

Supporting Information for

Efficient and Selective Oxidation of Sulfur Mustard using Singlet Oxygen Generated by a Pyrene-based Metal-Organic Framework.

Yangyang Liu,^{†a} Cassandra T. Buru,^{†a} Ashlee J. Howarth,^a John J. Mahle,^b James H. Buchanan,^b Jared B. DeCoste,^b Joseph T. Hupp^{*a} and Omar K. Farha^{*ac}

^a Department of Chemistry, Northwestern University
2145 Sheridan Road, Evanston, Illinois 60208, United States

^b Edgewood Chemical Biological Center, US Army Research, Development, and Engineering Command
5183 Black-hawk Rd., Aberdeen Proving Ground, MD 21010, United States

^c Department of Chemistry, Faculty of Science, King Abdulaziz University
Jeddah, Saudi Arabia

[†] These authors contributed equally to this work

o-farha@northwestern.edu

j-hupp@northwestern.edu

Table of Contents

Section S1. Instrumentation

Section S2. Characterizations of NU-1000

Section S3. Catalytic Studies

Section S4. Gas Chromatography

Section S5. ¹H NMR and ¹³C NMR Spectra

Section S6. ICP Analysis

Section S1. Instrumentation

NMR spectra were collected on a 500 MHz Bruker Avance III system equipped with DCH CryoProbe at IMSERC (Integrated Molecular Structure Education and Research Center) at Northwestern University. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku Smartlab instrument. Samples were scanned at 45 kV and 160 mA, a step size of $2\theta = 0.02^\circ$ (1.28 s per step) over a 2θ range of 2 to 30° . Inductively coupled plasma-optical emission spectroscopy (ICP-OES) measurements were performed on a Thermo iCap7600 ICP-OES Spectrometer. Standard solutions with Zr concentrations of 2, 8, 20 and 40 ppm were used for the calibration curve. The ICP sample was prepared by diluting 0.20 mL of the filtrate from the oxidation reaction (2.2 mg NU-1000 as catalyst) to 25 mL with millipore water. Nitrogen adsorption isotherm measurements were carried out on a Micromeritics Tristar II 3020 at 77 K. Samples were heated at 120°C under vacuum for 12 h prior to measuring the isotherms. GC-MS analysis was performed on a time-of-flight GC mass spectrometer from Waters Micromass GCT Premier. GC-FID analysis were carried out on an Agilent Technologies 7820A GC system equipped with an Agilent J&W GC HP-5 capillary column ($30\text{ m} \times 320\text{ }\mu\text{m} \times 0.25\text{ }\mu\text{m}$ film thickness). LED irradiation was performed using solderless LEDs purchased from RapidLED which were then mounted on aluminum to give a homemade irradiation setup. The LEDs were hooked up in series to a Mean Well LPC-35-700 constant current driver also purchased from RapidLED. The irradiation setup contains two UV LEDs ($\lambda_{\text{max}} = 390\text{-}400\text{ nm}$) that are mounted facing each other $\sim 1.5\text{ cm}$ apart.

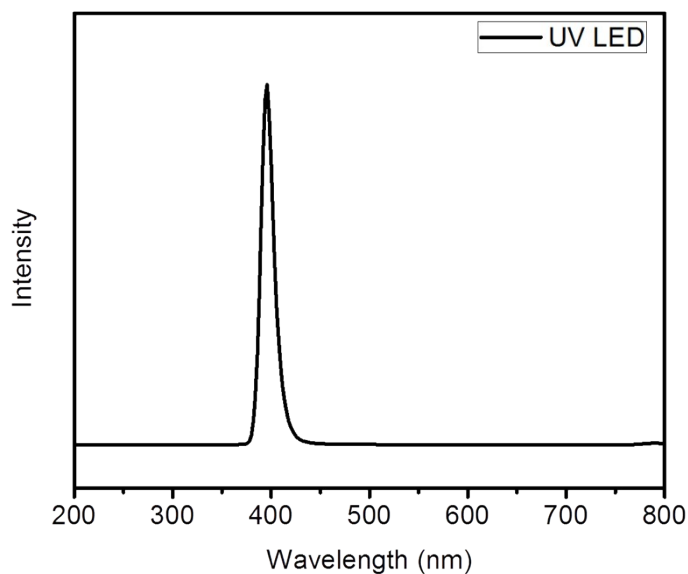


Fig. S1 Output wavelength of the UV LED (peak ~396 nm). Power density: 450mW/cm²

Section S2. Characterizations of NU-1000

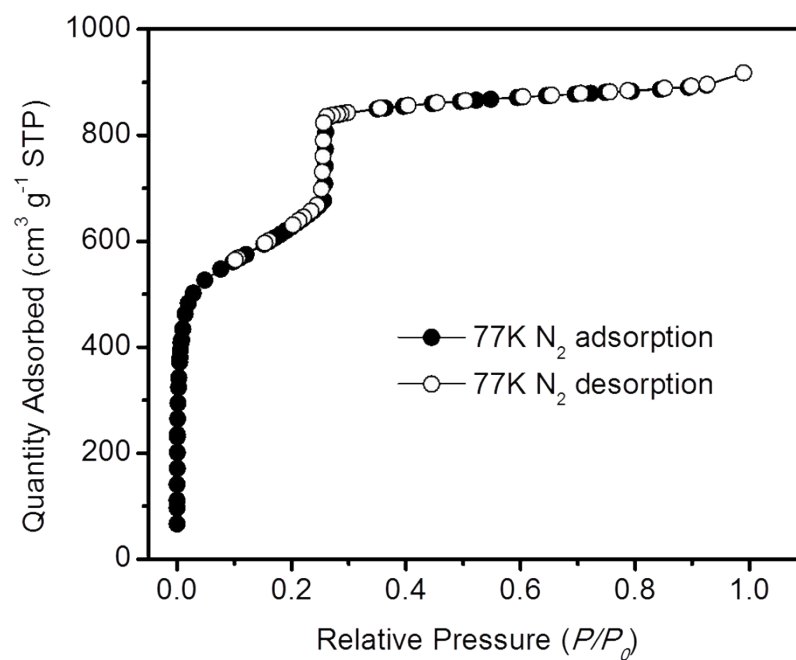


Fig. S2 N₂ isotherms of NU-1000 at 77K.

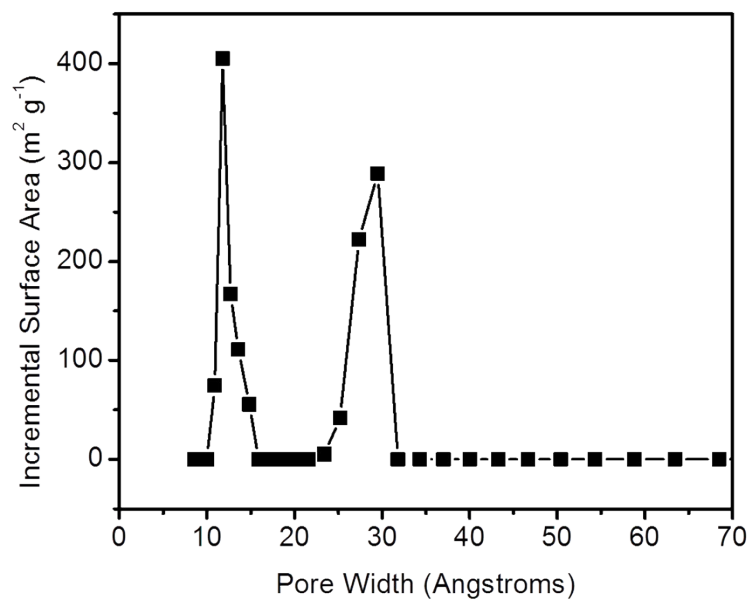


Fig. S3 Pore size distribution (PSD) of NU-1000 calculated by DFT.

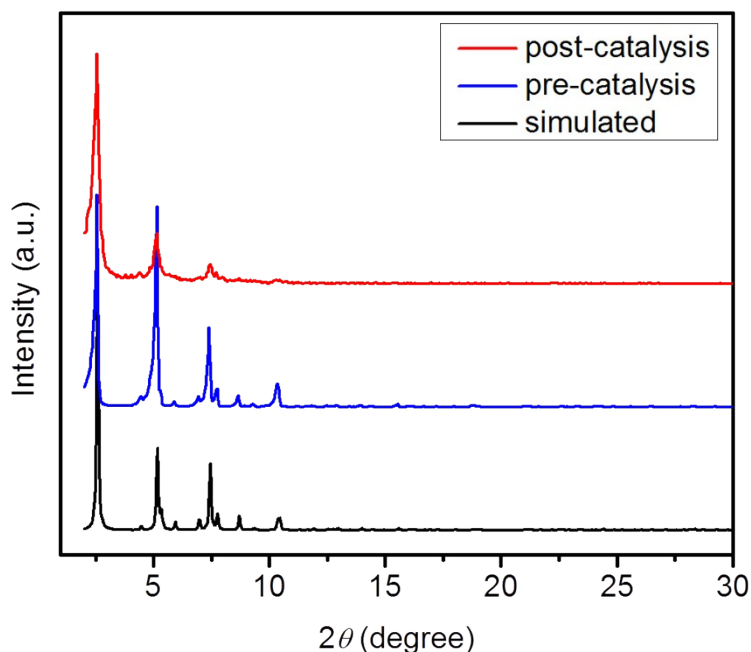


Fig. S4 PXRD of NU-1000, simulated (in black), pre-catalysis (in blue) and post-catalysis (in red).

Section S3. Catalytic Studies

CEES Oxidation with NU-1000: For catalytic tests, 1 mol% of NU-1000 (2.16mg, 2 μ mol by pyrene unit) was dispersed in 1 mL anhydrous methanol and sealed in a glass microwave vial. After purging with O₂ for 20 min, 23 μ L (0.2 mmol) 2-chloroethyl ethylsulfide (CEES) and 10 μ L (0.08 mmol) internal standard (1-bromo-3,5-difluorobenzene) were added to the microwave vial with a microsyringe. The microwave vial was then exposed to UV LED irradiation. Aliquots were withdrawn from the reaction with a syringe every 3 min, filtered and diluted with anhydrous methanol. Samples were then subjected to GC-FID to monitor the reaction and GC-MS to analyze the final products. NMR spectroscopy was also used to confirm the oxidation products. CD₃OD instead of MeOH was used in the reaction for NMR studies. To compare the pyrene-based linker to the MOF itself, 1.35 mg (2 μ mol, 1 mol%) 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrabenzoic acid (H₄TBAPy) was used in place of NU-1000.

Under optimized conditions, which is 1 mol% catalyst loading (catalyst loading is calculated based on moles of pyrenes in NU-1000) and UV LED irradiation, 0.2 mmol 2-chloroethyl ethylsulfide (CEES) can be completely oxidized to 1-chloro-2-(ethylsulfinyl)ethane (CEESO) within 15 min. GC results suggested there was no sulfone product formed in this process, even after an additional 24 hours of irradiation. Under the same condition but with different catalyst loading (0.5 mol % or 2 mol %), the oxidation takes longer than 15 min.

The reusability of the catalyst NU-1000 was studied by making multiple injections of CEES (0.2 mmol) into the same reaction. Before each injection, the solution was purged with O₂ for 20 min. GC-FID was used to monitor the reaction progress and calculate the conversion of the reaction after each injection.

HD Oxidation with NU-1000: 5.2 mg of NU-1000 was dispersed in 1 mL of methanol in a sealed quartz vial. After purging with O₂ for 20 min and irradiating with a UV LED for 20 min, 50 μ L (0.4 mmol) of HD was added to the vial with a syringe, and continue irradiating with UV LED. 25 μ L aliquots were taken at various time points, filtered, and removed from the light, before being analyzed by GC-FID, with the final time point analyzed by GC-MS.

CASARM (Chemical Agent Standard Analytical Reference Material) quality sulfur mustard (HD, >98%, Lot # HD-U-5038-CTF-N) was synthesized in house for research purposes only. **Danger!!! Sulfur mustard and other chemical warfare agents should only be handled in a lab and by personnel that are certified to do so. Even small doses of CWAs are known to be highly dangerous and potentially lethal.**

Section S4. Gas Chromatography

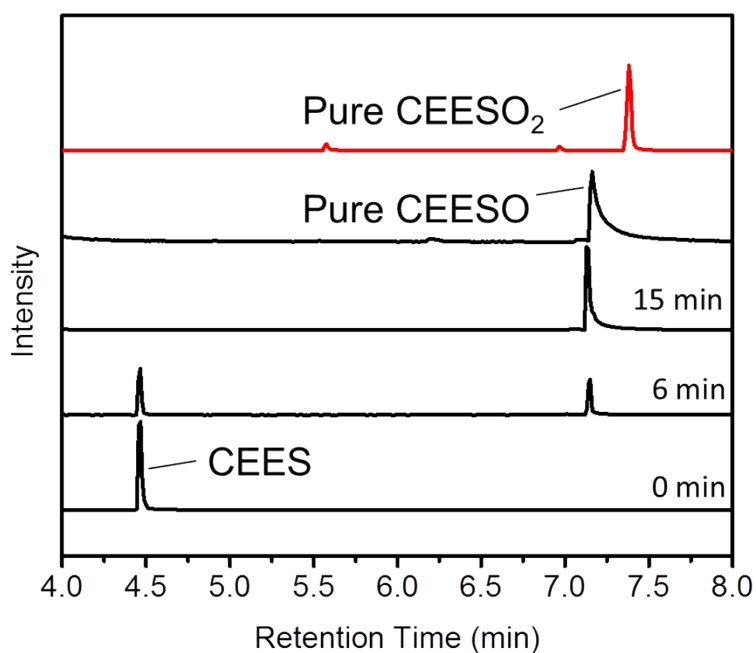


Fig. S5 Gas chromatography (GC) signals indicating the progress of the oxidation of CEES (4.45 min) to CEESO (7.14 min) in the presence of NU-1000 (2.2 mg). For comparison, chromatograms of pure CEESO (7.14 min) and pure CEESO₂ (7.38 min) were also recorded, confirming that CEESO was the only product.

Section S5. ^1H NMR and ^{13}C NMR spectra.

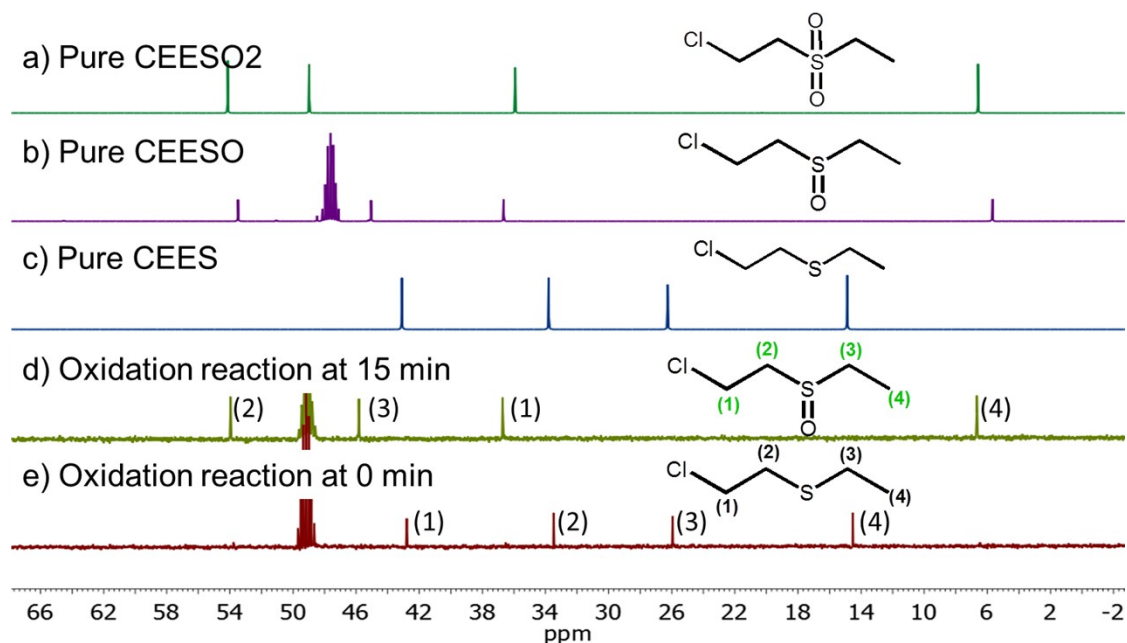


Fig. S6 ^{13}C NMR spectra of a) Pure 1-chloro-2-(ethylsulfonyl)ethane (CEESO₂) in CDCl_3 , b) Pure 2-chloroethyl ethyl sulfoxide (CEESO) in CD_3OD , c) pure 2-chloroethyl ethyl sulfide (CEES) in CDCl_3 , d) oxidation of CEES in the presence of 2.2 mg NU-1000. The reaction is performed in CD_3OD . NMR sample was taken at 15 min of the oxidation reaction, dissolved in CDCl_3 , indicating the oxidation is completed and only one product, 1-chloro-2-(ethylsulfinyl)ethane (CEESO), was obtained. e) NMR sample was taken at 0 min of the oxidation reaction, dissolved in CDCl_3 .

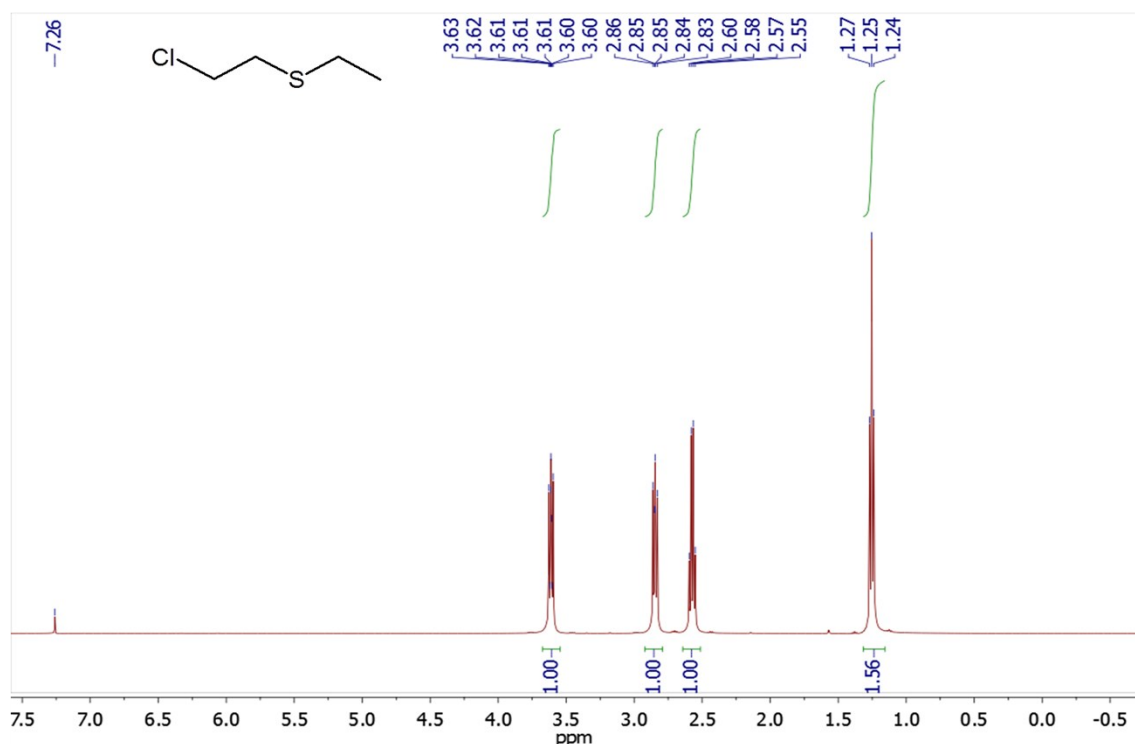


Fig. S7 ^1H NMR spectrum of pure CEES.

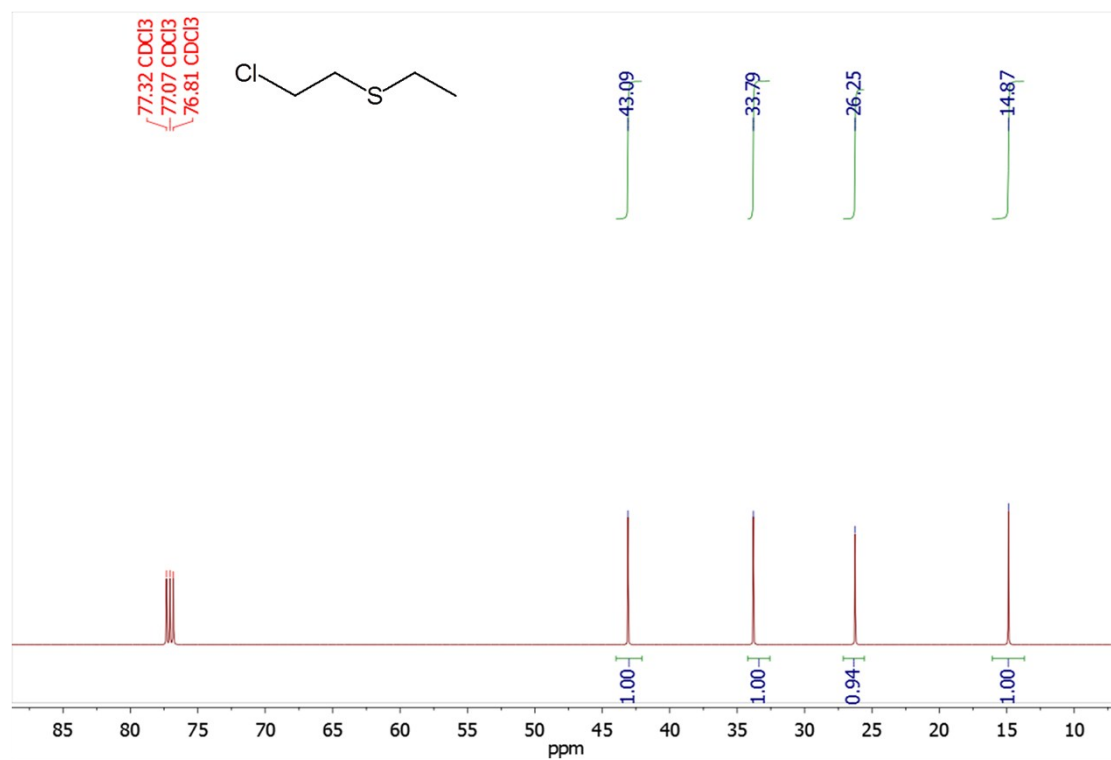


Fig. S8 ¹³C NMR spectrum of pure CEES.

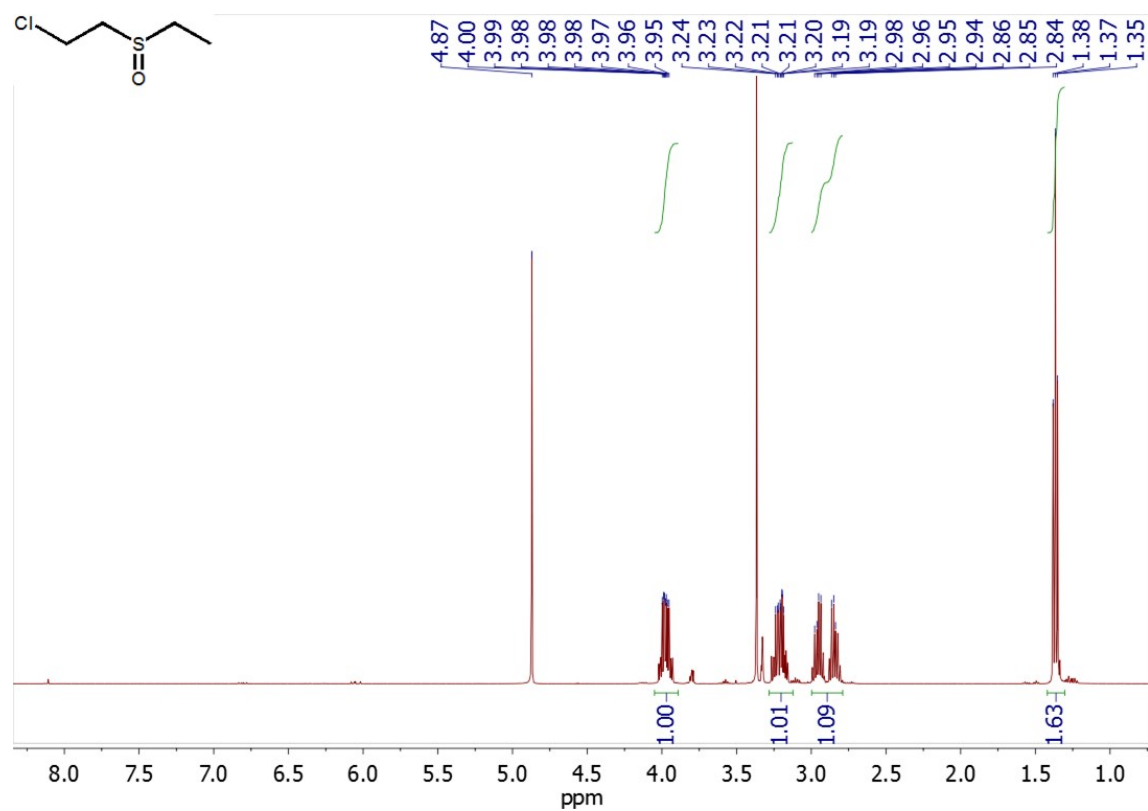


Fig. S9 ¹H NMR spectrum of pure CEESO.

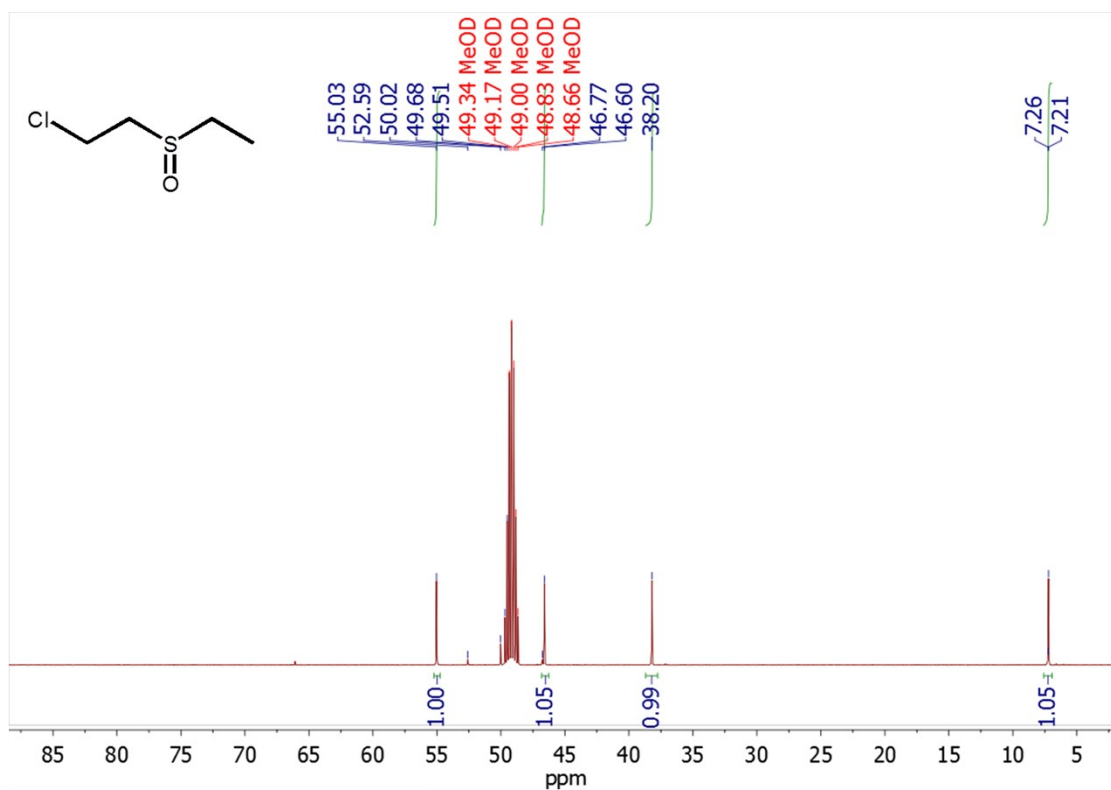


Fig. S10 ¹³C NMR spectrum of pure CEESO.

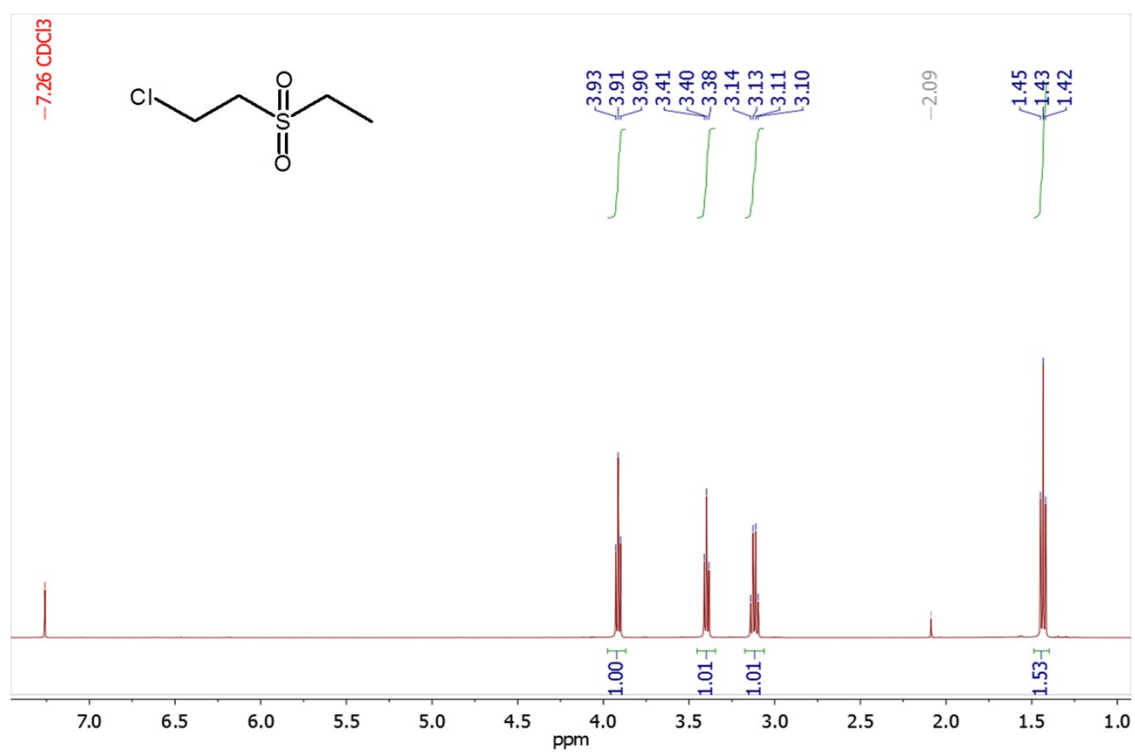


Fig. S11 ¹H NMR spectrum of pure CEESO₂.

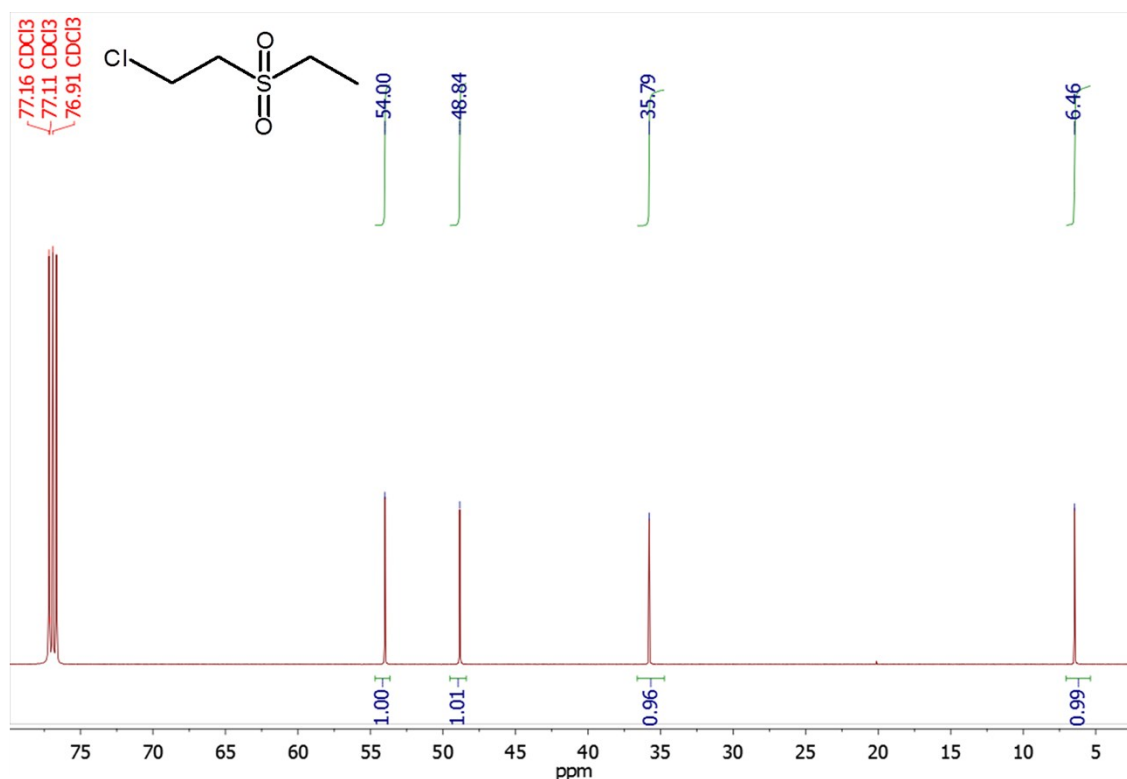


Fig. S12 ¹³C NMR spectrum of pure CEESO₂.

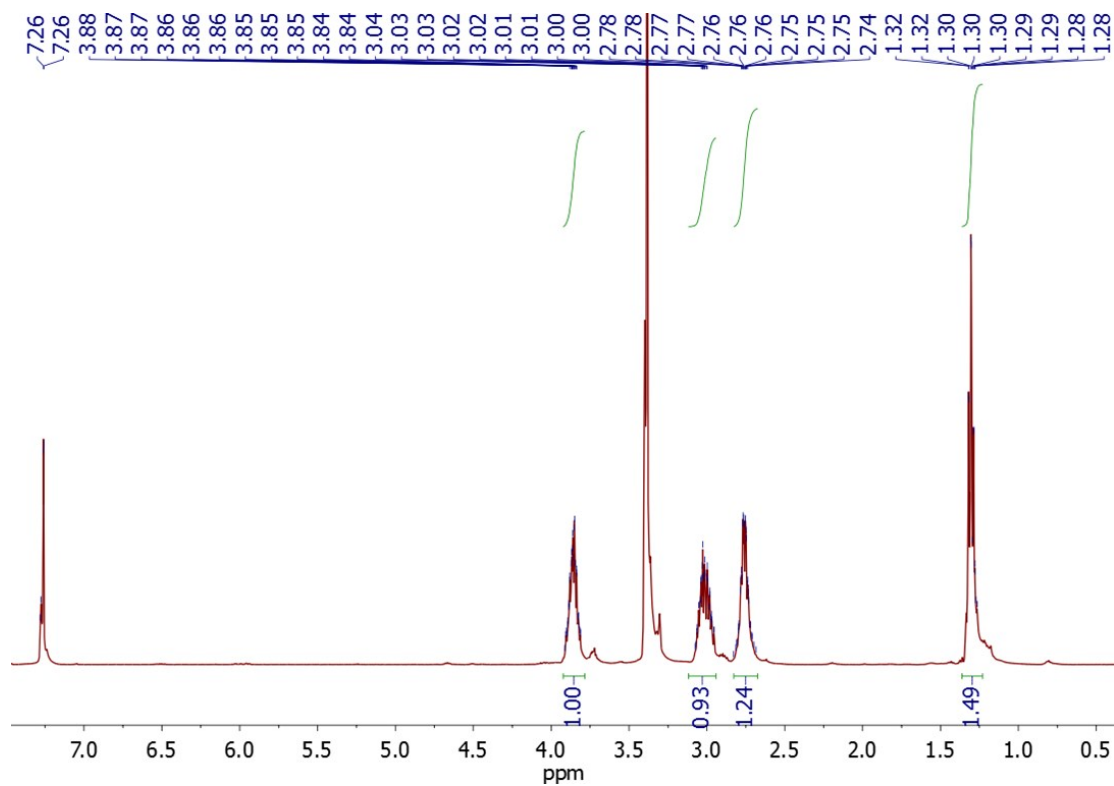


Fig. S13 ¹H NMR spectrum of oxidation reaction performed in CD₃OD in the presence of 2.2 mg NU-1000 under UV LED (t = 15 min).

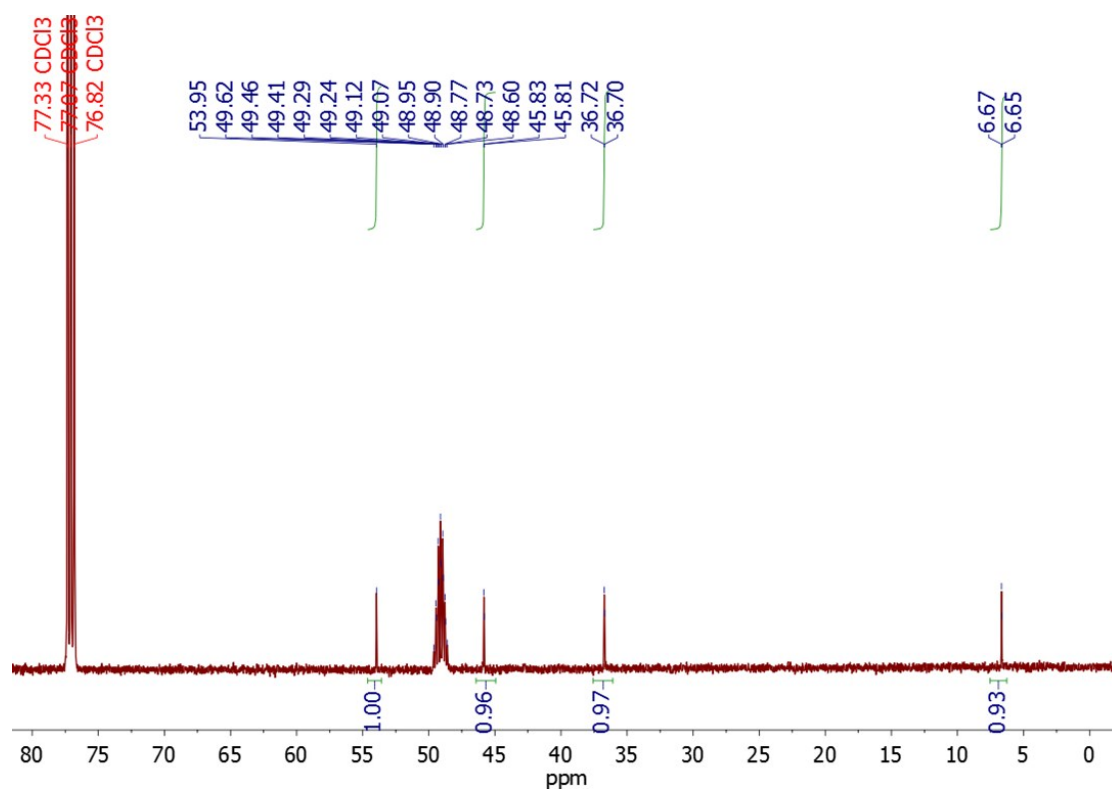


Fig. S14 ¹³C NMR spectrum of oxidation reaction performed in CD₃OD in the presence of 2.2 mg NU-1000 under UV LED (t = 15 min).

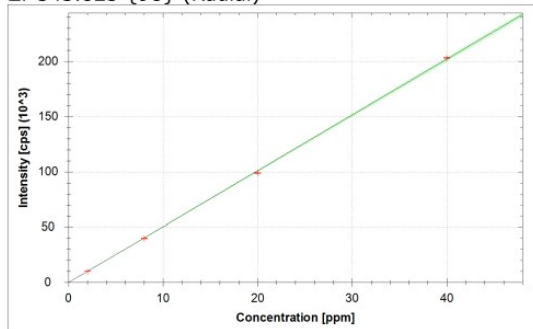
Section S6. ICP Analysis

Calibration details

	2	8	20	40
Zr 343.823 {98} (Radial)	2.000 ppm	8.000 ppm	20.000 ppm	40.000 ppm
Zr 327.305 {103} (Radial)	2.000 ppm	8.000 ppm	20.000 ppm	40.000 ppm
Zr 349.621 {96} (Radial)	2.000 ppm	8.000 ppm	20.000 ppm	40.000 ppm
Zr 339.198 {99} (Radial)	2.000 ppm	8.000 ppm	20.000 ppm	40.000 ppm

Symbol	Wavelength (nm) / Order	Fit Type	Weighting	Forcing
Zr	343.823 {98}	Linear	None	Blank
Zr	327.305 {103}	Linear	None	Blank
Zr	349.621 {96}	Linear	None	Blank
Zr	339.198 {99}	Linear	None	Blank

Zr 343.823 {98} (Radial)



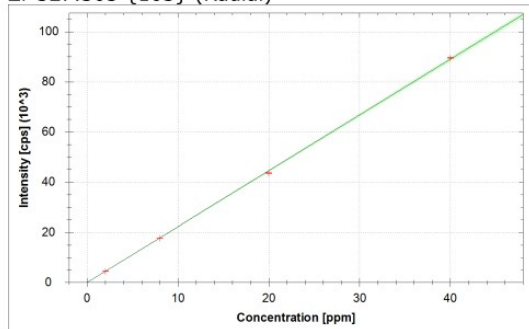
$$f(x) = 5049.5334 \cdot x + -4.3444$$

$$R^2 = 0.9997$$

$$BEC = -0.001 \text{ ppm}$$

$$LoD = 0.0040 \text{ ppm}$$

Zr 327.305 {103} (Radial)



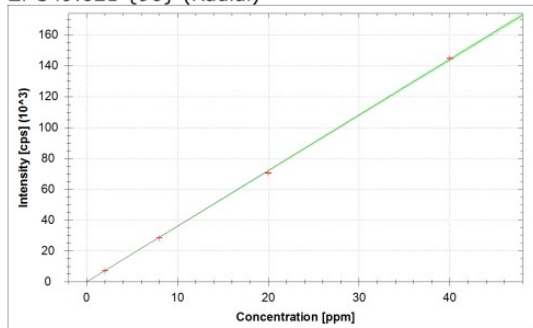
$$f(x) = 2224.3851 \cdot x + 12.6694$$

$$R^2 = 0.9997$$

$$BEC = 0.006 \text{ ppm}$$

$$LoD = 0.0125 \text{ ppm}$$

Zr 349.621 {96} (Radial)



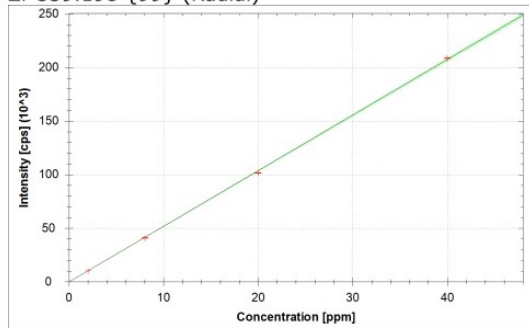
$$f(x) = 3601.5461 \cdot x + 30.5875$$

$$R^2 = 0.9998$$

$$BEC = 0.008 \text{ ppm}$$

$$LoD = 0.0114 \text{ ppm}$$

Zr 339.198 {99} (Radial)



$$f(x) = 5186.4607 \cdot x + -6.8181$$

$$R^2 = 0.9998$$

$$BEC = -0.001 \text{ ppm}$$

$$LoD = 0.0028 \text{ ppm}$$

Fig. S15 Calibration curves from Zr standards: 2, 8, 20, 40 ppm.

Table S1. ICP analysis of Zr in the filtrate after catalysis (RSD = relative standard deviation; SD = standard deviation)

	Zr 343.823 {98} (Radial)	Zr 327.305 {103} (Radial)	Zr 349.621 {96} (Radial)	Zr 339.198 {99} (Radial)
Concentration average	-0.006 ppm	-0.006 ppm	-0.005 ppm	-0.005 ppm
Concentration per Run 1	-0.007 ppm	-0.006 ppm	-0.004 ppm	-0.004 ppm
Concentration per Run 2	-0.006 ppm	-0.008 ppm	-0.004 ppm	-0.004 ppm
Concentration per Run 3	-0.006 ppm	-0.004 ppm	-0.007 ppm	-0.006 ppm
Concentration RSD	5.2 %	40.0 %	27.8 %	17.6 %
Concentration SD	0.0 ppm	0.0 ppm	0.0 ppm	0.0 ppm