The authors wish to thank all referees for their time and helpful comments concerning the manuscript "Proton affinities of candidates for positively charged ambient ions in the boreal forest" (acpd-13-10603-2013).

Here are our responses to each referee's comments:

Anonymous Referee 1:

Comment: "The text at P3 L11 & P8 L23 and in caption of Fig 2 in connection with the reference Ehn et al., 2010, should be opened a bit more. It is not obvious for a random reader whether the concentrations given (in 1/cm3) are for neutral gas molecules or molecules detected in cluster ions. I believe the latter, but the calculations were performed for neutral base compounds, after all, so this should be clarified."

Answer: The measurements performed by Ehn et al. (2010) were performed on ambient ions. Thus, all measured concentrations were either for positive or negative molecular ions and ionic clusters. We feel that a detailed explanation of the measurement setup is not within the scope of this paper, partly because for our purposes the relative magnitudes of the concentrations (i.e. the qualitative results) are more important than the absolute values. However, it is clear that these matters could be discussed more clearly and we shall do so in the revised manuscript.

In addition, the calculations were not performed on just neutral base compounds. In order to calculate the proton affinity of a molecule one needs to simulate both neutral and positively charged cases. This will be expressed more clearly in the revised manuscript.

Anonymous Referee 2:

Our answers to the correspondingly numbered comments:

1. A supporting information document of structures and thermodynamical data will be provided.
2. This will be expressed more clearly in the revised manuscript.
3. While it is true that semi-empirical methods could yield better initial guesses than UFF, the authors find that this extra step will give very small returns for the time invested in doing the calculations. The UFF optimizer is embedded in the ADF-GUI and can be run as the molecule geometry is being built. This phase usually only takes a few seconds and tends to result in initial geometries that look reasonable. It may of course be that some of the CBS-QB3 optimized geometries are local minima, but this uncertainty is an ever present problem in quantum chemistry and as the semi-empirical methods have their own limitations, we do not believe they would solve this issue.
4. The method that is deemed more accurate is the method that gives overall better results compared with the reference values. These reference values are defined on page 10607: "In the cases of methylamine, dimethylamine and trimethylamine, we compared all other methods with the W1BD. In the case of pyridine, all results were compared to the PA value listed in NIST. In the case of ammonia, all results were compared with the PA determined by Czakó et al. (2008)."

   The lines in Fig 1. did not originally correspond to the reference value for MMA, DMA and TMA, but instead represented the values listed in NIST. This could have been stated more

clearly. However, in the revised version of the manuscript, the lines will be changed to correspond to the reference values in order to make the figure more intuitive. The text part will also go through minor revision in order to make motivation behind the choice of method clearer to the reader.

5. By saying we were unable to resolve the issue we meant that we could not find a way around the problem. Trying different starting geometries resulted in the same optimized geometry - as could be expected since it is an aromatic species - and trying to model the McLafferty rearrangement might be comparing apples to oranges. While we believe the value of the calculated proton affinity should be quite accurate for the reaction it was calculated for, it is not clear whether the value is applicable to the actual chemical reaction forming the ion (the McLafferty rearrangement). This is why the calculated proton affinity needs to be questioned. It could of course be omitted, but we wished to include it in the tables for the sake of completeness. Also, we think the discussion about tropylium ion is a useful reminder that modeling seemingly simple things such as the proton affinity is not always straightforward, which is why we wish to include it.
6. This will be expressed more clearly in the revised manuscript and the section will be expanded to include a short discussion on the assumption and the error it may cause.
7. There were in total three cases where references or description of the method was missing. This was purely due to human error and will be corrected in the revised manuscript.
8. The explanations for the green squares and black circles will be added in the legend in the revised manuscript.

All of the typographical errors will be corrected.

Anonymous Referee 3:

There were no additional comments regarding changes in the manuscript.