Silenes: Novel Reagents for Organic Synthesis

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Abstract

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Whilst silenes have long been studied for their unique chemistry there has been little attempt to exploit this in other synthetic strategies. As part of a programme to explore this aspect the reactions of readily accessible silenes with alkenes and dienes were studied.

Silenes, generated by the thermolysis of acylpolysilanes, add to α,β-unsaturated esters to form silacyclobutanes and silyl-substituted cyclopropanes in moderate yields. Upon silicon-carbon bond oxidation the cyclopropanes were converted directly to 1,4-dicarbonyl compounds, thus demonstrating the formal acyl anion chemistry of acylpolysilanes.

In an alternative approach towards milder silene generation, the potential of *α*-silyl diazo carbonyl compounds was examined. It was found that *α*-silyl diazo esters undergo rhodium (II) catalysed decomposition to provide short-lived silenes. These intermediates rearrange to oxasilates which can be trapped with α,β-unsaturated ketones. The resulting products contain a high degree of functionality which offers considerable potential for further synthetic transformations.

Finally, more complex skeletons were approached through an exploration of intramolecular silene cycloaddition. In this respect, it was shown that thermolysis of acylpolysilanes at 180 ^{o}C produced [4+2] cycloadducts, while [2+2] cycloadducts and 'ene' products were not observed. Similarly, it was found that intramolecular cycloadducts can be generated at lower temperatures by the addition of MeLi·LiBr to acylpolysilanes. These two approaches allowed the cycloadducts to be synthesised in good yields and moderate diastereoselectivities.

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Declaration

The work in this thesis was carried out in the Department of Chemistry at the University of Durham, Department of Biochemistry and Organic Chemistry at Uppsala University or AstraZeneca at Macclesfield between October 2006 and March 2010. All the work is my own unless otherwise indicated. It has not been submitted for a degree at this or other university.

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Abbreviations

6-31G	Pople basis set
Ac	Acetyl
acac	acetylacetonate
Ad	Adamantyl
Anal	Elemental analysis
Ar	Aryl
ASAP	Atmospheric solids analysis probe
B3LYP	Becke-3 + LYP hybrid functional (method)
Boc	*tert*-Butoxycarbonyl
b.p.	Boiling point
BPW91	Becke's exchange functional combined with the Perdew and Wang's gradient-corrected correlation functional (method)
Bu	Butyl
cc-pVDZ	Correlation-consistent polarized valence double-zeta basis set
CCSD	Coupled cluster singles doubles
cm^{-1}	Wavenumbers
COSY	Correlation spectroscopy
d	Doublet (spectral)
DCM	Dichloromethane
dd	Doublet of doublets (spectral)
ddd	Doublet of doublet of doublets (spectral)
DEAD	Diethyl azodicarboxylate
DFT	Density Functional Theory
DIAD	Diisopropyl azodicarboxylate
DIPEA	*N*,*N*-Diisopropylethylamine
DMAP	4-Dimethylaminopyridine
DMF	*N*,*N*-Dimethylformamide
DMPU	1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone
ds	Diastereoselectivity
DTBAD	Di-*tert*-butyl azodicarboxylate
EDA	Ethyl diazoacetate

EI	Electron impact
eq	Equivalent
Et	Ethyl
g	Gramme
GC	Gas Chromatography
GC-MS	Gas Chromatography / Mass Spectrometry
GIAO	Gauge-including atomic orbitals (method)
h	Hour(s)
HMBC	Heteronuclear shift correlations *via* multiple bond connectivities
HMPA	Hexamethylphosphoramide
HOMO	Highest occupied molecular orbital
HRMS	High-resolution mass spectrometry
Hz	Hertz
IR	Infra red
J	Coupling constant
LDA	Lithium diisopropylamide
lit.	Literature
LUMO	Lowest unoccupied molecular orbital
m	Multiplet (spectral)
M	mol/L
m/z	Mass-to-charge ratio
mCPBA	*m*-Chloroperoxybenzoic acid
Me	Methyl
MHz	Megahertz
min	Minutes
mmol	Millimole(s)
m.p.	Melting point
MP2	Multi-Reference Moller-Plesset
MS	Mass spectrometry
NaHMDS	Sodium hexamethyldisilazide
NMO	*N*-Methylmorpholine-*N*-oxide
NMP	*N*-Methyl-2-pyrrolidinone
NMR	Nuclear magnetic resonance
NOE	Nuclear Overhauser effect

NOESY	Nuclear Overhauser effect spectroscopy
Nu	Nucleophile
pfb	Perfluorobutyrate
Ph	Phenyl
ppm	Part(s) per million
q	Quartet (spectral)
quin	Quintet (spectral)
R	Alkyl
R_f	Retention factor (for TLC)
RT	Room temperature
s	Singlet (spectral)
TASF	Tris(dimethylamino)sulfonium difluorotrimethylsilicate
TBAT	Tetrabutylammonium triphenyldifluorosilicate
TBDMS	*tert*-Butyldimethylsilyl
t-Bu	*tert*-Butyl
temp	Temperature
Tes	Triethylsilyl
Tf	Triflate
TFA	Trifluoroacetic acid
tfa	Trifluoroacetate
tfacac	Trifluoroacetylacetonate
TfOH	Trifluoromethanesulfonic acid
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TMS	Trimethylsilyl
TPAP	Tetra-n-propylylammonium perruthenate
UV	Ultraviolet
v/v	Volume-to-volume ratio

Contents

1 Introduction

This thesis describes the development of new methods for the generation of a range of structurally diverse silenes and applies these to the stereocontrolled functionalisation of π-bonded systems. The following chapter highlights selected aspects of organosilicon chemistry. Chapter 2 presents reactions of alkoxysilenes with electron-deficient alkenes. Chapter 3 focuses on silene generation from α-silyl diazo carbonyl compounds. Chapter 4 presents the first intramolecular silene cycloaddition reaction. Chapter 5 concludes the work presented and looks at prospects for future work arising from this thesis. Finally, Chapters 6 and 7 detail computational methods and experimental procedures, respectively.

1.1 Selected Aspects of Organosilicon Chemistry

1.1.1 Introduction

Silicon is a p-block element in group 14 immediately below carbon. It therefore shares many characteristics with carbon. The most obvious similarity is that both elements are tetravalent and both form tetrahedral compounds.[1] However, there are some important differences that distinguish silicon from carbon which have a broad impact on their chemistry.[2] This section will briefly outline some of the fundamental features of silicon chemistry.

1.1.2 Bond Length

Silicon atoms are approximately 50% larger than carbon atoms. Therefore the bonds between silicon and other atoms are, in general, longer than the equivalent bonds between carbon and the corresponding atoms (Table 1).[3,4] Compared to olefinic C=C bonds, which are about 14% shorter than C-C single bonds, Si=C bonds are approximately 9% shorter than the corresponding Si-C single bonds due to the weaker π-bonding which results from overlap of a 2p atomic orbital on carbon with a 3p orbital on silicon.

Bond to C	Bond length (Å)	Bond to Si	Bond length (Å)
C-C	1.54	Si-C	1.89
C=C	1.32	Si=C	1.72
C-O	1.41	Si-O	1.63
C-Cl	1.78	Si-Cl	2.05
C-F	1.39	Si-F	1.60

Table 1

1.1.3 Bond Strength

In relation to the bond length, silicon forms stronger bonds with electronegative elements in comparison to carbon (Table 2).[3,4] In particular, the silicon-fluorine bond is one of the strongest single bonds known. It is because of this that many of the reactions involving silicon are driven by the formation of strong silicon-fluorine or silicon-oxygen bonds at the expense of other weaker bonds.

Bond to C	Bond energy (kJ/mol)	Bond to Si	Bond energy (kJ/mol)
C-C	334	Si-C	318
C=C	620	Si=C	490
C-O	340	Si-O	531
C-Cl	335	Si-Cl	471
C-F	452	Si-F	808

Table 2

The silicon-carbon bond is weaker in comparison to the carbon-carbon bond (Table 2). However, the bond is strong enough for trialkyl silyl groups to survive a wide variety of synthetic transformations, but weak enough to be selectively cleaved when required.

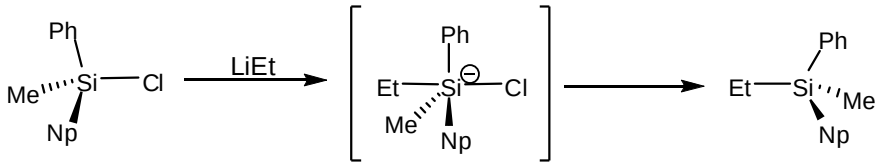
1.1.4 Bond Polarisation

Silicon is more electropositive than carbon resulting in polarisation of a silicon-carbon bond ($Si^{\delta+}-C^{\delta-}$) and is therefore susceptible to nucleophilic attack at the silicon atom.[4] In particular, silenes ($Si^{\delta+}=C^{\delta-}$) exhibit such high reactivity towards nucleophiles that most of the known

examples of these compounds are transient reactive intermediates. Silicon is also more electropositive than hydrogen ($Si^{\delta+}-H^{\delta-}$), which allows for Et_3SiH to act as a reducing agent.

1.1.5 Nucleophilic Substitution at Silicon

Nucleophilic substitution at silicon could proceed by either an S_N2 or an S_N1 type mechanism. Although silicon cations are more stable than their carbon analogues, substitution via an S_N1 mechanism is very rare because of the very high rate of the competing bimolecular process, sometimes referred to as the S_N2-Si mechanism. The long carbon-silicon bond and low-lying d-orbitals on silicon facilitate this process. With good leaving groups such as Cl, Br and I, substitution normally takes place with inversion of configuration at silicon (Scheme 1).[2,4]



1 **2** **3**

Scheme 1

The reaction proceeds via a pentacoordinate intermediate, e.g. **2**. This is in contrast to the S_N2 pathway for that of carbon where a loose pentacoordinate species exists only as a transition state.

1.1.6 Stabilisation of ß-carbocations and α-carbanions

The stabilisation of cations at the carbon atom in a ß-position to silicon is a result of the overlap of the vacant p orbital on the ß carbon atom and the σ orbital between the silicon atom and the α carbon atom (Figure 1).[2,4] The strongest stabilisation occurs when the vacant p orbital and the σ orbital of the carbon-silicon bond are in the same plane. One consequence of the increased stability of ß-carbocations determines the reaction pathway between electrophiles and organosilicon compounds such as allyl-, aryl-, vinyl- silanes and silyl enol ethers.

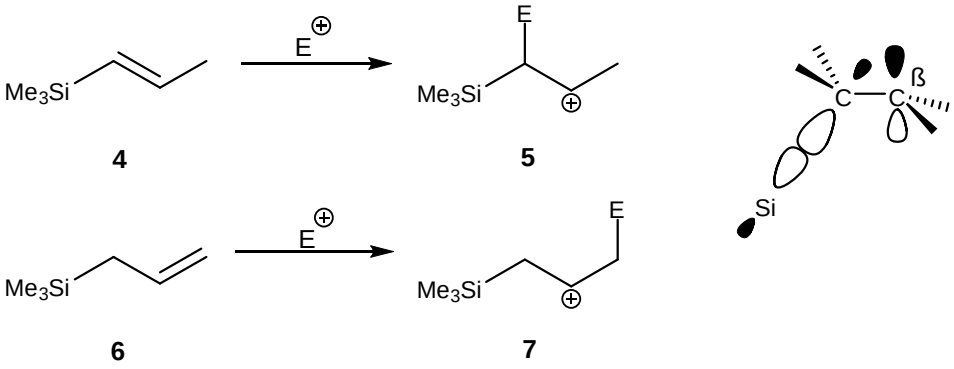


Figure 1

Silicon also stabilises a carbanion in the α-position.[2] In molecular orbital terms this ability can be attributed to two effects: a) Overlap of the α-carbon-metal bond with a silicon d orbital and b) Overlap of the α-carbon-metal with the adjacent σ* antibonding orbital between silicon and carbon (Figure 2).

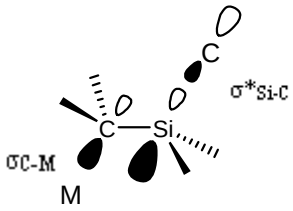


Figure 2

1.2 Organosilanes in synthesis

1.2.1 Introduction

Organosilicon reagents have been utilised in a plethora of reactions. The use of silicon-based protecting groups in the majority of multi-step natural product syntheses illustrates the necessity of organosilicon compounds. The use of other silicon reagents, such as silyl enol ethers, allyl-, vinyl- and aryl- silanes, has also become ubiquitous in the field of organic chemistry in powerful methods for carbon–carbon bond formation. The general aspects of organosilicon chemistry will be discussed in the following section.

1.2.2 Protecting group[5,6]

Silicon-based protecting groups are used extensively in organic synthesis. They are primarily employed as protecting groups for hydroxyl moieties, in which silicon is attached directly to oxygen, but can be used to protect other functional groups such as amines, thiols, carboxylic acids and phosphoric acids. The simplest protecting group used for hydroxyl protection is the trimethylsilyl group (TMS). Trimethylsilyl ethers however, are not particularly stable and are cleaved under mild acidic or basic conditions as well as by nucleophiles. To overcome these limitations, the use of other silyl ethers can be employed, as their relative stability can be finely tuned by varying the substituents on silicon. In general, the bulkier the substituents around silicon the harsher the conditions required for removal of the protecting group. The most common bulky silanes used for protection are shown in Figure 3.

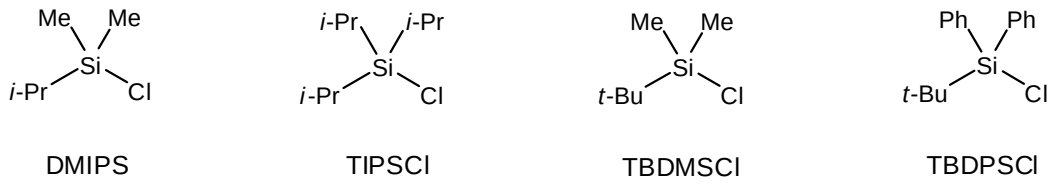
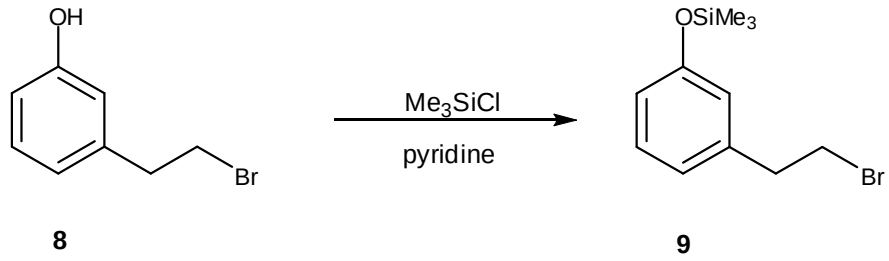


Figure 3

The general method of preparation of silyl ethers involves treatment of the alcohol with a silyl chloride in the presence of a weak base such as Et_3N, pyridine or imidazole (Scheme 2). More reactive silyl triflates have been used to protect tertiary or hindered secondary alcohols.

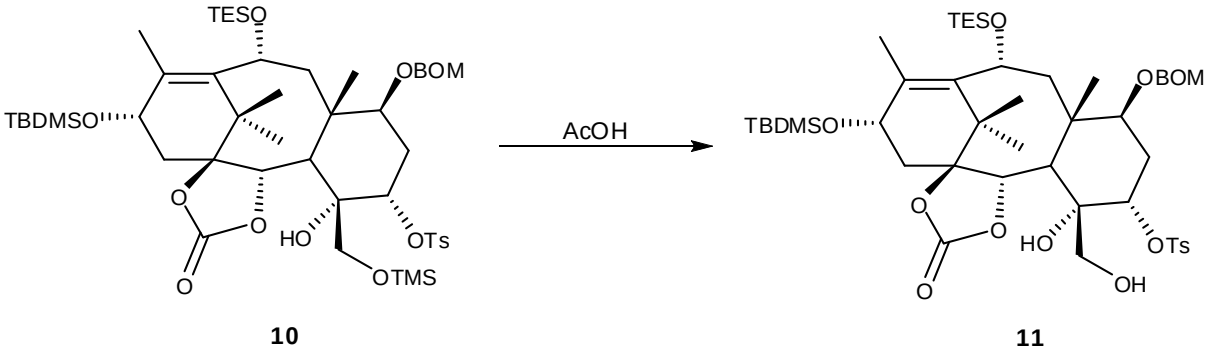


8 **9**

Scheme 2

A variety of methods are available for the cleavage of silyl ethers to their parent alcohols. Among the most widely used are fluorides, acids and bases. However, the use of catalysts, palladium (II) hydroxide,[7] PdO,[8] and Pd/C[9] has been also reported. Holton and co-workers took advantage of the varying lability of silyl ethers in the synthesis of the antitumor agent

taxol (Scheme 3)[10]. Treatment of **10** with acetic acid cleaved only the TMS ether leaving the other silyl groups intact. Consequently, the selective hydrolysis of different silyl protecting groups allowed selective modification of the molecule.

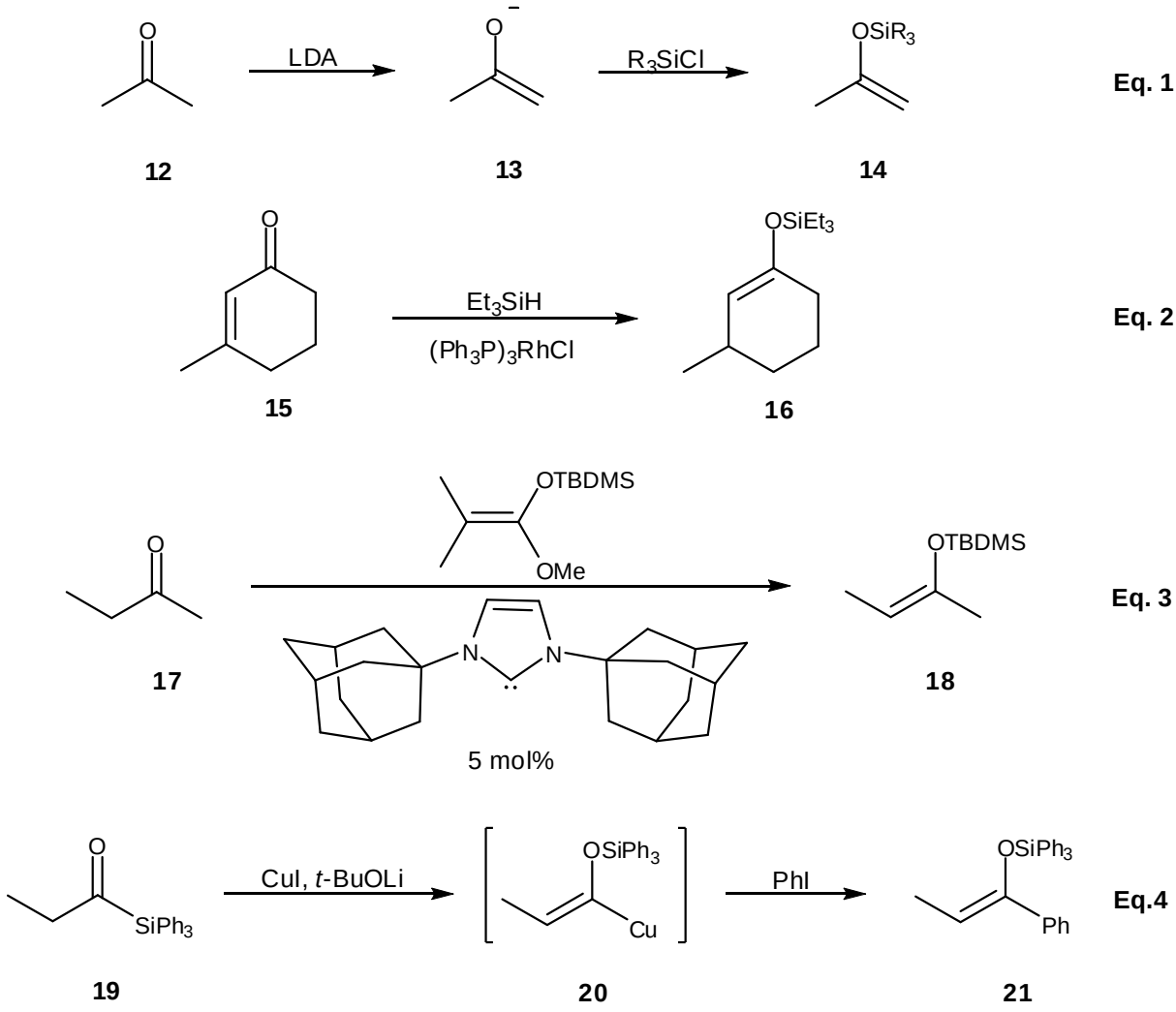


10 **11**

Scheme 3

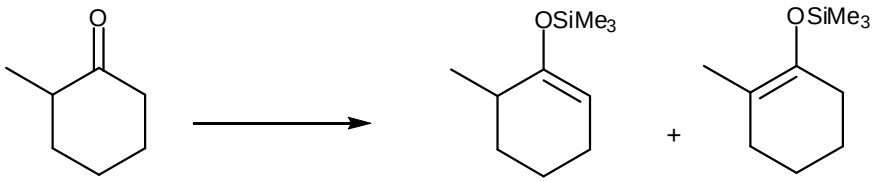
1.2.3 Silyl enol ethers

The second most important application of silicon in organic chemistry is stabilisation of an enolate anion as a silyl enol ether, which may be isolated, purified, and characterised using standard analytical procedures. Silyl enol ethers **14** are generally prepared by quenching enolate anions **13** with the corresponding silyl chloride (Scheme 4, Eq. 1). However, many other methods for their preparation have been reported, e.g. hydrosilylation of α,β-usaturated ketones (Eq. 2),[6] silyl transfer from trialkylsilyl ketene acetals to ketones (Eq. 3),[11] 1,2-silyl migration of the copper enolates of acyltriphenylsilanes (Eq. 4).[12]



Scheme 4

The formation of silyl enols ethers from unsymmetrical ketones is more difficult due to the formations of two isomeric enolate anions. Nevertheless, the regiochemistry of enolate formation can be effectively controlled using correct reaction conditions. Under kinetic conditions, deprotonation takes place at the less hindered site and the enolate anion with the less substituted double bond is formed. On the other hand, thermodynamic conditions give rise to the enolate anion containing the more substituted double bond (Scheme 5).

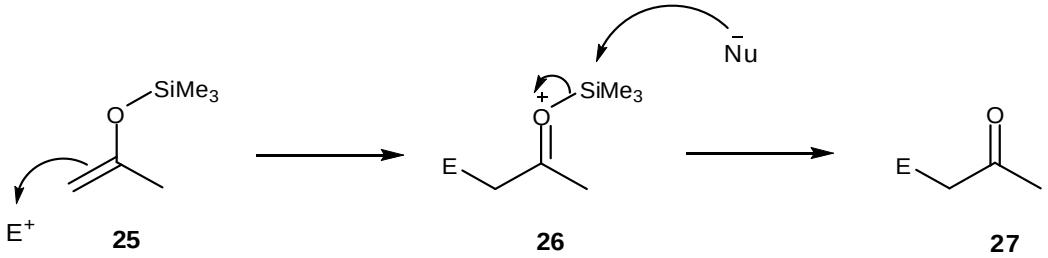


22 **23** **24**

kinetic control:	1. LDA, -78 ^{o}C, 1h 2. Me_3SiCl	99	:	1
thermodynamic control:	1. Me_3SiCl, Et_3N 130 ^{o}C, 90 h	12	:	88

Scheme 5

Silyl enol ethers are relatively weak nucleophiles, but in the presence of a Lewis acid they react readily with a wide range of electrophiles such as alkyl halides, aldehydes and ketones (Scheme 6). The reaction with aldehydes has been commonly used for preparation of β-hydroxy ketones in high yields. The increased stability of carbocations β to silicon determines the regioselectivity of the reaction.



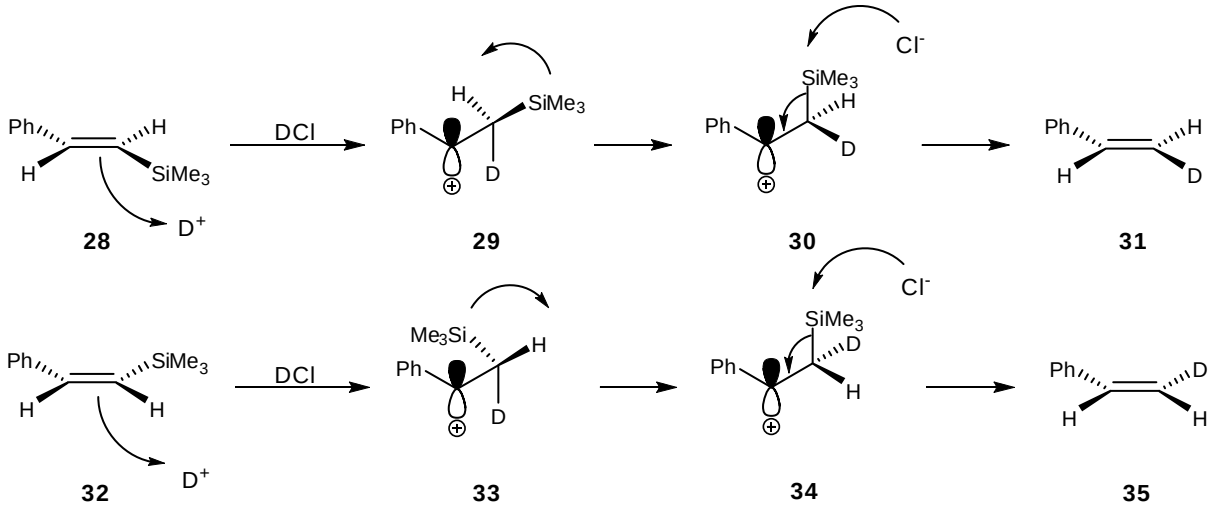
25 **26** **27**

Scheme 6

1.2.4 Vinylsilanes

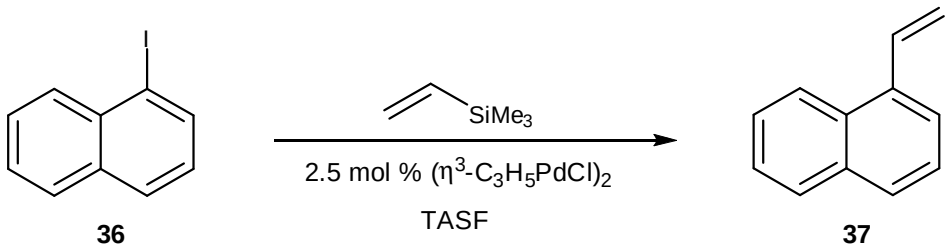
Vinylsilanes, like silyl enol ethers, have proved to be of value in a variety of useful synthetic transformations. Reflecting this, many methods for their preparation have been developed. The most common methods utilise the reductive alkylation of alkynyl silanes,[13] hydrosilylation of alkynes[14] and the coupling of vinylic organometallics with a silyl chloride.[15] Vinylsilanes react with electrophiles ranging from proton, carbon and main group heteroatoms with high stereoselectivity and regioselectivity.[3] In the example shown in Scheme 7 the silyl group of (*E*)- and (*Z*)-β-trimethylsilylstyrene is replaced by deuterium.[2] The retention of stereochemistry can be rationalised by initial addition of the electrophile to

the silicon-bearing carbon of the alkene generating the more stable β-carbocation. The rotation around the central carbon-carbon bond occurs in the direction which avoids bringing the empty p orbital and the silicon-carbon bond orthogonal to each other. Elimination to the alkene takes place when the empty p orbital and the silicon-carbon bond are in the same plane. In general, retention of configuration is usually observed, although inversion of configuration is also known.[3]



Scheme 7

A considerable amount of research has also been conducted on the applications of vinylsilanes in cross-coupling reactions (Scheme 8). Hiyama has shown that vinylsilanes react with aryl and vinyl iodides in the presence of a palladium catalyst and fluoride source.[16] The purpose of the fluoride is to activate the organosilicon compound by forming a pentavalent intermediate R_4SiF^-, which is more susceptible to transmetalation with the palladium (II) intermediate resulting from oxidative addition into the aryl iodide.



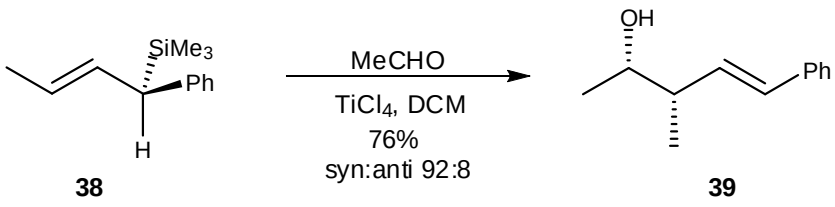
Scheme 8

1.2.5 Allylsilanes

Since allylsilanes are also very useful synthetic intermediates in organic synthesis, a number of procedures for their preparation have been reported. Among them, the methods utilising the Wittig reaction,[17] Peterson olefination[18] and metathesis[19] are the most attractive as they enable the preparation of regioisomerically pure allylsilanes. In contrast to vinylsilanes, allylsilanes are more reactive towards electrophiles as a result of the interaction between C-Si bonds that can be parallel to p orbitals of the π bond (Figure 4). In general, electrophiles attack the terminal carbon (γ) of the allylic group regioselectively, although sterically hindered alkyl halides may attack preferentially at the α position.[3]

Figure 4

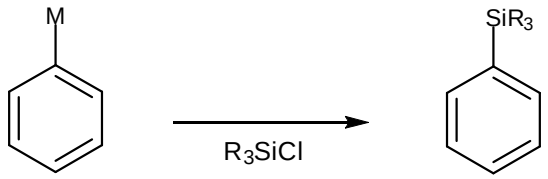
An example reported by Hayashi demonstrates the great potential of allylsilanes in the process of carbon-carbon bond formation (Scheme 9).[20] Optically active (*R*)-allylsilane **38** was allowed to react with acetaldehyde in the presence of titanium (IV) chloride in dichloromethane to give chiral homoallylic alcohol **39** with high stereoselectivity. Electrophilic attack occurs on the face of the alkene anti to the silyl group.



Scheme 9

1.2.6 Arylsilanes

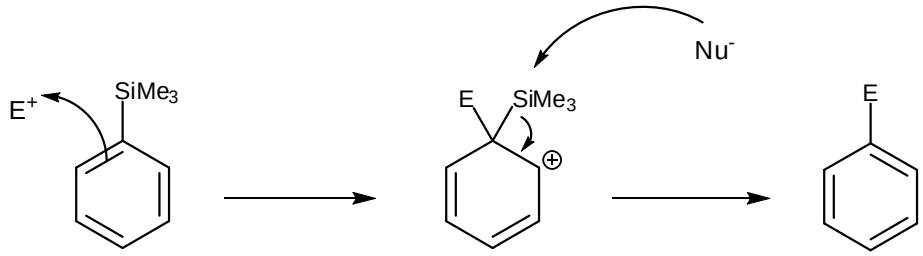
Arylsilanes **41** are generally prepared by the reaction of organometallic species **40** with a chlorosilane (Scheme 10). The organometallic component can be made either by metal-halogen exchange or by deprotonation of an activated C-H bond. The palladium-catalysed cross-coupling reaction of organic halides with hydrosilanes has also proved to be a versatile method for synthesising functionalised arylsilanes.[21]



40 **41**

Scheme 10

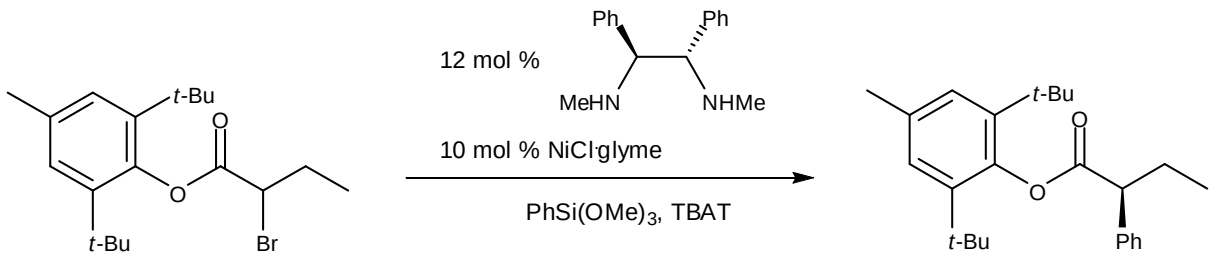
Arylsilanes react with electrophiles in a process known as *ipso* substitution (Scheme 11).[2] The result is the electrophile replaces the silyl group on the aromatic ring. The selectivity of *ipso* substitution comes from the same principle as that used to rationalise the reaction of vinyl and allylsilanes with electrophiles. The electrophile reacts with arylsilane **42** to produce the most stable carbocation **43** β to silicon.



42 **43** **44**

Scheme 11

Recently much attention has been focused on applications of aryl silanes in cross-coupling reactions.[22,23] Compared to other organometallic reagents (Zn, Mg, Sn, etc.) utilised in cross-coupling processes, arylsilanes are attractive due to their ease of handling and/or low toxicity. An example of a nickel/diamine-catalysed asymmetric Hiyama reaction is shown in Scheme 12.[24] A range of racemic α-bromo esters were cross-coupled with $PhSi(OMe)_3$ in good yield and enantioselectivity (80 - 99 % ee).

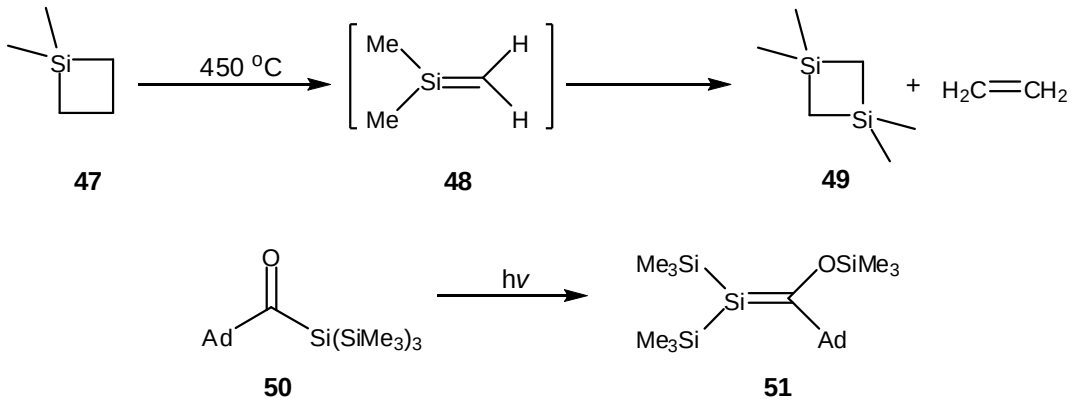


Scheme 12

1.3 Silenes

1.3.1 Introduction

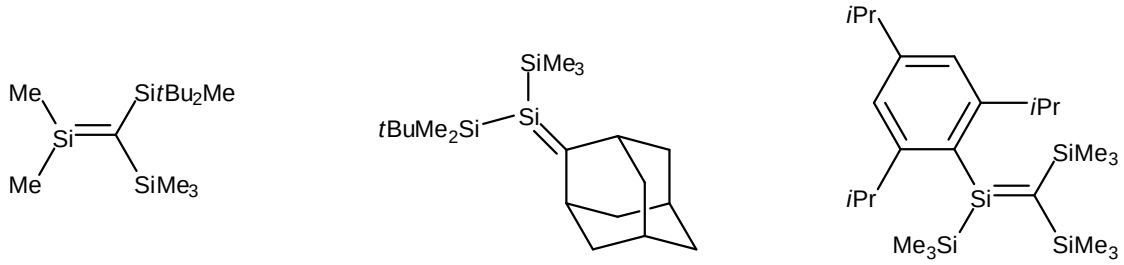
For a long time it was assumed that the Group 14 elements, with the exception of carbon, did not form multiple bonds. The so-called 'double-bond rule' stated that elements with principal quantum number greater than 2 do not form multiple bonds with themselves or with other elements.[25] The first strong evidence for the existence of a silicon-carbon double bond was established in 1967 by Gusel'nikov and Flowers.[26] They detected silene dimer **49** generated during the pyrolysis of silacyclobutane **47** (Scheme 13). A major breakthrough came in 1981 when Brook and co-workers found that the photolysis of the adamantyl-substituted acylpolysilane **50** gave a stable silene **51** which could be characterised by X-ray diffraction.[27] These findings led to the decisive overturning of the double-bond rule. Since then, the chemistry of the silicon-carbon double bond has been an area of active investigation.



Scheme 13

1.3.2 Stable silenes

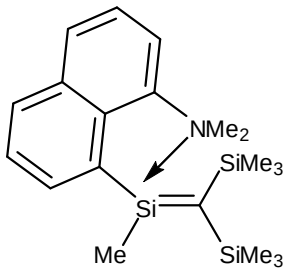
Brook and co-workers had succeeded for the first time in isolating a silene. They deduced that the steric bulk of the substituents on the carbon atom were a crucial factor in moderating silene reactivity. Since then, many other groups have utilised this approach and some common stable silenes (**52**[28], **53**[29], **54**[30]) formed from this technique are shown in Figure 5.



52 **53** **54**

Figure 5

However this is not the only strategy that can be employed to enhance silene stability. The use of electron donors to stabilise the electrophilic silicon atom was reported for the first time by Wiberg.[31] Even weak Lewis bases such as tetrahydrofuran easily coordinate to unsaturated silicon atoms to form remarkably stable adducts. It has been shown that Lewis basicity towards the silene **52** follows the order: THF < NMe_3 < C_5H_5N < F^-.[31] More recent work by Oehme has extended this principle to incorporate the amine group in the silene structure **55** as the electron donor (Figure 6).[30]

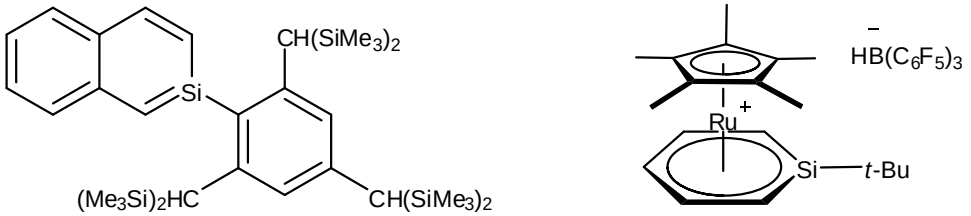


55

Figure 6

In 1997 Okazaki and co-workers successfully prepared the first stable silaaromatic **56** (Figure 7).[32] The aromatic character of the 2-silanaphthalene ring system was supported by quantum

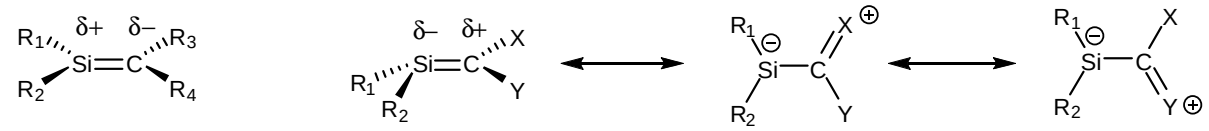
chemical calculations. Despite the increased stability gained in the aromatic resonance energy, this compound still requires steric protection with very bulky Tbt (2,4,6-tris[bis(trimethylsilyl)methyl]phenyl) protecting groups to stop dimerisation. An alternative strategy to steric stabilisation of silaaromatics was proposed in 2001 by Dysard and Tilley.[33] It has been shown that coordination to a transition metal fragment is a useful way to stabilise these reactive species. The ruthenium complex of silabenzene **57** is shown in Figure 7.



56 **57**

Figure 7

Alternatively, silene stability may also be increased by π-electron-donating substituents at the carbon atom of the silene (Figure 8). The substituent effect suppresses the natural $Si^{\delta+}=C^{\delta-}$ polarisation effectively and induces the zwitterionic effect, i.e. $Si^{\delta-}=C^{\delta+}$.[34] This causes substantial pyramidalisation at the silicon atom and increases the Si-C bond length. Indeed, Apeloig found through ab initio calculations that 'reverse polarisation' is the most important electronic factor that enhances the kinetic stability of silenes.[35]



58 **59** **60** **61**

R_1-R_4 = SiR_3, H, Alk, Ar

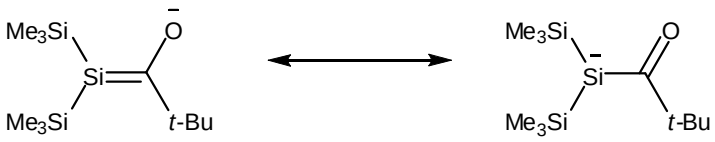
R_1,R_2 = SiR_3, H, Alk, Ar X,Y = NR_2, OR, SR

Naturally polarised silenes

Reverse polarised silenes

Figure 8

In 2003 Ottosson exemplified this concept in a report describing an isolable silanolate **62**, which can be kept under an inert atmosphere for three months (Figure 9).[36] X-ray diffraction of **62** shows a very long Si-C bond (1.926 Å) and thus silanolate is probably better described by the alternative resonance structure **63**.



62 **63**

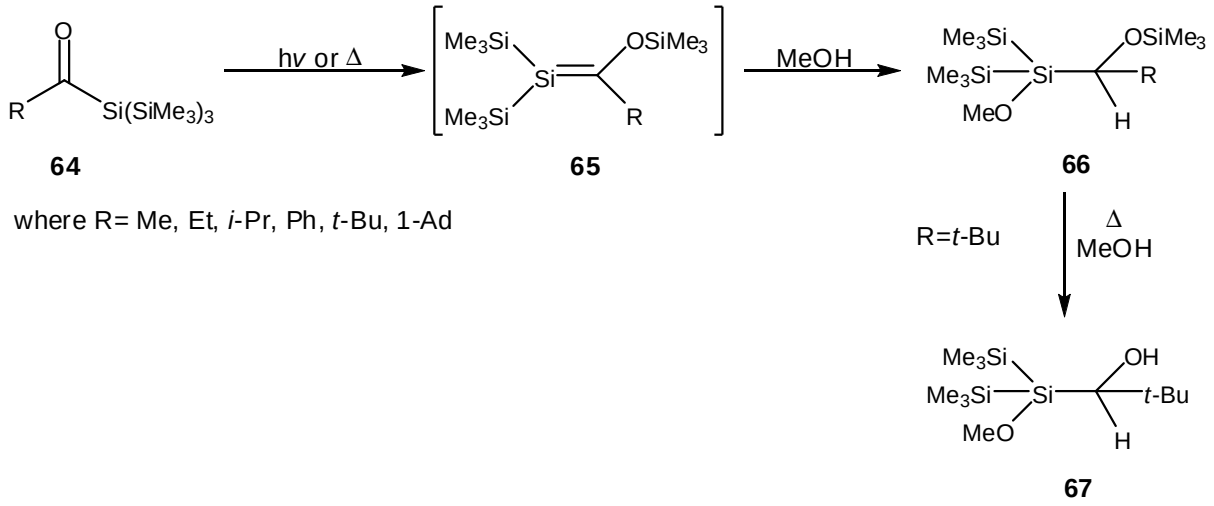
Figure 9

1.3.3 Generation of Silenes

The early methods of silene generation commonly involved thermolytic or photolytic fragmentations or rearrangements. However, there are now several alternative methods, which avoid these high energy conditions. This section will briefly outline some of the most commonly encountered techniques.

1.3.3.1 Acylpolysilanes

The photochemical and thermal rearrangement of acylpolysilanes into silenes was extensively studied by Brook and co-workers.[37,38] They found that the photolysis of acylpolysilanes **64** in methanol gave the adduct **66** from trapping of silene **65** (Scheme 14). Similarly, silene **65** can be generated thermally from the corresponding acylpolysilane **64**. For example, thermolysis of pivaloyltris(trimethylsilyl)silane **64** (R = *t*-Bu) in methanol in a sealed tube gave the alcohol **67** in 92% yield, which appears to be the methanolysis product of the expected silane **66**.[38]

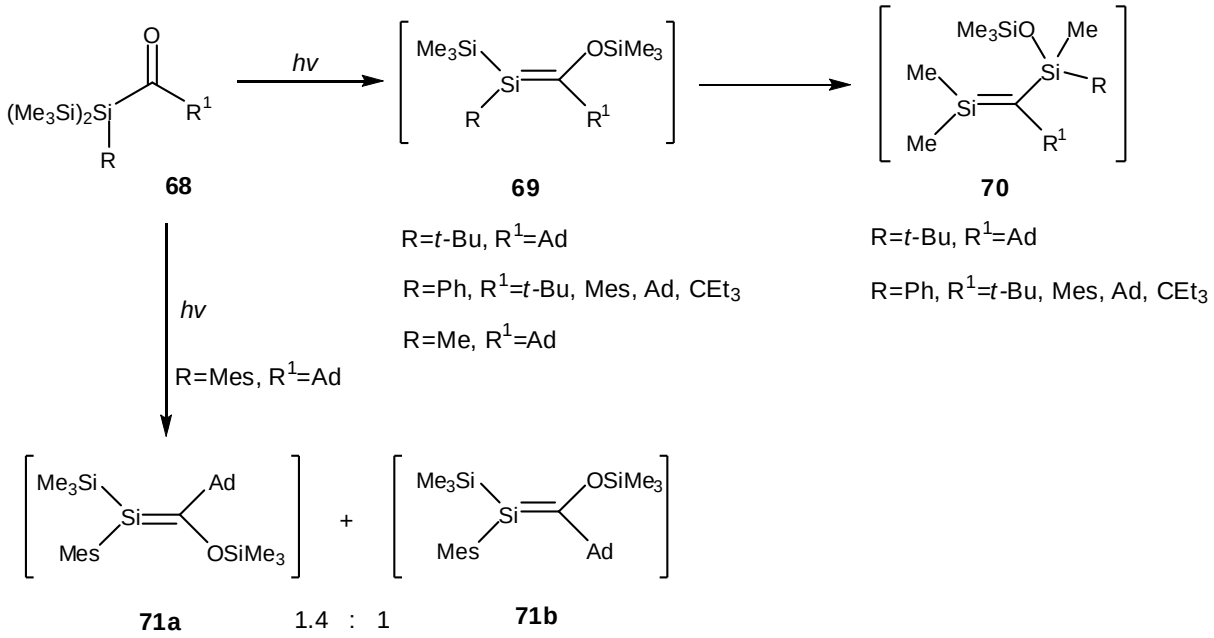


64 **65** **66** **67**

Scheme 14

The photochemical technique allowed Brook to prepare the first silene that could be characterised by X-ray crystallography and since then this method has been widely used to synthesise a variety of silenes.

It was subsequently found by Brook that replacement of the trimethylsilyl substituents with alkyl or phenyl groups generally leads to a reduction of the stability of the silene (Scheme 15).[39] Interestingly, the photolysis of the acylpolysilane **68** gave in only one case (R=Mes, R^1=Ad) two possible silene geometrical isomers in detectable amounts.[40] The structures of silene **71a** and **71b** were characterised by NMR spectroscopy in addition to their methanol and phenylacetylene adducts. In addition, it was found that silene **69** (R=Ph, *t*-Bu) isomerises during the photolysis to form species **70**.



Scheme 15

Ishikawa and co-workers have studied the mechanism of silene generation using a simple model to investigate the 1,3-silyl migration in acetylsilane (Figure 10).[41] There are two reaction pathways available with respect to the stereochemistry of the migrating silyl group: the retention pathway and the inversion pathway. The favoured retention pathway via TS_{ret} was computed to require 32.2 kcal/mol as the activation energy for the 1,3-silyl migration at the B3LYP/6-31G* level of theory.

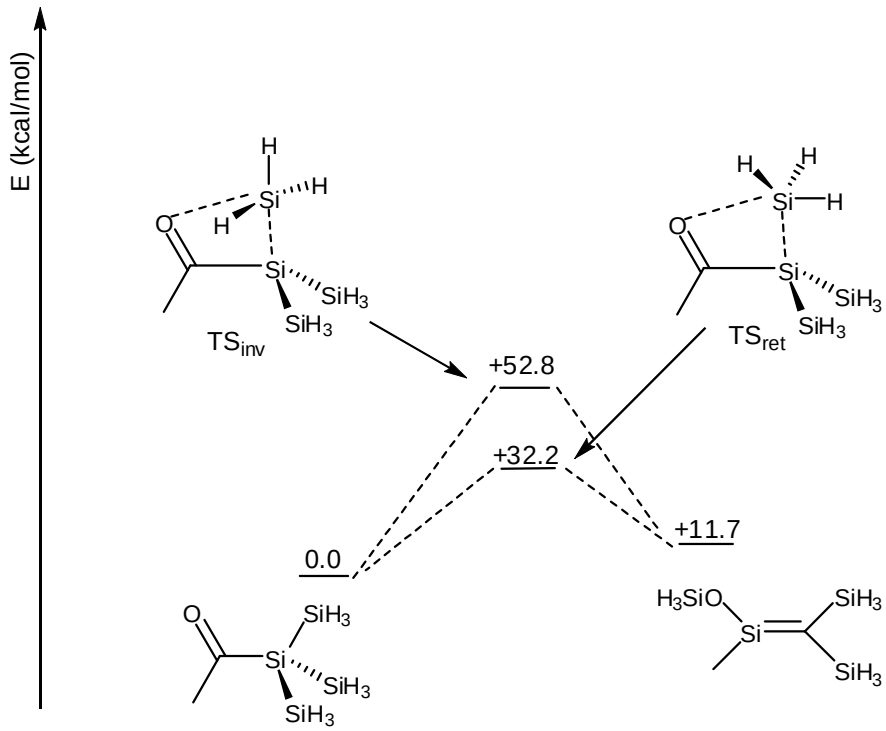
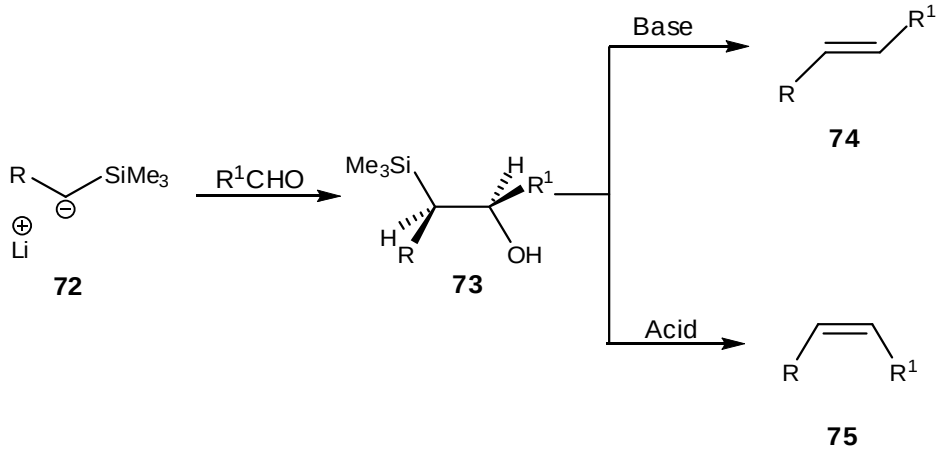


Figure 10

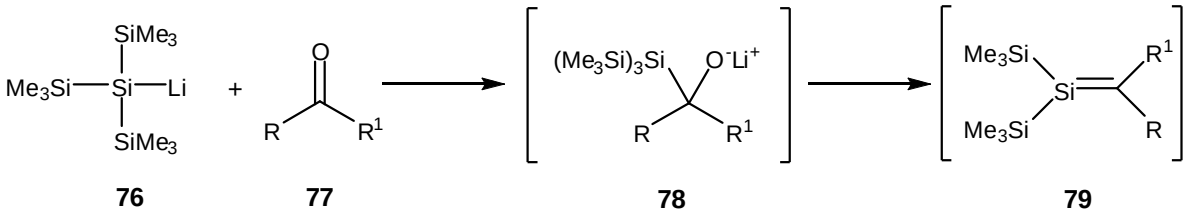
1.3.3.2 Modified Peterson Olefination

The original Peterson reaction is a method for preparing alkenes which was first described in 1968. The general reaction involves addition of an α-silylcarbanion to a ketone (or aldehyde) to form a ß-hydroxysilane which eliminates silanolate to form alkenes (Scheme 16).[2] The elimination follows two distinct mechanistic pathways to prepare either *cis* or *trans* alkenes depending on the reaction conditions. For example, compound **73** gives the *cis* product **75** or the *trans* product **74** depending on whether the elimination is carried out under acidic or basic conditions.



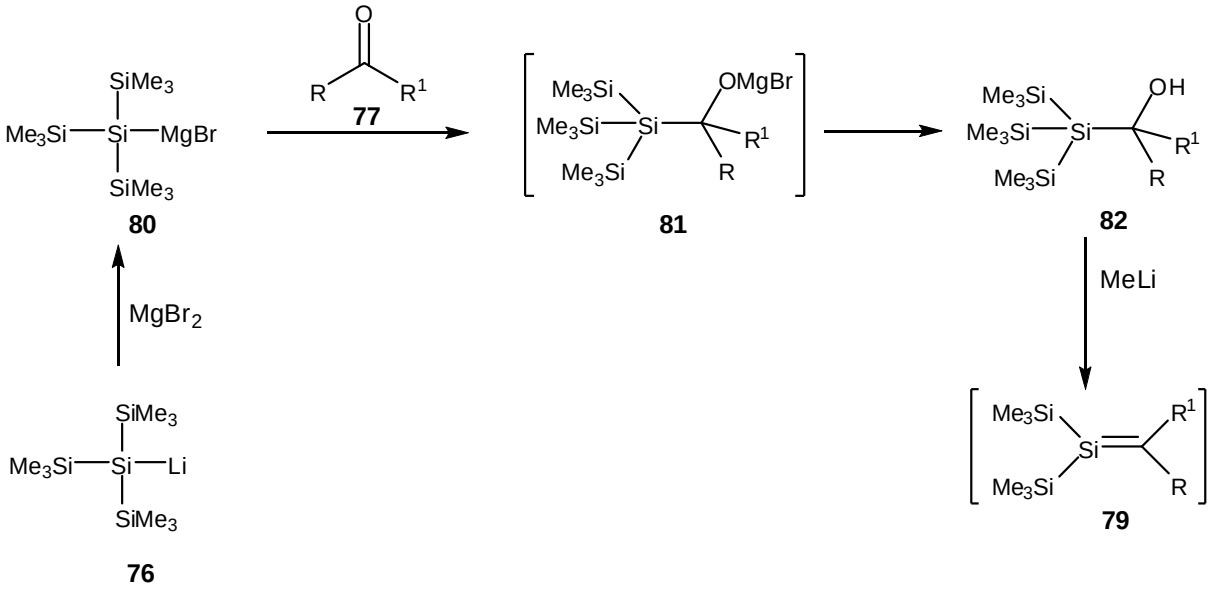
Scheme 16

Oehme and co-workers have adapted this methodology to form silenes by replacement of the carbon atom in the nucleophile by a silicon atom.[42] The reaction of silyllithium species **76** with carbonyl compounds **77** generates α-silyloxy anions **78** which are known to undergo spontaneous elimination to form silene **79** (Scheme 17).



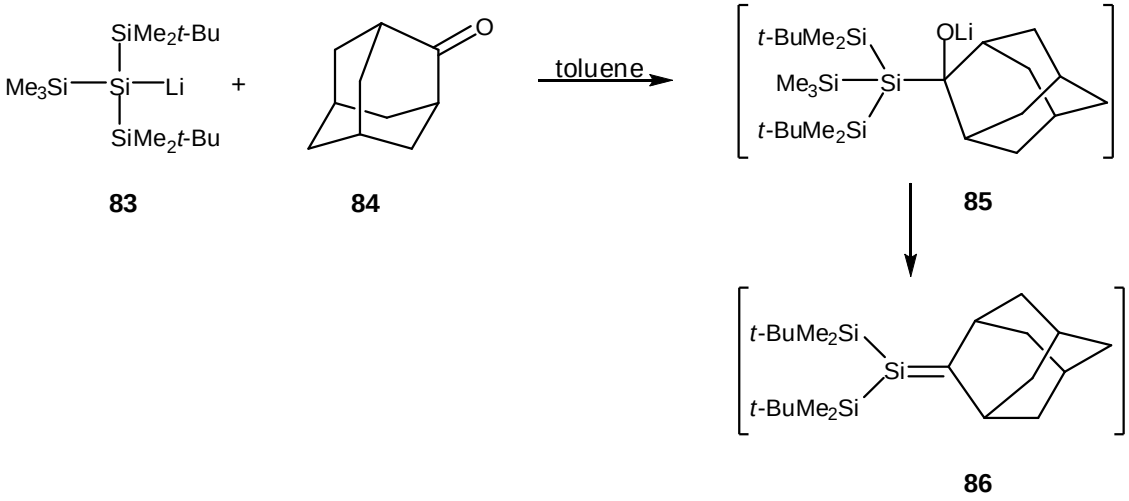
Scheme 17

Subsequently, Oehme has reported another approach to form silenes via a modified Peterson reaction.[43,44] The reaction of silyl Grignard reagent **80** with carbonyl compounds **77** generates magnesium alkoxide **81** which, after workup, affords silylalcohols **82** (Scheme 18). Silylalcohols **82** can be readily transformed into silenes **79** by treatment with methyllithium. This two-step procedure avoids potential problems of competing enolisation of carbonyl compounds and allows for the choice of reaction conditions in the second step.



Scheme 18

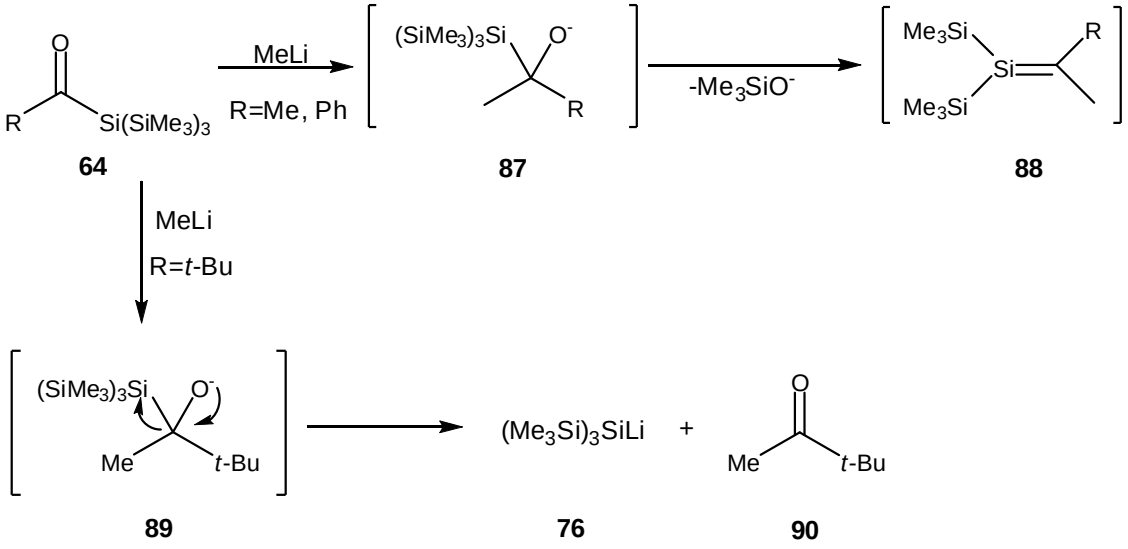
Almost all silenes from the modified Peterson olefination are transient species that usually dimerise in a head-to-head fashion. Apeloig was the first to use this methodology to generate an isolable silene.[29] The reaction of adamantanone with bulky silyllithium species **83** afforded a stable silene in good yields (Scheme 19). However, this silene was observed to react rapidly at room temperature with methanol and 1-methoxybutadiene.



Scheme 19

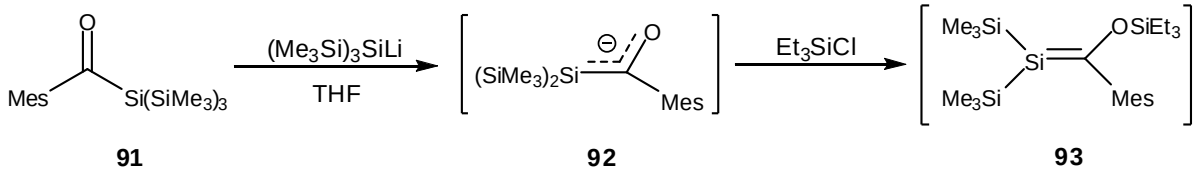
Ishikawa and co-workers later discovered that silenes could be generated by the addition of methyllithium to acylpolysilanes (Scheme 20).[45] The resulting α-silyloxy anion **87** underwent elimination of trimethylsilanolate to afford the silene **88** which underwent dimerisation.

However, all attempts to trap these silenes with other agents were unsuccessful. It was assumed that an increase in the steric bulk around the silene would lead to a stable isolable silene. Therefore, the reaction of pivaloyltris(trimethylsilyl)silane bearing a bulky *t*-Bu substituent was investigated. However, the expected product **88** was not observed. Instead, cleavage of the acyl-Si bond occurred to eliminate tris(trimethylsilyl)silyllithium **76**.



Scheme 20

Following this, Ishikawa found that the reaction of acyltris(trimethylsilyl)silane with silyllithium reagents proceeds in a different fashion from that above, giving lithium enolate **92**. These types of lithium species react readily with electrophiles, such as water, alkyl halides, and chlorosilanes, to produce coupled products. Treatment of the lithium enolate solution in THF with chlorotriethylsilane yielded silene **93** quantitatively (Scheme 21).[46,47]

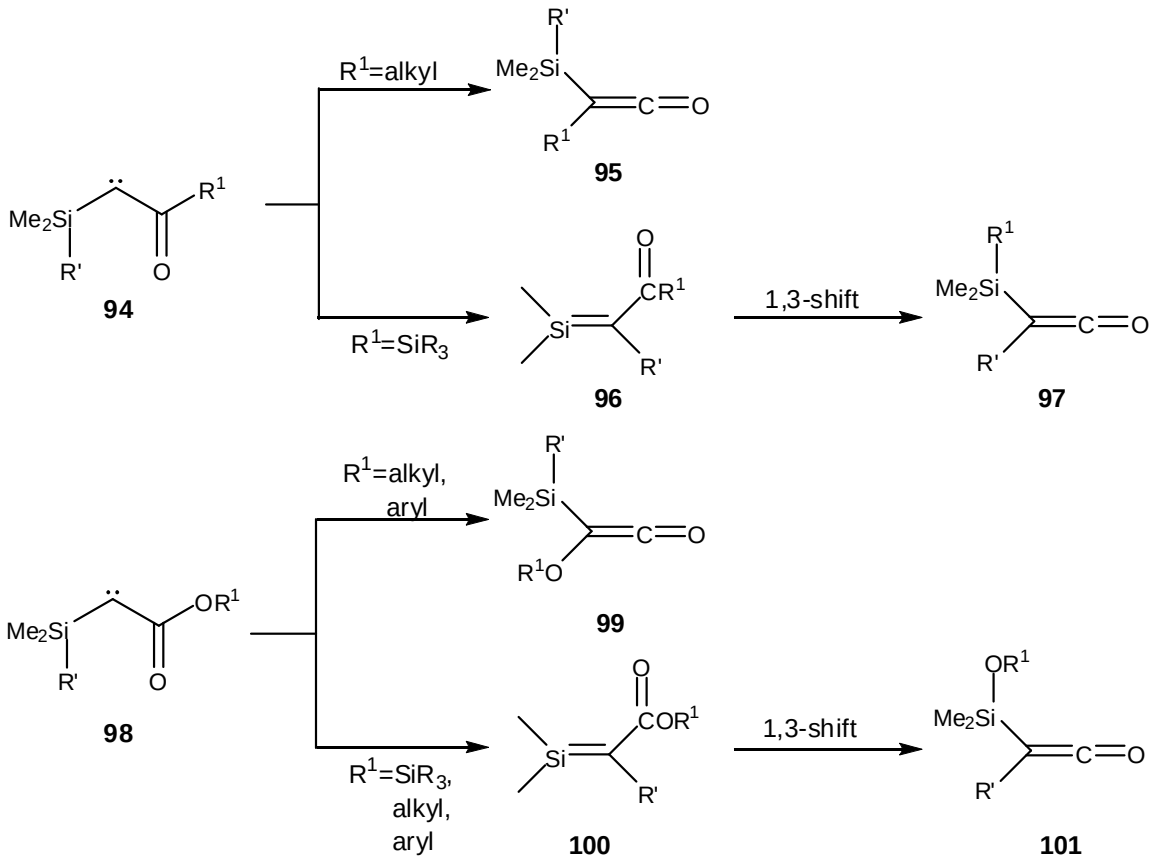


Scheme 21

1.3.3.3 Diazo compounds

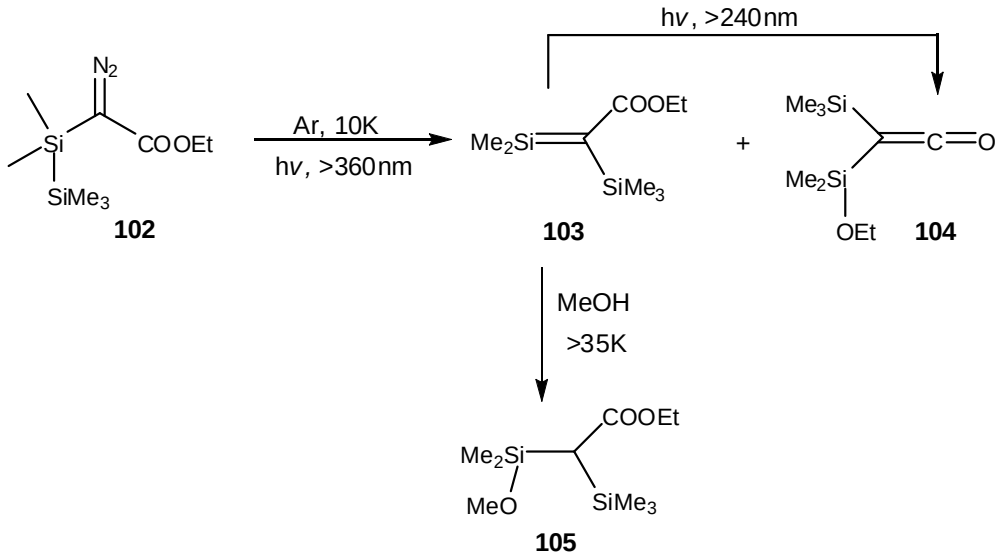
Another approach to the preparation of silenes relies on the photolysis or thermolysis of diazo compounds. The thermal decomposition is of less importance in comparison to photolysis methods since silyl-substituted diazo compounds are much more stable than their nonsilylated counterparts.

The extrusion of N_2 from silyl-substituted diazo compounds leads to silylcarbenes, which easily undergo transformation depending on the nature of the substituents. It appears that silyl ketocarbenes **94** rearrange cleanly to the corresponding silene **96** only in the presence of a disilanyl substituent (Si - Si) at the carbene.[48] In comparison, the Wolff rearrangement of a silylcarbene **94** to a silylketene **95** requires only silicon-carbon bonds. However, alkoxycarbonyl(trialkylsilanyl)carbenes **98** can undergo both types of rearrangement (Scheme 22).[48] It has been shown that some substituents on the silicon atom can migrate more easily than the others of the order: H > Me[49], $SiMe_3$ > Me[50,51,52], $(Me_3Si)_3Si$ > Me[53], Ph > Me[52,54]. Methoxy groups do not migrate at all.[55]



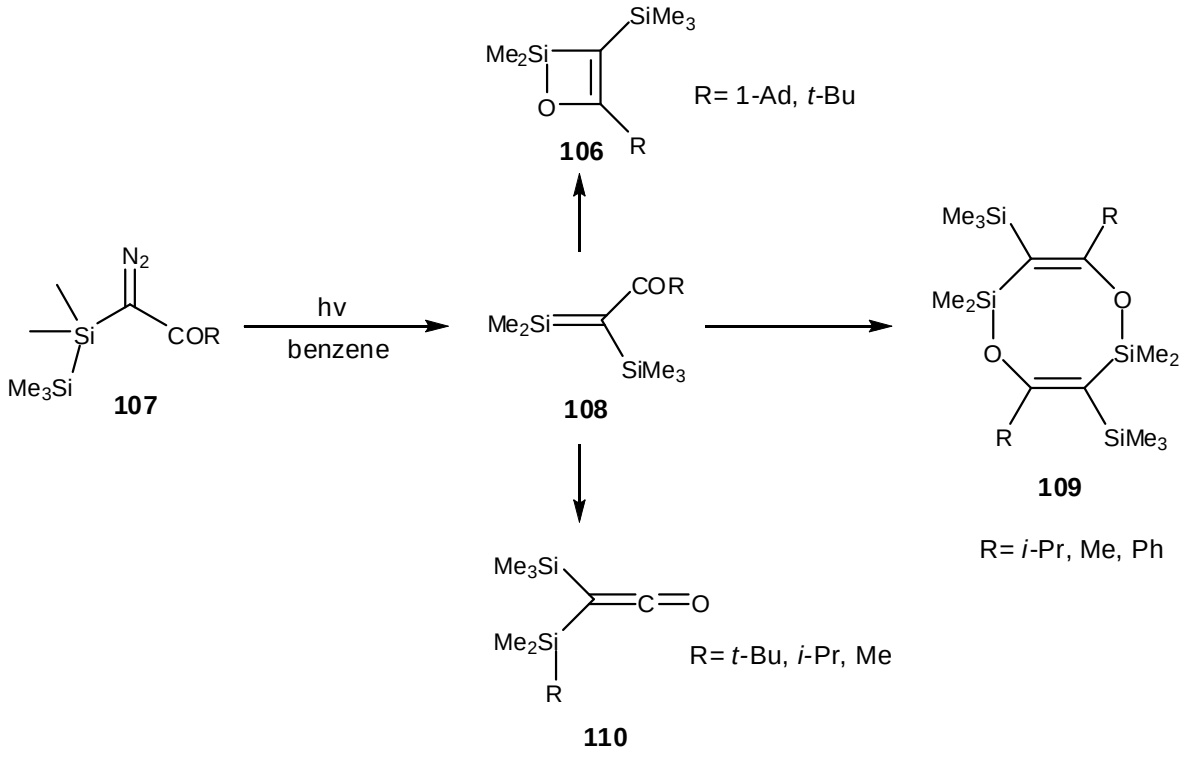
Scheme 22

Photolysis of methyl (pentamethyldisilanyl)diazoacetate **102** in inert matrices at low temperature allowed the isolation and spectroscopic characterisation of the silaacrylate **103** (Scheme 23).[56] Short-wavelength irradiation (>240nm) of silene **103** resulted in its rearrangement to ketene **104**. The observed 1,3-alkoxy migration has been assumed to proceed via an ion pair.[48] Addition of methanol at the double bond takes place after warming to >35K.



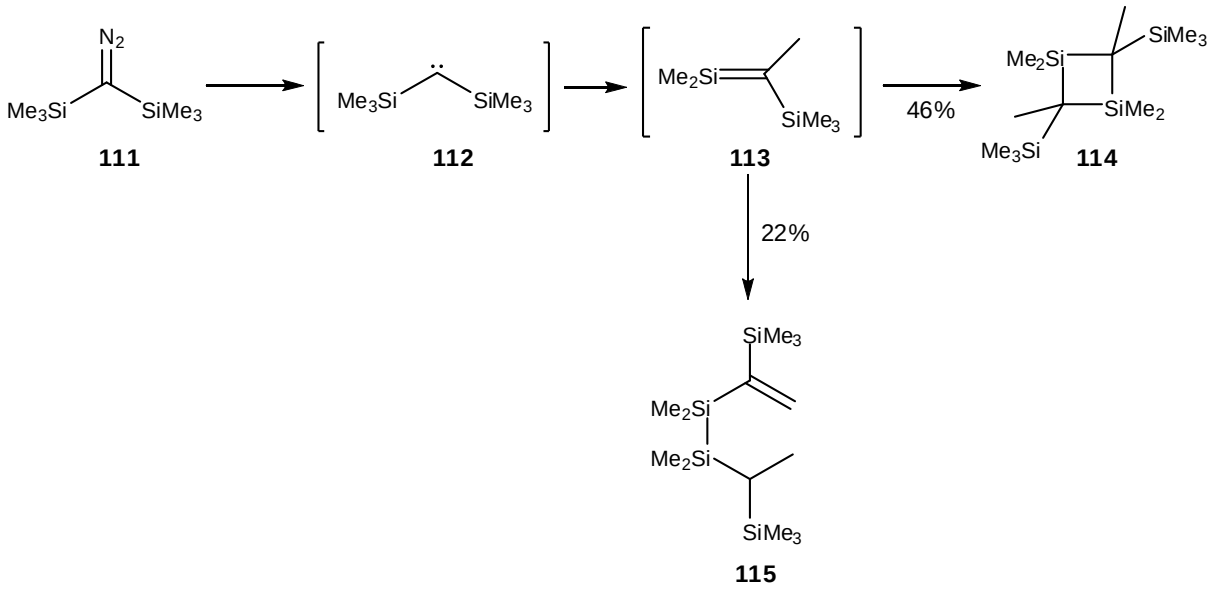
Scheme 23

Maas has further shown the fate of acylsilene **108** depends on the nature of the substituents (Scheme 24). Bulky substituents, such as 1-adamantyl or *tert*-butyl, yield the 1,2-silaoxetanes of type **106**, while acylsilenes with less sterically demanding substituents preferentially undergo dimerisation, to form 8-membered heterocycles of general type **109**.[53,57,58] In some cases, the rearrangement of acylsilene **108** to a silylketene **110** has been observed.[53]



Scheme 24

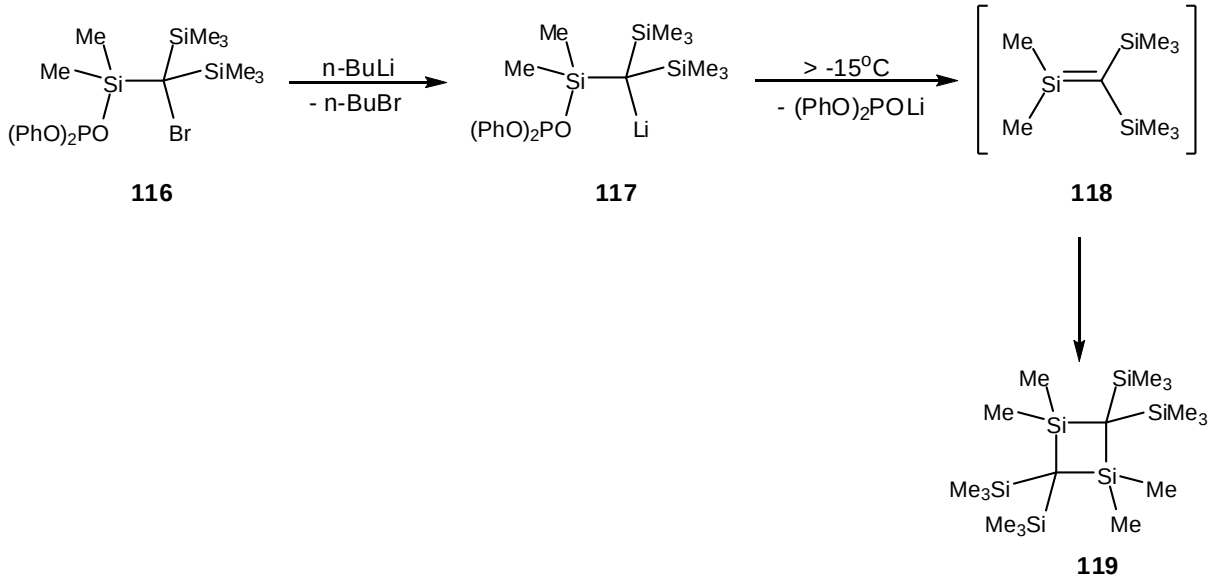
Barton showed that photolysis or thermolysis of bis(trimethylsilyl)diazomethane **111** cleanly affords silene products **113**. The reaction proceeds via the formation of an intermediate α-silylcarbene **112**, which then rearranges to give the silene.[59] In the absence of any trapping agent intermediate silene was found to form dimer **114** and ene product **115** (Scheme 25).



Scheme 25

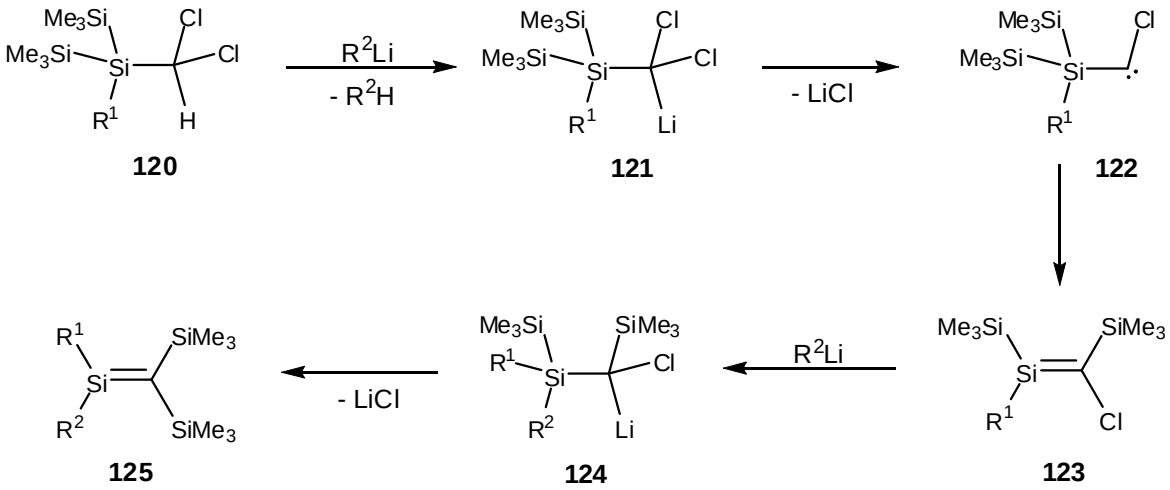
1.3.3.4 Elimination Techniques

Another approach to silenes is based on a salt elimination reaction. This technique was developed by Wiberg in 1977 and enables the synthesis of silenes under very mild conditions (Scheme 26).[60] Treatment of the bromosilane **116** with *n*-BuLi leads to the formation of intermediate silyllithium **117**, which undergoes salt elimination to furnish the silene **118**. In the absence of trapping agents silene **118** forms head to tail dimer **119**. This method was applied by Wiberg to generate stable silenes that cannot be formed thermally or photochemically.[61,62]



Scheme 26

Similarly, Oehme synthesised various stable silenes by employing similar methodology (Scheme 27).[63] When germinal dichloroalkylsilanes **120** are treated with alkyl lithium reagents, a deprotonation reaction produces a lithium carbenoid species **121**, with a metal atom and halogen attached to the same carbon atom. Lithium carbenoids are stable at very low temperatures, but under the reaction conditions they decompose to silylcarbenes **122**. Migration of one trimethylsilyl group from the central silicon atom to the carbene carbon atom affords intermediate silenes **123**. In the presence of a second equivalent of organolithium reagent silene **125** is formed.



Scheme 27

To conclude, the drive to develop new silene generation techniques has provided a great deal of information regarding their reactivity. These multiple bonded species are particularly susceptible to attack by nucleophiles, alkenes, alkynes and ketones. The general reactivity of silenes will be discussed in the next section.

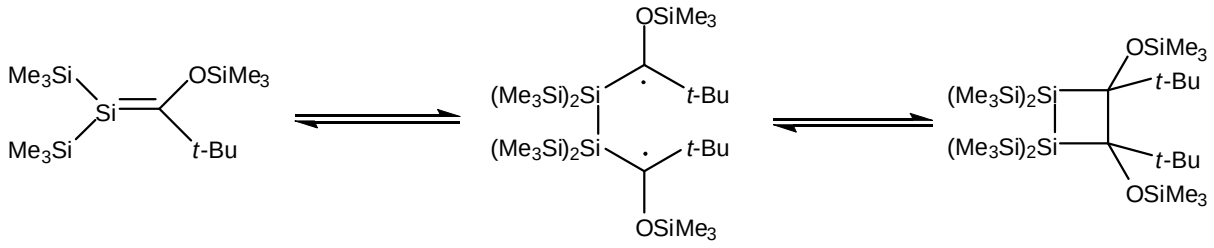
1.4 Reactions of Silenes

1.4.1 Dimerisation Reactions

Most silenes are highly reactive molecules at ambient conditions and, in contrast to alkenes, they often dimerise in the absence of trapping agents. As a result, isolation of dimerised products is usually taken as evidence for the formation of the corresponding intermediate silene.

Silenes usually dimerise to disilacyclobutanes in either a head-to-head or head-to-tail manner, depending on the nature of the substituents. Naturally polarised silenes that contain less bulky substituents at the Si and C atoms tend to form head to tail dimers. For example, Gusel'nikow observed such a dimer in the gas phase thermolysis of 1,1-dimethyl-1-silacyclobutane **47** (Section 1.3.1, Scheme 13).[26]

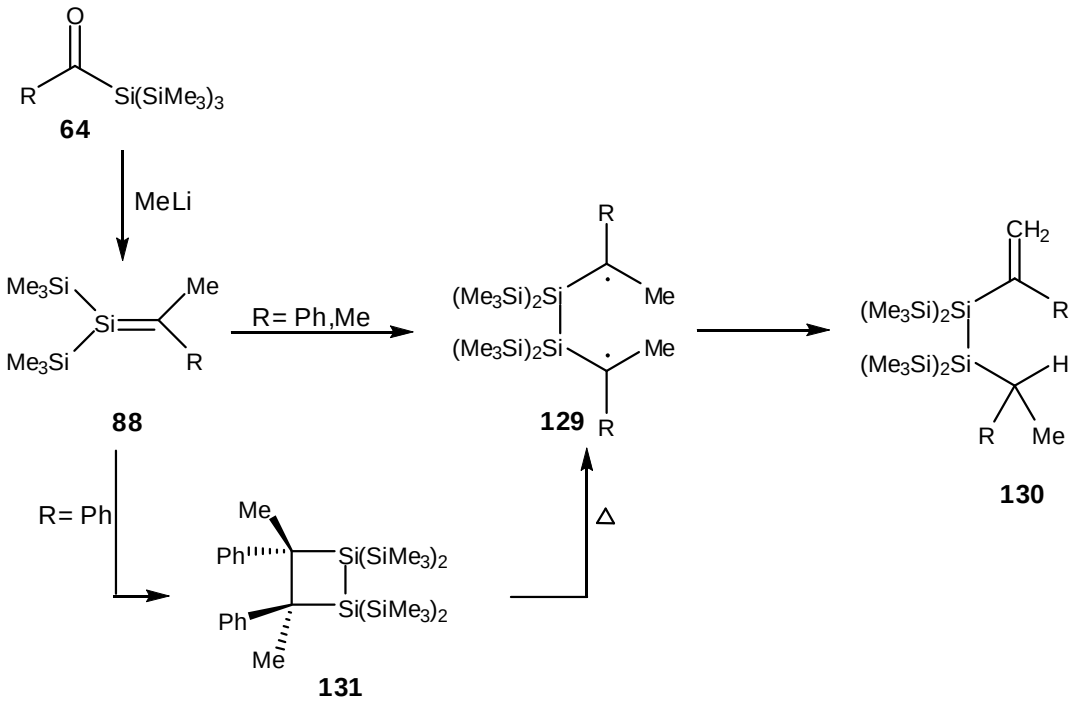
In contrast, Brook-type silenes generally undergo head-to-head dimerisation via a biradical intermediate (Scheme 28).[64] For example, photolysis of pivaloyltris(trimethylsilyl)silane gave the silene **126**, which exists in solution in equilibrium with its dimer **128**. The existence of biradical intermediate **127** is supported by the presence of a signal in the ESR spectrum. However, all attempts to trap this intermediate were unsuccessful.



126 **127** **128**

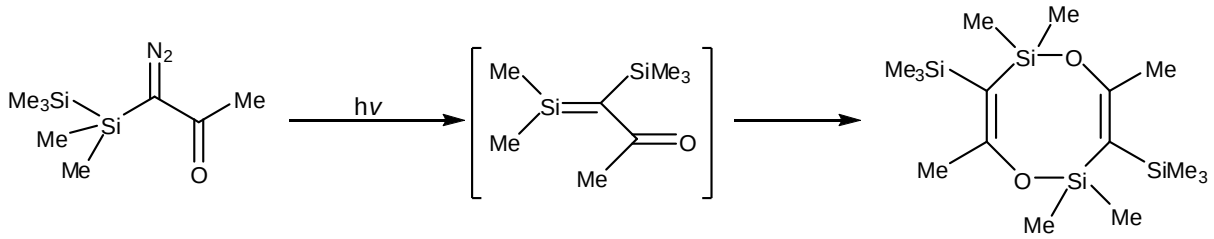
Scheme 28

Head to head dimerisation has also been observed by Ishikawa with silenes generated via a modified Peterson reaction.[45] However, the reaction of acetyltris(trimethylsilyl)silane **64** with methyllithium gave the linear dimer **130** as the major product (Scheme 29). The head-to-head dimer **131**, formed as the minor product, underwent isomerisation to the linear dimer upon thermolysis in a sealed tube.



Scheme 29

Dimers of different types have been observed by Maas and co-workers when forming acylsilenes from α-diazo-α-silyl carbonyl compounds. For instance, photolysis of the diazo compound **132** yielded the [4+4] adduct **134** which was characterised by X-ray analysis (Scheme 30).[58] However, acylsilenes with sterically more demanding substituents undergo intramolecular [2+2] cyclisation leading to 1,2-silaoxetanes.[58]



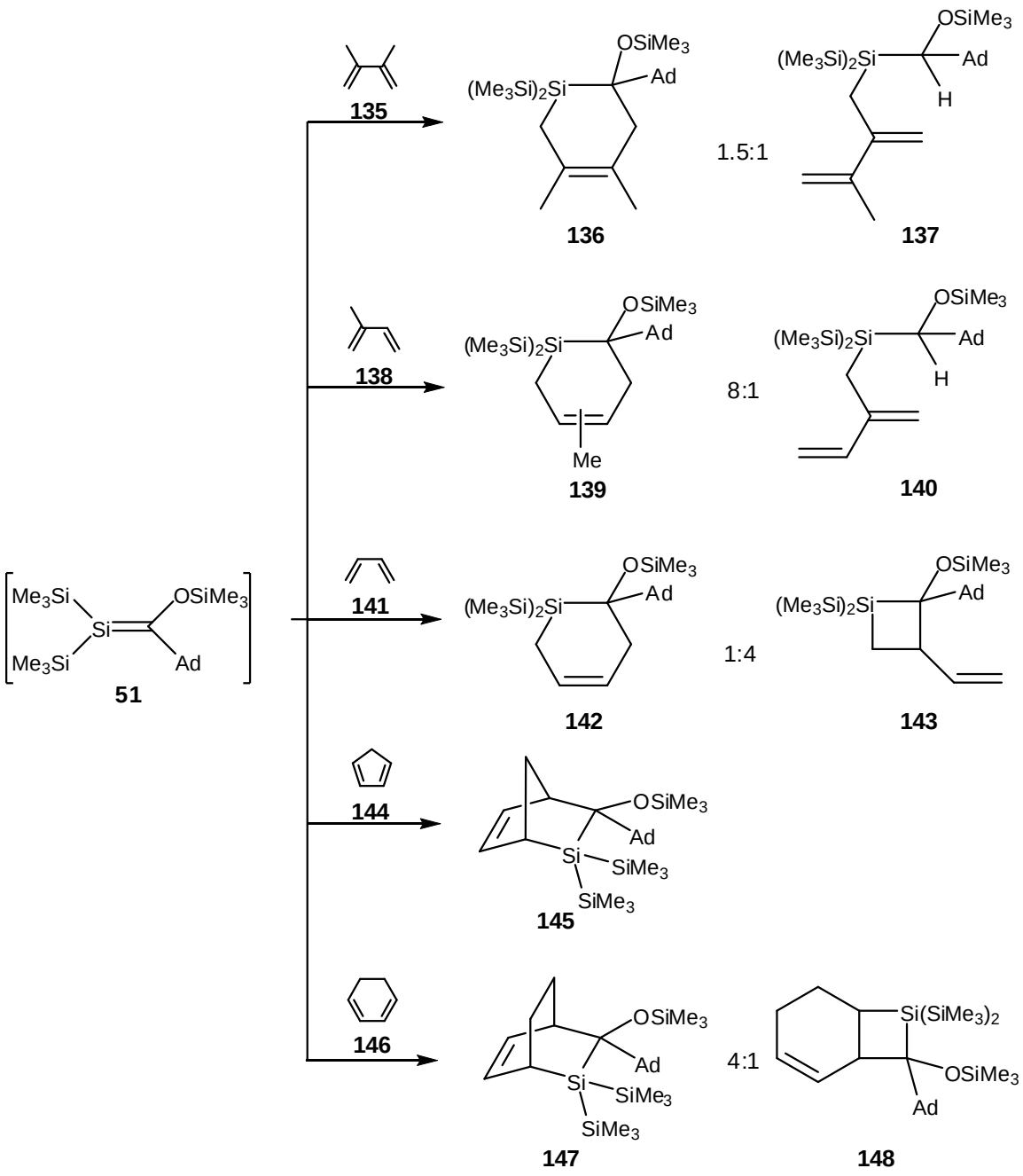
132 **133** **134**

Scheme 30

1.4.2 [4+2] Cycloaddition Reactions

Reactions of a variety of silenes with dienes and alkenes have been studied to prove their existence. Silenes normally form mixtures of [4+2] cycloaddition products and 'ene' products, occasionally accompanied by [2+2] products. The 'ene' products are the usual products from reactions with simple alkenes.

The reactions of stable silenes with dienes under photochemical conditions have been studied in detail by Brook.[64] It has been found that a [4+2] cycloaddition reaction predominated in the reactions of isoprene, 1,3-cyclohexadiene and 2,3-dimethylbutadiene with silene **51** (Scheme 31). In the case of cyclopentadiene only a single [4+2] adduct **145** was formed with 95% yield.



Scheme 31

In contrast, the thermolytic process appears to be more selective. For example, Griffiths has shown that heating a toluene solution of phenyl(trimethylsilyl)silane and a diene afforded the [4+2] silacycloadducts, whilst any [2+2] or 'ene' product could not be detected (Table 3).[65]

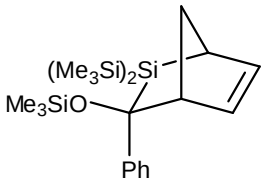
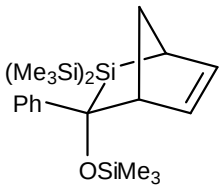
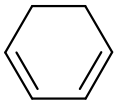
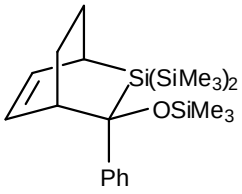
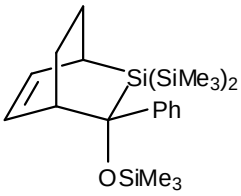
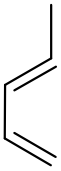
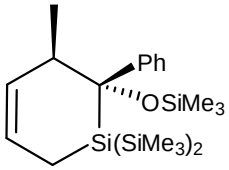
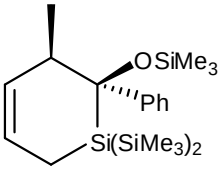
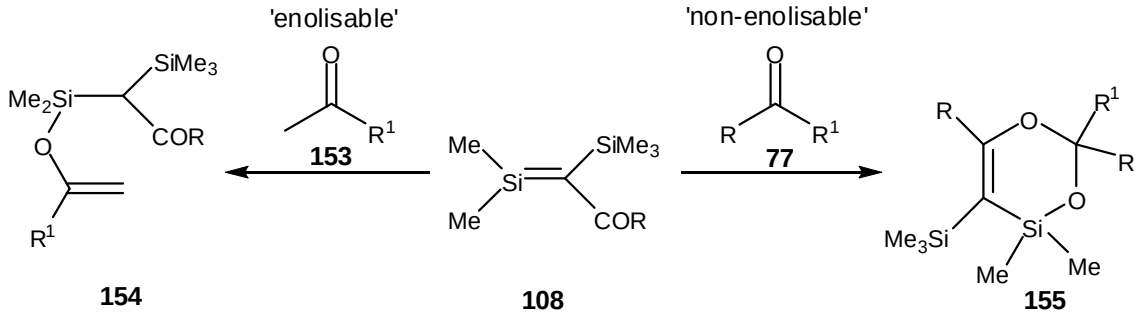
entry	diene	conditions	products		
1	 **144**	toluene 175 °C, 3 h	 **149a**	3:1 91%	 **149b**
2	 **146**	toluene 180 °C, 2 h	 **150a**	3:1 64%	 **150b**
3	 **151**	toluene 180 °C, 2 h	 **152a**	5.7:1 62%	 **152b**

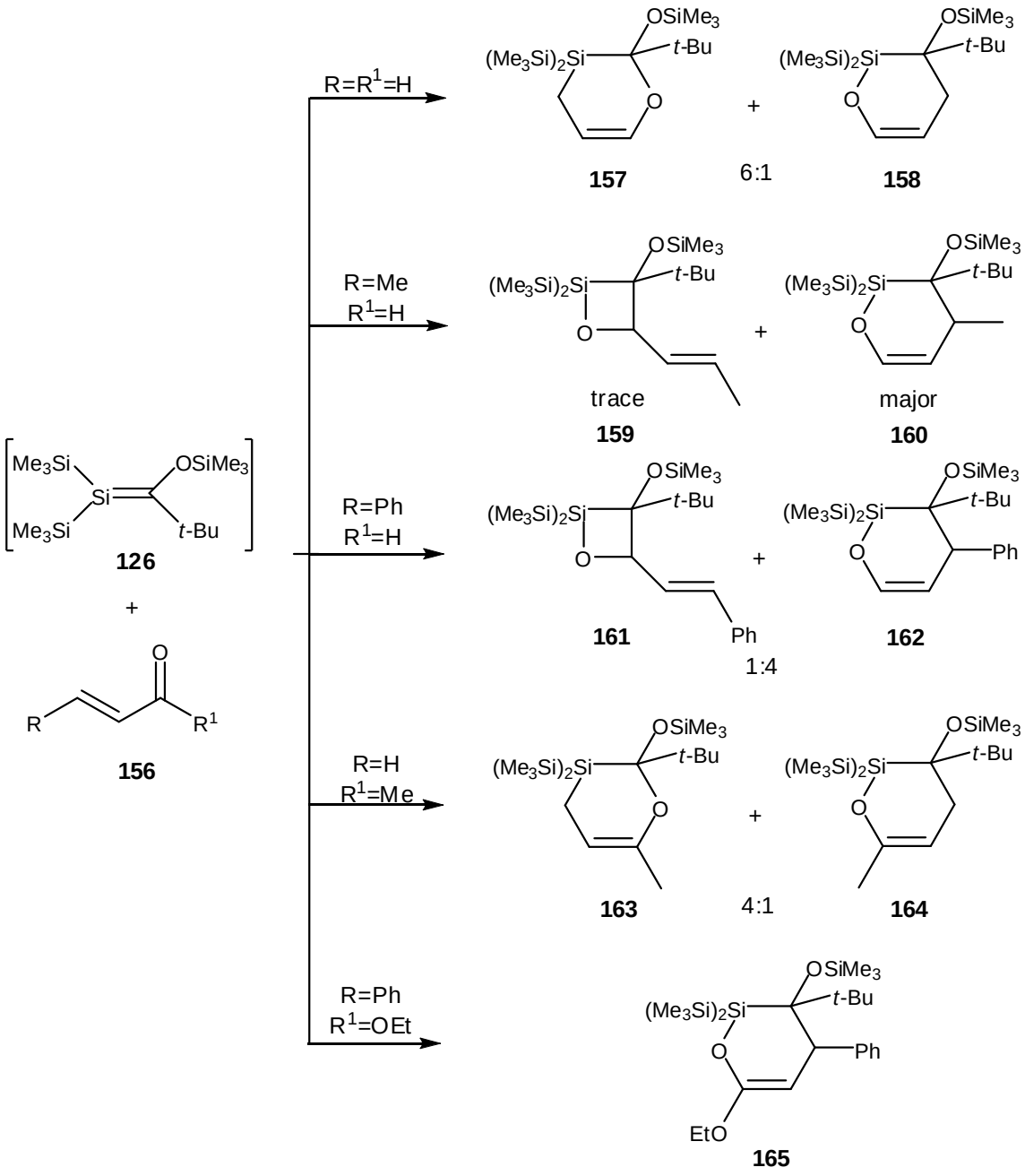
Table 3

Maas and co-workers have reported the formation of [4+2] cycloadducts during the photolysis of diazo ketones.[66] The acyl silenes **108** generated in this fashion reacted with non-enolisable carbonyl compounds such as benzophenone and crotonaldehyde forming 1,3-dioxa-4-sila-5-cyclohexanes **155**. In contrast, when **108** was reacted with enolisable ketones such as acetone, acetophenone and acetylacetone the corresponding 'ene' product **154** was generated (Scheme 32).



Scheme 32

Brook and co-workers have demonstrated that α,ß-unsaturated aldehydes, ketones and esters usually react in a [4+2] manner with silenes (Scheme 32).[67]



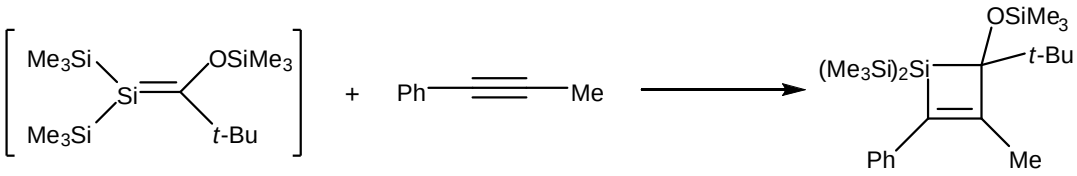
Scheme 33

The regiochemistry of the addition reaction of a silicon-carbon double bond to an α,ß-unsaturated aldehyde, ketone or ester[68] is sensitive to the nature of substituents on the conjugated system. In terms of frontier orbital theory, Fleming has shown that the energetically favoured pathway for cycloadditions involves the interaction of the LUMO of the heterodiene with the HOMO of the dienophile.[69] The regiochemistry of the cyclisation is

directed by the dominant interaction of the frontier orbitals having the larger coefficient, which are located on the β carbon of α,β-unsaturated compound and the silicon atom of the silene.[35] However, when β-substituents are present on an α,β-unsaturated compound, the coefficients of the atomic orbitals will be altered and steric interactions will be introduced.

1.4.3 [2+2] Cycloaddition Reactions

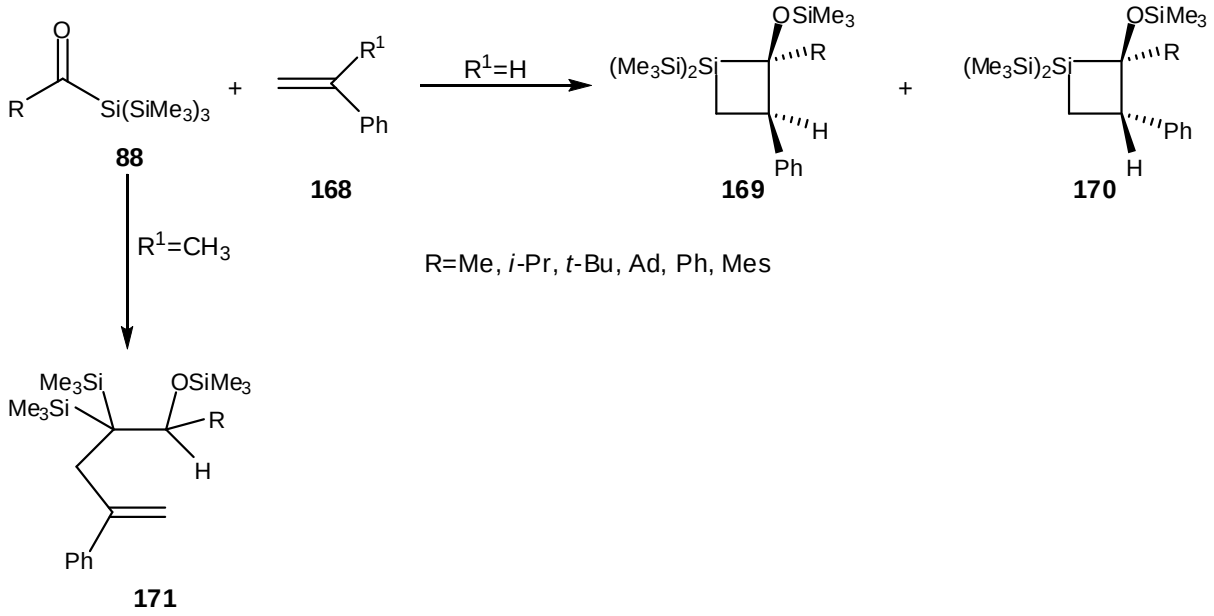
In general, cycloaddition of alkynes to silenes to afford silacyclobutenes proceeds cleanly and in high yields and consequently alkynes have been widely utilised as reliable trapping reagents. Brook has shown that silenes formed by photolysis of acylpolysilanes can be trapped using phenylpropyne (Scheme 34).[37,70]



126 **166** **167**

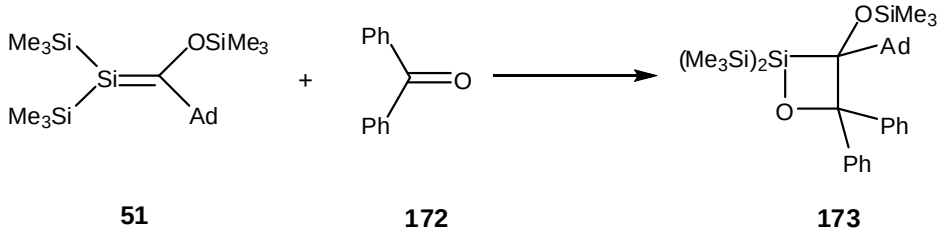
Scheme 34

Similarly, the reaction of alkenes with no α-proton and silenes usually gives the expected [2+2] product. For example, Ishikawa and co-workers examined the chemical behaviour of silenes towards styrenes.[71] They found that thermolysis of acyltris(trimethylsilyl)silane **88** (R = Me, *i*-Pr, *t*-Bu, Ad) in the presence of styrene gave [2+2] cycloadducts **169** and **170** in moderate yield. Interestingly, the reaction of acylpolysilanes bearing an aryl group on the carbonyl carbon (R= Ph, Mes) yielded only the *cis* product **169**. This is a marked contrast to α-methylstyrenes bearing an allylic hydrogen, which have been shown to give exclusively 'ene' products **171** (Scheme 35).



Scheme 35

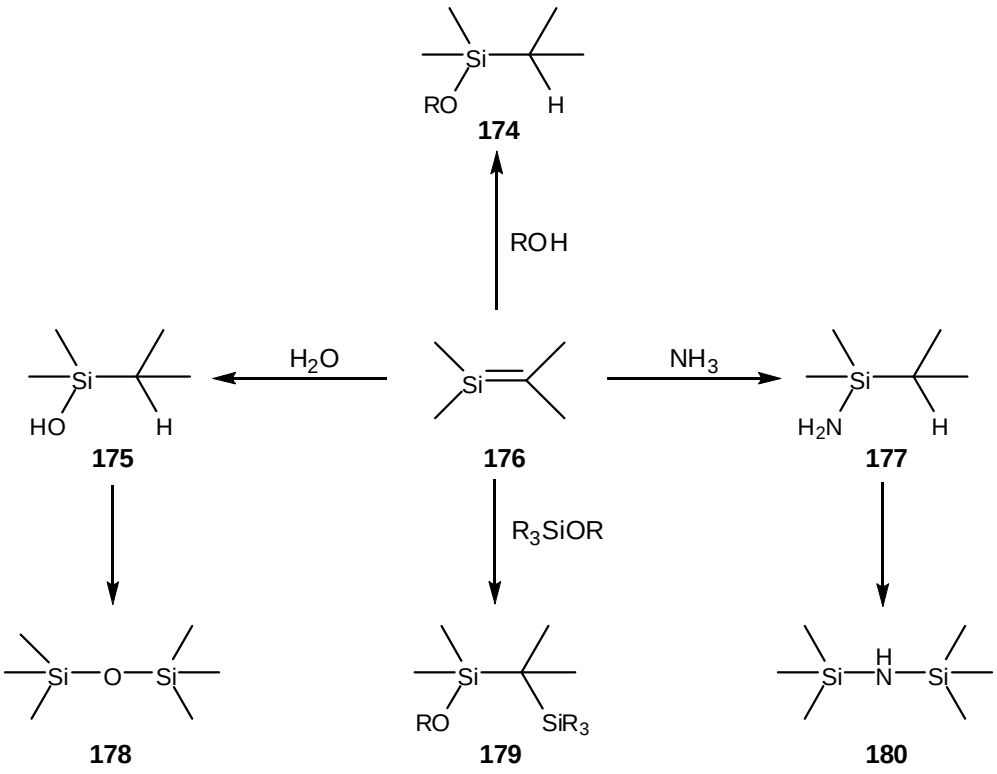
It has also been shown by Brook that silenes undergo [2+2] cycloadditions with nonenolisable carbonyl compounds.[72] Such reactions generate 1,2-siloxetanes which often undergo cycloreversion or complex rearrangements. However, the reaction of adamantylsilene **51** with benzophenone **172** gave the stable [2+2] cycloadduct **173** which could be characterised by X-ray crystallographic analysis (Scheme 36).



Scheme 36

1.4.4 Reaction of silenes with nucleophiles

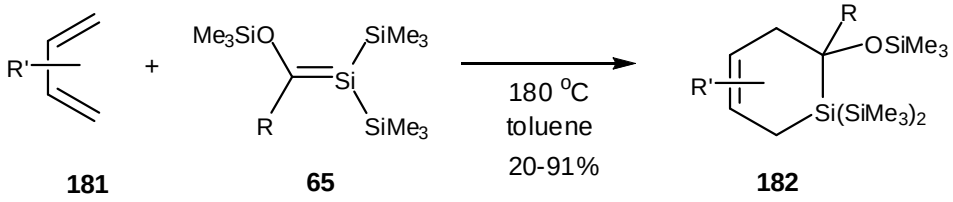
Silenes are potent electrophiles, reacting rapidly with a variety of nucleophiles such as alcohols, water, amines, carboxylic acids, and alkoxysilenes by 1,2-addition (Scheme 37).[73,74] The regioselectivity of the addition is a result of the polarisation of the silene $Si^{\delta+} = C^{\delta-}$ that allows for nucleophilic attack to occur at silicon. In particular, the reaction with alcohols is often used to trap transient silenes, providing evidence for their existence.



Scheme 37

1.5 Previous Work in the Group

Studies in the Steel group over the past few years have focused on developing silene cycloaddition chemistry to provide a novel strategy for the functionalisation of dienes. Griffiths showed that silenes **65** generated thermally from acylpolysilanes react with dienes **181** to afford [4+2] silacycloadducts **182** in good yield (Scheme 38).[75]

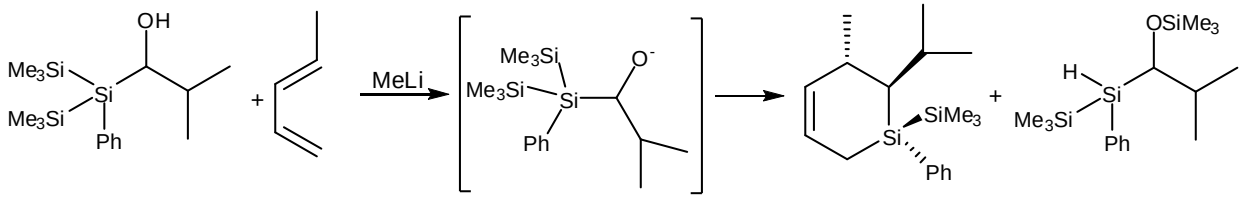


R= Ph, 4-$MeOC_6H_4$, 4-$CF_3C_6H_4$, 2,6-$(MeO)_2C_6H_4$, CH_3, *t*-Bu

diene: cyclopentadiene, isoprene, (*E*)-penta-1,3-diene

Scheme 38

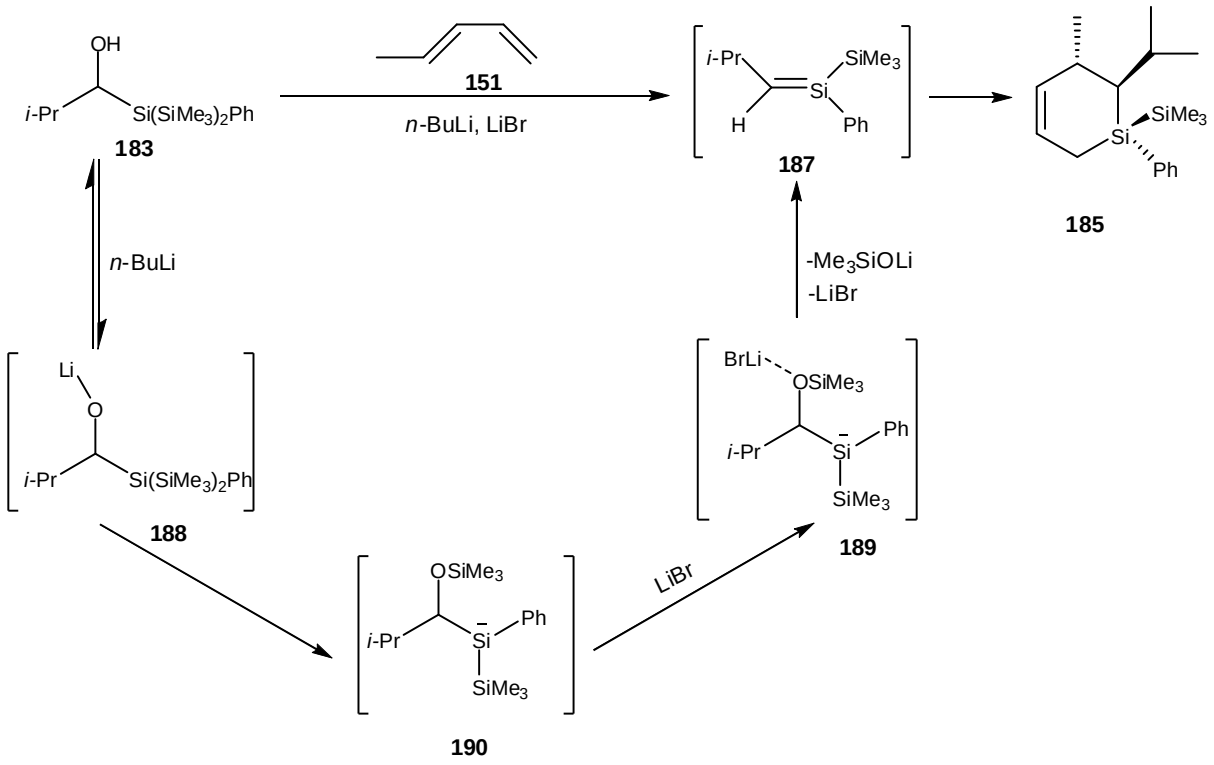
However, there was little effect on the diastereoselectivity of the cycloaddition reactions upon varying the substituents on the silene. Later work therefore focused on the synthesis of silenes via the modified Peterson reaction developed by Oehme.[76] The reaction proceeds through the elimination of -$OSiMe_3$ from the silyl-α-oxyanion **184** driving the generation of the transient silene. In the presence of 1,3-pentadiene **151** the reaction gave silacycle **185** in 52% yield (Scheme 39).[75] The use of this strategy also established a phenyl group on the central silicon atom of the silacycle, which was required to achieve the oxidative subsequent fragmentation.[77]



183 **151** **184** **185** **186**

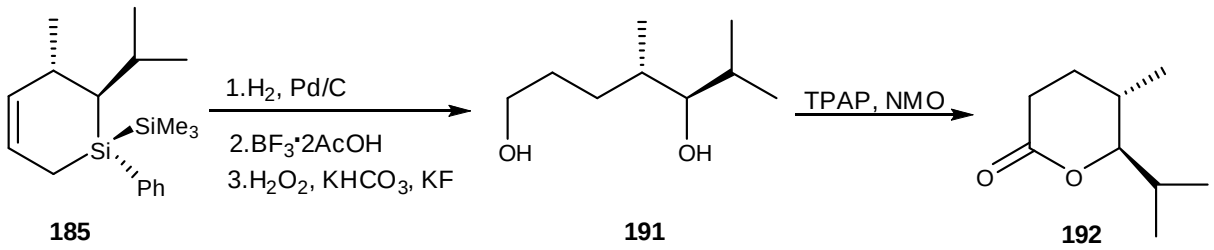
Scheme 39

Unfortunately, the reaction with methyllithium did not give reproducible results, whilst the use of other bases, such as NaH and *n*-BuLi led to the preferential formation of the silane **186**. To explain this observation Whelligan undertook a detailed analysis of the process. It was found that commercial ethereal methyllithium contains varying amounts of LiBr (≤6%), whereas other bases such as *n*-BuLi do not. A thorough investigation into the addition of lithium salts to the reaction mixture discovered that treatment of silyl alcohol **183** with *n*-BuLi in the presence of a catalytic amount of LiBr afforded the silacycle **185** in 50% yield (Scheme 40).[75]



Scheme 40

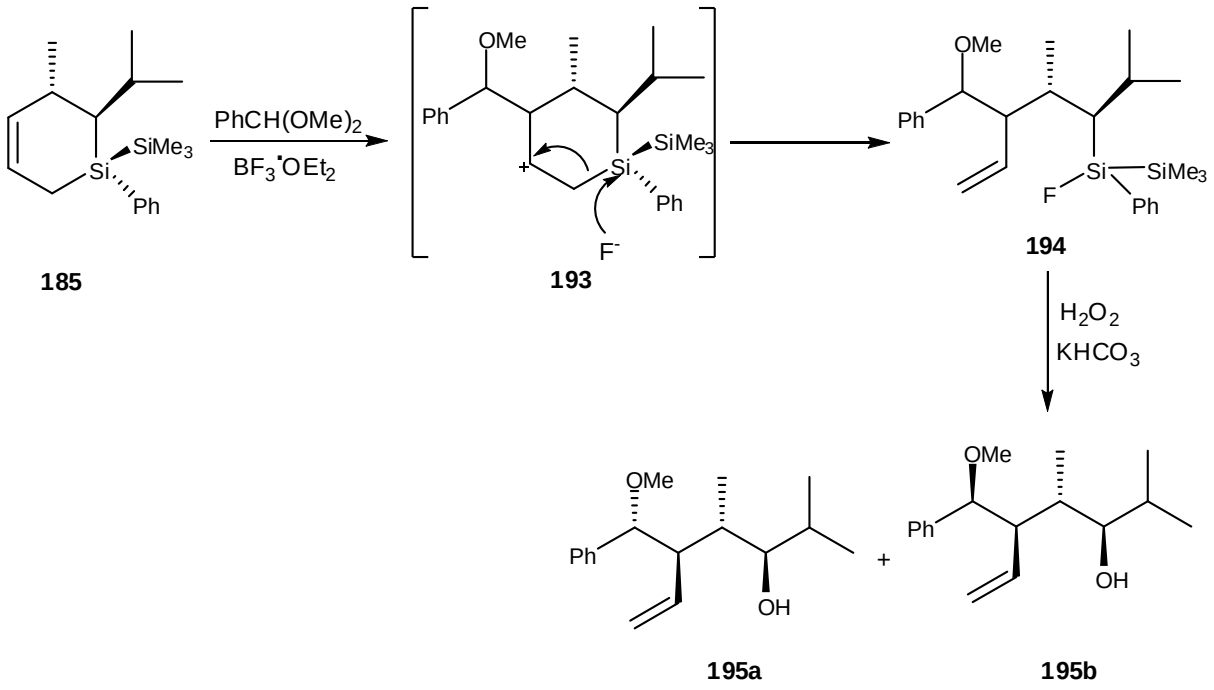
Subsequently, Whelligan utilising this methodology demonstrated that silenes can be used as novel reagents for alkene functionalisation providing stereoselective access to diols and lactones. Following reduction of the double bond, the silacycle **185** was treated with $BF_3 \cdot 2AcOH$ complex to afford the corresponding fluorosilane. The Fleming-Tamao oxidation of the silicon unit with H_2O_2, KF, $KHCO_3$ yielded the diol **191** in 43% yield. Further oxidation using TPAP, NMO produced the lactone **192** as a 98:2 mixture of diastereoisomers (Scheme 41).[78,77]



Scheme 41

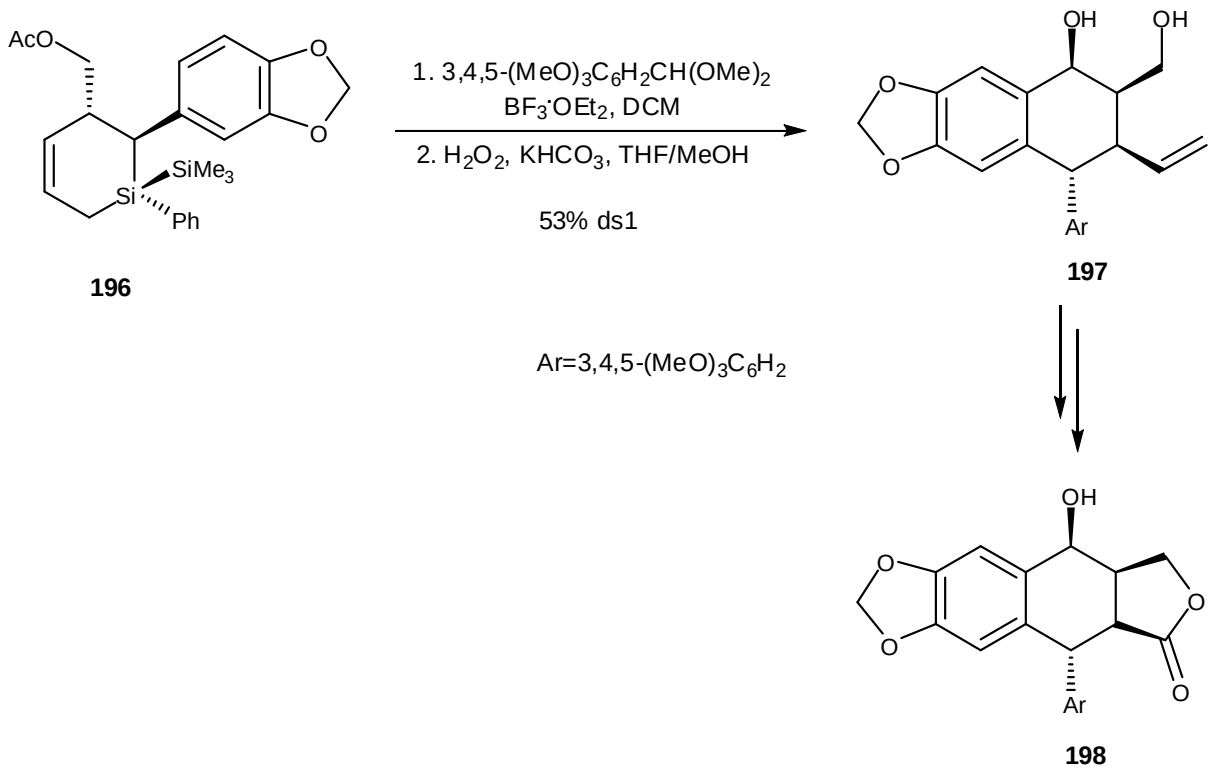
More recently, Sellars has shown that these silene-diene cycloadducts represent convenient sources of silacyclic allylsilanes which can undergo Hosomi-Sakurai reactions.[79] The reaction involves the Lewis-acid-promoted addition of allylsilanes **185** to acetals leading to the

formation of a carbocation intermediate **193**, stabilised by the ß-silicon substituent (Scheme 42). The fluoride-promoted fragmentation followed by oxidation with H_2O_2 in the presence of $KHCO_3$ afforded the monoprotected 1,4-diol as a mixture of diastereoisomers **195a** and **195b**.



Scheme 42

This has subsequently been exploited in the synthesis of (±)-*epi*-picropodophyllin **198** (Scheme 43).[80] The key step of the synthesis involves the Hosomi Sakurai reaction with an electron-rich acetal to give substituted aryl tetralol **197** with good diastereoselectivity.

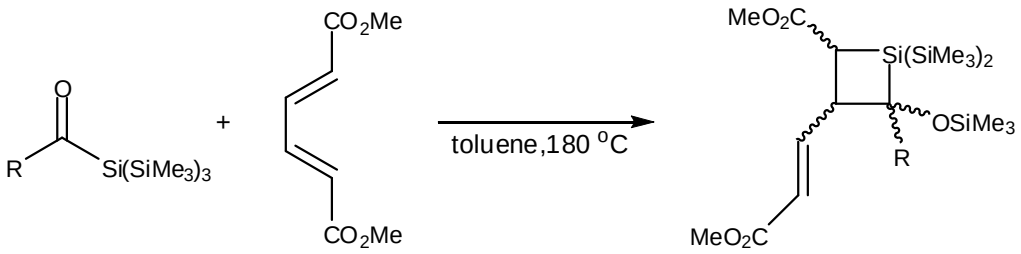


Scheme 43

1.6 Aims of the project

The general aim of this project was concerned with the development of methods for the stereocontrolled functionalisation of alkenes through the reaction with readily accessible silenes and the subsequent elaboration of the resultant adducts. More specifically, the goals were to explore how the diastereoselectivity of cycloaddition varies according to the nature of the silene and silenophile substituents and to develop new more practical and versatile methods for the generation of silenes.

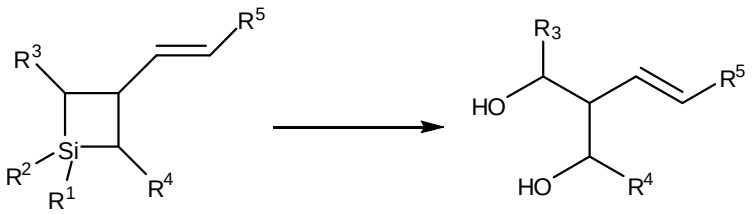
Initial work was focused on the unexpected observation made by Griffiths that alkoxysilenes undergo a very efficient thermal [2+2] cycloaddition with α,β-unsaturated esters to afford highly substituted silacyclobutanes with a high degree of stereocontrol (Scheme 44).[81] Consequently this requires facile access to suitable acylpolysilanes and electron-deficient alkenes.



64 **199** **200**

Scheme 44

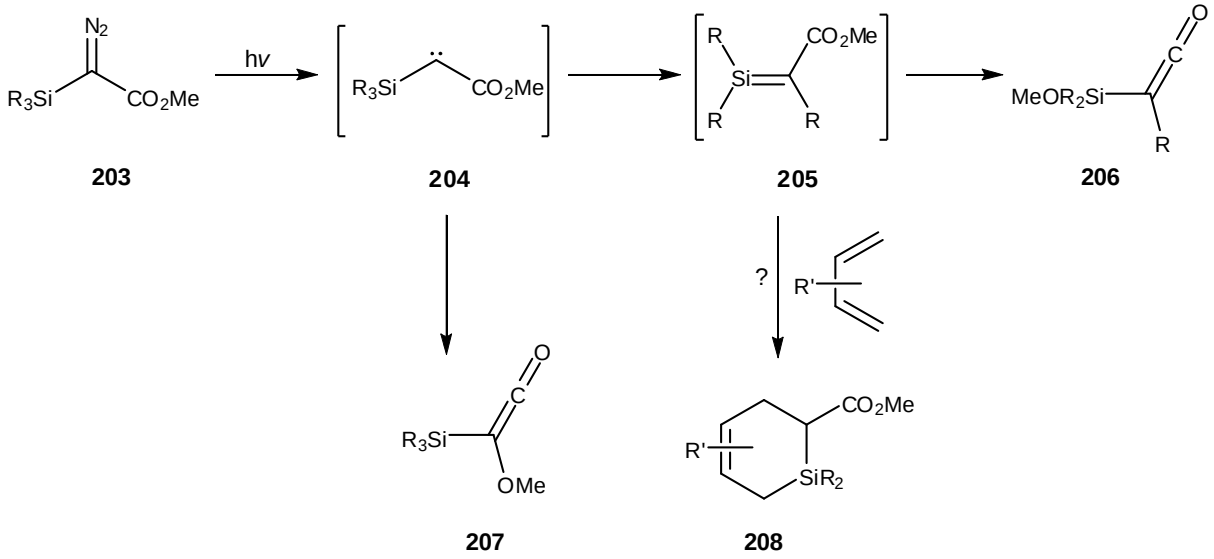
For each cycloadduct strategies for the conversion of these adducts into highly functionalised building blocks were explored (Scheme 45). For example, following the initial activation of the silicon moiety by treatment with HBF_4, direct oxidative cleavage of the silicon carbon bonds could lead to highly functionalised diols **202**.



201 **202**

Scheme 45

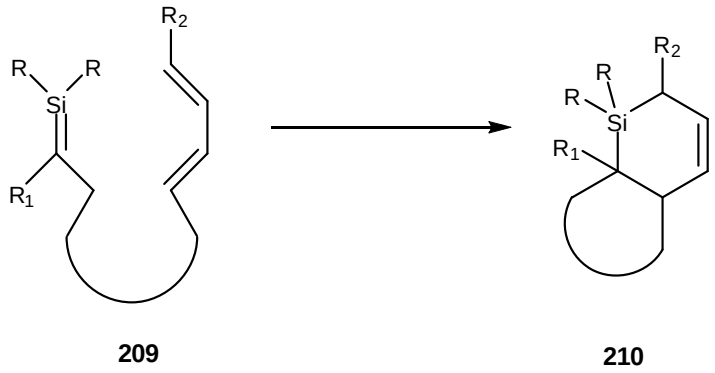
In an alternative approach towards milder silene generation, the synthetic potential of α-silyl diazo carbonyl compounds as silene precursors was examined. These compounds undergo photolytic or thermolytic decomposition to provide intermediate carbene species **204**, which then rearrange to give the silene **205** (Scheme 46).[48]



Scheme 46

The principal goal was to identify what types of substituents are needed in order to achieve increased stability of the intermediate silene **205**.

Finally intramolecular silene cycloaddition reactions were studied (Scheme 47). Surprisingly, such intramolecular reactions had not been explored in silene chemistry. Hence, the studies were focused on the investigation of synthetic as well as theoretical aspects of these reactions. For example, the preferred orientation of diene attack onto silene could be probed through variations in tether lengths and substituents on silicon.

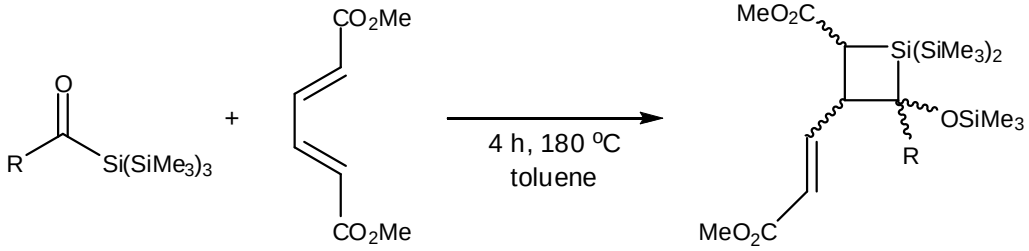


Scheme 47

2 Reaction of acylpolysilanes with electron-deficient alkenes

2.1 Introduction

As described in Section 1.7 of the previous chapter, initial work commenced in the area of [2+2] cycloaddition chemistry and focused on the observation made by Griffiths that alkoxysilenes undergo thermal [2+2] cycloaddition with (2*E*,4*E*)-dimethyl hexa-2,4-dienedioate to afford highly substituted silacyclobutanes (Table 4).[81] Interestingly, these adducts are formed as single stereoisomers, although the stereochemistry was not assigned.



entry	acylpolysilane	R	product	yield (%)
1	**211**	Ph	**212**	67
2	**213**	4-MeOAr	**214**	49
3	**215**	4-CF_3Ar	**216**	49
4	**217**	*t*-Bu	**218**	20

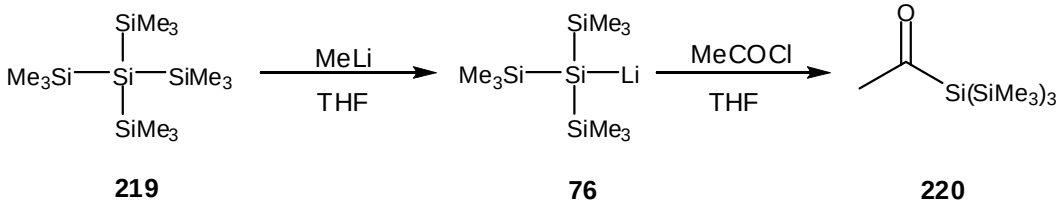
Table 4

Following Griffith's preliminary results in this area, the effect upon the diastereoselectivity of these cycloadditions, and variation of the silene/diene substituents were investigated. Consequently, this required facile access to suitable acyltris(trimethylsilyl)silanes.

2.2 Generation of acyltris(trimethylsilyl)silanes

In previous work, Griffiths[81] had generated acylpolysilanes by the treatment of tetrakis(trimethylsilyl)silane with methyllithium following a procedure outlined by Gilman.[82] Following this protocol, a solution of tetrakis(trimethylsilyl)silane **219** in THF was treated with methyllithium (Scheme 48). After approximately 24 h, ^{1}H NMR spectroscopic analysis showed a signal that corresponded to unreacted tetrakis(trimethylsilyl)silane (δ_H 0.20 ppm),

therefore a second portion of methyllithium (0.1 eq) was added and the reaction mixture was stirred for a further 12 h. The reaction mixture was then combined with a solution of acetyl chloride to give acyltris(trimethylsilyl)silane **220** in 32% yield. Unfortunately, the product was observed to decompose upon storage for a long period of time.

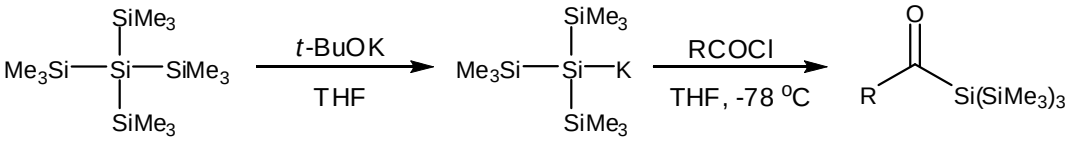


219 **76** **220**

Scheme 48

Evidence confirming the formation of **220** was obtained from the ^{13}C NMR spectrum, which showed the appearance of a characteristic signal at δ_C = 245 ppm, attributed to the carbonyl carbon. The significant downfield shift is due to the effect of the silyl groups attached to the carbonyl carbon.

The low yield was consistent with the earlier observation within the group, which indicated that this methodology does not give reproducible results, yields often ranging from 30 to 90%.[81] Similar observations have been made by Brook and co-workers.[83] This problem appears to be associated with many contributing factors, such as the quality of the methyllithium, the purity of the starting material, and the quality and dryness of the solvents. One possible solution is to isolate the silyllithium reagent as a crystalline solid ($(Me_3Si)_3SiLi \cdot 3THF$) and then perform the condensation reaction in a non-polar solvent which leads to fewer side reactions and generally leads to acylpolysilanes in better yields.[83] Although this represents a potential solution, a simple alternative was suggested from the work of Marschner, who had described the formation of silylpotassium reagents through the reaction of polysilanes with potassium *tert*-butoxide in THF or DME.[84] Following the procedure developed by Marschner, silylpotassium reagent **221** was generated in THF by the reaction of pre-dried potassium *tert*-butoxide and tetrakis(trimethylsilyl)silane. The solution of **221** was then combined with the appropriate acid chloride to give the desired acyltris(trimethylsilyl)silanes **211**, **213**, **217** and **222** (Table 5).

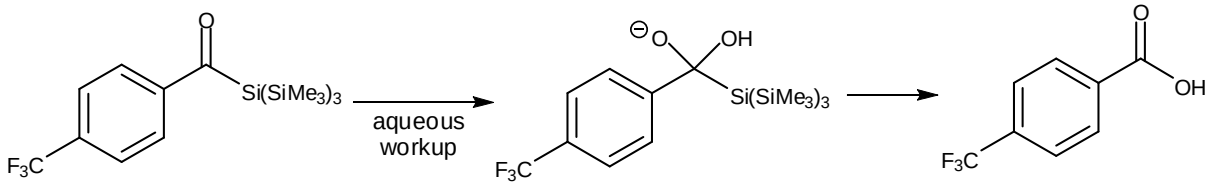


219 **221**

entry	product	R	yield (%)	C=O δ_C (ppm)
1	**211**	Ph	69	236
2	**213**	4-$MeOC_6H_4$	27	233
3	**215**	4-$CF_3C_6H_4$	58	237
4	**217**	*t*-Bu	85	248
5	**222**	2-furyl	36	223

Table 5

Whilst good yields could be obtained for most examples, it was observed that trifluoromethylphenyl analogue **215** decomposed during the aqueous workup. It was speculated that the presence of an electron-withdrawing group in the *para* position increases the electrophilicity of the carbonyl group and hence promotes hydrolysis of the product (Scheme 49). Fortunately, this could be avoided by simply eliminating the quenching stage from the procedure.

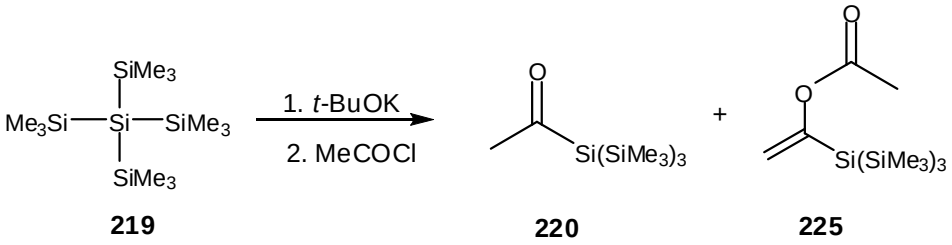


215 **223** **224**

Scheme 49

As before, evidence for the formation of acylpolysilanes was confirmed by the ^{13}C NMR spectrum with the signal at δ_C = 220-250 ppm corresponding to the carbonyl group.

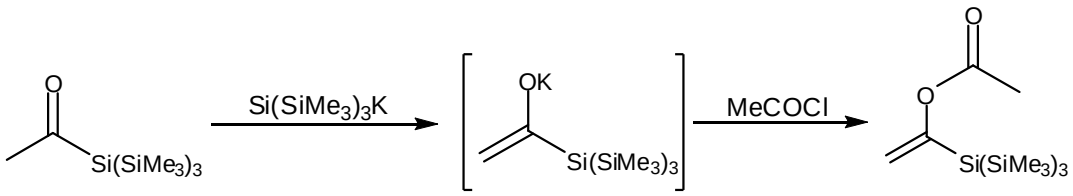
The same procedure was then used to make acetyl(tristrimethylsilyl)silane **220** (Scheme 50). Unfortunately, this yielded an inseparable mixture of acylpolysilane **220** and enol-ester **225** in a 1:3.7 ratio as determined by ^1H NMR spectroscopy. Formation of the latter product was confirmed by analysis of the ^1H NMR spectrum and MS data, which showed signals at δ_H = 5.46 ppm and δ_H = 5.21 ppm corresponding to the vinyl protons coupled with a *m/z* = 332 (M^+). All attempts to hydrolyse the enol-ester by treatment of the mixture containing **220** and **225** with base or acid were unsuccessful.



219 **220** **225**

Scheme 50

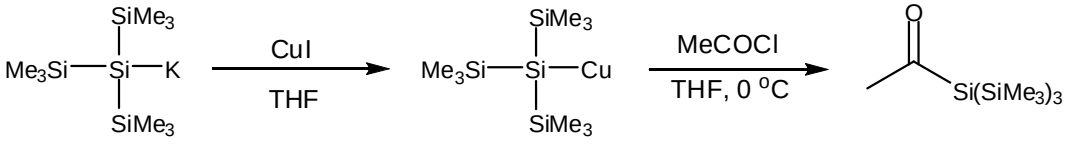
The above result indicates that the problem lies in the silylpotassium reagent, which is sufficiently basic to deprotonate acylpolysilane **220** (Scheme 51). The resulting potassium enolate reacts with acetyl chloride to form enol ester **225**.



220 **226** **225**

Scheme 51

To circumvent the problem of enolisation, silylpotassium reagent **221** was transmetalated with CuI (Scheme 52). This was considered to have occurred on the observation of a colour change of the orange silylpotassium solution to black and formation of a precipitate. The solution of silylcopper species **227** was then combined with acetyl chloride to give the desired product **220** in 50% yield.

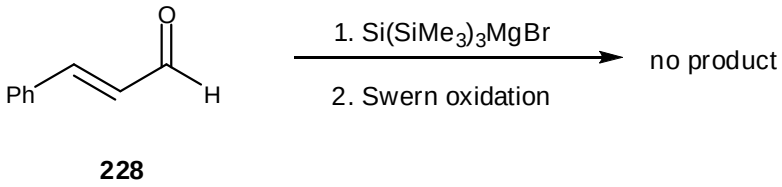


221 **227** **220** 50%

Scheme 52

Whilst the Marschner procedure ensures the synthesis of the acylpolysilanes **211**, **213**, **215**, **217**, **220** and **222** attempts to extend this to analogues derived from 4-nitrobenzoyl chloride, picolinoyl chloride, cinnamoyl chloride and (*E*)-but-2-enoyl chloride were not productive. Similarly, an alternative two-step protocol involving addition of the corresponding

silylmagnesium species to the aldehyde **228** and subsequent oxidation failed to produce the desired acylpolysilane (Scheme 53).



228

Scheme 53

2.3 Preliminary results

2.3.1 Introduction

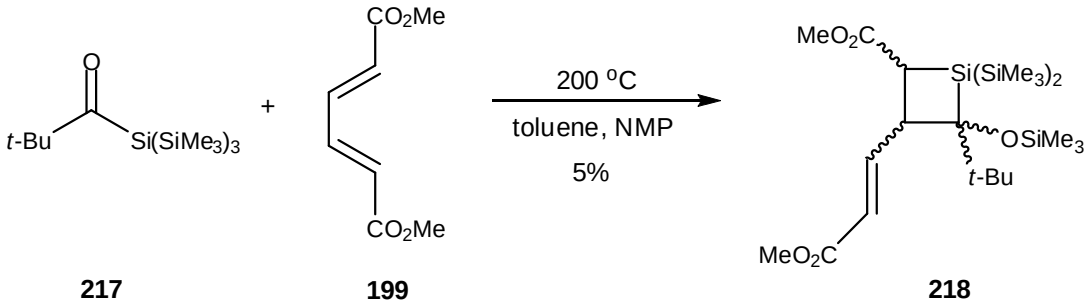
With a range of acylpolysilanes in hand, attention then turned to their reactions with electron-deficient alkenes. In his earlier studies Griffiths synthesised [2+2] cycloadducts using a sealed tube technique. The major disadvantages of this approach, however, are the time-consuming process of sample preparation and the hazard associated with heating a sealed vessel. Therefore a preliminary study was undertaken to ascertain the use of microwave irradiation in this respect. Recent developments in this field have suggested that microwave-assisted chemistry could be used in most reactions that require heating.[85] This technique has shown broad applications as a very efficient way to accelerate the course of many reactions often by orders of magnitude, producing high yields and higher selectivity, lower quantities of side products and, consequently, easier work-up and purification of the products.[86]

2.3.2 Reaction of pivaloylpolysilane with electron-deficient dienes

As mentioned in Section 2.1 of this chapter, the cycloaddition reactions reported by Griffiths were performed in toluene, which is microwave transparent. Therefore, in the initial experiments described below NMP was used as a polar additive to increase the microwave absorbance of the sample.

A solution of acylpolysilane **217** and diene **199** (2 eq) in a mixture of toluene and NMP (2ml, 9:1 v/v) was heated in a microwave reactor at 200 ^{o}C for 1.5 h (Scheme 54). Concentration,

followed by flash column chromatography afforded the product **218** in very low yield (5%), with a significant amount of impurities also observed.

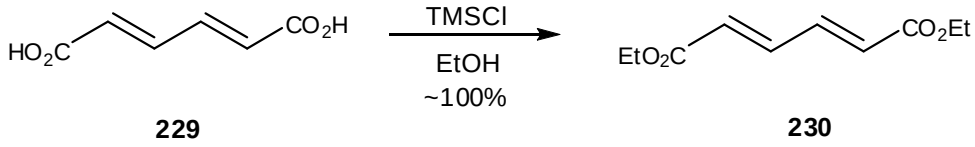


217 **199** **218**

Scheme 54

All spectroscopic data were consistent with those reported by Griffiths[81] providing evidence for the formation of the cycloaddition product **218**.

A major problem with this reaction was that compound **199** was not very soluble in non-polar solvents such as benzene and toluene, which are required for the synthesis of cycloadducts and may account for the poor yield. The trapping of silenes in a [2+2] cycloaddition reaction would be expected to proceed in higher yield if the concentration of the diene in solution was higher. Therefore, the more soluble (2*E*,4*E*)-diethyl hexa-2,4-dienedioate **230** was prepared by reaction of *trans*,*trans*-muconic acid **229** with ethanol in the presence of TMSCl (Scheme 55).[87]



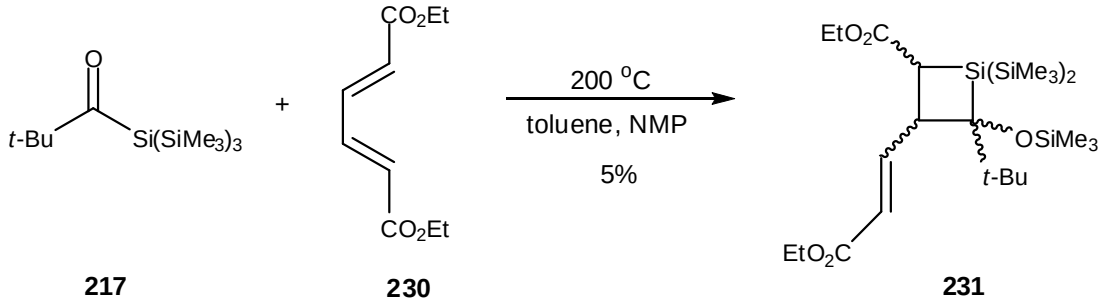
229 **230**

Scheme 55

Evidence for the formation of the ester was obtained from the ^{1}H NMR spectrum. Compound **230** shows characteristic signals corresponding to the olefinic protons at δ_H = 7.33-7.29 ppm and δ_H = 6.21-6.18 ppm and also signals attributed to the ethoxy protons at δ_H = 4.24 ppm and δ_H = 1.31 ppm.

With the more soluble diene **230** in hand, the microwave protocol was repeated. Silane **217** was dissolved in a mixture of toluene and NMP (2ml, 9:1 v/v), in the presence of a twofold excess of diene **230**. The mixture was heated at 200 ^{o}C for 1.5 h. Concentration, followed by

flash column chromatography afforded the product **231**, unfortunately also in a low yield (Scheme 56).



217 **230** **231**

Scheme 56

The spectroscopic data were similar to those reported by Griffiths[81] for compound **218** providing indirect evidence for the formation of the cycloaddition product **231**. Compound **231** shows characteristic signals corresponding to the olefinic protons at δ_H = 7.10 ppm and δ_H = 6.01 ppm and also signals attributed to the ring protons at δ_H = 2.33 ppm and δ_H = 2.31 ppm. In addition, formation of **231** was confirmed by analysis of the mass spectrum, showing *m/z* = 530 (M^+).

In order to improve the yield of the reaction, several experiments were carried out in which the reaction time (0.5 h – 24 h) and temperature (100 °C -220 °C) were varied. Unfortunately, all attempts to efficiently trap the generated silene were unsuccessful. Therefore, attention turned to the use of the sealed tube technique as previously described by Griffiths.[81]

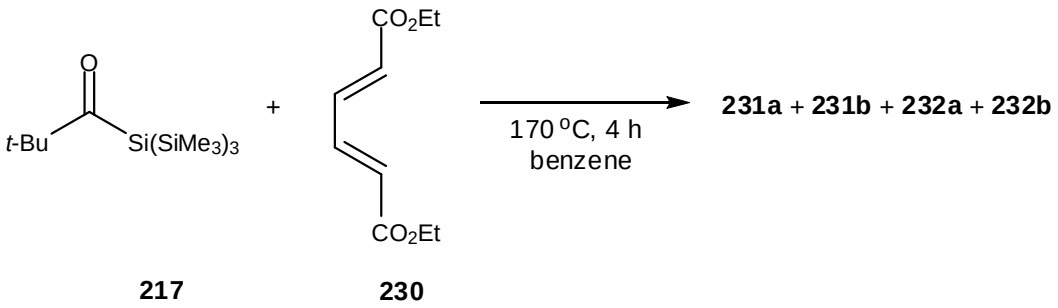
2.4 Thermolysis reactions

2.4.1 Introduction

In the work described below, all reactions were undertaken using similar conditions. A solution of polysilane and diene in dry benzene was prepared in a round-bottom flask and transferred to a Carius tube. The solution was then degassed using the freeze-pump-thaw technique, with a minimum of three cycles. The tube was then sealed and heated in a metal pipe. The resulting mixture was then concentrated, and purified by flash column chromatography. The diastereoselectivities were determined by ^{1}H NMR spectroscopy.

2.4.2 Thermolysis of pivaloylpolysilane with (2*E*,4*E*)-diethyl hexa-2,4-dienedioate

Thermolysis of trimethylacetyltris(trimethylsilyl)silane **217** with diene **230** gave a mixture of four products **231a**, **231b**, **232a** and **232b** (Scheme 57). Concentration, followed by flash column chromatography afforded two inseparable fractions of diastereoisomers **231a** + **231b** (ds 1.5:1) and **232a** + **232b** (ds 2.8:1) in an overall 32% yield.



Scheme 57

Mass spectrometry indicated molecular ions of *m/z* = 530, for all products **231a**, **231b**, **232a** and **232b** supporting the formation of a cycloadduct. Fortunately, product **232a** could be separated by crystallisation as a pure isomer. Recrystallisation from MeCN/$CHCl_3$ gave crystals suitable for X-ray diffraction (Figure 11). This revealed the structure of the adduct **232a** to be the substituted cyclopropane.

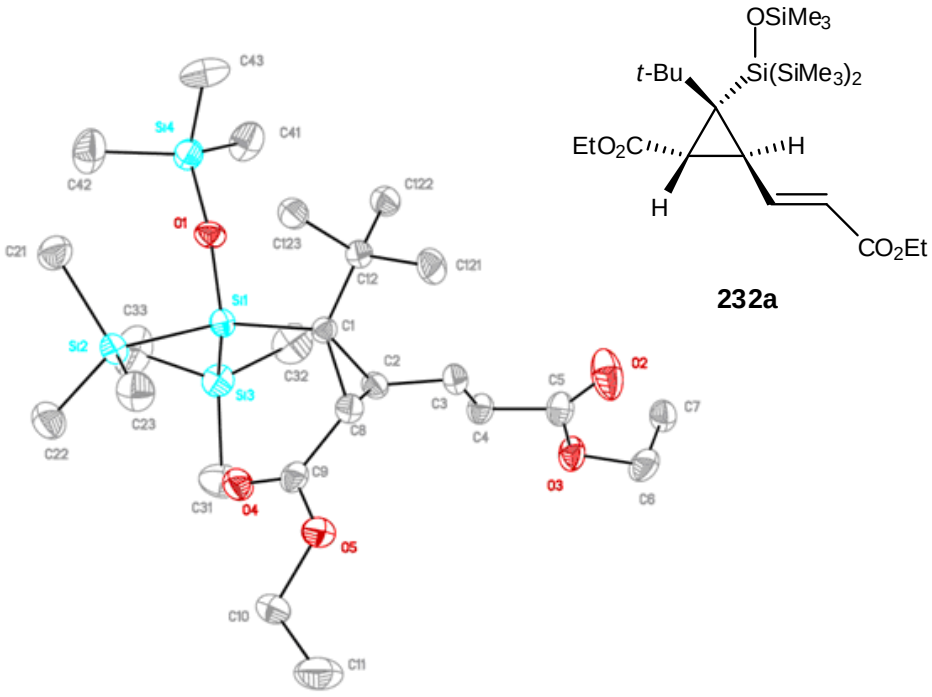
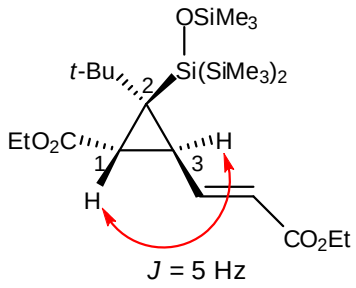


Figure 11

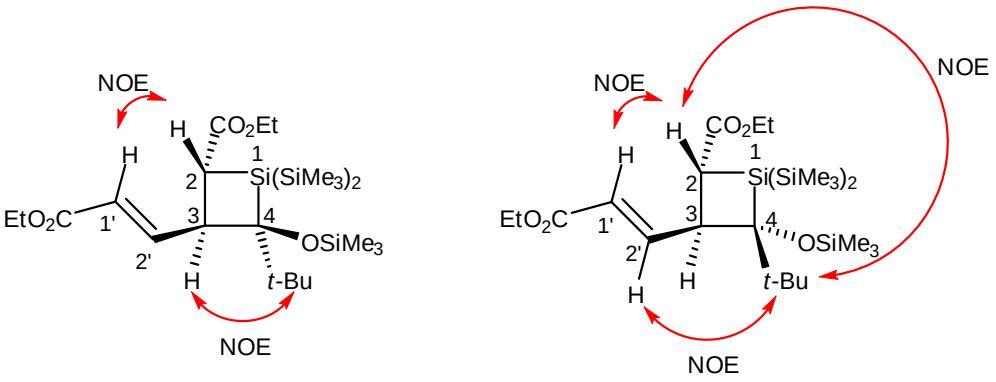
At first this product was surprising, as it was evident that some rearrangement reactions must have taken place. Furthermore, comparison of the product's ^{1}H NMR spectrum with that for compound **232a** indicated that **232b** was also a substituted cyclopropane. The configuration of the minor isomer **232b** was assigned on the basis of the observed coupling constant between 1-***H*** and 3-***H*** in the ^{1}H NMR (J = 5 Hz) spectrum similar to that observed for **232a**. The small vicinal coupling between those two protons indicates a mutual *trans* location and suggested that compound **232b** must have the configuration shown in Figure 12. In comparison, the coupling constant for the *cis* cyclopropanes is much larger (approx J = 8 Hz).[1]



232b

Figure 12

The configuration of the products **231a** and **231b** could be deduced from 2D correlation NMR experiments (Figure 13). The regiochemistry of the cycloaddition was confirmed by HMBC experiments which revealed a 3-bond correlation from proton 2´-***H*** to ring carbon ***C***-4 which confirms the location of the silicon atom to be between the ***C***-2 and ***C***-4 atoms in the ring. The analogous signal is present in the HMBC spectrum for compound **231b**. The stereochemistry of adduct **231a** was elucidated through ^{1}H NOESY experiments, and provided evidence that the *t*-Bu group was located *cis* to the proton 3-***H*** and *trans* to the proton 2-***H***. The ^{1}H NOESY spectrum of the adduct **231b** showed correlation between the *t*-Bu group and 2-***H*** indicating a mutual *cis* relationship.



231a **231b**

Figure 13

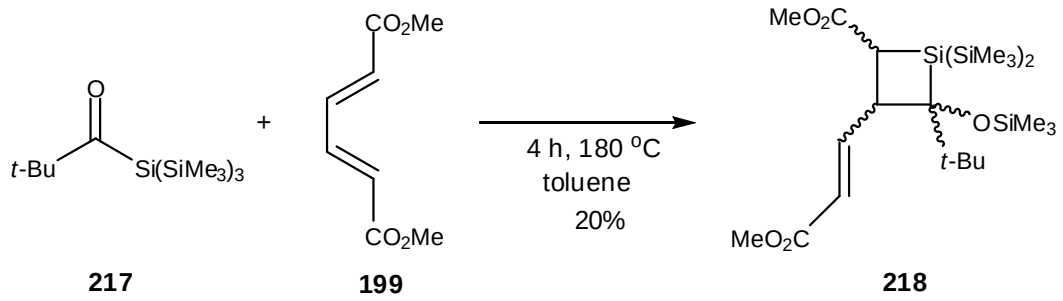
The cyclopropanes generate a characteristic ^{13}C NMR signal at 36-30 ppm that corresponds to ***C***-2. In comparison, the silacyclobutane **231b** shows a characteristic signal for the ring carbon ***C***-4 at 96 ppm, providing an easy method to distinguish between silacyclobutane and cyclopropane compounds.

In order to find optimal conditions for the cycloaddition reaction, several experiments were carried out, varying stoichiometry, time and temperature of the reaction (Table 6). It appears from the data presented in Table 3 that there is little effect upon varying the reaction conditions on the ratio of the products. However, **231b** was only observed when the reaction was performed at lower temperatures (150-170 ^{o}C), indicating its low relative stability. In addition, increasing the time of the reaction generally leads to lower yields, due to broad decomposition of the products. The best conversion was achieved when the reaction was carried out at 200 ^{o}C for 3 h (entry 7).

entry	**temp (^{o}C)**	**time (h)**	**diene (eq)**	**cyclobutane**	**cyclopropane**
				yield (%), ds (231a:231b)	**yield (%), ds (232a:232b)**
1	150	4.5	2.3	15 (1.6:1)	11 (2.3:1)
2	172	2	4	23 (1.5:1)	15 (2.8:1)
3	172	2	3	18 (1.4:1)	12 (3:1)
4	180	4	2	9 (2.9:0)	23 (6.4:1)
5	200	3	0.25	23 (3.9:0)	25 (3.3:1)
6	200	3	1	16 (1.4:0)	41 (2.7:1)
7	200	3	4	23 (1.9:0)	46 (2.7:1)
8	200	4	2	16 (2.2:0)	30 (3.2:1)
9	200	25	2	7 (3.6:0)	15 (6.1:1)

Table 6

In summary, the desired silacyclobutane **231** was synthesised in ≤ 23% yield. Moreover, it was found that simple variations in the time and/or temperature do not lead to increased yields of **231**. The reaction of trimethylacetyltris(trimethylsilyl)silane **217** with diethyl ester **230** at 180 ^{o}C gave a mixture of three products **231a**, **232a** and **232b** (Table 6, entry 4). This contrasts with the earlier reports by Griffiths describing the reaction of trimethylacetyltris(trimethylsilyl)silane **217** with dimethyl ester **199**, which afforded only silacyclobutane **218** (Scheme 58). The reasons for this difference in reaction outcome are not obvious and remain an open question.



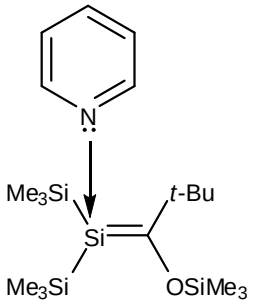
217 **199** **218**

Scheme 58

2.5 Microwave Techniques

2.5.1 Introduction

During work on the [2+2] cycloaddition between silenes and dienes, it was found that when the reaction was carried out in a Carius tube in the presence of NMP, multiple decomposition products were observed. It was therefore suggested that NMP was also the reason for failure of the preliminary microwave experiments (Chapter 2, Section 2.3). This led us to reinvestigate the use of the microwave-based method using alternative microwave absorbers. In the work described in the next paragraph, all reactions were undertaken in the presence of pyridine. It was speculated that pyridine can enhance the stability of the silene by providing an electron pair to stabilise the electrophilic silicon atom (Figure 14).

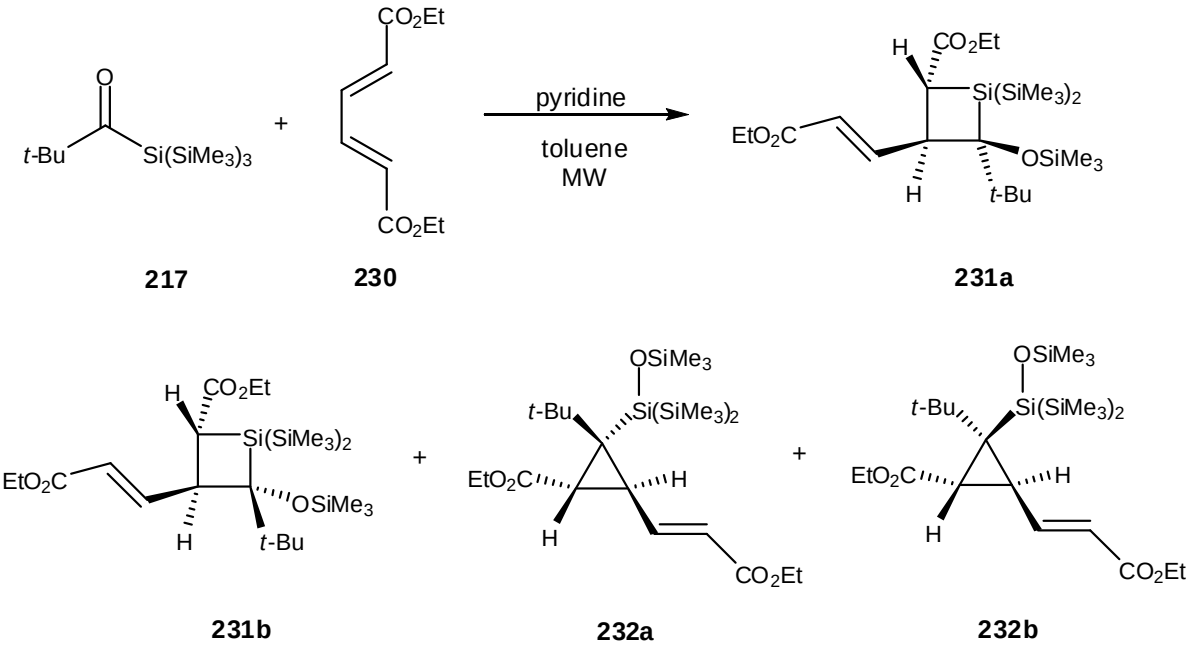


233

Figure 14

2.5.2 Reaction of pivaloylpolysilane with (2*E*,4*E*)-diethyl hexa-2,4-dienedioate

A solution of the trimethylacetyltris(trimethylsilyl)silane **217** and diene **230** in a mixture of toluene and pyridine (3 ml, 1-10% v/v of pyridine) was heated in a sealed microwave tube. The resulting mixture was then concentrated, and purified by flash column chromatography to afford a mixture of **231a**, **231b**, **232a** and **232b** (Scheme 59). The results are summarised in Table 7.



217 **230** **231a**

231b **232a** **232b**

Scheme 59

The data presented in Table 7 indicate that varying the conditions had little effect on the ratio of the products. Surprisingly and in contrast to many silene reactions, it was found that only one equivalent of diene is required to efficiently trap the generated silene when the reaction mixture was heated at 220 ^{o}C for 0.5 h (entry 7).

entry	temp (^{o}C)	time (h)	acylpolysilane (mg)	diene (eq)	pyridine (%)	cyclobutanes yield (%), ds (231a:231b)	cyclopropanes yield (%), ds (232a:232b)
1	160	8	500	1	10	17 (1:0)	33 (3.5:1)
2	160	0.5	100	4	10	6 (1.4:1)	12 (2.8:1)
3	190	4.25	300	2.5	5.5	17 (1:0)	35 (3.3:1)
4	160	0.5	500	4	1	6 (1:1)	6 (3.1:1)
5	190	4.25	300	2.5	5.5	21 (1:0)	41 (2.7:1)
6	220[a]	8	500	4	10	-	5 (5:1)
7	220[a]	0.5	500	1	1	24 (1:0)	38 (3:1)
8	160	8	100	1	1	19 (2.9:1)	28 (2.9:1)
9	220[a]	0.5	500	1	0	23 (1:0)	37 (3.1:1)
10	200[b]	1	250	3	0	7 (3.5:1)	20 (3:1)

[a]A tight seal is required for the microwave tube under these conditions, due to high pressure in the reaction vessel (approx 11 bars). [b]Reaction without solvent.

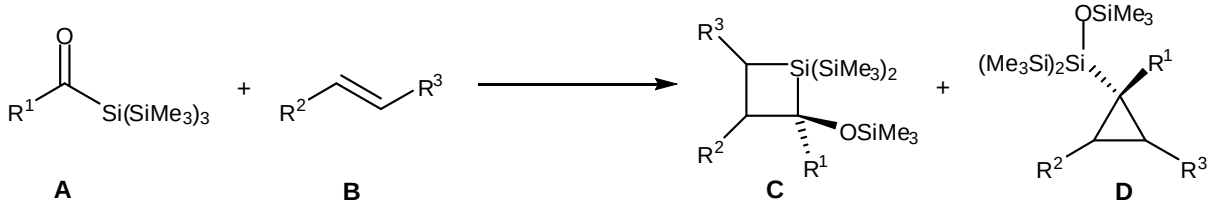
Table 7

Entry 9 shows that the reaction could be performed without addition of pyridine. This suggests that microwaves are efficiently absorbed by the polysilane/diene and that pyridine is not required when the concentration of the reaction mixture is sufficiently high. In addition, this experiment showed that pyridine in not involved in the stabilisation of the intermediate silene since the reaction gave essentially the same yield and ratio of the products (entry 7, 9). Subsequently, it was found that the reaction performed without solvent also leads to the formation of adducts, however in lower yields (entry 10).

The formation of the substituted cyclopropane is an interesting and unusual result. Intrigued by this unusual cyclopropanation reaction it was of interest to examine other electron-deficient silenophiles.

2.6 Reaction of acylpolysilanes with electron-deficient silenophiles

The acylpolysilanes described in Section 2.2 were reacted with electron-deficient silenophiles either in a Carius tube – *method A* or in a microwave reactor – *method B* (Table 8).



A **B** **C** **D**

entry	A		B			method[a]	product, yield (%), ds[b]	
	R^1	No	R^2	R^3	No		C	D
1	*t*-Bu	**217**	CH=CHCO$_2$Et	CO$_2$Et	**230**	A	**231**; 23 (1:0)	**232**; 43 (2.7:1)
2	*t*-Bu	**217**	CO$_2$Me	CO$_2$Me	**234**	A	-	**235**; 33 (1:0)
3	*t*-Bu	**217**	CH=CHMe	CO$_2$Et	**236**	A	-	**237**; 7 (1:0)
4	*t*-Bu	**217**	Ph	CO$_2$Me	**238**	A	-	**239**; 49 (1:0)
5	*t*-Bu	**217**	Ph	NO$_2$	**240**	A	alkene decomposed	
6	*t*-Bu	**217**	Ph	CN	**241**	A	**242**; 11 (7.2:2:1)	**243**; 32 (2.4:2.4:1:1)
7	*t*-Bu	**217**	H	CO$_2$Me	**244**	A	29[c]	
8	Ph	**211**	CH=CHMe	CO$_2$Et	**236**	A	-	**245**; 31 (2.8:1)
9	Ph	**211**	CH=CHCO$_2$Et	CO$_2$Et	**230**	A	-	**246**; 29 (1:0)
10	Ph	**211**	CO$_2$Me	CO$_2$Me	**234**	A	-	**247**; 40 (1:1)
11	Ph	**211**	Ph	CO$_2$Me	**238**	A	-	**248**; 53 (2.1:1)
12	4-MeOC$_6$H$_4$	**213**	CH=CHCO$_2$Et	CO$_2$Et	**230**	A	-	**249**; 16 (1:0)
13	4-MeOC$_6$H$_4$	**213**	Ph	CO$_2$Me	**238**	A	-	**250**; 21 (1:0)
14	Me	**220**	Ph	CO$_2$Me	**238**	A	-	**251**; 24 (1:0)
15	Ph	**211**	Ph	CONH$_2$	**252**	B (90 min)	intractable mixture	
16	4-MeOC$_6$H$_4$	**213**	Ph	CONEt$_2$	**253**	B (5 min)	-	**254**; 77[d] (2.9:1)
17	4-MeOC$_6$H$_4$	**213**	Ph	SO$_2$Ph	**255**	B (5 min)	**256**; 40 (1:1)	-
18	4-MeOC$_6$H$_4$	**213**	Ph	COPh	**257**	B (5 min)	[e]	
19	Ph	**211**	Ph	CO$_2$Me	**238**	B (90 min)	-	**248**; 49 (2.7:1)
20	*t*-Bu	**217**	Ph	CO$_2$Me	**238**	B (240 min)	-	**239**; 42 (1:0)
21	4-CF$_3$C$_6$H$_4$	**215**	Ph	CO$_2$Me	**238**	B (60 min)	-	**258**; 56 (4.9 :1)
22	4-MeOC$_6$H$_4$	**213**	Ph	CO$_2$Me	**238**	B (5 min)	-	**250**; 67 (2:1)
23	2-furyl	**222**	Ph	CO$_2$Me	**238**	B (50 min)	-	**259**; 40 (1:0)
24	Me	**220**	Ph	CO$_2$Me	**238**	B (180 min)	-	**251**; 50 (2.3:1)

[a]*Method A* involved heating a solution of the starting materials in benzene at 200 ^{o}C for 3 h in sealed tube. *Method B* employed the use of microwave radiation to heat a solution of the starting materials in toluene at 180 ^{o}C. In parentheses required time is given to achieve complete conversion of acylpolysilane. [b]Diastereoselectivity of the reaction was determined by ^{1}H NMR spectroscopy. [c]GC-MS showed formation of 12 adducts. [d]Product unstable. [e][4+2] cycloaddition product (Scheme 60).

Table 8

The configurations of the products in the Table 5 were deduced from 2D correlation NMR experiments as described for **231** and **232** previously. In addition, product **239** was crystalline and recrystallisation from MeCN/$CHCl_3$ gave crystals suitable for X-ray diffraction (Figure 15).

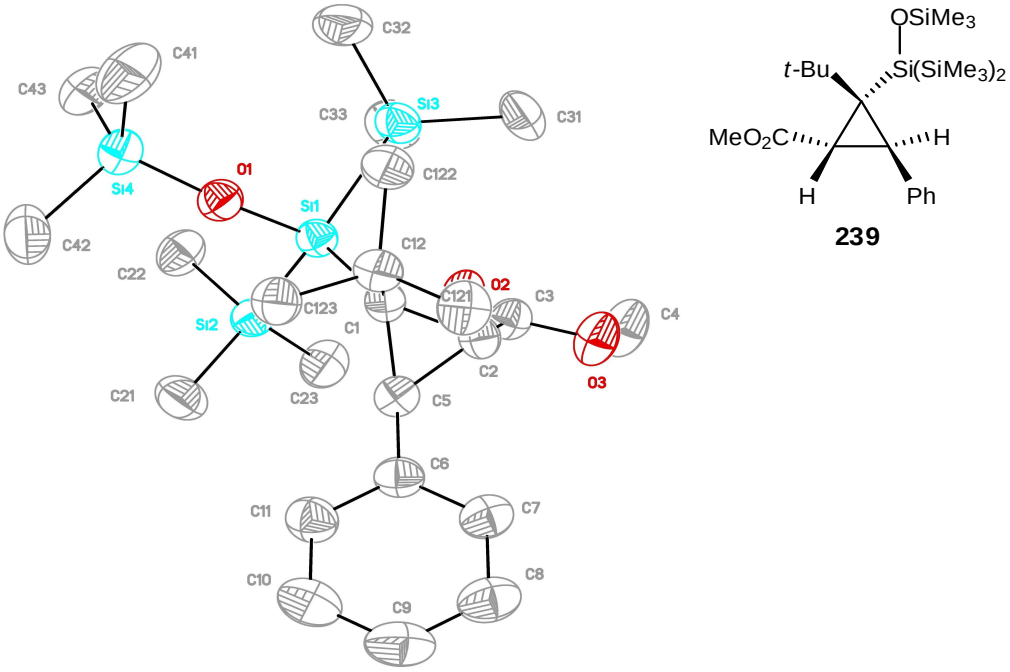
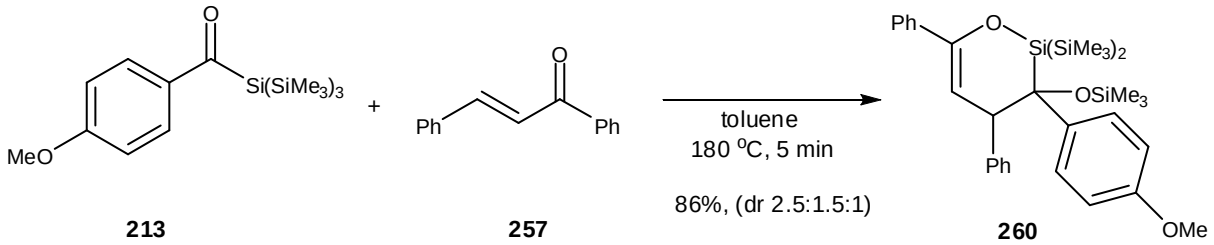


Figure 15

With the exception of phenyl vinyl sulfone (entry 17), which afforded only cyclobutanes, and chalcone **257** (entry 18), all these substrates led to the preferential if not exclusive formation of the cyclopropane. The reaction with chalcone **257** produced the [4+2] adduct **260** in which the α,β-unsaturated enone had behaved as the 4π component (Scheme 60). Whilst this latter outcome is consistent with the earlier reports by Brook describing the reaction of photochemically generated siloxysilenes with enals and enones, the formation of cyclopropanes contrasts with similar studies examining reactions with cinnamate esters.[67] The reasons for this difference in reaction outcome following these two approaches to silene generation are not obvious and still remain an open question.



213 **257** **260**

Scheme 60

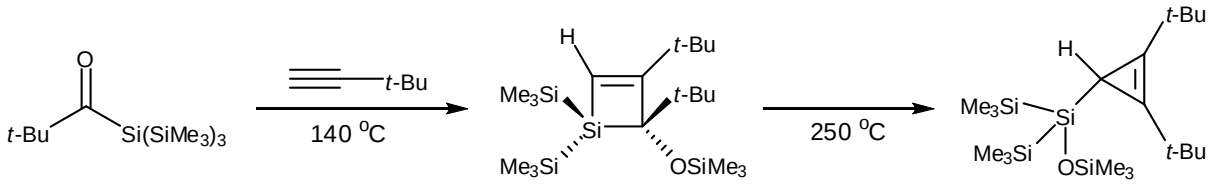
Whilst for the reaction of pivaloyl polysilane and diethyl hexadienoate, it was initially found that by running the reaction at higher temperature (220 ^{o}C) and shorter times (30 min), good yields could be obtained using only one equivalent of the silenophile, the high pressures generated in the tube made it practically difficult to translate this observation to other substrates. However, the use of microwave heating at slightly lower temperatures addressed this issue and using this somewhat operationally simpler protocol, a selection of different acylpolysilanes was reacted with methyl cinnamate as a model silenophile (entries 19-24). In all cases the cyclopropane was the only isolable product with no evidence for silacyclobutane being detected in the crude reaction mixture.

The acylpolysilanes **213** and **215** were synthesised to investigate the effect of electron–donating and withdrawing groups, on the diastereoselectivity. From the results presented in the Table 8 it appears that the presence of an electron-withdrawing group on the acylpolysilane increases the diastereoselectivity in the reaction with methyl cinnamate (entry 21). In addition, the reaction of bulky acylpolysilane **217** with the same ester gave only one diastereoisomer (entry 20). This finding could suggest that steric effects are far more important than electronic. In addition, it was observed that cyclopropane diastereoisomers have different thermal stability and longer reaction times or higher temperatures can increase diastereoselectivity significantly at the cost of yield. Furthermore, it is worth noting that it was not possible to apply one set of reaction conditions to all of the reactions presented in Table 8. For that reason interpretation of the results is more difficult.

2.7 Investigation of the Mechanism

2.7.1 Thermolysis of silacyclobutane

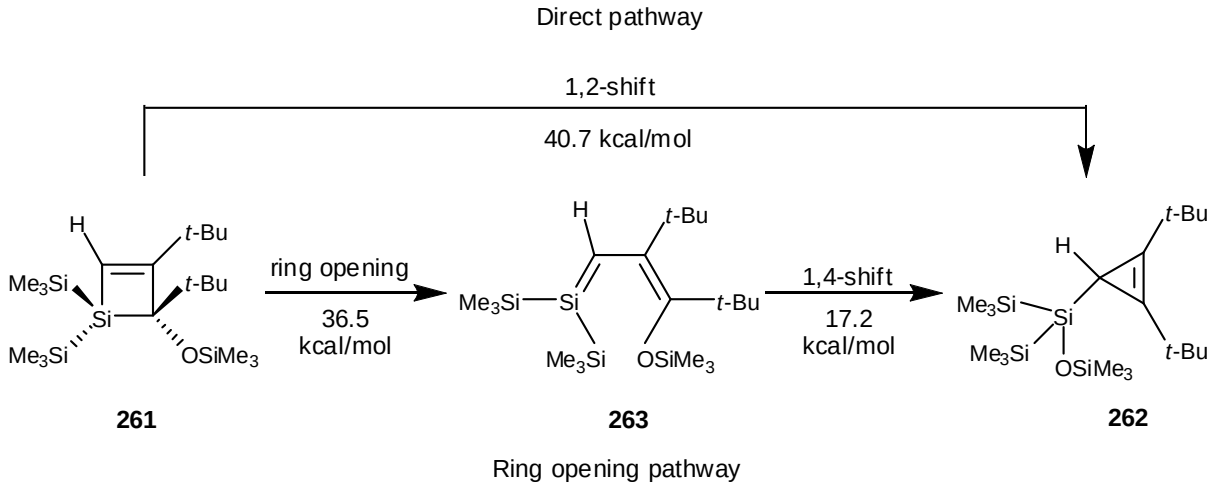
The unusual results of the acylpolysilane reactions prompted further investigations in order to understand the formation of cyclopropanes. It was hypothesised that cyclopropane products are formed by the rearrangement of the intended silacyclobutane products. There are many examples in the literature of thermally or photochemically induced rearrangements of organosilicon compounds.[88,72] Of these, a reaction studied by Ishikawa and co-workers appeared to be the most relevant to these results (Scheme 61).[89] Here, a mixture of pivaloyl polysilane and *tert*-butylacetylene was heated in a sealed tube at 140 ^{o}C for 24 h, to afford cyclobutene **261** in 94% yield. However, when silacyclobutene **261** was heated at 250 ^{o}C cyclopropane **262** was isolated exclusively.



217 **261** **262**

Scheme 61

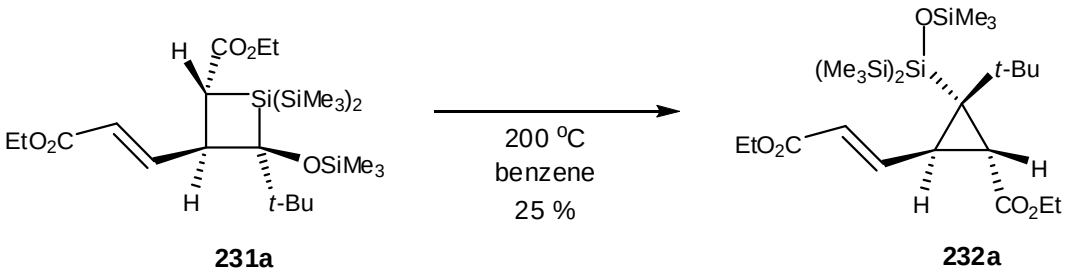
Theoretical studies were carried out to learn more about the isomerisation of silacyclobutene **261** to cyclopropene **262**. Ishikawa considered two reaction pathways for the formation **262** a ring-opening pathway and a direct pathway (Scheme 62).[90]



Scheme 62

The activation barrier of the direct formation of cyclopropene (40.7 kcal/mol) is energetically comparable to that of the ring-opening reaction (36.5 kcal/mol). This calculation suggests that both reaction pathways are likely to operate under the thermal conditions employed.

Given this precedent, it was proposed that cyclopropane products were formed by the rearrangement of the intended silacyclobutane product. In order to test this hypothesis a solution of silacyclobutane **231a** in benzene was heated for 1.5 h at 200 ^{o}C (Scheme 63).

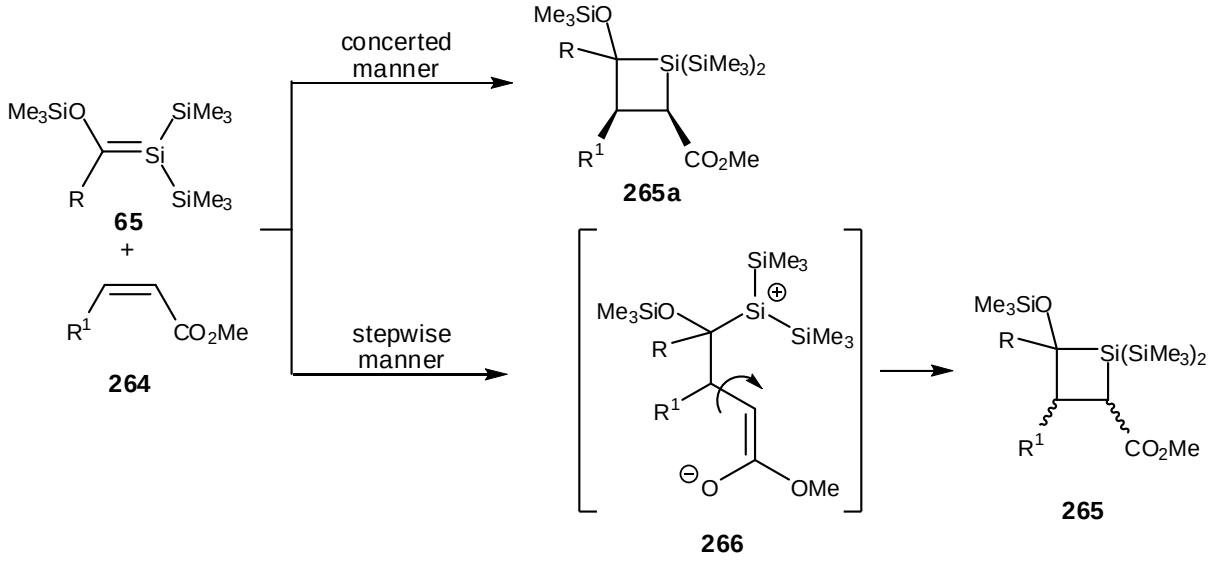


Scheme 63

In this case the cyclopropane product **232a** was isolated in 25% yield, however conversion was not complete and 46% of silacyclobutane was also recovered. This reaction supported the hypothesis that the cyclopropane is formed by rearrangement of silacyclobutane. Having established that **232a** was the product of the rearrangement, attention then turned on the initial [2+2] cycloaddition.

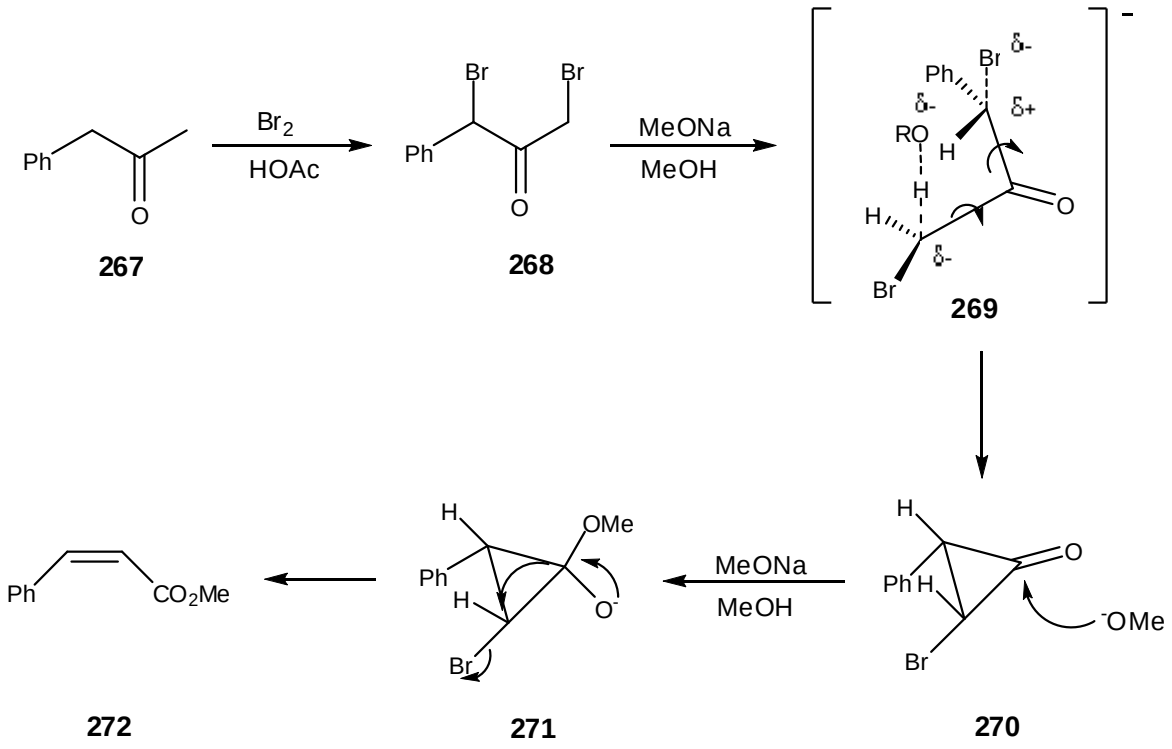
2.7.2 Reactions of *cis*–alkenes

It was hypothesised that siloxysilenes react with electron-deficient alkenes in a concerted manner. In order to prove this, a simple experiment was designed employing *cis*-alkenes (Scheme 64). The cycloaddition reaction which proceeds in a concerted manner gives *cis*-substituted products exclusively; whereas stepwise additions give a mixture of *cis*/*trans*-substituted products.



Scheme 64

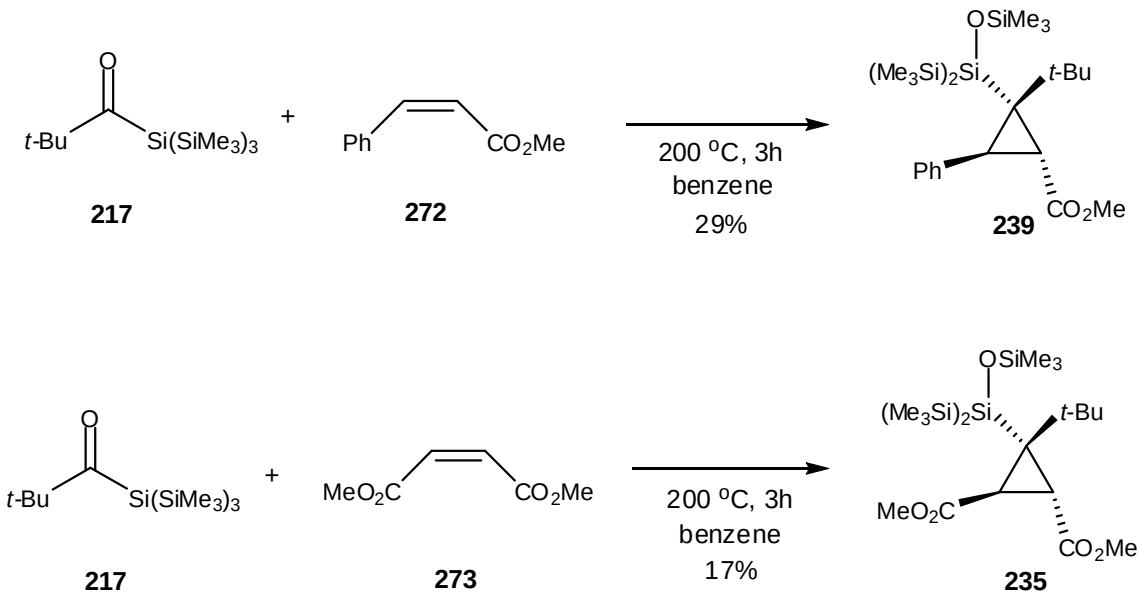
In order to prove the above hypothesis, the synthesis of *cis*-cinnamic methyl ester was carried out via a two-step sequence: bromination followed by Favorskii rearrangement.[74] The α,α-dibromophenylacetone **268** was prepared by direct bromination of 1-phenylpropan-2-one **267** (Scheme 65). Although the bromination product could be purified by flash column chromatography, extensive decomposition generally resulted in a low yield. For this reason the dibromoketone was used immediately without further purification. Subsequent reaction of the dibromoketone with two equivalents of sodium methoxide in methanol afforded the Favorski rearrangement product **272**. The rearrangement involves the initial concerted 1,3-elimination of hydrogen bromide from the least hindered rotamer **269** and disrotatory cyclisation, yielding the *cis* substituted intermediate cyclopropane **270**, which subsequently gave product **272** by a stereospecific S_N2-type ring-opening reaction.



Scheme 65

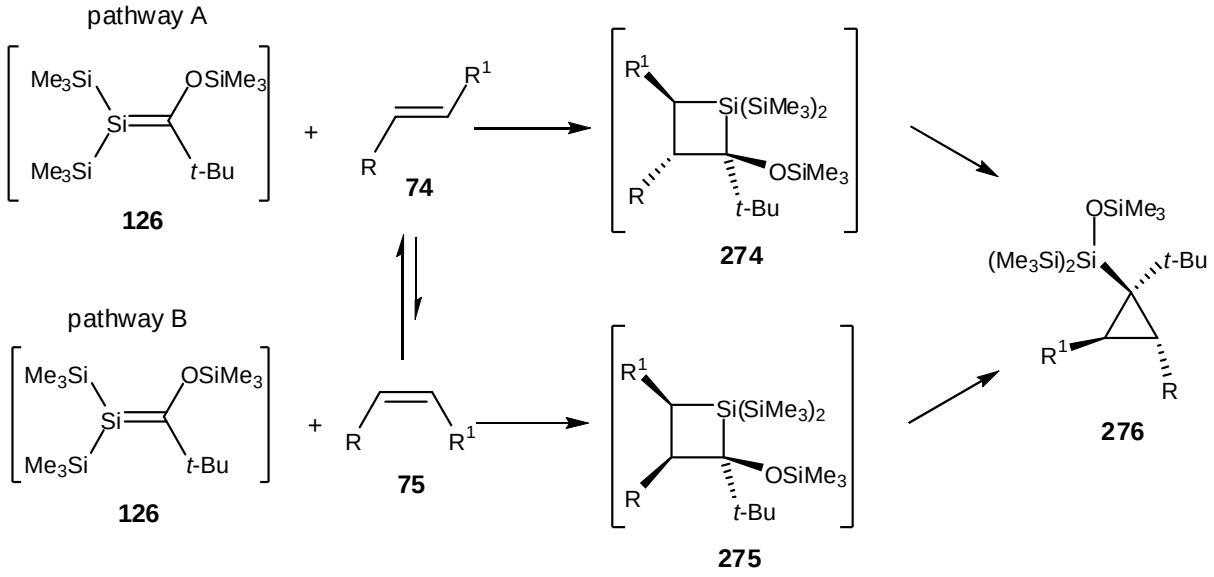
The *cis* double bond geometry in **272** was assigned on the basis of the observed coupling constants in the ^{1}H NMR spectrum (J = 12.5 Hz). In comparison, the coupling constant for the *trans*-cinnamic methyl ester is much larger (J = 16.0 Hz). With the *cis*-cinnamic methyl ester in hand, work then focused on investigating the cycloaddition mechanism.

Surprisingly, it was found that thermolysis of trimethylacetyltris(trimethylsilyl)silane with the *cis* olefins **272** and **273** gave the same product as with the *trans* olefins **238** (Table 8 entry 4) and **234** (Table 8 entry 2) respectively (Scheme 66). In addition, when subjected to the thermolysis conditions, the *cis* olefins isomerised and were recovered as a mixture of the *cis*/*trans* isomers (**272**:**238** - 1:2 *cis*/*trans*, **273**:**234** - 3.4:1 *cis*/*trans*).



Scheme 66

It appears that there are two possible pathways for the reaction (Scheme 67). In pathway **A** the *cis* olefin can isomerise to the *trans* compound and then react with the intermediate silene to form the intermediate silacyclobutane **274** which undergoes rearrangement to afford product **276**. In pathway **B**, the intermediate silene can react with the *cis* olefin to form the *cis* substituted intermediate silacyclobutane **275**. A final rearrangement causes the change of geometry between R and R^1 groups to afford product **276**.

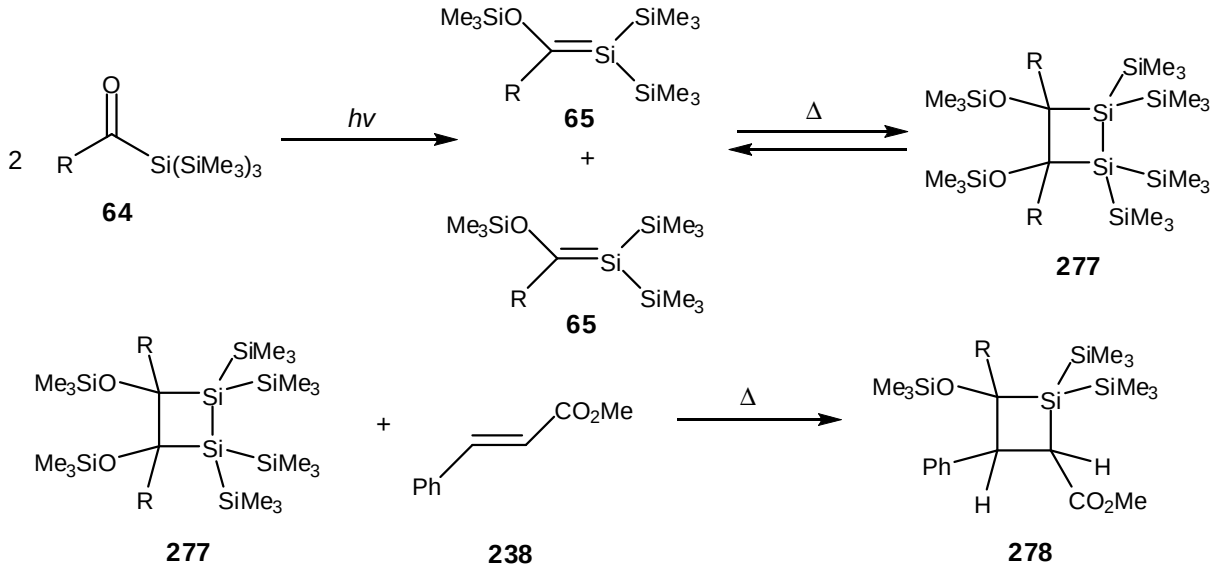


Scheme 67

To circumvent the problem of isomerisation of the double bond, trimethylacetyltris(trimethylsilyl)silane **217** was reacted with geometrically stable coumarin. Unfortunately, no desired product was ever detected and the NMR spectrum of the crude reaction mixture implied formation of an intractable mixture of products. In addition, it was found that the reaction of trimethylacetyltris(trimethylsilyl)silane with trisubstituted alkene, ethyl *trans*-β-methylcinnamate, also gives an intractable mixture of products. Those results indicate that either siloxysilenes do not react with sterically hindered and *cis* alkenes or that the resulting adducts are not stable at high temperature, which is needed for silene generation.

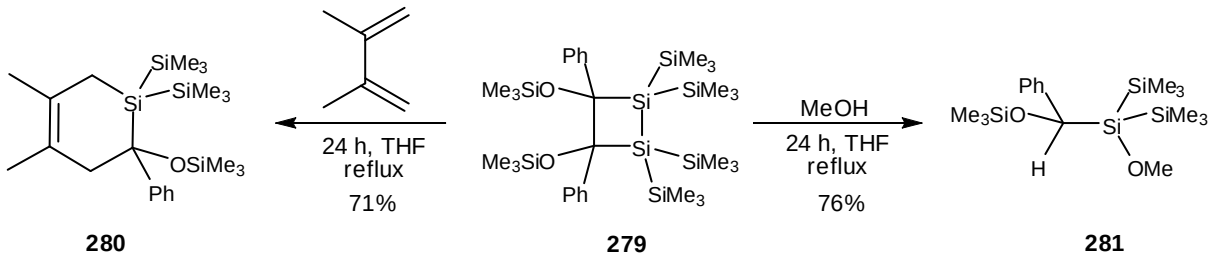
2.7.3 Silene Dimers

Attention then turned to alternative methods of silene generation to further investigate the mechanism. It was proposed that if the temperature of the reaction could be lowered, this would allow the silacyclobutane product to be isolated in larger amounts. This can be achieved by use of a silene dimer as a source of the silene (Scheme 68).



Scheme 68

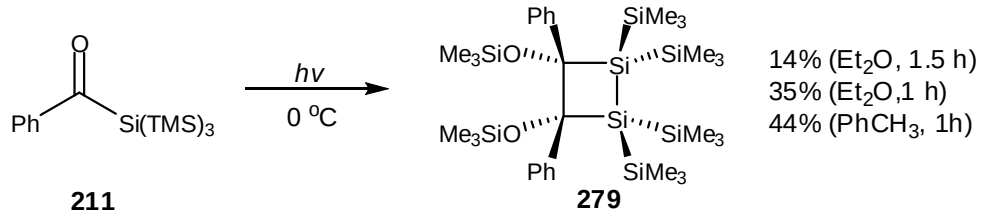
It has been shown by Brook that a silene dimer derived from acylpolysilanes can readily dissociate thermally to a monomeric silene.[38] When dimer **279** was refluxed in THF with methanol or 2,3-dimethylbutadiene, the appropriate adduct of the silaethylene was obtained in good yield (Scheme 69). The reaction did not occur at room temperature, suggesting that higher temperatures are required for complete dissociation of the dimer.



280 **279** **281**

Scheme 69

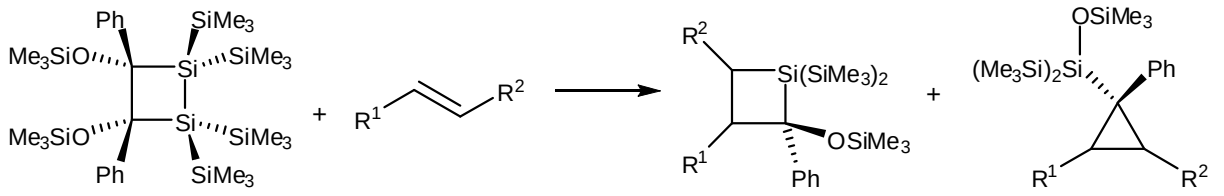
Following the procedure developed by Brook, a solution of benzoyl polysilane **211** was irradiated in a photochemical reactor to give the silene dimer **279** (Scheme 70).[38] The formation of the dimer was confirmed by analysis of the ^{1}H NMR spectrum, which showed peaks at δ_H = 0.42 (18H), δ_H = 0.08 (18H) and δ_H = -0.25 (18H) for the $SiMe_3$ groups. Unfortunately, it was not possible to obtain the silene dimer in the high yield reported by Brook (71%), probably because of the differences in the characteristics and/or power of irradiation source in the photochemical reactors.



211 **279**

Scheme 70

With the silene dimer **279** in hand, the next stage was to investigate the cycloreversion of the dimer in the presence of trapping agents. A solution of dimer **279** was stirred in the presence of a fourfold excess of silenophile under various conditions (Table 9).



entry	alkene			method	solvent	temp (°C)	time (h)	product, yield (%), ds	
	R^1	R^2	No					cyclobutane	cyclopropane
1	CH=CHCO$_2$Et	CO$_2$Et	**230**	NMR tube	d_8-toluene	RT	48	-	-
2	CH=CHCO$_2$Et	CO$_2$Et	**230**	flask	THF	45	24	-	-
3	CH=CHCO$_2$Et	CO$_2$Et	**230**	flask	THF	65	24	**282**, trace	**246**, 12 (1:0)
4	CH=CHCO$_2$Et	CO$_2$Et	**230**	microwave	benzene	120	0.3	**282**, 30 (1:1)	**246**, 24 (1:0)
5	Ph	CO$_2$Me	**238**	flask	THF	65	24	-	**248**, 36 (12:1)
6	Ph	CO$_2$Me	**238**	microwave	benzene	120	0.3	**283**, trace	**248**, 75(3.9:1)

Table 9

The first two entries in Table 9 show unsuccessful attempts to carry out the reaction at low temperature. In both cases, only slow decomposition of the silene dimer was observed. Consequently, to increase cycloreversion of the silene dimer, the temperature of the reaction was increased to 65 °C (entry 3, 5). This led to the formation of the cyclopropanes in low yield, but good diastereoselectivity. In addition, the silacyclobutane derived from diethyl hexadienoate was observed in the crude reaction mixture by NMR spectroscopy (entry 3). The ^{1}H NMR spectrum showed two characteristic peaks for the ring protons at δ_H = 4.27 ppm and δ_H = 3.09 ppm. This indicates that higher temperatures are needed for the reaction to occur. Bearing in mind that the silacyclobutanes are not stable at high temperatures, it was hypothesised that performing the reaction at even higher temperatures but for shorter periods of time may lead to a further increase in the yield of silacyclobutane. Consequently, the reaction was carried out under microwave conditions at 120 °C for 20 min to give the silacyclobutane **282** in 30% and cyclopropane **246** in 24% yield (Table 9, entry 4). In comparison, the same reaction carried out in a sealed tube at 200 °C for 3 h gave exclusively cyclopropane **246** in 29% yield (Table 8, entry 9). In the same way, the cycloreversion of the silene dimer **279** in the presence of *trans*-methyl cinnamate was also investigated (entry 6). The ^{1}H NMR spectrum of the crude reaction mixture suggests that the reaction carried out in microwave gave a mixture of the silacyclobutane and the cyclopropane in a 1:4 ratio

(determined by ^{1}H NMR spectroscopy). However, only the cyclopropane product was isolated after flash column chromatography in 75% yield.

Overall these experiments supported the hypothesis that the silacyclobutanes are unstable intermediate products which readily rearrange to form the corresponding cyclopropanes.

2.7.4 Cycloreversion of silacyclobutanes

In 1969, it was demonstrated by Gusel'nikov that 1,1-dimethylsilacyclobutane undergoes a thermally promoted reverse [2+2] cycloaddition to ethylene and dimethylsilene, which subsequently formed a head to tail dimer (Chapter 1, Section 1.3.1).[26] Gordon studied the mechanism of ring opening of silacyclobutanes under thermolysis conditions (Figure 16).[91] Theoretical investigations suggest that the most likely route from silacyclobutane to ethylene and silene involves the initial cleavage of a ring C-C bond to form diradical intermediate **286** (pathway B). However, it is very likely that pathway **A** involving Si-C bond cleavage and concerted pathway **C** also operate under thermolysis conditions as all transition states have similar energies.

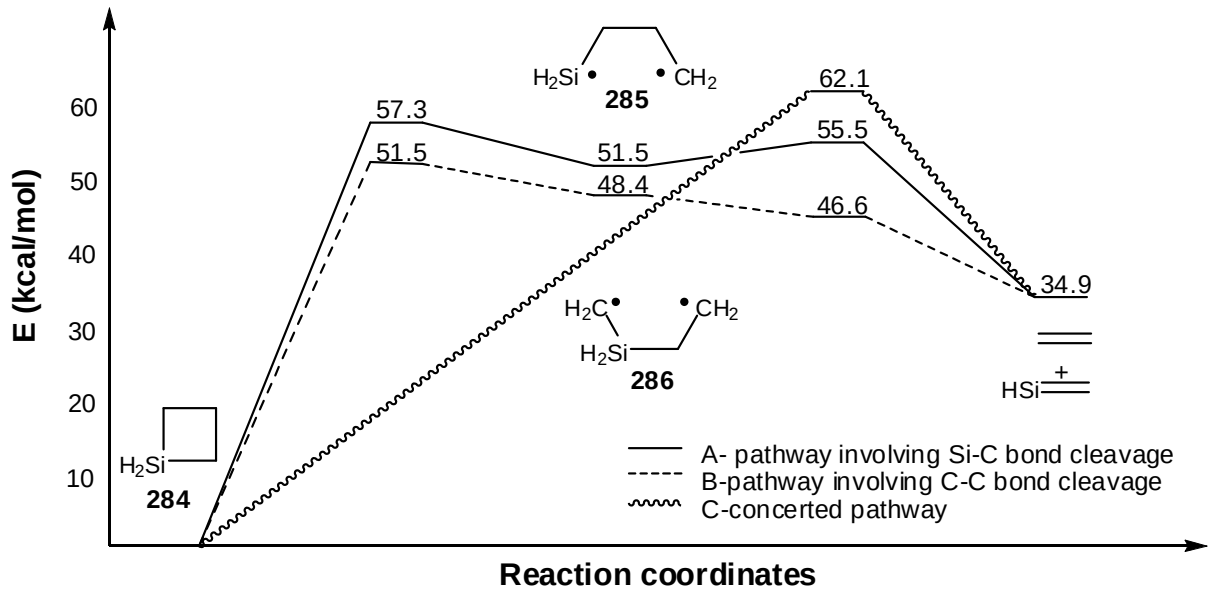
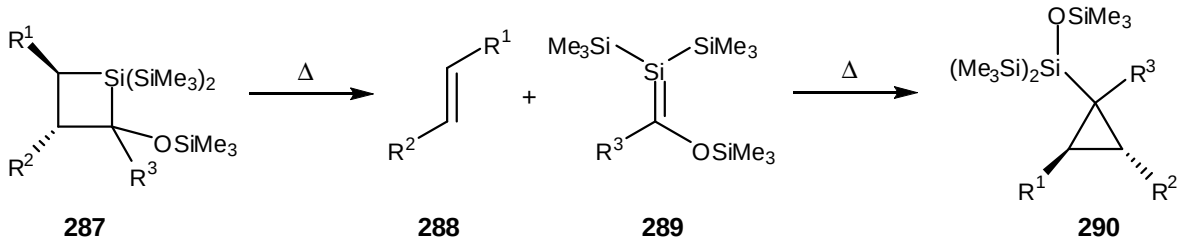


Figure 16

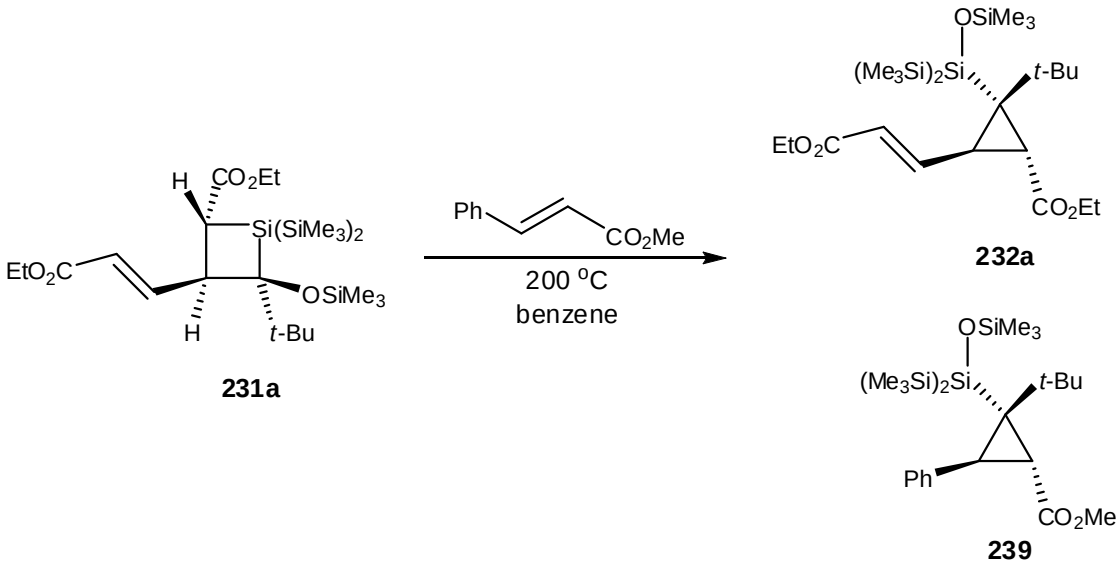
Based on the work by Gordon, it was suggested that an alternative route to the cyclopropanes must be operating under the thermolysis conditions (Scheme 71). This could involve a reverse [2+2] cycloaddition reaction followed by formation of the cyclopropane product.



287 **288** **289** **290**

Scheme 71

In order to test this hypothesis a solution of silacyclobutane **231a** was heated in the presence of a fourfold excess of *trans*-cinnamic methyl ester (Scheme 72). Removal of the solvent followed by purification by flash column chromatography gave exclusively the cyclopropane **232a** in 45% yield. The product **239** was not detected, suggesting that the initial [2+2] cycloaddition is not reversible.



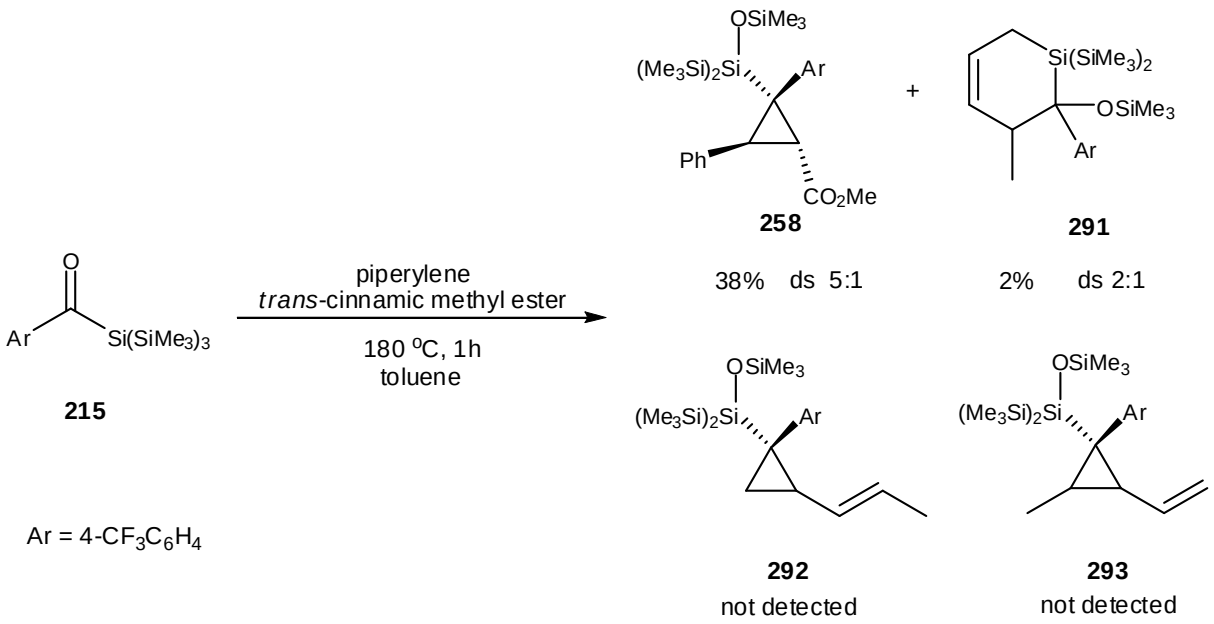
231a **232a** **239**

Scheme 72

2.7.5 Silene-carbene rearrangement

It was proposed that formation of a carbene in the reaction mixture may lead to the formation of cyclopropanes. To test the carbene hypothesis, a competition experiment was designed

(Scheme 73). A solution of acyltris(trimethylsilyl)silane **215**, piperylene and *trans*-cinnamic methyl ester in toluene was heated to 180 ^{o}C in a microwave tube. The resulting mixture was then concentrated and purified by flash column chromatography.

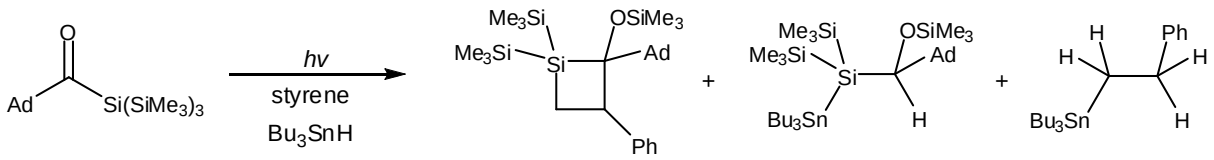


Scheme 73

In this case only the cyclopropane **258** and the [4+2] cycloadduct **291** were observed. Importantly, products **292** and **293** were not detected. Thus, these results disprove the carbene hypothesis. Spectroscopic data for the adduct **291** were consistent with data previously reported by Griffiths.[81] At this stage the best explanation for the formation of cyclopropane products is *via* rearrangement of the corresponding silacyclobutane.

2.7.6 Attempts to trap radical intermediates

It was plausible that both the [2+2] cycloaddition reaction and the rearrangement can proceed via radical intermediates. It appears that the thermolysis reaction can be carried out in the presence of Bu_3SnH in order to trap any radical intermediates. This methodology has been utilised by Brook to investigate the [2+2] cycloaddition reaction between silenes and alkenes under photochemical conditions.[68,64] In this, the acylpolysilane **50** was irradiated in the presence of styrene and tributyltin hydride (Scheme 74).

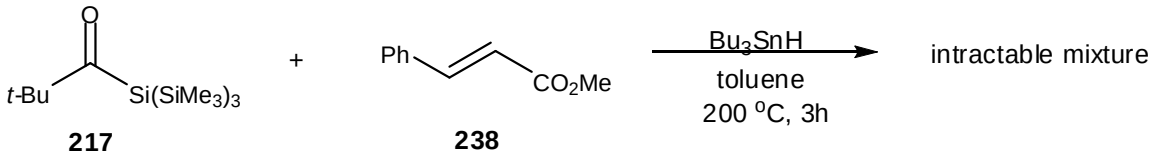


50 **294** **295** **296**

Scheme 74

The reaction gave the same cycloadduct **294** as was obtained when styrene was added to the polysilane alone, accompanied by a small amounts of the tributyltin hydride adducts **295** and **296**. This indicates that tributyltin hydride had no substantial effect on the course of the cycloaddition reaction.

Following this procedure, a solution of pivaloyl polysilane **217**, *trans*-cinnamic methyl ester and tributyltin hydride in toluene was thermolysed at 200 ^{o}C for 3 h (Scheme 75). Unfortunately, this experiment was inconclusive as none of the expected products were detected and crude NMR spectra implied formation of an intractable mixture of products.

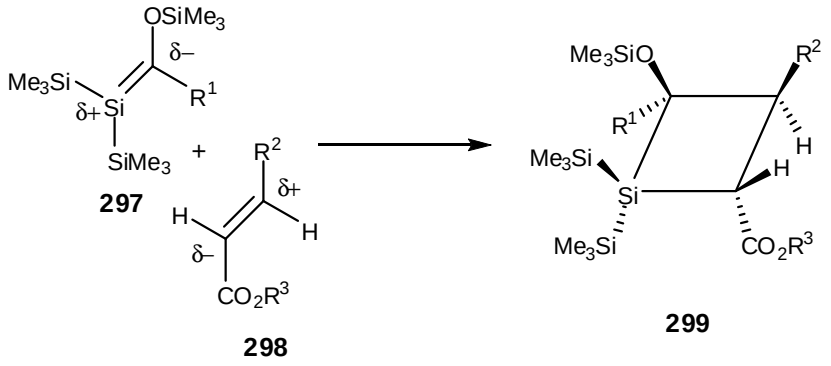


217 **238**

Scheme 75

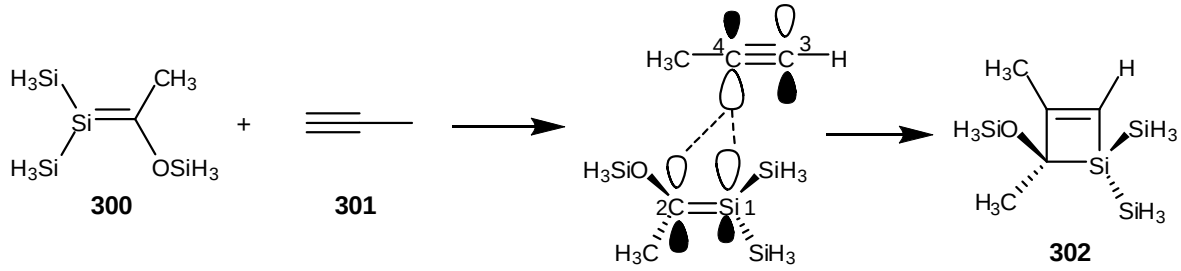
2.7.7 Mechanism

To account for the observed cyclobutane and cyclopropane products the following mechanism has been proposed (Scheme 76). The formation of product **299** can be rationalised by a [2+2] cycloaddition of the silene **297** generated from the corresponding acylpolysilane with alkene **298**.



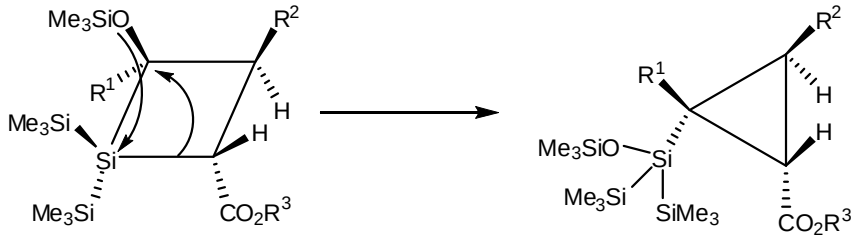
Scheme 76

The formation of silacyclobutene was investigated through quantum mechanical calculation by Ishikawa on a simple model presented in Scheme 77.[92] According to the Woodward-Hoffmann rules, such [2+2] cycloaddition reactions are symmetry-forbidden in carbon systems and do not proceed thermally. However, the orbital amplitude is significant on the Si atom of silene and the interaction between the silene Si atom and the diagonal acetylene ***C***-4 atom help to overcome symmetry restrictions arising from the unfavourable HOMO-LUMO overlap in the [2+2] cycloaddition. Overall, this [2+2] cycloaddition reaction can be viewed as a concerted but nonsynchronous process.



Scheme 77

Based on the Ishikawa theoretical calculations, this [2+2] cycloaddition reaction can be viewed as a concerted but nonsynchronous process. However, an alternative route via a diradical intermediate is also possible. The final process involves a 1,2-Si-$OSiMe_3$ migration, which is promoted by high temperatures, and subsequent ring contraction to form the three-membered cyclic system **303** (Scheme 78).



299 **303**

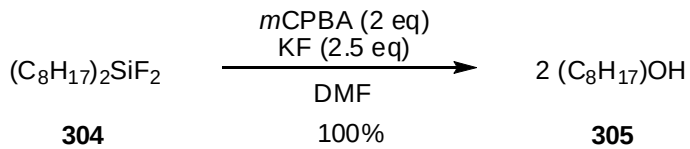
Scheme 78

In conclusion, it was found that siloxysilenes react with electron-deficient alkenes to form silacyclobutanes. These cycloadducts are thermally unstable and isomerise to the corresponding cyclopropanes. Despite these interesting observations, details of the rearrangement remain unclear.

2.8 Reactivity of the cycloadducts

2.8.1 Introduction

A key goal of the work involves the elaboration of the cycloadducts into synthetically useful target structures. It was shown previously in the group, that the oxidation of cyclic organosilanes provides a convenient route to a variety of dihydroxylated compounds (Chapter 1, Section 1.6). However, it is well known that organosilicon compounds are generally resistant to standard oxidation procedures used in organic synthesis. Nevertheless, under certain conditions an organosilicon group bearing an electronegative substituent or hydrogen can undergo oxidation as was shown by Tamao (Scheme 79).[93]

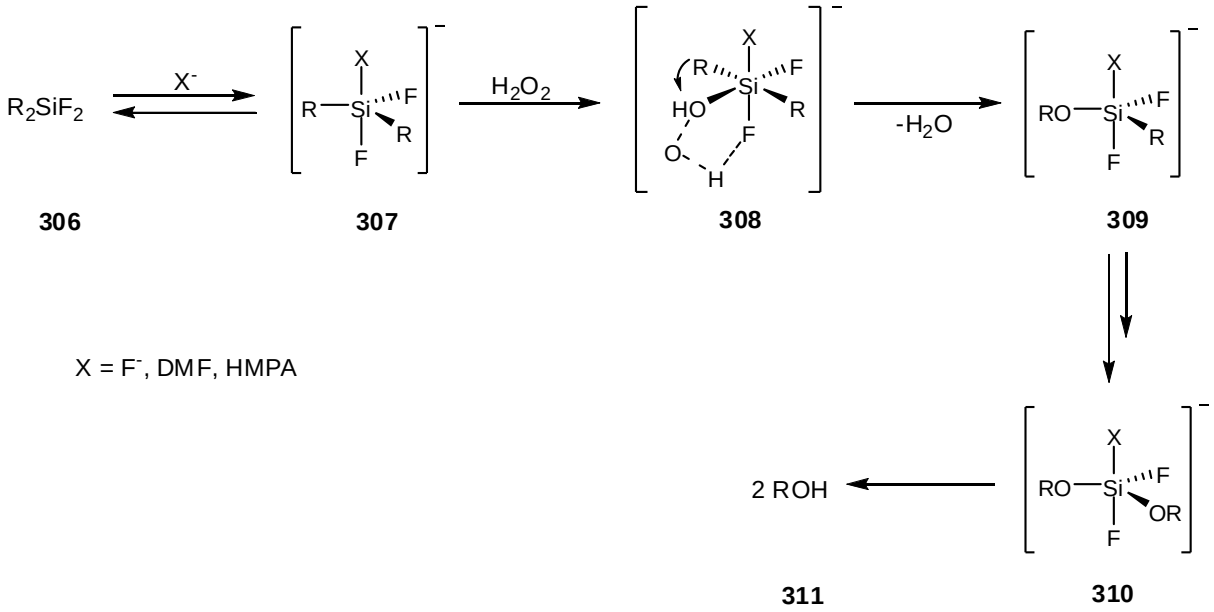


304 100% **305**

Scheme 79

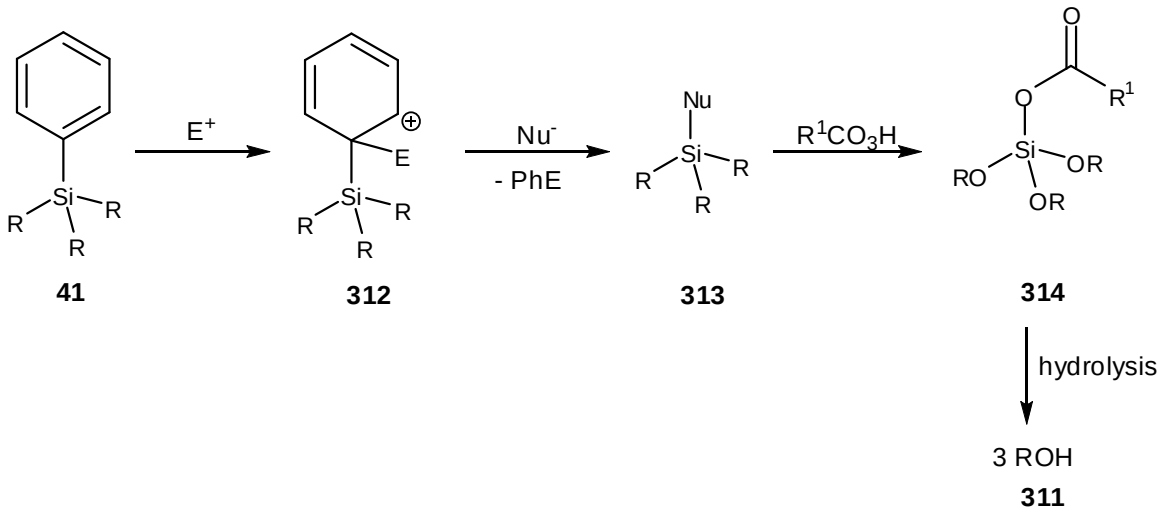
It is believed that the mechanism of the oxidation proceeds through the pentacoordinated species **307** formed by addition of fluoride or a donor solvent (DMF, HMPA) to the starting fluorosilane **306** (Scheme 80).[94] The resulting intermediate **307** is more electrophilic, thus

promoting attack by peroxide to produce the hexacoordinate species **308**, which undergoes concerted migration of an alkyl group from silicon to oxygen. Importantly, it was shown that the migration proceeds with retention of stereochemistry at the carbon centre. Finally the pentacoordinated species **310** undergoes hydrolysis to produce alcohol **311**.



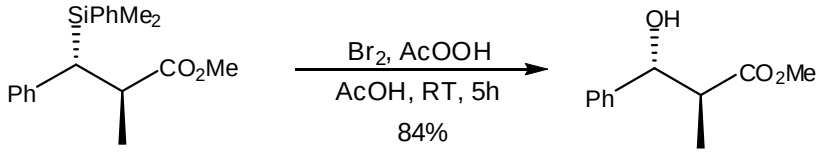
Scheme 80

The major disadvantage of the Tamao procedure is the necessity of using organosilicon compounds bearing electronegative substituents, which are generally unstable. This problem was solved eventually by Fleming, who showed that aryl-substituted silanes **41**, which are compatible with a broader range of reaction conditions, can serve as oxidation precursors (Scheme 81).[95]



Scheme 81

The first step of the Fleming oxidation involves the initial cleavage of the aryl group with an electrophilic reagent such as BF_3•2AcOH or HBF_4•Et_2O to give silane **313**. This cleavage proceeds via cationic intermediate **312** and can be treated as a classical electrophilic aromatic ipso substitution. In the second step the activated silanes **313** undergoes oxidation with peracid, giving the siloxane **314** which on hydrolysis produces the desired alcohol **311**. Subsequently, Fleming found that by using Br_2 or $Hg(OAc)_2$ as the electrophile, the two steps may be carried in one pot (Scheme 82).[96]

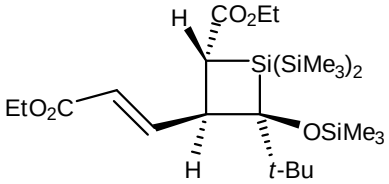


315 **316**

Scheme 82

2.8.2 Attempted oxidation of silacyclobutane

A solution of the silacyclobutane **231a** was treated with the reagents shown in Table 10. Unfortunately, the reaction under either oxidation conditions (entry 1, 2) or Lewis acid conditions (entry 3, 4) led to the formation of an intractable mixture of products.

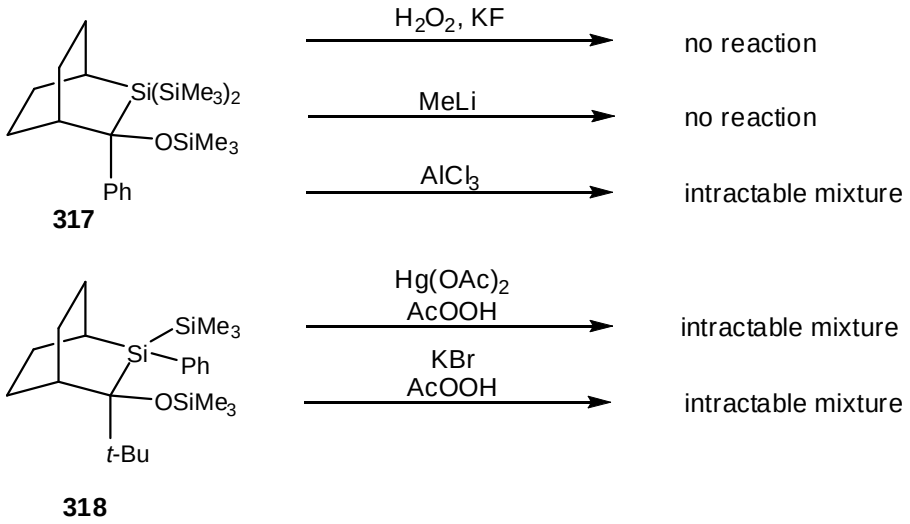


231a

entry	reaction conditions				outcome
	time (h)	temp (^oC)	solvent	reagent	
1	1	reflux	THF/MeOH	KF, $KHCO_3$, H_2O_2	intractable mixture
2	1	RT	THF/MeOH	KF, $KHCO_3$, H_2O_2	intractable mixture
3	0.75	RT	DCM	BF_3·2AcOH	intractable mixture
4	0.5	RT	DCM	BF_3·Et_2O	intractable mixture

Table 10

In earlier work, Griffiths encountered similar problems when attempting to oxidise silacycles derived from Brook siloxysilenes (Scheme 83). The Tamao oxidation of silacycle **317** or treatment with $AlCl_3$ or MeLi gave no reaction or caused decomposition of the starting material. In addition, even the oxidation of the silacycles **318** bearing a more easily displaceable phenyl group, gave a complex mixture of products.

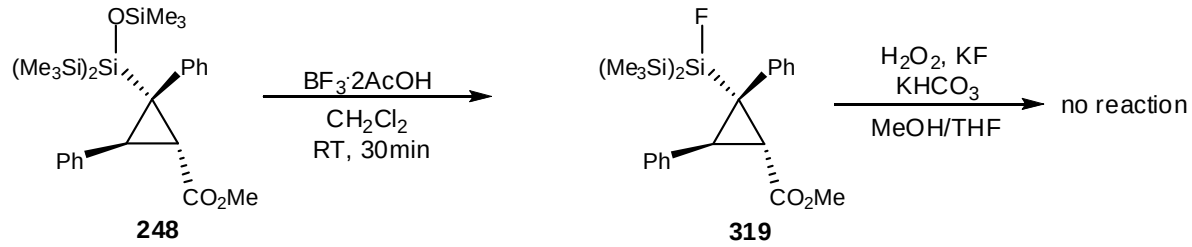


Scheme 83

It was suggested that problems encountered with the oxidation are associated with the $OSiMe_3$ group adjacent to the disilyl group. This simple factor may account for the lack of success with silacyclobutane **231a** and no further attempts to oxidise this substrate were made.

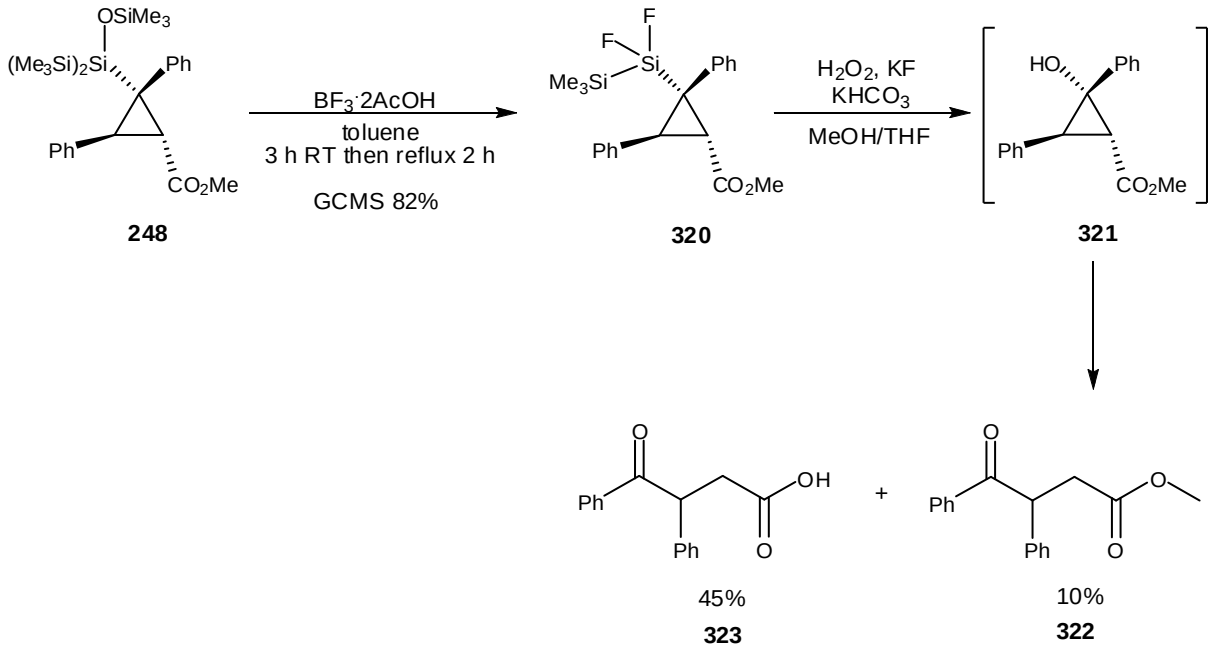
2.8.3 Oxidation of cyclopropane

Despite the difficulties in the elaboration of the silacyclobutane, the oxidation chemistry of the cyclopropanes was explored. It was anticipated that Fleming-Tamao oxidation of the silyl group would provide highly substituted cyclopropanols. However, despite the presence of the potentially activating siloxy group, initial attempts to directly oxidise the C-Si bond using the classic Tamao conditions (H_2O_2, KF, $KHCO_3$) failed. In such situations it can be beneficial to convert the silane precursors to the more nucleophilic fluorosilane. This was achieved by treatment of cyclopropane **248** with BF_3•2AcOH in dichloromethane at room temperature (Scheme 84). The formation of product **319** was supported by mass spectrometry which showed a molecular ion of *m/z* = 444, consistent with a substitution of the $OSiMe_3$ group by a fluoride ion. In addition, ^{19}F NMR spectroscopy indicated the presence of a fluorine atom.



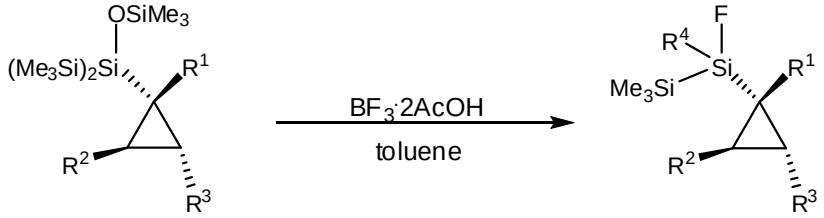
Scheme 84

Surprisingly, the fluorosilane **319** was also resistant to oxidation with hydrogen peroxide. However, enhancing the reactivity of the silicon centre by conversion into the difluorosilane **320** through prolonged treatment with BF_3•2AcOH overcame this problem (Scheme 85). Tamao oxidation of the difluorosilane **320** proceeded smoothly to afford a mixture of ketoester **322** and associated acid **323**, presumably arising from opening of the intermediate hydroxycyclopropane under the reaction conditions and concomitant ester hydrolysis. Identification of the difluorosilane was aided by the observation of a molecular ion of *m/z* = 390 in the GC-MS trace. It was found, however, that product **320** is not stable to column chromatography and was more efficiently oxidised without purification. The full characterisation of the difluoro species was carried out on analogous products derived from the cyclopropane **232a**, which appeared to be more stable to purification by flash column chromatography on silica (Table 11 entry 1).



Scheme 85

Disappointingly, attempts to extend this protocol to other silylcyclopropanes resulted in only low yields of the intermediate difluorosilane accompanied by extensive decomposition (Table 11).

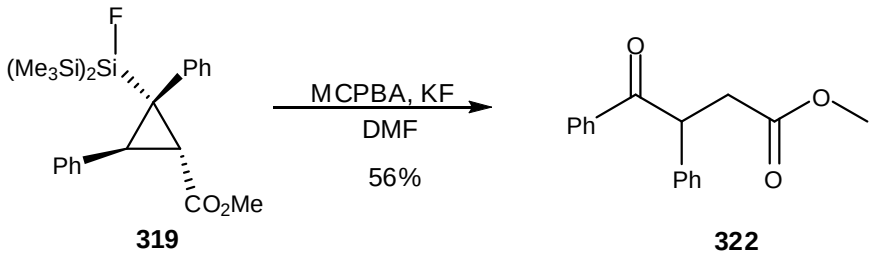


entry	cyclopropane				fluorosilane[a] R^4=$SiMe_3$		difluorosilane[b] R^4=F	
	No	**R^1**	**R^2**	**R^3**	**yield (%)**	**product**	**yield (%)**	**product**
1	**232**	*t*-Bu	CO_2Et	$CH=CHCO_2Et$	95	**324**	18	**325**
2	**239**	*t*-Bu	Ph	CO_2Me	97	**326**	trace	**327**
3	**250**	4-$OMeC_6H_4$	Ph	CO_2Me	98	**328**	trace	**329**

[a]RT, 30 min. [b]Reflux, 2 h.

Table 11

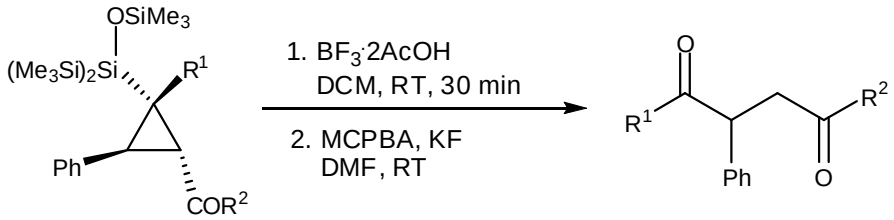
Consequently different methods were explored for the oxidation and, ultimately, it was found that, following a precedent established by Tamao,[93] the monofluorosilane could be oxidised, albeit slowly, using MCPBA in DMF. Following further optimisation it was found that the addition of KF to this oxidation provided both enhanced yields and shorter reaction times (Scheme 86).



319 **322**

Scheme 86

Pleasingly this two-step procedure proved to be applicable to all the other silylcyclopropanes to provide the corresponding 1,4-dicarbonyl compounds in reasonable yields (Table 12). Practically, the process can be simplified into a one-pot conversion with the intermediate fluorosilylcyclopropane being used directly in the subsequent oxidation.

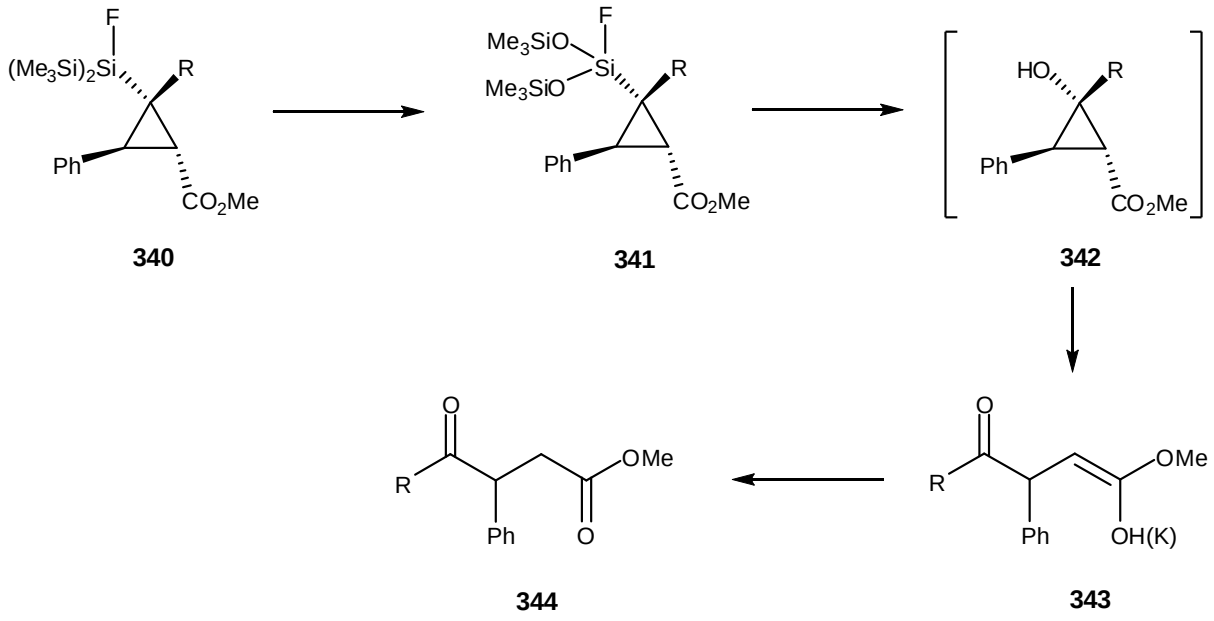


entry	cyclopropane			fluorosilane		diketone	
	No	R^1	R^2	product	yield (%)	product	yield (%)
1	**248**	Ph	OMe	**319**	96	**322**	56
2	**251**	CH_3	OMe	**330**	94	**331**	50
3	**239**	*t*-Bu	OMe	**326**	97	**332**	61
4	**250**	4-$MeOC_6H_4$	OMe	**328**	98	**333**	51
5	**258**	4-$CF_3C_6H_4$	OMe	**334**	98	**335**	45
6	**259**	2-furyl	OMe	**336**	61	**337**	78
7	**254**	4-$MeOC_6H_4$	NEt_2	**338**	-[a]	**339**	22

[a.]Fluorosilane **338** not stable to silica gel and used directly in oxidation without purification

Table 12

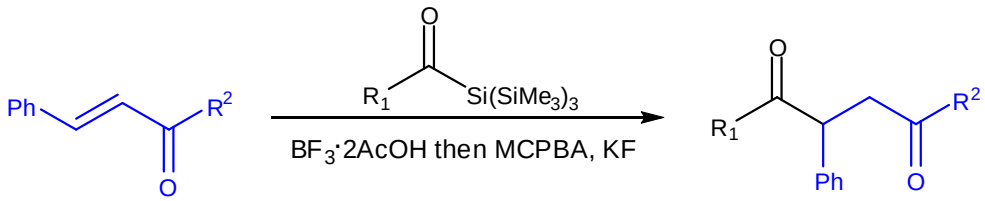
At this point it was clear that hydroxycyclopropane products were not sufficiently stable to survive the oxidation conditions and undergo a ring-opening reaction (Scheme 87). Presumably the ring opening of the cyclopropane proceeds *via* the intermediate enolate anion **343** but, to-date, all attempts to trap this with a variety of electrophiles (e.g methyl acrylate, benzyl bromide) have proved unsuccessful. The intermediate product **341** (R = 4-$MeOC_6H_4$) could be isolated suggesting that the reaction occurs according to the Tamao mechanism.



Scheme 87

2.9 Conclusions

The work described in this chapter was focused on the synthesis of silenes using methods that involve a thermal reaction and found that a microwave approach can be used as an alternative to sealed tube techniques. Key benefits of the microwave method are the ability to decrease the reaction time and also the possibility to monitor the internal pressure inside the reaction vessel. However, both approaches provide access to the cyclopropane products in moderate yields and varying diastereoselectivity. Furthermore, it was found that these products are formed at high temperatures from the silacyclobutanes. Finally, oxidation of the cyclopropanes gave access to the corresponding 1,4-dicarbonyl compounds. Overall, this two-step sequence involving silene generation and "cycloaddition" followed by oxidative cleavage of the cyclopropyl ring represents the product of the formal addition of an acyl anion to the cinnamate group (Scheme 88). These results continue to demonstrate that the unusual chemistry exhibited by silenes offers new prospects for synthetic methodology.

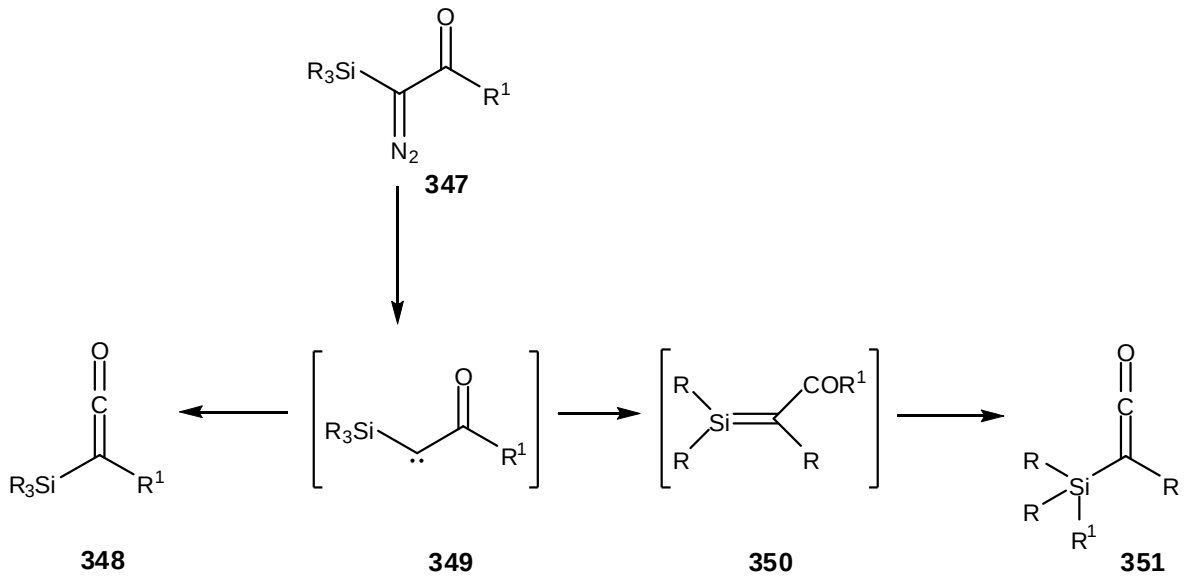


Scheme 88

3 Alternative silene generation strategies

3.1 Introduction

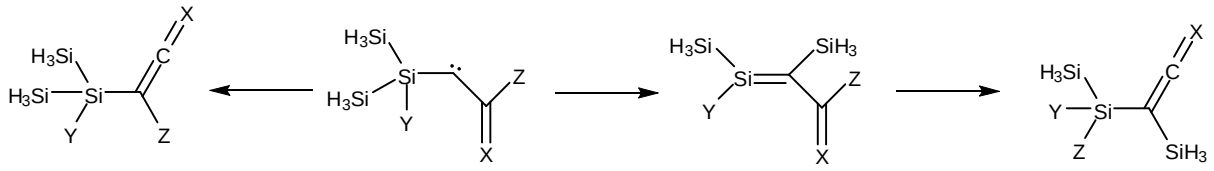
In the Steel group to-date, silenes have been principally generated from silylalcohols through a sila-Peterson reaction. In an alternative approach for milder silene generation the applicability of α-silyl diazo carbonyl compounds as silene precursors is described. As discussed in Chapter 1, Section 1.3.3.3, the extrusion of N_2 from α-silyl diazo compounds is usually achieved photochemically or thermally (Scheme 89). Transition metal catalysis, especially by copper (CuOTf,[97] $CuSO_4$,[98] CuCl[99]), rhodium ($Rh_2(OAc)_4$,[100] $Rh_2(pfb)_4$[101]) and palladium ($Pd(OAc)_2$,[97] $PdCl_2(CH_3CN)_2$[100]) has also been employed. This leads to the formation of carbene/metal carbenoid species which can rearrange to α-silyl ketene **348** or α-silyl ketene **351**. The formation of α-silyl ketene **351** is postulated to proceed via a silene intermediate, but attempts to explore the chemistry of these silenes have been limited.



Scheme 89

3.2 Silene stability

Anticipating that the lifetime and stability of the silene could be modulated by the degree and nature of substituents, initial attention turned to a computational study of their effect. The work described in this section was carried out at Uppsala University in Sweden under the supervision of Prof. Ottosson. The calculations were performed at B3LYP/6-31G(d)//B3LYP/6-31G(d) level on the model system shown in Table 13. The reaction began with the initial formation of carbene **353** which subsequently rearranged to form compound **352** or silene **354**. Although silene **354** can be trapped, it can also isomerise to compound **355** by fast 1,3-migration.



352 **353** **354** **355**

entry	No	X	Y	Z	$\Delta E_{355\text{-}354}$ (kcal/mol)	$\Delta E_{353\text{-}354}$ (kcal/mol)	$\Delta E_{352\text{-}354}$ (kcal/mol)
1	**a**	O	$-SiH_3$	$-CH_3$	-22.9	49.6	-9.1
2	**b**	O	$-SiH_3$	$-NH_2$	-22.0	53.9	13.1
3	**c**	O	$-SiH_3$	$-OCH_3$	-27.1	58.5	22.5
4	**d**	O	$-SiH_3$	$-SCH_3$	-30.7	57.1	-2.9
5	**e**	S	$-SiH_3$	$-CH_3$	-23.8	11.8	-11.8
6	**f**	S	$-SiH_3$	$-NH_2$	-22.9	24.6	8.6
7	**g**	S	$-SiH_3$	$-OCH_3$	-31.1	29.8	11.6
8	**h**	S	$-SiH_3$	$-SCH_3$	-32.6	18.9	-5.5
9	**i**	NH	$-SiH_3$	$-NH_2$	-22.4	40.3	7.5
10	**j**	O	-OMe	$-NH_2$	-28.8	55.4	15.2

Table 13

From the results the most obvious finding is that carbene **353** is always the most unstable species in calculated systems. Moreover, Z substituents $–CH_3$ and $–SCH_3$ lead to a more stable ketene product **352** when compared to silene **354** (entry 1, 4, 5, 8). On the other hand π-donor groups $–NH_2$ and $–OCH_3$ have the opposite destabilising effect (entry 2, 3, 6, 7, 9, 10). Entries 1-8 show that thiocarbenes (Z = S) are more stable than acylcarbenes (Z = O). In addition, in all the cases, ketene **355** is always more stable then the corresponding silene **354**.

These preliminary investigations suggest that carbenes derived from the model diazo compounds shown in Figure 17 should preferentially rearrange to the corresponding silenes. However, since silenes tend to isomerise to more stable ketenes, it was not known whether they can be efficiently trapped.

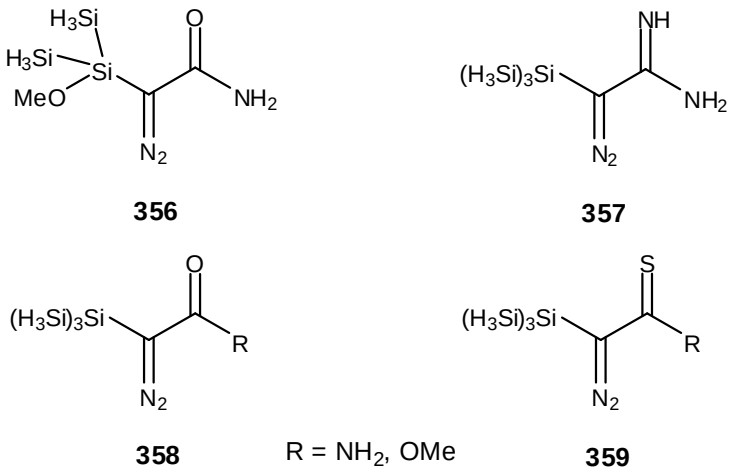


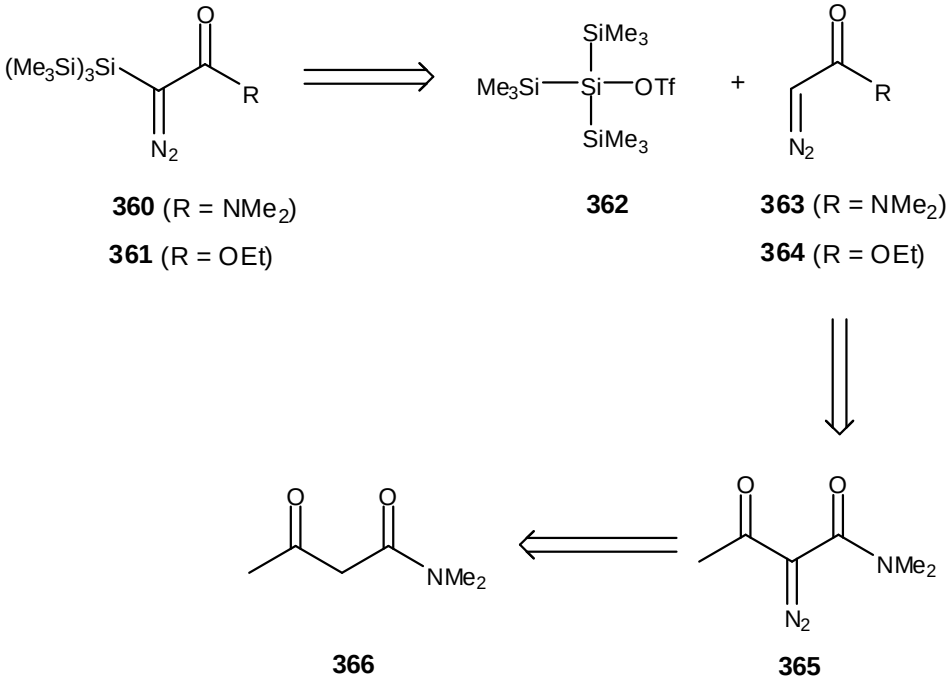
Figure 17

The model compounds shown in Figure 17 could be selected as synthetic targets in further studies. Nevertheless, certain modifications of the structure would be necessary to make these compounds more stable and less reactive. For example, SiH_3, NH_2 and NH groups can be replaced with $SiMe_3$, NMe_2 and NPh respectively.

In the following section, only the synthesis of an α-silyl diazo ester and an α-silyl diazo amide was performed since this would involve well established chemistry.

3.3 Synthesis of α-silyl diazo carbonyl compounds

Based on the results from the quantum chemical calculations, the synthesis of diazo amide **360** and diazo ester **361** was undertaken (Scheme 90). From the earlier work of Regitz it is known that α-diazo carbonyl compounds can be easily silylated with a silyl triflate in the presence of Hünig's base.[102] Following this precedent, the chosen synthetic route to afford diazo compound **360** involves coupling between silyl triflate **362** and diazo amide **363** prepared from *N*,*N*-dimethylacetoacetamide **366**.



360 (R = NMe_2)
361 (R = OEt)

362

363 (R = NMe_2)
364 (R = OEt)

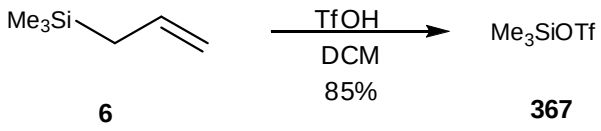
366

365

Scheme 90

In a similar manner, diazo ester **361** can be easily prepared from commercially available ethyl 2-diazoacetate **364**.

With the analysis in mind, a brief search of the literature suggested that a silyl triflate could be prepared from an allylsilane according to the Morita procedure.[103] This involves treatment of allyl silane **6** in DCM with triflic acid (Scheme 91).

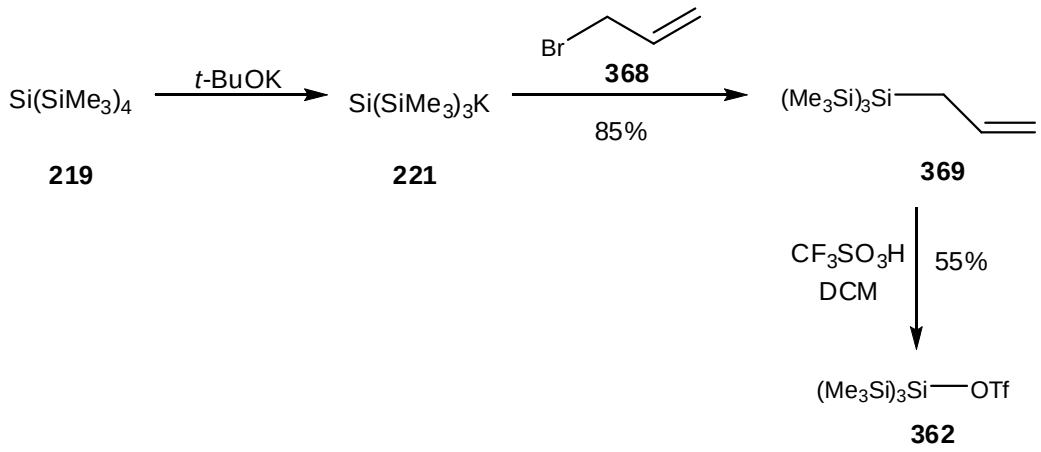


6

367

Scheme 91

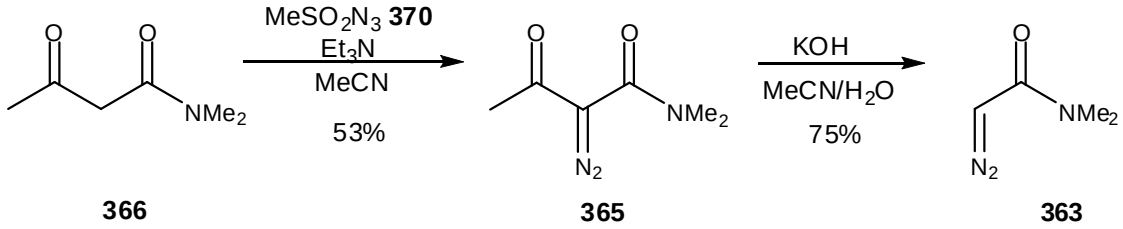
Following this strategy, allylsilane **369** was selected as the initial precursor (Scheme 92). This was generated from silane **219** by metalation with *t*-BuOK followed by alkylation with allyl bromide **368**. Subsequently, allylsilane **369** was treated with trifluoromethanesulfonic acid. Distillation under reduced pressure afforded the product **362** in 55% yield, albeit accompanied by a significant amount of impurities.



Scheme 92

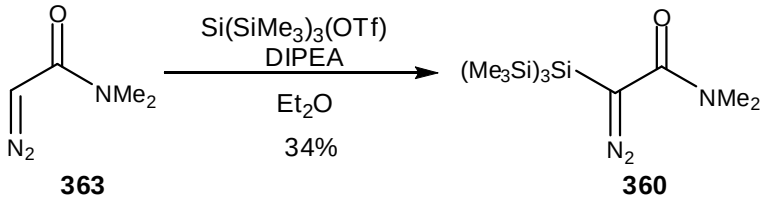
Evidence for the formation of triflate **362** was ascertained from the ^{13}C NMR spectrum which contained a signal corresponding to the CF_3 carbon at δ_C = 118.5 ppm ($^1J_{C\text{-}F}$ = 315.7Hz) and a signal attributed to the Si(***C***$H_3)_3$ carbons at δ_C = -0.7 ppm.

The diazo amide **363** could be generated in two steps following the procedure of Müller.[104] The first step involves the diazo transfer reaction of commercially available *N*,*N*-dimethylacetoacetamide **366** with methanesulfonyl azide **370**[105] (Scheme 93). Subsequent hydrolysis of **365** afforded the desired diazo compound **363** as confirmed by analysis of the IR and ^1H NMR spectrum, which showed a band at 2092 cm^{-1} corresponding to the diazo group and a signal at δ_H = 4.96 ppm arising from the α proton.



Scheme 93

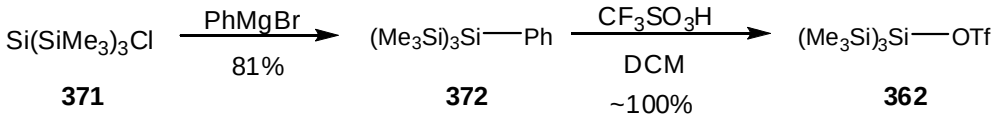
With the diazo amide in hand, attention then turned to the silylation reaction (Scheme 94). Following the Regitz protocol diazo amide **363** was treated with triflate **362** to afford α-silyl diazo carbonyl compound **360** in 34% yield, with a significant amount of impurities also observed.



Scheme 94

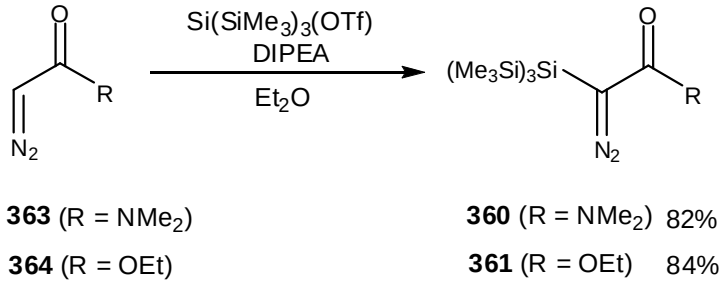
The α-silyl diazo amide **360** was confirmed by analysis of the IR spectrum which showed a signal at 2040 cm^{-1} corresponding to the diazo function. In addition, the ^1H NMR spectrum clearly indicated the disappearance of the signal attributed to the α-proton at δ_H = 9.63 ppm and the appearance of a signal corresponding to $Si(SiMe_3)_3$ group at δ_H = 0.24 ppm.

The low yield and purity of the product was attributed to the use of low quality silyl triflate **362**. Since impurities could affect the silene formation, an alternative source of the triflate was required. A survey of the literature revealed that Uhlig synthesised silyl triflates from the corresponding phenylsilanes.[106] Following this procedure, silyl triflate **362** was prepared with high purity and in very good yield (Scheme 95).



Scheme 95

With this reagent, reaction with amide **363** proceeded as planned to give the desired silyl amide **360** in very good yield (Scheme 96). In a similar manner diazo ester **361** was prepared from commercially available ethyl 2-diazoacetate **364** in 84% yield.



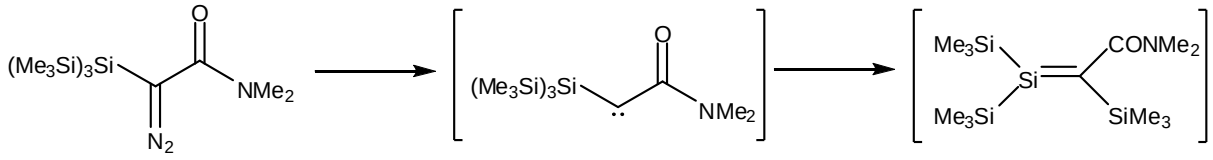
Scheme 96

The formation of silyl diazo ester **361** was confirmed by analysis of the IR spectrum, which showed a signal at 2071 cm^{-1} coupled with a peak at δ_H = 0.23 ppm in the ^1H NMR spectrum corresponding to $Si(SiMe_3)_3$ group.

3.4 Reactivity studies

3.4.1 Silyl diazo amide

With the silyl diazo carbonyl compounds in hand, the next stage was to attempt the formation of the corresponding silene species. Based on the computational work, initial attention turned to the use of amide **360** (Scheme 97). It was thought that transition metal-catalysed decomposition of diazo amide could be ideal, since higher temperature and photochemical methods are known to promote the silene-ketene rearrangement. Consequently a range of metal complexes were examined. In the work described below, all catalytic reactions were undertaken using similar conditions. To a solution of catalyst was added a solution of the diazo compound and trapping agent over a period of three hours. After an additional hour the solvent was evaporated and the residue examined by NMR and MS.



360 **373** **374**

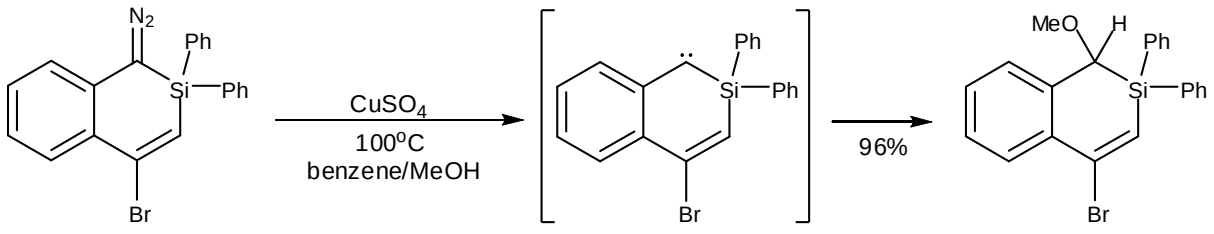
Scheme 97

Table 14 summarises the attempted silene generation in the presence of various trapping agents. Copper (I) triflate was tested first, as this is one of the most commonly used catalysts to generate intermediate carbenes. Surprisingly, this catalyst led to the formation of an intractable mixture of products (entry 1-3). Decomposition of the starting material did not occur with the catalyst in the presence of diethyl amine, probably due to the formation of the catalytically inactive complex with the amine (entry 4). Sadly, the other tested catalysts failed to produce any evidence for the silene species under the conditions examined (entry 5-12).

entry	catalyst (5-10%)	trapping agent	solvent	outcome
1	CuOTf	MeOH	PhH	intractable mixture
2	CuOTf	2-methyl-2-butene	PhH	intractable mixture
3	CuOTf	Phenylacetylene	PhH	intractable mixture
4	CuOTf	Et_2NH	PhH	starting material
5	$Cu(OAc)_2$	styrene	DCM	starting material
6	$Cu(tfacac)_2$	styrene	DCM	intractable mixture
7	$Cu(acac)_2$	styrene	DCM	intractable mixture
8	$Cu(acac)_2$	$PhCH_2OH$	DCM	intractable mixture
9	$Rh_2(pfb)_4$	Phenylacetylene	PhH	starting material
10	$Rh_2(OAc)_4$	Phenylacetylene	PhH	starting material
11	$Rh_2(tfa)_4$	Phenylacetylene	PhH	intractable mixture
12	$Pd(acac)_2$	Phenylacetylene	PhH	starting material

Table 14

It appears that some catalysts ($Pd(acac)_2$, $Rh_2(OAc)_4$, $Cu(OAc)_2$) are not sufficiently active to generate the intermediate carbene from the compound **360** at room temperature. A search of the literature revealed that Sekiguchi had found that elevated temperatures are sometimes needed to activate the catalyst (Scheme 98). For example, copper-catalysed decomposition of diazo compound **375** required heating at 100 ^oC to afford carbene **376** which underwent a simple O-H insertion reaction with methanol in 96% yield.



375 **376** **377**

Scheme 98

Following Sekiguchi's observation, a few catalysts were tested at elevated temperature (Table 15). The reactions were carried out in toluene in the presence of phenylacetylene. Unfortunately it was found that both the palladium and rhodium catalysts are unstable at higher temperature (entry 1, 2). In contrast, a small increase in the temperature (to 40 ^oC) in the case of the copper catalyst led to the formation of complex mixture of products (entry 3).

entry	catalyst	temp (^oC)	time (h)	outcome
1	$Pd(acac)_2$	90	0.5	starting material
2	$Rh_2(OAc)_4$	90	0.5	starting material
3	$Cu(OAc)_2$	40	2	intractable mixture

Table 15

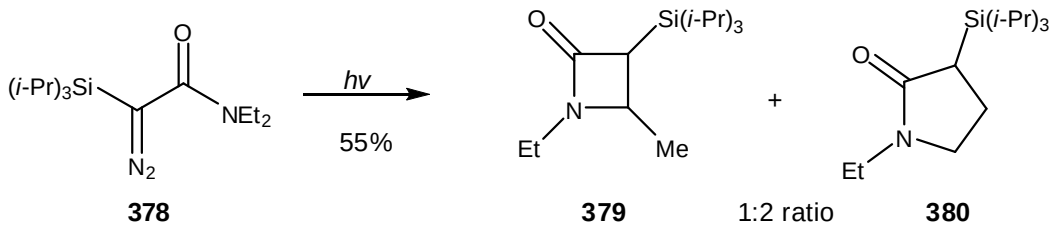
Subsequently, photochemical and thermal extrusion of N_2 from diazo compound **360** was investigated (Table 16). When the diazo compound was heated in toluene at reflux for 24 h, a complex mixture of products was obtained (entry 1). A similarly complex mixture of products was isolated when the reactions were performed at higher temperatures and for shorter periods of time under microwave conditions (entry 2-4). Sadly all the photochemical reactions were also equally unsuccessful and gave unidentified mixtures of products (entry 5-9).

entry	method	trapping agent	solvent	temp (^oC)	time (h)
1	flask	MeOH	PhH	110	24
2	microwave	MeOH	PhH	180	0.5
3	microwave	Et_2NH	PhH	180	0.5
4	microwave	2-methyl-2-butene	PhH	180	0.5
5	*hv*[a]	2-methyl-2-butene	PhH	RT	0.5
6	*hv*[a]	phenylacetylene	PhH	RT	0.5
7	*hv*[a]	MeOH	Et_2O	RT	0.5
8	*hv*[a]	MeOH	MeOH	RT	0.5
9	*hv*[a]	-	PhH	RT	0.5

[a]100W medium pressure Hg lamp.

Table 16

At this stage, it was proposed that the amide group may interfere with the silene formation. This could be related to carbene/metal carbenoid C-H insertion reactions. For instant, Maas has shown that photolysis of silyl diazo amide **378** leads to the formation of β and γ-lactams (Scheme 99).[107]



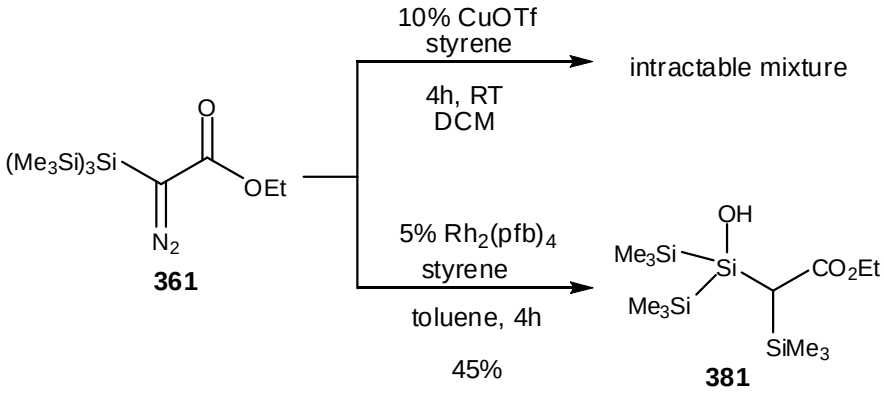
378 **379** 1:2 ratio **380**

Scheme 99

3.4.2 Silyl diazo ester

3.4.2.1 Decomposition of diazo ester

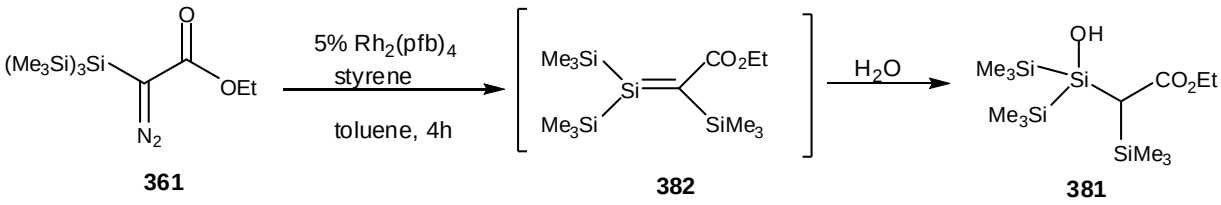
As in the above studies, metal-catalysed decomposition of diazo compound **361** was investigated first (Scheme 100). As before, attempted silene generation in the presence of copper (I) triflate led to the formation of an intractable mixture of products. In contrast, the reaction with $Rh_2(pfb)_4$ yielded the silyl alcohol **381**.



Scheme 100

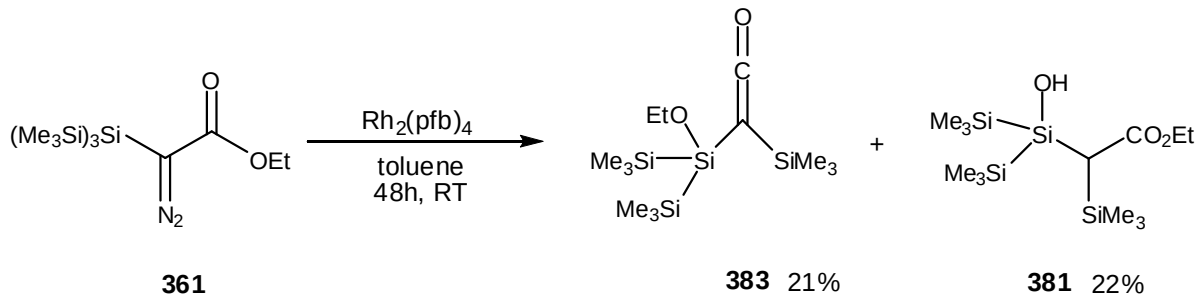
Formation of the product was confirmed by analysis of the IR and NMR spectra. The IR spectrum showed a characteristic signal at 3340 cm^{-1} corresponding to the hydroxyl group. The ^{29}Si NMR spectrum showed signals at δ_{Si} = 9.0 ppm, δ_{Si} = 3.8 ppm, δ_{Si} = -18.1 ppm and δ_{Si} = -18.2 ppm attributed to the Si-OH silicon, α-TMS group and two TMS groups bonded to silicon respectively. In addition, the formation of **381** was supported by mass spectrometry indicating molecular ions at m/z = 373 $[M+Na]^+$.

Although silanol **381** was not the desired silene [2+2] cycloadduct with styrene, its formation could be explained by the addition of water to the intermediate silene **382** (Scheme 101).



Scheme 101

As described in Chapter 1, Section 1.3.3.3, silenes derived from diazo esters tend to rearrange to the corresponding ketenes. Therefore, isolation of the ketene would indirectly provide further evidence for the presence of intermediate silene **382**. It was hypothesised that extension of the reaction time would lead to the formation of the corresponding ketene. Consequently, the following experiment was conducted to attempt the isolation of ketene **383** (Scheme 102). To a solution of the catalyst in dry toluene was added a solution of diazo compound **361**. The reaction mixture was stirred at RT for 48 h. Purification by flash column chromatography gave the product **383** in 21% yield and the product **381** in 22% yield.

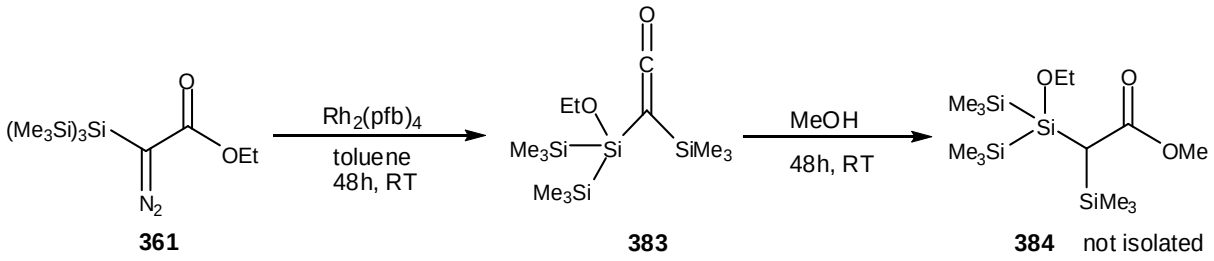


361 **383** 21% **381** 22%

Scheme 102

The ketene **383** was isolated in low yield due to its air sensitivity. Key evidence for the formation of the ketene was found in the IR spectrum where a signal corresponding to the cummulene group was observed at 2069 cm^{-1}. In addition, the ^1H NMR spectrum showed two signals for the TMS group at δ_H = 0.26 ppm (9H) and δ_H = 0.25 ppm (18H). The appearance of product **381** indicates the presence of water in the reaction mixture.

In order to produce further evidence for the ketene attempts were made to trap unstable ketene **383** with methanol (Scheme 103). To a solution of the catalyst was added a solution of diazo compound **361**. After stirring for 48 h, 2 equivalents of methanol were added and the reaction mixture was stirred for a further 48 h. This gave the expected product **384**, albeit accompanied by a significant amount of impurities. Disappointingly, all attempts to purify the product on silica and neutral alumina were unsuccessful.



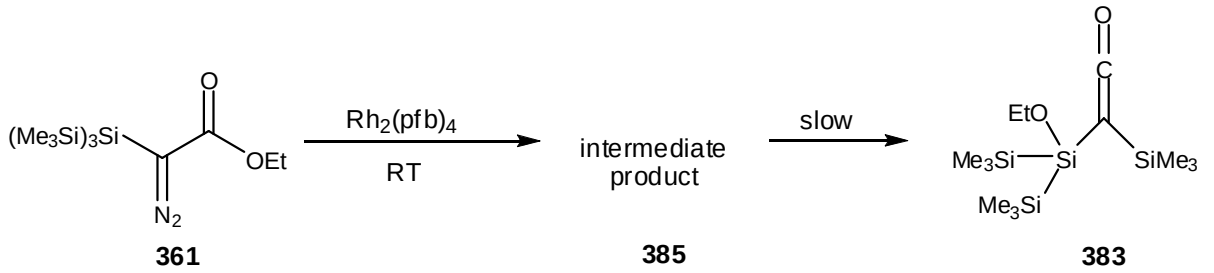
361 **383** **384** not isolated

Scheme 103

Formation of **384** was confirmed by analysis of the ^{1}H NMR and MS data, which showed a peak at δ_H =3.59 ppm characteristic of the methoxy protons along with a mass spectrum showing the molecular ion to have *m/z* = 364.

3.4.2.2 Intermediate product

As described in the previous section, the formation of silyl alcohol **381** and ketene **383** provide only indirect evidence for the formation of the intermediate silene species. Therefore, further studies were conducted to get additional information about the extrusion of N_2 from diazo compound **361**. Initial studies focused on identification of reaction intermediates by undertaking a reaction in an NMR tube and monitoring the reaction progress using ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy (Scheme 104).



361 **385** **383**

Scheme 104

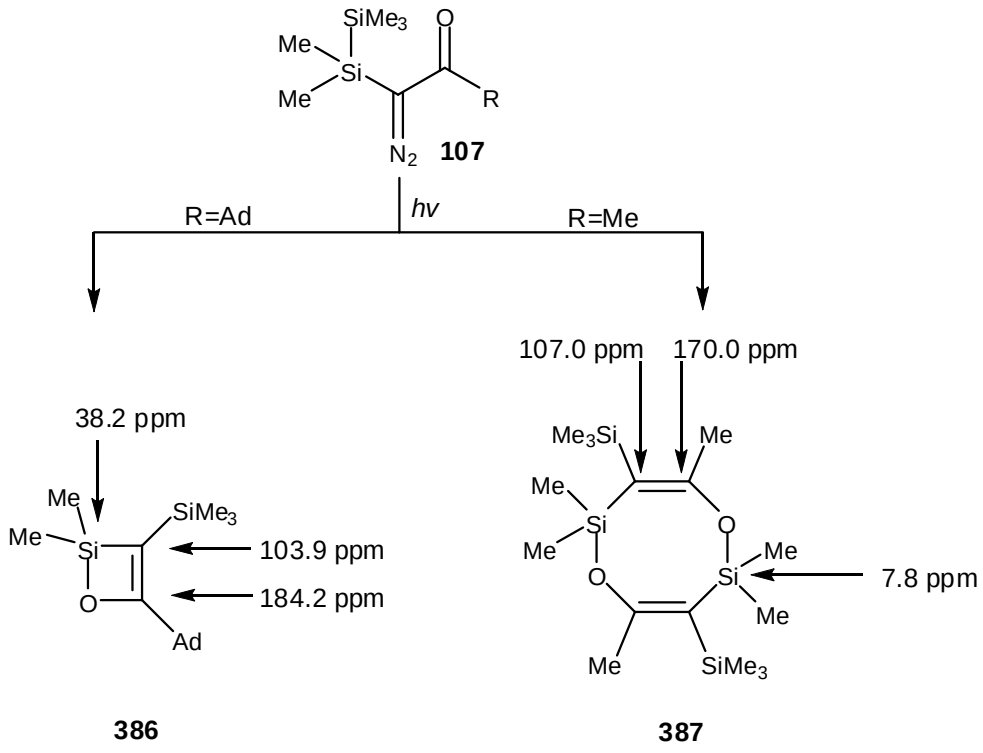
Through this it was possible to observe an intermediate product **385** in addition to the expected ketene **383** by NMR spectroscopy. It was found that full conversion of the diazo compound **361** in to the intermediate product **385** was achieved after approximately 25 min at room temperature. This product then slowly decomposes to form ketene **383**. The NMR data for the intermediate product are presented in Table 17.

NMR[a]	Data
^{1}H (ppm)	4.02 (2H, q, *J* = 7.2Hz, C***H***$_2$CH$_3$), 1.04 (1H, t, *J* = 7.2Hz, CH$_2$C***H***$_3$), 0.32 (9H, s, Si(C***H***$_3$)$_3$), 0.23 (18H, s, Si(C***H***$_3$)$_3$)
^{13}C (ppm)	161.1, 67.0, 62.8 (***C***H$_2$C*H*$_3$), 15 (CH$_2$***C***H$_3$), 1.4 (Si(***C***H$_3$)$_3$), -2.1 (Si(***C***H$_3$)$_3$)
^{29}Si (ppm)	35.6, -15.3, -17.1

[a]Since the intermediate product has a longer lifetime at lower temperatures all the NMR spectra were recorded at -80 ^{o}C.

Table 17

The ^{29}Si NMR spectrum showed a signal at δ_H = 35.6 which could be assigned to the C=***Si*** silicon. However, the signal which could correspond to the **C**=Si carbon was not observed in the ^{13}C NMR spectrum. In addition, it also appeared from the number of signals in the ^{1}H, ^{13}C and ^{29}Si NMR spectra that the intermediate compound was symmetrical or could easily interconvert between conformers on the NMR time scale. Consequently, the NMR data clearly showed that intermediate compound **385** was not the silene. Subsequently, it was suggested that compound **385** could be a product of silene dimerisation or intramolecular cycloaddition. A survey of the literature revealed that Maas has reported the formation of adduct **386** and dimer **387** during the photolysis of silyl diazo ketone **107** (Scheme 105). [108]



Scheme 105

Comparison of the NMR data shown in Scheme 105 with that obtained for compound **385** suggested that the structure of the intramolecular adduct was more probable (Figure 18). The shift of the ring silicon and the ***C***-4 carbon atom is similar to that reported for compound **386**. Furthermore, the large shift difference between ***C***-3 of **385** and ***C***-3 of **386** is expected as the presence of an ethoxy group at the ***C***-4 position in compound **385** will significantly shield the ***C***-3 carbon (compare **386**[109] and **389**[110]).

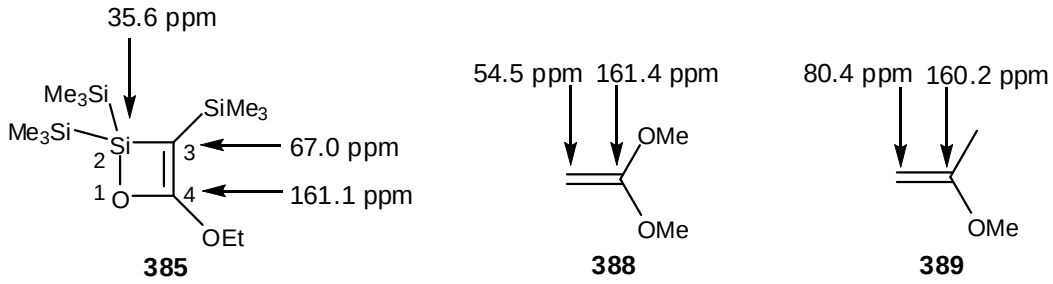
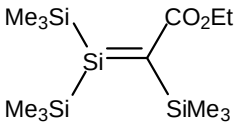


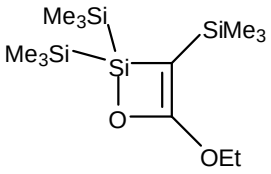
Figure 18

In order to provide further confirmation of the structure, calculations were undertaken to predict the ^{1}H, ^{13}C and ^{29}Si NMR spectra of silene **382**, oxasilete **385** and dimer **390**. In general, the chemical shifts are calculated more accurately with ab initio methods which include explicitly electron correlation, such as CCSD and MP2.[111] However, these methods are limited to relatively small molecules due to the prohibitively long CPU time and large disk space demands of such calculations. Consequently a DFT method was used to predict the chemical shifts.

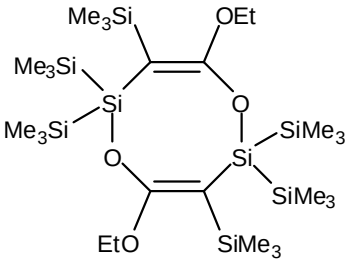
Table 18 summarises the calculated NMR shifts for silene **382**, oxasilete **385** and dimer **390** obtained using Gaussian 03. Geometries of these molecules were optimised using the hybrid density functional method B3LYP with the 6-31G(d) basis set. Vibrational analyses were performed on all fully optimised structures to ensure the absence of negative vibrational frequencies. For the calculation of the NMR shift the gauge-including atomic orbital method was used (GIAO) with the B3LYP and BPW91 hybrid functionals.



382



385



390

Silene 382

Method	NMR		
	^{1}H	^{13}C	^{29}Si
B3LYP/ 6-31G(d,p)	4.1 (C***H***$_2$), 1.3 (C***H***$_3$), 0.4/0.4/0.2 (Si(***C******H***$_3$))	167.5 (***C***=O), 157.4 (Si=***C***), 60.5 (***C***H$_2$), 15.2 (***C***H$_3$), 3.5/2.7/1.3 (Si(***C***H$_3$))	246.2 (***Si***=C), 7.2/2.3/-1.2 (***Si***(CH$_3$)$_3$)
BPW91/ 6-31G(d,p)	4.1 (C***H***$_2$), 1.3 (C***H***$_3$), 0.4/0.4/0.2 (Si(***C******H***$_3$))	167.6 (***C***=O), 156.4 (Si=***C***), 60.7 (***C***H$_2$), 15.3 (***C***H$_3$), 3.5/2.7/1.3(Si(***C***H$_3$))	244.2 (***Si***=C), 4.8/-0.5/-2.2 (***Si***(CH$_3$)$_3$)
B3LYP/aug-cc-pvDZ	4.1 (C***H***$_2$), 1.3 (C***H***$_3$), 0.4/0.3/0.2 (Si(***C******H***$_3$))	175.3 (***C***=O), 158.3 (Si=***C***), 61.5 (***C***H$_2$), 15.4 (***C***H$_3$), 2.8/2.5/1.5(Si(***C***H$_3$))	225.9 (***Si***=C), 8.0/-0.6/-2.5 (***Si***(CH$_3$)$_3$)

Oxasilete 385

Method	NMR		
	^{1}H	^{13}C	^{29}Si
B3LYP/ 6-31G(d,p)	4.3 (C***H***$_2$), 1.2 (C***H***$_3$), 0.2/0.2/0.0 (Si(***C******H***$_3$))	157.4 (***C***-4), 63.3 (***C***-3), 61.5 (***C***H$_2$), 15.2 (***C***H$_3$), 1.4/-1.4/-1.4 (Si(***C***H$_3$))	73.1 (***Si***O), -7.1/-7.1 (Si***Si***(CH$_3$)$_3$), -11.8 (C***Si***(CH$_3$)$_3$)
BPW91/ 6-31G(d,p)	4.2 (C***H***$_2$), 1.2 (C***H***$_3$), 0.2/0.2/0.0 (Si(***C******H***$_3$))	157.1 (***C***-4), 63.0 (***C***-3), 61.6 (***C***H$_2$), 15.3 (***C***H$_3$), 1.4/-1.3/-1.3 (Si(***C***H$_3$))	71.6 (***Si***O), -9.0/-9.0 (Si***Si***(CH$_3$)$_3$), -12.3 (C***Si***(CH$_3$)$_3$)
B3LYP/aug-cc-pvDZ	4.3 (C***H***$_2$), 1.3 (C***H***$_3$), 0.2/0.1/0.0 (Si(***C******H***$_3$))	162.4 (***C***-4), 65.2 (***C***-3), 62.9 (***C***H$_2$), 15.8 (***C***H$_3$), 1.3/-0.7/-1.5 (Si(***C***H$_3$))	43.8 (***Si***O), -7.4/-6.8 (Si***Si***(CH$_3$)$_3$), -12.4 (C***Si***(CH$_3$)$_3$)

Dimer 390

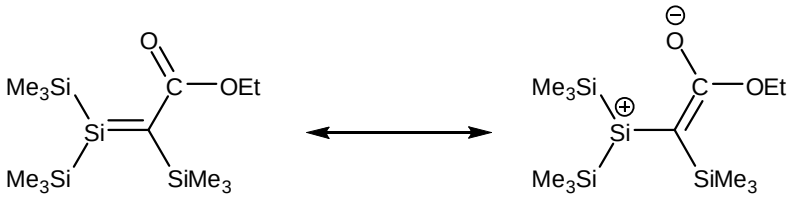
Method	NMR		
	^{1}H	^{13}C	^{29}Si
B3LYP/ 6-31G(d,p)	4.1 (C***H***$_2$), 1.3 (C***H***$_3$), 0.4/0.3/0.2(Si(***C******H***$_3$))	162.5 (SiC=***C***), 83.4 (Si***C***=C), 66.8 (***C***H$_2$), 15.8 (***C***H$_3$), 4.6/2.4/0.1 (Si(***C***H$_3$))	44.2 (***Si***O), 0.7 (C***Si***(CH$_3$)$_3$), -4.2/-2.3 (Si***Si***(CH$_3$)$_3$)
BPW91/ 6-31G(d,p)	4.1 (C***H***$_2$), 1.3 (C***H***$_3$), 0.3/0.3/0.2(Si(***C******H***$_3$))	162.5 (SiC=***C***), 83.5 (Si***C***=C), 67.0 (***C***H$_2$), 15.9 (***C***H$_3$), 4.6/2.5/0.1 (Si(***C***H$_3$))	41.6 (***Si***O),-0.7 (C***Si***(CH$_3$)$_3$), -6.3/-6.8(Si***Si***(CH$_3$)$_3$)
B3LYP/aug-cc-pvDZ	not calculated- too large molecule		

Table 18

It appears from the data presented in Table 18, that the computational method used has no significant effect on the calculated ^{1}H and ^{13}C chemical shifts. The ^{29}Si chemical shifts

calculated with B3LYP/aug-cc-pvDZ method are different to those calculated with the B3LYP/6-31G(d,p) and BPW91/6-31G(d,p) methods. This is mainly the effect of additional valence polarisation functions in the basis set, which has the biggest effect on heavy atoms.

Comparison of the NMR data in Table 17 with the data in Table 18 clearly support the suggestion that oxasilete **385** is the product of the diazo compound decomposition. The ^{13}C chemical shifts calculated with the B3LYP/aug-cc-pvDZ method for ***C***-3 (δ_C = 65.2 ppm) and ***C***-4 (δ_C = 162.4 ppm) are only slightly different from the corresponding experimental values (***C***-3 δ_C = 67.0 ppm; ***C***-4 δ_C = 161.1 ppm). Interestingly, the ^{29}Si calculations suggest that the doubly bonded silicon of silene **382** is significantly deshielded. This indicates a partial positive charge at Si is formed by electron delocalisation from the π-acceptor substituent at ***C*** (Scheme 106).



382 **391**

Scheme 106

Intrigued by the formation of oxasilete **385**, further studies were conducted to gain more understanding about the extrusion of N_2 from diazo ester **361**. As mentioned earlier, it was found that oxasilete **385** slowly rearranged to form ketene **383**. This can be easily followed by ^1H NMR spectroscopy by monitoring the change in integral for the methylene signal of the ethyl group (Figure 19).

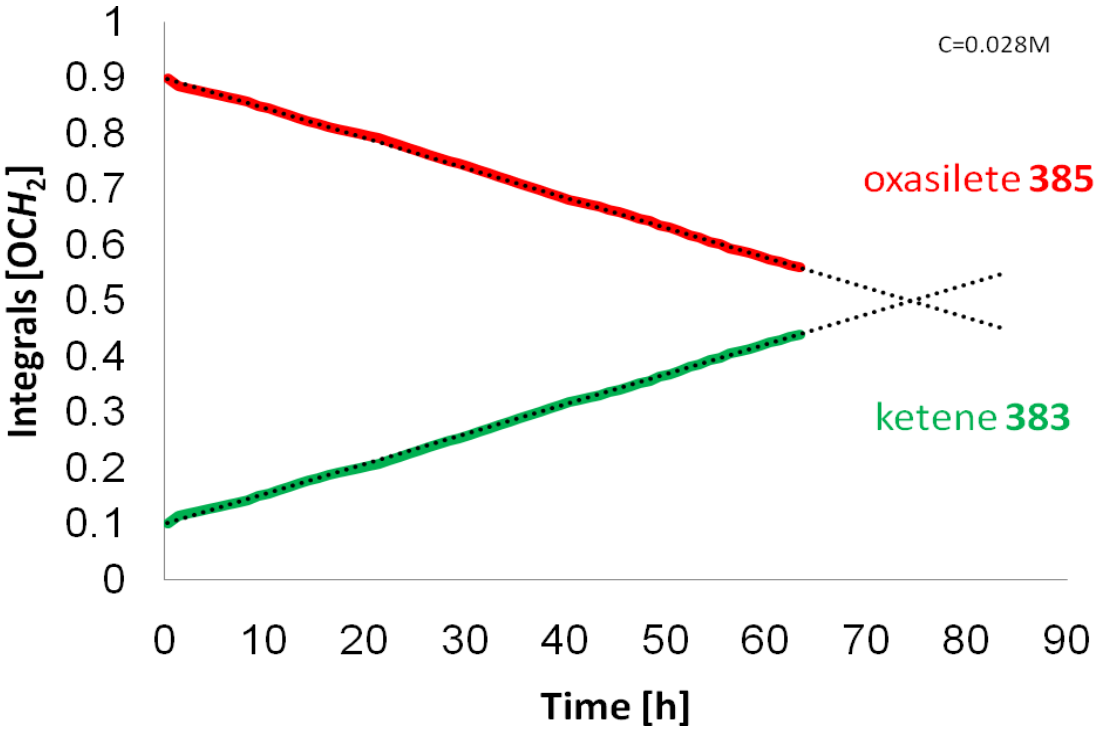
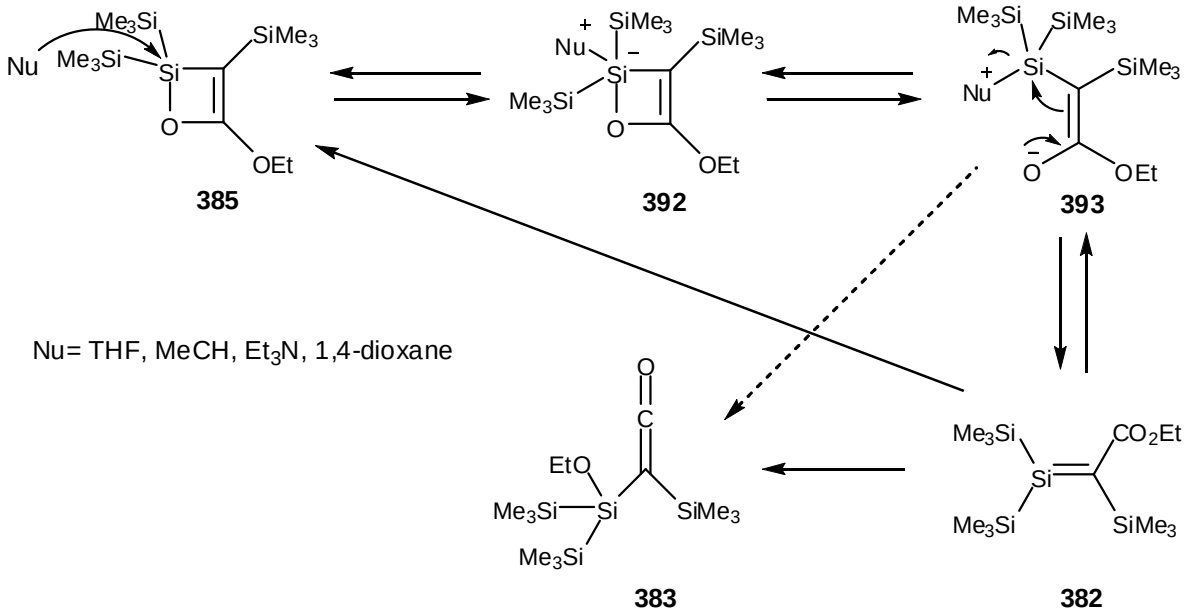


Figure 19

Interestingly, it was found that the rate of this rearrangement depends on the concentration of the reaction mixture. When a 0.11 M solution of diazo compound **361** was treated with $Rh_2(pfb)_4$ the expected oxasilate **385** was produced, but it was fully converted to the corresponding ketene **383** in approximately 24 h. In addition, it was found that additives such as 1,4-dioxane, THF, MeCN, Et_3N and pyridine significantly increase the rate of oxasilete-ketene rearrangement. Therefore, it was suggested that this rearrangement is promoted by weak nucleophiles and could involve a bimolecular process (Scheme 107).



Scheme 107

In general, silyl ketene acetals are quite stable, but in this case compound **385** is cleaved with weak nucleophiles such as THF or 1,4-dioxane because of the ring strain. Silene **382** can either reform oxasilete **385** or undergo isomerisation to ketene **383**. Since ketene formation appears to be irreversible, its concentration slowly increases. It is also plausible that intermediate **393** can rearrange directly to the ketene **383**.

3.4.2.3 Reaction pathway

To fully explain the outcome of the rearrangement of the carbene generated from diazo compound **361**, the mechanism of the isomerisation of a model carbene **353c** (Figure 20), was investigated using DFT calculations at B3LYP/6-31G(d)//B3LYP/6-31G(d) level. The copper carbenoid species was not considered, since this would involve more complicated calculations.

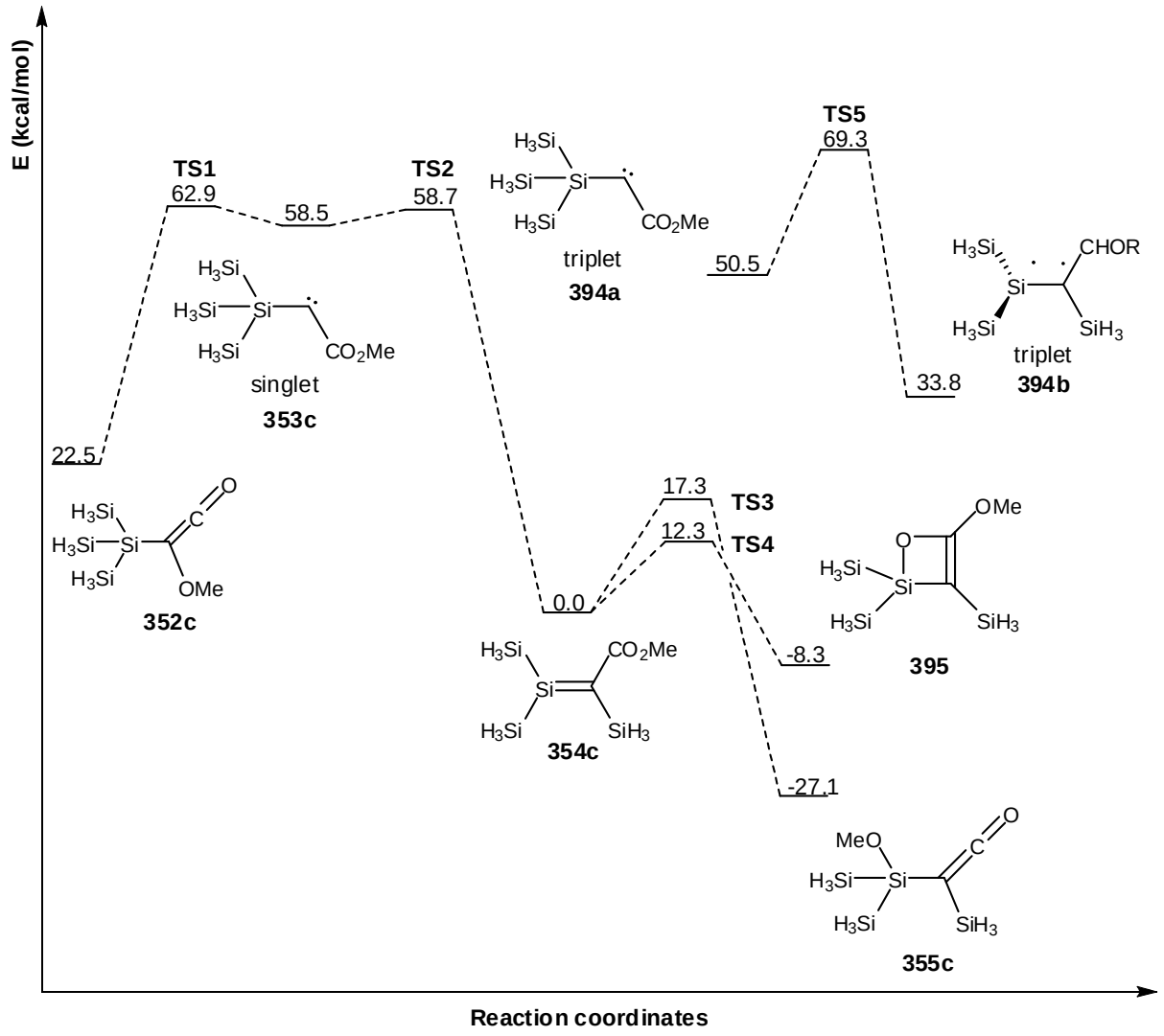


Figure 20

According to these calculations, the reaction starts with formation of singlet carbene **353c** which is less stable than the triplet state carbene **394a** by 8.0 kcal/mol. This is expected as silyl substituents stabilise the triplet ground state of a carbene.[3] The transition state leading to silene **354c** is separated from the carbene **353c** by 0.2 kcal/mol. The final products of the reaction are oxasilete **395** and ketene **355c**. The oxasilete **395** is formed preferentially since the transition state energy required for this transformation is only 12.3 kcal/mol. However, the ^{1}H NMR experiment showed that the silene-oxasilete transformation is reversible, thus eventually ketene **355c** is formed as it is the most stable molecule. The transition states for all transformations are shown in Figure 21.

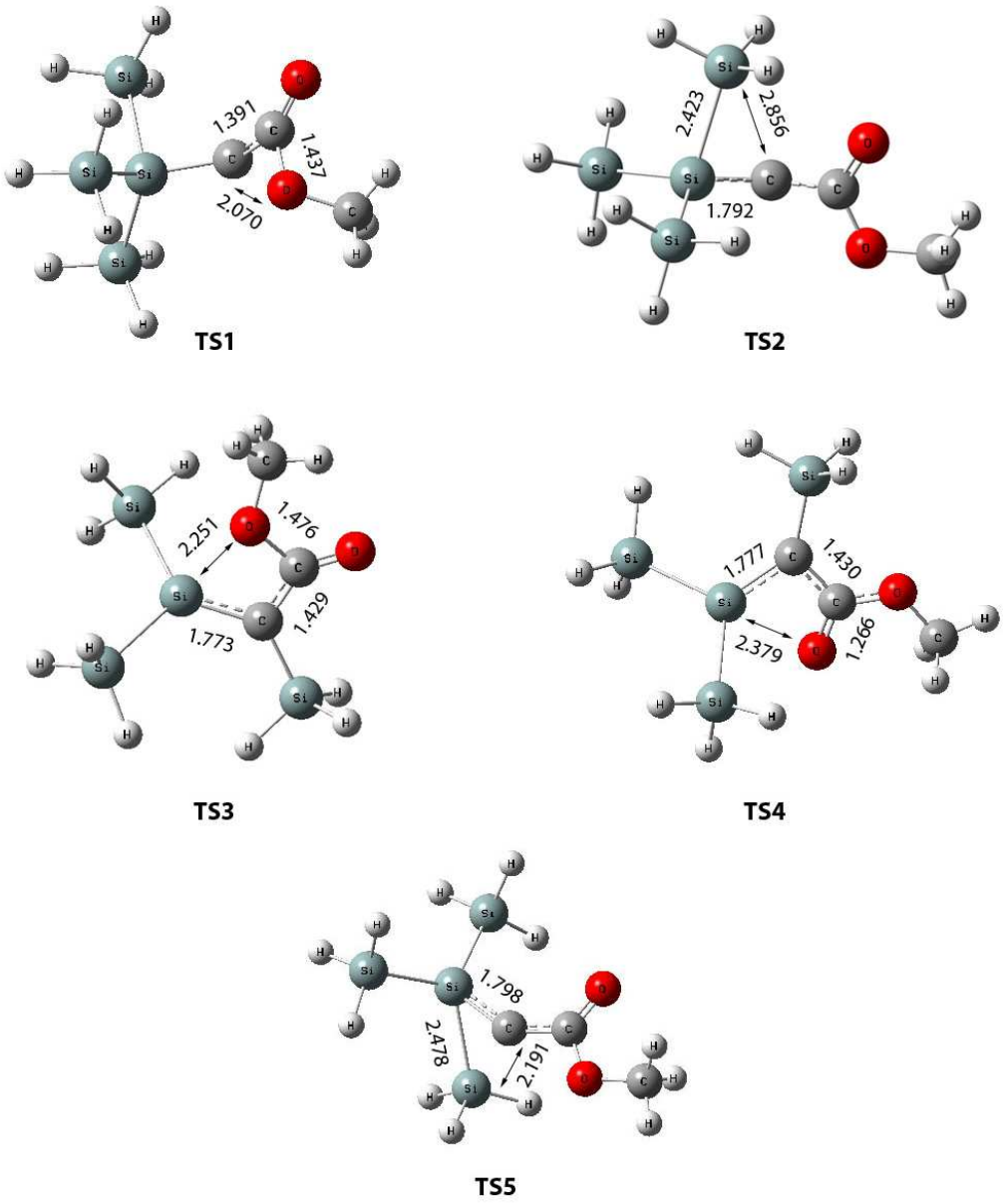
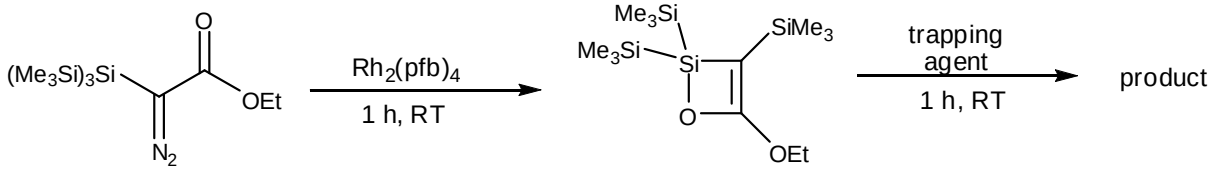


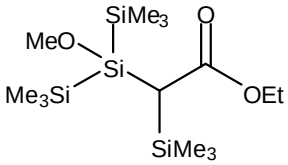
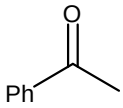
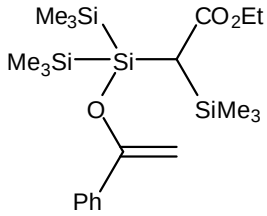
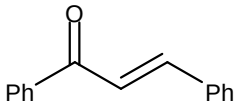
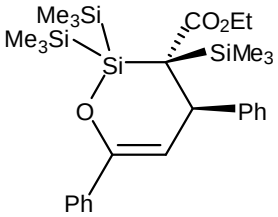
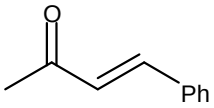
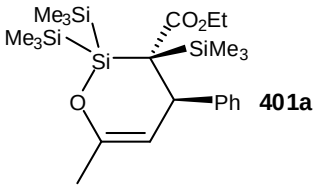
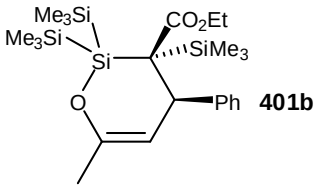
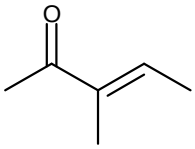
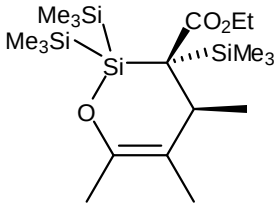
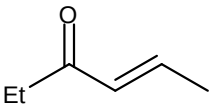
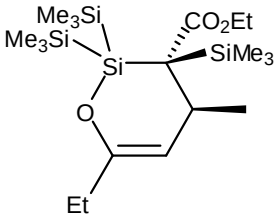
Figure 21

3.4.2.4 Further reactions

Disappointingly it was found that decomposition of the diazo compound **361** in the presence of styrene does not produce the expected [2+2] product. In addition, attempts to trap silene **382** with 2,3-dimethylbuta-1,3-diene, furan, 1-acetoxy-1,3-butadiene, and phenylacetylene had also proved to be unsuccessful. This suggests that silene **382** is too short lived and forms oxasilete **385** preferentially. Nevertheless, during the numerous attempts to trap silene **382** it was found that oxasilete **385** exhibits interesting reactivity (Table 19).



361 **385**

entry	trapping agent	product	yield (%)
1	MeOH	 **396**	43
2	 **397**	 **398**	25
3	 **257**	 **399**	51 (ds1)
4	 **400**	 **401a**  **401b**	**401a** 34 (ds 1) **401b** 18 (ds 1)[a] (crude ds 1:1)
5	 **402**	 **403**	56 (ds1)
6	 **404**	 **405**	47 (ds 1)

[a]Unstable diastereoisomer.

Table 19

It was found that oxasilete **385** forms adducts with methanol, acetophenone and α,β-unsaturated ketones. The formation of product **396** was supported by mass spectrometry showing a molecular ion at m/z = 365 $[M+H]^+$. In addition, the ^1H NMR spectrum showed a

signal attributed to the methoxy group at δ_H = 3.45 ppm. The formation of adduct **398** with acetophenone can most easily be detected from the presence of a pair of doublets at δ_H = 4.88 ppm (J = 2.8Hz) and δ_H = 4.40 ppm (J = 2.8Hz), corresponding to the vinyl protons. The acetophenone adduct is not stable to moisture and decomposes to form acetophenone and silanol **381** among other side products. Key evidence for the formation of adducts with α,β-unsaturated compounds was found in the ^{13}C NMR spectrum where signals corresponding to the ***C***-6 carbon were observed at around δ_C = 150 ppm and to ***C***-5 at around δ_C = 105 ppm. The configuration of the products could be deduced from the 2D correlation NMR experiments (Figure 22). ^{1}H NOESY experiments of the adduct **399** provide evidence that the Ph group is located *cis* to the adjacent TMS group and *trans* to the carboxyl group. Similarly, the configuration of the products **401a**, **401b**, **403** and **405** was deduced from the 2D correlation NMR experiments.

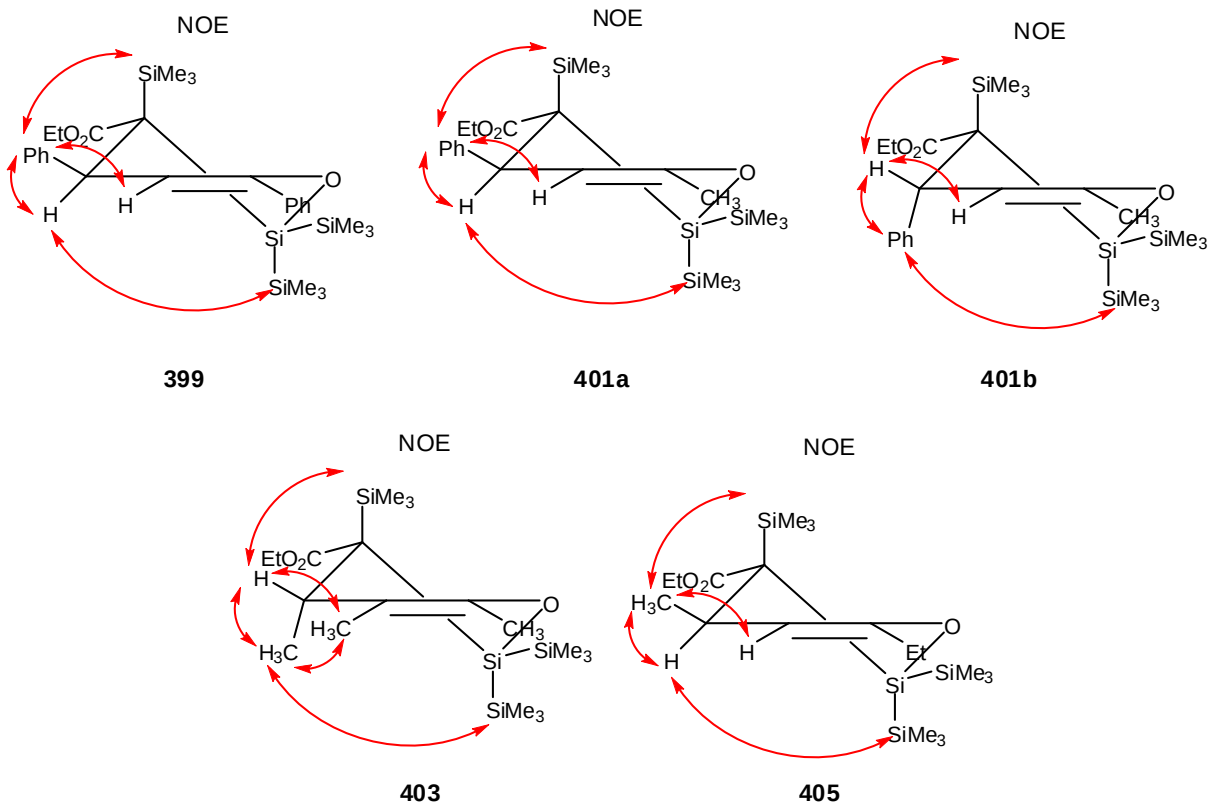
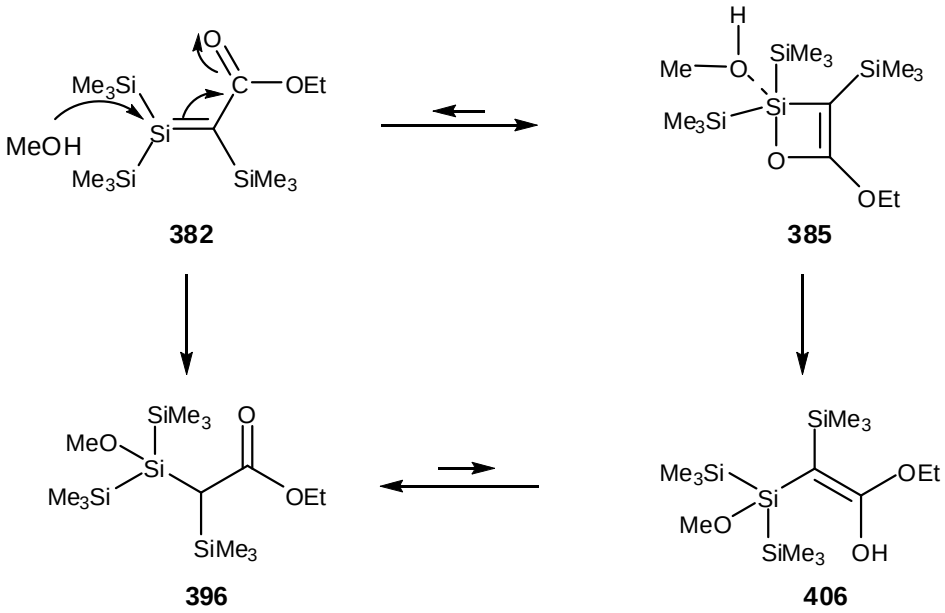


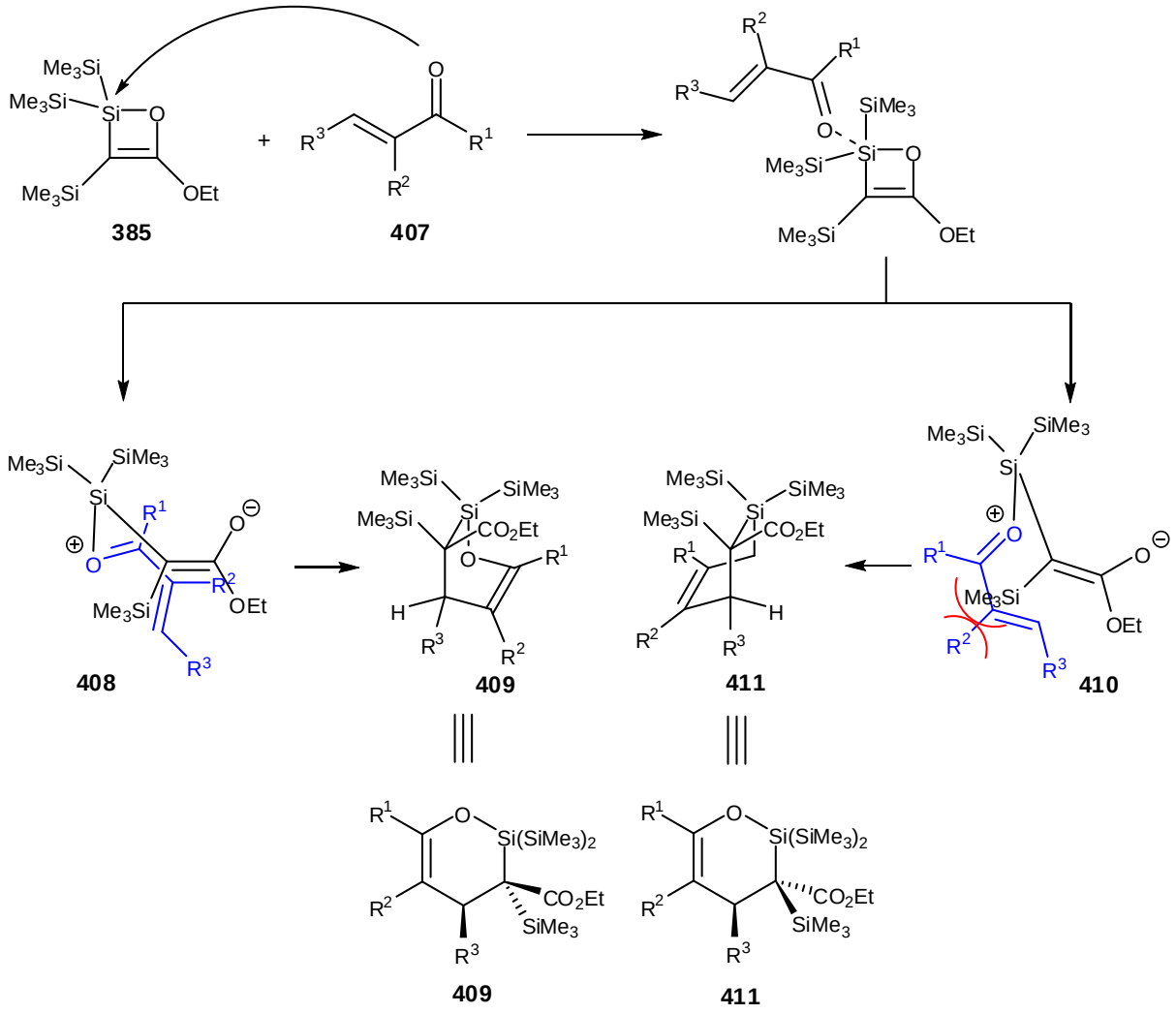
Figure 22

There are two possible explanations for the formation of adducts presented in Table 19. They can be a result of addition of trapping agents to oxasilete **385** or silene **382**. For example, addition of MeOH to oxasilete **385** or silene **382** would produce the same product **396** (Scheme 108).



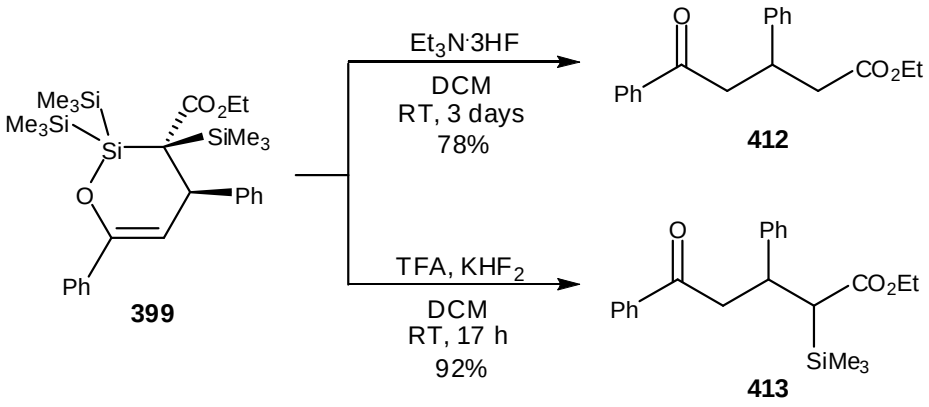
Scheme 108

With the exception of *trans*-benzylideneacetone, which afforded a mixture of diastereoisomers, all α,β-unsaturated ketones led to the preferential formation of one diastereoisomer (Table 19). It appears that the diastereoselectivity is mainly controlled by substituents R^1 and R^2 adjacent to the carbonyl group (Scheme 109). When R^2 is small and R^1 large then product **411** is favoured (entry 3 and 6). In addition, larger R^2 led to the preferential formation of product **409** (entry 5). It is hard, however, to explain the formation of diastereoisomers **401a** and **401b** (entry 4) with the model presented in Scheme 109 and further studies will be necessary to develop a full understanding of the mechanistic basis of the stereochemical course of these cycloadditions.



Scheme 109

The chemistry of adducts presented in Table 19 was not investigated in detail due to time constraints. However, it was found that the Si-C bond could be cleaved with a fluoride source (Scheme 110). When compound **399** was treated with triethylamine trihydrofluoride complex, 1,5-dicarbonyl compound **412** was isolated in 78% yield. In comparison, potassium hydrofluoride and trifluoroacetic acid led to formation of α-silyl ester **413** in 92% yield. These could represent useful building blocks for the generation of 1,5-dicarbonyl compounds.



Scheme 110

3.4.3 Silyl diazo amide vs silyl diazo ester

According to the DFT calculations described in section 3.2 of this chapter, the extrusion of N_2 from silyl diazo amide **360** and silyl diazo ester **361** should lead preferentially to the corresponding ketene. However, the experiments undertaken (Chapter 3, Section 3.4.2) showed that there is a significant difference in their chemical behaviour. Therefore, it was suggested that the calculation of the mechanism of carbene rearrangement could explain this observation. As before, the calculations were performed at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level for model carbene **353b** (Figure 23).

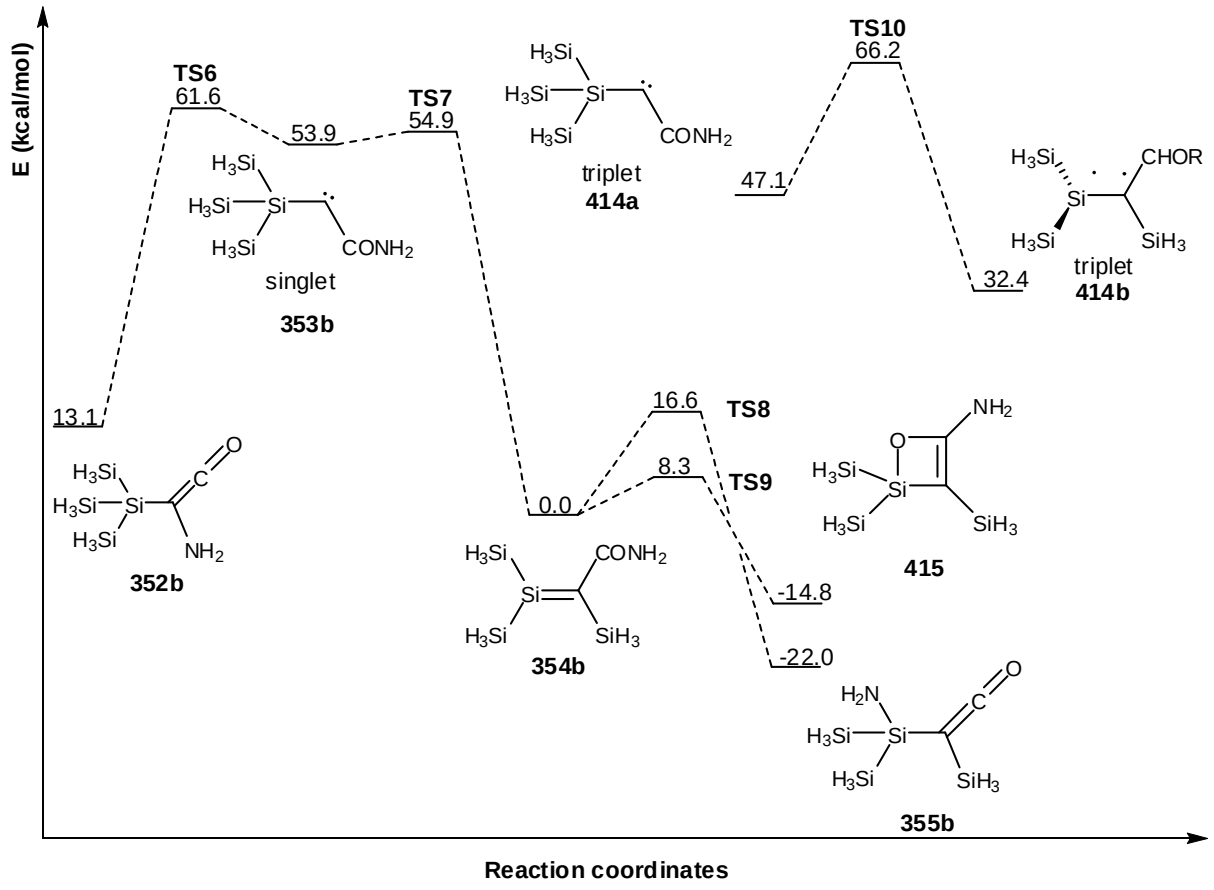


Figure 23

The transition state energy for transformation of **353b** to **352b** is 7.7 kcal/mol, and **352b** is 40.8 kcal/mol more stable than **353b**. However, this rearrangement is not likely to happen as carbene **353b** should more readily form the silene **354b**. In an analogous fashion to the ester carbene **353c**, **453b** can also isomerise to give the more stable triplet carbene **414a**. As can be seen in Figure 23, this silene can either form oxasilete **415** or ketene **355b**. The formation of **415** should be favoured as the transition state energy leading to this product is only 8.3 kcal/mol. The model ketene **355b** will be the final product if formation of oxasilete **415** is reversible. The transition states for all transformations are shown in Figure 24.

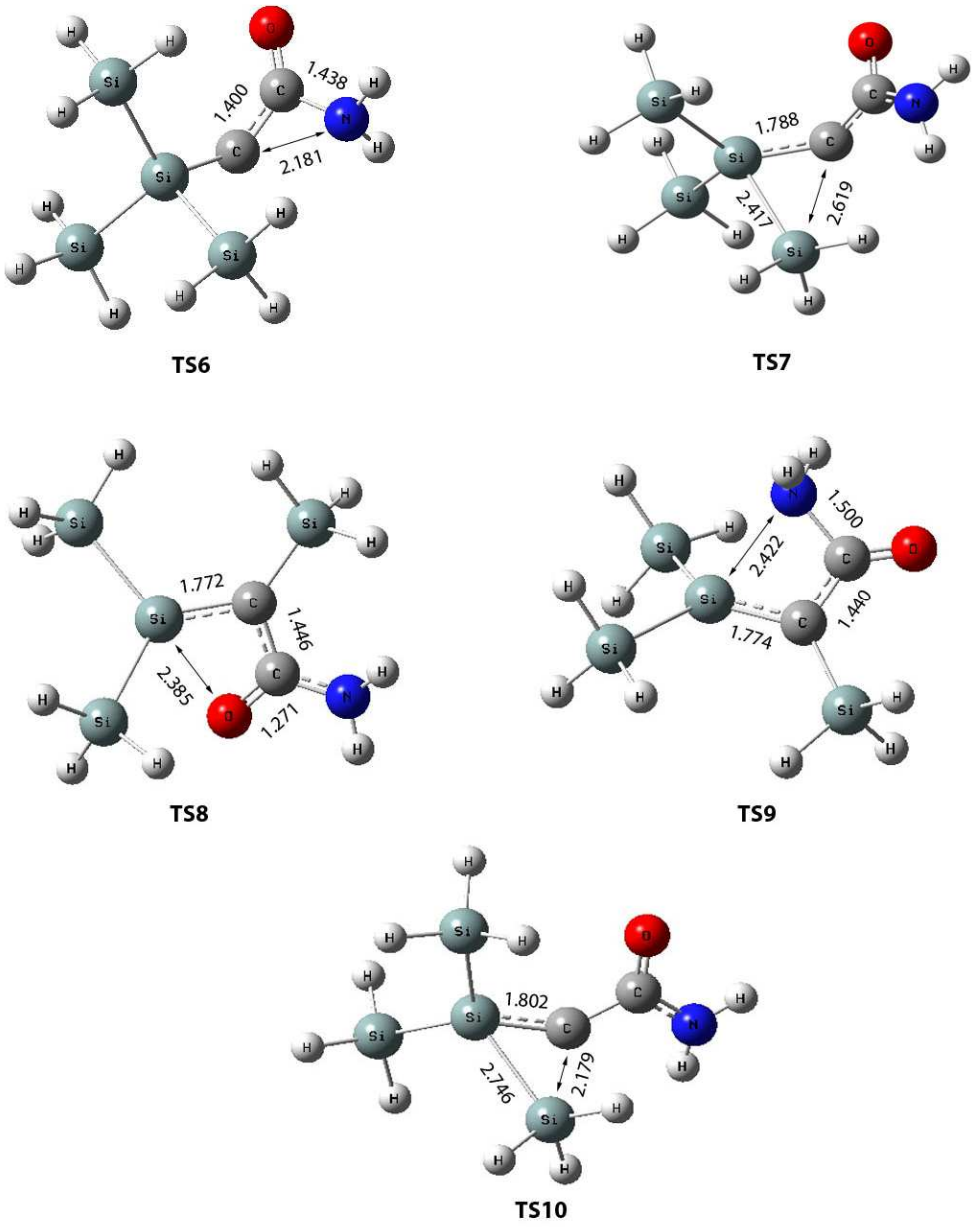
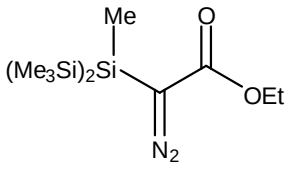


Figure 24

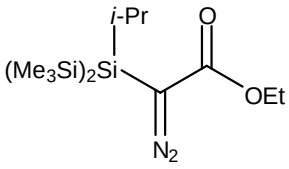
Unfortunately, these calculations did not provide any obvious reasons as to why extrusion of N_2 from silyl diazo amide **360** follows a different pathway to that of the ester **361**. One possibility is that there could be other reaction pathways which were not considered. For example, as mentioned in Section 3.4.1, the carbene generated from diazo compound **360** could undergo an C-H insertion reaction.

3.5 Effect of substituents

As described in Section 3.4 of this chapter, the decomposition of the diazo compound **361** in the presence of styrene, 2,3-dimethylbuta-1,3-diene, furan, 1-acetoxy-1,3-butadiene, and phenylacetylene did not produce the expected Diels-Alder cycloadduct. This suggests that silenes bearing an ester group on the silenic carbon do not react with alkenes, alkynes and dienes. A number of potential reasons for this can be proposed. These include the possibility that such 'cycloadditions' are sterically inhibited or that the rapid formation of the oxasilete 'protects' the silene. The latter possibility could be inhibited by creating steric bulk on the Si centre. To test these two competing proposals α-silyl diazo esters **416** and **417** were designed (Figure 25). The synthesis and reactivity of these esters is presented in the next section.



416

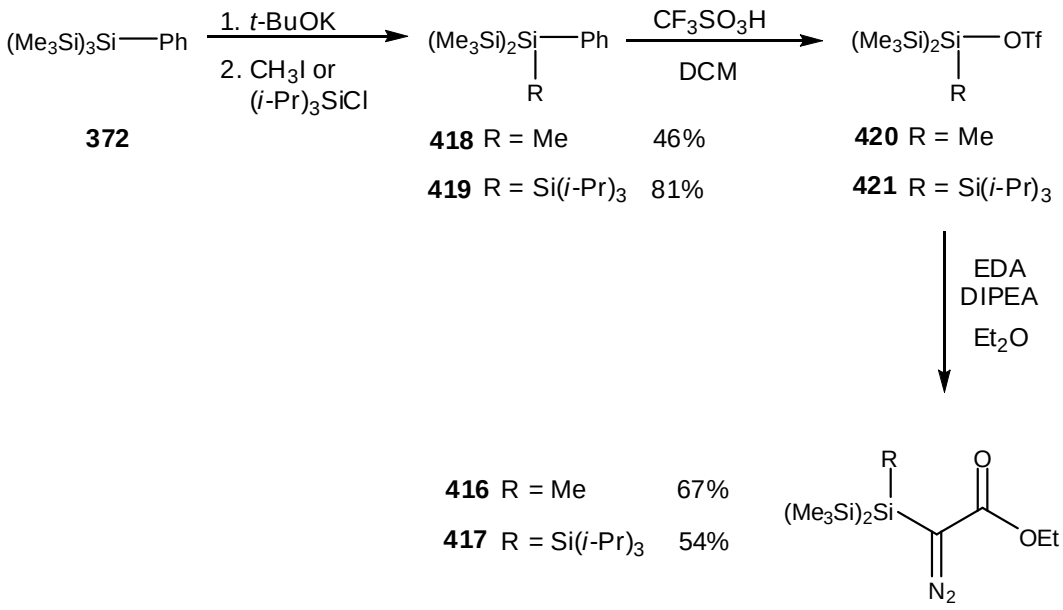


417

Figure 25

3.5.1 Synthesis of diazo esters

The synthesis began with the metalation of phenyltris(trimethylsilyl)silane **372** with *t*-BuOK followed by alkylation with methyl iodide or chlorotriisopropylsilane (Scheme 111). The resulting silanes were subsequently used to generate silyl triflates which were immediately combined with ethyl 2-diazoacetate to form silyl diazo esters **416** and **417**.

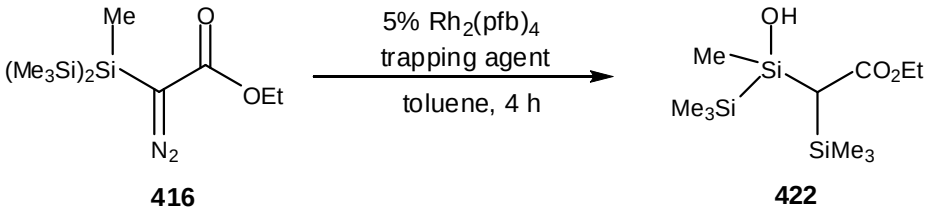


Scheme 111

As before, key evidence for the formation of the diazo compound **416** and **417** was obtained from the IR spectra. The IR spectrum showed a characteristic signal at 2075 cm^{-1} for **416** and 2069 cm^{-1} for **417** corresponding to the diazo function.

3.5.2 Reactivity studies

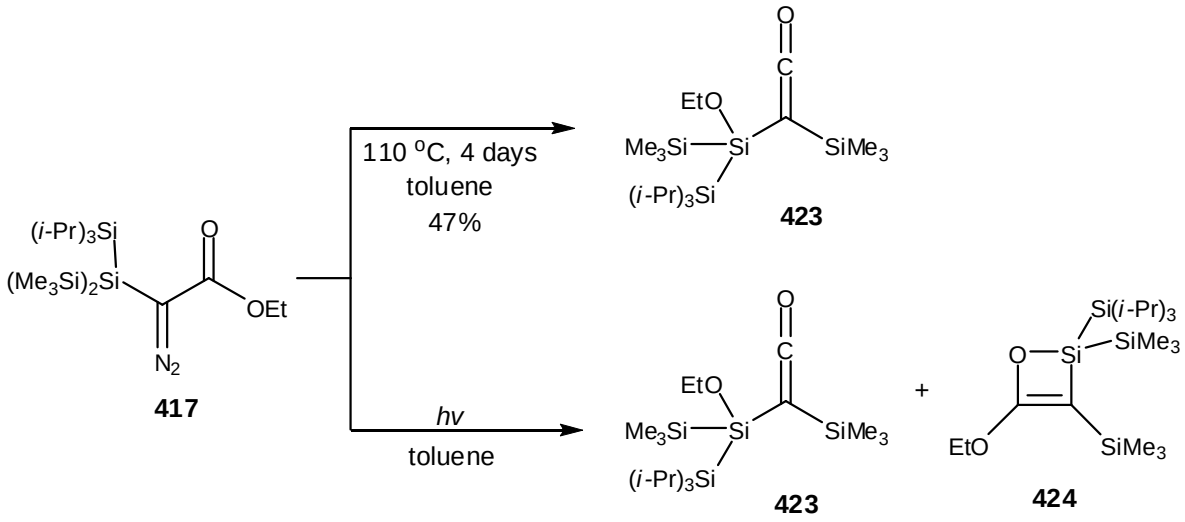
Initial work focused on the rhodium-catalysed decomposition of diazo ester **416** in the presence of various trapping agents such as cyclopentadiene, styrene and phenylacetylene (Scheme 112). Unfortunately, in all cases only water adduct **422** was isolated which was formed during the reaction work-up.



Scheme 112

Subsequently, the extrusion of N_2 from diazo ester **417** was investigated. Surprisingly, no reaction was observed when diazo ester **417** was added to a solution of $Rh_2(pfb)_4$ in toluene. In addition, other catalysts such as CuOTf, $Cu(tfacac)_2$, CuI, $Rh_2(tfa)_4$ have also been found to

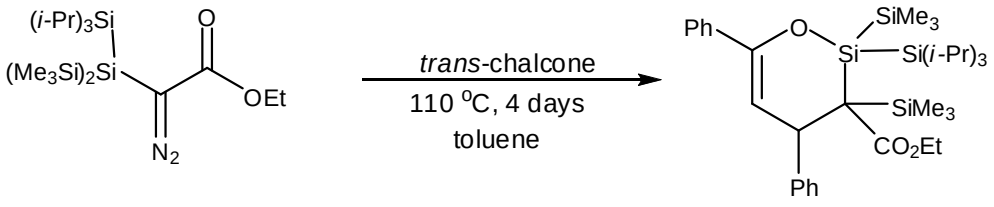
be inactive under the conditions used. This indicates that the $(i\text{-Pr})_3Si$ group effectively shields the diazo function from the catalyst. The lack of success in the decomposition of diazo ester **417** under catalytic conditions led to the investigation of thermal and photochemical techniques (Scheme 113). It was found that heating a solution of diazo ester **417** in toluene at 110 ^oC for 4 days led to the formation of corresponding ketene **423** in 47% yield. In comparison the reaction performed under photochemical conditions gave a mixture of oxasilete **424** and ketene **423** with significant amounts of impurities also observed.



Scheme 113

The formation of compound **423** was supported by the presence of a signal in the IR spectrum at 2069 cm^{-1} corresponding to the cummulene function. Interestingly in this case only one structural isomer of the ketene was detected, indicating that the $SiMe_3$ group migrates to the carbene carbon in preference to $(i\text{-Pr})_3Si$ group. Evidence for the formation of the oxasilete **424** was obtained from the ^{13}C and ^{29}Si NMR spectra. Compound **424** shows two characteristic signals in its ^{13}C NMR spectrum corresponding to the vinylic carbons at δ_C = 160.9 ppm and δ_C = 70.3 ppm. In addition ^{29}Si NMR shows a signal attributed to the ring silicon at δ_{Si} = 42.3 ppm.

Subsequently diazo ester **417** was decomposed thermally in the presence of trapping agents. It was found that the reaction carried out in the presence of phenylacetylene, styrene or 2,3-dimethylbuta-1,3-diene do not lead to the formation of any Diels-Alder product. On the other hand, the reaction performed in the presence of *trans*-chalcone **257** gave the expected [4+2] cycloadduct (Scheme 114). This, however, was unstable to purification by flash column chromatography.



417 **425**

Scheme 114

The formation of the adduct **425** with *trans*-chalcone can most easily be detected from the presence of a pair of doublets at δ_H = 5.91 ppm (J = 9.2Hz) and δ_H = 4.79 ppm (J = 9.2Hz) in the ^{1}H NMR spectrum, corresponding to the ring protons.

The above experiments confirm the hypothesis that silenes generated from silyl diazo esters do not react with alkenes, dienes and alkynes.

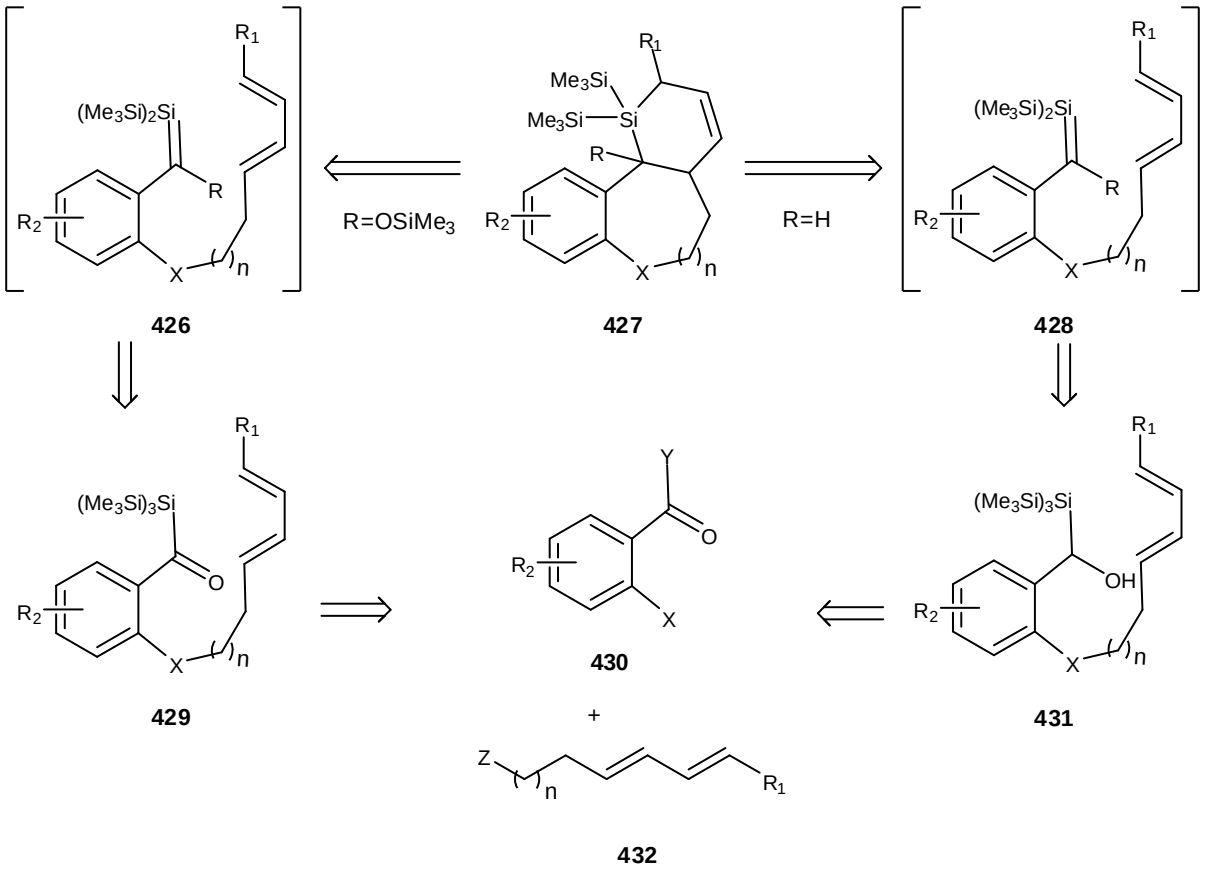
3.6 Conclusions

The extrusion of N_2 from α-silyl substituted diazo esters leads to a silylcarbene, which readily undergoes transformation in to the corresponding silene. However, this product is short-lived and forms an oxasilete, which appears to be the kinetically favourable product of this reaction. Prolonged reaction time leads to the formation of a thermodynamically stable ketene. Interestingly intermediate oxasilete can be trapped with α,β-unsaturated ketones in moderate yield and generally good diastereoselectivity. This could represent useful building blocks for the generation of 1,5-dicarbonyl compounds. In addition, it was found that silenes generated from diazo esters do not form [4+2] cycloadducts with dienes or [2+2] cycloadducts with alkenes and alkynes.

4 Intramolecular cycloaddition reactions

4.1 Introduction

As a part of the studies concerning the reaction of silenes with dienes, intramolecular silene cycloaddition reactions were examined. Surprisingly, such reactions are unknown in silene chemistry and, in addition to the synthetic applications, this thesis probes more theoretical aspects. It was expected that such intramolecular Diels-Alder reactions would give adducts in higher yields and diastereoselectivities than have been previously observed in intermolecular reactions (Section 2.6). To test this hypothesis the synthesis of cycloadduct **427** was proposed (Scheme 115). Initial studies focused on the synthesis of compound **427** via thermal rearrangement of acylpolysilane **429** and sila-Peterson reaction of silylalcohol **431** since those two methods are well established in the group.

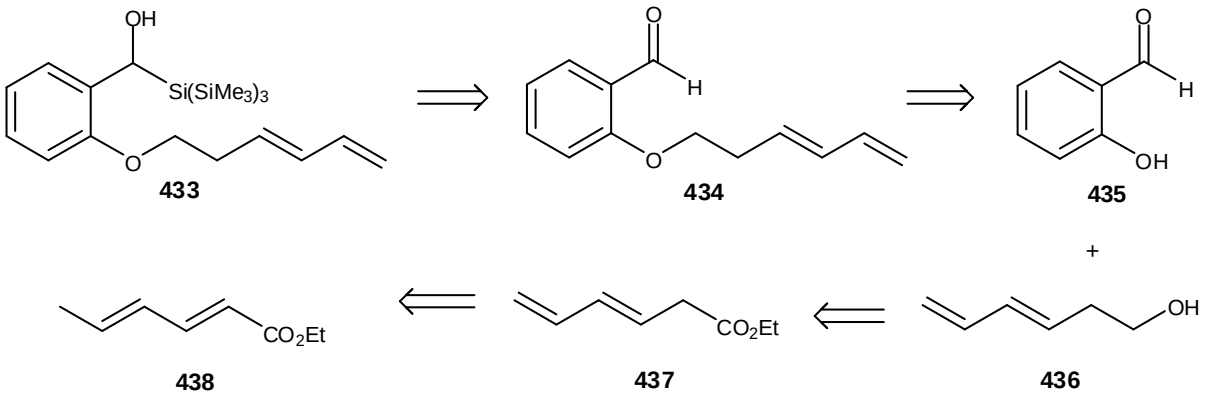


Scheme 115

Compound **427** was chosen as an initial target for a number of reasons. Firstly, the synthesis involves well known reactions and a wide range of aromatic carbonyl compounds with the required substitution pattern is commercially available. This would allow the quick synthesis of a library of acylpolysilanes and silyl alcohols needed for the investigation of the effect of substituents on the cycloaddition reaction. The aromatic ring in **426** and **428** restricts flexibility of the molecule and may therefore enhance efficiency and diastereoselectivity of the cycloaddition.

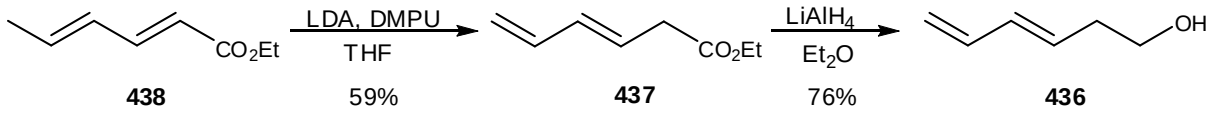
4.2 Sila-Peterson Reaction

Following this analysis the first approach explored the generation of the silene through a sila-Peterson reaction. The initial work involved the synthesis of silyl alcohol **433**. This was attempted by using the sequence of reactions shown in Scheme 116.



Scheme 116

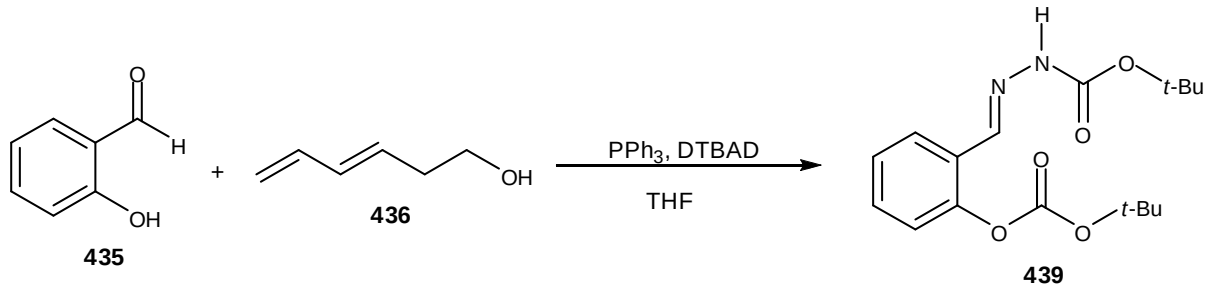
The alcohol **436** was prepared according to the literature procedure which involved deconjugation of commercially available ethyl sorbate **438** followed by reduction (Scheme 117).[112] The product was confirmed by analysis of the IR spectrum which showed a broad signal at 3326 cm^{-1} corresponding to the hydroxyl group, and ^{1}H NMR spectrum which contained peaks at δ_H = 6.33 ppm (ddd), δ_H = 5.14 ppm (d) and δ_H = 5.02 ppm (d) corresponding to the protons of the terminal double bond.



438 59% **437** 76% **436**

Scheme 117

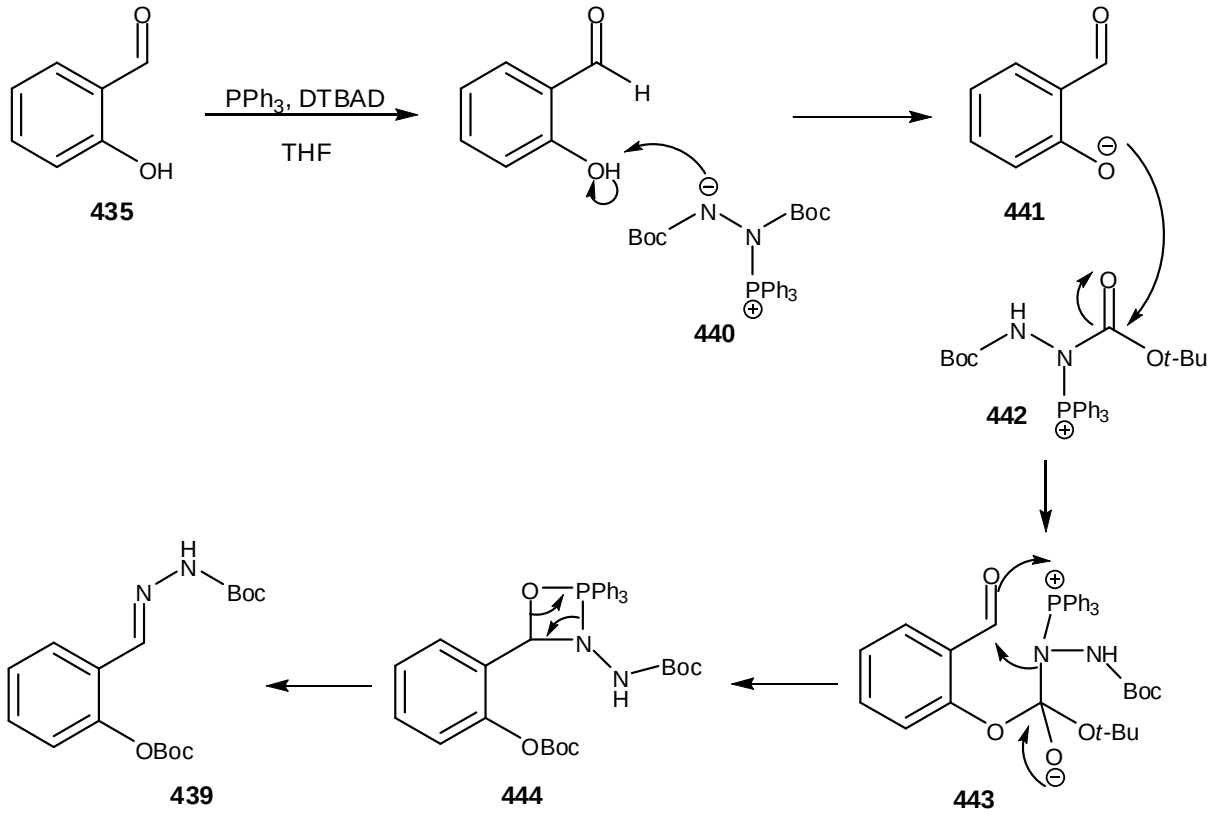
With the alcohol **436** in hand, attention turned to the coupling with salicylaldehyde. Hence, di-*tert*-butyl azodicarboxylate (DTBAD) was added to a solution of the alcohol and the reaction mixture was stirred for 24 h. Surprisingly, LCMS showed formation of hydrazone **439** (*m/z* = 359 (MNa^+)) instead of the expected ether **434** (Scheme 118).



435 **436** **439**

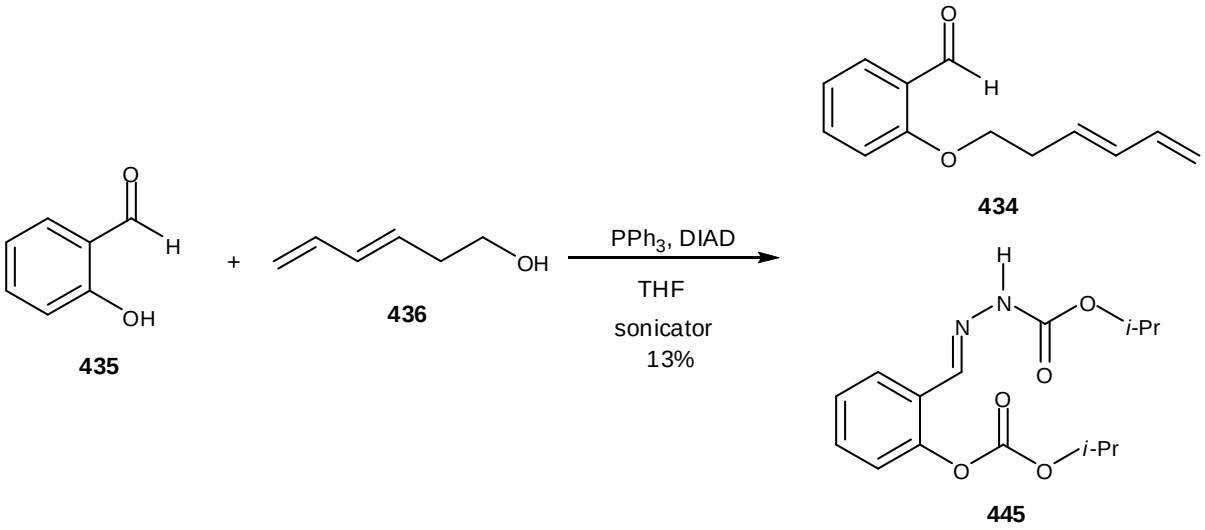
Scheme 118

A search of literature revealed that the particular problem of salicylaldehyde in the Mitsunobu reaction was described by the early work of Girard.[113] In this, ethers were not produced or were obtained only as minor products, when the phenol is substituted in its *ortho* position by a formyl group. Instead, hydrazones were obtained as the major products. These results were rationalised by the mechanism shown in Scheme 119. Initially, triphenylphosphine attacks DTBAD producing a betaine intermediate **440**, which deprotonates the phenol to form species **442**. The anion **441** then reacts with **442** to give the adduct **443**, which isomerises to oxazaphosphetane **444**. Finally, decomposition of **444** leads to the formation of hydrazone **439**.



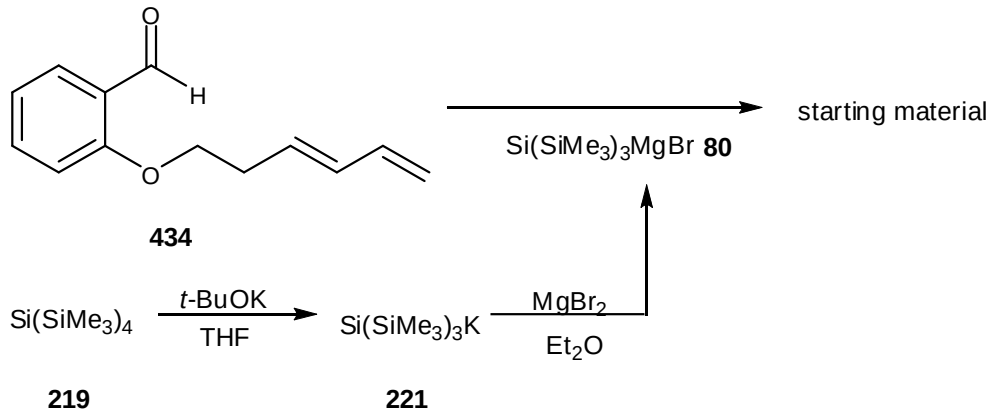
Scheme 119

Further examination of the literature revealed a report by Lepore describing the rapid coupling of crowded alcohols in the Mitsunobu reaction.[114] The procedure relies on sonication of a very concentrated solution of starting materials (3 M). It was speculated that under these conditions the coupling reaction could be faster than formation of the hydrazone. Thus, salicylaldehyde **435**, alcohol **436** and triphenylphosphine were dissolved in THF (Scheme 120). Subsequently, DIAD was added, and the reaction mixture was sonicated for 15 min at RT. The desired product was isolated in 13% yield as confirmed by analysis of the MS and IR data, which showed the molecular ion to have *m/z* = 202 (EI) and the absence of the broad signals attributed to the hydroxyl groups at 3183 cm^{-1} (**435**) and 3326 cm^{-1} (**436**). The hydrazone product was also present by crude NMR (**434**:**445** = 1:1), but was not isolated.



Scheme 120

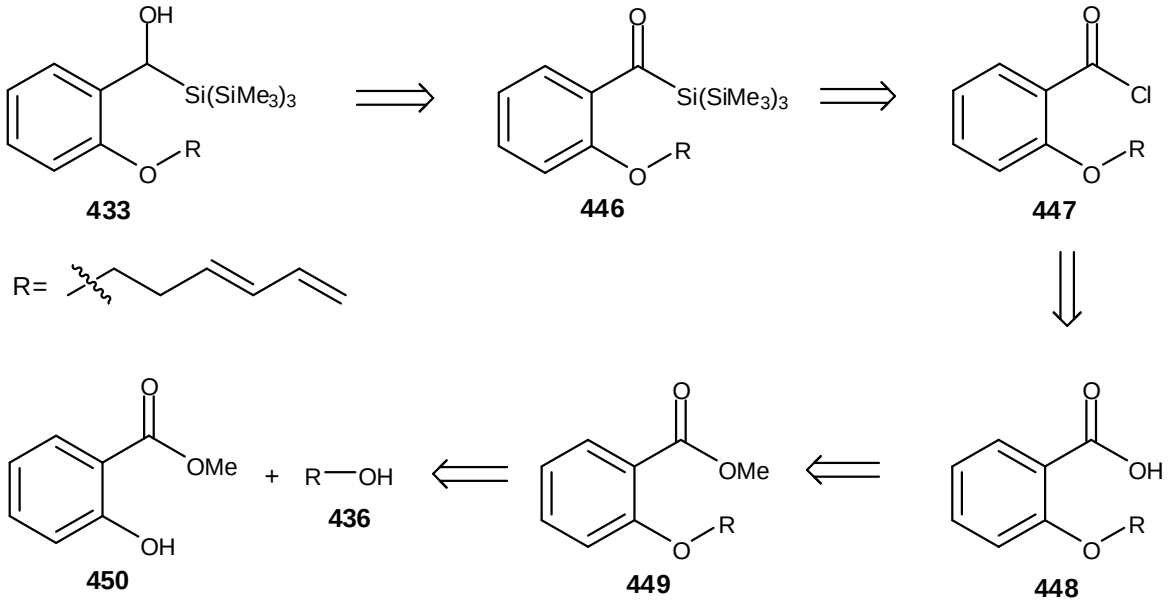
Although the yield of product **434** was low, the reaction gave a sufficient amount of material to attempt the synthesis of silyl alcohol **433**. Thus following Oehme's procedure, aldehyde **434** was treated with silylmagnesium species **80** freshly prepared from tetrakis(trimethylsilyl)silane **219** (Scheme 121).[115] Unfortunately, no product was detected and only aldehyde **434** was recovered quantitatively. The reason for this failure was not obvious; however this could suggest that the reactivity of the aldehyde group is significantly reduced by the *ortho* electron-donating substituent.



Scheme 121

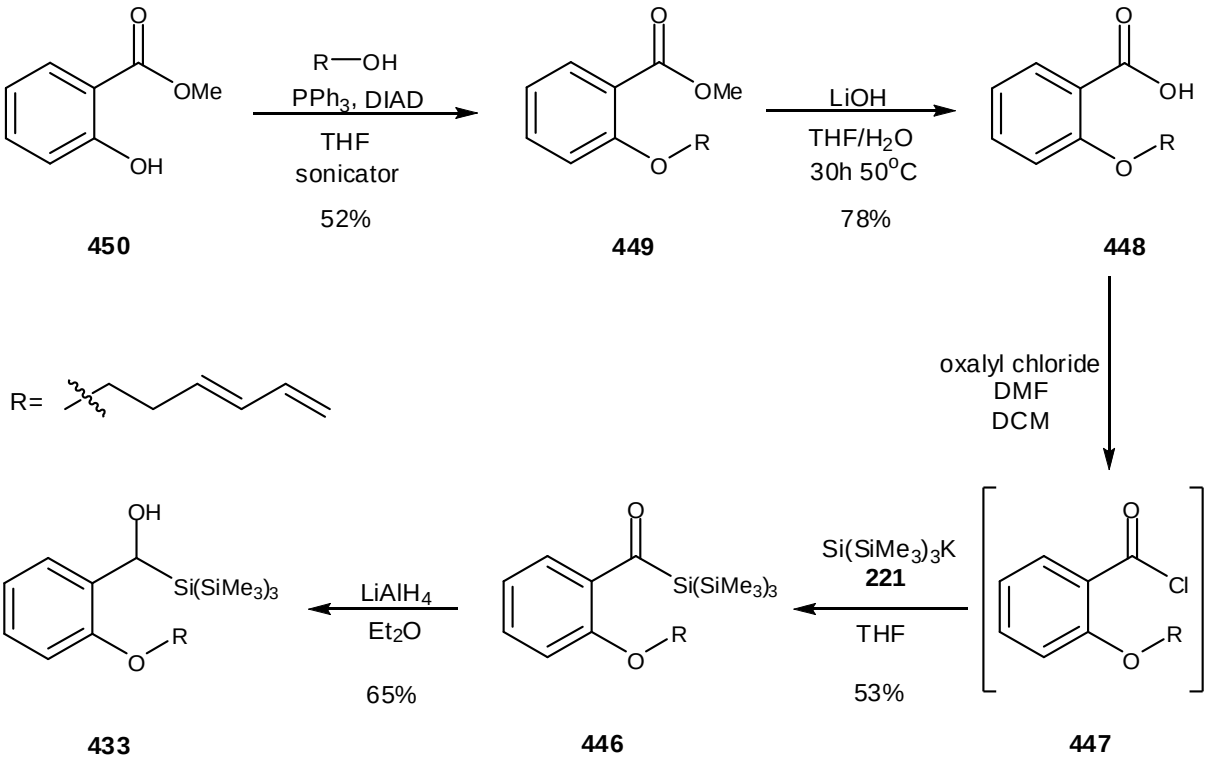
The failure of the above synthesis prompted investigations into an alternative method for the preparation of the silyl alcohols. This involved the synthesis and reduction of acylpolysilanes (Scheme 122). Unlike the silyl alcohols, these can be synthesised by direct addition of the silylpotassium reagent **221** to the appropriate acid chloride **447**. Importantly, this strategy

proceeds via acylpolysilanes **446** which could also be used in thermally-promoted silene generation.



Scheme 122

With this in mind, commercially available methyl salicylate **450** was reacted with alcohol **436** to give ether **449** in 52% yield (Scheme 123). It was found that the reaction can be carried out in the presence of either DIAD or DEAD as this does not have a significant effect on the reaction yield (DIAD 52%, DEAD 53%). As before, evidence for the formation of the Mitsunobu product **449** was confirmed by analysis of the IR and MS data. A comparison of the IR spectrum of the starting materials with that of the product showed the disappearance of signals corresponding to the hydroxyl group at 3187 cm^{-1} (**450**) and 3326 cm^{-1} (**436**). The mass spectrum showed a molecular ion at m/z=233 (MH^+).

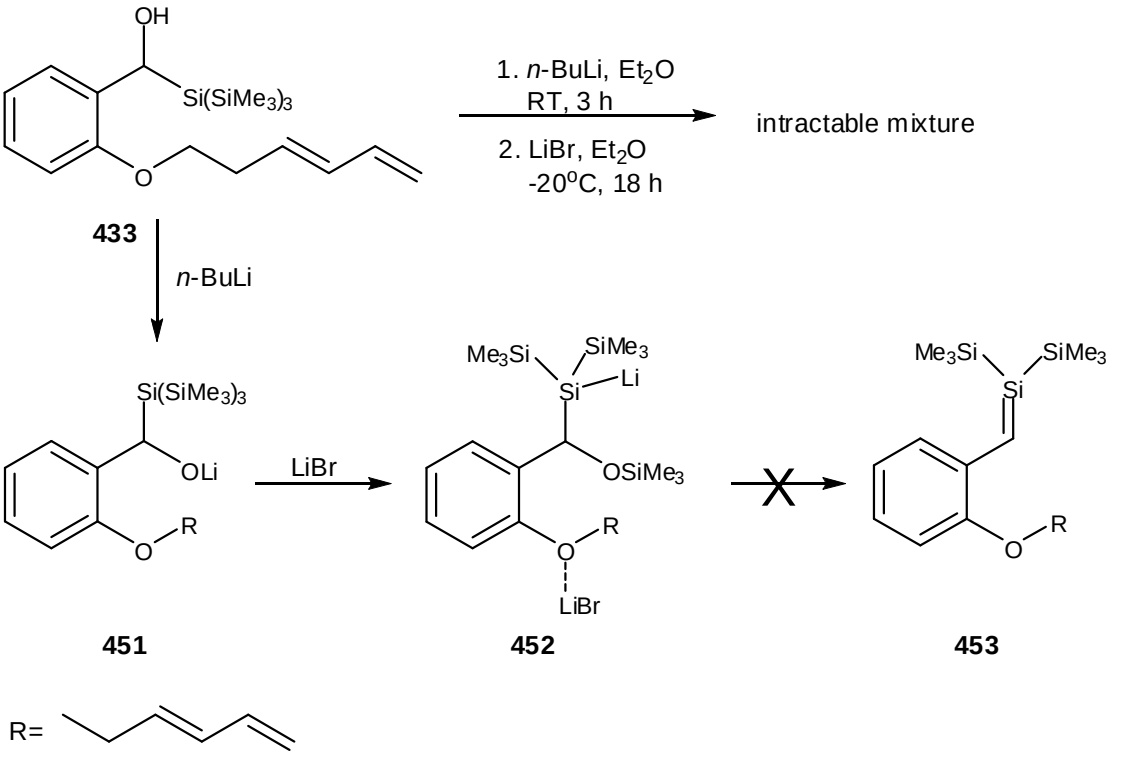


Scheme 123

Subsequently, ester **449** was hydrolysed to the corresponding acid **448** in 78% yield. Evidence for the formation of the acid was found in the ^{1}H NMR spectrum. A comparison of the ^{1}H NMR spectrum of the starting material and the product showed the appearance of the signal characteristic for a carboxylic acid at δ_H = 10.82 ppm and the disappearance of the ester signal at δ_H = 3.89 ppm. The next stage was to convert acid **448** into acid chloride **447**. This was achieved with oxalyl chloride and a catalytic amount of DMF. However, the acid chloride was not isolated but immediately combined with silylpotassium **221** to give acylpolysilane **446** in 53% yield. Evidence for the formation of the acylpolysilane was provided by the ^{13}C NMR spectrum, in which a characteristic signal corresponding to the carbonyl group at δ_C = 241.6 ppm was observed. Finally, acylpolysilane **446** was reduced with lithium aluminium hydride to afford silyl alcohol **433** in 65% yield. Reduction of the acylpolysilane was confirmed by analysis of the ^{1}H NMR spectrum, which showed a doublet at δ_H = 5.47 ppm (J = 4.2Hz) for the C***H***OH group and a doublet for the hydroxyl group at δ_H = 1.81 ppm (J = 4.2Hz). Interestingly, when sodium borohydride was used, the reduction of the acylpolysilane did not take place and starting material was recovered unchanged.

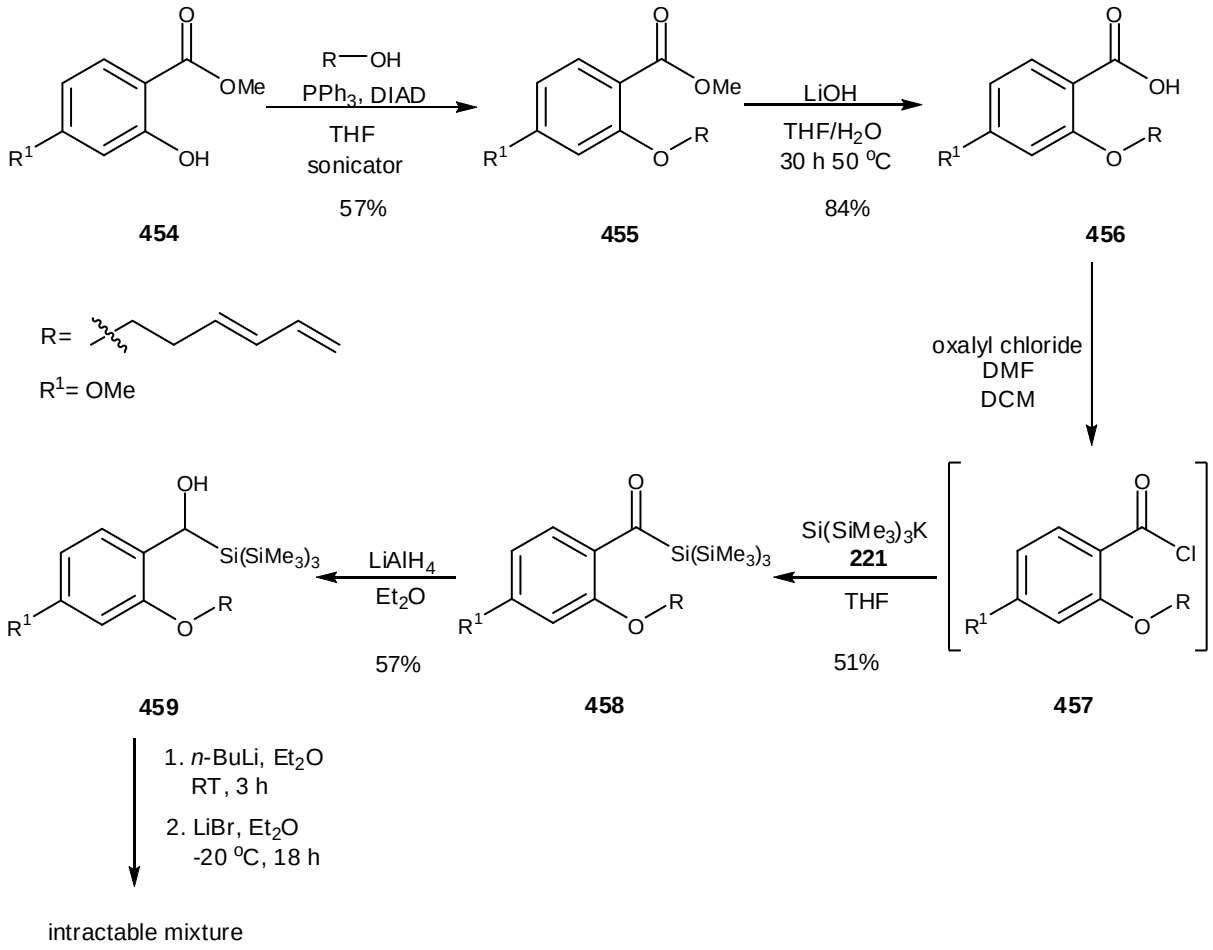
With silyl alcohol **433** in hand, the next stage was to attempt the formation of the corresponding silene species. Following the protocol developed by Whelligan, silyl alcohol

433 was treated with *n*-BuLi followed by addition of anhydrous LiBr (Scheme 124).[4] Disappointingly, the reaction led to the formation of an intractable mixture of products. This could be attributed to coordination of the lithium bromide to the ethereal oxygen rather than the more hindered $OSiMe_3$ group.



Scheme 124

It was speculated that the presence of an additional electron-donating substituent on the aromatic ring would encourage elimination of $LiOSiMe_3$, even without addition of LiBr. Silyl alcohol **459** was therefore prepared according to the previously established sequence (Scheme 125). Unfortunately, when the sila-Peterson reaction was carried out on alcohol **459** an intractable mixture of products was formed.



Scheme 125

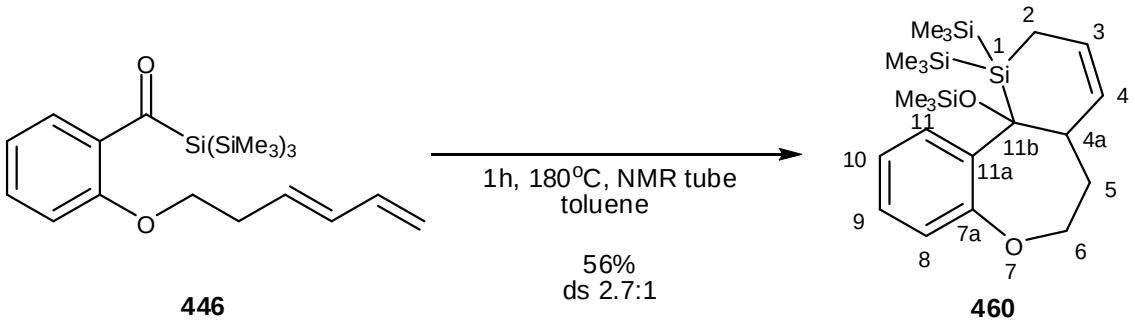
These preliminary investigations suggested that competitive coordination of the lithium bromide by the ethereal oxygen was occurring. Therefore, future research would involve the synthesis and use of a carbon-tethered diene, but time constraints precluded such work.

4.3 Thermolysis of acylpolysilanes

4.3.1 Preliminary results

Given the lack of success in the employment of silyl alcohols in the intramolecular silene cycloaddition, attention turned to the use of acylpolysilanes. Initial studies concentrated on the generation of silene species from acylpolysilane **446**. Hence, a solution of the polysilane in d_8-toluene was placed in an NMR tube under argon (Scheme 126). The NMR tube was sealed with a Young's tap and heated until all the acylpolysilane was consumed. The progress

of the reaction was followed by ^{1}H NMR spectroscopy. The resulting mixture was then concentrated, and purified by preparative TLC to give product **460** in 56% yield.



Scheme 126

Formation of the [4+2] adduct was confirmed by analysis of the MS and ^{1}H NMR data. The mass spectrum showed a molecular ion at m/z=448 (M^+). The ^{1}H NMR spectrum showed peaks at δ_H = 6.09 ppm and δ_H = 5.73 ppm attributed 3-***H*** and 4-***H*** respectively. The vicinal coupling J = 10.5Hz between those two protons indicates theirs mutual *cis* location. Finally, the connectivity was confirmed by HMBC experiments which revealed a 3-bond correlation from protons 2-***H*** and 5-***H*** to ring carbon ***C***-11b which confirms formation of the cycloadduct (Figure 26).

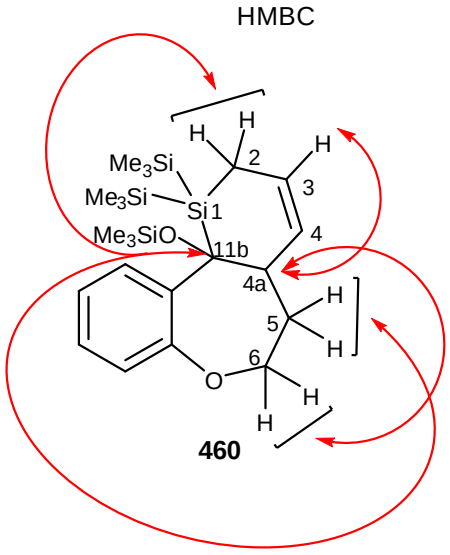
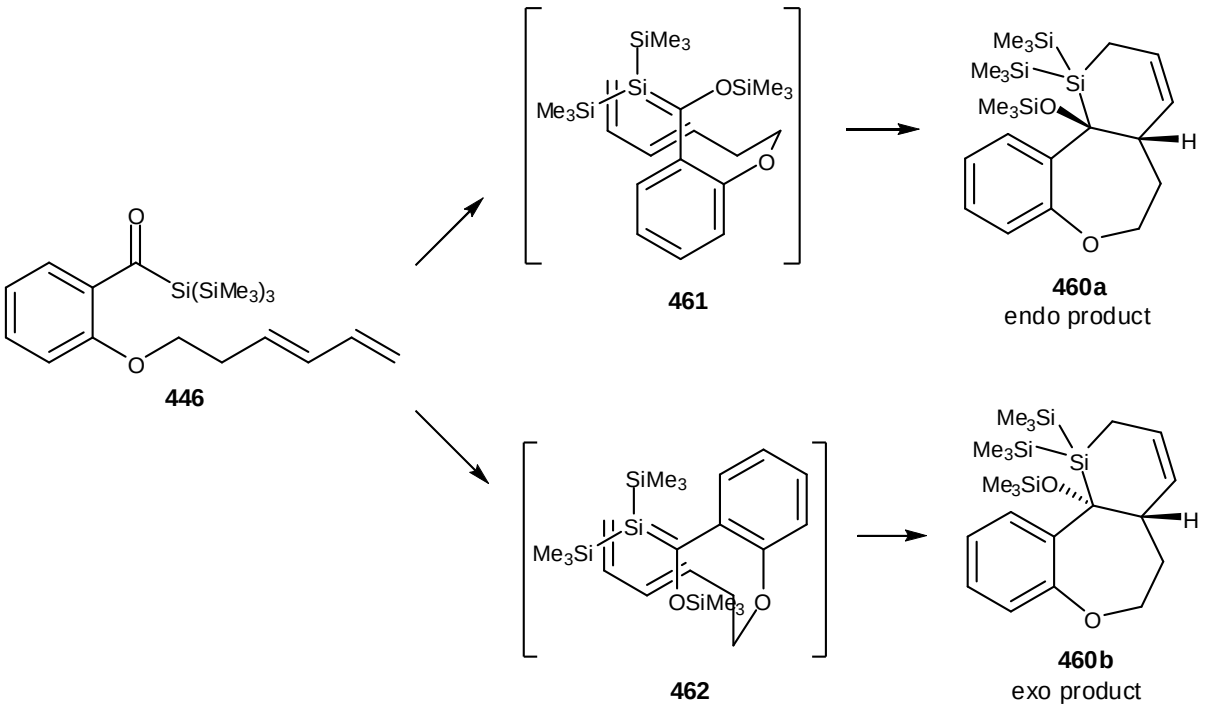


Figure 26

The configuration of the main diastereoisomer could not be deduced from the 2D correlation ^{1}H NMR experiments. However, it was suggested that the silene would react preferentially in an *endo* fashion, because of secondary orbital interactions between the diene and the phenyl tether (Scheme 127).



Scheme 127

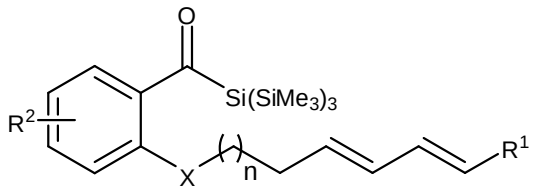
Subsequently investigations were undertaken to improve the diastereoselectivity by altering the time and temperature of the reaction (Table 20). It was hoped that lower temperatures may lead to an increase in the diastereoselectivity of the cycloaddition reaction, by increasing the relative difference in the energies for the *exo* and *endo* transition states. Unfortunately, the data presented in Table 20 indicates that there is no effect on varying these conditions upon the ratio of the diastereoisomers. It appears that to achieve full conversion of the acylpolysilane at lower temperature prolonged heating is required (entry 1, 2). However, this results in diminished yields probably due to product decomposition. The best conversion was achieved when the reaction was carried out under microwave conditions at 180 ^{o}C for 1 h (entry 4).

entry	**method**	**solvent**	**temp. (^{o}C)**	**time (h)**	**yield (%)**	**ds**	**recovery of 23 (%)**
1	flask	PhH	110	12	28	2.7:1	40
2	microwave	PhH	150	1	29	2.7:1	52
3	microwave	PhH	180	0.83	77	2.7:1	5
4	microwave	PhH	180	1	81	2.7:1	-

Table 20

4.3.2 Adducts derived from various acylpolysilanes

The preliminary investigations suggested that the intramolecular adducts resulting from acylpolysilanes could be synthesised in high yield and moderate diastereoselectivity. The work outlined in the following section describes further studies in this area, investigating the effect of changing acylpolysilane **429** (R^1, R^2, X and n) on the subsequent silene cycloaddition reaction (Figure 27).

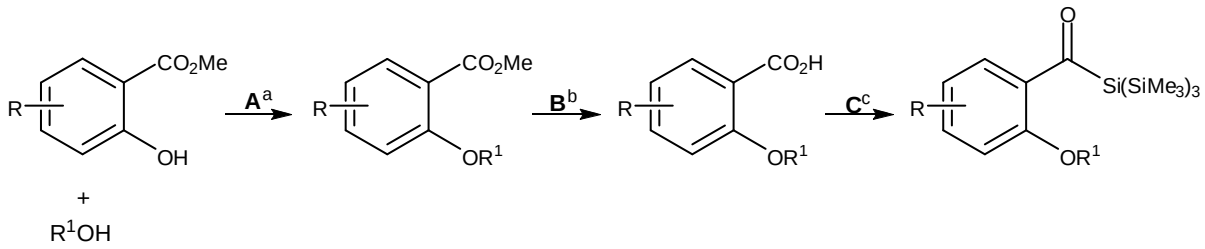


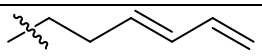
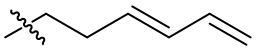
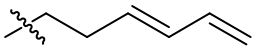
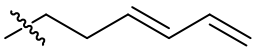
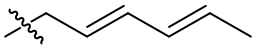
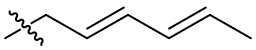
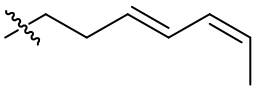
429

Figure 27

4.3.2.1 Acylpolysilane synthesis

The next stage in the project involved the synthesis of various acylpolysilanes. This could be accomplished by utilising the previously established sequence (Chapter 4, Section 4.2). The results are summarised in Table 21. As before, evidence for the formation of acylpolysilanes was confirmed through analysis of the ^{13}C NMR spectrum with a signal at δ_C = 245-230 ppm characteristic of the acylpolysilane carbonyl group.

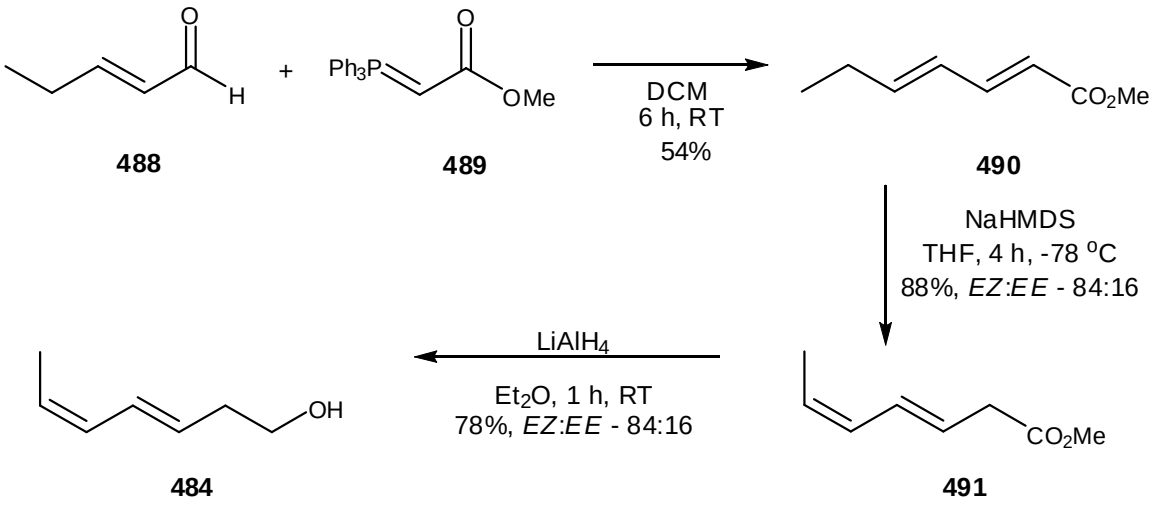


entry	ester		alcohol		Step A		Step B		Step C	
	No	R	No	R^1	No	yield (%)	No	yield (%)	No	yield (%)
1	**463**	5-Cl	**436**		**464**	78	**465**	86	**466**	10
2	**467**	3-Me	**436**		**468**	58	**469**	78	**470**	52
3	**471**	4-I	**436**		**472**	84	**473**	84	**474**	-
4	**475**	4,5-fused phenyl	**436**		**476**	52	**477**	86	**478**	53
5	**435**	H	**479**		**480**	41	**481**	-	-	-
6	**454**	4-OMe	**479**		**482**	44	**483**	[d]	-	-
7	**435**	H	**484**		**485**	54[e]	**486**	87[e]	**487**	54[e]

[a]PPh_3, DEAD, THF, RT, 20 min. [b]LiOH, THF/H_2O, 50 °C, 30 h. [c]1) $(COCl)_2$, DMF, DCM, 0 °C, 3 h; 2) $Si(SiMe_3)_3K$, THF, -78 °C, 3 h. [d]Sigmatropic rearrangement product **492** isolated in 56%; see Scheme 129. [e]Mixture of isomers *EZ*:*EE* 86:14.

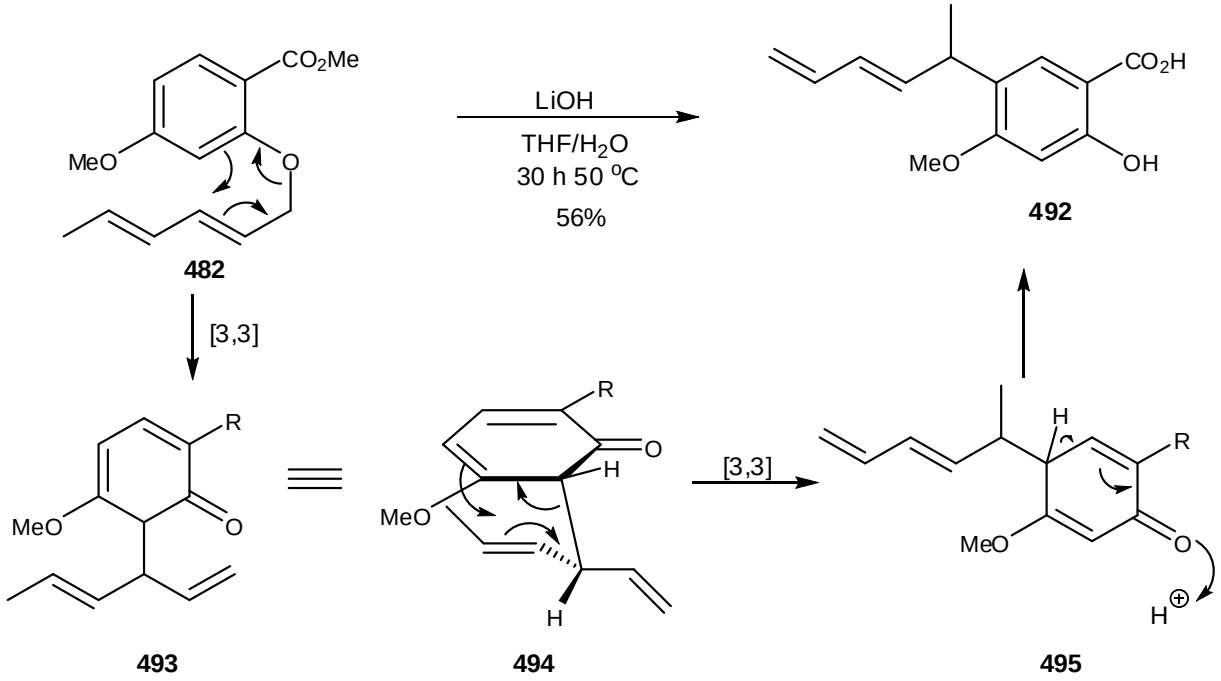
Table 21

The methyl esters used in the synthesis and (2*E*,4*E*)-hexa-2,4-dien-1-ol **479** are commercially available materials. The synthesis of diene **436** was described in Section 4.2 of this chapter. Diene **484** was prepared according to a well established procedure (Scheme 128).[116] The synthesis began with the reaction of aldehyde **488** with ylide **489** to afford **490** in 54% yield as a mixture of isomers *EZ*:*EE* 86:14. Unsaturated ester **490** was then deconjugated under basic conditions to give the corresponding ester **491**. This was subsequently reduced to alcohol **484** in 78% yield. All data on this compound agree with those given by Johnstone.[116]



Scheme 128

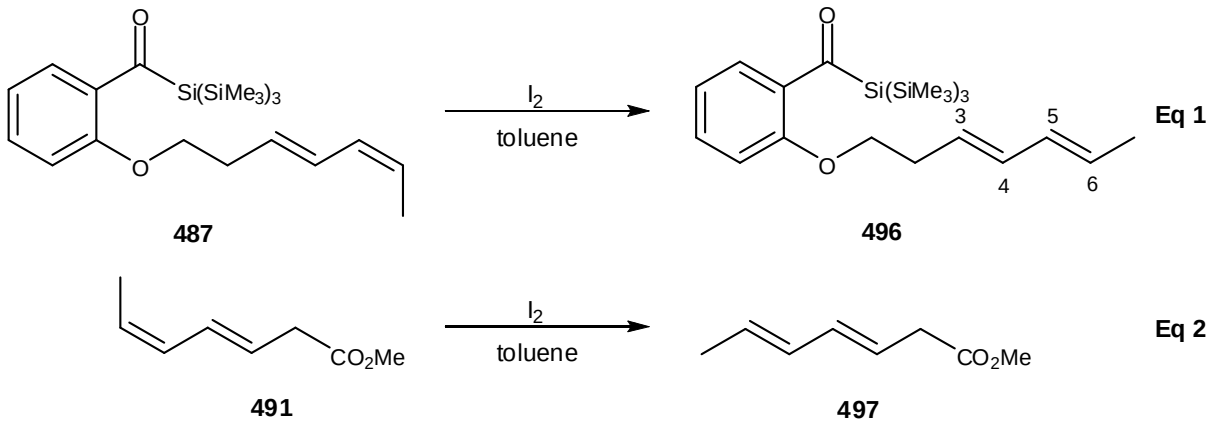
As can be seen from Table 21, the reaction of carboxylic acid **473** with silylpotassium **221** failed to produce the ccorresponding acylpolysilane **474** whereas carboxylic acid **465** gave the desired product in low yield (entry 3 and 1). This could indicate the unreliability of halo-substituted acid chlorides for the acylpolysilane synthesis. Furthermore, it was found that ethers **480** and **482** did not form the corresponding carboxylic acids **481** and **483** respectively. It was found that both compounds undergo a series of sigmatropic rearrangements. In the case of ester **482**, the product of the rearrangements was isolated and fully characterised (Scheme 129).



Scheme 129

Key evidence for the formation of product **492** was found in the ^{1}H NMR spectrum where only two singlets corresponding to the aromatic protons were observed at δ_H = 7.64 ppm and δ_H = 6.45 ppm. In addition, the ^{1}H NMR spectrum showed a doublet for the methyl group at δ_H = 1.33 ppm. Further evidence was obtained by analysis of the mass spectrum showing m/z = 247 (ES-, M-H).

Subsequently, the synthesis of a few acylpolysilane analogues was attempted using a different procedure. On this basis, it was speculated that acylpolysilane **496** could be simply prepared by isomerisation of **487** (Scheme 130, Eq 1). Johnstone had previously shown that *EE* ester **497** can be generated by treatment of *EZ* ester **491** with I_2 (Eq 2).[116] The reaction was carried out in toluene under artificial light for two days.

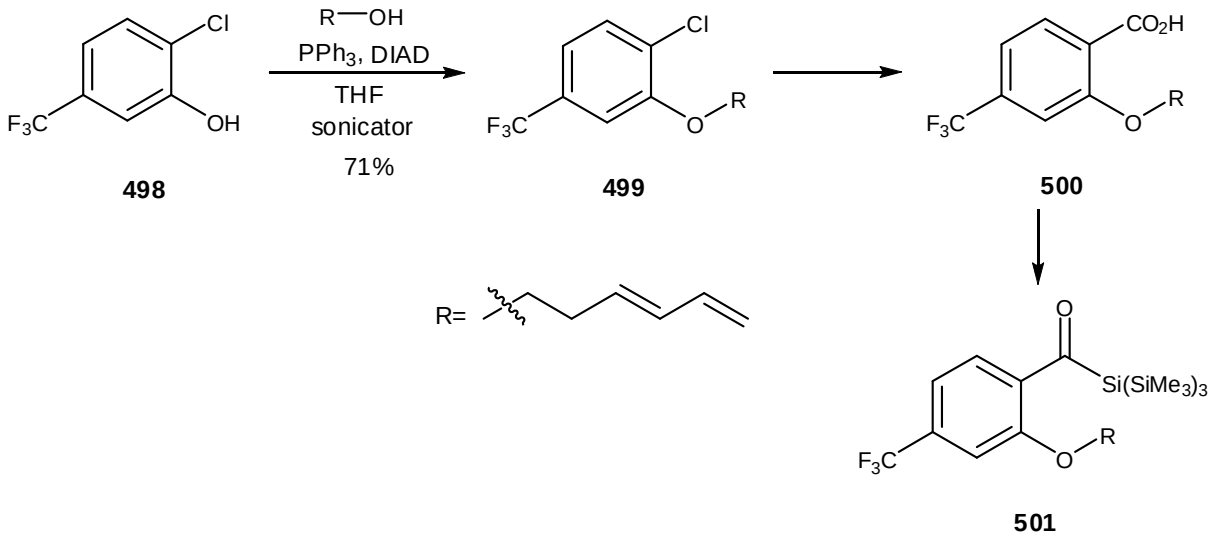


Scheme 130

Following the procedure developed by Johnstone, a solution of acylpolysilane **487** was treated with a single crystal of iodine. The presence of the desired compound in the crude product was established by ^{1}H NMR spectroscopy. The geometry of the product was ascertained by ^{1}H NMR spectroscopy where large coupling constants characteristic of *trans*-substituted double bonds were observed ($J_{\mathbf{3}H\text{-}\mathbf{4}H}$ = 15.4 Hz, $J_{\mathbf{5}H\text{-}\mathbf{6}H}$ = 15.4 Hz ppm). However, all attempts to purify this compound on silica and neutral alumina were unsuccessful. Interestingly, it was found later that after 6 h, the isomerisation reached thermodynamic equilibrium (*EE*:other isomers - 1.7:1) and prolonged exposure to artificial light caused only degradation of the product.

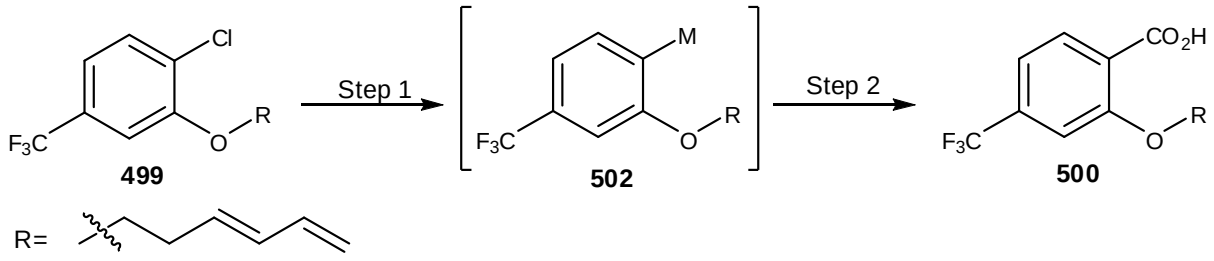
Subsequently, the synthesis of acylpolysilane **501** bearing an electron-withdrawing group in the *para*-position was carried out. It was speculated that this would increase the diastereoselectivity of the cycloaddition in a similar manner to that observed for intermolecular processes (Chapter 2, Section 2.6). In theory, the synthesis would involve the

Mitsunobu reaction of **498** followed by introduction of a carboxyl group and conversion of the carboxylic acid into the corresponding acylpolysilane (Scheme 131).



Scheme 131

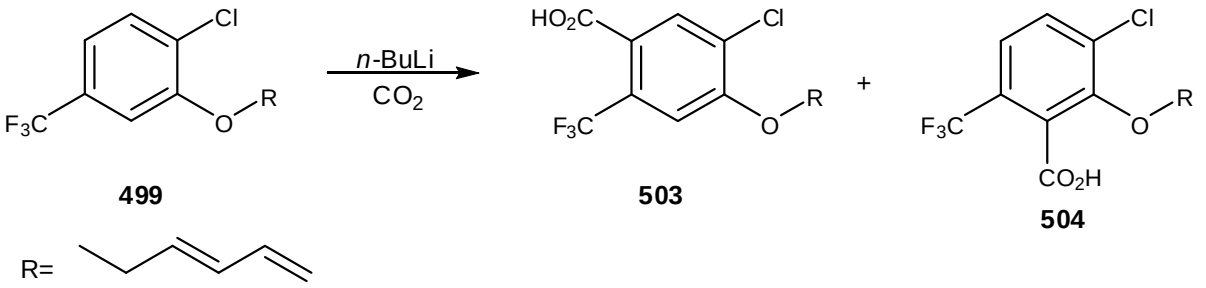
Following the above analysis, the synthesis began with the reaction of phenol **498** with alcohol **436** to afford **499** in 71% yield. Subsequently, synthesis of acid **500** was undertaken through a sequence involving preparation of organometallic reagent **502** and reaction with carbon dioxide (Table 22).



entry	conditions		outcome
	Step 1	**Step 2**	
1	Mg, 24 h at reflux	CO_2, 30 min at RT	starting material
2	Rieke Mg, 24 h at reflux	CO_2, 30 min at RT	starting material
3	*n*-BuLi, 30 min at -78 ^oC	CO_2, 30 min at RT	product **503**+**504**

Table 22

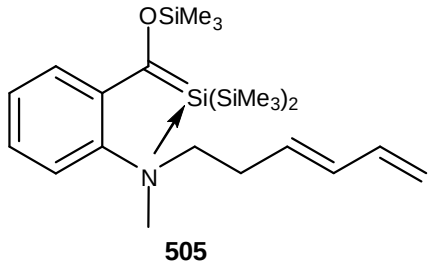
Disappointingly, every attempt to introduce a carboxyl group proved unsuccessful. Surprisingly, it was found that aryl chloride **499** did not form the corresponding Grignard reagent even with very reactive Rieke magnesium (entry 2).[117] However, the reaction with *n*-BuLi gave a mixture of products **503** and **504** (**503**:**504**-18:1) which arose from *ortho*-lithiation of **499** (Scheme 132).



Scheme 132

Evidence confirming the formation of **503** and **504** was obtained from the ^{1}H NMR spectrum which showed the appearance of the AB system (δ_H = 7.80 ppm and δ_H = 7.26, $^{5}J_{para}$ = 1.0Hz) and the AX system (δ_H = 7.57 ppm and δ_H = 7.40, $^{4}J_{ortho}$ = 8.8Hz) respectively.

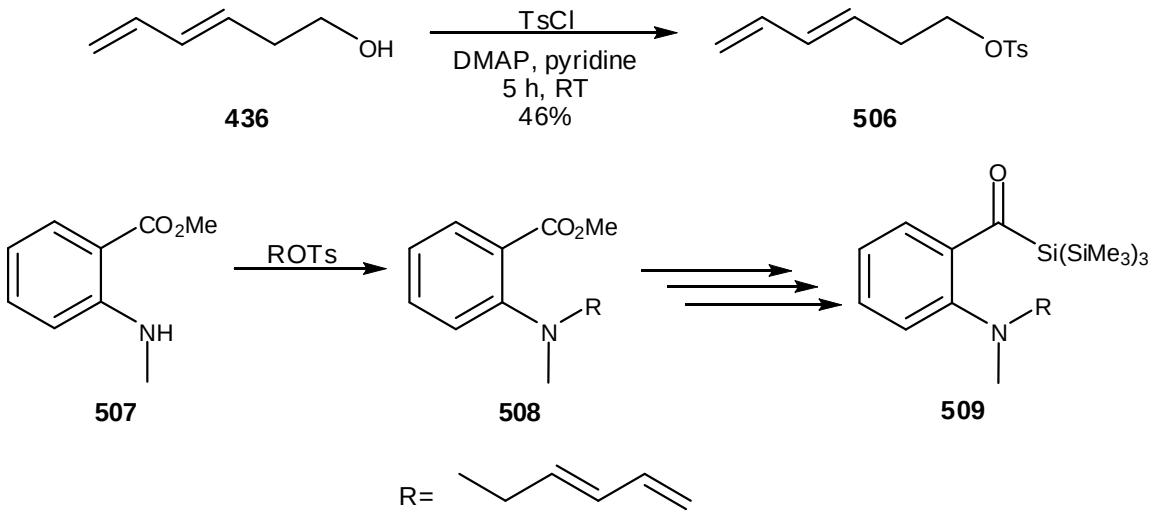
With the aim of varying the nature of the tether, attempts were then made to introduce an amine group. It was speculated that the presence of an amine group would make the silene less reactive and therefore would increase the diastereoselectivity of the cycloaddition (Figure 28). This type of stabilisation had been employed to make stable silenes (Chapter 1, Section 1.3.2).



505

Figure 28

It was anticipated this could be achieved by alkylation of amine **507** with tosylate **506** (Scheme 133). The required tosylate **506** was synthesised by treatment of the corresponding alcohol **437** with tosyl chloride in 46% yield.



Scheme 133

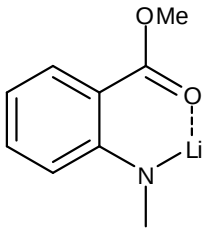
In order to find appropriate conditions for the alkylation, several different conditions were explored (Table 23). With the exception of KH, which afforded small amounts of impure product **508** (entry 2), every effort to introduce a diene chain proved unsuccessful. Moreover, it was found that prolonged heating of the reaction mixture led to decomposition of the tosylate. Formation of the product was confirmed by analysis of the GCMS trace showing a peak for the molecular ion at *m/z* = 245. In addition, the ^{1}H NMR spectrum showed the disappearance of the aromatic signals at δ_H = 7.80-7.79 ppm and δ_H = 7.36-7.35 ppm attributed to the tosyl group.

entry	base	solvent	conditions	yield (%)
1	KOH	DMF	24 h at 65 ^{o}C	starting material
2	NaH	DMF	6 h at RT then 24 h at 65 ^{o}C	13[a]
3	NaHMDS	DMF	24 h at RT then 24 h at 65 ^{o}C	starting material
4	LDA	THF	15 min at -78 ^{o}C then 24 h at RT	starting material
5	*n*-BuLi	THF	15 min at -78 ^{o}C then 24 h at RT	starting material
6	*n*-BuLi + HMPA	THF	15 min at -78 ^{o}C then 24 h at RT	starting material

[a]Flash column chromatography on silica gave an inseparable mixture of unreacted amine **507** and product **508**.

Table 23

The reason for this failure was not obvious, however in the case of lithium-based reagents it was suggested that internal coordination led to the formation of a very unreactive lithium species **510** (Figure 29). Unfortunately, an attempt to coordinate the lithium cation with HMPA and therefore generate the reactive anion gave no improvement (entry 6).

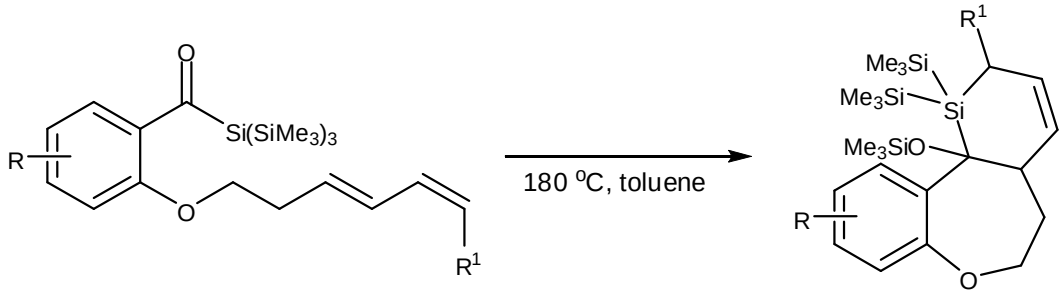


510

Figure 29

4.3.2.2 Cycloaddition

With the various acylpolysilanes in hand, the next stage was to attempt the thermolytic formation of the corresponding silene species. Thus, a solution of acylpolysilane in toluene was heated in a microwave reactor at 180 ^{o}C until full conversion was achieved. The table below summarises the products and diastereoselectivities obtained (Table 24).



entry	R	R^1	acylpolysilane	time (min)	product	yield (%)	ds
1	4-OMe	H	**458**	15	**511**	not stable	2:1
2	5-Cl	H	**466**	75	**512**	60	2.7:1
3	3-Me	H	**470**	90	**513**	87	3.7:1
4	4,5-fused phenyl	H	**478**	75	**514**	75	2.2:1
5	H	CH_3	**487**	60	**515**	-	-

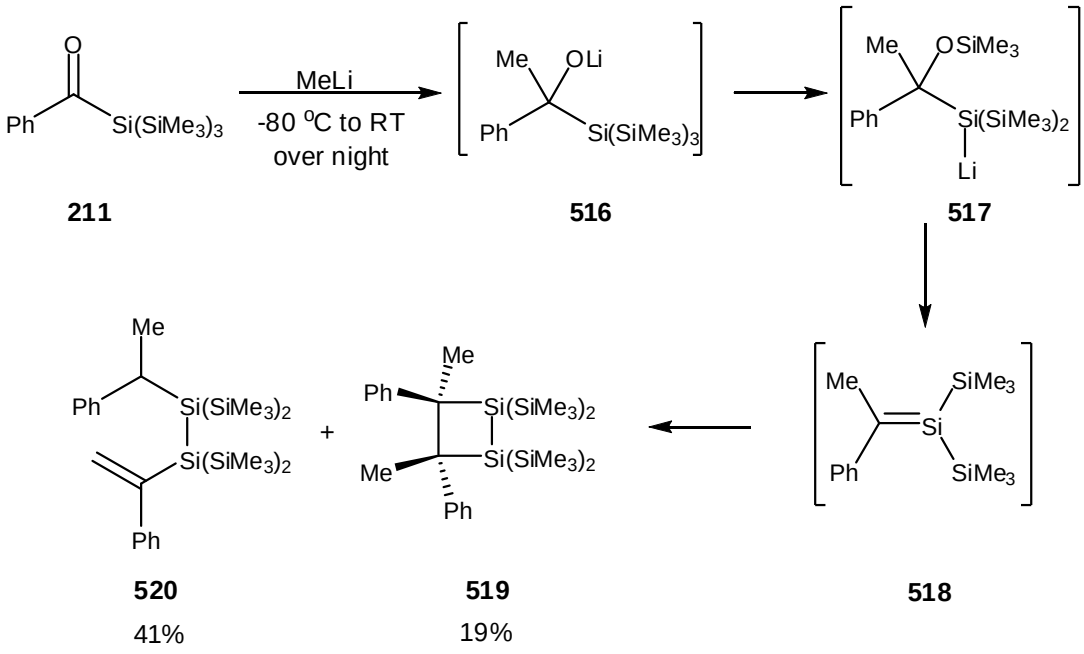
Table 24

Importantly, in all cases the main diastereoisomer possesses the same stereochemistry as that observed during earlier experiments with acylpolysilane **446**. In addition, it appears that there is little effect upon varying the substituents on the aromatic ring on the diastereoselectivity of the intramolecular cycloaddition reactions. Moreover, it was found that the 4-OMe substituted adduct **511** is very unstable and all attempts to purify and fully characterise this compound

were unsuccessful and led to decomposition. Entry 5 shows an unsuccessful attempt to synthesise adduct **515**. It is unclear whether thermolysis of the acylpolysilane **487** led directly to decomposition, or whether the cycloadduct **515** was decomposed by high temperature. Other adducts are much more stable, but, they decompose slowly in solution.

4.4 Use of MeLi

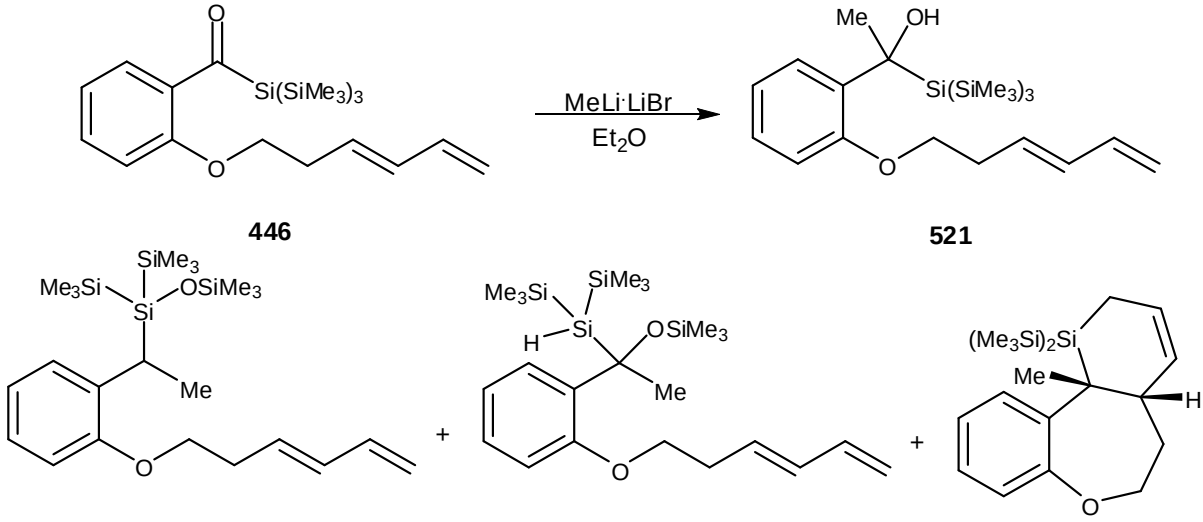
As discussed in the introduction (Section 4.1), the modified Peterson olefination and thermolysis of acylpolysilanes were chosen as the methods of silene generation in this project. However, since the modified Peterson olefination failed to produce any intramolecular adduct and thermolysis of acylpolysilanes gave the products with only moderate diastereoselectivity, an alternative method was explored. This involved addition of MeLi to acylpolysilanes at low temperature (Scheme 134). The reaction was investigated by Ishikawa and essentially follows the same pathway as the modified Peterson olefination via intermediates **516** and **517**.[118] Under the reaction conditions silene **518** forms dimer **519** and ene type product **520**. Interestingly, all attempts to trap silene **518** were unsuccessful.



Scheme 134

It was hypothesised that Ishikawa's protocol would allow the synthesis of intramolecular adducts with enhanced diastereoselectivity, since the reaction is performed at low

temperature. According to Whelligan's research, the presence of LiBr promotes elimination of $LiOSiMe_3$ and thus formation of silene.[75] Therefore the MeLi·LiBr complex was used instead of MeLi. The results of the experiments are summarised in Table 25.



446 **521**

522 **523** **524**

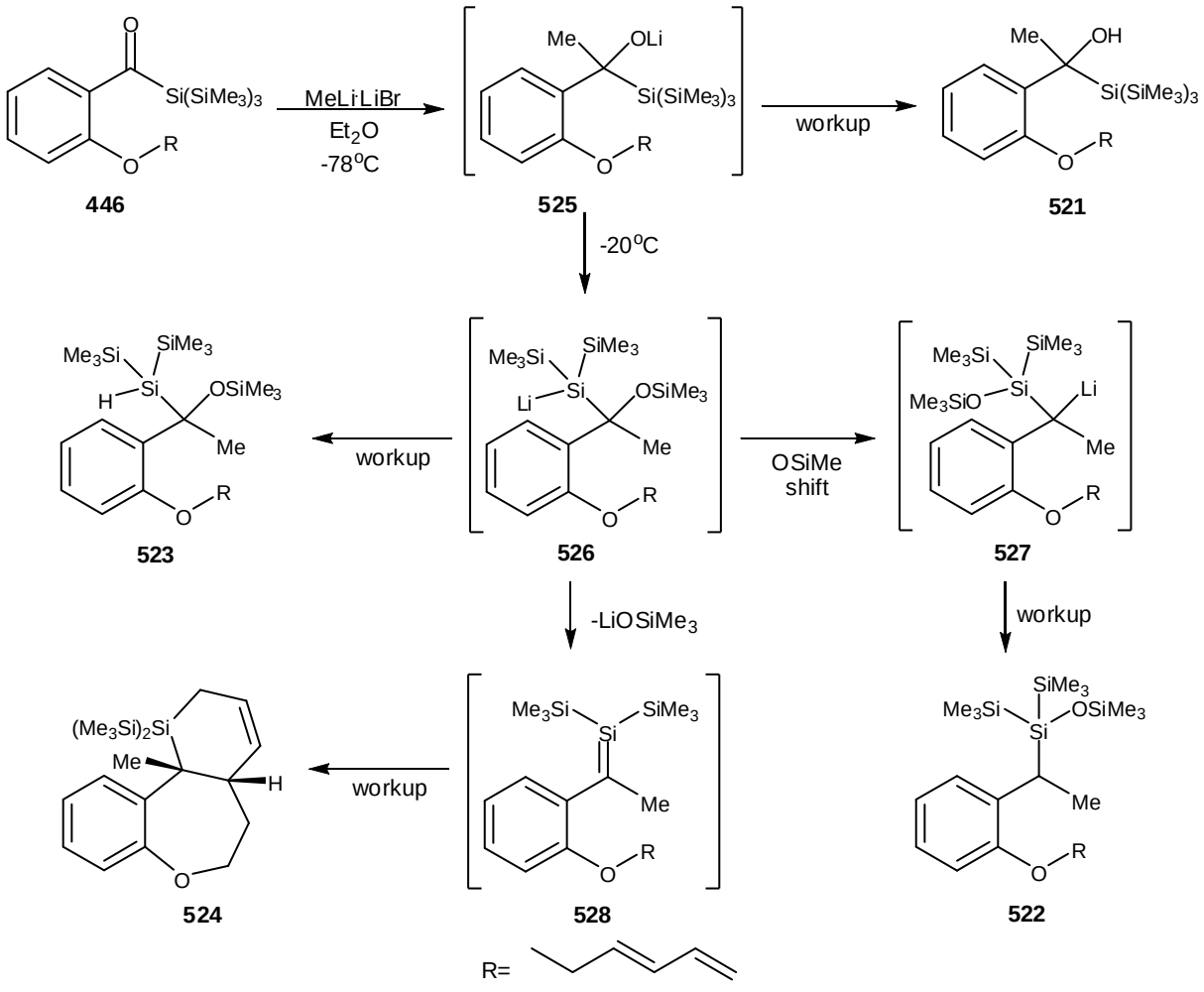
entry	conditions	product 524		product 522 and 523		product 521
		yield (%)	ds	yield (%)	ratio 522:523[a]	yield (%)
1	16 h at -78 °C	-	-	-	-	42
2	1 h at -78 °C then 16 h at -20 °C	32	2.5:1	29	1:1	-
3	addition of MeLi·LiBr at -78 °C, then 6 h at -20 °C and 16 h at 10 °C	57	2.5:1	12	25:1	-
4	30 min at -78 °C then 16 h at RT	38	2.3:1	17	1:0	-

[a] Products inseparable by flash column chromatography.

Table 25

In general four different products **521**, **522**, **523** and **524** could be obtained by varying the reaction conditions. Entry 1 describes the conversion of acylpolysilane **446** to silyl alcohol **521** in 42% yield. This showed that at -78 °C intermediate lithium alkoxide **525** is reasonably stable and did not isomerise to silyllithium species **526** (Scheme 135). The alcohol product was confirmed by the ^1H NMR spectrum, which showed a new signal at δ_H = 1.80 ppm corresponding to the methyl group, and IR data, which showed the appearance of the broad IR band characteristic of alcohols at 3506 cm^{-1}. Entries 2-4 show that the reaction proceeds through 1,3-$SiMe_3$ migration at higher temperatures. Silane **523** arises from unreacted silyllithium **526**, and silane **522** is a result of an $OSiMe_3$ shift (Scheme 135). Formation of

523 was confirmed by analysis of the ^{1}H NMR spectrum, which showed a signal at δ_H = 3.65 ppm for the ***H***-Si proton and a signal at δ_H = 2.02 ppm corresponding to the methyl group. Similarly, evidence for the formation of product **522** was confirmed by analysis of the ^{1}H NMR spectrum, which showed signals at δ_H = 3.06 ppm (d, *J* = 7.7Hz) and δ_H = 1.41 ppm (q, *J* = 7.7Hz) corresponding to the benzyl proton and methyl group respectively. Finally, elimination of $LiOSiMe_3$ led to the formation of intermediate silene **528**, which underwent intramolecular cycloaddition to form cycloadduct **524**. Interestingly, the cycloadduct was only formed in good yield when the reaction was carried out at -10 ^{o}C (entry 3). This indicates that at lower and higher temperatures side reactions compete with formation of the cycloadduct.



Scheme 135

Formation of the cycloadduct **524** was confirmed by examination of the ^{1}H NMR spectrum, which revealed new signals at δ_H = 6.15 ppm and δ_H = 5.63 ppm corresponding to the vinyl protons. The configuration of the major diastereoisomer was assigned on the basis of 2D correlation NMR experiments (Figure 30).

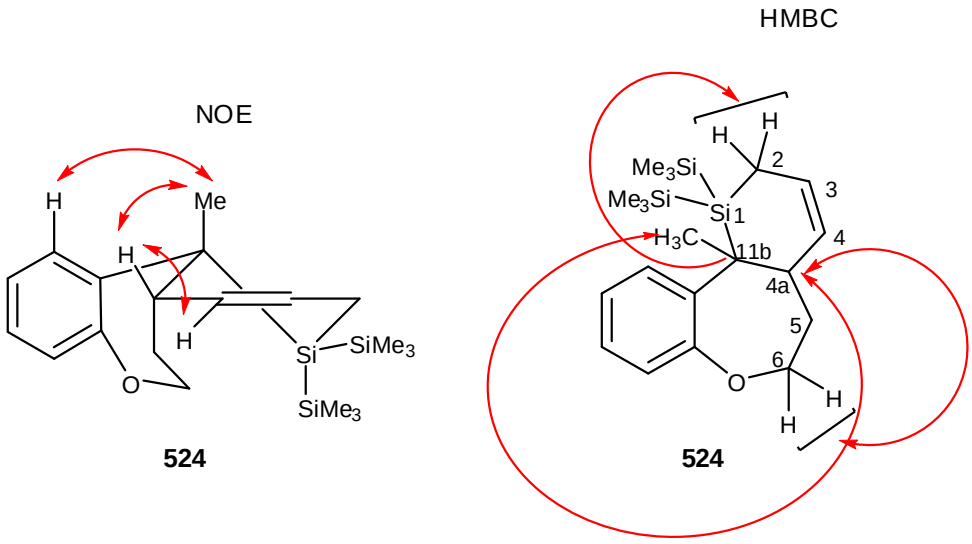
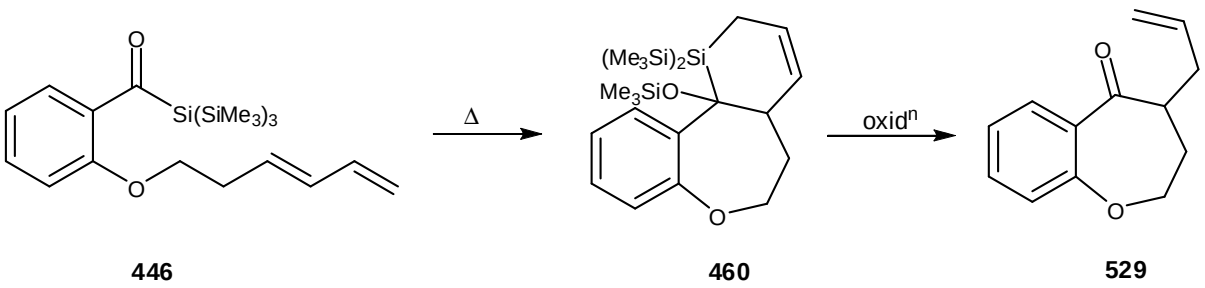


Figure 30

In summary, this experiment showed that Ishikawa's protocol could be employed in the silene intramolecular cycloaddition reaction. In addition, this experiment also suggests that this low-temperature silene generation method would give the cycloadducts with similar diastereoselectivity to the thermal method.

4.5 Attempted oxidation of silacycle 460

Preliminary investigations focused on the oxidation of cycloadduct **460** obtained by the thermolysis of the corresponding acylpolysilane **446**. In theory the oxidation of the cycloadduct should lead to the formation of ketone **529** (Scheme 136). Overall this sequence would represent a novel strategy for the generation of new C-C bonds.



Scheme 136

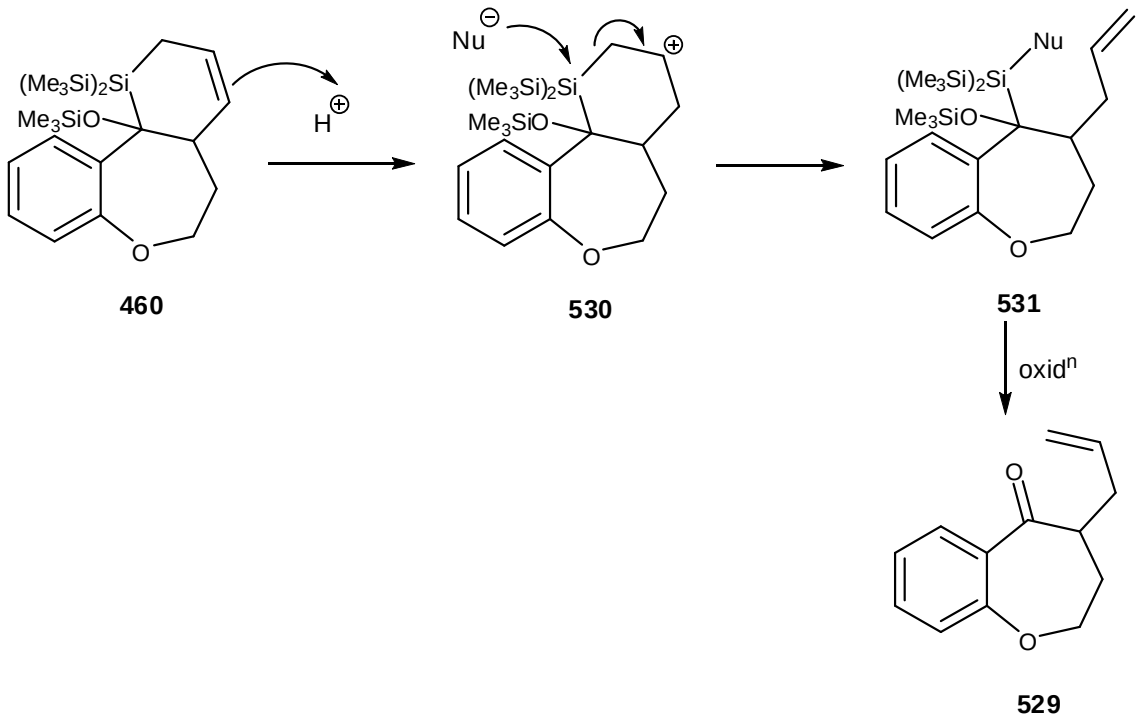
In view of this, a range of reagents were screened under various conditions (Table 26). Entry 1 shows the attempt to directly oxidise cycloadduct **460** with mCPBA. This reagent was used

previously with success to oxidise various cyclopropanes in good yield (Chapter 2, Section 2.8.3). Unfortunately, in this case cycloadduct **460** did not react with mCPBA at room temperature and decomposed when heated at 60 ^{o}C for 24 h.

entry	conditions	outcome
1	mCPBA, KF, DMF, 22 h at RT then 24 h at 60 ^{o}C	starting material decomposed upon heating at 60 ^{o}C
2	BF_3·2AcOH, DCM, 20 min at RT	intractable mixture
3	BF_3·2AcOH, DCM, 4 h at -78 ^{o}C	intractable mixture
4	TFA, KHF_2, DCM, 10 min at RT	product **532**
5	TFA, KHF_2, DCM, 6 h at RT	intractable mixture
6	1) TFA, KHF_2, DCM, 10 min at RT 2) mCPBA, DMF, 24 h at RT	intractable mixture
7	TfOH, DCM, 1h at -78 ^{o}C	intractable mixture

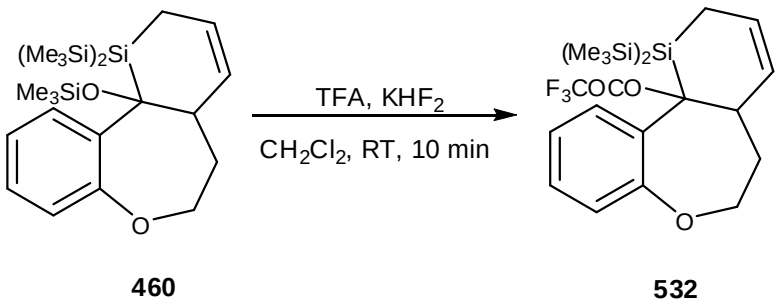
Table 26

Speculating that initial activation with a fluoride source was required, attempts were made to fragment the silacycle ring first. This could be achieved by employing the reactivity of the allylsilane system (Scheme 137). Therefore, the cycloadduct was treated with boron trifluoride acetic acid complex (entries 2-3). The reaction was completed after 20 min at room temperature and after 4 h at -78 ^{o}C, but led only to the formation of an intractable mixture of products.



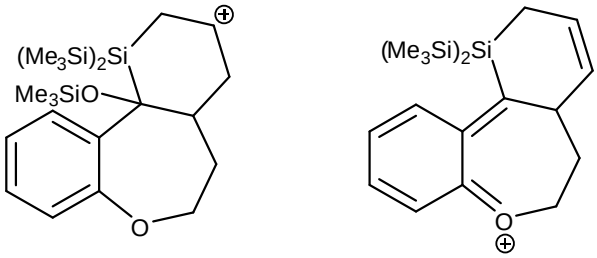
Scheme 137

Subsequently, trifluoroacetic acid was employed in an attempt to fragment the silacycle ring (entries 4-5). As can be seen, the reaction was complete after 10 min at room temperature and gave the product **532**, which decomposes when stirred for long periods of time (Scheme 138). The structure of this product was suggested by NMR spectroscopy. A comparison of the ^{1}H NMR spectrum of the starting material and the product showed the disappearance of the $OSiMe_3$ signal. Additional evidence for the formation of product **532** was found in the ^{19}F NMR spectrum where signals corresponding to the CF_3 group were observed for the major and minor isomers at δ_F = -76.8 ppm and δ_F = -76.4 ppm, respectively. Unfortunately, all attempts to purify and fully characterise this compound were unsuccessful and led to decomposition. Moreover an attempt to oxidise the crude product was unsuccessful leading to an intractable mixture of products (entry 6).



Scheme 138

Finally, a solution of cycloadduct **460** in DCM was treated with triflic acid at -78 ^{o}C (entry 7). Interestingly, the colour of the reaction mixture changed to deep red immediately after addition of the acid. This could indicate the formation of some ionic intermediate in the reaction mixture (Figure 31). However, only an intractable mixture of products was formed on aqueous work-up.



533 **534**

Figure 31

Overall, these preliminary results suggest that fragmentation of the intramolecular adduct can be problematic. This could be attributed to the rigidity of the molecule which does not allow the appropriate conformation to react with an electrophile (Figure 32).

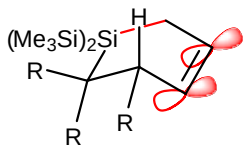


Figure 32

4.6 Conclusions

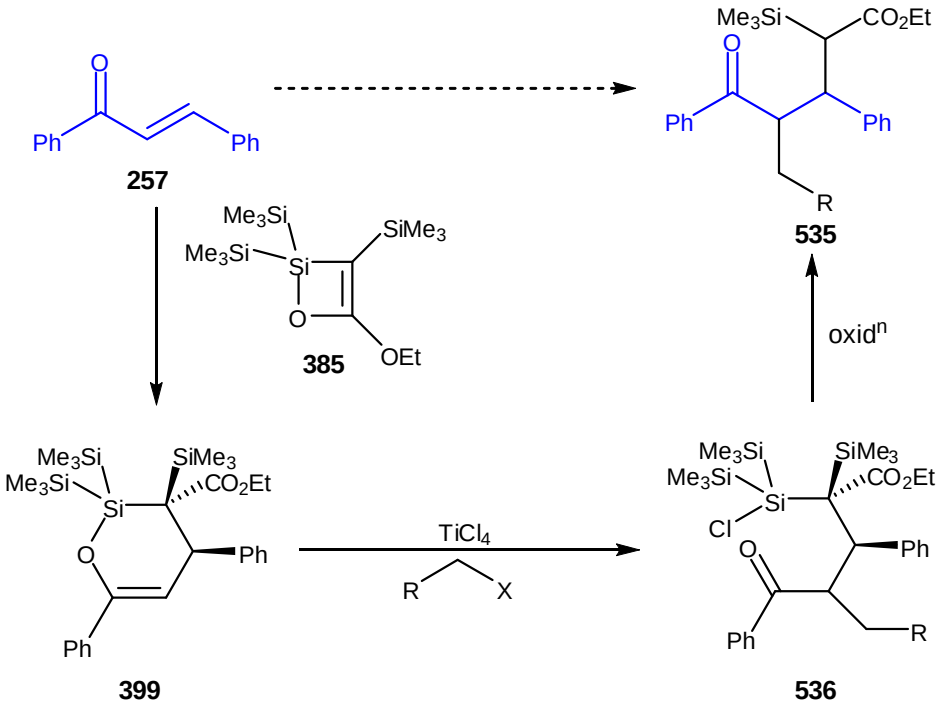
In conclusion, it is believed that this is the first report of an intramolecular silene cycloaddition reaction. Preliminary investigations indicate that this reaction proceeds to give silacycles in good yield, although with moderate diastereoselectivity. Disappointingly, initial attempts to oxidise the silacycle proved to be unsuccessful. However, it has to be emphasised that work in this area remains incomplete due to time constrains and the pressure of working on other aspects of the project.

5 Conclusions and Future work

This thesis deals with the development of novel methods for organic synthesis through the reactions of readily accessible silenes and the subsequent elaboration of the resultant adducts.

It was shown that the reaction of Brook siloxysilenes with electron-deficient dienes/alkenes led to the formation of silacyclobutanes, which under the reaction conditions underwent isomerisation to the corresponding cyclopropanes. These cyclopropanes were subsequently elaborated into 1,4-dicarbonyl compounds.

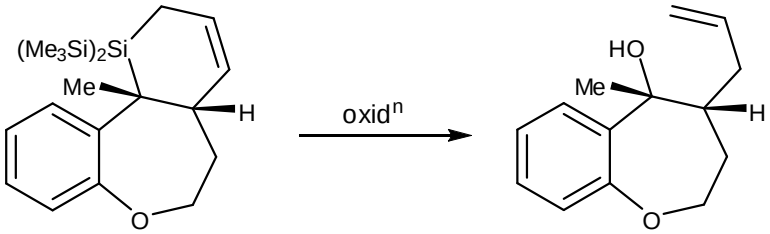
In the second phase of the work the synthetic potential of α-silyl diazo carbonyl compounds as silene precursors was examined. It was found that these compounds undergo decomposition to provide silylketenes. Such processes proceed via a short-lived silene and an oxasilete intermediate. These intermediates did not react with dienes, alkenes or alkynes. Interestingly, oxasiletes react with α,β-unsaturated ketones to form the corresponding adducts usually with good diastereoselectivity. In future, these adducts could be used in the synthesis of more complex structures (Scheme 139).



Scheme 139

Finally, it was shown in Chapter 4 that intramolecular silene cycloaddition reactions can be used to synthesise more complex skeletons. This involved thermolysis or addition of MeLi to

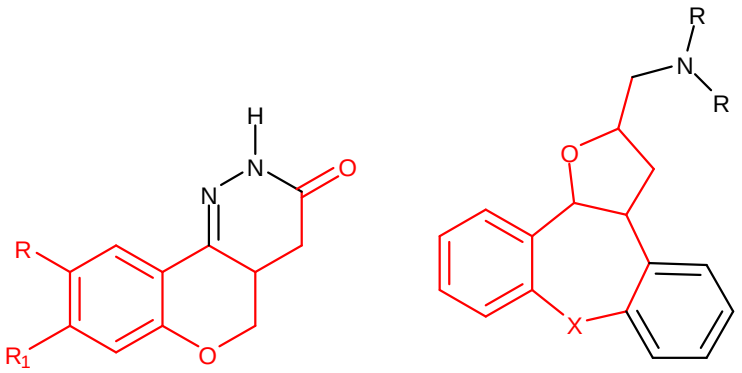
acylpolysilanes at low temperature. Both methods gave adducts with good yield and moderate diastereoselectivity. Unfortunately, the silacycle formed by thermolysis of acylpolysilanes proved difficult to oxidise. This is attributed to the presence of the $OSiMe_3$ group adjacent to the disilyl group. Therefore, future work could focus on the development of a suitable oxidation procedure. In addition, it is believed that the cycloadducts synthesised via Ishikawa's protocol could be easily oxidised since they do not have an $OSiMe_3$ group (Scheme 140).



523 **537**

Scheme 140

This methodology could present a novel approach to the synthesis of structurally interesting and biologically active natural products e.g. **538**[119], **539**[120] (Figure 33).



potentially antitumoric, antihypertensive

538

potential anxiolytic, antidepressant properties

539

Figure 33

6 Computational Details

Calculations were carried out using Gaussian03 software package.[121] The geometries were optimised with density functional theory using Becke's three parameter exchange functional and the correlation functional of Lee, Yang, and Parr (B3LYP),[122,123] with a 6-31G(d) basis set. Frequencies were calculated at B3LYP/6-31G(d) in order to identify them as minima. The NMR chemical shifts were evaluated by using the gauge-including atomic orbitals method (GIAO)[124] with the B3LYP and BPW91[122,125] functionals. These methods were accompanied by 6-31G(d,p) and aug-cc-pvDZ basis sets. In order to compare isotropic shieldings with experimental chemical shifts the NMR parameters for tetramethylsilane were calculated for each basis set and used as the reference molecule.

7 Experimental procedures

7.1 General Procedures

All air- and/or moisture-sensitive reactions were carried out under an argon atmosphere in oven-dried glassware.

Solvents

40-60 Petroleum ether was redistilled before use and refers to the fraction of light petroleum ether boiling in the range 40-60 ^{o}C. Benzene was dried over 4 Å molecular sieves. All other solvents were obtained dried from Innovative Technology Solvent Purification System (SPS).

Reagents

Commercially available reagents were used without further purification, apart from the following: trimethylacetyl chloride was distilled from anhydrous P_2O_{10}, Et_3N was distilled over KOH pellets, *t*-BuOK was dried under vacuum at 50 ^{o}C overnight before use.

Chromatography

Analytical thin layer chromatography (TLC) was performed using commercially available aluminium-backed plates coated with silica gel 60 F_{254} (UV_{254}) or neutral aluminium oxide 60 F_{254} (UV_{254}), and visualised under ultra-violet light (at 254 nm), or through staining with ethanolic phosphomolybdic acid followed by heating. Flash column chromatography was carried out using 200-400 mesh silica gel 40-63 μm or neutral alumina

Melting point

Melting points were determined either using Thermo Scientific 9100 or Gallenkamp melting point apparatus and are uncorrected.

Microwave

Microwave experiments were carried out using a Personal Chemistry Emrys Optimizer Workstation.

Gas chromatography

Gas Chromatography was carried out on a Hewlett-Packard 5890 series II gas chromatograph fitted with a 25 cm column and connected to a flame ionisation detector.

IR spectroscopy

Infrared spectra were recorded using a Diamond ATR (attenuated total reflection) accessory (Golden Gate) or as a solution in chloroform via transmission IR cells on a Perkin-Elmer FT-IR 1600 spectrometer.

NMR spectroscopy

^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were recorded in $CDCl_3$ (unless otherwise stated) on Varian Mercury-200 (^{1}H), Varian Mercury-400 (^{1}H, ^{13}C, ^{19}F), Bruker Avance-400 (^{1}H, ^{13}C, ^{29}Si), Varian Inova-500 (^{1}H, ^{13}C, ^{29}Si) or Varian VNMRS-700 (^{1}H, ^{13}C, ^{29}Si) spectrometers and reported as follows: chemical shift δ (ppm) (number of protons, multiplicity, coupling constant *J* (Hz), assignment). All ^{13}C NMR spectra were proton decoupled. The chemical shifts are reported using the residual signal of $CHCl_3$ as the internal reference (δ_H = 7.27 ppm; δ_C = 77.0 ppm). All chemical shifts are quoted in parts per million relative to tetramethylsilane (δ_H = 0.00 ppm) and coupling constants are given in Hertz to the nearest 0.5

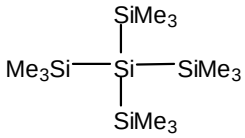
Hz. Assignment of spectra was carried out using COSY, NOESY, HSQC, and HMBC experiments.

Mass spectrometry

Gas-Chromatography mass spectra (EI) were taken using a Thermo-Finnigan Trace with a 25 cm column connected to a VG Mass Lab Trio 1000. Electrospray mass spectra (ES) were obtained on a Micromass LCT Mass Spectrometer. High resolution mass spectra were obtained using a Thermo-Finnigan LTQFT mass spectrometer or Xevo QToF mass spectrometer (Waters UK, Ltd) by Durham University Mass Spectrometry service, or performed by the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea.

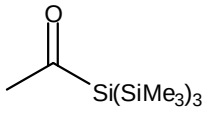
7.2 Experimental detail

Tetrakis(trimethylsilyl)silane[126,81] **219**



To a solution of chlorotrimethylsilylsilane (224 ml, 1.76 mol) in THF (400 ml) was added pieces of lithium ribbon (31.0 g, 4.46 mol) and stirred for 1 h at room temperature. A solution of silicon tetrachloride (43 ml, 0.38 mol) in THF (300 ml) was prepared. A portion of the resulting solution (40 ml) was added dropwise to the stirred solution of chlorotrimethylsilylsilane. After 4 h stirring, the remaining silicon tetrachloride solution was added over 2 h. The reaction mixture was stirred for 12 h and filtered through Celite®. The filtrate was added to dilute HCl (5 M, 300 ml). The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 x 150 ml). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Recrystallisation from acetone yielded tetrakis(trimethylsilyl)silane, (63.8 g, 53%). Mp: 249-251 ^oC (lit. 256-260 ^oC); IR (ATR) 2951, 2895, 1243, 825, 685, 620 cm^{-1}; δ_H (400 MHz) 0.20 (36H, s, C***H***$_3$); δ_C (100 MHz) 2.6 (***C***H_3); δ_{Si} (80 MHz) -9.9; m/z (EI) 320 ($[M]^{+\cdot}$, 36%), 305 ($[M\text{-}CH_3]^{+\cdot}$, 19), 232 ($[M\text{-}CH_3\text{-}Si(CH_3)_3]^{+\cdot}$, 100), 173 (36), 158 (29), 131 (16), 73 (84).

Acetyltris(trimethlsilyl)silane[81] **220**



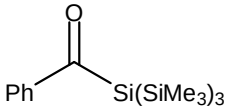
Method 1

To a solution of tetrakis(trimethylsilyl)silane (3.01 g, 9.38 mmol) in THF (39 ml) was added a solution of methyllithium (5.84 ml of a 1.6 M solution in Et_2O, 9.34 mmol) and stirred at room temperature. After 24 h ^{1}H NMR analysis showed a signal that correspond to unreacted tetrakis(trimethylsilyl)silane (δ_H 0.20 ppm) therefore a second portion of methyllithium (0.6 ml, 1.6 M) was added and the reaction mixture was stirred for a further 12 h (70% conversion by ^{1}H NMR). The solution was then cooled to -78 ^{o}C and added dropwise to a cooled solution (-78 ^{o}C) of acetylchloride (1.33 ml, 18.7 mmol) in THF (19 ml). The mixture was stirred at -78 ^{o}C for 3 h, before quenching by addition of diluted HCl (0.5 M, 50 ml) and extracting with Et_2O (3 x 60 ml). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. Flash column chromatography (pet. ether : diethyl ether 95:5) gave the title compound as a waxy colourless solid (0.80 g, 32%).

Method 2

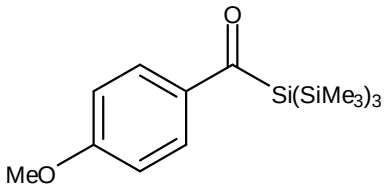
Tetrakis(trimethylsilyl)silane (2.26 g, 7.05 mmol) and dry potassium *tert*-butoxide (0.83 g, 7.40 mmol) were dissolved in THF (30 ml) and stirred for 3 h at room temperature. A suspension of CuI (1.41 g, 7.40 mmol) in THF (5 ml) was added and the reaction mixture was stirred for 5 min. The black solution was then added dropwise via cannula to a cooled (0 ^{o}C) solution of acetyl chloride (1.0 ml, 14.1 mmol) in THF (20 ml). After stirring for 3 h at 0 ^{o}C the reaction mixture was allowed to reach room temperature and then saturated $NaHCO_3$ solution (20 ml) was added. The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 x 20 ml). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash column chromatography (pet. ether : diethyl ether 95:5) gave the title compound as a waxy colourless solid (1.02 g, 50%). R_f 0.5 (pet. ether : diethyl ether 95:5); IR (ATR) 2952, 2895, 1633, 1244, 1112, 823, 688, 625 cm^{-1}; δ_H (500 MHz) 2.29 (3H, s, C(O)C$\boldsymbol{H}_3$), 0.24 (27H, s, Si(C$\boldsymbol{H}_3$)$_3$); δ_C (125 MHz) 244.0 (***C***O), 42.1 (***C***H$_3$), 1.0 (Si(***C***H$_3$)$_3$); δ_{Si} (80 MHz) -12.2; m/z (EI) 290 ([M]$^{+\cdot}$, 1%), 275 ([M-CH$_3$]$^{+\cdot}$, 9), 217 ([M-Si(CH$_3$)$_3$]$^{+\cdot}$, 12), 201 (16), 187 (18), 173 (30), 143 (35), 133 (36), 117 (13), 73 (100).

Benzoyltris(trimethylsilyl)silane[81] 211



Tetrakis(trimethylsilyl)silane (9.76 g, 30.4 mmol) and dry potassium *tert*-butoxide (3.75 g, 33.5 mmol) were dissolved in THF (60 ml). The solution was stirred for 3 h at room temperature. The orange solution was then added dropwise via cannula to a cooled (-78 ^{o}C) solution of trimethylacetyl chloride (10.6 ml, 91.2 mmol) in THF (60 ml). After stirring for 3 h at -78 ^{o}C the reaction mixture was allowed to reach room temperature and then NH_3/H_2O (1% w/w, 50 ml) and Et_2O (50 ml) were added. The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 x 50 ml). The combined organic layers were dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. Flash column chromatography (pet. ether : chloroform 7:3) gave the title compound (7.35 g, 69%) as a yellow oil. R_f 0.4 (pet. ether : chloroform 7:3); IR (ATR) 2950, 2894, 1608, 1245, 1200, 1070, 826, 765, 690 cm^{-1}; δ_H (500 MHz) 7.75-7.72 (2H, m, Ar-2,6-***H***), 7.53-7.43 (3H, m, Ar-3,4,5-***H***), 0.26 (27H, s, Si(C***H***$_3$)$_3$); δ_C (125 MHz) 236.4 (***C***O), 144.1 (Ar-***C***-1), 132.4 (Ar-***C***-4), 128.2 (Ar-***C***-2,6), 127.4 (Ar-***C***-3,5), 1.5 (Si(***C***H$_3$)$_3$); δ_{Si} (80 MHz) -11.5, -71.3; m/z (ES+) 353 ([M+H]$^{+\cdot}$, 40%), 295 (12), 124 (100).

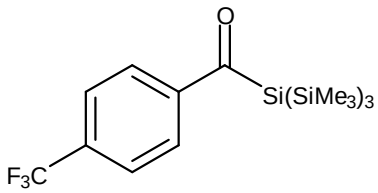
4-Methoxybenzoyltris(trimethylsilyl)silane[81] 213



Tetrakis(trimethylsilyl)silane (3.20 g, 10.0 mmol) and dry potassium *tert*-butoxide (1.28 g, 11.1 mmol) were dissolved in THF (20 ml) and stirred for 2 h at room temperature. The orange solution was then added dropwise via cannula to a cooled (-78 ^{o}C) solution of 4-methoxybenzoyl chloride (3.0 ml, 22.0 mmol) in THF (20 ml). After stirring for 4 h at -78 ^{o}C the reaction mixture was allowed to reach room temperature and then dilute HCl (1 M, 15 ml) was added. The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 x 20 ml). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash column chromatography (pet. ether : diethyl ether 9:1) gave the title compound as a yellow oil (1.04 g, 27%). R_f 0.5 (pet. ether : diethyl ether 9:1); IR (ATR) 2952, 2891, 1606, 1589, 1563, 1249, 1209, 1157, 1019, 822, 687, 618 cm^{-1}; δ_H (500 MHz)

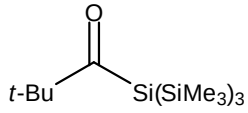
7.76-7.74 (2H, m, Ar-2,6-***H***), 6.94-6.92 (2H, m, Ar-3,5-***H***), 3.88 (3H, s, OC***H***$_3$), 0.26 (27H, s, Si(C***H***$_3$)$_3$); δ_C (125 MHz) 233.1 (***C***O), 163.2 (Ar-***C***-4), 137.6 (Ar-***C***-2,6), 130.0 (Ar-***C***-1), 113.3 (Ar-***C***-3,5), 55.4 (O***C***H$_3$), 1.50 (Si(***C***H$_3$)$_3$); δ_{Si} (80 MHz) -11.5, -72.3; m/z (ES+) 383 ([M+H]$^{+\cdot}$, 10%), 367 ([M-CH$_3$]$^{+\cdot}$, 100).

4-(Trifluoromethyl)benzoyltris(trimethylsilyl)silane[81] 215



Tetrakis(trimethylsilyl)silane (1.69 g, 5.3 mmol) and dry potassium *tert*-butoxide (0.62 g, 5.5 mmol) were dissolved in THF (20 ml) and stirred for 3 h at room temperature. The orange solution was then added dropwise via cannula to a cooled (-78 ^{o}C) solution of 4-(trifluoromethyl)benzoyl chloride (1.6 ml, 10.6 mmol) in THF (15 ml). After stirring for 2 h at -78 ^{o}C the reaction mixture was allowed to reach room temperature and then solvent was evaporated. Flash column chromatography, elution gradient 0 to 5% diethyl ether in hexane, gave the title compound as a yellow oil (1.29 g, 58%). R_f 0.8 (pet. ether : diethyl ether 95:5); IR (ATR) 2952, 2896, 1605, 1505, 1406, 1323, 1246, 1170, 1132, 1064, 1016, 825, 687, 624 cm^{-1}; δ_H (700 MHz) 7.82-7.81 (2H, m, Ar-2,6-***H***), 7.74-7.73 (2H, m, Ar-3,5-***H***), 0.27 (27H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 236.5 (***C***O), 146.2 (Ar-***C***-1), 133.7 (q, $^2J_{c\text{-}f}$ = 32.6Hz, Ar-***C***-4) 127.4 (Ar-***C***-2,6), 125.5 (q, $^3J_{c\text{-}f}$ = 3.8Hz, Ar-***C***-3,5), 123.8 (q, $^1J_{c\text{-}f}$ = 271.8Hz, ***C***F$_3$), 1.42 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) -11.3, -69.9; m/z (EI) 405 ([M-CH$_3$]$^{+\cdot}$, 30), 281 (56), 207 (32), 190 (29), 173 (62), 147 (61), 73 (100).

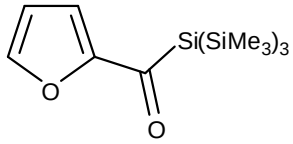
Trimethylacetyltris(trimethylsilyl)silane[81] 217



Tetrakis(trimethylsilyl)silane (15.0 g, 46.8 mmol) and dry potassium *tert*-butoxide (5.77 g, 51.4 mmol) were dissolved in THF (80 ml). The solution was stirred for 3 h at room temperature. The orange solution was then added dropwise via cannula (over a 1 hour period) to a cooled (-78 ^{o}C) solution of trimethylacetyl chloride (6.33 ml, 51.4 mmol) in THF (50 ml). After stirring for 5h at -78 ^{o}C the reaction mixture was allowed to reach room temperature and then dilute HCl (1 M, 52 ml) and Et$_2$O (50 ml) were added. The organic layer was separated,

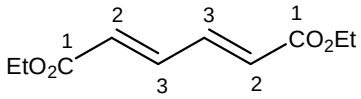
and the aqueous layer was extracted with Et_2O (2 x 50 ml). The combined organic layers were dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. Flash column chromatography (pet. ether : chloroform 7:3) gave the title compound (13.3 g, 85%) as a white solid. R_f 0.6 (pet. ether : chloroform 7:3); Mp: 176-178 ºC; IR (ATR) 2952, 2896, 1625, 1243, 824, 687, 621 cm^{-1}; δ_H (500MHz) 1.02 (9H, s, C(O)C(C***H***$_3$)$_3$), 0.22 (27H, s, Si(C***H***$_3$)$_3$); δ_C (125MHz) 248.2 (***C***O), 49.3 (***C***$(CH_3)_3$), 24.7 (C(***C***$H_3)_3$), 1.6 (Si(***C***$H_3)_3$); δ_{Si} (80MHz) -11.6, -78.2; m/z (EI) 317 ($[M\text{-}CH_3]^{+\cdot}$, 12%), 275 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 6), 247 (71), 173 (100), 159 (29), 147 (60), 131 (45), 117 (32), 73 (100), 45 (36).

2-Furoyltris(trimethylsilyl)silane 222



Tetrakis(trimethylsilyl)silane (4.95 g, 15.4 mmol) and dry potassium *tert*-butoxide (1.82 g, 16.2 mmol) were dissolved in THF (30 ml) and stirred for 2 h at room temperature. The orange solution was then added dropwise via cannula to a cooled (-78 ^oC) solution of 2-furoyl chloride (4.6 ml, 46.3 mmol) in THF (30 ml). After stirring for 3 h at -78 ^oC the reaction mixture was allowed to reach room temperature and then NH_3/H_2O (1% w/w, 25 ml) and Et_2O (25 ml) were added. The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 x 25 ml). The combined organic layers were dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. Flash column chromatography on silica, elution gradient 5 to 20% diethyl ether in hexane, afforded the product as an unstable yellow oil (1.92 g, 36%). R_f 0.5 (pet. ether : diethyl ether 4:1); IR (ATR) 2950, 2892, 1587, 1554, 1455, 1395, 1241, 1151, 1078, 1011, 823, 749 cm^{-1}; δ_H (700 MHz) 7.54 (1H, d, *J* = 1.4Hz, 5-***H***), 6.91 (1H, d, *J* = 3.5Hz, 3-***H***), 6.54 (1H, dd, *J* = 3.5Hz, *J* = 1.4Hz, 4-***H***), 0.25 (27H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 223.0 (***C***O), 159.2 (***C***-*2*), 144.9 (***C***-5), 112.4 (***C***-4), 110.5 (***C***-3), 1.3 (Si(***C***$H_3)_3$); δ_{Si} (140 MHz) -10.8, -70.2; m/z (ES+) 343 ($[M+H]^{+\cdot}$, 10%), 327 ($[M\text{-}CH_3]^{+\cdot}$, 100).

(2*E*,4*E*)-Diethyl hexa-2,4-dienedioate[87] 230

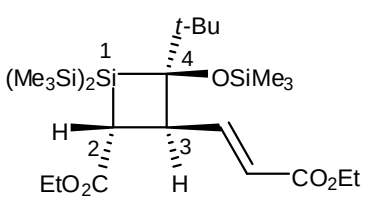


Chlorotrimethylsilane (30.0 ml, 236 mmol) was added to a solution of (2*E*, 4*E*)-diethyl hexa-2,4-dienedioate (10.0 g, 70.4 mmol) in EtOH (300 ml). The reaction mixture was heated to reflux and maintained for 20 h. The reaction was then quenched by addition of a saturated $NaHCO_3$ solution (200 ml) and diluted with Et_2O (100 ml).The aqueous layer was separated and extracted with Et_2O (2 x 100 ml). The combined organic fractions were washed with brine (50 ml), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to yield the title diester as a white solid (13.9 g, 100%). R_f 0.6 (diethyl ether : pet. ether 8:2); Mp: 54-55 ^oC (lit. [127] 57-59 ^oC); IR (ATR) 3068, 2981, 1696, 1610, 1312, 1239, 1153, 1022, 861, 694 cm^{-1}; δ_H (500 MHz) 7.33-7.29 (2H, m, 2-***H***), 6.21-6.18 (2H, m, 3-***H***), 4.24 (4H, q, *J* = 6.8Hz, C***H***$_2$CH$_3$), 1.31 (6H, t, *J* = 6.8Hz, CH$_2$C***H***$_3$); δ_C (125 MHz) 165.9 (***C***-1), 140.8 (***C***-2), 128.4 (***C***-3), 60.8 (***C***H$_2$CH$_3$), 14.2 (CH$_2$***C***H$_3$); m/z (EI) 198 ([M]$^{+\cdot}$, 5%), 153 ([M-OCH$_2$CH$_3$]$^{+\cdot}$ 36%), 125 ([M-OC(O)CH$_2$CH$_3$]$^{+\cdot}$, 39), 108 (10), 97 (100), 79 (20), 69 (15), 51 (32), 29 (43).

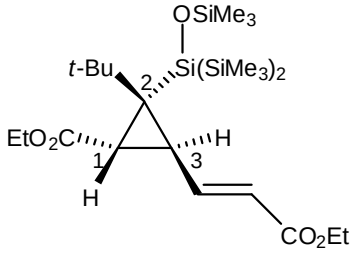
General procedure for the formation of cycloadduct in carius tube

A solution of polysilane and silenophile in dry benzene was prepared in a round bottom flask and transferred via syringe to a tube with tap under argon. The solution was then degassed by standard freeze-pump-thaw technique, repeating three times. The tube was then sealed and heated in a metal pipe. After heating, the tube was allowed to cool to ambient temperature and then further by immersion in liquid nitrogen before opening.

(2*RS*,3*SR*,4*SR*)-Ethyl 4-*tert*-butyl-3-((*E*)-3'-ethoxy-3'-oxoprop-1'-enyl)-1,1-bis(trimethylsilyl)-4-(trimethylsilyloxy)siletane-2-carboxylate 231a and **(1*RS*,2*RS*,3*SR*)--Ethyl 2-*tert*-butyl-3-((*E*)-3'-ethoxy-3'-oxoprop-1'-enyl)-2-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silylcyclopropanecarboxylate 232a**



231a



232a

Method A

A solution of trimethylacetyltris(trimethylsilyl)silane **217** (0.51 g, 1.53 mmol) and (2*E*,4*E*)-diethyl hexa-2,4-dienedioate **230** (1.22 g, 6.11 mmol) in dry benzene (7.0 ml) was heated in a sealed tube at 200 ^{o}C for 3 h. Concentration, followed by flash column chromatography (pet. ether : diethyl ether 9:1) afforded the product **231a** as a yellow oil (0.19 g, 23%) and product **232** as a mixture of diastereoisomers (0.36 g, 46%, 2.7:1). Recrystallisation from MeCN/$CHCl_3$ yielded compound **232** as a pure isomer **232a** (0.21 g, 58%).

Experimental data for compound **231a**:

R_f 0.3 (pet. ether : diethyl ether 9:1); IR (ATR) 2954, 2899, 1715, 1645, 1246, 1145, 1082, 1048, 834 cm^{-1}; δ_H (500 MHz) 7.01 (1H, dd, *J* = 15.6Hz, *J* = 7.0Hz, 1'-***H***), 5.82 (1H, dd, *J* = 15.6Hz, *J* = 1.2Hz, 2'-***H***), 4.20-4.12 (2H, m, 2'-$CO_2C\boldsymbol{H}_2CH_3$), 4.03 (2H, q, *J* = 7.0Hz, 2-$CO_2C\boldsymbol{H}_2CH_3$), 3.75 (1H, ddd, *J* = 12.0Hz, *J* = 7.0Hz, *J* = 1.2Hz, 3-***H***), 2.56 (1H, d, *J* = 12.0Hz, 2-***H***), 1.26 (3H, t, *J* = 7.0Hz, 2'-$CO_2CH_2C\boldsymbol{H}_3$), 1.21 (3H, t, *J* = 7.0Hz, 2-$OCH_2C\boldsymbol{H}_3$), 0.95 (9H, s, $C(C\boldsymbol{H}_3)_3$), 0.27 (9H, s, $Si(C\boldsymbol{H}_3)_3$), 0.23 (18H, s, $Si(C\boldsymbol{H}_3)_3$); δ_C (125 MHz) 174.0 (2-***C***O), 166.4 (2'-***C***O), 148.6 (***C***-2'), 121.7 (***C***-1'), 96.0 (***C***-4), 60.2 (2'-$CO_2\boldsymbol{C}H_2CH_3$), 59.7 (2-$CO_2\boldsymbol{C}H_2CH_3$), 49.6 (***C***-3), 37.4 ($\boldsymbol{C}(CH_3)_3$), 29.1 (***C***-2), 29.0 ($C(\boldsymbol{C}H_3)_3$), 14.3 (2'-$CO_2CH_2\boldsymbol{C}H_3$), 14.2 (2-$CO_2CH_2\boldsymbol{C}H_3$), 4.4 ($OSi(\boldsymbol{C}H_3)_3$), 0.8 ($Si(\boldsymbol{C}H_3)_3$), 0.5 ($Si(\boldsymbol{C}H_3)_3$); δ_{Si} (80 MHz) 6.4, -10.3, -14.8, -16.1; m/z (EI) 530 ($[M]^{+\cdot}$, 5%), 473 ($[M\text{-}C(CH_3)_3]^{+\cdot}$, 7), 457 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 19), 343 (20), 273 (49), 213 (52), 191 (49), 175(25), 147 (31), 117 (81), 73 (100), HRMS (EI) found $[M]^{+\cdot}$ 530.2743, $C_{24}H_{50}O_5Si_4$ requires $[M]^{+\cdot}$ 530.2741.

Experimental data for compound **232a**:

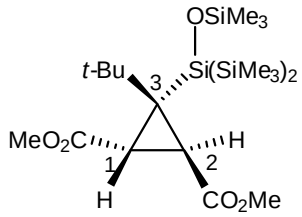
Mp: 104–106 ^{o}C; R_f 0.4 (pet. ether : diethyl ether 9:1); IR (ATR) 2956, 2898, 1713, 1635, 1251, 1175, 1135, 1027, 832 cm^{-1}; δ_H (500 MHz) 7.10 (1H, dd, *J* = 15.0Hz, *J* = 10.0Hz, 1'-***H***), 6.01 (1H, d, *J* = 15.0Hz, 2'-***H***), 4.22-4.16 (2H, m, 2'-$CO_2C\boldsymbol{H}_2CH_3$), 4.13-4.00 (2H, m, 1-$CO_2C\boldsymbol{H}_2CH_3$), 2.33 (1H, dd, *J* = 10.0Hz, *J* = 5.0Hz, 3-***H***), 2.31 (1H, d, *J* = 5.0Hz, 1-***H***), 1.29 (3H, t, *J* = 7.0Hz, 2'-$CO_2CH_2C\boldsymbol{H}_3$), 1.25 (3H, t, *J* = 7.0Hz, 1-$CO_2CH_2C\boldsymbol{H}_3$), 1.10 (9H, s, $C(C\boldsymbol{H}_3)_3$), 0.14 (9H, s, $OSi(C\boldsymbol{H}_3)_3$), 0.13 (9H, s, $Si(C\boldsymbol{H}_3)_3$), 0.12 (9H, s, $Si(C\boldsymbol{H}_3)_3$); δ_C (125 MHz) 172.6 (1-***C***O), 166.1 (2'-***C***O), 148.0 (***C***-1'), 122.3 (***C***-2'), 60.9 (1-$CO_2\boldsymbol{C}H_2CH_3$), 60.3 (2'-$CO_2\boldsymbol{C}H_2CH_3$), 37.9 ($\boldsymbol{C}(CH_3)_3$), 34.8 (***C***-3), 33.4 (***C***-1), 31.3 ($C(\boldsymbol{C}H_3)_3$), 29,0 (***C***-2), 14.3 (1-$CO_2CH_2\boldsymbol{C}H_3$), 14.2 (2'-$CO_2CH_2\boldsymbol{C}H_3$), 3.3 ($OSi(\boldsymbol{C}H_3)_3$), 0.8 ($Si(\boldsymbol{C}H_3)_3$), 0.6 ($Si(\boldsymbol{C}H_3)_3$); δ_{Si} (80 MHz) 4.6, -16.1, -16.9; m/z (EI) 515 ($[M\text{-}CH_3]^{+\cdot}$, 7%), 457 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 12), 207 (14),

191 (29), 147 (12), 117 (27), 73 (100), 57 (18), 45 (12), Anal. Calcd for $C_{24}H_{50}O_5Si_4$: C, 54.29; H, 9.49. Found: C, 54.07; H, 9.55.

Method B

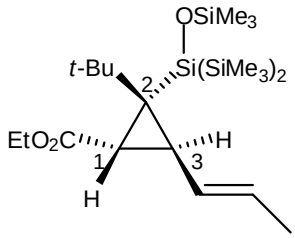
A solution of trimethylacetyltris(trimethylsilyl)silane (0.50 g, 1.50 mmol) and (2*E*,4*E*)-diethyl hexa-2,4-dienedioate (0.30 g, 1.50 mmol) in a mixture of toluene (2.97 ml) and pyridine (0.03 ml) was heated in a microwave tube at 220 ^oC for 0.5 h. Concentration, followed by flash column chromatography on silica (pet. ether : diethyl ether 9:1) afforded the product **231a** as a yellow oil (0.19 g, 24%) and product **232** as a mixture of diastereoisomers (0.31 g, 38%, 3:1). Recrystallisation from MeCN/$CHCl_3$ yielded compound **232** as a pure isomer **232a** (0.18 g, 57%). Spectroscopic data for both products **231a** and **232a** were consistent with data presented in *Method A*.

(1*RS*,2*RS*)-Dimethyl 3-*tert*-butyl-3-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silylcyclopropane-1,2-dicarboxylate 235



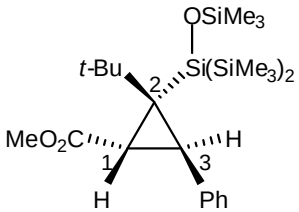
A solution of trimethylacetyltris(trimethylsilyl)silane (0.25 g, 0.75 mmol) and dimethyl fumarate (0.43 g, 3.00 mmol) in dry benzene (3.5 ml) was heated in a sealed tube at 200 ^oC for 3 h. Concentration, followed by flash column chromatography (pet. ether : diethyl ether 9:1) afforded the product as a colourless oil (0.12 g, 33%). R_f 0.5 (pet. ether : diethyl ether 9:1); IR ($CHCl_3$) 3021, 2955, 1740, 1438, 1252, 1213, 1055, 1032, 844, 755, 669 cm^{-1}; δ_H (500 MHz) 3.71 (3H, s, OC***H***$_3$), 3.64 (3H, s, OC***H***$_3$), 2.76 (1H, d, *J* = 6.0Hz, C***H***CO_2Me), 2.38 (1H, d, *J* = 6.0Hz, C***H***CO_2Me), 1.05 (9H, s, C(C***H***$_3)_3$), 0.17 (9H, s, Si(C***H***$_3)_3$), 0.14 (9H, s, Si(C***H***$_3)_3$), 0.12 (9H, s, OSi(C***H***$_3)_3$); δ_C (125 MHz) 172.1 (***C***O), 171.9 (***C***O), 52.8 (O***C***H_3), 52.1 (O***C***H_3), 38.4 (***C***$(CH_3)_3$), 34.4 (***C***-3), 31.7 (***C***HCO_2Me), 30.4 (C(***C***$H_3)_3$), 30.0 (***C***HCO_2Me), 3.4 (OSi(***C***$H_3)_3$), 0.5 (Si(***C***$H_3)_3$), 0.4 (Si(***C***$H_3)_3$); δ_{Si} (80 MHz) 6.3, 1.0, -17.3, -17.8 m/z (EI) 461 ($[M\text{-}CH_3]^{+\cdot}$, 6%), 403 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 93), 221(86), 207(26), 191(37), 147(55), 133 (49), 117 (90), 89 (30), 73 (100), 45 (36).

(1*RS*,2*RS*,3*SR*)-Ethyl 2-*tert*-butyl-2-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silyl-3-((*E*)prop-1'-enyl)cyclopropanecarboxylate 237



A solution of trimethylacetyltris(trimethylsilyl)silane (0.50 g, 1.50 mmol) and ethyl sorbate (0.44 ml, 3.00 mmol) in dry benzene (7.0 ml) was heated in a sealed tube at 200 ^{o}C for 4 h. Concentration, followed by flash column chromatography on silica (pet. ether : chloroform 8:2) afforded the product as a colourless oil (0.05 g, 7%). R_f 0.5 (pet. ether : chloroform 8:2); IR ($CHCl_3$) 3020, 2962, 1734, 1423, 1251, 1218, 1052, 930, 843, 669 cm^{-1}; δ_H (500 MHz) 5.67 (1H, dq, *J* = 15.1Hz, *J* = 6.5Hz, 2'-***H***), 5.58 (1H, dd, *J* = 15.1Hz, *J* = 8.1Hz, 1'-***H***), 4.05 (2H, q, *J* = 7.0Hz, OC***H***$_2$CH$_3$), 2.18 (1H, dd, *J* = 8.1Hz, *J* = 5.0Hz, 3-***H***), 2.00 (1H, d, *J* = 5.0Hz, 1-***H***), 1.71 (3H, d, *J* = 6.5Hz, 3'-***H***), 1.25 (3H, t, *J* = 7.0Hz, OCH$_2$C***H***$_3$), 1.08 (9H, s, C(C***H***$_3$)$_3$), 0.14 (9H, s, OSi(C***H***$_3$)$_3$), 0.13 (9H, s, Si(C***H***$_3$)$_3$), 0.10 (9H, s, Si(C***H***$_3$)$_3$); δ_C (125 MHz) 173.9 (***C***O), 129.0 (***C***-1'), 127.9 (***C***-2'), 60.5 (O***C***H$_2$CH$_3$), 34.7 (***C***-3), 34.4 (***C***-2) , 32.2 (***C***(CH$_3$)$_3$), 31.1 (C(***C***H$_3$)$_3$), 30.8 (***C***-1), 18.2 (***C***-3'), 14.3 (OCH$_2$***C***H$_3$), 3.3 (OSi(***C***H$_3$)$_3$), 0.8 (Si(***C***H$_3$)$_3$), 0.7 (Si(***C***H$_3$)$_3$); δ_{Si} (139 MHz) 3.8, -13.9, -16.0, -16.8; m/z (EI) 457 ([M-CH$_3$]$^{+\cdot}$, 4%), 399 ([M-Si(CH$_3$)$_3$]$^{+\cdot}$, 55), 235 (33), 207 (62), 191 (88), 147 (38), 133 (29), 117 (70), 73 (100); HRMS (ES+) found [M+H]$^{+\cdot}$ 473.2760, $C_{22}H_{49}O_3Si_4$ requires [M+H]$^{+\cdot}$ 473.2753.

(1*RS*,2*RS*,3*RS*)-Methyl 2-*tert*-butyl-2-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silyl-3-phenylcyclopropanecarboxylate 239



Method A

A solution of trimethylacetyltris(trimethylsilyl)silane (0.25 g, 0.75 mmol) and *trans*-cinnamic methyl ester (0.49 g, 3.02 mmol) in dry benzene (3.5 ml) was heated in a sealed tube at 200 ^{o}C for 3 h. Concentration, followed by flash column chromatography on silica (pet. ether : chloroform 8:2) afforded the product as a white solid (0.18 g, ds 1, 49%). Mp: 135-138 ^{o}C; R_f 0.4 (pet. ether : chloroform 8:2); IR (ATR) 2955, 1717, 1440, 1401, 1250, 1202, 1028, 831,

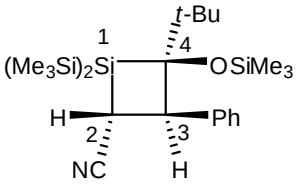
763, 685 cm^{-1}; δ_H (500 MHz) 7.41-7.39 (2H, m, Ar-3,5-***H***), 7.31-7.27 (2H, m, Ar-2,6-***H***), 7.23-7.19 (1H, m, Ar-4-***H***), 3.69 (3H, s, OC$\boldsymbol{H}_3$), 2.90 (1H, d, *J* = 6.0Hz, 3-***H***), 2.59 (1H, d, *J* = 6.0Hz, 1-***H***), 0.88 (9H, s, C(C$\boldsymbol{H}_3)_3$), 0.19 (9H, s, OSi(C$\boldsymbol{H}_3)_3$), 0.18 (9H, s, Si(C$\boldsymbol{H}_3)_3$), 0.17 (9H, s, Si(C$\boldsymbol{H}_3)_3$); δ_C (125 MHz) 174.4 (***C***O), 137.5 (Ar-***C***-1), 130.4 (Ar-***C***-2,6), 128.0 (Ar-***C***-3,5), 126.5 (Ar-***C***-4), 51.8 (O***C***H_3), 37.5 (***C***-3), 36.7 (***C***$(CH_3)_3$), 35.3 (***C***-2), 30.6 (C(***C***$H_3)_3$), 27.1 (***C***-1), 3.3 (OSi(***C***$H_3)_3$), 0.9 (Si(***C***$H_3)_3$), 0.8 (Si(***C***$H_3)_3$); δ_{Si} (80 MHz) 4.5, -16.2, -16.5; m/z (EI) 479 ($[M\text{-}CH_3]^{+\cdot}$, 7%), 421 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 82), 221(90), 191 (32), 147 (40), 133 (34), 73 (100), 59 (20), 45 (25); HRMS (ES+) found $[M+H]^{+\cdot}$ 495.2597, $C_{24}H_{46}O_3Si_4$ requires $[M+H]^{+\cdot}$ 495.2597.

Method B

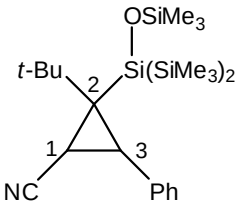
A solution of trimethylacetyltris(trimethylsilyl)silane (0.20 g, 0.61 mmol) and *trans*-cinnamic methyl ester (0.39 g, 2.42 mmol) in toluene (3.0 ml) was heated in a microwave tube at 180 ^oC for 4 h. Concentration, followed by flash column chromatography on silica (pet. ether : chloroform 8:2) afforded the product as a white solid (0.13 g, ds 1, 42%). Spectroscopic data for product **239** were consistent with data presented in *Method A*.

(2*RS*,3*SR*,4*SR*)-4-*tert*-Butyl-3-phenyl-1,1-bis(trimethylsilyl)-4-(trimethylsilyloxy)siletane-2-carbonitrile 242 and

2-*tert*-Butyl-2-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silyl-3-phenylcyclopropanecarbonitrile 243



242



243

A solution of trimethylacetyltris(trimethylsilyl)silane (0.32 g, 0.96 mmol) and *trans*-cinnamonitrile (0.49 ml, 3.86 mmol) in dry benzene (3.0 ml) was heated in a carious tube at 200 ^oC for 3 h. Concentration, followed by flash column chromatography on silica (pet. ether : diethyl ether 9:1) afforded the product **242** as a yellow solid (0.05 g, ds 7.2:2:1, 11%) and product **243** as yellow oil (0.14 g, ds 2.4:2.4:1:1, 32%). Recrystallisation from $CHCl_3$ yielded the product **242** as a single isomer.

Experimental data for compound (major diastereoisomer) **242**:

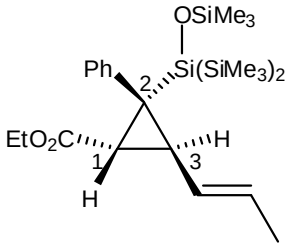
Mp: 122-123 ^{o}C; R_f 0.4 (pet. ether : diethyl ether 9:1); IR (ATR) 2952, 2896, 2215, 1247, 1079, 1025, 829, 741, 691 cm^{-1}; δ_H (500 MHz) 7.29-7.24 (4H, m, Ar-2,3,5,6-***H***), 7.20-7.17 (1H, m, Ar-4-***H***), 4.03 (1H, d, *J* = 13.0Hz, 3-***H***), 2.99 (1H, d, *J* = 13.0Hz, 2-***H***), 0.96 (9H, s, C(C***H***$_3$)$_3$), 0.36 (9H, s, Si(C***H***$_3$)$_3$), 0.24 (9H, s, Si(C***H***$_3$)$_3$), -0.25 (9H, s, Si(C***H***$_3$)$_3$); δ_C (125 MHz) 138.8 (Ar-***C***-1), 129.3 (Ar-***C***-2,6), 128,4 (Ar-***C***-3,5), 127,5 (Ar-***C***-4), 122.6 (***C***N), 99.1 (***C***-4), 54.5 (***C***-3), 37.5 (***C***(CH$_3$)$_3$), 29.1 (C(***C***H$_3$)$_3$), 8.1 (***C***-2), 3.8 (OSi(***C***H$_3$)$_3$), 0.7 (Si(***C***H$_3$)$_3$), 0.4 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) 7.8, -14.1, -15.8, -18.3; m/z (EI) 461 ([M]$^{+\cdot}$, 3%), 446 ([M-CH$_3$]$^{+\cdot}$, 3), 388 ([M-Si(CH$_3$)$_3$]$^{+\cdot}$, 14), 286 (30), 248 (67), 233 (36), 73 (100), 45 (16); HRMS (EI) found [M]$^{+\cdot}$ 461.2414, $C_{23}H_{43}NOSi_4$ requires [M]$^{+\cdot}$ 461.2416.

Experimental data for compound **243**:

^{1}H NMR – characteristic peaks: diastereoisomer *a*: 2.81-2.80 (1H, m, 3-***H***), 2.55 (1H, d, *J* = 2.4Hz, 2-***H***); diastereoisomer *b*: 2.81-2.80 (1H, m, 3-***H***), 2.52 (1H, d, *J* = 2.8Hz, 2-***H***); diastereoisomer *c*: 2.81-2.80 (1H, m, 3-***H***), 2.52 (1H, d, *J* = 2.8Hz, 2-***H***); diastereoisomer *d*: 2.76-2.75 (1H, m, 3-***H***), 2.47 (1H, d, *J* = 3.2Hz, 2-***H***).

GCMS – four peaks with similar fragmentation pattern: m/z (EI) 461 ([M]$^{+\cdot}$, 6%), 446 ([M-CH$_3$]$^{+\cdot}$, 4), 263 (53), 189 (16), 175 (30), 131 (27), 117 (29), 73 (100); m/z (EI) 461 ([M]$^{+\cdot}$, 1%), 446 ([M-CH$_3$]$^{+\cdot}$, 11), 388 ([M-Si(CH$_3$)$_3$]$^{+\cdot}$, 82), 302 (55), 259 (85), 204 (39), 185 (55), 171 (72), 147 (69), 131 (48), 117 (81), 73 (100), 45 (20); m/z (EI) 461 ([M]$^{+\cdot}$, 26%), 446 ([M-CH$_3$]$^{+\cdot}$, 30), 388 ([M-Si(CH$_3$)$_3$]$^{+\cdot}$, 36), 263 (100), 204 (37), 189 (54), 175 (55), 147 (50), 131 (52), 117 (51), 73 (59), 45 (18); m/z (EI) 461 ([M]$^{+\cdot}$, 1%), 446 ([M-CH$_3$]$^{+\cdot}$, 2), 388 ([M-Si(CH$_3$)$_3$]$^{+\cdot}$, 10), 302 (12), 157 (15), 147 (19), 117 (42), 73 (100), 45 (11).

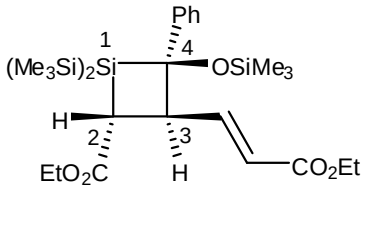
(1*RS*,2*RS*,3*SR*)-Ethyl 2-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silyl-2-phenyl-3-((*E*)-prop-1'-enyl)cyclopropanecarboxylate 245



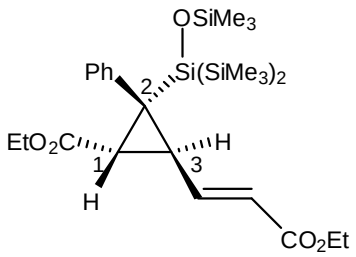
A solution of benzoyltris(trimethylsilyl)silane (0.36 g, 1.02 mmol) and ethyl sorbate (0.60 ml, 4.07 mmol) in dry benzene (5.0 ml) was heated in a sealed tube at 200 ^{o}C for 3 h. Concentration, followed by flash column chromatography, elution gradient 0 to 10% diethyl

ether in hexane, gave the title compound as a colourless oil (0.16 g, ds 7.1:1 (crude ds 2.8:1) 31%). R_f 0.7 (pet. ether : diethyl ether 95:5); IR (ATR) 2952, 2895, 1709, 1413, 1335, 1247, 1179, 1045, 964, 831, 749, 694 cm^{-1}; δ_H (700 MHz) 7.24-7.22 (2H, m, Ar-3,5-***H***), 7.15-7.12 (3H, m, Ar-2,4,6-***H***), 5.67 (1H, dq, *J* = 15.4Hz, *J* = 7.0Hz, 2'-***H***), 4.73 (1H, dd, *J* = 15.4Hz, *J* = 9.8Hz, 1'-***H***), 4.17 (1H, dq, *J* = 14.7Hz, *J* = 7.0Hz, OC***H***$_2$CH$_3$), 4.15 (1H, dq, *J* = 14.7Hz, *J* = 7.0Hz, OC***H***$_2$CH$_3$), 2.38 (1H, dd, *J* = 9.8Hz, *J* = 4.2Hz, 3-***H***), 2.04 (1H, d, *J* = 4.2Hz, 1-***H***), 1.64 (3H, d, *J* = 7.0Hz, 3'-***H***), 1.30 (3H, t, *J* = 7.0Hz, OCH$_2$C***H***$_3$), 0.18 (9H, s, Si(C***H***$_3$)$_3$), 0.03 (9H, s, Si(C***H***$_3$)$_3$), -0.16 (9H, s, OSi(C***H***$_3$)$_3$); δ_C (175 MHz) 173.2 (***C***O), 141.1 (Ar-***C***-1), 131.7 (Ar-***C***-2,6), 130.0 (***C***-1'), 127.8 (Ar-***C***-3,5), 126.4 (***C***-2'), 125.4 (Ar-***C***-4), 60.7 (O***C***H$_2$CH$_3$), 36.0 (***C***-3), 34.9 (***C***-1), 33.8 (***C***-2), 18.0 (***C***-3'), 14.3 (OCH$_2$***C***H$_3$), 2.3 (OSi(***C***H$_3$)$_3$), 0.2 (Si(***C***H$_3$)$_3$), 0.1 (Si(***C***H$_3$)$_3$); δ_{Si} (139 MHz) 4.6, 0.0, -16.9, -17.7; m/z (EI) 492 ($[M]^{+\cdot}$, 0.1%), 477 ($[M\text{-}CH_3]^{+\cdot}$, 2), 419 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 48), 235 (47), 207 (54), 191 (74), 147 (28), 117 (48), 73 (100); HRMS (EI) found $[M]^{+\cdot}$ 492.2361, $C_{24}H_{44}O_3Si_4$ requires $[M]^{+\cdot}$ 492.2362.

(2*RS*,3*SR*,4*SR*)-Ethyl 3-((*E*)-3'-ethoxy-3'-oxoprop-1'-enyl)-1,1-bis(trimethylsilyl)-4-(trimethyl-silyloxy)siletane-4-phenyl-2-carboxylate 282 and
(1*RS*,2*RS*,3*SR*)-Ethyl 3-((*E*)-3-ethoxy-3-oxoprop-1-enyl)-2-(1',1'-bistrimethylsilyl-1'-(trimethylsiloxy)silyl-2-phenylcyclopropanecarboxylate 246



282



246

Method A

A solution of benzoyltris(trimethylsilyl)silane (0.21 g, 0.60 mmol) and (2*E*,4*E*)-diethyl hexa-2,4-dienedioate (0.24 g, 1.20 mmol) in dry benzene (3.0 ml) was heated in a sealed tube at 200 ^oC for 3 h. Concentration, followed by flash column chromatography on silica, elution gradien 0 to 10% diethyl ether in hexane, afforded product **246** as a yellow oil (0.10 g, ds 1, 29%). R_f 0.5 (pet. ether : diethyl ether 7:3); IR (ATR) 2955, 1715, 1248, 1182, 1133, 1048, 834, 752, 702, 687 cm^{-1}; δ_H (500 MHz) 7.28-7.25 (2H, m, Ar-3,5-***H***), 7.19-7.14 (3H, m, Ar-2,4,6-***H***), 6.31 (1H, dd, *J* = 15.5Hz, *J* = 10.5Hz, 1'-***H***), 6.06 (1H, d, *J* = 15.5Hz, 2'-***H***), 4.26-4.21 (2H, m, 1-OC***H***$_2$CH$_3$), 4.20-4.15 (2H, m, 2'-OC***H***$_2$CH$_3$), 2.55 (1H, dd, *J* = 10.5Hz, *J* = 4.5Hz, 3-***H***), 2.38 (1H, d, *J* = 4.5Hz, 1-***H***), 1.34 (3H, t, *J* = 7.0Hz, 1-CO$_2$CH$_2$C***H***$_3$), 1.27 (3H,

t, *J* = 7.0Hz, 2'-$OCH_2C\boldsymbol{H}_3$), 0.21 (9H, s, $OSi(C\boldsymbol{H}_3)_3$), 0.06 (9H, s, $Si(C\boldsymbol{H}_3)_3$), -0.11 (9H, s, $Si(C\boldsymbol{H}_3)_3$); δ_C (125 MHz) 172.1 (1-***C***O), 165.9 (2'-***C***O), 148.3 (***C***-1'), 139.9 (Ar-***C***-1), 131.3 (Ar-***C***-2,6), 128.3 (Ar-***C***-3,5), 126.1 (Ar-***C***-4), 121.1 (***C***-2'), 61.1 (1-$CO_2\boldsymbol{C}H_2CH_3$), 60.1 (2'-$CO_2\boldsymbol{C}H_2CH_3$), 36.6 (***C***-2), 36.0 (***C***-1), 35.1 (***C***-3), 14.2 (3, 2'-$CO_2CH_2\boldsymbol{C}H_3$), 2.2 ($OSi(\boldsymbol{C}H_3)_3$), 0.2 ($Si(\boldsymbol{C}H_3)_3$), 0.0 ($Si(\boldsymbol{C}H_3)_3$); δ_{Si} (140 MHz) 5.4, -0.4, -16.8, -17.6; m/z (EI) 477 ([M-$Si(CH_3)_3$]$^{+\cdot}$, 10%), 207 (18), 191 (34), 147 (15), 117 (38), 73 (100), 45 (12).

Method B

A solution of 3,4-diphenyl-1,1,2,2-tetrakis(trimethylsilyl)-3,4-bis(trimethylsilyloxy)-1,2-disiletane (0.22 g, 0.31 mmol) and (2*E*,4*E*)-diethyl hexa-2,4-dienedioate (0.24 g, 1.22 mmol) in dry THF (10.0 ml) was heated at reflux for 24 h. Concentration, followed by flash column chromatography on silica, elution gradient 0 to 10% diethyl ether in hexane, afforded product **246** as a yellow oil (0.04 g, ds 1, 12%). Spectroscopic data for products **246** were consistent with data presented in *Method A*.

Method C

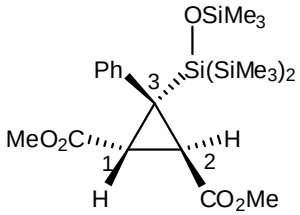
A solution of 3,4-diphenyl-1,1,2,2-tetrakis(trimethylsilyl)-3,4-bis(trimethylsilyloxy)-1,2-disiletane (0.15 g, 0.21 mmol) and (2*E*,4*E*)-diethyl hexa-2,4-dienedioate (0.34 g, 1.71 mmol) in dry benzene (3.0 ml) was heated in a microwave tube at 120 ^oC for 20 min. Concentration, followed by flash column chromatography on silica (pet. ether : diethyl ether 8:2) afforded the product **282** as a colourless oil (0.07 g, ds 1.0:0.9, 30%) and product **246** as yellow oil (0.06 g, ds 1, 24%). Spectroscopic data for products **246** were consistent with data presented in *Method A*.

Experimental data for compound (major diastereoisomer) **282**:

R_f 0.2 (pet. ether : diethyl ether 8:2); IR (ATR) 2950, 1710, 1642, 1443, 1367, 1243, 1174, 1144, 1061, 1035, 975, 831, 746, 693 cm^{-1}; δ_H (700 MHz) 7.29-7.27 (2H, m, Ar-3,5-***H***), 7.21 (1H, dd, *J* = 15.8Hz, *J* = 7.4Hz, 1'-***H***), 7.19-7.18 (3H, m, Ar-2,4,6-***H***), 6.01 (1H, dd, *J* = 15.8Hz, *J* = 0.7Hz, 2'-***H***), 4.27 (1H, ddd, *J* = 11.9Hz, *J* = 7.4Hz, *J* = 0.7Hz, 3-***H***), 4.21 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, 2'-$CO_2C\boldsymbol{H}_2CH_3$), 4.17 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, 2'-$CO_2C\boldsymbol{H}_2CH_3$), 4.06 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, 2-$CO_2C\boldsymbol{H}_2CH_3$), 4.21 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, 2-$CO_2C\boldsymbol{H}_2CH_3$), 3.09 (1H, d, *J* = 11.9Hz, 2-***H***), 1.27 (3H, t, *J* = 7.0Hz, 2'-$CO_2CH_2C\boldsymbol{H}_3$), 1.20 (3H, t, *J* = 7.0Hz, 2-$OCH_2C\boldsymbol{H}_3$), 0.35 (9H, s, $Si(C\boldsymbol{H}_3)_3$), -0.14 (9H, s, $Si(C\boldsymbol{H}_3)_3$), -0.20 (9H, s, $Si(C\boldsymbol{H}_3)_3$); δ_C (175 MHz) 174.0 (2-***C***O), 166.5 (2'-***C***O), 148.0 (***C***-1'),

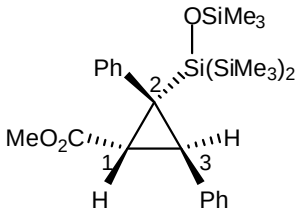
144.9 (Ar-***C***-1), 128.3 (Ar-***C***-2,6), 127.5 (Ar-***C***-3,5), 127.0 (Ar-***C***-4), 121.5 (***C***-2'), 81.3 (***C***-4), 60.2 (2'-CO_2***C***H_2CH_3), 59.8 (2-CO_2***C***H_2CH_3), 49.9 (***C***-3), 29.4 (***C***-2), 14.4 (2'-CO_2CH_2***C***H_3), 14.3 (2-CO_2CH_2***C***H_3), 2.3 (Si(***C***$H_3)_3$), -0.3 (Si(***C***$H_3)_3$), -1.1 (Si(***C***$H_3)_3$); δ_{Si} (140 MHz) 14.8, -5.5, -14.7, -16.4; m/z (EI) 550 ($[M]^{+\cdot}$, 1%), 535 ($[M\text{-}CH_3]^{+\cdot}$, 3), 477 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 37), 235 (15), 207 (37), 191 (70), 147 (27), 133 (18), 117 (58), 73 (100), 45 (15).

(1*RS*,2*RS*)-Dimethyl 3-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silyl-3-phenylcyclopropane-1,2-dicarboxylate 247



A solution of benzoyltris(trimethylsilyl)silane (0.26 g, 0.74 mmol) and dimethyl fumarate (0.43 g, 3.00 mmol) in dry benzene (4 ml) was heated in a sealed tube at 200 ^oC for 3 h. Concentration, followed by flash column chromatography (pet. ether : diethyl ether 7:3) afforded the product as a colourless oil (0.15 g, 40%). R_f 0.6 (pet. ether : diethyl ether 7:3); IR ($CHCl_3$) 2953, 1725, 1436, 1331, 1250, 1197, 1162, 1050, 834, 753, 701 cm^{-1}; δ_H (500 MHz) 7.28-7.26 (2H, m, Ar-3,5-***H***), 7.21-7.19 (1H, m, Ar-4-***H***), 7.12-7.11 (2H, m, Ar-2,6-***H***), 3.80 (3H, s, OC***H***$_3$), 3.62 (3H, s, OC***H***$_3$), 2.85 (1H, d, *J* = 5.0Hz, C***H***CO_2Me), 2.72 (1H, d, *J* = 5.0Hz, C***H***CO_2Me), 0.23 (9H, s, Si(C***H***$_3)_3$), 0.10 (9H, s, Si(C***H***$_3)_3$), -0.02 (9H, s, OSi(C***H***$_3)_3$); δ_C (125 MHz) 171.8 (**C**O), 169.9 (***C***O), 140.1 (Ar-***C***-1), 130.1 (Ar-***C***-2,6), 128.1 (Ar-***C***-3,5), 126.2 (Ar-***C***-4), 52.1 (O***C***H_3), 51.9 (O***C***H_3), 36.4 (***C***-3), 32.9 (***C***HCO_2Me), 32.7 (***C***HCO_2Me), 2.3 (OSi(***C***$H_3)_3$), -0.06 (Si(***C***$H_3)_3$), -0.09 (Si(***C***$H_3)_3$); δ_{Si} (139 MHz) 6.1, -0.8, -17.1, -17.9; m/z (EI) 496 ($[M]^{+\cdot}$, 1%), 481 ($[M\text{-}CH_3]^{+\cdot}$, 2%), 423 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 100), 221(24), 133 (11), 117 (23), 73 (32).

(1*RS*,2*RS*,3*RS*)-Methyl 2-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silyl-2,3-diphenylcyclopropanecarboxylate 248



Method A

A solution of benzoyltris(trimethylsilyl)silane (0.26 g, 0.74 mmol) and *trans*-cinnamic methyl ester (0.47 g, 2.91 mmol) in dry benzene (4.0 ml) was heated in a sealed tube at 180 ^{o}C for 3 h. Concentration, followed by flash column chromatography on silica (pet. ether : chloroform 7:3) afforded the product as a yellow oil (0.20 g, ds 5.5:1 (crude ds 2.1:1), 53%). R_f 0.6 (pet. ether : chloroform 7:3); IR (ATR) 2951, 1720, 1439, 1249, 1177, 1046, 831, 749, 700 cm^{-1}; δ_H (500 MHz) 7.12-7.11 (3H, m, Ar-***H***), 7.06-7.04 (3H, m, Ar-***H***), 6.84-6.82 (2H, m, Ar-***H***), 6.73-6.71 (2H, m, Ar-***H***), 3.75 (3H, s, OC***H***$_3$), 3.07 (1H, d, *J* =5.5Hz, 3-***H***), 2.63 (1H, d, *J* = 5.5Hz, 1-***H***), 0.23 (9H, s, OSi(C***H***$_3$)$_3$), 0.01 (9H, s, Si(C***H***$_3$)$_3$), -0.07 (9H, s, Si(C***H***$_3$)$_3$); δ_C (125 MHz) 173.3 (***C***O), 139.5 (Ar-***C***), 137.1 (Ar-***C***), 132.0 (Ar-***C***), 128.0 (Ar-***C***), 127.7 (Ar-***C***), 127.6 (Ar-***C***), 126.1 (Ar-***C***), 125.6 (Ar-***C***), 51.9 (O***C***H$_3$), 38.0 (***C***-2), 36.5 (***C***-3), 34.4 (***C***-1), 2.4 (OSi(***C***H$_3$)$_3$), 0.3 (Si(***C***H$_3$)$_3$), -0.06 (Si(***C***H$_3$)$_3$); δ_{Si} (139 MHz) 5.4, -0.5, -17.3, -18.0; m/z (EI) 499 ([M-CH$_3$]$^{+\cdot}$, 1%), 441 ([M-Si(CH$_3$)$_3$]$^{+\cdot}$, 58), 221(94), 191 (36), 147 (28), 133 (24), 117 (93), 74 (12), 73 (100), 45 (22); HRMS (ES+) found [M+H]$^{+\cdot}$ 515.2284, $C_{26}H_{43}O_3Si_4$ requires [M+H]$^{+\cdot}$ 515.2284.

Method B

A solution of benzoyltris(trimethylsilyl)silane (0.21 g, 0.60 mmol) and *trans*-cinnamic methyl ester (0.39 g, 2.38 mmol) in benzene (3.0 ml) was heated in a microwave tube at 180 ^{o}C for 1.5 h. Concentration, followed by flash column chromatography on silica (pet. ether : chloroform 7:3) afforded product **248** as yellow oil (0.15 g, ds 3.5:1 (crude ds 2.7:1), 49%). Spectroscopic data for the products **248** were consistent with data presented in *Method A*.

Method C

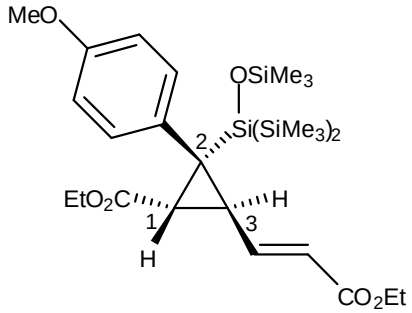
A solution of 3,4-diphenyl-1,1,2,2-tetrakis(trimethylsilyl)-3,4-bis(trimethylsilyloxy)-1,2-disiletane (0.16 g, 0.22 mmol) and *trans*-cinnamic methyl ester (0.29 g, 1.75 mmol) in dry benzene (3.0 ml) was heated in a microwave tube at 120 ^{o}C for 20 min. Concentration,

followed by flash column chromatography on silica, elution gradien 30 to 50% chloroform in hexane, afforded product **248** as a yellow oil (0.17 g, ds 6.7:1 (crude ds 3.9:1), 75%). Spectroscopic data for products **248** were consistent with data presented in *Method A*.

Method D

A solution of 3,4-diphenyl-1,1,2,2-tetrakis(trimethylsilyl)-3,4-bis(trimethylsilyloxy)-1,2-disiletane (0.17 g, 0.24 mmol) and *trans*-cinnamic methyl ester (0.15 g, 0.95 mmol) in dry THF (10.0 ml) was heated at reflux for 24 h. Concentration, followed by flash column chromatography on silica, elution gradient 0 to 10% diethyl ether in hexane, afforded product **248** as a yellow oil (0.09 g, ds 12:1, 36%). Spectroscopic data for products **248** were consistent with data presented in *Method A*.

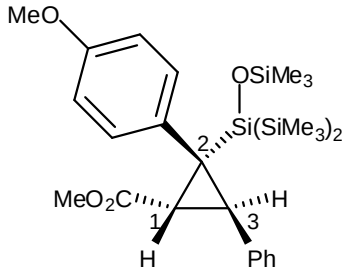
(1*RS*,2*RS*,3*SR*)-Ethyl 2-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silyl-3-((*E*)-3'-ethoxy-3'-oxoprop-1'-enyl)-2-(4-methoxyphenyl)cyclopropanecarboxylate 249



A solution of 4-methoxybenzoyltris(trimethylsilyl)silane (0.25 g, 0.65 mmol) and (2*E*,4*E*)-diethyl hexa-2,4-dienedioate (0.51 g, 2.61 mmol) in dry benzene (3.5 ml) was heated in a sealed tube at 200 ^{o}C for 3 h. Concentration, followed by flash column chromatography (pet. ether : diethyl ether 7:3) afforded the product as a yellow oil (0.06 g, 16%). R_f 0.6 (pet. ether : diethyl ether 7:3); IR (ATR) 2956, 1713, 1510, 1245, 1178, 1041, 833 cm^{-1}; δ_H (500 MHz) 7.44-7.42 (2H, m, Ar-2,6-***H***), 7.22-7.19 (2H, m, Ar-3,5-***H***), 6.71 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 1'-***H***), 6.43 (1H, d, *J* = 15.4Hz, 2'-***H***), 4.61-4.54 (4H, m, OC***H***$_2$CH$_3$), 4.19 (3H, s, OC***H***$_3$), 2.90 (1H, dd, *J* = 10.5Hz, *J* = 4.5Hz, 3-***H***), 2.72 (1H, d, *J* = 4.5Hz, 1-***H***), 1.71 (3H, t, *J* = 7.0Hz, 2'-OCH$_2$C***H***$_3$), 1.66 (3H, t, *J* = 7.0Hz, 1-OCH$_2$C***H***$_3$), 0.57 (9H, s, OSi(C***H***$_3$)$_3$), 0.43 (9H, s, Si(C***H***$_3$)$_3$), 0.30 (9H, s, Si(C***H***$_3$)$_3$); δ_C (125 MHz) 172.1 (1-***C***O), 166.0 (2'-***C***O), 158.0 (***C***-1'), 148.4 (Ar-***C***-4), 132.1 (Ar-***C***-1), 131.8 (Ar-***C***-2,6), 121.1 (***C***-2'), 113.8 (Ar-***C***-3,5), 61.0 (1-CO$_2$***C***H$_2$CH$_3$), 60.2 (2'-CO$_2$***C***H$_2$CH$_3$), 55.3 (O***C***H$_3$), 36.2 (***C***-2), 35.7 (***C***-1), 35.1 (***C***-3), 14.3 (1-OCH$_2$C***H***$_3$), 14.2 (2'-OCH$_2$C***H***$_3$), 2.3 (OSi(***C***H$_3$)$_3$), 0.2 (Si(***C***H$_3$)$_3$), 0.0 (Si(***C***H$_3$)$_3$);

δ_{Si} (80 MHz) 5.4, -17.0, -17.7; m/z (EI) 507 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 100%), 367 (10), 255(15), 235 (18), 207 (36), 191 (65), 147 (22), 117 (37), 73 (51).

(1*RS*,2*RS*,3*RS*)-Methyl 2-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silyl-2-(4-methoxyphenyl)-3-phenylcyclopropanecarboxylate 250



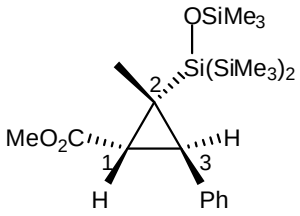
Method A

A solution of 4-methoxybenzoyltris(trimethylsilyl)silane (0.25 g, 0.66 mmol) and *trans*-cinnamic methyl ester (0.43 g, 2.63 mmol) in benzene (3.0 ml) was heated in a sealed tube at 180 ^{o}C for 3 h. Concentration, followed by flash column chromatography on silica (pet. ether : diethyl ether 95:5) afforded the product **X** as yellow oil (0.08 g, ds 1, 21%). R_f 0.5 (pet. ether : diethyl ether 9:1); IR (ATR) 2952, 1720, 1509, 1440, 1247, 1173, 1046, 827, 756, 695 cm^{-1}; δ_H (700 MHz) 7.28-7.27 (3H, m, 3-Ar-3,4,5-***H***), 6.89-6.88 (4H, m, 2,3-Ar-2,6-***H***), 6.77-6.76 (2H, m, 2-Ar-3,5-***H***), 3.89 (3H, s, $CO_2C\boldsymbol{H}_3$), 3.87 (3H, s, Ar-O$C\boldsymbol{H}_3$), 3.20 (1H, d, *J* = 4.9Hz, 3-***H***), 2.74 (1H, d, *J* = 4.9Hz, 1-***H***), 0.36 (9H, s, OSi($C\boldsymbol{H}_3)_3$), 0.15 (9H, s, Si($C\boldsymbol{H}_3)_3$), 0.12 (9H, s, Si($C\boldsymbol{H}_3)_3$); δ_C (175 MHz) 173.2 (***C***O), 157.6 (2-Ar-***C***-4), 137.1 (3-Ar-***C***-1), 132.8 (3-Ar-***C***-3,5), 131.5 (2-Ar-***C***-1), 128.1 (3-Ar-***C***-2,6), 127.7 (2-Ar-***C***-2,6), 126.0 (3-Ar-***C***-4), 113.2 (2-Ar-***C***-3,5), 55.2 (Ar-O$\boldsymbol{C}H_3$), 51.8 ($CO_2C\boldsymbol{H}_3$), 37.1 (***C***-2), 36.4 (***C***-3), 34.6 (***C***-1), 2.5 (OSi($\boldsymbol{C}H_3)_3$), 0.4 (Si($\boldsymbol{C}H_3)_3$), -0.1 (Si($\boldsymbol{C}H_3)_3$); δ_{Si} (140 MHz) 5.3, -1.2, -17.5, -18.2; m/z (EI) 544 ($[M]^{+\cdot}$, 1%), 529 ($[M\text{-}CH_3]^{+\cdot}$, 3), 471 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 96), 221 (100), 191 (23), 165 (10), 147 (27), 117 (97), 73 (86); HRMS (ES+) found $[M+H]^{+\cdot}$ 545.2386, $C_{27}H_{45}O_4Si_4$ requires $[M+H]^{+\cdot}$ 545.2389.

Method B

A solution of 4-methoxybenzoyltris(trimethylsilyl)silane (0.60 g, 1.57 mmol) and *trans*-cinnamic methyl ester (1.02 g, 6.30 mmol) in dry toluene (6.0 ml) was heated in a microwave tube at 180 ^{o}C for 5 min. Concentration, followed by flash column chromatography on silica (pet. ether : diethyl ether 95:5) afforded the product as a yellow oil (0.57 g, ds 2:1, 67%). Spectroscopic data for products **250** were consistent with data presented in *Method A*.

(1*RS*,2*RS*,3*RS*)-Methyl 2-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silyl-2-methyl-3-phenylcyclopropanecarboxylate 251



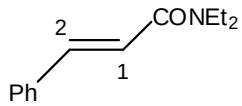
Method A

A solution of acetyltris(trimethylsilyl)silane (0.26 g, 0.90 mmol) and *trans*-cinnamic methyl ester (0.58 g, 3.60 mmol) in dry benzene (4.0 ml) was heated in a sealed tube at 200 ^{o}C for 3 h. Concentration, followed by flash column chromatography on silica (pet. ether : chloroform 7:3) afforded the product as a yellow oil (0.10 g, ds 1, 24%). R_f 0.6 (pet. ether : chloroform 7:3); IR (ATR) 2952, 1721, 1440, 1250, 1198, 1050, 830, 758, 697 cm^{-1}; δ_H (500 MHz) 7.37-7.34 (2H, m, Ar-3,5-***H***), 7.30-7.25 (3H, m, Ar-2,4,6-***H***), 3.74 (3H, s, OC***H***$_3$), 2.96 (1H, d, *J* = 5.5Hz, 3-***H***), 2.08 (1H, d, *J* = 5.5Hz, 1-***H***), 0.87 (3H, s, C***H***$_3$), 0.24 (9H, s, OSi(C***H***$_3$)$_3$), 0.183 (9H, s, Si(C***H***$_3$)$_3$), 0.177 (9H, s, Si(C***H***$_3$)$_3$); δ_C (125 MHz) 173.6 (***C***O), 137.0 (Ar-***C***-1), 129.1 (Ar-***C***-2,6), 128.1 (Ar-***C***-3,5), 126.4 (Ar-***C***-4), 51.7 (O***C***H$_3$), 36.2 (***C***-3), 32.4 (***C***-1), 22.8 (***C***-2), 18.5 (***C***H$_3$), 2.5 (OSi(***C***H$_3$)$_3$), 0.1 (Si(***C***H$_3$)$_3$), -0.4 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) 5.6, 1.1, -18.0, -18.7; m/z (EI) 452 ([M]$^{+\cdot}$, 10%), 437 ([M-CH$_3$]$^{+\cdot}$, 20), 379 ([M-Si(CH$_3$)$_3$]$^{+\cdot}$, 100), 279 (38), 222 (100), 217 (34), 191 (47), 147 (43), 133 (44), 117 (80), 89 (32), 73 (80), 59 (36), 45 (33).

Method B

A solution of acetyltris(trimethylsilyl)silane (0.23 g, 0.80 mmol) and trans-cinnamic methyl ester (0.52 g, 3.20 mmol) in benzene (3.0 ml) was heated in a microwave tube at 180 ^{o}C for 3 h. Concentration, followed by flash column chromatography on silica (pet. ether : chloroform 7:3) afforded the product **251** as yellow oil (0.18 g, ds 3.2:1 (crude ds 2.3:1), 50%). Spectroscopic data for products **251** were consistent with data presented in *Method A*.

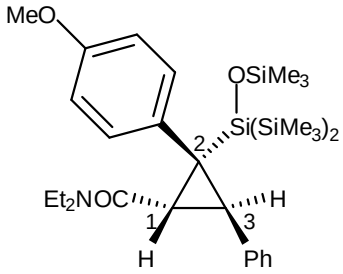
***N*,*N*-Diethylcinnamamide**[128] **253**



Diethylamine (4.78 ml, 46.2 mmol) was added to a stirred solution of cinnamoyl chloride (3.85 g, 23.1 mmol) in dry dichloromethane (40.0 ml) at 0 ^{o}C. The mixture was allowed to

warm to room temperature and stirred for 1 h, after which time a solution of 5% hydrochloric acid (20.0 ml) was added. The aqueous layer was separated and extracted with DCM (3 x 15 ml). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to yield the title amide as a white solid (4.44 g, 94%). Mp: 72.5–73.6 ^oC (lit.[129] 71-72 ^oC); R_f 0.3 (pet. ether : diethyl ether 2:3); IR (ATR) 2967, 2931, 1645, 1592, 1492, 1459, 1429, 1367, 1286, 1250, 1218, 1145, 1078, 973, 957, 865, 760, 707, 684 cm^{-1}; δ_H (700 MHz) 7.72 (1H, d, *J* = 15.2Hz, 2-***H***), 7.54-7.53 (2H, m, Ar-2,6-***H***), 7.39-7.34 (3H, m, Ar-3,4,5-***H***), 6.85-6.83 (1H, d, *J* = 15.2Hz, 1-***H***), 3.51 (2H, q, *J* = 7.0Hz, C***H***$_2$), 3.49 (2H, q, *J* = 7.0Hz, C***H***$_2$), 1.27 (3H, t, *J* = 7.0Hz, C***H***$_3$), 1.20 (3H, t, *J* = 7.0Hz, C***H***$_3$); δ_C (175 MHz) 165.7 (***C***O), 142.3 (***C***-2), 135.5 (Ar-***C***-1), 129.4 (Ar-***C***-4), 128.7 (Ar-***C***-3,5), 127.7 (Ar-***C***-2,6), 117.8 (***C***-1), 42.3 (***C***H_2), 41.1 (***C***H_2), 15.1 (***C***H_3), 13.2 (***C***H_3); m/z (EI) 203 ($[M]^{+\cdot}$, 29%), 131 (100), 103 (63), 77 (38).

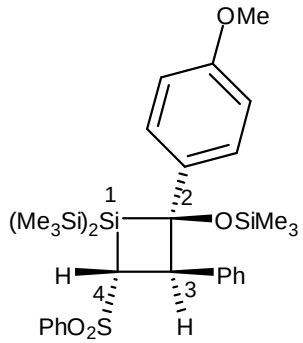
(1*RS*,2*RS*,3*RS*)-*N*,*N*-Diethyl-2-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silyl-2-(4-methoxyphenyl)-3-phenylcyclopropanecarboxamide 254



A solution of 4-methoxybenzoyltris(trimethylsilyl)silane (0.43 g, 1.14 mmol) and phenyl *N*,*N*-diethylcinnamamide (0.92 g, 4.53 mmol) in dry toluene (4.0 ml) was heated in a microwave tube at 180 ^oC for 5 min. Concentration, followed by fast flash column chromatography on silica (gradient elution pet. ether : diethyl ether 9:1, 4:6) afforded the product as a yellow oil (0.51 g, ds 3.6:1 (crude ds 2.9:1), 77%). Product was only partially characterised because of instability. R_f 0.6 and 0.3 (pet. ether : diethyl ether 7:3); IR (ATR) 2949, 2892, 1616, 1490, 1457, 1245, 1175, 1039, 825, 747, 687 cm^{-1}; δ_H (700 MHz) 7.13-7.10 (3H, m, 3-Ar-3,4,5-***H***), 6.75-6.74 (2H, m, 2-Ar-2,6-***H***), 6.71-6.70 (2H, m, 3-Ar-2,6-***H***), 6.63-6.62 (2H, m, 2-Ar-3,5-***H***), 3.73 (3H, s, OC***H***$_3$), 3.53 (1H, dq, *J* = 7.0Hz, *J* = 14.0Hz, C***H***$_2$CH$_3$), 3.48 (1H, dq, *J* = 7.0Hz, *J* = 14.0Hz, C***H***$_2$CH$_3$), 3.34 (1H, dq, *J* = 7.0Hz, *J* = 14.0Hz, C***H***$_2$CH$_3$), 3.27 (1H, dq, *J* = 7.0Hz, *J* = 14.0Hz, C***H***$_2$CH$_3$), 2.69 (1H, d, *J* = 5.6Hz, 3-***H***), 2.65 (1H, d, *J* = 5.6Hz, 1-***H***), 1.22 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$), 1.13 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$), 0.26 (9H, s, Si(C***H***$_3$)$_3$), 0.09 (9H, s, Si(C***H***$_3$)$_3$), -0.24 (9H, s, OSi(C***H***$_3$)$_3$); δ_C (175 MHz) 171.5 (***C***O), 157.2 (2-Ar-***C***-4), 138.1 (3-Ar-***C***-1), 133.0 (2-Ar-***C***-1), 132.9 (2-Ar-***C***-2,6), 127.8 (3-Ar-***C***-2,6), 127.6 (3-Ar-

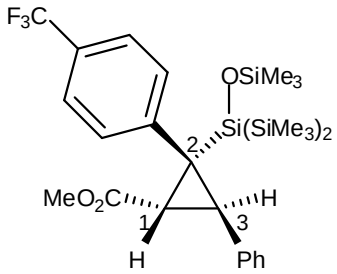
***C*-3,5), 125.6 (3-Ar-*C*-4), 113.1 (2-Ar-*C*-3,5), 55.3 (O*C*H_3), 42.6 (*C*H_2CH_3), 40.9 (*C*H_2CH_3), 37.4 (*C*-3), 35.8 (*C*-2), 34.4 (*C*-1), 15.0 (CH_2*C*H_3), 13.3 (CH_2*C*H_3), 2.4 (OSi(*C*H_3)$_3$), 0.8 (Si(*C*H_3)$_3$), 0.7 (Si(*C*H_3)$_3$); δ_{Si} (139 MHz) 1.4, -9.5, -16.0, -17.1.

(2*SR*,3*RS*,4*SR*)-2-(4-Methoxyphenyl)-3-phenyl-4-(phenylsulfonyl)-1,1-bis(trimethylsilyl)-2-(trimethylsilyloxy)siletane 256



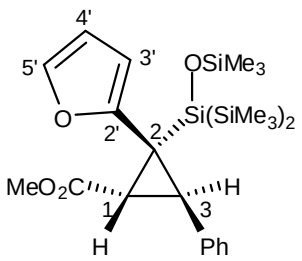
A solution of 4-methoxybenzoyltris(trimethylsilyl)silane (0.22 g, 0.57 mmol) and phenyl *trans*-styryl sulfone (0.55 g, 2.26 mmol) in dry toluene (3.0 ml) was heated in a microwave tube at 180 ^oC for 5 min. Concentration, followed by flash column chromatography on silica (gradient elution pet. ether , pet. ether : diethyl ether 85:15) afforded the product as a white solid (0.14 g, ds 5:1 (crude ds 1.2:1), 40%). Mp: 122–124 ^oC; R_f 0.3 (pet. ether : diethyl ether 8:2); IR (ATR) 2953, 2895, 1606, 1510, 1446, 1296, 1245, 1141, 1051, 830, 749, 691 cm^{-1}; δ_H (700 MHz) 7.46-7.45 (2H, m, 4-Ar-2,6-H), 7.23-7.20 (3H, m, 4-Ar-4-***H***, 2-Ar-*o*-***H***), 7.18-7.17 (2H, m, 3-Ar-2,6-***H***), 7.08-7.06 (2H, m, 4-Ar-3,5-***H***), 7.05-7.01 (3H, m, 3-Ar-3,4,5-***H***), 6.82-6.81 (2H, m, 2-Ar-3,5-***H***), 4.52 (1H, d, *J* = 12.6Hz, 3-***H***), 4.05 (1H, d, *J* = 12.6Hz, 4-***H***), 3.80 (3H, s, OC***H***$_3$), 0.49 (9H, s, Si(C***H***$_3$)$_3$), 0.16 (9H, s, Si(C***H***$_3$)$_3$), -0.56 (9H, s, OSi(C***H***$_3$)$_3$); δ_C (175 MHz) 158.6 (2-Ar-***C***-4), 141.8 (4-Ar-***C***-1), 138.1 (3-Ar-***C***-1), 137.3 (2-Ar-***C***-1), 131.7 (2-Ar-***C***-2,6), 130.0 (4-Ar-***C***-4), 129.9 (3-Ar-***C***-2,6), 128.2 (4-Ar-***C***-3,5), 127.7 (3-Ar-***C***-3,5), 127.1 (4-Ar-***C***-2,6), 126.7 (3-Ar-***C***-4), 113.1 (2-Ar-***C***-3,5), 81.6 (***C***-2), 55.3 (***C***-3), 55.2 (O***C***H_3), 53.6 (***C***-4), 2.1 (OSi(***C***H_3)$_3$), -0.2 (Si(***C***H_3)$_3$), -0.4 (Si(***C***H_3)$_3$); δ_{Si} (139 MHz) 14.2, -11.3, -14.5, -15.0; m/z (ES+) 644 ($[M+NH_4]^{+\cdot}$, 100%), 611 (24), 537 (6); HRMS (ES+) found $[M+NH_4]^{+\cdot}$ 644.2530, $C_{31}H_{50}O_4NSSi_4$ requires $[M+NH_4]^{+\cdot}$ 644.2532.

(1*RS*,2*RS*,3*RS*)-Methyl 2-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silyl-3-phenyl-2-(4-trifluoromethyl) phenyl)cyclopropanecarboxylate 258



A solution of 4-trifluoromethylbenzoyltris(trimethylsilyl)silane (0.36 g, 0.85 mmol) and *trans*-cinnamic methyl ester (0.55 g, 3.39 mmol) in dry toluene (3.0 ml) was heated in a microwave tube at 180 ^{o}C for 1 h. Concentration, followed by flash column chromatography on silica (pet. ether : diethyl ether 98:2) afforded the product as a yellow oil (0.28 g, ds 14:1 (crude ds 4.9:1), 56%). R_f 0.6 (pet. ether : diethyl ether 95:5); IR (ATR) 2952, 1718, 1615, 1323, 1250, 1163, 1125, 1041, 830, 747, 694 cm^{-1}; δ_H (700 MHz) 7.34-7.33 (2H, m, 2-Ar-3,5-***H***), 7.144-7.135 (3H, m, 3-Ar-3,4,5-***H***), 6.96-6.94 (2H, m, 2-Ar-2,6-***H***), 6.72-6.70 (2H, m, 3-Ar-2,6-***H***), 3.77 (3H, s, $CO_2C\boldsymbol{H}_3$), 3.11 (1H, d, *J* = 5.6Hz, 3-***H***), 2.65 (1H, d, *J* = 5.6Hz, 1-***H***), 0.27 (9H, s, $OSi(C\boldsymbol{H}_3)_3$), 0.05 (9H, s, $Si(C\boldsymbol{H}_3)_3$), -0.12 (9H, s, $Si(C\boldsymbol{H}_3)_3$); δ_C (175 MHz) 173.2 (***C***O), 144.4 (2-Ar-***C***-1), 136.3 (3-Ar-***C***-1), 132.2 (2-Ar-***C***-2,6), 127.9 (3-Ar-***C***-2,3,5,6), 127.8 (q, $^{2}J_{c\text{-}f}$ = 32.6Hz, 2-Ar-***C***-4), 126.5 (3-Ar-***C***-4), 124.6 (q, $^{3}J_{c\text{-}f}$ = 3.3Hz, 2-Ar-***C***-3,5), 124.3 (q, ^{1}J = 271.8Hz, 2-Ar-***C***F_3), 52.1 ($CO_2C\boldsymbol{H}_3$), 37.6 (***C***-2), 37.0 (***C***-3), 33.9 (***C***-1), 2.3 ($OSi(\boldsymbol{C}H_3)_3$), 0.4 ($Si(\boldsymbol{C}H_3)_3$), 0.1 ($Si(\boldsymbol{C}H_3)_3$); δ_{Si} (140 MHz) 5.7, 1.0, -16.7, -17.6; m/z (EI) 567 ($[M\text{-}CH_3]^{+\cdot}$, 8%), 509 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 89), 269 (51), 221 (100), 191 (34), 163 (15), 147 (27), 117 (90), 73 (86), 59 (15); HRMS (ES+) found $[M+NH_4]^{+\cdot}$ 600.2420, $C_{27}H_{45}O_3NF_3Si_4$ requires $[M+NH_4]^{+\cdot}$ 600.2423.

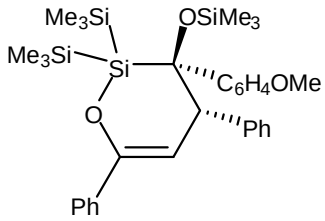
(1*RS*,2*RS*,3*RS*)-Methyl 2-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silyl-2-(furan-2'-yl)-3-phenylcyclopropanecarboxylate 259



A solution of 2-furoyltris(trimethylsilyl)silane (0.21 g, 0.61 mmol) and *trans*-cinnamic methyl ester (0.39 g, 2.43 mmol) in dry toluene (3.0 ml) was heated in a microwave tube at 180 ^{o}C

for 50 min. Concentration, followed by flash column chromatography on silica (pet. ether : diethyl ether 9:1) afforded the product as a yellowish solid (0.12 g, ds 1, 40%). Mp: 62–64 ^{o}C; R_f 0.7 (pet. ether : diethyl ether 8:2); IR (ATR) 2951, 2893, 1733, 1499, 1441, 1408, 1249, 1175, 1059, 831, 730, 687 cm^{-1}; δ_H (700 MHz) 7.24-7.20 (3H, m, Ar-3,4,5-***H***), 7.10 (1H, d, *J* = 2.1Hz, 5'-***H***), 7.04-7.03 (2H, m, Ar-2,6-***H***), 6.08 (1H, dd, *J* = 3.5Hz, *J* = 2.1Hz, 4'-***H***), 5.42 (1H, d, *J* = 3.5Hz, 3'-***H***), 3.76 (3H, s, $CO_2C\boldsymbol{H}_3$), 3.13 (1H, d, *J* = 6.3Hz, 3-***H***), 2.71 (1H, d, *J* = 6.3Hz, 1-***H***), 0.19 (9H, s, $Si(C\boldsymbol{H}_3)_3$), 0.13 (9H, s, $OSi(C\boldsymbol{H}_3)_3$), 0.02 (9H, s, $Si(C\boldsymbol{H}_3)_3$); δ_C (175 MHz) 171.9 (***C***O), 154.0 (***C***-2'), 140.8 (***C***-5'), 136.9 (Ar-***C***-1), 128.0 (Ar-***C***-2,6), 127.9 (Ar-***C***-3,5), 126.5 (Ar-***C***-4), 110.0 (***C***-4'), 108.1 (***C***-3'), 51.8 ($CO_2C\boldsymbol{H}_3$), 34.6 (***C***-3), 32.9 (***C***-1), 29.6 (***C***-2), 2.6 ($OSi(\boldsymbol{C}H_3)_3$), -0.1 ($Si(\boldsymbol{C}H_3)_3$), -1.0 ($Si(\boldsymbol{C}H_3)_3$); δ_{Si} (140 MHz) 6.2, -3.1, -17.8, -17.9; m/z (EI) 431 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 0.1%), 147 (1), 131 (1), 103 (1), 73 (100); HRMS (EI) found $[M]^{+\cdot}$ 504.1990, $C_{24}H_{40}O_4Si_4$ requires $[M]^{+\cdot}$ 504.1998.

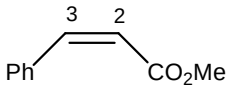
(3*RS*,4*SR*)-3-(4-Methoxyphenyl)-4,6-diphenyl-2,2-bis(trimethylsilyl)-3-(trimethylsilyloxy)-3,4-dihydro-2H-1,2-oxasiline 260



A solution of 4-methoxybenzoyltris(trimethylsilyl)silane (0.20 g, 0.53 mmol) and *trans*-chalcone (0.43 g, 2.11 mmol) in dry toluene (3.0 ml) was heated in a microwave tube at 180 ^{o}C for 5 min. Concentration, followed by flash column chromatography on silica (gradient elution pet. ether , pet. ether : diethyl ether 9:1) afforded the product as a pale yellow solid (0.26 g, ds 1:2.2 (crude ds 1:1.7), 86%). Mp: 36–38 ^{o}C; R_f 0.6 (pet. ether : diethyl ether 9:1); IR (ATR) 2954, 2896, 1604, 1505, 1447, 1327, 1247, 1183, 1019, 833, 745, 689 cm^{-1}; δ_H (700 MHz) 7.65-7.64 (2H, m, 6-Ar-2,5-***H***), 7.40-7.39 (3H, m, 3-Ar-2,6-***H***), 7.35-7.31 (2H, m, 6-Ar-3,5-***H***), 7.28-7.27 (1H, m, 6-Ar-4-***H***), 7.19-7.18 (2H, m, 4-Ar-2,6-***H***), 7.15-7.14 (3H, m, 4-Ar-3,4,5-***H***), 6.76-6.74 (2H, m, 3-Ar-3,5-***H***), 5.65 (1H, d, *J* = 4.2Hz, 5-***H***), 4.36 (1H, d, *J* = 4.2Hz, 4-***H***), 3.77 (3H, s, $OC\boldsymbol{H}_3$), 0.23 (9H, s, $Si(C\boldsymbol{H}_3)_3$), 0.07 (9H, s, $OSi(C\boldsymbol{H}_3)_3$), -0.08 (9H, s, $Si(C\boldsymbol{H}_3)_3$); δ_C (175 MHz) 156.8 (3-Ar-***C***-4), 148.3 (***C***-6), 145.0 (4-Ar-***C***-1), 137.0 (6-Ar-***C***-1), 133.0 (3-Ar-***C***-1), 131.1 (3-Ar-***C***-2,6), 129.8 (4-Ar-***C***-3,5), 128.1 (6-Ar-***C***-3,5), 127.9 (4-Ar-***C***-2,6), 127.5 (6-Ar-***C***-4), 126.3 (4-Ar-***C***-4), 124.4 (6-Ar-***C***-2,6), 113.3 (3-Ar-***C***-3,5), 107.7 (***C***-5), 55.2 ($O\boldsymbol{C}H_3$), 43.9 (***C***-4), 32.8 (***C***-3), 2.3 ($Si(\boldsymbol{C}H_3)_3$), 1.7 ($OSi(\boldsymbol{C}H_3)_3$), -1.0 ($Si(\boldsymbol{C}H_3)_3$);

δ_{Si} (139 MHz) 10.3, 4.8, -14.3, -19.7; m/z (EI) 590 ($[M]^{+\cdot}$, 4%), 575 ($[M\text{-}CH_3]^{+\cdot}$, 6), 517 ($[M\text{-}C(CH_3)_3]^{+\cdot}$, 3), 367 (24), 192 (16), 73 (100); HRMS (ES+) found $[M+H]^{+\cdot}$ 591.2589, $C_{32}H_{47}O_3Si_4$ requires $[M+H]^{+\cdot}$ 591.2597.

(*Z*) Methyl 3-phenylpropenoate[130] 272



Stage1

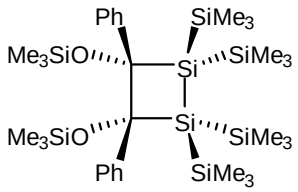
To a solution of phenylacetone (5.01 g, 37.3 mmol) in acetic acid (100 ml), under argon at room temperature, was added dropwise a solution of bromine (13.5g, 84.5 mmol) in acetic acid (75 ml). The reaction mixture was stirred for 40 min. The solution was diluted with Et_2O (100 ml) and made neutral by addition of aqueous NaOH (6M). The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 x 200 ml). The combined organic layers were dried over $MgSO_4$ and concentrated to yield 1,3-dibromo-1-phenylacetone **268** as a green oil (9.78 g) which was used immediately in *stage* 2 without further purification.

Stage2

The crude product from *stage 1* (9.78 g) was dissolved in methanol (10 ml) and added dropwise to a cooled solution (0 ^oC) of sodium methoxide prepared by dissolving sodium (1.76 g, 76.4 mmol) in dry methanol (35 ml). The reaction mixture was stirred for 30 min, quenched by the addition of diluted HCl (to pH=7) and the resultant solution extracted with Et_2O (3 x 100 ml). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel (pet. ether : dichloromethane 3.4:6.6) to afforded the title alkene **272** as a pale brown oil (2.41 g, 40%). R_f 0.6 (pet. ether : diethyl ether 6:4), IR (ATR) 1722, 1629, 1436, 1195, 1162, 826, 765, 695, 618 cm^{-1}; δ_H (500 MHz) 7.52-7.50 (2H, m, Ar-2,6-***H***), 7.29-7.24 (3H, m, Ar-3,4,5-***H***), 6.87 (1H, d, *J* = 12.5Hz, 2-***H***), 5.87 (1H, d, *J* = 12.5Hz, 3-*H*), 3.62 (3H, s, OC***H***$_3$); δ_C (125 MHz) 166.5 (***C***-1), 143.4 (***C***-3), 134.7 (Ar-***C***-1), 129.7 (Ar-***C***-3,5), 129.0 (Ar-***C***-2,6), 128.0 (Ar-***C***-4), 119.2 (***C***-2), 51.3 (O***C***H_3); m/z (EI) 162 ($[M]^{+\cdot}$, 30%), 131 ($[M\text{-}OCH_3]^{+\cdot}$, 84), 103 ($[M\text{-}CO_2CH_3]^{+\cdot}$, 100), 77 ($[C_6H_5]^{+\cdot}$, 66), 51 (50).

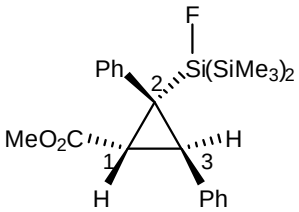
3,4-Diphenyl-1,1,2,2-tetrakis(trimethylsilyl)-3,4-bis(trimethylsilyloxy)-1,2-disiletane[38]

279



A solution of benzoyl(tristrimethylsilyl)silane (4.13 g, 11.7 mmol) in toluene (200 ml) was irradiated for 1 h at 0 ^{o}C using a 1 kW mercury lamp. Concentration followed by flash column chromatography (pet. ether) gave the title compound as a white crystalline solid (1.82 g, 35%); Mp: 147-149 ºC (lit.[38] 149-150 ºC); R_f 1 (pet. ether); IR (ATR) 2953, 2891, 1247, 1015, 827, 767, 709, 700, 675, 625 cm^{-1}; δ_H (700 MHz) 7.65-7.64 (4H, m, 3,4-Ar-2,6-***H***), 7.31-7.29 (4H, m, 3,4-Ar-3,5-***H***), 7.26-7.24 (2H, m, 3,4-Ar-4-***H***), 0.42 (18H, s, OSi(C***H***$_3$)$_3$), 0.08 (18H, s, Si(C***H***$_3$)$_3$), -0.25 (18H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 145.0 (3,4-Ar-***C***-1), 132.8 (3,4-Ar-***C***-2,6), 127.2 (3,4-Ar-***C***-3,5), 127.0 (3,4-Ar-***C***-4), 98.8 (***C***-3,4), 3.6 (Si(***C***H$_3$)$_3$), 3.1 (Si(***C***H$_3$)$_3$), 2.9 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) 8.8, -12.2, -13.3, -40.8; m/z (EI) 352 ([M/2]$^{+\cdot}$, 5%), 337 ([M/2]$^{+\cdot}$, 10).

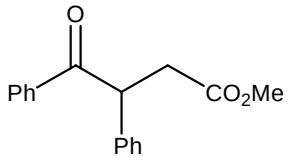
(1*RS*,2*RS*,3*RS*)-Methyl 2-(1'-fluoro-1',1'-bistrimethylsilyl)silyl-2,3-diphenylcyclopropanecarboxylate 319



To a solution of methyl 2-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silyl-2,3-diphenylcyclopropanecarboxylate (0.20 g, 0.39 mmol) in dry dichloromethane (4.0 ml) was added the trifluoroborane-acetic acid complex (0.05 ml, 0.39 mmol). The mixture was stirred at room temperature for 5 min after which time saturated sodium bicarbonate solution (5.0 ml) was added. The aqueous layer was separated and extracted with DCM (3 x 15 ml). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a pure title compound as white solid (0.16 g, 96%). Mp: 82-84 ^{o}C; R_f 0.4 (pet. ether : chloroform 7:3); IR (ATR) 2948, 1687, 1440, 1242, 1213, 830, 796, 732, 693 cm^{-1}; δ_H (700 MHz) 7.31-7.29 (2H, m, 2-Ar-3,5-***H***), 7.27-7.25 (4H, m, 2,3-Ar-***H***), 7.14-7.13 (2H, m, 2-Ar-2,6-***H***), 6.89-6.88 (2H, m, 3-Ar-2,6-***H***), 3.99 (3H, s, OC***H***$_3$), 3.19 (1H, d, *J* = 4.2Hz, 3-***H***), 2.98 (1H, d, *J* = 4.2Hz, 1-***H***), 0.52 (9H, s, Si(C***H***$_3$)$_3$), 0.29 (9H, s, Si(C***H***$_3$)$_3$); δ_C (175

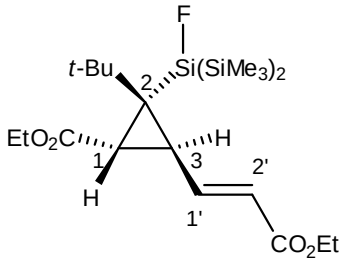
MHz) 175.2 (***C***O), 137.4 (2-Ar-***C***-1), 136.2 (3-Ar-***C***-1), 131.5 (2-Ar-***C***-2), 127.7 (2,3-Ar-***C***), 127.6 (3-Ar-***C***-3), 126.3 (3-Ar-***C***-4), 125.9 (2-Ar-***C***-4), 52.6 (O***C***H_3), 38.1 (***C***-3), 35.6 (***C***-2), 33.6 (***C***-1), -0.26 (Si(***C***H_3)$_3$), -0.72 (Si(***C***H_3)$_3$); δ_F (188 MHz) -186.3; δ_{Si} (139 MHz) 23.2 ($^1J_{Si-F}$ = 325.2Hz), -14.8 ($^2J_{Si-F}$ = 27.2Hz), -15.7 ($^2J_{Si-F}$ = 25.2Hz); m/z (EI) 429 ([M-CH_3]$^{+\cdot}$, 6%), 371 ([M-Si(CH_3)$_3$]$^{+\cdot}$, 88), 247(44), 235 (23), 191 (32), 131 (36), 89 (16), 73 (100), 59 (84), 45 (41); HRMS (ES+) found [M+NH_4]$^{+\cdot}$ 462.2109, $C_{23}H_{37}O_2NFSi_3$ requires [M+NH_4]$^{+\cdot}$ 462.2111.

Methyl 4-oxo-3,4-diphenylbutanoate[131] 322



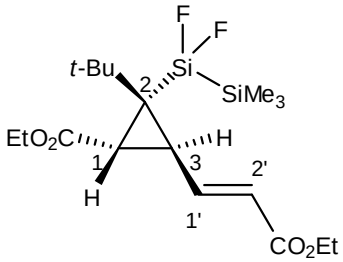
To a solution of methyl 2-(1'-fluoro-1',1'-bistrimethylsilyl)silyl-2,3-diphenylcyclopropanecarboxylate (0.20 g, 0.45 mmol) in DMF (4.0 ml) was added *m*CPBA (0.47 g, 2.70 mmol) and KF (0.05 g, 0.90 mmol). The mixture was stirred at RT for 12 h after which time it was diluted with ether (5.0 ml) and saturated sodium bicarbonate solution (5.0 ml) was added. The aqueous layer was separated and extracted with ether (3 x 10 ml). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash column chromatography (pet. ether : diethyl ether 1:1) give a title compound as a yellow oil (0.11 g, 56%); R_f 0.5 (pet. ether : diethyl ether 5:5); IR (ATR) 3031, 1733, 1707, 1493, 1453, 1239, 1026, 1010, 765, 699 cm^{-1}; δ_H (700 MHz) 7.99-7.97 (2H, m, 4-Ar-2,6-***H***), 7.49-7.47 (1H, m, 4-Ar-4-***H***), 7.45-7.43 (1H, m, 3-Ar-4-***H***), 7.40-7.38 (2H, m, 4-Ar-3,5-***H***), 7.30-7.29 (4H, m, 3-Ar-2,3,5,6-***H***), 5.11 (1H, dd, *J* = 9.8Hz, *J* = 4.9Hz, 3-***H***), 3.66 (3H, s, 1-OC***H***$_3$), 3.40 (1H, dd, *J* = 16.8Hz, *J* = 9.8Hz, 2-***H***), 2.74 (1H, dd, *J* = 16.8Hz, *J* = 4.9Hz, 2-***H***); δ_C (175 MHz) 198.6 (***C***O-4), 172.6 (***C***O-1), 138.1 (3-Ar-***C***-1), 136.2 (4-Ar-***C***-1), 133.0 (4-Ar-***C***-4), 129.8 (3-Ar-***C***-4), 129.2 (3-Ar-***C***-3,5), 128.9 (4-Ar-***C***-2,6), 128.5 (4-Ar-***C***-3,5), 128.1 (3-Ar-***C***-2,6), 51.8 (O***C***H_3), 49.6 (***C***-3), 38.4 (***C***-2); m/z (EI) 268 ([M]$^{+\cdot}$, 16%), 237 ([M-OCH_3]$^{+\cdot}$, 26), 121 (36), 106 (47), 105 (100), 103 (30), 78 (36), 77 (70), 51 (64).

(1*RS*,2*RS*,3*SR*)-Ethyl 2-*tert*-butyl-3-((*E*)-3'-ethoxy-3'-oxoprop-1'-enyl)-2-(1'-fluoro-1',1'-bistrimethylsilyl)silylcyclopropanecarboxylate 324



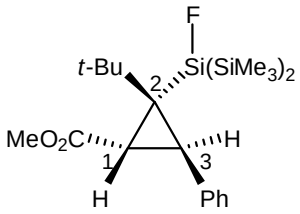
To a solution of ethyl 2-*tert*-butyl-3-((*E*)-3'-ethoxy-3'-oxoprop-1'-enyl)-2-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silylcyclopropanecarboxylate (0.20 g, 0.38 mmol) in dry dichloromethane (9.0 ml) was added the trifluoroborane-acetic acid complex (0.12 ml, 0.83 mmol). The mixture was stirred at room temperature for 30 min after which time saturated sodium bicarbonate solution (9.0 ml) was added. The aqueous layer was separated and extracted with DCM (3 x 15 ml). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a pure title compound (0.17 g, 95%). R_f 0.4 (pet. ether : diethyl ether 9:1); IR ($CHCl_3$) 3020, 2958, 1696, 1637, 1245, 1210, 1037, 840, 745, 670 cm^{-1}; δ_H (500 MHz) 7.10 (1H, dd, *J* = 15.0Hz, *J* = 10.0Hz, 1'-***H***), 6.04 (1H, d, *J* = 15.0Hz, 2'-***H***), 4.22-4.07 (4H, m, $CO_2C\boldsymbol{H}_2CH_3$), 2.37 (1H, d, *J* = 4.5Hz, 1-***H***), 2.18 (1H, dd, *J* = 10.0Hz, *J* = 4.5Hz, 3-***H***), 1.29 (3H, t, *J* = 7.0Hz, 2'-$CO_2CH_2C\boldsymbol{H}_3$), 1.28 (3H, t, *J* = 7.0Hz, 1-$CO_2CH_2C\boldsymbol{H}_3$), 1.11 (9H, s, $C(C\boldsymbol{H}_3)_3$), 0.18 (9H, s, $Si(C\boldsymbol{H}_3)_3$), 0.10(9H, s, $Si(C\boldsymbol{H}_3)_3$); δ_C (125 MHz) 175.5 (1-***C***O), 166.0 (2'-***C***O), 146.6 (***C***-1'), 123.1 (***C***-2'), 62.2 (1-$CO_2\boldsymbol{C}H_2CH_3$), 60.4 (2'-$CO_2\boldsymbol{C}H_2CH_3$), 37.1 ($\boldsymbol{C}(CH_3)_3$), 34.6 (***C***-3), 32.7 (***C***-1), 30.8 ($C(\boldsymbol{C}H_3)_3$), 29.7 (***C***-2), 14.3 (1-$CO_2CH_2\boldsymbol{C}H_3$), 14.1 (2'-$CO_2CH_2\boldsymbol{C}H_3$), -0.5 ($Si(\boldsymbol{C}H_3)_3$), -0.6 ($Si(\boldsymbol{C}H_3)_3$); δ_{Si} (139 MHz) 30.1 ($^1J_{Si\text{-}F}$ = 321.6Hz), -14.2 ($^2J_{Si\text{-}F}$ = 24.7Hz), -14.6 ($^2J_{Si\text{-}F}$ = 30.0Hz); δ_F (376 MHz) -169.46; m/z (EI) 445 ($[M\text{-}CH_3]^{+\cdot}$, 4%), 387 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 72), 205 (30), 177 (76), 131 (41), 73 (100), 57 (78), 45 (50); HRMS (EI) found $[M]^{+\cdot}$ 460.2283, $C_{21}H_{41}O_4Si_4$ requires $[M]^{+\cdot}$ 460.2291.

(1*RS*,2*RS*,3*SR*)-Ethyl 2-*tert*-butyl-2-(1',1'-difluoro-2',2',2'-trimethyldisilyl)-3-((*E*)-3'-ethoxy-3'-oxoprop-1'-enyl)cyclopropanecarboxylate 325



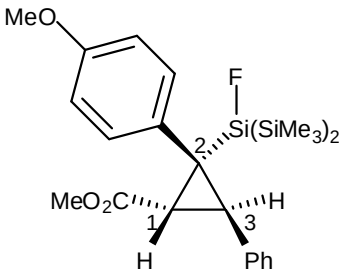
To a solution of ethyl 2-*tert*-butyl-3-((*E*)-3'-ethoxy-3'-oxoprop-1'-enyl)-2-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silylcyclopropanecarboxylate (0.19 g, 0.37 mmol) in dry dichloromethane (8.0 ml) was added the trifluoroborane-acetic acid complex (0.25 ml, 1.82 mmol). The mixture was stirred at reflux for 48 h after which time saturated sodium bicarbonate solution (10.0 ml) was added. The aqueous layer was separated and extracted with DCM (3 x 15 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica, elution gradient 0 to 20% diethyl ether in hexane, afforded the product as a colourless oil (0.03 g, 18%). R_f 0.3 (pet. ether : diethyl ether 8:2); IR ($CHCl_3$) 3020, 1702, 1522, 1477, 1424, 1225, 1014, 928, 777 cm^{-1}; δ_H (500 MHz) 6.98 (1H, dd, *J* = 15.0Hz, *J* = 10.0Hz, 1'-***H***), 6.11 (1H, d, *J* = 15.0Hz, 2'-***H***), 4.203 (2H, q, *J* = 7.0Hz, 2'-$CO_2C\boldsymbol{H}_2CH_3$), 4.197 (2H, q, *J* = 7.0Hz, 1-$CO_2C\boldsymbol{H}_2CH_3$), 2.48 (1H, d, *J* = 10.0, *J* = 5.0, Hz, 3-***H***), 2.38 (1H, d, *J* = 5.0Hz, 1-***H***), 1.32 (3H, t, *J* = 7.0Hz, 2'-$CO_2CH_2C\boldsymbol{H}_3$), 1.29 (3H, t, *J* = 7.0Hz, 1-$CO_2CH_2C\boldsymbol{H}_3$), 1.13 (9H, s, $C(C\boldsymbol{H}_3)_3$), 0.19 (9H, s, $Si(C\boldsymbol{H}_3)_3$); δ_C (125 MHz) 175.5 (1-***C***O), 166.0 (2'-***C***O), 144.9 (***C***-1'), 124.2 (***C***-2'), 62.4 (1-$CO_2\boldsymbol{C}H_2CH_3$), 60.4 (2'-$CO_2\boldsymbol{C}H_2CH_3$), 36.2 ($^2J_{C\text{-}F}$ = 6.7Hz, ***C***-2), 33.5 ($^3J_{C\text{-}F}$ = 1.9Hz, $\boldsymbol{C}(CH_3)_3$), 32.1 (***C***-3), 31.6 (***C***-1), 30.8 ($C(\boldsymbol{C}H_3)_3$), 14.3 (1-$CO_2CH_2\boldsymbol{C}H_3$), 14.1 (2'-$CO_2CH_2\boldsymbol{C}H_3$), -1.7 ($Si(\boldsymbol{C}H_3)_3$); δ_{Si} (139 MHz) -8.1 ($^1J_{Si\text{-}F}$ = 351.4Hz, $^1J_{Si\text{-}F}$ = 349.2Hz), -16.7 ($^2J_{Si\text{-}F}$ = 32.2Hz, $^2J_{Si\text{-}F}$ = 27.5Hz); δ_F (376 MHz) -127.32 ($^2J_{F\text{-}F}$ = 19.9Hz), -134.06 ($^2J_{F\text{-}F}$ = 19.9Hz); m/z (EI) 391 ($[M\text{-}CH_3]^{+\cdot}$, 1%), 333 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 32), 259 (49), 121 (20) 73 (100), 57 (98), 45 (26), 29 (50); HRMS (ES+) found $[M+NH_4]^{+\cdot}$ 424.2146, $C_{18}H_{36}O_4NF_2Si_2$ requires $[M+NH_4]^{+\cdot}$ 424.2145.

(1*RS*,2*RS*,3*RS*)-Methyl 2-*tert*-butyl-2-(1'-fluoro-1',1'-bistrimethylsilyl)silyl-3-phenylcyclopropanecarboxylate 326



To a solution of methyl 2-*tert*-butyl-2-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silyl-3-phenylcyclopropanecarboxylate (0.20 g, 0.39 mmol) in dry dichloromethane (4.0 ml) was added the trifluoroborane-acetic acid complex (0.05 ml, 0.39 mmol). The mixture was stirred at room temperature for 5 min after which time saturated sodium bicarbonate solution (5.0 ml) was added. The aqueous layer was separated and extracted with DCM (3 x 10 ml). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a pure title compound (0.16 g, 97%). R_f 0.5 (pet. ether : diethyl ether 9:1); IR (ATR) 2953, 1698, 1442, 1242, 1206, 833, 763, 732, 699, 686 cm^{-1}; δ_H (700 MHz) 7.41-7.40 (2H, m, Ar-2,6-***H***), 7.28-7.26 (2H, m, Ar-3,5-***H***), 7.23-7.19 (1H, m, Ar-4-***H***), 3.73 (3H, s, OC***H***$_3$), 2.77 (1H, d, *J* = 4.9Hz, 3-***H***), 2.59 (1H, d, *J* = 4.9Hz, 1-***H***), 0.87 (9H, s, C(C***H***$_3$)$_3$), 0.23 (9H, s, Si(C***H***$_3$)$_3$), 0.12 (9H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 177.1 (***C***O), 136.8 (Ar-C-1), 130.3 (Ar-***C***-2,6), 128.1 (Ar-***C***-3,5), 126.8 (Ar-***C***-4), 52.6 (O***C***H$_3$), 39.7 (***C***-3), 35.2 (***C***(CH$_3$)$_3$), 30.2 (C(***C***H$_3$)$_3$), 30.1 (***C***-2), 27.0 (***C***-1), -0.3 (Si(***C***H$_3$)$_3$), -0.4 (Si(***C***H$_3$)$_3$); δ_{Si} (139 MHz) 30.3 ($^1J_{Si\text{-}F}$ = 321.9Hz), -14.4 ($^2J_{Si\text{-}F}$ = 25.0Hz), -14.9 ($^2J_{Si\text{-}F}$ = 30.3Hz); δ_F (188 MHz) -163.8; m/z (EI) 409 ([M-CH_3]$^{+\cdot}$, 11%), 351 ([M-Si(CH$_3$)$_3$]$^{+\cdot}$, 89), 185 (15), 171 (23), 159 (45), 137 (29), 131 (58), 115 (32), 91 (16), 73 (100), 59 (81), 45 (44), 41 (26); HRMS (ES+) found [M+NH_4]$^{+\cdot}$ 442.2421, $C_{21}H_{41}O_2NFSi_3$ requires [M+NH_4]$^{+\cdot}$ 442.2424.

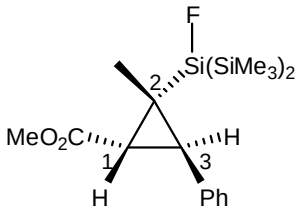
(1*RS*,2*RS*,3*RS*)-Methyl 2-(1'-fluoro-1',1'-bistrimethylsilyl)silyl-2-(4-methoxyphenyl)-3-phenylcyclopropanecarboxylate 328



To a solution of methyl 2-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silyl-2-(4-methoxyphenyl)-3-phenylcyclopropanecarboxylate (0.41 g, 0.75 mmol) in dry

dichloromethane (6.0 ml) was added the trifluoroborane-acetic acid complex (0.14 ml, 0.75 mmol). The mixture was stirred at room temperature for 5 min after which time saturated sodium bicarbonate solution (5.0 ml) was added. The aqueous layer was separated and extracted with DCM (3 x 15 ml). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give a pure title compound as a white solid (0.35 g, 98%). Mp: 80-82 ^oC; R_f 0.7 (pet. ether : diethyl ether 8:2); IR (ATR) 2952, 1688, 1510, 1442, 1242, 1176, 1033, 827, 750, 723, 694 cm^{-1}; δ_H (500 MHz) 7.10-7.09 (3H, m, 3-Ar-3,4,5-***H***), 6.85-6.83 (2H, m, 2-Ar-2,6-***H***), 6.71-6.69 (2H, m, 3-Ar-2,6-***H***), 6.68-6.66 (2H, m, 2-Ar-3,5-***H***), 3.80 (3H, s, $CO_2C\boldsymbol{H}_3$), 3.73 (3H, s, 2-Ar-$OC\boldsymbol{H}_3$), 2.95 (1H, d, *J* = 4.0Hz, 3-***H***), 2.73 (1H, d, *J* = 4.0Hz, 1-***H***), 0.31 (9H, s, $Si(C\boldsymbol{H}_3)_3$), 0.08 (9H, s, $Si(C\boldsymbol{H}_3)_3$); δ_C (125 MHz) 175.2 (***C***O), 157.7 (2-Ar-***C***-4), 136.3 (3-Ar-***C***-1), 132.4 (2-Ar-***C***-2,6), 129.7 (2-Ar-***C***-1), 127.74 (3-Ar-***C***-2,6), 127.70 (3-Ar-***C***-3,5), 126.2 (3-Ar-***C***-4), 113.2 (2-Ar-***C***-3,5), 55.1 (2-Ar-O***C***H_3), 52.6 ($CO_2C\boldsymbol{H}_3$), 38.3 (***C***-3), 34.6 (***C***-2), 33.8 (***C***-1), -0.3 ($Si(\boldsymbol{C}H_3)_3$), -0.7 ($Si(\boldsymbol{C}H_3)_3$); δ_F (376 MHz) -186.5; δ_{Si} (139 MHz) 23.1 ($^1J_{Si\text{-}F}$ = 322.2Hz), -14.9 ($^2J_{Si\text{-}F}$ = 27.0Hz), -15.8 ($^2J_{Si\text{-}F}$ = 24.9Hz); m/z (EI) 459 ($[M\text{-}CH_3]^{+\cdot}$, 6%), 401 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 100), 277 (27), 265 (21), 250 (38), 131 (33), 73 (93), 59 (81), 45 (19); HRMS (ES+) found $[M+NH_4]^{+\cdot}$ 492.2210, $C_{24}H_{39}O_3NFSi_3$ requires $[M+NH_4]^{+\cdot}$ 492.2216.

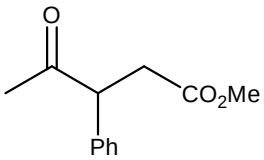
(1*RS*,2*RS*,3*RS*)-Methyl 2-(1'-fluoro-1',1'-bistrimethylsilyl)silyl-2-methyl-3-phenylcyclopropane-carboxylate 330



To a solution of methyl 2-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silyl-2-methyl-3-phenylcyclopropanecarboxylate (0.09 g, 0.19 mmol) in dry dichloromethane (2.0 ml) was added the trifluoroborane-acetic acid complex (0.02 ml, 0.19 mmol). The mixture was stirred at room temperature for 5 min after which time saturated sodium bicarbonate solution (5.0 ml) was added. The aqueous layer was separated and extracted with DCM (3 x 10 ml). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give a pure title compound (0.07 g, 94%). R_f 0.6 (pet. ether : diethyl ether 9:1); IR (ATR) 2953, 1702, 1442, 1244, 1206, 1068, 832, 758, 697 cm^{-1}; δ_H (700 MHz) 7.34-7.33 (2H, m, Ar-3,5-***H***), 7.27-7.26 (3H, m, Ar-2,4,6-***H***), 3.76 (3H, s, $OC\boldsymbol{H}_3$), 2.85 (1H, d, *J* = 4.2Hz, 3-***H***), 2.13

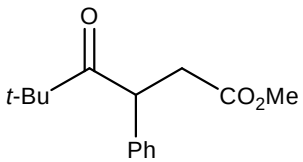
(1H, d, *J* = 4.2Hz, 1-***H***), 0.94 (3H, s, C***H***$_3$), 0.29 (9H, s, Si(C***H***$_3$)$_3$), 0.19 (9H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 175.8 (***C***O), 136.2 (Ar-***C***-1), 129.2 (Ar-***C***-2,6), 128.3 (Ar-***C***-3,5), 126.7 (Ar-***C***-4), 52.4 (O***C***H$_3$), 38.2 (***C***-3), 31.9 (***C***-1), 20.4 (***C***-2), 16.2 (***C***H$_3$), -0.4 (Si(***C***H$_3$)$_3$), -0.8 (Si(***C***H$_3$)$_3$); δ_F (188 MHz) -193.4; δ_{Si} (139 MHz) 27.1 ($^1J_{Si\text{-}F}$ = 315.7Hz), -15.4 ($^2J_{Si\text{-}F}$ = 26.3Hz), -16.4 ($^2J_{Si\text{-}F}$ = 25.0Hz); m/z 367 ([M-CH$_3$]$^{+\cdot}$, 30%), 309 ([M-Si(CH$_3$)$_3$]$^{+\cdot}$, 100), 209 (22), 185 (52), 173 (44), 158 (30), 131 (58), 115 (53), 89 (26), 73 (100), 59 (60), 45 (43).

Methyl 4-oxo-3-phenylpentanoate[132] 331



To a solution of methyl 2-(1'-fluoro-1',1'-bistrimethylsilyl)silyl-2-methyl-3-phenylcyclopropanecarboxylate (0.21 g, 0.54 mmol) in DMF (4.0 ml) was added mCPBA (0.57 g, 3.25 mmol) and KF (0.06 g, 1.08 mmol). The mixture was stirred at RT for 5 h after which time it was diluted with ether (10.0 ml) and saturated sodium bicarbonate solution (5.0 ml) was added. The aqueous layer was separated and extracted with ether (3 x 10 ml). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash column chromatography (pet. ether : diethyl ether 95:5) give title compound as a colourless liquid (0.06 g, 50%). R_f 0.1 (pet. ether : diethyl ether 95:5); IR (ATR) 2953, 1735, 1715, 1494, 1437, 1355, 1249, 1157, 1069, 841, 756, 701 cm^{-1}; δ_H (700 MHz) 7.33-7.31 (2H, m, Ar-3,5-***H***), 7.28-7.26 (1H, m, Ar-4-***H***), 7.20-7.19 (2H, m, Ar-2,6-***H***), 4.17 (1H, dd, *J* = 9.8Hz, *J* = 4.9 Hz, 3-***H***), 3.64 (3H, s, OC***H***$_3$), 3.20 (1H, dd, *J* = 16.8Hz, *J* = 9.8Hz, 2-***H***), 2.51 (1H, dd, *J* = 16.8Hz, *J* = 4.9Hz, 2-***H***), 2.10 (3H, s, C***H***$_3$); δ_C (175 MHz) 206.8 (***C***O), 172.5 (***C***OCH$_3$), 137.4 (Ar-C-*ipso*), 129.2 (Ar-***C***-*m*), 128.2 (Ar-***C***-*o*), 127.8 (Ar-***C***-*p*), 54.8 (***C***-3), 51.8 (O***C***H$_3$), 36.7 (***C***-2), 28.9 (***C***H$_3$); m/z (EI) 206 ([M]$^{+\cdot}$, 4%), 175 ([M-OCH$_3$]$^{+\cdot}$, 14), 164 (37), 131 (15), 121 (93), 104 (100), 91 (28), 77 (31), 43 (69).

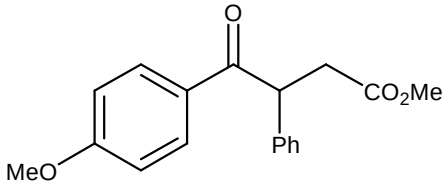
Methyl 5,5-dimethyl-4-oxo-3-phenylhexanoate 332



To a solution of methyl 2-*tert*-butyl-2-(1'-fluoro-1',1'-bistrimethylsilyl)silyl-3-phenylcyclopropanecarboxylate (0.27 g, 0.63 mmol) in DMF (4.0 ml) was added *m*CPBA

(0.65 g, 3.76 mmol) and KF (0.07 g, 1.25 mmol). The mixture was stirred at RT for 12 h after which time it was diluted with ether (5.0 ml) and saturated sodium bicarbonate solution (5.0 ml) was added. The aqueous layer was separated and extracted with ether (3 x 10 ml). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash column chromatography (pet. ether : diethyl ether 8:2) give the title compound as a yellow oil (0.10. g, 61%). R_f 0.4 (pet. ether : diethyl ether 8:2); IR (ATR) 2954, 1736, 1699, 1478, 1436, 1366, 1236, 1194, 1170, 1099, 1002, 970, 751, 703 cm^{-1}; δ_H (500 MHz) 7.30-7.27 (2H, m, Ar-3,5-***H***), 7.24-7.21 (1H, m, Ar-4-***H***), 7.21-7.19 (2H, m, Ar-2,6-***H***), 4.59 (1H, dd, *J* = 10.0Hz, *J* = 5.0 Hz, 3-***H***), 3.61 (3H, s, OC***H***$_3$), 3.16 (1H, dd, *J* = 17.0Hz, *J* = 10.0Hz, 2-***H***), 2.51 (1H, dd, *J* = 17.0Hz, *J* = 5.0Hz, 2-***H***), 1.07 (9H, s, C(C***H***$_3$)$_3$); δ_C (125 MHz) 214.3 (***C***O), 172.3 (***C***O_2CH_3), 138.0 (Ar-C-1), 128.9 (Ar-***C***-3,5), 128.1 (Ar-***C***-2,6), 127.3 (Ar-***C***-4), 51.6 (O***C***H_3), 48.9 (***C***-3), 45.0 (***C***$(CH_3)_3$), 39.3 (***C***-2), 27.2 (C(***C***$H_3)_3$); m/z (EI) 248 ($[M]^{+\cdot}$, 16%), 217 ($[M\text{-}OCH_3]^{+\cdot}$, 18), 191 (45), 164 (67), 157 (33), 131 (45), 121 (51), 104 (100), 85 (51), 77 (40), 57 (82), 41 (38); HRMS (EI) found $[M]^{+\cdot}$ 248.1404, $C_{15}H_{20}O_3$ requires $[M]^{+\cdot}$ 248.1407.

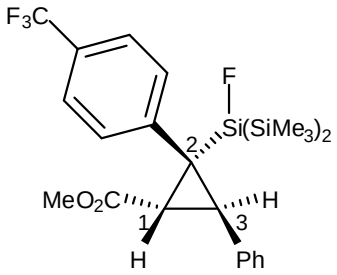
Methyl 4-(4-methoxyphenyl)-4-oxo-3-phenylbutanoate 333



To a solution of methyl 2-(1'-fluoro-1',1'-bistrimethylsilyl)silyl-2-(4-methoxyphenyl)-3-phenylcyclopropanecarboxylate (0.23 g, 0.49 mmol) in DMF (4.0 ml) was added *m*CPBA (0.50 g, 2.91 mmol) and KF (0.06 g, 0.97 mmol). The mixture was stirred at RT for 12 h after which time it was diluted with ether (5.0 ml) and saturated sodium bicarbonate solution (5.0 ml) was added. The aqueous layer was separated and extracted with ether (3 x 10 ml). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash column chromatography give title compound as a yellow oil (0.07. g, 51%). IR (ATR) 2952, 1732, 1670, 1598, 1574, 1511, 1436, 1317, 1248, 1162, 1027, 951, 830, 702 cm^{-1}; δ_H (700 MHz) 7.98-7.96 (2H, m, 4-Ar-2,6-***H***), 7.29-7.28 (4H, m, 3-Ar-2,3,5,6-***H***), 7.23-7.20 (1H, m, 3-Ar-4-***H***), 6.87-6.85 (2H, m, 4-Ar-3,5-***H***), 5.05 (1H, dd, *J* = 9.8Hz, *J* = 4.9Hz, 3-***H***), 3.82 (3H, s, 4-Ar-OC***H***$_3$), 3.65 (3H, s, 1-OC***H***$_3$), 3.37 (1H, dd, *J* = 16.8Hz, *J* = 9.8Hz, 2-***H***), 2.71 (1H, dd, *J* = 16.8Hz, *J* = 4.9Hz, 2-***H***); δ_C (175 MHz) 197.0 (***C***O-4), 172.6 (***C***O-1), 163.4 (4-Ar-***C***-4), 138.6 (3-Ar-***C***-1), 131.2 (4-Ar-***C***-2,6), 129.12 (4-Ar-***C***-1), 129.10 (3-Ar-***C***-3,5),

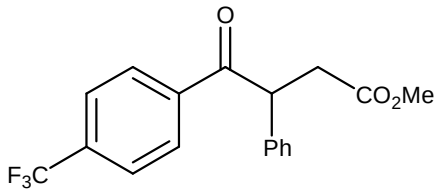
128.0 (3-Ar-***C***-2,6), 127.4 (3-Ar-***C***-4), 113.7 (4-Ar-***C***-3,5), 55.4 (4-Ar-O***C***H_3), 51.75 (1-O***C***H_3), 49.2 (***C***-3), 38.4 (***C***-2); m/z (EI) 298 ($[M]^{+\cdot}$, 6%), 267 ($[M\text{-}OCH_3]^{+\cdot}$, 27), 135(100), 121 (12), 107 (41), 92 (45), 77 (53), 64 (18); HRMS (EI) found $[M]^+$ 298.1201, $C_{18}H_{18}O_4$ requires $[M]^+$ 298.1200.

(1*RS*,2*RS*,3*RS*)-Methyl 2-(1'-fluoro-1',1'-bistrimethylsilyl)silyl-2-(4-(trifluoromethyl)phenyl)-3-phenylcyclopropanecarboxylate 334



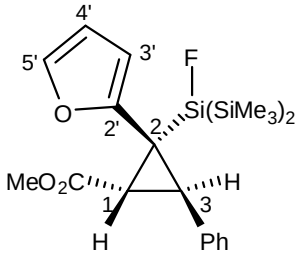
To a solution of methyl 2-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silyl-3-phenyl-2-(4-trifluoromethyl)phenyl)cyclopropanecarboxylate (0.19 g, 0.32 mmol) in dry dichloromethane (4.0 ml) was added the trifluoroborane-acetic acid complex (0.05 ml, 0.32 mmol). The mixture was stirred at room temperature for 5 min after which time saturated sodium bicarbonate solution (5.0 ml) was added. The aqueous layer was separated and extracted with DCM (3 x 10 ml). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a pure title compound (0.16 g, 98%). R_f 0.4 (pet. ether : diethyl ether 95:5); IR (ATR) 2954, 1702, 1616, 1444, 1323, 1243, 1163, 1122, 1068, 1017, 831, 745, 694, 605 cm^{-1}; δ_H (700 MHz) 7.37-7.36 (2H, m, 2-Ar-3,5-***H***), 7.11-7.09 (3H, m, 3-Ar-3,4,5-***H***), 7.04-7.03 (2H, m, 2-Ar-2,6-***H***), 6.68-6.66 (2H, m, 3-Ar-2,6-***H***), 3.83 (3H, s, $CO_2C\boldsymbol{H}_3$), 3.00 (1H, d, *J* = 4.2Hz, 3-***H***), 2.79 (1H, d, *J* = 4.2Hz, 1-***H***), 0.34 (9H, s, $OSi(C\boldsymbol{H}_3)_3$), 0.09 (9H, s, $Si(C\boldsymbol{H}_3)_3$), 0.08 (9H, s, $Si(C\boldsymbol{H}_3)_3$); δ_C (175 MHz) 175.2 (***C***O), 142.2 (2-Ar-***C***-1), 135.4 (3-Ar-***C***-1), 131.7 (2-Ar-***C***-2,6), 128.0 (q, $^2J_{C\text{-}F}$ = 31.2Hz, 2-Ar-***C***-4), 127.9 (3-Ar-***C***-3,5), 127.5 (3-Ar-***C***-2,6), 126.6 (3-Ar-***C***-4), 124.5 (q, $^3J_{C\text{-}F}$ = 3.5Hz, 2-Ar-***C***-3,5), 124.3 (q, $^1J_{C\text{-}F}$ = 271.1Hz, 2-Ar-***C***F_3), 52.9 ($CO_2C\boldsymbol{H}_3$), 38.4 (***C***-3), 35.3 (***C***-2), 33.1 (***C***-1), -0.3 ($Si(\boldsymbol{C}H_3)_3$), -0.7 ($Si(\boldsymbol{C}H_3)_3$); δ_F (376 MHz) -62.7, -184.5; δ_{Si} (139 MHz) 22.8 ($^1J_{Si\text{-}F}$ = 323.8Hz), -14.2 ($^2J_{Si\text{-}F}$ = 27.2Hz), -15.2 ($^2J_{Si\text{-}F}$ = 25.2Hz); m/z (EI) 497 ($[M\text{-}CH_3]^{+\cdot}$, 25%), 439 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 99), 315 (43), 303 (25), 283 (47), 269 (56), 241 (32), 220 (21), 191 (29), 151 (33), 131 (49), 73 (100), 59 (59), 45 (41); HRMS (ES+) found $[M+NH_4]^+$ 530.1986, $C_{24}H_{36}O_2NF_4Si_3$ requires $[M+NH_4]^+$ 530.1984.

Methyl 4-oxo-3-phenyl-4-(4-(trifluoromethyl)phenyl)butanoate 335



To a solution of methyl 2-(1'-fluoro-1',1'-bistrimethylsilyl)silyl-2-(4-(trifluoromethyl)phenyl)-3-phenylcyclopropanecarboxylate (0.11 g, 0.21 mmol) in DMF (4.0 ml) was added *m*CPBA (0.22 g, 1.28 mmol) and KF (0.03 g, 0.43 mmol). The mixture was stirred at RT for 12h after which time it was diluted with ether (10.0 ml) and saturated sodium bicarbonate solution (5.0 ml) was added. The aqueous layer was separated and extracted with ether (3 x 10 ml). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash column chromatography (pet. ether : diethyl ether 8:2) give title compound as a yellow oil (0.03. g, 45%). R_f 0.3 (pet. ether : diethyl ether 7:3); IR (ATR) 2956, 1732, 1688, 1409, 1320, 1231, 1165, 1125, 1066, 1016, 952, 829, 701 cm^{-1}; δ_H (700 MHz) 8.06-8.05 (2H, m, 4-Ar-2,6-***H***), 7.65-7.64 (2H, m, 4-Ar-3,5-***H***), 7.32-7.30 (2H, m, 3-Ar-3,5-***H***), 7.26-7.23 (3H, m, 3-Ar-2,4,6-***H***), 5.07 (1H, dd, *J* = 9.8Hz, *J* = 4.9 Hz, 3-***H***), 3.66 (3H, s, OC***H***$_3$), 3.41 (1H, dd, *J* = 17.2Hz, *J* = 9.8Hz, 2-***H***), 2.73 (1H, dd, *J* = 17.2Hz, *J* = 4.9Hz, 2-***H***); δ_C (175 MHz) 197.8 (***C***O), 172.4 (***C***OCH$_3$), 139.0 (4-Ar-C-1), 137.2 (3-Ar-***C***-1), 134.3 (q, $^2J_{c\text{-}f}$ = 32.7Hz, 4-Ar-***C***-4), 129.4 (3-Ar-***C***-3,5), 129.1 (4-Ar-***C***-2,6), 128.1 (3-Ar-***C***-2,6), 127.8 (3-Ar-***C***-4), 125.6 (q, $^3J_{c\text{-}f}$ = 3.3Hz, 4-Ar-***C***-3,5), 123.5 (q, $^1J_{c\text{-}f}$ = 273.1Hz, ***C***F$_3$), 51.9 (O***C***H$_3$), 50.0 (***C***-3), 38.3 (***C***-2); δ_F (376 MHz) -63.6; m/z (EI) 336 ([M]$^{+\cdot}$, 8%), 305 ([M-OCH$_3$]$^{+\cdot}$, 11), 173 (100), 145 (51), 121 (80), 104 (18), 91 (11), 77 (14); HRMS (EI) found [M]$^{+\cdot}$ 336.0965, $C_{18}H_{15}F_3O_3$ requires [M]$^{+\cdot}$ 461.0968.

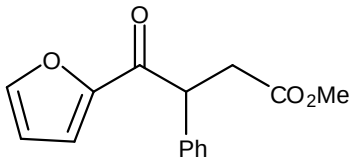
(1*RS*,2*RS*,3*RS*)-Methyl 2-(1'-fluoro-1',1'-bistrimethylsilyl)silyl-2-(furan-2'-yl)-3-phenylcyclopropanecarboxylate 336



To a solution of methyl 2-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silyl-2-(furan-2'-yl)-3-phenylcyclopropanecarboxylate (0.21 g, 0.42 mmol) in dry dichloromethane (4.0 ml) was

added the trifluoroborane-acetic acid complex (0.06 ml, 0.42 mmol). The mixture was stirred at room temperature for 5 min after which time saturated sodium bicarbonate solution (5.0 ml) was added. The aqueous layer was separated and extracted with DCM (3 x 15 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica (pet. ether : diethyl ether 9:1) afforded the product as a colourless oil (0.11 g, 61%). R_f 0.6 (pet. ether : diethyl ether 9:1); IR (ATR) 2951, 2894, 1704, 1499, 1442, 1404, 1243, 1202, 1179, 1013, 833, 730, 691 cm^{-1}; δ_H (700 MHz) 7.19-7.16 (4H, m, Ar-3,4,5-***H***, 5'-***H***), 6.94-6.93 (2H, m, Ar-2,6-***H***), 6.14 (1H, dd, *J* = 3.5Hz, *J* = 2.1Hz, 4'-***H***), 5.74 (1H, d, *J* = 3.5Hz, 3'-***H***), 3.79 (3H, s, $CO_2C\boldsymbol{H}_3$), 3.02 (1H, d, *J* = 5.6Hz, 3-***H***), 2.94 (1H, d, *J* = 5.6Hz, 2-***H***), 0.27 (9H, s, $Si(C\boldsymbol{H}_3)_3$), 0.09 (9H, s, $Si(C\boldsymbol{H}_3)_3$); δ_C (175 MHz) 174.0 (***C***O), 151.5 (***C***-2'), 141.0 (***C***-5'), 136.1 (Ar-***C***-1), 127.9 (Ar-***C***-2,6), 127.6 (Ar-***C***-3,5), 126.7 (Ar-***C***-4), 110.5 (***C***-4'), 109.2 (***C***-3'), 52.6 ($CO_2C\boldsymbol{H}_3$), 37.1 (***C***-3), 32.2 (***C***-2), 27.2 (***C***-1), -0.5 ($Si(\boldsymbol{C}H_3)_3$), -1.3 ($Si(\boldsymbol{C}H_3)_3$); δ_F (376MHz) -191.4; δ_{Si} (139 MHz) 23.9 ($^1J_{Si\text{-}F}$ = 327.5Hz), -14.9 ($^2J_{Si\text{-}F}$ = 24.3Hz), -15.9 ($^2J_{Si\text{-}F}$ = 21.7Hz); m/z (EI) 434 ($[M]^{+\cdot}$, 0.1%), 419 ($[M\text{-}CH_3]^{+\cdot}$, 0.5), 361 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 38), 165 (20), 131 (16), 73 (100), 59 (40), 45 (14); HRMS (EI) found $[M]^{+\cdot}$ 434.1562, $C_{21}H_{31}FO_3Si_3$ requires $[M]^{+\cdot}$ 434.1565.

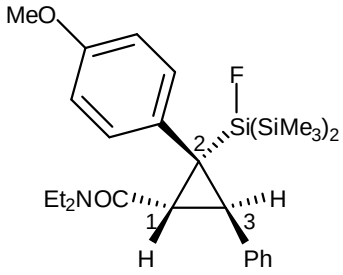
Methyl 4-(furan-2'-yl)-4-oxo-3-phenylbutanoate 337



To a solution of methyl 2-(1'-fluoro-1',1'-bistrimethylsilyl)silyl-2-(furan-2'-yl)-3-phenylcyclopropanecarboxylate (0.11 g, 0.25 mmol) in DMF (4.0 ml) was added *m*CPBA (0.25 g, 1.47 mmol) and KF (0.03 g, 0.49 mmol). The mixture was stirred at RT for 12 h after which time it was diluted with ether (5.0 ml) and saturated sodium bicarbonate solution (5.0 ml) was added. The aqueous layer was separated and extracted with ether (3 x 10 ml). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash column chromatography (pet. ether : diethyl ether 7:3) give title compound as a white solid (0.05. g, 78%). Mp: 86–88 ^oC; R_f 0.2 (pet. ether : diethyl ether 7:3); IR (ATR) 3125, 2954, 1730, 1656, 1464, 1404, 1331, 1279, 1235, 1167, 1092, 1035, 990, 962, 901, 777, 746, 702 cm^{-1}; δ_H (500 MHz) 7.54 (1H, dd, *J* = 1.5Hz, *J* = 0.5Hz, 5'-***H***), 7.35-7.29 (4H, m, 3-Ar-2,3,5,6-***H***), 7.26-7.22 (1H, m, 3-Ar-4-***H***), 7.20 (1H, dd, *J* = 3.5Hz, *J* = 0.5Hz, 3'-***H***), 6.47 (1H, dd, *J* = 3.5Hz, *J* = 1.5Hz, 4'-***H***), 4.90 (1H, dd, *J* = 10.0Hz, *J* = 5.0Hz, 3-***H***), 3.65 (3H, s,

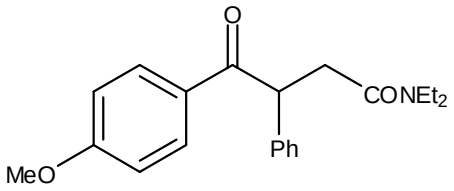
$CO_2C\boldsymbol{H}_3$), 3.39 (1H, dd, *J* = 17.0Hz, *J* = 10.0Hz, 2-***H***), 2.72 (1H, dd, *J* = 17.0Hz, *J* = 5.0Hz, 2-***H***); δ_C (125 MHz) 187.3 (***C***O), 172.3 (***C***O_2Me), 151.9 (***C***-2'), 146.6 (***C***-5'), 137.6 (Ar-***C***-1), 129.0 (Ar-***C***-3,5), 128.2 (Ar-***C***-2,6), 127.6 (Ar-***C***-4), 118.3 (***C***-3'), 112.3 (***C***-4'), 51.8 ($CO_2C\boldsymbol{H}_3$), 49.5 (***C***-3), 37.2 (***C***-2); m/z (EI) 258 ($[M]^{+\cdot}$, 10%), 121 (42), 103 (17), 95 (100), 77 (15); HRMS (ES+) found $[M+H]^{+\cdot}$ 259.0965, $C_{15}H_{15}O_4$ requires $[M+H]^{+\cdot}$ 259.0965.

(1*RS*,2*RS*,3*RS*)-*N*,*N*-Diethyl-2-(1'-fluoro-1',1'-bistrimethylsilyl)silyl-2-(4-methoxyphenyl)-3-phenylcyclopropanecarboxamide 338



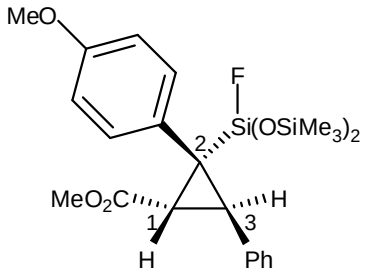
To a solution of *N*,*N*-diethyl-2-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silyl-2-(4-methoxyphenyl)-3-phenylcyclopropanecarboxamide (0.51 g, 0.87 mmol) in dry dichloromethane (10.0 ml) was added the trifluoroborane-acetic acid complex (0.12 ml, 0.87 mmol). The mixture was stirred at room temperature for 5 min after which time saturated sodium bicarbonate solution (10.0 ml) was added. The aqueous layer was separated and extracted with DCM (3 x 15 ml). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give a title compound (0.41 g, ds 3.8:1, 92%). Product was only partially characterised because of instability. IR (ATR) 2953, 2893, 1590, 1509, 1492, 1464, 1239, 1174, 1035, 828, 751, 693cm^{-1}; δ_H (700 MHz) 7.11-7.08 (3H, m, 3-Ar-3,4,6-***H***), 6.84-6.83 (2H, m, 2-Ar-2,6-***H***), 6.72-6.71 (2H, m, 3-Ar-2,6-***H***), 6.66-6.64 (2H, m, 2-Ar-3,5-***H***), 3.72 (3H, s, OC$\boldsymbol{H}_3$), 3.60 (1H, dt, *J* = 7.0Hz, *J* = 14.0Hz, C$\boldsymbol{H}_2CH_3$), 3.57 (1H, dt, *J* = 7.0Hz, *J* = 14.0Hz, C$\boldsymbol{H}_2CH_3$), 3.40 (1H, dt, *J* = 7.0Hz, *J* = 14.0Hz, C$\boldsymbol{H}_2CH_3$), 3.29 (1H, dt, *J* = 7.0Hz, *J* = 14.0Hz, C$\boldsymbol{H}_2CH_3$), 2.73 (1H, d, *J* = 4.9Hz, 1-***H***), 2.62 (1H, d, *J* = 4.9Hz, 3-***H***), 1.29 (3H, t, *J* = 7.0Hz, $CH_2C\boldsymbol{H}_3$), 1.18 (3H, t, *J* = 7.0Hz, $CH_2C\boldsymbol{H}_3$), 0.26 (9H, s, Si(C$\boldsymbol{H}_3)_3$), 0.03 (9H, s, Si(C$\boldsymbol{H}_3)_3$); δ_C (175 MHz) 173.3 (***C***O), 157.2 (2-Ar-***C***-4), 137.1 (3-Ar-***C***-1), 132.1 (2-Ar-***C***-2,6), 131.0 (2-Ar-***C***-1), 127.7 (3-Ar-***C***-3,5), 127.5 (3-Ar-***C***-2,6), 125.9 (3-Ar-***C***-4), 112.9 (2-Ar-***C***-3,5), 55.1 (O***C***H_3), 43.1 (***C***H_2CH_3), 41.6 (***C***H_2CH_3), 37.7 (***C***-3), 34.9 (***C***-2), 33.1 (***C***-1), 14.8 ($CH_2\boldsymbol{C}H_3$), 13.2 ($CH_2\boldsymbol{C}H_3$), 0.1 (Si(***C***$H_3)_3$), -0.4 (Si(***C***$H_3)_3$); δ_F (376MHz) -152.3; δ_{Si} (139 MHz) -10.9 ($^1J_{Si\text{-}F}$ = 309.7Hz), -14.4 ($^2J_{Si\text{-}F}$ = 38.1Hz), -14.9 ($^2J_{Si\text{-}F}$ = 33.5Hz).

***N*,*N*-Diethyl-4-(4-methoxyphenyl)-4-oxo-3-phenylbutanamide 339**



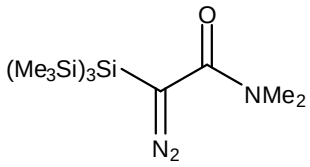
To a solution of *N*,*N*-diethyl-2-(1'-fluoro-1',1'-bistrimethylsilyl)silyl-2-(4-methoxyphenyl)-3-phenylcyclopropanecarboxamide (0.36 g, 0.70 mmol) in DMF (8.0 ml) was added mCPBA (0.72 g, 4.20 mmol) and KF (0.08 g, 1.40 mmol). The mixture was stirred at RT for 16 h after which time it was diluted with ether (20.0 ml) and saturated sodium thiosulfate solution (10.0 ml) was added. The aqueous layer was separated and extracted with ether (3 x 10 ml). The combined organic layers were washed with saturated sodium bicarbonate solution (20.0 ml) and dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash column chromatography (gradient elution pet. ether : diethyl ether 85:15, 3:7) fallowed by reverse phase column (gradient elution water : acetonitrile 8:2, 3:7) give title compound as a white solid (0.05 g, 22%). IR (ATR) 2961, 1673, 1631, 1596, 1511, 1481, 1449, 1405, 1362, 1309, 1245, 1163, 1025, 956, 833, 780, 699 cm^{-1}; δ_H (500 MHz) 8.02-8.00 (2H, m, 4-Ar-2,6-***H***), 7.34-7.33 (2H, m, 3-Ar-2,6-***H***), 7.30-7.27 (1H, m, 3-Ar-3,5-***H***), 7.22-7.19 (1H, m, 3-Ar-4-***H***), 6.86-6.84 (2H, m, 4-Ar-3,5-***H***), 5.25 (1H, dd, *J* = 10.0Hz, *J* = 4.0Hz, 3-***H***), 3.80 (3H, s, 4-Ar-OC***H***$_3$), 3.44 (1H, dd, *J* = 16.0Hz, *J* = 10.0Hz, 2-***H***), 3.42 (1H, dt, *J* = 7.0Hz, *J* = 21.0Hz, C***H***$_2$CH$_3$), 3.36-3.22 (3H, m, C***H***$_2$CH$_3$), 2.62 (1H, dd, *J* = 16.0Hz, *J* = 4.0Hz, 2-***H***), 1.18 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$), 1.06 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$); δ_C (125 MHz) 197.9 (***C***O-4), 170.1 (***C***O-1), 163.2 (4-Ar-***C***-4), 139.3 (3-Ar-***C***-1), 131.2 (4-Ar-***C***-2,6), 129.5 (4-Ar-***C***-1), 129.0 (3-Ar-***C***-3,5), 128.02 (3-Ar-***C***-2,6), 127.1 (3-Ar-***C***-4), 113.6 (4-Ar-***C***-3,5), 55.3 (4-Ar-O***C***H$_3$), 49.2 (***C***-3), 41.8 (***C***H$_2$CH$_3$), 40.2 (***C***H$_2$CH$_3$), 38.1 (***C***-2), 14.1 (CH$_2$***C***H$_3$), 13.0 (CH$_2$***C***H$_3$); m/z (EI) 339 ([M]$^{+\cdot}$, 1%), 135 (100), 77 (13); HRMS (ES+) found [M+H]$^{+\cdot}$ 340.1905, $C_{21}H_{26}O_3N$ requires [M+H]$^{+\cdot}$ 340.1907.

(1*RS*,2*RS*,3*RS*)-Methyl 2-(1'-fluoro-1',1'-bistrimethylsiloxy)silyl-2-(4-methoxyphenyl)-3-phenylcyclopropanecarboxylate 341



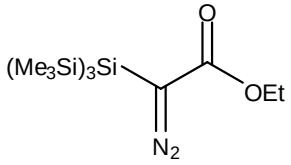
To a solution of methyl 2-(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silyl-2-(4-methoxyphenyl)-3-phenylcyclopropanecarboxylate (0.18 g, 0.37 mmol) in DMF (4.0 ml) was added *m*CPBA (0.26 g, 1.48 mmol) and KF (0.04 g, 0.74 mmol). The mixture was stirred at RT for 40 min after which time it was diluted with ether (5.0 ml) and saturated sodium bicarbonate solution (5.0 ml) was added. The aqueous layer was separated and extracted with ether (3 x 10 ml). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash column chromatography give the title compound as a colourless oil (0.07. g, 37%). R_f 0.5 (pet. ether : diethyl ether 8:2); IR (ATR) 2956, 1740, 1510, 1440, 1249, 1170, 1076, 841, 755, 696 cm^{-1}; δ_H (700 MHz) 7.07-7.06 (3H, m, 3-Ar-3,4,5-***H***), 6.79-6.78 (2H, m, 2-Ar-2,6-***H***), 6.70-6.69 (2H, m, 3-Ar-2,6-***H***), 6.61-6.60 (2H, m, 2-Ar-3,5-***H***), 3.74 (3H, s, $CO_2C\boldsymbol{H}_3$), 3.68 (3H, s, 2-Ar-O$C\boldsymbol{H}_3$), 3.12 (1H, d, *J* = 6.3Hz, 3-***H***), 2.58 (1H, d, *J* = 6.3Hz, 1-***H***), 0.05 (9H, s, OSi($C\boldsymbol{H}_3$)$_3$), 0.04 (9H, s, OSi($C\boldsymbol{H}_3$)$_3$); δ_C (175 MHz) 172.1 (***C***O), 157.9 (2-Ar-***C***-4), 135.8 (3-Ar-***C***-1), 132.3 (2-Ar-C-2,6), 129.8 (2-Ar-***C***-1), 128.1 (3-Ar-C-2,6), 127.7 (3-Ar-C-3,5), 126.3 (3-Ar-***C***-4), 113.2 (2-Ar-**C**-3,5), 55.1 (2-Ar-O$\boldsymbol{C}H_3$), 51.9 ($CO_2C\boldsymbol{H}_3$), 36.8 (***C***-2), 34.2 (***C***-3), 33.0 (***C***-1), 1.43 (OSi($\boldsymbol{C}H_3$)$_3$), 1.39 (OSi($\boldsymbol{C}H_3$)$_3$); δ_F (376 MHz) -192.8; δ_{Si} (139 MHz) 10.6 ($^1J_{Si\text{-}F}$ = 190.7Hz), -73.1 ($^3J_{Si\text{-}F}$ = 3.9Hz), -74.9 ($^3J_{Si\text{-}F}$ = 3.9Hz); m/z (EI) 506 ($[M]^{+\cdot}$, 22%), 491 ($[M\text{-}CH_3]^{+\cdot}$, 34), 431 (74), 416 (26), 373 (16), 250 (95), 241 (29), 222 (66), 211 (52), 178 (38), 91 (27), 73 (100), 59 (21); HRMS (ES+) found $[M+NH_4]^+$ 524.2115, $C_{24}H_{39}O_5NFSi_3$ requires $[M+NH_4]^+$ 524.2115.

2-Diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-*N*,*N*-dimethylacetamide[102] 360



Ethyldiisopropylamine (2.99 ml, 17.1 mmol) followed by tris(trimethylsilyl)silyl trifluoromethanesulfonate (5.93 g, 15.6 mmol) in diethyl ether (50 ml) were added at -78°C to a solution of 2-diazo-*N*,*N*-dimethylacetamide (1.76 g, 15.6 mmol) in diethyl ether (50 ml). The reaction mixture was allowed to warm up to room temperature, and stirred for 24 h. The reaction was then quenched by addition of a saturated $NaHCO_3$ solution (70 ml). The aqueous layer was separated and extracted with Et_2O (3 x 50 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica, elution gradient 0 to 10% diethyl ether in pet. ether, afforded the product as a yellow semi solid material (4.58 g, 82%). R_f 0.2 (pet. ether : diethyl ether 95:5); IR (ATR) 2949, 2893, 2040, 1617, 1369, 1243, 1167, 827, 745, 685 cm^{-1}; δ_H (700 MHz) 2.99 (6H, s, N(C***H***$_3$)$_2$), 0.24 (27H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 168.9 (***C***O), 37.7 (N(***C***H_3)$_2$), 1.0 (Si(***C***H_3)$_3$); δ_{Si} (139 MHz) -11.1, -75.7; m/z (EI) 217 (19%), 173 (37), 143 (12), 131 (21), 117 (23), 73 (100), 45 (14). HRMS (ASAP) found $[M+H]^{+\cdot}$ 360.1785, $C_{13}H_{34}ON_3Si_4$ requires $[M+H]^{+\cdot}$ 360.1779.

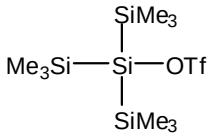
Ethyl 2-diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acetate[102] 361



Ethyldiisopropylamine (2.94 ml, 16.9 mmol) followed by tris(trimethylsilyl)silyl trifluoromethanesulfonate (5.83 g, 15.3 mmol) in diethyl ether (50 ml) were added at -78°C to a solution of ethyl 2-diazoacetate (1.61 g, 15.3 mmol) in diethyl ether (50 ml). The reaction mixture was allowed to warm up to room temperature, and stirred for 24 h. The reaction was then quenched by addition of a saturated $NaHCO_3$ solution (70 ml). The aqueous layer was separated and extracted with Et_2O (3 x 50 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica, elution gradient 0 to 10% diethyl ether in hexane, afforded the product as a yellow oil (4.6 g, 84%). R_f 0.7 (pet. ether : diethyl ether 9:1); IR (ATR) 2949, 2893, 2071, 1682, 1395, 1365, 1241, 1197, 1096, 1063, 825, 739 cm^{-1}; δ_H (500 MHz) 4.20 (2H, q, *J* = 7.0Hz, C***H***$_2$CH$_3$), 1.28 (3H, t, *J* = 7.0Hz,

$CH_2C\boldsymbol{H}_3$), 0.23 (27H, s, $Si(C\boldsymbol{H}_3)_3$); δ_C (125 MHz) 170.2 (***C***O), 60.9 (***C***H_2CH_3), 38.5 (***C***-2), 14.7 ($CH_2\boldsymbol{C}H_3$), 1.0 ($Si(\boldsymbol{C}H_3)_3$); δ_{Si} (140 MHz) -11.34, -80.2; m/z (EI) 332 ($[M\text{-}N_2]^{+\cdot}$, 0.1%), 215 (54), 117 (24), 73 (100), 45 ($[EtO]^{+\cdot}$, 34); HRMS (ASAP) found $[M+H]^{+\cdot}$ 361.1626, $C_{13}H_{33}O_2N_2Si_4$ requires $[M+H]^{+\cdot}$ 361.1619.

Tris(trimethylsilyl)silyl trifluoromethanesulfonate 362



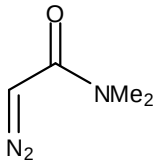
Method A[106]

Trifluoromethanesulfonic acid (1.38 ml, 15.6 mmol) was added dropwise (5 min) via syringe to a solution of phenyltris(trimethylsilyl)silane (5.05 g, 15.6 mmol) in dry dichloromethane (50.0 ml) at 0 ^oC. The reaction mixture was stirred for 20 min and then warmed to room temperature. The reaction mixture was stirred for a further 40 min after which time the solvent was evaporated directly using a vacuum manifold to give the product as a colourless semi solid material (5.93 g, 99%). Product must be used immediately. IR (ATR) 2954, 2896, 1381, 1245, 1200, 1151, 951, 828, 691 cm^{-1}; δ_H (400 MHz) 0.30 (27H, s, $Si(C\boldsymbol{H}_3)_3$); δ_C (100 MHz) 118.5 ((q, $^1J_{C\text{-}F}$ = 315.7Hz, ***C***F_3), -0.7 ($Si(\boldsymbol{C}H_3)_3$); δ_F (376MHz) -76.9; δ_{Si} (139 MHz) -11.7 (***Si***$(CH_3)_3$), -74.4 (***Si***-OTf).

Method B[103]

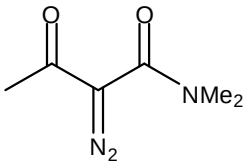
Trifluoromethanesulfonic acid (0.89 ml, 10.0 mmol) was added dropwise (5 min) via syringe to a solution of allyltris(trimethylsilyl)silane (4.14 g, 14.3 mmol) in dry dichloromethane (50.0 ml) at -78 ^oC. The reaction mixture was stirred for 40 min at room temperature after which time the solvent was evaporated directly using a vacuum manifold. Distillation gave the title compound as a colourless semi solid material along with several inseparable components (2.38 g, 60%). B.p. 94-97 ^oC/0.6 mbar. Spectroscopic data for product **362** were consistent with data presented in *Method A*.

2-Diazo-N,N-dimethylacetamide[104] 363



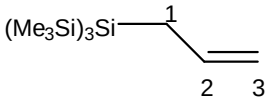
To a solution of 2-diazo-*N*,*N*-dimethyl-3-oxobutanamide (11.44 g, 73.8 mmol) in dry acetonitrile (80 ml) was added a solution of potassium hydroxide (8%, 80 ml) within 10 min. The mixture was stirred at room temperature for 16 h. After addition of water (80 ml) the mixture was extracted with ethyl acetate (3 x 80 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica (ethyl acetate) afforded the product as a yellow oil (6.26 g, 75%). R_f 0.2 (ethyl acetate); IR (ATR) 3069, 2931, 2092, 1604, 1487, 1450, 1393, 1261, 1175, 1127, 1060, 863, 723, 631 cm^{-1}; δ_H (700 MHz) 4.96 (1H, s, 2-***H***), 2.91 (6H, s, N(C***H***$_3$)$_2$); δ_C (175 MHz) 165.8 (***C***O), 46.1(***C***N_2), 36.2 (N(***C***H_3)$_2$); m/z (EI) 113 ($[M]^{+\cdot}$, 25%), 72 (38), 70 (21), 44 (20), 42 (100), 28 (20).

2-Diazo-*N*,*N*-dimethyl-3-oxobutanamide[104] 365



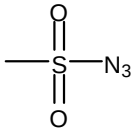
To a solution of *N*,*N*-dimethyl-3-oxobutanamide (18.3 g, 140 mmol) in dry acetonitrile (280 ml) was added methane sulfonyl azide (20.3 g, 168 mmol) and triethylamine (38.9 ml, 279 mmol). The mixture was stirred at room temperature for 3 h after which time sodium hydroxide solution (12%, 240 ml) was added. The aqueous layer was separated and extracted with ethyl acetate (3 x 150 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica (ethyl acetate) afforded the product as a yellow oil (11.44 g, 53%). R_f 0.3 (ethyl acetate); IR (ATR) 2930, 2099, 1624, 1491, 1442, 1385, 1362, 1261, 1228, 1145, 1049, 963, 891, 732, 683 cm^{-1}; δ_H (700 MHz) 3.01 (6H, s, N(C***H***$_3$)$_2$), 2.35 (3H, s, 4-***H***); δ_C (175 MHz) 189.5 (***C***O), 161.4 (***C***ON(CH_3)$_2$), 43.4 (***C***N_2), 37.5 (N(***C***H_3)$_2$), 27.3 (***C***-4); m/z (ES+) 156 ($[M+H]^{+\cdot}$, 100%).

Allyltris(trimethylsilyl)silane[133] **369**



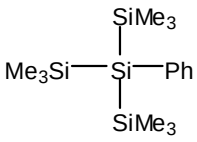
Tetrakis(trimethylsilyl)silane (10.67 g, 33.2 mmol) and dry potassium *tert*-butoxide (4.10 g, 36.6 mmol) were dissolved in THF (50 ml). The solution was stirred for 3h at room temperature. The orange solution was then added dropwise via cannula (over a 1 hour period) to a cooled (-78 ^{o}C) solution of allyl bromide (8.63 ml, 99.7 mmol) in THF (50 ml). The mixture was stirred at room temperature for 4 h after which time ammonium chloride solution (50 ml) was added. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 x 30 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (hexane) gave the title compound as a white semi solid material (8.12 g, 85%). R_f 0.8 (hexane); IR (ATR) 2949, 2893, 1394, 1243, 1047, 987, 892, 827, 763, 746 cm^{-1}; δ_H (700 MHz) 5.86 (1H, ddt, *J* = 16.8Hz, *J* = 9.1Hz, *J* = 8.4Hz, 2-***H***), 4.89 (1H, d, *J* = 16.8Hz, 3-***H***), 4.76 (1H, d, *J* = 9.1Hz, 3-***H***), 1.78 (2H, d, *J* = 8.4Hz, 1-***H***), 0.18 (27H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 138.5 (***C***-2), 111.8 (***C***-3), 14.9 (***C***-1), 1.1 (Si(***C***H$_3$)$_3$); δ_{Si} (139 MHz) -12.4, -81.4; m/z (EI) 288 ([M]$^{+\cdot}$, 6%), 247 ([M-C_3H_5]$^{+\cdot}$, 15), 215 ([M-Si(CH$_3$)$_3$]$^{+\cdot}$, 10), 199 (14), 173 (59), 141 (44), 131 (16), 73 (100), 45 (15).

Methanesulfonyl azide[105] **370**



To a solution of methanesulfonyl chloride (15.0 ml, 194 mmol) in acetone (100 ml) was added over a period of 30 min sodium azide (18.9 g, 290 mmol). The mixture was stirred at room temperature for 1.5 h after which time was filtered and concentrated. The product was obtained as a colourless oil (22.89 g, 97%). IR (ATR) 3029, 2937, 2133, 1349, 1193, 1151, 963, 773, 727 cm^{-1}; δ_H (200 MHz) 3.27 (3H, s, C***H***$_3$); δ_C (100 MHz) 42.8 (***C***H$_3$).

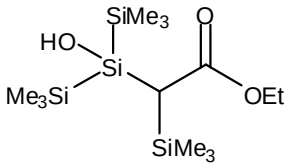
Phenyltris(trimethylsilyl)silane[81] **372**



A solution of phenyl magnesium bromide (88.3 ml, 88.3 mmol) in THF (1 M) was added dropwise (15 min) via syringe to a stirring solution of chlorotris(trimethylsilyl)silane (25.0 g,

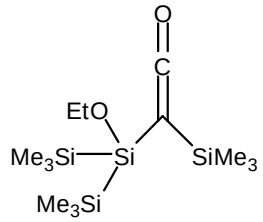
88.3mmol) in dry THF (50ml) at 0 ^{o}C. The reaction mixture was stirred for 22 h at room temperature after which time ammonium chloride solution (150 ml) was added slowly. The aqueous layer was separated and extracted with ether (3x100ml). The combined organic layers were dried over $MgSO_4$, filtered, concentrated and dried under reduced pressure. Flash column chromatography (pet. ether) gave the title compound as a white semi solid material (21.1 g , 74%). R_f 0.7 (pet. ether); IR (ATR) 2950, 2893, 1692, 1426, 1245, 777, 739, 728 cm^{-1}; δ_H (400 MHz) 7.47-7.44 (2H, m, Ar-2,6-***H***), 7.28-7.25 (3H, m, Ar-3,4,5-***H***), 0.23 (27H, s, Si(C***H***$_3$)$_3$); δ_C (100 MHz) 136.6 (Ar-***C***), 135.5 (Ar-***C***), 127.7 (Ar-***C***), 127.3 (Ar-***C***), 1.7 (Si(***C***H$_3$)$_3$); δ_{Si} (139 MHz) -12.7 (***Si***(CH$_3$)$_3$), -76.8 (Ar-***Si***); m/z (EI) 324 ($[M]^{+\cdot}$, 73%), 309 ($[M\text{-}CH_3]^{+\cdot}$, 29), 251 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 40), 236 (56), 174 (92) 73 (100).

Ethyl 2-(2-hydroxy-1,1,1,3,3,3-hexamethyltrisilan-2-yl)-2-(trimethylsilyl)acetate 381



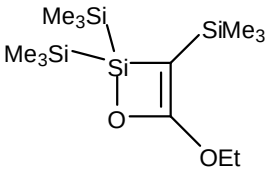
To a solution of $Rh_2(pfb)_4$ (23.3 mg, 0.022 mmol) in toluene (10.0 ml) was added dropwise (5 min) a solution of ethyl 2-diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acetate (0.16 g, 0.44 mmol) in toluene (10.0 ml). The solution was stirred for 1 h at room temperature after which time water (10 ml) was added. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 x 5 ml). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash column chromatography on silica, elution gradient 0 to 50% diethyl ether in hexane, afforded the silylalcohol as a white solid (89.6 mg, 58%). Mp: 57.1–58.5 ^{o}C; R_f 0.4 (pet. ether : diethyl ether 6:4); IR (ATR) 3340, 2953, 2895, 1655, 1365, 1243, 1182, 1039, 963, 831, 743 cm^{-1}; δ_H (700 MHz) 4.08 (2H, q, *J* = 7.0Hz, C***H***$_2$CH$_3$), 2.06 (1H, s, 2-***H***), 1.26 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$), 0.19 (18H, s, Si(C***H***$_3$)$_3$), 0.17 (9H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 174.5 (***C***O), 60.2 (***C***H$_2$CH$_3$), 31.0 (**C**-2), 14.5 (CH$_2$***C***H$_3$), 0.1 (Si(***C***H$_3$)$_3$), -1.0 (Si(***C***H$_3$)$_3$), -1.3 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) 9.0, 3.8, -18.1, -18.2; m/z (ES+) 373 ($[M+Na]^{+\cdot}$, 100%), 360 (42), 338 (17), 301 (20), 219 (16); Anal. Calcd for $C_{13}H_{34}O_3Si_4$: C, 44.52; H, 9.77. Found: C, 44.43; H, 9.70.

2-(2-Ethoxy-1,1,1,3,3,3-hexamethyltrisilan-2-yl)-2-(trimethylsilyl)ethenone 383



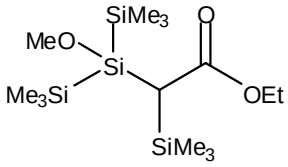
To a solution of $Rh_2(pfb)_4$ (23.0 mg, 0.022 mmol) in toluene (10.0 ml) was added dropwise (5 min) a solution of ethyl 2-diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acetate (0.16 g, 0.44 mmol) in toluene (10.0 ml). The reaction mixture was stirred for 48 h at room temperature. Concentration, followed by flash column chromatography on silica, elution gradient 0 to 10% diethyl ether in hexane, afforded the product as a colourless oil (29.9 mg, 21%). R_f 0.7 (hexane : diethyl ether 95:5); IR (ATR) 2954, 2895, 2069, 1387, 1245, 1101, 1074, 939, 893, 830, 755, 731 cm^{-1}; δ_H (C_7D_8, 700 MHz) 3.56 (2H, q, *J* = 7.0Hz, C***H***$_2$CH$_3$), 1.09 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$), 0.26 (9H, s, Si(C***H***$_3$)$_3$), 0.25 (18H, s, Si(C***H***$_3$)$_3$); δ_C (C_7D_8, 175 MHz) 165.6 (***C***O), 61.4 (***C***H$_2$CH$_3$), 18.7 (CH$_2$***C***H$_3$), 1.6 (Si(***C***H$_3$)$_3$), 0.2 (***C***CO), -0.7 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) 6.6, 5.7, -18.3; m/z (EI) 332 ($[M]^{+\cdot}$, 9%), 317 ($[M\text{-}CH_3]^{+\cdot}$, 49), 303 ($[M\text{-}CH_2CH_3]^{+\cdot}$, 49), 273 (30), 259 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 25), 215 (83), 199 (39), 191 (38), 155 (39), 147 (54), 131 (29), 117 (56), 99 (19), 97 (36), 83 (36), 73 (100), 59 (37), 45 (38); HRMS (EI) found $[M]^{+\cdot}$ 332.1478, $C_{13}H_{32}O_2Si_4$ requires $[M]^{+\cdot}$ 332.1474.

4-Ethoxy-2,2,3-tris(trimethylsilyl)-2H-1,2-oxasilete 385



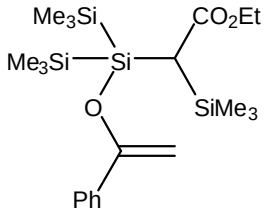
To a solution of $Rh_2(pfb)_4$ (0.7 mg, 0.0007 mmol) in d_8-toluene (0.5 ml) was added dropwise (1 min) a solution of ethyl 2-diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acetate (0.15 mg, 0.034 mmol) in d_8-toluene (0.5 ml). NMR spectroscopy indicated the formation of the intermediate product. δ_H (C_7D_8, -80 ^oC, 500 MHz) 4.02 (2H, q, *J* = 7.2Hz, C***H***$_2$CH$_3$), 1.04 (1H, t, *J* = 7.2Hz, CH$_2$C***H***$_3$), 0.32 (9H, s, Si(C***H***$_3$)$_3$), 0.23 (18H, s, Si(C***H***$_3$)$_3$); δ_C (C_7D_8, -80 ^oC, 125 MHz) 161.1 (***C***-4), 67.0 (***C***-3), 62.8 (***C***H$_2$CH$_3$), 15.0 (CH$_2$***C***H$_3$), 1.4 (Si(***C***H$_3$)$_3$), -2.1 (Si(***C***H$_3$)$_3$); δ_{Si} (C_7D_8, -80 ^oC, 99 MHz) 35.6, -15.3, -17.1.

Ethyl 2-(1-methoxy-1,2,2,2-tetramethyldisilyl)-2-(trimethylsilyl)acetate 396



To a solution of $Rh_2(pfb)_4$ (23.3 mg, 0.022 mmol) in toluene (10.0 ml) was added dropwise (5 min) a solution of ethyl 2-diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acetate (0.16 g, 0.44 mmol) in toluene (10.0 ml). The reaction mixture was stirred for 1 h at room temperature. Dry methanol (0.5 ml) was added and the reaction mixture was stirred for 5 min. Concentration, followed by flash column chromatography on silica, elution gradient 0 to 5% diethyl ether in hexane, afforded the product as a colourless oil (0.07 g, 43%). R_f 0.4 (hexane : diethyl ether 95:5); IR (ATR) 2950, 2897, 1696, 1244, 1163, 1107, 1083, 1039, 827, 761, 721 cm^{-1}; δ_H (700 MHz) 4.09 (1H, dq, *J* = 7.0Hz, *J* = 11.2Hz, C***H***$_2$CH$_3$), 4.02 (1H, dq, *J* = 7.0Hz, *J* = 11.2Hz, C***H***$_2$CH$_3$), 3.45 (3H, s, OC***H***$_3$), 2.23 (1H, s, 2-***H***), 1.24 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$), 0.21 (9H, s, Si(C***H***$_3$)$_3$), 0.19 (9H, s, Si(C***H***$_3$)$_3$), 0.17 (9H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 173.7 (***C***O), 60.0 (***C***H$_2$CH$_3$), 53.7 (O***C***H$_3$), 30.4 (***C***-2), 14.5 (CH$_2$***C***H$_3$), -0.08 (Si(***C***H$_3$)$_3$), -0.12 (Si(***C***H$_3$)$_3$), -0.7 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) 13.3, 4.1, -18.0, -18.5; m/z (ES+) 365 ([M+H]$^{+\cdot}$, 10%), 333 (100), 319 (27), 263 (10), 219 (17); HRMS (ES+) found [M+H]$^{+\cdot}$ 365.1812, $C_{14}H_{37}O_3Si_4$ requires [M+ H]$^{+\cdot}$ 365.1814.

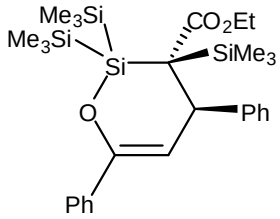
Ethyl 2-(1,1,1,3,3,3-hexamethyl-2-(1-phenylvinyloxy)trisilan-2-yl)-2-(trimethylsilyl)acetate 398



To a solution of $Rh_2(pfb)_4$ (58.7 mg, 0.056 mmol) in toluene (30.0 ml) was added dropwise (5 min) a solution of ethyl 2-diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acetate (0.40 g, 1.11 mmol) in toluene (20.0 ml). The reaction mixture was stirred for 1 h at room temperature. After that time, acetophenone (0.16 ml, 1.33 mmol) was added and the reaction mixture was stirred for 1 h. Concentration, followed by flash column chromatography on neutral alumina, elution gradient 0 to 10% diethyl ether in hexane, afforded the product as a colourless oil (0.12 g, 25%). R_f 0.6 (Al_2O_3 pH=7, hexane : diethyl ether 9:1); IR (ATR) 2953, 2896, 1694, 1314, 1300, 1285, 1244, 1158, 1105, 1075, 1027,

1003, 829, 771 cm^{-1}; δ_H (700 MHz) 7.59-7.58 (2H, m, Ar-2,6-***H***), 7.34-7.32 (2H, m, Ar-3,5-***H***), 7.30-7.27 (1H, m, Ar-4-***H***), 4.88 (1H, d, *J* = 2.8Hz, CC***H***$_2$), 4.40 (1H, d, *J* = 2.8Hz, CC***H***$_2$), 4.13 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 4.06 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 2.50 (1H, s, 2-***H***), 1.26 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$), 0.27 (9H, s, Si(C***H***$_3$)$_3$), 0.192 (9H, s, Si(C***H***$_3$)$_3$), 0.190 (9H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 173.4 (***C***O), 157.8 (SiO***C***), 137.5 (Ar-***C***-1), 128.2 (Ar-***C***-4), 128.0 (Ar-***C***-3,5), 125.3 (Ar-***C***-2,6), 90.0 (C***C***H$_2$), 60.2 (***C***H$_2$CH$_3$), 29.6 (***C***-2), 14.5 (CH$_2$***C***H$_3$), 0.1 (Si(***C***H$_3$)$_3$), -0.1 (Si(***C***H$_3$)$_3$), -0.2 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) 8.6, 4.3, -16.3, -16.7; m/z (ASAP) 451 ([M-H]$^{+\cdot}$, 7%); HRMS (ASAP) found [M+H]$^{+\cdot}$ 453.2153, $C_{21}H_{41}O_3Si_4$ requires [M+H]$^{+\cdot}$ 453.2133.

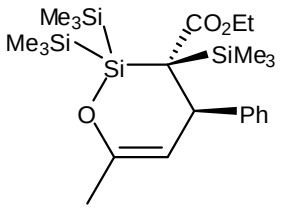
(3*SR*,4*RS*)-Ethyl 4,6-diphenyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2*H*-1,2-oxasiline-3-carboxylate 399



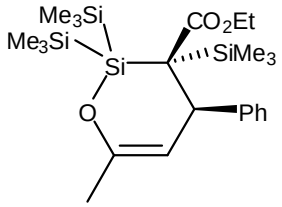
To a solution of $Rh_2(pfb)_4$ (25.3 mg, 0.024 mmol) in toluene (10.0 ml) was added dropwise (5 min) a solution of ethyl 2-diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acetate (0.17 g, 0.48 mmol) in toluene (10.0 ml). The reaction mixture was stirred for 1 h at room temperature. After that time, a solution of *trans*-chalcone (0.12 ml, 0.57 mmol) in toluene (2.0 ml) was added and the reaction mixture was stirred for 1 h. Concentration, followed by flash column chromatography on silica, elution gradient 0 to 10% diethyl ether in hexane, afforded the product as a white solid (0.13 g, 51%). Mp: 100.7–101.3 ^oC; R_f 0.6 (pet. ether : diethyl ether 95:5); IR (ATR) 2949, 2891, 1696, 1491, 1447, 1332, 1291, 1244, 1165, 1107, 1033, 832, 786, 753 cm^{-1}; δ_H (700 MHz) 7.74-7.73 (2H, m, 4-Ar-2,6-***H***), 7.62-7.61 (2H, m, 6-Ar-2,6-***H***), 7.35-7.33 (2H, m, 6-Ar-3,5-***H***), 7.31-7.29 (3H, m, 4-Ar-3,5-***H***, 6-Ar-4-***H***,), 7.25-7.23 (1H, m, 4-Ar-4-***H***), 5.50 (1H, d, *J* = 2.8Hz, 4-***H***), 4.91 (1H, d, *J* = 2.8Hz, 5-***H***), 4.37 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 4.06 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 1.33 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$), 0.40 (9H, s, Si(C***H***$_3$)$_3$), 0.16 (9H, s, Si(C***H***$_3$)$_3$), -0.18 (9H, s, CSi(C***H***$_3$)$_3$); δ_C (175 MHz) 176.1 (***C***O), 152.1 (***C***-6), 145.0 (4-Ar-***C***-1), 137.4 (6-Ar-***C***-1), 131.2 (4-Ar-***C***-2,6), 128.1 (6-Ar-***C***-2,6), 127.8 (4-Ar-***C***-3,5), 127.7 (6-Ar-***C***-4), 126.8 (4-Ar-***C***-4), 124.5 (6-Ar-***C***-3,5), 106.3 (***C***-5), 61.0 (***C***H$_2$CH$_3$), 44.5 (***C***-4), 37.2 (***C***-3), 14.8 (CH$_2$***C***H$_3$), 0.8 (Si(***C***H$_3$)$_3$), 0.7 (CSi(***C***H$_3$)$_3$), 0.3 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) 4.7, 3.1, -13.2, -

14.3; m/z (ASAP) 541 ($[M+H]^{+\cdot}$, 11%); Anal. Calcd for $C_{28}H_{44}O_3Si_4$: C, 62.16; H, 8.20. Found: C, 62.04; H, 8.20.

(3*SR*,4*RS*)-Ethyl 6-methyl-4-phenyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2*H*-1,2-oxasiline-3-carboxylate 401a and
(3*RS*,4*RS*)-Ethyl 6-methyl-4-phenyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2*H*-1,2-oxasiline-3-carboxylate 401b



401a



401b

To a solution of $Rh_2(pfb)_4$ (59.8 mg, 0.057 mmol) in toluene (30.0 ml) was added dropwise a solution of ethyl 2-diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acetate (0.41 g, 1.13 mmol) in toluene (20.0 ml). The reaction mixture was stirred for 1 h at room temperature. After that time, a solution of (*E*)-4-phenylbut-3-en-2-one (0.20 g, 1.36 mmol) in toluene (5.0 ml) was added and the reaction mixture was stirred for 1 h. Concentration, followed by flash column chromatography on neutral alumina, elution gradient 0 to 10% diethyl ether in hexane, afforded the product **401a** as a white solid (0.18 g, 34%) and product **401b** as a colourless oil (0.10 g, 18%). Ratio of the product changed after purification (crude ds 1:1).

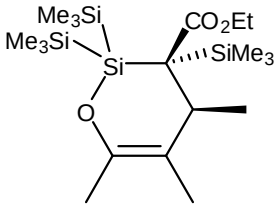
Experimental data for compound **401a**:
Mp: 42.1–46.2 ^{o}C; R_f 0.7 (Al_2O_3 pH=7, pet. ether : diethyl ether 9:1); IR (ATR) 2986, 2949, 2890, 1694, 1493, 1376, 1325. 1288, 1248, 1174, 1159, 1092, 1041, 1005, 909, 829, 765 cm^{-1}; δ_H (500 MHz) 7.68-7.67 (2H, m, Ar-2,6-***H***), 7.27-7.24 (2H, m, Ar-3,5-***H***), 7.22-7.18 (1H, m, Ar-4-***H***), 4.67 (1H, dd, *J* = 2.5Hz, *J* = 2.0Hz, 4-***H***), 4.52 (1H, d, *J* = 2.5Hz, 5-***H***), 4.34 (1H, dq, *J* = 11.0Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 4.01 (1H, dq, *J* = 11.0Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 1.82 (3H, d, *J* = 2.0Hz, C***H***$_3$), 1.29 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$), 0.31 (9H, s, Si(C***H***$_3$)$_3$), 0.20 (9H, s, Si(C***H***$_3$)$_3$), -0.20 (9H, s, CSi(C***H***$_3$)$_3$); δ_C (125 MHz) 176.1 (***C***O), 152.4 (***C***-6), 145.3 (Ar-***C***-1), 131.1 (Ar-***C***-2,6), 127.6 (Ar-***C***-3,5), 126.6 (Ar-***C***-4), 105.1 (***C***-5), 60.8 (***C***H$_2$CH$_3$), 44.1 (***C***-4), 36.8 (***C***-3), 22.8 (C***H***$_3$), 14.8 (CH$_2$***C***H$_3$), 0.72 (Si(***C***H$_3$)$_3$), 0.66 (CSi(***C***H$_3$)$_3$), 0.2 (Si(***C***H$_3$)$_3$); δ_{Si}

(140 MHz) 4.2, 1.7, -13.4, -14.9; m/z (ASAP) 479 ($[M+H]^{+\cdot}$, 18%); HRMS (ASAP) found $[M+H]^{+\cdot}$ 479.2284, $C_{23}H_{43}O_3Si_4$ requires $[M+H]^{+\cdot}$ 479.2289.

Experimental data for compound **401b**:

R_f 0.6 (Al_2O_3 pH=7, pet. ether : diethyl ether 9:1); IR (ATR) 2950, 2895, 1708, 1653, 1491, 1449, 1378, 1327, 1245, 1198, 1157, 1096, 1037, 1005, 979, 833, 743 cm^{-1}; δ_H (700 MHz) 7.39-7.37 (2H, m, Ar-2,6-***H***), 7.24-7.22 (2H, m, Ar-3,5-***H***), 7.19-7.16 (1H, m, Ar-4-***H***), 4.50 (1H, d, *J* = 4.2Hz, 5-***H***), 4.21 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 4.01 (1H, d, *J* = 4.2Hz, 4-***H***), 3.97 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 1.78 (3H, s, C***H***$_3$), 1.25 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$), 0.32 (9H, s, Si(C***H***$_3$)$_3$), 0.07 (9H, s, Si(C***H***$_3$)$_3$), 0.06 (9H, s, CSi(C***H***$_3$)$_3$); δ_C (175 MHz) 174.3 (***C***O), 150.1 (***C***-6), 145.1 (Ar-***C***-1), 130.2 (Ar-***C***-2,6), 127.9 (Ar-***C***-3,5), 126.6 (Ar-***C***-4), 104.0 (***C***-5), 60.2 (***C***H$_2$CH$_3$), 43.5 (***C***-4), 38.3 (***C***-3), 22.2 (C***H***$_3$), 14.2 (CH$_2$***C***H$_3$), 0.9 (Si(***C***H$_3$)$_3$), 0.7 (CSi(***C***H$_3$)$_3$), 0.0 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) 7.9, 3.7, -14.8, -15.7; m/z (ASAP) 479 ($[M+H]^{+\cdot}$, 8%); HRMS (ASAP) found $[M+H]^{+\cdot}$ 479.2297, $C_{23}H_{43}O_3Si_4$ requires $[M+H]^{+\cdot}$ 479.2289.

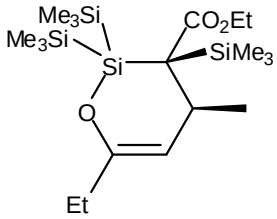
(3*RS*,4*SR*)-Ethyl 4,5,6-trimethyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2*H*-1,2-oxasiline-3-carboxylate 403



To a solution of $Rh_2(pfb)_4$ (59.0 mg, 0.056 mmol) in toluene (30.0 ml) was added dropwise (5 min) a solution of ethyl 2-diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acetate (0.40 g, 1.12 mmol) in toluene (20.0 ml). The reaction mixture was stirred for 1 h at room temperature. After that time, a solution of (*E*)-3-methylpent-3-en-2-one (0.15 ml, 1.34 mmol) in toluene (2.0 ml) was added and the reaction mixture was stirred for 1 h. Concentration, followed by flash column chromatography on neutral alumina, elution gradient 0 to 10% diethyl ether in hexane, afforded the product as a white solid (0.27 g, 56%). Mp: 148.3–151.2 ^oC; R_f 0.6 (Al_2O_3 pH=7, pet. ether : diethyl ether 9:1); IR (ATR) 2958, 2902, 1697, 1440, 1384, 1230, 1175, 1040, 944, 829, 768, 744 cm^{-1}; δ_H (700 MHz) 4.19 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 4.02 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 2.62 (1H, q, *J* = 7.0Hz, 4-***H***), 1.65 (3H, s, 6-C***H***$_3$), 1.61 (3H, s, 5-C***H***$_3$), 1.27 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$), 1.20

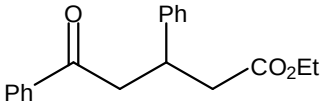
(3H, d, *J* = 7.0Hz, 4-C***H***$_3$), 0.26 (9H, s, Si(C***H***$_3$)$_3$), 0.17 (9H, s, Si(C***H***$_3$)$_3$), 0.12 (9H, s, CSi(C***H***$_3$)$_3$); δ_C (175 MHz) 174.9 (***C***O), 143.9 (***C***-6), 108.5 (***C***-5), 60.2 (***C***H$_2$CH$_3$), 38.0 (***C***-3), 37.4 (***C***-4), 20.1 (4-***C***H$_3$), 18.8 (6-***C***H$_3$), 18.7 (5-***C***H$_3$), 14.5 (CH$_2$***C***H$_3$), 1.1 (Si(***C***H$_3$)$_3$), 0.6 (Si(***C***H$_3$)$_3$), -0.3 (CSi(***C***H$_3$)$_3$); δ_{Si} (140 MHz) 8.0, 1.0, -14.8, -17.8; m/z (ASAP) 431 ([M+H]$^{+\cdot}$, 100%); HRMS (ASAP) found [M+H]$^{+\cdot}$ 431.2274, $C_{19}H_{43}O_3Si_4$ requires [M+H]$^{+\cdot}$ 431.2289.

(3*SR*,4*SR*)-Ethyl 6-ethyl-4-methyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2*H*-1,2-oxasiline-3-carboxylate 405



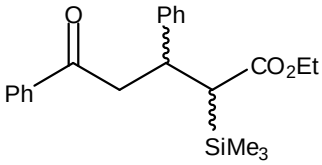
To a solution of $Rh_2(pfb)_4$ (59.0 mg, 0.056 mmol) in toluene (30.0 ml) was added dropwise a solution of ethyl 2-diazo-2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)acetate (0.41 g, 1.12 mmol) in toluene (20.0 ml). The reaction mixture was stirred for 1 h at room temperature. After that time, a solution of (*E*)-hex-4-en-3-one (0.15 ml, 1.35 mmol) in toluene (2.0 ml) was added and the reaction mixture was stirred for 1 h. Concentration, followed by flash column chromatography on neutral alumina, elution gradient 0 to 10% diethyl ether in hexane, afforded the product as a white semisolid (0.24 g, 47%). R_f 0.6 (Al_2O_3 pH=7, pet. ether : diethyl ether 9:1); IR (ATR) 2958, 2896, 1707, 1660, 1458, 1369, 1329, 1243, 1161, 1041, 1000, 948, 906, 829, 745 cm^{-1}; δ_H (700 MHz) 4.27 (1H, dq, *J* = 10.5Hz, *J* = 7.0Hz, OC***H***$_2$CH$_3$), 4.12 (1H, s, 5-***H***), 3.98 (1H, dq, *J* = 10.5Hz, *J* = 7.0Hz, OC***H***$_2$CH$_3$), 3.30 (1H, q, *J* = 7.0Hz, 4-***H***), 1.96 (2H, q, *J* = 7.0Hz, C***H***$_2$CH$_3$), 1.35 (3H, d, *J* = 7.0Hz, C***H***$_3$), 1.27 (3H, t, *J* = 7.0Hz, OCH$_2$C***H***$_3$), 0.99 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$), 0.29 (9H, s, Si(C***H***$_3$)$_3$), 0.21 (9H, s, CSi(C***H***$_3$)$_3$), -0.12 (9H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 175.5 (***C***O), 153.8 (***C***-6), 103.8 (***C***-5), 60.4 (O***C***H$_2$CH$_3$), 35.4 (***C***-3), 33.3 (***C***-4), 29.3 (***C***H$_2$CH$_3$), 23.5 (***C***H$_3$), 14.7 (OCH$_2$***C***H$_3$), 11.6 (CH$_2$***C***H$_3$), 2.1 (CSi(***C***H$_3$)$_3$), 0.4 (CSi(***C***H$_3$)$_3$), 0.2 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) 4.6, 2.0, -14.89, -14.91; m/z (ASAP) 431 ([M+H]$^{+\cdot}$, 100%); HRMS (ASAP) found [M+H]$^{+\cdot}$ 431.2272, $C_{19}H_{43}O_3Si_4$ requires [M+H]$^{+\cdot}$ 431.2289.

Ethyl 5-oxo-3,5-diphenylpentanoate[134] 412



To a solution of methyl ethyl 4,6-diphenyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2*H*-1,2-oxasiline-3-carboxylate (0.13 g, 0.24 mmol) in dry dichloromethane (4.0 ml) was added triethylamine trihydrofluoride complex (0.08 ml, 0.49 mmol). The mixture was stirred at room temperature for 3 days after which time saturated sodium bicarbonate solution (4.0 ml) was added. The aqueous layer was separated and extracted with DCM (3 x 5 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica, elution gradient 0 to 50% diethyl ether in hexane, afforded the product as a white solid (56.4 mg, 78%). Mp: 60.8-61.5 ^oC; R_f 0.4 (pet. ether : diethyl ether 1:1); IR (ATR) 3045, 2978, 1723, 1675, 1594, 1447, 1365, 1270, 1209, 1148, 1080, 1035, 984, 949, 852, 745 cm^{-1}; δ_H (700 MHz) 7.92-7.91 (2H, m, 5-Ar-2,6-***H***), 7.55-7.53 (1H, m, 5-Ar-4-***H***), 7.44-7.42 (1H, m, 5-Ar-3,5-***H***), 7.29-7.26 (4H, m, 3-Ar-2,3,5,6-***H***), 7.20-7.18 (1H, m, 3-Ar-4-***H***), 4.04 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 4.02 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 3.88 (1H, dq, *J* = 7.7Hz, *J* = 7.0Hz, 3-***H***), 3.39 (1H, dd, *J* = 16.8Hz, *J* = 7.0Hz, 4-***H***), 3.34 (1H, dd, *J* = 16.8Hz, *J* = 7.0Hz, 4-***H***), 2.80 (1H, dd, *J* = 15.4Hz, *J* = 7.0Hz, 2-***H***), 2.68 (1H, dd, *J* = 15.4Hz, *J* = 7.7Hz, 2-***H***), 1.33 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$); δ_C (175 MHz) 198.2 (***C***-5), 171.8 (***C***-1), 143.3 (3-Ar-***C***-1), 136.9 (5-Ar-***C***-1), 133.1 (5-Ar-***C***-4), 128.57 (5-Ar-***C***-3,5), 128.56 (3-Ar-***C***-3,5), 128.1 (5-Ar-***C***-2,6), 127.4 (3-Ar-***C***-2,6), 126.8 (3-Ar-***C***-4), 60.4 (***C***H$_2$CH$_3$), 44.6 (***C***-4), 40.8 (***C***-2), 37.6 (***C***-3), 14.1 (CH$_2$***C***H$_3$); m/z (EI) 296 ([M]$^{+\cdot}$, 14%), 251 ([M-OEt]$^{+\cdot}$, 14), 222 (35), 209 (53), 194 (16), 131 (47), 105 (100), 91 (16), 77 (58), 51 (20), 29 (22).

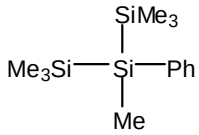
Ethyl 5-oxo-3,5-diphenyl-2-(trimethylsilyl)pentanoate[135] 413



To a solution of methyl ethyl 4,6-diphenyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2*H*-1,2-oxasiline-3-carboxylate (0.11 g, 0.21 mmol) in dry dichloromethane (4.0 ml) was added potassium hydrofluoride (0.02 g, 0.21 mmol) and trifluoroacetic acid (0.08 ml, 1.03 mmol). The mixture was stirred at room temperature for 17 h after which time saturated sodium bicarbonate solution (4.0 ml) was added. The aqueous layer was separated and extracted with

DCM (3 x 5 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica, elution gradient 0 to 50% diethyl ether in hexane, afforded the product as a white solid (69.7 mg, ds 1:1, 92%). Mp: 36.7-72.3 ^oC; R_f 0.5 (pet. ether : diethyl ether 1:1); IR (ATR) 2955, 2901, 1707, 1686, 1597, 1449, 1362, 1325, 1250, 1179, 1138, 1027, 985, 913, 841, 744 cm^{-1}; δ_H (700 MHz) 7.85-7.84 (2H, m, 5-Ar-2,6-***H***), 7.78-7.77 (2H, m, 5-Ar-2,6-***H***), 7.52-7.49 (2H, m, 5-Ar-4-***H***), 7.42-7.37 (2H, m, 5-Ar-3,5-***H***), 7.29-7.28 (2H, m, 3-Ar-2,6-***H***), 7.23-7.21 (2H, m, 3-Ar-2,3,5,6-***H***), 7.20-7.17 (2H, m, 3-Ar-3,5-***H***), 7.16-7.14 (1H, m, 3-Ar-4-***H***), 7.10-7.08 (1H, m, 3-Ar-4-***H***), 4.22 (1H, dq, *J* = 10.5Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 4.15 (1H, dq, *J* = 10.5Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 3.93-3.88 (2H, m, 3-***H***), 3.86 (1H, dq, *J* = 10.5Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 3.80 (1H, dq, *J* = 10.5Hz, *J* = 7.0Hz, C***H***$_2$CH$_3$), 3.43 (1H, dd, *J* = 15.8Hz, *J* = 10.5Hz, 4-***H***), 3.41 (1H, dd, *J* = 15.8Hz, *J* = 10.5Hz, 4-***H***), 3.28 (1H, dd, *J* = 15.8Hz, *J* = 3.5Hz, 4-***H***), 3.26 (1H, dd, *J* = 15.8Hz, *J* = 3.5Hz, 4-***H***), 2.64 (1H, d, *J* = 10.5Hz, 2-***H***), 2.54 (1H, d, *J* = 11.2Hz, 2-***H***), 1.31 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$), 0.98 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$), 0.20 (9H, s, Si(C***H***$_3$)$_3$), -0.19 (9H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 198.4 (***C***-5), 198.2 (***C***-5), 174.7 (***C***-1), 173.6 (***C***-1), 143.9 (3-Ar-***C***-1), 142.2 (3-Ar-***C***-1), 137.2 (5-Ar-***C***-1), 137.0 (5-Ar-***C***-1), 132.9 (5-Ar-***C***-4), 132.8 (5-Ar-***C***-4), 128.47 (Ar), 128.45 (Ar), 128.43 (Ar), 128.40 (Ar), 128.1 (5-Ar-***C***-2,6), 128.03 (Ar), 128.02 (Ar), 127.9 (5-Ar-***C***-2,6), 127.0 (3-Ar-***C***-4), 126.4 (3-Ar-***C***-4), 60.1 (***C***H$_2$CH$_3$), 59.6 (***C***H$_2$CH$_3$), 46.5 (***C***-4), 44.8 (***C***-2), 44.6 (***C***-4), 44.4 (***C***-2), 40.9 (***C***-3), 40.5 (***C***-3), 14.4 (CH$_2$***C***H$_3$), 14.1 (CH$_2$***C***H$_3$), -1.2 (Si(***C***H$_3$)$_3$), -2.1 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) 4.8, 3.9; m/z (EI) 368 ($[M]^{+\cdot}$, 11%), 340 ($[M\text{-}C_2H_4]^{+\cdot}$, 11), 322 ($[M\text{-EtOH}]^{+\cdot}$, 17), 307 (19), 281 (70), 263 (74), 131 (100), 105 (68), 77 ($[Ph]^{+\cdot}$, 36), 73 ($[EtOCO]^{+\cdot}$, 52), 45 ($[EtO]^{+\cdot}$, 11).

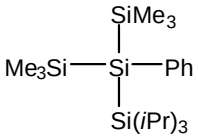
Methylphenylbis(trimethylsilyl)silane[136] **418**



Phenyltris(trimethylsilyl)silane (4.03 g, 12.4 mmol) and dry potassium *tert*-butoxide (1.53 g, 13.7 mmol) were dissolved in THF (30 ml). The solution was stirred for 6 h at room temperature. The orange solution was then added dropwise via cannula (over a 10 min period) to a cooled (-78 ^oC) solution of methyl iodide (0.93 ml, 14.9 mmol) in THF (30 ml). The mixture was stirred at room temperature for 3 h after which time ammonium chloride solution (50 ml) was added. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 x 30 ml). The combined organic layers were dried over $MgSO_4$, filtered and

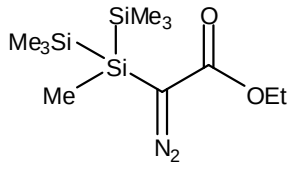
concentrated. Flash column chromatography (pet. ether) gave the title compound as a white semi solid material (1.53 g, 46%). R_f 0.5 (pet. ether); IR (ATR) 2948, 2891, 1427, 1396, 1244, 1096, 830, 777, 739, 728 cm^{-1}; δ_H (700 MHz) 7.41-7.40 (2H, m, Ar-2,6-***H***), 7.32-7.28 (3H, m, Ar-3,4,5-***H***), 0.39 (3H, s, C***H***$_3$), 0.13 (18H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 137.7 (Ar-***C***-1), 134.5 (Ar-***C***-2,6), 127.68 (Ar-***C***-4), 127.66 (Ar-***C***-3,5), -1.1 (Si(***C***H$_3$)$_3$), -9.0 (***C***H$_3$); δ_{Si} (139 MHz) -15.9 (***Si***(CH$_3$)$_3$), -46.3 (Ar-***Si***); m/z (EI) 266 ($[M]^{+\cdot}$, 36%), 251 ($[M\text{-}CH_3]^{+\cdot}$, 15), 193 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 100), 177 (29), 163 (28), 135 (96), 116 (50), 105 (16), 73 (88), 45 (26), 43 (17).

1-Phenyl-1-(triisopropylsilyl)-1,1-(trimethylsilyl)silane 419



Phenyltris(trimethylsilyl)silane (3.15 g, 9.69 mmol) and dry potassium *tert*-butoxide (1.14 g, 10.17 mmol) were dissolved in THF (25.0 ml). The solution was stirred for 3 h at room temperature. The orange solution was then added dropwise via cannula (over a 10 min period) to a cooled (-78 ^oC) solution of chlorotriisopropylsilane (2.46 ml, 11.62 mmol) in THF (20 ml). The mixture was stirred at room temperature for 1 h after which time ammonium chloride solution (30 ml) was added. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 x 20 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica (pet. ether) afforded the product as a white solid (3.21 g, 81%). Mp: 207.8–209.3 ^oC; R_f 0.5 (hexane); IR (ATR) 2944, 2863, 1461, 1243, 1063, 994, 828, 734 cm^{-1}; δ_H (700 MHz) 7.55-7.53 (2H, m, Ar-3,5-***H***), 7.24-7.22 (3H, m, Ar-2,4,6-***H***), 1.23 (3H, sep, *J* = 7.7Hz, C***H***(CH$_3$)$_2$), 1.08 (18H, d, *J* = 7.7Hz, CH(C***H***$_3$)$_2$), 0.30 (18H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 137.5 (Ar-***C***-2,6), 136.7 (Ar-***C***-1), 127.4 (Ar-***C***-3,5), 127.2 (Ar-***C***-4), 20.1 (CH(***C***H$_3$)$_2$), 13.8 (***C***H(CH$_3$)$_2$), 2.5 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) 7.5, -12.5, -75.7; m/z (EI) 408 ($[M]^{+\cdot}$, 6%), 393 ($[M\text{-}CH_3]^{+\cdot}$, 3), 281 (29), 258 (63), 236 (96), 221 (41), 209 (29), 191 (28), 177 (89), 162 (91), 157 (85), 145 (19), 135 (85), 129 (38), 115 (98), 101 (40), 87 (82), 73 (100), 59 (87), 45 (34); HRMS (ASAP) found $[M+NH_4]^{+\cdot}$ 426.2851, $C_{21}H_{48}NSi_4$ requires $[M+NH_4]^{+\cdot}$ 426.2858.

Ethyl 2-diazo-2-(1,1,1,2,3,3,3-heptamethyltrisilan-2-yl)acetate 416



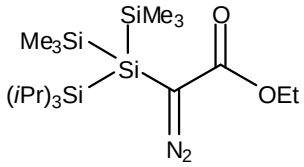
Stage1

To a solution of methylphenylbis(trimethylsilyl)silane (1.29 g, 4.85 mmol) in DCM (15.0 ml), under argon at 0 ^{o}C, was added dropwise triflic acid (0.43 ml, 4.85 mmol). The reaction mixture was stirred for 20 min and then warmed to room temperature. The reaction mixture was stirred for a further 40 min after which time solvent was evaporated directly using a vacuum manifold to yield methylphenyl(trimethylsilyl)silyl trifluoromethanesulfonate **420** as a white solid (1.64 g, ~100%) which was used immediately in *stage* 2 without purification.

Stage 2

Ethyldiisopropylamine (0.93 ml, 5.33 mmol) followed by methylphenyl(trimethylsilyl)silyl trifluoromethanesulfonate (1.64 g, 4.85 mmol) in diethyl ether (15 ml) were added at -78^{o}C to a solution of ethyl 2-diazoacetate (0.51 ml, 4.85 mmol) in diethyl ether (15 ml). The reaction mixture was allowed to warm up to room temperature, and stirred for 24 h. The reaction was then quenched by addition of a saturated $NaHCO_3$ solution (25 ml). The aqueous layer was separated and extracted with Et_2O (3 x 20 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica, elution gradient 0 to 10% diethyl ether in hexane, afforded the product as a yellow oil (0.99 g, 67%). R_f 0.5 (hexane : diethyl ether 95:5); IR (ATR) 2949, 2895, 2075, 1681, 1445, 1396, 1365, 1257, 1242, 1201, 1177, 1095, 1066, 833, 779, 739 cm^{-1}; δ_H (700 MHz) 4.20 (2H, q, *J* = 7.0Hz, C***H***$_2$CH$_3$), 1.28 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$), 0.26 (3H, s, C***H***$_3$), 0.17 (18H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 169.7 (***C***O), 68.1 (***C***-2), 60.7 (***C***H$_2$CH$_3$), 14.6 (CH$_2$***C***H$_3$), -1.2 (Si(***C***H$_3$)$_3$), -8.7 (***C***H$_3$); δ_{Si} (140 MHz) -14.3, -46.5; m/z (EI) 259 ([M-N$_2$-Me]$^{+\cdot}$, 11%), 245 ([M-COEt]$^{+\cdot}$, 49), 231 (16), 229 ([M-Si(CH$_3$)$_3$]$^{+\cdot}$, 8), 215 (35), 201 (36), 173 (58), 157 (66), 147 (15), 133 (27), 117 (28), 97 (53), 83 (23), 73 (100), 59 (37), 45 (47); HRMS (ES+) found [M+Na]$^{+\cdot}$ 325.1198, $C_{11}H_{26}O_2N_2NaSi_3$ requires [M+Na]$^{+\cdot}$ 325.1194.

Ethyl 2-diazo-2-(1,1,1-triisopropyl-3,3,3-trimethyl-2-(trimethylsilyl)trisilan-2-yl)acetate 417



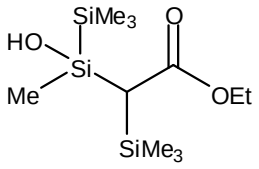
Stage1

To a solution of 1-phenyl-1-(triisopropylsilyl)-1,1-(trimethylsilyl)silane (1.50 g, 3.67 mmol) in DCM (15.0 ml), under argon at 0 ^{o}C, was added dropwise triflic acid (0.33 ml, 3.67 mmol). The reaction mixture was stirred at 0 ^{o}C for 1 h. The solvent was evaporated in *vacuo* to yield 1,1,1-triisopropyl-3,3,3-trimethyl-2-(trimethylsilyl)trisilan-2-yl trifluoromethanesulfonate **421** as a white solid (1.78 g) which was used immediately in *stage* 2 without purification.

Stage2

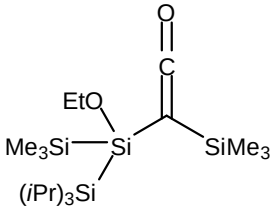
To a solution of ethyl 2-diazoacetate (0.37 ml, 3.66 mmol) in dry Et_2O (15.0 ml) at -78^{o}C were added DIPEA (0.70 ml, 4.03 mmol) fallowed by a solution of 1,1,1-triisopropyl-3,3,3-trimethyl-2-(trimethylsilyl)trisilan-2-yl trifluoromethanesulfonate (0.62g, 25.8 mmol) in Et_2O (15.0 ml). The reaction mixture was allowed to reach room temperature and stirred for 24 hours. The reaction was then quenched by addition of a saturated sodium bicarbonate solution (20 ml). The aqueous layer was separated and extracted with Et_2O (3 x 20 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica, elution gradient 0 to 10% diethyl ether in hexane, afforded the product as a yellow grease (0.88 g, 54%). R_f 0.6 (pet. ether : diethyl ether 9:1); IR (ATR) 2945, 2865, 2069, 1683, 1461, 1366, 1246, 1193, 1095, 1061, 997, 830, 739cm^{-1}; δ_H (700 MHz) 4.19 (2H, q, *J* = 7.0Hz, C***H***$_2$CH$_3$), 1.28 (3H, sep, *J* = 7.0Hz, C***H***(CH$_3$)$_2$), 1.27 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$), 1.14 (18H, d, *J* = 7.0Hz, CH(C***H***$_3$)$_2$), 0.28 (18H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 170.0 (***C***O), 60.9 (***C***H$_2$CH$_3$), 39.6 (***C***-2), 20.0 (CH(***C***H$_3$)$_2$), 14.7 (CH$_2$***C***H$_3$), 13.7 (***C***H(CH$_3$)$_2$), 2.1 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) 9.2, -10.7, -80.1; m/z (EI) 416 ([M-N$_2$]$^{+\cdot}$, 3%), 401 ([M-N$_2$-Me]$^{+\cdot}$, 20), 387 ([M-COEt]$^{+\cdot}$, 11), 343 ([M-N$_2$-SiMe$_3$]$^{+\cdot}$, 47), 303 (15), 259 (66), 230 (39), 215 (82), 201 (47), 191 (39), 171 (22), 157 (53), 147 (26), 133 (32), 115 (54), 103 (33), 87 (58), 73 (100), 59 (84), 45 (55).

Ethyl 2-(1-hydroxy-1,2,2,2-tetramethyldisilyl)-2-(trimethylsilyl)acetate 422



To a solution of $Rh_2(pfb)_4$ (17.7 mg, 0.017 mmol) in toluene (10.0 ml) was added dropwise a solution of ethyl 2-diazo-2-(1,1,1,2,3,3,3-heptamethyltrisilan-2-yl)acetate (0.10 g, 0.34 mmol) in toluene (10.0 ml). The solution was stirred for 1 h at room temperature after which time water (10 ml) was added. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 x 5 ml). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash column chromatography on silica, elution gradient 0 to 50% diethyl ether in hexane, afforded the product as a colourless oil (47.7 mg, ds 1.3:1, 49%). R_f 0.4 (pet. ether : diethyl ether 7:3); IR (ATR) 3438, 2953, 2895, 1670, 1365, 1247, 1169, 1107, 1038, 832, 777, 737 cm^{-1}; δ_H (700 MHz) 4.09 (2H, q, *J* = 7.0Hz, C***H***$_2$CH$_3$), 1.89 (1H, s, 2-***H***), 1.26 (1H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$), 0.35 (3H, s, C***H***$_3$), 0.18 (9H, s, Si(C***H***$_3$)$_3$), 0.14 (9H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 173.7 (***C***O), 60.0 (***C***H$_2$CH$_3$), 32.6 (***C***-2), 14.5 (CH$_2$***C***H$_3$), 0.0 (Si(***C***H$_3$)$_3$), -2.2 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) 11.6, 3.3, -21.1; m/z (EI) 292 ($[M]^{+\cdot}$, 0.1%), 277 ($[M\text{-}CH_3]^{+\cdot}$, 2), 221 (34), 219 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 59), 191 (33), 177 (48), 173 (26), 149 (91), 133 (100), 117 (41), 103 (24), 99 (17), 75 (41), 73 (96), 45 (20); HRMS (ES+) found $[M+H]^{+\cdot}$ 293.1421, $C_{11}H_{29}O_3Si_3$ requires $[M+H]^{+\cdot}$ 293.1419.

2-(2-Ethoxy-1,1,1,3,3,3-hexamethyltrisilan-2-yl)-2-(triisopropylsilyl)ethenone 423



A solution of ethyl 2-diazo-2-(1,1,1-triisopropyl-3,3,3-trimethyl-2-(trimethylsilyl)trisilan-2-yl)acetate (0.11 g, 0.25 mmol) in dry toluene (3.0 ml) was heated at 110 ^oC for 4 days. Concentration, followed by flash column chromatography on silica (hexane) afforded the product as a colourless semisolid (49.0 mg, 47%). IR (ATR) 2946, 2865, 2069, 1461, 1386, 1247, 1076, 1102, 939, 881, 833, 753, 723 cm^{-1}; δ_H (700 MHz) 3.68 (2H, q, *J* = 7.0Hz, C***H***$_2$CH$_3$), 1.30 (3H, sep, *J* = 7.0Hz, C***H***(CH$_3$)$_2$), 1.19 (3H, t, *J* = 7.0Hz, CH$_2$C***H***$_3$), 1.17 (18H, d, *J* = 7.0Hz, CH(C***H***$_3$)$_2$), 0.27 (9H, s, Si(C***H***$_3$)$_3$), 0.25 (9H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 163.2 (***C***O), 61.3 (***C***H$_2$CH$_3$), 20.0 (CH(***C***H$_3$)$_2$), 18.5 (CH$_2$***C***H$_3$), 12.4 (***C***H(CH$_3$)$_2$), 11.8 (***C***CO), 1.8

($Si(\boldsymbol{C}H_3)_3$), 0.2 ($Si(\boldsymbol{C}H_3)_3$); δ_{Si} (140 MHz) 9.3, 1.0, -0.6, -17.4; m/z (EI) 416 ($[M]^{+\cdot}$, 0.1%), 401 ($[M\text{-}CH_3]^{+\cdot}$, 1), 387 ($[M\text{-}CH_2CH_3]^{+\cdot}$, 5), 343 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 20), 259 (39), 230 (17), 215 (84), 201 (26), 191 (17), 157 (22), 133 (12), 115 (25), 103 (15), 87 (26), 73 (100), 59 (79), 45 (27).

Standard procedure for the Mitsunobu reaction (A)[114]

THF was added in one portion to triphenylphosphine, and alcohols at 25 ^{o}C under argon. The reaction vessel was then sonicated for a few minutes (approx. 5 min) giving a homogenous solution. To the sonicated reaction mixture azodicarboxylate ester was added dropwise over the course of 5-15 min. The reaction mixture was sonicated for 15 min and subsequently triturated with hexane to remove the majority of the triphenylphosphine. Flash column chromatography on silica, elution gradient 0 to 30% ethyl acetate in pet. ether, afforded the desired product.

Standard ester hydrolysis procedure (B)

To a solution of ester in THF was added a solution of lithium hydroxide (2 eq) in water. The reaction mixture was stirred at 50 ^{o}C for 30 h. The reaction was then quenched by addition of HCl (5 M, pH = 1) and diluted with Et_2O. The aqueous layer was separated and extracted three times with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash column chromatography on silica, elution gradient 0 to 50% ethyl acetate in pet. ether, afforded the desired carboxylic acid.

Standard procedure for acylpolysilane synthesis (C)

Stage 1

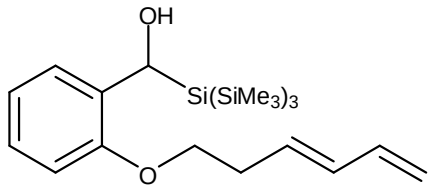
Tetrakis(trimethylsilyl)silane and dry potassium *tert*-butoxide were dissolved in THF and stirred for 3 h at room temperature. The resulting solution was used in *Stage 2*.

Stage 2

A solution of carboxylic acid in DCM was treated with oxalyl chloride and DMF (one drop) at 0 ^{o}C. The reaction mixture was stirred at that temperature for 3 h after which time volatiles were evaporated *in vacuo*. The residue was redissolved in THF and treated with

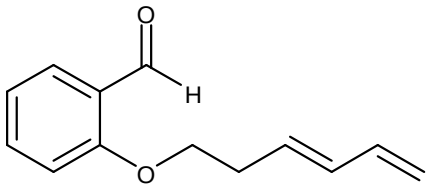
silylpotassium (*Stage 1*) at -78 ^{o}C. After stirring for 3 h at -78 ^{o}C saturated ammonium chloride solution was added. The organic layer was separated, and the aqueous layer was extracted three times with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash column chromatography, elution gradient 0 to 20% diethyl ether in pet. ether, afforded the desired product.

(*E*)-(2-(Hexa-3',5'-dienyloxy)phenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methanol 433



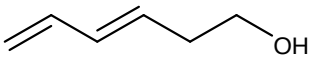
To a suspension of $LiAlH_4$ (0.029 g, 0.76 mmol) in diethyl ether (4.0 ml) was added a solution of (*E*)-(2-(hexa-3,5-dienyloxy)phenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methanone (0.34 g, 0.76 mmol) in diethyl ether (3.0 ml) at 0 °C, over a period of 3 minutes under nitrogen. The resulting suspension was stirred at RT for 1 h. The reaction mixture was quenched sequentially with H_2O (0.5 ml), NaOH (1M, 0.5 ml) and H_2O (0.5 ml). The mixture was then filtered through Celite®, the precipitate washed with EtOAc and the combined filtrate concentrated *in vacuo*. Flash column chromatography on silica, elution gradient 0 to 10% diethyl ether in hexane, afforded the product as a colourless oil (0.22 g, 65%). R_f 0.5 (pet. ether : diethyl ether 9:1); IR (ATR) 3428, 2946, 2891, 1597, 1487, 1471, 1451, 1232, 1161, 1048, 1029, 1001, 951, 827, 745 cm^{-1}; δ_H (700 MHz) 7.42-7.41 (1H, m, Ar-6-***H***), 7.14-7.11 (1H, m, Ar-4-***H***), 6.97-6.95 (1H, m, Ar-5-***H***), 6.79-6.78 (1H, m, Ar-3-***H***), 6.34 (1H, dt, *J* = 16.8Hz, *J* = 10.5Hz, 5'-***H***), 6.19 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.76 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.47 (1H, d, *J* = 4.2Hz, C***H***OH), 5.16 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.04 (1H, d, *J* = 10.5Hz, 6'-***H***), 4.10 (1H, dt, *J* = 9.1Hz, *J* = 7.0Hz, 1'-***H***), 3.97 (1H, dt, *J* = 9.1Hz, *J* = 7.0Hz, 1'-***H***), 2.63 (1H, dq, *J* = 14.0Hz, *J* = 7.0Hz, 2'-***H***), 2.59 (1H, dq, *J* = 14.0Hz, *J* = 7.0Hz, 2'-***H***), 1.81 (1H, d, *J* = 4.2Hz, O***H***), 0.15 (27H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 153.7 (***C***-2), 136.8 (***C***-5'), 135.8 (***C***-1), 133.5 (***C***-4'), 130.0 (***C***-3'), 127.7 (**C**-6), 126.8 (***C***-4), 120.9 (***C***-5), 116.1 (**C**-6'), 111.2 (***C***-3), 67.3 (**C**-1'), 62.1 (***C***HOH), 32.5 (**C**-2'), 1.5 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) -12.8, -68.0; m/z compound decomposes under all forms of ionisation.

(*E*)-2-(Hexa-3',5'-dienyloxy)benzaldehyde 434



Following standard procedure **A** (page 192), a solution of triphenylphosphine (0.65 g, 2.51 mmol), (*E*)-hexa-3,5-dien-1-ol (0.21 g, 2.09 mmol) and 2-hydroxybenzaldehyde (0.26 g, 2.09 mmol) in THF (1.0 ml) was treated with diisopropyl azodicarboxylate (0.49 ml, 2.51 mmol) to give the title compound as a colourless liquid (59.6 mg, 13%). R_f 0.4 (pet. ether : ethyl acetate 9:1); IR (ATR) 2942, 2862, 1685, 1597, 1485, 1456, 1382, 1285, 1238, 1188, 1160, 1102, 1041, 1003, 951, 901, 837, 755 cm^{-1}; δ_H (700 MHz) 10.51(1H, s, C***H***O), 7.85-7.84 (1H, m, 6-***H***), 7.55-7.53 (1H, m, 4-***H***), 7.04-7.02 (1H, m, 5-***H***), 6.99-6.97 (1H, m, 3-***H***), 6.34 (1H, dt, *J* = 17.5Hz, *J* = 9.8Hz, 5'-***H***), 6.21 (1H, dd, *J* = 16.1Hz, *J* = 9.8Hz, 4'-***H***), 5.79 (1H, dt, *J* = 16.1Hz, *J* = 7.0Hz, 3'-***H***), 5.17 (1H, d, *J* = 17.5Hz, 6'-***H***), 5.02 (1H, d, *J* = 9.8Hz, 6'-***H***), 4.14 (2H, t, *J* = 7.0Hz, 1'-***H***), 2.65 (2H, q, *J* = 7.0Hz, 2'-***H***); δ_C (175 MHz) 189.8 (***C***HO), 161.2 (***C***-2), 136.6 (***C***-5'), 135.9 (***C***-4), 133.7 (***C***-4'), 129.5 (***C***-3'), 128.3 (**C**-6), 125.0 (***C***-1), 120.7 (***C***-5), 116.4 (**C**-6'), 112.5 (***C***-3), 67.8 (***C***-1'), 32.3 (***C***-2'); m/z (EI) 202 ($[M]^{+\cdot}$, 0.5%), 174 ($[M\text{-}CO]^{+\cdot}$, 2), 135 (40), 81 (32), 80 (100), 77 (46), 65 (16), 53 (25), 51 (17), 41 (28), 39 (24), 27 (10); HRMS (EI) found $[M]^{+\cdot}$ 202.0986, $C_{13}H_{14}O_2$ requires $[M]^{+\cdot}$ 202.0988.

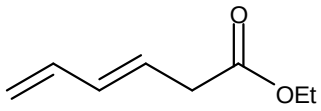
(*E*)-Hexa-3,5-dien-1-ol[112] 436



To a suspension of $LiAlH_4$ (3.69 g, 97.2 mmol) in diethyl ether (300 ml) was added a solution of (*E*)-ethyl hexa-3,5-dienoate (13.62 g, 97.2 mmol) in diethyl ether (50 ml) at 0 °C, over a period of 15 minutes under nitrogen. The resulting suspension was stirred at RT for 12 h. The reaction mixture was cooled with an ice bath and cautiously quenched sequentially with H_2O (4.0 ml), NaOH (1M, 4.0 ml) and H_2O (8.0 ml). The suspension was then filtered through Celite®. The residue was washed with EtOAc and then the combined filtrate concentrated *in vacuo*. Flash column chromatography on silica, elution gradient 0 to 50% ethyl acetate in hexane, afforded the product as a colourless liquid (7.2 g, 76%). R_f 0.4 (pet. ether : ethyl acetate 7:3); IR (ATR) 3326, 2936, 2886, 1654, 1603, 1415, 1042, 1001, 951, 897, 840 cm^{-1}; δ_H (400 MHz) 6.33 (1H, ddd, *J* = 16.8Hz, *J* = 10.4Hz, *J* = 10.1Hz, 5-***H***), 6.16 (1H, dd, *J* = 15.2Hz, *J* = 10.4Hz, 4-***H***), 5.69 (1H, dt, *J* = 15.2Hz, *J* = 7.2Hz, 3-***H***), 5.14 (1H, d, *J* = 16.8Hz, 6-***H***), 5.02 (1H, d, *J* = 10.1Hz, 6-***H***), 3.69 (2H, dt, *J* = 6.2Hz, *J* = 5.8Hz , 1-***H***), 2.37 (2H, dt, *J*

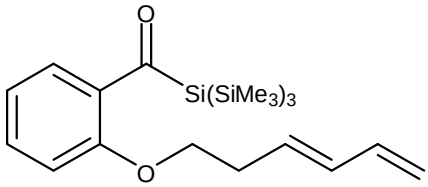
= 7.2Hz, *J* = 6.2Hz, 2-***H***), 1.29 (1H, t, *J* = 5.8Hz, O***H***); δ_C (100 MHz) 136.8 (**C**-5), 133.8 (***C***-4), 130.5 (**C**-3), 115.9 (***C***-6), 61.9 (***C***-1), 35.9 (***C***-2); m/z (EI) 98 ($[M]^{+\cdot}$, 35%), 80 ($[M\text{-}H_2O]^{+\cdot}$, 10), 67 ($[M\text{-}CH_2OH]^{+\cdot}$, 100), 53 ($[M\text{-}CH_2CH_2OH]^{+\cdot}$, 15), 41 (42).

(*E*)-Ethyl hexa-3,5-dienoate[112] 437



A solution of *n*-butyllithium (134 ml, 214.01 mmol) in hexane was added to a stirred solution of diisopropylamine (30.2 ml, 214.01 mmol) in THF (400 ml) at -78 °C, over a period of 15 minutes under nitrogen. The resulting solution was stirred at -78 °C for 1 h prior to the addition of DMPU (21.50 ml, 178.34 mmol). A room temperature solution of (2*E*,4*E*)-ethyl hexa-2,4-dienoate (27.0 ml, 178.34 mmol) in THF (50 ml) was slowly added to the yellow solution of LDA via cannula. The reaction was stirred at -78 °C for 1 h after which time EtOH (80ml) was added and the mixture was stirred for 5 min. The reaction mixture was poured onto water (200 ml) and EtOAc (100ml). The layers were separated and the aqueous layer was extracted with Et2O (2 x 200ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Distillation gave the title compound as a colourless liquid (14.66 g, 58.6 %). B.p 45 ^oC/10 mbar (lit.[112] 45 ^oC/0.7 mmHg); IR (ATR) 2980, 1732, 1603, 1407, 1368, 1335, 1243, 1177, 1139, 1097, 1025, 1003, 953, 902, 857 cm^{-1}; δ_H (700 MHz) 6.33 (1H, ddd, *J* = 17.0Hz, *J* = 10.4Hz, *J* = 10.2Hz, 5-***H***), 6.14 (1H, dd, *J* = 15.3Hz, *J* = 10.4Hz, 4-***H***), 5.79 (1H, dt, *J* = 15.3Hz, *J* = 7.2Hz, 3-***H***), 5.16 (1H, d, *J* = 17.0Hz, 6-***H***), 5.06 (1H, d, *J* = 10.2Hz, 6-***H***), 4.15 (2H, q, *J* = 7.1Hz, C***H***$_2$CH$_3$), 3.11 (2H, d, *J* = 7.2Hz, 2-***H***), 1.26 (3H, t, *J* = 7.1Hz, CH$_2$C***H***$_3$); δ_C (175 MHz) 171.4 (***C***-1), 136.4 (**C**-5), 134.3 (***C***-4), 125.7 (**C**-3), 116.8 (***C***-6), 60.7 (***C***H$_2$CH$_3$), 38.0 (***C***-2), 14.2 (CH$_2$***C***H$_3$); m/z (EI) 140 ($[M]^{+\cdot}$, 76%), 98 (19), 81 (12), 67 ($[M\text{-}CO_2Et]^{+\cdot}$, 100), 54 (22), 41(58).

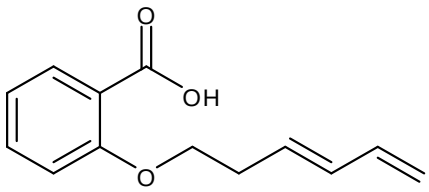
(*E*)-(2-(Hexa-3,5-dienyloxy)phenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methanone 446



Following standard procedure **C** (page 192), a solution of (*E*)-2-(hexa-3,5-dienyloxy)benzoic acid (2.02 g, 9.24 mmol) in DCM (32.0 ml) was treated with oxalyl chloride (1.03 ml, 12.0

mmol) and DMF (1 drop). The resulting acid chloride was redissolved in THF (32.0 ml) and treated with a solution of silylpotassium **221** in THF (32.0 ml), which was prepared from tetrakis(trimethylsilyl)silane (2.96g, 9.24 mmol) and potassium *tert*-butoxide (1.09g, 9.70 mmol). Flash column chromatography afforded the product as a yellow oil (2.20 g, 53%). R_f 0.5 (pet. ether : diethyl ether 9:1); IR (ATR) 2947, 2891, 1611, 1591, 1484, 1465, 1439, 1393, 1280, 1241, 1188, 1106, 1041, 1020, 999, 950, 895, 828, 747 cm^{-1}; δ_H (700 MHz) 7.29-7.26 (1H, m, 4-***H***), 7.01-7.00 (1H, m, 6-***H***), 6.97-6.94 (1H, m, 5-***H***), 6.88-6.87 (1H, m, 3-***H***), 6.32 (1H, dt, *J* = 17.5Hz, *J* = 10.5Hz, 5'-***H***), 6.15 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.73 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.15 (1H, d, *J* = 17.5Hz, 6'-***H***), 5.02 (1H, d, *J* = 10.5Hz, 6'-***H***), 3.99 (2H, t, *J* = 7.0Hz, 1'-***H***), 2.54 (2H, q, *J* = 7.0Hz, 2'-***H***), 0.19 (27H, s, $Si(C\boldsymbol{H}_3)_3$); δ_C (175 MHz) 241.6 (***C***O), 153.4 (***C***-2), 139.7 (***C***-1), 136.9 (***C***-5'), 133.3 (***C***-4'), 130.1 (***C***-4), 129.8 (**C**-3'), 125.6 (***C***-6), 120.2 (***C***-5), 115.9 (**C**-6'), 112.8 (***C***-3), 68.1 (**C**-1'), 32.3 (**C**-2'), 1.1 ($Si(\boldsymbol{C}H_3)_3$); δ_{Si} (140 MHz) -11.4, -70.4; m/z (EI) 448 ($[M]^{+\cdot}$, 0.2%), 375 ($[M-Si(CH_3)_3]^{+\cdot}$, 4), 147 (12), 73 (100); HRMS (EI) found $[M]^{+\cdot}$ 448.2096, $C_{22}H_{40}O_2Si_4$ requires $[M]^{+\cdot}$ 448.2100.

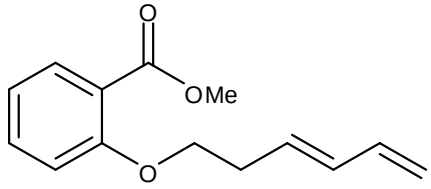
(*E*)-2-(Hexa-3,5-dienyloxy)benzoic acid 448



Following standard procedure **B** (page 192), a solution of (*E*)-methyl 2-(hexa-3,5-dienyloxy)benzoate (1.30 g, 5.58 mmol) in THF (30 ml) was treated with a solution lithium hydroxide (0.26 g, 11.2 mmol) in water (15 ml) to give the title compound as a white solid (0.95 g, 78%). Mp: 46.0–46.7 ^oC; R_f 0.4 (pet. ether : ethyl acetate 1:1); IR (ATR) 3248, 1726, 1602, 1581, 1488, 1473, 1455, 1399, 1355, 1296, 1237, 1217, 1161, 1123, 1040, 1001, 954, 930, 899, 834, 753, 728 cm^{-1}; δ_H (700 MHz) 10.82 (1H, s, $CO_2\boldsymbol{H}$), 8.21-8.20 (1H, m, 6-***H***), 7.57-7.55 (1H, m, 4-***H***), 7.16-7.14 (1H, m, 5-***H***), 7.05-7.04 (1H, m, 3-***H***), 6.34 (1H, ddd, *J* = 16.1Hz, *J* = 10.5Hz, *J* = 9.8Hz, 5'-***H***), 6.26 (1H, dd, *J* = 15.4Hz, *J* = 9.8Hz, 4'-***H***), 5.73 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.22 (1H, d, *J* = 16.1Hz, 6'-***H***), 5.10 (1H, d, *J* = 10.5Hz, 6'-***H***), 4.31 (2H, t, *J* = 7.0Hz , 1'-***H***), 2.72 (2H, q, *J* = 7.0Hz, 2'-***H***); δ_C (175 MHz) 165.2 ($\boldsymbol{C}O_2H$), 157.3 (***C***-2), 136.0 (***C***-5'), 134.94 (***C***-4), 134.90 (***C***-4'), 133.9 (***C***-6), 127.9 (**C**-3'), 122.3 (***C***-5), 117.8 (***C***-1), 117.4 (**C**-6'), 112.4 (***C***-3), 69.1 (C-1'), 32.3 (C-2'); m/z (ES-) 217

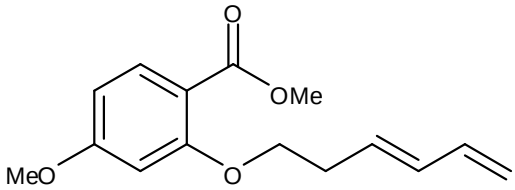
([M-H]$^-$, 15%), 137 (100); HRMS (ES-) found [M-H]$^-$ 217.0877, $C_{13}H_{13}O_3$ requires [M-H]$^-$ 217.0865.

(*E*)-methyl 2-(hexa-3,5-dienyloxy)benzoate 449



Following standard procedure **A** (page 192), a solution of triphenylphosphine (9.48 g, 36.2 mmol), (*E*)-hexa-3,5-dien-1-ol (2.96 g, 30.1 mmol) and methyl 2-hydroxybenzoate (3.91 ml, 30.1 mmol) in THF (10.0 ml) was treated with diisopropyl azodicarboxylate (7.12 ml, 36.2 mmol) to give the title compound as a colourless liquid (3.60 g, 52%). R_f 0.3 (pet. ether : ethyl acetate 7:3); IR (ATR) 2947, 1727, 1599, 1582, 1490, 1452, 1432, 1384, 1302, 1243, 1189, 1163, 1131, 1081, 1048, 1004, 953, 899, 836, 753, 704 cm^{-1}; δ_H (700 MHz) 7.79-7.78 (1H, m, 6-***H***), 7.45-7.43 (1H, m, 4-***H***), 6.99-6.97 (1H, m, 5-***H***), 6.96-6.96 (1H, m, 3-***H***), 6.35 (1H, dt, *J* = 16.8Hz, *J* = 10.5Hz, 5'-***H***), 6.20 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.83 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.16 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.03 (1H, d, *J* = 10.5Hz, 6'-***H***), 4.09 (2H, t, *J* = 7.0Hz, 1'-***H***), 3.89 (3H, s, C***H***$_3$), 2.63 (2H, q, *J* = 7.0Hz, 2'-***H***); δ_C (175 MHz) 167.0 (***C***O), 158.3 (***C***-2), 136.9 (***C***-5'), 133.33 (***C***-4), 133.27 (***C***-4'), 131.6 (***C***-6), 130.1 (**C**-3'), 120.7 (***C***-1), 120.3 (***C***-5), 115.9 (**C**-6'), 113.4 (***C***-3), 68.3 (C-1'), 51.9 (C***H***$_3$), 32.5 (C-2'); m/z (EI) 201 ([M-OCH$_3$]$^{+\cdot}$, 14%), 165 (49), 152 (52), 135 (44), 120 (52), 105 (14), 92 (46), 80 (100), 77 (57), 65 (30), 63 (23), 55 (16), 53 (49), 45 (49), 41 (44), 39 (37), 27 (23); HRMS (ES+) found [M+H]$^{+\cdot}$ 233.1175, $C_{14}H_{17}O_3$ requires [M+H]$^{+\cdot}$ 233.1172.

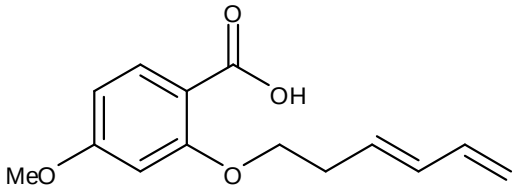
(*E*)-Methyl 2-(hexa-3',5'-dienyloxy)-4-methoxybenzoate 455



Following standard procedure **A** (page 192), a solution of triphenylphosphine (7.59 g, 28.9 mmol), (*E*)-hexa-3,5-dien-1-ol (2.37 g, 24.1 mmol) and methyl 2-hydroxy-4-methoxybenzoate (4.39 g, 24.1 mmol) in THF (8.0 ml) was treated with diethyl azodicarboxylate (4.56 ml, 28.9 mmol) to give the title compound as a colourless liquid (3.61 g, 57%). R_f 0.3 (pet. ether : ethyl acetate 4:1); IR (ATR) 2945, 1720, 1605, 1575, 1503, 1435,

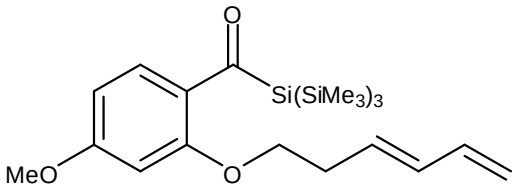
1384, 1249, 1200, 1167, 1136, 1087, 1029, 1007, 954, 904, 829, 768, 731 cm^{-1}; δ_H (700 MHz) 7.85-7.84 (1H, m, 6-***H***), 6.51-6.50 (1H, m, 5-***H***), 6.46-6.45 (1H, m, 3-***H***), 6.35 (1H, dt, *J* = 16.8Hz, *J* = 10.5Hz, 5'-***H***), 6.21 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.84 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.16 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.03 (1H, d, *J* = 10.5Hz, 6'-***H***), 4.06 (2H, t, *J* = 6.3Hz, 1'-***H***), 3.86 (3H, s, $CO_2C\boldsymbol{H}_3$), 3.84 (3H, s, $OC\boldsymbol{H}_3$), 2.64 (2H, dt, *J* = 7.0Hz, *J* = 6.3Hz, 2'-***H***); δ_C (175 MHz) 166.4 (***C***O), 164.1 (***C***-4), 160.5 (***C***-2), 136.9 (***C***-5'), 133.8 (***C***-6), 133.4 (**C**-4'), 130.1 (***C***-3'), 115.9 (***C***-6'), 112.8 (**C**-1), 104.9 (***C***-5), 100.1 (***C***-3), 68.4 (***C***-1'), 55.4 ($O\boldsymbol{C}H_3$), 51.6 ($CO_2\boldsymbol{C}H_3$), 32.4 (***C***-2'); m/z (ES+) 548 ($[2M+Na]^{+\cdot}$, 23%), 326 ($[M+Na+MeCN]^{+\cdot}$, 37), 285 ($[M+Na]^{+\cdot}$, 74), 263 ($[M+H]^{+\cdot}$, 100), 122 (61); HRMS (ES+) found $[M+H]^{+\cdot}$ 263.1281, $C_{15}H_{19}O_4$ requires $[M+H]^{+\cdot}$ 263.1283.

(*E*)-2-(Hexa-3,5-dienyloxy)-4-methoxybenzoic acid 456



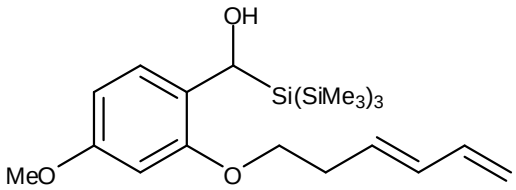
Following standard procedure **B** (page 192), a solution of methyl (*E*)-methyl 2-(hexa-3,5-dienyloxy)-4-methoxybenzoate (3.38 g, 12.9 mmol) in THF (60 ml) was treated with a solution lithium hydroxide (0.62g, 25.8 mmol) in water (30 ml) to give the title compound as a white solid (2.69 g, 84%). Mp: 69.3–70.1 ^oC; R_f 0.3 (pet. ether : ethyl acetate 1:1); IR (ATR) 3240, 2954, 2872, 1667, 1608, 1571, 1451, 1387, 1280, 1201, 1164, 1099, 1031, 996, 914, 825, 791 cm^{-1}; δ_H (700 MHz) 10.57 (1H, s, $CO_2\boldsymbol{H}$), 8.15-8.13 (1H, m, 6-***H***), 6.66-6.64 (1H, m, 5-***H***), 6.51-6.50 (1H, m, 3-***H***), 6.33 (1H, dt, *J* = 16.8Hz, *J* = 10.5Hz, 5'-***H***), 6.25 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.72 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.21 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.09 (1H, d, *J* = 10.5Hz, 6'-***H***), 4.26 (2H, t, *J* = 6.3Hz, 1'-***H***), 3.88 ($OC\boldsymbol{H}_3$), 2.70 (2H, dt, *J* = 7.0Hz, *J* = 6.3Hz, 2'-***H***); δ_C (175 MHz) 165.3 (***C***O), 165.2 (***C***-4), 158.9 (***C***-2), 136.2 (***C***-5'), 135.8 (***C***-6), 135.1 (**C**-4'), 128.1 (***C***-3'), 117.6 (***C***-6'), 110.8 (**C**-1), 106.9 (***C***-5), 99.6 (***C***-3), 69.2 (***C***-1'), 55.9 ($O\boldsymbol{C}H_3$), 32.4 (***C***-2'); m/z (ES+) 520 ($[2M+Na]^{+\cdot}$, 19%), 498 ($[2M]^{+\cdot}$, 26), 312 ($[M+Na+MeCN]^{+\cdot}$, 25), 271 ($[M+Na]^{+\cdot}$, 25), 249 ($[M+H]^{+\cdot}$, 100), 122 (38); HRMS (ES+) found $[M+H]^{+\cdot}$ 249.1123, $C_{14}H_{17}O_4$ requires $[M+H]^{+\cdot}$ 249.1127.

(*E*)-(2-(Hexa-3',5'-dienyloxy)-4-methoxyphenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)methanone 458



Following standard procedure **C** (page 192), a solution of (*E*)-2-(hexa-3,5-dienyloxy)-4-methoxybenzoic acid (2.16 g, 8.69 mmol) in DCM (40.0 ml) was treated with oxalyl chloride (1.43 ml, 11.3 mmol) and DMF (1 drop). The resulting acid was redissolved in THF (40.0 ml) and treated with a solution of silylpotassium **221** in THF (40.0 ml), which was prepared from tetrakis(trimethylsilyl)silane (2.79 g, 8.69 mmol) and potassium *tert*-butoxide (1.02 g, 9.11 mmol). Flash column chromatography afforded the product as a unstable yellow oil (2.11 g, 51%). R_f 0.3 (pet. ether : diethyl ether 9:1); IR (ATR) 2948, 2892, 1600, 1495, 1421, 1302, 1245, 1198, 1164, 1121, 1028, 1005, 949, 825, 734 cm^{-1}; δ_H (700 MHz) 7.18-7.17 (1H, m, Ar-6-***H***), 6.48-6.47 (1H, m, Ar-5-***H***), 6.42-6.41 (1H, m, Ar-3-***H***), 6.32 (1H, dt, *J* = 16.8Hz, *J* = 10.5Hz, 5'-***H***), 6.15 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.75 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.14 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.02 (1H, d, *J* = 10.5Hz, 6'-***H***), 3.98 (2H, t, *J* = 6.3Hz, 1'-***H***), 3.83 (3H, s, OC***H***$_3$), 2.55 (2H, dt, *J* = 7.0Hz, *J* = 6.3Hz, 2'-***H***), 0.21 (27H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 237.5 (***C***O), 162.1 (***C***-4), 155.7 (***C***-2), 136.9 (***C***-5'), 133.3 (***C***-4'), 131.9 (**C**-1), 130.2 (***C***-6), 129.9 (***C***-3'), 115.9 (**C**-6'), 103.8 (***C***-5), 100.2 (***C***-3), 68.2 (***C***-1'), 55.4 (O***C***H$_3$), 32.2 (***C***-2'), 1.3 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) -11.4, -70.2; m/z (EI) 463 ([M-CH_3]$^{+\cdot}$, 3%), 405 ([M-Si$(CH_3)_3$]$^{+\cdot}$, 43), 263 (62), 214 (83), 189 (30), 175 (40), 147 (39), 131 (26), 117 (33), 73 (100), 45 (11).

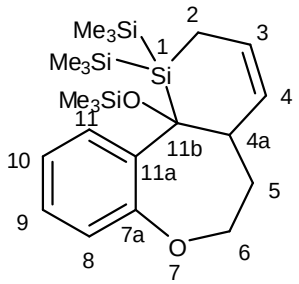
(*E*)-(2-(Hexa-3,5-dienyloxy)-4-methoxyphenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)methanol



To a suspension of $LiAlH_4$ (0.026 g, 0.68 mmol) in diethyl ether (3.0 ml) was added a solution of (*E*)-(2-(hexa-3',5'-dienyloxy)-4-methoxyphenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)methanone (0.33 g, 0.68 mmol) in diethyl ether (3.0 ml) at 0 °C, over a period of 3 minutes under nitrogen. The resulting suspension was stirred at RT for 1 h.

The reaction mixture was quenched sequentially with H_2O (0.5 ml), NaOH (1M, 0.5 ml) and H_2O (0.5 ml). The mixture was then filtered through Celite®, precipitate washed with EtOAc and the filtrate concentrated *in vacuo*. Flash column chromatography on neutral alumina, elution gradient 0 to 10% diethyl ether in hexane, afforded the product as a unstable colourless oil (0.29 g, 89%). R_f 0.3 (pet. ether : diethyl ether 9:1); IR (ATR) 3429, 2947, 2892, 1606, 1584, 1499, 1466, 1287, 1242, 1197, 1161, 1111, 1002, 829, 735 cm^{-1}; δ_H (700 MHz) 7.31-7.30 (1H, m, Ar-6-***H***), 6.51-6.50 (1H, m, Ar-5-***H***), 6.38-6.37 (1H, m, Ar-3-***H***), 6.33 (1H, dt, *J* = 16.8Hz, *J* = 10.5Hz, 5'-***H***), 6.19 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.76 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.39 (1H, d, *J* = 4.9Hz, C***H***OH), 5.15 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.04 (1H, d, *J* = 10.5Hz, 6'-***H***), 3.94 (2H, t, *J* = 7.0Hz, 1'-***H***), 3.80 (3H, s, OC$\boldsymbol{H}_3$), 2.60 (2H, q, *J* = 7.0Hz, 2'-***H***), 1.70 (1H, d, *J* = 4.9Hz, O***H***), 0.15 (27H, s, Si(C$\boldsymbol{H}_3)_3$); δ_C (175 MHz) 159.0 (***C***-4), 154.8 (***C***-2), 136.8 (***C***-5'), 133.5 (***C***-4'), 130.0 (**C**-3'), 128.6 (***C***-6), 121.8 (***C***-1), 116.1 (**C**-6'), 104.6 (***C***-5), 99.0 (***C***-3), 67.3 (***C***-1'), 61.5 (***C***HOH), 55.4 (O***C***H_3), 32.5 (***C***-2'), 1.5 (Si(***C***$H_3)_3$); δ_{Si} (140 MHz) -12.9, -68.9; m/z (ASAP) 463 ($[M\text{-}OH]^{+\cdot}$, 100%), 407 ($[M\text{-}SiMe_3]^{+\cdot}$, 11),. HRMS (ASAP) found $[M\text{-}OH]^{+\cdot}$ 463.2336, $C_{23}H_{43}O_2Si_4$ requires $[M\text{-}OH]^{+\cdot}$ 463.2335.

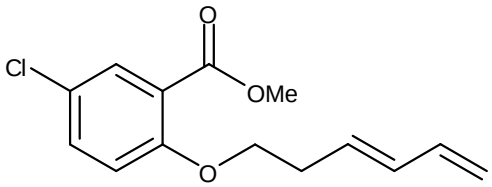
1,1-Bis(trimethylsilyl)-11b-(trimethylsilyloxy)-1,2,4a,5,6,11b-hexahydrobenzo[b]silino[2,3-d]oxepine 460



A solution of (*E*)-(2-(hexa-3,5-dienyloxy)phenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)methanone (0.21 g, 0.47 mmol) in dry toluene (2.0 ml) was heated in a microwave tube at 180 ^oC for 1 h. Concentration, followed by flash column chromatography on silica, elution gradient 0 to 5% diethyl ether in hexane, afforded the product as a greasy solid (0.17 g, ds 2.7:1, 81%). R_f 0.6 (pet. ether : diethyl ether 95:5); IR (ATR) 2951, 2895, 1479, 1441, 1242, 1210, 1059, 1025, 829, 767, 752 cm^{-1}; δ_H (700 MHz) 7.52-7.51 (1H, m, 11-***H***), 7.12-7.08 (2H, m, 9,10-***H***), 6.89-6.87 (1H, m, 8-***H***), 6.09 (1H, ddd, *J* = 10.5Hz, *J* = 7.7Hz, *J* = 2.8Hz, 3-***H***), 5.73 (1H, ddd, *J* = 10.5Hz, *J* = 6.3Hz, *J* = 2.8Hz, 4-***H***), 4.12 (1H, ddd, *J* = 11.2Hz, *J* = 7.0Hz, *J* = 6.3Hz, 6-***H***), 3.91 (1H, ddd, *J* = 11.2Hz, *J* = 6.3Hz, *J* = 5.6Hz, 6-***H***),

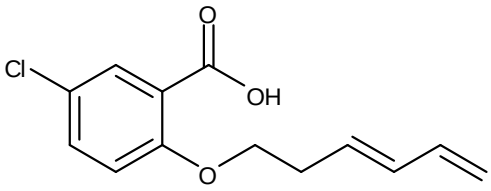
3.21-3.19 (1H, m, 4a-***H***), 2.07-2.03 (1H, m, 5-***H***), 1.88-1.83 (1H, m, 5-***H***), 1.66 (1H, dtd, *J* = 16.1Hz, *J* = 2.8Hz, *J* = 1.4Hz, 2-***H***), 1.40 (1H, dd, *J* = 16.1Hz, *J* = 7.7Hz, 2-***H***), 0.18 (9H, s, Si(C***H***$_3$)$_3$), 0.05 (9H, s, Si(C***H***$_3$)$_3$), -0.20 (9H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 152.6 (***C***-7a), 140.4 (***C***-11a), 132.9 (***C***-4), 131.0 (***C***-11), 127.8 (***C***-3), 127.4 (***C***-9), 124.0 (**C**-10), 122.6 (***C***-8), 82.4 (***C***-11b), 69.4 (**C**-6), 44.8 (***C***-4a), 30.1 (***C***-5), 8.4 (***C***-2), 2.8 (Si(***C***H$_3$)$_3$), 0.5 (Si(***C***H$_3$)$_3$), -0.5 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) 10.5, -15.5, -16.8, -26.8; m/z (EI) 448 ([M]$^{+\cdot}$, 0.2%), 433 ([M-Me]$^{+\cdot}$, 0.5%), 375 ([M-Si(CH$_3$)$_3$]$^{+\cdot}$, 14), 205 (10), 147 (16), 73 (100); HRMS (EI) found [M]$^{+\cdot}$ 448.2100, $C_{22}H_{40}O_2Si_4$ requires [M]$^{+\cdot}$ 448.2100.

(*E*)-Methyl 5-chloro-2-(hexa-3,5-dienyloxy)benzoate 464



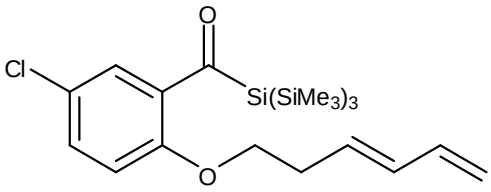
Following standard procedure **A** (page 192), a solution of triphenylphosphine (5.27 g, 20.1 mmol), (*E*)-hexa-3,5-dien-1-ol (1.45 g, 14.7 mmol) and methyl 5-chloro-2-hydroxybenzoate (2.50 g, 13.4 mmol) in THF (7.0 ml) was treated with diisopropyl azodicarboxylate (3.17 ml, 16.1 mmol) to give the title compound as a colourless liquid (2.79 g, 78%). R_f 0.4 (hexane : ethyl acetate 9:1); IR (ATR) 2949, 1732, 1598, 1487, 1465, 1435, 1403, 1298, 1273, 1233, 1151, 1113, 1079, 1003, 972, 953, 899, 811, 783, 731 cm^{-1}; δ_H (700 MHz) 7.76-7.75 (1H, m, 6-***H***), 7.40-7.38 (1H, m, 4-***H***), 6.90-6.89 (1H, m, 3-***H***), 6.34 (1H, ddd, *J* = 16.8Hz, *J* = 10.5Hz, *J* = 9.8Hz, 5'-***H***), 6.20 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.80 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.16 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.04 (1H, d, *J* = 9.8Hz, 6'-***H***), 4.06 (2H, t, *J* = 6.3Hz, 1'-***H***), 3.89 (3H, s, OC***H***$_3$), 2.62 (2H, dt, *J* = 7.0Hz, *J* = 6.3Hz, 2'-***H***); δ_C (175 MHz) 165.6 (***C***O), 156.9 (***C***-2), 136.8 (***C***-5'), 133.5 (***C***-4'), 133.0 (**C**-4), 131.3 (***C***-6), 129.8 (***C***-3'), 125.4 (**C**-5), 121.9 (***C***-1), 116.1 (***C***-6'), 114.8 (***C***-3), 68.8 (***C***-1'), 52.2 (O***C***H$_3$), 32.4 (***C***-2'); m/z (ES+) 289 ([M+Na]$^{+\cdot}$, 100), 555 ([2M+Na]$^{+\cdot}$, 5); HRMS (ES+) found [M+H]$^{+\cdot}$ 267.0778, $C_{14}H_{16}O_3Cl$ requires [M+H]$^{+\cdot}$ 267.0788.

(*E*)-5-Chloro-2-(hexa-3',5'-dienyloxy)benzoic acid 465



Following standard procedure **B** (page 192), a solution of (*E*)-methyl 5-chloro-2-(hexa-3,5-dienyloxy)benzoate (2.73 g, 10.2 mmol) in THF (40 ml) was treated with a solution lithium hydroxide (0.49 g, 20.5 mmol) in water (40 ml) to give the title compound as a white solid (2.20 g, 86%). Mp: 41.3–42.4 ^{o}C; R_f 0.4 (pet. ether : ethyl acetate 1:1); IR (ATR) 3258, 2946, 1722, 1655, 1599, 1480, 1456, 1414, 1397, 1274, 1237, 1203, 1149, 1111, 1039, 1004, 951, 899, 855, 826, 782, 767, 706 cm^{-1}; δ_H (700 MHz) 10.70 (1H, s, CO_2***H***), 8.161-8.158 (1H, m, 6-***H***), 7.51-7.50 (1H, m, 4-***H***), 7.00-6.99 (1H, m, 3-***H***), 6.33 (1H, ddd, *J* = 16.8Hz, *J* = 10.5Hz, *J* = 9.8Hz, 5'-***H***), 6.25 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.71 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.22 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.10 (1H, d, *J* = 9.8Hz, 6'-***H***), 4.29 (2H, t, *J* = 6.3Hz, 1'-***H***), 2.71 (2H, dt, *J* = 7.0Hz, *J* = 6.3Hz, 2'-***H***); δ_C (175 MHz) 164.0 (***C***O), 155.8 (***C***-2), 135.9 (***C***-5'), 135.1 (***C***-4'), 134.6 (**C**-4), 133.4 (***C***-6), 127.7 (***C***-5), 127.6 (**C**-3'), 119.2 (***C***-1), 117.6 (***C***-6'), 114.0 (***C***-3), 69.5 (***C***-1'), 32.2 (***C***-2'); m/z (ES+) 275 ([M+Na]$^{+\cdot}$, 100); HRMS (ES+) found [M+Na]$^{+\cdot}$ 275.0434, $C_{13}H_{13}O_3NaCl$ requires [M+Na]$^{+\cdot}$ 275.0451.

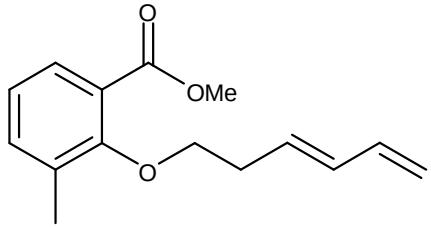
(*E*)-(5-Chloro-2-(hexa-3',5'-dienyloxy)phenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)methanone 466



Following standard procedure **C** (page 192), a solution of (*E*)-5-chloro-2-(hexa-3',5'-dienyloxy)benzoic acid (2.15 g, 8.53 mmol) in DCM (40.0 ml) was treated with oxalyl chloride (0.88 ml, 10.2 mmol) and DMF (1 drop). The resulting acid was redissolved in THF (45.0 ml) and treated with a solution of silylpotassium **221** in THF (45.0 ml), which was prepared from tetrakis(trimethylsilyl)silane (2.74 g, 8.53 mmol) and potassium *tert*-butoxide (1.01 g, 8.95 mmol). Flash column chromatography afforded the product as a yellow semisolid (0.43 g, 10%). R_f 0.5 (pet. ether : diethyl ether 9:1); IR (ATR) 2951, 2893, 1609, 1483, 1463, 1388, 1285, 1243, 1181, 1129, 1020, 1001, 952, 929, 901, 823, 750 cm^{-1}; δ_H (700 MHz) 7.24-7.22 (1H, m, 4-***H***), 6.984-6.980 (1H, m, 6-***H***), 6.82-6.81 (1H, m, 3-***H***), 6.32 (1H,

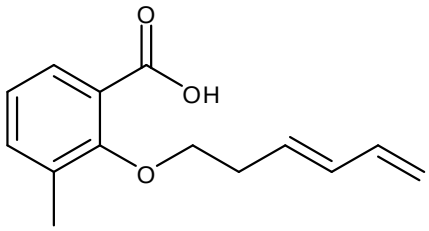
dt, *J* = 16.8Hz, *J* = 10.5Hz, 5'-***H***), 6.14 (1H, dd, *J* = 14.7Hz, *J* = 10.5Hz, 4'-***H***), 5.71 (1H, dt, *J* = 14.7Hz, *J* = 7.0Hz, 3'-***H***), 5.15 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.03 (1H, d, *J* = 10.5Hz, 6'-***H***), 3.96 (2H, t, *J* = 7.0Hz, 1'-***H***), 2.53 (2H, q, *J* = 7.0Hz, 2'-***H***), 0.21 (27H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 239.7 (***C***O), 152.0 (***C***-2), 140.4 (***C***-5), 136.8 (***C***-5'), 133.5 (**C**-4'), 129.8 (***C***-4), 129.4 (***C***-3'), 125.9 (**C**-6), 125.4 (***C***-1), 116.1 (***C***-6'), 114.4 (***C***-3), 68.6 (***C***-1'), 32.2 (***C***-2') 1.1 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) -11.2, -69.2; m/z (CI) 483 ([M+H]$^{+\cdot}$, 12), 393 (100), 90 (27); HRMS (ES+) found [M+H]$^{+\cdot}$ 483.1787, $C_{22}H_{40}O_2ClSi_4$ requires [M+H]$^{+\cdot}$ 483.1788.

(*E*)-Methyl 2-(hexa-3',5'-dienyloxy)-3-methylbenzoate 468



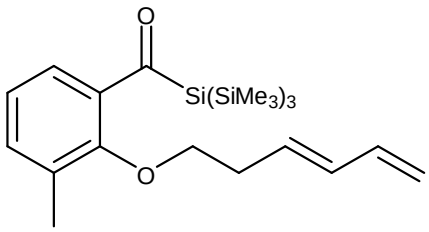
Following standard procedure **A** (page 192), a solution of triphenylphosphine (4.23 g, 16.1 mmol), (*E*)-hexa-3,5-dien-1-ol (1.16 g, 11.8 mmol) and methyl 2-hydroxy-3-methylbenzoate (2.00 g, 10.7 mmol) in THF (4.0 ml) was treated with diisopropyl azodicarboxylate (2.54 ml, 12.9 mmol) to give the title compound as a colourless liquid (1.52 g, 58%). R_f 0.5 (pet. ether : ethyl acetate 9:1); IR (ATR) 2949, 1725, 1652, 1592, 1460, 1433, 1377, 1292, 1258, 1221, 1189, 1173, 1137, 1002, 952, 898, 875, 761, 727 cm^{-1}; δ_H (700 MHz) 7.64-7.63 (1H, m, 6-***H***), 7.35-7.33 (1H, m, 4-***H***), 7.06-7.04 (1H, m, 5-***H***), 6.35 (1H, ddd, *J* = 16.1Hz, *J* = 10.5Hz, *J* = 9.8Hz, 5'-***H***), 6.20 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.82 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.45 (1H, d, *J* = 16.1Hz, 6'-***H***), 5.02 (1H, d, *J* = 9.8Hz, 6'-***H***), 3.95 (2H, t, *J* = 6.3Hz, 1'-***H***), 3.91 (3H, s, OC***H***$_3$), 2.62 (2H, dt, *J* = 7.0Hz, *J* = 6.3Hz, 2'-***H***), 2.31 (3H, s, C***H***$_3$); δ_C (175 MHz) 167.0 (***C***O), 157.1 (***C***-2), 137.0 (***C***-5'), 135.0 (***C***-4), 133.1 (**C**-4'), 132.7 (***C***-3), 130.5 (***C***-3'), 129.1 (**C**-6), 124.7 (***C***-1), 123.4 (***C***-5), 115.7 (***C***-6'), 73.4 (***C***-1'), 52.1 (O***C***H$_3$), 33.4 (***C***-2'), 16.3 (***C***H$_3$); m/z (ES+) 269 ([M+Na]$^{+\cdot}$, 100), 515 ([2M+Na]$^{+\cdot}$, 5); HRMS (ES+) found [M+Na]$^{+\cdot}$ 269.1151, $C_{15}H_{18}O_3Na$ requires [M+Na]$^{+\cdot}$ 269.1154.

(*E*)-2-(Hexa-3',5'-dienyloxy)-3-methylbenzoic acid 469



Following standard procedure **B** (page 192), a solution of (*E*)-methyl 2-(hexa-3,5-dienyloxy)-3-methylbenzoate (1.47 g, 5.97 mmol) in THF (30 ml) was treated with a solution lithium hydroxide (0.29g, 11.9 mmol) in water (30 ml) to give the title compound as a white solid (1.08 g, 78%). Flash column chromatography on silica, elution gradient 10 to 20% ethyl acetate in hexane, afforded the product as a white solid (1.08 g, 78%). Mp: 59.3–60.2 ^{o}C; R_f 0.5 (pet. ether : ethyl acetate 1:1); IR (ATR) 3252, 2912, 1700, 1675, 1593, 1407, 1383, 1303, 1276, 1225, 1187, 1165, 1093, 1016, 1000, 949, 912, 898, 865, 796, 747. 763, 719 cm^{-1}; δ_H (700 MHz) 11.21 (1H, s, CO_2***H***), 7.98-7.97 (1H, m, 6-***H***), 7.44-7.43 (1H, m, 4-***H***), 7.20-7.18 (1H, m, 5-***H***), 6.36 (1H, ddd, *J* = 16.81Hz, *J* = 10.5Hz, *J* = 9.8Hz, 5'-***H***), 6.24 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.75 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.19 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.08 (1H, d, *J* = 9.8Hz, 6'-***H***), 4.03 (2H, t, *J* = 7.0Hz, 1'-***H***), 2.68 (2H, q, *J* = 7.0Hz, 2'-***H***), 2.36 (3H, s, C***H***$_3$); δ_C (175 MHz) 165.9 (***C***O), 156.4 (***C***-2), 136.9 (***C***-4), 136.4 (***C***-5'), 134.7 (**C**-4'), 131.5 (***C***-3), 130.8 (***C***-6), 128.2 (**C**-3'), 125.1 (***C***-5), 122.2 (***C***-1), 116.9 (***C***-6'), 74.6 (***C***-1'), 33.1 (***C***-2'), 16.1 (***C***H$_3$); m/z (ES+) 255 ([M+Na]$^{+\cdot}$, 100), 487 ([2M+Na]$^{+\cdot}$, 6); HRMS (ES+) found [M+Na]$^{+\cdot}$ 255.1004, $C_{14}H_{16}O_3Na$ requires [M+Na]$^{+\cdot}$ 255.0997.

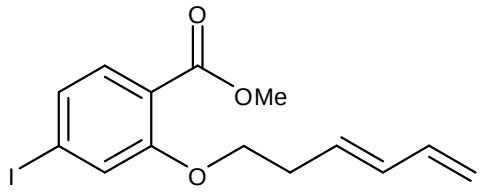
(*E*)-(2-(Hexa-3',5'-dienyloxy)-3-methylphenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)methanone 470



Following standard procedure **C** (page 192), a solution of (*E*)-2-(hexa-3',5'-dienyloxy)-3-methylbenzoic acid (0.83 g, 3.57 mmol) in DCM (20.0 ml) was treated with oxalyl chloride (0.37 ml, 4.28 mmol) and DMF (1 drop). The resulting acid was redissolved in THF (25.0 ml) and treated with a solution of silylpotassium **221** in THF (25.0 ml), which was prepared from tetrakis(trimethylsilyl)silane (1.15 g, 3.57 mmol) and potassium *tert*-butoxide (0.42 g, 3.75

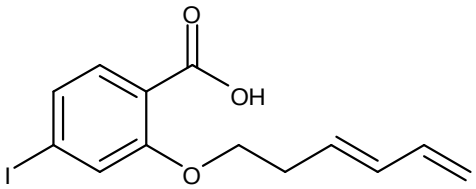
mmol). Flash column chromatography afforded the product as a yellow oil (0.86 g, 52%). R_f 0.7 (pet. ether : diethyl ether 9:1); IR (ATR) 2948, 2891, 1616, 1376, 1243, 1256, 1211, 1071, 1002, 953, 899, 827, 758 cm^{-1}; δ_H (700 MHz) 7.18-7.16 (1H, m, 6-***H***), 7.03-7.01 (1H, m, 5-***H***), 6.94-6.93 (1H, m, 4-***H***), 6.32 (1H, dt, *J* = 16.8Hz, *J* = 10.5Hz, 5'-***H***), 6.14 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.74 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.12 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.00 (1H, d, *J* = 10.5Hz, 6'-***H***), 3.80 (2H, t, *J* = 7.0Hz, 1'-***H***), 2.50 (2H, q, *J* = 7.0Hz, 2'-***H***), 2.26 (3H, s, C***H***$_3$), 0.20 (27H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 242.2 (***C***O), 152.1 (***C***-2), 143.2 (***C***-3), 137.0 (***C***-5'), 133.1 (**C**-4'), 132.3 (***C***-1), 132.1 (***C***-6), 130.5 (**C**-3'), 124.0 (***C***-4), 123.2 (***C***-5), 115.5 (***C***-6'), 74.5 (***C***-1'), 33.3 (***C***-2'), 16.1 (***C***H$_3$), 1.1 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) -11.4, -69.5; m/z (CI) 463 ([M+H]$^{+\cdot}$, 24), 373 (100), 90 (19); HRMS (ES+) found [M+H]$^{+\cdot}$ 463.2333, $C_{23}H_{43}O_2Si_4$ requires [M+H]$^{+\cdot}$ 463.2335.

(*E*)-Methyl 2-(hexa-3,5-dienyloxy)-4-iodobenzoate 472



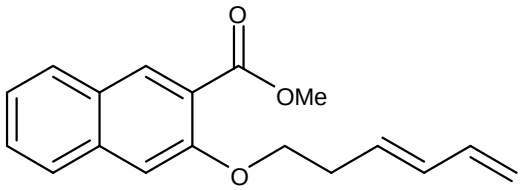
ollowing standard procedure **A** (page 192), a solution of triphenylphosphine (5.65 g, 22.0 mmol), (*E*)-hexa-3,5-dien-1-ol (1.41 g, 14.4 mmol) and methyl 2-hydroxy-4-iodobenzoate (4.00 g, 14.4 mmol) in THF (7.0 ml) was treated with diisopropyl azodicarboxylate (3.40 ml, 17.3 mmol) to give the title compound as a white solid (4.31 g, 84%). Mp: 43.8–45.1 ^oC; R_f 0.3 (pet. ether : ethyl acetate 9:1); IR (ATR) 3077, 2945, 1689, 1579, 1466, 1430, 1401, 1381, 1289, 1237, 1187, 1137, 1093, 1009, 959, 927, 890, 824, 769 cm^{-1}; δ_H (700 MHz) 7.50-7.49 (1H, m, 6-***H***), 7.35-7.34 (1H, m, 5-***H***), 7.30 (1H, m, 3-***H***), 6.34 (1H, ddd, *J* = 16.8Hz, *J* = 10.5Hz, *J* = 9.8Hz, 5'-***H***), 6.20 (1H, dd, *J* = 14.7Hz, *J* = 10.5Hz, 4'-***H***), 5.80 (1H, dt, *J* = 14.7Hz, *J* = 7.0Hz, 3'-***H***), 5.16 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.04 (1H, d, *J* = 9.8Hz, 6'-***H***), 4.06 (2H, t, *J* = 6.3Hz, 1'-***H***), 3.87 (3H, s, CO$_2$C***H***$_3$), 2.60 (2H, dt, *J* = 7.0Hz, *J* = 6.3Hz, 2'-***H***); δ_C (175 MHz) 166.3 (***C***O), 158.5 (***C***-2), 136.8 (***C***-5'), 133.6 (***C***-4'), 132.8 (**C**-6), 129.71 (***C***-5), 129.65 (***C***-3'), 122.8 (**C**-3), 120.1 (***C***-1), 116.1 (***C***-6'), 99.7 (***C***-4), 68.7 (***C***-1'), 52.1 (O***C***H$_3$), 32.3 (***C***-2'); m/z (ES+) 359 ([M+H]$^{+\cdot}$, 20%), 381 ([M+Na]$^{+\cdot}$, 100), 739 ([2M+Na]$^{+\cdot}$, 55); HRMS (ES+) found [M+H]$^{+\cdot}$ 359.0138, $C_{14}H_{16}O_3I$ requires [M+H]$^{+\cdot}$ 359.0144.

(*E*)-2-(Hexa-3,5-dienyloxy)-4-iodobenzoic acid 473



Following standard procedure **B** (page 192), a solution of (*E*)-methyl 2-(hexa-3,5-dienyloxy)-4-iodobenzoate (4.09 g, 11.4 mmol) in THF (50 ml) was treated with a solution lithium hydroxide (0.55g, 22.8 mmol) in water (25 ml) to give the title compound as a white solid (3.29 g, 84%). Mp: 91.5–93.2 ^{o}C; R_f 0.5 (pet. ether : ethyl acetate 1:1); IR (ATR) 3283, 3095, 1719, 1584, 1466, 1407, 1343, 1213, 1132, 1195, 1037, 999, 959, 899, 838, 768, 714 cm^{-1}; δ_H (700 MHz) 10.54 (1H, s, CO_2***H***), 7.87-7.86 (1H, m, 6-***H***), 7.52-7.50 (1H, m, 5-***H***), 7.395-7.393 (1H, m, 3-***H***), 6.33 (1H, ddd, *J* = 16.8Hz, *J* = 10.5Hz, *J* = 9.8Hz, 5'-***H***), 6.25 (1H, dd, *J* = 14.7Hz, *J* = 10.5Hz, 4'-***H***), 5.71 (1H, dt, *J* = 14.7Hz, *J* = 7.0Hz, 3'-***H***), 5.23 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.11 (1H, d, *J* = 9.8Hz, 6'-***H***), 4.29 (2H, t, *J* = 6.3Hz, 1'-***H***), 2.71 (2H, dt, *J* = 7.0Hz, *J* = 6.3Hz, 2'-***H***); δ_C (175 MHz) 164.7 (***C***O), 157.1 (***C***-2), 135.9 (***C***-5'), 135.1 (***C***-4'), 134.8 (***C***-6), 131.8 (**C**-5), 127.6 (***C***-3'), 122.1 (***C***-3), 117.6 (**C**-6'), 117.4 (***C***-1), 101.5 (***C***-4), 69.5 (***C***-1'), 32.2 (***C***-2'); m/z (ES+) 345 ([M+H]$^{+\cdot}$, 15%), 367 ([M+Na]$^{+\cdot}$, 100), 711 ([2M+Na]$^{+\cdot}$, 26); HRMS (ES-) found [M-H]$^{-\cdot}$ 342.9826, $C_{13}H_{12}O_3I$ requires [M-H]$^{-\cdot}$ 342.9831.

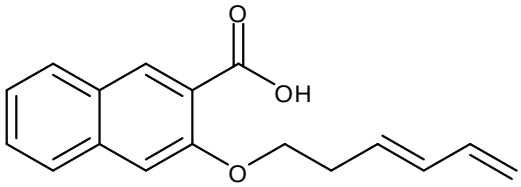
(*E*)-Methyl 3-(hexa-3,5-dienyloxy)-2-naphthoate 476



Following standard procedure **A** (page 192), a solution of triphenylphosphine (6.23 g, 23.7 mmol), (*E*)-hexa-3,5-dien-1-ol (1.94 g, 19.8 mmol) and methyl 3-hydroxy-2-naphthoate (4.00 g, 19.8 mmol) in THF (7.0 ml) was treated with diethyl azodicarboxylate (3.74 ml, 23.7 mmol) to give the title compound as a white solid (2.88 g, 52%). Mp: 37.9–38.4 ^{o}C; R_f 0.3 (pet. ether : ethyl acetate 9:1); IR (ATR) 3017, 2913, 1725, 1627, 1595, 1503, 1451, 1431, 1381, 1333, 1273, 1258, 1205, 1183, 1129, 1072, 1005, 951, 896, 861, 831, 780, 739 cm^{-1}; δ_H (700 MHz) 8.29 (1H, s, 1-***H***), 7.83-7.82 (1H, m, 8-***H***), 7.73-7.71 (1H, m, 5-***H***), 7.52-7.50 (1H, m, 6-***H***), 7.39-7.37 (1H, m, 7-***H***), 7.19 (1H, m, 4-***H***), 6.37 (1H, ddd, *J* = 16.8Hz, *J* = 10.5Hz, *J* = 9.8Hz, 5'-***H***), 6.24 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.87 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.17 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.04 (1H, d, *J* = 9.8Hz, 6'-***H***), 4.19 (2H, t, *J* =

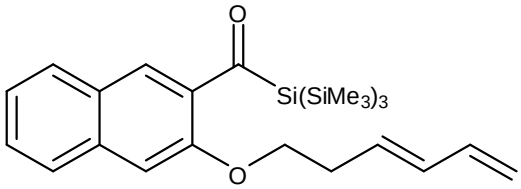
6.3Hz, 1'-***H***), 3.95 (3H, s, OC***H***$_3$), 2.70 (2H, dt, *J* = 7.0Hz, *J* = 6.3Hz, 2'-***H***); δ_C (175 MHz) 167.0 (***C***O), 154.8 (***C***-3), 137.0 (***C***-5'), 136.0 (***C***-4a), 133.4 (***C***-4'), 132.6 (***C***-1), 130.2 (***C***-3'), 128.7 (***C***-8), 128.3 (***C***-6), 127.6 (***C***-8a), 126.4 (***C***-5), 124.4 (***C***-7), 122.3 (***C***-2), 115.9 (***C***-6'), 107.9 (***C***-4), 68.1 (***C***-1'), 52.2 (O***C***H$_3$), 32.4 (***C***-2'); m/z (ES+) 283 ($[M+H]^{+\cdot}$, 25%), 305 ($[M+Na]^{+\cdot}$, 100), 587 ($[2M+Na]^{+\cdot}$, 70); HRMS (ES+) found $[M+H]^{+\cdot}$ 283.1326, $C_{18}H_{19}O_3$ requires $[M+H]^{+\cdot}$ 283.1334.

(*E*)-3-(Hexa-3',5'-dienyloxy)-2-naphthoic acid 477



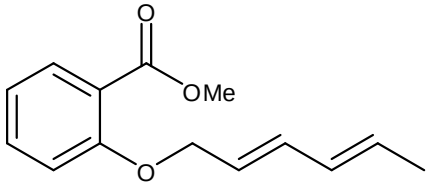
Following standard procedure **B** (page 192), a solution of (*E*)-methyl 3-(hexa-3,5-dienyloxy)-2-naphthoate (2.75 g, 9.75 mmol) in THF (45 ml) was treated with a solution lithium hydroxide (0.47g, 19.5 mmol) in water (22 ml) to give the title compound as a white solid (2.27 g, 86%). Mp: 61.9–63.1 ^oC; R_f 0.5 (pet. ether : ethyl acetate 1:1); IR (ATR) 3241, 1737, 1629, 1596, 1451, 1406, 1349, 1243, 1207, 1173, 1059, 1005, 983, 901, 824, 747, 709 cm^{-1}; δ_H (500 MHz) 11.00 (1H, s, CO_2***H***), 8.81 (1H, s, 1-***H***), 7.93-7.91 (1H, m, 8-***H***), 7.78-7.76 (1H, m, 5-***H***), 7.61-7.58 (1H, m, 6-***H***), 7.48-7.45 (1H, m, 7-***H***), 7.30 (1H, m, 4-***H***), 6.35 (1H, ddd, *J* = 16.0Hz, *J* = 10.5Hz, *J* = 9.0Hz, 5'-***H***), 6.29 (1H, dd, *J* = 15.0Hz, *J* = 10.5Hz, 4'-***H***), 5.78 (1H, dt, *J* = 15.0Hz, *J* = 7.0Hz, 3'-***H***), 5.24 (1H, d, *J* = 16.0Hz, 6'-***H***), 5.11 (1H, d, *J* = 9.0Hz, 6'-***H***), 4.41 (2H, t, *J* = 6.5Hz, 1'-***H***), 2.79 (2H, dt, *J* = 7.0Hz, *J* = 6.5Hz, 2'-***H***); δ_C (125 MHz) 165.3 (***C***O), 153.5 (***C***-3), 136.5 (***C***-4a), 136.3 (***C***-1), 136.1 (***C***-5'), 134.9 (***C***-4'), 129.5 (***C***-6, ***C***-8), 128.4 (***C***-8a), 128.1 (***C***-3'), 126.5 (***C***-7), 125.4 (***C***-5), 117.9 (***C***-2), 117.5 (***C***-6'), 107.9 (***C***-4), 69.0 (***C***-1'), 32.2 (***C***-2'); m/z (ES+) 269 ($[M+H]^{+\cdot}$, 49%), 291 ($[M+Na]^{+\cdot}$, 100), 537 ($[2M+H]^{+\cdot}$, 38), 559 ($[2M+Na]^{+\cdot}$, 77); HRMS (ES+) found $[M+H]^{+\cdot}$ 269.1186, $C_{17}H_{17}O_3$ requires $[M+H]^{+\cdot}$ 269.1178.

(*E*)-(3-(Hexa-3',5'-dienyloxy)naphthalen-2-yl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)methanone 478



Following standard procedure **C** (page 192), a solution of (*E*)-3-(hexa-3',5'-dienyloxy)-2-naphthoic acid (1.93 g, 7.19 mmol) in DCM (35.0 ml) was treated with oxalyl chloride (0.80 ml, 9.34 mmol) and DMF (1 drop). The resulting acid was redissolved in THF (35.0 ml) and treated with a solution of silylpotassium **221** in THF (35.0 ml), which was prepared from tetrakis(trimethylsilyl)silane (2.31 g, 7.19 mmol) and potassium *tert*-butoxide (0.85 g, 7.54 mmol). Flash column chromatography afforded the product as a pale yellow solid (1.90 g, 53%). Mp: 112.4–116.8 ^{o}C; R_f 0.5 (pet. ether : diethyl ether 9:1); IR (ATR) 2952, 2891, 1616, 1450, 1389, 1325, 1241, 1183, 1155, 1103, 1005, 949, 827, 743 cm^{-1}; δ_H (700 MHz) 7.77-7.75 (1H, m, 5-***H***), 7.71-7.70 (1H, m, 8-***H***), 7.48 (1H, s, 1-***H***), 7.48-7.46 (1H, m, 6-***H***), 7.38-7.36 (1H, m, 7-***H***), 7.13 (1H, m, 4-***H***), 6.35 (1H, dt, *J* = 17.5Hz, *J* = 10.5Hz, 5'-***H***), 6.19 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.79 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.17 (1H, d, *J* = 17.5Hz, 6'-***H***), 5.04 (1H, d, *J* = 10.5Hz, 6'-***H***), 4.11 (2H, t, *J* = 7.0Hz, 1'-***H***), 2.62 (2H, q, *J* = 7.0Hz, 2'-***H***), 0.22 (27H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 240.6 (***C***O), 152.3 (***C***-3), 140.4 (***C***-4a), 136.9 (***C***-5'), 134.6 (***C***-8a), 133.4 (***C***-4'), 129.8 (***C***-3'), 127.9 (***C***-5), 127.8 (***C***-2), 127.1 (***C***-6), 126.6 (***C***-8), 125.9 (***C***-1), 124.3 (***C***-7), 116.0 (***C***-6'), 107.4 (***C***-4), 67.9 (***C***-1'), 32.2 (***C***-2'), 1.2 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) -11.3, -69.6; m/z (EI) 498 ([M]$^{+\cdot}$, 2%), 425 ([M-Si(CH$_3$)$_3$]$^{+\cdot}$, 6), 397 (10), 205 (14), 147 (19), 73 (100); HRMS (EI) found [M]$^{+\cdot}$ 498.2256, $C_{26}H_{42}O_2Si_4$ requires [M]$^{+\cdot}$ 498.2256.

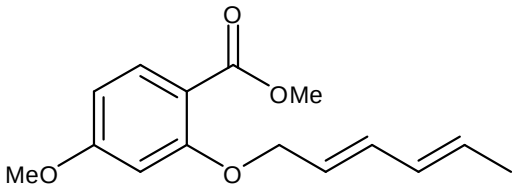
Methyl 2-((2'*E*,4'*E*)-hexa-2',4'-dienyloxy)benzoate 480



Following standard procedure **A** (page 192), a solution of triphenylphosphine (3.25 g, 12.4 mmol), (2*E*,4*E*)-hexa-2,4-dien-1-ol (1.01 g, 10.3 mmol) and methyl 2-hydroxybenzoate (1.57 g, 10.3 mmol) in THF (3.0 ml) was treated with diisopropyl azodicarboxylate (2.44 ml, 12.4 mmol) to give the title compound as a unstable white solid (0.99 g, 41%). Mp: 54.3–53.4 ^{o}C;

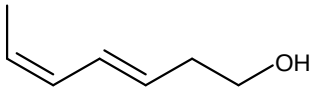
R_f 0.4 (pet. ether : ethyl acetate 9:1); IR (ATR) 2911, 2854, 1719, 1595, 1486, 1441, 1374, 1285, 1239, 1188, 1162, 1140, 1077, 996, 957, 923, 833, 762, 706 cm^{-1}; δ_H (700 MHz) 7.81-7.79 (1H, m, 6-***H***), 7.45-7.42 (1H, m, 4-***H***), 6.99-6.97 (2H, m, 3-***H***, 5-***H***), 6.38 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 3'-***H***), 6.10 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.78 (1H, dt, *J* = 15.4Hz, *J* = 6.3Hz, 2'-***H***), 5.75 (1H, dq, *J* = 15.4Hz, *J* = 6.3Hz, 5'-***H***), 4.65 (2H, d, *J* = 6.3Hz, 1'-***H***), 3.91 (3H, s, $CO_2C\boldsymbol{H}_3$), 1.78 (3H, d, *J* = 6.3Hz, 6'-***H***); δ_C (175 MHz) 166.8 (***C***O), 158.2 (***C***-2), 133.5 (***C***-3'), 133.3 (***C***-4), 131.7 (***C***-6), 130.7 (***C***-4'), 130.6 (**C**-5'), 124.6 (***C***-2'), 120.7 (***C***-1), 120.3 (**C**-5), 113.8 (***C***-3), 69.4 (***C***-1'), 51.9 ($CO_2\boldsymbol{C}H_3$), 18.1 (***C***-6'); m/z compound decomposes under all forms of ionisation.

Methyl 2-((2'*E*,4'*E*)-hexa-2',4'-dienyloxy)-4-methoxybenzoate 482



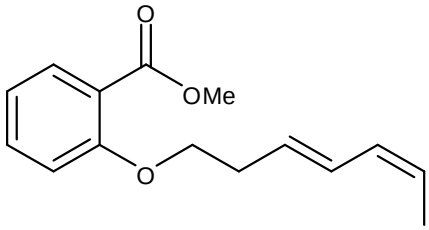
Following standard procedure **A** (page 192), a solution of triphenylphosphine (2.45 g, 9.33 mmol), (2*E*,4*E*)-hexa-2,4-dien-1-ol (0.76 g, 7.78 mmol) and methyl 2-hydroxy-4-methoxybenzoate (1.42 g, 7.78 mmol) in THF (2.0 ml) was treated with diisopropyl azodicarboxylate (1.84 ml, 9.33 mmol) to give the title compound as a white solid (0.90 g, 44%). Mp: 59.6–60.5 ^oC; R_f 0.2 (pet. ether : ethyl acetate 9:1); IR (ATR) 3009, 2941, 2842, 1692, 1611, 1570, 1502, 1433, 1385, 1304, 1270, 1200, 1172, 1141, 1099, 1035, 986, 926, 827, 761 cm^{-1}; δ_H (700 MHz) 7.87-7.85 (1H, m, 6-***H***), 6.51-6.50 (1H, m, 5-***H***), 6.481-6.478 (1H, m, 3-***H***), 6.41 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 3'-***H***), 6.10 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.80 (1H, dt, *J* = 15.4Hz, *J* = 5.6Hz, 2'-***H***), 5.76 (1H, dq, *J* = 15.4Hz, *J* = 6.3Hz, 5'-***H***), 4.63 (2H, d, *J* = 5.6Hz, 1'-***H***), 3.87 (3H, s, $CO_2C\boldsymbol{H}_3$), 3.84 (3H, s, $OC\boldsymbol{H}_3$), 1.78 (3H, d, *J* = 6.3Hz, 6'-***H***); δ_C (175 MHz) 166.2 (***C***O), 164.0 (***C***-4), 160.4 (***C***-2), 133.9 (***C***-6), 133.6 (***C***-3'), 130.7 (***C***-4'), 130.6 (**C**-5'), 124.4 (***C***-2'), 112.8 (***C***-1), 105.0 (**C**-5), 100.5 (***C***-3), 69.4 (***C***-1'), 55.4 ($ArO\boldsymbol{C}H_3$), 51.7 ($CO_2\boldsymbol{C}H_3$), 18.1 (***C***-6'); m/z (ES+) 263 ($[M+H]^+$, 100%), 285 ($[M+Na]^+$ 45), 547 ($[2M+Na]^+$ 47); Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.80; H, 6.92.

(3*E*,5*Z*)-hepta-3,5-dien-1-ol[116] 484



To a suspension of $LiAlH_4$ (0.96 g, 25.4 mmol) in diethyl ether (80 ml) was added a solution of (3*E*,5*Z*)-methyl hepta-3,5-dienoate (3.56 g, 25.4 mmol) in diethyl ether (20 ml) at 0°C, over a period of 15 minutes. The resulting suspension was stirred at RT for 1 h. The reaction mixture was cooled with an ice bath and cautiously quenched sequentially with H_2O (3.0 ml), NaOH (1M, 3.0 ml) and H_2O (6.0 ml). The suspension was then filtered through Celite®, the precipitate washed with EtOAc and the combined filtrate concentrated under reduced preasure. Flash column chromatography on silica, elution gradient 0 to 30% ethyl acetate in hexane, afforded the title product as a clear liquid (2.23 g, *EZ*:*EE* - 84:16, 78%). R_f 0.4 (pet. ether : ethyl acetate 7:3); IR (ATR) 3326, 3018, 2923, 2879, 1432, 1371, 1179, 1041, 982, 945, 911, 839, 729 cm^{-1}; δ_H (500 MHz) 6.46 (1H, dd, *J* = 15.0Hz, *J* = 11.0Hz, 4-***H***), 6.00 (1H, td, *J* = 11.0Hz, *J* = 1.5Hz, 5-***H***), 5.64 (1H, dt, *J* = 15.0Hz, *J* = 7.0Hz, 3-***H***), 5.45 (1H, dq, *J* = 11.0Hz, *J* = 7.0Hz, 6-***H***), 3.70 (2H, q, *J* = 6.0Hz, 1-***H***), 2.40 (2H, dt, *J* = 7.0Hz, *J* = 6.0Hz, 2-***H***), 1.76 (3H, dd, *J* = 7.0Hz, *J* = 1.5Hz, 7-***H***), 1.43 (1H, t, *J* = 6.0Hz, O***H***); δ_C (125 MHz) 129.4 (***C***-5), 129.0 (***C***-3), 128.5 (***C***-4), 125.3 (***C***-6), 62.0 (***C***-1), 36.3 (***C***-2), 13.3 (***C***-7); m/z (EI) 112 ($[M]^{+\cdot}$, 78%), 94 ($[M\text{-}H_2O]^{+\cdot}$, 10), 81 ($[M\text{-}CH_2OH]^{+\cdot}$, 100), 79 ($[M\text{-}H_2O\text{-}CH_3]^{+\cdot}$, 85), 77 (40), 67 (84), 65 (28), 55 (44), 53 (74), 51 (19), 41 (72), 39 (63), 31 (31), 27 (37).

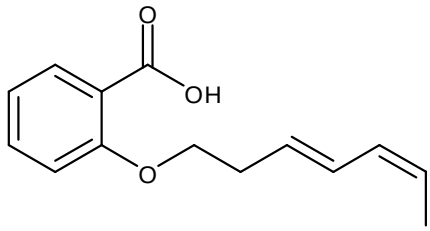
Methyl 2-((3*E*,5*Z*)-hepta-3',5'-dienyloxy)benzoate 485



Following standard procedure **A** (page 192), a solution of triphenylphosphine (5.79 g, 22.1 mmol), (3*E*,5*Z*)-hepta-3,5-dien-1-ol (2.06 g, 18.4 mmol) and methyl 2-hydroxybenzoate (2.38 ml, 18.4 mmol) in THF (6.0 ml) was treated with diethyl azodicarboxylate (3.47 ml, 22.1 mmol) to give the title compound as a colourless liquid (2.46 g, *EZ*:*EE* - 84:16, 54%). R_f 0.4 (pet. ether : ethyl acetate 7:3); IR (ATR) 3017, 2945, 1725, 1599, 1489, 1450, 1300, 1243, 1163, 1131, 1081, 1044, 1017, 985, 947, 836, 753, 707 cm^{-1}; δ_H (700 MHz) 7.79-7.78 (1H, m, Ar-6-***H***), 7.46-7.43 (1H, m, Ar-4-***H***), 6.99-6.96 (2H, m, Ar-5-***H***, Ar-3-***H***), 6.49 (1H, dd, *J* = 14.7Hz, *J* = 11.2Hz, 4'-***H***), 6.02 (1H, ddd, *J* = 11.2Hz, *J* = 10.5Hz, *J* = 1.4Hz, 5'-***H***), 5.77

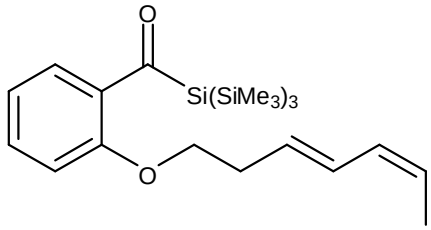
(1H, dt, *J* = 14.7Hz, *J* = 7.0Hz, 3'-***H***), 5.45 (1H, dq, *J* = 10.5Hz, *J* = 7.0Hz, 6'-***H***), 4.09 (2H, t, *J* = 7.0Hz, 1'-***H***), 3.89 (3H, s, OC***H***$_3$), 2.66 (2H, q, *J* = 7.0Hz, 2'-***H***), 1.76 (3H, dd, *J* = 7.0Hz, *J* = 1.4Hz, 7'-***H***); δ_C (175 MHz) 167.0 (***C***O), 158.3 (***C***-2), 133.3 (***C***-4), 131.6 (***C***-6), 129.2 (***C***-5'), 129.0 (***C***-3'), 127.9 (***C***-4'), 125.2 (***C***-6'), 120.7 (***C***-1), 120.3 (***C***-5), 113.4 (***C***-3), 68.6 (***C***-1'), 51.9 (O***C***H$_3$), 32.8 (***C***-2'), 13.3 (***C***-7'); m/z (EI) 246 ([M]$^{+\cdot}$, 5%), 215 ([M-OCH$_3$]$^{+\cdot}$, 8), 185 (61), 135 (10), 120 (12), 94 (100), 79 (86), 67 (40), 55 (22), 45 (33), 41 (20), 39 (14); HRMS (ES+) found [M+H]$^{+\cdot}$ 247.1329, $C_{15}H_{19}O_3$ requires [M+H]$^{+\cdot}$ 247.1329.

2-((3*E*,5*Z*)-Hepta-3,5-dienyloxy)benzoic acid 486



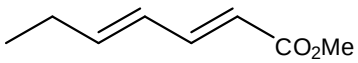
Following standard procedure **B** (page 192), a solution of methyl 2-((3*E*,5*Z*)-hepta-3',5'-dienyloxy)benzoate (1.74 g, 7.1 mmol) in THF (35 ml) was treated with a solution lithium hydroxide (0.34g, 14.1 mmol) in water (15 ml) to give the title compound as a colourless liquid (1.43 g, *EZ*:*EE* - 84:16, 87%). R_f 0.5 (pet. ether : ethyl acetate 1:1); IR (ATR) 3276, 3020, 2928, 1728, 1601, 1581, 1486, 1456, 1395, 1295, 1234, 1219, 1163, 1125, 1041, 984, 947, 909, 834, 752 cm^{-1}; δ_H (700 MHz) 10.85 (1H, s, CO$_2$***H***), 8.21-8.19 (1H, m, Ar-6-***H***), 7.57-7.55 (1H, m, Ar-4-***H***), 7.15-7.13 (1H, m, Ar-5-***H***), 7.05-7.04 (1H, m, Ar-3-***H***), 6.55 (1H, dd, *J* = 15.4Hz, *J* = 11.2Hz, 4'-***H***), 6.00 (1H, ddd, *J* = 11.2Hz, *J* = 10.5Hz, *J* = 1.4Hz, 5'-***H***), 5.67 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.51 (1H, dq, *J* = 10.5Hz, *J* = 7.0Hz, 6'-***H***), 4.31 (2H, t, *J* = 6.3Hz, 1'-***H***), 2.74 (2H, dt, *J* = 7.0Hz, *J* = 6.3Hz, 2'-***H***), 1.77 (3H, dd, *J* = 7.0Hz, *J* = 1.4Hz, 7'-***H***); δ_C (175 MHz) 165.3 (***C***O), 157.4 (***C***-2), 134.9 (***C***-4), 133.9 (***C***-6), 129.5 (***C***-4'), 128.4 (***C***-5'), 126.8 (***C***-3'), 126.7 (***C***-6'), 122.3 (***C***-5), 117.8 (***C***-1), 112.5 (***C***-3), 69.2 (***C***-1'), 32.6 (***C***-2'), 13.4 (***C***-7'); m/z (ES+) 487 ([2M+Na]$^{+\cdot}$, 24%), 465 ([2M+H]$^{+\cdot}$, 100), 250 ([M+NH$_4$]$^{+\cdot}$, 28), 233 ([M+H]$^{+\cdot}$, 20); HRMS (ES+) found [M+NH$_4$]$^{+\cdot}$ 250.1440, $C_{14}H_{20}O_3N$ requires [M+NH$_4$]$^{+\cdot}$ 250.1438.

(2-((3*E*,5*Z*)-Hepta-3',5'-dienyloxy)phenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methanone 487



Following standard procedure **C** (page 192), a solution of 2-((3*E*,5*Z*)-hepta-3,5-dienyloxy)benzoic acid (1.91 g, 8.21 mmol) in DCM (40.0 ml) was treated with oxalyl chloride (0.92 ml, 10.7 mmol) and DMF (1 drop). The resulting acid was redissolved in THF (45.0 ml) and treated with a solution of silylpotassium **221** in THF (45.0 ml), which was prepared from tetrakis(trimethylsilyl)silane (2.63 g, 8.21 mmol) and potassium *tert*-butoxide (0.97 g, 8.62 mmol). Flash column chromatography afforded the product as a yellow oil (1.90 g, *EZ*:*EE* - 84:16, 50%). R_f 0.5 (pet. ether : diethyl ether 9:1); IR (ATR) 2948, 2891, 1614, 1591, 1484, 1465, 1441, 1393, 1242, 1188, 1157, 1106, 1040, 1018, 979, 824, 746cm^{-1}; δ_H (700 MHz) 7.29-7.26 (1H, m, 4-***H***), 7.01-6.99 (1H, m, 6-***H***), 6.96-6.94 (1H, m, 5-***H***), 6.88-6.87 (1H, m, 3-***H***), 6.44 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.99 (1H, ddd, *J* = 11.2Hz, *J* = 10.5Hz, *J* = 1.4Hz, 5'-***H***), 5.68 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.44 (1H, dq, *J* = 11.2Hz, *J* = 7.0Hz, 6'-***H***), 3.99 (2H, t, *J* = 7.0Hz, 1'-***H***), 2.56 (2H, dt, *J* = 7.0Hz, *J* = 7.0Hz, 2'-***H***), 1.76 (3H, dd, *J* = 7.0Hz, *J* = 1.4Hz, 7'-***H***), 0.19 (27H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 241.6 (***C***O), 153.4 (***C***-2), 139.7 (***C***-1), 130.1 (***C***-4), 129.2 (***C***-5'), 128.7 (***C***-3'), 127.9 (***C***-4'), 125.5 (***C***-6), 125.2 (***C***-6'), 120.2 (***C***-5), 112.9 (***C***-3), 68.3 (***C***-1'), 32.7 (***C***-2'), 13.3 (***C***-7'), 1.1 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) -11.4, -70.5; m/z (ES+) 942 ([2M+NH$_4$]$^{+\cdot}$, 100%), 463 ([M+H]$^{+\cdot}$, 75); HRMS (ES+) found [M+H]$^{+\cdot}$ 463.2331, $C_{23}H_{43}O_2Si_4$ requires [M+H]$^{+\cdot}$ 463.2335.

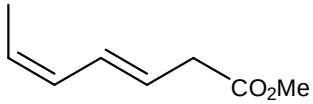
(2*E*,4*E*)-Methyl hepta-2,4-dienoate[116] 490



To a solution of methyl (triphenylphosphoranylidene)acetate (19.88 g, 59.4 mmol) in DCM (125 ml) was added (*E*)-pent-2-enal. The reaction mixture was stirred at RT for 6 h after which time the solvent was evaporated under reduced pressure. The residue was than triturated with hexane to remove the majority of the triphenylphosphine oxide. Kugelrohr distillation (95 ^{o}C, 0.4 mbar) afforded the product as a colourless liquid (4.50 g, 54%). IR (ATR) 2964, 2879, 1713, 1643, 1617, 1434, 1301, 1259, 1236, 1187, 1139, 1039, 999, 874, 720 cm^{-1}; δ_H (700 MHz) 7.28 (1H, ddd, *J* = 15.4Hz, *J* = 7.0Hz, *J* = 3.5Hz, 3-***H***), 6.18-6.17

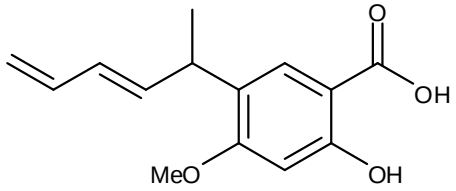
(2H, m, 4-***H***, 5-***H***), 5.80 (1H, d, *J* = 15.4Hz, 2-***H***), 3.74 (3H, s, $CO_2C\boldsymbol{H}_3$), 2.20 (2H, dq, *J* = 7.0Hz, *J* = 4.9Hz, 6-***H***), 1.05 (3H, t, *J* = 7.0Hz, 7-***H***); δ_C (175 MHz) 167.7 (***C***O), 146.2 (***C***-5), 145.4 (***C***-3), 127.4 (***C***-4), 118.7 (***C***-2), 51.4 ($CO_2\boldsymbol{C}H_3$), 26.0 (***C***-6), 12.8 (***C***-7); m/z (EI) 140 ($[M]^{+\cdot}$, 48%), 111 (100), 109 ($[M\text{-}OMe]^{+\cdot}$, 43), 81 ($[M\text{-}CO_2Me]^{+\cdot}$, 100), 79 (73), 53 (43), 39 (38), 27 (20).

(3*E*,5*Z*)-Methyl hepta-3,5-dienoate[116] 491



To a solution of sodium bis(trimethylsilyl)amide (61.8 ml, 1M in THF) in THF (90 ml) was added a solution of (2*E*,4*E*)-methyl hepta-2,4-dienoate (4.33 g, 30.9 mmol) in THF (20 ml) at -78 ^oC. The reaction mixture was stirred at -78 ^oC for 4 h after which time a solution of acetic acid (5.0 ml) in THF/H_2O (45 ml, 1:1) was added. The reaction mixture was allowed to reach room temperature and then volatiles were evaporated under reduced pressure. The residue was extracted with Et_2O (3 x 40 ml). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash column chromatography on silica, elution gradient 0 to 10% diethyl ether in hexane, afforded the product as a clear liquid (3.83 g, EZ:EE - 84:16, 88%). R_f 0.4 (pet. ether : diethyl ether 9:1); IR (ATR) 3021, 2952, 1737, 1435, 1339, 1255, 1198, 1161, 985, 945, 827 cm^{-1}; δ_H (500 MHz) 6.45 (1H, dd, *J* = 15.0Hz, *J* = 11.0Hz, 4-***H***), 6.01 (1H, td, *J* = 11.0Hz, *J* = 1.5Hz, 5-***H***), 5.74 (1H, dt, *J* = 15.0Hz, *J* = 7.0Hz, 3-***H***), 5.50 (1H, dq, *J* = 11.0Hz, *J* = 7.0Hz, 6-***H***), 3.70 (3H, s, $OC\boldsymbol{H}_3$), 3.16 (2H, d, *J* = 7.0Hz, 2-***H***), 1.75 (3H, dd, *J* = 7.0Hz, *J* = 1.5Hz, 7-***H***); δ_C (125 MHz) 172.1 (***C***O), 129.0 (***C***-4), 128.6 (***C***-5), 126.3 (***C***-6), 124.4 (***C***-3), 51.9 ($O\boldsymbol{C}H_3$), 38.1 (***C***-2), 13.3 (***C***-7); m/z (EI) 140 ($[M]^{+\cdot}$, 56%), 111 (10), 98 (64), 80 (100), 77 (35), 67 (15), 65 (22), 59 (36), 53 (50), 51 (20), 41 (45), 39 (40), 29 (11), 27 (18).

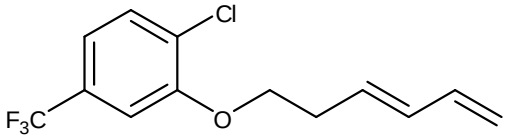
(*E*)-5-(Hexa-3',5'-dien-2'-yl)-2-hydroxy-4-methoxybenzoic acid 492



Following standard procedure **B** (page 192), a solution of methyl 2-((2'*E*,4'*E*)-hexa-2',4'-dienyloxy)-4-methoxybenzoate (0.80 g, 3.05 mmol) in THF (20 ml) was treated with a solution of lithium hydroxide (0.15 g, 6.10 mmol) in water (10 ml) to give the title compound

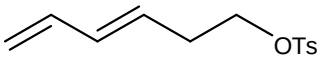
as a white solid (0.42 g, 56%). Mp: 121.6–122.8 ^{o}C; R_f 0.2 (pet. ether : ethyl acetate 3:2); IR (ATR) 3241, 1737, 1629, 1596, 1451, 1406, 1349, 1243, 1207, 1173, 1059, 1005, 983, 901, 747, 709 cm^{-1}; δ_H (700 MHz) 10.54 (1H, s, O***H***), 7.64 (1H, s, 6-***H***), 6.45 (1H, s, 3-***H***), 6.35 (1H, ddd, *J* = 16.8Hz, *J* = 10.5Hz, *J* = 9.8Hz, 5'-***H***), 6.07 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.87 (1H, dd, *J* = 15.4Hz, *J* = 6.3Hz, 3'-***H***), 5.14 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.01 (1H, d, *J* = 9.8Hz, 6'-***H***), 3.88 (3H, s, OC***H***$_3$), 3.84 (1H, quin, *J* = 6.3Hz, 2'-***H***), 1.33 (3H, d, *J* = 6.3Hz, 1'-***H***); δ_C (175 MHz) 174.2 (***C***O), 164.0 (***C***-2), 163.2 (***C***-4), 138.6 (***C***-3'), 137.3 (***C***-5'), 129.6 (***C***-4'), 129.2 (**C**-6), 126.6 (***C***-5), 115.5 (***C***-6'), 103.5 (**C**-1), 99.1 (***C***-3), 55.8 (O***C***H$_3$), 34.3 (***C***-2'), 19.8 (***C***-1'); m/z (ES-) 247 ([M-H]$^{-\cdot}$, 100%), 495 ([2M-H]$^{-\cdot}$, 10%); HRMS (ES-) found [M-H]$^{-\cdot}$ 247.0959, $C_{14}H_{15}O_4$ requires [M-H]$^{-\cdot}$ 247.0970.

(*E*)-1-Chloro-2-(hexa-3',5'-dienyloxy)-4-(trifluoromethyl)benzene 499



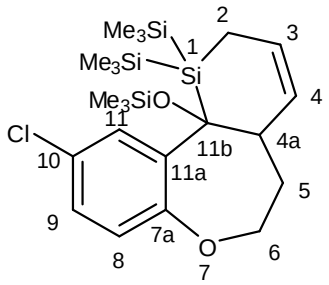
Following standard procedure **A** (page 192), a solution of triphenylphosphine (3.66 g, 14.0 mmol), (*E*)-hexa-3,5-dien-1-ol (1.14 g, 12.0 mmol) and 2-chloro-5-(trifluoromethyl)phenol (2.29 g, 12.0 mmol) in THF (4.0 ml) was treated with diethyl azodicarboxylate (2.20 ml, 14.0 mmol) to give the title compound as a colourless liquid (2.28 g, 71%). R_f 0.6 (pet. ether : diethyl ether 95:5); IR (ATR) 2940, 2882, 1600, 1492, 1423, 1388, 1326, 1247, 1168, 1123, 1079, 1003, 950, 903, 858, 817, 745 cm^{-1}; δ_H (700 MHz) 7.48-7.47 (1H, m, 6-***H***), 7.17-7.16 (1H, m, 5-***H***), 7.12 (1H, m, 3-***H***), 6.35 (1H, ddd, *J* = 16.8Hz, *J* = 10.5Hz, *J* = 9.8Hz, 5'-***H***), 6.23 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.82 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.18 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.06 (1H, d, *J* = 9.8Hz, 6'-***H***), 4.12 (2H, t, *J* = 6.3Hz, 1'-***H***), 2.67 (2H, dt, *J* = 7.0Hz, *J* = 6.3Hz, 2'-***H***); δ_C (175 MHz) 154.7 (***C***-2), 136.7 (***C***-5'), 133.8 (***C***-4'), 130.6 (***C***-6), 130.1 (q, $^2J_{c\text{-}f}$ = 32.6Hz, ***C***-4), 129.2 (***C***-3'), 127.0 (***C***-1), 123.6 (q, $^1J_{c\text{-}f}$ = 271.1Hz, ***C***F$_3$), 118.1 (q, $^3J_{c\text{-}f}$ = 3.3Hz, ***C***-5), 116.3 (***C***-6'), 110.0 (***C***-3), 68.8 (***C***-1'), 32.2 (***C***-2'); δ_F (375 MHz) -63.0; m/z (ASAP) 277 ([M+H]$^{+\cdot}$, 100%), 553 ([2M+H]$^{+\cdot}$, 14); HRMS (ASAP) found [M+H]$^{+\cdot}$ 277.0599, $C_{13}H_{13}OClF_3$ requires [M+H]$^{+\cdot}$ 277.0602.

(*E*)-Hexa-3,5-dienyl 4-methylbenzenesulfonate[137] 506



To a solution of (*E*)-hexa-3,5-dien-1-ol (2.00 g, 20.4 mmol) in pyridine (18 ml) tosyl chloride (6.22 g, 32.6 mmol) and *N*,*N*-dimethyl-4-aminopyridine (0.25 g, 2.0 mmol) were added. After 5 h, the reaction mixture was diluted with DCM (40 ml) and washed with saturated sodium bicarbonate solution (40 ml). The aqueous layer was separated and extracted with DCM (3 x 10 ml). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Flash column chromatography (pet. ether : etyl acetate 85:15) give the title compound as a colourless liquid (2.37. g, 46%). R_f 0.4 (pet. ether : etyl acetate 85:15); IR (ATR) 2967, 1598, 1355, 1301, 1173, 1096, 1043, 1002, 961, 907, 814, 758 cm^{-1}; δ_H (700 MHz) 7.80-7.79 (2H, m, Ar-2,6-***H***), 7.36-7.35 (2H, m, Ar-3,5-***H***), 6.24 (1H, ddd, *J* = 16.8Hz, *J* = 10.5Hz, *J* = 9.8Hz, 5-***H***), 6.06 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4-***H***), 5.52 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3-***H***), 5.12 (1H, d, *J* = 16.8Hz, 6-***H***), 5.03 (1H, d, *J* = 9.8Hz, 6-***H***), 4.07 (2H, t, *J* = 7.0Hz, 1-***H***), 2.46 (3H, s, C***H***$_3$), 2.44 (2H, q, *J* = 7.0Hz, 2-***H***); δ_C (175 MHz) 144.7 (Ar-***C***-1), 136.4 (***C***-5), 134.2 (***C***-4), 133.1 (Ar-***C***-4), 129.8 (Ar-***C***-3,5), 127.9 (Ar-**C**-2,6), 127.9 (***C***-3), 116.6 (**C**-6), 69.4 (***C***-1), 32.0 (***C***-2), 21.6 (***C***H$_3$); m/z (ES+) 275 ([M+Na]$^{+\cdot}$, 100%), 527 ([2M+Na]$^{+\cdot}$, 5).

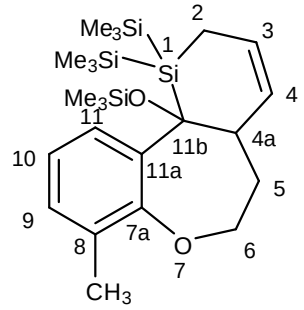
10-Chloro-1,1-bis(trimethylsilyl)-11b-(trimethylsilyloxy)-1,2,4a,5,6,11b-hexahydrobenzo [b]silino[2,3-d]oxepine 512



A solution of (*E*)-(5-chloro-2-(hexa-3',5'-dienyloxy)phenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)methanone (0.16 g, 0.33 mmol) in dry toluene (2.0 ml) was heated in a microwave tube at 180 ^oC for 75 min. Concentration, followed by flash column chromatography on silica, elution gradient 0 to 5% diethyl ether in hexane, afforded the product as a greasy colourless solid (0.10 g, ds 3.5:1 (crude ds 2.7:1), 60%). R_f 0.6 (pet. ether : diethyl ether 95:5); IR (ATR) 2952, 2894, 1477, 1244, 1027, 831, 749 cm^{-1}; δ_H (700 MHz) 7.51-7.50 (1H, m, 11-***H***), 7.06-7.05 (1H, m, 9-***H***), 6.83-6.82 (1H, m, 8-***H***), 6.09 (1H, ddd, *J* = 10.5Hz, *J* = 7.7Hz, *J* = 2.8Hz, 3-***H***), 5.68 (1H, ddd, *J* = 10.5Hz, *J* = 6.3Hz, *J* = 2.8Hz, 4-***H***), 4.13 (1H, ddd, *J* = 11.2Hz, *J* = 7.0Hz, *J* = 6.3Hz, 6-***H***), 3.86 (1H, ddd, *J* = 11.2Hz, *J* = 6.3Hz,

J = 5.6Hz, 6-***H***), 3.14-3.12 (1H, m, 4a-***H***), 2.10-2.06 (1H, m, 5-***H***), 1.87-1.82 (1H, m, 5-***H***), 1.64 (1H, dtd, *J* = 16.1Hz, *J* = 2.8Hz, *J* = 1.4Hz, 2-***H***), 1.38 (1H, dd, *J* = 16.1Hz, *J* = 7.7Hz, 2-***H***), 0.19 (9H, s, Si(C***H***$_3$)$_3$), 0.09 (9H, s, Si(C***H***$_3$)$_3$), -0.15 (9H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 151.1 (***C***-7a), 142.5 (***C***-10), 132.5 (***C***-4), 130.5 (***C***-11), 129.2 (***C***-11a), 127.9 (***C***-3), 127.0 (***C***-9), 124.1 (***C***-8), 81.9 (***C***-11b), 69.6 (**C**-6), 45.0 (***C***-4a), 29.9 (***C***-5), 8.2 (***C***-2), 2.9 (Si(***C***H$_3$)$_3$), 0.5 (Si(***C***H$_3$)$_3$), -0.6 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) 11.5, -15.4, -16.6, -26.2; m/z (EI) 482 ([M]$^{+\cdot}$, 0.5%), 467 ([M-Me]$^{+\cdot}$, 2%), 409 ([M-Si(CH$_3$)$_3$]$^{+\cdot}$, 19), 293 (12), 263 (34), 243 (15), 205 (56), 191 (27), 175 (25), 147 (76), 133 (48), 117 (47), 73 (100), 59 (23), 45 (31); HRMS (EI) found [M]$^{+\cdot}$ 482.1713, $C_{22}H_{39}O_2ClSi_4$ requires [M]$^{+\cdot}$ 482.1710.

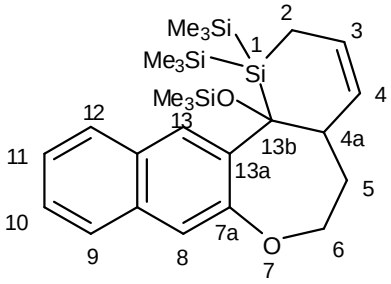
8-Methyl-1,1-bis(trimethylsilyl)-11b-(trimethylsilyloxy)-1,2,4a,5,6,11b-hexahydrobenzo [b]silino[2,3-d]oxepine 513



A solution of (*E*)-(2-(hexa-3',5'-dienyloxy)-3-methylphenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl) trisilan-2-yl)methanone (0.17 g, 0.36 mmol) in dry toluene (2.0 ml) was heated in a microwave tube at 180 ^{o}C for 90 min. Concentration, followed by flash column chromatography on silica, elution gradient 0 to 5% diethyl ether in hexane, afforded the product as a greasy colourless solid (0.14 g, ds 4.3:1 (crude ds 3.7:1), 87%). R_f 0.6 (pet. ether : diethyl ether 95:5); IR (ATR) 2949, 2893, 1469, 1432, 1243, 1193, 1043, 1020, 954, 829, 749 cm^{-1}; δ_H (700 MHz) 7.32-7.31 (1H, m, 10-***H***), 7.00-6.96 (2H, m, 9,11-***H***), 6.13 (1H, ddd, *J* = 10.5Hz, *J* = 7.7Hz, *J* = 4.2Hz, 3-***H***), 5.68 (1H, ddd, *J* = 10.5Hz, *J* = 6.3Hz, *J* = 2.8Hz, 4-***H***), 4.07 (1H, ddd, *J* = 11.2Hz, *J* = 7.7Hz, *J* = 6.3Hz, 6-***H***), 3.85 (1H, ddd, *J* = 11.2Hz, *J* = 6.3Hz, *J* = 4.2Hz, 6-***H***), 3.16-3.14 (1H, m, 4a-***H***), 2.22 (3H, s, C***H***$_3$), 2.12-2.08 (1H, m, 5-***H***), 1.81-1.75 (1H, m, 5-***H***), 1.66 (1H, dddd, *J* = 16.1Hz, *J* = 4.2Hz, *J* = 2.8Hz, *J* = 1.4Hz, 2-***H***), 1.39 (1H, dd, *J* = 16.1Hz, *J* = 7.7Hz, 2-***H***), 0.16 (9H, s, Si(C***H***$_3$)$_3$), 0.08 (9H, s, Si(C***H***$_3$)$_3$), -0.21 (9H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 150.2 (***C***-7a), 140.6 (***C***-11a), 132.6 (***C***-4), 131.0 (***C***-8), 128.6 (***C***-9), 128.2 (***C***-3), 127.9 (***C***-11), 123.5 (***C***-10), 81.9 (***C***-11b), 69.1 (**C**-6), 45.4 (***C***-4a), 29.9 (***C***-5), 16.0 (C***H***$_3$), 8.4 (***C***-2), 2.9 (Si(***C***H$_3$)$_3$), 0.6 (Si(***C***H$_3$)$_3$), -0.5 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) 10.3, -15.6, -16.6, -27.5; m/z (EI) 462 ([M]$^{+\cdot}$, 1%), 447 ([M-Me]$^{+\cdot}$, 3%), 389 ([M-

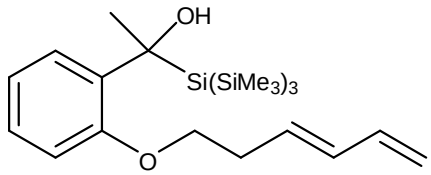
$Si(CH_3)_3]^{+\cdot}$, 51), 361 (10), 321 (16), 301 (14), 273 (55), 223 (38), 205 (46), 157 (26), 147 (87), 133 (38), 117 (30), 73 (100), 45 (24); HRMS (EI) found $[M]^{+\cdot}$ 462.2250, $C_{23}H_{42}O_2Si_4$ requires $[M]^{+\cdot}$ 462.2256.

1,1-Bis(trimethylsilyl)-13b-(trimethylsilyloxy)-1,2,4a,5,6,13b-hexahydronaphtho[2,3-b]silino[2,3-d]oxepine 514



A solution of (*E*)-(3-(hexa-3',5'-dienyloxy)naphthalen-2-yl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methanone (0.32 g, 0.65 mmol) in dry toluene (3.2 ml) was heated in a microwave tube at 180 ^oC for 75 min. Concentration, followed by flash column chromatography on silica, elution gradient 0 to 5% diethyl ether in hexane, afforded the product as a colourless viscous oil (0.25 g, ds 2.7:1 (crude ds 2.2:1), 75%). R_f 0.5 (pet. ether : diethyl ether 95:5); IR (ATR) 2951, 2891, 1495, 1443, 1398, 1242, 1165, 1093, 1029, 904, 830, 730 cm^{-1}; δ_H (700 MHz) 7.97 (1H, m, 13-***H***), 7.77-7.76 (1H, m, 12-***H***), 7.74-7.71 (1H, m, 9-***H***), 7.41-7.38 (2H, m, 10-***H***, 11-***H***), 6.18 (1H, ddd, *J* = 10.5Hz, *J* = 7.7Hz, *J* = 4.2Hz, 3-***H***), 5.67 (1H, ddd, *J* = 10.5Hz, *J* = 4.9Hz, *J* = 2.1Hz, 4-***H***), 4.23 (1H, ddd, *J* = 11.2Hz, *J* = 7.0Hz, *J* = 6.3Hz, 6-***H***), 3.91 (1H, ddd, *J* = 11.2Hz, *J* = 5.6Hz, *J* = 4.2Hz, 6-***H***), 3.20-3.18 (1H, m, 4a-***H***), 2.18-2.13 (1H, m, 5-***H***), 1.83-1.78 (1H, m, 5-***H***), 1.72 (1H, dddd, *J* = 16.1Hz, *J* = 4.2Hz, *J* = 2.1Hz, *J* = 1.4Hz, 2-***H***), 1.43 (1H, dd, *J* = 16.1Hz, *J* = 7.7Hz, 2-***H***), 0.18 (9H, s, $Si(C\boldsymbol{H}_3)_3$), 0.16 (9H, s, $Si(C\boldsymbol{H}_3)_3$), -0.27 (9H, s, $Si(C\boldsymbol{H}_3)_3$); δ_C (175 MHz) 151.7 (***C***-7a), 141.9 (***C***-13a), 133.1 (***C***-8a), 132.2 (***C***-4), 130.9 (***C***-12a), 128.4 (***C***-3), 128.2 (**C**-13), 127.3 (***C***-12), 126.5 (***C***-9), 125.4 (***C***-10), 124.9 (***C***-11), 118.8 (***C***-8), 81.9 (***C***-13b), 69.7 (**C**-6), 46.2 (***C***-4a), 30.0 (***C***-5), 8.2 (***C***-2), 3.1 ($Si(\boldsymbol{C}H_3)_3$), 0.8 ($Si(\boldsymbol{C}H_3)_3$), -0.4 ($Si(\boldsymbol{C}H_3)_3$); δ_{Si} (140 MHz) 10.7, -15.6, -16.8, -26.9; m/z (EI) 498 ($[M]^{+\cdot}$, 7%), 470 (12), 425 ($[M\text{-}Si(CH_3)_3]^{+\cdot}$, 22), 397 (24), 309 (24), 259 (20), 233 (18), 205 (78), 191 (46), 157 (36), 147 (74), 133 (49), 117 (48), 73 (100), 59 (33), 45 (39); HRMS (EI) found $[M]^{+\cdot}$ 498.2252, $C_{26}H_{42}O_2Si_4$ requires $[M]^{+\cdot}$ 498.2256.

(*E*)-1-(2-(Hexa-3',5'-dienyloxy)phenyl)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)ethanol 521

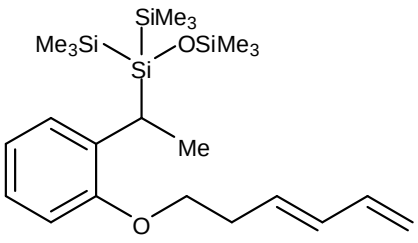


To a solution o of (*E*)-(2-(hexa-3,5-dienyloxy)phenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methanone (0.34 g, 0.77 mmol) in diethyl ether (6.0 ml) was added methyllithium lithium bromide complex (1.5 M, 0.51 ml, 0.77 mmol) at -78^{o}C. The mixture was stirred at RT for 16 h after which time saturated sodium bicarbonate solution (6.0 ml) was added. The aqueous layer was separated and extracted with diethyl ether (3 x 5 ml), The combined organic extracts were dried over $MgSO_4$, filtered, concentrated and dried *in vacuo*. Flash column chromatography on silica, elution gradient 0 to 10% diethyl ether in hexane, afforded the product as a unstable colourless oil (0.15 g, 42%). R_f 0.6 (pet. ether : diethyl ether 9:1); IR (ATR) 3506, 2947, 2892, 1598, 1487, 1443, 1395, 1282, 1241, 1223, 1048, 1020, 1001, 903, 827, 745, 733 cm^{-1}; δ_H (700 MHz) 7.21-7.20 (1H, m, Ar-6-***H***), 7.15-7.12 (1H, m, Ar-4-***H***), 6.92-6.90 (1H, m, Ar-5-***H***), 6.87-6.86 (1H, m, Ar-3-***H***), 6.33 (1H, ddd, *J* = 17.5Hz, *J* = 10.5Hz, *J* = 9.8Hz, 5'-***H***), 6.21 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.73 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.17 (1H, d, *J* = 17.5Hz, 6'-***H***), 5.05 (1H, d, *J* = 9.8Hz, 6'-***H***), 4.89 (1H, s, O***H***), 4.15 (1H, dt, *J* = 9.1Hz, *J* = 7.0Hz, 1'-***H***), 4.07 (1H, dt, *J* = 9.1Hz, *J* = 7.0Hz, 1'-***H***), 2.64 (1H, q, *J* = 7.0Hz, 2'-***H***), 1.80 (3H, s, C***H***$_3$), 0.18 (27H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 155.3 (Ar-***C***-2), 138.3 (Ar-***C***-1), 136.6 (***C***-5'), 134.1 (***C***-4'), 129.3 (***C***-3'), 128.5 (Ar-**C**-6), 126.9 (Ar-***C***-4), 121.0 (Ar-***C***-5), 116.4 (**C**-6'), 113.0 (Ar-***C***-3), 76.0 (**C**OH), 68.0 (***C***-1'), 33.1 (***C***H$_3$), 32.5 (**C**-2'), 2.2 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) -13.3, -54.7; m/z compound decomposes under all forms of ionisation.

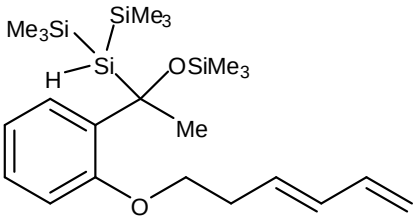
(*E*)-2-(1-(2-(Hexa-3',5'-dienyloxy)phenyl)ethyl)-1,1,1,3,3,3-hexamethyl-2-(trimethylsiloxy)trisilane 522 and

(*E*)-2-(1-(2-(Hexa-3',5'-dienyloxy)phenyl)-1-(trimethylsilyloxy)ethyl)-1,1,1,3,3,3-hexamethyltrisilane 523 and

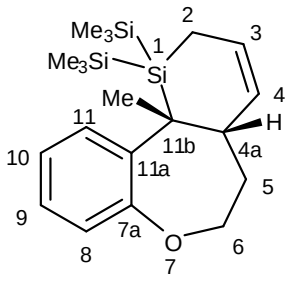
(4a*SR*,11b*RS*)-11b-methyl-1,1-bis(trimethylsilyl)-1,2,4a,5,6,11b-hexahydrobenzo[b]silino[2,3-d]oxepine 524



522



523



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To a solution of (*E*)-(2-(hexa-3,5-dienyloxy)phenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methanone (0.23 g, 0.52 mmol) in diethyl ether (4.0 ml) was added methyllithium lithium bromide complex (1.5 M in Et_2O, 0.34 ml, 0.52 mmol) at -78 ^oC. The mixture was stirred at -20 ^oC for 6 h and then at 10 ^oC for 16 h. After that time saturated sodium bicarbonate solution (6.0 ml) was added. The aqueous layer was separated and extracted with diethyl ether (3 x 5 ml), The combined organic extracts were dried over $MgSO_4$, filtered, concentrated and dried under reduced preasure. Flash column chromatography on silica, elution gradient 0 to 10% diethyl ether in hexane, afforded the product **524** as a colourless oil (0.11 g, 57%, ds 2.5:1) and products **522** and **523** as a colourless inseparable mixture (28.6 mg, 12%, 25:1).

Experimental data for compound **522**:

R_f 0.7 (pet. ether : diethyl ether 95:5); IR (ATR) 2951, 2893, 1595, 1487, 1447, 1238, 1051, 1002, 831, 743 cm^{-1}; δ_H (700 MHz) 7.19-7.17 (1H, m, Ar-6-***H***), 7.06-7.03 (1H, m, Ar-4-***H***), 6.90-6.88 (1H, m, Ar-5-***H***), 6.79-6.77 (1H, m, Ar-3-***H***), 6.34 (1H, ddd, *J* = 16.8Hz, *J* = 10.5Hz, *J* = 9.8Hz, 5'-***H***), 6.19 (1H, dd, *J* = 15.4Hz, *J* = 10.5Hz, 4'-***H***), 5.80 (1H, dt, *J* = 15.4Hz, *J* = 7.0Hz, 3'-***H***), 5.14 (1H, d, *J* = 16.8Hz, 6'-***H***), 5.02 (1H, d, *J* = 9.8Hz, 6'-***H***), 4.03 (1H, dt, *J* = 9.1Hz, *J* = 7.0Hz, 1'-***H***), 3.93 (1H, dt, *J* = 9.1Hz, *J* = 7.0Hz, 1'-***H***), 3.06 (1H, q, *J* = 7.7Hz, C***H***CH_3), 2.62 (1H, dq, *J* = 14.0Hz, *J* = 7.0Hz, 2'-***H***), 2.59 (1H, dq, *J* = 14.0Hz, *J* = 7.0Hz, 2'-***H***), 1.41 (3H, d, *J* = 7.7Hz, CHC***H***$_3$), 0.11 (9H, s, Si(C***H***$_3$)$_3$), 0.08 (9H, s,

OSi(C***H***$_3$)$_3$), -0.10 (9H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 154.9 (Ar-***C***-2), 136.9 (***C***-5'), 135.7 (Ar-***C***-1), 133.2 (***C***-4'), 130.6 (***C***-3'), 128.4 (Ar-**C**-6), 125.1 (Ar-***C***-4), 120.6 (Ar-***C***-5), 115.7 (**C**-6'), 111.2 (Ar-***C***-3), 67.3 (**C**-1'), 32.7 (**C**-2'), 21.6 (C***H***CH$_3$), 17.4 (CHC***H***$_3$), 2.1 (OSi(***C***H$_3$)$_3$), -0.7 (Si(***C***H$_3$)$_3$), -1.2 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) 6.8, 1.9, -19.8, -20.1; m/z (GC-MS, EI) 391 ([M-Si(CH$_3$)$_3$]$^{+\cdot}$, 28), 323 (20), 309 (12), 263 (46), 207 (25), 189 (42), 175 (44), 147 (45), 117 (42), 81 (100), 73 (64), 53 (32), 41 (24).

Experimental data for compound **523**:

^{1}H NMR – characteristic peaks: 3.65 (1H, s, Si***H***), 2.02 (3H, s, C***H***$_3$), 0.21 (9H, s, Si(C***H***$_3$)$_3$), 0.17 (9H, s, OSi(C***H***$_3$)$_3$), -0.13 (9H, s, Si(C***H***$_3$)$_3$); m/z (GCMS, EI) 446 ([M-CH$_3$]$^{+\cdot}$, 1%), 147 (22), 81 (100), 73 (60).

Experimental data for compound **524**:

R_f 0.6 (pet. ether : diethyl ether 95:5); IR (ATR) 2947, 2891, 1481, 1439, 1396, 1241, 1215, 1113, 1069, 1008, 909, 829, 769, 735 cm^{-1}; δ_H (700 MHz) 7.22-7.21 (1H, m, 11-***H***), 7.09-7.07 (2H, m, 9,10-***H***), 6.92-6.90 (1H, m, 8-***H***), 6.15 (1H, ddd, *J* = 10.5Hz, *J* = 7.7Hz, *J* = 2.1Hz, 3-***H***), 5.63 (1H, ddd, *J* = 10.5Hz, *J* = 4.9Hz, *J* = 2.8Hz, 4-***H***), 4.12 (1H, td, *J* = 10.5Hz, *J* = 6.3Hz, 6-***H***), 3.81 (1H, ddd, *J* = 10.5Hz, *J* = 6.3Hz, *J* = 2.1Hz, 6-***H***), 2.68-2.66 (1H, m, 4a-***H***), 2.09-2.04 (1H, m, 5-***H***), 1.78 (1H, ddt, *J* = 16.1Hz, *J* = 2.8Hz, *J* = 2.1Hz, 2-***H***), 1.69-164 (1H, m, 5-***H***), 1.66 (3H, s, C***H***$_3$), 1.26 (1H, dd, *J* = 16.1Hz, *J* = 7.7Hz, 2-***H***), 0.21 (9H, s, Si(C***H***$_3$)$_3$), -0.23 (9H, s, Si(C***H***$_3$)$_3$); δ_C (175 MHz) 154.6 (***C***-7a), 143.1 (***C***-11a), 133.8 (***C***-4), 128.6 (***C***-11), 128.0 (***C***-3), 126.4 (***C***-9), 124.7 (**C**-10), 123.0 (***C***-8), 68.9 (**C**-6), 44.9 (***C***-4a), 33.4 (***C***-11b), 30.0 (C***H***$_3$), 28.1 (***C***-5), 7.8 (***C***-2), 1.1 (Si(***C***H$_3$)$_3$), -0.6 (Si(***C***H$_3$)$_3$); δ_{Si} (140 MHz) -16.0, -16.8, -27.9; m/z (EI) 374 ([M]$^{+\cdot}$, 8%), 359 ([M-Me]$^{+\cdot}$, 7), 301 ([M-Si(CH$_3$)$_3$]$^{+\cdot}$, 71), 273 (30), 257 (22), 233 (47), 221 (29), 199 (74), 193 (60), 175 (58), 161 (42), 141 (32), 117 (43), 115 (46), 99 (30), 97 (20), 73 (100), 59 (60), 45 (54), 43 (16); HRMS (ASAP) found [M+H]$^{+\cdot}$ 375.1987, $C_{20}H_{35}OSi_3$ requires [M+H]$^{+\cdot}$ 375.1996.

8 Appendix

Research conferences attended

'Modern Aspects of stereochemistry', Stereochemistry at Sheffield, Dec **2006**

'22nd Postgraduate Heterocyclic Symposium', Organon, Newhouse, Scotland, Sep **2007**

'Modern Aspects of Stereochemistry', Stereochemistry at Sheffield, Dec **2007**

'Modern Aspects of Stereochemistry', Stereochemistry at Sheffield, Jan **2009**

Workshop attended

'Investigating Chemical Processes through Designed Experiments', University of Southampton, UK, Sept **2007**

Poster presentations

'Silenes: Novel Reagents for Organic Synthesis', 5th European Silicon Days, Vienna, Austria, Sep **2009**

'*Formation and Oxidation of Silylcyclopropanes',* RSC North East Regional Meeting, Newcastle, United Kingdom, Feb **2008**

'Reactions of Siloxysilenes with Electron Deficient Alkenes', 4th European Silicon Days, Bath, United Kingdom, Sep **2007**

Oral presentation

'Silenes: Novel Reagents for Organic Synthesis', CASE Student Symposium, Warwick, United Kingdom, Sep **2009**

Publication

J. Bower M. Box, M. Czyzewski, A. Goerta, P. G Steel, '*Acyl polysilanes: New acyl anion equivalents for additions to electron deficient alkene'*, Org. Lett., **2009**, *11*, 2744.

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