Supporting Information for:

A safe and compact flow platform for the neutralization of a mustard gas simulant with air and light

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1. **Continuous flow setu**ps

1.1 Microfluidic setups and parts

All microfluidic setups were assembled with commercially available parts.

1.1.1 Pumps

ThalesNano microHPLC® pumps (wetted parts: SS 316, ruby and sapphire) were utilized to handle the liquid feeds.

1.1.2 Gas module

The gas flow rate was controlled with a Bronkhorst® F210CTM mass flow controller (MFC).

1.1.3 Connectors, ferrules and mixers

1/8” PFA tubings (Swagelok®) were equipped with Super Flangeless PEEK nuts, ETFE ferrules and SS rings. 1/4” PFA tubings (Swagelok®) were equipped with 1/4” PFA Swagelok Tube Fitting unions and elbows. Connectors, ferrules and unions were purchased from IDEX/Upchurch (details in Table S1).

1.1.4 Check-valves

Check-valves (IDEX/Upchurch Scientific) were inserted between the pumps and the reactor.

1.1.5 Back-pressure regulator

A dome-type BPR (Zaiput Flow Technologies, BPR-10) was inserted downstream. The dome-type BPR was connected to a compressed gas cylinder (air or nitrogen) to set the working pressure.

1.1.6 Reactor setups

The flow reactor setups were manufactured by Corning SAS. The preliminary experiments relied on a Corning® Advanced-Flow™ Lab Photo Reactor (1 fluidic module, 2.6 mL internal volume) and the final optimized setup relied on a Corning® Advanced-Flow™ LF/G1 skid Photo Reactor (5 fluidic modules integrated with static mixers and connected in series, 13 mL total internal volume).

1.1.7 Thermoregulatory devices

The reactor was maintained at reaction temperature with a LAUDA Integral XT 280 thermostat. The LED panels were maintained at 10 °C with a LAUDA RP845 (LAUDA Therm 180 silicone oil).

1.2 Part numbers & vendors

Standard fluidic elements and connectors were purchased from IDEX/Upchurch Scientific or from Swagelok (Table S1).

Table S1. Connectors, ferrules and unions

Item	Details	Vendor	Reference
Connectors	Super Flangeless™ Nut PEEK, 1/4-28 Flat-Bottom, for 1/8"	IDEX/ Upchurch Scientific	P-331
	Super Flangeless™ Ferrule Tefzel™ (ETFE), 1/4-28 Flat-Bottom, for 1/8" OD	IDEX/ Upchurch Scientific	P-359
	PFA Swagelok Tube Fitting, Union, 1/4 in. Tube Fitting	Swagelok	PFA-420-6
	PFA Swagelok Tube Fitting, Union Elbow, 1/4 in. Tube Fitting	Swagelok	PFA-420-9
Unions	Large Bore Union PEEK for 3/16" OD	IDEX/ Upchurch Scientific	P-134
Check-valve	Check-valve inline cartridge 1.5 psi and cartridge holder, PEEK	IDEX/ Upchurch Scientific	CV-3000
Dome-type BPR	Dome-type BPR, metal-free, with adjustable set point	Zaiput Flow Techn.	BPR-10
Tubing	PFA Tubing, 1/8 in. OD x 0.030 in. wall x 100 feet	Swagelok	PFA-T2-030-100
	PFA Tubing, 1/4 in. OD x 0.047 in. wall x 100 feet	Swagelok	PFA-T4-047-100

1.3 Detailed continuous flow setup

Photooxidation of thioethers in a Corning® Advanced-Flow™ LF/G1 skid Photo Reactor. See manuscript for experimental details (Tables 2 and 3).

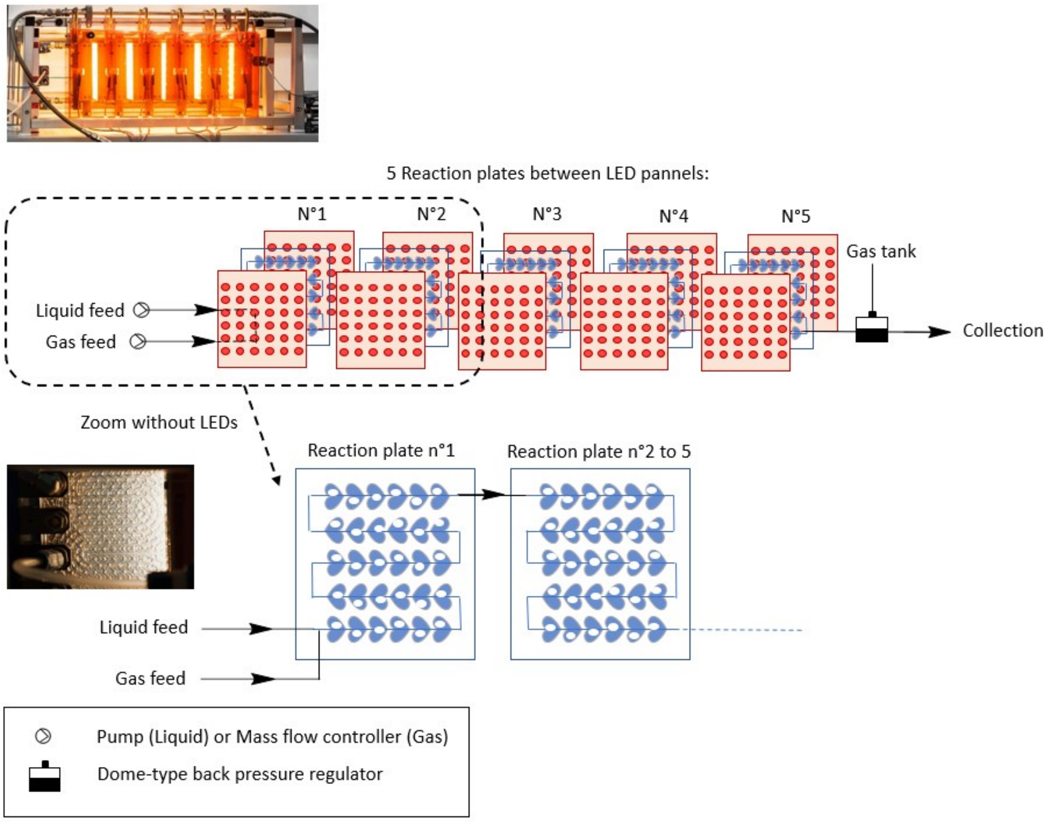


Figure S1. Detailed setup for the continuous flow photooxidation of sulfides.

2. Additional experimental details

2.1 Chemicals

Chemicals, purities, CAS numbers and suppliers are provided in Table S2.

Table S2. Solvents, chemicals and suppliers

Solvents	Purity (%)	CAS number	Supplier
Ethanol	99	64-17-5	VWR
Acetonitrile	≥99.8	75-05-8	VWR
2-Methyltetrahydrofuran	≥99	96-47-9	Merck
Chemicals	**Purity (%)**	**CAS number**	**Supplier**
Thioanisole (methyl phenyl sulfide)	>99	100-68-5	TCI
Thioanisole sulfoxide (methyl phenyl sulfoxide)	>98	1193-82-4	TCI
Thioanisole sulfone (methyl phenyl sulfone)	>97	3112-85-4	TCI
Dipropyl sulfide	>98	111-47-7	TCI
Dipropyl sulfone	>99	598-03-8	TCI
Thiodipropionic acid	>99	111-17-1	TCI
Benzyl sulfide	>98	538-74-9	TCI
Benzyl sulfoxide	>98	621-08-9	TCI
Benzyl sulfone	>98	620-32-6	Alfa Aesar
Diphenyl sulfide	>98	139-66-2	TCI
Diphenyl sulfoxide	>99	945-51-7	TCI
Diphenyl sulfone	>99	127-63-9	TCI
Tetrahydrothiophene sulfide	>99	110-01-0	TCI
Tetrahydrothiophene sulfoxide	>95	1600-44-8	TCI
Tetrahydrothiophene sulfone	>99	126-33-0	TCI
Benzyl phenyl sulfide	98	831-91-4	Alfa Aesar
Diethyl sulfide	>98	352-93-2	TCI
Benzyl methyl sulfide	>98	766-92-7	TCI
Benzyl methyl sulfone	>98	3112-90-1	Alfa Aesar
Dibenzothiophene sulfide	98	132-65-0	Alfa Aesar
Dibenzothiophene sulfone	>98	1016-05-3	TCI
2-Chloroethylethyl sulfide	>98	693-07-2	TCI
2-Chloroethylethyl sulfone	95	25027-40-1	Sigma Aldrich
Ethyl vinyl sulfide	>93	627-50-9	TCI
Ethyl vinyl sulfone	98	1889-59-4	Sigma Aldrich
Methyl vinyl sulfone	95	3680-02-2	Alfa Aesar
2-Chloroethylphenyl sulfide	>98	5535-49-9	TCI
2-Chloroethylphenyl sulfone	98	938-09-0	abcr
Phenyl vinyl sulfone	99	5535-48-8	Sigma Aldrich
Gas	**Purity (%)**	**Ref**	**Supplier**
Alphagaz 1 Oxygen	O_2 ≥ 99.995	P0361L50S2A 001	Air Liquide
Alphagaz 1 Air	$N_2 + O_2$ ≥ 99.999	P0291L50S2A 001	Air Liquide

2.2 Additional experimental data

2.2.1 Analytical methods

Conversions and selectivities were determined by GC-FID or by HPLC-DAD using the following methods:

GC method: The GC-FID oven program consisted of the following steps: a 3 min hold at 50 °C, a 20 °C min^{-1} ramp to 250 °C, and a 2 min hold at 250 °C. The temperature of the injector was set at 250 °C and the temperature of the FID detector was set at 270 °C. Prior to analysis unless specified otherwise, the sample was homogenized, 50 µL of the sample was mixed with 1 mL of EtOH (denaturated with 5% MeOH) in a 1.5 mL Eppendorf® vial. Conversions and selectivities for compounds **1a** and **CEES** were determined using this method.

HPLC method:

Eluent:

A: Water + 0.1% CF_3COOH (v:v)

B: Acetonitrile

Gradient Table:

Time (min)	A (%)	B (%)
0	100	0
20	20	80
23	20	80
25	100	0
31	100	0

Flow: 1 mL min^{-1}

Injection Volume: 10 µL

Column: C18, 100 × 4.6 mm, 3 µm

Oven Temperature: 40 °C

Diode Array Detector: 180-800 nm (processed at 240 nm)

Conversions and selectivities for compounds **1c**, **1d**, **1e** and **1f** were determined using this method.

2.2.2 Representative GC results for **CEES** oxidation

GC chromatogram – see manuscript: Table 3, Entry 1

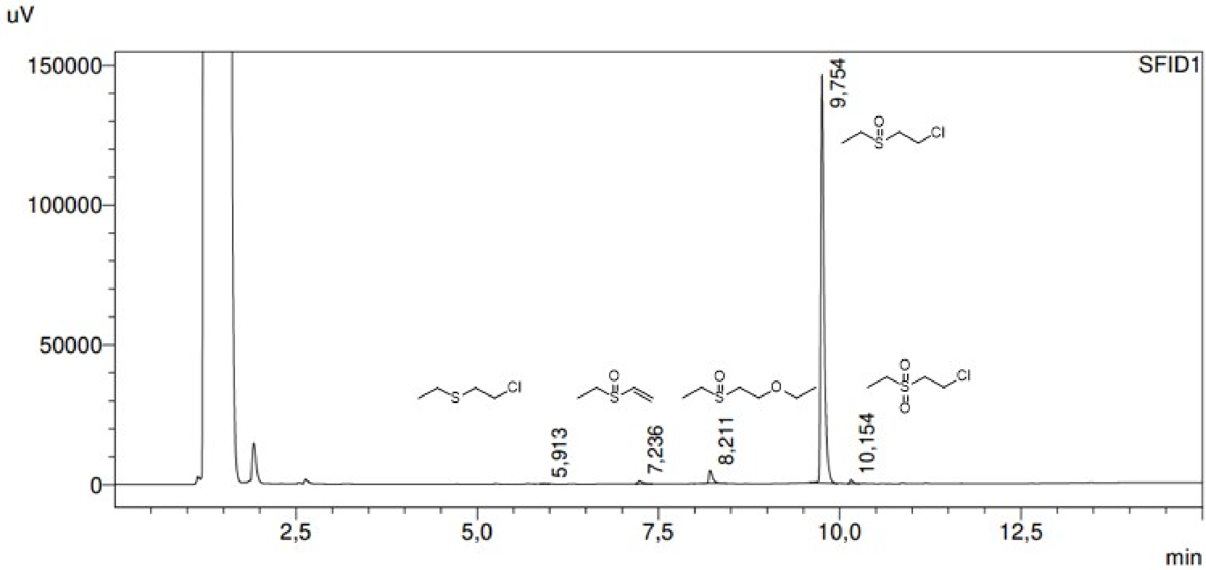


Figure S2. GC chromatogram of the oxidation of **CEES**. See manuscript for experimental details (Table 3, Entry 1).

	Ret. time (min)	Conversion (%)
CEES	5.9	0.10
EVSO (I-2)	7.2	0.94
I-3	8.2	3.39
CEESO	9.75	94.70
CEESO$_2$	10.15	0.85

Conversion 99.92%

Selectivity for **CEESO** = 94.8%

GC chromatogram – see manuscript: Table 3, Entry 6

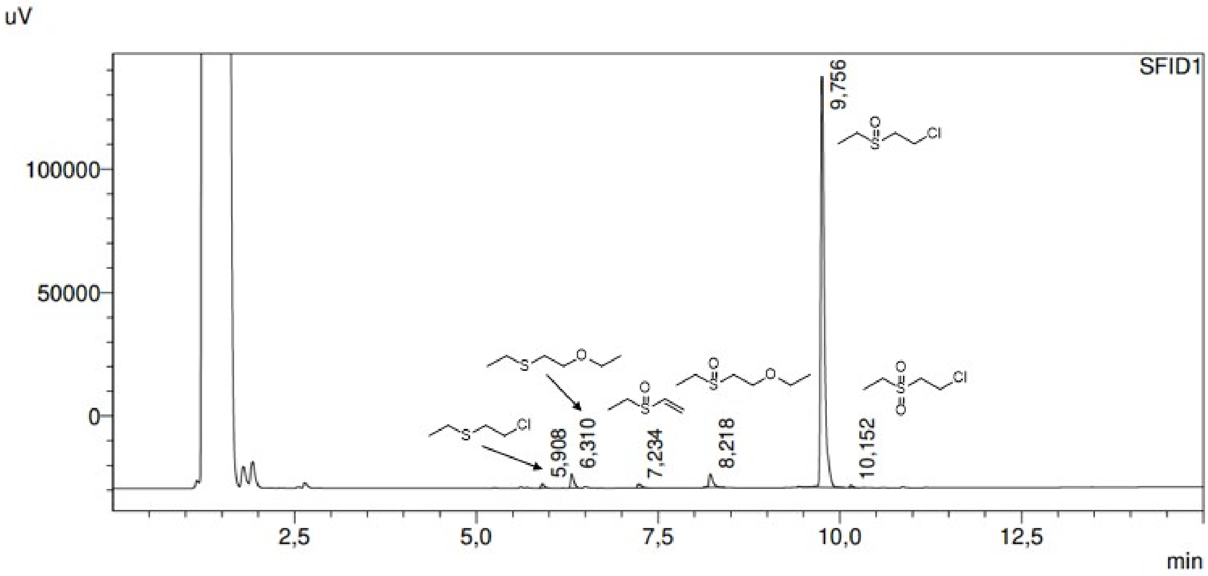


Figure S3. GC chromatogram of the oxidation of **CEES**. See manuscript for experimental details (Table 3, Entry 6).

	Ret. time (min)	Conversion (%)
CEES	5.9	0.79
I-1	6.3	2.79
EVSO (I-2)	7.2	0.95
I-3	8.2	3.36
CEESO	9.75	91.69
$CEESO_2$	10.15	0.43

Conversion 99.26%

Selectivity for **CEESO** = 92.4%

GC chromatogram – see manuscript: Table 3, Entry 4

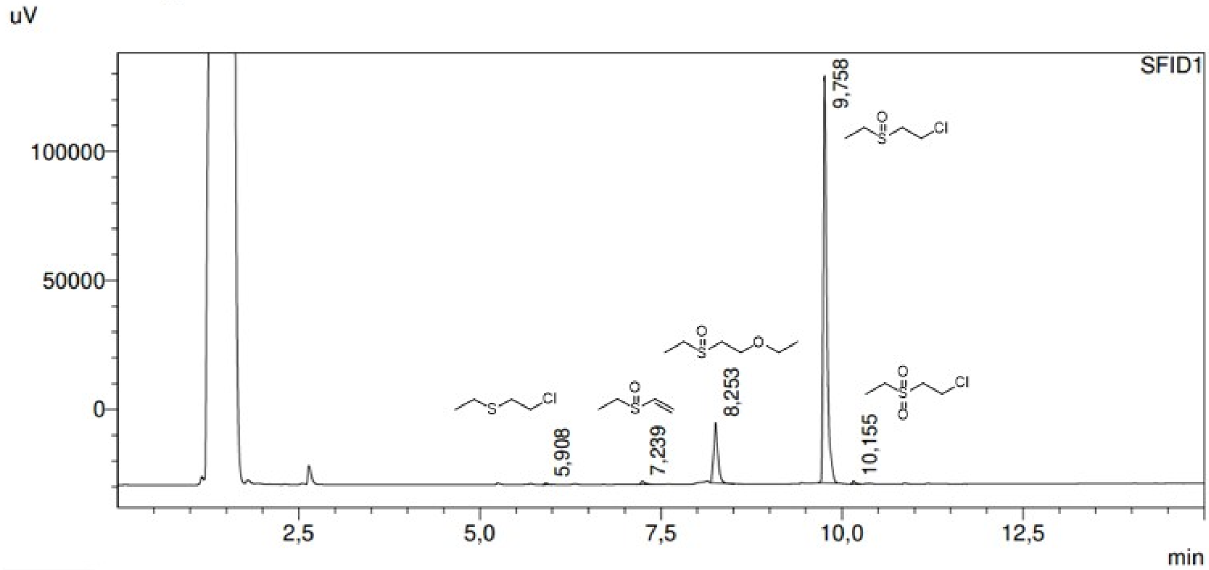


Figure S4. GC chromatogram of the oxidation of **CEES**. See manuscript for experimental details (Table 3, Entry 4).

	Ret. time (min)	Conversion (%)
CEES	5.9	0.27
EVSO (I-2)	7.2	0.79
I-3	8.2	14.56
CEESO	9.75	83.81
$CEESO_2$	10.15	0.57

Conversion 99.74%

Selectivity for **CEESO** = 84.0%

GC chromatogram – see manuscript: Table 3, Entry 5

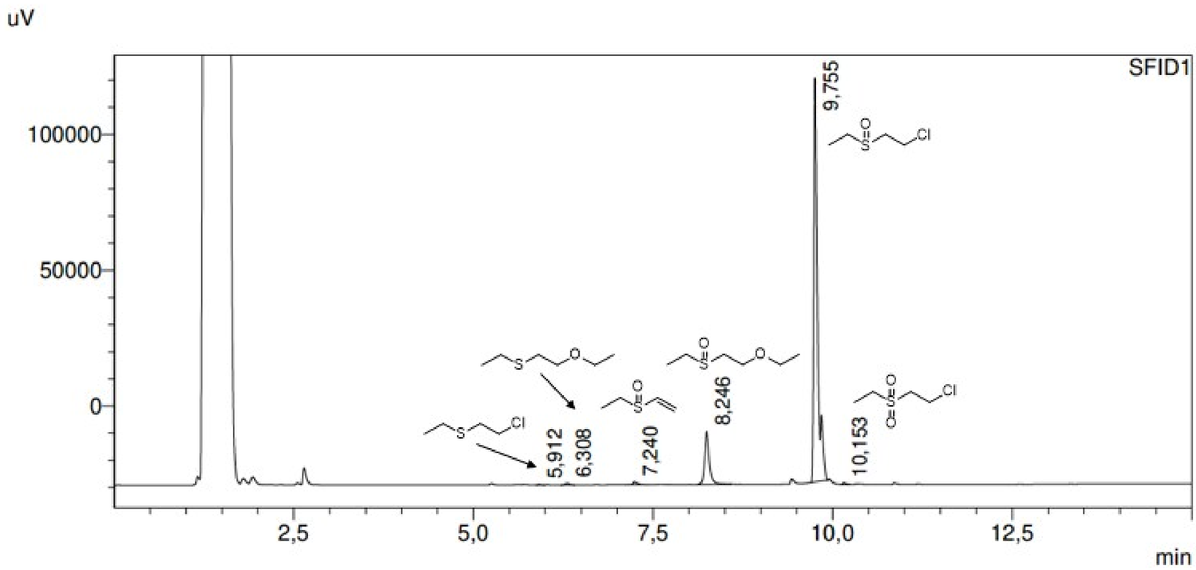


Figure S5. GC chromatogram of the oxidation of **CEES**. See manuscript for experimental details (Table 3, Entry 5).

	Ret. time (min)	Conversion (%)
CEES	5.9	0.13
I-1	6.3	0.43
EVSO (I-2)	7.2	0.76
I-3	8.2	13.71
CEESO	9.75	84.71
CEESO$_2$	10.15	0.27

Conversion 99.88%

Selectivity for **CEESO** = 84.8%

GC chromatogram – see manuscript: Table 3, Entry 2

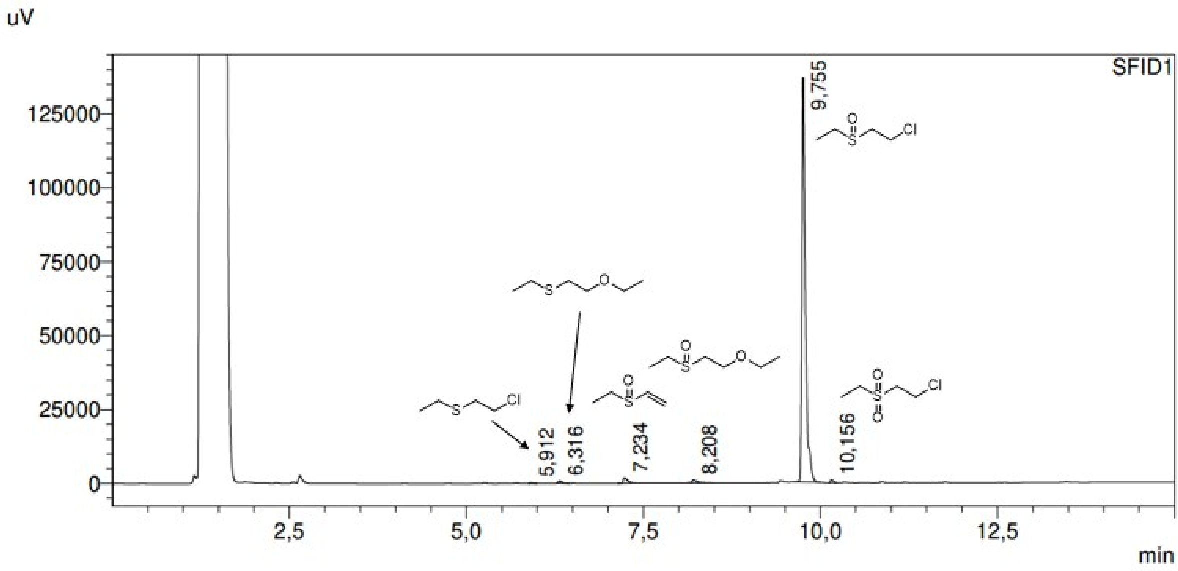


Figure S6. GC chromatogram of the oxidation of **CEES**. See manuscript for experimental details (Table 3, Entry 2).

	Ret. time (min)	Conversion (%)
CEES	5.9	0.12
I-1	6.3	0.49
EVSO (I-2)	7.2	1.58
I-3	8.2	1.26
CEESO	9.75	95.94
$CEESO_2$	10.15	0.60

Conversion 99.91%

Selectivity for **CEESO** = 96.1%

GC chromatogram – see manuscript: Table 3, Entry 3

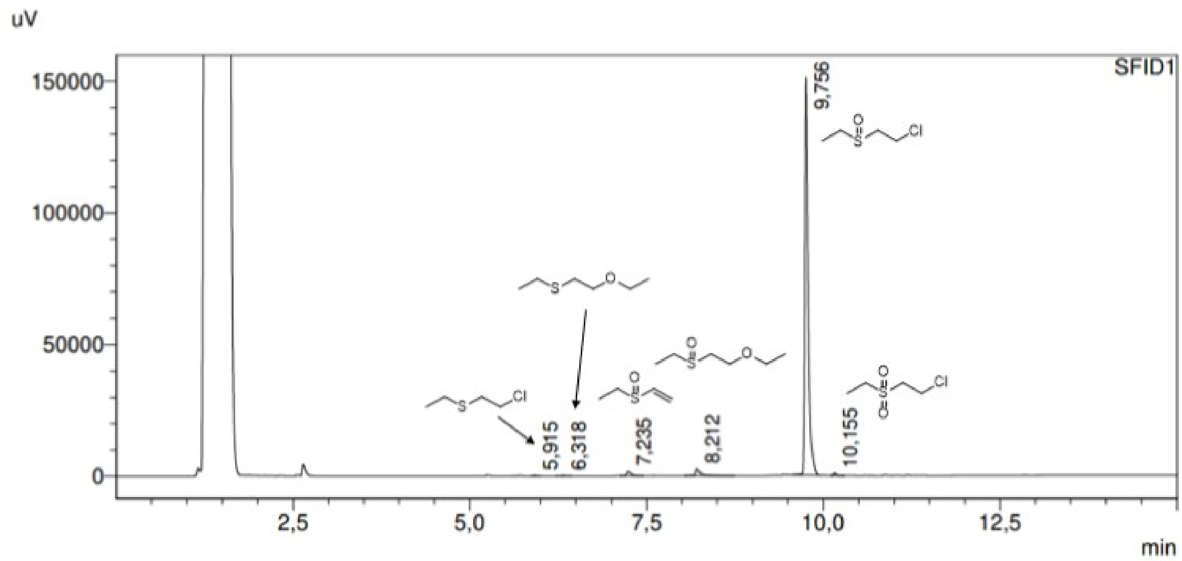


Figure S7. GC chromatogram of the oxidation of **CEES**. See manuscript for experimental details (Table 3, Entry 3).

	Ret. time (min)	Conversion (%)
CEES	5.9	0.10
I-1	6.3	0.12
EVSO (I-2)	7.2	1.41
I-3	8.2	2.51
CEESO	9.75	95.30
CEESO$_2$	10.15	0.56

Conversion 99.92%

Selectivity for **CEESO** = 95.4%

GC chromatogram – see manuscript: Table 3, Entry 10

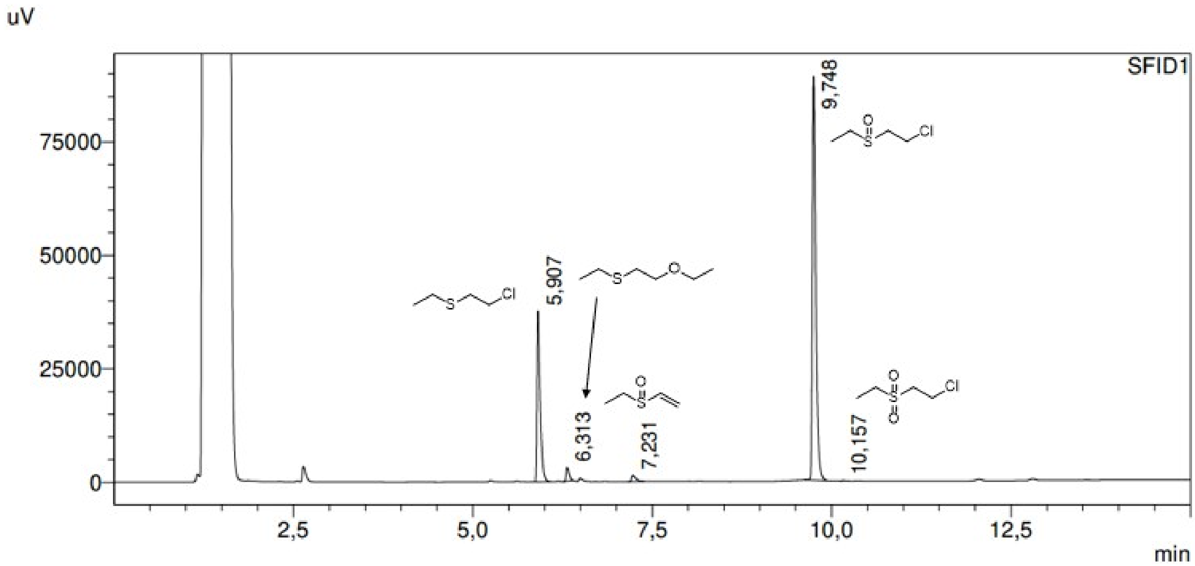


Figure S8. GC chromatogram of the oxidation of **CEES**. See manuscript for experimental details (Table 3, Entry 10).

	Ret. time (min)	Conversion (%)
CEES	5.9	28.15
I-1	6.3	2.02
EVSO (I-2)	7.2	1.28
CEESO	9.75	68.47
$CEESO_2$	10.15	0.08

Conversion 81.88%

Selectivity for **CEESO** = 95.3%

GC chromatogram – see manuscript: Table 3, Entry 7

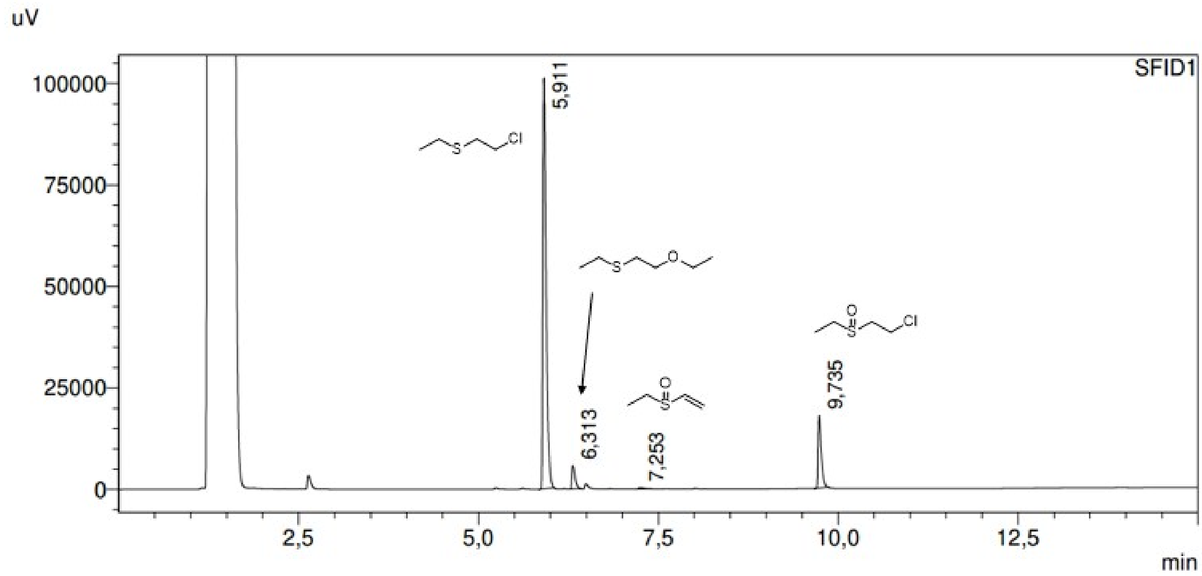


Figure S9. GC chromatogram of the oxidation of **CEES**. See manuscript for experimental details (Table 3, Entry 7).

	Ret. time (min)	Conversion (%)
CEES	5.9	81.06
I-1	6.3	4.48
EVSO (I-2)	7.2	0.44
CEESO	9.75	14.02

Conversion 51.42%

Selectivity for **CEESO** = 74.0%

GC chromatogram – see manuscript: Table 3, Entry 8

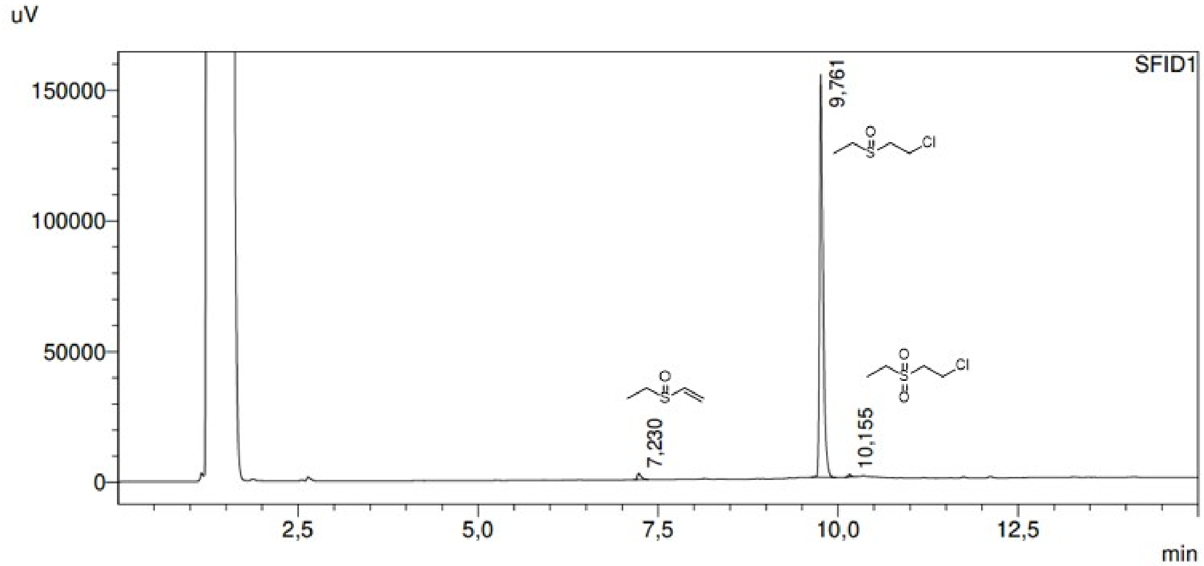


Figure S10. GC chromatogram of the oxidation of **CEES**. See manuscript for experimental details (Table 3, Entry 8).

	Ret. time (min)	Conversion (%)
EVSO (I-2)	7.2	1.68
CEESO	9.75	97.79
CEESO$_2$	10.15	0.53

Conversion 100%

Selectivity for **CEESO** = 97.8%

GC chromatogram – See manuscript: Table 3, Entry 9

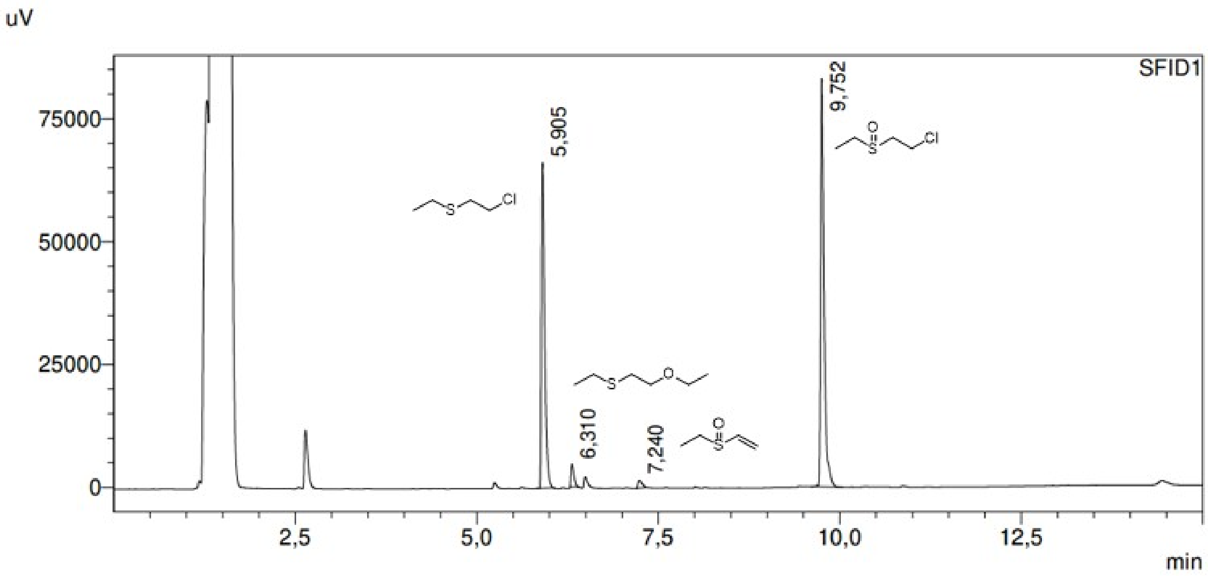


Figure S11. GC chromatogram of the oxidation of **CEES**. See manuscript for experimental details (Table 3, Entry 9).

	Ret. time (min)	Conversion (%)
CEES	5.9	41.43
I-1	6.3	2.56
EVSO (I-2)	7.2	1.27
CEESO	9.75	54.74

Conversion 68.23%

Selectivity for **CEESO** = 93.5%

2.2.3 Continuous flow procedure for the photooxidation of sulfides

2.2.3.1 Continuous flow procedure for the photooxidation of 2-chloroethylethyl sulfide (**CEES**)

A solution of **CEES** (1 M) and MB (560 µM) was prepared in EtOH. The pump used to deliver the solution of sulfide/catalyst and the gas flow meter used to deliver oxygen were set to 1 mL min^{-1} and 20 mL_N min^{-1}, respectively. Both streams were mixed in the fluidic modules (5 x 2.6 mL internal volume, estimated 4 min residence time) at room temperature under 9 bar of counterpressure. White LEDs (4000K) were selected and used at 100% of their maximum intensity. The reactor effluent was collected at steady state, diluted with ethanol and analyzed by GC-FID (>99% conversion, 97.8% selectivity). Photooxidation of 2-chloroethylethyl sulfide with air was conducted following the same procedure with conditions described in Table 3 (>99% conversion, 84% selectivity).

2.2.3.2 Continuous flow procedure for the photooxidation of dipropyl sulfide **1a**

A solution of dipropyl sulfide (**1a**, 1 M) and MB (560 µM) was prepared in EtOH. The pump used to deliver the solution of sulfide/catalyst and the gas flow meter used to deliver oxygen were set to 0.5 mL min^{-1} and 10 mL_N min^{-1}, respectively. Both streams were mixed in the fluidic modules (5 x 2.6 mL internal volume, estimated 10 min residence time) at room temperature under 9 bar of counterpressure. Orange LEDs (610 nm) were selected and used at 70% of their maximum intensity. The reactor effluent was collected at steady state, diluted with ethanol and analyzed by GC-FID (>99% conversion, 97.2% selectivity).

2.2.3.3 Continuous flow procedure for the photooxidation of benzyl methyl sulfide **1c**

A solution of benzyl methyl sulfide (**1c**, 1 M) and MB (560 µM) was prepared in EtOH. The pump used to deliver the solution of sulfide/catalyst and the gas flow meter used to deliver oxygen were set to 0.5 mL min^{-1} and 10 mL_N min^{-1}, respectively. Both streams were mixed in the fluidic modules (5 x 2.6 mL internal volume, estimated 10 min residence time) at room temperature under 9 bar of counterpressure. Orange LEDs (610 nm) were selected and used at 70% of their maximum intensity. The reactor effluent was collected at steady state, diluted with ethanol and analyzed by HPLC-DAD (>99% conversion, >99% selectivity).

2.2.3.4 Continuous flow procedure for the photooxidation of thioanisole **1d**

A solution of thioanisole (**1d**, 1 M) and MB (560 µM) was prepared in EtOH. The pump used to deliver the solution of sulfide/catalyst and the gas flow meter used to deliver oxygen were set to 0.5 mL min^{-1} and 10 mL_N min^{-1}, respectively. Both streams were mixed in the fluidic modules (5 x 2.6 mL internal volume, estimated 10 min residence time) at room temperature under 9 bar of counterpressure. Orange LEDs (610 nm) were selected and used at 70% of their maximum intensity. The reactor effluent was collected at steady state, diluted with ethanol and analyzed by HPLC-DAD (>99% conversion, >99% selectivity).

2.2.3.5 Continuous flow procedure for the photooxidation of diphenyl sulfide **1e**

A solution of diphenyl sulfide (**1e**, 0.1 M) and 9,10-dicyanoanthracene (56 µM) was prepared in MeCN. The pump used to deliver the solution of sulfide/catalyst and the gas flow meter used to deliver oxygen were set to 0.5 mL min^{-1} and 10 mL_N min^{-1}, respectively. Both streams were mixed in the fluidic modules (5 x 2.6 mL internal volume, estimated 10 min residence time) at room temperature under 9 bar of counterpressure. Purple LEDs (395 nm) were selected and used at 70% of their maximum intensity. The reactor effluent was collected at steady state, diluted with MeCN and analyzed by HPLC-DAD (46.6% conversion, >99% selectivity).

2.2.3.6 Continuous flow procedure for the photooxidation of dibenzothiophene **1f**

A solution of dibenzothiophene (**1f**, 0.1 M) and 9,10-dicyanoanthracene (56 µM) was prepared in MeCN. The pump used to deliver the solution of sulfide/catalyst and the gas flow meter used to deliver oxygen were set to 0.5 mL min^{-1} and 10 mL_N min^{-1}, respectively. Both streams were mixed in the fluidic modules (5 x 2.6 mL internal volume, estimated 10 min residence time) at room temperature under 9 bar of counterpressure. Orange LEDs (610 nm) were selected and used at 70% of their maximum intensity. The reactor effluent was collected at steady state, diluted with MeCN and analyzed by HPLC-DAD (48.9% conversion, 20.3% selectivity).

2.2.3.7 Continuous flow procedure for the photooxidation of diethyl sulfide

A solution of diethyl sulfide (1 M) and MB (560 µM) was prepared in EtOH. The pump used to deliver the solution of sulfide/catalyst and the gas flow meter used to deliver oxygen were set to 0.5 mL min^{-1} and 10 mL_N min^{-1}, respectively. Both streams were mixed in the fluidic modules (5 x 2.6 mL internal volume, estimated 10 min residence time) at room temperature under 9 bar of counterpressure. Orange LEDs (610 nm) were selected and used at 70% of their maximum intensity. The reactor effluent was collected at steady state, diluted with ethanol and analyzed by GC-FID (>99% conversion, 97.3% selectivity).

2.2.3.8 Continuous flow procedure for the photooxidation of thiodipropionic acid

A solution of thiodipropionic acid (1 M) and MB (560 µM) was prepared in EtOH. The pump used to deliver the solution of sulfide/catalyst and the gas flow meter used to deliver oxygen were set to 0.5 mL min^{-1} and 10 mL_N min^{-1}, respectively. Both streams were mixed in the fluidic modules (5 x 2.6 mL internal volume, estimated 10 min residence time) at room temperature under 9 bar of counterpressure. Orange LEDs (610 nm) were selected and used at 70% of their maximum intensity. The reactor effluent was collected at steady state, diluted with ethanol and analyzed by NMR (>99% conversion, >99% selectivity).

2.2.3.9 Continuous flow procedure for the photooxidation of tetrahydrothiophene

A solution of tetrahydrothiophene (1 M) and MB (560 µM) was prepared in EtOH. The pump used to deliver the solution of sulfide/catalyst and the gas flow meter used to deliver oxygen were set to 0.5 mL min^{-1} and 10 mL_N min^{-1}, respectively. Both streams were mixed in the fluidic modules (5 x 2.6 mL internal volume, estimated 10 min residence time) at room temperature under 9 bar of counterpressure. Orange LEDs (610 nm) were selected and used at 70% of their maximum intensity. The reactor effluent was collected at steady state, diluted with ethanol and analyzed by GC-FID (>99% conversion, >99% selectivity).

2.2.3.10 Continuous flow procedure for the photooxidation of dibenzyl sulfide

A solution of dibenzyl sulfide (0.1 M) and MB (560 µM) was prepared in EtOH/2-MeTHF. The pumps used to deliver the solution of sulfide/catalyst and the gas flow meter used to deliver oxygen were set to 0.5 mL min^{-1} and 10 mL_N min^{-1}, respectively. Both streams were mixed in the fluidic modules (5 x 2.6 mL internal volume, estimated 10 min residence time) at 60 °C under 9 bar of counterpressure. Orange LEDs (610 nm) were selected and used at 70% of their maximum intensity. The reactor effluent was collected at steady state, diluted with ethanol and analyzed by HPLC-DAD (>99% conversion, >63.9% selectivity).

2.2.3.11 Continuous flow procedure for the photooxidation of benzyl phenyl sulfide

A solution of benzyl phenyl sulfide (1 M) and MB (560 µM) was prepared in EtOH. The pump used to deliver the solution of sulfide/catalyst and the gas flow meter used to deliver oxygen were set to 0.1 mL min^{-1} and 25 mL_N min^{-1}, respectively. Both streams were mixed in the fluidic modules (1 x 2.6 mL internal volume, estimated 1 min residence time) at room temperature under 9 bar of counterpressure. Orange LEDs (610 nm) were selected and used at 70% of their maximum intensity. The reactor effluent was collected at steady state, diluted with ethanol and analyzed by HPLC-DAD (13.1% conversion, 55.7% selectivity).

2.2.3.12 Continuous flow procedure for the photooxidation of 2-chloroethylphenyl sulfide

A solution of 2-chloroethylphenyl sulfide (0.1 M) and MB (56 µM) was prepared in EtOH. The pump used to deliver the solution of sulfide/catalyst and the gas flow meter used to deliver oxygen were set to 0.5 mL min^{-1} and 10 mL_N min^{-1}, respectively. Both streams were mixed in the fluidic modules (5 x 2.6 mL internal volume, estimated 10 min residence time) at room temperature under 9 bar of counterpressure. Orange LEDs (610 nm) were selected and used at 70% of their maximum intensity. The reactor effluent was collected at steady state, diluted with ethanol and analyzed by GC-MS (>93.1% conversion, >99% selectivity).

2.2.4 Batch procedures for the synthesis of products and by-products resulting from 2-chloroethylethylsulfide oxidation

2.2.4.1 Batch procedure for the synthesis of vinyl ethyl sulfoxide (**EVSO, I-2**)

A solution of ethyl vinyl sulfide (1 M, 5 mL) was prepared in EtOH and oxidized with an aqueous solution of 30% H_2O_2 (1 mL). An aliquot was taken after 5 min, diluted in EtOH, analyzed by GC-FID. Vinyl ethyl sulfoxide (**EVSO**) was detected alongside with vinyl ethyl sulfone (**$EVSO_2$**) and identified by MS.

2.2.4.2 Batch procedure for the synthesis of 2-ethoxyethylethyl sulfane (**I-1**)

A solution of 2-chloroethyl ethyl sulfide (1 M, 5 mL) was prepared in EtOH and heated in a microwave oven (CEM Discovery, 150 °C, 3 x 20 min, 150 W). An aliquot was diluted in EtOH, analyzed by GC-FID and identified by NMR and MS.

The formation of 2-ethoxyethylethyl sulfane (**I-1**) was also studied by leaving a solution of **CEES** (1 M) in EtOH for a week at room temperature without mixing. An aliquot was diluted in EtOH and analyzed by GC-FID over 4 days. From day 1 to day 4, the quantity of 2-ethoxyethylethylsulfane (**I-1**) increased from 1.19% to 4.03%. Even if **I-1** is detectable in GC when a fresh solution of **CEES** in EtOH is injected, this increase over time demonstrates that the formation of additional **I-1** occurs slowly upon standing in solution at room temperature.

2.2.4.3 Batch procedure for the synthesis of 1-ethoxy-2-(ethylsulfinyl)ethane (**I-3**)

A solution of 2-ethoxyethylethyl sulfane (0.1 M, 2 mL) was prepared in EtOH and oxidized with an aqueous solution of 30% H_2O_2 (0.3 mL). An aliquot was taken immediately, diluted in EtOH, analyzed by GC-FID. 1-Ethoxy-2-(ethylsulfinyl)ethane (**I-3**) was identified by MS.

I-3 was not detected in GC when a solution of **EVSO** (**I-2**) in EtOH was injected; thus rejecting the filiation between **EVSO** and **I-3**.

2.2.4.4 Batch procedure for the synthesis of 1-ethoxy-2-(ethylsulfonyl)ethane

A solution of 2-ethoxyethylethyl sulfane (0.1 M, 2 mL) was prepared in EtOH and oxidized with an aqueous solution of 30% H_2O_2 (0.3 mL). An aliquot was taken after 5 min, diluted in EtOH, analyzed by GC-FID. 1-Ethoxy-2-(ethylsulfonyl)ethane was identified by MS.

2.3 Characterization of compounds

Commercial references for sulfoxides were purchased for **CEES**, **1d** and **1e** (see Table S2). For compounds **1a**, **1c** and **1f**, reference sulfoxides were synthesized by oxidation with H_2O_2 for peak identification in HPLC or GC. Commercial references for sulfones were purchased for **CEES**, **1a**, **1c**, **1d**, **1e** and **1f** (see Table S2).

2.3.1 In-line NMR

A study of the evolution of **1d** oxidation regarding to an increase of light intensity was conducted. An In-line NMR was equipped downstream (43 MHz Spinsolve™ Carbon NMR spectrometer from Magritek® equipped with the flow-through module). A T-mixer was used to vent the excess gas before entering the NMR flow cell.

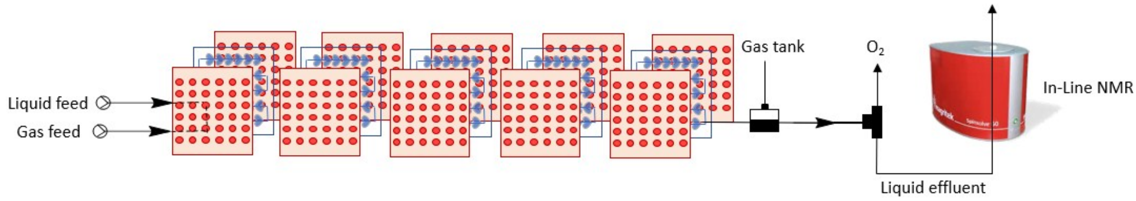


Figure S12. Detailed setup for the continuous flow photooxidation of sulfides.

A solution of **1d** (1 M) and MB (560 µM) was prepared in EtOH. The pumps used to deliver the solution of sulfide/catalyst and the gas flow meter used to deliver oxygen were set to 0.5 mL min^{-1} and 10 mL_N min^{-1}, respectively. Both streams were mixed in the fluidic modules (5 x 2.6 mL internal volume, estimated 10 min residence time) at 20 °C under 9 bar of counterpressure. LEDs were set on a 610 nm wavelength with an increasing intensity (from 0% to 100% with a 10% increment). A first ^{1}H NMR spectrum was recorded for the solvent alone. When the reaction started, a ^{1}H NMR spectrum was recorded after each increment of light intensity. The evolution of the oxidation can be studied by following the shift of the $-CH_3$ signal from 2.42 ppm to 2.81 ppm. The reaction reached completion upon irradiation at 70% of light intensity (see Figure S13).

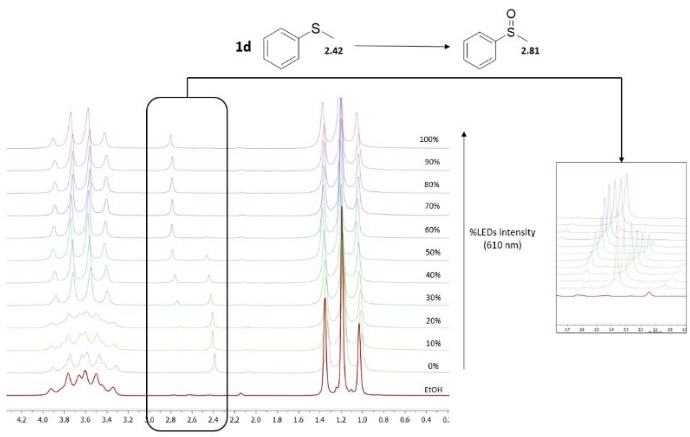


Figure S13. In-line ^{1}H NMR (43 MHz) spectra of **1d** photooxidation. Evolution of the sulfoxide appearance with an increase of light intensity.

2.3.2 In-line IR

To assess the efficiency of the In-line IR as an analytical tool to follow the oxidation of **CEES**, a first set of experiments was carried out on **1a** as a model thioether (see Figure S14).

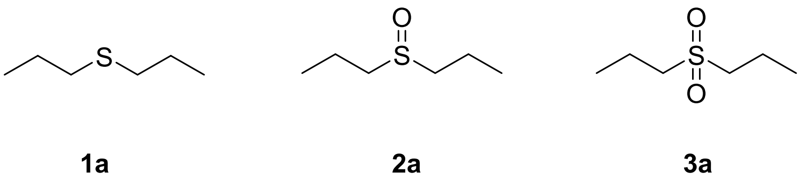


Figure S14. Structures of **1a**, **2a** and **3a**

A solution of dipropyl sulfide (**1a**, 1 M) was prepared in EtOH and injected first. Every 2 min, the amount of **1a** was reduced and the amount of dipropyl sulfoxide (**2a**) was increased to the point where the solution only contained the sulfoxide (1 M). The same procedure was applied with a decrease in sulfoxide and an increase in the corresponding sulfone **3a** until a concentration of 1 M was reached. Compound **1a** does not show any easily distinguishable signals from the solvent backbone and fingerprint. The corresponding sulfoxide **2a** shows a characteristic broad peak between 980 and 1020 cm^{-1} that can be utilized to monitor the appearance of **2a**. The IR spectrum of dipropyl sulfone (**3a**) also displays characteristic vibration bands at 1130, 1280 and 1315 cm^{-1} (see Figure S15) that can be utilized to monitor variations in its concentration.

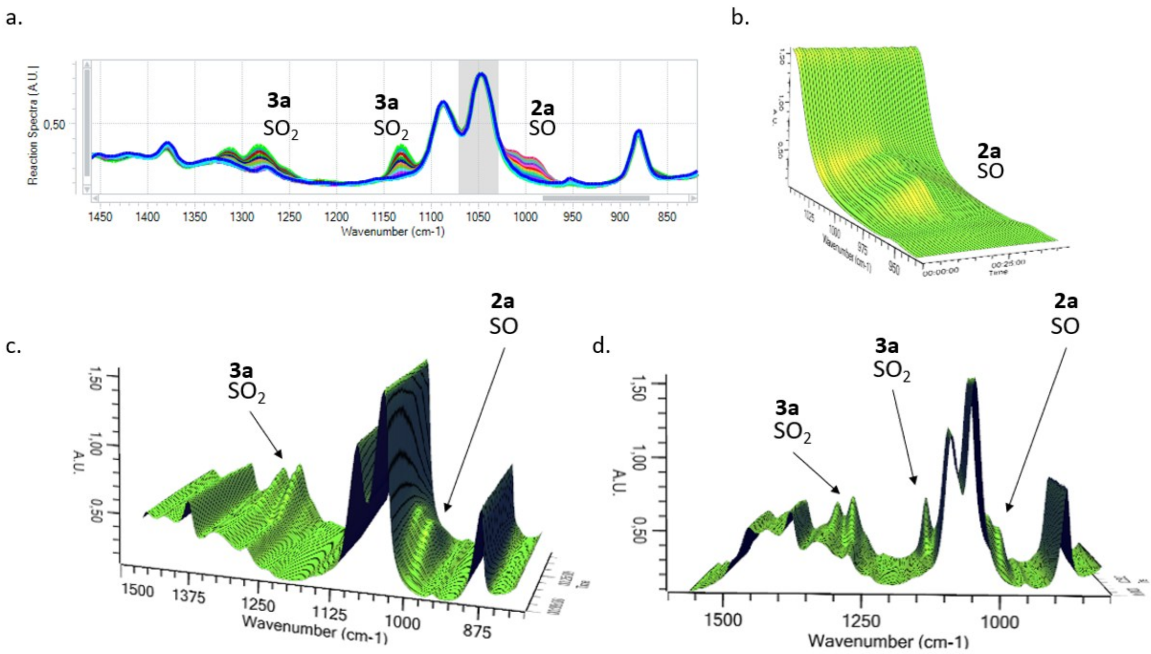
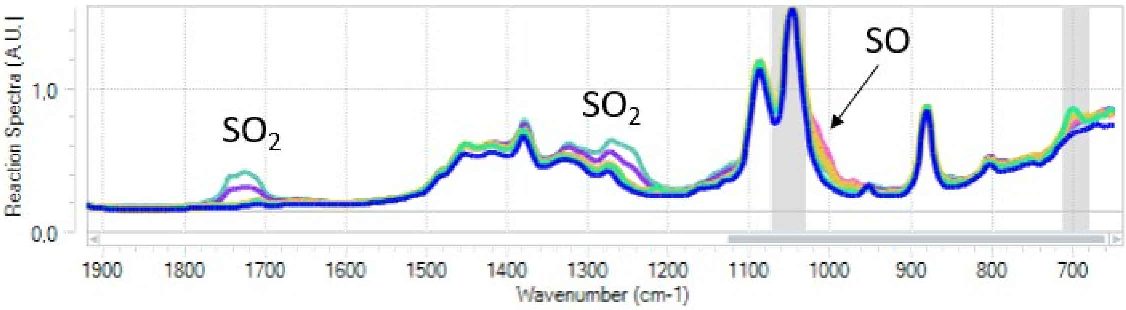


Figure S15. In-line IR spectra following **1a** oxidation to sulfoxide and overoxidation to sulfone.

The same procedure was applied to the oxidation of **CEES** for establishing a usable library of IR spectra. The characteristic vibration bands for the corresponding sulfoxide **CEESO** can be seen at 980 and 1020 cm^{-1}, while the characteristic vibration bands for the sulfone **CEESO$_2$** appear between 1220 and 1360 cm^{-1} and at about 1730 cm^{-1} (see Figure S16). These experiments confirm that In-line IR can be used as a suitable monitoring tool for the monitoring of **CEES** oxidation.



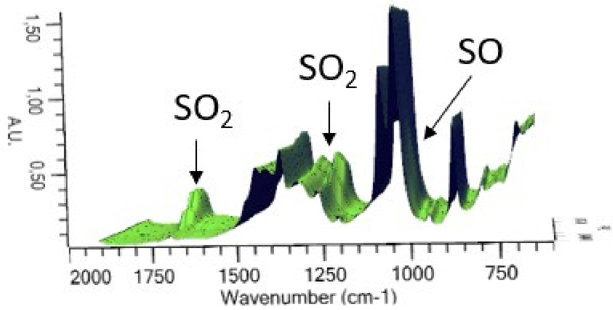
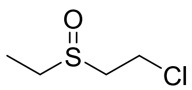


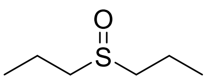
Figure S16. In-line IR spectra following **CEES** oxidation to sulfoxide and overoxidation to sulfone.

2.4 Structural identity of compounds



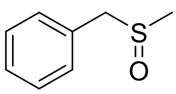
C_4H_9ClOS
MW 140,01

CEESO. ^1H NMR ($CDCl_3$, 400 MHz): δ = 3.96 (m, 2H), 3.21 (m, 2H), 2.91 (m, 2H), 1.37 (t, J = 7.5 Hz, 3H) ppm. The NMR data match those reported in the literature.[S1] **ESI HRMS** *m/z* $C_4H_{10}O^{35}Cl^{32}S^+$ [M+H]$^+$: calcd 141.01354; found 141.01366.



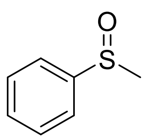
$C_6H_{14}OS$
MW 134,24

Dipropyl sulfoxide (**2a**). ^1H NMR (MeOD, 400 MHz): δ = 2.66 – 8.62 (m, 4H), 1.74 – 1.63 (m, 4H), 1.00 – 0.96 (t, J = 7.4 Hz, 6H) ppm. The NMR data match those reported in the literature.[S2]



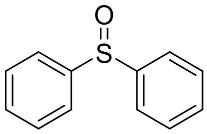
$C_8H_{10}OS$
MW 154,23

Benzyl methyl sulfoxide (**2c**). ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.31 – 7.22 (m, 5H), 3.99 (d, J = 12.9 Hz, 1H), 3.92 (d, J = 12.9 Hz, 1H), 2.42 (s, 3H) ppm. The NMR data match those reported in the literature.[S3]



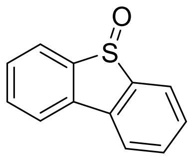
C_7H_8OS
MW 140,20

Phenyl methyl sulfoxide (**2d**). ^1H NMR ($CDCl_3$, 43 MHz): δ = 7.69 – 7.62 (m, 5H), 2.79 (s, 3H) ppm. The NMR data match the commercial reference and those reported in the literature.[S4]



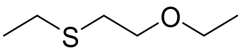
$C_{12}H_{10}OS$
MW 202,27

Diphenyl sulfoxide (**2e**). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.54 – 7.51 (m, 4H), 7.35 – 7.34 (m, 6H) ppm. The NMR data match the commercial reference and those reported in the literature.[S3]



$C_{12}H_8OS$
MW 200,26

Dibenzothiophene (**2f**). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.98 (d, *J* = 7.6 Hz, 2H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.70 – 7.63 (m, 3H), 7.57 – 7.52 (m, 2H) ppm. The NMR data match those reported in the literature.[S2]



$C_6H_{14}OS$
MW 134,24

2-ethoxyethylethyl sulfane (**I-1**). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.52 – 3.32 (m, 4H), 2.63 – 2.53 (m, 2H), 2.48 – 2.38 (m, 2H), 1.15 – 1.03 (m, 6H) ppm. GC-MS: m/z = 134

2.5 Copies of NMR spectra

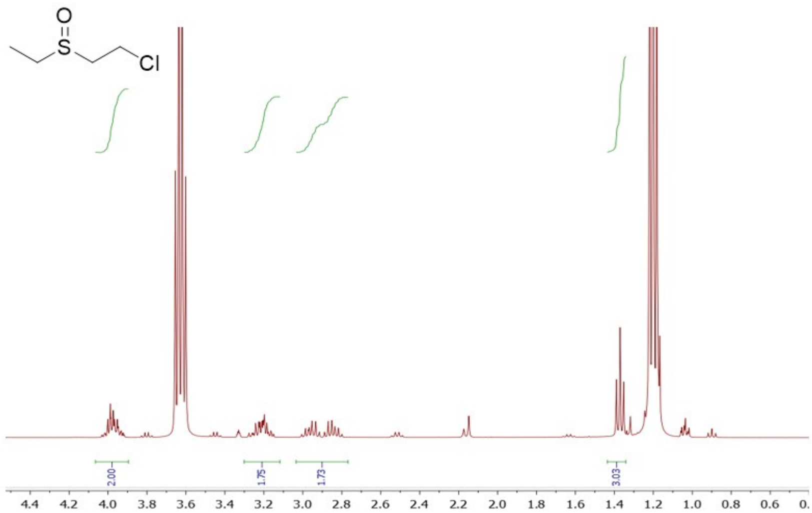


Figure S17. ^{1}H NMR spectrum (400 MHz) of **CEESO** in $CDCl_3$.

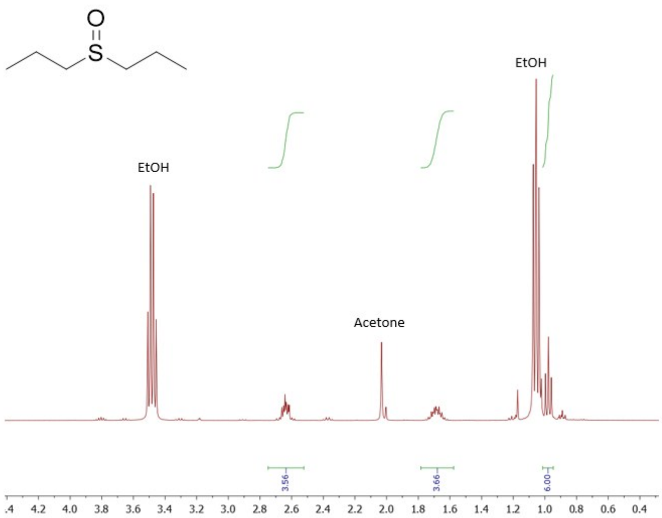


Figure S18. ^{1}H NMR spectrum (400 MHz) of dipropyl sulfoxide (**2a**) in $CDCl_3$.

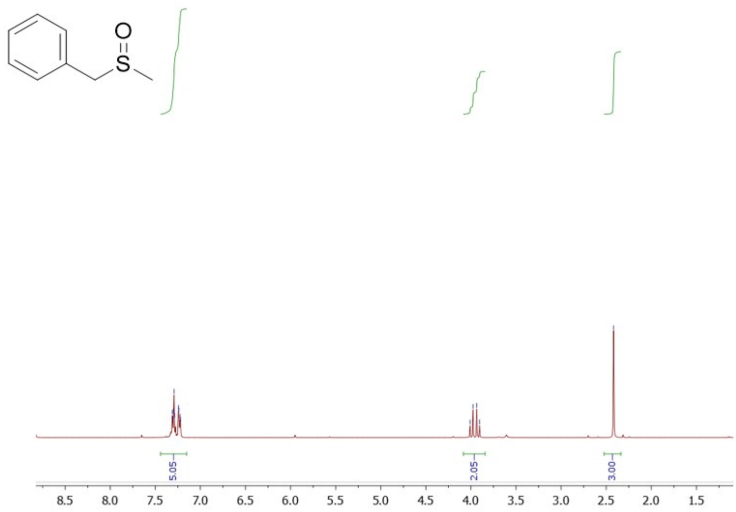


Figure S19. ^{1}H NMR spectrum (400 MHz) of benzyl methyl sulfoxide (**2c**) in $CDCl_3$.

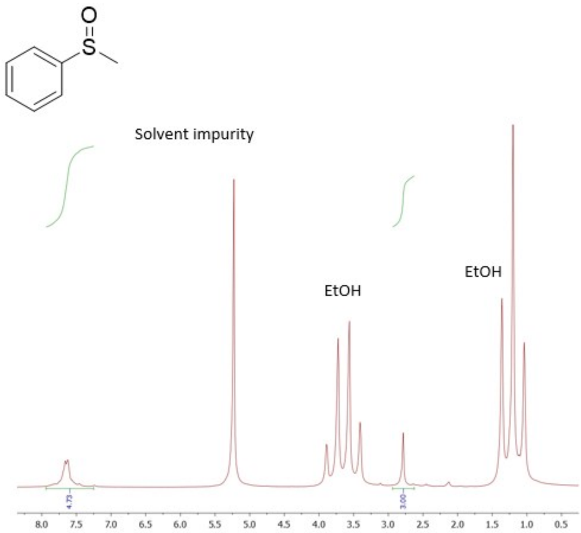


Figure S20. ^{1}H NMR spectrum (400 MHz) of phenyl methyl sulfoxide (**2d**) in $CDCl_3$.

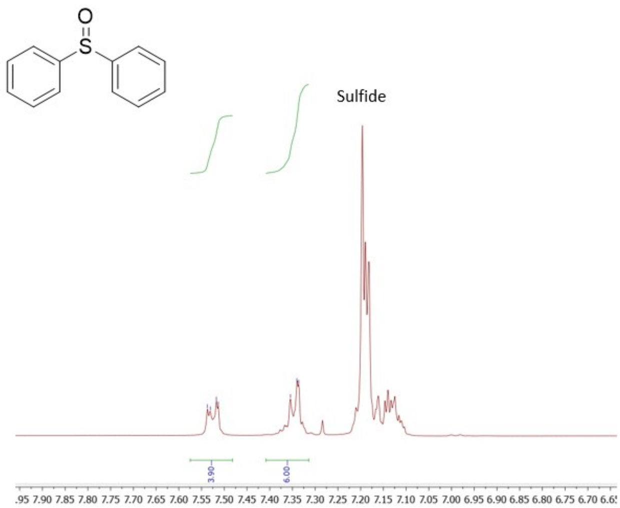


Figure S21. [1]H NMR spectrum (400 MHz) of diphenyl sulfide (**2e**) in $CDCl_3$.

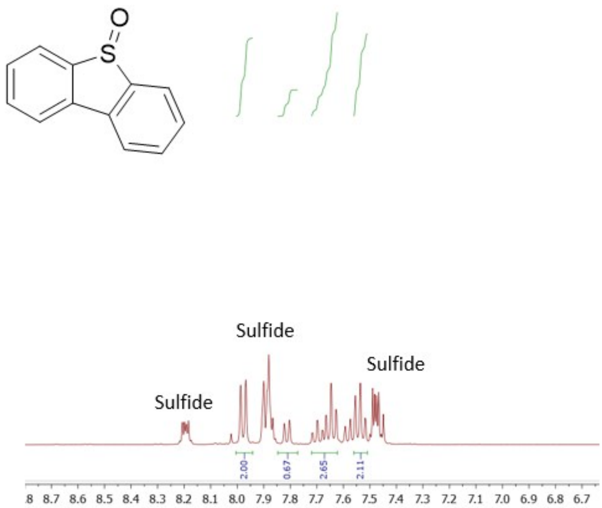


Figure S22. [1]H NMR spectrum (400 MHz) of dibenzothiophene sulfoxide (**2f**) in $CDCl_3$.

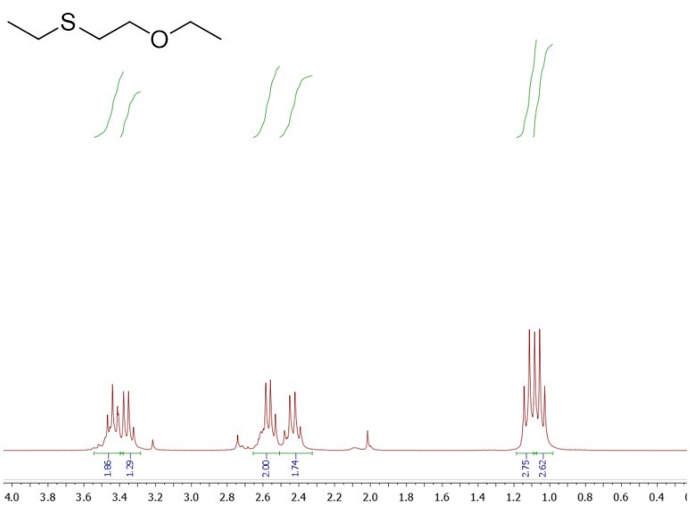


Figure S23. [1]H NMR spectrum (400 MHz) of 2-ethoxyethylethyl sulfane (**I-1**) in $CDCl_3$.

3. Detailed data on the photooxidation trials

3.1 Photooxidation of model thioethers

Table S3. General table of oxidation tests (part 1). Selectivity is only specified when not total towards the sulfoxide.

						Concentration (M)		Flow rate (mL.min^{-1})						
n°exp	Substrate	Oxidant	Photosensib.	Solvent	Temp. (°C)	Substrate	Photosensib.	Substrate	O_2	BPR (bar)	Light (nm) (Intensity (%))	Res. Time (min)	Conversion (%)	Selectivity (%)
1	thioanisole	O_2	MB	EtOH	rt	1	0.00056	1.5	15	8	610 (50)	~4	14.6	
2	thioanisole	O_2	MB	EtOH	rt	1	0.00056	1.5	15	8	610 (50)	~4	14.4	
3	thioanisole	O_2	MB	EtOH	rt	1	0.00056	1.5	15	8	610 (50)	~4	14.5	
4	thioanisole	O_2	MB	EtOH	rt	1	0.00056	2	15	8	610 (50)	~3	10.9	
5	thioanisole	O_2	MB	EtOH	rt	1	0.00056	2	15	8	610 (50)	~3	11.12	
6	thioanisole	O_2	MB	EtOH	rt	1	0.00056	2	15	8	610 (50)	~3	10.8	
7	thioanisole	O_2	MB	EtOH	rt	1	0.00056	20.2	15	8	610 (100)	~3	27.3	
8	thioanisole	O_2	MB	EtOH	rt	1	0.00056	2.5	15	8	610 (50)	~3	7.8	
9	thioanisole	O_2	MB	EtOH	rt	1	0.00056	3	15	8	610 (50)	~3	7.1	
10	thioanisole	O_2	MB	EtOH	rt	1	0.00056	3.5	15	8	610 (50)	~3	6.3	
11	thioanisole	O_2	MB	EtOH	rt	1	0.00056	1.5	15	8	610 (50)	~4	10.7	
12	thioanisole	O_2	MB	EtOH	rt	1	0.00056	2	15	8	610 (50)	~3	8.7	
13	thioanisole	O_2	MB	EtOH	rt	1	0.00056	2.5	15	8	610 (50)	~3	6.7	
14	thioanisole	O_2	MB	EtOH	rt	1	0.00056	3	15	8	610 (50)	~3	7.2	
15	thioanisole	O_2	MB	EtOH	rt	1	0.00056	3.5	15	8	610 (50)	~3	7.0	
16	thioanisole	O_2	MB	EtOH	rt	1	0.00056	1.5	20	8	610 (50)	~3	0.14	
17	thioanisole	O_2	MB	EtOH	rt	1	0.00056	1.5	25	8	610 (50)	~3	14.2	
18	thioanisole	O_2	MB	EtOH	rt	1	0.00056	1.5	30	8	610 (50)	~3	10.9	
19	thioanisole	O_2	MB	EtOH	rt	1	0.00056	1.5	35	8	610 (50)	~2	10.44	
20	thioanisole	O_2	MB	EtOH	rt	1	0.00056	2	20	8	610 (50)	~3	10.6	
21	thioanisole	O_2	MB	EtOH	rt	1	0.00056	2	25	8	610 (50)	~3	10.1	
22	thioanisole	O_2	MB	EtOH	rt	1	0.00056	2	30	8	610 (50)	~3	9.9	
23	thioanisole	O_2	MB	EtOH	rt	1	0.00056	2	35	8	610 (50)	~2	9.8	
24	thioanisole	O_2	MB	EtOH	rt	1	0.00056	1.5	10	8	610 (50)	~5	14.6	
25	thioanisole	O_2	MB	EtOH	rt	1	0.00056	2	10	8	610 (50)	~4	10.9	
26	thioanisole	O_2	MB	EtOH	rt	1	0.00056	1	15	8	610 (50)	~4	19.8	
27	thioanisole	O_2	MB	EtOH	rt	1	0.00056	1.5	20	8	610 (60)	~3	16.7	
28	thioanisole	O_2	MB	EtOH	rt	1	0.00056	1.5	20	8	610 (70)	~3	21.9	
29	thioanisole	O_2	MB	EtOH	rt	1	0.00056	1.5	20	8	610 (80)	~3	23.9	
30	thioanisole	O_2	MB	EtOH	rt	1	0.00056	1.5	20	8	610 (90)	~3	32.8	
31	thioanisole	O_2	MB	EtOH	rt	1	0.00056	1.5	20	8	610 (100)	~3	35.8	
32	thioanisole	O_2	MB	EtOH	rt	1	0.00056	1	50	8	610 (50)	~2	15.5	
33	thioanisole	O_2	MB	EtOH	rt	1	0.000056	1	50	8	610 (50)	~2	3.4	
34	thioanisole	O_2	MB	EtOH	rt	1	0.000056	1	15	8	610 (50)	~4	3.4	
35	thioanisole	O_2	MB	EtOH	rt	1	0.000056	1.5	15	8	610 (50)	~4	2.6	
36	thioanisole	O_2	MB	EtOH	rt	1	0.000056	2	15	8	610 (50)	~3	2.2	
37	thioanisole	O_2	RB	EtOH	rt	1	0.00056	1	50	8	532 (50)	~2	9.2	
38	thioanisole	O_2	RB	EtOH	rt	1	0.00056	1	15	8	532 (50)	~4	3.7	
39	thioanisole	O_2	RB	EtOH	rt	1	0.00056	1.5	15	8	532 (50)	~4	10.4	
40	thioanisole	O_2	RB	EtOH	rt	1	0.00056	2	15	8	532 (50)	~3	10.9	
41	thioanisole	O_2	MB	EtOH	rt	1	0.00056	1	15	8	610 (100)	~4	43.9	
42	thioanisole	O_2	MB	EtOH	rt	1	0.00056	0.5	10	8	610 (50)	~7	61.2	
43	thioanisole	O_2	MB	EtOH	rt	1	0.00056	0.5	15	8	610 (50)	~6	40.8	
44	thioanisole	O_2	MB	EtOH	rt	1	0.00056	0.5	10	8	610 (100)	~7	88.8	
45	thioanisole	O_2	MB	EtOH	rt	1	0.0056	0.5	10	8	610 (50)	~7	25.9	
46	thioanisole	O_2	MB	EtOH	rt	1	0.0056	1	15	8	610 (50)	~4	25.6	
47	thioanisole	O_2	MB	EtOH	rt	1	0.0056	1.5	15	8	610 (50)	~4	15.05	
48	thioanisole	O_2	MB	EtOH	rt	1	0.0056	2	15	8	610 (50)	~4	11.6	
49	thioanisole	O_2	MB	EtOH	rt	1	0.000056	0.5	10	8	610 (50)	~6	6.7	
50	thioanisole	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (50)	~10	N.D	
51	thioanisole	O_2	MB	EtOH	rt	1	0.00056	0.5	10	7	610 (50)	~6	45.4	
52	thioanisole	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (50)	~10	94.0	
53	thioanisole	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (50)	~10	94.8	
54	thioanisole	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (80)	~10	66.2	
55	thioanisole	O_2	MB	EtOH	rt	1	0.001	0.5	10	9	610 (50)	~10	33.9	
56	thioanisole	O_2	MB	EtOH	rt	1	0.001	0.5	10	9	610 (50)	~10	39.1	
57	thioanisole	O_2	MB	EtOH	rt	1	0.001	0.5	10	9	610 (60)	~10	72.8	
58	thioanisole	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (70)	~10	99.4	
59	thioanisole	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (70)	~10	93.2	
60	thioanisole	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (70)	~10	total	
61	thioanisole	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (70)	~10	97.6	
62	benzyl methyl sulfide	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (50)	~10	total	
63	benzyl methyl sulfide	O_2	MB	EtOH	t	1	0.00056	0.5	10	9	610 (60)	~10	total	
64	benzyl methyl sulfide	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (80)	~10	total	
65	benzyl methyl sulfide	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (70)	~10	total	
66	tetrathiophene	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (60)	~10	94.8	
67	tetrathiophene	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (80)	~10	97.6	97.0
68	tetrathiophene	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (70)	~10	total	
69	dipropylsulfide	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (80)	~10	total	97.2
70	dipropylsulfide	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (70)	~10	total	92.5
71	diphenyl sulfide	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (70)	~10	6.2	
72	diphenyl sulfide	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (70)	~10	3.8	
73	diphenyl sulfide	O_2	MB	EtOH	rt	1	0.00056	0.5	10	11	610 (70)	~10	6.0	
74	diethyl sulfide	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (70)	~10	total	97.3
75	dibenzothiophene	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (70)	~10	0.0	
76	Thiodipropionic acid	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (70)	~10	total	
77	dibenzyl sulfide	O_2	MB	EtOH/2-MeTHF (1:1)	rt	1	0.00056	0.5	10	9	610 (70)	~10	clogged reactor	
78	dibenzyl sulfide	O_2	MB	EtOH/2-MeTHF (1:1)	60	0.1	0.00056	0.5	10	9	610 (70)	~10	total	63.9
79	dibenzyl sulfide	O_2	MB	EtOH/2-MeTHF (1:1)	70	1	0.00056	0.5	10	9	610 (70)	~10	total	60.5
80	diphenyl sulfide	O_2	MB	ACN/eau 85:15	rt	1	0.00056	0.5	10	9	610 (70)	~10	0.0	
81	diphenyl sulfide	O_2	MB	ACN/eau 85:15	rt	1	0.00056	1.5	20	11,6	610 (70)	~ 4	0.0	
87	thioanisole	air	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (70)	~10	21.5	
88	thioanisole	air	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (70)	~10	19.3	
89	thioanisole	air	MB	EtOH	rt	1	0.00056	1	20	9	610 (70)	~ 4	15.6	
90	thioanisole	air	MB	EtOH	rt	1	0.00056	1	20	9	610 (70)	~ 4	15.3	
91	thioanisole	air	MB	EtOH	rt	0.1	0.000056	0.5	10	9	610 (70)	~10	total	
92	thioanisole	air	MB	EtOH	rt	0.1	0.000056	0.5	10	9	610 (70)	~10	total	
93	thioanisole	air	MB	EtOH	rt	0.1	0.000056	1.5	30	5	610 (70)	~ 2	46.7	
94	thioanisole	air	MB	EtOH	rt	0.1	0.000056	1.5	30	5	610 (70)	~ 2	46.3	

Table S3. General table of oxidation tests (part 2). Selectivity is only specified when not total toward the sulfoxide.

						Concentration (M)		Flow rate (mL.min^{-1})						
n°exp	Substrate	Oxidant	Photosensib.	Solvent	Temp. (°C)	Substrate	Photosensib.	Substrate	O_2	BPR (bar)	Light (nm) (Intensity (%))	Res. Time (min)	Conversion (%)	Selectivity (%)
95	propylS	air	MB	EtOH	rt	0.1	0.000056	0.5	10	9	610 (70)	~10	total	
96	propylS	air	MB	EtOH	rt	0.1	0.000056	0.5	10	9	610 (70)	~10	total	
97	diphenyl sulfide	O_2	MB	ACN	rt	0.1	0.00056	0.5	10	9	610 (70)	~10	0.0	
98	diphenyl sulfide	O_2	MB	ACN	rt	0.1	0.00056	0.5	10	9	610 (70)	~10	0.0	
99	diphenyl sulfide	O_2	DCA	ACN	rt	0.1	0.000056	0.5	10	9	395 (100)	~10	N.D	
100	diphenyl sulfide	O_2	DCA	ACN	rt	0.1	0.000056	0.5	10	9	395 (70)	~10	46.6	
101	dibenzothiophene	O_2	DCA	MeCN	rt	0.1	0.000056	0.5	10	9	395 (100)	~10	20.1	12.5
102	dibenzothiophene	O_2	DCA	MeCN	rt	0.1	0.000056	0.5	10	9	395 (70)	~10	22.7	7.9
103	dibenzothiophene	O_2	DCA	MeCN	rt	0.1	0.00056	0.5	10	9	395 (100)	~10	48.9	20.3
104	dibenzothiophene	O_2	DCA	MeCN	rt	0.1	0.00056	0.5	10	9	395 (70)	~10	47.8	17.2
105	dibenzyl sulfide	O_2	DCA	MeCN	rt	0.1	0.00056	0.5	10	9	395 (100)	~10	total	19.0
106	dibenzyl sulfide	O_2	DCA	MeCN	rt	0.1	0.00056	0.5	10	9	395 (70)	~10	total	21.2
107	CEES	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (100)	~10	99.92	94.8
108	CEES	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (70)	~10	99.92	95.5
109	CEES	O_2	MB	EtOH	rt	1	0.00056	1	20	9	610 (100)	~ 4	99.26	92.4
110	CEES	Air	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (100)	~10	99.74	84.0
111	CEES	Air	MB	EtOH	rt	0.1	0.000056	0.5	10	9	610 (100)	~10	99.88	84.8
112	CEES	Air	MB	EtOH	rt	0.1	0.000056	0.5	10	9	610 (70)	~10	total	83.4
113	CEES	Air	RB	EtOH	rt	0.1	0.000056	0.5	10	9	530 (100)	~10	83.69	83.4
114	CEES	Air	RB	EtOH	rt	0.1	0.000056	0.5	10	9	530 (70)	~10	80.94	79.5
115	CEES	O_2	RB	EtOH	rt	1	0.00056	0.5	10	9	530 (70)	~10	94.51	97.3
116	CEES	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	white light (100)	~10	99.91	96.1
117	CEES	O_2	RB	EtOH	rt	1	0.00056	0.5	10	9	white light (100)	~10	99.92	95.4
118	CEES	O_2	MB	EtOH	rt	1	0.00056	2	40	9	610 (100)	~ 2	81.88	95.3
119	CEES	Air	MB	EtOH	rt	1	0.00056	1	20	9	610 (100)	~ 4	51.42	74.0
120	CEES	O_2	MB	EtOH	rt	1	0.00056	1	20	9	white light (100)	~ 4	total	97.8
121	CEES	Air	MB	EtOH	rt	1	0.00056	1	20	9	white light (100)	~ 4	68.23	93.5
122	CEPS	O_2	MB	EtOH	rt	1	0.00056	1	20	9	610 (100)	~ 4	58.0	97.6
123	CEPS	O_2	MB	EtOH	rt	1	0.00056	0.5	10	9	610 (100)	~10	57.8	97.6
124	CEPS	O_2	MB	EtOH	rt	0.1	0.000056	1	20	9	610 (100)	~ 4	65.4	98.1
125	CEPS	O_2	MB	EtOH	rt	0.1	0.000056	0.5	10	9	610 (100)	~10	93.11	99.9
126	CEPS	O_2	MB	EtOH	rt	0.1	0.000056	0.5	10	10	white light (100)	~10	74.7	99.99

3.2 **CEES** photooxidation tests

3.2.1 Impact of the residence time

Table S4. Comparison of residence time for the neutralization of **CEES**. PS is always MB when not specified, Rose Bengal when (RB) is specified.

				Flow rate (mL.min^{-1})						
In Table 3	[CEES] (M)	[PS] (µM)	Oxidant	Liquid	Gas	BPR (bar)	Light (nm) (Intensity (%))	Res. time (min)	Conversion (%)	Selectivity (%)
Entry 1	1	560	O_2	0.5	10	9	610 (100)	~10	99.92	94.8
Entry 6	1	560	O_2	1	20	9	610 (100)	~ 4	99.26	92.4
Entry 10	1	560	O_2	2	40	9	610 (100)	~ 2	81.88	95.3

3.2.2 Comparison of oxygen and air

Table S5. Comparison of oxidant gas for the neutralization of **CEES**. PS is always MB when not specified, Rose Bengal when (RB) is specified.

				Flow rate (mL.min^{-1})						
In Table 3	[CEES] (M)	[PS] (µM)	Oxidant	Liquid	Gas	BPR (bar)	Light (nm) (Intensity (%))	Res. time (min)	Conversion (%)	Selectivity (%)
Entry 1	1	560	O_2	0.5	10	9	610 (100)	~10	99.92	94.8
Entry 4	1	560	Air	0.5	10	9	610 (100)	~10	99.74	84
Entry 6	1	560	O_2	1	20	9	610 (100)	~ 4	99.26	92.4
Entry 7	1	560	Air	1	20	9	610 (100)	~ 4	51.42	74
entry 8	1	560	O_2	1	20	9	white light (100)	~ 4	total	97.8
Entry 9	1	560	Air	1	20	9	white light (100)	~ 4	68.23	93.5

3.2.3 Comparison of photosensitizers

Table S6. Comparison of photosensitizers for **CEES** oxidation. PS is always MB when not specified, Rose Bengal when (RB) is specified.

				Flow rate ($mL.min^{-1}$)						
In Table 3	[CEES] (M)	[PS] (µM)	Oxidant	Liquid	Gas	BPR (bar)	Light (nm) (Intensity (%))	Res. time (min)	Conversion (%)	Selectivity (%)
not shown 1	1	560	O_2	0.5	10	9	610 (70)	~10	99.92	95.5
not shown 2	1	560 (RB)	O_2	0.5	10	9	530 (70)	~10	94.51	97.3
Entry 5	0.1	56	Air	0.5	10	9	610 (100)	~10	99.88	84.8
not shown 3	0.1	56 (RB)	Air	0.5	10	9	530 (100)	~10	83.69	83.4
Entry 2	1	560	O_2	0.5	10	9	white light (100)	~10	99.91	96.1
Entry 3	1	560 (RB)	O_2	0.5	10	9	white light (100)	~10	99.92	95.4

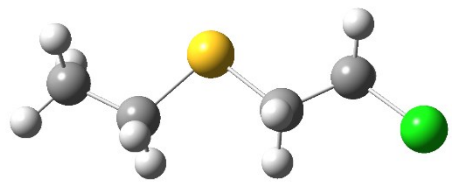
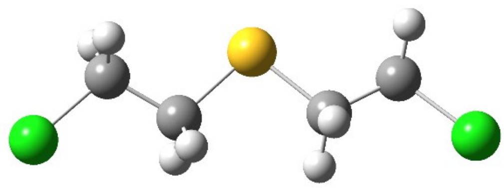
3.2.4 Comparison of light (wavelength and intensity)

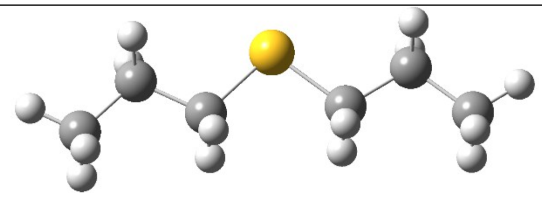
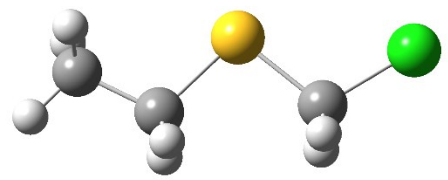
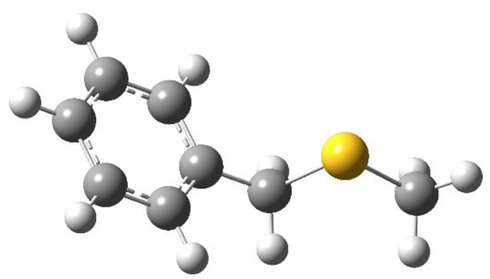
Table S7. Comparison of light for **CEES** oxidation. PS is always MB when not specified, Rose Bengal when (RB) is specified.

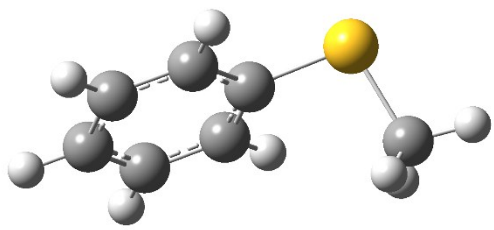
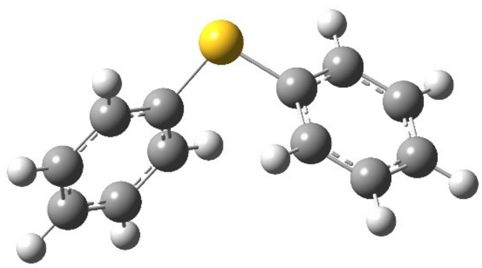
				Flow rate ($mL.min^{-1}$)						
In Table 3	[CEES] (M)	[PS] (µM)	Oxidant	Liquid	Gas	BPR (bar)	Light (nm) (Intensity (%))	Res. time (min)	Conversion (%)	Selectivity (%)
Entry 1	1	560	O_2	0.5	10	9	610 (100)	~10	99.92	94.8
not shown 1	1	560	O_2	0.5	10	9	610 (70)	~10	99.92	95.5
Entry 2	1	560	O_2	0.5	10	9	white light (100)	~10	99.91	96.1
Entry 6	1	560	O_2	1	20	9	610 (100)	~ 4	99.26	92.4
Entry 8	1	560	O_2	1	20	9	white light (100)	~ 4	total	97.8
Entry 5	0.1	56	Air	0.5	10	9	610 (100)	~10	99.88	84.8
not shown 4	0.1	56	Air	0.5	10	9	610 (70)	~10	total	83.4
not shown 3	0.1	56 (RB)	Air	0.5	10	9	530 (100)	~10	83.69	83.4
not shown 5	0.1	56 (RB)	Air	0.5	10	9	530 (70)	~10	80.94	79.5
not shown 2	1	560 (RB)	O_2	0.5	10	9	530 (70)	~10	94.51	97.3
Entry 3	1	560 (RB)	O_2	0.5	10	9	white light (100)	~10	99.92	95.4
Entry 7	1	560	Air	1	20	9	610 (100)	~ 4	51.42	74
Entry 9	1	560	Air	1	20	9	white light (100)	~ 4	68.23	93.5

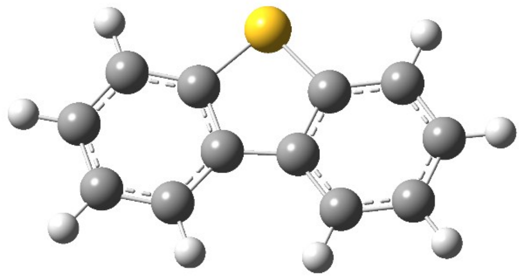
4. Computations

4.1 Stationary points for compounds **CEES**, **HD** and **1a-f**

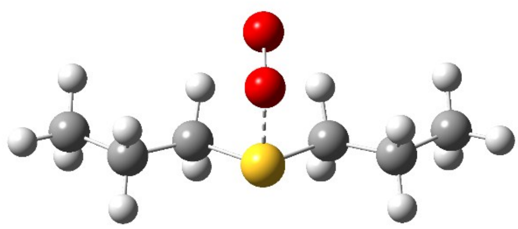
CEES	**MP2/6-31+G**** (Hartree)
15 scf done: -1014.569720 S 0.000000 0.000000 0.000000 C 0.000000 0.000000 1.792323 C 1.778165 0.000000 -0.253799 C -1.418766 0.077061 2.322684 C 2.091289 -0.114762 -1.733662 Cl 3.863064 -0.185112 -1.939820 H 0.611517 0.833668 2.134774 H 0.479444 -0.958472 2.040217 H -1.897513 1.018484 2.068487 H -2.018943 -0.753796 1.961510 H 2.125054 -0.881495 0.298219 H 2.182014 0.912821 0.181894 H 1.679041 -1.029718 -2.149896 H 1.729914 0.743979 -2.292796 H -1.389099 0.008742 3.390088	H = -1014.432024 G = -1014.476153 
HD	**MP2/6-31+G**** (Hartree)
15 scf done: -1473.592520 S 0.000000 0.000000 0.000000 C 0.000000 0.000000 1.820206 C 1.804791 0.000000 -0.236227 C 2.110725 -0.346458 -1.679465 Cl 3.880480 -0.306183 -1.959382 C -1.388127 0.359382 2.310690 Cl -1.437711 0.315289 4.101684 H 0.717538 0.740596 2.173039 H 0.290074 -0.982675 2.190699 H -1.664799 1.365389 2.008006 H -2.133454 -0.347168 1.954439 H 2.246850 -0.747053 0.422788 H 2.210736 0.980069 0.012172 H 1.771139 -1.348830 -1.924631 H 1.663803 0.368500 -2.365524	H = -1473.462357 G = -1473.509951 
1a	**MP2/6-31+G**** (Hartree)
21 scf done: -633.914467 S 0.000000 0.000000 0.000000 C 0.000000 0.000000 1.540000 C 1.451926 0.000000 -0.513333 C -1.451926 0.000025 2.053333 C 1.451926 -0.000634 -2.053333	H = -633.708181 G = -633.756180

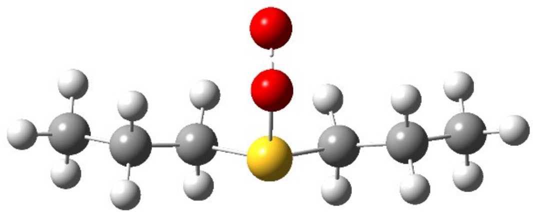
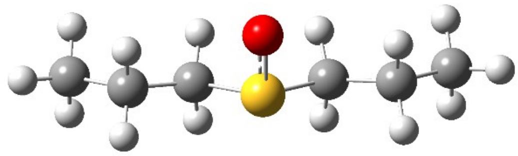
C 2.903849 0.002154 -2.566668 C -1.451926 0.000025 3.593333 H 3.410060 -0.870298 -2.209628 H 3.406441 0.877001 -2.210375 H 2.903849 0.001696 -3.636668 H 0.945720 0.871827 -2.410359 H 0.949329 -0.875471 -2.409640 H 1.956202 0.873871 -0.157026 H 1.956456 -0.873431 -0.156307 H 0.504418 0.873643 1.896667 H 0.504388 -0.873660 1.896667 H -1.956344 -0.873617 1.696667 H -1.956314 0.873685 1.696667 H -0.947508 0.873668 3.950000 H -2.460732 0.000043 3.950000 H -0.947538 -0.873635 3.950000	
1b	**MP2/6-31+G**** (Hartree)
12 scf done: -975.379095 S 0.000000 0.000000 0.000000 C 0.000000 0.000000 1.818307 C 1.799460 0.000000 -0.265304 C -1.424972 0.088353 2.345894 H 0.584580 0.852002 2.166642 H 0.479485 -0.914758 2.168073 H -1.906056 1.011875 2.026113 H -2.025321 -0.752543 1.999923 H 2.254083 -0.717680 0.417964 H 2.208892 0.989390 -0.062891 H -1.412332 0.070800 3.435348 Cl 2.135823 -0.470131 -1.927662	H = -975.272292 G = -975.314752 
1c	**MP2/6-31+G**** (Hartree)
19 scf done: -668.343358 S -2.053586 -0.000084 -0.680770 C -3.684737 0.000088 0.102417 C -1.021695 -0.000008 0.821936 C 0.429459 -0.000008 0.436546 C 1.116949 -1.208986 0.251973 C 2.461562 -1.210638 -0.131914 C 3.138224 0.000028 -0.320319 C 2.461522 1.210676 -0.131948 C 1.116910 1.208989 0.251936 H -3.821623 -0.890355 0.713532 H -4.429205 0.000060 -0.691155 H -3.821512 0.890660 0.713367 H -1.257091 0.887812 1.411464 H -1.257086 -0.887764 1.411563	H = -707.359079 G = -707.405066 

H 0.595190 -2.148260 0.401851 H 2.981818 -2.150839 -0.269979 H 4.180855 0.000040 -0.613839 H 2.981745 2.150892 -0.270040 H 0.595118 2.148249 0.401784	
1d	**MP2/6-31+G**** (Hartree)
16 scf done: -668.343357 S 0.000000 0.000000 0.000000 C 0.000000 0.000000 1.782446 C 1.789167 0.000000 -0.300110 C 0.511104 -1.092331 2.501333 C 0.486722 -1.085431 3.898840 C -0.073107 -0.003484 4.588916 C -0.599080 1.077646 3.874408 C -0.558043 1.084222 2.475656 H 0.923556 -1.943237 1.971916 H 0.887379 -1.930398 4.445687 H -0.099439 -0.004497 5.671551 H -1.033777 1.918284 4.401491 H -0.950451 1.928941 1.922456 H 2.252006 0.873983 0.152735 H 1.931386 0.041215 -1.378688 H 2.251737 -0.907353 0.080207	H = -668.204306 G = -668.246695 
1e	**MP2/6-31+G**** (Hartree)
23 scf done: -859.512841 S 0.000000 0.000000 0.000000 C 0.000000 0.000000 1.783633 C 1.760523 0.000000 -0.284007 C 2.568803 1.020720 0.241188 C 3.944685 1.011514 0.000690 C 4.517217 0.007196 -0.790861 C 3.707571 -0.996516 -1.331341 C 2.331385 -1.006744 -1.074285 C -0.838860 0.892889 2.464438 C -0.894860 0.871065 3.862937 C -0.111651 -0.034442 4.585381 C 0.728501 -0.923675 3.902836 C 0.770391 -0.924513 2.506508 H -1.427658 1.611064 1.906155 H -1.543407 1.565895 4.382645 H -0.148118 -0.043179 5.667647 H 1.333639 -1.632348 4.455451 H 1.411825 -1.622689 1.981196 H 2.124972 1.804515 0.844196 H 4.565503 1.796256 0.415988 H 5.583159 0.007845 -0.982002	H = -859.318588 G = -859.371122 

H 4.143571 -1.778185 -1.941561 H 1.706606 -1.796681 -1.473691	
1f	**MP2/6-31+G**** (Hartree)
21 sfc done: -858.3527375 S 0.000000 0.000000 0.000000 C 0.000000 0.000000 1.754929 C 1.754671 0.000000 -0.030842 C 2.557844 0.000000 -1.180068 C 3.943026 0.000000 -1.021781 C 4.522511 0.000000 0.262174 C 3.722322 0.000000 1.402038 C 2.321976 0.000000 1.265399 C 1.306029 0.000000 2.299326 C 1.467328 0.000000 3.697018 C 0.341788 0.000000 4.517234 C -0.952155 0.000000 3.960456 C -1.134810 0.000000 2.578280 H 5.600907 0.000000 0.362802 H 4.578977 0.000000 -1.898668 H 2.114729 0.000000 -2.168810 H 4.174636 0.000000 2.387342 H -2.131183 0.000000 2.152723 H -1.817686 0.000000 4.611781 H 0.461410 0.000000 5.593691 H 2.460476 0.000000 4.131761	H = -858.185869 G = -858.231417 

4.2 Selected transition states, peroxysulfoxides and sulfoxides

TS$^{1}_{1a}$	**MP2/6-31+G**** (Hartree)
23 scf done : -783.8306078 S 0.001090 -0.230173 -0.802643 C 1.371445 -0.560524 0.302297 C -1.368535 -0.567589 0.300751 O -0.003749 1.635150 -0.548470 O -0.007288 1.962681 0.769973 H 1.211938 0.151555 1.124357 H 1.256531 -1.580546 0.672130 H -1.253045 -1.590475 0.662164 H -1.209147 0.138421 1.127929 C 2.714263 -0.343585 -0.380861 H 2.815401 -1.024173 -1.228255 H 2.759935 0.675783 -0.768102 C -2.711302 -0.344919 -0.380645 H -2.754759 0.676224 -0.763369 H -2.814224 -1.021559 -1.230966 C 3.854936 -0.570112 0.607725	H = -783.617775 G = -783.672039 

H 4.817150 -0.413167 0.121601 H 3.781632 0.121402 1.447398 H 3.833986 -1.587507 0.999295 C -3.852298 -0.572873 0.607316 H -4.814169 -0.411296 0.121994 H -3.834290 -1.591904 0.994727 H -3.777135 0.114974 1.449864	
1Aa	**MP2/6-31+G**** (Hartree)
23 scf done: -705.4646392 S 0.000000 0.000000 0.000000 O 0.000000 0.000000 1.632804 O 1.372865 0.000000 2.142795 C 1.061157 1.390146 -0.429241 C 1.054479 -1.393613 -0.437150 C 0.467723 -2.699838 0.080800 C 0.420700 2.709889 -0.020802 H 2.007000 1.219826 0.083053 H 1.198791 1.320790 -1.510676 H -0.547928 2.819379 -0.512472 H 0.247740 2.704755 1.056036 H 2.036733 -1.192678 -0.013099 H 1.103495 -1.374989 -1.528368 H -0.538012 -2.839294 -0.320754 H 0.388104 -2.646164 1.166718 C 1.355687 -3.874880 -0.319864 H 0.942369 -4.808516 0.059741 H 1.433731 -3.953551 -1.404446 H 2.359631 -3.757324 0.088486 C 1.330023 3.877669 -0.393965 H 1.504217 3.908339 -1.469761 H 0.875846 4.821920 -0.096115 H 2.294371 3.791752 0.107114	H = -705.310617 G = -705.355168 
2a	**MP2/6-31+G**** (Hartree)
23 scf done: -708.9285944 S 0.000000 0.000000 0.000000 O 0.000000 0.000000 1.632804 O 1.372865 0.000000 2.142795 C 1.061157 1.390146 -0.429241 C 1.054479 -1.393613 -0.437150 C 0.467723 -2.699838 0.080800 C 0.420700 2.709889 -0.020802 H 2.007000 1.219826 0.083053 H 1.198791 1.320790 -1.510676 H -0.547928 2.819379 -0.512472 H 0.247740 2.704755 1.056036 H 2.036733 -1.192678 -0.013099	H = -708.717905 G = -708.766896 

H	1.103495	-1.374989	-1.528368
H	-0.538012	-2.839294	-0.320754
H	0.388104	-2.646164	1.166718
C	1.355687	-3.874880	-0.319864
H	0.942369	-4.808516	0.059741
H	1.433731	-3.953551	-1.404446
H	2.359631	-3.757324	0.088486
C	1.330023	3.877669	-0.393965
H	1.504217	3.908339	-1.469761
H	0.875846	4.821920	-0.096115
H	2.294371	3.791752	0.107114

TS^1_{CEES}

MP2/6-31+G** (Hartree)

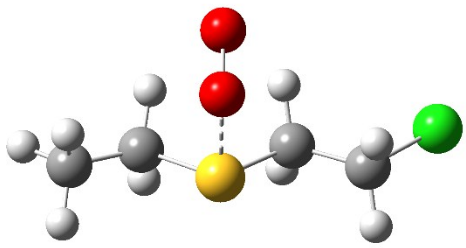
17

scf done: -1164.482060

S	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.789866
C	1.774045	0.000000	-0.283965
O	-0.258618	1.826513	-0.186958
O	0.566664	2.535674	0.633915
C	2.085775	0.116971	-1.766937
C	-1.415598	-0.099510	2.324229
Cl	-1.369695	0.020003	4.105785
H	2.166592	-0.916977	0.155039
H	2.131050	0.866780	0.281900
H	1.688229	-0.726025	-2.329350
H	1.683864	1.041752	-2.176465
H	0.462901	0.967797	2.035413
H	0.627229	-0.821659	2.132371
H	-2.029965	0.720006	1.960869
H	-1.880032	-1.048909	2.073243
H	3.167516	0.132391	-1.890482

H = -1164.337868

G = -1164.386512



CEESOO

MP2/6-31+G** (Hartree)

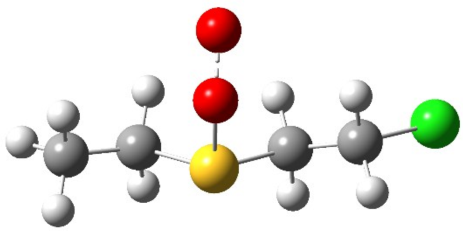
17

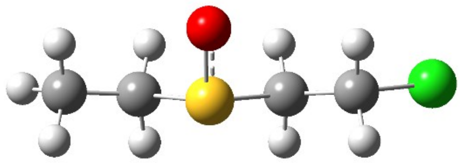
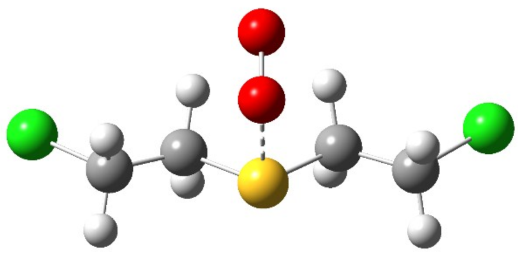
scf done: -1164.4888327

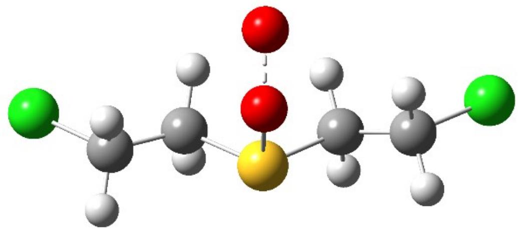
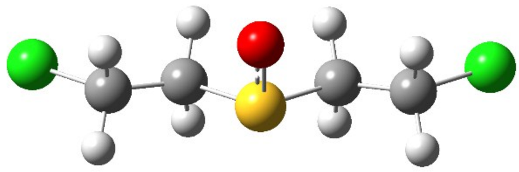
S	0.888064	-0.272016	-0.659449
O	0.999348	1.351888	-0.559551
O	0.774977	1.788057	0.819654
C	-0.682107	-0.630748	0.156663
C	2.042211	-0.870504	0.588597
C	3.474415	-0.583499	0.166704
C	-1.794041	0.138153	-0.531620
Cl	-3.343617	-0.250641	0.265914
H	1.839625	-1.939456	0.671268
H	1.770784	-0.362256	1.511530
H	3.721778	-1.070824	-0.774761
H	3.643386	0.487130	0.071114
H	-0.582742	-0.336324	1.198192
H	-0.818441	-1.709080	0.067109

H = -1164.342699

G = -1164.391685



H -1.632012 1.207033 -0.435266 H -1.888347 -0.136564 -1.578951 H 4.140964 -0.966479 0.937524	
CEESO	**MP2/6-31+G**** (Hartree)
16 scf done: -1089.5818305 S 0.000000 0.000000 0.000000 O 0.000000 0.000000 1.630775 C 1.757404 0.000000 -0.414364 C -0.433364 1.692868 -0.440747 C -1.883155 1.978776 -0.083066 C 2.426993 -1.197316 0.233266 Cl 4.156509 -1.201202 -0.210771 H -0.248817 1.761431 -1.513955 H 0.262301 2.328306 0.103370 H -2.565928 1.313874 -0.609142 H -2.044355 1.882773 0.988724 H 2.177967 0.933885 -0.050597 H 1.801083 -0.049989 -1.502941 H 2.363749 -1.128356 1.314601 H 1.999820 -2.135586 -0.110879 H -2.110621 3.003502 -0.371716	H = -1089.439828 G = -1089.485407 
TS^1_{HD}	**MP2/6-31+G**** **(**Hartree)
17 scf done: -1623.501380 S 0.000000 0.000000 0.000000 C 0.000000 0.000000 1.792322 C 1.778165 0.000000 -0.253799 O -0.221301 1.830609 -0.194652 O 0.635652 2.526376 0.604954 C 2.091289 0.114762 -1.733662 C -1.418767 -0.077036 2.322683 Cl -1.369262 0.036962 4.103784 H 2.182014 -0.912821 0.181894 H 2.125075 0.881481 0.298229 H 1.729914 -0.743979 -2.292796 H 1.679041 1.029718 -2.149896 H 0.479444 0.958472 2.040216 H 0.611517 -0.833669 2.134774 H -2.018930 0.753831 1.961509 H -1.897531 -1.018450 2.068487 Cl 3.863063 0.185112 -1.939820	H = -1623.364778 G = -1623.416916 
HDOO	**MP2/6-31+G**** (Hartree)
17 scf done: -1623.5013185 S 0.000000 0.000000 0.000000	H = -1623.364796 G = -1623.417406

C 0.000000 0.000000 1.792323 C 1.778164 0.000000 -0.253799 O -0.221301 -1.830611 -0.194652 O 0.635666 -2.526379 0.604936 C -1.418767 0.077036 2.322684 Cl -1.369262 -0.036962 4.103785 C 2.091287 -0.114737 -1.733664 Cl 3.863062 -0.185088 -1.939823 H 0.611503 0.833679 2.134775 H 0.479444 -0.958472 2.040217 H -1.897531 1.018450 2.068488 H -2.018930 -0.753831 1.961510 H 2.125053 -0.881495 0.298219 H 2.182016 0.912813 0.181910 H 1.679038 -1.029685 -2.149914 H 1.729915 0.744015 -2.292783	
HDO	MP2/6-31+G** (Hartree)
16 scf done: -1548.6024474 S 0.000000 0.000000 0.000000 C 0.000000 0.000000 1.818220 C 1.808010 0.000000 -0.187222 O -0.478699 -1.395541 -0.430838 C -1.427710 -0.105771 2.316231 Cl -1.443668 -0.130669 4.104558 C 2.155318 -0.116456 -1.658278 Cl 3.932253 -0.134343 -1.860394 H 0.464737 0.931059 2.145582 H 0.594233 -0.853590 2.147648 H -2.024582 0.746006 1.999767 H -1.892606 -1.026858 1.977126 H 2.198552 -0.848668 0.376037 H 2.179326 0.935341 0.233369 H 1.773842 -1.042852 -2.077579 H 1.774077 0.728807 -2.225859	H = -1548.468056 G = -1548.517443 

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