

Electronic Supporting Information (ESI)

An Environmentally Benign Electrochemical Oxidation of Sulfides and Thiols in a Continuous-Flow Microreactor

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1. *General information*

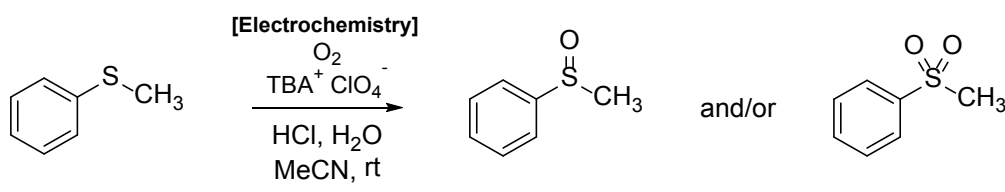
All reagents and solvents were used as received without further purification, unless stated otherwise. Reagents and solvents were bought from Sigma Aldrich and TCI and if applicable, kept under argon atmosphere. Technical solvents were bought from VWR International and Biosolve, and are used as received. All capillary tubing and microfluidic fittings were purchased from IDEX Health & Science. Used syringes were of BD Discardit II® or NORM-JECT®, purchased from VWR Scientific. Syringe pumps were purchased from Chemix Inc. model Fusion 200 Touch. ¹H (400MHz), ¹³C (100MHz) and ¹⁹F (376 MHz) NMR spectra were recorded on ambient temperature using a Bruker-Avance 400 or Mercury 400. ¹H NMR spectra are reported in parts per million (ppm) downfield relative to CDCl₃ (7.26 ppm) and DMSO-*d*₆ (2.50 ppm), all ¹³C NMR spectra are reported in ppm relative to CDCl₃ (77.2 ppm) and DMSO-*d*₆ (39.52 ppm). NMR spectra uses the following abbreviations to describe the multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet, ddd = double double doublet, td = triple doublet. NMR data was processed using the MestReNova 9.0.1 software package. Known products were characterized by comparing to the corresponding ¹H NMR and ¹³C NMR from literature. Melting points were determined with a Buchi B-540 capillary melting point apparatus in open capillaries and are uncorrected. The names of all products were generated using the PerkinElmer Chem-BioDraw Ultra v.12.0.2 software package.

For all electrochemical reactions, a Syrris Asia Flux module was used. The module, via which the potential or the current can be set, is connected to the electrochemical cell. The cell consists of a working electrode and a counter electrode, with a PTFE (Polytetrafluoroethylene) gasket containing micro-channels in between. The volume of the reactor is fixed at 300 μL. This results in an undivided electrochemical cell. In the cell, direct contact between the electrode surface and the reaction mixture is established. The reaction mixture is pumped through the system via syringe pump, and is collected in a glass vial. During the project, for both the working- and the counter electrode, stainless steel was used as electrode material. Both electrodes can be set to be the anode or the cathode at any time.

2. Optimization of reaction conditions – Batch experiments

A series of batch reactions was performed as reference experiments. These reactions are performed both in the open and closed setup described below.

Table S1: Preliminary batch experiments



Entry	Potential (V)	Conversion 2 ^a (%)	Conversion 3 ^a (%)
1	2	Traces	0
2	4	Traces	0
3	6	Traces	0

Results electrochemical batch reaction after 6 hours. General info: The reaction was performed with 0.15 M thioanisole in an oxygen saturated 3:1 (v/v) mixture of acetonitrile and a 0.1M HCl solution in water, with 10 mol% tetrabutyl ammonium perchlorate as supporting electrolyte. The electrodes used are identical (Fe). ^aData recorded on GC-MS (uncorrected yield).

Using an open setup was in general unsuccessful as no reaction occurred. The electrodes were oxidized before any reaction could occur, even after acidification. The closed system did enable a reaction as electrode oxidation occurred at higher potentials. The closed system was put under argon atmosphere with the oxygen mainly in solution, this delayed oxidation as the oxidising agent was only present in controlled amounts, in contrary to the open system where the solution was in constant contact with the air.

A point of notice was the detection of gas formation, due to the electrolysis of water, generating oxygen and hydrogen gas. This gas formation is not problematic in the continuous flow cell as the quantities present are much lower and gas build-up is prevented by the imposed flow, but in such close glassware devices the handling of this setup resulted cumbersome.

The first setup example is an open air single cell configuration (Fig. S1A). The two electrodes are hung in a 500 ml borosilicate glass beaker, they are placed in a way that no contact is made with the beaker itself, only with the residing mixture. The electrode are then connected to a potentiostat (electronic hardware required to control the electrodes) as power source. The beaker is filled with 25 ml of reaction

mixture and the mixture submerges part of the electrode surface. A capillary tube is run into the mixture to provide for oxygen and a stirrer is added to increase mixing in the system.

The second setup example is a closed single cell setup (Fig S1B). The electrodes are pushed through septa, these septa are then put on the side ends of a three-neck flask. A third septa is put on the last opening to close the system. A stirrer is added and the entire system is put under argon atmosphere. A needle is pushed through the septum into the mixture, this needle is connected to a dry oxygen balloon. A second needle is added, this one only reaching the head-space, an argon balloon is connected to the needle, this is done to prevent overpressure in the system. The electrodes are subsequently connected to the negative and positive poles of a potentiostat.

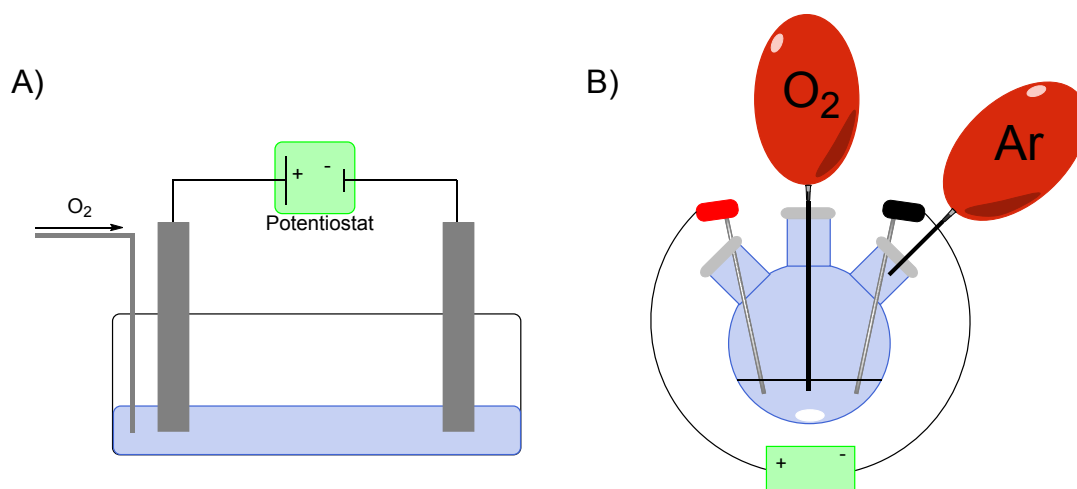


Figure S 1: A) Open air single cell configuration B) Closed single cell setup

3. Optimization of reaction conditions – Flow experiments

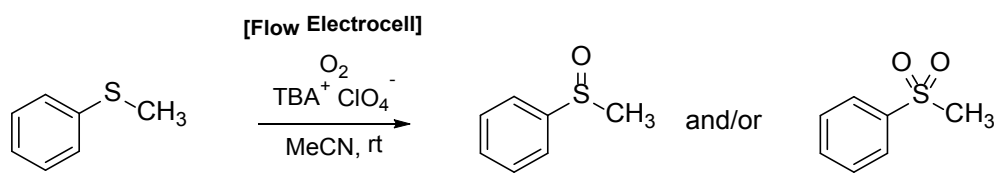
The initial reaction mixture contained thioanisole (0.15 M) dissolved in acetonitrile which was saturated with oxygen gas (Fig. 11). This reactions was screened over a variety of potentials (0.5 – 4.5 V), flow rates (0.1 – 0.02 mL min⁻¹) and electrode materials (Steel, Cu, C and Pt).

Unfortunately, none of the reactions conditions gave conversion. Furthermore, a current was only detected past the potential window at 4.5 V, which corresponded with the electrode oxidation at the cathode. This result led us to the conclusion that the apparent solvent system was not capable enough to maintain a stable current at lower potentials (<4.0 V), indicating a lack of reaction media conductivity.

Henceforth, the conductivity was improved by adding a supporting electrolyte to the reaction mixture, which supposedly participates in the transfer of electrons through the reaction mixture. Therefore 10 mol% tetrabutyl ammonium perchlorate (TBA ClO₄) was added to the reaction medium. TBA ClO₄ is commonly used in previously reported literature. The performed screening and corresponding results are reported in Table S2.

Table S2. Flow experiment with oxygen saturated ACN ^a

[Flow Electrocell]



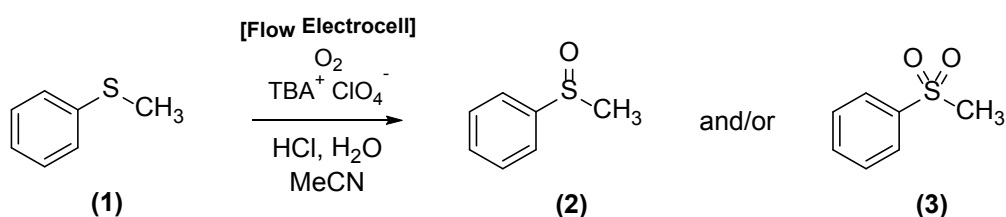
Entry	Potential (V)	Current (mA)	Yield 2 (%) ^a	Yield 3 (%) ^a
1	0.5	0	n.r.	
2	1.0	0	n.r.	
3	1.5	0	n.r.	
4	2.0	0	n.r.	
5	2.5	0	n.r.	
6	3.0	3	n.r.	
7	3.5	5	n.r.	
8	4.0	15	7.5	0.0
9	4.5	30	2.0	16.6

Screening conditions and results for sulfoxidation. General info: The reaction was performed using 0.1 M thioanisole in oxygen saturated acetonitrile, with 10 mol% tetrabutyl ammonium perchlorate as supporting electrolyte. Fe electrodes are used and the reaction was run over 6 min. Data recorded on GC-MS (uncorrected yield).

Fortunately, with these slight adaptations a current was observed at lower potential than previously observed (3.0 V), this demonstrated that the conductivity of the reaction mixture was improved due to the addition of a electrolyte. Furthermore, the detected current corresponds with the conversion of the thioanisole to the wanted product. Albeit the perceived conversions were rather low, it can be appreciated that selectively towards single oxidation occurs at 4.0 V.

The oxidation of the materials normally signals the end of the potential boundaries of the system. The steel electrodes were usable up to 2.5 V, when potential was increased further the electrodes become unstable allowing them to oxidize or be damaged. To enable a higher potential other materials can be used or the system can be stabilized by altering its environment. *Pourbaix diagrams* show that there is a relation between redox potentials and the pH of compound. The *Pourbaix diagram* of Fe(II)/Fe(III), clearly shows that the oxidising potential is increases with lower pH.¹ Using this relationship it is opted to stabilize the electrodes by adding an acid, such as HCl (0.1 M in H₂O), to the reaction mixture. The new reaction conditions are shown below, with the performed screenings and corresponding results reported in Table S3.

Table S3. Flow experiment with aqueous HCl addition ^a

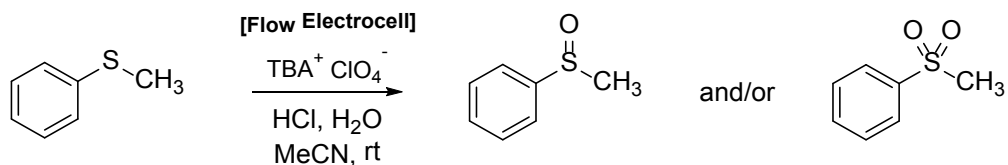


Entry	Potential (V)	Current (mA)	Yield 2 (%)	Yield 3 (%)
1	0.5	0	n.r.	
2	1.0	0	n.r.	
3	1.5	0	n.r.	
4	2.0	5	n.r.	
5	2.5	21	39	0
6	3.0	30	62	21
7	3.5	47	60	35
8	4.0	108	10	87
9	4.5	112	15	82

^aGeneral info: The reaction was performed using 0.1 M thioanisole in an oxygen saturated 3:1 (v/v) mixture of acetonitrile and a 0.1M HCl solution in water, with 10 mol% tetrabutyl ammonium perchlorate as supporting electrolyte. Fe electrodes are used and the reaction was run over 6 min .Data recorded on GC-MS (uncorrected yield).

The critical potential at which oxidation of the electrodes occurs, has increased (from 2.5 V to 3.5 V), enlarging the potential window of the system. Another observation is that the current starts at 2 V, which is considerably earlier in comparison to the previous reported reactions. Furthermore, the increased current corresponds with higher conversion rates. A possible reason for this increase is that the HCl can act as an complementary electrolyte. The conversion has noticeably increased, suggesting that the additives have had an effect on the reaction productivity.

Table S4. Flow experiment with aqueous HCl addition without oxygen^a



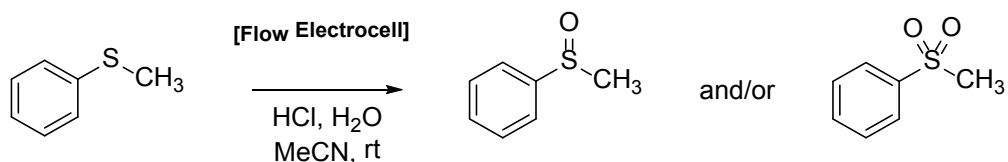
Entry	Potential (V)	Current (mA)	Yield 2 (%)	Yield 3 (%)
1	0.5	0	n.r.	
2	1.0	0	n.r.	
3	1.5	0	n.r.	
4	2.0	5	n.r.	
5	2.5	21	62	0
6	3.0	30	65	27
7	3.5	47	59	39
8	4.0	108	7	92
9	4.5	112	17	83

^aGeneral info: The reaction was performed using 0.1 M thioanisole in a 3:1 (v/v) mixture of acetonitrile and a 0.1M HCl solution in water, with 10 mol% tetrabutyl ammonium perchlorate as supporting electrolyte. Fe electrodes are used and the reaction was run over 6 min. Data recorded on GC-MS (uncorrected yield).

Comparing these results with the previous results from Table S3, it can be established that oxygen gas was not a necessity for this reaction, as its presence only causes a slight change in reaction conversion. Excluding possible oxygen activity cannot be done, as in Table S2 product formation is observed, which was performed in the absence of other possible oxygen sources. It is possible that H₂O present in the HCl solution acts as oxygen source in Table S4 & 3, being preferred over the oxygen gas.

In Table S2 it is observed that electrolyte addition increases conductivity in the system, however in Table S3, HCl and H₂O are added, which as mentioned before, can also act as charge carriers and increase conductivity of the reaction media. In the next test reaction, the electrolyte will be omitted (Table S5). The reaction was screened over multiple potentials (0.5 - 3.5 V), residence times (1 – 15 min) and different electrode materials (steel, Cu, C and Pt).

Table S5. Flow experiment with aqueous HCl addition without electrolyte ^a

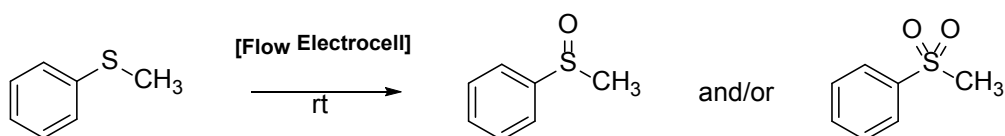


Entry	Potential (V)	Current (mA)	Yield ^a 2 (%)	Yield ^a 3 (%)
1	0.5	0		n.r.
2	1.0	0		n.r.
3	1.5	0		n.r.
4	2.0	0		n.r.
5	2.5	0		n.r.
6	3.0	0		n.r.
7	3.5	2		n.r.
8	4.0	5		n.r.
9	4.5	12		n.r.

^aGeneral info: The reaction was performed using 0.15 M thioanisole in a 3:1 (v/v) mixture of acetonitrile and a 0.1 M HCl solution in water. Fe electrodes are used and the reaction was run over 6 min. Data recorded on GC-MS (uncorrected yield).

Considering the reactions above, it is concluded that the conditions applied in Table S4 are the most optimal for the sulfur transformation. An overview of all earlier mentioned reactions, with corresponding conversions, is shown in Table S6.

Table S6. Overview condition tested ^a



Reaction	TBA ClO ₄	HCl solution	O ₂ saturated	Conversion ^a (%)
1	No	No	Yes	0
2	Yes	No	Yes	0 - 16
3	Yes	Yes	Yes	39 - 99
4	Yes	Yes	No	43 - 98
5	No	Yes	No	0

^aGeneral info: Depending on the screening the reaction was performed using 0.1 M thioanisole in oxygen saturated acetonitrile or a 3:1 (v/v) mixture of acetonitrile and a 0.1M HCl solution in water, with 10 mol% tetrabutyl ammonium perchlorate as supporting electrolyte. Fe electrodes are used and the reaction was run over 6 min. Data recorded on GC-MS (uncorrected yield).

4. Optimization of reaction conditions – Flow rate and residence time

The reaction was initially performed using a flow rate of 0.06 mL/min. The reactor had a fixed volume of 0.3 mL, which then corresponds to a residence time of 5 minutes. To achieve a higher residence time, the reaction mixture was pumped through the reactor multiple times, without lowering the flow rate. This is called ‘fixed flow rate’ method. Alternatively, the flow rate can be altered to achieve a different residence time. This is called ‘varying flow rate’ method. These two methods were applied to the model reaction (Figure S2A and B, varying flow rate and fixed flow rate methods, respectively).

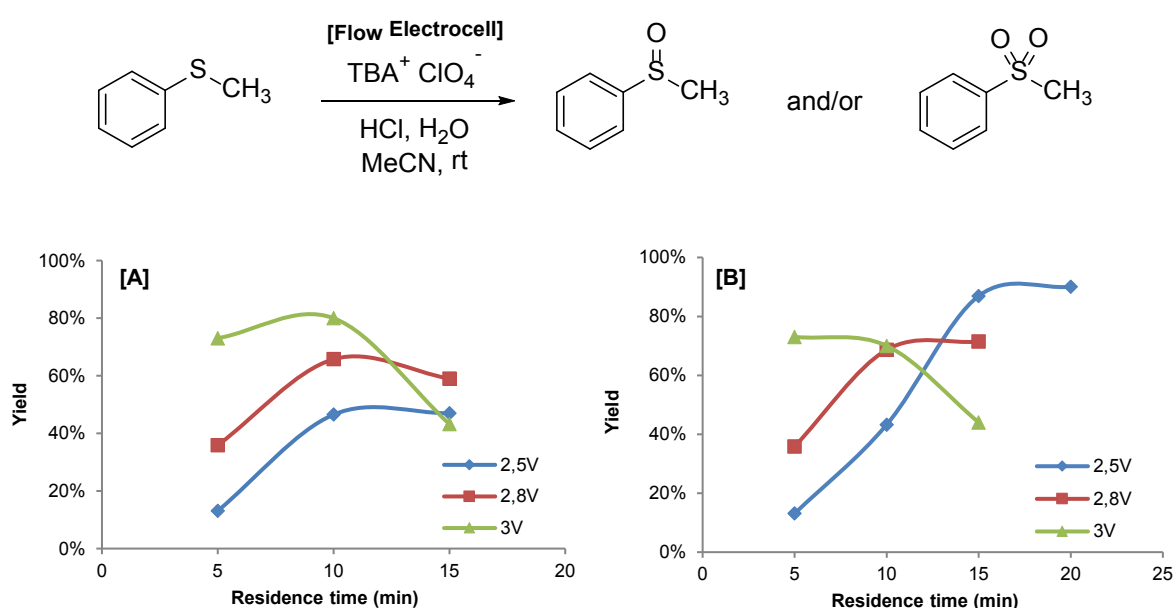


Figure S2. Electrochemical oxidation of thioanisole. *General reagents and conditions:* unless stated otherwise, thioanisole (c = 0.15 M), TBAClO₄ (10 mol%), MeCN/HCl (3:1, v/v), HCl = 0.1 M in H₂O), Q_L = 0.06 mL min⁻¹, t_R = see graph, applied potential = see graph. [A] (Left graph) Varying flow rate method (Q_L = 0.02, 0.03, 0.06 mL min⁻¹). [B] (Right graph) Fixed flow rate method (Q_L = 0.06 mL min⁻¹).

The results in Figure S2 show that the fixed flow rate method provides higher yields at higher residence times than the varying flow rate method. As can be seen when comparing Figure S2A with Figure S2B, the yields at a residence time of 5 and 10 minutes are the same in both cases, but is significantly higher at a residence time of 15 minutes with a fixed flow rate. This is especially prevalent at a voltage of 2.5 V, where it appears that although a higher residence time generally leads to better results, the low flow rate hampers this increase. To further examine this effect, the reaction selectivity and conversion were monitored (Figure S3, see below).

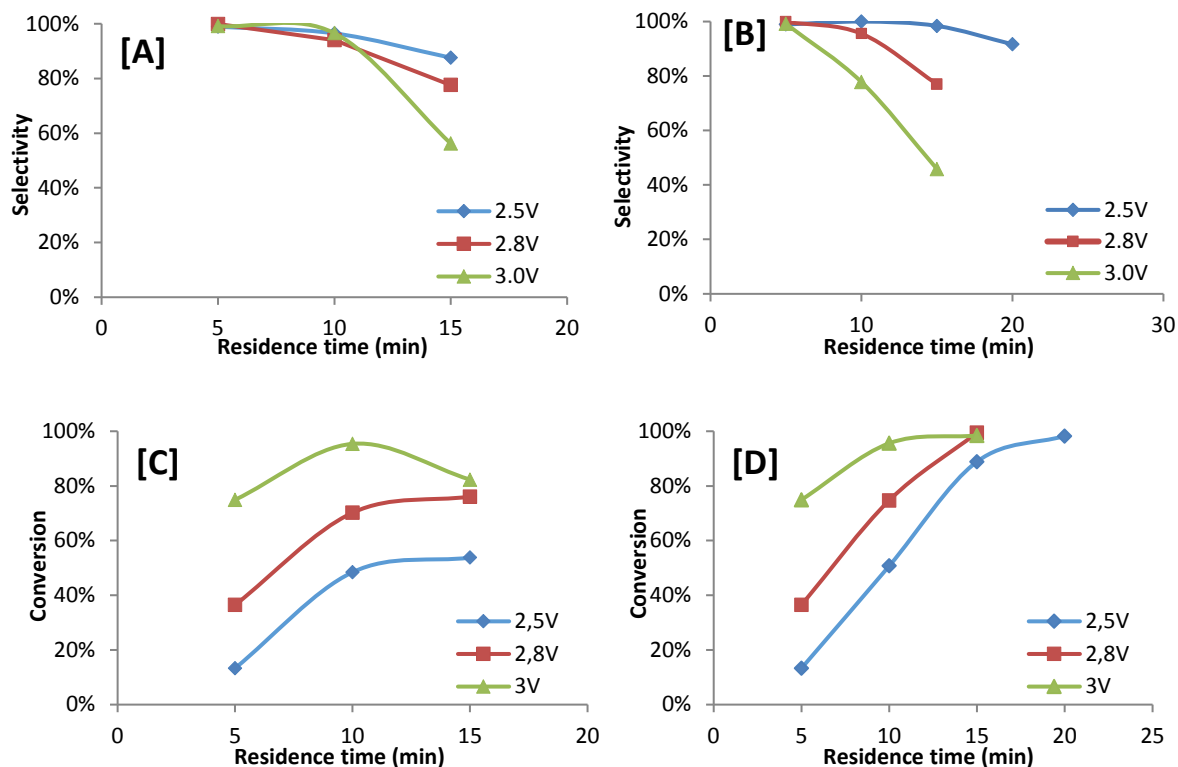
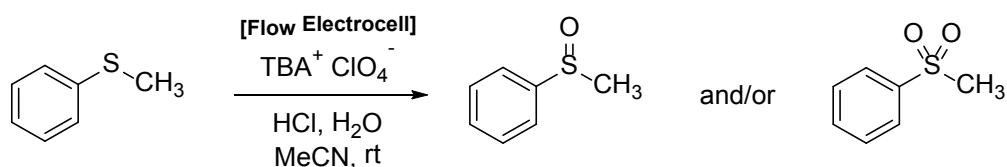


Figure S3. General reagents and conditions: unless stated otherwise, thioanisole ($c = 0.15 \text{ M}$), $\text{Bu}_4\text{N}/\text{ClO}_4$ (10 mol%), MeCN/HCl (3:1, v/v), $\text{HCl} = 0.1 \text{ M}$ in H_2O , $Q_L = 0.06 \text{ mL min}^{-1}$, $t_R = \text{see graph}$, applied potential = see graph. [A] (Left above graph) Selectivity, Varying flow rate method ($Q_L = 0.06 \text{ mL min}^{-1}$). [B] (Right above graph) Selectivity, Fixed flow rate method ($Q_L = 0.02, 0.03, 0.06 \text{ mL min}^{-1}$). [C] (Left under graph) Conversion, Varying flow rate method ($Q_L = 0.06 \text{ mL min}^{-1}$). [D] (Right under graph) Conversion, Fixed flow rate method ($Q_L = 0.02, 0.03, 0.06 \text{ mL min}^{-1}$).

The selectivity (Figure S5 A and S5 B) was not effected significantly between the two methods. This might indicate that the effective flow rate does not affect the selectivity of the oxidation reaction. In figure S5 C, it can be seen that a varying flow rate results in an optimum conversion between 10 and 15 minutes residence time, while using a fixed flow rate (Figure S5 D) no optimum was found. As the flow rate is kept fixed, the conversion reaches 100% at any given applied potential (Figure S5 D). From this observation, it can be concluded that a varying flow rate has an optimum between mixing and residence time, while the fixed flow rate always reaches 100% conversion. It is possible that if the flow rate gets too low, the conversion decreases. This might be attributed to the decrease in mass transfer.

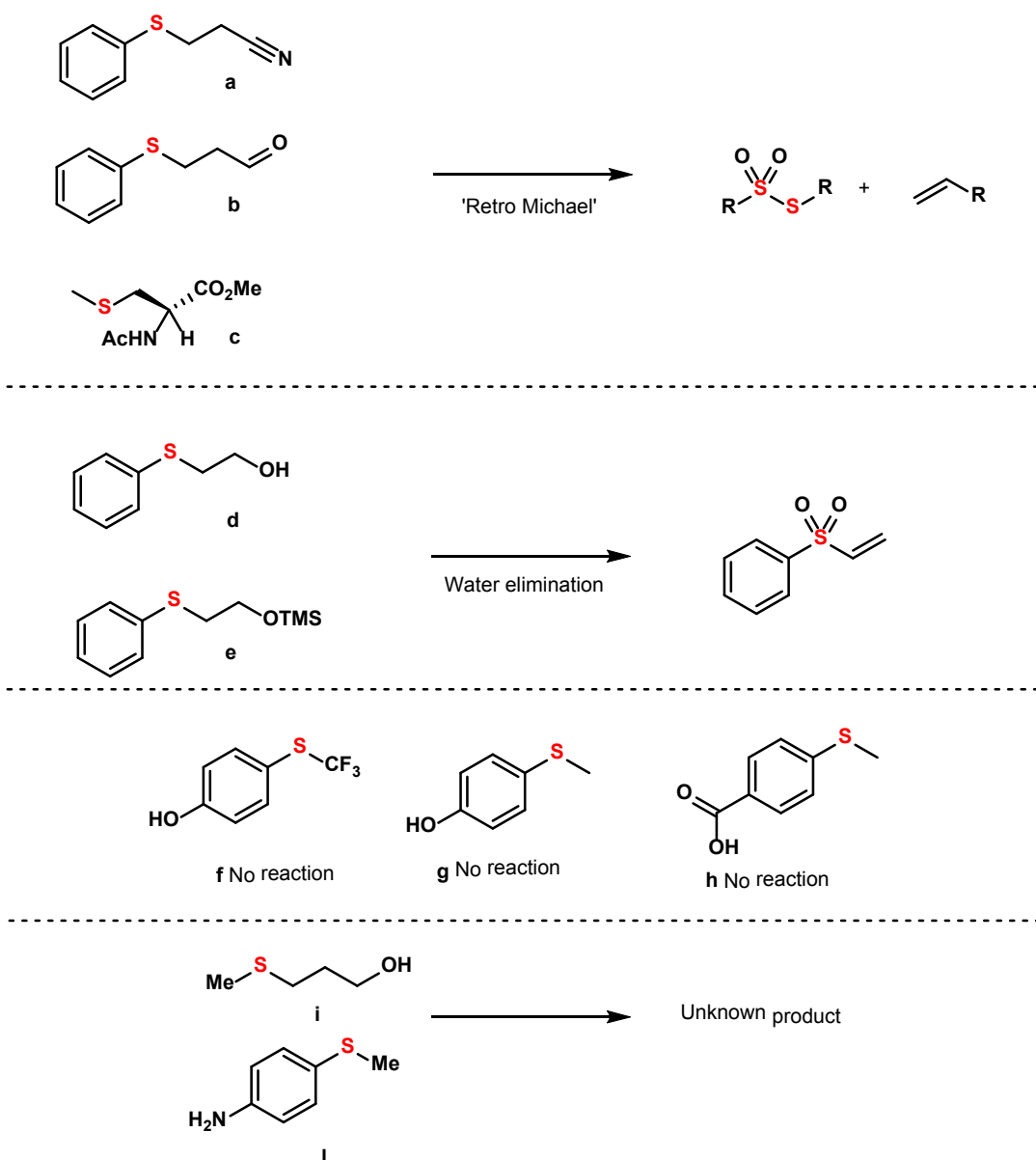
5. *Substrate limitations*

One reoccurring issue was the formation of sulfonothionate moieties. According to the GC-MS results (these compounds have never been isolated), if the compound was unsaturated on the β position, a sort of ‘radical retro-Michael addition’ could take place, resulting in the corresponding alkene and sulfonothionate. Interesting to note is that when doing this reaction with the cysteine derivative methyl *N*-acetyl-*S*-methyl-*D*-cysteinate (**c**), vinyl-glycine was formed, a bioactive compound as well.

A similar problem occurs if an alcohol group is incorporated on the β position. If this is the case, even when the alcohol is trimethylsilyl (TMS) protected (**e**), water can eliminate to form the alkene. A possible explanation is that this product is thermodynamically favoured, and as both oxidation and reduction can theoretically occur in the electrochemical cell, reduction via water elimination seems feasible.

It was found that phenols show no reactivity whatsoever. This can be explained by the known antioxidative capacities of phenols as radical quenchers. Alcohols in general do not inhibit reactions, only phenols do actively quench the reaction to prevent oxidation.

Compounds **i** and **l** showed no conversion towards the sulfoxide and sulfone, but resulted in side-reactions instead. These products were not further analysed.



Scheme S1: Unsuccessful substrates Figure 1 Unsuccessful substrate scope for formation of sulfoxides and sulfones. General info: The reaction was performed with 0.15 M substrate dissolved in an oxygen saturated 3:1 (v/v) mixture of acetonitrile and a 0.1M HCl solution in water, with 10 mol% tetrabutylammonium perchlorate as supporting electrolyte. The electrodes used are identical (Fe).

6. Flow reactor design

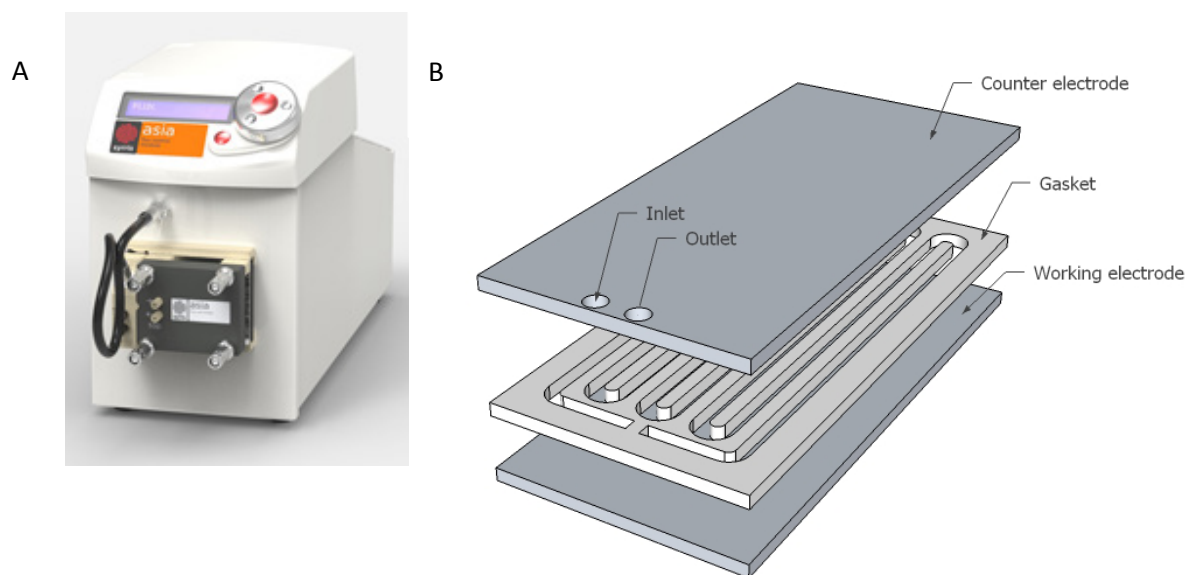
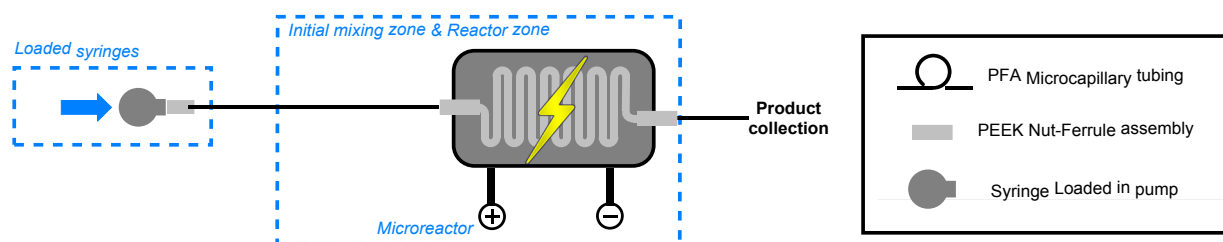


Figure S4: A) Picture of the module Syrris Asia Flux B) Working reactor ($V_{int} = 0.3$ mL).



Scheme S2: Schematic representation of the flow design

7. General procedures

7.1. Synthesis of sulfoxides and sulfones

7.1.1. General protocol for the screening of electrochemical oxidation reactions of sulfides

The concerning thioether was dissolved in the corresponding amount of stock solution (3:1 v/v acetonitrile/0.1 M HCl (aq) and 10 mol% tetrabutylammonium perchlorate) to yield a 0.15 M solution of thioether in stock solution. The amount of solution varied between 5 – 7.5 mL. The solution was flown through the electrochemical setup with a fixed flowrate of 0.06 mL/min to give a residence time of 5 minutes. During the experiment, the potential was varied between 2.3 V – 4 V. After every 6.6 minutes (400 μ L) a sample was taken at the corresponding potential. For each fraction, the current was determined. The fraction was diluted with ethyl acetate or acetone, and analysed without further purification using TLC and GC-MS.

7.1.2. General protocol for the electrochemical oxidation of sulfides

The concerning thioether was dissolved in the corresponding amount of stock solution (3:1 v/v acetonitrile/0.1 M HCl (aq) and 10 mol% tetrabutylammonium perchlorate) to yield a 0.15 M solution of thioether in stock solution. The amount of solution varied between 5 mL – 7.5 mL. The solution was flown through the electrochemical setup with a fixed flowrate of 0.06 mL/min to give a residence time of 5 minutes. During the experiment, the potential was set at the optimal potential determined in the screening experiment. All of the solution was collected in a vial, covered by a parafilm tape. If the conversion was found to be sufficiently high after collecting, the solution was diluted with saturated bicarb solution (15 mL) and transferred to a separation funnel. The water phase was extracted with ethyl acetate (three times 25 mL). The resulting organic fractions were washed with brine, dried over MgSO_4 and concentrated *in vacuo*. The product was then purified using flash chromatography (PE/EtOAc, CyHex/EtOAc or DCM/MeOH) and analysed by H-NMR, C-NMR, GC-MS, FT-IR, HR-MS and TLC. The electrode surface was cleaned after every experiment by sonicating the plates, gasket and seal in 1 M HCl (aq) for 5 minutes, followed by sonicating in acetone for 5 minutes. The plates were dried, scrubbed with an abrasive sponge, and polished with paper towels drenched in 1 M HCl (aq) and acetone.

7.2. *Synthesis of disulfides*

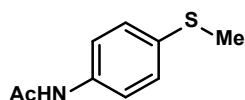
7.2.1. General protocol for the screening of electrochemical oxidation reactions of thiols

The concerning thiol was dissolved in the corresponding amount of stock solution (3:1 v/v acetonitrile/0.1 M HCl (aq) and 10 mol% tetrabutylammonium perchlorate) to yield a 0.15 M solution of thioether in stock solution. The amount of solution varied between 5 – 7.5 mL. The solution was flown through the electrochemical setup with a fixed flowrate of 0.06 mL/min to give a residence time of 5 minutes. During the experiment, the potential was varied between 2.3 V – 4 V. After every 6.6 minutes (400 μ L) a sample was taken at the corresponding potential. For each fraction, the current was determined. The fraction was diluted with ethyl acetate or acetone, and analysed without further purification using TLC and GC-MS.

7.2.2. General protocol for the electrochemical oxidation of thiols

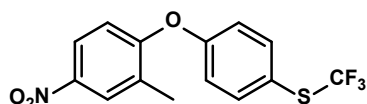
The concerning thiol was dissolved in the corresponding amount of stock solution (3:1 v/v acetonitrile/0.1 M HCl (aq) and 10 mol% tetrabutylammonium perchlorate) to yield a 0.15M solution of thiol in stock solution. The amount of solution varied between 5 mL – 7.5 mL. The solution was flown through the electrochemical setup with a fixed flowrate of 0.06 mL/min to give a residence time of 5 minutes. During the experiment, the potential was set at the optimal potential determined in the screening experiment. All of the solution was collected in a vial, covered by a parafilm tape. If the conversion was found to be sufficiently high after collecting, the solution was diluted with saturated bicarb solution (15 mL) and transferred to a separation funnel. The water phase was extracted with ethyl acetate (three times 25 mL). The resulting organic fractions were washed with brine, dried over MgSO_4 and concentrated *in vacuo*. The product was then purified using flash chromatography (PE/EtOAc, CyHex/EtOAc or DCM/MeOH) and analysed by H-NMR, C-NMR, GC-MS, FT-IR, HR-MS and TLC. The electrode surface was cleaned after every experiment by sonicating the plates, gasket and seal in 1 M HCl (aq) for 5 minutes, followed by sonicating in acetone for 5 minutes. The plates were dried, scrubbed with an abrasive sponge, and polished with paper towels drenched in 1 M HCl (aq) and acetone.

7.3. Synthesis of precursors



N-(4-(methylthio)phenyl)acetamide (9).² 4-(methylthio)aniline (557 mg, 4 mmol) was placed in a 50 mL flask and dissolved in dichloromethane (20 mL). The mixture was cooled to 0 °C. Triethylamine (0.72 mL, 5.2 mmol) and acetyl chloride (0.345 mL, 4.8 mmol) was added and the mixture was stirred for 1 hour. The mixture was treated with saturated ammonium chloride solution (15 mL) and extracted with dichloromethane. The combined organic phase was washed with brine, dried over MgSO₄, and concentrated *in vacuo*. The remaining solid was triturated with 1 mL of diethylether and 8 mL of hexane, resulting in the product (606 mg, 3.34 mmol, 84%).

¹H NMR (399 MHz, Chloroform-*d*) δ 7.53 – 7.35 (m, 2H), 7.32 – 7.19 (m, 3H), 2.46 (s, 3H), 2.16 (s, 3H).
¹³C NMR (100 MHz, Chloroform-*d*) δ 168.24, 135.50, 133.60, 127.98, 120.52, 24.56, 16.68.

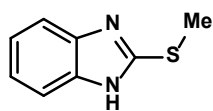


(4-(2-methyl-4-nitrosophenoxy)phenyl)(trifluoromethyl)sulfane (11).³ K₂CO₃ (1.8 g, 12.5 mmol) was placed in a 25 mL flask. The flask was covered by a septum, after which vacuum-argon cycles were performed three times. Dimethylsulfoxide (10 mL) and 4-((trifluoromethyl)thio)phenol (1.0 g, 5 mmol) were added. The mixture was heated to 70 °C and stirred for 20 minutes after which 2-chloro-5-nitrotoluene (1.17 g, 7.5 mmol) was added. The mixture was stirred for 18 hours after which the mixture was cooled to room temperature. Et₂O (50 mL) was added and the mixture was washed with water (3 times) and brine (one time). The aqueous layers were extracted with Et₂O, dried over MgSO₄, and the crude mixture was purified using column chromatography (EtOAc/PE 1:99) to obtain the product as a yellow solid (958 mg, 3.06 mmol, 60%).

¹H NMR (399 MHz, Chloroform-*d*) δ 8.19 (dd, *J* = 2.8, 0.9 Hz, 1H), 8.06 (dd, *J* = 8.9, 2.8 Hz, 1H), 7.73 – 7.63 (m, 2H), 7.07 – 6.98 (m, 2H), 6.93 (d, *J* = 8.9 Hz, 1H), 2.38 (s, 3H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 159.45, 158.30, 143.72, 138.65, 130.96, 130.72, 127.07, 123.26, 119.57, 119.41, 118.08, 16.35.

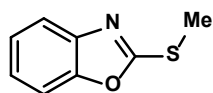
¹⁹F NMR (376 MHz, Chloroform-*d*) δ -43.22.



2-(methylthio)-1H-benzo[d]imidazole (13).⁴ 1H-benzo[d]imidazole-2-thiol (1.20 g, 8 mmol), was placed in a 100 mL flask and dissolved in acetone (25 mL). Iodomethane (1.14 g, 0.50 mL, 8 mmol) and N-ethyl-diisopropylamine (1.03 g, 1.36 mL, 8 mmol) was added, after which the mixture was sonicated for 15 minutes. Water was added (25 mL) which results in the crystallization of the product, which was filtrated and collected (1.01 g, 6.1 mmol, 76%).

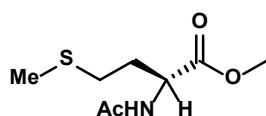
¹H NMR (399 MHz, Chloroform-*d*) δ 7.45 (dd, *J* = 6.0, 3.3 Hz, 2H), 7.14 (dd, *J* = 6.1, 3.2 Hz, 2H), 2.73 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 151.63, 135.80, 123.90, 113.62, 15.36.



2-(methylthio)benzo[d]oxazole (14).⁴ benzo[d]oxazole-2-thiol (365 mg, 2.5 mmol), was placed in a 15 mL flask and dissolved in acetone (8 mL). Iodomethane (342 mg, 0.150 mL, 2.5 mmol) and N-ethyl-diisopropylamine (309 mg, 0.410 mL, 2.5 mmol) was added, after which the mixture was sonicated for 15 minutes. Water was added (15 mL) which results in the crystallization of the product, which was filtrated and collected (376 mg, 2.28 mmol, 91%).

¹H NMR (399 MHz, Chloroform-*d*) δ 7.62 – 7.58 (m, 1H), 7.45 – 7.41 (m, 1H), 7.31 – 7.20 (m, 2H), 2.76 (s, 3H).
¹³C NMR (100 MHz, Chloroform-*d*) δ 165.72, 151.98, 141.94, 124.26, 123.80, 118.31, 109.84, 14.51.



methyl acetyl-D-methioninate (15). Methionine (5g, 33.6 mmol) was placed in a 250 mL flask, and dissolved in glacial acetic acid (75 mL). Acetic anhydride (4.74 g, 5.12 mL, 46 mmol) was added, and the mixture was refluxed for 1.5 hours. The solvent was removed *in vacuo*. Diethylether was added in order to recrystallize the product to form a white solid (5.54 g, 29 mmol, 86%).⁵

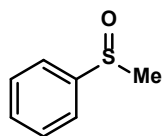
¹H NMR (400 MHz, Deuterium Oxide) δ 4.43 (dd, $J = 9.3, 4.6$ Hz, 1H), 2.62 – 2.44 (m, 2H), 2.10 (dtd, $J = 14.1, 8.1, 4.8$ Hz, 1H), 2.03 (s, 3H), 1.97 (s, 3H), 2.00 – 1.89 (m, 1H).

acetyl-D-methionine (1.916 g, 10 mmol) was placed in a 100 mL flask. Methanol (35 mL) was added, followed by the addition of thionyl chloride (3.108 mL, 42.6 mmol). DMF was added (100 μ L) after which the solution was stirred overnight. The solvent was evaporated *in vacuo*. Purification using column chromatography (EtOAc) yielded the product as a white solid (1.27 g, 6.2 mmol, 62%).⁶

¹H NMR (399 MHz, Chloroform-*d*) δ 6.22 (d, $J = 7.8$ Hz, 1H), 4.71 (td, $J = 7.5, 5.2$ Hz, 1H), 3.75 (s, 3H), 2.50 (ddd, $J = 8.0, 6.7, 2.9$ Hz, 2H), 2.15 (dddd, $J = 14.0, 8.2, 7.0, 5.1$ Hz, 1H), 2.08 (s, 3H), 2.02 (s, 3H), 2.04 – 1.89 (m, 1H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 172.56, 169.85, 52.54, 51.56, 31.74, 29.96, 23.20, 15.49.

8. Characterization data



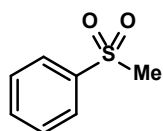
Methyl phenyl sulfoxide (1-A) was prepared as described in the general procedure (7.1). Thioanisole (130.4 mg) was dissolved in 7 mL ACN-stock solution. The mixture was exposed to 3 V over 5 minutes. Flash chromatography was used for purification (EtOAc). Yielding 95.6 mg of product (0.68 mmol, 65 %).

White solid, Mp.: 30 °C (Lit. 30-35 °C)⁷

HRMS (ESI) calculated for C₇H₈OS [M+H]: 141.0374, found: 141.0369

¹H-NMR (399 MHz, Chloroform-*d*) δ 7.68 – 7.62 (m, 2H), 7.57 – 7.45 (m, 3H), 2.73 (s, 3H).

¹³C-NMR (100 MHz, Chloroform-*d*) δ 146.08, 131.37, 129.69, 123.83, 44.32.

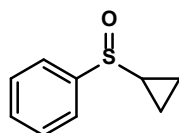


Methyl phenyl sulfone (1-B) was prepared as described in the general procedure (7.1). Thioanisole (130.4 mg) was dissolved in 7 mL ACN-stock solution. The mixture was exposed to 3.5 V over 10 minutes. Flash chromatography was used for purification (EtOAc: PE, 1:4). Yielding 129.6 mg of product (0.83 mmol, 92 %).

White solid, Mp.: 91 °C (Lit. 88-90 °C)⁸

¹H NMR (399 MHz, Chloroform-*d*) δ 7.98 – 7.90 (m, 2H), 7.70 – 7.62 (m, 1H), 7.61 – 7.52 (m, 2H), 3.05 (s, 3H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 140.90, 134.00, 129.67, 127.65, 44.80.



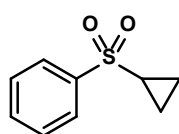
Cyclopropyl phenyl sulfoxide (2-A) was prepared as described in the general procedure (7.1). Cyclopropyl phenyl sulfide (157.5 mg) was dissolved in 7 mL ACN-stock solution. The mixture was exposed to 3 V over 10 minutes. Flash chromatography was used for purification (EtOAc). Yielding 106.3 mg of product (0.64 mmol, 61 %).

Colourless oil⁹

HRMS (ESI) calculated for C₉H₁₀OS [M+H]: 167.0531, found: 167.0520

¹H NMR (400 MHz, Chloroform-*d*) δ 7.64 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.49 (d, *J* = 6.6 Hz, 3H), 2.24 (ddd, *J* = 12.8, 8.1, 4.8 Hz, 1H), 1.22 (dq, *J* = 10.9, 4.8 Hz, 1H), 1.01 (dq, *J* = 9.1, 5.1 Hz, 1H), 0.97 – 0.86 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 145.17, 131.17, 129.41, 124.26, 34.07, 3.68, 3.03.



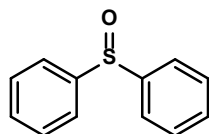
Cyclopropyl phenyl sulfone (2-B) was prepared as described in the general procedure (7.1). Cyclopropyl phenyl sulfide (157.5 mg) was dissolved in 7 mL ACN-stock solution. The mixture was exposed to 3.5 V over 10 minutes. Flash chromatography was used for purification (EtOAc:PE, 1:3). Yielding 59.4 mg of product (0.32 mmol, 31 %).

White solid, Mp.: 32°C (Lit. 33 °C)¹⁰

HRMS (ESI) calculated for C₉H₁₀O₂S [M+H]: 183.04798, found: 183.0472

¹H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.87 (m, 2H), 7.67 – 7.59 (m, 1H), 7.55 (t, *J* = 7.6 Hz, 2H), 2.46 (ddd, *J* = 12.7, 8.2, 4.8 Hz, 1H), 1.41 – 1.14 (m, 2H), 1.11 – 0.91 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 141.01, 133.64, 129.51, 127.82, 33.20, 6.26.



Diphenyl sulfoxide (3-A) was prepared as described in the general procedure (7.1).

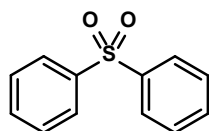
Diphenyl sulfide (195.6 mg) was dissolved in 7 mL ACN-stock solution. The mixture was exposed to 3 V over 10 minutes. Flash chromatography was used for purification (EtOAc). Yielding 131.7 mg of product (0.65 mmol, 62 %).

White solid, Mp.: 67-69 °C (Lit. 68-70 °C)¹¹

HRMS (ESI) calculated for C₁₂H₁₀O₂S [M+H]: 203.0531, found: 203.0534

¹H NMR (399 MHz, Chloroform-*d*) δ 7.68 – 7.61 (m, 4H), 7.50 – 7.39 (m, 6H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 145.91, 131.37, 129.65, 125.10.



Diphenyl sulfone (3-B) was prepared as described in the general procedure (7.1).

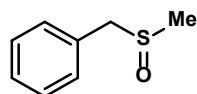
Diphenyl sulfide (195.6 mg) was dissolved in 7 mL ACN-stock solution. The mixture was exposed to 3.5 V over 10 minutes. Flash chromatography was used for purification (EtOAc:Pe, 1:1). Yielding 185.6 mg of product (0.85 mmol, 81 %).

Colorless solid, Mp.: 123-124 °C (Lit. 123-125 °C)⁸

HRMS (ESI) calculated for C₁₂H₁₀O₂S [M-H]: 219.0480, found: 219.0479

¹H NMR (399 MHz, Chloroform-*d*) δ 7.98 – 7.88 (m, 4H), 7.55 – 7.42 (m, 6H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 142.01, 133.76, 129.81, 128.10.



Benzyl methyl sulfoxide (4-A) was prepared as described in the general procedure (7.1).

Benzyl methyl sulfide (144.9 mg) was dissolved in 7 mL ACN-stock solution. The mixture was exposed to 3 V over 10 minutes. Flash chromatography was used for purification (EtOAc). Yielding 95.4 mg of product (0.62 mmol, 59 %).

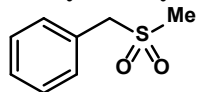
White solid, Mp.: 52-53 °C (Lit. 55-57°C)¹²

HRMS (ESI) calculated for C₈H₁₀S [M-H]: 155.0531, found: 155.0526

¹H NMR (400 MHz, Chloroform-*d*) δ 7.38 (q, *J* = 7.7, 7.0 Hz, 3H), 7.31 – 7.28 (m, 2H), 4.06 (d, *J* = 12.8 Hz, 1H), 3.92 (d, *J* = 12.8 Hz, 1H), 2.45 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 130.36, 129.34, 128.80, 60.73, 37.66.

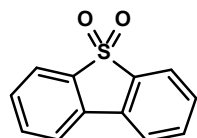
Benzyl methyl sulfone (4-B) was prepared as described in the general procedure (7.1). Benzyl methyl sulfide (144.9 mg) was dissolved in 7 mL ACN-stock solution. The mixture was exposed to 3.5 V over 15 minutes. Flash chromatography was used for purification (EtOAc:PE, 1:4). Yielding 153.5 mg of product (0.90 mmol, 86 %).



White solid, Mp.: 124-125 °C (Lit. 124-126 °C)¹²

¹H NMR (400 MHz, Chloroform-*d*) δ 7.42 (s, 5H), 4.25 (s, 2H), 2.75 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 130.84, 129.51, 128.65, 61.72, 39.34.

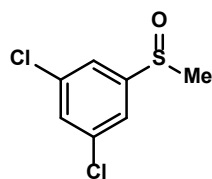


Dibenzo[b,d]thiophene 5,5-dioxide (5-B) Following the general procedure (7.1). dibenzo[b,d]thiophene (165 mg, 0.90 mmol) was dissolved in 6 mL DMF-stock solution. The mixture was exposed to 4.5 V over 5 minutes. Flash chromatography was used for purification (EtOAc/PE 50:50). Yielding 101 mg of product (0.47 mmol, 52 %).

White solid, Mp.: 201-203 °C (Lit. 204-205 °C)⁷

¹H NMR (399 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.79 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 145.23, 137.17, 132.64, 129.63, 127.60, 122.01.

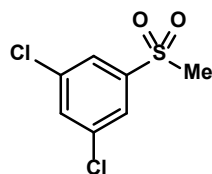


3,5-Dichlorophenyl methyl sulfoxide (6-A) was prepared as described in the general procedure (7.1). 3,5-dichlorophenyl methyl sulfide (203.7 mg) was dissolved in 7 mL ACN-stock solution. The mixture was exposed to 3 V over 7.5 minutes. Flash chromatography was used for purification (EtOAc:Pe, 1:1). Yielding 120.7 mg of product (0.58 mmol, 55 %).

White solid, Mp.: 72-74 °C (Lit. 71-72 °C)¹³

HRMS (ESI) calculated for C₇H₆Cl₂OS [M+H]: 208.9595, found: 208.9590

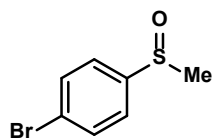
¹H NMR (399 MHz, Chloroform-*d*) δ 7.48 (s, 2H), 7.43 (s, 1H), 2.73 (s, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 149.74, 136.50, 131.25, 122.17, 44.40. MZ *e/z*: (M⁺) 209, 193, 165, 145, 125, 109, 85, 75, 63, 45, 38.



3,5-Dichlorophenyl methyl sulfone (6-B) was prepared as described in the general procedure (7.1). 3,5-dichlorophenyl methyl sulfide (203.7 mg) was dissolved in 7 mL ACN-stock solution. The mixture was exposed to 3.5 V over 10 minutes. Flash chromatography was used for purification (EtOAc:PE, 1:9). Yielding 151.2 mg of product (0.67 mmol, 64 %).

Colorless solid, Mp.: 201-203 °C (Lit. 204-205 °C)¹⁴

^1H NMR (399 MHz, Chloroform-*d*) δ 7.98 – 7.77 (m, 2H), 7.65 – 7.51 (m, 1H), 3.09 (d, J = 1.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.58, 136.81, 134.16, 126.29, 44.76. MZ m/z : (M^+) 225, 209, 193, 177, 162, 145, 133, 109, 84, 75, 63, 50, 37.



1-bromo-4-(methylsulfinyl)benzene (7-A) Following the general procedure (7.1). (4-bromophenyl)(methyl)sulfane (230 mg, 1.13 mmol) was dissolved in 7.5 mL ACN-stock solution. The mixture was exposed to 2.5V over 20 minutes.

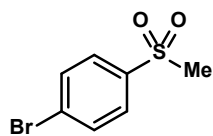
Flash chromatography was used for purification (EtOAc/PE 50:50). Yielding 206.2 mg of product (0.94 mmol, 83 %).

White solid, Mp.: 86-89 °C (Lit.: 85-87 °C)¹⁵

HRMS (ESI) calculated for $\text{C}_7\text{H}_7\text{BrOS}$ [$\text{M}+\text{H}$]: 218.9480, found: 218.9477

^1H NMR (399 MHz, Chloroform-*d*) δ 7.67 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 8.2 Hz, 2H), 2.72 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.88, 132.59, 125.49, 125.15, 44.01.

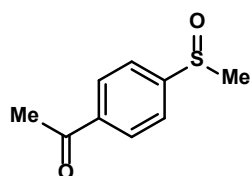


1-bromo-4-(methylsulfonyl)benzene (7-B) Following the general procedure (7.1). (4-bromophenyl)(methyl)sulfane (153 mg, 0.75 mmol) was dissolved in 5 mL ACN-stock solution. The mixture was exposed to 3.8V over 10 minutes. Flash chromatography was used for purification (EtOAc/PE 40:60). Yielding 90.8 mg of product (0.39 mmol, 52 %).

Yellow solid, Mp.: 103-105 °C (Lit.: 103-105 °C)¹⁶

^1H NMR (399 MHz, Chloroform-*d*) δ 7.82 (d, J = 8.6 Hz, 2H), 7.72 (d, J = 8.5 Hz, 1H), 3.05 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.57, 132.72, 129.01 (d, J = 4.7 Hz), 44.54.



1-(4-(methylsulfinyl)phenyl)ethan-1-one (8-A) Following the general procedure (7.1). 1-(4-(methylthio)phenyl)ethan-1-one (150 mg, 0.90 mmol) was dissolved in 6 mL ACN-stock solution. The mixture was exposed to 2.5 V over 20 minutes. Flash chromatography was used for purification (MeOH/DCM 4:96). Yielding 120 mg of product (0.65 mmol, 72 %).

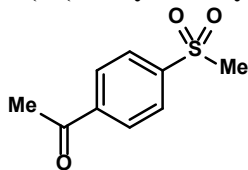
White solid, Mp.: 100-105 °C (Lit.: 108-109 °C)¹⁵

HRMS (ESI) calculated for $\text{C}_9\text{H}_{10}\text{O}_2\text{S}$ [$\text{M}+\text{H}$]: 183.0480, found: 183.0474

^1H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.5 Hz, 2H), 2.76 (s, 3H), 2.65 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.01, 150.83, 139.13, 129.17, 123.78, 43.81, 26.81.

1-(4-(methylsulfonyl)phenyl)ethan-1-one (8-B) Following the general procedure (7.1). 1-(4-(methylthio)phenyl)ethan-1-one (150 mg, 0.90 mmol) was dissolved in 7 mL ACN-

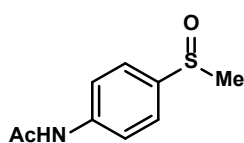


stock solution. The mixture was exposed to 3.8 V over 10 minutes. Flash chromatography was used for purification (MeOH/DCM 2.5:97.5). Yielding 122 mg of product (0.61 mmol, 68 %).

White solid, Mp.: 125-128 °C (Lit.: 128-130 °C)¹⁷

¹H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.6 Hz, 2H), 8.05 (d, *J* = 8.6 Hz, 2H), 3.08 (s, 3H), 2.66 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 196.76, 144.32, 141.04, 129.27, 127.94, 44.45, 27.07.



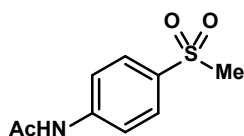
N-(4-(methylsulfonyl)phenyl)acetamide (9-A) Following the general procedure (7.1). N-(4-(methylthio)phenyl)acetamide (134 mg, 0.75 mmol) was dissolved in 5 mL ACN-stock solution. The mixture was exposed to 2.5V over 10 minutes. Flash chromatography was used for purification (MeOH/DCM 3:97).

Yielding 46 mg of product (0.23 mmol, 32 %).

White off solid, Mp.: 140-145 °C (Lit.: 126 °C)¹⁸

¹H NMR (399 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 2.72 (s, 3H), 2.19 (s, 3H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 169.01, 141.18, 139.93, 124.81, 120.46, 44.03, 24.74.



N-(4-(methylsulfonyl)phenyl)acetamide (9-B) Following the general procedure (7.1). N-(4-(methylthio)phenyl)acetamide (162 mg, 0.90 mmol) was dissolved in 6 mL ACN-stock solution. The mixture was exposed to 3.8 V over 10 minutes. Flash chromatography was used for purification (MeOH/DCM 3:97).

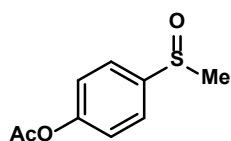
Yielding 103 mg of product (0.46 mmol, 51 %).

White off solid, Mp.: 183-186 °C (Lit.: 185-187 °C)¹⁷

HRMS (ESI) calculated for C₉H₁₁NO₂S [M+H]: 198.0589, found: 198.0592

¹H NMR (399 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.55 (s, 1H), 3.04 (s, 3H), 2.23 (s, 3H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 168.86, 142.98, 135.09, 128.68, 119.54, 77.34, 44.71, 13.58.



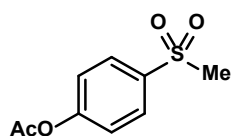
4-(Methylsulfonyl)phenyl acetate (10-A) was prepared as described in the general procedure (7.1). 4-(Methylthio)phenyl acetate (191.1 mg) was dissolved in 7 mL ACN-stock solution. The mixture was exposed to 3 V over 10 minutes. Flash chromatography was used for purification (EtOAc). Yielding 124.7 mg of product (0.63 mmol, 60 %).

White off solid, Mp.: 90-92 °C

HRMS (ESI) calculated for C₉H₁₁NO₂S [M+H]: 214.0538, found: 214.0543

¹H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 2.76 (s, 3H), 2.65 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 197.65, 151.64, 139.78, 129.81, 124.41, 44.51, 27.45.

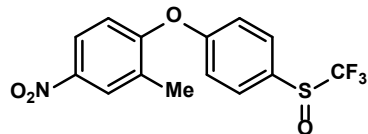


4-(Methylsulfonyl)phenyl acetate (10-B) was prepared as described in the general procedure (7.1). 4-(Methylthio)phenyl acetate (191.1 mg) was dissolved in 7 mL ACN-stock solution. The mixture was exposed to 3.5 V over 10 minutes. Flash chromatography was used for purification (EtOAc:PE, 1:7). Yielding 164.2 mg of product (0.77 mmol, 73 %).

White solid, Mp.: 96 °C (Lit. 97°C)

¹H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.2 Hz, 2H), 8.04 (d, *J* = 8.1 Hz, 2H), 3.08 (s, 3H), 2.66 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 196.93, 144.57, 141.28, 129.48, 128.16, 44.68, 27.27.



2-methyl-4-nitroso-1-(4-((trifluoromethyl)sulfinyl)phenoxy)benzene (11-A) Following the general procedure (7.1). (4-(2-methyl-4-nitrosophenoxy)phenyl)(trifluoromethyl)sulfane (234 mg, 0.75

mmol) was dissolved in 5 mL ACN-stock solution. The mixture was exposed to 3.0 V over 40 minutes. Flash chromatography was used for purification (EtOAc/PE 5:95). Yielding 118 mg of product (0.36 mmol, 48 %).

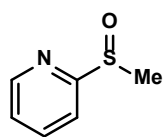
Yellow solid, Mp.: 100-105 °C

HRMS (ESI) calculated for C₁₄H₁₀F₃NO₄S [M+H]: 346.0361, found: 346.0355

¹H NMR (399 MHz, Chloroform-*d*) δ 8.24 – 8.17 (m, 1H), 8.09 (dd, *J* = 8.9, 2.8 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.22 – 7.16 (m, 2H), 7.00 (d, *J* = 8.9 Hz, 1H), 2.36 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 160.60, 158.66, 144.25, 131.24, 130.31, 130.29, 128.49, 127.24, 126.29, 123.36, 122.96, 119.16, 119.04, 16.35.

¹⁹F NMR (376 MHz, CDCl₃) δ -74.70.



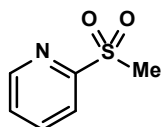
2-(Methylsulfinyl)pyridine (12-A) was prepared as described in the general procedure (7.1). 2-(Methylthio)pyridine (131.2 mg) was dissolved in 7 mL ACN-stock solution. The mixture was exposed to 2.5 V over 10 minutes. Flash chromatography was used for purification (EtOAc). Yielding 67.6 mg of product (0.54 mmol, 51 %).

Colourless oil¹⁹

HRMS (ESI) calculated for C₆H₇NOS [M+H]: 142.0327, found: 142.0321

¹H NMR (400 MHz, Chloroform-*d*) δ 8.62 (dd, *J* = 4.8, 1.5 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.95 (td, *J* = 7.7, 1.7 Hz, 1H), 7.38 (ddd, *J* = 7.7, 4.7, 1.2 Hz, 1H), 2.85 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 166.36, 149.88, 138.44, 124.90, 119.60, 41.65.



2-(Methylsulfonyl)pyridine (12-B) was prepared as described in the general procedure (7.1). 2-(Methylthio)pyridine (131.2 mg) was dissolved in 7 mL ACN-stock solution.

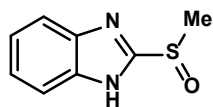
The mixture was exposed to 3.5 V over 10 minutes. Flash chromatography was used for purification (EtOAc:PE 1:9). Yielding 95.6 mg of product (0.61 mmol, 58 %).

Colourless oil¹⁹

HRMS (ESI) calculated for C₆H₇NO₂S [M+H]: 158.0276, found: 158.0270

¹H NMR (399 MHz, Chloroform-*d*) δ 8.70 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 8.05 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.95 (td, *J* = 7.7, 1.7 Hz, 1H), 7.54 (ddd, *J* = 7.6, 4.7, 1.2 Hz, 1H), 3.19 (d, *J* = 0.6 Hz, 3H).

¹³C NMR (100 MHz, Chloroform-*d*) δ 158.16, 150.32, 138.56, 127.74, 121.30, 40.28. MZ *e/z*: (M⁺) 157, 93, 78, 67, 51, 39.



2-(methylsulfonyl)-1H-benzo[d]imidazole (13-A) Following the general procedure (7.1). 2-(methylthio)-1H-benzo[d]imidazole (147 mg, 0.90 mmol) was dissolved in 6 mL ACN-stock solution.

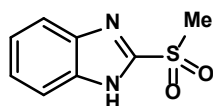
The mixture was exposed to 3.0 V over 15 minutes. Flash chromatography was used for purification (EtOAc). Yielding 65 mg of product (0.36 mmol, 40 %).

White solid, Mp.: 131-134 °C (Lit.: 139-140 °C)²⁰

HRMS (ESI) calculated for C₈H₈N₂OS [M+H]: 181.0436, found: 181.0452

¹H NMR (400 MHz, Chloroform-*d*) δ 10.92 (s, 1H), 7.68 (dd, *J* = 6.1, 3.2 Hz, 2H), 7.33 (dd, *J* = 6.1, 3.2 Hz, 2H), 3.18 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 152.54, 138.15, 122.87, 115.20, 40.43.



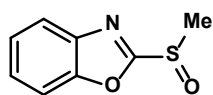
2-(methylsulfonyl)-1H-benzo[d]imidazole (13-B) Following the general procedure (7.1). 2-(methylthio)-1H-benzo[d]imidazole (125 mg, 0.75 mmol) was dissolved in 6 mL ACN-stock solution.

The mixture was exposed to 4.0 V over 15 minutes. Flash chromatography was used for purification (EtOAc/PE 50:50). Yielding 80 mg of product (0.41 mmol, 54 %).

White off solid, Mp.: 190-195 °C (Lit.: 199-201 °C)²¹

HRMS (ESI) calculated for C₈H₈N₂O₂S [M+H]: 197.0384, found: 197.0387

^1H NMR (399 MHz, Chloroform-*d*) δ 7.87 – 7.65 (m, 2H), 7.45 (dt, J = 5.4, 1.9 Hz, 2H), 3.42 (s, 3H).
 ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.21, 125.63, 124.67, 100.13, 77.16, 42.97.

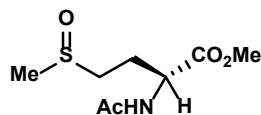


2-(methylsulfinyl)benzo[d]oxazole (14-A) Following the general procedure (7.1). 2-(methylthio)benzo[d]oxazole (124 mg, 0.75 mmol) was dissolved in 5 mL ACN-stock solution. The mixture was exposed to 4 V over 10 minutes. Flash chromatography was used for purification (EtOAc/PE 50:50). Yielding 63 mg of product (0.35 mmol, 46 %).

White off solid, Mp.: 75-77 °C

^1H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, J = 7.4 Hz, 1H), 7.65 (d, J = 7.5 Hz, 1H), 7.53 – 7.36 (m, 2H), 3.21 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.83, 151.86, 140.39, 127.23, 125.69, 121.36, 111.58, 39.95.



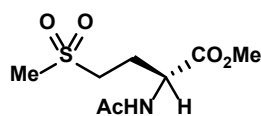
Methyl (2R)-2-acetamido-4-(methylsulfinyl)butanoate (15-A) Following the general procedure (7.1). methyl acetyl-D-methioninate (184 mg, 0.90 mmol) was dissolved in 6 mL ACN-stock solution. The mixture was exposed to 2.8 V over 15 minutes. Flash chromatography was used for purification (MeOH/DCM 8:92). Yielding 93 mg of product (0.42 mmol, 46 %).

White solid, Mp.: 117-120 °C (Lit.: 102 °C)²²

HRMS (ESI) calculated for C₈H₁₅NO₄S [M-H]: 222.0800, found: 222.0794

^1H NMR (399 MHz, Chloroform-*d*) δ 6.97 (dd, J = 31.7, 7.4 Hz, 1H), 4.65 (tt, J = 8.0, 4.5 Hz, 1H), 3.73 (s, 3H), 2.86 – 2.60 (m, 2H), 2.56 (d, J = 1.8 Hz, 3H), 2.38 – 2.25 (m, 2H), 2.00 (d, J = 2.5 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.83 (d, J = 4.4 Hz), 170.72 – 170.17 (m), 52.59 (d, J = 3.2 Hz), 51.09 (d, J = 19.6 Hz), 50.18 (d, J = 22.5 Hz), 38.41 (d, J = 2.4 Hz), 25.46 (d, J = 44.0 Hz), 22.88 (d, J = 1.2 Hz).

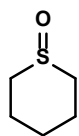


Methyl (2R)-2-acetamido-4-(methylsulfonyl)butanoate (15-B) Following the general procedure (7.1). methyl acetyl-D-methioninate (184 mg, 0.90 mmol) was dissolved in 6 mL ACN-stock solution. The mixture was exposed to 3.8 V over 10 minutes. Flash chromatography was used for purification (MeOH/DCM 8:92). Yielding 75 mg of product (0.32 mmol, 36 %).

White solid, Mp.: 223-225 °C (Lit.: 245-246)²³

HRMS (ESI) calculated for C₈H₁₅NO₅S [M-H]: 238.0749, found: 238.0759

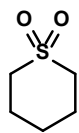
^1H NMR (399 MHz, Chloroform-*d*) δ 6.62 (d, $J = 7.7$ Hz, 1H), 4.67 (td, $J = 8.1, 5.0$ Hz, 1H), 3.75 (s, 3H), 3.10 (dddd, $J = 42.9, 14.0, 10.7, 5.3$ Hz, 2H), 2.92 (s, 3H), 2.47 – 2.07 (m, 2H), 2.02 (s, 3H).
 ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.57, 170.58, 52.96, 51.21, 50.72, 40.87, 25.38, 23.10.



Tetrahydro-2H-thiopyran 1-oxide (16-A) Following the general procedure (7.1). tetrahydro-2H-thiopyran (94 mg, 0.91 mmol) was dissolved in 6 mL ACN-stock solution. The mixture was exposed to 2.8 V over 10 minutes. Flash chromatography was used for purification (DCM/MeOH 95:5). Because the corresponding sulfone and the electrolyte could not be spotted on TLC, the yield was determined by ^1H -NMR, yielding 80 mg of product (0.41 mmol, 46 %).

HRMS (ESI) calculated for $\text{C}_5\text{H}_{10}\text{OS}$ [$\text{M}+\text{H}$]: 119.0531, found: 119.0529

^1H NMR (400 MHz, Chloroform-*d*) δ 2.87 (ddd, $J = 12.3, 9.1, 2.8$ Hz, 2H), 2.74 (ddd, $J = 12.6, 8.6, 3.1$ Hz, 2H), 2.29 – 2.14 (m, 2H), 1.71 – 1.60 (m, 4H).²⁴



Tetrahydro-2H-thiopyran 1,1-dioxide (16-B) Following the general procedure (7.1). tetrahydro-2H-thiopyran (92 mg, 0.90 mmol) was dissolved in 6 mL ACN-stock solution. The mixture was exposed to 4.0 V over 10 minutes. Flash chromatography was used for purification (EtOAc). Yielding 101 mg of product (0.75 mmol, 84 %).

Colorless oil

^1H NMR (399 Mz, Chloroform-*d*) δ 3.03 – 2.92 (m, 4H), 2.07 (ddt, $J = 12.0, 8.5, 4.9$ Hz, 4H), 1.67 – 1.54 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 52.16, 24.26, 23.83.

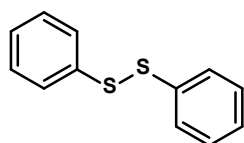


(methylsulfonyl)methane (16-B) Following the general procedure (7.1). (methylsulfinyl)methane (70.3 mg, 0.90 mmol) was dissolved in 6 mL ACN-stock solution. The mixture was exposed to 3.8 V over 10 minutes. Flash chromatography was used for purification (EtOAc). Yielding 68 mg of product (0.72 mmol, 80 %).

White solid, Mp.: 101-105 °C (Lit.: 107-109 °C)²⁵

^1H NMR (399 MHz, Chloroform-*d*) δ 2.98 (s, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 42.82.



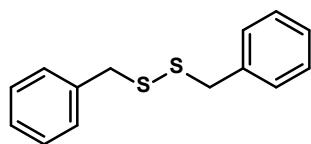
Diphenyl disulfide (18-C) was prepared as described in the general procedure (7.2). Thiophenol (115.5 mg) was dissolved in 6 mL ACN-stock solution. The mixture was exposed to 2.5 V over 10 minutes. Flash chromatography was used for purification (EtOAc with $\text{N}(\text{CH}_2\text{CH}_3)_3$ (2 %)). Yielding 104.1 mg of product (0.48 mmol, 91 %).

White solid, Mp.: 59-60 °C (Lit: 59-61 °C)²⁶

HRMS (ESI) calculated for C₁₂H₁₀S₂ [M-H]: 217.0146, found: 217.0141

¹H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.13 (m, 10H), 3.52 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 137.61, 129.65, 128.72, 127.66, 43.54.

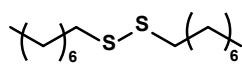


Dibenzyl disulfide (19-C) was prepared as described in the general procedure (7.2). Benzyl mercaptan (128.1 mg) was dissolved in 6 mL ACN-stock solution. The mixture was exposed to 2.5 V over 10 minutes. Flash chromatography was used for purification (EtOAc with N(CH₂CH₃)₃(2 %)). Yielding 89.1 mg of product (0.36 mmol, 69 %).

White solid, Mp.: 70 °C (Lit: 69-70 °C)²⁷

¹H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.13 (m, 10H), 3.52 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 137.61, 129.65, 128.72, 127.66, 43.54.

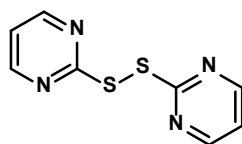


Di-n-octyl disulfide (20-C) was prepared as described in the general procedure (7.2). n-Octane thiol (128.1 mg) was dissolved in 6 mL ACN-stock solution. The mixture was exposed to 2.5 V over 10 minutes. Flash chromatography was used for purification (EtOAc). Yielding 82.1 mg of product (0.28 mmol, 65 %).

Colorless oil²⁶

¹H NMR (400 MHz, CDCl₃) δ: 2.68 (t, *J* = 7.4 Hz, 4H), 1.71-1.63 (m, 4H), 1.40-1.28 (m, 20H), 0.90-0.86 (m, 6H) ppm.

¹³C NMR (101 MHz, CDCl₃) δ 77.34, 77.02, 76.70, 39.24, 31.83, 29.25, 29.22, 29.19, 28.55, 22.66, 14.10.

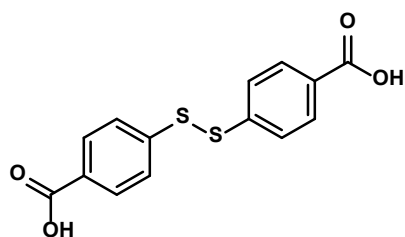


1,2-Di(pyrimidin-2-yl)disulfane (21-C) Following the general procedure (7.2). pyrimidine-2-thiol (101 mg, 0.90 mmol) was dissolved in 12 mL DMF-stock solution. The mixture was exposed to 3.0 V over 15 minutes. Crystallization was used for purification (H₂O). Yielding mg of product (mmol, %).

White solid, Mp.: 133-135 °C (133-135 °C)²⁸

¹H NMR (400 MHz, Chloroform-*d*) δ 8.56 (d, *J* = 4.8 Hz, 2H), 7.07 (t, *J* = 4.8 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 169.72, 157.91, 118.19, 77.38, 77.06, 76.74.



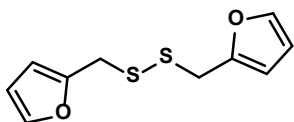
4,4'-disulfanediyldibenzoic acid (22-C) Following the general procedure (7.2). 4-mercaptobenzoic acid (139 mg, 0.90 mmol) was dissolved in 12 mL DMF-stock solution. The mixture was exposed to 3.0 V over 15 minutes. Crystallization was used for purification (H₂O). Yielding 50 mg of product (0.16 mmol, 36 %).

White solid, Mp.: decomposes at 337-342 °C (Lit.: decomposes at 319-322 °C)²⁹

HRMS (ESI) calculated for C₁₄H₁₀O₄S₂ [M-H]: 304.9942, found: 304,9951

¹H NMR (400 MHz, Dimethylsulfoxide-*d*₆) δ 13.06 (s, 2H), 8.06 – 7.84 (m, 4H), 7.77 – 7.53 (m, 4H).

¹³C NMR (101 MHz, Dimethylsulfoxide-*d*₆) δ 167.08, 141.22, 130.79, 130.16, 126.57.



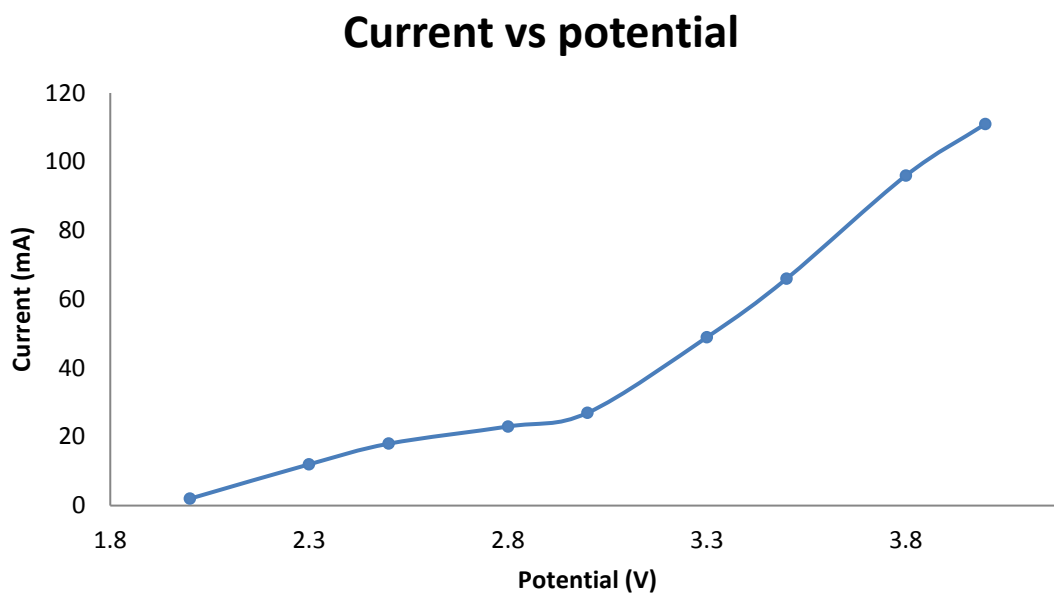
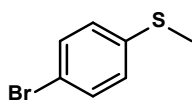
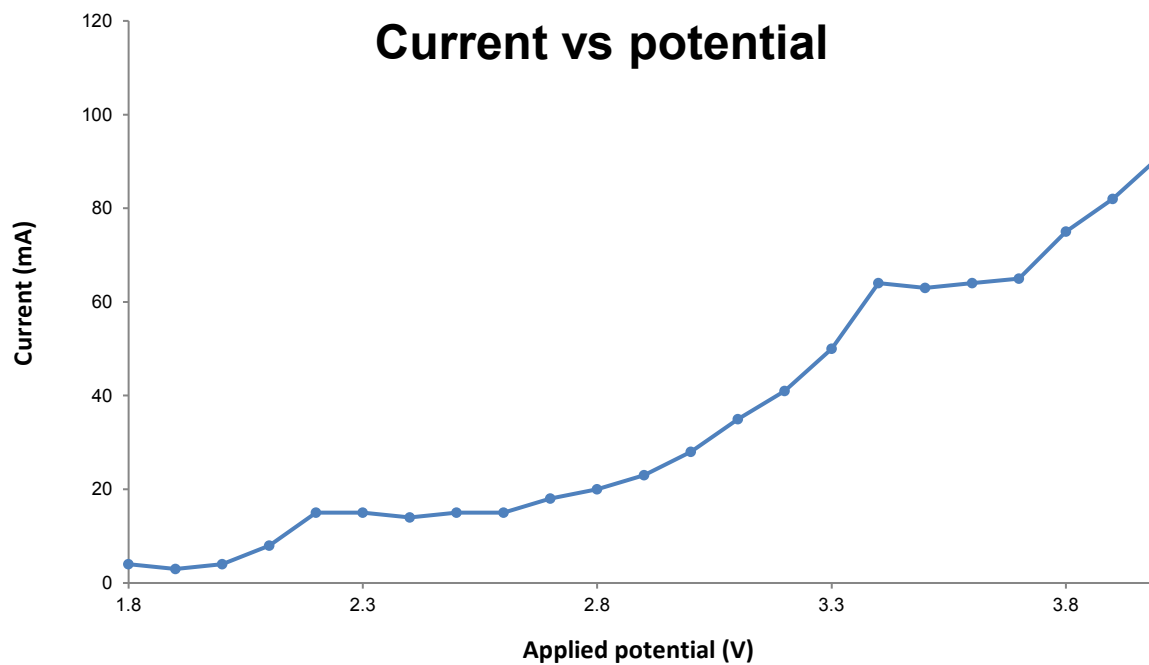
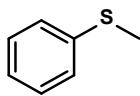
1,2-bis(furan-2-ylmethyl)disulfane (23-C) Following the general procedure (7.2). 2-furanylmethanethiol (103 mg, 0.90 mmol) was dissolved in 6 mL ACN-stock solution. The mixture was exposed to 2.5 V over 15 minutes. Flash chromatography was used for purification (EtOAc). Yielding 86 mg of product (0.16 mmol, 36 %).

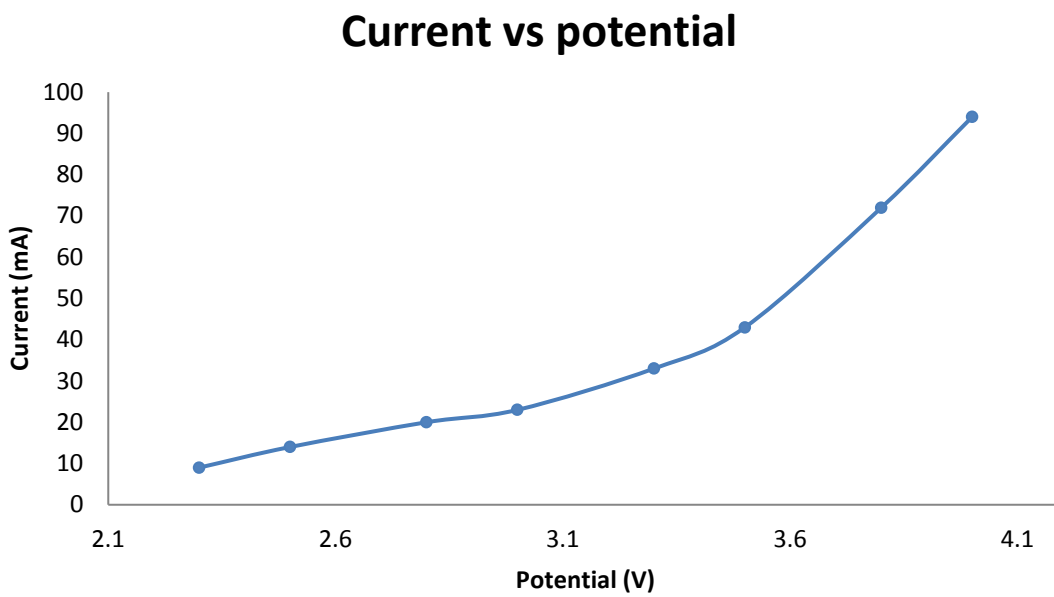
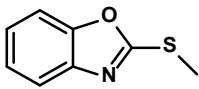
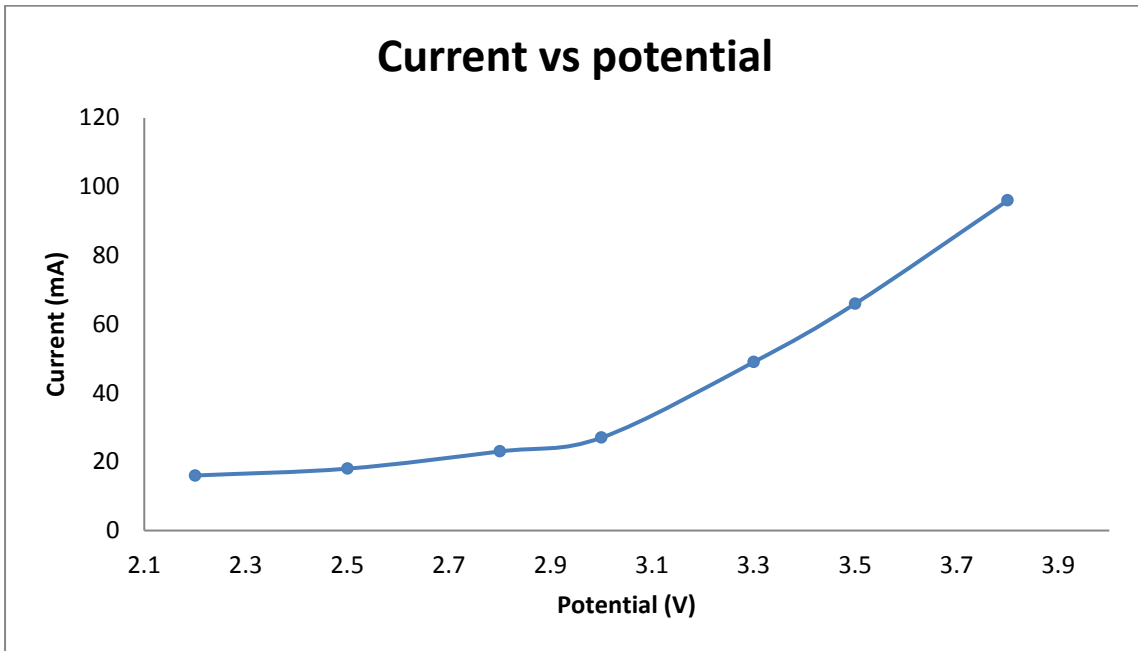
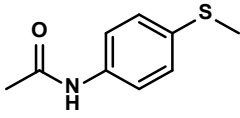
Brown oil.²⁶

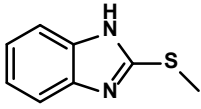
¹H NMR (400 MHz, CDCl₃) δ: 7.40 (dd, J = 0.9, 1.9 Hz, 2H), 6.35 (dd, J = 1.9, 3.3 Hz, 2H), 6.24 (d, J = 3.3 Hz, 2H), 3.70 (s, 4H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ: 35.7, 109.1, 110.9, 142.6, 150.3 ppm.

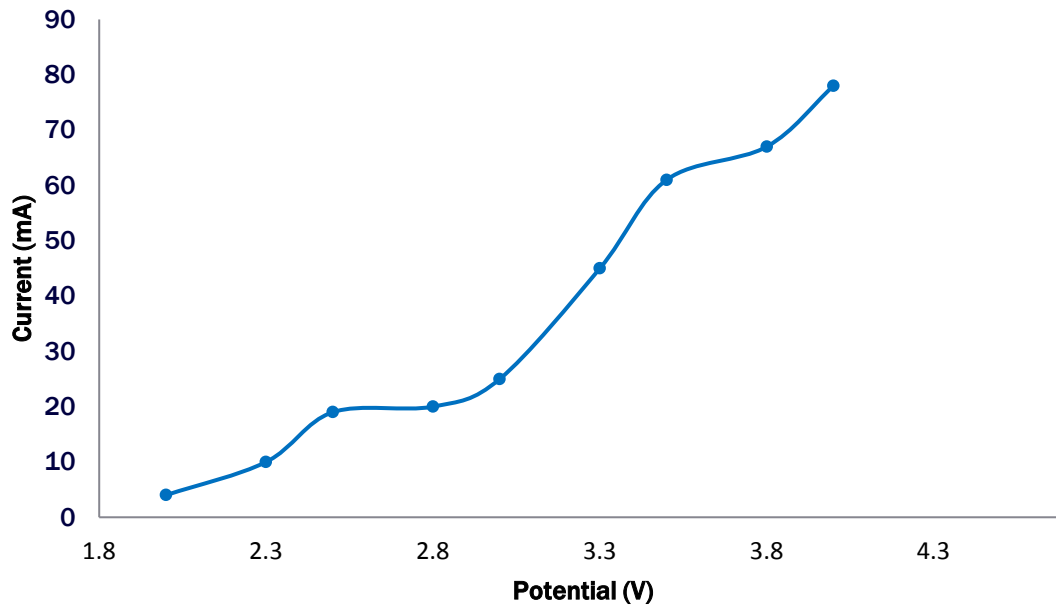
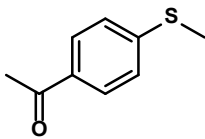
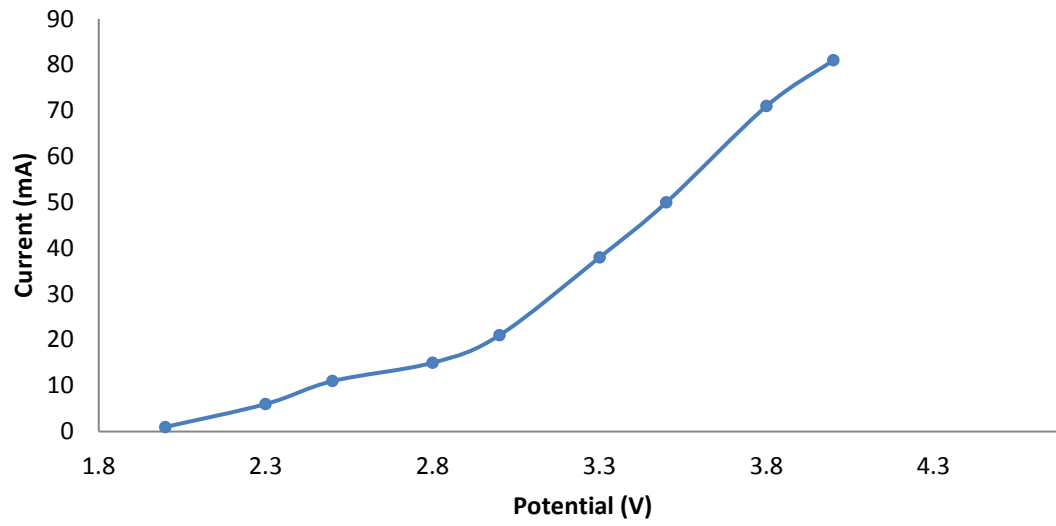
9. Polarograms

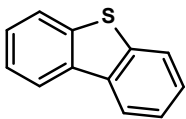




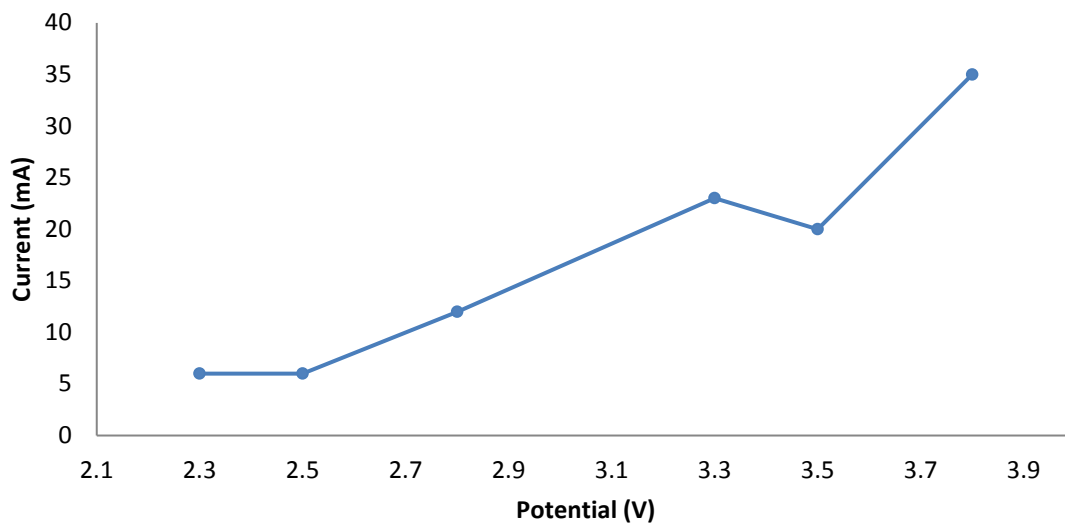


Current vs potential

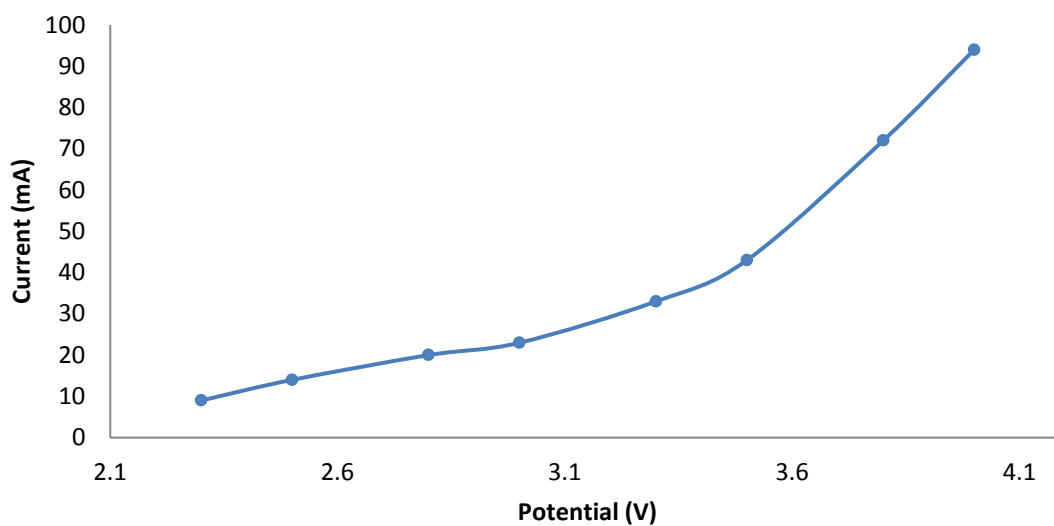


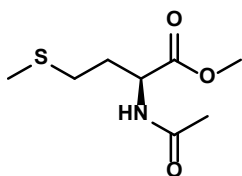


Current vs potential

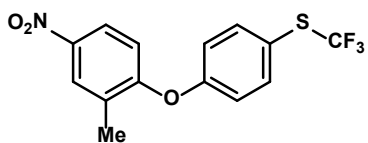
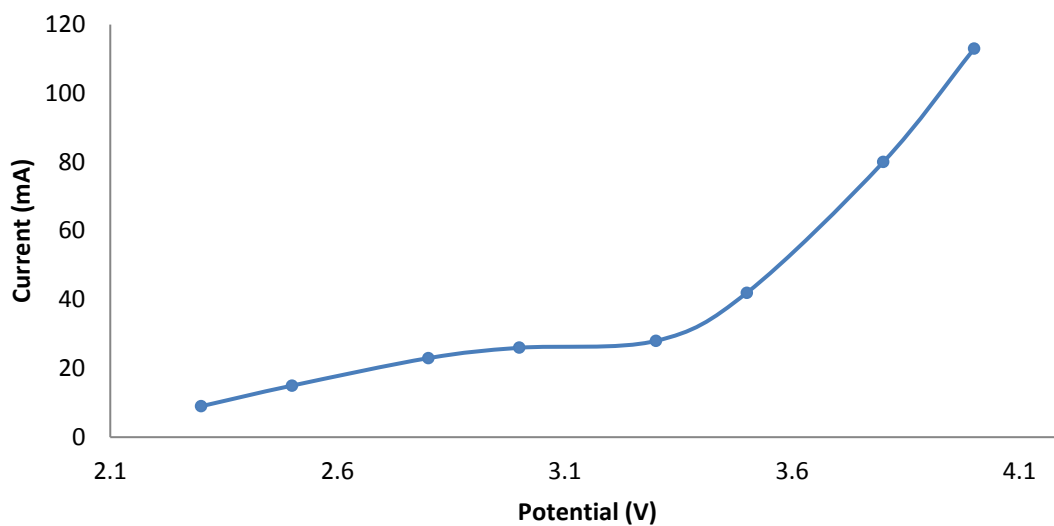


Current vs potential

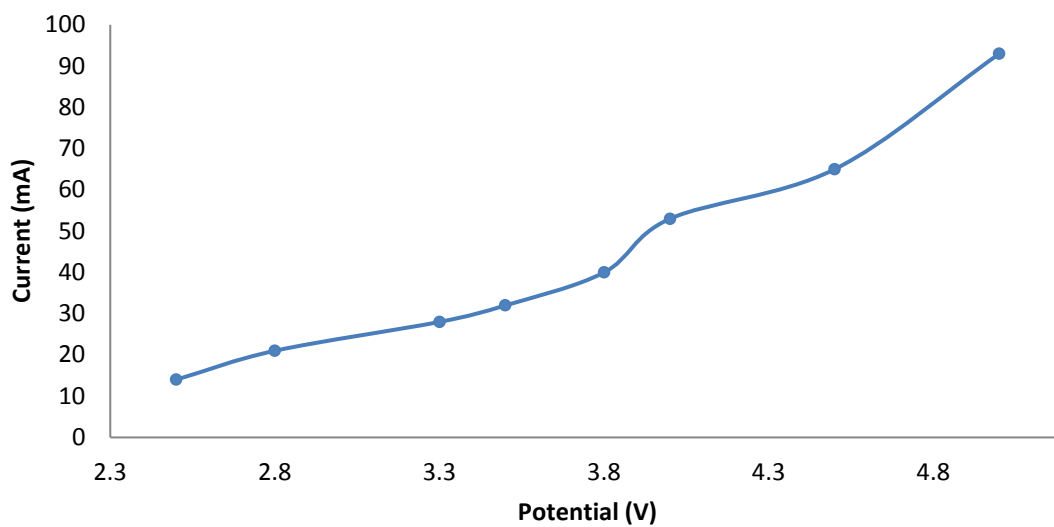


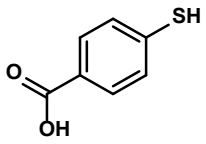


Current vs potential

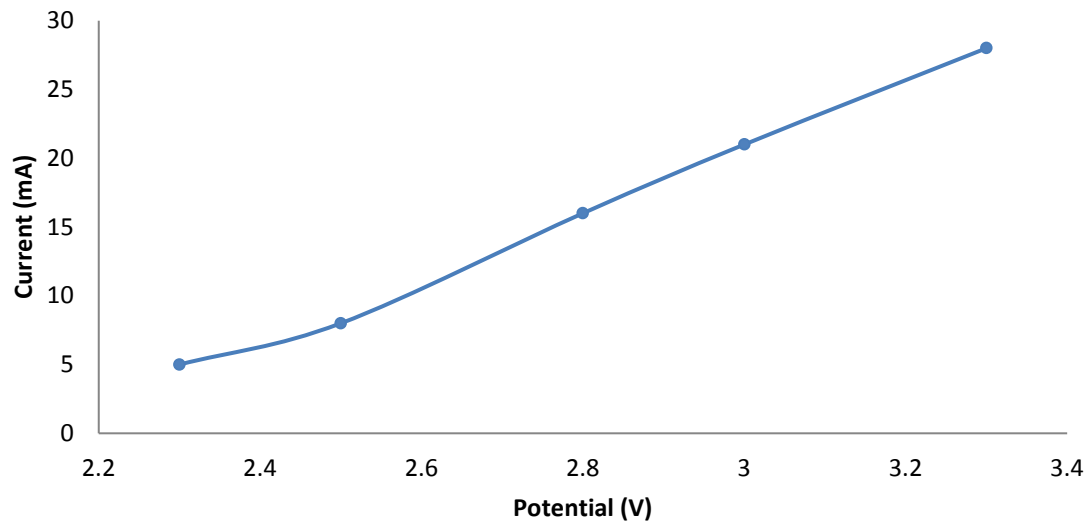


Current vs potential





Current vs potential



10. References

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11. NMR spectra

