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 present. The subsequent addition of $(C, H_2) N^+F$ should clearly and quantitatively remove the O silvel present.
- 10 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.
- 15 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.

5 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.

10 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. Mass spectra (EI, NI) of synthesised isoprene nitrates (3,4)-IN (A and B), Z-(1,4)-IN (C and D), E-(1,4)-IN (E and F), Z-(4,1)-IN (G and H), E-(4,1)-IN (I and J), species X (K and L), Z-(4,1)-al-IN (M and N), E-(1,4)-al-IN (O and P), Z-(1,4)-al-IN (Q and R), acetone nitrate (S and T). A, C, E, G, I, K, M, O, Q and S are EI mass spectra and B, D, F, H, J, L, N, P, R and T are NI mass spectra.



Figure S2.2. 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.



Figure S3.1. GCMS response for 7 consecutive 200 ml samples of a mixture of INs and a stable C₈ 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 ¹/₄ " glass thermal desorption tube. Injection was at 150 °C for 3 minutes. **A**) Absolute GCMS response for a C₈ alkyl nitrate and (4,3)-IN, **B**) Response C₈ 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 CHBr₃ (a more volatile, stable compound as a control) with drum temperature normalised to their responses at 20.5 $^{\circ}$ 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. Synthesised aldehydic isoprene nitrate data.



Figure S4.1: ¹H NMR (500 MHz, CDCl₃) 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 ¹H NMR to that reported by Xiong et al. 2016.



Figure S4.2. 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 S4.3. 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 S4.4. 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.

S5. Synthesised Isoprene Nitrate Data (taken from Bew et al. 2016)



Figure S5.1. E-(4,1)-IN ((*E*)-4-hydroxy-2-methylbut-2-enyl nitrate) NMR data. ¹H NMR (500 MHz, CDCl₃) 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). ¹³C NMR (126 MHz, CDCl₃) δ 131.29, 129.89, 77.89, 58.92, 14.33. FT-IR KBr (neat):3349(OH), 2924(alkene), 1633 and 1280 (ONO₂) cm⁻¹.



Figure S5.2. Z-(4,1)-IN ((*Z*)-4-hydroxy-2-methylbut-2-enyl nitrate) NMR data. ¹**H NMR** (500 MHz, CDCl₃) 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, CDCl₃) δ 132.09, 130.21, 71.43, 58.58, 21.40. **FT-IR** KBr (neat):3340 (OH), 2921 (alkene), 1630 and 1277 (ONO₂) cm⁻¹

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Figure S5.3. E-(1,4)-IN ((*E*)-4-hydroxy-3-methylbut-2-enyl nitrate). NMR data. ¹H NMR (500 MHz, CDCl₃) 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). ¹³C NMR (126 MHz, CDCl₃) δ 145.3, 113.9, 69.3, 67.0, 13.9. **FT-IR** KBr (neat) : 3353 (OH), 2920 (ene), 1633 and 1279 (ONO₂) cm⁻¹.



Figure S5.4. Z-(1,4)-IN ((*Z*)-4-hydroxy-3-methylbut-2-enyl nitrate) NMR data. ¹**H NMR** (500 MHz, CDCl₃) 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, CDCl₃) δ 145.07, 117.56, 68.87, 61.60, 21.41. **FT-IR** KBr (neat): 3348 (OH), 2920 (ene), 1634 and 1279 (ONO₂).



Figure S5.5. (4,3)-IN (2-hydroxy-3-methylbut-3-enyl nitrate) NMR data. ¹H NMR (500 MHz, CDCl₃) 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).¹³C NMR (126 MHz, CDCl₃) 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:

¹H NMR (500 MHz, CDCl₃) δ 4.94 (s, 2H), 2.22 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 197.97, 73.22, 24.97. FT-IR KBr(neat): 2927, 2284, 1722, 1651, 1287 cm⁻¹.

5 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.