## **Supporting information:**

## Mass spectrometry-based identification of ortho-, meta- and paraisomers using infrared ion spectroscopy

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Figure S1. CID MS/MS spectra showing the fragmentation of the (a)  $R_1$ -meta-isomer (m/z 460) and (b)  $R_1$ -para-isomer (m/z 460).



Figure S2. (a) Comparison of the IR spectra of the ortho-, meta- and para-isomers with the  $R_2$ -group (m/z 460) (b) IR spectrum of the ortho-isomer of the  $R_3$ -compound (m/z 347) (c) Comparison of the IR spectra of the m/z 202 fragments of the ortho-, meta- and para-isomers from the  $R_2$ -compound. (d) IR spectrum of the m/z 202 fragment of the  $R_3$ -ortho-isomer.



Figure S3. Comparison of the IR spectra of the m/z 202 fragments of the R1-, R2 and R3-ortho-isomers.



Figure S4. (a) IR spectrum of the ortho-isomer with the  $R_4$ -group (m/z 315) (b) Comparison of the IR spectrum of the ortho- and para-isomers with the  $R_5$ -group (m/z 303)



Figure S5. Comparison of the IR spectrum of the m/z 202 fragment of the  $R_1$ -ortho-isomer to calculated IR spectra for the (a) ortho-, (b) meta- and (c) para-phenylethylpiperidine fragment ions. Qualitatively, the best match is indeed found in panel a.



Figure S6. Comparison of the IR spectrum of the m/z 202 fragment of the  $R_1$ -meta-isomer to calculated IR spectra for the (a) ortho-, (b) meta- and (c) para-phenylethylpiperidine fragment ions. Qualitatively, the best match is indeed found in panel b.



Figure S7. Comparison of the IR spectrum of the m/z 202 fragment of the  $R_1$ -para-isomer to calculated IR spectra for the (a) ortho-, (b) meta- and (c) para-phenylethylpiperidine fragment ions. Qualitatively, the best match is indeed found in panel c.



Figure S8. Comparison of the calculated IR spectra of (a) the ortho-, meta- and para-phenylethylpiperidine fragment ions and (b) the cesium-adducts of 2-, 3- and 4-fluorobenzylalcohol.



Figure S9. Comparison of the IRIS spectra (of cesium-adducts) and FTIR spectra (of neutrals) of (a) 2-fluorobenzyl alcohol, (b) 3-fluorobenzyl alcohol and (c) 4-fluorobenzyl alcohol.





Figure S10. Comparison of the predicted IR spectra of (a) protonated and (b) deprotonated ortho- (left), meta- (middle) and paraaminobenzoic acid (right). The most prominent CH-out-of-plane vibrations in the predicted spectra are indicated with green, red and blue for the ortho-, meta-, and para-isomers, respectively.