

# Atmospheric breakdown kinetics and air quality impact of potential “green” solvents the oxymethylene ethers OME3 and OME4

## Supplementary Information (S1-5a)

James D. D’Souza Metcalf<sup>1,2</sup>, Ruth K. Winkless<sup>1</sup>, Caterina Mapelli<sup>1,2,3</sup>, C. Rob McElroy<sup>2,4</sup>, Claudiu Roman<sup>5,6</sup>, Cecilia Arsene<sup>5,6,7</sup>, Romeo I. Olariu<sup>5,6,7</sup>, Iustinian G. Bejan<sup>5,7</sup> and Terry J. Dillon<sup>1</sup>.

<sup>1</sup>Wolfson Atmospheric Chemistry Laboratories, Department of Chemistry, University of York, York, YO10 5DD, UK.

<sup>2</sup>Green Chemistry Centre of Excellence, Department of Chemistry, University of York, York, YO10 5DD, UK

<sup>3</sup>now at: National Research Council - Institute of Methodologies for Environmental Analysis (IMAA), Tito Scalo, Potenza, 85050, Italy

<sup>4</sup>now at: Department of Chemistry, School of Natural Sciences, University of Lincoln, Brayford Pool, Lincoln, LN6 7TS, UK

<sup>5</sup>Faculty of Chemistry, “Alexandru Ioan Cuza” University of Iasi, 700506, Iasi, Romania

<sup>6</sup>Research Center with Integrated Techniques for Atmospheric Aerosol Investigation in Romania (RECENT-AIR), “Alexandru Ioan Cuza” University of Iasi, 11th Carol I, Iasi, 700506, Romania

<sup>7</sup>Integrated Center of Environmental Science Studies in the North Eastern Region – CERNESIM, “Alexandru Ioan Cuza” University of Iasi, 700506, Iasi, Romania

Correspondence to: Terry J. Dillon (terry.dillon@york.ac.uk) and Iustinian G. Bejan (iustinian.bejan@uaic.ro)

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# S1 – OME Characterisation Data

## S1.2 – Procedures

### APCI-MS

Mass spectra were taken on a Bruker MicroTOF time of flight mass spectrometer fitted with and APCI II ionisation source. Samples were diluted *quantum satis* in dichloromethane (Fischer Scientific, 99.8%, HPLC Grade) and introduced *via* a syringe pump.

The APCI source was run in positive mode and spectra were scanned between  $m/z = 50 - 1000$ . The capillary voltage was 4500V and the corona was 5000 nA. The nebuliser gas pressure was 2.1 bar. The dry gas heater was set to 250 °C with a flow rate of 2 l min<sup>-1</sup>. The vaporiser temperature was 400 °C.

The instrument was calibrated using a calibration solution (SCIEX, part number 4460131).

### NMR

NMR spectra were taken at room temperature in Chloroform-d (Apollo Scientific, >99.8% D atom count) on a JEOL ECS400 instrument operating at a nominal proton frequency of 400 MHz. Samples were spun at 20 Hz. Spectra were referenced to the residual chloroform peak (7.26 ppm for <sup>1</sup>H spectra, 77.16 ppm for <sup>13</sup>C spectra)

### GC-FID

Gas chromatographic measurements were made with an Agilent Technologies HP 6890N gas chromatograph, with a flame ionisation detector (GC-FID), fitted with a Restex Stabilwax capillary column (30 m 250 mm x 0.25 mm nominal, max temperature 260°C). Hydrogen was used as the carrier gas at a flow rate of 0.8 mL min<sup>-1</sup> (10.1 psi) with a split ratio of 15:1 and a 0.5 µl injection.

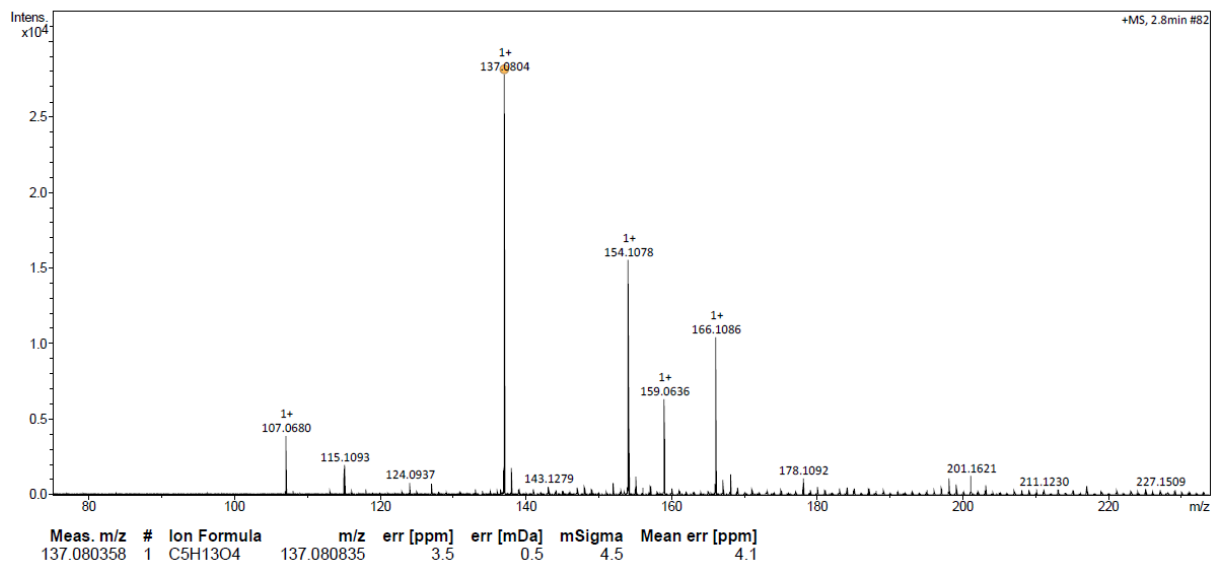
The initial oven temperature was 50 °C and was increased instantly at a rate of 20 °C min<sup>-1</sup> to 260 °C and held at this temperature for 9 minutes, giving a total run time of 19.5 minutes. Injection temperature was 260 °C and the detector temperature was 260 °C.

## S1.2 – OME3 (2,4,6,8-tetraoxanonane, CH<sub>3</sub>O(CH<sub>2</sub>O)<sub>3</sub>CH<sub>3</sub>)

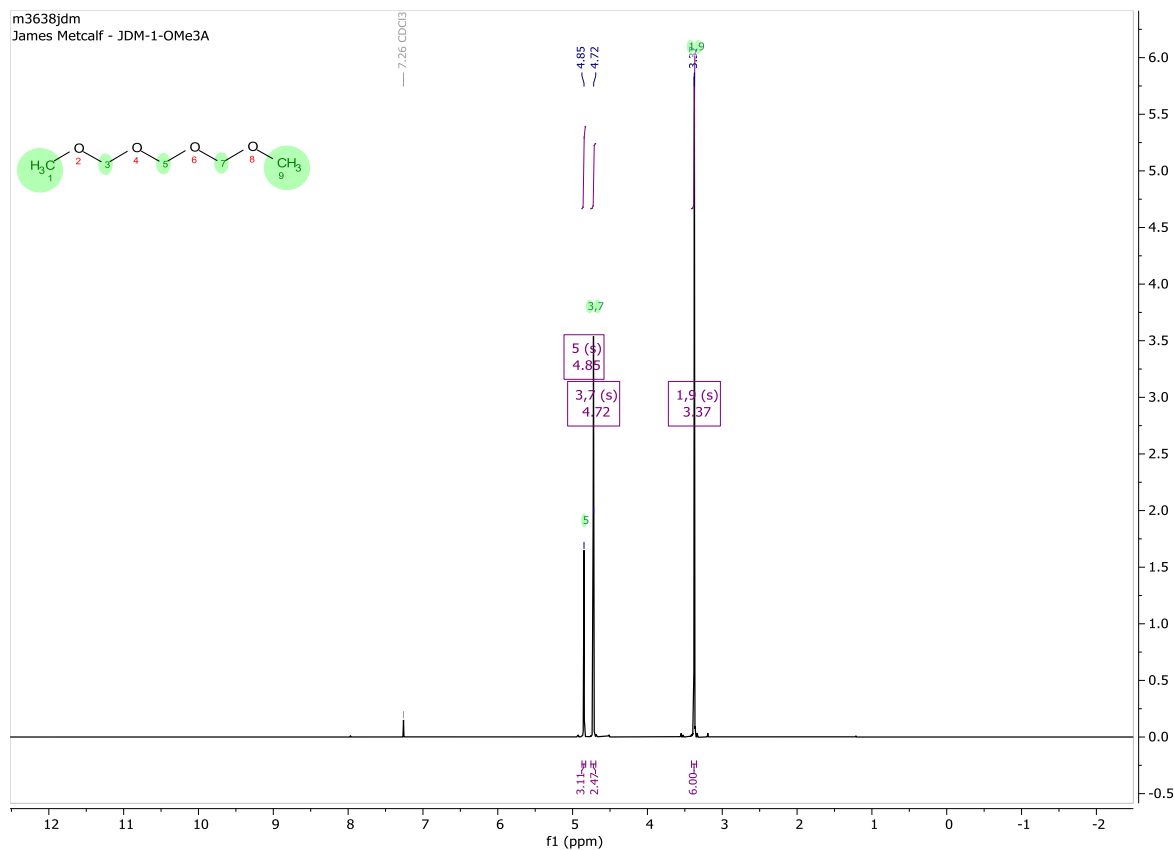
### APCI-MS

# Analysis Information

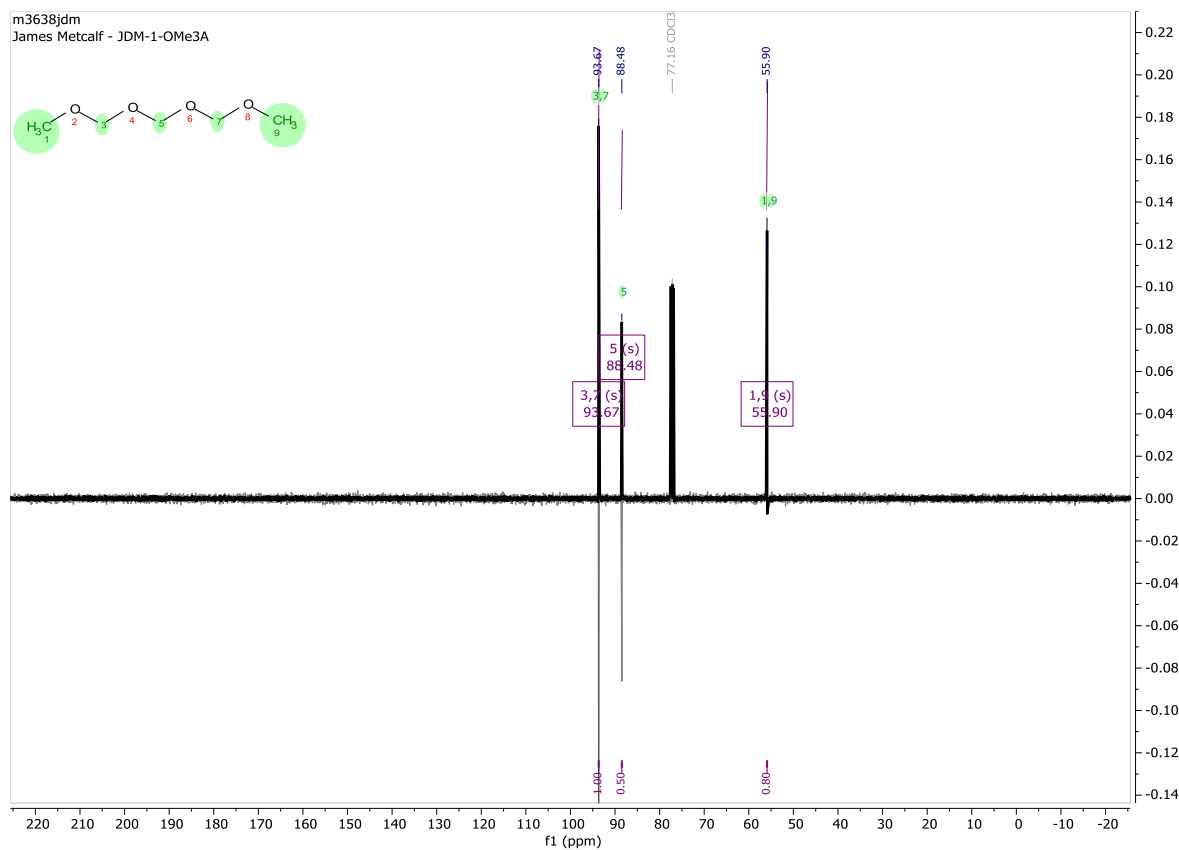
Analysis Filename hfs106955jm.d Acquisition Date 31/10/2023 06:23:49  
 Method APCL LOW MASS\_oTOF34 METHODS.m Instrument micrOTOF  
 Submission Name jwg71051rm\_3 APCI Positive



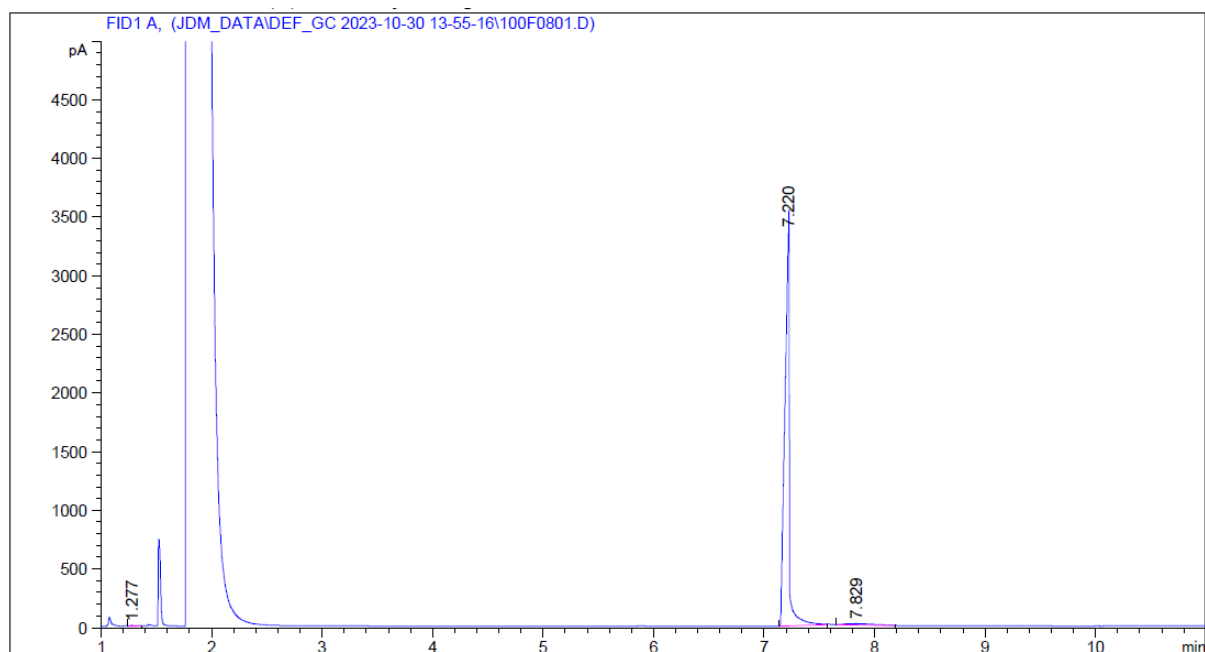
## <sup>1</sup>H NMR



## <sup>13</sup>C NMR (Black) with DEPT-135 overlaid (grey)



## GC-FID

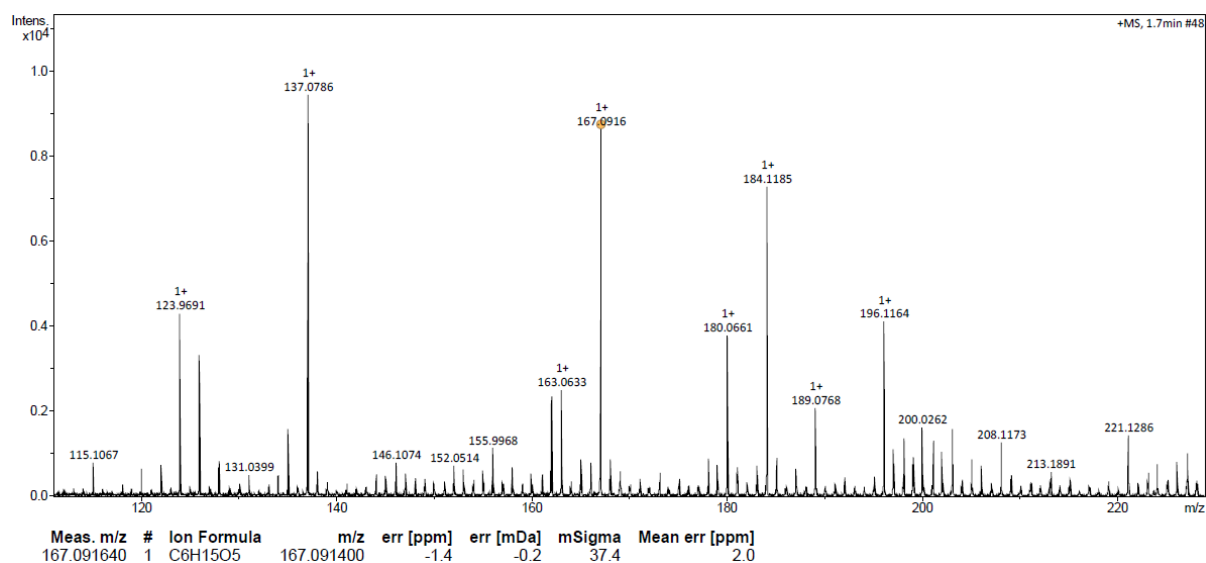


Peak #	RetTime [min]	Sig	Type	Area [pA*s]	Height [pA]	Area %
1	1.277	1	VB	17.00299	4.76025	0.16727
2	7.220	1	BB	9942.40430	3366.13940	97.80796
3	7.829	1	BB	205.82256	12.85588	2.02477

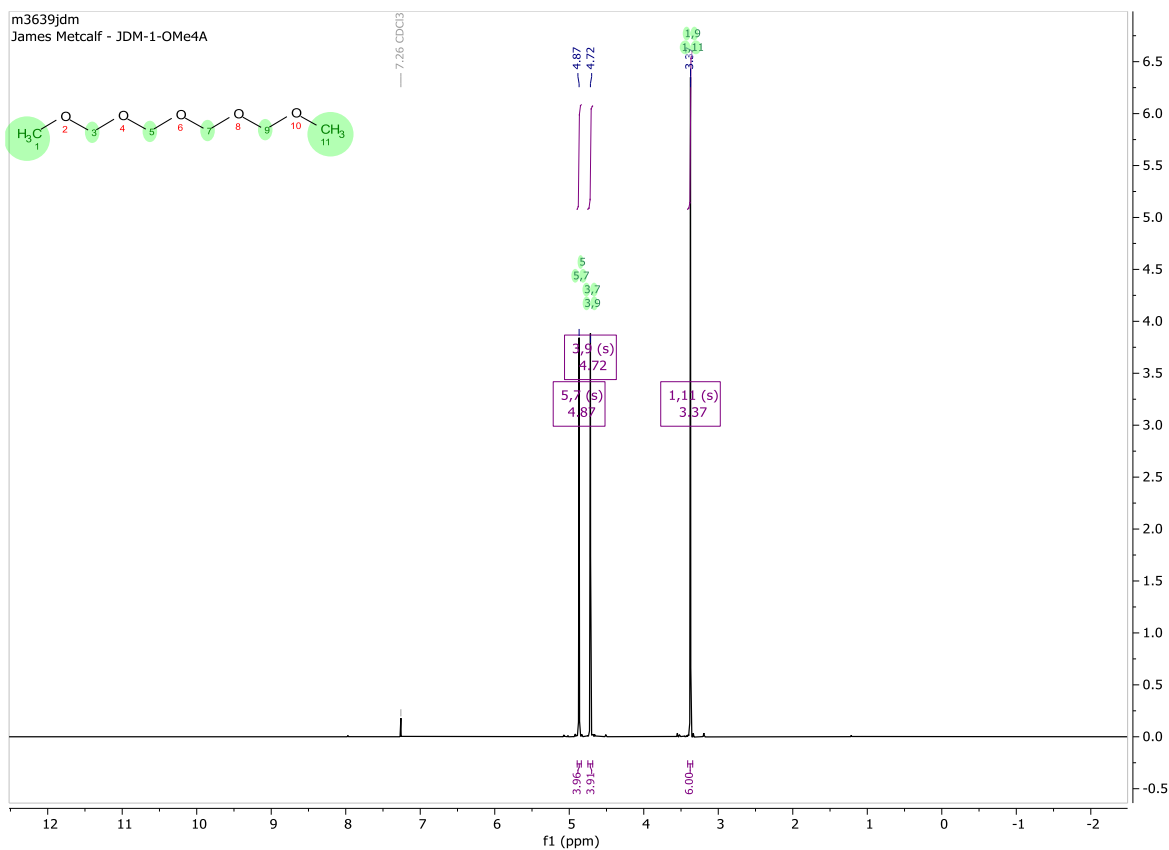
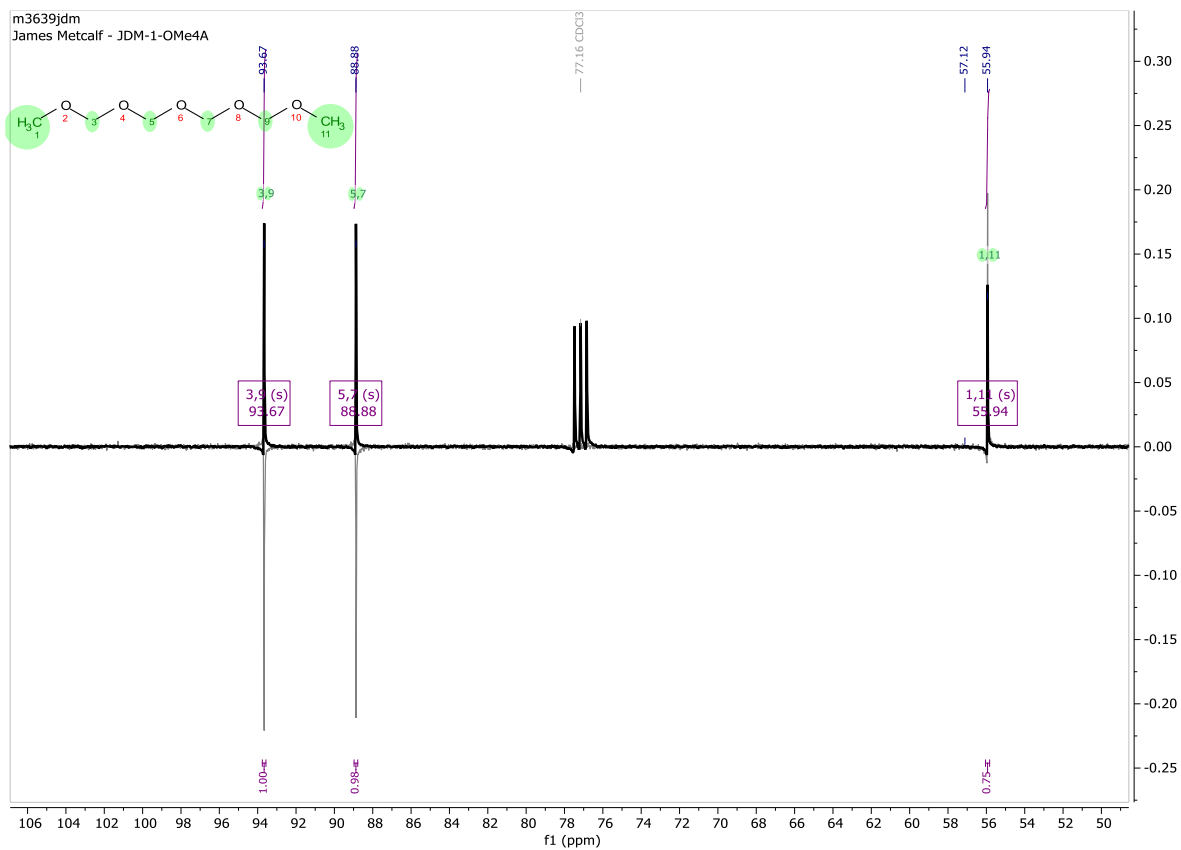
Totals : 1.01652e4 3383.75554

### S1.3 – OME4 (2,4,6,8,10-Pentaoxaundecane, CH<sub>3</sub>O(CH<sub>2</sub>O)<sub>4</sub>CH<sub>3</sub>)

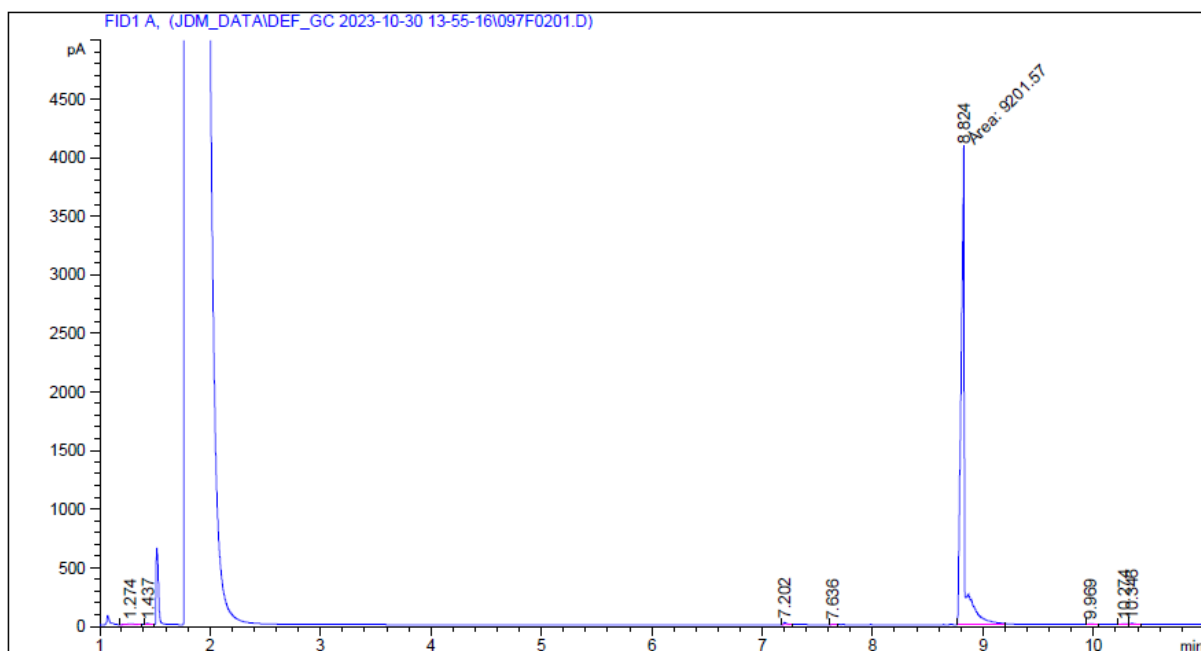
#### ACPI-MS



#### <sup>1</sup>H NMR

<sup>13</sup>C NMR (Black) with DEPT-135 overlaid (grey)

## GC-FID



Peak #	RetTime [min]	Sig	Type	Area [pA*s]	Height [pA]	Area %
1	1.274	1	BB	42.35159	7.60741	0.45182
2	1.437	1	BV	23.36383	10.62514	0.24925
3	7.202	1	BB	32.36141	18.21927	0.34524
4	7.636	1	BB	7.91826	4.47685	0.08447
5	8.824	1	MM	9201.57227	4062.82886	98.16507

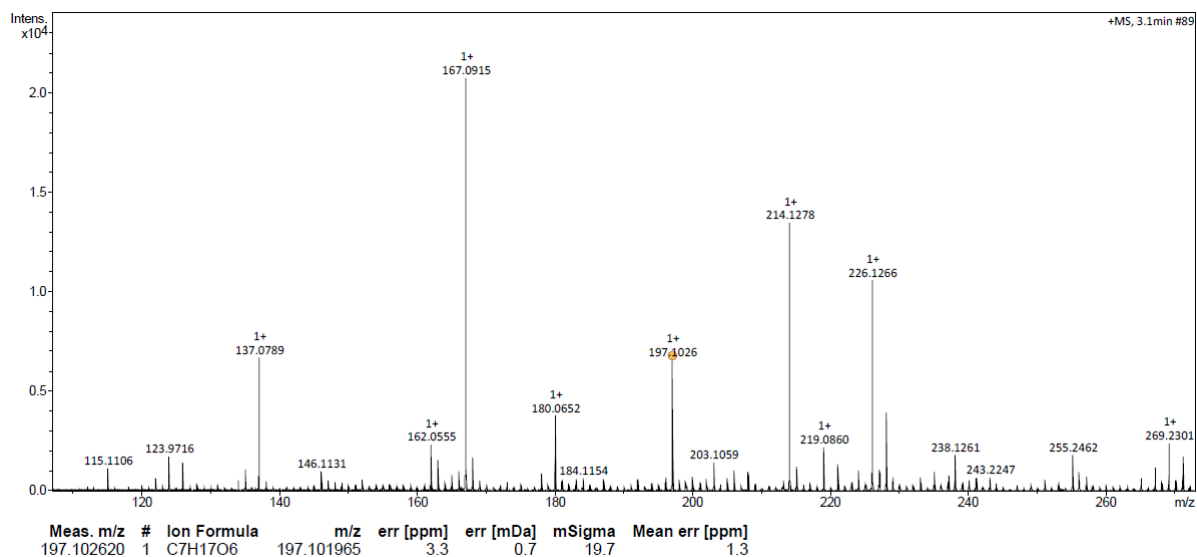
Peak #	RetTime [min]	Sig	Type	Area [pA*s]	Height [pA]	Area %
6	9.969	1	BB	21.11243	7.49390	0.22523
7	10.274	1	BV	21.90153	6.98396	0.23365
8	10.346	1	VB	22.98904	8.47070	0.24525

Totals : 9373.57036 4126.70608

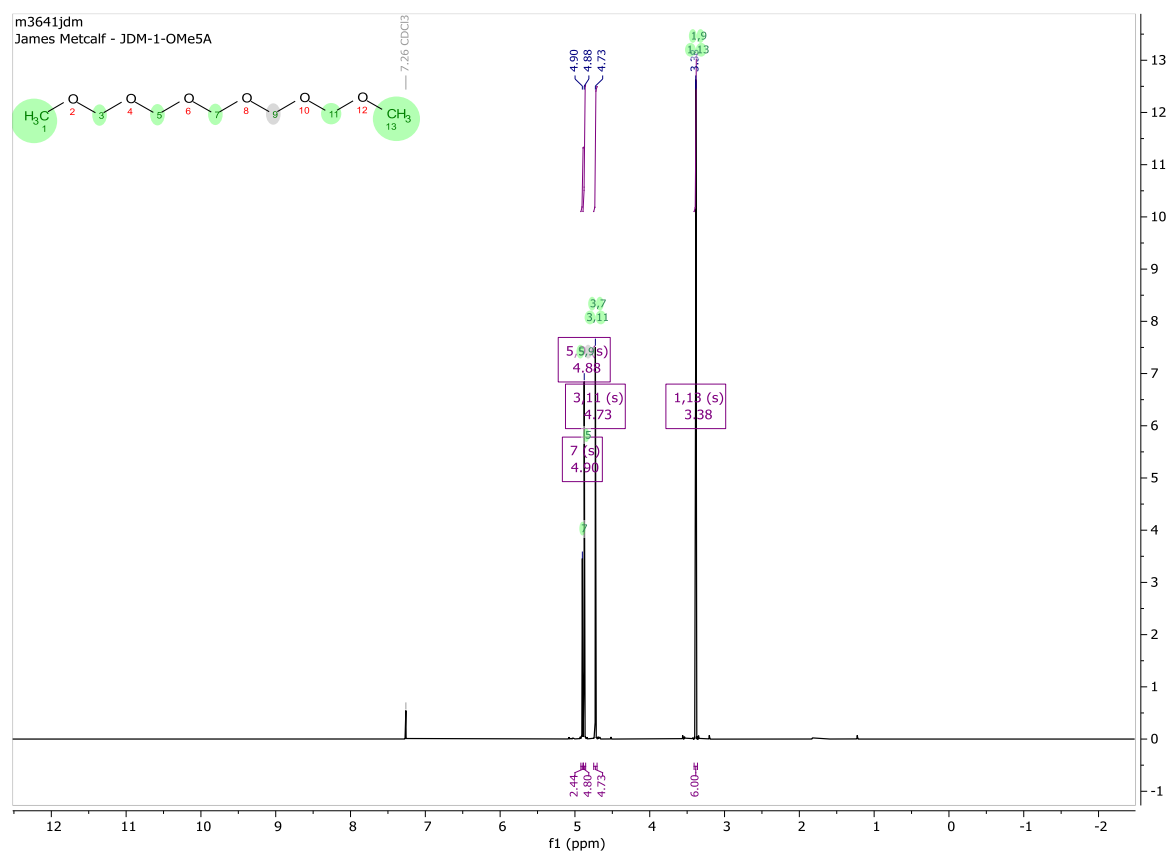
S1.4 – OME5 (2,4,6,8,10,12-hexaoxatridecane,  $\text{CH}_3\text{O}(\text{CH}_2\text{O})_5\text{CH}_3$ )

APCI-MS

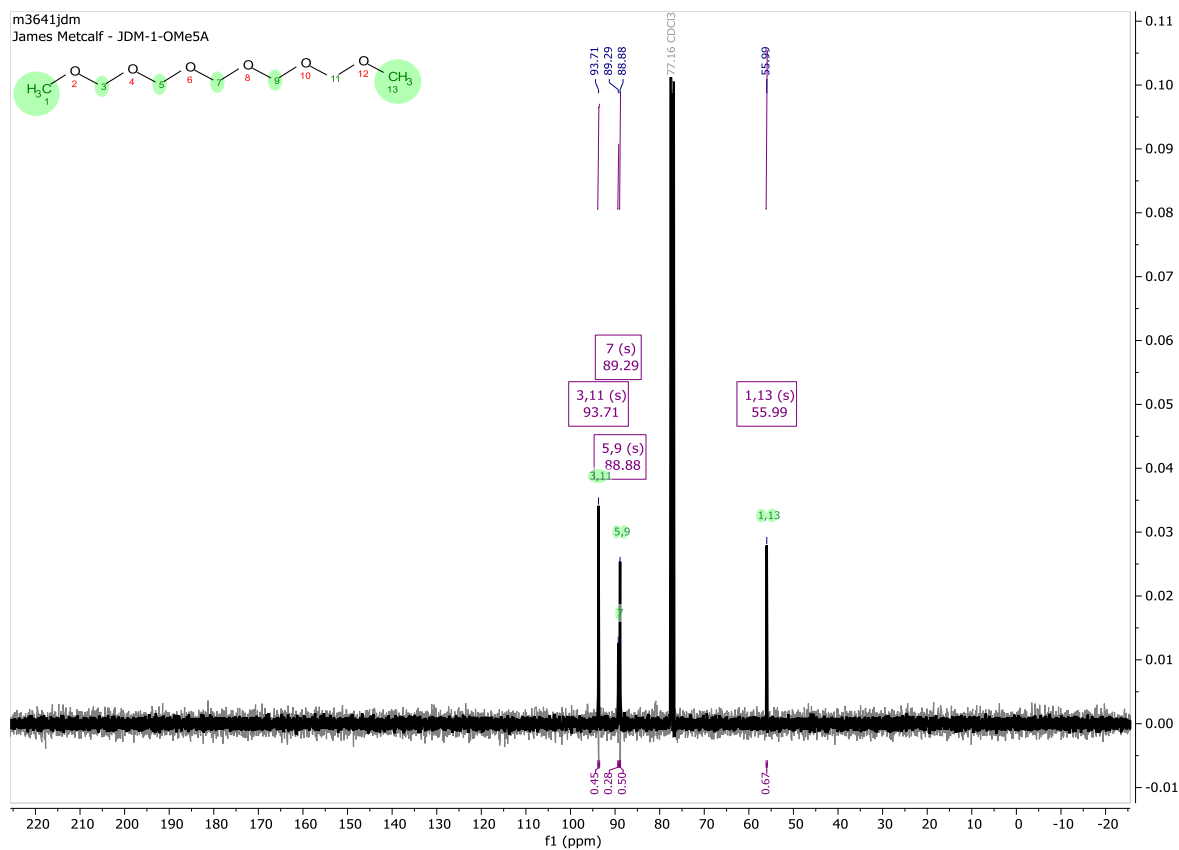




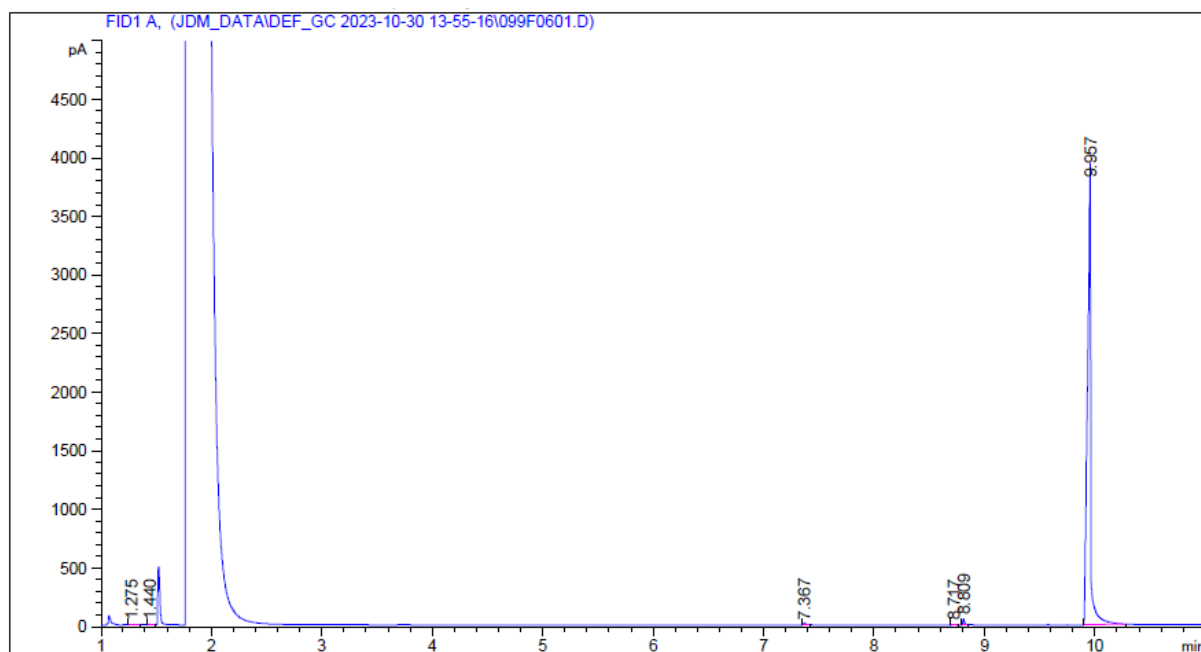
## <sup>1</sup>H NMR



## <sup>13</sup>C NMR (Black) with DEPT-135 overlaid (grey)



## GC-FID



Peak #	RetTime [min]	Sig	Type	Area [pA*s]	Height [pA]	Area %
1	1.275	1	VB	10.34972	4.08246	0.12977
2	1.440	1	BB	9.11106	4.63338	0.11424
3	7.367	1	BB	23.61317	13.32308	0.29608
4	8.717	1	BB	4.54751	3.30458	0.05702
5	8.809	1	BB	54.93659	50.72303	0.68884

Peak #	RetTime [min]	Sig	Type	Area [pA*s]	Height [pA]	Area %
6	9.957	1	BB	7872.70264	3778.80347	98.71405
Totals :				7975.26069	3854.86999	

## S2 – Relative Rate Plots

### S2.1 – OME3 + OH (R3)

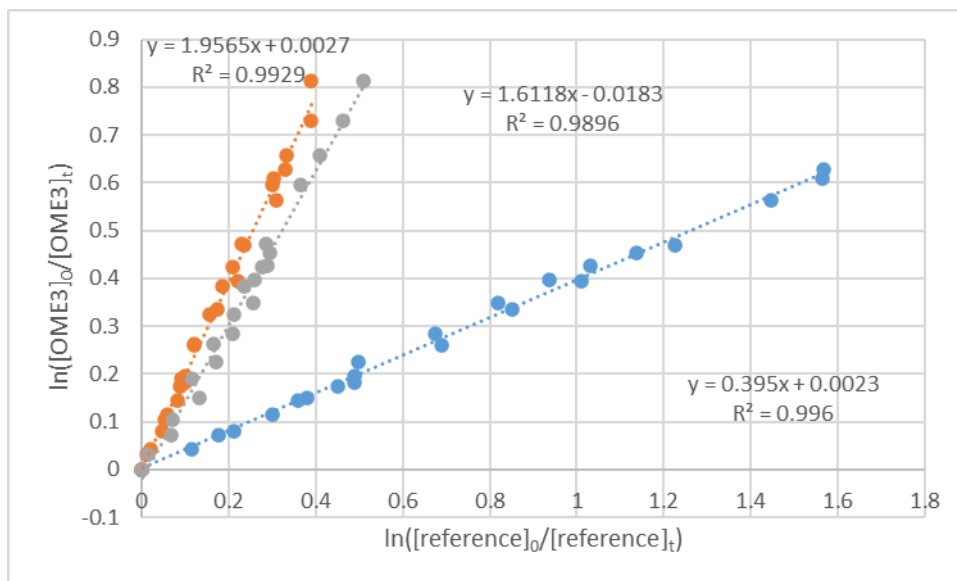


Figure 1: Relative rate plot and fits used to determine  $k_{3RR}$ . Orange data are relative to toluene, grey to cyclohexane and blue to propene.

### S2.2 – OME4 + OH (R4)

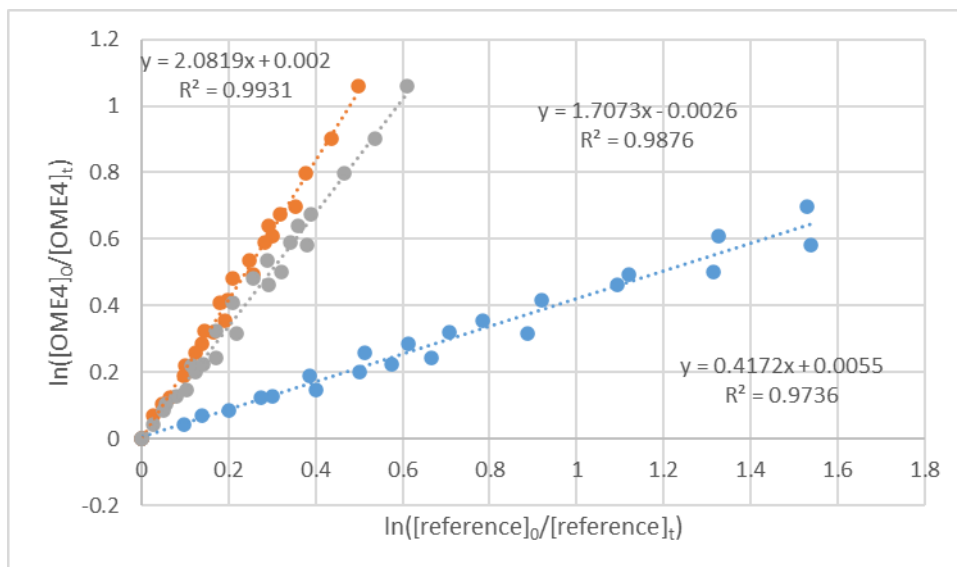


Figure 2: Relative rate plot and fits used to determine  $k_{4RR}$ . Orange data are relative to toluene, grey to cyclohexane and blue to propene.

### S2.3 – OME3 + Cl (R5)

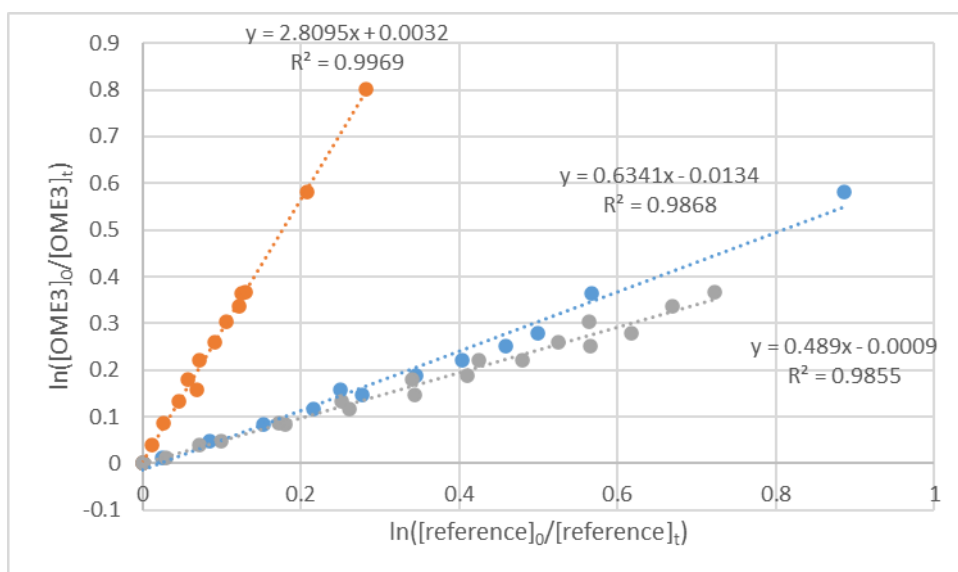


Figure 3: Relative rate plot and fits used to determine  $k_5$ . Orange data are relative to toluene, grey to cyclohexane and blue to propene.

### S2.4 – OME4 + Cl (R6)

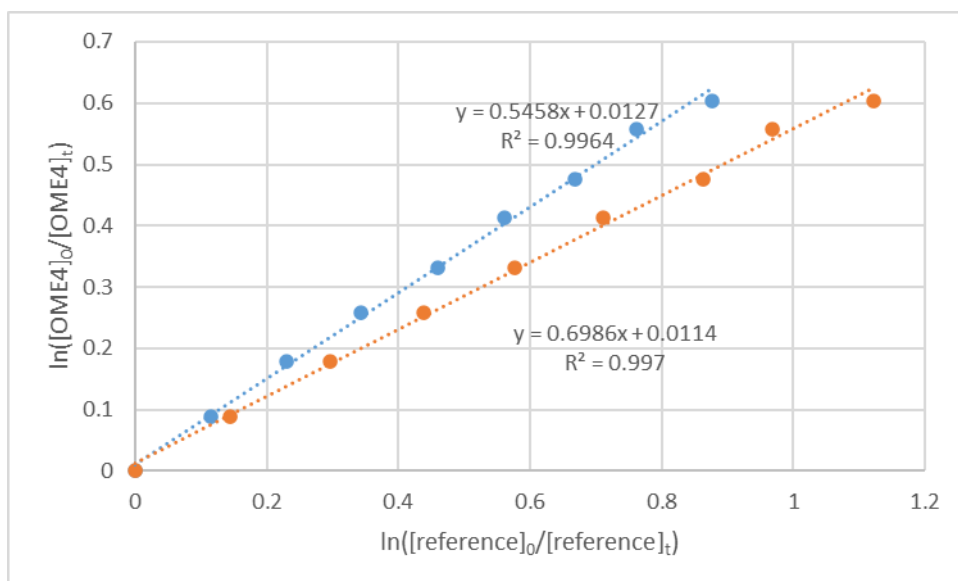


Figure 4: Relative rate plot and fits used to determine  $k_6$ . Orange data are relative to toluene and blue to propene.

## S3 – Gaussian Estimated Spectra

Raw data and Gaussian Files are provided in a separate .zip file (see below, S5a).

### S3.1 – OME3 Estimated Spectrum

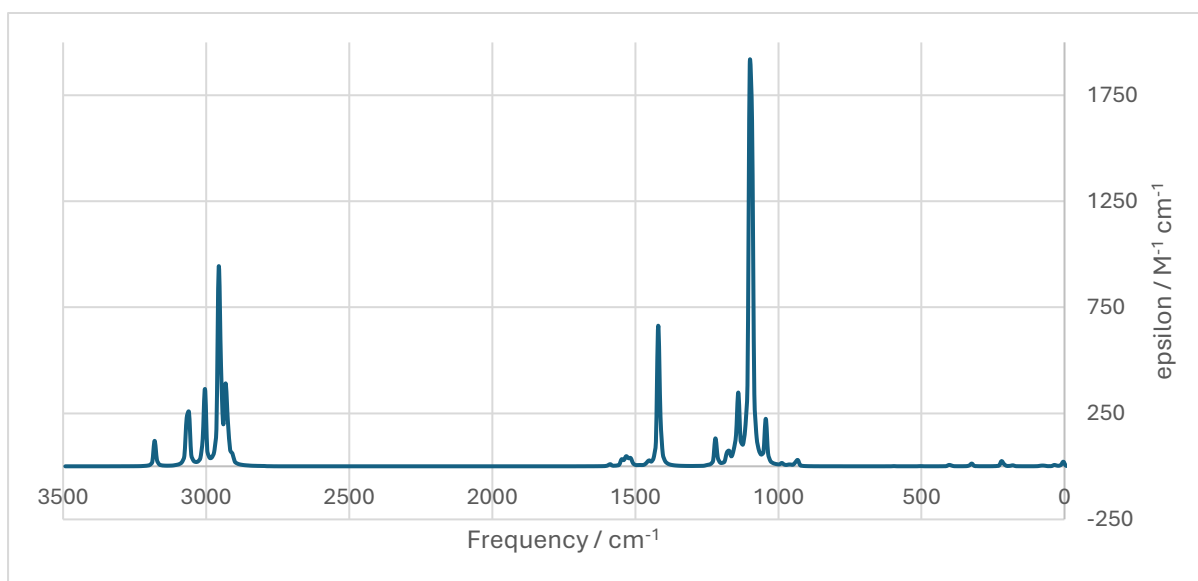


Figure 5: IR spectrum predicted for OME3 by Gaussian calculations

Table 1: IR peaks predicted by Gaussian calculations for OME3

Peak Table	
Frequency / cm <sup>-1</sup>	epsilon / M <sup>-1</sup> cm <sup>-1</sup>
5.5408	5176.611763
33.3311	294.3175651
72.5355	81.56387338
85.636	31.65951784
182.3784	36.53443352
217.5926	177.9907444
267.3563	0.001492165
325.8053	54.81230201
400.8943	29.62087585
503.2738	2.879840107
594.5938	1.806183951
934.9269	55.31486613
960.1656	8.24167068
986.5033	12.36284438
1043.5712	226.8055653
1096.2987	3686.426994
1114.4314	30.51280373
1121.7742	3.649504158
1139.3457	315.3367319
1148.762	66.26549926
1158.0958	33.46717302
1175.865	101.2653125
1218.6486	38.43332872
1218.8159	92.45671176

1242.7177	0.691481419
1418.2064	647.8465771
1454.942	20.45394855
1487.1334	1.719820609
1504.5801	0.08511322
1514.4092	26.5457695
1528.6124	52.76474184
1543.5322	14.14209935
1545.6278	20.4873656
1580.3213	0.397848861
1590.0912	8.484384526
2910.3354	16.55834059
2917.0798	2.496963492
2929.2599	197.2055599
2945.8526	66.6314162
2954.2031	423.9984144
3005.574	111.9420842
3005.9047	47.62105925
3063.7689	178.7869234
3179.0678	14.22674857
3179.1114	31.37860432

### S3.2 – OME4 Estimated Spectrum

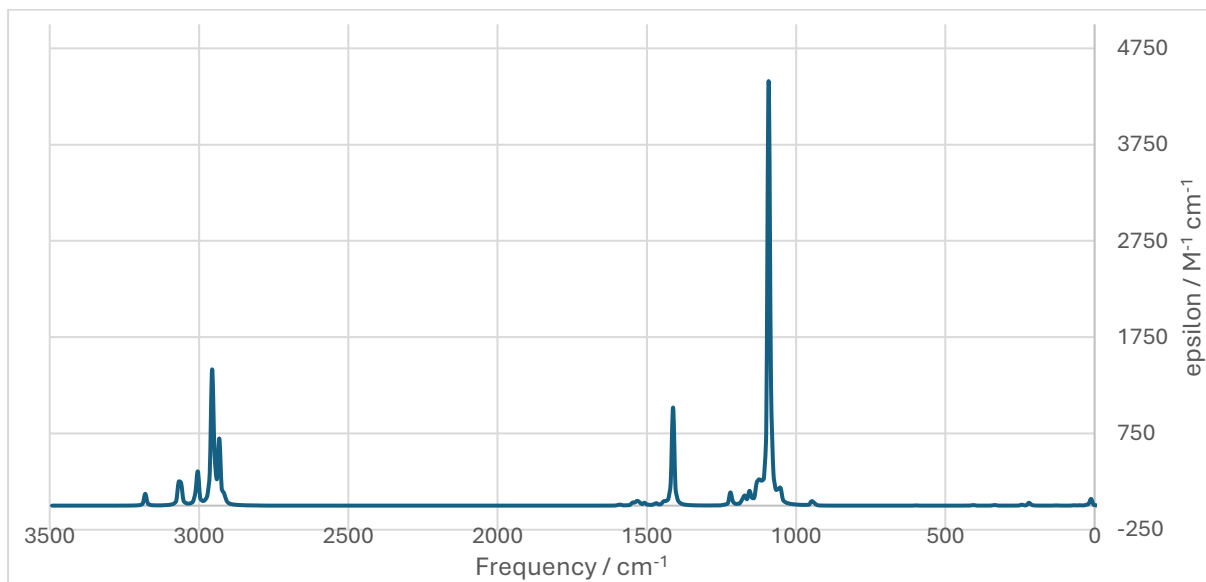


Figure 6: IR spectrum predicted for OME4 by Gaussian calculations

Table 2: IR peaks predicted by Gaussian calculations for OME4

Peak Table	
Frequency / cm <sup>-1</sup>	epsilon / M <sup>-1</sup> cm <sup>-1</sup>
12.7617	6505.071373

25.5234	275.9226131
43.8872	0.009090116
49.6301	94.37723241
69.1487	61.07383194
128.0174	31.15358206
218.1262	1.260139683
218.2257	159.6357115
218.3476	25.82402682
244.0112	43.92386515
335.3588	32.5198434
407.059	24.12598559
430.9758	2.35304353
566.8888	0.064039925
598.0605	5.624614707
943.4756	11.86025453
945.1199	70.84397566
988.8316	0.066165075
1002.6586	0.278517352
1055.2115	236.8697792
1090.7364	5120.250489
1116.7372	109.1047945
1120.1316	0.005342315
1127.1958	9.238787939
1128.0724	352.7879203
1138.5432	0.000350395
1153.5046	84.00043041
1157.437	66.7746008
1162.1768	3.622865309
1172.0157	0.000680775
1175.0422	124.6059652
1218.557	90.65182768
1219.107	45.60636161
1241.1976	0.714505926
1249.2553	0.01724447
1412.5776	849.3125684
1440.7442	36.26759643
1470.611	20.86293286
1494.0276	2.664088523
1506.7669	19.81583676
1515.6839	2.141194995
1528.7962	53.15191115
1543.8095	21.95007827
1545.0607	15.60270777
1567.32	0.13948586

1576.232	0.206274132
1584.5593	0.652076527
1591.3916	11.29290703
2910.6342	1.062511002
2914.6841	30.59042866
2923.1519	6.016129918
2932.1836	251.1394265
2946.8212	0.00013538
2947.2806	104.5310754
2956.5597	536.4903182
3005.8779	124.0482239
3006.0499	37.15041429
3064.0593	0.000390599
3064.1086	178.1075211
3179.6946	11.01932225
3179.7178	33.75743761

## S4 – COSMO-RS Validation

COSMO Files are provided in a separate .zip file (S5).

To the best of our knowledge,  $k_{OH}$  estimation using the COSMOTermX software is carried out as described by Klamt (Klamt, 1993, 1996) however there is little publicly available information describing what, if any modifications have been made since its implementation into the current software package. In order to investigate the accuracy of the COSMO-RS method of VOC + OH rate constant estimation it's estimates for a series of oxygenated VOCs were compared to their IUPAC recommended values (Atkinson et al., 2006; Mellouki et al., 2021), (figure 5). A linear fit of the data, shown in Table 3 gives equation 1:

$$k_{COSMO-RS} = (0.81 \pm 0.10)k_{IUPAC} + (0.47 \pm 2.43) \times 10^{-12} \quad (1)$$

Where N = 27 and  $R^2 = 0.741$ .



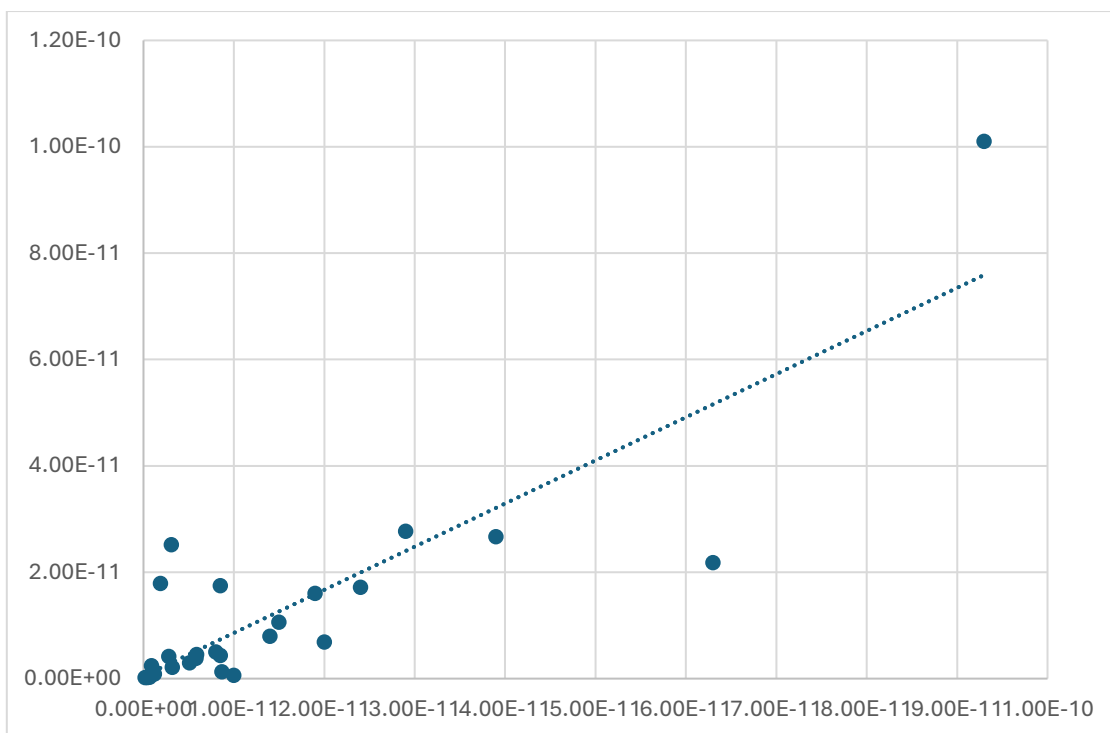


Figure 7: A plot of IUPAC recommended rate constants for a series of oxygenates (table 3) against their values estimated via the COSMO-RS method.

Table 3: Estimated and IUPAC recommended values for the OH rate constants of a series of saturated VOCs.

Compound	Estimated	IUPAC Recommended
acetaldehyde	1.06E-11	1.50E-11
propanal	1.60E-11	1.90E-11
propanone	2.11E-13	1.80E-13
butanone	1.51E-12	1.10E-12
methanol	2.42E-12	9.00E-13
ethanol	2.10E-12	3.20E-12
propanol	3.81E-12	5.80E-12
2-propanol	2.94E-12	5.10E-12
1-butanol	4.35E-12	8.50E-12
2-butanol	1.26E-12	8.70E-12
dimethyl ether	4.19E-12	2.80E-12
formic acid	2.01E-13	4.50E-13
acetic acid	2.27E-13	6.90E-13
propionic acid	8.53E-13	1.20E-12
2-hydroxy-2-methylpropanal	7.96E-12	1.40E-11
2-methyl-3-buten-2-ol	2.18E-11	6.30E-11
3-methylfuran	1.01E-10	9.30E-11
butyraldehyde	1.72E-11	2.40E-11
formaldehyde	1.75E-11	8.50E-12
glycolaldehyde	5.01E-12	8.00E-12
glyoxal	2.52E-11	3.10E-12
methacrolein	2.77E-11	2.90E-11

<b>methyl peroxide</b>	6.35E-13	1.00E-11
<b>hydroxyacetone</b>	4.51E-12	5.90E-12
<b>methyl vinyl ketone</b>	6.89E-12	2.00E-11
<b>methyl glyoxal</b>	1.79E-11	1.90E-12
<b>pinonaldehyde</b>	2.67E-11	3.90E-11

## S5a – Details of included files

Included alongside this document are the files associated with Gaussian and COSMO calculations. A brief description of these files, and what is required to open them is detailed here.

### S5a.1 Gaussian Files

Four files are included per calculation, for a total of 8 files:

**.chk** files are Gaussian checkpoint files and are only openable in Gaussian. These can be used to view the minimised structure and view the details of the calculation method and results that are beyond the scope of this paper.

**.gif** files are gaussian input files. These are openable as text files (i.e. in Notepad) and give details on the calculation method and initial structure in Gaussian format. They can also be opened in packages such as Chem3D to view the unoptimised 3D structure

**.LOG** files are gaussian log/output files. They contain full details of the calculations and results and are openable as text files (i.e. in Notepad).

**.txt** files contain raw predicted IR spectra and peak tables

### S5a.2 COSMO-RS Files

Files are divided by type into two folders. One folder contains optimised structures, with two files per compound (describing on the lowest energy gas-phase conformer, which is used in  $k_{\text{OH}}$  calculations). The second folder contains files relating to the  $k_{\text{OH}}$  estimation calculations. Here we have provided overall tabulated results (OMEs.tab). A subfolder then contains the raw output and .tab files for each compound. One quirk of the COSMOTermX software is that 1-octanol, *n*-heptane and water are added to every set of compounds, regardless of if they are needed for the requested calculation. We have included the files corresponding to these compounds for completeness, but they are of no practical importance. All files in this section can be opened as text files (i.e. in Notepad), a total of 25 files are provided.

**.cosmo** files contain the optimised structure and screening charge surface of each molecule.

**.energy** files contain additional energy information for each compound, required by the COSMOTermX software.

**.out** files contain full details of the calculations and results for each compound in the set, analogous to gaussian .LOG files

**.tab** files contain the parameters used for the  $k_{\text{OH}}$  estimation for each compound in the set, with the exception of OMEs.tab, which contains the overall results (see above).