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The synthesis of HMF-based α-amino phosphonates *via* one-pot Kabachnik–Fields reaction†

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The first use of biomass-derived HMF in the one-pot Kabachnik–Fields reaction is reported here. A wide range of furan-based α-amino phosphonates were prepared in moderate to excellent yields under mild, effective and environmentally-benign conditions: iodine as a non-metal catalyst, biobased 2-MeTHF as the solvent and room or moderate temperature. The hydroxymethyl group of HMF persists in the Kabachnik–Fields products, widening the scope of further modification and derivatization compared to those arising from furfural. Issues involving the diastereoselectivity and double Kabachnik–Fields condensation were also faced.

Recently, the production of chemicals from renewable biomass has attracted growing interests due to the dwindling reserves of fossil resources and the increasing awareness of environmental concerns.[1] 5-Hydroxymethylfurfural (HMF), a promising primary biomass-derived platform chemical readily obtained from acid-catalyzed dehydration of six-carbon carbohydrates, displays a strong potential in organic synthesis.[2] Besides the well-developed conversions of HMF towards monomers and biofuels *via* oxidation or reduction reactions,[3] some remarkable strategies converting HMF to high value-added fine chemicals have been disclosed.[4] Nevertheless, the specific reactivity and reduced stability of HMF, in comparison with the pentose-derived furfural homolog, have limited its use in synthetic applications.[5] Furthermore, its commercial availability, though not anymore a barrier nowadays, has limited the number of investigations in the past. In this regard, developing efficient and economic routes to existing or novel fine chemicals from HMF, with its different reactivity compared to simpler aldehydes, is still a challenge.

Multi-component reactions (MCRs) are extremely convenient and efficient strategies to prepare highly functionalized compounds from simple starting materials by one-pot procedures. Since they have many advantages, such as high atom economy, high convergence, time and energy saving, MCRs have gained much attention in modern synthetic organic chemistry.[6] Nevertheless, to our knowledge, the direct utilization of HMF in MCR processes has been only rarely explored.

α-Amino phosphonates, due to the structural analogy to natural α-amino acids and their significant biological activities, such as antitumor, antitubercular, cytotoxic activities, and so on,[7] have been the subject of considerable interest in the past decades both in synthetic organic and medicinal chemistry.[8] Among several methods for preparing α-amino phosphonates, the Kabachnik–Fields reaction, a one-pot condensation of an aldehyde, an amine and a dialkyl phosphite is the most effective and convenient strategy.[9] A large number of conditions have been reported for the acid-catalyzed (Lewis/Brønsted)[10] and catalyst-free[11] Kabachnik–Fields reaction, affording the α-amino phosphonates from various aldehydes. However, none of studies have included HMF as a substrate in their scope although the products from HMF can offer more possibilities for further functionalization, thanks to its CH_2OH appendage. The sole synthesis of α-amino phosphonates from HMF was reported by Cottier and Skowroński in a two-step reaction strategy, consisting in pre-formation of the imine which upon isolation reacted with dialkyl phosphites as nucleophilic species at high temperature using trifluoroacetic acid as catalyst.[12] Thus, a milder and more direct procedure for the synthesis of α-amino phosphonates from HMF is still to be developed.

As part of our on-going interest on the application of HMF towards fine chemicals and on green and sustainable chemistry,[13] we explored the possibility to synthesize furan-based α-amino phosphonates *via* the one-pot Kabachnik–Fields condensation, directly from HMF.

For this study, we selected molecular iodine as a mild and effective Lewis acid catalyst, as often used in multicomponent synthesis because of its operational simplicity, low cost and toxicity and likely to be compatible with HMF sensitivity to acidic conditions.[14] Wu and co-workers have confirmed its efficiency in Kabachnik–Fields reactions of simple aldehydes such as benzaldehyde and furfural.[15] The primary set of

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experimental conditions has been fixed as 5 mol% iodine in ethanol [0.5 M] with equimolar stoichiometric ratio of all partners (HMF, aniline, diethyl phosphite). The corresponding Kabachnik–Fields product **4a** was obtained in 71% isolated yield after 24 h, together with around 11% of unreacted HMF and 6% of the intermediate imine (Table 1, entry 1).

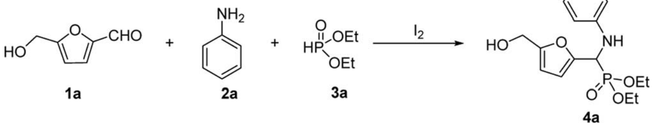
Based on this preliminary result, the reaction conditions were optimized, first by studying the influence of the solvent. THF was found to provide a better yield than EtOH, MeCN and DCM, affording product **4a** in 84% yield (Table 1, entries 1–4). The bio-based 2-methyltetrahydrofuran (2-MeTHF), considered as a greener alternative to THF proved to be also efficient (Table 1 entry 5). Using excess diethyl phosphite (1.5 equivalents) led to better yields both in THF and in 2-MeTHF (Table 1, entries 6 and 7). Considering all the benefits (production from renewable resources, easy degradation, low miscibility with water and enhanced stability),[16] we decided to continue the investigation with 2-MeTHF as the solvent.

Decreasing the catalyst loading to 2.5 mol% and 1 mol% led to slightly slower reactions (77% and 61% respectively) (Table 1, entries 8 and 9). It is important to note that the reaction could proceed even without any catalyst, though giving the expected product in a moderate yield (54%) after 8 h, but in a satisfactory 80% yield after 24 h (Table 1, entry 10). Even though the catalyst-free conditions afford good yields in long enough reaction time, the 5 mol% I_2 conditions give the best balance between reaction efficiency and reaction duration, and were preserved for the rest of the study. With respect to temperature, performing the reaction at 50 °C led to total conversion of HMF within 4 h but with a slight decrease of the yield (Table 1, entry 11). Prolongation of the reaction time led to lower yields. The same result was observed when the reaction time (equimolar quantities of all reactants) was refluxed in 2-MeTHF (Table 1, entry 12).

With the optimized conditions in hand (Table 1, entry 7), the scope of the reaction was investigated with respect to the nature of the amine and the phosphite, allowing the access to a library of novel α-amino phosphonates. In Scheme 1 is depicted the scope of amines used in the reaction.

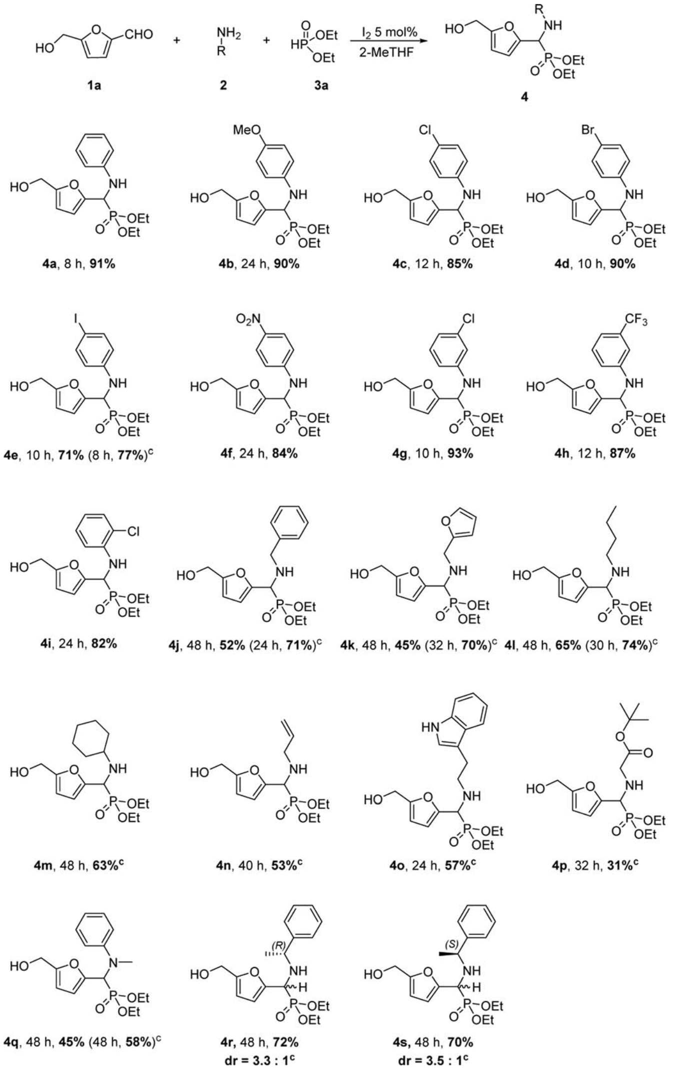
Whatever the electron-donating or electron-withdrawing nature of the *para* substituent (methoxy-, chloro-, bromo-, iodo- and nitro-) on the aniline, the corresponding α-amino phosphonates **4b–4f** were obtained in good to excellent yields (71–90%). An exception was observed for *p*-iodo-aniline requiring a 50 °C temperature for producing **4e** in 77% yield. The same tendency was noticed for *meta*-substituted anilines, presumed to display low electronic influence on the reactivity (yields of 93% for **4g** and 87% for **4h**), and in a more unexpected way for 2-chloroaniline (82% for **4i**). These results revealed that the substituted group on phenyl ring of aniline has globally a low impact on the reaction. Compared to anilines, aliphatic amines were found consistently as less reactive. In the case of aliphatic amines, elevated temperature (50 °C) was required to promote the reaction. Benzylamine and furfurylamine provided the corresponding α-amino phosphonates **4j** and **4k** in moderate yields, respectively 71% and 70%. Similar results were obtained for *n*-butylamine, cyclohexylamine and allylamine (**4l–4n**). Non-protected tryptamine afforded compound **4o** in 57% yield. The product possibly arising from the reaction of the pyrrolic amine of tryptamine was not observed. ^{tert}-Butyl glycinate also worked under the conditions but gave a poor yield of **4p** (31%). *N*-Methyl aniline, as an example of secondary amine, was also less reactive than aniline, giving **4q** in 58% yield. When the chiral amine (*R*)-α-methylbenzylamine was used, the mixture of products was obtained **4r** in 72% yield, from which the two isomers could not be separated entirely by column chromatography. A moderate diastereoselectivity was observed,

Table 1 The Optimization of Kabachnik–Fields reaction of HMF[a]



Entry	Cat. loading	Solvent [0.5 M]	Temp.	Ratio **1a**/**2a**/**3a**	Time	Isolated yield
1	5 mol%	EtOH	25 °C	1 : 1 : 1	24 h	71%
2	5 mol%	MeCN	25 °C	1 : 1 : 1	24 h	60%
3	5 mol%	DCM	25 °C	1 : 1 : 1	24 h	31%
4	5 mol%	THF	25 °C	1 : 1 : 1	24 h	84%
5	5 mol%	2-MeTHF	25 °C	1 : 1 : 1	24 h	74%
6	5 mol%	THF	25 °C	1 : 1 : 1.5	24 h	90%
7	**5 mol%**	**2-MeTHF**	**25 °C**	**1 : 1 : 1.5**	**8 h**	**91%**
8	2.5 mol%	2-MeTHF	25 °C	1 : 1 : 1.5	8 h	77%
9	1 mol%	2-MeTHF	25 °C	1 : 1 : 1.5	8 h	61%
10	—	2-MeTHF	25 °C	1 : 1 : 1.5	8 h	54% (80%)[b]
11	5 mol%	2-MeTHF	50 °C	1 : 1 : 1.5	4 h	83%
12	5 mol%	2-MeTHF	78 °C	1 : 1 : 1	3 h	71%

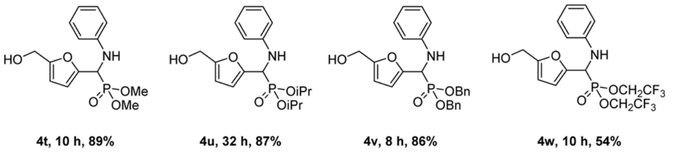
[a] The reaction was carried out in a sealed tube with HMF, aniline, diethyl phosphite, solvent and iodine, stirred at corresponding temperature for indicated time. [b] 24 h.



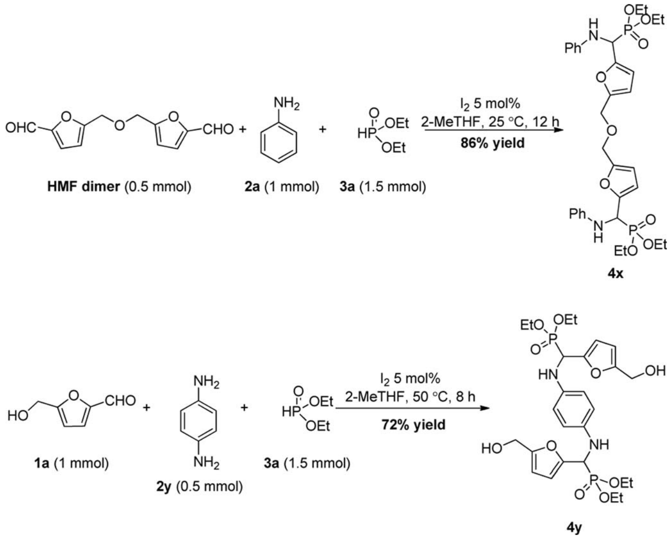
Scheme 1 The Kabachnik–Fields reaction of HMF and different amines.[a,b] [a]The reaction was carried out with HMF (1 mmol), amine (1 mmol), diethyl phosphite (1.5 mmol) with I_2 (5 mol%) in 2-MeTHF (2 mL), stirred at 25 °C for indicated time. [b]Isolated yield. [c]At 50 °C.

with a 3.3 : 1 ratio of two diastereoisomers observed on the base of ^{31}P NMR spectra. Similarly, (*S*)-α-methylbenzylamine gave the products **4s** as a 3.5 : 1 mixture of two diastereoisomers in 70% yield.

The nature of the dialkyl phosphite was also examined but to a minor extent due to the low diversity of commercially available phosphite reagents (Scheme 2). Dimethyl-, diisopropyl- and dibenzyl-phosphites afforded the corresponding products (**4t**–**4v**) in a range of yields of 86–89%. Surprisingly, phosphite with two strongly electron-withdrawing CF_3– groups could also be used affording **4w** in a modest 54% yield under the optimized conditions.



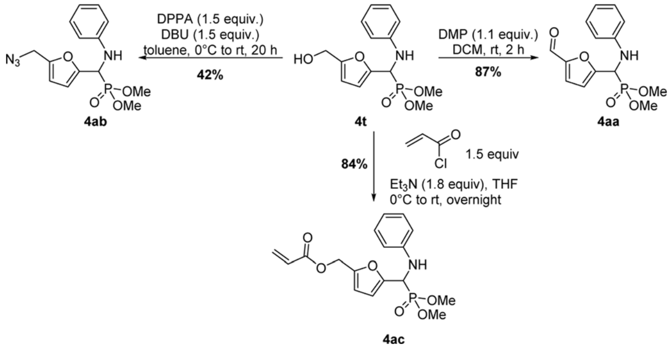
Scheme 2 The Kabachnik–Fields reaction of HMF and commercially available phosphites.



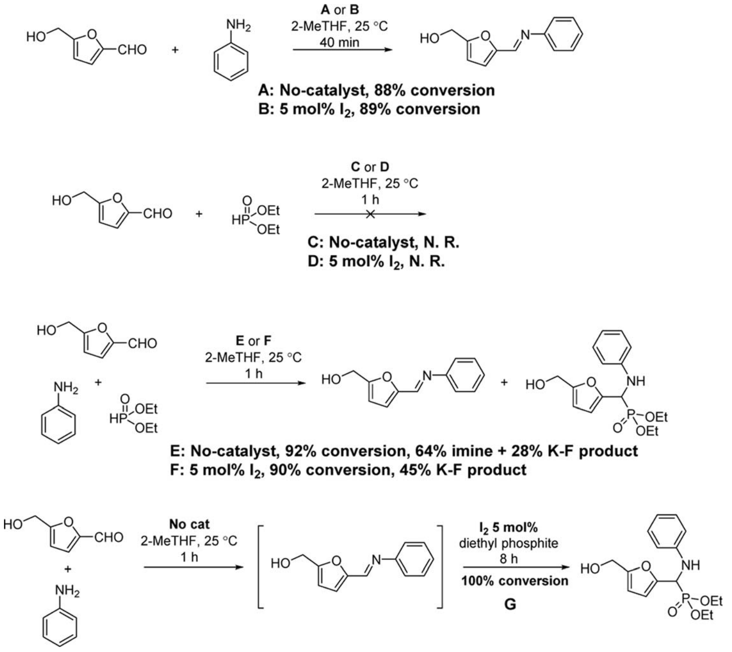
Scheme 3 The double Kabachnik–Fields reaction.

In order to expand the application of HMF, a pre-prepared 5,5′-[oxybis(methylene)]bis-2-furfural *via* self-etherification of HMF was subjected to the optimized conditions, resulting into the expected double Kabachnik–Fields product **4x** in 86% yield. Alternatively, using *p*-phenylenediamine instead of aniline led to the other type of double Kabachnik–Fields product **4y**. The results above undoubtedly indicate the possible application of the strategy towards highly functional polymers *via* Kabachnik–Fields polycondensation of 5,5′-[oxybis(methylene)]bis-2-furfural and suitable diamines (Scheme 3).[17]

A couple of derivatizations on hydroxyl group of the Kabachnik–Fields product were investigated using **4t** as model substrate (Scheme 4). The aldehyde **4aa** could be prepared in 87% yield by oxidation of **4t** using Dess–Martin periodinane (DMP). The hydroxyl group of **4t** could be also converted into an azido group after treatment with diphenylphosphoryl azide in the presence of DBU in 42% yield (compound **4ab**). The acrylate **4ac** was also easily obtained in a good yield. Diversification and optimization of these reactions are now in progress in the lab for further illustrating the usefulness of the hydroxymethyl appendage and providing a library of new α-amino phosphonates.



Scheme 4 The derivatizations on hydroxyl group.



Scheme 5 Control experiments.

Usually in a multicomponent reaction, the mechanism is not distinct because the reaction may undergo different pathways depending on which reactants react at first step. In order to gain insight into the mechanism of the Kabachnik–Fields reaction in our case, a series of control stepwise experiments were carried out (Scheme 5 and for more details see ESI†). Mixing HMF (1 mmol) and aniline (1 mmol) in 2-MeTHF yielded the imine rapidly with and without iodine, with around 90% conversion observed in the crude NMR after 40 min in both cases (Exp. A and B). Subsequent addition of diethyl phosphite (1.5 mmol) and I_2 (5 mol%) to the solution of the *in situ* formed imine (HMF, aniline, 1 h) afforded cleanly **4a** after 8 h as seen by NMR (Exp. G). On the other hand, no reaction occurred when HMF (1 mmol) and diethyl phosphite (1.5 mmol) were mixed, either in the presence or absence of iodine (Exp. C and D). The above results indicate that the reaction likely undergoes the imine pathway, followed by nucleophilic attack by the phosphite to afford the α-amino phosphonate.[8e,18] It is also known that iodine, as a Lewis acid, can activate imines in nucleophilic addition reactions.[8e,19] This imine pathway was corroborated by the observation of the imine in the crude NMR of the three-component reaction mixture in the absence of iodine (Exp. E). In the presence of iodine, the proton of CH═N is shifted from 8.17 ppm to 8.42 ppm which made it difficult to identify, but the imine component was clearly detected in the crude reaction mixture by MS (imine plus H^+: 202.0), thus also supporting the imine pathway (Exp. F).

Conclusion

To summarize, we have reported the first application of biomass-derived HMF in the one-pot Kabachnik–Fields reaction, leading to hydroxymethylated heterocyclic α-amino phosphonates. The conditions are simple to settle, effective and environmentally benign. The hydroxymethylfuran moiety in the targeted Kabachnik–Fields products provides additional opportunities for further modification widening the scope of possibly reachable α-amino phosphonates by this route. Moreover, a new possibility for the synthesis of functional polymers *via* Kabachnik–Fields polycondensation from the 5,5′-[oxybis(methylene)]bis-2-furfural was proposed.

Conflicts of interest

There are no conflicts to declare.

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