Flow Electrosynthesis of Sulfoxides, Sulfones and Sulfoximines without Supporting Electrolytes

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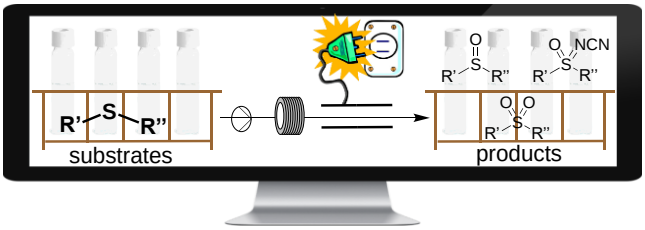
Graphical abstract:



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]

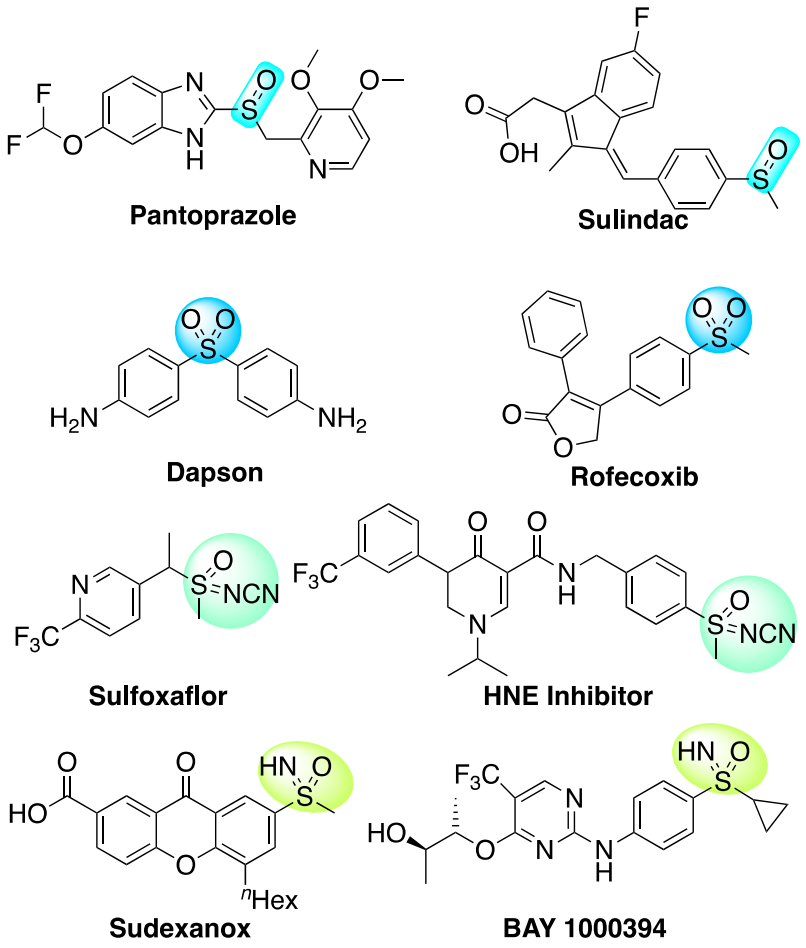


Figure 1. Examples of biological relevant sulfoxide, sulfone and sulfoximine compounds.

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,[10,11] photocatalytic processes,[8,12] or hypervalent iodine reagents.[13,14,15] Continuous processes have been investigated as well.[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.[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.[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.[24] Yudin *et al.* reported a method for the amination of sulfoxides in batch electrolysis using a divided cell.[25] Potentiostatic anodic oxidation conditions have been applied in these reactions. Generally, using a divided cell leads to increased cell potentials.[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.[27,28,29,30]

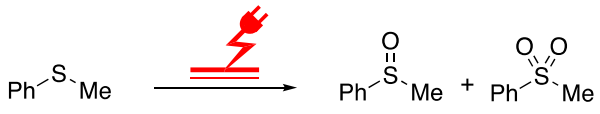
Results and Discussion

In extension of our previous efforts towards the development of flow tools and techniques to implement flow transformations,[31,32] we recently have reported a reaction without using supporting electrolyte[33] and disclosed the first use of an integrated flow electrochemical reactor in an automated way.[34,35] We saw this as an opportunity to further improve and simplify the oxidation methodologies of organosulfur compounds.[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 Vapourtec 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 examined 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).[33,37] 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 selectivity towards sulfoxide formation in 98% yield (Table 1, entries 1-10). The formation of sulfone 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-efficient electrode material (Table 1, entries 6-8). To reduce the reaction time, the flow rate was increased 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 supporting 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.



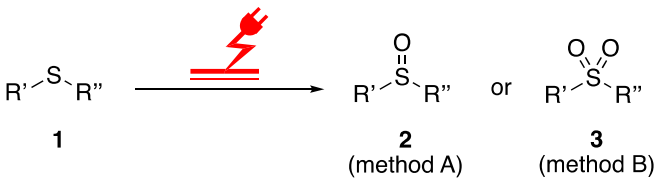
Entry	Anode	Cathode	Current [mA]	Conversion [%][a]	**2a** [%][a]	**3a** [%][a]
1	Pt	Pt	64 (2F)	90	83	7
2	Pt	Pt on Ti	64 (2F)	95	92	3
3	Pt	Gr	64 (2F)	98	86	12
4	Pt on Ti	Pt	64 (2F)	90	90	0
5	Gr	Gr	64 (2F)	96	96	0
6	Gr	Pt	64 (2F)	98	98	0
7	**Gr**	**Fe**	**64 (2F)**	**98**	**98**	**0**
8	GC	Pt	64 (2F)	98	98	0
9	Fe	Fe	64 (2F)	48	48	0
10	Gr	Fe	128 (4F)	100	27	73
11	Pt	Fe	128 (4F)	98	40	58
12	**Pt**	**Fe**	**160 (5F)**	**98**	**11**	**87**
13	Pt	Fe	192 (6F)	98	12	87

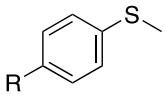
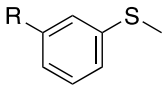
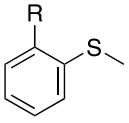
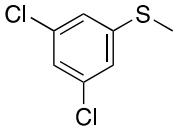
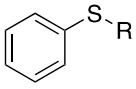
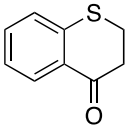
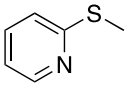
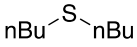
Table 1. Conditions: [**1a**] = 0.1 M, MeCN/H_2O (9:1), flow rate = 0.2 mL min^{-1}, at room temperature, reactor volume: 0.6 mL. [a] Determined by ^1H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard.

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.



	**1a** R = H **1b** R = Me **1c** R = Br **1d** R = Cl **1e** R = F **1f** R = CN **1g** R = OMe **1h** R = CHO **1i** R = NO_2	**2a** (87%) **2b** (89%) **2c** (86%) **2d** (83%) **2e** (80%) **2f** (82%) **2g** (88%) **2h** (68%) **2i** (63%)	**3a** (81%) **3b** (83%) **3c** (79%) **3d** (73%) **3e** (66%) **3f** (68%) **3g** (78%) **3h** (35%) **3i** (28%)
	**1j** R = Me **1k** R = Br **1l** R = Cl	**2j** (86%) **2k** (90%) **2l** (85%)	**3j** (78%) **3k** (71%) **3l** (74%)
	**1m** R = Br **1n** R = Cl **1o** R = I	**2m** (72%) **2n** (79%) **2o** (34%)	**3m** (51%) **3n** (53%) **3o** (15%)
	**1p**	**2p** (89%)	**3p** (60%)
	**1q** R = Et **1r** R = *n*Pr **1s** R = cyclopropyl **1t** R = allyl **1u** R = benzyl **1v** R = Ph	**2q** (91%) **2r** (86%) **2s** (84%) **2t** (67%) **2u** (78%) **2v** (70%)	**3q** (74%) **3r** (71%) **3s** (72%) **3t** (18%) **3u** (0%) **3v** (70%)
	**1w**	**2w** (47%)	**3w** (48%)
	**1x**	**2x** (73%)	**3x** (67%)
	**1y**	**2y**[a] (66%)	**3y**[a] (34%)
	**1z** X = CH_2 **1aa** X = O	**2z**[a] (72%) **2aa**[a] (67%)	**3z**[a] (51%) **3aa**[a] (48%)

Scheme 1 Substrate scope for the electrochemical oxidation of sulfides. Method A: [**1**] = 0.1 M, MeCN/H_2O (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/H_2O (9:1), Pt(+)/Fe(-), 160 mA, flow rate = 0.2 mL min^{-1}, reactor volume: 0.6 mL, RT. [a] 0.01 M of Bu_4NBF_4 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 Bu_4NBF_4 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.

2a **4** **5a**

Entry	Anode	Cathode	Solvent	Conversion [%][a]
1	C	C, Pt or Fe	HFIP	0
2	Pt	C	HFIP	8
3	Pt	Pt	HFIP	25
4	Pt	Pt	MeCN	18
5	Pt	Pt	MeOH	4
6	Pt	Pt	TFE	6
7	Pt	Pt	HFIP	0[b]
8	Pt	Pt	HFIP	34[c]

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_4NCl (0.01 M), reactor volume: 0.3 mL. [a] Determined by ^1H NMR spectroscopy. [b] supporting electrolyte: Et_4NI, Et_4NBr or *n*-Bu_4NBr. [c] Without supporting electrolyte.

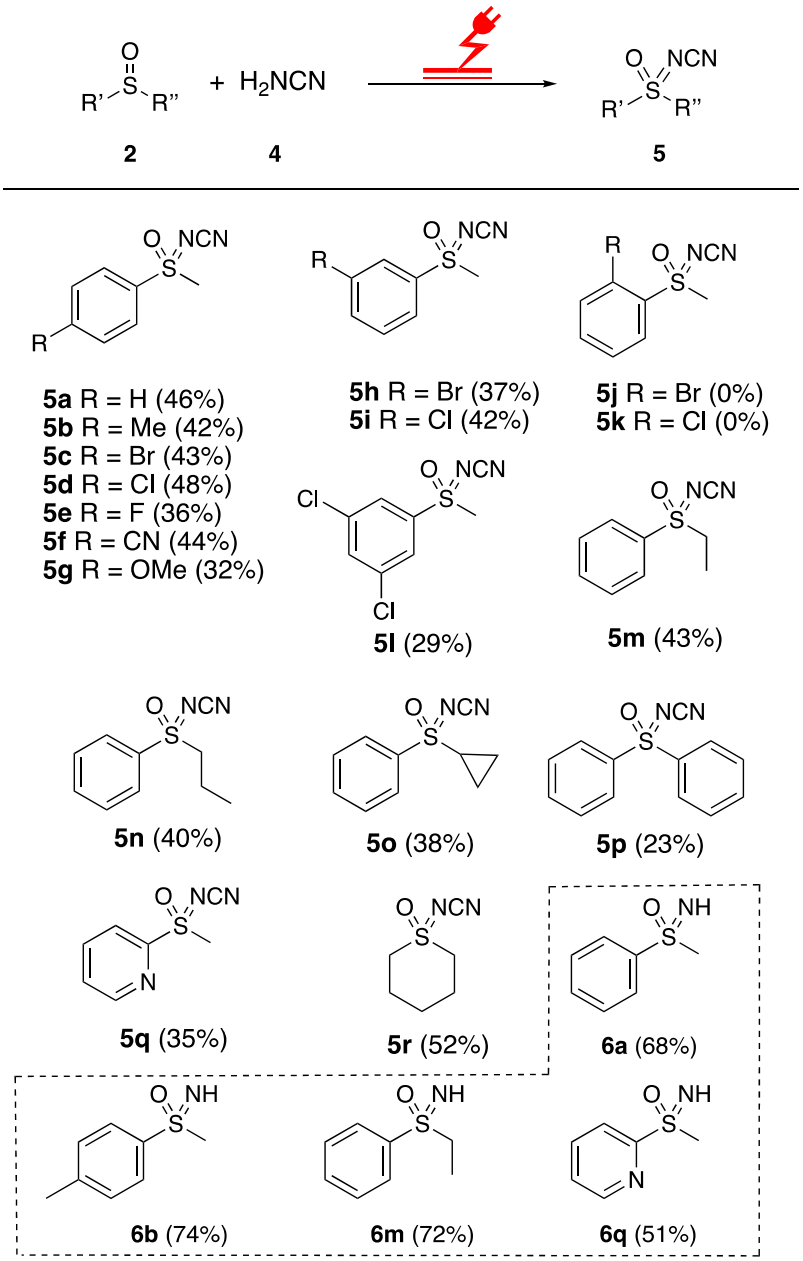
Initial screening showed that the platinum electrodes and hexafluoro-2-propanol (HFIP) were the appropriate materials for this reaction. It is known that HFIP has the ability to stabilize radicals in electrochemical reactions.[38] To study the effect of the reaction time, the flow rate was screened from 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).

Entry	Flow rate (mL min^{-1})	I (mA)	F	Conversion [%][a]
1	0.075	18	3	33
2	0.1	24	3	34
3	0.15	36	3	40
4	0.2	48	3	17
5	0.15	48	4	48
6	0.15	72	6	68
7	0.15	36	6[b]	43
8	0.15	144	6[c]	62

Table 3. Conditions: [**2a**] = 0.05 M, [**4**] 0.075 M, reactor volume: 0.3 mL. [a] Determined by ^1H 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 *para*- and *meta*-positions of alkyl aryl sulfoxides delivered good yields of the corresponding *N*-cyanosulfoximines **5a−i**. No reaction occurred with *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*-pyridinylsulfoximine **5q** and cyclic sulfoximines **5r** were also obtained in moderate yields as shown in

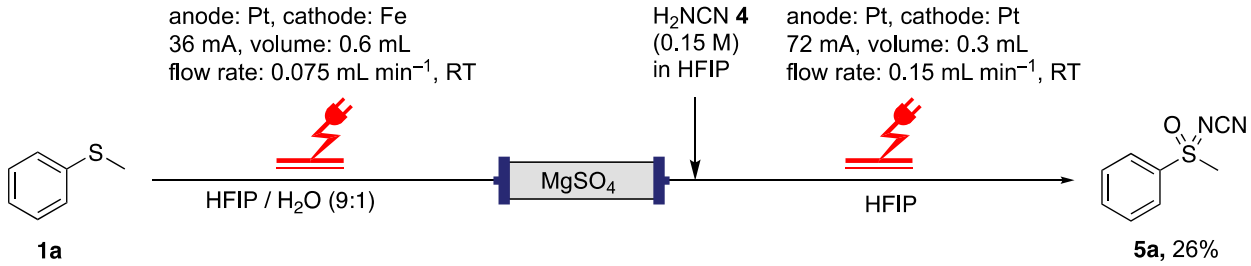
Scheme 2. Finally, the protected *N*-cyanosulfoximines were converted into NH-sulfoximines **6** by treatment with trifluoroacetic anhydride (TFAA), followed by the addition of K_2CO_3.[39]



Scheme 2. Substrate scope for the electrochemical formation of *N*-cyanosulfoximines. Conditions: [**2**] = 0.05 M, [**4**] = 0.125 M, HFIP, Pt (+)/Pt (-), 72 mA, flow rate = 0.15 mL min^{-1}, reactor volume: 0.3 mL, RT.

A combination of both oxidation sequences from sulfides to *N*-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 $MgSO_4$ in between, which allowed an in-

line removal of water. As shown in Scheme 3, the thioanisol **1a** in HFIP/H_2O 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_4NBF_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 Ep = 1.57 V and Ep = 1.9 V (Figure 2a, yellow line), while there was only one apparent oxidation peak for sulfoxide **2a** at Ep = 2.05 V (Figure 2a, blue line). Also, the cyclic voltammetry of sulfoxide **2a** in HFIP showed one oxidation peak at Ep = 2.1 V (Figure 2b, orange line), while there was no oxidation peak for cyanamide **4** (Figure 2b, gray line).

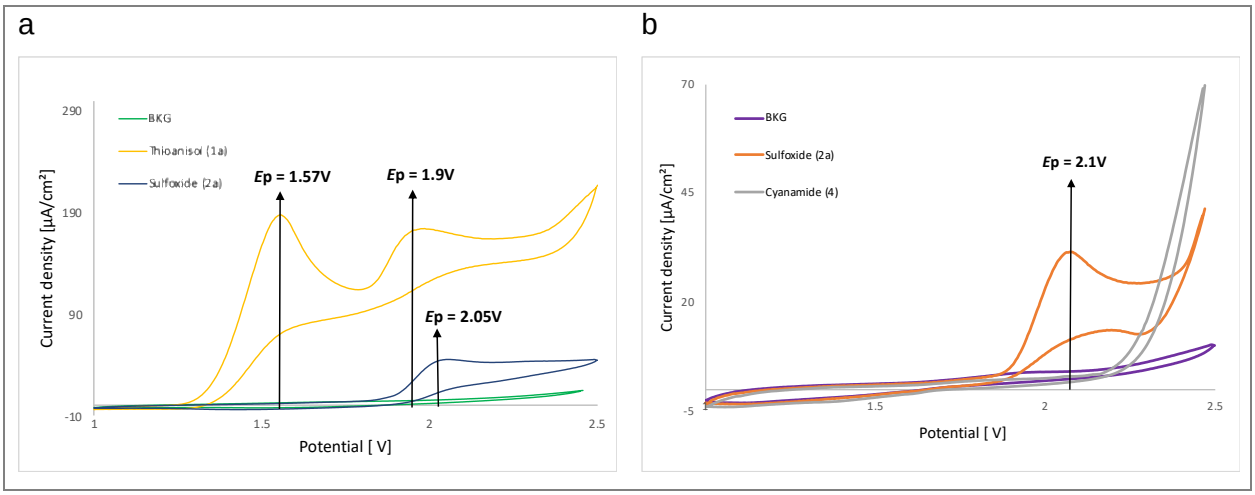
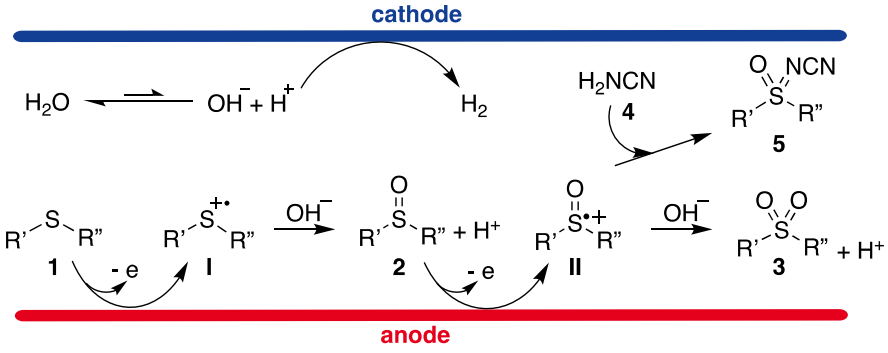


Figure 2. Cyclic voltammetry (CV) studies of thioanisol **1a** (yellow line**)** and sulfoxide **2a** (blue line) in MeCN (a). Sulfoxide **2a** (orange line) and cyanamide **4** (gray line) in HFIP (b). GC carbon disk working electrode (immersed surface area: 3 mm^2), Pt counter electrode (immersed surface area: 1.2 mm^2), Ag/0.01 M AgCl refence electrode, 20 mV s^{-1}.

Based on our initial studies and according to previous literature reports on the oxygenation of sulfides, [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. 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. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were measured on Bruker DPX 400 or 500 apparatus and were referenced to the residual proton solvent peak (^{1}H: $CDCl_3$, δ 7.26 ppm; DMSO-d_6, δ 2.50 ppm) and solvent ^{13}C signal ($CDCl_3$, δ 77.2 ppm, DMSO-d_6, 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 voltammogram 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 cm^2). A solution of sulfide (0.1 M) in mixture of CH_3CN and H_2O (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 cm^2). A solution of sulfide (0.1 M) in mixture of CH_3CN and H_2O (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 rector. 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 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 rector. 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_2Cl_2 (10 mL) at 0 ºC, 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_2Cl_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. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 145.7, 131.1, 129.4, 123.6, 44.0 ppm. The spectroscopic data agree with the literature.[43]

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. $^{13}C\{^1H\}$ 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.[43]

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].[44] ^{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. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 145.1, 132.8, 125.7, 125.4, 44.2 ppm. The spectroscopic data agree with the literature.[43]

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. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 144.3, 137.4, 129.8, 125.1, 44.2 ppm. The spectroscopic data agree with the literature.[43]

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, $CDCl_3$) δ 7.68 – 7.61 (m, 2H), 7.25 – 7.16 (m, 2H), 2.70 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ –152.06 ppm. The spectroscopic data agree with the literature.[40]

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, $CDCl_3$) δ 7.96 – 7.68 (m, 4H), 2.76 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 151.6, 133.1, 124.4, 117.8, 114.9, 44.0 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.: 42-44 °C [Lit.: 42-44 °C].[44] ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 162.1, 136.8, 125.6, 114.9, 55.6, 44.1 ppm. The spectroscopic data agree with the literature.[43]

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, $CDCl_3$) δ 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, $CDCl_3$) δ 191.1, 152.4, 138.0, 130.3, 124.1, 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, $CDCl_3$) δ 8.43 – 8.34 (m, 2H), 7.88 – 7.78 (m, 2H), 2.79 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 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).

^{1}H NMR (500 MHz, $CDCl_3$) 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. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) 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.[43]

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). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 – 7.76 (m, 1H), 7.64 – 7.50 (m, 2H), 7.42 – 7.36 (m, 1H), 2.72 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 148.1, 134.2, 130.9, 126.6, 123.7, 122.2, 44.1 ppm. The spectroscopic data agree with the literature.[40]

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). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.50 – 7.43 (m, 3H), 2.73 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 148.0, 135.8, 131.3, 130.7, 123.7, 121.7, 44.1 ppm. The spectroscopic data agree with the literature.[40]

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). ^{1}H NMR (500 MHz, $CDCl_3$) 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. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 145.5, 133.0, 132.4, 128.8, 125.8, 118.5, 42.0 ppm. The spectroscopic data agree with the literature.[45]

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). ^{1}H NMR (500 MHz, $CDCl_3$) 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. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 143.7, 132.1, 129.9, 128.3, 125.4, 41.7 ppm. The spectroscopic data agree with the literature.[40]

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). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (t, *J* = 6.6 Hz, 1H), 7.82 – 7.79 (t, *J* = 6.6 Hz, 1H), .63 – 7.56 (m, 1H), 7.24 – 7.17 (m, 1H), 2.77 (s, 3H) ppm. $^{13}C\{^{1}H\}$ 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. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 149.5, 136.4, 131.2, 122.0, 44.1 ppm. The spectroscopic data agree with the literature.[40]

(Ethylsulfinyl)benzene (2q). Compound **2q** was synthesized following **GP1**, 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 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. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 143.3, 131.0, 129.2, 124.3, 50.4, 6.0 ppm. The spectroscopic data agree with the literature.[43]

(Propylsulfinyl)benzene (2r). Compound **2r** was synthesized following **GP1**, using phenyl(propyl)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. $^{13}C\{^1H\}$ 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.[48]

(Cyclopropylsulfinyl)benzene (2s). Compound **2s** was synthesized following **GP1**, using cyclopropyl(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. $^{13}C\{^1H\}$ 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(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 (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. $^{13}C\{^1H\}$ 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, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ 7.69 – 7.58 (m, 2H), 7.47 – 7.41 (m, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CDCl_3$) δ 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 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 66% yield (160 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 52.1, 24.6, 22.1, 13.7 ppm. The spectroscopic data agree with the literature.[43]

Tetrahydro-2*H*-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. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 48.8, 24.7, 19.0 ppm. The spectroscopic data agree with the literature.[51]

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. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 59.1, 46.2 ppm. The spectroscopic data agree with the literature.[52]

(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°C [Lit.: 91 °C].[25] ^{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. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 140.7, 133.7, 129.4, 127.4, 44.8 ppm. The spectroscopic data agree with the literature.[40]

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°C [Lit.: 87-88 °C].[53]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 7.3 Hz, 2H), 2.99 (s, 3H), 2.40 (s, 3H) ppm. $^{13}C\{^{1}H\}$ 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.[51]

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°C [Lit.: 100-102 °C] .[40]¹ ^{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. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 139.7, 132.8, 129.1, 44.6 ppm. The spectroscopic data agree with the literature.[40]

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].[40] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 2H), 7.57 – 7.51 (m, 2H), 3.08 – 3.01 (m, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 140.6, 139.2, 129.8, 129.0, 44.6 ppm. The spectroscopic data agree with the literature.[40]

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 NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 2H), 7.26 – 7.20 (m, 2H), 3.04 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 165.8 (d, *J* = 256.1 Hz), 136.8 (d, *J* = 3.2 Hz), 130.4 (d, *J* = 9.6 Hz), 116.7 (d, *J* = 22.7 Hz), 44.7 (s) ppm. $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$) δ –103.59 ppm. The spectroscopic data agree with the literature.[40]

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].[54] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.03 (m, 2H), 7.91 – 7.84 (m, 2H), 3.08 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 144.6, 133.3, 128.3, 117.7, 117.1, 44.3 ppm. The spectroscopic data agree with the literature.[51]

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].[40] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.72 (m, 2H), 7.10 – 6.90 (m, 2H), 3.86 (s, 3H), 3.01 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 163.8, 132.4, 129.6, 114.6, 55.8, 44.9 ppm. The spectroscopic data agree with the literature.[40]

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].[55] ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.14 (s, 1H), 8.11 (dd, *J* = 19.4, 8.3 Hz, 4H), 3.10 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 190.8, 145.5, 139.8, 130.5, 128.4, 44.4 ppm. The spectroscopic data agree with the literature.[56]

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 NMR (500 MHz, $CDCl_3$) δ 8.46 – 8.39 (m, 2H), 8.20 – 8.10 (m, 2H), 3.12

(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 e 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, $CDCl_3$) 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. ^{1}H NMR (500 MHz, $CDCl_3$) 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. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.9, 142.9, 134.6, 131.0, 129.0, 92.7, 42.0 ppm. The spectroscopic data agree with the literature.[59]

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].[25] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 1.9 Hz, 2H), 7.62 (t, *J* = 1.9 Hz, 1H), 3.08 (s, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 14.4, 136.5, 133.9, 126.0, 44.5 ppm. The spectroscopic data agree with the literature.[25]

(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). ^{1}H NMR (500 MHz, $CDCl_3$) 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. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) 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). ^{1}H NMR (500 MHz, $CDCl_3$) 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. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) 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). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.80 (m, 2H), 7.65 – 7.58 (m, 1H), 7.57 – 7.47 (m, 2H), 2.51 – 2.36 (m, 1H), 1.35 – 1.27 (m, 2H), 1.04 – 0.94 (m, 2H) ppm. ^{13}C{^{1}H} NMR

(126 MHz, $CDCl_3$) δ 140.7, 133.4, 129.3, 127.5, 32.9, 6.0 ppm. The spectroscopic data agree with the literature.[40]

(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). ^{1}H NMR (500 MHz, $CDCl_3$) 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. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 138.4, 133.9, 129.2, 128.7, 124.9, 124.8, 61.0 ppm. The spectroscopic data agree with the literature.[61]

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].[62] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.89 (m, 2H), 7.61 – 7.46 (m, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.7, 133.3, 129.4, 127.8 ppm. The spectroscopic data agree with the literature.[40]

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].[63] ^{1}H NMR (500 MHz, $CDCl_3$) 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. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) 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.[64]

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). ^{1}H NMR (500 MHz, $CDCl_3$) 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. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.1, 150.1, 138.4, 127.6, 121.1, 40.1 ppm. The spectroscopic data agree with the literature.[40]

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). ^{1}H NMR (500 MHz, $CDCl_3$) 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.[51]

Tetrahydro-2*H*-thiopyran 1,1-dioxide (3z). Compound **3z** was synthesized following **GP2**, 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 (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.[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].[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 (101 MHz, $CDCl_3$) δ 66.3, 53.0 ppm. The spectroscopic data agree with the literature.[66]

***N*-(Methyl(oxo)(phenyl)-λ^{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.[67]

***N*-(Methyl(oxo)(*p*-tolyl)-λ^{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 = 8.3 Hz, 2H), 7.47 (d, J = 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.[67]

***N*-((4-Bromophenyl)(methyl)(oxo)-λ^{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 –

7.78 (m, 4H), 3.35 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 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)-λ^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, $CDCl_3$) δ 8.00 – 7.88 (m, 2H), 7.72 – 7.61 (m, 2H), 3.35 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 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)-λ^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, $CDCl_3$) δ 8.06 – 8.00 (m, 2H), 7.39 – 7.33 (m, 2H), 3.35 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ –99.69 ppm. The spectroscopic data agree with the literature.[68]

***N*-((4-Cyanophenyl)(methyl)(oxo)-λ^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, $CDCl_3$) δ 8.18 – 8.11 (m, 2H), 8.02 – 7.95 (m, 2H), 3.40 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 140.4, 134.0, 128.9, 119.4, 116.6, 111.0, 44.5 ppm. The spectroscopic data agree with the literature.[69]

***N*-((4-Methoxyphenyl)(methyl)(oxo)-λ^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, $CDCl_3$) δ 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, $CDCl_3$) δ 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)-λ^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, $CDCl_3$) δ 8.12 (s,

1H), 7.97 – 7.88 (m, 2H), 7.57 (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.[67]

***N*-((3-Chlorophenyl)(methyl)(oxo)-λ^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 (101 MHz, $CDCl_3$) δ 137.9, 136.8, 135.8, 131.7, 128.1, 126.1, 111.4, 44.8 ppm. The spectroscopic data agree with the literature.[70]

***N*-((3,5-Dichlorophenyl)(methyl)(oxo)-λ^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, 1091, 844, 688 cm^{-1}. HRMS (ESI) m/z: [M+H] calcd for $C_8H_7N_2OSCl_2$ 248.9656; found 248.9655.

***N*-(Ethyl(oxo)(phenyl)- λ^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.[68]

***N*-(Oxo(phenyl)(propyl)-λ^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 $C_{10}H_{13}N_2OS$ 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 sulfinyldibenzene (**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-2*H*-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 cm^{-1}. HRMS (ESI) m/z: [M+H] calcd for $C_6H_{11}N_2OS$ 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.[71]

Imino(methyl)(*p*-tolyl)-λ^6-sulfanone (6b). Compound **6b** was synthesized following **GP4**, using *N*-(methyl(oxo)(*p*-tolyl)-λ^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.[71]

Ethyl(imino)(phenyl)-λ^6-sulfanone (6m). Compound **6m** was synthesized following **GP4**, using *N*-(ethyl(oxo)(phenyl)-λ^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.[71]

Imino(methyl)(pyridin-2-yl)-λ^6-sulfanone (6q). Compound **6q** was synthesized following **GP4**, using *N*-(methyl(oxo)(pyridin-2-yl)-λ^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_2Cl_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.[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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