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Carbon–Oxygen Homocoupling of 2-Naphthols through Electrochemical Oxidative Dearomatization

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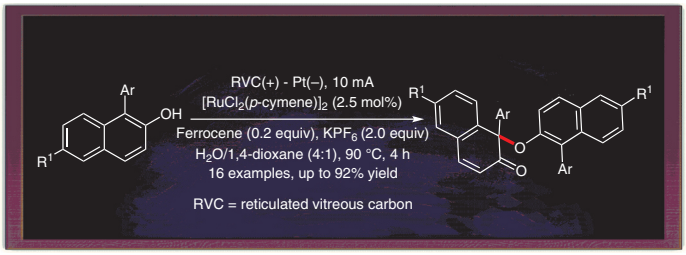

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Abstract A homocoupling reaction of 2-naphthols with formation of a C–O bond through electrochemical oxidative dearomatization in the presence of catalytic amounts of ferrocene and a ruthenium complex was developed. Mechanistic studies revealed that the reaction might proceed through coupling between two identical radical species. Moreover, a gram-scale experiment was performed to illustrate the potential practicability of this methodology in organic synthesis.

Key words electrochemistry, homocoupling, C–O bond formation, naphthols, dearomatization, naphthyloxynaphthalenones

Deconjugated C–O bonded dimeric molecules have found uses in organic syntheses and bioresearch. Lapachol, a naphthoquinone isolated from the heartwood of the lapacho tree (*Handroanthus impetiginosus*, formerly *Tabebuia avellanedae*) ,[1] has diverse bioactivities, such as anticancer,[2] analgesic,[3] and trypanocidal activities.[4] The C–O bonded dimer of laplachol can be prepared by Hooker's oxidation method (Figure 1, left).[1c–e] Biological probing has shown that this dimer exhibits activity against HCT-8 (colon) cancer cells (IC_{50}, 9.76 μM).[5]

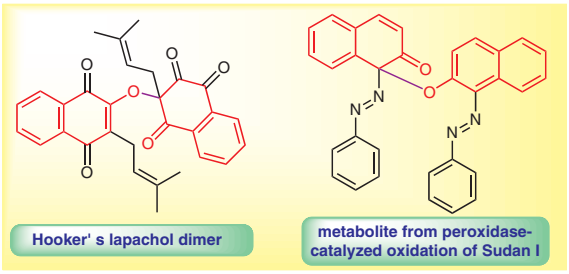
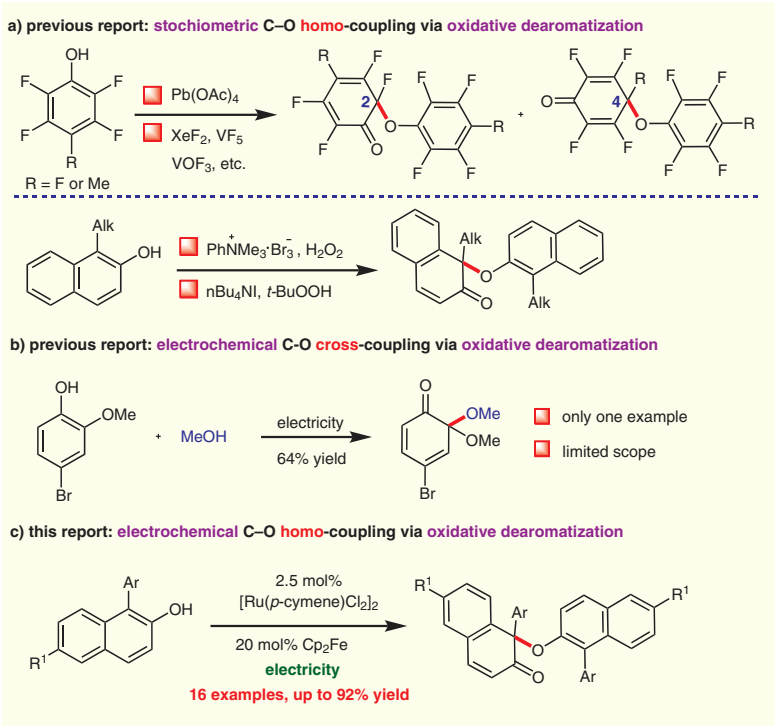


Figure 1 Deconjugated C–O bond naphthol dimers

Sudan I [1-(phenyldiazenyl)-2-naphthol] is a diazo dye once used as a food coloring in some countries,[6] but is now recommended as unsafe because it causes cancers in some animals such as mice and rabbits,[7] and is also considered to be a potential human carcinogen. Stiborová and co-workers reported peroxidase-mediated oxidation of Sudan I, and characterized the Sudan I dimer (Figure 1, right) as one a major peroxidase-mediated metabolites. The isolation and characterization of this dimer will help understand the mechanism by which metabolites are formed during the oxidation of Sudan I by peroxidase.[8]

Because these C–O bonded dimeric molecules have potential bioactivities and uses, the discovery of efficient methodologies for the construction of such compounds could play a vital role in further investigations. Intermolecular C–O homocoupling reactions through oxidative dearomatization form an efficient method for synthesizing the core skeletons of these C–O bonded dimeric compounds. Kovtonyuk and co-workers have disclosed such reactions of tetra- or pentafluoro phenols in the presence of various oxidants, such as $Pb(OAc)_4$, XeF_2, VOF_3, or VF_5 [Scheme 1(a)].[9] C–O homocouplings of 2-naphthols have been conducted through oxidative dearomatization with $PhNMe_3{\cdot}Br_3$ (PTAB)/H_2O_2[10] or TBAI/*t*-BuOOH.[11] The substrates in these works were limited to 1-alkyl-2-naphthols [Scheme 1(b)]. It is apparent that to complement current progress in relation to this reaction, more attempts need to be made to discover novel C–O bond homocoupling approaches through oxidative dearomatization.

In the past decade, electroorganic chemistry has been shown to provide a green alternative to common chemical oxidizing or reducing agents[12] and, in some cases, to induce extraordinary reactivity, superior to that attainable by conventional methods.[13] Notably, Quideau et al. reported an electrochemical C–O cross-coupling reaction of 2-methoxyphenols through oxidative dearomatization in MeOH, al-



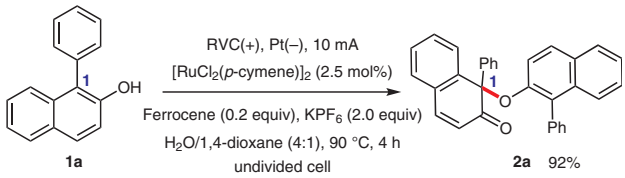
Scheme 1 C–O bond coupling reactions through oxidative dearomatization

though only one example was showcased [Scheme 1(b)].[14] We were therefore motivated by the prospect of exploiting electrochemical synthesis to induce a dearomatization reaction leading to C–O homocoupling although, to the best of our knowledge, there was no precedent for this. Here, we described our findings on an electrochemical oxidative dearomatization approach to the C–O homocoupling of 2-naphthols [Scheme 1(c)]. The reaction is compatible with various 1-aryl-2-naphthols in the presence of inexpensive ferrocene (Cp_2Fe) as a redox catalyst.

We began this project by using 1-phenyl-2-naphthol (**1a**) as a substrate to probe the optimal reaction condition to give the homocoupling product **2a** (Table 1). Besides extensive NMR characterization, the molecular structure of **2a** was confirmed by single-crystal X-ray diffraction analysis (see Scheme 2, below).[15] After extensive examination [See Supplementary Information (SI) for details], a maximum yield of 92% was obtained when the electrochemical synthesis was conducted at a constant current of 10 mA in an undivided cell with a reticulated vitreous carbon anode [RVC (+)] and a platinum plate cathode [Pt (–)] with 20 mol% Cp_2Fe as a redox catalyst and 2.5 mol% [$RuCl_2$(*p*-cymene)]$_2$ as an additive in an electrolyte solution of KPF_6 in H_2O–1,4-dioxane (4:1) at 90 °C.

It was found that the electrode materials had a marked effect on the reaction, since a lower yield was obtained with electrode materials other than an RVC anode and a platinum plate cathode (Table 1, entries 1–4). Notably, when the platinum cathode was replaced with an inexpensive copper plate, the product yield decreased markedly (entry 3). Not surprisingly, performing the electrolysis without an electric current or in the absence of Cp_2Fe suppressed the reaction completely (entries 5 and 6). It has been reported that cyclizations of phenols or benzoic acid can be catalyzed by a Ru complex through weak O-coordination under electrochemical conditions.[16] Because our reaction was also performed without a base, we reasoned that the introduction of a Ru complex to coordinate with naphthols **1a** and to increase the acidity of the proton would accelerate the production of H_2 at the cathode and would promote the reaction. Notably, the product was obtained in 65% yield under electrolysis in the absence of [$RuCl_2$(*p*-cymene)]$_2$ (entry 7), demonstrating that this ruthenium salt was not essential for the reaction and might act as an additive, albeit in a catalytic amount. Changing the amount of Cp_2Fe from 20 mol% in the absence of [$RuCl_2$(*p*-cymene)]$_2$ gave inferior results (entries 8 and 9) (See SI for details). A slightly lower yield was observed when the amount of ruthenium salt was reduced from 2.5 mol% to 1 mol% (entry 10). Not surprisingly, the supporting electrolyte also affected the efficacy of this reaction (entries 11 and 12). In addition, altering the current from 10 mA to 20 mA or 5 mA proved detrimental to this electrochemical reaction (entries 13 and 14). Control

Table 1 Screening of reaction conditions



Entry	Deviations from standard conditions	Yield[a] (%)
1	graphite (–)	79
2	RVC (–)	72
3	Cu (–)	trace
4	Pt (+)	76
5	no current	0
6	no ferrocene	trace
7	no $[RuCl_2(p\text{-cymene})]_2$	65
8	ferrocene (0.1 equiv), no $[RuCl_2(p\text{-cymene})]_2$	45
9	ferrocene (0.3 equiv), no $[RuCl_2(p\text{-cymene})]_2$	62
10	$[RuCl_2(p\text{-cymene})]_2$ (1.0 mol%)	87
11	Bu_4NOAc as electrolyte	83
12	Bu_4NClO_4 as electrolyte	54
13	current: 5 mA	69
14	current: 20 mA	76
15	H_2O–acetone (1:4), 70 °C	50
16	H_2O–MeOH, 60 °C	14
17	70 °C	32
18	r.t.	trace
19	gram scale	76 (0.765g)

[a] Isolated yield.

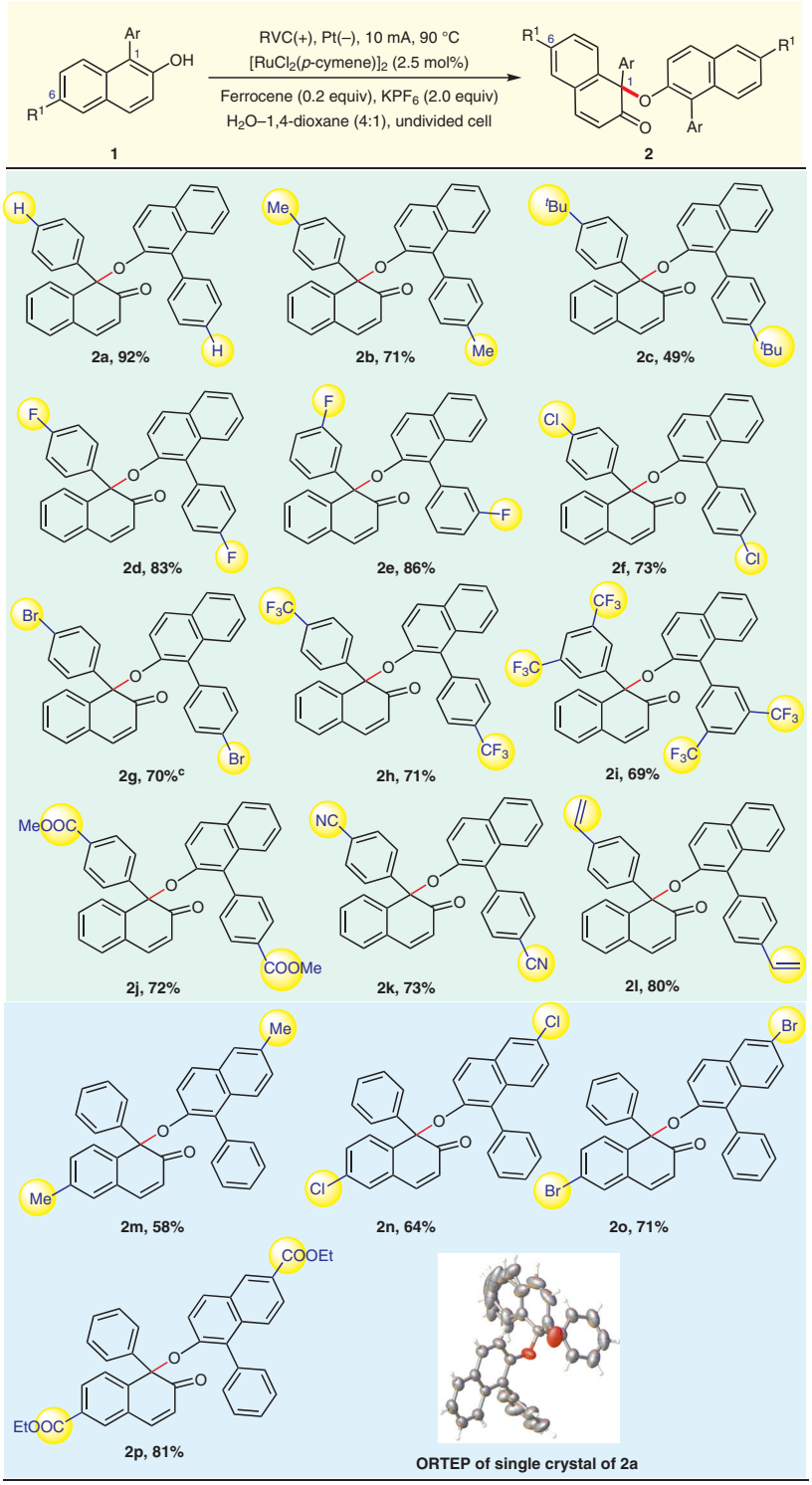
experiments verified that the best solvent system is a 4:1 mixture of H_2O and 1,4-dioxane; other solvent systems such as H_2O–acetone or H_2O–MeOH gave inferior yields (entries 15 and 16), unlike the results obtained by Quideau et al. [Scheme 1(b)].[14] Notably, when the reaction was performed at a lower temperature, the electrolysis gave disappointing results (entries 17 and 18). The reaction could be scaled up to a gram scale, with 76% yield (entry 19).

With these optimal reaction conditions, we set about exploring the scope of this method (Scheme 2). A broad range of functional groups on the phenyl ring (Ar) were tolerated. Substrates with 4-methyl or 4-*tert*-butyl substituents on the phenyl ring (**1b** and **1c**, respectively) gave the corresponding homocoupling products **2b** and **2c** in yields of 71 and 49%, respectively. Fluoro- (**2d** and **2e**), chloro- (**2f**), bromo- (**2g**), and trifluoromethyl-substituted substrates (**2h** and **2i**) exhibited good reactivity and afforded the corresponding homocoupling products in satisfactory yields of 69–86%. The presence of other electron-deficient groups on the aryl ring, such as ester (**2j**) or cyano (**2k**) groups, was found to benefit the electrochemical homocoupling under the standard conditions. Notably, it had previously been found that a styryl group could be electrochemically oxidized to a radical-cation intermediate that was captured by alcohols, H_2O, or other nucleophiles.[17] Interestingly, a styryl group was left intact under our reaction conditions, and compound **2l** was obtained in a satisfactory 80% yield; this might be due to the higher electrical potential ($E_{p/2}$ > 1.5 V vs. SCE)[17a,18] preventing oxidation of the styryl group to alkene radical-cation intermediates.

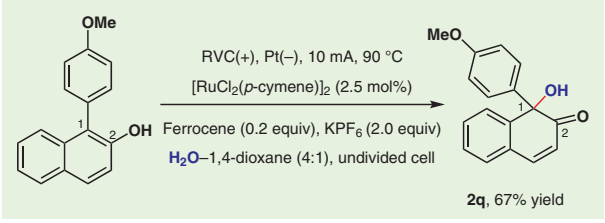
Additionally, a variety of functional groups at the C-6 position of the naphthalene ring, including methyl (**2m**), chloro (**2n**), bromo (**2o**), or ester groups (**2p**), were found to be compatible with the reaction. Unfortunately, substrates with heteroaryl substituents at the C-1 position of 2-naphthol did not give the desired product (see SI for details).

Specifically, a methoxy-substituted substrate did not give the corresponding homocoupling product, but instead gave the hydroxylated compound **2q** (Scheme 3). We reasoned that the presence of a methoxy group would make the electrochemically generated intermediate with a radical at C-1 prone to release an electron to generate a cationic carbon atom at the C-1 position. This cationic species would be stabilized by two phenyl groups, one of which is electron-rich, and then captured by water to give compound **2q**.

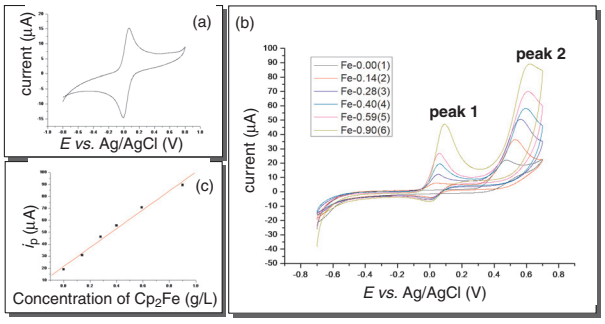
To probe the reaction mechanism, we performed cyclic voltammetry (CV) on the RVC electrode in a solution of 0.15 g/L Cp_2Fe in 2:1 H_2O–1,4-dioxane with 0.8 M KPF_6 as the supporting electrolyte at a scan rate of 10 mV·s^{-1} at 50 °C (Figure 2). A pair of quasi-reversible peaks were observed centered at about 0.1 V versus Ag/AgCl; these were superimposed on a large capacitive background in the absence of the substrate **1a** [Figure 2(a)]. The waves showed a typical CV pattern of a $Cp_2Fe(II) \leftrightarrow Cp_2Fe(III)^+$ pair. When substrate **1a** was gradually added to the above system, the reduction peak for $Cp_2Fe(III)^+$ fell markedly when the concentration of **1a** reached 3.5 g/L, showing that most of the $Cp_2Fe(III)^+$ species was probably reduced in solution rather than on the electrode. On the other hand, two oxidation peaks appeared in the CV curves [Figure 2(b)]. The first peak, centered at 0.1 V, arose from oxidation of $Cp_2Fe(II)$, and its peak current (i_p) showed a linear relationship to the amount of $Cp_2Fe(II)$. The second peak was attributed to oxidation of substrate **1a**, and its i_p also showed a good linear correlation with the concentration of $Cp_2Fe(II)$ [Figure 2(c)]. These results indicate that $Cp_2Fe(III)^+$, generated by electronic oxidation on the anode, mediates the oxidation of **1a**, which is followed by reduction to $Cp_2Fe(II)$ in the solution.[19]



Scheme 2 Substrate scope. *Reaction conditions*: RVC anode [100 pores per linear inch, 10 × 10 × 12 mm], Pt cathode (10 × 12 × 0.1 mm), substrate (0.15 mmol), H_2O (12 mL), 1,4-dioxane (3.0 mL), 4 h. Isolated yields are reported.[a] 0.1 mmol scale.



Scheme 3 Electrolysis of a methoxy-substituted substrate

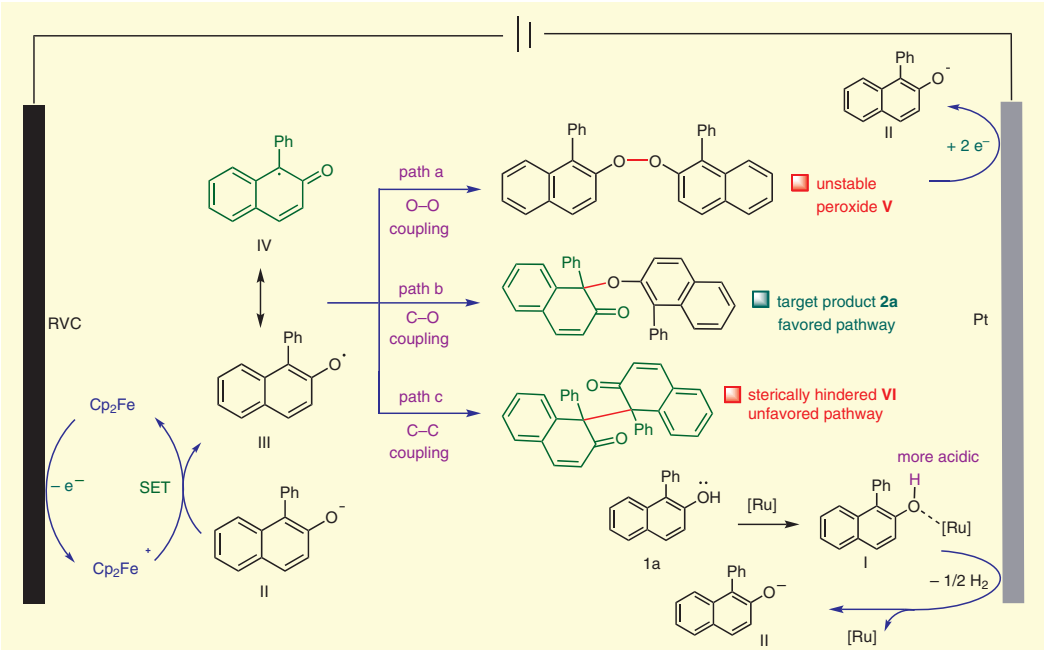


a) CV of 0.15g/L Cp_2Fe; b) CV of **1a** of 3.5 g/L with the different amount of Cp_2Fe. CV was conducted on the RVC electrode in the H_2O/1,4-dioxane (2:1) solution with 0.8 M KPF_6 over 10 mV/s scan rate at 50 °C.

Figure 2 Cyclic voltammetry of the tested reaction system

Based on the above study, a possible mechanism for electrochemical synthesis of the homocoupling product was proposed with 2-naphthol (**1a**) as a model substrate (Scheme 4). The electrolytic process commences with anodic oxidation of Cp_2Fe to generate Cp_2Fe^+. Meanwhile, substrate **1a** coordinates with the [Ru] complex to give intermediate **I**, which is reduced at the cathode to produce **II** and H_2 efficiently. Then, single-electron transfer (SET) between **II** and Cp_2Fe^+ gives the oxygen-centered radical **III**, with regeneration of Cp_2Fe. A carbon-centered radical **IV** might then be formed, which has a resonance structure associated with intermediate **III**.[20] Theoretically, three coupling pathways should then be possible. For Path a, O–O bond formation through homocoupling of **III** might generate peroxide **V**, which is likely to be unstable and would be reduced at the cathode to regenerate **II** under the current electrochemical condition. For Path b, C–O bond formation through coupling of **III** and **IV** produces the stable product. Hence, this pathway is predominant among the three possible pathways. For Path c, C–C bond formation through homocoupling of radical **IV** would suffer from considerable steric hindrance, disfavoring this pathway; this is supported by the fact that we did not observe any compound **VI** in the reaction.

In summary, we have reported an electrochemical oxidative dearomatization method for C–O homocoupling of 2-naphthols.[21] A gram-scale experiment illustrated the potential practicability of our method. Further studies on applications of this electrochemical system in syntheses of related C–O homocoupling dimers that are bioactive and useful are underway in our laboratory.



Scheme 4 Plausible mechanism

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611777.

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(21) **Electrochemical Oxidative Homocoupling of 2-Naphthols; General Procedure**

A 25 mL four-necked flask equipped with stirrer bar, a reflux condenser, an RVC anode (100 pores/inch, 10 × 10 × 12 mm; Goodfellow Cambridge Ltd.), and a Pt plate cathode (10 × 12 × 0.1 mm; Beijing Global International Science and Technology Co., Ltd) was charged with the appropriate substituted 2-naphthol, $[RuCl_2(p\text{-cymene})]_2$ (2.5 mol%), Cp_2Fe (0.2 equiv), KPF_6 (2.0 equiv), H_2O (12.0 mL), and 1,4-dioxane (3.0 mL). Constant-current electrolysis (10 mA) was performed at 90 °C with magnetic stirring for 4 h. The resulting solution was then cooled to

r.t., the layers was separated, and the aqueous phase was extracted with EtOAc (3 × 20 mL). The organic phases were combined, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography.

1-Phenyl-1-[(1-phenyl-2-naphthyl)oxy]naphthalen-2(1*H*)-one (2a)

Yellow foam solid; yield: 40.1 mg (92%); TLC: R_f = 0.45 (EtOAc–PE, 1:5). IR (neat): 2973, 1923, 1734, 1684, 1507, 1053, 697 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 7.4 Hz, 1 H), 7.71–7.64 (m, 2 H), 7.62 (d, *J* = 10.0 Hz, 1 H), 7.57–7.47 (m, 6 H), 7.39 (td, *J* = 7.2, 1.8 Hz, 1 H), 7.35–7.27 (m, 4 H), 7.16–7.11 (m, 1 H), 7.06 (dd, *J* = 10.1, 4.9 Hz, 2 H), 7.01–6.97 (m, 2 H), 6.42 (d, *J* = 9.1 Hz, 1 H), 6.25 (d, *J* = 10.0 Hz, 1 H).^{13}C NMR (101 MHz, $CDCl_3$): δ = 196.78, 150.02, 145.09, 143.89, 139.57, 137.11, 133.97, 131.81, 131.37, 130.79, 130.56, 129.71, 128.91, 128.87, 128.44, 128.21, 128.16, 127.82, 127.19, 126.94, 126.37, 125.93, 125.75, 125.48, 123.78, 116.41, 85.58, 29.84. HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{32}H_{22}NaO_2$: 461.1512; found: 461.1508.