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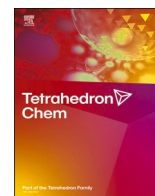
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Selective C3- or C5-Borylation of furfural derivatives: Enabling the synthesis of tri- and tetra-substituted furan Analogues

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ABSTRACT

A strategy of C3/C4 and C5/C4 bis-C–H functionalization of furfural and 5-hydroxymethylfurfural is presented. This task has been accomplished by the initial iridium-catalyzed C–H borylation of furfural, equipped with an appropriate imine function. Depending on the nature of the ligand employed, the borylation takes place selectively at C3 or C5, the products serving in turn as partners in Suzuki-Miyaura cross-couplings. After aldehyde function regeneration, some of the resulting heterobiaryl compounds underwent a, C3- or C5-directed, C4-selective Pd-catalyzed Fujiwara-Moritani olefination. These hitherto unknown serial C3/C4 and C5/C4 bis C–H functionalization strategies allow the straightforward conversion of the bio-sourced platform molecules furfural and 5-hydroxymethylfurfural into tri- and tetra-substituted furfuraldehyde derivatives.

1. Introduction

In recent years, there has been a growing societal focus on moving away from fossil as an energy source, due to its threatening environmental impact, and the search of more sustainable solutions [1]. Among other things, this change has led to increased exploration of biomass as a viable alternative, not only as a source of energy, but also for the production of both known and new intermediates [2]. For example, furfural, a key biomass derivative, is emerging as a promising chemical platform, offering considerable potential for the synthesis of a diverse range of heterocyclic compounds [3,4]. However, studies on the conversion of furfural, or derivatives of it, into more elaborated building blocks have highlighted challenges associated to the low stability of the furan core compared to more stable benzene core [5]. To solve this problem, the introduction of substituents at the C3, C4, and/or C5 in the furan nucleus may be an interesting approach. These modifications are expected to enable the synthesis of novel biomass-derived building blocks endowed with improved chemical and thermal stability. These advancements are promising for various industrial applications in materials science and organic synthesis [6].

A few years ago, we initiated a project centered on the sustainable functionalization of furfural derivatives through the selective activation of C3–H bonds [7], with a special focus on methods catalyzed by transition metals (TMs) [8]. Our primary objective was to forge bonds while

preserving the redox state of the aldehyde function. Over time, our investigations have yielded significant progress, notably in the realm of Ru(0)-catalyzed C3–functionalizations of furfurylimines, encompassing alkylation (in batch and flow processes), arylation, alkenylation, and acylation (Scheme 1-a) [9]. The outcome of these processes depends significantly on the grafted imine, which, depending on its nature, can override (or not) the intrinsic electronic bias of the substrate, directing the coupling.

In addition, we developed the Ir(I)-catalyzed C3–H directed silylation of furfurylimines [10], which, in the case of the C3–SiMe(OSiMe₃)₂ manifold, allowed us to expand the horizons of our endeavors to fluoride-based post-functionalization strategies (Scheme 1-b). As part of our ongoing interest in the selective decoration of the furan core of platform molecules derived from lignocellulose, we started the study of the C–H borylation. Indeed, due to their low toxicity and remarkable versatility, organoboron compounds stand out as an excellent alternative to organometallic compounds in cross-coupling reactions [11]. Herein, we present our results in the Ir(I)-catalyzed C–H borylation of furfural derivatives using an imine as a directing/protecting group. This strategy enables the selective activation/borylation at C3 or C5 of the furan core depending on the ligand employed (Scheme 2 - steps 1 and 2), and the resulting borylated products could in turn be reacted *in situ* with a variety of aryl-halides in Suzuki-Miyaura cross-couplings (step 3). After imine hydrolysis, the directed C4–H functionalization of the C3–

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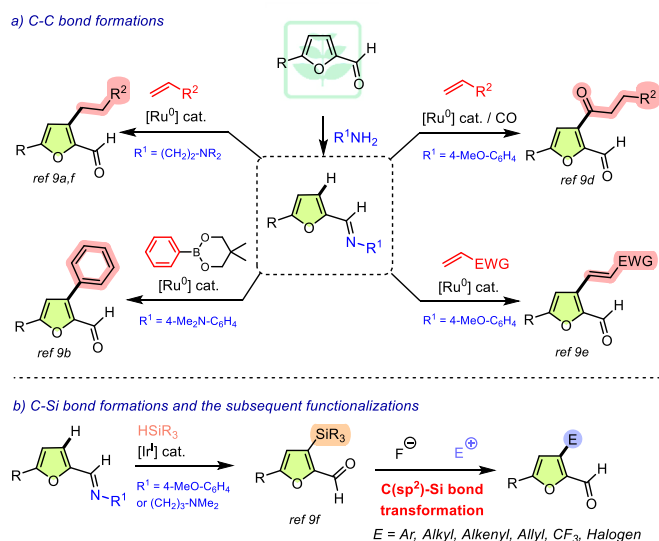
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Scheme 1. Ru- and Ir-catalyzed selective C3-H functionalizations of furfurylimines previously developed by our group.

and C5-substituted intermediates was considered. In order to obtain the desired steering effect, the furanic products incorporating an *ortho*-positioned coordinating group in the aryl substituent were selected as coupling partners, choosing the Pd-catalyzed coupling with alkenes (Fujiwara-Moritani olefination) for the second C-H functionalization (step 4).

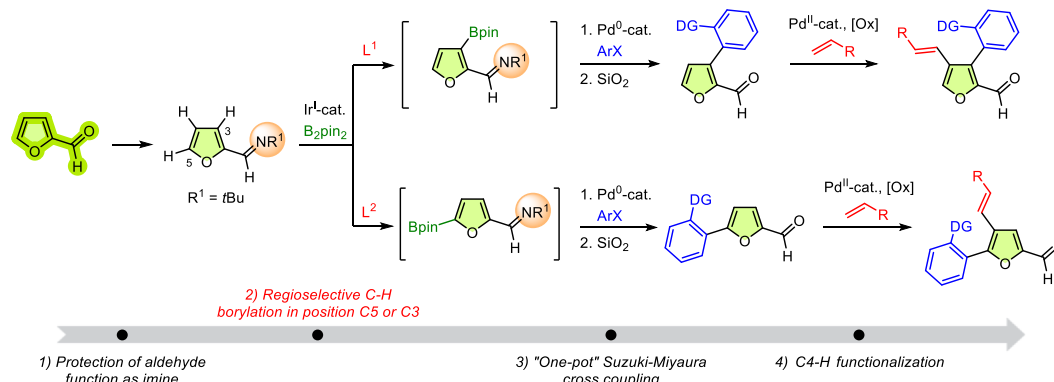
2. Results & discussion

The reported Ir-catalyzed C-H borylation of 5-substituted 2-formylfurans protected as pentafluoroaniline imines represented a valuable starting point for our study [12]. However, our main objective being the C-H borylation of furfural, which bears a free furan C5-H position. In this case, reactivity at C3 or C5 may be expected, depending on the operation of a directed or undirected control, respectively. Preliminary tests of borylation on different imines derived from furfural (see SI) indicated *tert*-butylfurfuryl imine **1a** as the substrate of choice. Furthermore, it has been reported that *tert*-butylimines of substituted benzaldehydes undergo C-H-directed borylations [13]. Accordingly, we decided to focus our optimization on this imine. Various parameters were optimized, including boron source, Ir-catalyst, ligand and temperature. Some results are presented in Table 1 (and in the SI). Using [Ir(COD)(Cl)]₂ as pre-catalyst and 0.5 equivalents of B₂pin₂ in the presence (entry 1), or absence (entry 2), of 8-aminoquinoline (**8-AQ**) as ligand, at 120 °C after 1 h predominantly led to the formation of the C3-borylated product **2a**, with only traces of the C5-borylated **3** or diborylated

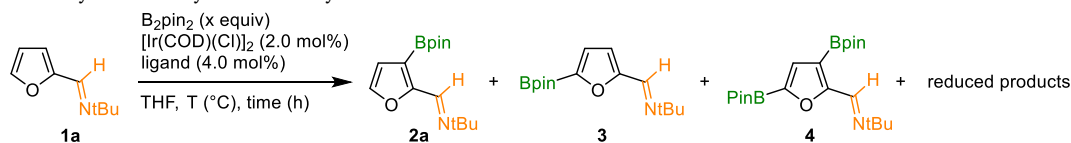
product **4**, as well as traces of reduced products (furfurylamine derivatives, see SI). When the amount of B₂pin₂ was increased to 0.7 equivalents, product **2a** was obtained in 50 % spectroscopic yield, regardless of whether operating in the presence or absence of ligand **8-AQ** (entries 3–4). While rising the temperature to 140 °C did not improve the borylation efficiency at C3 (entry 5), the increase of B₂pin₂ equivalents up to 2.0 mainly led to product **4**, bis-borylated at C3 and C5 (entries 5 and 7). It is worthy to point out that direct reaction on furfural, or in the presence of substoichiometric amounts of *tert*-butylamine, proved ineffective. Therefore, incorporation of the imine group serves both as a directing group, and protecting group for the aldehyde function against decarbonylation or reduction.

Gratifyingly, by switching the ligand from **8-AQ** to 1,10-phenanthroline (**1,10-phen**) gave the C5-borylated product **3** in 76 % spectroscopic yield (entry 8). Here again, use of an excess of the B₂pin₂ gave mainly the bis-borylated product **4** (entry 9). Finally, applying the protocol with **8-AQ** to the C5-substituted furfural derivatives 5-methylfurfural **1b** and *O*-TBS-protected 5-hydroxymethylfurfural (HMF) **1c** gave the C3-borylated products **2b** and **2c** in 68 % and 63 % yield, respectively (Scheme 3).

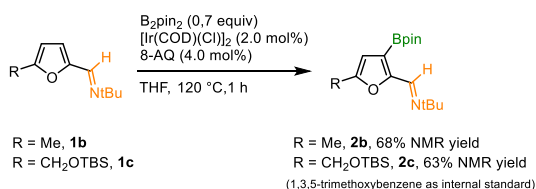
Unfortunately, all efforts to observe, isolate, and characterize the intermediates involved in these couplings through stoichiometric experiments [14] met with failure. Nevertheless, in light of our experimental findings, and on the basis of the reported mechanistic studies on both C-H borylation [15] and C-H functionalization of furfural [8], we can propose the following two mechanisms (Scheme 4). In both cases, the active catalysts are first formed by the interaction between the ligand and the dinuclear [Ir(COD)(Cl)]₂ precatalyst, with rupture of the chloride bridges and displacement of the 1,5-cyclooctadiene (COD) ligand. On the one hand, its combination with the LX ligand **8-AQ** is expected to give a mononuclear Ir(I) complex that further evolves into the 14-valence electrons Ir(III) complex **A** following oxidative addition of B₂Pin₂. The subsequent imine coordination sets the stage for a directed oxidative addition of the C3-H bond to the metal, to afford the iridium(V) complex **C**. Upon reductive elimination, the C3-borylated product **2** and an Ir(III) complex **D** are obtained. Finally, oxidative addition of a new B₂pin₂ unit with reductive elimination of HBpin regenerates the active species **A** [16]. On the other hand, interaction of the L2 ligand 1,10-phenanthroline with the precatalyst, after oxidative addition of two units of B₂pin₂ and reductive elimination of ClBpin is expected to generate the 16-valence electron trisborylated Ir(III) complex **E**, which is not prone to accept imine coordination. Accordingly, oxidative addition of **1** to intermediate **E** generates the iridium(V) intermediate **G**, most likely *via* the Wheland-type intermediate (or transition state) **F**, deriving from electrophilic addition to the most electron-rich C5 position. Subsequent reductive elimination yields the C5-borylated product **3**, as well as a bisboryl iridium monohydride complex **G**. Finally, reductive elimination of HB(pin) with oxidative addition of B₂pin₂ regenerates the trisboryl complex **E**.



Scheme 2. This work: Ir-Catalyzed regioselective C-H borylation of furfurylimine and post-functionalization of borylated-furan intermediates.

Table 1Optimization of the Ir-catalyzed C–H borylation on *t*-butyl imine.

Entry	Ligand	B (x equiv.)	T(°C)	Time (h)	Conv.(%) ^a	2 (%) ^a	3 (%) ^a	4 (%) ^a	Red. Prod. (%) ^a
1	8-AQ	0.5	120	1	71	39	3	3	12
2	/	0.5	120	1	70	39	3	3	10
3	8-AQ	0.7	120	1	91	50	2	5	16
4	/	0.7	120	1	95	53	2	6	18
5	/	0.7	140	0.5	97	47	1	6	18
6	/	1.0	120	1	<99	30	/	16	21
7	/	2.0	120	3	<99	12	/	40	9
8	1,10-phen	0.7	120	1	96	3	76	6	3
9 ^b	1,10-phen	1.4	120	1	<99	4	/	55	2

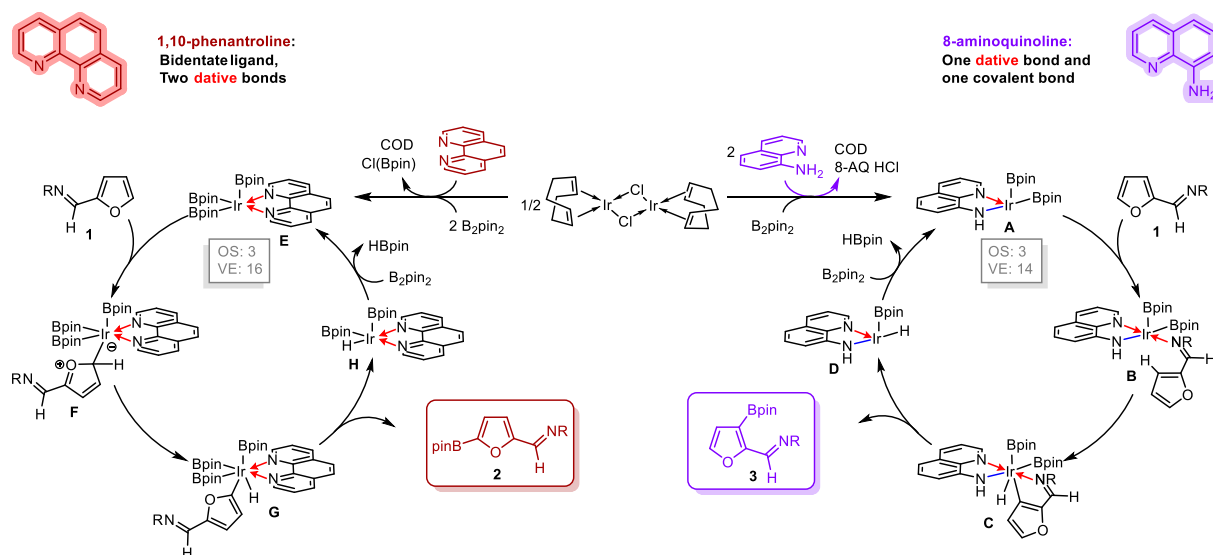
^b Ligand (8.0 mol%), [Ir(COD)(Cl)]₂ (4.0 mol%). 8-aminoquinoline (8-AQ); 1,10-phenanthroline (1,10-phen).^a ¹H NMR yield with 1,3,5-trimethoxybenzene as internal standard.**Scheme 3.** Ir-Catalyzed C3-borylation of C5-substituted furfurylimines.

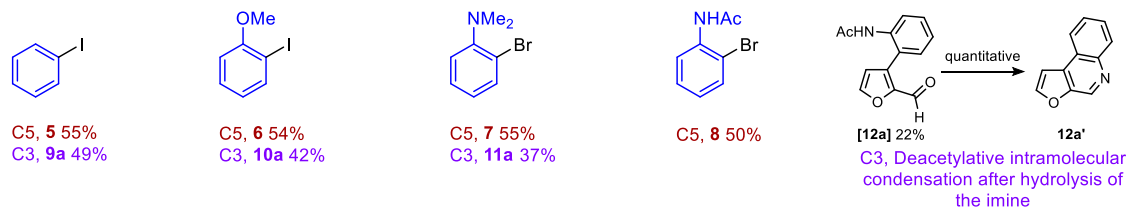
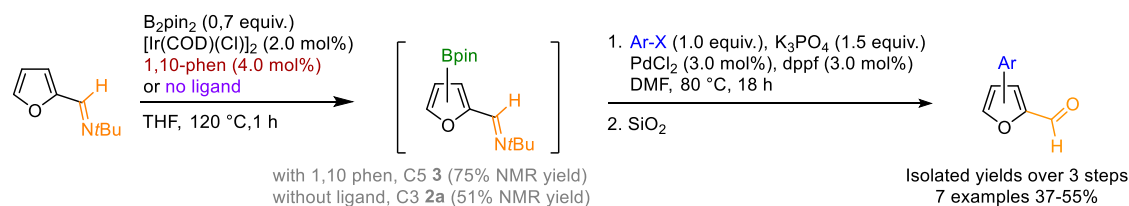
Regrettably, all attempts of isolation of these newly formed C3- and C5-borylated compounds were fruitless. Indeed, attempts the selective hydrolysis of the imine with silica gel, or of the hydrolysis of both the imine and the boronic ester with aqueous HCl, or of oxidative cleavage of the boronic ester [17] led solely to degradation products [18]. Faced with these problems, we decided to forego purification of the C3- and C5-borylated products **2a** and **3**, whose characterization at the crude stage was still possible (see SI). We thus decided to react the *in situ*-generated borylated products with aryl halides under Pd(0) catalysis, according to a Suzuki-Miyaura coupling (Scheme 2 - step 2–3).

Accordingly, following a reported procedure [19], the crude products coming from the Ir-catalyzed C–H borylations after evaporation of

THF, were directly submitted to the Suzuki-Miyaura couplings by addition of DMF, PdCl₂ (3 mol%), 1,1'-bis(diphenylphosphine)ferrocene (dppf) (3 mol%), K₃PO₄ (1.5 equiv.), and the aryl halide (1.0 equiv.), stirring at 80 °C during 18 h (Scheme 5). The coupling between the C3- and the C5-borylated imines **2a** or **3** and iodobenzene, afforded compounds **9a** and **5** in 49 % and 55 % isolated yields after 3 steps, respectively. Aryl halides bearing *ortho*-located electron-donating groups, such as iodo-2-methoxybenzene and 2-bromo-*N,N*-dimethylaniline, led to the expected coupling products in comparable yields. While the coupling between *N*-(2-bromophenyl)acetamide and the C5-borylated product **3** took place as expected, generating **8** in 50 % yield, the corresponding reaction with the C3-borylated substrate gave the tricyclic heteroaromatic furo[2,3-*c*]quinoline **12a'**, which results from a deacetylate intramolecular condensation between the amine and the aldehyde functions, occurred in the NMR tube after imine hydrolysis [20]. The use of 2-bromoaniline, *N*-(2-bromophenyl)-methanesulfonamide or *N*-(2-bromophenyl)-tosylamide failed to yield the desired coupling products [21].

After having successfully completed the C–H borylation/Suzuki-Miyaura cross-coupling sequence at the C3 and C5 positions of furfural, our next objective was to further explore the functionalization at the C4 position, which has been rarely studied [22]. Specifically, we

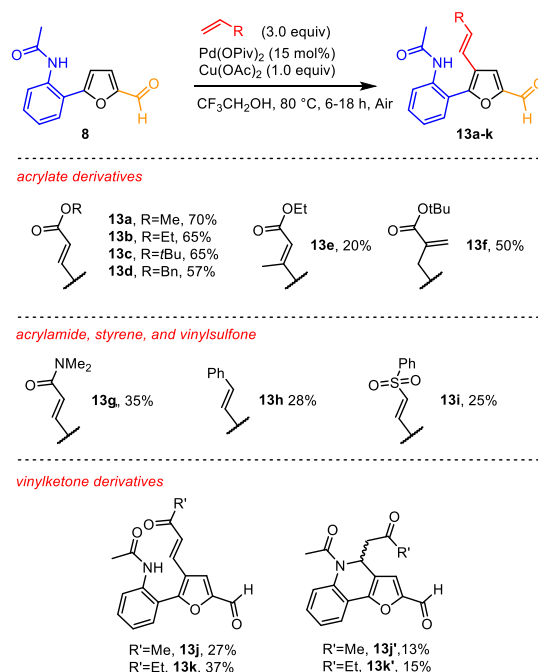
**Scheme 4.** Proposed mechanisms for Ir-Catalyzed regioselective C–H borylations of furfurylimine.



Scheme 5. One-pot sequence: Borylation/Suzuki Miyaura coupling/deprotection of aldehyde function.

aimed to implement a palladium-catalyzed oxidative olefination using electron-deficient alkenes, according to a Fujiwara-Moritani coupling [23]. As to the steering aspect, Chuang and colleagues previously reported that the *N*-acyl group of 2-aminobiphenyls can enable a directed palladium-catalyzed oxidative olefinations in the *ortho* or *ortho'* position (Fig. 1, left) [24]. This work inspired us to adopt the above strategy in the hope to obtain a C3- or C5-directed C4-olefination (Fig. 1, right).

To our satisfaction, subjecting the C5-arylated furfural **8** to the same reaction conditions as those described by Chuang and co-workers [24] [Pd(OAc)₂ 10 mol%, Cu(OAc)₂ 1 equiv., methylacrylate 1.5 equiv., in TFEtOH (CF₃CH₂OH) at 120 °C for 24 h under an oxygen atmosphere] led to the C4-H alkenylated product **13a**, although in a low (15%) yield, which corresponds to a full *ortho'* selectivity. Optimization of the reaction conditions (see SI) gave as best protocol [Pd(OPiv)₂ (15 mol%)], acrylate (3.0 equiv.), 80 °C, air] (Scheme 6). Using these optimized conditions, the Fujiwara-Moritani coupling of **8** with various unsubstituted acrylates gave exclusively the *E*-configured C4-alkenylation products **13a-d** with yields ranging between 57 and 70% (Scheme 6). Ethyl-*E*-but-2-enoate led to the corresponding alkylation product **13e**, while reaction with *tert*-butyl methacrylate favored the α -methylidene ester **13f**. This outcome indicates that the β -H elimination step of the coupling involved the methyl group, as opposed to the methylene group. The coupling worked also with acrylamide, styrene and vinylsulfone, although in rather low yields, giving products **13g**, **13h**, and **13i**, respectively. Finally, both methyl vinyl ketone and ethyl vinyl ketone gave rise to a separable mixture of the “regular” C4-alkenylation products **13j-k** and to **13j'**-**13k'**, which suffered an additional intramolecular aza-Michael addition. Attempts of direct coupling from the crude reaction



Scheme 6. C4-alkylation directed by the *N*-phenylacetamide group in position C5.

mixture of the borylation/Suzuki-Miyaura coupling (*i.e.* on the imine) resulted in traces of the olefination product. In addition, attempts to carry out the coupling with 5-methyl-, 5-phenyl- (**5**) or 5-(2-methoxyphenyl) (**6**) furfurals also proved unsuccessful, underlining the importance of the nitrogen-based directing group.

Steering of the oxidative C-H olefination was not restricted to the *N*-acetamide as directing group. Indeed, employing the same reaction conditions as above, we successfully carried out C5-directed Fujiwara-Moritani couplings between **7**, which bears a C5-located *ortho*-*N,N*-dimethylaminophenyl (ONDAP) group, and a range of unsubstituted acrylates, or an acrylamide, obtaining the coupled products **14a-d** and **14g** (Scheme 7). The yields in most cases are comparable to those obtained with compound **8**. The additional bonus of this group lies in the fact that coupling of the C3-ONDAP substituted furfural **11a** with the same acrylates and the acetamide as used before, allowed to obtain the C3-arylated/C4-alkenylation furfurals **15a-d,g** in yields comparable to those of the C5-substituted series. It has to be noted that the previously observed cyclization of the C3-substituted *ortho*-acetamidophenyl

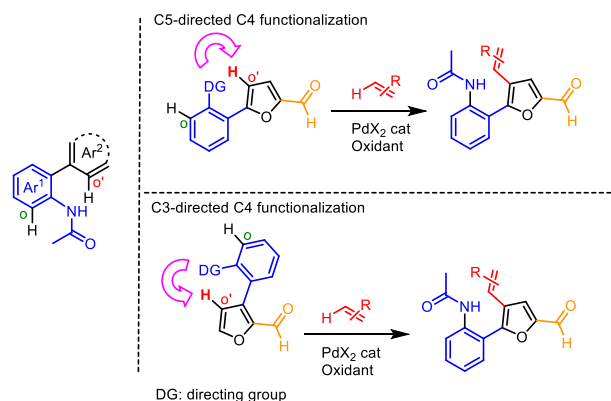
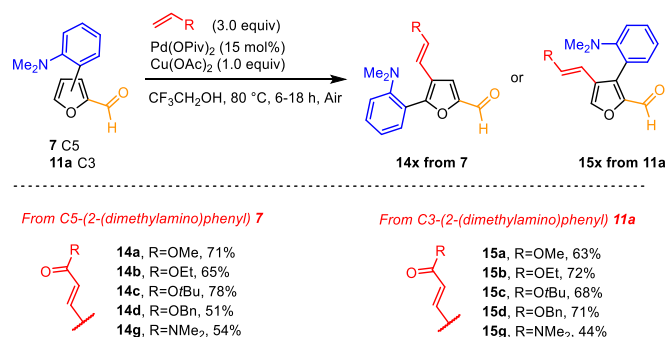


Fig. 1. Left: position *ortho* and *ortho'* in *N*-acyl 2-aminobiphenyl systems. Right: envisaged strategy for the C3- and C5-directed C4 C-H functionalization.



Scheme 7. C4-alkylation directed by the ONDAP group in position C5 or C3.

furfural derivative **12a** to **12a'** prohibits a directed C4-functionalization from that C3-substituted furfural derivative.

This approach was further extended to the synthesis of five peri-substituted furan derivatives. Accordingly, C3-borylation/Suzuki-Miyaura coupling between the HMF-derived imine **2c** and 2-bromo-*N,N*-dimethylaniline yielded intermediate **11c** in 37 % yield over 3 steps. Subsequent Fujiwara-Moritani couplings with the same five electron-poor alkenes as used before afforded the corresponding peri-substituted furans **16b-d,f,g** (**Scheme 8**), marking a pioneering instance of such double C–H activation-based functionalization strategy.

3. Conclusion

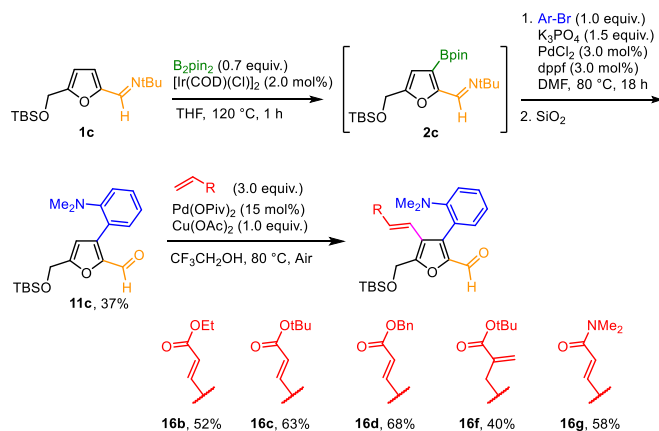
In conclusion, we have developed a new strategy to selectively decorate the furan core of the lignocellulosic biomass-derived molecules furfural and 5-HMF. This task was accomplished through the initial temporary conversion of the formyl group of these two platform molecules into the corresponding *tert*-butyl imines. This protection/activation step allows to develop efficient Ir-catalyzed borylations at the C3 or C5 (when this position is unsubstituted), depending on the nature of the ligand used. While the ligand 8-aminoquinoline favors an imine-directed borylation at C3, the presence of 1,10-phenanthroline promotes an undirected borylation at the most electron-rich C5 position of the furan core. Subsequent treatment of the crude borylated molecules with a number of aryl halides under Pd(0)-catalysis allows to perform efficient Suzuki-Miyaura cross-couplings that generate 3- or 5-substituted 2-formylfuran derivatives. In particular, when the aryl moiety introduced in the Suzuki-Miyaura coupling bears an appropriate *ortho*-located directing group, the resulting product can in turn undergo further C3- or C5-directed C–H functionalizations at position C4, namely a Fujiwara-Moritani cross-coupling. Overall, this strategy allows to smoothly convert the bioderived furfural molecule into a number of C3,C4- or C5, C4-difunctionalized 2-formyl-furans. Furthermore, application of this same strategy to 5-HMF allows to peri-functionalize furan. Given the importance of the selective and multiple functionalization of furfural and 5-HMF, we believe that this strategy will find considerable interest in the chemical community in the future.

CRedit authorship contribution statement

Alessia Mori: Methodology, Investigation, Formal analysis. **Mariana Isabel Crespo Monteiro:** Methodology, Investigation. **Filipa Siopa:** Methodology, Investigation, Funding acquisition. **Giovanni Poli:** Writing – original draft, Supervision, Funding acquisition. **Julie Oble:** Writing – review & editing, Writing – original draft, Validation, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial



Scheme 8. Synthesis of peri-substituted furan derivatives.

interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.tchem.2024.100079>.

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