

Response to Referee #4

Thank you for the valuable comments and suggestions. Our answers are in bullet points below the original referee comments in **bold**, changes to the manuscript are in *italics*.

The manuscript presents synthesis methods for nitrate esters with relevance to terpene oxidation products in the atmosphere. The authors report preparation and purification of nine nitrate esters and additionally provide some details on unsuccessful methods. The information contained in this manuscript will be of interest to atmospheric chemists looking into nitrate radical oxidation products and I recommend acceptance after the following comments are addressed.

Thank you for the general comments on the importance of our work.

1. Was the HPLC listed on page 3 line 12 used on the Orbitrap? If so, what conditions were used (solvents, gradient, spray conditions, etc.). Were both positive and negative ion mode used? How was the instrument mass calibrated?

- The HRMS data was generated by direct infusion, bypassing the HPLC. The ion mode is indicated as either “ESI+” or “ESI-” as well as in the charge of the masses observed. The facility technician loaded the most recent tune files (for both positive and negative modes) and checked the calibration with a standard sample (reserpine).

2. Acronyms I noticed that should be added to the list: CV, TLC, br, dq and qd, vs, Rf etc.

- abbreviations have been added to section 2.1.

3. Exact mass measurements were only provided for a subset of the samples. Why is this the case? Also, the expected exact masses for the anions are incorrect, check to make sure the mass of the electron has been added. The expected exact mass for C₁₀H₁₆O₄N⁻ is 214.10848. (page 9 line 6 and page 10 line 16)

- HRMS data has been added for all previously unreported compounds.
- exact mass for C₁₀H₁₆O₄N⁻ was corrected to 214.10848.

4. Methanolysis products were observed when methanol was used as the analysis solvent (page 18). Were these the only products observed or were the desired products also observed? Did this occur for all the nitrate esters? Also, please clarify what M⁺ is for each of the masses. I can see how m/z 185.1 is formed but I do not see where m/z 223.13 is coming from. Also, are these exact mass measurements? If so, providing more numbers after the decimal is a good idea.

- These were low resolution GC-MS data. The *m/z* 223.1 is consistent with M+K (it was incorrectly indicated as M+Na).

5. Figure 7 is very crowded, especially at the far right side on top. I recommend providing a little more space between compounds 22, 23 and 24 so that they are easier to see.

- added spacing to figure 7 as allowed by document margins.

6. Incomplete citation on page 2, line 10

- replaced with “Nozière et al., 2015”

7. m/z should be italic throughout

- corrected to italicized *m/z*.

8. Formatting on the citations looks a little odd, especially the spacing between the comma and the dates

- Deleted extra spacing in citations.