Response to Referee #2

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*.

In the manuscript titled "Preparation and purification of atmospherically relevant a-hydroxynitrate esters of monoterpenes", McKnight et al described the synthesis of a series of nitrate esters. Currently there is large uncertainties in secondary organic aerosol formation especially from organic nitrate esters derived from biogenic volatile organic compounds, in part hindered by the availability of standards. Thus, availability of nitrate ester standard would bridge the critical knowledge gap exists in our further understanding of the mechanism of aerosol formation. This would be of interest to the reader of ACP.

Thank you for this positive assessment. We also hope that the availability of these compounds will help fill this critical knowledge gap.

1. **First of all, since this is a journal on atmospheric science and the title stated "Preparation and purification of atmospherically relevant a-hydroxynitrate esters of monoterpenes", the reviewer feels that it is worthwhile to more specifically spell out the relevance of the synthetic targets with atmospheric chemistry mechanistically. The way the authors frame the whole set of compounds as a general class "nitrate ester of monoterpenes" is good in a general way with the synthesis of variously nitrate esters as the general aim, a little bit more detailed account on the relevance of all the targeted compounds with atmospheric chemistry would be appropriate for majority of the reader of this journal. The author did an extensive investigation on the reaction of nitrate with epoxide, if that were to be emphasized for its relevance, it would be better to spell out clearly.**
    - We have clearly delineated the importance of these compounds in terms of atmospheric chemistry in the introduction section. As a technical note, we believe that the introduction is sufficient background information to convey the importance of our work and will leave descriptions of the detailed and complicated mechanistic fates to the references sited therein.
2. **As the author presented in the manuscript, IR would provide characteristic peaks for NO2 group, supporting the existence of nitro group in the analyzed molecule. As the indicated in table 1 of this manuscript, compared to the corresponding alcohols, the nitrate esters likely would have very similar NMR spectral profile with only the proton and carbon at the alpha position to the nitrate ester group to likely exhibit significant chemical shift difference. On the other hand, mass spectroscopy would be very important in such characterization if a good spectrum is feasible. The absence of such data from many nitrate ester target compounds in this manuscript would be better to be explained since only the HRMS of a few of them are provided.**
    - HRMS data have been added for all previously unreported nitrate esters.
3. **The opening of the cis and trans-1,2-limonene oxide with Bi(NO2)3 under the same conditions led to different nitrate ester with nitro group attached to different positions to afford different constitutional isomer, instead of stereoisomer. The reason behind it might be the same as the kinetic resolution of the cis and trans-1,2-limonene oxide. This fact merits more discussion and more detailed 2-D NMR spectroscopy evidence in**

addition to those original 1-D NMR spectrum provided by the author would be very helpful to go with the description text.

- Added clarifying text and updated figure 5. *"The nitration of the cis isomer was predicted to produce the tertiary nitrate ester via stereoelectronic effects. The dominant conformation of cis-1,2-limonene oxide is expected to be a pseudo-half chair (Figure 5). Nucelophilic substitution at the less substituted position would proceed through a lower energy chair-like transition state, whereas attack at the more substituted carbon leads to a very unstable twist-boat. The nitration of cis-1,2-limonene oxide (**cis-12**) proceeded smoothly in both dioxane (53%) and dichloromethane (63%). Respectively, the trans isomer was expected to produce the secondary nitrate ester."*
- HSQC data have been added to the supplement document

4. **The characterization of limonene-diol doesn't seem to match with other report (J. Am. Chem. Soc. 2018, 140, 1502−1507). Since the other report provided the original NMR spectrum, it would be feasible for the author to provide an explanation of the discrepancy. Furthermore, in figure 4, the author attributed the transformation of compound 10 to 11 and back an interchange equilibrium. That interpretation is better to be explained further since it is not obvious.**
   - Thank you for bringing this to our attention. We revisited the reaction of **9** in acetonitrile & dioxane. Upon further characterization (^{13}C NMR, gHSQC) we determined that the product formed in acetonitrile is actually a 1:1 diastereomeric mixture of oxazolidine **10a**. Of note were ^{13}C signals at: 162.62, 162.55 ppm (carbonyl carbon), 72.77, 72.62 ppm (tetrasubstituted C), 13.87, 13.86 ppm ($\underline{C}H_3C$). The structure was further confirmed by an IR stretch at 1674 cm^{-1} and an *m/z* 193.8 (M+). This type of reactivity with bismuth nitrate and acetonitrile opening epoxides was also observed by Pinto, et al., 2007.
   - The interchange of either limonene-diol or nitrate **10** can be rationalized by an intramolecular elimination and tautomerization.
5. **There are other suggestions**

Page 1 Line 21. The abbreviation "ON" is not necessary as it is used only once.

- Amended the text to utilize the abbreviation for organonitrate.

Page 2 Figure 1. Compound 1 is basically compound 13 without stereo isomer indication.

- The reports of compounds 1 & 2 lacked reference to relative stereochemistry. Due to the possible presence of two diastereomers, we prefer to keep our compounds (that are single diastereomers and indicated relative stereochemistry) labeled separately.

Page 3 Line 17. "0.86 mL, 1 g" incorrect.

- Corrected to "0.86 g, 1 mL"

Page 3 Line 25. Citation year incorrect.

- Corrected to 2009

Page 3 Line 27. Citation better to be placed at the first mention.

- Amended to "Crocker and Grayson, 1969" at first mention.

Page 4 line 10. "(9 am – 11 am)" relevant?

- deleted

Page 5 line 7. Citation better to be placed at the first mention

- Amended to "Steiner, et al., 2002" at first mention.