C–H Activation

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Rhodium(III)/Copper(II)-Promoted *trans*-Selective Heteroaryl Acyloxylation of Alkynes: Stereodefined Access to *trans*-Enol Esters**

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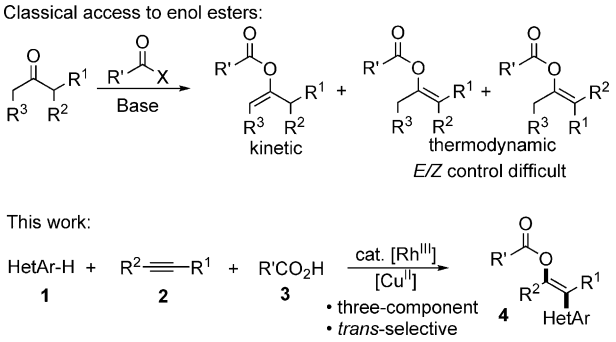
Abstract: *Enol esters are versatile synthetic building blocks which can be elaborated by a wide variety of transformations. The classical synthesis by O-selective enolate acylation often hampers control of the E/Z selectivity with highly substituted substrates. A rhodium(III)/copper(II)-mediated process is reported to provide tetrasubstituted enol esters in a trans-selective fashion. Overall, the reaction consists of a heteroaryl acyloxylation of alkynes. The process is initiated by a rhodium-(III)-catalyzed C2-selective activation of electron-rich hetero-arenes, such as benzofuran, furan, and thiophene. Upon addition across an alkyne, a transmetalation to copper(II) enables reductive C–O bond formation. The transformation allows the three-component couplings of heteroarenes, alkynes, and carboxylic acids. Application of the method in the functionalization of bioactive furocoumarin natural products is also described.*

Enol ester derivatives are key synthetic building blocks and are amenable to a wide variety of synthetic transformations including asymmetric hydrogenations,[1] aldol reactions, Mannich-type reactions,[2] cyclizations,[3] and cross-coupling reactions.[4] The enol ester motif is also found in natural products.[5] The classical synthetic access to enol esters is based on deprotonation of the corresponding ketones and subsequent O acylation,[6] thus impeding the use of substrates with base-sensitive functional groups. More recent approaches include metal-catalyzed direct additions of carboxylic acids to alkynes,[7] rearrangements of propargylic esters,[8] isomerizations of allylic esters,[9] carbonylative arylations of aryl ketones,[10] Chan–Lam couplings,[11] and zirconium-catalyzed methylalumination of terminal alkynes.[12] A control of the *E*/*Z* stereochemistry of especially fully substituted enol esters is highly desirable, but often very challenging to achieve. Herein, we report a complementary and *trans*-selective access to enol esters by a three-component assembly from heteroarenes, alkynes, and carboxylates (Scheme 1).



Scheme 1. Three-component access to *trans*-enol esters by rhodium(III)/copper(II) catalysis.

Benzofurans, furans, and thiophenes are important class of heterocycles. For instance, benzofurans are frequently encountered in bioactive furocoumarin natural products such as psoralen, khellin, and karanjin.[13] Moreover, these heterocycles have drawn attention in the pharmaceutical industry because of their broad biological activities,[14] and are an important structural design element for new organic materials.[15] As a consequence, major efforts have been reported for their direct and regioselective C–H functionalization with different transition-metal catalysts.[16] Among them, [Cp*Rh^{III}]-catalyzed reactions have emerged as a powerful synthetic tool.[17,18]

With the exemption of intramolecularly predisposed processes,[17e] reductive C–O bond formations have been only scarcely observed with rhodium(III) catalysis.[19,20] Most commonly, the organometallic intermediate is undergoing a protonolysis pathway or β-hydride elimination when possible, thus avoiding reductive C–O bond formations. After screening different oxidants, we observed the incorporation of a pivalate group into the product when $Cu(OPiv)_2$ was used instead of the classical $Cu(OAc)_2$ oxidant. In this uncommon *trans*-selective heteroaryl acyloxylation of an alkyne, both pivalate and copper(II), were essential for the acyloxylation. The rhodium(III)/copper(II) catalyst system allows the introduction of two functionalities at once. While the [Cp*Rh^{III}] fragment is enabling the C–H activation and C–C bond forming, a subsequent swap to copper(II) carries out the reductive C–O bond formation. We then investigated the process with 5-decyne and benzofuran (Table 1). Under optimized reaction conditions, the arylated enol ester **4aa** was obtained in 70% yield by using 2.5 mol% $[(Cp^*RhCl_2)_2]$ and $Cu(OPiv)_2$ as the terminal oxidant (entry 1). Both, the addition of catalytic amounts of perbromodiphenyl ether, an inexpensive and widely available flame retardant,[17g,21] as well as running the reaction under wet conditions are required for

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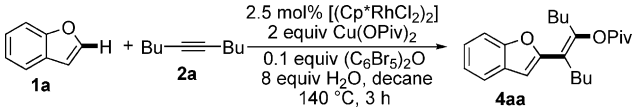
Table 1: Optimization of the *trans*-selective aryl acyloxylation.[a]

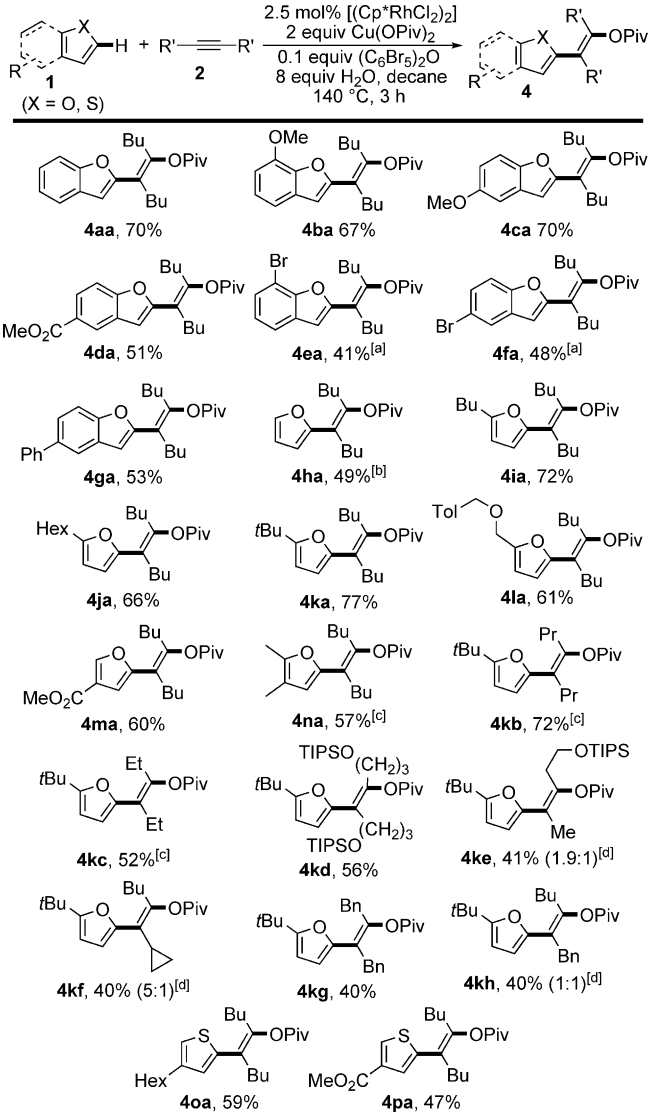


Entry	Deviations from the standard conditions	Yield [%][b]
1	–	70[c]
2	1.25 mol% [(Cp*RhCl$_2$)$_2$]	62[c]
3	no H_2O	50
4	no $(C_6Br_5)_2O$ and H_2O	37
5	no [(Cp*RhCl$_2$)$_2$]	0
6	no Cu(OPiv)$_2$	0
7	5 mol% $RhCl_3 \cdot 3H_2O$	55
8	2 equiv $Cu(OAc)_2 \cdot H_2O$	0
9	2 equiv AgOPiv (no Cu^{II})	0
10	2 equiv PhI(OPiv)$_2$ (no Cu^{II})	0
11	with 2 equiv PivOH	60
12	with 2 equiv Cs_2CO_3	0
13	with 0.15 mmol **1a**	52

[a] Standard reaction conditions: 0.10 mmol **2a**, 0.30 mmol **1a**, 2.50 μmol [(Cp*RhCl$_2$)$_2$], 0.20 mmol Cu(OPiv)$_2$, 0.01 mmol $(C_6Br_5)_2O$, 0.8 mmol H_2O, decane 0.25 M, 140 °C for 3 h. [b] Determined by ^{1}H NMR spectroscopy. [c] Yield of isolated product. Cp* = C_5Me_5, Piv = pivaloyl.

good yields (entries 3 and 4). The reaction still works well with a reduced catalyst loading (entry 2). Control experiments showed that no reaction took place in the absence of either [(Cp*RhCl$_2$)$_2$] or Cu(OPiv)$_2$ (entries 5 and 6). Simple $RhCl_3$ gave the product, albeit in lower yield (entry 7). Surprisingly, no product was obtained when $Cu(OAc)_2$ was used instead of Cu(OPiv)$_2$ (entry 8), thus indicating the importance of the bulk of the carboxylate. In the absence of copper, other common oxidants such as silver salts or PhI(OPiv)$_2$ did not give the desired product at all (entries 9 and 10). The reaction proved to be insensitive to acid, but a basic additive shut down the reaction completely (entries 11 and 12). The use of 1.5 equivalents of benzofuran is possible, but caused some reduction in yield (entry 13).

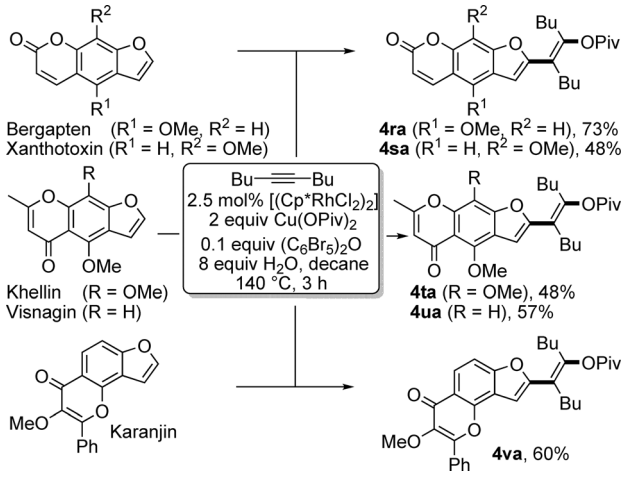
With the optimized reaction conditions, the scope of the transformation was explored (Scheme 2). The reaction proved to be tolerant of different substitution patterns on the aromatic core. Electron-rich benzofurans provided the desired product in good yields, whereas electron-deficient benzofurans led to slightly reduced yields. Despite their propensity to engage in hydrodebromination side reactions, brominated benzofuran substrates afforded the functionalized products. Not surprisingly, steric bulk close to the reaction site, such as a methyl group at the 3-position of the benzofuran shut the reaction down. The methodology could be further extended to furan as well as thiophene derivatives. In these cases, the transformation worked well with either C2- or C3-substituted substrates, thus tolerating ester and ether functionalities. Indoles and pyrroles do not undergo activation and can be largely recovered. In addition to different symmetrical dialkyl alkynes, unsymmetrically substituted alkyne provided the desired products with moderate regioselectivities. However, aryl alkynes react only sluggishly and bulky silyl alkynes are not competent substrates.



Scheme 2. Scope of alkyne heteroaryl acyloxylation. Reaction conditions: 0.10 mmol **2**, 0.30 mmol **1**, 2.50 μmol [(Cp*RhCl$_2$)$_2$], 0.20 mmol Cu(OPiv)$_2$, 0.01 mmol $(C_6Br_5)_2O$, 0.8 mmol H_2O, decane 0.25 M, 140 °C for 3 h. Yields are those of isolated products. [a] At 120 °C for 14 h. [b] Reaction performed with 2 mmol **1h**, microwave heating in heptane 0.25 M. [c] Microwave heating in heptane 0.25 M. [d] Regioisomers. TIPS = triisopropylsilyl.

The frequent occurrence of the benzofuran scaffolds in bioactive natural products prompted us to showcase this functionalization reaction with some representative members (Scheme 3). For instance bergapten,[13c] xanthotoxin,[13d] khellin,[13e] visnagin,[13e,f] and karanjin[13g] were subjected to standard reaction conditions. Gratifyingly all these functionalized substrates reacted well and delivered the desired products **4ra**–**va**. Moreover, X-ray crystallographic analyses of **4ra** and **4sa** confirmed the C2 selectivity of the reaction and the *trans*-configuration of enol pivalate products.[22]

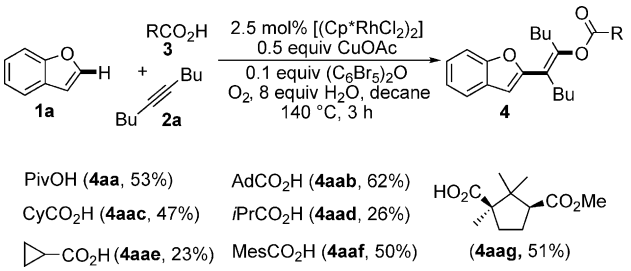
The reluctance of acetate to engage in the acetoxylation process could be used as convenient handle to introduce different carboxylic acids without the requirement of preparing the respective copper carboxylate. In a three-component



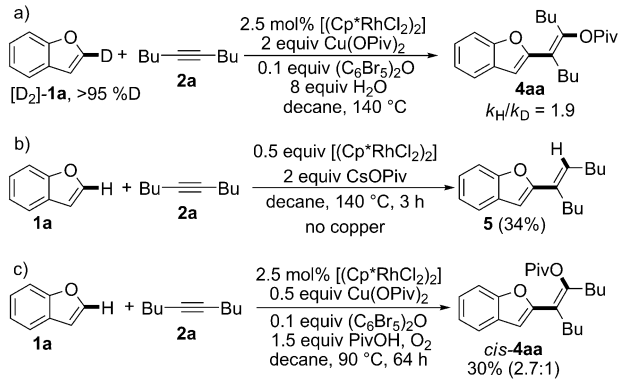
Scheme 3. Selective functionalizations of bioactive natural products.

reaction of benzofuran, alkyne and a free carboxylic acid gave the enol esters **4** using substoichiometric amounts of CuOAc and molecular oxygen as the oxidant (Scheme 4). The yields correlate strongly with the steric bulk of the acid **3**.

To gain mechanistic insights into the reaction pathway, several experiments were performed (Scheme 5). The radical inhibitor *tert*-butylhydroxytoluene had no influence on the reaction outcome and the enol ester **4aa** was obtained in comparable yield. Deuterium-labeling experiments were conducted with [D_2]benzofuran. Initial rate measurements of two parallel reactions revealed a kinetic isotope effect of 1.9 (Scheme 5a). Moreover, exposure of [D_2]-**1a** with **2a** to



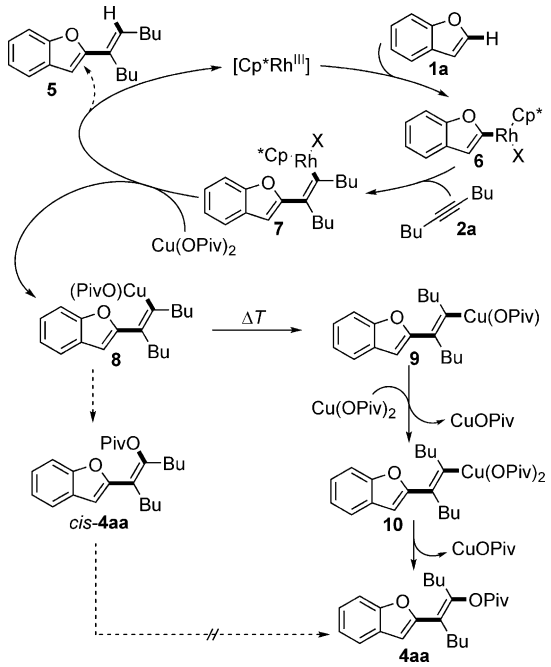
Scheme 4. Three-component enol ester formation.



Scheme 5. Control experiments for the reaction mechanism.

the standard reaction conditions for 25 minutes led to significant deuterium loss (60% recovery of **1a** with 62%D), thus suggesting a reversible C–H activation step. Omitting $Cu(OPiv)_2$ and using stoichiometric amounts of [$(Cp^*RhCl_2)_2$] and CsOPiv gave the hydroarylation product **5** and no trace of **4aa** was detected (Scheme 5b). This clearly underscores the pivotal role of the copper additive in the transformation. A reduction of the reaction temperature to 90 °C gave *cis*-**4aa** as major isomer (Scheme 5a). Even under forcing reaction conditions, *cis*-**4aa** could not be isomerized to its *trans*-**4aa**, thus suggesting that the observed *trans* product stems from an thermal isomerization step during the catalysis.[23]

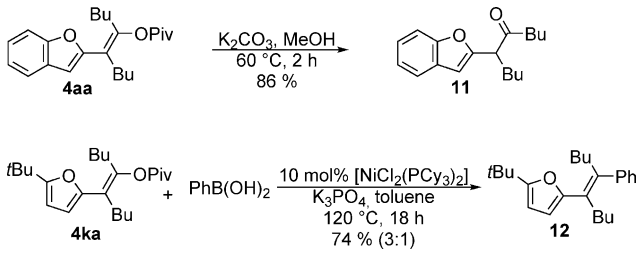
Based on these results, we suggest the following mechanistic scenario for the reaction (Scheme 6). A reversible



Scheme 6. Mechanistic working model for the *trans*-selective alkyne heteroaryl acyloxylation (X = OPiv, Cl, Br).

metalation of benzofuran (**1a**) at the C2-position provides the heteroaryl rhodium species **6**. Association of **2a** and migratory insertion leads to the intermediate **7**. Without copper hydroarylation the compound **5** is formed. Subsequent transmetalation of **7** to copper(II) provides **8** and releases the rhodium catalyst. At higher temperatures, a double-bond isomerization step occurs, thus giving the thermodynamically more stable *trans*-vinyl copper species **9**.[24] Presumed disproportionation of **9** with $Cu(OPiv)_2$ would form the copper(III) intermediate **10**[25] followed by reductive elimination, thus delivering the *trans*-**4aa**. Lower reaction temperature slows down the isomerization step and leads preferentially to *cis*-**4aa** by a similar pathway.

The versatility of the enol ester products is shown by further transformations into valuable products (Scheme 7). For instance, the enol esters are smoothly hydrolyzed under



Scheme 7. Transformations of enol ester products.

mildly basic conditions with potassium carbonate in methanol, thus yielding the α-heteroaryl-substituted ketone **11** in good yields. Moreover, enol pivalates are competent substrates for nickel-catalyzed cross-coupling reactions.[4,26] In this respect, the furan **4ka** provides access to tetrasubstituted olefin **12** by a nickel-catalyzed coupling with phenylboronic acid.

In summary, we report the *trans*-selective heteroaryl acyloxylations of alkynes by cooperative rhodium(III)/copper(II) catalysis. The reaction is initiated by a direct C2 metalation of the electron-rich heterocycles by the [Cp*Rh^{III}] catalyst. Upon alkyne insertion, a transmetalation to copper(II) occurs, followed by thermally driven double-bond isomerization. Reductive elimination with bulky carboxylates finally forges the C–O bond. A three-component version is described and incorporates a heteroarene, an alkyne, and a bulky carboxylic acid. The resulting *trans*-enol esters are synthetically attractive building blocks which are otherwise difficult to synthesize in a stereodefined fashion. Moreover, the method was shown to be suitable for the late-stage functionalization of a range of bioactive benzofuran natural products.

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[22] CCDC 1024414 (**4ra**) and 1024415 (**4sa**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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