Microwave-Assisted Thermolysis of ortho-Substituted Aroylsilanes

by

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A thesis submitted in conformity with the requirements for the degree of Master of Science

Department of Chemistry
University of Toronto

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Department of Chemistry
University of Toronto
2008

Abstract

The microwave-assisted thermolysis of ortho-substituted aroylsilanes has been investigated. When irradiated at 250°C in DMSO or o-dichlorobenzene for 10 minutes, aroylsilanes form siloxycarbenes that react following different pathways depending on the solvent and the structure of the starting material. It is shown that in the case of substrates having an O-allyl or an O-propargyl chain ortho to the acylsilane, cycloaddition occurs followed by a cascade ring opening to give respectively chroman-4-one and chromen-4-one derivatives in up to 66% yield. Among the major competitive pathways were the insertion of the siloxycarbene into allylic C–H bonds and decomposition of the acylsilane group to the corresponding aldehyde, followed by Claisen rearrangement.
Acknowledgements

I would like to thank Dr. Zengming Shen for having been a great mentor and a strong model of perseverance to me. Your work ethic and your discipline were truly inspiring. You always encouraged me to go higher and to reach my goals. Working with you has been a great pleasure and I keep tons of wonderful memories that I will cherish all my life. Most of all, I found in you an extraordinary friend. Thank you so much for everything you did for me!

I am also very grateful to my family and friends, old and new, who supported me throughout my time in Toronto. Merci à tous, je vous aime!
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>µwaves</td>
<td>microwaves</td>
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<tr>
<td>AcOH</td>
<td>acetic acid</td>
</tr>
<tr>
<td>AgOAc</td>
<td>silver acetate</td>
</tr>
<tr>
<td>AIBN</td>
<td>2,2’-azobis(2-methylpropionitrile)</td>
</tr>
<tr>
<td>Ar</td>
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<td>aq</td>
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</tr>
<tr>
<td>Bu</td>
<td>butyl</td>
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<td>cat.</td>
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<td>concentrated</td>
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<td>dimethylformamide</td>
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<td>DMSO</td>
<td>dimethyl sulfoxide</td>
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<tr>
<td>EI</td>
<td>electron ionization</td>
</tr>
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<td>equivalent</td>
</tr>
<tr>
<td>ESI</td>
<td>electrospray ionization</td>
</tr>
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<td>EtOAc</td>
<td>ethyl acetate</td>
</tr>
<tr>
<td>EtOH</td>
<td>ethanol</td>
</tr>
<tr>
<td>GC/MS</td>
<td>gas chromatography-mass spectrometry</td>
</tr>
<tr>
<td>h</td>
<td>hour</td>
</tr>
<tr>
<td>HRMS</td>
<td>high resolution mass spectrometry</td>
</tr>
<tr>
<td>iPr</td>
<td>isopropyl</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>LDA</td>
<td>lithium diisopropylamide</td>
</tr>
<tr>
<td>LRMS</td>
<td>low resolution mass spectrometry</td>
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<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
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</tr>
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<tr>
<td>n</td>
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</tr>
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<td>NBS</td>
<td>N-bromosuccinimide</td>
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<tr>
<td>NMP</td>
<td>1-methyl-2-pyrrolidinone</td>
</tr>
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<td>nuclear magnetic resonance</td>
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</table>
o ortho
p para
Ph phenyl
ppm parts per million
R carbon chain
rt room temperature
t tert
THF tetrahydrofuran
TLC thin layer chromatography
TMS trimethylsilyl
TMSCl chlorotrimethylsilane
UV-Vis ultraviolet-visible
Chapter 1
Introduction

The term acylsilane refers to the functional group where a carbonyl is substituted with a silicon moiety. The study of this class of compounds began in 1957 when Brook achieved the synthesis of benzoyltriphenylsilane (1), the first reported acylsilane (Scheme 1).¹

Scheme 1. First acylsilane synthesis by Brook¹

Most of the early investigations focused on the intriguing physical properties of these compounds, many of them being quite different from ketones. Brook extensively studied their spectroscopic properties² and suggested that they could all be accounted for by both the higher atomic mass and the stronger inductive effect of silicon (χ = 1.90) in comparison to carbon (χ = 2.55).³ The question of possible σ(p-d) and π(π-d) interactions in the ground state between the carbonyl and the silicon atom has been heavily debated in the literature,⁴a-d but all experimental evidence points toward the inductive effect of silicon as the dominant electronic effect in the acylsilane functionality.²,⁵ This release of

---

electrons by the silicon results in a more polarized carbonyl bond than in ketones (Figure 1), accounting for the shift of about 50-70 cm\(^{-1}\) of the IR C=O stretch band to a smaller wavenumber than in the corresponding ketone.\(^6\) A similar effect is observed in the UV-Vis spectra. The bright yellow color of conjugated acylsilanes such as aroylsilanes and \(\alpha,\beta\)-unsaturated acylsilanes is the result of a bathochromic shift of about 100 nm of their \(n \rightarrow \pi^*\) transitions to reach about 420 nm.\(^6\) A shift of this magnitude is also observed with alkyl acylsilanes, but in this case, the absorption falls below the lower limit of the visible spectrum, hence rendering the compounds colorless like their carbon analogues. It is worth noting that the nature of the substituents on the silicon does not influence the frequency of absorption in both IR and UV-Vis spectroscopy.\(^4a\) An other evidence to support the polarization of the carbonyl bond was found by Yates and Agolini when they demonstrated that the oxygen of the carbonyl group was notably more basic in acylsilanes than in their carbon analogues,\(^7\) presumably because of its negative character.

Figure 1. Resonance structures of acylsilanes\(^6\)

Resonance structure 2 has an important consequence on the \(^{13}\)C NMR spectra of acylsilanes and to a lower extent, on their \(^1\)H spectra. The carbonyl-carbon is indeed significantly deshielded and its peak is shifted downfield by 25 to 103 ppm\(^8,9\) relative to the corresponding ketone-carbon. In agreement with the polarized nature of the carbonyl bond in acylsilanes, substitution of the alkyl group adjacent to the C=O by an aromatic ring results in a much more significant change in the \(^{13}\)C signals than for their corresponding ketones. For instance, MeCO-t-Bu and PhCO-t-Bu have chemical shifts of 210 and

\(^9\) The 103 ppm shift is for bis(trimethylsilyl) ketone.
208 ppm, respectively.\textsuperscript{8} However, MeCOSiMe\textsubscript{3} and PhCOSiMe\textsubscript{3} show chemical shifts of 248 and 234 ppm, respectively. This observation can be rationalized by the stabilization by the benzene ring of the positive charge of the carbonyl-carbon (Figure 2) resulting in an increase of its shielding. As for the \textsuperscript{1}H NMR of acylsilanes, only small downfield shifts of protons alpha to the carbonyl (due to anisotropy and differences in electronegativity) are observed.\textsuperscript{10}

![Figure 2. Resonance structures of benzoylsilanes](image)

Trotter’s crystallographic studies\textsuperscript{11} have shown that in acetyltriphenylsilane the Si–CO bond (1.926 Å) was longer than usual saturated Si–C bonds (1.84 to 1.87 Å).\textsuperscript{6} Based on his previous work on acetyltriphenylgermane,\textsuperscript{12} the author suggested that structure 3 (Figure 1) was also a contributing resonance structure, an assumption in agreement with the large electronegativity difference between silicon and carbon. Surprisingly, the C=O bond length (1.21 Å) was found to be very similar to ketones.\textsuperscript{11} There is currently no satisfactory explanation of this phenomenon that would be consistent with both the basicity and the spectroscopic properties previously described.

Even though they often react in the same way as ketones,\textsuperscript{6} acylsilanes have distinct chemistry. Nucleophilic attacks can occur not only on the carbonyl-carbon, but also on the silicon atom due to its low-lying 3\textit{d} orbitals.\textsuperscript{6} Because of the oxophilicity of silicon, most of the nucleophilic attacks lead to a 1,2-migratory shift of the silicon to the oxygen,\textsuperscript{2} a process known as the Brook rearrangement. This transformation accounts for the rapid decomposition of acylsilanes in the presence of hydroxide or alkoxides. Three pathways have historically been proposed to explain the formation of the different

\textsuperscript{10} \textit{α},\textit{β}-unsaturated acylsilanes do not follow this rule. See reference 6.
Scheme 2. Decomposition of acylsilanes in the presence of hydroxide or alkoxides\textsuperscript{13,15}

**Pathway A (for hydroxide and alkoxides):**

\[
\begin{align*}
R^2 \text{Si}(R^1)_3 + \text{OR}^3 & \rightarrow R^2 \text{Si}(R^1)_3 \text{OR}^3 \\
& \xrightarrow{1,2\text{-silyl shift}} R^2 \text{OSi}(R^1)_3 \\
& \xrightarrow{\text{Brook rearrangement}} R^2 \text{Si}(R^1)_3 \text{OR}^3 \\
& \xrightarrow{R^3 \text{O} \cdot H} R^3 \text{O} \cdot H
\end{align*}
\]

**Pathway B (for alkoxides only):**

\[
\begin{align*}
R^3 \text{OSi}(R^1)_3 & \xrightarrow{\text{OR}^3} R^2 \text{Si}(R^1)_3 \text{OR}^3 \\
& \xrightarrow{1,2\text{-shift}} R^2 \text{Si}(R^1)_2(\text{OR}^3) \\
& \xrightarrow{\text{Brook}} R^2 \text{Si}(R^1)_2(\text{OR}^3) \xrightarrow{R^3 \text{O} \cdot H} R^3 \text{O} \cdot H
\end{align*}
\]

**Rejected pathway C (for hydroxide and alkoxides):**

\[
\begin{align*}
R^2 \text{Si}(R^1)_3 + \text{OR}^3 & \rightarrow R^2 \text{Si}(R^1)_3 \text{OR}^3 \\
& \xrightarrow{R^3 \text{O} \cdot H} R^2 \text{Si}(R^1)_2(\text{OR}^3) \\
& \xrightarrow{\text{Brook}} R^2 \text{Si}(R^1)_2(\text{OR}^3) \xrightarrow{R^3 \text{O} \cdot H} R^3 \text{O} \cdot H
\end{align*}
\]

decomposition products (Scheme 2). Using acylsilanes with chiral silicon moieties, Brook has showed that alkoxides-catalysed decomposition follows both pathways A and B, the former being the major one only when steric hindrance prevents bulky bases (e.g., t-butoxide) from attacking the silicon.\textsuperscript{13}

In the case of hydroxide-catalysed decomposition, only aldehydes and silanol products are obtained.\textsuperscript{14}

Between the two possible pathways (A and C), kinetic studies by Ricci concluded that only direct nucleophilic attack at the carbonyl occurred in the presence of aqueous hydroxide.\textsuperscript{15}

Acylsilanes are known to form siloxycarbenes by both thermolysis and photolysis. The latter has received a great deal of attention since Brook first observed that a sample of cyclic acylsilane 4 was oxidized when exposed to air and ambient light to give the lactone 5 (Scheme 3).\textsuperscript{2,16} Brook also observed that irradiation with a mercury lamp of a solution of 4 in dry methanol\textsuperscript{17} lead to triphenylmethoxysilane (6) and benzaldehyde dimethylacetal (7) (Scheme 3).\textsuperscript{4c,18} In addition, production of small amount of benzaldehyde (8) and triphenylsilanol (9) was observed. However, when a catalytic amount of base was added, the major product was the mixed acetal 10. Independently, Kuivila observed that a sample of benzoyltrimethylsilane decomposed to benzaldehyde (traces) and hexamethyldisiloxane in presence of water and ethanol when irradiated.\textsuperscript{19}

\textbf{Scheme 3. Examples of photocatalysed reactions of acylsilanes}\textsuperscript{2,18}

\begin{align*}
\text{Ph}_3\text{Si} & \overset{\text{hν}}{\longrightarrow} \text{Ph}_3\text{SiO}^+ \\
\text{MeOH} & \text{MeOH} \\
\text{Ph}_3\text{SiOMe} & + \text{Ph}_3\text{SiOH} \\
(\text{major}) & (\text{minor})
\end{align*}

\begin{align*}
\text{Ph}_3\text{Si} & \overset{\text{hν}}{\longrightarrow} \text{Ph}_3\text{SiOMe} + \text{Ph}_3\text{SiOMe} \\
\text{MeOH} & \text{MeOH} \\
(\text{major}) & (\text{minor})
\end{align*}

\begin{align*}
\text{Ph}_3\text{Si} & \overset{\text{hν}}{\longrightarrow} \text{Ph}_3\text{SiO}^+ \\
\text{MeOH} & \text{MeOH} \\
\text{Ph}_3\text{SiOMe} & + \text{Ph}_3\text{SiOMe} \\
(\text{major}) & (\text{minor})
\end{align*}

\textsuperscript{17} Catalytic amount of acid could also be added.
Brook explained his experimental results through mechanisms involving the formation of carbenes (Scheme 4)\(^2,18\). In the case of 4, the 1,2-migration of the silicon to the oxygen of the acylsilane causes a ring expansion to the cyclic siloxycarbene 11 which subsequently reacts with oxygen to yield the lactone 5. A similar rearrangement happens to benzoyltriphenylsilane in presence of pyridine to give the intermediate 12 which inserts into the O–H bond of the solvent to form 10. In neutral or acidic conditions, the mechanism is different and thought to involve a concerted addition between the acylsilane and the alcohol.

**Scheme 4.** Formation of oxacarbenes by photolysis of acylsilanes\(^6\)

Brook obtained direct evidence that acylsilanes could generate siloxycarbenes upon photolysis. By irradiating 4 in presence of diethyl fumarate, he was able to isolate the cyclopropane 13 in
78% yield (Scheme 5). This intermolecular reaction involved a highly electron deficient olefin, which made the author speculate that the siloxycarbene acted as a nucleophile. Brook also obtained NMR evidence that the cyclopropanation occurred with another electron-poor alkene (1,2-dichloroethene), but only in trace amount. Importantly, all his attempts to do the cyclopropanation with electron-rich olefins, notably cyclohexene, 2,3-dimethylbut-2-ene and 1,1-dimethoxyethene, failed. In 1984, Frei was able to isolate, though in very low yield, the tricyclic system 15 after either the photolysis or the thermolysis of acylsilane 14 (Scheme 5). To the best of our knowledge, this is the only published example of cyclopropanation of an electron-rich alkene with a siloxycarbene formed by thermolysis of an acylsilane.

**Scheme 5. Trapping of siloxycarbenes with olefins**

The formation of siloxycarbenes by thermolysis of acylsilanes has received little attention since Brook's initial report. At high temperature (320°C) and with a prolonged reaction time (24h), Brook

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showed that pivaloyltrimethylsilane (17) rearranged to give cyclopropane 19 (Scheme 6). He proposed that a 1,2-silyl migration gave the siloxycarbene 18 which underwent insertion into the γ C–H bond. In the case of acylsilanes having β-hydrogens, the products obtained depended on the concentration and the temperature of the reaction. At low concentration and extremely high temperature (650ºC), substrate 20 gave 98% yield of insertion product 21. However, at lower temperature and higher concentration, the competing intermolecular reaction depicted in Scheme 6 gave two more products (22 and 23) in 25% yield each. Swenton demonstrated another example of an intramolecular C–H bond insertion while trying to synthesize benzocyclobutenol from the ortho-substituted benzoysilane 24.23 However, the benzocyclobutyl silyl ether 25 was not stable and rearranged to yield the thermodynamically favored aldehyde 26 (Scheme 6).

Selective C–H bond activation has redefined the way organic chemists think about connectivity and as such has become an active research field in modern organic synthesis. It is thus somewhat surprising that no further efforts have been made to study the thermolysis of acylsilanes and find milder reaction conditions for the development of novel and useful organic transformations. With this in mind, our group started to study the microwave-assisted thermolysis of acylsilanes. We chose microwave irradiation because of its efficiency to rapidly heat a solution to a precise temperature.24 Because of the shorter reaction times usually involved with microwave-assisted chemistry, we felt that it would help make the thermolysis conditions milder.

We envisioned that benzoyltrimethylsilane 27 (Scheme 7) could generate a siloxycarbene which would undergo an intramolecular C–H insertion. Based on Swenton's studies and the kinetic preference for five-membered rings formation,25 we thought that this substrate would present ideal characteristics to maximize the chances of insertion. Moreover, since siloxycarbenes have a nucleophilic character, it was believed that having an electronegative atom next to the benzylic protons would create a small polarization that would orientate the carbene toward them. A post-doctoral fellow in our laboratory,

Scheme 6. C–H bonds insertions with thermally-generated siloxycarbenes

![Scheme diagram](image-url)
Dr. Zengming Shen, demonstrated that under microwave irradiation, the insertion effectively occurred in moderate to very good yields at 250ºC with short reaction time (Scheme 7). Interestingly, the direct insertion product of the siloxycarbene was the only product formed in o-dichlorobenzene (29). However, in DMSO, elimination leading to 2-phenylbenzofuran (28) inevitably occurred. It was found that conventional heating with oil bath at 150ºC in toluene for 4 days gave 84% yield (by NMR) of 29 with a cis/trans ratio of 3/1.

Encouraged by these preliminary results, we aimed to explore in more depth the microwave-assisted thermolysis of different o-substituted aroylsilanes. Our goal was to gain a better understanding of the reaction mechanism involved and to eventually develop new synthetic methods toward structurally interesting compounds.

Scheme 7. Microwave-assisted intramolecular C–H bonds insertions

![Scheme 7 Diagram](image-url)

26. Shen, Z.; Dong, V. M. unpublished results
Chapter 2
Results and Discussion

2.1 Preliminary Studies

Based on Dr. Shen previous results, it was envisioned that aroylsilanes bearing different alkyl chains ortho to the acylsilane group could possibly undergo C–H insertion with high temperature microwave heating. Four initial substrates were chosen for study (Scheme 8). Substrates 30 and 31 would allow us to compare the selectivity of the reaction for the formation of five versus six-membered rings. Based on intramolecular insertions of rhodium carbenoids, it was expected that the kinetic product (i.e., the five-membered ring), would be favored. Substrate 32, despite being more sterically hindered than its O-methyl and O-ethyl analogues, should undergo C–H insertion more easily because of its secondary C–H bond. Finally, because of its nucleophilic character, the siloxycarbene derived from substrate 33 was expected to insert at the allylic position instead of undergoing a cyclopropanation with the electron-rich olefin that would lead to a strained tricyclic system (39).

Scheme 8. Expected products from the microwave-assisted thermolysis of acylsilanes 30-33
Acylsilanes 30-33 were synthesized following Prakash's method of reductive silylation of methyl benzoates (Scheme 9).\textsuperscript{27} This method was chosen for its ease of operation and the reasonable yields reported. However, in our case, the isolated yields were low, possibly due to steric factors not encountered in Prakash's \textit{meta} and \textit{para}-substituted benzoates.\textsuperscript{28} Also, it was observed that these acylsilanes were not completely stable on normal phase silica gel, decomposing to give the corresponding aldehydes. This decomposition accounts for some product loss during the purification steps.

**Scheme 9.** Acylsilanes synthesis by reductive silylation of methyl benzoates\textsuperscript{27}

![Scheme 9](image)

The reactivity of substrates 30, 31 and 32 was further investigated. Preliminary analyses seemed to indicate that no expected simple C–H insertion products were detected in the crude reaction mixtures (Table 1). For substrates 30 and 31, it appeared that most of the starting material remained unchanged after the reaction (entries 1-4). Since Dr. Shen's results suggested the easy formation of a siloxycarbene with a benzoyltrimethylsilane substrate using the same solvents and temperature, it


\textsuperscript{28} Only two \textit{ortho}-substituted substrates are reported: \textit{o}-methylbenzoyltrimethylsilane (40\%) and \textit{o}-methylbenzoyldimethyl-(vinyl)silane (11\%).
seems that the lack of reactivity with the saturated O-alkyl substrates might be due to the high energy barrier of the C–H insertion rather than the reversible formation of the carbene itself.\textsuperscript{29} Substrate 32 was almost completely consumed in either DMSO or o-dichlorobenzene but the expected product was not detected.\textsuperscript{30}

Table 1. Preliminary studies on the microwave-assisted thermolysis of acylsilanes 30, 31 and 32\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Solvent</th>
<th>Concentration (M)</th>
<th>Time (min)</th>
<th>Compounds observed</th>
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<tr>
<td>1</td>
<td>30</td>
<td>DMSO</td>
<td>0.050</td>
<td>7</td>
<td>starting material and aldehyde\textsuperscript{b}</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>o-dichlorobenzene</td>
<td>1.0</td>
<td>10</td>
<td>mostly starting material, traces of aldehyde\textsuperscript{b}</td>
</tr>
<tr>
<td>3</td>
<td>31</td>
<td>DMSO</td>
<td>0.050</td>
<td>15</td>
<td>starting material, aldehyde and traces of unknown material\textsuperscript{b}</td>
</tr>
<tr>
<td>4</td>
<td>31</td>
<td>o-dichlorobenzene</td>
<td>0.10</td>
<td>45</td>
<td>mostly starting material, traces of aldehyde and of unknown material\textsuperscript{c}</td>
</tr>
<tr>
<td>5</td>
<td>32</td>
<td>DMSO</td>
<td>0.050</td>
<td>7</td>
<td>mostly aldehyde, traces of starting material and of unknown material\textsuperscript{c}</td>
</tr>
<tr>
<td>6</td>
<td>32</td>
<td>o-dichlorobenzene</td>
<td>0.049</td>
<td>10</td>
<td>unknown material and traces of starting material\textsuperscript{c}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: A solution of \textit{ortho}-substituted benzoylsilane in the indicated solvent was heated to 250ºC under microwave irradiation for the time specified in the Table. \textsuperscript{b} By TLC analysis of the crude mixture. \textsuperscript{c} By \textit{1}H NMR analysis of the crude mixture. \textsuperscript{d} By \textit{1}H NMR analysis of the crude mixture after aqueous work-up (5 mL) and extraction with Et\textsubscript{2}O (3 x 5 mL).

The case of substrate 33 differed. As with the substrates discussed above, microwave heating of 33 at 250ºC for 10 minutes in DMSO did not produce any detectable traces of 33\textit{a} or 33\textit{b} in the \textit{1}H NMR spectrum of the crude mixture. However, product 33\textit{c} was detected in 37% yield accompanied by 33\textit{d} in

\textsuperscript{29} Trommer, M.; Sander, W. \textit{Organometallics}, 1996, 15, 189.

\textsuperscript{30} Further investigations would be needed to identify the product containing a silicon moiety (according to \textit{1}H NMR) that was formed by the thermolysis of this substrate.
11% yield (eq. 1). 31,32 33c was clearly the major product of the reaction according to NMR analysis, with only traces of starting material remaining and traces of unidentified by-products.

\[
\begin{array}{ccc}
& \text{DMSO, \mu waves} & \\
& 250^\circ \text{C, 10 min} & \\
\text{33} & \text{33c: 37\% (by NMR)} & \text{33d: 11\% (by NMR)}
\end{array}
\]

Scheme 10 shows the proposed mechanism for the formation of 33c. The first step consists of the Brook rearrangement of the acylsilane to give the siloxycarbene 38 which then undergoes cyclopropanation with the olefin. This step is surprising considering the electron-rich character of that double bond and the presence of reactive allylic C–H bonds that would allow the formation of a five-membered ring rather than a strained tricyclic system. To our knowledge, this transformation is only the second example of a cyclopropanation between a siloxycarbene generated by the Brook rearrangement of an acylsilane and an electron-rich alkene. 21 We believe that the short allyl chain, the rigidity conferred by the phenyl ring and the six-membered transition state decrease the entropic barrier to cyclopropanation. Ring strain of the cyclopropane intermediate (39) is relieved by a cascade ring opening process to generate the β,γ-unsaturated aromatic ketone 40 which quickly isomerizes to ketone 41 under the reaction conditions. The phenolic oxygen stabilizes the negative charge generated, making that step irreversible and explaining why cyclopropane 39 was not detected in the crude mixture by 1H NMR. Finally, conjugate addition of the phenoxide anion would give the final product 33c.

31. According to the analysis of the 1H NMR spectrum of the crude mixture.
32. Formation of 33d is discussed in details further.
Scheme 10. Proposed mechanism for the formation of 2-methylchroman-4-one (33c)

The main side product of this reaction was 33d for which the proposed mechanism of formation is detailed in Scheme 11. The first step is rate-determining and involves the reversible [3,3]-sigmatropic rearrangement of the allyl aryl ether moiety (Claisen rearrangement) to generate the dienone 42. This intermediate quickly and irreversibly enolizes to regain aromaticity (43). The final protodesilylation step probably occurs by interaction with the solvent since the intermolecular mechanism detailed in Scheme 6 would require the presence of a β-hydrogen.

Scheme 11. Proposed mechanism for the formation of 3-allyl-2-hydroxybenzaldehyde (33d)

2.2 Optimization and Mechanistic Investigations

In order to increase the yield of 33c and to reduce the amount of side product 33d formed, an optimization study was conducted with different temperatures and reaction times (Table 2). For these reactions, NMR yields based on the $^1$H signals of the internal standard 1,3,5-trimethoxybenzene were calculated. In all cases, it was possible to find strong and distinct signals for 33c. However, in the case of 33d, only the phenol and the aldehyde peaks did not interfere with other signals. That, combined with the fact that smaller unidentified side products were formed, can reasonably account for the fact that the total yields of 33c and 33d are lower than 100%.

Important trends can be drawn from this optimization study. At 200ºC, increasing the reaction time had a noticeable effect on the yield of 33c (Table 2, entries 7-9). However, at 250ºC, the yield remained essentially the same (ca. 35%) whether the reaction mixture was heated for 5, 10 or 35. These peaks were used even if their integration might be somewhat inaccurate.
Table 2. Optimization of 2-methylchroman-4-one (33c) formation in DMSO\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Yield 33c(^b) (%)</th>
<th>Yield 33d(^b) (%)</th>
<th>Ratio 33c/33d(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>250</td>
<td>5</td>
<td>35</td>
<td>17</td>
<td>2.1</td>
</tr>
<tr>
<td>2</td>
<td>250</td>
<td>10</td>
<td>37</td>
<td>11</td>
<td>3.4</td>
</tr>
<tr>
<td>3</td>
<td>250</td>
<td>20</td>
<td>34</td>
<td>8</td>
<td>4.3</td>
</tr>
<tr>
<td>4</td>
<td>225</td>
<td>5</td>
<td>30</td>
<td>10</td>
<td>3.0</td>
</tr>
<tr>
<td>5</td>
<td>225</td>
<td>10</td>
<td>36</td>
<td>17</td>
<td>2.1</td>
</tr>
<tr>
<td>6</td>
<td>225</td>
<td>20</td>
<td>35</td>
<td>14</td>
<td>2.5</td>
</tr>
<tr>
<td>7</td>
<td>200</td>
<td>5</td>
<td>11</td>
<td>8</td>
<td>1.4</td>
</tr>
<tr>
<td>8</td>
<td>200</td>
<td>10</td>
<td>18</td>
<td>8</td>
<td>2.3</td>
</tr>
<tr>
<td>9</td>
<td>200</td>
<td>20</td>
<td>24</td>
<td>13</td>
<td>1.9</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: 0.1 mmol of 33 in 2.0 mL of DMSO was heated to the specified temperature under microwave irradiation. No unreacted starting material was detected in the crude \(^1\)H NMR spectra. \(^b\) NMR yields. \(^c\) Calculated according to the respective NMR yields of 33c and 33d.

20 min (entries 1-3). This yield was also obtained at 225°C, but only for a reaction time of at least 10 min. At this temperature, the reaction was significantly slower than at 250°C but much faster than at 200°C. Thus, the maximum yield of 33c was about 35-37%.

As a general trend, the proportion of product 33c increased as the temperature was raised. Thus, the amount of side product 33d was considerably more important at 200°C (a temperature at which most of the Claisen rearrangements occur).\(^{36}\) This study shows that siloxycarbenes are still formed and undergo cyclopropanation at 200°C, a temperature much milder than the one used by Frei (Scheme 5). The slow formation of 33c at that temperature could be accounted for by the difficulty to overcome the energy barrier of either the carbene formation or the cyclopropanation step.

Overall, the best compromise for a small amount of Claisen by-product, a fast reaction time and a maximum yield of 33c was microwave heating for 10 min at 250°C. However, the best yield obtained was still only 37%. In order to further improve the yield, a solvent screen was performed. Because of the

high pressure generated at the elevated temperature needed for the reaction, the choice of solvent was limited to those having high boiling points (Table 3).

Table 3. Effect of the solvent on the yield of 33c versus 33d

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield 33c (%)</th>
<th>Yield 33d (%)</th>
<th>Ratio 33c/33d</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DMSO</td>
<td>37 (29)</td>
<td>11</td>
<td>3.4</td>
</tr>
<tr>
<td>2</td>
<td>α-dichlorobenzene&lt;sup&gt;de&lt;/sup&gt;</td>
<td>42 (54)</td>
<td>10 (27&lt;sup&gt;f&lt;/sup&gt;)</td>
<td>4.2 (2.0)</td>
</tr>
<tr>
<td>3</td>
<td>α-dichlorobenzene&lt;sup&gt;dg&lt;/sup&gt;</td>
<td>53</td>
<td>31</td>
<td>1.7</td>
</tr>
<tr>
<td>4</td>
<td>DMF</td>
<td>39</td>
<td>23</td>
<td>1.7</td>
</tr>
<tr>
<td>5</td>
<td>NMP</td>
<td>32</td>
<td>31</td>
<td>1.0</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: 0.1 mmol of 33 in 2.0 mL of solvent was heated to 250°C for 10 min under microwave irradiation. <sup>b</sup>NMR yields (isolated yields are in parentheses). <sup>c</sup>Calculated according to the respective NMR or isolated yields (in parentheses) of 33c and 33d. <sup>d</sup>After treatment with 2.5M NaOH. <sup>e</sup>Internal standard added after removal of the solvent by flash chromatography. Trace amount of unreacted starting material was isolated. <sup>f</sup>Mixture of 33d and other unidentified by-products. <sup>g</sup>Internal standard added before removal of the solvent by flash chromatography. Reaction time was 15 min.

NMP gave only a slightly lower yield of 33c than DMSO, but the proportion of Claisen rearrangement side product was more than three times higher (Table 3, entries 1 and 5). A similar phenomenon was encountered with DMF (entry 4). Between these three polar solvents, DMSO thus seemed to be the best choice for this reaction. However, the most interesting result came from the reaction in α-dichlorobenzene. Using freshly distilled solvent, no traces of the expected product 33c were detected by 1H NMR in the crude mixture. The main product formed was α-hydroxycrotonophenone (44, Scheme 12). An aqueous work-up with sodium hydroxide efficiently closed the ring of the chromanone product leaving no detectable traces of 44. An acidic work-up was also possible, but in that case, the ring closure was rather slow. Overall, among the solvents screened under the optimized conditions, α-dichlorobenzene appeared to offer the best yield of 33c and the lowest amount of Claisen rearrangement side product. The latter observation probably results from the lower polarity of that solvent (a factor known to decrease the rate of aromatic Claisen rearrangement).<sup>36</sup> The possibility of stopping the reaction at the enone intermediate was also interesting from a synthetic point
of view. For these reasons, DMSO and o-dichlorobenzene were selected as the two solvents used for further studies.

**Scheme 12.** Formation of o-hydroxy crotonophenone (44) in o-dichlorobenzene

\[
\begin{align*}
\text{SiMe}_3 & \quad \text{o-dichlorobenzene} \\
33 & \quad \mu\text{waves, 250ºC, 10 min} \\
44 & \quad \text{H}^+ \text{ or } \text{OH} \\
& \quad \text{33c}
\end{align*}
\]

Experiments were performed to find the right conditions to get the chromanone product directly after the microwave irradiation process with o-dichlorobenzene as the solvent (Table 4). Even though the basic work-up was found to be more efficient than the acidic one to yield the desired chromanone product, use of Arrhenius bases as additives for the microwave reactions was not possible because it is well-known that these catalyse the decomposition of acylsilanes to aldehydes (Scheme 2). We attempted a ring closure with distilled water as the additive to test neutral conditions. Unfortunately, no desired product was obtained (Table 4, entry 1), possibly due to the non-miscibility of water in o-dichlorobenzene. A weak organic acid, namely benzoic acid, was then used with little success at 1.5 equivalent loading (entry 2). However, this additive also favored the Claisen rearrangement to give 33d as the major product. Using a catalytic amount of acid did not produce any detectable traces of 33c (entry 3).

**Table 4.** Effect of Brønsted acids on the course of the formation of 33c<sup>a</sup>

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive</th>
<th>Equiv</th>
<th>Yield 33c&lt;sup&gt;b&lt;/sup&gt; (%)</th>
<th>Yield 33d&lt;sup&gt;b&lt;/sup&gt; (%)</th>
<th>Ratio 33c/33d&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>distilled water</td>
<td>1.1</td>
<td>0</td>
<td>traces</td>
<td>———</td>
</tr>
<tr>
<td>2</td>
<td>benzoic acid</td>
<td>1.5</td>
<td>8</td>
<td>36</td>
<td>0.2</td>
</tr>
<tr>
<td>3</td>
<td>benzoic acid</td>
<td>0.025</td>
<td>0</td>
<td>traces</td>
<td>———</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: 0.1 mmol of 33 in 2.0 mL of solvent was heated to 250ºC for 10 min under microwave irradiation. <sup>b</sup>NMR yields. <sup>c</sup>Calculated according to the respective NMR yields of 33c and 33d.
The isolation and characterization of 44 was direct evidence that the final cyclization of the reaction proceeded through a conjugate addition as proposed in Scheme 10. That was also in agreement with the formation of β-γ ketone 40 which could isomerize to give the much more stable aromatic conjugate ketone 41. Since that isomerization occurred in aprotic solvents, it is possible that the postulated phenoxide anion or the trimethylsilanol by-product play the role of acid or base to promote formation of the conjugate ketone. The high temperature at which this reaction takes place probably also favors intermediate 41.

The key feature of our proposed mechanism is the cyclopropanation of the alkene by the siloxycarbene derived by Brook rearrangement of the acylsilane (Scheme 10). To obtain direct evidence that cyclopropanation occurred, it was envisioned that using acylsilanes 45 and 46, it would be possible to isolate the tricyclic products 45a and 46a (Scheme 13). With compound 45, the carbaisostere of 33, the tricyclic compound 45a was expected to be obtained as the final product of the reaction because it does not have a heteroatom to stabilize the negative charge created by the opening of the ring system. 45 has the advantage of having essentially the same six-membered transition state as for 33, which seems to be appropriate for the cyclopropanation to occur (Scheme 10). Substrate 46 is interesting because it necessarily undergoes a seven-membered transition state. Also, because of the larger ring formed, the cascade ring opening would not put the negative charge on the phenolic oxygen and hence 46a should be the final product of the reaction.

Scheme 14 details the synthetic route followed to synthesize substrate 45. Bromination at the benzylic position of methyl o-toluate (47) afforded 48 in good yield. Formation of an organozinc reagent followed by nucleophilic attack on allyl bromide gave 49 in 33% yield and a significant amount of 47 was recovered (likely due to the introduction of trace water in the reaction). After many attempts to purify 49 using silica gel chromatography and Kugelhror distillation, we were not able to obtain spectroscopically pure material. This compound was nevertheless subjected to the usual conditions to yield acylsilane 45. This final compound was purified without problem.
Scheme 13. Proposed formation of isolable cyclopropanes

Scheme 14. Preparation of substrate 45

In DMSO, the major product of the reaction was the aldehyde 45b (31% yield, Table 5, entry 3). Only 3% of the cyclopropane product was detected by $^1$H NMR in the crude mixture (entry 1). In o-dichlorobenzene, 45a was formed in 46% yield and only 4% of 45b was detected (entries 2 and 4).
However, it turned out to be difficult to isolate 45a and only impure material could be obtained. Its $^1$H and $^{13}$C NMR spectra were in perfect agreement with published data.\textsuperscript{37}

### Table 5. Major products of the microwave-assisted thermolysis of 45\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Product</th>
<th>Solvent</th>
<th>Yield (%)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me$_3$SiO$\text{45a}$</td>
<td>DMSO (3)</td>
<td>(3)$^{c,e}$</td>
</tr>
<tr>
<td>2</td>
<td>$\text{45a}$</td>
<td>o-dichlorobenzene</td>
<td>(46)$^{d,e}$</td>
</tr>
<tr>
<td>3</td>
<td>$\text{45b}$</td>
<td>DMSO</td>
<td>(31)$^{f}$</td>
</tr>
<tr>
<td>4</td>
<td>$\text{45b}$</td>
<td>o-dichlorobenzene</td>
<td>(4)$^{f}$</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>DMSO</td>
<td>traces</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>o-dichlorobenzene</td>
<td>not detected</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reaction conditions: 0.1 mmol of 45 in 2.0 mL of solvent was heated to 250°C for 10 min under microwave irradiation. When o-dichlorobenzene was used, no treatment with NaOH(aq) was performed (see the experimental section for more details). \textsuperscript{b}Isolated yields (NMR yields are in parentheses). \textsuperscript{c}Yield of the major diastereoisomer (no literature data available for this diastereoisomer for confirmation). Trace amount of what seemed to be the other diastereoisomer was detected. \textsuperscript{d}Yield of the major diastereoisomer (opposite configuration than the one in entry 1). Small amount (11% NMR yield) of what seemed to be the other diastereoisomer (same diastereoisomer as in entry 1) was detected. \textsuperscript{e}Compound detected in the crude mixture by $^1$H NMR but not isolated. The signals were in agreement with those reported in the literature.\textsuperscript{37} \textsuperscript{f}Compound detected in the crude mixture by $^1$H NMR but not isolated. The signals were in agreement with those reported in the literature.\textsuperscript{38}

In DMSO, the thermolysis of 46 also gave the protodesilylation product (Table 6, entry 1). Once again, in o-dichlorobenzene, the formation of the aldehyde product was less important (entry 2). A significant difference with substrate 45 is that a large portion of unreacted starting material could be recovered after the reaction, especially in o-dichlorobenzene (entries 3 and 4). In this case, no


cyclopropanation or C–H bond insertion products were detected in the crude $^1$H NMR spectrum for both solvents. That seems to indicate that with substrate 46 at 250ºC, there is not sufficient energy to overcome the barrier of a seven-membered ring formation by cyclopropanation or a six-membered ring formation by C–H insertion.

Table 6. Major products of the microwave-assisted thermolysis of 46°

<table>
<thead>
<tr>
<th>Entry</th>
<th>Product</th>
<th>Solvent</th>
<th>Yield (%)°</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>DMSO</td>
<td>48 (55)</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>o-dichlorobenzene</td>
<td>4 (6)</td>
</tr>
<tr>
<td>3</td>
<td>Unreacted starting material (46)</td>
<td></td>
<td>18 (19)</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>o-dichlorobenzene</td>
<td>60 (72)</td>
</tr>
</tbody>
</table>

°Reaction conditions: 0.1 mmol of 46 in 2.0 mL of solvent was heated to 250ºC for 10 min under microwave irradiation. When o-dichlorobenzene was used, no treatment with NaOH(aq) was performed (see the experimental section for more details). b Isolated yields (NMR yields are in parentheses).

To increase the yield of chroman-4-one derivative and reduce the amount of Claisen rearrangement side product, we envisioned the addition of a methyl group at the position ortho to the O-allyl chain on the phenyl ring (substrate 50). As pointed out in Scheme 15, rearomatization of the system after the first [3,3]-sigmatropic rearrangement would be inhibited and perhaps allow for cyclopropanation. However, it was also highly possible that dienone 51 underwent a Cope-rearrangement (intermediate 52) and enolization to generate the aromatic para-Claisen product 53. To rule out this possibility, we synthesized substrates with both ortho and para positions blocked with alkyl chains (Scheme 16).
Scheme 15. Proposed side product formation by a tandem Claisen-Cope rearrangement of 50

\[
\begin{align*}
\text{Scheme 15. Proposed side product formation by a tandem Claisen-Cope rearrangement of 50} \\
\text{Scheme 16. Proposed substrates to prevent the formation of Claisen and Cope side products} \\
\end{align*}
\]

Substrates 50 and 55 were synthesized from the commercially available 3-methylsalicylic and 3,5-diisopropylsalicylic acids, respectively (see the experimental section for more details). Unfortunately, 3,5-dimethylsalicylic acid (59) is not available from major suppliers and had to be synthesized. The route chosen is outlined in Scheme 17.
Scheme 17. Synthesis of 3,5-disubstituted methyl salicylates as precursors to 2,3,5-trisubstituted benzoylsilanes 39

\[
\begin{array}{c}
\text{Scheme 17. Synthesis of 3,5-disubstituted methyl salicylates as precursors to 2,3,5-trisubstituted benzoylsilanes}^{39} \\
\end{array}
\]

\[
\begin{array}{c}
\text{(R}^1 = \text{R}^2 = \text{Me})
\end{array}
\]

**Scheme 17.** Synthesis of 3,5-disubstituted methyl salicylates as precursors to 2,3,5-trisubstituted benzoylsilanes

\[
\begin{array}{c}
\text{R}^2
\end{array}
\]

\[
\begin{array}{c}
\text{OH} \\
\text{OH}
\end{array}
\]

\[
\begin{array}{c}
\text{AcOH (glacial)} \\
\text{reflux, 30 min}
\end{array}
\]

\[
\begin{array}{c}
\text{R}^1
\end{array}
\]

\[
\begin{array}{c}
\text{OH} \\
\text{OH}
\end{array}
\]

\[
\begin{array}{c}
\text{p-toluidine, AcOH (glacial)} \\
\text{reflux, 2 days}
\end{array}
\]

\[
\begin{array}{c}
\text{R}^2
\end{array}
\]

\[
\begin{array}{c}
\text{OH} \\
\text{OH}
\end{array}
\]

\[
\begin{array}{c}
\text{R}^1
\end{array}
\]

\[
\begin{array}{c}
\text{OH} \\
\text{OH}
\end{array}
\]

\[
\begin{array}{c}
\text{MeOH} \\
\text{H}_2\text{SO}_4 \text{(conc.)}
\end{array}
\]

\[
\begin{array}{c}
\text{MeOH}
\end{array}
\]

\[
\begin{array}{c}
\text{H}_2\text{SO}_4 \text{(conc.)}
\end{array}
\]

\[
\begin{array}{c}
\text{1) NaOH(aq)} \\
\text{2) HCl(aq)}
\end{array}
\]

\[
\begin{array}{c}
\text{R}^2
\end{array}
\]

\[
\begin{array}{c}
\text{OH}
\end{array}
\]

\[
\begin{array}{c}
\text{R}^1
\end{array}
\]

\[
\begin{array}{c}
\text{N}
\end{array}
\]

\[
\begin{array}{c}
\text{O}
\end{array}
\]

\[
\begin{array}{c}
\text{O}
\end{array}
\]

\[
\begin{array}{c}
\text{O}
\end{array}
\]

\[
\begin{array}{c}
\text{OH}
\end{array}
\]

\[
\begin{array}{c}
\text{R}^2
\end{array}
\]

\[
\begin{array}{c}
\text{OH}
\end{array}
\]

\[
\begin{array}{c}
\text{R}^1
\end{array}
\]

\[
\begin{array}{c}
\text{OMe}
\end{array}
\]

\[
\begin{array}{c}
\text{OH}
\end{array}
\]

\[
\begin{array}{c}
\text{R}^1
\end{array}
\]

\[
\begin{array}{c}
\text{R}^2
\end{array}
\]

\[
\begin{array}{c}
\text{(R}^1 = \text{R}^2 = \text{Me}): 92% \\
\text{reflux, 30 min}
\end{array}
\]

\[
\begin{array}{c}
\text{AcOH (glacial)} \\
\text{reflux, 2 days}
\end{array}
\]

\[
\begin{array}{c}
\text{(R}^1 = \text{R}^2 = \text{Me}): 48%
\end{array}
\]

\[
\begin{array}{c}
\text{59 (R}^1 = \text{R}^2 = \text{Me): 96%}
\end{array}
\]

\[
\begin{array}{c}
\text{58 (R}^1 = \text{R}^2 = \text{Me): 48%}
\end{array}
\]

\[
\begin{array}{c}
\text{60 (R}^1 = \text{Me}, \text{R}^2 = \text{H): 94%}
\end{array}
\]

\[
\begin{array}{c}
\text{61 (R}^1 = \text{R}^2 = \text{Me): 90%}
\end{array}
\]

\[
\begin{array}{c}
\text{62 (R}^1 = \text{R}^2 = \text{tBu): 96%}
\end{array}
\]

2.3 Substrate Scope

In DMSO, the yield of chroman-4-one derivative increased up to 66% (the highest yield of our substrate scope study) with the microwave-assisted thermolysis of 50 (Table 7, entry 3). Only 4% of Claisen-rearrangement product was detected compared to 11% with substrate 33 (Table 8, entry 1). However, in o-dichlorobenzene, the yield of 50a was notably lower at only 32% (Table 7, entry 4). This contrasts with substrate 33 which gave a higher yield of 2-methylchroman-4-one in o-dichlorobenzene (entries 1 and 2). With substrates having both positions 3 and 5 blocked by alkyl substituents

(entries 5-8), the yield in DMSO was higher than with substrate 33, but lower than with 50. Once again, the yield in o-dichlorobenzene was lower than with the model substrate 33.

Though it was surprising that the cyclopropanation occurs with the electron-rich substrate 33, it was even more impressive that it occurs with substrates 63 and 64 (Table 7, entries 9-12). The success of these reactions strengthens our suggestion that the rigidity of the phenyl ring backbone and the short allyl chain help the six-membered ring addition of the nucleophilic siloxycarbene to the olefin. According to the isolated yield of 64a and 64b (entries 11 and 12), this reaction has no diastereoselectivity. However, analysis of the crude mixture by 1H NMR showed that there were about two times more trans than cis isomers formed (entries 11 and 12).

Table 7. Substrate scope

<table>
<thead>
<tr>
<th>Entry</th>
<th>Starting material</th>
<th>Expected product</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>DMSO</td>
<td>29 (37)</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td>o-dichlorobenzene</td>
<td>54 (42)</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>DMSO</td>
<td>66 (51)</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>o-dichlorobenzene</td>
<td>32 (31)</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td>DMSO</td>
<td>46 (53)</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td>o-dichlorobenzene</td>
<td>14 (52)</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td>DMSO</td>
<td>47 (51)</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td>o-dichlorobenzene</td>
<td>39 (5)</td>
</tr>
</tbody>
</table>
Table 7. (continued)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Starting material</th>
<th>Expected product</th>
<th>Solvent</th>
<th>Yield (%)\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td><img src="Image9" alt="Image" /></td>
<td><img src="Image10" alt="Image" /></td>
<td>DMSO</td>
<td>15 (30)</td>
</tr>
<tr>
<td>10</td>
<td><img src="Image11" alt="Image" /></td>
<td><img src="Image12" alt="Image" /></td>
<td>o-dichlorobenzene</td>
<td>23 (16)</td>
</tr>
<tr>
<td>11</td>
<td><img src="Image13" alt="Image" /></td>
<td><img src="Image14" alt="Image" /></td>
<td>DMSO</td>
<td>64a: 15 (12) 64b: (22)</td>
</tr>
<tr>
<td>12</td>
<td><img src="Image15" alt="Image" /></td>
<td><img src="Image16" alt="Image" /></td>
<td>o-dichlorobenzene</td>
<td>64a: 16 (8) 64b: 15 (15)</td>
</tr>
<tr>
<td>13</td>
<td><img src="Image17" alt="Image" /></td>
<td><img src="Image18" alt="Image" /></td>
<td>DMSO</td>
<td>4 (4)</td>
</tr>
<tr>
<td>14</td>
<td><img src="Image19" alt="Image" /></td>
<td><img src="Image20" alt="Image" /></td>
<td>o-dichlorobenzene</td>
<td>(2)</td>
</tr>
<tr>
<td>15</td>
<td><img src="Image21" alt="Image" /></td>
<td><img src="Image22" alt="Image" /></td>
<td>DMSO</td>
<td>33 (41)</td>
</tr>
<tr>
<td>16</td>
<td><img src="Image23" alt="Image" /></td>
<td><img src="Image24" alt="Image" /></td>
<td>o-dichlorobenzene</td>
<td>44 (30)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reaction conditions: 0.1 mmol of starting material in 2.0 mL of solvent was heated to 250°C for 10 min under microwave irradiation. When o-dichlorobenzene was used, a treatment with 2.5M NaOH for 1h was also performed (see the experimental section for more details). \textsuperscript{b}Isolated yields (NMR yields are in parentheses). \textsuperscript{c}For an unknown reason, there was a loss of material for this reaction. \textsuperscript{d}For an unknown reason, there was a loss of material during the work-up of this reaction.

Changing the phenyl for a naphthyl backbone had a dramatic effect on the course of the reaction. The expected product 65a was isolated in 4% yield in DMSO and observed in only 2% yield by \textsuperscript{1}H NMR when the reaction was performed in o-dichlorobenzene (Table 7, entries 13 and 14). 4-allyl-3-hydroxy-2-naphthaldehyde (65c) was the major product as shown in Table 11 (entries 3 and 4).

The reaction also worked with alkyne 66, giving 2,3-dimethylchromen-4-one (66a) as the main product (Table 7, entries 15 and 16). The proposed mechanism for this reaction is similar to the one for O-allyl substrates (Scheme 18). The addition of the siloxycarbene 67 would generate a cyclopropene.
(68) that would open to give the allene 69. We propose that conjugate addition of the phenoxide anion followed by isomerization of the intermediate 70 gives 2,3-dimethylchromen-4-one as the final product (66a).

**Scheme 18. Proposed mechanism for the formation of 2,3-dimethylchromen-4-one (66a)**

2.4 Competitive Reactions

Tables 8 to 14 show the main by-products obtained during our substrate scope study. As predicted, substrate 50 underwent protodesilylation followed by a tandem Claisen-Cope rearrangement to give 50b (Table 8, entries 1 and 2), but in much lower yield than the side product 33d.
To our delight, we were able to isolate and fully characterize the direct cyclopropanation product 64c (Table 13, entry 2) in support of our proposed mechanism. We were also able to detect and partially characterize the cyclopropane 63b (Table 12, entry 2), though we could not obtain it completely pure. In both cases, the cyclopropanes were only observed when the reactions were performed in o-dichlorobenzene, which suggests that DMSO favors ring openings.

We observed two examples of direct C–H bond insertions (Table 12, entry 4 and Table 13, entry 4). In four cases, we observed benzofuran derivatives as indirect evidence of C–H bond insertion reactions (products 54b, 55b, 64e and 65b). These products were all observed in DMSO, which is in agreement with results obtained by Dr. Shen. Surprisingly, one benzofuran was also observed to form in o-dichlorobenzene (Table 9, entry 2).

It has been previously reported that upon photolysis, acylsilanes can undergo decarbonylation, possibly via an intramolecular concerted extrusion of CO. To the best of our knowledge, this has not been reported for the thermolysis of acylsilanes and 55d (Table 10, entry 6) would represent the first example of this kind of reaction. A representation of the proposed mechanism is shown in Scheme 19.

We also observed some cases of complete loss of the acylsilane functionality (54c and 55c). As the first step of the mechanism of formation, we propose a protodesilylation to form an aldehyde that would then undergo decarbonylation to extrude carbon monoxide (Scheme 20). An ortho-Claisen rearrangement followed by rearomatization of the phenyl ring would give the final product.

---

Table 8. Major by-product of the microwave-assisted thermolysis of 50

<table>
<thead>
<tr>
<th>Entry</th>
<th>Product</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;c&lt;/sup&gt;</td>
<td><img src="image" alt="Aldehyde structure" /></td>
<td>DMSO</td>
<td>(4)</td>
</tr>
<tr>
<td>2&lt;sup&gt;c&lt;/sup&gt;</td>
<td><img src="image" alt="Phenol structure" /></td>
<td>o-dichlorobenzene</td>
<td>traces</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: 0.1 mmol of 50 in 2.0 mL of solvent was heated to 250°C for 10 min under microwave irradiation. No unreacted starting material was detected in the crude 1H NMR spectra. When o-dichlorobenzene was used, a treatment with 2.5M NaOH for 1h was also performed (see the experimental section for more details). <sup>b</sup>NMR yields. <sup>c</sup>Proposed structure to explain the presence of aldehyde and phenol peaks in the crude mixtures. This molecule was detected in the crude mixture by 1H NMR and compared to literature data,<sup>41</sup> but not isolated.

Table 9. Major by-products of the microwave-assisted thermolysis of 54

<table>
<thead>
<tr>
<th>Entry</th>
<th>Product</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image" alt="Furan structure" /></td>
<td>DMSO</td>
<td>8 (5)</td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="Phenol structure" /></td>
<td>o-dichlorobenzene</td>
<td>(5)</td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="Phenol structure" /></td>
<td>DMSO</td>
<td>7 (8)</td>
</tr>
<tr>
<td>4</td>
<td><img src="image" alt="Phenol structure" /></td>
<td>o-dichlorobenzene</td>
<td>(11)</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: 0.1 mmol of 54 in 2.0 mL of solvent was heated to 250°C for 10 min under microwave irradiation. No unreacted starting material was detected in the crude 1H NMR spectra. When o-dichlorobenzene was used, a treatment with 2.5M NaOH for 1h was also performed (see the experimental section for more details). <sup>b</sup>Isolated yields (NMR yields are in parentheses).

Table 10. Major by-products of the microwave-assisted thermolysis of 55

<table>
<thead>
<tr>
<th>Entry</th>
<th>Product</th>
<th>Solvent</th>
<th>Yield (%) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Image" /></td>
<td>DMSO</td>
<td>12 (10)</td>
</tr>
<tr>
<td>2</td>
<td><img src="image2.png" alt="Image" /></td>
<td>o-dichlorobenzene</td>
<td>not detected</td>
</tr>
<tr>
<td>3</td>
<td><img src="image3.png" alt="Image" /></td>
<td>DMSO</td>
<td>28 (28)</td>
</tr>
<tr>
<td>4</td>
<td><img src="image4.png" alt="Image" /></td>
<td>o-dichlorobenzene</td>
<td>not detected</td>
</tr>
<tr>
<td>5</td>
<td><img src="image5.png" alt="Image" /></td>
<td>DMSO</td>
<td>not detected</td>
</tr>
<tr>
<td>6</td>
<td><img src="image6.png" alt="Image" /></td>
<td>o-dichlorobenzene</td>
<td>8</td>
</tr>
<tr>
<td>7</td>
<td><img src="image7.png" alt="Image" /></td>
<td>DMSO</td>
<td>not detected</td>
</tr>
<tr>
<td>8</td>
<td><img src="image8.png" alt="Image" /></td>
<td>o-dichlorobenzene</td>
<td>traces</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: 0.1 mmol of 55 in 2.0 mL of solvent was heated to 250°C for 10 min under microwave irradiation. When o-dichlorobenzene was used, a treatment with 2.5M NaOH for 1h was also performed (see the experimental section for more details). \(^b\) Isolated yields (NMR yields are in parentheses).
Table 11. Major by-products of the microwave-assisted thermolysis of 65

<table>
<thead>
<tr>
<th>Entry</th>
<th>Product</th>
<th>Solvent</th>
<th>Yield (%)&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image" alt="65b" /></td>
<td>DMSO</td>
<td>(1)</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>o-dichlorobenzene</td>
<td>not detected</td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="65c" /></td>
<td>DMSO</td>
<td>66 (78)</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>o-dichlorobenzene</td>
<td>62 (70)</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: 0.1 mmol of 65 in 2.0 mL of solvent was heated to 250°C for 10 min under microwave irradiation. No unreacted starting material was detected in the crude ¹H NMR spectra. When o-dichlorobenzene was used, a treatment with 2.5M NaOH for 1h was also performed (see the experimental section for more details). <sup>b</sup>An impure compound which ¹H NMR spectrum looked like a direct cyclopropanation product was also detected when the reaction was performed in o-dichlorobenzene. However, the characteristic peak of the TMS group was not detected: ¹H NMR (400 MHz, CDCl₃) δ 8.05 (s, 1H, ArH), 7.79 (app d, J = 8.0 Hz, 1H, ArH), 7.70 (app d, J = 8.0 Hz, 1H, ArH), 7.40-7.35 (m, 2H, ArH), 7.24 (s, 1H, ArH), 4.30 (dd, J = 10.6, 1.3 Hz, 1H, OCH(H)), 3.98 (app d, J = 10.5 Hz, 1H, OCH(H)), 2.00 (ddt, J = 9.5, 6.2, 1.4 Hz, 1H, OCCH), 1.48 (dd, J = 9.7, 5.5 Hz, 1H, OCCH(H)), 1.36 (app t, J = 5.8 Hz, 1H, OCCH(H)). <sup>c</sup>Isolated yields (NMR yields are in parentheses).

Scheme 19. Proposed mechanism for the formation of 55d
Scheme 20. Proposed mechanism for the formation of 54c and 55c

Unexpectedly, the thermolysis of acylsilane 63 gave 63g (Table 12, entries 9 and 10), a configuration isomer of 63a. The proposed mechanism (Scheme 21) starts by the migration of the double bond of 63 to the internal position of the alkyl chain, generating a very electron-rich alkene (71). After the Brook rearrangement (72) and the cyclopropanation steps (73), we propose that a ring expansion cascade process including an intermolecular protonation step (perhaps from a trimethylsilanol molecule generated in situ by another reaction) gives the final product 63g. If this mechanism is correct, then it would indicate that cyclopropanations of very electron-rich alkenes are possible with siloxycarbenes.
Table 12. Major by-products of the microwave-assisted thermolysis of 63

<table>
<thead>
<tr>
<th>Entry</th>
<th>Product</th>
<th>Solvent</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="63b" alt="Image" /></td>
<td>DMSO</td>
<td>not detected</td>
</tr>
<tr>
<td>2</td>
<td><img src="63b" alt="Image" /></td>
<td>o-dichlorobenzene</td>
<td>(18)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td><img src="63c" alt="Image" /> + <img src="63d" alt="Image" /></td>
<td>DMSO</td>
<td>not detected</td>
</tr>
<tr>
<td>4</td>
<td><img src="63c" alt="Image" /> + <img src="63d" alt="Image" /></td>
<td>o-dichlorobenzene</td>
<td>63c: (9) 63d: (13)</td>
</tr>
<tr>
<td>5</td>
<td><img src="63e" alt="Image" /></td>
<td>DMSO</td>
<td>(7)&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>6</td>
<td><img src="63e" alt="Image" /></td>
<td>o-dichlorobenzene</td>
<td>(16)&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>7</td>
<td><img src="63f" alt="Image" /></td>
<td>DMSO</td>
<td>(21)</td>
</tr>
<tr>
<td>8</td>
<td><img src="63f" alt="Image" /></td>
<td>o-dichlorobenzene</td>
<td>6 (18)</td>
</tr>
<tr>
<td>9</td>
<td><img src="63g" alt="Image" /></td>
<td>DMSO</td>
<td>(1)</td>
</tr>
<tr>
<td>10</td>
<td><img src="63g" alt="Image" /></td>
<td>o-dichlorobenzene</td>
<td>16 (1)</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: 0.1 mmol of 63 in 2.0 mL of solvent was heated to 250ºC for 10 min under microwave irradiation. No unreacted starting material was detected in the crude <sup>1</sup>H NMR spectra. When o-dichlorobenzene was used, a treatment with 2.5M NaOH for 1h was also performed (see the experimental section for more details).<sup>b</sup>Isolated yields (NMR yields are in parentheses).<sup>c</sup>Only one isomer observed.<sup>d</sup>This product was not isolated. <sup>1</sup>H NMR signals from the unpurified reaction mixture were in agreement with published data.<sup>42</sup>

---

**Scheme 21. Proposed mechanism for the formation of 63g**

Scheme 21 illustrates the proposed mechanism for the formation of 63g. The process involves isomerization, Brook rearrangement, cyclopropanation, and ring expansion. The compound 63g is thought to be formed in low yield by the thermolysis of 64 in o-dichlorobenzene (Table 13, entry 10). If the proposed structure is right, then its mechanism of formation, though not investigated in this study, would be quite interesting to examine since it involves an elimination step without the loss of the O-silyl group.

**Table 13. Major by-products of the microwave-assisted thermolysis of 64**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Product</th>
<th>Solvent</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image" alt="64c" /></td>
<td>DMSO</td>
<td>not detected</td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="64c" /></td>
<td>o-dichlorobenzene</td>
<td>7 (15)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="64d" /></td>
<td>DMSO</td>
<td>not detected</td>
</tr>
<tr>
<td>4</td>
<td><img src="image" alt="64d" /></td>
<td>o-dichlorobenzene</td>
<td>(2)&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
</tbody>
</table>
Table 13. (continued)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Product</th>
<th>Solvent</th>
<th>Yield (%)&lt;sup&gt;o&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>DMSO</td>
<td>8 (5)</td>
</tr>
<tr>
<td>6</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>o-dichlorobenzene</td>
<td>not detected</td>
</tr>
<tr>
<td>7&lt;sup&gt;a&lt;/sup&gt;</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>DMSO</td>
<td>(7)&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
<tr>
<td>8&lt;sup&gt;a&lt;/sup&gt;</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>o-dichlorobenzene</td>
<td>traces&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
<tr>
<td>9</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>DMSO</td>
<td>not detected</td>
</tr>
<tr>
<td>10</td>
<td><img src="image" alt="Chemical Structure" /></td>
<td>o-dichlorobenzene</td>
<td>(4)&lt;sup&gt;g&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>Reaction conditions: 0.1 mmol of 64 in 2.0 mL of solvent was heated to 250ºC for 10 min under microwave irradiation. No unreacted starting material was detected in the crude <sup>1</sup>H NMR spectra. When o-dichlorobenzene was used, a treatment with 2.5M NaOH for 1h was also performed (see the experimental section for more details).<sup>b</sup>Isolated yields (NMR yields are in parentheses).<sup>c</sup>Only one isomer observed.<sup>d</sup>Yield of the trans-<sup>E</sup> diastereoisomer (no literature data available for this diastereoisomer for confirmation). Trace amount of what seemed to be the cis-<sup>E</sup> diastereoisomer was detected.<sup>e</sup>Proposed structure to explain the presence of aldehyde and phenol peaks in the crude <sup>1</sup>H NMR spectra. This molecule was not further characterized.<sup>f</sup>Yields based on the integration of the peak of the aldehyde proton.<sup>g</sup>Detectected by <sup>1</sup>H NMR and GC/MS in a mixture along with 64c.

Indirect evidence for the cyclopropenation step in the thermolysis of substrate 66 was found when the vinylsilane 66b was isolated (Table 14, entries 1 and 2). Two possible mechanisms for this reaction are shown in Scheme 22. It is possible that a concerted [2,2]-sigmatropic rearrangement directly gives the vinylsilane from the cyclopropene 74 (pathway A). One could also imagine a stepwise mechanism starting with the expansion of the cyclopropene ring to form a five-membered ring that would collapse to give 66b (pathway B).
Table 14. Major by-product of the microwave-assisted thermolysis of 66

<table>
<thead>
<tr>
<th>Entry</th>
<th>Product</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="image" /></td>
<td>DMSO</td>
<td>(8)</td>
</tr>
<tr>
<td>2</td>
<td>66b</td>
<td>o-dichlorobenzene</td>
<td>13 (8)</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>DMSO</td>
<td>traces</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>o-dichlorobenzene</td>
<td>not detected</td>
</tr>
</tbody>
</table>

*aReaction conditions: 0.1 mmol of 66 in 2.0 mL of solvent was heated to 250°C for 10 min under microwave irradiation. When o-dichlorobenzene was used, a treatment with 2.5M NaOH for 1h was also performed (see the experimental section for more details). bIsolated yields (NMR yields are in parentheses).*

Scheme 22. Proposed mechanisms for the formation of vinylsilane 66b

**Pathway A (concerted):**

1) Brook rearrangement  
2) cyclopropanation  

**Pathway B (stepwise):**

1) Brook rearrangement  
2) cyclopropanation  
   - ring expansion  
   - ketone formation
2.5 Attempted intramolecular aromatic C–H bond insertion and intermolecular cyclopropanation

Encouraged by our success with intramolecular additions of siloxycarbenes to unsaturated carbon-carbon bonds, we envisioned that an intermolecular reaction between benzoyltrimethylsilane (75) and allyloxybenzene (76) could be possible (Scheme 23).\textsuperscript{43} Unfortunately, in DMSO (250°C, 10 min) only products resulting from the ortho and para-Claisen rearrangement of allyloxybenzene were detected after the microwave-assisted thermolysis. At the end of the reaction, there was no benzoyltrimethylsilane left which indicated that it decomposed instead of undergoing the desired intermolecular reaction to generate 75a or 75b. Also, no product arising from the insertion of the siloxycarbene into the allylic C–H bonds was detected. Future work could involve studying this reaction in o-dichlorobenzene.

Scheme 23. Proposed intermolecular cyclopropanation of a thermally-generated siloxycarbene

With the goal of widening the scope of the microwave-assisted C–H bond functionalization with siloxycarbenes, we designed the aliphatic acylsilane 80 (Scheme 24) as a potential candidate for an intramolecular aromatic C–H insertion. The lack of β-hydrogen in this substrate should prevent

\textsuperscript{43} 75 was synthesized by Dr. Zengming Shen.
undesirable elimination reactions. Also, the Thorpe-Ingold effect\textsuperscript{44} induced by the geminal methyl groups and the possibility of forming a five-membered ring should favor the C–H insertion process. Because of the aliphatic nature of the acylsilane needed, we used the acid chloride\textsuperscript{79} and lithium tetrakis(trimethylsilyl)aluminate\textsuperscript{45} to synthesize \textit{80} in good yield.\textsuperscript{46,47} Unfortunately, even though there was almost no starting material left after the thermolysis of \textit{80} in DMSO and \textit{o}-dichlorobenzene, the expected product \textit{80a} was not detected.\textsuperscript{48} To make sure that the aliphatic siloxycarbene actually formed under these conditions, we tried to reproduce Brook’s experiment\textsuperscript{22} with pivaloyltrimethylsilane (\textit{81}, scheme 25). The reaction was performed in DMSO-d\textsubscript{6} so that no work-up was necessary. After 1h of microwave heating at 250\degree C, no starting material was left, but no C–H insertion product (\textit{81a}) was detected by \textit{^1}H NMR. The presence of other unknown products indicated that under our conditions, other reactions proceeded in preference to intramolecular C–H insertion.

\textbf{Scheme 24}. Synthesis of aliphatic acylsilane \textit{80} and proposed intramolecular siloxycarbene insertion into an aromatic C–H bond

\begin{center}
\begin{tikzpicture}
\node at (0.5,0) {\textbf{Scheme 24.} Synthesis of aliphatic acylsilane \textit{80} and proposed intramolecular siloxycarbene insertion into an aromatic C–H bond};
\node at (0,0) {
\begin{minipage}{0.9\textwidth}
\begin{align*}
&\text{MeO} &\text{MeO} \\
&\text{1) LDA, THF, -60\degree C} &\text{1) KOH, MeOH, reflux} \\
&\text{2) Mel, THF, -60\degree C} &\text{2) HCl(aq)} \\
&\text{2 times} &\text{77: 38\%} \\
\rightarrow &\text{MeO} &\text{HO} \\
\rightarrow &\text{MeO} &\text{78: 47\%} \\
\rightarrow &\text{(COCl)}_2, \text{CH}_2\text{Cl}_2 &\text{79: quantitative yield} \\
\rightarrow &\text{DMF (cat.), 0\degree C} &\text{80: 62\%} \\
\rightarrow &\text{DMSO or} &\text{Cl} \\
\rightarrow &\text{\textit{o}-dichlorobenzene} &\text{\mu waves, 250\degree C, 10 min} \\
\rightarrow &\text{Me}_3\text{Si} &\text{\textit{80a}} \\
&\text{Li[Al(SiMe}_3\text{)]}_4, \text{CuCN,} &\text{not detected by \textit{^1}H NMR} \\
&\text{THF, -75\degree C \rightarrow 0\degree C} &\text{by \textit{^1}H NMR} \\
&\text{2) H}_2\text{SO}_4(aq)}
\end{align*}
\end{minipage}}
\end{tikzpicture}
\end{center}

\textsuperscript{47} This methodology was also employed to synthesize acylsilanes \textit{63, 64} and \textit{81}.
\textsuperscript{48} The side products were not identified.
Scheme 25. Attempted reproduction of Brook's intramolecular C–H bond insertion reaction\textsuperscript{22} under microwave irradiation

\begin{align*}
\text{O} & \quad 1) \text{Li}[\text{Al}(\text{SiMe}_3)_4], \text{CuCN}, \text{THF, } -75^\circ\text{C} \rightarrow 0^\circ\text{C} \\
\text{Cl} & \quad 2) \text{H}_2\text{SO}_4(\text{aq}) \\
\rightarrow & \quad \text{O} \\
\text{SiMe}_3 & \quad \text{DMSO-d}_6, \mu\text{waves} \\
81 & \quad 250^\circ\text{C}, 1\text{h} \\
\rightarrow & \quad \text{H} \\
81a & \quad \text{SiMe}_3 \\
& \quad \text{not detected} \\
& \quad \text{by } ^1\text{H NMR}
\end{align*}

2.6 Summary and Future Directions

We investigated the microwave-assisted thermolysis of \textit{ortho}-substituted aroylsilanes. At high temperature, aroylsilanes form siloxycarbenes that readily add to electron-rich carbon-carbon unsaturations to form fused six-membered rings and cyclopropanes or cyclopropenes. We showed that in the case of substrates having an \textit{ortho} aryl ether bond, an \textit{in situ} cascade ring opening of the cyclopropanes or cyclopropenes formed leads to chroman-4-one and chromen-4-one derivatives in low to good yield. The reaction efficiency depends on the heating time, temperature, solvent and the substitution pattern of the starting material.

Studies should be done to further improve the yield and the selectivity of this transformation. Development of a transition metal catalysed version of this reaction may allow for reactivity under milder conditions and improved selectivity. Such a methodology may be ultimately applied to the synthesis of structurally challenging molecules.
Chapter 3
Experimental Methods

3.1 General Information

Microwave-assisted reactions were performed within sealed vials using a Biotage Initiator 2.0 reactor. $^1$H and $^{13}$C NMR spectra were acquired on either a Varian Mercury 300 (300 MHz and 75 MHz), Varian Mercury 400 (400 MHz and 100 MHz), Varian 400 (400 MHz and 100 MHz) or Varian Unity 500 (500 MHz) spectrometer using the residual peak of the indicated solvent as reference. $^1$H NMR data are reported as follow: chemical shift ($\delta$ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, app = apparent), $J$ coupling constant (Hz), integration and assignment. $^{13}$C NMR data are reported as chemical shifts ($\delta$ ppm). IR spectra were obtained from a Perkin Elmer Spectrum 1000 spectrometer. Absorptions are reported in terms of wavenumbers (cm$^{-1}$). Routine GC/MS analyses were performed on an Agilent 5975C GC/MS. High resolution mass spectra were obtained from the University of Toronto Mass Spectrometry facility.

Analytical TLC analyses were performed on EMD fluorescent 250 $\mu$m silica gel 60 glass plates (F$^{254}$). Chromatograms were visualized by fluorescence quenching (254 nm) or water-based KMnO$\textsubscript{4}$ stain. Preparative TLC were performed on EMD fluorescent 2 mm silica gel 60 glass plates (F$^{254}$) and revealed by fluorescence quenching (254 nm). Purifications by flash column chromatography were performed using either a glass column (Silicycle ultra pure silica gel, 60 Å, 40-63 $\mu$m) or an automated system (Biotage SP1, 60 Å, 40-63 $\mu$m).

Prior to use, 1-methyl-2-pyrrolidinone and dimethyl sulfoxide were distilled over calcium hydride under reduced pressure. Chlorotrimethylsilane was dried over calcium hydride and then distilled under atmospheric pressure. Unless otherwise noted, acetonitrile, dichloromethane, diethyl ether, dimethylformamide, hexanes and tetrahydrofuran were dried on a basic alumina oxide column. Air sensitive
solids were manipulated in a glovebox under nitrogen atmosphere. Organic solutions were concentrated by rotary evaporation under reduced pressure (Büchi Rotavapor R-200).

3.2 Preparation of Starting Materials

3.2.1 General Procedures

General procedure A: O-alkylation and O-allylation of phenols. Based on a modification of the procedure by Che and Yu, a three-neck flask equipped with a reflux condenser was charged with methyl salicylate, K$_2$CO$_3$, alkyl or allyl halide and acetone. The magnetically stirred heterogeneous mixture was heated to reflux under N$_2$(g) or Ar(g) until TLC (9:1 Hexanes:EtOAc) showed complete disappearance of the starting material. Most of the acetone was removed by rotary evaporation under reduced pressure and water was then added. The aqueous solution was extracted three times with EtOAc. The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered and concentrated by rotary evaporation under reduced pressure. The crude product was then purified by flash column chromatography on silica gel.

General procedure B: O-alkylation and O-allylation of phenols. Idem as procedure A except for the work-up where the K$_2$CO$_3$ was removed by simple filtration. The filtrate was then concentrated by rotary evaporation under reduced pressure to afford the crude product that was then purified by flash column chromatography on silica gel.

General procedure C: Reductive silylation of methyl benzoates. Based on a modification of the Prakash's procedure, a three-neck flask or a Schlenk flask under Ar(g) was charged with magnesium powder, iodine, TMSCl and NMP. The mixture was stirred at rt and a solution of the appropriate ester in NMP was added dropwise. The solution typically turned green over time and was followed by TLC.

When starting material completely disappeared, saturated aqueous NH₄Cl solution was slowly added followed by aqueous 2M HCl. The orange mixture was stirred a few hours at rt and then extracted with pentanes or hexanes. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated by rotary evaporation under reduced pressure. The crude product was then purified by flash column chromatography on silica gel.

**General procedure D: Esterification.** Based on Vogel's procedure,⁵⁰ a round-bottomed flask was charged with a solution of the appropriate carboxylic acid in methanol. Concentrated sulfuric acid was added and the mixture was heated to reflux until TLC showed no remaining starting material. Water was then added and the aqueous solution was extracted with chloroform. Specific work-up and purification procedures are detailed for each reaction.

### 3.2.2 Syntheses and Characterization Data

![Methyl o-methoxybenzoate (34)](image)

**Methyl o-methoxybenzoate (34).** Prepared following general procedure A from methyl salicylate (3.9 mL, 30 mmol), K₂CO₃ (8.33 g, 60.3 mmol), methyl iodide (3.8 mL, 61 mmol) and acetone (110 mL) for a total reaction time of 8h. Crude product was obtained as a yellow oil in quantitative yield and was used without further purification. ¹H and ¹³C NMR spectra were in agreement with published data.⁵¹

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**o-Methoxybenzoyltrimethylsilane (30).** Prepared following general procedure C from magnesium powder (0.72 g, 30 mmol), iodine (0.13 g, 0.51 mmol), TMSCl (15.0 mL, 119 mmol), NMP (30 mL) and a solution of 34 (2.49 g, 15.0 mmol) in NMP (6.0 mL). After a total reaction time of 19h, the silyl ketal was hydrolysed for 2h with NH₄Cl(aq) (30 mL) and 2M HCl (30 mL). The aqueous layer was extracted five times with pentanes. Purification afforded the title product as a yellow liquid in 21% yield (643 mg, 3.09 mmol). IR (neat) 2959, 2901, 2840, 1692, 1608, 1587, 1483, 1469, 1435, 1396, 1283, 1243, 1192, 1161, 1107, 1046, 1023, 950, 841, 756, 699 cm⁻¹; ¹H NMR spectra was in agreement with published data.⁵²

**Methyl o-ethoxybenzoate (35).** Prepared following general procedure A from methyl salicylate (4.5 mL, 35 mmol), K₂CO₃ (9.65 g, 69.9 mmol), iodoethane (5.6 mL, 70 mmol) and acetone (110 mL) for a total reaction time of 18h. Combined organic layers were washed once with brine and then dried over anhydrous Na₂SO₄. Purification afforded a colorless liquid in 89% yield (5.57 g, 30.9 mmol). IR (neat) 2982, 2949, 2909, 2881, 1731, 1601, 1582, 1493, 1476, 1454, 1433, 1393, 1305, 1252, 1189, 1165, 1133, 1111, 1084, 1044, 965, 924, 827, 756, 707, 665 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.77 (dd, J = 7.9, 1.8 Hz, 1H, ArH), 7.43 (ddd, J = 8.5, 7.5, 1.8 Hz, 1H, ArH), 6.98-6.93 (m, 2H, ArH), 4.12 (q, J = 7.0 Hz, 1H, OCH₂CH₃), 3.89 (s, 3H, OCH₃), 1.46 (t, J = 7.0 Hz, 3H, OCH₂CH₃). ¹³C NMR (100 MHz, CDCl₃) δ...
o-Ethoxybenzoyltrimethylsilane (31). Prepared following general procedure C from magnesium powder (0.73 g, 30 mmol), iodine (0.13 g, 0.51 mmol), TMSCl (15.5 mL, 123 mmol), NMP (30 mL) and a solution of 35 (2.75 g, 15.3 mmol) in NMP (6.0 mL). After a total reaction time of 13 h, the silyl ketal was hydrolysed for 2 h with NH₄Cl(aq) (30 mL) and 2 M HCl (30 mL). The aqueous layer was extracted eight times with pentanes. Purification afforded the title product as a yellow liquid in 24% yield (814 mg, 3.66 mmol). IR (neat) 3071, 2981, 2955, 2900, 1741, 1606, 1585, 1472, 1446, 1391, 1284, 1234, 1194, 1161, 1118, 1045, 951, 919, 842, 754, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.42-7.38 (m, 1H, ArH), 7.31 (app dd, J = 7.5, 1.7 Hz, 1H, ArH), 6.97 (app t, J = 7.4 Hz, 1H, ArH), 6.92 (d, J = 8.4 Hz, 1H, ArH), 4.18 (q, J = 7.0 Hz, 2H, CH₂CH₃), 1.47 (t, J = 7.1 Hz, 3H, CH₂CH₃), 0.25 (s, 9H, Si(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ 236.0, 156.3, 132.8, 131.9, 126.0, 120.0, 110.7, 64.1, 16.4, -0.2; HRMS (ESI) m/z calcd for C₁₂H₁₉O₂Si [M+H]+ 223.1148, found 223.1148.

Methyl o-isopropoxybenzoate (36). Prepared following general procedure A from methyl salicylate (3.4 mL, 26 mmol), K₂CO₃ (7.13 g, 51.6 mmol), 2-iodopropane (5.0 mL, 51 mmol) and acetone (110 mL)
for a total reaction time of 23h. Purification afforded a pale yellow oil in 51% yield (2.62 g, 13.5 mmol).

\(^1\)H NMR spectrum was in agreement with published data.\(^{53}\)

![Image 32](image)

**O-Isopropoxybenzoyltrimethylsilane (32).** Prepared following general procedure C from magnesium powder (0.32 g, 13 mmol), iodine (62 mg, 0.24 mmol), TMSCl (6.8 mL, 54 mmol), NMP (10 mL) and a solution of 36 (1.29 g, 6.66 mmol) in NMP (6.0 mL). After a total reaction time of 15h, the silyl ketal was hydrolysed for 1h30 with NH\(_4\)Cl(aq) (13 mL) and 2M HCl (13 mL). The aqueous layer was extracted four times with pentanes. Purification afforded the title product as a yellow liquid in 17% yield (260 mg, 1.10 mmol). IR (neat) 3069, 2979, 2938, 2901, 1687, 1604, 1586, 1478, 1446, 1385, 1375, 1282, 1235, 1195, 1118, 1050, 949, 841, 753, 700, 623 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.40-7.35 (m, 1H, ArH), 7.24 (dd, \(J\) = 8.2, 0.7 Hz, 1H, ArH), 6.96-6.90 (m, 2H, ArH), 4.71 (septet, \(J\) = 6.1 Hz, 1H, CH(CH\(_3\))\(_2\)), 1.40 (d, \(J\) = 6.2 Hz, 6H, CH(CH\(_3\))\(_2\)), 0.26 (s, 9H, Si(CH\(_3\))\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 237.6, 154.9, 134.2, 131.4, 127.0, 126.1, 119.7, 111.8, 70.7, 23.5, -0.03; HRMS (EI) m/z calcd for C\(_{13}\)H\(_{20}\)O\(_2\)Si [M]\(^+\) 236.1233, found 236.1232.

![Image 37](image)

**Methyl o-allyloxybenzoate (37).** Prepared following general procedure A from methyl salicylate (3.4 mL, 26 mmol), K\(_2\)CO\(_3\) (7.29 g, 52.8 mmol), allyl bromide (4.6 mL, 53 mmol) and acetone (110 mL)

for a total reaction time of 17h. Purification afforded a colorless liquid in 93% yield (4.71 g, 24.5 mmol).

\(^1\)H and \(^{13}\)C NMR spectra were in agreement with published data.\(^{54}\)

![Structural formula of \(\text{o-Allyloxybenzoyltrimethylsilane (33).} \)](image)

**o-Allyloxybenzoyltrimethylsilane (33).** Prepared following general procedure C from magnesium powder (0.60 g, 25 mmol), iodine (0.11 g, 0.42 mmol), TMSCl (12.5 mL, 98.8 mmol), NMP (30 mL) and a solution of 37 (2.34 g, 12.2 mmol) in NMP (6.0 mL). After a total reaction time of 13h, the silyl ketal was hydrolysed for 2h with NH\(_4\)Cl(aq) (30 mL) and 2M HCl (30 mL). The aqueous layer was extracted eight times with pentanes. Purification afforded the title product as a yellow liquid in 25% yield (717 mg, 3.06 mmol). IR (neat) 3072, 3025, 2955, 2909, 1607, 1587, 1479, 1447, 1425, 1283, 1247, 1232, 1222, 1011, 995, 935, 842, 755, 701 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta \) 7.43-7.34 (m, 2H, ArH), 6.99 (td, \(J = 7.4, 0.8 \text{ Hz}, 1H, \text{ArH})

6.93 (d, \(J = 8.3 \text{ Hz}, 1H, \text{ArH})

6.08 (ddt, \(J = 17.2, 10.6, 5.7 \text{ Hz}, 1H, \text{CH} = \text{CH}_2\)

5.40 (dq, \(J = 17.3, 1.4 \text{ Hz}, 1H, \text{CH} = \text{CH(H)}\)), 5.33 (dq, \(J = 10.4, 1.3 \text{ Hz}, 1H, \text{CH} = \text{CH(H)}\)), 4.67 (dt, \(J = 5.7, 1.3 \text{Hz}, 2H, \text{OCH}_2\)), 0.24 (s, 9H, Si(CH\(_3\))\(_3\)); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta \) 239.0, 157.9, 133.9, 133.2, 132.9, 127.2, 121.3, 119.2, 112.0, 69.4, -1.9; HRMS (ESI) m/z calcd for C\(_{10}\)H\(_{15}\)O\(_2\)Si [M+H]\(^+ \) 235.1154, found 235.1148.

Methyl o-(bromoethyl)benzoate (48). Following Laufer's procedure, to a solution of methyl o-toluate (3.6 mL, 26 mmol) in CHCl₃ (25 mL) was added NBS (4.82 g, 27.1 mmol) followed by AIBN (43 mg, 0.26 mmol). The mixture was heated to reflux for 1h45 (it turned dark orange after 10 min). The mixture was filtered and the filtrate was washed with distilled water (2 x 10 mL), dried over anhydrous Na₂SO₄, filtered and concentrated by rotary evaporation under reduced pressure. Purification by flash column chromatography afforded the title compound as a colorless liquid in 71% yield (4.18 g, 18.2 mmol). ¹H and ¹³C NMR spectra were in agreement with published data.

Methyl 2-(but-3-enyl)benzoate (49). Following Knochel's procedures, under an atmosphere of N₂(g), zinc dust (1.38 g, 21.1 mmol) and a solution of 1,2-dibromoethane (0.06 mL, 0.7 mmol) in dry THF (1 mL) were heated to a boil for a few seconds in order to activate the zinc. A solution of 48 (4.03 g, 17.6 mmol) in dry THF (10 mL) was slowly added (1 drop every 5 s) at 0°C. The resulting solution was warmed up to 5°C and stirred 3h. The mixture was cooled to -70°C and added dropwise to a solution of LiCl (1.57 g, 37.0 mmol) and CuCN (1.58 g, 17.6 mmol) in dry THF (15 mL) also at -70°C. The resulting mixture was slowly warmed up to -20°C and stirred 5 min. It was then cooled back to -70°C and a solution of allyl bromide (1.6 mL, 19 mmol) in dry THF (2 mL) was then added. The reaction mixture was

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slowly brought to 0°C and stirred 50 min at that temperature. Water (30 mL) was then added and the precipitate formed was removed by vacuum filtration. The filtrate was extracted with Et₂O (3 x 60 mL). The combined organic layers were washed with brine (60 mL), dried over anhydrous Na₂SO₄, filtered and concentrated by rotary evaporation under reduced pressure. Purification by flash column chromatography was not effective at isolating 49 from 47. Kugelrohr distillation afforded 49 (1.11 g, 5.76 mmol, ≈33% yield) with about 7.7% (by NMR) of 47 as an impurity. 49 was not further purified. ¹H NMR spectrum was in agreement with published data.⁵⁹

**o-(But-3-enyl)benzoyltrimethylsilane (45).** Prepared following general procedure C from magnesium powder (263 mg, 10.8 mmol), iodine (45 mg, 0.18 mmol), TMSCl (5.4 mL, 43 mmol), NMP (10 mL) and a solution of 49 (1.02 g, 5.38 mmol)⁶⁰ in NMP (5.0 mL). After a total reaction time of 13h, the silyl ketal was hydrolysed for 4h with NH₄Cl(aq) (15 mL) and 2M HCl (15 mL). The aqueous layer was extracted with pentanes (4 x 30 mL). Purification afforded the title product as a yellow liquid in 12% yield (150 mg, 0.65 mmol). IR (neat) 3073, 2957, 1613, 1250, 1202, 911, 843, 776, 750 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.51 (dd, J = 7.6, 1.5 Hz, 1H, ArH), 7.37-7.27 (m, 2H, ArH), 7.24 (dd, J = 7.4, 0.6 Hz, 1H, ArH), 5.83 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H, CH=CH₂), 5.00 (app dq, J = 17.2, 1.7 Hz, 1H, CH=CH₂(H)), 4.95 (ddt, J = 10.2, 2.1, 1.1 Hz, 1H, CH=CH₂(H)), 2.83 (app t, J = 7.8 Hz, 2H, ArCH₂), 2.29 (dtt, J = 9.0, 6.8, 1.3 Hz, 2H, CH₂CH=CH₂), 0.31 (s, 9H, Si(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ 239.3, 141.1, 138.2, 137.0, 130.2, 129.5, 128.1, 124.7, 114.2, 37.1, 34.0, 0.4; HRMS (ESI) m/z calcd for C₁₄H₂₀OSi [M+H]+ 232.1283, found 232.1291.

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⁶⁰. The starting material was not completely pure.
Methyl 2-(but-3-enyloxy)benzoate (82). Prepared following a modified version of general procedure B where a mixture of methyl salicylate (3.2 mL, 25 mmol), K₂CO₃ (6.8 g, 49.6 mmol), KI (4.09 g, 24.6 mmol), 4-bromobutene (3.0 mL, 30 mmol) and acetone (110 mL) was heated to reflux for 116h. TLC then showed considerable amount of starting material. Acetone was removed by rotary evaporation under reduced pressure and butan-2-one (100 mL) was added. The resulting mixture was heated to reflux for an additional 22h. Purification afforded a pale yellow liquid in 15% yield (766 mg, 3.72 mmol).

1H NMR (400 MHz, CDCl₃) δ 7.78 (dd, J = 7.7, 1.6 Hz, 1H, ArH), 7.44 (ddd, J = 8.3, 7.4, 1.9 Hz, 1H, ArH), 6.99-6.95 (m, 2H, ArH), 5.95 (ddt, J = 17.1, 10.3, 6.8 Hz, 1H, CH=CH₂), 5.18 (ddd, J = 17.2, 3.4, 1.6, 1H, CH=CH(H)), 5.11 (ddt, J = 10.2, 2.0, 1.2 Hz, 1H, CH=CH(H)), 4.09 (t, J = 6.7 Hz, 2H, OCH₂), 3.88 (s, 1H, OCH₃), 2.59 (tq, J = 6.7, 1.3 Hz, 2H, CH₂CH=CH₂); 13C NMR (100 MHz, CDCl₃) δ 167.2, 158.6, 134.6, 133.5, 131.8, 120.9, 120.5, 117.3, 113.6, 68.6, 52.1, 33.9.

O-(But-3-enyloxy)benzoyltrimethylsilane (46). Prepared following general procedure C from magnesium powder (173 mg, 7.11 mmol), iodine (30 mg, 0.12 mmol), TMSCl (3.5 mL, 28 mmol), NMP (10 mL) and a solution of 82 (732 mg, 3.56 mmol) in NMP (5.0 mL). After a total reaction time of 8 days, the silyl ketal was hydrolysed for 4h with NH₄Cl(aq) (10 mL) and 2M HCl (10 mL). The aqueous layer was extracted with pentanes (3 x 40 mL). Purification afforded the title product as a yellow liquid in 22% yield (616 mg, 2.2 mmol).

1H NMR (400 MHz, CDCl₃) δ 7.2 (overlapping m, 2H, ArH), 6.7 (overlapping m, 2H, ArH), 5.7 (qt, 1H, CH=CH₂), 5.1-4.7 (m, 2H, CH=CH₂), 3.8 (t, 2H, OCH₂CH₂), 3.5 (s, 3H, CH₃), 2.3 (t, 2H, OCH₂CH₂).
yield (198 mg, 0.80 mmol). IR (neat) 3074, 2955, 2900, 1643, 1608, 1587, 1478, 1470, 1447, 1284, 1236, 1194, 1162, 1108, 1049, 1025, 990, 920, 842, 754, 699, 622 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.40 (ddd, J = 8.3, 7.3, 1.9 Hz, 1H, ArH), 7.28 (dd, J = 7.4, 1.8 Hz, 1H, ArH), 6.98 (td, J = 7.5, 1.0 Hz, 1H, ArH), 6.93 (dd, J = 8.3, 0.5 Hz, 1H, ArH), 5.85 (ddt, J = 17.0, 10.2, 6.7 Hz, 1H, CH=CH₂), 5.17 (dq, J = 17.2, 1.7 Hz, 1H, CH=CH₂(H)), 5.13 (dq, J = 10.4, 1.5 Hz, 1H, CH=CH₂(H)), 4.14 (t, J = 7.4 Hz, 2H, OCH₃), 2.61 (app q, J = 7.1 Hz, 2H, CH₂CH=CH₂), 0.24 (s, 9H, Si(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ 240.2, 157.8, 134.5, 133.7, 133.0, 127.2, 121.2, 118.0, 111.7, 67.6, 33.5, -2.0; HRMS (EI) m/z calcd for C₁₄H₁₉O₂Si [M-H]⁺ 247.1154, found 247.1152.

**Methyl 2-hydroxy-3-methylbenzoate (60).** Prepared following general procedure D from 2-hydroxy-3-methylbenzoic acid (10.0 g, 65.8 mmol), MeOH (100 mL) and concentrated H₂SO₄ (16 mL) for a total reaction time of 44h. Water (100 mL) was then added and the aqueous phase was extracted with Et₂O (3 x 100 mL). Combined organic layers were washed with a saturated aqueous solution of NaHCO₃ (2 x 50 mL), washed once with brine (50 mL), dried over anhydrous Na₂SO₄, filtered and then concentrated by rotary evaporation under reduced pressure. Crude product was obtained as a yellow oil in 94% yield (10.3 g, 62.0 mmol) and was used without further purification. ¹H NMR spectrum was in agreement with published data.⁶²

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Methyl 2-allyloxy-3-methylbenzoate (93). Prepared following general procedure B from 60 (9.89 g, 59.5 mmol), K₂CO₃ (16.5 g, 119 mmol), allyl bromide (10.5 mL, 121 mmol) and acetone (200 mL) for a total reaction time of 46h. Purification afforded a colorless liquid in 83% yield (10.2 g, 49.6 mmol). 

¹H NMR spectra was in agreement with published data.⁵⁴

2-Allyloxy-3-methylbenzoyltrimethylsilane (50). Prepared following a modified version of general procedure C from magnesium powder (1.42 g, 58.2 mmol), iodine (0.26 g, 1.0 mmol), TMSCl (30.0 mL, 237 mmol), NMP (70 mL) and a solution of 93 (6.00 g, 29.1 mmol) in NMP (10 mL). After a total reaction time of 110h, the mixture was heated to 45 ºC for 27 h. TLC showed the reaction had stopped progressing with about half the starting material left unreacted. The silyl ketal was hydrolysed for 40 min with NH₄Cl(aq) (80 mL) and 2M HCl (80 mL). The aqueous layer was extracted with hexanes (3 x 100 mL). Purification afforded the title product as a yellow liquid in 11% yield (778 mg, 3.13 mmol).

IR (neat) 3071, 3016, 2956, 2900, 2861, 1620, 1615, 1580, 1463, 1455, 1418, 1372, 1354, 1246, 1203, 1086, 985, 926, 865, 844, 783, 754, 700, 623 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.27 (multiplet overlapping with chloroform residual peak, 1H, ArH), 7.07 (t, J = 7.5 Hz, 1H, ArH), 7.00 (ddd, J = 7.6, 1.8, 0.4 Hz, 1H, ArH), 6.03-5.93 (m, 1H, CH=CH₂), 5.35 (dq, J = 17.2, 1.6 Hz, 1H, CH=CH(H)), 5.23 (dq, J = 10.5, 1.4 Hz, 1H, CH=CH(H)), 4.24 (dt, J = 5.5, 1.5 Hz, 2H, OCH₂), 2.30 (s, 3H, ArCH₃), 0.23 (s, 9H,
Si(CH$_3$)$_3$); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 243.7, 155.5, 139.8, 134.0, 133.7, 131.9, 124.6, 124.3, 117.9, 76.2, 16.1, -2.0; HRMS (ESI) m/z calcd for C$_{14}$H$_{20}$O$_2$Si [M+H]$^+$ 271.1130, found 271.1124.

2-Hydroxy-2-(2-hydroxy-3,5-dimethylphenyl)indane-1,3-dione (57). Following Laude's procedure,$^{39}$ a blue heterogeneous mixture of ninhydrin (5.90 g, 33.1 mmol) and glacial acetic acid (22 mL) was heated up to 105°C until it became homogeneous. 2,4-dimethylphenol (4.0 mL, 33 mmol) was then added and the mixture was heated to reflux under air for 30 min. The green solution turned yellow upon cooling and when it reached rt, a solid crashed out. The precipitate was recovered by vacuum filtration and washed with glacial acetic acid. The pale yellow solid was dried 15 min at 45°C under high vacuum, giving the pure title compound in 92% yield (8.59 g, 30.4 mmol). $^1$H NMR (400 MHz, acetone-d$_6$)$^{63}$ δ 8.01 (d, J = 7.7 Hz, 1H, ArH), 7.88 (t, J = 7.4 Hz, 1H, ArH), 7.74 (d, J = 7.6 Hz, 1H, ArH), 7.63 (t, J = 7.4 Hz, 1H, ArH), 7.08 (s, 1H, ArH), 6.90 (s, 1H, ArH), 6.53 (s, 1H, OH), 5.68 (s, 1H, OH), 2.21 (s, 3H, CH$_3$), 2.09 (s, 3H, CH$_3$).

63. This spectrum was in agreement with published data (see reference 39) but our spectrum gave more information about coupling patterns between protons.
3-(2-Hydroxy-3,5-dimethylbenzoyl)-2-(4-methylphenyl)isoindolone (58). Based on a modification of Laude’s procedure, a round-bottomed flask was charged with 57 (8.38 g, 29.7 mmol) and glacial acetic acid (50 mL). The mixture was heated, but it remained heterogeneous. It turned purple upon addition of p-toluidine (6.36 g, 59.3 mmol). The reaction mixture was heated to reflux under air for 52h. Acetic acid was then removed by rotary evaporation under reduced pressure. The crude solid obtained was recrystallized in EtOH and dried in a vacuum oven, affording the pure product as yellow crystals in 48% yield (5.31 g, 14.3 mmol). $^1$H NMR (400 MHz, acetone-d$_6$) $^64$ δ 11.78 (s, 1H, OH), 8.35 (s, 1H, NCHCO), 7.90-7.16 (m, 10H, ArH), 2.44 (s, 3H, ArCH$_3$), 2.27 (s, 3H, ArCH$_3$), 2.19 (s, 3H, ArCH$_3$); $^{13}$C NMR (100 MHz, acetone-d$_6$) $^65$ δ 200.2, 168.0, 160.8, 141.0, 140.6, 137.3, 135.2, 133.6, 133.4, 130.42, 130.37, 129.7, 128.7, 128.4, 125.1, 123.9, 121.5, 121.4, 118.4, 65.4, 20.9, 20.7, 15.5; HRMS (EI) m/z calcd for C$_{24}$H$_{21}$NO$_3$ [M]$^+$ 371.1521, found 371.1529.

3,5-Dimethylsalicylic acid (59). Based on a modification of Laude’s procedure, a round-bottomed flask was charged with 58 (5.12 g, 13.8 mmol) and 50 mL of aqueous 2M NaOH. The heterogeneous

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64. Literature reports (see reference 39): δ 11.8 (s, OH), 8-7 (m, 9H), 6.9 (s, 1H), 6.65 (s, 1H), 2.4 (s, CH$_3$), 2.25 (s, CH$_3$), 2.15 (s, CH$_3$).
65. Only 23 carbons were detected, probably due to equivalence in the phenyl ring of the p-toluidine moiety.
mixture was heated to reflux 5 min and then vacuum filtered to remove the precipitate. The filtrate was cooled and acidified with concentrated HCl until precipitation was complete. The beige precipitate was recovered by vacuum filtration and dried in a vacuum oven, affording the title compound in 96% yield (2.19 g, 13.2 mmol). \(^1\)H NMR spectrum was in agreement with published data.\(^{39}\) \(^{13}\)C NMR (75 MHz, acetone-d\(_6\)) \(\delta\) 173.2, 159.4, 138.6, 128.5, 128.4, 126.8, 112.1, 20.4, 15.6.

Methyl 3,5-dimethylsalicylate (61). Prepared following general procedure D from 59 (2.13 g, 12.8 mmol), MeOH (20 mL) and concentrated H\(_2\)SO\(_4\) (0.7 mL) for a total reaction time of 88h. Water (20 mL) was then added and the aqueous phase was extracted with CHCl\(_3\) (3 x 20 mL). Combined organic layers were washed with a saturated aqueous solution of NaHCO\(_3\) (2 x 30 mL), washed once with brine (50 mL), dried over anhydrous Na\(_2\)SO\(_4\), filtered and then concentrated by rotary evaporation under reduced pressure. Crude product was obtained as a beige solid in 90% yield (2.08 g, 11.6 mmol). \(^1\)H NMR showed it was pure so it was not further purified. IR (neat) 1660, 1440, 1347, 1281, 1222, 1206, 1137, 1127 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 10.81 (s, 1H, OH), 7.48 (s, 1H, ArH), 7.15 (s, 1H, ArH), 3.93 (s, 3H, OCH\(_3\)), 2.25 (s, 3H, ArCH\(_3\)), 2.24 (s, 3H, ArCH\(_3\)); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 171.3, 158.2, 137.9, 127.7, 127.2, 126.5, 111.4, 52.4, 20.6, 15.8. HRMS (EI) m/z calcd for C\(_{10}\)H\(_{12}\)O\(_3\) [M]\(^+\) 180.0786, found 180.0787.
Methyl 2-allyloxy-3,5-dimethylbenzoate (83). Prepared following general procedure B from 61 (1.90 g, 10.5 mmol), K₂CO₃ (2.91 g, 21.1 mmol), allyl bromide (1.8 mL, 21 mmol) and acetone (50 mL) for a total reaction time of 59h. Purification afforded a pale yellow oil in 95% yield (2.21 g, 10.0 mmol). IR (neat) 3022, 2990, 2950, 2919, 2874, 1730, 1588, 1476, 1435, 1378, 1357, 1317, 1261, 1204, 1131, 1018, 989, 925, 870, 790, 757, 619 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.44 (s, 1H, ArH), 7.15 (s, 1H, ArH), 6.15-6.06 (m, 1H, CH=CH₂), 5.39 (app d, J = 17.2 Hz, 1H, CH=CH(H)), 5.24 (app d, J = 10.6 Hz, 1H, CH=CH(H)), 4.40 (app d, J = 5.6 Hz, 2H, CH₂CH=CH₂), 3.89 (s, 3H, OCH₃), 2.29 (s, 3H, CCH₃), 2.28 (s, 3H, CCH₃); ¹³C NMR (100 MHz, CDCl₃) δ 167.3, 155.0, 136.0, 134.2, 133.3, 132.8, 129.5, 124.7, 117.7, 75.2, 52.3, 20.8, 16.5; HRMS (EI) m/z calcd for C₁₃H₁₆O₃ [M]+ 220.1099, found 220.1105.

2-Allyloxy-3,5-dimethylbenzoyltrimethylsilane (54). Prepared following general procedure C from magnesium powder (0.47 g, 19 mmol), iodine (0.81 g, 0.32 mmol), TMSCl (10.0 mL, 79.1 mmol), NMP (20 mL) and a solution of 83 (2.13 g, 9.69 mmol) in NMP (5.0 mL). After a total reaction time of 17h, the silyl ketal was hydrolysed for 4h with NH₄Cl(aq) (20 mL) and 2M HCl (20 mL). The aqueous layer was extracted with pentanes (3 x 50 mL). Purification afforded the title product as a yellow liquid in 19% yield (481 mg, 1.83 mmol). IR (neat) 3070, 3017, 2955, 2919, 1617, 1586, 1472, 1420, 1375, 1295, 1246, 1208, 1148, 1100, 986, 923, 844, 791, 758, 730, 699, 624 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.08 (m,
Methyl 3,5-diisopropylsalicylate (62). Prepared following a modified version of general procedure D from 3,5-diisopropylsalicylic acid (6.63 g, 29.8 mmol), MeOH (15 mL), concentrated H₂SO₄ (1.8 mL) and glacial acetic acid (1.8 mL, added by mistake). After 28h of heating to reflux, another 1 mL of concentrated H₂SO₄ was added. After a total of 51h, 100 mL of water were added and the aqueous phase was extracted with CHCl₃ (4 x 30 mL). Combined organic layers were washed with a saturated aqueous solution of NaHCO₃ (2 x 100 mL), dried over anhydrous Na₂SO₄, filtered and then concentrated by rotary evaporation under reduced pressure. Crude product was obtained as a light brown liquid (pure according to ¹H NMR) in 96% yield (6.77 g, 28.7 mmol) and was used without further purification. IR (neat) 3171, 2959, 2870, 1674, 1611, 1465, 1441, 1383, 1344, 1309, 1239, 1209, 1170, 1119, 996, 891, 800, 780, 747, 736, 637 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 10.95 (d, J = 0.4 Hz, OH), 7.53 (d, J = 2.1 Hz, 1H, ArH), 7.25 (d overlapping with chloroform residual peak, 1H, ArH), 3.94 (s, 3H, CO₂CH₃), 3.36 (septet, J = 6.9 Hz, 1H, (CH₃)₂CH), 2.85 (septet, J = 6.9 Hz, 1H, (CH₃)₂CH), 1.25 (d, J = 5.9 Hz, 6H, (CH₃)₂CH), 1.23 (d, J = 5.9 Hz, 6H, (CH₃)₂CH); ¹³C NMR (100 MHz, CDCl₃) δ 171.5, 157.7, 139.1, 136.8, 131.2, 124.3, 111.5, 52.4, 33.7, 27.0, 24.3, 22.6; HRMS (EI) m/z calcd for C₁₄H₂₀O₃ [M]^+ 236.1412, found 236.1409.
Methyl 2-allyloxy-3,5-diisopropylbenzoate (84). Prepared following general procedure B from 62 (6.00 g, 25.4 mmol), K$_2$CO$_3$ (7.02 g, 50.7 mmol), allyl bromide (4.4 mL, 51 mmol) and acetone (110 mL) for a total reaction time of 68h. Purification afforded a pale yellow oil in 86% yield (6.02 g, 21.8 mmol). IR (neat) 3082, 2961, 2870, 1731, 1715, 1647, 1604, 1584, 1470, 1384, 1363, 1342, 1294, 1260, 1244, 1221, 1204, 1171, 1149, 1111, 991, 925, 891, 863, 840, 802, 750, 733, 646 cm$^{-1}$; $^1$H NMR (300 MHz, acetone-$d_6$) $\delta$ 7.44 (d, $J = 2.2$ Hz, 1H, ArH), 7.40 (d, $J = 2.4$ Hz, 1H, ArH), 5.40 (app dd, $J = 17.3, 1.7$ Hz, 1H, CH=CH$_2$), 5.21 (app dd, $J = 10.5, 1.0$ Hz, 1H, CH=CH$_2$), 4.42 (app d, $J = 5.5$ Hz, 2H, CH$_2$CH=CH$_2$), 3.85 (s, 3H, CO$_2$CH$_3$), 3.40 (septet, $J = 6.9$ Hz, 1H, (CH$_3$)$_2$CH), 2.93 (septet, $J = 6.9$ Hz, 1H, (CH$_3$)$_2$CH), 2.42 (d, $J = 3.8$ Hz, 6H, (CH$_3$)$_2$CH), 1.22 (d, $J = 3.8$ Hz, 6H, (CH$_3$)$_2$CH); $^{13}$C NMR (100 MHz, acetone-$d_6$) $\delta$ 167.8, 155.0, 145.1, 143.9, 135.6, 129.4, 126.9, 126.2, 117.0, 76.7, 52.3, 34.5, 27.2, 24.4, 24.0; HRMS (EI) m/z calcd for C$_{17}$H$_{24}$O$_3$ [M]$^+$ 276.1725, found 276.1728.

2-Allyloxy-3,5-diisopropylbenzoyltrimethylsilane (55). Prepared following general procedure C from magnesium powder (883 mg, 36.3 mmol), iodine (161 mg, 0.63 mmol), TMSCl (18 mL, 140 mmol), NMP (36 mL) and a solution of 84 (5.00 g, 18.1 mmol) in NMP (5.0 mL). After a total reaction time of 8 days,
the silyl ketal was hydrolysed for 3h with NH₄Cl(aq) (35 mL) and 2M HCl (35 mL). The aqueous layer was extracted with pentanes (3 x 60 mL). Purification afforded the title product as a yellow liquid in 26% yield (1.49 g, 4.67 mmol). IR (neat) 2961, 2928, 2900, 2870, 1623, 1591, 1581, 1465, 1448, 1422, 1383, 1363, 1314, 1246, 1207, 1178, 1130, 1107, 985, 922, 892, 843, 789, 760, 734, 700, 628 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.19 (d, J = 2.3 Hz, 1H, ArH), 6.84 (d, J = 2.4 Hz, 1H, ArH), 5.98 (ddt, J = 17.2, 10.5, 5.2 Hz, 1H, CH=CH₂), 5.37 (dd, J = 17.2, 1.6 Hz, 1H, CH=CH(H)), 5.23 (dq, J = 10.6, 1.4 Hz, 1H, CH=CH(H)), 4.18 (dt, J = 5.3, 1.6 Hz, 2H, CH₂CH=CH₂), 3.28 (septet, J = 6.9 Hz, 1H, (CH₃)₂CH), 1.24 (d, J = 1.9 Hz, 6H, (CH₃)₂CH), 1.23 (d, J = 1.9 Hz, 6H, (CH₃)₂CH), 0.23 (s, 9H, Si(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ 244.2, 152.6, 145.3, 142.0, 139.5, 133.9, 127.6, 121.5, 117.4, 77.5, 34.0, 26.5, 24.2, 23.8, -1.9; HRMS (EI) m/z calcd for C₁₉H₃₀O₂Si [M⁺] 318.2015, found 318.1998.

Methyl o-(2-methylallyloxy)benzoate (85). Prepared following a modified version of general procedure A where a mixture of methyl salicylate (3.8 mL, 29 mmol), K₂CO₃ (8.16 g, 59.0 mmol), KI (4.81 g, 29.0 mmol), 3-chloro-2-methylpropene (6.0 mL, 61 mmol) and acetone (120 mL) was heated to reflux for 18h. Combined organic layers were washed once with brine, dried over anhydrous Na₂SO₄ and filtered. Fractions that contained the pure product after purification by flash column chromatography were decolorized with activated carbon and then concentrated by rotary evaporation under reduced pressure, affording the title compound as a colorless oil in 83% yield (5.06 g, 24.5 mmol). ¹H and ¹³C NMR spectra were in agreement with published data. ⁶⁶

o-(2-Methylallyloxy)benzoic acid (86). Prepared by standard saponification of ester 85. The ester (2.51 g, 12.2 mmol) was dissolved in warm MeOH (48 mL) and 30% w/v aqueous KOH (30 mL) was added. The mixture was stirred at rt for 1h and then most of the solvent was removed by rotary evaporation under reduced pressure. Water (50 mL) was added, followed by 2M HCl until the solution became acidic. The product crashed out as a white solid and was recovered by vacuum filtration and washed with water. The solid was dried under vacuum at 50ºC overnight to give the pure title compound in 97% yield (2.27 g, 11.8 mmol). ¹H and ¹³C spectra were in agreement with published data.

o-(2-Methylallyloxy)benzoyl chloride (87). Following McKervey's procedure, 86 (1.12 g, 5.82 mmol) was dissolved in dry CH₂Cl₂ (13 mL) and the solution was cooled to 0ºC. Oxalyl chloride (0.59 mL, 7.0 mmol) was added slowly followed by 2 drops of dry DMF. The reaction mixture was stirred 7h at 0ºC under N₂(g) atmosphere and then concentrated by rotary evaporation under reduced pressure to afford the title compound as an orange liquid in 99% yield (1.21 g, 5.76 mmol). ¹H NMR (400 MHz, CDCl₃) δ 8.09 (dd, J = 8.0, 1.7 Hz, 1H, ArH), 7.55 (ddd, J = 8.5, 7.4, 1.8 Hz, 1H, ArH), 7.05 (ddd, J = 8.2, 7.4, 1.0 Hz, 1H, ArH), 6.98 (dd, J = 8.4, 0.6 Hz, 1H, ArH), 5.20-5.19 (m, 1H, C=CH(H)), 5.04-5.02 (m, 1H, 1H,

C=CH(H)), 4.53 (s, 2H, OCH₂), 1.86 (m, 3H, CH₃); ¹³C NMR (75 MHz, CDCl₃) δ 163.9, 158.8, 139.8, 136.2, 134.8, 122.8, 120.6, 113.4, 113.3, 72.5, 19.5.

**Lithium tetrakis(trimethylsilyl)aluminate.** Following Altnau’s procedure,⁴⁵ aluminum powder (20.1 g, 745 mmol), aluminum gritty (5.12 g, 190 mmol), mercury (1.5 mL, 100 mmol), TMSCl (120 mL, 950 mmol) and Et₂O (186 mL) were stirred 2h at rt under Ar(g). Small pieces of lithium wire (7 g, 1 mol) were then added and the mixture was heated to reflux for 4 days. The top green layer was transferred via canula to a Schlenk flask under Ar(g). The gray solid left was washed with Et₂O (2 x 60 mL). Et₂O used to wash the solid was transferred to the Schlenk flask. The solvent was removed under vacuum, giving a green solid that was washed four times with dry hexanes. The white solid obtained was dried under vacuum overnight and then sublimed under vacuum, affording Li[Al(SiMe₃)₄] in 2% yield (5.60 g, 17.1 mmol).

![Image of o-(2-Methylallyloxy)benzoyltrimethylsilane (63)](image_url)

**o-(2-Methylallyloxy)benzoyltrimethylsilane (63).** Following Kang’s procedure,⁴⁶ to a solution of CuCN (21 mg, 0.23 mmol) in dry THF (13 mL) cooled to -78ºC and kept under Ar(g) atmosphere was added dropwise a solution of Li[Al(SiMe₃)₄] (745 mg, 2.28 mmol) in dry Et₂O (16 mL). The solution was warmed to 0ºC and stirred 30 min. The dark red mixture was then cooled back to -78ºC and a solution of 87 (1.20 g, 5.71 mmol) in dry THF (5 mL) was added dropwise. The mixture was stirred 3h45 at a temperature kept between -70ºC and -75ºC. 1M H₂SO₄ (3 mL) was added and the mixture was stirred 1 h at 0ºC upon which it turned green. The organic layer was separated and the aqueous layer was extracted with Et₂O (3 x 20mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated under high vacuum. Purification by flash chromatography afforded the title compound as a yellow oil in 17% yield (243 mg, 0.98 mmol). IR (neat) 3073, 2972,
2954, 1608, 1587, 1478, 1446, 1298, 1280, 1246, 1217, 1193, 1161, 1108, 1049, 1006, 903, 841, 754, 700 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.40-7.35 (m, 1H, ArH), 7.32 (dd, \(J = 7.5, 1.9\) Hz, 1H, ArH), 6.98 (app t, \(J = 7.4\) Hz, 1H, ArH), 6.91 (d, \(J = 8.3\) Hz, 1H, ArH), 5.05 (app s, 1H, C=CH(H)), 5.02 (m, 1H, C=CH(H)), 4.56 (s, 2H, OCH\(_2\)), 1.80 (m, 3H, CCH\(_3\)), 0.23 (s, 9H, Si(CH\(_3\))\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 239.5, 158.1, 140.4, 134.1, 133.0, 127.1, 121.3, 113.8, 112.5, 72.2, 19.6, -2.06; HRMS (ESI) m/z calcd for C\(_{14}\)H\(_{21}\)O\(_2\)Si [M+H]\(^+\) 249.1311, found 249.1305.

![Structure of 88](image)

**Methyl o-cinnamylxybenzoate (88).** Prepared following a modified version of general procedure A where a mixture of methyl salicylate (2.4 mL, 19 mmol), K\(_2\)CO\(_3\) (5.15 g, 37.2 mmol), (E)-(3-bromoprop-1-enyl)benzene (5.51 g, 28.0 mmol), and acetone (80 mL) was heated to reflux for 21h. Combined organic layers were washed with brine, dried over anhydrous Na\(_2\)SO\(_4\) and then filtered. Major impurities were removed by flash column chromatography and the solid obtained was recrystallized in EtOH, affording the title product as a white solid in 91% yield (4.55 g, 16.9 mmol). \(^1\)H NMR (400 MHz, CDCl\(_3\))\(^{69}\) \(\delta\) 7.82 (dd, \(J = 7.7, 1.8\) Hz, 1H, ArH), 7.48-7.40 (m, 3H, ArH), 7.35-7.31 (m, 2H, ArH), 7.28-7.24 (m, 1H, ArH), 7.04-6.98 (m, 2H, ArH), 6.81 (app d, \(J = 16.0\) Hz, 1H, CH=CHPh), 6.43 (dt, \(J = 16.0, 5.4\) Hz, 1H, CH=CHPh), 4.81 (dd, \(J = 5.4, 1.6\) Hz, 2H, OCH\(_2\)), 3.92 (s, 3H, OCH\(_3\)); \(^{13}\)C NMR spectrum was in agreement with published data (see reference in footnote 69).

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\(^{69}\) This spectrum was in agreement with published data (Okada, Y.; Adachi, M.; Hayashi, T. *J. Oleo Sci.* **2002**, *51*, 359) but our spectrum gave more information about coupling patterns between protons.
o-Cinnamyloxybenzoic acid (89). Prepared by standard saponification of ester 88. The ester (2.10 g, 7.84 mmol) was dissolved in warm MeOH (48 mL) and 30% w/v aqueous KOH (30 mL) was added. The mixture was heated to reflux for 1h and then most of the solvent was removed by rotary evaporation under reduced pressure. Water (50 mL) was added, followed by 2M HCl until the solution became acidic. The product crashed out as a white solid that was recovered by vacuum filtration and washed with water. The solid was dried under vacuum at 50°C overnight to give the pure title compound in quantitative yield. ^1H and ^13C NMR spectra were in agreement with published data (see reference in footnote 69).

o-Cinnamyloxybenzoyl chloride (90). Following McKervey’s procedure, 89 (843 mg, 3.31 mmol) was dissolved in dry CH₂Cl₂ (7.5 mL) and the solution was cooled to 0°C. Oxaly chloride (0.34 mL, 4.0 mmol) was added slowly followed by 2 drops of dry DMF. The reaction mixture was stirred 4h30 at 0°C under N₂(g) atmosphere. The solution was then concentrated by rotary evaporation under reduced pressure and dried under high vacuum to afford the title compound in 76% yield (689 mg, 2.53 mmol).^70

^1H NMR (400 MHz, CDCl₃) δ 8.10 (dd, J = 7.9, 1.6 Hz, 1H, ArH), 7.60-7.54 (m, 1H, ArH), 7.44-7.24 (m, 5H, ArH), 7.09-6.99 (m, 2H, ArH), 6.84 (app d, J = 16.0 Hz, 1H, CH=CPh), 6.40 (dt, J = 16.1, 5.4 Hz, CH=CHPh), 4.83 (dd, J = 5.4, 1.5 Hz, 2H, OCH₂).

^70. ^1H NMR showed the presence of some impurities.
o-Cinnamylbenzoyltrimethylsilane (64). Following Kang's procedure, to a solution of CuCN (8 mg, 0.09 mmol) in dry THF (5 mL) cooled to -78ºC and kept under Ar(g) atmosphere was added dropwise a solution of Li[Al(SiMe$_3$)$_4$] (278 mg, 0.85 mmol) in dry Et$_2$O (6 mL). The dark red solution was stirred 35 min at 0ºC. The mixture was then cooled back to -78ºC and a solution of 90 (576 mg, 2.11 mmol) in THF (5 mL) was added dropwise. The mixture was stirred 2h30 at -75ºC, then 2h at -40ºC, 2h at -25ºC and finally 40 min at 0ºC. 1M H$_2$SO$_4$ (1 mL) was added and the mixture turned green. Water (15 mL) was added and the mixture was extracted with EtOAc (3 x 25 mL). The organic layers were combined, washed with brine, dried over anhydrous Na$_2$SO$_4$, filtered and concentrated by rotary evaporation under reduced pressure. Purification by flash chromatography afforded the title compound as a yellow oil in 55% yield (358 mg, 1.15 mmol). IR (neat) 3061, 3026, 2957, 2899, 2869, 1605, 1585, 1477, 1447, 1377, 1283, 1246, 1232, 1221, 1161, 1107, 997, 967, 841, 753, 692, 621 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45-7.28 (m, 7H, ArH), 7.03-6.98 (m, 2H, ArH), 6.72 (d, $J$ = 16.0 Hz, 1H, CH=CHPh), 6.43 (dt, $J$ = 15.9, 6.2 Hz, 1H, CH=CHPh), 4.83 (dd, $J$ = 6.1, 1.2 Hz, 2H, OCH$_2$), 0.25 (s, 9H, Si(CH$_3$)$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 235.4, 156.2, 134.9, 133.1, 132.7, 132.0, 127.8, 127.7, 127.3, 126.1, 125.7, 122.8, 120.3, 111.2, -0.1; HRMS (EI) m/z calcd for C$_{19}$H$_{21}$O$_2$Si [M-H]$^-$ 309.1311, found 309.1315.
Methyl 3-allyloxy-2-naphthoate (91). Prepared following general procedure B from methyl 3-hydroxy-2-naphthoate (5.50 g, 27.2 mmol), K$_2$CO$_3$ (7.52 g, 54.4 mmol), allyl bromide (4.8 mL, 55 mmol) and acetone (125 mL) for a total reaction time of 20h. Purification afforded a pale yellow oil in 80% yield (5.26 g, 21.7 mmol). $^1$H NMR spectrum was in agreement with published data.$^{71}$ $^{13}$C NMR (75 MHz, CDCl$_3$) δ 167.0, 154.8, 136.2, 133.1, 132.9, 128.9, 128.6, 127.8, 126.7, 124.9, 122.3, 117.6, 108.4, 69.5, 52.4.

3-Allyloxy-2-naphthoyltrimethylsilane (65). Prepared following general procedure C from magnesium powder (1.09 g, 41.5 mmol), iodine (188 mg, 0.74 mmol), TMSCl (20.0 mL, 158 mmol), NMP (60 mL) and a solution of 91 (5.00 g, 20.6 mmol) in NMP (10.0 mL). After a total reaction time of 12h30, the silyl ketal was hydrolysed for 2h40 with NH$_4$Cl(aq) (40 mL) and 2M HCl (40 mL). The aqueous layer was extracted with hexanes (4 x 80 mL). Purification afforded the title product as a yellow oil in 19% yield (1.09 g, 3.84 mmol). IR (neat) 3055, 3023, 2954, 2900, 1633, 1606, 1589, 1501, 1455, 1445, 1422, 1359, 1330, 1243, 1180, 1158, 1109, 1010, 997, 917, 842, 787, 748, 707, 628 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.83 (d, $J = 8.0$ Hz, 1H, ArH), 7.73 (s, 1H, ArH), 7.72 (d, $J = 8.2$ Hz, 1H, ArH), 7.48 (ddd, $J = 8.2, 6.9, 1.3$ Hz, 1H, ArH), 7.36 (ddd, $J = 8.1, 6.9, 1.2$ Hz, 1H, ArH), 7.16 (s, 1H, ArH), 6.15 (ddt, $J = 17.2, 10.4, 5.8$ Hz, 1H, CH=CH$_2$), 5.46 (dq, $J = 17.3, 1.4$ Hz, 1H, CH=CH(H)), 5.37 (dq, 71. Prajer-Janczewska, L.; Wroblewski, J. Pol. J. Chem. 1980, 54, 1431.
$J = 10.4, 1.2 \text{ Hz}, 1\text{H, CH}=\text{CH(H)}, 4.75 (dt, J = 5.9, 1.3 \text{ Hz}, 2\text{H, OCH}_2), 0.26 (s, 9\text{H, Si(CH}_3)_3); ^{13}\text{C NMR}$

(100 MHz, CDCl$_3$) $\delta$ 240.3, 154.9, 136.1, 136.0, 132.8, 129.6, 128.7, 128.1, 127.2, 126.7, 124.6, 119.4, 106.8, 69.6, -2.0; HRMS (EI) m/z calcd for C$_{17}$H$_{20}$O$_2$Si [M$^+$] 284.1233, found 284.1229.

Methyl 2-(but-2-ynyloxy)benzoate (92). Prepared following general procedure A from methyl salicylate (1.2 mL, 9.3 mmol), K$_2$CO$_3$ (2.57 g, 18.6 mmol), 1-bromo-2-butyne (0.98 mL, 11 mmol) and acetone (30 mL) for a total reaction time of 21h30. Purification afforded the title compound in 73% yield (1.40 g, 6.86 mmol). IR (neat) 3077, 2998, 2951, 2920, 2876, 2303, 2229, 1731, 1714, 1600, 1583, 1489, 1454, 1434, 1370, 1304, 1252, 1190, 1167, 1133, 1085, 1051, 999, 849, 829, 756, 705, 659 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (dd, $J = 7.8, 1.8 \text{ Hz}, 1\text{H, ArH}), 7.49 (m, 1\text{H, ArH}), 7.13 (dd, J = 8.5, 0.9 \text{ Hz}, 1\text{H, ArH}), 7.02 (td, J = 7.6, 1.0 \text{ Hz}, 1\text{H, ArH}), 4.75 (q, J = 2.3 \text{ Hz}, 2\text{H, OCH}_2), 3.89 (s, 3\text{H, CO}_2\text{CH}_3), 1.84 (t, J = 2.4 \text{ Hz}, 3\text{H, CCCH}_3); ^{13}\text{C NMR}$ (100 MHz, CDCl$_3$) $\delta$ 166.8, 157.6, 133.5, 131.9, 121.1, 121.1, 114.6, 84.5, 74.0, 57.7, 52.3, 3.9; HRMS (EI) m/z calcd for C$_{12}$H$_{12}$O$_3$ [M$^+$] 204.0786, found 204.0788.

o-(But-2-ynyloxy)benzoyltrimethylsilane (66). Prepared following general procedure C from magnesium powder (0.33 g, 13 mmol), iodine (69.4 mg, 0.27 mmol), TMSCl (6.7 mL, 53 mmol), NMP (30 mL) and a solution of 92 (1.36 g, 6.65 mmol) in NMP (6.0 mL). After a total reaction time of 19h, the silyl ketal was hydrolysed for 4h with NH$_4$Cl(aq) (13 mL) and 2M HCl (13 mL). The aqueous layer was
extracted four times with hexanes. Purification afforded the title product as a yellow liquid in 14% yield (235 mg, 0.95 mmol). IR (neat) 3073, 2955, 2921, 2899, 1733, 1689, 1608, 1587, 1479, 1448, 1369, 1285, 1247, 1218, 1193, 1161, 1107, 1048, 999, 842, 754, 699, 623 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.46-7.41 (m, 1H, ArH), 7.40-7.37 (dd, \(J = 7.6, 1.9\) Hz, 1H, ArH), 7.05-7.00 (m, 2H, ArH), 4.74 (q, \(J = 2.3\) Hz, 2H, OCH\(_2\)), 1.86 (t, \(J = 2.4\) Hz, 3H, CCH\(_3\)), 0.26 (s, 9H, Si(CH\(_3\))\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 234.7, 155.4, 132.5, 131.9, 126.0, 120.6, 111.4, 84.8, 73.6, 56.7, 5.5, -0.2; HRMS (EI\(^+\)) m/z calcd for C\(_{14}\)H\(_{19}\)O\(_2\)Si [M+H]\(^+\) 247.1154, found 247.1156.

![Benzoyltrimethylsilane (75)](image)

**Benzoyltrimethylsilane (75).** Prepared by Dr. Zengming Shen following Prakash's procedure\(^{27}\) from methyl benzoate.

![Allyloxybenzene (76)](image)

**Allyloxybenzene (76).** Prepared following a modified version of general procedure B where a mixture of phenol (3.50 g, 37.2 mmol), K\(_2\)CO\(_3\) (10.3 g, 74.4 mmol), allyl bromide (6.5 mL, 75 mmol) and acetone (110 mL) was heated to reflux for 5h. Purification afforded a colorless liquid in 81% yield (4.06 g, 30.3 mmol). \(^1\)H NMR spectrum was in agreement with published data.\(^{72}\)

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Methyl 2,2-dimethyl-3-phenylpropanoate (77). Following Wills' procedure, under an atmosphere of N₂(g), freshly distilled diisopropylamine (8.0 mL, 57 mmol) was dissolved in dry THF (120 mL) and the solution was cooled to -60°C. n-BuLi (2.5M in hexanes, 22.8 mL, 57 mmol) was then added dropwise. The mixture was stirred 10 min and methyl benzenepropanoate (6.0 mL, 38 mmol) was then added. After 10 min of stirring, methyl iodide (6.2 mL, 100 mmol) was added and the resulting mixture was stirred 20 min at -60°C. The mixture was poured into 1M HCl (110 mL) at rt. The organic layer was separated and the aqueous layer extracted with Et₂O (4 x 150 mL). Combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated by rotary evaporation under reduced pressure to afford a crude dark red liquid. This material was subjected to a second methylation reaction as previously described. This time, the deprotonation step lasted 30 min and the reaction with methyl iodide lasted 40 min. The mixture was poured in 1M HCl (150 mL) at rt and then another extraction with Et₂O was performed. The combined organic layers were decolorized with activated carbon, giving a yellow liquid that was dried over anhydrous Na₂SO₄, filtered and concentrated by rotary evaporation under reduced pressure. Purification by flash column chromatography followed by decolorization with activated carbon gave the title compound as a yellow liquid in 38% yield (2.82 g, 14.7 mmol). ¹H and ¹³C NMR spectra were in agreement with published data.⁷³

2,2-Dimethyl-3-phenylpropanoic acid (78). Prepared by standard saponification of ester 77. The ester (2.81 g, 14.6 mmol) was dissolved in MeOH (50 mL) and 30% w/v aqueous KOH (30 mL) was added. The mixture was heated to reflux for 10 h and then most of the solvent was removed by rotary evaporation under reduced pressure. Water (50 mL) was added, followed by 5 M HCl until the solution became acidic. The solution was extracted with EtOAc (4 x 50 mL). Combined organic layers were concentrated by rotary evaporation under reduced pressure. The crude material was purified by flash column chromatography to afford the pure title compound as a colorless oil in 47% yield (1.23 g, 6.90 mmol). $^1$H and $^{13}$C NMR spectra were in agreement with published data.74

2,2-Dimethyl-3-phenylpropanoyl chloride (79). Following McKervey’s procedure,68 78 (1.22 g, 6.86 mmol) was dissolved in dry CH$_2$Cl$_2$ (15 mL) and the solution was cooled to 0°C. Oxalyl chloride (0.70 mL, 8.3 mmol) was added slowly followed by 2 drops of dry DMF. The reaction mixture was stirred 4 h at 0°C under N$_2$(g) atmosphere. The solution was then concentrated by rotary evaporation under reduced pressure and dried under high vacuum to afford the title compound in quantitative yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.31-7.24 (m, 3H, ArH), 7.19-7.18 (m, 1H, ArH), 7.18-7.17 (m, 1H, ArH), 2.99 (s, 2H, CH$_2$), 1.30 (s, 6H, C(CH$_3$)$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 179.9, 136.4, 130.4, 128.5, 127.3, 54.1, 45.8, 25.3.

2,2-Dimethyl-3-phenylpropanoyltrimethylsilane (80). Following Kang's procedure,\(^\text{46}\) to a solution of CuCN (15 mg, 0.17 mmol) in dry THF (14 mL) cooled to -75ºC and kept under Ar(g) atmosphere was added dropwise a solution of Li[Al(SiMe\(_3\))\(_4\)] (562 mg, 1.72 mmol) in dry Et\(_2\)O (13 mL). The solution was warmed to 0ºC and stirred until it became dark red. The mixture was then cooled back to -75ºC and 79 (845 mg, 4.29 mmol) diluted with a minimum of dry Et\(_2\)O was added dropwise. The mixture was stirred 11h at -75ºC, then 2h at -20ºC and finally 1h40 at 0ºC. 1M H\(_2\)SO\(_4\) (2 mL) was added and the mixture was stirred 30 min at 0ºC. Water (25 mL) was added and the mixture was extracted with EtOAc (3 x 25 mL). The organic layers were combined, washed with brine, dried over anhydrous Na\(_2\)SO\(_4\), filtered and concentrated by rotary evaporation under reduced pressure, affording a yellow oil. Purification by flash chromatography (0 → 2% EtOAc in hexanes) afforded the title compound as a pale yellow oil in 62% yield (629 mg, 2.68 mmol). IR (neat) 3084, 3063, 3028, 2964, 1631, 1604, 1495, 1466, 1453, 1361, 1249, 842, 739, 702, 660 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.27-7.17 (m, 3H, ArH), 7.07-7.04 (m, 2H, ArH), 2.76 (s, 2H, CH\(_2\)), 1.06 (s, 6H, C(CH\(_3\))\(_2\)), 0.23 (s, 9H, Si(CH\(_3\))\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 246.4, 136.8, 129.5, 127.0, 125.3, 53.7, 44.3, 23.9, 1.2; HRMS (EI) m/z calcd for C\(_{14}\)H\(_{22}\)OSi [M]+ 234.1440, found 234.1435.

Pivaloyltrimethylsilane (81). Following Kang's procedure,\(^\text{46}\) to a solution of CuCN (11 mg, 0.13 mmol) in dry THF (10 mL) cooled to -78ºC and kept under Ar(g) atmosphere was added dropwise a solution of Li[Al(SiMe\(_3\))\(_4\)] (415 mg, 1.27 mmol) in dry Et\(_2\)O (8.6 mL). The clear yellow solution was warmed to 0ºC
and stirred 30 min at 0°C. The dark red mixture was then cooled back to -78°C and a solution of pivaloyl chloride (0.39 mL, 3.2 mmol) was added dropwise. The mixture was stirred overnight at -78°C and then warmed up to 0°C. 1M H₂SO₄ (20 mL) was added and the mixture was extracted with Et₂O (3 x 20 mL). The organic layers were combined, dried over anhydrous Na₂SO₄, filtered and concentrated by rotary evaporation under reduced pressure. Purification by flash chromatography (100% hexanes) afforded the title compound as a colorless liquid in 6% yield (32 mg, 0.20 mmol). ¹H NMR spectrum was in agreement with published data.²⁶ ¹³C NMR (100 MHz, CDCl₃) δ 245.9, 49.8, 26.1, 1.2.

3.3 Microwave-Assisted Thermolysis of Aroylsilanes

3.3.1 Experimental Procedures

**General procedure E: Microwave-assisted thermolysis of aroylsilanes in DMSO.** A solution of aroylsilane (0.10 mmol) in dry DMSO (2.0 mL) was heated to 250°C under microwave irradiation in a sealed vial for 10 min. Water (5 mL) was added to the mixture which was then extracted with Et₂O (3 x 5 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated by rotary evaporation under reduced pressure. Flash column chromatography afforded the different products. Each reaction was run twice, once to get isolated yields and once to get NMR yields. 1,3,5-trimethoxybenzene was used as internal standard to get NMR yields and was added to the crude mixture just before the NMR spectrum was taken.

**General procedure F: Microwave-assisted thermolysis of aroylsilanes in o-dichlorobenzene.** A solution of aroylsilane (0.10 mmol) in dry o-dichlorobenzene (2.0 mL) was heated to 250°C under microwave irradiation in a sealed vial for 10 min. The reaction mixture was then passed trough a column of silica gel to get rid of the solvent (100% pentanes until all the o-dichlorobenzene came off, then 100%

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²⁵ This low yield can be accounted for by the several aliquots taken to monitor the reaction.
Et₂O). The fractions containing the products were combined and concentrated by rotary evaporation under reduced pressure to a volume of about 1 mL. 2.5M NaOH (1.0 mL) was then added and the mixture were vigorously stirred 1h at rt. 5M HCl was then added until the mixture became acidic. The organic layer was separated and the aqueous layer was extracted with Et₂O (3 x 1 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated by rotary evaporation under reduced pressure. Flash column chromatography afforded the different products. Each reaction was run twice, once to get isolated yields and once to get NMR yields. 1,3,5-trimethoxybenzene was used as internal standard to get NMR yields and was added to the crude mixture just before the NMR spectrum was taken.

**Attempted intermolecular reaction between benzoyltrimethylsilane (75) and allyloxybenzene (76):**
A solution of 75 (22 mg, 0.12 mmol) and 76 (466 mg, 3.48 mmol) in dry DMSO (1.0 mL) was heated to 250°C under microwave irradiation in a sealed vial for 10 min. Water (20 mL) was added to the mixture which was then extracted with Et₂O (3 x 10 mL) in the presence of brine (5 mL) to prevent emulsion to form. The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated by rotary evaporation under reduced pressure. The crude mixture was then purified by flash column chromatography on silica gel.

**Attempted reproduction of Brook’s intramolecular C–H bond insertion reaction** under our conditions. 81 (8 mg, 0.05 mmol) was dissolved in DMSO-d₆ (0.85 mL) and heated to 250°C under microwave irradiation for 1h. The reaction mixture was directly analyzed by 'H NMR.
3.3.2 Characterization Data

**2-Methylchroman-4-one (33c).** IR (neat) 2956, 2921, 2852, 1693, 1607, 1578, 1463, 1385, 1307, 1229, 1152, 1122, 1071, 1036, 948, 877, 828, 763 cm\(^{-1}\); \(^1\)H and \(^{13}\)C NMR spectra were in agreement with published data.\(^{77}\) HRMS (EI) m/z calcd for C\(_{10}\)H\(_{10}\)O\(_2\) [M\(^+\)] 162.0681, found 162.0678.

**3-Allyl-2-hydroxybenzaldehyde (33d).** This product was obtained\(^{79}\) from a thermolysis reaction not included in our discussion in 14% yield (4.8 mg, 0.030 mmol) following a modified version of general procedure F from 33 (51 mg, 0.22 mmol) and o-dichlorobenzene (2.0 mL). No basic work-up was performed. IR (neat) 3065, 2922, 1718, 1654, 1647, 1635, 1458, 1266, 751 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 11.30 (s, 1H, OH), 9.89 (s, 1H, CHO), 7.46-7.40 (m, 2H, ArH), 6.97 (t, \(J = 7.6\) Hz, 1H, ArH), 6.07-5.93 (m, 1H, CH=CH\(_2\)), 5.14-5.11 (m, 1H, CH=CH(H)), 5.08-5.06 (m, 1H, CH=CH(H)), 3.44 (d, \(J = 6.6\) Hz, 2H, CH\(_2\)CH=CH\(_2\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 196.9, 159.8, 137.4, 136.0, 132.1, 129.0, 120.5, 119.8, 116.5, 33.3; HRMS (EI) m/z calcd for C\(_{10}\)H\(_{10}\)O\(_2\) [M\(^+\)] 162.0681, found 162.0682.


\(^{78}\) This known compound was fully characterized because the reported \(^{13}\)C NMR data (\(\delta\) 196.6, 137.5, 136.0, 131.2, 119.8, 116.5, 33.0) did not matched the molecular structure (Ramin, M.; Jutz, F.; Grunwaldt, J.-D.; Baiker, A. *J. Mol. Catal. A: Chem.* 2005, 242, 32).

\(^{79}\) The characterization data of this compound was used to analyze the NMR spectra from the thermolysis reactions of 33.
**o-Hydroxycrotonophenone (44).** This product was obtained from a thermolysis reaction not included in our discussion. A solution of 33 (51 mg, 0.22 mmol) in dry o-dichlorobenzene (2.0 mL) was heated to 250°C under microwave irradiation in a sealed vial for 20 min. The reaction mixture was then purified by flash column chromatography, giving among other products 44 in 7% yield (2.5 mg, 0.015 mmol). IR (neat) 3020, 2915, 2871, 1724, 1652, 1681, 1588, 1443, 1344, 1307, 1271, 1236, 1207, 1158, 1033, 961, 923, 838, 803, 753, 663 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 12.71 (s, 1H, OH), 7.81 (dd, J = 8.0, 1.8 Hz, 1H, ArH), 7.47 (ddd, J = 8.4, 7.1, 1.4 Hz, 1H, ArH), 7.22 (dq, J = 15.1, 6.8 Hz, 1H, CH=CHCH₃), 7.00 (dd, J = 8.4, 1.0 Hz, 1H, ArH), 6.91 (dd, J = 8.0, 7.2, 1.2 Hz, 1H, ArH), 2.04 (dd, J = 6.7, 1.5 Hz, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 194.3, 163.8, 146.1, 136.4, 130.0, 125.7, 119.7, 119.0, 118.7, 19.0; HRMS (EI) m/z calcd for C₁₀H₁₀O₂ [M]⁺ 162.0681, found 162.0683.

**2-(But-3-enyloxy)benzaldehyde (46b).** ¹H and ¹³C NMR spectra were in agreement with published data.⁸⁰

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2,8-Dimethylchroman-4-one (50a). Obtained as a colorless liquid. IR (neat) 2977, 2916, 2875, 1694, 1599, 1478, 1464, 1429, 1385, 1346, 1302, 1258, 1222, 1143, 1123, 1076, 1029, 948, 869, 784, 744, 701 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.73 (app dd, \(J = 8.0, 1.2\) Hz, 1H, ArH), 7.34-7.32 (m, 1H, ArH), 6.90 (t, \(J = 7.5\) Hz, 1H, ArH), 4.64-4.53 (m, 1H, OCH), 2.68 (s, 1H, (C=O)CH(H)), 2.66 (d, \(J = 1.6\) Hz, 1H, (C=O)CH(H)), 2.24 (s, 3H, ArCH\(_3\)), 1.54 (d, \(J = 6.3\) Hz, 3H, OCH\(_2\)CH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 193.2, 160.2, 137.0, 127.3, 124.7, 120.73, 120.68, 74.3, 44.7, 21.2, 15.9; HRMS (ESI) m/z calcd for C\(_{11}\)H\(_{13}\)O\(_2\) [M+H]\(^+\) 177.0910, found 177.0901.

2,6,8-Trimethylchroman-4-one (54a). Obtained as a white solid. IR (neat) 2973, 2950, 2922, 2880, 1692, 1614, 1476, 1381, 1352, 1295, 1261, 1221, 1210, 1173, 1142, 1102, 1035, 948, 875, 791, 741, 615 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.52 (s, 1H, ArH), 7.16 (s, 1H, ArH), 4.59-4.49 (m, 1H, OCH), 2.65 (s, 1H, (C=O)CH(H)), 2.63 (d, \(J = 1.0\) Hz, 1H, (C=O)CH(H)), 2.26 (s, 3H, ArCH\(_3\)), 2.26 (s, 3H, ArCH\(_3\)), 1.52 (d, \(J = 6.3\) Hz, 3H, OCH\(_2\)CH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 190.8, 156.5, 136.8, 128.8, 125.9, 123.2, 119.4, 74.3, 45.5, 22.5, 21.9, 17.2; HRMS (ESI) m/z calcd for C\(_{12}\)H\(_{15}\)O\(_2\) [M+H]\(^+\) 191.1066, found 191.1065.
5,7-Dimethyl-2-vinylbenzofuran (54b). IR (neat) 2952, 2922, 2870, 2852, 1468, 1204, 1132, 1023, 979, 941, 907, 846, 749 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.13 (s, 1H, ArH), 6.89 (s, 1H, ArH), 6.64 (dd, \(J = 17.5, 11.2\) Hz, 1H, CH=CH\(_2\)), 6.51 (s, 1H, OC=CH), 5.94 (dd, \(J = 17.4, 0.9\) Hz, 1H, CH=CH(H)), 5.35 (dd, \(J = 11.2, 1.2\) Hz, 1H, CH=CH(H)) 2.49 (s, 3H, CH\(_3\)), 2.38 (s, 3H, CH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 153.1, 150.7, 131.1, 127.4, 126.1, 124.7, 119.9, 117.5, 114.4, 104.4, 22.7, 16.6; HRMS (EI) m/z calcd for C\(_{12}\)H\(_{12}\)O [M]+ 172.0888, found 172.0889.

2-Allyl-4,6-dimethylphenol (54c). IR (neat) 3521, 2953, 2919, 2873, 2851, 1672, 1636, 1484, 1442, 1294, 1248, 1201, 1147, 1017, 996, 912, 855 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.84 (s, 1H, ArH), 6.77 (s, 1H, ArH), 6.01 (ddt, \(J = 16.5, 10.1, 6.4\) Hz, 1H, CH=CH\(_2\)), 5.21-5.14 (m, 2H, CH=CH\(_2\)), 4.76 (s, 1H, OH), 3.37 (app d, \(J = 6.4\) Hz, 2H, CH\(_2\)CH=CH\(_2\)), 2.23 (s, 3H, ArCH\(_3\)), 2.21 (s, 3H, ArCH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 148.8, 135.5, 128.9, 128.6, 127.5, 123.5, 123.1, 115.8, 36.8, 21.9, 17.4; HRMS (EI) m/z calcd for C\(_{11}\)H\(_{14}\)O [M]+ 162.1045, found 162.1043.
6,8-Diisopropyl-2-methylchroman-4-one (55a). Obtained as a colorless oil. IR (neat) 2960, 2930, 2870, 1692, 1586, 1472, 1384, 1363, 1347, 1306, 1268, 1218, 1187, 1166, 1145, 1033, 951, 889, 879, 757 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.60 (d, \(J = 2.3\) Hz, 1H, ArH), 7.27 (d overlapping with chloroform residual peak, 1H, ArH), 4.54 (m, 1H, OCH), 3.29 (septet, \(J = 6.9\) Hz, 1H, CH(CH\(_3\))\(_2\)), 2.86 (septet, \(J = 6.9\) Hz, 1H, CH(CH\(_3\))\(_2\)), 2.66 (s, 1H, (C=O)CH(H)), 2.64 (d, \(J = 2.8\) Hz, 1H, (C=O)CH(H)), 1.52 (d, \(J = 6.3\) Hz, 3H, OCHCH\(_3\)), 1.25 (d, \(J = 0.9\) Hz, 3H, CH(CH\(_3\))(CH\(_3\))), 1.24 (s, 3H, CH(CH\(_3\))(CH\(_3\))), 1.23 (d, \(J = 0.9\) Hz, 3H, CH(CH\(_3\))(CH\(_3\))), 1.22 (s, 3H, CH(CH\(_3\))(CH\(_3\))); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 191.0, 155.9, 139.9, 136.1, 130.4, 120.3, 119.6, 74.3, 45.6, 34.7, 28.5, 25.41, 25.39, 24.0, 23.9, 22.5; HRMS (EI) m/z calcd for C\(_{16}\)H\(_{22}\)O\(_2\) [M]+ 246.1620, found 246.1616.

5,7-Diisopropyl-2-vinylbenzofuran (55b). Obtained as a colorless liquid. IR (neat) 2959, 2926, 2870, 1639, 1604, 1551, 1471, 1460, 1425, 1382, 1362, 1203, 1179, 1023, 978, 943, 906, 864, 799, 762, 651 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.19 (d, \(J = 1.7\) Hz, 1H, ArH), 6.98 (d, \(J = 1.7\) Hz, 1H, ArH), 6.63 (dd, \(J = 17.4, 11.2\) Hz, 1H, CH=CH\(_2\)), 6.53 (s, 1H, OC=CH), 5.93 (dd, \(J = 17.4, 1.1\) Hz, 1H, CH=CH(H)), 5.33 (dd, \(J = 11.2, 1.3\) Hz, 1H, CH=CH(CH)), 3.40 (septet, \(J = 6.9\) Hz, 1H, CH(CH\(_3\))\(_2\)), 2.97 (septet, \(J = 6.9\) Hz, 1H, CH(CH\(_3\))\(_2\)), 1.40 (d, \(J = 6.9\) Hz, 6H, CH(CH\(_3\))\(_2\)), 1.28 (d, \(J = 6.9\) Hz, 6H, CH(CH\(_3\))\(_2\));
$^{13}$C NMR (100 MHz, CDCl$_3$) δ 153.0, 149.8, 142.4, 130.6, 127.7, 124.7, 120.2, 114.7, 114.2, 104.5, 35.4, 30.5, 26.0, 24.1; HRMS (EI) m/z calcd for C$_{16}$H$_{20}$O [M]$^+$ 228.1514, found 228.1509.

![Structure of 55c](image)

2-Allyl-4,6-diisopropylphenol (55c). IR (neat) 3553, 3528, 2959, 2925, 2869, 1636, 1475, 1382, 1362, 1259, 1199, 1174, 998, 917, 877, 763, 754 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 6.96 (d, $J = 2.2$ Hz, 1H, ArH), 6.81 (d, $J = 2.2$ Hz, 1H, ArH), 6.04 (ddt, $J = 16.6$, 10.0, 6.5 Hz, 1H, CH=CH$_2$), 5.26-5.17 (m, 2H, CH=CH$_2$), 4.90 (s, 1H, OH), 3.41 (dt, $J = 6.4$ Hz, 1.4 Hz, 2H, CH$_2$C=CH$_2$), 3.22 (septet, $J = 6.9$ Hz, 1H, CH(CH$_3$)$_2$), 2.83 (septet, $J = 6.9$ Hz, 1H, CH(CH$_3$)$_2$), 1.25 (d, $J = 6.8$ Hz, 6H, CH(CH$_3$)$_2$), 1.23 (d, $J = 7.0$ Hz, 6H, CH(CH$_3$)$_2$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.9, 141.1, 137.0, 134.9, 125.6, 124.4, 123.0, 116.9, 36.5, 33.8, 27.4, 24.5, 22.9; HRMS (EI) m/z calcd for C$_{15}$H$_{22}$O [M]$^+$ 218.1671, found 218.1666.

![Structure of 55d](image)

(2-(Allyloxy)-3,5-diisopropylphenyl)trimethylsilane (55d). IR (neat) 2959, 2926, 2870, 1638, 1470, 1362, 1317, 1284, 1253, 1220, 1178, 1131, 995, 914, 843, 772, 752, 692, 644 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 6.91 (d, $J = 2.4$ Hz, 1H, ArH), 6.80 (d, $J = 2.2$ Hz, 1H, ArH), 5.97 (ddt, $J = 16.8$, 10.4, 6.5 Hz, 1H, CH=CH$_2$), 5.08 (app sextet, $J = 1.8$ Hz, 1H, CH=CH(H)), 5.04 (dq, $J = 10.3$, 1.7 Hz, 1H, CH=CH(H)),
3.32 (app d, \( J = 6.4 \) Hz, 2H, \( \text{CH}_2\text{CH}=\text{CH}_2 \)), 3.20 (septet, \( J = 6.9 \) Hz, 1H, \( \text{CH}_3\text{CH}_2\text{CH} \)), 2.81 (septet, \( J = 7.0 \) Hz, 1H, \( \text{CH}_3\text{CH}_2\text{CH} \)), 1.21 (d, \( J = 7.1 \) Hz, 6H, \( \text{CH}_3\text{CH}_2\text{CH} \)), 1.18 (d, \( J = 7.0 \) Hz, 6H, \( \text{CH}_3\text{CH}_2\text{CH} \)), 0.25 (s, 9H, Si(\( \text{CH}_3 \))3); 13C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 147.0, 140.4, 137.4, 136.2, 128.7, 124.1, 121.1, 114.9, 36.4, 34.8, 28.2, 25.6, 24.9, 2.8; HRMS (EI) m/z calcd for C\(_{18}\)H\(_{30}\)OSi [M]+ 290.2066, found 290.2035.

![63a](image)

**2,2-Dimethylchroman-4-one (63a).** Obtained as a white solid. IR (neat) 2976, 2934, 2874, 1691, 1604, 1575, 1455, 1370, 1328, 1306, 1256, 1229, 1203, 1167, 1147, 1120, 1057, 1025, 954, 929, 8.96, 872, 837, 807, 775, 766, 727, 651 cm\(^{-1}\); \(^1\)H and \(^{13}\)C NMR spectra were in agreement with published data;\(^{81}\) HRMS (ESI) m/z calcd for C\(_{11}\)H\(_{13}\)O\(_2\) [M+H]+ 177.0910, found 177.0902.

![63b](image)

(1a-Methyl-1,1a,2,7b-tetrahydrocyclopropa[c]chromen-7b-yloxy)trimethylsilane (63b).\(^{82}\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.42 (dd, \( J = 7.6 \), 1.7 Hz, 1H, ArH), 7.09 (ddd, \( J = 7.8 \), 7.4, 1.7 Hz, 1H, ArH), 6.99 (td, \( J = 7.5 \), 1.3 Hz, 1H, ArH), 6.81 (dd, \( J = 7.9 \), 1.3 Hz, 1H, ArH), 4.06 (d, \( J = 10.3 \) Hz, 1H, OCH(H)), 3.60 (d, \( J = 10.2 \) Hz, 1H, OCH(H)), 1.39 (d, \( J = 5.6 \) Hz, 1H, OCCH(H)), 1.30 (s, 9H, Si(\( \text{CH}_3 \))3), 1.04 (d, \( J = 5.6 \) Hz, 1H, OCCH(H)). LRMS (EI) m/z calcd for C\(_{14}\)H\(_{20}\)O\(_2\)Si [M]+ 248.1, found 248.1.

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82. Based on the analysis of a mixture of 63b, 63c and 63d. There was not enough material to further characterize these compounds.
cis-(2-(Prop-1-en-2-yl)-2,3-dihydrobenzofuran-3-yloxy)trimethylsilane (63c).\(^{82}\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) aromatic signals are hidden behind those of compound 63d, 5.20 (d, \(J = 4.1\) Hz, 1H, Me\(_3\)SiOCH), signal hidden by the signal at 5.14 ppm from compound 63d (should be t, 1H, C=CH(H)), 4.94 (t, \(J = 1.5\) Hz, 1H, C=CH(H)), 4.84 (d, \(J = 4.0\) Hz, 1H, CH\(_2\)=CCH), 1.72 (t, \(J = 1.1\) Hz, 3H, CH\(_2\)=CCH\(_3\)), 0.19 (s, 9H, Si(CH\(_3\))\(_3\)). LRMS (EI) m/z calcd for C\(_{14}\)H\(_{20}\)O\(_2\)Si [M]+ 248.1, found 248.1.

\begin{center}
\includegraphics[width=2cm]{63c}
\end{center}

trans-(2-(Prop-1-en-2-yl)-2,3-dihydrobenzofuran-3-yloxy)trimethylsilane (63d).\(^{82}\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.29-7.22 (m, 2H, ArH), 6.94-6.87 (m, 2H, ArH), 5.29 (d, \(J = 6.5\) Hz, 1H, Me\(_3\)SiOCH), 5.14 (t, \(J = 0.8\) Hz, 1H, C=CH(H)), 5.08 (t, \(J = 0.8\) Hz, 1H, C=CH(H)), 4.86 (d, \(J = 6.3\) Hz, 1H, CH\(_2\)=CCH), 1.85 (s, 3H, CH\(_2\)=CCH\(_3\)), 0.12 (s, 9H, Si(CH\(_3\))\(_3\)). LRMS (EI) m/z calcd for C\(_{14}\)H\(_{20}\)O\(_2\)Si [M]+ 248.1, found 248.1.

\begin{center}
\includegraphics[width=2cm]{63d}
\end{center}

2-Hydroxy-3-(2-methylallyl)benzaldehyde (63f). IR (neat) 2955, 2923, 2852, 1737, 1693, 1659, 1651, 1615, 1478, 1446, 1387, 1325, 1278, 1218, 1166, 990, 892, 850, 756, 689, 649 cm\(^{-1}\); \(^1\)H NMR (400 MHz,
CDCl$_3$ $\delta$ 11.29 (s, 1H, CHO), 9.89 (s, 1H, OH), 7.44 (dd, $J$ = 7.7 Hz, 1H, ArH), 7.41 (dm, $J$ = 7.4 Hz, 1H, ArH), 6.98 (t, $J$ = 7.5 Hz, 1H, ArH), 4.85-4.83 (m, 1H, C=CH(H)), 4.70-4.67 (m, 1H, C=CH(H)), 3.39 (s, 2H, ArCH$_2$), 1.75 (s, 3H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 194.2, 158.2, 142.6, 136.5, 131.0, 127.5, 119.6, 118.7, 111.4, 37.7, 23.8; HRMS (EI) m/z calcd for C$_{11}$H$_{12}$O$_2$ [M]$^+$ 176.0837, found 176.0844.

3,3-Dimethylchroman-4-one (63g). $^1$H NMR spectrum was in agreement with published data.$^{84}$

$cis$-2-Methyl-3-phenylchroman-4-one (64a). Obtained as a colorless liquid. IR (neat) 2927, 1685, 1607, 1577, 1472, 1461, 1383, 1355, 1304, 1262, 1224, 1151, 1121, 1025, 955, 762, 700 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95 (dd, $J = 8.2$, 1.7 Hz, 1H, ArH), 7.55 (ddd, $J = 8.4$, 7.2, 1.8 Hz, 1H, ArH), 7.34-7.18 (m, 5H, ArH), 7.09-7.05 (m, 2H, ArH), 4.86 (dq, $J = 6.5$, 3.5 Hz, 1H, OCHCH$_3$), 3.66 (d, $J = 3.5$ Hz, 1H, (C=O)CH), 1.33 (d, $J = 6.6$ Hz, 3H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 192.7, 161.7, 136.5, 134.0, 129.6, 129.0, 128.2, 127.9, 122.0, 120.6, 118.2, 77.0, 57.6, 17.9; HRMS (EI) m/z calcd for C$_{16}$H$_{14}$O$_2$ [M]$^+$ 238.0994, found 238.1002.

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83. NMR spectrum showed some impurities.
trans-2-Methyl-3-phenylchroman-4-one (64b). Obtained as a colorless liquid. IR (neat) 1691, 1608, 1580, 1473, 1463, 1382, 1321, 1223, 1150, 1083, 1063, 954, 763, 748, 700, 650, 622 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.94 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.51 (ddd, J = 8.3, 7.2, 1.8 Hz, 1H, ArH), 7.39-7.29 (m, 3H, ArH), 7.18-7.15 (m, 2H, ArH), 4.75 (dq, J = 11.4, 6.3 Hz, 1H, OCH₂CH₃), 3.72 (d, J = 11.1 Hz, 1H, (C=O)CH), 1.34 (d, J = 6.4 Hz, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 193.2, 161.4, 136.2, 135.8, 129.5, 129.1, 127.9, 127.8, 121.6, 121.1, 118.1, 78.8, 59.9, 20.3; HRMS (EI) m/z calcd for C₁₆H₁₄O₂ [M]+ 238.0994, found 238.0989.

(1-Phenyl-1,1a,2,7b-tetrahydrocyclopropa[c]chromen-7b-yloxy)trimethylsilane (64c). IR (neat) 3062, 3033, 2957, 2920, 2864, 1604, 1580, 1499, 1485, 1453, 1335, 1250, 1213, 1199, 1097, 1014, 920, 872, 841, 758, 748, 734, 696 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.54 (dd, J = 7.6, 1.7 Hz, 1H, ArH), 7.32-7.28 (m, 2H, ArH), 7.23-7.20 (m, 3H, ArH), 7.14 (ddd, J = 8.0, 7.5, 1.8 Hz, 1H, ArH), 6.99 (td, J = 7.5, 1.3 Hz, 1H, ArH), 6.87 (dd, J = 8.0, 1.2 Hz, 1H, ArH), 4.39 (dd, J = 10.5, 1.4 Hz, 1H, OCH(H)), 4.05 (dq, J = 10.5, 0.8 Hz, 1H, OCH(H)), 2.47 (d, J = 6.4 Hz, 1H, PhCH), 2.25 (dt, J = 6.2, 1.6 Hz, 1H, OCH₂CH), 0.12 (s, 9H, Si(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ 149.5, 135.0, 128.7, 127.7, 126.9, 126.1, 125.2, 124.5, 120.6, 116.3, 62.0, 58.5, 34.2, 32.9, 3.2; HRMS (EI) m/z calcd for C₁₉H₂₃O₂Si [M]+ 310.1389, found 310.1374.
trans-(E)-(2-Styryl-2,3-dihydrobenzofuran-3-yloxy)trimethylsilane (64d).\textsuperscript{46,85,86} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.46-7.28 (m, 7H, ArH), 6.95 (m, 1H, ArH), 6.89 (d, J = 8.1 Hz, 1H, ArH), 6.79 (d, J = 15.8 Hz, 1H, CH=CHPh), 6.51 (dd, J = 16.0, 8.3 Hz, 1H, CH=CHPh), 5.27 (d, J = 6.0 Hz, 1H, CHOSiMe\textsubscript{3}), 5.0 (ddd, J = 8.3, 6.0, 0.8 Hz, 1H, OCHC=CHPh), 0.13 (s, 9H, Si(CH\textsubscript{3})\textsubscript{3}). LRMS (EI) m/z calcd for C\textsubscript{19}H\textsubscript{22}O\textsubscript{2}Si [M]\textsuperscript{+} 310.1, found 310.1.

(E)-2-Styrylbenzofuran (64e). Obtained as a white solid. \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were in agreement with published data.\textsuperscript{87} HRMS (EI) m/z calcd for C\textsubscript{16}H\textsubscript{12}O [M]\textsuperscript{+} 220.0888, found 220.0888.

(2-Methyl-3-phenyl-2H-chromen-4-yloxy)trimethylsilane (64g).\textsuperscript{88} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.47-7.44 (m, 2H, ArH), 7.38-7.30 (m, 3H, ArH), 7.25-7.17 (m, 3H, ArH), 6.94 (td, J = 7.5, 1.1 Hz, 1H, ArH).

\textsuperscript{85} Trace amount of cis-(E) diastereoisomer was also detected.
\textsuperscript{86} Based on the analysis of an impure \textsuperscript{1}H NMR spectrum. There was not enough material to obtain \textsuperscript{13}C NMR and IR data.
\textsuperscript{88} Based on the analysis of a mixture with 64c.
ArH), 5.34 (q, \( J = 6.4 \) Hz, 1H, OCH), 1.30 (d, \( J = 6.5 \) Hz, 3H, OCHCH\(_3\)), -0.12 (s, 9H, Si(CH\(_3\))\(_3\)). LRMS (EI) m/z calcd for C\(_{19}\)H\(_{22}\)O\(_2\)Si [M]+ 310.1, found 310.1.

![Image 65a](image)

2-Methylbenzo[g]chroman-4-one (65a). IR (neat) 2974, 2932, 2871, 1694, 1629, 1601, 1500, 1455, 1388, 1351, 1329, 1242, 1214, 1190, 1131, 1026, 875, 749, 666 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.50 (s, 1H, ArH), 7.88 (dd, \( J = 8.4, 0.4 \) Hz, 1H, ArH), 7.71 (dd, \( J = 8.3, 0.4 \) Hz, 1H, ArH), 7.51 (ddd, \( J = 8.2, 6.8, 1.2 \) Hz, 1H, ArH), 7.36 (ddd, \( J = 8.2, 6.9, 1.2 \) Hz, 1H, ArH), 7.34 (s, 1H, ArH), 4.69-4.61 (m, 1H, OCH), 2.81 (s, 1H, (C=O)CH(H)), 2.79 (d, \( J = 4.5 \) Hz, 1H, (C=O)CH(H)), 1.56 (d, \( J = 6.3 \) Hz, 3H, CH\(_3\)); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 190.8, 155.2, 136.8, 129.0, 128.2, 128.1, 127.4, 125.8, 123.8, 120.8, 112.1, 74.2, 46.4, 22.7; HRMS (EI) m/z calcd for C\(_{14}\)H\(_{12}\)O\(_2\) [M]+ 212.0837, found 212.0841.

![Image 65b](image)

2-Vinylnaptho[2,3-b]furan (65b). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.97 (s, 1H, ArH), 7.92-7.90 (m, 2H, ArH), 7.83 (s, 1H, ArH), 7.45-7.38 (m, 2H, ArH), 6.71 (s, 1H, OC=CH), 6.70 (dd, \( J = 17.4, 11.1 \) Hz, 1H, CH=CH\(_2\)), 6.07 (dm, \( J = 16.7 \) Hz, 1H, CH=CH(H)), 5.48 (dd, \( J = 11.4, 1.0 \) Hz, 1H, CH=CH(H)); HRMS (EI) m/z calcd for C\(_{14}\)H\(_{10}\)O [M]+ 194.0732, found 194.0737.
4-Alllyl-3-hydroxy-2-naphthaldehyde (65c). Obtained as a yellow liquid. IR (neat) 3217, 3074, 2978, 2920, 2947, 1651, 1560, 1512, 1505, 1445, 1392, 1356, 1321, 1285, 1213, 1180, 1027, 993, 952, 912, 889, 850, 828, 787, 763, 750, 695 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 10.62 (s, 1H, CHO), 10.08 (s, 1H, OH), 8.08 (s, 1H, ArH), 7.93 (d, J = 8.7 Hz, 1H, ArH), 7.89 (d, J = 8.2 Hz, 1H, ArH), 7.62 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H, ArH), 7.39 (ddd, J = 8.0, 6.8, 1.0 Hz, 1H, ArH), 6.05 (ddt, J = 16.2, 10.3, 5.9 Hz, 1H, CH=CH₂), 5.06-4.99 (m, 2H, CH=CH₂), 3.86 (dt, J = 5.9, 1.7 Hz, 2H, ArCH₂); ¹³C NMR (100 MHz, CDCl₃) δ 197.1, 153.3, 137.2, 136.9, 135.9, 130.44, 130.43, 127.8, 124.2, 123.7, 122.0, 120.2, 115.7, 28.6; HRMS (EI) m/z calcd for C₁₄H₁₂O₂ \([M]^+\) 212.0837, found 212.0837.

2,3-Dimethylchromen-4-one (66a). Obtained as a white solid. ¹H and ¹³C NMR spectra were in agreement with published data.⁸⁹

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(Z)-3-(1-(Trimethylsilyl)ethylidene)chroman-4-one (66b). IR (neat) 2952, 2897, 2851, 1668, 1606, 1578, 1477, 1465, 1326, 1309, 1246, 1222, 1147, 1116, 1031, 1008, 911, 843, 757, 678, 619 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (dd, J = 7.8, 1.7 Hz, 1H, ArH), 7.46 (ddd, J = 8.4, 7.2, 1.8 Hz, 1H, ArH), 7.03 (ddd, J = 8.0, 7.3, 1.0 Hz, 1H, ArH), 6.96 (dd, J = 8.4 Hz, 1H, ArH), 5.13 (q, J = 1.1 Hz, 2H, OCH₂), 2.00 (t, J = 1.1 Hz, 3H, C=CCH₃), 0.21 (s, 9H, Si(CH₃)₃); ¹³C NMR (100 MHz, CDCl₃) δ 182.7, 161.7, 157.4, 138.2, 135.7, 128.1, 122.5, 121.8, 117.8, 69.1, 19.6, 0.1; HRMS (El) m/z calcd for C₁₄H₁₇O₂Si [M-H]⁺ 245.0998, found 245.0993.
Appendix
Selected NMR Spectra
35

ppm

ppm
58 in acetone-d$_6$
84
in acetone-\textsubscript{d}_6
$66b$