Referee #5

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 paper by McKnight et al. presents successful synthetic routes to the preparation of the hydroxy nitrates that are produced in nature by the atmospheric oxidation of monoterpenes. In recent years it has been shown that formation of these organic nitrates are an important sink for NOx in the atmosphere, as well as an important mechanism for the production of atmospheric aerosol. Such aerosol results from an interaction between anthropogenic NOx, and biogenic monoterpenes. Thus, interestingly, control of NOx emissions (from combustion) can influence the role of production of atmospheric aerosol from biogenic emissions. There is thus considerable interest in these compounds, and their atmospheric chemistry, and, e.g. the ability to study their hydrolysis rates. However, the atmospheric chemistry community has not had much success in making these compounds, and that is a major stumbling block to progress. Here is a paper that connects the organic synthesis community to the atmospheric chemistry community in a useful way, and the atmospheric chemistry community increasingly needs this connection, in more general terms. This paper is technically important, and will stimulate a great deal of badly needed research, likely to start with atmospheric chemists at Reed. So, this paper should be published, and I think can be done with only editorial changes. That said, the authors need to be aware that the audience here is indeed atmospheric chemists, who are not versed in the editorial jargon of synthetic organic chemists. So, the paper could be made more readable and useful if the authors shed the notion that they are writing to organic chemists. They are, at best, writing to organic chemists existing with the labs of atmospheric chemistry professors.

Thank you for the assessment of the need for this work. In addition to filling the need for nitrate ester standards, we hope that our work will help bridge the gap between the synthetic and atmospheric communities. We attempted to mitigate the use of jargon and tried to write to a more general audience. We appreciate your input and comments for improving the manuscript.

1. **The last sentence of the Introduction is unclear – 30-40% of MT emissions are at night, or the nitrate radical consumes 30-40% of the emitted MTs at night? Please note that the OH radical oxidation pathway is still an important source of MT-nitrates, e.g. as discussed in Pratt et al., 2012.**
   - Clarified page 1, line 20: Replaced "This nitrate oxidation pathway has been shown to be important with 30-40% of monoterpene emissions occurring at night (Pye et al., 2010)."
   - "*Nitrate oxidation pathways have been shown to be important particularly during nighttime. A large portion (30-40%) of monoterpene emissions occur at night (Pye et al., 2010). These emissions can then react with NO_3 radicals, formed from the oxidation of NO_2 emissions by O_3, (Pye et al., 2010).*"
2. **Line 21, page 2 – is there a better reference for this quite general organic chemistry laboratory hazard?**
   - Despite the well-known hazards of nitric acids, explosions and other accidents occur nearly every year. I believe that it is important to reference examples of recent accidents, such as the incident at UC Berkeley.
   - A second reference (Parker, 1995) was also added.
3. **The Ma et al. paper should not be cited. If you go to the ACP web site, it says "This paper has been retracted."**
   - The reference to the original Ma paper was removed. The citation for the retraction remains.
4. **Page 3, line 17 – what is CPBA? (Good example of my comment above; most organic chemists will know that it doesn't stand for Certified Professional Behavioral Analyst).**
   - We added meta-chloroperoxybenzoic acid (m-CPBA) to the list of abbreviations.

5. **Page 3, line 27 – should the reference be Crocker and Grayson, 1969? And on Page 4, line 8.**
    - Reference for trans-carene oxide (page 3, line 27) is correct.
    - Page 4 line 8 was corrected from Croker, 1969 to Crocker and Grayson, 1969.
6. **Page 5, line 8 should be Steiner et al., 2002. And line 16.**
    - replaced "Steiner" with *"Steiner et al., 2002"*
7. **Page 7, at 2.3.1 title, refer the Table 1 for structures. The reader needs to see the structures. Line 2 – do you mean the trans-3-carene epoxide? Also on line 10, the epoxide?**
    - Inserted structures for each experimental procedure.
    - Corrected "trans-3-carene" to *"trans-3-carene oxide"*
8. **Page 8, line 4, those percentages are the yields? Please try to avoid organic synthetic chemists shorthand. Also line 13. For structures 16 and 17, line 22, are there yields?**
    - Replaced "(53% in dioxane; 62% in DCM)" with *"(53% yield in dioxane; 62% yield in DCM)"*
    - The yields for 16 & 17 were reported in their individual descriptions. Added %yields in the summary description.
9. **Page 8, line 24, what is "the title compound"? Also page 9, lines 4, 17, and 23. There is sloppy shorthand on this page, e.g. line 13 – "the following". What following?**
    - This nomenclature and formatting is standard for organic chemistry experimental procedures.
    - Deleted "the following" and replaced the title compound with "nitrate ester," where indicated.
10. **Line 11 – you mean the a-pinene oxide? Line 17 – by "title compound" you mean the aldehyde? Similarly, I find line 23 confusing. You synthesized the alcohol?**
    - Page 9, line 11, replaced with a-pinene oxide.
    - Clarified by replacing the title compound with the appropriate nitrate ester.
11. **Page 10, lines 13 and 14 – "The title compound", when the title compound is "Nitrate ester 23" does not make for great/easy reading. Perhaps it would be helpful that in each case, the structure should be shown next to the name, as a graphic? That would really make the paper more readable.**
    - Clarified by replacing the title compound with the appropriate nitrate ester and added a graphic with the structure of the compound
12. **Page 14, line 8 – provide a reference for the fast hydrolysis rates.**
    - Added citations to Boyd et al., 2015; Darer et al., 2011; Liu et al., 2012.
13. **Page 19, line 6, re decomposition of ester 14 – does this depend on water content in the solvent? Do you know what the decomposition products are? The corresponding diol?**
    - Nitrate ester **14** was stored as a neat (i.e. water and solvent-free) liquid.
    - Decomposition produces a complex mixture of products that have not been identified.
    - Rephrased to clarify *"For example, tertiary nitrate ester **4** is particularly stable stored as a solid at 0 ºC. In contrast, when secondary nitrate ester **14** was stored as a neat oil at 0 ºC, it decomposed to a complex mixture within a few weeks."*
14. **Page 19, line 9 – the "the" methods, but "successful methods".**
    - corrected to *"successful methods"*
15. **Line 17 – insert "for" after "important".**

- corrected to *"is important for"*