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Microwave-Assisted 1,3-Dioxa-[3,3]-Sigmatropic Rearrangement of Substituted Allylic Carbamates: Application to the Synthesis of Novel 1,3-Oxazine-2,4-Dione Derivatives

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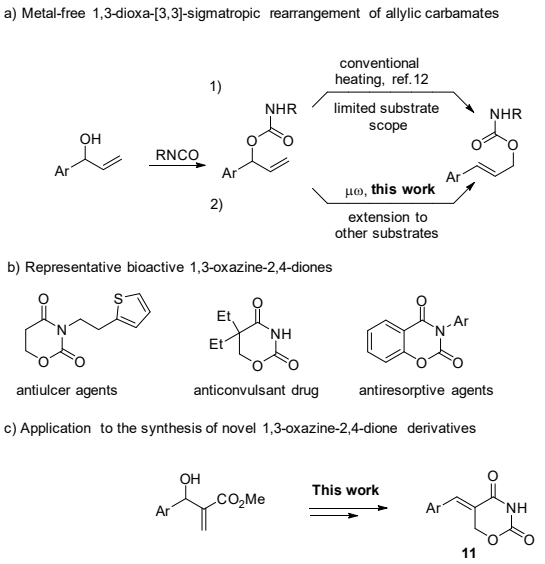
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Abstract: In a first instance, the effect of the microwave irradiation on the 1,3-Dioxa-[3,3]-sigmatropic rearrangement of aryl allylic carbamates was investigated. Under these new conditions, the reaction acceleration was clearly highlighted compared to conventional heating conditions. Depending on the electronic nature of substituents on the aromatic group, this type of rearrangement can be faster with similar or improved yields. Due to this experimental improvement, the diversity of aryl allylic carbamates able to undergo this rearrangement in a reasonable reaction time (30 min.) and with acceptable to high yields was greatly extended. Finally, an original synthetic way involving this microwave-assisted process to access new six-membered heterocyclic structures such as (*E*)-5-arylidene-1,3-oxazinane-2,4-diones was developed from Morita-Baylis-Hillman (MBH) adducts showing the interest of this molecular rearrangement approach. DFT and Fragment Distortion studies showed in general polar transition structures and connected high deformation and interaction energies with lower activation barriers.

Introduction

[3,3]-Sigmatropic rearrangements involving the stereoselective construction of carbon-heteroatom bonds constitute powerful methods for the synthesis of heterocyclic compounds, which can be easily incorporated in sequential reactions.[1] Probably, the most popular carbon-nitrogen bond forming reaction is the Overman rearrangement[2-3] although other methods[4-5] including the allyl cyanate-to-isocyanate rearrangement[6-7] are becoming efficient alternatives for the synthesis of allylamine derivatives. With regard to [3,3]-sigmatropic rearrangements generating a C-O bond formation, those have been much less employed in multistep synthesis of important scaffolds such as heterocycles. Thermal rearrangement of allyl esters was one of first examples to be reported.[8] Afterwards, the employment of metal catalysts allowed the allylic ester transposition under milder conditions[9] as well as the rearrangement of other allyl groups such as, for instance, carbamates.[10] The *in situ* [3,3]-sigmatropic rearrangement resulting from the acylation of *N*-oxyenamines and derivatives can be also mentioned.[11]

Recently, we brought to light an unexpected metal-free 1,3-dioxa-[3,3]-sigmatropic rearrangement of allylic carbamates from α-aryl allylic alcohols (Figure 1a$_1$).[12] The first step is a carbamoylation reaction followed, in some cases, by a spontaneous rearrangement to afford the corresponding linear carbamates. However, the transposition is more or less favored according to the electronic nature of substituents on the phenyl group. The more the aromatic ring is electron-deficient, the more the rate of the reaction is slow and so requires additional energy to reach an appropriate conversion. In order to expand this metal-free process to a larger number of aryl substituted allylic alcohols due to synthetic interest of allyl carbamates,[13] we investigated the usefulness of the microwave (MW) technology as a non-conventional heating to improve the sequential reaction (Figure 1a$_2$). In a second step, we envisioned that using conveniently functionalized starting materials, this methodology followed by an intramolecular cyclisation approach, could be helpful to access original heterocyclic systems. In particular, six-membered rings such as 1,3-oxazine-2,4-diones are a class of compounds which can be not only useful building blocks[14] but also exhibit many biological activities (Figure 1b).[15]



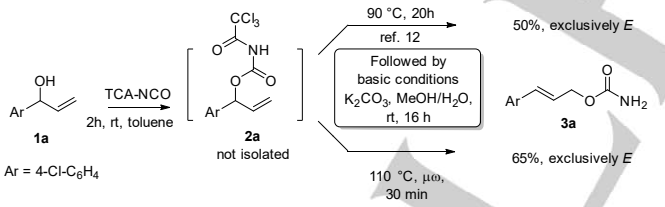
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Figure 1. Effect of the microwave heating on the 1,3-dioxa-[3,3]-sigmatropic rearrangement of *O*-allyl carbamates and application to the synthesis of (*E*)-5-arylidene-1,3-oxazine-2,4-diones **11**.

In this paper, we report our findings on this subject. The improvement obtained using the microwave irradiation allowed us to applied this sequential reaction to the Morita-Baylis-Hillman (MBH) adducts opening the synthetic way to prepare hitherto new heterocyclic scaffolds such as 1,3-oxazine-2,4-dione derivatives **11**, which are promising candidates as biologically active compounds (Figure 1c).

Results and Discussion

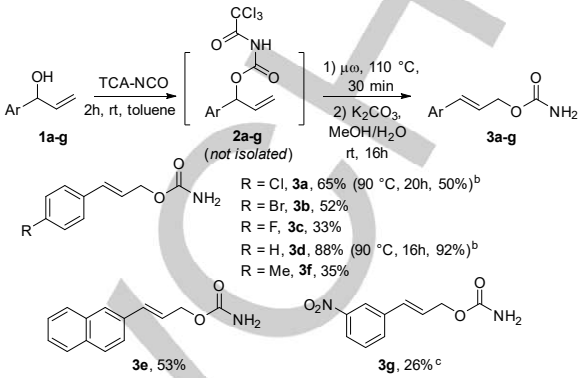
1-(4-chlorophenyl)prop-2-en-1-ol **1a** was chosen as model substrate to evaluate the effect of the microwave heating on the tandem reaction (Scheme 1). The first step was the carbamoylation of **1a** with 2,2,2-trichloroacetyl isocyanate (TCA-NCO) in toluene leading to the formation of the branched carbamate **2a** in a quantitative way monitored by ^{1}H NMR. In a previous paper, we showed that when the mixture reaction was undergone under conventional thermal conditions (90 °C, 20h), the linear primary carbamate **3a** was isolated in a 50% overall yield from **1a** after hydrolysis of the rearranged intermediate.[12] Under microwave conditions (110 °C), we were pleased to observe a complete stereoselective rearrangement only after 30 minutes. After evaporation of solvent, the residue was treated under basic conditions to afford the expected product (*E*)-**3a** in a better overall yield (65%).[16] it is interesting to note when the reaction is performed at the same temperature (110 °C, toluene) under conventional thermal conditions for 30 minutes in a sealed microwave reactor, a partial rearrangement is observed (37% conversion).



Scheme 1. Improvement of the tandem reaction using the microwave heating.

Considering the positive effect of the microwave irradiation on the bond reorganization and the overall yield of the reaction sequence, a set of secondary allylic alcohols with deactivating groups and poorly activating substituents (relative to H) on the aromatic ring have been evaluated under this new protocol (Table 1). In all cases, the expected products **3** resulting from the carbamoylation/rearrangement/hydrolysis sequence were obtained as a single stereoisomer (*E*) and with moderate to good yields. Compound **3d** with an unsubstituted phenyl group was isolated with a similar yield to that obtained with a conventional heating. The benefit of using this microwave conditions is clearly highlighted in the case of compound **3g**, for which the rearrangement of **2g** was not observed by heating under neat conditions at 110 °C for 1h. Under solvent-free microwave conditions (110 °C, 1h) in the same reactor, the allyl carbamate **3g,** after hydrolysis, can be obtained with a 26% non-optimized yield from **1g**.

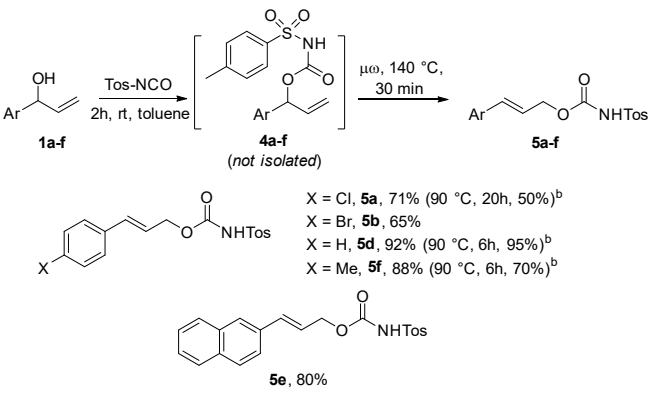
Table 1. Microwave-assisted 1,3-dioxa-[3,3]-sigmatropic rearrangement using the TCA-NCO reagent.[a]



[a] Isolated yields from **1**. [b] The yield in bracket was obtained under conventional heating in toluene (ref. 12). [c] the reaction was carried out without solvent for 60 minutes at the same temperature.

The acceleration produced by the microwave heating on the 1,3-dioxa-[3,3]-sigmatropic rearrangement of allyl carbamates was also checked using another isocyanate reagent (Table 2). Allylic alcohol **1a** was treated with *p*-toluenesulfonyl isocyanate to afford **4a** and further submitted to the previously described irradiation conditions. However, the complete conversion into the linear *N*-tosyl carbamate **5a** required an increased temperature from 110 °C to 140 °C. Under these new conditions, the only stereoisomer (*E*) is formed and **5a** was isolated with a better yield (71%) than that obtained (50%) by conventional heating (Table 2).[17] The same beneficial impact was observed starting from other aryl allylic alcohols.

Table 2. Microwave-assisted 1,3-dioxa-[3,3]-sigmatropic rearrangement using the Tos-NCO reagent.[a]

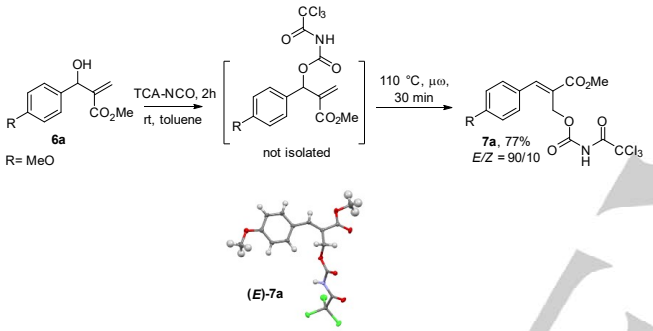


[a] Isolated yields from **1**. [b] The yield in bracket was obtained under conventional heating in toluene (ref. 12).

Having demonstrated the microwave positive effect on the rate of the rearrangement, particularly for the unfavored substrates under conventional thermal conditions, we turned our attention to the Morita-Baylis-Hillman adducts. We speculated that these functionalized scaffolds could serve as potential substrates for an access to a new class of heterocycles using our methodology. Indeed, the primary carbamate function

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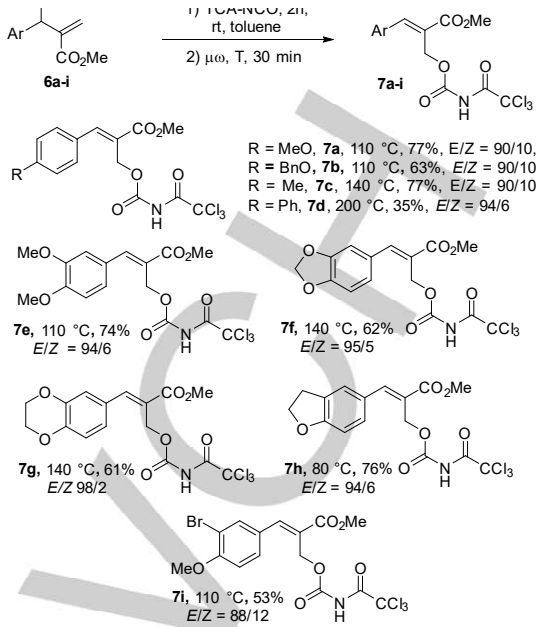
generated through the bond reorganization could react with the ester group via an intramolecular cyclisation leading to 5-arylidene-1,3-oxazine-2,4-dione derivatives. First of all, we optimized the sigmatropic rearrangement conditions of this type of substrates using the methyl 2-(hydroxy(4-methoxyphenyl)methyl)acrylate **6a** as reference model (Scheme 2). After carbamoylation reaction with TCA-NCO in a microwave reactor (toluene, r.t., 2h), the mixture was heated by microwave irradiations (110 °C, 30 min.).[18] Under these conditions, we have been pleased to observe by NMR monitoring that the rearrangement is still highly stereoselective (*E*/*Z* = 90/10) leading to compound **7a** in a good overall yield (77%) starting from **6a** after purification. Fortunately, the two isomers can be separated by a simple trituration in diisopropyl ether and the configuration *E* of the predominant isomer was established by X-ray crystallography and confirmed by NOESY (see the Supporting Information).[19] It should be pointed out that this rearrangement under conventional heating at 110 °C (toluene, sealed microwave reactor) is complete only after 4h with a poorer stereoselectivity 80/20 in favor of the isomer *E* and an isolated yield of 68%.



Scheme 2. Stereoselective synthesis of (*E*)-**7a** involving a microwave-assisted rearrangement.

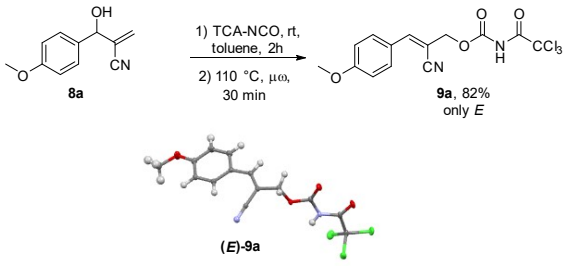
Given this encouraging outcome, this one-pot process was extended to other Morita-Baylis-Hillman (MBH) adducts (Table 3). In any case, the internal double bond configuration of compounds **7** was largely in favor of the isomer *E* which may be obtained in a pure form by a trituration process of the isolated mixture (see experimental section). In all studied examples, the obtained yields were acceptable excepted for the compound **7d**, for which a significant temperature increase was required to improve the conversion of the rearrangement. It should be noted that the presence of an electron donating group (+M) at the para-position on the aromatic ring is the guarantee of a successful rearrangement even with the existence of other substituents having an opposite inductive effect (**7e-i**).

Table 3. Microwave-assisted 1,3-dioxa-[3,3]-sigmatropic rearrangement from Morita-Baylis Hillman adducts.[a]



[a] Isolated yields. The ratio of stereoisomers is given before trituration in diisopropyl ether.

This kind of sigmatropic rearrangement can be extended to other allylic alcohols containing an activated alkene functionality. Indeed, the product **8a**, resulting from the MBH reaction between the acrylonitrile and the 4-methoxybenzaldehyde, led to the formation of rearranged compound **9a** in good yield and excellent stereoselectivity after treatment with TCA-NCO under microwave conditions (Scheme 3).[20] The configuration of the double bond was established by X-ray analysis and confirmed by NOESY (see the Supporting Information). Considering the results obtained from acrylate esters derivatives **6**, the isomer **9a** was not that we expected.[21]

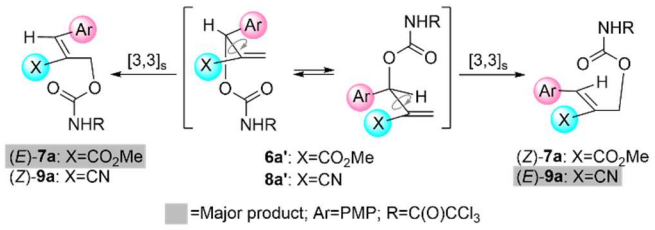


Scheme 3. Stereoselective synthesis of (*E*)-**9a** involving a microwave-assisted rearrangement.

In order to get a better understanding of the behavior of substrates **6a-i** and **8a** in these oxa-[3,3] pericyclic reactions, we explored computationally the reaction of carbamoyl derivatives **6a'** and **8a'** stemming from alcohols **6a** and **8a**, to yield (*E*) and (*Z*) carbamates **7a** and **9a**. In principle, rotation about the C(Ar)-C(sp^2) bond should permit the formation of both stereoisomers, as it is shown in Scheme 4. If a concerted dioxa-[3,3] suprafacial sigmatropic shift is assumed for this reaction, formation of products **7a** and **9a** stems from the relative energies of the corresponding transition states. Within this context, we explored computationally within Density Functional Theory (DFT, see the

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Computational Methods section for further information) the **6a'**→**7a** and **8a'**→**9a** reactions shown in Scheme 4.



Scheme 4. Formation of compounds (*E*)/(*Z*)-**7a** and **9a** via sigmatripic shifts of carbamoyl intermediates **6a'** and **8a**'. The connection between the formal rotation about the C(sp^3)-C(sp^2) bond in the reactants and the configuration of the final double bonds in the products is highlighted.

Computational analysis of **6a'**→**7a** transformation showed two transition structures leading to (*E*) and (*Z*) isomers of the reaction product (Figure 2). Only the boat transition structures were found in both cases. Optimization of chair initial structures with both B3LYP-D3BJ and M06-2X dispersion-corrected functionals spontaneously converged to boat geometries. Our results indicate that saddle point (*E*)-**TS1** is ca. 1.2 kcal/mol less energetic than (*Z*)-**TS1**. Both transition structures are quite synchronous and polar, with a negatively charged carboxylate moiety and a partially positively charged allyl cation, in line with previous results.[12] This polar character should favor the progress of the reaction under microwave irradiation.[22] Under a Curtin-Hammett kinetics scheme, this corresponds to a (*E*)-**7a**:(*Z*)-**7a** ratio of 83:17, in good agreement with the experimental results observed for X=CO_2Me substrates. The lower energy of (*E*)-**TS1** stems from the relatively large steric demand of the methoxycarbonyl group, which favors the *trans* relationship with the para-methoxyphenyl (PMP) group, and the lower steric congestion between the carbamoyl group and this latter aromatic substituent, favored by the boat arrangement. It is interesting to note that in this case both kinetic and thermodynamic control point to the preferred formation of (*E*)-**7a**. Therefore, microwave irradiation should not affect significantly the stereochemical outcome of this and related reactions.

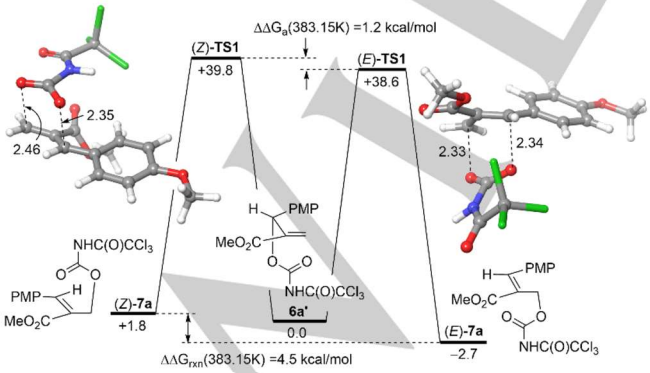


Figure 2. Reaction profile of the dioxa-[3,3] sigmatropic shift of carbamoyl intermediate **6a'** to both (*E*) and (*Z*) isomers of **7a**, computed at the M06-2X(PCM,toluene)/6-31+G* level of theory. Relative free energies, in kcal/mol, have been computed at 383.15 K. Bond distances are given in Å.

A similar computational analysis of the **8a'**→**9a** transformation yielded the reaction profile shown in Figure 3. In contrast with the previous case, in (*E*)-**9a** the cyano (X=CN, Scheme 4) and PMP groups are *cis* to each other. In this reaction, (*Z*)-**TS2** showed a late sofa geometry, whereas its congener (*E*)-**TS2** exhibited an earlier boat conformation. This latter saddle point was calculated to lie 4.6 kcal/mol lower than (*Z*)-**TS2** and therefore our calculations predict the exclusive formation of (*E*)-**9a**, in nice agreement with the experimental results. In addition, the computed free activation energies are lower than those found for the **6a'**→**7a** reaction. Moreover, in this case, the Gibbs reaction energy associated with the formation of (*E*)-**9a** is more exergonic than the value corresponding to (*Z*)-**9a**. Therefore, exclusive formation of this latter product is predicted under both kinetic and thermodynamic control.

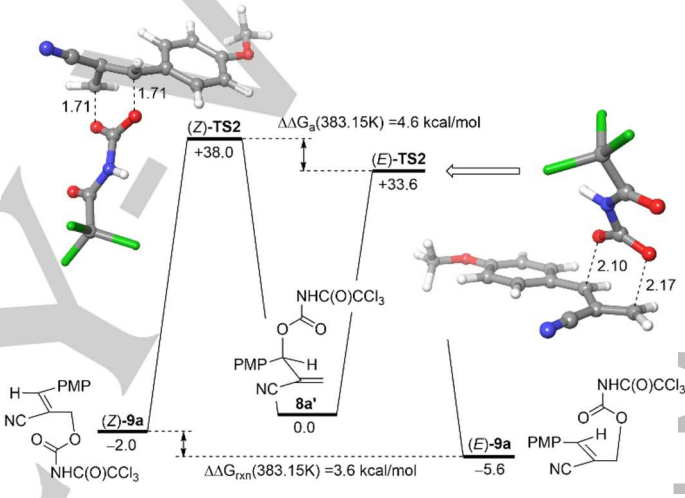
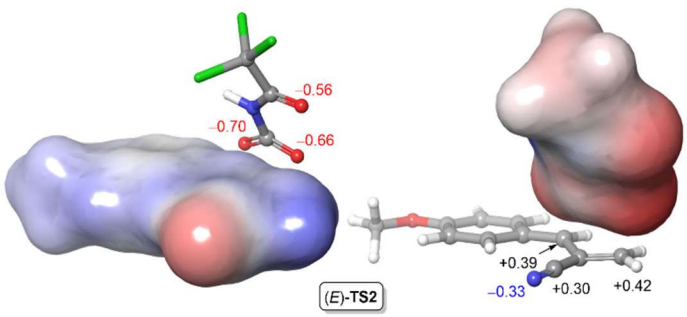


Figure 3. Reaction profile of the dioxa-[3,3] sigmatropic shift of carbamoyl intermediate **6a'** to both (*E*) and (*Z*) isomers of **7a**, See Figure 2 caption for additional details.

The preferential formation of (*E*)-**9a** via (*E*)-**TS2** is compatible with the polar character of the saddle point and the boat geometry that puts the carbamoyl moiety away from the PMP group and generates a quite compact structure, favored by solvent effects and microwave irradiation. Thus, the arrangement of charges (Figure 4) results in an attractive Coulombic interaction between both components. In addition, the linear cyano moiety is sterically less demanding in its cis interaction with the aryl group, thus favoring the formation of (*E*)-**9a**.



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Figure 4. Electrostatic potentials projected on the electron densities of the carboxy and allylic parts of (*E*)-**TS2**. Colors range from blue (+0.3 a .u.) to red (-0.3 a. u.). Point NBO charges are given in a. u.

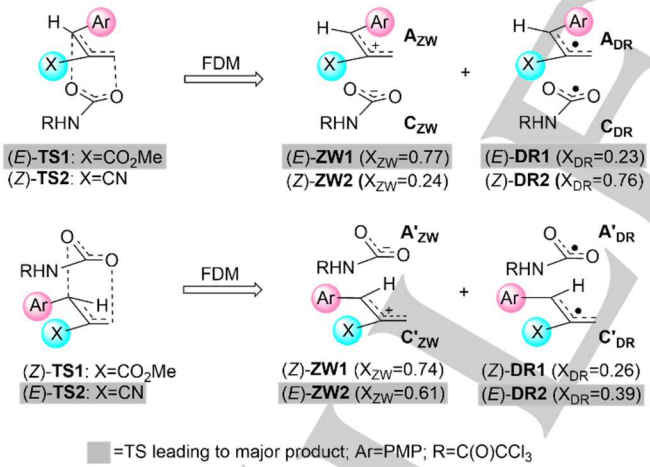
We have also investigated the origins of the (*Z*)-selectivity in **TS1** and **TS2** by means of a modified distortion-strain model based on the partitioning of the transition structure in fragments (Fragment Distortion Model).[23] According to this modification, previously reported by our group,[12] we described the activation energy $\Delta E^{\ddagger}$ as the contribution of the deformation (FDEF) and interaction (FINT) terms between the carboxylate (C) and allylic (A) componnets of the TS under study:

$$\Delta E^{\ddagger} = \Delta E^{\ddagger}_{FDEF} + \Delta E^{\ddagger}_{FINT}$$

In turn, the deformation term of the activation energy results as the sum of the zwitterionic (ZW) and diradical (DR) contributions of the C and A fragments (Scheme 5):

$$\Delta E^{\ddagger}_{FDEF} = X_{ZW}\Delta E^{\ddagger}_{ZW} + X_{DR}\Delta E^{\ddagger}_{DR}$$

In this latter equation, X_{ZW} is the weight of the zwitterionic contribution normalized to one. Therefore, the equivalent term for the diradical contribution is X_{DR}=1-X_{ZW}. The value of X_{ZW} was estimated from the net NBO charge δ of the allylic terms in the corresponding transition structures **TS1** and **TS2** (X_{ZW}=δ). In general, these δ values lie in the range 0.6-0.8 a.u., which is consistent with the polar character of these saddle points (see Figure 4). The exception is (*Z*)-**TS2**, with δ=0.24. This result is compatible with the advanced character of this latter saddle point, which has C···O bond distances of ca. 1.7 Å (see Figure 3) and a more diradical character, with X_{DR}=0.76.



Scheme 5. Decomposition of saddle points **TS1** and **TS2** in the carboxylate (C) and allylic (A) fragments, according to the Fragment Distortion Model (see text). The contributions of the zwitterionic (ZW) and diradical (DR) resonance forms are also highlighted.

The $\Delta E^{\ddagger}_{ZW}$ and $\Delta E^{\ddagger}_{DR}$ terms were calculated as the contributions of single-point energies of the A and C fragments computed at the required charges and multiplicities (singlet for the ZW parts, doublet for the DR contributions):

$$\Delta E^{\ddagger}_{ZW} = (\Delta E^{\ddagger}_{C^-} + \Delta E^{\ddagger}_{A^+}) - E_0$$

$$\Delta E^{\ddagger}_{DR} = (\Delta E^{\ddagger}_{C^{\bullet}} + \Delta E^{\ddagger}_{A^{\bullet}}) - E_0$$

In this latter equation, E_0 is the reference energy (without zero-point corections) of the reactants **6a'** (for **TS1**) and **8a'** (for **TS2**).

The results of the FDM calculations on both **TS1** and **TS2** series are gathered in Figure 5. From these data, it can be concluded that transition structures (*E*)-**TS1,2** have larger deformation energies. This larger distortion of the C and A fragments results in fragments that are more reactive and therefore develop larger FINT terms. These larger stabilization terms overcome the relative energy cost associated with the deformation energies. As a consequence, the activation energies associated with (*E*)-**TS1,2** are lower than those found for their (*Z*)-**TS1,2** congeners because of a more adequate tradeoff between distortion and reactivity.

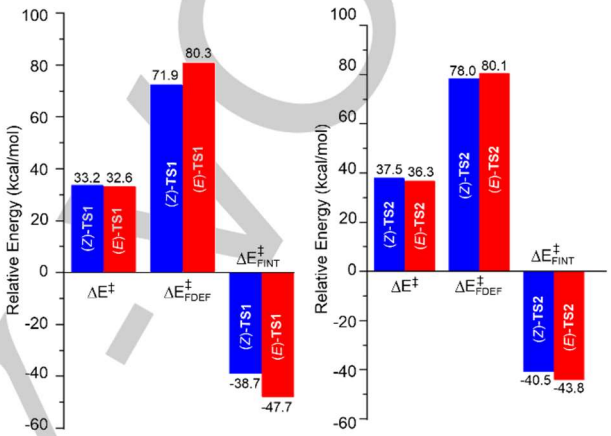
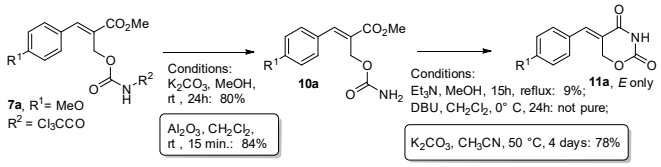


Figure 5. Fragment Distortion Analysis of **TS1** and **TS2** series corresponding to **6a'**→**7a** and **8a'**→**9a** reactions, respectively. Activation energies are decomposed in fragment deformation (FDEF) and fragment interaction (FINT) terms. See text for further details.

To reach our final objective, the first step was to cleave the *N*-protective group in order to generate the corresponding primary carbamate which would be able to react on the ester function to form the heterocyclic scaffold by cyclisation (Scheme 6). Usually, hydrolysis of the 2,2,2-trichloroacetylamide is performed under basic conditions (K_2CO_3) in the presence of methanol. In our case, we obtained similar yields of **10a** employing neutral alumina without further purification and in a shorter reaction time (15 min. instead of 24h in conventional conditions).[24] Several cyclisation conditions inspired from the literature for the synthesis of 2,4-oxazolidinediones have been explored.[25] Treatment of **10a** with Et_3N, in EtOH at reflux for 15h led to the formation of desired heterocyclic compound **11a** in a low rate of conversion. When DBU was used as base, the conversion was complete but unfortunately, an unidentified side compound was also formed making difficult the purification of **11a**. Finally, a clean process was implemented using K_2CO_3 in acetonitrile despite a longer reaction time. Under these conditions, **11a** was isolated in a pure form with a 78% yield after a simple filtration and without erosion of the double bond stereoselectivity confirmed by NOESY (see the Supporting Information).

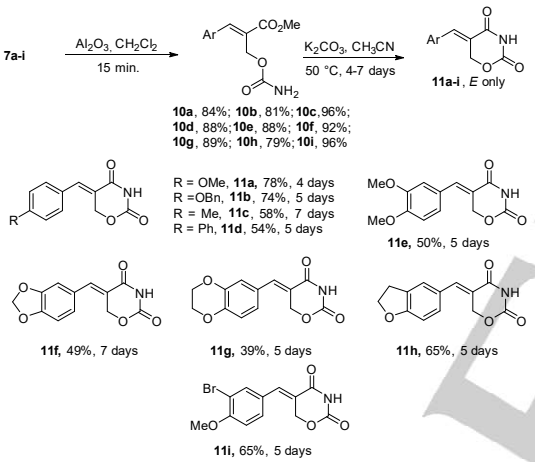
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Scheme 6. Stereoselective synthesis of heterocyclic compound **11a**

This optimized sequence without any chromatographic purification to access hitherto unknown heterocyclic compounds was applied to other substrates **7** (Table 4). In all cases, the (*E*)-1,3-oxazine-2,4-dione derivatives **11** were obtained in moderate to good yields showing the good level of reliability of this approach. The reaction time of the cyclisation step may range from 4 to 7 days depending on the solubility of final product in the reaction solvent.

Table 4. Transformation of compounds **7** into new 1,3-oxazine-2,4-dione derivatives **11**.[a]



[a] Isolated yields.

Conclusion

As a conclusion, we showed in this paper the positive effect of the microwave heating on the 1,3-dioxa-[3,3]-sigmatropic rearrangement of substituted allylic carbamates whatever the electronic nature of the substituent on the aromatic group. In a general way, the reaction time is shortened compared to conventional heating conditions as well as the overall yield of the reaction sequence is improved. DFT calculations support the main features of these reactions in terms of relative activation energies and stereocontrol. Analysis of the transition structures (TS's) by means of the Fragment Distortion model showed a polar zwitterionic character (with the exception of advanced (*Z*)-**TS2**). In addition, this analysis indicated that the higher the deformation of the carboxy and allyl fragments, the higher stabilizing interaction between them, thus resulting in lower activation energies for (*E*)-**TS1,2** with respect to their respective (*Z*)-**TS1,2** analogs. The implementation of these microwave conditions allowed us to extend this kind of rearrangement to a larger number of substrates opening the route to the synthesis of new heterocyclic structures such as the (*E*)-1,3-oxazine-2,4-dione derivatives. Taking into account the structural analogy with benzoxazine-2,4-diones, the biological activity of these new compounds will be evaluated in the near future.

Computational Methods

DFT calculations were performed by using the dispersion-corrected M06-2X functional[26] and the 6-31+G* basis set[27] in order to describe adequately the possible polar character of the stationary points. Solvent effects (toluene) were computed by means of the Polarization Continuum Model (PCM),[28] within the Self-Consistent Reaction Field (SCRF) approach.[29] Free energies were computed at 383.15 K, according to the experimental conditions. The concerted character of the **6'a**→**7a** and **8'a**→**9a** reactions was verified by Intrinsic Reaction Coordinate (IRC) calculations (see Figures S1 and S2 of the Supporting Information).[30] These calculations were performed using the Gaussian suite of programs.[31] Electrostatic charges were computed within the Natural Bond Orbitals (NBO) scheme.[32] Electrostatic potentials with NBO charges were calculated by using the Jaguar program.[33] Optimized molecular structures were drawn with the Maestro interface.[34]

Experimental Section

All air- and water-sensitive reactions were performed in flame-dried glassware under argon atmosphere. Tetrahydrofuran (THF) was distilled over sodium/benzophenone, dichloromethane (DCM) and ethanol were distilled over calcium hydride (CaH_2) and toluene was distilled over sodium. All aldehydes were washed before use with a saturated aqueous solution of $NaHCO_3$. ^1H NMR spectra (300 MHz, 400 MHz, 500 MHz), ^{13}C NMR (75 MHz, 101 MHz), were recorded on a Bruker AC 300, AC 400 and AC 500 spectrometers. Chemical shifts are given in ppm and coupling constants *J* in Hz. All high-resolution mass spectra (HRMS) were recorded on a Bruker MaXis 4G or on an Agilent 6510 at the CRMPO (Centre Régional de Mesures de Physiques de l'Ouest – Rennes- France) using ion Electrospray ionization technique. Purifications on silica gel were carried out on Acros silica gel 0.006-0.200 mm, 60 A. 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}. X-ray crystallographic data were collected on an APEXII crystal diffractometer at the Centre de Diffraction, Rennes. Reactions under microwave irradiations were realized in the Anton Paar Monowave® 300 apparatus (ScanMat platform-ISCR- Rennes, France). Microwave irradiation reactions were carried out in borosilicate glass vials of 10 mL equipped with snap caps using stirring option. The target temperature was reached with a ramp of 2-5 minutes and the chosen microwave power remained constant to hold the mixture at this temperature. The reaction temperature is monitored using calibrated infrared sensor and the reaction time included the ramp period. Melting points were measured on a melting point apparatus Stuart SMP10 and Stuart SMP3.

General procedure for the synthesis of allylic carbamates 3: Trichloroacetyl isocyanate (0.328 mmol) was added dropwise to a solution of allylic alcohol **1** (0.273 mmol) in 1 mL of dry toluene in a microwave vial cooled at 0 °C. Once the reaction was completed, the vial

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was placed in the Anton Paar monowave reactor and the reaction was stirred during 30 minutes at 110 °C (800 W). In the case of **1g**, no solvent was used (60 min., 110 °C). The resulting mixture was concentrated *in vacuo* and dissolved in a mixture of methanol/water (1.8 mL/0.4 mL) and potassium carbonate (1.12 mmol) was added. The solution was stirred at room temperature overnight and then methanol was removed *in vacuo*. The aqueous layer was extracted with dichloromethane (3 x 5 mL). The organic layers were dried over magnesium sulfate, filtered and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel to afford the corresponding product.

(*E*)-3-(4-chlorophenyl)allyl carbamate 3a:[12] Prepared from **1a** and the desired product was obtained as a white solid (38 mg) in 65% yield without any need for a purification. Mp = 144–146 °C.^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.64-4.66 (br s, 2H), 4.74 (d, *J* = 6.5 Hz, 2H), 6.29 (dt, *J* = 16.0, 6.3 Hz, 1H), 6.63 (d, *J* = 15.9 Hz, 1H), 7.30-7.37 (m, 4H). Spectral data were identical to those reported in literature.

(*E*)-3-(4-bromophenyl)allyl carbamate 3b:[35] Prepared from **1b** and purified using a cyclohexane/ethyl acetate mixture (60/40, R_f = 0.26). The product was isolated as a white solid (36 mg) in 52% yield. Mp = 161-164 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.67-4.69 (br s, 2H), 4.71 (dd, *J* = 6.2, 1.1 Hz, 2H), 6.28 (dt, *J* = 15.9, 6.2 Hz, 1H), 6.59 (d, *J* = 15.9 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 65.4, 121.8, 124.4, 128.1, 131.7, 132.5, 135.2, 156.4. HRMS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{10}H_{10}BrNO_2Na$, 277.9787; found, 277.9789.

(*E*)-3-(4-fluorophenyl)allyl carbamate 3c:[35] Prepared from **1c** and purified using a cyclohexane/ethyl acetate mixture (60/40, R*f* = 0.28). The product was isolated as a white solid (18 mg) in 33% yield. Mp = 111-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.71 (dd, *J* = 6.4, 1.2 Hz, 2H), 4.81-4.83 (br s, 2H), 6.20 (dt, *J* = 15.9, 6.4 Hz, 1H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.97-7.04 (m, 2H), 7.31-7.39 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 65.6, 115.5 (d, *J* = 21 Hz), 123.3 (d, *J* = 3 Hz), 128.1 (d, *J* = 8 Hz), 132.4 (d, *J* = 4 Hz), 132.7, 156.7, 162.5 (d, *J* = 247 Hz). HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{10}H_{10}FNO_2Na$, 218.0588; found 218.0590.

(*E*)-3-(phenyl)allyl carbamate 3d: [35] Prepared from **1d** and the desired product was obtained as a white solid (43 mg) in 88% yield without any need for a purification. Mp = 116-119 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.64-4.66 (br s, 2H), 4.75 (dd, *J* = 6.3, 1.4 Hz, 2H), 6.31 (dt, *J* = 15.9, 6.4 Hz, 1H), 6.68 (d, *J* = 15.9 Hz, 1H), 7.29-7.44 (m, 5H). Spectral data were identical to those reported in literature

(*E*)-3-(naphthalen-2-yl)allyl carbamate 3e: Prepared from **1e** and purified using a cyclohexane/ethyl acetate mixture (65/35, R*f* = 0.3). The product was isolated as a white solid (33 mg) in 53% yield. Mp = 175-178 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.67-4.69 (br s, 2H), 4.81 (dd, *J* = 6.4, 1.4 Hz, 2H), 6.44 (dt, *J* = 15.9, 6.3 Hz, 1H), 6.84 (d, *J* = 15.9 Hz, 1H), 7.43-7.54 (m, 2H), 7.62 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.76-7.88 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 65.8, 123.5, 123.9, 126.1, 126.3, 126.8, 127.7, 128.0, 128.3, 133.2, 133.5, 133.7, 134.0, 156.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_{13}NO_2Na$, 250.0838; found 250.0837.

(*E*)-3-(*p*-tolyl)allyl carbamate 3f:[35] Prepared from **1f** and purified using a cyclohexane/ethyl acetate mixture (70/30, R*f* = 0.26). The product was isolated as a white solid (18 mg) in 35% yield. Mp = 145-151 °C.^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (s, 3H), 4.74 (dd, *J* = 6.4, 1.1 Hz, 2H), 4.77-4.79 (br s, 2H), 6.26 (dt, *J* = 15.9, 6.4 Hz, 1H), 6.65 (d, *J* = 15.9 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2, 65.8, 122.4, 126.5, 129.3, 133.5, 133.9, 137.9, 156.7. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{11}H_{13}NO_2Na$, 214.0838; found 214.0839.

(*E*)-3-(3-nitrophenyl)allyl carbamate 3g: Prepared from **1g** (110 °C, 60 min., without solvent) and purified using a cyclohexane/ethyl acetate mixture (60/40, R_f = 0.3). The product was isolated as a white solid (16 mg) in 26% yield. Mp = 115-118 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.75-4.80 (br s, 2H), 4.77 (dd, *J* = 5.7, 1.4 Hz, 2H), 6.43 (dt, *J* = 15.9, 5.9 Hz, 1H), 6.70 (d, *J* = 15.9 Hz, 1H), 7.49 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.24-8.26 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 64.9, 121.2, 122.5, 127.2, 129.5, 130.8, 132.3, 138.1, 148.6, 156.3. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{10}H_{10}N_2O_4Na$, 245.0533; found 245.0533.

General procedure for the synthesis of allylic carbamates 5: *p*-Toluenesulfonyl isocyanate (0.328 mmol) was added dropwise to a solution of allylic alcohol (0.273 mmol) in 1 mL of dry toluene in a microwave vial cooled at 0 °C. Once the reaction was completed, the vial was placed in the Anton Paar monowave reactor and the reaction was stirred during 30 minutes at 140 °C (800 W). The resulting mixture was concentrated *in vacuo* and directly purified by column chromatography on silica gel to afford the desired product.

(*E*)-3-(4-chlorophenyl)allyl tosylcarbamate 5a:[12] Prepared from **1a** and purified using a cyclohexane/ethyl acetate mixture (65/35, R_f = 0.26). The product was isolated as a white solid (71 mg) in 71% yield. Mp = 85-87 °C. NMR spectra of **5a** in $CDCl_3$ at 298 K indicated the presence of two conformers in a ratio (60/40). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.42 (s, 1.2H), 2.43 (s, 1.8H), 4.71 (dd, *J* = 6.6, 1.3 Hz, 2H), 4.81-4.83 (br s, 1H), 6.12 (dt, *J* = 16.0, 6.6, 1H), 6.53 (d, *J* = 16.0, 1H), 7.22-7.37 (m, 6H), 7.82 (d, *J* = 8.1 Hz, 0.8H), 7.93 (d, *J* = 8.1 Hz, 1.2H). Spectral data were identical to those reported in literature.

(*E*)-3-(4-bromophenyl)allyl tosylcarbamate 5b:[36] Prepared from **1b** and purified using a cyclohexane/ethyl acetate mixture (75/25, R_f = 0.26). The product was isolated as a white solid (73 mg) in 65% yield. Mp = 116-119 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.44 (s, 3H), 4.73 (dd, *J* = 6.4, 1.4 Hz, 2H), 6.15 (dt, *J* = 15.8, 6.4 Hz, 1H), 6.53 (d, *J* = 15.8 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.7, 67.1, 122.3, 122.4, 128.2, 128.4, 129.6, 131.8, 134.0, 134.7, 135.4, 145.2, 150.2. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{16}BrNO_4NaS$, 431.9876; found 431.9875.

(*E*)-3-(phenyl)allyl tosylcarbamate 5d:[12] Prepared from **1d** and purified using a cyclohexane/ethyl acetate mixture (60/40, R_f = 0.39). The product was isolated as a white solid (83 mg) in 92% yield. Mp = 73-76 °C. NMR spectra of **5d** in $CDCl_3$ at 298 K indicated the presence of two conformers in a ratio (75/25). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.42 (s, 2.25H), 2.43 (s, 0.75H), 4.72 (dd, *J* = 6.6, 1.3 Hz, 2H), 6.14 (dt, *J* = 15.9, 6.6 Hz, 1H), 6.58 (d, *J* = 15.8 Hz, 1H), 7.25-7.37 (m, 7H), 7.82 (m, 0.5H), 7.90-7.97 (m, 1.5H). Spectral data were identical to those reported in literature.

(*E*)-3-(naphthalen-2-yl)allyl tosylcarbamate 5e:[36] Prepared from **1e** and purified using a cyclohexane/ethyl acetate mixture (75/25, R_f = 0.24). The product was isolated as a white solid (83 mg) in 80% yield. Mp = 132-135 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 3H), 4.80 (dd, *J* = 6.5, 1.4 Hz, 2H), 6.28 (dt, *J* = 15.9, 6.5 Hz, 1H), 6.75 (d, *J* = 15.9 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.45-7.57 (m, 3H), 7.70 (s, 1H), 7.80-7.83 (m, 3H), 7.97 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6, 67.4, 121.9, 123.3, 126.3, 126.4, 127.1, 127.7, 128.1, 128.3, 128.4, 129.6, 133.2, 133.3, 133.4, 135.4, 145.1, 150.4. Spectral data were identical to those reported in literature.

(*E*)-3-(*p*-tolyl)allyl tosylcarbamate 5f:[12] Prepared from **1f** and purified using a cyclohexane/ethyl acetate mixture (65/35, R_f = 0.28). The product

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was isolated as a white solid (83 mg) in 88% yield. Mp = 110-116 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (s, 3H), 2.43 (s, 3H), 4.73 (dd, *J* = 6.6, 1.4 Hz, 2H), 6.11 (dt, *J* = 15.9, 6.6 Hz, 1H), 6.57 (d, *J* = 15.9 Hz, 1H), 7.14 (d, *J* = 7.9 Hz, 2H), 7.23-7.27 (m, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.95 (d, *J* = 8.3 Hz, 2H). Spectral data were identical to those reported in literature.

General procedure for the synthesis of allylic carbamates 7: Alcohol **6** or **8** (1.15 mmol) was dissolved in 2.5 mL of dry toluene in a microwave vial and the mixture was cooled in ice. Trichloroacetyl isocyanate (1.38 mmol) was added dropwise to the stirred solution. Once the reaction was completed at room temperature, the vial was placed in the Anton Paar monowave reactor and the reaction was stirred during the adequate time and temperature (800 W). Solvent was then removed *in vacuo* to obtain a solid which was triturated in isopropyl ether to yield the pure product **7 or 9**.

Methyl (*E*)-3-(4-methoxyphenyl)-2-((((2,2,2-trichloroacetyl) carbamoyl)oxy)methyl)acrylate 7a: Prepared from **6a** (110 °C, 30 min). The product was obtained as a white solid (364 mg) in 77% yield (*E* only). Mp = 168-171 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.87 (d, 3H), 3.88 (d, 3H), 5.23 (s, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 8.03 (s, 1H), 8.43-8.45 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.4, 55.4, 62.3, 91.7, 114.5, 122.5, 126.2, 131.6, 146.8, 149.3, 157.6, 161.2, 167.3. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{14}NO_6Cl_3Na$, 431.9779; found 431.9777.

Methyl (*E*)-3-(4-(benzyloxy)phenyl)-2-((((2,2,2-trichloroacetyl) carbamoyl)oxy)methyl)acrylate 7b: Prepared from **6b** (110 °C, 30 min,). The product was obtained as a white solid (353 mg) in 63% yield (*E*/*Z*: 90/10). Mp = 160-163 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.78 (s, 0.3H), 3.88 (s, 2.7H), 5.09 (s, 0.2H), 5.11 (s, 0.2H), 5.14 (s, 1.8H), 5.23 (s, 1.8H), 7.06 (d, *J* = 8.8 Hz, 2H), 7.35-7.48 (m, 7H), 8.02 (s, 1H), 8.42-8.44 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.0, 52.4, 62.3, 69.3, 70.1, 91.7, 114.6, 115.4, 122.7, 123.7, 126.4, 126.8, 127.4, 127.5, 128.1, 128.2, 128.6, 128.7, 129.0, 131.2, 131.6, 136.3, 142.8, 146.7, 149.3, 157.6, 160.4, 167.3. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{18}NO_6Cl_3Na$, 508.0092; found 508.0097.

Methyl (*E*)-3-(*p*-tolyl)-2-((((2,2,2-trichloroacetyl)carbamoyl)oxy) methyl)acrylate 7c: Prepared from **6c** (140 °C, 60 min). The product was obtained as a white solid (269 mg) in 77% yield (*E* only). Mp = 146-149 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.41 (s, 3H), 3.88 (s, 3H), 5.21 (s, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 8.05 (s, 1H), 8.43-8.46 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4, 52.4, 62.1, 91.7, 124.2, 129.6, 129.7, 130.9, 140.5, 147.0, 149.2, 157.6, 167.1. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{14}NO_5Cl_3Na$, 415.9830; found 415.9834

Methyl (*E*)-3-([1,1'-biphenyl]-4-yl)-2-((((2,2,2-trichloroacetyl) carbamoyl)oxy)methyl)acrylate 7d: Prepared from **6d** (200 °C, 30 min). The product was obtained as a yellow solid (184 mg) in 35% yield (*E*/*Z*: 94/6). Mp = 142-146 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.76 (s, 0.18H), 3.91 (s, 2.82H), 5.26 (s, 2H), 7.38-7.44 (m, 1H), 7.46-7.56 (m, 4H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 8.12 (s, 1H), 8.46-8.49 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.5, 62.1, 91.7, 124.9, 127.1, 127.6, 128.0, 129.0, 130.1, 132.6, 139.9, 142.9, 146.5, 149.2, 157.6, 167.0. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{16}NO_5Cl_3Na$, 477.9986; found 477.9988.

Methyl (*E*)-3-(3,4-dimethoxyphenyl)-2-((((2,2,2-trichloroacetyl) carbamoyl)oxy)methyl)acrylate 7e: Prepared from **6e** (110 °C, 30 min). The product was obtained as a white solid (375 mg) in 74% yield (*E* only). Mp = 134-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.88 (s, 3H), 3.90 (s, 3H), 3.94 (s, 3H), 5.25 (s, 2H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.99 (d, *J* = 2.0 Hz, 1H), 7.08 (dd, *J* = 8.3, 2.0 Hz, 1H), 8.02 (s, 1H), 8.48-8.50 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.4, 55.9, 56.0, 62.4, 91.7, 111.2, 112.5, 122.7, 123.5, 126.4, 147.1, 149.1, 149.4, 150.9, 157.6, 167.2. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{16}NO_7Cl_3Na$, 461.9885; found 461.9885.

Methyl (*E*)-3-(benzo[d][1,3]dioxol-5-yl)-2-((((2,2,2-trichloroacetyl) carbamoyl)oxy)methyl)acrylate 7f: Prepared from **6f** (140 °C, 30 min). The product was obtained as a white solid (303 mg) in 62% yield (*E*/*Z*: 95/5). Mp = 118-122 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.79 (s, 0.15H), 3.88 (s, 2.85H), 5.08 (s, 0.1H), 5.21 (s, 1.9H), 6.02 (s, 0.1H), 6.05 (s, 1.9H), 6.8-7.02 (m, 3H), 7.98 (s, 1H), 8.41-8.43 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.4, 62.1, 91.7, 101.7, 108.8, 109.3, 123.3, 125.1, 127.7, 146.7, 148.3, 149.4, 157.6, 167.1. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{12}NO_7Cl_3Na$, 445.9572; found 445.9576.

Methyl (*E*)-3-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2-((((2,2,2-trichloroacetyl)carbamoyl)oxy)methyl)acrylate 7g: Prepared from **6g** (140 °C, 30 min). The product was obtained as a white solid (308 mg) in 61% yield (*E*/*Z*: 98/2). Mp = 146-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 0.06H), 3.87 (s, 2.94H), 4.31 (d, *J* = 4.5 Hz, 4H), 5.08 (s, 0.04H), 5.22 (s, 1.96H), 6.96 (m, 3H), 7.96 (s, 1H), 8.42-8.44 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.4, 62.1, 64.2, 64.6, 91.7, 117.8, 118.7, 123.2, 123.5, 127.0, 143.7, 145.5, 146.6, 149.3, 157.6, 167.1. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{14}NO_7Cl_3Na$, 459.9728; found 459.9730.

Methyl (*E*)-3-(2,3-dihydrobenzofuran-5-yl)-2-((((2,2,2-trichloroacetyl) carbamoyl)oxy)methyl)acrylate 7h: Prepared from **6h** (80 °C, 30 min). The product was obtained as a white solid (369 mg) in 76% yield (*E* only). Mp = 123-127 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.28 (t, *J* = 8.7 Hz, 2H), 3.88 (s, 3H), 4.67 (t, *J* = 8.7 Hz, 2H), 5.24 (s, 2H), 6.86 (d, *J* = 8.3 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 1H), 7.33 (s, 1H), 8.02 (s, 1H), 8.41-8.43 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.3, 52.3, 62.4, 71.9, 109.9, 121.9, 126.2, 126.6, 128.2, 131.1, 147.2, 149.3, 157.6, 162.1, 167.4. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{14}NO_6Cl_3Na$, 443.9779; found 443.9779.

Methyl (*E*)-3-(3-bromo-4-methoxyphenyl)-2-((((2,2,2-trichloroacetyl) carbamoyl)oxy)methyl)acrylate 7i: Prepared from **6i** (110 °C, 30 min). The product was obtained as a white solid (298 mg) in 53% yield (*E*/*Z*: 88/12). Mp = 142-145 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 0.36H), 3.88 (s, 2.64H), 3.94 (s, 0.36H), 3.96 (s, 2.64H), 5.09 (s, 0.24H), 5.20 (s, 1.76H), 6.88 (d, J = 8.6 Hz, 0.12H), 6.98 (d, *J* = 8.6 Hz, 0.88H), 7.08 (s, 0.12H), 7.28 (s, 0.88H), 7.41 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.65 (d, *J* = 2.1 Hz, 1H), 7.95 (s, 1H), 8.43-8.45 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.5, 56.4, 61.9, 91.7, 112.0, 112.2, 124.2, 127.5, 130.0, 134.9, 145.1, 149.2, 157.3, 157.5, 166.8. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{15}H_{13}NO_6Cl_3BrNa$, 509.8884; found 509.8888.

(*E*)-2-cyano-3-(4-methoxyphenyl)allyl (2,2,2-trichloroacetyl)carbamate 9a: Prepared from **8a** (100 °C, 30 min.). The product was obtained as a white solid (356 mg) in 82% yield (*E* only). Mp = 126-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.89 (s, 3H), 5.00 (s, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 7.30 (s, 1H), 7.84 (d, *J* = 8.8 Hz, 2H), 8.50 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.5, 68.3, 91.5, 100.5, 117.7, 124.9, 131.5, 149.0, 149.3, 157.7, 162.3. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_{11}N_2O_4Cl_3Na$, 398.9677; Found 398.9680.

General procedure for the synthesis of primary allylic carbamates 10: To a solution of carbamate **7** (0.163 mmol) in dichloromethane (2 mL) was added alumina in powder (2 g, 14.7 mmol) and the mixture was stirred for 15 minutes. Afterwards, the reaction mixture was filtered and alumina was washed with ethyl acetate (3 x 25 mL). The filtrate was evaporated *in vacuo* to yield the pure primary carbamate.

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Methyl (*E*)-2-((carbamoyloxy)methyl)-3-(4-methoxyphenyl)acrylate 10a: Prepared from **7a** and obtained as a white solid (36 mg) in 84 % yield (*E* only). Mp = 118-121 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.85 (s, 3H), 3.86 (s, 3H), 4.89-4.91 (br s, 2H), 5.00 (s, 2H), 6.95 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.93 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.2, 55.4, 60.1, 114.3, 124.1, 126.7, 131.6, 145.4, 156.7, 160.9, 167.8. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{15}NO_5Na$, 288.0842; found 288.0840.

Methyl (*E*)-3-(4-(benzyloxy)phenyl)-2-((carbamoyloxy)methylacrylate 10b: Prepared from **7b** and obtained as a white solid (45 mg) in 81% yield (E/Z: 90/10). Mp = 115-120 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.75 (s, 0.3H), 3.86 (s, 2.7H), 4.79 (br s, 2H), 4.90 (s, 0.2H), 5.01 (s, 1.8H), 5.10 (s, 0.2H), 5.12 (s, 1.8H), 6.94-7.05 (m, 2H), 7.35-7.48 (m, 7H), 7.94 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.2, 60.1, 70.1, 115.2, 124.3, 126.9, 127.4, 128.1, 128.7, 131.6, 136.4, 145.3, 156.6, 160.1, 167.7. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{19}NO_5Na$, 364.1155; found 364.1158.

Methyl (*E*)-2-((carbamoyloxy)methyl)-3-(*p*-tolyl)acrylate 10c: Prepared from **7c** and obtained as a white solid (39 mg) in 96% yield (*E* only). Mp = 142-145 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 3H), 3.87 (s, 3H), 4.67-4.69 (br s, 2H), 4.99 (s, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.98 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4, 52.2, 60.0, 125.7, 129.5, 129.7, 131.3, 140.1, 145.6, 156.6, 167.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{15}NO_4Na$, 272.0893; found 272.0891.

Methyl (*E*)-3-([1,1'-biphenyl]-4-yl)-2-((carbamoyloxy)methyl)acrylate 10d: Prepared from **7d** and obtained as a yellow solid (45 mg) in 88% yield. (*E*/*Z*: 96/4). Mp = 150-156 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.76 (s, 0.12H), 3.89 (s, 2.88H), 4.77-4.80 (br s, 2H), 5.04 (s, 2H), 7.36-7.57 (m, 5H), 7.61-7.73 (m, 4H), 8.03 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.3, 60.0, 126.5, 127.1, 127.4, 127.9, 128.9, 130.2, 133.0, 140.1, 142.5, 145.1, 156.4, 167.5. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{17}NO_4Na$, 334.1050; found 334.1052.

Methyl (*E*)-2-((carbamoyloxy)methyl)-3-(3,4-dimethoxyphenyl) acrylate 10e: Prepared from **7e** and obtained as a white solid (42 mg) in 88% yield (*E* only). Mp = 167-170 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.87 (s, 3H), 3.92 (s, 3H), 3.94 (s, 3H), 4.67-4.69 (br s, 2H), 5.04 (s, 2H), 6.93 (d, *J* = 8.2 Hz, 1H), 7.02-7.12 (m, 2H), 7.95 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.2, 55.8, 55.9, 60.3, 111.1, 112.4, 123.9, 124.1, 126.9, 145.7, 149.0, 150.6, 156.5, 167.7. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_{17}NO_6Na$, 318.0948; found 318.0946.

Methyl (*E*)-3-(benzo[d][1,3]dioxol-5-yl)-2-((carbamoyloxy) methyl)acrylate 10f: Prepared from **7f** and obtained as a white solid (42 mg) in 92% yield (E/Z: 97/3). Mp = 138-140 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.76 (s, 0.09H), 3.85 (s, 2.91H), 4.81-4.83 (br s, 2H), 4.87 (s, 0.06H), 4.98 (s, 1.94H), 6.03 (s, 2H), 6.84-6.89 (m, 1H), 6.96-6.98 (m, 2H), 7.89 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.3, 60.0, 101.5, 108.6, 109.4, 124.8, 125.1, 128.1, 145.4, 148.1, 149.0, 156.5, 167.6. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{13}NO_6Na$, 302.0635; found 302.0636.

Methyl (*E*)-2-((carbamoyloxy)methyl)-3-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)acrylate 10g: Prepared from **7g** and obtained as a white solid (43 mg) in 89% yield (E/Z: 97/3). Mp = 154-159 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.86 (s, 0.09H), 3.88 (s, 2.91H), 4.26-4.37 (m, 4H), 4.64-4.66 (br s, 2H), 4.89 (s, 0.06H), 5.00 (s, 1.94H), 6.88-7.04 (m, 3H), 7.88 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 52.2, 60.0, 64.2, 64.5, 117.6, 118.8, 123.7, 124.8, 127.5, 143.5, 145.2, 145.3, 156.5, 167.7. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_{15}NO_6Na$, 316.0792; found 316.0793.

Methyl (*E*)-2-((carbamoyloxy)methyl)-3-(2,3-dihydrobenzofuran-5-yl)acrylate 10h: Prepared from **7h** and obtained as a white solid (36 mg) in 79% yield (*E* only). Mp = 136-138 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.25 (t, *J* = 8.7 Hz, 2H), 3.85 (s, 3H), 4.64 (t, *J* = 8.7 Hz, 2H), 4.82 (br s, 2H), 5.01 (s, 2H), 6.83 (d, *J* = 8.3 Hz, 1H), 7.25 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.32 (d, *J* = 1.8 Hz, 1H), 7.93 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.4, 52.2, 60.2, 71.8, 109.7, 123.5, 126.6, 126.7, 127.9, 131.1, 145.9, 156.6, 161.8, 167.9. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_{15}NO_5Na$, 300.0842; found 300.0844.

Methyl (*E*)-3-(3-bromo-4-methoxyphenyl)-2-((carbamoyloxy)methyl)acrylate 10i: Prepared from **7i** and obtained as a white solid (54 mg) in 96% yield (*E*/*Z*: 88/12). Mp = 140-144 °C.^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.75 (s, 0.36H), 3.85 (s, 2.64H), 3. 92 (s, 0.36H), 3.95 (s, 2.64H), 4.86-4.89 (br s, 2H), 4.97 (s, 2H), 6.84-6.96 (m, 1H), 7.40 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.66 (d, *J* = 2.2 Hz, 1H), 7.85 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.9, 52.3, 56.3, 59.8, 60.4, 111.2, 111.8, 112.0, 125.6, 127.4, 127.9, 128.4, 129.6, 130.2, 134.0, 134.9, 137.6, 143.8, 156.4, 157.0, 167.4. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{14}NO_5BrNa$, 365.9947; found 365.9947.

General procedure for the synthesis of 5-arylidene-1,3-oxazinane-2,4-dione 11: To a solution of carbamate **10** (0.43 mmol) in acetonitrile (3 mL) was added solid potassium carbonate (0.645 mmol, 1.5 eq). The mixture was stirred at 50 °C for 4-7 days to form the corresponding oxazinane-2,4-dione that precipitated in the medium. After the reaction was completed (NMR monitoring), the solid was filtered and washed successively with hot acetonitrile (3 mL) and 3 mL of HCl solution 0.1N and finally dried to yield the pure product.

(*E*)-5-(4-methoxybenzylidene)-1,3-oxazinane-2,4-dione 11a: Prepared from **10a** (4 days) and obtained as a white solid (78 mg) in 78% yield (*E* only). Mp = 230-233 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.82 (s, 3H), 5.33 (d, *J* = 1.9 Hz, 2H), 7.05 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.69 (s, 1H), 11.10-11.12 (br s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6,): δ = 55.8, 65.6, 114.8, 121.2, 126.5, 132.7, 137.0, 152.2, 160.9, 165.4. IR (neat, cm^{-1}): 3170, 3051, 2865, 1740, 1694, 1590, 1564, 1513, 1413, 1372, 1260, 1246, 1210, 1177, 1019, 831, 801, 533, 519, 508, 425. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{11}NO_4Na$, 256.0580; found 256.0582.

(*E*)-5-(4-(benzyloxy)benzylidene)-1,3-oxazinane-2,4-dione 11b: Prepared from **10b** (5 days) and obtained as a white solid (98 mg) in 74% yield (*E* only). Mp = 179-181 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 5.19 (s, 2H), 5.32 (d, *J* = 1.3 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.31-7.52 (m, 7H), 7.68 (s, 1H), 11.10-11.12 (br s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 64.1, 68.1, 113.9, 118.5, 124.7, 126.5, 126.7, 127.2, 131.2, 135.3, 136.4, 149.2, 158.5, 162.5. IR (neat, cm^{-1}): 3199, 3104, 2740, 1741, 1708, 1598, 1512, 1417, 1360, 1248, 1205, 1180, 1026, 838, 733, 695, 540, 517, 424. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{15}NO_4Na$, 332.0893; found 332.0893.

(*E*)-5-(4-methylbenzylidene)-1,3-oxazinane-2,4-dione 11c: Prepared from **10c** (7 days) and obtained as a white solid (54 mg) in 58% yield (*E* only). Mp = 230-233 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.36 (s, 3H), 5.31 (d, *J* = 2.0 Hz, 2H), 7.28-7.35 (m, 4H), 7.68-7.71 (m, 1H), 11.14-11.20 (br s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ = 21.5, 65.7, 121.9, 129.9, 130.9, 138.3, 140.5, 151.0, 164.3. IR (neat, cm^{-1}): 3191, 3100, 2857, 1728, 1702, 1619, 1605, 1410, 1357, 1246, 1207, 1184, 1069, 819, 525, 507, 490, 430, 418. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{11}NO_3Na$, 240.0631; found 240.0632.

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(*E*)-5-([1,1'-biphenyl]-4-ylmethylene)-1,3-oxazinane-2,4-dione 11d: Prepared from **10d** (5 days) and obtained as a white solid (65 mg) in 54% yield (*E* only). Mp = 196-199 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 5.36 (d, *J* = 1.6 Hz, 2H), 7.38-7.55 (m, 5H), 7.72-7.82 (m, 5H), 10.6-11.7 (br s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6, δ ppm): 65.7, 123.4, 127.2, 127.4, 128.5, 129.5, 131.5, 133.0, 137.2, 139.5, 141.7, 151.6, 164.7. IR (neat, cm-1): 3160, 3097, 2820, 1736, 1698, 1619, 1408, 1364, 1245, 1189, 837, 764, 689, 655, 541, 429. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{13}NO_3Na$, 302.0788; found 302.0790.

(*E*)-5-(3,4-dimethoxybenzylidene)-1,3-oxazinane-2,4-dione 11e: Prepared from **10e** (5 days) and obtained as a white solid (57 mg) in 50% yield (*E* only). Mp = 175-178 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.80 (s, 3H), 3.82 (s, 3H), 5.35 (d, *J* = 1.9 Hz, 2H), 6.93-7.10 (m, 3H), 7.68 (s, 1H), 11.15-11.19 (br s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ = 56.0, 56.1, 65.8, 112.1, 114.4, 120.7, 124.4, 126.5, 138.2, 149.1, 150.8, 151.4, 164.7. IR (neat, cm^{-1}): 3150, 3075, 2862, 1774, 1695, 1612, 1593, 1515, 1411, 1378, 1271, 1227, 1165, 1156, 1018, 934, 862, 806, 754, 613, 537, 529, 481, 425. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{13}NO_5Na$, 286.0686; found 286.0687.

(*E*)-5-(benzo[d][1,3]dioxol-5-ylmethylene)-1,3-oxazinane-2,4-dione 11f: Prepared from **10f** (7 days) and obtained as a white solid (52 mg) in 49% yield (*E* only). Mp = 222-225 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 5.32 (d, *J* = 1.9 Hz, 2H), 6.11 (s, 2H), 6.93-7.08 (m, 3H), 7.65 (s, 1H), 11.11-11.15 (br s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 65.8, 102.2, 109.2, 110.5, 120.7, 127.7, 138.5, 148.3, 149.4, 150.8, 164.1. IR (neat, cm^{-1}): 3152, 3087, 2856, 1754, 1690, 1596, 1500, 1455, 1390, 1365, 1236, 1076, 1025, 921, 861, 831, 815, 755, 608, 516, 496, 445, 425. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_9NO_5Na$, 270.0373; found 270.0375.

(*E*)-5-((2,3-dihydrobenzo[b][1,4]dioxin-6-yl)methylene)-1,3-oxazinane-2,4-dione 11g: Prepared from **10g** (5 days) and obtained as a white solid (44 mg) in 39% yield (*E* only). Mp = 213-217 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.27-4.31 (m, 4H), 5.27 (d, *J* = 2.1 Hz, 2H), 6.88-7.00 (m, 3H), 7.58-7.60 (br s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ = 64.4, 64.8, 65.7, 117.9, 119.6, 121.3, 124.6, 127.1, 137.5, 143.8, 145.6, 151.6, 164.8. IR (neat, cm^{-1}): 3086, 2870, 1740, 1693, 1604, 1575, 1516, 1409, 1359, 1290, 1263, 1239, 1218, 1064, 814, 612, 546, 490, 423. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{11}NO_5Na$, 284.0529; found 284.0530.

(*E*)-5-((2,3-dihydrobenzofuran-5-yl)methylene)-1,3-oxazinane-2,4-dione 11h: Prepared from **10h** (5 days) and obtained as a white solid (69 mg) in 65% yield (*E* only). Mp = 197-200 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.23 (t, *J* = 8.7 Hz, 2H), 4.61 (t, *J* = 8.7 Hz, 2H), 5.31 (d, *J* = 1.9 Hz, 2H), 6.87 (d, *J* = 8.3 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 7.33 (s, 1H), 7.66 (s, 1H), 11.02-11.25 (br s, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 29.1, 65.9, 72.2, 109.8, 119.6, 126.3, 128.0, 129.0, 132.3, 138.7, 151.1, 161.9, 164.4. IR (neat, cm^{-1}): 3071, 2865, 1736, 1692, 1574, 1493, 1412, 1362, 1324, 1232, 1203, 1104, 1076, 942, 819, 600, 572, 494, 421. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_{11}NO_4Na$, 268.0580; found 268.0581.

(*E*)-5-(3-bromo-4-methoxybenzylidene)-1,3-oxazinane-2,4-dione 11i: Prepared from **10i** (5 days) and obtained as a white solid (87 mg) in 65% yield (*E* only). Mp = 225-228 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.91 (s, 3H), 5.25-5.27 (m, 2H), 7.20 (d, *J* = 8.6 Hz, 1H), 7.41 (d, *J* = 8.6 Hz, 1H), 7.60 (s, 1H), 7.68-7.70 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6): δ = 57.0, 65.6, 111.5, 113.2, 122.1, 127.8, 131.9, 135.3, 136.3, 151.4, 156.9, 164.5. IR (neat, cm^{-1}): 3207, 3107, 1734, 1694, 1590, 1499, 1403, 1378, 1351, 1290, 1247, 1200, 1192, 1051, 1008, 937, 814, 803, 563, 555, 474, 423. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{12}H_{10}NO_4BrNa$, 333.9685; found 333.9688.

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Conflict of interest

The authors declare no conflict of interest

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[16] The difference of overall yield with that obtained under conventional heating can be explained, inter alia, by a faster reaction under microwave conditions causing less formation of side-products. We have not been able to determine the structure of these side-products.

[17] When the rearrangement was performed at 140 °C for 30 minutes under conventional heating (toluene, sealed microwave reactor), a low conversion rate was observed (25%).

[18] When the carbamoylation/rearrangement sequence is directly performed under microwave conditions at 110 °C for 30 minutes, some impurities are generated making difficult the purification of **7a**. For further work, the two-stage process (room temperature followed by heating) was preferred.

[19] CCDC 2074213 contains the supplementary crystallographic data for compound **7a**.

[20] In this case, the reaction can be also performed by heating the reaction mixture just after addition of TCA-NCO with a similar yield.

[21] CCDC 2074212 contains the supplementary crystallographic data for compound **9a**.

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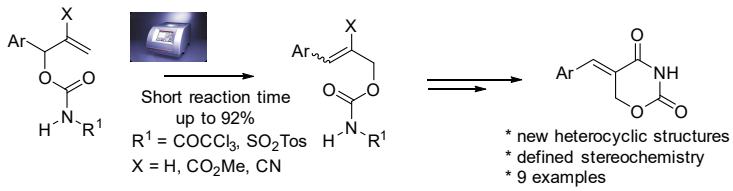
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The acceleration of 1,3-dioxa-[3,3]-sigmatropic rearrangement of aryl allylic carbamates under microwave irradiation was described. The implementation of these unconventional thermal conditions allowed the development of an original synthetic route to new heterocycle products such as (*E*)-5-arylidene-1,3-oxaninane-2,4-diones.

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