Supporting information for

Miniaturized Ozonolysis Flow Platform for Expeditious Sulfur Mustard Warfare Simulant Neutralization

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1. Computations

1.1. Equations

Computations of the activation barriers corrected by concentration and quasi-harmonic factors (Grimme method for entropy and Head-Gordon method for enthalpy correction),[S1] as well as reaction times, were performed using our open-access SnapPy toolkit (v1.0.0.).[S2] For each species, three Gaussian output files were required to calculate the corrected energy. Electronic energies were computed at the M08HX/6-311+G** level whereas solvation energies and Gibbs free energy corrections were obtained at the B3LYP-D3BJ/6-31+G* level. Activation barriers ($\Delta G^{\ddagger}$) were then calculated by subtracting the corrected energy of the reagents **1** and O_3 from the one of the transition state (TS). The extraction of the kinetic rate constant ($k(T)$) from $\Delta G^{\ddagger}$ was done based on the Eyring equation (1).

$$k = \frac{\kappa k_B T}{h} e^{\left(\frac{-\Delta G^{\ddagger}}{RT}\right)} \quad (1)$$

k = reaction rate constant, κ = transmission coefficient, H = Planck's constant (J s), k_B = Boltzmann constant (J K^{-1}), T = temperature (K), R = gas constant (cal K^{-1} mol^{-1}), $\Delta G^{\ddagger}$ = activation barrier (cal mol^{-1})

The time to reach the target conversion ($t_{conv.}$) at a given concentration (C_0) was calculated from the second-order integrated rate law (equation (2)) where $k(T)$ was extracted from the Eyring equation (1) using the activation barrier computed at the target temperature.

$$\frac{1}{C} = \frac{1}{C_0} + k(T) * t_{conv.} \quad (2)$$

k(T) = reaction rate constant at temperature T (K), C = concentration at the desired conversion, C_0 = initial concentration, $t_{conv.}$ = desired conversion

For more detailed information and instructions, please refer to the README file located in the installation folder of SnapPy.

Sulfur nucleophilicity (N_s) was calculated based on equations from the Conceptual Density Functional Theory (CDFT). The global nucleophilicity index was determined following equation (3) suggested by Domingo, where **TCE** stands for tetracyanoethylene and is characterized by E_{HOMO} = -8.9 eV at the B3LYP-GD3BJ/6-31+G* level (SMD = ethanol).[S3] The Fukui function for the electrophilic attack on the sulfur atom (f_S^-) was used as a local descriptor and calculated based on equation (4) from Yang and Mortier.[S4] N_s (equation (5)) was then calculated by multiplying equations (3) with (4).

$$N = E_{HOMO(Nu)} - E_{HOMO(TCE)} \quad (3)$$

N = global nucleophilicity index, E_{HOMO} = energy of the HOMO orbital

$$f_S^- = q_S(N) - q_S(N-1) \quad (4)$$

f_s^-= Fukui function for the electrophilic attack on the sulfur atom, q_S(N) = charge on the sulfur atom from the neutral form, q_S(N-1) = charge on the sulfur atom from the cationic form

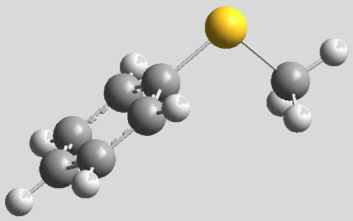
$$N_S = N * f_S^- \quad (5)$$

N_S = local sulfur nucleophilicity, N = global nucleophilicity index, f_s^-= Fukui function for the electrophilic attack on the sulfur atom

1.2. Conceptual Density Functional Theory

Stationary points for thioethers **1a-d**, **CEES**, **CEPS**, and **HD** at the B3LYP-D3BJ/6-31+G* level (SMD = ethanol) are presented in Table S1. Only the most stable form is represented.

Table S*1*: Geometries of the most stable stationary point of thioethers 1a-d, CEES, CEPS and HD



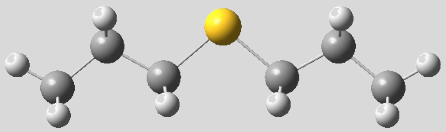
Methyl phenyl sulfide (1a)

H = -669.66262 Hartree
G = -669.70204 Hartree

E_{HOMO} (eV)	E_{LUMO} (eV)	q_S	f^-_S	N_S
-6.3	-0.8	0.2	0.7	1.8

0 1

C	-0.127799	-0.005618	-0.284320
C	0.568117	-1.214925	-0.147393
C	1.940959	-1.206724	0.116221
C	2.625245	0.006428	0.240369
C	1.933510	1.213602	0.099414
C	0.560886	1.209765	-0.164980
H	0.036917	-2.157552	-0.245991
H	2.474252	-2.148062	0.221945
H	3.693032	0.011125	0.443395
H	2.461148	2.159516	0.191811
H	0.024218	2.147711	-0.277825
S	-1.890996	-0.013727	-0.635176
C	-2.554390	0.019203	1.075340
H	-2.234595	0.926298	1.596005
H	-3.646153	0.016081	0.994412
H	-2.232056	-0.865887	1.631163



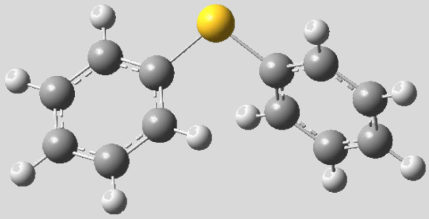
Dipropyl sulfide (1b)

H = -635.11567 Hartree
G = -635.16348 Hartree

E_{HOMO} (eV)	E_{LUMO} (eV)	q_S	f^-_S	N_S
-5.9	0.3	0.1	0.7	2.1

0 1

S	-0.000007	0.810225	0.000087
C	1.403131	-0.377811	-0.000064
H	1.318583	-1.016460	0.887337
H	1.318557	-1.016190	-0.887655
C	2.743484	0.356866	0.000022
H	2.804720	1.008008	0.882153
H	2.804727	1.008199	-0.881967
C	3.922529	-0.620798	-0.000086
H	4.877794	-0.081433	-0.000088
H	3.901608	-1.266772	0.887143
H	3.901546	-1.266663	-0.887393
C	-1.403128	-0.377817	0.000250
H	-1.318740	-1.016003	0.887999
H	-1.318411	-1.016651	-0.887002
C	-2.743477	0.356866	-0.000269
H	-2.804581	1.007713	-0.882626
H	-2.804854	1.008492	0.881494
C	-3.922523	-0.620799	-0.000011
H	-3.901701	-1.266328	0.887544
H	-4.877788	-0.081433	-0.000387
H	-3.901441	-1.267108	-0.886992



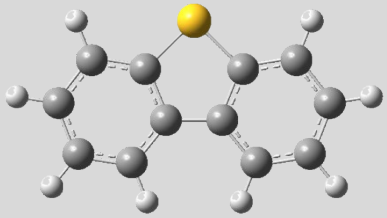
Diphenyl sulfide (1c)

H = -861.37472 Hartree
G = -861.42562 Hartree

E_{HOMO} (eV)	E_{LUMO} (eV)	q_S	f^-_S	N_S
-5.9	-0.8	0.3	0.4	1.0

0 1

C	-1.401648	0.507550	0.060984
C	-1.331355	-0.697076	0.774956
C	-2.446729	-1.534857	0.831932
C	-3.640741	-1.172591	0.198190
C	-3.710761	0.034867	-0.501888
C	-2.593513	0.871793	-0.579793
H	-0.413541	-0.982014	1.280317
H	-2.382993	-2.470278	1.382217
H	-4.506806	-1.827056	0.248649
H	-4.630915	0.324264	-1.003141
H	-2.647816	1.799076	-1.144160
S	-0.027582	1.659995	0.000388
C	1.391805	0.565261	-0.066873
C	1.511591	-0.397428	-1.079926
C	2.413107	0.719616	0.877890
C	2.643562	-1.211357	-1.131966
H	0.721915	-0.513155	-1.816847
C	3.554639	-0.086445	0.806963
H	2.314772	1.457642	1.669054
C	3.669971	-1.055616	-0.192196
H	2.729135	-1.961232	-1.914311
H	4.345080	0.037980	1.542610
H	4.552908	-1.687444	-0.240240



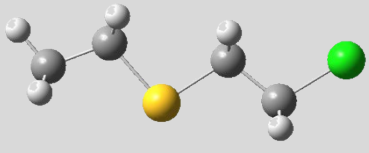
Dibenzothiophene (1d)

H = -860.21702 Hartree
G = -860.26211 Hartree

E_{HOMO} (eV)	E_{LUMO} (eV)	q_S	f^-_S	N_S
-6.1	-1.3	0.4	0.3	0.8

0 1

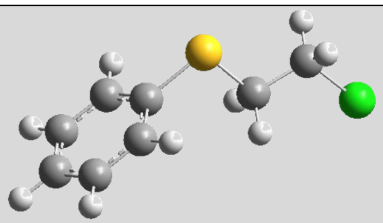
C	1.261615	0.733269	0.000073
C	2.640235	0.963235	0.000066
C	3.496084	-0.138442	0.000001
C	2.983281	-1.447559	-0.000052
C	1.608282	-1.669969	-0.000017
C	0.727517	-0.576740	0.000022
H	3.038912	1.973839	0.000110
H	4.571021	0.021165	-0.000007
H	3.665874	-2.293039	-0.000093
H	1.214901	-2.683070	-0.000058
S	0.000004	1.974782	-0.000035
C	-1.261611	0.733277	-0.000001
C	-0.727522	-0.576737	-0.000029
C	-2.640232	0.963238	-0.000028
C	-1.608287	-1.669965	0.000015
C	-3.496084	-0.138438	0.000002
H	-3.038911	1.973841	0.000002
C	-2.983288	-1.447558	0.000030
H	-1.214910	-2.683066	0.000041
H	-4.571020	0.021176	0.000010
H	-3.665880	-2.293039	0.000070



2-Chloroethyl ethyl sulfide (CEES)

H = -1016.1444 Hartree
G = -1016.1890 Hartree

E_{HOMO} (eV)	E_{LUMO} (eV)	q_S	f^-_S	N_S
-6.2	-0.2	0.1	0.7	1.9



2-Chloroethyl phenyl sulfide (CEPS)

H = -1168.5632 Hartree
G = -1168.6138 Hartree

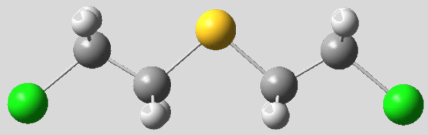
E_{HOMO} (eV)	E_{LUMO} (eV)	q_S	f^-_S	N_S
-6.5	-0.9	0.2	0.7	1.6

0 1

S	-1.111994	-0.678701	0.000074
C	0.440292	0.312243	-0.000838
H	0.457852	0.946676	-0.892463
H	0.457687	0.948202	0.889696
C	1.622961	-0.636339	-0.000006
H	1.653543	-1.262109	-0.893006
H	1.652921	-1.261370	0.893513
C	-2.320268	0.710743	0.000387
H	-2.137780	1.325932	-0.887462
H	-2.138049	1.325222	0.888787
Cl	3.189116	0.314817	0.000193
C	-3.746760	0.171800	-0.000053
H	-3.946316	-0.438458	0.888776
H	-4.454179	1.010103	0.000305
H	-3.946115	-0.437551	-0.889544

0 1

S	-0.242511	1.377605	0.047415
C	-1.408703	-0.060936	-0.003812
H	-1.218597	-0.631858	-0.916603
H	-1.219377	-0.694476	0.866850
C	-2.827447	0.472398	0.013975
H	-3.051414	1.086349	-0.859576
H	-3.051197	1.027947	0.925815
Cl	-4.013557	-0.921008	-0.031136
C	1.312058	0.477187	0.016691
C	1.927996	0.182383	-1.207395
C	1.922942	0.091001	1.217692
C	3.146469	-0.502098	-1.227783
H	1.455902	0.486166	-2.137470
C	3.141296	-0.593451	1.191623
H	1.446993	0.324269	2.165996
C	3.754308	-0.890372	-0.029769
H	3.620555	-0.728304	-2.179430
H	3.611398	-0.890706	2.125538
H	4.702883	-1.420620	-0.047773



Bis(2-chloroethyl)sulfide (HD)

H = -1475.7537 Hartree
G = -1475.8029 Hartree

E_{HOMO} (eV)	E_{LUMO} (eV)	q_S	f^-_S	N_S
-6.4	-0.5	0.2	0.7	1.8

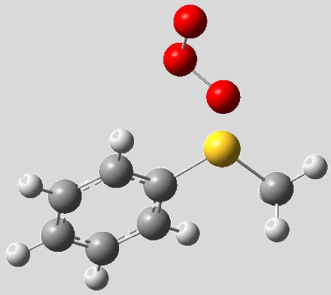
0 1

S	-0.000010	-1.000113	-0.018937
C	-1.386062	0.214701	-0.038276
H	-1.284551	0.879813	0.824278
H	-1.329749	0.805667	-0.957068
C	-2.694877	-0.548874	0.028064
H	-2.792946	-1.123596	0.949937
H	-2.839743	-1.200790	-0.834486
C	1.386246	0.214345	-0.045908
H	1.279604	0.889945	0.807861
H	1.335432	0.794139	-0.972100
C	2.694558	-0.548357	0.038012
H	2.843301	-1.213702	-0.813575
H	2.788144	-1.108695	0.969131
Cl	-4.098774	0.626204	0.013964
Cl	4.098861	0.626039	0.011781

1.3. Oxidation of thioethers with ozone

Stationary points at the B3LYP-D3BJ/6-31+G* level (SMD = ethanol) for starting materials and their corresponding TS during ozonolysis of thioethers **1a-d**, **CEES**, **CEPS**, and **HD** are presented in Table S2. Only the most stable form is represented. Gibbs free (G) and enthalpies (H) energies are uncorrected. Activation barriers are determined at 25 °C.

Table S2: Geometries of the most stable stationary point of thioethers 1a-d, CEES, CEPS, and HD and their corresponding TS during ozonolysis

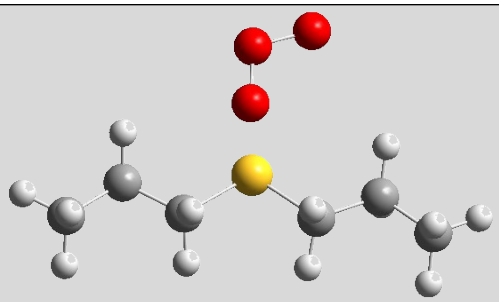


Methyl phenyl sulfide (1a)

$\Delta G^{\ddagger}$(298 K) = 2.3 kcal mol^{-1}

Reagent			
H = -895.09259 Hartree			
G = -895.14684 Hartree			
0 1			
C	1.635539	-0.844380	0.992499
C	0.893038	0.172130	0.363685
C	1.435222	0.884517	-0.716978
C	2.724311	0.579171	-1.156722
C	3.466834	-0.429874	-0.536091
C	2.918035	-1.140908	0.537674
S	-0.735867	0.446422	0.990895
C	-1.255623	2.017558	0.253441
O	-1.745256	-0.791371	-0.784893
O	-2.889583	-1.310213	-0.479097
O	-3.889006	-0.443560	-0.412904
H	3.491021	-1.924537	1.025294
H	1.213351	-1.393108	1.830437
H	0.870863	1.665331	-1.213720
H	3.145670	1.132229	-1.991600
H	4.469033	-0.661072	-0.885954
H	-1.368376	1.917494	-0.828589
H	-2.225555	2.250313	0.700226
H	-0.535508	2.802478	0.499684

TS			
H = -895.09165 Hartree			
G = -895.14241 Hartree			
0 1			
O	1.985648	0.045318	0.805048
S	1.036365	0.640681	-0.737755
O	1.887998	-1.330012	0.945252
O	2.682653	-1.979311	0.023853
C	1.301716	2.368766	-0.283794
C	-0.627817	0.265613	-0.312480
C	-1.369565	0.988324	0.635778
C	-2.668913	0.577488	0.919483
C	-3.214820	-0.543492	0.279968
C	-2.463212	-1.262861	-0.652798
C	-1.162464	-0.863318	-0.955981
H	-2.886076	-2.132520	-1.146561
H	-0.572990	-1.414804	-1.682903
H	-0.951816	1.851251	1.142022
H	-3.257101	1.130518	1.645844
H	-4.229238	-0.854971	0.512293
H	1.177761	2.508791	0.791701
H	2.324448	2.608267	-0.585125
H	0.593230	2.981489	-0.847485



Dipropyl sulfide (1b)

$\Delta G^{\ddagger}$(298 K) = 0.7 kcal mol^{-1}

Reagent
H = -860.54850 Hartree
G = -860.60718 Hartree

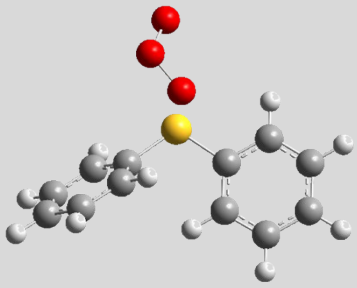
0 1

C	-3.653456	-1.656348	0.420201
C	-2.564159	-0.928062	-0.372545
C	-1.188788	-1.189015	0.237338
S	0.128461	-0.318425	-0.679245
C	1.615662	-0.936793	0.185472
C	2.884534	-0.289390	-0.365585
C	4.123209	-0.820426	0.361462
O	0.099438	1.484978	0.700971
O	-0.174046	2.611286	0.112026
O	-1.471767	2.787358	-0.155914
H	-1.136077	-0.845274	1.277043
H	-0.938049	-2.256151	0.213204
H	1.484438	-0.726000	1.253102
H	1.630365	-2.024257	0.047473
H	-2.766188	0.149519	-0.376723
H	-2.574511	-1.266497	-1.416165
H	2.823606	0.799102	-0.247522
H	2.967621	-0.496999	-1.439872
H	-4.639712	-1.469566	-0.020818
H	-3.484628	-2.740620	0.423322
H	-3.679205	-1.313740	1.462207
H	4.219390	-1.906525	0.238525
H	5.032028	-0.353728	-0.036427
H	4.074536	-0.603240	1.435853

Reagent
H = -860.54850 Hartree
G = -860.60718 Hartree

0 1

C	-3.653456	-1.656348	0.420201
C	-2.564159	-0.928062	-0.372545
C	-1.188788	-1.189015	0.237338
S	0.128461	-0.318425	-0.679245
C	1.615662	-0.936793	0.185472
C	2.884534	-0.289390	-0.365585
C	4.123209	-0.820426	0.361462
O	0.099438	1.484978	0.700971
O	-0.174046	2.611286	0.112026
O	-1.471767	2.787358	-0.155914
H	-1.136077	-0.845274	1.277043
H	-0.938049	-2.256151	0.213204
H	1.484438	-0.726000	1.253102
H	1.630365	-2.024257	0.047473
H	-2.766188	0.149519	-0.376723
H	-2.574511	-1.266497	-1.416165
H	2.823606	0.799102	-0.247522
H	2.967621	-0.496999	-1.439872
H	-4.639712	-1.469566	-0.020818
H	-3.484628	-2.740620	0.423322
H	-3.679205	-1.313740	1.462207
H	4.219390	-1.906525	0.238525
H	5.032028	-0.353728	-0.036427
H	4.074536	-0.603240	1.435853



Diphenyl sulfide (1c)

$\Delta G^{\ddagger}$(298 K) = 7.3 kcal mol^{-1}

Reagent

H = -1086.8032 Hartree

G = -1086.8633 Hartree

0 1

C	-4.154064	-0.551244	0.615875
C	-3.055239	-0.470380	1.479181
C	-1.792678	-0.146900	0.984823
C	-1.635487	0.080339	-0.390933
C	-2.732002	0.009233	-1.261797
C	-3.991923	-0.308126	-0.750898
S	-0.077442	0.571476	-1.092357
C	1.120485	-0.587483	-0.494651
C	0.789151	-1.838803	0.048977
C	1.809835	-2.689811	0.466881
C	3.151609	-2.306428	0.347323
C	3.474848	-1.064959	-0.205280
C	2.465290	-0.199369	-0.628829
O	0.337799	2.145092	0.733800
O	1.605529	2.322596	0.914613
O	2.151938	3.256044	0.155308
H	4.513289	-0.762499	-0.306466
H	2.721686	0.761408	-1.064538
H	-0.245496	-2.151306	0.132657
H	1.554965	-3.660742	0.882685
H	3.939576	-2.976797	0.678865
H	-0.944353	-0.071948	1.655757
H	-2.601678	0.191969	-2.324636
H	-3.181676	-0.651686	2.542922
H	-4.842791	-0.368564	-1.423529
H	-5.135537	-0.799723	1.010186

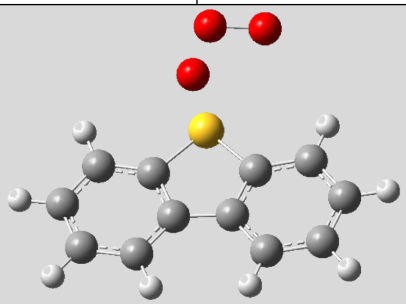
TS

H = -1086.7981 Hartree

G = -1086.8565 Hartree

0 1

O	-0.187494	1.826683	0.850381
S	-0.035936	0.728963	-0.682136
O	0.705545	2.898935	0.799273
O	0.267611	3.865471	-0.079603
C	1.370040	-0.258230	-0.265984
C	-1.479416	-0.233933	-0.296626
C	-1.421341	-1.611042	-0.052792
C	-2.613274	-2.297545	0.179774
C	-3.835751	-1.619436	0.168069
C	-3.877125	-0.244748	-0.088001
C	-2.699422	0.458931	-0.332820
C	2.338219	-0.405841	-1.268597
C	3.487582	-1.145404	-0.986713
C	3.664391	-1.706592	0.280605
C	2.696399	-1.532433	1.278533
C	1.540300	-0.803504	1.015235
H	4.243682	-1.274497	-1.755248
H	2.195468	0.041223	-2.248250
H	0.791192	-0.655916	1.785693
H	2.845129	-1.962020	2.264783
H	4.563637	-2.276195	0.497617
H	-2.729684	1.524971	-0.537491
H	-0.477890	-2.143764	-0.055485
H	-4.826122	0.282896	-0.101929
H	-2.581547	-3.366725	0.367733
H	-4.757807	-2.163422	0.352251



Dibenzothiophene (1d)

$\Delta G^{\ddagger}$(298 K) = 7.8 kcal mol^{-1}

Reagent

H = -1085.6396 Hartree

G = -1085.6989 Hartree

0 1

S	-0.332186	-0.844747	1.186440

TS

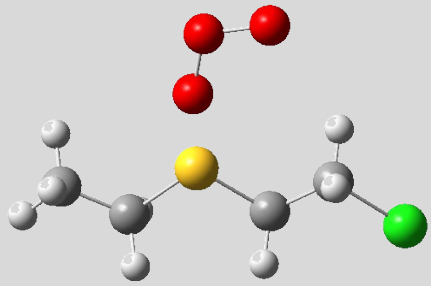
H = -1085.6306 Hartree

G = -1085.6847 Hartree

0 1

O	-0.699989	-2.000176	0.872214

C	-0.921721	0.708751	0.593972	S	-0.414834	-1.051063	-0.688936
C	0.085024	1.439646	-0.078212	O	-1.655870	-3.007653	0.584347
C	1.357938	0.726232	-0.106645	O	-2.841078	-2.412165	0.231294
C	1.283175	-0.524404	0.547571	C	1.256791	-0.569987	-0.328657
C	-0.232573	2.696654	-0.604310	C	-1.011539	0.578122	-0.340953
C	-1.529150	3.194441	-0.459916	C	0.032283	1.448259	0.041193
C	-2.516302	2.450817	0.205705	C	1.339836	0.785506	0.047997
C	-2.221969	1.195255	0.740234	C	2.594380	1.313583	0.351257
C	2.576506	1.118664	-0.671981	C	3.720469	0.485260	0.276880
C	3.681948	0.270687	-0.578820	C	3.610358	-0.858507	-0.102138
C	3.586687	-0.967529	0.075239	C	2.362887	-1.407757	-0.417167
C	2.381241	-1.379682	0.647036	C	-0.282661	2.775021	0.327633
O	-0.921204	-2.109097	-0.968895	C	-1.615011	3.196431	0.236146
O	-1.813281	-3.014521	-0.803816	C	-2.633377	2.312682	-0.142126
O	-3.035324	-2.585346	-0.664777	C	-2.340784	0.977224	-0.437037
H	-1.776831	4.169660	-0.869612	H	4.697780	0.895380	0.514254
H	-3.520872	2.851635	0.306036	H	4.496989	-1.482810	-0.155424
H	-2.984810	0.614658	1.250416	H	2.265982	-2.447868	-0.712362
H	0.526175	3.278224	-1.120396	H	2.694155	2.355557	0.640118
H	2.302620	-2.338166	1.151418	H	-3.120712	0.278160	-0.718869
H	4.456520	-1.615153	0.138068	H	-3.659793	2.660790	-0.204290
H	4.627984	0.574183	-1.018273	H	-1.860886	4.229810	0.462923
H	2.657836	2.075420	-1.180031	H	0.497531	3.472920	0.615617



2-Chloroethyl ethyl sulfide (CEES)

$\Delta G^{\ddagger}$(298 K) = 1.6 kcal mol^{-1}

Reagent

H = -1241.5741 Hartree

G = -1241.6297 Hartree

0 1

C	1.856562	-0.225412	0.565574
Cl	3.442883	-0.581639	-0.263667
C	0.735762	-0.919966	-0.185462
S	-0.859434	-0.575093	0.640751
C	-1.990390	-1.483001	-0.478776
C	-3.430639	-1.361460	0.001796
O	-1.274783	1.339923	-0.661303
O	-1.125386	2.458704	-0.034434
O	0.134449	2.818133	0.159841
H	0.661557	-0.559462	-1.216162

TS

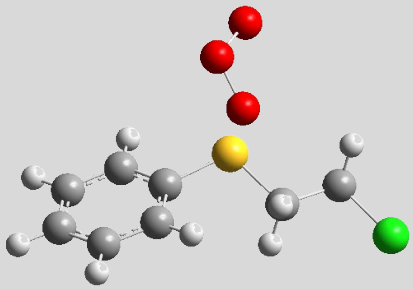
H = -1241.5737 Hartree

G = -1241.6267 Hartree

0 1

O	-1.241489	1.062277	-0.737785
S	-0.832977	-0.400254	0.543867
O	-1.312787	2.268379	-0.133691
O	-0.073055	2.727232	0.217574
C	0.791051	-0.877240	-0.140460
C	-1.921674	-1.585356	-0.328663
C	-3.376435	-1.367562	0.061594
C	1.882859	-0.025140	0.482937
Cl	3.487186	-0.534887	-0.211966
H	0.735010	-0.747315	-1.225936

H	0.876541	-2.005565	-0.191750	H	0.923382	-1.939096	0.093658
H	-1.858784	-1.063736	-1.482210	H	-1.747830	-1.444725	-1.400525
H	-1.655783	-2.525475	-0.491509	H	-1.563404	-2.579490	-0.040614
H	1.740688	0.858482	0.559880	H	1.754617	1.031361	0.249767
H	1.957521	-0.589132	1.588900	H	1.952593	-0.168838	1.561894
H	-4.078543	-1.912673	-0.689459	H	-3.986658	-2.099073	-0.480005
H	-3.559624	-1.789836	1.001885	H	-3.534924	-1.520486	1.134367
H	-3.763636	-0.318300	0.019120	H	-3.723482	-0.366510	-0.212284



2-Chloroethyl phenyl sulfide (CEPS)

$\Delta G^{\ddagger}$(298 K) = 4.4 kcal mol^{-1}

Reagent

H = -1393.9929 Hartree

G = -1394.0537 Hartree

0 1

O	0.201836	1.850572	-0.811905
S	0.321790	0.224560	1.026845
O	-1.024431	2.232417	-0.939961
O	-1.365579	3.268780	-0.199076
C	-1.144794	-0.556872	0.439974
C	1.681543	-0.612632	0.127829
C	2.980695	0.071042	0.524755
Cl	4.360277	-0.735496	-0.350249
C	-1.161338	-1.575257	-0.527274
C	-2.383983	-2.104833	-0.937175
C	-3.584957	-1.623162	-0.403585
C	-3.563451	-0.603094	0.552178
C	-2.349726	-0.065878	0.977121
H	-4.491190	-0.220276	0.967630
H	-2.337306	0.728390	1.718658
H	-0.242732	-1.959532	-0.954619
H	-2.396473	-2.896969	-1.680728
H	-4.532049	-2.040605	-0.733453
H	1.502463	-0.519427	-0.945403
H	1.688597	-1.667489	0.414814
H	3.003003	1.121271	0.232161
H	3.193810	-0.024912	1.590269

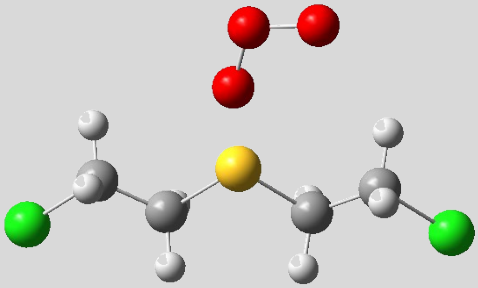
TS

H = -1393.9888 Hartree

G = -1394.0460 Hartree

0 1

O	-0.470543	1.518526	0.935398
S	-0.162736	0.432345	-0.595806
O	0.148459	2.755215	0.829164
O	-0.526762	3.575351	-0.045575
C	1.391420	-0.314535	-0.245756
C	-1.412063	-0.779823	-0.032046
C	-2.779019	-0.326945	-0.524012
Cl	-4.015235	-1.533004	0.042658
C	1.586537	-1.214198	0.814490
C	2.862176	-1.729443	1.024064
C	3.927159	-1.344063	0.198712
C	3.723067	-0.438050	-0.845389
C	2.451398	0.085176	-1.076692
H	4.549671	-0.138759	-1.482641
H	2.284253	0.785135	-1.890294
H	0.768538	-1.505102	1.464039
H	3.027872	-2.430307	1.836848
H	4.918709	-1.751664	0.373913
H	-1.368959	-0.830254	1.059147
H	-1.121684	-1.741712	-0.463382
H	-3.069867	0.638386	-0.109519
H	-2.839056	-0.303618	-1.612524



Bis(2-chloroethyl)sulfide (HD)

$\Delta G^{\ddagger}$(298 K) = 3.2 kcal mol^{-1}

Reagent

H = -1701.1806 Hartree

G = -1701.2401 Hartree

0 1

C	2.543695	-0.605512	0.530129
Cl	3.867225	-1.409047	-0.433984
C	1.201766	-0.945486	-0.092677
S	-0.132927	-0.142256	0.871516
C	-1.570817	-0.754375	-0.086996
C	-2.841717	-0.179737	0.513428
Cl	-4.276703	-0.789985	-0.431775
O	-0.207242	1.790228	-0.586374
O	0.348320	2.838969	-0.093747
O	1.662069	2.817267	-0.081764
H	1.135241	-0.580288	-1.121866
H	1.019944	-2.024491	-0.077113
H	-1.442726	-0.440410	-1.127537
H	-1.565199	-1.847167	-0.036255
H	2.748944	0.464816	0.503697
H	2.635796	-0.982322	1.549385
H	-2.872734	0.908219	0.450201
H	-2.994049	-0.499781	1.544901

TS

H = -1701.1782 Hartree

G = -1701.2344 Hartree

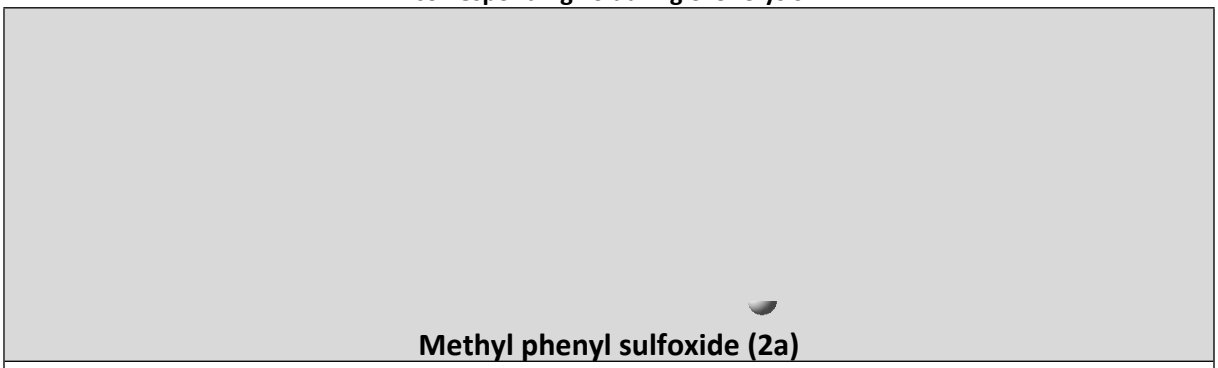
0 1

O	-0.183343	1.488077	-0.702514
S	-0.098736	0.126671	0.674213
O	0.195866	2.708399	-0.219295
O	1.542056	2.732830	0.030632
C	1.231028	-0.903956	-0.041544
C	-1.553614	-0.756282	-0.001702
C	-2.825040	-0.028567	0.403725
Cl	-4.244380	-0.932583	-0.285626
C	2.583565	-0.417018	0.448976
Cl	3.872278	-1.453015	-0.311416
H	1.134306	-0.831770	-1.129142
H	1.027549	-1.931181	0.278310
H	-1.430791	-0.802792	-1.087662
H	-1.515578	-1.767519	0.415082
H	2.777798	0.611445	0.147006
H	2.692955	-0.523428	1.528853
H	-2.870700	0.981495	-0.002613
H	-2.962292	-0.007336	1.485173

1.4. Oxidation of sulfoxides with ozone

Stationary points at the B3LYP-D3BJ/6-31+G* level (SMD = ethanol) for starting materials and their corresponding TS during ozonolysis of sulfoxides **2a-d**, **CEESO**, **CEPSO** and **HDO** are presented in Table S3. Only the most stable form is represented. Gibbs free (G) and enthalpies (H) energies are uncorrected. Activation barriers are determined at 25 °C.

Table S*3*: Geometries of the most stable stationary point of sulfoxides 2a-d, CEESO, CEPSO and HDO and their corresponding TS during ozonolysis



Methyl phenyl sulfoxide (2a)

$\Delta G^{\ddagger}$(298 K) = 5.8 kcal mol^{-1}

Reagent

H = -970.27068 Hartree

G = -970.32733 Hartree

0 1

O	-0.154550	2.640318	-0.406550
S	-0.546269	1.183029	-0.166751
O	-2.552954	-0.377006	-1.127080
C	0.968762	0.200354	-0.088582
C	-1.083817	1.050235	1.565897
C	2.203105	0.846545	-0.151230
C	3.365788	0.073334	-0.097811
C	3.281628	-1.318531	0.007598
C	2.032930	-1.948361	0.055524
C	0.862006	-1.190558	-0.002962
H	1.967810	-3.030272	0.129160
H	-0.108968	-1.677498	0.018165
H	2.251988	1.927799	-0.232832
H	4.335823	0.561077	-0.137489
H	4.189313	-1.914536	0.045304
H	-0.321990	1.518511	2.195827
H	-2.040168	1.573021	1.655355
H	-1.203281	-0.007895	1.813785
O	-3.254909	-0.861614	-0.177365
O	-2.801664	-1.921296	0.392263

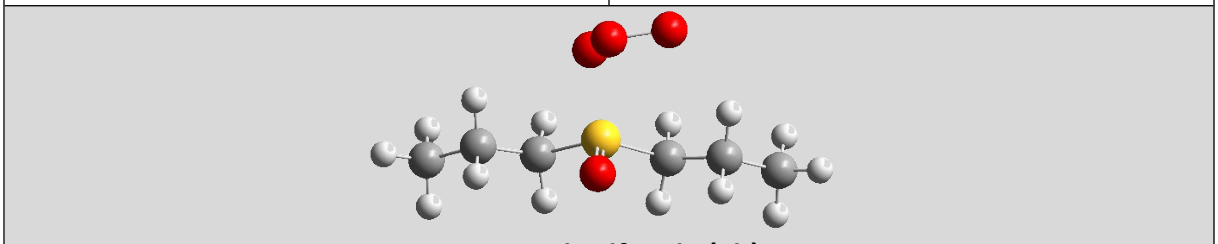
TS

H = -970.26555 Hartree

G = -970.31750 Hartree

0 1

O	2.039295	0.177976	-1.109294
S	0.779806	-0.943207	-0.001306
O	2.815894	0.987104	-0.342559
O	2.197278	2.156795	-0.022651
O	0.752265	-2.380923	-0.387874
C	1.455785	-0.708470	1.646847
C	-0.848679	-0.231447	-0.006824
C	-0.975707	1.146724	0.192256
C	-2.260542	1.687128	0.199069
C	-3.372137	0.864097	-0.016513
C	-3.212599	-0.508307	-0.237022
C	-1.938806	-1.075946	-0.240299
H	-2.390830	2.753695	0.355672
H	-0.096865	1.775102	0.318742
H	-1.796278	-2.138947	-0.403464
H	-4.079007	-1.140892	-0.405463
H	-4.368364	1.297045	-0.022270
H	0.888687	-1.373280	2.305569
H	2.511521	-0.989460	1.613350
H	1.332509	0.337771	1.932690



Dipropyl sulfoxide (2b)

$\Delta G^{\ddagger}$(298 K) = 3.8 kcal mol^{-1}

Reagent

H = -935.73218 Hartree

G = -935.79507 Hartree

TS

H = -935.72887 Hartree

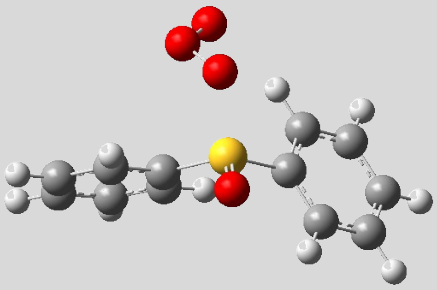
G = -935.78854 Hartree

0 1

O	-0.001331	-0.920663	1.840767
S	-0.000716	-0.253914	0.456850
C	-1.396405	-0.957307	-0.498529
C	1.393999	-0.959604	-0.498233
C	2.736426	-0.653184	0.157208
C	3.888410	-1.231917	-0.670198
C	-2.738344	-0.650751	0.157863
C	-3.891072	-1.227047	-0.670215
H	-1.212464	-2.035788	-0.566202
H	-1.318373	-0.515076	-1.498138
H	1.209094	-2.038019	-0.564341
H	1.315928	-0.518693	-1.498427
H	-2.756894	-1.078135	1.167111
H	-2.862176	0.434337	0.260349
H	2.754929	-1.078810	1.167206
H	2.861071	0.431990	0.257692
H	-4.853255	-1.009872	-0.191457
H	-3.909191	-0.794560	-1.678409
H	-3.801324	-2.315975	-0.769773
H	3.906482	-0.801379	-1.679228
H	4.850932	-1.014547	-0.192212
H	3.797800	-2.320966	-0.767628
O	1.083259	2.325793	-0.281297
O	0.003529	2.865954	0.146322
O	-1.076605	2.328539	-0.283731

0 1

O	0.206969	1.619179	-0.786607
S	0.139994	-0.167360	0.206794
O	-0.380991	2.551883	-0.021297
O	-1.734189	2.569707	-0.178940
O	0.099974	0.093807	1.674786
C	-1.188666	-1.294092	-0.347768
C	1.692668	-0.942058	-0.335038
C	2.914885	-0.171958	0.160344
C	4.194256	-0.873803	-0.305160
C	-2.546599	-0.896476	0.215799
C	-3.629080	-1.837002	-0.324549
H	-0.866310	-2.288866	-0.015772
H	-1.146765	-1.243801	-1.441804
H	1.656211	-1.966515	0.054719
H	1.622538	-0.971541	-1.428849
H	-2.517172	-0.946631	1.309369
H	-2.772249	0.138723	-0.063184
H	2.895180	-0.118972	1.254169
H	2.888206	0.853245	-0.223494
H	-4.605980	-1.556219	0.085120
H	-3.690961	-1.782899	-1.418115
H	-3.429742	-2.878222	-0.043660
H	4.244491	-0.922187	-1.399639
H	5.073730	-0.325690	0.051298
H	4.250033	-1.896941	0.085832



Diphenyl sulfoxide (2c)

$\Delta G^{\ddagger}$(298 K) = 6.5 kcal mol^{-1}

Reagent

H = -1161.9781 Hartree

G = -1162.0439 Hartree

0 1

C	1.923686	-1.663172	0.382240
C	1.489011	-0.335042	0.365445
C	2.167966	0.661632	-0.334598
C	3.308760	0.308825	-1.062865
C	3.756125	-1.014321	-1.064768
C	3.067170	-1.997342	-0.342040

TS

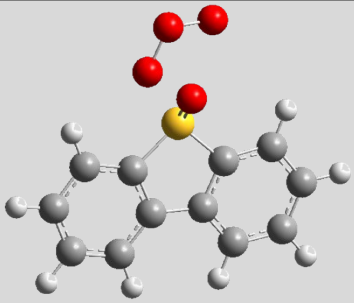
H = -1161.9719 Hartree

G = -1162.0327 Hartree

0 1

O	-0.412472	2.382221	0.335063
S	0.025521	0.535498	0.976762
O	-1.215563	2.381081	-0.760123
O	-0.506971	2.282339	-1.923257
O	0.026806	0.564071	2.465806
C	-1.293497	-0.440985	0.309878

S	0.010209	0.127277	1.294499	C	1.568751	-0.044705	0.321039
C	-1.270734	-0.543465	0.203285	C	1.916253	0.299474	-0.987967
C	-1.327593	-0.121867	-1.128698	C	3.124725	-0.184123	-1.488642
C	-2.353686	-0.606268	-1.941038	C	3.957526	-0.967182	-0.682456
C	-3.307608	-1.487886	-1.420644	C	3.592993	-1.278465	0.632823
C	-3.239163	-1.888979	-0.083261	C	2.387268	-0.814631	1.155799
C	-2.219578	-1.410126	0.744353	C	-2.574934	-0.161117	0.804284
O	-0.026442	-0.682975	2.587299	C	-3.649921	-0.889355	0.300098
O	-0.599076	2.793571	1.077502	C	-3.439085	-1.862443	-0.682757
O	-1.011817	3.069026	-0.096907	C	-2.152455	-2.117383	-1.168718
O	-0.114225	3.370559	-0.965500	C	-1.060480	-1.401866	-0.680774
H	3.848333	1.071548	-1.617077	H	3.419380	0.063342	-2.503992
H	1.818704	1.690077	-0.318905	H	1.259562	0.927896	-1.586063
H	1.378493	-2.416535	0.943254	H	2.087697	-1.050323	2.171552
H	3.418726	-3.025312	-0.346704	H	4.245805	-1.884642	1.253771
H	4.646704	-1.283000	-1.626294	H	4.901695	-1.330669	-1.077935
H	-2.155368	-1.713748	1.784184	H	-2.729185	0.598878	1.563869
H	-0.584114	0.556839	-1.536496	H	-0.062927	-1.599620	-1.055377
H	-3.977974	-2.575588	0.320674	H	-4.650887	-0.692047	0.671391
H	-2.405962	-0.293483	-2.980047	H	-1.994077	-2.877429	-1.927725
H	-4.104532	-1.860599	-2.058204	H	-4.282667	-2.424356	-1.073241



Dibenzothiophene 5-oxide (2d)

$\Delta G^{\ddagger}$(298 K) = 7.3 kcal mol^{-1}

Reagent

H = -1160.8060 Hartree

G = -1160.8671 Hartree

0 1

O	0.218390	-1.160092	2.487289
S	0.216664	-1.002594	0.959501
C	1.050353	0.523788	0.476515
C	-1.359150	-0.310892	0.406925
C	-1.211095	0.960353	-0.172124
C	0.177347	1.441508	-0.131636
C	0.694492	2.653502	-0.594261
C	2.056806	2.922675	-0.424295
C	2.906163	1.996053	0.193082
C	2.405896	0.768180	0.643745
C	-2.341998	1.598485	-0.686344
C	-3.584218	0.960963	-0.597548

TS

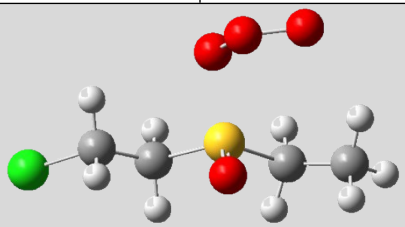
H = -1160.7982 Hartree

G = -1160.8548 Hartree

0 1

O	1.168620	-1.924350	-0.996407
S	0.557933	-0.804036	0.468714
O	2.359568	-2.486068	-0.620433
O	3.399949	-1.629851	-0.827339
O	1.098032	-1.420345	1.704833
C	0.762214	0.944058	0.266154
C	-1.189267	-0.753517	0.222016
C	-2.052642	-1.840875	0.266833
C	-3.400829	-1.587317	-0.006040
C	-3.828257	-0.292945	-0.326792
C	-2.932567	0.783262	-0.378417
C	-1.586836	0.559707	-0.097977

C	-3.708197	-0.303614	-0.008986	C	-0.475478	1.526301	-0.072282
C	-2.580300	-0.963183	0.495926	C	-0.505319	2.898676	-0.309554
H	2.461254	3.866761	-0.778420	C	0.680783	3.636330	-0.199752
H	3.960610	2.224423	0.317774	C	1.894953	3.024851	0.137529
H	3.059349	0.037193	1.110802	C	1.955170	1.646147	0.363749
H	0.045284	3.378882	-1.076203	H	0.656516	4.706228	-0.384398
H	-2.664340	-1.949371	0.943884	H	2.800278	3.618642	0.214122
H	-4.681642	-0.781242	0.052567	H	2.889957	1.148049	0.600990
H	-4.466581	1.456641	-0.992584	H	-1.438681	3.388705	-0.568981
H	-2.256919	2.579064	-1.145631	H	-1.701147	-2.839634	0.505962
O	0.368797	-2.098117	-1.668743	H	-4.115419	-2.403722	0.026915
O	1.336679	-2.888383	-1.427766	H	-4.878021	-0.117098	-0.542532
O	2.331105	-2.385630	-0.814556	H	-3.281309	1.780250	-0.629530



2-Chloroethyl ethyl sulfoxide (CEESO)

$\Delta G^{\ddagger}$(298 K) = 6.3 kcal mol^{-1}

Reagent

H = -1316.7574 Hartree

G = -1316.8162 Hartree

0 1

O	0.543829	-1.395811	1.643220
S	0.644121	-0.529936	0.380188
C	-0.992153	-0.595771	-0.458787
C	1.602198	-1.480491	-0.862903
C	3.044177	-1.657744	-0.410954
C	-2.057662	-0.016203	0.450374
Cl	-3.675025	-0.101953	-0.391251
H	-1.187595	-1.646896	-0.692636
H	-0.884426	-0.019614	-1.382659
H	1.084814	-2.438575	-0.982103
H	1.527029	-0.907528	-1.792853
H	-2.163794	-0.585632	1.373441
H	-1.886781	1.036221	0.676830
H	3.586389	-2.220533	-1.179314
H	3.548035	-0.694031	-0.277754
H	3.103190	-2.221417	0.525792
O	0.275761	2.439749	0.264793
O	1.548837	2.520750	0.211724
O	2.114481	1.736741	-0.620598

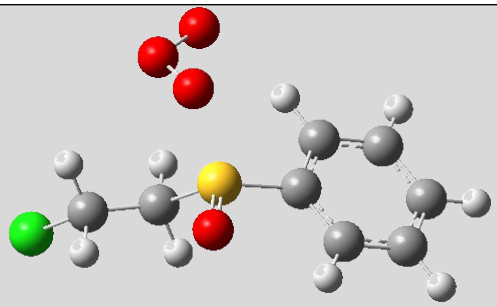
TS

H = -1316.7505 Hartree

G = -1316.8055 Hartree

0 1

O	0.797109	1.417908	-0.647288
S	0.465294	-0.375845	0.164212
O	1.740749	2.051109	0.087618
O	2.995965	1.630804	-0.241080
O	0.640245	-0.322351	1.640145
C	1.381277	-1.754351	-0.625267
C	-1.268591	-0.630493	-0.334289
C	-2.166129	0.412253	0.313493
Cl	-3.882256	0.059796	-0.168087
C	2.796180	-1.851195	-0.087485
H	-1.518185	-1.649219	-0.018395
H	-1.269294	-0.569206	-1.427605
H	0.775417	-2.642217	-0.408716
H	1.334803	-1.527367	-1.695537
H	-2.129240	0.365086	1.401417
H	-1.942621	1.421445	-0.029488
H	3.296519	-2.660452	-0.630546
H	3.353113	-0.923818	-0.253565
H	2.804159	-2.094310	0.978641



2-Chloroethyl phenyl sulfoxide (CEPSO)

$\Delta G^{\ddagger}$(298 K) = 8.1 kcal mol^{-1}

Reagent

H = -1469.1704 Hartree

G = -1469.2341 Hartree

0 1

C	2.377705	-1.441776	0.216058
C	1.573716	-0.302168	0.269307
C	1.958974	0.906731	-0.313803
C	3.174246	0.961488	-1.000372
C	3.989681	-0.172272	-1.074619
C	3.593967	-1.368699	-0.465989
S	-0.008910	-0.372657	1.139796
C	-1.070719	-0.765540	-0.319578
C	-2.508566	-0.937785	0.129311
Cl	-3.544963	-1.319783	-1.322986
O	-0.012215	-1.617410	2.028790
O	-1.105443	2.234797	1.299713
O	-1.544736	2.624457	0.170303
O	-0.713427	3.206248	-0.606935
H	3.486897	1.892912	-1.463913
H	1.329574	1.789367	-0.237097
H	2.057430	-2.362816	0.693614
H	4.230722	-2.247260	-0.522757
H	4.938704	-0.121795	-1.601296
H	-0.663207	-1.679827	-0.761669
H	-0.953283	0.068093	-1.018267
H	-2.626239	-1.774520	0.817836
H	-2.921113	-0.029950	0.570718

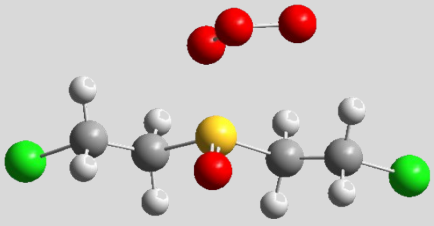
TS

H = -1469.1618 Hartree

G = -1469.2204 Hartree

0 1

O	-0.571421	1.711733	1.363501
S	-0.060294	-0.157016	0.914805
O	-1.269822	2.333870	0.364031
O	-0.456455	2.909291	-0.562903
O	-0.184453	-1.069494	2.082334
C	-1.252546	-0.576248	-0.406661
C	1.550194	-0.255525	0.168145
C	2.392713	-1.300070	0.564874
C	3.640495	-1.393087	-0.049759
C	4.019308	-0.460406	-1.022131
C	3.158624	0.580418	-1.388183
C	1.908742	0.703091	-0.782635
C	-2.655158	-0.716741	0.163607
Cl	-3.767697	-1.148652	-1.206136
H	3.464965	1.308633	-2.132979
H	1.237989	1.525952	-1.023113
H	2.078917	-2.019046	1.314088
H	4.314140	-2.197281	0.230546
H	4.995978	-0.540059	-1.490835
H	-0.873008	-1.515318	-0.822483
H	-1.168301	0.219484	-1.151058
H	-2.721274	-1.525561	0.890511
H	-3.030876	0.210761	0.593524



Bis(2-chloroethyl)sulfoxide (HDO)

$\Delta G^{\ddagger}$(298 K) = 9.2 kcal mol^{-1}

Reagent

H = -1776.3636 Hartree

TS

H = -1776.3532 Hartree

G = -1776.4282 Hartree				G = -1776.4119 Hartree			
0 1				0 1			
C	2.703374	-0.417659	0.331780	O	0.274579	1.756899	-0.750586
Cl	4.057457	-1.178347	-0.624569	S	0.117375	0.108440	0.317736
C	1.378614	-0.786716	-0.306990	O	-0.417394	2.749400	-0.131595
S	0.002814	-0.032399	0.656265	O	-1.758121	2.628603	-0.354562
C	-1.369889	-0.792679	-0.306764	O	0.095167	0.374625	1.778152
C	-2.696025	-0.429379	0.332440	C	-1.249683	-0.979929	-0.235166
Cl	-4.047424	-1.192990	-0.625349	C	1.615042	-0.764938	-0.242392
O	0.004413	-0.686140	2.043171	C	2.860737	-0.009932	0.197624
O	1.062354	2.549626	-0.376833	Cl	4.308857	-0.989371	-0.291456
O	-0.014605	3.119796	-0.008733	C	-2.568046	-0.504352	0.347121
O	-1.095245	2.547227	-0.362294	Cl	-3.881390	-1.583250	-0.292752
H	-1.200275	-1.873524	-0.305092	H	-0.971212	-1.982173	0.108754
H	-1.285236	-0.399092	-1.324009	H	-1.221191	-0.930827	-1.328261
H	1.213683	-1.868257	-0.305071	H	1.553377	-1.763412	0.203153
H	1.292016	-0.393772	-1.324308	H	1.521471	-0.835540	-1.331456
H	-2.783138	-0.817575	1.347166	H	-2.589148	-0.590326	1.432909
H	-2.882998	0.644745	0.324826	H	-2.800247	0.516041	0.040070
H	2.791708	-0.803925	1.347147	H	2.908946	0.105618	1.280139
H	2.886888	0.657044	0.322423	H	2.950906	0.958812	-0.291927

2. Continuous flow setup

2.1. Microfluidic setup and parts

All microfluidic setups were assembled with commercially available parts.

2.1.1. Pumps

HPLC pumps Knauer – Azura P4.1S and metal-free HiTec Zang SyrDos™ 2 XLP equipped with two 1-mL glass syringes were used to handle liquid feeds.

2.1.2. Connectors, ferrules, unions

PFA coils were assembled both with coned PEEK fittings or Super Flangeless PEEK nuts, ETFE ferrules and SS rings from IDEX/Upchurch and 1/16in, 1/8in and 1/4in PFA and SS nuts and unions from Swagelok® (details in Table S4).

2.1.3. Back-pressure regulator

Dome-type BPRs were purchased from Zaiput Flow Technologies (BPR-10). The dome-type BPR was connected to a compressed gas cylinder (pressurized air) to set the working pressure.

2.1.4. Liquid-gas separator

Liquid-gas separation was per connected vertically to the outlet of the BPR (down) and g (up) as the bubbling part (see **Figure S1**).

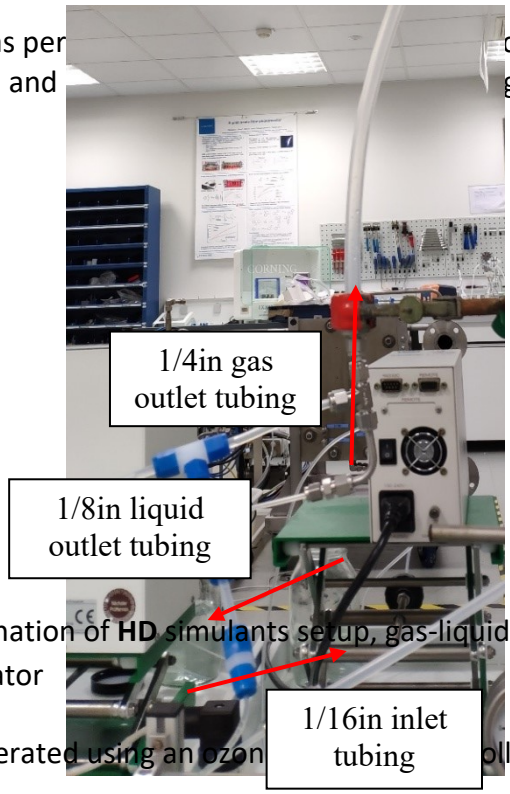


Figure S1: Ozonation of **HD** simulants setup, gas-liquid separation section.

2.1.5. Ozone generator

The ozone feed was generated using an ozon ollows:

Figure S2: Picture of the exterior of the ozone dosing line from Corning®

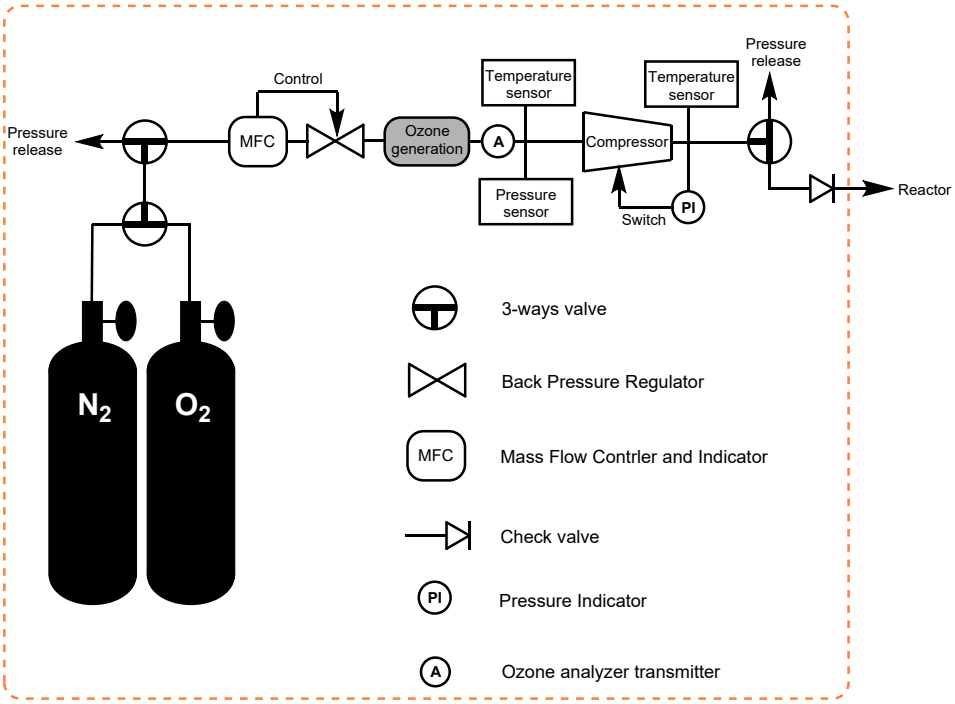


Figure S3: Detailed scheme of the interior of the ozone dosing line used at the Corning® site.

2.2. Table of parts and vendors

Table S4: Parts list for fluidic elements and connectors.

Items	Details	Vendor	Reference
Connectors	SuperFlangeless™ Male Nut 1/16in PEEK	INACOM Instruments/IDEX	P-255
	SuperFlangeless™ Ferrule Assembly 1/16in	INACOM	P-259

		Instruments/IDEX	
	FingerTight I PEEK	INACOM Instruments/IDEX	F-120
Mixers	Stainless Steel Swagelok Tube Fitting, Male Run Tee, 1/8 in. Tube OD x 1/8 in. Male NPT x 1/8 in. Tube OD	Swagelok	SS-200-3TMT
	Stainless Steel Swagelok Tube Fitting, Male Run Tee, 1/4 in. Tube OD x 1/4 in. Male NPT x 1/4 in. Tube OD	Swagelok	SS-400-3-4TMT
	PFA Swagelok Tube Fitting, Union Tee, 1/8 in. Tube Fitting	Swagelok	PFA-220-3
	PFA Swagelok Tube Fitting, Union Tee, 1/4 in. Tube Fitting	Swagelok	PFA-420-3
Unions	Union body 1/4-28 - 1/16in PEEK	INACOM Instruments/IDEX	P702-01
	Stainless Steel Swagelok Tube Fitting, Male Connector, 1/8 in. Tube OD x 1/16 in. Male NPT	Swagelok	SS-200-1-1
	Stainless Steel Swagelok Tube Fitting, Male Connector, 1/8 in. Tube OD x 1/4 in. Male NPT	Swagelok	SS-200-1-4
	Stainless Steel Swagelok Tube Fitting, Male Connector, 1/4 in. Tube OD x 1/2 in. Male NPT	Swagelok	SS-400-1-8
	Stainless Steel Swagelok Tube Fitting, Male Connector, 1/8 in. Tube OD x 1/8 in. Male NPT	Swagelok	SS-200-1-2
	Stainless Steel Swagelok Tube Fitting, Male Connector, 1/4 in. Tube OD x 1/4 in. Male NPT	Swagelok	SS-400-1-4
	Stainless Steel Swagelok Tube Fitting, Male Connector, 1/16 in. Tube OD x 1/16 in. Male NPT	Swagelok	SS-100-1-1
	PFA Swagelok Tube Fitting, Male Connector, 1/4 in. Tube Fitting x 1/4 in. Male NPT	Swagelok	PFA-420-1-4
	PFA Swagelok Tube Fitting, Male Connector, 1/8 in. Tube Fitting x 1/8 in. Male NPT	Swagelok	PFA-220-1-2
Back pressure regulator	Dome-type back pressure regulator	Zaiput Flow Techn.	BPR-10
Tubing	Tubing PFA High Purity 1/16” OD, 0.020” ID (50 ft)	INACOM Instruments/IDEX	1622L
	Tubing PFA High Purity 1/8” OD, 0.062” ID (50 ft)	INACOM Instruments/IDEX	1641L
	Tubing PFA High Purity 1/4” OD, 0.188” ID (100 ft)	INACOM Instruments/IDEX	1645XL

2.3. Continuous flow setup at the microfluidic scale

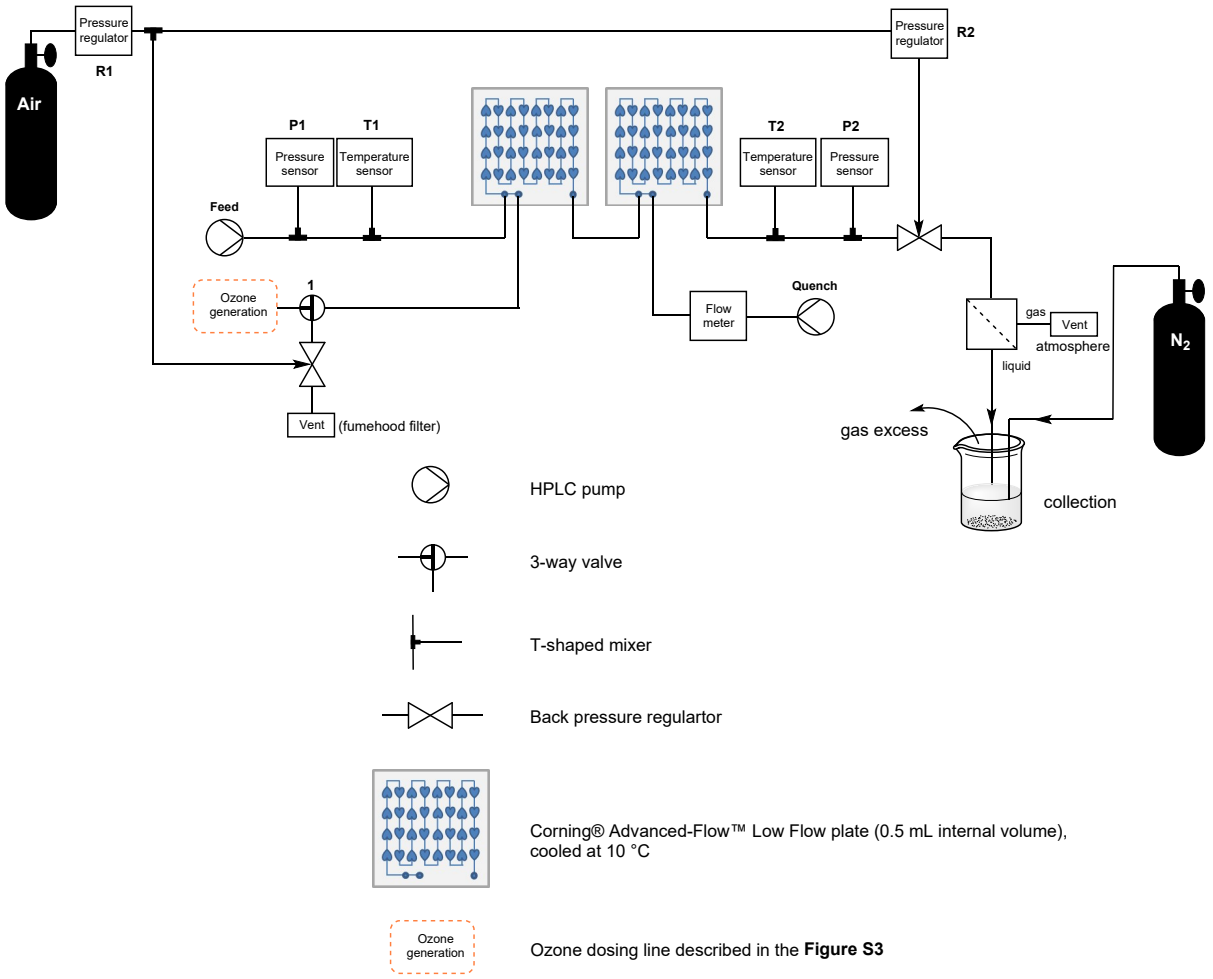


Figure S4: Detailed scheme of the microfluidic setup for the oxidation of sulfides and mustard gas simulants using one Corning® Advanced-Flow™ reactor LF plate for the reaction and another to quench the remaining ozone. Both BPRs were Zaiput BPR-10 back pressure regulators. The 3-way valve 1 controls the input of ozone in the system. Pressure regulator R2 lets the operator control the pressure of both BPRs separately for a more refined control.

3. Additional details on methods

3.1. Purchased chemicals

Table S5: Table of the purchased chemicals.

Solvents	Purity (%)	CAS Number	Supplier
Absolute Ethanol	≥99.8	64-17-5	Fisher Scientific
DI water			
Chemicals	Purity (%)	CAS Number	Supplier
Sodium thiosulfate	99%	7772-98-7	Sigma Aldrich
Methyl phenyl sulfide (**1a**)	>99%	100-68-5	TCI
Methyl phenyl sulfone (**3a**)	>97%	3112-85-4	TCI
2-Chloroethyl ethyl sulfide (**CEES**)	97%	693-07-2	TCI
2-Chloroethyl ethyl sulfone (**CEESO$_2$**)	>99%	25027-40-1	Sigma-Aldrich
2-Chloroethyl phenyl sulfide (**CEPS**)	98%	105-57-7	Sigma-Aldrich
2-Chloroethyl phenyl sulfone (**CEPSO$_2$**)	98%	938-09-0	abcr
Dipropyl sulfide (**1b**)	97%	111-47-7	TCI
Dipropyl sulfone (**3b**)	>99%	598-03-8	TCI
Acetaldehyde diethyl acetal	>99%	105-57-7	Sigma-Aldrich
Colorimetric peroxide test, 0.5-25 mg/L	Vendor reference: 1100110001		Sigma-Aldrich

3.2. Analysis methods

HPLC analyses were conducted with a Shimadzu LC-2030 3D – Prominence-I PDA liquid chromatograph equipped with a diode array detector (DAD) and a reverse phase Shim-pack GIST C18 (Shimadzu) column (100 mm × 4.6 mm i.d., 3 µm) at 40 °C using a gradient of eluent A (0.1% formic acid in H_2O, *v*:*v*) and B (acetonitrile) at a flow rate of 1 mL min^{-1} and an injection volume of 10 µL. The monitoring was achieved using DAD within 180-800 nm.

GC analyses were conducted with a Shimadzu GC-2014 gas chromatograph equipped with a flame-ionization (FID) detector and a SH-Rtx-1701 (Shimadzu) capillary column (30 m × 0.25 mm i.d., 0.25 µm).

3.2.1. HPLC method for methyl phenyl sulfide (**1a**) oxidation

Table S6: Elution gradient for HPLC analysis of methyl phenyl sulfide (**1a**).

Time (min)	A	B
0	100	0
20	20	80
23	20	80
23	100	0
26	100	0

Total time: 26 min. Detection wavelength: 254 nm.

3.2.2. HPLC method for 2-chloroethyl phenyl sulfide (**CEPS**) oxidation

Table S7: Elution gradient for HPLC analysis of 2-chloroethyl phenyl sulfide (**CEPS**).

Time (min)	A	B
0	100	0
20	80	20
30	20	80
33	20	80
33	100	0
36	100	0

Total time: 36 min. Detection wavelength: 254 nm.

3.2.3. GC method for dipropyl sulfide (**1b**) oxidation

Table S8: Elution gradient for GC-FID analysis of dipropyl sulfide (**1b**).

Hold Time (min)	Rate (°C/min)	T (°C)
0.33	0	50
6.67	30	250
2	0	250

Total time: 9 min

3.2.4. GC method for 2-chloroethyl ethyl sulfide (**CEES**) oxidation

Table S9: Elution gradient for GC-FID analysis of 2-chloroethyl ethyl sulfide (**CEES**).

Hold Time (min)	Rate (°C/min)	T (°C)
3	0	30
7.33	30	250
6	0	250

4.

Total time: 16.33 min

4. Safety assessment

A comprehensive "what if" analysis was systematically conducted, resulting in the development of detailed checklists. These checklists serve as a decisive guide to be followed in the event of an emergency, ensuring swift and appropriate responses. Additionally, these measures encompass strategies for safe equipment startup and shutdown protocols.

1. The potential risk of gas leakage demands meticulous consideration due to the hazardous nature of the gas involved.

a. The laboratory exclusively serves this specific task, thereby preventing any inadvertent interplay with concurrent chemical reactions occurring within the facility.

b. The ozone dosing line is enveloped within a protective shell with minimal perforations.

c. The ozone dosing line is connected to an exhaust system boasting a magnitude far exceeding the gas throughput capacity of the dosing line itself. Ensuring a secure connection is facilitated through the presence of several exhaust measurement probes. A lack of vacuum triggers an automatic gas inlet flow shutdown.

d. A verified ozone detection device is integrated with the laboratory's power supply, promptly deactivating the power source upon detection. Moreover, this mechanism triggers an emergency alert.

e. During operations, the operator is equipped with a secondary, compact ozone detector affixed to their lab coat.

f. The exhaust lines are integrated with the vent system of the fume hood, and tightly secured to the fume hood structure. This precaution prevents any potential abrupt pressure surges due to gas release that could dislodge the exhaust line, safeguarding personnel.

g. At the reactor outlet, a T-shaped connector effectively segregates the gas streams, preventing any residual ozone or oxygen from entering the sample.

h. Routine testing of each equipment component is conducted regularly prior to starting the setup.

i. The dosing line encompasses crucial safety features including a pressure relief valve and pressure probes. Additionally, the cooling of the ozone compressor is facilitated via a liquid flow mechanism.

j. Experiments are consistently conducted with the presence of multiple operators simultaneously.

2. Another significant concern involves the potential presence of peroxides and their associated risks.

a. The ozone dosing line undergoes thorough rinsing with a high-grade Nitrogen line to eliminate any traces of humidity. The same procedure is repeated after each run.

b. The equipment is systematically stored under a positive Nitrogen atmosphere in between uses.

c. All wetted parts of the equipment (*i.e.,* parts that come in contact with reactive materials) are grease-free grade.

d. The quenching line is activated before the reagent lines (ozone and thioether simulants) and is subsequently halted post-experimentation.

e. Regular and frequent use of peroxide test strips are used to check the absence of peroxides.

f. Before initiating operations, meticulous tests involving all reagents, known products, and intermediates are conducted to ensure comprehensive validation of the peroxide test. These

evaluations encompass a wide range of concentrations, including dilutions and reagent mixtures, to account for potential false-positive and false-negative outcomes.
g. A batch of suitable reductive reagent (aqueous sodium thiosulfate), prepared within a fume hood and stirred, is pre-cooled and kept ready for immediate utilization. This batch serves a dual purpose – either for direct infusion into the flow reactor or for instant transfer into the collection tank.

3. Another significant concern involves the presence of oxygen and flammable organics.
a. A continuous flow of nitrogen is employed throughout the experiment to effectively dilute and degas the oxygen present in the collection tank.
b. The system is systematically flushed with Nitrogen prior and after all runs.
c. The presence of a purging system situated between the dosing line and the reactor effectively prevents any undesired backflow.

5. General protocol for the oxidation of sulfides under continuous flow

The feed solution containing the sulfide compounds was pumped using a Knauer – Azura P4.1S HPLC pump. The quench solution was pumped using a HiTec Zang SyrDos™ 2 XLP pump. Before each experiment, the ozone dosing line was pressurized to 10 bars with oxygen. The reactor was cooled to 10 °C and the downstream pressure was set at 10 bar (Zaiput BPR-10). The reactor setup was thoroughly flushed with nitrogen, and then with 1:1 EtOH/H_2O mixture for 5 min. The pumps handling the feed solution (sulfide) and quench solution (0.5 M sodium thiosulfate in 9:1 (v:v) water/ethanol mixture) were set to the desired flow rate (Table S10). Once the temperature and pressure of the system were stable, the ozone was set to the desired flow rate (Table S10) and the valve connecting the ozone dosing line was changed from "vent" to "reactor". Samples were collected after 10 minutes of equilibration once stable conditions were achieved. The crude samples were tested for peroxides using test tapes and analyzed with proton NMR using a benchtop Spinsolve 43 Carbon Ultra from Magritek without the addition of deuterated solvent.

Table S10. Flow rates used for each of the conditions tested for the oxidation of sulfide compounds.

Sufide	Concentration (M)	Ozone equiv	Sulfide flow rate (mL min^{-1})	Ozone flow rate (mLN min^{-1})	Quench flow rate (mL/min)
Thioanisole	0.1	1.4	5.07	249	2.03
Dipropyl sulfide	0.1	1.4	5.07	249	2.03
CEPS	0.2	1.4	2.95	271	2.36
CEES	0.2	1.2	3.39	266	2.71
CEES	0.2	1	3.97	260	3.18
CEES	0.2	0.8	4.81	252	3.85
CEES	0.5	1	1.76	282	3.51

A note on the calculation of the flow rates

The dosing line for ozone was operated under 10 bar and afforded ozone in a concentration of 10 %wt (6.9 %mol). The molarity of ozone in the dosing line was calculated assuming ideal gas behavior:

$$\frac{n}{V} = \frac{P}{RT}$$

$$\frac{mol}{L} = \frac{10}{(0.0821)(283)} = 0.43\ M_{gas}$$

$$0.43\ M_{gas}\ x\ 6.9\% = 0.03\ M_{ozone}$$

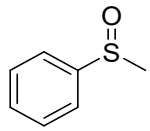
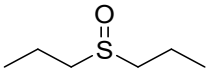
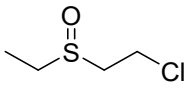
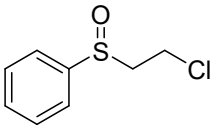
The flow rates for each feed were then calculated to afford the desired stoichiometry, considering a reactor volume of 0.5 mL with a target residence time of 1 second.

The flow rate of the quench line (sodium thiosulfate 0.5 M) was calculated to provide 2 equivalents of thiosulfate as compared to the sulfide.

6. General protocol for the batch synthesis of the references

The corresponding sulfide (1 mmol, 1 eq) was dissolved in MTBE (5 mL). A solution of hydrogen peroxide at 50 *wt%* (60 µL, 1.05 mmol, 1.05 eq) was added and the mixture was stirred at room temperature for 4 h. The remaining peroxide was quenched by the addition of sodium thiosulfate (220 mg, 1 mmol, 1eq). The crude was then stirred again for 20 min, dried on $MgSO_4$, filtered and evaporated under high vacuum.

Table S*11*: Table of sulfoxide references.

	methyl phenyl sulfoxide (**2a**) C_7H_8OS MW = 140.20	**HPLC:** 6.8 min (Figure S13) **^{1}H NMR (400 MHz, $CDCl_3$) δ** 2.64 – 2.66 (s, 3H), 7.41 – 7.48 (m, 3H), 7.55 – 7.62 (dd, *J* = 8.0, 1.6 Hz, 2H). (Figure S5) **^{13}C NMR (101 MHz, $CDCl_3$) δ** 145.51, 130.97, 129.28, 123.41, 43.81. (Figure S6)
	dipropyl sulfoxide (**2b**) $C_6H_{14}OS$ MW = 134.24	**GC-FID:** 9.6 min (Figure S15) **^{1}H NMR (400 MHz, $CDCl_3$) δ** 0.99 – 1.10 (t, *J* = 7.4 Hz, 6H), 1.71 – 1.87 (m, 4H), 2.52 – 2.63 (ddd, *J* = 12.9, 8.6, 7.5 Hz, 2H), 2.68 – 2.78 (ddd, *J* = 12.9, 8.2, 6.0 Hz, 2H). (Figure S7) **^{13}C NMR (101 MHz, $CDCl_3$) δ** 53.97, 16.43, 13.33. (Figure S8)
	2-chloroethyl ethyl sulfoxide (**CEESO**) C_4H_9ClOS MW = 140.1	**GC-FID:** 9.1 min (Figure S17) **^{1}H NMR (400 MHz, $CDCl_3$) δ** 1.19 – 1.30 (t, *J* = 7.5 Hz, 3H), 2.64 – 2.75 (pent, *J* = 7.5 Hz, 2H), 2.89 – 3.03 (ddd, *J* = 8.7, 5.7, 2.5 Hz, 2H), 3.75 – 3.88 (m, 2H). (Figure S9) **^{13}C NMR (101 MHz, $CDCl_3$) δ** 53.82, 45.83, 37.06, 6.56. (Figure S10)
	2-chloroethyl phenyl sulfoxide (**CEPSO**) C_8H_9ClOS MW = 188.67	**HPLC:** 22.6 min (Figure S14) **^{1}H NMR (400 MHz, $CDCl_3$) δ** 3.05 – 3.11 (ddd, *J* = 7.4, 6.3, 3.4 Hz, 2H), 3.55 – 3.63 (m, 1H), 3.82 – 3.95 (dt, *J* = 11.7, 7.5 Hz, 1H), 7.39 – 7.51 (m, 3H), 7.51 – 7.60 (m, 2H). (Figure S11) **^{13}C NMR (101 MHz, $CDCl_3$) δ** 142.60, 131.25, 129.33, 123.72, 59.07, 36.60. (Figure S12)

7. Characterization of the crude reference compounds

7.1. Methyl phenyl sulfoxide (**2a**)

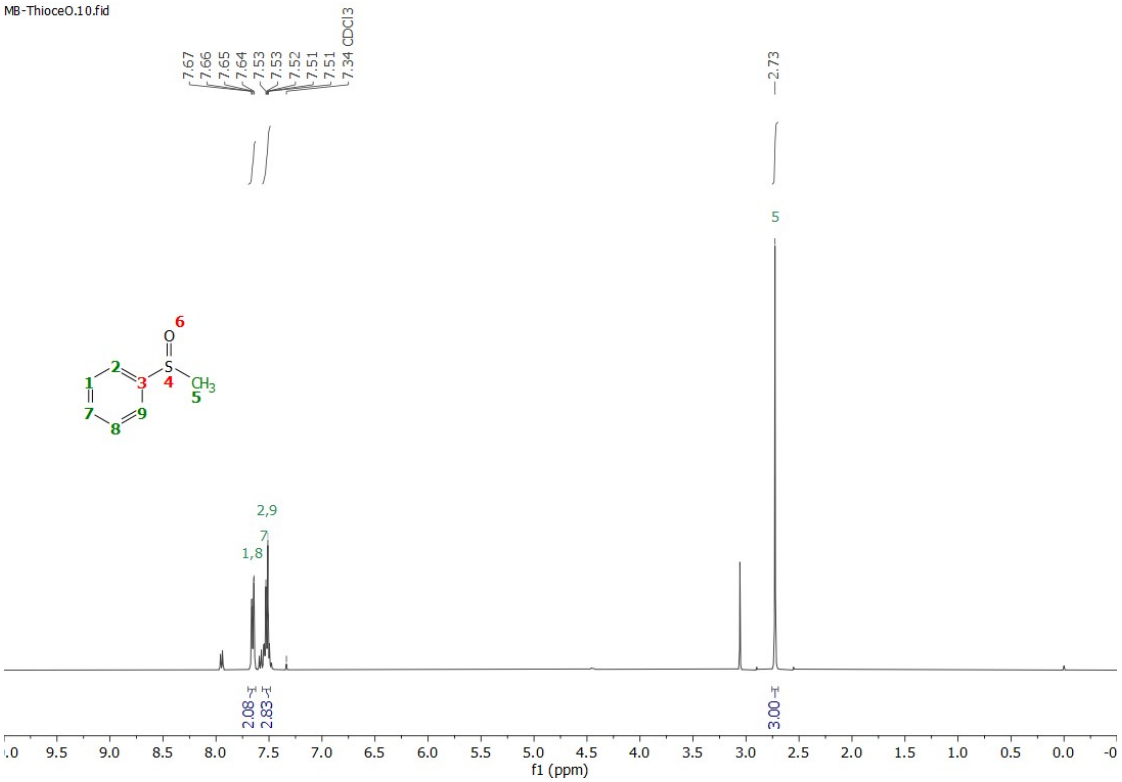


Figure S5: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude mixture for the synthesis of methyl phenyl sulfoxide (**2a**).

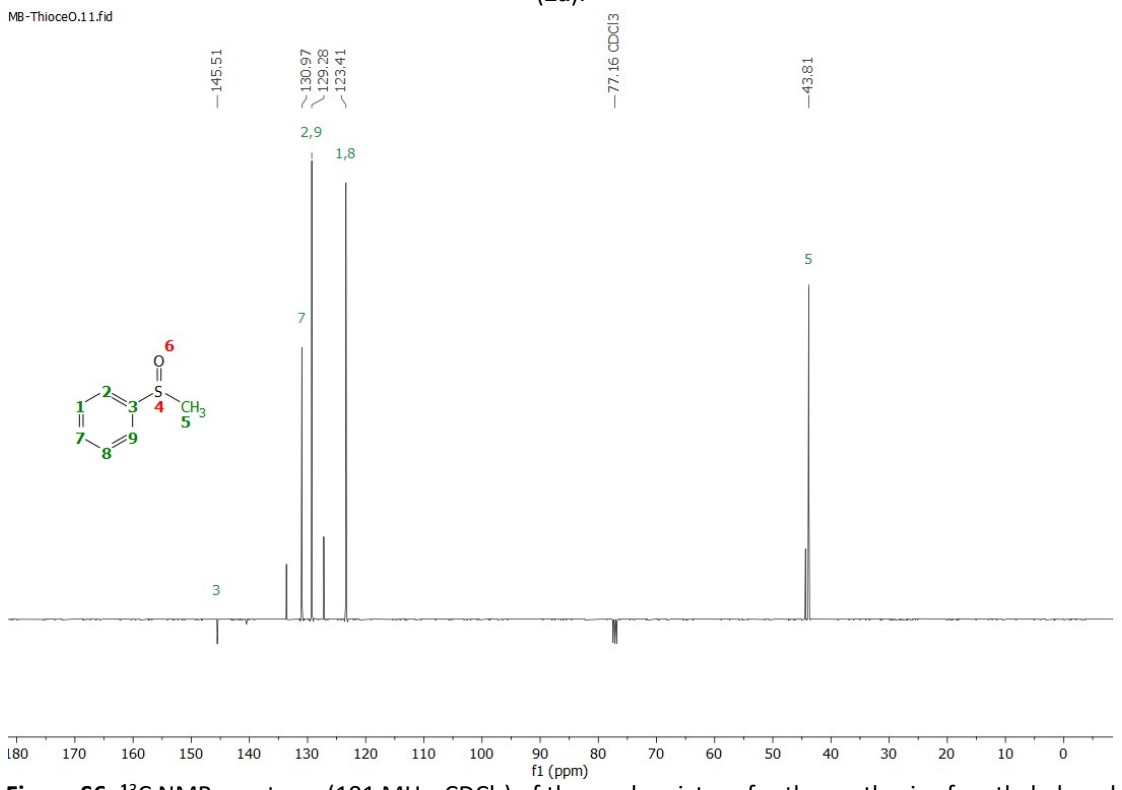


Figure S6: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of the crude mixture for the synthesis of methyl phenyl sulfoxide (**2a**).

7.2. Dipropyl sulfoxide (**2b**)

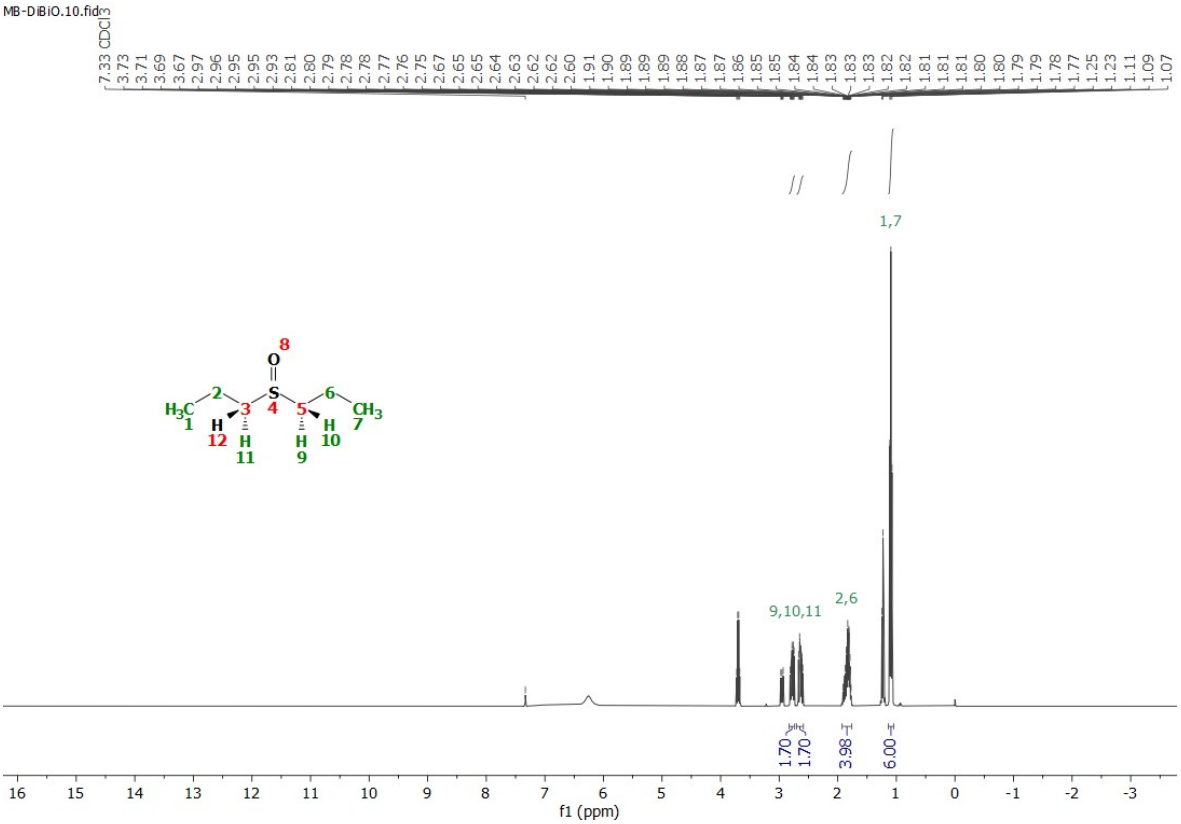


Figure S7: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude mixture for the synthesis of dipropyl sulfoxide (**2b**).

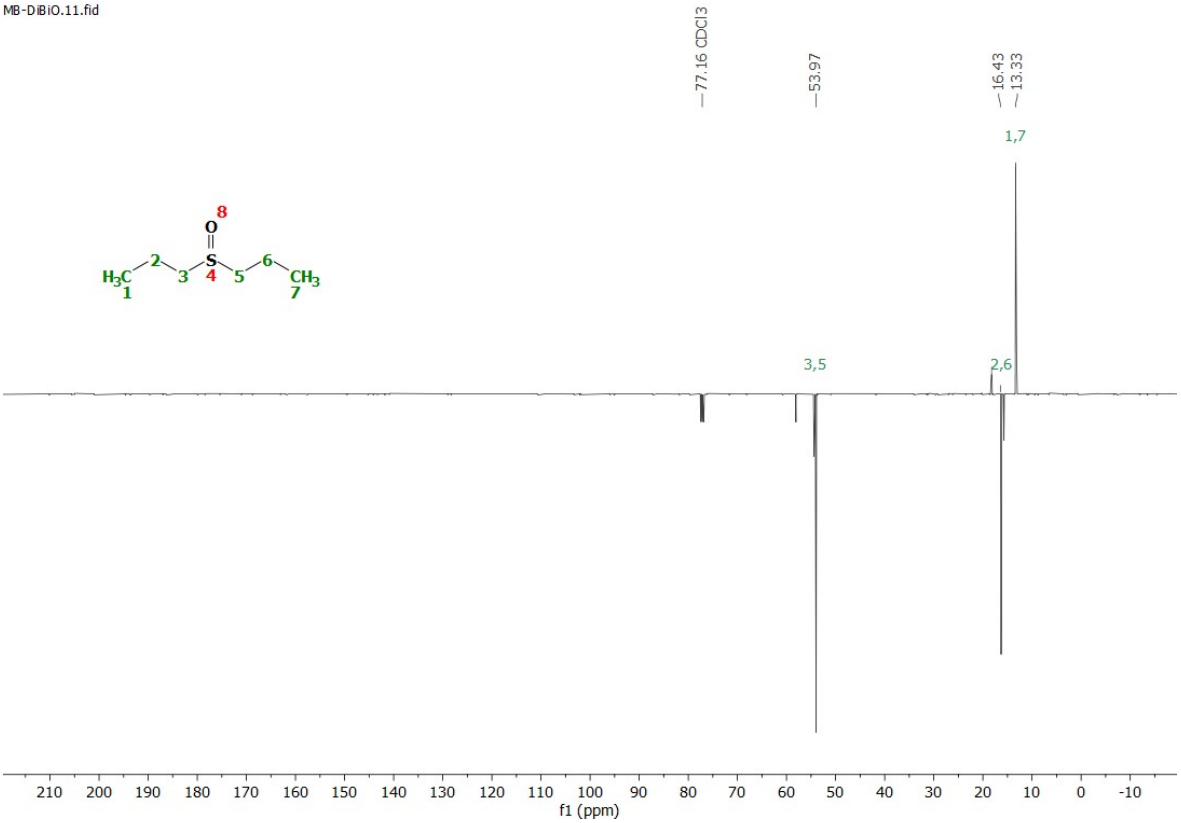


Figure S8: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of the crude mixture for the synthesis of dipropyl sulfoxide (**2b**).

7.3. 2-Chloroethyl ethyl sulfoxide (**CEESO**)

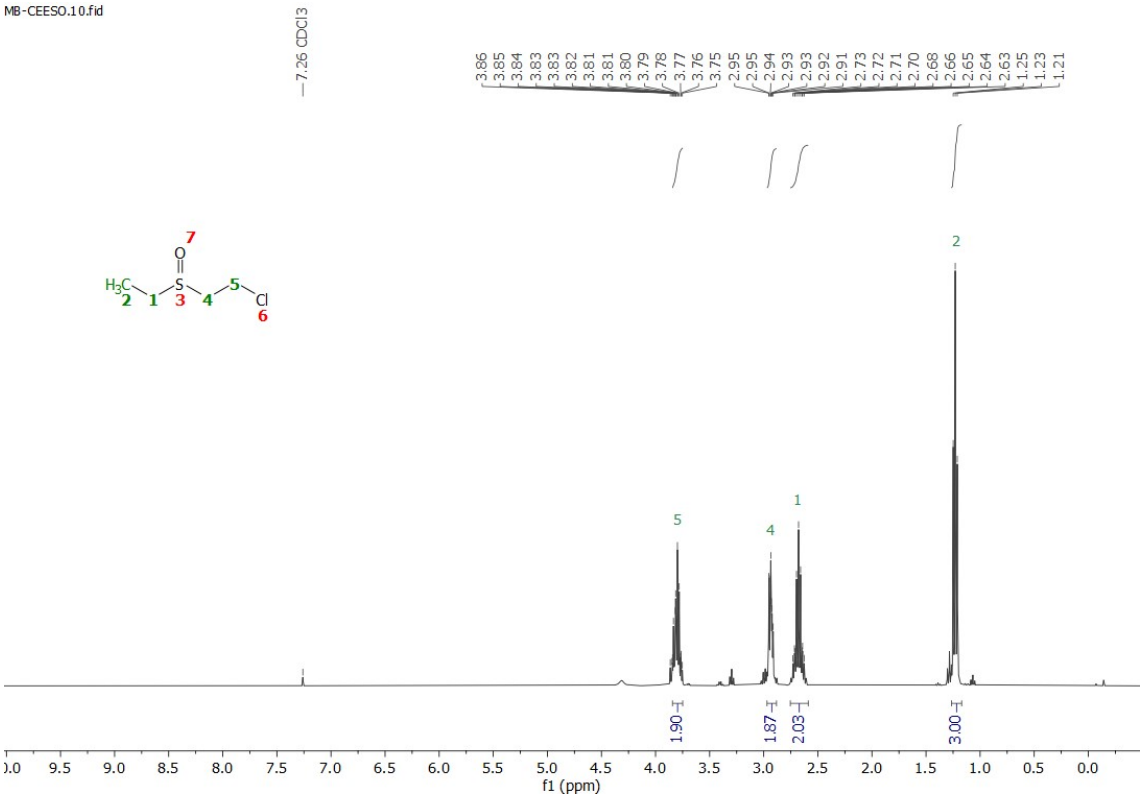


Figure S9: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude mixture for the synthesis of 2-chloroethyl ethyl sulfoxide (**CEES**).

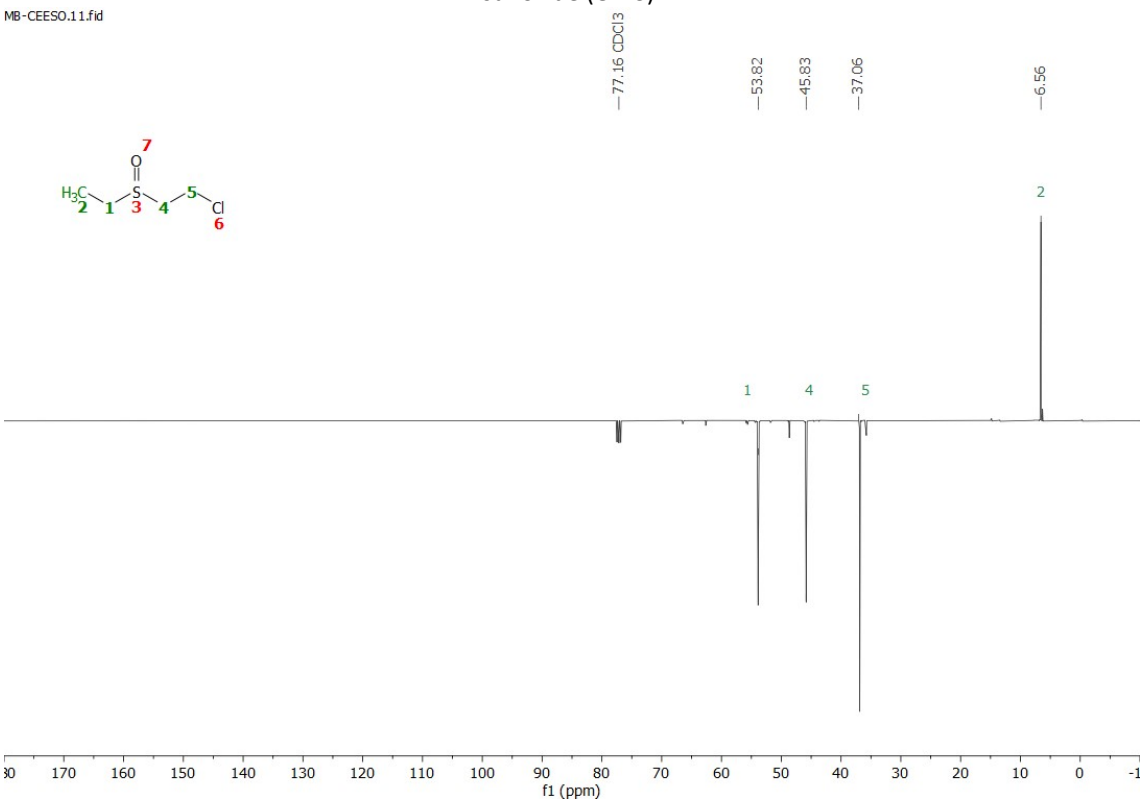


Figure S10: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of the crude mixture for the synthesis of 2-chloroethyl ethyl sulfoxide (**CEES**).

7.4. 2-Chloroethyl phenyl sulfoxide (**CEPSO**)

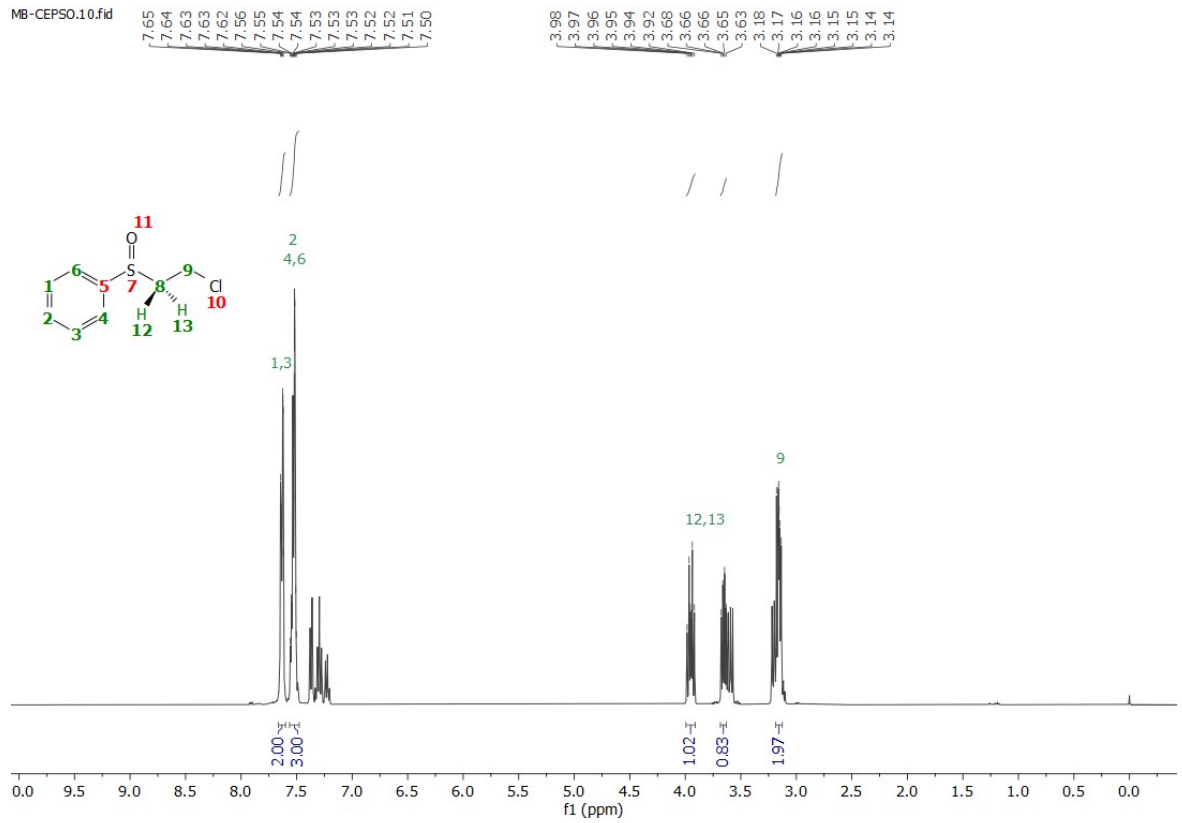


Figure S11: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the crude mixture for the synthesis of 2-chloroethyl phenyl sulfoxide (**CEPSO**).

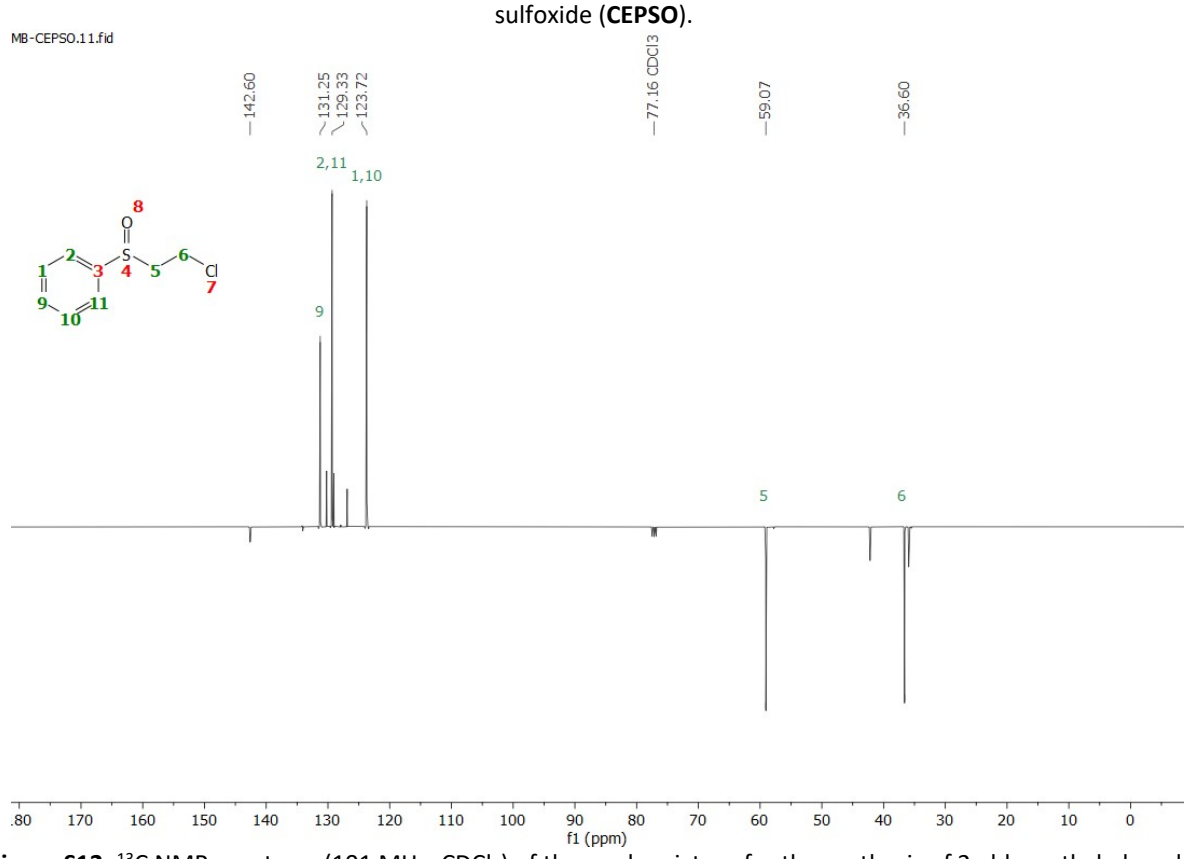


Figure S12: ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of the crude mixture for the synthesis of 2-chloroethyl phenyl sulfoxide (**CEPSO**).

8. Representative LC chromatograms

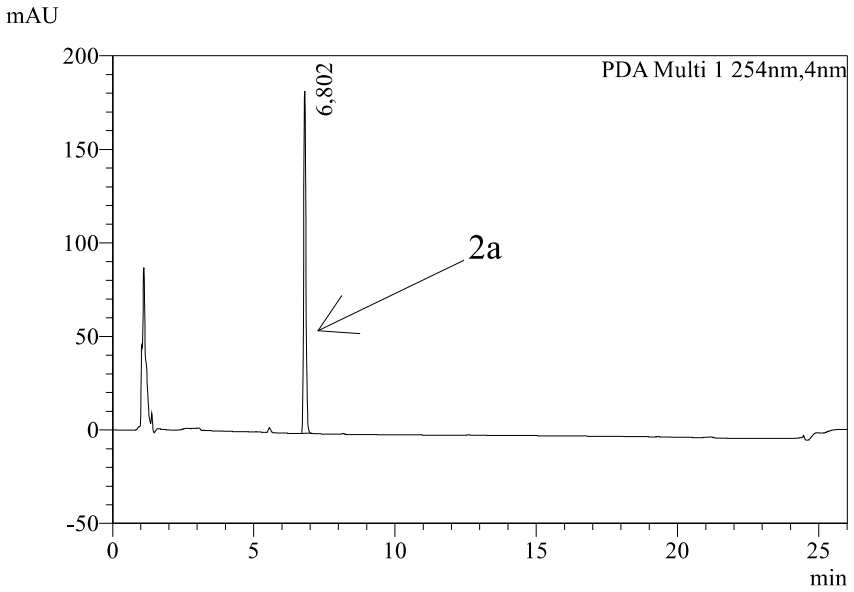


Figure S13. HPLC-DAD chromatogram (254 nm) of the reaction crude from Table 1, entry 2.

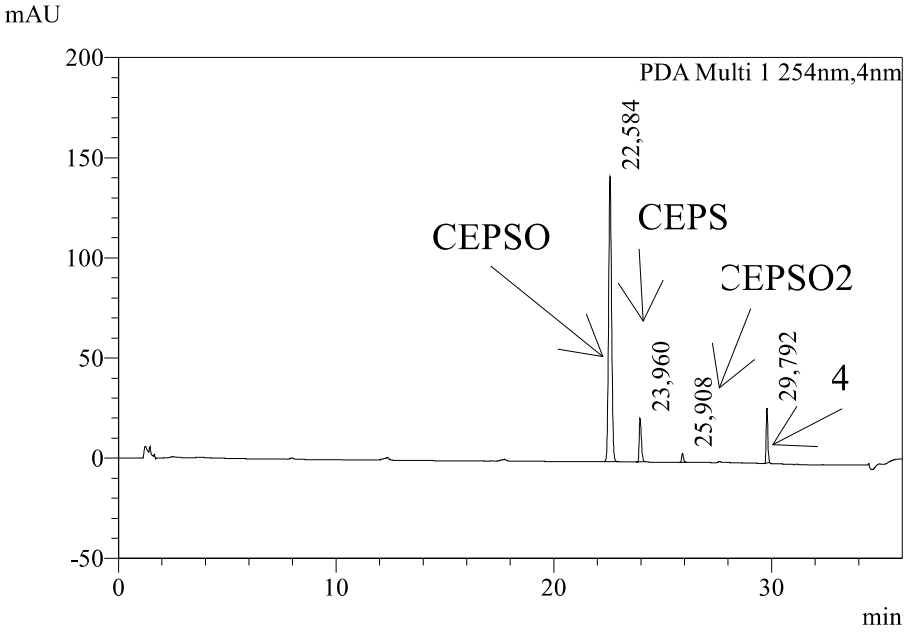


Figure S14. HPLC-DAD chromatogram (254 nm) of the reaction crude from Table 1, entry 4.

9. Representative GC chromatograms

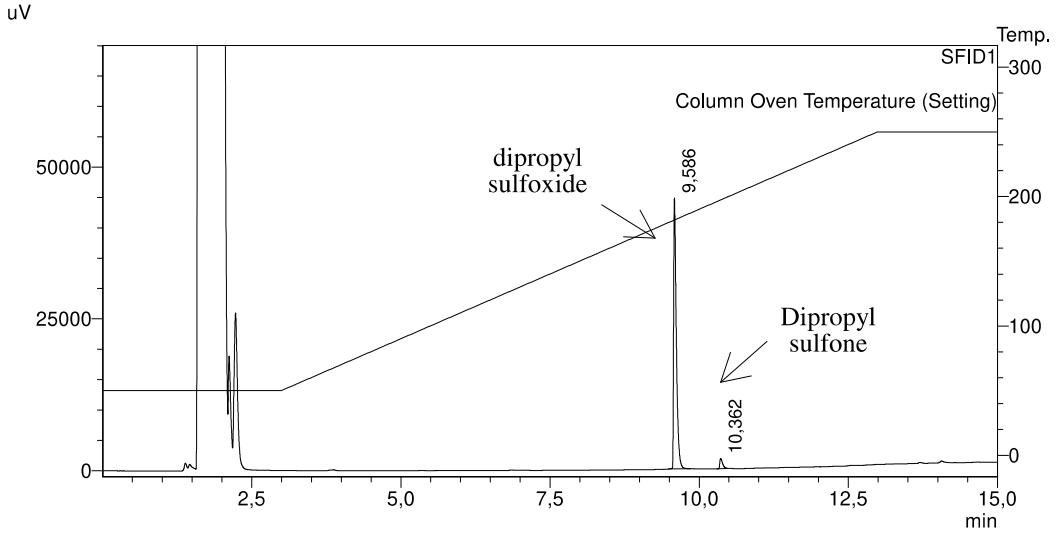


Figure S15. GC-FID chromatogram of the reaction crude from Table 1, entry 3.

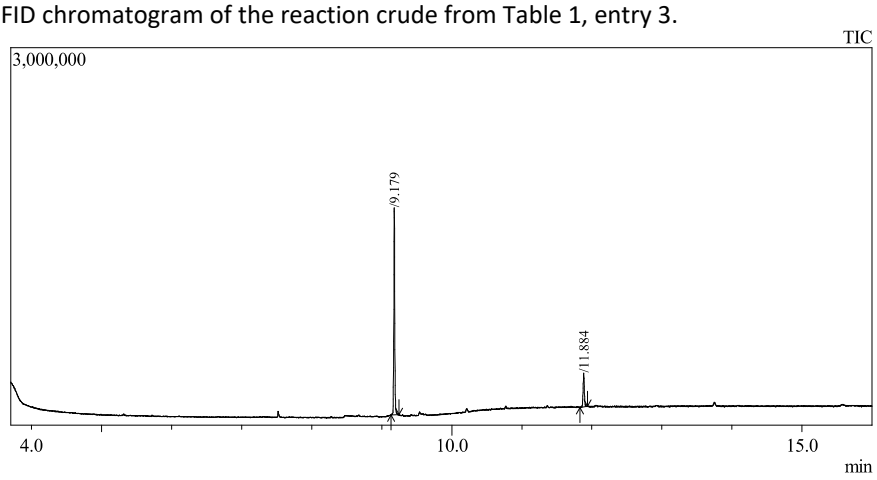


Figure S16. GC-MS chromatogram of the reaction crude from Table 1, entry 7. The signal at 11.9 min was assigned as compound **5**,[S5] as supported by the GC-MS mass spectrum.

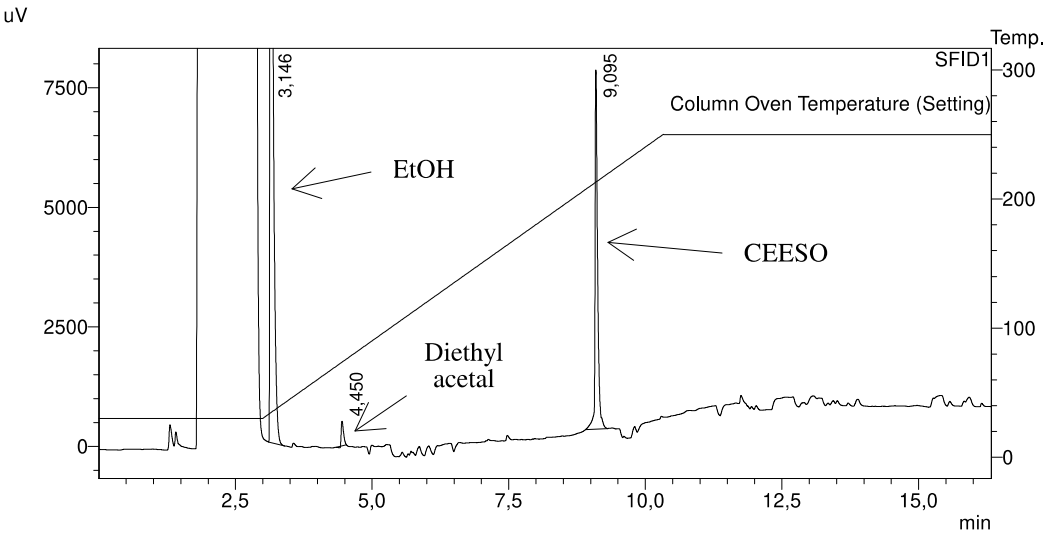


Figure S17. GC-FID chromatogram of the reaction crude from Table 1, entry 8. The Diethyl acetal label stands for acetaldehyde diethyl acetal. The identity of this compound was verified with a commercial reference.

10. References

S1 I. Funes-Ardoiz and R. S. Paton, GoodVibes (v3.0.0), Zenodo, 2019, https://doi.org/10.5281/zenodo.33461662018.

S2 J. C. M. Monbaliu and P. Bianchi, SnapPy (v1.0.0), Zenodo, 2023, https://doi.org/10.5281/zenodo.8116089.

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S4 W. Yang and W. J. Mortier, *J. Am. Chem. Soc.*, 1986, **108**, 5708–5711.

S5 B. Picard, B. Gouilleux, T. Lebleu, J. Maddaluno, I. Chataigner, M. Penhoat, F.-X. Felpin, P. Giraudeau, J. Legros, *Angew. Chem. Int. Ed.* **2017**, *56*, 7568.