

Supporting information for:

Synthesis of Polyhedral Phenylsilsesquioxanes with KF as the Source of Fluoride Ion

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General Procedures. ^{29}Si -MAS NMR spectra were recorded on Varian NMR systems 600 spectrometer. All spectra were obtained at 25° C. FT-IR spectra of compounds were recorded as KBr pellets on Bruker IFS 66/S, FT-Raman spectra as powder pellets on Perkin Elmer 2000; X-ray powder diffractograms on X-ray powder diffractometer Siemens D 5000; mass spectra on a AutoSpec Q spectrometer with EI (electron ionization) for Ph-T₈ and Q-TOF methods for Ph-T₁₂.

Spectral characterization data.

FT-Infrared and Raman spectra. In the IR spectra, the absorption bands of silsesquioxane skeleton of the pre-polymer and T cages were clearly seen in the region from 1110 to 1130 cm^{-1} . The additional sharp and strong band observed in the IR spectra of pre-polymer at 1136 cm^{-1} was attributed to the phenyl ring mode (**Fig. 1**). This band could still be seen in the IR spectra of Ph-T₈ but not in the corresponding Ph-T₁₂ spectra (**Fig. 2**), suggesting clear distinction between both compounds. The shoulder band at 1044 cm^{-1} observed in the IR spectra of pre-polymer we ascribed to the Si-O-Si mode of the double chain (ladder-like) polymer, which was absent in the IR spectra of Ph-T₈ and Ph-T₁₂, inferring the formation of cage-like structures instead of double chain polymers. Additional band, which could serve for easy identification of cages, was noted at 424 cm^{-1} , enabling the distinction of cages from the pre-polymers, which showed the corresponding symmetric stretching Si-O-Si mode at 494 cm^{-1} .

Raman spectra (**Fig. 3**), even though they did not show very strong bands attributed to the Si-O-Si skeleton, showed weak bands in the region from 524 to 300 cm^{-1} which were absent from the Raman spectra of pre-polymer.

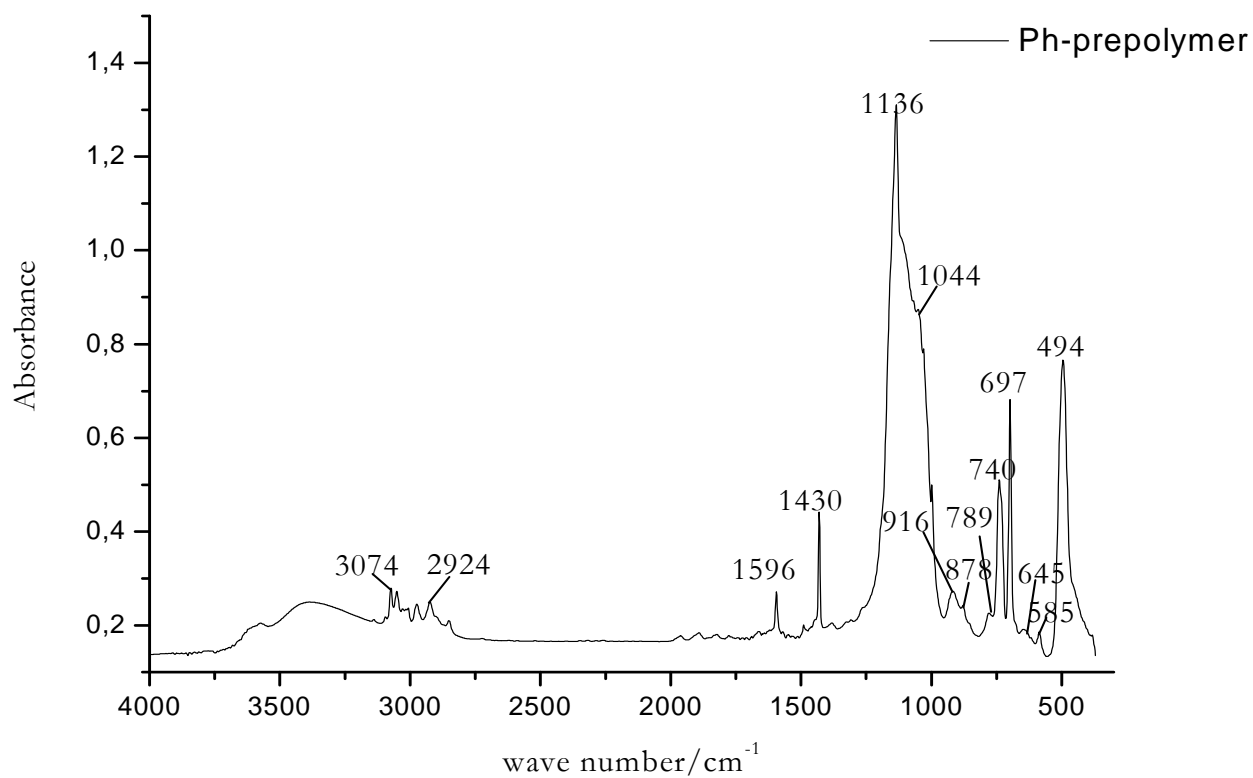


Figure 1: FT-IR spectra of prepolymer.

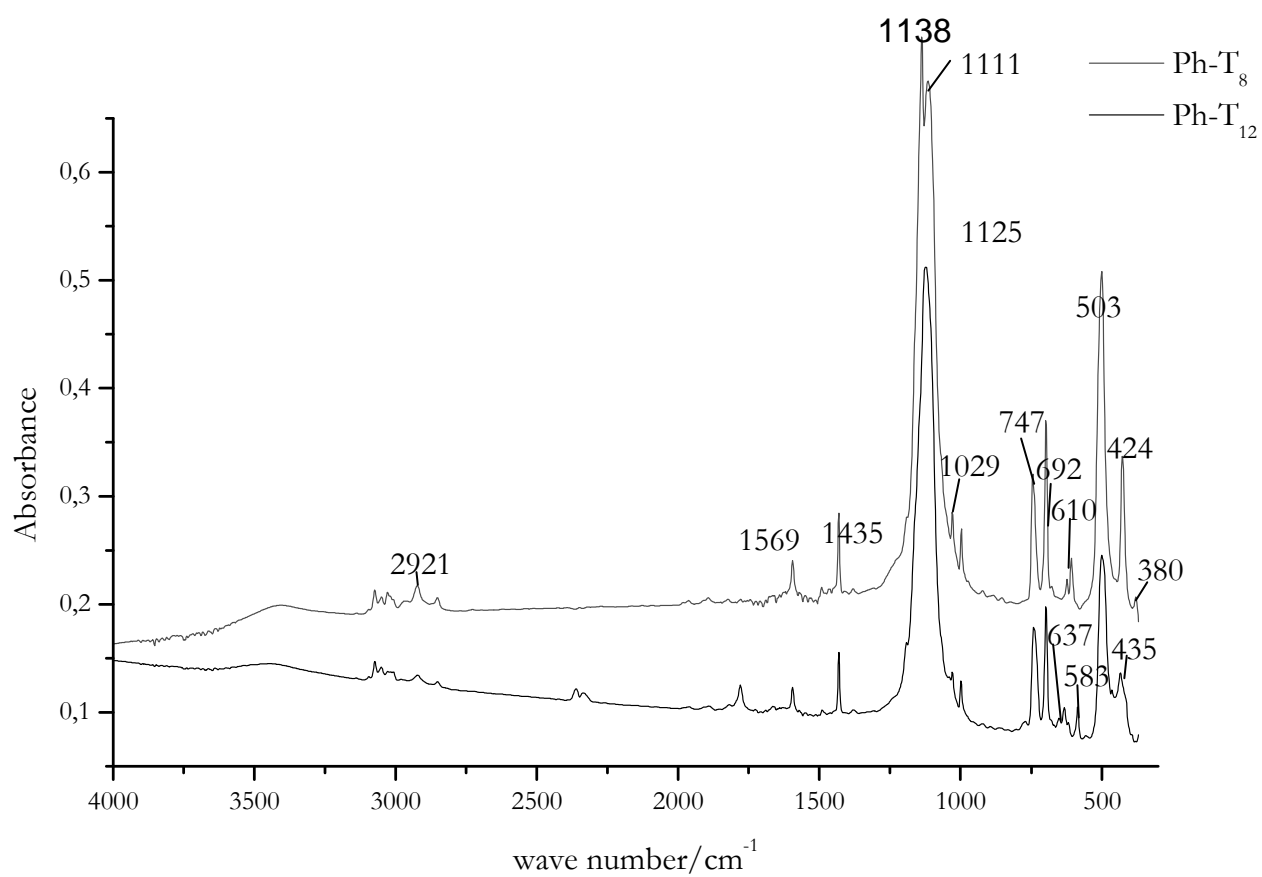


Figure 2: FT-IR spectra of Ph-T₈ and T₁₂.

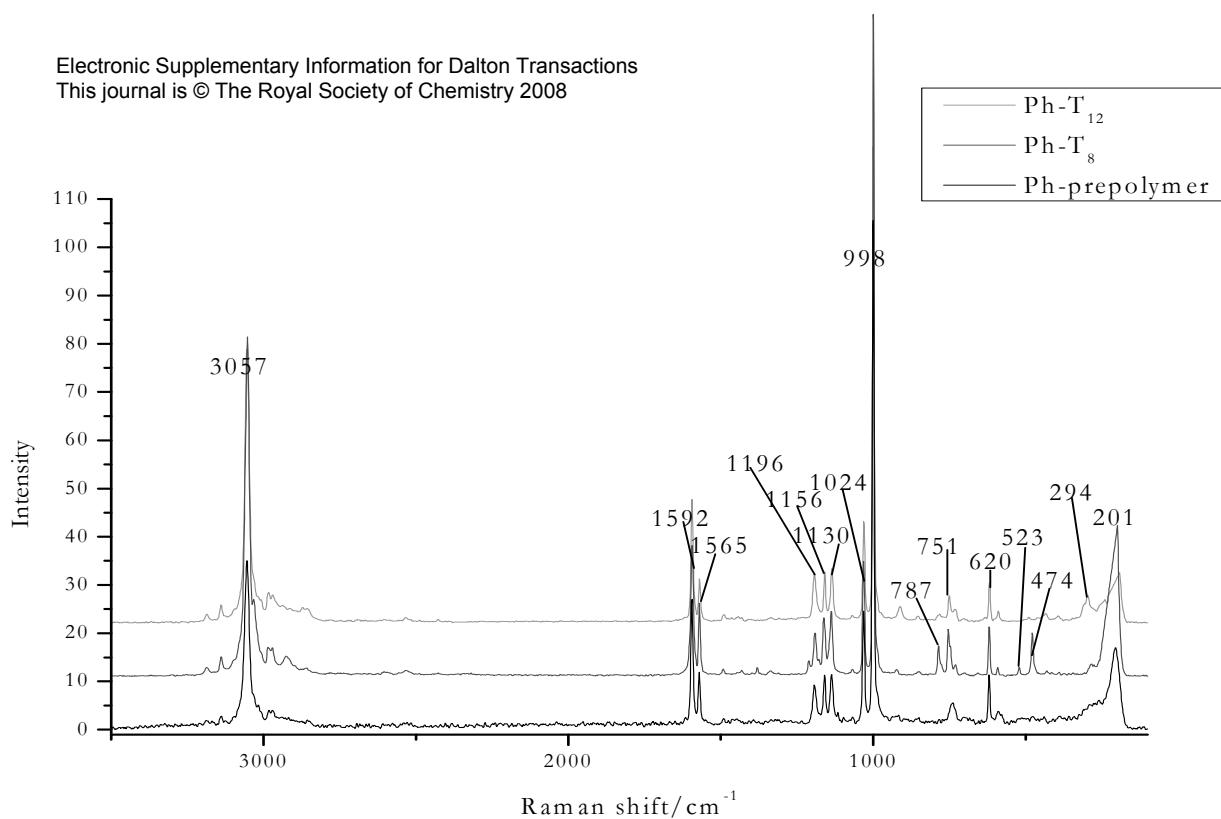


Figure 3: FT-Raman spectra of all three compounds.

^{29}Si -MAS NMR spectra: ^{29}Si NMR spectra are represented on **Fig. 4 and 5**. While the Ph-T₈ (**Fig. 5**) showed just one signal at -77.71 ppm, two signals were noted in the ^{29}Si -NMR spectra of Ph-T₁₂. It should be stressed that Bassindale et al. [[A. R. Bassindale, Z. Liu, I. A. MacKinnon, P. G. Taylor, Y. Yang, M. E. Light, P. N. Horton and M. B. Hursthouse, *Dalton Trans.* 2003, 2945], reported two signals at -76.82 and -80.40 ppm for Ph-T₈, contrasting single band at 77.71 ppm observed in or spectra of Ph-T₈. Spectra of synthesized Ph-T₁₂ showed practically the same signals (**Fig. 4**) as reported by Bassindale et al., for Ph-T₈.

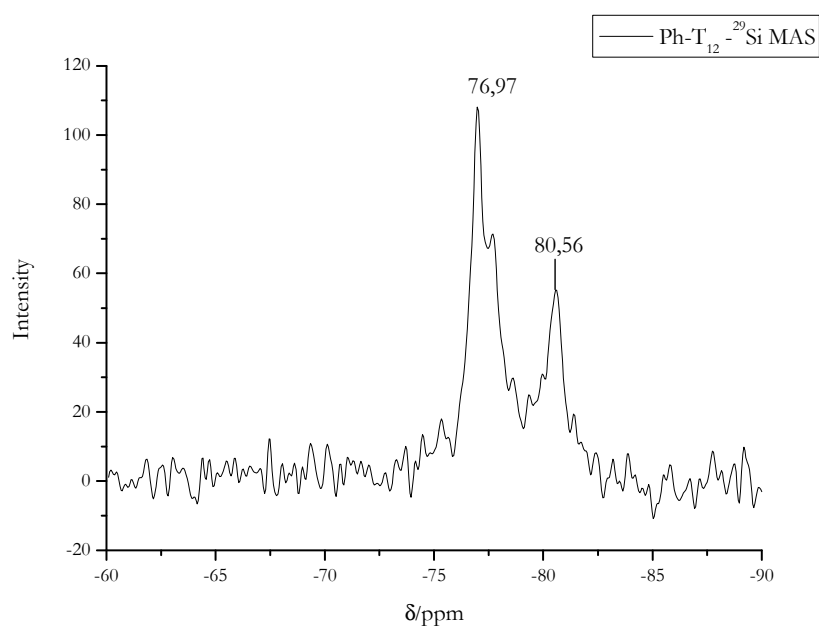


Figure 4: ^{29}Si -MAS NMR spectra of Ph-T₁₂.

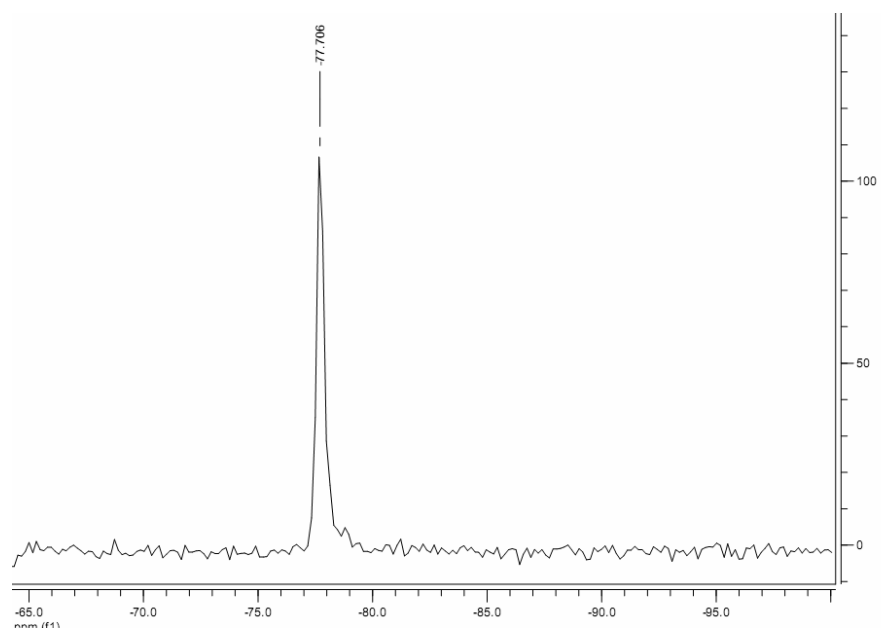


Figure 5: ^{29}Si -MAS NMR spectra of Ph- T_8 .

iBu- T_8 exhibited in the ^{29}Si -NMR spectra just one signal at -67, 82 ppm (**Fig. 6**). ^1H -NMR spectra independently confirmed the presence of iBu groups on the T_8 as could be conceived from **Fig. 7**.

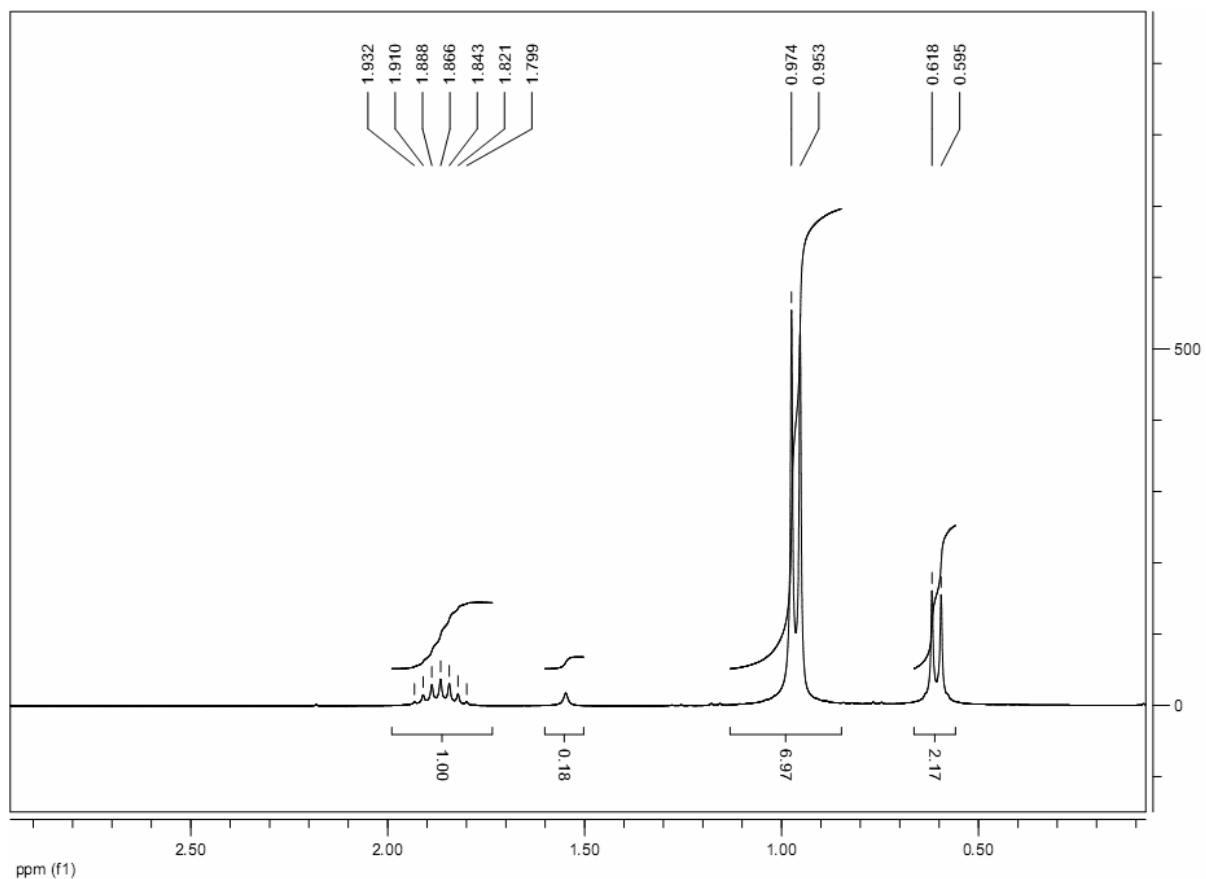


Figure 6: ^1H -NMR spectra of iBu- T_8 (CDCl_3). (signal at 1,56 ppm is water from impure NMR solvent)

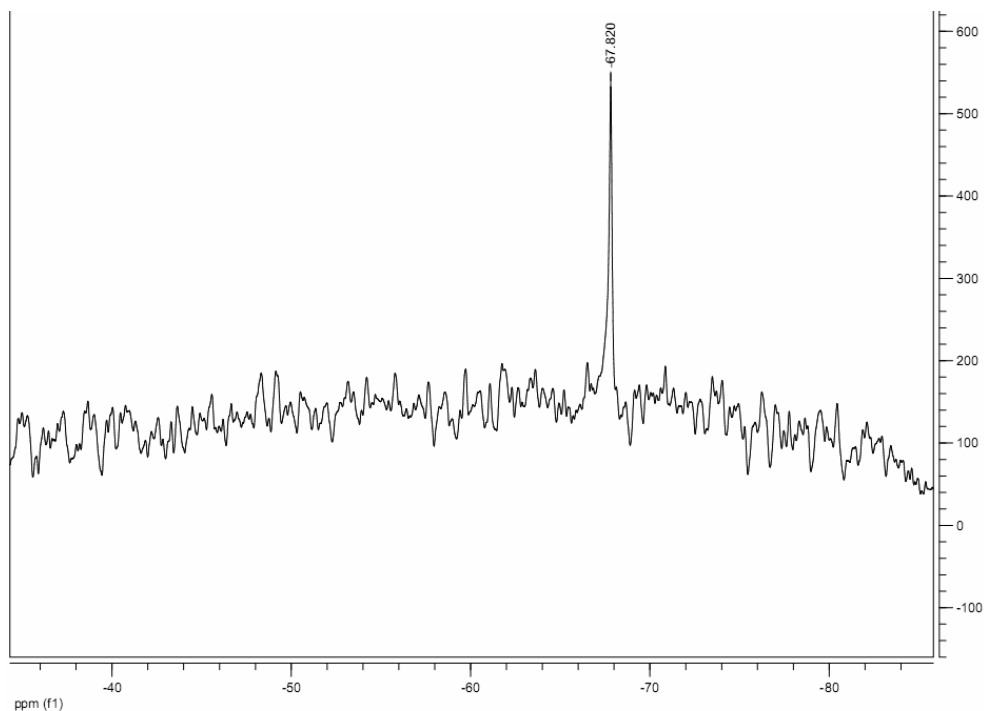


Figure 7: ^{29}Si -NMR spectra of iBu-T_8 (CDCl_3).

Powder XRD: These data are confirming structure and purity of compounds, no additional recrystallization was performed.

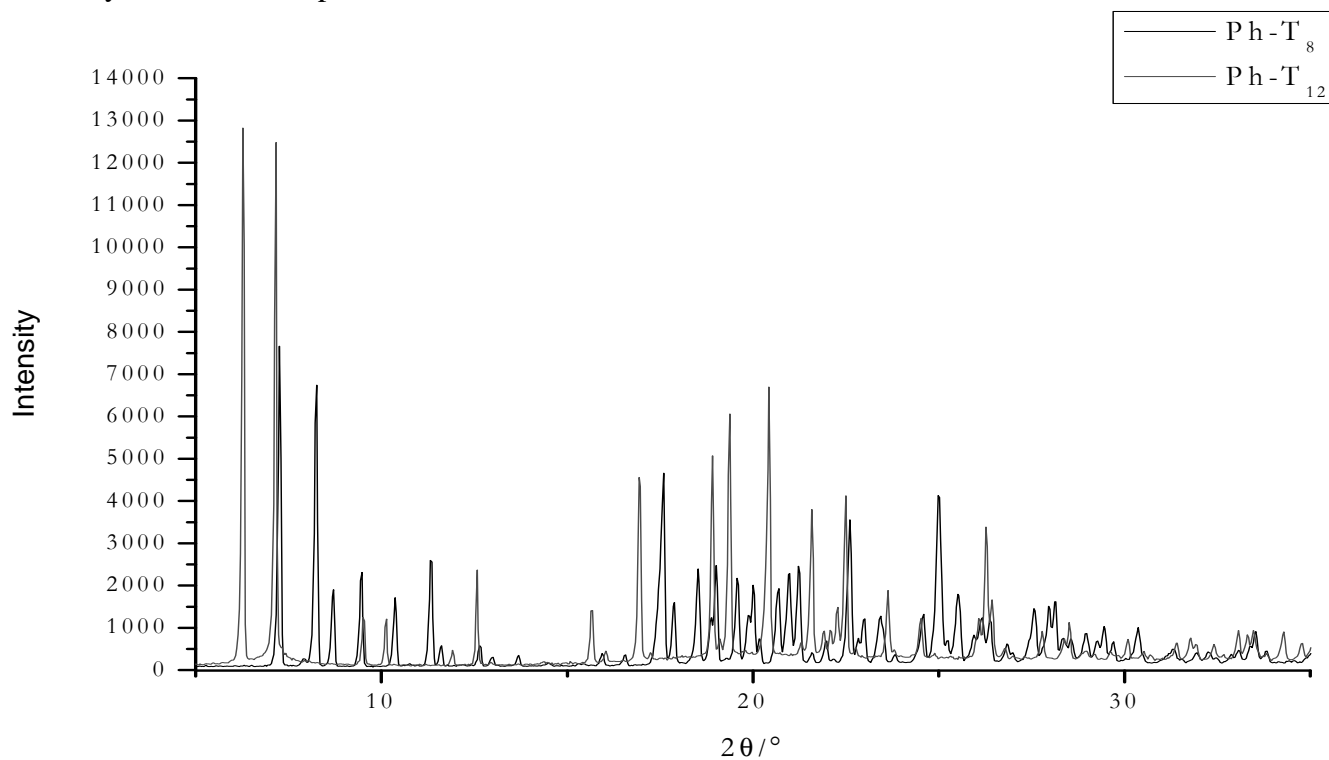


Figure 8: Powder XRD of both compounds recorded as obtained from reaction mixture.

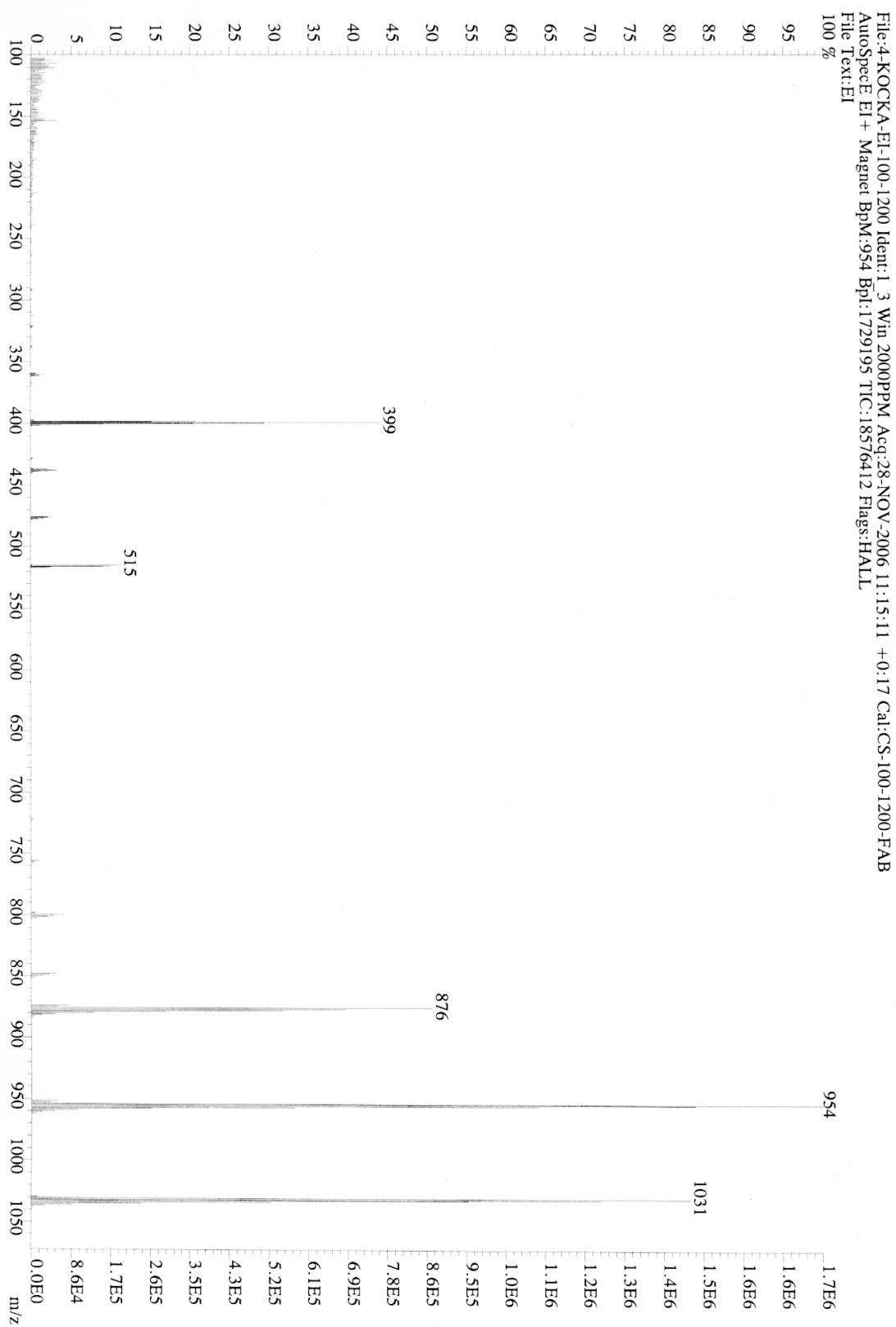


Figure 9: EI MS spectra of Ph-T₈.

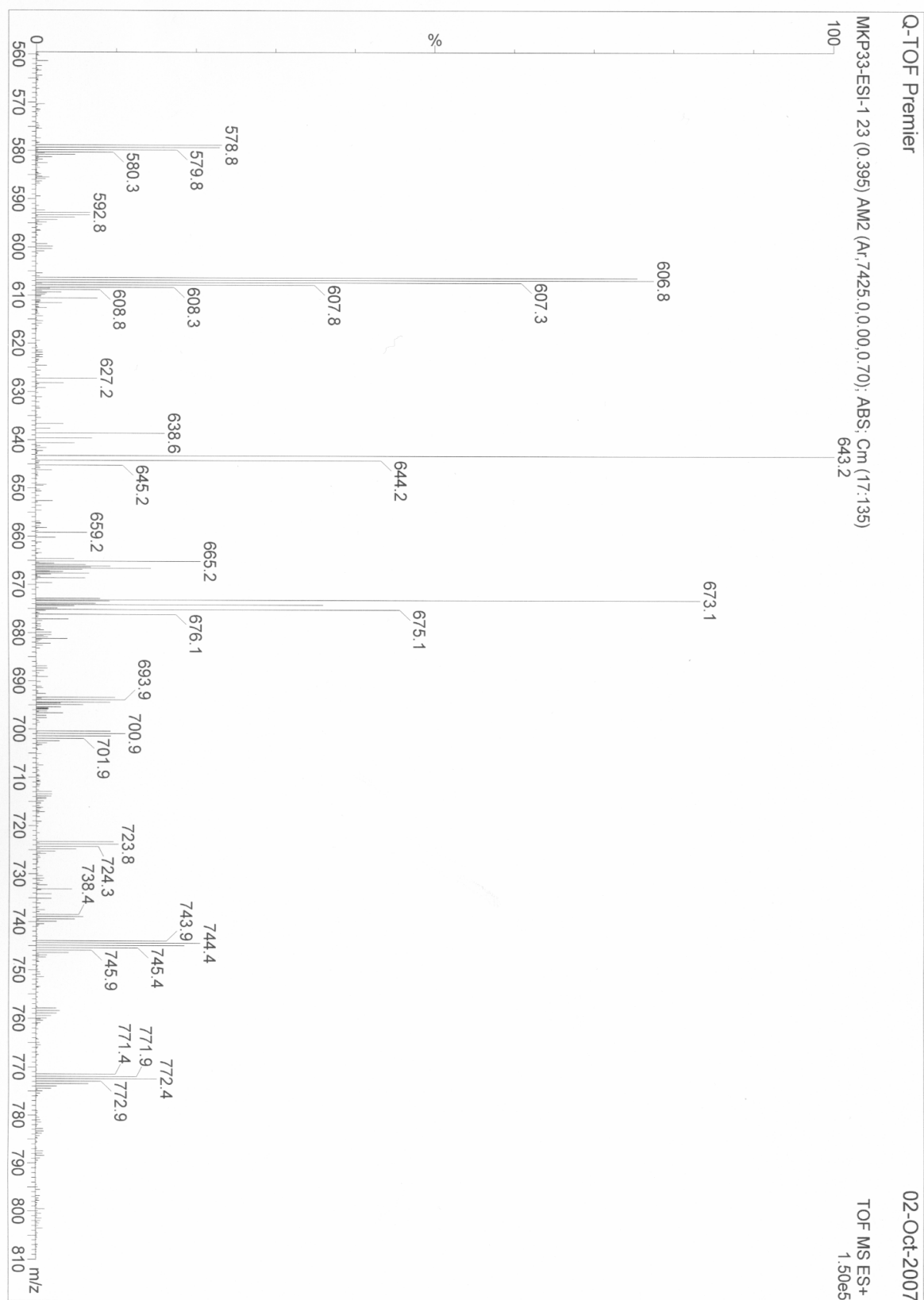


Figure 10: Q-TOF MS spectra of Ph-T₁₂. There can be seen double charged molecular peaks at around 772 m/z.