



A Strategy for Site- and Chemoselective C–H Alkenylation through Osmaelectrooxidative Catalysis

Isaac Choi, Antonis M. Messinis, Xiaoyan Hou, and Lutz Ackermann*

Abstract: Herein, we disclose osmaelectrocatalyzed C–H activations that set the stage for electrooxidative alkyne annulations by benzoic acids. The osmium electrocatalysis enables site- and chemoselective electrooxidative C–H activations with unique levels of selectivity. The isolation of unprecedented osmium(0) and osmium(II) intermediates, along with crystallographic characterization and analyses by spectrometric and spectroscopic in operando techniques delineate a synergistic osmium redox catalyst regime. Detailed mechanistic studies revealed a facile C–H cleavage, which allows for an ample substrate scope, providing provide robust and user-friendly access to annulated heterocycles.

Introduction

C–H activation has emerged as a powerful tool in molecular sciences, of which tremendous progress has been witnessed in recent years.^[1] Particularly, considerable advances in carboxylate-assisted^[2] oxidative C–H annulations^[3] by weak O-coordination^[4] have been realized by consecutive C–H and O–H bond scission of aromatic carboxylic acids (Figure 1 a). With pioneering contributions by Miura/Satoh,^[5] Ackermann,^[6] and Ison,^[7] among others,^[8] the modular assembly of five- or six-membered heterocycles has been established.^[9] Despite indisputable advances, these reactions generally require the additional use of stoichiometric chemical oxidants, such as copper(II) or silver(I) salts, to facilitate the catalyst reoxidation.

In sharp contrast, electrocatalysis has recently gained significant attention, providing chemists with a transformative platform for sustainable syntheses.^[10] Specifically, C–H activation has allowed for oxidative chemical transformations with electricity for the crucial catalyst reoxidation by an

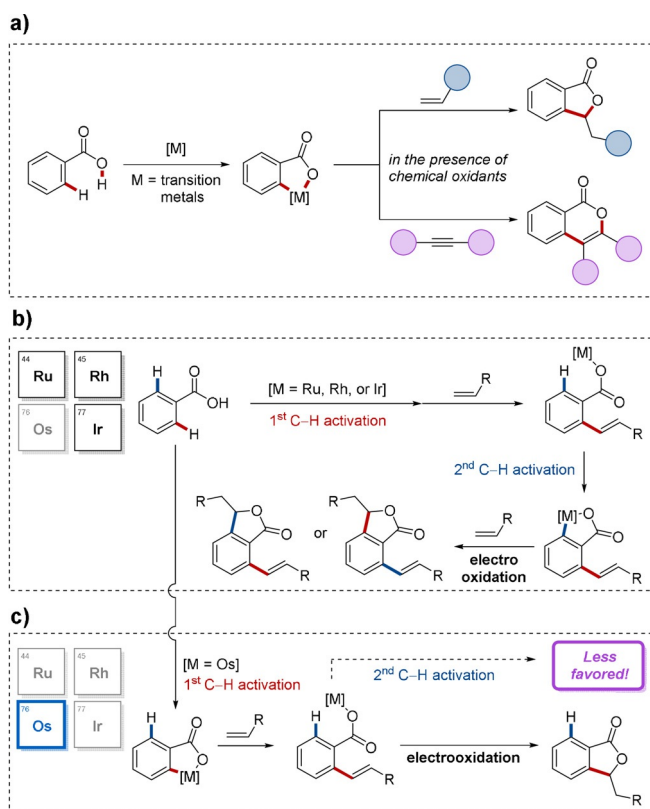


Figure 1. Transition-metal-catalyzed C–H annulations. a) General C–H annulations of benzoic acids. b) Mode of C–H activations by ruthenium, rhodium, and iridium catalysts. c) This work, presenting chemo-selective osmaelectrocatalyzed C–H activation.

anodic event, thus avoiding expensive or toxic chemical oxidants.^[11] Hence, electrooxidative C–H annulations^[12] by ruthenium,^[13] rhodium,^[14] and iridium^[15] catalysis have thus far become viable (Figure 1 b). However, these catalytic processes largely suffer from a lack of product selectivity.

Osmium^[16] complexes feature prominently in stereoselective olefin difunctionalizations,^[17] but have been rarely used in organometallic catalysis^[18] compared to the homologues iron and ruthenium, arguably due to the inherently lower kinetic reactivity.^[19] Specifically, osmium-catalyzed electrooxidative C–H activations have thus far proven elusive to the best of our knowledge (Figure 1 c).

At the outset, we hypothesized that the metal center would enable selectivity control by repulsive steric interactions. Thus, we envisioned that unique regio- and chemo-selectivity could arise from osmium complexes, which have distinct physicochemical features compared with other metals.^[20] As a result, we have established a novel osmium(II)-

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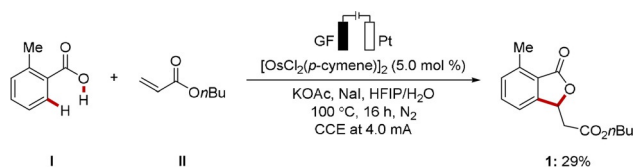
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catalyzed electrooxidative C–H annulation by making use of a weak *O*-directing group. Notable features of our strategy include a) the first osmium-catalyzed C–H activation with electricity as a sustainable oxidant, b) a powerful regio- and chemoselective approach by osmaelectrocatalyzed C–H activation, c) ample substrate scope enabling the synthesis of five- and six-membered heterocycles, d) spectroscopic and spectrometric analysis, as well as e) detailed mechanistic and kinetic insights through the identification of key intermediates.

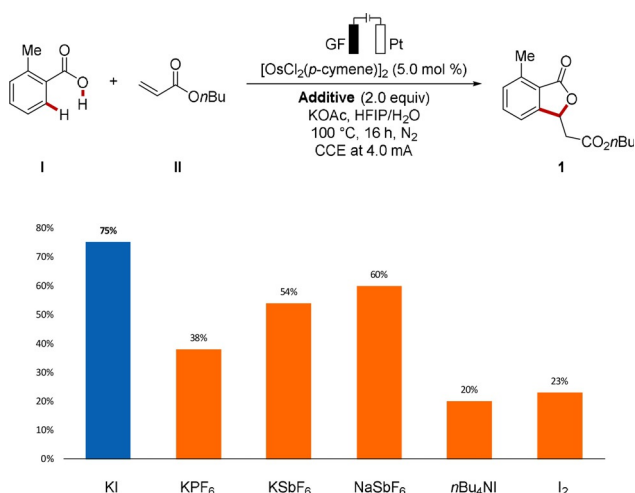
Results and Discussion

Based on our hypothesis, we set out to explore viable reaction conditions for the electrooxidative C–H annulation of *o*-toluic acid **I** with olefin **II** in an undivided cell setup (Scheme 1).^[21] Orienting experimentation showed that $[\text{OsCl}_2(p\text{-cymene})]_2$ was a viable catalyst in combination with a graphite felt (GF) anode and a platinum plate cathode, which provided 29% of the C–H annulated product **1**.



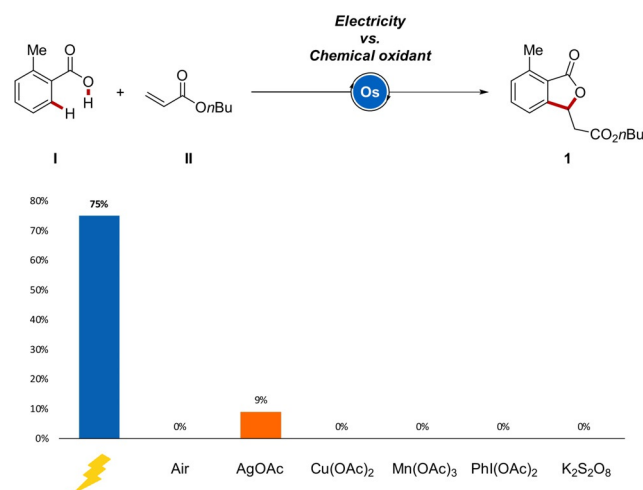
Scheme 1. Initial observation of osmaelectrocatalyzed C–H annulation. Reaction conditions: **I** (0.2 mmol), **II** (0.6 mmol), $[\text{OsCl}_2(p\text{-cymene})]_2$ (5.0 mol%), KOAc (2.0 equiv), NaI (2.0 equiv), HFIP (2.0 mL), H_2O (2.0 mL). See the Supporting Information for the reaction setup and detailed optimization studies (Table S1 and Figure S1).

On the basis of these initial results, the effect of the additive was probed to improve conductivity and reaction performance (Scheme 2). Hence, a variety of additives, such as alkali metal based salts, organic salts, and iodine, were included in the osmaelectrocatalyzed C–H annulation. Interestingly, non-toxic and inexpensive potassium iodide provid-



Scheme 2. Examination of various additives.

ed the desired [4+1] annulated product **1** in 75% yield by osmaelectrocatalysis. To highlight the advantages of the electrochemical approach, a set of experiments were carried out under air or with commonly employed chemical oxidants, such as AgOAc, $\text{Cu}(\text{OAc})_2$, $\text{Mn}(\text{OAc})_3$, $\text{PhI}(\text{OAc})_2$, or $\text{K}_2\text{S}_2\text{O}_8$. All of the attempts met with unsatisfactory results, showing that electricity not only played a crucial role in the sustainable oxidation, but also gave optimal and unique efficiency for the osmium-catalyzed oxidative C–H annulation (Scheme 3).^[21]

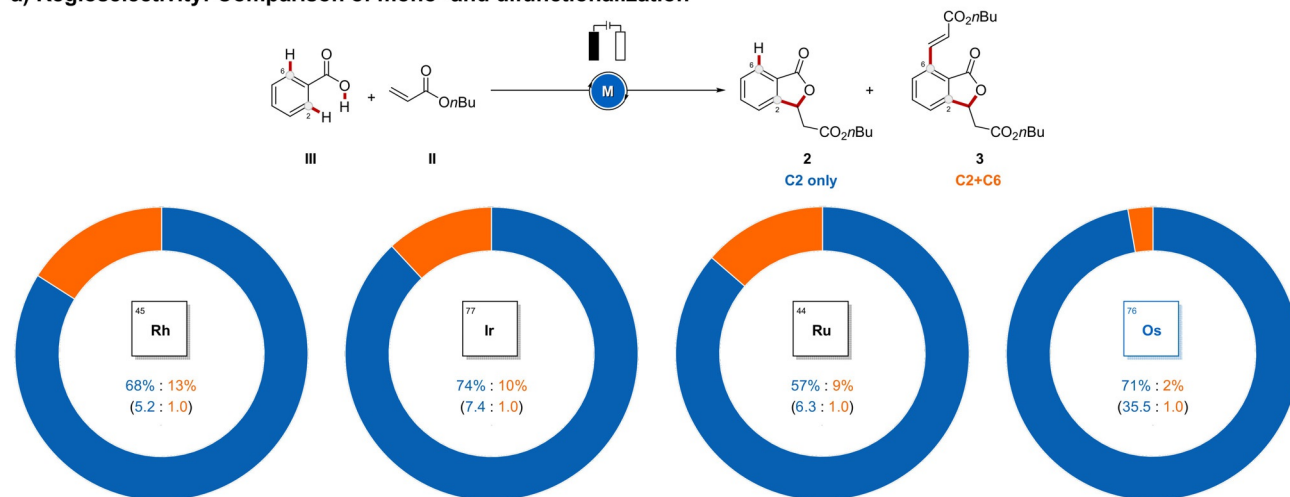


Scheme 3. Reaction comparison between electricity and representative chemical oxidants.

Inspired by this unprecedented reactivity, we were interested in interrogating its robustness (Scheme 4).^[21] To this end, we performed a series of metallaelectrocatalyzed reactions with benzoic acid **III** possessing two accessible *ortho*-C–H bonds (Scheme 4a). Interestingly, osmaelectrocatalysis showed unique chemoselectivity (35.5:1), while rhodium, iridium, and ruthenium catalysis gave significantly lower selectivities (5.2:1, 7.4:1, and 6.3:1 respectively). This aspect was also displayed in H/D scrambling experiments in the presence of an isotopically labeled solvent mixture (Scheme 4b). With the present osmium electrocatalysis regime, deuterations occurred at the C6 position in a highly selective fashion. In sharp contrast, comparable C2 and C6 deuterations were observed in the reaction with the other Group 8 metal, ruthenium. These findings hence represent a novel tool for selective hydrogen isotopic exchange (HIE).^[22]

With these observations in mind, we set about to study the working mode of the electrooxidative osmium-catalyzed C–H annulation (Scheme 5).^[21] To this end, novel key intermediates, **Os-I** and **Os-II**, were selectively prepared, which were found to afford the desired products **5** and **6**, respectively, in both stoichiometric and catalytic reactions (Scheme 5a). Also, in operando NMR studies revealed the consumption of **Os-I** and alkyne **VI** with concomitant formation of the new osmium(0) sandwich complex **Os-II**, while an induction period was not detected (Scheme 5b). Interestingly, the seven-membered intermediate formed by migratory insertion

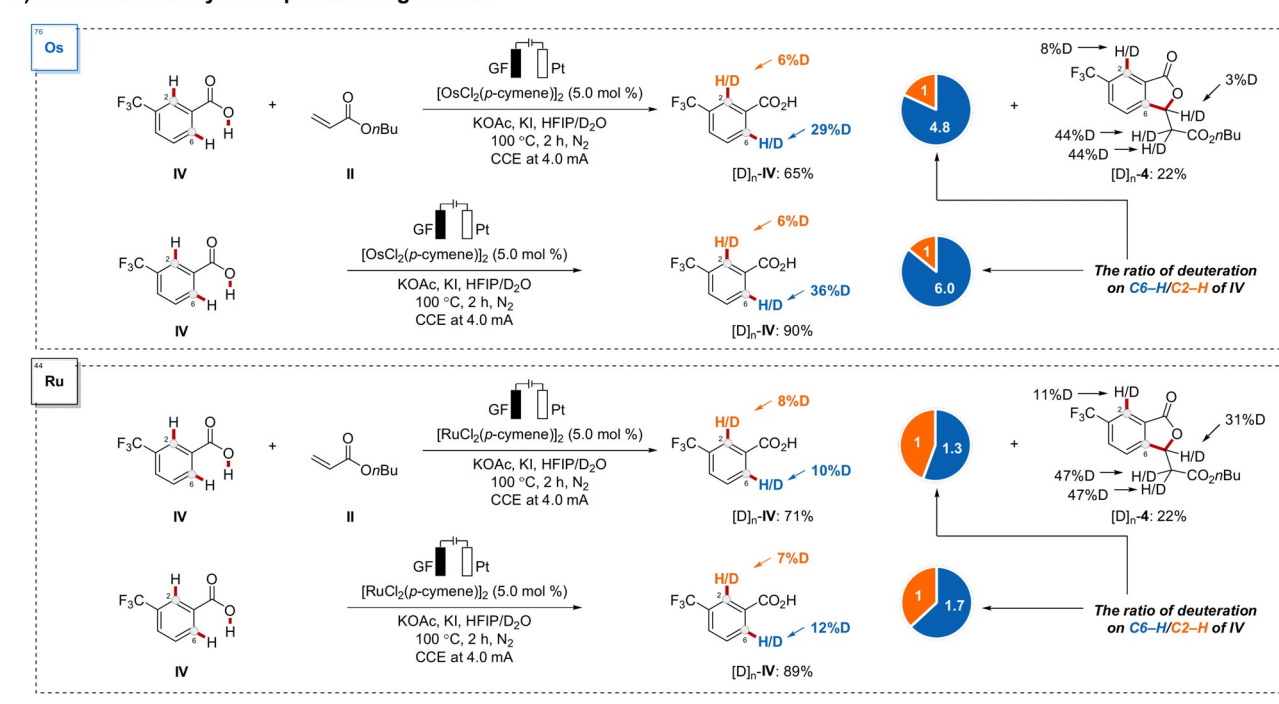
a) Regioselectivity: Comparison of mono- and difunctionalization*



*Reaction conditions

- [Rh] **III** (0.4 mmol), **II** (0.2 mmol), [Cp*RhCl₂]₂ (2.5 mol %), KOAc (2.0 equiv), *t*AmOH/H₂O (3.0 mL/1.0 mL), 100 °C, 8 h, CCE = 4.0 mA (Cathode: Pt, Anode: GF).
 [Ir] **III** (0.2 mmol), **II** (0.4 mmol), [Cp*IrCl₂]₂ (2.5 mol %), benzoquinone (10 mol %), KOAc (2.0 equiv), *t*AmOH/H₂O (3.0 mL/1.0 mL), 100 °C, 18 h, CCE = 4.0 mA (Cathode: Pt, Anode: GF).
 [Ru] **III** (0.4 mmol), **II** (0.2 mmol), [RuCl₂(*p*-cymene)]₂ (5.0 mol %), NaOPiv (2.0 equiv), *t*AmOH/H₂O (3.0 mL/1.0 mL), 100 °C, 18 h, CCE = 4.0 mA (Cathode: Pt, Anode: GF).
 [Os] **III** (0.2 mmol), **II** (0.6 mmol), [OsCl₂(*p*-cymene)]₂ (5.0 mol %), KOAc (2.0 equiv), HFIP/H₂O (2.0 mL/2.0 mL), 100 °C, 16 h, CCE = 4.0 mA (Cathode: Pt, Anode: GF).

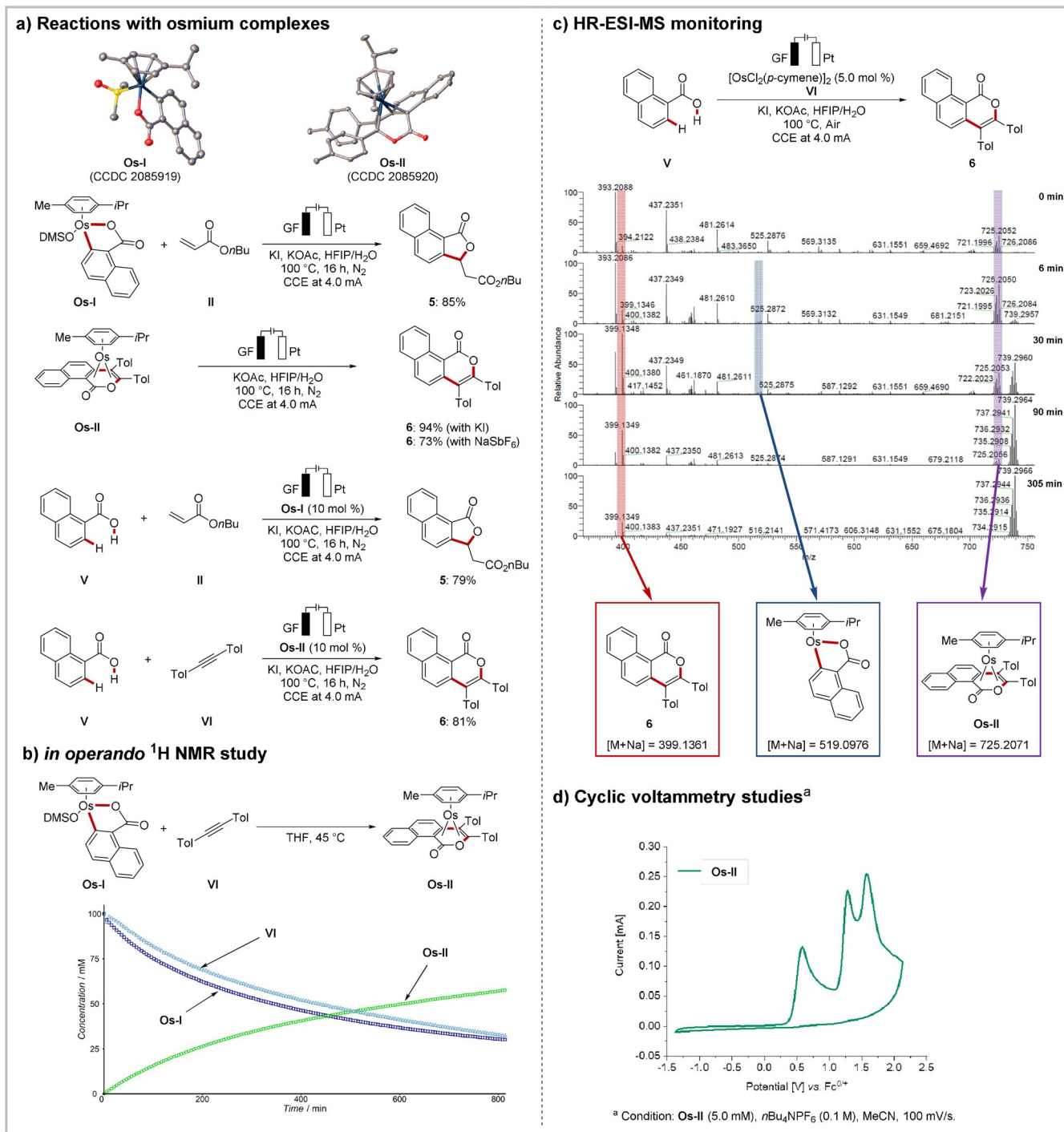
b) Chemoselectivity: Isotopic labelling studies



Scheme 4. Selectivity of electrochemical osmium catalysis.

of alkyne **IV** was hardly observed, which presumably suggests the facile formation of the osmium(0) complex **Os-II** after the insertion step. Furthermore, the successive formation and consumption of key species were also clearly demonstrated by high-resolution electrospray ionization mass-spectrometric (HR-ESI-MS) analysis (Scheme 5c). Additionally, cyclovoltammetric analysis of **Os-II** showed that the oxidation event occurred at $E = 0.58$ V vs. Fc/Fc⁺, representing a slightly lower value than for the Ru⁰ to Ru^{II} oxidation potential (Scheme 5d and Figures S11–S13).^[13f]

Next, we performed detailed kinetic studies (Scheme 6).^[21] First, intermolecular competition experiments with differently substituted benzoic acids were carried out (Scheme 6a). The competition experiments showed that electron-donating groups in benzoic acid **VII** gave a higher reactivity while an alkyne **VI** with an electron-donating group afforded less product formation. Recent studies have proposed a base-assisted internal electrophilic substitution-type (BIES) mechanism to be operative in such a scenario.^[23] Additionally, a Hammett correlation was found for benzoic

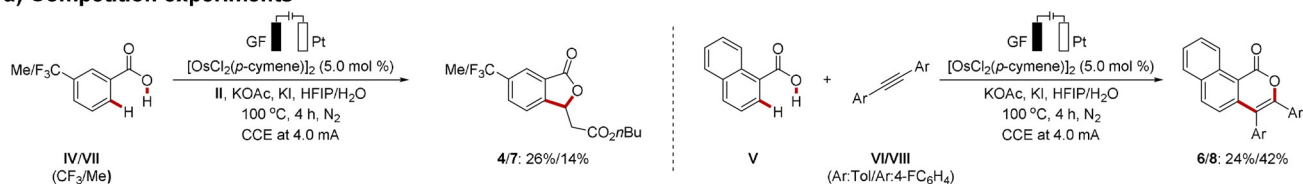


Scheme 5. Mechanistic understanding of osmaelectrocatalysis.^[25]

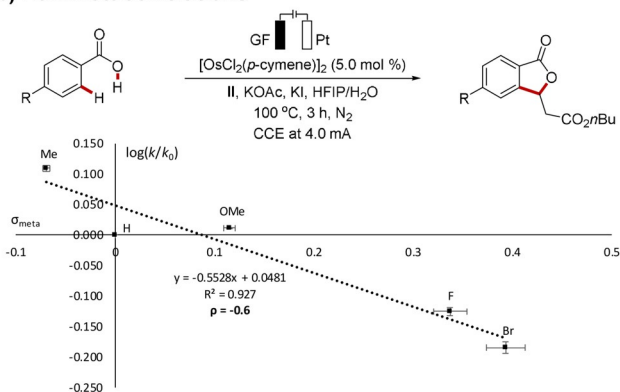
acids with different substituents in the *meta*-position to the C–H bond to be cleaved (Scheme 6b). A linear correlation with a negative ρ value was found, indicating that an electrophilic mechanism is likely operative in the C–H bond cleavage step.^[23] Importantly, we observed a considerable dependence of the conversion upon an alteration of the current, being suggestive of a turnover-limiting electron transfer step (Scheme 6c).^[14d] Subsequently, an intermolecular competition reaction and a pair of parallel reactions were performed with *o*-toluic acid **I** and an isotopically labeled compound

[D]₇-I to determine the kinetic isotope effect (Scheme 6d). In both cases, a negligible KIE of 1.1 and 1.2 was observed, respectively, suggesting a facile C–H scission. On the basis of our mechanistic findings, a plausible catalytic cycle for the osmaelectrocatalyzed C–H activation is depicted in Scheme 6e. The mechanistic rationale commences with a facile C–H bond cleavage, which constructs osmacycle **B**. Thereafter, migratory insertion of the alkene or alkyne occurs, which enables the formation of intermediate **D**. Next, reductive elimination—in the case of a [4+1] annulation, a β -hydride

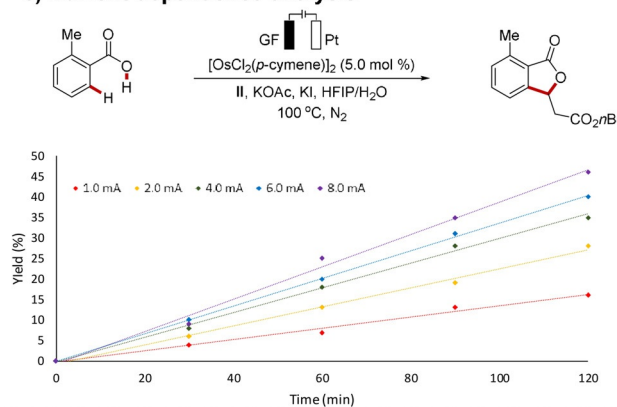
a) Competition experiments



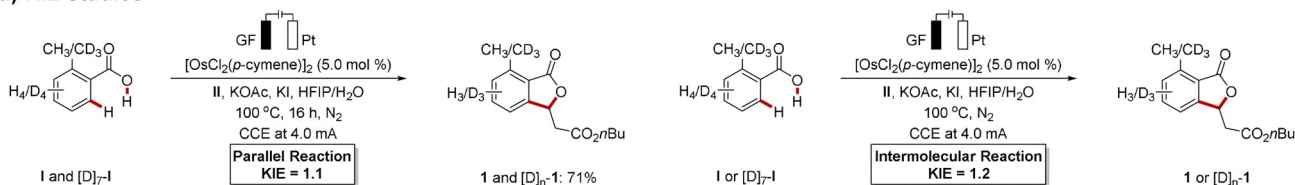
b) Hammett correlations



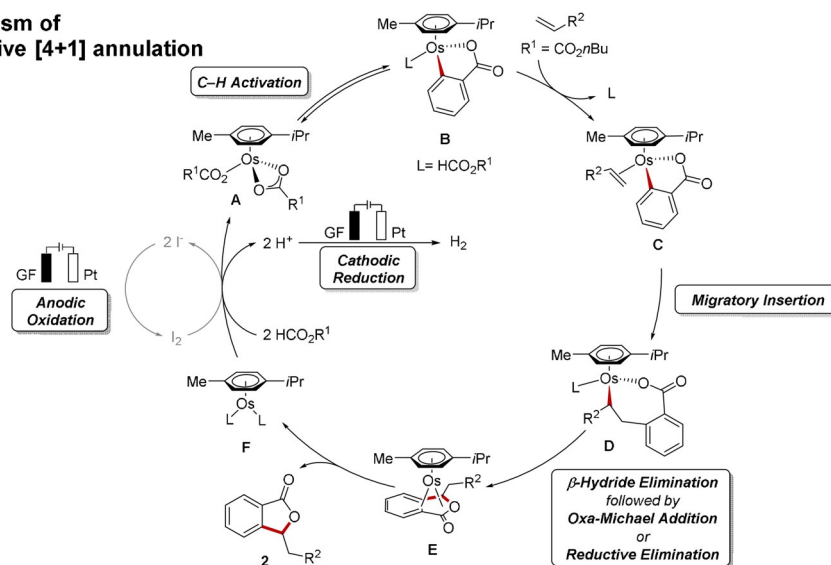
c) Current-dependence analysis



d) KIE studies



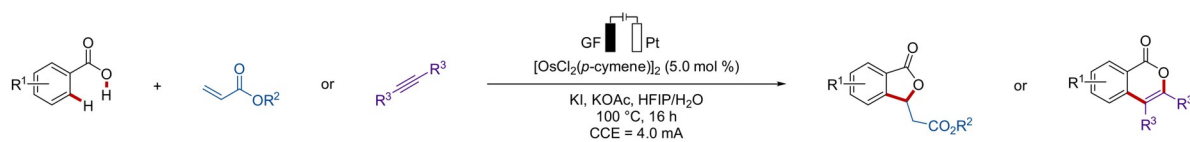
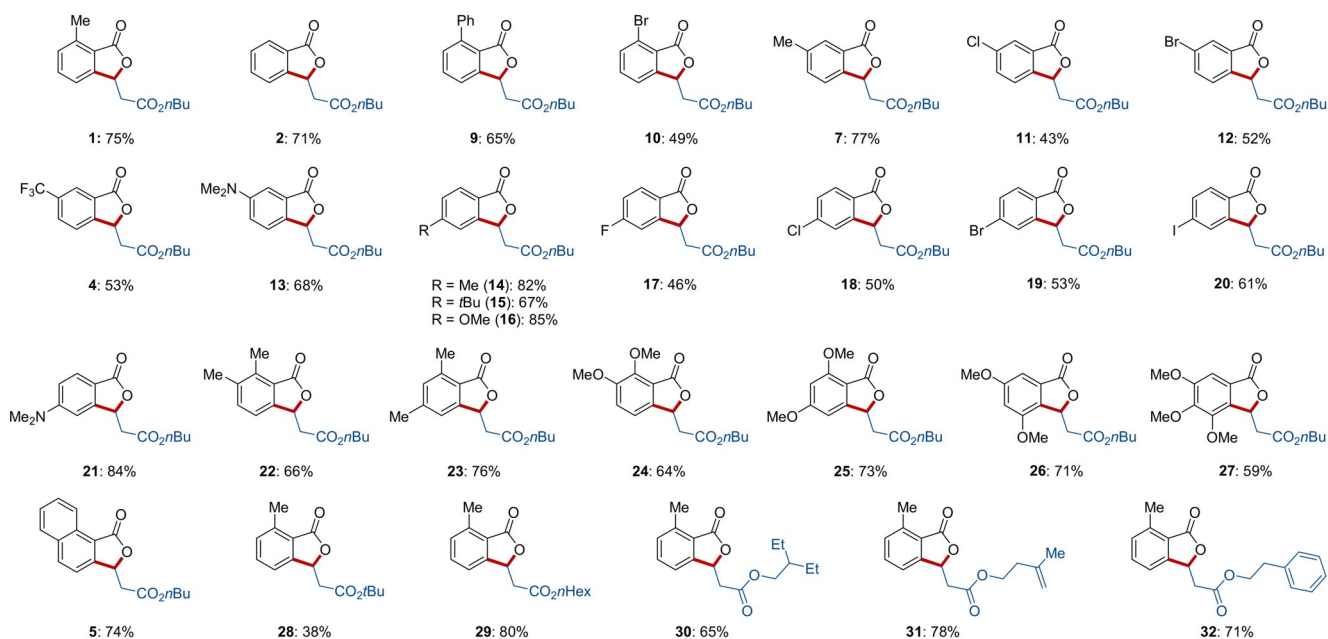
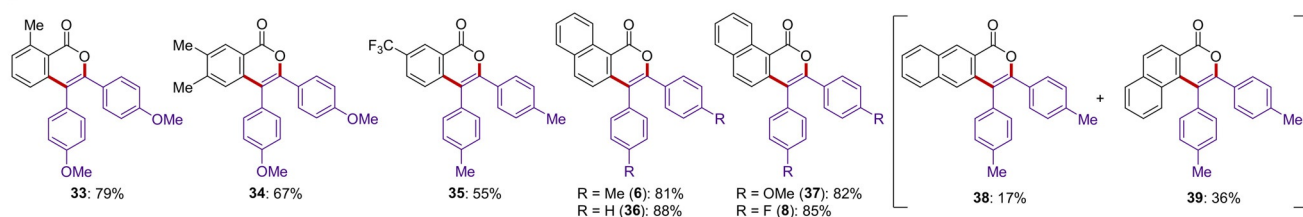
e) Proposed mechanism of osmaelectrooxidative [4+1] annulation



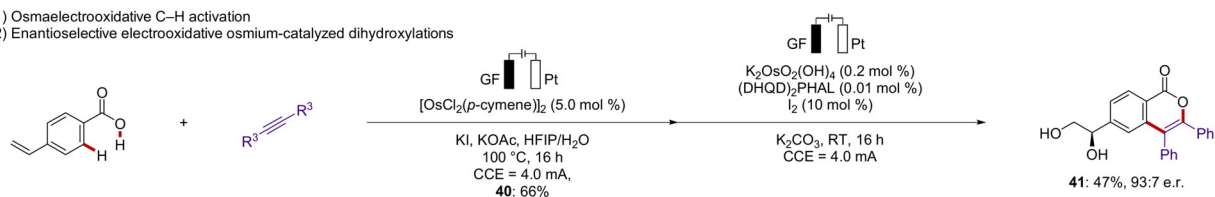
Scheme 6. Detailed kinetic studies and proposed mechanism.

elimination step is additionally involved—delivers osmium(0) sandwich complex **E**. Finally, the key anodic oxidation—via a proposed redox-mediator event when iodide is present—regenerates the catalytically active complex **A**, while liberating the desired product.

With detailed mechanistic insights in hand, we finally explored the viable substrate scope of the electrochemical osmium-catalyzed [4+1] and [4+2] C–H/O–H annulation of benzoic acids with alkenes **2** and alkynes **4** (Scheme 7). A wide range of benzoic acids gave the desired heterocycles, and

**[4+1] Annulations****[4+2] Annulations****One-pot reaction**

- 1) Osmoelectrooxidative C–H activation
- 2) Enantioselective electrooxidative osmium-catalyzed dihydroxylations



Scheme 7. Versatility of the electrochemical osmium-catalyzed C–H annulation.

valuable functional groups, such as halides (**10**, **11**, **12**, **17**, **18**, **19**, and **20**) or amines (**13** and **21**), were fully tolerated. Particularly, the reaction with a substrate having two competing olefins selectively afforded a single annulated product (**31**). The annulation manifold was not limited to the construction of five-membered rings, but six-membered heterocycle assembly with differently-substituted alkynes was also found to be viable, thus providing the extension of conjugated π -system. Notably, the synthetic utility of our electrooxidative osmium catalysis was mirrored by the

development of a one-pot strategy of C–H/O–H activation (**35**) followed by enantioselective dihydroxylations (**36**).^[24]

Conclusion

In summary, we have reported on the first electrochemical osmium(II)-catalyzed C–H activation involving benzoic acids by weak *O*-coordination. Detailed reaction analyses with analogous transition-metal catalytic systems highlighted ad-

vantageous characteristics of the osmium catalysis. Key osmium intermediates were isolated and characterized by X-ray crystallography. Spectrometric, spectroscopic, and kinetic mechanistic studies revealed the electrocatalytic mode of action. Mechanistic investigations provided strong support for a facile organometallic C–H osmation by a BIES mechanism. The ample substrate scopes of the [4+1] and [4+2] annulations reflected the robust and versatile features of the electrooxidative osmium catalysis.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: C–H activation · electrocatalysis · electrochemistry · osmium · selectivity

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