# Base Mediated Cascade Rearrangements of Aryl Substituted Diallyl Ethers



| | |
|---|---|
| Journal: | *The Journal of Organic Chemistry* |
| Manuscript ID: | jo-2014-02403n.R1 |
| Manuscript Type: | Article |
| Date Submitted by the Author: | n/a |





| | |
|---|---|
| Complete List of Authors: | Reid, Jolene; Queen's University Belfast, School of Chemistry and Chemical Engineering<br>McAdam, Catherine; Queens University Belfast, Chemistry and Chemical Engineering<br>Johnston, Adam; Queen's University Belfast, School of Chemistry and Chemical Engineering<br>Grayson, Matthew; University of Cambridge, Chemistry<br>Goodman, Jonathan; University of Cambridge, Department of Chemistry<br>Cook, Matthew; Queen's University Belfast, School of Chemistry and Chemical Engineering |

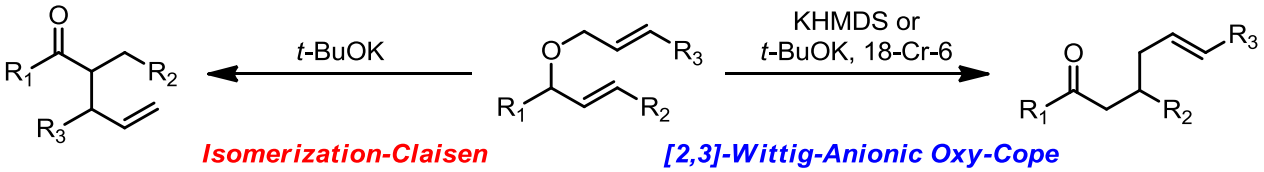
# Base Mediated Cascade Rearrangements of Aryl Substituted Diallyl Ethers

*Jolene P. Reid,[†,‡] Catherine A. McAdam,[†] Adam J. S. Johnston,[†] Matthew N. Grayson,[‡] Jonathan M. Goodman[‡] and Matthew J. Cook[†]**

[†]School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast BT9 5AG, Northern Ireland and [‡] Centre for Molecular Science Informatics, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom

m.cook@qub.ac.uk

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




ABSTRACT. Two base mediated cascade rearrangement reactions of diallyl ethers were developed leading to selective [2,3]-Wittig-oxy-Cope and isomerization-Claisen rearrangements. Both diaryl and aryl-silyl substituted 1,3-substituted propenyl substrates were examined and each exhibits unique reactivity and different reaction pathways. Detailed mechanistic and computational analysis was conducted which demonstrated that the role of the base and solvent were key to the reactivity and selectivity observed. Crossover experiments also suggest that these reactions proceed with a certain degree of dissociation and the mechanistic pathway is highly complex with multiple competing routes.

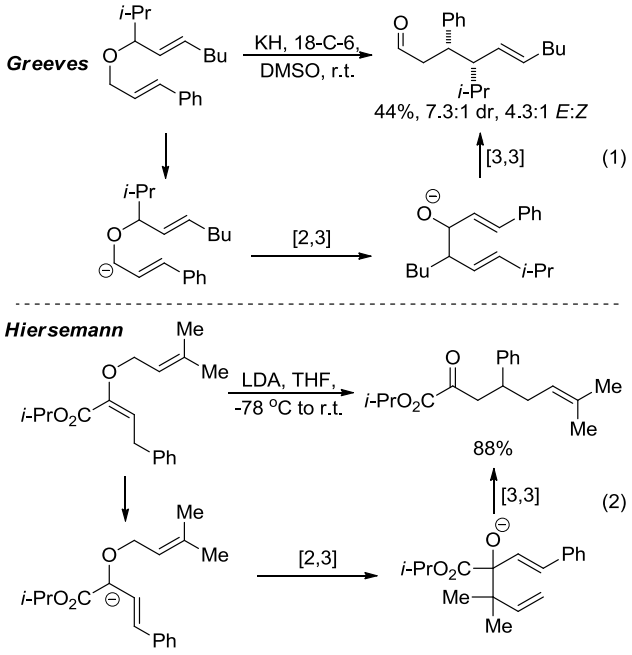
INTRODUCTION

The development of new transformations that efficiently produce molecular complexity in a step and atom efficient manner is an important aspect of synthetic organic chemistry. One of the most powerful strategies involves the use of cascade reactions whereby multiple reactions can be performed in a domino fashion. The result of which is many new bonds being formed and broken in a single transformation which can lead to impressive skeletal rearrangements and the formation of multiple stereogenic centers.[1] Historically significant examples of cascade reactions include squalene oxide biosynthesis,[2] the Robinson Tropinoine synthesis[3] and Johnson's synthesis of progesterone.[4] In particular, pericyclic reactions are excellent candidates for these types of transformations due to their concerted nature and high levels of stereocontrol.[5] Many of these transformations also occur under similar reaction conditions therefore the cascade sequence can proceed without intervention allowing for the formation of complex molecules such as the endriandic acids in a single step.[6]

Sigmatropic rearrangements are a particularly attractive for cascade processes[7] with both the [2,3] and [3,3] variations having found widespread use in synthesis.[8] These rearrangements generally occur with high levels of stereocontrol and proceed through highly ordered cyclic transition states where the most favorable geometry can often be predicted.[9,10] Cascades that contain one or more sigmatropic rearrangements are particularly appealing due to the significant skeletal rearrangements possible. Notable examples include aza-Claisen-Mannich,[11] oxy-Cope-aldol,[12] oxy-Cope-ene[13] and oxy-Cope-ene-Claisen reactions.[14,15] In contrast to the numerous [3,3]-[3,3] cascades that have been reported, there are only isolated examples of [2,3]-[3,3] cascades.[16]

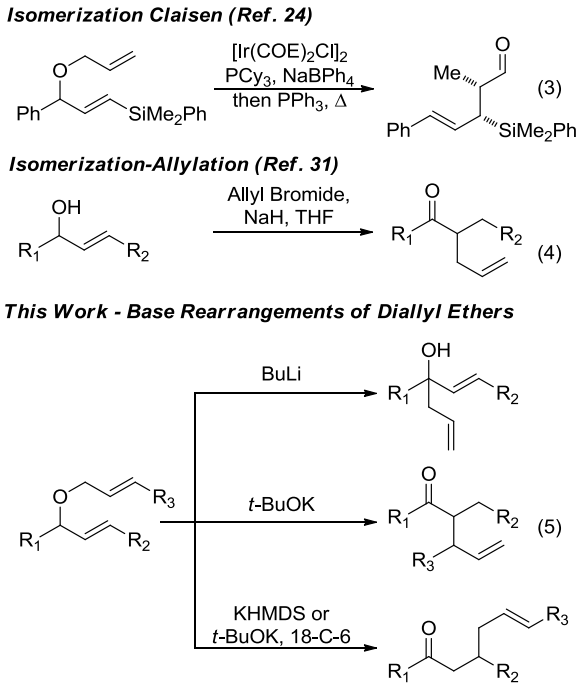
Greeves first reported the combination of the [2,3]-Wittig rearrangement and the anionic oxy-Cope in a tandem process by treating an diallyl ether with KH and 18-Crown-6.[17] This led to aldehyde products which could be isolated with good *E*/*Z* control when large substituents were present and contiguous stereogenic centers could be formed with good *syn* selectivity (Eq. 1).[18] Following this initial report, Hiersemann demonstrated an LDA mediated approach through the formation of an extended

enolate which produced α-ketoesters (Eq. 2).[19] There have also been reports of a sequential [2,3]-Wittig rearrangement followed by an anionic oxy-Cope which are performed under separate reaction conditions,[20] however, the only reports of a true cascade sequence have come from the Greeves and Heirsemann laboroatories.[17-19]




An alternative rearrangement pathway for diallyl ethers is an isomerization-Claisen reaction. There are two main strategies to perform the isomerization of allyl ethers into vinyl ethers: a transition metal catalyzed isomerization or a base mediated approach. Indeed, the transition metal catalyzed isomerization-Claisen reaction is well developed with a range of catalysts used. Isomerizations can be performed at elevated temperatures using ruthenium, rhodium, palladium and iridium catalysts which allow for a concomitant Claisen rearrangement.[21] These approaches generally lead to epimerization of the α-stereogenic center in the presence of the Lewis acidic metal catalysts at these elevated temperatures. Highly active cationic iridium (I) complexes can be used to perform this isomerization at ambient temperature.[22] This can be coupled with a thermal Claisen, following sequestration of the Lewis acidic catalyst with $PPh_3$, to provide isomerization-Claisen products in with high stereocontrol.[23] We have previous utilized this approach to form highly substituted allylsilanes (Eq. 3).[24]

Base mediated isomerizations of allyl ethers proceed *via* an allylic anion which is reprotonated as the thermodynamically more stable enol ether product.[25,26] Base mediated methods do generally provide the *Z*-enol ether product making the two pathways both distinct and complementary. The most commonly applied conditions to mediate this transformation are *t*-BuOK in DMSO however the elevated temperatures required can lead to side reactions and functional group incompatibility.[27] Alternative bases include butyllithium,[28] although unwanted side reactions can occur,[29] and an excess of LDA which allows isomerization to occur at ambient temperature.[30] To the best of our knowledge no reports of base mediated isomerization-Claisen rearrangements have been disclosed to date.



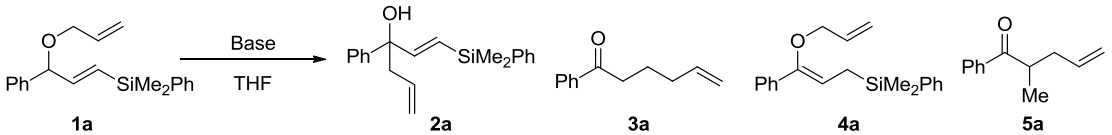

We recently reported the treatment of γ-silyl allylic alcohols[31] with sodium hydride and allyl bromide which results in an isomerization-allylation reaction affording α-allylated ketones (Eq. 4).[32] During the course of studying this reaction we investigated the possibility of this reaction proceeding via diallyl ether **1**. Herein, we report our studies on the base mediated cascade rearrangements of these diallyl ethers whereby complete selectivity can be achieved for three different reaction pathways using the same starting material simply by modulating the base and conditions used (Eq. 5).

## RESULTS AND DISCUSSION

We examined the reaction of γ-silylated allyl ether **1a** with a variety of bases. *n*-Butyllithium resulted in a very facile [2,3]-Wittig rearrangement to form **2a** as had previously reported by Takeda in similar systems.[33] The use of sodium bases such as sodium hydride and NaHMDS led to no reaction or decomposition when 15-crown-5 was added. The use of KHMDS provided a somewhat unexpected product with linear ketone **3a** being produced as a single product and in excellent yield. When tertiary-b

utoxide bases were used other products were formed, with three equivalents of potassium or sodium *tert*-butoxide, an isomerization took place to form allyl vinyl ether **4a**. Interestingly, when the equivalents of base were reduced, a second product began to appear with α-methyl ketone **5a** being produced as the major product. Ketone **5a** could be isolated as the only product by elevating the temperature of the reaction to 80 °C. If the reaction was performed at higher temperatures selectivity is lost and a mixture of products is produced again, where linear ketone **3a** is the minor product.

**Table 1:** Optimization Studies




**1a** **2a** **3a** **4a** **5a**

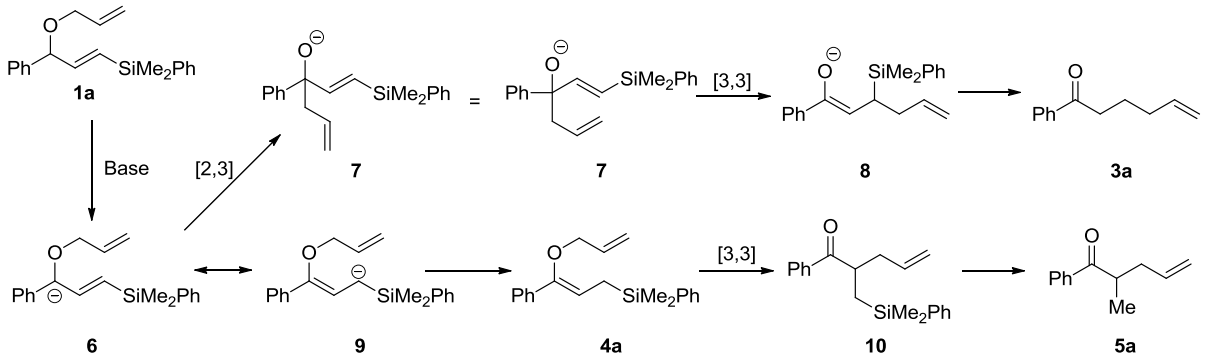
| | | | | | Product Ratios[a,b] | | | |
|---|---|---|---|---|---|---|---|---|
| **Entry** | **Base** | **Equiv.** | **Temp. (°C)** | **Conversion (%)[a]** | **2a** | **3a** | **4a** | **5a** |
| 1 | *n*-BuLi | 3 | 23 | 100 | 100 (90) | - | - | - |
| 2 | NaH | 3 | 60 | n.r. | - | - | - | - |
| 3 | NaH/15-C-5 | 3 | 60 | Decomp. | - | - | - | - |
| 4 | NaHMDS | 3 | 60 | n.r. | - | - | - | - |
| **5** | **KHMDS** | **3** | **60** | **100** | **-** | **100 (85)** | **-** | **-** |
| 6 | KHMDS | 1 | 60 | 65 | - | 100 | - | - |
| 7 | *t*-BuONa | 3 | 60 | 37 | - | - | 100 | - |
| 8 | *t*-BuOK | 3 | 60 | 100 | - | - | 100 (67) | - |
| 9 | *t*-BuOK | 1 | 60 | 52 | - | - | 57 | 43 |
| 10 | *t*-BuOK | 0.5 | 60 | 80 | - | - | 39 | 61 |
| **11** | ***t*-BuOK** | **0.5** | **80** | **100** | **-** | **-** | **-** | **100 (75)** |
| 12 | *t*-BuOK | 0.5 | 100[c] | 100 | - | 26 | - | 74 |

[a] Conversion & product distribution determined by $^1$H NMR; [b] Values in parentheses indicate isolated yields of a single isomer; [c] Performed in a sealed tube.

The proposed mechanisms that lead to **2-5** are shown in Scheme 1. The first step is deprotonation at the benzylic position to form an allylic anion **6** which is a common intermediate for all pathways. This can then undergo one of two pathways: the first is a [2,3]-Wittig rearrangement to form a tertiary

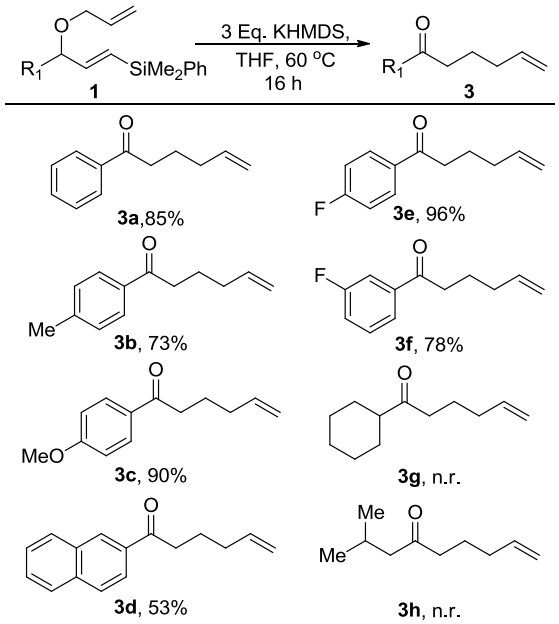
homoallylic alkoxide **7** which is perfectly orientated to perform an anion assisted oxy- Cope rearrangement to form enolate **8**, which following protodesilylation provides linear ketone **3**. The alternative reaction pathway is for the allylic anion to be reprotonated as the allylsilane form **9** which provides allyl vinyl ether **4**.[34] This then performs a Claisen rearrangement to form ketone **10** followed by protodesilylation to form the observed ketone **5**. The protodesilylation process appears to be mediated by the base and not from the work-up procedure. We have previously been able to isolate silane product **10** following a similar workup procedure and appears to be stable.[32] Indeed, the stoichiometry of the base can dictate the amount of protodesilylation observed (*vide infra*).

**Scheme 1: Possible mechanistic Pathways**




Next we proceeded to study the scope of the base mediated rearrangements beginning with the [2,3]-Wittig-anionic oxy-Cope pathway examined initially (Table 2). Using the optimized conditions (3 equivalents of KHMDS, THF, 60 °C) it was found to be very general for aromatic substrates with little difference between electron rich and poor substitution patterns **1a-f**, all of which are produced in good to excellent yields. When alkyl substituted groups **1g-h** were used, no reaction was observed with quantitive recovery of starting material. This can be explained by the lower p*K*a of the allylic proton when the anion stabilizing aromatic groups are present.

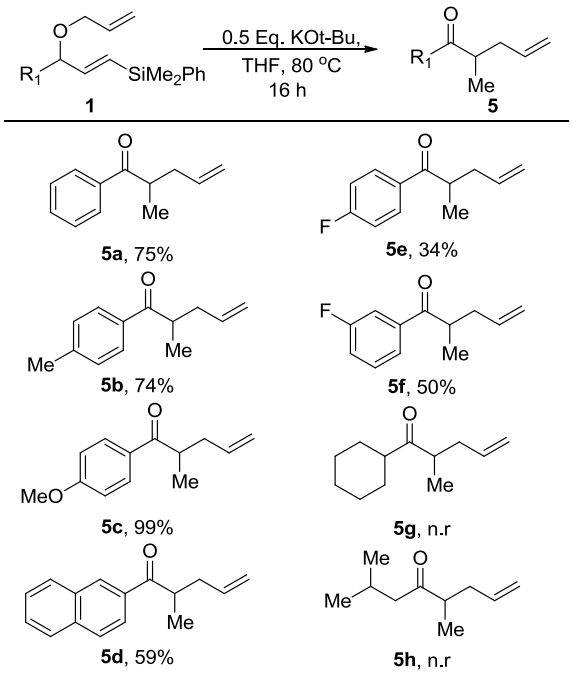
**Table 2: [2,3]-Wittig-oxy-Cope Substrate Scope**




Next the scope of the isomerization-Claisen-protodesilylation pathway was examined (Table 3). Using the optimized conditions of 0.5 equivalents of *t*-BuOK in THF at 80 °C, it was discovered that electron rich substrates promote this reaction with high yields of the α-methyl ketones **5** being obtained. When electron deficient aromatic substrates are used the reaction is much less efficient with fluoro substituted compounds **5e-f** providing low yields of the ketone product. In these cases, a large amount of the [2,3]-Wittig-oxy-Cope-protodesilylation product **3** was obtained as a by-product. Once again alkyl substituted compounds **1g-h** provided no reaction with quantitive recovery of starting materials. There is a clear trend that electron rich groups provide excellent yields whereas the electron poor groups provide more moderate yields and product selectivities. More electron density and less stabilization on the intermediate allylic anion **9** would result in this becoming more basic and hence faster to reprotonate *via*

the isomerization pathway. Contrary to this, stabilization of the anion provides a long enough lived intermediate for the [2,3]-Wittig rearrangement to occur and begin the alternative cascade reaction.

**Table 3: Isomerization-Claisen Substrate Scope**

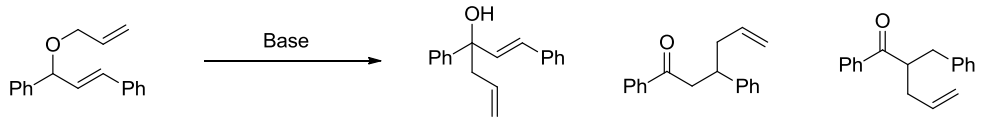



As the silyl group is an anion stabilizing group, in this case through a vinyligous α-effect, we examined other anion stabilizing groups in the form of aromatic groups. Again we began screening basic conditions to examine the regiochemical outcomes of the rearrangements. The use of *n*-butyl lithium once again provided the [2,3]-Wittig product **12** as a single isomer as had been reported previously by Takeda.[33] Using the optimized [2,3]-Wittig-oxy-Cope conditions for the vinyl silanes **1** (3 Equiv. KHMDS, THF, 80 °C), we found that this did not translate to this class of substrates in the same manner providing a mixture of compounds with the [2,3]-Wittig-oxy-Cope **13a** and isomerization-Claisen **14a** products formed in a 9:1 ratio. Lowering the temperature of the reaction provided an almost

1:1 mixture of compounds as did lowering the equivalents of base. Sodium bases gave a preference for the isomerization-Claisen pathway albeit in moderate conversions. Potassium *tert*-butoxide gave poor conversions and selectivities with substoichiometric and equimolar amounts of base however when an excess of base is used, the [2,3]-Wittig-oxy-Cope product **13a** is formed in good conversions. Dissociating the anion through the use of 18-Crown-6 provided complete conversion and 78% isolated yield of **13a** as a single regioisomer. A range of solvents were examined however THF was optimal for this reaction.

We also wanted access to the regioisomeric isomerization-Claisen product **14a**. When 0.5 equivalents of *t*-BuOK are used (Table 4, Entry 7), a 60:40 mixture of **13a:14a** are obtained. Simply by lowering the temperature to 60 °C complete selectivity for **14a** can be obtained, however the reaction is very slow (46% conversion after 3 days). Increasing the equivalents of base reverses the selectivity however the use of toluene as solvent at elevated temperature provides much higher conversions with **14a** being the major product (Entry 20). Under these conditions the product selectivity is eroded over time possibly through the isomerization of **14a** to **13a** during the reaction. Finally the optimal combination of conversion and selectivity was obtained by performing the reaction in a sealed tube at 130 °C providing 100% conversion (72% isolated yield) and 89:11 selectivity **14a:13a** (Entry 23).

## Table 4: Diaryl Substrates Optimization Studies



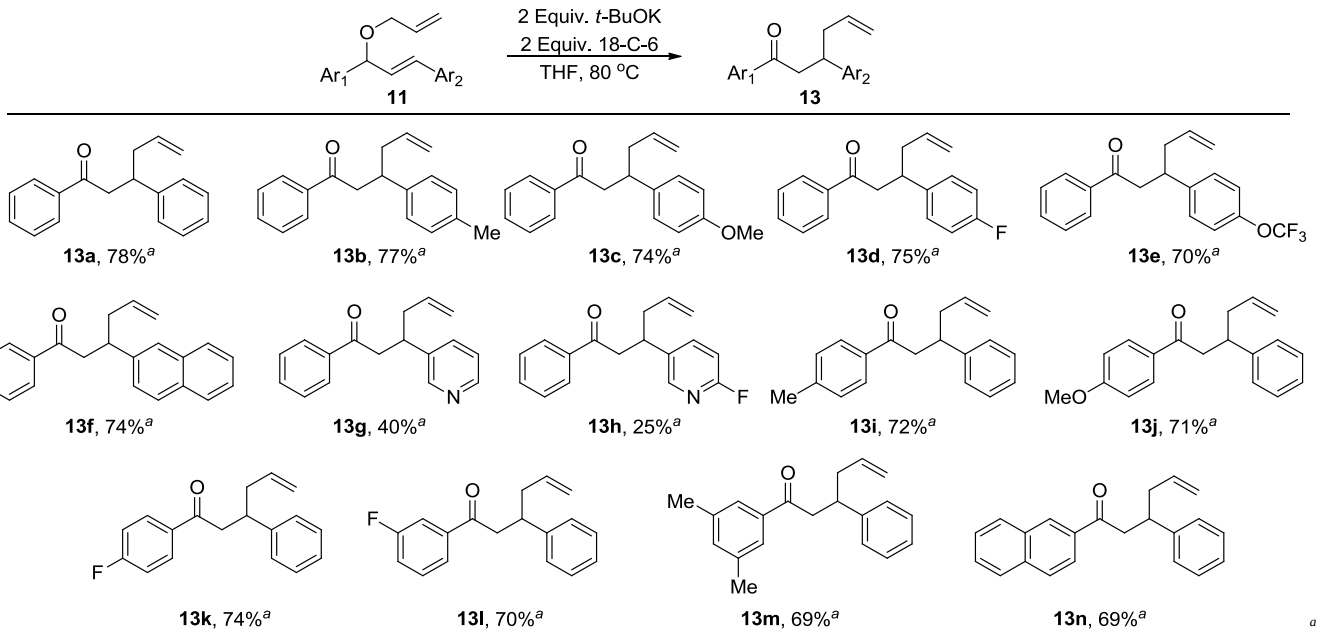

**11a** **12a** **13a** **14a**

| Entry | Base | Equiv. | Solvent | Temp. (°C) | Conversion (%)[a] | Product Ratios[a,b] 12a | 13a | 14a |
|---|---|---|---|---|---|---|---|---|
| 1 | *n*-BuLi | 3 | THF | 23 | 100 | 100 | - | - |
| 2 | KHMDS | 3 | THF | 80 | 100 | - | 90 | 10 |
| 3 | KHMDS | 3 | THF | 60 | 75 | - | 57 | 43 |
| 4 | KHMDS | 1 | THF | 80 | 100 | - | 50 | 50 |
| 5 | NaH | 2 | THF | 80 | 75 | - | 38 | 62 |
| 6 | *t*-BuONa | 2 | THF | 80 | 64 | - | 1 | 99 |
| 7 | *t*-BuOK | 0.5 | THF | 80 | 25 | - | 60 | 40 |
| 8 | *t*-BuOK | 1 | THF | 80 | 52 | - | 89 | 11 |
| 9 | *t*-BuOK | 1.5 | THF | 80 | 80 | - | 100 (64) | - |
| 10 | *t*-BuOK | 2 | THF | 80 | 85 | - | 100 (68) | - |
| 11 | *t*-BuOK | 3 | THF | 80 | 84 | - | 100 (65) | - |
| **12** | ***t*-BuOK/18-C-6** | **2** | **THF** | **80** | **100** | **-** | **100(78)** | **-** |
| 13 | *t*-BuOK/18-C-6 | 2 | DMF | 80 | 47 | - | 100 (39) | - |
| 14 | *t*-BuOK/18-C-6 | 2 | DMSO | 80 | 72 | - | 100 (61) | - |
| 15 | *t*-BuOK/18-C-6 | 2 | CPME | 80 | 58 | - | 100 (53) | - |
| 16 | *t*-BuOK/18-C-6 | 2 | PhCl | 80 | 60 | - | 100 (44) | - |
| 17 | *t*-BuOK/18-C-6 | 2 | Dioxane | 80 | 52 | - | 100 (40) | - |
| 18 | *t*-BuOK | 0.5 | THF | 60 | 46 | - | - | 100 |
| 19 | *t*-BuOK | 1 | THF | 60 | 100 | - | 93 | 7 |
| 20 | *t*-BuOK | 0.5 | Toluene | 110 | 76 | - | 1 | 99 |
| 21[c] | *t*-BuOK | 0.5 | Toluene | 110 | 96 | - | 14 | 86 |
| 22 | *t*-BuOK | 1 | Toluene | 110 | 100 | - | 44 | 56 |
| **23**[d] | ***t*-BuOK** | **0.5** | **Toluene** | **130** | **100 (72)**[e] | **-** | **11** | **89** |

[a] Conversion and product distribution determined by $^1$H NMR; [b] Values in parentheses indicate isolated yields of a single isomer; [c] Reaction was performed over 72 hours; [d] Reaction performed in a sealed tube; [e] Combined isolated yield of a partially separable mixture of isomers

With both sets of optimized conditions in hand we began examining the scope of the reaction. In the case of the [2,3]-Wittig-oxy-Cope reaction, the scope was very general, with the substituents on the aryl ring showing essentially no effect on the reactivity. Good isolated yields were obtained with both electron rich and poor groups and all products **13a-n** were produced as a single regioisomer. Pyridines **13g** and **13h** were tolerated with complete conversion being observed, however the yields are reduced in these cases due problems encountered in their isolation.

**Table 5: Diaryl [2,3]-Wittig-oxy-Cope Substrate Scope**

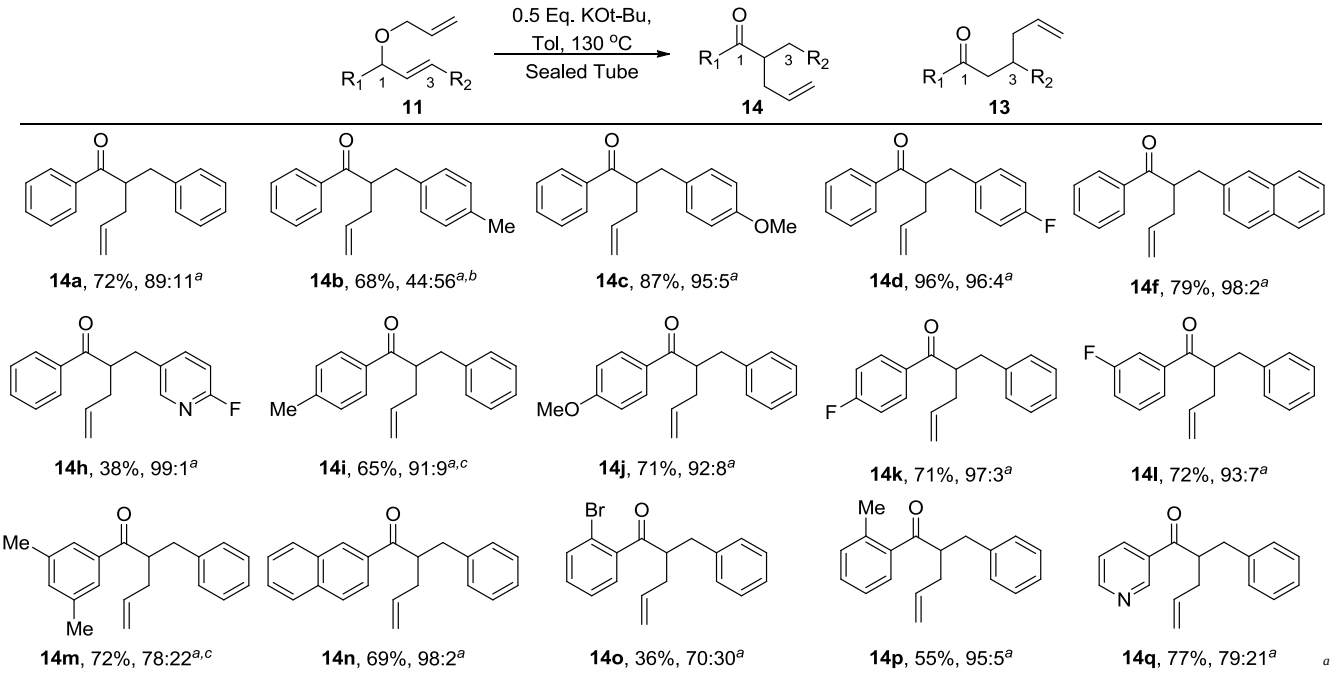



[a] Isolated yields of a single regioisomer.

We next turned our attention to the isomerization-Claisen reaction using the conditions outlined above (Table 4, Entry 23). In general, this reaction was tolerant of most functionality used providing good yields and >90:10 product ratios for the isomerization-Claisen **14** over the [2,3]-Wittig-anionic-oxy-Cope rearrangement **13**. Under these standard conditions, substrates containing aromatic methyl groups failed to react (**11b**, **11i** and **11m**), providing quantative recovery of starting diallyl ether. Reactivity could be achieved through the modulation of the solvent from toluene to THF, however this affected the selectivity of the reaction. Substrate **11b** was reluctant to rearrange solely *via* solvent modification and also required elevated temperatures to achieve complete conversion. As a consequence, no selectivity was observed with a mixture of products being obtained in a 44:56 ratio of **14b**:**13b**. Methyl substituted aromatics at the 1-position were better tolerated with reactions proceeding at 80 °C in THF. When *para*-methyl substituent **11i** was used, good selectivity was observed, however this was eroded in *m*-xylyl substituent **11m** possibly due to increased steric effect of the group. Interestingly, when an ortho-methyl group is present **11p**, the reaction proceeds in toluene under standard reaction conditions. This provided

**14p** with an excellent 95:5 regioselectivity, however sterically encumbered ortho-substitution led to less efficient reactions with lower conversions and yields being obtained.

**Table 6: Diaryl Isomerization-Claisen Substrate Scope**



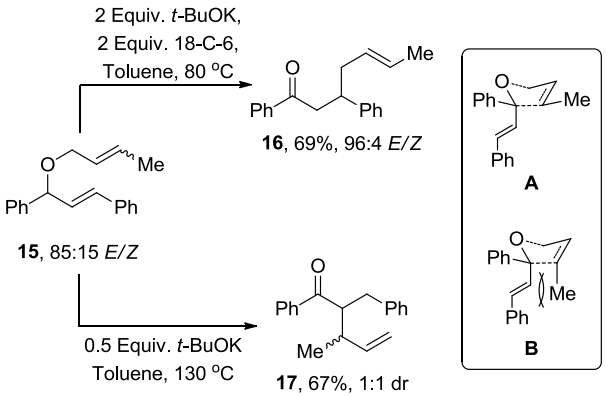

Isolated total yields of the isomeric mixture; [b] Reaction performed in THF at 130 °C; [c] Reaction performed in THF at 80 °C

## Mechanistic Studies

Due to the unusual and very subtle reactivity observed we began to examine the mechanism of these reactions. We first of all examined the use of substituted allyl ethers and prepared the crotyl analog **15** as an 75:25 mixture *E/Z* isomers (Scheme 2).[35] When this was subjected to the [2,3]-Wittig-oxy-Cope conditions, a very smooth reaction proceeded to provide the corresponding 3-substituted ketone **16** in good yields and enhanced *E/Z* selectivity. The methyl group at the terminal position suggests the proposed mechanistic pathway of a [2,3]-Wittig-oxy-Cope pathway is in effect. The enhancement of the *E/Z* ratio is due to a kinetic The methyl group at the terminal position suggests the proposed mechanistic pathway of a [2,3]-Wittig-oxy-Cope pathway is in effect. The enhancement of the *E/Z* ratio is due to a kinetic preference for the *E*-isomer in the [2.3]-Wittg rearrangement (**A** versus **B**). The isomerization-Claisen reaction also resulted in our expected product with the branched methyl product **17** being

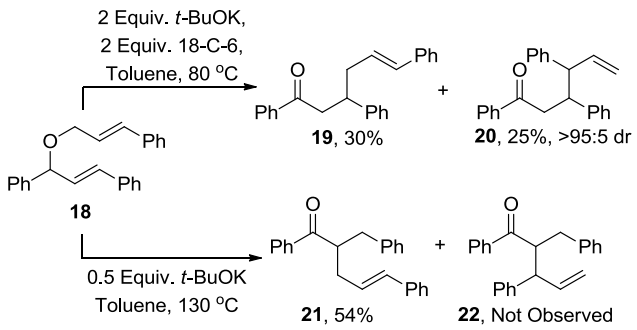
obtained in good yield and a 1:1 mixture of diastereoisomers. This is most likely due to epimerization of the α-stereogenic center under the forcing reaction conditions but could also be due to a dissociative ion-pair or biradical Claisen pathway.

**Scheme 2: Isomerization of Allyl Vinyl Ethers**

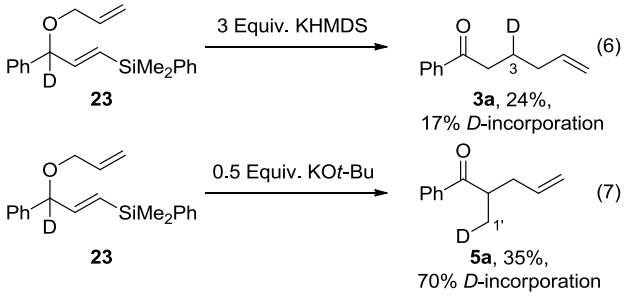



We also examined the cinnamyl rearrangement to probe whether these reactions were concerted in all cases (Scheme 3). When cinnamyl ether **18** was subjected to the 3-allylation conditions, a 1.75:1 mixture of products were observed which included the expected styryl product **19** and the terminal olefin **20** which was formed as a single diastereoisomer. This suggests that in this case at least a significant degree of dissociation is present due to the two regioisomeric products being formed. In the case of the 2-allylated conditions, only one product was formed and this was the styryl product **21** with no isomerisation-Claisen product **22** being observed. This product demonstrates that either the Claisen rearrangement is dissociative and the resulting ion pair or diradical intermediates recombine to provide a single regioisomer as the [1,3]-rearrangement product.

**Scheme 3: Isomerization of Allyl-Vinyl Ethers**

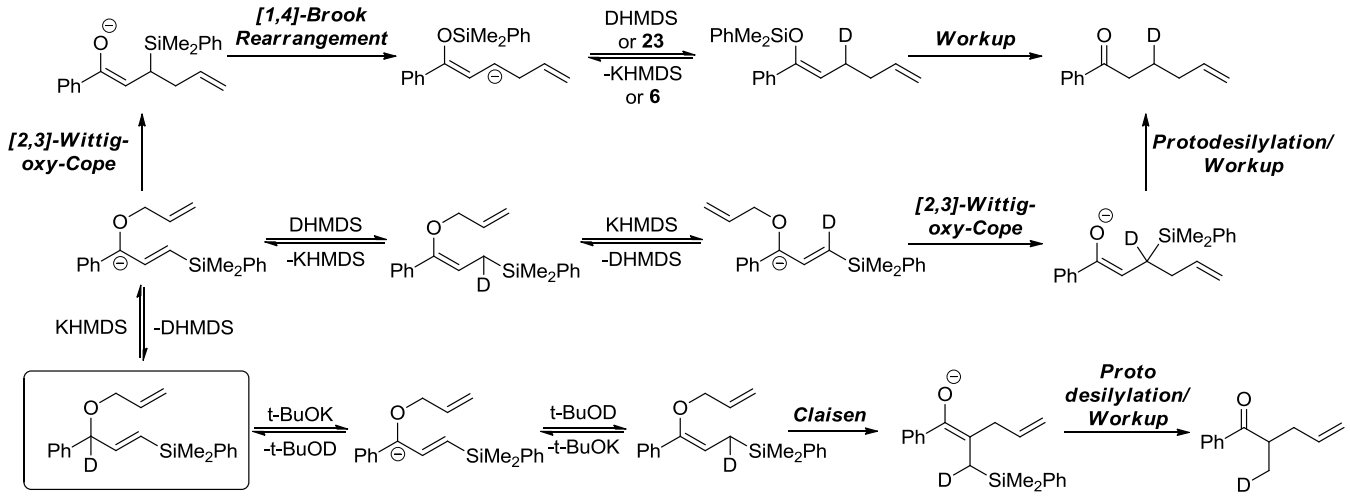


To further strengthen our mechanistic understanding of these reactions a series of deuterium labeling experiments were conducted. Firstly, the vinyl silane was investigated and deuterated analog **23** was prepared and subjected to the reaction conditions. Under the [2,3]-Wittig-oxy-Cope conditions the reaction proceeded with a 17% deuteration at the C-3 position **3a** (Eq. 6). Alternatively, the isomerization-Claisen conditions provided 70% deuteration at the C-1' position **5a** (Eq. 7).




The small amount of deuteration at the C-3 position can be explained by one of two mechanisms both of which would be a minor reaction pathway (Scheme 4). Firstly, following the initial deprotonation of at the benzylic position, the allylic anion is then reprotonated by the conjugate acid α to the silyl group. This can then undergo a second deprotonation to form an alternative allylic anion which then performs the rearrangement. Alternatively, following the [2,3]-Wittig-oxy-Cope reaction, the enolate product can perform a [1,4]-Brook rearrangement to form a silyl enol ether and allylic anion which can be reprotonated by the conjugate acid. Both of these pathways are possible however, no recovered starting material was isolated with the deuterium isomerized from the original position and no silyl enol ethers were ever detected despite our efforts to isolate these sensitive intermediates. However the silicon-oxygen bond could be cleaved during the reaction pathway prior to work-up in a similar pathway to the protodesilylation observed.

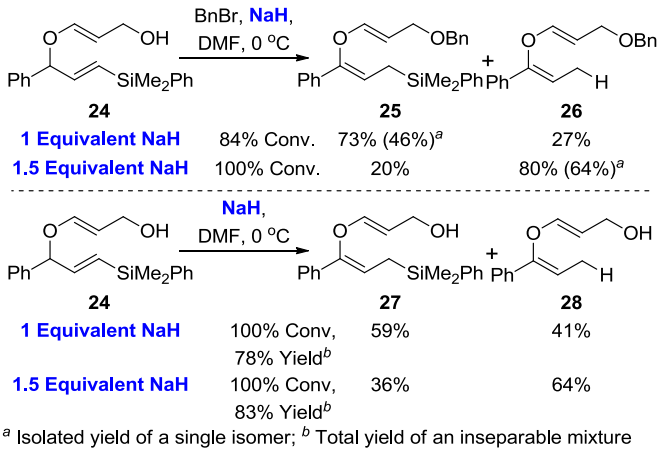
**Scheme 4: Possible Deuterium Incorporation Mechanisms**




We also discovered that the isomerization of the allyl vinyl ethers[36] to divinyl ethers can occur utilizing an internal base (Scheme 5). When an allyl vinyl ether containing an alcohol **24** is treated with NaH and benzyl bromide under standard benzylation conditions, both the isomerization of the allyl ether and the benzylation occurs. The amount of base used also determines the degree of protodesilylation. When one equivalent of base is used the major product is the allyl silane **25**, whereas when 1.5 equivalents are used the protodesilyation predominates to afford **26** which suggests the base is mediating the protodesilylation. In all cases there was complete benzylation of the primary alcohol with no observed *O*-silylation.

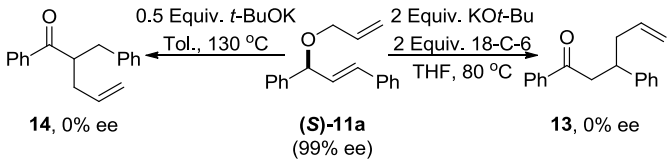
To investigate this further we removed the benzyl bromide from the mixture and found a similar scenario with isomerization occurring to form **27** and **28**. The level of protodesilylation was once again determined by the stoichiometry of base and no *O*-silylation was observed. A similar internal isomerization process has been reported by Maulide for the conversion of alkynyl pyrrolidines to their corresponding allenamine followed by subsequent cyclization reaction.[37] In all cases, no *O*-silylation was ever detected thus suggesting that the protodesilylation is being performed by the excess base.

**Scheme 5: Isomerization of Allyl Vinyl Ethers**



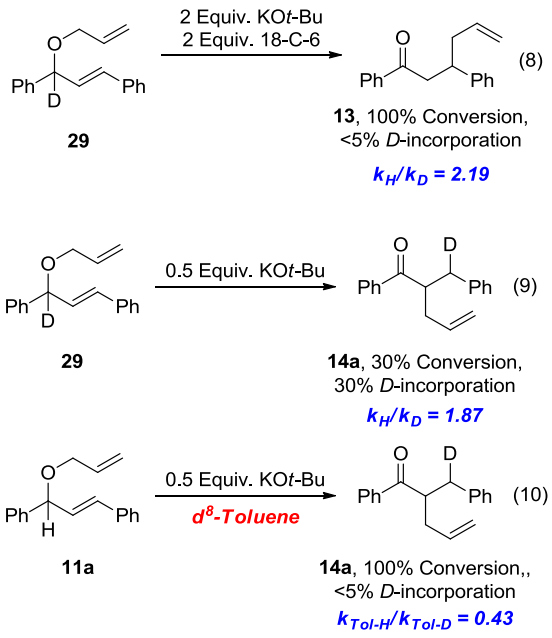

To probe any potential stereospecificity of the reaction we prepared diallyl ether **(*S*)-11a** in 99% ee and subjected this to both sets of reaction conditions (Scheme 6). When the 2-allylation pathway was tested, which we assumed to proceed *via* an isomerization Claisen pathway, a racemic product was obtained thus suggesting the intermediacy of a planar achiral intermediate. When the 3-allylation pathway was used, once again completely racemic product was obtained indicating an achiral intermediate is also present in this pathway.

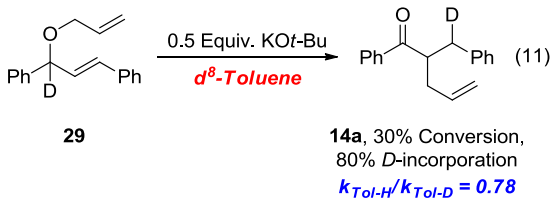
**Scheme 6: Stereospecificity of Rearrangements**




In the case of the deuterated diaryl substrate **29**, the [2,3]-Wittig-oxy-Cope rearrangement occurs with no visible sign of deuterium in the resulting *C*-3 allylated ketone. A kinetic isotope effect was also measured and it was found to be 2.19 which is a small primary effect suggesting proton transfer is rate limiting (Eq. 8).[38,39] When the isomerization-Claisen rearrangement occurs, the corresponding C-2 allylated ketone was isolated with just 30% deuterium incorporation and a smaller primary KIE (Eq. 9).[40] The deuterium content of the product **14a** is significantly different from when vinylsilane **1a** is

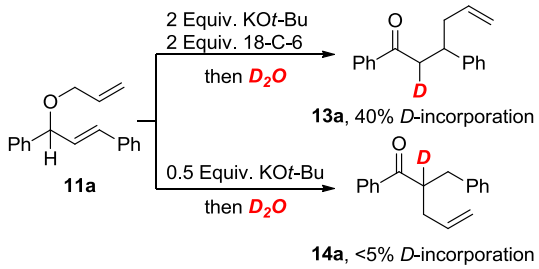
used and led us to speculate where the additional proton content originated from as there were no other obvious proton sources in the reaction. These results, coupled with the issues that were encountered when the methyl substituted aromatic substrates **11b**, **11i** and **11m** were used led us to believe that the additional protons were coming from the toluene solvent and that deprotonation at the benzylic position was inhibiting the reaction. To probe this, we performed the reaction with the protio variant **11a** in $d^8$-toluene and found that the product was formed with no deuterium present (Eq. 10). A solvent KIE study showed that there was a significant inverse solvent effect which resulted in the rate of reaction in the deuterated solvent being nearly 2.5 times that of the protio solvent.[41] This suggests that the solvent is involved in the reaction and that a competing deprotonation reaction with the toluene solvent slows the reaction rate. The deprotonation of $d^8$-toluene occurs at a much slower rate therefore this side reaction is negligible which allows the base to shuttle the proton efficiently with no incorporation of deuterium in the product. We also performed the control experiment whereby the reaction was performed with the deuterated substrate and in $d^8$-toluene (Eq. 11). In this case almost complete deuteration is observed and once again an inverse solvent kinetic isotope effect is observed albeit much less pronounced.[42]





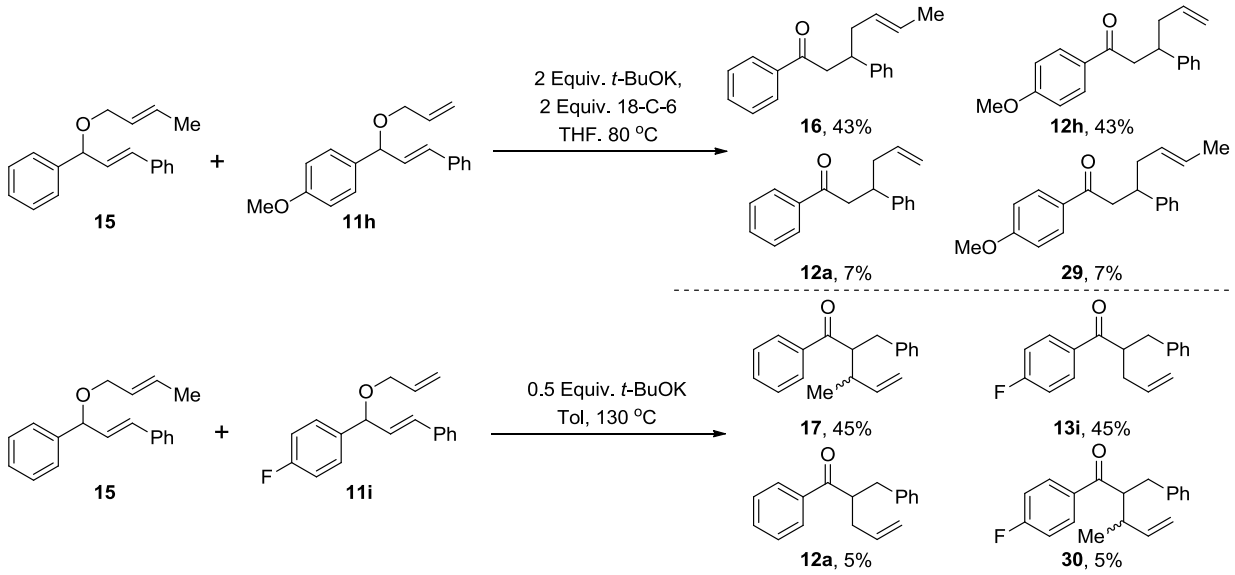

A deuterium trapping experiment was also performed whereby the reactions were quenched with $D_2O$ (Scheme 7). In the [2,3]-Wittig-oxy-Cope reaction 40% deuterium was obsvered α to the ketone thus confirming the presence of an enolate product at the end of the reaction. In the isomerization-Claisen reaction no deuterium was observed thus suggesting that following the rearrangement, the resulting ketone **14a** does not exists as an enolate.

**Scheme 7: Deuterium Quenching Experiments**




We conducted crossover experiments with the allyl groups whereby a mixture of allyl **11h** and crotyl **15** ethers were subjected to the reaction conditions (Scheme 8). When the mixture was subjected to the [2,3]-Wittig-oxy-Cope reaction conditions, the products were observed with 14% crossover. The majority of the products were the expected products **16** and **12h** however a relatively large proportion of the products did show crossover suggesting a dissociative pathway in the reaction. When the isomerization-Claisen reaction conditions were utilized, once again crossover was observed albeit in a lower proportion. Again, this requires dissociation of the allyl vinyl ether for this crossover to occur.

**Scheme 8: Cross-Over Studies**[a]




[a] Product distributions determined by $^1$H NMR and LCMS analysis of the crude reaction mixtures.

**DFT Calculations**

To further probe the pathways involved in these rearrangements the reactions were investigated using computational methods.

**Computational methods**

The B3LYP density functional,[43,44] and split-valence polarized 6-31G** basis set,[45,46] were used for all geometry optimizations. All activation free energies are quoted relative to infinitely separated reagents. Quantum mechanical calculations were performed using Gaussian03 (Revision E.01).[47] Single point energies were taken using the M06-2X density functional,[48] and the 6-31G** basis set using the Jaguar program (version 7.6).[49] This energy was used to correct the gas phase energy obtained from the B3LYP calculations.[50,51]

Free energies in solution were derived from gas phase optimized structures (B3LYP/6-31G**) by means of a single point calculation using M06-2X/6-31G** with the polarizable continuum model (PCM),[52] as implemented in the Jaguar program (version 7.6) using toluene (probe radius = 2.76 Å) or THF (probe radius = 2.52 Å) as the solvent. These values were used to correct the Gibbs free energy derived from the B3LYP calculations.[53,54]

**Anion-assisted oxy-Cope rearrangement**

Calculations using PCM show that the products of radical dissociation in the 3-allylation pathway which yield an intermediate alkoxide and an allylic radical are disfavored relative to the undissociated anion **31** (*ca*. 5 kcal.mol$^{-1}$). If these radical intermediates escape the solvent cage, they could recombine with the alternate partner to form the observed crossover product. Investigation of the anion-assisted oxy-Cope rearrangement identified two unique TSs corresponding to chair conformations for both possible diastereomers resulting from the [2.3]-Wittig rearrangement (**TS-1** and **TS-2**, Figure 1 and Table 7). These TSs were strongly asymmetrical with the much longer forming bond interatomic distances than those of breaking bonds previously observed for rearrangements of this kind (Table 8).[55]

However, TSs corresponding to the C-C bond cleavage reaction were found to have lower activation energies than both concerted TSs (**TS-3** and **TS-4**). Houk *et al.* consider this bond cleavage reaction to be the rate limiting step and that the subsequent C-C bond forming step is fast.[56] Heterolytic cleavage prior to C-C bond formation has been observed for anionic amino-Cope reactions.[55] Whilst generally oxy-Cope rearrangements proceed via concerted mechanisms,[56] the pathway taken is substrate dependant and non-concerted reactions have also been reported.[57] Experimental observation of the rearranged product suggests the cleavage reaction must be followed by a rapid recombination step of the two closely associated intermediates.[55] A small amount of these intermediates that may escape the solvent cage and dissipate into the solution could help account for the observed crossover. Solvent effects were shown to have more of an impact on the relative free energies of these competing TSs compared to those of the Claisen rearrangement due to the net charge associated with the TSs (Table 7). The crown ether present in solution allows examination of the anion alone, without associated cation, and therefore the stabilisation seen from the solvent for the unassociated anion is representative of the experimental conditions. The calculated Boltzmann ratios indicate that both bond cleavage TSs are significantly populated under the experimental reaction conditions.

**Table 7: Reaction barriers and Boltzmann ratios for the competing TSs of the 3-allylation pathway**

| TS | $\Delta\Delta G^{\ddagger}$ | $\Delta\Delta G_{sol}^{\ddagger}$ | Boltzmann ratio (gas phase 298 K) | Boltzmann ratio (THF 353 K) |
|---|---|---|---|---|
| TS-1 | 4.1 | 3.8 | $9.6 \times 10^{-4}$ | $4.6 \times 10^{-3}$ |
| TS-2 | 3.6 | 4.1 | $2.4 \times 10^{-3}$ | $2.7 \times 10^{-3}$ |
| TS-3 | 0.4 | 0.7 | 0.5 | 0.4 |
| TS-4 | 0 | 0 | 1 | 1 |

Geometries B3LYP/6-31G**, single point energies M06-2X/6-31G**. All energies in kcal $mol^{-1}$

**Table 8: 3-Allylation Interatomic distances of competing TSs.**

| | Interatomic distance (Å) | |
|---|---|---|
| TS | C-C (breaking) | C-C (forming) |
| TS-1 | 2.16 | 3.96 |
| TS-2 | 2.19 | 4.22 |
| TS-3 | 2.14 | - |
| TS-4 | 2.09 | - |

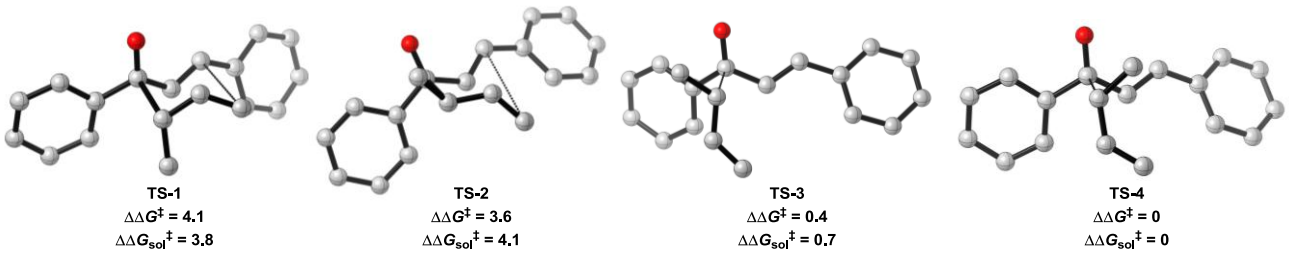



**Figure 1:** Competing TSs for the 3-allylation pathway. Geometries B3LYP/6-31G**, single point energies M06-2X/6-31G**. **TS-1/2** are for the concerted anion-assisted oxy-Cope rearrangement, **TS3/4** correspond to the dissociative C-C cleavage reaction.

## Claisen rearrangement

Solvent phase calculations suggest that the dissociative pathway responsible for the observed crossover in the Claisen rearrangement proceeds via radical intermediates. The calculated free energy

difference between infinitely separated reactants corresponding to the radical and ionic pathways suggests radical intermediates are favored (*ca.* 60 kcal $mol^{-1}$). Comparing free energies of infinitely separated reactants neglects the ionic stabilization between anion and cation, but does more accurately reflect the situation required for crossover to occur with the ions having broken free of this stabilization. The radical intermediates were calculated to be disfavored relative to the undissociated diallyl ether suggesting the preferred pathway proceeds via a concerted mechanism as is generally observed for Claisen rearrangements of this kind.[58]

Investigation of the concerted pathway for diallyl ether Claisen rearrangement identified four unique transition structures TSs) corresponding to chair and boat conformations (Figure 2). Both geometries of the newly formed double bond were considered. The values of $\Delta G_{sol}^{\ddagger}$ suggest the most favorable TS to be reaction of the *E* alkene in a chair conformation (Table 9, TS-5). The corresponding *Z* alkene chair TS is destabilized by 2.7 kcal $mol^{-1}$ (TS-6). Similarly higher energies were observed for both boat TSs (TS-7 and TS-8). Solvent effects were shown to have minimal impact on the relative free energies of the competing TSs due to their concerted and apolar nature.[54] The calculated Boltzmann ratios indicate that the only significantly populated TS under the experimental reaction conditions is TS-5

**Table 9: Reaction barriers and Boltzmann ratios for the competing TSs of the 2-allylation pathway**

| TS | $\Delta\Delta G^{\ddagger}$ | $\Delta\Delta G_{sol}^{\ddagger}$ | Boltzmann ratio (gas phase 298 K) | Boltzmann ratio (Toluene 403K) |
|---|---|---|---|---|
| TS-5 | 0 | 0 | 1 | 1 |
| TS-6 | 3.1 | 2.7 | $5.3 \times 10^{-4}$ | $6.2 \times 10^{-3}$ |
| TS-7 | 4.9 | 4.6 | $2.5 \times 10^{-4}$ | $3.1 \times 10^{-3}$ |
| TS-8 | 8.4 | 7.6 | $8.1 \times 10^{-8}$ | $1.3 \times 10^{-5}$ |

Geometries B3LYP/6-31G**, single point energies M06-2X/6-31G**. All energies in kcal $mol^{-1}$.

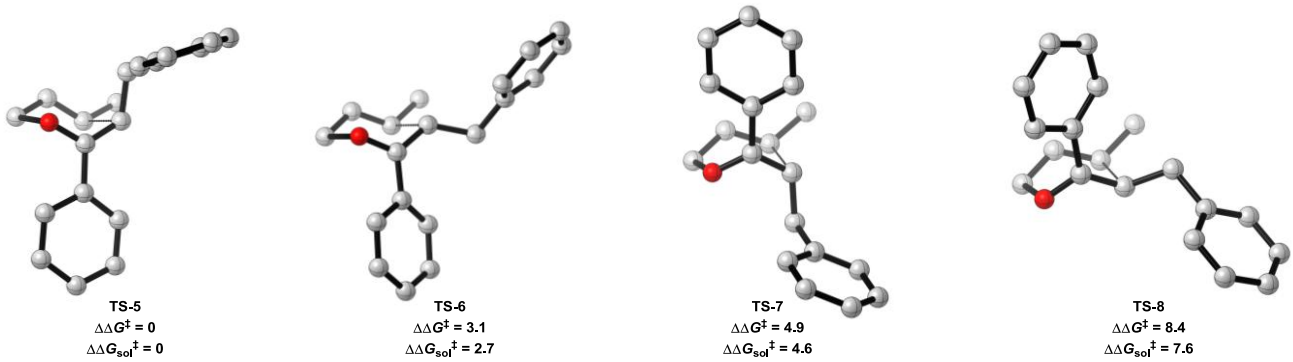



**Figure 2:** Competing TSs (TS-5-8) for diallyl ether Claisen rearrangement. Geometries B3LYP/6-31G**, single point energies M06-2X/631G**

## Proposed Mechanism

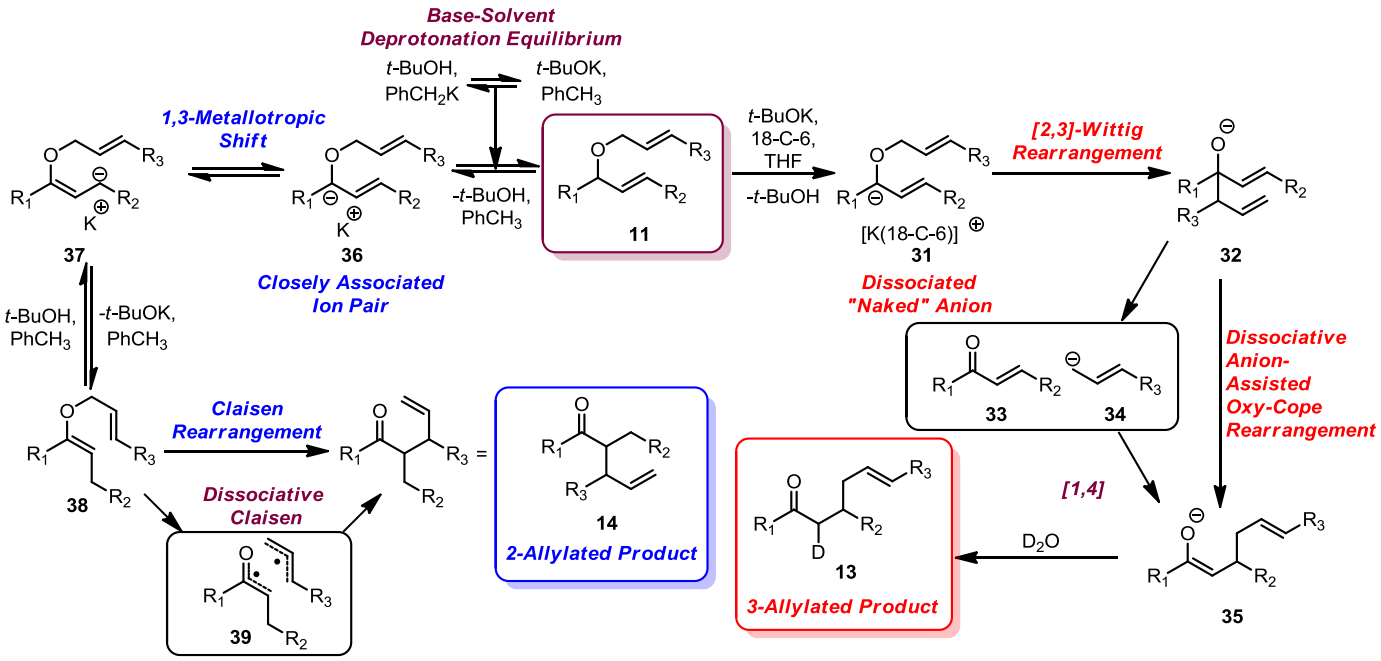
Through the combination of experimental observations and computational analysis we can propose detailed mechanisms for both processes (Scheme 9). Firstly, the 3-allylated product was proposed to proceed *via* a [2,3]-Wittig anionic oxy-Cope pathway to provide **13**. This proceeds through deprotonation at the benylic position to form a highly dissociated "naked" anion **31** due to the presence of the 18-crown-6. This dissociated anion then performs a [2,3]-Wittig rearrangement to form 1,5-diene **32** which can further undergo an anionic oxy-Cope to form enolate **35**. However the presence of cross-over product suggests that the classical concerted mechanisms for these two pathways were not in effect. An alternative dissociative pathway could be through diradical pair as similar to the [1,2]-Wittig rearrangement. At elevated temperatures the [1,2]-Wittig rearrangement is promoted where the intermediate anion can undergo a radical dissociation to form an alkoxide and an allylic radical.[59] These can usually recombine to form the direct [2,3]-rearrangement product **12** however, should these intermediates escape the solvent cage, they could recombine with the alternate partner to form the observed crossover product. Although much rarer than the [1,2] variant there have been several examples of the [1,4]-Wittig rearrangement however its mechanism has not been fully elucidated.[60] Calculations suggest a second dissociative pathway which involves the classical [2,3]- Wittig rearrangement followed by a heterolytic dissociative Cope rearrangement. This pathway which forms an enone **33** and an allylic anion **34** was found to have the lowest transition state energy by 3.8 kcal.mol$^{-1}$.

These intermediates can recombine in a 1,4-sense to form enolate **36** which provides 3-allylated product **13** following workup. This explains the presence of cross-over product, however this is a minor pathway suggesting the recombination is fast which does not allow the allylic anion to escape the solvent cage readily. The small amount that does escape the solvent cage and dissipates into the solution accounts for the cross-over observed.

The 2-allylated product **14** can occur through an isomerization-Claisen pathway as described earlier however; this does not take into account all the mechanistic data. The strong inverse solvent kinetic isotope effect observed indicates there is a competitive deprotonation of the toluene solvent alongside the diallyl ether. There are two possible scenarios which could be occurring; the toluene anion is conducting the deprotonation or the competitive reaction slows the rate of deprotonation. Once the allylic anion **37** is formed, this will exist as a closely associated ion pair due to the non-polar solvent disfavoring solvent separation. A 1,3-metallotropic shift provides allylic anion **37** which can be reprotonated by the conjugate acid or toluene to provide our requisite allyl vinyl ether **38**. As the reaction is performed at elevated temperatures, **38** undergoes a spontaneous Claisen rearrangement to form our 2-allylated product **14**.

The Claisen appears to proceed with some degree of dissociation as judged by the crossover experiments. Although Claisen rearrangements do generally proceed *via* a concerted closed transition state,[61] some can proceed through more dissociative pathways. These can include dipolar ionizations to form either a close contact or solvent separated ion pair[62] or alternatively proceed through a homolytic pathway whereby a diradical intermediate is formed.[63] The DFT calculations suggest that the concerted pathway is the lowest energy pathway however a homolytic cleavage to provide diradical pair **39** is the most likely cause of the cross-over products. These radical pairs can escape the solvent cage and recombine with the alternate partner to provide the cross-over product.

**Scheme 9: Proposed Mechanisms**




## CONCLUSIONS

In conclusion, we have developed and investigated the mechanism of new base mediated rearrangements of diallyl ethers. The reaction can proceed through a combination of mechanisms which account for all the observations. Two classes of compounds were examined aryl vinylsilanes and diaryl substrates. Each of these classes react in their own unique manner to provide similar products however the silanes always proceed with protodesilylation. The rearrangement to the 3-allylated species appears to proceed *via* a [2,3]-Wittig anionic oxy-Cope rearrangement, however there appears to be a small degree of [1,4]-Wittig rearrangement occurring due to the presence of intermolecular rearrangements in crossover experiments. The 2-allylated products proceed through an isomerization-Claisen pathway however the reaction is slowed through a competitive deprotonation of the solvent. It also appears that a small proportion of the Claisen rearrangement occurs through dissociative mechanism either through a diradical or dipolar intermediate.

## EXPERIMENTAL SECTION

All reactions were carried out under an atmosphere of argon in oven- dried glassware otherwise mentioned elsewhere. All reaction were monitored by thin layer chromatography (TLC) using Merck TLC silica gel 60 sheets, which were visualized with ultraviolet light and then developed with Iodine and basic potassium permanganate or anisaldehyde solution. Flash chromatography was performed on Sigma-Aldrich silica gel 60 as the stationary phase and the solvents employed were of analytical grade. Unless stated otherwise, all commercially available reagents were used as received. When necessary, commonly used organic solvents were dried prior to use according to standard laboratory practices.[64] NMR spectra were recorded at 400MHz ($^{1}$H) and 100MHz ($^{13}$C) and were referenced to $CDCl_3$ δ 7.26 ppm and 77.2 ppm respectively. Infrared spectra were recorded as a thin film on KBr discs. High-resolution mass spectra were obtained on mass spectrometers using electrospray ionization (ESI) or electron impact ionization at 70 eV and TOF analyzers.

### General Procedure A: Formation of Propargylic alcohols

A hexane solution of n-BuLi (2.5 M) (1.1 equiv.) was added to a THF (0.5 M) solution of phenylacetylene (1.1 equiv.) at -78°C. The mixture was stirred at 1 hr at that temperature, before the aryl aldehyde was added (1 equiv.). The reaction mixture was warmed to room temperature and stirred for 1hr, and quenched with a saturated aqueous $NH_4Cl$ solution. The aqueous solution was extracted with EtOAc (2 x 15 mL), and the combined organic layers were washed with brine (20 mL). After the organic layer was dried with $NaSO_4$ and concentrated in vacuo. The crude product was loaded onto a column and chromatographed to afford the requisite propargylic alcohol.

### General Procedure B: Formation of Allylic Alcohols[65]

An oven dried round bottomed flask, purged with argon, and cooled to 0$^{O}$C, Red-Al (65% in PhMe) (2 equiv.) was dissolved in diethyl ether (0.5 M) followed by the dropwise addition of a solution of the propargylic alcohol (1 equiv.) in $Et_2O$ (0.5 M). The mixture was stirred for 4 hours, maintaining the temperature at 0$^{o}$C after which the reaction was quenched with several drops of 1 M HCl solution (CAUTION: Rapid evolution of hydrogen gas). The mixture was extracted with $Et_2O$ (2 x 25 mL), washed with brine (25 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude mixture was applied directly onto the top of a column and chromatographed to afford the requisite 1,3-diaryl propenol.

**General Procedure C: Formation of Diallyl Ethers (1a- 1h and 11i-11q)** [66]

A solution of the diaryl allylic alcohol or vinyl silane (1 equiv.) in DMF (0.08 M) was made up in an oven-dried, 50 mL round-bottomed flask, purged with argon and cooled to 0 $^{o}$C. Allyl bromide (2 equiv.) followed by sodium hydride (60% suspension in mineral oil; unwashed) (2 equiv.) were added, after which the reaction mixture turned pale yellow. The mixture was stirred at 0$^{o}$C under argon for one hour followed by quenching with saturated $NH_4Cl$ solution (30 mL). The aqueous solution was extracted with diethyl ether (3x60 mL) and the ether layer washed with distilled water (3 x 25 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude mixture was applied directly onto the top of a column and chromatographed to afford the requisite allyl ether.

**General Procedure D: [2,3]-Wittig-oxy-Cope Cascade (3a – 3f)**

KHMDS solution (0.5 M in toluene, 3 equiv.) was added to a THF solution (0.05 M) of the diallylic alcohol (1 equiv.) in a dry, argon purged 10 mL round-bottomed flask at room temperature. The flask was fitted with a condenser and heated to 60 $^{o}$C and allowed to stir overnight. The reaction mixture slowly turned deep brown after addition of the KHMDS. After quenching with a few drops of $NH_4Cl$, the reaction was diluted with diethyl ether (25 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The

crude mixture was applied directly onto the top of a column and chromatographed to afford the requisite ketone.

**General Procedure E: Isomerisation-Claisen Cascade (5a – 5f)**

Potassium *t*-butoxide (0.5 equiv.) was added to a THF solution (0.13 M) of the γ-silyl allylic alcohol in a clean, dry, argon purged 5 mL round-bottomed flask at room temperature. A condenser was attached and the reaction heated to 60 $^{o}$C and allowed to stir overnight. After quenching with distilled water (10 mL) and extracted with EtOAc (2 x 25 mL), the combined organic phases were washed with distilled water (25 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude mixture was applied directly onto the top of a column and chromatographed to afford the requisite ketone.

**General Procedure F: [2,3]-Wittig-oxy-Cope Cascade(13a-13n)**

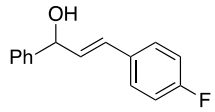
18-Crown-6 (2 equiv.) followed by potassium *t*-butoxide (2 equiv.) was added to a THF solution (0.13 M) of the diallyl ether (1 equiv.) in a dry, argon purged 10 mL round-bottomed flask at room temperature, after which the reaction mixture turned dark red. The flask was fitted with a condenser and heated to 80 $^{o}$C and allowed to stir overnight. After quenching with distilled water (10 mL) and extracted with EtOAc (2 x 25 mL), the combined organic phases were washed with distilled water (25 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude mixture was applied directly onto the top of a column and chromatographed to afford the requisite ketone.

**General Procedure G: Isomerisation-Claisen Cascade (14a – 14q)**

Potassium *t*-butoxide (0.5 equiv.) was added to a toluene solution (0.13 M) of the diallyl ether in a dry, argon purged sealed tube at room temperature. The reaction heated to 130 $^{o}$C in a sealed tube and allowed to stir for 16h. After quenching with distilled water (10 mL) and extracted with EtOAc (2 x 25 mL), the combined organic phases were washed with distilled water (25 mL) and brine (25 mL), dried

over $MgSO_4$ and concentrated *in vacuo*. The crude mixture was applied directly onto the top of a column and chromatographed to afford the requisite ketone.

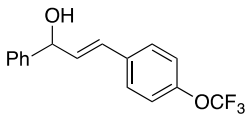
**(*E*)-1-phenyl-3-(4-fluorophenyl)prop-2-en-1-ol (S1)**




The title compound was prepared according to general procedure B, from 3-(4-fluorophenyl)-1-phenylprop-2-yn-1-ol[67] (307 mg, 1.36 mmol) using Red-Al (65% in PhMe) (0.83 mL, 2.72 mmol). The crude product was applied directly onto the top of a column and chromatographed (10% EtOAc in hexane) to afford **S1** (250 mg, 81%) as a colorless oil.

$R_f$ (9:1 Hexane/EtOAc) =0.13; $\upsilon_{max}$ (thin film) / $cm^{-1}$; 3415, 1656, 1640, 1505, 1266, 1227, 1158, 834, 741, 701; $^1$H NMR: (400 MHz, $CDCl_3$) $\delta$ 7.45 – 7.28 (7H, m), 7.02 – 6.94 (2H, m), 6.63 (1H, d, $J$ = 15.8 Hz), 6.28 ( 1H, dd, $J$ = 15.6, 6.3 Hz), 5.34 (1H, dd, $J$ = 6.4, 2.4 Hz), 2.02 (1H, d, $J$ = 2.4 Hz);; $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 162.4 (d, $J_{C-F}$ = 245.4 Hz), 142.7, 132.7 (d, $J_{C-F}$ = 3.3 Hz), 131.3 (d, $J_{C-F}$ = 2.2 Hz), 129.4, 128.7, 128.1 (d, $J_{C-F}$ = 8.0 Hz), 127.9, 126.3, 115.5 (d, $J_{C-F}$ = 21.5 Hz), 75.1; HRMS (ES+) Calcd. for $C_{15}H_{12}OF$ $[M+H]^+$ 227.0872. Found 227.0864.

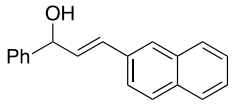
***(E)*-1-phenyl-3-(4-trifluoromethoxyphenyl)prop-2-en-1-ol (S2)**




The title compound was prepared according to general procedure B, from 1-phenyl-3-(4-trifluoromethoxyphenyl)prop-2-yn-1-ol[32] (116 mg, 0.41 mmol) using Red-Al (65% in PhMe) (0.26 mL, 0.82 mmol). The crude product was applied directly onto the top of a column and chromatographed (10% EtOAc in hexane) to afford **S2** (95 mg, 79%) as a colorless oil.

$R_f$ (9:1 Hexane/EtOAc) =0.23; $\nu_{max}$ (thin film) / $cm^{-1}$; 3339, 1508, 1263, 1219, 1164, 966, 670; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.29 (7H, m), 7.22 – 7.11 (2H, m), 6.69 (1H, dd, *J* = 15.8, 1.3 Hz), 6.38 (1H, dd, *J* = 16.0, 6.2 Hz), 5.40 (1H, dd, *J* = 6.4, 2.3 Hz), 2.05 (1H, d, *J* = 3.3 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 145.6 (q, $J_{C-F}$ = 245.8 Hz), 142.5, 135.3, 132.5, 128.9, 128.7, 128.0, 127.8, 126.3, 121.1, 74.9; HRMS (ES+) Calcd. for $C_{16}H_{13}F_3O_2Na$ $[M+Na]^+$ 317.0765. Found 317.0761.

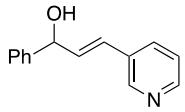
**(*E*)-1-phenyl-3-(2-naphthyl)prop-2-en-1-ol (S3)**




The title compound was prepared according to general procedure B, from 1-phenyl-3-(2-naphthyl)prop-2-yn-1-ol[32] (381 mg, 1.48 mmol) using Red-Al (65% in PhMe) (0.90 mL, 2.96 mmol). The crude product was applied directly onto the top of a column and chromatographed (10% EtOAc in hexane) to afford **S3** (278 mg, 72%) as a yellow oil.

$R_f$ (9:1 Hexane/EtOAc) =0.11; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.18 – 8.14 (1H, m), 7.90 – 7.77 (2H, m), 7.62 – 7.31 (10H, m), 6.46 (1H, dd, *J* = 15.3, 6.2 Hz), 5.53 (1H, d, *J* = 6.04 Hz), 2.15 (1H, s); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 142.8, 134.7, 134.3, 133.6, 131.2, 128.7, 128.5, 128.1, 127.9, 127.7, 126.4, 126.1, 125.8, 125.6, 124.0, 123.7, 75.3. Characterisation in accordance with literature data.[32]

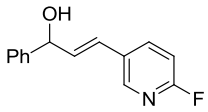
**(*E*)-1-phenyl-3-(pyridin-3-yl)prop-2-en-1-ol (S4)**




The title compound was prepared according to general procedure B, from 1-phenyl-3-(3-pyridyl)prop-2-yn-1-ol[32] (304 mg, 1.50 mmol) using Red-Al (65% in PhMe) (0.69 mL, 2.25 mmol). The crude crude product was applied directly onto the top of a column and chromatographed (10% EtOAc in hexane) to afford **S4** (214 mg, 68%) as a colorless oil.

$R_f$ (3:1 Hexane:EtOAc) =0.09; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 3200, 2925, 1416, 1026, 968, 700; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.59 (1H, s), 8.46 – 8.44 (1H, m,) 7.71 – 7.68 (1H, m), 7.45- 7.21 (6H, m), 6.69 (1H, d, *J* = 16.0 Hz), 6.46 (1H, dd, *J* = 15.8, 6.0 Hz), 5.42 (1H, d, *J* = 6.0 Hz), 3.20 (1H, s, br); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 148.7, 148.5, 142.5, 133.9, 133.0, 132.3, 128.8,128.1, 126.6, 126.4, 123.5, 74.9; HRMS (ES+) Calcd. for $C_{14}H_{13}NO$ $[M + H]^+$ 212.1072. Found 212.1060.

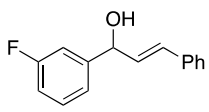
**(E)-3-(2-fluoropyridin-5-yl)-1-phenylprop-2-en-1-ol (S5)**




The title compound was prepared according to general procedure B, from 1-phenyl-3-(2-fluoro-pyrid-5-yl)prop-2-yn-1-ol[32] (300 mg, 1.32 mmol) using Red-Al (65% in PhMe) (0.69 mL, 2.25 mmol). The crude crude product was applied directly onto the top of a column and chromatographed (10% EtOAc in hexane) to afford **S5** (248 mg, 80%) as a colorless solid.

Rf (3:1 Hexane/EtOAc) =0.31; $\nu_{max}$ (thin film) / $cm^{-1}$; 3217, 3061, 3029, 1573, 1492, 1453, 1416, 1092, 1026, 969, 701; $^1H$ NMR: (400 MHz, $CDCl_3$) δ 8.17 – 8.11 (1H, m), 7.83 – 7.75 (1H, m), 7.44 – 7.28 (5H, m), 6.86 (1H, dd, *J* = 8.5, 2.8 Hz), 6.66 (1H, d, *J* = 15.8 Hz), 6.37 (1H, dd, *J* = 15.8, 6.04 Hz), 5.39 (1H, d, *J* = 5.8 Hz), 2.49 (1H, s); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 162.9 (d, $^1J_{C\text{-}F}$ = 238.8Hz), 146.0 (d, $^3J_{C\text{-}F}$ = 14.2 Hz), 142.3, 138.1 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 133.7 (d, $^4J_{C\text{-}F}$ = 1.82 Hz), 130.4 (d, $^3J_{C\text{-}F}$ = 4.7 Hz), 128.7, 128.1, 126.3, 125.1, 109.4 (d, $^2J_{C\text{-}F}$ = 37.1 Hz), 74.7; HRMS (ES+) Calcd. for $C_{14}H_{13}FNO$ $[M + H]^+$ 230.0981. Found 230.0993.

**(*E*)-1-(3-fluorophenyl)-3-phenylprop-2-en-1-ol (S6)**

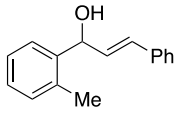



The title compound was prepared according to general procedure B, from 1-(4-fluorophenyl)-3-phenylprop-2-yn-1-ol (329 mg, 1.45 mmol)[68] using Red-Al (65% in PhMe) (0.88 mL, 2.90 mmol). The

crude product was applied directly onto the top of a column and chromatographed (10% EtOAc in hexane) to afford **S6** (295 mg, 89%) as a colorless oil.

$R_f$ (10% EtOAc in hexane) = 0.13; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.38 (2H, m), 7.36 – 7.29 (3H, m), 7.28 – 7.24 (1H, m), 7.22 – 7.15 (2H, m), 7.02 – 6.59 (1H, m), 6.70 (1H, dd, *J* = 16.0, 1.0 Hz), 6.34 (1H, dd, *J* = 15.8, 6.8 Hz), 5.39 (1H, dd, *J* = 6.8, 3.8 Hz), 2.03 (1H, d, *J* = 3.5 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 163.1 (d, *J* = 250.0 Hz), 145.4 (d, *J* = 7.0 Hz), 136.3, 131.2, 130.9, 130.1 (d, *J* = 8.0 Hz), 128.7, 128.0, 126.7, 121.9 (d, *J* = 3.0Hz), 114.6 (d, *J* = 22.0 Hz), 113.2 (d, *J* = 22.0 Hz), 74.6 (d, *J* = 1.0 Hz).; Characterization in accordance with literature data.[66]

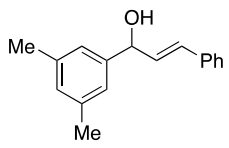
**(*E*)-1-(o-toyl)-3-phenylprop-2-en-1-ol (S7)**




The title compound was prepared according to general procedure B, from 3-phenyl-1-(*o*-tolyl)prop-2-yn-1-ol (683 mg, 3.07 mmol) using Red-Al (65% in PhMe) (1.87 mL, 6.14 mmol). The crude product was applied directly onto the top of a column and chromatographed (10% EtOAc in hexane) to afford **S7** (600 mg, 93%) as a colorless oil.

$R_f$ (10% EtOAc in hexane) = 0.16; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.54- 7.52 (1H, m), 7.39 – 7.36 (2H, m), 7.32 – 7.15 (6H, m), 6.65 (1H, d, *J* = 16.0 Hz), 6.36 (1H, dd, *J* = 16.0, 6.2 Hz), 5.58 (1H, d, *J* = 6.0 Hz), 2.39 (3H, s), 1.96 (1H, s, br); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 140.7, 136.6, 135.3, 130.8, 130.7, 130.6, 128.6, 127.8, 127.7, 126.6, 126.4, 125.9, 71.9, 19.2; Characterization in accordance with literature data.[69]

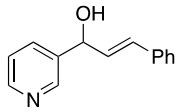
**(*E*)-1-(3,5-dimethylphenyl)-3-phenylprop-2-en-1-ol (S8)**



Magnesium turnings (100 mg, 3.96 mmol) and a single crystal of iodine was added to an oven dried round bottomed flask purged with argon. A reflux condenser was fitted and $Et_2O$ (7.3 mL, 0.5 M) added. This mixture was stirred for 10 minutes, after which 1-bromo-3,5-dimethylbenzene (0.50 mL, 3.63 mmol) was added dropwise. The reaction mixture was heated to reflux for 20 minutes and then cooled to room temperature at which point the majority of Mg turnings had disappeared. The freshly prepared Grignard solution was added dropwise to a cooled (0°C) solution of cinnamaldehyde (0.40 mL, 3.30 mmol) in THF (7.3 mL, 0.5 M). Once addition was complete, the reaction mixture was warmed to room temperature and stirred overnight. The reaction was quenched with saturated $NH_4Cl$ solution (20 mL) and extracted with EtOAc (2 x 20 mL), the combined organic layers were washed with distilled water (20 mL) and brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated. The crude product was applied to a column and chromatographed (5% EtOAc in hexane) to afford **S8** (380 mg, 48%) as a yellow oil.

$R_f$ (10% EtOAc in hexane) = 0.24; IR: $\nu_{max}$ (thin film) / $cm^{-1}$; 3347, 2918, 1601.4, 1495, 965, 754; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.41 – 7.21 (5H, m), 7.04 (2H, s), 6.94 (1H, s), 6.69 (1H, d, $J$ = 16.0 Hz), 6.38 (1H, dd, $J$ = 16.0, 6.4 Hz), 5.33 – 5.31 (1H, m), 2.32 (6H, s), 1.96 (1H, d, $J$ = 3.6Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 142.8, 138.3, 136.7, 131.7, 130.3, 129.5, 128.6, 127.7, 126.6, 124.11, 75.2, 21.3; HRMS (ES+) Calcd. for $C_{17}H_{18}ONa$ $[M+Na]^+$ 261.1255. Found 261.1264

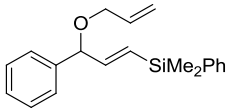
### *(E)*-1-(pyridin-3-yl)-3-phenylprop-2-en-1-ol (S9)




The title compound was prepared according to general procedure B, from 1-(3-pyridyl)-3-phenyl-prop-2-yn-1-ol[32] (278 mg, 1.32 mmol) using Red-Al (65% in PhMe) (0.6 mL, 1.98 mmol). The crude product was applied directly onto the top of a column and chromatographed (10% EtOAc in hexane) to afford **S9** (200 mg, 72%) as a colorless oil.

$R_f$ (10% EtOAc in hexane) = 0.06; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 1579, 1424, 1275, 1027, 967; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.67 (1H, s), 8.55 – 8.53 (1H, m), 7.79 – 7.76 (1H, m), 7.40 – 7.24 (6H, m), 6.72 (1H, d, *J* = 16.0 Hz), 6.35 (1H, dd, *J* = 16.0, 6.8 Hz), 5.45 (1H, d, *J* = 6.4 Hz), 2.42 (1H, s, br); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 149.1, 148.2, 138.1, 136.1, 134.0, 131.6, 130.6, 128.7, 128.2, 126.7, 123.5, 73.1; HRMS (ES+) Calcd. for $C_{14}H_{13}NNaO$ $[M + Na]^+$ 234.0895. Found 234.0866.

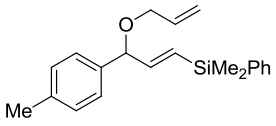
**(E)-(3-(allyloxy)-3-phenylprop-1-en-1-yl)dimethyl(phenyl)silane (1a)**




The title compound was prepared according to general procedure C from (*E*)-3-(dimethyl(phenyl)silyl)-1-phenylprop-2-en-1-ol[31a] (200 mg, 0.746 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (36 mg, 1.49 mmol) and allyl bromide (181 mg, 1.49 mmol) in DMF (10 mL) which following conversion to the allyl ether and column chromatography (9:1 hexane/EtOAc) afforded **1a** as a colorless oil (161 mg, 70%).

$R_f$ (9:1 hexane-ethyl acetate) = 0.80; $^1H$ NMR: (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (2H, m), 7.42 – 7.30 (8H, m), 6.26 (1H, ddd, *J* = 18.8, 5.8, 1.7 Hz), 6.12 (1H, d, *J* = 18.8 Hz), 6.05 – 5.94 (1H, m), 5.33 (1H, ddd, *J* = 17.3, 3.0, 3.0 Hz), 5.23 (1H, ddd, *J* = 10.5, 2.8, 2.8 Hz), 4.89 (1H, d, *J* = 5.8 Hz), 4.03 (1H, m), 0.39 ( 3H, d, *J* = 1.5 Hz), 0.38 (3H, d, J = 1.5 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 147.6, 140.8, 138.5, 134.8, 133.8, 129.2, 128.9, 128.4, 127.7, 127.6, 127.1, 116.9, 83.7, 69.3, -2.6, -2.7. Characterization in accordance with literature data.[24]

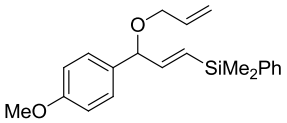
**(*E*)-(3-(allyloxy)-3-(*p*-tolyl)prop-1-en-1-yl)dimethyl(phenyl)silane (1b)**




The title compound was prepared according to general procedure C from (E)-3-(dimethyl(phenyl)silyl)-1-(p-tolyl)prop-2-en-1-ol[31b] (876 mg, 3.10 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (248 mg, 6.20 mmol) and allyl bromide (750 mg, 6.20 mmol) in DMF (39 mL) which following conversion to the allyl ether and column chromatography (19:1 hexane/EtOAc) afforded **1b** as a colourless oil (0.892 g, 89%).

Rf (9:1 hexane-ethyl acetate) = 0.63 IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 3735, 3068, 3048, 2956, 2856, 1512, 1427, 1247, 1114, 822, 730, 699; $^{1}H$ NMR: (400 MHz, $CDCl_3$) δ7.54 – 7.49 (2H, m), 7.39 – 7.34 (3H, m), 7.26 – 7.16 (4H, m), 6.23 (1H, dd, *J* = 18.6, 5.52 Hz), 6.07 (1H, dd, *J* = 18.8, 1.3 Hz), 5.96 (1H, ddd, *J* = 17.3, 3.0, 3.0 Hz), 5.29 (1H, ddd, *J* = 17.3, 2.0, 1.8 Hz), 5.19 (1H, m), 4.83 (1H, d, *J* = 5.8), 3.98 (2H, d, *J* = 5.5 Hz), 2.37 (3H, s), 0.36 (3H, s), 0.35 (3H, s); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ147.8, 138.6, 137.8, 137.3, 134.9, 133.8, 129.1, 128.9, 128.8, 127.7, 127.1, 116.8, 83.6, 69.3, 21.1, -2.6; HRMS (ES+) Calcd. for $C_{21}H_{26}ONaSi$ $[M + Na]^+$ 345.1651. Found 345.1664.

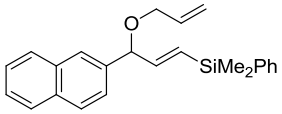
**(*E*)-(3-(allyloxy)-3-(4-methoxyphenyl)prop-1-en-1-yl)dimethyl(phenyl)silane (1c)**




The title compound was prepared according to general procedure C from (*E*)-3-(dimethyl(phenyl)silyl)-1-(4-methoxyphenyl)prop-2-en-1-ol[31b] (399 mg, 1.34 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (112 mg, 2.81 mmol) and allyl bromide (343 mg, 2.25 mmol) in DMF (17.5 mL) which following conversion to the allyl ether and column chromatography (9:1 hexane/EtOAc) afforded **3b** as a colorless oil (389 mg, 86%).

$R_f$ (9:1 hexane-ethyl acetate) = 0.67 IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 3446, 1614, 1510, 1248, 823, 730, 699; $^1H$ NMR: (400 MHz, $CDCl_3$) δ7.51 – 7.46 (2H, m), 7.35 - 7.30 (3H, m), 7.26 – 7.22 (2H, m), 6.90 – 6.85 (2H, m), 6.20 (1H, dd, *J* = 18.6, 5.5 Hz), 6.02 (1H, d, J = 18.6 Hz), 5.97 - 5.86 (1H, m), 5.25 (1H, ddd, *J* = 17.4, 2.5, 2.4 Hz), 5.16 (1H, ddd, *J* = 10.7, 2.9, 2.9 Hz), 4.78 (1H, d, *J* = 5.5 Hz), 3.94 (2H, d, *J* = 5.5 Hz), 3.79 (3H, s), 0.33 (3H, s), 0.32 (3H, s); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ159.1, 147.9, 138.6, 134.9, 133.8, 128.9, 128.7, 128.4, 127.7, 116.8, 113.8, 83.2, 69.1, 55.2, -2.6, -2.6; HRMS (EI+) Calcd. for $C_{21}H_{26}O_2SiNa$ $[M + Na]^+$ 361.1600. Found 361.1618.

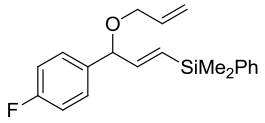
**(*E*)-(3-(allyloxy)-3-(naphthalen-2-yl)prop-1-en-1-yl)dimethyl(phenyl)silane (1d)**




The title compound was prepared according to general procedure C from (*E*)-3-(dimethyl(phenyl)silyl)-1-(naphthalen-2-yl)prop-2-en-1-ol[31b] (401 mg, 1.26 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (101 mg, 2.52 mmol) and allyl bromide (301 mg, 2.52 mmol) in DMF (16 mL) which following conversion to the allyl ether and column chromatography (9:1 hexane/EtOAc) afforded **1d** as a colorless oil (453 mg, 99%.)

$R_f$ (9:1 hexane-ethyl acetate) = 0.77 IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 3437, 3054, 2956, 1647, 1601, 1508, 1427, 1249, 1114, 1086, 990, 819, 732, 670, 478; $^1H$ NMR: (400 MHz, $CDCl_3$) δ 7.88 – 7.84 (3H, m), 7.85 – 7.80 (1H, m), 7.54 – 7.47 (5H, m), 7.41 – 7.31 (3H, m), 6.31 (1H, dd, *J* = 18.8, 5.5 Hz), 6.14 (1H, dd, *J* = 18.8, 1.3 Hz), 6.01 – 5.90 (1H, m), 5.33 (1H, ddd, *J* = 17.3, 1.9, 1.8 Hz), 5.22 (1H, ddd, *J* = 10.3, 1.2, 1.1 Hz), 5.04 (1H, d, *J* = 5.8 Hz), 4.02 – 3.99 (2H, m), 0.37 (3H, s), 0.36 (3H, s); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ147.6, 138.6, 134.8, 134.4 133.8, 133.2, 133.0, 129.4, 128.9, 128.3, 128.0 127.9, 127.7, 126.2, 126.0, 125.9, 125.0, 117.0, 83.8, 69.4, -2.6, -2.6; HRMS (EI+) Calcd. for $C_{24}H_{30}ONSi$ $[M + NH_4]^+$ 376.2097. Found 376.2098.

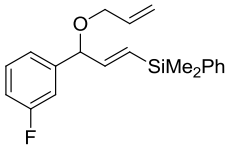
**(E)-(3-(allyloxy)-3-(4-fluorophenyl)prop-1-en-1-yl)dimethyl(phenyl)silane (1e)**




The title compound was prepared according to general procedure C from (*E*)-3-(dimethyl(phenyl)silyl)-1-(4-fluorophenyl)prop-2-en-1-ol[31b] (300 mg, 1.12 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (90 mg, 2.24 mmol) and allyl bromide (273 mg, 2.25 mmol) in DMF (14 mL) which following conversion to the allyl ether and column chromatography (3% EtOAc in hexane) afforded **3e** as a colorless oil (237 mg, 65%)

$R_f$ (9:1 hexane-ethyl acetate) = 0.83 IR: $\upsilon_{max}$ (thin film) / $cm^{-1}$ 3433, 2957, 1604, 1508, 1223, 1114, 838, 670; 1H NMR: (400 MHz, $CDCl_3$) δ 7.52 – 7.49 (2H, m), 7.38 – 7.29 (5H, m), 7.07 – 7.02 (2H, m), 6.18 (1H, dd, J = 18.8, 5.8 Hz), 6.05 (1H, dd, J = 18.6, 1.0 Hz), 5.94 (1H, ddd, J = 17.1, 11.0, 5.52 Hz), 5.28 (1H, ddd, J = 17.0, 1.5, 1.5 Hz), 5.20 (1H, ddd, J = 10.2, 1.2, 1.2 Hz), 4.83 (1H, d, J = 5.8 Hz), 3.98 – 3.93 (2H, m), 0.36 (3H,s), 0.35 (3H, s); 13C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, $J_{C-F}$ = 243.9 Hz), 147.4, 138.4, 136.6 (d $J_{C-F}$ = 3.3 Hz), 134.7, 133.8, 129.7, 129.0, 128.7 (d, $J_{C-F}$ = 8.02 Hz), 127.8, 117.0, 115.3 (d, $J_{C-F}$ = 21.1 Hz), 83.0, 69.4, -2.6, -2.6; HRMS (EI+) Calcd. for $C_{19}H_{20}OFSi$, [M – CH3]+ 311.1267. Found 311.1289.

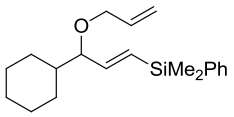
**(*E*)-(3-(allyloxy)-3-(3-fluorophenyl)prop-1-en-1-yl)dimethyl(phenyl)silane (1f)**




The title compound was prepared according to general procedure C from (*E*)-3-(dimethyl(phenyl)silyl)-1-(3-fluorophenyl)prop-2-en-1-ol[31b] (1.0 g, 3.49 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (279 mg, 6.98 mmol) and allyl bromide (844 mg, 6.98 mmol) in DMF (44 mL) which following conversion to the allyl ether and column chromatography (19:1 hexane/EtOAc) afforded **1f** as a colorless oil (892 mg, 89%)

$R_f$ (9:1 hexane-ethyl acetate) = 0.89 IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 3656, 3069, 2956, 2946, 2855, 1591, 1485, 1448, 1428, 1249, 1114, 991, 843, 699, 469; $^1$H NMR: (400 MHz, $CDCl_3$) δ7.51 – 7.44 (2H, m), 7.36 – 7.25 (4H, m), 7.11 – 7.04 (2H, m), 6.99 – 6.92 (1H, m), 6.14 (1H, dd, *J* = 18.6, 5.2 Hz), 6.06 (1H, 18.6, 0.8 Hz), 5.93 (1H, m), 5.27 (1H, ddd, *J* = 17.3, 1.7, 1.7 Hz), 5.18 (1H, ddd, *J* = 10.3, 1.5, 1.2 Hz), 5.01 (1H, d, *J* = 5.8 Hz), 4.04 (2H, m), 0.34 (3H, s), 0.33 (3H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) δ163.0 (d, $J_{C-F}$ = 244.3 Hz), 147.0, 143.6 (d, $J_{C-F}$ = 6.9 Hz), 138.3, 134.5, 133.9, 130.1, 129.9 (d, $J_{C-F}$ = 8.0), 129.0, 127.8, 122.6 (d, $J_{C-F}$ = 2.9 Hz), 117.1, 114.4 (d, $J_{C-F}$ = 21.2 Hz), 113.8 (d, $J_{C-F}$ = 21.9 Hz), 83.1 (d, $J_{C-F}$ = 1.5 Hz), 69.4, -2.7; HRMS (ES+) Calcd. for $C_{20}H_{23}OFNaSi$ $[M + Na]^+$ 349.1395. Found 349.1389.

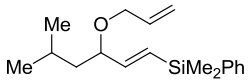
**(E)-(3-(allyloxy)-3-cyclohexylprop-1-en-1-yl)dimethyl(phenyl)silane (1g)**




The title compound was prepared according to general procedure C from (E)-1-cyclohexyl-3-(dimethyl(phenyl)silyl)prop-2-en-1-ol[31a] (399 mg, 1.46 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (117 mg, 2.94 mmol) and allyl bromide (350 mg, 2.89 mmol) in DMF (18 mL) which following conversion to the allyl ether and column chromatography (9:1 hexane/EtOAc) afforded **1g** as a colorless oil (376 mg, 82%)

$R_f$ (9:1 hexane-ethyl acetate) = 0.80; $^1$H NMR: (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (2H, m), 7.40 – 7.35 (3H, m), 6.02 - 5.88 (3H, m), 5.26 (1H, ddd, *J* = 17.3, 2.0, 1.8 Hz), 5.16 (1H, ddd, *J* = 10.2, 1.9, 1.8 Hz), 4.06 (1H ddd, *J* = 12.8, 5.1, 1.8 Hz), 3.81 (1H, ddd, *J* = 12.8, 6.1, 1.8 Hz), 3.47 (1H, t, *J* = 6.1 Hz), 1.82 – 1.69 (2H, m), 1.68 – 1.56 (3H, m), 1.52 -1.45 (3h, m), 0.91 – 0.82 (3H, m), 0.38 (3H, s), 0.37 (3H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 147.4, 138.8, 135.4, 133.8, 131.1, 129.0, 127.8, 116.4, 87.3, 69.6, 42.3, 29.0, 26.7, 26.2, -2.4, -2.5. Characterization in accordance with literature data.[24]

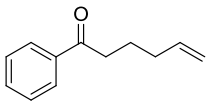
**(E)-(3-(allyloxy)-5-methylhex-1-en-1-yl)dimethyl(phenyl)silane (1h)**




The title compound was prepared according to general procedure C from (E)-1-(dimethyl(phenyl)silyl)-5-methylhex-1-en-3-ol[31a] (319 mg, 1.10 mmol), sodium hydride (60% suspension in mineral oil; unwashed) (110 mg, 2.75 mmol) and allyl bromide (336 mg, 2.72 mmol) in DMF (14 mL) which following conversion to the allyl ether and column chromatography (19:1 hexane/EtOAc) afforded **1h** as a colorless oil (299 mg, 81%).

$R_f$ (9:1 hexane-ethyl acetate) = 0.74; $^1$H NMR: (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (2H, m), 7.40 – 7.34 (3H, m), 5.99 – 5.88 (3H, m), 5.27 (1H, ddd, *J* = 17.1, 1.5 Hz), 5.18 (1H, ddd, *J* = 10.3, 1.5 Hz), 4.07 ( 1H, ddd, *J* = 12.8, 5.3, 1.5 Hz), 3.87 – 3.79 (2H, m), 1.84 – 1.73 (1H, m), 1.61 – 1.53 (1H, m), 1.36 – 1.27 (2H, m), 0.93 (6H, dd, *J* = 6.7, 0.6 Hz), 0.38 (3H, s), 0.37 (3H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 148.9, 138.6, 135.2, 133.8, 129.7, 129.0, 127.8, 116.6, 80.8, 69.4, 44.5, 24.4, 23.0, 22.5, -2.5, -2.6 Characterization in accordance with literature data.[24]

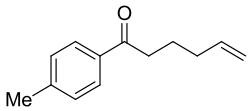
**1-phenylhex-5-en-1-one (3a)**




The title compound was prepared according to general procedure D from **1a** (144 mg, 0.371 mmol) and KHMDS (0.5 M in toluene) (225 mg, 1.13 mmol) in THF (3.5 mL) which following conversion to the ketone and column chromatography (4:1 hexane/DCM) afforded **3a** as a colorless oil (55.5 mg, 85%).

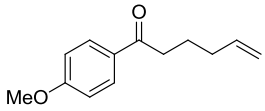
$R_f$ (9:1 hexane-ethyl acetate) = 0.83; $^1$H NMR: (400 MHz, $CDCl_3$) δ8.00 – 7.94 (2H, m), 7.59 – 7.73 (1H, m), 7.50 – 7.44 (2H, m), 5.83 (1H, ddd, J = 17.1, 10.2, 6.1 Hz), 5.06 (1H, ddd, *J* = 17.0 2.0, 1.5 Hz), 5.01 (1H, dd, *J* = 10.3, 2.0Hz), 2.99 (2H, t, *J* = 7.0 Hz), 2.17 (2H, dddd, *J* = 7.2, 6.8, 6.0, 0.5 Hz) 1.87 (2H, dt , *J* = 7.7, 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ200.2, 138.0, 137.1, 132.9, 128.5, 128.0, 115.3, 37.7, 33.2, 23.3; Characterisation in accordance with literature data.[69]

**1-(*p*-tolyl)hex-5-en-1-one (3b)**



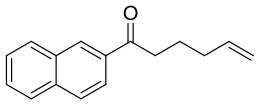

The title compound was prepared according to general procedure D from **1b** (57.3 mg, 0.178 mmol) and KHMDS (0.5 M in toluene) (106 mg, 0.534 mmol) in THF (3.6 mL) which following conversion to the ketone and column chromatography (1% EtOAc/hexane) afforded **3b** as a colorless oil (24.6 mg, 73%). $R_f$ (9:1 hexane-ethyl acetate) = 0.57; $^1$H NMR: (400 MHz, $CDCl_3$) δ7.89 – 7.84 (2H, m), 7.29 – 7.24 (2H, m), 5.83 (1H, m), 5.05 (1H, ddd, *J* = 17.0, 3.5, 1.5 Hz), 5.00 (1H, ddd, *J* = 10.3, 2.0, 1.2 Hz), 2.96 (2H, t, *J* = 7.3 Hz), 2.41 (3H, s), 2.16 (2H, qt, *J* = 8.6, 1.3 Hz), 1.85 (2H, dt, *J* = 7.5, 7.3 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ199.8, 143.6, 138.1, 134.6, 129.2, 128.1, 115.2, 37.6, 33.2, 23.4, 21.6; Characterisation in accordance with literature data.[69]

**1-(4-methoxyphenyl)hex-5-en-1-one (3c)**



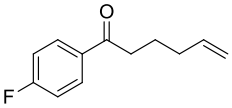

The title compound was prepared according to general procedure D from **1c** (49.9mg, 0.147 mmol) and KHMDS (0.5 M in toluene) (82.0 mg, 0.441 mmol) in THF (3.0 mL) which following conversion to the ketone and column chromatography (1% EtOAc/hexane) afforded **3c** as a colorless oil (26.9 mg, 90%). $R_f$ (9:1 hexane-ethyl acetate) = 0.42; $^1$H NMR: (400 MHz, $CDCl_3$) δ7.95 (2H, m), 6.94 (2H, m), 5.83 (1H, m), 5.05 (1H, ddd, *J* = 17.1, 2.0, 1.5 Hz), 5.00 (1H, ddd, *J* = 10.3, 2.0, 1.3 Hz), 3.87 (3H, s), 2.93 (2H, t, *J* = 7.3 Hz), 2.16 (2H, br dd, *J* = 7.3, 1.2 Hz), 1.85 (2H, dt, *J* = 7.6, 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ198.4, 163.3, 138.1, 130.3, 130.2, 115.7, 113.7, 55.4, 37.4, 33.2, 23.6; ; Characterisation in accordance with literature data.[70]

**1-(naphthalen-2-yl)hex-5-en-1-one (3d)**



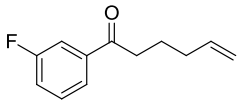
The title compound was prepared according to general procedure D from **1d** (50.2 mg, 0.140 mmol) and KHMDS (0.5 M in toluene) (83.8 mg, 0.420 mmol) in THF (2.8 mL) which following conversion to the ketone and column chromatography (2% EtOAc/hexane) afforded **3d** as a colorless oil (17.2 mg, 55%). $R_f$ (9:1 hexane-ethyl acetate) = 0.72; $^1$H NMR: (400 MHz, $CDCl_3$) δ8.48 (1H, m), 8.06 – 8.02 (1H, m), 8.00 – 7.96 (1H, m), 7.92 - 7.86 (2H, m), 7.64 – 7.54 (2H, m), 5.87 (1H, m), 5.09 (1H, ddd, *J* = 17.0, 2.0, 1.5 Hz), 5.03 (1H, ddd, *J* = 10.3, 2.0, 1.2 Hz), 3.13 (2H, d, *J* = 7.3 Hz), 2.22 (2H, m), 1.93 (2H, dt, *J* = 7.4, 7.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ200.2, 138.1, 135.5, 134.4, 132.5, 129.6, 129.5, 128.4, 128.3, 127.7, 126.7, 123.9, 115.3, 37.7, 33.2, 23.5; Characterisation in accordance with literature data.[71]

**1-(4-fluorophenyl)hex-5-en-1-one (3e)**



The title compound was prepared according to general procedure D from **1e** (54.5 mg, 0.167 mmol) and KHMDS (0.5 M in toluene) (99.9 mg, 0.501 mmol) in THF (3.3 mL)which following conversion to the ketone and column chromatography (4:1 hexane/DCM) afforded **3e** as a colorless oil (15.6 mg, 49%). $R_f$ (9:1 hexane-ethyl acetate) = 0.74; $^1$H NMR: (400 MHz, $CDCl_3$) δ8.02 – 7.96 (2H, m), 7.17 – 7.10 (2H, m), 5.83 (1H, m), 5.03 (2H, m), 2.96 (2H, t, *J* = 7.3 Hz), 2.16 (2H, br dd, *J* = 7.2, 1.2 Hz), 1.86 (2H, dt, *J* = 7.6, 7.1 Hz), $^{13}$C NMR (100 MHz, $CDCl_3$) δ198.6, 165.6 (d, $J_{C-F}$ = 253 Hz), 138.0, 133.5 (d, $J_{C-F}$ = 2.9 Hz), 130.6 (d, $J_{C-F}$ = 9.1 Hz), 115.6 (d, $J_{C-F}$ = 21.5 Hz), 115.4, 37.6, 33.1, 22.2 ; Characterisation in accordance with literature data.[70]

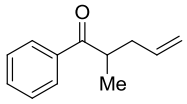
**1-(3-fluorophenyl)hex-5-en-1-one (3f)**




The title compound was prepared according to general procedure D from **1f** (51.6 mg, 0.159 mmol) and KHMDS (0.5 M in toluene) (95 mg, 0.477 mmol) in THF (3.2 mL) which following conversion to the ketone and column chromatography (2% EtOAc/hexane) afforded **3f** as a colorless oil (23.8 mg, 78%).

Rf (9:1 hexane-ethyl acetate) = 0.83; $^{1}$H NMR: (400 MHz, $CDCl_3$) δ7.76 – 7.73 (1H, m), 7.66 – 7.62 (1H, m), 7.48 – 7.41 (1H, m), 7.29 – 7.23 (1H, m), 5.83 (1H, m), 5.04 (2H, m), 2.97 (2H, t, $J$ = 7.3 Hz), 2.17 (2H, dr dd, $J$ = 7.3 Hz), 1.86 (2H, dt, $J$ = 7.7, 7.1 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ199.9, 162.9 (d, $J_{C\text{-}F}$ = 246 Hz), 139.2 (d, $J_{C\text{-}F}$ = 6.2 Hz), 137.9, 130.2 (d, $J_{C\text{-}F}$ = 7.6 Hz), 123.7 (d, $J_{C\text{-}F}$ = 2.9 Hz), 119.9 (d, $J_{C\text{-}F}$ = 21.1 Hz), 115.4, 114.7 (d, $J_{C\text{-}F}$ =22.2 Hz), 37.8, 33.0, 23.1; Characterisation in accordance with literature data.[71]

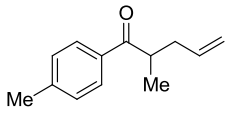
**2-methyl-1-phenylpent-4-en-1-one (5a)**




The title compound was prepared according to general procedure E from **1a** (54.4 mg, 0.176 mmol) and potassium *t*-butoxide (9.9 mg, 0.088 mmol) in THF (1.5 mL) which following conversion to the ketone and column chromatography (0.25% $Et_2O$, 0.25% THF in pentane) afforded **5a** as a colorless oil (23.1 mg, 75%).

$R_f$ (1% $Et_2O$ in hexane) = 0.40; IR: $\nu_{max}$ (thin film) / cm$^{-1}$ 3420, 2975, 2931, 1680, 1607, 1240, 1205, 1182, 974, 827, 748; $^{1}$H NMR: (400 MHz, $CDCl_3$) δ7.99 – 7.94 (2H, m), 7.60 – 7.54 (1H, m), 7.51 – 7.45 (2H, m), 5.80 (1H, m), 5.09 – 5.00 (2H, m), 3.55 (1H, td, $J$ = 13.8, 7.0 Hz), 2.57 (1H, dtt, $J$ = 14.1, 6.5, 1.5 Hz), 2.21 (1H, dtt, $J$ = 14.3, 7.3, 1.2 Hz), 1.22 (3H, d, $J$ = 6.8 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ201.6, 136.5, 135.8, 132.9, 128.6, 128.3, 116.7, 40.4, 37.6, 17.0; HRMS (EI+) Calcd. for $C_{12}H_{14}O$ $[M]^+$ 174.1045. Found 174.1051. Characterisation in accordance with literature data.[72]

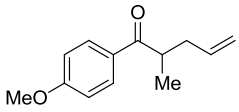
**2-methyl-1-(*p*-tolyl)pent-4-en-1-one (5b)**




The title compound was prepared according to general procedure E from **1b** (62.0 mg, 0.192 mmol) and potassium *t*-butoxide (10.8 mg, 0.096 mmol) in THF (1.5 mL) which following conversion to the ketone and column chromatography (0.25% $Et_2O$, 0.25% THF in pentane) afforded **5b** as a colorless oil (26.7 mg, 74%).

$R_f$ (5% $Et_2O$ in pentane) = 0.54; $^1H$ NMR: (400 MHz, $CDCl_3$) δ7.89 – 7.85 (2H, m), 7.30 – 7.25 (2H, m), 5.79 (1H, m), 5.09 – 4.99 (2H, m), 3.52 (1H, td, *J* = 13.6, 6.8 Hz), 2.56 (1H, ddd, *J* = 14.0, 6.5, 1.2), 2.42 (3H, s), 2.20 (1H, dtt, *J* = 14.3, 7.3, 1.2 Hz), 1.20 (3H, d, *J* = 6.8 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ203.2, 143.6, 135.9, 133.9, 129.3, 128.4, 116.6, 40.4, 37.7, 21.6, 17.1; Characterisation in accordance with literature data.[72]

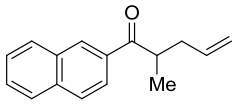
**1-(4-methoxyphenyl)-2-methylpent-4-en-1-one (5c)**




The title compound was prepared according to a modified general procedure E, where the reaction was carried out in an argon purged 5 mL sealed tube at 100 $^oC$ from **1c** (43.1 mg, 0.127 mmol) and potassium *t*-butoxide (7.0 mg, 0.062 mmol) in THF (1 mL). Following conversion to the ketone and column chromatography (2% THF in hexane) afforded **5c** as a colorless oil (25.7 mg, 99%).

$R_f$ (1% $Et_2O$ in hexane) = 0.56; $^1H$ NMR: (400 MHz, $CDCl_3$) δ7.98 – 7.94 (2H, m), 6.97 – 6.93 (2H, m), 5.79 (1H, m), 5.05 (1H, ddd, *J* = 16.8, 3.2, 1.5 Hz), 5.01 (1H, ddd, *J* = 10.0, 1.8, 1.2 Hz), 3.88 (3H, s), 3.50 (1H, td, *J* = 13.9, 6.8 Hz), 2.55 (1H, dtt, *J* = 14.3, 5.0, 1.3 Hz), 2.20 (1H, dtt, *J* = 14.1, 6.3, 1.2 Hz), 1.20 (3H, d, *J* = 6.9 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ202.1, 163.4, 136.0, 130.5, 129.4, 116.5, 113.8, 55.4, 40.0, 37.8, 17.2; Characterisation in accordance with literature data.[73]

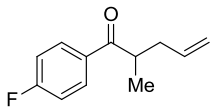
**2-methyl-1-(naphthalen-2-yl)pent-4-en-1-one (5d)**




The title compound was prepared according to general procedure E from **1d** (49.1 mg, 0.137 mmol) and potassium *t*-butoxide (7.7 mg, 0.069 mmol) in THF (1.0 mL) which following conversion to the ketone and column chromatography (0.5% $Et_2O$, 0.5% THF in pentane) afforded **5d** as a colorless oil (18.1 mg, 59%).

$R_f$ (5% $Et_2O$ in pentane) = 0.62; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 3425, 1677, 1187, 1122, 915, 760; $^1H$ NMR: (400 MHz, $CDCl_3$) δ8.48 (1H, m), 8.07 – 7.87 (4H, m), 7.64 – 7.53 (2H, m), 5.84 (1H, m), 5.09 (1H, m), 5.04 (1H, m), 3.73 (1H, td, *J* = 13.7, 6.8 Hz), 2.64 (1H, dtt, *J* = 14.3, 6.3, 1.5 Hz), 2.28 (1H, dtt, *J* = 14.3, 7.2, 1.3 Hz), 1.29 (3H, d, *J* = 6.8 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ203.6, 135.8, 135.5, 133.8, 132.6, 129.7, 129.6, 128.5, 128.4, 127.7, 126.7, 124.2, 116.8, 40.5, 37.8, 17.2; HRMS (ES+) Calcd. for $C_{16}H_{17}O$ $[M+H]^+$ 225.1279. Found 225.1273.

**1-(4-fluorophenyl)-2-methylpent-4-en-1-one (5e)**

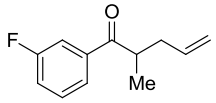



The title compound was prepared according to general procedure E from **1e** (55.1 mg, 0.163 mmol) and potassium *t*-butoxide (9.1 mg, 0.082 mmol) in THF (1.6 mL) which following conversion to the ketone and column chromatography (0.25% $Et_2O$, 0.25% THF in pentane) afforded an inseparable mixture of **5e** (10.7 mg, 34%) and regioisomeric product **3e** (11.3 mg, 36%) as a colorless oil.

$R_f$ (1% $Et_2O$ in hexane) = 0.39; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 3066, 2976, 2932, 1684, 1598, 1409, 1233, 1157, 978, 846, 759; $^1H$ NMR: (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (2H, m), 7.17 – 7.10 (2H, m), 5.77 (1H, m), 5.04 (2H, m), 3.49 (1H, td, *J* = 13.6, 6.8 Hz), 2.55 (1H, ddd, *J* = 13.0, 6.5, 1.2 Hz), 2.20 (1H, ddd, *J* = 14.6, 7.5, 1.2 Hz), 1.20 (3H, d, *J* = 7.0 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ202.0, 165.6 (d, $J_{C-F}$

= 252 Hz), 135.6, 132.8 (d, $J_{C-F}$ = 3.3 Hz), 130.8 (d, $J_{C-F}$ = 9.12 Hz), 116.9, 115.7 (d, $J_{C-F}$ = 21.9 Hz), 40.4, 37.6, 17.0; HRMS (ES+) Calcd. for $C_{12}H_{13}FO$ $[M + 2H]^+$ 194.1107. Found 194.1132.

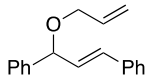
**1-(3-fluorophenyl)-2-methylpent-4-en-1-one (5f)**




The title compound was prepared according to general procedure E from **1f** (52.1 mg, 0.160 mmol) and potassium *t*-butoxide (9.0 mg, 0.080 mmol) in THF (1.2 mL) which following conversion to the ketone and column chromatography (0.25% $Et_2O$, 0.25% THF in pentane) afforded **5f** as a colorless oil (15.4 mg, 50%).

$R_f$ (1% $Et_2O$ in pentane) = 0.65; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 3076, 2977, 2934, 1688, 1588, 1441, 1255, 991, 917, 750; $^1H$ NMR: (400 MHz, $CDCl_3$) δ7.75 – 7.72 (1H, m), 7.65 – 7.61 (1H, m), 7.49 – 7.43 (1H, m), 7.30 – 7.24 (1H, m), 5.78 (1H, m), 5.05 (2H, m), 3.48 (1H, td, *J* = 13.2, 6.5 Hz), 2.56 (1H, dtt, *J* = 11.5, 6.4, 1.2 Hz), 2.21 (1H, dtt, *J* = 14.3, 7.3, 1.2 Hz), 1.22 (3H, d, *J* = 6.8 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ202.3, 162.9 (d, $J_{C-F}$ = 246 Hz), 138.6 (d, $J_{C-F\ F}$ = 5.8 Hz), 135.5, 130.2 (d, $J_{C-F}$ = 7.3 Hz), 123.9 (d, $J_{C-F}$ = 2.9 Hz), 119.8 (d, $J_{C-F}$ = 21.1 Hz), 117.0, 115.0 (d, $J_{C-F}$ = 21.9 Hz), 40.7, 37.5, 16.9; HRMS (ES+) Calcd. for $C_{12}H_{13}FNaO$ $[M+Na]^+$ 215.0848. Found 215.0861.

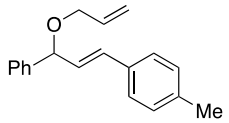
**(*E*)-1-Allyoxy-1,3-diphenyl-prop-2-ene (11a)**




Three drops of conc. $H_2SO_4$ was added to a THF solution of (*E*)-1,3-diphenylpropen-2-ol (837 mg, 3.99 mmol) and allyl alcohol (290 mg, 5.0 mmol). The solution was allowed to stir at room temperature for 1 hour. The reaction was diluted with distilled water (20 mL), extracted with $Et_2O$ (3 x 20 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude product was loaded onto a column and chromatographed (2% EtOAc in hexane) to afford **11a** (847 mg, 85%) as a colorless oil.

$R_f$ (10% EtOAc in hexane) = 0.91; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.34 (6H, m), 7.34 – 7.24 (3H, m), 7.24 – 7.18 (1H, m), 6.62 (1H, d, *J* = 16.1 Hz), 6.30 (1H, dd, *J* = 15.6, 6.5 Hz), 5.96 (1H, m), 5.31 (1H, m), 5.20 (1H, m), 4.98 (1H, d, *J* = 7.0 Hz), 4.03 (2H, m); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 141.2, 136.6, 134.9, 131.5, 130.3, 128.6, 127.8, 127.7, 127.1, 127.0, 126.6, 117.0, 81.8, 69.3. Characterisation in accordance with literature data.[74]

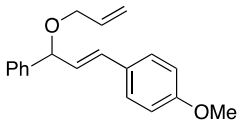
**(*E*)-1-Allyoxy-1-phenyl-3-(4-methylphenyl)prop-2-ene (11b)**




The title compound was prepared according to general procedure C, from (*E*)-1-phenyl-3-(*p*-tolyl)prop-2-en-1-ol[66] (219 mg, 0.97 mmol) using allyl bromide (0.17 mL, 1.94 mmol) and NaH (78.0 mg, 1.94 mmol). The crude product was applied directly onto the top of a column and chromatographed (2% EtOAc in hexane) to afford **11b** (219 mg, 86%) as a colorless oil.

$R_f$ (10% EtOAc in hexane) = 0.53; IR $\nu_{max}$ (thin film) / $cm^{-1}$ 3025, 2923, 2854, 1512, 1495, 1449, 1260, 1071, 966, 922, 745; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.25 (7H, m), 7.10 (2H, d, J = 8.2Hz), 6.58 (1H, d, J = 15.4 Hz), 6.24 (1H, dd, J = 16.1, 7.2 Hz), 5.97 (1H, ddd, J = 17.2, 10.4, 5.6 Hz), 5.31 (1H, ddd, J = 17.4, 1.6, 1.5 Hz), 5.20 (1H, ddd, J = 10.4, 1.4, 1.4 Hz), 4.97 (1H, d, J = 7.2 Hz), 4.06 (1H, ddd, J = 12.8, 5.5, 1.6 Hz), 4.01 (1H, ddd, J = 13.2, 5.3, 1.5Hz, 2.32 (3H, s); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 141.3, 137.6, 134.9, 133.8, 131.5, 129.2,129.2, 128.5, 127.6, 126.9, 126.5, 116.9, 81.9, 69.2, 21.2 HRMS (ES+) Calcd. for $C_{19}H_{20}NaO$ $[M + Na]^+$ 287.1412. Found 287.1426.

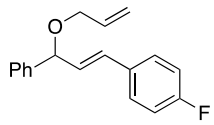
**(*E*)-1-Allyoxy-1-phenyl-3-(4-methoxyphenyl)prop-2-ene (11c)**



The title compound was prepared according to general procedure C, from (*E*)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-ol[75] (142 mg, 0.6 mmol) using allyl bromide (0.10 mL, 1.20 mmol) and NaH (60% suspension in mineral oil; unwashed) (48.0 mg, 1.20 mmol). The crude product was applied directly onto the top of a column and chromatographed (1% EtOAc in hexane) to afford **11c** (84 mg, 50%) as a colorless oil.

$R_f$ (10% EtOAc in hexane) = 0.30; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2923, 1607, 1511, 1452, 1252, 750; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 7.34 – 7.15 (7H, m), 6.75 – 6.73 (2H, m), 6.47 (1H, d, J = 15.8 Hz), 6.08 (1H, dd, J = 15.6, 7.2 Hz), 5.89 (1H, ddd, J = 17.2, 10.4, 5.6 Hz), 5.23 (1H, ddd, J = 17.2, 1.6 Hz), 5.11 (1H, ddd, J = 10.4, 1.6 Hz), 4.88 (1H, dd, J = 7.2 Hz), 3.98 (1H, ddd, J = 12.8, 5.2, 1.6 Hz), 3.92 (1H, ddd, J = 12.8, 5.6, 1.6 Hz), 3.70 (3H, s); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 158.3, 140.4, 130.9, 130.0, 128.3, 127.5, 127.1, 126.8, 126.6, 125.8, 115.8, 112.9, 80.9, 68.2, 54.2; HRMS (ES+) Calcd. for $C_{19}H_{21}O_2$ $[M + H]^+$ 281.1542. Found 281.1547.

### (*E*)-1-Allyoxy-1-phenyl-3-(4-fluorophenyl)prop-2-ene (11d)

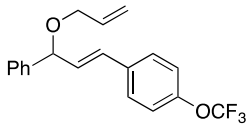



The title compound was prepared according to general procedure C, from (*E*)-3-(4-fluorophenyl)-1-phenylprop-2-en-1-ol **S1** (274 mg, 1.2 mmol) using allyl bromide (0.21 mL, 2.40 mmol) and NaH (60% suspension in mineral oil; unwashed) (96.0 mg, 2.40 mmol). The crude product was applied directly onto the top of a column and chromatographed (1% EtOAc in hexane) to afford **11d** (221 mg, 69%) as a light yellow oil.

$R_f$ (10% EtOAc in hexane) = 0.63; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2924, 1508, 1275, 1227, 750; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 7.41 – 7.27 (7H, m), 6.99 -6.95 (2H, m), 6.59 – 6.55 (1H, d, J = 15.6 Hz), 6.22 (1H, dd, J = 16.0, 6.8 Hz), 5.97 (1H, ddd, J = 17.2, 10.4, 5.6Hz), 5.31 (1H, ddd, J = 17.6, 1.6 Hz), 5.20 (1H, ddd, J = 10.4, 1.2 Hz), 4.97 (1H, d, J = 7.2 Hz), 4.04 (1H, ddd, J = 13.2, 5.6, 1.2 Hz), 4.00 (1H,

ddd, J =13.2, 5.2, 1.6 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 162.4 (d, $J_{C-F}$ = 246.0 Hz), 141.1, 134.8, 132.8 (d, $J_{C-F}$ = 3.0 Hz), 130.2 (m), 128.6, 128.1, 128.0 (d, $J_{C-F}$ = 40.0), 126.9, 117.0, 115.6, 115.3, 81.7, 69.3; HRMS (ES+) Calcd. for $C_{18}H_{18}FO$ $[M + H]^+$ 269.1347. Found 269.1342.

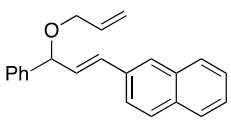
**(*E*)-1-Allyoxy-1-phenyl-3-(4-trifluoromethoxyphenyl)prop-2-ene (11e)**




The title compound was prepared according to general procedure C, from (E)-1-phenyl-3-(4-(trifluoromethoxy)phenyl)prop-2-en-1-ol **S2** (164 mg, 0.560 mmol) using allyl bromide (0.10 mL, 1.12 mmol) and NaH (60% suspension in mineral oil; unwashed) (45.0 mg, 1.12 mmol). The crude product was applied directly onto the top of a column and chromatographed (2% EtOAc in hexane) to afford **11e** (127 mg, 68%) as a yellow oil.

$R_f$ (10% EtOAc in hexane) = 0.28; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2926, 1508, 1260, 1220, 1166, 700; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.27 (7H, m), 7.19 – 7.09 (2H, m), 6.60 (1H, d, J = 16.0 Hz), 6.29 (1H, d, J = 16.0, 6.8 Hz), 5.96 (1H, ddd, J = 17.2, 10.4, 5.6 Hz), 5.31 (1H, ddd, J = 17.2, 1.6 Hz), 5.21 (1H, ddd, J = 10.4, 1.2), 4.98 (1H, d, J = 6.8 Hz), 4.07 – 3.98 (2H, m); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 148.6 (q, $J_{C-F}$ = 245.1 Hz),, 140.9, 135.4, 134.7, 131.5, 129.7, 128.6, 127.9, 127.8, 127.0, 121.0 (q, $J_{C-F}$ = 1.0 Hz), 117.1, 81.5, 69.4; 357.1078 HRMS (ES) Calcd. for $C_{19}H_{17}F_3Na\ O_2$ $[M + Na]^+$ 357.1078. Found 357.1102.

**(*E*)-1-Allyoxy-1-phenyl-3-(2-naphthyl)prop-2-ene (11f)**

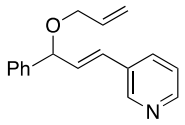



The title compound was prepared according to general procedure C, from (*E*)-3-(naphthalen-2-yl)-1-phenylprop-2-en-1-ol **S3** (263 mg, 1.01 mmol) using allyl bromide (0.18 mL, 2.02 mmol) and NaH

(60% suspension in mineral oil; unwashed) (81.0 mg, 2.02 mmol). The crude product was applied directly onto the top of a column and chromatographed (1% EtOAc in hexane) to afford **11f** (234 mg, 77%) as a colorless oil.

$R_f$ (10% EtOAc in hexane) = 0.60; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2854, 1451, 1066, 969, 775, 771, 619; $^1$H-NMR (400 MHz, $CDCl_3$): δ 8.11 – 8.09 (1H, m), 7.85 – 7.75 (2H, m), 7.60 – 7.28 (10H, m,) 6.35 (1H, dd, J = 16.0, 6.8Hz), 6.01 (1H, ddd, J = 17.2, 10.4, 5.6 Hz), 5.36 (1H, ddd, J = 17.2,1.6 Hz), 5.23 (1H, ddd, 1H, J = 10.4, 1.2 Hz), 5.12 (1H, d, J = 6.8 Hz), 4.14 (1H, ddd, J = 13.6, 5.6, 1.2 Hz), 4.09 (1H, ddd, J = 11.2, 5.6, 1.6 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 141.2, 134.9, 134.4, 133.6, 133.5, 131.2, 128.6, 128.6, 128.5, 128.1,127.8, 127.0, 126.1, 125.8, 125.6, 124.0, 123.7, 117.0, 81.9, 69.4; HRMS (ES+) Calcd. for $C_{22}H_{21}O$ $[M + H]^+$ 301.1592.. Found 301.1576.

**(*E*)-1-Allyoxy-1-phenyl-3-(pyridin-3-yl)prop-2-ene (11g)**

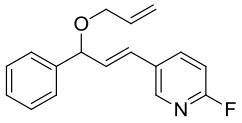



The title compound was prepared according to general procedure C, from (*E*)-1-phenyl-3-(pyridin-3-yl)prop-2-en-1-ol **S4** (113 mg, 0.53 mmol) using allyl bromide (0.09 mL, 1.06 mmol) and NaH (60% suspension in mineral oil; unwashed) (43.0 mg, 1.06 mmol). The crude product was applied directly onto the top of a column and chromatographed (20% EtOAc in hexane) to afford **11g** (94.2 mg, 90%) as a light yellow oil.

$R_f$ (50% Et2O in hexane) = 0.19; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 3028, 1422, 1070, 967, 751, 700; $^1$H-NMR (400 MHz, $CDCl_3$): δ 8.59 (1H, s, br), 8.46 (1H, d, *J* = 3.8 Hz), 7.70 -7.67 (1H, m), 7.41 – 7.24 (5H, m), 7.23 – 7.18 (1H, m), 6.62 (1H, d, *J* = 16.0 Hz), 6.39 (1H, dd, *J* = 16.0, 8.4 Hz), 5.97 (1H, ddt, *J* = 18.8, 12.0, 3.6 Hz), 5.31 (1H, dq, J = 17.4, 1.6 Hz) 5.21 (1H, dq, *J* = 10.4, 1.2 Hz), 5.01 (1H, d, *J* = 6.8 Hz), 4.03 (2H, dt, *J* = 5.6, 1.4 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 148.8, 148.6, 140.6, 134.6, 132.9, 132.8,

132.3, 128.7, 128.0, 127.4, 127.0, 123.4, 117.2, 81.4, 69.4; HRMS (ES+) Calcd. for $C_{17}H_{18}NO$ $[M + H]^+$ 252.1388. Found 252.1393.

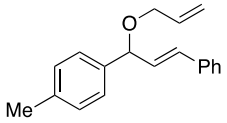
### (*E*)-1-Allyoxy-1-phenyl-3-(2-fluoropyridin-3-yl)prop-2-ene (11h)




The title compound was prepared according to general procedure C, from *(E)*-1-phenyl-3-(2-fluoropyridin-3-yl)prop-2-enol **S5** (163 mg, 0.71 mmol) using allyl bromide (0.13 mL, 1.42 mmol) and NaH (60% suspension in mineral oil; unwashed) (57.0 mg, 1.42 mmol). The crude product was applied directly onto the top of a column and chromatographed (10% EtOAc in 60:40 petroleum ether) to afford **11h** (139 mg, 73%) as a yellow oil.

$R_f$ (10% EtOAc in 60:40 petroleum:ether) = 0.40; $^1$H-NMR (300 MHz, $CDCl_3$) δ 8.17 (1H, d, *J* = 2.4 Hz), 7.81 (1H, td, *J* = 8.1, 2.6 Hz), 7.41 – 7.28 (6H, m), 6.88 (1H, dd, *J* = 8.7, 3.0 Hz), 6.60 (1H, d, *J* = 16.1 Hz), 6.30 (1H, dd, *J* = 15.9, 6.3 Hz), 6.03 – 5.89 (1H, m), 5.35 – 5.27 (1H, m), 5.25 – 5.19 (1H, m), 5.02 – 4.98 (1H, m), 4.03 – 3.99 (2H, m): $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 146.2, 146.1, 139.3 (d, $J_{C-F}$ = 237 Hz), 138.0, 134.6, 132.6 (d, $J_{C-F}$ = 1.0 Hz), 128.7, 128.0, 127.0, 126.7, 125.9, 117.2, 109.4 (d, $J_{C-F}$ = 38.0 Hz), 81.3, 69.4; HRMS (ES+) Calcd. for $C_{17}H_{17}NFO$ $[M + H]^+$ 270.1294. Found 270.1298.

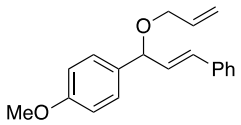
### *(E)*-1-Allyoxy-1-(2-methoxyphenyl)-3-phenylprop-2-ene (11i)




The title compound was prepared according to general procedure C, from *(E)*-3-phenyl-1-(*p*-tolyl)prop-2-en-1-ol[76] (239 mg, 1.07 mmol) using allyl bromide (0.18 mL, 2.14 mmol) and NaH (60% suspension in mineral oil; unwashed) (86.0 mg, 2.14 mmol). The crude product was applied directly onto the top of a column and chromatographed (2% EtOAc in hexane) to afford **11i** (226 mg, 80%) as a colorless oil.

$R_f$ (10% EtOAc in hexane) = 0.68 ; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.28 (2H, m), 7.23 – 7.08 (7H, m), 6.53 (1H, d, J = 16.0 Hz), 6.22 (1H, dd, J = 16.0, 6.8 Hz), 5.89 (1H, ddd, J = 17.2, 10.4, 5.6 Hz), 5.23 (1H, ddd, 1H, J = 17.0, 1.7, 1.6 Hz), 5.11 (1H, ddd, 1H, J = 10.4, 1.4, 1.2 Hz), 4.88 (1H, d, J = 7.2 Hz), 3.97 (1H, ddd, J = 12.8, 5.6, 1.6 Hz), 3.92 (1H, ddd, J = 12.8, 5.6, 1.6 Hz), 2.27 (3H, s) $^{13}$C NMR (100 MHz, $CDCl_3$): δ 137.1, 136.4, 135.7, 133.9, 130.1, 129.5, 128.2, 127.5, 126.6, 125.9, 125.6, 115.8, 80.6, 68.2, 20.1; Characterization in accordance with literature data.[33]

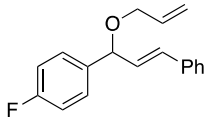
**(*E*)-1-Allyoxy-1-(4-methoxyphenyl)-3-phenylprop-2-ene (11j)**




The title compound was prepared according to general procedure C, from (*E*)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-ol[77] (463 mg, 1.93 mmol) using allyl bromide (0.33 mL, 3.86 mmol) and NaH (60% suspension in mineral oil; unwashed) (155 mg, 3.86 mmol). The crude product was applied directly onto the top of a column and chromatographed (2% EtOAc in hexane) to afford **11j** (448 mg, 83%) as a colorless oil.

$R_f$ (10% EtOAc in hexane) = 0.3; IR: $\nu_{max}$ (thin film) / cm$^{-1}$ 2835, 1610, 1511, 1248, 830, 693; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.19 (7H, m), 6.90 – 6.88 (2H, m), 6.59 (1H, d, *J* = 16.0 Hz), 6.30 (1H, dd, *J* = 16.0, 6.8 Hz), 5.96 (1H, ddd, *J* = 17.2, 10.4, 5.2) 5.30 (1H, ddd, *J* = 17.2, 1.6), 5.19 (1H, ddd, *J* = 10.4, 1.2 Hz), 4.94 (1H, d, J = 6.8 Hz), 4.04 (1H, ddd, J = 12.8, 5.2, 1.6 Hz), 3.98 (1H, ddd, J = 13.2, 5.6, 1.6 Hz) 3.80 (3H, s); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 159.2, 136.7, 135.0, 133.3, 131.1, 130.5, 128.5, 128.2, 127.7, 126.6, 116.9, 114.0, 81.3, 69.2, 55.3; Calcd. for $C_{19}H_{21}O_2$ $[M + H]^+$ 281.1542. Found 281.1533.

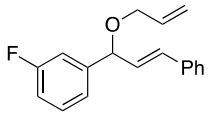
**(*E*)-1-Allyoxy-1-(4-fluorophenyl)-3-phenylprop-2-ene (11k)**



The title compound was prepared according to general procedure C, from (*E*)-1-(4-fluorophenyl)-3-phenylprop-2-en-1-ol[78](447 mg, 1.96 mmol) using allyl bromide (0.34 mL, 3.92 mmol) and NaH (60% suspension in mineral oil; unwashed) (157 mg, 3.92 mmol). The crude product was applied directly onto the top of a column and chromatographed (2% EtOAc in hexane) to afford **11k** (447 mg, 85%) as a light yellow oil.

$R_f$ (20% EtOAc in hexane) = 0.71; IR $\nu_{max}$ (thin film) / $cm^{-1}$ 3060, 3026, 2924, 2855, 1646, 1603, 1508, 1449, 1409, 1294, 1222, 1155, 1071, 1014, 968, 925, 833, 745; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.21 (7H, m), 7.06 – 7.02 (2H, m), 6.60 (1H, d, J = 16.0 Hz), 6.26 (1H, dd, J = 15.9, 6.8 Hz), 5.96 (1H, ddd, J = 17.2, 10.4, 5.6 Hz), 5.30 (1H, ddd, J = 17.2, 1.3 Hz) 5.20 (1H, ddd, 1H, J = 10.4, 1.3 Hz), 4.96 (1H, d, J = 7.0 Hz), 4.06 (1H, ddd, J = 12.8, 5.3, 1.3 Hz), 4.00 (1H, ddd, J = 12.8, 5.2, 1.6 Hz) $^{13}$C NMR (100 MHz, $CDCl_3$): δ 162.3 (d, $J_{C-F}$ = 244.0 Hz), 137.0 (d, $J_{C-F}$ = 3.0 Hz), 136.5, 134.7, 131.7, 130.0 (d, $J_{C-F}$ = 1.0Hz), 128.6, 128.5, 127.8, 126.6, 117.0, 115.3 (d, $J_{C-F}$ =21.0 Hz), 81.0, 69.2; HRMS (ES+) Calcd. for $C_{18}H_{18}FO$ $[M + 2H]^+$ 270.1420. Found 270.1447.

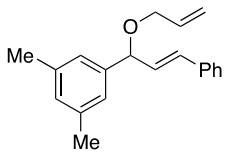
**(*E*)-1-Allyoxy-1-(3-fluorophenyl)-3-phenylprop-2-ene (11l)**



The title compound was prepared according to general procedure C, from (*E*)-1-(3-fluorophenyl)-3-phenylprop-2-en-1-ol **S6** (203 mg, 0.89 mmol) using allyl bromide (0.15 mL, 1.78 mmol) and NaH (60% suspension in mineral oil; unwashed) (71.2 mg, 1.78 mmol). The crude product was applied directly onto the top of a column and chromatographed (1% EtOAc in hexane) to afford **11l** (226 mg, 95%) as a colorless oil.

$R_f$ (10% EtOAc in hexane) = 0.62; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2924, 1591, 1486, 1070, 764, 692; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.13 (8H, m), 6.99 – 6.94 (1H, m), 6.62 (1H, d, J = 16.2 Hz), 6.24 (1H, dd, J = 16.0, 7.2 Hz), 5.96 (1H, ddd, J = 17.2, 10.4, 5.6 Hz), 5.32 (1H, ddd, 1H, J = 17.2, 1.6 Hz) 5.21 (1H, ddd, 1H, J = 10.4, 1.2 Hz), 4.97 (1H, d, J = 7.4 Hz), 4.08 (1H, ddd, J = 13.2, 5.8, 1.2 Hz), 4.02 (1H, ddd, J = 12.8, 5.6, 1.6 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 163.0 (d, $J_{C-F}$ = 244.0 Hz), 144.0 (d, $J_{C-F}$ = 7.0 Hz), 136.4, 134.6, 132.1, 130.0 (d, $J_{C-F}$ = 8.0Hz), 129.6, 128.6, 127.9, 126.7, 122.4 (d, $J_{C-F}$ = 3.0Hz), 117.2 114.5 (d, $J_{C-F}$ =22.0 Hz), 113.7 (d, $J_{C-F}$ = 21.0 Hz), 81.1 (d, $J_{C-F}$ = 2.0 Hz), 69.4; Calcd. for $C_{18}H_{18}OF$ $[M + H]^+$ 269.1342. Found 269.1342.

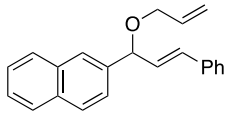
### *(E)*-1-Allyoxy-1-(3,5-dimethylphenyl)-3-phenylprop-2-ene (11m)




The title compound was prepared according to general procedure C, from (*E*)-1-(3,5-dimethylphenyl)-3-phenylprop-2-en-1-ol **S8** (149 mg, 0.430 mmol) using allyl bromide (0.075 mL, 0.860 mmol) and NaH (60% suspension in mineral oil; unwashed) (35.0 mg, 0.860 mmol). The crude product was applied directly onto the top of a column and chromatographed (2% EtOAc in hexane) to afford **11m** (122 mg, 70%) as a colorless oil.

$R_f$ (10% EtOAc in hexane) = 0.84; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2921, 1602, 1449, 1070, 966, 693; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.36 (2H, m), 7.29 – 7.25 (2H, m), 7.22 – 7.18 (1H, m), 7.02 – 7.00 (2H, m), 6.92 – 6.89 (1H, m), 6.61 (1H, d, J = 16.0 Hz), 6.29 (1H, dd, J = 16.0, 7.2 Hz), 5.97 (1H, ddd, J = 17.6, 10.6, 5.2 Hz), 5.30 (1H, ddd, J = 17.2, 1.2 Hz), 5.19 (1H, ddd, J = 10.8, 1.6, 1.6 Hz), 4.90 (1H, d, J = 6.8 Hz), 4.05 (1H, ddd, J = 13.2, 6.0, 1.2 Hz), 4.00 (1H, ddd, J = 13.2, 5.2, 1.6 Hz), 2.31 (6H,s) $^{13}$C NMR (100 MHz, $CDCl_3$): δ 141.1, 138.1, 136.8, 135.0, 131.2, 130.5, 129.4, 128.6, 127.7, 126.7, 124.7, 116.9, 81.9, 69.3, 21.4 ;HRMS (ES+) Calcd. for $C_{40}H_{44}O_2Na$ $[2M + Na]^+$ 579.3239 Found 579.3209.

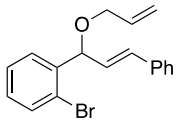
**(*E*)-1-Allyoxy-1-(2-naphthyl)-3-phenylprop-2-ene (11n)**




The title compound was prepared according to general procedure C, from (E)-1-(naphthalen-2-yl)-3-phenylprop-2-en-1-ol[79] (203 mg, 0.78 mmol) using allyl bromide (0.13 mL, 1.56 mmol) and NaH (60% suspension in mineral oil; unwashed) (63.0 mg, 1.56 mmol). The crude product was applied directly onto the top of a column and chromatographed (1% EtOAc in hexane) to afford **11n** (154 mg, 66%) as a light yellow oil.

$R_f$ (20% EtOAc in hexane) = 0.91; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2924, 1071, 819, 748, 692, 478; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 7.85 – 7.83 (4H, m), 7.54 – 7.20 (8H, m), 6.66 (1H, d, J = 15.6 Hz), 6.38 (1H, dd, J = 16.0, 6.8Hz), 6.00 (1H, ddd, J = 17.2, 10.4, 5.6 Hz), 5.33 (1H, ddd, 1H, J = 17.2, 2.1, 1.8 Hz), 5.22 (1H, ddd, 1H, J = 10.1, 1.2, 1.2 Hz), 5.16 (1H, d, J = 6.8 Hz), 4.10 (1H, ddd, J = 12.4, 5.8, 1.2 Hz), 4.01 (1H, ddd, J = 13.2, 5.4, 1.2 Hz) $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 138.6, 136.6, 134.8, 133.4, 133.1, 131.6, 130.2, 128.5, 128.4, 128.0, 127.7, 127.7, 126.6, 126.1, 125.9, 125.8, 125.0, 117.0, 81.8, 69.4; HRMS (ES+) Calcd. for $C_{22}H_{21}O$ $[M + H]^+$ 301.1592. Found 301.1576.

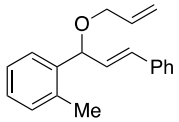
***(E)*-1-Allyoxy-1-(o-bromo)-3-phenylprop-2-ene (11o)**




The title compound was prepared according to general procedure C, from (E)-1-(2-bromophenyl)-3-phenylprop-2-en-1-ol[80] (238 mg, 0.82 mmol) using allyl bromide (0.14 mL, 1.64 mmol) and NaH (60% suspension in mineral oil; unwashed) (66.0 mg, 1.64 mmol). The crude product was applied directly onto the top of a column and chromatographed (1% EtOAc in hexane) to afford **11o** (220 mg, 81%) as a colorless oil.

$R_f$ (10% EtOAc in hexane) = 0.67; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2924, 1438, 1071, 965, 748, 693; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.59 (1H, dd, J = 7.6, 1.6 Hz), 7.54 (1H, dd, J = 7.6, 0.8 Hz), 7.38 – 7.12 (m, 7H), 6.69 (d, 1H, J = 15.6 Hz), 6.22 (dd, 1H, J = 16.0, 6.8 Hz), 5.97 (1H, ddd, J = 17.2, 10.4, 5.6 Hz), 5.42 (1H, d, J = 6.8 Hz), 5.32 (1H, ddd, J = 17.2, 3.5, 1.5 Hz), 5.21 (1H, ddd, J = 10.4, 3.1, 1.2 Hz), 4.08 – 3.99 (2H, m) $^{13}$C NMR (100 MHz, $CDCl_3$): δ 140.3, 136.6, 134.6, 132.8, 131.7, 129.1, 128.5, 128.5, 128.4, 127.9, 127.8, 126.7, 123.2, 117.2, 80.0, 69.6; HRMS (ES+) Calcd. for $C_{18}H_{18}BrO$ $[M + H]^+$ 329.0541. Found 329.0556.

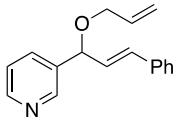
**(*E*)-1-Allyoxy-1-(o-tolyl)-3-phenylprop-2-ene (11p)**




The title compound was prepared according to general procedure C, from (*E*)-3-phenyl-1-(o-tolyl)prop-2-en-1-ol **S7**(442 mg, 1.97 mmol) using allyl bromide (0.34 mL, 3.94 mmol) and NaH (60% suspension in mineral oil; unwashed) (158 mg, 3.94 mmol). The crude product was applied directly onto the top of a column and chromatographed (1% EtOAc in 60:40 petroleum ether) to afford **11p** (466 mg, 90%) as a light yellow oil.

$R_f$ (10% EtOAc in 60:40 petroleum ether) = 0.85; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2925, 1449, 1276, 1071, 967, 750; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.49 (1H, m), 7.38 – 7.35 (2H, m), 7.30 – 7.14 (6H, m) 6.56 (1H, d, J = 16.2 Hz), 6.27 (1H, dd, J = 16.0, 5.6 Hz), 5.97 (1H, ddd, J = 17.2, 10.6, 5.6 Hz), 5.30 (1H, ddd, 1H, J = 17.4, 3.3, 1.6 Hz), 5.20 (1H, ddd, 1H, J = 10.4, 3.0, 1.3 Hz), 5.16 (1H, d, J = 7.0 Hz), 4.06 – 3.98 (2H, m), 2.36 (3H, s); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 138.9, 136.7, 135.7, 134.9, 131.4, 130.5, 129.3, 128.5, 127.7, 127.5, 126.7, 126.6, 126.3, 117.0, 78.8, 69.3, 19.3; HRMS (ES+) Calcd. for $C_{19}H_{21}O$ $[M + H]^+$ 265.1592. Found 265.1561.

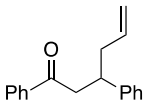
**(*E*)-1-Allyoxy-1-(pyridine-3-yl)-3-phenylprop-2-ene (11q)**



The title compound was prepared according to general procedure C, from (*E*)-3-phenyl-1-(pyridine-3-yl)prop-2-en-1-ol **S9** (172 mg, 0.82 mmol) using allyl bromide (0.14 mL, 1.64 mmol) and NaH (60% suspension in mineral oil; unwashed) (66.0 mg, 1.64 mmol). The crude product was applied directly onto the top of a column and chromatographed (20% EtOAc in hexane) to afford **11q** (174 mg, 84%) as a light yellow oil.

$R_f$ (50% Et2O in hexane) = 0.22 ; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2855, 1577, 1423, 1071, 750, 714; $^1$H-NMR (400 MHz, $CDCl_3$): δ 8.65 (1H, s), 8.55 – 8.54(1H, m), 7.76 – 7.73 (1H, m), 7.40 – 7.23 (6H, m), 6.65 (1H, d, J = 16.0 Hz), 6.26 (1H, dd, J = 16.4 , 7.2 Hz), 5.97 (1H, ddt, J = 17.2, 10.0, 6.0 Hz), 5.32 (dq, 1H, J = 17.6, 1.6 HZ), 5.23 (1H, dq, J = 10.4, 1.2 Hz), 5.03 (1H, d, J = 7.2 Hz), 4.11 (1H, ddt, J = 12.8, 5.6, 1.6 Hz) 4.03 (1H, ddt, J = 13.2, 5.6, 1.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 149.2, 148.7, 136.7, 136.2, 134.4, 134.4, 132.5, 129.2, 128.6, 128.1, 126.7, 123.5, 117.3, 79.5, 69.4; HRMS (ES+) Calcd. for $C_{17}H_{18}NO$ $[M + H]^+$ 252.1388. Found 252.1386.

**1,3-diphenylhex-5-en-1-one (13a)**

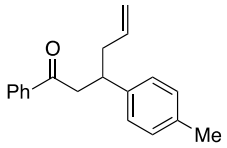


The title compound was prepared according to general procedure F from (*E)*-1-allyoxy-1,3-diphenylprop-2-ene **11a** (170 mg, 0.68 mmol), using 18-crown-6 (360 mg, 136 mmol) and potassium *t*-butoxide (153mg, 1.36 mmol). The crude product was applied directly onto the top of a column and chromatographed (1% $Et_2O$ in hexane) to afford **13a** (132 mg, 78%) as a colorless oil.

$R_f$ (2% $Et_2O$ in hexane) = 0.25; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.90 – 7.88 (2H, m), 7.54 – 7.51 (1H, m), 7.44 – 7.40 (2H, m), 7.30 – 7.15 (5H, m), 5.69 (1H, ddd, J = 17.2, 10.0, 7.2 Hz), 5.02 – 4.94 (2H, m), 3.51 – 3.44 (1H, m), 3.34 – 3.24 (2H, m), 2.52 – 2.40 (2H, m) $^{13}$C NMR (100 MHz, $CDCl_3$): δ

198.9, 144.4, 137.3, 136.3, 132.9, 128.5, 128.4, 128.0, 127.6, 126.4, 116.8, 44.6, 40.8, 40.7 Characterization in accordance with literature data.[81]

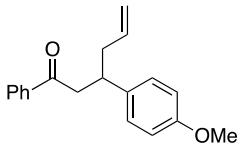
**1-phenyl-3-(4-methylphenyl)hex-5-en-1-one (13b)**




The title compound was prepared according to general procedure F from (*E)*-1-allyoxy-1-phenyl-3-(4-methylphenyl)-prop-2-ene **11b** (58.5 mg, 0.22 mmol), using 18-crown-6 (116 mg, 0.44 mmol) and potassium *t*-butoxide (49.0 mg, 0.44 mmol). The crude product was applied directly onto the top of a column and chromatographed (1% $Et_2O$ in60:40 petroleum ether) to afford **13b** (45.0 mg, 77%) as a colorless oil.

$R_f$ (4% $Et_2O$ in 60:40 petroleum ether) = 0.43; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2921, 1686, 1515, 1448, 815, 690; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 7.90 – 7.88 (2H, m), 7.55 – 7.50 (1H, m), 7.44 – 7.40 (2H, m), 7.13 – 7.07 (4H, m), 5.69 (ddd, 1H, J = 17.2, 12.8, 6.8 Hz), 5.02 – 4.94 (2H, m), 3.47 – 3.40 (1H, m), 3.32 – 3.21 (2H, m), 2.50 -2.38 (2H, m), 2.29 (3H, s) $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 199.0, 141.3, 137.3, 136.4, 135.8, 132.9, 129.1, 128.5, 128.1, 127.4, 116.7, 44.7, 40.8, 40.4, 21.0; HRMS (ES+) Calcd. for $C_{19}H_{21}O$ $[M + H]^+$ 265.1592. Found 265.1594. Characterization in accordance with literature data.[82]

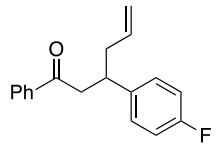
**1-phenyl-3-(4-methoxyphenyl)hex-5-en-1-one (13c)**




The title compound was prepared according to general procedure F from (*E)*-1-allyoxy-1-phenyl-3-(4-methoxyphenyl)-prop-2-ene **11c** (64.0 mg, 0.32 mmol), using 18-crown-6 (122 mg, 0.46 mmol) and potassium *t*-butoxide (52.0 mg, 0.46 mmol). The crude product was applied directly onto the top of a column and chromatographed (4% $Et_2O$ in hexane) to afford **13c** (47.6 mg, 74%) as a light yellow oil.

$R_f$ (8% $Et_2O$ in hexane) = 0.33: IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2920, 1248, 1179, 1685, 1036, 1513; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.90 – 7.87 (2H, m), 7.54 – 7.51 (1H, m), 7.44 – 7.40 (2H, m), 7.16 – 7.13 (2H, m), 6.83 – 6.80 (2H, m), 5.69 (1H, ddd, J = 17.2, 10.0, 6.8 Hz), 5.02 – 4.95 (2H, m), 3.76 (3H, s), 3.46 – 3.39 (1H, m), 3.31 – 3.20 (2H, m), 2.49 – 2.37 (2H, m) $^{13}$C NMR (100 MHz, $CDCl_3$): δ 199.1, 158.0, 137.3, 136.4, 136.4, 132.9, 128.5, 128.5. 128.0, 116.7, 113.8, 55.2, 44.8, 40.9, 40.1; HRMS (ES+) Calcd. for $C_{19}H_{21}O_2$ $[M + H]^+$ 281.1542. Found 281.1544. Characterization in accordance with literature data.[82b]

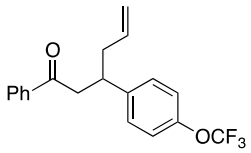
**1-phenyl-3-(4-fluorophenyl)hex-5-en-1-one (13d)**




The title compound was prepared according to general procedure F from (*E)*-1-allyoxy-1-phenyl-3-(4-fluorophenyl)-prop-2-ene **11d** (67.0 mg, 0.25 mmol), using 18-crown-6 (132 mg, 0.50 mmol) and potassium *t*-butoxide (56.0 mg, 0.50 mmol). The crude product was applied directly onto the top of a column and chromatographed (2% $Et_2O$ in hexane) to afford **13d** (50.3 mg, 75%) as a colorless oil.

$R_f$ (4% $Et_2O$ in hexane) = 0.21; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2921, 1684, 1448, 1001, 796, 778; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.89 – 7.87 (2H, m), 7.56 – 7.52 (1H, m), 7.45 – 7.41 (2H, m), 7.20 – 7.17 (2H, m), 6.98 – 6.93 (2H, m), 5.67 (1H, ddd, J = 17.2, 10.0, 7.2 Hz), 5.02 – 4.96 (2H, m), 3.50 – 3.43 (1H, m), 3.32 – 3.21 (2H, m), 2.50 – 2.37 (2H, m) $^{13}$C NMR (100 MHz, $CDCl_3$): δ 198.8, 161.4 (d, $J_{C-F}$ = 243.0 Hz), 140.0 (d, $J_{C-F}$ = 3.0 Hz), 137.2, 136.0, 133.0, 129.0 (d, $J_{C-F}$ = 8.0 Hz), 128.6, 128.0, 117.0, 115.2 (d, $J_{C-F}$ = 21.0 Hz), 44.6, 40.8, 40.1; HRMS (ES+) Calcd. for $C_{18}H_{18}FO$ $[M + H]^+$ 269.1342. Found 269.1331.

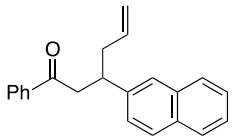
**1-phenyl-3-(4-trifluoromethyoxyphenyl)hex-5-en-1-one (13e)**



The title compound was prepared according to general procedure F from (*E)*-1-allyoxy-1-phenyl-3-(4-trifluoromethoxyphenyl)-prop-2-ene **11e** (40.0 mg, 0.13 mmol), using 18-crown-6 (69.0 mg, 0.26 mmol) and potassium *t*-butoxide (29 mg, 0.26 mmol). The crude product was applied directly onto the top of a column and chromatographed (4% $Et_2O$ in hexane) to afford **13e** (28.0 mg, 70%) as a yellow oil.

$R_f$ (4% $Et_2O$ in hexane) = 0.16; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2926, 1687, 1598, 1233, 1015, 700; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.90 – 7.87 (1H, m), 7.56 – 7.50 (1H, m), 7.45 – 7.41 (2H, m), 7.36 – 7.10 (5H, m), 5.67 (1H, ddd, J = 17.2, 10.0, 6.8 Hz), 5.03 – 4.97 (2H, m), 3.54 – 3.47 (1H, m), 3.34 – 3.22 (2H, m), 2.51 – 2.39 (2H, m) $^{13}$C NMR (100 MHz, $CDCl_3$): δ 198.5, 147.9 (q, $J_{C-F}$ = 245.6 Hz) 143.1, 137.1, 135.8, 133.1, 128.9, 128.6, 128.0, 127.8, 120.9, 117.2, 44.4, 40.7, 40.1; HRMS (ES+) Calcd. for $C_{19}H_{17}F_3O_2Na$ $[M + Na]^+$ 357.1078. Found 357.1077.

**1-phenyl-3-(2-naphthyl)-hex-5-en-1-one (13f)**

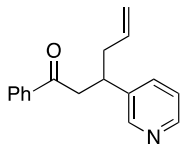


The title compound was prepared according to general procedure F from (*E)*-1-allyoxy-1-phenyl-3-(2-naphthyl)-prop-2-ene **11f** (59.7 mg, 0.195 mmol), using 18-crown-6 (103 mg, 0.39 mmol) and potassium *t*-butoxide (44.0 mg, 0.39 mmol). The crude product was applied directly onto the top of a column and chromatographed (1% $Et_2O$ in hexane) to afford **13f** (44.0 mg, 74%) as a yellow oil.

$R_f$ (4% $Et_2O$ in hexane) = 0.40; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2921, 1684, 1597, 1448, 1001, 778; $^1$H-NMR (400 MHz, $CDCl_3$): δ 8.24 – 8.22 (1H, m), 7.93 – 7.91 (2H, m), 7.86 – 7.84 (1H, m), 7.73 – 7.70 (1H, m), 7.55 – 7.41 (7H, m), 5.72 (1H, ddd, J = 17.2, 10.4, 6.8 Hz) 5.04 – 4.91 (2H, m), 4.50 – 4.43 (1H, m),

3.48 (1H, dd, J = 16.8, 7.6 Hz), 3.38 (1H, dd, J = 17.4, 5.6 Hz), 2.68 – 2.57 (2H, m) $^{13}$C NMR (100 MHz, $CDCl_3$): δ 198.9, 140.4, 137.3, 136.2, 134.0, 133.0, 131.7, 129.0, 128.6, 128.1, 126.9, 126.1, 125.5, 125.3, 125.3, 123.5, 123.4, 116.9, 44.3, 40.0; HRMS (ES+) Calcd. for $C_{22}H_{21}O$ $[M + H]^+$ 301.1592. Found 301.1601.

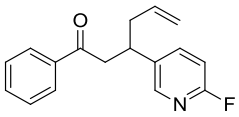
**1-phenyl-3-(pyridin-3-yl)hex-5-en-1-one (13g)**




The title compound was prepared according to general procedure F from (*E)*-1-allyoxy-1-phenyl-3-(pyridine-3-yl)-prop-2-ene **11g** (52.3 mg, 0.21 mmol), using 18-crown-6 (111 mg, 0.42 mmol) and potassium *t*-butoxide (47.0 mg, 0.42 mmol). The crude product was applied directly onto the top of a column and chromatographed (50% $Et_2O$ in hexane) to afford **13g** (21.1 mg, 40%) as a yellow oil.

$R_f$ (50% $Et_2O$ in hexane) = 0.18; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2923, 1685, 1448, 1426, 715, 690; $^1$H-NMR (400 MHz, $CDCl_3$): δ 8.58 – 8.53 (2H, m), 7.90 – 7.88 (2H, m), 7.58 – 7.42 (4H, m), 7.23 – 7.20 (1H, m), 5.68 (1H, ddt, J = 17.2, 10.0, 7.2 Hz), 5.04 – 4.99 (2H, m), 3.55 – 3.48 (1H, m), 3.40 – 3.27 (2H, m), 2.55 – 2.41 (2H, m);$^{13}$C NMR (100 MHz, $CDCl_3$): δ 198.2, 149.5, 147.9, 136.9, 135.4, 135.2, 133.2, 128.7, 128.0, 123.4, 117.6, 44.0, 40.1, 38.3; HRMS (ES+) Calcd. for $C_{17}H_{17}ONNa$ $[M + Na]^+$ 274.1208. Found 274.1200.

**1-phenyl-3-(2-fluoropyridin-5-yl)hex-5-en-1-one (13h)**

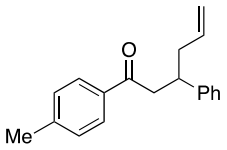



The title compound was prepared according to general procedure F from (*E)*-1-allyoxy-1-phenyl-3-(2-fluoropyridine-5-yl)-prop-2-ene **11h** (45.0 mg, 0.17 mmol), using 18-crown-6 (90.0 mg, 0.34 mmol) and potassium *t*-butoxide (38.2 mg, 0.34 mmol). The crude product was applied directly onto the top of

a column and chromatographed (10% EtOAc in hexane) to afford **13h** (11.0 mg, 25%) as a light yellow oil.

$R_f$ (10% $Et_2O$ in hexane) = 0.21; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2926, 1687, 1598, 1233, 1015, 700; $^1$H-NMR (400 MHz, $CDCl_3$): δ 8.09 (1H, d, J = 2.0 Hz), 7.88 (2H, dd, J = 7.3, 1.3 Hz), 7.67 (1H, td, J = 8.0, 2.5 Hz), 7.58 – 7.53 (1H, m), 7.44 (2H, t, J = 7.8 Hz), 6.85 (1H, dd, J = 8.3, 2.8 Hz), 5.67 (1H, ddd, J = 16.3, 10.5, 7.3 Hz), 5.03 (1H, br d, J = 1.0 Hz), 5.01 – 4.99 (1H, m), 3.56 – 3.49 (1H, m), 3,36 (1H, dd, J = 17.0, 5.8 Hz), 3.27 (1H, dd, J = 17.3, 8.3 Hz), 2.54 – 2.39 (2H, m); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 198.1, 162.5 (d, $J_{C-F}$ = 237.6 Hz), 146.7 (d, $J_{C-F}$ = 14.7 Hz), 140.4 (d, $J_{C-F}$ = 7.7 Hz), 137.3 (d, $J_{C-F}$ = 4.1 Hz), 135.2, 133.3, 128.7, 128.0, 117.8, 109.4, 108.9, 44.3, 39.8, 37.2; HRMS (ES+) Calcd. for $C_{17}H_{16}ONF$ $[M + H]^+$ 270.1294. Found 270.1305.

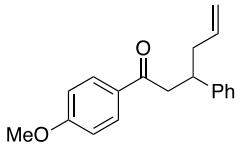
**1-(4-methylphenyl)-3-phenylhex-5-en-1-one (13i)**




The title compound was prepared according to general procedure F from (*E)*-1-allyoxy-1-(4-methylphenyl)-3phenyl-prop-2-ene **11i** (58.0 mg, 0.22 mmol), using 18-crown-6 (116 mg, 0.44 mmol) and potassium *t*-butoxide (49.0 mg, 0.44 mmol). The crude product was applied directly onto the top of a column and chromatographed (2% $Et_2O$ in hexane) to afford **13i** (41.8 mg, 72%) as a colorless oil.

$R_f$ (4% $Et_2O$ in hexane) = 0.16; IR: $\nu_{max}$ (thin film) / $cm^{-1}$2923, 1682, 1468, 1124, 821, 700; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.81 – 7.79 (2H, m), 7.34 – 7.15 (7H, m), 5.68 (1H, ddd, J = 16.8, 10.0, 6.8 Hz), 5.01 – 4.93 (2H, m), 3.50 – 3.43 (1H, m), 3.31 – 3.20 (2H, m), 2.51 – 2.41 (2H, m), 2.39 (3H, s); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 198.6, 144.5, 143.7, 136.3, 134.8, 129.2, 128.4, 128.2, 127.6, 126.4, 116.7, 44.5, 40.8, 40.7, 21.7; HRMS (ES+) Calcd. for $C_{19}H_{21}O$ $[M + H]^+$ 265.1592. Found 265.1595.

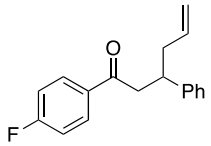
**1-(4-methoxyphenyl)-3-phenylhex-5-en-1-one (13j)**




The title compound was prepared according to general procedure F from (*E)*-1-allyoxy-1-(4-methoxyphenyl)-3phenyl-prop-2-ene **11j** (76.4 mg, 0.27 mmol), using 18-crown-6 (143 mg, 0.54 mmol) and potassium *t*-butoxide (65.3 mg, 0.54 mmol). The crude product was applied directly onto the top of a column and chromatographed (10% $Et_2O$ in hexane) to afford **13j** (54.2 mg, 71%) as a colorless oil.

$R_f$ (10% $Et_2O$ in hexane) = 0.40; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2924, 1586, 1255, 834, 750, 700; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.90 -7.86 (2H, m), 7.29 – 7.15 (5H, m), 6.91 – 6.88 (2H, m), 5.68 (1H, ddd, J = 17.2, 10.0, 6.8 Hz), 5.01 – 4.93 (2H, m), 3.85 (3H, s), 3.49 – 3.42 (1H, m), 3.28 – 3.18 (2H, m), 2.51 – 2.39 (2H, m) $^{13}$C NMR (100 MHz, $CDCl_3$): δ 197.5, 163.4, 144.5, 136.4, 130.4, 130.3, 128.4, 127.6, 126.3, 116.7, 113.7, 55.5, 44.3, 41.0, 40.7; HRMS (ES) Calcd. for $C_{19}H_{21}O_2$ $[M + H]^+$ 281.1542. Found 281.1534.[82a]

**1-(4-fluorophenyl)-3-phenylhex-5-en-1-one (13k)**

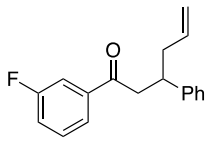



The title compound was prepared according to general procedure F from (*E)*-1-allyoxy-1-(4-fluorophenyl)-3phenyl-prop-2-ene **11k** (52.6 mg, 0.20 mmol), using 18-crown-6 (106 mg, 0.40 mmol) and potassium *t*-butoxide (45.0 mg, 0.40 mmol). The crude product was applied directly onto the top of a column and chromatographed (2% $Et_2O$ in hexane) to afford **13k** (49.1 mg, 74%) as a colorless oil.

$R_f$ (4% $Et_2O$ in hexane) = 0.30; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.92 – 7.89 (2H, m), 7.29 – 7.15 (5H, m), 7.10 – 7.06 (2H, m), 5.69 (1H, ddd, J = 17.2, 10.4, 6.8 Hz), 5.03 – 4.95 (2H, m), 3.49 – 3.42 (1H, m), 3.26 – 3.24 (2H, m), 2.48 – 2.44 (2H, m) $^{13}$C NMR (100 MHz, $CDCl_3$): δ 197.3, 165.7 (d, $J_{C-F}$ = 223

Hz), 144.2, 136.2, 133.7 (d, $J_{C\text{-}F}$ = 4.0 Hz), 130.6 (d, $J_{C\text{-}F}$ = 9.0 Hz), 128.5, 127.6, 126.5, 116.9, 115.6 (d, $J_{C\text{-}F}$ = 22 Hz), 44.5, 40.9, 40.7; HRMS (ES) Calcd. for $C_{18}H_{18}OF$ $[M + H]^+$ 269.1342. Found 269.1349.

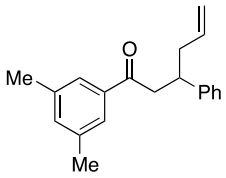
**1-(3-fluorophenyl)-3-phenylhex-5-en-1-one (13l)**




The title compound was prepared according to general procedure F from (*E)*-1-allyoxy-1-(3-fluorophenyl)-3phenyl-prop-2-ene **11l** (59.0 mg, 0.22 mmol), using 18-crown-6 (116 mg, 0.44 mmol) and potassium *t*-butoxide (50.0 mg, 0.44 mmol). The crude product was applied directly onto the top of a column and chromatographed (2% $Et_2O$ in hexane) to afford **13l** (41.0 mg, 70%) as a colorless oil.

$R_f$ (4% $Et_2O$ in hexane) = 0.33; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2925, 1690, 1589, 1443, 1249, 700; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.67 – 7.65 (1H, m), 7.57 – 7.54 (1H, m), 7.42 – 7.37 (1H, m), 7.30 – 7.15 (6H, m), 5.69 (1H, ddd, J = 17.2, 10.4, 6.8 Hz), 5.03 – 4.95 (2H, m), 3.50 – 3.42 (1H, m), 3.31 – 3.21 (2H, m), 2.48 -2.44 (2H, m) $^{13}$C NMR (100 MHz, $CDCl_3$): δ 197.7 (d, J $_{C\text{-}F}$ = 2.0 Hz), 162.8 (d, $J_{C\text{-}F}$ = 247 Hz), 144.1, 139.3 (d, $J_{C\text{-}F}$ = 6.0 Hz), 136.2, 130.2 (d, $J_{C\text{-}F}$ = 7.0 Hz), 128.5, 127.5, 126.5, 123.7 (d, $J_{C\text{-}F}$ = 3.0 Hz), 119.9 (d, J $_{C\text{-}F}$ = 21.0 Hz), 116.9, 114.8 (d, J $_{C\text{-}F}$ = 22.0 Hz), 44.7, 40.8, 40.7; HRMS (ES) Calcd. for $C_{18}H_{17}FNaO$ $[M + Na]^+$ 291.1161. Found 291.1174.

**1-(3,5-dimethylphenyl)-3-phenylhex-5-en-1-one (13m)**

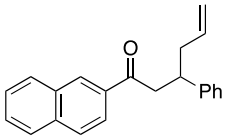



The title compound was prepared according to general procedure F from (*E)*-1-allyoxy-1-(3,3-dimethylphenyl)-3phenyl-prop-2-ene **11m** (86.0 mg, 0.32 mmol), using 18-crown-6 (169 mg, 0.64 mmol) and potassium *t*-butoxide (72.0 mg, 0.64 mmol). The crude product was applied directly onto

the top of a column and chromatographed (2% $Et_2O$ in hexane) to afford **13m** (59.2 mg, 69%) as a clear oil.

$R_f$ (4% $Et_2O$ in hexane) = 0.40; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2926, 1687, 1598, 1233, 1015, 700; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.49 (2H, s), 7.29 – 7.15 (6H, m), 5.68 (1H, ddt, J = 17.2, 10.4, 7.2 Hz), 5.02 – 4.93 (2H, m) 3.50 – 3.43 (1H, m), 3.30 – 3.20 (2H, m), 2.51 – 2.39 (2H, m), 2.33 (6H, s); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 199.3, 144.5, 138.2, 137.4, 136.4, 134.6, 128.4, 127.6, 126.4, 125.9, 116.7, 44.7, 40.8, 40.6, 21.3; HRMS (ES+) Calcd. for $C_{20}H_{23}O$ $[M + H]^+$ 279.1749. Found 279.1744.

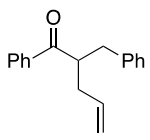
**1-(2-naphthyl)-3-phenylhex-5-en-1-one (13n)**




The title compound was prepared according to general procedure F from (*E)*-1-allyoxy-1-(2-naphthyl)-3phenyl-prop-2-ene **11n** (63.4 mg, 0.21 mmol), using 18-crown-6 (111 mg, 0.42 mmol) and potassium *t*-butoxide (47.0 mg, 0.42 mmol). The crude product was applied directly onto the top of a column and chromatographed (2% $Et_2O$ in hexane) to afford **13n** (44.0 mg, 69%) as a yellow oil.

$R_f$ (4% $Et_2O$ in hexane) = 0.40; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2922, 1682, 1607, 1180, 808, 700; $^1$H-NMR (400 MHz, $CDCl_3$): δ 8.41 – 8.38 (1H, m), 7.98 – 7.92 (2H, m), 7.87 – 7.84 (2H, m), 7.60 – 7.52 (2H, m), 7.32 – 7.16 (5H, m), 5.72 (1H, ddd, J = 17.2, 10.2, 7.0 Hz), 5.05 – 4.96 (2H, m), 3.57 – 3.50 (1H, m), 3.43 – 3.41 (2H, m), 2.57 – 2.45 (2H, m) $^{13}$C NMR (100 MHz, $CDCl_3$): δ 198.9, 144.4, 136.3, 135.5, 134.6, 132.5, 129.7, 129.6, 128.5, 128.4, 128.4, 127.8, 127.6, 126.8, 126.4, 123.9, 116.8, 44.7, 41.0, 40.7; HRMS (ES) Calcd. for $C_{22}H_{21}O$ $[M + H]^+$ 301.1592. Found 301.1576.

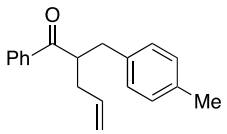
**2-Benzyl-1-phenylpent-4-en-1-one (14a)**



The title compound was prepared according to general procedure G from (*E)*-1-allyoxy-1,3-diphenyl-prop-2-ene **11a** (143 mg, 0.57 mmol), using potassium *t*-butoxide (33.0 mg, 0.29 mmol). The crude product was applied directly onto the top of a column and chromatographed (2% $Et_2O$ in hexane) to afford **14a** (103 mg, 72%) as a colorless oil.

$R_f$ (4% $Et_2O$ in hexane) = 0.42 $^1$H NMR (400 MHz, $CDCl_3$): δ 7.85 – 7.83 (2H, m), 7.52 – 7.49 (1H, m), 7.42 – 7.38 (2H, m), 7.24 – 7.12 (5H, m), 5.73 (ddd, 1H, J = 17.2, 10.0, 7.0), 5.04 – 4.97 (2H, m), 3.83 – 3.76 (1H, m), 3.10 (1H, dd, J = 13.6, 7.6 Hz), 2.81 (1H, dd, J = 14.0, 6.6 Hz), 2.57 -2.50 (1H, m), 2.33 – 2.26 (1H, m) $^{13}$C NMR (100 MHz, $CDCl_3$): δ 203.0, 139.7, 137.3, 135.3, 132.9, 129.1, 128.6, 128.4, 128.2, 126.3, 117.2, 48.1, 37.7, 36.3 Characterisation in accordance with literature data.[83]

**2-Ally-1-phenyl-3-(p-toyl)prop-1-one (14b)**

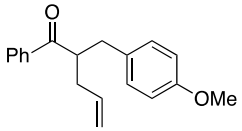



Potassium *t*-butoxide (14.0 mg, 0.12 mmol) was added to a THF solution (1.8 mL) of (*E)*-1-allyoxy-1-phenyl-3- (4-methylphenyl)-prop-2-ene **11b** (60.0 mg, 0.23 mmol) in a dry, argon purged sealed tube flask at room temperature. The reaction heated to 130 $^o$C and allowed to stir for 16 h. After quenching with distilled water (10 mL) and extraction (2 x 25 mL EtOAc), the organic layer was washed with distilled water (25 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude mixture was applied directly onto the top of a column and chromatographed (2% $Et_2O$ in hexane) to afford **5i** (41.0 mg, 68%) as a yellow oil.

$R_f$ (4% $Et_2O$ in hexane) = 0.24; IR: $\nu_{max}$ (thin film) / cm$^{-1}$ 2924, 1684, 1448, 1001, 915, 753; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.83 – 7.77 (2H, m), 7.47 – 7.42 (1H, m), 7.36 – 7.32 (2H, m), 7.06 – 6.97 (4H, m), 5.70 – 5.56 (1H, m), 4.96 – 4.87 (2H, m), 3.73 – 3.66 (1H, m), 2.99 (1H, dd, J = 14.0, 7.2 Hz), 2.68 (1H, dd, J = 14.0, 6.8 Hz), 2.48 – 2.41 (1H, m), 2.27 – 2.21 (1H, m), 2.21 (3H, s); $^{13}$C NMR (100 MHz,

$CDCl_3$): δ 203.4, 141.3, 137.3, 136.5, 135.7, 135.4, 132.9, 129.1, 129.0, 128.6, 128.2, 48.1, 37.2, 36.2, 21.0; HRMS(ES+) Calcd. for $C_{19}H_{21}O$ $[M + H]^+$ 265.1592. Found 265.1563

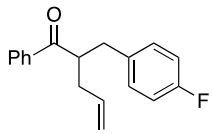
**2-Ally-1-phenyl-3-(4-methoxyphenyl)prop-1-one (14c)**




The title compound was prepared according to general procedure G from (*E)*-1-allyoxy-1- phenyl-3- (4-methoxyphenyl)-prop-2-ene **11c** (48.0 mg, 0.17 mmol), using potassium *t*-butoxide (10.0 mg, 0.085 mmol). The crude product was applied directly onto the top of a column and chromatographed (4% $Et_2O$ in hexane) to afford **14c** (41.8 mg, 87%) as a colorless oil.

$R_f$ (8% $Et_2O$ in hexane) = 0.36; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2921, 1681, 1513, 1247, 1036, 700; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.86 – 7.83 (2H, m), 7.53 – 7.50 (1H, m), 7.43 – 7.39 (2H, m), 7.09 – 7.07 (2H, m), 6.78 – 6.76 (2H, m), 5.73 (1H, ddt, J = 17.2, 10.4, 7.2 Hz), 5.04 – 4.97 (2H, m), 3.74 (4H, m), 3.04 (1H, dd, J = 14.0, 7.6 Hz), 2.75 (1H, dd, J = 14.0, 6.4 Hz), 2.55 – 2.48 (1H, m), 2.32 – 2.25 (1H, m); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 203.2, 158.1, 137.3, 135.4, 132.4, 131.7, 130.0, 128.6, 128.2, 117.1, 113.8, 55.2, 48.3, 36.8, 36.2; HRMS (ES+) Calcd. for $C_{19}H_{21}O_2$ $[M + H]^+$ 281.1542. Found 281.1545.[84]

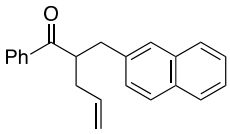
**2-Ally-1-phenyl-3-(4-methoxyphenyl)prop-1-one (14d)**




The title compound was prepared according to general procedure G from (*E)*-1-allyoxy-1- phenyl-3- (4-fluorophenyl)-prop-2-ene **11d** (45.5 mg, 0.17 mmol), using potassium *t*-butoxide (0.095 mg, 0.085 mmol). The crude product was applied directly onto the top of a column and chromatographed (2% $Et_2O$ in hexane) to afford **14d** (43.0 mg, 96%) as a yellow oil.

$R_f$ (4% $Et_2O$ in hexane) = 0.22 $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.87 (2H, m), 7.23 – 7.19 (2H, m), 7.16 - 7.12 (3H, m), 7.08 – 7.02 (2H, m), 5.72 (1H, ddd, J = 17.1, 10.0, 7.0 Hz), 5.05 – 4.97 (2H, m), 3.74 (1H, ddd, J = 13.8, 6.3, 6.0 Hz), 3.07 (1H, dd, J = 13.6, 7.8 Hz), 2.82(1H, dd, J = 13.6, 6.3 Hz), 2.52 (1H, dddd, J = 13.1, 7.0, 6.0, 1.3 Hz), 2.30 (1H, dddd, J = 13.1, 7.0, 6.0, 1.3 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 201.5, 165.8 (d, $J_{C-F}$ = 254.9 Hz), 139.5, 135.1, 133.7 (d, $J_{C-F}$ = 2.9 Hz), 130.8 (d, $J_{C-F}$ = 10.0 Hz), 129.0, 128.4, 126.3, 117.2, 115.6 (d, $J_{C-F}$ =22.0 Hz), 48.0, 37.9, 36.4; HRMS (ES+) Calcd. for $C_{18}H_{17}OFNa$ $[M + Na]^+$ 291.1161. Found 291.1148

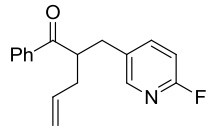
**2-Ally-1-phenyl-3-(2-naphthyl)prop-1-one (14f)**




The title compound was prepared according to general procedure G from (*E)*-1-allyoxy-1- phenyl-3-(2-naphthyl)-prop-2-ene **11f** (58.0 mg, 0.19 mmol), using potassium *t*-butoxide (11.0 mg, 0.095 mmol). The crude product was applied directly onto the top of a column and chromatographed (1% $Et_2O$ in hexane) to afford **14f** (45.8 mg, 79%) as a yellow oil.

$R_f$ (4% $Et_2O$ in hexane) = 0.39; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2922, 1678, 1607, 1454, 1181, 916; $^1$H-NMR (400 MHz, $CDCl_3$): δ 8.06 – 8.04 (1H, m), 7.84 – 7.82 (1H, m), 7.71 – 7.64 (2H, m), 7.56 -7.41 (4H, m), 7.32 – 7.27 (4H, m), 5.79 (1H ddd, J = 16.8, 10.2, 7.2 Hz), 5.09 – 5.01 (2H, m), 4.02 -3.95 (1H, m), 3.50 (1H, dd, J = 13.6, 8.0 Hz), 3.35 (1H, dd, J = 14.0, 6.2), 2.66 – 2.59 (1H, m), 2.41 – 2.34 (1H, m); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 203.4, 137.3, 135.6, 135.2, 134.0, 132.9, 131.9, 129.0, 128.5, 128.1, 127.5, 127.1, 126.0, 125.5, 125.4, 123.5, 117.5, 46.8, 37.0, 34.7; Calcd. for $C_{22}H_{21}O$ $[M + H]^+$ 301.1592. Found 301.1594.

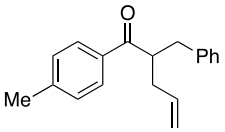
**2-Ally-1-phenyl-3-(2-fluoropyridin-3-yl)prop-1-one (14h)**



The title compound was prepared according to general procedure G from (*E)*-1-allyoxy-1-phenyl-3-(2-fluoropyridine-5-yl)-prop-2-ene **11h** (68.0 mg, 0.25 mmol), using potassium *t*-butoxide (14.0 mg, 0.125 mmol). The crude product was applied directly onto the top of a column and chromatographed (5% EtOAc in hexane) to afford **14h** (26.0 mg, 38%) as a yellow oil.

$R_f$ (5% $Et_2O$ in hexane) = 0.22; IR: $\nu_{max}$ (thin film) / $cm^{-1}$; 2926, 1680, 1596, 1488, 1250, 831; $^1$H-NMR (400 MHz, $CDCl_3$): δ 8.04 -8.02 (1H, m), 7.84 – 7.82 (2H, m), 7.59 – 7.52 (2H, m), 7.45 – 7.41 (2H, m), 6.77 (1H, dd, J = 8.0, 2.8 Hz), 5.75 (1H, ddd, J = 17.2, 10.8, 6.8 Hz), 5.09 – 5.05 (2H, m), 3.80 – 3.73 (1H, m), 3.11 (1H, dd, J = 14.0, 8.8 Hz), 2.84 (1H, dd, J = 14.0, 5.6 Hz), 2.57 – 2.50 (1H, m), 2.34 – 2.27 (1H, m); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 202.0, 162.4 (d, $J_{C-F}$ = 236.0 Hz), 147.7 (d, $J_{C-F}$ = 14.0 Hz), 141.8 (d, $J_{C-F}$ = 7.0 Hz), 136.8, 134.5, 133.3, 132.8 (d, $J_{C-F}$ = 5.0 Hz), 128.8, 128.2, 117.9, 109.1 (d, $J_{C-F}$ = 37.0 Hz), 47.7 (d, $J_{C-F}$ = 1.0 Hz), 36.7, 33.2 (d, $J_{C-F}$ = 2.0 Hz); Calcd. for $C_{17}H_{17}NOF$ $[M + H]^+$ 270.1294. Found 270.1298.

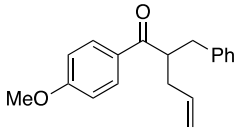
**2-Benzyl-1-(4-methylphenyl)pent-4-en-1-one (14i)**



Potassium *t*-butoxide (9.0 mg, 0.08 mmol) was added to a THF solution (1.3 mL) of (*E)*-1-allyoxy-1-(4-methylphenyl)-3-phenyl-prop-2-ene **11i** (42.8 mg, 0.16 mmol) in a dry, argon purged 10 mL rounded bottomed flask at room temperature. The reaction heated to 80 $^o$C and allowed to stir for 16 h. The reaction was quenched with distilled water (10 mL) and extracted with EtOAc (2 x 25 mL), the combined organic phases were washed with distilled water (25 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude mixture was applied directly onto the top of a column and chromatographed (2% $Et_2O$ in hexane) to afford **14i** (28.0 mg, 65%) as a yellow oil.

$R_f$ (4% $Et_2O$ in hexane) = 0.27; IR $\nu_{max}$ (thin film) / $cm^{-1}$ 3028, 2921, 1701, 1606, 1494, 1453, 1238, 1180, 917, 824, 752, 699; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.77 – 7.75 (2H, m), 7.27 – 7.12 (7H, m), 5.73 (1H, ddd, J = 17.2, 10.0, 7.2 Hz), 5.03 – 4.96 (2H, m), 3.80 – 3.73 (1H, m), 3.10 (1H, dd, J = 14.0, 8.0 Hz), 2.79 (1H, dd, J = 13.6, 6.4 Hz), 2.56 – 2.48 (1H, m), 2.37 (3H, s), 2.31 – 2.25 (1H, m) $^{13}$C NMR (100 MHz, $CDCl_3$): δ 202.5, 143.7, 139.8, 135.4, 134.8, 129.3, 129.1, 128.4, 128.4, 126.2, 117.1, 47.9, 37.7, 36.4, 21.6; Calcd. for $C_{19}H_{21}O$ $[M + H]^+$ 265.1592. Found 265.1598.

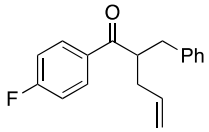
**2-Benzyl-1-(4-methoxyphenyl)pent-4-en-1-one (14j)**




The title compound was prepared according to general procedure G from (*E)*-1-allyoxy-1-(4-methoxyphenyl)-3-phenyl-prop-2-ene **11j** (70.0 mg, 0.25 mmol), using potassium *t*-butoxide (14.0 mg, 0.125 mmol). The crude product was applied directly onto the top of a column and chromatographed (10% $Et_2O$ in hexane) to afford **14j** (49.8 mg, 71%) as a colorless oil.

$R_f$ (10% $Et_2O$ in hexane) = 0.42; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2922, 1671, 1599, 1243, 1170, 750; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.85 – 7.83 (2H, m), 7.25 – 7.12 (5H, m), 6.89 – 6.86 (2H, m), 5.72 (dtt, 1H, J = 17.2, 10.4, 6.8 Hz), 5.04 – 4.96 (2H, m), 3.84 (3H, s), 3.77 – 3.70 (1H, m), 3.09 (1H, dd, J = 13.6, 7.6 Hz), 2.80 (1H, dd, J = 13.6, 6.4 Hz), 2.56 – 2.49 (1H, m), 2.32 – 2,25 (1H, m) $^{13}$C NMR (100 MHz, $CDCl_3$): δ 201.4, 163.4, 139.9, 135.5, 130.5, 130.3, 129.1, 128.4, 126.2, 117.0, 113.7, 55.4, 47.6, 37.9, 36.5; HRMS (ES+) Calcd. for $C_{19}H_{21}O_2$ $[M + H]^+$ 281.1542. Found 281.1541.

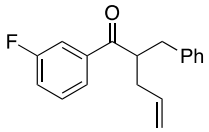
**2-Benzyl-1-(4-fluorophenyl)pent-4-en-1-one (14k)**



The title compound was prepared according to general procedure G from (*E)*-1-allyoxy-1-(4-fluorophenyl)-3-phenyl-prop-2-ene **11k** (56.0 mg, 0.21 mmol), using potassium *t*-butoxide (12.0 mg, 0.105 mmol). The crude product was applied directly onto the top of a column and chromatographed (2% $Et_2O$ in hexane) to afford **14k** (40.0 mg, 71%) as a yellow oil.

$R_f$ (4% $Et_2O$ in hexane) = 0.31; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 1681, 1598, 1506, 1234, 1156, 700; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.86 – 7.82 (2H, m), 7.25 – 7.03 (7H, m), 5.72 (1H, ddt, J = 17.2, 10.0, 7.2 Hz), 5.04 – 4.98 (2H, m), 3.77 -3.7 (1H, m), 3.07 (1H, dd, J = 14.0, 6.4 Hz), 2.82 (1H, dd, J = 13.6, 6.4 Hz), 2.56 – 2.49 (1H, m), 2.33 – 2.27 (1H, m); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 201.5, 165.6 (d, $J_{C-F}$ = 254 Hz), 139.5, 135.2, 133.8 (d, $J_{C-F}$ = 3.0 Hz), 130.8 (d, $J_{C-F}$ = 10.0 Hz), 129.0, 128.4, 126.3, 117.2, 115.6 (d, $J_{C-F}$ =22.0 Hz), 48.1, 37.9, 36.5; Calcd. for $C_{18}H_{18}OF$ $[M + H]^+$ 269.1342. Found 269.1354.

**2-Benzyl-1-(3-fluorophenyl)pent-4-en-1-one (14l)**

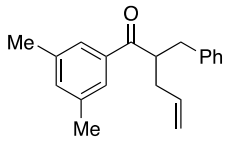



The title compound was prepared according to general procedure G from (*E)*-1-allyoxy-1-(3-fluorophenyl)-3-phenyl-prop-2-ene **11l** (47.3 mg, 0.176 mmol), using potassium *t*-butoxide (10.0 mg, 0.09 mmol). The crude product was applied directly onto the top of a column and chromatographed (2% $Et_2O$ in hexane) to afford **14l** (34.2 mg, 72%) as a yellow oil.

$R_f$ (4% $Et_2O$ in hexane) = 0.33 ; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2926, 1683, 1587, 1490, 1443, 1257, 757; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.60 – 7.58 (1H, m), 7.51 – 7.48 (1H, m), 7.40 – 7.34 (1H, m), 7.25 – 7.14 (6H, m), 5.72 (1H, ddd,, J = 17.2, 10.0, 6.8 Hz), 5.05 – 4.99 (2H, m), 3.76 – 3.69 (1H, m), 3.08 (1H , dd, J = 13.6, 8.0 Hz), 2.82 (1H, dd, J = 13.6, 6.4 Hz), 2.56 -2.49 (1H, m), 2.34 – 2.27 (1H, m) $^{13}$C NMR (100 MHz, $CDCl_3$): δ 201.9 (d, $J_{C-F}$ = 2.0 Hz), 162.8 (d, $J_{C-F}$ =246 Hz), 139.5 (d, $J_{C-F}$ = 6.0Hz), 139.4, 135.0, 130.2 (d, $J_{C-F}$ = 8Hz), 129.0, 128.5, 126.4, 123.9 (d, $J_{C-F}$ = 4.0 Hz), 119.9 (d, $J_{C-F}$ = 21.0

Hz), 117.4, 115.0 (d, $J_{C-F}$ = 22.0 Hz), 48.4, 37.8, 36.3; HRMS (ES+) Calcd. for $C_{18}H_{18}OF$ $[M + H]^+$ 269.1342. Found 269.1348.

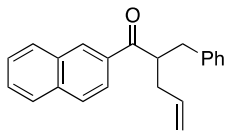
**2-Benzyl-1-(3,5-methylphenyl)pent-4-en-1-one (14m)**




Potassium *t*-butoxide (9.0 mg, 0.08 mmol) was added to a THF solution (1.3 mL) of (*E)*-1-allyoxy-1-(3,5-dimethylphenyl)-3-phenyl-prop-2-ene **11m** (42.9 mg, 0.16 mmol) in a dry, argon purged 10 mL rounded bottomed flask at room temperature. The reaction heated to 80$^o$C and allowed to stir for 16h. After quenching with distilled water (10 mL) and extraction (2x25 mL EtOAc), the organic layer was washed with distilled water (25 mL) and brine (25 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude mixture was applied directly onto the top of a column and chromatographed (2% $Et_2O$ in hexane) to afford **14m** (31.0 mg, 72%) as a colorless oil.

$R_f$ (4% $Et_2O$ in hexane) = 0.45; IR: $\nu_{max}$ (thin film) / $cm^{-1}$; 2921, 1679, 1604, 1293, 915, 700; $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 7.43 (2H, s), 7.29 – 7.14 (6H, m), 5.72 (1H, ddd, J = 17.2, 10.0, 6.8 Hz), 5.04 – 4.94 (2H, m), 3.79 – 3.72 (1H, m), 3.08 (1H, dd, J = 13.6, 7.6), 2.79 (1H, dd,J = 13.6, 6.4 Hz), 2.55 – 2.48 (1H, m), 2.35 – 2.24 (1H, m), 2.32 (6H, s) $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 203.3, 139.9, 138.2, 135.4, 134.6, 129.1, 128.4, 126.2, 126.0, 117.1, 48.1, 37.7, 36.3, 21.2; HRMS (ES+) Calcd. for $C_{20}H_{23}O$ $[M + H]^+$ 279.1749. Found 279.1752.

**2-Benzyl-1-(2-naphthyl)pent-4-en-1-one (14n)**

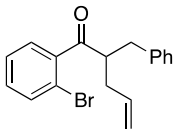



The title compound was prepared according to general procedure G from (*E)*-1-allyoxy-1-(2-naphthyl)-3-phenyl-prop-2-ene **11n** (48.9 mg, 0.16 mmol), using potassium *t*-butoxide (9.0 mg, 0.080 mmol). The

crude product was applied directly onto the top of a column and chromatographed (2% $Et_2O$ in hexane) to afford **14n** (39.1 mg, 80%) as a colorless oil.

$R_f$ (4% $Et_2O$ in hexane) = 0.40; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2925, 1375, 1675, 1276, 1186, 917; $^1$H-NMR (400 MHz, $CDCl_3$): δ 8.22 (1H, s), 7.88 – 7.75 (4H, m), 7.52 – 7.42 (2H, m), 7.21 – 7.03 (5H, m), 5.70 (1H, ddd, J = 17.2, 10.4, 6.8 Hz), 4.99 – 4.90 (2H, m), 3.91 – 3.84 (1H, m), 3.09 (1H, dd, J = 13.6, 8.0 Hz), 2.80 (1H, dd, J = 13.6, 6.8 Hz), 2.56 – 2.49 (1H, m), 2.32 – 2.26 (1H, m) $^{13}$C NMR (100 MHz, $CDCl_3$): δ 203.0, 139.8, 135.5, 135.3, 134.6, 132.5, 129.8,129.6, 129.1, 128.5, 128.4, 128.4, 127.7, 126.7, 126.3, 124.1, 117.2, 48.2, 37.2, 36.6; HRMS (ES+) Calcd. for $C_{22}H_{20}ONa$ $[M + Na]^+$ 323.1407. Found 323.1436.

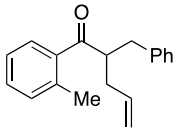
**2-Benzyl-1-(2-bromophenyl)pent-4-en-1-one (14o)**




The title compound was prepared according to general procedure G from (*E)*-1-allyoxy-1-(2-bromophenyl)-3-phenyl-prop-2-ene **11o** (58.2 mg, 0.18 mmol), using potassium *t*-butoxide (10.0 mg, 0.090 mmol). The crude product was applied directly onto the top of a column and chromatographed (1% $Et_2O$ in hexane) to afford **14o** (19.6 mg, 34 %) as a colorless oil.

$R_f$ (4% $Et_2O$ in hexane) = 0.39; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2924, 1679, 1583, 1257, 974, 757; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.58 – 7.56 (1H, m), 7.28 – 7.16 (7H, m), 7.09 – 7.07 (1H, m), 5.76 (1H, ddd, J = 17.2, 10.0, 7.2 Hz), 5.09 – 5.03 (2H, m), 3.66 – 3.60 (1H, m), 3.14 (1H, dd, J = 13.6, 7.6 Hz), 2.80 (1H, dd, J = 13.6, 6.8 Hz), 2.52 – 2.43 (1H, m), 2.30 – 2.23 (1H, m) $^{13}$C NMR (100 MHz, $CDCl_3$): δ 205.9, 141.6, 139.5, 134.9, 133.7, 131.5, 129.2, 128.9, 128.4, 127.2, 126.3, 119.3, 117.7, 52.5, 36.6, 35.4; HRMS (ES+) Calcd. for $C_{36}H_{34}O_2Br_2Na$ $[2M + Na]^+$ 679.0823. Found 679.0836

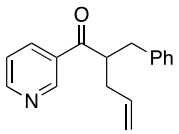
**2-Benzyl-1-(2-methylphenyl)pent-4-en-1-one (14p)**




The title compound was prepared according to general procedure G from (*E)*-1-allyoxy-1-(2-methylphenyl)-3-phenyl-prop-2-ene **11p** (56.1 mg, 0.21 mmol), using potassium *t*-butoxide (12.0 mg, 0.105 mmol). The crude product was applied directly onto the top of a column and chromatographed (0.5% EtOAc in hexane) to afford **14p** (31.0 mg, 55%) as a colorless oil.

$R_f$ (4% $Et_2O$ in hexane) = 0.31; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2926, 1684, 1455, 1232, 918, 749; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.14 (9H, m), 5.73 (1H, ddd, J = 16.8, 10.0, 7.2 Hz), 5.06 – 4.99 (2H, m), 3.66- 3.59 (1H, m), 3.09 (1H, dd, J = 13.6, 8.0 Hz), 2.77 (1H, dd, J = 13.6, 6.4 Hz), 2.52 – 2.45 (1H, m), 2.37 (3H, s), 2.29 – 2.23 (1H, m) $^{13}$C NMR (100 MHz, $CDCl_3$): δ 206.9, 139.0, 138.8, 138.1, 135.3, 131.7, 131.0, 129.1, 128.4, 127.9, 126.3, 125.5, 117.3, 51.4, 37.4, 36.3, 20.8; Calcd. for $C_{19}H_{21}O$ $[M + H]^+$ 265.1592. Found 265.1599.

**2-Benzyl-1-(pyridin-3-yl)pent-4-en-1-one (14q)**

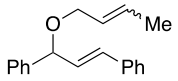



The title compound was prepared according to general procedure G from (*E)*-1-allyoxy-1-(pyridine-3-yl)-3-phenyl-prop-2-ene **11q** (40.0 mg, 0.16 mmol), using potassium *t*-butoxide (9.0 mg, 0.080 mmol). The crude product was applied directly onto the top of a column and chromatographed (50% $Et_2O$ in hexane) to afford **14q** (31.0 mg, 77%) as a colorless oil.

$R_f$ (50% $Et_2O$ in hexane) = 0.19; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2924, 1684, 1584, 1417, 1244, 701; $^1$H-NMR (400 MHz, $CDCl_3$): δ 9.01 – 8.97 (1H, m), 8.73 – 8.68 (1H, m), 8.06 – 8.03 (1H, m), 7.36 – 7.12 (6H, m), 5.71 (1H, ddd, J = 17.2, 10.0, 6.8 Hz), 5.00 – 4.97 (2H, m), 3.80 – 3.73 (1H, m), 3.08 (1H, dd, J = 13.6, 8.4 Hz), 2.86 (1H, dd, J = 13.6, 6.0 Hz), 2.59 – 2.52 (1H, m), 2.37 – 2.31 (1H, m); $^{13}$C NMR (100

MHz, $CDCl_3$): δ 202.2, 153.2, 149.6, 139.1, 135.5, 134.8, 128.9, 128.5, 127.5, 126.5, 123.5, 117.6, 48.8, 37.9, 36.4; HRMS (ES+) Calcd. for $C_{17}H_{18}NO$ $[M + H]^+$ 252.1388. Found 252.1389.

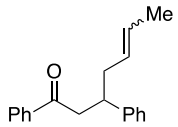
### (*E*)-1-(2-Butenyloxy)-1,3-diphenylprop-2-ene (15)




The title compound was prepared according to general procedure D, from (*E*)-1,3-diphenylpropen-2-ol (266 mg, 1.26 mmol), using crotyl bromide (0.26 mL, 2.52 mmol) and NaH (60% suspension in mineral oil; unwashed) (101 mg, 2.52 mmol). The crude product was applied directly onto the top of a column and chromatographed (1% EtOAc in hexane) to afford **15** (290 mg, 87%) as a yellow oil.

$R_f$ (10% EtOAc in hexane) = 0.61;IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 2854, 1395, 1276, 1067, 764, 700; $^1$H-NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.19 (10H, m), 6.60 (1H, d, J =16.0 Hz), 6.30 (1H, dd, J = 16.0, 7.2 Hz), 5.77 – 5.60 (2H, m), 4.97 (1H, d, J = 6.8 Hz), 4.00 – 3.91 (2H, m), 1.72 (d, 3H, J= 6.0 Hz) $^{13}$C NMR (100 MHz, $CDCl_3$): δ 141.3, 136.7, 131.3, 130.5, 129.5, 128.5, 127.6, 127.0, 126.6, 81.6, 69.1, 17.9 HRMS (ES+) Calcd. for $C_{19}H_{20}NaO$ $[M + Na]^+$ 287.1412. Found 287.1389. Characterization in accordance with literature data.[23a]

### 1,3-diphenylhept-5-en-1-one (16)

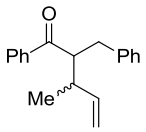



The title compound was prepared according to general procedure F from (*E*)-1-(2-butenyloxy)-1,3-diphenylprop-2-ene **15** (86.0 mg, 0.32 mmol), using 18-crown-6 (169 mg, 0.64 mmol) and potassium *t*-butoxide (72.0 mg, 0.64 mmol). The crude product was applied directly onto the top of a column and chromatographed (2% $Et_2O$ in hexane) to afford **16** (59.2 mg, 69%) as a colorless oil.

Rf (2% $Et_2O$ in hexane) = 0.35; $\upsilon_{max}$ (thin film) / $cm^{-1}$; 3407, 3170, 2936, 1690, 1571, 1561, 1506, 1463, 1336, 1301, 962, 750; $^1$H-NMR (400 MHz, $CDCl_3$): δ = 7.91 – 7.88 (2H, m), 7.55 – 7.50 (1H, m), 7.44

– 7.40 (2H, m), 7.29 – 7.14 (5H, m), 5.50 – 5.27 (2H, m), 3.47 – 3.36 (1H, m), 3.32 – 3.20 (2H, m), 2.54 – 2.35 (2H, m), 1.57 – 1.52 (3H, m) $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 199.2, 144.8, 137.9, 132.9, 128.7, 128.5, 128.4, 128.0, 127.9, 127.6, 127.4, 44.5, 41.2, 39.7, 17.9; HRMS (ES+) Calcd. for $C_{19}H_{22}O$ $[M + 2H]^+$ 266.1671. Found 266.1701.

**2-benzyl-3-methyl-1-phenylpent-4-en-1-one (17)**

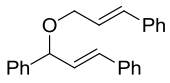



The title compound was prepared according to general procedure G from **15** (100.0 mg, 0.38 mmol), using potassium *t*-butoxide (21.1 mg, 0.19 mmol). The crude product was applied directly onto the top of a column and chromatographed (2% $Et_2O$ in hexane) to afford **17** (67.3 mg, 67%) as a clear oil and as an inseparable mix of isomers.

Rf (2% $Et_2O$ in hexane) = 0.41; $\upsilon_{max}$ (thin film) / $cm^{-1}$; 3434, 3120, 3074, 1684, 1571, 1549, 1506, 1463, 1336, 1207, 974, 750; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.77 – 7.64 (2H, m), 7.48 – 7.31 (2H, m), 7.19 – 7.04 (6H, m), 5.87 (0.5H, ddd, J = 17.4, 10.1, 7.0), 5.77 (0.5H, ddd, J = 17.4, 10.1, 7.0), 5.12 – 5.00 (2H, m), 3.76 (0.5H, ddd, J = 10.2, 6.3, 3.6 Hz), 3.62 (0.5H, ddd, J = 10.2, 6.3, 3.6 Hz), 3.21 – 2.93 (1H, m), 2.83 (1H, dd, J = 13.4, 8.0 Hz), 2.69 -2.59 (1H, m), 1.02 (3H, dd, J = 9.3, 6.9 Hz)

$^{13}$C NMR (100 MHz, $CDCl_3$): δ144.8, 137.3, 132.9, 128.8, 128.5(0.5 C), 128.4(0.5 C), 128.0, 127.9, 127.4, 126.3(0.5 C),, 126.2(0.5 C),, 125.8, 44.7 (0.5 C), 44.5(0.5 C),, 41.3, , 39.7, 33.5, 17.9,; HRMS (ES+) Calcd. for $C_{19}H_{20}ONa$ $[M + Na]^+$ 287.1412 Found 287.1404

**(*E*)-1-(3-phenylallyloxy)-1,3-diphenylprop-2-ene (18)**




Cinnamyl alcohol (0.146 mL, 1.14 mmol) was added to an oven dried round bottom flask and placed under argon. Dry diethyl ether (3 mL) was added and the reaction was cooled to 0ºC and $PBr_3$ (154 mg,

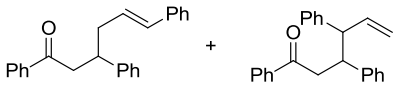
53.6 µL, 0.57 mmol) was added via syringe. The solution was stirred at this temperature for 30 minutes, followed by the addition of brine (10 mL). Solution was extracted with $Et_2O$ (2 x 20 mL), dried and concentrated to give a yellow oil.

This was then transferred to a separate flask containing diphenyl-2-propen-1-ol (0.571 mml, 120 mg) using DMF (2 mL). The resultant clear solution was cooled to 0ºC and NaH (60% suspension in mineral oil; unwashed) (45.6 mg, 1.14 mmol ) was added as a single portion.

After stirring at the same temperature for 1.5 hours, the reaction was quenched with $NH_4Cl$ (10 mL), extracted with ether (3 x 10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was applied directly onto the top of a column and chromatographed (2.5 % EtOAc in hexane) to afford **18** (157 mg, 83%) as a colorless oil.

$R_f$ (10% EtOAc in hexane) = 0.59; $^1$H NMR: (400 MHz, $CDCl_3$) δ 7.46 – 7.37 (6H, m), 7.37 – 7.28 (5H, m), 7.28 – 7.19 (4H, m), 6.65 (1H, d, J = 16.0 Hz), 6.63 (1H, dt, J = 16.0, 2.4 Hz), 6.34 (1H, dd, J= 16.9, 0.8 Hz), 6.32 (1H, d, J= 16.0 Hz), 5.05 (1H, d, J = 7.0 Hz), 4.21 (2H, ddd, J = 6.0, 3.6, 1.3 Hz) Characterization in accordance with literature data.[85]

**(E)-1,3,6-triphenylhex-5-en-1-one (19) and 1,3,4-triphenylhex-5-en-1-one (20)**




The title compounds were prepared according to general procedure F from (*E*)-1-(3-phenylallyloxy)-1,3-diphenylprop-2-ene **18** (50.9 mg, 0.15 mmol), using 18-crown-6 (80.4 mg, 0.305 mmol) and potassium *t*-butoxide (34.1 mg, 0.305 mmol). The crude product was applied directly onto the top of a column and chromatographed (0.5 % $Et_2O$ in hexane) to afford **21** and **22** (30.0 mg, 59%) as an inseparable mixture in the form of a clear oil.

**19** and **20:** $R_f$ (19:1 Hexane/$Et_2O$) = 0.34

**19** and **20:** $\upsilon_{max}$ (thin film) / $cm^{-1}$; 3531 (br), 2977, 2861, 1679, 1662, 1645, 1412, 1238, 1054, 1032, 1012, 896, 766

**19:** $^{1}$H NMR: (400 MHz, $CDCl_3$) δ 7.77 – 7.64 (2H, m), 7.48 – 7.31 (2H, m), 7.33 – 7.27 (3H, m), 7.19 – 7.04 (6H, m), 7.03 – 6.99 (2H, m) 6.33 (1H, dt, J = 15.8, 6.0 Hz), 6.14 (1H, dt, J = 15.8, 9.2 Hz), 5.21 (1H, d, J = 5.8 Hz), 4.22 (1H, dd, J = 6.0, 1.3 Hz), 3.75 (1H, t, J = 9.5 Hz), 3.11 (2H, d, J = 9.8 Hz)

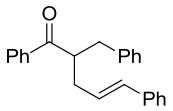
**20:** $^{1}$H NMR: (400 MHz, $CDCl_3$) δ 7.77 – 7.64 (2H, m), 7.48 – 7.31 (2H, m), 7.33 – 7.27 (3H, m), 7.19 – 7.04 (6H, m), 7.03 – 6.99 (2H, m) 5.89 (1H, ddd, J = 18.3, 17.0, 7.0 Hz), 4.91 (1H, dt, J = 16.8, 1.0 Hz), 4.87 (1H, dt, J – 16.8, 1.0 Hz), 4.14 – 4.06 (1H, m), 2.93 (1H, dd, J = 13.0, 11.4 Hz), 2.66 (1H, dd, J = 13.0, 3.3 Hz)

**19** $^{13}$C NMR (100 MHz, $CDCl_3$) δ 204.0, 132.6, 132.5, 128.5, 128.3, 128.2, 128.0, 127.7, 127.0, 126.9, 126.6, 126.1, 126.0, 116.4, 60.8, 55.0, 53.7, 37.9

**20:** $^{13}$C NMR (100 MHz, $CDCl_3$) δ 203.1, 142.0, 139.9, 138.6, 132.2, 129.0, 128.9, 128.4, 128.3, 127.9, 127.9, 127.6, 126.5, 126.1, 117.3, 70.8, 54.1, 53.8, 37.3

**19** and **20:** HRMS (ES+) Calcd. for $C_{24}H_{22}ONa$ $[M+ Na]^+$ 349.1568 Found 349.1572

**(E)-2-benzyl-1,5-diphenylpent-4-en-1-one (21)**

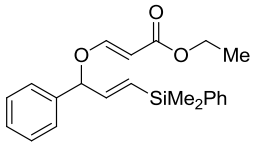



The title compound was prepared according to general procedure G from (*E*)-1-(3-phenylallyloxy)-1,3-diphenylprop-2-ene **18** (50.8mg, 0.152 mmol), using potassium *t*-butoxide (8.5 mg, 0.076 mmol). The crude product was applied directly onto the top of a column and chromatographed (0.5% $Et_2O$ in hexane) to afford **19** (67.3 mg, 64 %) as a colorless solid.

$R_f$ (29:1 Hexane/$Et_2O$) = 0.17; $\upsilon_{max}$ (thin film) / $cm^{-1}$ 3536 (br), 2906, 2771, 1679, 1650, 1492, 1423, 1257, 1054, 1032, 1012, 897, 766; $^{1}$H NMR: (400 MHz, $CDCl_3$) δ 7.89 (1H, d, J = 7.3 Hz), 7.57 – 7.48 (2H, m), 7.47 – 7.43 (3H, m), 7.41 (2H, t, J = 7.8 Hz), 7.30 – 7.23 (6H, m), 7.16 – 7.12 (1H, m). 6.35 (1H, d, *J* = 15.8 Hz), 6.13 – 6.04 (1H, m), 3.56 (1H, dd, J = 14.3, 5.0 Hz), 3.39 (1H, dd, J = 14.3, 5.0 Hz), 3.33 (1H, dd, J = 7.0, 5.3 Hz), 2.61 (2H, t, J = 8.3 Hz);$^{13}$C NMR (100 MHz, $CDCl_3$) δ 133.0, 132.1, 129.1, 128.5, 128.5, 128.0, 127.9, 127.6, 126.0, 125.2, 125.1, 72.4, 62.0, 49.2, 44.3, 36.5,31.9 , ;

HRMS (ES+) Calcd. for $C_{24}H_{22}ONa$ $[M+ Na]^+$ 349.1568 Found 349.1579

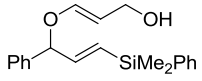
**(E)-ethyl 3-((E)-3-(dimethyl(phenyl)silyl)-1-phenylallyl)oxy)acrylate (S10)**




Following a modified form of the procedure reported by Wulff,[36] to an oven dried round bottomed flask equipped with a magnetic stirrer bar and purged with argon was added dry methylene chloride (4 mL), followed by (*E*)-3-(dimethyl(phenyl)silyl)-1-phenylprop-2-en-1-ol[23a] (300 mg, 1.125 mmol) (1 equiv.) and ethyl propiolate (0.114 mL, 1.125 mmol) (1 equiv.). The resultant solution was cooled to 0 $^oC$. In a separate oven dried round bottom flask, a solution of trimethyl phosphine (1M in a solution of THF) (0.22 mL, 0.225 mmol) (0.2 equiv.) in dry methylene chloride (4 mL) was prepared and cooled to 0 $^oC$, This solution was then slowly transferred, *via* cannula, to the flask containing the alcohol and alkyne solution. The reaction was allowed to warm to room temperature over the course of an hour, then heated to 40 $^oC$ and stirred at this temperature for 48 hourss. When the reaction was found to be complete by TLC, the methylene chloride was removed under reduced pressure, and the crude mixture was applied directly to a column containing base washed silica. Column chromatograpy (9:1 EtOAc:Hexane) afforded **S11** as a yellow oil (412 mg, 90%).

$R_f$ (9:1 hexane-ethyl acetate) = 0.26; $^1H$ NMR: (400 MHz, $CDCl_3$) δ 7.58 (1H, d, J = 12.6 Hz), 7.50 – 7.46 (2H, m), 7.40 – 7.28 (8H, m), 6.20 ( 1H, dd, *J* = 18.6, 5.0 Hz), 6.10 (1H, dd, *J* = 18.6, 1.0 Hz), 5.37 (1H, d, *J* = 5.0 Hz), 5.31 (1H, d, *J* = 12.6 Hz), 4.13 (2H, dq, J = 7.3, 0.7 Hz), 1.26 (3H, t, J = 7.0), 0.37 (3H,s), 0.36 (3H, s) $^{13}C$ NMR (100 MHz, $CDCl_3$) δ167.7, 160.9, 144.5, 138.3, 137.7, 133.9, 131.4, 129.2, 128.8, 128.5, 128.4, 127.9, 126.9, 98.9, 86.2, 59.7, 14.4, -2.8; HRMS (EI+) Calcd. for $C_{22}H_{26}O_3NaSi$ $[M + Na]^+$ 398.1549. Found 398.1396.

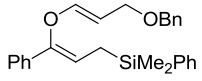
**(E)-2-((E)-3-(dimethyl(phenyl)silyl)-1-phenylallyl)oxy)ethanol (24)**




To a dried round 10 mL bottomed flask equipped with a magnetic stirrer bar and purged with argon was added ether (**not dried**) (2 mL), followed by **S11**(161 mg, 0.44 mmol) (1 equiv.). The resultant solution was cooled to -78 $^{o}$C. DIBAL (1.5M solution in toluene) (0.78mL, 0.968 mmol) (2.2 equiv.) was added dropwise, and the solution stirred at -78% $^{o}$C for one hour. The temperature was then brought up to -40 $^{o}$C and the reaction stirred for a further two hours. When the reaction was found to be complete by TLC, it was quenched with $NH_4Cl$ and allowed to warm to room temperature. This was then transferred to a conical flask and stirred rigorously in NaOH to dissolve aluminium salts. The resultant solution was extracted with $Et_2O$ and the combined organic layers were washed with brine. Column chromatograpy in base washed silica (25% EtOAc:Hexane) afforded **24** as a colorless oil (98 mg, 69%).

$R_f$ (9:1 hexane-ethyl acetate) = 0.09; $^{1}$H NMR: (400 MHz, $CDCl_3$) δ 7.55 – 7.44 (2H, m), 7.41 – 7.28 (8H, m), 6.54 (1H, dt, J = 12.3, 0.8 Hz), 6.20 (1H, dd, J = 18.8, 5.3 Hz), 6.08 (1H, dd, J = 18.8, 1.3 Hz), 2.20 (1H, s), 5.18 (1H, dt, *J* = 12.6, 7.5 Hz), 3.99 (2H, dd, J= 6.5, 5.3 Hz), 0.34 (3H, s), 0.33 (3H, s) $^{13}$C NMR (100 MHz, $CDCl_3$) δ148.6, 145.8, 139.4, 138.1, 133.8, 130.2, 129.7, 129.1, 128.7, 128.1, , 126.8, 105.8, 84.3, 60.7, -2.7, -2.7; HRMS (ES+) Calcd. for $C_{20}H_{25}O_2Si$ $[M + H]^+$ 325.1624. Found 325.1611.

**((Z)-3-((E)-3-(benzyloxy)prop-1-en-1-yl)oxy)-3-phenylallyl)dimethyl(phenyl)silane (25)**

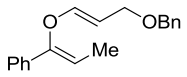



To a dried round 5 mL bottomed flask equipped with a magnetic stirrer bar and purged with argon was added dry DMF (0.25 mL), followed by alcohol **22** (49.8 mg, 0.156 mmol). The resultant solution was cooled to 0 $^{o}$C. NaH (60% in mineral oil; unwashed) (6.22 mg, 0.156 mmol) was added in one portion, swiftly followed by dropwise addition of benzyl bromide (18.6 µL, 0.156 mmol). The reaction was stirred at this temperature for one hour, before warming to room temperature. The reaction was stirred overnight. When the reaction was found to be complete by TLC, it was quenched with saturated $NH_4Cl$

solution (5 mL). The resultant solution was extracted with $Et_2O$ (3 x 10 mL) and the combined organic layers were washed with brine (2 x 10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Column chromatograpy (pure Hexane) afforded **25** (26.5 mg, 46 %) as a colorless oil.

$R_f$ (9:1 Hexane/EtOAc) = 0.67; $\upsilon_{max}$ (thin film) / cm-1; 2924, 2854, 1654, 1456, 1275, 972, 749, 698; $^1$H NMR: (400 MHz, CDCl3) δ 7.57 – 7.51 (2H, m), 7.48 – 7.42 (2H, m), 7.39 – 7.29 (13H, m), 6.46 (1H, d, J = 12.3 Hz), 5.70 (1H, q, J = 7.0 Hz), 5.17 (1H, dt, J = 12.6, 5.3 Hz), 4.40 (2H, s), 3.90 (2H, d, J = 7.53 Hz), 1.79 (2H, d, J = 7.5 Hz), 0.32 (6H, s); $^{13}$C NMR (100 MHz, CDCl3) δ140.0, 137.5, 134.4, 132.9, 132.1, 128.4, 127.6, 127.5, 127.0, 127.0, 126.9, 126.8, 126.7, 124.3, 110.1, 102.6, 71.3, 70.2, 66.1, 10.4, -4.0, -4.1; HRMS (ES+) Calcd. for $C_{27}H_{31}O_2Si$ $[M+H^+]^+$ 415.2093. Found 415.2115.

**(1-((E)-3-(benzyloxy)prop-1-en-1-yl)oxy)prop-1-en-1-yl)benzene (26)**

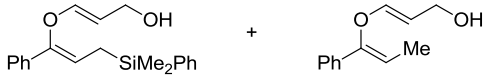



To a dried round 5 mL bottomed flask equipped with a magnetic stirrer bar and purged with argon was added dry DMF (0.75 mL), followed by alcohol **22** (148 mg, 0.462 mmol). The resultant solution was cooled to 0 $^o$C. NaH (60% in mineral oil; unwashed) (27.7 mg, 0.693 mmol) was added in one portion, swiftly followed by dropwise addition of benzyl bromide (0.185 mL, 1.39 mmol). The reaction was stirred at this temperature for one hour, before warming to room temperature. The reaction was stirred overnight. When the reaction was found to be complete by TLC, it was quenched with saturated $NH_4Cl$ solution (5 mL). The resultant solution was extracted with $Et_2O$ (3 x 10 mL) and the combined organic layers were washed with brine (2 x 10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Column chromatograpy (pure Hexane) afforded the desired product (81 mg, 64 %) as a colorless oil.

$R_f$ (9:1 Hexane/EtOAc) = 0.55; $\upsilon_{max}$ (thin film) / $cm^{-1}$;2856, 1654, 1495, 1453, 1275, 1261, 1155, 1066, 929, 763, 749, 697; $^1$H NMR: (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (2H, m), 7.36 – 7.24 (8H, m), 6.46 (1H, d, *J* = 12.3 Hz), 5.69 (1H, q, *J* = 7.0 Hz), 5.17 (1H, dt, J = 12.6, 5.3 Hz), 4.40 (2H, s), 3.90 (2H, d, J = 7.53 Hz), 1.78 (3H, d, J = 7.5 Hz);$^{13}$C NMR (100 MHz, $CDCl_3$) δ 151.1, 148.3, 128.4, 128.3, 127.9,

127.8, 127.5, 127.4, 125.3, 111.0, 103.5, 85.6 71.2, 66.6, 11.5; HRMS (ES+) Calcd. for $C_{19}H_{21}O_2$ [M + $H^+$]$^+$ 281.1542 Found 281.1531.

**Dimethyl(phenyl)((Z)-3-phenyl-3-((E)-prop-1-en-1-yloxy)allyl)silane and (1-((E)-prop-1-en-1-yloxy)prop-1-en-1-yl)benzene (27 +28)**




To a dried round 5 mL bottomed flask equipped with a magnetic stirrer bar and purged with argon was added dry DMF (0.25 mL), followed by alcohol **22.** The resultant solution was cooled to 0 $^oC$. NaH of the quantity stated (60% in mineral oil; unwashed) was added in one portion. The reaction was stirred at this temperature for one hour, before warming to room temperature. The reaction was stirred overnight. When the reaction was found to be complete by TLC, it was quenched with saturated $NH_4Cl$ solution (5 mL). The resultant solution was extracted with $Et_2O$ (3 x 10 mL) and the combined organic layers were washed with brine (2 x 10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Column chromatograpy (pure hexane) provided **27** and **28** as an inseparable mixture.

**27** and **28:** $\upsilon_{max}$ (thin film) / $cm^{-1}$; 2941, 2906, 2856, 2743, 1632, 1493, 1450, 1274, 1137, 1013, 971, 930, 860.

**27:** $^1H$ NMR: (400 MHz, $CDCl_3$) δ 7.59 – 7.51 (2H, m), 7.48 – 7.40 (2H, m), 7.36 – 7.27 (3H, m), 7.25 – 7.21 (2H, m), 6.32 (1H, d, J = 12.4 Hz), 5.07 (1H, dt, J = 12.4, 7.5 Hz), 4.57 (2H, t, J = 6.6 Hz), 3.91 (2H, d, J = 7.5 Hz), 0.94 – 0.85 (2H, m), 0.24 (6H, s)

**28:** $^1H$ NMR: (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (2H, m), 7.36 – 7.27 (3H, m), 6.49 (1H, d, J = 12,4 Hz), 5.72 (1H, q, J = 7.0 Hz), 5.25 (1H, dt, J = 11.9, 7.5 Hz), 4.02 (2H, d, J = 7.3 Hz), 1.78 (3H, d, J = 7.0 Hz)

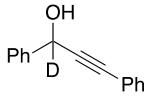
**27** $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 147.6, 139.1, 132.7, 132.2, 128.4, 127.6, 127.5, 127.0, 126.9, 124.3, 110.1, 102.6, 70.2, 66.1, -3.9, -4.0

**28:** $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 150.2, 137.5, 134.4, 128.1, 127.4, 126.8, 125.6, 101.3, 83.8, 71.3

**27**: HRMS (ES+) Calcd. for $C_{20}H_{24}O_2Si$ $[M]^+$ 325.1624 Found 325.2452.

**28**: HRMS (ES+) Calcd. for $C_{12}H_{14}NaO_2$ $[M + Na]^+$ 213.0891. Found 213.0889.

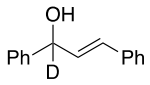
### 1-deutero-1-phenylprop-2-yn-1-ol (S11)




The title compound was prepared according to general procedure A, from benzaldehyde-α-*d*1 (321 mg, 0.30 mL, 3.00 mmol) using phenylacetylene (0.36 mL, 3.30 mmol) and *n*-butyllithium (2.5 M in hexane) (1.32 mL, 3.30 mmol). To afford **S1** (430 mg, 69%) as a colorless oil.

$R_f$ (20% EtOAc in hexane) = 0.35; IR: $\nu_{max}$ (thin film) / $cm^{-1}$; 3295, 1489, 1063, 1010, 756, 691; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.64 – 7.62 (2H, m), 7.49 – 7.31 (8H, m), 2.23 (1H, s); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 140.6, 131.8, 128.7, 128.6, 128.5, 128.3, 126.8, 122.4, 88.7, 86.7. Characterization in accordance with literature data.[86]

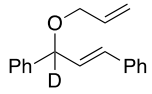
### 1-deutero-1,3-diphenylprop-2-yn-1-ol (S12)




The title compound was prepared according to general procedure B, from **S1** (277 mg, 1.32 mmol) using Red-Al (65% in PhMe) (0.80 mL, 2.64 mmol). The crude product was applied directly onto the top of a column and chromatographed (20% EtOAc in hexane) to afford **S1** (241 mg, 86%) as a colorless oil.

$R_f$ (20% EtOAc in hexane) = 0.29; IR: $\nu_{max}$ (thin film) / $cm^{-1}$ 3348, 1494, 1448, 965, 746, 695; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.44 – 7.17 (10H, m), 6.68 (1H, d, J = 16.0 Hz), 6.37 (1H, d, J = 16.0 Hz), 2.11 (s, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 142.8, 136.6, 131.5, 130.6, 128.7, 128.6, 127.8, 127.8, 126.7, 126.4, 74.6 (t, J = 22.0 Hz). Characterisation in accordance with literature data.[87]

**1-deutero-(*E*)-1-Allyoxy-1,3-diphenyl-prop-2-ene (29)**




The title compound was prepared according to general procedure D, from **S11** (579 mg, 2.74 mmol) using Red-Al (65% in PhMe) (1.59 mL, 5.20 mmol). The crude product was applied directly onto the top of a column and chromatographed (10% EtOAc in hexane) to afford **27** (429 mg, 72%) as a colorless oil.

$R_f$ (10% EtOAc in hexane) = 0.57; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.16 (10H, m), 6.62 (1H, d, *J* = 16.4 Hz), 6.30 (1H, d, *J* = 15.6 Hz), 6.02 – 5.92 (1H, m), 5.33 -5.29 (1H, m), 5.21- 5.19 (1H, m), 4.09 – 3.99 (1H, m); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 141.1, 136.6, 134.9, 131.5, 130.2, 128.5, 127.7 (d, J = 3.0 HZ), 126.9, 126.6, 117.0, 69.2; Characterization in accordance with literature data.[66]

ACKNOWLEDGMENT. We thank Eli Lilly (Dr Magnus Walter and Dr Maria Whatton) for a CASE award to C.A.M. and Queen's University Belfast for funding. We also thank Girton College, Cambridge (Research Fellowship to M.N.G.) and Unilever for support.

SUPPORTING INFORMATION AVAILABLE $^1$H and $^{13}$C NMR spectra, additional experimental information and tables containing the full computational analysis are provided in the supporting information. This material is available free of charge via the Internet at http://pubs.acs.org

REFERENCES

(1) For reviews see: (a) Tietze; L. F. *Chem. Rev.* **1996**, *96*, 115; (b) Nicalou, K. C.; Edmonds, D. J.; Bulger, P. G. *Angew. Chem. Int. Ed.* **2006**, *45*, 7134; (c) Tietze, L.F.; Brasche, G.; Gericke. K. Domino *Reactions in Organic Synthesis*, Wiley-VCH, Weinhem, 2006 (d) Pellisier, H.

*Tetrahedron*, **2006**, *62*, 1619 (e) Padwa, A.; Bur, S. K. *Tetrahedron* **2007**, *63*, 5341; (f) Nicolaou, K. C.; Chen, J. S. *Chem. Soc. Rev.* **2009**, *38*, 2993; (g) Barriault, L.; Grisé-Bard, C. M.; Poulin J. *Chem. Rev. Soc*. **2009**, *38*, 3092; (h) Anderson, E. A., *Org. Biomol. Chem.* **2011**, *9*, 3997.

(2) (a) Stork, G.; Burgstahler, A. W., *J. Am. Chem. Soc.* **1955**, *77*, 5068; (b) Johnson, W. S.; Lindell, S. D.; Steele, J., *J. Am. Chem. Soc.* **1987**, *109*, 5852.

(3) Robinson, R. *J. Chem. Soc. Trans.* **1917**, 762

(4) Johnson, W. S.; Gravestock, M. B.; McCarry, B. E. J. *Am. Chem. Soc*. **1971**, *93*, 4332

(5) Reviews: (a) Greer, E. M.; Cosgriff, C. V. *Annu. Rep. Prog. Chem., Sect. B: Org. Chem.* **2012**,*108*, 251; (b) Greer, E. M.; Cosgriff, C. V. *Annu. Rep. Prog. Chem., Sect. B: Org. Chem.* **2013**, *109*, 328.

(6) (a) Nicolaou, K. C.; Petasis, N. A.; Zipkin, R. E.; Uenishi, J., *J. Am. Chem. Soc.* **1982**, *104*, 5555; (b) Nicolaou, K. C.; Petasis, N. A.; Uenishi, J.; Zipkin, R. E., *J. Am. Chem. Soc.* **1982**, *104*, 5557; (c) Nicolaou, K. C.; Zipkin, R. E.; Petasis, N. A., *J. Am. Chem. Soc.* **1982**, *104*, 5558; (d) Nicolaou, K. C.; Petasis, N. A.; Zipkin, R. E., *J. Am. Chem. Soc.* **1982**, *104*, 5560.

(7) For Review of Cascade Sigmatropic Rearrangements see: Jones, A. C.; May, J. A.; Sarpong, R.; Stoltz, B. M. *Angew. Chem. Int. Ed.* **2014**, *53*, 2556.

(8) Reviews on synthetic applications of sigmatropic rearrangements: (a) Bartlett, P.A. *Tetrahedron* **1980**, *36*, 2 (b) Desimoni, G.; Tacconi, G.; Barco, A.; Pollini, G. P. *Natural Products Synthesis Through Pericyclic Reactions*; American Chemical Society; Washington, DC, 1983, Chapter (c) Nakai, T.; Mikami, K.; Sayo, N. *Yuki Gosei Kagaku Kyokaishi* **1983**, *41*, 100; *Chem. Abstr*. **1983**, *98*, 178323. (d) Hill, R. K. *Asymmetric Synthesis*; Academic: New York, 1984; Vol. 3B, Chapter 8; (e) Nubbemeyer, U. *Synthesis*, **2003**, 961; (f) Castro, A. M. M. *Chem. Rev.* **2004**, *104*,

2939; (g) *The Claisen Rearrangement: Methods and Applications* Wiley-VCH 2007, Hiersemann, M.; Nubbemeyer, U (Ed).

(9) Nakai, T.; Mikami, K. *Chem. Rev.* **1986**, *86*, 885.

(10) Woodward, R.B.; Hoffmann, R. *The Conservation of Orbital Symmetry*, Academic Press, New York, 1970, 114

(11) For representative Examples See: (a) Overman, L. E.; Mendelson, L. T. *J. Am. Chem. Soc.* **1981**, *103*, 5579; (b) Overman, L. E.; Mendelson, L. T; Jacobsen, E. J. *J. Am. Chem. Soc.* **1983**, *105*, 6629; (c) Knight, S. D.; Overman, L. E.; Pairaudeau, G. *J. Am. Chem. Soc.* **1993**, *115*, 9293; For Review See: (d) Yamago, S.; Nakamura, E. *Org. React.* **2002**, *61*, 1.

(12) Sworin, M.; Lin, K. C., *J. Am. Chem. Soc*. **1989**, *111*, 1815

(13) Arns, S.; Barriault, L. *Chem. Commun.* **2007**, 2211.

(14) (a) Barriault, L.; Gauvreau, D. *J. Org. Chem.* **2005**, *70*, 1382; (b) Barriault, L.; Sauer, E. L. O.; Hooper, J.; Woo, T. *J. Am. Chem. Soc.* **2007**, *129*, 2112; (c) Barriault, L.; Woo. T.; Hooper, J.; Sauer, E. L. O., *Chem. Eur. J.* **2010**, *16*, 14124; (d) Barriault, L.; Denissova, I,; Goulet, *Synthesis*, **2012**, 1833.

(15) For uses in total synthesis see: (a) Barriault, L.; Deon, D.H. *Org. Lett.* **2001**, *3*, 1925; (b) Barriault, L.; Arns, S. *J. Org. Chem.* **2006**, *71*, 1809.

(16) Davies, P. W.; Albrecht, S. J. -C. *Chem. Commun*. **2008**, 238.

(17) (a) Greeves, N.; Vines, K. J. *J. Chem. Soc., Chem. Commun*. **1994**, 1469; (b) Greeves, N.; Vines, K. J. *Tetrahedron Lett.* **1994**, *35*, 7077.

(18) (a) Greeves, N.; Lee, W. –M. *Tetrahedron Lett.* **1997**, *38*, 6445; (b) Greeves, N.; Lee, W. –M.; McLachlan, S. P.; Oakes, G. H.; Purdie, M.; Bickley, J. F. *Tetrahedron Lett.* **2003**, *44*, 9035.

(19) (a) Hiersemann, M. *Synlett* **1999**, 415; (b) Hiersemann, M. *Eur. J. Org. Chem*. **2001**, 483.

(20) For representative examples see: (a) Mikami,K.; Kishi, N.; Nakai, T.; Fujita, Y. *Tetrahedron* **1986**, *42*, 2911; (b) Nakai, T.; Mikami, K. *Org. React.* **1994**, *46*, 105.

(21) (a) Mitchell, T. N.; Gießelmann, F. *Synlett* **1996**, 475; (b) Higashino, T.; Sakaguchi, S.; Ishii, Y. *Org. Lett.* **2000**, *2*, 4193 (c) Ben Ammar, H.; Le Notre, J.; Salem, M.; Kaddachi, M. T.; Dixneuf, P. H. *J. Organomet. Chem.* **2002**, *662*, 63; (d) Le Notre, J.; Brissieux, L.; Semeril, D.; Bruneau, C.; Dixneuf, P. H. *Chem. Commun.* **2002**, 1772; (e) Schmidt, B. *Synlett* **2004**, 1541; (f) Nevado, C.; Echavarren, A. M. *Tetrahedron* **2004**, 60, 9735; (g) Trost, B. M.; Zhang, T. *Org. Lett.* **2006**, *8*, 6007; (h) Okamato, R.; Tanaka, K. *Org. Lett.* **2013**, *15*, 2112 and references therein.

(22) (a) Ohumura, T.; Yamamoto, Y.; Miyaura, N. *Organometallics* **1998**, *18*, 413. (b) Ohumura, T.; Yamamoto, Y.; Miyaura, N. *Chem. Commun.* **1998**, 1337.

(23) (a) Nelson, S. G.; Bungard, C. J.; Wang, K. *J. Am. Chem. Soc.* **2003**, *125*, 13000. (b) Nelson, S. G.; Wang, K. *J. Am. Chem. Soc*. **2006**, *128*, 4232. (c) Stevens, B. D.; Bungard, C. J.; Nelson, S. G. *J. Org. Chem.* **2006**, *71*, 6397. (d) Wang, K.; Bungard, C. J.; Nelson, S. G. J. *Org. Lett.* **2007**, *9*, 2325. (e) Kerrigan, N. J.; Bungard, C. J.; Nelson, S. G. *Tetrahedron* **2008**, *64*, 6863; (f) Geherty, M. E.; Dura, R. D.; Nelson, S. G. *J. Am. Chem. Soc.* **2010**, *132*, 11875.

(24) McLaughlin, M. G.; Cook, M. J. *J. Org. Chem.* **2012**, *77*, 2058.

(25) (a) Price, C. C.; Snyder, W. H. *J. Am. Chem. Soc.* **1961**, *83*, 1773; (b) Taskinen, E.; Laine, M. *Struct. Chem.* **1997**, *8*, 367; (c) Mereyala, H. B.; Gurrala, S. R.; Mohan, S. K. *Tetrahedron* **1999**, *55*, 11331.

(26) (a) Taskinen, E.; Virtanen, R. *J. Org. Chem.* **1977**, *42*, 1443; (b) Taskinen, E. *J. Chem. Soc., Perkin Trans.1* **2001**, 1824

(27) (a) Endo, K.; Otsu, T. *Polymer* **1991**, *32*, 2856; (b) Crivello, J. V.; Kong, S. *J. Org. Chem.* **1998**, *63*, 6745 (c) Davis, C. E.; Duffy, B. C.; Coates, R. M. *J. Org. Chem.* **2003**, *68*, 6935; (d) Evans, D. A.; Kværnø, L.; Dunn, T. B.; Beauchemin, A.; Raymer, B.; Mulder, J. A.; Olhava, E. J.; Juhl, M.; Kagechika, K.; Favor, D. A. *J. Am. Chem. Soc.* **2008**, *130*, 16295.

(28) Harmata, M.; Lee, D. R.; Barnes, C. L. *Org. Lett.* **2005**, *7*, 1881.

(29) Bailey, W. F.; England, M. D.; Mealy, M. J.; Thongsornkleeb, C.; Teng, L. *Org. Lett.* **2000**, *2*, 489; (b) Schollkopf, U. *Angew. Chem., Int. Ed.* **1970**, *9*, 763.

(30) Su, C.; Willard, P. G. *Org. Lett.* **2010**, *12*, 5378.

(31) For hydrosilylation of progarylic and allylic alcohols see: (a) McLaughlin, M. G.; Cook, M. J. *Chem. Commun,* **2011**, *47*, 11104; (b) McAdam, C. A.; McLaughlin, M. G.; Johnston, J. S.; Chen, J.; Walter, M. W.; Cook, M. J. *Org. Biomol. Chem.* **2013**, *11*, 4488; (c) McLaughlin, M. G.; Cook, M. J. *Chem. Commun.* **2014**, *50*, 3501; for other uses see: (d) Chavhan, S. W.; Cook, M. J. *Chem. Eur. J.* **2014**, *20*, 4891.

(32) Johnston, A. J. S.; McLaughlin, M. G.; Reid, J. P.; Cook, M. J. *Org.Biomol. Chem.* **2013**, *11*, 7662.

(33) Sasaki, M.; Ikemoto, H.; Kawahata, M.; Yamaguchi, K.; Takeda, K. *Chem. Eur. J.* **2009**, *15*, 4663.

(34) For competing [2,3]-Wittig and Claisen Rearrangements See: (a) Thomas, A.; Dubini, R. *Helv. Chim. Acta.* **1974**, *57*, 2084; (b) Koreeda, M.; Luengo, J. *J. Am. Chem. Soc*. **1985**, *107*, 5572.

(35) Commercially available crotyl bromide is sold as a 85:15 E/Z mixture from Sigma-Aldrich.

(36) (a) Davies, K. A.; Wulff, J. E. *Org. Lett.* **2011**, *13*, 5552; (b) O'Rourke, N. F.; Davies, K. A.; Wulff, J. E. *J. Org. Chem.* **2012**, *77*, 8634.

(37) Shaaban, S.; Peng, B.; Maulide, N. *Synlett* **2013**, 1722.

(38) KIE experiments were performed by independently measuring the initial rate of the proto and deutero reactions up to 10% conversion under identical conditions in triplicate. The averages were these experiments were then directly compared. For review of kinetic isotope measurements see: Simmons, E. M.; Hartwig, J. F. *Angew. Chem. Int. Ed.* **2012**, *51*, 3066.

(39) Initial rates of reaction: **11a** to **13a** ($k_H$); = 1.74 (±0.03) x $10^{-5}$ mol.dm$^{-3}$.s$^{-1}$; **29** to **13a** ($k_D$); = 7.91 (±0.02) x $10^{-6}$ mol.dm$^{-3}$.s$^{-1}$.

(40) Initial rates of reaction: **11a** to **14a** in $d^0$-toluene ($k_H$); = 2.97 (±0.01) x $10^{-6}$ mol.dm$^{-3}$.s$^{-1}$; **29** to **14a** in $d^0$-toluene ($k_D$); = 1.59 (±0.07) x $10^{-6}$ mol.dm$^{-3}$.s$^{-1}$.

(41) Initial rate of reaction: **11** to **14a** in $d^8$-toluene ($k_{D\text{-}Tol}$); = 6.83 (±0.09) x $10^{-6}$ mol.dm$^{-3}$.s$^{-1}$.

(42) Initial rate of reaction: **29** to **14a** in $d^8$-toluene ($k_{D\text{-}Tol}$); = 2.05 (±0.05) x $10^{-6}$ mol.dm$^{-3}$.s$^{-1}$.

(43) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(44) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(45) Krishnan R.; Binkley J. S.; Seeger R.; Pople J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(46) Gill, P. M. W.; Johnson, B. G.; Pople, J. A.; Frisch, M. J. *Chem. Phys. Lett.* **1992**, *197*, 499.

(47) Gaussian 03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.;

Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

(48) Zhao, Y.; Truhlar, D. *Theor. Chem. Acc.* **2008**, *120*, 215.

(49) Jaguar, version 7.6, Schrodinger, LLC, New York, NY, 2009.

(50) Simon, L.; Goodman, J. M. *Org. Biomol. Chem.* **2011**, *9*, 689.

(51) Grayson, M. N.; Pellegrinet, S. C.; Goodman, J. M. *J. Am. Chem. Soc.* **2012**, *134*, 2716.

(52) Mennucci B.; Tomasi J. *J. Chem. Phys.* **1997**, *106*, 5151.

(53) Grayson, M. N.; Goodman, J. M. *J. Org. Chem.* **2013**, *78*, 8796.

(54) Grayson, M. N.; Goodman, J. M. *J. Am. Chem. Soc.* **2013**, *135*, 6142.

(55) Yoo, H. Y.; Houk, K. N.; Lee, J. K.; Scialdone, M. A.; Meyers, A. I. *J. Am. Chem. Soc.* **1998**, *120*, 205..

(56) Haeffner, F.; Houk, K. N.; Schulze, S. M.; Lee, J. K. *J. Org. Chem.* **2003**, *68*, 2310.

(57) Baumann, H.; Chen, P. *Helv. Chim. Acta* **2001**, *84*, 124.

(58) Hou, S.; Li, X.; Xu, J. *J. Org. Chem.* **2012**, *77*, 10856

(59) (a) Wittig, G., Doser, H., Lorenz, I. *Leibigs Ann. Chem.* **1949**, *562*, 192; (b) Wittig, G., Löhmann, L. *Ann.* **1942**, *550*, 260. (c) Cast, J., Stevens, T.S., Holmes, J. *J. Chem. Soc.***1960**, 3521; (d) Rautenstrach, V., *J. Chem. Soc., Chem. Commun.* **1970**, 4.

(60) (a) Schöllkopf, U. ; Fellenberger, K.; Rizk, M. *Justus Liebigs Ann. Chem.* **1970**, *734*, 106; (b) Felkin, H.; Frajeermann, C. *Tetrahedron Lett*., **1977**, *18*, 3485 and references cited therein; (c) Sayo, K.; Kumara, Y.; Nakai, T. *Tetrahedron Lett*., **1982**, *23*, 3931; (d) Hayakawa, K.; Hayashida, A.; Kanematsu, K. *J. Chem. Soc., Chem. Commun*., **1988**, 1108; (e) Schlösser M.; Strunk, S. *Tetrahedron*, **1989**, *45*, 2649; (f) Bailey, W. F.; Zarcone, L.M. *Tetrahedron Lett.* **1991**, *32*, 4425; (g) Bailey, W. F.; Punzalan, E. R.; Zarcone, L. M. *Heteroat. Chem.* **1992**, *3*, 55; (h) Tomooka, K.; Yamamoto, H.; Nakai, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 4500; (i) Nakazaki, A.; Nakai T.; Tomooka, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 2235; (j) Onyeozili, E. N.; Maleczka Jr., R. E. *Chem. Commun.* **2006**, 2466.

(61) (a) McMichael K. D., Korver, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 2746; (b) Gajewski, J. J.; Conrad, N. D. *J. Am. Chem. Soc*. **1979**, *101*, 2747; (c) Gajewski, J. J.; Conrad, N. D. *J. Am. Chem. Soc.* **1979**, *101*, 6693; (d) Kupczyk-Subotkowska, L.; Saunders Jr., W. H.; Shine, H. J.; Subotkowski, W. *J. Am. Chem. Soc.* **1993**, *115*, 5957.

(62) (a) Gajewski, J. J.; Jurayj, J.; Kimbrough, D. R.; Gande, M. E.; Ganem B.; Carpenter, B. K. *J. Am. Chem. Soc.* **1987**, *109*, 1170; (b) Coates, R. M.; Rogers, B. D.; Hobbs, S. J.; Peck, D. R.; Curran, D. P. *J. Am. Chem. Soc.* **1987**, *109*, 1160; (c) Copley, S. D.; Knowles, J. R. *J. Am. Chem. Soc.* **1987**, *109*,5008; (d) O'Rourke, N. F.; Wulff, J. E. *Org. Biomol. Chem.* **2014**, *12*, 1292.

(63) (a) Dewar, M. J. S.; Healy, E. F. *J. Am. Chem. Soc*. **1984**, *106*, 7127; (b) Gajewski, J. J.; Emrani, J. *J. Am. Chem. Soc.* **1984**, *106*, 5733; (c) Vance, R. L.; Rondan, N. G.; Houk, K. N.; Jensen, F.; Borden, W. T.; Komornicki, A.; Wimmer, E. *J. Am. Chem.Soc.* **1988**, *110*, 2314; (d) Dewar, M. J. S.; Jie, C. *J. Am. Chem. Soc.* **1989**, *111*, 511; (e) Gajewski, J. J.; Gee, K. R.; Jurayj, J. *J. Org. Chem.* **1990**,*55*, 1813; (f) Wiest, O.; Black K. A.; Houk, K. N. *J. Am. Chem. Soc.* **1994**, *116*, 10336; (g) Gajewski, J. J.; Brichford, N. L. *J. Am. Chem. Soc.* **1994**,*116*, 3165; (h) Houk, K. N.;

Yoo, H. Y. J. *Am. Chem. Soc.* **1994**, *116*,12047. (i) Ramadhar, T. R.; Batey, R. A. *Comp. Theor. Chem.* **2011**, *976*, 167.

(64) Perrin, D. D.; Armarego, W. L. F. purification of laboratory Chemicals; 3rd ed. Pergaman press, Oxford, 1988.

(65) Stoner, E. J.; Peterson, M. J.; Allen, M. S.; DeMattei, J. A.; Haight, A. R.; Leanna, M. R.; Patel, S. R.; Plata, D. J.; Premchandran, R. H.; Rasmussen, M., *J. Org. Chem.* **2003,** *68,* 8847.

(66) Ikemoto, H.; Sasaki, M.; Takeda, K., *Eur. J. Org. Chem.* **2010,** 6643.

(67) Liu, P.; Deng, C.-L.; Lei, X.; Lin, G.-q., *Eur. J. Org. Chem.* **2011,** *2011,* 7308.

(68) Leven, M.; Mueller, D.; Goldfuss, B., *Synlett* **2011,** 2505.

(69) Tarantino, K. T.; Liu, P.; Knowles, R. R., *J. Am. Chem. Soc.* **2013,** *135,* 10022.

(70) Zhu, J.-L.; Su, Y.-L.; Chan, Y.-H.; Chen, I. C.; Liao, C.-C., *Heterocycles* **2009,** *78,* 369.

(71) Motiwala, H. F.; Gulgeze, B.; Aube, J., *J. Org. Chem.* **2012,** *77,* 7005.

(72) Edwards, G. L.; Motherwell, W. B.; Powell, D. M.; Sandham, D. A. *J. Chem. Soc., Chem. Commun.* **1991**, 1399.

(73) Hanessian, S.; Chenard, E., *Org. Lett.* **2012,** *14,* 3222.

(74) Li, Y.; Bao, W., *Adv. Synth. Catal.* **2009,** *351,* 865.

(75) Gabbutt, C. D.; Heron, B. M.; Kilner, C.; Kolla, S. B., *Org. Biomol. Chem.* **2010,** *8,* 4874.

(76) Zheng, H.; Lejkowski, M.; Hall, D. G., *Chem. Sci.* **2011,** *2,* 1305.

(77) Xu, W.; Wang, R.; Wu, G.; Chen, P. *RSC Adv.* **2012**, *2*, 6005.

(78) Lu, S.-M.; Gao, Q.; Li, J.; Liu, Y.; Li, C. *Tetrahedron Lett.* **2013**, *54*, 7013.

(79) Arai, N.; Azuma, K.; Nii, N.; Ohkuma, T., *Angew. Chem., Int. Ed.* **2008,** *47,* 7457.

(80) Krishna, J.; Reddy, A. G. K.; Ramulu, B. V.; Mahendar, L.; Satyanarayana, G., *Synlett* **2012,** *23,* 375.

(81) Shibata, I.; Kano, T.; Kanazawa, N.; Fukuoka, S.; Baba, A., *Angew. Chem., Int. Ed.* **2002,** *41,* 1389.

(82) (a) Xu, L.-W.; Yang, M.-S.; Qiu, H.-Y.; Lai, G.-Q.; Jiang, J.-X., *Synth. Commun.* **2008,** *38,* 1011; (b) Yadav, J. S.; Reddy, B. V. S.; Sadasiv, K.; Satheesh, G., *Tetrahedron Lett.* **2002,** *43,* 9695.

(83) Ketcham, J. M.; Biannic, B.; Aponick, A., *Chem. Commun.* **2013,** *49,* 4157.

(84) Fukuda, S.; Tsuji, K.; Musashi, J.; Nonaka, R.; Kimura, T.; Satoh, T., *Synthesis* **2011,** 3615.

(85) Arai, S.; Koike, Y.; Hada, H.; Nishida, A., *J. Org. Chem.* **2010,** *75,* 7573.#

(86) Ueda, T.; Tanaka, K.; Ichibakase, T.; Orito, Y.; Nakajima, M., *Tetrahedron* **2010,** *66,* 7726.

(87) Evans, P.; Johnson, P.; Taylor, R. J. K., *Eur. J. Org. Chem.* **2006,** 1740.