Supplementary Information

Destruction of chemical warfare agent simulants by air and moisture stable metal NHC complexes

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Contents

1. General Experimental Procedures:

NMR spectra were recorded on a Bruker AVA400 spectrometer for ^{1}H (399.90 MHz), ^{31}P (161.98 MHz) and a Bruker AVA600 spectrometer ^{1}H (599.81 MHz).

Gas Chromatography Mass Spectrometry (GCMS) data was collected on a Shimadzu GC-2010 plus with a 30 m, 0.25 mmID, 0.25 µm df column.

Photolysis was carried out using a Pen-Ray Light Source 11SC-1.75 - 254 nm, Effective 2200 μW/cm^2 @1" and 18 mA, Maximum 6W.

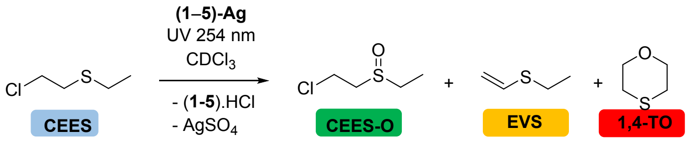
UV/vis spectra were recorded on a JASCO V-670 spectrophotometer.

Synthesis of all complexes (**1-5**)-**Ag**[1], **6-Ag**[2], (**1-5**)-**Cu**[3], and (**1-3**)-**V**[4, 5] were carried out according to literature preparations. Imidazoline and Imidazolinium salts were purchased from Sigma-Aldrich and used as supplied, *o*-aryloxide imidazoline salt[6] was prepared according to literature. All chemicals were purchased from Sigma-Aldrich and used as supplied without further purification. Deuterated solvents were purchased from Cambridge Isotopes. Extreme caution must be taken when handling the chemical warfare simulants.

2. Destruction by Group 11 metal-NHC complexes

General experimental procedure:

CEES (2.0 µL, 0.017 mmol) was added to a quartz NMR tube containing 0.5 mL $CDCl_3$ and **#-Ag** or **#-Cu** (0.017 mmol). A ^1H NMR was taken after addition and then placed under UV light (254 nm) and monitored every 30 minutes until CEES had been consumed. A small aliquot was taken every hour for GC-MS.



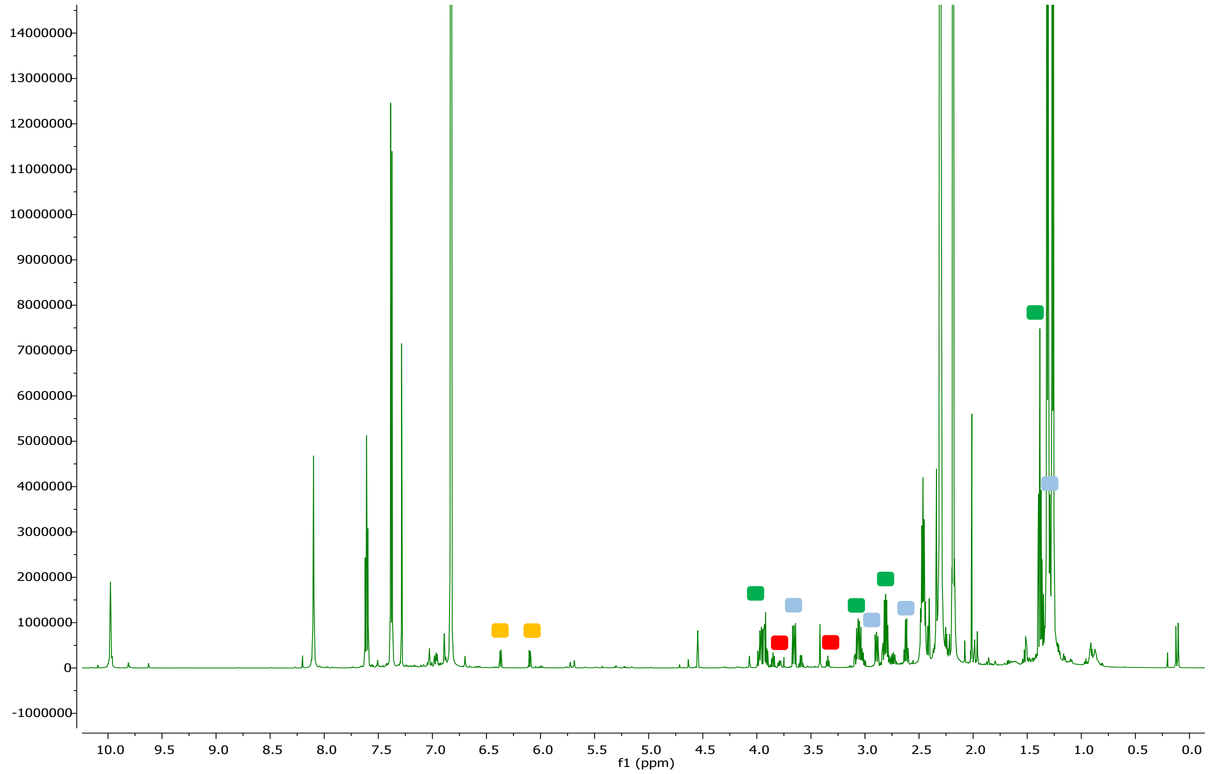


Figure 1. 1-Ag and 1 eq CEES, UV (254 nm) 5hr

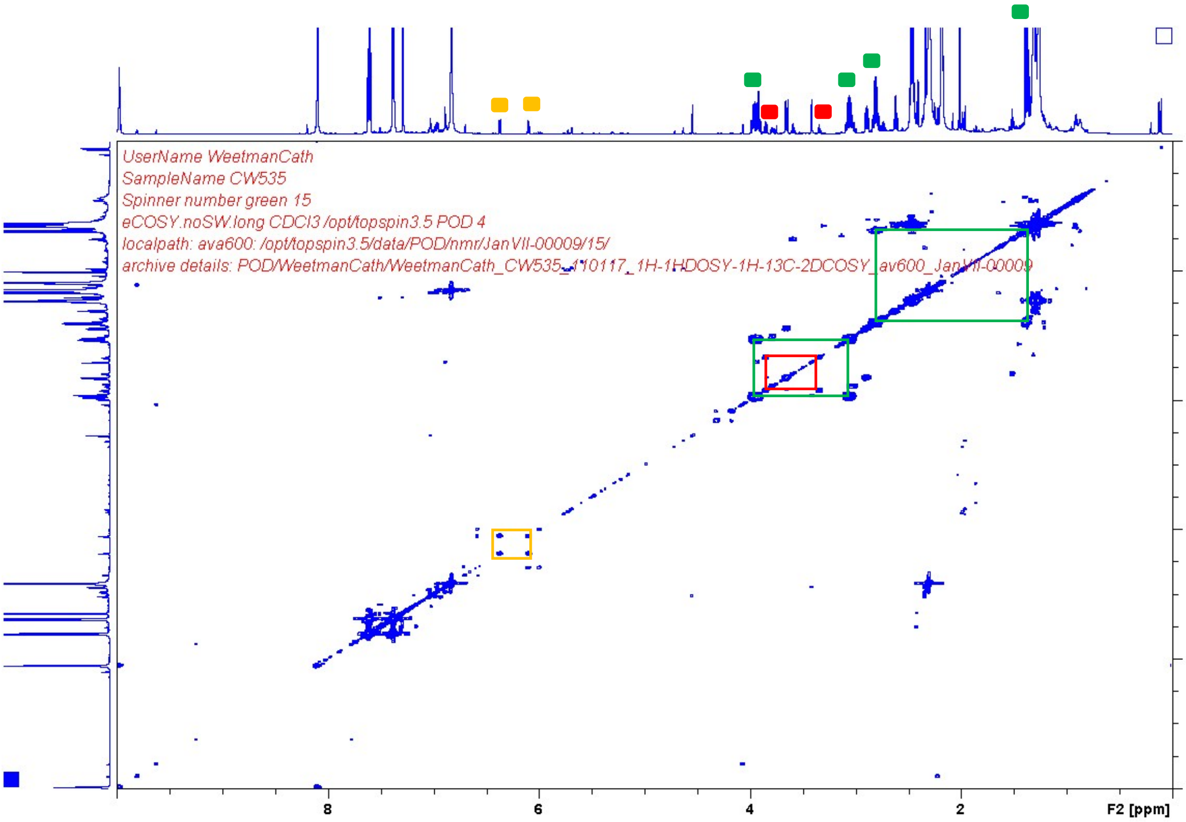


Figure 2. 1H-1H COSY NMR for reaction of 1-Ag with CEES

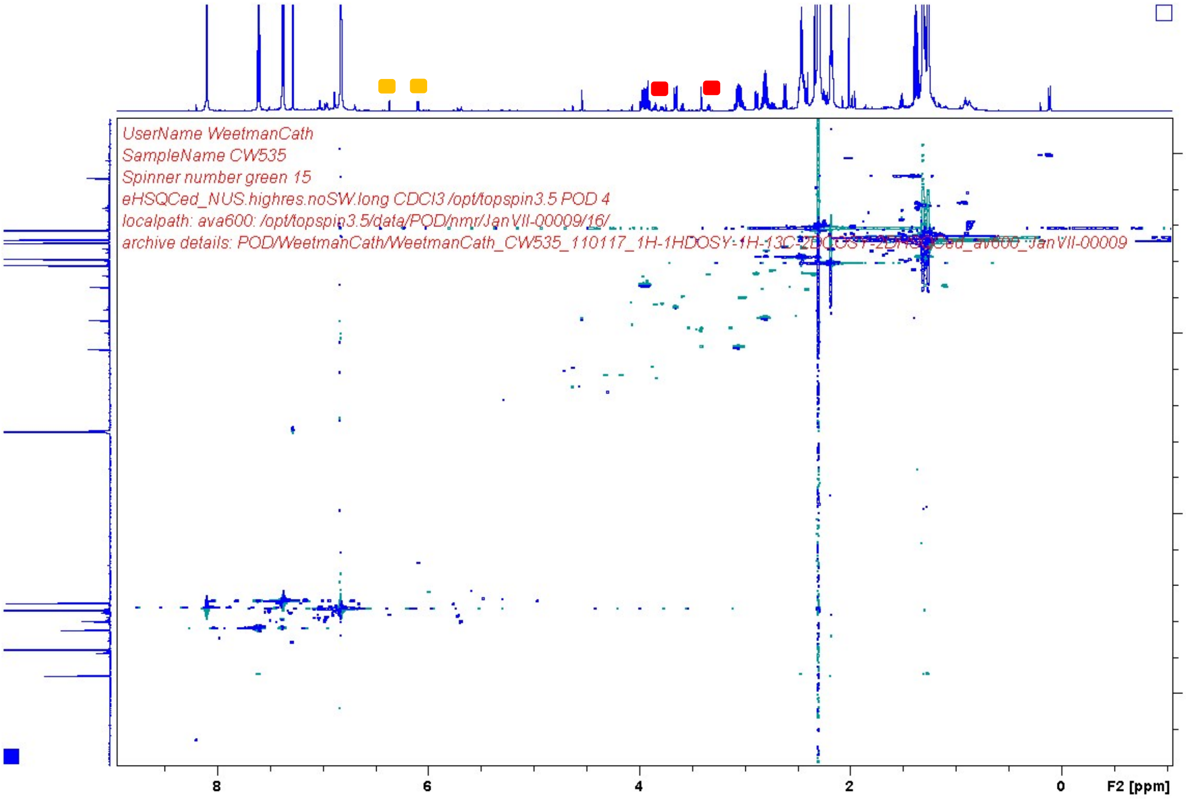


Figure 3. 1H-13C HSQC NMR for reaction of 1-Ag with CEES

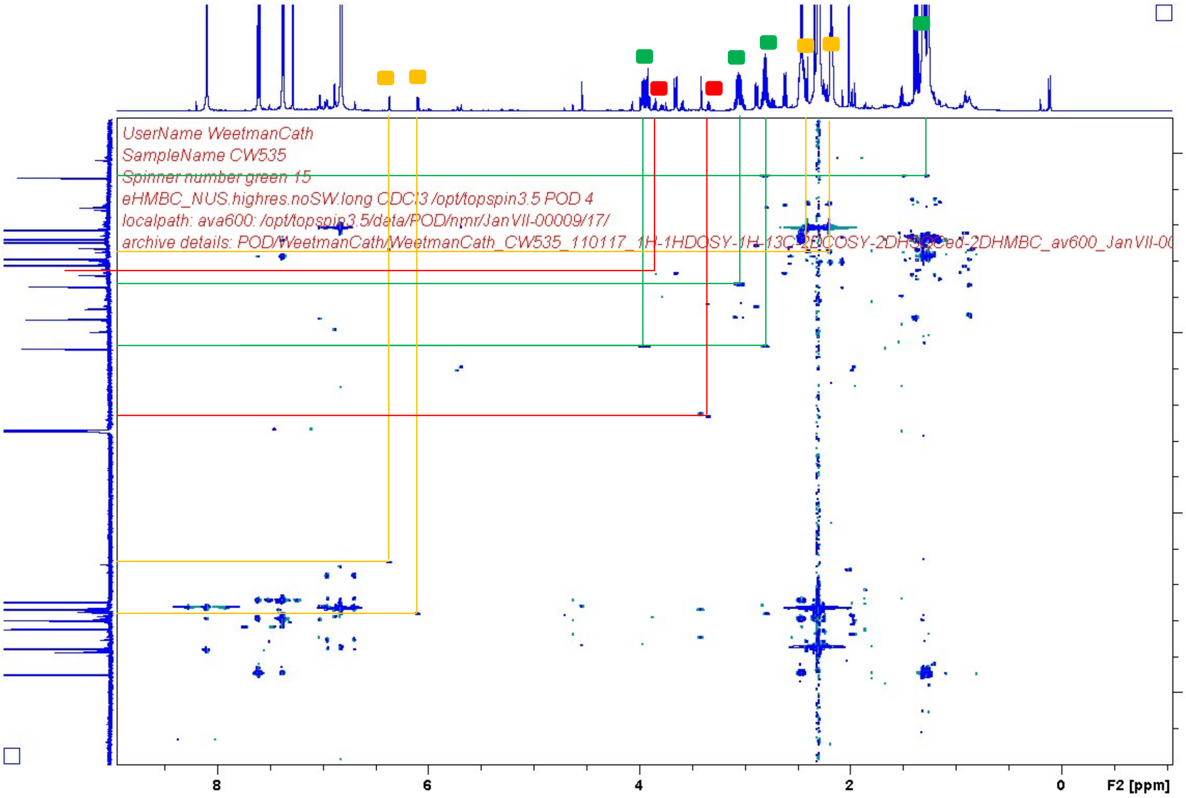


Figure 4. 1H-13C HMBC NMR for reaction of 1-Ag with CEES

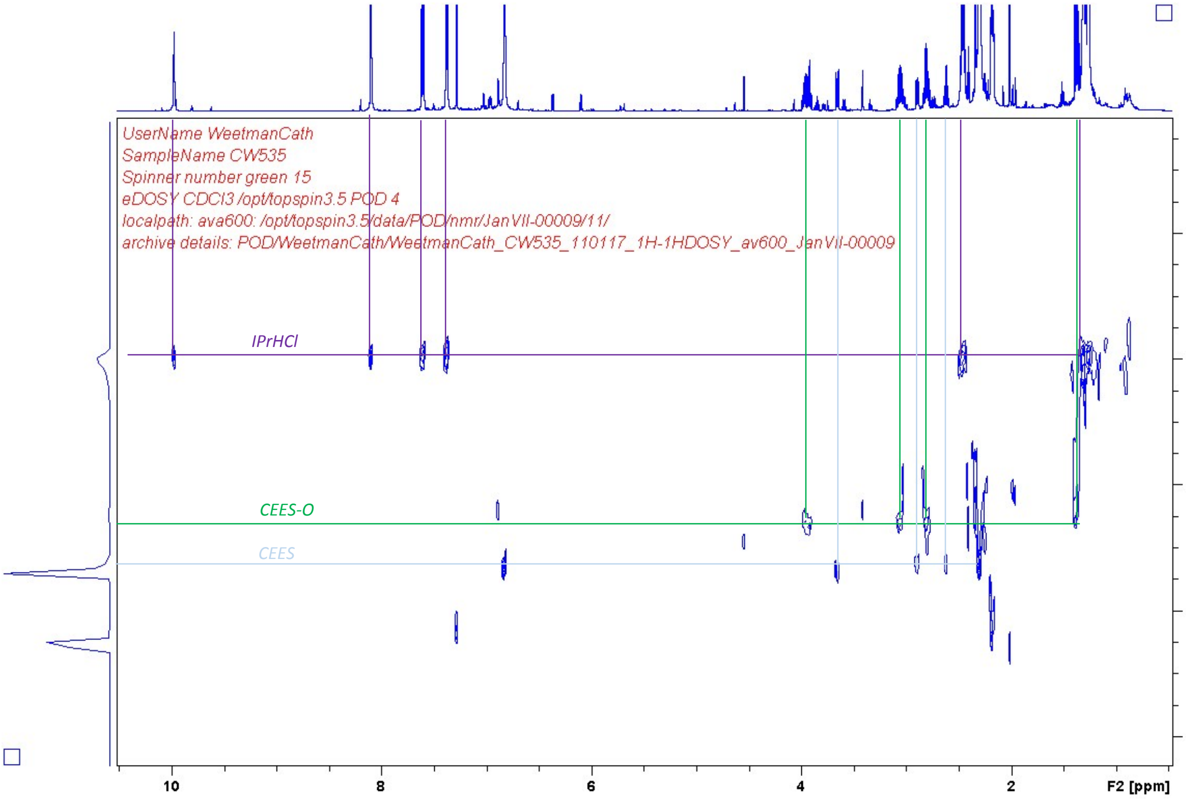


Figure 5. DOSY NMR for reaction of 1-Ag and CEES

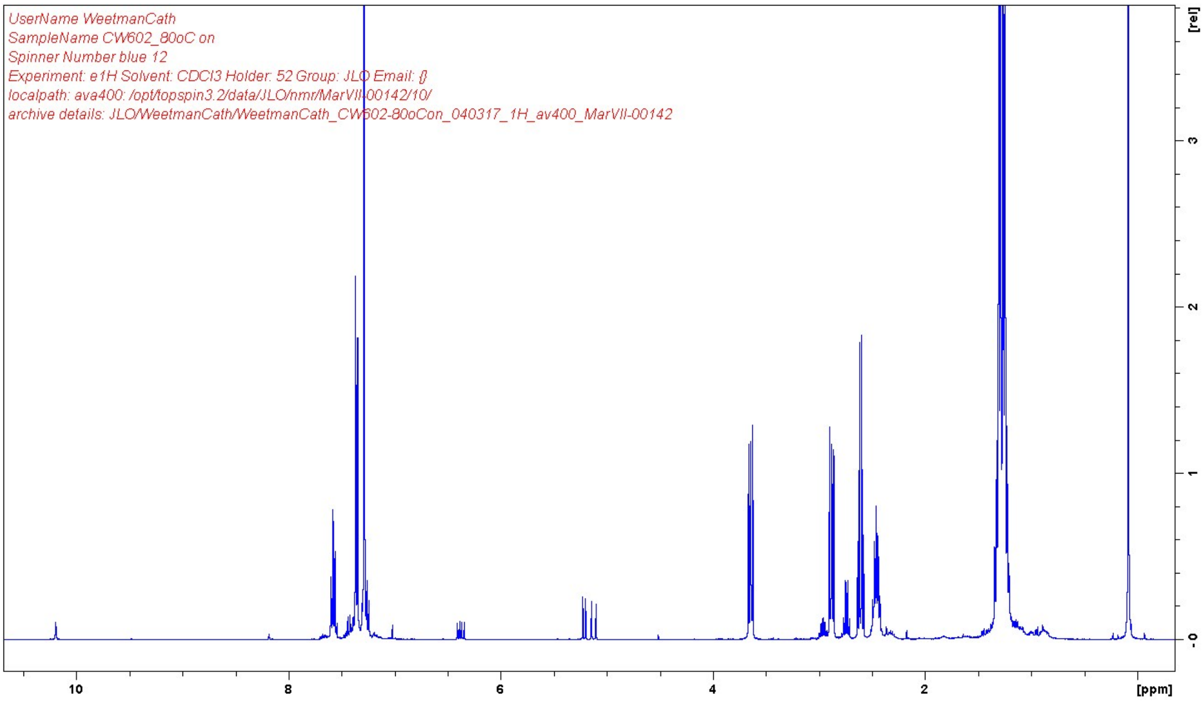


Figure 6. IPr and 1 eq CEES, after 24 hr at 80 ^{o}C

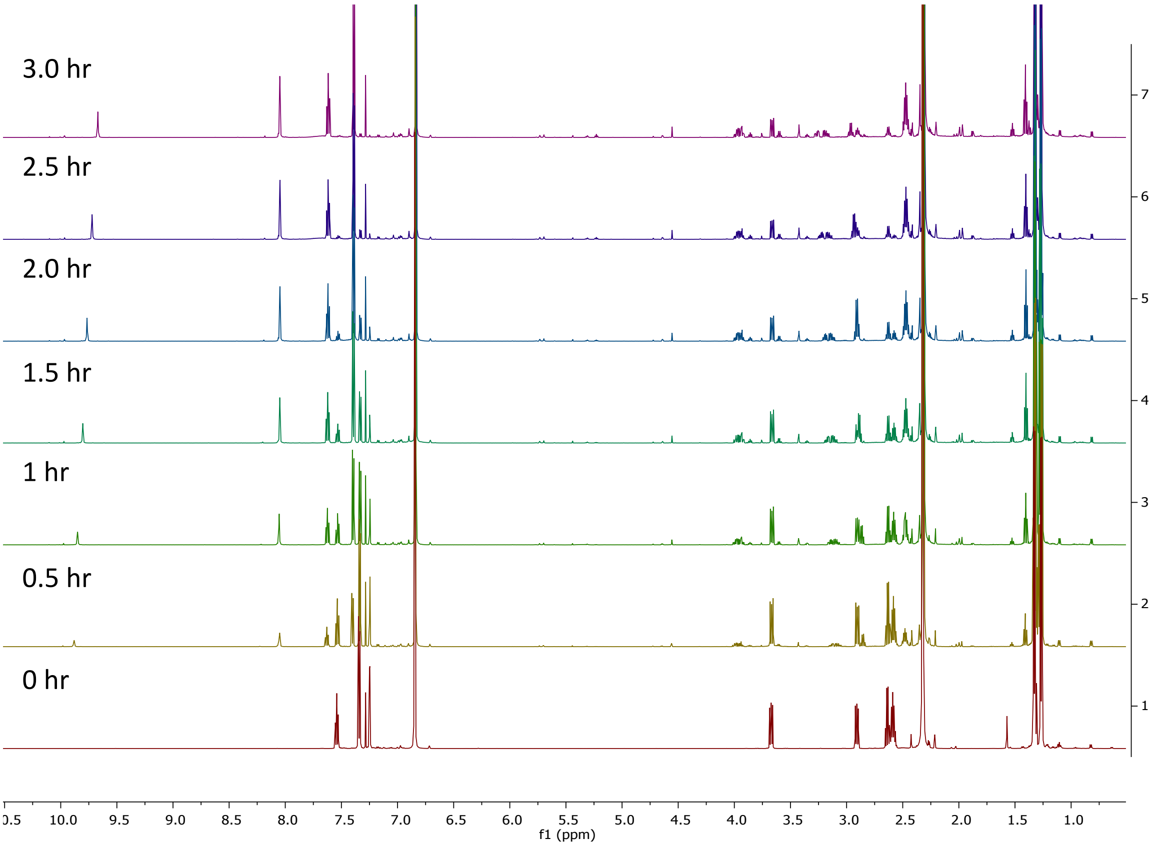


Figure 7. 1H NMR stack plot 30 minute intervals, 1-Ag + CEES

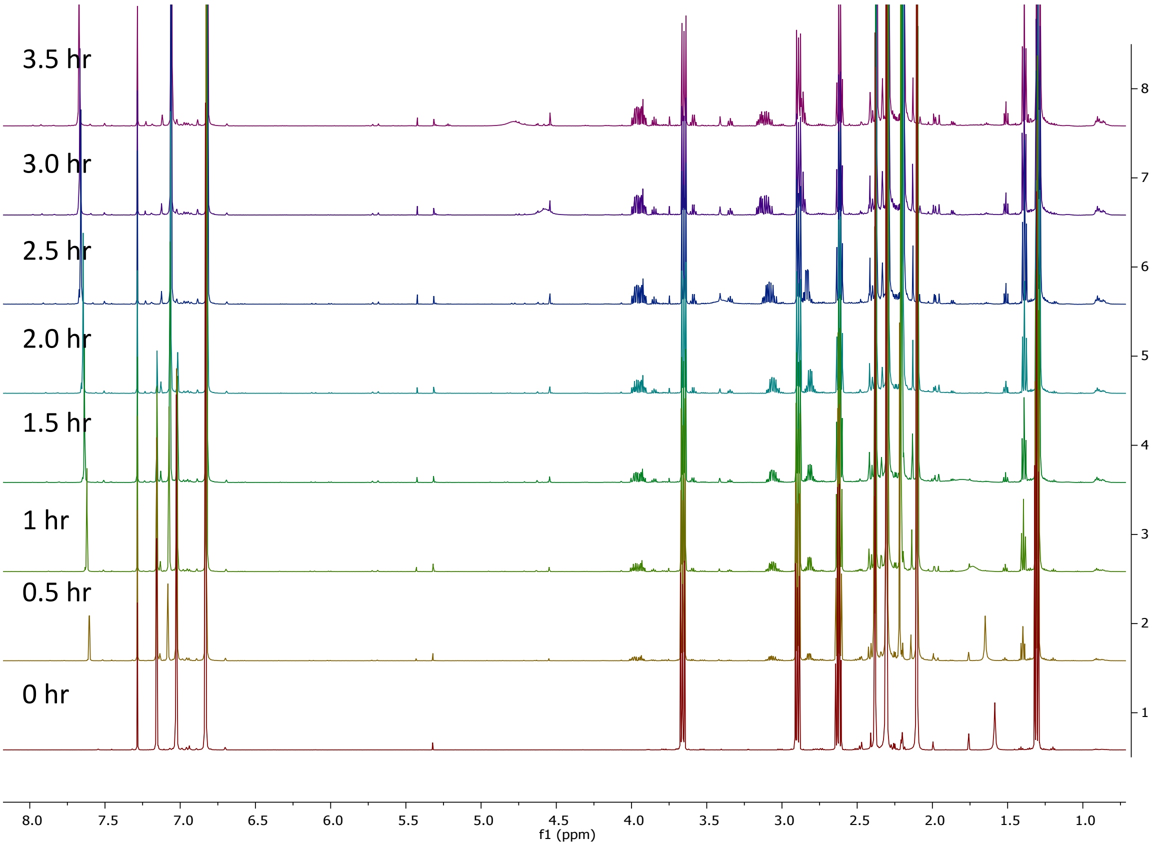


Figure 8. 1H NMR stack plot 30 minute intervals, 2-Ag + CEES

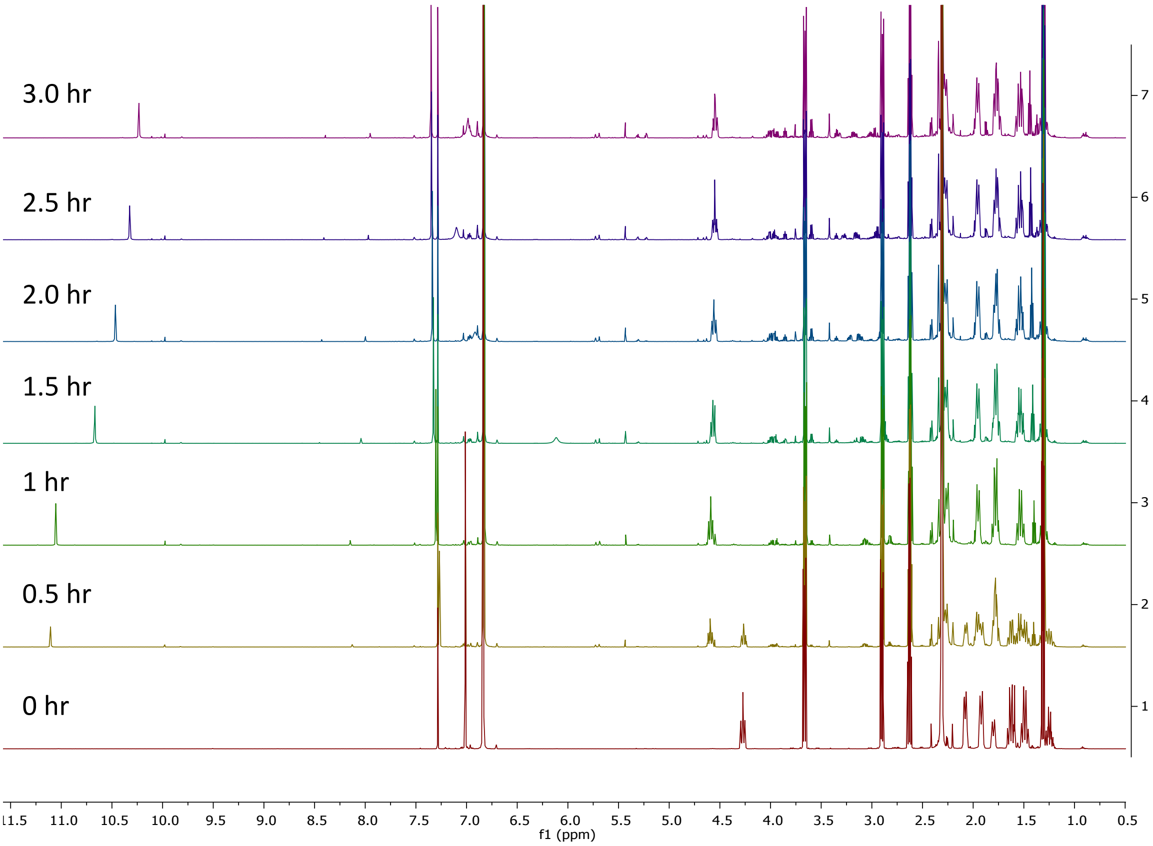


Figure 9. 1H NMR stack plot 30 minute intervals, 3-Ag + CEES

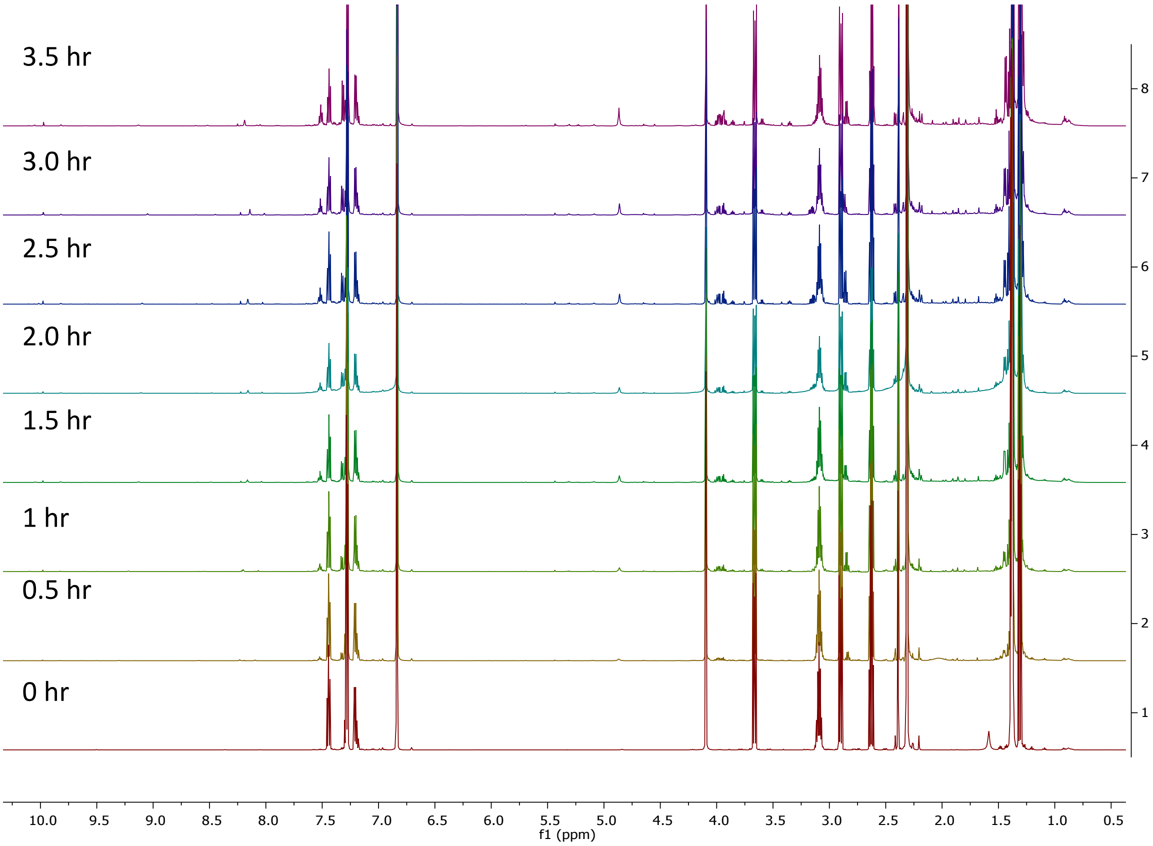


Figure 10. 1H NMR stack plot 30 minute intervals, 4-Ag + CEES

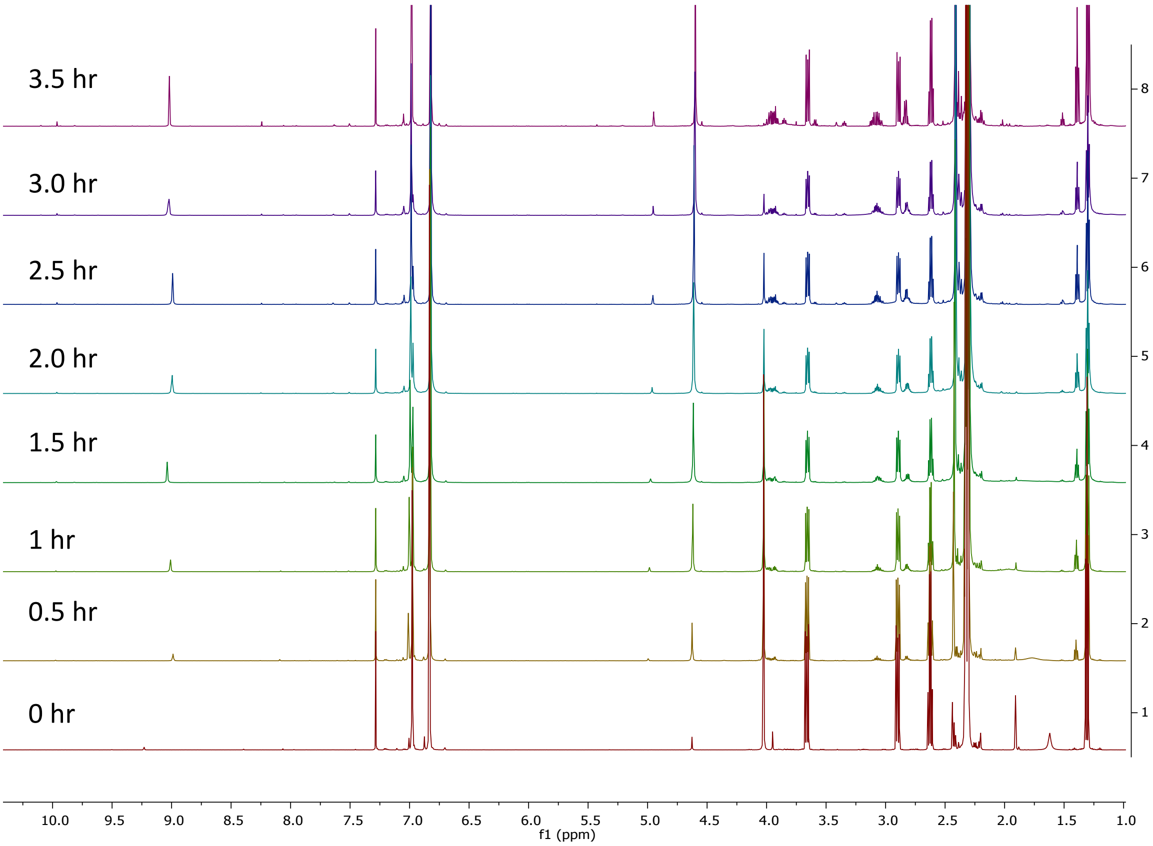


Figure 11. 1H NMR stack plot 30 minute intervals, 5-Ag + CEES

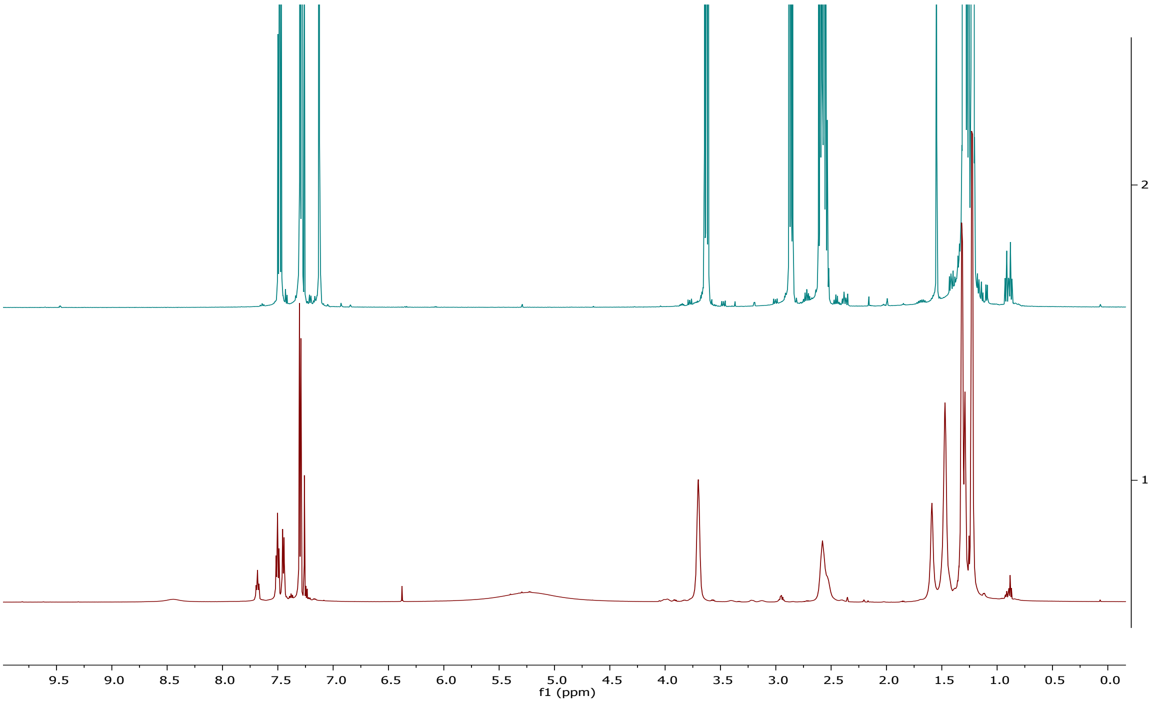
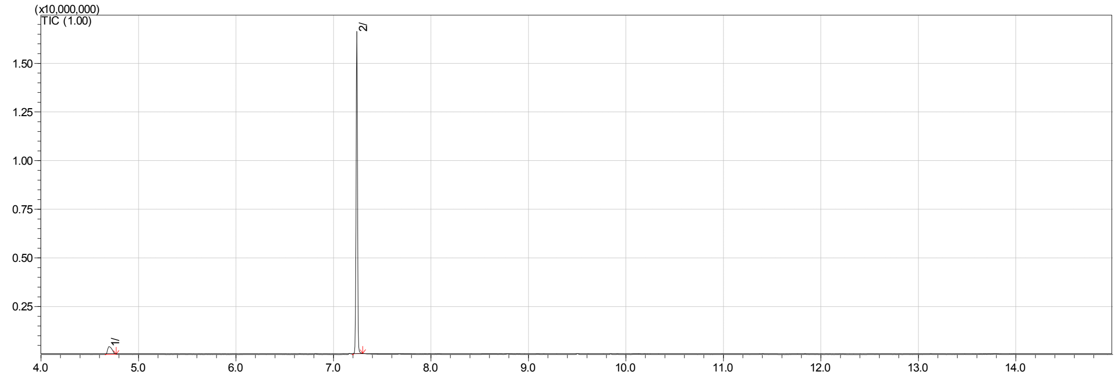


Figure 12. Stacked ^{1}H NMR spectra (top spectra – 1-Cu + CEES after addition; bottom spectra – after 5 hrs UV 254nm)



PEAK	RET. TIME	START TIME	END TIME	AREA	AREA %	HEIGHT	HEIGHT %	A/H	NAME
1	4.697	4.660	4.770	1265603	6.88	399073	2.35	3.17	Toluene
2	7.240	7.200	7.300	17129314	93.12	16568668	97.65	1.03	2-Chloroethyl ethyl sulfide

Figure 13. GC-MS trace of 1-Cu + CEES, after 5hrs UV (254 nm)

3. Destruction by vanadium-NHC complexes

General experimental procedure:

CEES (2.0 µL, 0.017 mmol) was added to a quartz NMR tube containing 0.5 mL $CDCl_3$ and #-Ag (0.017 mmol). A ^1H NMR was taken after addition and then placed under UV light (254 nm) and monitored every 30 minutes until CEES had been consumed. A small aliquot was taken every hour for GC-MS.

Paraoxon-ethyl (8.8 µmol) or Profenofos (8.8 µmol) was added to a quartz NMR tube containing 0.5 mL of **#-V** (8.8 µmol). ^1H, ^{31}P and ^{51}V NMR were taken after addition, and then placed under UV light (254 nm) and monitored at regular intervals using GC-MS.

On one occasion, crystals of a vanadium-containing decomposition product were isolated from a chloroform reaction mixture of $IMesVOCl_3$ and a stoichiometric amount of Paraoxon-ethyl after photolysis. The crystals were isolated in approx. 15% yield, and characterised by single crystal X-ray diffraction as the 1-D polymer of $(VO_2Cl_2PO_2)_n$.

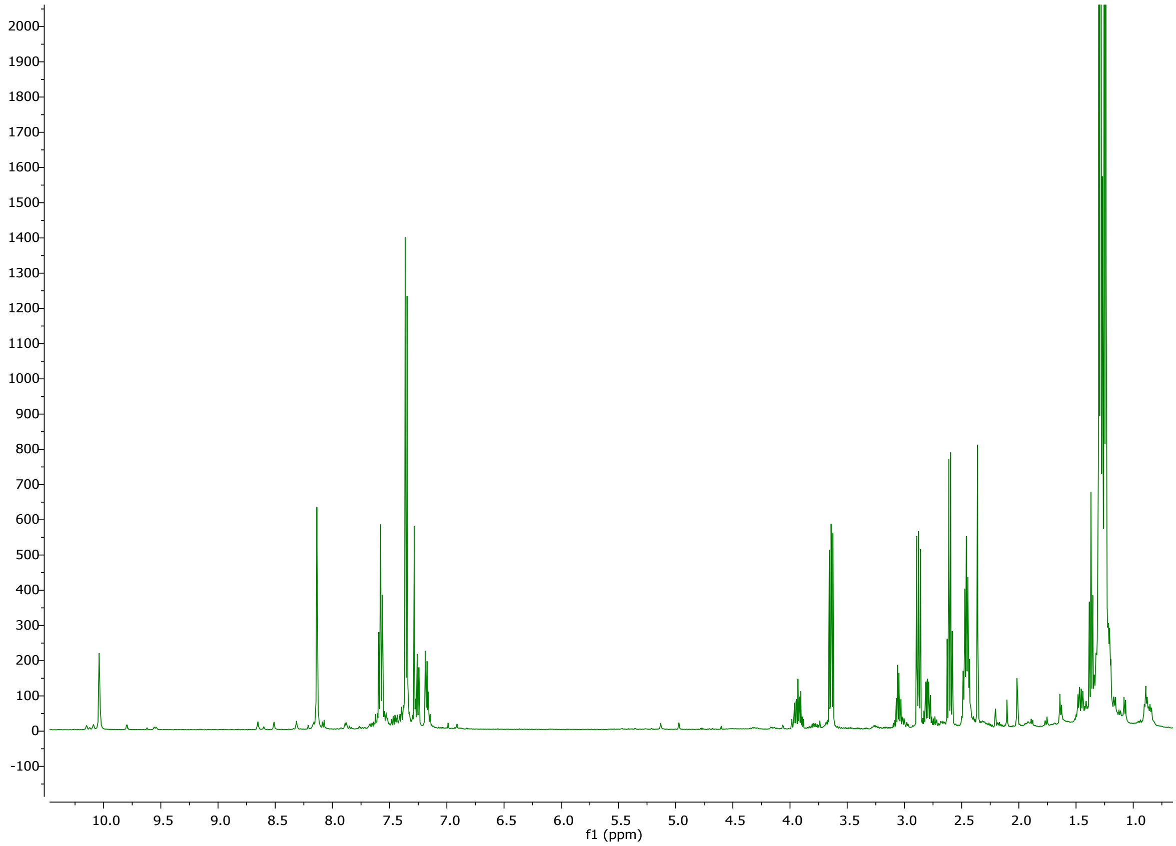
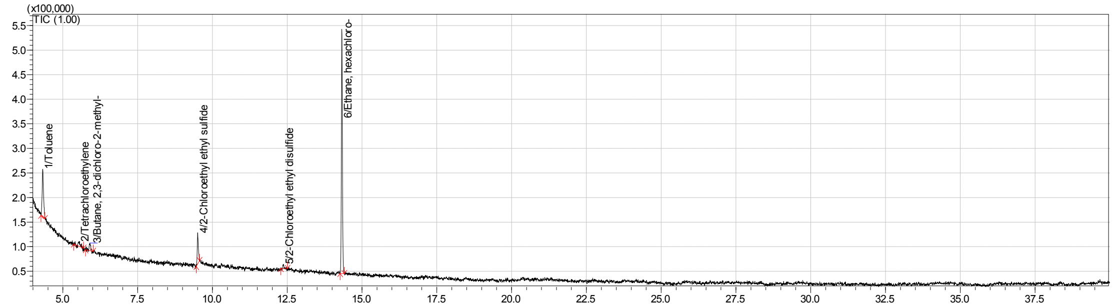
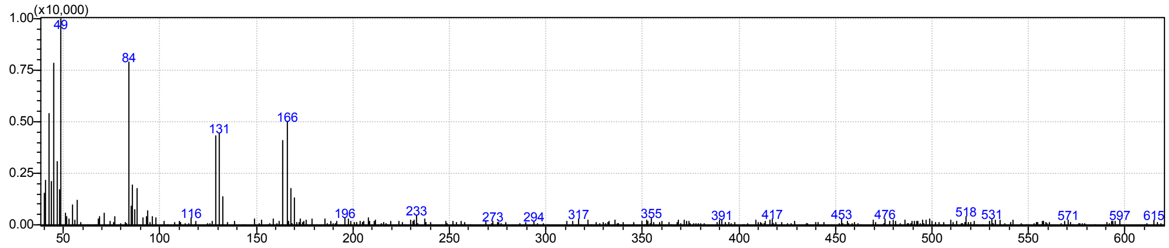


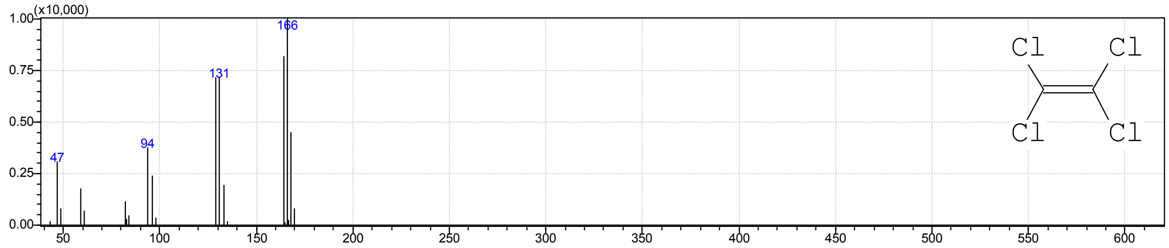
Figure 14. ^1H NMR of 1-V + CEES after 3 hours exposure to UV light (254 nm)

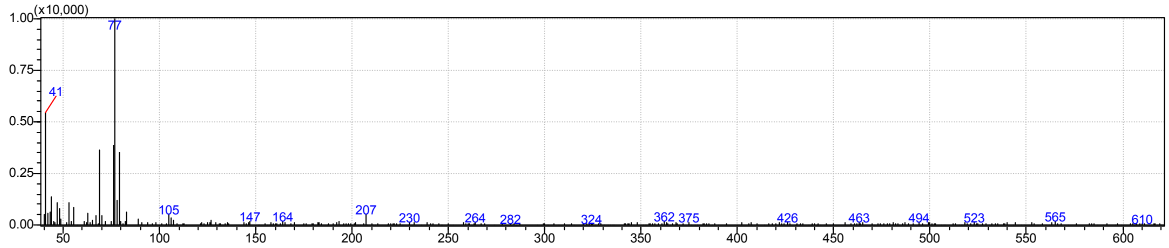


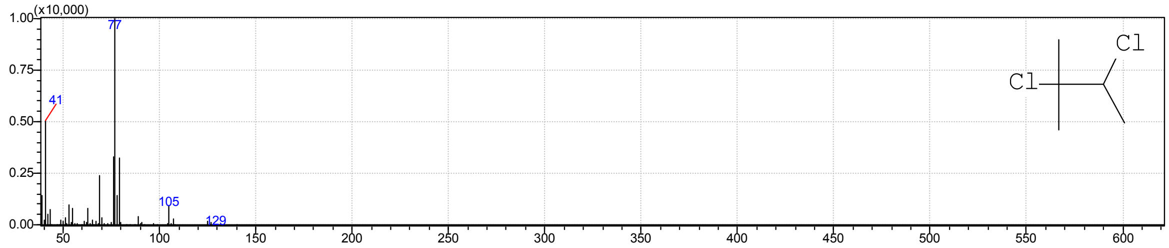
PEAK	R. TIME	I. TIME	F. TIME	AREA	AREA %	HEIGHT	HEIGHT %	A/H	NAME
1	4.326	4.270	4.400	316214	17.48	96633	13.99	3.27	Toluene
2	5.538	5.365	5.690	32243	1.78	9894	1.43	3.26	Tetrachloroethylene
3	5.903	5.755	6.015	45847	2.53	15446	2.24	2.97	Butane, 2,3-dichloro-2-methyl-
4	9.507	9.460	9.570	173293	9.58	63395	9.18	2.73	2-Chloroethyl ethyl sulfide
5	12.374	12.285	12.510	12101	0.67	8430	1.22	1.44	2-Chloroethyl ethyl disulfide
6	14.326	14.270	14.410	1229014	67.96	496811	71.94	2.47	Hexachloroethane

Figure 15. GC-MS trace 2-V and CEES (3 hours)









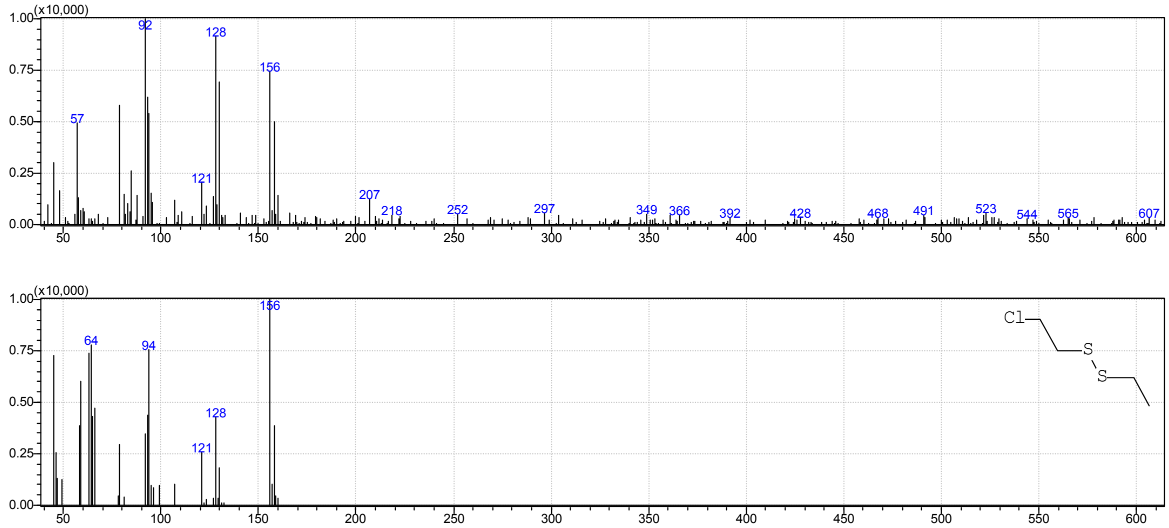
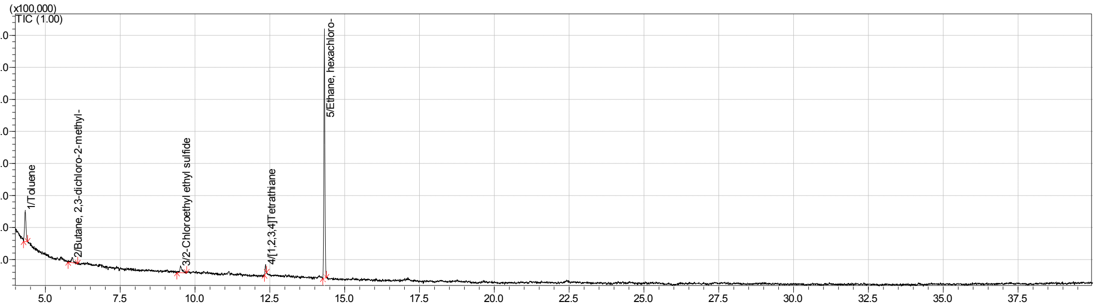
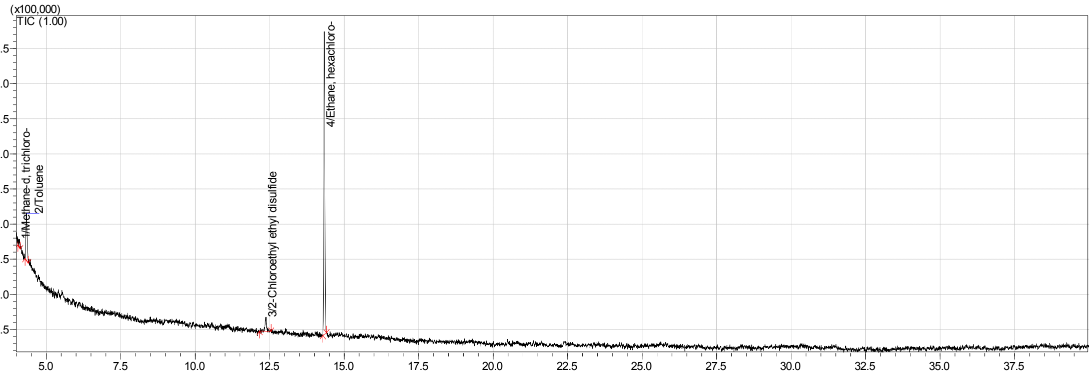


Figure 16. Selected MS peaks from GC-MS trace (upper found, lower predicted structure)



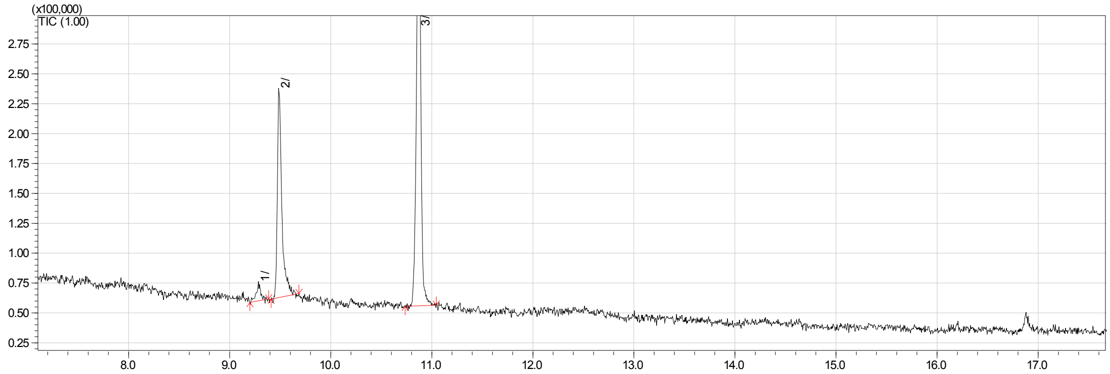
PEAK	R. TIME	I. TIME	F. TIME	AREA	AREA %	HEIGHT	HEIGHT %	A/H	NAME
1	4.325	4.270	4.405	328925	13.34	98065	10.39	3.35	Toluene
2	5.892	5.755	6.080	82512	3.35	16355	1.73	5.05	Butane, 2,3-dichloro-2-methyl-
3	9.515	9.395	9.720	114381	4.64	21791	2.31	5.25	2-Chloroethyl ethyl sulfide
4	12.355	12.320	12.390	60614	2.46	29177	3.09	2.08	2-Chloroethyl ethyl disulfide
5	14.321	14.270	14.390	1879240	76.21	778216	82.48	2.41	Ethane, hexachloro-

Figure 17. GC-MS trace of 2-V and CEES (5 hours)



PEAK	R. TIME	I. TIME	F. TIME	AREA	AREA %	HEIGHT	HEIGHT %	A/H	NAME
1	4.100	4.045	4.125	25965	1.93	12116	2.28	2.14	Methane-d, trichloro-
2	4.334	4.290	4.395	201162	14.95	67298	12.68	2.99	Toluene
3	12.375	12.160	12.545	71531	5.32	20324	3.83	3.52	2-Chloroethyl ethyl disulfide
4	14.332	14.280	14.405	1047027	77.80	431042	81.21	2.43	Ethane, hexachloro-

Figure 18. GC-MS trace of 2-V and CEES (6 hours)



PEAK	R. TIME	I. TIME	F. TIME	AREA	AREA %	HEIGHT	HEIGHT %	A/H	NAME
1	9.285	9.200	9.385	44861	2.64	16203	2.76	2.77	Diethyl disulfide
2	9.487	9.410	9.685	537544	31.58	175148	29.80	3.07	2-Chloroethyl ethyl sulfide
3	10.871	10.735	11.045	1119935	65.78	396390	67.44	2.83	Mesitylene

Figure 19. GC-MS trace of 2-V and CEES in C6D6

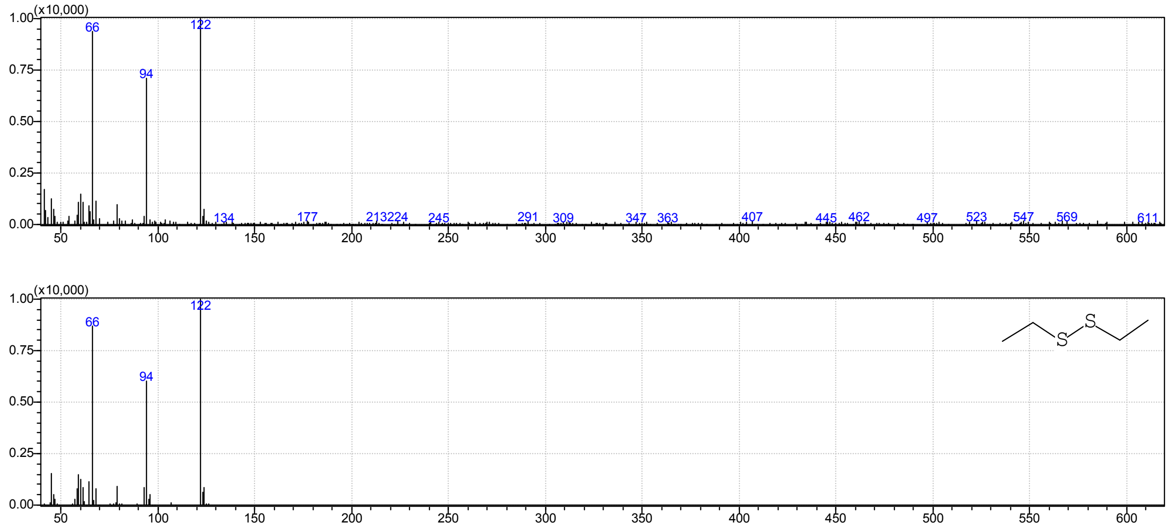
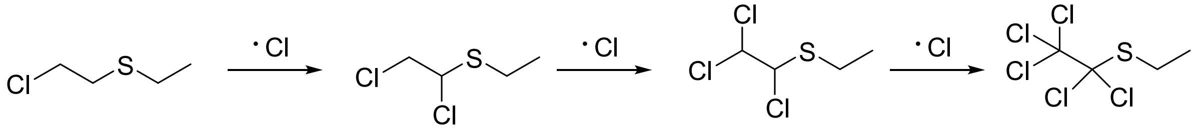


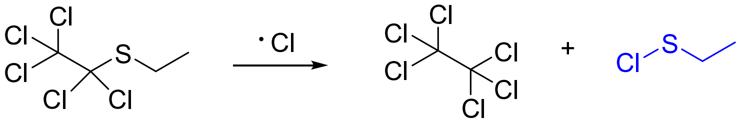
Figure 20. Selected MS peaks from GC-MS trace (Top found, bottom predicted)

Chlorination of CEES - proposed mechanism via chloride radical for **both solvents**

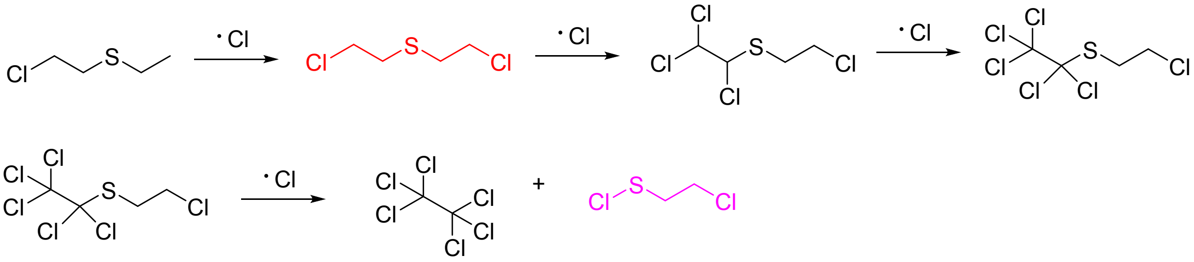
Initial ·Cl attack to form tri, tet & hexachloride species - chlorination is fast through to hexachloroethane



hexachloridesulphide reacts further to form hexachloroethane and ethyl hypochlorothioite



Chlorination of CEES - proposed mechanism in **Chloroform**



Excess chloride radicals in solution increase chances of attack on ethyl group leading to initial formation of mustard gas which rapidly undergoes attack via a second chloride radical and so on.

Combination of 2 products

Benzene

Chloroform

Figure 21. Proposed mechanism for chloride radical destruction of CEES

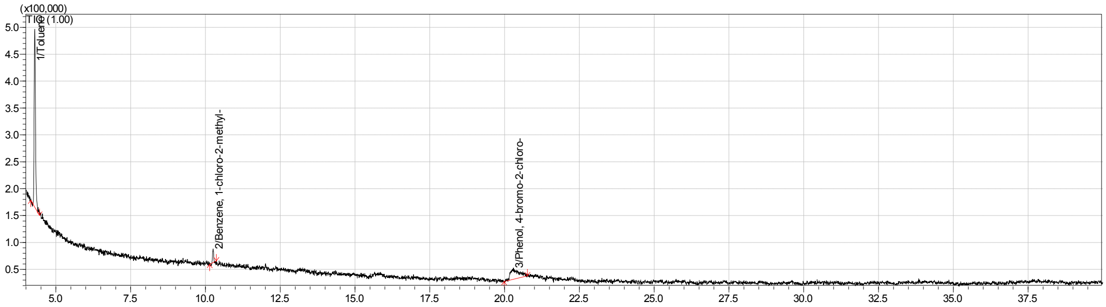
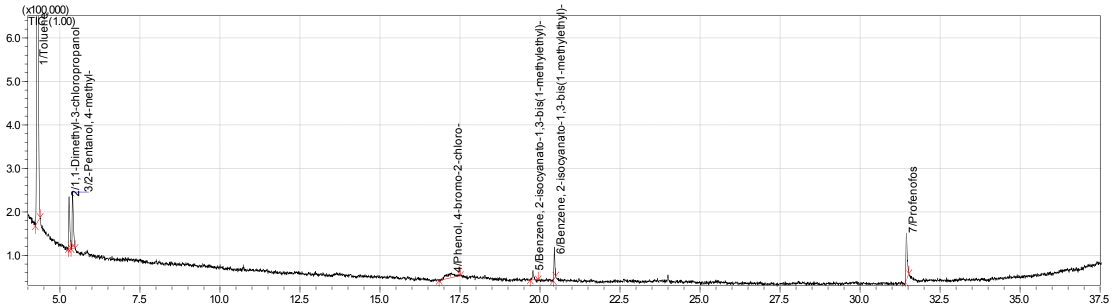


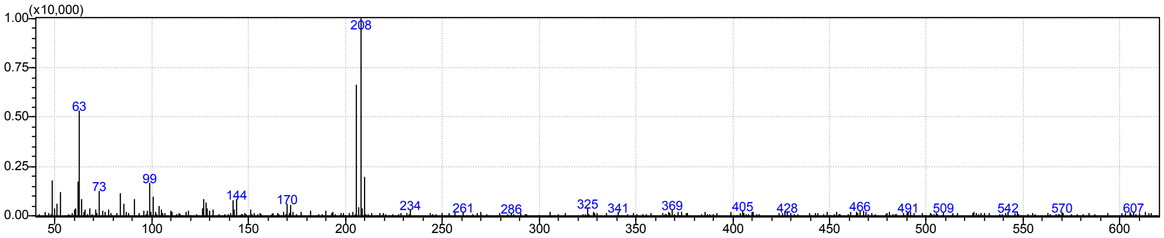
Figure 22. 2-V and Profenofos (3.5hr)

PEAK	R. TIME	I. TIME	F. TIME	AREA	AREA %	HEIGHT	HEIGHT %	A/H	NAME
1	4.293	4.160	4.455	1056900	71.02	330590	87.58	3.20	Toluene
2	10.256	10.140	10.365	45803	3.08	25607	6.78	1.79	Benzene, 1-chloro-2-methyl-
3	20.294	19.985	20.765	385507	25.90	21276	5.64	18.12	Phenol, 4-bromo-2-chloro-



PEAK	R. TIME	I. TIME	F. TIME	AREA	AREA %	HEIGHT	HEIGHT %	A/H	NAME
1	4.295	4.230	4.385	3228512	71.26	1046364	69.41	3.09	Toluene
2	5.284	5.260	5.345	286610	6.33	120086	7.97	2.39	1,1-Dimethyl-3-chloropropanol
3	5.394	5.345	5.475	355732	7.85	129616	8.60	2.74	2-Pentanol, 4-methyl-
4	17.235	16.845	17.515	175106	3.87	11279	0.75	15.52	Phenol, 4-bromo-2-chloro-
5	19.779	19.695	19.945	47741	1.05	21551	1.43	2.22	Benzene, 2-isocyanato-1,3-bis(1-methylethyl)-
6	20.450	20.415	20.490	137160	3.03	72201	4.79	1.90	Benzene, 2-isocyanato-1,3-bis(1-methylethyl)-
7	31.453	31.410	31.525	299509	6.61	106271	7.05	2.82	Profenofos

Figure 23. GC-MS trace of 1-V + Profenofos (4 hr)



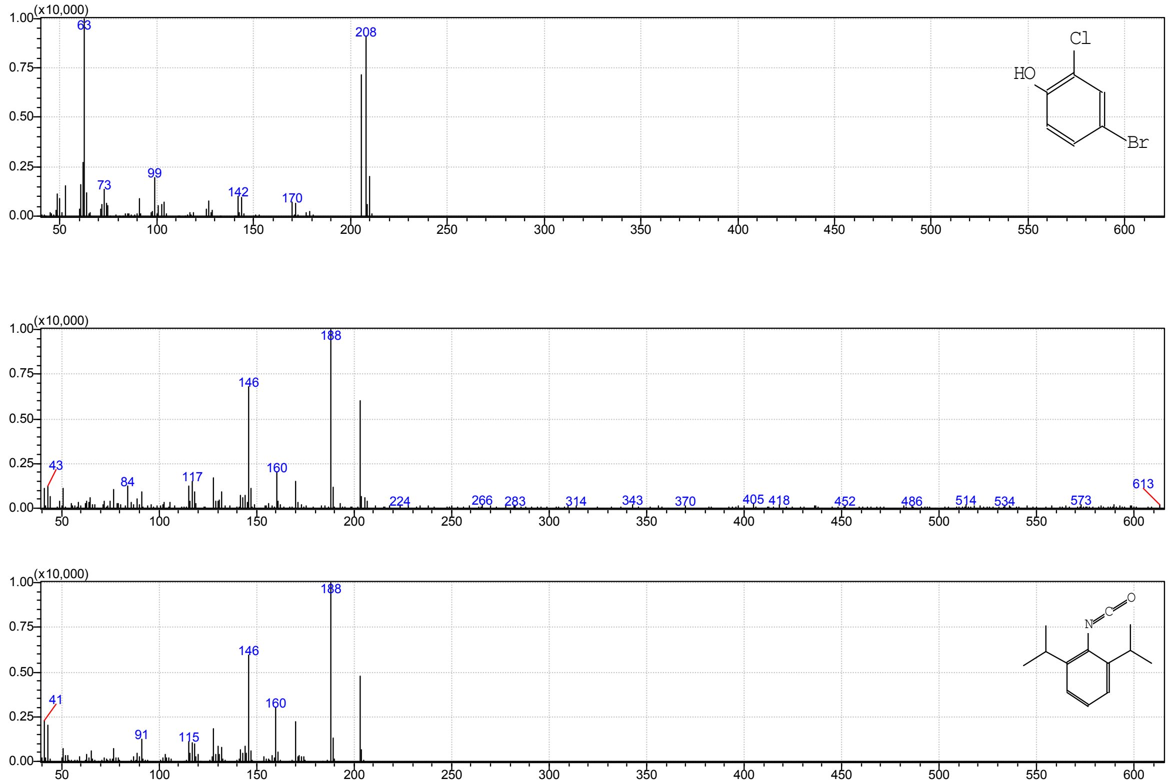


Figure 24. Selected MS peaks from GC-MS trace (Top found, bottom predicted)

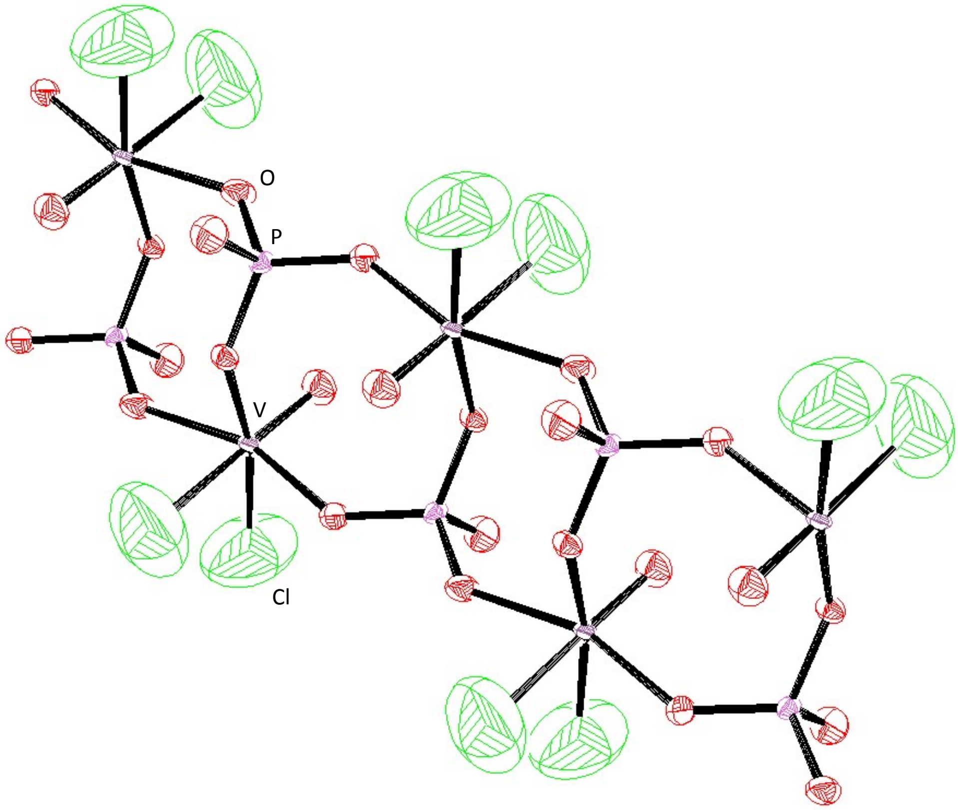


Figure 25. ORTEP representation of a section of the 1-D polymer of $(VO_2Cl_2PO_2)_n$; isolated in low yield from a nerve-agent simulant destruction reaction. Thermal ellipsoids drawn at the 50% probability level. Sodium counter ion omitted for clarity.

Table S1. Crystallographic data summary for 1D polymer $(VO_2Cl_2PO_2)$

Complex	$(VO_2Cl_2PO_2)_n$
Local code	p16148a_mono
Chemical formula	$ClO_{2.5}P_{0.5}V_{0.5}\cdot Na$
M_r	139.40
Crystal system, space group	Monoclinic, *I*2/*m*
Temperature (K)	170
a, *b*, *c* (Å)	7.3580 (6), 6.3903 (6), 15.2247 (16)
α, β, γ (°)	90.318 (9)
V (Å^3)	715.85 (12)
Z	8
Radiation type	Mo *K*a

μ (mm^{-1})	2.44
Crystal size (mm)	0.16 × 0.07 × 0.04
Diffractometer	Xcalibur, Eos
Absorption correction	Multi-scan
T_{min}, T_{max}	0.859, 0.953
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	5177, 675, 566
R_{int}	0.057
$(\sin \theta/\lambda)_{max}$ ($Å^{-1}$)	0.588
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.098, 0.263, 1.13
No. of reflections	675
No. of parameters	51
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	1.53, -1.72
CCDC number	1580495

4. Destruction by complexes of tethered-NHCs

CEES (2.8 µL, 0.024 mmol) was added to a NMR tube containing 0.5 mL $CDCl_3$ and **6-M** (0.024 mmol). A ^1H NMR was taken after addition and then placed in a pre-heated oil bath to 80 °C and monitored at regular intervals using ^1H NMR and GC-MS spectroscopy.

Paraoxon-ethyl (2.6 µL, 12 µmol) or Profenofos (3.0 µL, 12 µmol) were added to a NMR tube containing 0.5 mL of $CDCl_3$ with **6-M** (12 µmol). ^1H, ^{31}P were taken after addition, and then placed in a pre-heated oil bath to 80 °C and monitored at regular intervals using ^1H, ^{31}P and GC-MS.

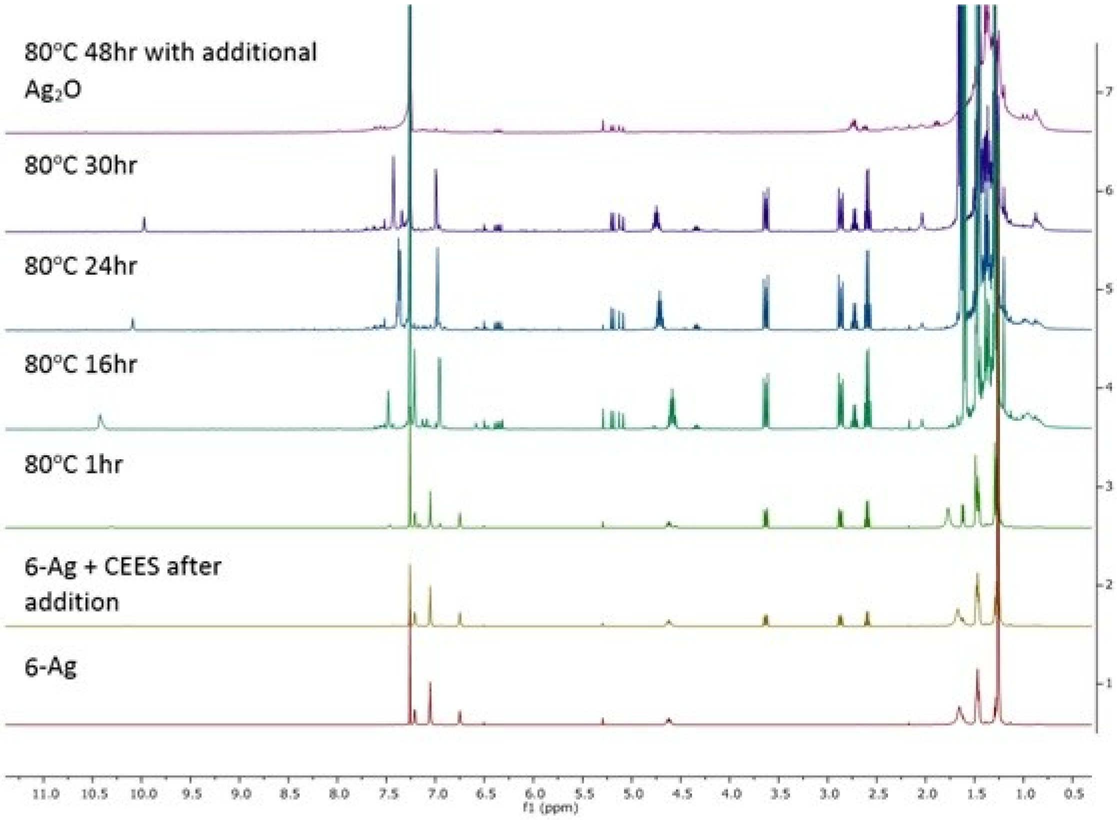


Figure 26. 1H NMR stack plot for reaction of 6-Ag and CEES

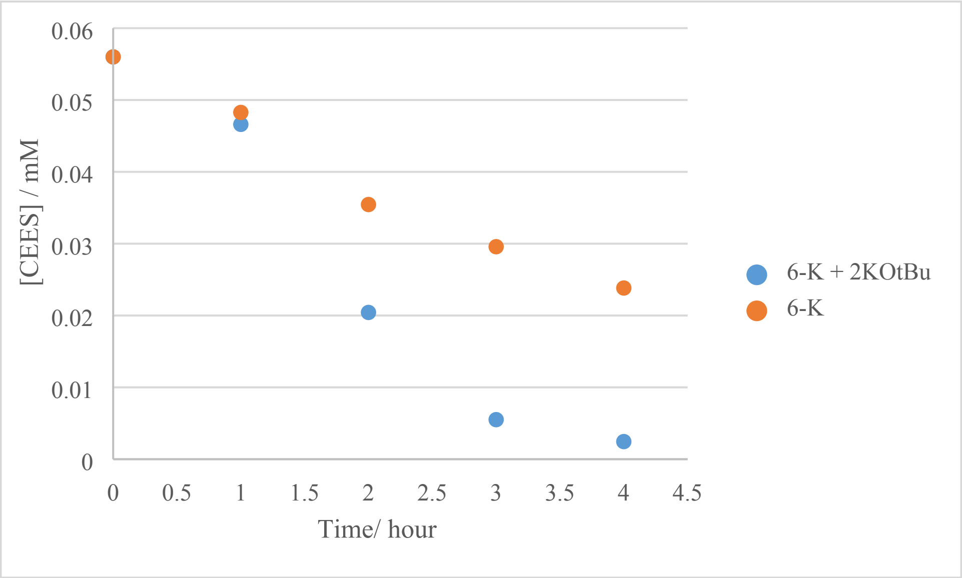
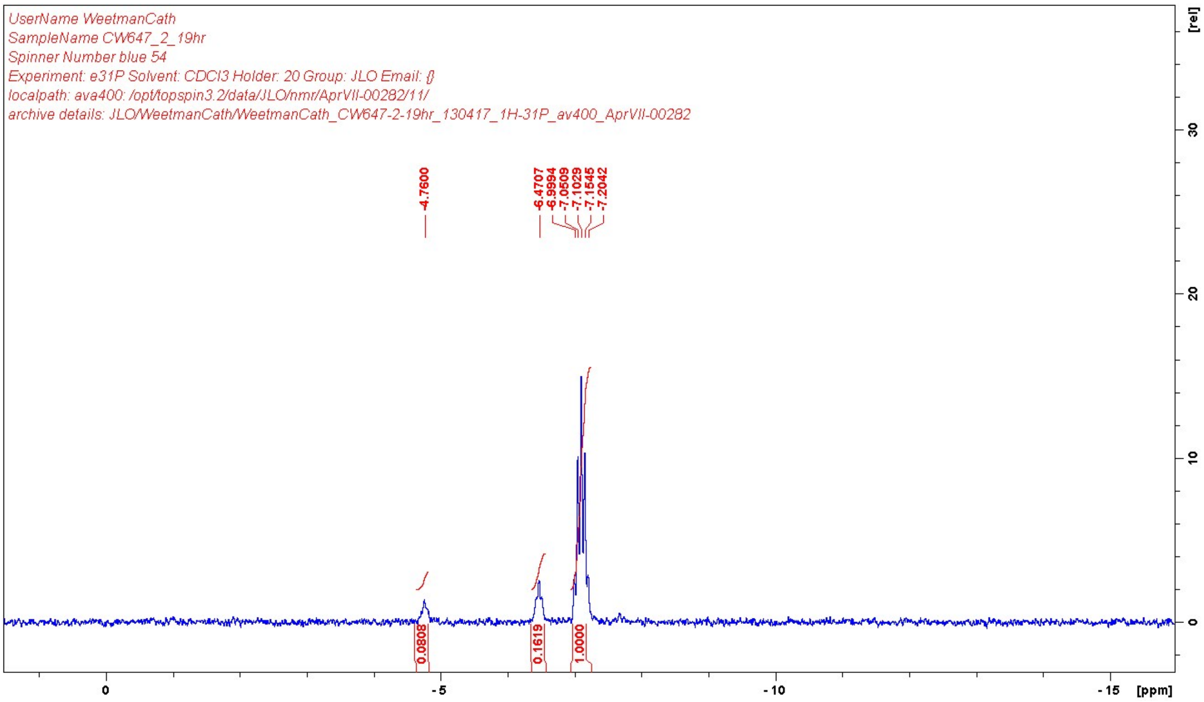


Figure 27. Graph showing destruction of CEES with 6-K (orange) and 6-K with an additional 2 equivalents of KOtBu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SampleName CW647_2_19hr
Spinner Number blue 54
Experiment: e31P Solvent: CDCl3 Holder: 20 Group: JLO Email: {}
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archive details: JLO/WeetmanCath/WeetmanCath_CW647-2-19hr_130417_1H-31P_av400_AprVII-00282

Figure 28. 31P NMR spectrum of 6-Ag and Paraoxon after 19 hrs at 80 ^{o}C

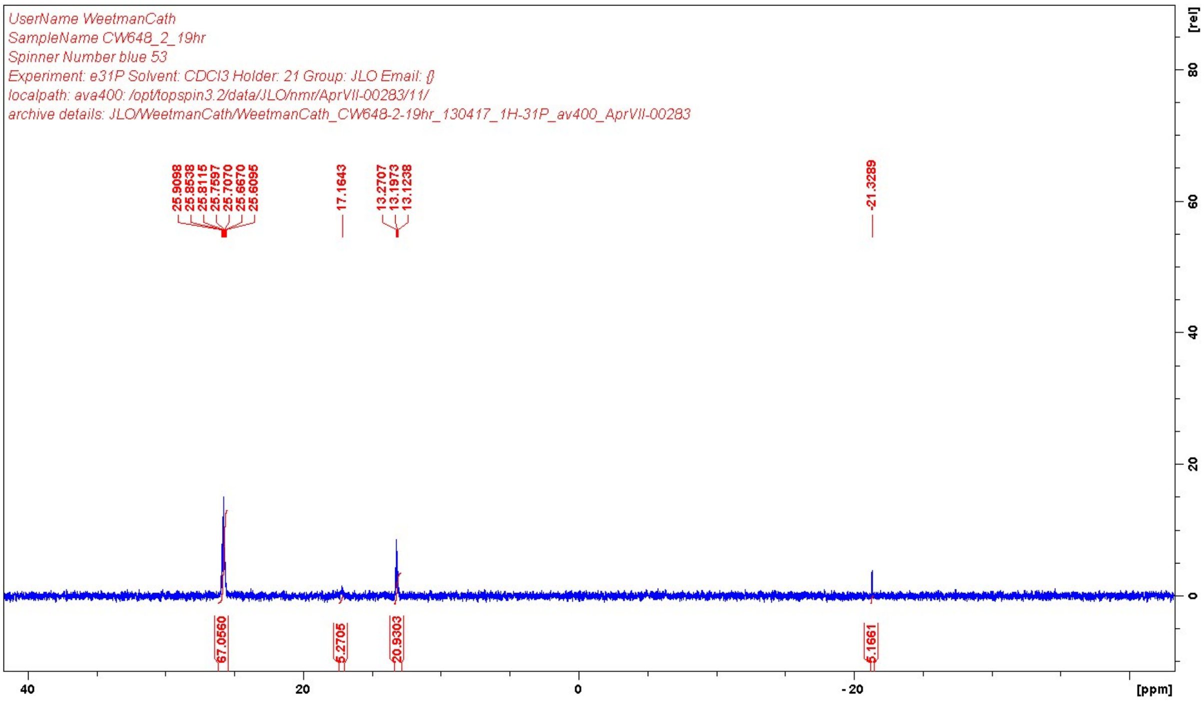


Figure 29. 31P NMR spectrum of 6-Ag and Profenofos after 19 hrs at 80 ^{o}C

5. Catalytic CWA destruction

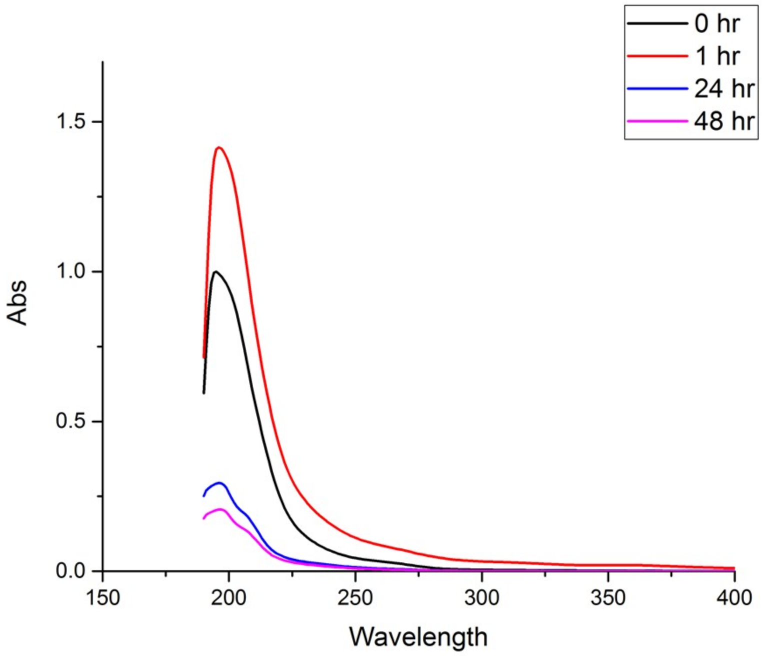


Figure 30. 5 mol% IMes.HCl, 5 mol% $NiCl_2$, 20 mol% KOtBu and CEES over 48 hr period at 80 ◦C in MeCN

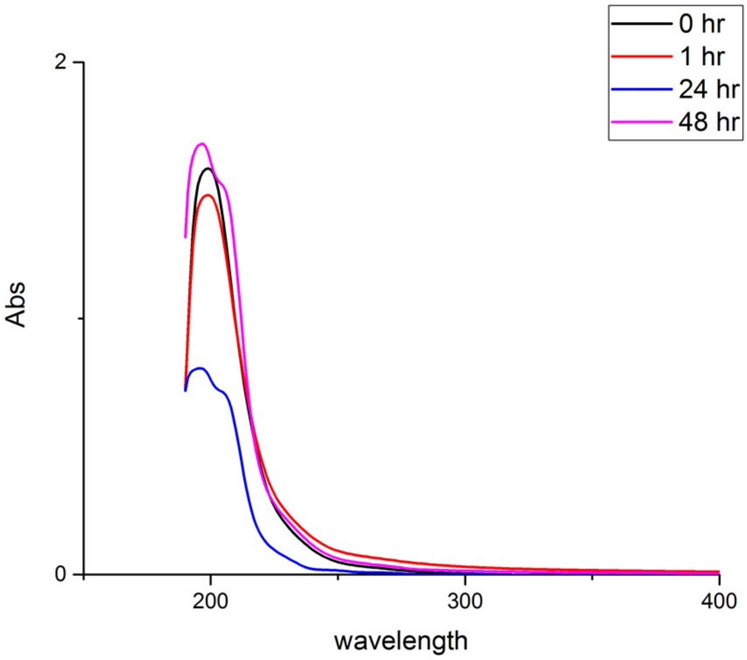


Figure 31. 5 mol% IMes.HCl, 5 mol% $FeBr_2$, 20 mol% KOtBu and CEES over 48 hr period at 80 ◦C in MeCN

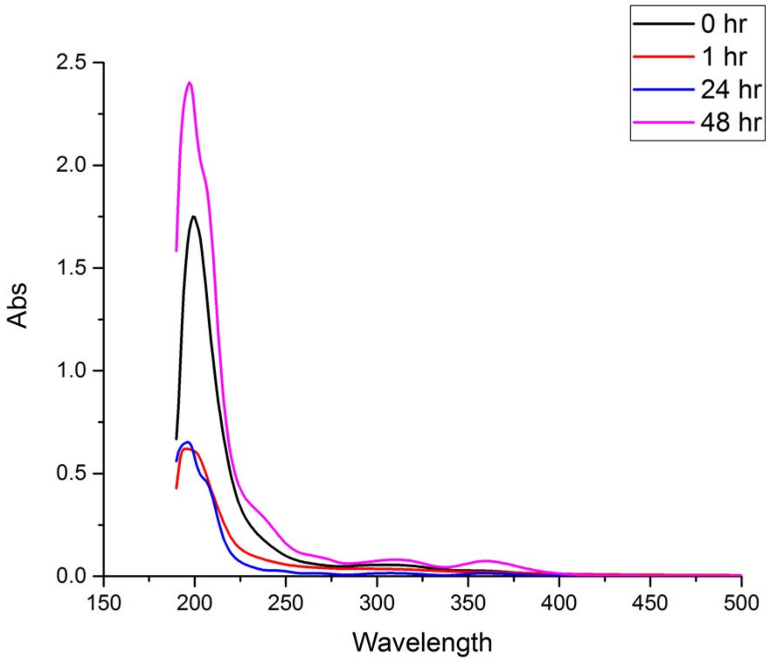


Figure 32. 5 mol% IMes.HCl, 5 mol% $FeCl_3$, 20 mol% KOtBu and CEES over 48 hr period at 80 ◦C in MeCN

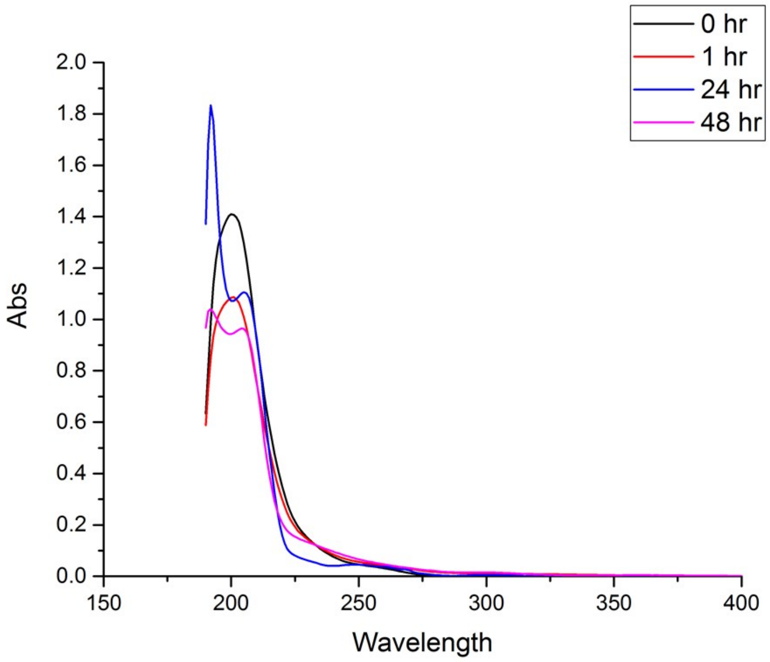


Figure 33. 5 mol% ICy.HCl, 5 mol% $NiCl_2$, 20 mol% KOtBu and CEES over 48 hr period at 80 ◦C in MeCN

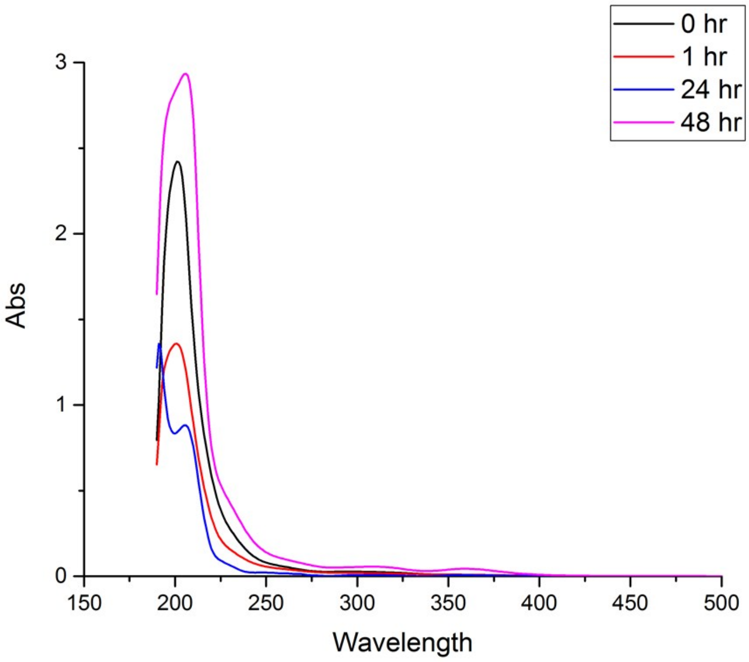


Figure 34. 5 mol% ICy.HCl, 5 mol% $FeBr_2$, 20 mol% KOtBu and CEES over 48 hr period at 80 ◦C in MeCN

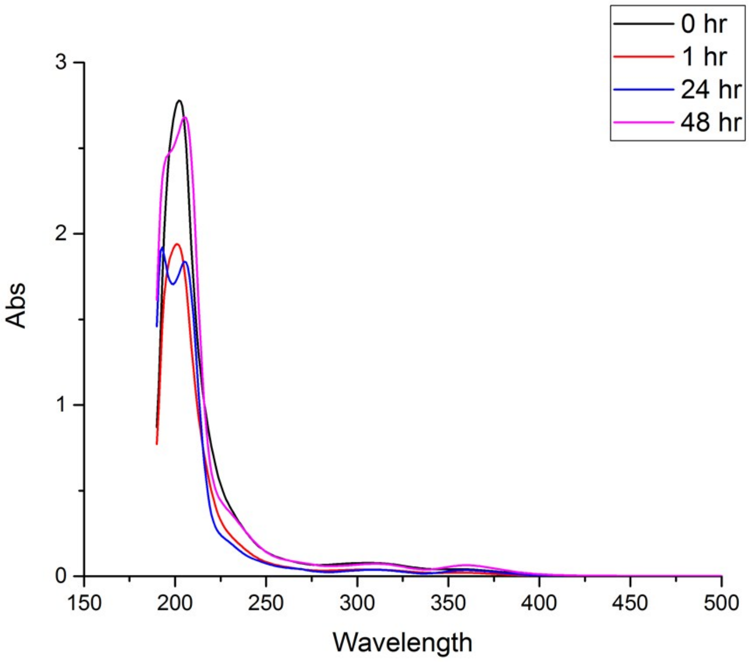


Figure 35. 5 mol% ICy.HCl, 5 mol% $FeCl_3$, 20 mol% KOtBu and CEES over 48 hr period at 80 ◦C in MeCN

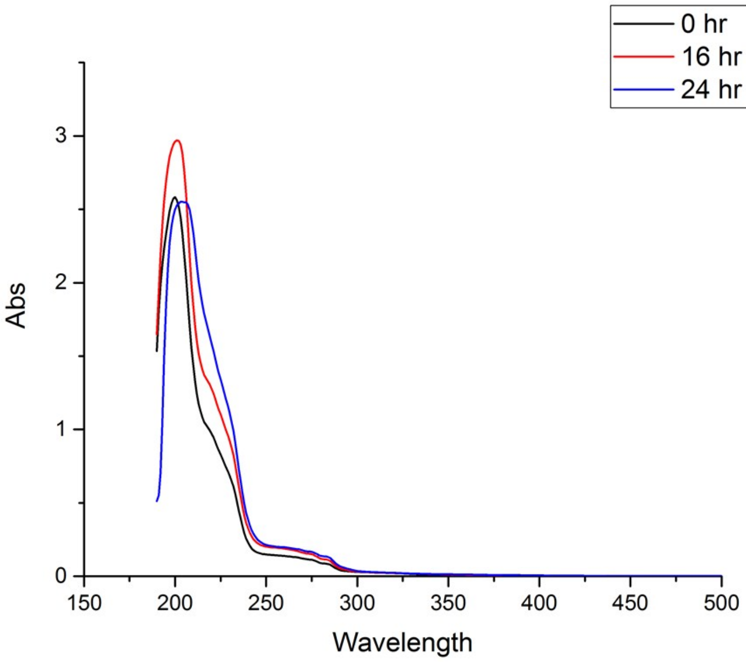


Figure 36. 5 mol% IMes.HCl, 5 mol% $FeCl_2$, 20 mol% KOtBu and Profenofos over 24 hr period at 80 ◦C in MeCN

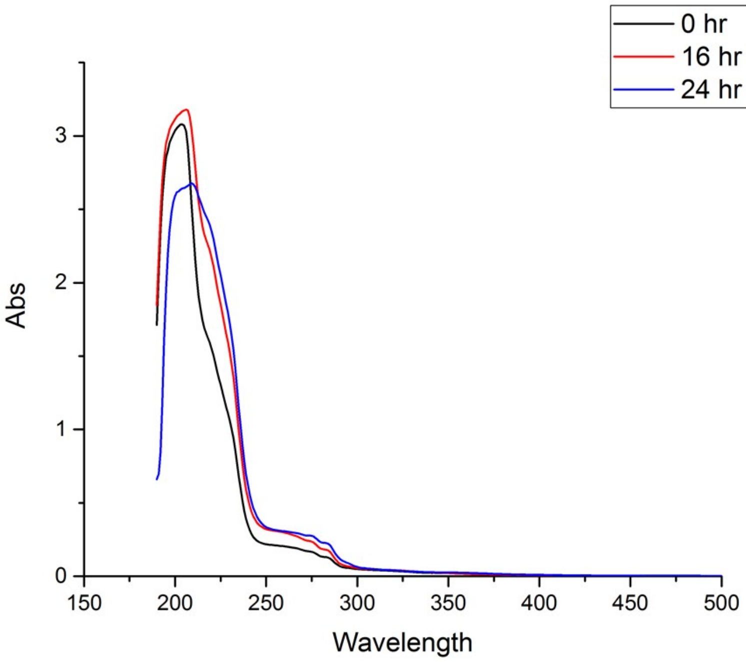
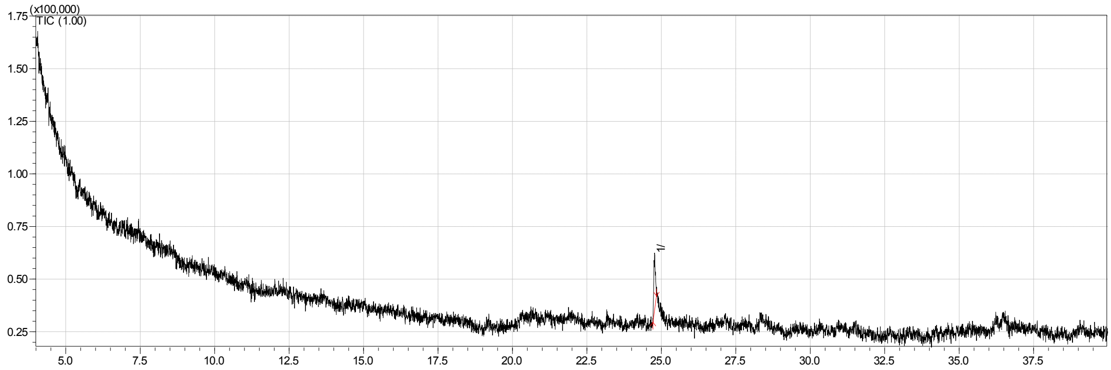
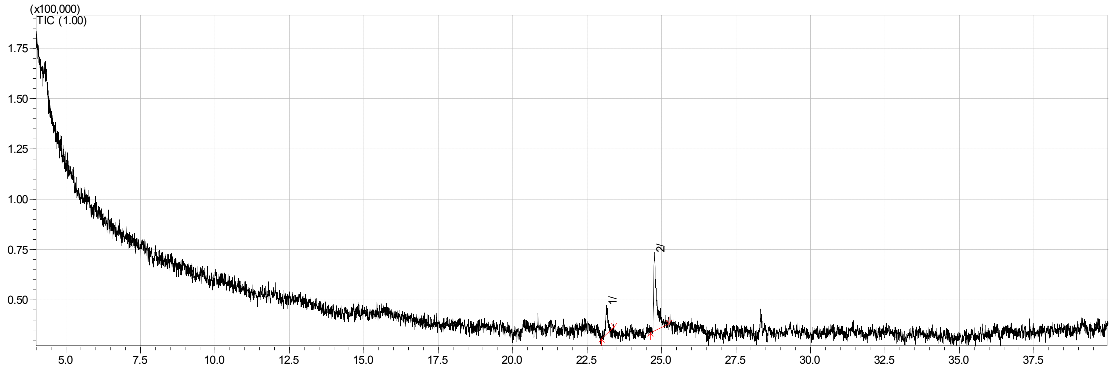


Figure 37. 5 mol% IMes.HCl, 5 mol% $FeCl_3$, 20 mol% KOtBu and Profenofos over 24 hr period at 80 ◦C in MeCN



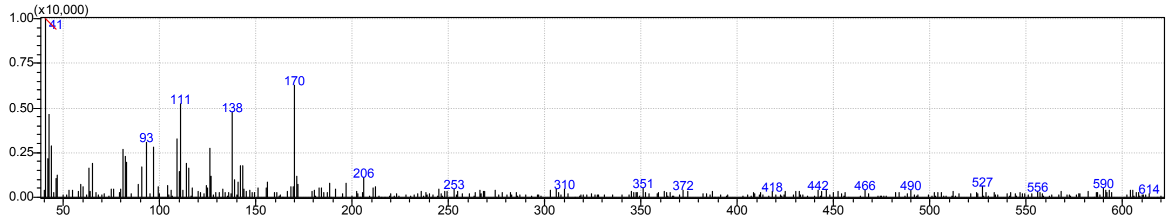
PEAK	R. TIME	I. TIME	F. TIME	AREA	AREA %	HEIGHT	HEIGHT %	A/H	NAME
1	24.772	24.720	24.835	103634	74.50	27270	77.29	3.80	Phenol, 4-bromo-2-chloro-

Figure 38. GC-MS trace of 5 mol% IMes.HCl, 5 mol% $FeCl_3$, 20 mol% KOtBu and Profenofos after 24 hrs at 80 ◦C in MeCN



PEAK	R. TIME	I. TIME	F. TIME	AREA	AREA %	HEIGHT	HEIGHT %	A/H	NAME
1	23.145	22.980	23.400	56054	16.47	14515	27.13	3.86	o-Butyl O,O-diethyl phosphorothioate
2	24.753	24.625	25.255	284342	83.53	38982	72.87	7.29	Phenol, 4-bromo-2-chloro-

Figure 39. GC-MS trace of 5 mol% IPr.HCl, 5 mol% $FeCl_3$, 20 mol% KOtBu and Profenofos after 24 hrs at 80 ◦C in MeCN



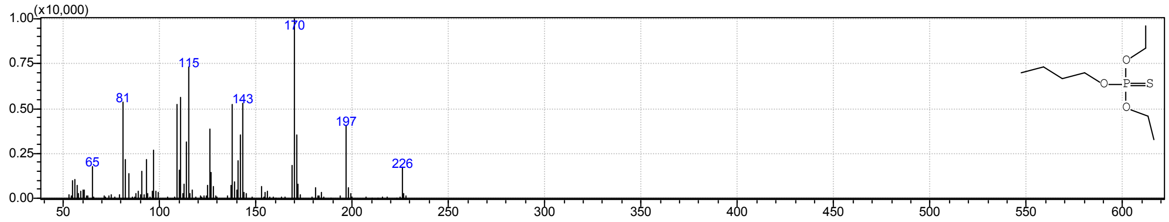


Figure 40. Selected MS peaks from GC-MS trace (Top found, bottom predicted)

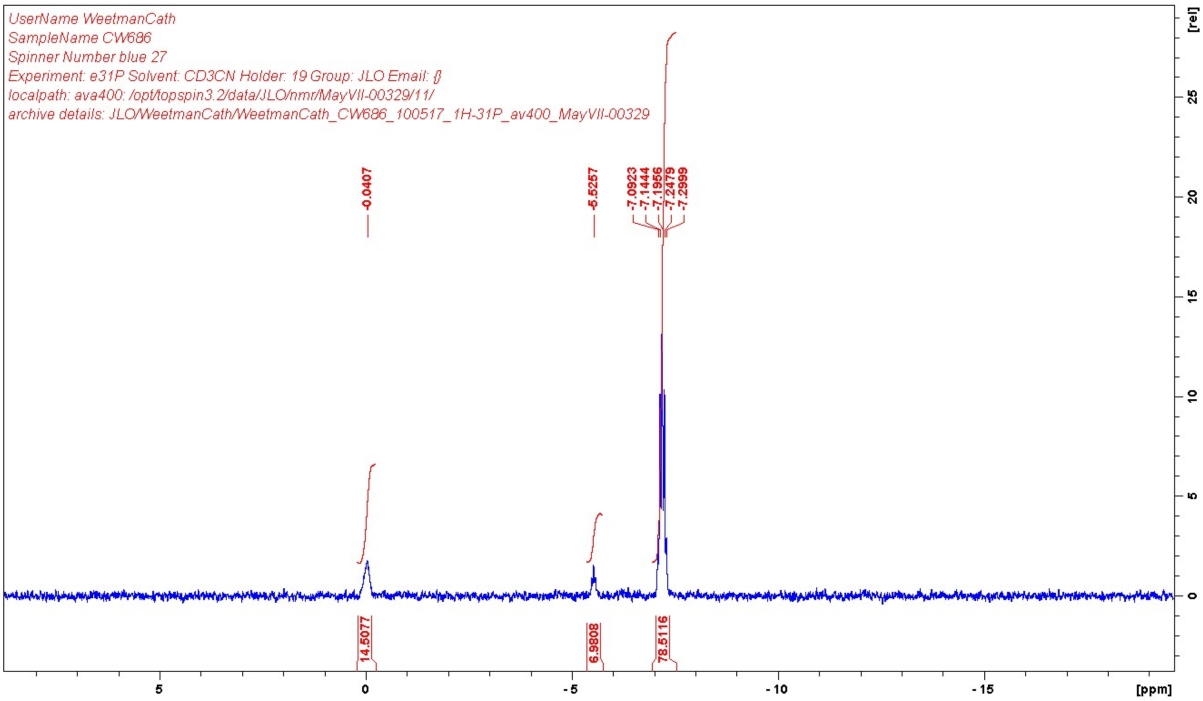


Figure 41. 31P NMR after 24 hrs of 5 mol% ICy.HCl, 5 mol% $NiCl_2$, 20 mol% KOtBu and Paraoxon at 80 ◦C in d-MeCN

6. References

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