Selective Hydrofunctionalization of N-Allenyl Derivatives with Heteronucleophiles Catalyzed by Brønsted Acids

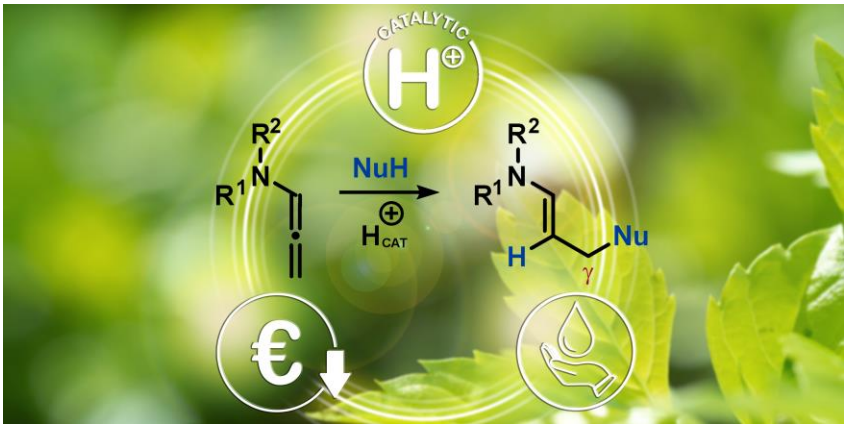
A Selective Hydrofunctionalization of *N*-Allenyl Derivatives with Heteronucleophiles Catalyzed by Brønsted Acids

Arianna Quintavalla[a,b*], Davide Carboni[a,b], Alessandro Brusa[a], and Marco Lombardo[a,b*]

[a] Alma Mater Studiorum - University of Bologna, Department of Chemistry "G. Ciamician", Via P. Gobetti 85, 40129 Bologna, Italy.

[b] Alma Mater Studiorum - University of Bologna, Center for Chemical Catalysis - C3, Via P. Gobetti 85, 40129 Bologna, Italy.

* Email: arianna.quintavalla@unibo.it; marco.lombardo@unibo.it



Abstract. In this study, we present a novel and environmentally sustainable protocol for the γ-hydrofunctionalization of *N*-allenyl compounds using various heteronucleophiles, catalyzed solely by simple Brønsted acids. The method displays remarkable attributes, highlighting its sustainability, efficiency, regio- and stereoselectivity, as well as its versatile applicability to diverse heteroatom-containing enamides. Notably, our approach eliminates the need for metal catalysts and toxic solvents, representing a significant advancement in greener chemistry practices. We demonstrate the broad scope of our protocol by successfully scaling up reactions to gram-scale syntheses, underscoring its robustness for potential industrial implementation. The resulting γ-heterosubstituted enamides offer new possibilities for further synthetic transformations, yielding highly functionalized compounds with diverse applications. Mechanistic investigations reveal the pivotal role of CSA as a catalyst, enabling alcohol addition *via* a covalent activation mode.

Introduction

Enamides and enamines are stable, highly polarized compounds characterized by an electron-rich π-system and are extensively used in synthetic chemistry.[1] These moieties play a crucial role in medicinal chemistry, being widely present in pharmacologically relevant natural and synthetic products.[2] In particular, γ-oxygenated enamines and enamides are often found as structural elements in the scaffold of bioactive compounds (Figure 1),[3] and they also serve as intermediates in the preparation of hepatitis C virus inhibitors,[4] fungicides,[5] 4-hydroxyisoleucine and analogues for diabetes treatment,[6] among others. Furthermore, γ-oxygenated enamines and enamides, bearing a leaving group in the allylic position, are universally recognized as valuable substrates for allylic substitution reactions.[7]

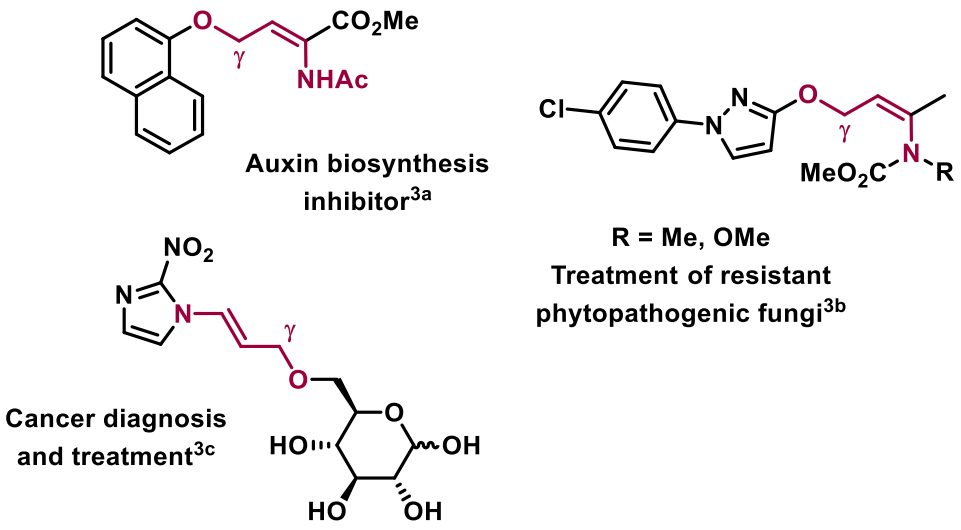
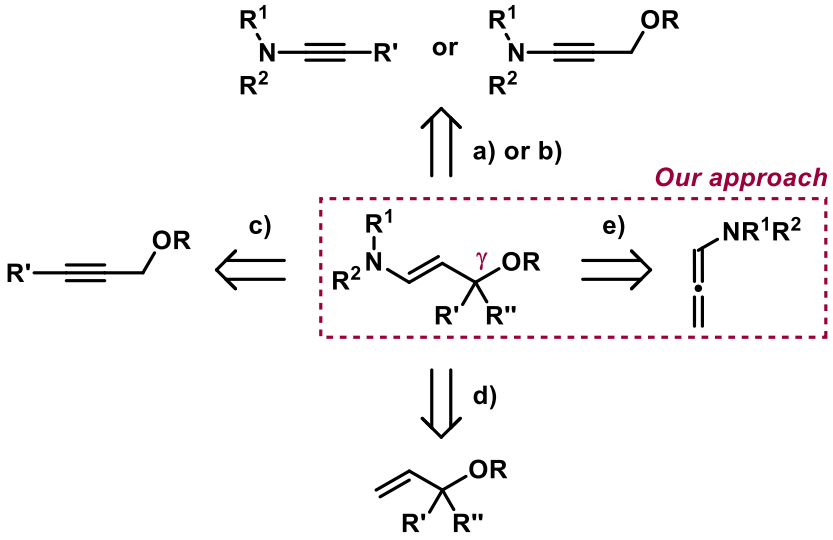


Figure 1. Examples of bioactive γ-oxygenated enamines and enamides.

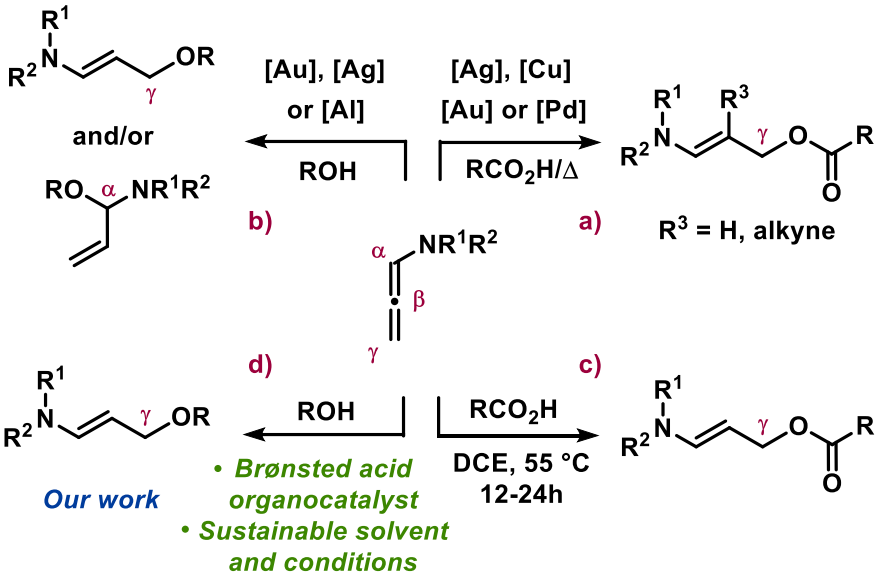
For these reasons, various synthetic approaches have been proposed for constructing these γ-oxygenated compounds. Among them, the most notable ones start from ynamides (**a** and **b**, Scheme 1),[8] alkynes (**c**),[9] oxygenated terminal alkenes (**d**),[10] or *N*-allenyl derivatives (**e**).[11] The use of *N*-

substituted allenes in organic synthesis has recently experienced a substantial growth due to their peculiar reactivity and their usefulness and versatility in incorporating nitrogen functionalities into structurally different scaffolds.[12]



Scheme 1. Synthetic approaches to γ-oxygenated enamides.

However, only a limited number of protocols use oxygen-nucleophiles with *N*-allenyl substrates[13] and many of them employ carboxylic acids as nucleophiles[11g] and metal-based catalysts (Scheme 2a).[11c-d,11f] A few methods focus on the addition of alcohols[11e,14] and they invariably rely on metal-catalysis[11b,15] and/or preferential α-functionalization, generating *N*,*O*-acetals[13,16] (Scheme 2b).

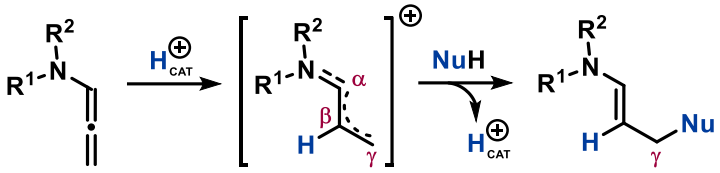


Scheme 2. Prior art and our proposal.

Despite the remarkable results, the current state of the art for synthesizing γ-oxygenated enamines or enamides from *N*-substituted allenes has one or more of the following limitations: i) the catalysts are based on expensive metals, often used in high loading; ii) the nucleophile is the solvent or is used in large excess; iii) the solvents are not sustainable, according to the accepted solvent sustainability guides and the green chemistry principles;[17] iv) limited scope, being applicable to a structurally restricted subset of substrates; v) additional reagents or ligands are required (poor atom economy); vi) elevated temperatures and long reaction times are required, which are unsuitable for sensitive or highly functionalized reagents; vii) poor regioselectivity or heavily dependent on the specific substrate. On this basis, an efficient, sustainable and widely applicable protocol for the synthesis of γ-oxygenated enamides is highly desirable.

As part of our ongoing research interests in the reactivity of alkenyl-systems[18] and, in particular, of *N*-allenyl substrates,[18d] we focused our efforts to the development of an effective, simple, inexpensive and sustainable synthetic approach to γ-oxygenated enamides starting from *N*-substituted allenes and alcohols (Scheme 2d). Aiming to avoid the use of metal-based catalysts, we envisaged that a Brønsted

acid could mimic the activation ability of some metal complexes, exploiting the electron-rich nature of the allenamides[12a] (Scheme 3).



Scheme 3. Proposed Brønsted acid activation and nucleophilic addition.

The reactivity of *N*-allenyl compounds in the presence of Brønsted acids has been reported,[12b,19] but it is limited to a few examples describing almost only the construction of C−C bonds. Only very recently two publications reported on the organocatalyzed C−O bond formation, but still with remarkable limitations. The method proposed by Cheong and Park (Scheme 2c)[20a] was limited to carboxylic acids as nucleophiles (already extensively developed) and the process sustainability was undermined by the use of a hazardous chlorinated solvent (DCE).[21a] On the other hand, Yang described the asymmetric synthesis of macrocycles promoted by chiral phosphoric acids through intramolecular alcohol addition.[20b] However, the protocol was restricted to specially synthesized substrates, the yields were low, the reaction medium was highly toxic (CCl_4),[21b] and the authors did not develop an intermolecular version of their process.

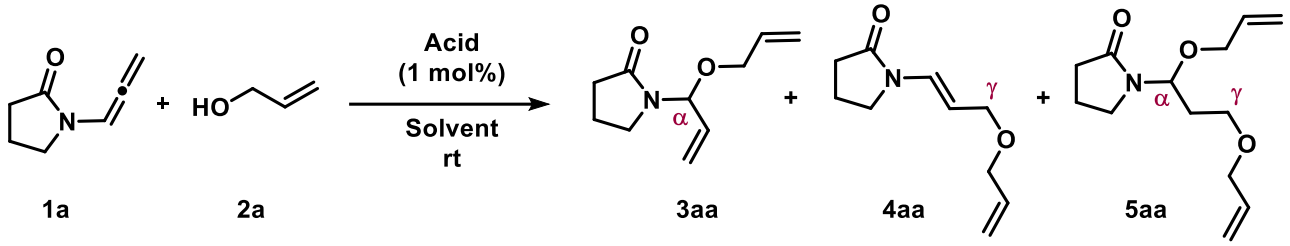
Therefore, our objective focused on the development of an efficient and sustainable Brønsted acid-promoted protocol applicable to intermolecular addition of alcohols (Scheme 2d) and extendable to other heteronucleophiles.

Results and Discussion

To assess the viability of our approach, we started using 3-(propa-1,2-dien-1-yl)pyrrolidin-2-one **1a** and allyl alcohol **2a** as model substrates. The reaction was conducted at room temperature in

dichloromethane as solvent, in the presence of a catalytic amount of (1*S*)-(+)-10-camphorsulfonic acid (CSA) as Brønsted acid (Table 1).

Table 1. Optimization of the reaction conditions.[a]



Entry	**2a** (mmol)	Acid	Solvent	Time (h)	Conversion (%)[b]	Yield (%)[b] **3aa**	**4aa**	**5aa**
1	5	CSA	DCM	0.5	88	8	71	6
2	2.5	CSA	DCM	1	88	traces	55	traces
3	1.2	CSA	DCM	3	94	6	72	traces
4	1.2	CSA	MeCN	3	>95	traces	30	10
5	1.2	CSA	*t*BuOAc	2	70	25	15	-
6	1.2	CSA	*t*BuOMe	2	75	15	<5	-
7	1.2	CSA	CPME	2	40	38	<5	-
8	1.2	CSA	PhOMe	2	98	5	70	10
9	1.2	*p*TSA	PhOMe	2	>95	4	70	13
10	1.2	MsOH	PhOMe	2	>95	-	50	13
11	1.2	TfOH	PhOMe	2	97	-	30	6
12	1.2	Tf_2NH	PhOMe	2	90	-	55	-
13	1.2	TFA	PhOMe	2	66	28	-	-

[a] Reaction conditions: **1a** (0.1 mmol), **2a**, acid (1 mol%, stock solution 0.025 M in the reaction solvent), solvent (0.2 M), rt. [b] Conversion and products yield determined by ^{1}H-NMR analysis of the crude using methyl acetoacetate as internal standard. eq. = equivalents, DCM = dichloromethane, CSA = (1*S*)-(+)-10-camphorsulfonic acid, CPME = cyclopentyl methylether, *p*TSA = *p*-toluenesulfonic acid hydrate, MsOH = methanesulfonic acid, TfOH = trifluoromethanesulfonic acid, TFA = trifluoroacetic acid, Tf_2NH = bis(trifluoromethane)sulfonimide.

In the presence of only 1 mol% catalyst and an excess of alcohol **2a** (5 eq.), the reaction proceeded rapidly (0.5 h), yielding three different products (α-adduct **3aa**, γ-adduct **4aa**, and α,γ-adduct **5aa**), with the γ-adduct **4aa** being predominantly formed (71%, entry 1). This result not only demonstrated the feasibility of the intermolecular hydroalkoxylation of allenamides solely promoted by Brønsted acids, but also highlighted its good performance and γ-product selectivity. Furthermore, the desired enamide **4aa** was exclusively generated as the *E*-isomer. On this basis, we focused on the process sustainability by reducing the alcohol amount to 1.2 equivalents (entries 2-3). As expected, the reaction rate decreased; however, complete conversion was achieved within three hours, affording a good yield of the desired γ-adduct **4aa** (72%, entry 3).

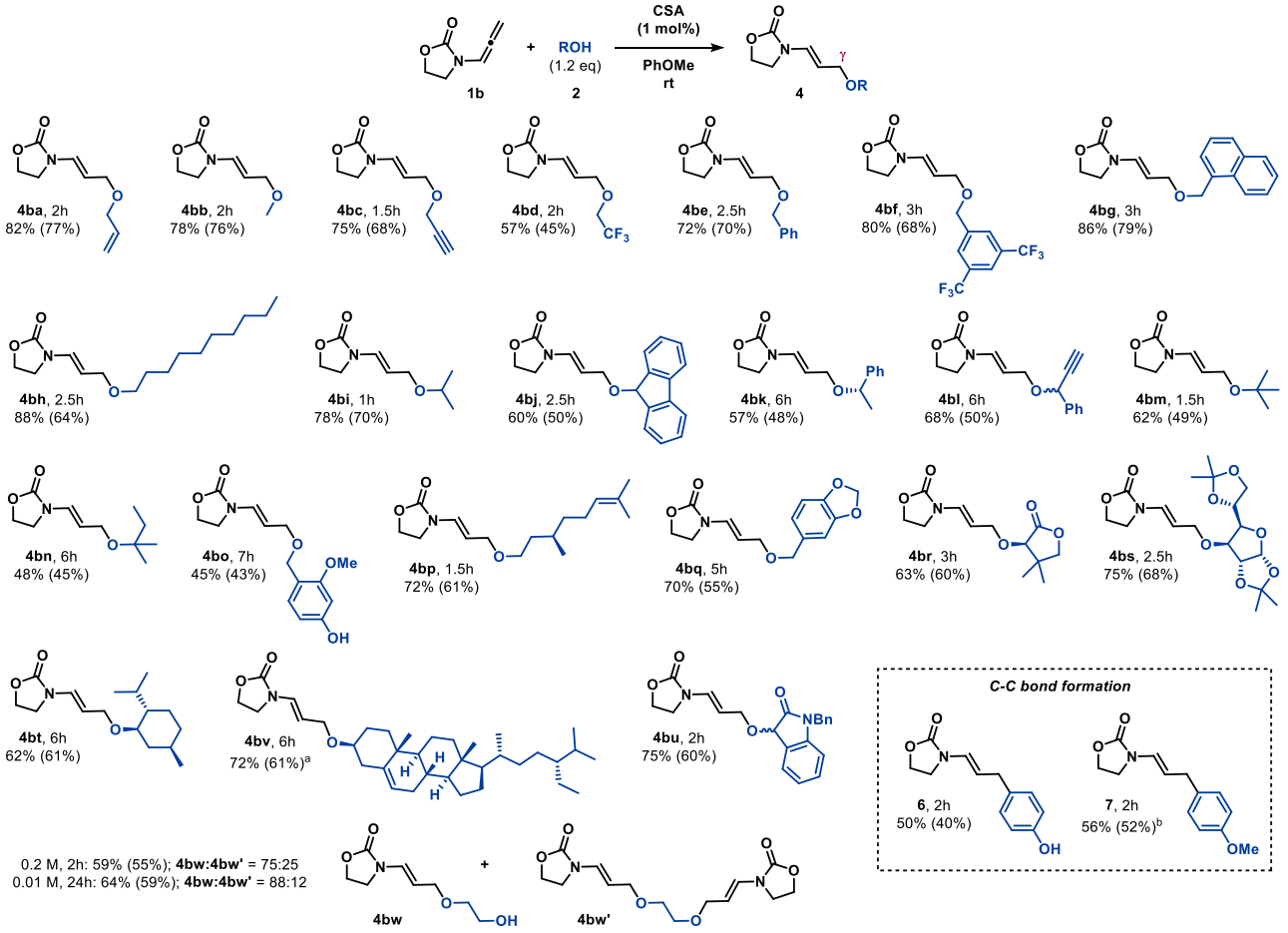
Since solvents represent the main source of waste produced in industrial chemical processes and, based on their hazardous nature and toxicity, they significantly impact on process safety,[22a-b] we carried out a screening of different solvents to identify a more environmentally friendly reaction medium compared to DCM. Results obtained with the most sustainable solvents are summarized in Table 1 (entries 4-8; for the full solvents screening see Supporting Information). While allenamide conversion was high in many cases, MeCN and *t*BuOAc yielded low amounts of **4aa** (entries 4-5), whereas *t*BuOMe and CPME provided **3aa** as the major product, although in low yields (entries 6-7). We noticed that, in solvents where the allene conversion was lower, the main product was **3aa**. This evidence suggests that these solvents slow down the alcohol addition and, consequently, the possible interconversion between the products.[22c] Conversely, anisole allowed a remarkable yield of enamide **4aa**, and the reaction proceeded even faster than in DCM (entry 8 *vs* 3). Anisole is a starting material for chemical transformations in the pharmaceutical industry and it finds a wide range of different applications, including the synthesis of intermediates or products (e.g. cosmetics and fragrances), the use as a flavoring agent in food additives, and as a solvent for chemical reactions and electronics.[23] In particular, anisole as reaction medium shows an optimal sustainability rank in recent solvent selection guidelines,[17] being low-cost, non-toxic and biodegradable. Although its actual

production is based on petrochemicals, it can also be derived from renewable sources such as lignin and guaiacol.[24] Therefore, anisole is an excellent alternative to traditional fossil fuel-derived solvents.[25]

Once we identified the best sustainable medium for our transformation, the efficacy of various catalytic Brønsted acids was investigated (entries 9-13, Table 1). *p*-TSA (entry 9) provided results comparable to CSA, while MsOH, TfOH and Tf_2NH afforded **4aa** with significantly lower yields (entries 10-12). TFA gave poor allene conversion, affording the α-adduct **3aa** as the only product (entry 13). A similar behaviour was observed for HCl (for the complete acids screening see Supporting Information). Phosphoric acids gave mixtures of **3aa** and **4aa** in low yields, while weaker acids as acetic or benzoic acid were unable to promote the alcohol addition. To optimize the process sustainability, particularly focusing on process safety for potential large-scale applications, we selected CSA as the preferred catalyst, due to its non-toxic nature.[26]

Once we found the most suitable reaction conditions, we examined the applicability of the developed sustainable protocol to different alcohols **2** (Scheme 4). Given the convenient synthesis of the 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b**, we investigated the alcohols scope with this substrate possessing a behavior analogous to **1a** (see product **4ba**, Scheme 4).

We were pleased to observe a very broad alcohols scope. Variably substituted primary alcohols, both aliphatic and aromatic, provided good results (**4ba**-**4bh**). Notably, secondary (**4bi**-**4bl**) and tertiary (**4bm**-**4bn**) alcohols also displayed a good reactivity. It is noteworthy that only a limited number of procedures allow the addition of hindered alcohols to allenamides, resulting in low yields or poor product selectivity.[11e,16,27] Prompted by these achievements, structurally more complex natural product- or drug-like alcohols were used, such as vanillol (**4bo**), citronellol (**4bp**), piperonyl alcohol (**4bq**), *D*-(−)-pantolactone (**4br**), *D*-glucose diacetonide (**4bs**), (−)-menthol (**4bt**), isatin-derived alcohol (**4bu**), and stigmasterol (**4bv**).

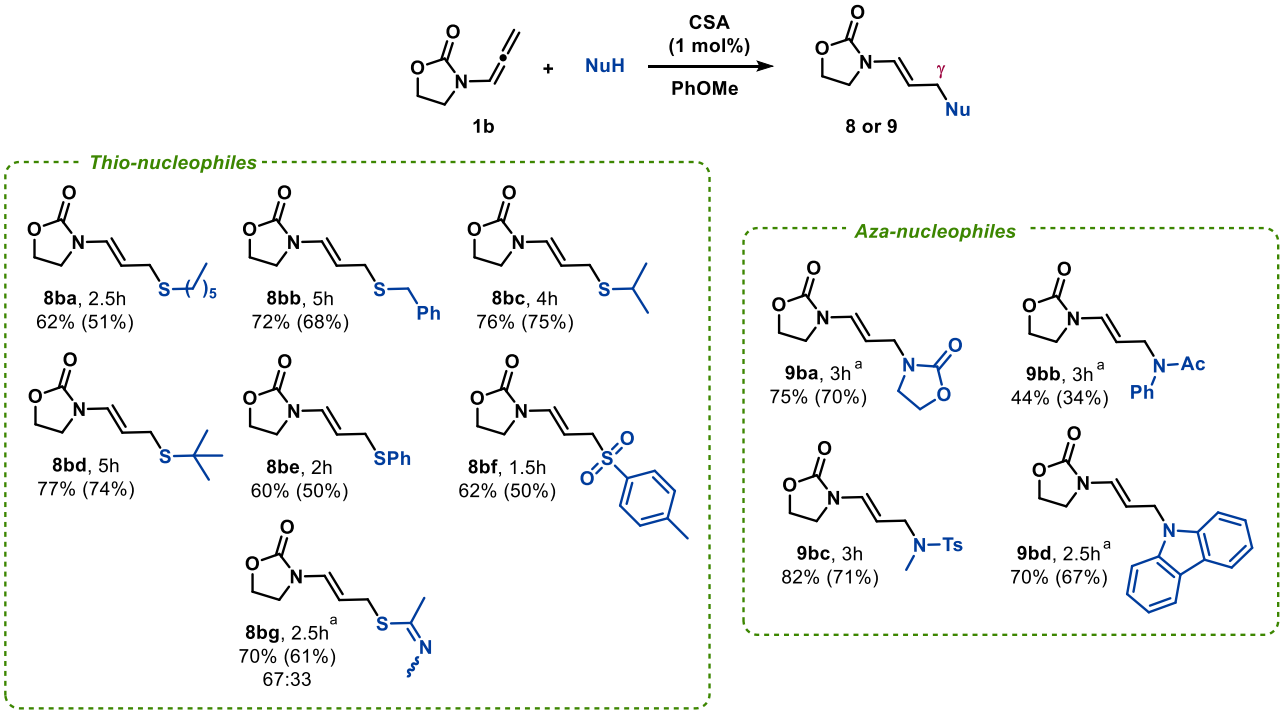


Scheme 4. Reaction conditions: **1b** (0.1 mmol), CSA (1 mol%, stock solution 0.025 M in PhOMe), PhOMe (0.2 M). Yields determined by ^{1}H-NMR analysis of the crude using methyl acetoacetate as internal standard. Yields after purification in parentheses. [a] 1 eq. of HFIP added to improve the alcohol solubility. [b] 1.2 equivalents of HFIP were present in the reaction mixture.

Good performances were obtained in all cases, with excellent functional group tolerance, regio- and stereoselectivity. We also tested ethylene glycol aiming to evaluate the possible formation of the corresponding cyclic *N,O*-acetal. However, we only isolated mixtures of two enamides: the expected **4bw** as the major product, and **4bw'** derived from the glycol addition to two allenamide units. Investigating the structural diversity of alcohols, we observed that phenol took part in a Friedel-Crafts-type addition, generating a C-C bond and providing compound **6** (Scheme 4). Conversely, HFIP (1,1,1,3,3,3-hexafluoro-2-propanol) was unable to add to allenamide **1b**. In this case, we

isolated compound **7** in a significant yield, deriving from a Friedel-Crafts addition of the solvent anisole. According to Mayr's database of reactivity parameters[28] and pKa values,[29] we supposed that the poor nucleophilicity of HFIP prevents its addition under our reaction conditions. However, it evidently played a role in promoting the reactivity of anisole, which was much lower in the absence of HFIP (see Supporting Information). We attributed this result to the ionizing ability of HFIP which strongly affects the processes generating positively charged intermediates, such as electrophilic aromatic substitutions.[30a] The cooperation between the Brønsted acid catalyst and the HFIP hydrogen-bond clusters could significantly affect the reaction outcome.[30b] Furthermore, HFIP is characterized by a certain acidity (pK_a ~ 17.9 in DMSO,[29a] pK_a ~ 9.3 in water[29b]). While the formation of C-C bonds was not a primary objective of our study, it is worth noting that only one example is reported in the literature describing the γ-addition of anisole to allenamides.[31] This protocol is limited to allenyl-*N*-sulfonamides and its sustainability is penalized by the use of boronic acids, a Pd-based catalyst, and 1,4-dioxane as solvent. In all other protocols, anisole results unreactive, since much more electron-rich compounds must be used to ensure an acceptable reactivity.[32]

Based on the remarkable results obtained with alcohols, we extended our sustainable metal-free protocol to different hetero-nucleophiles and, in particular, we tested some sulfur- and nitrogen-based substrates (Scheme 5).

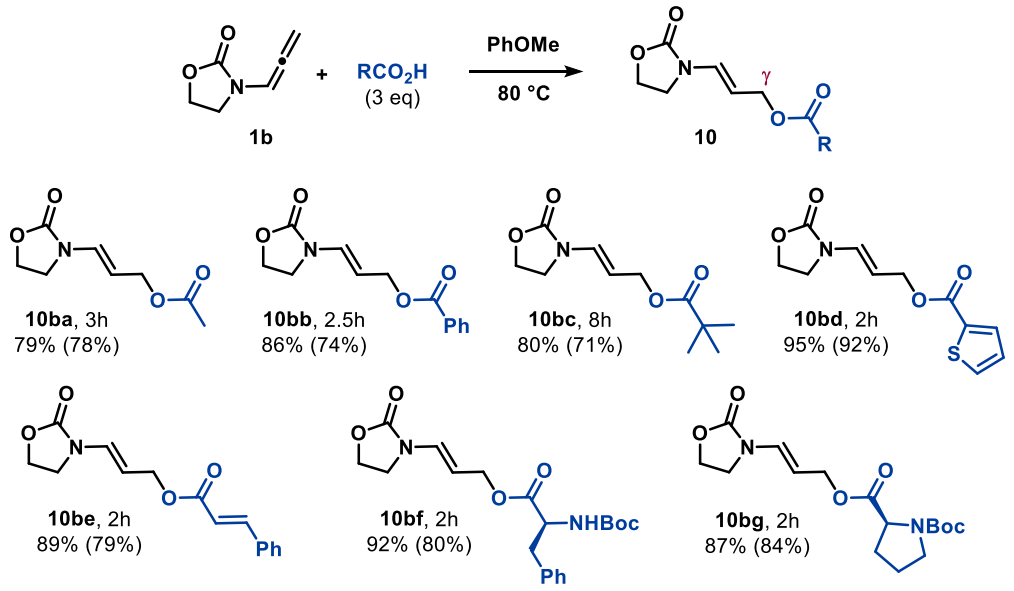


Scheme 5. Reaction conditions: **1b** (0.1 mmol), NuH (1.2 eq.), CSA (1 mol%, stock solution 0.025 M in PhOMe), PhOMe (0.2 M), rt. Yields determined by ^{1}H-NMR analysis of the crude using methyl acetoacetate as internal standard. Yields after purification in parentheses. [a] 80 °C. Ac = acetyl, Ts = tosyl.

We were pleased to observe good results with primary, secondary and tertiary aliphatic thiols (**8ba-8bd**) as well as with toluensulfinic acid (**8bf**), all yielding the corresponding γ-sulfur-substituted enamides at room temperature. These results are particularly noteworthy, since the addition of thiols to allenamides is rarely described in the literature and the reported methods lead to structurally different products[33] or require metal-catalysis[34] or stoichiometric TFA addition.[19c] It is interesting to note that thiophenol acts as thio-nucleophile selectively yielding the corresponding γ-sulfur enamide **8be**, contrary to phenol which takes part in a Friedel-Crafts-type reaction (Scheme 4). Additionally, we demonstrated that thioamides, which are remarkable scaffolds in medicinal chemistry,[35] can be successfully employed as nucleophiles, with the addition taking place at the sulfur atom and providing a mixture of the two stereoisomers (**8bg**).

Concerning the nitrogen-based nucleophiles, sulphonamides, carbamates and amides provided the corresponding γ-functionalized enamides in this order of reactivity, reflecting the nucleophilicity of the species. Specifically, the sulphonamide product **9bc** was obtained at room temperature, while both the carbamate- (**9ba**) and the amide- (**9bb**) derivatives required heating. In general, with less reactive nucleophiles (thioamide, carbamate and amide, Scheme 5) a higher temperature was necessary to push the nucleophilic addition, but especially to obtain the desired γ-adducts from the initially formed α-adducts, being the products interconversion particularly slow (see the mechanistic studies below). It is worth noting that our protocol represents the first example of a metal-free, Brønsted acid-catalysed intermolecular addition of *amide*-type substrates to allenamides. Indeed, all the previously reported methods are not catalytic, or require metal-catalysts and/or focused on the addition of amines or heteroaromatics.[32a,36] Finally, carbazole was successfully added to an allenamide, yielding for the first time the corresponding product **9bd** in the absence of metal catalysis.[37]

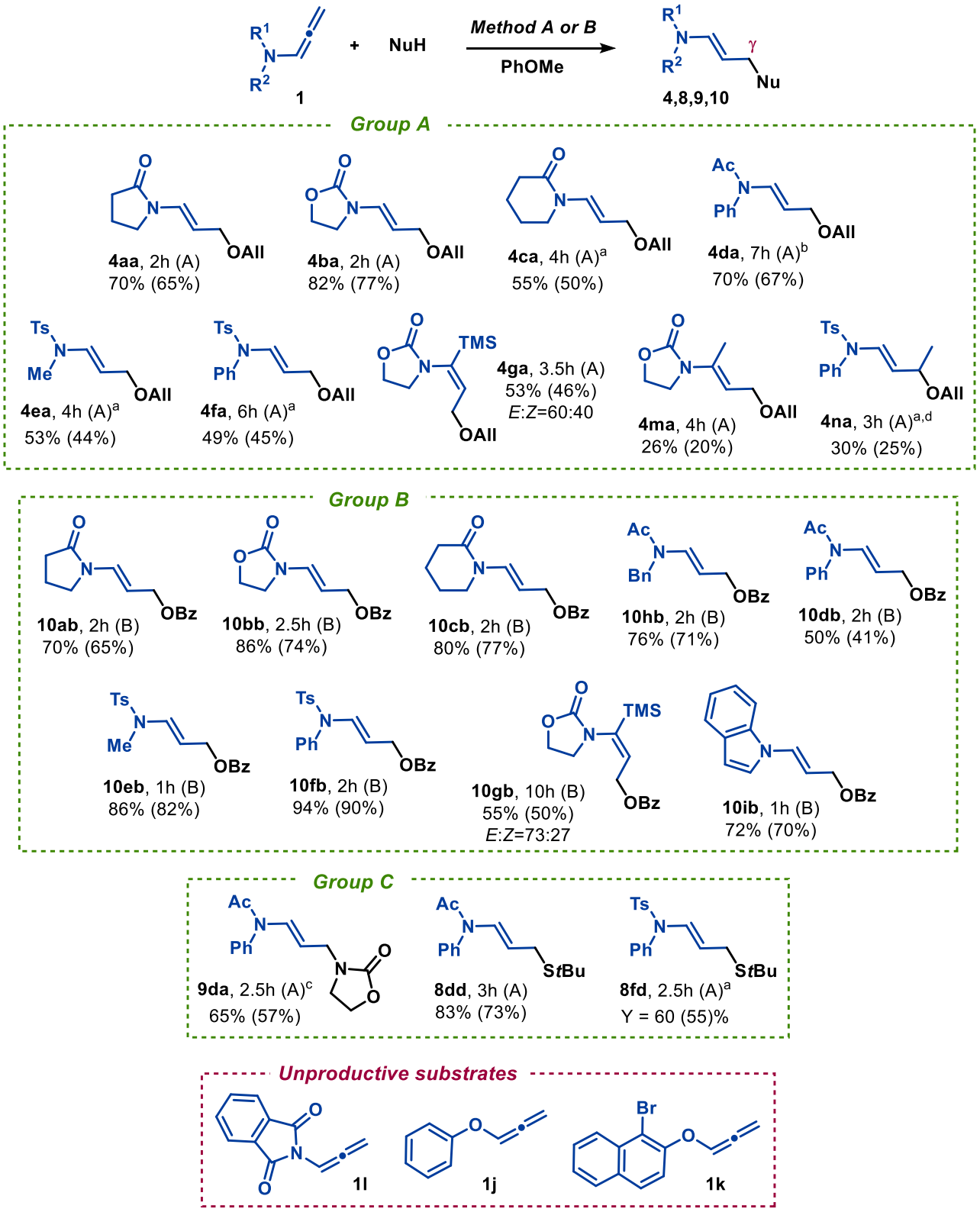
We concluded our exploration of heteronucleophiles by assessing the reactivity of carboxylic acids (Scheme 6). These substrates have previously been employed in reactions with allenamides, under metal-catalysis or metal-free conditions (Scheme 2a and 2c, respectively). However, limited attention has been given to the use of sustainable solvents.



Scheme 6. Reaction conditions: **1b** (0.1 mmol), RCOOH (3 eq.), PhOMe (0.2 M), 80 °C. Yields determined by ^{1}H-NMR analysis of the crude using methyl acetoacetate as internal standard. Yields after purification in parentheses.

The first attempts, carried out under our standard conditions (1 mol% CSA at room temperature in anisole), provided the desired enamides **10** (Scheme 6) with average yields around 50% (see Supporting Information). However, the allenamide **1b** was completely consumed, suggesting a partial substrate degradation likely promoted by the strong acid (CSA) employed, as reported in the literature.[12a] In this case, the degradation side reaction became competitive because of the lower nucleophilicity of the carboxylic acids compared to alcohols.[28] Therefore, we decided to avoid the use of strong acids and to directly exploit the nucleophile acidity to activate the allenamide. The best results were obtained at 80 °C in the presence of three equivalents of acid (Scheme 6, see Supporting Information for the conditions optimization). The unreacted carboxylic acid was easily fully recovered, enhancing the protocol sustainability. Under these conditions, aliphatic (**10ba**), aromatic (**10bb**), heteroaromatic (**10bd**), α,β-unsaturated (**10be**) and also sterically hindered (**10bc**) carboxylic acids provided excellent results. The γ-regioselectivity was particularly remarkable, being the α- and α,γ-adducts never observed. The excellent stereopreference for the *E*-isomer was also confirmed. The protocol was successfully applied to natural product-like structures, such as α-aminoacids (**10bf** and **10bg**), proving the good functional groups tolerance of the method (*N*-Boc remained unaltered).

Once we evaluated the applicability of our sustainable protocol to very different families of heteronucleophiles, we tested their addition to some structurally different allenamides **1** (Scheme 7).



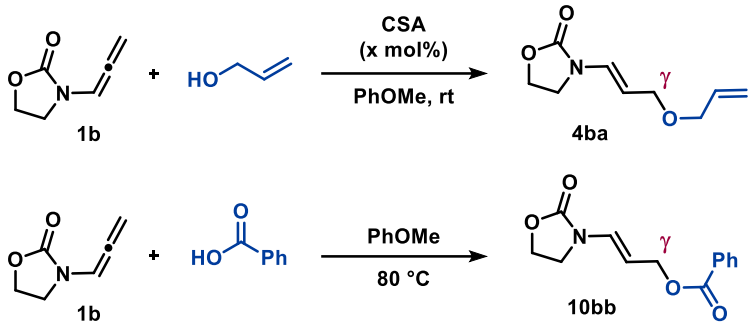
Scheme 7. Reaction conditions: **1** (0.1 mmol), PhOMe (0.2 M); *Method A*: NuH (1.2 eq.), CSA (1 mol%, stock solution 0.025 M in PhOMe), rt; *Method B*: NuH (3 eq.), 80 °C. Yields determined by ^{1}H-NMR analysis of the crude using methyl acetoacetate as internal standard. Yields after purification

in parentheses. [a] 1.5 mol% of CSA. [b] 50 °C. [c] 80 °C. [d] 20% of α-adduct **3na** was also isolated; overall yield after purification = 45%. All = allyl; Bn = benzyl; TMS = trimethylsilyl; Bz = benzoyl; *t*Bu = *tert*-butyl.

The screening involved cyclic and acyclic allenamides (**1a** and **1c** *vs* **1d** and **1h**), different ring sizes (**1a** *vs* **1c**), carbamates (**1b** and **1g**), *N*-alkyl and *N*-aryl tosylamides (**1e** and **1f**), α,α-disubstituted allenamides (**1g** and **1m**), a γ-monosubstituted allenamide (**1n**), and the indolyl allene **1i**. Using allyl alcohol as the nucleophile (*Group A*, Scheme 7) we obtained acceptable to high yields with all substrates, except for **1m**, **1n** and **1i**. The indolyl derivative **1i** proved to be sensitive to strong acids. The α-methyl derivative **1m** suffers from the remarkable tendency to rearrange to the corresponding 1,3-butadiene.[50] Conversely, α-TMS derivative **1g** provided good results, demonstrating that α,α-disubstituted allenamides can be suitable substrates for our protocol. Lastly, we evaluated the reactivity of γ-monosubstituted allenamide **1n**, although only an example is present in the literature reporting on the nucleophilic γ-addition to this kind of compounds, providing poor results.[19b] Under our reaction conditions, we obtained a 45% overall yield and the products distribution (**3na**:**4na** = 44:56) suggested that the γ-substituent might interfere with the products isomerization. Concerning the reactivity of carboxylic acids (*Group B*, Scheme 7), the addition of benzoic acid as a nucleophile provided in general excellent results, including the particularly sensitive indolyl allene **1i**. Notably, we successfully extended the addition of a carbamate (oxazolidinone) and a sterically hindered thiol (2-methyl-2-propanethiol) to allenamides **1d** and **1f** (*Group C*, Scheme 7), thereby definitively demonstrating the broad applicability of our protocol compared to those already published, in terms of both nucleophiles and allenamides. Finally, we tested some allenyl ethers (**1j** and **1k**), which were unreactive,[38] and the phthalimido-allene **1l** which proved to be too electron-poor to take part in the reaction (Scheme 7).

Once we established the broad reaction scope, we focused on the process scale up (Table 2).

Table 2. Process scale up.[a]

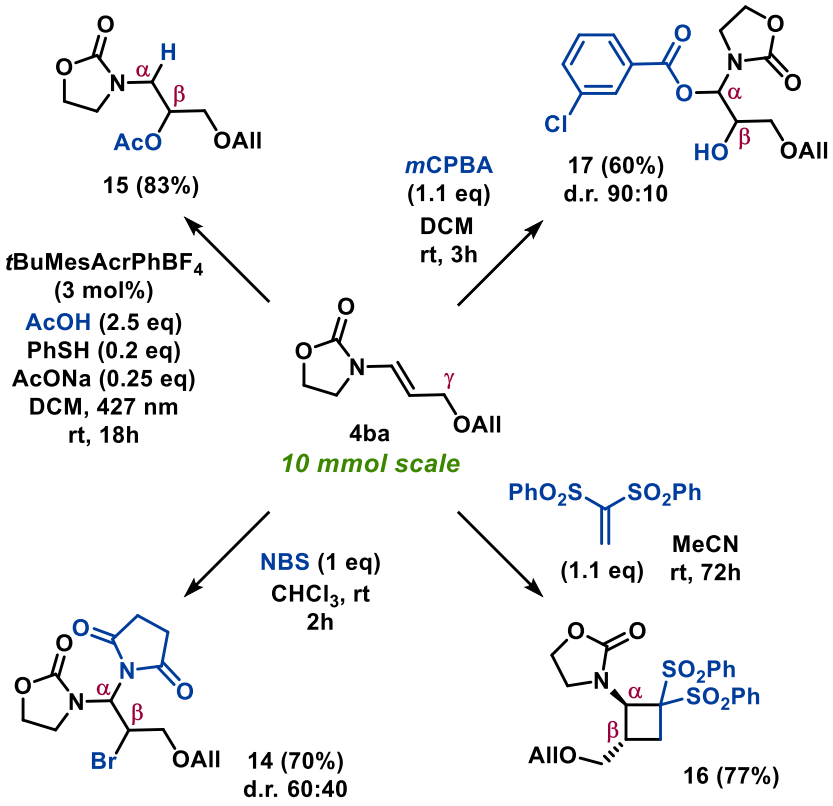


Entry	**1b** (mmol)	NuH (eq.)	CSA (mol%)	PhOMe (M)	Time (h)	Yield (%)[b]
1	0.1	Allyl-OH (1.2)	1	0.2	2	82 (77)
2	0.1	Allyl-OH (1.2)	0.5	0.2	7	39
3	0.1	Allyl-OH (1.2)	0.5	0.4	1.25	74
4	1	Allyl-OH (1.2)	0.5	0.4	1.5	88 (78)
5	10	Allyl-OH (1.2)	0.5	0.4	1.25	78 (72)
6	0.1	BzOH (3)	-	0.2	2.5	86 (74)
7	1	BzOH (1.5)	-	0.4	3	82 (76)

[a] Reaction conditions: **1b** (limiting reagent). [b] Product yield determined by ^{1}H-NMR analysis of the crude using methyl acetoacetate as internal standard. Yields after purification in parentheses.

Aiming to further improve efficiency and sustainability, we reduced the catalyst loading to 0.5 mol% but the reaction rate significantly dropped (entry 2 *vs* 1). Increasing of the concentration from 0.2 to 0.4 M brought us a double benefit, enhancing the process sustainability and restoring a good reactivity (entry 3). These further optimized conditions were applied to 1 mmol of limiting substrate **1b** (10 times scaled, entry 4) and to 10 mmol (100 times scaled, entry 5) providing excellent results (143 mg and 1.32 g of product, respectively) in short reaction times. The addition of benzoic acid was also optimized, halving the amount of both nucleophile and solvent (entry 7 *vs* 6), and it was scaled up by a factor of 10, while maintaining excellent performance (entry 7).

Further synthetic elaborations were made to demonstrate the synthetic utility of the obtained enamides (Scheme 8). In fact, γ-heterosubstituted enamides are valuable intermediates[39] for the synthesis of densely functionalized products.

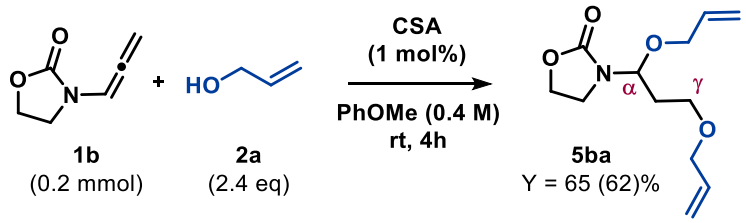


Scheme 8. Synthetic elaborations on enamide **4ba**. Yields after purification in parentheses. All = allyl; NBS = *N*-bromosuccinimide; *m*CPBA = *meta*-chloroperoxybenzoic acid; *t*BuMesAcrPhBF$_4$ = 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate.

We focused on metal-free synthetic elaborations and we first carried out two electrophile-promoted difunctionalizations. In particular, the bromoamination furnished product **14** in good yield, albeit with modest diastereomeric ratio. Conversely, the hydroxycarboxylation led to compound **17** with good diastereoselectivity. Subsequently, we successfully synthesized the unprecedented cyclobutane **16**, characterized by three substituted carbons, including a fully substituted one. The transformation was fully regio- and diastereoselective, yielding a single product. Notably, the cyclobutane motif is

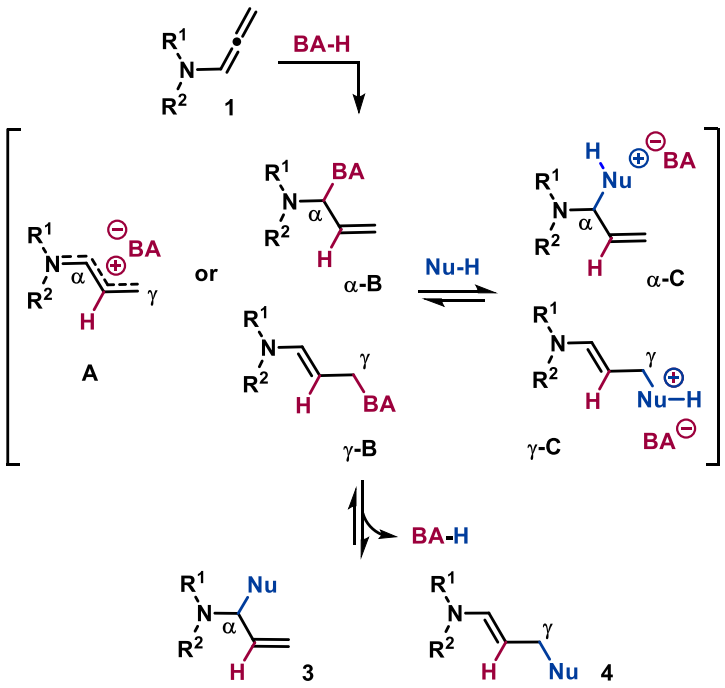
present in a variety of compounds showing significant pharmacological properties and, among the derivatives bearing two heteroatom(O,N,S)-containing substituents, the 1,2-arrangement is the least reported in the literature.[40] Lastly, we applied the light-promoted anti-Markovnikov hydrofunctionalization recently proposed by Nicewicz[41] to our γ-oxygenated enamide **4ba**, obtaining **15** with excellent yield and regioselectivity.

The optimized protocol (method A, Scheme 7) can be further applied to achieve a different class of products. In fact, by doubling the alcohol amount we obtained in good yield the one-pot and metal-free formation of the α,γ bis-hydroalkoxylation product **5ba** (Scheme 9).[15a] *N,O*-acetals are remarkable structural motifs present in bioactive natural products and this peculiar functional group is usefully exploited as the precursor of unstable *N*-acylimines, to introduce different structural moieties.[42]



Scheme 9. One-pot preparation of α,γ bis-hydroalkoxylation product **5ba**.

Mechanistic Investigations. Once we established an efficient, sustainable and versatile protocol to synthesize γ-functionalized enamides, we decided to investigate the reaction mechanism aiming to rationalize the observed regioselectivity. Two are the previously hypothesized activation modes for the addition of nucleophiles (mostly C-nucleophiles) to allenamides activated by Brønsted acids (Scheme 10).[12b,43]



Scheme 10. Possible activation modes and reaction pathway.

The selective protonation of the most electron-rich β-carbon of the allenamide **1** by the Brønsted acid (**BA-H**) should provide the π-system activation, generating an intermediate α,β-unsaturated iminium ion. At this stage, the anionic counterion ($\mathbf{BA^-}$) might behave differently. According to a *non-covalent* activation mode, it takes part in an ion pair (**A**) and the following nucleophilic addition is driven by electrostatic and hydrogen bonding interactions. Conversely, the *covalent* activation mode[44] suggests a temporary covalent binding between the iminium ion and the counterion (**B**), being **α-B** the most favoured intermediate by electrostatic interactions and hydrogen bonding with the amide. Subsequently, a substitution process allows the nucleophile to provide the final products (**3** and/or **4**). The whole transformation consists of equilibrium steps, therefore, in the presence of acidic traces, the two products **3** and **4** could be interconverted. Experiments were carried out to explore the underlying reaction mechanism, giving some crucial insights: a) CSA plays a fundamental role in catalysing the alcohol addition, because the reaction does not proceed in its absence (even at 80 °C; see Supporting Information for details); b) high resolution mass spectrometry (HRMS) analysis of the reaction mixture composition during the reaction course, revealed the presence of intermediate **B**

(see Supporting Information for details); this evidence could support a covalent activation mode, otherwise **B** might revert back to **A** which reacts with the nucleophile; c) by analysing the reaction mixture composition over the time with ^{1}H-NMR spectroscopy (see Supporting Information for details), we found that, under our reaction conditions, the α-adduct **3** appears to be the kinetically favoured product, being the major one at short reaction times (with alcohols and thiols) and when the reactivity is poor (with amides). On the other hand, the γ-adduct **4** seems to be the thermodynamically favoured product, whose amount increases over the time and/or at higher temperatures (amides), suggesting that it is mainly generated from **3**.[45] However, almost all the papers describing mechanistic studies on this type of transformations[12b,19a,43,46] and postulating a covalent activation mode propose a S_N2'-like displacement on **α-B** directly leading to the γ-adduct **4**, without observing the temporary formation of the α-adduct **3**. To get further insights on the nucleophilic substitution mechanism taking place under our reaction conditions, we performed some DFT calculations at the M06-2X/cc-pvtz-IEFPCM (anisole)//M06-2X/6-31G(d)-IEFPCM (anisole) level of theory, on a simplified system consisting of the allenamide **1b**, methanol as the nucleophile and methanesulfonic acid as the catalyst. An initial conformational analysis on allenamide **1b** revealed that the s-*trans* conformation is more stable than the corresponding s-*cis* by 4.0 kcal·mol^{-1}, with a low interconversion barrier (**TS1**, $\Delta G^{\ddagger}$ 7.1 kcal·mol^{-1}, Figure 2). On the other hand, no suitable adduct with acid and methanol on the s-*trans* conformer was found productive to give the protonation product **I2**. Indeed, all pre-reaction complexes examined were characterized by a strong hydrogen-bond (~1.6 Å) between the acid catalyst and the oxygen atom of the oxazolidinone motif. Thus, the intramolecular proton transfer was hindered in the case of the s-*trans* conformer, due to the excessive distance between the proton and the allene system. Conversely, in the s-*cis* conformation, the position of the allene system in the pre-reaction complex **I1** was found to be favorable for the occurrence of the proton transfer and the corresponding transition state **TS2** leading to the carbocation intermediate **I2** was immediately found.

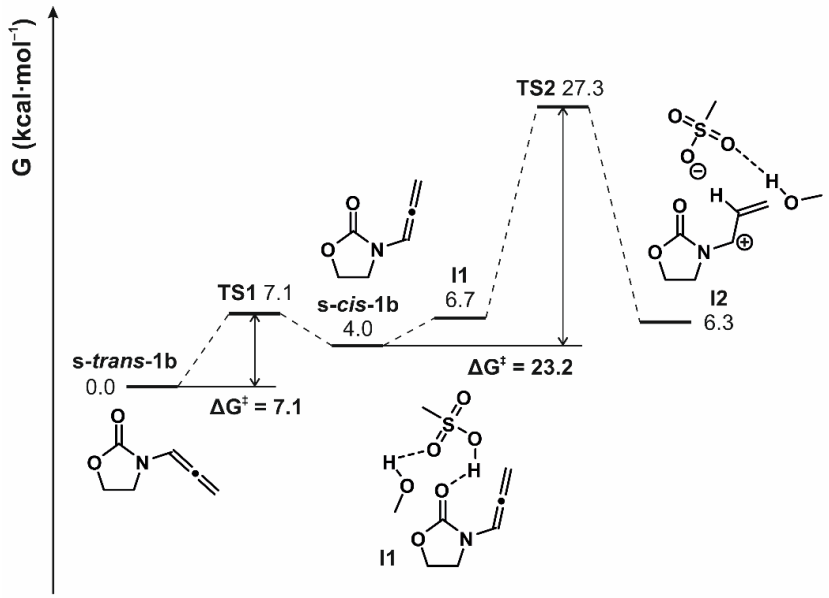


Figure 2. Overall reaction profile for the protonation of allenamide **1b**, giving cabocation intermediate **I2**. Free-energy profile at the M06-2X/cc-pvtz-IEFPCM (anisole)//M06-2X/6-31G(d)-IEFPCM (anisole) level of theory. Energies from single points calculations, corrected using the program GoodVibes (Truhlar's quasi-harmonic approximation).

Overall, by considering the complete reaction pathway starting from the most stable s-*trans* conformer, the protonation reaction is a slightly endoergonic process (ΔG_{298} = 6.3 kcal·mol^{-1}), with an activation barrier of 27.3 kcal·mol^{-1} (Figure 2).

The direct addition of methanol to the carbocation **I2** (Figure 3, green profile) revealed to be a strongly exergonic reaction (ΔG_{298} = –17.3 kcal·mol^{-1}) occurring through an almost barrierless process (**TS3**, $\Delta G^{\ddagger}$ 1.5 kcal·mol^{-1}), leading first to intermediate α-**I3** and finally to the α-adduct **3**. Starting from the same intermediate **I2**, the direct addition of methanesulfonate was also calculated (Figure 3, red profile). Indeed, intermediate **I2** spontaneously rearrange to the more stable intermediate **I4** (ΔG_{298} = –3.9 kcal·mol^{-1}), where the sulfonate anion is in close proximity to the reactive carbocation. The subsequent addition is thus very rapid (**TS4**, $\Delta G^{\ddagger}$ 2.8 kcal·mol^{-1}), leading to the intermediate α-**I2**. Starting from α-**I2**, the reaction pathway for the γ-addition of methanol was subsequently located (Figure 3, blue profile).

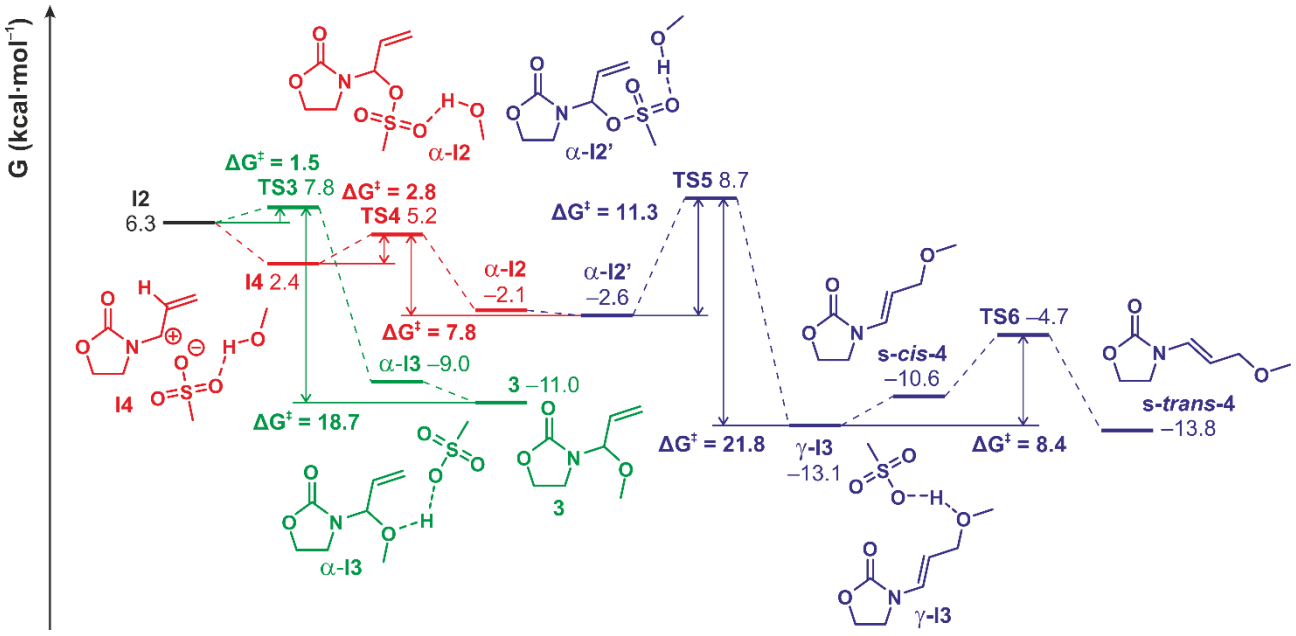


Figure 3. Overall reaction profiles for the α-addition of sulfonate anion (red profile), the α-addition (green profile) and the γ-addition (blue profile) of methanol to carbocation intermediate **I2**. Free-energy profiles at the M06-2X/cc-pvtz-IEFPCM (anisole)//M06-2X/6-31G(d)-IEFPCM (anisole) level of theory. Energies from single points calculations, corrected using the program GoodVibes (Truhlar's quasi-harmonic approximation).

First, the sulfonate group rotates around the C-O bond bringing the methanol molecule closer to the double bond (α-**I2'**), then methanol addition occurs via **TS5** leading to γ-intermediate γ-**I3** ($\Delta G^{\ddagger}$ 11.3 kcal·mol^{-1}, ΔG_{298} = –10.5 kcal·mol^{-1}) and to the s-*cis* γ-adduct **4**. Finally, the most stable s-*trans* γ-adduct conformer **4** is obtained (**TS6**, $\Delta G^{\ddagger}$ 8.4 kcal·mol^{-1}, ΔG_{298} = –3.2 kcal·mol^{-1}). Notably, all γ-derivatives found were characterized by an *E* configured double bond, as experimentally observed.

By examining the reaction profiles so far identified, the most favorable reaction pathway from the common intermediate **I2** appears to be the sulfonate addition (Figure 3, red profile), leading to α-**I2** and α-**I2'**. From here, both products **3** or **4** can be formed, with a barrier of 10.4 kcal·mol^{-1} in the first case (Figure 3, green profile), and of 11.3 kcal·mol^{-1} in the second case (Figure 3, blue profile), corresponding to a **3**:**4** ratio of ~ 85:15. Overall, the Brønsted acid adduct α-**I2'** seems to be the most favorable intermediate, acting as a reservoir from which first the product **3** is kinetically formed and

through which the most thermodynamically stable s-*trans* γ-product **4** accumulates over time, confirming what we have found experimentally.

Lastly, it is worth mentioning that we have modeled the entire reaction profile also for the more sterically hindered allenamide **1g** bearing a TMS group in the α-position (see Supporting Information for details). We observed also in this case that the α-addition of the sulfonate anion to the protonated allenamide intermediate is the reversible kinetically favored pathway, from which first α-methanol addition product is kinetically generated and through which the thermodynamically more stable γ-addition product is formed.

Conclusions

In summary, we have developed a straightforward and environmentally friendly protocol for the intermolecular γ-hydrofunctionalization of *N*-allenyl compounds with heteronucleophiles, catalyzed solely by a Brønsted acid. The key features of the proposed transformation include: i) ***sustainability***, being metal-free, atom-economical and requiring no excess reagents or further additives, being the acid catalyst not toxic, cheap and used in low loading, while employing a green solvent; ii) ***efficiency***, affording the desired products in good yields and short reaction times; iii) ***regio- and stereoselectivity***, preferentially providing the linear allylic products (γ-functionalization) and the *E*-configuration of the double bond exclusively; iv) ***versatility***, allowing the preparation of different heteroatom (O,N,S)-containing enamides. In contrast to previously reported methods, our process not only significantly enhances sustainability, avoiding metal catalysts and toxic solvents, but also remarkably broadens the scope for both reaction partners. This intermolecular methodology has successfully been applied to different allenamides and structurally complex and sterically hindered nucleophiles, even on the gram-scale, demonstrating its robustness and its potential for industrial applications. Finally, γ-heterosubstituted enamides offer further opportunities as valuable and versatile starting materials for the synthesis of unprecedented, highly functionalized compounds.

Experimental Section

General Methods. The ^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR spectra were recorded on a Varian INOVA 400 NMR instrument with a 5 mm probe, or on a Varian INOVA 600 NMR instrument or on a Bruker Ascend-600 spectrometer. The spectra were recorded at 400 MHz or 600 MHz for ^{1}H, at 100 MHz or 150 MHz for ^{13}C, and at 376 MHz for ^{19}F, respectively. All chemical shifts have been quoted relative to residue solvent signal; chemical shifts (δ) are reported in ppm and coupling constants (J) are reported in hertz (Hz). The following abbreviations are used to indicate the multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), hept (heptet), m (multiplet), br (broad), app (apparent). Structural assignments were made with additional information from gCOSY, gHSQC, and gHMBC experiments, as detailed in the Supporting Information. HPLC analyses were performed on an Agilent Technologies HP1260 instrument. A Phenomenex Gemini C18 3 μm (100 x 3 mm) column was employed for the chromatographic separation: mobile phase H_2O/CH_3CN, gradient from 30% to 80% of CH_3CN in 8 min, 80% of CH_3CN until 22 min, then up to 90% of CH_3CN in 2 min, flow rate 0.4 mL/min. Low-resolution MS (LRMS) ESI analyses were performed on an Agilent Technologies MSD1260 single-quadrupole mass spectrometer. Mass spectrometric detection was performed in the full-scan mode from m/z 50 to 2500, with a scan time of 0.1 s in the positive ion mode, ESI spray voltage of 4500 V, nitrogen gas pressure of 35 psi, drying gas flow rate of 11.5 mL/min and fragmentor voltage of 30 V. High-resolution MS (HRMS) ESI analyses were performed on a Xevo G2-XS QTof (Waters) mass spectrometer. Mass spectrometric detection was performed in the full-scan mode from m/z 50 to 1200, with a scan time of 0.15 s in the positive ion mode, cone voltage: 40 V, collision energy: 6.00 eV. ESI: capillary: 3kV, cone: 40 V, source temperature: 120 °C, desolvation temperature: 600 °C, cone gas flow: 50 L/h, desolvation gas flow: 1000 L/h. Melting point (m.p.) measurements were performed on Bibby Stuart Scientific SMP3 apparatus. Optical rotation measurements were performed on a polarimeter Schmidt+Haensch UniPol L1000. Flash chromatography purifications were carried out using VWR silica gel (40 – 63 μm particle size). Thin-

layer chromatography was performed on Merck 60 F254 plates, using UV light as the visualizing agent and basic aqueous potassium permanganate ($KMnO_4$) as developing agent. All the commercial chemicals were purchased from Sigma-Aldrich, VWR, Alfa Aesar, Fluorochem or TCI Chemicals and used without additional purification unless otherwise stated. CSA ((1*S*)-(+)-10-camphorsulfonic acid) was dried under vacuum heating with the heating gun and stored in a Schlenk tube under argon, anisole was dried on molecular sieves (3Å), **2a** was dried by refluxing it on Mg and distilled on molecular sieves (3Å), the CSA stock solution was prepared in a Schlenk tube and kept under argon, the catalytic reaction was performed in a Schlenk tube dried under vacuum and refilled with argon. Alcohols **2a**–**2i**, **2k**–**2t**, **2v** and phenol were commercially available and were used as received. Thio-nucleophiles **11a**–**11g**, aza-nucleophiles **12a**–**12d** and carboxylic acids **13a**–**13g** were commercially available and used without further purification. Allenamides **1** and other nucleophiles were prepared according to the literature: **1a-c** and **1e**;[47] **1d**;[48] **1f**;[49] **1g** and **1m**;[50] **1h**;[51] **1i**;[52] **1j**;[53] **1k**;[54] **1l**;[55] **1n**;[11c] **2j**;[56] **2u**;[57] **12c**.[58] The regioisomeric ratio was determined by ^{1}H NMR analysis of the crude product through integration of diagnostic signals.

The reaction setup doesn't require specialized equipment or procedures. No significant hazards or risks are associated with the reported work.

*General Procedure A (**GP-A**) for the synthesis of products **4,5aa,6,7,8** and **9bc**.* A Schlenk tube equipped with a magnetic stirring bar was dried under vacuum and refilled with Argon. The reaction vessel was then charged with the allenamide **1** (0.1 mmol, 1 eq.), anisole (0.46 mL, 0.2 M), the nucleophile (alcohol **2**, thiol **11** or sulfonamide **12c**) (0.12 mmol, 1.2 eq) and 40 µL of a 0.025 M (1.0 µmol, 0.01 eq., 1 mol%) stock solution of CSA in anisole. The reaction mixture was then allow to stir at room temperature until complete consumption of the starting material, as observed by TLC analysis. After the reported time, the reaction was diluted with ca. 3 mL of ethyl acetate and added to a separatory funnel containing 5 mL of a saturated aqueous solution of $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with EtOAc (2 x 3 mL). The combined organic extracts were dried over sodium sulphate, and concentrated under vacuum (0.5 mbar). The NMR

yield was determined by adding methyl acetoacetate (0.1 mmol, 1 eq.) as internal standard to the crude mixture dissolved in $CDCl_3$. Purification of the crude product by flash chromatography (FC) on silica gel afforded the desired product.

(*E*)-1-(3-(allyloxy)prop-1-en-1-yl)pyrrolidin-2-one (4aa). Prepared according to **GP-A** using 1-(propa-1,2-dien-1-yl)pyrrolidin-2-one **1a** (0.1 mmol, 12.3 mg, 1 eq.), allyl alcohol **2a** (0.12 mmol, 8.6 µL, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 2 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 40:60) to afford the product as a colourless oil (11.8 mg, 65%). R_f (CyH:EtOAc 1:1) = 0.51. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 14.4 Hz, 1H), 5.98 – 5.84 (m, 1H), 5.28 (dq, J = 17.3, 1.6 Hz, 1H), 5.19 (d, J = 10.4 Hz, 1H), 5.06 (dt, J = 14.1, 6.9 Hz, 1H), 4.02 (d, J = 7.0 Hz, 2H), 3.97 (d, J = 6.3 Hz, 2H), 3.53 (t, J = 7.2 Hz, 2H), 2.49 (t, J = 8.1 Hz, 2H), 2.11 (p, J = 7.7 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.5, 134.8, 127.5, 117.3, 107.4, 70.9, 69.2, 45.3, 31.3, 17.6. HPLC-LRMS (ESI) Rt = 3.8 min; *m/z* 182.20 $[M + H]^+$. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{16}NO_2^+$ 182.1176; Found 182.1182.

(*E*)-3-(3-(allyloxy)prop-1-en-1-yl)oxazolidin-2-one (4ba). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), allyl alcohol **2a** (0.12 mmol, 8.6 µL, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of Anisole (0.2 M). The reaction was stirred 2 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 50:50) to afford the product as a colourless oil (14.1 mg, 77%). R_f (CyH:EtOAc 1:1) = 0.34. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (d, J = 14.2 Hz, 1H), 5.91 (m,1H), 5.28 (dq, J = 17.2, 1.6 Hz, 1H), 5.20 (dq, J = 10.4, 1.6 Hz, 1H), 4.96 (dt, J = 14.2, 6.9 Hz, 1H), 4.50 – 4.41 (m, 2H), 4.01 (dd, J = 6.9, 0.8 Hz, 1H), 3.98 (dt, J = 5.7, 1.4 Hz, 1H), 3.77 – 3.68 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.4, 134.7, 127.9, 117.4, 106.6, 77.5, 77.2, 76.8, 71.0, 68.7, 62.4, 42.6. HPLC-LRMS (ESI) R_t = 3.5 min; *m/z* 389.10 $[2M+Na]^+$, 206.10 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_9H_{13}NNaO_3^+$ 206.0788; Found 206.0780.

(*E*)-3-(3-methoxyprop-1-en-1-yl)oxazolidin-2-one (4bb). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), methanol **2b** (0.12 mmol, 4.9 µL, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 2 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 30:70) to afford the product as a colourless oil (11.9 mg, 76%). R_f (CyH:EtOAc 1:1) = 0.18. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (d, J = 15.4 Hz, 1H), 4.94 (dt, J = 14.2, 7.0 Hz, 1H), 4.50 – 4.39 (m, 2H), 3.95 (dd, J = 7.0, 1.1 Hz, 2H), 3.79 – 3.68 (m, 2H), 3.32 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.4, 128.0, 106.5, 71.1, 62.4, 57.7, 42.6. HPLC-LRMS (ESI) R_t = 2.0 min; *m/z* 337.16 $[2M+Na]^+$, 180.15 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_7H_{11}NNaO_3^+$ 180.0631; Found 180.0649.

(*E*)-3-(3-(prop-2-yn-1-yloxy)prop-1-en-1-yl)oxazolidin-2-one (4bc). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), 2-propynol **2c** (0.12 mmol, 6.9 µL, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 1.5 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 40:60) to afford the product as a colourless oil (12.3 mg, 68%). R_f (CyH:EtOAc 1:1) = 0.36. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (d, J = 14.2 Hz, 1H), 4.93 (dt, J = 14.2, 7.1 Hz, 1H), 4.50 – 4.40 (m, 2H), 4.13 (d, J = 2.4 Hz, 2H), 4.10 (dd, J = 7.1, 1.1 Hz, 2H), 3.77 – 3.66 (m, 2H), 2.44 (t, J = 2.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.2, 128.5, 105.5, 79.5, 74.6, 68.0, 62.2, 56.6, 42.3. HPLC-LRMS (ESI) R_t = 3.1 min; *m/z* 385.06 $[2M+Na]^+$, 204.04 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_9H_{11}NNaO_3^+$ 204.0631; Found 204.0637.

(*E*)-3-(3-(2,2,2-trifluoroethoxy)prop-1-en-1-yl)oxazolidine-2-one (4bd). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), 2,2,2-trifluoroethanol **2d** (0.12 mmol, 8.7 µL, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 2 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 50:50) to afford the product as a yellow oil (12.9 mg, 45%). R_f (CyH:EtOAc 1:1) = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (d, J = 14.3 Hz,

1H), 4.92 (dt, J = 14.3, 7.1 Hz, 1H), 4.52 – 4.43 (m, 2H), 4.17 (d, J = 7.0 Hz, 2H), 3.80 (q, J = 8.5 Hz, 2H), 3.79 – 3.70 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.01 (t, J = 8.5 Hz, 3F). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 155.4, 129.2, 124.1 (4, J = 279.6 Hz), 104.9, 71.0, 66.8 (q, J = 34.1 Hz), 62.4, 42.5. HPLC-LRMS (ESI) R_t = 5.1 min; *m/z* 473.10 $[2M+Na]^+$, 248.10 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_8H_{10}F_3NNaO_3^+$ 248.0505; Found 248.0512.

(*E*)-3-(3-(benzyloxy)prop-1-en-1-yl)oxazolidine-2-one (4be). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), benzyl alcohol **2e** (0.12 mmol, 12.5 µL, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 2.5 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 50:50) to afford the product as a colourless oil (16.3 mg, 70%). R_f (CyH:EtOAc 1:1) = 0.36. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 4H), 7.33 – 7.26 (m, 1H), 6.92 (d, J = 14.3 Hz, 1H), 4.98 (dt, J = 14.3, 7.0 Hz, 1H), 4.51 (s, 2H), 4.50 – 4.38 (m, 2H), 4.06 (dd, J = 7.0, 1.1 Hz, 2H), 3.72 (d, J = 7.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.4, 138.3, 128.6, 128.0, 128.0, 127.8, 106.7, 72.1, 68.8, 62.4, 42.6. HPLC-LRMS (ESI) R_t = 14.7 min; *m/z* 489.00 $[2M+Na]^+$, 256.00 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{15}NNaO_3^+$ 256.0944; Found 256.0923.

(*E*)-3-(3-((3,5-bis(trifluoromethyl)benzyl)oxy)prop-1-en-1-yl)oxazolidin-2-one (4bf). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), (3,5-bis(trifluoromethyl)phenyl)methanol **2f** (0.12 mmol, 29.3 mg, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 3 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 80:20 to 60:40) to afford the product as a colourless oil (25.1 mg, 68%). R_f (CyH:EtOAc 7:3) = 0.41. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 3H), 6.96 (d, J = 14.3 Hz, 1H), 4.98 (dt, J = 14.3, 7.0 Hz, 1H), 4.60 (s, 2H), 4.51 – 4.43 (m, 2H), 4.14 (dd, J = 7.0, 1.1 Hz, 2H), 3.79 – 3.71 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.9 (s, 6F). $^{13}C\{^1H\}$ NMR(100 MHz, $CDCl_3$) δ 155.4, 141.1, 131.8 (q, J = 33.6 Hz), 128.7, 127.6 – 127.4 (m), 123.4 (q, J = 272.8 Hz), 121.7 (h, J = 3.7 Hz), 105.7, 70.4, 69.8, 62.4, 42.5. HPLC-LRMS

(ESI) R_t = 7.4 min; *m/z* 761.00 $[2M+Na]^+$, 392.00 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{13}F_6NNaO_3^+$ 392.0692; Found 392.0689.

(*E*)-3-(3-((3,5-bis(trifluoromethyl)benzyl)oxy)prop-1-en-1-yl)oxazolidin-2-one (4bg). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), naphthalen-1-ylmethanol **2g** (0.12 mmol, 19.0 mg, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 3 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 50:50) to afford the product as a colourless oil (22.4 mg, 79%). R_f (CyH:EtOAc 1:1) = 0.49. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, J = 9.4 Hz, 1H), 7.87 (d, J = 9.0 Hz, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.51 – 7.48 (m, 2H), 7.44 (dd, J = 8.2, 6.9 Hz, 1H), 6.93 (d, J = 14.4 Hz, 1H), 4.99 (dt, J = 14.4, 7.1 Hz, 1H), 4.96 (s, 2H), 4.47 – 4.36 (m, 2H), 4.13 (dd, J = 7.1, 1.2 Hz, 2H), 3.72 – 3.65 (m, 2H). ^{13}C{^{1}H} NMR(150 MHz, $CDCl_3$) δ 155.4, 133.9, 133.7, 131.9, 128.8, 128.7, 128.0, 126.7, 126.4, 125.9, 125.3, 124.1, 106.7, 70.6, 68.9, 62.3, 42.5. HPLC-LRMS (ESI) R_t = 5.9 min; *m/z* 589.20 $[2M+Na]^+$, 306.20 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{17}H_{17}NNaO_3^+$ 306.1101; Found 306.1110.

(*E*)-3-(3-(decyloxy)prop-1-en-1-yl)oxazolidine-2-one (4bh). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), decan-1-ol **2h** (0.12 mmol, 19.0 mg, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 2.5 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 50:50) to afford the product as a colourless oil (18.3 mg, 64%). R_f (CyH:EtOAc 1:1) = 0.40. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.90 (d, J = 14.4 Hz, 1H), 4.96 (dt, J = 14.4, 6.9 Hz, 1H), 4.51 – 4.37 (m, 2H), 3.98 (dd, J = 6.9, 1.2 Hz, 2H), 3.76 – 3.70 (m, 2H), 3.40 (t, J = 6.8 Hz, 2H), 1.61 – 1.53 (m, 2H), 1.36 – 1.20 (m, 14H), 0.87 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR(150 MHz, $CDCl_3$) δ 155.5, 127.6, 106.9, 70.5, 69.4, 62.3, 42.6, 32.0, 29.9, 29.8, 29.7, 29.6, 29.5, 26.3, 22.8, 14.3. HPLC-LRMS (ESI) R_t = 9.4 min; *m/z* 589.40 $[2M+Na]^+$, 306.20 $[M + Na]^+$.HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{29}NNaO_3^+$ 306.2040; Found 306.2049.

(*E*)-3-(3-isopropoxyprop-1-en-1-yl)oxazolidin-2-one (4bi). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), 2-propanol **2i** (0.12 mmol, 9.2 µL, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 1 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 40:60) to afford the product as a colourless oil (13.0 mg, 70%). R_f (CyH:EtOAc 1:1) = 0.27. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (d, J = 14.3 Hz, 1H), 4.96 (dt, J = 14.3, 6.9 Hz, 1H), 4.47 – 4.40 (m, 2H), 3.98 (d, J = 6.9 Hz, 2H), 3.77 – 3.69 (m, 2H), 3.63 (p, J = 6.1 Hz, 1H), 1.17 (d, J = 6.1 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.5, 127.4, 107.3, 70.9, 66.7, 62.3, 42.6, 22.2. HPLC-LRMS (ESI) R_t = 12.7 min; *m/z* 393.20 $[2M+Na]^+$, 208.20 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_9H_{15}NNaO_3^+$ 208.0944; Found 208.0955.

(*E*)-3-(3-((9H-fluoren-9-yl)oxy)prop-1-en-1-yl)oxazolidin-2-one (4bj). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), 9H-fluoren-9-ol **2j** (0.12 mmol, 21.9 mg, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 2.5 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 40:60) to afford the product as a white crystalline solid (15.4 mg, 50%). R_f (CyH:EtOAc 1:1) = 0.32. m.p. = 96 – 99 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, J = 7.5 Hz, 2H), 7.62 (dd, J = 7.4, 1.0 Hz, 2H), 7.40 (t, J = 7.2 Hz, 2H), 7.33 (td, J = 7.4, 1.2 Hz, 2H), 6.75 (d, J = 14.3 Hz, 1H), 5.68 (s, 1H), 4.86 (dt, J = 14.3, 6.9 Hz, 1H), 4.43 – 4.37 (m, 2H), 3.73 (dd, J = 6.9, 1.1 Hz, 2H), 3.66 – 3.60 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 155.3, 142.9, 141.0, 129.2, 127.7, 127.7, 125.6, 120.2, 107.0, 80.6, 63.4, 62.3, 42.5. HPLC-LRMS (ESI) R_t = 6.5 min; *m/z* 637.20 $[2M+Na]^+$, 330.20 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{17}NNaO_3^+$ 330.1101; Found 330.1112.

(*S,E*)-3-(3-(1-phenylethoxy)prop-1-en-1-yl)oxazolidin-2-one (4bk). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), (*S*)-1-phenylethan-1-ol **2k** (0.12 mmol, 14.5 µL, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 6 h at rt. The crude mixture was

purified by FC (CyH:EtOAc, from 70:30 to 40:60) to afford the product as a yellow oil (11.9 mg, 48%). R_f (CyH:EtOAc 1:1) = 0.38. $[\alpha]_D^{20}$ = -56.2 (c = 0.71, $CDCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H), 6.84 (d, J = 14.4 Hz, 1H), 4.94 (dt, J = 14.4, 6.9 Hz, 1H), 4.49 – 4.40 (m, 3H), 3.86 (qdd, J = 11.3, 6.9, 1.1 Hz, 2H), 3.70 (td, J = 7.9, 5.3 Hz, 2H), 1.45 (d, J = 6.6 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.4, 143.7, 128.7, 127.6, 127.6, 126.4, 126.3, 106.9, 77.3, 67.1, 62.3, 42.5, 24.3. HPLC-LRMS (ESI) R_t = 6.7 min; *m/z* 517.2 $[2M+Na]^+$, 270.2 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{17}NNaO_3^+$ 270.1101; Found 270.1097.

(*E*)-3-(3-(but-3-yn-2-yloxy)prop-1-en-1-yl)oxazolidin-2-one (4bl). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), (1-phenylprop-2-yn-1-ol **2l** (0.12 mmol, 14.5 µL, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 6 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 50:50) to afford the product as a yellow oil (12.9 mg, 50%). R_f (CyH:EtOAc 1:1) = 0.42. ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 2H), 7.44 – 7.31 (m, 3H), 6.95 (d, J = 14.3 Hz, 1H), 5.20 (d, J = 2.2 Hz, 1H), 4.97 (ddd, J = 14.3, 7.5, 6.7 Hz, 1H), 4.52 – 4.40 (m, 2H), 4.23 (ddd, J = 11.2, 6.7, 1.1 Hz, 1H), 4.12 (ddd, J = 11.3, 7.5, 1.1 Hz, 1H), 3.76 – 3.68 (m, 2H), 2.66 (d, J = 2.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.4, 138.1, 128.8, 128.6, 127.6, 106.0, 81.5, 76.0, 70.4, 66.9, 62.4, 42.5. HPLC-LRMS (ESI) R_t = 5.1 min; *m/z* 537.20 $[2M+Na]^+$, 280.20 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{15}NNaO_3^+$ 280.0944; Found 280.0950.

(*E*)-3-(3-(tert-butoxy)prop-1-en-1-yl)oxazolidin-2-one (4bm). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), 2-methylpropan-2-ol **2m** (0.12 mmol, 11.4 µL, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 1.5 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 50:50) to afford the product as a yellow oil (9.8 mg, 49%). R_f (CyH:EtOAc 7:3) = 0.31. ^1H NMR (400 MHz, $CDCl_3$) δ 6.89 (d, J = 14.3 Hz, 1H), 4.95 (dt, J = 14.2, 6.8 Hz, 1H), 4.49 – 4.37 (m, 2H), 3.93 (app. dd, J = 6.8, 1.2 Hz, 2H), 3.79 – 3.67 (m, 2H),

1.23 (s, 9H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 155.5, 126.9, 108.0, 73.5, 62.3, 60.8, 42.6, 27.8. HPLC-LRMS (ESI) R_t = 4.5 min; *m/z* 421.2 $[2M+Na]^+$, 222.2 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{10}H_{17}NNaO_3^+$ 222.1101; Found 222.1115.

(*E*)-3-(3-(*tert*-pentyloxy)prop-1-en-1-yl)oxazolidin-2-one (4bn). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), 2-methylbutan-2-ol **2n** (0.12 mmol, 13.1 µL, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 6 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 60:40 to 30:70) to afford the product as a yellow oil (9.6 mg, 45%). R_f (CyH:EtOAc 7:3) = 0.59. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (dt, J = 14.3, 1.4 Hz, 1H), 5.00 – 4.89 (m, 1H), 4.46 – 4.39 (m, 2H), 3.89 (dd, J = 6.7, 1.2 Hz, 2H), 3.76 – 3.68 (m, 2H), 1.52 (q, J = 7.5 Hz, 2H), 1.16 (s, 6H), 0.87 (t, J = 7.5 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 155.5, 126.8, 108.0, 75.5, 62.3, 60.3, 42.6, 32.5, 25.3, 8.4. HPLC-LRMS (ESI) R_t = 3.9 min; *m/z* 449.20 $[2M+Na]^+$, 236.20 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_{19}NNaO_3^+$ 236.1257; Found 236.1263.

(*E*)-3-(3-((4-hydroxy-2-methoxybenzyl)oxy)prop-1-en-1-yl)oxazolidin-2-one (4bo). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), 4-(hydroxymethyl)-3-methoxyphenol **2o** (0.12 mmol, 18.5 mg, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 7 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 60:40 to 30:70) to afford the product as a white crystalline solid (12.0 mg, 43%). R_f (CyH:EtOAc 1:1) = 0.19. m.p. =104 – 107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, J = 14.4 Hz, 1H), 6.89 – 6.86 (m, 2H), 6.82 (dd, J = 8.1, 1.9 Hz, 1H), 5.61 (s, 1H), 4.97 (dt, J = 14.1, 7.0 Hz, 1H), 4.48 – 4.43 (m, 2H), 4.42 (s, 2H), 4.03 (dd, J = 7.0, 1.1 Hz, 2H), 3.90 (s, 3H), 3.78 – 3.68 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 155.3, 146.6, 145.3, 130.0, 127.8, 121.2, 114.1, 110.6, 106.5, 72.1, 68.4, 62.2, 55.9, 42.4. HPLC-LRMS (ESI) R_t = 1.9 min; *m/z* 581.00 $[2M+Na]^+$, 302.00 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{17}NNaO_5^+$ 302.0999; Found 302.0989.

(*S*,*E*)-3-(3-((3,7-dimethyloct-6-en-1-yl)oxy)prop-1-en-1-yl)oxazolidin-2-one (4bp). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1eq.), (*S*)-(−)-β-citronellol **2p** (0.12 mmol, 21.9 µL, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 1.5 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 80:20 to 50:50) to afford the product as a yellow oil (17.2 mg, 61%). R_f (CyH:EtOAc 65:35) = 0.27. $[\alpha]_D^{20}$ = +1.8 (c = 0.94, $CDCl_3$).^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (d, J = 14.3 Hz, 1H), 5.09 (tt, J = 7.1, 1.4 Hz, 1H), 4.95 (dt, J = 14.3, 7.1 Hz, 1H), 4.49 – 4.38 (m, 2H), 3.98 (d, J = 7.1 Hz, 2H), 3.76 – 3.68 (m, 2H), 3.49 – 3.38 (m, 2H), 2.05 – 1.88 (m, 2H), 1.67 (d, J = 1.4 Hz, 3H), 1.66 – 1.61 (m, 1H), 1.59 (s, 3H), 1.58 – 1.50 (m, 1H), 1.45 – 1.28 (m, 2H), 1.22 – 1.09 (m, 1H), 0.89 (d, J = 6.7 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.5, 131.3, 127.6, 124.9, 106.9, 69.4, 68.6, 62.3, 42.5, 37.4, 36.8, 29.7, 25.9, 25.6, 19.7, 17.8. HPLC-LRMS (ESI) R_t = 8.1 min; *m/z* 304.20 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{27}NNaO_3^+$ 304.1883; Found 304.1876.

(*E*)-3-(3-(benzo[d][1,3]dioxol-5-ylmethoxy)prop-1-en-1-yl)oxazolidin-2-one (4bq). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), piperonyl alcohol **2q** (0.12 mmol, 18.3 mg, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 5 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 80:20 to 50:50) to afford the product as a yellow oil (15.3 mg, 55%). R_f (CyH:EtOAc 6:4) = 0.53. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (d, J = 14.2 Hz, 1H), 6.84 (s, 1H), 6.81 – 6.75 (m, 2H), 5.95 (s, 2H), 4.97 (dt, J = 14.2, 7.0 Hz, 1H), 4.48 – 4.43 (m, 2H), 4.40 (s, 2H), 4.02 (dd, J = 7.0, 1.1 Hz, 2H), 3.77 – 3.68 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.4, 147.9, 147.3, 132.1, 128.0, 121.6, 108.7, 108.3, 106.6, 101.2, 72.0, 68.6, 62.4, 42.5. HPLC-LRMS (ESI) R_t = 4.0 min; *m/z* 577.2 $[2M + Na]^+$, 300.0 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{15}NNaO_5^+$ 300.0842; Found 300.0845.

(*R*,*E*)-3-(3-((4,4-dimethyl-2-oxotetrahydrofuran-3-yl)oxy)prop-1-en-1-yl)oxazolidin-2-one (4br). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol,

12.5 mg, 1 eq.), D-(−)-pantolactone **2r** (0.12 mmol, 15.6 mg, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 3 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 60:40 to 30:70) to afford the product as a yellow oil (15.4 mg, 60%). R_f (CyH:EtOAc 1:1) = 0.17. $[\alpha]_D^{20}$ = +21.0 (c = 0.84, $CDCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 6.92 (d, J = 14.4 Hz, 1H), 5.00 (dt, J = 14.2, 7.0 Hz, 1H), 4.46 (dd, J = 8.6, 7.6 Hz, 2H), 4.42 (ddd, J = 11.8, 6.6, 1.2 Hz, 1H), 4.26 (ddd, J = 11.8, 7.4, 1.1 Hz, 1H), 3.99 (d, J = 8.8 Hz, 1H), 3.90 (d, J = 8.8 Hz, 1H), 3.78 – 3.72 (m, 3H), 1.19 (s, 3H), 1.09 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 175.4, 155.4, 128.5, 105.9, 80.8, 76.4, 70.0, 62.4, 42.5, 40.5, 23.5, 19.5. HPLC-LRMS (ESI) R_t = 2.2 min; *m/z* 533.2 $[2M + Na]^+$, 278.2 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{17}NNaO_5^+$ 278.0999; Found 278.0997.

3-((*E*)-3-(((3a*R*,5*R*)-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl)oxy)prop-1-en-1-yl)oxazolidin-2-one (4bs). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), D-glucose diacetonide **2s** (0.12 mmol, 31.2 mg, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 2.5 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 50:50) to afford the product as a yellow oil (26.2 mg, 68%). R_f (CyH:EtOAc 1:1) = 0.52. $[\alpha]_D^{20}$ = -18.9 (c = 1.66, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 6.93 (d, J = 14.2 Hz, 1H), 5.87 (d, J = 3.7 Hz, 1H), 4.91 (dt, J = 14.2, 6.9 Hz, 1H), 4.52 (d, J = 3.7 Hz, 1H), 4.46 (dd, J = 8.5, 7.6 Hz, 2H), 4.27 (dt, J = 8.1, 5.7 Hz, 1H), 4.21 – 4.12 (m, 2H), 4.12 – 4.06 (m, 2H), 4.00 (dd, J = 8.6, 5.5 Hz, 1H), 3.96 (d, J = 3.0 Hz, 1H), 3.73 (td, J = 7.6, 1.5 Hz, 2H), 1.49 (s, 3H), 1.42 (s, 3H), 1.36 (s, 3H), 1.31 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.4, 128.2, 112.0, 109.2, 106.0, 105.3, 83.1, 81.3, 80.9, 72.5, 69.2, 67.5, 62.3, 42.5, 27.0, 26.9, 26.4, 25.6. HPLC-LRMS (ESI) R_t = 13.9 min; *m/z* 408.20 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{27}NNaO_8^+$ 408.1629; Found 408.1640.

3-((*E*)-3-(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)prop-1-en-1-yl)oxazolidin-2-one (4bt). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol,

12.5 mg, 1 eq.), (−)-menthol **2t** (0.12 mmol, 18.8 mg, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 6 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 50:50) to afford the product as a colorless oil (17.2 mg, 61%). R_f (CyH:EtOAc 1:1) = 0.60. $[\alpha]_D^{20}$ = -39.9 (c = 1.02, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (d, J = 14.3 Hz, 1H), 4.95 (dt, J = 14.3, 7.0 Hz, 1H), 4.48 – 4.38 (m, 2H), 4.15 (ddd, J = 11.2, 6.7, 1.2 Hz, 1H), 3.89 (ddd, J = 11.3, 7.2, 1.1 Hz, 1H), 3.77 – 3.68 (m, 2H), 3.07 (td, J = 10.6, 4.2 Hz, 1H), 2.19 – 2.14 (m, 1H), 2.12 – 2.03 (m, 1H), 1.69 – 1.58 (m, 3H), 1.41 – 1.28 (m, 1H), 1.27 – 1.17 (m, 1H), 0.92 (d, J = 6.6 Hz, 3H), 0.89 (d, J = 7.0 Hz, 3H), 0.76 (d, J = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.5, 127.2, 107.6, 78.4, 67.0, 62.3, 48.4, 42.6, 40.6, 34.6, 31.7, 25.6, 23.4, 22.5, 21.1. HPLC-LRMS (ESI) R_t = 8.2 min; *m/z* 585.40 $[2M + Na]^+$, 304.20 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{27}NNaO_3^+$ 304.1883; Found 304.1894.

(*E*)-3-(3-((1-benzyl-2-oxoindolin-3-yl)oxy)prop-1-en-1-yl)oxazolidin-2-one (4bu). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidine-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), 1-benzyl-3-hydroxyindolin-2-one **2u** (0.12 mmol, 28.7 mg, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 2 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 40:60) to afford the product as a yellow oil (21.9 mg, 60%). R_f (CyH:EtOAc 1:1) = 0.27. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (d, J = 7.8 Hz, 1H), 7.34 – 7.27 (m, 5H), 7.21 (t, J = 7.6, 1H), 7.05 (td, J = 7.5, 1.0 Hz, 1H), 6.93 (d, J = 14.4 Hz, 1H), 6.70 (d, J = 7.6 Hz, 1H), 5.06 (dt, J = 14.3, 7.1 Hz, 1H), 5.03 (s, 1H), 4.92 (d, J = 15.7 Hz, 1H), 4.82 (d, J = 15.7 Hz, 1H), 4.48 – 4.40 (m, 3H), 4.30 (ddd, J = 11.2, 7.3, 1.0 Hz, 1H), 3.75 – 3.70 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 174.9, 155.4, 143.4, 135.6, 130.1, 129.0, 128.7, 127.9, 127.4, 125.5, 125.2, 123.1, 109.6, 106.2, 74.9, 67.7, 62.4, 43.8, 42.5. HPLC-LRMS (ESI) R_t = 5.7 min; *m/z* 751.00 $[2M + Na]^+$, 387.00 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{21}H_{20}N_2NaO_4^+$ 387.1315; Found 387.1309.

3-(*E*-3-(((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-17-((2*R*,5*S*,*E*)-5-ethyl-6-methylhept-3-en-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]oxazolidine-3-

yl)oxy)prop-1-en-1-yl)oxazolidine-2-one (4bv). Prepared according to a slightly modified **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), stigmasterol **2v** (0.12 mmol, 49.5 mg, 1.2 eq.), 1,1,1,3,3,3-hexafluoropropan-2-ol (0.1 mmol, 10.5 µL, 1 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 6 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 90:10 to 50:50) to afford the product as a yellow oil (32.8 mg, 61%). R_f (CyH:EtOAc 1:1) = 0.27. $[\alpha]_D^{20}$ = -20.5 (c = 1.00, $CHCl_3$). m.p. = 182 – 184 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (d, J = 14.3 Hz, 1H), 5.35 (d, J = 5.4 Hz, 1H), 5.15 (dd, J = 15.2, 8.6 Hz, 1H), 5.07 – 4.91 (m, 2H), 4.48 – 4.37 (m, 2H), 4.08 – 4.01 (m, 2H), 3.76 – 3.69 (m, 2H), 3.26 – 3.17 (m, 1H), 2.41 – 2.30 (m, 1H), 2.27 – 2.15 (m, 1H), 2.08 – 1.81 (m, 6H), 1.76 – 1.64 (m, 1H), 1.62 – 1.45 (m, 6H), 1.34 – 1.07 (m, 7H), 1.06 – 0.98 (m, 9H), 0.88 – 0.77 (m, 9H), 0.69 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.5, 141.0, 138.5, 129.4, 127.5, 121.9, 107.3, 78.4, 66.5, 62.3, 57.0, 57.0, 56.1, 51.4, 50.4, 42.6, 42.4, 40.6, 39.8, 39.3, 37.4, 37.0, 32.1, 32.0, 29.1, 28.6, 25.6, 24.5, 21.4, 21.2, 21.2, 19.5, 19.1, 12.4, 12.2. HPLC-LRMS (ESI) R_t = 5.3 min; *m/z* 576.20 $[M + K]^+$. HRMS (ESI) *m/z*: $[M + K]^+$ Calcd for $C_{35}H_{55}NKO_3^+$ 576.3814; Found 576.3827.

(*E*)-3-(3-(2-hydroxyethoxy)prop-1-en-1-yl)oxazolidin-2-one (4bw). Prepared according to **GP-A** or its modification using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), ethylene glycol **2w** (0.12 mmol, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and Anisole (0.2 M or 0.01 M). The reaction was stirred 2 h or 24 h at rt. The crude mixture was purified by FC (EtOAc:MeOH, from 100:0 to 95:5) to afford the product as a colourless oil and as a not separable mixture of **4bw** and **4bw'** (0.2 M: 55%, **4bw:4bw'** = 75:25; 0.01 M: 59%, **4bw:4bw'** = 88:12). R_f (EtOAc 100%) = 0.20. The NMR spectra of the major product **4bw** are described as follows: ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.92 (d, J = 14.3 Hz, 1H), 4.97 (dq, J = 14.0, 6.9 Hz, 1H), 4.50 – 4.41 (m, 2H), 4.06 (ddd, J = 6.3, 5.1, 1.1 Hz, 2H), 3.77 – 3.70 (m, 4H), 3.57 – 3.53 (m, 2H), 1.91 (t, J = 6.0 Hz, 1H).^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 155.4, 128.1, 106.3, 71.0, 69.8,

62.4, 62.0, 42.5. HPLC-LRMS (ESI) R_t = 1.5 min; *m/z* 413.1 $[2M+K]^+$, 397.2 $[2M+Na]^+$, 210.1 $[M+Na]^+$.

(*E*)-1-(3-(allyloxy)prop-1-en-1-yl)piperidin-2-one (4ca). Prepared according to a modification of **GP-A** using 1-(propa-1,2-dien-1-yl)piperidin-2-one **1c** (0.1 mmol, 13.7 mg, 1 eq.), allyl alcohol **2a** (0.12 mmol, 8.6 µL, 1.2 eq.), 60 µL of a stock solution 0.025 M of CSA in anisole (1.5 mol%, 0.015 eq.) and 0.44 mL of anisole (0.2 M). The reaction was stirred 4 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 50:50) to afford the product as a colourless oil (9.8 mg, 50%). R_f (CyH:EtOAc 1:1) = 0.38. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 14.6 Hz, 1H), 5.96 – 5.84 (m, 1H), 5.27 (dq, J = 17.3, 1.4 Hz, 1H), 5.17 (dq, J = 10.4, 1.4 Hz, 1H), 5.12 (dt, J = 14.6, 7.0 Hz, 1H), 4.03 (d, J = 7.0 Hz, 2H), 3.96 (app. dt, J = 5.7, 1.3 Hz, 2H), 3.41 (t, J = 6.2 Hz, 2H), 2.48 (t, J = 6.6 Hz, 2H), 1.92 – 1.85 (m, 2H), 1.84 – 1.76 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.9, 134.8, 130.7, 117.3, 106.5, 70.8, 69.6, 45.3, 33.0, 22.7, 20.6. HPLC-LRMS (ESI) R_t = 4.6 min; *m/z* 413.8 $[2M+Na]^+$, 218.0 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_{17}NNaO_2^+$ 218.1151; Found . 218.1171.

(*E*)-N-(3-(allyloxy)prop-1-en-1-yl)-N-phenylacetamide (4da). Prepared according to a modification of **GP-A** using *N*-phenyl-*N*-(propa-1,2-dien-1-yl)acetamide **1d** (0.1 mmol, 17.3 mg, 1 eq.), allyl alcohol **2a** (0.12 mmol, 8.6 µL, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 7 h at 50 °C. The crude mixture was purified by FC (CyH:EtOAc, from 95:5 to 60:40) to afford the product as a colourless oil (15.5 mg, 67%). R_f (CyH:EtOAc 7:3) = 0.45. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, J = 14.4 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.45 – 7.40 (m, 1H), 7.20 – 7.16 (m, 2H), 5.87 (ddt, J = 17.3, 10.4, 5.7 Hz, 1H), 5.23 (dq, J = 17.3, 1.6 Hz, 1H), 5.15 (dq, J = 10.4, 1.3 Hz, 1H), 4.53 (dt, J = 14.4, 7.1 Hz, 1H), 3.94 (dd, J = 7.1, 1.1 Hz, 2H), 3.91 (d, J = 5.7 Hz, 2H), 1.86 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 169.0, 139.7, 134.8, 131.8, 130.3, 129.0, 117.3, 109.5, 70.9, 69.2, 23.4. HPLC-LRMS (ESI) R_t = 7.1 min; *m/z* 485.1 $[2M+Na]^+$, 254.1 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{17}NNaO_2^+$ 254.1151; Found 254.1163.

(*E*)-*N*-(3-(allyloxy)prop-1-en-1-yl)-N,4-dimethylbenzenesulfonamide (4ea). Prepared according to a modification of **GP-A** using *N*,4-dimethyl-*N*-(propa-1,2-dienyl)benzenesulfonamide **1e** (0.1 mmol, 22.3 mg, 1 eq.), allyl alcohol **2a** (0.12 mmol, 8.6 µL, 1.2 eq.), 60 µL of a stock solution 0.025 M of CSA in anisole (1.5 mol%, 0.015 eq.) and 0.44 mL of anisole (0.2 M). The reaction was stirred 4 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 90:10 to 70:30) to afford the product as a colorless oil (12.4 mg, 44%). R_f (CyH:EtOAc 1:1) = 0.72. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 14.1 Hz, 1H), 5.97 – 5.83 (m, 1H), 5.26 (dq, J = 17.3, 1.7 Hz, 1H), 5.19 (dd, J = 10.5, 1.5 Hz, 1H), 4.83 (dt, J = 14.1, 7.0 Hz, 1H), 3.97 (dd, J = 7.0, 1.1 Hz, 2H), 3.94 (dt, J = 5.7, 1.4 Hz, 2H), 2.88 (s, 3H), 2.42 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.1, 134.9, 134.8, 131.8, 130.0, 127.2, 117.4, 106.0, 70.8, 69.1, 32.2, 21.7. HPLC-LRMS (ESI) R_t = 6.8 min; *m/z* 585.0 $[2M+Na]^+$, 304.2 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{19}NNaO_3S^+$ 304.0978; Found 304.0984.

(*E*)-*N*-(3-(allyloxy)prop-1-en-1-yl)-4-methyl-*N*-phenylbenzenesulfonamide (4fa). Prepared according to a modification of **GP-A** using 4-methyl-*N*-phenyl-*N*-(propa-1,2-dienyl)benzenesulfonamide **1f** (0.1 mmol, 28.5 mg, 1 eq.), allyl alcohol **2a** (0.12 mmol, 8.6 µL, 1.2 eq.), 60 µL of a stock solution 0.025 M of CSA in anisole (1.5 mol%, 0.015 eq.) and 0.44 mL of anisole (0.2 M). The reaction was stirred 6 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 95:5 to 70:30) to afford the product as a colourless oil (15.5 mg, 45%). R_f (CyH:EtOAc 1:1) = 0.83. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.4 Hz, 2H), 7.36 – 7.29 (m, 3H), 7.27 – 7.18 (m, 3H), 7.00 – 6.89 (m, 2H), 5.84 (ddt, J = 17.2, 10.3, 5.7 Hz, 1H), 5.21 (dq, J = 17.3, 1.7 Hz, 1H), 5.17 – 5.12 (m, 1H), 4.45 (dt, J = 14.0, 7.1 Hz, 1H), 3.91 – 3.82 (m, 4H), 2.41 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.2, 134.8, 132.8, 130.4, 129.8, 129.7, 129.3, 127.7, 117.4, 107.0, 70.9, 69.0, 21.7. HPLC-LRMS (ESI) R_t = 10.4 min; *m/z* 709.1 $[2M+Na]^+$, 366.2 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{21}NNaO_3S^+$ 366.1134; Found 366.1137.

3-(3-(allyloxy)-1-(trimethylsilyl)prop-1-en-1-yl)oxazolidin-2-one (4ga). Prepared according to **GP-A** using 3-(1-(trimethylsilyl)propa-1,2-dien-1-yl)oxazolidin-2-one **1g** (0.1 mmol, 19.7 mg, 1 eq.),

allyl alcohol **2a** (0.12 mmol, 8.6 µL, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 3.5 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 50:50) to afford the product as a colourless oil and as a mixture of diastereoisomers (*d.r.* 60:40, 11.7 mg, 46%). R_f (CyH:EtOAc 1:1) = 0.52. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 – 5.94 (m, 2H, *major and minor diastereoisomers*), 5.94 – 5.84 (m, 2H, *major and minor diastereoisomers*), 5.31 – 5.23 (m, 2H, *major and minor diastereoisomers*), 5.23 – 5.15 (m, 2H, *major and minor diastereoisomers*), 4.47 – 4.25 (m, 4H, *major and minor diastereoisomers*), 4.08 (d, J = 6.9 Hz, 2H, *major diasteroisomer*), 4.04 (d, J = 5.7 Hz, 2H, *minor diastereoisomer*), 3.97 (app. tt, J = 4.1, 1.2 Hz, 4H, *major and minor diastereoisomers*), 3.72 (app. ddd, J = 15.9, 8.6, 7.2 Hz, 4H, *major and minor diastereoisomers*), 0.26 (s, 9H, *major diastereoisomer*), 0.18 (s, 9H, *minor diastereoisomer*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, *reported as mixture of diastereoisomers*) δ 156.8, 156.3, 143.4, 140.0, 137.8, 134.6, 134.6, 131.8, 117.7, 117.7, 72.0, 71.7, 67.2, 67.0, 62.5, 62.3, 47.4, 46.7, 0.8, -0.8. HPLC R_t (*Z isomer)*: 7.3 min. HPLC-MS (ESI) *m/z* 533.1 $[2M+Na]^+$, 278.1 $[M + Na]^+$. HPLC-LRMS (ESI) R_t (*E major isomer)* = 7.6 min; *m/z* 533.1 $[2M+Na]^+$, 278.1 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{21}NNaO_3Si^+$ 278.1183; Found 278.1163.

(*E*)-3-(4-(allyloxy)but-2-en-2-yl)oxazolidin-2-one (4ma). Prepared according to **GP-A** using 3-(buta-2,3-dien-2-yl)oxazolidin-2-one **1m** (0.1 mmol, 13.9 mg, 1 eq.), allyl alcohol **2a** (0.12 mmol, 8.6 µL, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of Anisole (0.2 M). The reaction was stirred 4 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 40:60) to afford the product as a colourless oil (3.9 mg, 20%). R_f (CyH:EtOAc 1:1) = 0.31. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.93 (ddt, J = 17.3, 10.4, 5.8 Hz, 1H), 5.29 (ddd, J = 16.1, 3.3, 1.6 Hz, 1H), 5.24 – 5.18 (m, 1H), 5.06 (td, J = 7.0, 1.1 Hz, 1H), 4.38 – 4.31 (m, 2H), 4.06 (dd, J = 7.1, 0.6 Hz, 2H), 3.99 (dt, J = 5.7, 1.4 Hz, 2H), 3.83 – 3.76 (m, 2H), 2.21 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 155.2, 137.9, 134.8, 117.6, 109.2, 71.3, 65.7, 61.4, 45.8, 14.5.

HPLC-LRMS (ESI) R_t = 3.1 min; *m/z* 417.1 $[2M+Na]^+$, 220.1 $[M+Na]^+$. HRMS(ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{10}H_{15}NNaO_3^+$ 220.0944; Found 220.0947.

(*E*)-*N*-(3-(allyloxy)but-1-en-1-yl)-4-methyl-*N*-phenylbenzenesulfonamide (4na). Prepared according to a modification of **GP-A** using *N*-(buta-1,2-dien-1-yl)-4-methyl-*N*-phenylbenzenesulfonamide **1n** (0.1 mmol, 29.9 mg, 1 eq.), allyl alcohol **2a** (0.12 mmol, 8.6 µL, 1.2 eq.), 60 µL of a stock solution 0.025 M of CSA in anisole (1.5 mol%, 0.015 eq.) and 0.44 mL of anisole (0.2 M). The reaction was stirred 3 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 100:0 to 90:10) to afford the product as a colourless oil (8.9 mg, 25%). R_f (CyH:EtOAc 7:3) = 0.68. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.0 Hz, 1H), 7.37 – 7.30 (m, 3H), 7.24 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 14.0 Hz, 1H), 6.98 – 6.91 (m, 2H), 5.91 – 5.77 (m, 1H), 5.25 – 5.16 (m, 1H), 5.17 – 5.09 (m, 1H), 4.25 (dd, J = 14.0, 8.4 Hz, 1H), 3.96 – 3.82 (m, 2H), 3.78 (dd, J = 12.7, 6.1 Hz, 2H), 2.42 (s, 3H), 1.15 (d, J = 6.4 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.0, 136.3, 135.7, 135.1, 131.0, 130.1, 129.6, 129.5, 129.0, 127.5, 116.6, 112.8, 74.1, 68.6, 22.1, 21.6. HPLC-LRMS (ESI) R_t = 8.8 min; *m/z* 358.1 $[M+H]^+$. HRMS(ESI) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{24}NO_3S^+$ 358.1471; Found 358.1468.

1-(1,3-bis(allyloxy)propyl)pyrrolidin-2-one (5aa). Prepared according to **GP-A** using 1-(propa-1,2-dien-1-yl)pyrrolidin-2-one **1a** (0.1 mmol, 12.3 mg, 1 eq.), allyl alcohol **2a** (0.12 mmol, 8.6 µL, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 5 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 40:60) to afford the product as a colourless oil (7.2 mg, 30%). R_f (CyH:EtOAc 1:1) = 0.39. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 – 5.80 (m, 2H), 5.43 (t, J = 6.8 Hz, 1H), 5.32 – 5.25 (m, 1H), 5.28 – 5.20 (m, 1H), 5.21 – 5.12 (m, 2H), 3.93 (app. dd, J = 10.0, 5.3 Hz, 4H), 3.51 – 3.43 (m, 2H), 3.37 (q, J = 6.5 Hz, 2H), 2.47 – 2.38 (m, 2H), 2.08 – 1.95 (m, 3H), 1.87 (dq, J = 13.6, 6.8 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.0, 134.9, 134.2, 117.3, 117.1, 78.9, 72.2, 69.1, 66.3, 41.5, 33.2, 31.9, 18.4. HPLC-LRMS (ESI) R_t = 3.4 min; *m/z* 501.2 $[2M+Na]^+$, 262.20 $[M + H]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{21}NNaO_3^+$ 262.1414; Found 262.1424.

(*E*)-3-(3-(4-hydroxyphenyl)prop-1-en-1-yl)oxazolidin-2-one (6). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidine-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), phenol **2x** (0.12 mmol, 14.5 mg, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 2 h at rt. The crude mixture was purified by FC (from 50:50 CyH:EtOAc to 80:20 EtOAc:MeOH) to afford the product as a yellow oil (8.8 mg, 40%). R_f (EtOAc:MeOH 9:1) = 0.40. ^{1}H NMR (400 MHz, CD_3OD) δ 7.06 – 6.98 (m, 2H), 6.74 – 6.69 (m, 2H), 6.63 (d, J = 14.2, 1H), 5.10 (dt, J = 14.2, 7.0 Hz, 1H), 4.51 – 4.39 (m, 2H), 3.80 – 3.70 (m, 2H), 3.31 (bs, J = 1.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD) δ 157.9, 156.8, 132.6, 130.4, 125.2, 116.2, 112.8, 64.1, 44.0, 36.2. HPLC-LRMS (ESI) R_t = 3.9 min; *m/z* 461.8 $[2M+Na]^+$, 242.8 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{13}NNaO_3^+$ 242.0788; Found 242.0776.

(*E*)-3-(3-(4-methoxyphenyl)prop-1-en-1-yl)oxazolidin-2-one (7). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), 1,1,1,3,3,3-hexafluoropropan-2-ol (0.12 mmol, 12.6 µL, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 2 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 40:60) to afford the product as a yellow oil (12.1 mg, 52%). R_f (CyH:EtOAc 1:1) = 0.37. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 8.8 Hz, 1H), 6.84 (d, J = 8.8 Hz, 1H), 6.75 (app. dt, J = 14.3, 1.5 Hz, 1H), 4.94 (dt, J = 14.3, 7.2 Hz, 1H), 4.45 – 4.39 (m, 2H), 3.79 (s, 3H), 3.71 – 3.66 (m, 2H), 3.34 (d, J = 7.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.3, 132.6, 129.5, 124.8, 114.3, 114.1, 110.7, 62.3, 55.4, 42.8, 35.5. HPLC-LRMS (ESI) R_t = 6.3 min; *m/z* 488.6 $[2M+Na]^+$, 256.0 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{15}NNaO_3^+$ 256.0944; Found 256.0953.

(*E*)-3-(3-(hexylthio)prop-1-en-1-yl)oxazolidin-2-one (8ba). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), 1-hexanethiol **11a** (0.12 mmol, 17.0 µL, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 2.5 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 50:50) to afford the product as a yellow oil (12.4 mg, 51%). R_f

(CyH:EtOAc 1:1) = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (d, J = 14.2 Hz, 1H), 4.82 (dt, J = 14.2, 7.6 Hz, 1H), 4.47 – 4.42 (m, 2H), 3.75 – 3.68 (m, 2H), 3.17 (d, J = 7.6 Hz, 2H), 2.48 – 2.41 (m, 2H), 1.60 – 1.51 (m, 2H), 1.41 – 1.23 (m, 6H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.4, 125.8, 107.4, 62.3, 42.7, 32.0, 31.6, 31.1, 29.5, 28.7, 22.7, 14.2. HPLC-LRMS (ESI) R_t = 7.1 min; *m/z* 509.2 $[2M+Na]^+$, 266.2 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{21}NNaO_2S^+$ 266.1185; Found 266.1197.

(*E*)-3-(3-(benzylthio)prop-1-en-1-yl)oxazolidin-2-one (8bb). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), phenylmethanethiol **11b** (0.12 mmol, 14.0 µL, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 5 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 80:20 to 50:50) to afford the product as a yellow oil (16.9 mg, 68%). R_f (CyH:EtOAc 1:1) = 0.66. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 4H), 7.23 – 7.16 (m, 1H), 6.66 (d, J = 14.2 Hz, 1H), 4.70 (dt, J = 14.2, 7.6 Hz, 1H), 4.42 – 4.35 (m, 2H), 3.64 (s, 2H), 3.62 – 3.56 (m, 2H), 3.06 (dd, J = 7.6, 1.2 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 155.3, 138.5, 129.1, 128.7, 127.1, 126.3, 107.0, 62.3, 42.6, 35.6, 31.6. HPLC-LRMS (ESI) R_t = 7.4 min; *m/z* 521.00 $[2M + Na]^+$, 272.10 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{15}NNaO_2S^+$ 272.0716; Found 272.0709.

(*E*)-3-(3-(isopropylthio)prop-1-en-1-yl)oxazolidin-2-one (8bc). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), propane-2-thiol **11c** (0.12 mmol, 18.2 µL, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 4 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 50:50) to afford the product as a yellow oil (15.1 mg, 75%). R_f (CyH:EtOAc 1:1) = 0.51. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (d, J = 14.2 Hz, 1H), 4.84 (dt, J = 14.2, 7.6 Hz, 1H), 4.48 – 4.41 (m, 2H), 3.82 – 3.61 (m, 2H), 3.22 (app. dd, J = 7.6, 1.2 Hz, 2H), 2.87 (hept, J = 6.7 Hz, 1H), 1.25 (d, J = 6.7 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.4, 125.6, 107.6,

62.3, 42.6, 34.0, 30.8, 23.3. HPLC-LRMS (ESI) R_t = 14.9 min; *m/z* 425.0 $[2M+Na]^+$, 224.2 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_9H_{15}NNaO_2S^+$ 224.0716; Found 224.0723.

(*E*)-3-(3-(*tert*-butylthio)prop-1-en-1-yl)oxazolidin-2-one (8bd). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), 2-methylpropane-2-thiol **11d** (0.12 mmol, 13.5 µL, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 5 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 80:20 to 50:50) to afford the product as a yellow oil (15.9 mg, 74%). R_f (CyH:EtOAc 1:1) = 0.68. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.81 (d, J = 14.2 Hz, 1H), 4.85 (dt, J = 14.2, 7.6 Hz, 1H), 4.47 – 4.39 (m, 2H), 3.73 – 3.66 (m, 2H), 3.26 (dd, J = 7.5, 1.3 Hz, 2H), 1.33 (s, 9H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 155.3, 125.9, 107.4, 62.3, 43.0, 42.6, 31.1, 28.9. HPLC-LRMS (ESI) R_t = 6.8 min; *m/z* 453.2 $[2M + Na]^+$, 238.10 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{10}H_{17}NNaO_2S^+$ 238.0872; Found 238.0866.

(*E*)-3-(3-(phenylthio)prop-1-en-1-yl)oxazolidin-2-one (8be). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), benzenethiol **11e** (0.12 mmol, 15.4 µL, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 2 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 80:20 to 50:50) to afford the product as white waxy solid (11.7 mg, 50%). R_f (CyH:EtOAc 1:1) = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.18 (m, 4H), 7.16 – 7.11 (m, 1H), 6.68 (d, J = 14.1 Hz, 1H), 4.80 (dt, J = 14.1, 7.5 Hz, 1H), 4.38 – 4.32 (m, 2H), 3.59 (t, J = 8.1 Hz, 2H), 3.54 (d, J = 7.5 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.3, 135.7, 130.3, 129.1, 126.8, 126.7, 106.1, 62.3, 42.6, 34.8. HPLC-LRMS (ESI) R_t = 7.1 min; *m/z* 493.1 $[2M+Na]^+$, 258.2 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{13}NNaO_2S^+$ 258.0559; Found 258.0549.

(*E*)-3-(3-tosylprop-1-en-1-yl)oxazolidin-2-one (8bf). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), benzenesulfinic acid **11f** (0.12 mmol, 17.0 mg, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 1.5 h at rt. The crude mixture was purified by FC

(CyH:EtOAc, from 60:40 to 30:70) to afford the product as a colourless oil (14.0 mg, 50%). R_f (CyH:EtOAc 1:1) = 0.19. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 6.66 (d, J = 14.2 Hz, 1H), 4.81 (dt, J = 14.2, 7.8 Hz, 1H), 4.50 – 4.42 (m, 2H), 3.78 (d, J = 7.8 Hz, 1H), 3.76 – 3.67 (m, 2H), 2.45 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.0, 145.1, 135.4, 131.5, 130.0, 128.5, 96.1, 62.4, 58.3, 42.4, 21.8. HPLC-LRMS (ESI) R_t = 13.2 min; *m/z* 585.00 $[2M+Na]^+$, 304.00 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{15}NNaO_4S^+$ 304.0614; Found 304.0632.

(*E*)-*N*-methyl-N-(3-(2-oxooxazolidin-3-yl)allyl)ethanethioamide (8bg). Prepared according to a modification of **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), *N*-methylethanethioamide **11g** (0.12 mmol, 10.7 mg, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 2.5 h at 80 °C. The crude mixture was purified by FC (CyH:EtOAc, from 50:50 to 0:100) to afford the product as a colourless oil and as a mixture of diastereoisomers (*d.r.* 67:33, 13.1 mg, 61%). R_f (CyH:EtOAc 1:1) = 0.15. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (d, J = 14.2 Hz, 1H, *minor diastereoisomer*), 6.80 (d, J = 14.2 Hz, 1H *major diastereoisomer*), 4.83 (dt, J = 14.2, 7.1 Hz, 1H, *major diastereoisomer*), 4.75 (dt, J = 14.2, 6.8 Hz, 1H, *minor diastereoisomer*), 4.52 – 4.41 (m, 2H *minor diastereoisomer, 2H, major diastereoisomer*), 3.97 (d, J = 7.1 Hz, 2H, *major diastereoisomer*), 3.91 (d, J = 6.8 Hz, 2H, *minor diastereoisomer*), 3.75 – 3.65 (m, 2H *minor diastereoisomer, 2H, major diastereoisomer*), 2.94 (s, 3H, *major diastereoisomer*), 2.8 9 (s, 3H, *minor diastereoisomer*), 2.12 (s, 3H, *minor diastereoisomer*), 2.09 (s, 3H, *major diastereoisomer*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, reported as mixture of diastereoisomers) δ 170.7, 170.4, 155.5, 155.4, 127.3, 127.0, 105.4, 104.5, 62.4, 50.6, 47.3, 42.6, 42.6, 35.4, 32.9, 22.0, 21.6, 21.5. HPLC-LRMS (ESI) R_t = 7.9 min; *m/z* 237.00 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_9H_{14}N_2NaO_2S^+$ 237.0668; Found 237.0679.

(*E*)-*N*-(3-(*tert*-butylthio)prop-1-en-1-yl)-*N*-phenylacetamide (8dd). Prepared according to **GP-A** using *N*-phenyl-*N*-(propa-1,2-dien-1-yl)acetamide **1d** (0.1 mmol, 17.3 mg, 1 eq.), 2-methylpropane-2-thiol **11d** (0.12 mmol, 13.5 µL, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1

mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 3 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 95:5 to 70:30) to afford the product as a colourless oil (19.2 mg, 73%). R_f (CyH:EtOAc 7:3) = 0.47. ^{1}H NMR (400 MHz, $CDCl_3$) 7.63 (d, J = 14.4 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.44 – 7.38 (m, 1H), 7.19 – 7.13 (m, 2H), 4.43 (dt, J = 14.4, 7.6 Hz, 1H), 3.20 (d, J = 7.6 Hz, 2H), 1.84 (s, 3H), 1.28 (s, 9H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 168.7, 139.8, 130.2, 130.1, 128.9, 128.9, 110.4, 42.7, 31.1, 29.3, 23.3. HPLC-LRMS (ESI) R_t = 9.4 min; *m/z* 549.2 $[2M+Na]^+$, 286.1 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{21}NNaOS^+$ 286.1236; Found 286.1241.

(*E*)-*N*-(3-(*tert*-butylthio)prop-1-en-1-yl)-4-methyl-*N*-phenylbenzenesulfonamide (8fd). Prepared according to a modification of **GP-A** using 4-methyl-*N*-phenyl-*N*-(propa-1,2-dienyl)benzenesulfonamide **1f** (0.1 mmol, 28.5 mg, 1 eq.), 2-methylpropane-2-thiol **11d** (0.12 mmol, 13.5 µL, 1.2 eq.), 60 µL of a stock solution 0.025 M of CSA in anisole (1.5 mol%, 0.015 eq.) and 0.44 mL of anisole (0.2 M). The reaction was stirred 2.5 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 90:10 to 60:40) to afford the product as a colourless oil (20.6 mg, 55%). R_f (CyH:EtOAc 1:1) = 0.62. ^{1}H NMR (400 MHz, $CDCl_3$) 7.53 (d, J = 8.4 Hz, 2H), 7.37 – 7.28 (m, 2H), 7.25 (d, J = 8.1 Hz, 2H), 7.17 – 7.08 (m, 1H), 7.00 – 6.91 (m, 2H), 4.38 (dt, J = 14.0, 7.6 Hz, 1H), 3.16 (dd, J = 7.6, 1.1 Hz, 2H), 2.42 (s, 3H), 1.26 (s, 9H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 143.9, 136.4, 135.8, 130.8, 130.2, 129.6, 129.5, 129.0, 127.5, 107.9, 42.7, 30.8, 28.9, 21.6. HPLC-LRMS (ESI) R_t = 12.0 min; *m/z* 773.1 $[2M+Na]^+$, 398.1 $[M + Na]^+$, 376.1 $[M + H]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{25}NNaO_2S_2^+$ 398.1219; Found 398.1209.

(*E*)-*N*,4-dimethyl-*N*-(3-(2-oxooxazolidin-3-yl)allyl)benzenesulfonamide (9bc). Prepared according to **GP-A** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), *N*,4-dimethylbenzenesulfonamide **12c** (0.12 mmol, 22.2 mg, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 3 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 40:60) to afford the product as a colourless oil (22.0 mg, 71%). R_f (CyH:EtOAc 1:1) = 0.19. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66

(d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 6.73 (d, J = 14.3 Hz, 1H), 4.76 (dt, J = 14.3, 7.3 Hz, 1H), 4.48 – 4.41 (m, 1H), 3.70 – 3.64 (m, 1H), 3.62 (app. dd, J = 7.3, 1.2 Hz, 1H), 2.64 (s, 3H), 2.43 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 155.3, 143.7, 134.4, 129.9, 128.1, 127.6, 104.7, 62.4, 50.5, 42.5, 34.1, 21.6. HPLC-LRMS (ESI) R_t = 6.1 min; *m/z* 643.6 $[2M+Na]^+$, 333.8 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{18}N_2NaO_4S^+$ 333.0879; Found 333.0891.

*General Procedure B (**GP-B**) for the synthesis of products **9**.* A Schlenk tube equipped with a magnetic stirring bar was dried under vacuum and refilled with Argon. The reaction vessel was then charged with the allenamide **1** (0.1 mmol, 1 eq.), anisole (0.46 mL, 0.2M), the aza-nucleophile (0.12 mmol, 1.2 eq) and 40 µL of a 0.025 M (1.0 µmol, 0.01 eq., 1 mol%) stock solution of CSA in anisole. The reaction mixture was then allow to stir at 80 °C until complete consumption of the starting material, as observed by TLC analysis. After the reported time the reaction was cooled down, diluted with ca. 3 mL of ethyl acetate and added to a separatory funnel containing 5 mL of a saturated aqueous solution of $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with EtOAc (2 x 3 mL). The combined organic extracts were dried over sodium sulphate, and concentrated under vacuum (0.5 mbar). The NMR yield was determined by adding methyl acetoacetate (0.1 mmol, 1 eq.) as internal standard to the crude mixture dissolved in $CDCl_3$. Purification of the crude product by flash chromatography on silica gel afforded the desired product.

(*E*)-3,3'-(prop-1-ene-1,3-diyl)bis(oxazolidin-2-one) (9ba). Prepared according to **GP-B** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), 2-oxazolidinone **12a** (0.12 mmol, 10.4 mg, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 3 h at 80 °C. The crude mixture was purified by FC (CyH:EtOAc, from 30:70 to 0:100) to afford the product as a colourless oil (14.9 mg, 70%). R_f (EtOAc) = 0.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (d, J = 14.4 Hz, 1H), 4.81 (dt, J = 14.4, 7.2 Hz, 1H), 4.51 – 4.42 (m, 2H), 4.35 – 4.29 (m, 2H), 3.90 (app. dd, J = 7.4, 1.1 Hz, 2H), 3.75 – 3.68 (m, 2H), 3.57 – 3.46 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 158.3, 155.4, 128.2, 103.9, 62.4, 62.0,

44.3, 44.1, 42.6. HPLC-LRMS (ESI) R_t = 8.6 min; *m/z* 447.20 $[2M+Na]^+$, 235.2 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_9H_{12}N_2NaO_4^+$ 235.0689; Found 235.0677.

(*E*)-*N*-(3-(2-oxooxazolidin-3-yl)prop-1-en-1-yl)-*N*-phenylacetamide (9bb). Prepared according to **GP-B** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), *N*-phenylacetamide **12b** (0.12 mmol, 16.2 mg, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 3 h at 80 °C. The crude mixture was purified by FC (CyH:EtOAc, from 90:10 to 60:40) to afford the product as a colorless oil (8.9 mg, 34%). R_f (CyH:EtOAc 75:25) = 0.32. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 2H), 7.36 – 7.32 (m, 1H), 7.13 – 7.09 (m, 2H), 6.62 (d, J = 14.4 Hz, 1H), 4.99 (dt, J = 14.4, 7.2 Hz, 1H), 4.45 – 4.40 (m, 2H), 4.28 (dd, J = 7.2, 1.2 Hz, 2H), 3.71 – 3.65 (m, 2H), 1.85 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 170.4, 155.4, 142.8, 129.9, 128.2, 128.2, 127.3, 105.5, 62.3, 49.6, 42.6, 22.9. HPLC-LRMS (ESI) R_t = 2.2 min; *m/z* 543.20 $[2M+Na]^+$, 238.2 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{16}N_2NaO_3^+$ 283.1053; Found 283.1047.

(*E*)-3-(3-(9H-carbazol-9-yl)prop-1-en-1-yl)oxazolidin-2-one (9bd). Prepared according to **GP-B** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), 9H-carbazole **12d** (0.12 mmol, 20.1 mg, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 2.5 h at 80 °C. The crude mixture was purified by FC (CyH:EtOAc, from 90:10 to 60:40) to afford the product as a colourless oil (19.6 mg, 67%). R_f (CyH:EtOAc 1:1) = 0.63. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, J = 7.8 Hz, 2H), 7.51 – 7.45 (m, 2H), 7.43 (d, J = 8.1 Hz, 2H), 7.30 – 7.23 (m, 2H), 7.07 (d, J = 13.2 Hz, 1H), 4.99 – 4.90 (m, 3H), 4.39 – 4.33 (m, 2H), 3.58 – 3.53 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 155.4, 140.1, 127.2, 125.9, 123.2, 120.6, 119.3, 108.8, 105.0, 62.3, 42.8, 42.5. HPLC-LRMS (ESI) R_t = 8.6 min; *m/z* 607.2 $[2M+Na]^+$, 315.2 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{16}N_2NaO_2^+$ 315.1104; Found 315.1118.

(*E*)-*N*-(3-(2-oxooxazolidin-3-yl)prop-1-en-1-yl)-*N*-phenylacetamide (9da). Prepared according to **GP-B** using *N*-phenyl-*N*-(propa-1,2-dien-1-yl)acetamide **1d** (0.1 mmol, 17.3 mg, 1 eq.), 2-

oxazolidinone **12a** (0.12 mmol, 10.4 mg, 1.2 eq.), 40 µL of a stock solution 0.025 M of CSA in anisole (1 mol%, 0.01 eq.) and 0.46 mL of anisole (0.2 M). The reaction was stirred 2.5 h at 80 °C. The crude mixture was purified by FC (CyH:EtOAc, from 50:50 to 0:100) to afford the product as a colourless oil (14.8 mg, 57%). R_f (CyH:EtOAc 1:1) = 0.10. ^{1}H NMR (400 MHz, $CDCl_3$) 7.67 (d, J = 14.2 Hz, 1H), 7.53 – 7.41 (m, 3H), 7.18 – 7.11 (m, 2H), 4.34 (dt, J = 14.2, 7.3 Hz, 1H), 3.83 (d, J = 7.3 Hz, 2H), 3.47 – 3.40 (m, 4H), 1.86 (s, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 169.1, 158.2, 139.4, 132.2, 130.4, 129.2, 128.7, 106.8, 61.8, 44.6, 44.0, 23.3. HPLC-LRMS (ESI) R_t = 3.9 min; *m/z* 543.2 $[2M+Na]^+$, 283.1 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{16}N_2NaO_3^+$ 283.1053; Found 283.1064.

*General Procedure C (**GP-C**) for the synthesis of products **10***. A Schlenk tube equipped with a magnetic stirring bar was dried under vacuum and refilled with Argon. The reaction vessel was then charged with the allenamide **1** (0.1 mmol, 1 eq.), anisole (0.5 mL, 0.2 M) and the carboxylic acid **13** (0.3 mmol, 3 eq.). The reaction mixture was then allow to stir at 80 °C until complete consumption of the starting material, as observed by TLC analysis. After the reported time the reaction was cooled down, diluted with ca. 3 mL of ethyl acetate and added to a separatory funnel containing 5 mL of a saturated aqueous solution of $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with EtOAc (2 x 3 mL). The combined organic extracts were dried over sodium sulphate, and concentrated under vacuum (0.5 mbar). The NMR yield was determined by adding methyl acetoacetate (0.1 mmol, 1 eq.) as internal standard to the crude mixture dissolved in $CDCl_3$. Purification of the crude product by flash chromatography on silica gel afforded the desired product.

(*E*)-3-(2-oxooxazolidin-3-yl)allyl acetate (10ba). Prepared according to **GP-C** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), acetic acid **13a** (0.3 mmol, 17.2 µL, 3 eq.) and 0.5 mL of anisole (0.2 M). The reaction was stirred 3 h at 80 °C. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 40:60) to afford the product as a colourless oil (14.4 mg, 78%). R_f (CyH:EtOAc 1:1) = 0.29. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, J = 14.3 Hz, 1H), 4.98 (dt, J = 14.3, 7.2 Hz, 1H), 4.59 (d, J = 7.2, 2H), 4.50 – 4.39 (m, 2H), 3.77 – 3.63 (m, 2H), 2.05 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 171.0, 155.3, 129.5, 104.1, 63.3, 62.4, 42.5, 21.2. HPLC-LRMS (ESI) R_t = 10.8 min; *m/z* 393.00 $[2M+Na]^+$, 208.00 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_8H_{11}NNaO_4^+$ 208.0580; Found 208.0560.

(*E*)-3-(2-oxooxazolidin-3-yl)allyl benzoate (10bb). Prepared according to **GP-C** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), benzoic acid **13b** (0.3 mmol, 36.6 mg, 3 eq.) and 0.5 mL of anisole (0.2 M). The reaction was stirred 2.5 h at 80 °C. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 50:50) to afford the product as a colourless oil (18.3 mg, 74%). In this case, the aqueous phase was acidified and extracted with EtOAc (3 x 4 mL) allowing us to fully (94%) recover benzoic acid **13b**. R_f (CyH:EtOAc 1:1) = 0.42. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.95 (m, 2H), 7.56 (ddt, J = 7.9, 6.9, 1.3 Hz, 1H), 7.48 – 7.38 (m, 2H), 7.07 (d, J = 14.2 Hz, 1H), 5.11 (dt, J = 14.2, 7.3 Hz, 1H), 4.85 (app. dd, J = 7.3, 1.0 Hz, 2H), 4.50 – 4.43 (m, 2H), 3.79 – 3.70 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 166.6, 155.3, 133.2, 130.3, 129.7, 129.7, 128.5, 104.3, 63.9, 62.4, 42.5. HPLC-LRMS (ESI) R_t = 6.2 min; *m/z* 517.00 $[2M+Na]^+$, 270.20 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{13}NNaO_4^+$ 270.0737; Found 270.0748.

(*E*)-3-(2-oxooxazolidin-3-yl)allyl pivalate (10bc). Prepared according to **GP-C** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), pivalic acid **13c** (0.3 mmol, 30.6 mg, 3 eq.) and 0.5 mL of anisole (0.2 M). The reaction was stirred 8 h at 80 °C. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 50:50) to afford the product as a colourless oil (16.1 mg, 71%). R_f (CyH:EtOAc 1:1) = 0.39. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (d, J = 14.3 Hz, 1H), 4.98 (dt, J = 14.3, 7.1 Hz, 1H), 4.57 (app. dd, J = 7.1, 1.1 Hz, 2H), 4.50 – 4.40 (m, 2H), 3.77 – 3.68 (m, 2H), 1.19 (s, 9H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 178.6, 155.3, 129.2, 104.5, 63.3, 62.4, 42.5, 38.8, 27.3. HPLC-LRMS (ESI) R_t = 15.1 min; *m/z* 477.20 $[2M+Na]^+$, 250.20 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_{17}NNaO_4^+$ 250.1050; Found 250.1038.

(*E*)-3-(2-oxooxazolidin-3-yl)allyl thiophene-2-carboxylate (10bd). Prepared according to **GP-C** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), thiophene-2-carboxylic acid **13d** (0.3 mmol, 38.3 mg, 3 eq.) and 0.5 mL of anisole (0.2 M). The reaction was stirred 2 h at

80 °C. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 40:60) to afford the product as a colourless oil (23.3 mg, 92%). R_f (CyH:EtOAc 1:1) = 0.38. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.55 (dd, *J* = 4.9, 1.3 Hz, 1H), 7.09 (dd, *J* = 4.9, 3.8 Hz, 1H), 7.04 (d, *J* = 14.2 Hz, 1H), 5.08 (dt, *J* = 14.2, 7.3 Hz, 1H), 4.81 (d, *J* = 7.3 Hz, 1H), 4.51 – 4.38 (m, 2H), 3.79 – 3.68 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.2, 155.3, 133.8, 133.7, 132.6, 129.9, 127.9, 104.0, 64.0, 62.4, 42.5. HPLC-LRMS (ESI) R_t = 14.2 min; *m/z* 529.00 $[2M+Na]^+$, 276.00 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_{11}NNaO_4S^+$ 276.0301; Found 276.0311.

(*E*)-3-(2-oxooxazolidin-3-yl)allyl cinnamate (10be). Prepared according to **GP-C** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), cinnamic acid **13e** (0.3 mmol, 44.4 mg, 3 eq.) and 0.5 mL of anisole (0.2 M). The reaction was stirred 2 h at 80 °C. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 40:60) to afford the product as a colourless oil (21.6 mg, 79%). R_f (CyH:EtOAc 1:1) = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 16.0 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.43 – 7.35 (m, 3H), 7.03 (d, J = 14.3 Hz, 1H), 6.43 (d, J = 16.0 Hz, 1H), 5.05 (dt, J = 14.3, 7.2 Hz, 1H), 4.73 (app. dd, J = 7.2, 1.1 Hz, 2H), 4.54 – 4.42 (m, 2H), 3.80 – 3.66 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.9, 155.3, 145.2, 134.4, 130.5, 129.5, 129.0, 129.0, 128.2, 118.0, 104.2, 63.4, 62.4, 42.5. HPLC-LRMS (ESI) R_t = 3.3 min; *m/z* 569.2 $[2M+Na]^+$, 296.20 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{15}NNaO_4^+$ 296.0893; Found 296.0900..

(*E*)-3-(2-oxooxazolidin-3-yl)allyl (*tert*-butoxycarbonyl)-*L*-phenylalaninate (10bf). Prepared according to **GP-C** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), (*tert*-butoxycarbonyl)-*L*-phenylalanine **13f** (0.3 mmol, 79.6 mg, 3 eq.) and 0.5 mL of anisole (0.2 M). The reaction was stirred 2 h at 80 °C. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 40:60) to afford the product as a colourless oil (31.2 mg, 80%). R_f (CyH:EtOAc 1:1) = 0.27. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.21 (m, 3H), 7.12 (d, J = 6.5 Hz, 2H), 6.95 (d, J = 14.3 Hz, 1H), 4.98 (d, J = 8.8 Hz, 1H), 4.89 (dt, J = 14.3, 7.4 Hz, 1H), 4.61 (app. t, J = 7.8 Hz, 2H), 4.66 – 4.52 (m, 1H), 4.49 – 4.43 (m, 2H), 3.78 – 3.62 (m, 2H), 3.07 (qd, J = 14.0, 6.4 Hz, 2H), 1.41 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.8, 155.2, 155.1, 136.1, 130.1, 129.5, 128.6, 127.1, 103.5, 80.0, 64.2,

62.4, 54.6, 42.4, 38.5, 28.4. HPLC-LRMS (ESI) R_t = 16.5 min; *m/z* 803.20 $[2M+Na]^+$, 413.2 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{26}N_2NaO_6^+$ 413.1683; Found 413.1694.

(*E*)-1-(*tert*-butyl) 2-(3-(2-oxooxazolidin-3-yl)allyl) (*S*)-pyrrolidine-1,2-dicarboxylate (10bg). Prepared according to **GP-C** using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (0.1 mmol, 12.5 mg, 1 eq.), (*tert*-butoxycarbonyl)-*L*-proline **13g** (0.3 mmol, 64.6 mg, 3 eq.) and 0.5 mL of anisole (0.2 M). The reaction was stirred 2 h at 80 °C. The crude mixture was purified by FC (CyH:EtOAc, from 80:20 to 50:50) to afford the product as a colourless oil (28.7 mg, 84%). R_f (CyH:EtOAc 1:1) = 0.53. ^{1}H NMR (400 MHz, $CDCl_3$, reported as mixture of rotamers due to the Boc protecting group) δ 7.01 – 6.90 (m, 1H), 4.97 (dt, J = 14.4, 7.4 Hz, 1H), 4.62 (app. t, J = 7.6 Hz, 2H), 4.50 – 4.39 (m, 2H), 4.24 (ddd, J = 35.6, 8.8, 3.8 Hz, 1H), 3.70 (app. t, J = 8.1 Hz, 2H), 3.56 – 3.34 (m, 2H), 2.28 – 2.10 (m, 1H), 2.00 – 1.80 (m, 3H), 1.44 (s, 4H), 1.40 – 1.35 (m, 5H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, reported as mixture of rotamers due to the Boc protecting group) δ 173.2, 173.0, 155.3, 154.5, 153.9, 129.8, 129.4, 104.1, 103.7, 80.0, 79.9, 63.8, 63.8, 62.4, 59.3, 59.0, 46.7, 46.4, 42.5, 42.4, 31.0, 30.0, 28.5, 28.5, 24.5, 23.8. HPLC-LRMS (ESI) R_t = 6.0 min; *m/z* 703.6 $[2M+Na]^+$, 363.6 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{24}N_2NaO_6^+$ 363.1527; Found 363.1540.

(*E*)-3-(2-oxopyrrolidin-1-yl)allyl benzoate (10ab). Prepared according to **GP-C** using 1-(propa-1,2-dien-1-yl)pyrrolidin-2-one **1a** (0.1 mmol, 12.3 mg, 1 eq.), benzoic acid **13b** (0.3 mmol, 36.6 mg, 3 eq.) and 0.5 mL of anisole (0.2 M). The reaction was stirred 2 h at 80 °C. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 50:50) to afford the product as a colourless oil (15.9 mg, 65%). R_f (CyH:EtOAc 1:1) = 0.41. ^{1}H NMR (400 MHz, $CDCl_3$) 8.07 – 8.00 (m, 2H), 7.59 – 7.50 (m, 1H), 7.46 – 7.39 (m, 2H), 7.26 (d, J = 14.5 Hz, 1H), 5.20 (dt, J = 14.5, 7.2 Hz, 1H), 4.85 (app. dd, J = 7.2, 1.1 Hz, 2H), 3.54 (t, J = 7.2 Hz, 2H), 2.50 (app. dd, J = 8.7, 7.2 Hz, 2H), 2.12 (app. qd, J = 8.7, 6.9 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.7, 166.6, 133.1, 130.4, 129.7, 129.2, 128.5, 105.0, 64.4, 45.2, 31.2, 17.6. HPLC-LRMS (ESI) R_t = 3.8 min; *m/z* 268.2 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{15}NNaO_3^+$ 268.0944; Found 268.0965.

(*E*)-3-(2-oxopiperidin-1-yl)allyl benzoate (10cb). Prepared according to **GP-C** using 1-(propa-1,2-dien-1-yl)piperidin-2-one **1c** (0.1 mmol, 13.7 mg, 1 eq.), benzoic acid **13b** (0.3 mmol, 36.6 mg, 3 eq.) and 0.5 mL of anisole (0.2 M). The reaction was stirred 2 h at 80 °C. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 50:50) to afford the product as a colourless oil (19.9 mg, 77%). R_f (CyH:EtOAc 1:1) = 0.54. ^{1}H NMR (400 MHz, $CDCl_3$) 8.06 – 8.00 (m, 2H), 7.78 (d, *J* = 14.6 Hz, 1H), 7.59 – 7.50 (m, 1H), 7.43 (dd, *J* = 8.2, 7.0 Hz, 2H), 5.27 (dt, *J* = 14.6, 7.2 Hz, 1H), 4.87 (d, *J* = 7.2 Hz, 2H), 3.43 (t, *J* = 6.3 Hz, 2H), 2.50 (t, *J* = 6.6 Hz, 2H), 1.96 – 1.85 (m, 2H), 1.86 – 1.75 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.0, 166.7, 133.0, 132.4, 130.5, 129.7, 128.5, 104.1, 64.8, 45.4, 33.1, 22.7, 20.6. HPLC-LRMS (ESI) R_t = 4.1 min; *m/z* 541.20 $[2M+Na]^+$, 282.10 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{15}H_{17}NNaO_3^+$ 282.1101; Found 282.1115.

(*E*)-3-(*N*-benzylacetamido)allyl benzoate (10hb). Prepared according to **GP-C** using *N*-benzyl-*N*-(propa-1,2-dien-1-yl)acetamide **1h** (0.1 mmol, 18.7 mg, 1 eq.), benzoic acid **13b** (0.3 mmol, 36.6 mg, 3 eq.) and 0.5 mL of anisole (0.2 M). The reaction was stirred 2 h at 80 °C. The crude mixture was purified by FC (CyH:EtOAc, from 95:5 to 80:20) to afford the product as a colourless oil (21.9 mg, 71%). R_f (CyH:EtOAc 1:1) = 0.73. ^{1}H NMR (400 MHz, $CDCl_3$, *reported as mixture of rotamers*) 8.02 – 7.96 (m, 2H *major*, 2H *minor*), 7.79 (d, J = 14.8 Hz, 1H, *minor*), 7.54 (app. q, J = 6.9 Hz, 1H *minor*, 1H *major*), 7.47 – 7.38 (m, 2H, *major*, 2H *minor*), 7.35 (app. t, J = 7.3 Hz, 1H *major*, 1H *minor*), 7.31 – 7.26 (m, 1H *major*, 2H *minor*), 7.22 (d, J = 7.3 Hz, 1H *major*), 7.21 – 7.12 (m, 2H *major*, 2H *minor*), 7.04 (d, J = 13.7 Hz, 1H, *major*), 5.20 (tt, J = 13.4, 7.2 Hz, 1H *major*, 1H, *minor*), 4.90 (s, 2H, *major*), 4.81 (app d, J = 6.7 Hz, 4H, *minor*), 4.76 (d, J = 7.3 Hz, 2H, *major*), 2.37 (s, 3H, *major*), 2.18 (s, 3H, *minor*). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, *reported as mixture of rotamers*) δ 170.1, 169.7, 166.5, 136.6, 135.6, 133.7, 133.2, 133.1, 133.0, 131.8, 130.3, 129.7, 129.7, 129.1, 128.7, 128.5, 128.4, 127.8, 127.7, 127.2, 126.9, 125.6, 105.3, 105.2, 64.6, 64.3, 49.6, 46.3, 29.8, 22.2. HPLC-LRMS (ESI) R_t = 4.4 min; *m/z* 641.4 $[2M+Na]^+$, 332.2 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{19}NNaO_3^+$ 332.1257; Found 332.1268.

(*E*)-3-(*N*-phenylacetamido)allyl benzoate (10db). Prepared according to **GP-C** using *N*-phenyl-*N*-(propa-1,2-dien-1-yl)acetamide **1d** (0.1 mmol, 18.7 mg, 1 eq.), benzoic acid **13b** (0.3 mmol, 36.6 mg, 3 eq.) and 0.5 mL of anisole (0.2 M). The reaction was stirred 2 h at 80 °C. The crude mixture was purified by FC (CyH:EtOAc, from 90:10 to 60:40) to afford the product as a colourless oil (12.10 mg, 41%). R_f (CyH:EtOAc 1:1) = 0.71. ^{1}H NMR (400 MHz, $CDCl_3$) 8.02 – 7.96 (m, 2H), 7.87 (d, J = 14.4 Hz, 1H), 7.56 – 7.47 (m, 3H), 7.46 – 7.38 (m, 3H), 7.23 – 7.17 (m, 2H), 4.78 (app. dd, J = 7.1, 1.3 Hz, 2H), 4.64 (app. ddd, J = 14.4, 7.7, 6.7 Hz, 1H), 1.88 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.1, 166.5, 139.5, 133.5, 133.0, 130.4, 130.4, 129.7, 129.1, 128.9, 128.4, 106.8, 64.2, 23.4. HPLC-LRMS (ESI) R_t = 18.9 min; *m/z* 613.2 $[2M+Na]^+$, 318.2 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{17}NNaO_3^+$ 318.1101; Found 318.1118.

(*E*)-3-((*N*,4-dimethylphenyl)sulfonamido)allyl benzoate (10eb). Prepared according to **GP-C** using *N*,4-dimethyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide **1e** (0.1 mmol, 22.3 mg, 1 eq.), benzoic acid **13b** (0.3 mmol, 36.6 mg, 3 eq.) and 0.5 mL of anisole (0.2 M). The reaction was stirred 1 h at 80 °C. The crude mixture was purified by FC (CyH:EtOAc, from 90:10 to 60:40) to afford the product as a colourless oil (28.3 mg, 82%). R_f (CyH:EtOAc 1:1) = 0.68. ^{1}H NMR (400 MHz, $CDCl_3$) 8.05 – 8.00 (m, 2H), 7.68 – 7.62 (m, 2H), 7.60 – 7.51 (m, 1H), 7.47 – 7.41 (m, 2H), 7.31 – 7.26 (m, 2H), 7.19 (d, J = 13.9 Hz, 1H), 4.97 (dt, J = 13.0, 6.9 Hz, 1H), 4.80 (d, J = 6.9 Hz, 1H), 2.89 (s, 3H), 2.40 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.6, 144.2, 134.7, 133.9, 133.1, 130.4, 130.0, 129.7, 128.5, 127.2, 103.6, 64.2, 32.2, 27.0. HPLC-LRMS (ESI) R_t = 9.7 min; *m/z* 713.2 $[2M+Na]^+$, 368.0 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{19}NNaO_4S^+$ 368.0927; Found 368.0936.

(*E*)-3-((4-methyl-*N*-phenylphenyl)sulfonamido)allyl benzoate (10fb). Prepared according to **GP-C** using 4-methyl-*N*-phenyl-*N*-(propa-1,2-dien-1-yl)benzenesulfonamide **1f** (0.1 mmol, 28.6 mg, 1 eq.), benzoic acid **13b** (0.3 mmol, 36.6 mg, 3 eq.) and 0.5 mL of anisole (0.2 M). The reaction was stirred 2 h at 80 °C. The crude mixture was purified by FC (CyH:EtOAc, from 80:20 to 50:50) to afford the product as a colourless oil (36.7 mg, 90%). R_f (CyH:EtOAc 1:1) = 0.76. ^{1}H NMR (400 MHz, $CDCl_3$) 8.02 – 7.97 (m, 2H), 7.59 – 7.53 (m, 2H), 7.45 – 7.39 (m, 3H), 7.38 – 7.34 (m, 3H),

7.30 – 7.23 (m, 3H), 7.01 – 6.95 (m, 2H), 4.74 (d, J = 7.9 Hz, 2H), 4.58 (dt, J = 14.3, 7.9 Hz, 1H), 2.43 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 166.5, 144.3, 136.0, 135.7, 134.8, 133.0, 130.3, 129.8, 129.7, 129.7, 129.4, 128.4, 127.7, 104.4, 64.0, 21.8. HPLC-LRMS (ESI) R_t = 9.3 min; *m/z* 837.0 $[2M+Na]^+$, 430.0 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{23}H_{21}NNaO_4S^+$ 430.1084; Found 430.1093.

3-(2-oxooxazolidin-3-yl)-3-(trimethylsilyl)allyl benzoate (10gb). Prepared according to **GP-C** using 3-(1-(trimethylsilyl)propa-1,2-dien-1-yl)oxazolidin-2-one **1g** (0.1 mmol, 19.7 mg, 1 eq.), benzoic acid **13b** (0.3 mmol, 36.6 mg, 3 eq.) and 0.5 mL of anisole (0.2 M). The reaction was stirred 10 h at 80 °C. The crude mixture was purified by FC (CyH:EtOAc, from 80:20 to 50:50) to afford the product as a colourless oil and as a mixture of diastereoisomers (*d.r.* 73:27, 16.0 mg, 50%). R_f (CyH:EtOAc 1:1) = 0.59. ^{1}H NMR (400 MHz, $CDCl_3$, *reported as mixture of diastereoisomers*) 8.09 – 8.02 (m, 2H, *major and minor diastereoisomers*), 7.60 – 7.54 (m, 1H, *major and minor diastereoisomers*), 7.48 – 7.42 (m, 2H, *major and minor diastereoisomers*), 6.05 (t, *J* = 7.6 Hz, 1H, *minor diastereoisomer*), 6.01 (t, J = 5.9 Hz, 1H, *major and minor diastereoisomers*), 4.96 (d, *J* = 7.6 Hz, 2H, *minor diastereoisomer*), 4.92 (d, J = 5.9 Hz, 2H, *major and minor diastereoisomers*), 4.46 – 4.39 (m, 2H, *major and minor diastereoisomers*), 3.84 – 3.76 (m, 2H, *major and minor diastereoisomers*), 0.35 (s, 9H, *minor diastereoisomer*), 0.23 (s, 9H, *major and minor diastereoisomers*). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, only the major diastereoisomer is detected) δ 166.4, 156.4, 141.7, 135.0, 133.3, 133.2, 130.2, 129.8, 128.6, 62.4, 61.6, 47.2, -0.8. HPLC-LRMS (ESI) R_t = 8.9 min; *m/z* 661.1 $[2M+Na]^+$, 343.2 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{21}NNaO_4Si^+$ 342.1132; Found 342.1142.

(*E*)-3-(1H-indol-1-yl)allyl benzoate (10ib). Prepared according to **GP-C** using 1-(propa-1,2-dien-1-yl)-1H-indole **1i** (0.1 mmol, 15.5 mg, 1 eq.), benzoic acid **13b** (0.3 mmol, 36.6 mg, 3 eq.) and 0.5 mL of anisole (0.2 M). The reaction was stirred 1 h at 80 °C. The crude mixture was purified by FC (CyH:EtOAc, from 95:5 to 80:20) to afford the product as a colourless oil (19.4 mg, 70%). R_f (CyH:EtOAc 8:2) = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$) 8.11 – 8.06 (m, 2H), 7.62 (dt, J = 7.8, 1.0 Hz,

1H), 7.59 – 7.54 (m, 1H), 7.52 – 7.36 (m, 5H), 7.33 – 7.24 (m, 1H), 7.18 (ddd, J = 8.0, 7.1, 1.0 Hz, 1H), 6.65 (d, J = 3.3 Hz, 1H), 5.97 (dt, J = 14.4, 7.9 Hz, 1H), 5.02 (app. dd, J = 7.4, 1.0 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 166.5, 135.5, 133.0, 130.2, 129.6, 129.3, 129.2, 128.4, 123.7, 122.9, 121.2, 121.1, 109.5, 106.4, 105.7, 64.0. HPLC-LRMS (ESI) R_t = 25.6 min; *m/z* 577.2 $[2M+Na]^+$, 300.2 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{15}NNaO_2^+$ 300.0995; Found 300.1006.

*Procedure D for the synthesis of product **5ba***. A Schlenk tube equipped with a magnetic stirring bar was dried under vacuum and refilled with Argon. The reaction vessel was then charged with the allenamide **1b** (31 mg, 0.2 mmol, 1 eq.), anisole (0.92 mL, 0.2 M), allyl alcohol **2a** (32.6 µL, 0.48 mmol, 2.4 eq.) and 80 µL of a 0.025 M (2.0 µmol, 0.01 eq., 1 mol%) stock solution of CSA in anisole. The reaction was stirred 4 h at rt. The reaction was cooled down, diluted with ca. 5 mL of ethyl acetate and added to a separatory funnel containing 8 mL of a saturated aqueous solution of $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with EtOAc (2 x 5 mL). The combined organic extracts were dried over sodium sulphate, and concentrated under vacuum (0.5 mbar). The NMR yield was determined by adding methyl acetoacetate (0.2 mmol, 1 eq.) as internal standard to the crude mixture dissolved in $CDCl_3$. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 50:50) to afford the product as a colourless oil (30 mg, 62%).

3-(1,3-bis(allyloxy)propyl)oxazolidin-2-one (5ba). R_f (CyH:EtOAc 1:1) = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 – 5.80 (m, 2H), 5.32 – 5.22 (m, 3H), 5.22 – 5.12 (m, 2H), 4.42 – 4.27 (m, 2H), 4.07 – 3.92 (m, 2H), 3.97 – 3.90 (m, 2H), 3.56 (t, J = 8.0 Hz, 2H), 3.49 (t, J = 6.5 Hz, 2H), 2.08 – 1.94 (m, 1H), 1.96 – 1.86 (m, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 158.3, 134.8, 133.9, 117.7, 117.2, 81.4, 77.5, 77.2, 76.8, 72.2, 69.2, 66.1, 62.4, 39.0, 33.3. HPLC-LRMS (ESI) R_t = 5.6 min; *m/z* 264.40 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{19}NNaO_4^+$ 264.1206; Found 264.1180.

*General Procedure E (**GP-E**) for the synthesis of product **4ba** in mmol and gram scale*. A Schlenk tube equipped with a magnetic stirring bar was dried under vacuum and refilled with Argon. The reaction vessel was then charged with the allenamide **1b** (1 eq.), anisole (0.4 M), allyl alcohol **2a** (1.2

eq) and the right amount of a 0.025 M stock solution of CSA in anisole. The reaction mixture was then allow to stir at room temperature until complete consumption of the starting material, as observed by TLC analysis. After the reported time, the reaction was diluted with ethyl acetate and added to a separatory funnel containing a saturated aqueous solution of $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted two times with EtOAc. The combined organic extracts were dried over sodium sulphate, concentrated under reduced pressure and anisole was then removed and recovered by means of a vacuum distillation (0.5 mbar). The NMR yield was determined by adding methyl acetoacetate (1 eq.) as internal standard to the crude mixture dissolved in $CDCl_3$. Purification of the crude product by flash chromatography on silica gel afforded the desired product.

Product **4ba** prepared in **mmol scale** following **GP-E** and using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (1.0 mmol, 125.1 mg, 1 eq.), allyl alcohol **2a** (1.2 mmol, 81.6 µL, 1.2 eq.), 200 µL of a stock solution 0.025 M of CSA in anisole (0.5 mol %, 0.005 eq.) and 2.3 mL of anisole (0.4 M). The reaction was stirred 1.5 h at rt. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 50:50) to afford the product as a colourless oil (143.7 mg, 78%).

Product **4ba** prepared in **gram scale** following **GP-E** and using 3-(propa-1,2-dien-1-yl)oxazolidin-2-one **1b** (10.0 mmol, 1.25 g, 1 eq.), allyl alcohol **2a** (12.0 mmol, 816 µL, 1.2 eq.), 2 mL of a stock solution 0.025 M of CSA in anisole (0.5 mol%, 0.005 eq.) and 23 mL of anisole (0.4 M). The reaction was stirred 1.25 h at rt. Then, the mixture was diluted with ethyl acetate (7 mL) and added to a separatory funnel containing a saturated aqueous solution of $NaHCO_3$ (30 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (2 x 20 mL). The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 50:50) to afford the product as a colourless oil (1.32 g, 72%).

3-(1-(allyloxy)allyl)oxazolidin-2-one (3ba). Product **3ba** was isolated from the gram scale reaction (10 mmol) between allenamide **1b** and allyl alcohol **2a** by FC (CyH:EtOAc, from 70:30 to 50:50). The product was obtained as colourless oil in 7% yield (128.7 mg). R_f (CyH:EtOAc 1:1) = 0.54. ^1H NMR (400 MHz, $CDCl_3$) δ 5.91 (ddt, J = 17.1, 10.5, 5.6 Hz, 1H), 5.79 (ddd, J = 17.3, 10.6, 4.5 Hz,

1H), 5.59 (d, J = 4.5 Hz, 1H), 5.50 (dt, J = 17.3, 1.5 Hz, 1H), 5.38 – 5.29 (m, 2H), 5.21 (dq, J = 10.4, 1.3 Hz, 1H), 4.44 – 4.27 (m, 2H), 4.10 – 4.01 (m, 2H), 3.62 – 3.45 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 158.2, 133.8, 133.2, 119.1, 117.7, 82.2, 77.5, 77.2, 76.8, 69.1, 62.6, 39.3. HPLC-LRMS (ESI) R_t = 4.2 min; *m/z* 389.10 [2M+Na]+, 206.10 [M + Na]+. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_9H_{13}NNaO_3^+$ 206.0788; Found 206.0779.

*Synthesis of product **14***: Product **14** was prepared applying conditions adapted from Coleman *et al.*.[59] A Schlenk tube equipped with a magnetic stirring bar was dried under vacuum and refilled with Argon. The reaction vessel was then charged with the enamide **4ba** (0.2 mmol, 36.6 mg, 1 eq.), $CHCl_3$ (0.4 mL, 0.5 M) and *N*-bromosuccinimide (0.2 mmol, 35.6 mg, 1 eq.). The reaction mixture was then allow to stir at room temperature for 2 h, then it was diluted with *ca.* 3 mL of DCM and added to a separatory funnel containing 5 mL of a saturated aqueous solution of $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with DCM (2 x 4 mL). The combined organic extracts were dried over sodium sulphate, and concentrated under vacuum. The crude mixture was purified by FC (CyH:EtOAc, from 60:40 to 0:100) to afford the product as a colourless oil and as a mixture of diastereoisomers (*d.r.* 60:40, 50.5 mg, 70%). R_f (CyH:EtOAc 1:1) = 0.10. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.21 (d, J = 11.1 Hz, 1H, *minor diastereoisomer*), 6.17 (d, J = 10.9 Hz, 1H, *major diastereoisomer*), 5.88 (ddt, J = 17.3, 10.4, 5.9 Hz, 1H, *minor diastereoisomer*), 5.80 (ddt, J = 17.3, 10.4, 5.8 Hz, 1H, *major diastereoisomer*), 5.29 (dq, J = 17.3, 1.6 Hz, 1H *minor diastereoisomer*), 5.25 (dq, J = 15.5,1.5 Hz, 1H, *major diastereoisomer*), 5.22 – 5.17 (m, 3H, *major and minor diastereoisomers*), 4.82 (ddd, J = 10.9, 7.4, 4.7 Hz, 1H, *major diastereoisomer*), 4.41 – 4.31 (m, 2H, *major diastereoisomer*), 4.27 (ddd, J = 8.6, 7.2, 1.5 Hz, 2H, *minor diastereoisomer*), 4.09 – 3.97 (m, 3H, *major and minor diastereoisomers*), 3.96 – 3.89 (m, 2H, *major and minor diastereoisomers*), 3.88 – 3.80 (m, 3H, *major and minor diastereoisomers*), 3.79 – 3.74 (m, 2H, *major and minor diastereoisomers*), 3.62 (td, J = 8.6, 7.4 Hz, 1H, *minor diastereoisomer*), 2.77 (q, J = 1.5 Hz, 4H, *minor diastereoisomer*), 2.65 (q, J = 2.7 Hz, 4H, *major diastereoisomer*). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$, reported as mixture of diastereoisomers) δ 176.9, 176.5, 157.7, 157.4, 133.9, 133.6, 118.4,

118.3, 72.7, 72.7, 72.4, 72.3, 63.4, 63.3, 62.9, 62.5, 45.0, 44.0, 43.0, 42.9, 28.2, 28.1. HPLC-LRMS (ESI) R_t (*major diastereoisomer*) = 4.8 min; *m/z* 742.9 $[2M+Na]^+$, 382.9 $[M + Na]^+$. HPLC-LRMS (ESI) R_t (*minor diastereoisomer*) = 4.9 min; *m/z* 742.9 $[2M+Na]^+$, 382.9 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{13}H_{17}BrN_2NaO_5^+$ 383.0213; Found 383.0225.

*Synthesis of product **15***: Product **15** was prepared applying conditions adapted from Nicewicz *et al*..[41] A 4 mL screw cap septum vial equipped with a magnetic stir bar, enamide **4ba** (0.1 mmol, 18.32 mg, 1 eq.), 3,6-di-*tert*-butyl-9-mesityl-10-phenylacridin-10-ium tetrafluoroborate (3 µmol, 1.72 mg, 0.03 eq, 3 mol%), sodium acetate (25.0 µmol, 2.1 mg, 0.25 eq), acetic acid (0.25 mmol, 14.3 µL, 2.5 eq.), benzenethiol (20.0 µmol, 2.0 µl, 0.20 eq) and DCM (0.4 ml) were added. The vial was closed and the reaction mixture was degassed with 3 cycles of Freeze – Pump – Thaw (3 x 10 minutes, backfilling with Argon after each degassing cycle). Then, the vial was sealed with grease on the septum and with parafilm®, and the reaction was set to stir approximately 10 cm from a 50W 427 nm Kessil® Lamp at room temperature (a fan was employed to blow air over the vial and to maintain the temperature between 25 and 30 °C). After 18 hours, the solvent was removed under vacuum and the crude was purified by FC on silica gel (CyH: EtOAc from 60:40 to 40:60) to afford the product as a colourless oil (20.3 mg, 83%). R_f (CyH:EtOAc 1:1) = 0.42. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (ddt, J = 17.2, 10.4, 5.7 Hz, 1H), 5.27 (dq, J = 17.3, 1.6 Hz, 1H), 5.22 – 5.13 (m, 2H), 4.35 – 4.25 (m, 2H), 4.06 – 3.96 (m, 2H), 3.71 (td, J = 8.4, 7.1 Hz, 1H), 3.60 (dd, J = 14.8, 7.7 Hz, 1H), 3.58 – 3.54 (m, 3H), 3.40 (dd, J = 14.7, 3.9 Hz, 1H), 2.09 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.7, 158.8, 134.3, 117.7, 72.5, 70.3, 69.3, 62.0, 45.6, 21.2. HPLC-LRMS (ESI) R_t = 3.2 min; *m/z* 506.2 $[2M+Na]^+$, 266.2 $[M + Na]^+$, 244.2 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{11}H_{17}NNaO_5^+$ 266.0999; Found 266.1012.

*Synthesis of product **16***: Product **16** was prepared applying conditions adapted from Wilson *et al*..[60] A Schlenk tube equipped with a magnetic stirring bar was dried under vacuum and refilled with Argon. The reaction vessel was then charged with the enamide **4ba** (0.2 mmol, 36.6 mg, 1 eq.), dry MeCN (0.4 mL, 0.5 M) and (ethene-1,1-diyldisulfonyl)dibenzene (0.22 mmol, 67.8 mg, 1.1 eq.). The

reaction mixture was then allow to stir at room temperature for 72 h. The solvent was then removed under vacuum and the obtained oil was purified by FC (CyH:EtOAc, from 70:30 to 50:50) to afford the product as a pale yellow oil and as a single diastereoisomer (73.3 mg, 77%). R_f (CyH:EtOAc 1:1) = 0.49. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.09 (m, 2H), 8.03 – 7.99 (m, 2H), 7.77 – 7.66 (m, 2H), 7.62 – 7.55 (m, 4H), 5.78 (ddt, J = 17.2, 10.4, 5.6 Hz, 1H), 5.28 (dd, J = 10.1, 1.1 Hz, 1H), 5.22 (dq, J = 17.3, 1.7 Hz, 1H), 5.17 (dq, J = 10.5, 1.6 Hz, 1H), 4.29 – 4.21 (m, 2H), 4.20 – 4.13 (m, 1H), 3.88 (dt, J = 5.5, 1.5 Hz, 2H), 3.67 – 3.58 (m, 2H), 3.43 (dd, J = 9.8, 4.9 Hz, 1H), 3.36 (dd, J = 9.8, 5.8 Hz, 1H), 2.73 (ddd, J = 13.5, 9.7, 1.2 Hz, 1H), 2.62 (dd, J = 13.5, 9.5 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 157.1, 136.9, 134.9, 133.9, 133.7, 133.3, 130.1, 129.7, 127.8, 127.8, 116.2, 86.0, 71.1, 69.2, 61.5, 57.0, 43.1, 35.2, 25.3. HPLC-LRMS (ESI) R_t = 8.0 min; *m/z* 1005.0 $[2M+Na]^+$, 313.9 $[M + Na]^+$, 492.0 $[M + H]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{23}H_{25}NNaO_7S_2^+$ 514.0965; Found 514.0947.

*Synthesis of product **17***: Product **17** was prepared applying conditions adapted from Hahn *et al*..[61] A Schlenk tube equipped with a magnetic stirring bar was dried under vacuum and refilled with Argon. The reaction vessel was then charged with the enamide **4ba** (0.2 mmol, 36.6 mg, 1 eq.), dry DCM (0.4 mL, 0.5 M) and 3-chlorobenzoperoxoic acid (0.22 mmol, 38.0 mg, 1.1 eq.). The reaction mixture was then allow to stir at room temperature for 3 hours, then it was diluted with *ca.* 4 mL of DCM and added to a separatory funnel containing 6 mL of a saturated aqueous solution of $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with DCM (2 x 5 mL). The combined organic extracts were dried over sodium sulphate, and concentrated under vacuum. The crude mixture was purified by FC (CyH:EtOAc, from 70:30 to 40:60) to afford the product as a colourless oil and as a mixture of diastereoisomers (*d.r.* 90:10, 42.8 mg, 60%). R_f (CyH:EtOAc 1:1) = 0.40. ^{1}H NMR (600 MHz, $CDCl_3$, reported as mixture of diastereoisomers) δ 8.03 (t, J = 1.9 Hz, 1H), 8.01 – 7.92 (m, 1H), 7.60 – 7.55 (m, 1H), 7.44 – 7.38 (m, 1H), 6.48 (d, J = 4.9 Hz, 1H), 6.45 (d, J = 7.3 Hz, 0H), 5.89 – 5.79 (m, 1H), 5.27 – 5.22 (m, 1H), 5.20 – 5.15 (m, 1H), 4.43 – 4.35 (m, 3H), 4.35 – 4.28 (m, 1H), 4.04 – 3.97 (m, 2H), 3.95 (dd, J = 8.7, 7.3 Hz, 1H), 3.80 (td, J = 8.8, 7.6 Hz, 1H), 3.59 (dd, J = 4.9,

1.9 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 164.4, 163.7, 157.8, 157.6, 134.8, 134.0, 133.8, 133.8, 131.1, 130.1, 130.1, 130.0, 130.0, 130.0, 128.3, 128.3, 118.1, 118.0, 79.1, 78.6, 72.6, 72.6, 70.9, 70.2, 69.9, 69.3, 63.0, 62.9, 43.3, 42.3. HPLC-LRMS (ESI) R_t (*major diastereoisomer*) = 6.7 min; *m/z* 733.1 $[2M+Na]^+$, 378.0 $[M + Na]^+$. HPLC-LRMS (ESI) R_t (*minor diastereoisomer*) = 7.0 min; *m/z* 733.1 $[2M+Na]^+$, 378.0 $[M + Na]^+$. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{18}ClNNaO_6^+$ 378.0715; Found 378.0734.

Computational Details. Calculations were performed using Gaussian 16, Revision C.01.[62] Geometries were optimized using the M06-2X density functional[63] and the 6-31G(d) basis set within the IEFPCM model (solvent = anisole)[64] and further confirmed to be stationary points on the potential energy surface by frequency calculations. Transition states were confirmed to join the correct minimum energy structures by IRC calculations. Single point energies were calculated using the M06-2X density functional and cc-pvtz basis set within the IEFPCM model (solvent = anisole)[64] and corrected using the program GoodVibes (Truhlar's quasiharmonic approximation).[65] Molecules possessing conformational mobility were first optimized using molecular mechanics (MMFF94 force field); all the conformers within a 10 kcal·mol^{-1} window were then reoptimized using DFT and only the lowest energy conformer was used in all subsequent calculations. All molecule illustrations were made using with CYLView.[66]

AUTHOR INFORMATION

Corresponding Authors

Arianna Quintavalla − Department of Chemistry "Giacomo Ciamician" and Center for Chemical Catalysis – C3; University of Bologna, Via P. Gobetti 85, I-40129 Bologna, Italy; orcid.org/0000-0002-0993-6855; Email: arianna.quintavalla@unibo.it

Marco Lombardo − Department of Chemistry "Giacomo Ciamician" and Center for Chemical Catalysis – C3; University of Bologna, Via P. Gobetti 85, I-40129 Bologna, Italy; orcid.org/0000-0001-8415-8363; Email: marco.lombardo@unibo.it

Authors

Davide Carboni − Department of Chemistry "Giacomo Ciamician" and Center for Chemical Catalysis – C3; University of Bologna, Via P. Gobetti 85, I-40129 Bologna, Italy; orcid.org/0000-0002-9376-2025; Email: davide.carboni4@unibo.it

Alessandro Brusa − Department of Chemistry "Giacomo Ciamician"; University of Bologna, Via P. Gobetti 85, I-40129 Bologna, Italy; orcid.org/0009-0003-7658-3169; Email: alessandro.brusa@graduate.univaq.it

Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications Web site. Optimization of the reaction conditions, investigation on the HFIP role, mechanistic studies, time-dependent formation of the products, NMR yields determination method, products characterization and stereochemistry determinations, NMR spectra for all the new products, computational data details.

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