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Electrochemically Induced Synthesis of *N*-Allyloxyphthalimides via Cross-Dehydrogenative C−O Coupling of *N*-Hydroxyphthalimide with Alkenes Bearing the Allylic Hydrogen Atom

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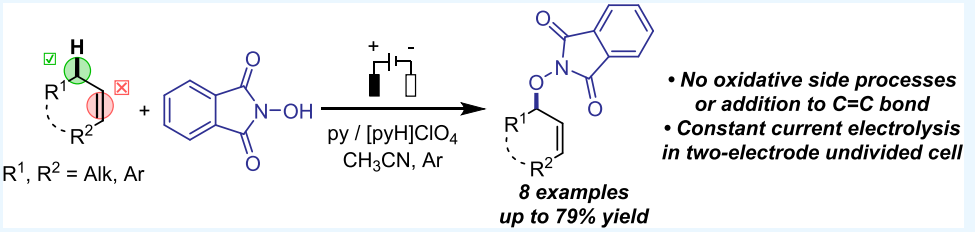

ABSTRACT: The electrochemically induced reaction between alkenes, bearing an allylic hydrogen atom, and *N*-hydroxyphthalimide was investigated. Cross-dehydrogenative C−O coupling with phthalimide-*N*-oxyl radical, derived from *N*-hydroxyphthalimide, occurs instead of oxidation of the allylic site, with the formation of a carbonyl group or functionalization of the double C=C bond. The discovered transformation proceeds in an undivided electrochemical cell equipped with a carbon felt anode and a platinum cathode. Coupling products were obtained with yields up to 79%. The developed process is based on the abstraction of hydrogen atom from the allylic position for functionalization while the C=C bond remains unreacted. The method exploits the ability of the phthalimide-*N*-oxyl radical to abstract hydrogen atoms with the following interception of the intermediate *C*-centered radical.

INTRODUCTION

Over the last few decades, cross-coupling reactions have become one of the main tools in organic synthesis for construction of C−C and C-heteroatom bonds.[1−4] This approach allows for the formation of a new bond with superior efficiency and selectivity. Traditionally, cross-coupling reactions proceed under transition metal catalysis, which requires prefunctionalization of the starting substrates.[4−6] In contrast, cross-dehydrogenative (oxidative) coupling via selective activation of C−H and heteroatom-H bonds allows direct functionalization of molecules with high atom and step economy. The main challenge of the oxidative approach is the search for an optimal oxidizing system, which allows to overcome overoxidation of the starting material, ensuring the required chemo- and regioselectivity.

Recently, electrochemical methodology was used for C−H functionalization of various substrates.[7−11] The transition from the usage of material oxidants to anodic oxidation meets the principles of green chemistry,[12−14] while allowing one to conduct oxidative coupling reactions with oxidatively labile compounds. A substantial number of works are devoted to photo- and electrochemical functionalization of activated molecules bearing benzylic[15] or allylic[16−18] sites. Such processes are often accompanied by the formation of stabilized benzyl and allyl radicals, which play a crucial role in the target process.

Radical transformations of alkenes bearing an allylic hydrogen atom can proceed via a great variety of mechanism routes, opening the way to a wide range of products.[19] This variety can affect the selectivity and efficiency of the desired process. One of the possible reactions is allylic oxygenation, leading to the formation of unsaturated ketones or alcohols.[20] The formation of such products mainly occurs under the action of oxygen-containing oxidizing agents, for example peroxides.[21,22] Besides this route, allylic oxygenation can occur in the presence of atmospheric oxygen[23] or *O*-nucleophiles.[24,25]

It is also necessary to keep in mind the possibility of C=C bond entering the reaction,[26,27] leading to mono- and difunctionalization of alkenes, which is another thriving area in the chemistry of unsaturated compounds.[28−33] The regioselectivity of the reactions may shift from allylic C−H functionalization toward addition to the C=C bond if it

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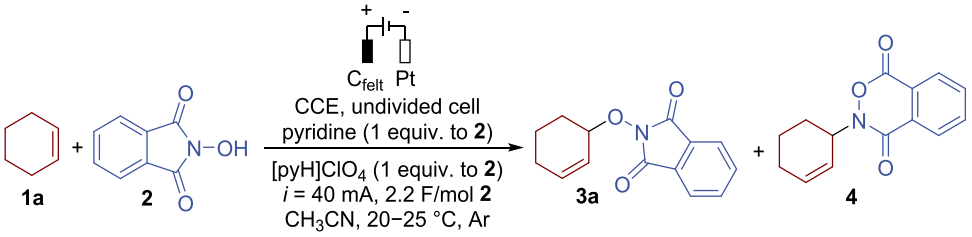
Table 1. Optimization of the Electrochemical Reaction of Cyclohexene 1a with *N*-Hydroxyphthalimide 2



entry	variation from the initial reaction conditions[a]	3a yield, %[b]	4 yield, %[b]
1	none[a]	72	14
2	*n*-Bu_4NClO_4 instead of [pyH]ClO_4	14	n.d.
3	acetone instead of CH_3CN	29	5
4	MeOH instead of CH_3CN	26	5
5	2,6-lutidine instead of pyridine	66	15
6	Et_3N instead of pyridine	49	13
7	reaction without base	59	12
8	Pt plate anode instead of carbon felt anode	39	7
9	Ni foam cathode instead of Pt wire cathode	29	6
10	reaction under air	58	8
11	2 equiv of **1a** instead of 3 equiv	45	10
12	4 equiv of **1a** instead of 3 equiv	67	12
13	**50 mA instead of 40 mA**	**73 (70)**	**14 (10)**
14	60 mA instead of 40 mA	65	13
15	2.0 F/mol passed instead of 2.2	55	10
16	2.5 F/mol passed instead of 2.2	55	10

[a]Initial reaction conditions: **1a** (1.5 mmol, 123 mg), **2** (0.5 mmol, 82 mg), [pyH]ClO_4 (0.5 mmol, 90 mg), pyridine (0.5 mmol, 40 mg), CH_3CN (10.0 mL), undivided cell, carbon felt anode (10 × 30 × 3 mm), Pt wire cathode, constant current electrolysis with i = 40 mA (j_{anode} = 13.3 mA/cm^2), F = 2.2 F/mol **2** (reaction time 44 min, Faraday efficiency = 78%), 20−25 °C, Ar atmosphere. n.d. − not detected. [b]Yields based on NHPI **2** were determined by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as an internal standard; isolated yields are given in parentheses.

produces a stabilized radical, such as a benzyl; in such cases, a mixture of regioisomeric products is often formed.[27]

Until recently the electrochemical utility of imide-*N*-oxyl radicals was limited to their usage as mediators of atom hydrogen abstraction in various C−H functionalization processes.[34−37] A number of papers[16,17,34,38] reported electrochemical allylic oxygenation of alkenes catalyzed by the *N*-oxyl radical derived from *N*-hydroxyimides. In our recent works we have described an approach for preparative electrochemical generation of the PINO radical and its following addition to the double C═C bond of styrenes[39] and vinyl azides.[40]

A 2022 paper by Stahl et al. disclosed electrochemical phthalimide-*N*-oxyl (PINO) radical-mediated C−H functionalization of alkyl arenes with the incorporation of PINO moiety into the final product.[41] In this work, along with the alkylarene derivatives, an example of oxidative C−O coupling of NHPI with alkene containing an allylic hydrogen atom (cyclohexene) was shown. The successful formation of such a product critically depends on the simultaneous presence in the reaction system of the allylic and PINO radicals and their selective recombination. On the other hand, it is crucial to fine-tune the electrochemical parameters to overcome possible side overoxidation of the allylic site. Thus, this work raises the fundamental question of the reactivity of allylic radicals under electrochemical conditions. Inspired by this result, we aimed to establish how the nature of allylic radicals derived from other alkenes affects the selectivity of the desired C−O coupling. Despite the presence of different reaction centers that can interact with the PINO radical, only the allylic hydrogen atom undergoes the target transformation with retention of the double C═C bond, and no side allylic oxidation occurs. Additionally, in contrast to *N*-oxyl radical-mediated living polymerization, characterized by the formation of labile alkoxyamine intermediates, the discovered radical transformation terminates with the formation of stable C−O coupling products.[42]

RESULTS AND DISCUSSION

We began our studies with an evaluation of the conditions for the model reaction between cyclohexene **1a** and NHPI **2** under constant current electrolysis in an undivided cell. Carbon felt and platinum were used as anode and cathode materials while passing 2.2 F/mol **2** electricity. The reaction was conducted in CH_3CN in the presence of pyridine as the base and pyridinium perchlorate as the supporting electrolyte. Argon atmosphere was employed to prevent side oxidation processes involving atmospheric oxygen. Under these initial conditions (Table 1, entry 1) along with the product of C−O coupling **3a** (72% yield), we were able to isolate a product of C−N coupling **4** (14% yield).

During the optimization, the following parameters were screened: nature of base and electrolyte, solvents, cathode and anode materials, and different electrochemical parameters (Table 1, see Supporting information for the full optimization table).

When *n*-Bu_4NClO_4 was used instead of [pyH]ClO_4, the yield of **3a** dropped to 14% (Table 1, entry 2). At the same time, the formation of **4** was not detected. During variation of the solvent (Table 1, entries 3 and 4), the yield of **3a** dropped to 29% in case of acetone and 26% in case of MeOH; the yields of **4** in both cases dropped to 5%. When the base was changed to 2,6-lutidine or Et_3N (Table 1, entries 5 and 6), we

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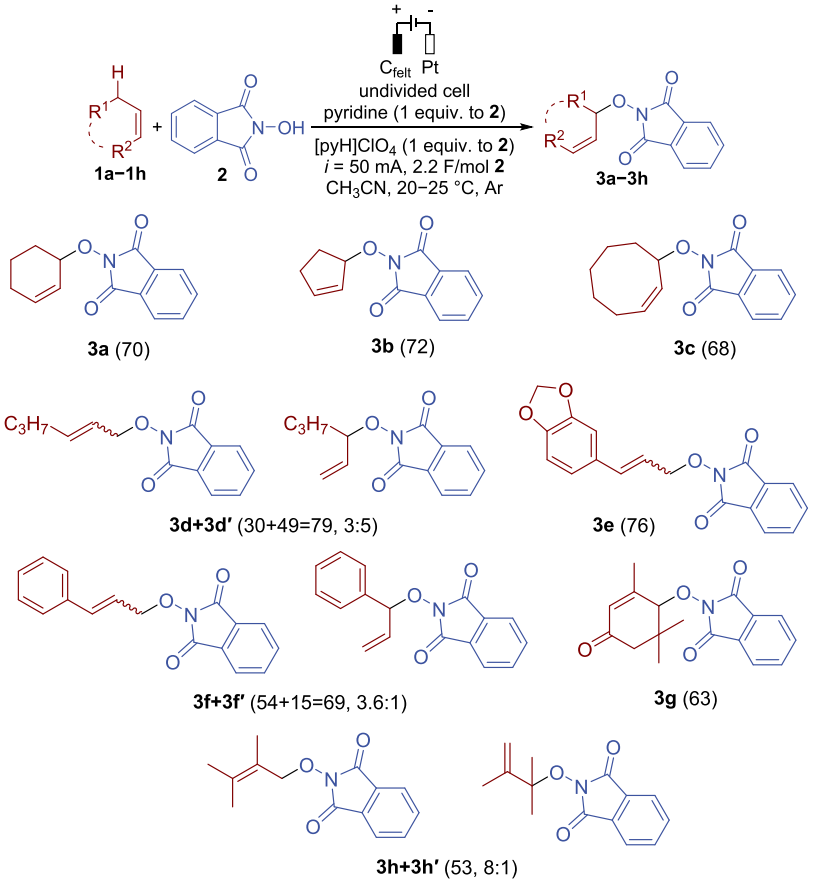
Table 2. Scope of *N*-Alkoxyphthalimides 3a−3h Synthesized from Alkenes 1a−1h and NHPI 2[a,b]



[a]Reaction conditions: **1a−1h** (1.5 mmol, 102−243 mg), **2** (0.5 mmol, 82 mg), [pyH]ClO_4 (0.5 mmol, 90 mg), pyridine (0.5 mmol, 40 mg), CH_3CN (10.0 mL), undivided cell, carbon felt anode (10 × 30 × 3 mm), Pt wire cathode, constant current electrolysis with i = 50 mA (j_{anode} = 16.7 mA/cm^2), F = 2.2 F/mol **2** (reaction time 35 min), 20−25 °C, Ar atmosphere. [b]Isolated yields.

observed decreasing of the yield of **3a** to 66 and 49%, respectively; the yields of **4** were 15 and 13%. When the reaction was conducted omitting the base (Table 1, entry 7), the yields of **3a** and **4** were only 59 and 12%, respectively.

When the anode and cathode materials were changed (Table 1, entries 8 and 9), the yields of **3a** were 39% in the case of Pt plate anode and 29% in the case of Ni foam cathode. The yields of **4** were 7 and 6%, respectively. Reaction under an air atmosphere (Table 1, entry 10) gave us **3a** in 58% yield and **4** in 8% yield. Upon increasing the equivalent of **1a** to 4 or decreasing to 2 (Table 1, entries 11 and 12), **3a** was yielded in 67 and 45%, and **4** in 10 and 12% yield, respectively. During optimization of the current density (Table 1, entries 13 and 14), the yield of **3a** was 73% in case of 50 mA and 65% in case of 60 mA. The yield of **4** was 14 and 13%, respectively. Increasing or decreasing the passed charge lowered the yields of **3a** and **4** to 55 and 10%, respectively (Table 1, entries 15 and 16). Thus, we were able to obtain **3a** in 70% yield and **4** in 10% yield in the reaction of NHPI **2** with 3 equiv of cyclohexene **1a** under constant current conditions using carbon felt anode and Pt wire cathode by passing 2.2 F/mol of electricity (Table 1, entry 13).

Under optimized conditions, the scope of the developed electrochemical allylic C−O coupling of alkenes **1a−1g** with NHPI **2** yielding *N*-alkoxyphthalimides **3a−3g** was evaluated (Table 2). Cyclic alkenes **1a−1c** were tested in the developed process, providing products **3a−3c** in good yields (63−79%). In the case of hex-1-ene **1d**, allylbenzene **1f** and 2,3-dimethylbut-2-ene **1h** pairs of regioisomeric products **3d**/**3d′** (79%), **3f**/**3f′** (69%), and **3h**/**3h′** (53%) were obtained. Safrole **1e** and isophorone **1g** also react with NHPI with the formation of products **3e** and **3g** in 76 and 63% yields, respectively.

To clarify the reaction mechanism, cyclic voltammetry (CV) studies were carried out. According to the results of the CV experiments (Figure 1), we conclude that cyclohexene **1a** and pyridine are electrochemically inert in the range of −0.3 to 1.5 V vs. Fc/Fc$^+$ (curves b and c). On the voltammogram of NHPI **2** solution (curve d), we observe minor peaks in the 0.6−1.2 V region, corresponding to the reversible oxidation of NHPI **2** to PINO radical. Addition of 1 equiv of pyridine to the NHPI **2** solution (curve e) led to a significant increase of the oxidation and reduction currents (peaks at 0.86 and 0.29 V, respectively). In the presence of cyclohexene **1a**, the peak of reduction of the phthalimide-*N*-oxyl radical disappeared (curve f), which indicated its interaction with cyclohexene **1a**.

Based on literature data and CV experiments, a possible mechanism of the discovered process was proposed (Scheme 1). Initially, deprotonation of NHPI **2** under the action of pyridine occurs. Then, anion **A** anodically oxidates into the **PINO** radical. After PINO-mediated hydrogen atom abstraction, alkene **1** forms the stabilized allylic radical **B**. Products **3** and **3′** result in the reaction between radical **B** and **PINO**, acting as both *O*- and *N*-centered radicals. In the case of the

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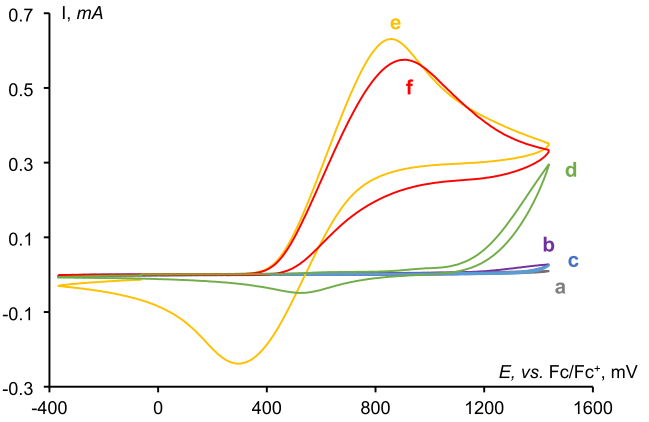


Figure 1. CV curves: (a) background; (b) pyridine (0.05 M); (c) **1a** (0.025 M); (d) **2** (0.05 M); (e) **2** (0.05 M) and pyridine (0.05 M); (f) **1a** (0.025 M), **2** (0.05 M), and pyridine (0.05 M) in $[pyH]ClO_4$/MeCN (0.1 M). Working electrode—glassy carbon (d = 3 mm, unseparated from the counter electrode), counter electrode—platinum wire, reference electrode—Ag/Ag^+, argon atmosphere, 25 ± 0.5 °C. Starting point—0 mV, the direction of the scan—forward, scan rate—100 mV/s.

C−N coupling product formation, the resulting intermediate **C** is then rearranged into **3′**.[41] The reduction of protons from the pyridinium ion with the evolution of molecular hydrogen occurs at the cathode.

CONCLUSIONS

The electrochemically induced reaction between various alkenes bearing an allylic hydrogen atom and *N*-hydroxyphthalimide was disclosed. Instead of deep oxidation of the allylic site, the formation of *N*-allyloxyphthalimides as unforeseen C−O coupling products was observed. The reaction was implemented in a simple undivided cell, and the target *N*-allyloxyphthalimides were obtained in moderate to good yields (53−79%). The developed approach exploits the dual reactivity of the PINO radical both as HAT mediator and as a coupling partner. The process starts with the generation of the PINO radical, followed by abstraction of an allylic hydrogen atom under the action of the PINO radical and recombination of PINO and *C*-centered allylic radicals. Along with the target *N*-allyloxyphthalimides, an unusual product of C−N coupling and subsequent rearrangement was obtained. The developed process can be used for selective allylic introduction of the hydroxylamine fragment into alkenes bearing the allylic hydrogen atom.

EXPERIMENTAL SECTION

General Information. ^1H and $^{13}C\{^1H\}$ spectra were obtained using the Bruker AVANCE II 300 spectrometer (300 and 75 MHz, respectively) in $CDCl_3$. Chemical shifts are given in parts per million (ppm), using the residual solvent peak as a reference: ^1H ($CDCl_3$ δ 7.26 ppm), $^{13}C\{^1H\}$ ($CDCl_3$ δ 77.16 ppm). Multiplicity was indicated as follows: s (singlet), bs (broad singlet), d (doublet), dd (doublet of doublet), t (triplet), q (quartet), quin (quintet), sept (septet), and m (multiplet).

High-resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF II instrument by using electrospray ionization (ESI). The measurements were performed in a positive ion mode (interface capillary voltage −4500 V); mass range from m/z 50 to m/z 3000 Da; external calibration with Electrospray Calibrant Solution.

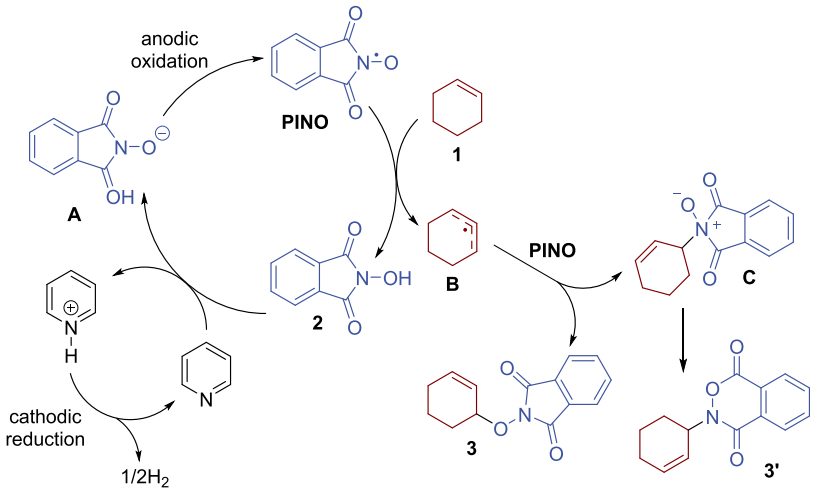
The thin-layer chromatography (TLC) analysis was carried out with the use of ALUGRAMR Xtra SIL G/UV_{254} silica gel chromatography plates and visualized with a 254 nm UV lamp. Column chromatography was performed with the use of a 0.060−0.200 mm, 60 Å silica gel (Acros).

Ethyl acetate and acetonitrile (MeCN) were distilled over P_2O_5. Petroleum ether, 40−60 (PE), and dichloromethane (DCM) were distilled over K_2CO_3. Acetone was distilled over $KMnO_4$. Pyridine was distilled over KOH and stored over 4 Å molecular sieves. 2,6-Lutidinium perchlorate ($[LutH]ClO_4$) and pyridinium perchlorate ($[PyH]ClO_4$) were synthesized according to the literature and stored in a desiccator over anhydrous $CaCl_2$. Alkenes **1a−1h** and NHPI **2** were commercial reagents and used as supplied without further purification, unless stated otherwise.

All of the obtained products (**3a−3h**) were characterized using ^1H, $^{13}C\{^1H\}$ NMR spectroscopy and HRMS ESI. For the previously described compounds (**3a,b,f**), all of the characterization data were in good agreement with the literature.

General Procedure for Optimization of 3a Electrosynthesis from Cyclohexene 1a and *N*-Hydroxyphtha-

Scheme 1. Proposed Mechanism for Electrochemical Oxidative C−O Coupling of Cyclohexene 1a with NHPI 2



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limide 2 (Experimental for Table 1). An undivided 10 mL cell, equipped with a carbon felt anode (10 × 30 × 3 mm, S = 3.0 cm^2) and a platinum wire cathode, was connected to a DC-regulated power supply (Korad KA3005D). A solution of cyclohexene 1a (0.5−2.0 mmol, 41−164 mg), *N*-hydroxyphthalimide 2 (0.5 mmol, 82 mg), base (pyridine, 2,6-lutidine, Et_3N or *n*-Bu_4NOH (30% aq.), 0.5 mmol, 40−432 mg), and supporting electrolyte ($[LutH]ClO_4$, $[PyH]ClO_4$, *n*-Bu_4NClO_4, or *n*-Bu_4NBF_4, 0.5 mmol, 89−171 mg) in 10.0 mL of solvent (DCM, CH_3CN, acetone, CH_3CN/H_2O) was electrolyzed using constant current conditions (I = 30−60 mA, j_{anode} = 10−20 mA/cm^2) at 25 °C under magnetic stirring. After passing 2−2.5 F/mol **2** of electricity (reaction time 29−59 min), the electrodes were washed with DCM (2 × 20.0 mL). The combined organic phases were concentrated under reduced pressure using a rotary evaporator (15−20 mmHg), bath temperature ca. 50−55 °C. The yields of products **3a** and **3a′** were determined by ^1H NMR analysis of a crude mixture using *p*-methoxyacetophenone as the internal standard. In the selected entries, products **3a** and **3a′** were isolated by flash column chromatography on silica gel using DCM as eluent.

General Procedure for Electrochemical Synthesis of *N*-Alkoxyphthalimides 3a−3h (Experimental for Table 2). An undivided 10 mL cell, carbon felt anode (10 × 30 × 3 mm, S = 3.0 cm^2), and a platinum wire cathode were connected to a DC-regulated power supply (Korad KA3005D). A solution of alkene **1a−1h** (1.5 mmol, 102−243 mg), *N*-hydroxyphthalimide **2** (0.5 mmol, 82 mg), pyridine (0.5 mmol, 40 mg), and $[pyH]ClO_4$ (0.5 mmol, 90 mg) in 10.0 mL of CH_3CN was electrolyzed using constant current conditions (I = 50 mA, j_{anode} = 16.7 mA/cm^2) at 25 °C under magnetic stirring. After passing 2.2 F/mol **2** of electricity (reaction time of 35 min), the electrodes were washed with DCM (2 × 20.0 mL). The combined organic phases were concentrated under reduced pressure using a rotary evaporator (15−20 mmHg), bath temperature ca. 50−55 °C. All products were isolated by flash column chromatography on silica gel using the corresponding eluent.

General Procedure for Cyclic Voltammetry. Cyclic voltammetry (CV) experiments were performed with the use of a computer-assisted potentiostat (IPC-Pro M, ≪Econix≫) (starting potential setting 0.25 mV; scan rate error 1.0%; scan rate 0.1 V·s^{-1}). The experiments were implemented in a pearl-shaped 10 mL electrochemical cell, externally thermostated at 25 ± 0.5 °C with a water jacket. Voltammetry curves were recorded using a disc glassy-carbon electrode (d = 3 mm, polished with chromium oxide-based polishing paste before each recording) as the working electrode, platinum wire auxiliary electrode, and $Ag/AgNO_3$ (0.01 M) reference electrode. CV experiments were performed under an inert argon atmosphere; the analyte was bubbled with argon for 1 min before recording of the curve.

*2-(Cyclohex-2-en-1-yloxy)isoindoline-1,3-dione (**3a**).*[43] According to the general procedure, cyclohexene (123 mg, 1.5 mmol, 3.0 equiv) and *N*-hydroxyphthalimide (82 mg, 0.5 mmol, 1.0 equiv) gave **3a** as a white powder in 70% yield (85 mg, 0.30 mmol) after column chromatography (eluent: DCM). Mp 82−83 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.91−7.66 (m, 4H), 6.17−5.99 (m, 1H), 5.98−5.85 (m, 1H), 4.73 (d, J = 5.0 Hz, 1H), 2.25−2.07 (m, 1H), 2.06−1.89 (m, 2H), 1.89−1.74 (m, 1H), 1.68−1.51 (m, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 166.1, 135.1, 134.5, 129.9, 124.0, 123.5, 81.5, 78.7, 27.4, 25.3, 18.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{13}NO_3$ 244.0968; found 244.0966.

*3-(Cyclohex-2-en-1-yl)-1H-benzo[d][1,2]oxazine-1,4(3H)-dione (**3a′**).* According to the general procedure, cyclohexene (123 mg, 1.5 mmol, 3.0 equiv) and *N*-hydroxyphthalimide (82 mg, 0.5 mmol, 1.0 equiv) gave **3a′** as a white powder in 10% yield (12 mg, 0.05 mmol) after column chromatography (eluent: DCM). Mp 105−106 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.29 (dd, J_1 = 7.8 Hz, J_2 = 1.4 Hz, 1H), 8.23 (dd, J_1 = 7.8 Hz, J_2 = 1.4 Hz, 1H), 7.92 (td, J_1 = 7.6 Hz, J_2 = 1.4 Hz, 1H), 7.83 (td, J_1 = 7.6 Hz, J_2 = 1.4 Hz, 1H), 6.08−5.98 (m, 1H), 5.65 (dq, J_1 = 10.2 Hz, J_2 = 2.2 Hz, 1H), 5.59−5.47 (m, 1H), 2.25−1.88 (m, 5H), 1.82−1.62 (m, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 160.3, 156.8, 135.8, 133.9, 133.0, 130.1, 129.6, 128.0, 124.9, 123.8, 53.9, 26.3, 24.4, 21.0. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{14}H_{13}NO_3$ 266.0788; found 266.0788.

*2-(Cyclopent-2-en-1-yloxy)isoindoline-1,3-dione (**3b**).*[43] According to the general procedure, cyclopentene (102 mg, 1.5 mmol, 3.0 equiv) and *N*-hydroxyphthalimide (82 mg, 0.5 mmol, 1.0 equiv) gave **3b** as a white powder in 72% yield (83 mg, 0.36 mmol) after column chromatography (eluent: DCM). Mp 95−97 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.95, 7.60 (m, 4H), 6.30, 6.14 (m, 1H), 6.02, 5.85 (m, 1H), 5.48, 5.30 (m, 1H), 2.69, 2.48 (m, 1H), 2.43, 2.11 (m, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 164.5, 138.9, 134.0, 129.1, 128.2, 125.1, 94.2, 37.0, 27.2. HRMS (ESI) m/z: $[M + NH_4]^+$ calcd for $C_{13}H_{11}NO_3$ 247.1077; found 247.1084.

*(Z)-2-(Cyclooct-2-en-1-yloxy)isoindoline-1,3-dione (**3c**).* According to the general procedure, cyclooctene (165 mg, 1.5 mmol, 3.0 equiv) and *N*-hydroxyphthalimide (82 mg, 0.5 mmol, 1.0 equiv) gave **3c** as a white powder in 68% yield (92 mg, 0.34 mmol) after column chromatography (eluent: DCM/PE = 5:1 (v/v)). Mp 169−171 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.88−7.77 (m, 2H), 7.76−7.66 (m, 2H), 5.90−5.79 (m, 1H), 5.78−5.65 (m, 1H), 5.34−5.20 (m, 1H), 2.25−1.97 (m, 3H), 1.77,1.29 (m, 7H). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 164.3, 134.5, 132.3, 130.3, 129.1, 123.6, 85.5, 33.8, 29.0, 26.5, 26.1, 23.6. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{17}NO_3$ 272.1281; found 272.1274.

*2-(Hex-2-en-1-yloxy)isoindoline-1,3-dione (**3d**).* According to the general procedure, hex-1-ene (126 mg, 1.5 mmol, 3.0 equiv) and *N*-hydroxyphthalimide (82 mg, 0.5 mmol, 1.0 equiv) gave **3d** as a colorless oil in 30% yield (37 mg, 0.15 mmol) after column chromatography (eluent: DCM/PE = 3:2 (v/v)). Mixture of E/Z isomers with a ratio of 0.15:1. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.85−7.79 (m, 2.3H), 7.75−7.71 (m, 2.3H), 5.84−5.70 (m, 2.3H), 4.79 (d, J = 6.6 Hz, 0.3H), 4.64 (d, J = 6.6 Hz, 2H), 2.06 (q, J = 7.1 Hz, 0.3H), 1.99 (q, J = 6.8 Hz, 2H), 1.34−1.24 (m, 2.3H), 0.83−0.75 (m, 3.45H). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 163.9, 155.5, 140.8, 139.0, 134.5, 134.5, 129.0, 123.9, 123.2, 122.2, 78.7, 73.0, 33.6, 30.4, 22.6, 21.5, 13.6, 13.6. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{15}NO_3$ 246.1125; found 246.1128.

*2-(Hex-1-en-3-yloxy)isoindoline-1,3-dione (**3d′**).* According to the general procedure, hex-1-ene (126 mg, 1.5 mmol, 3.0 equiv) and *N*-hydroxyphthalimide (82 mg, 0.5 mmol, 1.0 equiv) gave **3d′** as a colorless oil in 49% yield (60 mg, 0.25 mmol) after column chromatography (eluent: DCM/PE = 3:2 (v/v)). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.81−7.68 (m, 4H), 5.96−5.81 (m, 1H), 5.22−5.11 (m, 2H), 4.63 (dt, J_1 = 9.3 Hz, J_2 = 6.7 Hz, 1H), 1.98−1.82 (m, 1H), 1.72−1.57 (m, 1H), 1.54−1.40 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR

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ACS Omega 2024, 9, 49825−49831

(75.47 MHz, $CDCl_3$): δ 164.1, 136.5, 134.4, 129.0, 123.5, 121.2, 89.4, 35.2, 18.5, 14.0. HRMS (ESI) *m/z:* $[M + Na]^+$ calcd for $C_{14}H_{15}NO_3$ 268.0944; found 268.0933.

*2-((3-(Benzo[d][1,3]dioxol-5-yl)allyl)oxy)isoindoline-1,3-dione (**3e**).* According to the general procedure, safrole (243 mg, 1.5 mmol, 3.0 equiv) and *N*-hydroxyphthalimide (82 mg, 0.5 mmol, 1.0 equiv) gave **3e** as a white powder in 76% yield (123 mg, 0.38 mmol) after column chromatography (eluent: DCM). Mp 158−160 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.85−7.64 (m, 4H), 6.90 (s, 1H), 6.78 (d, J = 8.4 Hz, 1H), 6.71 (d, J = 8.0 Hz, 1H), 6.56 (d, J = 15.8 Hz, 1H), 6.27 (dt, J_1 = 15.3 Hz, J_2 = 7.2 Hz, 1H), 5.93 (s, 2H), 4.82 (d, J = 7.1 Hz, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 162.6, 161.7, 135.3, 133.4, 131.1, 129.2, 127.7, 123.6. HRMS (ESI) *m/z:* $[M + Na]^+$ calcd for $C_{18}H_{13}NO_5$ 346.0686; found 346.0681.

*2-((3-Phenylallyl)oxy)isoindoline-1,3-dione (**3f**).*[43] According to the general procedure, allylbenzene (177 mg, 1.5 mmol, 3.0 equiv) and *N*-hydroxyphthalimide (82 mg, 0.5 mmol, 1.0 equiv) gave **3f** as a white powder in 54% yield (73 mg, 0.27 mmol) after column chromatography (eluent: DCM). Mp 150−152 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.88−7.69 (m, 4H), 7.43−7.22 (m, 5H), 6.70 (d, J = 15.9 Hz, 1H), 6.60−6.40 (m, 1H), 4.90 (d, J = 7.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 163.9, 137.6, 135.9, 134.5, 129.6, 128.7, 128.5, 127.0, 124.8, 122.2, 78.7. HRMS (ESI) *m/z:* $[M + H]^+$ calcd for $C_{17}H_{13}NO_3$ 280.0968; found 280.0967.

*2-((1-Phenylallyl)oxy)isoindoline-1,3-dione (**3f′**).* According to the general procedure, allylbenzene (177 mg, 1.5 mmol, 3.0 equiv) and *N*-hydroxyphthalimide (82 mg, 0.5 mmol, 1.0 equiv) gave **3f′** as a white powder in 15% yield (21 mg, 0.075 mmol) after column chromatography (eluent: DCM). Mp 90−91 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.90−7.73 (m, 4H), 7.61 (d, J = 7.2 Hz, 2H), 7.50−7.36 (m, 3H), 6.40−6.22 (m, 1H), 5.75 (d, J = 8.5 Hz, 1H), 5.51−5.34 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 163.94, 136.98, 135.34, 134.48, 129.18, 128.94, 128.69, 128.05, 123.56, 121.54, 90.15. HRMS (ESI) *m/z:* $[M + Na]^+$ calcd for $C_{17}H_{13}NO_3$ 302.0788; found 302.0793.

*2-((2,6,6-Trimethyl-4-oxocyclohex-2-en-1-yl)oxy)-isoindoline-1,3-dione (**3g**).* According to the general procedure, isophorone (207 mg, 1.5 mmol, 3.0 equiv) and *N*-hydroxyphthalimide (177 mg, 0.5 mmol, 1.0 equiv) gave **3g** as a white powder in 63% yield (94 mg, 0.32 mmol) after column chromatography (eluent: DCM). Mp 127−131 °C. ^1H NMR ($CDCl_3$, 300.13 MHz): δ 7.85−7.68 (m, 4H), 5.80 (s, 1H), 4.23 (s, 1H), 3.31 (d, J = 12.7 Hz, 1H), 2.30 (d, J = 12.5 Hz, 1H), 2.05 (s, 3H), 1.25 (s, 3H), 0.99 (s, 3H).$^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$) δ: 206.7, 162.3, 142.1, 135.2, 129.0, 127.5, 124.3, 85.3, 49.9, 37.8, 32.5, 29.7, 21.7. HRMS (ESI) *m/z:* $[M + H]^+$ calcd for $C_{17}H_{13}NO_3$ 302.0788; found 302.0793.

*2-((2,3-Dimethylbut-2-en-1-yl)oxy)isoindoline-1,3-dione (**3h**) and 2-((2,3-dimethylbut-3-en-2-yl)oxy)isoindoline-1,3-dione (**3h′**).* According to the general procedure, 2,3-dimethylbut-2-ene (126 mg, 1.5 mmol, 3.0 equiv) and *N*-hydroxyphthalimide (177 mg, 0.5 mmol, 1.0 equiv) gave a mixture of **3h** and **3h′** as a white powder in 53% yield (65 mg, 0.27 mmol) after column chromatography (eluent: DCM). Mixture of regioisomers with the ratio of 8:1. Mp 77−81 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.85−7.68 (m, 4.44H), 4.55 (d, J = 27.6 Hz, 1H), 4.24 (s, 2H), 1.58 (s, 0.33H), 1.44 (s, 3H), 1.29 (s, 3H), 1.23 (s, 3H), 1.06 (s, 0.66H).$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 163.8, 136.2, 134.4, 129.3, 129.1, 123.4, 122.2, 113.5, 88.9, 78.9, 24.8, 21.1, 20.4, 19.3, 17.7. HRMS (ESI) *m/z:* $[M + H]^+$ calcd for $C_{14}H_{15}NO_3$ 246.1125; found 246.1120.

■ ASSOCIATED CONTENT

Data Availability Statement

All underlying data are available in the article itself and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c08532.

Pictures of the equipment used, cyclic voltammetry studies, copies of ^1H, $^{13}C\{^1H\}$ NMR, and HRMS (ESI) spectra (PDF)

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Notes

The authors declare no competing financial interest.

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