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1,3-DIOXA-[3,3]-SIGMATROPIC OXO-REARRANGEMENT OF SUBSTITUTED ALLYLIC CARbamates: SCOPE AND MECHANISTIC STUDIES

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ABSTRACT: An unexpected 1,3-dioxa-[3,3]-sigmatropic rearrangement during the treatment of aryl- and alkenyl-substituted allylic alcohols with activated isocyanates is reported. The reorganization of bonds is highly dependent on the electron density of the aromatic ring and the nature of isocyanate used. This metal-free tandem reaction from branched allyl alcohols initiated by a carbamoylation reaction and followed by a sigmatropic rearrangement thus
offers a new access to \((E)\)-cinnamyl and conjugated \((E,E)\)-diene carbamates such as \(N\)-acyl and \(N\)-sulfonyl derivatives. A computational study was conducted in order to rationalize this phenomenon as well as a rearrangement progress kinetic analysis was performed.

INTRODUCTION

Among the plethora of tools at the disposal of synthetic organic chemists, the [3,3]-sigmatropic rearrangements represent very useful methods for the regio and stereoselective formation of carbon-carbon or carbon-heteroatom bonds.\(^1\) Among the C-N bond forming reactions, the sigmatropic rearrangement of allylic trichloroacetimidates, namely the Overman rearrangement,\(^2\) occupies a place of choice as shown by the number of total synthesis involving this method.\(^3\) The decarboxylative [3,3]-rearrangement of allylic carbamates represents also a very useful strategy for the preparation of protected allylic amines from allylic alcohols with an excellent regio-and stereoselectivity.\(^4,5\) Initially reported by Holm et al. in 1970,\(^6\) the allyl cyanate/isocyanate rearrangement can be now considered as an attractive alternative method to those above-mentioned, due to the fact that the transposition occurs at or below ambient temperature, under metal-free conditions and with a complete transfer of chirality.\(^7\) The first step of this process is the formation of the transient allyl cyanate from a carbamate-type \(B\), under dehydration conditions, followed by a spontaneous [3,3]-sigmatropic bond reorganization to afford the corresponding allyl isocyanate \(C\) (Figure 1). This domino dehydration/rearrangement sequence was successfully applied on a wide variety of carbamates coming from alkyl-substituted allylic alcohols such as \(A\).\(^8\) As a continuation of our studies on the use of this methodology for the synthesis of new reagents or original compounds,\(^9\) we envisaged the formation of branched substituted carbamates of \(B\)-type in which \(R\) would be an aryl group since they have never been employed to date in this kind of rearrangement.\(^7\) However, as preliminary result, we observed that treatment of 1-(4-methoxyphenyl)prop-2-en-1-ol with trichloroacetyl isocyanate followed by a basic hydrolysis following a standard sequential process did not provide the expected branched compound (Figure 1). The only product formed was a primary carbamate \(4a\) with a well-defined stereochemistry of the double bond \((E)\). In view of previous works concerning the thermal rearrangement of allylic esters,\(^10,11\) we envisioned at this stage that the formation of \(4a\) could be the outcome of a rapid 1,3-dioxa-[3,3]-sigmatropic rearrangement\(^12\) from the branched trichloroacetyl carbamate intermediate before hydrolysis.
Surprisingly, this rearrangement does not require any metal catalyst and takes place under neutral conditions. Indeed, the scarce examples described in literature require catalytic methods based on palladium (II) or mercury (II) salts. Taking into account the important role of molecules bearing a carbamate group as synthetic intermediates as well as in modern drug discovery, and that this one-pot process starting from 2-alken-1-ols (A, R = aryl or alkenyl) could constitute a valuable access to linear allyl carbamates (Figure 2), we decided to further explore the substrate scope and limitations of this methodology in order to offer a rationalization of this phenomenon.

**Figure 1.** Observation of the uncatalyzed 1,3-dioxa-[3,3]-sigmatropic rearrangement.

**Figure 2.** Proposed 1,3-dioxa-[3,3]-sigmatropic rearrangement of O-allyl carbamates.
In this paper, we report the results of our study. We show that the rate of the 1,3-dioxa-[3,3] sigmatropic rearrangement depends mainly on the electron density of the aromatic ring. These experimental observations have been confirmed by a kinetic study establishing that the rearrangement is of first kinetic order. The nature of the isocyanate used is also important for the transposition to occur. Activated reagents such as trichloroacetyl or p-toluenesulfonyl isocyanates were required. Other substrates, in which an aryl group at the allylic position (C1) was replaced by an alkenyl group, were also examined with success. In addition, a computational study of the mechanism has also been carried out in order to seed some light on the nature of this stereoselective thermal rearrangement.

RESULTS AND DISCUSSION

Experimental studies. First of all, we carefully examined the reaction of 1-(4-methoxyphenyl)prop-2-en-1-ol 1a with trichloroacetyl isocyanate by monitoring the carbamoylation over time by ¹H NMR (Scheme 1). At room temperature, the reaction is complete after 15 minutes in favor of the formation of 3a, product which may result of a [3,3] sigmatropic rearrangement from intermediate 2a. At no moment during this NMR study was the branched carbamate 2a detected indicating the short-lived nature of this reaction intermediate even at lower temperature (-70 °C). In all cases only the linear carbamate 3a was formed, with (E)-stereochemistry of the internal double bond. After evaporation of solvent, 18 3a could be isolated from the reaction medium by trituration techniques or used without further purification. Treatment of crude mixture under basic conditions in the presence of K₂CO₃ afforded the expected compound 4a with 73% overall yield from 1a and 62% from 4-methoxybenzaldehyde. It is noteworthy that this new compound 4a was also prepared from the same starting material, according to a conventional longer strategy (four steps instead of three) and a poorer overall yield (52%). 19

Scheme 1. Synthesis of 4a Using a Rearrangement/Hydrolysis Sequence.
In order to determine the main factors that influence this sigmatropic rearrangement, different secondary allylic alcohols bearing both electron withdrawing and electron donating groups at para position on the aromatic ring were tested in the presence of trichloroacetyl isocyanate (TCA-NCO). As summarized in Table 1, the bond reorganization is highly dependent on the nature of the substituent. Except when the mesomeric effect is positive (+ M, R = OMe, entry 1), heating the reaction mixture was required for all other cases (entries 2-4). During the NMR study, the formation of intermediates 2b-d was clearly identified as being the first step before rearrangement can occur. The results obtained confirmed that the rate of this reaction is much slower with electron-deficient aromatic rings. Indeed, conversion of 2c into 3c (R = Cl, -I and +M effects) was complete after 20 h at 90 °C (entry 3) while with R = NO2 (-I and -M effects), the time of reaction was increased sixfold to reach only 50% conversion to 3d (entry 4). These results suggest a significant electron-deficient character for the allyl moiety along this sigmatropic process. After evaporation of solvent and hydrolysis under basic conditions, all linear carbamates 4 were obtained as single stereoisomer (E) and with moderate to good yields.

Table 1. Synthesis of Linear Carbamates 4 from Allyl Alcohols 1 Using Trichloroacetyl Isocyanate.
Considering the potential importance of dienyl carbamates in the synthesis of natural products, the carbamoylation/rearrangement/hydrolysis sequence was also extended to other substrates such as C3-alkenyl-substituted allylic alcohols. The results indicated in Table 2 led to similar conclusions regarding the electronic effects that promote the rearrangement. More the aromatic ring was electron-rich, faster was the sigmatropic process. The difference of reaction rate between starting materials 1 and 5, both of them possessing the same substitution pattern on the aromatic ring can be in part explained by the generation of a conjugated diene unit acting as the driving force due to the higher stability of products 6. For instance, the rearrangement took place from 5c in the presence of trichloroacetyl isocyanate (Table 2, entry 3) without heating, whereas a temperature of 90 °C was required for starting alcohol 1c (Table 1, entry 3). In the case of nitro group (entry 4, Table 2), the rearranged product 6d was not observed by NMR analysis even after 7 days of reaction at 90 °C, most likely due to the instability of the corresponding reaction intermediates at this temperature. In all other cases, the linear conjugated diene carbamates 7 were obtained after basic hydrolysis.
in good yields, except for R = OMe (Table 2, entry 1), for which the purification on silica gel led to lose of product.

Table 2. Carbamoylation/Rearrangement/Hydrolysis Sequence of C3-Alkenyl-Substituted Allyl Alcohols 5.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Time (h)</th>
<th>Product (Yield, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MeO</td>
<td>2</td>
<td>7a, 24(65)</td>
</tr>
<tr>
<td>2</td>
<td>H</td>
<td>4</td>
<td>7b, 65</td>
</tr>
<tr>
<td>3</td>
<td>Cl</td>
<td>4</td>
<td>7c, 75</td>
</tr>
<tr>
<td>4</td>
<td>NO₂</td>
<td>178</td>
<td>-</td>
</tr>
</tbody>
</table>

* Reactions were monitored by \(^1\)H-NMR until total consumption of starting material. \(^b\) Isolated yield of pure product. \(^c\) Reaction carried out in toluene-d8 at 90 °C. \(^d\) No formation of desired product was observed. \(^e\) Determined by \(^1\)H-NMR using 1,3,5-trimethoxybenzene as internal reference.

In order to bring to light the utility of this new process, the synthetic interest of linear carbamates such as 4a was evaluated through a [3,3]-allyl cyanate rearrangement.\(^{21}\) Treatment of 4a with trifluoroacetic anhydride (TFAA, 1.5 equiv) in the presence of a large excess of Et₃N at 0 °C for 30 min. led to the complete formation of isocyanate which can be quenched with various nucleophiles to afford compounds 8, 9 and 10 in unoptimized yields (Scheme 2). When benzyl alcohol was used as nucleophile, a catalytic amount of Ti(Or-Bu)₄ was required.\(^{22}\)

Scheme 2. Selected In Situ Transformations of Rearranged Carbamate 4a.
In our quest to determine the parameters influencing this 1,3-dioxo-\([3,3]\)-sigmatropic rearrangement, the nature of the reagent was afterwards examined using deactivated isocyanates. As expected, treatment of \(1a\) with aliphatic or aromatic isocyanates in the presence of \(\text{Et}_3\text{N}\) and a catalytic amount of DMAP gave rise to the corresponding branched carbamates \(11\) (\(R = \text{Ph}\)) and \(12\) (\(R = \text{i-Pr}\)) with no trace of linear rearranged carbamates, as revealed by NMR analysis of the corresponding crude reaction mixtures (Scheme 3).\(^{23,24}\) When the phenyl isocyanate was used, the conversion was incomplete, which justifies the low yield obtained for the isolated compound \(11\) (30%). From these last results, the presence of the \(N\)-trichloroacetyl group in carbamates, such as \(2a\), appears to be critical for the implementation of the rearrangement, likely by making the NH group less basic.

**Scheme 3. No Rearrangement Observed with Deactivated Isocyanates During The Carbamoylation Reaction**
In order to validate our hypothesis that the reorganization of branched aryl allyl carbamates could be reliant on the acidity of the carbamate NH, we tried the reaction between the allyl alcohol 1a and p-toluenesulfonyl isocyanate. After 15 minutes at room temperature in CH₂Cl₂, the conversion into linear N-tosyl carbamate 14a was complete leading exclusively the (E)-isomer. In these conditions, the product was obtained after purification with an excellent yield (90%) from 1a (Table 3). The one-pot reaction was extended to other aryl allyl alcohols 1 with good to high yields of purified products 14, except for 14h and 14i because of their weak stability on silica gel. For substrates with electron-poor aromatic rings (1b, 1c, 1d, 1e), heating in toluene solution was required. In all cases, the exclusive E-isomer formation of the internal double bond was maintained. Structure of 14e was determined by X-ray crystallography.

Table 3. 1,3-dioxa-[3,3]-Sigmatropic Rearrangement Using p-Toluenesulfonyl Isocyanate as Reagent.
Benzoyl isocyanate was also successfully employed to yield the rearranged product 15 from 1a (Scheme 4). After 30 minutes in CDCl₃, the starting material was completely consumed and the primary carbamate 15 was obtained in 63% yield after purification.

Scheme 4. Carbamoylation/Rearrangement Sequence Using Benzoyl Isocyanate.

In the same way, the one-pot process using tosyl isocyanate reagent was carried out successfully from C3-alkenyl-substituted allyl alcohols 5 to afford the corresponding (E,E)-
conjugated linear carbamates 16 (Table 4). Nevertheless, compound 16d (R = NO$_2$, Table 4, entry 4) was obtained in moderate yield after separation of the unreacted starting material.

Table 4. Carbamoylation/Rearrangement Sequence Using Tosyl Isocyanate From C3-Alkenyl-Substituted Allyl Alcohols 5.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Time (h)$^a$</th>
<th>Product (Yield,%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MeO</td>
<td>0.5</td>
<td>16a, 25(85)$^c$</td>
</tr>
<tr>
<td>2</td>
<td>H</td>
<td>4</td>
<td>16b, 75</td>
</tr>
<tr>
<td>3</td>
<td>Cl</td>
<td>4</td>
<td>16c, 68</td>
</tr>
<tr>
<td>4$^c$</td>
<td>NO$_2$</td>
<td>120$^d$</td>
<td>16d, 36</td>
</tr>
</tbody>
</table>

$^a$ Reactions were monitored by $^1$H-NMR until total consumption of starting material. $^b$ Isolated yield of pure product. $^c$ Reaction carried out in toluene-$d_8$ at 90 °C. $^d$ 50 % conversion was observed. $^e$ Determined by $^1$H-NMR using 1,3,5-trimethoxybenzene as internal reference.

In order to test whether the carbamoylation reaction could be followed by a sequential double sigmatropic oxo-rearrangement in a one-pot process, 1-aryl-2,4-butadien-1-ols 17 as a mixture of stereoisomers were prepared from hexanedial according to a described procedure (Scheme 5).$^{25}$ Treatment of 17 with tosyl and benzoyl isocyanates led to the formation of the corresponding rearranged products 18ab, 18ba and 18bb respectively. The reactions took place at room temperature with a complete conversion after 2 h in CH$_2$Cl$_2$, but unfortunately the purification of these compounds is difficult due to their instability on silica gel (see Experimental Section). It should be noted, however, that even in the presence of a deactivating group on the aromatic ring, these substrates are prone to undergo this consecutive double rearrangement under mild conditions, as demonstrated with alcohol 17b.

Scheme 5. Consecutive [3,3]-Sigmatropic Rearrangements from Starting Alcohols 17.
Finally, we studied the stereoselectivity of the rearrangement in terms of the transfer of chirality when a chiral allyl alcohol is used as starting reactant. To this end, we analyzed the behavior of racemic (E)-1-phenylbut-2-en-1-ol 20 and its (S)-enantiomer (Figure 3). This latter starting alcohol was separated from a racemic mixture by HPLC using a chiral stationary phase (see the Experimental Section). After this chromatographic separation, (S)-20 was obtained with an enantiomeric excess of 98%. Both racemic and (S)-20 were transformed into carbamates 21 (not isolated, see Figure 3) by reaction with (R)-[1-(4-fluorophenyl)ethyl]isocyanate (R)-19 in the presence of triethylamine. After two days of reaction at 110 °C in toluene the corresponding rearranged products 22 was obtained. The HPLC profile of the diastereomeric mixture of (S,R)+(R,R) carbamates 22 showed two well-defined peaks compatible, within the experimental error, with that would be expected for the reaction product stemming from racemic 20. In the case of the product formed using (S)-20 as reactant, formation of (S,R)-22 was observed with 95% diastereomeric excess, according to the HPLC profile. These results, show that, within the experimental error, most of –if not all– the observed rearrangement takes place via a symmetry allowed concerted supra-supra mechanism, with virtually complete 1,3-transfer of the chiral information contained in the starting alcohol, together with retention of configuration of the double bond. The mechanistic aspects derived from this observation shall be discussed in the following section.
**Mechanistic studies.** Conversion of alcohols 1b,c (R=H, Cl, respectively) into the rearranged products 14b,c in the presence of p-toluenesulfonyl isocyanate was monitored by $^1$H-NMR in deuterated toluene at 90 °C. A selected ensemble of spectra recorded at different reaction times is gathered in Figure 4. These data indicate that alcohol 1c is immediately converted into carbamate 13c, as it can be appreciated by comparison of both spectra. This intermediate
carbamate evolves towards the rearranged product 14c with no detectable intermediate species. Using these NMR data and applying first-order kinetics in eq 1

\[ \ln[13c]_t - \ln[13c]_0 = -k_{obs}t \] (1)

we obtained \( k_{obs} = 1.08( \pm 0.04) \times 10^{-4} \) s\(^{-1}\). A similar study for alcohol 1b (R=H) led to a measured kinetic constant of \( k_{obs} = 1.62( \pm 0.06) \times 10^{-4} \) s\(^{-1}\) (see the Supporting Information). These results were confirmed in a combined experiment using a 1:1 mixture of 1b and 1c, to which a 50 % of p-toluenesulfonyl isocyanate was added. After 5 min. of reaction at room temperature, the \(^1\)H-NMR analysis revealed that ca. 50 % of both alcohols remained unreacted, whereas carbamates 13b and 13c were observed in a 1.0:1.2 ratio. After 6h of reaction at 90 ºC, a complete 13b→14b (R=H) conversion was observed, whereas for the 13c→14c (R=Cl) rearrangement the conversion was of ca. 40 %. These results showed that the fast formation of carbamates 13 from alcohols 1 is not selective and that the subsequent dioxa-[3,3]-sigmatropic rearrangements occur through a kinetically independent process, not related to the formation of the starting carbamate. In the case of alcohol 1a (R=OMe) the reaction was too fast to obtain a reliable first-order kinetic under the same experimental conditions used for 1b and 1c. However, we could measure the first-order reaction rate until 15 min of reaction at room temperature and obtained \( k_{obs} = 1.63( \pm 0.05) \times 10^{-3} \) s\(^{-1}\), one order of magnitude faster than in the preceding cases. Similar experiments with 1d (R=NO\(_2\)) were not possible because the reaction was too slow. We also examined the efficiency of the reaction in the presence of polar solvents. When alcohol 1b and tosyl isocyanate were allowed to react in DMSO or DMF no reaction was observed, whereas in acetonitrile only 35 % conversion was observed after three days of reaction at 90 ºC. These results are in agreement with those reported in Table 3 (vide supra). We concluded from these data that electron withdrawing groups at the aryl moiety of the starting alcohols result in lower reactivity. On the contrary, electron releasing groups such as methoxy accelerate the sigmatropic rearrangement. This conclusion is compatible with an electron deficient character of the allyl moiety at the corresponding transition state, an aspect (among others) that was analyzed by DFT calculations.
Figure 4. \textsuperscript{1}H-NMR plots (500 MHz) corresponding to the reaction of 1-(4-chlorophenyl)prop-2-en-1-ol 1c with N-tosyl isocyanate at 90 °C to yield rearranged carbamate 14c via intermediate 13c. The successive spectra, recorded at different reaction times, show the evolution of the allylic hydrogens of both carbamates. The spectrum of the allylic region of 1c is also shown.

Since the \textsuperscript{1}H-NMR showed that the formation of 1-arylallyl tosylcarbamates 13b,c from alcohols 1b,c was not kinetically relevant, we carried out DFT calculations on these transformations. These calculations were performed at the B3LYP-D3(PCM)/6-311G++G(d,p) level of theory. Toluene was used as solvent and the Gibbs energies were calculated at 90 °C (363.15 K).

Previous work on the rearrangement of allyl esters\textsuperscript{10a,b} suggested that both [3,3] and [1,3] mechanisms could occur (Scheme 6). In addition, Birney,\textsuperscript{11,27} Duncan\textsuperscript{28} and respective co-workers have indicated that in esters and acetimidates both pericyclic and pseudopericyclic mechanisms can compete. In order to elucidate the preference for the [1.3] or [3,3] topologies...
associated with these 1,3-dioxa-sigmatropic rearrangements, we studied computationally the degenerate rearrangement of allyl tosylcarbamate 23 via [1,3] or [3,3] sigmatropic shifts. In turn, within the [3,3] reaction path, we considered chair and boat geometries for the corresponding saddle points (Scheme 6) as well as the possible occurrence of pseudopericyclic mechanisms.

Scheme 6. Possible [3,3] and [1,3] Mechanisms for the 1,3-Dioxa Rearrangement of Allyl Tosylcarbamate 23.

The chief geometric and energetic features of transition structures chair-TS(3,3), boat-TS(3,3) and TS(1,3) are gathered in Figure 5. Our calculations indicate that the dioxa-[3,3]-sigmatropic mechanism is clearly preferred with respect to the [1,3] rearrangement involving only one of the oxygen atoms of the carboxylate moiety. Within the [3,3] mechanism, the chair geometry of the corresponding transition state is 4.6 kcal/mol less energetic than that associated with the boat analogue. These results are in agreement with the empirical observations reported by Lewis and Hill, who established that the [1,3] mechanism is substantially more energetic than the [3,3] reaction path. On the other hand, the dihedral angles calculated for the three transition structures shown in Figure 5 indicate $\pi-\pi$ interactions between both reactants, with dihedral angles $\omega$ of 85-110 deg. Since the participation of the lone pairs (orbitally disconnected to the C=O $\pi$-orbitals) of one or two oxygen atoms should lead to $\omega$ values close to 180 deg. (vide infra), we concluded that both
[1,3] and [3,3] geometries shown in Figure 5 correspond to pericyclic and not to pseudopericyclic processes. In addition, these 1,3-dioxa-[3,3]-sigmatropic rearrangements take place via chair geometries and symmetry allowed\textsuperscript{29} supra-supra topologies.

![Optimized structures of transition structures](image)

**Figure 5.** Optimized structures (B3LYP-D3(PCM=toluene)/6-311++G(d,p) level of theory) of transition structures chair-\(\text{TS(3,3)}\), boat-\(\text{TS(3,3)}\) and \(\text{TS(1,3)}\) depicted in Scheme 6. Bond distances are in Å. Dihedral angle \(\omega\) (in deg.) is defined by the \(a-b-c-d\) atoms. Numbers in parenthesis are the relative energies, in kcal/mol.

We also performed isotope labeling NMR experiments in order to verify the previously discussed computational results. These experiments were carried out by using a mixture of 11.1% H\(_{2}\text{O}^{17}\), 29.7% H\(_{2}\text{O}^{18}\) and 59.2% H\(_{2}\text{O}^{16}\). Conversion of (trichloromethyl)benzene \(24\) into doubly labeled benzoic acid \(25\) under microwave irradiation\textsuperscript{30} permitted two synthetic routes (Figure 6A). In the first one, we prepared diester \(26\) following a described procedure.\textsuperscript{31} The \(^{17}\text{O}-\text{NMR}\) spectrum is shown in Figure 6B. In this spectrum two well separated signals at 340 and 136 ppm can be observed, associated with the sp\(^2\) and sp\(^3\)-hybrydized \(^{17}\text{O}\) nuclei, respectively. This process permitted us to calibrate the performance of \(^{17}\text{O}-\text{NMR}\) to distinguish the starting and final resonances associated with the \([^{17}\text{O}]_{13b} \rightarrow [^{17}\text{O}]_{14b}\) transformation.
Figure 6. (A) Synthesis of labelled allyl tosylcarbamates [*O_1]13b and [*O_2]14b, and diester [*O_2]26. The [*^{17}O]-labeled compounds were synthesized from a mixture of 11.1% H_{2}^{17}O, together with 29.7% H_{2}^{18}O and 59.2% H_{2}^{16}O. The δ(^{17}O) chemical shifts of the [*^{17}O]-labelled compounds are given in ppm. (B) ^{17}O-NMR spectrum of diester [*^{17}O_2]26, in which the sp^2 and sp^3-hybridized oxygen atoms can be distinguished. (C) ^{17}O-NMR spectra of the [*^{17}O_1]13b → [*^{17}O_1]14b transformation recorded in d_8-PhMe at different reaction times. The signals of sulfone oxygen atoms (c' and c'', natural abundances) are also given.

The second synthetic route of labeling experiments consisted of the conversion of labeled benzoic acid 25 into allyl alcohol 1b via a sequence of reduction, oxidation and addition reactions involving O-labeled benzyl alcohol 27 and benzaldehyde 28, whose diagnostic δ(^{17}O) chemical shifts are gathered in Figure 6A (see the Supporting Information for further details). Reaction of labeled 1b with tosyl isocyanate led almost immediately (vide
supra) to labeled 13b. The $^{17}$O-NMR spectrum of labeled $[{^{17}}\text{O}]_{13b}$ showed a very broad signal at 150 ppm, partially superimposed to the signal associated with the sulfone moiety (natural abundance, see the Supporting Information for further details). Heating of $[{^{17}}\text{O}]_{13b}$ led us to observe a new signal at 264 ppm (Figure 6C), which was interpreted as associated with the sp$^2$-hybridized $^{17}$O nucleus of $[{^{17}}\text{O}]_{14b}$ on the basis of the related signal of $[{^{17}}\text{O}]_{26}$ shown in Figure 6B. The emergent signal of $[{^{17}}\text{O}]_{14b}$ was coincident with the decrease of the broad signal of $[{^{17}}\text{O}]_{13b}$, the broad signals of the SO$_2$ groups of both tosyl carbamates being of similar chemical shift. These results, together with the above described calculations and experiments involving chiral species, led us to the conclusion that, as suggested by Lewis and Hill, the conversion of carbamates 13 into their regioisomers 14 takes place via concerted pericyclic 1,3-dioxo-[3,3]-sigmatropic rearrangements.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{rearrangement_diagram.png}
\caption{Reaction profiles of the thermal rearrangement of 1-phenylallyl tosylcarbamate 13b to yield cinnamyl tosylcarbamate 14b. All stationary points were calculated at the B3LYP-D3(PCM,solvent=toluene)/6-311++G(d,p) level of theory. Numbers in parentheses are the relative free energies, in kcal/mol, calculated at 363.15 K with respect to 13b. The experimental Gibbs activation energy, estimated at the same temperature, is also provided.}
\end{figure}
Bond distances are given in Å. Σq(CO$_2$) values, displayed in red, correspond to the natural charges of the carboxy moieties and are given in a. u. Numbers in blue correspond to the respective bond orders. The $\bar{S}y$ parameter stands for the synchronicity of each elementary process via TSb and TSb'. For a perfectly synchronous transformation, $\bar{S}y$=1 (see text).

The reaction coordinate associated with the [3,3] sigmatropic rearrangement of 1-phenylallyl tosylcarbamate 13b to yield cinnamyl tosylcarbamate 14b (R=H) was analyzed first. The chief features of this reaction are gathered in Figure 7. We found two transition structures TSb and TSb' corresponding to chair and boat geometries, respectively. The former saddle point was found to be ca. 4.2 kcal/mol less energetic than its boat congener, which indicates that only the 13b$\rightarrow$TSb$\rightarrow$14b reaction coordinate is kinetically relevant. The theoretical activation energy was calculated to be 21.7 kcal/mol. From the $^1$H-NMR data (vide supra), the experimental Gibbs activation energy at 363.15 K was estimated from the Eyring equation (eq.2) associated with $k_{obs}$:

$$k_{obs} = \kappa \frac{k_B 363.15}{h} \exp \left[ - \frac{\Delta G_{363.15}^{\text{ex}}}{R \cdot 363.15} \right]$$  \hspace{1cm} (2)

Assuming $\kappa \approx$ 1, the estimated activation energy was calculated to be 22.4 kcal/mol, in good agreement with the computational value. In addition, using the bond orders associated with the suprafacial [3,3] sigmatropic shift, we computed the earliness of the reaction path via TSb as the average of the degree of advancement $\delta B_{AV}$ of both saddle points, according to the following expression (eq.3):

$$\delta B_{AV} = \frac{1}{6} \sum_{i=1}^{6} \delta B_i = \frac{1}{6} \sum_{i=1}^{6} B_{TS}^i - B_{TS}^p$$

(3)

where $B_i$ is the bond order of the $i$-th bond involved in the pericyclic reaction at the reactant (R) 13b, transition state (TS) TSb and product (P) 14b. For the 13b$\rightarrow$TSb$\rightarrow$14b transformation it was found that $\delta B_{AV}$ =0.42. Since for an exactly midway transition structure $\delta B_{AV}$=0.5, this result indicates an slightly early saddle point, with $\Delta G_{\text{rxn}}$=-5.5 kcal/mol. We also calculated the synchronicity $\bar{S}y$ of the reaction as

$$\bar{S}y = 1 - \frac{1}{10} \sum_{i=1}^{6} \frac{\left| \delta B_i - \delta B_{AV} \right|}{\delta B_{AV}}$$

(4)

According to this expression (eq.4), for a perfectly synchronous [3,3] sigmatropic reaction, $\delta B_i=\delta B_{AV}$ for any $i=1,2, \ldots, 6$ and therefore $\left| \delta B_i - \delta B_{AV} \right| = 0$ and $\bar{S}y$=1. In our case, we obtained $\bar{S}y$=0.75 for the 13b$\rightarrow$14b reaction mediated by TSb, which suggests a noticeable
asynchronicity. When the same reaction is mediated by $\text{TSb'}$, the reaction was computed to be slightly more asynchronous (see Figure 7). These results are in line with the geometries obtained for both saddle points, with two C···O distances associated with the bonds being broken and formed (see Figure 7). This partially asynchronous but still concerted character of the reaction mechanism agrees with the preservation of the chiral information contained in the starting enantiopure allyl alcohol (see Figure 3). Finally, the charge analysis of the carboxylate moiety along the reaction coordinate showed that this charge was ca. 0.2 e higher in the transition structures than in the reactant and product (Figure 7). This result points to relatively polar transition structures, with an associated positive charge delocalized in the allyl moiety. As a consequence, electron-withdrawing groups in the starting allyl alcohol should destabilize this partial cationic character, thus leading to higher activation energies. Likewise, electron releasing substituents should accelerate the sigmatropic rearrangement, in good agreement with our experimental results (see Tables 1-4).

We also performed the above described DFT study with tosylcarbamate 13c (R=Cl) to yield 4-chlorocynnamyl tosylcarbamate 14c (see the Supporting Information for further details). The computed reaction profile for this series was similar to that found for R=H case. As expected, the activation energy computed for the 13c→14c reaction via $\text{TSc}$ was calculated to be 22.6 kcal/mol, a value slightly higher than that found for the parent 13b→14b reaction. The excellent agreement between this latter computational value and the corresponding experimental estimate (22.7 kcal/mol, see the Supporting Information) reflects the reliability of our calculations and reproduces correctly the lower reaction rate with respect to the parent reaction (R=H) for allyl alcohols when R=Cl.

In order to analyze the reasons for the preference for the chair conformation in $\text{TSb}$, we considered applying the distortion/interaction-activation strain model\textsuperscript{33} to both saddle points. However, the intramolecular nature of the sigmatropic rearrangement hampered the analysis in terms of interacting molecules. Therefore, we decomposed the activation energy $\Delta E^\ddagger$ as the sum of the deformation (FDEF) and interaction (FINT) terms between two carboxylic (C) and allylic (A) fragments at transition structure $\text{TSb}$:

$$\Delta E^\ddagger = \Delta E_{\text{FDEF}}^\ddagger + \Delta E_{\text{FINT}}^\ddagger \quad (5)$$

The deformation of both fragments can be envisaged as the sum of the zwitterionic (ZW) and diradical (DR) contributions of both fragments:
\[ \Delta E_{\text{DEF}}^\pm = X_{ZW} \Delta E_{ZW}^\pm + (1 - X_{ZW}) \Delta E_{DR}^\pm \] (6)

where \( X_{ZW} \) is the weight of the zwitterionic contribution, the corresponding diradical coefficient \( X_{DR} \) satisfying the relation \( X_{ZW} + X_{DR} = 1 \). Since for the DR structures the charges of both fragments are zero, we approximated the contribution of the ZW form as \( X_{ZW} = \delta \), namely the NBO charge of the allylic fragment \( A \) in TSb (Figure 8).

The \( \Delta E_{ZW}^\pm \) term was computed as the sum of the single-point energies of isolated carboxylate (\( C^- \)) and allyl cation (\( A^+ \)) fragments at the geometry of TSb, with respect to the energy \( E_0 \) of the reactant 13b:

\[ \Delta E_{ZW}^\pm = (\Delta E_{C^-}^\pm + \Delta E_{A^+}^\pm) - E_0 \] (7)

The \( \Delta E_{DR}^\pm \) term was computed in a similar way, but considering the contributions of the carboxy (\( C^- \)) and allyl (\( A^- \)) isolated radical fragments, also computed at the geometries of the transition state TSb:

\[ \Delta E_{DR}^\pm = (\Delta E_{C}^\pm + \Delta E_{A}^\pm) - E_0 \] (8)

Our results indicate that both in the chair and boat conformations of TSb the contributions of the ZW forms are ca. 1 kcal/mol larger than those associated with the DR forms. Thus, in chair-TSb the respective values are \( \Delta E_{ZW}^\pm = 73.3 \) kcal/mol and \( \Delta E_{DR}^\pm = 72.3 \) kcal/mol, whereas the corresponding values for boat-TSb are \( \Delta E_{ZW}^\pm = 78.4 \) kcal/mol and \( \Delta E_{DR}^\pm = 77.6 \) kcal/mol. The computed total values of \( \Delta E^\pm, \Delta E_{\text{DEF}}^\pm \) and \( \Delta E_{\text{INT}}^\pm \) terms of eq. (1) are shown in Figure 8. Our calculations indicate that the fragment deformation term \( \Delta E_{\text{DEF}}^\pm \) is 5.1 kcal/mol higher in boat-TSb than in chair-TSb, the difference in \( \Delta E_{\text{INT}}^\pm \) being of only 1.2 kcal/mol in favor of boat-TSb. Therefore, in the boat geometry both the deformation (destabilizing) and interaction (stabilizing) terms between the C and A fragments are higher in magnitude because of closer steric, Coulombic and electronic contacts in boat-TSb with respect to its chair congener. We conclude that \( \Delta E_{\text{DEF}}^\pm \) is responsible for the preference for the chair conformation in these pericyclic transition structures, since the more congested boat geometry induces a larger departure of the C and A fragments from their respective optimal geometries.
Figure 8. (A) Fragment deformation/interaction analysis (see text) of TSb in terms of resonant zwitterionic (ZW) and diradical (DR) contributions between carboxy (C) and allyl (A) fragments. $\Sigma q$ is the formal charge of the corresponding fragment. The expected $\langle S^2 \rangle$ values, in atomic units (a.u.) are also given. The sum of NBO charges of each fragment at chair- and boat-TSb, in a.u., are denoted as $\delta$. (B) Calculated activation ($\Delta E^\ddagger$), deformation ($\Delta E_{FDEF}$) and interaction energies ($\Delta E_{FINT}$) for the chair and boat conformations of TSb, in kcal/mol.

In order to assess whether this relatively polar character of the sigmatropic shift can be extended to other para-substituted allyl alcohol derivatives, we computed at the B3LYP-D3(SCRF,solvent=toluene)/6-311++G(d,p) level the activation free energies associated with different reactants and we plotted these energies with respect to the combined Hammett parameter\(^34\) $\langle \sigma \rangle$ of the corresponding substituents in the form

$$\langle \sigma \rangle = Z_W \sigma_p^+ + (1 - Z_W) \sigma_p$$

where $\sigma_p^+$ is the Taft resonance parameter for positive charges and $\sigma_p$ is the Hammett parameter for a para-substituent (Figure 9). Our results show a moderate linear correlation between the Gibbs activation energies and the combined polar Hammett-Taft parameter $\langle \sigma \rangle$. 

\(^34\text{See text for details.}\)
However, there is no linear correlation between the $\Delta G_a$ and $\Delta G_{\text{rxn}}$ values, as it is shown in Figure 9B. This result does not follow the behavior observed for other pericyclic reactions such as 1,4-dihydrogenations and [4+2] cycloadditions of aromatic molecules, thus suggesting that the relationship between activation and reaction energies is not reducible to Marcus-Hammond models. In our opinion, this supports our conclusion that the transition structures of these sigmatropic rearrangements follow a polar-radical carboxy/allyl model not directly connected to the reactants or products. Within this context, it is interesting to note that Houk and Ess have shown a departure from the Marcus-Hammond framework in 1,3-dipolar reactions, in which the nature of the different dipoles generates different $\Delta H^\ddagger / \Delta H_{\text{rxn}}$ plots.

Finally, we explored computationally the conversion of alcohols 17a,b into carbamates 18ab-bb (Scheme 5). As a model case, we chose the thermal transformation of (Z)-buta-1,3-dien-1-yl formate 29a into (E)- or (Z)-31a (Figure 10A). From the $s$-trans conformation of (Z)-29a, the 1,3-dioxo-[3,3]-sigmatropic rearrangement gives rise to
intermediate 30a via saddle point TS1a. This latter intermediate has a novel terminal C=C bond and yields diene (E)-31a via TS2a, which in this model case is identical to TS1a. In turn, as we have seen in the previous cases, this model transition structure can adopt chair and boat geometries. Another possibility consists of a degenerate pseudopericyclic reaction\textsuperscript{27,28}—not subjected to the Woodward-Hoffmann\textsuperscript{29} rules for thermal sigmatropic rearrangements—involving the s-cis conformation of (Z)-29a to yield again (Z)-31a (Figure 10A). This latter process should occur via $C_s$-symmetric transition structure TS3 by through interconversion between C-O $\sigma$-bonds, C-C $\pi$-bonds and one of the lone pairs of one oxygen of the carboxy group.
Our calculations showed that, in effect, chair-TS1b, boat-TS1b and TS3a are practically isoenergetic. In particular, the [3,3] transition structures correspond to pericyclic
supra, supra topologies, as indicated by the corresponding dihedral angles \( \omega \) (Figure 10B). On the contrary, TS3a eludes the geometrically demanding supra, antara pericyclic topology by adopting a pseudopericyclic [3,5] geometry reflected by a \( \omega \) value of ca. 180 deg. Next, we computed the realistic case associated with the conversion of alcohol (E,Z)-17a into carbamate (E)-18ab (Scheme 5) through analysis of the (Z)-29b→(E/Z)-18ab transformation. In this case, the [3,5] pseudopericyclic mechanism disappeared from the potential energy hypersurface and only the pericyclic [3,3] mechanism survived. In addition, saddle point boat-TS1b was calculated to lie 1.7 kcal/mol above its congener chair-TS1b (Figure 10C). These computational permitted us to conclude that, although the pseudopericyclic [3,5] mechanism is conceivable, in this particular case the conversion of (Z)-29b into (E)-18ab via two consecutive suprafacial [3,3] processes is the only accessible mechanism. These results agree with the experimental findings summarized in Scheme 5, since a hypothetical pseudopericyclic [3,5] mechanism should preserve the Z-stereochemistry of the starting alcohol (Z)-17a.

CONCLUSIONS

In this paper, we have described a tandem reaction from 1-arylallyl alcohols involving an initial carbamoylation reaction followed by an unexpected metal-free 1,3-dioxo-[3,3]-sigmatropic rearrangement for a non-conventional access to linear allyl carbamates. Scope and limitations of this one-pot process were carried out showing the crucial importance of the electron density from aromatic ring as well as the nature of the isocyanate used. The synthetic interest of this methodology is all greater given that this kind of sigmatropic rearrangement can occur rapidly under mild reaction conditions (room temperature) and with a complete transfer of chiral information.

The mechanism of these [3,3] sigmatropic reactions has been investigated both experimentally and computationally. \(^1\)H-NMR studies show the very fast conversion of starting alcohols 1b,c to give rise to intermediate tosylcarbamates 13b,c whose [3,3] sigmatropic rearrangements yielded cinnamyl tosylcarbamates 14b,c without any noticeable reaction intermediate. The corresponding first-order reaction rates showed a relative reactivity following the order H>Cl. Computational DFT studies showed asynchronous, but concerted, suprafacial processes mediated by chair transition structures, in agreement with the observed stereoselectivities with an enantiopure substrate and NMR experiments with a \(^17\)O labeled
substrate. These latter saddle points reflect correctly the relative reaction rates and activation energies and show a polar character, in which the carboxy moiety bears a significant negative charge.

**EXPERIMENTAL SECTION**

**General Information and Materials.** Tetrahydrofuran (THF) was distilled over sodium/benzophenone and dichloromethane (DCM) was distilled over P₂O₅. All other commercially available chemicals were used without further purification. NMR spectra were recorded at 300, 400 or 500 MHz for ¹H and 75, 101 or 126 MHz for ¹³C. Chemical shifts of ¹H were referenced to Me₄Si as internal reference. Data are represented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet), coupling constant ⁴J (Hz) and integration. Assignments were done with the aid of DEPT 135, COSY and HSQC experiments. High-resolution mass spectra (HRMS) were recorded on a Micro-Tof-Q II or on a Q-Tof 2 using positive ion electrospray. Purifications on silica gel were carried out on silica gel 0.006-0.200 mm, 60 Å. Infrared spectra were recorded on a FT-IR spectrometer equipped with a diamond detection and an ATR unit or a single reflection ATR module; wavenumbers are given in cm⁻¹. Analytical thin layer chromatography was performed on Silica gel 60 F₂₅₄ plates. Optical rotations were measured using 10-cm cell at 22 °C (sodium D-line: 589 nm), and the concentration is expressed in g/dL. Melting points were measured without correction on a digital melting point apparatus. All analytical high-performance liquid chromatography (HPLC) were performed, using Daicel Chiralpak IB column. 1-(Phenyl)prop-2-en-1-ol (1b) is a commercially available compound. The [¹⁷O] labelled H₂O (11.1% H₂¹⁷O, 29.7% H₂¹⁸O and 59.2% H₂¹⁶O) was purchased from Corteccnet. NMR spectra were recorded at 68 MHz for ¹⁷O.

**General procedure for the synthesis of allylic alcohols 1, 5 and 20.** To a solution of aldehyde (1.50 mmol) in THF (10 mL) was slowly added at 0° C a solution of vinyl or phenylmagnesium bromide in THF (1.80 mmol, 1 M). The reaction mixture was stirred at room temperature for 16 hours after which a saturated NH₄Cl solution (5 mL) was added. The aqueous layer was extracted with Et₂O (4 x 10 mL). The organic layers were dried over MgSO₄, filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to afford the corresponding product.

1-(4-Methoxyphenyl)prop-2-en-1-ol (1a).³⁸ Prepared from 4-methoxybenzaldehyde and vinyl magnesium bromide. Purified using a hexane/ethyl acetate mixture (80/20, Rₗ 0.25) as eluent. The product was isolated as a yellow oil (210 mg) in 85% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, ⁴J = 8.2 Hz, 2H), 6.89 (d, ⁴J = 8.2 Hz, 2H), 6.05 (ddd, ⁴J = 17.2, 10.3, 5.9 Hz, 1H), 5.34 (dd, ⁴J = 17.2, 1.7 Hz, 1H), 5.22–5.12 (m, 2H), 3.81 (s, 3H), 1.89–1.86 (br s, 1H).

1-(4-Chlorophenyl)prop-2-en-1-ol (1c).³⁹ Prepared from 4-chlorobenzaldehyde and vinyl magnesium bromide. Purified using a hexane/ethyl acetate mixture (85/15, Rₗ 0.30) as eluent. The product was isolated as a pale yellow oil (187 mg) in 74% yield. ¹H NMR (300 MHz, CDCl₃): δ 7.33–7.31 (m, 4H), 6.01 (dd, ⁴J = 8.2 Hz, 2H), 6.05 (ddd, J = 17.2, 10.3, 5.9 Hz, 1H), 5.34 (dd, J = 17.2, 1.7 Hz, 1H), 5.22–5.12 (m, 2H), 3.81 (s, 3H), 1.89–1.86 (br s, 1H).

1-(4-Nitrophenyl)prop-2-en-1-ol (1d).⁴⁰ Prepared from 4-nitrobenzaldehyde and vinyl magnesium bromide. Purified using a hexane/ethyl acetate mixture (80/20, Rₗ 0.20) as eluent. The product was isolated as an
isolated as a pale yellow oil (117 mg) in 40% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.15 (d, $J = 8.7$ Hz, 2H), 7.52 (d, $J = 8.7$ Hz, 2H), 5.96 (ddd, $J = 17.1, 10.2, 6.4$ Hz, 1H), 5.36 (ddd, $J = 17.1, 1.2, 1.2$ Hz, 1H), 5.28 (d, $J = 6.4$ Hz, 1H), 5.23 (ddd, $J = 10.3, 1.1, 1.1$ Hz, 1H), 2.67–2.65 (br s, 1H).

1-(4-Methylphenyl)prop-2-en-1-ol ($^{1e}$). Prepared from 4-methylbenzaldehyde and vinyl magnesium bromide. Purified using a hexane/ethyl acetate mixture (80/20, $R_f$ 0.32) as eluent. The product was isolated as a yellow oil (218 mg) in 98% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.48–7.35 (m, 5H), 7.35–7.22 (m, 2H), 6.97 (d, $J = 8.3$ Hz, 2H), 6.05 (ddd, $J = 17.1, 10.3, 5.9$ Hz, 1H), 5.34 (d, $J = 17.1$ Hz, 1H), 5.21–5.15 (m, 2H), 5.07 (s, 2H), 1.86 (d, $J = 3.4$ Hz, 1H).

1-(4-Benzoyloxyphenyl)prop-2-en-1-ol ($^{1f}$). Prepared from 4-benzoyloxybenzaldehyde and vinyl magnesium bromide. Purified using a hexane/ethyl acetate mixture (80/20, $R_f$ 0.33) as eluent. The product was isolated as a colorless oil (259 mg) in 98% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.4–7.3 (m, 7H), 7.25 (d, $J = 8.2$ Hz, 1H), 6.81 (d, $J = 8.2$ Hz, 1H), 6.10 (ddd, $J = 17.2, 10.4, 5.6$ Hz, 1H), 5.41 (dd, $J = 5.6, 5.6$ Hz, 1H), 5.31 (dd, $J = 17.2, 1.4$ Hz, 1H), 5.17 (dd, $J = 10.4, 1.4$ Hz, 1H), 3.87 (s, 3H), 2.77 (dd, $J = 4.5, 3.8$ Hz, 1H).

1-(2-Methoxyphenyl)prop-2-en-1-ol ($^{1g}$). Prepared from 2-methoxybenzaldehyde and vinyl magnesium bromide. Purified using a hexane/ethyl acetate mixture (85/15, $R_f$ 0.44) as eluent. The product was isolated as a colorless oil (172 mg) in 70% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.32–7.25 (m, 2H), 7.01–6.94 (m, 1H), 6.90 (d, $J = 8.2$ Hz, 1H), 6.14 (ddd, $J = 17.2, 10.4, 5.6$ Hz, 1H), 5.34 (d, $J = 17.1$ Hz, 1H), 5.24 (ddd, $J = 10.4, 1.4$ Hz, 1H), 5.19 (d, $J = 5.8$ Hz, 1H), 4.63 (t, $J = 8.7$ Hz, 2H), 3.26 (t, $J = 7.5$ Hz, 2H), 1.92–1.86 (br s, 1H).

1-(3,4-Dimethoxyphenyl)prop-2-en-1-ol ($^{1h}$). Prepared from 3,4-dimethoxybenzaldehyde and vinyl magnesium bromide. Purified using a hexane/ethyl acetate mixture (75/25, $R_f$ 0.30) as eluent. The product was isolated as a pale yellow oil (324 mg) in 80% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.4–7.3 (m, 5H), 7.32–7.25 (m, 2H), 6.97 (d, $J = 8.3$ Hz, 2H), 6.05 (ddd, $J = 17.1, 10.3, 5.9$ Hz, 1H), 5.34 (d, $J = 17.1$ Hz, 1H), 5.21–5.15 (m, 2H), 5.07 (s, 2H), 1.86 (d, $J = 3.4$ Hz, 1H).

1-(3-(Benzyl)oxy-4-methoxyphenyl)prop-2-en-1-ol ($^{1i}$). Prepared from 3-benzylxoy-4-methoxybenzaldehyde and vinyl magnesium bromide. Purified using a hexane/ethyl acetate mixture (80/20, $R_f$ 0.21) as eluent. The product was isolated as a pale yellow oil (324 mg) in 80% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.45 (d, $J = 7.5$ Hz, 2H), 7.36 (ddd, $J = 7.4, 7.4$ Hz, 2H), 7.31 (d, $J = 7.2$ Hz, 1H), 6.96 (s, 1H), 6.94–6.90 (m, 1H), 6.87 (d, $J = 8.2$ Hz, 1H), 5.99 (ddd, $J = 17.2, 10.3, 5.7$ Hz, 1H), 5.30 (d, $J = 17.2$ Hz, 1H), 5.19–5.16 (m, 1H), 5.14 (s, 2H), 5.12–5.10 (m, 1H), 3.87 (s, 3H), 1.87 (d, $J = 3.8$ Hz, 1H), $^{13}$C{1H} NMR (101 MHz, CDCl$_3$): $\delta$ 149.1, 148.1, 140.3, 136.9, 135.3, 128.4, 127.7, 127.4, 119.2, 114.6, 112.3 (d, $J = 5.7$ Hz), 111.6 (d, $J = 4.6$ Hz), 74.6, 70.9, 55.9. IR (cm$^{-1}$) 3488, 3054, 1511, 1263, 1157, 1135, 1021, 730, 698. HRMS (ESI): m/z calcd. for C$_{17}$H$_{10}$O$_3$ [M+H]$^+$ 271.1334; found: 271.1335.
1-(Benzo[d][1,3]dioxol-5-yl)prop-2-en-1-ol (1K). Prepared from piperonal and vinyl magnesium bromide. Purified using a hexane/ethyl acetate mixture (90/10, \( R_f \) 0.17) as eluent. The product was isolated as a colorless oil (203 mg) in 76% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 6.88 (d, \( J = 1.6 \) Hz, 1H), 6.83 (dd, \( J = 8.0, 1.6 \) Hz, 1H), 6.78 (d, \( J = 8.0 \) Hz, 1H), 6.02 (ddd, \( J = 17.1, 10.3, 5.9 \) Hz, 1H), 5.95 (s, 2H), 5.34 (ddd, \( J = 17.1, 1.4, 1.4 \) Hz, 1H), 5.19 (ddd, \( J = 10.4, 1.4, 1.4 \) Hz, 1H), 5.13 (m, 1H), 1.88 (d, \( J = 3.6 \) Hz, 1H).

\( (E)\)-1-(4-Methoxyphenyl)penta-1,4-dien-3-ol (5a). Prepared from (E)-3-(4-methoxyphenyl)-2-propenal and vinyl magnesium bromide. Purified using a hexane/ethyl acetate mixture (75/25, \( R_f \) 0.24) as eluent. The product was isolated as a pale yellow oil (242 mg) in 85% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.34–7.24 (m, 2H), 7.30–7.20 (m, 2H), 6.62 (d, \( J = 16.1 \) Hz, 1H), 6.23 (dd, \( J = 16.1, 6.4 \) Hz, 1H), 5.98 (ddd, \( J = 17.2, 10.4, 5.9 \) Hz, 1H), 5.34 (ddd, \( J = 17.2, 1.4, 1.4 \) Hz, 1H), 5.20 (ddd, \( J = 10.4, 1.3, 1.3 \) Hz, 1H), 4.89–4.76 (m, 1H), 1.77–1.74 (m, 1H).

General procedure for the synthesis of allylic carbamates 3, 6, 4, 7, 13, 14, 15, 16, 18, 22.

Using trichloroacetyl isocyanate. A solution of allylic alcohol 1 or 5 (0.3 mmol) in anhydrous toluene
CHCl₃ or CH₂Cl₂ (0.2 M) under argon atmosphere was cooled to 0 °C and trichloroacetyl isocyanate (0.36 mmol)
was added slowly. The reaction mixture was stirred during the time and temperature indicated in Table 1 and 2.
Solvent was removed in vacuo and in some cases, intermediates have been identified.

(E)-3-(4-methoxyphenyl)allyl (2,2,2-trichloroacetyl)carbamate (3a). Prepared from allylic alcohol 1a
(rt, 0.25 h). The product was isolated as a colorless oil (103 mg) in 98% yield and used in the next step without
further purification. ¹H NMR (300 MHz, CDCl₃): δ 8.50–8.45 (br s, 1H); 7.34 (d, J = 8.7 Hz, 2H), 6.86 (d, J =
8.7 Hz, 2H), 6.69 (d, J = 15.8 Hz, 1H), 6.17 (dt, J = 15.7, 6.9 Hz, 1H), 4.88 (dd, J = 6.9, 1.2 Hz, 2H), 3.81 (s,
3H). ¹³C{¹H} NMR (75 MHz, CDCl₃) δ 159.9, 157.9, 149.8, 136.2, 128.1, 118.9, 114.1, 91.8, 68.3, 55.3.

(2E,4E)-5-phenylpenta-2,4-dien-1-yl (2,2,2-trichloroacetyl)carbamate (6b). Prepared from allylic
alcohol 5b (rt, 4 h). The product was isolated as a white solid (102 mg) in 98% yield and used in the next step
without further purification; mp 101–104 °C. ¹H NMR (300 MHz, CDCl₃) δ 8.50–8.45 (br s, 1H); 7.42–7.36 (m,
2H), 7.35–7.28 (m, 2H), 7.27–7.21 (m, 1H), 6.76 (dd, J = 15.6, 10.2 Hz, 1H), 6.62 (d, J = 15.6 Hz, 1H), 6.53
(dd, J = 15.1, 1.1, 1.1 Hz, 1H), 5.88 (dt, J = 15.1, 6.9 Hz, 1H), 4.83 (dd, J = 6.9, 1.1 Hz, 2H). ¹³C{¹H} NMR
(75 MHz, CDCl₃) δ 157.8, 149.7, 134.1, 130.5, 128.8, 122.7, 115.0, 66.4, 55.7. IR (cm⁻¹) 3423, 3329, 3263, 3203, 2954, 2834, 1682, 1603, 1509, 1244, 1028, 510.

To the resulting mixture or pure compound 3 or 6, K₂CO₃ (1.2 mmol) in a mixture of MeOH (1.6 mL)
and water (0.4 mL) was added. The solution was stirred at room temperature overnight and then MeOH was
removed in vacuo. The aqueous layer was extracted with CH₂Cl₂ (4 x 1 mL). The organic layers were dried over
MgSO₄, filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica
gel to afford the corresponding product.

(E)-3-(4-Methoxyphenyl)allyl carbamate (4a). Prepared from 3a. Purified using a hexane/ethyl acetate
mixture (70/30, Rf 0.31) as eluent. The product was isolated as a white solid (45 mg) in 73% yield from 1a. mp
131–134 °C. ¹H NMR (400 MHz, acetone-d₆) δ 7.35 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 6.57 (d, J =
15.9 Hz, 1H), 6.17 (dt, J = 15.9, 6.3 Hz, 1H), 5.9–0.55.84 (br s, 2H), 4.57 (dd, J = 6.3, 1.5 Hz, 2H), 3.75 (s, 3H).
¹³C{¹H} NMR (126 MHz, CDCl₃) δ 161.0, 159.8, 134.1, 130.5, 128.8, 122.7, 115.0, 66.4, 55.7. IR (cm⁻¹) 3423,
3329, 3263, 3203, 2954, 2834, 1682, 1603, 1509, 1244, 1028, 510. HRMS (ESI): m/z calcd. for C₁₁H₁₂NO₂Na
[M+Na]⁺ 230.0793; found 230.0789.

(E)-3-(phenyl)allyl carbamate (4b). Prepared from the commercially available
1-(Phenyl)prop-2-en-1-ol (90 °C, 16 h). Purified using a hexane/ethyl acetate mixture (70/30, Rf 0.28) as eluent.
The product was isolated as a white solid (49 mg) in 92% yield. mp 116–119 °C. ¹H NMR (400 MHz, CDCl₃) δ
7.37 (d, J = 7.1 Hz, 2H), 7.33–7.27 (m, 2H), 7.27–7.21 (m, 1H), 6.63 (d, J = 15.9 Hz, 1H), 6.27 (dt, J = 15.9, 6.3
Hz, 1H), 5.01–4.92 (br s, 2H), 4.70 (dd, J = 6.3, 1.4 Hz, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 156.9, 136.4,
133.9, 128.7, 128.1, 126.7, 123.7, 65.8. HRMS (ESI): m/z calcd. for C₁₀H₇NO₂Na [M+Na]⁺ 200.0687; found
200.0686.

(E)-3-(4-Chlorophenyl)allyl carbamate (4c). Prepared from allylic alcohol 1c (90 °C, 20 h). Purified
using a hexane/ethyl acetate mixture (70/30, Rf 0.27) as eluent. The product was isolated as a white solid (32 mg)
in 50% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.32–7.28 (m, 4H), 6.60 (d, \(J = 15.9\) Hz, 1H), 6.26 (dt, \(J = 15.9, 6.3\) Hz, 1H), 4.78–4.74 (br s, 2H), 4.72 (dd, \(J = 6.3, 1.4\) Hz, 2H).

\textit{(E)-3-((4-Nitrophenyl)allyl carbamate (4d).} \textsuperscript{15} Prepared from allylic alcohol 1d (90 °C, 120 h). Purified using a hexane/ethyl acetate mixture (70/30, \(R_f\) 0.10) as eluent. The product was isolated as a yellow solid (28 mg) in 43% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.19 (d, \(J = 8.5\) Hz, 2H), 7.52 (d, \(J = 8.5\) Hz, 2H), 6.71 (d, \(J = 16.0\) Hz, 1H), 6.46 (dt, \(J = 16.0, 5.8\) Hz, 1H), 4.78 (dd, \(J = 5.8, 1.5\) Hz, 2H), 4.73–4.66 (br s, 2H).

\textit{(2E,4E)-5-(4-methoxyphenyl)penta-2,4-dien-1-yl carbamate (7a).} Prepared from allylic alcohol 5a (rt, 2 h). Purified using a hexane/ethyl acetate mixture (65/35, \(R_f\) 0.29) as eluent. The product was isolated as a pale yellow solid (17 mg) in 24% yield. mp 150–153 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.33 (d, \(J = 8.7\) Hz, 2H), 6.85 (d, \(J = 8.7\) Hz, 2H), 6.65 (dd, \(J = 15.6, 10.3\) Hz, 1H), 6.53 (d, \(J = 15.6\) Hz, 1H), 6.43 (dd, \(J = 15.2, 10.2\) Hz, 1H), 5.83 (dt, \(J = 15.1, 6.6\) Hz, 1H), 4.71–4.67 (br s, 2H), 4.64 (dd, \(J = 6.6, 1.3\) Hz, 2H), 3.81 (s, 3H). \textsuperscript{13}C{\textsuperscript{1}H} NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 159.6, 156.8, 134.9, 133.5, 129.7, 127.9, 126.2, 114.36, 65.7, 55.5. IR (cm\textsuperscript{-1}) 3436, 3394, 3331, 3269, 3216, 3014, 2955, 1685, 1600, 1508, 1418, 1351, 1246, 1028, 988, 820, 552, 522. HRMS (ESI): m/z calcd. for C\textsubscript{13}H\textsubscript{14}NO\textsubscript{3}Na [M+Na\textsuperscript{+}] 256.0950; found 256.0953.

\textit{(2E,4E)-5-phenylpenta-2,4-dien-1-yl carbamate (7b).} \textsuperscript{20} Prepared from 6b. Purified using a hexane/ethyl acetate mixture (70/30, \(R_f\) 0.27) as eluent. The product was isolated as a yellow solid (40 mg) in 65% yield from 5b. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.45–7.37 (m, 2H), 7.37–7.29 (m, 2H), 7.29–7.22 (m, 1H), 6.78 (dd, \(J = 15.8, 10.4\) Hz, 1H), 6.59 (d, \(J = 15.8\) Hz, 1H), 6.46 (dd, \(J = 15.3, 10.4\) Hz, 1H), 5.89 (dt, \(J = 15.3, 6.4\) Hz, 1H), 4.77–4.68 (br s, 2H), 4.66 (dd, \(J = 6.6, 1.5\) Hz, 2H).

\textit{(2E,4E)-5-(4-Chlorophenyl)penta-2,4-dien-1-yl carbamate (7c).} Prepared from allylic alcohol 5c (rt, 4 h). Purified using a hexane/ethyl acetate mixture (70/30, \(R_f\) 0.27) as eluent. The product was isolated as a pale yellow solid (53 mg) in 75% yield. mp 167–170 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.36–7.24 (m, 4H), 6.74 (dd, \(J = 15.8, 10.4\) Hz, 1H), 6.53 (d, \(J = 15.7\) Hz, 1H), 6.44 (dd, \(J = 15.2, 10.5\) Hz, 1H), 5.90 (dt, \(J = 15.2, 6.4\) Hz, 1H), 4.66 (dd, \(J = 6.4, 1.5\) Hz, 2H), 4.63–4.58 (br s, 2H). \textsuperscript{13}C{\textsuperscript{1}H} NMR (126 MHz, CD\textsubscript{3}OD) \(\delta\) 159.7, 137.3, 134.4, 134.2, 132.9, 130.0, 129.9, 129.8, 128.9, 65.8. IR (cm\textsuperscript{-1}) 3410, 3348, 3286, 3210, 3028, 2955, 1644, 1486, 1421, 1348, 1318, 1053, 986, 827, 508. HRMS (ESI): m/z calcd. for C\textsubscript{13}H\textsubscript{14}ClNO\textsubscript{3}Na [M+Na\textsuperscript{+}] 260.0454; found 260.0457.

\textbf{Using p-toluenesulfonyl isocyanate.} To a solution of allylic alcohol 1, 5 or 17 (0.3 mmol) in chloroform, dichloromethane or toluene (0.2 M) under argon atmosphere, p-toluensulfonyl isocyanate (0.36 mmol) was added dropwise and the mixture was stirred at room temperature or warmed at 90 °C during the time indicated in Table 3, Table 4 and Scheme 5. The conversion of the reaction can be followed by \textsuperscript{1}H NMR using deuterated solvent. The resulting mixture was concentrated in vacuo and the product was purified by flash column chromatography on silica gel to afford the desired product.

\textit{1-phenylallyl tosylcarbamate (13b).} \textsuperscript{2c} Prepared from 1b (rt, 5 min) and purified using a hexane/ethyl acetate mixture (80/20, \(R_f\) 0.31) as eluent. The product was isolated as a colorless oil (91 mg) in 92% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.88 (d, \(J = 8.3\) Hz, 2H), 7.55–7.53 (br s, 1H), 7.34–7.26 (m, 5H), 7.21 (dd, \(J = 6.8, 3.0\) Hz, 2H), 6.11 (dd, \(J = 6.0, 1.5\) Hz, 1H), 5.92 (ddd, \(J = 16.7, 10.5, 5.9\) Hz, 1H), 5.27–5.23 (m, 2H), 2.43 (s, 3H). \textsuperscript{13}C{\textsuperscript{1}H} NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 149.6, 145.2, 137.5, 135.1, 129.7, 128.7, 128.5, 127.3, 118.2, 79.4, 21.8; HRMS (ESI): m/z calcd. for C\textsubscript{13}H\textsubscript{14}NO\textsubscript{3}SK [M+K\textsuperscript{+}] 370.0515; found: 370.0514.
1-(4-chlorophenyl)allyl tosylcarbamate (13c). Prepared from 1c (rt, 5 min) and purified using a hexane/ethyl acetate mixture (80/20, Rf 0.30) as eluent. The product was isolated as a colorless oil (93 mg) in 85% yield. 1H NMR (400 MHz, CDCl3) δ 7.86 (d, J = 8.5 Hz, 2H), 7.70–7.67 (br s, 1H), 7.33–7.23 (m, 4H), 7.14 (d, J = 8.5 Hz, 2H), 6.07 (d, J = 5.9 Hz, 1H), 5.87 (ddd, J = 16.7, 10.8, 5.9 Hz, 1H), 5.27–5.23 (m, 2H), 2.44 (s, 3H). 13C{1H} NMR (101 MHz, CDCl3) δ 149.6, 145.3, 136.1, 135.6, 134.6, 129.8, 128.9, 128.7, 128.5, 118.6, 78.5, 21.8. IR (cm⁻¹) 3301, 2997, 1725, 1448, 1435, 1155, 1088, 706, 728, 664, 647, 547. HRMS (ESI): m/z calcd. for C17H16ClNO3SNa [M+Na]+: 388.0381; found: 388.0380.

1-(4-nitrophenyl)allyl tosylcarbamate (13d). Prepared from 1d (rt, 5 min) and purified using a hexane/ethyl acetate mixture (60/40, Rf 0.31) as eluent. The product was isolated as a yellow oil (101 mg) in 90% yield. 1H NMR (400 MHz, CDCl3) δ 8.14 (d, J = 8.5 Hz, 2H), 7.88 (d, J = 8.1 Hz, 2H), 7.37 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 6.16 (d, J = 6.1 Hz, 1H), 5.85 (ddd, J = 16.8, 10.5, 6.1 Hz, 1H), 5.33–5.24 (m, 2H), 2.44 (s, 3H). 13C{1H} NMR (126 MHz, CDCl3) δ 149.5, 147.9, 145.5, 144.7, 135.5, 133.9, 129.8, 128.4, 127.8, 123.9, 119.7, 77.9, 21.8. IR (cm⁻¹) 3236, 3112, 2858, 1748, 1520, 1444, 1345, 1241, 1158, 1098, 853, 665, 548. HRMS (ESI) m/z calcd. for C18H15NO4S [M+H]⁺: 394.1073; found: 394.1070.

(E)-3-(4-Methoxyphenyl)allyl tosylcarbamate (14a). Prepared from 1a (rt, 15 min.) and purified using a hexane/ethyl acetate mixture (70/30, Rf 0.23) as eluent. The product was isolated as a colorless oil (98 mg) in 90% yield. NMR spectra of 14a in CDCl3 at 298K revealed the presence of two conformers (rotamers) in a ratio (55:45). 1H NMR (400 MHz, CDCl3) δ 7.93 (d, J = 8.5 Hz, 1.1H), 7.81 (d, J = 8.6 Hz, 0.9H), 7.37–7.28 (m, 4H), 6.85 (d, J = 4.7 Hz, 2H), 6.53 (d, J = 15.9 Hz, 1H), 6.01 (dt, J = 15.9, 6.6 Hz, 1H), 4.77–4.75 (br s, 1H), 4.69 (dd, J = 6.6, 1.3 Hz, 2H), 3.81 (s, 3H), 2.43 (s, 1.65H), 2.42 (s, 1.35H). 13C{1H} NMR (126 MHz, CDCl3) δ 159.9, 150.6, 145.1, 143.6, 139.2, 135.6, 135.3, 129.8, 129.7, 128.6, 128.5, 128.1, 126.5, 119.4, 114.2, 67.8, 55.4, 21.8, 21.6. IR (cm⁻¹) 3356, 3259, 2959, 1744, 1606, 1510, 1442, 1300, 1245, 1153, 1088, 812, 660, 545, 532. HRMS (ESI): m/z calcd. for C18H15NO4S [M+H]⁺: 379.1328; found: 379.1324.

(E)-3-(phenyl)allyl tosylcarbamate (14b). Prepared from 1b (90 °C, 6 h) and purified using a hexane/ethyl acetate mixture (60/40, Rf 0.39) as eluent. The product was isolated as a white solid (94 mg) in 95% yield. mp 73–76 °C. NMR spectra of 14b in CDCl3 at 298K revealed the presence of two conformers (rotamers) in a ratio (75:25). 1H NMR (400 MHz, CDCl3) δ 7.97–7.90 (m, 1.5H), 7.82 (m, 0.5H), 7.37–7.25 (m, 7H), 6.58 (d, J = 15.8 Hz, 1H), 6.14 (dt, J = 15.9, 6.6 Hz, 1H), 4.72 (ddd, J = 6.6, 1.3 Hz, 2H), 2.43 (s, 0.75H), 2.42 (s, 2.25H). 13C{1H} NMR (126 MHz, CDCl3): δ 150.7, 145.1, 143.5, 139.2, 135.8, 135.5, 135.2, 129.7, 129.6, 128.7, 128.4, 128.3, 126.7, 126.4, 121.7, 67.3, 21.7, 21.5. HRMS (ESI): m/z calcd. for C18H16NO4S [M+H]⁺: 349.1222; found 349.1222.

(E)-3-(4-Chlorophenyl)allyl tosylcarbamate (14c). Prepared from 1c (90 °C, 20 h) and purified using a hexane/ethyl acetate mixture (65/35, Rf 0.26) as eluent. The product was isolated as a white solid (77 mg) in 70% yield. mp 86–87 °C. NMR spectra of 14c in CDCl3 at 298K revealed the presence of two conformers (rotamers) in a ratio (60/40). 1H NMR (400 MHz, CDCl3) δ 7.93 (d, J = 8.1 Hz, 1.2H), 7.82 (d, J = 8.1 Hz, 0.8H), 7.37–7.22 (m, 6H), 6.53 (d, J = 15.9 Hz, 1H), 6.12 (dt, J = 16.0, 6.6 Hz, 1H), 4.83–4.81 (br s, 1H), 4.71 (dd, J = 6.6, 1.3 Hz, 2H), 2.43 (s, 1.8H), 2.42 (s, 1.2H). 13C{1H} NMR (126 MHz, CDCl3): δ 150.6, 145.2, 143.7, 139.2, 134.4, 134.1, 133.9, 129.8, 129.7, 129.6, 128.9, 128.5, 128.3, 127.9, 126.5, 122.5, 67.1, 21.8. IR (cm⁻¹) 3355,
3259, 3086, 2849, 1737, 1304, 1285, 1160, 1080, 969, 813, 658, 583, 533. HRMS (ESI): m/z calcd. for C_{15}H_{20}ClN_{2}O_{3}S [M+Na]^{-} 383.0832; found 383.0829.

(E)-3-(4-Nitrophenyl)allyl tosylcarbamate (14d). Prepared from 1d (90 °C, 4 days, 70% conversion) and purified using a hexane/ethyl acetate mixture (80/20, R_{f} 0.15) as eluent. The product was isolated as a yellow oil (45 mg) in 40% yield. NMR spectra of 14d in CDCl3 at 298K revealed the presence of two conformers (rotamers) in a ratio (99/1). 1H NMR (400 MHz, CDCl3) δ 8.18 (d, J = 8.5 Hz, 2H), 7.94 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 6.64 (d, J = 16.0 Hz, 1H), 6.34 (dt, J = 16.0, 6.2 Hz, 1H), 4.77 (dd, J = 6.2, 1.4 Hz, 2H), 2.43 (s, 3H). 13C{1H} NMR (101 MHz, CDCl3) δ 145.4, 142.3, 135.5, 132.41, 129.8, 128.6, 127.4, 126.8, 124.2, 66.6, 21.9. IR (cm⁻¹) 3450, 2996, 2950, 1723, 1448, 1434, 1272, 1241, 1190, 1148, 907, 727, 641. HRMS (ESI): m/z calcd. for C_{15}H_{20}N_{2}O_{3}S [M+Na]^{-}: 394.1067; found: 394.1067.

(E)-3-(4-Methylphenyl)allyl tosylcarbamate (14e). Prepared from 1e (90 °C, 6 h) and purified using a hexane/ethyl acetate mixture (70/30, R_{f} 0.26) as eluent. The product was isolated as a white solid (72 mg) in 70% yield. mp 82–85 °C. NMR spectra of 14e in CDCl3 at 298K revealed the presence of two conformers (rotamers) in a ratio (65/35). 1H NMR (400 MHz, CDCl3) δ 7.93 (d, J = 8.1 Hz, 1.3H), 7.82 (d, J = 8.1 Hz, 0.7H), 7.32 (d, J = 7.9 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 7.9 Hz, 2H), 6.55 (d, J = 15.8 Hz, 1H), 6.09 (dt, J = 15.8, 6.7 Hz, 1H), 4.73–4.69 (br s, 1H), 4.71 (dd, J = 6.7, 1.2 Hz, 2H), 2.43 (s, 1.05H), 2.42 (s, 2.27H), 2.34 (s, 3H). IR (cm⁻¹) 3354, 3229, 3048, 2948, 1754, 1596, 1436, 1344, 1219, 1147, 1088, 970, 875, 665, 582, 544. HRMS (ESI): m/z calcd. for C_{15}H_{19}N_{2}O_{3}S [M+NH₄]⁺: 363.1378; found 363.1378.

(E)-3-(4-(Benzyloxy)phenyl)allyl tosylcarbamate (14f). Prepared from 1f (rt, 15 min.) and purified using a hexane/ethyl acetate mixture (65/35, R_{f} 0.38) as eluent. The product was isolated as a white solid (97 mg) in 74% yield. mp 106–109 °C. NMR spectra of 14f in CDCl3 at 298K revealed the presence of two conformers (rotamers) in a ratio (65/35). 1H NMR (400 MHz, CDCl3) δ 7.97–7.88 (d, J = 8.4 Hz, 1.3H), 7.86–7.78 (d, J = 8.4 Hz, 0.7H), 7.50–7.25 (m, 9H), 6.97–6.86 (d, J = 8.4 Hz, 2H), 6.53 (d, J = 15.8 Hz, 1H), 6.01 (dt, J = 15.8, 6.8 Hz, 1H), 5.07 (s, 2H), 4.76–4.73 (br s, 1H), 4.69 (dd, J = 6.9, 1.3 Hz, 2H), 2.43 (s, 1.05H), 2.42 (s, 1.95H). 13C{1H} NMR (126 MHz, CDCl3) δ 159.1, 150.6, 145.2, 143.6, 139.2, 136.8, 135.6, 135.2, 129.8, 129.7, 128.9, 128.7, 128.5, 128.2, 128.1, 127.6, 126.5, 119.6, 115.1, 70.1, 67.7, 21.76, 21.62. IR (cm⁻¹) 3356, 3250, 2950, 2869, 1738, 1605, 1512, 1433, 1300, 1153, 1064, 813, 660, 530. HRMS (ESI): m/z calcd. for C_{25}H_{26}N_{2}O_{4}S [M+NH₄]⁺: 455.1641; found 455.1643.

(E)-3-(2-Methoxyphenyl)allyl tosylcarbamate (14g). Prepared from 1g (rt, 16 h) and purified using a hexane/ethyl acetate mixture (70/30, R_{f} 0.24) as eluent. The product was isolated as a yellow oil (92 mg) in 85% yield. NMR spectra of 14g in CDCl3 at 298K revealed the presence of two conformers (rotamers) in a ratio (65/35). 1H NMR (400 MHz, CDCl3) δ 7.92 (d, J = 8.1 Hz, 1.3H), 7.81 (d, J = 8.1 Hz, 0.7H), 7.34–7.22 (m, 4H), 6.94–6.84 (m, 2H), 6.16 (dt, J = 16.0, 6.6 Hz, 1H), 5.25–5.20 (br s, 1H), 4.70 (dd, J = 6.6, 1.3 Hz, 2H), 3.82 (s, 3H), 2.40 (s, 1.05H), 2.39 (s, 1.95H). 13C{1H} NMR (126 MHz, CDCl3) δ 157.0, 150.6, 145.1, 143.5, 139.3, 135.6, 130.6, 129.8, 129.7, 129.5, 128.5, 127.3, 126.5, 124.9, 122.3, 120.7, 111.0, 68.0, 55.5, 21.7, 21.6. IR (cm⁻¹) 3355, 2946, 1744, 1596, 1488, 1437, 1343, 1242, 1152, 1067, 868, 812, 751, 659, 576, 544. HRMS (ESI): m/z calcd. for C_{18}H_{22}N_{2}O_{5}S [M+NH₄]⁺: 379.1328; found 379.1325.
(E)-3-(2,3-dihydrobenzofuran-5-yl)allyl tosylcarbamate (14h). Prepared from 1h (rt, 1 h) and purified using a hexane/ethyle acetate mixture (60/40 Rf, 0.30) as eluent. The product was isolated as a colorless oil (40 mg) in 36% yield. NMR spectra of 14h in CDCl3 at 298K revealed the presence of two conformers (rotamers) in a ratio (99/1). 1H NMR (400 MHz, CDCl3) δ 7.97–7.88 (m, 2H), 7.31 (m, 2H), 7.22–7.19 (m, 1H), 7.07 (dd, J = 8.2, 1.9 Hz, 1H), 6.72 (d, J = 8.2 Hz, 1H), 6.52 (d, J = 15.7 Hz, 1H), 5.98 (dt, J = 15.7, 6.8 Hz, 1H), 4.68 (dd, J = 6.8, 1.2 Hz, 2H), 4.58 (t, J = 8.7 Hz, 2H), 3.19 (t, J = 8.7 Hz, 2H), 2.42 (s, 3H). 13C{1H} NMR (101 MHz, CDCl3) δ 160.6, 150.5, 145.2, 135.9, 135.6, 129.7, 128.6, 127.5, 123.2, 118.7, 109.5, 71.7, 67.9, 29.6, 21.8. IR (cm⁻¹) 3374, 3280, 3054, 1746, 1599, 1491, 1264, 1161, 731, 702, 546. HRMS (ESI): m/z calcd. for C16H19NO3SNa [M+Na]+ 396.0882; found 396.0881.

(E)-3-(3,4-dimethoxyphenyl)allyl tosylcarbamate (14i). Prepared from 1i (rt, 45 min.) and purified using a hexane/ethyle acetate mixture (60/40 Rf, 0.20) as eluent. The product was isolated as a colorless oil (38 mg) in 32% yield. NMR spectra of 14i in CDCl3 at 298K revealed the presence of two conformers (rotamers) in a ratio (99/1). 1H NMR (400 MHz, CDCl3) δ 7.96–7.89 (m, 2H), 7.29 (d, J = 8.0 Hz, 2H), 6.90–6.84 (m, 2H), 6.79 (d, J = 8.1 Hz, 1H), 6.51 (d, J = 15.8 Hz, 1H), 6.02 (dt, J = 15.8, 6.7 Hz, 1H), 4.69 (dd, J = 6.7, 0.9 Hz, 2H), 3.86 (s, 6H), 2.39 (s, 3H). 13C{1H} NMR (126 MHz, CDCl3) δ 150.6, 149.5, 149.1, 145.1, 135.6, 135.5, 129.7, 128.9, 128.57, 120.3, 119.7, 111.1, 108.9, 67.6, 56.0, 55.9, 21.7. IR (cm⁻¹) 3254, 3057, 2957, 2936, 1746, 1746, 1597, 1513, 1451, 1343, 1263, 1158, 1089, 1024, 732, 510. HRMS (ESI): m/z calcd. for C19H20NO3S [M+NH4]+ 409.1433; found 409.1431.

(E)-3-(3-(benzyloxy)-4-methoxyphenyl)allyl tosylcarbamate (14j). Prepared from 1j (rt, 45 min.) and purified using a hexane/ethyle acetate mixture (60/40 Rf, 0.33) as eluent. The product was isolated as a yellow oil (76 mg) in 54% yield. NMR spectra of 14j in CDCl3 at 298K revealed the presence of two conformers (rotamers) in a ratio (90/10). 1H NMR (400 MHz, CDCl3) δ 7.95–7.89 (d, J = 8.3 Hz, 1.8H), 7.80 (d, J = 8.3 Hz, 0.2H), 7.44 (d, J = 7.1 Hz, 2H), 7.40–7.30 (m, 5H), 6.95–6.83 (m, 3H), 6.47 (d, J = 15.7 Hz, 1H), 5.95 (dt, J = 15.7, 6.7 Hz, 1H), 5.13 (s, 2H), 4.67 (dd, J = 6.7, 1.3 Hz, 2H), 3.88 (s, 3H), 2.42 (s, 0.3H), 2.40 (s, 2.7H). 13C{1H} NMR (101 MHz, CDCl3) δ 150.4, 150.3, 148.4, 145.2, 137.1, 135.6, 129.73, 128.90, 128.71, 128.6, 128.1, 127.5, 120.8, 119.6, 112.2, 111.8, 71.3, 67.7, 56.2, 21.8. IR (cm⁻¹) 3258, 2958, 2930, 1744, 1596, 1510, 1440, 1257, 1155, 1135, 1016, 660, 545. HRMS (ESI): m/z calcd. for C21H20NO3S [M+NH4]+ 485.1746; found 485.1745.

(E)-3-(benzo[d][1,3]dioxol-5-yl)allyl tosylcarbamate (14k). Prepared from 1k (rt, 3 h) and purified using a hexane/ethyle acetate mixture (65/35 Rf, 0.27) as eluent. The product was isolated as a white solid (95 mg) in 84% yield. mp 89–91 °C. NMR spectra of 14k in CDCl3 at 298K revealed the presence of two conformers (rotamers) in a ratio (90/10). 1H NMR (400 MHz, CDCl3) δ 7.92 (d, J = 8.1 Hz, 1.6H), 7.81 (d, J = 8.1 Hz, 0.4H), 7.33–7.29 (m, 2H), 6.84 (s, 1H), 6.75 (d, J = 2.2 Hz, 2H), 6.47 (d, J = 15.8 Hz, 1H), 6.04–5.88 (m, 3H), 5.05–5.00 (br s, 1H), 4.68 (dd, J = 6.9, 1.3 Hz, 2H), 2.41 (s, 3H). 13C{1H} NMR (101 MHz, CDCl3) δ 150.6, 148.2, 147.9, 145.2, 135.6, 135.3, 130.3, 129.7, 128.5, 126.5, 121.8, 119.9, 108.4, 105.9, 101.3, 67.5, 21.7, 21.6. IR (cm⁻¹) 3355, 3258, 1737, 1492, 1451, 1250, 1156, 1086, 1036, 852, 810, 662, 576, 549. HRMS (ESI): m/z calcd. for C18H14NO3SNa [M+Na]+ 398.0670; found 398.0672.

(2E,4E)-5-(4-methoxyphenyl)penta-2,4-dien-1-yl tosylcarbamate (16a). Prepared from 5a (rt, 30 min.) and purified using a hexane/ethyle acetate mixture (65/35 Rf, 0.24) as eluent. The product was isolated as a yellow oil (29 mg) in 25% yield. NMR spectra of 16a in CDCl3 at 298K revealed the presence of two conformers...
(rotamers) in a ratio (75/25). 1H NMR (400 MHz, CDCl₃) δ 7.93 (d, J = 8.2 Hz, 1.5H), 7.82 (d, J = 8.2 Hz, 0.5H), 7.36–7.30 (m, 4H), 6.86 (d, J = 8.7 Hz, 2H), 6.63–6.52 (m, 2H), 6.36 (dd, J = 15.1, 9.8 Hz, 1H), 5.70 (dt, J = 14.5, 6.9 Hz, 1H), 4.75–4.74 (br s, 1H), 4.63 (d, J = 6.9 Hz, 2H), 3.81 (s, 3H), 2.44 (s, 2.25H), 2.41 (s, 0.75H). 13C{1H} NMR (101 MHz, CDCl₃) δ 159.8, 150.4, 145.2, 136.4, 134.4, 129.8, 128.6, 127.9, 126.6, 124.0,114.3, 67.4, 55.5, 21.8, 21.7. IR (cm⁻¹) 3268, 2957, 2925, 1735, 1601, 1510, 1458, 1341, 1249, 1160, 814, 644, 547. HRMS (ESI): m/z calcd. for C₉₀H₁₁₀NO₅SNa [M+Na]⁺ 410.1038; found 410.1036.

(2E,4E)-5-phenylpenta-2,4-dien-1-y1 tosylcarbamate (16b). Prepared from 5b (rt, 4 h) and purified using a hexane/ethyl acetate mixture (70/30 R{19} 0.29) as eluent. The product was isolated as a yellow oil (80 mg) in 75% yield. NMR spectra of 16b in CDCl₃ at 298K revealed the presence of two conformers (rotamers) in a ratio (63/37). 1H NMR (400 MHz, CDCl₃) δ 7.95–7.91 (m, 1.3H), 7.84–7.80 (m, 0.7H), 7.41–7.36 (m, 2H), 7.36–7.29 (m, 4H), 7.27–7.24 (m, 1H), 6.71 (dd, J = 15.7, 10.3 Hz, 1H), 6.56 (d, J = 15.7 Hz, 1H), 6.37 (dd, J = 15.2, 10.4 Hz, 1H), 5.75 (dt, J = 14.1, 6.7 Hz, 1H), 5.02–4.93 (br s, 1H), 4.64 (d, J = 6.7 Hz, 2H), 2.43 (s, 1.9H), 2.42 (s, 1.1H). 13C{1H} NMR (126 MHz, CDCl₃) δ 150.6, 145.2, 143.6, 139.2, 136.8, 135.6, 134.5, 129.8, 128.7, 128.4, 128.1, 127.4, 126.6, 126.5, 125.4, 67.1, 21.7, 21.6. IR (cm⁻¹) 3355, 3259, 1745, 1441, 1302, 1152, 660, 544. HRMS (ESI): m/z calcd. for C₉₀H₁₁₀NO₅SNa [M+Na]⁺ 380.0932; found 380.0929.

(2E,4E)-5-(4-chlorophenyl)pentai-2,4-dien-1-y1 tosylcarbamate (16c). Prepared from 5c (rt, 4 h) and purified using a hexane/ethyl acetate mixture (70/30 R{19} 0.22) as eluent. The product was isolated as pale yellow oil (80 mg) in 68% yield. NMR spectra of 16c in CDCl₃ at 298K revealed the presence of two conformers (rotamers) in a ratio (75/25). 1H NMR (400 MHz, CDCl₃) δ 7.96–7.88 (m, 1.5H), 7.85–7.76 (m, 0.5H), 7.31 (d, J = 8.1 Hz, 2H), 7.29–7.22 (m, 4H), 6.64 (dd, J = 15.7, 10.5 Hz, 1H), 6.46 (d, J = 15.7 Hz, 1H), 6.33 (dd, J = 15.2, 10.4 Hz, 1H), 5.75 (dt, J = 15.2, 6.5 Hz, 1H), 4.62 (d, J = 6.5 Hz, 2H), 2.40 (s, 2.25H), 2.39 (s, 0.75H). 13C{1H} NMR (126 MHz, CDCl₃) δ 150.5, 145.2, 143.7, 139.2, 135.5, 135.2, 133.7, 131.1, 129.8, 127.9, 128.9, 128.5, 127.9, 127.8, 126.5, 125.9, 67.0, 21.8, 21.6. IR (cm⁻¹) 3272, 3055, 1749, 1595, 1344, 1264, 1159, 1089, 732, 510. HRMS (ESI): m/z calcd. for C₉₀H₈₂ClNO₅SNa [M+Na]⁺ 414.0543; found 414.0542.

(2E,4E)-5-(4-nitrophenyl)pentai-2,4-dien-1-y1 tosylcarbamate (16d). Prepared from 5d (90 °C, 5 days) and purified using a hexane/ethyl acetate mixture (60/40 R{19} 0.26) as eluent. The product was isolated as an orange oil (44 mg) in 36% yield. NMR spectra of 16d in CDCl₃ at 298K revealed the presence of two conformers (rotamers) in a ratio (99/1). 1H NMR (400 MHz, CDCl₃) δ 8.18 (d, J = 8.5 Hz, 2H), 7.93 (d, J = 8.1 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 6.85 (dd, J = 15.7, 10.5 Hz, 1H), 6.60 (d, J = 15.7 Hz, 1H), 6.41 (dd, J = 15.3, 10.6 Hz, 1H), 5.90 (dt, J = 15.3, 5.9 Hz, 1H), 4.67 (d, J = 5.9 Hz, 2H), 2.44 (s, 3H). 13C{1H} NMR (101 MHz, CDCl₃) δ 150.3, 147.1, 145.4, 143.3, 135.5, 134.3, 131.9, 129.8, 128.7, 128.5, 127.1, 124.2, 66.6, 21.8. IR (cm⁻¹) 3237, 2957, 2927, 1749, 1594, 1514, 1450, 1340, 1158, 1089, 860, 662, 577, 547. HRMS (ESI): m/z calcd. for C₉₀H₈₂NO₃SNa [M+Na]⁺ 425.0783; found 425.0785.

(3E,5E)-6-(4-Chlorophenyl)hexa-3,5-dien-2-y1 tosylcarbamate (18ba). Prepared from 17b (rt, 2 h). The compound is unstable on silica gel but a pure sample can be obtained by flash chromatography using a cyclohexane/ethyl acetate mixture (70/30 R{19} 0.28) as eluent. The product was isolated as a yellow oil. 1H NMR (300 MHz, CD₂Cl₂) δ 7.90 (d, J = 8.4 Hz, 2H), 7.80–7.77 (br s, 1H), 7.38–7.34 (m, 2H), 7.36–7.25 (m, 4H), 6.75–6.63 (m, 1H), 6.51 (d, J = 15.7 Hz, 1H), 6.32 (ddd, J = 15.2, 10.3, 1.1 Hz, 1H), 5.71 (dd, J = 15.2, 6.8 Hz, 1H), 5.36–5.24 (m, 1H), 2.43 (s, 3H), 1.32 (d, J = 6.5 Hz, 3H). 13C{1H} NMR (75 MHz, CD₂Cl₂) δ 149.8, 145.3, 135.6, 135.5, 133.2, 132.5, 132.2, 131.9, 129.6, 128.7, 128.3, 128.2, 127.6, 126.3, 74.1, 21.4, 19.9. IR (cm⁻¹) 36
3227, 1740, 1596, 1490, 1436, 1344, 1222, 1157, 1088, 986, 813, 767, 660. HRMS (ESI): m/z calcd. for C_{38}H_{35}ClNO_{6}S [M-H]^{+} 404.0729; found 404.0729.

**Using phenyl and isopropyl isocyanate.** To a solution of allylic alcohol 1a (0.7 mmol) in dry dichloromethane (0.35M) were added the desired isocyanate (1.05 mmol, 1.5 eq), Et_{3}N (1.05 mmol, 1.5 eq) and DMAP (0.04 mmol, 5 mol%). The reaction was stirred at reflux for 16 hours. Dichloromethane was evaporated and the crude product was purified by silica gel chromatography to afford the branched carbamate.

1-(4-Methoxyphenyl)allyl phenylcarbamate (11). Prepared from phenyl isocyanate and purified using a cyclohexane/ethyl acetate mixture (80/20, R_{f} 0.28) as eluent. The product was isolated as a colorless oil (53 mg) in 30% yield. \(^{1}H\) NMR (300 MHz, CDCl_{3}) \(\delta\) 7.43–7.26 (m, 6H), 7.11–7.05 (m, 1H), 6.93 (d, \(J = 8.7\) Hz, 2H), 6.87–6.83 (br s, 1H), 6.28 (d, \(J = 5.7\) Hz, 1H), 6.10 (ddd, \(J = 17.2, 10.4, 5.6\) Hz, 1H), 5.42–5.26 (m, 2H), 3.83 (s, 3H). \(^{13}C\{^{1}H\}\) NMR (101 MHz, Acetone- \(d_{6}\)) \(\delta\) 165.2, 159.8, 159.5, 154.9, 137.1, 131.7, 128.7, 116.1, 114.0, 113.6, 76.0, 55.3, 23.1. IR (cm\(^{-1}\)) 3329, 2972, 1685, 1612, 1523, 1512, 1242, 1175, 1070, 1031, 926, 828, 816, 778. HRMS (ESI) m/z calcd. for C_{17}H_{12}NO_{3}Na [M+Na]^{+} 306.1101; found 306.1099.

1-(4-Methoxyphenyl)allyl isopropylcarbamate (12). Prepared from isopropyl isocyanate and purified using a cyclohexane/ethyl acetate mixture (90/10, R_{f} 0.18) as eluent. The product was isolated as a yellow solid (62 mg) in 65% yield. m.p. 120–123 °C. \(^{1}H\) NMR (300 MHz, CDCl_{3}) \(\delta\) 7.28 (d, \(J = 8.8\) Hz, 2H), 6.13 (d, \(J = 5.7\) Hz, 1H), 6.01 (ddd, \(J = 17.1, 10.4, 5.6\) Hz, 1H), 5.34–5.11 (m, 2H), 4.60–4.55 (br s, 1H), 3.88–3.80 (m, 1H), 3.80 (s, 3H), 1.14 (dd, \(J = 8.7, 6.4\) Hz, 6H). \(^{13}C\{^{1}H\}\) NMR (75 MHz, CDCl_{3}) \(\delta\) 159.5, 154.9, 137.1, 131.7, 128.7, 116.1, 114.0, 113.6, 76.0, 55.3, 23.1. IR (cm\(^{-1}\)) 3329, 2972, 1685, 1612, 1523, 1512, 1242, 1175, 1070, 1031, 926, 828, 816, 778. HRMS (ESI) m/z calcd. for C_{17}H_{12}NO_{3}Na [M+Na]^{+} 272.1257; found 272.1254.

Using benzoyl isocyanate. To a solution of allylic alcohol 1a or 17 (0.7 mmol) in dry CH_{2}Cl_{2} or CDCl_{3} (0.70M) was added the desired isocyanate (0.84 mmol, 1.2 eq). The reaction was stirred at room temperature for desired time (Scheme 4 and Scheme 5). Solvent was evaporated and the crude product was purified by silica gel chromatography to afford the desired compound.

(E)-3-(4-Methoxyphenyl)allyl benzoylcarbamate (15). Prepared from 1a in 30 min. and purified using a cyclohexane/ethyl acetate mixture (70/30, R_{f} 0.31) as eluent. The product was isolated as a colorless oil (137 mg) in 62% yield. \(^{1}H\) NMR (400 MHz, CDCl_{3}) \(\delta\) 8.57–8.53 (br s, 1H), 7.81 (d, \(J = 7.2\) Hz, 2H), 7.53–7.47 (m, 1H), 7.39 (dd, \(J = 8.3, 7.1\) Hz, 2H), 7.23 (d, \(J = 8.8\) Hz, 2H), 6.79 (d, \(J = 8.8\) Hz, 2H), 6.56 (d, \(J = 15.8\) Hz, 1H), 6.09 (dt, \(J = 15.9, 6.8\) Hz, 1H), 4.75 (dd, \(J = 6.8, 1.2\) Hz, 2H), 3.74 (s, 3H). \(^{13}C\{^{1}H\}\) NMR (101 MHz, CDCl_{3}) \(\delta\) 165.2, 159.8, 151.2, 135.2, 133.0, 130.6, 128.8, 128.7, 128.0, 127.8, 119.9, 114.1, 67.7, 67.0, 55.3. IR (cm\(^{-1}\)) 3241, 3189, 3035, 2835, 1747, 1683, 1606, 1507, 1488, 1192, 1173, 1054, 1033, 1025, 969, 834, 778, 701. HRMS (ESI) m/z calcd. for C_{18}H_{17}NO_{3}Na [M+Na]^{+} 334.1050; found 334.1050.

(3E,5E)-6-Phenylhexa-3,5-dien-2-yl benzoylcarbamate (18ab). Prepared from 17a (rt, 2 h). The compound is unstable on silica gel but a pure sample can be obtained by flash chromatography using a cyclohexane/ethyl acetate mixture (70/30, R_{f} 0.24) as eluent. The product was isolated as a slight yellow oil. \(^{1}H\) NMR (300 MHz, CDCl_{3}) \(\delta\) 8.02–7.59 (br s, 1H), 7.87–7.77 (m, 2H), 7.62–7.54 (m, 1H), 7.52–7.45 (m, 3H), 7.45–7.33 (m, 2H), 7.35–7.28 (m, 2H), 6.74 (dd, \(J = 15.6, 10.2\) Hz, 1H), 6.61 (d, \(J = 15.7\) Hz, 1H), 6.50 (dd, \(J = 15.1, 9.8\) Hz, 1H), 5.82 (dd, \(J = 15.1, 7.0\) Hz, 1H), 5.54 (m, 1H), 1.47 (d, \(J = 6.5\) Hz, 3H). \(^{13}C\{^{1}H\}\) NMR (75 MHz, CDCl_{3}) \(\delta\) 166.5, 151.4, 150.6, 134.2, 133.2, 133.0, 132.9, 132.0, 128.8, 128.6, 128.5, 128.3, 127.9, 127.7,
127.5, 126.5, 73.3, 20.3. IR (cm⁻¹) 3285, 3028, 2984, 1754, 1665, 1510, 1488, 1192, 1035, 989, 690. HRMS (ESI) m/z calcd. for C_{20}H_{19}NO_{3}Na [M+Na]^+ 344.1257; found 344.1257.

(3E,5E)-6-(4-Chlorophenyl)hexa-3,5-dien-2-yl benzoylecarbamate (18bb). Prepared from 17b (rt, 2 h).

The compound is unstable on silica gel but a pure sample can be obtained by flash chromatography using a cyclohexane/ethyl acetate mixture (70/30, v/v) as eluent. The product was isolated as a yellow oil. ¹H NMR (300 MHz, CD₂Cl₂) δ 8.32–8.30 (br s, 1H), 7.86–7.80 (m, 2H), 7.64–7.55 (m, 1H), 7.53–7.45 (m, 2H), 7.39–7.25 (m, 4H), 6.75 (dd, J = 15.4, 10.6 Hz, 1H), 6.56 (d, J = 15.7 Hz, 1H), 6.48 (dd, J = 15.2, 10.4, 1.1 Hz, 1H), 5.86 (dd, J = 15.2, 6.8 Hz, 1H), 5.49 (m, 1H), 1.44 (d, J = 6.5 Hz, 3H). ¹³C {¹H} NMR (75 MHz, CD₂Cl₂) δ 164.8, 150.1, 135.6, 133.3, 133.2, 132.9, 132.5, 132.4, 132.2, 128.8, 128.7, 128.5, 128.4, 127.7, 127.5, 127.3, 72.9, 20.0. IR (cm⁻¹) 3252, 2982, 2930, 1742, 1683, 1519, 1488, 1288, 1202, 1121, 1088, 992, 830, 776, 703. HRMS (ESI) m/z calcd. for C_{20}H_{18}ClNO₂ [M-H] 336.1376; found 336.1371. HPLC (ChiralPak IB, hexane/iPrOH = 97:3, flow rate 1 mL/min, λ 210 nm), tₚ (minor) 13.64 min, tₖ (major) 15.71 min; 95% de. [α]²⁰D = -15.91 (c 0.35, CHCl₃).

Using (+)-(+)-(4-fluorophenyl)ethyl isocyanate.

(S,E)-4-phenylbut-3-en-2-yl ((R)-1-(4-fluorophenyl)ethyl)carbamate (22). To a solution of (+)-(S,E)-1-phenylbut-2-enol 20 (ee 98%, 0.15 mmol) in toluene (0.2 M) under argon atmosphere, (+)-(+)-(4-fluorophenyl)ethyl isocyanate 19 (0.17 mmol) and triethylamine (0.05 mmol) were added and the mixture was stirred at 90 °C for 6 h. The initial mixture was concentrated in vacuo, diluted with Et₂O (2 mL) and washed with saturated NaCl (3x 2mL). The resulting crude mixture was diluted in toluene (0.2 M) and stirred at 110 °C for 48 h. The final mixture was purified by flash column chromatography on neutral aluminium oxide using a hexane/ethyl acetate mixture (83:17, v/v) as eluent. The product was isolated as a colorless oil (19 mg) in 98% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.39–7.26 (m, 7H), 7.00 (dd, J = 8.6, 8.6 Hz, 2H), 6.56 (d, J = 16.0 Hz, 1H), 6.17 (dd, J = 16.0, 6.5 Hz, 1H), 5.41 (dd, J = 6.5, 6.5 Hz, 1H), 4.92–4.90 (br s, 1H), 4.86–4.78 (m, 1H), 1.50–1.45 (m, 3H), 1.43–1.36 (m, 3H). ¹³C {¹H} NMR (101 MHz, CDCl₃) δ 162.08 (d, ¹JC = 244.9 Hz), 155.21, 136.56, 131.24, 129.38, 128.68, 127.97, 127.68 (d, ¹JC = 8.3 Hz), 126.68, 115.53 (d, ¹JC = 21.1 Hz), 71.66, 50.15, 22.68, 20.75; ¹⁹F NMR (376 MHz, CDCl₃) δ -115.58. IR (cm⁻¹) 3343, 2979, 2931, 1680, 1529, 1508, 1221, 1058, 548. HRMS (ESI) m/z calcd. for C_{19}H_{20}FNO₂Na [M+Na]^+ 336.1376; found 336.1371. HPLC (ChiralPak IB, hexane/iPrOH = 97:3, flow rate 1 mL/min, λ 210 nm), tₚ (minor) 13.64 min, tₖ (major) 15.71 min; 95% de. [α]²⁰D = -15.91 (c 0.35, CHCl₃).

General procedure for the synthesis of allylamine derivatives 8, 9 and 10 via an allyl cyanate/isocyanate rearrangement from 4a.

To a solution of carbamate 4a (0.25 mmol) in dry dichloromethane (0.13M) cooled at 0 °C under argon atmosphere was added TFAA (0.75 mmol) and triethylamine (1.13 mmol). The reaction mixture was stirred at 0°C for 1 hour and then the desired nucleophile (0.38 mmol), and Ti(OR-Bu)₄ (0.025 mmol) if necessary, were added at 0 °C. The reaction mixture was stirred at room temperature during the required time (Scheme 2). Water was added and the aqueous layer was extracted three times with CH₂Cl₂. The collected organic layers were dried over MgSO₄, filtered and concentrated under vacuo. The crude product was purified by silica gel chromatography.

1,1-Diethyl-3-(1-(4-methoxyphenyl)allyl)urea (8). Prepared using HNEt₂ as nucleophile and purified using a cyclohexane/ethyl acetate mixture (70/30, Rₚ 0.51) as eluent. The product was isolated as a colorless oil (33 mg) in 50% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 6.04
(dd, J = 16.8, 10.6, 5.2 Hz, 1H), 5.50 (ddddd, J = 7.2, 5.2, 1.7, 1.7 Hz, 1H), 5.24–5.14 (m, 2H), 4.52 (d, J = 7.6 Hz, 1H), 3.79 (s, 3H), 3.27 (q, J = 7.4 Hz, 4H), 1.14 (t, J = 7.4 Hz, 6H). 13C{1H} NMR (101 MHz, CDCl3) δ 159.0, 156.5, 139.1, 134.2, 128.5, 115.0, 114.1, 55.8, 55.4, 41.4, 14.1. IR (cm⁻¹) 3348, 2977, 2931, 1618, 1510, 1249, 1177, 1031, 908, 828, 810, 762. HRMS (ESI) m/z calcd. for C15H22N2O2Na [M+Na]⁺ 285.1574; found 285.1574.

1- Allyl-1-benzyl-3-(1-(4-methoxyphenyl)allyl)urea (9). Prepared using N-benzyl allylamine as nucleophile and purified using a cyclohexane/ethyl acetate mixture (70/30, Rf 0.54) as eluent. The product was isolated as a colorless oil (46 mg) in 55% yield. 1H NMR (400 MHz, CDCl3) δ 7.36–7.27 (m, 2H), 7.28–7.23 (m, 3H), 7.12 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 5.95 (dddd, J = 17.2, 10.4, 5.2 Hz, 1H), 5.78 (ddt, J = 17.5, 9.9, 5.5 Hz, 1H), 5.52–5.45 (m, 1H), 5.20–5.15 (m, 2H), 5.13–5.04 (m, 2H), 4.73 (d, J = 7.8 Hz, 1H), 4.57–4.40 (m, 2H), 3.88 (dd, J = 5.5, 1.6 Hz, 2H), 3.78 (s, 3H). 13C{1H} NMR (101 MHz, CDCl3) δ 158.9, 157.5, 138.9, 138.1, 134.1, 133.9, 128.8, 128.3, 127.5, 117.1, 114.8, 114.0, 56.0, 55.4, 50.5, 49.9. IR (cm⁻¹) 3316, 2960, 2917, 2849, 1613, 1531, 1511, 1249, 1177, 1031, 908, 828, 810, 762. HRMS (ESI) m/z calcd. for C21H26N2O2Na [M+Na]⁺ 359.1730; found 359.1729.

Benzyl (1-(4-methoxyphenyl)allyl)carbamate (10). Prepared using benzyl alcohol as nucleophile and purified using a cyclohexane/ethyl acetate mixture (80/20, Rf 0.50) as eluent. The product was isolated as a colorless oil (33 mg) in 45% yield. 1H NMR (300 MHz, CDCl3) δ 7.37–7.32 (m, 5H), 7.21 (d, J = 8.3 Hz, 2H), 6.83 (d, J = 8.3 Hz, 2H), 6.00 (dd, J = 17.4, 10.1, 5.2 Hz, 1H), 5.34–5.07 (m, 6H), 3.80 (s, 3H).

Preparation of [17O] labelled compounds.

17O/13C benzilic acid ([17O]J25). (Trichloromethyl)benzene (1.75 mmol) and 0.59 mL of HCl (0.54) as eluent. The product was isolated as a white solid (200 mg) in 93% yield. 1H NMR (400 MHz, CDCl3) δ 8.07 – 8.02 (m, 2H), 7.66 – 7.60 (m, 1H), 7.51 (dd, J = 8.4, 7.1 Hz, 2H). 17O NMR (68 MHz, Acetone-d6): δ 245.

[17O]2-ethoxy-2-oxoethyl benzoate ([17O]J26). To a solution of [17O]J25 (1.62 mmol) and Cu(OtBu)2 (5.9 mg) in toluene (10 mL) ethyl diazoacetate was added dropwise (3.24 mmol) and the resulting mixture was warmed up to 80 °C and stirred for 12h. After completion, the reaction mixture was filtered and toluene was evaporated in vacuo. The final product was used without further purification. 1H NMR (500 MHz, Acetone-d6): δ 8.09 (d, J = 7.7 Hz, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.56 (q, J = 8.0 Hz, 2H), 4.91 (s, 2H), 4.23 (q, J = 7.1 Hz, 2H), 1.27 (q, J = 7.2, 3.6, 2.6 Hz, 3H). 17O NMR (68 MHz, Acetone-d6): δ 340, 136.

[17O]Benzyl alcohol ([17O]J27). Compound [17O]J25 (1.60 mmol) was dissolved in THF (20 mL). A solution of LiAlH₄ in THF (1.48 mL, 2.5 M) was slowly added to the resulting mixture at 0 °C and the reaction was allowed to stir at room temperature until total consumption of starting material. After completion, a solution of NaOH 1N (10 mL) was used to quench the reaction and the aqueous layer was extracted with CH₂Cl₂ (3 x 10 mL). The organic layers were dried over MgSO₄, filtered and concentrated in vacuo. The final product was purified by flash column chromatography on silica gel using a hexane/ethyl acetate mixture (60/40, Rf 0.59) as
eluent, and isolated as a pale yellow oil (149 mg) in 85% yield. 1H NMR (500 MHz, CDCl3): δ 7.37 (d, J = 4.5 Hz, 4H), 7.32 – 7.28 (m, 1H), 4.70 (d, J = 2.3 Hz, 2H), 1.67 (s, 1H). 13C NMR (68 MHz, Acetone-d6): δ 0.

[^17]O-Benzaldehyde ([^17]O[28]).[^32] A solution of oxalyl chloride (2.33 mmol) in CH2Cl2 (3 mL) was cooled to -84 °C and dimethyl sulfoxide (4.65 mmol) was added slowly. The resulting mixture was stirred for additional 15 minutes. [^17]O[27] (1.37 mmol) was added to the reaction and the mixture was allowed to stir for 15 minutes. Triethylamine (6.85 mmol) was slowly added and the resulting white suspension was stirred at the indicated temperature for 2h. After completion, the reaction was warmed up to 0 °C, quenched with HCl 3 mL) and extracted with CH2Cl2 (3x 5 mL). The organic layer was washed with NaHCO3 sat. (2 x 5 mL) and the combined organic layers were dried over MgSO4, filtered and concentrated in vacuo at 0 °C. The desired compound was isolated as a colorless oil (95 mg) in 65% yield. 1H NMR (400 MHz, CDCl3): δ 10.06 (s, 1H), 7.95 – 7.88 (m, 2H), 7.72 – 7.63 (m, 1H), 7.57 (dd, J = 8.2, 6.9 Hz, 2H). ^^O NMR (68 MHz, CDCl3): δ 554.

[^17]O/[1-Phenylprop-2-en-1-ol ([^17]O[28]).[^32] 1) A solution of [^17]O[28] (0.89 mmol) in THF (6 mL) was slowly added at 0 °C a solution of vinylmagnesium bromide in THF (1.07 mmol, 1 M). The reaction mixture was stirred at room temperature for 4 hours after which a saturated NH4Cl solution (3 mL) was added. The aqueous layer was extracted with Et2O (4 x 6 mL). The organic layers were dried over MgSO4, filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel using a hexane/ethyl acetate mixture (80/20, 30%).

[^17]O/[1-Phenylallyl tosylcarbamate ([^17]O[13b]).[^32] To a solution of [^17]O[1b] (0.073 mmol) in toluene (0.2 M) under argon atmosphere, p-toluenesulfonylisocyanate (0.447 mmol) was added dropwise and the mixture was stirred at room temperature for 5 minutes. The resulting mixture was concentrated in vacuo and purified using a hexane/ethyl acetate mixture (80/20, Rf 0.31) as eluent. The product was isolated as a colorless oil (21 mg) in 90% yield. 1H NMR (400 MHz, CDCl3) δ 7.42 – 7.34 (m, 4H), 7.29 (td, J = 5.7, 2.5 Hz, 1H), 6.06 (ddd, J = 16.7, 10.3, 6.0 Hz, 1H), 5.35 (ddd, J = 16.7, 1.6 Hz, 1H), 5.24 – 5.18 (m, 2H). ^^O NMR (68 MHz, CDCl3): δ 31.

[^17]O/[1-phenylallyl tosylcarbamate ([^17]O[14b]).[^32] Prepared from 1-phenylprop-2-en-1-ol [^17]O[1b] (0.373 mmol) in toluene (0.2 M) under argon atmosphere, p-toluenesulfonylisocyanate (0.088 mmol) was added dropwise and the mixture was stirred at room temperature for 5 minutes. The resulting mixture was concentrated in vacuo and purified using a hexane/ethyl acetate mixture (80/20, Rf 0.39) as eluent. The product was isolated as a white solid (21 mg) in 86% yield. 1H NMR (400 MHz, CDCl3) δ 7.97–7.90 (m, 1.5H), 7.82 (m, 0.5H), 7.37–7.25 (m, 7H), 6.58 (d, J = 15.8 Hz, 1H), 6.14 (dt, J = 15.9, 6.6 Hz, 1H), 4.72 (dd, J = 6.6, 1.3 Hz, 2H), 2.43 (s, 0.75H), 2.42 (s, 2.25H). ^^O NMR (68 MHz, Chloroform-d) δ 264, 125. HRMS (ESI): m/z calcd. for [^17]O[14b]: calculated for C17H17NO2SNa [M+Na]+ 354.0763; found: 354.0763 (59%); calculated for C17H17NO2SNa [(M+1)+Na]+ 355.0805; found: 355.0799 (11%); calculated for C17H17NO2SNa [(M+2)+Na]+ 356.0806; found: 356.0799 (30%).


To a solution of 1-phenylprop-2-en-1-ol [^17]O[1b] (0.373 mmol) in toluene (0.2 M) under argon atmosphere, p-toluenesulfonylisocyanate (0.447 mmol) was added dropwise. The reaction was heated to 90 °C,
and 200 µL were taken from the reaction medium every 20 minutes. The solvent was removed and the resulting colorless oil was dissolved in CDCl₃ to perform ¹⁷O NMR experiments at room temperature.

**Computational Methods.** All of the calculations reported in this work were carried out with the GAUSSIAN 09 suite of programs and using the hybrid DFT functional B3LYP with the D3 dispersion empirical correction and the 6-311++G(d,p) basis set. The most stable conformations of reactants and products were previously determined by MM Monte Carlo simulations using the OPLS force field as implemented in the MacroModel program implemented in the Shrödinger Maestro suite and then subjected to DFT optimizations. All the stationary points were characterized by harmonic analysis. Reactants and products showed positive definite Hessians. Transition structures (TSs) showed one and only one imaginary frequency associated with nuclear motion along the chemical transformation under study. Free energies at 363.15 K were calculated by including the corresponding thermal corrections to Gibbs free energies (TCGE). Solvent effects were considered by means of the PCM method. The solvent introduced in the calculations was toluene. Natural bonding analysis calculations were performed using the NBO program as implemented in Gaussian 09.

**ASSOCIATED CONTENT**

**Supporting Information.** This material is available free of charge via the Internet at http://pubs.acs.org.

- Copies of ¹H, ¹³C NMR spectra and chiral HPLC chromatography of all new compounds.
- Copies of ¹⁷O NMR of 25, 26, 27, 28, 1b, 13b, 14b. First order linear plot obtained for compounds 14a-c. Cartesian coordinates, number of imaginary frequencies (NIMAG), and energy data of stationary points gathered in Figure 5, 7, 8, 9 and 10.
- Crystal data, CCDC 1824810 for 14e (CIF)

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**Notes**

The authors declare no competing financial interest.

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(13) A similar rearrangement was observed as side-reaction, see ref. 5c.


(17) This kind of allyl carbamates are generally synthesized from the reaction of primary allyl alcohols with isocyanates.

(18) CDCl3 can be efficiently replaced by CH2Cl2.

(19) The (E)-3-(4-methoxyphenyl)prop-2-en-1-ol was prepared from anisaldehyde according to the following publication: Bouziane, A.; Carboni, B.; Bruneau, C.; Carreaux, F.; Renaud, J.-L. Pentamethylcyclopentadienyl Ruthenium: an Efficient Catalyst for the Redox Isomerization of Functionalized Allylic Alcohols into Carbonyl Compounds. *Tetrahedron* 2008, 64, 11745–11750.


(23) No formation of **11** and **12** at room temperature in the absence of Et$_3$N and DMAP. Alkyl carbamate **12** can also be prepared from **1a** and isopropyl isocyanate using CuCl as catalyst, see: Duggan, M. E.; Imagire, J. S. Copper(I) Chloride Catalyzed Addition of Alcohols to Alkyl Isocyanates. A Mild and Expedient Method for Alkyl Carbamate Formation. *Synthesis* **1989**, 131–132.

(24) To avoid a slight formation of rearranged products during the purification, a prior deactivation of silica gel with triethylamine has been necessary.


(26) From (S)-**20**, the carbamoylation/rearrangement sequence is complete after 1 h at room temperature using tosyl isocyanate. However, the enantiomeric excess of this rearranged product could not be determined due to its instability during HPLC analysis.


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