C–H Activation

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Regioselective C–H Hydroarylation of Internal Alkynes with Arenecarboxylates: Carboxylates as Deciduous Directing Groups

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Dedicated to K. Peter C. Vollhardt on the occasion of his 70th birthday

Abstract: *In the presence of catalytic $[Ru(p\text{-}cym)I_2]_2$ and the base guanidine carbonate, benzoic acids react with internal alkynes to give the corresponding 2-vinylbenzoic acids. This alkyne hydroarylation is generally applicable to diversely substituted electron-rich and electron-poor benzoic and acrylic acids. Aryl(alkyl)acetylenes react regioselectively with formation of the alkyl-branched hydroarylation products, and propargylic alcohols are converted into γ-alkylidene-δ-lactones. The hydroarylation can also be conducted decarboxylatively with a different choice of catalyst and reaction conditions. This reaction variant, which does not proceed via intermediate formation of 2-vinylbenzoic acids, opens up a regioselective, waste-minimized synthetic entry to vinylarenes.*

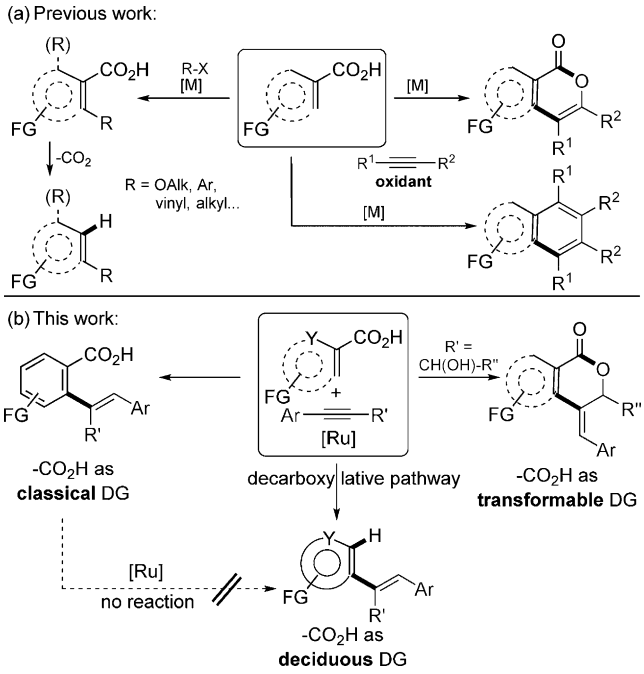
Given the prevalence of vinylarene moieties in functional materials, pharmaceuticals, and natural products,[1] efficient methods for the construction of this structural motif are constantly sought. Established synthetic approaches include Mizoroki–Heck[2] and Fujiwara–Moritani reactions,[3] as well as various catalytic cross-couplings of organometallic reagents with alkynes.[4]

C–H hydroarylations of alkynes are advantageous over these processes, because they require neither prefunctionalized substrates nor oxidants. Since the pioneering studies by Murai and co-workers,[5] various metals have been found to efficiently catalyze the hydroarylation of alkynes, for example Ru,[6] Rh,[7] Re,[8] Co,[9] and others.[10] However, these C–H functionalizations are highly regioselective only when directed by ketone, pyridine, amide, sulfoxide, or other strong directing groups, groups which need to be synthesized in additional reaction steps and are not easily removed.

Arguably, the most advantageous directing groups in *ortho*-functionalizations are carboxylates, because benzoic acids are widely available in great structural diversity and at low cost, and can subsequently be derivatized further, utilized as leaving groups in decarboxylative couplings,[11] or removed tracelessly by protodecarboxylation.[12] However, the weak coordinating ability of this group poses additional challenges in the development of regiospecific C–H-activating processes. In recent years, substantial advances in carboxylate-directed C–H activation have been made,[13] for example, by the groups of Yu,[14] Miura,[15] Ackermann,[16] and Larrosa,[12b,c] as well as our own group.[12d,17]

In this context, oxidative couplings of benzoic acids with alkynes to form isocoumarins, naphthalenes, and other cyclic structures have intensively been studied. These reactions involve carboxylate-directed C–H activation to give vinylmetal intermediates, which immediately undergo cyclization steps before either reductive elimination or protonolysis can occur (Scheme 1 a).[15,18] Moreover, in the presence of electron-deficient transition-metal catalysts or ruthenium(II), alkynes preferentially react with the nucleophilic carboxylate, to form enol esters, rather than with the C–H moiety.[19] This reactivity points to the challenges associated with developing selective C–H hydroarylations in the proximity of a reactive carboxylate.[20]

In continuation of our research on the use of carboxylic acids as substrates in transition-metal catalysis,[11,12d,17] we explored whether carboxylate groups could be utilized as directing groups in redox-neutral intermolecular hydroaryla-



Scheme 1. Carboxylate-directed C–H activation and coupling with alkynes. DG = directing group, FG = functional group.

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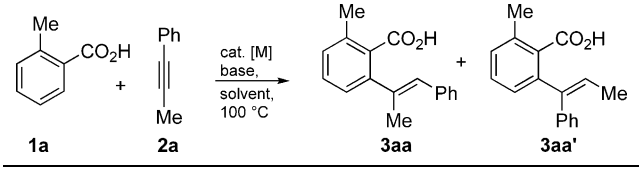
tions of alkynes (Scheme 1b). The desired process would have to be initiated by a carboxylate-directed *ortho*-C–H alkyne insertion step. The resulting vinyl–metal species would then need to be forced towards a reductive elimination step to yield alkenylbenzoic acids, despite the abundance of facile pathways leading to cyclized products.

To probe the feasibility of this concept, we investigated the reaction of 2-methylbenzoic acid (**1a**) with 1-phenyl-1-propyne (**2a**) in the presence of various metal catalysts (Table 1). Many complexes known for their ability to mediate

Table 1: Optimization of the directed hydroarylation conditions.[a]



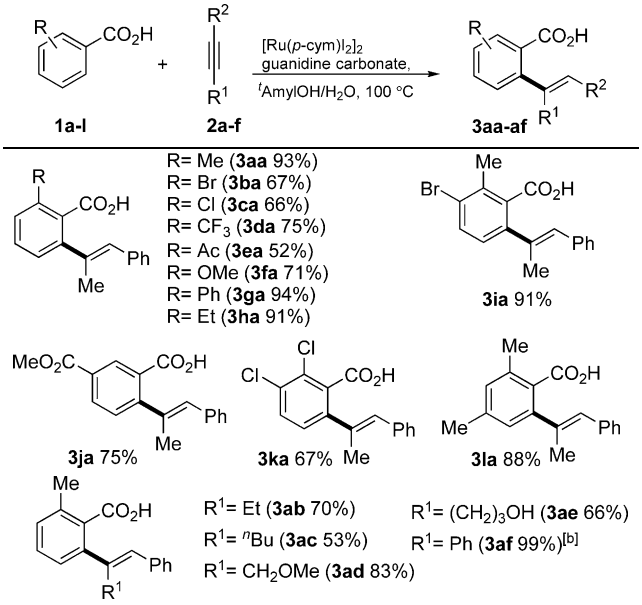
Entry	[M] (mol%)	Base	Yield [%] (**3aa**/**3aa'**)[b]
1	[Ru(*p*-cym)Cl_2]$_2$ (4)	0.3 equiv K_2CO_3	43:5
2	[Ru(*p*-cym)I_2]$_2$ (4)	0.3 equiv K_2CO_3	52:10
3	[Ru(*p*-cym)I_2]$_2$ (2)	0.3 equiv K_2CO_3	60:6
4	[Ru(*p*-cym)I_2]$_2$ (2)	0.1 equiv K_2CO_3	39:7
5	[Ru(*p*-cym)I_2]$_2$ (2)	0.5 equiv K_2CO_3	46:trace
6	[Ru(*p*-cym)I_2]$_2$ (2)	1.0 equiv K_2CO_3	n.d.
7	[Ru(*p*-cym)I_2]$_2$ (2)	0.5 equiv Cs_2CO_3	53:14
8	[Ru(*p*-cym)I_2]$_2$ (2)	0.5 equiv Li_2CO_3	44:9
9	[Ru(*p*-cym)I_2]$_2$ (2)	0.5 equiv guanidine carbonate	68:7
10[c]	[Ru(*p*-cym)I_2]$_2$ (2)	0.5 equiv guanidine carbonate	74:5
11[c,d]	[Ru(*p*-cym)I_2]$_2$ (2)	0.5 equiv guanidine carbonate	73:6
12[c,e]	[Ru(*p*-cym)I_2]$_2$ (2)	0.5 equiv guanidine carbonate	90 (93):5

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), [M] (4 mol%), base, 1,4-dioxane:H_2O (10:1, 1.1 mL), 100°C, 12 h. [b] Yields of corresponding methyl esters determined by GC after esterification with K_2CO_3 (2 equiv) and MeI (5 equiv) in MeCN using *n*-tetradecane as the internal standard. Yields of isolated products are given within parentheses. [c] ^{t}AmOH/H_2O = 10:1 as solvent. [d] 0.6 mmol **1a**. [e] 0.75 mmol **2a**. n.d. = not determined. cym = cymene.

C–H functionalizations, including $Pd(OAc)_2$, [{IrCp*Cl_2}$_2$], [{Ir(cod)$_2$Cl}$_2$], and [{Rh(cod)$_2$Cl}$_2$] were investigated, but none of them gave the hydroarylation product **3aa** in the desired selectivity (see the Supporting Information for details). However, the simple ruthenium complex [Ru(*p*-cym)Cl_2]$_2$, usually an efficient hydroacyloxylation catalyst,[19] surprisingly furnished **3aa** in an encouraging 48% yield with a high 7:1 regioselectivity in favor of the methyl-branched stilbene derivative (entry 1). The iodine-bridged analogue [Ru(*p*-cym)I_2]$_2$ proved to be an even more active and selective catalyst (entries 2 and 3). The process requires the presence of substoichiometric amounts of base, ideally 50 mol%, thus giving the best balance between conversion and selectivity. If stoichiometric amounts of base are present, the reaction is completely suppressed, thus indicating that protons are required in the overall process (entries 4–6). Carbonate bases, and guanidinium carbonate in particular, were found to be most effective (entries 7–9). The remarkable reactivity of the guanidinium base may result from the known ability of guanidine to form stable ruthenium(II) complexes.[21] A thorough solvent screening revealed that a 10:1 mixture of ^{t}AmOH and H_2O gives the highest yields and selectivities (entry 10; see the Supporting Information). Substrates **1a** and **2a** were best employed in a 1:1.5 ratio (entries 11 and 12).

The scope of the hydroarylation reaction with regard to the acid component was investigated using 1-phenyl-1-propyne (**2a**) as the coupling partner (Table 2). Benzoic acids

Table 2: Substrate scope of the directed hydroarylation.[a]

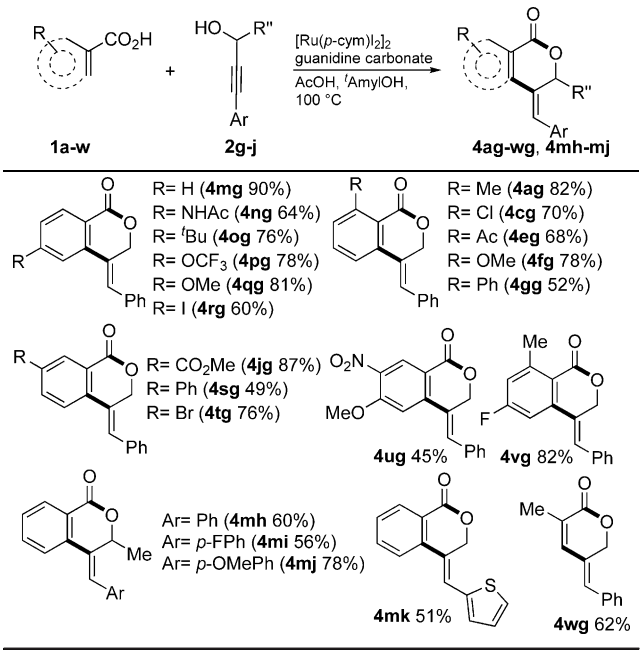


[a] Reaction conditions: **1a–l** (0.5 mmol), **2a–f** (0.75 mmol), [Ru(*p*-cym)I_2]$_2$ (2 mol%), guanidine carbonate (0.5 equiv.), ^{t}AmOH/H_2O = 10:1 (1.1 mL), 100°C, 12–24 h. Yields of the corresponding methyl ester isolated after derivatization with MeI. [b] **2f** (0.5 mmol).

bearing various functional groups, including halides (**1b–c**), electron-withdrawing groups such as CF_3, Ac, CO_2Me (**1d–e**,**j**), or electron-donating moieties (**1a**,**f–g**) all gave good to moderate yields. Multisubstituted benzoic acids (**1i**,**k**,**l**)were also suitable substrates for this transformation. Next, several alkynes were evaluated as coupling partners in combination with toluic acid (**1a**). All gave reasonable yields, with best results being obtained with diphenylacetylene (**2f**). Unprotected hydroxy groups remained intact when at a distance from the C–C triple bond (**2e**).

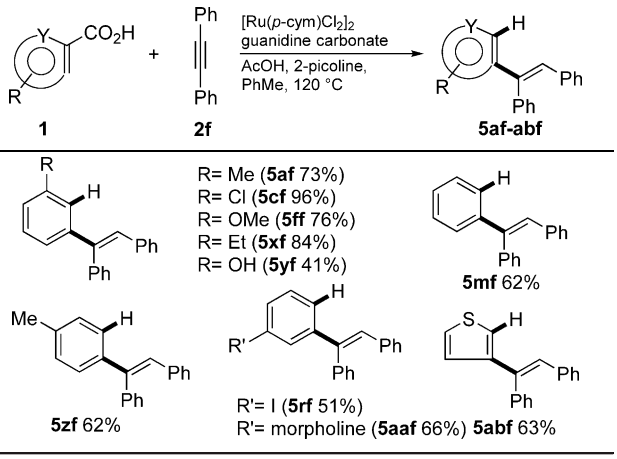
With propargylic alcohols (**2g–k**) as substrates, the C–H hydroarylation was followed by intramolecular lactonization, so that γ-alkylidene-δ-lactones were formed in high yields (Table 3). This reaction nicely complements the oxidative C–H functionalizations/lactonizations, which lead to endocyclic C–C double bonds (Scheme 1). The broad scope spans from electron-rich to electron-deficient benzoic acids bearing a wealth of functional groups in the *para*-, *ortho*-, or *meta*-position (Table 3; **1m–v**). Various propargylic alcohols were smoothly converted into the corresponding lactones (**2h–k**). Not only benzoic acid, but also methacrylic acid (**1w**) was successfully converted. During the optimization of the

Table 3: Substrate scope of benzoic acids for hydroarylation and annulation.[a]



[a] Reaction conditions: **1a–w** (0.5 mmol), **2g–k** (0.75 mmol), [Ru(*p*-cym)I_2]$_2$ (2 mol%), guanidine carbonate (0.5 equiv), HOAc (1.0 equiv), ^{t}AmOH (1 mL), 100°C, 12–24 h.

Table 4: Scope with respect to benzoic acids for decarboxylative hydroarylation.[a]

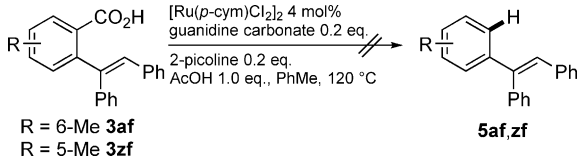


[a] Reaction conditions: **1a–ab** (0.5 mmol), **2f** (0.5 mmol), [Ru(*p*-cym)Cl_2]$_2$ (4 mol%), guanidine carbonate (0.2 equiv), 2-picoline (0.2 equiv), HOAc (1.0 equiv), toluene (2 mL), 120°C, 24 h.

reaction conditions, we had occasionally observed the formation of decarboxylation products.

Intrigued by this observation, we optimized the catalyst and reaction conditions using the model reaction of **2f** with **1a** until the decarboxylative reaction pathway became predominant (see the Supporting Information). In the presence of [Ru(*p*-cym)Cl_2]$_2$ (4 mol%), guanidine carbonate (0.2 equiv), 2-picoline (0.2 equiv), HOAc (1.0 equiv), and in the nonpolar solvent toluene (2 mL), the decarboxylative coupling product **5af** was finally obtained in 73% yield at 120°C (Table 4). In this decarboxylative reaction variant, various functional groups are tolerated including halides, methoxy, and alkyl groups (Table 4). It also extends to heterocyclic substrates. The tolerance of chloro and even iodo groups demonstrates the orthogonality of the present transformation into traditional cross-coupling processes. However, this prototype protocol does not presently allow a high-yielding coupling of alkyl-substituted alkynes.

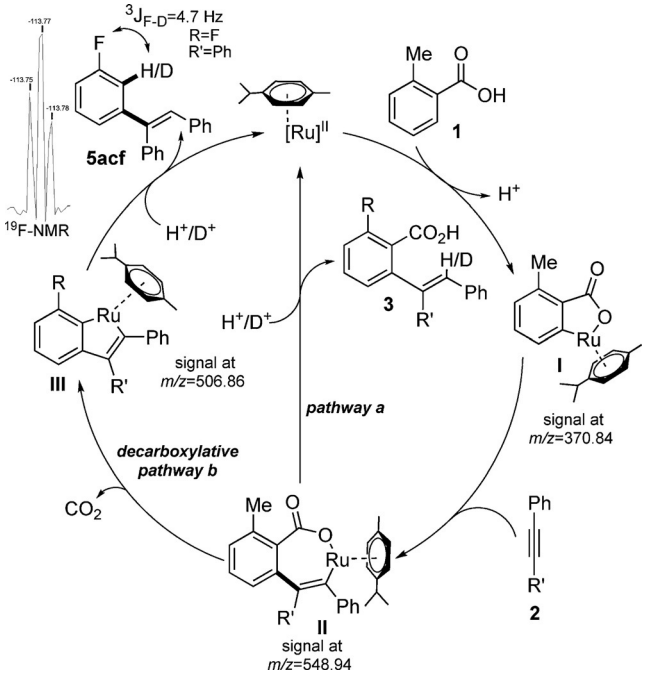
In a control experiment, we submitted the products **3af**,**zf** of the non-decarboxylative hydroarylation to the decarboxylative hydroarylation conditions (Scheme 2). These did not decarboxylate, which suggests that the decarboxylated products are not formed by a hydroarylation/protodecarboxylation sequence, but by an alternative mechanistic pathway. The carboxylate group may thus be considered to act as a deciduous directing group, remaining in place for as long as it is required to direct C–H functionalization, but being shed tracelessly within the catalytic cycle.[12] The key advantage of the concept of deciduous directing groups is that the unwanted formation of byproducts resulting from C–H functionalization on both sides of the directing group is impossible, because the directing group is removed in course of the first C–H functionalization, and is no longer in place to activate a second C–H bond.



Scheme 2. Protodecarboxylation experiment under standard reaction conditions.

Based on the above findings and mechanistic investigations for related processes,[18] a tentative catalytic cycle for the ruthenium-catalyzed C–H hydroarylation of alkynes can be outlined (Scheme 3). It starts with formation of the cyclometallated ruthenium complex **I**, which coordinates to the alkyne substrate. Migratory insertion affords the seven-membered alkenyl–ruthenium species **II**. In pathway a, which predominates in polar solvents, protonolysis occurs (or reductive elimination, if the proton resides at the ruthenium), thus releasing the hydroarylation product **3aa**. The alternative pathway b, leading to the decarboxylated product **5acf**, becomes more favorable at higher temperatures, when protonolysis is slower, that is, in less polar solvents, and when coordinating chloride ions are present. These factors contribute to facilitate extrusion of CO_2 from **II**. In-depth mechanistic studies are underway to fully clarify the reaction pathways of this intriguing transformation.

In conclusion, the carboxylate-directed C–H hydroarylation of internal alkynes with benzoic or acrylic acids catalyzed by the inexpensive, easy-to-handle [Ru(*p*-cym)I_2]$_2$ complex opens up a convenient and waste-free entry to a wide variety of 2-vinylbenzoic acids or aromatic δ-lactones from abundant precursors. In a less-polar solvent mixture and at higher temperatures, the carboxylate group is removed directly within the hydroarylation process. Beyond being removable, the carboxylates thus become deciduous directing groups,



Scheme 3. Proposed mechanism for the ruthenium-catalyzed (decarboxylative) C–H hydroarylation of alkynes. ESI-MS results provided for compounds where R = Me, R′ = Ph.

intrinsically preventing disubstitution in this directed C–H functionalization.

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Keywords: alkynes · C–H activation · decarboxylation · ruthenium · synthetic methods

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