Ruthenium-Catalyzed C-H Arylation and Alkenylation of Furfural Imines with Boronates

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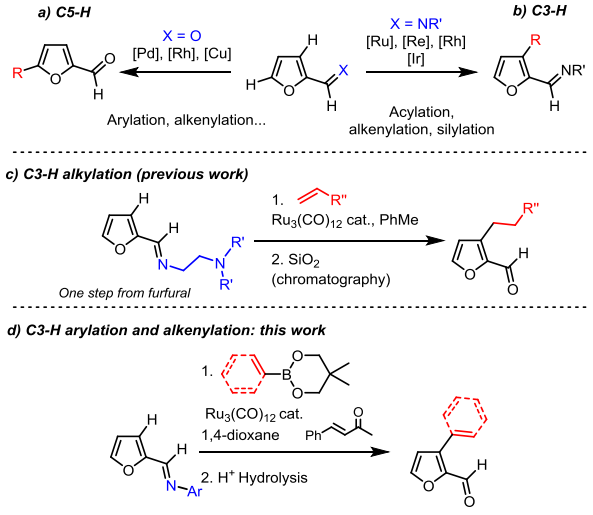
Abstract: A Ru(0)-catalyzed direct C-H arylation and alkenylation of furfural imines with aryl- or alkenyl-boronates, in the presence of benzylideneacetone as a sacrificial hydride acceptor, is disclosed. This reaction provides access, after hydrolysis, to C3-arylated or vinylated furfural derivatives, and thus valorizes these relevant building-blocks obtained from lignocellulosic biomass. This approach, involving C-H activation by a Ru(0)/Ru(II), cycle offers several advantages, notably simple, mild and neutral reaction conditions.

Introduction

Over the past decade, environmentally benign organic reactions featuring the direct functionalization of non-activated C-H bonds have emerged to maximize the step- as well as the atom-economy of a synthetic route.[1] Furthermore, the implementation of these catalytic C-H transformations on renewable feedstocks is becoming an attractive strategy that paves the way toward greener chemical supplies by merging two eco-compatible approaches. In particular, lignocellulosic biomass valorization has recently received significant attention as an alternative to the shortage of petroleum resources, for the sustainable production of chemicals and bio-fuels.[2] Furfural **1**[3] and 5-(hydroxymethyl)furfural (HMF) **2**,[4] readily obtained by cyclodehydration of abundant natural carbohydrate materials, are among the most important unsaturated bulk available from biomass. Thus, efficient transformations of **1** and **2** into more complex chemicals and fuels,[5,6] as well as applications of these molecules in the fields of polymers[7] and pharmaceuticals,[4] represent highly desirable projects. Some transition metal (TM)-catalyzed direct C-H functionalizations of furfural have been reported. Most of these studies addressed the functionalization at the C5 position of the furan ring (arylation,[8] alkylation,[9] alkenylation[10] and alkynylation[11]) (Scheme 1a). In contrast, C3-H functionalization via directing groups that force the natural C5 preference has been much less studied (Scheme 1b).[12] For our part, we recently reported a directed Ru(0)-catalyzed addition of vinylsilanes (Murai reaction) to furfural imines, leading to C3-alkylated furfurals (Scheme 1c).[13] We now describe the Ru(0)-catalyzed[14] C3-H arylation and alkenylation of furfural imines with boronate derivatives (Scheme 1d). The adopted protocol takes inspiration from the reported Ru(0)-catalyzed C-H arylations (or alkenylations) of aryl-ketones,[15] amides,[16] nitriles[17] and imines,[18] which make use of a sacrificial hydride scavenger to prevent the reduction of the directing group by the in situ generated Ru-H species. Pinacolone is the most common hydride acceptor, while benzylideneacetone (BA) has been recently used for the reaction with aryl-imines.[18] The optimization and the scope of this C-H activation-based transformation of furfural imines are here summarized.



Scheme 1. TM-catalyzed direct C-H functionalizations of furfural derivatives.

Results and Discussion

We started our study by adopting the same conditions as recently reported by Szostak for the Ru-catalyzed C-H bond arylation of aromatic imines with arylboronates,[18] namely: 5 mol% of $Ru_3(CO)_{12}$, 1.5 equiv. of phenylboronic acid neopentylglycol ester (PhBnep) and 1.1 equiv. of BA, in toluene at 125 °C (oil bath), in sealed tube. A series of furfural-imines **3a-c**, readily prepared in one-step from furfural **1** (see SI), was examined under the above conditions (Scheme 2). On the one hand, the N,N'-bidentate imine **3a**, which previously showed satisfactory results in the Murai reaction (Scheme 1b),[13] did not furnish the desired product, whereas benzyl-imine **3b** displayed a low reactivity. On the other hand, use of *p*-methoxyphenyl-imine (PMP-imine) **3c** lead to the desired C3-phenylated imine **4ca**[19] in 43% NMR yield.

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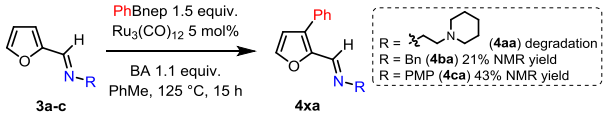
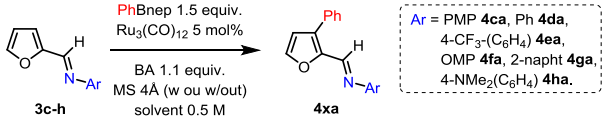


Scheme 2. Ru-catalyzed C3-phenylation of imines **3a-c**.

Following this promising result, we carried on the optimization with the PMP-imine **3c** testing different solvents and temperatures (Table 1). While the reaction carried out in toluene at 125 or 140 °C led to similar NMR yields as before, the use of 1,4-dioxane at 130 °C gave 55% NMR yield of **4ca** (entries 1-4). An experiment realized at 140 °C in pinacolone as both the solvent provided an inferior result (entry 5).

Table 1. Ru-catalyzed C3-phenylation of aryl imines **3c-h**.[a]

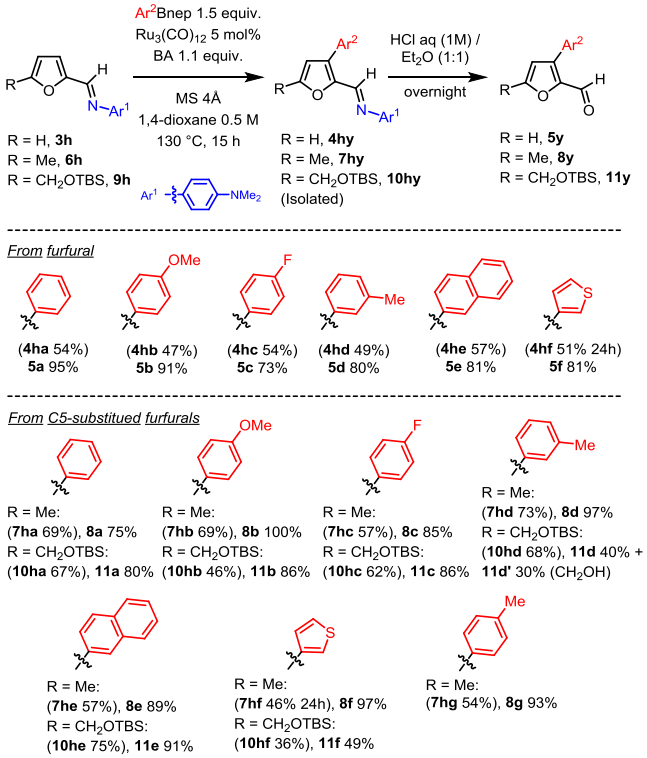


Entry	Ar	MS 4Å	Solvent, T (°C)	Yield %[b]
1	PMP (**3c**)	-	PhMe, 125	43 (**4ca**)
2	PMP (**3c**)	-	PhMe, 140	47 (**4ca**)
3	PMP (**3c**)	-	1,4-dioxane, 140	38 (**4ca**)
4	PMP (**3c**)	-	1,4-dioxane, 130	55 (**4ca**)
5	PMP (**3c**)	-	Pinacolone, 140	13 (**4ca**)
6	Ph (**3d**)	-	1,4-dioxane, 140	22 (**4da**)
7	4-F_3C-(C_6H_4) (**3e**)	-	1,4-dioxane, 140	4 (**4ea**)
8	PMP (**3c**)	✓	1,4-dioxane, 130	58 (**4ca**)
9	2,4-(MeO)$_2$-(C_6H_3) (**3f**)	✓	1,4-dioxane, 130	47 (**4fa**)
10	2-napht (**3g**)	✓	1,4-dioxane, 130	51 (**4ga**)
11	**4-Me_2N-(C_6H_4) (3h)**	✓	**1,4-dioxane, 130**	**71 (4ha)**
12[c]	4-Me_2N-(C_6H_4) (**3h**)	✓	1,4-dioxane, 130	47 (**4ha**)

[a] Reaction conditions: **3c-h** (0.5 mmol), PhBnep (0.75 mmol), $Ru_3(CO)_{12}$ (0.025 mmol), BA (0,55 mmol), MS 4Å (270 mg), solvent (1 mL). [b] ^{1}H-NMR yield of corresponding phenylated imines **4xa**, determined using 1,3,5-trimethoxybenzene as internal standard. [c] 1.5 equiv. of $MgSO_4$ instead of MS 4Å. PMP = *p*-methoxyphenyl.

The nature of the imine was considered next. The use of the phenyl-imine **3d** or the electron-poor aromatic imine **3e** led to a clear reactivity drop (compare entries 3 and 6-7), and the encouraging result of the electron-rich aromatic imine **3c** (entry 4) could be further improved by addition of 4Å molecular sieves (MS) (entry 8). Additional electron-rich aromatic imines (**3f-h**) were next tested (entries 9-11). In the event, use of *p*-dimethylaminophenyl-imine (PDMAPh-imine) **3h** afforded the desired C-H arylation product **4ha** with the highest NMR yield (71%). Finally, the use of $MgSO_4$ instead of MS gave a modest result (entry 12).[20] The sensitivity of the reaction to the electron richness of the aldimine nitrogen atom is evident and suggests that increase of basicity of the nitrogen atom is key. Indeed, the *para*-located electron-donors of the best-behaved imines **3c** and **3h** compete with the nitrogen atom in lone pair delocalization into the aromatic ring, rendering the aldimine nitrogen atom more basic via an arylogous alpha-effect. We speculate that such enhanced basicity of the nitrogen atom may favor nitrogen coordination to ruthenium throughout the catalytic cycle (*vide infra* the proposed mechanism).

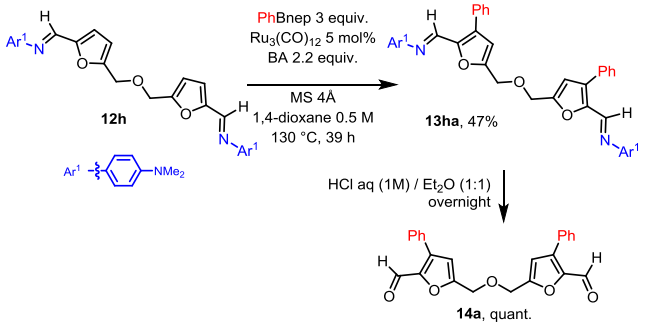
With the optimal conditions in hand (entry 11), the scope of this C-H arylation between PDMAPh-imine **3h** and various arylboronic acids neopentylglycol esters ArBnep was investigated. Direct isolation of the C-H arylated products in the form of the corresponding aldehydes, although initially attempted, was unsuccessful. However, acid hydrolysis of the arylated-imine **4hy**[19] after a rapid silica gel chromatographic purification took place uneventfully.[21] First, we reacted imine **3h** with a variety of ArBnep bearing *para* or *meta* located electron-withdrawing or -donating groups, as well as with a 2-thienyl boronate derivatives. In all the cases, arylated-imines **4hy** were obtained with moderate yields (47-57% isolated yields after chromatography or 52-76% NMR yields, see SI) (Scheme 3, top). The subsequent acid hydrolysis enabled access to the arylated-furfurals **5y** with very good yields.



Scheme 3. Scope of Ru-catalyzed C3-arylation.[22]

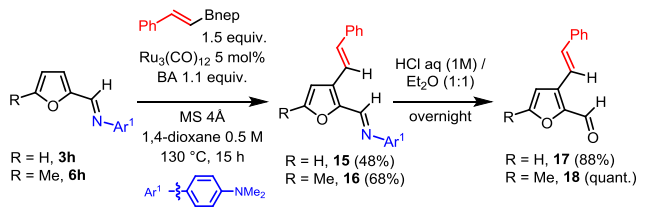
The scope of the study was next extended to C5 substituted furfural-imines, such as 5-methylfurfural-imine **6h** and the TBS-protected HMF imine **9h** (readily prepared from HMF **2** see SI) (Scheme 3, bottom rows). With these two starting materials, various arylboronic neopentylglycol esters bearing electron-rich and electron-poor functional groups in *para* or *meta* position also afforded the desired arylated-imines (**7hy** or **10hy** respectively) in reasonable to good yields. However, coupling of 2-

MeC_6H_4Bnep was inefficient, very likely due to the steric hindrance of the boronate partner. The C3-arylated furfurals were isolated with excellent yields after mild hydrolysis, except for the TBS protected furfural-imines **10hd** and **10hf**, which suffered partial deprotection of the TBS group (**10hd**) or degradation (**10hf**). Additionally, a double coupling was successfully achieved with the HMF-dimer diimine **12h** and two equivalents of PhBnep, which gave the di-phenylated HMF imine dimer **13ha** and the corresponding dialdehyde **14a** after hydrolysis (Scheme 4).



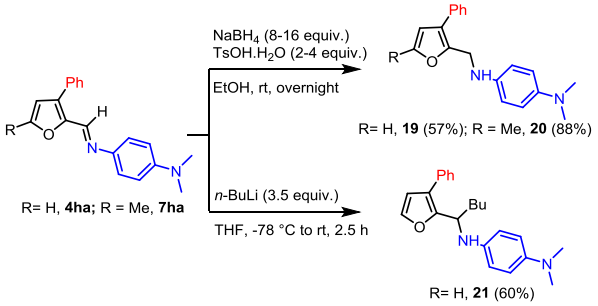
Scheme 4. Ru-catalyzed C3-phenylation of HMF-dimer derivative.

Then, the scope of the reaction was studied with an alkenylboronate derivative, namely cinnamylboronic neopentylglycol ester. This boronate partner proved to be effective, and furfural-imines **3h** and **6h** gave the desired alkenylated imine derivatives **15** (48%) and **16** (68%), which were successfully hydrolyzed to the corresponding alkenylated furfurals **17** (88%) and **18** (quant.) (Scheme 5).



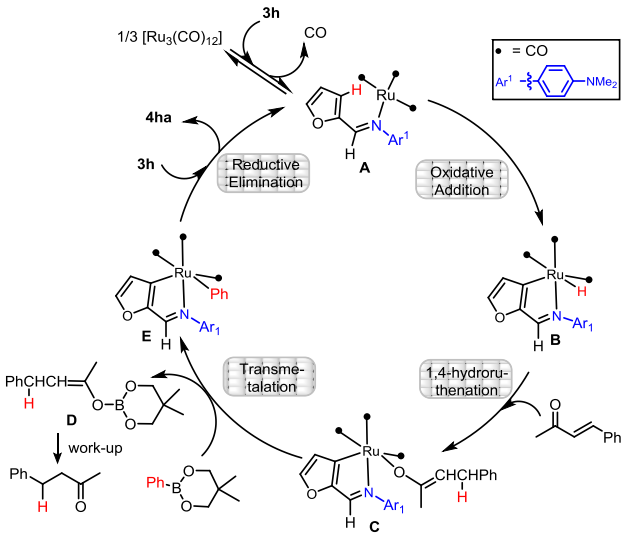
Scheme 5. Ru-catalyzed C3-alkenylation of furfural-imines.

Other synthetic applications of the C3-arylated furfuryl-imines were then evaluated (Scheme 6).[18] First, treatment of imines **4ha** and **7ha** with $NaBH_4$ in presence of TsOH gave the corresponding furfural-amines **19** and **20** in moderate to good yields. Furthermore, treatment of **4ha** with *n*-BuLi gave smoothly the alkylated amine **21**.



Scheme 6. Synthetic applications.

A plausible mechanism for this Ru-catalyzed C3-arylation[15b] is presented in Scheme 7 for the reaction between PDMAPh-imine **3h** and PhBnep. By analogy with our previous study,[13] we anticipate the initial decarbonylative Ru-Ru cleavage of $Ru_3(CO)_{12}$ pre-catalyst to generate the mononuclear complex $Ru(0)(CO)_3$,[23] and coordination by PDMAPh-imine **3h** affords complex **A**. Oxidative addition of the C3-H furfural position - likely through agostic C3-H / Ru(0) interaction - takes then place, to form the Ru(II)-H species **B**. Subsequent 1,4-addition of the ruthenium hydride to benzylideneacetone (BA) gives the vinyloxy-ruthenium intermediate **C**.[24] Following transmetalation between PhBnep and the alkoxy-ruthenium complex **C** results in the formation of furfuryl-phenyl ruthenium intermediate **E** and the boryl enol ether **D**. Finally, reductive elimination from **E** followed by a trans-imination in the presence of a new molecule of starting furylimine **3h** releases product **4ha** and regenerates catalyst **A**. The boryl enol ether **D** is hydrolyzed to 4-phenylbutan-2-one during the work-up, as detected in the ^1H NMR of the crude product.



Scheme 7. Proposed mechanism of the catalytic cycle.

Conclusions

In summary, we have developed the directed C3-arylation of furfural imines with arylboronic acid neopentylglycol esters, under Ru-catalysis. This straightforward C-H functionalization method requires the use of electron-rich aromatic imines, such as a *p*-dimethylaminophenyl-imine. When using cinnamylboronic neopentylglycol ester, the same catalytic system promotes C3-cinnamylation. The mild acid hydrolysis enables access to arylated- or cinnamylated-furfural derivatives. Further work is ongoing to demonstrate the synthetic value of the new C3 functionalized furfurals by accessing relevant target molecules of synthetic, industrial and / or biological value.

Experimental Section

All experimental procedures and compound characterizations are described in Supporting Information available online.

General procedure for Ru-catalyzed arylation or alkenylation of furfural imines. In a sealed tube, a solution of $Ru_3(CO)_{12}$ (0.025 mmol, 5 mol%), furfural imine (0.5 mmol, 1.0 equiv.), aryl- or cinnamyl-boronic acid neopentylglycol ester (0.75 mmol, 1.5 equiv.), benzylideneacetone (BA) (0.55 mmol, 1.1 equiv.) and molecular sieves 4Å (typically, 264 mg) in 1,4-dioxane (0.5 M) was stirred for 15 h at 130 °C. The reaction mixture was let cool to room temperature, diluted with CH_2Cl_2 and filtered through Celite. The solvent was removed and the crude product was purified by silica gel chromatography affording the corresponding C3-functionnalized products.

(*E*)-N,N-dimethyl-4-(((3-phenylfuran-2-yl)methylene)amino)aniline (4ha): Prepared according to general procedure from (*E*)-4-((furan-2-ylmethylene)amino)-N,N-dimethylaniline **3h** (107.1 mg, 0.5 mmol), 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane **a** (142.5 mg, 0.75 mmol), benzylideneacetone (80.4 mg, 0.55 mmol), $Ru_3(CO)_{12}$ (16.0 mg, 0.025 mmol), molecular sieves 4Å (264 mg). The crude product (71% NMR yield) was purified by flash chromatography on silica gel eluting with CyHex/EtOAc (80/20) to afford 78.7 mg of **4ha** (54% yield) as a brown solid. m.p. 92 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.47 (s, 1H), 7.63 (dd, *J* = 1.8, 0.5 Hz, 1H), 7.51-7.43 (m, 5H), 7.32-7.28 (m, 2H), 6.75 (d, *J* = 9.0 Hz, 2H), 6.70 (d, *J* = 1.8 Hz, 1H), 3.00 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 149.8, 147.7, 144.7, 142.8, 140.7, 132.6, 131.9, 129.0, 128.9, 128.1, 122.6, 113.2, 112.9, 40.8. **IR (cm^{-1})** ν 3139, 2922, 2854, 1670, 1590, 1512, 1443, 1359, 1227, 1059, 759. **HRMS** m/z calculated for $C_{19}H_{19}N_2O$ $[M+H]^+$: 291.1492; found 291.1500.

(*E*)-4-(((3-(4-methoxyphenyl)furan-2-yl)methylene)amino)-N,N-dimethylaniline (4hb): Prepared according to general procedure from (*E*)-4-((furan-2-ylmethylene)amino)-N,N-dimethylaniline **3h** (107.1 mg, 0.5 mmol), 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane **b** (165.1 mg, 0.75 mmol,), benzylideneacetone (80.4 mg, 0.55 mmol), $Ru_3(CO)_{12}$ (16.0 mg, 0.025 mmol), molecular sieves 4Å (275 mg). The crude product (58% NMR yield) was purified by flash chromatography on silica gel eluting with CyHex/EtOAc (80/20) to afford 75.9 mg of **4hb** (47% yield) as a brown solid. m.p. 112 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.33 (s, 1H), 7.49-7.48 (m, 1H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.18 (d, *J* = 9.2 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.63 (d, *J* = 9.1 Hz, 2H), 6.53 (d, *J* = 1.8 Hz, 1H), 3.75 (s, 3H), 2.87 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 159.6, 149.6, 147.2, 144.6, 142.9, 140.7, 131.6, 129.9, 124.8, 122.5, 114.4, 113.1, 112.8, 55.4, 40.7. **IR (cm^{-1})** ν 2960, 2923, 1663, 1511, 1439, 1351, 1244, 1061, 747. **HRMS** m/z calculated for $C_{20}H_{21}N_2O_2$ $[M+H]^+$: 321.1598; found 321.1608.

(*E*)-4-(((5-(((tert-butyldimethylsilyl)oxy)methyl)-3-phenylfuran-2-yl)methylene)amino)-N,N-dimethylaniline (10ha): Prepared according to general procedure from (E)-1-(5-(((tert-butyldimethylsilyl)oxy)methyl)furan-2-ylmethylene)amino)-N,N-dimethylaniline **9h** (179.3 mg, 0.5 mmol), 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane **a** (142.5 mg, 0.75 mmol), benzylideneacetone (80.4 mg, 0.55 mmol), $Ru_3(CO)_{12}$ (16.0 mg, 0.025 mmol), molecular sieves 4Å (274 mg). The crude product (71% NMR yield) was purified by flash chromatography on silica gel eluting with CyHex/EtOAc (90/10) to afford 145.5 mg of **10ha** (67% yield) as a brown solid. m.p. 88.0 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.24 (s, 1H), 7.35-7.24 (m, 5H), 7.11-7.98 (m, 2H), 6.58-6.56 (m, 2H), 6.41 (s, 1H), 4.69 (s, 2H), 2.81 (s, 6H), 0.81 (s, 9H), -0.00 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.8, 149.6, 146.7, 143.1, 140.9, 133.1, 132.7, 128.9, 128.0, 122.5, 112.9, 112.8, 109.7, 59.1, 40.8, 25.9, 18.5, -5.2. **IR (cm^{-1})** ν 3051, 2930, 2854, 1675, 1613, 1511, 1457, 1351, 1256, 1219, 1064, 841, 771. **HRMS** m/z calculated for $C_{26}H_{35}N_2O_2Si[M+H]^+$: 435.2462; found 435.2475.

(E)-4-(((5-(((tert-butyldimethylsilyl)oxy)methyl)-3-(4-methoxyphenyl)furan-2-yl)methylene)amino)-N,N-dimethylaniline (10hb): Prepared according to general procedure from (E)-1-(5-(((tert-butyldimethylsilyl)oxy)methyl)furan-2-ylmethylene)amino)-N,N-dimethylaniline **9h** (179.3 mg, 0.5 mmol), 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane **b** (165.1 mg, 0.75 mmol), benzylideneacetone (80.4 mg, 0.55 mmol), $Ru_3(CO)_{12}$ (16.0 mg, 0.025 mmol), molecular sieves 4Å (266 mg). The crude product (73% NMR yield) was purified by flash chromatography on silica gel eluting with CyHex/EtOAc (90/10) to afford 106.0 mg of **10hb** (46% yield) as a brown solid. m.p. 107.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.22 (s, 1H), 7.28 (d, *J* = 8.7 Hz, 2H), 7.13-7.09 (m, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.59 (d, *J* = 9.0 Hz, 2H), 6.38-6.37 (m, 1H), 4.69 (s, 2H), 3.72 (s, 3H), 2.83 (s, 6H), 0.81 (s, 9H), -0.00 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.7, 157.8, 149.6, 146.4, 143.4, 141.3, 133.0, 130.1, 125.1, 122.5, 114.5, 112.9, 109.7, 59.2, 55.5, 40.9, 26.0, 18.6, -5.2. **IR (cm^{-1})** ν 2956, 2852, 1668, 1608, 1507, 1457, 1352, 1249, 1075, 842, 774. **HRMS** m/z calculated for $C_{27}H_{37}N_2O_3Si[M+H]^+$: 465.2568; found 465.2583.

General procedure for acid hydrolysis of C3-arylated or vinylated furfural imines. To a solution of C3-arylated or vinylated furfural imine (0.05 mmol, 1 equiv.) in diethyl ether (0.02 M) was added dropwise HCl (aq, 1 N, 2.5 mL). The mixture was stirred overnight at room temperature and diluted with diethyl ether (10 mL). The aqueous layer was extracted with diethyl ether (3 x 20 mL) and the organic layers were combined, dried over $MgSO_4$, filtered and concentrated affording the corresponding C3-functionnalized furfural derivatives.

3-Phenylfuran-2-carbaldehyde (5a): Prepared according to general procedure from (E)-N,N-dimethyl-4-(((3-phenylfuran-2-yl)methylene)amino)aniline **4ha** (15.1 mg, 0.05 mmol). 8.2 mg of product **5a** was obtained as a brown oil (95% yield). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 9.75 (s, 1H), 7.70 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.58-7.45 (m, 5H), 6.74 (d, *J* = 1.7 Hz, 1H). The spectral data are in good agreement with those previously reported.[25]

3-(4-methoxyphenyl)furan-2-carbaldehyde (5b): Prepared according to general procedure from (*E*)-4-(((3-(4-methoxyphenyl)furan-2-yl)methylene)amino)-N,N-dimethylaniline **4hb** (12.0 mg, 0.04 mmol). 6.8 mg of product **5b** was obtained as a brown oil (90% yield). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 9.74 (s, 1H), 7.67 (d, *J* = 2.2 Hz, 1H), 7.53 (dd, *J* = 9.0, 2.4 Hz, 2H), 7.02-6.97 (m, 2H), 6.70 (d, *J* = 1.7 Hz, 1H), 3.87 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 178.0, 160.7, 147.6, 147.5, 138.6, 130.5, 122.9, 114.6, 113.7, 55.6. **IR (cm^{-1})** ν 2959, 2838, 1762, 1662, 1512, 1426, 1365, 1247, 1028, 768. **HRMS** m/z calculated for $C_{12}H_{11}O_3$ $[M+H]^+$: 203.0703; found 203.0702.

5-(((tert-butyldimethylsilyl)oxy)methyl)-3-phenylfuran-2-carbaldehyde (11a): Prepared according to general procedure from (*E*)-4-(((5-(((tert-butyldimethylsilyl)oxy)methyl)-3-phenylfuran-2-yl)methylene)amino)-N,N-dimethylaniline **10ha** (21.7 mg, 0.05 mmol). 12.7 mg of product **11a** was obtained as a brown oil (80% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.68 (s, 1H), 7.57-7.54 (m, 2H), 7.47-7.45 (m, 3H),

6.61 (s, 1H), 4.78 (s, 2H), 0.94 (s, 9H), 0.14 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.7, 161.0, 146.9, 140.2, 130.9, 129.4, 129.2, 125.7, 110.4, 58.9, 25.9, 18.5, -5.2. **IR (cm^{-1})** ν 2928, 2856, 1768, 1668, 1538, 1449, 1357, 1255, 1089, 765. **HRMS** m/z calculated for $C_{18}H_{25}O_3Si$ $[M+H]^+$: 317.1567; found 317.1566.

5-(((tert-butyldimethylsilyl)oxy)methyl)-3-(4-methoxyphenyl)furan-2-carbaldehyde (11b): Prepared according to general procedure from (*E*)-4-(((5-(((tert-butyldimethylsilyl)oxy)methyl)-3-(4-methoxyphenyl)furan-2-yl)methylene)amino)-N,N-dimethylaniline **10hb** (23.6 mg, 0.05 mmol). 15.1 mg of product **11b** was obtained as a brown oil (86% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.67 (s, 1H), 7.52 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.57 (s, 1H), 4.76 (s, 2H), 3.86 (s, 3H), 0.94 (s, 9H), 0.13 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.7, 160.9, 160.6, 146.7, 139.9, 130.4, 130.4, 123.2, 114.6, 114.5, 110.9, 110.3, 58.9, 55.6, 25.9, 18.5, -5.2. **IR (cm^{-1})** ν 2929, 2856, 1765, 1663, 1541, 1356, 1249, 1032, 777. **HRMS** m/z calculated for $C_{19}H_{27}O_4Si$ $[M+H]^+$: 347.1673; found 347.1669.

Acknowledgements

The authors would like to acknowledge Horizon 2020 ERANet-LAC project CelluloseSynThech for financial support (ref. ELAC2014/BEE-0341), as well as CNRS, Sorbonne Université and Labex Michem (Investissements d'Avenir programme, ref. ANR-11-IDEX-0004-02) and Fundação para a Ciência e Tecnologia (SFRH/BPD/88666/2012). Support through CMST COST Action, CA15106 (CHAOS) and Dr. Svilen P. Simeonv for providing sample of **12h** is also gratefully acknowledged.

Keywords: C-H activation • ruthenium • furfurals • boronate derivatives • imines

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[19] In compounds **4-14 xy**, **x** refers to the imine starting material and **y** refers to the aryl introduced.

[20] Use of other hydride acceptors (acetone, (*E*)-1,4-diphenylbut-2-en-1,4-dione or (*E*)-chalcone), catalysts ($RuH_2(CO)(PPh_3)_3$ or $RhCl(PPh_3)_3$) or boron partners (PhBPin, $PhB(OH)_2$, $PhBF_3K$) only gave very sluggish reactions or afforded complex mixtures.

[21] In a few cases, minor traces (~5%) of imine hydrolysis occurred during chromatographic purification.

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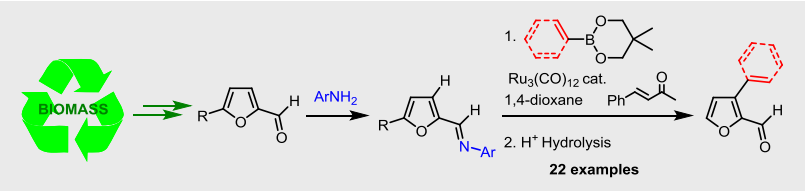

Furfural activated again: a Ru-catalyzed arylation and alkenylation of furfural imines with aryl- or alkenyl-boronates, involving a directed C-H activation occurring at C3 of the furan ring, was developed. A thorough experimental study revealed that an electron-rich aromatic imine, such as a *p*-dimethylaminophenyl-imine, enables the coupling with good yields. After the coupling, a smooth hydrolytic removal of the imine directing-group releases the C3-functionalized furfurals.

C-H activation

Filipa Siopa, Valérie-Anne Ramis Cladera, Carlos Alberto Mateus Afonso, Julie Oble, and Giovanni Poli**

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Ruthenium-Catalyzed C-H Arylation and Alkenylation of Furfural Derivatives