Formation of Polycyclic Aromatic Hydrocarbons from Bimolecular Reactions of Phenyl Radicals at High Temperatures

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The supporting information contains figures S1-S11.

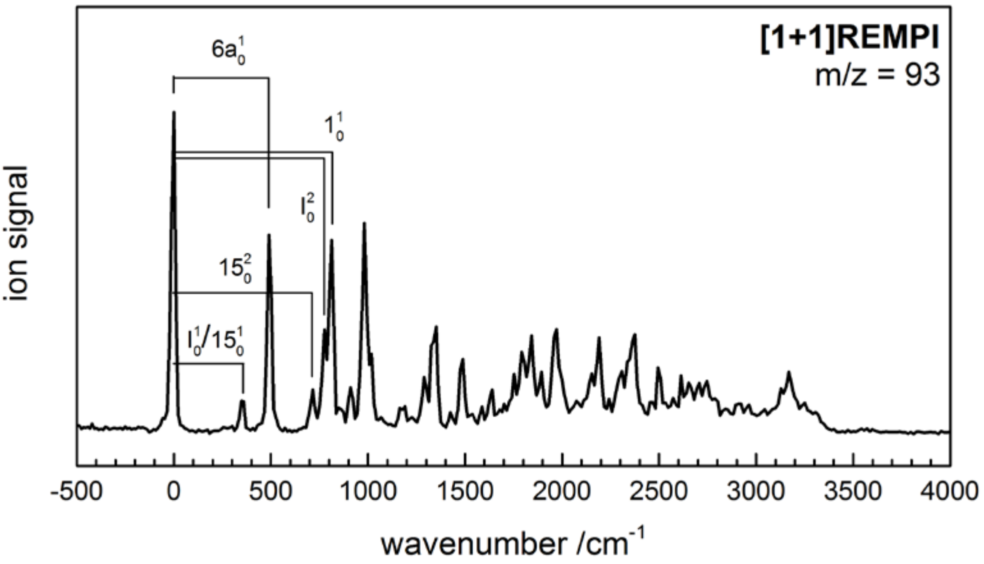

Figure S1: In a control experiment without pyrolysis and in the absence of FEL radiation trace amounts of aniline from the heated diazobenzene sample were identified by its REMPI spectrum, using a ps laser system. Aniline was identified by comparison with the spectra given in Ref 1 and 2.

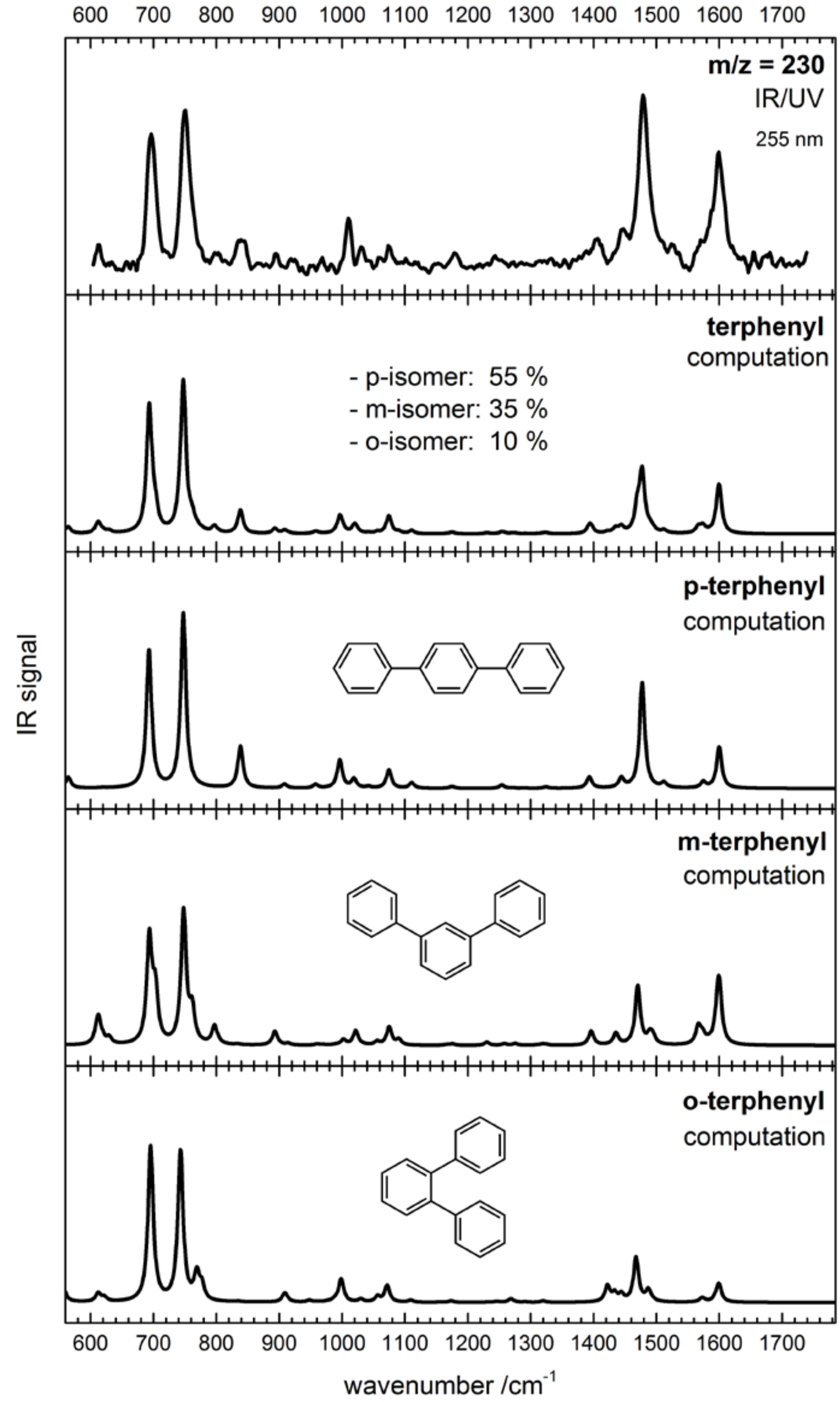

Figure S2: IR/UV-spectrum of the peak at m/z = 230 (top trace) and computed IR spectra for the terphenyl isomers (lower traces). The best fit to the experimental spectrum shows the dominant contribution of the para isomer (second trace).

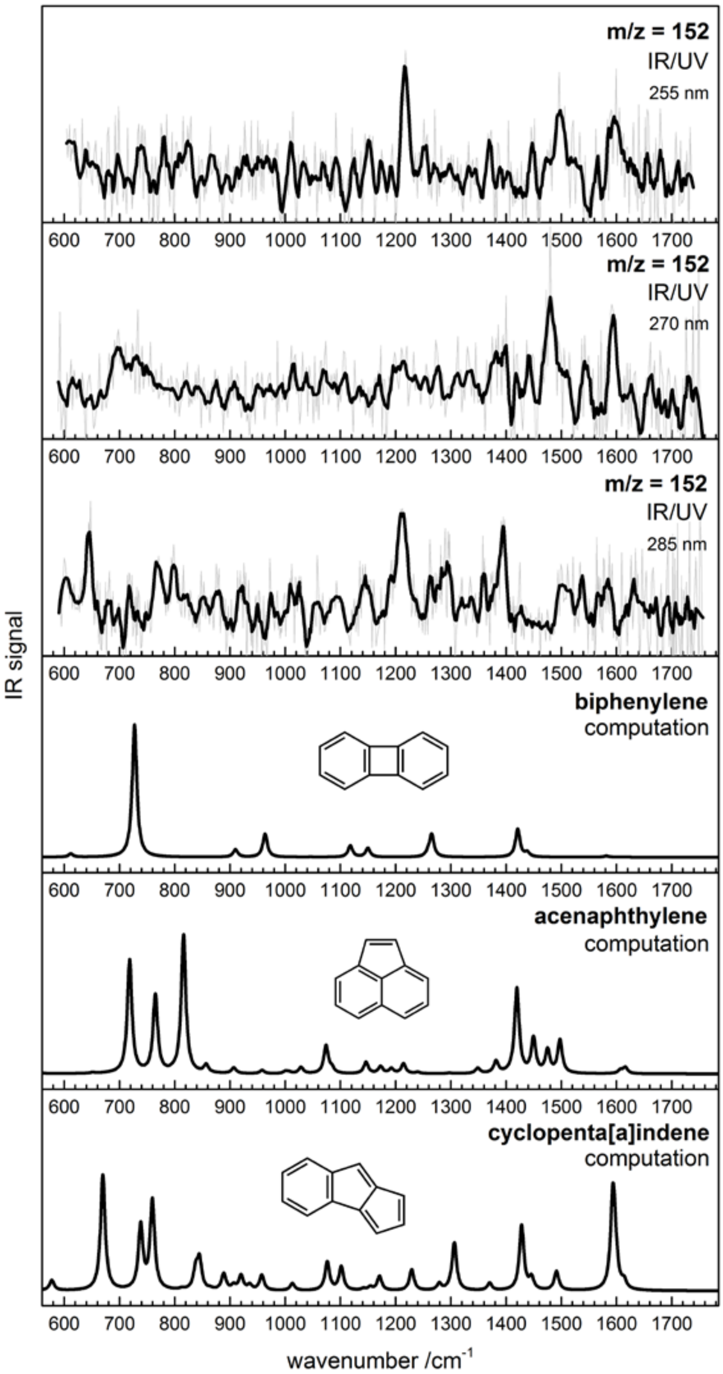

Figure S3: IR/UV-spectra of the mass peak at m/z = 152 recorded at 255 nm (top trace), 270 nm (second trace) and 285 nm (third trace) UV radiation. The two bands around 1500 and 1600 cm^{-1} are probably due to dissociative photoionization of biphenyl associated with H_2 loss. The characteristic peak around 1210 cm^{-1} does not appear in the computed IR spectra of biphenylene (fourth trace), acenaphthylene (fifth trace) and cyclopenta[a]indene (lowest trace), which are possible candidates for m/z = 152. In turn peaks computed with high intensity do not appear in the experimental spectrum. Thus there is no evidence for formation of any of these species.

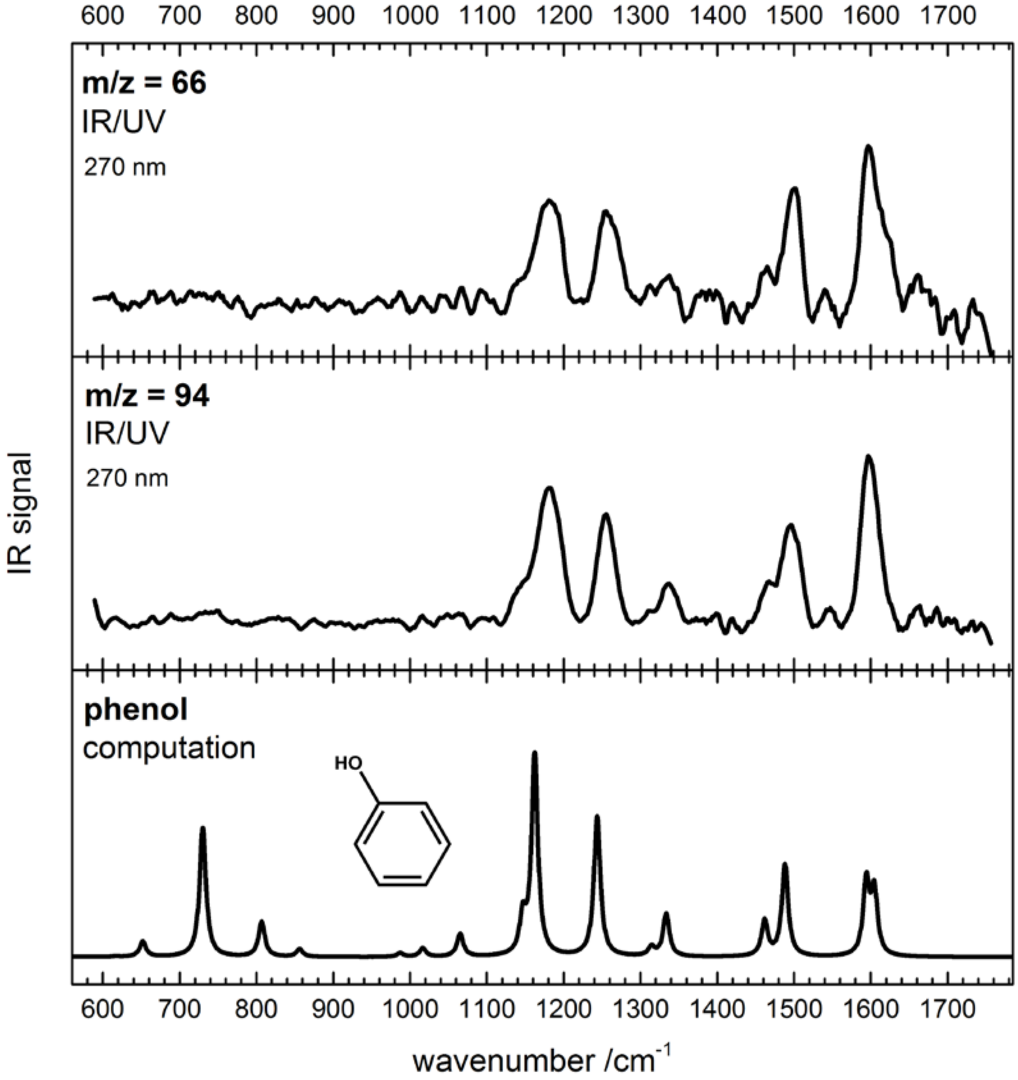

Figure S4: As visible in the center trace, small amounts of oxygen present in the pyrolysis lead to the formation of phenol (m/z = 94) from phenyl radical. The top trace shows, that the signal at m/z=66 is due to dissociative photoionisation of phenol.

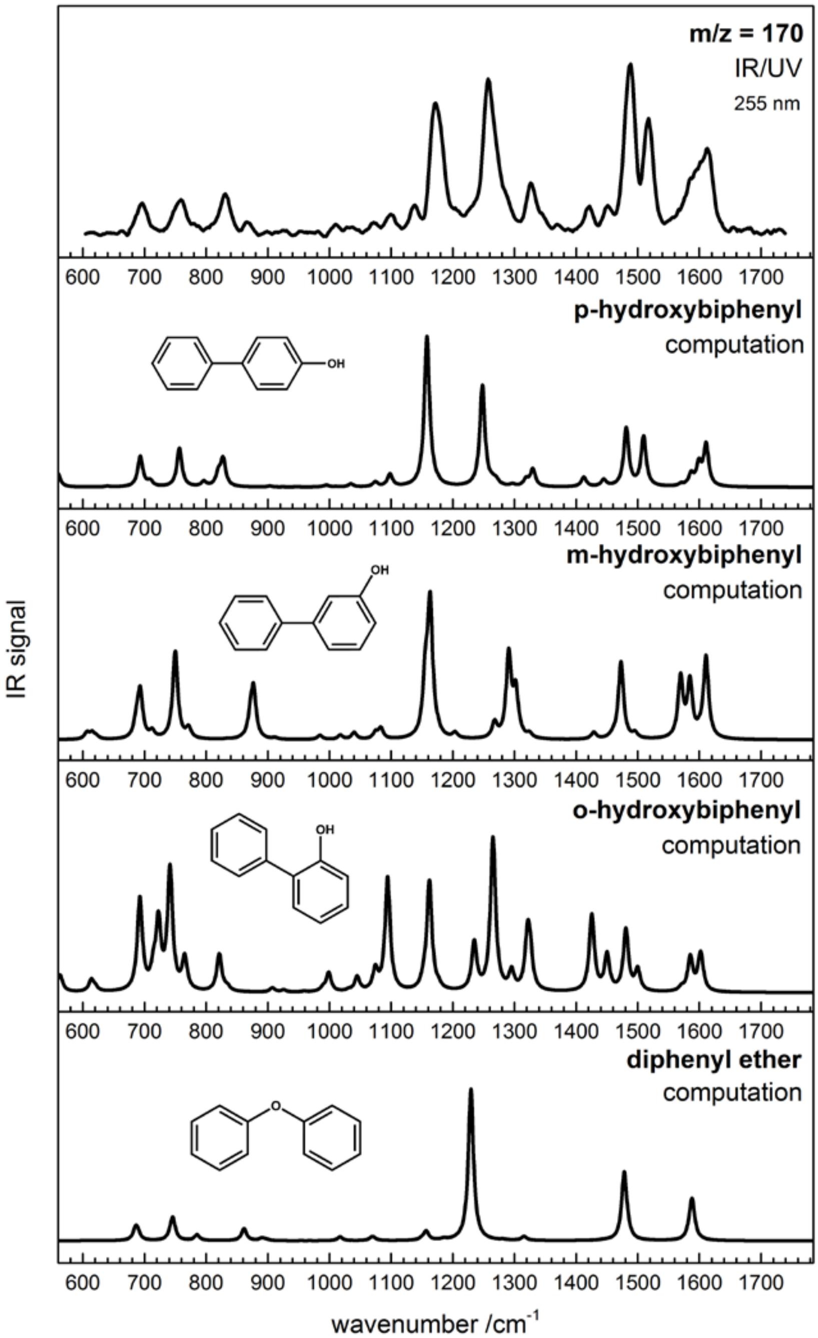

Figure S5: The pyrolysis product m/z = 170 is identified as p-hydroxybiphenyl, which is formed in the presence of trace amounts of oxygen in the pyrolysis.

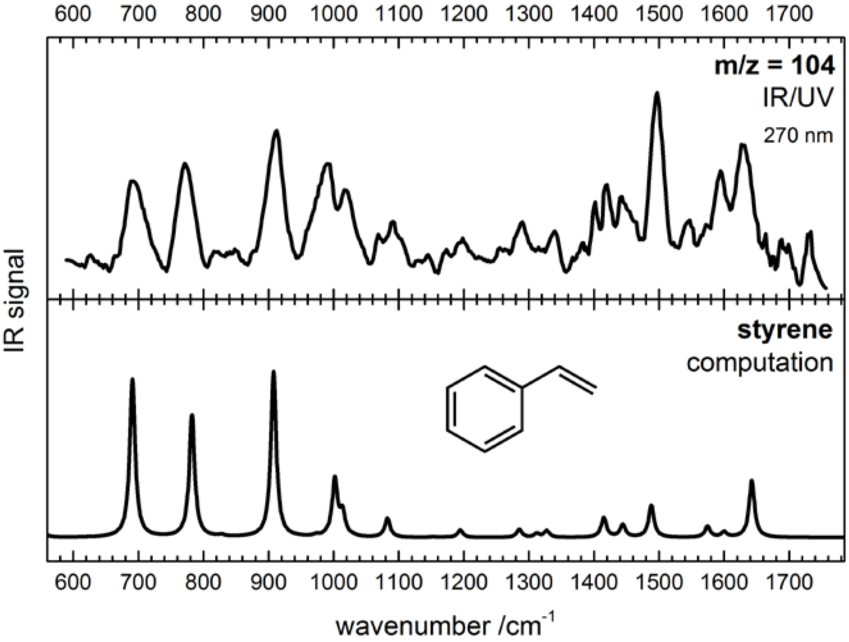

Figure S6: The IR/UV-spectrum of the peak at m/z = 104 (upper trace) was identified as styrene by its computed IR spectrum (lower trace).

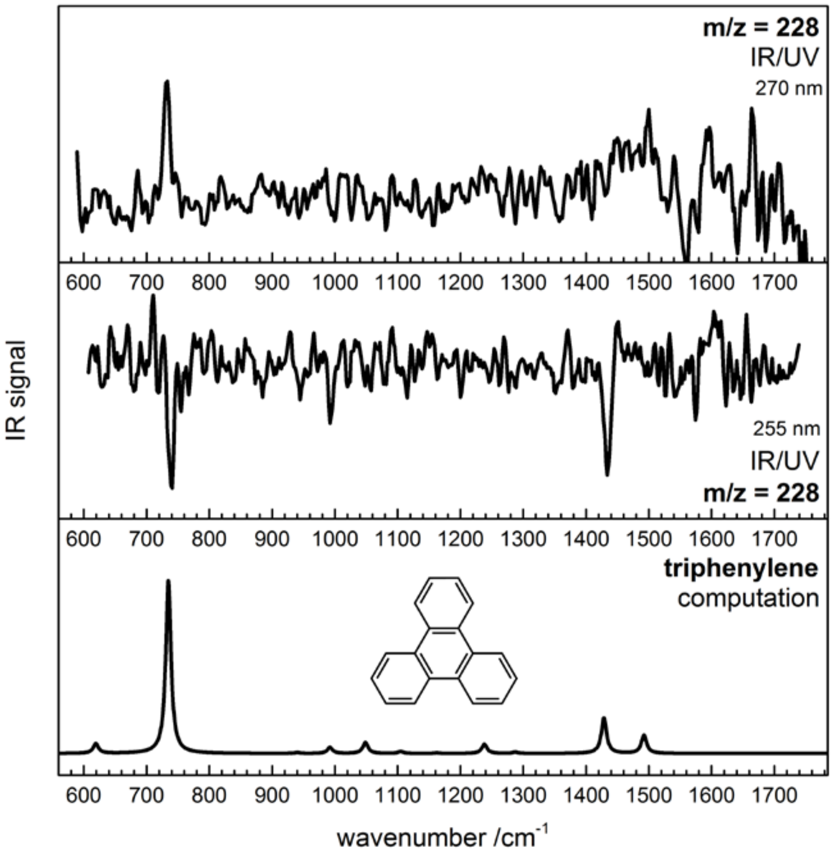

Figure S7: The IR/UV-spectrum of the peak at m/z = 228 is rather noisy, but shows only a single peak in the low-wavenumber region at around 740 cm^{-1}. Ruling out 1-phenylethynyl naphthalene and chrysene by their experimental spectra, we assign this mass to triphenylene due to its high symmetry. Note that the IR/UV spectrum recorded at 255 nm shows a signal gain rather than a depletion.

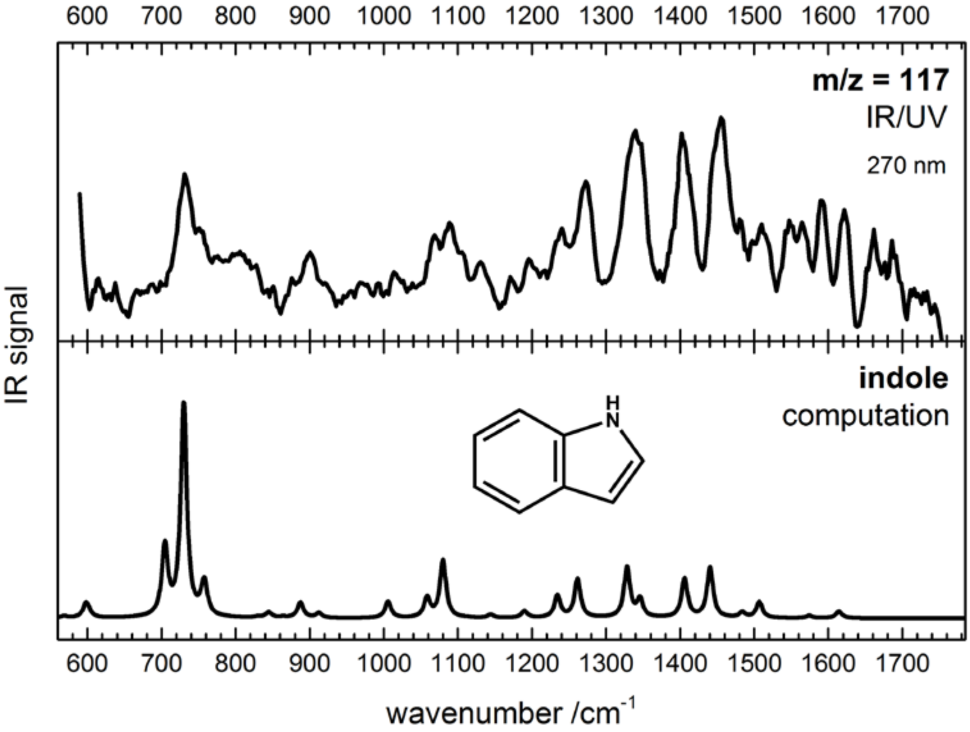

Figure S8: The IR/UV-spectrum of the peak at m/z = 117 (upper trace) was assigned to indole by its computed IR spectrum (lower trace).

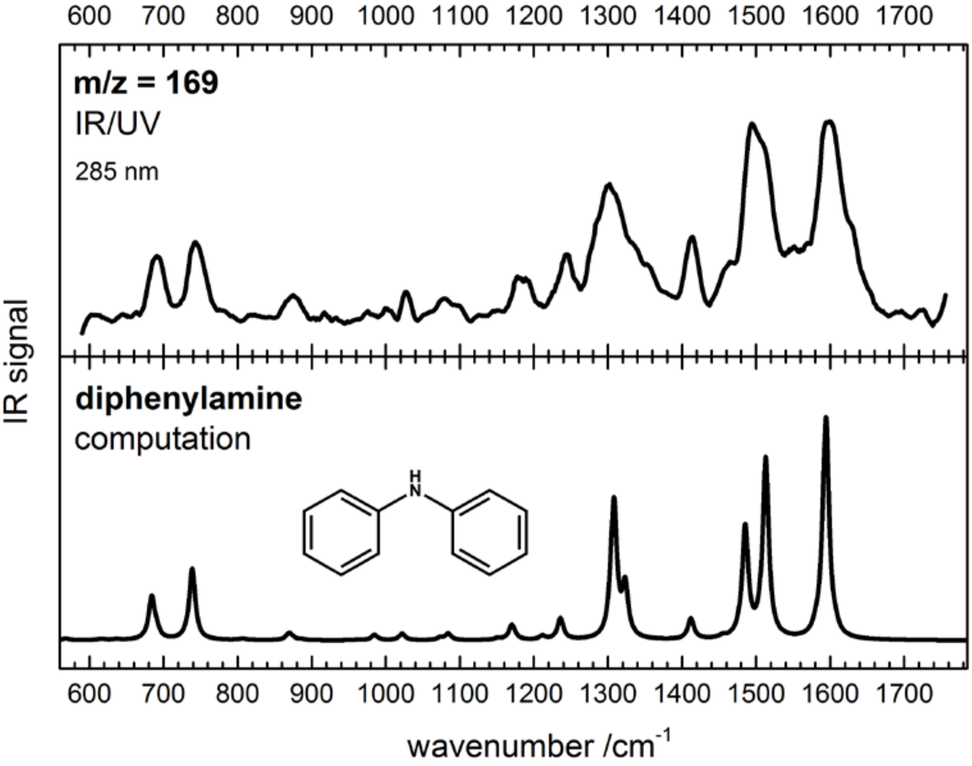

Figure S9: The IR/UV-spectrum of the peak at m/z = 169 (upper trace) was assigned to diphenylamine by its computed IR spectrum (lower trace).

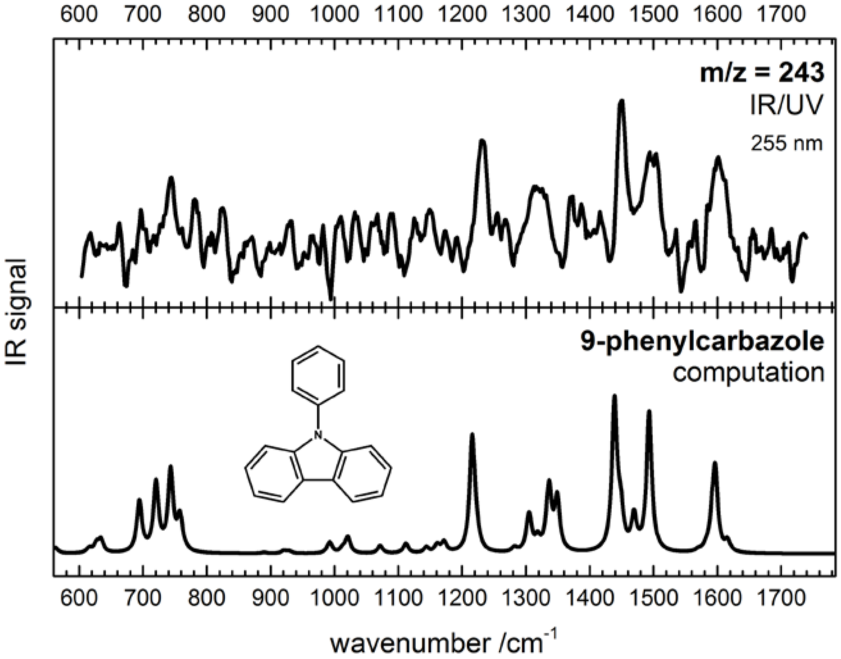

Figure S10: The IR/UV-spectrum of the peak at m/z = 243 (upper trace) was assigned to 9-phenylcarbazole by its computed IR spectrum (lower trace).

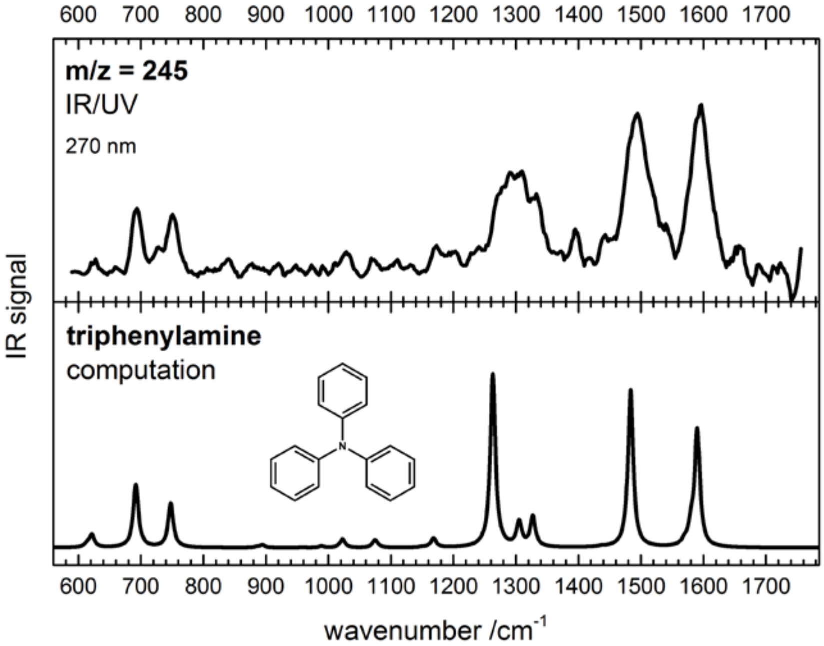

Figure S11: The IR/UV-spectrum of the peak at m/z = 245 (upper trace) was assigned to triphenylamine by its computed IR spectrum (lower trace).

References

1. M. A. Smith, J. W. Hager and S. C. Wallace, *J. Chem. Phys.*, 1984, **80**, 3097.
2. N. Mikami, A. Hiraya, I. Fujiwara and M. Ito, *Chem. Phys. Lett.*, 1980, **74**, 531.