An electrochemical approach to prepare aziridines via an oxidative coupling between alkenes and primary alkyl amines was realized. The reaction is carried out in an electrochemical flow reactor, leading to short reaction/residence times (5 min), high yields, and broad scope. At the cathode, hydrogen is generated, which can be used in a second reactor to reduce the aziridine yielding the corresponding hydroaminated product.
Electrochemical Aziridination of Internal Alkenes with Primary Amines

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SUMMARY
Aziridines are useful synthetic building blocks, widely employed for the preparation of various nitrogen-containing derivatives. As the current methods require the use of prefunctionalized amines, the development of a synthetic strategy toward aziridines that can establish the union of alkenes and amines would be of great synthetic value. Herein, we report an electrochemical approach, which realizes this concept via an oxidative coupling between alkenes and primary alkylamines. The reaction is carried out in an electrochemical flow reactor leading to short reaction/residence times (5 min), high yields, and broad scope. At the cathode, hydrogen is generated, which can be used in a second reactor to reduce the aziridine, yielding the corresponding hydroaminated product. Mechanistic investigations and DFT calculations revealed that the alkene is first anodically oxidized and subsequently reacted with the amine coupling partner.

INTRODUCTION
Aziridines are a synthetically useful class of three-membered N-containing saturated heterocycles, which play an essential role in the preparation of different nitrogen-containing derivatives.1–7 Despite their remarkable reactivity, imparted by the ring-strain (28 kcal mol−1), aziridines are also present in many pharmacologically active natural products, such as antibiotics and anticancer agents.8,9 Consequently, the development of new methods to prepare aziridine structural motifs remains a contemporary subject of interest to synthetic organic chemists. Promising results have been obtained for the synthesis of both racemic and enantiomerically enriched aziridines,10,11 which can be essentially categorized in three main categories: (1) addition of a nitrogen-containing moiety to an alkene, (2) addition of substituted carbene to a C=N bond, and (3) cyclization of 2-haloamines or 2-amino alcohols.1 Among these different approaches,12–14 the addition of a nitrogen-containing reagent to an alkene is the most popular due to its efficiency and versatility.15–17 However, most of these methodologies require the use of a transition metal catalyst, such as copper,18–21 rhodium,22 gold,23 cobalt,24–27 iron,28 or palladium,29 in combination with a suitable and activated nitrene precursor, such as iminoidinanes and organic azides (Figure 1A).30,31

In order to foster more sustainable and transition-metal-free alternatives, new strategies to access aziridines have been devised using electrochemical activation (Figure 1B).32–35 Yudin and coworkers developed an electrochemical aziridination, which uses N-amino-phthalimide as the source of electrophilic nitrogen.7,36,37

The Bigger Picture
The central tenet in modern synthetic methodology is to develop new methods only using widely available organic building blocks. As a direct consequence, new activation strategies are required to cajole the coupling partners to react and, subsequently, forge new and useful chemical bonds. Using electrochemical activation, our methodology enables for the first time the direct coupling between olefins and amines to yield aziridines. Aziridines display interesting pharmacological activity and serve as valuable synthetic intermediates to prepare diverse nitrogen-containing derivatives. Interestingly, the sole byproduct generated in this process is hydrogen, which can be subsequently used to reduce the aziridine into the corresponding hydroaminated product. Hence, this electrochemical methodology can be regarded as green and sustainable from the vantage point of upgrading simple and widely available commodity chemicals.
An iodide-mediated electrocatalytic variant of this protocol was realized by Little, Zheng, and coworkers. Recently, Cheng et al. established an electrochemical strategy, which utilizes a trifluoromethylated sulfamate as a coupling partner. Despite the synthetic value of these electrochemical and other approaches toward aziridines, the scope of the nitrogen-containing coupling partners remains restricted to a limited set of prefunctionalized amines, either PhNH₂ or HfsNH₂ (Figure 1B). It is, however, manifest that an electrochemical coupling between olefins and amines would be of significant value given the broad availability and the low cost of these building blocks (Figure 1C). Such a strategy would also remove the requirement for substrate prefunctionalization, thereby increasing the atom efficiency of the transformation while expanding the scope of available molecular fragments. Based on recent work from our lab involving the electrochemical synthesis of sulfonamides and sulfonyl fluorides, we surmised that direct electrochemical activation of either olefins or amines via anodic oxidation might enable the expedient formation of a carbon-nitrogen bond, eventually leading to the targeted aziridines. Herein, we report on our efforts to develop such an approach, enabling...
for the first time the union of olefins and amines, as convenient and widely available starting materials, to prepare aziridines.

**RESULTS AND DISCUSSION**

**Initial Experiments and Optimization**

Our investigation into this aziridination protocol began with the introduction of trans-anethole and cyclohexylamine into an electrochemical microflow reactor with a small interelectrode gap (250 μm) between the carbon anode and stainless steel cathode (Table 1). After an extensive optimization of the different reaction variables (see Section S2), a good isolated yield (72% yield) could be obtained in only 5 min of reaction/residence time under galvanostatic conditions using an excess of amine (5 equiv) in CH$_3$CN (Table 1, entry 1). Addition of 5 equiv of hexafluoroisopropanol (HFIP) proved beneficial for the targeted transformation and serves as a radical-stabilizing cosolvent and as a proton source for the cathodic half-reaction, generating hydrogen as a useful byproduct (Table 1, entries 1 and 2). Reducing the amount of amine resulted in lower yields (Table 1, entry 3). Interestingly, the presence of a substoichiometric amount of γ-terpinene proved beneficial to prevent overoxidation of the starting material (Table 1, entry 4). Other electrode combinations did not lead to improved results or were less effective for different substrate combinations (Table 1, entry 5; see also Section S2.6). HFIP was the optimal proton source for the electrochemical aziridination, while other acids proved less effective (Table 1, entry 6; see also Section S2.4). As expected, the reaction was electrochemical in nature as no conversion was observed in the absence of electricity (Table 1, entry 7).

![Microflow Electrocell](image)

Table 1. Optimization of the Electrochemical Aziridination between Alkenes and Primary Amines

<table>
<thead>
<tr>
<th>Entry</th>
<th>Variation from the Standard Conditions</th>
<th>Yield (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^a$</td>
<td>none</td>
<td>88 (72)$^c$</td>
</tr>
<tr>
<td>2</td>
<td>neat HFIP</td>
<td>Traces</td>
</tr>
<tr>
<td>3</td>
<td>2.5 equiv amine</td>
<td>75</td>
</tr>
<tr>
<td>4</td>
<td>no γ-terpinene</td>
<td>78</td>
</tr>
<tr>
<td>5</td>
<td>graphite cathode</td>
<td>59</td>
</tr>
<tr>
<td>6</td>
<td>p-TsOH (1 equiv)</td>
<td>32</td>
</tr>
<tr>
<td>7</td>
<td>no electricity</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>batch (16 h)</td>
<td>14$^d$</td>
</tr>
</tbody>
</table>

$^a$Reaction Conditions: anethole (2 mmol), γ-terpinene (0.5 equiv), cyclohexylamine (5 equiv), HFIP (5 equiv), CH$_3$CN (0.1 M), C anode/Fe cathode, 2.5-5 mA cm$^{-2}$

$^b$Yield determined by GC-FID with biphenyl as an internal standard

$^c$Isolated yield

$^d$Batch reaction conditions: Electrasyn, 3.1 mA cm$^{-2}$, 3.5 F, C anode/Fe cathode, 0.5 mmol scale
**Amine Scope**

<table>
<thead>
<tr>
<th></th>
<th>1-A</th>
<th>1-B</th>
<th>2-A</th>
<th>2-B</th>
<th>3-A</th>
<th>3-B</th>
<th>4-A</th>
<th>4-B</th>
<th>5-A</th>
<th>5-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeO</td>
<td>19%</td>
<td>48%</td>
<td>50%</td>
<td>72%</td>
<td>71%</td>
<td>80%</td>
<td>41%</td>
<td>69%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-A</td>
<td>45%</td>
<td>65%</td>
<td>53%</td>
<td>64%</td>
<td>72%</td>
<td>82%</td>
<td>9-A</td>
<td>10-A</td>
<td>traces</td>
<td>traces</td>
</tr>
<tr>
<td>MeO</td>
<td>45%</td>
<td>65%</td>
<td>53%</td>
<td>64%</td>
<td>72%</td>
<td>82%</td>
<td>9-A</td>
<td>10-A</td>
<td>traces</td>
<td>traces</td>
</tr>
<tr>
<td>11-A</td>
<td>62%</td>
<td>77%</td>
<td>57%</td>
<td>78%</td>
<td>70%</td>
<td>94%</td>
<td>14-A</td>
<td>15-A</td>
<td>84%</td>
<td></td>
</tr>
</tbody>
</table>

**Alkene Scope**

<table>
<thead>
<tr>
<th></th>
<th>16-A</th>
<th>17-A</th>
<th>18-A</th>
<th>19-A</th>
<th>20-A</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeO</td>
<td>58%</td>
<td>72%</td>
<td>72%</td>
<td>25%</td>
<td>59%</td>
</tr>
<tr>
<td>21-A</td>
<td>29%</td>
<td>33%</td>
<td>30%</td>
<td>93%</td>
<td>78%</td>
</tr>
<tr>
<td>22-A</td>
<td>27%</td>
<td>88%</td>
<td>27%</td>
<td>51%</td>
<td>61%</td>
</tr>
</tbody>
</table>

**Microflow Electrocell**

- **C|Fe**
- 2.5 - 5.0 mA cm$^{-2}$
- HFIP (5 equiv.)
- γ-terpinene (0.5 equiv.)
- CH$_3$CN (0.1 M)
- room temperature, $t_R = 5$ min

**Aziridine (Product A)**

- 2-B, 48%  
- 3-B, 72%  
- 4-B, 80%  
- 5-B, 69%  
- 9-B, 82%  
- 10-B, 25%  

**Product B**

- 19-A, 25%, (26%)$^b$
- 25-A, 78%  
- 27-A, 27%  
- 28-A, 51%  
- (NH$_3$, 7 M in MeOH) 51%  
- (NH$_3$, 40% w/w in H$_2$O) 61%
entry 7). Finally, the reaction was less effective in a batch reactor, requiring longer reaction times, which resulted in an increased generation of byproducts (Table 1, entry 8). The difference in efficacy between a microflow electrochemical cell and a batch cell to enable the aziridination reaction is significant (Table 1, entry 1 versus entry 8). This can be attributed to the high electrode surface-to-volume ratio, the short diffusion distances (250 \( \mu \text{m} \) interelectrode gap) between anode and cathode, and the reduced Ohmic drop observed in the flow reactor. Hence, reaction/residence times are significantly reduced (5 min in flow versus 16 h in batch), which minimizes effectively the extent to which these degradation-sensitive compounds are exposed to the electrochemical conditions. In addition, due to the continuous operation of the flow reactor, less deposition of organic residue was observed at the electrodes in flow compared to batch. Such a deposition leads to faster passivation of the electroactive surface, which further prolongs the required reaction times in batch.

### Reaction Scope

Having established optimal reaction conditions, we next investigated the generality of this electrochemical aziridination reaction. As shown in Figure 2, a wide variety of structurally and electronically diverse primary alkyl amines and alkenes can be readily engaged in this transformation. In most cases, the targeted aziridines could be isolated as pure compounds (product A) in good isolated yields, while other compounds proved to be too fragile to be isolated via standard workup and chromatographic procedures. This non-productive degradation is especially problematic for aziridines bearing small \( N \)-alkyl substituents and for very electron-rich aziridines, where nucleophilic ring-opening reactions with excess amine or HFIP can occur. We opted to isolate those compounds after subsequent ring opening with a suitable nucleophile, i.e., 4-bromothiophenol as the corresponding 1,2-amino thiether (product B). Interestingly, unprotected \( N \)-H aziridines (1 and 28) can be prepared by using ammonia in either water (40% w/w) or methanol (7 M). It should be noted that these \( N \)-H aziridines are extremely challenging to make and only recently a method toward these compounds using rhodium catalysis and \( O \)-(2,4-dinitrophenyl)hydroxylamine, as an electrophilic nitrogen reagent, was reported. Furthermore, a variety of primary amines are competent coupling partners in this electrochemical aziridination protocol, including methylamine (2), butylamine (3), isopropylamine (4), tert-butylamine (5), cyclopropanemethylamine (6), cyclobutylamine (7), cyclopentylamine (8) and cyclohexylamine (9), furnishing the targeted products in good isolated yields. The use of a narrow-gap flow cell allows us to readily scale the reaction conditions without the need for reoptimization; by pumping the reagents continuously into the reactor for a prolonged amount of time, compound 9 was isolated on a 10 mmol scale. Also activated amines, such as propargylamine (10), benzylamine (11–12), and \( \alpha \)-methylbenzylamine (13) are effective in this transformation. Finally, the esters of amino acids glycine (14) and phenylalanine (15) can be readily engaged in this aziridination protocol, providing opportunities for peptide modification. Notably, no racemization of the chiral center occurs under the electrochemical reaction conditions.

**Figure 2. Substrate Scope for the Electrochemical Aziridine Synthesis**

(A) Reaction Conditions: alkene (1 mmol), amine (5 equiv), HFIP (5 equiv), \( \gamma \)-terpinene (0.5 equiv), CH\(_3\)CN (0.1 M), C anode/Fe cathode, 2.5–5 mA cm\(^{-2}\). Decomposition refers to the instability of the product making isolation of the compound impossible. (B) Reaction Conditions: isolated yields refer to the ring-opened product. The nucleophilic quenching was carried out in the collection vial with 4-bromothiophenol (1.2 equiv) in the presence of BF\(_3\).OEt\(_2\) (10 mol %). Decomposition indicates full decomposition of the aziridine during the reaction or workup. Traces denote an inseparable mixture in which small amounts of aziridine (<5%) are still apparent. a10 mmol scale reaction, b\( cis\)-Stilbene used as a substrate.

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Similarly, we investigated the variability of the alkene reaction partner that is compatible with the reaction conditions. Both electro-neutral and electron-rich internal alkenes can be effectively reacted with cyclohexylamine. For instance, \((E)-1\)-methoxy-2-(prop-1-en-1-yl)benzene (16) and \((E)-1,2\)-dimethoxy-4-(prop-1-enyl)benzene (17) delivered the desired functionalized product in good yield. When the substrate contained two double bonds, the terminal double bond remained intact providing exclusively the internal trans-aziridine (18). This site specificity may be exploited for the selective aziridination of other polyene compounds. Next, a variety of stilbenes (19–22) were subjected to the reaction conditions, highlighting the breadth of our transformation in comparison with previous electrochemical aziridination strategies. Both cis- and trans-stilbene led to the same trans-aziridine (19-A). In addition, heterocyclic moieties like thiophene (23-A) are compatible with the electrochemical conditions, yielding synthetically useful quantities of the targeted aziridine. The cyclic alkene of precocene I (24-A), a natural chromene, was found to be an adequate reaction partner and furnished the targeted product in excellent yield. Next, we moved our attention to the functionalization of trisubstituted alkenes. Even for such sterically congested double bonds, the targeted product can be obtained in good to excellent yields for both electron-rich (25-A) and electron-neutral (26-A) alkenes. Notably, a spirocyclic aziridine (27-A) could be accessed as well using this electrochemical aziridination strategy.

**Formal Hydroamination**

All single electron transfer events relevant for the electrochemical aziridination occur at the anode, while the other half-reaction generates hydrogen as a useful yet hazardous byproduct at the cathode. We wondered if this hydrogen could be productively used in a follow-up hydrogenation step to form the corresponding hydroaminated product (Figure 3A). Indeed, by connecting a packed-bed reactor filled with Pd/C to the electrochemical flow reactor, the gas-liquid flow (Figure 3D) exiting the first reactor can be directed over the Pd/C bed without intermediate isolation (Figure 3C). To our delight, the corresponding hydroaminated products (Figure 3B) could be promptly obtained in good overall yield. Furthermore, we observed a single-phase exiting the packed-bed reactor indicating that nearly all hydrogen gas was consumed. In contrast, when this experiment was conducted in batch, additional hydrogen to compensate for leakage to the headspace was required to obtain a full conversion, albeit at a lower isolated yield (For 9-C: 50% for the batch hydrogenation versus 58% for the two-step flow protocol). It should be further noted that this paired reaction sequence in flow not only increases the yield and the atom efficiency of the process but also allows for facile reuse and recycling of the Pd/C bed and it reduces the risks associated with the handling of combustible hydrogen gas due to its immediate consumption in a follow-up reaction.48,53,54

**Mechanistic Investigation**

To obtain insights into the underlying mechanism, we performed additional experiments and studied possible mechanistic pathways by means of density functional theory (DFT) calculations (Figure 4). Cyclic voltammetry (CV) experiments revealed two subsequent oxidations of the alkene moiety (Figure 4A). The first oxidation results in the formation of a radical cation while the second oxidation leads to oxidative cleavage of the olefin. Small quantities of the corresponding Schiff base could be found in the reaction mixture confirming this hypothesis (Figure 4B).55,56 We anticipated that this overoxidation could be countered by adding a suitable donor of hydrogens and electrons. Indeed, 0.5 equivalents 1,4-cyclohexadiene (1,4-CHD) allowed for the reduction in the amount of imine significantly. Also, γ-terpinene, which is a more stable, non-toxic, and a cheaper alternative for 1,4-CHD, enabled the suppression of the overoxidation of the alkene as shown in
While our experimental results indicate that oxidation of the alkene is most likely the first step, CV analysis showed that a competitive activation of cyclohexylamine could occur as well (See Section S3). However, due to the irreversible nature of the oxidation of both reaction partners and the similar set-off potentials, it is difficult to predict the first anodic event in this aziridination protocol. Hence, we decided to

**Figure 3. Two-Step Hydroamination Protocol by Combining the Electrochemical Aziridine Synthesis and a Subsequent Hydrogenation**

(A) Schematic representation of the two-step protocol.

(B) Representative examples. Yields denote the overall yield over two steps.

(C) Picture of the two-step flow protocol: (i) syringe pump, (ii) potentiostat, (iii) electrochemical flow reactor, (iv) packed bed filled with Pd/C, and (v) collection vessel.

(D) Hydrogen gas bubbles exiting the electrochemical flow reactor.

Reaction conditions (C): alkene (1 mmol), amine (5 equiv), HFIP (5 equiv), γ-terpinene (0.2 equiv), CH₃CN (0.1 M), C anode/Fe cathode, 2.7 mA cm⁻². Flow conditions: Pd/C (150 mg cartridge). Batch conditions: Pd/C (5 mol %), H₂ (1 bar) resulted in 50% isolated yield. Additional hydrogenation in batch was carried out to achieve full conversion.

the CV (Figure 4A). While our experimental results indicate that oxidation of the alkene is most likely the first step, CV analysis showed that a competitive activation of cyclohexylamine could occur as well (See Section S3). However, due to the irreversible nature of the oxidation of both reaction partners and the similar set-off potentials, it is difficult to predict the first anodic event in this aziridination protocol. Hence, we decided to
obtain further insights via DFT calculations. These computational studies revealed that the anodic oxidation of anethole is indeed the first step in the electrochemical aziridinization ($\Delta G_{298K}^0 = +28.3 \text{ kcal mol}^{-1}$ and +1.226 V versus saturated calomel electrode [SCE]) (Figure 4D). An alternative pathway starting from the oxidation of the amine coupling partner, yielding the aminium radical, is energetically disfavored due to the higher required energy input ($\Delta G_{298K}^0 = +38.4 \text{ kcal mol}^{-1}$ and +1.665 V versus SCE) (see Section S4.2). However, we cannot exclude that for some substrate combinations, the reaction can be initiated via the formation of the aminium radical. Once the radical cation of
anethole is formed, it readily reacts with an amine coupling partner yielding intermediate C (Figure 4D) via a low-barrier transition state. After deprotonation and subsequent single electron transfer, a carbocation (E) is formed, which can undergo a rapid barrier-less intramolecular ring closure and deprotonation to yield the target aziridine (F). The reaction is exergonic after the initial oxidation (ΔG° 298K = -11.7 kcal mol⁻¹) but endergonic with respect to the starting materials, which is consistent with the required energy input in the form of electrons during the reaction. Further, the conversion of both cis- and trans-alkenes to the same trans-aziridine supports this stepwise mechanistic proposal (Figure 2, 19-A).

Finally, this mechanistic rationale also explains the observed scope and limitations. The protocol is currently limited to electron-rich β-substituted styrenes, which can be attributed to a combination of their accessible oxidation potential and the steric protection of the radical cation intermediate. Alkenes with higher oxidation potentials (e.g., styrene or trans-β-methylstyrene, see Section S8) did not afford the desired aziridines, likely due to excessive amine oxidation at the electrode prior to alkene oxidation. 4-Methoxystyrene, as a terminal alkene substrate, has an accessible oxidation potential (see Table S11), but lacks steric protection of the β-substituent, therefore making it prone to degradative side-reactions after anodic oxidation. With regard to the amine coupling partner, a broad scope of nucleophilic alkyl amines was compatible with the reaction conditions (Figure 2). In contrast, less-nucleophilic aryl amines were not able to react with the radical cation B (Figure 4D).

Conclusion
The electrochemical approach reported herein demonstrates the possibility to directly convert olefins and primary alkyl amines into synthetically useful aziridines. We expect that the operational simplicity of this protocol and its potential to use common and broadly available starting materials will find widespread use among organic chemistry practitioners both in academia and industry.

EXPERIMENTAL PROCEDURES
Resource Availability
Lead Contact
Further information and requests for resources should be directed to and will be fulfilled by the Lead Contact, Timothy Noël (t.noel@uva.nl).

Materials Availability
Unique and stable reagents generated in this study will be made available on request, but we might require a payment and/or a completed materials transfer agreement if there is potential for commercial application.

Data and Code Availability
There is no dataset and code associated with the paper. Full experimental procedures are provided in the Supplemental Information.

General Procedure for Electrochemical Aziridination in Flow
Procedure A
Alkene (1.0 equiv, 2.0 mmol), together with amine (5.0 equiv, 10.0 mmol), hexafluoroisopropanol (HFIP, 5.0 equiv, 10.0 mmol, 1.05 mL), and γ-terpinene (0.5 equiv, 1.0 mmol, 0.16 mL) were dissolved in acetonitrile using a 20 mL volumetric flask (0.1 M). The mixture was swirled until homogeneous and taken up in a 20 ml disposable syringe. The solution was pumped through the electrochemical setup with a fixed flowrate of 0.15 mL/min to give a residence time of 5 min in the active part.
of the electrochemical flow reactor, equipped with a graphite anode, a steel cathode, and distanced by a 0.25 mm thick Teflon gasket. The first fraction was discarded to ensure steady-state data collection, after which a constant current (selected on the basis of the voltammograms recorded) was applied. The reaction mixture was collected in a vial cooled at 0°C for 67 min, which corresponds to 1.0 mmol scale. The crude mixture was concentrated under vacuum at room temperature to prevent decomposition of the product and directly purified by flash column chromatography on silica gel.

Procedure B
Alkene (1.0 equiv, 2.0 mmol), together with amine (5.0 equiv, 10.0 mmol), hexafluoroisopropanol (HFIP, 5.0 equiv, 10.0 mmol, 1.05 mL), and γ-terpinene (0.5 equiv, 1.0 mmol, 0.16 mL) were dissolved in acetonitrile using a 20 mL volumetric flask (0.1 M). The mixture was swirled until homogeneous and taken up in a 20 mL disposable syringe. The solution was pumped through the electrochemical setup with a fixed flow rate of 0.15 mL/min to give a residence time of 5 min in the active part of the electrochemical flow reactor, equipped with a graphite anode, a steel cathode, and distanced by a 0.25-mm thick Teflon gasket. The first fraction was discarded to ensure steady-state data collection, after which a constant current (selected on the basis of the voltammograms recorded) was applied. The reaction mixture was collected in a vial containing a stirred solution of 4-bromothiophenol (1.2 mmol, 227 mg) and BF₃·Et₂O (0.1 mmol, 12.7 μL) in acetonitrile (5 mL) for 67 min, which corresponds to 1.0 mmol scale. The crude mixture was concentrated under vacuum and dissolved in methanol (5 mL). Subsequently, NaBH₄ (0.26 mmol, 10 mg) was added and the solution was stirred for 1 h at room temperature. The crude mixture was concentrated under vacuum and purified by flash column chromatography on silica gel.

General Procedure for Formal Electrochemical Hydroamination in Flow
Alkene (1.0 equiv, 2.0 mmol), together with amine (5.0 equiv, 10.0 mmol), hexafluoroisopropanol (HFIP, 5.0 equiv, 10.0 mmol, 1.05 mL), and γ-terpinene (0.2 equiv, 0.4 mmol, 64 μL) were dissolved in acetonitrile using a 20 mL volumetric flask (0.1 M). The mixture was swirled until homogeneous and taken up in a 20 mL disposable syringe. The solution was pumped through the electrochemical setup with a fixed flow rate of 0.15 mL/min to give a residence time of 5 min in the active part of the electrochemical flow reactor, equipped with a graphite anode, a steel cathode and distanced by a 0.25-mm thick Teflon gasket. A self-made packed bed reactor (1 mL), filled with Pd/C (200 mg) and glass beads (500 mg), was connected to the outlet of the electrochemical reactor. The first fraction was discarded to ensure steady-state data collection, after which a constant current (selected on the basis of the voltammograms recorded) was applied. The reaction mixture was collected in a vial for 67 min, which corresponds to a 1.0 mmol scale. The crude mixture was concentrated under vacuum and purified by flash column chromatography on silica gel.

SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.chempr.2020.12.002.

ACKNOWLEDGMENTS
We acknowledge financial support from the Dutch Science Foundation (NWO) for a VIDI grant for T.N. (SensPhotoFlow, no. 14150) and the Estonian Research Council
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**AUTHOR CONTRIBUTIONS**

T.N. coordinated the project and secured the project funding. T.N., M.O., and G.L. wrote the manuscript with the help of all co-authors. T.N., M.O., and G.L. conceived the initial project idea. M.O. and G.L. designed and carried out the majority of the experiments. N.P.L. and B.d.B. carried out the DFT calculations. M.D. contributed to the synthesis of some substrates and electrochemical aziridination. M.O., G.L., and A.A.B. carried out the optimization reactions and demonstrated the feasibility of the transformation. All authors discussed the project progress together at regular intervals and provided input for future experiments.

**DECLARATION OF INTERESTS**

The authors declare no competing interests.

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