Supplement of Atmos. Meas. Tech., 9, 4533–4545, 2016
http://www.atmos-meas-tech.net/9/4533/2016/
doi:10.5194/amt-9-4533-2016-supplement

Atmospheric Measurement Techniques
Open Access
EGU

Supplement of

Measurement of isoprene nitrates by GCMS

Graham P. Mills et al.

Correspondence to: Graham P. Mills (g.mills@uea.ac.uk)

S1. Attempted synthesis of (2,1)-IN

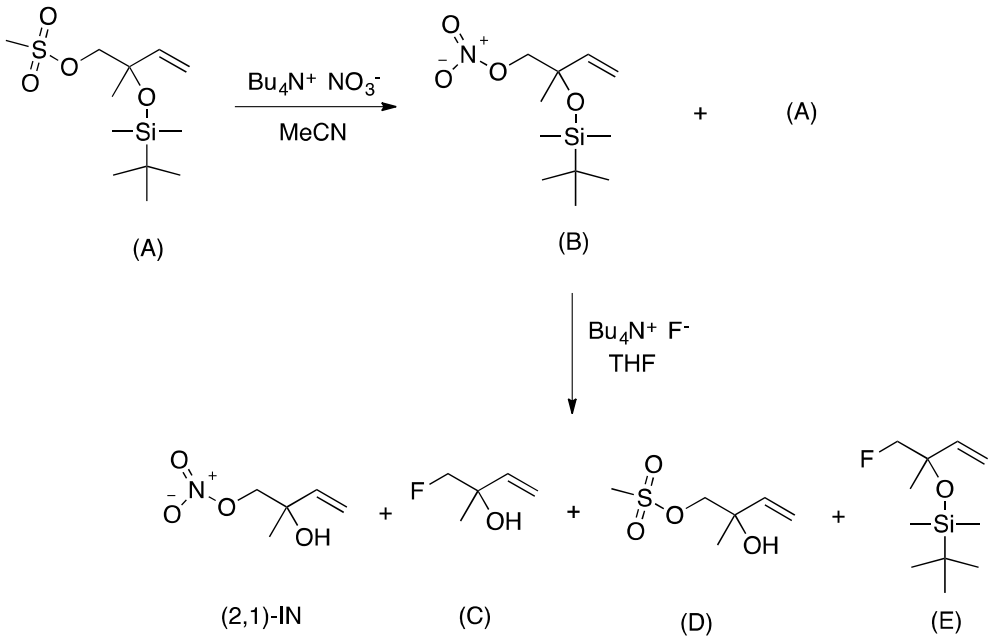

Figure S1.1: Attempted synthesis of (2,1)-IN from starting material (A). THF is tetrahydrofuran.

Despite the low yields and failure to separate the products of nitration from the starting material, we took one of the nitration mixtures and reacted it with tetrabutylammonium fluoride [$(C_4H_9)_4N^+ F^-$] in THF to remove the OTBDMS-protecting group and release the hydroxyl group, as shown in Fig. S1.1. Nitration of the starting material can occur at three possible locations although the mild nitration conditions effectively eliminate the possibility of nitration on the C=C bond. The mesylate group is generally considered to be an excellent leaving group, and the OTBDMS ether a poor one which leads us to the conclusion that nitration of the precursor should occur by displacement of the mesylate almost exclusively to yield (B), though only at a few percent. The subsequent addition of $(C_4H_9)_4N^+ F^-$ should cleanly and quantitatively remove the O-silyl protecting group, however, it is also possible that it can react with the mesylate group in (A) to yield a fluoride (Claesener et al. 2012) or it may not react with either. If both nitration and de-protection occur, then we would produce (2,1)-IN in low yield, and where only one or no reaction has occurred we would make compounds (B)-(E). This final mixture had the solvent removed, but was otherwise untreated.

The possible fluorinated alcohol (C) is expected to be volatile and elute much earlier on the column than similar nitrated alcohols. Furthermore it would not be expected to undergo electron capture efficiently and would thus not be visible in NI mode and additionally the high abundance of the m/z 46 ions in both the EI and NI mass spectra are difficult to rationalise. In summary, these factors collectively suggest that (C) is not the volatile component we observe.

The mesylate group displays characteristic ions (m/z 79, 80 and 95) in EI mass spectra (Sitaram et al. 2011), and since it is an excellent leaving group, we would expect to see similar masses in the NI mass spectrum. The absence of such 'fingerprint ions' strongly suggests that (D) is also not a likely candidate. Furthermore the O-silyl ether protecting group would be expected to produce significant abundances of at least some of the m/z 57, 58, 115 and 131 fragment ions in the EI mass

spectrum, as well as small contributions from larger fragments derived from the parent molecule. These ions were not observed at significant abundances.

The nitration agent is a non-volatile salt which, consequently, should not be present in the gas phase and if it were, we would expect to see abundant m/z 57 from the butyl groups in the EI mass spectrum, which we do not.

The limited evidence available suggests that the volatile component contains an -ONO_2 group, and that the molecule contains none of the starting material's large functional groups and the late-elution suggests it is not fluorinated. This limited evidence seems to exclude the majority of the likely reaction products from the reactions in Figure S1.1. However, there is not enough evidence to reliably identify the volatile component as the (2,1)-IN isomer, and the possibility remains that it is some other nitrated species, for example, a dinitrate of some sort.

References:

Claesener M., Breyholz, H-J., Hermann,S., Faust, A., Wagner, S., Schober,O., Schäfers,M., Kopka, K., Efficient synthesis of a fluorine-18 labeled biotin derivative, Nuclear Medicine and Biology, 39 (8), 1189-1194, 2012. doi:10.1016/j.nucmedbio.2012.08.001

Sitaram C, Rupakula R B, Reddy B N, Sastry C. Determination of alkyl methanesulfonates in doxazosin mesylate by gas chromatography-mass spectrometer. Indian J. Pharm. Sci. 73,107-10, 2011.

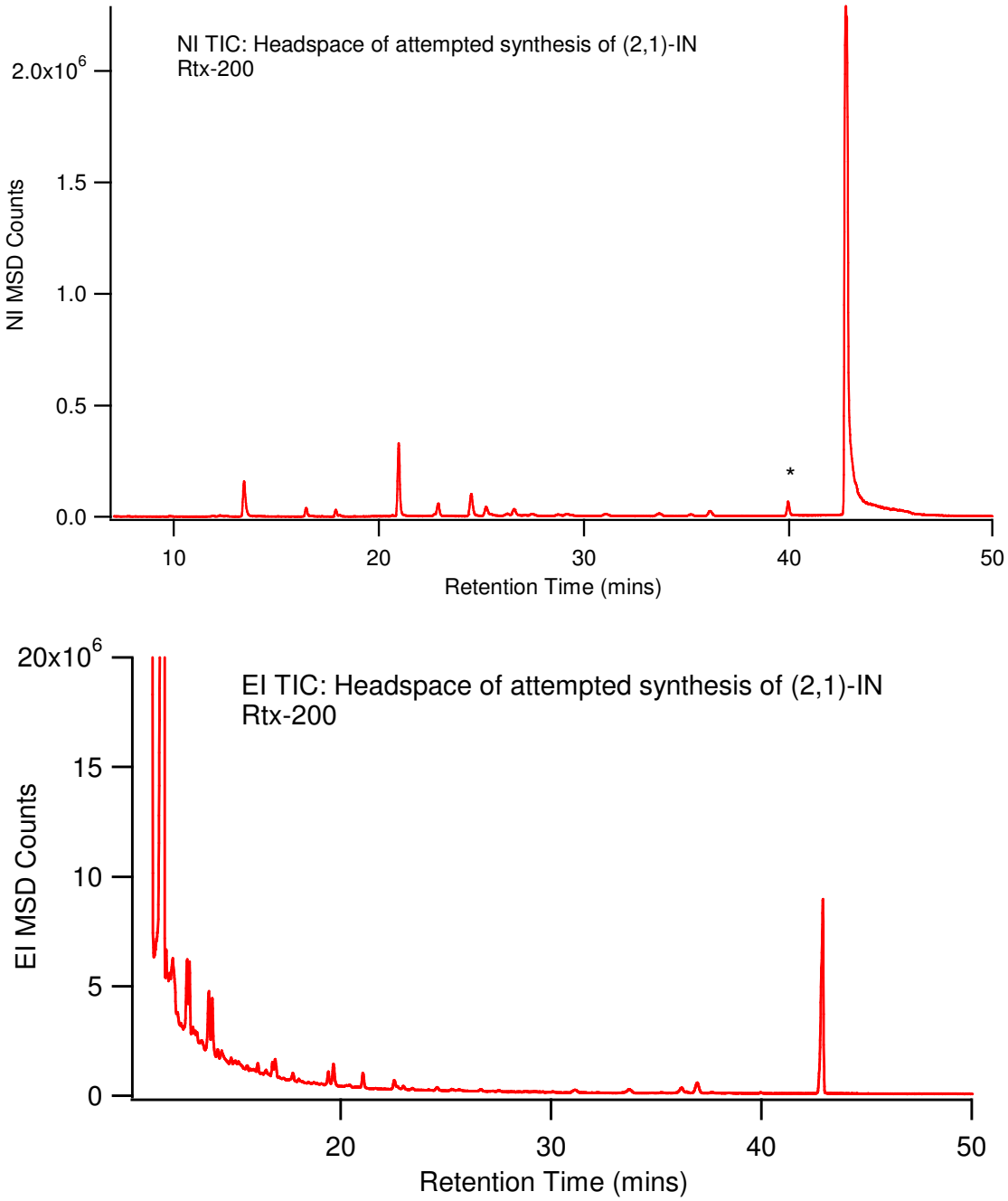

Figure S1.2. Total Ion Chromatograms (TIC) of the headspace of the mixture of products from the attempted synthesis of (2,1)-IN. The peak at approx. 43 mins is species X and the peak marked (*) is a trace impurity that has an identical NI mass spectrum to species X and whose EI mass spectrum is shown in Figure S2.2.

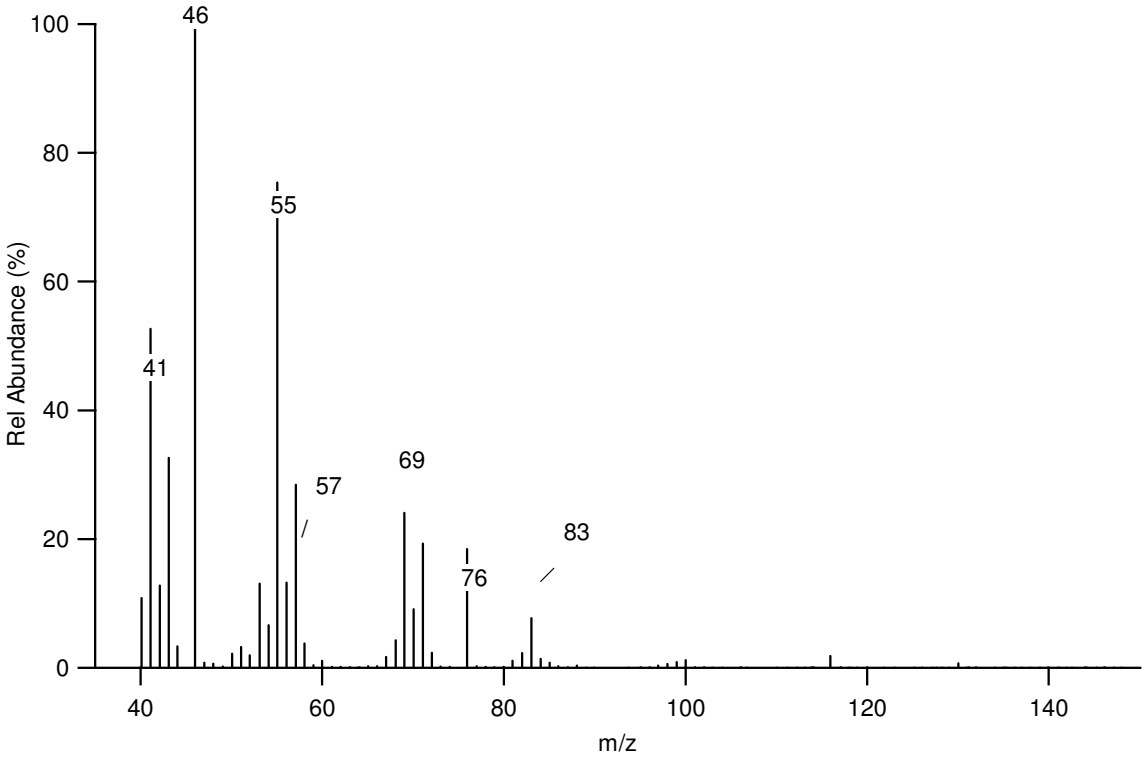

Figure S1.3. EI (70eV) mass spectrum of the volatile component (species X) from the attempted synthesis of (2,1)-IN.

S2. Mass spectra

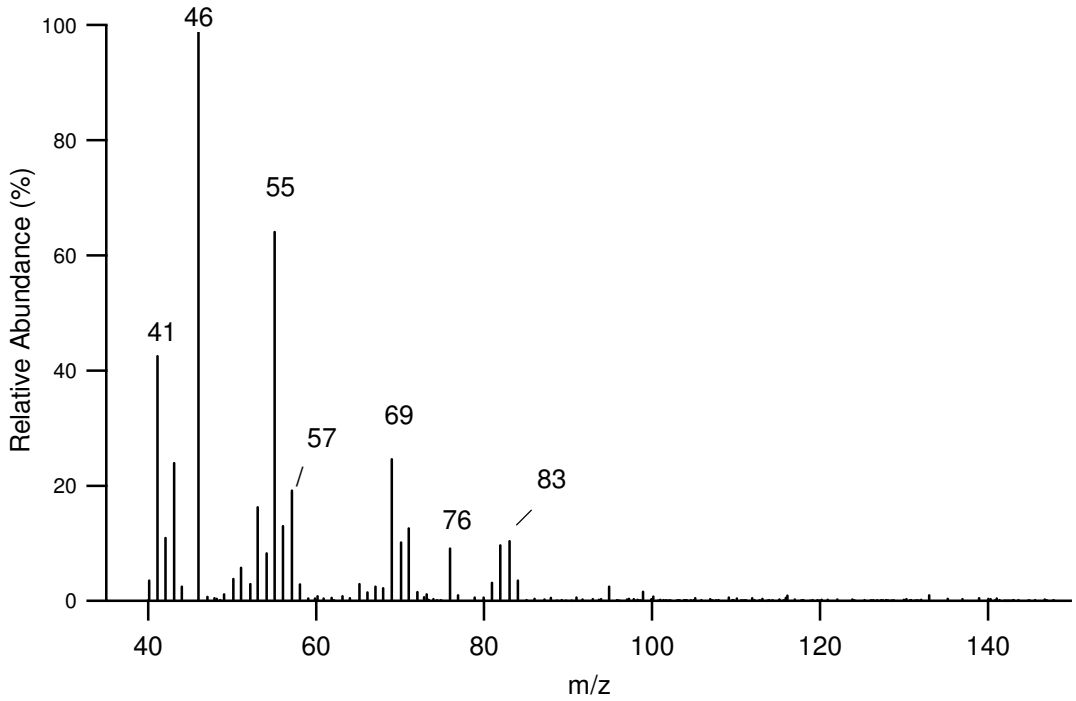

Figure S2.1. EI mass spectrum of the trace impurity in the synthesised species X. Mass scan was to m/z 400, but only data to m/z 150 shown for clarity since no larger masses were observed. No ions were observed that are not shown in the figure.

S3. Instrument performance.

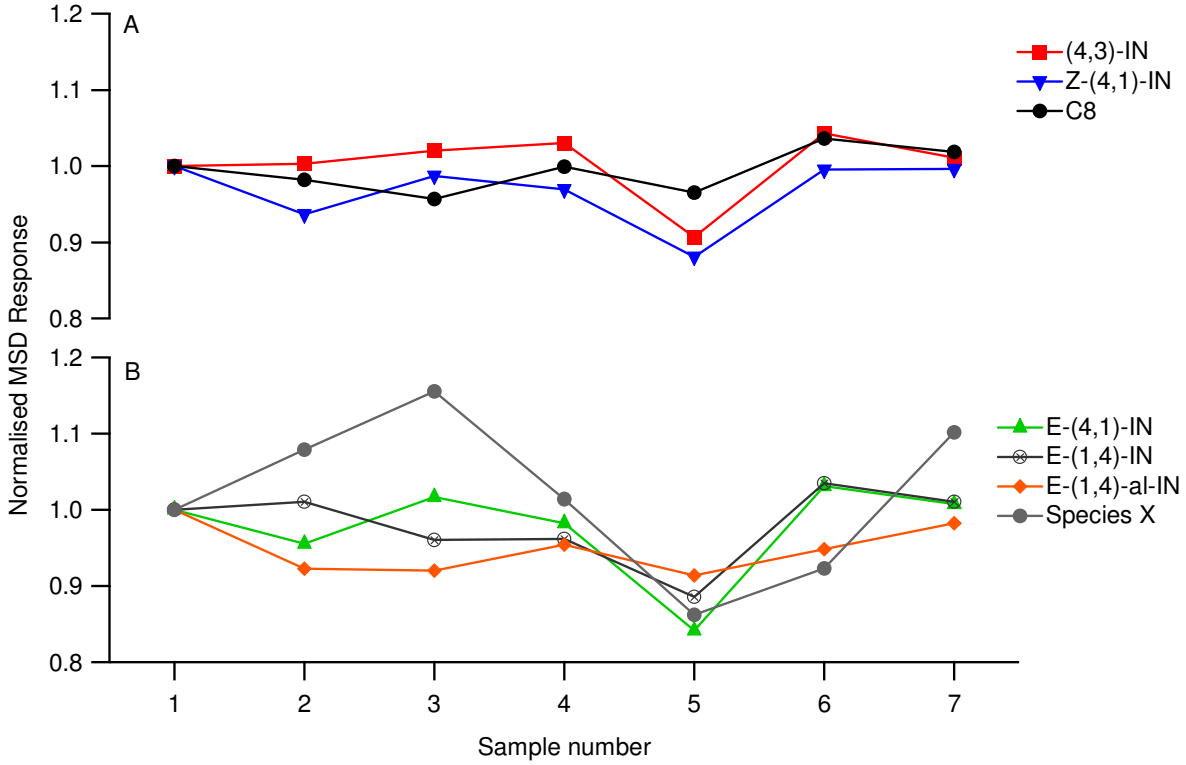

Figure S3.1. GCMS response for 7 consecutive 200 ml samples of a mixture of INs and a stable C_8 nitrate (ethylhexylnitrate) in a temperature controlled aluminium drum. Data for each component are normalised to the response of the first injection of that component.

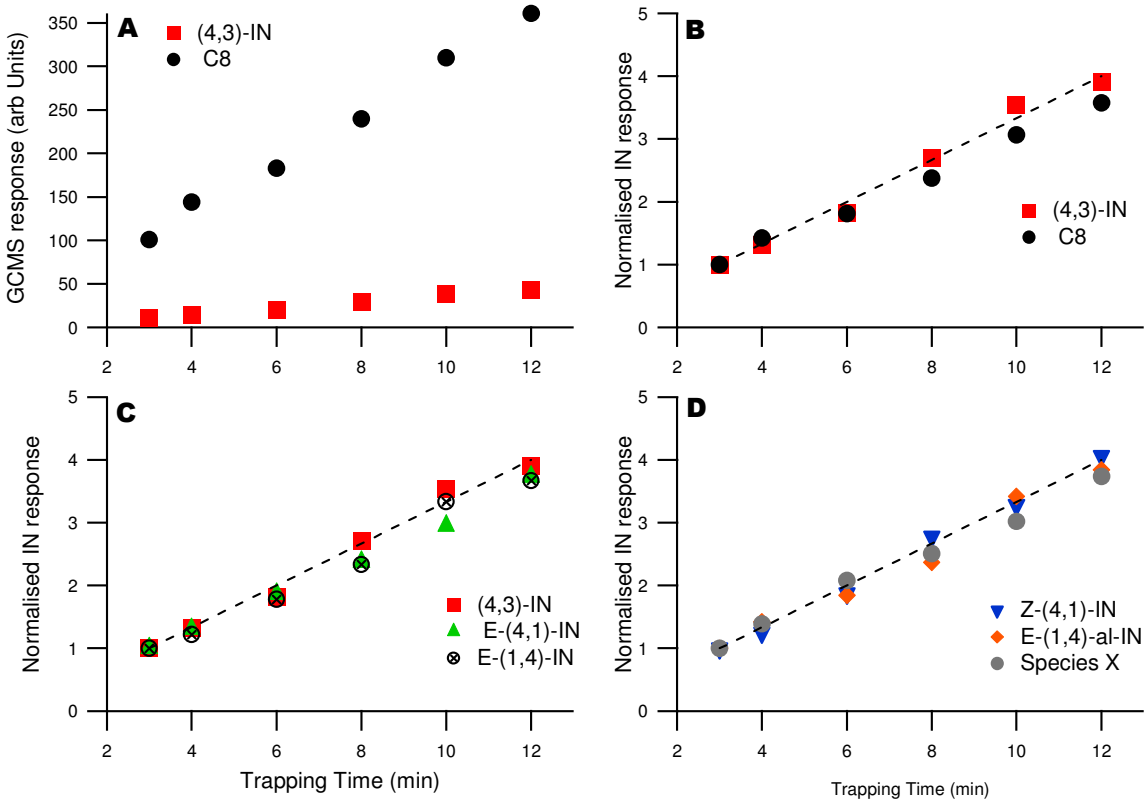

Figure S3.2. GCMS response as a function of trapping time (and thus volume). Samples were trapped at 40 ml min^{-1} at 35 °C on a 3 cm bed of 60/80 Tenax TA in a standard ¼ " glass thermal desorption tube. Injection was at 150 °C for 3 minutes. **A**) Absolute GCMS response for a C_8 alkyl nitrate and (4,3)-IN, **B**) Response C_8 alkyl nitrate and (4,3)-IN normalised to that of the sample trapped at 3 minutes. Also shown are normalised responses of (4,3)-IN, E-(4,1)-IN and E-(1,4)-IN in plot (**C**) and of Z-(4,1)-IN, species X and E-(1,4)-al-IN in plot (**D**). In each plot, the line represents a 1:1 linear increase in response with volume.

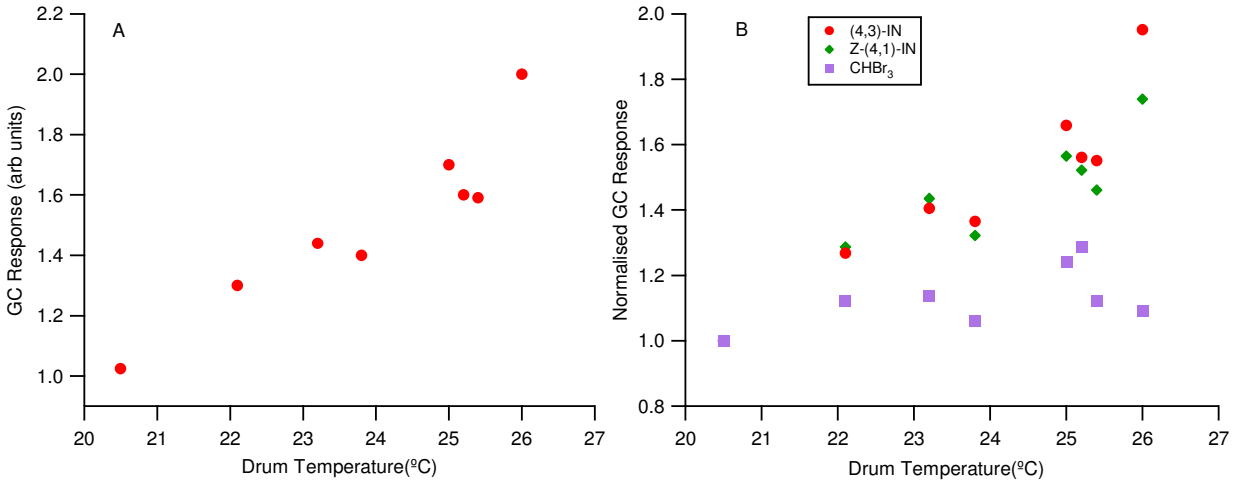

Figure S3.3. The effect of drum temperature on the observed GCMS response to isoprene nitrates. A) shows the absolute GCMS response to (4,3)-IN as a function of drum temperature. B) The responses of two INs and $CHBr_3$ (a more volatile, stable compound as a control) with drum temperature normalised to their responses at 20.5 °C. The measurements were made over two days, and the temperature of the drum was increased or decreased by blowing cold air over it with an external fan or by insulating it and allowing the heat from the internal fan to warm the drum. The temperature was measured with a pt100 sensor mounted on the drum wall (on the opposite side to the external cooling fan)

S4 Chemiluminscence measurements

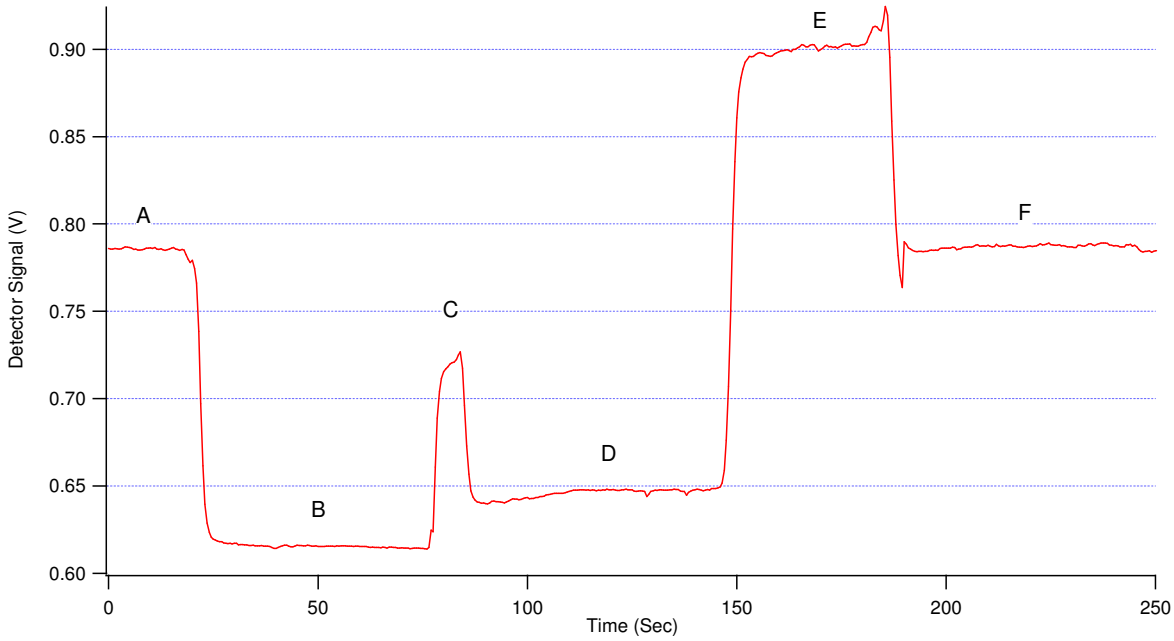

Figure S4.1 Signal from the chemiluminescence analysis of a (4,3)-IN dilution in a glass calibration volume. A and F are NO_2 calibrations (at 15.0 ppb), B is Zero air, C is lab air, D and E are the IN dilution sampled through cold (D) and hot quartz (E). E-D is the measured IN (22.7 ppb), D-B is the measured NO_2 (2.7ppb).

Figure S4.1 shows the CL analysis of a dilution of (4,3)-IN. In the paper we assume that the signal D-B represents NO_2 in the calibration volume and that IN is determined by E-D, however any decomposition in the CL instrument itself and direct reaction with luminol would also contribute to D-B and thus give an underestimate of the true IN concentration.

In our experiments the magnitude of the D-B signal showed no strong correlation to either E-D nor E-B (total NO_Y) and varied between 6% and 30%of the total NO_Y signal. Direct reaction of the IN with luminol is possible, and PAN is well known to react quantitatively, although Hao et al (1994) report that gas-phase C_6 alkyl- and hydroxy nitrates do not react with luminol directly. The residence times of gases, temperatures, solution compositions etc are constant in the CL system, so we would expect that any direct reaction would thus produce a signal that is a constant fraction of the IN. The lowest fraction of 6% for the D-B signal thus represents the maximum possible contribution from the direct reaction (if zero NO_2 is present)

Similarly for decomposition within the CL system, if there is no direct reaction and NO_2 is absent in the IN dilution, then internal decomposition can result in a maximum of 6% underestimation of the IN concentration. The wetted materials of the CL system are as inert as possible consisting only of a short capillary column inlet, the quartz tube and PFA .Given the residence time of approximately 10 seconds inside the CL system (of which

<1 second is in contact with quartz) compared to the several hours to a day inside the glass calibration volume, it seems very likely that NO_2 formed in the calibration volume contributes the majority of the D-B signal at all times.

Reference: Hao, C., Shepson, P.B., Drummond, J.W., Muthuramut, K., Gas Chromatographic Detector for Selective and Sensitive Detection of Atmospheric Organic Nitrates, Anal. Chem., 66, 3137-3143, 1994.

S5 Observation of (1,2)-IN using direct injection

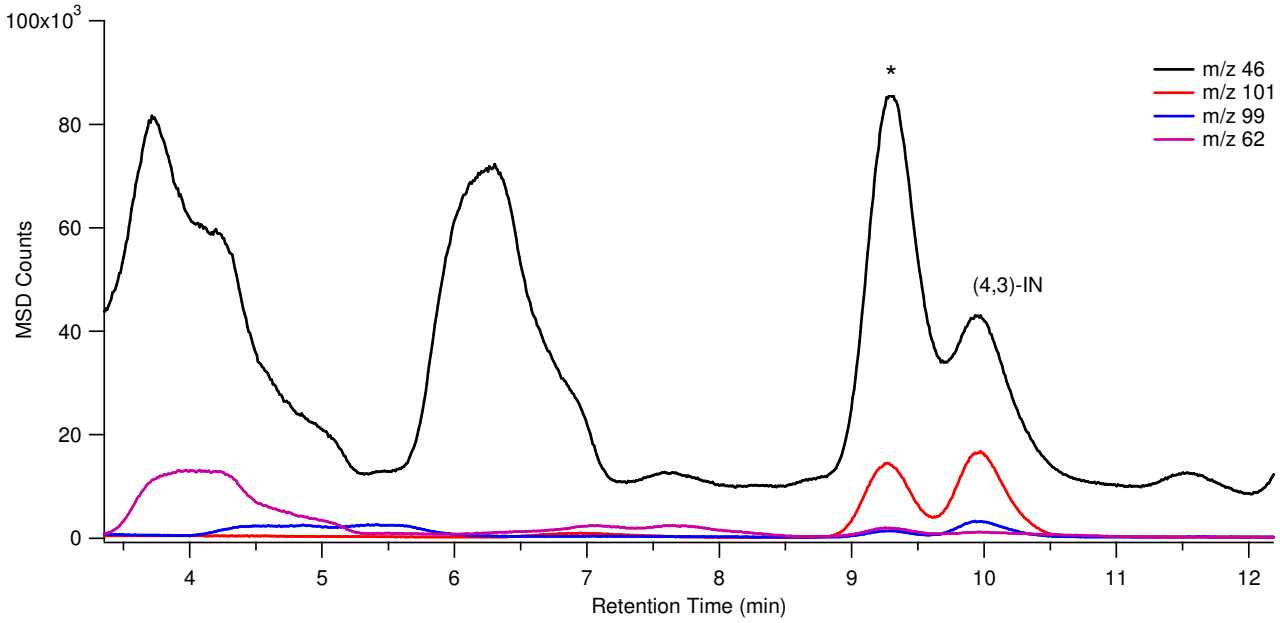

Fig S5.1. Chromatogram of the direct injection (not using preconcentration) of a bag photochemistry experiment showing the presumed (1,2)-IN isomer (*). Sample separated using a 4 m Rtx-200 + 0.6 m Rtx-1701 combination column (J.Crounse, pers. Comm.) at 15 °C, joined with a non-metal union. Injection: 5 ml of air from a PFA loop through a PEEK valve held at 50 °C. The mass spectrometer was operated in SIM mode, so a full mass spectrum was not obtained.

Fig. S5.1 illustrates that using a direct injection method, short cooled column and no metal parts gives a peak eluting before (4,3)-IN which has similar ion fragments to the (4,3)-IN on our system. While we do not have a full mass spectrum of this (or identification from a pure sample), the elution prior to (4,3)-IN would suggest that this is (1,2)-IN based on the order of elution found by Nguyen et al. (2014). The fact that we do not see a peak with these ion fragments prior to (4,3)-IN when we use the Tenax based pre-concentration method as described in the main paper confirms that that (1,2)-IN is indeed lost on that system.

Reference: Nguyen, T. B., Crounse, J. D., Schwantes, R. H., Teng, A. P., Bates, K. H., Zhang, X., St. Clair, J. M., Brune, W. H., Tyndall, G. S., Keutsch, F. N., Seinfeld, J. H., and Wennberg, P. O.: Overview of the Focused Isoprene eXperiment at the California Institute of Technology (FIXCIT): mechanistic chamber studies on the oxidation of biogenic compounds, Atmos. Chem. Phys., 14, 13531-13549, doi:10.5194/acp-14-13531-2014, 2014.

.

S6. Synthesised aldehydic isoprene nitrate data.

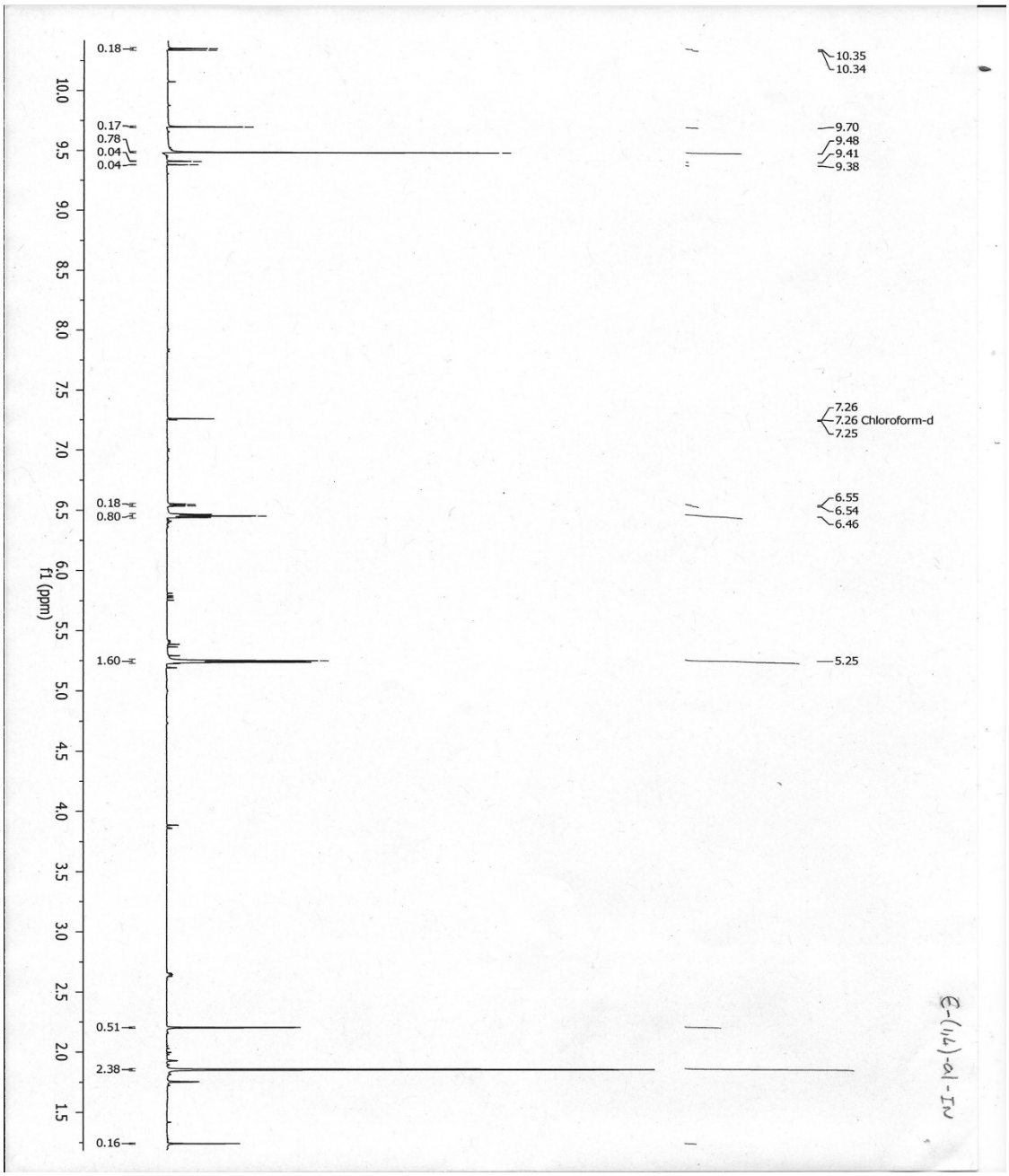

Figure S6.1: ^{1}H NMR (500 MHz, $CDCl_3$) of E-(1,4)-al-IN synthesised from E-(1,4)-IN. The major component in the spectrum (δ 1.85(3H), 5.25(2H), 6.46(1H), 9.48 (1H)) has an identical ^{1}H NMR to that reported by Xiong et al. 2016.

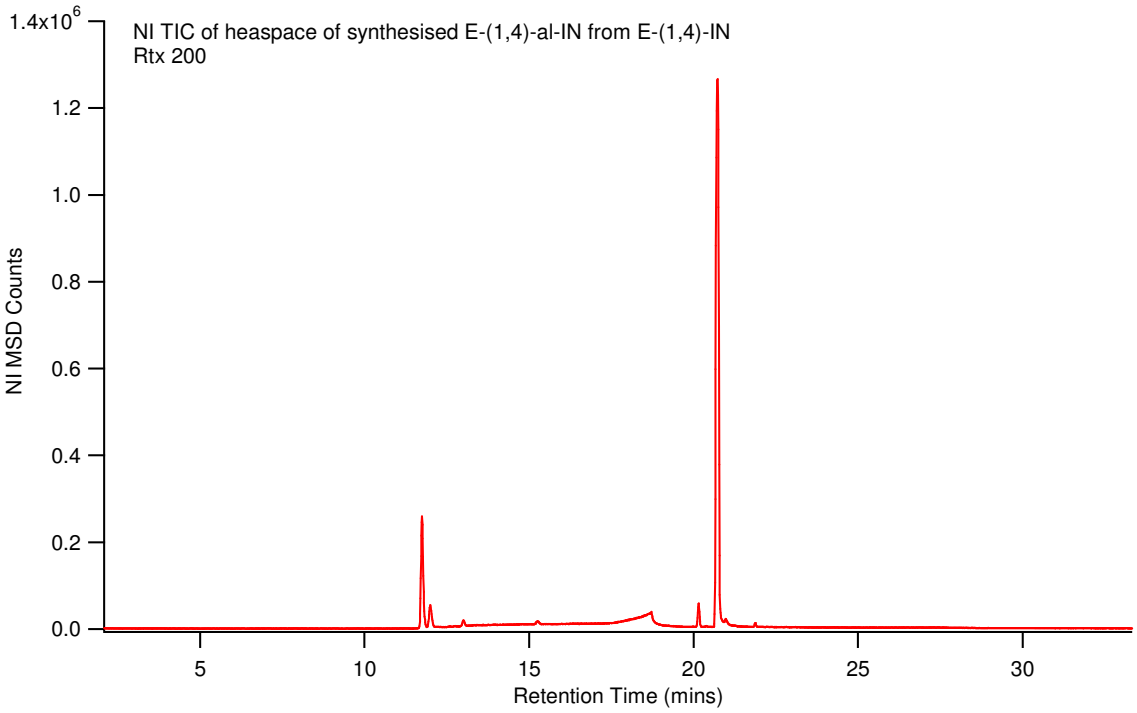

Figure S6.2. NI TIC of headspace of E-(1,4)-al-IN. The slightly different retention times to that reported in the main paper are due to different column lengths and analytical conditions used when this sample was analysed.

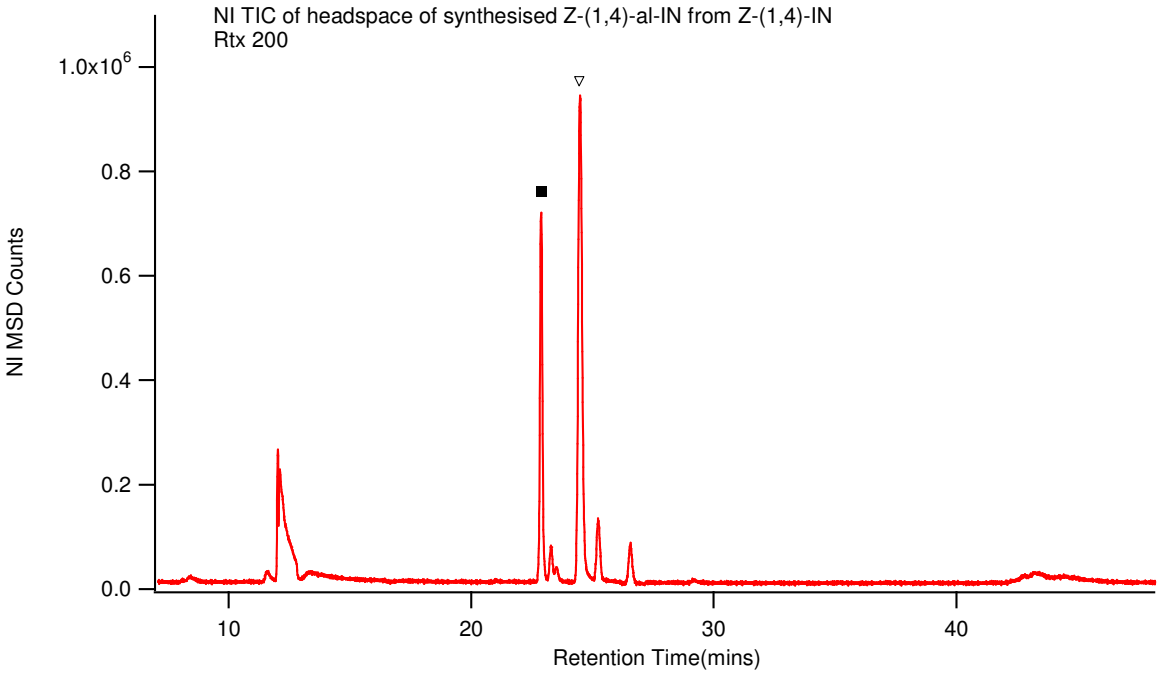

Figure S6.3. Headspace of Z-(1,4)-al-IN synthesised from Z-(1,4)-IN. The peak marked with a triangle is E-(1,4)-al-IN and Z-(1,4)-al-IN is marked with a solid square.

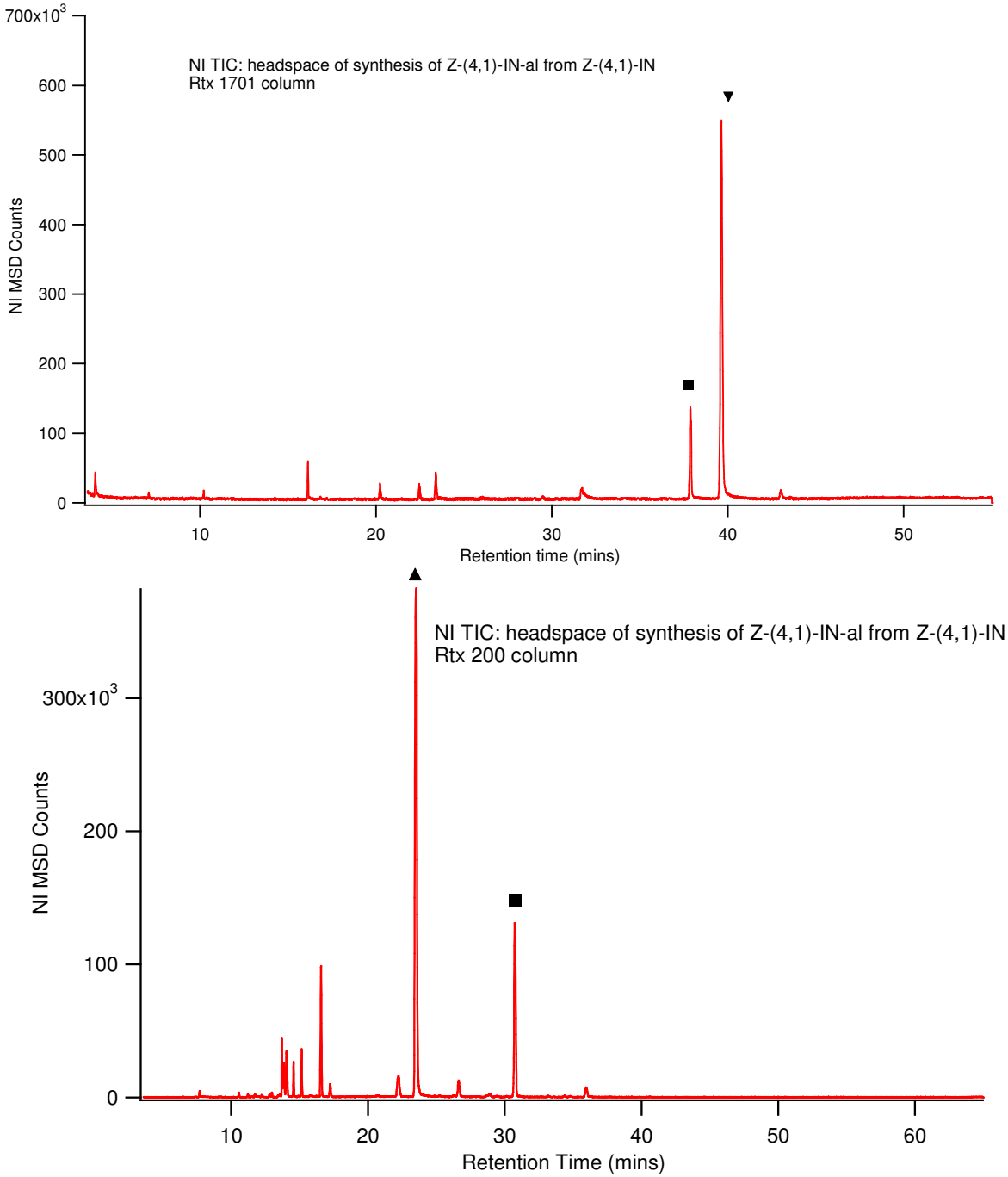

Figure S6.4. GCMS Negative Ion Total Ion Chromatogram (TIC) of the headspace of Z-(4,1)-al-IN made by the oxidation of Z-(4,1)-IN with MnO_2 and analysed on the two different column phases used in this study. In each case, the parent Z-(1,4)-IN hydroxy nitrate is indicated with a triangle symbol, and the aldehyde with a square.

S7. Synthesised Isoprene Nitrate Data (taken from Bew et al. 2016)

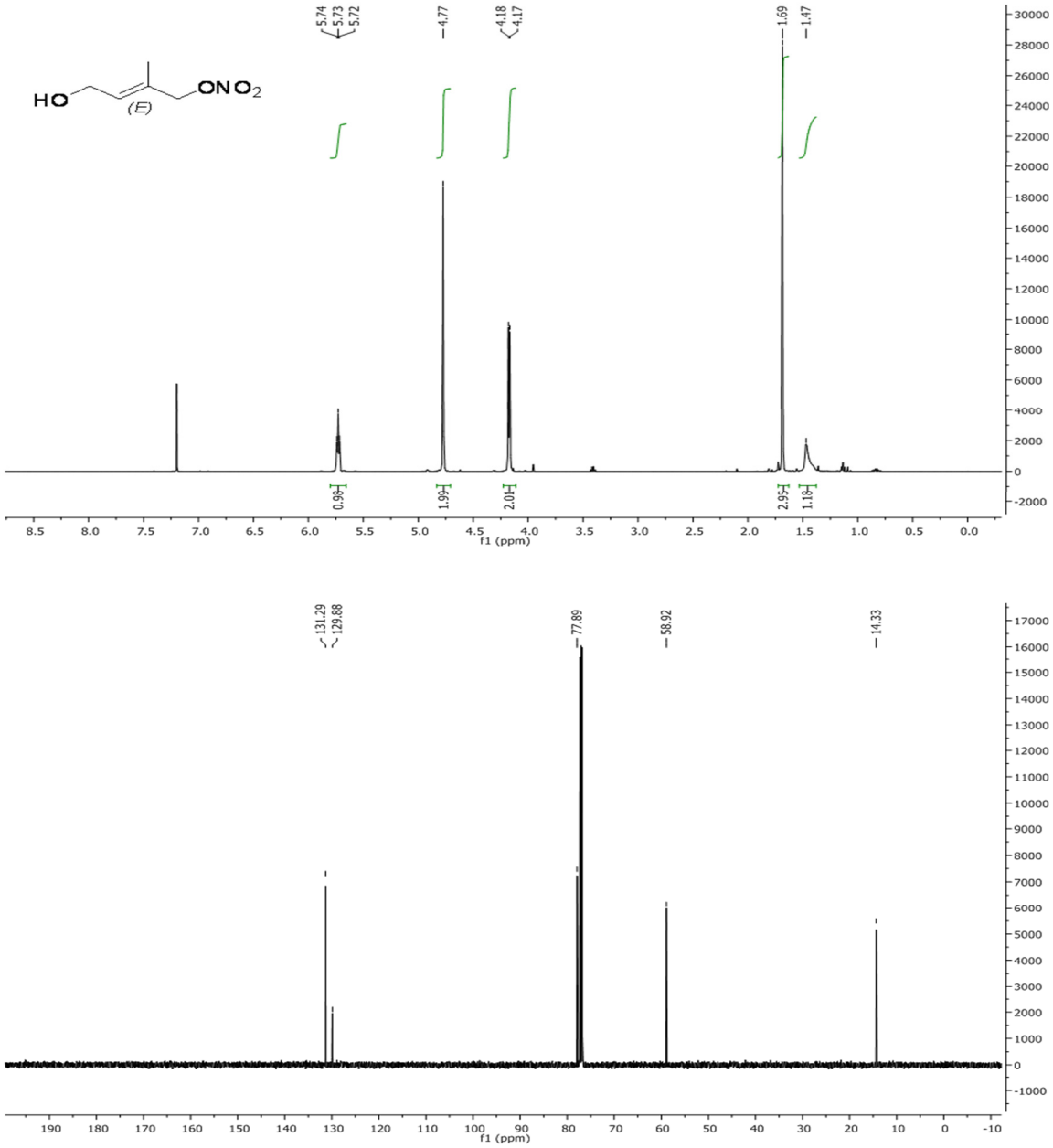

Figure S7.1. E-(4,1)-IN ((*E*)-4-hydroxy-2-methylbut-2-enyl nitrate) NMR data. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.79 (t, *J*5.8 Hz, 1H), 4.84 (s, 2H), 4.24 (d, *J*6.4 Hz, 2H), 1.75 (s, 3H), 1.58 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 131.29, 129.89, 77.89, 58.92, 14.33. **FT-IR** KBr (neat):3349(OH), 2924(alkene), 1633 and 1280 (ONO_2) cm^{-1}.

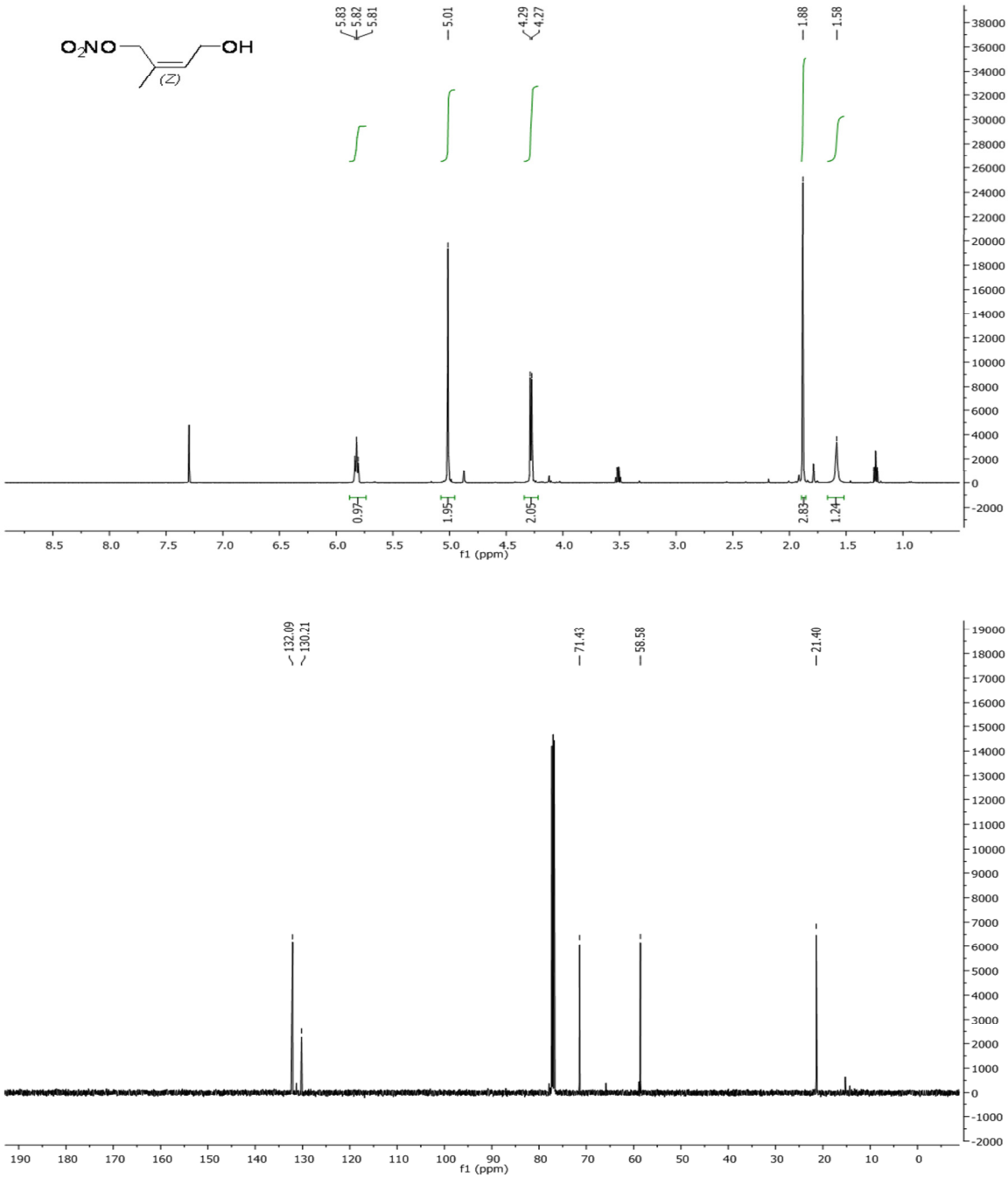

Figure S7.2. Z-(4,1)-IN ((*Z*)-4-hydroxy-2-methylbut-2-enyl nitrate) NMR data. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.78 (t, *J*6.4 Hz, 1H), 4.97 (s, 2H), 4.24 (d, *J*6.7 Hz, 2H), 1.84 (d, *J*1.0 Hz, 3H), 1.60 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 132.09, 130.21, 71.43, 58.58, 21.40. **FT-IR** KBr (neat):3340 (OH), 2921 (alkene), 1630 and 1277 (ONO_2) cm^{-1}

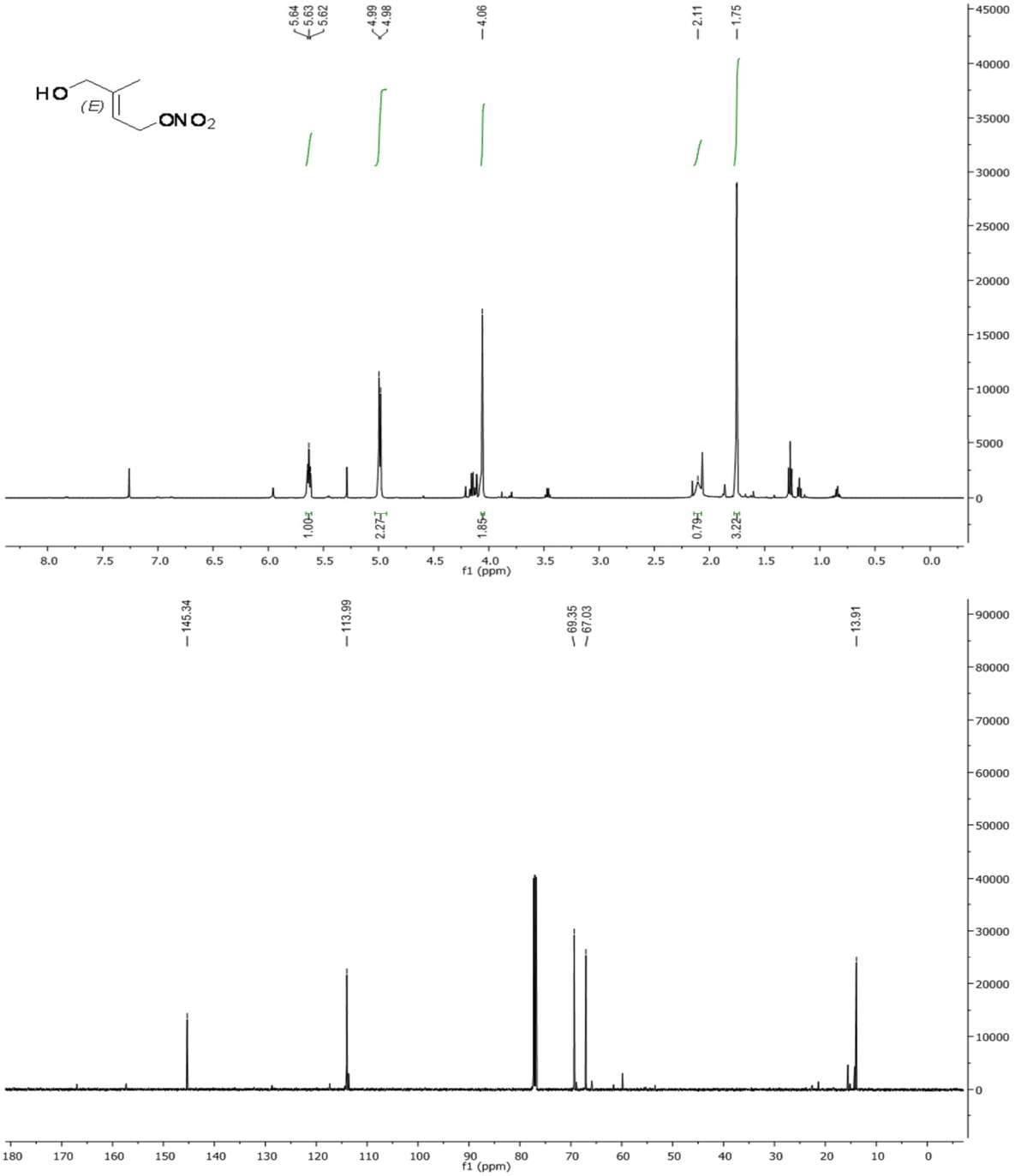

Figure S7.3. E-(1,4)-IN ((*E*)-4-hydroxy-3-methylbut-2-enyl nitrate)**.** NMR data**.** **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.63 (t, *J*6.5 Hz, 1H), 4.99 (d, *J*7.2 Hz, 2H), 4.06 (s, 2H), 2.11 (s, 1H), 1.75 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.3, 113.9, 69.3, 67.0, 13.9. **FT-IR** KBr (neat) : 3353 (OH), 2920 (ene), 1633 and 1279 (ONO_2) cm^{-1}.

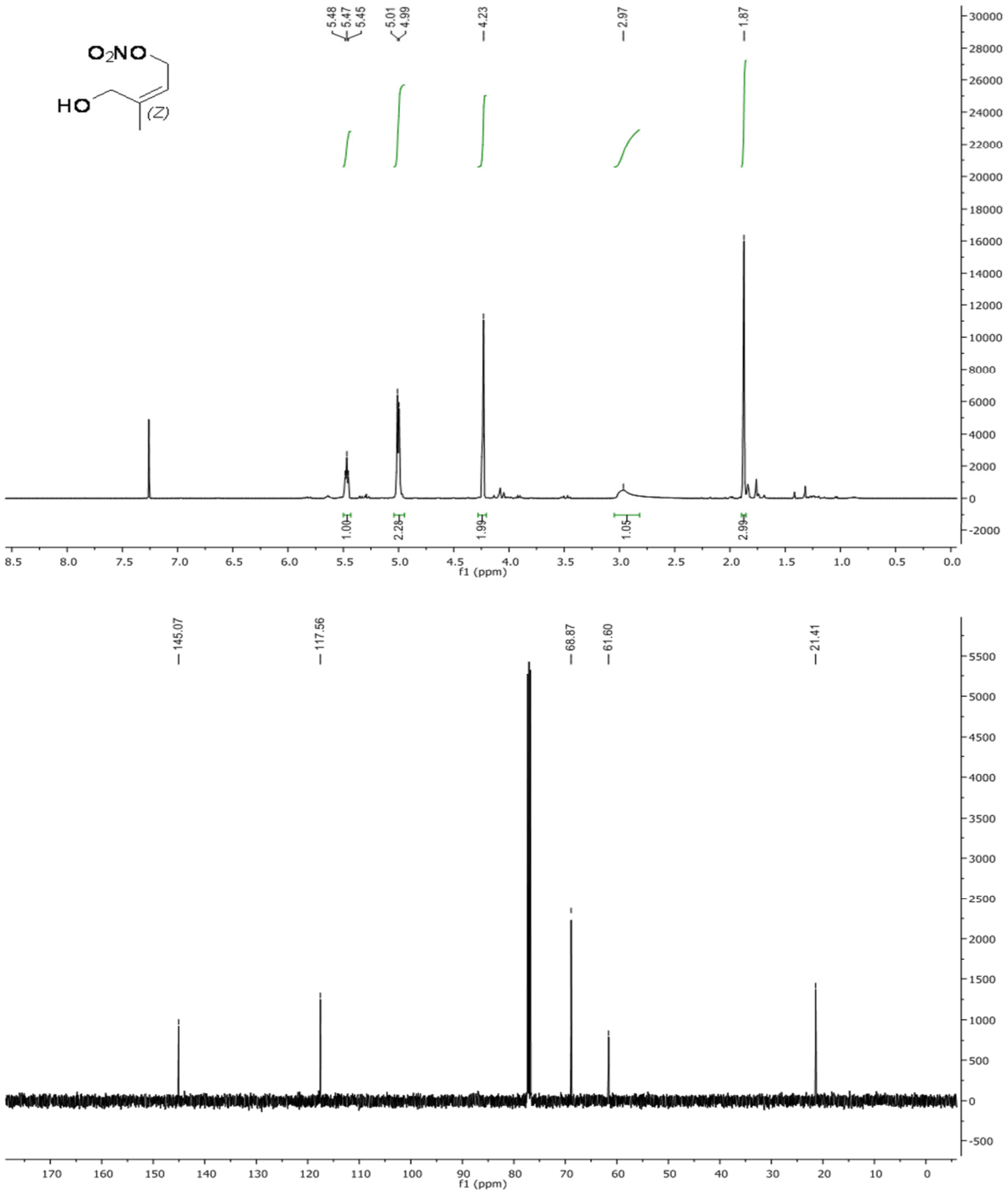

Figure S7.4. Z-(1,4)-IN ((*Z*)-4-hydroxy-3-methylbut-2-enyl nitrate) NMR data. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.47 (t, *J*7.4 Hz, 1H), 5.00 (d, *J*7.3 Hz, 2H), 4.23 (s, 2H), 2.96 (s, 1H), 1.87 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.07, 117.56, 68.87, 61.60, 21.41. **FT-IR** KBr (neat): 3348 (OH), 2920 (ene), 1634 and 1279 (ONO_2).

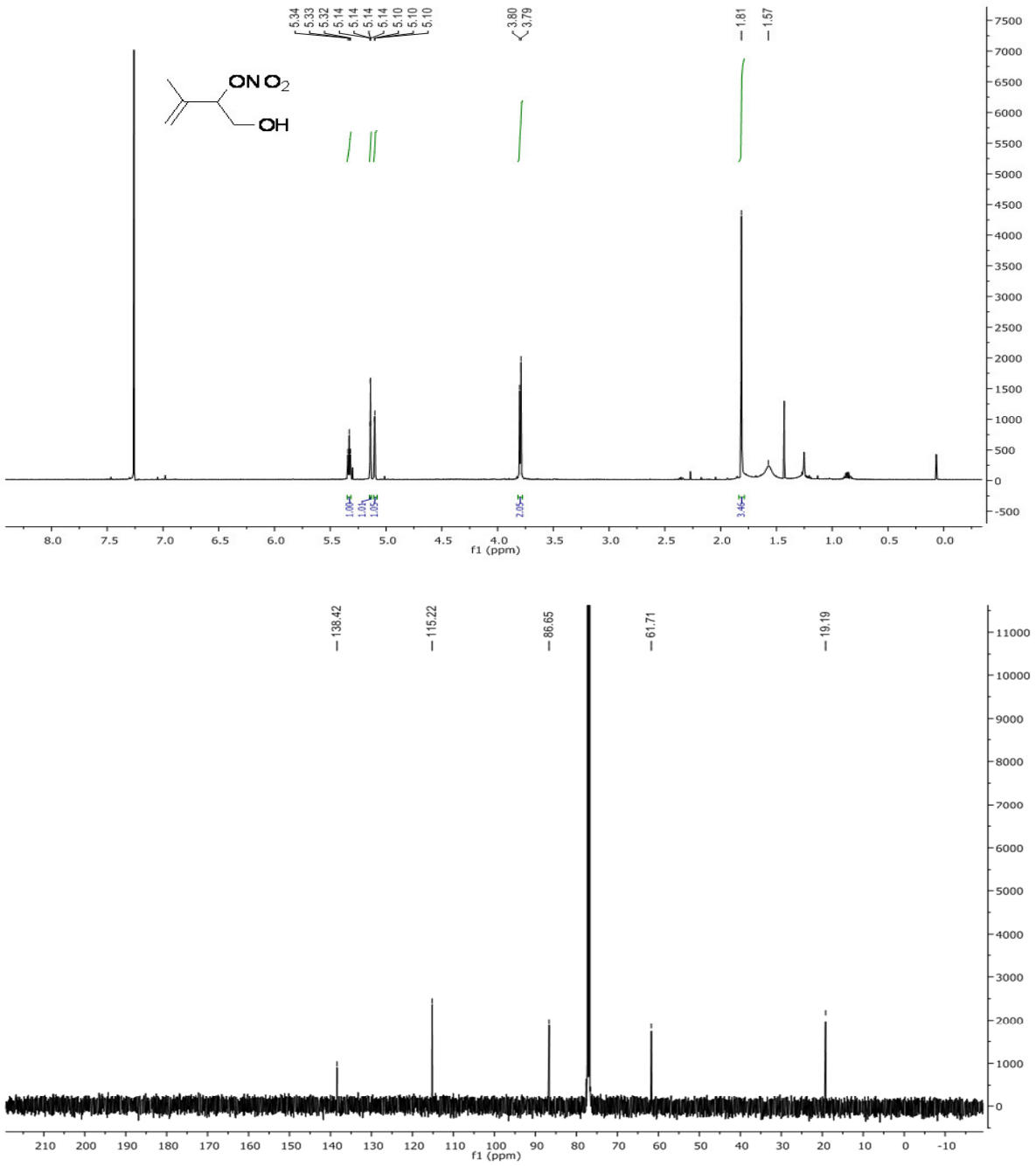

Figure S7.5. (4,3)-IN (2-hydroxy-3-methylbut-3-enyl nitrate) NMR data. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.33 (t, *J*5.7 Hz, 1H), 5.14 (dd, *J*1.8, 0.9 Hz, 1H), 5.11 – 5.08 (m, 1H), 3.80 (d, *J*6.0 Hz, 2H), 1.81 (s, 3H), 1.57 (s, 1H)**.^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.42, 115.22, 86.65, 61.71, 19.19. **FT-IR** KBr (neat) : 3359, 1634, 1274, 856 cm^{-1}

Acetone Nitrate NMR data:

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.94 (s, 2H), 2.22 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 197.97, 73.22, 24.97. **FT-IR** KBr(neat): 2927, 2284, 1722, 1651, 1287 cm^{-1}.

Reference:

Bew, S.P., Hiatt-Gipson, G.D., Mills, G.P., Reeves, C.E., Efficient syntheses of climate impacting isoprene nitrates and (1R,5S)-(-)-myrtenol nitrate. Submitted: Beilstein Jounal of Organic Chemistry, 2016.