Flow Electrosynthesis of Sulfoxides, Sulfones and Sulfoximines without Supporting Electrolytes

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Graphical abstract:

Abstract:
An efficient electrochemical flow process for the selective oxidation of sulfides to sulfoxides and sulfones and of sulfoxides to $N$-cyanosulfoximines has been developed. In total, 69 examples of sulfoxides, sulfones, and $N$-cyanosulfoximines have been synthesized in good to excellent yields and with high current efficiencies. The synthesis was assisted and facilitated through a supporting electrolyte-free, fully automated electrochemical protocol highlighting the advantages of flow electrolysis.
Introduction

Since ancient times, organosulfur compounds have attracted attention of chemists because of their importance in medicine and pharmaceutical products.\(^1,2\) Many biologically active compounds and natural products contain sulfoximine, sulfoxide, or sulfone functional groups. Notably, sulfoximine, sulfoxide, or sulfone functional groups are very important in antibiotic, musculoskeletal, metabolism, alimentary tract, or anti-inflammatory drugs (Figure 1).\(^3,4,5\)

![Chemical structures of biological relevant sulfoxide, sulfone and sulfoximine compounds.](image)

**Figure 1.** Examples of biological relevant sulfoxide, sulfone and sulfoximine compounds.

Additionally, there is an exceptionally rich chemistry of organosulfur compounds in organic synthesis. The oxygen of the sulfinyl group has the ability to coordinate with different carbon ligands and metal ions, in addition to the stereoelectronic effects and the conformational stability that exists in the sulfinyl group. Sulfoximines and sulfoxides are stable functional groups which have been used as ligands as enantiopure compounds also in asymmetric synthesis.\(^6,7,8,9\).
Many variations of the organosulfur oxidation process have been developed to generate more viable and long-lasting oxidative procedures that will have an impact on the pharmaceutical industry to reduce cost, waste, and by-products. Generally, such oxidation processes can be performed using different oxidants such as peroxides,\textsuperscript{10,11} photocatalytic processes,\textsuperscript{8,12} or hyper-valent iodine reagents.\textsuperscript{13,14,15} Continuous processes have been investigated as well.\textsuperscript{16} Despite these developments in organosulfur oxidation processes, most lack industrial interest owing to sustainability, scaling-up, and safety concerns.

Recently, a resurgence of organic electrosynthesis has been observed in the context of modern synthesis.\textsuperscript{17,18,19,20,21} As a sustainable tool, electrons can be used to perform oxidation and reduction processes in clean and often environmentally benign procedures by replacing chemical oxidants and reductants with inexpensive electricity.\textsuperscript{22,23} Anodic oxidation of sulfur has been applied in the successful synthesis of organosulfur compounds through controlled potential electrolysis. Noël and co-workers have reported the direct oxidation of thioethers to the corresponding sulfoxides or sulfones in the presence of supporting electrolytes under flow reaction conditions.\textsuperscript{24} Yudin \textit{et al.} reported a method for the amination of sulfoxides in batch electrolysis using a divided cell.\textsuperscript{25} Potentiostatic anodic oxidation conditions have been applied in these reactions. Generally, using a divided cell leads to increased cell potentials.\textsuperscript{26}

There has been significant growth in the field of electroorganic synthesis over the last few years. Electroorganic synthesis in a flow reactor is a highly useful tool to perform redox transformations in a more proficient manner while overcoming some of the constraints such as low reaction rates, large current gradients, and low conductivity of organic solvents in batch electrolysis. In addition, there have been innovations in flow cells that have permitted selective and successful synthesis exploiting the usually high electrode surface-to-reactor volume ratio, which in turn translates to a higher mass transfer and higher productivity.\textsuperscript{27,28,29,30}

\textbf{Results and Discussion}

In extension of our previous efforts towards the development of flow tools and techniques to implement flow transformations,\textsuperscript{31,32} we recently have reported a reaction without using supporting electrolyte\textsuperscript{33} and disclosed the first use of an integrated flow electrochemical reactor in an automated way.\textsuperscript{34,35} We saw this as an opportunity to further improve and simplify the oxidation methodologies of organosulfur compounds.\textsuperscript{36}

In this work, we report a green synthesis method of sulfoxides, sulfones and sulfoximines without any additional supporting electrolyte through a controlled current using an
electrochemical flow reactor attached to a fully automated system. Unique features of the Va-
pourtec automatic flow system with integrated electrochemical ion microflow reactor speed up
the reaction while largely reducing the amount of manpower needed to execute the reactions.
The device self-loads chemicals, collects reaction products, and auto-cleans the system while
allowing for specific reaction temperatures, flow rates, and current control for each reaction.

Initially, the reaction of thioanisol (1a) in a mixture of acetonitrile/water (9:1) was exam-
ined using different reaction conditions, electrode materials, and electrical current. The reaction
proceeds in absence of any additional supporting electrolyte due to the close distance of the
electrodes in the flow reactor (0.5 mm). In this reaction, different electrodes such as graphite
(Gr), platinum (Pt), platinum coated on Ti, glassy carbon (GC) and stainless steel (Fe) were
screened and among these, Gr as anode and stainless steel as cathode showed the highest se-
lectivity towards sulfoxide formation in 98% yield (Table 1, entries 1-10). The formation of sul-
fone as over oxidized product in 3-12% yield was observed with Pt as anode material (Table 1,
entries 1-3). Gr and GC anode gave similar yields, and Gr was selected as the most cost-effi-
cient electrode material (Table 1, entries 6-8). To reduce the reaction time, the flow rate was in-
creased from 0.1 mL min\(^{-1}\) to 0.3 mL min\(^{-1}\). At 0.2 mL min\(^{-1}\) still 98% yield was obtained but at
higher flow rates lower yields were observed (see supporting information). Replacing acetonitrile
with methanol or water with hexafluoro-2-propanol (HFIP) resulted in decreased yields (see sup-
porting information). An increase in the sulfide concentration led to reduced yields of the product
and traces of sulfone were detected (see the supporting information). An increase in the charge
from 2 F to 4 F led to the formation of sulfone in 73% yield. Replacing the Gr by Pt electrode
and applying 5 F led to significant yields of sulfone (Table 1, entry 12). Passing more charge did
not improve the yield further (Table 1, entry 13). The optimal reaction conditions for sulfoxide
and sulfone formation are shown in entry 7 and entry 12 of Table 1, respectively.
Table 1. Conditions: [1a] = 0.1 M, MeCN/H₂O (9:1), flow rate = 0.2 mL min⁻¹, at room temperature, reactor volume: 0.6 mL. ¹ Determined by ¹H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Anode</th>
<th>Cathode</th>
<th>Current [mA]</th>
<th>Conversion [%]⁰</th>
<th>2a [%]⁰</th>
<th>3a [%]⁰</th>
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<tr>
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<td>Pt</td>
<td>Pt</td>
<td>64 (2F)</td>
<td>90</td>
<td>83</td>
<td>7</td>
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<tr>
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<td>Pt</td>
<td>Pt on Ti</td>
<td>64 (2F)</td>
<td>95</td>
<td>92</td>
<td>3</td>
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<tr>
<td>3</td>
<td>Pt</td>
<td>Gr</td>
<td>64 (2F)</td>
<td>98</td>
<td>86</td>
<td>12</td>
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<td>4</td>
<td>Pt on Ti</td>
<td>Pt</td>
<td>64 (2F)</td>
<td>90</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>Gr</td>
<td>Gr</td>
<td>64 (2F)</td>
<td>96</td>
<td>96</td>
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<tr>
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<td>Gr</td>
<td>Pt</td>
<td>64 (2F)</td>
<td>98</td>
<td>98</td>
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</tr>
<tr>
<td>7</td>
<td>Gr</td>
<td>Fe</td>
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<td>98</td>
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<td>GC</td>
<td>Pt</td>
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<td>64 (2F)</td>
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<td>Fe</td>
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<tr>
<td>11</td>
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<td>Fe</td>
<td>128 (4F)</td>
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<tr>
<td>12</td>
<td>Pt</td>
<td>Fe</td>
<td>160 (5F)</td>
<td>98</td>
<td>11</td>
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<td>13</td>
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<td>192 (6F)</td>
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<td>12</td>
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With the optimized reaction conditions in hand, the influence of the applied current on the observed high selectivity was explored in the synthesis of sulfoxides and sulfones derivatives as shown in Scheme 1. Aryl thioethers with electron-donating and electron-withdrawing substituents offered sulfoxides or sulfones in good to excellent yields. Thioanisol (1a) provided sulfoxide and sulfone in excellent yield of 87% and 81% respectively. Thioanisol derivatives 1b–o reacted efficiently to afford the desired sulfoxides 2b–o and sulfones 3b–o in 15–90% yield. Functional groups, such as fluoro-, chloro-, bromo- and aldehyde-substitutions were well tolerated. Also, 3,5-dichlorothioanisol 1p delivered the desired products 2p and 3p in reasonable yields.

Furthermore, sulfides containing different alkyl and aryl groups such as ethyl, propyl, cyclopropyl, allyl, benzyl, and phenyl 1q–1v were oxidized under optimized conditions, giving
moderate to good, isolated yields. Sulfide 1w bearing a ketone also offered sulfoxide 2w and sulfone 3w products. Of note is that benzyl substituted 1u did not form the desired sulfone.

\[
\begin{array}{c}
1 \\
\text{R}^1-S\text{R}^2
\end{array} \xrightarrow{\text{method A}} \begin{array}{c}
2 \\
\text{R}^1\text{S}^\circ\text{R}^2
\end{array} \text{ or } \begin{array}{c}
3 \\
\text{R}^1\text{S}^\circ\text{O}\text{R}^2
\end{array}
\]

<table>
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<tr>
<th>Substrate</th>
<th>Method A</th>
<th>Method B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a R = H</td>
<td>2a (87%)</td>
<td>3a (81%)</td>
</tr>
<tr>
<td>1b R = Me</td>
<td>2b (89%)</td>
<td>3b (83%)</td>
</tr>
<tr>
<td>1c R = Br</td>
<td>2c (86%)</td>
<td>3c (79%)</td>
</tr>
<tr>
<td>1d R = Cl</td>
<td>2d (83%)</td>
<td>3d (73%)</td>
</tr>
<tr>
<td>1e R = F</td>
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</tr>
<tr>
<td>1f R = CN</td>
<td>2f (82%)</td>
<td>3f (68%)</td>
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<tr>
<td>1g R = OMe</td>
<td>2g (88%)</td>
<td>3g (78%)</td>
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<tr>
<td>1h R = CHO</td>
<td>2h (68%)</td>
<td>3h (35%)</td>
</tr>
<tr>
<td>1i R = NO₂</td>
<td>2i (63%)</td>
<td>3i (28%)</td>
</tr>
<tr>
<td>1j R = Me</td>
<td>2j (86%)</td>
<td>3j (78%)</td>
</tr>
<tr>
<td>1k R = Br</td>
<td>2k (90%)</td>
<td>3k (71%)</td>
</tr>
<tr>
<td>1l R = Cl</td>
<td>2l (85%)</td>
<td>3l (74%)</td>
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<td>1m R = Br</td>
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<td>3m (51%)</td>
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<tr>
<td>1n R = Cl</td>
<td>2n (79%)</td>
<td>3n (53%)</td>
</tr>
<tr>
<td>1o R = I</td>
<td>2o (34%)</td>
<td>3o (15%)</td>
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<tr>
<td>1p</td>
<td>2p (89%)</td>
<td>3p (60%)</td>
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<td>1q R = Et</td>
<td>2q (91%)</td>
<td>3q (74%)</td>
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<tr>
<td>1r R = nPr</td>
<td>2r (86%)</td>
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<tr>
<td>1s R = cyclopropyl</td>
<td>2s (84%)</td>
<td>3s (72%)</td>
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<tr>
<td>1t R = allyl</td>
<td>2t (67%)</td>
<td>3t (18%)</td>
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<tr>
<td>1u R = benzyl</td>
<td>2u (78%)</td>
<td>3u (0%)</td>
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<tr>
<td>1v R = Ph</td>
<td>2v (70%)</td>
<td>3v (70%)</td>
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<tr>
<td>2w</td>
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<td>2x</td>
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</tr>
<tr>
<td>1y</td>
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</tr>
<tr>
<td>1z X = CH₂</td>
<td>2z\textsuperscript{a} (72%)</td>
<td>3z\textsuperscript{a} (51%)</td>
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<tr>
<td>1aa X = O</td>
<td>2aa\textsuperscript{a} (67%)</td>
<td>3aa\textsuperscript{a} (48%)</td>
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</table>

**Scheme 1** Substrate scope for the electrochemical oxidation of sulfides. Method A: \[ [1] \] = 0.1 M, MeCN/H₂O (9:1), Gr (+)/Pt(-), 64 mA, flow rate = 0.2 mL min⁻¹, reactor volume: 0.6 mL, RT. Method B: \[ [1] \] = 0.1 M, MeCN/H₂O (9:1), Pt(+) /Fe(-), 160 mA, flow rate = 0.2 mL min⁻¹, reactor volume: 0.6 mL, RT. \[ \textsuperscript{a} \] 0.01 M of Bu₄NBF₄ was used.
Heterocyclic thioether 1x was also amenable to the reaction conditions. Moreover, these two methods were successfully applied to oxidize dibutyl sulfide 1y and cyclic sulfide 1z and heterocyclic sulfide containing one oxygen atom 1aa to offer the corresponding sulfoxide and sulfone products. In these reactions, a catalytic amount of supporting electrolyte Bu₄NBF₄ was added to increase the cell conductivity and decrease the high cell voltage. For sulfoxides 2 using method A and sulfones 3 using method B, high selectivities were observed in all cases.

This method was then extended to the synthesis of sulfoximines 5. However, a simple addition of cyanamide 4 to the electrolysis solution led only to the formation of the corresponding sulfoxides. Therefore, sulfoxide 2a prepared in the previous reaction was examined as a starting material together with cyanamide 4 under different reaction conditions for the formation of 5a.

Initially, Gr anode and different cathodes materials such as Gr, Pt and Fe were investigated but the reaction did not occur (Table 2, entry 1). The use of platinum anode and graphite cathode led only to a low yield of 8% (Table 2, entry 2) while the yield increased when platinum was used as anode and cathode (Table 2, entry 3). Hexafluoro-2-propanol (HFIP) was determined to be the solvent of choice, other solvents such as acetonitrile, methanol and trifluoroethanol (TFE) led to lower product yields (Table 2, entry 4-6). No product was formed when different supporting electrolytes were examined (Table 2, entry 7). Interestingly, the highest yield was observed in the absence of any supporting electrolyte (Table 2, entry 8), although for all these experiments a thinner spacer (0.25 mm thickness) was used to reduce the high voltage observed in the reactions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Anode</th>
<th>Cathode</th>
<th>Solvent</th>
<th>Conversion [%]a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C</td>
<td>C, Pt or Fe</td>
<td>HFIP</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Pt</td>
<td>C</td>
<td>HFIP</td>
<td>8</td>
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<tr>
<td>3</td>
<td>Pt</td>
<td>Pt</td>
<td>HFIP</td>
<td>25</td>
</tr>
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<td>4</td>
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<td>Pt</td>
<td>MeCN</td>
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<td>5</td>
<td>Pt</td>
<td>Pt</td>
<td>MeOH</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>Pt</td>
<td>Pt</td>
<td>TFE</td>
<td>6</td>
</tr>
<tr>
<td>7</td>
<td>Pt</td>
<td>Pt</td>
<td>HFIP</td>
<td>0b</td>
</tr>
<tr>
<td>8</td>
<td>Pt</td>
<td>Pt</td>
<td>HFIP</td>
<td>34c</td>
</tr>
</tbody>
</table>

- a: Conversion determined by spectroscopic methods
- b: No product formed
- c: Highest yield
Table 2. Conditions: [2a] = 0.05 M, [4] 0.075 M, flow rate = 0.1 mL min\(^{-1}\), \(I = 24\) mA (3 F), supporting electrolyte: Et\(_4\)NCl (0.01 M), reactor volume: 0.3 mL. \(^a\) Determined by \(^1\)H NMR spectroscopy. \(^b\) supporting electrolyte: Et\(_4\)NI, Et\(_4\)NBr or \(n\)-Bu\(_4\)NBr. \(^c\) Without supporting electrolyte.

Initial screening showed that the platinum electrodes and hexafluoro-2-propanol (HFIP) were the appropriate materials for this reaction. It is known that HFIP has the ability to stabilize radicals in electrochemical reactions.\(^{38}\) To study the effect of the reaction time, the flow rate was screened from 0.075 mL min\(^{-1}\) to 0.2 mL min\(^{-1}\) and an improvement in yield was observed with a flow rate of 0.15 mL min\(^{-1}\) (Table 3, entry 3). Then, increasing the electrical charge from 3 F to 6 F led to a further increase in the yield to 68% (Table 3, entries 5+6). A decrease or increase in the sulfoxide concentration (0.025 M or 0.1 M) led to reduced yields of the product (Table 3, entries 7+8).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Flow rate (mL min(^{-1}))</th>
<th>I (mA)</th>
<th>F</th>
<th>Conversion [%](^a)</th>
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<tr>
<td>1</td>
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<td>18</td>
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<td>33</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>24</td>
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<td>34</td>
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<td>3</td>
<td>0.15</td>
<td>36</td>
<td>3</td>
<td>40</td>
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<tr>
<td>4</td>
<td>0.2</td>
<td>48</td>
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<td>17</td>
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<td>68</td>
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<tr>
<td>7</td>
<td>0.15</td>
<td>36</td>
<td>6(^b)</td>
<td>43</td>
</tr>
<tr>
<td>8</td>
<td>0.15</td>
<td>144</td>
<td>6(^c)</td>
<td>62</td>
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</table>

Table 3. Conditions: [2a] = 0.05 M, [4] 0.075 M, reactor volume: 0.3 mL. \(^a\) Determined by \(^1\)H NMR spectroscopy. \(^b\) [2a] = 0.025 M. \(^c\) [2a] = 0.1 M.

With the optimized conditions in hand, different sulfoxides obtained from the previous method was evaluated. Both electron-donating and electron-withdrawing substituents in the \textit{para}- and \textit{meta}-positions of alkyl aryl sulfoxides delivered good yields of the corresponding \textit{N}-cyanosulfoximines \(5a\)–\(i\). No reaction occurred with \textit{ortho}-substituted sulfoxides \(5j\)–\(k\), probably because of steric reasons. Replacing the S-methyl group to other alkyl groups resulted corresponding sulfoximine where S-ethyl-S-phenylsulfoximine \(5m\), S-propyl-S-phenylsulfoximine \(5n\) and S-cyclopropyl-S-phenylsulfoximine \(5o\) were obtained in 43%, 40% and 38% yield, respectively. However, diaryl sulfoxide provided only a low yield of \(5p\). Notably, S-methyl-S-pyridinyl-sulfoximine \(5q\) and cyclic sulfoximines \(5r\) were also obtained in moderate yields as shown in
Scheme 2. Finally, the protected \( N \)-cyanosulfoximines were converted into \( NH \)-sulfoximines 6 by treatment with trifluoroacetic anhydride (TFAA), followed by the addition of \( K_2CO_3 \).^{39}

\[
\begin{align*}
\text{Scheme 2. Substrate scope for the electrochemical formation of } N \text{-cyanosulfoximines. Conditions: } & [2] = 0.05 \text{ M, } [4] = 0.125 \text{ M, HFIP, Pt (+)/Pt (-), 72 mA, flow rate } = 0.15 \text{ mL min}^{-1}, \text{ reactor volume: 0.3 mL, RT.} \\
\text{A combination of both oxidation sequences from sulfides to } N \text{-cyanosulfoximines as the final product in one flow setup was investigated. For this purpose, two electrochemical flow reactors were connected with a packed bed column of } MgSO_4 \text{ in between, which allowed an in-}
\end{align*}
\]
line removal of water. As shown in Scheme 3, the thioanisol 1a in HFIP/H$_2$O was injected to the first reactor to form sulfoxide 2a, followed by the packed bed filled with MgSO$_4$ to remove the remaining water. The cyanamide 4 in HFIP was added before the second reactor to deliver the N-cyanosulfoximine 5a as final product in 26% yield overall. The use of HFIP as solvent in place of MeCN in the first step had an adverse impact on the sulfoxide formation.

Scheme 3. Amination of sulfide 1a to sulfoximine 5a in a combined flow setup.

To further explore the reaction mechanism, the oxidation of 1a was carried out in the absence of water with addition of Bu$_4$NBF$_4$ as supporting electrolyte and no sulfoxide product was observed and only starting material was detected. Also, we conducted the oxidation of thioanisol 1a in presence of H$_2^{18}$O under the same reaction conditions. The sulfoxide product contained $^{18}$O labeling which was confirmed by HRMS analysis. This result proves that the oxygen atom stems from water and any dissolved O$_2$ did not play a role in this reaction.

Additionally, cyclic voltammetry studies of the sulfide and sulfoxide in acetonitrile were conducted to obtain insight into the reaction mechanism in various solutions. Two one-electron oxidation peaks of thioanisol 1a were observed in acetonitrile at $E_p = 1.57$ V and $E_p = 1.9$ V (Figure 2a, yellow line), while there was only one apparent oxidation peak for sulfoxide 2a at $E_p = 2.05$ V (Figure 2a, blue line). Also, the cyclic voltammetry of sulfoxide 2a in HFIP showed one oxidation peak at $E_p = 2.1$ V (Figure 2b, orange line), while there was no oxidation peak for cyanamide 4 (Figure 2b, gray line).
Figure 2. Cyclic voltammetry (CV) studies of thioanisol 1a (yellow line) and sulfoxide 2a (blue line) in MeCN (a). Sulfoxide 2a (orange line) and cyanamide 4 (gray line) in HFIP (b). GC carbon disk working electrode (immersed surface area: 3 mm$^2$), Pt counter electrode (immersed surface area: 1.2 mm$^2$), Ag/0.01 M AgCl reference electrode, 20 mV s$^{-1}$.

Based on our initial studies and according to previous literature reports on the oxygenation of sulfides,\textsuperscript{40,41,42} the proposed mechanism for the oxygenation and amination of sulfides / sulfoxides is shown in Scheme 4. In the initial step, sulfide 1 is oxidised at the anode to produce sulfide radical cation intermediate I while water is reduced at the cathode to generate the hydroxide ions (OH$^-$), which then react with I to generate the sulfoxide 2. Subsequently, sulfoxide 2 undergoes a second single electron transfer (SET) generating sulfoxide radical cation intermediate II which reacts with hydroxide ions (OH$^-$) to produce sulfone 3 or react with cyanamide 4 to produce N-cyanosulfoximines 5. The proton generated in this process will be finally reduced to hydrogen at the cathode.

scheme 4

Scheme 4. Proposed mechanism for the electrochemical synthesis of sulfoxides, sulfones and sulfoximines.
Conclusions

In conclusion, an electrochemical flow protocol for the rapid synthesis of sulfoxides, sulfones and N-cyanosulfoximines has been developed. A broad range of sulfoxides (27 examples), sulfones (26 examples), and N-cyanosulfoximines (16 examples) were synthesized in good to excellent yields using an automated electrochemical flow system in the absence of any supporting electrolyte.

Experimental Section

All solvents, reagents, thioether substrates 1, and cyanamide 4 were purchased from Sigma-Aldrich, Acros organic, fluorochem, alfa aesar and TCI chemicals and used as received without purification or drying. Thin-layer chromatography (TLC) was performed on pre-coated aluminium sheets of Merck silica gel 60 F254 (0.20 mm) and visualized by UV radiation (254 nm). Automated column chromatography was performed on a Biotage® Isolera Four using Biotage® cartridges SNAP Ultra 10 g. 1H NMR, 13C NMR and 19F NMR spectra were measured on Bruker DPX 400 or 500 apparatus and were referenced to the residual proton solvent peak (1H: CDCl₃, δ 7.26 ppm; DMSO-d₆, δ 2.50 ppm) and solvent 13C signal (CDCl₃, δ 77.2 ppm, DMSO-d₆, δ 39.5). Chemical shifts δ were reported in ppm, multiplicity of the signals was declared as followed: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex = sextet, hep = septet, dd = doublet of doublets, m = multiplet, b = broad; and coupling constants (J) in Hertz. IR spectra were recorded on a Shimadzu FTIR Affinity-1S apparatus. Wavenumbers are quoted in cm⁻¹. All compounds were measured neat directly on the crystal of the IR machine. Mass spectrometric measurements were performed by R. Jenkins, R. Hick, T. Williams and S. Waller at Cardiff University on a Water LCR Premier XEtof. Ions were generated by Electron Ionisation (EI) and Electron Spray (ES). The molecular ion peaks values quoted for either molecular ion [M]+, molecular ion plus hydrogen [M+H]+ or molecular ion plus sodium [M+Na]+. Melting points were measured using a Gallenkamp variable heater with samples in open capillary tubes. The electrochemical reactions were carried out in a galvanostatic mode using a Vapourtec Ion Electrochemical flow reactor powered up by an Ion electrochemical power supply. The cyclic voltamogram studies were performed using an Orygalys OGF500 Potentiostat / Galvanostat with OGFPWR power supply.

General procedure for the electrochemical oxidation of sulfides to sulfoxides (GP1). The electrolysis was performed in an undivided cell using a Vapourtec Ion Electrochemical Flow Reactor (reactor volume = 0.6 mL, spacer 0.5 mm) using a graphite (Gr) electrode as the anode
and a stainless steel (Fe) electrode as the cathode (active surface area: $A = 12 \text{ cm}^2$). A solution of sulfide (0.1 M) in mixture of $\text{CH}_3\text{CN}$ and $\text{H}_2\text{O}$ (9:1) placed in 20 mL vial screw cap with hole with PTFE/silicone septum. The reaction mixture was injected to 18 mL sample loop. After that, the reactor temperature was set at room temperature with the flow rate 0.2 mL/min and the current was set at 64 mA turn on automatically. Then, solutions were pumped into the electrochemical reactor. After reaching a steady state, the solution (15 mL, 1.5 mmol) was collected automatically into a glass vial. The solvent was removed under vacuum. The crude product was purified by column chromatography (EtOAc/cyclohexane).

**General procedure for the electrochemical oxidation of sulfides to sulfones (GP2).** The electrolysis was performed in an undivided cell using a Vapourtec Ion Electrochemical Flow Reactor (reactor volume = 0.6 mL, spacer 0.5 mm) using a graphite (Pt) electrode as the anode and a stainless steel (Fe) electrode as the cathode (active surface area: $A = 12 \text{ cm}^2$). A solution of sulfide (0.1 M) in mixture of $\text{CH}_3\text{CN}$ and $\text{H}_2\text{O}$ (9:1) placed in 20 mL vial screw cap with hole with PTFE/silicone septum. The reaction mixture was injected to the 18 mL sample loop. After that, the reactor temperature was set at room temperature with the flow rate 0.2 mL/min and the current was set at 160 mA turn on automatically. Then, solutions were pumped into the electrochemical reactor. After reaching a steady state, the solution (15 mL, 1.5 mmol) was collected automatically into a glass vial. The solvent was removed under vacuum. The crude product was purified by column chromatography (EtOAc/cyclohexane).

**General procedure for the electrochemical imination of sulfoxides (GP3).** The electrolysis was performed in an undivided cell using a Vapourtec Ion Electrochemical Flow Reactor (reactor volume = 0.3 mL, spacer 0.3 mm) using a platinum (Pt) electrode as anode and cathode (active surface area: $A = 12 \text{ cm}^2$). A solution of sulfoxide (0.05 M) and cyanamide (1.5 equiv.) in HFIP (12 mL) was placed in a 20 mL vial screw cap with hole with PTFE/silicone septum. The reaction mixture was injected to the 12 mL sample loop. After that, the reactor temperature was set at room temperature with the flow rate 0.15 mL/min and the current was set at 72 mA turn on automatically. Then, solutions were pumped into the electrochemical reactor. After reaching a steady state, the solution (10 mL, 0.5 mmol) was collected automatically into a glass vial. The solvent was removed under vacuum. The crude product was purified by column chromatography (EtOAc/cyclohexane).
General procedure for the reduction of $N$-cyanosulfoximines (GP4). To a mixture solution of $N$-cyanosulfoximine (0.5 mmol) in CH$_2$Cl$_2$ (10 mL) at 0 °C, TFAA (1.5 mmol) was added. The reaction mixture was allowed to stirrer at room temperature until the starting material was consumed (monitored by TLC). The mixture was quenched with water (10 mL). The aqueous layer was extracted with CH$_2$Cl$_2$ (3 x 10 mL). The combined organic layers were dried over anhydrous MgSO$_4$, filtered and evaporated. The residue was purified by column chromatography (EtOAc/cyclohexane).

(Methylsulfinyl)benzene (2a). Compound 2a was synthesized following GP1, using methyl(phenyl)sulfane (1a, 186 mg, 1.5 mmol) to give the product as colourless oil. It was purified by column chromatography on silica gel using ethyl acetate (100 %) to obtain 87% yield (183 mg). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.72 – 7.63 (m, 2H), 7.57 – 7.48 (m, 2H), 2.72 (s, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$): δ 145.7, 131.1, 129.4, 123.6, 44.0 ppm. The spectroscopic data agree with the literature.

1-Methyl-4-(methylsulfinyl)benzene (2b). Compound 2b was synthesized following GP1, using methyl(p-tolyl)sulfane (1b, 207 mg, 1.5 mmol) to give the product as colourless oil. It was purified by column chromatography on silica gel using ethyl acetate (100 %) to obtain 89% yield (207 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.54 (d, $J$ = 7.4 Hz, 2H), 7.33 (d, $J$ = 7.6 Hz, 2H), 2.70 (s, 3H), 2.41 (s, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) δ 142.6, 141.7, 130.2, 123.7, 44.1, 21.5 ppm. The spectroscopic data agree with the literature.

1-Bromo-4-(methylsulfinyl)benzene (2c). Compound 2c was synthesized following GP1, using (4-bromophenyl)(methyl)sulfane (1c, 305 mg, 1.5 mmol) to give the product as white solid. It was purified by column chromatography on silica gel using ethyl acetate (100 %) to obtain 86% yield (282 mg). m.p.: 86-88 °C [Lit.: 85-87 °C]. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.67 (d, $J$ = 8.3 Hz, 2H), 7.52 (d, $J$ = 8.3 Hz, 2H), 2.71 (s, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) δ 145.1, 132.8, 125.7, 125.4, 44.2 ppm. The spectroscopic data agree with the literature.

1-Chloro-4-(methylsulfinyl)benzene (2d). Compound 2d was synthesized following GP1, using (4-chlorophenyl)(methyl)sulfane (1d, 238 mg, 1.5 mmol) to give the product as colourless oil. It was purified by column chromatography on silica gel using ethyl acetate (100 %) to obtain 83% yield (217 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.58 (d, $J$ = 8.5 Hz, 2H), 7.50 (d, $J$ = 8.4 Hz, 2H), 2.71 (s, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) δ 144.3, 137.4, 129.8, 125.1, 44.2 ppm. The spectroscopic data agree with the literature.

1-Fluoro-4-(methylsulfinyl)benzene (2e). Compound 2e was synthesized following GP1, using (4-fluorophenyl)(methyl)sulfane (1e, 213 mg, 1.5 mmol) to give the product as yellow oil. It was
purified by column chromatography on silica gel using ethyl acetate (100 %) to obtain 80% yield (190 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.68 – 7.61 (m, 2H), 7.25 – 7.16 (m, 2H), 2.70 (s, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) $\delta$ 164.4 (d, $J = 251.4$ Hz), 141.2 (d, $J = 3.1$ Hz), 125.9 (d, $J = 8.9$ Hz), 116.8 (d, $J = 22.6$ Hz) ppm. $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ –152.06 ppm. The spectroscopic data agree with the literature.

4-(Methylsulfinyl)benzonitrile (2f). Compound 2f was synthesized following GP1, using (4-(methylthio)benzonitrile (1f, 224 mg, 1.5 mmol) to give the product as White solid. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 82% yield (204 mg). m.p.: 86-88 °C [Lit.: 87-89 °C].$^{44}$ $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.63 – 7.55 (m, 2H), 7.06 – 6.99 (m, 2H), 3.85 (s, 3H), 2.69 (s, 3H) ppm. $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) $\delta$ 162.1, 136.8, 125.6, 114.9, 55.6, 44.1 ppm. The spectroscopic data agree with the literature.$^{45}$

1-Methoxy-4-(methylsulfinyl)benzene (2g). Compound 2g was synthesized following GP1, using (4-methoxyphenyl)(methyl)sulfane (1g, 231 mg, 1.5 mmol) to give the product as colourless oil. It was purified by column chromatography on silica gel using ethyl acetate (100 %) to obtain 88% yield (224 mg). m.p.: 86-88 °C [Lit.: 87-89 °C].$^{44}$ $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63 – 7.55 (m, 2H), 7.06 – 6.99 (m, 2H), 3.85 (s, 3H), 2.69 (s, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) $\delta$ 161.1, 136.8, 125.6, 114.9, 55.6, 44.1 ppm. The spectroscopic data agree with the literature.$^{45}$

4-(Methylsulfinyl)benzaldehyde (2h). Compound 2h was synthesized following GP1, using 4-(methylthio)benzaldehyde (1h, 228 mg, 1.5 mmol) to give the product as white solid. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 68% yield (174 mg). m.p.: 83-86 °C [Lit.: 84-87 °C].$^{46}$ $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 10.09 (s, 1H), 8.05 (d, $J = 7.7$ Hz, 2H), 7.82 (d, $J = 7.7$ Hz, 2H), 2.78 (s, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) $\delta$ 191.1, 152.4, 138.0, 124.1, 124.4, 117.8, 114.9, 43.7 ppm. The spectroscopic data agree with the literature.$^{45}$

1-(Methylsulfinyl)-4-nitrobenzene (2i). Compound 2i was synthesized following GP1, using methyl(4-nitrophenyl)sulfane (1i, 254 mg, 1.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using ethyl acetate (100 %) to obtain 63% yield (174 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.43 – 8.34 (m, 2H), 7.88 – 7.78 (m, 2H), 2.79 (s, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) $\delta$ 153.4, 149.6, 124.8, 124.6, 44.0 ppm. The spectroscopic data agree with the literature.$^{43}$

1-Methyl-3-(methylsulfinyl)benzene (2j). Compound 2j was synthesized following GP1, using methyl(m-tolyl)sulfane (1j, 207 mg, 1.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using ethyl acetate (100 %) to obtain 86% yield (200 mg).
1H NMR (500 MHz, CDCl₃) δ 7.49 – 7.45 (m, 1H), 7.41 – 7.36 (m, 2H), 7.30 – 7.26 (m, 1H), 2.70 (s, 3H), 2.41 (s, 3H) ppm. 13C{¹H} NMR (126 MHz, CDCl₃) δ 145.6, 139.7, 131.9, 129.2, 123.9, 120.7, 44.0, 21.5 ppm. The spectroscopic data agree with the literature.

1-Bromo-3-(methylsulfinyl)benzene (2k). Compound 2k was synthesized following GP1, using (3-bromophenyl)(methyl)sulfane (1k, 305 mg, 1.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using ethyl acetate (100%) to obtain 90% yield (296 mg). 1H NMR (500 MHz, CDCl₃) δ 7.84 – 7.76 (m, 1H), 7.64 – 7.50 (m, 2H), 7.42 – 7.36 (m, 1H), 2.72 (s, 3H) ppm. 13C{¹H} NMR (126 MHz, CDCl₃) δ 148.1, 134.2, 130.9, 126.6, 123.7, 122.2, 44.1 ppm. The spectroscopic data agree with the literature.

1-Chloro-3-(methylsulfinyl)benzene (2l). Compound 2l was synthesized following GP1, using (3-chlorophenyl)(methyl)sulfane (1l, 238 mg, 1.5 mmol) to give the product as colourless oil. It was purified by column chromatography on silica gel using ethyl acetate (100% ) to obtain 85% yield (224 mg). 1H NMR (500 MHz, CDCl₃) δ 7.65 (s, 1H), 7.50 – 7.43 (m, 3H), 2.73 (s, 3H) ppm. 13C{¹H} NMR (126 MHz, CDCl₃) δ 148.0, 135.8, 131.3, 130.7, 123.7, 121.7, 44.1 ppm. The spectroscopic data agree with the literature.

1-Bromo-2-(methylsulfinyl)benzene (2m). Compound 2m was synthesized following GP1, using (2-bromophenyl)(methyl)sulfane (1m, 305 mg, 1.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 72% yield (238 mg). 1H NMR (500 MHz, CDCl₃) δ 7.94 (dd, J = 7.8, 1.7 Hz, 1H), 7.62 – 7.54 (m, 2H), 7.39 – 7.35 (m, 1H), 2.82 (s, 3H) ppm. 13C{¹H} NMR (126 MHz, CDCl₃) δ 145.5, 133.0, 132.4, 128.8, 125.8, 118.5, 42.0 ppm. The spectroscopic data agree with the literature.

1-Chloro-2-(methylsulfinyl)benzene (2n). Compound 2n was synthesized following GP1 GP1, using (2-chlorophenyl)(methyl)sulfane (1n, 238 mg, 1.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 79% yield (208 mg). 1H NMR (500 MHz, CDCl₃) δ 7.94 (dd, J = 7.8, 1.6 Hz, 1H), 7.53 (td, J = 7.5, 1.2 Hz, 1H), 7.44 (td, J = 7.4, 1.5 Hz, 1H), 7.39 (d, J = 1.2 Hz, 1H), 2.81 (s, 3H) ppm. 13C{¹H} NMR (126 MHz, CDCl₃) δ 143.7, 132.1, 129.9, 128.3, 125.4, 41.7 ppm. The spectroscopic data agree with the literature.

1-Iodo-2-(methylsulfinyl)benzene (2o). Compound 2o was synthesized following GP1, using(2-iodophenyl)(methyl)sulfane (1o, 375 mg, 1.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 34% yield (136 mg). 1H NMR (500 MHz, CDCl₃) δ 7.89 (t, J = 6.6 Hz, 1H), 7.82 – 7.79 (t, J = 6.6 Hz, 1H), 6.3 – 7.56 (m, 1H), 7.24 – 7.17 (m, 1H), 2.77 (s, 3H) ppm. 13C{¹H} NMR (126
MHz, CDCl$_3$ δ 148.4, 139.4, 132.6, 129.7, 125.9, 91.5, 42.3 ppm. The spectroscopic data agree with the literature.$^{47}$

1,3-Dichloro-5-(methylsulfinyl)benzene (2p). Compound 2p was synthesized following GP1, using (3,5-dichlorophenyl)(methyl)sulfane (1n, 290 mg, 1.5 mmol) to give the product as white solid. It was purified by column chromatography on silica gel using ethyl acetate (100 %) to obtain 89% yield (278 mg). m.p.: 71-73°C [Lit.: 72-74 °C].$^{25}$ $^1$H NMR (500 MHz, CDCl$_3$) δ 7.50 (d, $J =$ 1.6 Hz, 2H), 7.46 – 7.44 (m, 1H), 2.74 (s, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) δ 149.5, 136.4, 131.2, 122.0, 44.1 ppm. The spectroscopic data agree with the literature.

(Ethylsulfinyl)benzene (2q). Compound 2q was synthesized following GP1, using ethyl(phe- nyl)sulfane (1q, 207 mg, 1.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using ethyl acetate (100 %) to obtain 91% yield (210 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.63 – 7.55 (m, 2H), 7.53 – 7.46 (m, 3H), 2.89 (dq, $J =$ 13.3, 7.4 Hz, 1H), 2.76 (dq, $J =$ 13.3, 7.4 Hz, 1H), 1.18 (t, $J =$ 7.4 Hz, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) δ 143.3, 131.0, 129.2, 59.3, 16.0, 13.3 ppm. The spectroscopic data agree with the literature.$^{43}$

(Propylsulfinyl)benzene (2r). Compound 2r was synthesized following GP1, using phenyl(pro- pyl)sulfane (1r, 228 mg, 1.5 mmol) to give the product as colourless oil. It was purified by column chromatography on silica gel using ethyl acetate (100 %) to obtain 86% yield (218 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.67 – 7.53 (m, 2H), 7.52 – 7.41 (m, 3H), 2.81 – 2.69 (m, 2H), 1.83 – 1.72 (m, 1H), 1.69 – 1.59 (m, 1H), 1.02 (t, $J =$ 7.4 Hz, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) δ 144.1, 131.0, 129.3, 124.1, 59.3, 16.0, 13.3 ppm. The spectroscopic data agree with the literature.$^{43}$

(Cyclopropylsulfinyl)benzene (2s). Compound 2s was synthesized following GP1, using cy- clopropyl(phenyl)sulfane (1s, 225 mg, 1.5 mmol) to give the product as colourless. It was purified by column chromatography on silica gel using ethyl acetate (100 %) to obtain 84% yield (209 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.73 – 7.56 (m, 2H), 7.55 – 7.42 (m, 3H), 2.29 – 2.17 (m, 1H), 1.28 – 1.19 (m, 1H), 1.06 – 0.89 (m, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) δ 144.9, 131.0, 129.2, 124.1, 33.9, 3.5, 2.9 ppm. The spectroscopic data agree with the literature.$^{40}$

(Allylsulfinyl)benzene (2t). Compound 2t was synthesized following GP1, using allyl(phe- nyl)sulfane (1t, 225 mg, 1.5 mmol) to give the product as colourless oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 67% yield (166 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.64 – 7.55 (m, 2H), 7.55 – 7.46 (m, 3H), 5.78 – 5.52 (m, 1H), 5.37 – 5.30 (m, 1H), 5.19 (dq, $J =$ 17.0, 1.2 Hz, 1H), 3.54 (ddd, $J =$ 32.0, 12.7, 7.5 Hz, 2H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) δ 143.0, 131.2, 129.2, 125.4, 124.4, 124.0, 61.0 ppm. The spectroscopic data agree with the literature.$^{49}$
(Benzylsulfinyl)benzene (2u). Compound 2u was synthesized following GP1, using allyl(phenyl)sulfane (1u, 300 mg, 1.5 mmol) to give the product as white solid. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 78% yield (254 mg). m.p.: 120-122°C [Lit.: 122-123 °C].\(^{40}\) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.51 – 7.33\) (m, 3H), 7.32 – 7.22 (m, 2H), 6.98 (d, \(J = 7.2\) Hz, 1H), 4.05 (dd, \(J = 50.0, 12.6\) Hz, 1H) ppm. \(^{13}\)C\(^{\{1\}H}\) NMR (126 MHz, CDCl\(_3\)) \(\delta 142.8, 131.3, 130.5, 129.2, 128.9, 128.5, 128.3, 124.6, 63.7\) ppm. The spectroscopic data agree with the literature.\(^{49}\)

Sulfinyldibenzene (2v). Compound 2v was synthesized following GP1, using diphenylsulfane (1v, 279 mg, 1.5 mmol) to give the product as white solid. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (6:4) to obtain 70% yield (212 mg). m.p.: 68-70°C [Lit.: 69-70 °C].\(^{25}\) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.69 – 7.58\) (m, 2H), 7.47 – 7.41 (m, 3H) ppm. \(^{13}\)C\(^{\{1\}H}\) NMR (126 MHz, CDCl\(_3\)) \(\delta 145.6, 131.1, 129.3, 124.8\) ppm. The spectroscopic data agree with the literature.\(^{43}\)

Thiochroman-4-one 1-oxide (2w). Compound 2w was synthesized following GP1, using thiochroman-4-one (1w, 246 mg, 1.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 47% yield (128 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 8.11\) (dd, \(J = 7.8, 1.2\) Hz, 1H), 7.83 (dd, \(J = 7.7, 0.9\) Hz, 1H), 7.72 (td, \(J = 7.6, 1.3\) Hz, 1H), 7.62 (td, \(J = 7.6, 1.2\) Hz, 1H), 3.49 – 3.39 (m, 3H), 2.90 – 2.81 (m, 1H) ppm. \(^{13}\)C\(^{\{1\}H}\) NMR (126 MHz, CDCl\(_3\)) \(\delta 192.1, 145.6, 134.7, 132.2, 129.3, 128.9, 128.5, 46.7, 30.4\) ppm. The spectroscopic data agree with the literature.\(^{50}\)

2-(Methylsulfinyl)pyridine (2x). Compound 2x was synthesized following GP1, using 2-(methylthio)pyridine (1x, 188 mg, 1.5 mmol) to give the product as colourless oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 73% yield (155 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 8.65 – 8.54\) (m, 1H), 8.00 (dt, \(J = 7.9, 1.0\) Hz, 1H), 7.93 (td, \(J = 7.7, 1.7\) Hz, 1H), 7.36 (ddd, \(J = 7.4, 4.8, 1.1\) Hz, 1H), 2.83 (s, 3H) ppm. \(^{13}\)C\(^{\{1\}H}\) NMR (126 MHz, CDCl\(_3\)) \(\delta 166.0, 149.6, 138.3, 124.7, 119.5, 41.4\) ppm. The spectroscopic data agree with the literature.\(^{40}\)

1-(Butylsulfinyl)butane (2y). Compound 2y was synthesized following GP1, using dibutyldisulfane (1y, 219 mg, 1.5 mmol) to give the product as colourless oil. It was purified by column chromatography on silica gel using ethyl acetate (100 %) to obtain 66% yield (160 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 2.67 – 2.54\) (m, 4H), 1.76 – 1.62 (m, 4H), 1.51 – 1.33 (m, 4H), 0.90 (t, \(J = 7.4\) Hz, 6H) ppm. \(^{13}\)C\(^{\{1\}H}\) NMR (101 MHz, CDCl\(_3\)) \(\delta 52.1, 24.6, 22.1, 13.7\) ppm. The spectroscopic data agree with the literature.\(^{43}\)
Tetrahydro-2H-thiopyran 1-oxide (2z). Compound 2z was synthesized following GP1, using tetrahydro-2H-thiopyran (1z, 153 mg, 1.5 mmol) to give the product as colourless oil. It was purified by column chromatography on silica gel using ethyl acetate/methanol (98:2) to obtain 72% yield (128 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 2.88 – 2.74 (m, 1H), 2.73 – 2.64 (m, 1H), 2.21 – 2.09 (m, 1H), 1.64 – 1.46 (m, 2H) ppm. \(^{13}\)C\(^{\text{1}}\)H NMR (126 MHz, CDCl\(_3\)) δ 48.8, 24.7, 19.0 ppm. The spectroscopic data agree with the literature.\(^5\)

1,4-Oxathiane 4-oxide (2aa). Compound 2aa was synthesized following GP1, using 1,4-oxathiane (1aa, 156 mg, 1.5 mmol) to give the product as colourless oil. It was purified by column chromatography on silica gel using ethyl acetate/methanol (98:2) to obtain 67% yield (120 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 4.36 – 4.23 (m, 1H), 3.80 – 3.70 (m, 1H), 2.92 – 2.78 (m, 1H), 2.73 – 2.60 (m, 1H) ppm. \(^{13}\)C\(^{\text{1}}\)H NMR (126 MHz, CDCl\(_3\)) δ 59.1, 46.2 ppm. The spectroscopic data agree with the literature.\(^5\)

(Methylsulfonyl)benzene (3a). Compound 3a was synthesized following GP2, using methyl(phenyl)sulfane (1a, 186 mg, 1.5 mmol) to give the product as White solid. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (6:4) to obtain 81% yield (189 mg). m.p.: 89-91\(^\circ\)C [Lit.: 91 \(^\circ\)C].\(^2\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.93 (d, \(J = 8.2\) Hz, 2H), 7.68 – 7.51 (m, 3H), 3.04 (s, 3H) ppm. \(^{13}\)C\(^{\text{1}}\)H NMR (101 MHz, CDCl\(_3\)) δ 140.7, 133.7, 129.4, 127.4, 44.8 ppm. The spectroscopic data agree with the literature.\(^4\)

1-Methyl-4-(methylsulfonyl)benzene (3b). Compound 3b was synthesized following GP2, using methyl(\(p\)-tolyl)sulfane (1b, 207 mg, 1.5 mmol) to give the product as white solid. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (6:4) to obtain 83% yield (212 mg). m.p.: 86-87\(^\circ\)C [Lit.: 87-88 \(^\circ\)C].\(^3\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.85 – 7.77 (m, 2H), 7.73 – 7.66 (m, 2H), 3.04 (s, 3H) ppm. \(^{13}\)C\(^{\text{1}}\)H NMR (101 MHz, CDCl\(_3\)) δ 144.7, 137.7, 123.0, 127.3, 44.6, 21.6 ppm. The spectroscopic data agree with the literature.\(^5\)

1-Bromo-4-(methylsulfonyl)benzene (3c). Compound 3c was synthesized following GP2, using (4-bromophenyl)(methyl)sulfane (1c, 305 mg, 1.5 mmol) to give the product as white solid. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (6:4) to obtain 79% yield (280 mg). m.p.: 100-102\(^\circ\)C [Lit.: 100-102 \(^\circ\)C].\(^4\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.85 – 7.77 (m, 2H), 7.73 – 7.66 (m, 2H), 3.04 (s, 3H) ppm. \(^{13}\)C\(^{\text{1}}\)H NMR (101 MHz, CDCl\(_3\)) δ 139.7, 132.8, 129.1, 44.6 ppm. The spectroscopic data agree with the literature.\(^4\)

1-Chloro-4-(methylsulfonyl)benzene (3d). Compound 3d was synthesized following GP2, using (4-chlorophenyl)(methyl)sulfane (1d, 238 mg, 1.5 mmol) to give the product as white solid. It
was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (6:4) to obtain 73% yield (210 mg). m.p.: 92-94 °C [Lit.: 94-95 °C].

\[ ^{1}H \text{NMR (400 MHz, CDCl}_3] \delta 7.91 - 7.84 \text{ (m, 2H), 7.57 - 7.51 \text{ (m, 2H), 3.08 - 3.01 \text{ (m, 3H) ppm.}} \]

\[ ^{13}C\text{\{}^{1}H\text{\}} \text{NMR (101 MHz, CDCl}_3] \delta 140.6, 139.2, 129.8, 129.0, 44.6 \text{ ppm. The spectroscopic data agree with the literature.} \]

1-Fluoro-4-(methylsulfonyl)benzene (3e). Compound 3e was synthesized following GP2, using (4-fluorophenyl)(methyl)sulfane (1e, 213 mg, 1.5 mmol) to give the product as colourless oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (6:4) to obtain 66% yield (172 mg). 

\[ ^{1}H \text{NMR (500 MHz, CDCl}_3] \delta 7.98 - 7.90 \text{ (m, 2H), 7.26 - 7.20 \text{ (m, 2H), 3.04 \text{ (s, 3H) ppm.}} \]

\[ ^{13}C\text{\{}^{1}H\text{\}} \text{NMR (101 MHz, CDCl}_3] \delta 165.8 (d, J = 256.1 \text{ Hz}), 136.8 \text{ (d, J = 3.2 Hz), 130.4 \text{ (d, J = 9.6 Hz), 116.7 \text{ (d, J = 22.7 Hz), 44.7 \text{ (s) ppm.}} \]

\[ ^{19}F\text{\{}^{1}H\text{\}} \text{NMR (471 MHz, CDCl}_3] \delta -103.59 \text{ ppm. The spectroscopic data agree with the literature.} \]

4-(Methylsulfonyl)benzonitrile (3f). Compound 3f was synthesized following GP1 using (4-(methylthio)benzonitrile (1f, 224 mg, 1.5 mmol) to give the product as white solid. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (2:8) to obtain 68% yield (68 mg). m.p.: 142-143 °C [Lit.: 142-143 °C].

\[ ^{1}H \text{NMR (500 MHz, CDCl}_3] \delta 8.11 - 8.03 \text{ (m, 2H), 7.91 - 7.84 \text{ (m, 2H), 3.08 \text{ (s, 3H) ppm.}} \]

\[ ^{13}C\text{\{}^{1}H\text{\}} \text{NMR (101 MHz, CDCl}_3] \delta 144.6, 133.3, 128.3, 117.7, 117.1, 44.3 \text{ ppm. The spectroscopic data agree with the literature.} \]

1-Methoxy-4-(methylsulfonyl)benzene (3g). Compound 3g was synthesized following GP2, using (4-methoxyphenyl)(methyl)sulfane (1g, 231 mg, 1.5 mmol) to give the product as white solid. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (6:4) to obtain 78% yield (218 mg). m.p.: 118-120 °C [Lit.: 120-122 °C].

\[ ^{1}H \text{NMR (400 MHz, CDCl}_3] \delta 7.93 - 7.72 \text{ (m, 2H), 7.10 - 6.90 \text{ (m, 2H), 3.86 \text{ (s, 3H), 3.01 \text{ (s, 3H) ppm.}} \]

\[ ^{13}C\text{\{}^{1}H\text{\}} \text{NMR (101 MHz, CDCl}_3] \delta 163.8, 132.4, 129.6, 114.6, 55.8, 44.9 \text{ ppm. The spectroscopic data agree with the literature.} \]

4-(Methylsulfonyl)benzaldehyde (3h). Compound 3h was synthesized following GP2, using 4-(methylthio)benzaldehyde (1h, 228 mg, 1.5 mmol) to give the product as white solid. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (6:4) to obtain 35% yield (96 mg). m.p.: 157-158 °C [Lit.: 157-158 °C].

\[ ^{1}H \text{NMR (400 MHz, CDCl}_3] \delta 10.14 \text{ (s, 1H), 8.11 \text{ (dd, J = 19.4, 8.3 Hz, 4H), 3.10 \text{ (s, 3H) ppm.}} \]

\[ ^{13}C\text{\{}^{1}H\text{\}} \text{NMR (101 MHz, CDCl}_3] \delta 190.8, 145.5, 139.8, 130.5, 128.4, 44.4 \text{ ppm. The spectroscopic data agree with the literature.} \]

1-(Methylsulfonyl)-4-nitrobenzene (3i). Compound 3i was synthesized following GP2, using methyl(4-nitrophenyl)sulfane (1i, 254 mg, 1.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (6:4) to obtain 28% yield (85 mg). 

\[ ^{1}H \text{NMR (500 MHz, CDCl}_3] \delta 8.46 - 8.39 \text{ (m, 2H), 8.20 - 8.10 \text{ (m, 2H), 3.12 \text{ ppm.}} \]
(s, 3H) ppm. $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) δ 151.0, 146.1, 129.1, 124.8, 44.5 ppm. The spectroscopic data agree with the literature.$^{51}$

1-Methyl-3-(methylsulfonyl)benzene (3j). Compound 3k was synthesized following GP2, using methyl(m-tolyl)sulfane (1j, 207 mg, 1.5 mmol) to give the product as colourless oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (6:4) to obtain 78% yield (198 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.79 – 7.63 (m, 2H), 7.49 – 7.40 (m, 2H), 3.03 (s, 3H), 2.43 (s, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) δ 140.5, 139.8, 134.5, 129.3, 127.7, 124.5, 44.6, 21.4 ppm. The spectroscopic data agree with the literature.$^{57}$

1-Bromo-3-(methylsulfonyl)benzene (3k). Compound 3k was synthesized following GP2, using (3-bromophenyl)(methyl)sulfane (1k, 305 mg, 1.5 mmol) to give the product as white solid. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (6:4) to obtain 71% yield (252 mg). m.p.: 102-103 °C. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.10 – 8.05 (m, 1H), 7.89 – 7.85 (m, 1H), 7.79 – 7.76 (m, 1H), 7.49 – 7.42 (m, 1H), 3.06 (s, 3H) ppm. $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) δ 142.5, 136.9, 131.1, 130.5, 125.9, 123.4, 44.6. The spectroscopic data agree with the literature.$^{58}$

1-Chloro-3-(methylsulfonyl)benzene (3l). Compound 3l was synthesized following GP2, using (3-chlorophenyl)(methyl)sulfane (1l, 283 mg, 1.5 mmol) to give the product as white solid. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (6:4) to obtain 74% yield (212 mg). m.p.: 55-56°C [Lit.: 56-58 °C].$^{40}$ $^1$H NMR (500 MHz, CDCl$_3$) δ 7.93 (t, $J$ = 1.9 Hz, 1H), 7.85 – 7.81 (m, 1H), 7.64 – 7.60 (m, 1H), 7.52 (t, $J$ = 7.9 Hz, 1H), 3.06 (s, 3H) ppm. $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) δ 142.3, 135.7, 134.0, 130.9, 127.7, 125.6, 44.5 ppm. The spectroscopic data agree with the literature.$^{40}$

1-Bromo-2-(methylsulfonyl)benzene (3m). Compound 3m was synthesized following GP2, using (2-bromophenyl)(methyl)sulfane (1m, 305 mg, 1.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (6:4) to obtain 51% yield (180 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.19 (dd, $J$ = 7.7, 1.9 Hz, 1H), 7.77 (dd, $J$ = 7.8, 1.3 Hz, 1H), 7.50 (dtd, $J$ = 17.1, 7.5, 1.5 Hz, 2H), 3.28 (s, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) δ 139.8, 135.6, 134.9, 131.3, 128.2, 120.8, 42.5 ppm. The spectroscopic data agree with the literature.$^{40}$

1-Chloro-2-(methylsulfonyl)benzene (3n). Compound 3n was synthesized following GP2, using (2-chlorophenyl)(methyl)sulfane (1n, 238 mg, 1.5 mmol) to give the product as white solid. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (6:4) to obtain 53% yield (152 mg). m.p.: 82-84°C [Lit.: 80-82 °C].$^{40}$ $^1$H NMR (500 MHz, CDCl$_3$) δ 8.13 (dd, $J$ = 8.3, 1.5 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.49 – 7.43 (m, 1H), 3.26 (s, 3H) ppm. $^{13}$C($^1$H)
NMR (126 MHz, CDCl₃) δ 138.1, 134.9, 132.6, 132.0, 130.9, 127.6, 42.8 ppm. The spectroscopic data agree with the literature.⁴⁰

1-iodo-2-(methylsulfonyl)benzene (3o). Compound 3o was synthesized following GP2, using (2-iodophenyl)(methyl)sulfane (1o, 375 mg, 1.5 mmol) to give the product as white solid. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (6:4) to obtain 15% yield (64 mg). m.p.: 108-109 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.23 (dd, J = 7.9, 1.7 Hz, 1H), 8.11 (dd, J = 7.9, 1.2 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.27 (dt, J = 7.7, 1.7 Hz, 1H), 3.26 (s, 3H) ppm. ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 142.9, 142.9, 134.6, 131.0, 129.0, 92.7, 42.0 ppm. The spectroscopic data agree with the literature.⁴⁰

1,3-Dichloro-5-(methylsulfonyl)benzene (3p). Compound 3p was synthesized following GP2, using (3,5-dichlorophenyl)(methyl)sulfane (1n, 290 mg, 1.5 mmol) to give the product as white solid. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (6:4) to obtain 60% yield (204 mg). m.p.: 202-205 °C [Lit.: 201-203 °C]. ¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, J = 1.9 Hz, 2H), 7.62 (t, J = 1.9 Hz, 1H), 3.08 (s, 3H) ppm. ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 14.4, 136.5, 133.9, 126.0, 44.5 ppm. The spectroscopic data agree with the literature.⁵⁹

(Ethylsulfonyl)benzene (3q). Compound 3q was synthesized following GP2, using ethyl(phenyl)sulfane (1q, 207 mg, 1.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (6:4) to obtain 74% yield (188 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.94 – 7.80 (m, 2H), 7.68 – 7.51 (m, 3H), 3.10 (q, J = 7.4 Hz, 2H), 1.25 (t, J = 7.4 Hz, 3H) ppm. ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 138.6, 133.8, 129.3, 128.3, 50.7, 7.5 ppm. The spectroscopic data agree with the literature.⁵¹

(Propylsulfonyl)benzene (3r). Compound 3r was synthesized following GP2, using phenyl(propyl)sulfane (1r, 228 mg, 1.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (6:4) to obtain 71% yield (196 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.90 – 7.84 (m, 2H), 7.64 – 7.59 (m, 1H), 7.56 – 7.51 (m, 2H), 3.06 – 3.00 (m, 2H), 1.75 – 1.66 (m, 2H), 0.95 (t, J = 7.5 Hz, 3H) ppm. ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 139.2, 133.7, 129.3, 128.0, 57.9, 16.5, 12.9 ppm. The spectroscopic data agree with the literature.⁶⁰

(Cyclopropylsulfonyl)benzene (3s). Compound 3s was synthesized following GP2, using cyclopropyl(phenyl)sulfane (1s, 225 mg, 1.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (6:4) to obtain 72% yield (198 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.93 – 7.80 (m, 2H), 7.65 – 7.58 (m, 1H), 7.57 – 7.47 (m, 2H), 2.51 – 2.36 (m, 2H), 1.35 – 1.27 (m, 2H), 1.04 – 0.94 (m, 2H) ppm. ¹³C{¹H} NMR
(126 MHz, CDCl₃) δ 140.7, 133.4, 129.3, 127.5, 32.9, 6.0 ppm. The spectroscopic data agree with the literature.

**Allylsulfonyl)benzene (3t).** Compound 3t was synthesized following GP2, using allyl(phenyl)sulfane (1t, 225 mg, 1.5 mmol) to give the product as colourless oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (6:4) to obtain 18% yield (48 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.91 – 7.82 (m, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.56 (t, J = 7.7 Hz, 2H), 5.80 (ddt, J = 17.4, 10.1, 7.4 Hz, 1H), 5.24 (dd, J = 92.6, 13.6 Hz, 2H), 3.81 (d, J = 7.4 Hz, 2H) ppm. ¹³C(¹H) NMR (126 MHz, CDCl₃) δ 138.4, 133.9, 129.2, 124.9, 124.8, 61.0 ppm. The spectroscopic data agree with the literature.

**Sulfonyldibenzene (3v).** Compound 3v was synthesized following GP2, using diphenylsulfane (1v, 279 mg, 1.5 mmol) to give the product as white solid. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (6:4) to obtain 70% yield (230 mg). m.p.: 121-122°C [Lit.: 117-118 °C]. ¹H NMR (400 MHz, CDCl₃) δ 8.02 – 7.89 (m, 2H), 7.61 – 7.46 (m, 3H) ppm. ¹³C(¹H) NMR (101 MHz, CDCl₃) δ 141.7, 133.3, 129.4, 127.8 ppm. The spectroscopic data agree with the literature.

**Thiochroman-4-one 1,1-dioxide (3w).** Compound 3w was synthesized following GP2, using thiochroman-4-one (1w, 246 mg, 1.5 mmol) to give the product as white solid. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (6:4) to obtain 48% yield (142 mg). m.p.: 142-144°C [Lit.: 142-144 °C]. ¹H NMR (500 MHz, CDCl₃) δ 8.09 (d, J = 7.8 Hz, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.80 (t, J = 7.6 Hz, 1H), 7.72 (t, J = 7.7 Hz, 1H), 3.77 – 3.61 (m, 2H), 3.46 – 3.30 (m, 2H) ppm. ¹³C(¹H) NMR (126 MHz, CDCl₃) δ 190.26, 141.5, 135.0, 133.5, 130.3, 128.9, 123.7, 49.3, 36.8 ppm. The spectroscopic data agree with the literature.

**2-(Methylsulfonyl)pyridine (3x).** Compound 3x was synthesized following GP2, using 2-(methylthio)pyridine (1x, 188 mg, 1.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 67% yield (158 mg). ¹H NMR (500 MHz, CDCl₃) δ 8.75 – 8.69 (m, 1H), 8.07 (dt, J = 7.9, 1.0 Hz, 1H), 7.96 (td, J = 7.8, 1.7 Hz, 1H), 7.55 (ddd, J = 7.7, 4.7, 1.1 Hz, 1H), 3.21 (s, 3H) ppm. ¹³C(¹H) NMR (101 MHz, CDCl₃) δ 158.1, 150.1, 138.4, 127.6, 121.1, 40.1 ppm. The spectroscopic data agree with the literature.

**1-(Butylsulfonyl)butane (3y).** Compound 3y was synthesized following GP2, using dibutylsulfane (1y, 219 mg, 1.5 mmol) to give the product as colourless oil. It was purified by column chromatography on silica gel using ethyl acetate (100 %) to obtain 34% yield (92 mg). ¹H NMR (500 MHz, CDCl₃) δ 3.11 – 2.80 (m, 2H), 1.84 – 1.76 (m, 2H), 1.50 – 1.42 (m, 2H), 0.95 (t, J =...
7.4 Hz, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) δ 52.6, 24.0, 21.9, 13.7 ppm. The spectroscopic data agree with the literature.\textsuperscript{51}

**Tetrahydro-$2$H-thiopyran $1,1$-dioxide ($3z$).** Compound $3z$ was synthesized following GP2, using tetrahydro-$2$H-thiopyran ($1z$, 153 mg, 1.5 mmol) to give the product as colourless oil. It was purified by column chromatography on silica gel using ethyl acetate (100 %) to obtain 51% yield (102 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 3.01 – 2.88 (m, 4H), 2.10 – 2.00 (m, 4H), 1.63 – 1.55 (m, 2H) ppm. $^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$) δ 52.16, 24.28, 23.8 ppm. The spectroscopic data agree with the literature.\textsuperscript{51}

**$1,4$-Oxathiane $4,4$-dioxide ($3aa$).** Compound $3aa$ was synthesized following GP2, using $1,4$-oxathiane ($1aa$, 156 mg, 1.5 mmol) to give the product as white solid. It was purified by column chromatography on silica gel using ethyl acetate (100 %) to obtain 48% yield (98 mg). m.p.: 130-132 °C [Lit.: 130-131 °C].\textsuperscript{65} $^1$H NMR (500 MHz, CDCl$_3$) δ 4.14 – 4.08 (m, 2H), 3.13 – 3.05 (m, 2H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) δ 66.3, 53.0 ppm. The spectroscopic data agree with the literature.\textsuperscript{66}

**$N$-(Methyl($\text{oxo}$)($\text{phenyl}$)-$\lambda^6$-sulfaneylidene)cyanamide ($5a$).** Compound $5a$ was synthesized following GP3, using (methylsulfinyl)benzene ($2a$, 70 mg, 0.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 46% yield (42 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.98 – 7.89 (m, 2H), 7.76 – 7.70 (m, 1H), 7.66 – 7.60 (m, 2H), 3.28 (s, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) δ 136.1, 135.6, 130.4, 128, 112, 44.9 ppm. The spectroscopic data agree with the literature.\textsuperscript{67}

**$N$-(Methyl($\text{oxo}$)($\rho$-tolyl)-$\lambda^6$-sulfaneylidene)cyanamide ($5b$).** Compound $5b$ was synthesized following GP3, using 1-methyl-$4$-(methylsulfinyl)benzene ($2b$, 77 mg, 0.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 42% yield (41 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.86 (d, $J_{\text{Hz}}$ = 8.3 Hz, 2H), 7.47 (d, $J_{\text{Hz}}$ = 8.2 Hz, 2H), 3.31 (s, 3H), 2.49 (s, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) δ 147.2, 133.0, 131.0, 128.1, 112.2, 45.1, 21.9 ppm. The spectroscopic data agree with the literature.\textsuperscript{67}

**$N$-((4-Bromophenyl)(methyl)($\text{oxo}$)-$\lambda^6$-sulfaneylidene)cyanamide ($5c$).** Compound $5c$ was synthesized following GP3, using 1-bromo-$4$-(methylsulfinyl)benzene ($2c$, 110 mg, 0.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 43% yield (56 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.93 – 7.89 (m, 2H), 7.76 – 7.70 (m, 1H), 7.66 – 7.60 (m, 2H), 3.31 (s, 3H), 2.49 (s, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) δ 136.3, 135.8, 130.8, 128.8, 112.1, 44.9 ppm. The spectroscopic data agree with the literature.\textsuperscript{67}
7.78 (m, 4H), 3.35 (s, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) $\delta$ 135.1, 133.8, 131.4, 129.5, 111.6, 44.8 ppm. The spectroscopic data agree with the literature.$^{67}$

$N$-((4-Chlorophenyl)(methyl)(oxo)-$\lambda^6$-sulfaneylidene)cyanamide (5d). Compound 5d was synthesized following GP3, using 1-chloro-4-(methylsulfinyl)benzene (2d, 87 mg, 0.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 48% yield (52 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.00 – 7.88 (m, 2H), 7.72 – 7.61 (m, 2H), 3.35 (s, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) $\delta$ 142.8, 134.5, 130.8, 129.5, 111.6, 45.0 ppm. The spectroscopic data agree with the literature.$^{67}$

$N$-((4-Fluorophenyl)(methyl)(oxo)-$\lambda^6$-sulfaneylidene)cyanamide (5e). Compound 5e was synthesized following GP3, start with 1-fluoro-4-(methylsulfinyl)benzene (2e, 79 mg, 0.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 36% yield (36 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.06 – 8.00 (m, 2H), 7.39 – 7.33 (m, 2H), 3.35 (s, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) $\delta$ 167.0 (d, $J$ = 260.2 Hz), 132.0 (d, $J$ = 3.2 Hz), 131.2 (d, $J$ = 10.1 Hz), 118.0 (d, $J$ = 23.1 Hz), 112.0, 45.1 ppm. $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ –99.69 ppm. The spectroscopic data agree with the literature.$^{67}$

$N$-((4-Cyanophenyl)(methyl)(oxo)-$\lambda^6$-sulfaneylidene)cyanamide (5f). Compound 5f was synthesized following GP3, using 4-(methylsulfinyl)benzonitrile (2f, 83 mg, 0.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 44% yield (45 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.18 – 8.11 (m, 2H), 8.02 – 7.95 (m, 2H), 3.40 (s, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) $\delta$ 140.4, 134.0, 128.9, 119.4, 116.6, 111.0, 44.5 ppm. The spectroscopic data agree with the literature.$^{67}$

$N$-((4-Methoxyphenyl)(methyl)(oxo)-$\lambda^6$-sulfaneylidene)cyanamide (5g). Compound 5g was synthesized following GP3, using 1-methoxy-4-(methylsulfinyl)benzene (2g, 85 mg, 0.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 32% yield (34 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.01 – 7.80 (m, 2H), 7.18 – 7.03 (m, 2H), 3.92 (s, 3H), 3.32 (s, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) $\delta$ 165.4, 130.4, 126.6, 115.7, 113.8, 56.2, 45.4 ppm. The spectroscopic data agree with the literature.$^{67}$

$N$-((3-Bromophenyl)(methyl)(oxo)-$\lambda^6$-sulfaneylidene)cyanamide (5h). Compound 5h was synthesized following GP3, using 1-bromo-3-(methylsulfinyl)benzene (2k, 110 mg, 0.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 37% yield (48 mg). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.12 (s,
$N$-((3-Chlorophenyl)(methyl)(oxo)$\lambda^6$-sulfaneylidene)cyanamide (5i). Compound 5i was synthesized following GP3, using 1-chloro-3-(methylsulfinyl)benzene (2l, 87 mg, 0.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 42% yield (45 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.97 (t, $J = 1.9$ Hz, 1H), 7.89 (ddd, $J = 7.9$, 1.9, 1.0 Hz, 1H), 7.75 (ddd, $J = 8.1$, 2.0, 1.0 Hz, 1H), 7.64 (t, $J = 8.0$ Hz, 1H), 3.36 (s, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) δ 138.7, 138.0, 131.8, 130.8, 126.6, 124.4, 111.4, 44.9 ppm. The spectroscopic data agree with the literature.  

$N$-((3,5-Dichlorophenyl)(methyl)(oxo)$\lambda^6$-sulfaneylidene)cyanamide (5l). Compound 5l was synthesized following GP3, using 1,3-dichloro-5-(methylsulfinyl)benzene (2p, 105 mg, 0.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 29% yield (36 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.87 (d, $J = 1.8$ Hz, 2H), 7.75 (t, $J = 1.8$ Hz, 1H), 3.38 (s, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) δ 139.1, 137.5, 135.7, 126.4, 110.9, 44.7 ppm. IR (neat): 2934, 2185, 1444, 1211, 1167, 844, 688 cm$^{-1}$. HRMS (ESI) m/z: [M+H] calcd for C$_8$H$_7$N$_2$OSCl$_2$ 248.9656; found 248.9655.  

$N$-(Ethyl(oxo)(phenyl)$\lambda^6$-sulfaneylidene)cyanamide (5m). Compound 5m was synthesized following GP3, using (ethylsulfinyl)benzene (2q, 77 mg, 0.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 43% yield (42 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.98 – 7.90 (m, 2H), 7.82 – 7.77 (m, 1H), 7.71 – 7.66 (m, 2H), 3.52 – 3.33 (m, 2H), 1.34 (t, $J = 7.4$ Hz, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) δ 135.6, 134.0, 130.3, 128.7, 112.3, 51.7, 7.3 ppm. The spectroscopic data agree with the literature.  

$N$-(Oxo(phenyl)(propyl)$\lambda^6$-sulfaneylidene)cyanamide (5n). Compound 5n was synthesized following GP3, using (propylsulfinyl)benzene (2r, 84 mg, 0.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 40% yield (42 mg). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.01 – 7.88 (m, 2H), 7.80 – 7.75 (m, 1H), 7.71 – 7.64 (m, 2H), 3.40 (ddd, $J = 14.2$, 10.6, 5.4 Hz, 1H), 3.30 (ddd, $J = 14.2$, 10.5, 5.5 Hz, 1H), 1.87 – 1.72 (m, 2H), 1.02 (t, $J = 7.5$ Hz, 3H) ppm. $^{13}$C($^1$H) NMR (126 MHz, CDCl$_3$) δ 135.5, 134.8, 130.3, 128.6, 112.3, 58.4, 16.3, 12.6 ppm. IR (neat): 2923, 2191, 1447, 1241, 1186, 1091, 825, 683 cm$^{-1}$. HRMS (ESI) m/z: [M+H] calcd for C$_{10}$H$_{13}$N$_2$OS 209.0749; found 209.0746.
**N-(Cyclopropyl(oxo)(phenyl)-λ^6-sulfaneylidene)cyanamide (5o).** Compound 5o was synthesized following GP3, using (cyclopropylsulfinyl)benzene (2s, 83 mg, 0.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 38% yield (39 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 8.02 – 7.87 (m, 2H), 7.78 – 7.74 (m, 1H), 7.69 – 7.61 (m, 2H), 2.73 – 2.65 (m, 1H), 1.72 – 1.65 (m, 1H), 1.40 – 1.28 (m, 2H), 1.15 – 1.08 (m, 1H) ppm. \(^{13}\)C{\(^1\)H} NMR (126 MHz, CDCl\(_3\)) δ 136.5, 135.2, 130.2, 128.0, 112.2, 33.7, 7.2, 6.1 ppm. The spectroscopic data agree with the literature.\(^{67}\)

**N-(Oxodiphenyl-λ^6-sulfaneylidene)cyanamide (5p).** Compound 5p was synthesized following GP3, using sulfinyldibenzen (2v, 101 mg, 0.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 23% yield (28 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 7.72 – 7.64 (m, 2H), 7.63 – 7.55 (m, 3H) ppm. \(^{13}\)C{\(^1\)H} NMR (126 MHz, CDCl\(_3\)) δ 135.8, 133.1, 130.4, 127.6, 113.8 ppm. The spectroscopic data agree with the literature.\(^{67}\)

**N-(Methyl(oxo)(pyridin-2-yl)-λ^6-sulfaneylidene)cyanamide (5q).** Compound 5q was synthesized following GP3, using 2-(methylsulfinyl)pyridine (2x, 101 mg, 0.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (4:6) to obtain 35% yield (32 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 8.75 (d, J = 4.7 Hz, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.99 (td, J = 7.8, 1.6 Hz, 1H), 7.62 – 7.53 (m, 1H), 3.24 (s, 3H) ppm. \(^{13}\)C{\(^1\)H} NMR (126 MHz, CDCl\(_3\)) δ 158.2, 150.6, 138.8, 128.0, 121.6, 113.7, 40.5 ppm. The spectroscopic data agree with the literature.\(^{67}\)

**N-(1-Oxidotetrahydro-2H-1λ^6-thiopyran-1-ylidene)cyanamide (5r).** Compound 5r was synthesized following GP3, using tetrahydro-2H-thiopyran 1-oxide (2z, 59 mg, 0.5 mmol) to give the product as yellow oil. It was purified by column chromatography on silica gel using ethyl acetate (100%) to obtain 52% yield (41 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 3.60 – 3.37 (m, 2H), 3.34 – 3.08 (m, 2H), 2.23 – 2.04 (m, 4H), 1.80 – 1.57 (m, 2H) ppm. \(^{13}\)C{\(^1\)H} NMR (126 MHz, CDCl\(_3\)) δ 112.2, 51.8, 23.8, 22.9 ppm. IR (neat): 2148, 1416, 1174, 872, 756 cm\(^{-1}\). HRMS (ESI) m/z: [M+H] calcd for C\(_6\)H\(_{11}\)N\(_2\)OS 159.0592; found 159.0593.

**Imino(methyl)(phenyl)-λ^6-sulfanone (6a).** Compound 6a was synthesized following GP4, using N-(methyl(oxo)(phenyl)-λ^6-sulfaneylidene)cyanamide (5a, 90 mg, 0.5 mmol) to give the product as colourless oil. It was purified by column chromatography on silica gel using ethyl acetate (100%) to obtain 68% yield (53 mg). \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 8.02 – 7.90 (m, 2H), 7.61 – 7.55 (m, 1H), 7.55 – 7.45 (m, 2H), 3.06 (s, 3H), 2.70 (s, 1H) ppm. \(^{13}\)C{\(^1\)H} NMR (126
MHz, CDCl$_3$ δ 143.5, 133.1, 129.3, 127.7, 46.2 ppm. The spectroscopic data agree with the literature.\textsuperscript{71}

**Imino(methyl)(p-tolyl)-λ\textsuperscript{6}-sulfanone (6b).** Compound 6b was synthesized following GP4, using \(N\)-(methyl(oxo)(p-tolyl)-λ\textsuperscript{6}-sulfaneylidene)cyanamide (5b, 97 mg, 0.5 mmol) to give the product as pale-yellow oil. It was purified by column chromatography on silica gel using ethyl acetate (100\%) to obtain 74\% yield (63 mg). \(^1\)H NMR (500 MHz, CDCl$_3$) δ 7.87 (d, \(J = 8.3\) Hz, 2H), 7.33 (d, \(J = 8.3\) Hz, 2H), 3.08 (br.s, 3H), 2.94 (s, 1H), 2.43 (s, 3H) ppm. \(^{13}\)C\({^1}\)H NMR (126 MHz, CDCl$_3$) δ 144.1, 140.6, 130.0, 127.9, 46.4, 21.6 ppm. The spectroscopic data agree with the literature.\textsuperscript{71}

**Ethyl(imino)(phenyl)-λ\textsuperscript{6}-sulfanone (6m).** Compound 6m was synthesized following GP4, using \(N\)-(ethyl(oxo)(phenyl)-λ\textsuperscript{6}-sulfaneylidene)cyanamide (5m, 97 mg, 0.5 mmol) to give the product as pale-yellow oil. It was purified by column chromatography on silica gel using ethyl acetate (100\%) to obtain 72\% yield (61 mg). \(^1\)H NMR (500 MHz, CDCl$_3$) δ 7.96 – 7.86 (m, 2H), 7.59 – 7.54 (m, 1H), 7.52 – 7.46 (m, 2H), 3.12 (q, \(J = 7.5\) Hz, 2H), 2.69 (s, 1H), 1.20 (t, \(J = 7.4\) Hz, 3H) ppm. \(^{13}\)C\({^1}\)H NMR (126 MHz, CDCl$_3$) δ 141.3, 133.0, 129.1, 128.5, 51.8, 7.9 ppm. The spectroscopic data agree with the literature.\textsuperscript{71}

**Imino(methyl)(pyridin-2-yl)-λ\textsuperscript{6}-sulfanone (6q).** Compound 6q was synthesized following GP4, using \(N\)-(methyl(oxo)(pyridin-2-yl)-λ\textsuperscript{6}-sulfaneylidene)cyanamide (5q, 97 mg, 0.5 mmol) to give the product as pale-yellow oil. It was purified by column chromatography on silica gel using CH$_2$Cl$_2$/MeOH (20:1) to obtain 51\% yield (40 mg). \(^1\)H NMR (500 MHz, CDCl$_3$) δ 8.72 (d, \(J = 4.7\) Hz, 1H), 8.12 (dt, \(J = 7.9, 1.0\) Hz, 1H), 7.94 (td, \(J = 7.8, 1.7\) Hz, 1H), 7.50 (ddd, \(J = 7.6, 4.7, 1.1\) Hz, 1H), 3.25 (s, 3H), 2.73 (s, 1H) ppm. \(^{13}\)C\({^1}\)H NMR (126 MHz, CDCl$_3$) δ 160.6, 150.7, 138.4, 126.9, 121.2, 42.4 ppm. The spectroscopic data agree with the literature.\textsuperscript{39}

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**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021xxxxx, containing: automated flow and electrochemical reactor setup, optimization of reaction conditions, NMR spectra.
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