

Response to Referee #1

Our answers are in bullet points below the original referee comments in **bold**, changes to the manuscript are in *italics*.

This manuscript describes the synthesis and characterization of a number of hydroxy nitrate esters of monoterpene compounds. Specifically, the work refines a previously identified route to hydroxy nitrate esters – reaction of epoxide precursors with bismuth nitrate – and shows that it is a general pathway to a variety of potentially important nitrate esters. Because of the need for analytical standards for organic nitrates, this work will be of interest to readers of Atmospheric Chemistry and Physics. I recommend publication after the authors consider the following suggestions for improvement of the manuscript.

Thank you for the acknowledgement of the importance of our work.

- 1. p. 2 line 24: The cited work was not controversial - it was a case of scientific fraud. I would change this last clause to "and has been subject of a retracted study."**
 - We were unaware of the specific circumstances of the retraction and have corrected the last sentence to read "*and has been subject of a retracted study.*"
- 2. p. 3 line 7: It seems as if the column chromatography method is critical to the success of this work (intractable mixtures turn out to be tractable). Is this particular system critical to this success? I'm not familiar with it.**
 - Automated chromatography systems have become common in both academic and industrial organic laboratories. Teldyne Isco and Biotage are two of the major companies that manufacture such systems. Typically the chromatography systems can handle higher pressures and also finer grades of silica. The increased pressure, finer grades of silica, coupled with the accuracy of pumps for gradient elutions leads to better separations than standard glass column chromatography. We have not tested the purification of these compounds by methods other than the CombiFlash Isco. We have tested other lower grades (40-63 μm irregular) of silica and have found that the finer grade (25 μm spherical silica) gives optimal separation.
- 3. p. 3 line 25: ^{13}C NMR data is very useful when using reference data to analyze complex mixtures. I see that some species have ^{13}C characterization, and some don't (like this species). It would strengthen the utility of this work if as much ^{13}C characterization were included.**
 - We have included full characterization (^1H & ^{13}C NMR, IR, HRMS, melting point, R_f) for all new compounds. Known compounds, such as *trans*-carene oxide, have been described by their ^1H NMR and a literature reference, as is standard practice.
- 4. p. 7 line 1: There should be a reference to the numbering system here (or preceding this section) and the information given that the structures are given later in the paper. I also think the name should include monoterpene precursor to help keep track of the various species.**
 - We have appended structures for each experimental procedure to clarify the numbers and structures.
- 5. p. 19 line 18: The authors should expand on how their results bear on previous work. Generally, it would be valuable to point out that these reactions generally lead to ring**

opening of the bicyclic backbone of the monoterpene. The atmospheric chemistry literature contains a number of proposed monoterpene epoxide reaction products in which the bicyclic backbone is retained (for example, see Duporte, G et al. Experimental Study of the Formation of Organosulfates from α -Pinene Oxidation. Part I: Product Identification, Formation Mechanisms and Effect of Relative Humidity. The Journal of Physical Chemistry A 2016, 120 (40), 7909–7923) even though the synthetic literature shows that this is not usually the case. Specifically, it should be pointed out that Rindelaub's compounds 1 and 2 are the present work's compounds 17 and 22, and some comparison of the two methods should be given. The authors should also summarize the species for which they were not able to isolate compounds (such as several tertiary nitrates, which have previously been shown to highly susceptible to hydrolysis) since this is valuable information concerning the potential stability of these compounds in the atmosphere.

- We have added the following to the conclusions section “*Interestingly, we did not observe the formation of α -pinene oxide and β -pinene oxide products that retained their bicyclic ring structures. This is consistent with the solution phase synthetic literature (Kaminska et al., 1992) but in contrast to many atmospheric reports (For example, see: Rindelaub, 2016b; Duporte, G., et al., 2016).*”
 - The reports of compounds 1 & 2 lacked reference to relative stereochemistry. Due to the potential presence of diastereomers, we prefer to keep our compounds (that are single diastereomers and indicated relative stereochemistry) labeled separately.
6. **p. 2 line 10: typo (incomplete citation)**
 - citation corrected to (*Nozière et al., 2015*)
 7. **p. 11 line 1: type: add “oxide” to heading name**
 - name corrected to “ *β -pinene oxide*”
 8. **Figure 7, Compounds 23 and 24: It is very difficult to see the dashed line bonds to the nitrate groups.**
 - Decreased the hatch spacing/increased the number of hatches for dashed bonds
 9. **p. 16 line 3: typo: slashed “o” should be lower case**
 - corrected to “Brønsted”
 10. **p. 16 line 12: typo: author name is currently in all capital letters**
 - corrected capitalization of author names in reference.