Silenes: Novel Reagents for Organic Synthesis

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Silenes: Novel Reagents for Organic Synthesis

Michal Czyzewski
Ph.D. Thesis

University of Durham
Department of Chemistry
October 2010
Abstract

Silenes: Novel Reagents for Organic Synthesis
Michal Czyzewski
Ph.D. 2010

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 \( \alpha,\beta \)-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 \( \alpha \)-silyl diazo carbonyl compounds was examined. It was found that \( \alpha \)-silyl diazo esters undergo rhodium (II) catalysed decomposition to provide short-lived silenes. These intermediates rearrange to oxasilates which can be trapped with \( \alpha,\beta \)-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 °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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Special thanks to my case supervisors from AstraZeneca, Dr Justin Bower and Matthew Box for valuable discussions and ideas.

Prof. Henrik Ottosson, thank you for teaching me about computational chemistry and for a warm welcome during my placement in your group.

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Special thanks to the staff at the University of Durham: NMR – Dr Alan Kenwright, Ian McKeag and Catherine Hefferman; MS – Dr Mike Jones, Dr Jackie Mosely; Elemental analysis – Dr Ritu Kataky; X-Ray – Dr Andrés Goeta; Glassblowers – Peter Coyne, Malcolm Richardson; entire team of High Performance Computing service, thank you for all you have done.

Many thanks to all past and current members of CG1: Tom Woods, Kathryn Knight, Nick Hughes, Peter Harrisson, Marvis Erhunmwunse, John Dunwell, John Mina, Hazmi Tajuddin, Matt Burton and Jon Sellars for a great time over the past three years and for all the help and support.

I would also like to thank EPSRC and AstraZeneca for their generous financial support.

And most of all, I would like to thank my wife Maria for support during these years. I will always be immensely indebted to her for all the help and inspiration.
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-31G</td>
<td>Pople basis set</td>
</tr>
<tr>
<td>Ac</td>
<td>Acetyl</td>
</tr>
<tr>
<td>acac</td>
<td>acetylacetonate</td>
</tr>
<tr>
<td>Ad</td>
<td>Adamantyl</td>
</tr>
<tr>
<td>Anal</td>
<td>Elemental analysis</td>
</tr>
<tr>
<td>Ar</td>
<td>Aryl</td>
</tr>
<tr>
<td>ASAP</td>
<td>Atmospheric solids analysis probe</td>
</tr>
<tr>
<td>B3LYP</td>
<td>Becke-3 + LYP hybrid functional (method)</td>
</tr>
<tr>
<td>Boc</td>
<td>tert-Butoxycarbonyl</td>
</tr>
<tr>
<td>b.p.</td>
<td>Boiling point</td>
</tr>
<tr>
<td>BPW91</td>
<td>Becke's exchange functional combined with the Perdew and Wang's gradient-corrected correlation functional (method)</td>
</tr>
<tr>
<td>Bu</td>
<td>Butyl</td>
</tr>
<tr>
<td>cc-pVDZ</td>
<td>Correlation-consistent polarized valence double-zeta basis set</td>
</tr>
<tr>
<td>CCSD</td>
<td>Coupled cluster singles doubles</td>
</tr>
<tr>
<td>cm⁻¹</td>
<td>Wavenumbers</td>
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<tr>
<td>COSY</td>
<td>Correlation spectroscopy</td>
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<tr>
<td>d</td>
<td>Doublet (spectral)</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>dd</td>
<td>Doublet of doublets (spectral)</td>
</tr>
<tr>
<td>ddd</td>
<td>Doublet of doublet of doublets (spectral)</td>
</tr>
<tr>
<td>DEAD</td>
<td>Diethyl azodicarboxylate</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>DIAD</td>
<td>Diisopropyl azodicarboxylate</td>
</tr>
<tr>
<td>DIPEA</td>
<td>N,N-Diisopropylethylamine</td>
</tr>
<tr>
<td>DMAP</td>
<td>4-Dimethylaminopyridine</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-Dimethylformamide</td>
</tr>
<tr>
<td>DMPU</td>
<td>1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone</td>
</tr>
<tr>
<td>ds</td>
<td>Diastereoselectivity</td>
</tr>
<tr>
<td>DTBAD</td>
<td>Di-tert-butyl azodicarboxylate</td>
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<tr>
<td>EDA</td>
<td>Ethyl diazoacetate</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>EI</td>
<td>Electron impact</td>
</tr>
<tr>
<td>eq</td>
<td>Equivalent</td>
</tr>
<tr>
<td>Et</td>
<td>Ethyl</td>
</tr>
<tr>
<td>g</td>
<td>Gramme</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas Chromatography / Mass Spectrometry</td>
</tr>
<tr>
<td>GIAO</td>
<td>Gauge-including atomic orbitals (method)</td>
</tr>
<tr>
<td>h</td>
<td>Hour(s)</td>
</tr>
<tr>
<td>HMBC</td>
<td>Heteronuclear shift correlations via multiple bond connectivities</td>
</tr>
<tr>
<td>HMPA</td>
<td>Hexamethylphosphoramide</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>HRMS</td>
<td>High-resolution mass spectrometry</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>IR</td>
<td>Infra red</td>
</tr>
<tr>
<td>J</td>
<td>Coupling constant</td>
</tr>
<tr>
<td>LDA</td>
<td>Lithium diisopropylamide</td>
</tr>
<tr>
<td>lit.</td>
<td>Literature</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>m</td>
<td>Multiplet (spectral)</td>
</tr>
<tr>
<td>M</td>
<td>mol/L</td>
</tr>
<tr>
<td>m/z</td>
<td>Mass-to-charge ratio</td>
</tr>
<tr>
<td>mCPBA</td>
<td>m-Chloroperoxybenzoic acid</td>
</tr>
<tr>
<td>Me</td>
<td>Methyl</td>
</tr>
<tr>
<td>MHz</td>
<td>Megahertz</td>
</tr>
<tr>
<td>min</td>
<td>Minutes</td>
</tr>
<tr>
<td>mmol</td>
<td>Millimole(s)</td>
</tr>
<tr>
<td>m.p.</td>
<td>Melting point</td>
</tr>
<tr>
<td>MP2</td>
<td>Multi-Reference Moller-Plesset</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrometry</td>
</tr>
<tr>
<td>NaHMDS</td>
<td>Sodium hexamethyldisilazide</td>
</tr>
<tr>
<td>NMO</td>
<td>N-Methylmorpholine-N-oxide</td>
</tr>
<tr>
<td>NMP</td>
<td>N-Methyl-2-pyrrolidinone</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>NOE</td>
<td>Nuclear Overhauser effect</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>NOESY</td>
<td>Nuclear Overhauser effect spectroscopy</td>
</tr>
<tr>
<td>Nu</td>
<td>Nucleophile</td>
</tr>
<tr>
<td>pfb</td>
<td>Perfluorobutyrate</td>
</tr>
<tr>
<td>Ph</td>
<td>Phenyl</td>
</tr>
<tr>
<td>ppm</td>
<td>Part(s) per million</td>
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<tr>
<td>q</td>
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<tr>
<td>quin</td>
<td>Quintet (spectral)</td>
</tr>
<tr>
<td>R</td>
<td>Alkyl</td>
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<tr>
<td>$R_f$</td>
<td>Retention factor (for TLC)</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>s</td>
<td>Singlet (spectral)</td>
</tr>
<tr>
<td>TASF</td>
<td>Tris(dimethylamino)sulfonium difluorotrimethylsilicate</td>
</tr>
<tr>
<td>TBAT</td>
<td>Tetrabutylammonium triphenyldifluorosilicate</td>
</tr>
<tr>
<td>TBDMS</td>
<td>tert-Butyldimethylsilyl</td>
</tr>
<tr>
<td>t-Bu</td>
<td>tert-Butyl</td>
</tr>
<tr>
<td>temp</td>
<td>Temperature</td>
</tr>
<tr>
<td>Tes</td>
<td>Triethylsilyl</td>
</tr>
<tr>
<td>Tf</td>
<td>Triflate</td>
</tr>
<tr>
<td>TFA</td>
<td>Trifluoroacetic acid</td>
</tr>
<tr>
<td>tfa</td>
<td>Trifluoroacetate</td>
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<tr>
<td>tfacac</td>
<td>Trifluoroacetylacetonate</td>
</tr>
<tr>
<td>TfOH</td>
<td>Trifluoromethanesulfonic acid</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
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<tr>
<td>TLC</td>
<td>Thin layer chromatography</td>
</tr>
<tr>
<td>TMS</td>
<td>Trimethylsilyl</td>
</tr>
<tr>
<td>TPAP</td>
<td>Tetra-n-propylammonium perruthenate</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>v/v</td>
<td>Volume-to-volume ratio</td>
</tr>
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</table>
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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 alkoxy silenes 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).³⁴ 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.
<table>
<thead>
<tr>
<th>Bond to C</th>
<th>Bond length (Å)</th>
<th>Bond to Si</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>1.54</td>
<td>Si-C</td>
<td>1.89</td>
</tr>
<tr>
<td>C≡C</td>
<td>1.32</td>
<td>Si≡C</td>
<td>1.72</td>
</tr>
<tr>
<td>C-O</td>
<td>1.41</td>
<td>Si-O</td>
<td>1.63</td>
</tr>
<tr>
<td>C-Cl</td>
<td>1.78</td>
<td>Si-Cl</td>
<td>2.05</td>
</tr>
<tr>
<td>C-F</td>
<td>1.39</td>
<td>Si-F</td>
<td>1.60</td>
</tr>
</tbody>
</table>

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). 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.

<table>
<thead>
<tr>
<th>Bond to C</th>
<th>Bond energy (kJ/mol)</th>
<th>Bond to Si</th>
<th>Bond energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>334</td>
<td>Si-C</td>
<td>318</td>
</tr>
<tr>
<td>C≡C</td>
<td>620</td>
<td>Si≡C</td>
<td>490</td>
</tr>
<tr>
<td>C-O</td>
<td>340</td>
<td>Si-O</td>
<td>531</td>
</tr>
<tr>
<td>C-Cl</td>
<td>335</td>
<td>Si-Cl</td>
<td>471</td>
</tr>
<tr>
<td>C-F</td>
<td>452</td>
<td>Si-F</td>
<td>808</td>
</tr>
</tbody>
</table>

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$^+$–C$^-$) and is therefore susceptible to nucleophilic attack at the silicon atom. In particular, silenes (Si$^+$=C$^-$) 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$^{δ+}$–H$^{δ-}$), which allows for Et$_3$SiH to act as a reducing agent.

1.1.5 Nucleophilic Substitution at Silicon

Nucleophilic substitution at silicon could proceed by either an S$_N$2 or an S$_N$1 type mechanism. Although silicon cations are more stable than their carbon analogues, substitution via an S$_N$1 mechanism is very rare because of the very high rate of the competing bimolecular process, sometimes referred to as the S$_N$2–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). \(^{2,4}\)

\[ \text{Ph} \quad \text{Me} \quad \text{Si} \quad \text{Cl} \quad \text{LiEt} \quad \text{Et} \quad \text{Si} \quad \text{Cl} \quad \text{Et} \quad \text{Si} \quad \text{Me} \quad \text{Np} \]

Scheme 1

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

1.1.6 Stabilisation of β-carbocations and α-carbanions

The stabilisation of cations at the carbon atom in a β-position to silicon is a result of the overlap of the vacant p orbital on the β 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 β-carbocations determines the reaction pathway between electrophiles and organosilicon compounds such as allyl-, aryl-, vinyl- silanes and silyl enol ethers.
Silicon also stabilises a carbanion in the α-position. 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).

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\textsuperscript{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](image)

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\textsubscript{3}N, pyridine or imidazole (Scheme 2). More reactive silyl triflates have been used to protect tertiary or hindered secondary alcohols.

![Scheme 2](image)

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,\textsuperscript{7} PdO,\textsuperscript{8} and Pd/C\textsuperscript{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)\textsuperscript{10}. Treatment of \textbf{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.

\textbf{Scheme 3}

\textbf{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 \textbf{14} are generally prepared by quenching enolate anions \textbf{13} with the corresponding silyl chloride (Scheme 4, Eq. 1). However, many other methods for their preparation have been reported, e.g. hydrosilylation of $\alpha,\beta$-unsaturated ketones (Eq. 2),\textsuperscript{6} silyl transfer from trialkylsilyl ketene acetals to ketones (Eq. 3),\textsuperscript{11} 1,2-silyl migration of the copper enolates of acyltriphenylsilanes (Eq. 4).\textsuperscript{12}
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).
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 $\beta$-hydroxy ketones in high yields. The increased stability of carbocations $\beta$ to silicon determines the regioselectivity of the reaction.

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,\textsuperscript{13} hydrosilylation of alkynes\textsuperscript{14} and the coupling of vinylic organometallics with a silyl chloride.\textsuperscript{15} Vinylsilanes react with electrophiles ranging from proton, carbon and main group heteroatoms with high stereoselectivity and regioselectivity.\textsuperscript{3} In the example shown in Scheme 7 the silyl group of ($E$)- and ($Z$)-$\beta$-trimethylsilylstyrene is replaced by deuterium.\textsuperscript{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 \( \beta \)-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.\(^3\)

\[
\begin{align*}
\text{Ph} & \quad \text{H} \\
\swarrow & \quad \searrow \\
\circ & \quad \circ \\
\text{SiMe}_3 & \quad \text{H} \\
\downarrow & \quad \downarrow \\
\text{Ph} & \quad \text{H} \\
\leftarrow & \quad \\
\text{D} & \quad \text{D} \\
\text{D} & \quad \text{D} \\
\end{align*}
\]

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 \( \text{R}_4\text{SiF} \), which is more susceptible to transmetalation with the palladium (II) intermediate resulting from oxidative addition into the aryl iodide.

\[
\begin{align*}
\text{36} & \quad \text{37} \\
\text{2.5 mol %} \ (\eta^3\text{-C}_3\text{H}_5\text{PdCl})_2 & \quad \text{TASF} \\
\end{align*}
\]

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,\textsuperscript{17} Peterson olefination\textsuperscript{18} and metathesis\textsuperscript{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 $\pi$ bond (Figure 4). In general, electrophiles attack the terminal carbon ($\gamma$) of the allylic group regioselectively, although sterically hindered alkyl halides may attack preferentially at the $\alpha$ position.\textsuperscript{3}

![Figure 4](image)

An example reported by Hayashi demonstrates the great potential of allylsilanes in the process of carbon-carbon bond formation (Scheme 9).\textsuperscript{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](image)
### 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.\(^\text{21}\)

![Scheme 10](image)

Arylsilanes react with electrophiles in a process known as *ipso* substitution (Scheme 11).\(^\text{2}\) 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.

![Scheme 11](image)

Recently much attention has been focused on applications of aryl silanes in cross-coupling reactions.\(^\text{22,23}\) 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.\(^\text{24}\) A range of racemic α-bromo esters were cross-coupled with PhSi(OMe)\(_3\) in good yield and enantioselectivity (80 - 99 % ee).
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. The first strong evidence for the existence of a silicon-carbon double bond was established in 1967 by Gusel’nikov and Flowers. 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. 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.
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, 53, 54) formed from this technique are shown in Figure 5.

![Silene Molecule 52](image)

![Silene Molecule 53](image)

![Silene Molecule 54](image)

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\(_5\)H\(_5\)N < 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).

![Silene Molecule 55](image)

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.\textsuperscript{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.

![Figure 7](image)

Alternatively, silene stability may also be increased by $\pi$-electron-donating substituents at the carbon atom of the silene (Figure 8). The substituent effect suppresses the natural $\text{Si}^{\delta-}=\text{C}^{\delta+}$ polarisation effectively and induces the zwitterionic effect, i.e. $\text{Si}^{\delta-}=\text{C}^{\delta+}$.\textsuperscript{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.\textsuperscript{35}

![Figure 8](image)

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).\textsuperscript{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.
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 \(66\).\(^{38}\)

![Scheme 14](image-url)
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). Interestingly, the photolysis of the acylpolysilane 68 gave in only one case (R=Mes, R’=Ad) two possible silene geometrical isomers in detectable amounts. 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.

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). 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\textsubscript{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.
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 \( \alpha \)-silylcarbanion to a ketone (or aldehyde) to form a \( \beta \)-hydroxysilane which eliminates silanolate to form alkenes (Scheme 16).\(^2\) The elimination follows two distinct mechanistic pathways to prepare either \( \textit{cis} \) or \( \textit{trans} \) alkenes depending on the reaction conditions. For example, compound 73 gives the \( \textit{cis} \) product 75 or the \( \textit{trans} \) product 74 depending on whether the elimination is carried out under acidic or basic conditions.
Oehme and co-workers have adapted this methodology to form silenes by replacement of the carbon atom in the nucleophile by a silicon atom. The reaction of silyllithium species with carbonyl compounds generates α-silyloxy anions which are known to undergo spontaneous elimination to form silene (Scheme 17).

Subsequently, Oehme has reported another approach to form silenes via a modified Peterson reaction. The reaction of silyl Grignard reagent with carbonyl compounds generates magnesium alkoxide which, after workup, affords silylalcohols (Scheme 18). Silylalcohols can be readily transformed into silenes 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.
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.\textsuperscript{29} The reaction of adamantanone with bulky silyllithium species \textsuperscript{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.

Ishikawa and co-workers later discovered that silenes could be generated by the addition of methyllithium to acylpolysilanes (Scheme 20).\textsuperscript{45} The resulting α-silyloxy anion \textsuperscript{87} underwent elimination of trimethylsilanolate to afford the silene \textsuperscript{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](image)

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 chlorotritylsilane yielded silene 93 quantitatively (Scheme 21).

![Scheme 21](image)
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\textsubscript{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.\textsuperscript{48} In comparison, the Wolff rearrangement of a silylcarbene 94 to a silylketene 95 requires only silicon-carbon bonds. However, alkoxy carbonyl(trialkylsilanyl)carbenes 98 can undergo both types of rearrangement (Scheme 22).\textsuperscript{48} It has been shown that some substituents on the silicon atom can migrate more easily than the others of the order: H > Me\textsuperscript{49}, SiMe\textsubscript{3} > Me\textsuperscript{50,51,52}, (Me\textsubscript{3}Si)\textsubscript{3}Si > Me\textsuperscript{53}, Ph > Me\textsuperscript{52,54}. Methoxy groups do not migrate at all.\textsuperscript{55}

![Scheme 22](image-url)
Photolysis of methyl (pentamethyldisilanyl)diazoacetate 102 in inert matrices at low temperature allowed the isolation and spectroscopic characterisation of the silaacrylate 103 (Scheme 23).\textsuperscript{56} Short-wavelength irradiation (\textgreater 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.\textsuperscript{48} Addition of methanol at the double bond takes place after warming to \textgreater 35K.

\[
\begin{align*}
\text{Si} & \text{COOEt} \\
\text{N}_2 & \text{SiMe}_3 \\
\text{Me}_2 & \text{Si} \\
\text{SiMe}_3 & \text{COOEt} \\
\text{Me}_2 & \text{Si} \\
\text{SiMe}_3 & \text{OEt} \\
\text{MeOH} & \text{MeOH} \\
\text{hv, } \text{>240nm} & \text{>360nm} \\
\text{Ar, 10K} & \text{10K} \\
\end{align*}
\]

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.\textsuperscript{53,57,58} In some cases, the rearrangement of acylsilene 108 to a silylketene 110 has been observed.\textsuperscript{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. 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). 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.

Similarly, Oehme synthesised various stable silenes by employing similar methodology (Scheme 27). 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.
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’nikov observed such a dimer in the gas phase thermolysis of 1,1-dimethyl-1-silacyclobutane 47 (Section 1.3.1, Scheme 13).
In contrast, Brook-type silenes generally undergo head-to-head dimerisation via a biradical intermediate (Scheme 28). 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.

Scheme 28

Head to head dimerisation has also been observed by Ishikawa with silenes generated via a modified Peterson reaction. 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). However, acylsilenes with sterically more demanding substituents undergo intramolecular [2+2] cyclisation leading to 1,2-silaoxetanes.

![Scheme 30](image)

### 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. 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).
Maas and co-workers have reported the formation of [4+2] cycloadducts during the photolysis of diazo ketones. The acyl silenes generated in this fashion reacted with non-enolisable carbonyl compounds such as benzophenone and crotonaldehyde forming 1,3-dioxo-4-sila-5-cyclohexanes. In contrast, when was reacted with enolisable ketones such as acetone, acetophenone and acetylacetone the corresponding ‘ene’ product was generated (Scheme 32).
Brook and co-workers have demonstrated that α,β-unsaturated aldehydes, ketones and esters usually react in a [4+2] manner with silenes (Scheme 32).  

Scheme 33

The regiochemistry of the addition reaction of a silicon-carbon double bond to an α,β-unsaturated aldehyde, ketone or ester 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. 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. 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).\(^{37,70}\)

\[ \begin{align*}
\text{Me}_3\text{Si} & \quad \text{Me}_3\text{Si} \\
\text{Si} & \quad \text{Me}_3\text{Si} \\
\text{OSiMe}_3 & \quad \text{OSiMe}_3 \\
t-\text{Bu} & \quad (\text{Me}_3\text{Si})_2\text{Si} \\
\text{Ph} & \quad \text{Ph} \\
\text{Me} & \quad \text{Me} \\
\end{align*} \]

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).
It has also been shown by Brook that silenes undergo [2+2] cycloadditions with nonenolisable carbonyl compounds. 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).

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 alkoxy silenes by 1,2-addition (Scheme 37). The regioselectivity of the addition is a result of the polarisation of the silene Si^{δ^+} = C^{δ^-} 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.
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

\[ \text{Scheme 38} \]

\[ \text{R} = \text{Ph, 4-MeOC}_6\text{H}_4, 4-\text{CF}_3\text{C}_6\text{H}_4, 2,6-(\text{MeO})_2\text{C}_6\text{H}_4, \text{CH}_3, \text{t-Bu} \]
\[ \text{dienen: cyclopentadiene, isoprene, } (\text{E})\text{-penta-1,3-diene} \]
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. 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). 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.

![Scheme 39](image)

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).
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$_3$·2AcOH complex to afford the corresponding fluorosilane. The Fleming-Tamao oxidation of the silicon unit with H$_2$O$_2$, 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).

More recently, Sellars has shown that these silene-diene cycloadducts represent convenient sources of silacyclic allylsilanes which can undergo Hosomi-Sakurai reactions. 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 β-silicon substituent (Scheme 42). The fluoride-promoted fragmentation followed by oxidation with H₂O₂ in the presence of KHCO₃ 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). 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.
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 alkoxy silenes undergo a very efficient thermal [2+2] cycloaddition with \(\alpha,\beta\)-unsaturated esters to afford highly substituted silacyclobutanes with a high degree of stereocontrol (Scheme 44). Consequently this requires facile access to suitable acylpolysilanes and electron-deficient alkenes.
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.

In an alternative approach towards milder silene generation, the synthetic potential of $\alpha$-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).
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.
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 alkoxy silenes undergo thermal [2+2] cycloaddition with (2E,4E)-dimethyl hexa-2,4-dienedioate to afford highly substituted silacyclobutanes (Table 4). Interestingly, these adducts are formed as single stereoisomers, although the stereochemistry was not assigned.

\[
\begin{align*}
\text{acylpolysilane} & \quad \text{R} & \quad \text{product} & \quad \text{yield (\%)} \\
1 & 211 & \text{Ph} & 212 & 67 \\
2 & 213 & 4-\text{MeOAr} & 214 & 49 \\
3 & 215 & 4-\text{CF}_3\text{Ar} & 216 & 49 \\
4 & 217 & \text{t-Bu} & 218 & 20
\end{align*}
\]

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 had generated acylpolysilanes by the treatment of tetrakis(trimethylsilyl)silane with methyllithium following a procedure outlined by Gilman. Following this protocol, a solution of tetrakis(trimethylsilyl)silane 219 in THF was treated with methyllithium (Scheme 48). After approximately 24 h, \textsuperscript{1}H NMR spectroscopic analysis showed a signal that corresponded to unreacted tetrakis(trimethylsilyl)silane (\textit{d}_{\text{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.

Evidence confirming the formation of 220 was obtained from the $^{13}$C NMR spectrum, which showed the appearance of a characteristic signal at $\delta_C = 245$ 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%. Similar observations have been made by Brook and co-workers. 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$_3$Si)$_3$SiLi·3THF) and then perform the condensation reaction in a non-polar solvent which leads to fewer side reactions and generally leads to acylnpolysilanes in better yields.

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. 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).
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.

As before, evidence for the formation of acylpolysilanes was confirmed by the $^{13}$C NMR spectrum with the signal at $\delta_{C} = 220$-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 $^1$H NMR spectroscopy. Formation of the latter product was confirmed by analysis of the $^1$H NMR spectrum and MS data, which showed signals at $\delta_{H} = 5.46$ ppm and $\delta_{H} = 5.21$ 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.
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.

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.

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).

\[
\begin{align*}
\text{Ph} & \quad \text{H} \\
\text{228} & \\
& \quad 1. \text{Si(SiMe}_3\text{)}_3\text{MgBr} \\
& \quad 2. \text{Swern oxidation} \\
& \quad \text{no product}
\end{align*}
\]

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 °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.

Scheme 54

All spectroscopic data were consistent with those reported by Griffiths\cite{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 (2E,4E)-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).\cite{87}

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 $\delta_H = 7.33-7.29$ ppm and $\delta_H = 6.21-6.18$ ppm and also signals attributed to the ethoxy protons at $\delta_H = 4.24$ ppm and $\delta_H = 1.31$ 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 °C for 1.5 h. Concentration, followed by
flash column chromatography afforded the product 231, unfortunately also in a low yield (Scheme 56).

\[
\begin{align*}
&\text{t-Bu}^+\text{Si(SiMe}_3\text{)}_3 \quad + \quad \text{CO}_2\text{Et} \quad \text{CO}_2\text{Et} \\
&\quad \xrightarrow{200 \text{ } ^\circ\text{C}} \quad \text{toluene, NMP} \\
&\quad 5\% \quad \text{EtO}_2\text{C} \quad \text{Si(SiMe}_3\text{)}_2 \quad \text{EtO}_2\text{C} \\
&\quad \text{EtO}_2\text{C} \quad \text{t-Bu} \quad \text{OSiMe}_3 \\
&\text{217} \quad \text{230} \quad \text{231}
\end{align*}
\]

Scheme 56

The spectroscopic data were similar to those reported by Griffiths\textsuperscript{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 $\delta_H = 7.10$ ppm and $\delta_H = 6.01$ ppm and also signals attributed to the ring protons at $\delta_H = 2.33$ ppm and $\delta_H = 2.31$ 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\textdegree C – 220\textdegree 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.\textsuperscript{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 pivaloylpolsilane with (2E,4E)-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.

\[

t\text{-BuSi(SiMe}_3\text{)}_3 + \text{CO}_2\text{Et} \quad \rightarrow \quad 231a + 231b + 232a + 232b
\]

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).\(^1\)

![Figure 12](image_url)

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.
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 °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 °C for 3 h (entry 7).

<table>
<thead>
<tr>
<th>entry</th>
<th>temp (°C)</th>
<th>time (h)</th>
<th>diene (eq)</th>
<th>cyclobutane yield (%)</th>
<th>cyclopropane yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(231a:231b)</td>
<td>(232a:232b)</td>
</tr>
<tr>
<td>1</td>
<td>150</td>
<td>4.5</td>
<td>2.3</td>
<td>15 (1.6:1)</td>
<td>11 (2.3:1)</td>
</tr>
<tr>
<td>2</td>
<td>172</td>
<td>2</td>
<td>4</td>
<td>23 (1.5:1)</td>
<td>15 (2.8:1)</td>
</tr>
<tr>
<td>3</td>
<td>172</td>
<td>2</td>
<td>3</td>
<td>18 (1.4:1)</td>
<td>12 (3:1)</td>
</tr>
<tr>
<td>4</td>
<td>180</td>
<td>4</td>
<td>2</td>
<td>9 (2.9:0)</td>
<td>23 (6.4:1)</td>
</tr>
<tr>
<td>5</td>
<td>200</td>
<td>3</td>
<td>0.25</td>
<td>23 (3.9:0)</td>
<td>25 (3.3:1)</td>
</tr>
<tr>
<td>6</td>
<td>200</td>
<td>3</td>
<td>1</td>
<td>16 (1.4:0)</td>
<td>41 (2.7:1)</td>
</tr>
<tr>
<td>7</td>
<td>200</td>
<td>3</td>
<td>4</td>
<td>23 (1.9:0)</td>
<td>46 (2.7:1)</td>
</tr>
<tr>
<td>8</td>
<td>200</td>
<td>4</td>
<td>2</td>
<td>16 (2.2:0)</td>
<td>30 (3.2:1)</td>
</tr>
<tr>
<td>9</td>
<td>200</td>
<td>25</td>
<td>2</td>
<td>7 (3.6:0)</td>
<td>15 (6.1:1)</td>
</tr>
</tbody>
</table>

Table 6
In summary, the desired silacyclobutane 231 was synthesised in \( \leq 23\% \) 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 °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.

\[
\begin{align*}
&\text{t-BuSi(SiMe}_3\text{)}_3 + \\
&\text{CO}_2\text{Me} + \\
&\text{CO}_2\text{Me} \rightarrow \\
&\text{MeO}_2\text{C} \quad \text{Si(SiMe}_3\text{)}_2 \quad \text{MeO}_2\text{C} \\
&\text{MeO}_2\text{C} \quad \text{t-Bu} \\
&\text{4 h, 180 °C} \\
&\text{toluene} \\
&\text{20%}
\end{align*}
\]

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).
2.5.2 Reaction of pivaloylpolysilane with (2\textit{E},4\textit{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 231\textit{a}, 231\textit{b}, 232\textit{a} and 232\textit{b} (Scheme 59). The results are summarised in Table 7.

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 °C for 0.5 h (entry 7).

<table>
<thead>
<tr>
<th>entry</th>
<th>temp (°C)</th>
<th>time (h)</th>
<th>acylpolysilane (mg)</th>
<th>diene (eq)</th>
<th>pyridine (%)</th>
<th>cyclobutanes yield (%), ds (231a:231b)</th>
<th>cyclopropanes yield (%), ds (232a:232b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>160</td>
<td>8</td>
<td>500</td>
<td>1</td>
<td>10</td>
<td>17 (1:0)</td>
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</tr>
<tr>
<td>2</td>
<td>160</td>
<td>0.5</td>
<td>100</td>
<td>4</td>
<td>10</td>
<td>6 (1:4:1)</td>
<td>12 (2.8:1)</td>
</tr>
<tr>
<td>3</td>
<td>190</td>
<td>4.25</td>
<td>300</td>
<td>2.5</td>
<td>5.5</td>
<td>17 (1:0)</td>
<td>35 (3.3:1)</td>
</tr>
<tr>
<td>4</td>
<td>160</td>
<td>0.5</td>
<td>500</td>
<td>4</td>
<td>1</td>
<td>6 (1:1)</td>
<td>6 (3.1:1)</td>
</tr>
<tr>
<td>5</td>
<td>190</td>
<td>4.25</td>
<td>300</td>
<td>2.5</td>
<td>5.5</td>
<td>21 (1:0)</td>
<td>41 (2.7:1)</td>
</tr>
<tr>
<td>6</td>
<td>220</td>
<td>8</td>
<td>500</td>
<td>4</td>
<td>10</td>
<td>-</td>
<td>5 (5:1)</td>
</tr>
<tr>
<td>7</td>
<td>220</td>
<td>0.5</td>
<td>500</td>
<td>1</td>
<td>1</td>
<td>24 (1:0)</td>
<td>38 (3:1)</td>
</tr>
<tr>
<td>8</td>
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<td>8</td>
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<td>1</td>
<td>1</td>
<td>19 (2.9:1)</td>
<td>28 (2.9:1)</td>
</tr>
<tr>
<td>9</td>
<td>220</td>
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<td>23 (1:0)</td>
<td>37 (3.1:1)</td>
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<td>10</td>
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<td>250</td>
<td>3</td>
<td>0</td>
<td>7 (3.5:1)</td>
<td>20 (3:1)</td>
</tr>
</tbody>
</table>

*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 \text{R}^1 \text{Si(SiMe}_3\text{)}_3 + B \text{R}^2 \text{C} = \text{CH} \text{R}^3 \overset{}{\rightarrow} C \text{Si(SiMe}_3\text{)}_2 \text{R}^3 \text{OSiMe}_3 + D \text{Me}_3\text{Si} \text{R}^1 \text{O}_2\text{SiMe}_3

<table>
<thead>
<tr>
<th>entry</th>
<th>A</th>
<th>B</th>
<th>method\textsuperscript{a}</th>
<th>product, yield (%)</th>
<th>ds\textsuperscript{b}</th>
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<tr>
<td></td>
<td>\text{R}^1</td>
<td>\text{No}</td>
<td>\text{R}^2</td>
<td>\text{R}^3</td>
<td>\text{No}</td>
</tr>
<tr>
<td>1</td>
<td>\text{t-Bu}</td>
<td>217</td>
<td>\text{CH}=\text{CHCO}_2\text{Et}</td>
<td>\text{CO}_2\text{Et}</td>
<td>230</td>
</tr>
<tr>
<td>2</td>
<td>\text{t-Bu}</td>
<td>217</td>
<td>\text{CO}_2\text{Me}</td>
<td>\text{CO}_2\text{Me}</td>
<td>234</td>
</tr>
<tr>
<td>3</td>
<td>\text{t-Bu}</td>
<td>217</td>
<td>\text{CH}=\text{CHMe}</td>
<td>\text{CO}_2\text{Et}</td>
<td>236</td>
</tr>
<tr>
<td>4</td>
<td>\text{t-Bu}</td>
<td>217</td>
<td>\text{Ph}</td>
<td>\text{CO}_2\text{Me}</td>
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</tr>
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<td>\text{Ph}</td>
<td>\text{NO}_2</td>
<td>240</td>
</tr>
<tr>
<td>6</td>
<td>\text{t-Bu}</td>
<td>217</td>
<td>\text{Ph}</td>
<td>\text{CN}</td>
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<td>\text{t-Bu}</td>
<td>217</td>
<td>\text{H}</td>
<td>\text{CO}_2\text{Me}</td>
<td>244</td>
</tr>
<tr>
<td>8</td>
<td>\text{Ph}</td>
<td>211</td>
<td>\text{CH}=\text{CHMe}</td>
<td>\text{CO}_2\text{Et}</td>
<td>236</td>
</tr>
<tr>
<td>9</td>
<td>\text{Ph}</td>
<td>211</td>
<td>\text{CH}=\text{CHCO}_2\text{Et}</td>
<td>\text{CO}_2\text{Et}</td>
<td>230</td>
</tr>
<tr>
<td>10</td>
<td>\text{Ph}</td>
<td>211</td>
<td>\text{CO}_2\text{Me}</td>
<td>\text{CO}_2\text{Me}</td>
<td>234</td>
</tr>
<tr>
<td>11</td>
<td>\text{Ph}</td>
<td>211</td>
<td>\text{Ph}</td>
<td>\text{CO}_2\text{Me}</td>
<td>238</td>
</tr>
<tr>
<td>12</td>
<td>4-MeOC\text{C}_6\text{H}_4</td>
<td>213</td>
<td>\text{CH}=\text{CHCO}_2\text{Et}</td>
<td>\text{CO}_2\text{Et}</td>
<td>230</td>
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<tr>
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<td>\text{Ph}</td>
<td>\text{CO}_2\text{Me}</td>
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<tr>
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<td>213</td>
<td>\text{Ph}</td>
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<td>238</td>
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<tr>
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<tr>
<td>24</td>
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<td>220</td>
<td>\text{Ph}</td>
<td>\text{CO}_2\text{Me}</td>
<td>238</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Method A involved heating a solution of the starting materials in benzene at 200 °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 °C. In parentheses required time is given to achieve complete conversion of acylpolysilane. \textsuperscript{b}Diastereoselectivity of the reaction was determined by \textsuperscript{1}H NMR spectroscopy. \textsuperscript{c}GC-MS showed formation of 12 adducts. \textsuperscript{d}Product unstable. \textsuperscript{e}[4+2] cycloaddition product (Scheme 60).
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/CHCl₃ gave crystals suitable for X-ray diffraction (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. The reasons for this difference in reaction outcome following these two approaches to silene generation are not obvious and still remain an open question.
Whilst for the reaction of pivaloyl polysilane and diethyl hexadienoate, it was initially found that by running the reaction at higher temperature (220 °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. Of these, a reaction studied by Ishikawa and co-workers appeared to be the most relevant to these results (Scheme 61). Here, a mixture of pivaloyl polysilane and tert-butylacetylene was heated in a sealed tube at 140 °C for 24 h, to afford cyclobutene 261 in 94% yield. However, when silacyclobutene 261 was heated at 250 °C cyclopropane 262 was isolated exclusively.

![Scheme 61](image)

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).
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 °C (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.

![Image of 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. 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.
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).
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.
To circumvent the problem of isomerisation of the double bond, trimethylecetyltrimethylsilylsilane 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 trimethylecetyltrimethylsilylsilane 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.\textsuperscript{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.
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). The formation of the dimer was confirmed by analysis of the $^1$H NMR spectrum, which showed peaks at $\delta_H = 0.42$ (18H), $\delta_H = 0.08$ (18H) and $\delta_H = -0.25$ (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.

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).
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 $\delta_H = 4.27$ ppm and $\delta_H = 3.09$ 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). Gordon studied the mechanism of ring opening of silacyclobutanes under thermolysis conditions (Figure 16). 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 (pathway B). However, it is very likely that pathway involving Si-C bond cleavage and concerted pathway C also operate under thermolysis conditions as all transition states have similar energies.

![Figure 16](image-url)
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.

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.

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

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 Bu₃SnH 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).
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 °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.

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.
The formation of silacyclobutene was investigated through quantum mechanical calculation by Ishikawa on a simple model presented in Scheme 77. 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.

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-OSiMe₃ migration, which is promoted by high temperatures, and subsequent ring contraction to form the three-membered cyclic system 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).\(^{93}\)

![Scheme 79](image)

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.

\[
\begin{align*}
R_2SiF_2 & \xrightarrow{X^-} [R \text{Si}^{\text{II}}F_2]^- \\
306 & \xrightarrow{H_2O_2} [R \text{Si}^{III}F_2]^- \\
307 & \xrightarrow{-H_2O} [R \text{Si}^{IV}F_2]^- \\
308 & \xrightarrow{} [R \text{Si}^{IV}F_2]^- \\
309 & \xrightarrow{} [R \text{Si}^{III}F_2]^- \\
310 & \xrightarrow{2 \text{ROH}} [R \text{Si}^{II}F_2]^- \text{ROH}
\end{align*}
\]

\(X = F^-, \text{DMF, HMPA}\)

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).

\[
\begin{align*}
\text{aryl} & \xrightarrow{E^+} [\text{aryl} \text{Si}^{III}E]^- \\
41 & \xrightarrow{Nu^-} [\text{aryl} \text{Si}^{III}E]^- \xrightarrow{-\text{PhE}} [\text{aryl} \text{Si}^{III}E]^- \xrightarrow{R'\text{CO}_2H} [\text{aryl} \text{Si}^{III}E]^- \\
312 & \xrightarrow{} [\text{aryl} \text{Si}^{III}E]^- \xrightarrow{} [\text{aryl} \text{Si}^{III}E]^- \xrightarrow{} [\text{aryl} \text{Si}^{III}E]^- \\
313 & \xrightarrow{} [\text{aryl} \text{Si}^{III}E]^- \xrightarrow{} [\text{aryl} \text{Si}^{III}E]^- \xrightarrow{} [\text{aryl} \text{Si}^{III}E]^- \\
314 & \xrightarrow{\text{hydrolysis}} 3 \text{ROH}
\end{align*}
\]

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$_2$O 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

![Scheme 82](image)

**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.

<table>
<thead>
<tr>
<th>entry</th>
<th>time (h)</th>
<th>temp (°C)</th>
<th>solvent</th>
<th>reagent</th>
<th>outcome</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>reflux</td>
<td>THF/MeOH</td>
<td>KF, KHCO$_3$, H$_2$O$_2$</td>
<td>intractable mixture</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>RT</td>
<td>THF/MeOH</td>
<td>KF, KHCO$_3$, H$_2$O$_2$</td>
<td>intractable mixture</td>
</tr>
<tr>
<td>3</td>
<td>0.75</td>
<td>RT</td>
<td>DCM</td>
<td>BF$_3$·2AcOH</td>
<td>intractable mixture</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>RT</td>
<td>DCM</td>
<td>BF$_3$·Et$_2$O</td>
<td>intractable mixture</td>
</tr>
</tbody>
</table>

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 AlCl₃ 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](image)

It was suggested that problems encountered with the oxidation are associated with the OSiMe₃ 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 (H₂O₂, KF, KHCO₃) 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 BF₃•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 OSiMe₃ group by a fluoride ion. In addition, ¹⁹F NMR spectroscopy indicated the presence of a fluorine atom.
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 BF₃•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).
Disappointingly, attempts to extend this protocol to other silylcyclopropanes resulted in only low yields of the intermediate difluorosilane accompanied by extensive decomposition (Table 11).

$$\text{BF}_3 \cdot 2\text{AcOH} \quad \text{toluene}$$

$$\text{SiMe}_3$$

<table>
<thead>
<tr>
<th>entry No</th>
<th>cyclopropane</th>
<th>fluorosilane$$^a$$</th>
<th>difluorosilane$$^b$$</th>
<th>yield (%)</th>
<th>product</th>
<th>yield (%)</th>
<th>product</th>
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<tr>
<td>1</td>
<td>232</td>
<td>t-Bu</td>
<td>CO$_2$Et</td>
<td>95</td>
<td>324</td>
<td>18</td>
<td>325</td>
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<tr>
<td>2</td>
<td>239</td>
<td>t-Bu</td>
<td>Ph</td>
<td>97</td>
<td>326</td>
<td>trace</td>
<td>327</td>
</tr>
<tr>
<td>3</td>
<td>250</td>
<td>4-OMeC$_6$H$_4$</td>
<td>Ph</td>
<td>98</td>
<td>328</td>
<td>trace</td>
<td>329</td>
</tr>
</tbody>
</table>

$$^a$$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,$^9$ 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).

$$\text{Ph}$$

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.
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 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 (R = 4-MeOC₆H₄) could be isolated suggesting that the reaction occurs according to the Tamao mechanism.

Table 12

<table>
<thead>
<tr>
<th>entry</th>
<th>cyclopropane</th>
<th>fluorosilane</th>
<th>diketone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No</td>
<td>R¹</td>
<td>R²</td>
</tr>
<tr>
<td>1</td>
<td>248</td>
<td>Ph</td>
<td>OMe</td>
</tr>
<tr>
<td>2</td>
<td>251</td>
<td>CH₃</td>
<td>OMe</td>
</tr>
<tr>
<td>3</td>
<td>239</td>
<td>t-Bu</td>
<td>OMe</td>
</tr>
<tr>
<td>4</td>
<td>250</td>
<td>4-MeOC₆H₄</td>
<td>OMe</td>
</tr>
<tr>
<td>5</td>
<td>258</td>
<td>4-CF₃C₆H₄</td>
<td>OMe</td>
</tr>
<tr>
<td>6</td>
<td>259</td>
<td>2-furyl</td>
<td>OMe</td>
</tr>
<tr>
<td>7</td>
<td>254</td>
<td>4-MeOC₆H₄</td>
<td>NEt₂</td>
</tr>
</tbody>
</table>

*Fluorosilane 338 not stable to silica gel and used directly in oxidation without purification

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.

\[
\begin{array}{c}
\text{Ph} \quad \text{Ph} \\
\text{O} & \text{R}^2 \\
\text{O} & \text{O}
\end{array}
\xrightarrow{\text{BF}_3\cdot 2\text{AcOH then MCPBA, KF}}
\begin{array}{c}
\text{R}_1 \\
\text{O} & \text{R}^2
\end{array}
\]

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 N₂ from α-silyl diazo compounds is usually achieved photochemically or thermally (Scheme 89). Transition metal catalysis, especially by copper (CuOTf, CuSO₄, CuCl), rhodium (Rh₂(OAc)₄, Rh₂(pfb)₄) and palladium (Pd(OAc)₂, PdCl₂(CH₃CN)₂) 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](image-url)
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.

![Diagram of reaction](image)

<table>
<thead>
<tr>
<th>entry</th>
<th>No</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>∆E_{352-354} (kcal/mol)</th>
<th>∆E_{353-354} (kcal/mol)</th>
<th>∆E_{354-355} (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>a</td>
<td>O</td>
<td>-SiH₃</td>
<td>-CH₃</td>
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<td>49.6</td>
<td>-9.1</td>
</tr>
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<td>2</td>
<td>b</td>
<td>O</td>
<td>-SiH₃</td>
<td>-NH₂</td>
<td>-22.0</td>
<td>53.9</td>
<td>13.1</td>
</tr>
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<td>-OCH₃</td>
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<td>58.5</td>
<td>22.5</td>
</tr>
<tr>
<td>4</td>
<td>d</td>
<td>O</td>
<td>-SiH₃</td>
<td>-SCH₃</td>
<td>-30.7</td>
<td>57.1</td>
<td>-2.9</td>
</tr>
<tr>
<td>5</td>
<td>e</td>
<td>S</td>
<td>-SiH₃</td>
<td>-CH₃</td>
<td>-23.8</td>
<td>11.8</td>
<td>-11.8</td>
</tr>
<tr>
<td>6</td>
<td>f</td>
<td>S</td>
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<td>-NH₂</td>
<td>-22.9</td>
<td>24.6</td>
<td>8.6</td>
</tr>
<tr>
<td>7</td>
<td>g</td>
<td>S</td>
<td>-SiH₃</td>
<td>-OCH₃</td>
<td>-31.1</td>
<td>29.8</td>
<td>11.6</td>
</tr>
<tr>
<td>8</td>
<td>h</td>
<td>S</td>
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<td>-SCH₃</td>
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<td>18.9</td>
<td>-5.5</td>
</tr>
<tr>
<td>9</td>
<td>i</td>
<td>NH</td>
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<td>-NH₂</td>
<td>-22.4</td>
<td>40.3</td>
<td>7.5</td>
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<tr>
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<td>-OMe</td>
<td>-NH₂</td>
<td>-28.8</td>
<td>55.4</td>
<td>15.2</td>
</tr>
</tbody>
</table>

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 –CH₃ and –SCH₃ 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 –NH₂ and –OCH₃ 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](image)

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, SiH₃, NH₂ and NH groups can be replaced with SiMe₃, NMe₂ 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. 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.
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.\textsuperscript{103} This involves treatment of allyl silane 6 in DCM with triflic acid (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.
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 $\delta_C = 118.5$ ppm ($^1J_{C-F} = 315.7$Hz) and a signal attributed to the Si(CH$_3$)$_3$ carbons at $\delta_C = -0.7$ 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 $^1$H NMR spectrum, which showed a band at 2092 cm$^{-1}$ corresponding to the diazo group and a signal at $\delta_H = 4.96$ ppm arising from the $\alpha$ proton.

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 $\alpha$-silyl diazo carbonyl compound 360 in 34% yield, with a significant amount of impurities also observed.
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 \(^1\)H NMR spectrum clearly indicated the disappearance of the signal attributed to the α-proton at \(\delta_H = 9.63\) ppm and the appearance of a signal corresponding to Si(SiMe\(_3\))\(_3\) group at \(\delta_H = 0.24\) 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).

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.
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 \(\delta_H = 0.23\) ppm in the \(^1\)H 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.

![Scheme 97](image)

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).
Table 14

It appears that some catalysts (Pd(acac)₂, Rh₂(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 °C to afford carbene 376 which underwent a simple O-H insertion reaction with methanol in 96% yield.

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 °C) in the case of the copper catalyst led to the formation of complex mixture of products (entry 3).
Table 15

Subsequently, photochemical and thermal extrusion of N₂ 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).

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

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 \(\delta_{\text{Si}} = 9.0\ \text{ppm}, \delta_{\text{Si}} = 3.8\ \text{ppm}, \delta_{\text{Si}} = -18.1\ \text{ppm}\) and \(\delta_{\text{Si}} = -18.2\ \text{ppm}\) attributed to the Si-OH silicon, \(\alpha\)-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 \(m/z = 373\ [\text{M+Na}]^+\).

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.

![Scheme 102](image)

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 \(^1\)H NMR spectrum showed two signals for the TMS group at \(\delta_H = 0.26\) ppm (9H) and \(\delta_H = 0.25\) 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.
Formation of 384 was confirmed by analysis of the $^1$H NMR and MS data, which showed a peak at $\delta_{\text{H}} = 3.59$ 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).

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.
Since the intermediate product has a longer lifetime at lower temperatures all the NMR spectra were recorded at -80 °C.

Table 17

The $^{29}$Si NMR spectrum showed a signal at $\delta_H = 35.6$ 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).$$^{108}$$

\[ \text{MeSiMe}_3 \quad \text{O} \quad \text{N}_2 \quad \text{R} \quad 107 \]

\[ \text{hv} \quad \text{R=Ad} \quad \text{R=Me} \]

\[ \text{MeSiMe}_3 \quad \text{N} \quad \text{MeSiMe}_3 \]

\[ 38.2 \text{ ppm} \quad 107.0 \text{ ppm} \quad 170.0 \text{ ppm} \]

\[ \text{MeSiMe}_3 \quad \text{Si} \quad \text{Me} \quad \text{Si} \quad \text{Me} \quad \text{Si} \quad \text{Me} \quad \text{Si} \quad \text{Me} \]

\[ 103.9 \text{ ppm} \quad 7.8 \text{ ppm} \quad 184.2 \text{ ppm} \]

\[ \text{Scheme 105} \]
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\textsuperscript{109} and 389\textsuperscript{110}).

![Comparison of NMR shifts for compounds 385, 386, and 389.](image)

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.\textsuperscript{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.
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

Table 18

<table>
<thead>
<tr>
<th>Method</th>
<th>NMR</th>
<th>$^1$H</th>
<th>$^{13}$C</th>
<th>$^{29}$Si</th>
</tr>
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<td><strong>Silene 382</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>B3LYP/6-31G(d,p)</td>
<td>$^{1}$H 4.1 (CH$_2$), 1.3 (CH$_3$),</td>
<td>167.5 (C=O),</td>
<td>15.2 (CH$_3$),</td>
<td>246.2 (Si=C), 7.2/2.3/-</td>
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<td></td>
<td>$^{13}$C 0.3/0.3/0.2 (Si(C$_2$H$_5$)),</td>
<td>157.4 (Si=C),</td>
<td>3.5/2.7/1.3 (Si(CH$_3$))</td>
<td>1.2 (Si(CH$_3$)$_3$)</td>
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<td></td>
<td>$^{29}$Si 0.4/0.3/0.2 (Si(C$_2$H$_5$)),</td>
<td>60.5 (CH$_2$),</td>
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<tr>
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</tr>
<tr>
<td><strong>Oxasilete 385</strong></td>
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<td></td>
</tr>
<tr>
<td>B3LYP/6-31G(d,p)</td>
<td>$^{1}$H 4.3 (CH$_2$), 1.2 (CH$_3$),</td>
<td>157.4 (C-4),</td>
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<td>73.1 (SiO), -7.1/-7.1 (SiSi)</td>
</tr>
<tr>
<td></td>
<td>$^{13}$C 63.3 (C-3), 61.5 (CH$_2$),</td>
<td>1.4/-1.4/-1.4 (Si(CH$_3$))</td>
<td>(CH$_3$)$_3$,</td>
<td>-11.8 (CSi(CH$_3$)$_3$)</td>
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<td>71.6 (SiO),</td>
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<tr>
<td></td>
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<td>-9.0/-9.0 (SiSi)</td>
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<tr>
<td><strong>Dimer 390</strong></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>B3LYP/6-31G(d,p)</td>
<td>$^{1}$H 4.1 (CH$_2$), 1.3 (CH$_3$),</td>
<td>162.4 (C-4),</td>
<td>15.8 (CH$_3$),</td>
<td>43.8 (SiO), -7.4/-6.8 (SiSi)</td>
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<td></td>
<td>$^{13}$C 65.2 (C-3), 62.9 (CH$_2$),</td>
<td>1.3/-0.7/-1.5 (Si(CH$_3$))</td>
<td>1.2 (SiSi),</td>
<td>-12.4 (CSi(CH$_3$)$_3$)</td>
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<tr>
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<td>71.6 (SiO),</td>
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<tr>
<td><strong>Table 18</strong></td>
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</table>

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 ($\delta_C = 65.2$ ppm) and C-4 ($\delta_C = 162.4$ ppm) are only slightly different from the corresponding experimental values (C-3 $\delta_C = 67.0$ ppm; C-4 $\delta_C = 161.1$ 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 $\pi$-acceptor substituent at $C$ (Scheme 106).

![Scheme 106](image)

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 $^1$H NMR spectroscopy by monitoring the change in integral for the methylene signal of the ethyl group (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$_3$N and pyridine significantly increase the rate of oxasiletet ketene rearrangement. Therefore, it was suggested that this rearrangement is promoted by weak nucleophiles and could involve a bimolecular process (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.
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. 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.
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).
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 $\delta_H = 3.45$ ppm. The formation of adduct 398 with acetophenone can most easily be detected from the presence of a pair of doublets at $\delta_H = 4.88$ ppm ($J = 2.8$Hz) and $\delta_H = 4.40$ ppm ($J = 2.8$Hz), 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 $\alpha,\beta$-unsaturated compounds was found in the $^{13}$C NMR spectrum where signals corresponding to the C-6 carbon were observed at around $\delta_C = 150$ ppm and to C-5 at around $\delta_C = 105$ 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.

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).
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.
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).
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 oxasilet e $415$ 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 oxasilet e $415$ is reversible. The transition states for all transformations are shown in Figure 24.
Unfortunately, these calculations did not provide any obvious reasons as to why extrusion of N₂ 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.

Figure 24
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.

![Figure 25](image-url)

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.
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.

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 \((i\text{-Pr})_3\text{Si}\) 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 °C 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](image)

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 \((i\text{-Pr})_3\text{Si}\) group. Evidence for the formation of the oxasilete 424 was obtained from the \(^{13}\text{C}\) and \(^{29}\text{Si}\) NMR spectra. Compound 424 shows two characteristic signals in its \(^{13}\text{C}\) NMR spectrum corresponding to the vinylic carbons at \(\delta_C = 160.9\) ppm and \(\delta_C = 70.3\) ppm. In addition \(^{29}\text{Si}\) NMR shows a signal attributed to the ring silicon at \(\delta_{\text{Si}} = 42.3\) 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 \(\text{trans}\)-chalcone 257 gave the expected [4+2] cycloadduct (Scheme 114). This, however, was unstable to purification by flash column chromatography.
The formation of the adduct 425 with trans-chalcone can most easily be detected from the presence of a pair of doublets at $\delta_H = 5.91$ ppm ($J = 9.2$Hz) and $\delta_H = 4.79$ ppm ($J = 9.2$Hz) 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 $\alpha$-silyl substituted diazo esters leads to a silylcarbene, which readily undergoes transformation into 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 $\alpha,\beta$-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.
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](image)

The alcohol 436 was prepared according to the literature procedure which involved deconjugation of commercially available ethyl sorbate 438 followed by reduction (Scheme 117). 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 \(\delta_H = 6.33\) ppm (ddd), \(\delta_H = 5.14\) ppm (d) and \(\delta_H = 5.02\) ppm (d) corresponding to the protons of the terminal double bond.
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).

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. 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.
Further examination of the literature revealed a report by Lepore describing the rapid coupling of crowded alcohols in the Mitsunobu reaction. 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, alcohol 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). 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.

\[
\begin{align*}
\text{Scheme 122} \\
\text{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\(^+\)).}
\end{align*}
\]
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 $\delta_H = 10.82$ ppm and the disappearance of the ester signal at $\delta_H = 3.89$ 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 $\delta_C = 241.6$ 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 $\delta_H = 5.47$ ppm ($J = 4.2$Hz) for the $\text{CHOH}$ group and a doublet for the hydroxyl group at $\delta_H = 1.81$ ppm ($J = 4.2$Hz). 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
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 \( \text{OSiMe}_3 \) group.

It was speculated that the presence of an additional electron-donating substituent on the aromatic ring would encourage elimination of \( \text{LiOSiMe}_3 \), 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 d₈-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 $\delta_H = 6.09$ ppm and $\delta_H = 5.73$ ppm attributed 3-$H$ and 4-$H$ respectively. The vicinal coupling $J = 10.5$Hz between those two protons indicates their 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 \textit{exo} and \textit{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 °C for 1 h (entry 4).

<table>
<thead>
<tr>
<th>entry</th>
<th>method</th>
<th>solvent</th>
<th>temp. (°C)</th>
<th>time (h)</th>
<th>yield (%)</th>
<th>ds</th>
<th>recovery of 23 (%)</th>
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<tbody>
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<td>flask</td>
<td>PhH</td>
<td>110</td>
<td>12</td>
<td>28</td>
<td>2.7:1</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>microwave</td>
<td>PhH</td>
<td>150</td>
<td>1</td>
<td>29</td>
<td>2.7:1</td>
<td>52</td>
</tr>
<tr>
<td>3</td>
<td>microwave</td>
<td>PhH</td>
<td>180</td>
<td>0.83</td>
<td>77</td>
<td>2.7:1</td>
<td>5</td>
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<tr>
<td>4</td>
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<td>PhH</td>
<td>180</td>
<td>1</td>
<td>81</td>
<td>2.7:1</td>
<td>-</td>
</tr>
</tbody>
</table>

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 (R¹, R², X and n) on the subsequent silene cycloaddition reaction (Figure 27).

![Figure 27](image)

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 ¹³C NMR spectrum with a signal at δ_C = 245-230 ppm characteristic of the acylpolysilane carbonyl group.


\[ \text{ester} + \text{R'}OH \rightarrow \text{alcohol} \]

<table>
<thead>
<tr>
<th>entry</th>
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<th>alcohol</th>
<th>Step A</th>
<th>Step B</th>
<th>Step C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No</td>
<td>R</td>
<td>No</td>
<td>yield (%)</td>
<td>No</td>
</tr>
<tr>
<td>1</td>
<td>463</td>
<td>5-Cl</td>
<td>436</td>
<td>464</td>
<td>78</td>
</tr>
<tr>
<td>2</td>
<td>467</td>
<td>3-Me</td>
<td>436</td>
<td>468</td>
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<td>471</td>
<td>4-I</td>
<td>436</td>
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<td>84</td>
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<td>476</td>
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</tr>
<tr>
<td>5</td>
<td>435</td>
<td>H</td>
<td>479</td>
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<td>4-OMe</td>
<td>479</td>
<td>482</td>
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</tr>
<tr>
<td>7</td>
<td>435</td>
<td>H</td>
<td>484</td>
<td>485</td>
<td>54(^c)</td>
</tr>
</tbody>
</table>

\(^{a}\)PPh\(_{3}\), DEAD, THF, RT, 20 min. \(^{b}\)LiOH, THF/H\(_2\)O, 50 °C, 30 h. \(^{\text{c1}}\) (COCl\(_2\), DMF, DCM, 0 °C, 3 h; 2) Si(SiMe\(_3\))\(_3\)K, THF, -78 °C, 3 h. \(^{\text{d1}}\)Sigmatropic rearrangement product 492 isolated in 56%; see Scheme 129. \(^{\text{e1}}\)Mixture of isomers EZ:EE 86:14.

Table 21

The methyl esters used in the synthesis and (2E,4E)-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.\(^{116}\)
As can be seen from Table 21, the reaction of carboxylic acid 473 with silylpotassium 221 failed to produce the corresponding 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).
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 $\delta_H = 7.64$ ppm and $\delta_H = 6.45$ ppm. In addition, the $^1$H NMR spectrum showed a doublet for the methyl group at $\delta_H = 1.33$ 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](image)

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 ($J_{3H-4H} = 15.4$ Hz, $J_{5H-6H} = 15.4$ 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).

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).

<table>
<thead>
<tr>
<th>entry</th>
<th>conditions</th>
<th>Step 1</th>
<th>Step 2</th>
<th>outcome</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mg, 24 h at reflux</td>
<td>CO₂, 30 min at RT</td>
<td>starting material</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Rieke Mg, 24 h at reflux</td>
<td>CO₂, 30 min at RT</td>
<td>starting material</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>n-BuLi, 30 min at -78 °C</td>
<td>CO₂, 30 min at RT</td>
<td>product 503+504</td>
<td></td>
</tr>
</tbody>
</table>

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). However, the reaction with n-BuLi gave a mixture of products 503 and 504 (503:504-18:1) which arose from ortholithiation of 499 (Scheme 132).

![Scheme 132](image)

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

![Figure 28](image)

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.
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 \( \delta_H = 7.80-7.79 \) ppm and \( \delta_H = 7.36-7.35 \) ppm attributed to the tosyl group.

<table>
<thead>
<tr>
<th>entry</th>
<th>base</th>
<th>solvent</th>
<th>conditions</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>KOH</td>
<td>DMF</td>
<td>24 h at 65 °C</td>
<td>starting material</td>
</tr>
<tr>
<td>2</td>
<td>NaH</td>
<td>DMF</td>
<td>6 h at RT then 24 h at 65 °C</td>
<td>13(^a)</td>
</tr>
<tr>
<td>3</td>
<td>NaHMDS</td>
<td>DMF</td>
<td>24 h at RT then 24 h at 65 °C</td>
<td>starting material</td>
</tr>
<tr>
<td>4</td>
<td>LDA</td>
<td>THF</td>
<td>15 min at -78 °C then 24 h at RT</td>
<td>starting material</td>
</tr>
<tr>
<td>5</td>
<td>( n )-BuLi</td>
<td>THF</td>
<td>15 min at -78 °C then 24 h at RT</td>
<td>starting material</td>
</tr>
<tr>
<td>6</td>
<td>( n )-BuLi + HMPA</td>
<td>THF</td>
<td>15 min at -78 °C then 24 h at RT</td>
<td>starting material</td>
</tr>
</tbody>
</table>

\(^a\)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).
4.3.2.2 Cycloaddition

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

<table>
<thead>
<tr>
<th>entry</th>
<th>R</th>
<th>R¹</th>
<th>acylpolysilane</th>
<th>time (min)</th>
<th>product</th>
<th>yield (%)</th>
<th>ds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-OMe</td>
<td>H</td>
<td>458</td>
<td>15</td>
<td>511</td>
<td>not stable</td>
<td>2:1</td>
</tr>
<tr>
<td>2</td>
<td>5-Cl</td>
<td>H</td>
<td>466</td>
<td>75</td>
<td>512</td>
<td>60</td>
<td>2.7:1</td>
</tr>
<tr>
<td>3</td>
<td>3-Me</td>
<td>H</td>
<td>470</td>
<td>90</td>
<td>513</td>
<td>87</td>
<td>3.7:1</td>
</tr>
<tr>
<td>4</td>
<td>4,5-fused phenyl</td>
<td>H</td>
<td>478</td>
<td>75</td>
<td>514</td>
<td>75</td>
<td>2.2:1</td>
</tr>
<tr>
<td>5</td>
<td>H</td>
<td>CH₃</td>
<td>487</td>
<td>60</td>
<td>515</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 24

Importantly, in all cases the main diastereoisomer possesses the same stereochemistry as that observed during earlier experiments with acyl polysilane 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. 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.

![Scheme](image)

In general four different products 521, 522, 523 and 524 could be obtained by varying the reaction conditions. Entry 1 describes the conversion of acylopolsilane 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 $^1$H NMR spectrum, which showed a new signal at $\delta_H$ = 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

<table>
<thead>
<tr>
<th>entry</th>
<th>conditions</th>
<th>product 524 yield (%)</th>
<th>ds</th>
<th>product 522 and 523 yield (%)</th>
<th>ratio 522:523</th>
<th>product 521 yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16 h at -78 °C</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>42</td>
</tr>
<tr>
<td>2</td>
<td>1 h at -78 °C then 16 h at -20 °C addition of MeLi LiBr at -78 °C, then 6 h at -20 °C and 16 h at 10 °C</td>
<td>32</td>
<td>2.5:1</td>
<td>29</td>
<td>1:1</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>-78 °C, then 6 h at -20 °C and 16 h at 10 °C</td>
<td>57</td>
<td>2.5:1</td>
<td>12</td>
<td>25:1</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>30 min at -78 °C then 16 h at RT</td>
<td>38</td>
<td>2.3:1</td>
<td>17</td>
<td>1:0</td>
<td>-</td>
</tr>
</tbody>
</table>

*Products inseparable by flash column chromatography.*

Table 25
was confirmed by analysis of the $^1$H NMR spectrum, which showed a signal at $\delta_{H} = 3.65$ ppm for the $H$-Si proton and a signal at $\delta_{H} = 2.02$ 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 $\delta_{H} = 3.06$ ppm ($d, J = 7.7$Hz) and $\delta_{H} = 1.41$ ppm ($q, J = 7.7$Hz) 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 $^\circ$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 $\delta_{H} = 6.15$ ppm and $\delta_{H} = 5.63$ ppm corresponding to the vinyl protons. The configuration of the major diastereoisomer was assigned on the basis of 2D correlation NMR experiments (Figure 30).
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](image)

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 °C for 24 h.

<table>
<thead>
<tr>
<th>entry</th>
<th>conditions</th>
<th>outcome</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>mCPBA, KF, DMF, 22 h at RT then 24 h at 60 °C</td>
<td>starting material decomposed upon heating at 60 °C</td>
</tr>
<tr>
<td>2</td>
<td>BF₃·2AcOH, DCM, 20 min at RT</td>
<td>intractable mixture</td>
</tr>
<tr>
<td>3</td>
<td>BF₃·2AcOH, DCM, 4 h at -78 °C</td>
<td>intractable mixture</td>
</tr>
<tr>
<td>4</td>
<td>TFA, KHF₂, DCM, 10 min at RT</td>
<td>product 532</td>
</tr>
<tr>
<td>5</td>
<td>TFA, KHF₂, DCM, 6 h at RT</td>
<td>intractable mixture</td>
</tr>
<tr>
<td>6</td>
<td>1) TFA, KHF₂, DCM, 10 min at RT</td>
<td>intractable mixture</td>
</tr>
<tr>
<td>7</td>
<td>2) mCPBA, DMF, 24 h at RT</td>
<td>intractable mixture</td>
</tr>
<tr>
<td>7</td>
<td>TfOH, DCM, 1 h at -78 °C</td>
<td>intractable mixture</td>
</tr>
</tbody>
</table>

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 °C, but led only to the formation of an intractable mixture of products.
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 $\delta_F = -76.8$ ppm and $\delta_F = -76.4$ 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).
Finally, a solution of cycloadduct 460 in DCM was treated with triflic acid at -78 °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.

![Figure 31](image1)

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](image2)

### 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).

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 OSiMe₃ 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 OSiMe₃ group
(Scheme 140).

![Scheme 140](image)

This methodology could present a novel approach to the synthesis of structurally interesting
and biologically active natural products e.g. 538₁¹⁹, 539₁²⁰ (Figure 33).

![Figure 33](image)
6 Computational Details

Calculations were carried out using Gaussian03 software package.\textsuperscript{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),\textsuperscript{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)\textsuperscript{124} with the B3LYP and BPW91\textsuperscript{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 °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 °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 $\delta$ (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 ($\delta_\text{H} = 7.27$ ppm; $\delta_\text{C} = 77.0$ ppm). All chemical shifts are quoted in parts per million relative to tetramethylsilane ($\delta_\text{H} = 0.00$ ppm) and coupling constants are given in Hertz to the nearest 0.5
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**

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 Et₂O (3 x 150 ml). The combined organic layers were dried over MgSO₄, filtered, and concentrated under reduced pressure. Recrystallisation from acetone yielded tetrakis(trimethylsilyl)silane, (63.8 g, 53%). Mp: 249-251 °C (lit. 256-260 °C); IR (ATR) 2951, 2895, 1243, 825, 685, 620 cm⁻¹; δ_H (400 MHz) 0.20 (36H, s, CH₃); δ_C (100 MHz) 2.6 (CH₃); δ_Si (80 MHz) -9.9; m/z (EI) 320 ([M]+, 36%), 305 ([M-CH₃]+, 19), 232 ([M-CH₃-Si(CH₃)₃]+, 100), 173 (36), 158 (29), 131 (16), 73 (84).
Acetyltris(trimethylsilyl)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$_2$O, 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 ($\delta_H$ 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 °C and added dropwise to a cooled solution (-78 °C) of acetyl chloride (1.33 ml, 18.7 mmol) in THF (19 ml). The mixture was stirred at -78 °C for 3 h, before quenching by addition of diluted HCl (0.5 M, 50 ml) and extracting with Et$_2$O (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 °C) solution of acetyl chloride (1.0 ml, 14.1 mmol) in THF (20 ml). After stirring for 3 h at 0 °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$_2$O (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$^{-1}$; $\delta_H$ (500 MHz) 2.29 (3H, s, C(O)CH$_3$), 0.24 (27H, s, Si(CH$_3$)$_3$); $\delta_C$ (125 MHz) 244.0 (CO), 42.1 (CH$_3$), 1.0 (Si(CH$_3$)$_3$); $\delta_Si$ (80 MHz) -12.2; m/z (EI) 290 ([M]$^+$, 1%), 275 ([M-CH$_3$]$^+$, 9), 217 ([M-Si(CH$_3$)$_3$]$^+$, 12), 201 (16), 187 (18), 173 (30), 143 (35), 133 (36), 117 (13), 73 (100).
Benzoyltriphenylsilane\textsuperscript{81} 211

\[
\text{Ph} \quad \text{Si(\text{SiMe}_3)_3}
\]

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 °C) solution of trimethylacetyl chloride (10.6 ml, 91.2 mmol) in THF (60 ml). After stirring for 3 h at -78 °C the reaction mixture was allowed to reach room temperature and then NH\textsubscript{3}/H\textsubscript{2}O (1% w/w, 50 ml) and Et\textsubscript{2}O (50 ml) were added. The organic layer was separated, and the aqueous layer was extracted with Et\textsubscript{2}O (2 x 50 ml). The combined organic layers were dried over MgSO\textsubscript{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\textsubscript{f} 0.4 (pet. ether : chloroform 7:3); IR (ATR) 2950, 2894, 1608, 1245, 1200, 1070, 826, 765, 690 cm\textsuperscript{-1}; \(\delta\text{H} (500 MHz)\) 7.75-7.72 (2H, m, Ar-2,6-\textit{H}), 7.53-7.43 (3H, m, Ar-3,4,5-\textit{H}), 0.26 (27H, s, Si(CH\textsubscript{3})\textsubscript{3}); \(\delta\text{C} (125 MHz)\) 236.4 (CO), 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(CH\textsubscript{3})\textsubscript{3}); \(\delta\text{Si} (80 MHz)\) -11.5, -71.3; m/z (ES+) 353 ([M+H]\textsuperscript{+}, 40%), 295 (12), 124 (100).

4-Methoxybenzoyltriphenylsilane\textsuperscript{81} 213

\[
\text{MeO}^' \quad \text{Si(\text{SiMe}_3)_3}
\]

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 °C) solution of 4-methoxybenzoyl chloride (3.0 ml, 22.0 mmol) in THF (20 ml). After stirring for 4 h at -78 °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\textsubscript{2}O (2 x 20 ml). The combined organic layers were dried over MgSO\textsubscript{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\textsubscript{f} 0.5 (pet. ether : diethyl ether 9:1); IR (ATR) 2952, 2891, 1606, 1589, 1563, 1249, 1209, 1157, 1019, 822, 687, 618 cm\textsuperscript{-1}; \(\delta\text{H} (500 MHz)\)
7.76-7.74 (2H, m, Ar-2,6-H), 6.94-6.92 (2H, m, Ar-3,5-H), 3.88 (3H, s, OCH₃), 0.26 (27H, s, Si(CH₃)₃); \( \delta_C \) (125 MHz) 233.1 (CO), 163.2 (Ar-C-4), 137.6 (Ar-C-2,6), 130.0 (Ar-C-1), 113.3 (Ar-C-3,5), 55.4 (OCH₃), 1.50 (Si(CH₃)₃); \( \delta_{Si} \) (80 MHz) -11.5, -72.3; m/z (ES+) 383 ([M+H]⁺, 10%), 367 ([M-CH₃]⁺, 100).

4-(Trifluoromethyl)benzoyltris(trimethylsilyl)silane

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 °C) solution of 4-(trifluoromethyl)benzoyl chloride (1.6 ml, 10.6 mmol) in THF (15 ml). After stirring for 2 h at -78 °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, 1246, 1170, 1132, 1064, 1016, 825, 687, 624 cm⁻¹; \( \delta_H \) (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(CH₃)₃); \( \delta_C \) (175 MHz) 236.5 (CO), 146.2 (Ar-C-1), 133.7 (q, \( 2J_{c-f} = 32.6 \text{Hz}, \) Ar-C-4) 127.4 (Ar-C-2,6), 125.5 (q, \( 3J_{c-f} = 3.8 \text{Hz}, \) Ar-C-3,5), 123.8 (q, \( 1J_{c-f} = 271.8 \text{Hz}, \) CF₃), 1.42 (Si(CH₃)₃); \( \delta_{Si} \) (140 MHz) -11.3, -69.9; m/z (EI) 405 ([M-CH₃]⁺, 30), 281 (56), 207 (32), 190 (29), 173 (62), 147 (61), 73 (100).

Trimethylacetyltris(trimethylsilyl)silane

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 °C) solution of trimethylacetyl chloride (6.33 ml, 51.4 mmol) in THF (50 ml). After stirring for 5h at -78 °C the reaction mixture was allowed to reach room temperature and then dilute HCl (1 M, 52 ml) and Et₂O (50 ml) were added. The organic layer was separated,
and the aqueous layer was extracted with Et₂O (2 x 50 ml). The combined organic layers were
dried over MgSO₄, 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. Rₛ 0.6 (pet. ether : chloroform 7:3); Mp: 176-178 °C; IR (ATR) 2952, 2896, 1625,
1243, 824, 687, 621 cm⁻¹; δ_H (500MHz) 1.02 (9H, s, C(O)C(CH₃)₃), 0.22 (27H, s, Si(CH₃)₃);
δ_C (125MHz) 248.2 (CO), 49.3 (C(CH₃)₃), 24.7 (C(CH₃)₃), 1.6 (Si(CH₃)₃); δ_Si (80MHz) -11.6,
-78.2; m/z (EI) 317 ([M-CH₃]+·, 12%), 275 ([M-Si(CH₃)₃]+·, 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 °C) solution of 2-furoyl
chloride (4.6 ml, 46.3 mmol) in THF (30 ml). After stirring for 3 h at -78 °C the reaction
mixture was allowed to reach room temperature and then NH₃/H₂O (1% w/w, 25 ml) and
Et₂O (25 ml) were added. The organic layer was separated, and the aqueous layer was
extracted with Et₂O (2 x 25 ml). The combined organic layers were dried over MgSO₄,
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%). Rₛ 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-Η), 6.91 (1H, d, J = 3.5Hz, 3-Η), 6.54 (1H, dd, J = 3.5Hz, J = 1.4Hz, 4-Η), 0.25
(27H, s, Si(CH₃)₃); δ_C (175 MHz) 223.0 (CO), 159.2 (C-2), 144.9 (C-5), 112.4 (C-4), 110.5
(C-3), 1.3 (Si(CH₃)₃); δ_Si (140 MHz) -10.8, -70.2; m/z (ES+) 343 ([M+H]+, 10%), 327 ([M-
CH₃]+·, 100).
(2E,4E)-Diethyl hexa-2,4-dienedioate\(^{87} \) 230

Chlorotrimethylsilane (30.0 ml, 236 mmol) was added to a solution of (2E, 4E)-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\(_2\)O (100 ml). The aqueous layer was separated and extracted with Et\(_2\)O (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 °C (lit. \(^{127} 57-59 \)°C); IR (ATR) 3068, 2981, 1696, 1610, 1312, 1239, 1153, 1022, 861, 694 cm\(^{-1}\); \(\delta\)\(_H\) (500 MHz) 7.33-7.29 (2H, m, 2-H), 6.21-6.18 (2H, m, 3-H), 4.24 (4H, q, \(J = 6.8\)Hz, \(\text{C}_2\text{H}_5\text{CH}_3\)), 1.31 (6H, t, \(J = 6.8\)Hz, \(\text{CH}_2\text{C}_3\)); \(\delta\)\(_C\) (125 MHz) 165.9 (C-1), 140.8 (C-2), 128.4 (C-3), 60.8 (\(\text{CH}_2\text{C}_3\)), 14.2 (\(\text{CH}_2\text{C}_3\)); m/z (El) 198 ([M\(^+\), 5\%]), 153 ([M-OCH\(_2\text{C}_3\)]\(^+\), 36\%), 125 ([M-OC(O)\(\text{CH}_2\text{C}_3\)]\(^+\), 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.

\((2RS,3SR,4SR)\)-Ethyl 4-tert-butyl-3-((E)-3’-ethoxy-3’-oxoprop-1’-enyl)-1,1-bis(trimethylsilyl)-4-(trimethylsilyloxy)siletane-2-carboxylate 231a and

\((1RS,2RS,3SR)\)--Ethyl 2-tert-butyl-3-((E)-3’-ethoxy-3’-oxoprop-1’-enyl)-2-(1’,1’-bistrimethylsilyl-1’-trimethylsiloxyl)silylcyclopropane-carboxylate 232a
Method A

A solution of trimethylacetyltrimethylsilane 217 (0.51 g, 1.53 mmol) and (2E,4E)-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 °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/CHCl₃ yielded compound 232 as a pure isomer 232a (0.21 g, 58%).

Experimental data for compound 231a:

Rf 0.3 (pet. ether : diethyl ether 9:1); IR (ATR) 2954, 2899, 1715, 1645, 1246, 1145, 1082, 1048, 834 cm⁻¹; δH (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'-CO₂CH₂CH₃), 4.03 (2H, q, J = 7.0Hz, 2'-CO₂CH₂CH₃), 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'-CO₂CH₂CH₃), 1.21 (3H, t, J = 7.0Hz, 2-OCH₂CH₃), 0.95 (9H, s, C(CH₃)₃), 0.27 (9H, s, Si(CH₃)₃), 0.23 (18H, s, Si(CH₃)₃); δC (125 MHz) 174.0 (2-CO), 166.4 (2'-CO), 148.6 (C-2'), 121.7 (C-1'), 96.0 (C-4), 60.2 (2'-CO₂CH₂CH₃), 59.7 (2-CO₂CH₂CH₃), 49.6 (C(CH₃)₃), 37.4 (C(CH₃)₃), 29.1 (C-2), 29.0 (C(CH₃)₃), 14.3 (2'-CO₂CH₂CH₃), 14.2 (2-CO₂CH₂CH₃), 4.4 (OSi(CH₃)₃), 0.8 (Si(CH₃)₃), 0.5 (Si(CH₃)₃); δSi (80 MHz) 6.4, -10.3, -14.8, -16.1; m/z (EI) 530 ([M]+, 5%), 473 ([M-C(CH₃)₃]+, 7), 457 ([M-Si(CH₃)₃]+, 19), 343 (20), 273 (49), 213 (52), 191 (49), 175(25), 147 (31), 117 (81), 73 (100), HRMS (ED) found [M]+ 530.2743, C₂₃H₅₀O₄Si₄ requires [M]+ 530.2741.

Experimental data for compound 232a:

Mp: 104–106 °C; Rf 0.4 (pet. ether : diethyl ether 9:1); IR (ATR) 2956, 2898, 1713, 1635, 1251, 1175, 1135, 1027, 832 cm⁻¹; δH (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'-CO₂CH₂CH₃), 4.13-4.00 (2H, m, 1-CO₂CH₂CH₃), 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'-CO₂CH₂CH₃), 1.25 (3H, t, J = 7.0Hz, 1-CO₂CH₂CH₃), 1.10 (9H, s, C(CH₃)₃), 0.14 (9H, s, OSi(CH₃)₃), 0.13 (9H, s, Si(CH₃)₃), 0.12 (9H, s, Si(CH₃)₃); δC (125 MHz) 172.6 (1-CO), 166.1 (2'-CO), 148.0 (C-1'), 122.3 (C-2'), 60.9 (1-CO₂CH₂CH₃), 60.3 (2'-CO₂CH₂CH₃), 37.9 (C(CH₃)₃), 34.8 (C-3), 33.4 (C-1), 31.3 (C(CH₃)₃), 29.0 (C-2), 14.3 (1-CO₂CH₂CH₃), 14.2 (2'-CO₂CH₂CH₃), 3.3 (OSi(CH₃)₃), 0.8 (Si(CH₃)₃), 0.6 (Si(CH₃)₃); δSi (80 MHz) 4.6, -16.1, -16.9; m/z (EI) 515 ([M-CH₃]+, 7%), 457 ([M-Si(CH₃)₃]+, 12), 207 (14), 144
191 (29), 147 (12), 117 (27), 73 (100), 57 (18), 45 (12), Anal. Calcd for C_{24}H_{50}O_{5}Si_{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 (2E,4E)-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 °C 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.

(1RS,2RS)-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 °C 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, 755, 669 cm^{-1}; δ_{H} (500 MHz) 3.71 (3H, s, OCH_{3}), 3.64 (3H, s, OCH_{3}), 2.76 (1H, d, J = 6.0Hz, CHCO_{2}Me), 2.38 (1H, d, J = 6.0Hz, CHCO_{2}Me), 1.05 (9H, s, C(CH_{3})_{3}), 0.17 (9H, s, Si(CH_{3})_{3}), 0.14 (9H, s, Si(CH_{3})_{3}), 0.12 (9H, s, OSi(CH_{3})_{3}); δ_{C} (125 MHz) 172.1 (CO), 171.9 (CO), 52.8 (OCH_{3}), 52.1 (OCH_{3}), 38.4 (C(CH_{3})_{3}), 34.4 (C-3), 31.7 (CHCO_{2}Me), 30.4 (C(CH_{3})_{3}), 30.0 (CHCO_{2}Me), 3.4 (OSi(CH_{3})_{3}), 0.5 (Si(CH_{3})_{3}), 0.4 (Si(CH_{3})_{3}); δ_{Si} (80 MHz) 6.3, 1.0, -17.3, -17.8 m/z (EI) 461 ([M-CH_{3}]^{+}, 6%), 403 ([M-Si(CH_{3})_{3}]^{+}, 93), 221(86), 207(26), 191(37), 147(55), 133 (49), 117 (90), 89 (30), 73 (100), 45 (36).
(1RS,2RS,3SR)-Ethyl 2-tert-butyl-2-(1’,1’-bistrimethylsilyl-1’-trimethylsiloxysilyl)-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 °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%). Rf 0.5 (pet. ether : chloroform 8:2); IR (CHCl₃) 3020, 2962, 1734, 1423, 1251, 1218, 1052, 930, 843, 669 cm⁻¹; δH (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, OCH₂CH₃), 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, OCH₂CH₃), 1.08 (9H, s, C(CH₃)₃), 0.14 (9H, s, OSi(CH₃)₃), 0.13 (9H, s, Si(CH₃)₃), 0.10 (9H, s, Si(CH₃)₃); δC (125 MHz) 173.9 (C=O), 129.0 (C-1’), 127.9 (C-2’), 60.5 (OCH₂CH₃), 34.7 (C-3), 34.4 (C-2), 32.2 (C(CH₃)₃), 31.1 (C(CH₃)₃), 30.8 (C-1), 18.2 (C-3’), 14.3 (OCH₂CH₃), 3.3 (OSi(CH₃)₃), 0.8 (Si(CH₃)₃), 0.7 (Si(CH₃)₃); δSi (139 MHz) 3.8, -13.9, -16.0, -16.8; m/z (EI) 457 ([M-CH₃]⁺, 4%), 399 ([M-Si(CH₃)₃]⁺, 55), 235 (33), 207 (62), 191 (88), 147 (38), 133 (29), 117 (70), 73 (100); HRMS (ES+) found [M+H]⁺ 473.2760, C₂₂H₄₉O₂Si₄ requires [M+H]⁺ 473.2753.

(1RS,2RS,3RS)-Methyl 2-tert-butyl-2-(1’,1’-bistrimethylsilyl-1’-trimethylsiloxysilyl)-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 °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 °C; Rf 0.4 (pet. ether : chloroform 8:2); IR (ATR) 2955, 1717, 1440, 1401, 1250, 1202, 1028, 831,
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 °C 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.

(2RS,3SR,4SR)-4-tert-Butyl-3-phenyl-1,1-bis(trimethylsilyl)-4-(trimethylsilyloxy)siletane-2-carbonitrile 242 and
2-tert-Butyl-2-(1’,1’-bistrimethylsilyl-1’-trimethylsiloxysilyl)-3-phenylcyclopropanecarbonitrile 243

A solution of trimethylacetyltris(trimethylsilyl)silane (0.32 g, 0.96 mmol) and trans-cinnamonicarbonitrile (0.49 ml, 3.86 mmol) in dry benzene (3.0 ml) was heated in a carious tube at 200 °C 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 CHCl₃ yielded the product 242 as a single isomer.
Experimental data for compound (major diastereoisomer) 242:

Mp: 122-123 °C; Rf 0.4 (pet. ether : diethyl ether 9:1); IR (ATR) 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(CH₃)₃), 0.36 (9H, s, Si(CH₃)₃), 0.24 (9H, s, Si(CH₃)₃), -0.25 (9H, s, Si(CH₃)₃); δC (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 (CN), 99.1 (C-4), 54.5 (C-3), 37.5 (C(CH₃)₃), 29.1 (C(CH₃)₃), 8.1 (C-2), 3.8 (OSi(CH₃)₃), 0.7 (Si(CH₃)₃), 0.4 (Si(CH₃)₃); δSi (140 MHz) 7.8, -14.1, -15.8, -18.3; m/z (EI) 461 ([M]+·, 3%), 446 ([M-CH₃]+·, 3), 388 ([M-Si(CH₃)₃]+·, 14), 286 (30), 248 (67), 233 (36), 73 (100), 45 (16); HRMS (EI) found [M]+ 461.2414, C₂₃H₄₃NOSi₄ requires [M]+ 461.2416.

Experimental data for compound 243:

¹H 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]+, 6%), 446 ([M-CH₃]+, 4), 263 (53), 189 (16), 175 (30), 131 (27), 117 (29), 73 (100); m/z (EI) 461 ([M]+, 1%), 446 ([M-CH₃]+, 11), 388 ([M-Si(CH₃)₃]+, 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]+, 26%), 446 ([M-CH₃]+, 30), 388 ([M-Si(CH₃)₃]+, 36), 263 (100), 204 (37), 189 (54), 175 (55), 147 (50), 131 (52), 117 (51), 73 (59), 45 (18); m/z (EI) 461 ([M]+, 1%), 446 ([M-CH₃]+, 2), 388 ([M-Si(CH₃)₃]+, 10), 302 (12), 157 (15), 147 (19), 117 (42), 73 (100), 45 (11).

(1RS,2RS,3SR)-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 °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%). Rf 0.7 (pet. ether : diethyl ether 95:5); IR (ATR) 2952, 2895, 1709, 1413, 1335, 1247, 1179, 1045, 964, 831, 749, 694 cm⁻¹; δH (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, dd, J = 15.4Hz, J = 14.7Hz, J = 7.0Hz, 3’-H), 4.03 (9H, s, Si(CH₃)₃), 0.18 (9H, s, Si(CH₃)₃), -0.16 (9H, s, OSi(CH₃)₃); δC (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 (OCH₂CH₃), 36.0 (C-3), 34.9 (C-1), 33.8 (C-2), 18.0 (C-3’), 14.3 (OCH₂CH₃), 2.3 (OSi(CH₃)₃), 0.2 (Si(CH₃)₃), 0.1 (Si(CH₃)₃); δSi (139 MHz) 4.6, 0.0, -16.9, -17.7; m/z (EI) 492 ([M⁺], 0.1%), 477 ([M-Si(CH₃)₃⁺], 48), 235 (47), 207 (54), 191 (74), 147 (28), 117 (48), 73 (100); HRMS (EI) found [M⁺] 492.2361, C₂⁴H₴₄O₃Si₄ requires [M⁺] 492.2362.

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

Method A
A solution of benzoyltris(trimethylsilyl)silane (0.21 g, 0.60 mmol) and (2E,4E)-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 °C 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%). Rf 0.5 (pet. ether : diethyl ether 7:3); IR (ATR) 2955, 1715, 1248, 1182, 1133, 1048, 834, 752, 702, 687 cm⁻¹; δH (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-OCH₂CH₃), 4.20-4.15 (2H, m, 2’-OCH₂CH₃), 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-CO₂CH₂CH₃), 1.27 (3H,
**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 °C 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\(^{-1}\); \(\delta_H\) (700 MHz) 7.29-7.27 (2H, m, Ar-3,5-\(H\)), 7.21 (1H, dd, \(J = 15.8\)Hz, \(J = 7.4\)Hz, 1'-\(H\)), 7.19-7.18 (3H, m, Ar-2,4,6-\(H\)), 6.01 (1H, dd, \(J = 15.8\)Hz, \(J = 0.7\)Hz, 2'-\(H\)), 4.27 (1H, ddd, \(J = 11.9\)Hz, \(J = 7.4\)Hz, \(J = 0.7\)Hz, 2-CO\(_2\)C\(_6\)H\(_5\)), 4.17 (1H, dq, \(J = 11.2\)Hz, \(J = 7.0\)Hz, 2'CO\(_2\)C\(_6\)H\(_5\)), 4.06 (1H, dq, \(J = 11.2\)Hz, \(J = 7.0\)Hz, 2-CO\(_2\)CH\(_2\)CH\(_3\)), 4.21 (1H, dq, \(J = 11.2\)Hz, \(J = 7.0\)Hz, 2'-CO\(_2\)CH\(_2\)CH\(_3\)), 3.09 (1H, d, \(J = 11.9\)Hz, 2-\(H\)), 1.27 (3H, t, \(J = 7.0\)Hz, 2'-CO\(_2\)CH\(_2\)CH\(_3\)), 1.20 (3H, t, \(J = 7.0\)Hz, 2-OCH\(_2\)CH\(_3\)), 0.35 (9H, s, Si(CH\(_3\))\(_3\)), -0.14 (9H, s, Si(CH\(_3\))\(_3\)), -0.20 (9H, s, Si(CH\(_3\))\(_3\)); \(\delta_C\) (175 MHz) 174.0 (2-CO), 166.5 (2'-CO), 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$_2$CH$_2$CH$_3$), 59.8 (2-CO$_2$CH$_2$CH$_3$), 49.9 (C-3), 29.4 (C-2), 14.4 (2'-CO$_2$CH$_2$CH$_3$), 14.3 (2-CO$_2$CH$_2$CH$_3$), 2.3 (Si(CH$_3$)$_3$), -0.3 (Si(CH$_3$)$_3$), -1.1 (Si(CH$_3$)$_3$); $\delta$$_{\text{Si}}$ (140 MHz) 14.8, -5.5, -14.7, -16.4; m/z (EI) 550 ([M]$^+$, 1%), 535 ([M-CH$_3$]$^+$, 3), 477 ([M-Si(CH$_3$)$_3$]$^+$, 37), 235 (15), 207 (37), 191 (70), 147 (27), 133 (18), 117 (58), 73 (100), 45 (15).

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

![Chemical structure](image)

A solution of benzoyltrimethylsilylsilane (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 °C 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$^{-1}$; $\delta$$_H$ (500 MHz) 7.28-7.26 (2H, m, Ar-3,5-H), 7.21-7.19 (1H, m, Ar-4-H), 7.12-7.11 (2H, m, Ar-2,6-H), 3.80 (3H, s, OCH$_3$), 3.62 (3H, s, OCH$_3$), 2.85 (1H, d, J = 5.0Hz, CHCO$_2$Me), 2.72 (1H, d, J = 5.0Hz, CHCO$_2$Me), 0.23 (9H, s, Si(CH$_3$)$_3$), 0.10 (9H, s, Si(CH$_3$)$_3$), -0.02 (9H, s, OSi(CH$_3$)$_3$); $\delta$$_C$ (125 MHz) 171.8 (CO), 169.9 (CO), 140.1 (Ar-C-1), 130.1 (Ar-C-2,6), 128.1 (Ar-C-3,5), 126.2 (Ar-C-4), 52.1 (OCH$_3$), 51.9 (OCH$_3$), 36.4 (C-3), 32.9 (CHCO$_2$Me), 32.7 (CHCO$_2$Me), 2.3 (OSi(CH$_3$)$_3$), -0.06 (Si(CH$_3$)$_3$), -0.09 (Si(CH$_3$)$_3$); $\delta$$_{\text{Si}}$ (139 MHz) 6.1, -0.8, -17.1, -17.9; m/z (EI) 496 ([M]$^+$, 1%), 481 ([M-CH$_3$]$^+$, 2%), 423 ([M-Si(CH$_3$)$_3$]$^+$, 100), 221(24), 133 (11), 117 (23), 73 (32).
(1RS,2RS,3RS)-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 °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%). Rf 0.6 (pet. ether : chloroform 7:3); IR (ATR) 2951, 1720, 1439, 1249, 1177, 1046, 831, 749, 700 cm⁻¹; δH (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, OC₃H₃), 3.07 (1H, d, J =5.5Hz, 3-H), 2.63 (1H, d, J = 5.5Hz, 1-H), 0.23 (9H, s, OSi(C₃H₃)₃), 0.01 (9H, s, Si(C₃H₃)₃), -0.07 (9H, s, Si(C₃H₃)₃); δC (125 MHz) 173.3 (CO), 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 (OCH₃), 38.0 (C-2), 36.5 (C-3), 34.4 (C-1), 2.4 (OSi(CH₃)₃), 0.3 (Si(CH₃)₃), -0.06 (Si(CH₃)₃); δSi (139 MHz) 5.4, -0.5, -17.3, -18.0; m/z (EI) 499 ([M-CH₃]+, 1%), 441 ([M-Si(CH₃)₃]⁺, 58), 221(94), 191 (36), 147 (28), 133 (24), 117 (93), 74 (12), 73 (100), 45 (22); HRMS (ES+) found [M+H]+ 515.2284, C₂₆H₄₃O₃Si₄ requires [M+H]+ 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 °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 °C for 20 min. Concentration,
followed by flash column chromatography on silica, elution gradient 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.

\[(1RS,2RS,3SR)-\text{Ethyl 2-}(1',1'-bistrimethylsilyl-1'-trimethylsiloxy)silyl-3-((E)-3'-ethoxy-3'-oxoprop-1'-enyl)-2-(4-methoxyphenyl)cyclopropanecarboxylate 249\]

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 °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<sub>f</sub> 0.6 (pet. ether : diethyl ether 7:3); IR (ATR) 2956, 1713, 1510, 1245, 1178, 1041, 833 cm\(^{-1}\); δ<sub>H</sub> (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, OCH<sub>2</sub>CH<sub>3</sub>), 4.19 (3H, s, OCH<sub>3</sub>), 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<sub>2</sub>CH<sub>3</sub>), 1.66 (3H, t, J = 7.0Hz, 1-OCH<sub>2</sub>CH<sub>3</sub>), 0.57 (9H, s, OSi(CH<sub>3</sub>)<sub>3</sub>), 0.43 (9H, s, Si(CH<sub>3</sub>)<sub>3</sub>), 0.30 (9H, s, Si(CH<sub>3</sub>)<sub>3</sub>); δ<sub>C</sub> (125 MHz) 172.1 (1-CO), 166.0 (2'-CO), 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<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 60.2 (2'-CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 55.3 (OCH<sub>3</sub>), 36.2 (C-2), 35.7 (C-1), 35.1 (C-3), 14.3 (1-OCH<sub>2</sub>CH<sub>3</sub>), 14.2 (2'-OCH<sub>2</sub>CH<sub>3</sub>), 2.3 (OSi(CH<sub>3</sub>)<sub>3</sub>), 0.2 (Si(CH<sub>3</sub>)<sub>3</sub>), 0.0 (Si(CH<sub>3</sub>)<sub>3</sub>);
δ<sub>Si</sub> (80 MHz) 5.4, -17.0, -17.7; m/z (EI) 507 ([M-Si(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>, 100%), 367 (10), 255(15), 235 (18), 207 (36), 191 (65), 147 (22), 117 (37), 73 (51).

(1RS,2RS,3RS)-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 °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<sub>f</sub> 0.5 (pet. ether : diethyl ether 9:1); IR (ATR) 2952, 1720, 1509, 1440, 1247, 1173, 1046, 827, 756, 695 cm<sup>-1</sup>; δ<sup>H</sup> (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<sub>2</sub>C<sub>H</sub><sub>3</sub>), 3.87 (3H, s, Ar-OC<sub>2</sub>H<sub>5</sub>), 3.20 (1H, d, J = 4.9Hz, 3-H), 2.74 (1H, d, J = 4.9Hz, 1-H), 0.36 (9H, s, OSi(CH<sub>3</sub>)<sub>3</sub>), 0.15 (9H, s, Si(CH<sub>3</sub>)<sub>3</sub>), 0.12 (9H, s, Si(CH<sub>3</sub>)<sub>3</sub>); δ<sup>C</sup> (175 MHz) 173.2 (CO), 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-OC<sub>2</sub>H<sub>5</sub>), 51.8 (CO<sub>2</sub>C<sub>H</sub><sub>3</sub>), 37.1 (C-2), 36.4 (C-3), 34.6 (C-1), 2.5 (OSi(CH<sub>3</sub>)<sub>3</sub>), 0.4 (Si(CH<sub>3</sub>)<sub>3</sub>), -0.1 (Si(CH<sub>3</sub>)<sub>3</sub>); δ<sub>Si</sub> (140 MHz) 5.3, -1.2, -17.5, -18.2; m/z (EI) 544 ([M]<sup>+</sup>, 1%), 529 ([M-CH<sub>3</sub>]<sup>+</sup>, 3), 471 ([M-Si(CH<sub>3</sub>)<sub>3</sub>]<sup>+</sup>, 96), 221 (100), 191 (23), 165 (10), 147 (27), 117 (97), 73 (86); HRMS (ES+) found [M+H]<sup>+</sup> 545.2386, C<sub>27</sub>H<sub>43</sub>O<sub>4</sub>Si<sub>4</sub> requires [M+H]<sup>+</sup> 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 °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.
(1RS,2RS,3RS)-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 °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%). Rf 0.6 (pet. ether : chloroform 7:3); IR (ATR) 2952, 1721, 1440, 1250, 1198, 1050, 830, 758, 697 cm⁻¹; δH (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, OC₃H₃), 2.96 (1H, d, J = 5.5Hz, 3-H), 2.08 (1H, d, J = 5.5Hz, 1-H), 0.87 (3H, s, CH₃), 0.24 (9H, s, OSi(CH₃)₃), 0.183 (9H, s, Si(CH₃)₃), 0.177 (9H, s, Si(CH₃)₃); δC (125 MHz) 173.6 (CO), 137.0 (Ar-C-1), 129.1 (Ar-C-2,6), 128.1 (Ar-C-3,5), 126.4 (Ar-C-4), 51.7 (OCH₃), 36.2 (C-3), 32.4 (C-1), 22.8 (C-2), 18.5 (CH₃), 2.5 (OSi(CH₃)₃), 0.1 (Si(CH₃)₃), -0.4 (Si(CH₃)₃); δSi (140 MHz) 5.6, 1.1, -18.0, -18.7; m/z (EI) 452 ([M]+, 10%), 437 ([M-CH₃]+, 20), 379 ([M-Si(CH₃)₃]+, 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 °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 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 °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<sub>4</sub>, filtered, and concentrated in vacuo to yield the title amide as a white solid (4.44 g, 94%). Mp: 72.5–73.6 °C (lit. 129–129.71–72 °C); R<sub>f</sub> 0.3 (pet. ether : diethyl ether 2:3); IR (ATR) 2967, 2931, 1645, 1592, 1492, 1459, 1429, 1367, 1286, 1250, 1145, 1078, 973, 957, 865, 760, 707, 684 cm<sup>−1</sup>; δ<sub>H</sub> (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, CH₂), 3.49 (2H, q, J = 7.0Hz, CH₂), 1.27 (3H, t, J = 7.0Hz, CH₃), 1.20 (3H, t, J = 7.0Hz, CH₃); δ<sub>C</sub> (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 (CH₂), 41.1 (CH₂), 15.1 (CH₃), 13.2 (CH₃); m/z (EI) 203 ([M]+·, 29%), 131 (100), 103 (63), 77 (38).

(1RS,2RS,3RS)-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 °C 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<sub>f</sub> 0.6 and 0.3 (pet. ether : diethyl ether 9:1, 4:6); IR (ATR) 2949, 2892, 1616, 1490, 1457, 1245, 1175, 1039, 825, 747, 687 cm<sup>−1</sup>; δ<sub>H</sub> (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, OC₃H₃), 3.53 (1H, dq, J = 7.0Hz, J = 14.0Hz, CH₂CH₃), 3.48 (1H, dq, J = 7.0Hz, J = 14.0Hz, CH₂CH₃), 3.34 (1H, dq, J = 7.0Hz, J = 14.0Hz, CH₂CH₃), 3.27 (1H, dq, J = 7.0Hz, J = 14.0Hz, CH₂CH₃), 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, CH₂CH₃), 1.13 (3H, t, J = 7.0Hz, CH₂CH₃), 0.26 (9H, s, Si(CH₃)₃), 0.09 (9H, s, Si(CH₃)₃), -0.24 (9H, s, OSi(CH₃)₃); δ<sub>C</sub> (175 MHz) 171.5 (CO), 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 (OCH₃), 42.6 (CH₂CH₃), 40.9 (CH₂CH₃), 37.4 (C-3), 35.8 (C-2), 34.4 (C-1), 15.0 (CH₂CH₃), 13.3 (CH₂CH₃), 2.4 (OSi(CH₃)₃), 0.8 (Si(CH₃)₃), 0.7 (Si(CH₃)₃); δSi (139 MHz) 1.4, -9.5, -16.0, -17.1.

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

![Chemical structure](attachment:image)

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 °C 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 °C; Rf 0.3 (pet. ether : diethyl ether 8:2); IR (ATR) 2953, 2895, 1606, 1510, 1446, 1296, 1245, 1141, 1051, 749, 691 cm⁻¹; δH (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-4-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, OCH₃), 0.49 (9H, s, Si(CH₃)₃), 0.16 (9H, s, Si(CH₃)₃), -0.56 (9H, s, OSi(CH₃)₃); δC (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 (OCH₃), 53.6 (C-4), 2.1 (OSi(CH₃)₃), -0.2 (Si(CH₃)₃), -0.4 (Si(CH₃)₃); δSi (139 MHz) 14.2, -11.3, -14.5, -15.0; m/z (ES+) 644 ([M+NH₄]⁺, 100%), 611 (24), 537 (6); HRMS (ES+) found [M+NH₄]⁺ 644.2530, C₃₁H₅₀O₄NSSi₄ requires [M+NH₄]⁺ 644.2532.
(1RS,2RS,3RS)-Methyl 2-(1′,1′-bistrimethylsilyl-1′-trimethylsiloxy)silyl-3-phenyl-2-(4-trifluoromethyl) phenylcyclopropanecarboxylate 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 °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, 749 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_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(CH_3)_3), 0.05 (9H, s, Si(CH_3)_3), -0.12 (9H, s, Si(CH_3)_3); δ_C (175 MHz) 173.2 (CO), 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, 2J_C-F = 32.6Hz, 2-Ar-C-4), 126.5 (3-Ar-C-4), 124.6 (q, 3J_C-F = 3.3Hz, 2-Ar-C-3,5), 124.3 (q, 1J_C-F = 271.8Hz, 2-Ar-CF_3), 52.1 (CO_2CH_3), 37.6 (C-2), 37.0 (C-3), 33.9 (C-1), 2.3 (OSi(CH_3)_3), 0.4 (Si(CH_3)_3), 0.1 (Si(CH_3)_3); δ_Si (140 MHz) 5.7, 1.0, -16.7, -17.6; m/z (EI) 567 ([M-CH_3]^+, 8%), 509 ([M-Si(CH_3)_3]^+, 89), 269 (51), 221 (100), 191 (34), 163 (15), 147 (27), 117 (90), 73 (86), 59 (15); HRMS (ES+) found [M+NH_4]^+ 600.2420, C_{27}H_{45}O_{2}NF_3Si_4 requires [M+NH_4]^+ 600.2423.

(1RS,2RS,3RS)-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 °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 °C; Rf 0.7 (pet. ether : diethyl ether 8:2); IR (ATR) 2951, 2893, 1733, 1499, 1441, 1408, 1249, 1175, 1059, 831, 730, 687 cm⁻¹; δH (700 MHz) 7.24-7.20 (3H, m, Ar-3,4,5-H), 7.10 (1H, d, J = 2.1 Hz, 5'-H), 7.04-7.03 (2H, m, Ar-2,6-H), 6.08 (1H, dd, J = 3.5 Hz, J = 2.1 Hz, 4'-H), 5.42 (1H, d, J = 3.5 Hz, 3'-H), 3.76 (3H, s, CO₂CH₃), 3.13 (1H, d, J = 6.3 Hz, 1-H), 0.19 (9H, s, Si(CH₃)₃), 0.13 (9H, s, OSi(CH₃)₃), 0.02 (9H, s, Si(CH₃)₃); δC (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 (CO₂CH₃), 34.6 (C-3), 32.9 (C-1), 29.6 (C-2), 2.6 (OSi(CH₃)₃), -0.1 (Si(CH₃)₃), -1.0 (Si(CH₃)₃); δSi (140 MHz) 6.2, -3.1, -17.8, -17.9; m/z (EI) 431 ([M-Si(CH₃)₃]⁺·, 0.1%), 147 (1), 131 (1), 103 (1), 73 (100); HRMS (EI) found [M]⁺ 504.1990, C₂₄H₄₀O₄Si₄ requires [M]⁺ 504.1998.

(3RS,4SR)-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 °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 °C; Rf 0.6 (pet. ether : diethyl ether 9:1); IR (ATR) 2954, 2896, 1604, 1505, 1447, 1327, 1247, 1183, 1019, 833, 745, 689 cm⁻¹; δH (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 = 4.2 Hz, 5-H), 4.36 (1H, d, J = 4.2 Hz, 4-H), 3.77 (3H, s, OCH₃), 0.23 (9H, s, Si(CH₃)₃), 0.07 (9H, s, OSi(CH₃)₃), -0.08 (9H, s, Si(CH₃)₃); δC (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 (OCH₃), 43.9 (C-4), 32.8 (C-3), 2.3 (Si(CH₃)₃), 1.7 (OSi(CH₃)₃), -1.0 (Si(CH₃)₃);
δSi (139 MHz) 10.3, 4.8, -14.3, -19.7; m/z (EI) 590 ([M]+, 4%), 575 ([M-CH3]+, 6), 517 ([M-C(CH3)3]+, 3), 367 (24), 192 (16), 73 (100); HRMS (ES+) found [M+H]+ 591.2589, C32H47O3Si4 requires [M+H]+ 591.2597.

(Z) Methyl 3-phenylpropenoate130 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 Et2O (100 ml) and made neutral by addition of aqueous NaOH (6M). The organic layer was separated, and the aqueous layer was extracted with Et2O (2 x 200 ml). The combined organic layers were dried over MgSO4 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 °C) 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 Et2O (3 x 100 ml). The combined organic layers were dried over MgSO4, 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%). Rf 0.6 (pet. ether : diethyl ether 6:4 ), IR (ATR) 1722, 1629, 1436, 1195, 1162, 826, 765, 695, 618 cm⁻¹; δH (500 MHz) 7.52-7.50 (2H, m, Ar-2,6-H), 5.87 (1H, d, J = 12.5Hz, 3-H), 3.62 (3H, s, OCH3); δC (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 (OCH3); m/z (EI) 162 ([M]+, 30%), 131 ([M-OCH3]+, 84), 103 ([M-CO2CH3]+, 100), 77 ([C6H5]+, 66), 51 (50).
3,4-Diphenyl-1,1,2,2-tetrakis(trimethylsilyl)-3,4-bis(trimethylsilyloxy)-1,2-disiletane

A solution of benzoyl(trimethylsilyl)silane (4.13 g, 11.7 mmol) in toluene (200 ml) was irradiated for 1 h at 0 °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 °C (lit. 149-150 °C); Rf 1 (pet. ether); IR (ATR) 2953, 2891, 1247, 1015, 827, 767, 625 cm⁻¹; δH (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(CH₃)₃), 0.08 (18H, s, Si(CH₃)₃), -0.25 (18H, s, Si(CH₃)₃); δC (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(CH₃)₃), 3.1 (Si(CH₃)₃), 2.9 (Si(CH₃)₃); δSi (140 MHz) 8.8, -12.2, -13.3, -40.8; m/z (EI) 352 ([M/2]^+·, 5%), 337 ([M/2]^+, 10).

(1RS,2RS,3RS)-Methyl 2-(1’-fluoro-1’,1’-bistrimethylsilyl)silyl-2,3-diphenylcyclopropanecarboxylate

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 MgSO₄, filtered, and concentrated under reduced pressure to give a pure title compound as white solid (0.16 g, 96%). Mp: 82-84 °C; Rf 0.4 (pet. ether : chloroform 7:3); IR (ATR) 2948, 1687, 1440, 1242, 1213, 830, 796, 732, 693 cm⁻¹; δH (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, OCH₃), 3.19 (1H, d, J = 4.2Hz, 3-H), 2.98 (1H, d, J = 4.2Hz, 1-H), 0.52 (9H, s, Si(CH₃)₃), 0.29 (9H, s, Si(CH₃)₃); δC (175
MHZ) 175.2 (CO), 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 (2-Ar-C-4), 125.9 (2-Ar-C-4), 125.2 (OCH3), 38.1 (C-3), 35.6 (C-2), 33.6 (C-1), -0.26 (Si(CH3)3), -0.72 (Si(CH3)3); δF (188 MHz) -186.3; δSi (139 MHz) 23.2 (1JSi-F = 325.2Hz), -14.8 (2JSi-F = 27.2Hz), -15.7 (2JSi-F = 25.2Hz); m/z (EI) 429 ([M-CH3]+, 6%), 371 ([M-Si(CH3)3]+, 88), 247(44), 235 (23), 191 (32), 131 (36), 89 (16), 73 (100), 59 (84), 45 (41); HRMS (ES+) found [M+NH4]+ 462.2109, C23H37O2NF3 requires [M+NH4]+ 462.2111.

Methyl 4-oxo-3,4-diphenylbutanoate

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 mCPBA (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 MgSO4, 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%); Rf 0.5 (pet. ether : diethyl ether 5:5); IR (ATR) 3031, 1733, 1707, 1493, 1453, 1239, 1026, 1010, 765, 699 cm⁻¹; δH (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-OCH3), 3.40 (1H, dd, J = 16.8Hz, J = 9.8Hz, 2-H), 2.74 (1H, dd, J = 16.8Hz, J = 4.9Hz, 2-H); δC (175 MHz) 198.6 (CO-4), 172.6 (CO-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 (OCH3), 49.6 (C-3), 38.4 (C-2); m/z (EI) 268 ([M]+, 16%), 237 ([M-OCH3]+, 26), 121 (36), 106 (47), 105 (100), 103 (30), 78 (36), 77 (70), 51 (64).
(1RS,2RS,3SR)-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 MgSO₄, filtered, and concentrated under reduced pressure to give a pure title compound (0.17 g, 95%).

Rf 0.4 (pet. ether: diethyl ether 9:1); IR (CHCl₃) 3020, 2958, 1696, 1637, 1245, 1210, 1037, 840, 745, 670 cm⁻¹; δH (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, CO₂CH₂CH₃), 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’-CO₂CH₂CH₃), 1.28 (3H, t, J = 7.0Hz, 1-CO₂CH₂CH₃), 1.11 (9H, s, C(CH₃)₃), 0.18 (9H, s, Si(CH₃)₃), 0.10 (9H, s, Si(CH₃)₃); δC (125 MHz) 175.5 (1-CO), 166.0 (2’-CO), 146.6 (C-1’), 123.1 (C-2’), 62.2 (1-CO₂CH₂CH₃), 60.4 (2’-CO₂CH₂CH₃), 37.1 (C(CH₃)₃), 34.6 (C-3), 32.7 (C-1), 30.8 (C(CH₃)₃), 29.7 (C-2), 14.3 (1-CO₂CH₂CH₃), 14.1 (2’-CO₂CH₂CH₃), -0.5 (Si(CH₃)₃), -0.6 (Si(CH₃)₃); δSi (139 MHz) 30.1 (1JSi-F = 321.6Hz), -14.2 (2JSi-F = 24.7Hz), -14.6 (2JSi-F = 30.0Hz); δF (376 MHz) -169.46; m/z (EI) 445 ([M-CH₃]+, 4%), 387 ([M-Si(CH₃)₃]+, 72), 205 (30), 177 (76), 131 (41), 73 (100), 57 (78), 45 (50); HRMS (EI) found [M]+ 460.2283, C₂₁H₄₁O₄Si₄ requires [M]+ 460.2291.
(1RS,2RS,3SR)-Ethyl 2-tert-butyl-2-(1’',1’'-difluoro-2',2',2'-trimethylidisilyl)-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$^{-1}$; $\delta_H$ (500 MHz) 6.98 (1H, dd, $J$ = 15.0 Hz, $J$ = 10.0 Hz, 1’-H), 6.11 (1H, d, $J$ = 15.0 Hz, 2’-H), 4.20 (2H, q, $J$ = 7.0 Hz, 1-CO$_2$CH$_2$CH$_3$), 4.19 (2H, q, $J$ = 7.0 Hz, 2’-CO$_2$CH$_2$CH$_3$), 2.48 (1H, d, $J$ = 10.0, $J$ = 5.0 Hz, 3-H), 2.38 (1H, d, $J$ = 5.0 Hz, 1-H), 1.32 (3H, t, $J$ = 7.0 Hz, 2’-CO$_2$CH$_2$CH$_3$), 1.29 (3H, t, $J$ = 7.0 Hz, 1-CO$_2$CH$_2$CH$_3$), 1.13 (9H, s, C(CH$_3$)$_3$), 0.19 (9H, s, Si(CH$_3$)$_3$); $\delta_C$ (125 MHz) 175.5 (1-CO), 166.0 (2’-CO), 144.9 (C-1’), 124.2 (C-2’), 62.4 (1-CO$_2$CH$_2$CH$_3$), 60.4 (2’-CO$_2$CH$_2$CH$_3$), 36.2 ($^2J_{C-F}$ = 6.7Hz, C-2), 33.5 ($^3J_{C-F}$ = 1.9Hz, C(CH$_3$)$_3$), 32.1 (C-3), 31.6 (C-1), 30.8 (C(CH$_3$)$_3$), 14.3 (1-CO$_2$CH$_2$CH$_3$), 14.1 (2’-CO$_2$CH$_2$CH$_3$), -1.7 (Si(CH$_3$)$_3$); $\delta_{Si}$ (139 MHz) -8.1 ($^1J_{Si-F}$ = 351.4Hz, $^1J_{Si-F}$ = 349.2Hz), -16.7 ($^2J_{Si-F}$ = 32.2Hz, $^3J_{Si-F}$ = 27.5Hz); $\delta_F$ (376 MHz) -127.32 ($^2J_{F-F}$ = 19.9Hz), -134.06 ($^2J_{F-F}$ = 19.9Hz); m/z (El) 391 ([M-CH$_3$]$^+$, 1%), 333 ([M-Si(CH$_3$)$_3$]$^+$, 32), 259 (49), 121 (20) 73 (100), 57 (98), 45 (26), 29 (50); HRMS (ES+) found [M+NH$_4$]$^+$ 424.2146, C$_{18}$H$_{36}$O$_4$NF$_2$Si$_2$ requires [M+NH$_4$]$^+$ 424.2145.
(1RS,2RS,3RS)-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 MgSO₄, filtered, and concentrated under reduced pressure to give a pure title compound (0.16 g, 97%). Rf 0.5 (pet. ether : diethyl ether 9:1); IR (ATR) 2953, 1698, 1442, 1242, 1206, 833, 732, 699, 686 cm⁻¹; δH (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, OCH₃), 2.77 (1H, d, J = 4.9Hz, 3-H), 2.59 (1H, d, J = 4.9Hz, 1-H), 0.87 (9H, s, C(CH₃)₃), 0.23 (9H, s, Si(CH₃)₃), 0.12 (9H, s, Si(CH₃)₃); δc (175 MHz) 177.1 (CO), 136.8 (Ar-C), 130.3 (Ar-C-2,6), 128.1 (Ar-C-3,5), 126.8 (Ar-C-4), 52.6 (OCH₃), 39.7 (C-3), 35.2 (C(CH₃)₃), 30.2 (C(CH₃)₃), 30.1 (C-2), 27.0 (C-1), -0.3 (Si(CH₃)₃), -0.4 (Si(CH₃)₃); δSi (139 MHz) 30.3 (¹JSi-F = 321.9Hz), -14.4 (²JSi-F = 25.0Hz), -14.9 (²JSi-F = 30.3Hz); δF (188 MHz) -163.8; m/z (EI) 409 ([M-CH₃]⁺, 11%), 351 ([M-Si(CH₃)₃]⁺, 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+NH₄]⁺ 442.2421, C₂₁H₄₁O₂NFSi₃ requires [M+NH₄]⁺ 442.2424.

(1RS,2RS,3RS)-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 MgSO₄, filtered, and concentrated in vacuo to give a pure title compound as a white solid (0.35 g, 98%). Mp: 80-82 °C; Rf 0.7 (pet. ether : diethyl ether 8:2); IR (ATR) 2953, 1702, 1442, 1244, 1206, 1068, 832, 758, 697 cm⁻¹; δH (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, CO₂CH₃), 3.73 (3H, s, 2-Ar-OC₂H₅), 2.95 (1H, d, J = 4.0Hz, 3-H), 2.73 (1H, d, J = 4.0Hz, 1-H), 0.31 (9H, s, Si(CH₃)₃), 0.08 (9H, s, Si(CH₃)₃); δC (125 MHz) 175.2 (CO), 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-OCH₃), 52.6 (CO₂CH₃), 38.3 (C-3), 34.6 (C-2), 33.8 (C-1), -0.3 (Si(CH₃)₃), -0.7 (Si(CH₃)₃); δF (376 MHz) -186.5; δSi (139 MHz) 23.1 (J₁Si-F = 322.2Hz), -14.9 (J₂Si-F = 27.0Hz), -15.8 (J₂Si-F = 24.9Hz); m/z (EI) 459 ([M-CH₃]+, 6%), 401 ([M-Si(CH₃)₃]+, 100), 277 (27), 265 (21), 250 (38), 131 (33), 73 (93), 59 (81), 45 (19); HRMS (ES+) found [M+NH₄]⁺ 492.2210, C₂₄H₃₀O₃NFSi₃ requires [M+NH₄]⁺ 492.2216.

(1RS,2RS,3RS)-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 MgSO₄, filtered, and concentrated in vacuo to give a pure title compound (0.07 g, 94%). Rf 0.6 (pet. ether : diethyl ether 9:1); IR (ATR) 2953, 1702, 1442, 1244, 1206, 1068, 832, 758, 697 cm⁻¹; δH (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, OCH₃), 2.85 (1H, d, J = 4.2Hz, 3-H), 2.13
(1H, d, $J = 4.2$ Hz, 1-$H$), 0.94 (3H, s, CH$_3$), 0.29 (9H, s, Si(CH$_3$)$_3$), 0.19 (9H, s, Si(CH$_3$)$_3$); $\delta$C (175 MHz) 175.8 (CO), 136.2 (Ar-C-1), 129.2 (Ar-C-2,6), 128.3 (Ar-C-3,5), 126.7 (Ar-C-4), 52.4 (OCH$_3$), 38.2 (C-3), 31.9 (C-1), 20.4 (C-2), 16.2 (CH$_3$), -0.4 (Si(CH$_3$)$_3$), -0.8 (Si(CH$_3$)$_3$); $\delta_F$ (188 MHz) -193.4; $\delta_{Si}$ (139 MHz) 27.1 ($^1$J$_{Si-F}$ = 315.7 Hz), -15.4 ($^2$J$_{Si-F}$ = 26.3 Hz), -16.4 ($^3$J$_{Si-F}$ = 25.0 Hz); m/z 367 ([M-CH$_3$]$^+$, 30%), 309 ([M-Si(CH$_3$)$_3$]$^+$, 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 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$^{-1}$; $\delta_H$ (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, $J = 9.8$ Hz, $J = 4.9$ Hz, 3-$H$), 3.64 (3H, s, OCH$_3$), 3.20 (1H, dd, $J = 16.8$ Hz, $J = 9.8$ Hz, 2-$H$), 2.51 (1H, dd, $J = 16.8$ Hz, $J = 4.9$ Hz, 2-$H$), 2.10 (3H, s, CH$_3$); $\delta$C (175 MHz) 206.8 (CO), 172.5 (COCH$_3$), 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 (OCH$_3$), 36.7 (C-2), 28.9 (CH$_3$); m/z (EI) 206 ([M]$^+$, 4%), 175 ([M-OCH$_3$]$^+$, 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 mCPBA...
(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$^{-1}$; $\delta_H$ (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, OCH$_3$), 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(CH$_3$)$_3$); $\delta_C$ (125 MHz) 214.3 (CO), 172.3 (CO$_2$CH$_3$), 138.0 (Ar-C-1), 128.9 (Ar-C-3,5), 128.1 (Ar-C-2,6), 127.3 (Ar-C-4), 51.6 (OCH$_3$), 48.9 (C-3), 45.0 (C(CH$_3$)$_3$), 39.3 (C-2), 27.2 (C(CH$_3$)$_3$); m/z (EI) 248 ([M]$^+$, 16%), 217 ([M-OCH$_3$]$^+$, 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]$^+$ 248.1404, C$_{15}$H$_{20}$O$_3$ requires [M]$^+$ 248.1407.

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

![Methyl 4-(4-methoxyphenyl)-4-oxo-3-phenylbutanoate](image)

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 mCPBA (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$^{-1}$; $\delta_H$ (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-OCH$_3$), 3.65 (3H, s, 1-OCH$_3$), 3.37 (1H, dd, $J$ = 16.8Hz, $J$ = 9.8Hz, 2-H), 2.71 (1H, dd, $J$ = 16.8Hz, $J$ = 4.9Hz, 2-H); $\delta_C$ (175 MHz) 197.0 (CO-4), 172.6 (CO-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), 168
128.0 (3-Ar-C-2,6), 127.4 (3-Ar-C-4), 113.7 (4-Ar-C-3,5), 55.4 (4-Ar-OCH₃), 51.75 (1-OCH₃), 49.2 (C-3), 38.4 (C-2); m/z (EI) 298 ([M]⁺, 6%), 267 ([M-OCH₃]⁺, 27), 135(100), 121 (12), 107 (41), 92 (45), 77 (53), 64 (18); HRMS (EI) found [M]⁺ 298.1201, C₁₈H₁₈O₄ requires [M]⁺ 298.1200.

(1RS,2RS,3RS)-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 MgSO₄, filtered, and concentrated under reduced pressure to give a pure title compound (0.16 g, 98%). Rf 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; δH (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, CO₂C₃H₃), 3.00 (1H, d, J = 4.2Hz, 3-H), 2.79 (1H, d, J = 4.2Hz, 1-H), 0.34 (9H, s, OSi(CH₃)₃), 0.09 (9H, s, Si(CH₃)₃), 0.08 (9H, s, Si(CH₃)₃); δC (175 MHz) 175.2 (CO), 142.2 (2-Ar-C-1), 135.4 (3-Ar-C-1), 131.7 (2-Ar-C-2,6), 128.0 (q, ²J_C-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-F = 3.5Hz, 2-Ar-C-3,5), 124.3 (q, ¹J_C-F = 271.1Hz, 2-Ar- CF₃), 52.9 (CO₂C₃H₃), 38.4 (C-3), 35.3 (C-2), 33.1 (C-1), -0.3 (Si(CH₃)₃), -0.7 (Si(CH₃)₃); δF (376 MHz) -62.7, -184.5; δSi (139 MHz) 22.8 (¹J_{Si-F} = 323.8Hz), -14.2 (²J_{Si-F} = 27.2Hz), -15.2 (²J_{Si-F} = 25.2Hz); m/z (EI) 497 ([M-CH₃]⁺, 25%), 439 ([M-Si(CH₃)₃]⁺, 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+NH₄]⁺ 530.1986, C₂₄H₃₆O₂NF₄Si₃ requires [M+NH₄]⁺ 530.1984.
Methyl 4-oxo-3-phenyl-4-(4-(trifluoromethyl)phenyl)butanoate 335

To a solution of methyl 2-(1’-fluoro-1’,1’-bistrimethylsilylsilyl)-2-(4-(trifluoromethyl)phenyl)-3-phenylcyclopropanecarboxylate (0.11 g, 0.21 mmol) in DMF (4.0 ml) was added mCPBA (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 MgSO₄, filtered, and concentrated in vacuo. Flash column chromatography (pet. ether : diethyl ether 8:2) gave title compound as a yellow oil (0.03 g, 45%).

(1RS,2RS,3RS)-Methyl 2-(1’-fluoro-1’,1’-bistrimethylsilylsilyl)-2-(furan-2’-yl)-3-phenylcyclopropanecarboxylate 336

To a solution of methyl 2-(1’,1’-bistrimethylsilyl-1’-trimethylsiloxysilyl)-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 MgSO₄, 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%). Rf 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; δH (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, CO₂CH₃), 3.02 (1H, d, J = 5.6Hz, 2-H), 2.94 (1H, d, J = 5.6Hz, 2-H), 0.27 (9H, s, Si(CH₃)₃), 0.09 (9H, s, Si(CH₃)₃); δC (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 (CO₂CH₃), 37.1 (C-3), 32.2 (C-2), 27.2 (C-1), -0.5 (Si(CH₃)₃), -1.3 (Si(CH₃)₃); δF (376MHz) -191.4; δSi (139 MHz) 23.9 (1JSi-F = 327.5Hz), -14.9 (2JSi-F = 21.7Hz); m/z (EI) 434 ([M]+, 0.1%), 419 ([M-CH₃]+, 0.5), 361 ([M-Si(CH₃)₃]+, 38), 165 (20), 131 (16), 73 (100), 59 (40), 45 (14); HRMS (EI) found [M]+ 434.1562, C₂₁H₃₁FO₃Si₃ requires [M]+ 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 mCPBA (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 MgSO₄, filtered, and concentrated in vacuo. Flash column chromatography (pet. ether : diethyl ether 7:3) gave title compound as a white solid (0.05 g, 78%). Mp: 86–88 °C; Rf 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; δH (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,
CO₂CH₃), 3.39 (1H, dd, J = 17.0Hz, J = 10.0Hz, 2-H), 2.72 (1H, dd, J = 17.0Hz, J = 5.0Hz, 2-H); δC (125 MHz) 187.3 (CO), 172.3 (CO₂Me), 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 (CO₂CH₃), 49.5 (C-3), 37.2 (C-2); m/z (EI) 258 ([M]⁺, 10%), 121 (42), 103 (17), 95 (100), 77 (15); HRMS (ES+) found [M+H]⁺ 259.0965, C₁₅H₁₅O₄ requires [M+H]⁺ 259.0965.

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

![Structure](attachment:image.png)

To a solution of N,N-diethyl-2-(1',1'-bistrimethylsilyl-1'-trimethylsil oxy)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 MgSO₄, 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, 693 cm⁻¹; δH (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, OCH₃), 3.60 (1H, dt, J = 7.0Hz, J = 14.0Hz, CH₂CH₃), 3.57 (1H, dt, J = 7.0Hz, J = 14.0Hz, CH₂CH₃), 3.40 (1H, dt, J = 7.0Hz, J = 14.0Hz, CH₂CH₃), 3.29 (1H, dt, J = 7.0Hz, J = 14.0Hz, CH₂CH₃), 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, CH₃CH₂), 1.18 (3H, t, J = 7.0Hz, CH₃CH₂), 0.26 (9H, s, Si(CH₃)₃), 0.03 (9H, s, Si(CH₃)₃); δC (175 MHz) 173.3 (CO), 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 (OCH₃), 43.1 (CH₂CH₃), 41.6 (CH₂CH₃), 37.7 (C-3), 34.9 (C-2), 33.1 (C-1), 14.8 (CH₂CH₃), 13.2 (CH₂CH₃), 0.1 (Si(CH₃)₃), -0.4 (Si(CH₃)₃); δF (376MHz) -152.3; δSi (139 MHz) -10.9 (J_{Si-F} = 309.7Hz), -14.4 (J_{Si-F} = 38.1Hz), -14.9 (J_{Si-F} = 33.5Hz).
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) followed 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\(^{-1}\); \( \delta \)\(_{\text{H}}\) (500 MHz) 8.02-8.00 (2H, m, 4-Ar-2,6-\( \text{H} \)), 7.34-7.33 (2H, m, 3-Ar-2,6-\( \text{H} \)), 7.30-7.27 (1H, m, 3-Ar-3,5-\( \text{H} \)), 7.22-7.19 (1H, m, 3-Ar-4-\( \text{H} \)), 6.86-6.84 (2H, m, 4-Ar-3,5-\( \text{H} \)), 5.25 (1H, dd, \( J = 10.0 \text{Hz} \), \( J = 4.0 \text{Hz} \), 3-\( \text{H} \)), 3.80 (3H, s, 4-Ar-O\( \text{CH}_3 \)), 3.36-3.22 (3H, m, \( \text{CH}_2\text{CH}_3 \)), 2.62 (1H, dd, \( J = 16.0 \text{Hz} \), \( J = 4.0 \text{Hz} \), 2-\( \text{H} \)), 1.18 (3H, t, \( J = 7.0 \text{Hz} \), \( \text{CH}_2\text{CH}_3 \)), 1.06 (3H, t, \( J = 7.0 \text{Hz} \), \( \text{CH}_2\text{CH}_3 \)); \( \delta \)\(_{\text{C}}\) (125 MHz) 197.9 (CO-4), 170.1 (CO-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\( \text{CH}_3 \)), 49.2 (C-3), 41.8 (\( \text{CH}_2\text{CH}_3 \)), 40.2 (\( \text{CH}_2\text{CH}_3 \)), 38.1 (C-2), 14.1 (\( \text{CH}_2\text{CH}_3 \)), 13.0 (\( \text{CH}_2\text{CH}_3 \)); m/z (EI) 339 ([M]+, 1%), 135 (100), 77 (13); HRMS (ES+) found [M+H]\(^+\) 340.1905, \( \text{C}_{21}\text{H}_{28}\text{O}_3\text{N} \) requires [M+H]\(^+\) 340.1907.

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

**Diagram:**

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MeO
\( \text{N} \)
\( \text{Ph} \)
CONEt\(_2\)
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(1RS,2RS,3RS)-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 mCPBA (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 MgSO₄, filtered, and concentrated in vacuo. Flash column chromatography give the title compound as a colourless oil (0.07 g, 37%). Rf 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, CO₂CH₃), 3.68 (3H, s, 2-Ar-OCH₃), 3.12 (1H, d, J = 6.3Hz, 3-H), 2.58 (1H, d, J = 6.3Hz, 1-H), 0.05 (9H, s, OSi(CH₃)₃), 0.04 (9H, s, OSi(CH₃)₃); δ_C (175 MHz) 172.1 (CO), 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-OCH₃), 51.9 (CO₂CH₃), 36.8 (C-2), 34.2 (C-3), 33.0 (C-1), 1.43 (OSi(CH₃)₃), 1.39 (OSi(CH₃)₃); δ_F (376 MHz) -192.8; δ_Si (139 MHz) 10.6 (J_Si-F = 190.7Hz), -73.1 (J_Si-F = 3.9Hz), -74.9 (J_Si-F = 3.9Hz); m/z (EI) 506 ([M]⁺, 22%), 491 ([M-CH₃]⁺, 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+NH₄]⁺ 524.2115, C₂₄H₉₉O₃NFSi₃ requires [M+NH₄]⁺ 524.2115.
2-Diazo-2-(1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-N,N-dimethylacetamide

Ethylidiisopropylamine (2.99 ml, 17.1 mmol) followed by tris(trimethylsilyl)silyl trifluoromethanesulphonate (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 NaHCO₃ solution (70 ml). The aqueous layer was separated and extracted with Et₂O (3 x 50 ml). The combined organic layers were dried over MgSO₄, 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%). Rₛ 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(C₃H₃)₂), 0.24 (27H, s, Si(C₃H₃)₃); δ_C (175 MHz) 168.9 (CO), 37.7 (N(CH₃)₂), 1.0 (Si(CH₃)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]^+ 360.1785, C₁₃H₃₄ON₃Si₄ requires [M+H]^+ 360.1779.

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

Ethylidiisopropylamine (2.94 ml, 16.9 mmol) followed by tris(trimethylsilyl)silyl trifluoromethanesulphonate (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 NaHCO₃ solution (70 ml). The aqueous layer was separated and extracted with Et₂O (3 x 50 ml). The combined organic layers were dried over MgSO₄, 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%). Rₛ 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, CH₂CH₃), 1.28 (3H, t, J = 7.0Hz,
CH₂CH₃), 0.23 (27H, s, Si(CH₃)₃); δC (125 MHz) 170.2 (CO), 60.9 (CH₂CH₃), 38.5 (C-2), 14.7 (CH₂CH₃), 1.0 (Si(CH₃)₃); δSi (140 MHz) -11.34, -80.2; m/z (EI) 332 ([M-N₂]+, 0.1%), 215 (54), 117 (24), 73 (100), 45 ([EtO]+, 34); HRMS (ASAP) found [M+H]⁺ 361.1626, C₁₃H₃₃O₂N₂Si₄ requires [M+H]⁺ 361.1619.

**Tris(trimethylsilyl)silyl trifluoromethanesulfonate 362**

![Chemical structure](image)

**Method A**

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 °C. 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; δH (400 MHz) 0.30 (27H, s, Si(CH₃)₃); δC (100 MHz) 118.5 ((q, ¹J_C-F = 315.7Hz, CF₃), -0.7 (Si(CH₃)₃); δF (376MHz) -76.9; δSi (139 MHz) -11.7 (Si(CH₃)₃), -74.4 (Si-OTf).

**Method B**

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 °C. 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 °C/0.6 mbar. Spectroscopic data for product 362 were consistent with data presented in Method A.
2-Diazo-N,N-dimethylacetamide\textsuperscript{104} 363

\[ \begin{array}{c}
\text{O} \\
\text{NMe}_2 \\
\text{N}_2 \\
\end{array} \]

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 \(\text{MgSO}_4\), 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\(^{-1}\); \(\delta_H\) (700 MHz) 4.96 (1H, s, 2-\(H\)), 2.91 (6H, s, N(\(\text{CH}_3\))\(_2\)); \(\delta_C\) (175 MHz) 165.8 (\(\text{CO}\)), 46.1(CN\(_2\)), 36.2 (N(\(\text{CH}_3\))\(_2\)); m/z (EI) 113 ([M]+, 25%), 72 (38), 70 (21), 44 (20), 42 (100), 28 (20).

2-Diazo-\(N,N\)-dimethyl-3-oxobutanamide\textsuperscript{104} 365

\[ \begin{array}{c}
\text{O} \\
\text{NMe}_2 \\
\text{N}_2 \\
\end{array} \]

To a solution of \(\text{N,N\)-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 \(\text{MgSO}_4\), 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\(^{-1}\); \(\delta_H\) (700 MHz) 3.01 (6H, s, N(\(\text{CH}_3\))\(_2\)), 2.35 (3H, s, 4-\(H\)); \(\delta_C\) (175 MHz) 189.5 (\(\text{CO}\)), 161.4 (\(\text{CON(CH}_3)_2\)), 43.4 (CN\(_2\)), 37.5 (N(CH\(_3\))\(_2\)), 27.3 (\(\text{C-4}\)); m/z (ES+) 156 ([M+H]+, 100%).
Allyltris(trimethylsilyl)silane

\[
\text{Allyltrimethylsilylsilane} = \text{(Me}_3\text{Si)}_3\text{Si} 
\]

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 °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 Et₂O (3 x 30 ml). The combined organic layers were dried over MgSO₄, filtered and concentrated. Flash column chromatography (hexane) gave the title compound as a white semi solid material (8.12 g, 85%). Rf 0.8 (hexane); IR (ATR) 2949, 2893, 1394, 1243, 1047, 987, 892, 827, 763, 746 cm⁻¹; δH (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(CH₃)₃); δC (175 MHz) 138.5 (C-2), 111.8 (C-3), 14.9 (C-1), 1.1 (Si(CH₃)₃); δSi (139 MHz) -12.4, -81.4; m/z (EI) 288 ([M⁺], 6%), 247 ([M-C₃H₅S]+, 15), 215 ([M-Si(CH₃)₃]+, 10), 199 (14), 173 (59), 141 (44), 131 (16), 73 (100), 45 (15).

Methanesulfonyl azide

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; δH (200 MHz) 3.27 (3H, s, CH₃); δC (100 MHz) 42.8 (CH₃).

Phenyltris(trimethylsilyl)silane

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,
88.3 mmol) in dry THF (50 ml) at 0 °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 (3 x 100 ml). The combined organic layers were dried over MgSO₄, 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, 739, 728 cm⁻¹; \( \delta_H \) (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(CH₃)₃); \( \delta_C \) (100 MHz) 136.6 (Ar-\( C \)), 135.5 (Ar-\( C \)), 127.7 (Ar-\( C \)), 127.3 (Ar-\( C \)), 1.7 (Si(CH₃)₃); \( \delta_Si \) (139 MHz) -12.7 (Si(CH₃)₃), -76.8 (Ar-Si); m/z (EI) 324 ([M]+, 73%), 309 ([M-CH₃]+, 29), 251 ([M-Si(CH₃)₃]+, 40), 236 (56), 174 (92) 73 (100).

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

![Chemical Structure](image)

To a solution of Rh₂(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 Et₂O (3 x 5 ml). The combined organic layers were dried over MgSO₄, 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 ºC; \( R_f \) 0.4 (pet. ether : diethyl ether 6:4); IR (ATR) 3340, 2953, 2895, 1655, 1365, 1243, 1182, 1039, 963, 831, 743 cm⁻¹; \( \delta_H \) (700 MHz) 4.08 (2H, q, J = 7.0Hz, CH₂CH₃), 2.06 (1H, s, 2-\( H \)), 1.26 (3H, t, J = 7.0Hz, CH₂CH₃), 0.19 (18H, s, Si(CH₃)₃), 0.17 (9H, s, Si(CH₃)₃); \( \delta_C \) (175 MHz) 174.5 (CO), 60.2 (CH₂CH₃), 31.0 (C-2), 14.5 (CH₂CH₃), 0.1 (Si(CH₃)₃), -1.0 (Si(CH₃)₃), -1.3 (Si(CH₃)₃); \( \delta_Si \) (140 MHz) 9.0, 3.8, -18.1, -18.2; m/z (ES+) 373 ([M+Na]+, 100%), 360 (42), 338 (17), 301 (20), 219 (16); Anal. Calcd for C₁₃H₃₄O₃Si₄: 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, 893, 830, 755, 731 cm$^{-1}$; $\delta_H$ (C$_7$D$_8$, 700 MHz) 3.56 (2H, q, $J = 7.0$Hz, $\mathrm{CH}_2$CH$_3$), 1.09 (3H, t, $J = 7.0$Hz, CH$_2$CMe$_3$), 0.26 (9H, s, Si(CMe$_3$)$_3$), 0.25 (18H, s, Si(CMe$_3$)$_3$); $\delta_C$ (C$_7$D$_8$, 175 MHz) 165.6 (CO), 61.4 (CH$_2$CH$_3$), 18.7 (CH$_2$CH$_3$), 1.6 (Si(CH$_3$)$_3$), 0.2 (CCO), -0.7 (Si(CH$_3$)$_3$); $\delta_{Si}$ (140 MHz) 6.6, 5.7, -18.3; m/z (EI) 332 ([M]$^+$, 9%), 317 ([M-CH$_3$]$^+$, 49), 303 ([M-CH$_2$CH$_3$]$^+$, 49), 273 (30), 259 ([M-Si(CH$_3$)$_3$]$^+$, 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]$^+$ 332.1478, C$_{13}$H$_{32}$O$_2$Si$_4$ requires [M]$^+$ 332.1474.

4-Ethoxy-2,2,3-tris(trimethylsilyl)-2H-1,2-oxasiletetra-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. $\delta_H$ (C$_7$D$_8$, -80 $^\circ$C, 500 MHz) 4.02 (2H, q, $J = 7.2$Hz, CH$_2$CH$_3$), 1.04 (1H, t, $J = 7.2$Hz, CH$_2$CH$_3$), 0.32 (9H, s, Si(CH$_3$)$_3$), 0.23 (18H, s, Si(CH$_3$)$_3$); $\delta_C$ (C$_7$D$_8$, -80 $^\circ$C, 125 MHz) 161.1 (C-4), 67.0 (C-3), 62.8 (CH$_2$CH$_3$), 15.0 (CH$_2$CH$_3$), 1.4 (Si(CH$_3$)$_3$), -2.1 (Si(CH$_3$)$_3$); $\delta_{Si}$ (C$_7$D$_8$, -80 $^\circ$C, 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, 827, 761, 721 cm$^{-1}$; $\delta_H$ (700 MHz) 4.09 (1H, dq, $\text{J} = 7.0\text{Hz}$, $\text{J} = 11.2\text{Hz}$, CH$_2$CH$_3$), 4.02 (1H, dq, $\text{J} = 7.0\text{Hz}$, $\text{J} = 11.2\text{Hz}$, CH$_2$CH$_3$), 3.45 (3H, s, OC$_2$H$_3$), 2.23 (1H, s, 2-H), 1.24 (3H, t, $\text{J} = 7.0\text{Hz}$, CH$_2$CH$_3$), 0.21 (9H, s, Si(CH$_3$)$_3$), 0.19 (9H, s, Si(CH$_3$)$_3$), 0.17 (9H, s, Si(CH$_3$)$_3$); $\delta_C$ (175 MHz) 173.7 (CO), 60.0 (CH$_2$CH$_3$), 53.7 (OCH$_3$), 30.4 (C-2), 14.5 (CH$_2$CH$_3$), -0.08 (Si(CH$_3$)$_3$), -0.12 (Si(CH$_3$)$_3$), -0.7 (Si(CH$_3$)$_3$); $\delta_{Si}$ (140 MHz) 13.3, 4.1, -18.0, -18.5; m/z (ES+) 365 ([M+H]$^+$, 10%), 333 (100), 319 (27), 263 (10), 219 (17); HRMS (ES+) found [M+H]$^+$ 365.1812, C$_{14}$H$_{37}$O$_3$Si$_4$ requires [M+H]$^+$ 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$_2$O$_3$ 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; \( \delta_H \) (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, \( J = 2.8\text{Hz}, \text{CCH}_2 \)), 4.40 (1H, d, \( J = 2.8\text{Hz}, \text{CCH}_2 \)), 4.13 (1H, dq, \( J = 11.2\text{Hz}, J = 7.0\text{Hz}, \text{CH}_2\text{CH}_3 \)), 4.06 (1H, dq, \( J = 11.2\text{Hz}, J = 7.0\text{Hz}, \text{CH}_2\text{CH}_3 \)), 2.50 (1H, s, 2-H), 1.26 (3H, t, \( J = 7.0\text{Hz}, \text{CH}_2\text{C}_3 \)), 0.27 (9H, s, Si(C\_3H\_3)), 0.192 (9H, s, Si(C\_3H\_3)), 0.190 (9H, s, Si(C\_3H\_3)); \( \delta_C \) (175 MHz) 173.4 (CO), 157.8 (SiOC), 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\_CH\_2), 60.2 (C\_CH\_2CH\_3), 29.6 (C-2), 14.5 (C\_CH\_2), 0.1 (Si(C\_3H\_3)), -0.1 (Si(C\_3H\_3)), -0.2 (Si(C\_3H\_3)); \( \delta_Si \) (140 MHz) 8.6, 4.3, -16.3, -16.7; m/z (ASAP) 451 ([M-H]⁺, 7%); HRMS (ASAP) found [M+H]⁺ 453.2153, C\_21H\_41O\_3Si\_4 requires [M+H]⁺ 453.2133.

(3SR,4RS)-Ethyl 4,6-diphenyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2H-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 °C; \( R_f \) 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; \( \delta_H \) (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, \( J = 2.8\text{Hz}, 4-H \)), 4.91 (1H, d, \( J = 2.8\text{Hz}, 5-H \)), 4.37 (1H, dq, \( J = 11.2\text{Hz}, J = 7.0\text{Hz}, \text{CH}_2\text{CH}_3 \)), 4.06 (1H, dq, \( J = 11.2\text{Hz}, J = 7.0\text{Hz}, \text{CH}_2\text{CH}_3 \)), 1.33 (3H, t, \( J = 7.0\text{Hz}, \text{CH}_2\text{CH}_3 \)), 0.40 (9H, s, Si(CH\_3)_3), 0.16 (9H, s, Si(CH\_3)_3), -0.18 (9H, s, CSi(CH\_3)_3); \( \delta_C \) (175 MHz) 178.0 (CO), 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 (CH\_2CH\_3), 44.5 (C-4), 37.2 (C-3), 14.8 (CH\_2CH\_3), 0.8 (Si(CH\_3)_3), 0.7 (CSi(CH\_3)_3), 0.3 (Si(CH\_3)_3); \( \delta_Si \) (140 MHz) 4.7, 3.1, -13.2, -
14.3; m/z (ASAP) 541 ([M+H]+, 11%); Anal. Calcd for C_{28}H_{44}O_{3}Si_{4}: C, 62.16; H, 8.20. Found: C, 62.04; H, 8.20.

(3SR,4RS)-Ethyl 6-methyl-4-phenyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2H-1,2-oxasiline-3-carboxylate 401a and
(3RS,4RS)-Ethyl 6-methyl-4-phenyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2H-1,2-oxasiline-3-carboxylate 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 °C; R_{f} 0.7 (Al_{2}O_{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, CH_{2}CH_{3}), 4.01 (1H, dq, J = 11.0Hz, J = 7.0Hz, CH_{2}CH_{3}), 1.82 (3H, d, J = 2.0Hz, CH_{3}), 1.29 (3H, t, J = 7.0Hz, CH_{2}CH_{3}), 0.31 (9H, s, Si(CH_{3})_{3}), 0.20 (9H, s, Si(CH_{3})_{3}), -0.20 (9H, s, CSi(CH_{3})_{3}); δ_{C} (125 MHz) 176.1 (CO), 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 (CH_{2}CH_{3}), 44.1 (C-4), 36.8 (C-3), 22.8 (CH_{3}), 14.8 (CH_{2}CH_{3}), 0.72 (Si(CH_{3})_{3}), 0.66 (CSi(CH_{3})_{3}), 0.2 (Si(CH_{3})_{3}); δ_Si
(140 MHz) 4.2, 1.7, -13.4, -14.9; m/z (ASAP) 479 ([M+H]⁺, 18%); HRMS (ASAP) found [M+H]⁺ 479.2284, C₂₃H₄₃O₃Si₄ requires [M+H]⁺ 479.2289.

Experimental data for compound 401b:
R₇ 0.6 (Al₂O₃ pH=7, pet. ether : diethyl ether 9:1); IR (ATR) 2950, 2895, 1708, 1653, 1491, 1449, 1378, 1245, 1198, 1157, 1096, 1037, 1005, 979, 833, 743 cm⁻¹; δₗ (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), 3.95 (1H, dq, J = 11.2Hz, J = 7.0Hz, CH₂CH₃), 4.01 (1H, d, J = 4.2Hz, 4-H), 3.91 (1H, dq, J = 11.2Hz, J = 7.0Hz, CH₂CH₃), 1.84 (3H, s, CH₃), 1.28 (3H, t, J = 7.0Hz, CH₂C₃H₇), 0.32 (9H, s, Si(CH₃)₃), 0.07 (9H, s, Si(CH₃)₃), 0.06 (9H, s, CSi(CH₃)₃); δc (175 MHz) 174.3 (CO), 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 (CH₂CH₃), 43.5 (C-4), 38.3 (C-3), 22.2 (CH₃), 14.2 (CH₂CH₃), 0.9 (Si(CH₃)₃), 0.7 (CSi(CH₃)₃), 0.0 (Si(CH₃)₃); δSi (140 MHz) 7.9, 3.7, -14.8, -15.7; m/z (ASAP) 479 ([M+H]⁺, 8%); HRMS (ASAP) found [M+H]⁺ 479.2297, C₂₃H₄₃O₃Si₄ requires [M+H]⁺ 479.2289.

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

To a solution of Rh₂(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 °C; R₇ 0.6 (Al₂O₃ pH=7, pet. ether : diethyl ether 9:1); IR (ATR) 2950, 2902, 1697, 1440, 1384, 1230, 1175, 1040, 944, 829, 768, 744 cm⁻¹; δₗ (700 MHz) 4.19 (1H, dq, J = 11.2Hz, J = 7.0Hz, CH₂CH₃), 4.02 (1H, dq, J = 11.2Hz, J = 7.0Hz, CH₂CH₃), 2.62 (1H, q, J = 7.0Hz, 4-H), 1.65 (3H, s, 6-CH₃), 1.61 (3H, s, 5-CH₃), 1.27 (3H, t, J = 7.0Hz, CH₂CH₃), 1.20
(3H, d,  J = 7.0Hz, 4-CH₃), 0.26 (9H, s, Si(CH₃)₃), 0.17 (9H, s, Si(CH₃)₃), 0.12 (9H, s, CSi(CH₃)₃); δC (175 MHz) 174.9 (CO), 143.9 (C-6), 108.5 (C-5), 60.2 (CH₂CH₃), 38.0 (C-3), 37.4 (C-4), 20.1 (4-CH₃), 18.8 (6-CH₃), 18.7 (5-CH₃), 14.5 (CH₂CH₃), 1.1 (Si(CH₃)₃), 0.6 (Si(CH₃)₃), -0.3 (CSi(CH₃)₃); δSi (140 MHz) 8.0, 1.0, -14.8, -17.8; m/z (ASAP) 431 ([M+H]+, 100%); HRMS (ASAP) found [M+H]+ 431.2274, C₁₉H₄₃O₃Si₄ requires [M+H]+ 431.2289.

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

To a solution of Rh₂(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%). Rf 0.6 (Al₂O₃ 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; δH (700 MHz) 4.27 (1H, dq, J = 10.5Hz, J = 7.0Hz, OC₂H₂CH₃), 4.12 (1H, s, 5-H), 3.98 (1H, dq, J = 10.5Hz, J = 7.0Hz, OCH₂CH₃), 3.30 (1H, q, J = 7.0Hz, 4-H), 1.96 (2H, q, J = 7.0Hz, CH₂CH₃), 1.35 (3H, d, J = 7.0Hz, CH₃), 1.27 (3H, t, J = 7.0Hz, OCH₂CH₃), 0.99 (3H, t, J = 7.0Hz, CH₂CH₃), 0.29 (9H, s, Si(CH₃)₃), 0.21 (9H, s, CSi(CH₃)₃), -0.12 (9H, s, Si(CH₃)₃); δC (175 MHz) 175.5 (CO), 153.8 (C-6), 103.8 (C-5), 60.4 (OCH₂CH₃), 35.4 (C-3), 33.3 (C-4), 29.3 (CH₂CH₃), 23.5 (CH₃), 14.7 (OCH₂CH₃), 11.6 (CH₂CH₃), 2.1 (Csi(CH₃)₃), 0.4 (Csi(CH₃)₃), 0.2 (Si(CH₃)₃); δSi (140 MHz) 4.6, 2.0, -14.89, -14.91; m/z (ASAP) 431 ([M+H]+, 100%); HRMS (ASAP) found [M+H]+ 431.2272, C₁₉H₄₃O₃Si₄ requires [M+H]+ 431.2289.
Ethyl 5-oxo-3,5-diphenylpentanoate\textsuperscript{134} 412

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{CO}_2\text{Et}
\end{array}
\]

To a solution of methyl ethyl 4,6-diphenyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2\textit{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\textsubscript{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 °C; \(R_f\) 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\textsuperscript{-1}; \(\delta_H\) (700 MHz) 7.92-7.91 (2H, m, 5-Ar-2,6-\textit{H}), 7.55-7.53 (1H, m, 5-Ar-4-\textit{H}), 7.44-7.42 (1H, m, 5-Ar-3,5-\textit{H}), 7.29-7.26 (4H, m, 3-Ar-2,3,5,6-\textit{H}), 7.20-7.18 (1H, m, 3-Ar-4-\textit{H}), 4.04 (1H, dq, \(J = 11.2\text{Hz}, J = 7.0\text{Hz}, \text{CH}_2\text{CH}_3\)), 4.02 (1H, dq, \(J = 11.2\text{Hz}, J = 7.0\text{Hz}, \text{CH}_2\text{CH}_3\)), 3.88 (1H, dq, \(J = 7.7\text{Hz}, J = 7.0\text{Hz}, 3\-\text{H}\)), 3.39 (1H, dd, \(J = 16.8\text{Hz}, J = 7.0\text{Hz}, 4\-\text{H}\)), 3.34 (1H, dd, \(J = 16.8\text{Hz}, J = 7.0\text{Hz}, 4\-\text{H}\)), 2.80 (1H, dd, \(J = 15.4\text{Hz}, J = 7.0\text{Hz}, 2\-\text{H}\)), 2.68 (1H, dd, \(J = 15.4\text{Hz}, J = 7.7\text{Hz}, 2\-\text{H}\)), 1.33 (3H, t, \(J = 7.0\text{Hz}, \text{CH}_2\text{CH}_3\)); \(\delta_C\) (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 (CH\textsubscript{2}CH\textsubscript{3}), 44.6 (C-4), 40.8 (C-2), 37.6 (C-3), 14.1 (CH\textsubscript{2}CH\textsubscript{3}); m/z (El) 296 ([M]\textsuperscript{+}, 14\%), 251 ([M-OEt]\textsuperscript{+}, 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\textsuperscript{135} 413

\[
\begin{array}{c}
\text{Ph} \\
\text{O} \\
\text{CO}_2\text{Et} \\
\text{SiMe}_3
\end{array}
\]

To a solution of methyl ethyl 4,6-diphenyl-2,2,3-tris(trimethylsilyl)-3,4-dihydro-2\textit{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 MgSO₄, 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 °C; Rf 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; δH (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, CH₂CH₃), 4.15 (1H, dq, J = 10.5Hz, J = 7.0Hz, CH₂CH₃), 3.93-3.88 (2H, m, 3-H), 3.86 (1H, dq, J = 10.5Hz, J = 7.0Hz, CH₂CH₃), 3.43 (1H, dd, J = 15.8Hz, J = 10.5Hz, 4-H), 3.41 (1H, dd, J = 15.8Hz, J = 10.5Hz, 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, CH₂CH₃), 0.98 (3H, t, J = 7.0Hz, CH₂CH₃), 0.20 (9H, s, Si(CH₃)₃), -0.19 (9H, s, Si(CH₃)₃); δC (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 (CH₂CH₃), 59.6 (CH₂CH₃), 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 (CH₂CH₃), 14.1 (CH₂CH₃), -1.2 (Si(CH₃)₃), -2.1 (Si(CH₃)₃); δSi (140 MHz) 4.8, 3.9; m/z (EI) 368 ([M]+, 11%), 340 ([M-C₂H₄]⁺, 11), 322 ([M-EtOH]+, 17), 307 (19), 281 (70), 263 (74), 131 (100), 105 (68), 77 ([Ph]+, 36), 73 ([EtOCO]+, 52), 45 ([EtO]+, 11).

Methylphenylbis(trimethylsilyl)silane

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 °C) 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 Et₂O (3 x 30 ml). The combined organic layers were dried over MgSO₄, filtered and
concentrated. Flash column chromatography (pet. ether) gave the title compound as a white semi solid material (1.53 g, 46%). Rf 0.5 (pet. ether); IR (ATR) 2948, 2891, 1427, 1396, 1244, 1096, 777, 739, 728 cm⁻¹; δH (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(CH₃)₃); δC (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(CH₃)₃), -9.0 (CH₃); δSi (139 MHz) -15.9 (Si(CH₃)₃), -46.3 (Ar-Si); m/z (EI) 266 ([M]+·, 36%), 251 ([M-CH₃]+, 15), 193 ([M-Si(CH₃)₃]+, 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 °C) 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 Et₂O (3 x 20 ml). The combined organic layers were dried over MgSO₄, 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 °C; Rf 0.5 (hexane); IR (ATR) 2944, 2863, 1461, 1243, 1063, 994, 828, 734 cm⁻¹; δH (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, CH(CH₃)₂), 1.08 (18H, d, J = 7.7Hz, CH(CH₃)₂), 0.30 (18H, s, Si(CH₃)₃); δC (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(CH₃)₂), 13.8 (CH(CH₃)₂), 2.5 (Si(CH₃)₃); δSi (140 MHz) 7.5, -12.5, -75.7; m/z (EI) 408 ([M]+, 6%), 393 ([M-CH₃]+, 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+NH₄]⁺ 426.2851, C₂₁H₄₈NSi₄ requires [M+NH₄]⁺ 426.2858.
Ethyl 2-diazo-2-(1,1,1,2,3,3,3-heptamethyltrisilan-2-yl)acetate 416

\[
\text{Me}_3\text{Si} - \text{SiMe}_3 - \text{N}_2 - \text{OEt}
\]

Stage 1
To a solution of methylphenylbis(trimethylsilyl)silane (1.29 g, 4.85 mmol) in DCM (15.0 ml), under argon at 0 °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
Ethyl diisopropylamine (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 °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$_2$O (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$^{-1}$; $\delta_H$ (700 MHz) 4.20 (2H, q, $J$ = 7.0Hz, CH$_2$CH$_3$), 1.28 (3H, t, $J$ = 7.0Hz, CH$_2$CH$_3$), 0.26 (3H, s, CH$_3$), 0.17 (18H, s, Si(CH$_3$)$_3$); $\delta_C$ (175 MHz) 169.7 (CO), 68.1 (C-2), 60.7 (CH$_2$CH$_3$), 14.6 (CH$_2$CH$_3$), -1.2 (Si(CH$_3$)$_3$), -8.7 (CH$_3$); $\delta_{\text{Si}}$ (140 MHz) -14.3, -46.5; m/z (EI) 259 ([M-N$_2$-Me]$^+$, 11%), 245 ([M-COEt]$^+$, 49), 231 (16), 229 ([M-Si(CH$_3$)$_3$]$^+$, 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]$^+$ 325.1198, C$_{11}$H$_{26}$O$_2$N$_2$NaSi$_3$ requires [M+Na]$^+$ 325.1194.
**Ethyl 2-diazo-2-(1,1,1-triisopropyl-3,3,3-trimethyl-2-(trimethylsilyl)trisilan-2-yl)acetate**

![Chemical Structure](image)

**Stage 1**

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 °C, was added dropwise triflic acid (0.33 ml, 3.67 mmol). The reaction mixture was stirred at 0 °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 (1.78 g) as a white solid which was used immediately in *stage 2* without purification.

**Stage 2**

To a solution of ethyl 2-diazoacetate (0.37 ml, 3.66 mmol) in dry Et₂O (15.0 ml) at -78°C were added DIPEA (0.70 ml, 4.03 mmol) followed by a solution of 1,1,1-triisopropyl-3,3,3-trimethyl-2-(trimethylsilyl)trisilan-2-yl trifluoromethanesulfonate (0.62 g, 25.8 mmol) in Et₂O (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 Et₂O (3 x 20 ml). The combined organic layers were dried over MgSO₄, 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%). Rf (pet. ether : diethyl ether 9:1); IR (ATR) 2945, 2865, 2689, 1461, 1366, 1246, 1193, 1095, 1061, 997, 739 cm⁻¹; δH (700 MHz) 4.19 (2H, q, J = 7.0 Hz, CH₂CH₃), 1.28 (3H, sep, J = 7.0 Hz, CH(CH₃)₂), 1.27 (3H, t, J = 7.0 Hz, CH₂CH₃), 1.14 (18H, d, J = 7.0 Hz, CH(CH₃)₂), 0.28 (18H, s, Si(CH₃)₃); δC (175 MHz) 170.0 (CO), 60.9 (CH₂CH₃), 39.6 (C-2), 20.0 (CH(CH₃)₂), 14.7 (CH₂CH₃), 13.7 (CH(CH₃)₂), 2.1 (Si(CH₃)₃); δSi (140 MHz) 9.2, -10.7, -80.1; m/z (EI) 416 ([M-N₂]⁺, 3%), 401 ([M-N₂-Me]⁺, 20), 387 ([M-COEt]⁺, 11), 343 ([M-N₂-SiMe₃]⁺, 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$_2$O (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$^{-1}$; $\delta_H$ (700 MHz) 4.09 (2H, q, $J = 7.0$Hz, CH$_2$CH$_3$), 1.89 (1H, s, 2-H), 1.26 (1H, t, $J = 7.0$Hz, CH$_2$CH$_3$), 0.35 (3H, s, CH$_3$), 0.18 (9H, s, Si(CH$_3$)$_3$), 0.14 (9H, s, Si(CH$_3$)$_3$); $\delta_C$ (175 MHz) 173.7 (CO), 60.0 (CH$_2$CH$_3$), 32.6 (CO-2), 14.5 (CH$_2$CH$_3$), 0.0 (Si(CH$_3$)$_3$), -2.2 (Si(CH$_3$)$_3$); $\delta_Si$ (140 MHz) 11.6, 3.3, -21.1; m/z (EI) 292 ([M]+·, 0.1%), 277 ([M-Ch$_3$]+, 2), 221 (34), 219 ([M-Si(CH$_3$)$_3$]+, 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]$^+$ 293.1421, C$_{11}$H$_{29}$O$_3$Si$_3$ requires [M+ H]$^+$ 293.1419.

2-(2-Ethoxy-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 °C 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$^{-1}$; $\delta_H$ (700 MHz) 3.68 (2H, q, $J = 7.0$Hz, CH$_2$CH$_3$), 1.30 (3H, sep, $J = 7.0$Hz, CH(CH$_3$)$_2$), 1.19 (3H, t, $J = 7.0$Hz, CH$_2$CH$_3$), 1.17 (18H, d, $J = 7.0$Hz, CH(CH$_3$)$_2$), 0.27 (9H, s, Si(CH$_3$)$_3$), 0.25 (9H, s, Si(CH$_3$)$_3$); $\delta_C$ (175 MHz) 163.2 (CO), 61.3 (CH$_2$CH$_3$), 20.0 (CH(CH$_3$)$_2$), 18.5 (CH$_2$CH$_3$), 12.4 (CH(CH$_3$)$_2$), 11.8 (CCO), 1.8
\((\text{Si}(\text{CH}_3)_3), 0.2 (\text{Si}(\text{CH}_3)_3); \delta_{\text{Si}} (140 \text{ MHz}) 9.3, 1.0, -0.6, -17.4; m/z \text{ (EI}) 416 ([M]^+, 0.1\%),
401 ([M-\text{CH}_3]^+, 1), 387 ([M-\text{CH}_2\text{CH}_3]^+, 5), 343 ([M-\text{Si}(\text{CH}_3)_3]^+, 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)**

THF was added in one portion to triphenylphosphine, and alcohols at 25 °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 °C for 30 h. The reaction was then quenched by addition of HCl (5 M, pH = 1) and diluted with Et₂O. The aqueous layer was separated and extracted three times with Et₂O. The combined organic layers were dried over MgSO₄, 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 °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 (\textit{Stage 1}) at -78 °C. After stirring for 3 h at -78 °C saturated ammonium chloride solution was added. The organic layer was separated, and the aqueous layer was extracted three times with \(\text{Et}_2\text{O}\). The combined organic layers were dried over \(\text{MgSO}_4\), filtered, and concentrated \textit{in vacuo}. Flash column chromatography, elution gradient 0 to 20\% diethyl ether in pet. ether, afforded the desired product.

\((E)-(2-(\text{Hexa}-3',5'-\text{dienyloxy})\text{phenyl})(1,1,1,3,3,3-\text{hexamethyl}-2-(\text{trimethylsilyl})\text{trisilan}-2-yl)\text{methanol 433}\)

To a suspension of \(\text{LiAlH}_4\) (0.029 g, 0.76 mmol) in diethyl ether (4.0 ml) was added a solution of \((E)-(2-(\text{hexa}-3,5-\text{dienyloxy})\text{phenyl})(1,1,1,3,3,3-\text{hexamethyl}-2-(\text{trimethylsilyl})\text{trisilan}-2-yl)\text{methanone (0.34 g, 0.76 mmol)}\) 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 \(\text{H}_2\text{O}\) (0.5 ml), \(\text{NaOH}\) (1M, 0.5 ml) and \(\text{H}_2\text{O}\) (0.5 ml). The mixture was then filtered through Celite®\textsuperscript{®}, the precipitate washed with \(\text{EtOAc}\) and the combined filtrate concentrated \textit{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\(^{-1}\); \(\delta_H\) (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, \(J = 16.8\text{Hz}, J = 10.5\text{Hz}, 5'\)-\(H\)), 6.19 (1H, dd, \(J = 15.4\text{Hz}, 5'\)-\(H\)), 5.76 (1H, dt, \(J = 15.4\text{Hz}, J = 7.0\text{Hz}, 3'\)-\(H\)), 5.47 (1H, d, \(J = 4.2\text{Hz}, \text{CHOH}\)), 5.16 (1H, d, \(J = 16.8\text{Hz}, 6'\)-\(H\)), 5.04 (1H, d, \(J = 10.5\text{Hz}, 6'\)-\(H\)), 4.10 (1H, dt, \(J = 9.1\text{Hz}, J = 7.0\text{Hz}, 1'\)-\(H\)), 2.63 (1H, dq, \(J = 14.0\text{Hz}, J = 7.0\text{Hz}, 2'\)-\(H\)), 2.59 (1H, dq, \(J = 14.0\text{Hz}, J = 7.0\text{Hz}, 2'\)-\(H\)), 1.81 (1H, d, \(J = 4.2\text{Hz}, \text{OH}\)), 0.15 (27H, s, \(\text{Si(CH}_3)_3\)); \(\delta_C\) (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 (\(\text{CHOH}\)), 32.5 (\(C\)-2’), 1.5 (\(\text{Si(CH}_3)_3\)); \(\delta_{\text{Si}}\) (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, 951, 901, 837, 755 cm^{-1}; δ_H (700 MHz) 10.51(1H, s, CHO), 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 (CHO), 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]^+·, 0.5%), 174 ([M-CO]^+, 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]^+ 202.0986, C_{13}H_{14}O_{2} requires [M]^+ 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-\textit{H}), 1.29 (1H, t, J = 5.8Hz, \textit{OH}); \delta_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]+, 35%), 80 ([M-H_2O]^+, 10), 67 ([M-CH_2OH]^+, 100), 53 ([M-CH_2CH_2OH]^+, 15), 41 (42).

\textit{(E)}-Ethyl hexa-3,5-dienoate$^{112} 437$

A solution of \textit{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\textit{E},4\textit{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 °C/10 mbar (lit.$^{112}$ 45 °C/0.7 mmHg); IR (ATR) 2980, 1732, 1603, 1407, 1368, 1335, 1243, 1177, 1139, 1097, 1025, 1003, 953, 902, 857 \text{cm}$^{-1}$; \delta_h (700 MHz) 6.33 (1H, ddd, \textit{J} = 17.0Hz, \textit{J} = 10.4Hz, 5-\textit{H}), 6.14 (1H, dd, \textit{J} = 15.3Hz, \textit{J} = 10.4Hz, 4-\textit{H}), 5.79 (1H, dt, \textit{J} = 15.3Hz, \textit{J} = 7.2Hz, 3-\textit{H}), 5.16 (1H, d, \textit{J} = 17.0Hz, 6-\textit{H}), 5.06 (1H, d, \textit{J} = 10.2Hz, 6-\textit{H}), 4.15 (2H, q, \textit{J} = 7.1Hz, \textit{CH}_2\textit{CH}_3), 3.11 (2H, d, \textit{J} = 7.2Hz, 2-\textit{H}), 1.26 (3H, t, \textit{J} = 7.1Hz, \textit{CH}_2\textit{CH}_3); \delta_c (175 MHz) 171.4 (C-1), 136.4 (C-3, C-5), 134.3 (C-4), 125.7 (C-3), 116.8 (C-6), 60.7 (\textit{CH}_2\textit{CH}_3), 38.0 (C-2), 14.2 (\textit{CH}_2\textit{CH}_3); m/z (EI) 140 ([M]$^+$, 76%), 98 (19), 81 (12), 67 ([M-CO$_2$Et]$^+$, 100), 54 (22), 41(58).

\textit{(E)}-(2-(Hexa-3,5-dienyloxy)phenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methanone 446

Following standard procedure \textit{C} (page 192), a solution of \textit{(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 \textbf{221} in THF (32.0 ml), which was prepared from tetrakis(trimethylsilyl)silane (2.96 g, 9.24 mmol) and potassium \textit{tert}-butoxide (1.09 g, 9.70 mmol). Flash column chromatography afforded the product as a yellow oil (2.20 g, 53%). R<sub>f</sub> 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<sup>-1</sup>; δ<sub>H</sub> (700 MHz) 7.29-7.26 (1H, m, 4-<i>H</i>), 7.01-7.00 (1H, m, 6-<i>H</i>), 6.97-6.94 (1H, m, 5-<i>H</i>), 6.88-6.87 (1H, m, 3-<i>H</i>), 6.32 (1H, dt, <i>J</i> = 17.5Hz, <i>J</i> = 10.5Hz, 5'-<i>H</i>), 6.15 (1H, dd, <i>J</i> = 15.4Hz, <i>J</i> = 10.5Hz, 4'-<i>H</i>), 5.73 (1H, dt, <i>J</i> = 15.4Hz, <i>J</i> = 7.0Hz, 3'-<i>H</i>), 5.15 (1H, d, <i>J</i> = 17.5Hz, 6'-<i>H</i>), 5.02 (1H, d, <i>J</i> = 10.5Hz, 6'-<i>H</i>), 3.99 (2H, t, <i>J</i> = 7.0Hz, 1'-<i>H</i>), 2.54 (2H, q, <i>J</i> = 7.0Hz, 2'-<i>H</i>), 0.19 (27H, s, Si(CH<sub>3</sub>)<sub>3</sub>); δ<sub>C</sub> (175 MHz) 241.6 (C<sub>2</sub>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(CH<sub>3</sub>)<sub>3</sub>); δ<sub>Si</sub> (140 MHz) -11.4, -70.4; m/z (EI) 448 ([M]+·, 0.2%), 375 ([M-Si(CH<sub>3</sub>)<sub>3</sub>]+·, 4), 147 (12), 73 (100); HRMS (EI) found [M]+ 448.2096, C<sub>22</sub>H<sub>40</sub>O<sub>2</sub>Si<sub>4</sub> requires [M]+ 448.2100.

\textbf{(E)-2-(Hexa-3,5-dienyloxy)benzoic acid 448}

Following standard procedure B (page 192), a solution of \textit{(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 °C; R<sub>f</sub> 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<sup>-1</sup>; δ<sub>H</sub> (700 MHz) 10.82 (1H, s, CO<sub>2</sub>H), 8.21-8.20 (1H, m, 6-<i>H</i>), 7.57-7.55 (1H, m, 4-<i>H</i>), 7.16-7.14 (1H, m, 5-<i>H</i>), 7.05-7.04 (1H, m, 3-<i>H</i>), 6.34 (1H, ddd, <i>J</i> = 16.1Hz, <i>J</i> = 10.5Hz, <i>J</i> = 9.8Hz, 5'-<i>H</i>), 6.26 (1H, dd, <i>J</i> = 15.4Hz, <i>J</i> = 9.8Hz, 4'-<i>H</i>), 5.73 (1H, dt, <i>J</i> = 15.4Hz, <i>J</i> = 7.0Hz, 3'-<i>H</i>), 6.15 (1H, dd, <i>J</i> = 15.4Hz, <i>J</i> = 10.5Hz, 6'-<i>H</i>), 5.22 (1H, d, <i>J</i> = 16.1Hz, 6'-<i>H</i>), 5.10 (1H, d, <i>J</i> = 10.5Hz, 6'-<i>H</i>), 4.31 (2H, t, <i>J</i> = 7.0Hz, 1'-<i>H</i>), 2.72 (2H, q, <i>J</i> = 7.0Hz, 2'-<i>H</i>); δ<sub>C</sub> (175 MHz) 165.2 (CO<sub>2</sub>H), 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\textsubscript{13}H\textsubscript{13}O\textsubscript{3} requires [M-H\^-] 217.0865.

\textbf{\((E)\)-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\(^{-1}\); \(\delta\)\(_{H}\) (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, \(J = 16.8Hz, J = 10.5Hz\)), 5.83 (1H, dt, \(J = 15.4Hz, J = 7.0Hz\)), 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, CH\(_3\)), 2.63 (2H, q, \(J = 7.0Hz, 2'-\(H\))\)), \(\delta\)\(_{C}\) (175 MHz) 167.0 (CO), 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 (CH\(_3\)), 32.5 (C-2'); m/z (EI) 201 ([M-OCH\(_3\)]\(^+\), 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]\(^+\) 233.1175, C\textsubscript{14}H\textsubscript{17}O\textsubscript{3} requires [M+H]\(^+\) 233.1172.

\textbf{\((E)\)-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,
(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 (0.62 g, 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 °C; Rf 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; δH (700 MHz) 10.57 (1H, s, CO₂H), 8.15-8.13 (1H, m, 6'-H), 6.66-6.64 (1H, m, 5'-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 (OCH₃), 2.70 (2H, dt, J = 7.0Hz, J = 6.3Hz, 2'-H); δC (175 MHz) 165.3 (CO), 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 (OCH₃), 32.4 (C-2'); m/z (ES+) 548 ([2M+Na]⁺, 23%), 326 ([M+MeCN]⁺, 37), 285 ([M+Na]⁺, 74), 263 ([M+H]⁺, 100), 122 (61); HRMS (ES+) found [M+H]⁺ 263.1281, C₁₅H₁₉O₄ requires [M+H]⁺ 263.1283.
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 an 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\(^{-1}\); \( \delta_H \) (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, \( J = 16.8 \)Hz, \( J = 10.5 \)Hz, 5’-H), 6.15 (1H, dd, \( J = 15.4 \)Hz, \( J = 10.5 \)Hz, 4’-H), 5.75 (1H, dt, \( J = 15.4 \)Hz, \( J = 7.0 \)Hz, 3’-H), 5.14 (1H, d, \( J = 16.8 \)Hz, 6’-H), 5.02 (1H, d, \( J = 10.5 \)Hz, 6’-H), 3.98 (2H, t, \( J = 6.3 \)Hz, 1’-H), 3.83 (3H, s, OCH\(_3\)), 2.55 (2H, dt, \( J = 6.3 \)Hz, 2’-H), 0.21 (27H, s, Si(CH\(_3\))\(_3\)); \( \delta_C \) (175 MHz) 237.5 (CO), 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 (OCH\(_3\)), 32.2 (C-2’), 1.3 (Si(CH\(_3\))\(_3\)); \( \delta_Si \) (140 MHz) -11.4, -70.2; m/z (EI) 463 ([M-CH\(_3\)]\(^+\), 3%), 405 ([M-Si(CH\(_3\))\(_3\)]\(^+\), 43), 263 (62), 214 (83), 189 (30), 175 (40), 147 (39), 131 (26), 117 (33), 73 (100), 45 (11).

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$_2$O (0.5 ml), NaOH (1M, 0.5 ml) and H$_2$O (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 an unstable colourless oil (0.29 g, 89%). R$_f$ 0.3 (pet. ether : diethyl ether 9:1); IR (ATR) 3429, 2947, 1606, 1584, 1499, 1466, 1287, 1242, 1197, 1161, 1111, 1002, 829, 735 cm$^{-1}$; $\delta$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, $J = 16.8$Hz, $J = 10.5$Hz, 5’-H), 6.19 (1H, dd, $J = 15.4$Hz, $J = 10.5$Hz, 4’-H), 5.76 (1H, dt, $J = 15.4$Hz, $J = 7.0$Hz, 3’-H), 5.39 (1H, d, $J = 4.9$Hz, CHOH), 5.15 (1H, d, $J = 16.8$Hz, 6’-H), 5.04 (1H, d, $J = 10.5$Hz, 6’-H), 3.94 (2H, t, $J = 7.0$Hz, 1’-H), 3.80 (3H, s, OC$_3$H$_3$), 2.60 (2H, q, $J = 7.0$Hz, 2’-H), 1.70 (1H, d, $J = 4.9$Hz, OHH), 0.15 (27H, s, Si(C$_3$H$_3$)$_3$); $\delta$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 (CHOH), 55.4 (OCH$_3$), 32.5 (C-2’), 1.5 (Si(CH$_3$)$_3$); $\delta$Si (140 MHz) -12.9, -68.9; m/z (ASAP) 463 ([M-OH]$^+$, 100%), 407 ([M-SiMe$_3$]$^+$, 11%). HRMS (ASAP) found [M-OH]$^+$ 463.2336, C$_{23}$H$_{43}$O$_2$Si$_4$ requires [M-OH]$^+$ 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 °C 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$^{-1}$; $\delta$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, $J = 10.5$Hz, $J = 7.7$Hz, $J = 2.8$Hz, 3-H), 5.73 (1H, ddd, $J = 10.5$Hz, $J = 6.3$Hz, $J = 2.8$Hz, 4-H), 4.12 (1H, ddd, $J = 11.2$Hz, $J = 7.0$Hz, $J = 6.3$Hz, 6-H), 3.91 (1H, ddd, $J = 11.2$Hz, $J = 6.3$Hz, $J = 5.6$Hz, 6-H), 2.60 (2H, q, $J = 7.0$Hz, 2’-H), 1.70 (1H, d, $J = 4.9$Hz, OHH), 0.15 (27H, s, Si(C$_3$H$_3$)$_3$); $\delta$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 (CHOH), 55.4 (OCH$_3$), 32.5 (C-2’), 1.5 (Si(CH$_3$)$_3$); $\delta$Si (140 MHz) -12.9, -68.9; m/z (ASAP) 463 ([M-OH]$^+$, 100%), 407 ([M-SiMe$_3$]$^+$, 11%). HRMS (ASAP) found [M-OH]$^+$ 463.2336, C$_{23}$H$_{43}$O$_2$Si$_4$ requires [M-OH]$^+$ 463.2335.
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(CH$_3$)$_3$), 0.05 (9H, s, Si(CH$_3$)$_3$), -0.20 (9H, s, Si(CH$_3$)$_3$); δC (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(CH$_3$)$_3$), 0.5 (Si(CH$_3$)$_3$), -0.5 (Si(CH$_3$)$_3$); δSi (140 MHz) 10.5, -15.5, -16.8, -26.8; m/z (EI) 448 ([M]+, 0.2%), 433 ([M-Me]+, 0.5%), 375 ([M-Si(CH$_3$)$_3$]+, 14), 205 (10), 147 (16), 73 (100); HRMS (EI) found [M]+ 448.2100, C$_{22}$H$_{40}$O$_2$Si$_4$ requires [M]+ 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$^{-1}$; δH (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, OCH$_3$), 2.62 (2H, dt, J = 7.0Hz, J = 6.3Hz, 2'-H); δC (175 MHz) 165.6 (CO), 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 (OCH$_3$), 32.4 (C-2'); m/z (ES+) 289 ([M+Na]+, 100), 555 ([2M+Na]+, 5); HRMS (ES+) found [M+H]$^+$ 267.0778, C$_{14}$H$_{16}$O$_2$Cl requires [M+H]$^+$ 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 °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, CO₂H), 8.16-8.158 (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 (CO), 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]+, 100); HRMS (ES+) found [M+Na]+ 275.0434, C_{13}H_{13}O_3NaCl requires [M+Na]+ 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, $J = 16.8$Hz, $J = 10.5$Hz, 5'-$H$), 6.14 (1H, dd, $J = 14.7$Hz, $J = 10.5$Hz, 4'-$H$), 5.71 (1H, dt, $J = 14.7$Hz, $J = 7.0$Hz, 3'-$H$), 5.15 (1H, d, $J = 16.8$Hz, 6'-$H$), 5.03 (1H, d, $J = 10.5$Hz, 6'-$H$),
3.96 (2H, t, $J = 7.0$Hz, 1'-$H$), 2.53 (2H, q, $J = 7.0$Hz, 2'-$H$), 0.21 (27H, s, Si(CH$_3$)$_3$);
$\delta_C$ (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'); $\delta_{Si}$ (140 MHz) -11.2, -69.2; m/z (Cl) 483 ([M+H]$^+$, 12), 393 (100), 90 (27); HRMS (ES+) found [M+H]$^+$ 483.1787, C$_{22}$H$_{40}$O$_2$ClSi$_4$ requires [M+H]$^+$ 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$^{-1}$; $\delta_H$ (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, $J = 16.1$Hz, $J = 10.5$Hz, $J = 9.8$Hz, 5'-H), 6.20 (1H, dd, $J = 15.4$Hz, $J = 10.5$Hz, 4'-H), 5.82 (1H, dt, $J = 15.4$Hz, $J = 7.0$Hz, 3'-H), 5.45 (1H, d, $J = 16.1$Hz, 6'-H), 5.02 (1H, dt, $J = 9.8$Hz, 6'-H), 3.95 (2H, t, $J = 6.3$Hz, 1'-H), 3.91 (3H, s, OCH$_3$), 2.62 (2H, dt, $J = 7.0$Hz, $J = 6.3$Hz, 2'-H), 2.31 (3H, s, CH$_3$); $\delta_C$ (175 MHz) 167.0 (CO), 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 (OCH$_3$), 33.4 (C-2'), 16.3 (CH$_3$); m/z (ES+) 269 ([M+Na]$^+$, 100), 515 ([2M+Na]$^+$, 5); HRMS (ES+) found [M+Na]$^+$ 269.1151, C$_{15}$H$_{18}$O$_3$Na requires [M+Na]$^+$ 269.1154.
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 (0.29 g, 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 °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, $J = 16.81$Hz, $J = 10.5$Hz, 5'-H), 6.24 (1H, dd, $J = 15.4$Hz, $J = 10.5$Hz, 4'-H), 5.75 (1H, dt, $J = 15.4$Hz, $J = 7.0$Hz, 3'-H), 5.19 (1H, d, $J = 16.8$Hz, 6'-H), 5.08 (1H, d, $J = 9.8$Hz, 6'-H), 4.03 (2H, t, $J = 7.0$Hz, 1'-H), 2.68 (2H, q, $J = 7.0$Hz, 2'-H), 2.36 (3H, s, CH$_3$); δ$_C$ (175 MHz) 165.9 (CO), 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 (CH$_3$); m/z (ES+) 255 ([M+Na]$^+$, 100), 487 ([2M+Na]$^+$, 6); HRMS (ES+) found [M+Na]$^+$ 255.1004, C$_{14}$H$_{16}$O$_3$Na requires [M+Na]$^+$ 255.0997.

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%). Rf 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; δH (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, CH₃), 0.20 (27H, s, Si(CH₃)₃); δC (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-2), 123.2 (C-5), 115.5 (C-6'), 74.5 (C-1'), 33.3 (C-2'), 16.1 (CH₃), 1.1 (Si(CH₃)₃); δSi (140 MHz) -11.4, -69.5; m/z (CI) 463 ([M+H]+·, 24), 373 (100), 90 (19); HRMS (ES+) found [M+H]+ 463.2333, C₂₃H₄₃O₂Si₄ requires [M+H]+ 463.2335.

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

Following 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 °C; Rf 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; δH (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 = 9.8Hz, 6'-H), 5.04 (1H, d, J = 9.8Hz, 6'-H), 4.06 (2H, t, J = 6.3Hz, 1'-H), 3.87 (3H, s, CO₂CH₃), 2.60 (2H, dt, J = 7.0Hz, J = 6.3Hz, 2'-H); δC (175 MHz) 166.3 (CO), 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 (OCH₃), 32.3 (C-2'); m/z (ES+) 359 ([M+H]+, 20%), 381 ([M+Na]+, 100), 739 ([2M+Na]+, 55); HRMS (ES+) found [M+H]+ 463.2333, C₂₃H₄₃O₂Si₄ requires [M+H]+ 463.2335.
(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 (0.55 g, 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 °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), 7.39–7.37 (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 (CO), 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]$, 15$%), 367 ([M+Na]$^+$, 100), 711 ([2M+Na]$^+$, 26); HRMS (ES-) found [M-H]$^-$ 342.9826, C$_{13}$H$_{12}$O$_3$I requires [M-H]$^-$ 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 °C; R$_f$ 0.3 (pet. ether : ethyl acetate 9:1); IR (ATR) 3017, 2913, 1725, 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, OCH₃), 2.70 (2H, dt, J = 7.0Hz, J = 6.3Hz, 2’-H); δC (175 MHz) 167.0 (CO), 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 (OCH₃), 32.4 (C-2’); m/z (ES+) 283 ([M+H]+, 25%), 305 ([M+Na]+, 100), 587 ([2M+Na]+, 70); HRMS (ES+) found [M+H]+ 283.1326, C₁₈H₁₉O₃ requires [M+H]+ 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 °C; Rf 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; δH (500 MHz) 11.00 (1H, s, CO₂H), 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); δC (125 MHz) 165.3 (CO), 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]+, 49%), 291 ([M+Na]+, 100), 537 ([2M+H]+, 38), 559 ([2M+Na]+, 77); HRMS (ES+) found [M+H]+ 269.1186, C₁₇H₁₇O₃ requires [M+H]+ 269.1178.
(E)-(3-(Hexa-3’,5’-dienyloxy)naphthalen-2-yl)(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 °C; Rf 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\(_{\text{H}}\) (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, \(J = 17.5\)Hz, \(J = 10.5\)Hz, 5’-\(H\)), 6.19 (1H, dd, \(J = 15.4\)Hz, \(J = 10.5\)Hz, 4’-\(H\)), 5.79 (1H, dt, \(J = 15.4\)Hz, \(J = 7.0\)Hz, 3’-\(H\)), 5.17 (1H, q, \(J = 7.0\)Hz, 2’-\(H\)), 0.22 (27H, s, Si(CH\(_3\))\(_3\)); δ\(_{\text{C}}\) (175 MHz) 240.6 (CO), 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(CH\(_3\))\(_3\)); δ\(_{\text{Si}}\) (140 MHz) -11.3, -69.6; m/z (EI) 498 ([M]+, 2%), 425 ([M-Si(CH\(_3\))\(_3\)]\(^+\), 6), 397 (10), 205 (14), 147 (19), 73 (100); HRMS (EI) found [M]+ 498.2256, C\(_{26}\)H\(_{42}\)O\(_2\)Si\(_4\) requires [M]+ 498.2256.

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

Following standard procedure A (page 192), a solution of triphenyolphosphine (3.25 g, 12.4 mmol), (2E,4E)-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 an unstable white solid (0.99 g, 41%). Mp: 54.3–53.4 °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-\textit{H}), 7.45-7.42 (1H, m, 4-\textit{H}), 6.99-6.97 (2H, m, 3-\textit{H}, 5-\textit{H}), 6.38 (1H, dd, \textit{J} = 15.4Hz, \textit{J} = 10.5Hz, 3’-\textit{H}), 6.10 (1H, dd, \textit{J} = 15.4Hz, \textit{J} = 10.5Hz, 4’-\textit{H}), 5.78 (1H, dt, \textit{J} = 15.4Hz, \textit{J} = 6.3Hz, 2’-\textit{H}), 5.75 (1H, dq, \textit{J} = 15.4Hz, \textit{J} = 6.3Hz, 5’-\textit{H}), 4.65 (2H, d, \textit{J} = 6.3Hz, 1’-\textit{H}), 3.91 (3H, s, CO₂CH₃), 1.78 (3H, d, \textit{J} = 6.3Hz, 6’-\textit{H}); δ_C (175 MHz) 166.8 (CO), 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 (CO₂CH₃), 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\textit{E},4\textit{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 °C; 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-\textit{H}), 6.51-6.50 (1H, m, 5-\textit{H}), 6.481-6.478 (1H, m, 3-\textit{H}), 6.41 (1H, dd, \textit{J} = 15.4Hz, \textit{J} = 10.5Hz, 3’-\textit{H}), 6.10 (1H, dd, \textit{J} = 15.4Hz, \textit{J} = 10.5Hz, 4’-\textit{H}), 5.80 (1H, dt, \textit{J} = 15.4Hz, \textit{J} = 5.6Hz, 2’-\textit{H}), 5.76 (1H, dq, \textit{J} = 15.4Hz, \textit{J} = 6.3Hz, 5’-\textit{H}), 4.63 (2H, d, \textit{J} = 5.6Hz, 1’-\textit{H}), 3.87 (3H, s, CO₂CH₃), 3.84 (3H, s, OCH₃), 1.78 (3H, d, \textit{J} = 6.3Hz, 6’-\textit{H}); δ_C (175 MHz) 166.2 (CO), 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 (ArOCH₃), 51.7 (CO₂CH₃), 18.1 (C-6’); m/z (ES+) 263 ([M+H]^+ 100%), 285 ([M+Na]^+ 45), 547 ([2M+Na]^+ 47); Anal. Calcd for C₁₅H₁₈O₄: C, 68.68; H, 6.92. Found: C, 68.80; H, 6.92.
(3E,5Z)-hepta-3,5-dien-1-ol$^{16}$ 484

To a suspension of LiAlH$_4$ (0.96 g, 25.4 mmol) in diethyl ether (80 ml) was added a solution of (3E,5Z)-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$_2$O (3.0 ml), NaOH (1 M, 3.0 ml) and H$_2$O (6.0 ml). The suspension was then filtered through Celite$^{8}$, the precipitate washed with EtOAc and the combined filtrate concentrated under reduced pressure. 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$^{-1}$; $\delta_H$ (500 MHz) 6.46 (1H, dd, $J = 15.0$Hz, $J = 11.0$Hz, 4-H), 6.00 (1H, td, $J = 11.0$Hz, $J = 1.5$Hz, 5-H), 5.64 (1H, dt, $J = 15.0$Hz, $J = 7.0$Hz, 3-H), 5.45 (1H, dq, $J = 11.0$Hz, $J = 7.0$Hz, 6-H), 3.70 (2H, q, $J = 6.0$Hz, 1-H), 2.40 (2H, dt, $J = 7.0$Hz, $J = 6.0$Hz, 2-H), 1.76 (3H, dd, $J = 7.0$Hz, $J = 1.5$Hz, 7-H), 1.43 (1H, t, $J = 6.0$Hz, OH); $\delta_C$ (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]$^{+}$, 78%), 94 ([M-H$_2$O]$^{+}$, 10), 81 ([M-CH$_2$OH]$^{+}$, 100), 79 ([M-H$_2$O-CH$_3$]$^{+}$, 85), 77 (40), 67 (84), 65 (28), 55 (44), 53 (74), 51 (19), 41 (72), 39 (63), 31 (31), 27 (37).

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

Following standard procedure A (page 192), a solution of triphenylphosphine (5.79 g, 22.1 mmol), (3E,5Z)-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$^{-1}$; $\delta_H$ (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, $J = 14.7$Hz, $J = 11.2$Hz, 4'-H), 6.02 (1H, ddd, $J = 11.2$Hz, $J = 10.5$Hz, $J = 1.4$Hz, 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, OCH₃), 2.66 (2H, q, J = 7.0Hz, 2’-H), 1.76 (3H, dd, J = 7.0Hz, J = 1.4Hz, 7’-H); δC (175 MHz) 167.0 (CO), 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 (OCH₃), 32.8 (C-2’), 13.3 (C-7’); m/z (EI) 246 ([M]⁺, 5%), 215 ([M-OCH₃]⁺, 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]⁺ 247.1329, C₁₅H₁₉O₃ requires [M+H]⁺ 247.1329.

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

Following standard procedure B (page 192), a solution of methyl 2-((3E,5Z)-hepta-3’,5’-dienyloxy)benzoate (1.74 g, 7.1 mmol) in THF (35 ml) was treated with a solution lithium hydroxide (0.34 g, 14.1 mmol) in water (15 ml) to give the title compound as a colourless liquid (1.43 g, EZ:EE - 84:16, 87%). Rf 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; δH (700 MHz) 10.85 (1H, s, CO₂H), 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), 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); δC (175 MHz) 165.3 (CO), 157.4 (C-2), 134.9 (C-4), 133.9 (C-6), 129.5 (C-5’), 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]⁺, 24%), 465 ([2M+H]⁺, 100), 250 ([M+NH₄]⁺, 28), 233 ([M+H]⁺, 20); HRMS (ES+) found [M+NH₄]⁺ 250.1440, C₁₄H₂₀O₃N requires [M+NH₄]⁺ 250.1438.
Following standard procedure C (page 192), a solution of 2-((3E,5Z)-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 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%). Rf 0.3 (pet. ether : diethyl ether 9:1); IR (ATR) 2948, 2891, 1614, 1591, 1484, 1465, 1441, 1393, 1242, 1188, 1157, 1106, 1040, 1018, 979, 824, 746 cm\(^{-1}\); \(\delta\)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(CH\(_3\))\(_3\)); \(\delta\)C (175 MHz) 241.6 (CO), 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(CH\(_3\))\(_3\)); \(\delta\)Si (140 MHz) -11.4, -70.5; m/z (ES+) 942 ([2M+NH\(_4\)]\(^+\), 100%), 463 ([M+H]\(^+\), 75); HRMS (ES+) found [M+H]\(^+\) 463.2331, C\(_{23}\)H\(_{43}\)O\(_2\)Si\(_4\) requires [M+H]\(^+\) 463.2335.

**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 °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\(^{-1}\); \(\delta\)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, CO₂CH₃), 2.20 (2H, dq, J = 7.0Hz, J = 4.9Hz, 6-H), 1.05 (3H, t, J = 7.0Hz, 7-H); δC (175 MHz) 167.7 (CO), 146.2 (C-5), 145.4 (C-3), 127.4 (C-4), 118.7 (C-2), 51.4 (CO₂CH₃), 26.0 (C-6), 12.8 (C-7); m/z (EI) 140 ([M⁺], 48%), 111 (100), 109 ([M-OMe]+, 43), 81 ([M-CO₂Me]+, 100), 79 (73), 53 (43), 39 (38), 27 (20).

(3E,5Z)-Methyl hepta-3,5-dienoate

To a solution of sodium bis(trimethylsilyl)amide (6.1 ml, 1M in THF) in THF (90 ml) was added a solution of (2E,4E)-methyl hepta-2,4-dienoate (4.33 g, 30.9 mmol) in THF (20 ml) at -78 °C. The reaction mixture was stirred at -78 °C for 4 h after which time a solution of acetic acid (5.0 ml) in THF/H₂O (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 Et₂O (3 x 40 ml). The combined organic layers were dried over MgSO₄, 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%). Rf 0.4 (pet. ether : diethyl ether 9:1); IR (ATR) 3021, 2952, 1737, 1435, 1339, 1255, 1198, 1161, 985, 945, 827 cm⁻¹; δH (500 MHz) 6.45 (1H, dd, J = 15.0Hz, J = 11.0Hz, 4-H), 6.01 (1H, td, J = 11.0Hz, J = 1.5Hz, 6-H), 5.74 (1H, dt, J = 15.0Hz, J = 7.0Hz, 3-H), 5.50 (1H, dq, J = 11.0Hz, J = 7.0Hz, 5-H), 3.70 (3H, s, OCH₃), 3.16 (2H, d, J = 7.0Hz, 2-H), 1.75 (3H, dd, J = 7.0Hz, J = 1.5Hz, 7-H); δC (125 MHz) 172.1 (CO), 129.0 (C-4), 128.6 (C-5), 126.3 (C-6), 124.4 (C-3), 51.9 (OCH₃), 38.1 (C-2), 13.3 (C-7); m/z (EI) 140 ([M⁺], 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

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 °C; Rf 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\(_T\) (700 MHz) 10.54 (1H, s, O\(_H\)), 7.64 (1H, s, 6-\(_H\)), 6.45 (1H, s, 3-\(_H\)), 6.35 (1H, ddd, \(J = 16.8\)Hz, \(J = 10.5\)Hz, 5'-\(_H\)), 6.07 (1H, dd, \(J = 15.4\)Hz, \(J = 10.5\)Hz, 4'-\(_H\)), 5.87 (1H, dd, \(J = 15.4\)Hz, \(J = 6.3\)Hz, 3'-\(_H\)), 5.14 (1H, d, \(J = 16.8\)Hz, 6'-\(_H\)), 5.01 (1H, d, \(J = 9.8\)Hz, 6'-\(_H\)), 3.88 (3H, s, OCH\(_3\)), 3.84 (1H, quin, \(J = 6.3\)Hz, 2'-\(_H\)), 1.33 (3H, d, \(J = 6.3\)Hz, 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 (OCH\(_3\)), 34.3 (C-2'), 19.8 (C-1'); m/z (ES-) 247 ([M-H]\(^{-}\), 100%), 495 ([2M-H]\(^{-}\), 10%); HRMS (ES-) found [M-H]\(^{-}\) 247.0959, C\(_{14}\)H\(_{15}\)O\(_4\) requires [M-H]\(^{-}\) 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%). Rf 0.6 (pet. ether : diethyl ether 95:5); IR (ATR) 2940, 2882, 1600, 1388, 1326, 1247, 1168, 1123, 1079, 1003, 950, 903, 858, 817, 745 cm\(^{-1}\); δ\(_T\) (700 MHz) 7.48-7.47 (1H, m, 6-\(_H\)), 7.17-7.16 (1H, m, 5-\(_H\)), 6.35 (1H, ddd, \(J = 16.8\)Hz, \(J = 10.5\)Hz, \(J = 9.8\)Hz, 5'-\(_H\)), 6.23 (1H, dd, \(J = 15.4\)Hz, \(J = 10.5\)Hz, 4'-\(_H\)), 5.82 (1H, dt, \(J = 15.4\)Hz, \(J = 7.0\)Hz, 3'-\(_H\)), 5.18 (1H, d, \(J = 16.8\)Hz, 6'-\(_H\)), 5.06 (1H, d, \(J = 9.8\)Hz, 6'-\(_H\)), 4.12 (2H, t, \(J = 6.3\)Hz, 1'-\(_H\)), 2.67 (2H, t, \(J = 7.0\)Hz, \(J = 6.3\)Hz, 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, \(^{1}J_{c-f} = 32.6\)Hz, C-4), 129.2 (C-3'), 127.0 (C-1), 123.6 (q, \(^{1}J_{c-f} = 271.1\)Hz, CF\(_3\)), 118.1 (q, \(^{3}J_{c-f} = 3.3\)Hz, 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]+, 100%), 553 ([2M+H]+, 14); HRMS (ASAP) found [M+H]+ 277.0599, C\(_{13}\)H\(_{13}\)OClF\(_3\) requires [M+H]+ 277.0602.
(E)-Hexa-3,5-dienyl 4-methylbenzenesulfonate

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 MgSO₄, filtered, and concentrated in vacuo. Flash column chromatography (pet. ether : ethyl acetate 85:15) gave the title compound as a colourless liquid (2.37 g, 46%). Rf 0.4 (pet. ether : ethyl acetate 85:15); IR (ATR) 2967, 1598, 1355, 1096, 814, 758 cm⁻¹; δH (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, CH₃), 2.44 (2H, q, J = 7.0Hz, 2-H); δC (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 (CH₃); m/z (ES+) 275 ([M+Na]⁺, 100%), 527 ([2M+Na]⁺, 5).

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

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 °C 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%). Rf 0.6 (pet. ether : diethyl ether 95:5); IR (ATR) 2952, 2894, 1477, 1244, 1027, 831, 749 cm⁻¹; δH (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, 6-H), 2.46 (3H, s, CH₃), 2.44 (2H, q, J = 7.0Hz, 2-H); δC (175 MHz) 110.4 (Ar-C-1), 113.4 (C-5), 133.1 (C-4), 132.9 (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 (CH₃); m/z (ES+) 275 ([M+Na]⁺, 100%), 527 ([2M+Na]⁺, 5).
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 °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%). Rf 0.6 (pet. ether : diethyl ether 95:5); IR (ATR) 2949, 2893, 1469, 1432, 1243, 1193, 1043, 1020, 954, 829, 749 cm⁻¹; δH (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, CH₃), 2.12-2.08 (1H, m, 5-H), 1.81-1.75 (1H, m, 5-H), 1.66 (1H, ddd, 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(CH₃)₃), 0.08 (9H, s, Si(CH₃)₃), -0.21 (9H, s, Si(CH₃)₃); δC (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 (CH₃), 8.4 (C-2), 2.9 (Si(CH₃)₃), 0.6 (Si(CH₃)₃), -0.5 (Si(CH₃)₃); δSi (140 MHz) 10.3, -15.6, -16.6, -27.5; m/z (EI) 462 ([M]⁺, 1%), 447 ([M-Me]⁺, 3%), 389 ([M-
Si(CH$_3$)$_3$]$^+$, 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]$^+$ 462.2250, C$_2$H$_4$O$_2$Si$_4$ requires [M]$^+$ 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 °C 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$^{-1}$; $\delta$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, $J = 10.5$Hz, $J = 7.7$Hz, $J = 4.2$Hz, 3-H), 5.67 (1H, ddd, $J = 10.5$Hz, $J = 4.9$Hz, $J = 2.1$Hz, 4-H), 4.23 (1H, ddd, $J = 11.2$Hz, $J = 7.0$Hz, $J = 6.3$Hz, 6-H), 3.91 (1H, ddd, $J = 11.2$Hz, $J = 5.6$Hz, $J = 4.2$Hz, 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, $J = 16.1$Hz, $J = 4.2$Hz, $J = 2.1$Hz, 1-H), 1.43 (1H, dd, $J = 16.1$Hz, $J = 7.7$Hz, 2-H), 0.18 (9H, s, Si(CH$_3$)$_3$), 0.16 (9H, s, Si(CH$_3$)$_3$), -0.27 (9H, s, Si(CH$_3$)$_3$); $\delta$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(CH$_3$)$_3$), 0.8 (Si(CH$_3$)$_3$), -0.4 (Si(CH$_3$)$_3$); $\delta$Si (140 MHz) 10.7, -15.6, -16.8, -26.9; m/z (EI) 498 ([M]$^+$, 7%), 470 (12), 425 ([M-Si(CH$_3$)$_3$]$^+$, 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]$^+$ 498.2252, C$_{26}$H$_{42}$O$_2$Si$_4$ requires [M]$^+$ 498.2256.
(E)-1-(2-(Hexa-3’,5’-dienyloxy)phenyl)-1-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)ethanol

To a solution of (E)-(2-(hexa-3,5-dienyloxy)phenyl)(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methanone (0.34 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°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 MgSO₄, filtered, concentrated and dried in vacuo. Flash column chromatography on silica, elution gradient 0 to 10% diethyl ether in hexane, afforded the product as an unstable colourless oil (0.15 g, 42%). Rf 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; δH (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, OH), 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, CH₃), 0.18 (27H, s, Si(CH₃)₃); δC (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 (COH), 68.0 (C-1’), 33.1 (CH₃), 32.5 (C-2’), 2.2 (Si(CH₃)₃); δSi (140 MHz) -13.3, -54.7; m/z compound decomposes under all forms of ionisation.
To a solution of \((E)-(2-(\text{hexa}-3',5'-\text{dienyloxy})\text{phenyl})\text{methyl})\text{trimethylsilyl})\text{methanone}\) (0.23 g, 0.52 mmol) in diethyl ether (4.0 ml) was added methyllithium lithium bromide complex (1.5 M in Et$_2$O, 0.34 ml, 0.52 mmol) at -78 °C. The mixture was stirred at -20 °C for 6 h and then at 10 °C 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 pressure. 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:

$\text{R}_f$ 0.7 (pet. ether : diethyl ether 95:5); IR (ATR) 2951, 2893, 1595, 1487, 1447, 1238, 1051, 1002, 831, 743 $\text{cm}^{-1}$; $\delta_{\text{H}}$ (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, $J = 16.8$Hz, $J = 10.5$Hz, $J = 9.8$Hz, 5'-H), 6.19 (1H, dd, $J = 15.4$Hz, $J = 10.5$Hz, 4'-H), 5.80 (1H, dt, $J = 15.4$Hz, $J = 7.0$Hz, 3'-H), 5.14 (1H, d, $J = 16.8$Hz, 6'-H), 5.02 (1H, d, $J = 9.8$Hz, 6'-H), 4.03 (1H, dt, $J = 9.1$Hz, $J = 7.0$Hz, 1'-H), 3.93 (1H, dt, $J = 9.1$Hz, $J = 7.0$Hz, 1'-H), 3.06 (1H, d, $J = 7.7$Hz, CH$_2$), 2.62 (1H, dq, $J = 14.0$Hz, $J = 7.0$Hz, 2'-H), 2.59 (1H, dq, $J = 14.0$Hz, $J = 7.0$Hz, 2'-H), 1.41 (3H, d, $J = 7.7$Hz, CH$_3$), 0.11 (9H, s, Si(CH$_3$)$_3$), 0.08 (9H, s,
OSi(CH$_3$)$_3$, -0.10 (9H, s, Si(CH$_3$)$_3$); $\delta$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 (CHCH$_3$), 17.4 (CHCH$_3$), 2.1 (OSi(CH$_3$)$_3$), -0.7 (Si(CH$_3$)$_3$), -1.2 (Si(CH$_3$)$_3$); $\delta$Si (140 MHz) 6.8, 1.9, -19.8, -20.1; m/z (GC-MS, EI) 391 ([M-Si(CH$_3$)$_3$]$,^-$, 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, SiH), 2.02 (3H, s, CH$_3$), 0.21 (9H, s, Si(CH$_3$)$_3$), 0.17 (9H, s, OSi(CH$_3$)$_3$), -0.13 (9H, s, Si(CH$_3$)$_3$); m/z (GCMS, EI) 446 ([M-CH$_3$]$^-$, 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$^{-1}$; $\delta$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, $J = 10.5$Hz, $J = 7.7$Hz, $J = 2.1$Hz, 3-H), 5.63 (1H, ddd, $J = 10.5$Hz, $J = 4.9$Hz, $J = 2.8$Hz, 4-H), 4.12 (1H, td, $J = 10.5$Hz, $J = 6.3$Hz, 6-H), 3.81 (1H, ddd, $J = 10.5$Hz, $J = 6.3$Hz, $j = 2.1$Hz, 6-H), 2.68-2.66 (1H, m, 4a-H), 2.09-2.04 (1H, m, 5-H), 1.78 (1H, ddt, $J = 16.1$Hz, $j = 2.8$Hz, $J = 2.1$Hz, 2-H), 1.69-1.64 (1H, m, 5-H), 1.66 (3H, s, CH$_3$), 1.26 (1H, dd, $j = 16.1$Hz, $j = 7.7$Hz, 2-H), 0.21 (9H, s, Si(CH$_3$)$_3$), -0.23 (9H, s, Si(CH$_3$)$_3$); $\delta$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 (CH$_3$), 28.1 (C-5), 7.8 (C-2), 1.1 (Si(CH$_3$)$_3$), -0.6 (Si(CH$_3$)$_3$); $\delta$Si (140 MHz) -16.0, -16.8, -27.9; m/z (EI) 374 ([M]$^+$, 8%), 359 ([M-Me]$^+$, 7), 301 ([M-Si(CH$_3$)$_3$]$^+$, 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]$^+$ 375.1987, C$_{20}$H$_{35}$OSi$_3$ requires [M+H]$^+$ 375.1996.

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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

‘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

9 References


