Furan Synthesis

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A Modular and Scalable One-Pot Synthesis of Polysubstituted Furans

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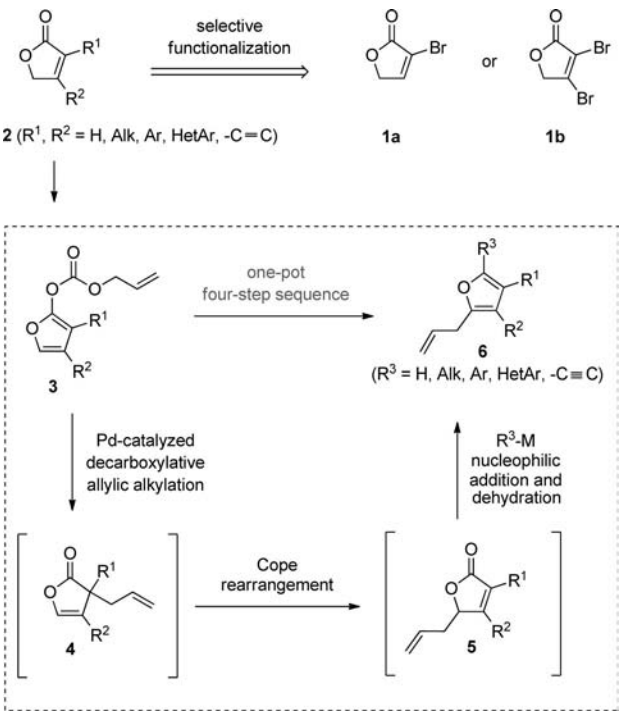
Functionalized furans represent an important class of five-membered heterocycles prevalent in a number of biologically active natural products as well as in various pharmaceuticals and agrochemicals.[1] They are also particularly useful building blocks, finding use in fields such as synthetic organic chemistry,[2] material science,[3] nonlinear optics,[4] and even supramolecular chemistry.[5] As a consequence, a number of synthetic methods have been specifically designed to access functionalized furans.[6–10] Nonetheless, the development of flexible and predictable de novo approaches to diversely substituted furans starting from inexpensive and readily available compounds still remains an area of ongoing interest,[11] particularly since the emergence of fragment-based drug discovery[12] for the development of small molecules as novel potent therapeutic agents.

The palladium-catalyzed decarboxylative allylic alkylation (PDAA) reaction, most commonly referred to as the Tsuji–Trost reaction,[13] has become a remarkably powerful synthetic tool for the construction of C–C bonds. This transformation, which typically displays broad functional-group tolerance, has been successfully applied to a wide variety of substrates bearing either an allyl ester or an allyl enol carbonate moiety.[14–17]

As part of an ongoing research program aimed at developing new methods for the synthesis of functionalized heterocycles,[18] we became particularly interested in the outcome of the PDAA reaction when applied to a new type of substrate, namely allyl dienol carbonates **3**. Indeed, we reasoned that by analogy with allyl vinyl carbonates, such substrates could also undergo facile oxidative addition followed by decarboxylation to afford the corresponding palladium-dienolate species which, in turn, should generate the α-allyl product **4**. The latter could then be engaged in a [3,3]-sigmatropic Cope rearrangement[19] to form the corresponding γ-allyl furanone **5**, which could eventually be treated with a variety of hard nucleophiles followed by an acidic work-up to promote sequential functionalization and dehydration and potentially generate the corresponding bis-, tris- or tetrasubstituted furan **6** in an entirely tailored fashion (Scheme 1). If successful, this reaction sequence would represent a practical, a highly versatile, and an exceptionally atom-economical method for accessing diversely substituted furans starting from readily available starting materials. Herein, we report the results of our endeavors.



Scheme 1. One-pot approach to polysubstituted furans.

To test our hypothesis, allyl dienol carbonate **3a** was chosen as a model substrate. The latter, was prepared in two steps and 60% overall yield starting from bromo furanone **1a** through a $[PdCl_2(PPh_3)_2]$-catalyzed Suzuki coupling followed by treatment with NaHMDS and allyl chloroformate (THF, −60 °C). Compound **3a** was then subjected to standard PDAA reaction conditions ($[Pd(PPh_3)_4]$ (3 mol%), $CDCl_3$, RT; Scheme 2). In less than ten minutes, complete conversion of the starting material was observed and, to our delight, we were able to isolate both the α- and the γ-allyl products **4a** and **5a** in 76% and 18% yield, respectively. Interestingly, after conducting a kinetic study by monitoring the reaction through ^1H NMR analysis (see the Supporting Information), we were able to determine that the formation of the γ-allyl product **5a** was solely the result of a competitive γ-allylation rather than an in situ [3,3]-sigmatropic Cope rearrangement, which could have been triggered during the PDAA reaction. The resulting α-allyl product **4a** was eventually engaged in the actual Cope rearrangement. After exploring various reaction conditions, we found that microwave (MW) irradiation of a solution of **4a** in CH_3CN (closed vessel, 400 W, 180 °C, 1 hour) cleanly afforded the γ-allyl furanone **5a** in 92% yield.

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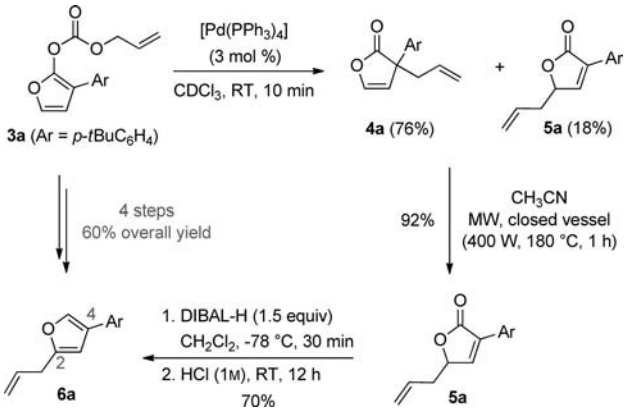
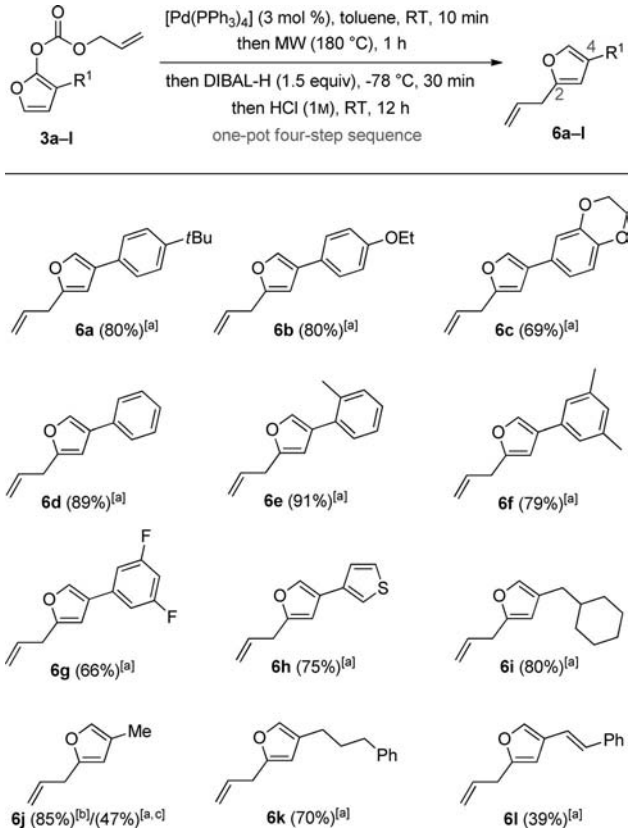


Scheme 2. Sequential approach to 2,4-disubstituted furans. DIBAL-H = diisobutylaluminum hydride.



Scheme 3. One-pot synthesis of 2,4-disubstituted furans. [a] Yield of product upon isolation. [b] Yield determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxy-benzene as an internal reference. [c] Reaction sequence run in CH_2Cl_2 instead of toluene.

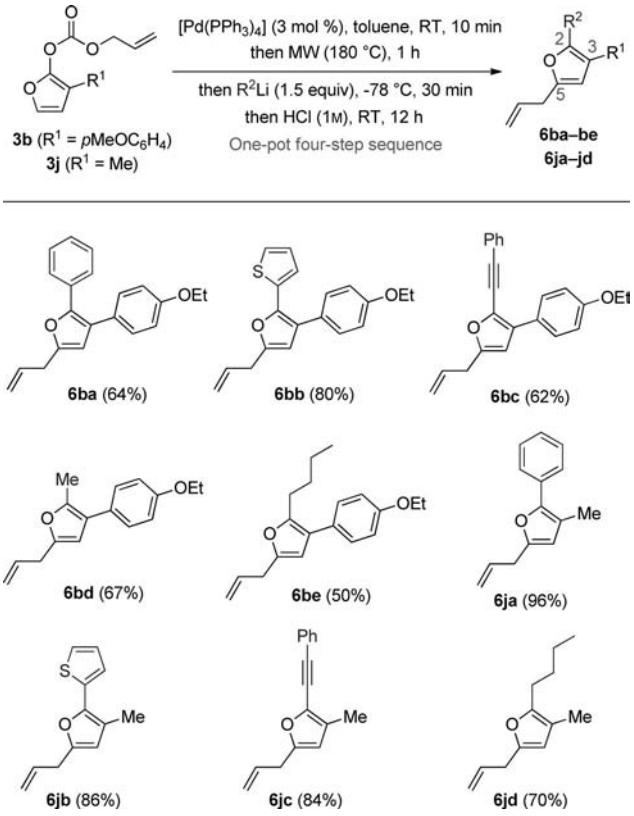
The latter was finally treated with DIBAL-H[20] (CH_2Cl_2, −78 °C, 30 minutes) followed by an acidic work-up (1M HCl, RT, 12 hours) to afford the corresponding 2,4-disubstituted furan **6a** in 70% yield after purification over alumina (60% overall yield starting from allyl dienol carbonate **3a**). As a general trend, these preliminary results showed that allyl dienol carbonates such as **3a** could be converted into the corresponding 2,4-disubstituted furans through a simple four-step sequence, which features a palladium-catalyzed decarboxylative allylic alkylation, a Cope rearrangement, a nucleophilic addition, and a dehydration reaction (Scheme 2).

In the last decade, research efforts have increasingly been dedicated to the development of more sustainable synthetic methods, which take into account new constraints such as atom-, step-, redox-, and pot economy.[21,22] In this context, we aimed to conduct the entire sequence in the same flask to avoid unnecessary and tedious purification steps and thus offer a more straightforward and practical synthetic method. After much experimentation, not only were we able to perform the entire four-step sequence in toluene without isolating any of the intermediates, but we were also able to improve the overall yield from 60% to 80% in the case of 2,4-disubstituted furan **6a** (Scheme 3).

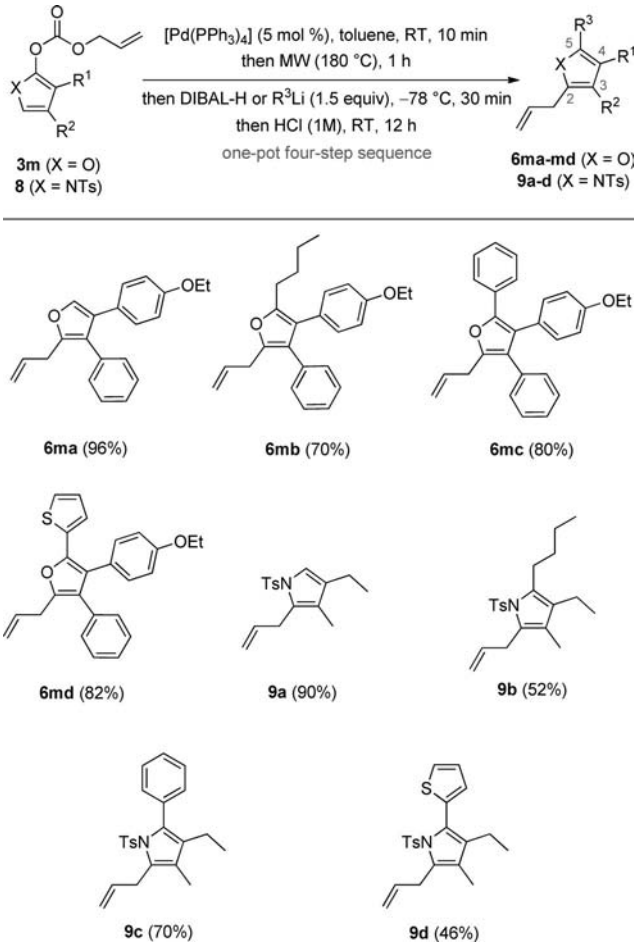
Having identified a useful set of reaction conditions, we next examined the scope and limitations of this transformation. To this end, several aryl- (**3a**–**g**), heteroaryl- (**3h**), alkyl- (**3i**–**k**), and vinyl-substituted (**3l**) dienol carbonates were synthesized and subjected to our one-pot four-step sequence. The results are summarized in Scheme 3. As a general trend, the expected furans **6a**–**k** were obtained in high yields ranging from 69 to 91%, independent of the substitution pattern on the starting allyl dienol carbonates **3a—k**; an exception was the allyl dienol carbonate **3l** (corresponding product isolated in 39% yield) bearing a vinyl moiety, which is prone to polymerization during the Cope rearrangement. Notably, the isolation of furan **6j** was quite challenging because of its high volatility. In this specific case, the reaction was performed in dichloromethane and the yield (85%) was determined by ^{1}H NMR spectroscopy of the crude residue using 1,3,5-trimethoxybenzene as an internal reference (47% yield upon isolation).

To introduce more structural diversity around the furan ring, the one-pot four-step sequence was slightly modified. Hence, after the traditional PDAA and the Cope rearrangement, the nucleophilic addition was carried out using a selection of organolithium reagents (R^2Li) instead of DIBAL-H under otherwise identical conditions (Scheme 4). Interestingly, whether an alkyl-, an aryl-, a heteroaryl-, or a propargyl lithium reagent was used as the nucleophile in conjunction with the two allyl dienol carbonates tested (**3b** and **3j**), the corresponding 2,3,5-trisubstituted furans (**6ba**–**be** and **6ja**–**jd**) were obtained in good to excellent yields (50–96% overall yield, Scheme 4).

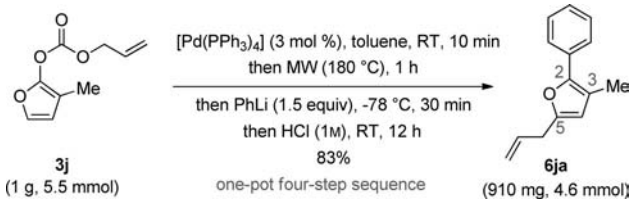
With the aim of generating further structural diversity, we then applied the one-pot four-step sequence to the disubstituted allyl dienol carbonate **3m**. The latter was prepared in three steps and 29% overall yield (unoptimized) starting from dibromo furanone **1b** through consecutive and regioselective $[PdCl_2(PPh_3)_2]$-catalyzed Suzuki coupling [23] and treatment of the resulting disubstituted furanone **2** with NaHMDS and allyl chloroformate in THF at −60 °C. After subjecting allyl dienol carbonate **3m** to the PDAA reaction and the subsequent microwave-mediated Cope rearrangement, the in situ nucleophilic addition reactions were carried out using either DIBAL-H or an organolithium reagent, such as *n*BuLi, PhLi, or 2-thienyllithium, thus affording, after acidic work-up, the corresponding 2,3,4-trisubstituted furans **6ma** and



Scheme 4. One-pot synthesis of 2,3,5-trisubstituted furans. Yield of isolated product is given in parentheses.



Scheme 5. One-pot synthesis of 2,3,4-trisubstituted- and 2,3,4,5-tetrasubstituted furans and pyrroles. Yields represent products isolated. Ts = *p*-toluenesulfonyl.



Scheme 6. Gram-scale synthesis of 2,3,5-trisubstituted furan **6ja**.

2,3,4,5-tetrasubstituted furans **6mb–md**. As a general trend, the desired heterocycles were obtained in particularly high yields, ranging from 70% to 96%, yields, which compare favorably with those of other methods reported in the literature (Scheme 5).

Although the feasibility of generating polysubstituted furans in a laboratory setting on a milligram scale was demonstrated, another important challenge was to perform this one-pot four-step sequence on a gram scale in order to validate the efficacy and the practicality of the method. Unsurprisingly, the reaction proved scalable, with the use of allyl dienol carbonate **3j** giving 83% of the desired product **6ja** (Scheme 6).

Finally, with an efficient synthesis of polysubstituted furans established, we turned our attention to the application of the method to the synthesis of pyrroles, which are another important class of heterocycle.[24,25] In the event, the *N*-tosyl precursor **8** was prepared and subjected to the same reaction conditions that were used for the synthesis of the furans. To our delight, we were able to isolate the corresponding 2,3,4-trisubstituted pyrrole **9a** and the 2,3,4,5-tetrasubstituted pyrroles **9b–d** in relatively high yield ranging from 46% to 90% (Scheme 5).

In summary, we have developed an extremely mild and efficient method for the preparation of diversely substituted furans, including 2,4-disubstituted-, 2,3,4- and 2,3,5-trisubstituted-, and 2,3,4,5-tetrasubstituted furans, starting from simple and readily available substrates. Overall, this reaction sequence represents an operationally simple, an easily scalable and, most of all, a particularly flexible method for constructing furans in an entirely tailored fashion. Notably, this is probably the only method that allows access to furans of virtually any substitution pattern. Additionally, this method was also successfully applied to the synthesis of polysubstituted pyrroles. The implementation of the present method to the synthesis of other key heterocycles is currently being investigated and will be reported in due course.

Experimental Section

Typical procedure for the synthesis of 2,5-disubstituted furan **6a** from allyl dienol carbonate **3a**: to a solution of allyl dienol carbonate **3a**

(50 mg, 0.17 mmol) in toluene (1 mL) at RT was added $[Pd(PPh_3)_4]$ (5.8 mg, 0.005 mmol) and the resulting reaction mixture was stirred at the same temperature until complete conversion of the starting material was detected; the reaction was monitored by TLC analysis and was usually complete within 10 min. The crude reaction mixture was then heated under microwave irradiation (closed vessel, 400 W, 180 °C) for 1 h; the temperature of the reaction mixture was lowered to −78 °C and then a solution of DIBAL-H (250 μL of a 1 M solution in CH_2Cl_2, 0.25 mmol) was added slowly to the reaction mixture. After complete conversion of the furanone intermediate **5a**, a 1 M aqueous solution of HCl was added and stirring was continued for 12 h at RT. The organic layer was then separated and the aqueous phase was extracted twice with EtOAc (2 mL). The combined organic layers were then washed with brine (2 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to afford a crude residue, which was purified by flash column chromatography over alumina using hexane as eluent. Pure furan **6a** (32 mg, 80 %) was isolated as a colorless oil.

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