

Synthesis and Characterization of Fluorinated Polyionomers

I. Polyperfluoro-Sulfonylethoxy Propylene Vinyl Ether Sulfonimides Containing Aryl Sulfonic Acids

Anna Flach, Frederick E. Johnson and Israel Cabasso*

The Michael Szwarc Polymer Research Institute , Department of Chemistry

State University of New York-esf, Syracuse New York 13210

Supplemental Information

Figures S1 and S2 show the ^1H NMR spectra of the poly(perfluoro-sulfonylethoxy propylene vinyl ether) (PSEPVE) sulfonimide derivatives and aromatic sulfonyl chlorides based on o-terphenyl and triphenylene. Comparison of the spectra of the polymers and aromatic sulfonyl chlorides shows splitting of the proton peaks at ~7.1 and ~7.5 ppm, corresponding to terminal phenyl rings, in the case of poly(PSEPVE) sulfonimides bearing the di- and trisubstituted o-terphenyl side groups. The linkage of one of the sulfur containing groups to the polymer chain probably results in different environments for these protons in the case of the polymers.

Figures S3-S10 display two-dimensional $^1\text{H}^1\text{H}$ COSY, $^1\text{H}^{13}\text{C}$ HSQC and $^1\text{H}^{13}\text{C}$ HMBC spectra of o-terphenyl sulfonyl chloride, o-terphenyl disulfonyl chloride, o-terphenyl trisulfonyl chloride and triphenylene trisulfonyl chloride with ^1H and ^{13}C assignments. Quaternary carbon atoms resonate in the 130-145 ppm range with the carbon atoms bearing the sulfonyl chloride group shifted the furthest downfield. The symmetry of o-terphenyl 4',4''-disulfonyl chloride results a simplified spectrum with *para* substitution on the two terminal phenylene rings while the monosulfonyl chloride shows substitution on the terminal phenylene ring. o-Terphenyl trisulfonyl chloride shows *para* substitution on

the two terminal phenylene rings as in the case of the disulfonyl chloride with the third sulfonyl chloride group located on the central phenylene ring *meta* to one of the terminal aromatic rings and *para* to the other ring. Figures S11-S15 give the $^1\text{H}^{13}\text{C}$ HSQC spectra of poly(PSEPVE) o-terphenyl sulfonimide sulfonic acid and disulfonic acid, respectively and the ^{13}C , $^1\text{H}^{13}\text{C}$ HSQC and $^1\text{H}^{13}\text{C}$ HMBC spectra of the model compound, PSEPVE o-terphenyl sylfonimide

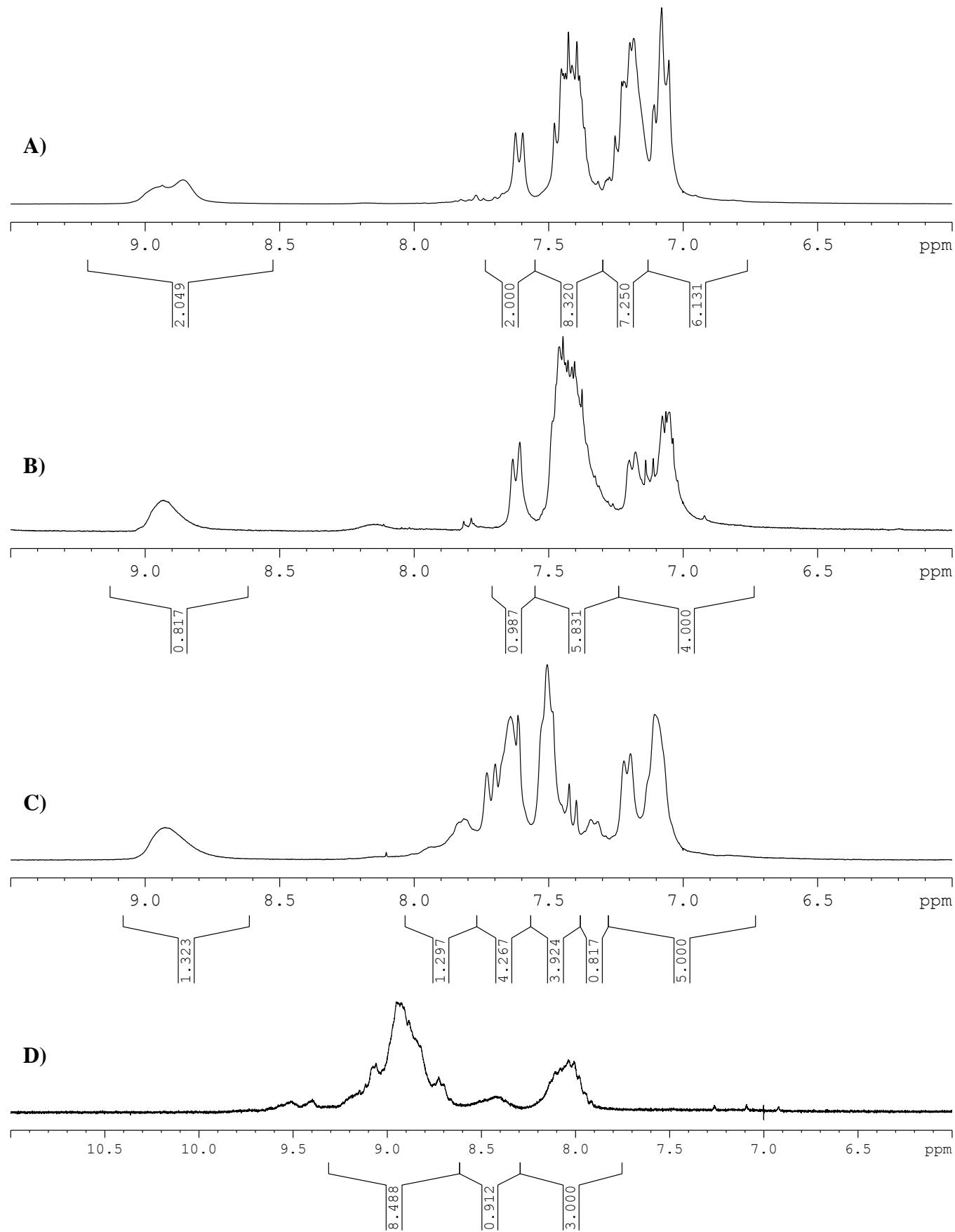


Figure S1. ¹H NMR spectra of A) poly(PSEPVE) o-terphenyl sulfonimide, B) poly(PSEPVE) o-terphenyl sulfonic acid, C) poly(PSEPVE) o-terphenyl sulfonimide disulfonic acid and D) poly(PSEPVE) triphenylene sulfonimide disulfonic acid, solvent d_6 -DMSO, 300 MHz.

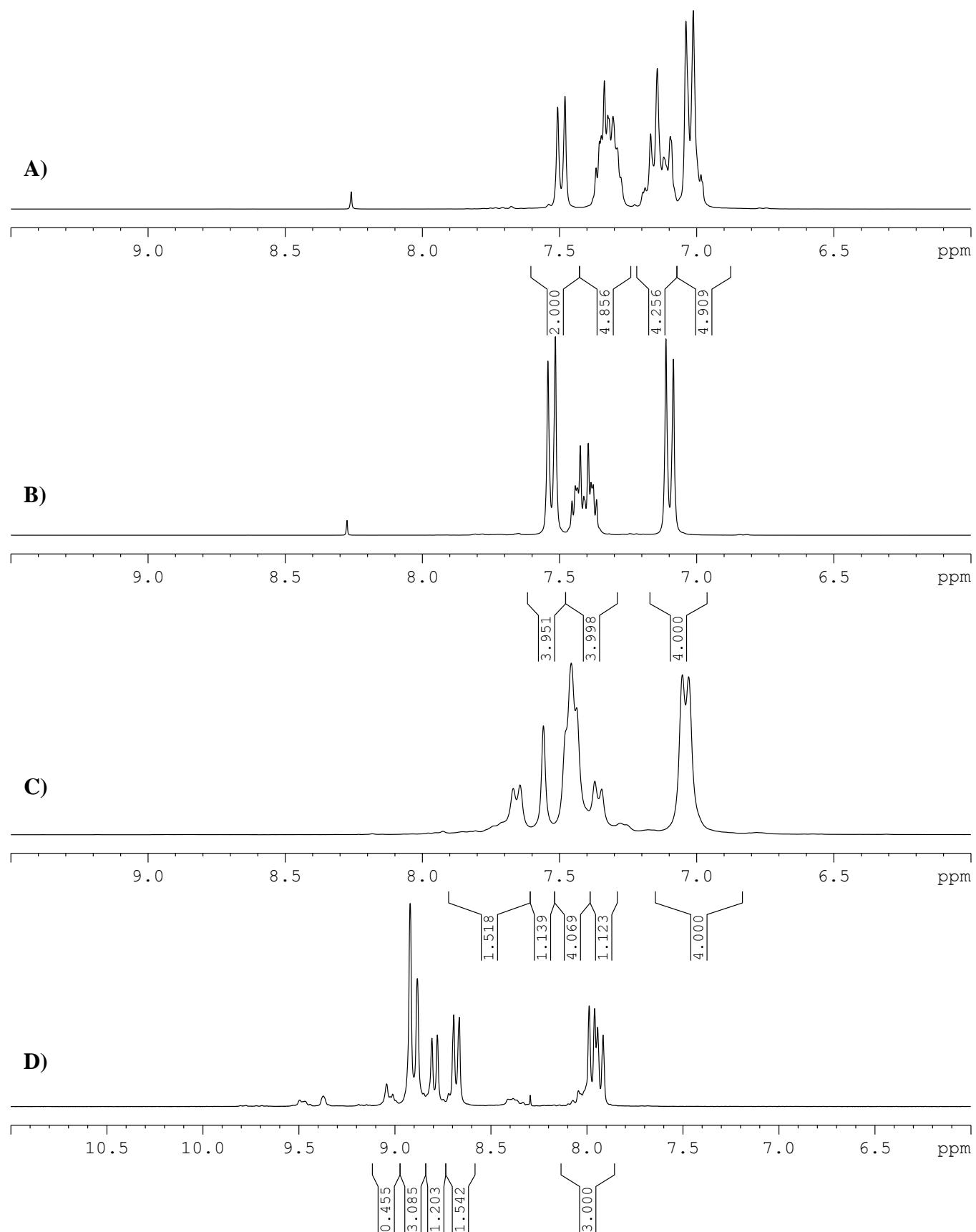


Figure S2. ¹H NMR spectra of A) o-terphenyl sulfonyl chloride, B) o-terphenyl disulfonyl chloride, C) o-terphenyl trisulfonyl chloride and D) triphenylene trisulfonyl chloride, solvent DMSO, 300 MHz.

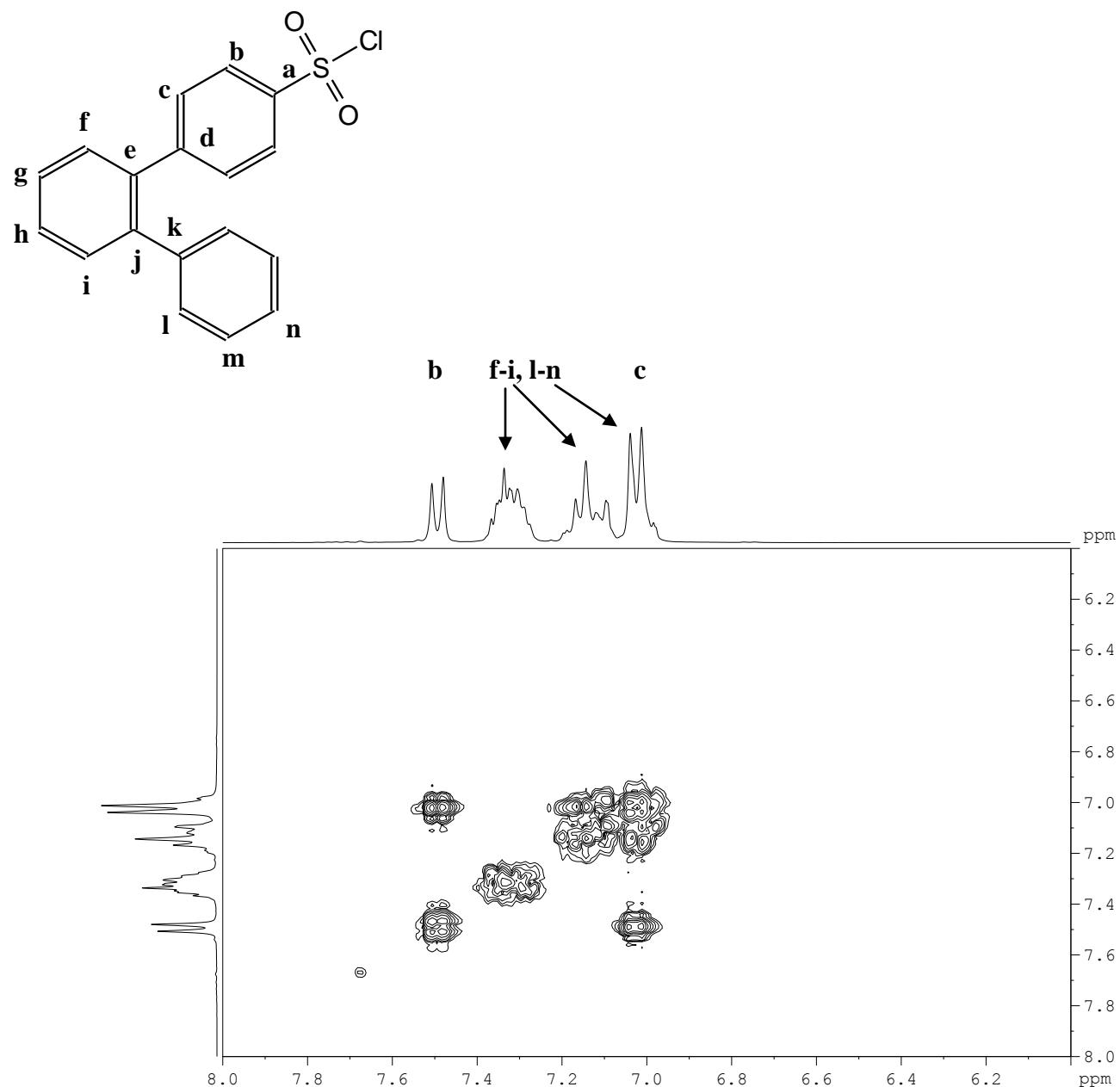


Figure S3. ^1H ^1H COSY spectrum of o-terphenyl sulfonyl chloride, solvent DMSO, 300 MHz.

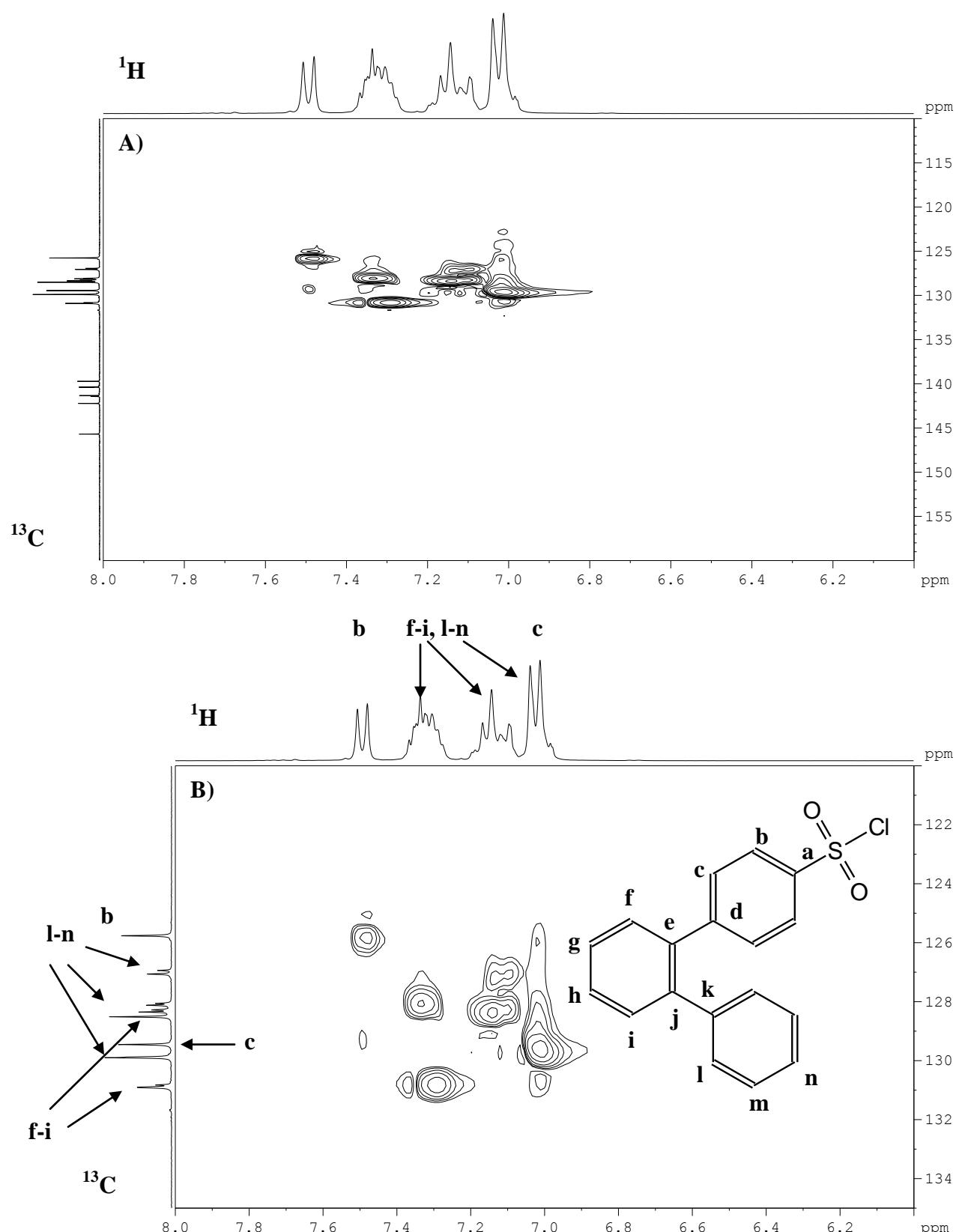


Figure S4. ^1H - ^{13}C HSQC spectrum of o-terphenyl sulfonyl chloride, solvent DMSO, 300 MHz.

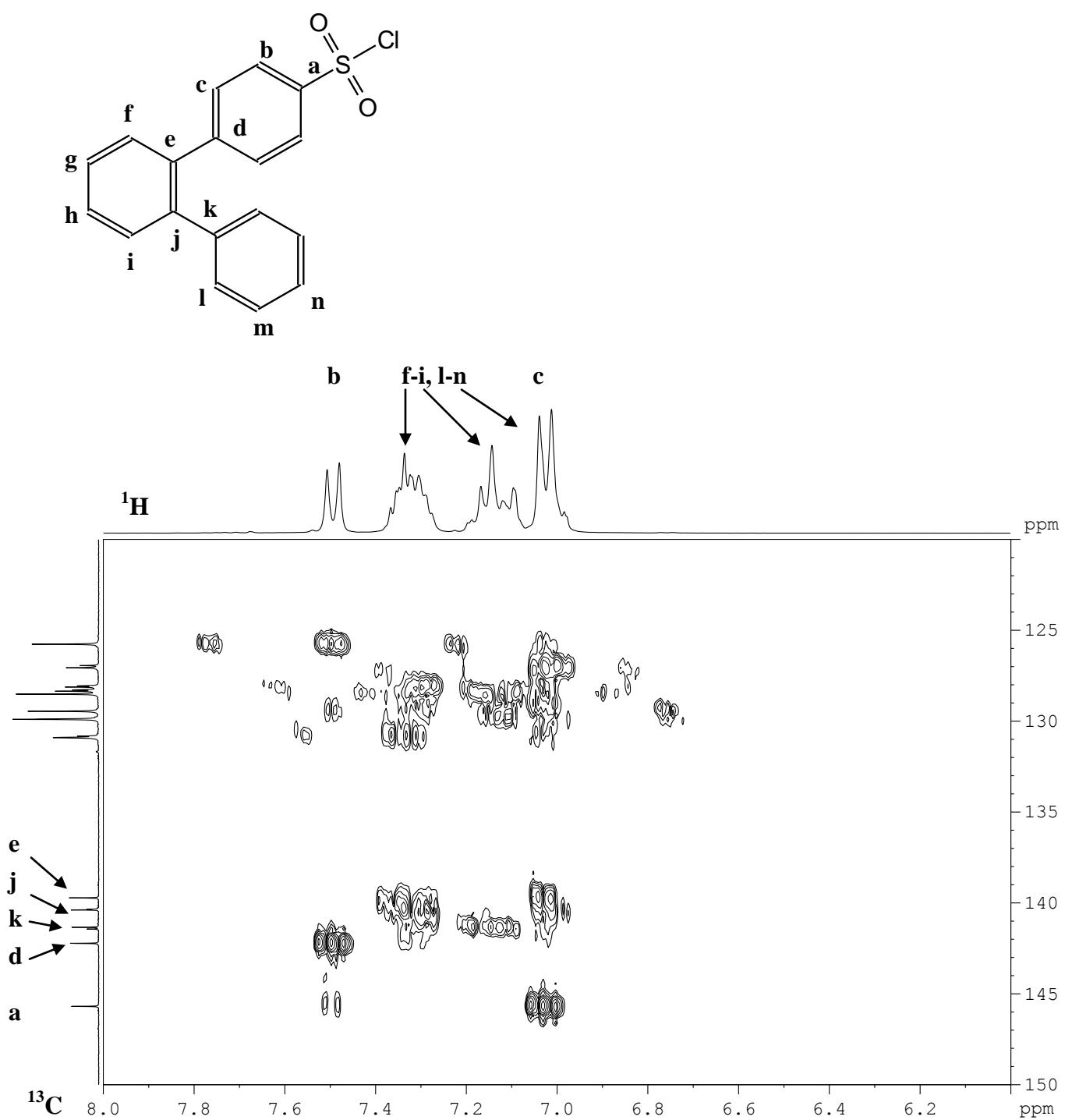


Figure S5. $^1\text{H}^{13}\text{C}$ HMBC spectrum of o-terphenyl sulfonyl chloride, solvent DMSO, 300 MHz.

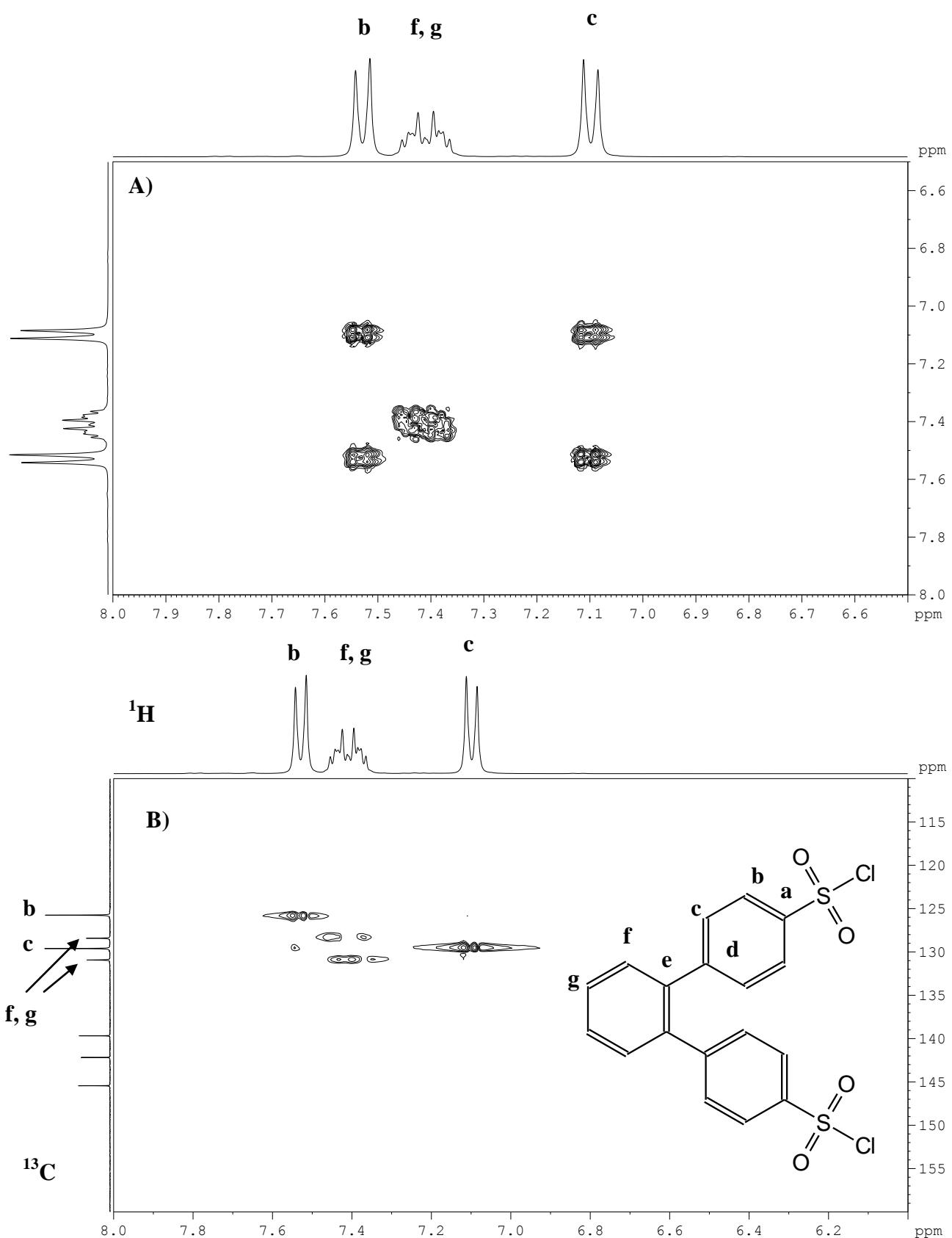


Figure S6. A) ^1H COSY spectrum and B) ^1H - ^{13}C HSQC spectrum of o-terphenyl disulfonyl chloride, solvent DMSO, 300 MHz.

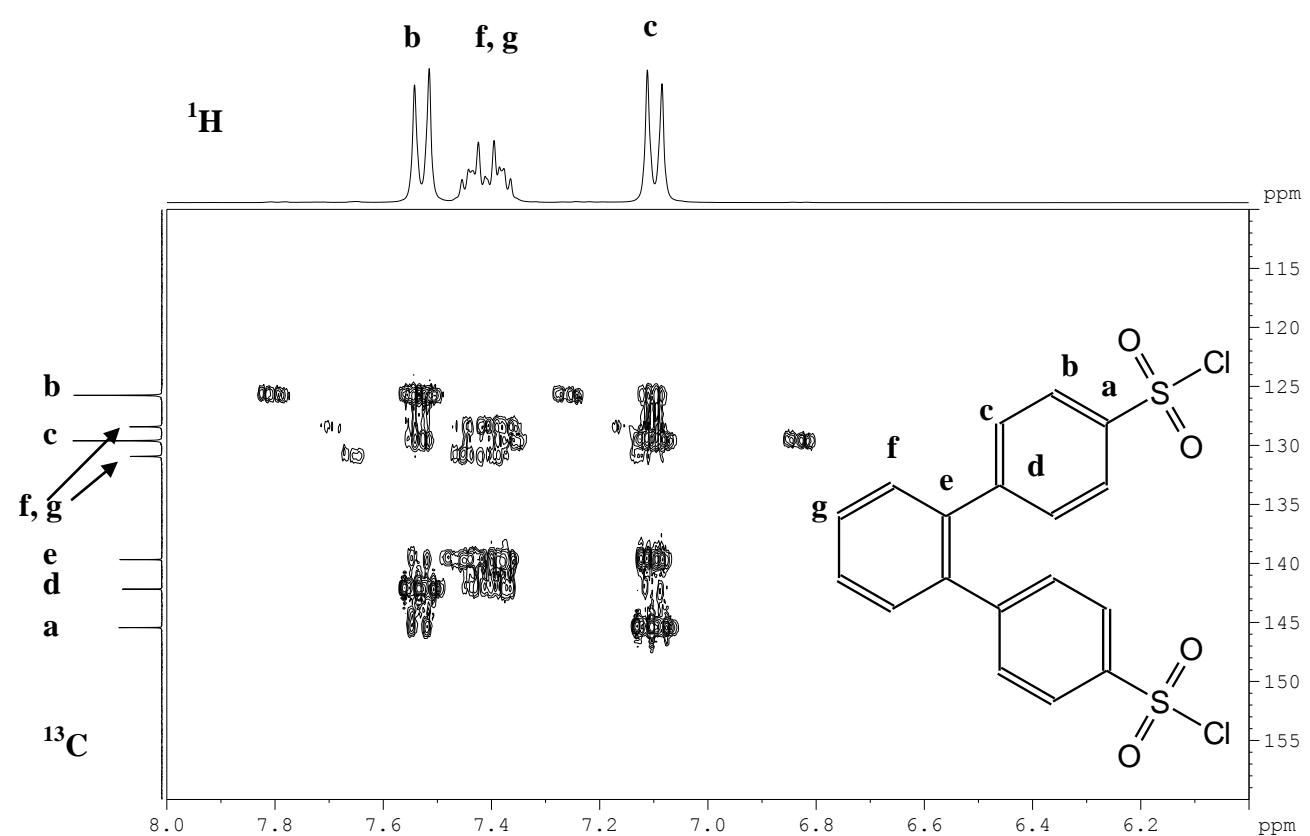


Figure S7. A) ^1H - ^1H COSY spectrum and B) ^1H - ^{13}C HSQC spectrum of o-terphenyl disulfonyl chloride, solvent DMSO, 300 MHz.

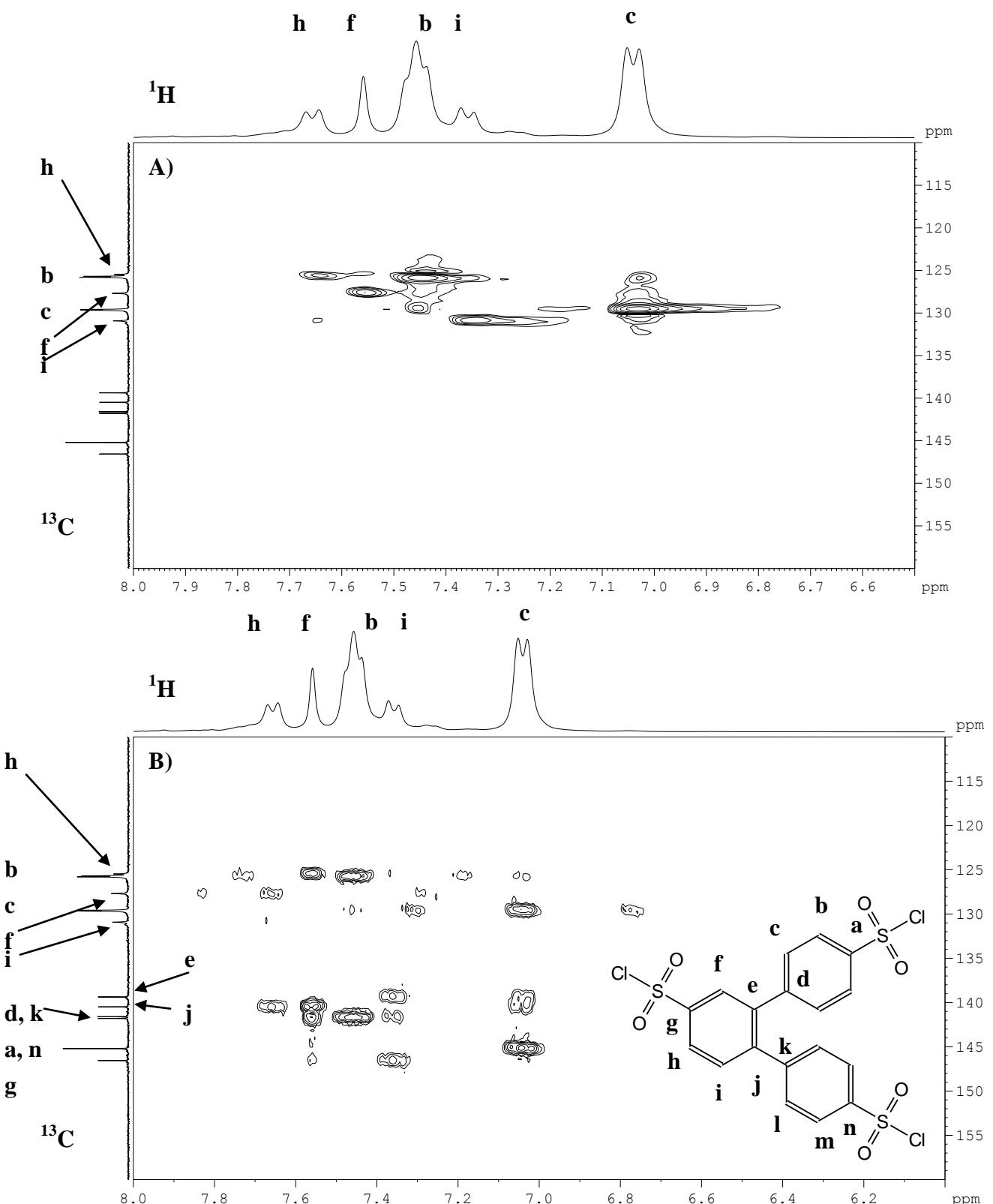


Figure S8. A) ^1H - ^{13}C HSQC spectrum and B) ^1H - ^{13}C HMBC spectrum of o-terphenyl trisulfonyl chloride, solvent DMSO, 300 MHz.

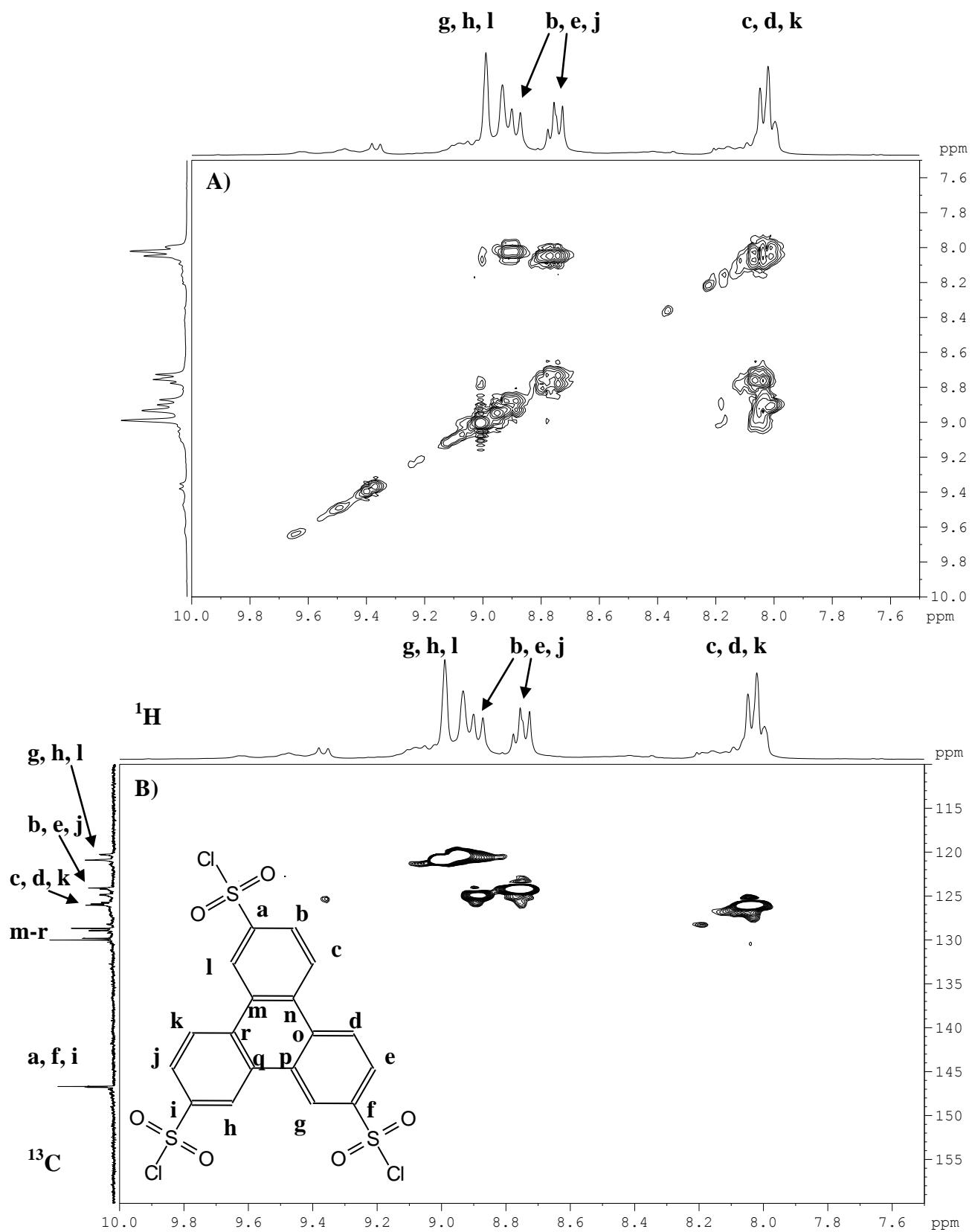


Figure S9. A) ^1H ^1H COSY spectrum and B) ^1H ^{13}C HSQC spectrum of triphenylene trisulfonyl chloride, solvent DMSO, 300 MHz.

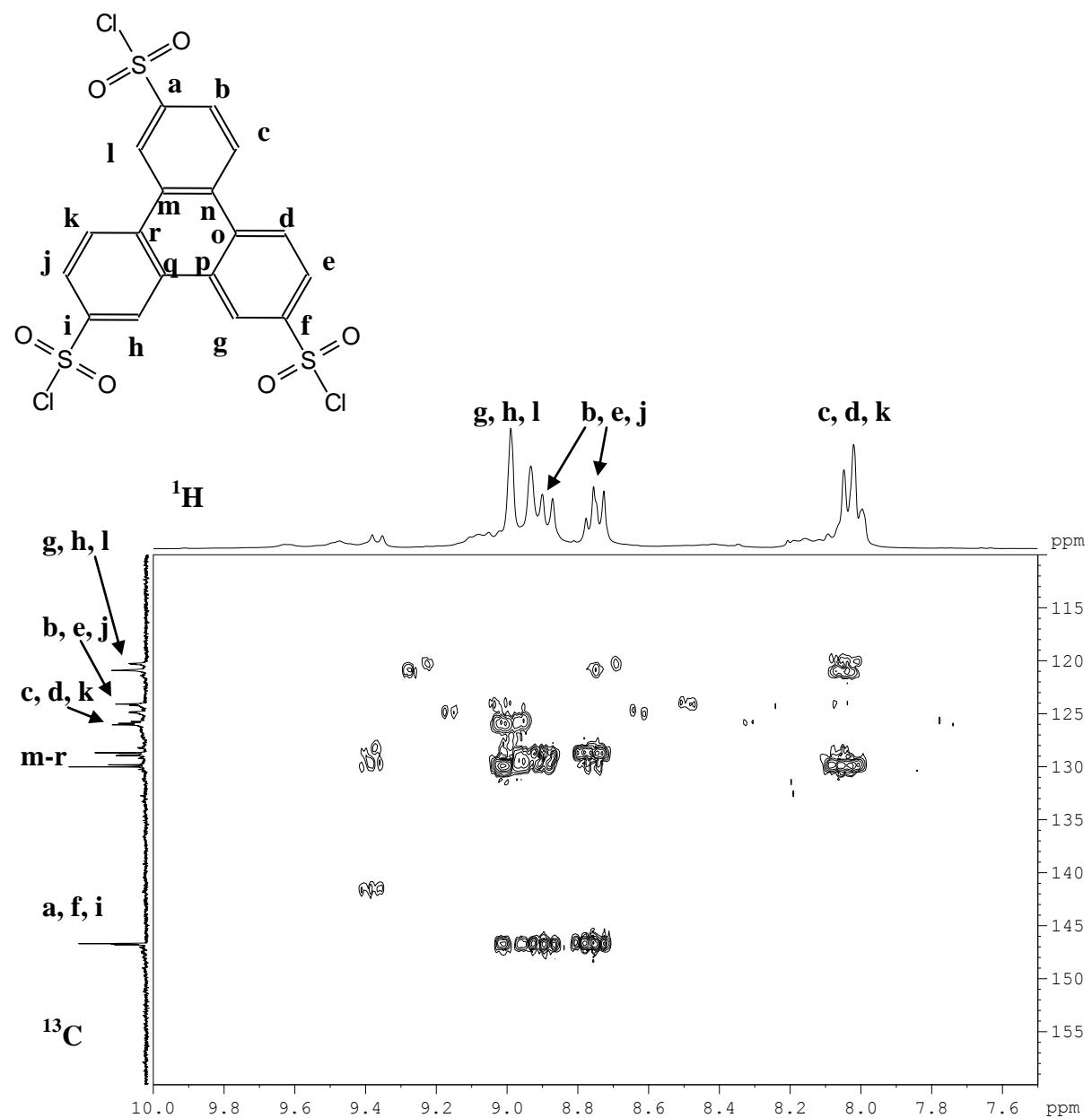


Figure S10. ¹H-¹³C HMBC spectrum of triphenylene trisulfonyl chloride, solvent DMSO, 300 MHz.

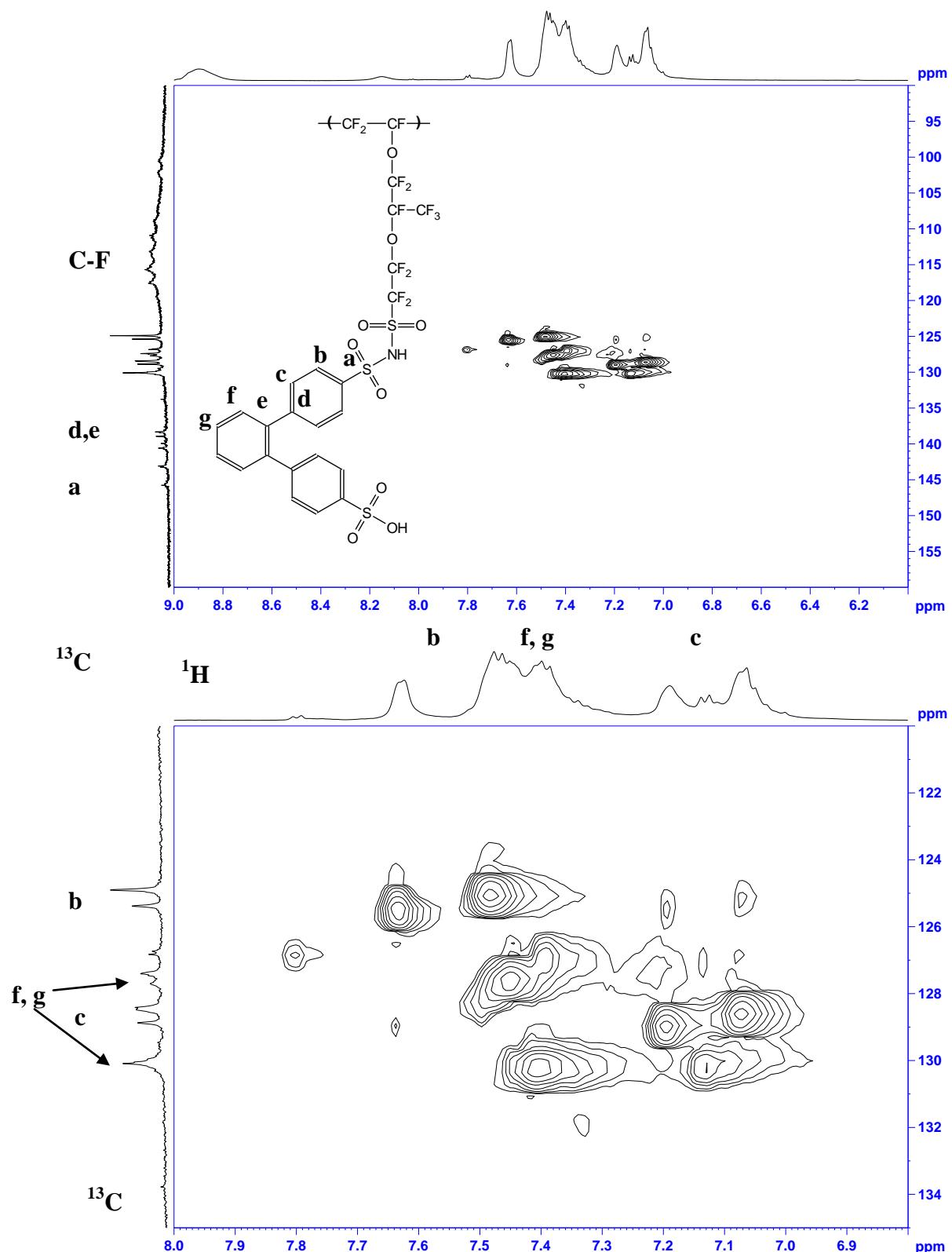


Figure S11. ^1H - ^{13}C HSQC spectrum of poly(PSEPVE) o-terphenyl sulfonimide sulfonic acid, solvent DMSO, 600 MHz.

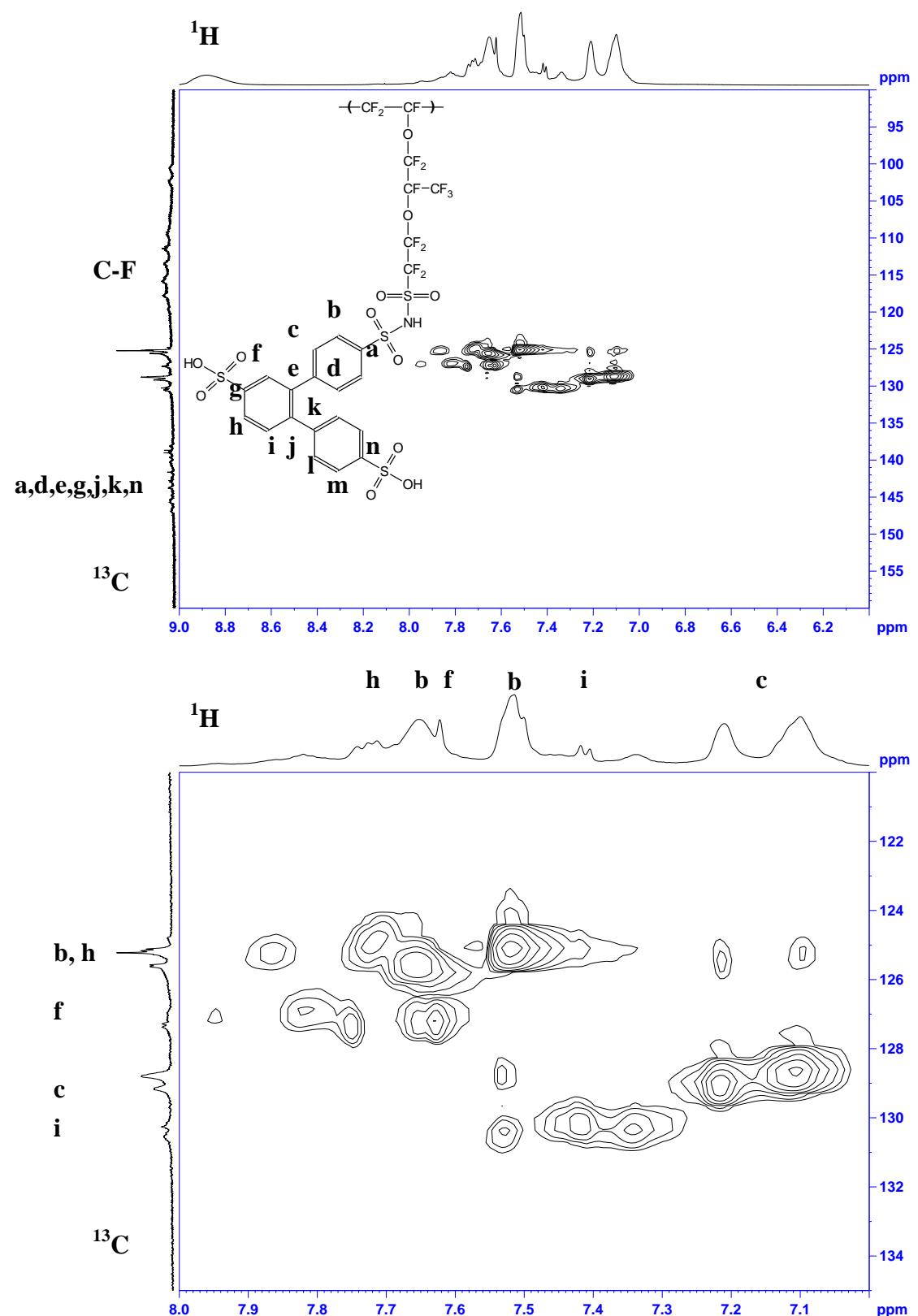


Figure S12. ^1H - ^{13}C HSQC spectrum of poly(PSEPVE) o-terphenyl sulfonimide disulfonic acid, solvent DMSO, 600 MHz.

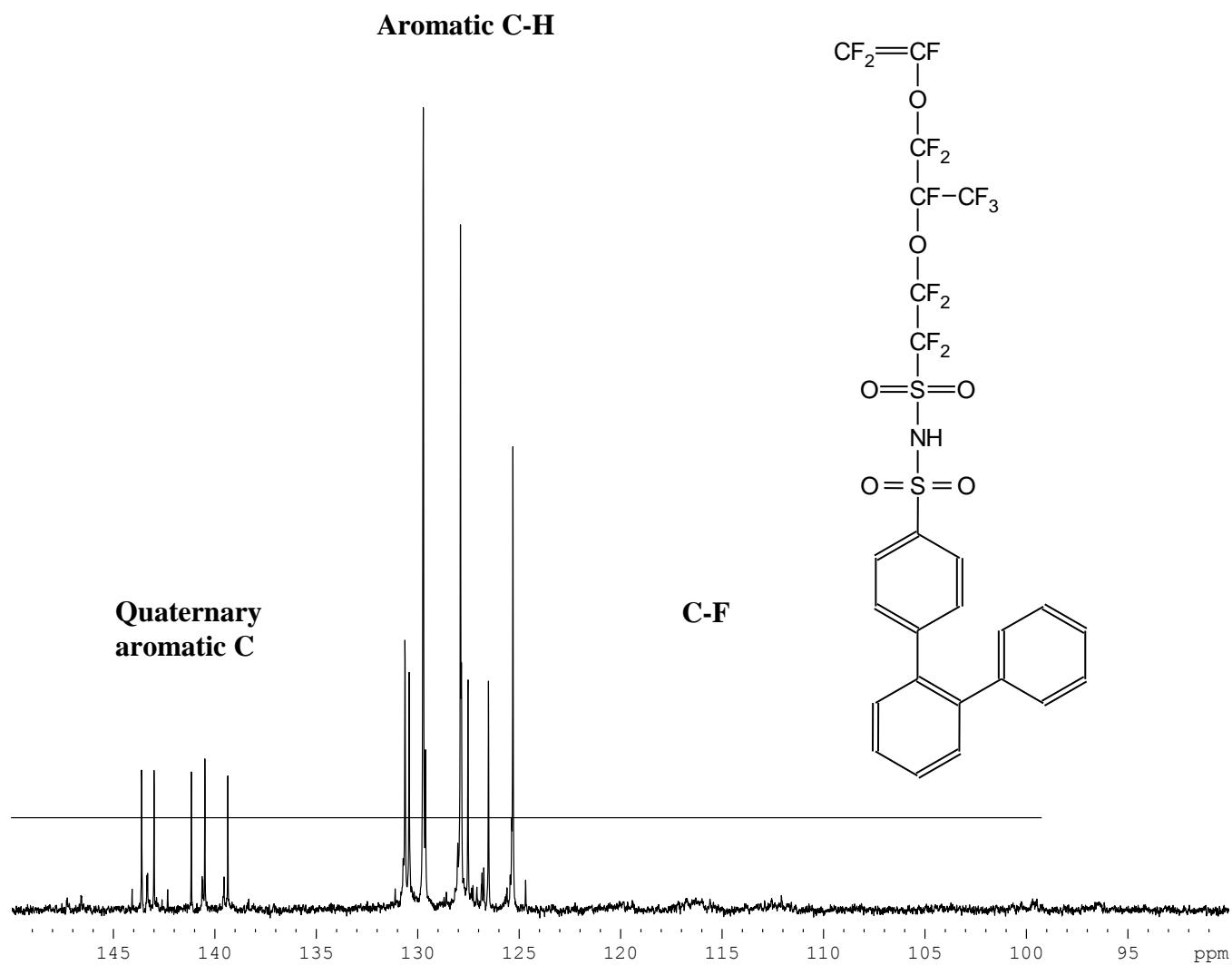


Figure S13. ^{13}C NMR spectrum of PSEPVE o-terphenyl sulfonimide, solvent CDCl_3 , 75 MHz.

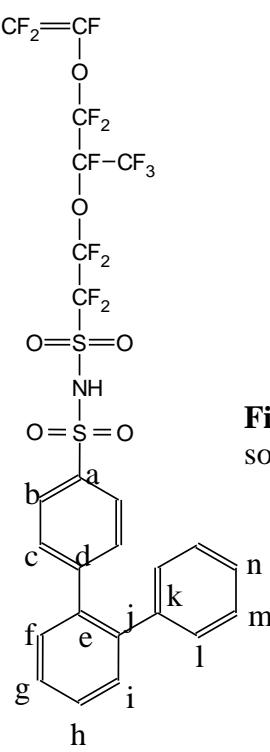
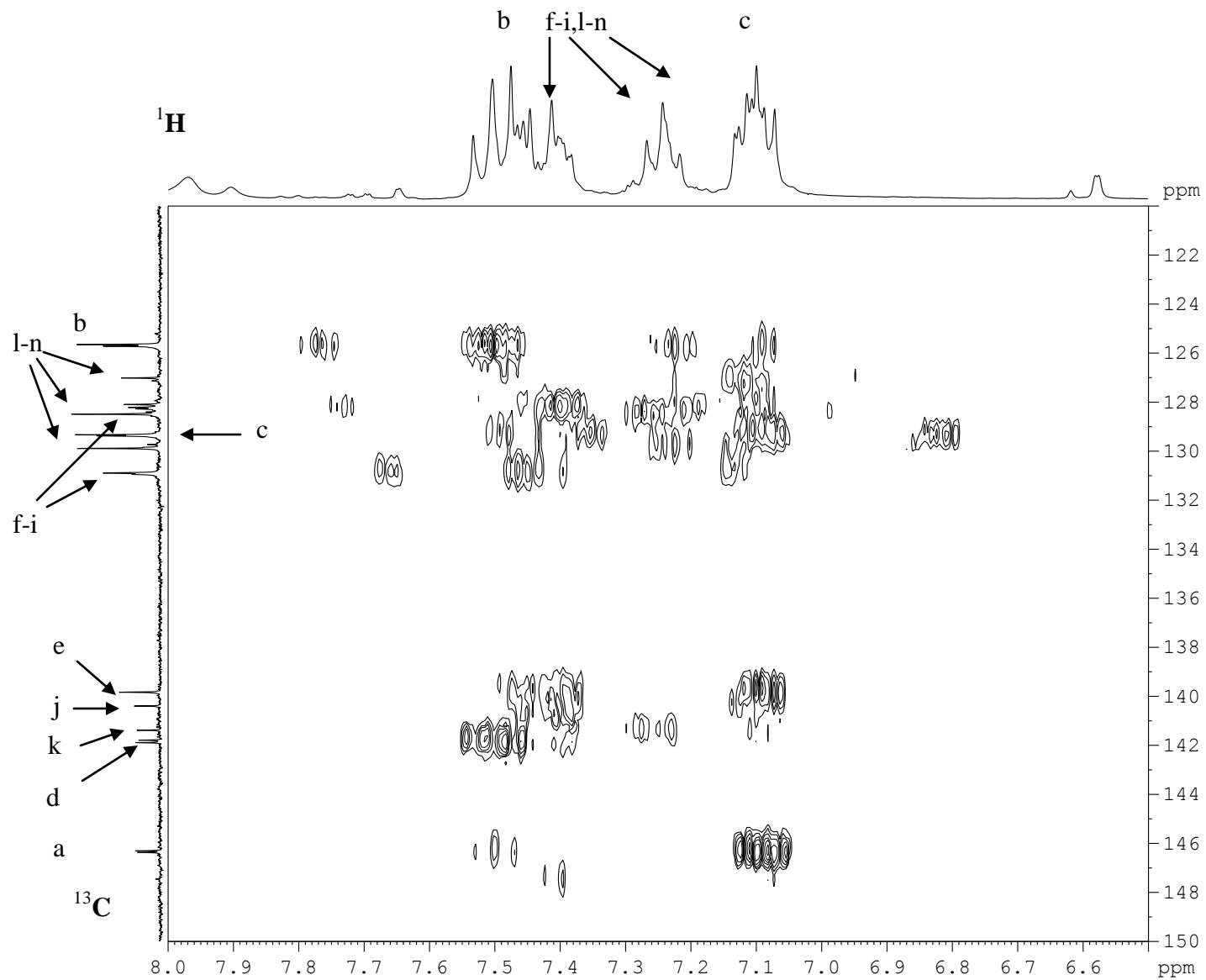


Figure S14. ^1H - ^{13}C HMBC spectrum of PSEPVE o-terphenyl sulfonimide, solvent DMSO, 300 MHz.

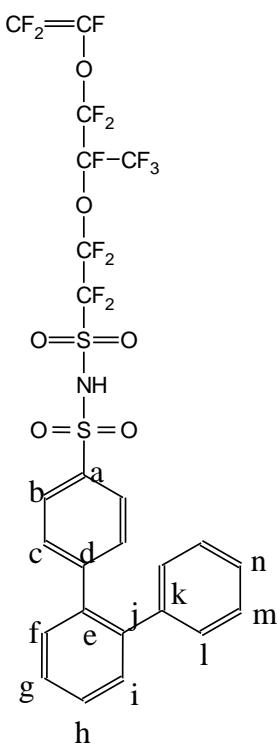
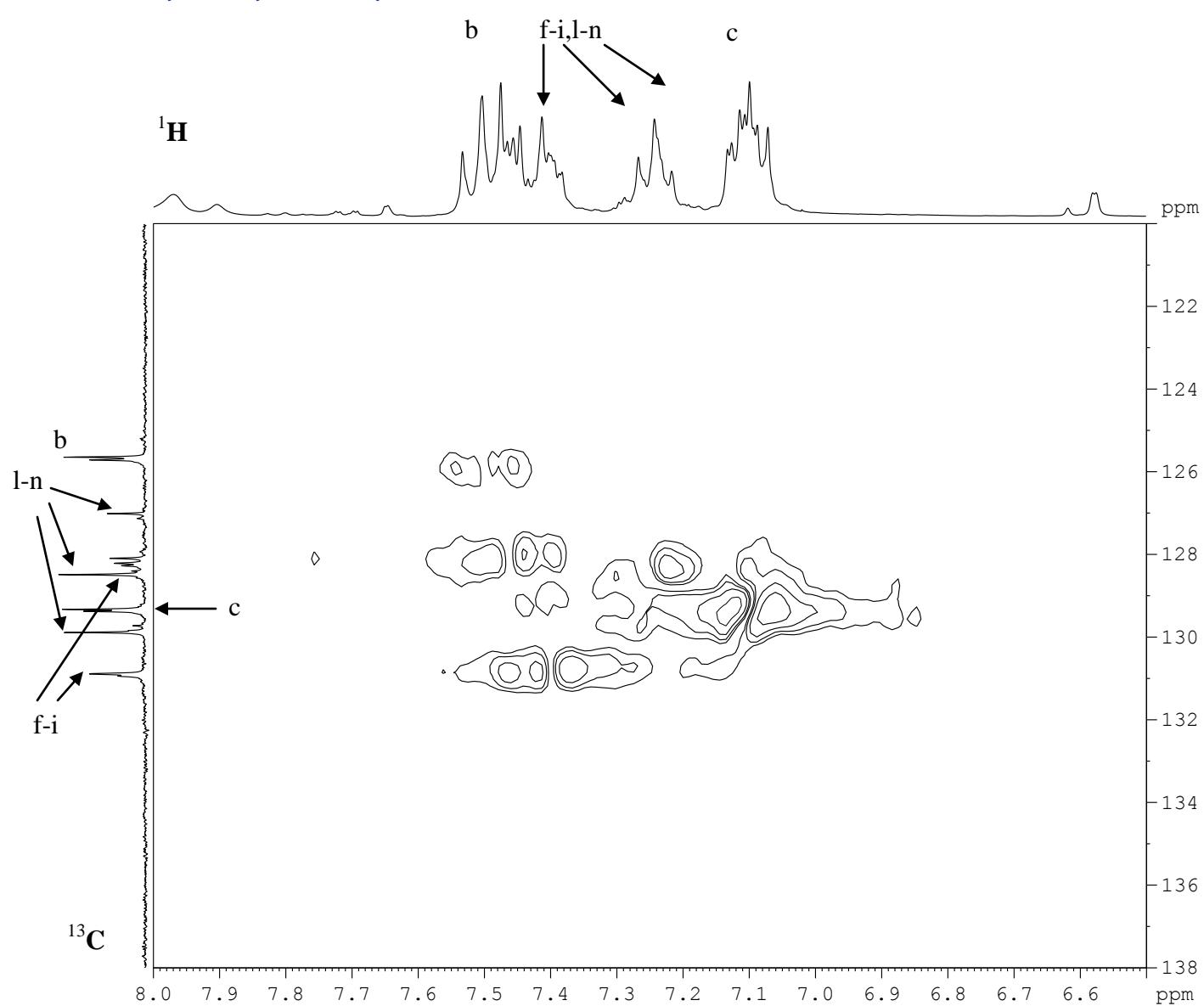


Figure S15. ¹H-¹³C HSQC spectrum of PSEPVE o-terphenyl sulfonimide, solvent DMSO, 300 MHz.