


C–H Activation Hot Paper

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Rhodalectro-Catalyzed *peri*-Selective Direct Alkenylations with Weak *O*-Coordination Enabled by the Hydrogen Evolution Reaction (HER)

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In memory of Professor Ulf Diederichsen

Abstract: Direct C–H functionalizations by electrocatalysis is dominated by strongly coordinating N(sp²)-directing groups. In sharp contrast, direct electrocatalytic transformations of weakly-coordinating phenols remain underdeveloped. Herein, electrooxidative *peri* C–H alkenylations of challenging 1-naphthols were achieved by versatile rhodium(III) catalysis via user-friendly constant current electrolysis. The rhodalectrocatalysis employed readily-available alkenes and a protic reaction medium and features ample scope, good functional group tolerance and high site- and stereoselectivity. The strategy was successfully applied to high-value, nitrogen-containing heterocycles, thereby providing direct access to uncommon heterocyclic motifs based on the dihydropyranoquinoline skeleton.

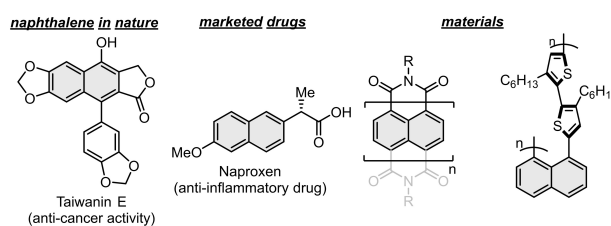
Introduction

Metal-catalyzed C–H activation has emerged as a transformative platform for molecular syntheses.^[1] Particularly, oxidative C–H/C–H functionalizations^[2] constitute one of the most attractive approaches for the construction of C–C and C–Het bonds, since it employs non-prefunctionalized substrates, thus enabling ideal resource economy. The past decade has witnessed major progress in electrochemical organic synthesis.^[3] The replacement of chemical oxidants by the hydrogen evolution reaction (HER)^[3b,4] have received major attention, as this approach offers an alternative to conventional methods that require non-environmentally-friendly stoichiometric amounts of expensive chemical

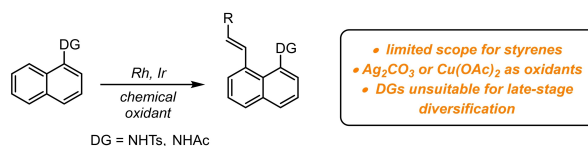
oxidants.^[4d,5] Despite of indisputable advances in the field of electrosynthesis, electrooxidative C–H/C–H alkenylation reactions are highly underdeveloped.^[6]

Naphthalene is the smallest polycyclic aromatic hydrocarbon and its significance is reflected by remarkable pharmaceutical core structures,^[7] natural products,^[8] powerful ligands for asymmetric catalysis,^[9] photocatalysts^[10] and in materials chemistry^[11] (Scheme 1a). Given the importance

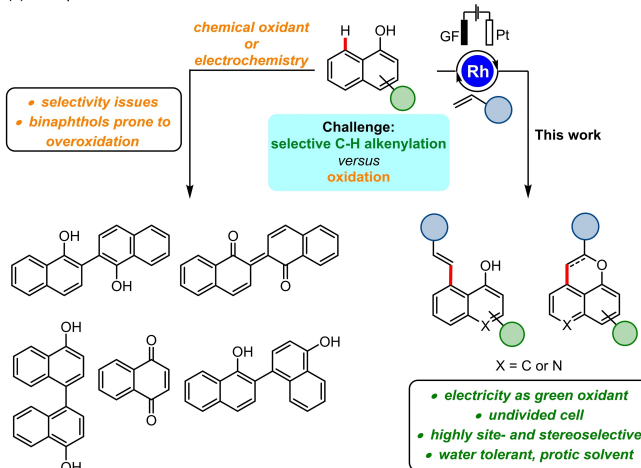
(a) Importance of the naphthalene scaffold



(b) Previous works on alkenylation of naphthalene assisted with directing groups (DGs)



(c) 1-Naphthols under oxidative conditions



Scheme 1. a) Examples of important naphthalene molecules. b) Previous studies on the alkenylation of the naphthalene scaffold. c) Electrooxidative alkenylation of 1-naphthols by HER.

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of 1,8-disubstituted (*peri*-substituted) naphthalene derivatives, there has been continuous strong interest in the C8 functionalization towards C–C formation by metal-catalyzed C–H functionalizations.^[12] In this context, methods for the construction of the C–C bonds via *peri*-selective naphthalene functionalization have been developed, such as arylations,^[13] alkenylations,^[14] alkynylations^[15] or annulations.^[16] While the oxidative, *peri*-selective alkenylation with styrenes was enabled with chemical oxidants by difficult to remove sulfonamide directing groups^[14a] (Scheme 1b), oxidative 1-naphthol alkenylations, either in a chemical or an electrochemical manner are yet to be developed.

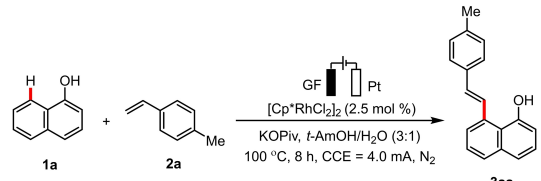
The oxidative functionalization of naphthols^[17] is particularly difficult, because the chemo-selective C–H activation is challenged by undesired dimerizations^[18] or polymerizations^[19] (Scheme 1c). Within our ongoing interest in material syntheses via electrochemical C–H activation,^[20] we have now devised the first electrochemical, organometallic and *peri*-selective C–H alkenylation with 1-naphthols (Scheme 1c). Salient features of our findings include 1) electro-oxidative rhodium-catalyzed *peri*-selective alkenylation reaction; 2) weakly coordinating^[21] and electrochemically challenging 1-naphthols; 3) oxidative alkenylation enabled by HER and 4) excellent site- and stereoselectivity. Notably, the presence of the synthetically meaningful hydroxyl^[22] group and the arylalkene^[23] moiety in the *peri* relationship within the designed molecular structures creates an opportunity for further late-stage modifications.

Results and Discussion

We initiated our studies with 1-naphthol (**1a**) and 4-methylstyrene (**2a**) as substrates to evaluate the envisioned *peri*-C–H alkenylations employing user-friendly galvanostatic condition, in an undivided cell equipped with a graphite felt (GF) anode and a platinum cathode (Table 1 and Table S1 in the Supporting Information). Initial attempts revealed that while similar efficacy could be obtained in 1,4-dioxane/H₂O (3:1) or *t*-AmOH/H₂O (3:1) solvent mixtures under air, the reaction performed under N₂ atmosphere in the latter solvent system gave slightly improved yield of product **3aa** (entries 1 and 2). When testing various additives (entries 3 and 4 and Table S1), we found that KOPIV was optimal for this transformation. The electricity amount was recognized as 4.0 mA/8 h (entries 6–8) with a Faradaic efficiency (FE) being 51 % for entry 6. Other frequently used catalysts fell short in providing the desired product **3aa** (entry 9). Control experiments demonstrated the key importance of the rhodium catalyst and the electricity (entries 10 and 11). The reaction also proceeded efficiently under potentiostatic conditions at 0.8 V (entry 12), however an increased reaction time was required to achieve full conversion of naphthol **1a**. Applying a reduced catalyst loading (entry 13) or a higher temperature (entry 14) led to slightly diminished yields.

The essential role of electricity in this transformation, a set of experiments was performed under air or using typical chemical oxidants (Figure 1a). All attempts gave unsatisfac-

Table 1: Optimization of the rhodium-catalyzed C–H olefination of 1-naphthol.^[a]



Entry	Deviation from standard conditions	Yield [%]
1	none	77
2	NaOPiv instead of KOPIV	69/54 ^[b]
3	1-AdCO ₂ Na instead of KOPIV	65
4	LiOAc:2 H ₂ O instead of KOPIV	41
5	85 °C	39
6	with benzoquinone (10 mol %)	6
7	14 h, 3 mA	69
8	4 h, 8 mA	53
9	[Cp*IrCl ₂] ₂ , [RuCl ₂ (<i>p</i> -cymene)] ₂ , RuCl ₃ ·H ₂ O, RhCl ₃ ·3 H ₂ O, Cp*Co(CO)I ₂ or Pd(OAc) ₂ instead of [Cp*RhCl ₂] ₂	NR
10	no [Cp*RhCl ₂] ₂	NR
11	no electricity	7
12	CPE at 0.8 V for 14 h	67
13	1.5 mol % of [Cp*RhCl ₂] ₂	59
14	120 °C	54 ^[c]

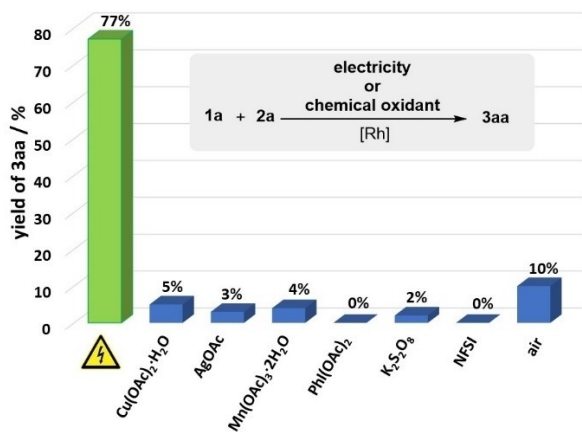
[a] Standard reaction conditions: Undivided cell, GF anode, Pt-plate cathode, constant current electrolysis (CCE) = 4.0 mA, **1a** (0.40 mmol), **2a** (0.80 mmol), NaOPiv (0.80 mmol), [Cp*RhCl₂]₂ (2.5 mol %), *t*-AmOH/H₂O (3:1, 4 mL), under N₂, 18 h, isolated yields. [b] Under air. [c] Obtained as a mixture with a compound bearing the hydrogenated double bond in a ratio of 96:4 (**3aa**:**3aa^{red}**). Ad: adamantyl. NR: no reaction.

tory result to deliver the desired product **3aa**, concluding that electricity not only played a crucial role in the sustainable oxidation by HER, but also enabled an unique performance in the rhodium-catalyzed oxidative C–H alkenylation. The formation of the *peri*-alkenylated product **3aa** was strongly suppressed in the absence of electricity (Figure 1b), as revealed by an on/off experiment. The robustness of the strategy was reflected by the direct comparison with the alkenylation of tosylated 1-naphthylamines (Scheme S1).^[14a]

Thereafter, we probed the influence of the chelation-assistance on the outcome of the electro-C–H-alkenylation (Scheme 2). Thus, only a carbamoyl group provided the C8 alkenylation product with comparable efficiency. However, the hydroxyl group has a greater potential^[22] for late-stage synthetic modifications. Interestingly, applying 2-pyridyl as a directing group led to the alkenylated products with complementary site-selectivity, as the C2-alkenylated derivative was obtained. These results clearly underlined the importance of the five-membered rhodacycles for the introduction of alkenyl substituents onto the naphthalene scaffold via rhodoelectrocatalysis.

With the optimized reaction conditions in hand, we next examined the viable substrate scope of the rhodoelectrocatalyzed alkenylation of 1-naphthol (**1a**) employing a set of styrenes **2** (Schemes 3 and 4). In general, differently

(a) Electricity versus chemical oxidants



(b) On/Off experiment

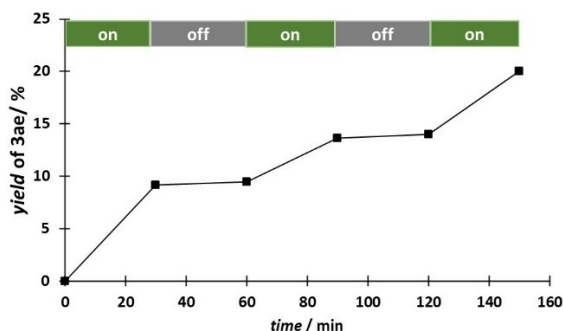
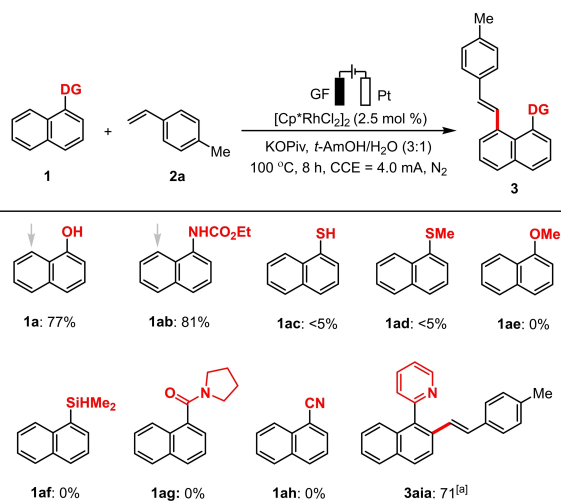
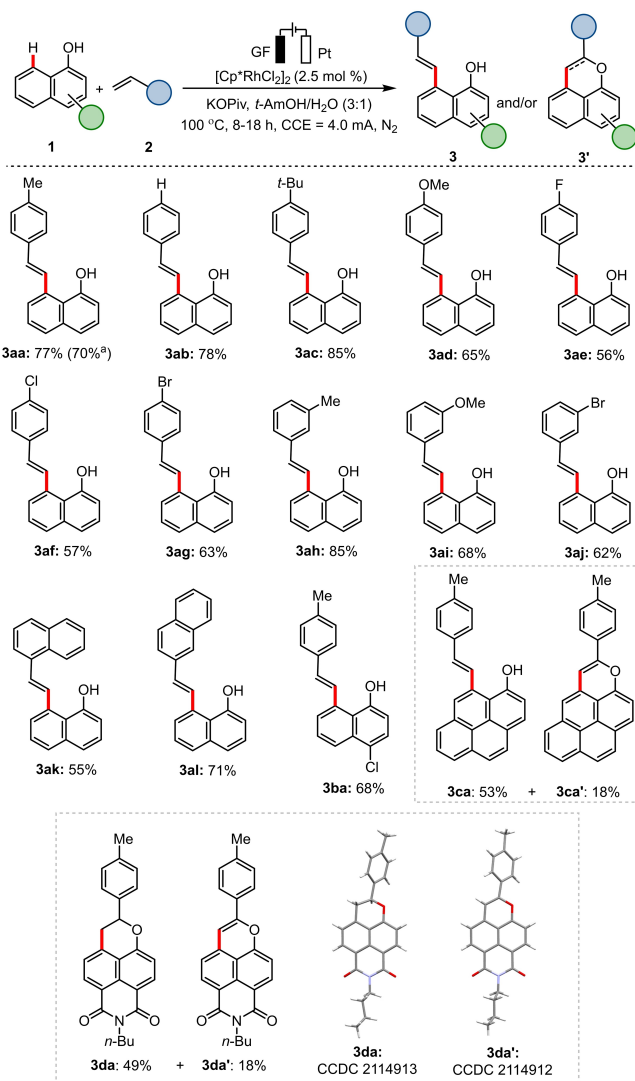


Figure 1. a) Comparison between electricity and representative chemical oxidants. Isolated yields are given. b) On/Off experiment for the reaction of **1a** with alkene **2e**. ¹⁹F NMR yields are given.

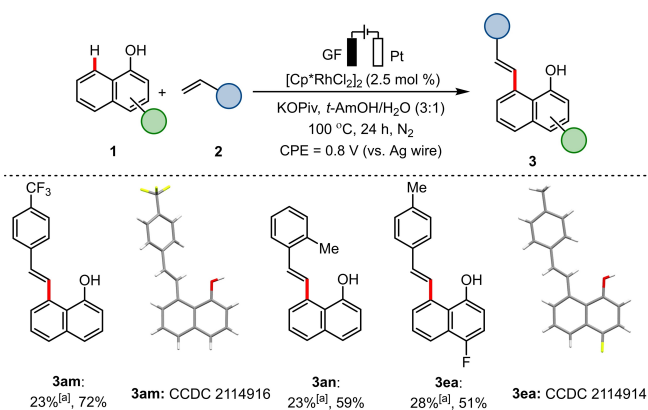


Scheme 2. Examination of different directing groups. Isolated yields are given. [a] Reaction time: 18 h. DG: directing group.

decorated styrenes **2** bearing *para*-, *meta*-, or even sterically hindered *ortho*-substituents were thus efficiently converted into desired products **3**. Sensitive electrophilic functional groups, such as chloro or bromo (**3af** and **3ag**) were fully



Scheme 3. Electrocatalytic C–H alkenylation of 1-naphthols **1** with alkenes under constant current regime (CCE = 4 mA). [a] 8.0 mmol scale. Isolated yields are given.



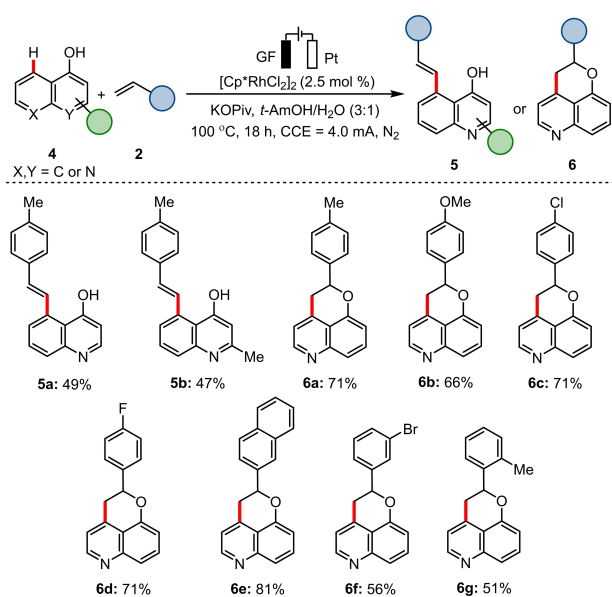
Scheme 4. Electrocatalytic C–H alkenylation by potentiostatic electrolysis at 0.8 V vs. Ag wire. [a] CCE = 4 mA. Isolated yields are given.

tolerated, which should prove invaluable for further synthetic modifications.

Next, we turned our attention to differently-substituted naphthols **1** for the rhodaelectro-catalyzed alkenylation (Schemes 3 and 4). Chloro- or fluoro-substituted 1-naphthols effectively delivered the desired products **3ba** and **3ea**, respectively. Given the importance of polycyclic aromatic hydrocarbons (PAHs)^[24] or naphthalene imides^[11] as functional materials, substrates **1c** and **1d** were tested. For 1-hydroxypyrene (**1c**) we obtained a mixture of alkenylated derivative **3ca** and **3ca'** through oxidative C–H/O–H functionalization. In turn, substrate **1d** did not give the alkenylated compound. It appeared that the expected alkenylation product immediately underwent two competing reactions, giving rise to the oxa-Michael^[25] product **3da** and the oxidative C–H/O–H activation **3da'** product. Under otherwise identical reaction conditions, the use of alkyl, methoxy- or amino-substituted 1-naphthols led thus far to less satisfactory results (for detailed information, see paragraph 11 in the Supporting Information).

Our strategy could be readily scaled to gram quantities with high efficiency, as 1.17 g of product **3aa** was isolated, corresponding to 70% yield (Scheme 3). It should be mentioned that the application of the optimized reaction conditions to substrates bearing electron-withdrawing (**1e** and **2m**) or sterically demanding groups (**2n**) initially led to a rather poor mass balance attributed to the decomposition of the starting material. We successfully addressed this obstacle by applying a constant potential electrolysis (CPE) regime. Thereby the expected products **3am**, **3an** and **3ea** were obtained in greatly improved yields (Scheme 4).

The versatility of our approach was further illustrated by high-value molecule^[26] modifications (Scheme 5). 4-Hydroxyquinolines were successfully converted into alkenylated derivatives **5**. Interestingly, employing 5-hydroxyquinoline



Scheme 5. Electrocatalytic C–H alkenylation of 4-hydroxy- and 5-hydroxyquinoline.

as a starting material led exclusively to unprecedented heterocycles **6**, bearing the 2-phenyl-2,3-dihydropyrano[4,3,2-*de*]quinoline skeleton.

Given the efficacy of the rhodaelectro-catalyzed alkenylation, we became interested in delineating the catalyst's mode of action. Therefore, we performed a series of experiments in the presence of deuterated water as a co-solvent (Scheme 6a). H/D-scrambling at the C8 and C2 positions within 1-naphthol was observed in the absence of alkene **2a**, indicating the reversible nature of the C–H cleavage events. The same experiment performed in the absence of both styrene **2a** and the rhodium catalyst revealed H/D scrambling solely at the C2 position, implying that the presence of the rhodium catalyst was key to success for selective C8–H bond activation. In sharp contrast, a H/D exchange experiment in the presence of alkene **2a** provided evidence for a facile and irreversible new C–C bond formation, giving excellent site-selectivity of the C8–H activation of 1-naphthol. Kinetic studies provided strong support for a fast C–H metalation with a minor kinetic isotope effect (KIE) of only $k_H/k_D \approx 1.1$ (Scheme 6b). A competition experiment performed with differently substituted alkenes **2a/2m** revealed the preferential conversion of alkenes bearing an electron-withdrawing group (Scheme 6c). When performing the reaction at different currents, a strong dependence of the reaction rate was observed, being indicative of a turnover-limiting electron transfer (Scheme 6d). The reaction between substrates **1a** and **2l** in the presence of a stoichiometric amount of the rhodium(III) catalyst delivered product **3al** in only 40% yield, suggesting a distinct role of the electricity beyond being only the sacrificial oxidant (Scheme 6e).

To gain deeper insight into the catalyst mode of action, DFT calculations were carried out for the reductive elimination (RE) elementary step from rhodium(III) versus from rhodium(IV) at the PW6B95-D4/def2-TZVP+SMD(*i*-PrOH)//PBE0-D3BJ/def2-SVP level of theory (Figure 2). The rhodium(IV/II) manifold pathway was shown to be energetically preferred over the rhodium(III/I) pathway by 2.1 kcal mol⁻¹, generating the thermodynamically more sta-

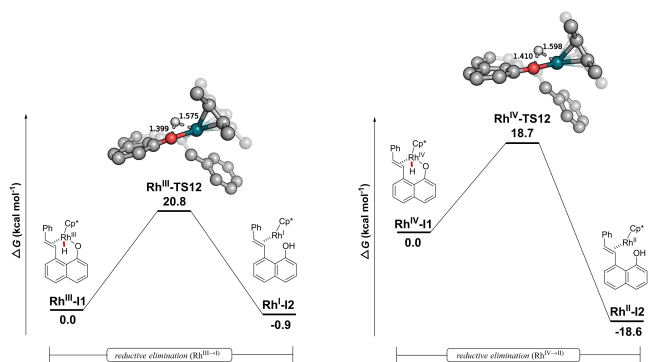
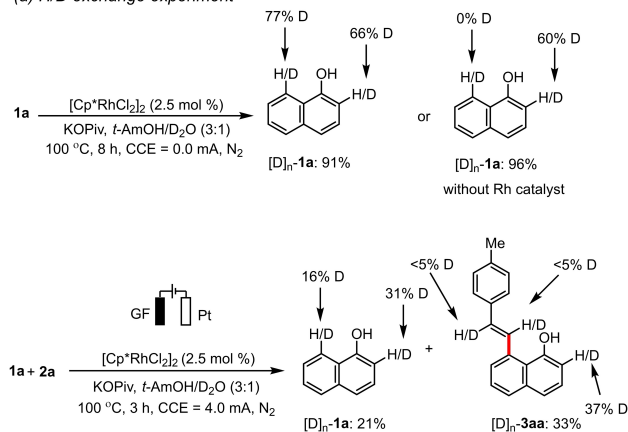
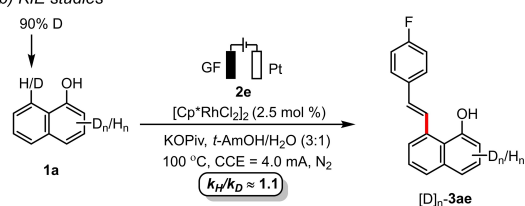


Figure 2. Computed relative Gibbs free energy profile ($\Delta G_{373.15}$) in kcal mol⁻¹ for two different reductive elimination pathways at the PW6B95-D4/def2-TZVP+SMD(*i*-PrOH)//PBE0-D3BJ/def2-SVP level of theory. Non-participating hydrogen atoms in the transition state structures were omitted for clarity. Key bond lengths given in Å.

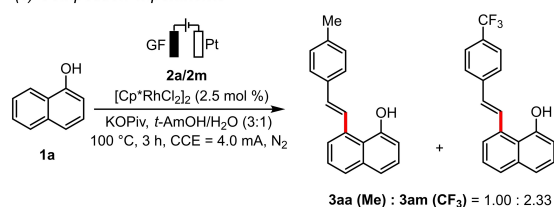
(a) H/D exchange experiment



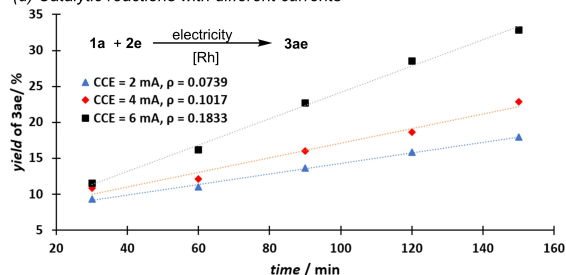
(b) KIE studies



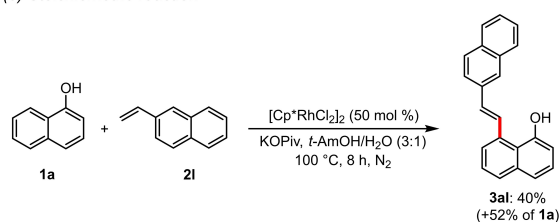
(c) Competition experiments



(d) Catalytic reactions with different currents



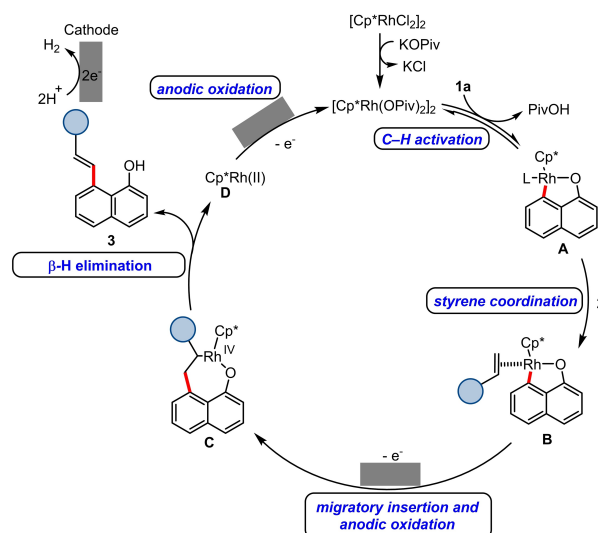
(e) Stoichiometric reaction



Scheme 6. Summary of key mechanistic findings.

ble intermediate $\text{Rh}^{\text{II}}\text{-I2}$ ($17.7 \text{ kcal mol}^{-1}$). Thus, our computational results provide strong support for a preferential oxidation-induced reductive elimination pathway.

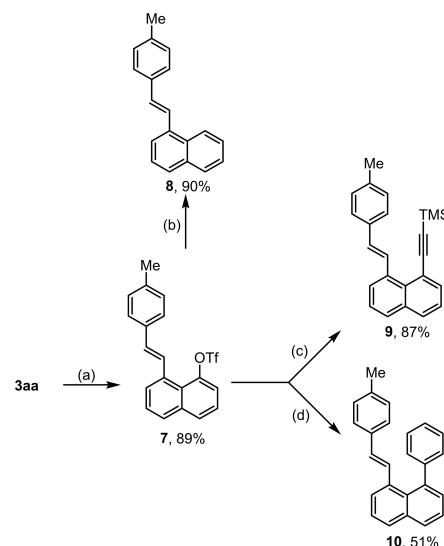
On the basis of our experimental findings, a plausible catalytic cycle is presented for the rhodium(III)-catalyzed electrochemical C–H alkenylation. As depicted in Scheme 7,



Scheme 7. Proposed catalytic cycle for the electrooxidative alkenylation.

O-type coordination of deprotonated 1-naphthol **1a** to rhodium species and subsequent directed cyclorhodation at the *peri* position leads to rhodacycle **A**. Thereafter, migratory alkene insertion followed by an anodic oxidation furnish the seven-membered, high-valent^[4b,27] rhodacycle **C**, which subsequently undergoes β -H elimination to afford the desired product **3** and rhodium(II) species **D**. Finally, the rhodium(II) species is re-oxidized at the anode, generating molecular hydrogen as the by-product at the cathode.

The obtained alkenylated naphthols could be readily late-stage diversified, thus providing more complex molecules in an efficient manner (Scheme 8). Namely, triflate **7** underwent reduction (**8**), alkylation (**9**) or arylation (**10**),



Scheme 8. Derivatization of compound **3aa**. Conditions: a) TiF_2O , Et_3N , CH_2Cl_2 , $0-5^\circ\text{C}$ to rt, overnight; b) HCOOH , $\text{Pd}(\text{PPh}_3)_4$ (10 mol %), Et_3N , DMF, 80°C , 2 h; c) $\text{TMSC}\equiv\text{CH}$, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (10 mol %), CuBr (5 mol %), DIPEA, 80°C , 5 h; d) $\text{PhB}(\text{OH})_2$, $\text{Pd}(\text{PPh}_3)_4$ (10 mol %), K_2CO_3 , 4 Å MS, PhMe, 80°C , 2 h.

showcasing the synthetic power of *peri*-alkenylated naphthols that were assembled via robust rhodaelectrocatalysis.

Conclusion

In summary, we have described the first electrochemical functionalization of oxidation-sensitive 1-naphthols which features high site- and stereoselectivity. Our strategy provided a general and robust access to a variety of *peri*-substituted naphthalene derivatives under mild and environmentally-benign conditions. Our findings showcase an underdeveloped opportunity for the electrocatalytic functionalization of easily oxidizable molecules, which provides an entry to new building blocks which will prove useful for the assembly of more complex materials.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Alkenylation · C–H Activation · Electrocatalysis · Materials · Rhodium

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