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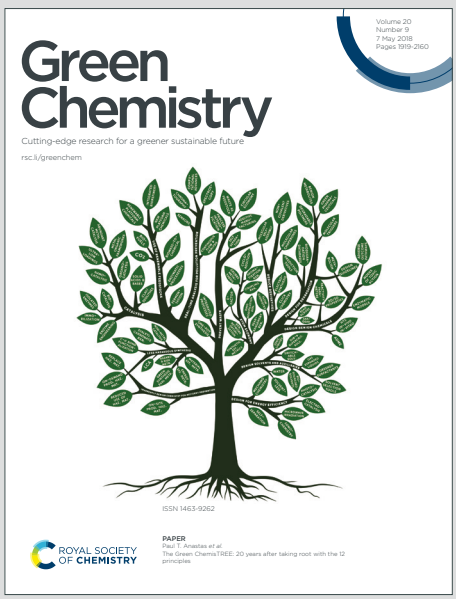

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Dipolar Cycloadditions of HMF- based nitrones: stepwise and multicomponent reactions, stereochemical outcome and structural scope

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Abstract

The straightforward preparation of new 3-furanyl isoxazolidines by 1,3-dipolar cycloaddition of 5-hydroxymetylfurfural (HMF) derived nitrones with electro-deficient olefins is investigated. The study addresses the stepwise reaction, with isolation of the intermediate nitrone, and the multicomponent protocol involving directly HMF and other reaction partners and reagents. Optimal reaction parameters (solvent, temperature, stoichiometry) for the stepwise and multicomponent reactions are defined, resulting on a choice a clean and direct conditions leading to cycloadducts in good yields. Isopropanol is found the most appropriate solvents both in terms of acceptability and efficiency depending on the solubility of the different substrates and on specific requirements for either the stepwise or multicomponent protocols. The stereochemical outcome of the reaction and the structural scope with respect to various dipolarophiles (acrylates, cycloalkenones, acrylamides, acrylonitrile), variously substituted hydroxylamines, using HMF and *O*-substituted HMF analogs are also fully assessed. The structural considerations allowing more regioselective reactions are also defined. This study

provides the basic elements necessary for considering the use of HMF in such strategies.

Keywords: Dipolar cycloadditions, nitrones, isoxazolidines, HMF, bio-based chemistry

Introduction

The chemistry of renewable small molecules has become an active field of research in the last decades, in order to contribute to more sustainable solutions in the whole scope of the chemical industry, and propose the integration of bio-based building blocks in a wider range of molecular designs.[1-7] Among these molecules, small biobased aldehydes appear extremely promising for accessing a variety of molecular architectures, from simple to more complex ones, targeting the whole scope of chemistry from basic to specialty and fine chemicals. The sugar-derived furanic platform 5-(hydroxymethyl)furfural (HMF) is believed to play a key role in the future, and promising applications have actually already been found, notably in polymer and material science or in fuel chemistry, with reductive or oxidative transformations towards compounds like 2,5-dimethyl furan or 2,5-furandicarboxylic acid, or hydrolysis towards molecules such as levulinic acid or hydroxyhexanedione.[8-21] With respect to applications in the design of novel fine chemicals, the densely functionalized HMF has also found a growing interest for its use as a platform, relying on its specific multiple functional decorations including an aldehyde, a primary alcohol and a furanic ring constituting 3 handles for selective chemical transformations.[11-16, 22-26] HMF has been for years less investigated than other aldehydes as substrate for elaborating complex structures, however its improved availability encourage to assess its reactivity in novel directions.[27]

Heterocyclic systems are important in many facets of the chemical and pharmaceutical industry, and within the green chemistry community, some efforts are made for

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reaching them from biobased aldehydes, such as the example of the formation of quinaldic acids from furfural or that of indolyldihydrofurans from glycolaldehyde.[28,29] In the present study aiming at proposing novel molecular design in biobased chemistry and diversification of the use of HMF platform in original and straightforward synthetic schemes towards more complex building blocks, we have opened a new section of HMF chemistry by investigating the reactivity of HMF-based nitrones in 1,3-dipolar cycloadditions with activated alkenes, which has never been investigated previously.

The nitrone-olefin 1,3-dipolar cycloaddition reaction is a useful reaction in organic synthesis as the resulting isoaxazolidine ring is a widely encountered heterocyclic backbone.[30-35] Besides its synthetic interest, the 1,3-dipolar cycloaddition reaction is also direct and atom-economical, creating new C-C bond and C-O bonds in a single step with all atoms of the reactants found in the product. The starting nitrones exhibit satisfactory stability, are easy to handle and easy to prepare by simple condensation of a carbonyl compound with a hydroxylamine.[36] Alternatives starting from nitro-derivatives using reductive coupling in presence of metallic nanoparticles [37] or electrosynthesis are also efficient alternatives.[38] The whole sequence (from the aldehyde to the cycloadduct) can even be performed in a multicomponent approach in which the aldehyde, the hydroxylamine and the dipolarophile are mixed together, with *in situ* formation of the nitrone.

All these features designate the nitrone-olefin 1,3-dipolar cycloaddition reaction as an interesting one for being investigated in the case of HMF (Figure 1). Below are reported the results of our investigation defining the basics of HMF reactivity in this reaction, studying all aspects, namely: i) the influence of reaction conditions (solvent, temperature, stoichiometry, concentration), ii) a detailed stereochemical outcome, iii) the structural scope with variations in the aldehyde (HMF and *O*-substituted analogs), the hydroxylamine, and the activated alkene, and iv) a study of the alternative multicomponent approach.

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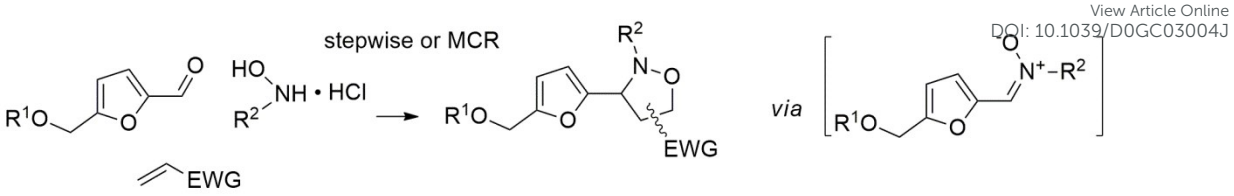


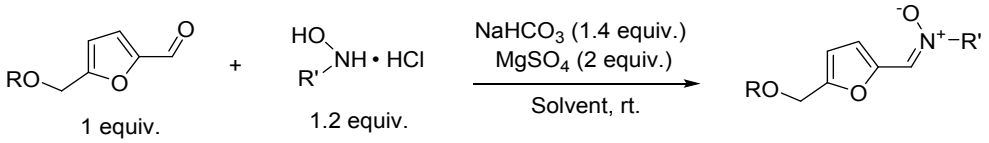
Figure 1. HMF-based nitrones in 1,3-dipolar cycloaddition with activated alkenes

Results and discussion

Stepwise reaction

Nitrone formation- The condensation of the commercially available *N*-methyl hydroxylamine hydrochloride with HMF in isopropanol led to the desired nitrone **1a**. Using a small excess (1.2 equiv.) of *N*-methyl hydroxylamine hydrochloride to secure full conversion of HMF, 1.4 equiv. of $NaHCO_3$ to neutralize the hydrochloride, and 2.0 equiv. of anhydrous $MgSO_4$ in isopropanol, nitrone **1a** was obtained quantitatively after simple filtration over celite, as a bench-stable solid (entry 1). Under similar conditions, benzyl and *tert*-butyl hydroxylamines gave the corresponding nitrones in high yields (Table 1, entry 2, 3). Similar condensation of a fluorescent hydroxylamine with HMF was recently proposed as a mean of quantitative analytical method of HMF in foods.[39] Using TBDPS-protected HMF, nitrone **1d** could also be obtained readily and in excellent yields (Table 1, entry 4). The glucosylated analog of HMF, glusosyloxymethylfurfural (GMF),[40-43] was also converted to its corresponding nitrone **1e** using MeOH as solvent. With this clean, efficient, and fast protocol in hands, the subsequent cycloaddition step of the isolated nitrone was then undertaken.

Table 1. Preparation of furanic aldonitrones [a]



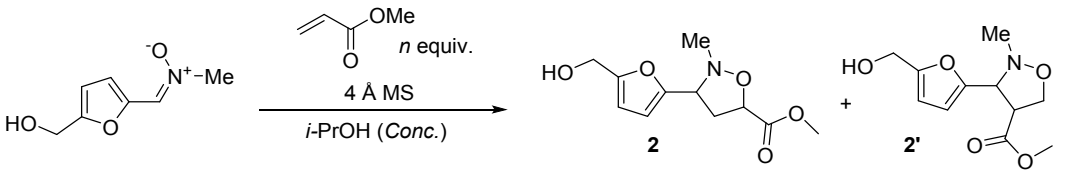
Entry	R	R'	Solvent	Nitrone	Yield
1	H	Me	*i*-PrOH	**1a**	99%
2	H	Bn	*i*-PrOH	**1b**	98%

3	H	*t*-Bu	*i*-PrOH	**1c**	99%
4	TBDPS	Me	*i*-PrOH	**1d**	99%
5	α-glucosyl	Me	MeOH	**1e**	94%

(a) Reaction conditions: aldehyde (1.0 eq), *N*-substituted hydroxylamine hydrochloride (1.2 eq), $NaHCO_3$ (1.4 eq) and $MgSO_4$ (2.0 eq) were stirred at room temperature for 1-3 h.

Cycloadditions - Isopropanol was selected again as solvent for the cycloaddition step, based on its wide solubilizing properties, safety, easiness to evaporate,[44] and its reasonable price. The reaction was investigated with respect to the stoichiometry, the reaction time, the concentration and the temperature. Results are given below in Table 2. The reaction at room temperature and 40 °C was found too slow (entry 1 and 2), while heating it up to 80°C gave satisfactory results, however preserving the thermally sensitive HMF-scaffold (entries 1-3). At this temperature, a 73% yield of cycloadducts **2** and **2'** was formed as a 1:1.5 mixture of inseparable isomers (regio and diastereo; see next section on stereochemical issues). The yield could be increased to 80% using a large excess of acrylate (5 equiv., entry 4), or, alternatively, by increasing the concentration up to 2M, though keeping only 2 equiv. of acrylate, leading to the corresponding isoxazolidines up to the multigram scale and in yields up to 84% (entries 5-7). Running the reaction in neat conditions was also possible though being slightly less efficient (70% yield) due to partial degradation of the nitrone (entry 8).

Table 2. Influence of reaction parameters on the cycloaddition step[a]



Entry	n	Conc.	Time (h)	T (°C)	Yield[b]
1	2	1M	168	r.t.	≤5%
2	2	1M	48	40	18%

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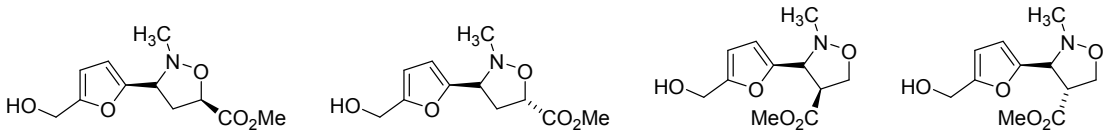
Entry	n	Conc.	Time (h)	T (°C)	Yield[b]
3	2	1M	16	80	73%
4	5	1M	16	80	80%
5	1.2	1M	16	80	62%
6	1.2	2M	16	80	72%
7	2	2M	16	80	84%[c]
8	2	neat	16	80	70%[d]

(a) Reaction condition: nitrone (1mmol) and methyl acrylate were treated in sealed MW tubes with concentration of 1M or 2M in isopropanol.
(b) Overall isolated yield for cycloadducts as a 1.5/1 mixture of 3,5 (**2**) and 3,4- (**2'**) oxazolidines
(c) 10 mmol scale reaction.
(d) Degradation was observed.

Stereochemical outcome - 1,3-Dipolar cycloaddition reaction can provide regioisomers (3,5- and 3,4-disubstituted isoxazolidines), as well as *cis/trans* diastereoisomers with respect to the relationship between susbtituents on the isoxazolidine ring. Using HMF nitone and methylacrylate, the four distinct products, *cis* and *trans* **2** and *cis* and *trans* **2',** were found in a 45:15:22:18 ratio (Scheme 1). This ratio was mostly constant, independently of the reaction conditions.



Scheme 1: Stereochemical distribution of the isomeric mixture HMF-derived isoxazolidines, 3,5-disubstituted (left) and 3,4-disubstituted (right).

Identification of the isomers could be achieved by detailed NMR analysis of the mixture of isomers based on ^{1}H, ^{13}C and 2D NMR spectra (HMBC, HSQC, NOSEY) allowed for the stereochemical attribution of each isomer. NMR spectra appeared to be complicated by the presence of broad signals in the ^{1}H and ^{13}C NMR spectra, especially around the protons of interest for the structural attribution C3 and C4 (Fig S1 and S2).

This broadness can be explained by the slow rotation around the simple bond between the two heterocycles at room temperature. By running the NMR experiments in DMSO at 90°C (fig. S3), signals became well defined and coupling constant could be measured. From the ^{1}H NMR and ^{13}C DEPT NMR, four isomers were distinctly identified in the mixture (Figure S4 and S5). The protons H_5 in **2** are found at δ 4.65 ppm and δ 4.71 ppm, correlate with the δ 74.5 ppm and δ 73.7 ppm corresponding carbon signals respectively. The proton H_5 at δ 4.65 ppm in 2D NOESY spectrum (Figure 2). shows strong correlation with H_3, which indicates the *cis*-configuration relationship between H_3 and H_5. Therefore, the proton at δ 4.71 ppm is *trans*-H_5 (Figure S4). The proton of H_4 in **2'** at δ 3.85 ppm, combining with the δ 50.4 ppm carbon signal, has the $J_{H4\text{-}H3}$ value of 8.9 Hz. The proton at δ 3.85 ppm should be in *cis*-configuration (Figure S6 and S7) as it shows a larger J value than *trans*-configuration found in similar furfural derivatives (*trans*-$J_{H4\text{-}H3}$ = 6.9 Hz).[45] The integration of these peaks in the various spectra of the crude mixtures allows the measurement of the ratio of the four isomers. The 3,5-isoxazolidine **2** was found to be the major regio-isomer constituting 60% of the mixture with a cis/trans relation of 45:15. The 3,4-isoxazolidine was the minor isomer, with the formation of the most sterically constrained **cis2'** in 22%, while this isomer was absent from the furfural adducts.[45] This difference in reactivity can be attributed to the presence of the 5-hydroxymethyl substituent of HMF, raising the HOMO of the nitrone allowing a better interaction with the LUMO of the dienophile.

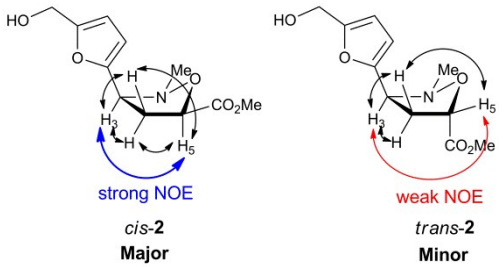


Figure 2. Structure of *cis* and *trans* **2** based on 2D NOESY indications on the H_3- H_5 relationship.

Structural scope - With a set of biobased furanic nitrones in hands, we then tested the scope of the cycloaddition reaction, in the optimized conditions for the reaction of

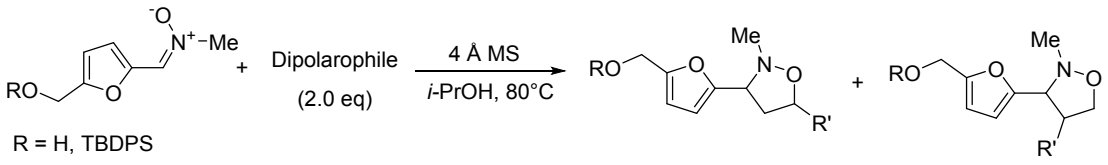
HMF-*N*-methyl nitrone and methyl acrylate (Table 3). Changing the nitrone substituent from methyl to benzyl and *tert*-butyl groups led to a slower reaction, due to increasing steric hindrance. A lower yield is indeed already observed for the benzyl derivative **3** was obtained in 65% yield, whereas the more hindered *tert*-butyl one **4** was only formed in 19% yield after 16 h and 42% yield after prolonged the reaction time to 64 h. The effect of steric hindrance was also observed on regioselectivity of those cycloadditions, bulkiness of the N-substituent favoring the formation of the 5-isoxazolidine product (respectively 76:24 and 90:10 for benzyl and *t*-butyl substituents). This could be clearly seen by checking the integration of the H_5 of each regio-isomers in ^1H NMR. The TBDPS-protected HMF-*N*-methyl nitrone **1d** was found to react similarly to the regular HMF one, giving the cycloaddition product **5** in 80% yield. Selectivity was also slightly improved; however, the substituent is rather far away from the reactive center and it is not easy to hypothesize on this effect.

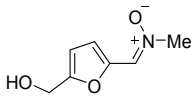
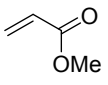
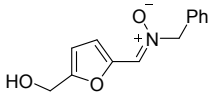
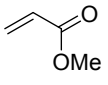
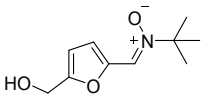
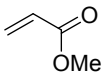
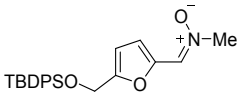
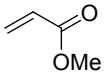
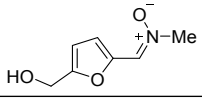
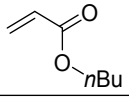
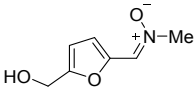
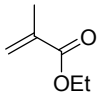
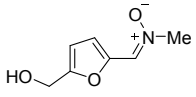
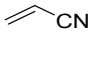
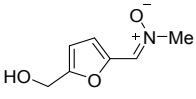
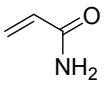
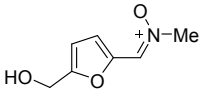
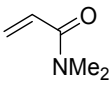
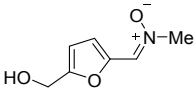
Different acrylates were then evaluated as dipolarophiles. Using *n*-butyl acrylate, the corresponding isoxazolidine **6** was obtained in 87% yield and the same moderate 65:35 regioselectivity as for methyl acrylate. Interestingly, the less polarized ethyl methacrylate provided almost exclusively the 3,5-isoxazolidine **7** in 86% yield. Nitrogen-containing dipolarophiles proved also suitable for the cycloaddition: the acrylonitrile derivative **8** could be obtained in 71% yield and 68:32 regioselectivity. While acrylamide provided the corresponding products **9** in 83% yield and better regioselectivity of 87:13; *N*,*N*-dimethyl acrylamide afforded the corresponding isoxazolidine in 88% yield with 83:17 regioselectivity. Diethyl vinylphosphonate could be also engaged in the reaction with moderate efficiency as the phosphonate containing product **11** was isolated in 39% yield.

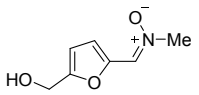
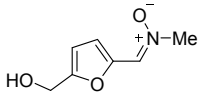
Finally, cyclic enones were successfully engaged in the cycloaddition, the cyclohexenone provided the bicyclic products **12** in 66% yield, and cyclopentenone in 44% yield. The reactions with cycloalkenones exhibited excellent reversal regioselectivity yielding almost exclusively the 4-carbonyl products. These results are

consistent with reports in literature which the more electron withdrawing group is attached to C-4 position when using 1,2-disubstituted alkenes.[46-48]

Table 3. Structural scope of the cycloaddition of HMF derived nitrone and dipolarophiles[(a)].



Nitrone	Dipolarophile	Product	Ratio[(b)]	Time (h)	Yield
		**2**	68:32	16	84%
		**3**	76:24	16	65%
		**4**	90:10	16 64	19% 42%
		**5**	80:20	16	80%
		**6**	65:35	16	87%
		**7**	>95:5	16	86%
		**8**	68:32	16	71%
		**9**	87:13	16 64	46% 83%
		**10**	83:17	16 64	56% 88%
		**11**	83:17	16	39%

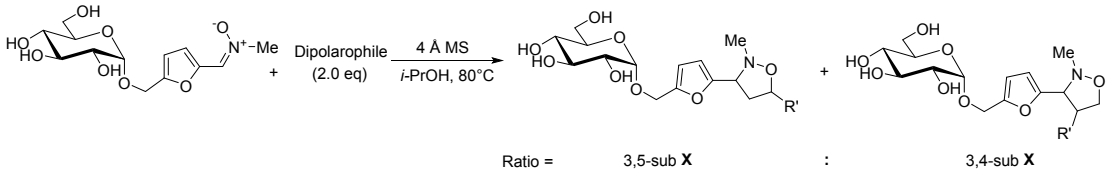
Nitrone	Dipolarophile	Product	Ratio[(b)]	Time (h)	Yield
		**12**	<5:95	16 64	44% 66%
		**13**	<5:95	8 16	29% 44%

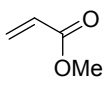
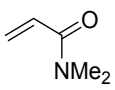
(a) General condition: nitrone (1.0 mmol) and dipolarophile (2.0 mmol) were treated in sealed MW tube with the nitrone concentration of 2M in isopropanol at 80°C in the given time.

(b) For cycloalkenones products, the major isomers are ones that carbonyl group adjacent to C-4 position.

We then extended the investigation to GMF, the glucosylated analog of HMF, much less available than HMF but interesting by exhibiting a remaining polar and functional moiety.[40-43] GMF-derived *N*-methyl nitrone **1e** yielded the corresponding carbohydrate containing isoxazolidine **14** in 69% yield and moderate 65:35 regioselectivity. The cycloaddition reaction between **1e** and *N*,*N*-dimethyl acrylamide led to product **15** with higher yield of 78% and a better 78:22 regioselectivity. Interestingly, with acrylamide, GMF nitrone **1e** gave a moderate 62% yield, and high regioselectivity more than 95:5 (Table 4). Unsurprisingly, the chiral information brought by the sugar moiety, quite far away from the nitrone group, did not seem to transfer to the chiral heterocycle during its formation.

Table 4. Scope of the cycloaddition of the GMF derived nitrone and dipolarophiles[(a)].



Dipolarophile	Product	Ratio[(b)]	Time (h)	Yield
	**14**	65:35	16	69%
	**15**	78:22	64	78%

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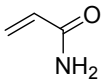
	**16**	>95:5	64	62%

(a) General condition: nitrone (1.0 mmol) and dipolarophile (2.0 mmol) were treated in sealed MW tube with the nitrone concentration of 2M in isopropanol at 80°C in the given time.

Multicomponent reaction

The multicomponent strategy relying on simply mixing the three starting materials, HMF, the hydroxylamine and the alkene, was also examined. The reaction conditions involve the mixing in a closed vessel of *N*-methylhydroxylamine hydrochloride, $NaHCO_3$ and a desiccating agent to trap the water formed during the reaction and methyl acrylate used as the dipolarophile, and heating to trigger the thermal cycloaddition.

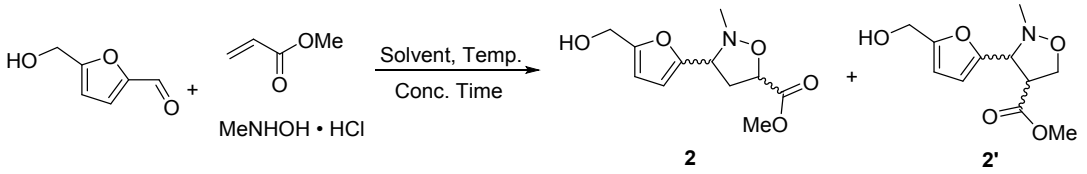
The influence of the solvent, concentration, temperature, reaction time, amount of hydroxylamine and acrylate, type and quantity of base was investigated and the results are summarized in Table 5. A short survey of possible solvents was first performed (entry 1-5) showing that apart from MeOH which gave a lower yield, DMSO, DMF, CH_3CN and *i*PrOH led to similar results. Considering the easiness to evaporate due to its low boiling point and its reasonable price, *i*-PrOH was selected as solvent for the study. Addition of ytterbium triflate as catalyst did not improve the yield (entry 6).

Changing the amount of amine down to 1.2 equiv. or up to 3.0 equiv. was not beneficial (entry 7-9). Moreover, when 3.0 equiv. of amine was used, more abundant CO_2 release could provoke leaks which could modify the content of the mixture. Increasing the temperature and concentration of the reaction increased the yield (entry 10-12), but a degradation was observed when the temperature reached 100°C (entry 15). Increasing the concentration to 2M increased the yield up to 75% even though much less amount of acrylate and hydroxylamine were used (2.0 equiv. and 1.2 equiv. respectively) (entry 14). Increasing the reaction time to 40 h did not improve the yield (entry 16). Moving from 5 equiv. of acrylate to 10 equiv. increased the NMR yield up to 74% (entry 17). However, it is not desirable to use a large excess of acrylate for atom-economy concerns.

Running the condensation at room temperature for 4h prior to the addition of acrylate in a one-pot two-step manner did not give better results (entry 18). Using other inorganic bases or a tertiary amine gave similar or lower yields (entry 19-22).

Overall, the MCR appears nearly as efficient than the step-wise reaction with yields up to 75%,. Though preferable in terms of number of steps, it is nevertheless slightly less practically effective due to uncomplete conversion of HMF resulting in more difficult isolation of the products requiring chromatography, whereas simple filtration/evaporation can be envisaged in most cases when starting from the isolated nitrone in the stepwise protocol.

Table 5. Multicomponent approach for reactions between HMF, hydroxylamine and methyl acrylate.



Entry	Solvent	Conc. (M)	Temp (°C)	Time (h)	Amine (equiv.)	Acrylate (equiv.)	Base (equiv.)	Yield (**2**+**2'**)
1	MeOH	0.5	65	65	2	5	$NaHCO_3$/ 2.5	38%
2	*i*PrOH	0.5	65	65	2	5	$NaHCO_3$/ 2.5	60%
3	DMF	0.5	65	65	2	5	$NaHCO_3$/ 2.5	64%
4	CH_3CN	0.5	65	65	2	5	$NaHCO_3$/ 2.5	55%
5	DMSO	0.5	65	65	2	5	$NaHCO_3$/ 2.5	65%
6[b]	*i*PrOH	0.5	65	16	2	5	$NaHCO_3$/ 2.5	28%
7	*i*PrOH	0.5	65	16	2	5	$NaHCO_3$/ 2.5	29%
8	*i*PrOH	0.5	65	16	1.2	5	$NaHCO_3$/ 1.5	32%

Entry	Solvent	Conc. (M)	Temp (°C)	Time (h)	Amine (equiv.)	Acrylate (equiv.)	Base (equiv.)	Yield (**2+2'**)
9	*i*PrOH	0.5	65	16	3	5	$NaHCO_3$/ 3.5	25%
10	*i*PrOH	1	65	16	2	5	$NaHCO_3$/ 2.5	50%
11	*i*PrOH	0.5	80	16	2	5	$NaHCO_3$/ 2.5	60%
12	*i*PrOH	1	80	16	2	5	$NaHCO_3$/ 2.5	65%
13[c]	*i*PrOH	1	80	16	2	2	$NaHCO_3$/ 2.5	65%
14	*i*PrOH	2	80	16	1.2	2	$NaHCO_3$/ 1.5	75%
15	*i*PrOH	1	100	16	2	5	$NaHCO_3$/ 2.5	62%
16	*i*PrOH	1	80	40	2	10	$NaHCO_3$/ 2.5	62% [d]
17	*i*PrOH	1	80	16	2	5	$NaHCO_3$/ 2.5	74%
18	*i*PrOH	1	r.t - 80	4 + 12 [f]	2	5 [d]	$NaHCO_3$/ 2.5	67%
19	*i*PrOH	1	80	16	2	5	K_2CO_3/ 2.5	56%
20	*i*PrOH	1	80	16	2	5	Li_2CO_3/ 2.5	52%
21	*i*PrOH	1	80	16	2	5	NaOAc/ 2.5	50%
22	*i*PrOH	1	8	16	2	5	Et_3N/ 2.5	36%

(a) Reaction condition: All the experiments were carried out mixing all the components: HMF (1 mmol), *N*-methylhydroxylamine and methyl acrylate (5 mmol) in a sealed MW tube. The NMR yields were determined using 1,3,6-trimethoxybenzene as internal standard (0.33 mmol), comparing the furan signals of the products to the aromatic C-H of the standard.

(b) Addition of ytterbium triflate as catalyst.

(c) Significant degradation was observed.

(d) Condensation before acrylate added.

Conclusion

The complete study of the use of HMF for accessing isoxazolines via the 1,3-dipolar cycloaddition of its intermediate nitrone reaction with activated alkenes has been unveiled, comparing the stepwise and the multicomponent approaches. Good yields of

cycloadducts are reached either through both protocols using isopropanol as a clean and convenient solvent. In the stepwise protocol, the first step forms readily the nitrone in high yield isolated by simple filtration. Both the stepwise and the multicomponent appear therefore as efficient and direct. Stoichiometries as low as 1.2 equiv of activated alkene can be used. The stereochemical outcome of the reaction has been fully established, showing for some cases (hindered nitrones or alkenes) significant levels of regioselectivity. The reaction can be applied to a wide range of activated alkenes, alkylhydroxylamines and HMF ethers offering diversity in the possible uses of the reaction towards novel heterocyclic compounds in direct and clean conditions.

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