C–H Activation

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# Aromatic Homologation by Non-Chelate-Assisted Rh$^{III}$-Catalyzed C–H Functionalization of Arenes with Alkynes**

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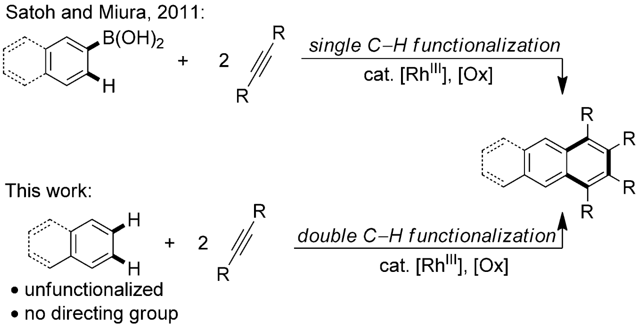
***Abstract:** Larger condensed arenes are of interest owing to their electro- and photochemical properties. An efficient synthesis is the catalyzed aromatic annulation of a smaller arene with two alkyne molecules. Besides difunctionalized starting materials, directed C–H functionalization can be used for such aromatic homologation. However, thus far the requirement of either pre-functionalized substrates or suitable directing groups were limiting this approach. Herein, we describe a rhodium(III)-catalyzed method allowing the use of completely unbiased arenes and internal alkynes. The reaction works best with copper(II) 2-ethylhexanoate and decabromodiphenyl ether as the oxidant combination. This aromatic annulation tolerates a variety of functional groups and delivers homologated condensed arenes. Aside from simple benzenes, naphthalenes and higher condensed arenes provide access to highly substituted and highly soluble acenes structures having important electronic and photophysical properties.*

Larger condensed arenes and heteroarenes have received much interest due to their electro- and photochemical properties, rendering them attractive materials for organic electronics and luminescence applications.[1] The introduction of multiple substituents/side chains generally makes these compounds more soluble and stable, as well as allowing for modulation and improvement of their fluorescence and charge mobility properties.[2] A modular and attractive method for their synthesis is an arene homologation that provides the next higher acene by the condensation of an aromatic ring with two alkyne units. A range of methods and different starting materials have been devised. These comprise metal-catalyzed reactions of difunctionalized starting materials[3] and, synthetically more efficiently, monofunctionalized educts, whereas the second C–C bond formation is initiated by a C–H bond functionalization.[4,5] So far, the most general method using monofunctionalized starting materials is the Rh$^{III}$-catalyzed annulation of arylboronic acids and internal alkynes reported by Satoh and Miura (Scheme 1).[6] However, despite the availability of a wide range of aryl boronic acid substrates and methods to access them, the requirement of a functionalized starting material represents a restricting limitation. In the view of efficiency and step-economy, the use of a totally unbiased aromatic substrate is therefore highly desirable.



***Scheme 1.*** Acene annulation by an undirected double oxidative Rh$^{III}$-catalyzed C–H functionalization.

Recently, Rh$^{III}$-directed C–H functionalization[7] has emerged as valuable tool to access polycondensed aromatic ring systems.[5c,8] However, reactions lacking any directing group on the substrate,[9] and thus allowing the use of unbiased arenes, are scarce[10] and would be a highly desirable tool (Scheme 1). Herein, we report a Rh$^{III}$-catalyzed homologation of directing group-free arenes and alkynes operating by double C–H functionalization under oxidative conditions.

The influence of the different reaction parameters was initially evaluated with 5-decyne (**1a**) as the limiting reactant, and naphthalene (**2a**) as aromatic acceptor (Table 1). Under carefully optimized conditions, 60 % of anthracene **3aa** is obtained using [(Cp*RhCl$_2$)$_2$] (Cp* = pentamethylcyclopentadienyl) as catalyst and a combination of copper(II) 2-ethylhexanoate and decabromo diphenyl ether as oxidants (entry 1). Both the electron-poor complex reported by Tanaka et al.[11] and simple RhCl$_3$ were less efficient (entries 3–4). The employed oxidant combination is essential for the success of the annulation. The high solubility of copper(II) 2-ethylhexanoate in apolar solvents makes it largely superior to Cu(OAc)$_2$ (entry 5). The perbromobenzene co-oxidant introduced by Glorius et al.[12] improved the yield, however the separation of its degradation products from **3aa** is quite tedious (entry 6). The addition of substoichiometric amounts of decabromodiphenyl ether (decaBDE), an inexpensive and widely available flame retardant,[13] mitigates this issue. Silver salts were detrimental for the reaction outcome (entries 8–9). Moreover, both acidic and basic additives decrease the yield significantly (entries 10–11). The reaction proceeded equally well in cyclohexane and less efficiently in dichloroethane, *i*Pr$_2$O,

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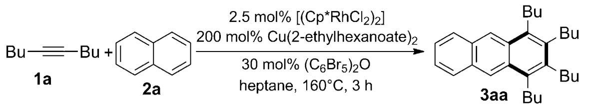
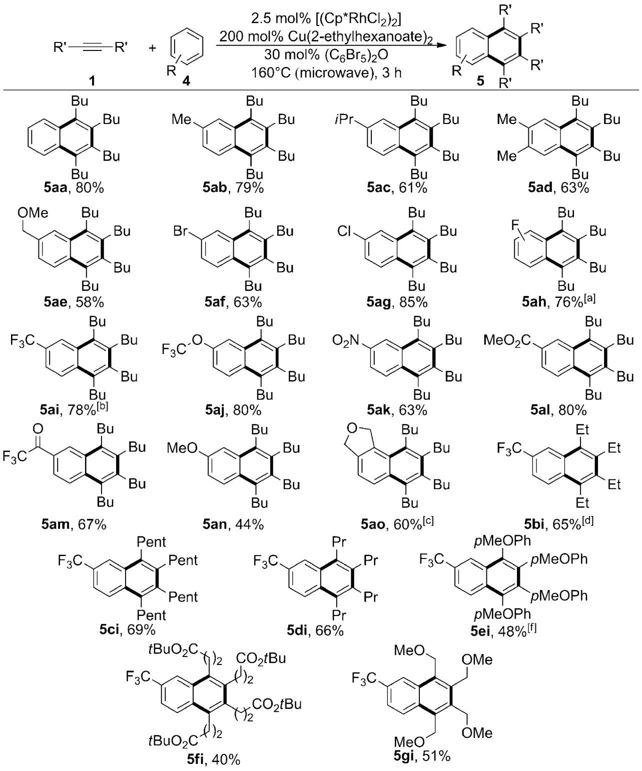
***Table 1:*** Optimization studies of the C−H annulation reaction.[a]



| Entry | Changes from standard conditions | Yield [%][b] |
|---|---|---|
| 1 | – | 60[c] |
| 2 | without $[(Cp^*RhCl_2)_2]$ | 0 |
| 3 | 2.5 mol % $[\{Me_3(CO_2Et)_2CpRhCl_2\}_2]$ | 42 |
| 4 | 5 mol % $RhCl_3{\cdot}3\,H_2O$ | 23 |
| 5 | 200 mol % $Cu(OAc)_2{\cdot}H_2O$ | 5 |
| 6 | with 50 mol % $C_6Br_6$ | 53 |
| 7 | without $(C_6Br_5)_2O$ | 20 |
| 8 | with 10 mol % $AgSbF_6$ | 15 |
| 9 | with 200 mol % AgOPiv | 3 |
| 10 | with 200 mol % $Cs_2CO_3$ | 3 |
| 11 | with 200 mol % PivOH | 33 |
| 12 | in cyclohexane | 57 |
| 13 | in DCE | 40 |
| 14 | in $i\mathrm{Pr}_2O$ | 50 |
| 15 | in *t*BuOH | 51 |
| 16 | with conventional heating | 42 |
| 17 | at 140 °C | 45 |
| 18 | with 0.2 mmol **2a** | 40 |

[a] Standard conditions: **1a** (0.20 mmol), **2a** (0.50 mmol), $[(Cp^*RhCl_2)_2]$ (2.50 μmol), 0.20 mmol Cu(2-ethylhexanoate)$_2$, 0.03 mmol $(C_6Br_5O)_2$, 1.0 M in heptane at 160 °C microwave heating for 3 h; [b] Determined by $^1$H NMR spectroscopy with an internal standard; [c] Yield of isolated **3aa**. DCE = 1,2-dichloroethane, Piv = pivaloyl.



***Scheme 2.*** Scope of the annulation process for monocyclic arenes. Reaction conditions: 0.20 mmol **1**, 2.00 mmol arene **4**, 2.50 μmol $[(Cp^*RhCl_2)_2]$, 0.20 mmol Cu(2-ethylhexanoate)$_2$, 0.03 mmol $(C_6Br_5)_2O$, 160 °C microwave heating for 3 h; All yields are isolated pure **5**. [a] 2.3:1 *meta/ortho*. [b] 74 % yield was obtained upon 40-fold scale up (8.0 mmol **1a**). [c] Reaction performed with 0.01 mmol $(C_6Br_5)_2O$; 1.5:1 linear/angular isomer. [d] At 120 °C for 12 h. [e] At 140 °C for 6 h. [f] Reaction performed with 5.00 μmol $[(Cp^*RhCl_2)_2]$ at 180 °C.

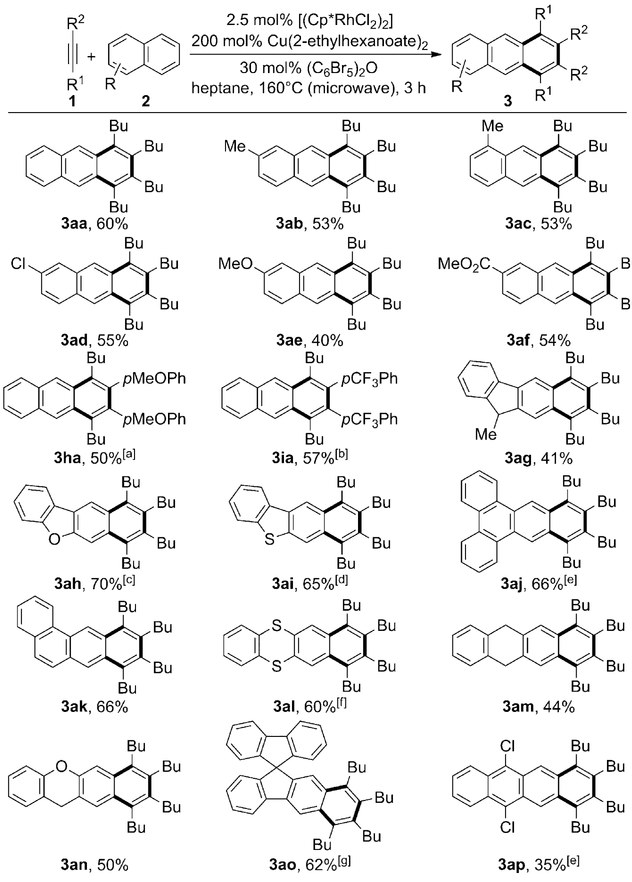
and *t*BuOH (entries 12–15). Conventional heating, or lowering the reaction temperature or the equivalents of naphthaline reduces the yield as well (entries 16–18).

To explore the scope of the optimized process, we evaluated different simple benzenes (**4**; Scheme 2). The annulation of benzene and toluene gave the corresponding naphthalenes **5aa** and **5ab** in 80 % and 79 % yield, respectively. The substrate *o*-xylene delivers product **5ad** in comparable yield, whereas *m*-xylene is not a competent substrate. Halobenzenes[14] and other electron-poor derivatives display an enhanced reactivity. Notably, esters and trifluoroacetyl groups bearing both carbonyl directing groups, also yield the distal activation product. Anisole, exemplifying an electron-rich substrate, provides naphthaline **5an** in somewhat reduced yields. Aside from different internal alkyl alkynes,[15] ω-functionalized alkynes and diaryl alkynes can be used and provide naphthalenes **5bi–gi**. The reaction is also scalable (8.0 mmol of alkyne **1a** provides a 74 % yield (1.25 g) of **5ai**).

Besides the formation of substituted naphthalenes, the method was further employed for the synthesis of a range of anthracenes from their corresponding naphthalenes (Scheme 3). The reaction is tolerant to α- and β-substitution of the substrate. In these cases, the activation exclusively takes place at the unsubstituted ring. Notably, a methyl ester does not act as directing group (**3af**). Reaction with unsymmetrically substituted alkyl aryl alkynes (**1h** and **1i**) provide the corresponding anthracenes **3ha** and **3ia** with a regioselectivity clearly favoring an orientation of the aromatic substituents at the 2,3-position over the 2,4-position.[16] We next tested larger polycyclic aromatic substrates for their viability in this reaction. Such ring systems are at the center of interest due to their physical properties, which are favorable for applications in materials, such as organic electronics.[1] In this respect, fluorene,[17] dibenzofurane,[18] dibenzothiophene,[19] triphenylene,[20] thianthrene,[21] phenanthrene,[22] 9,10-dihydroanthracene,[23] 9*H*-xanthene, and 9,9-spirobi[fluorene][24] participated well in the process to give the corresponding annulated products **3ag–ao**. Notably, 9,10-dichloroanthracene gave tetracene **3ap** when appropriate precautions are taken to exclude light and oxygen during isolation.[25]

A common problem for material sciences is the dramatically reduced solubility of larger polyarenes, which hampers exploitation of the properties of the products, and makes the fabrication of devices challenging.[2] To overcome this, the installation of solubilizing side chains is required. In this respect, the reported direct annulation method opens convenient opportunities for the direct introduction of such solubilizing substituents or other functionalized tails. For example, tetracene **3ap** displays excellent solubility in pure hydrocarbon solvents (minimum 290 mg mL$^{-1}$ in hexane at 23 °C). We then measured its photophysical properties in *n*-hexane as solvent and obtained values for **3ap** in the expected range for tetracenes (Figure 1).[25]

We propose the following scenario for the reaction mechanism (Scheme 4): First, a non-chelation-assisted metalation[26] of the napthalene **2a** leads to aryl rhodium inter-



***Scheme 3.*** Scope of the annulation process for polycyclic arenes. Reaction conditions: **1** (0.20 mmol), arene **2** (0.50 mmol), $[(Cp^*RhCl_2)_2]$ (2.50 μmol), Cu(2-ethylhexanoate)$_2$ (0.20 mmol), $(C_6Br_5)_2O$ (0.03 mmol), 1.00 M in heptane, 160 °C microwave heating for 3 h; All yields shown are of isolated **3**. [a] Aryl groups are 23:8:1 2,3-/2,4-/1,4-. [b] Aryl groups are 30:10:1 2,3-/2,4-/1,4-. [c] 2:1 linear/angular isomer. [d] 3.7:1 linear/angular isomer. [e] 0.50 M in heptane. [f] 3:1 linear/angular isomer. [g] reaction performed with 5.00 μmol $[(Cp^*RhCl_2)_2]$ in heptane 0.50 M for 6 h.

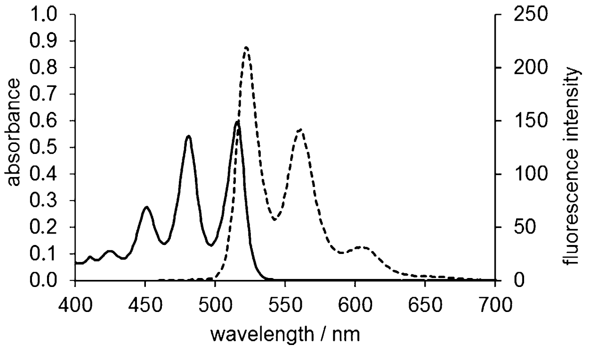
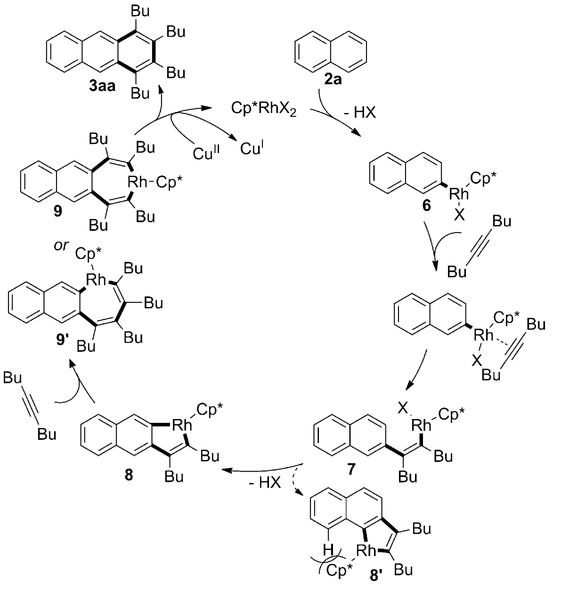


***Figure 1.*** Absorbance spectra (——) and fluorescence emission spectra (-----) of tetracene **3ap** ($5\times10^{-5}$ M in *n*-hexane). Excitation wavelength: 450 nm.

mediate **6**. Subsequent migratory insertion of the first molecule of alkyne gives **7**, which in turn triggers an intramolecular C–H activation leading to rhodacycle **8**; this process strongly favors the linear isomer over the angular **8′**.



***Scheme 4.*** Mechanistic proposal for the annulation reaction (X = Cl, Br, or 2-ethylhexanoate).

Incorporation of the second molecule of alkyne provides **9** or **9′**, followed by reductive elimination, which expels annulated product **3aa**. Reoxidation by Cu$^{II}$ then regenerates the Cp*Rh$^{III}$ catalyst. Based on the report of Satoh and Miura for the annulation of aryl boronic acids,[6] we assume the first undirected intermolecular metalation is the challenging and rate-limiting step of the overall transformation.

In summary, we reported Cp*Rh$^{III}$-catalyzed non-chelate-assisted C–H activation of a broad range of simple and condensed arenes. The reaction with internal alkynes results in annulative condensation to give the homologated acene. The method is suited for larger aromatic substrates of interest to material science and allows installation of solubilizing chains and functional tails.

## Experimental Section

Typical procedure for **3aa**: $[(Cp^*RhCl_2)_2]$ (1.54 mg, 2.50 μmol), decabromodiphenyl ether (28.8 mg, 0.03 mmol), copper(II) 2-ethylhexanoate (70.0 mg, 0.20 mmol), and naphthalene (64.1 mg, 0.50 mmol) were weighed into a 0.5 mL microwave vial equipped with a magnetic stir bar and sealed. The vial was evacuated and backfilled with nitrogen. 5-decyne (36.4 μL, 0.20 mmol) and 0.2 mL heptane were then added. The mixture was heated to 160 °C in a microwave apparatus. After 3 h, the reaction mixture was cooled to 23 °C and the volatiles were evaporated in vacuo. The residue was purified by chromatography on silica gel, eluting with pentane to yield 24.0 mg (60 % yield) of **3aa**.

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**Keywords:** acenes · alkynes · C-H activation · naphthalenes · rhodium

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