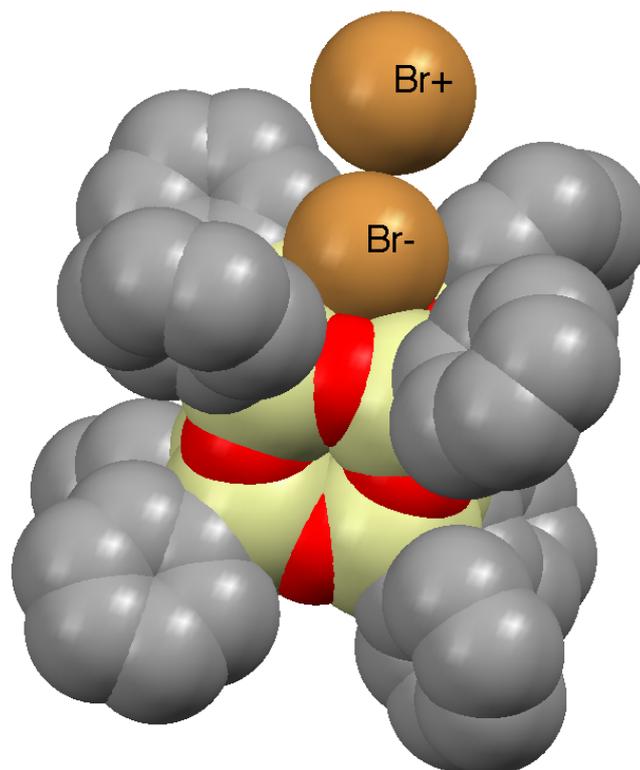


**Figure S.1** MALDI-TOF MS of octa(bromophenyl)silsesquioxane(Ag<sup>+</sup>/Dithranol).



**Figure S.2** Proposed complexation of bromide ion with silsesquioxane cage face.

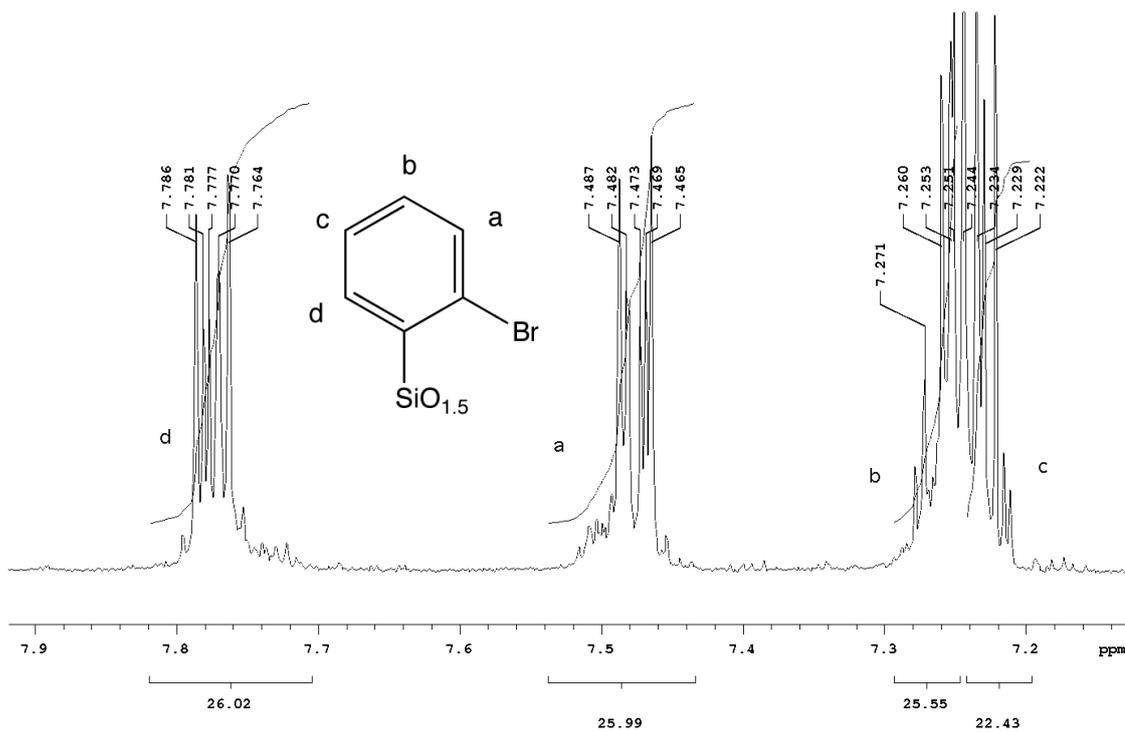


Figure S.3  $^1\text{H}$  NMR spectrum of octa(*o*-bromophenyl)silsesquioxane in  $\text{CS}_2/\text{CDCl}_3$

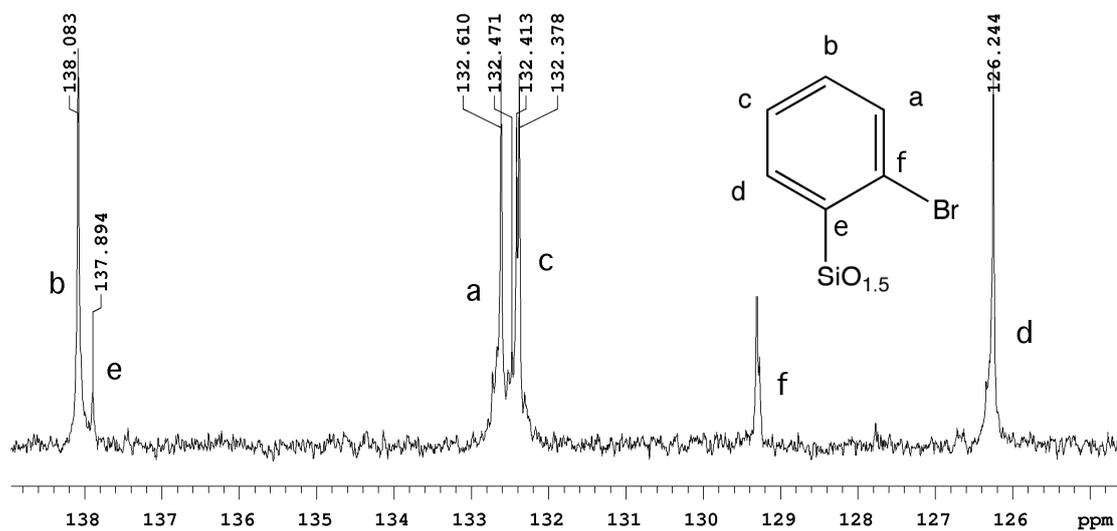
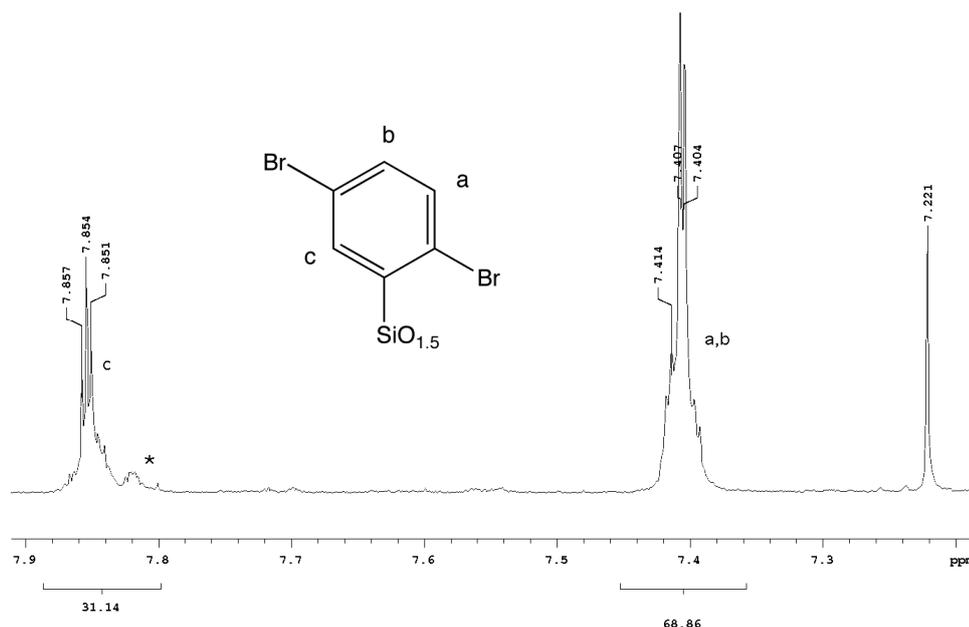
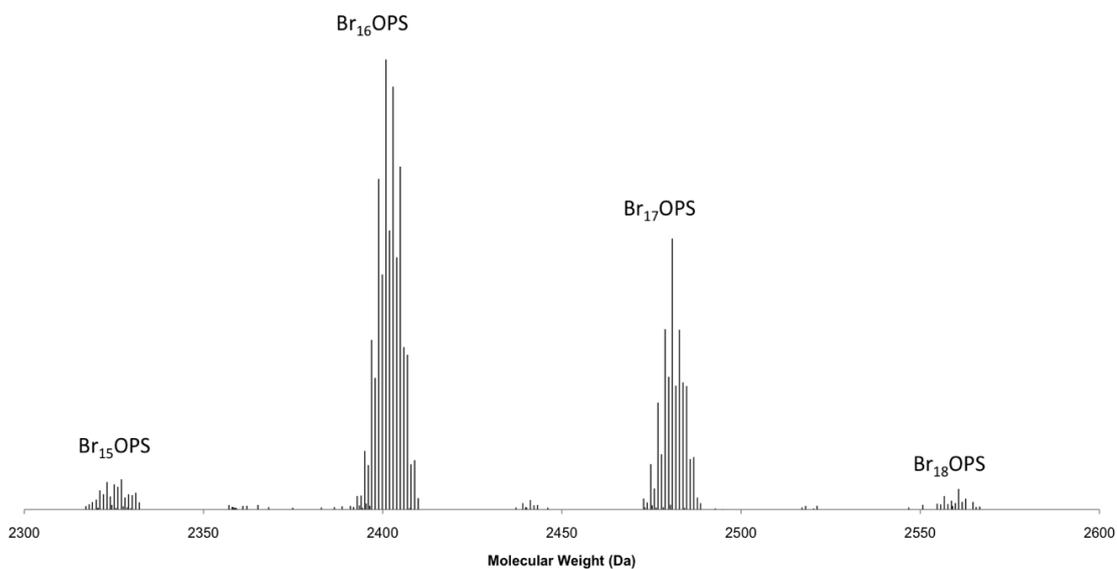


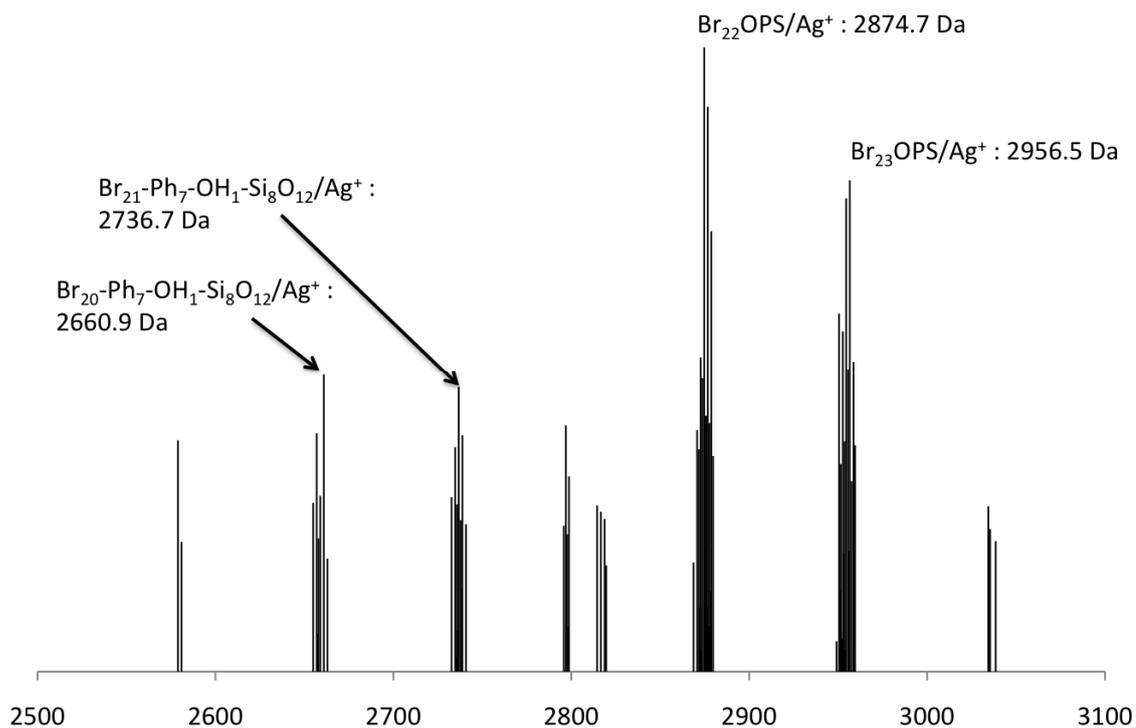
Figure S.4  $^{13}\text{C}$  NMR spectrum of octa(*o*-bromophenyl)silsesquioxane in  $\text{CS}_2/\text{CDCl}_3$ .



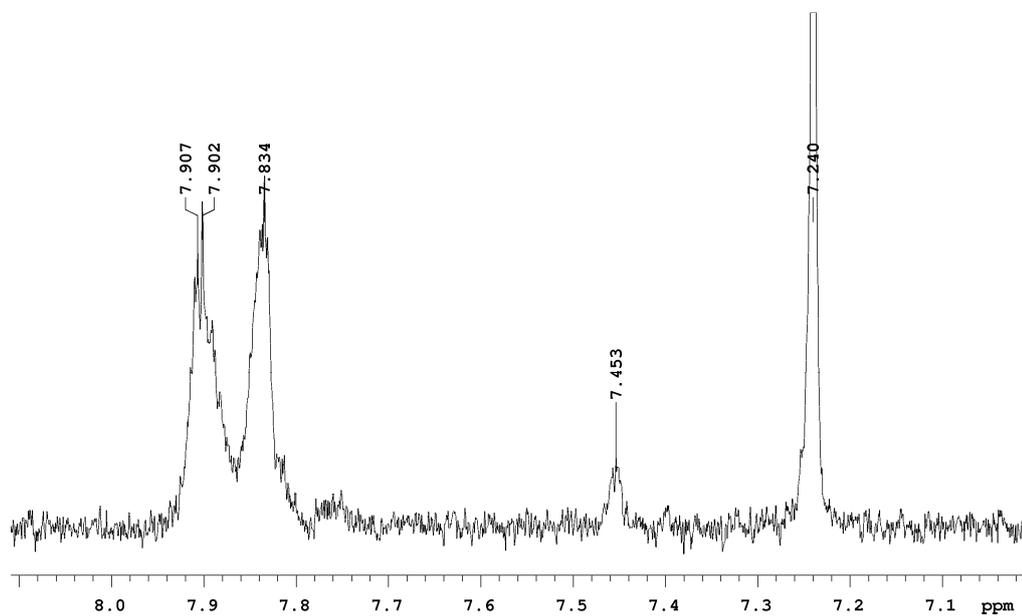
**Figure S.5**  $^1\text{H}$  NMR spectrum of octa(2,5-dibromophenyl)silsesquioxane in  $\text{CS}_2/\text{CDCl}_3$ .



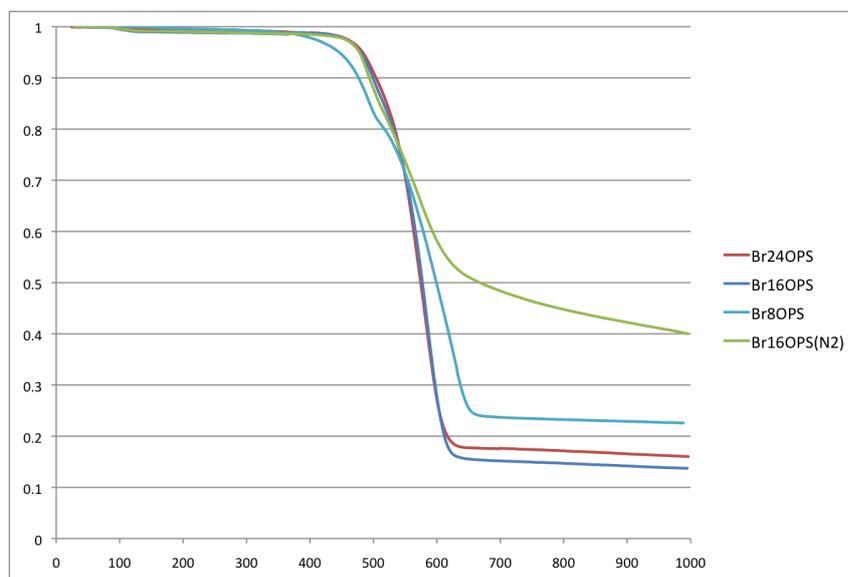
**Figure S.6** MALDI-TOF MS of amorphous  $\text{Br}_{16}\text{OPS}$ . ( $\text{Ag}^+$ /Dithranol).



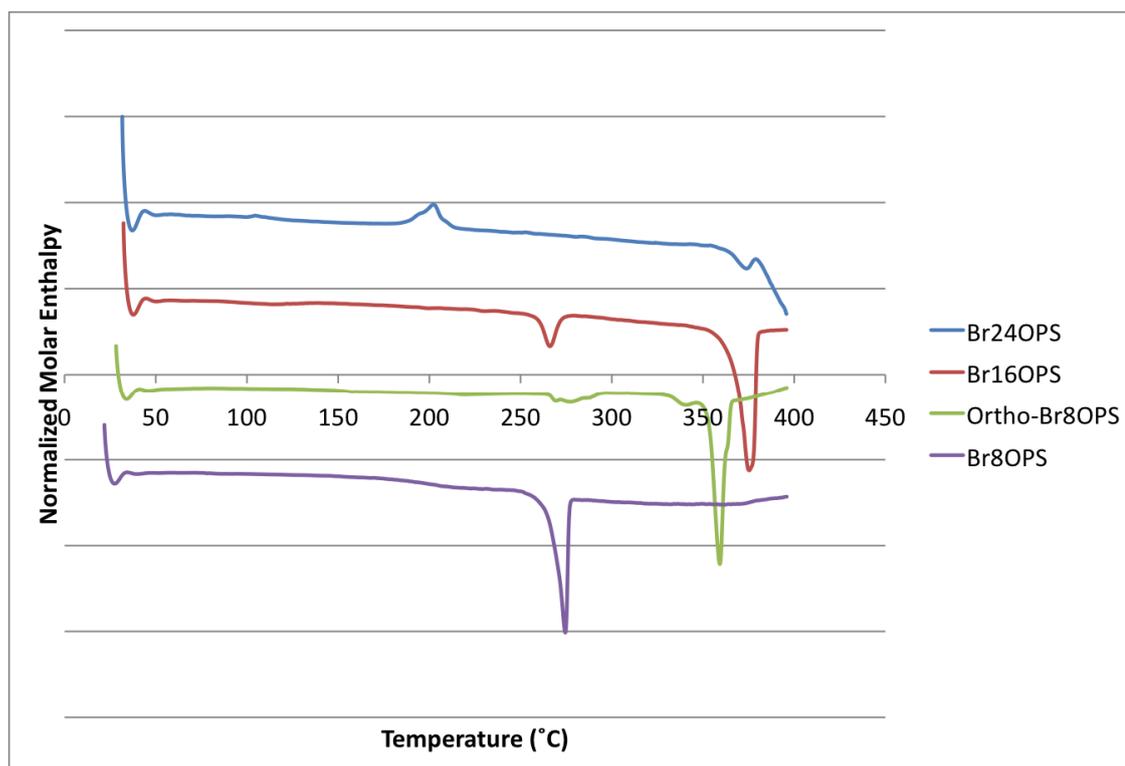
**Figure S.7** MALDI-TOF MS showing corner cleavage during bromination. ( $\text{Ag}^+$ /Dithranol).



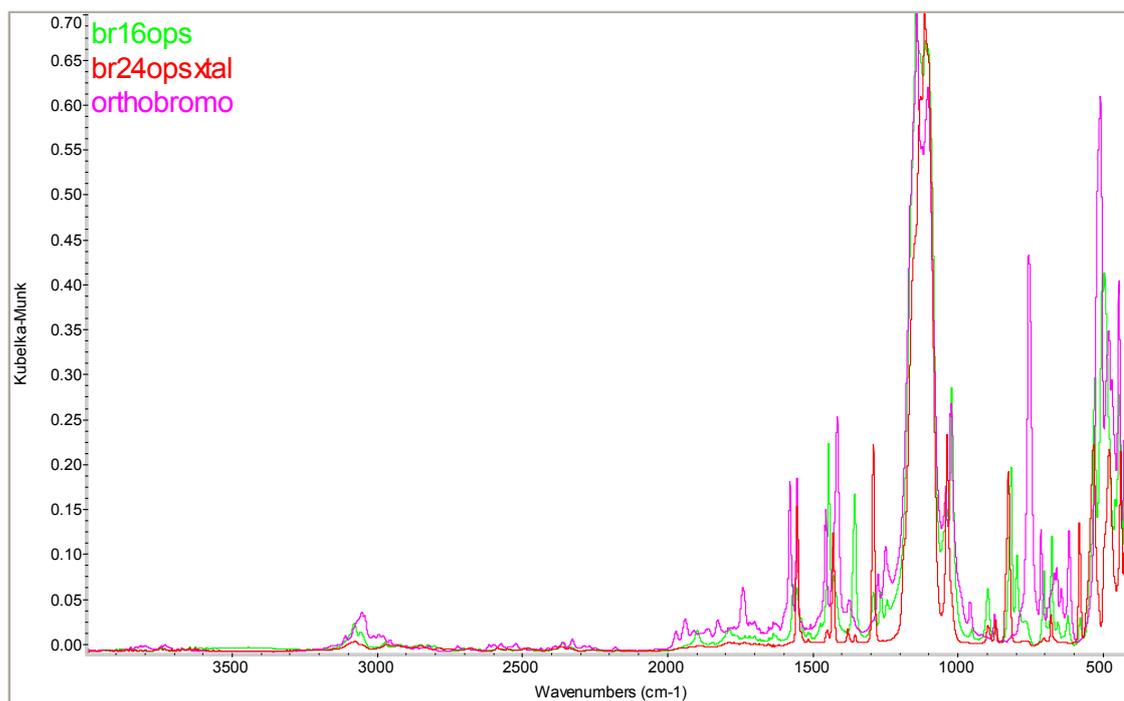
**Figure S.8**  $^1\text{H}$  NMR spectrum of tetraicosabrominated OPS in  $\text{CS}_2/\text{CDCl}_3$



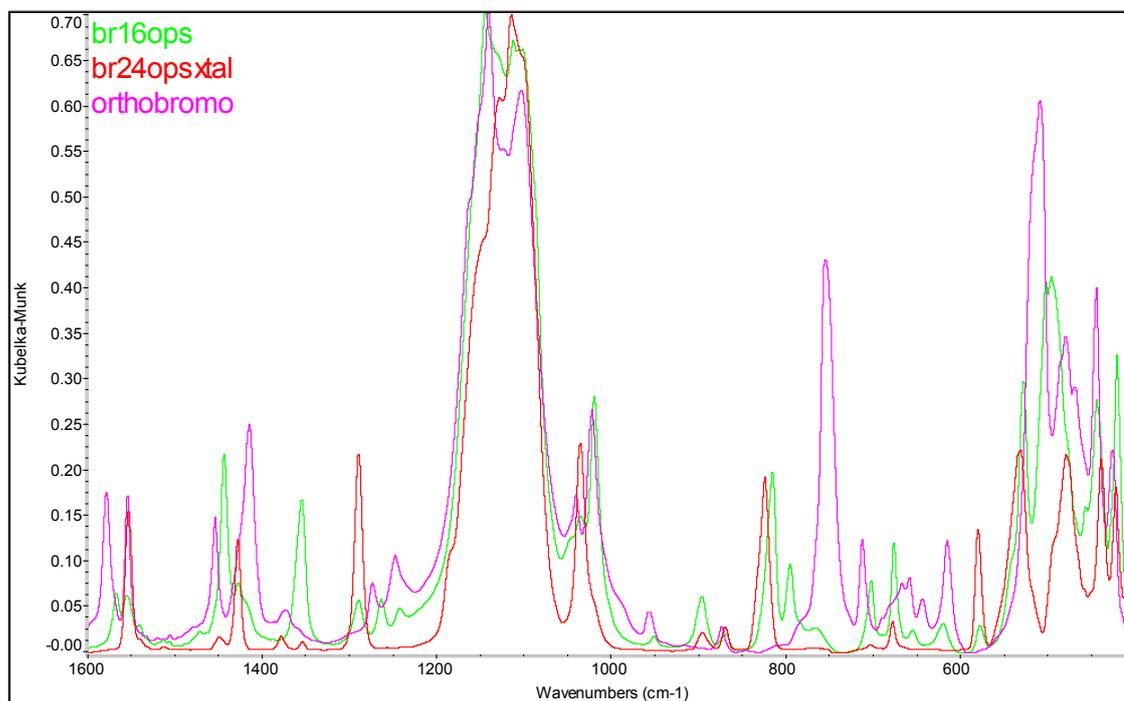
**Figure S.9.** TGAs of brominated OPS derivatives in air. Table 4 lists the ceramic yields.



**Figure S.10.** DSC traces of brominated OPS derivatives, showing melting of the crystalline phases.



**Figure S.11.** FTIR spectra of brominated OPS derivatives, 3200-400 cm<sup>-1</sup>.



**Figure S.12.** FTIR spectra of brominated OPS derivatives 1600-400 cm<sup>-1</sup>.