

A tandem Mannich addition–palladium catalyzed ring-closing route toward 4-substituted-3(2*H*)-furanones

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Abstract

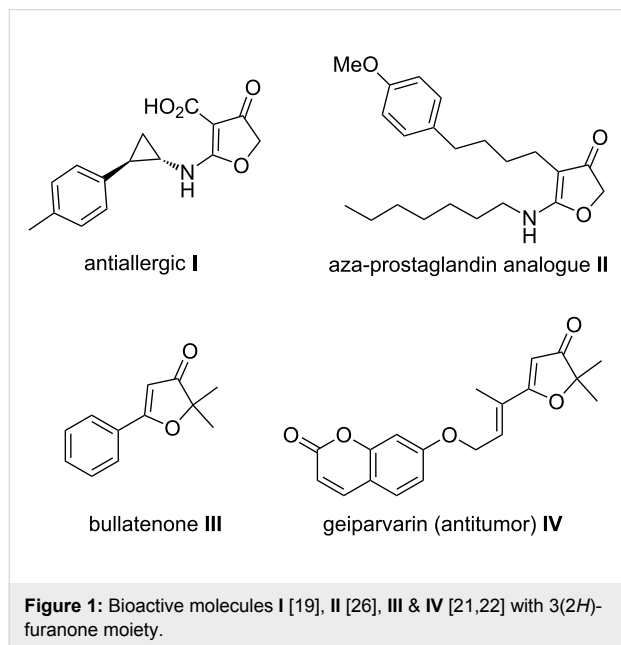
A facile route towards highly functionalized 3(2*H*)-furanones via a sequential Mannich addition–palladium catalyzed ring closing has been elaborated. The reaction of 4-chloroacetoacetate esters with imines derived from aliphatic and aromatic aldehydes under palladium catalysis afforded 4-substituted furanones in good to excellent yields. 4-Hydrazino-3(2*H*)-furanones could also be synthesized from diazo esters in excellent yields by utilising the developed strategy. We could also efficiently transform the substituted furanones to aza-prostaglandin analogues.

Introduction

Organic chemists welcome the introduction of facile tandem protocols because of the advantages of multiple bond formation in one-pot processes, which in turn makes the process economic and most importantly eco-friendly [1,2]. Conjugate addition is a very efficient tool used by synthetic chemists for the construction of carbon–carbon or carbon–heteroatom bonds [3]. Much effort has been invested to develop different variants of conjugate additions, both in catalyzed and non-catalyzed pathways.

α -Halo ketones are known to react with zero-valent palladium like allyl halides to form oxa- π -allylpalladium complexes. Despite this fact, only minor attention has been paid to the formation of oxa- π -allylpalladium species from α -halo ketones and to their reactivity [4-8]. In this report we describe the use of a tandem methodology involving a Mannich addition/palladium-catalyzed ring-closing protocol for the facile synthesis of 4-substituted furanones.

Since 3(2*H*)-furanones form the main component of many natural products and pharmaceutically important compounds (Figure 1) a number of routes for their synthesis [9-18] to have been reported in the literature.



Substituted 3(2*H*)-furanones exhibit a wide range of biological activities such as antiallergic, antiulcer, antiinflammatory, and antitumor activities or selective COX-2 inhibition [19-26]. Syn-

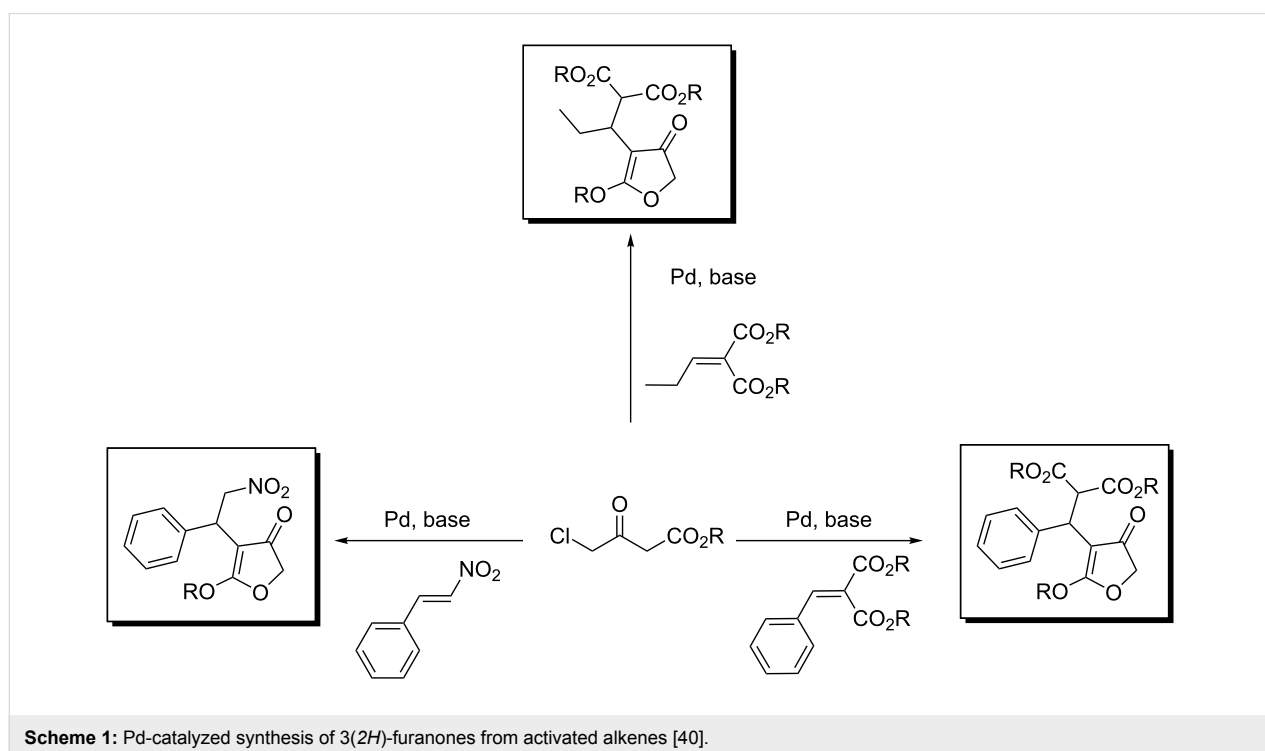
thetic routes for the preparation of these compounds involve transformations of substituted α -hydroxy-1,3-diketones [15,17], substituted furans [27-29], cyclization of allenic hydroxyketones [30], transition metal-catalyzed strategies (Au [31-33], Pt [34,35], Pd [36], Hg [37]), etc. Lately, organo-catalyzed asymmetric routes towards 3(2*H*)-furanones from 4-haloacetoacetates and nitrostyrene were reported by Lu et al. [38] and Yan et al. [39].

We have recently reported on a palladium-catalyzed tandem methodology for the synthesis of 4-substituted-3(2*H*)-furanones from activated alkenes and 4-chloroacetoacetates (Scheme 1) [40].

The reaction was found to be general for a wide range of alkenes derived from aromatic and aliphatic aldehydes. The reaction proceeded via Michael addition of the acetoacetate to the alkene with a subsequent palladium-catalyzed ring closure of the primary adduct to form the furanone. In this paper, we report our investigations that extend the reaction to heteroatom-containing electrophiles such as imines and diazo esters.

Results and Discussion

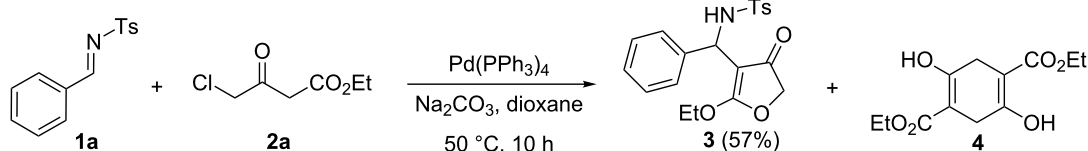
Following the work on nitrostyrenes, Yan et al. also reported a two-step asymmetric route towards 4-substituted-furanones from imines [41]. Recently Fructos et al. have shown that *N*-*p*-toluenesulfonyl-protected imines were better candidates for gold catalyzed Mannich addition of acetoacetates when



compared to *N*-Boc (*tert*-butoxycarbonyl) and *N*-PMP (*p*-methoxyphenyl) imines [42]. Hence, we commenced our investigations with the reaction of tosylimine **1a** and ethyl 4-chloroacetoacetate (**2a**) in the presence of 5 mol % of Pd(PPh₃)₄ and 2.0 equivalents of Na₂CO₃, in dioxane at 50 °C for 10 hours. The reaction afforded 4-substituted-3(2*H*)-furanone **3** in 57% yield (Scheme 2). Interestingly, we could not detect the formation of diene-2,5-dicarboxylate **4** (formed by the dimerization of **2a**) as a side product, although this was observed previously in the reaction of activated alkenes [40] and 4-chloroacetoacetates.

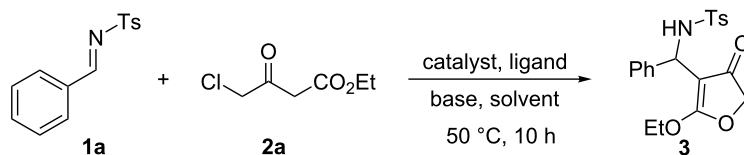
Table 1 summarizes our efforts towards optimizing various reaction parameters with **1a** and **2a** as model substrates. Screening of bases revealed that Na₂CO₃ was more effective

than either K₂CO₃ or KO*t*-Bu (Table 1, entries 1–3). When KO*t*-Bu was employed as base, byproduct **4** (formed by the dimerisation of **2a**) was formed in higher amounts (Table 1, entry 3). From the tested catalysts, Pd(PPh₃)₄ and Pd₂dba₃·CHCl₃, and ligands, dppe and P(*o*-furyl)₃, the combination of Pd₂dba₃·CHCl₃ and dppe afforded the furanone **3** in 88% yield (Table 1, entry 8). A solvent screen revealed that dioxane was best for the present transformation from which the product **3** was obtained in 88% yield (Table 1, entries 8–10). It was found that lowering the temperature had a negative influence on the yield as **3** was obtained only in 43% even after 24 hours when the substrates **1a** and **2a** were stirred in the presence of Pd₂dba₃·CHCl₃/dppe/Na₂CO₃ in dioxane at room temperature. When the catalyst loading was decreased to 1 mol %, the reaction afforded the furanone **3** in 78% yield after



Scheme 2: Pd-catalyzed synthesis of 3(2*H*)-furanone from tosylimine **1a**.

Table 1: Optimisation studies^a.



Entry	Catalyst	Ligand	Base	Yield 3 ^b (%)
1	Pd(PPh ₃) ₄	–	Na ₂ CO ₃	57
2	Pd(PPh ₃) ₄	–	K ₂ CO ₃	34
3	Pd(PPh ₃) ₄	–	KO <i>t</i> -Bu	19 ^c
4	Pd(PPh ₃) ₄	P(<i>o</i> -furyl) ₃	Na ₂ CO ₃	66
5	Pd(PPh ₃) ₄	dppe	Na ₂ CO ₃	70
6	Pd ₂ dba ₃ ·CHCl ₃	–	Na ₂ CO ₃	85
7	Pd ₂ dba ₃ ·CHCl ₃	P(<i>o</i> -furyl) ₃	Na ₂ CO ₃	82
8	Pd₂dba₃·CHCl₃	dppe	Na₂CO₃	88
9	Pd ₂ dba ₃ ·CHCl ₃	dppe	Na ₂ CO ₃	80 ^d
10	Pd ₂ dba ₃ ·CHCl ₃	dppe	Na ₂ CO ₃	84 ^e
11	Pd ₂ dba ₃ ·CHCl ₃	dppe	Na ₂ CO ₃	43 ^f
12	–	–	Na ₂ CO ₃	65
13	Pd ₂ dba ₃ ·CHCl ₃	dppe	–	trace
14	Pd ₂ dba ₃ ·CHCl ₃	dppe	Na ₂ CO ₃	78 ^g

^aReaction conditions: **1a** (1.0 equiv), **2a** (1.1 equiv), catalyst (5 mol %), ligand (10 mol %), base (2.0 equiv), dioxane (2 mL), 50 °C, 10 h. ^bIsolated yield. ^cDimerisation product **4** was formed in 27% yield. ^dCH₃CN instead of dioxane. ^eTHF instead of dioxane. ^frt, 24 h. ^g1 mol % of Pd₂dba₃·CHCl₃, 5 mol % of dppe.

10 hours (Table 1, entry 14). The catalytic role of palladium in the present transformation was proved by conducting two control experiments. The first reaction was performed only in the presence of base (Table 1, entry 12) and the second one only in the presence of the Pd₂dba₃·CHCl₃/dppe combination (Table 1, entry 13). Furanone **3** was obtained in 65% yield from the first reaction whereas the second reaction afforded only trace amounts of the desired product. Thus we can see that under palladium catalysis there is an increase in the yield of 3(2*H*)-furanone **3** by 23% by comparing the first control experiment and the reaction depicted in entry 8 of Table 1, thereby proving that palladium is catalyzing the reaction.

With optimal conditions in hand (imine (1.0 equiv), 4-chloroacetoacetate (1.1 equiv), Pd₂dba₃·CHCl₃ (5 mol %), dppe (10 mol %) Na₂CO₃ (2.0 equiv) in dioxane at 50 °C for 10 h), studies towards the generality of the reaction were carried out with different imines **1a–c** derived from aromatic aldehydes with 4-chloro-acetoacetates **2a,b**.

In all the cases substituted 3(2*H*)-furanones were obtained in good to excellent yields (Figure 2). The reaction was also extended to tosylimines derived from aliphatic aldehydes, pentanal (for **1d**) and 3-phenylpropionaldehyde (for **1e**) and thus we could rule out any influence of the aromatic moiety on the outcome of the reaction. The corresponding 4-substituted-3(2*H*)-furanones were obtained from these two substrates in good yields (Figure 2). We also tried a reaction with *N*-Boc protected imine under optimized conditions and the corresponding furanone was obtained in good yield (Figure 2, compound **14**). The structure elucidation of the furanone products **3**, and **5–14** was accomplished by the usual spectroscopic methods (see Supporting Information File 1) and also by X-ray structure determination [43] for furanones **7** (product formed by the reaction of **1b** with **2b**) and **10** (product formed by the reaction of **1d** with **2a**) (Figure 3).

We believe that the mechanism of the present furanone synthesis from imines is similar to that reported for activated

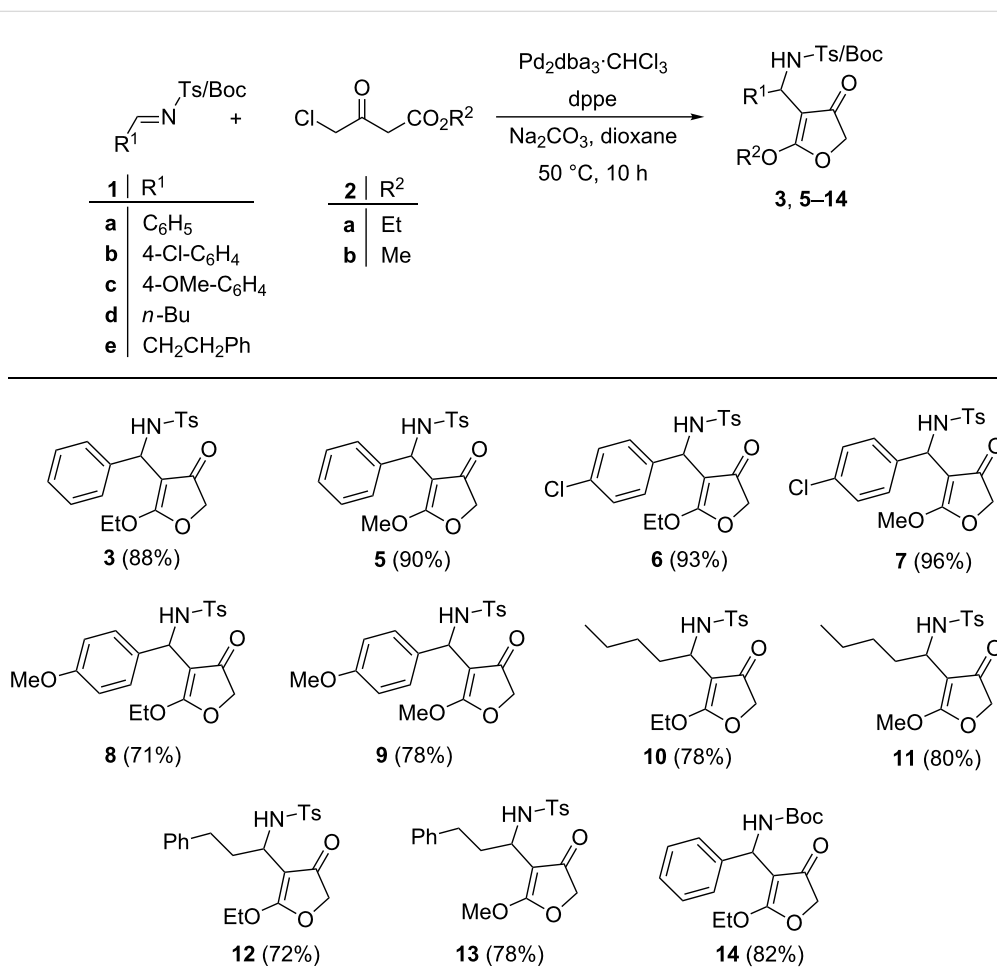


Figure 2: Generalisation with aromatic and aliphatic imines (reaction conditions: **1** (1.0 equiv), **2** (1.1 equiv), Pd₂dba₃·CHCl₃ (5 mol %), dppe (10 mol %), Na₂CO₃ (2.0 equiv), dioxane (2 mL), 50 °C, 10 h, isolated yield).

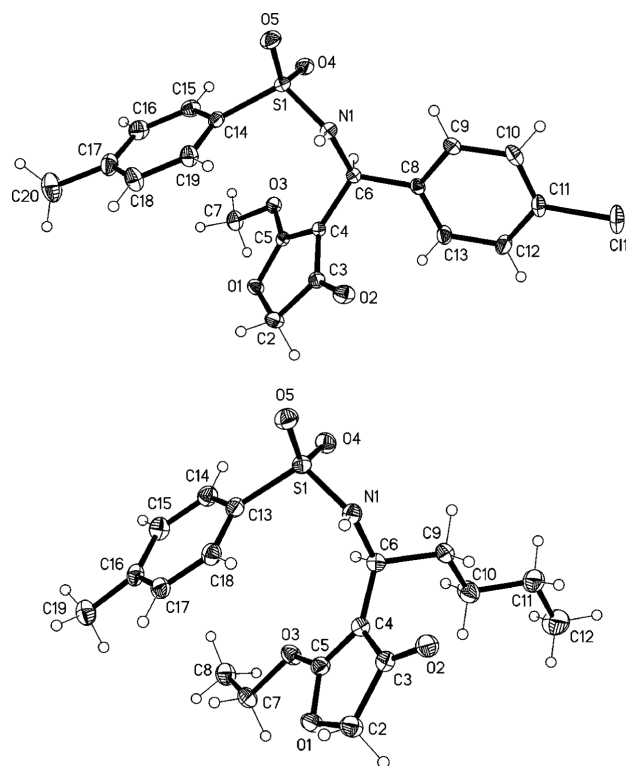


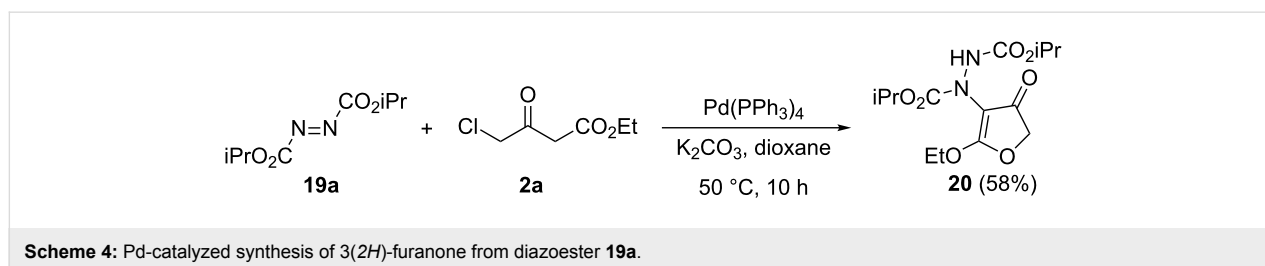
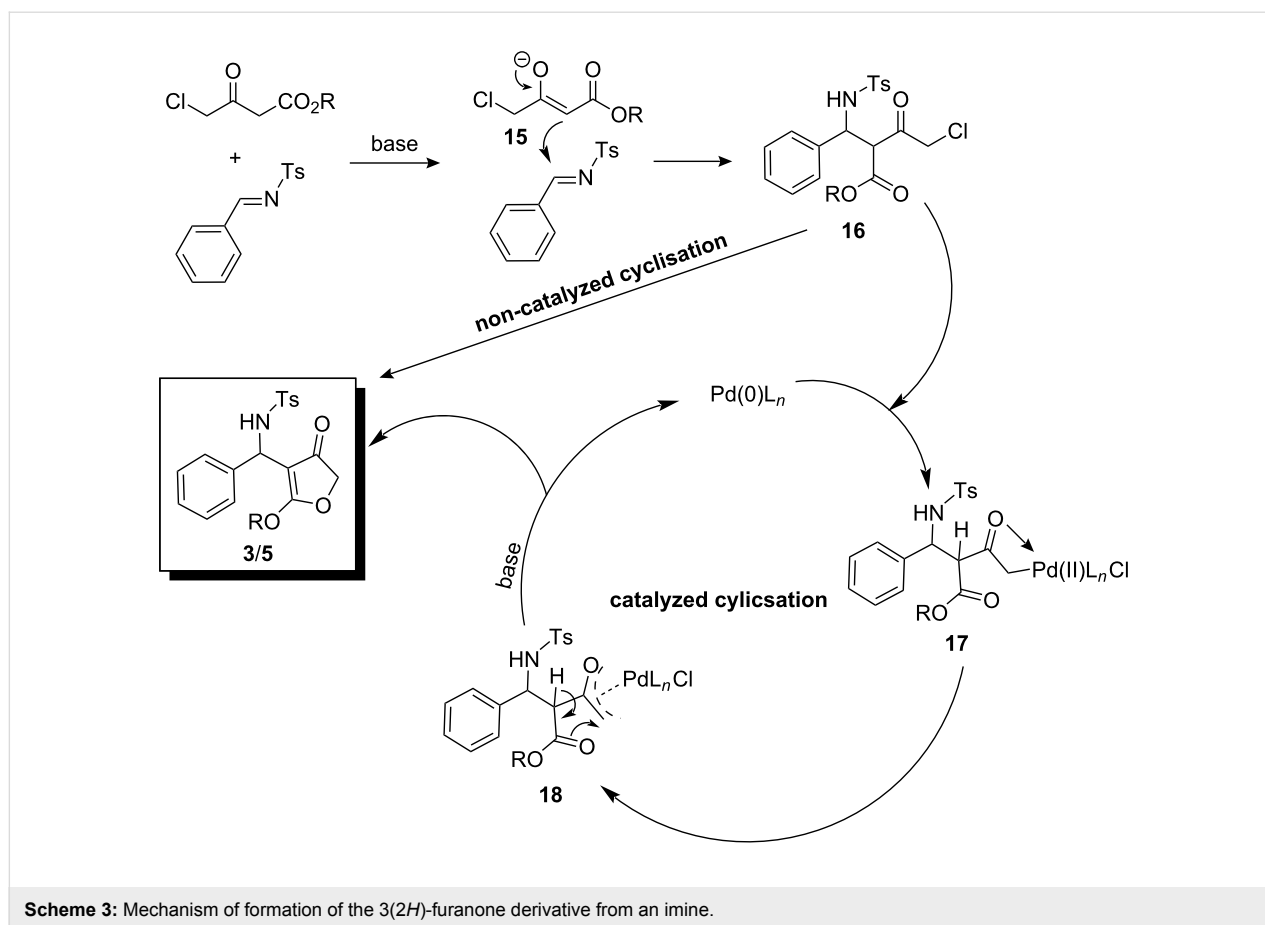
Figure 3: Thermal ellipsoid diagrams (50% probability levels) of 4-substituted-3(2*H*)-furanones **7** (above) and **10** (below).

alkenes [40]. This tandem protocol has two steps, the first being a Mannich addition of the enolate to the imine. To find out whether Mannich addition is palladium catalyzed, we carried out two reactions of tosylimine **1a** with methyl acetoacetate. The first transformation was carried out under basic conditions (Na_2CO_3 (1.0 equiv), dioxane, 50 °C, 6 h) and the second under optimized conditions. Both reactions afforded the Mannich addition product in similar yields, proving that Mannich addition was uncatalyzed.

Based on these results, we propose a plausible mechanism for 3(2*H*)-furanone synthesis from tosylimines and 4-chloroacetoacetate (Scheme 3). The reaction starts with the Mannich addition of the enolate **15** to the carbon atom of the imine double bond to form intermediate **16**. This step is the same for both the catalyzed and the uncatalyzed pathway. The second step of the catalyzed route involves the oxidative addition of $\text{Pd}(0)\text{L}_n$ to the C–Cl bond of Mannich adduct **16** to form **17**. The oxy- π -allylpalladium intermediate **18** can then be formed from intermediate **17** [4–8]. The final step of the catalyzed mechanism, i.e., the ring closure towards the formation of 3(2*H*)-furanone is initiated by the abstraction of the acidic proton by the base and consequent ester enolate attack to the end carbon of the oxy- π -allylpalladium intermediate.

Having established an efficient method for the synthesis of highly functionalized furanones from imines, we were interested next in extending the range of the electrophiles by introducing different functionalities at the 4-position of the 3(2*H*)-furanone. We chose to check the reactivity of diisopropylazodicarboxylate (**19a**) with ethyl 4-chloroacetoacetate (**2a**) under palladium catalysis. In the initial reaction, **19a** was treated with **2a** in the presence of $\text{Pd}(\text{PPh}_3)_4$ as catalyst and base (K_2CO_3) in dioxane at 50 °C. After 10 hours, the expected product 4-hydrazino-3(2*H*)-furanone **20** was isolated in 58% yield (Scheme 4).

Table 2 describes the screening of different reaction conditions to improve the yield of **20**. First we tested the efficacy of different bases K_2CO_3 , Na_2CO_3 and $\text{KO}t\text{-Bu}$, of which Na_2CO_3 proved to be the best (Table 2, entries 1–3). The highest yield for 4-hydrazino-3(2*H*)-furanone was given when $\text{Pd}(\text{PPh}_3)_4$ alone was used among different catalyst/ligand combinations tested with $\text{Pd}(\text{PPh}_3)_4$ and $\text{Pd}_2\text{dba}_3\cdot\text{CHCl}_3$ as catalysts and *dpe* and *P(o-furyl)*₃ as ligands (Table 2, entries 2, and 4–8). The product was obtained in better yields when dioxane was used as the solvent (Table 2, entries 2, 9 and 10). At room temperature the reaction with optimised catalyst/solvent system furnished only 38% of the substituted furanone even after 24 hours



(Table 2, entry 11). A control experiment was done without the catalyst/ligand combination but only in the presence of base, which afforded the furanone in 69% yield (Table 2, entry 12). Thus by comparing the control experiment and the reaction depicted in entry 2 of Table 2 we can confirm that palladium catalyzes the reaction.

The generality of the reaction was checked with different diazo esters **19a–c** with 4-chloroacetate esters **2a** and **2b** under the optimized conditions (diazo ester (1.0 equiv), 4-chloroacetate (1.1 equiv), Pd(PPh₃)₄ (5 mol %), Na₂CO₃ (2.0 equiv) in dioxane at 50 °C for 10 h). All reactions afforded the corresponding 4-hydrazino-3(2*H*)-furanones in excellent yields (Figure 4).

The possibility for further functionalization of 4-substituted furanones was checked by treating **11** with *n*-heptylamine in MeOH at 40 °C. After 10 hours the aza-prostaglandin analogue [26] **27** was isolated in 85% yield (Scheme 5).

Conclusion

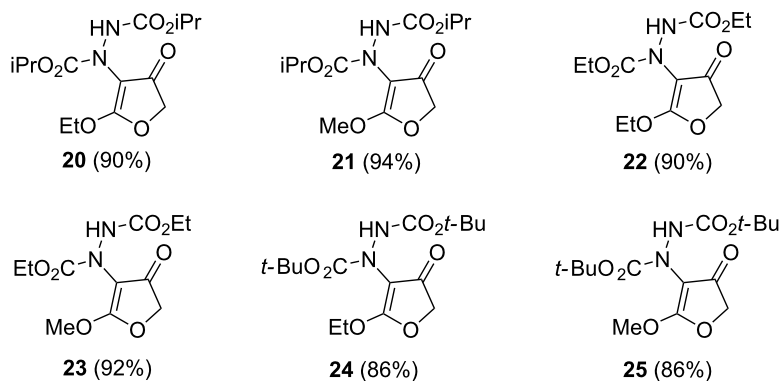
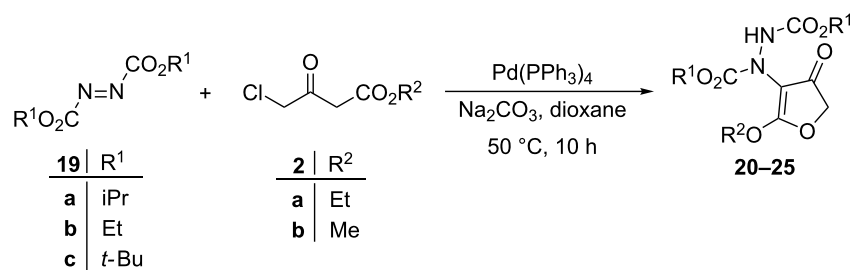
We have developed an efficient protocol for the synthesis of 4-substituted 3(2*H*)-furanones by the reaction of imines or diazo esters with 4-chloroacetates under palladium catalysis. We could extend the reaction to imines derived from aromatic and aliphatic aldehydes. The reaction proceeded via a catalyzed tandem Mannich addition–palladium-catalyzed ring-closing pathway to afford various 3(2*H*)-furanones in good to excellent yields. We could further apply this route to the preparation of an

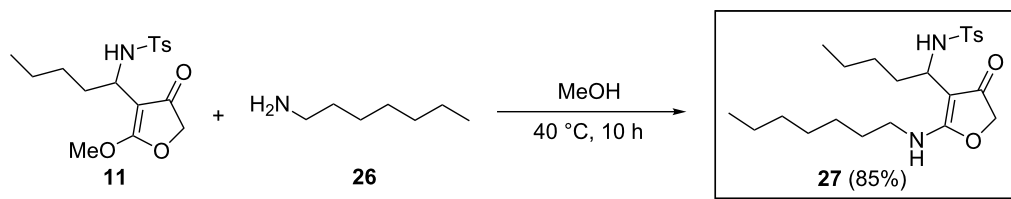
Table 2: Optimisation studies^a.

Reaction scheme showing the synthesis of **20** from **19a** and **2a** using a catalyst, ligand, base, and solvent at 50 °C for 10 h.

Entry	Catalyst	Ligand	Base	Yield 20 ^b (%)
1	Pd(PPh ₃) ₄	–	K ₂ CO ₃	58
2	Pd(PPh₃)₄	–	Na₂CO₃	90
3	Pd(PPh ₃) ₄	–	KOt-Bu	35 ^c
4	Pd(PPh ₃) ₄	P(<i>o</i> -furyl) ₃	Na ₂ CO ₃	75
5	Pd(PPh ₃) ₄	dppe	Na ₂ CO ₃	79
6	Pd ₂ dba ₃ ·CHCl ₃	–	Na ₂ CO ₃	83
7	Pd ₂ dba ₃ ·CHCl ₃	P(<i>o</i> -furyl) ₃	Na ₂ CO ₃	80
8	Pd ₂ dba ₃ ·CHCl ₃	dppe	Na ₂ CO ₃	76
9	Pd(PPh ₃) ₄	–	Na ₂ CO ₃	58 ^d
10	Pd(PPh ₃) ₄	–	Na ₂ CO ₃	82 ^e
11	Pd(PPh ₃) ₄	–	Na ₂ CO ₃	38 ^f
12	–	–	Na ₂ CO ₃	69

^aReaction conditions: **19a** (1.0 equiv), **2a** (1.1 equiv), catalyst (5 mol %), ligand (10 mol %), base (2.0 equiv), dioxane (2 mL), 50 °C, 10 h. ^bIsolated yield. ^cDimerization product **4** was formed in 23% yield. ^dCH₃CN instead of dioxane. ^eTHF instead of dioxane. ^frt, 24 h.

**Figure 4:** Generalisation with diazo esters (reaction conditions: **19** (1.0 equiv), **2** (1.1 equiv), Pd(PPh₃)₄ (5 mol %), Na₂CO₃ (2.0 equiv), dioxane (2 mL), 50 °C, 10 h, isolated yield).



Scheme 5: Synthesis of aza-prostaglandin analogue.

aza-prostaglandin analogue. The synthesized molecules are currently being screened for biological activities. We have also extended the reaction to triple-bonded electrophiles such as acetylenes, benzyne and nitriles; the results will be reported in due course. Studies are in progress to develop a stereoselective version of the process.

Supporting Information

Supporting Information File 1

Experimental part and NMR spectra.

[<http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-10-150-S1.pdf>]

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