Electronic Supplementary Material (ESI) for RSC Advances.

Design, synthesis and thermal behaviour of a series of well-defined clickable and triggerable sulfonate polymers

Joanna Kolomanska,[a] Priscilla Johnston,[a] Alberto Gregori,[b,a] Isabel Fraga Dominguez,[c,d,a] Hans-Joachim Egelhaaf[e†], Sébastien Perrier,[f,g] Agnès Rivaton,[c,d] Christine Dagron-Lartigau[b] and Paul D. Topham[a*]

a. Chemical Engineering and Applied Chemistry, Aston University, Birmingham, B4 7ET, UK.

b. Université de Pau et des Pays de l'Adour, Institut Plurisdisciplinaire de Recherche sur l'Environnement et les Matériaux, UMR 5254, Technopole Helioparc2, av. Pdt Angot 64 053 Pau cedex 09, France

c. Institut de Chimie de Clermont-Ferrand, Equipe Photochimie, UMR 6296, Université Blaise Pascal, , 24, Avenue des Landais, BP80026, 63171 Aubière Cedex, France.

d. CNRS, UMR 6296, ICCF, Équipe Photochimie, BP 80026, F-63171 Aubière, France.

e. Belectric OPV GmbH, Landgrabenstr. 94, 90443 Nürnberg, Germany; currently: ZAE Bayern, Fürther Str. 250, 90429 Nürnberg, Germany

f. Department of Chemistry, University of Warwick, CV4 7AL, UK.

g. Faculty of Pharmacy and Pharmaceutical Sciences, Monash University, 381 Royal Parade, Parkville, VIC 3052, Australia.

† Current address: ZAE Bayern, Fürther Str. 250, D-90429, Nürnberg, Germany.

*Corresponding author: p.d.topham@aston.ac.uk

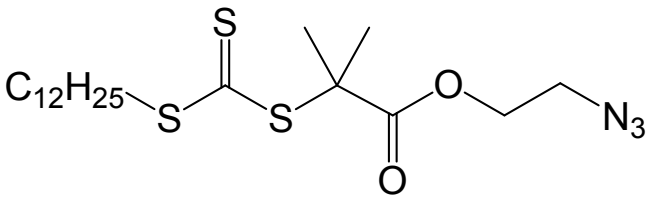

Figure S1. Structure of the chain transfer agent, 2-azidoethyl 2-(dodecylthiocarbonothioylthio)-2-methylpropionate (CTA-N_3).

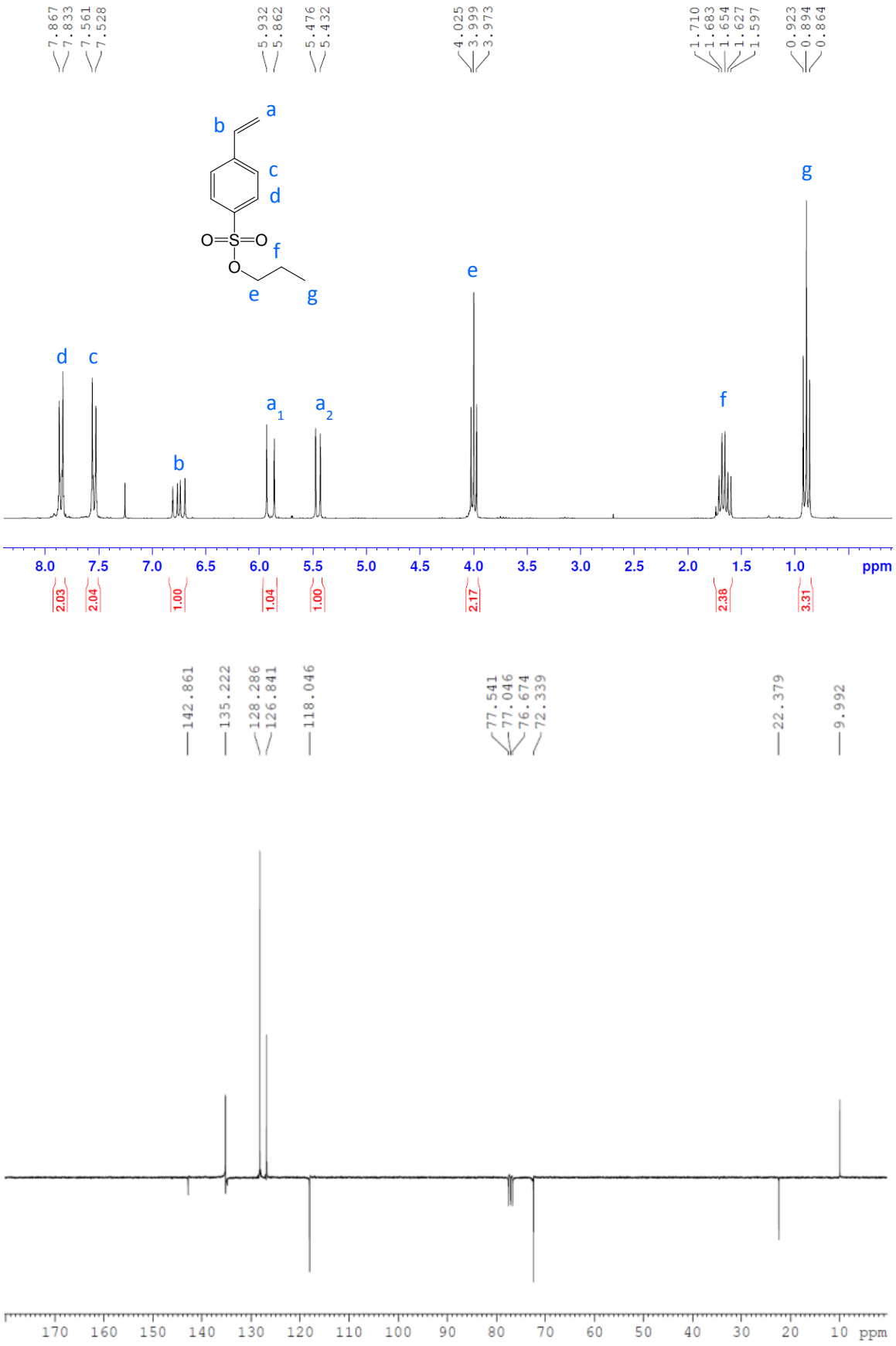

Figure S2. ^{1}H NMR and ^{13}C NMR spectra of *n*-propyl styrene sulfonate, **2**.

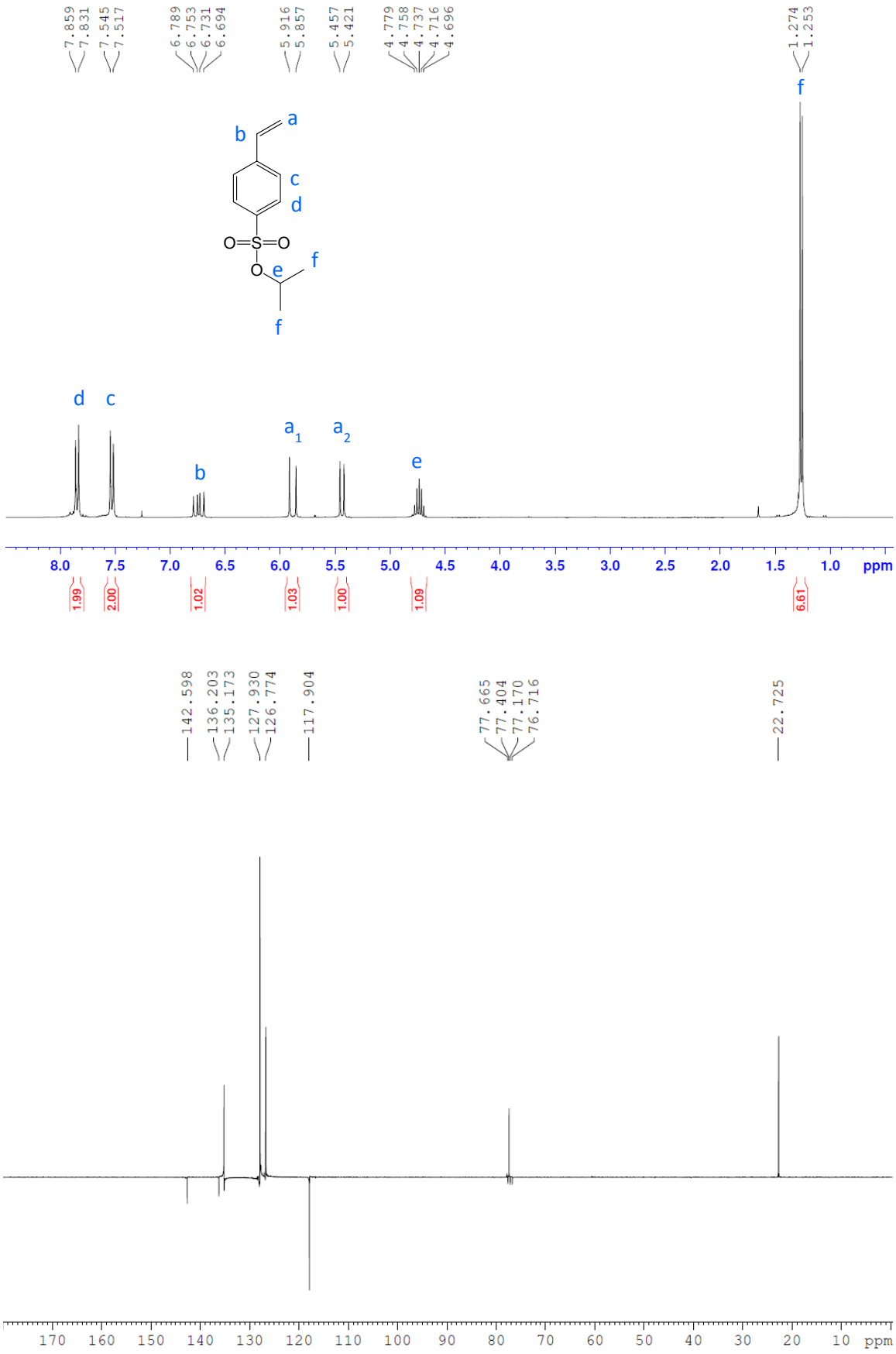

Figure S3. ^{1}H NMR and ^{13}C NMR spectra of isopropyl styrene sulfonate, **3**.

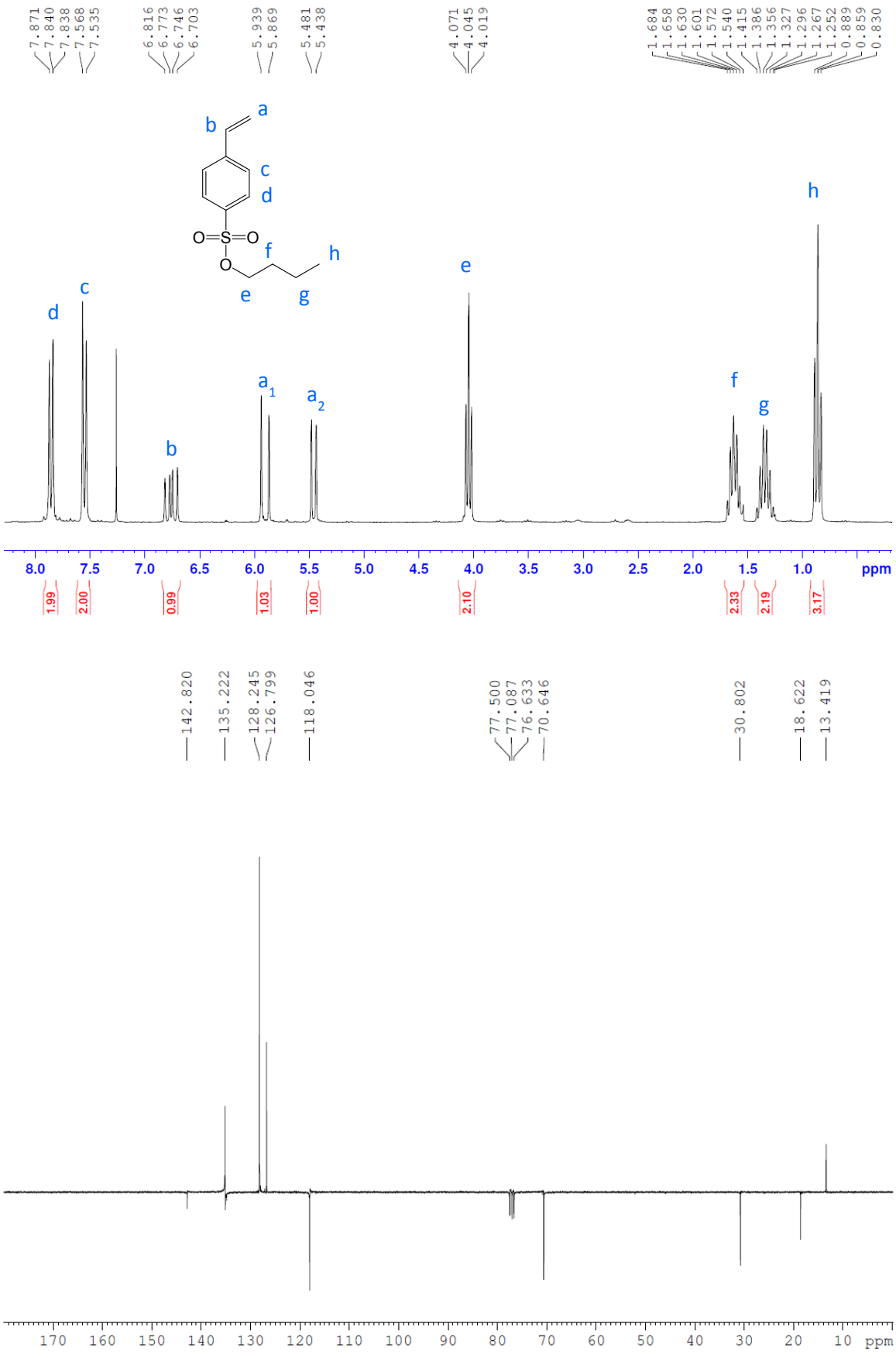

Figure S4. ^{1}H NMR and ^{13}C NMR spectra of *n*-butyl styrene sulfonate, **4**.

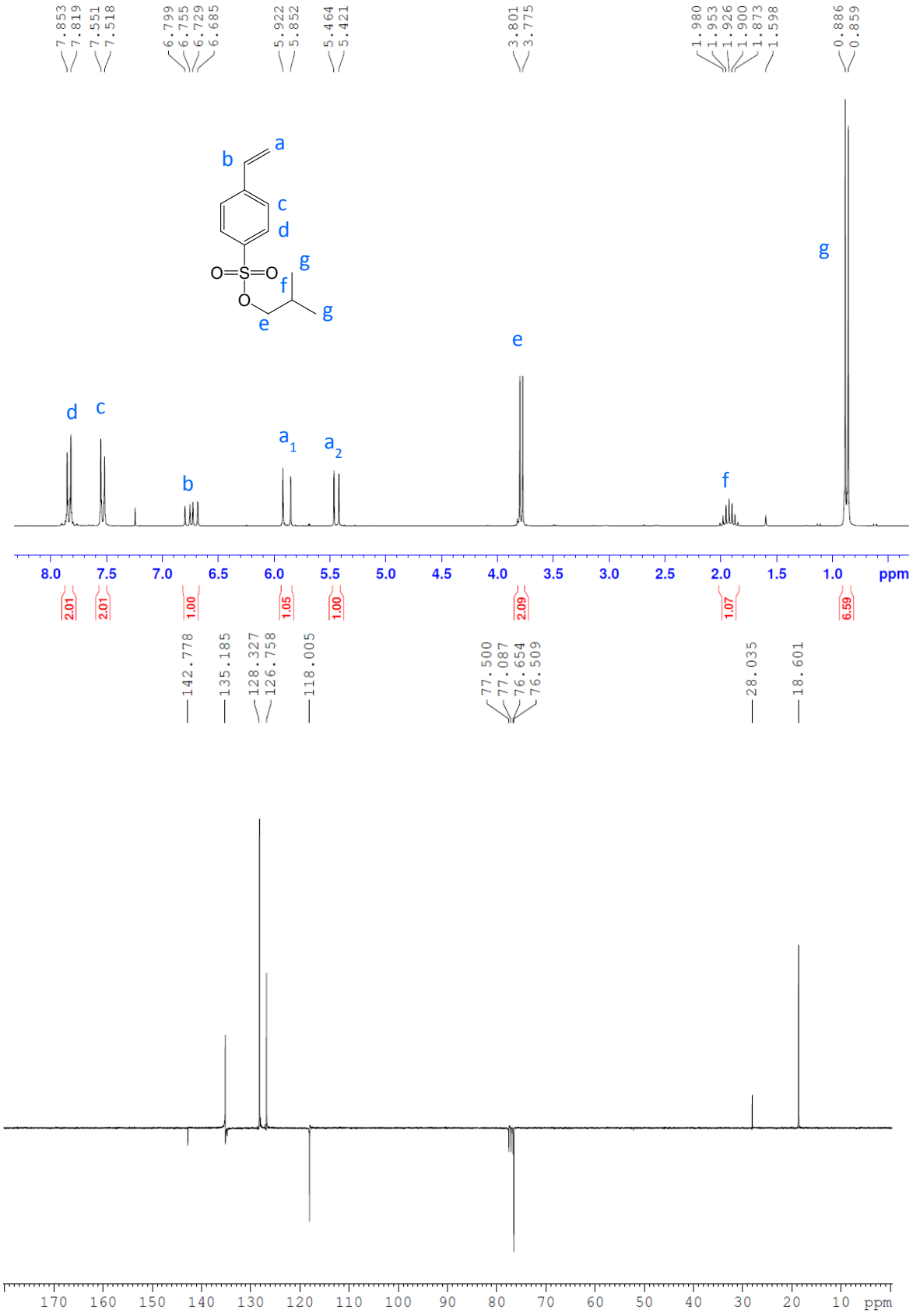

Figure S5. ^{1}H NMR and ^{13}C NMR spectra of isobutyl styrene sulfonate, **5**.

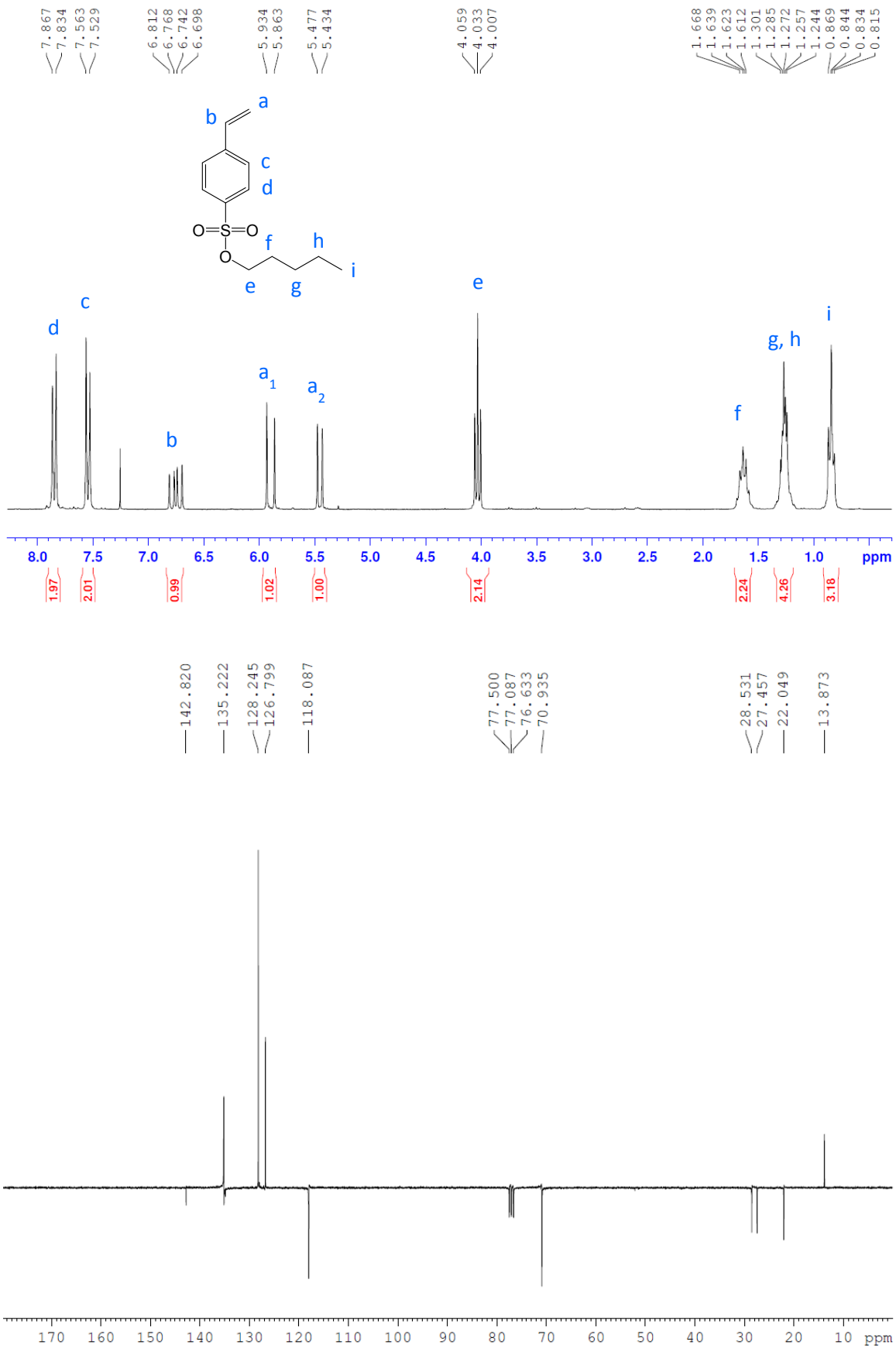

Figure S6. ^{1}H NMR and ^{13}C NMR spectra of *n*-pentyl styrene sulfonate, **6**.

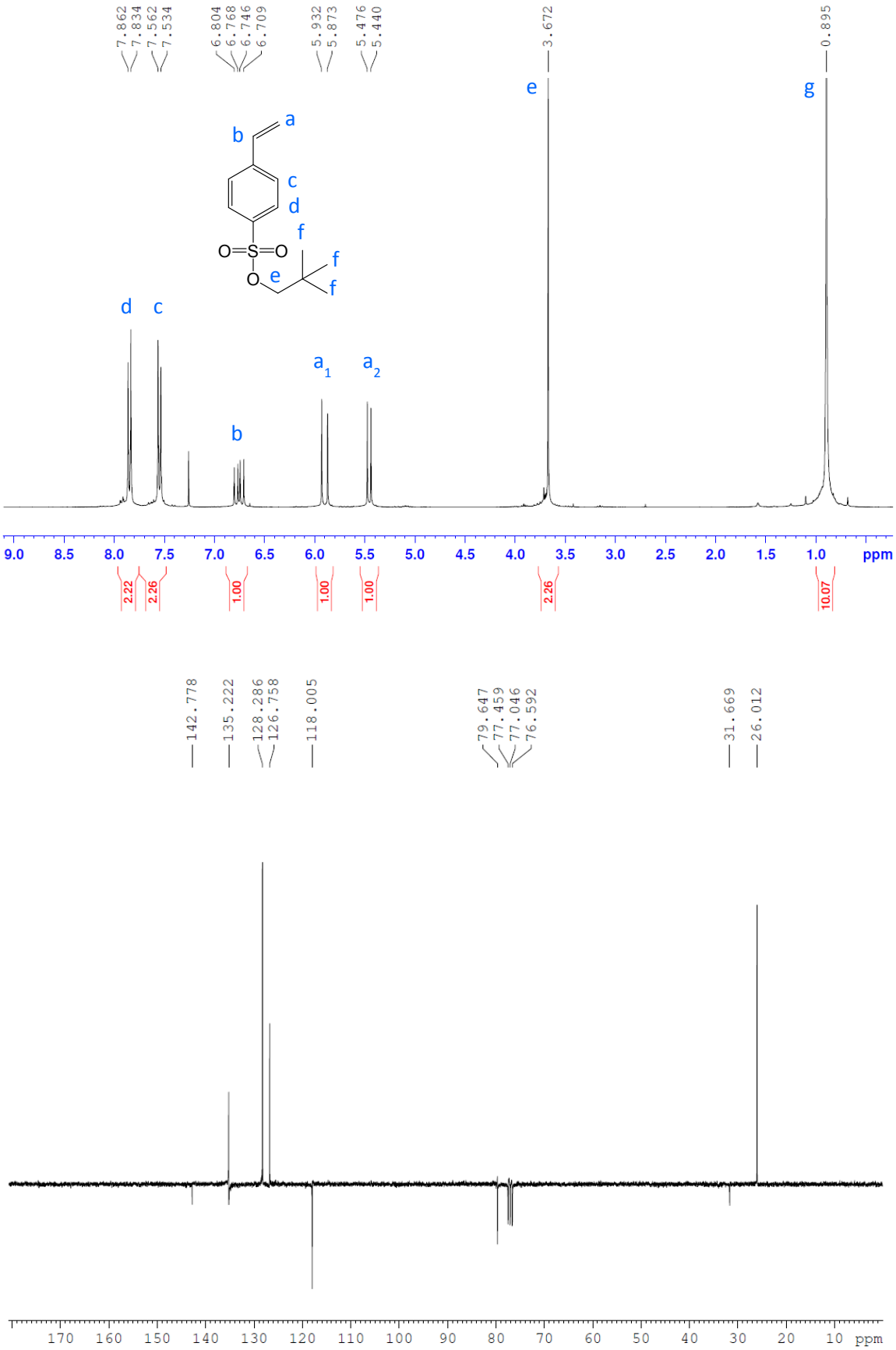

Figure S7. ^{1}H NMR and ^{13}C NMR spectra of neopentyl styrene sulfonate, **7**.

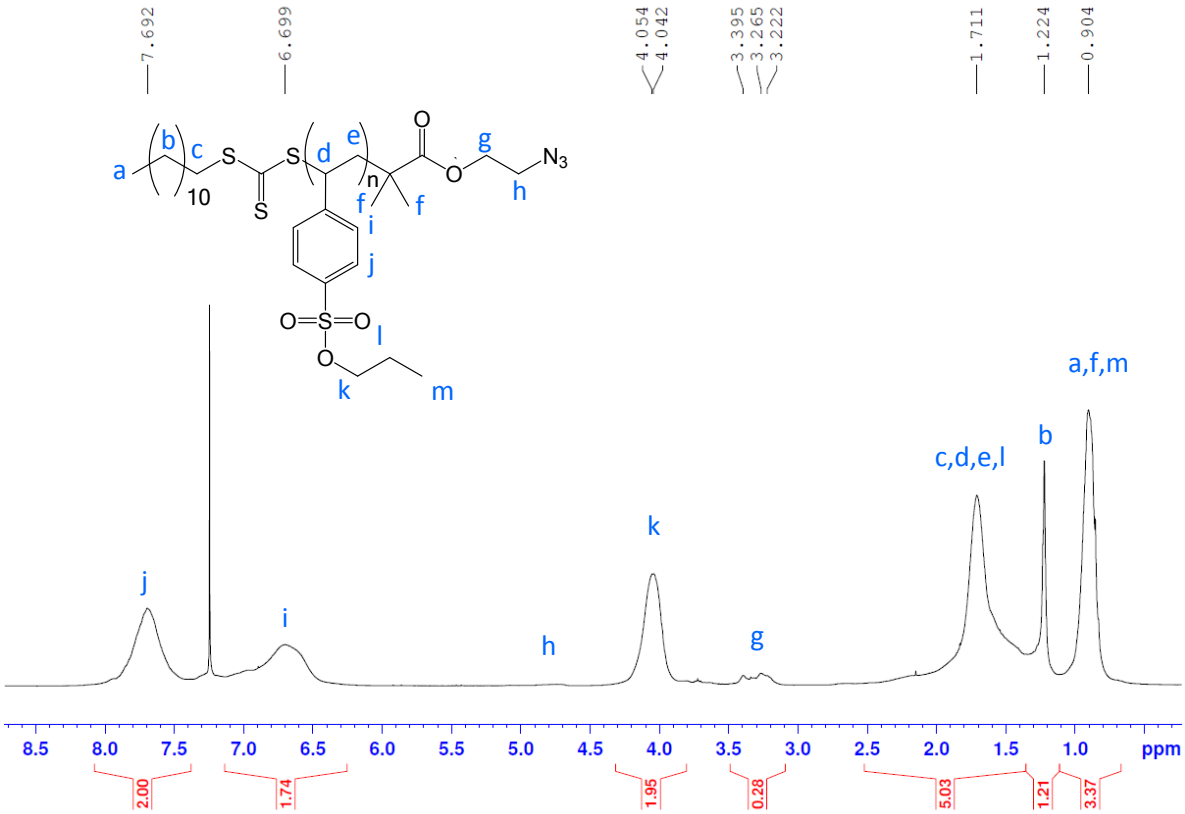

Figure S8. ^{1}H NMR spectrum of poly(*n*-propyl styrene sulfonate), **8**.

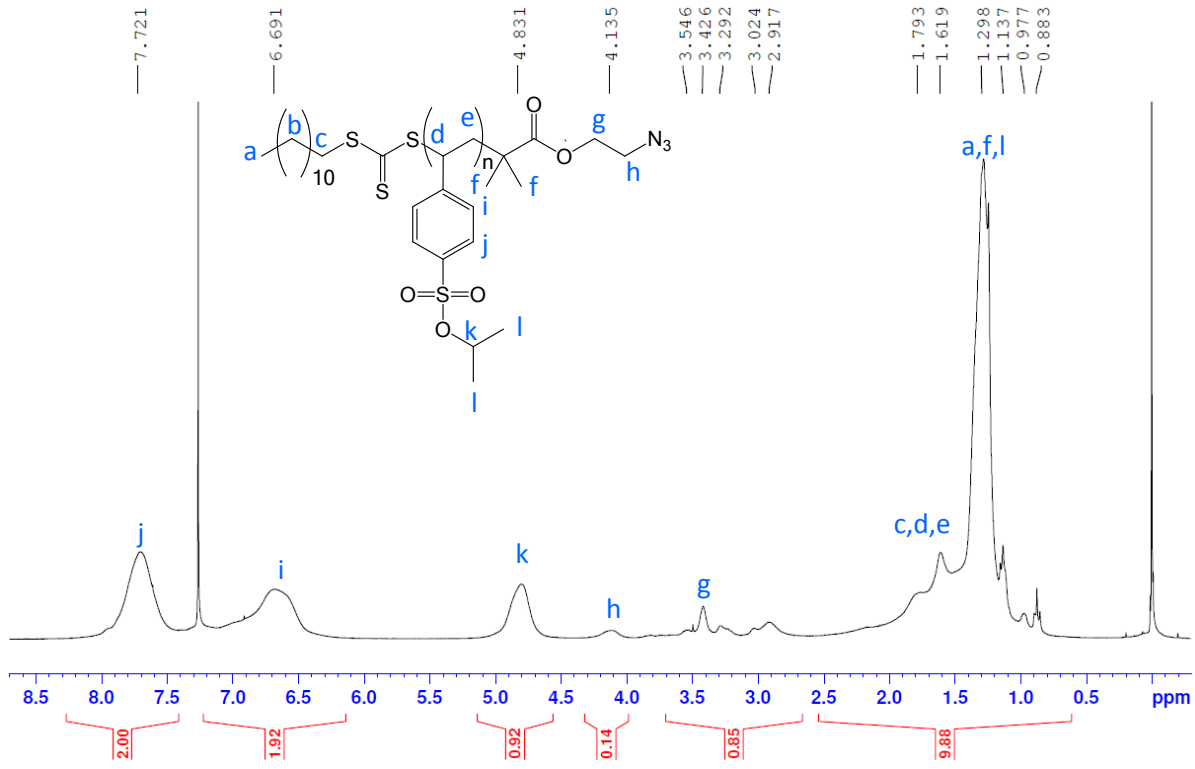

Figure S9. ^{1}H NMR spectrum of poly(isopropyl styrene sulfonate), **9**.

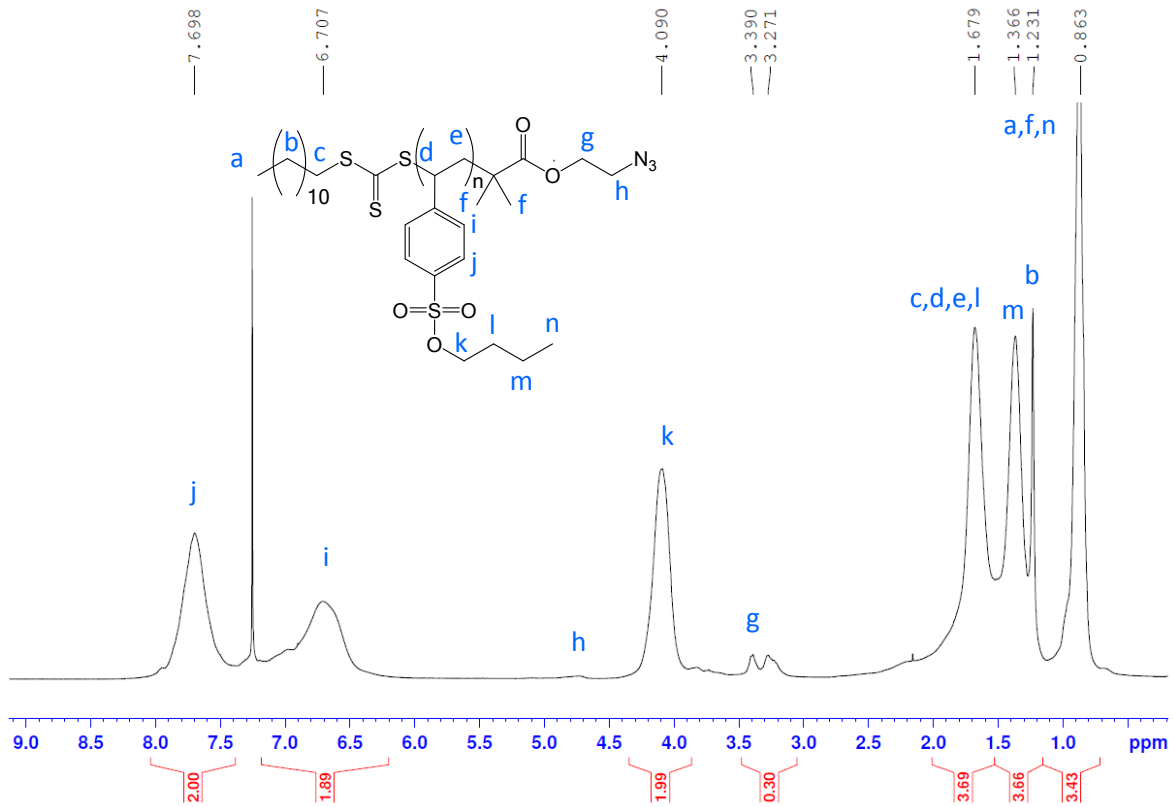

Figure S10. ^{1}H NMR spectrum of poly(*n*-butyl styrene sulfonate), **10**.

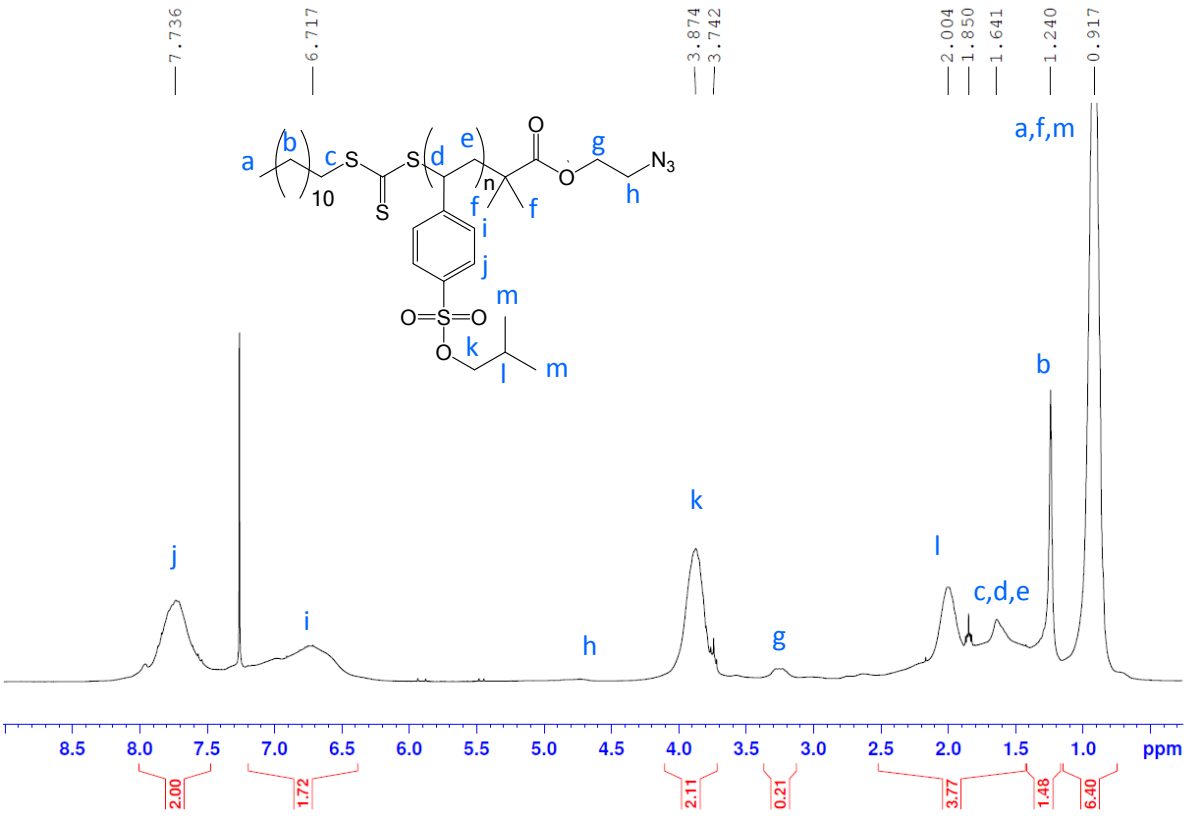

Figure S11. ^{1}H NMR spectrum of poly(isobutyl styrene sulfonate), **11**.

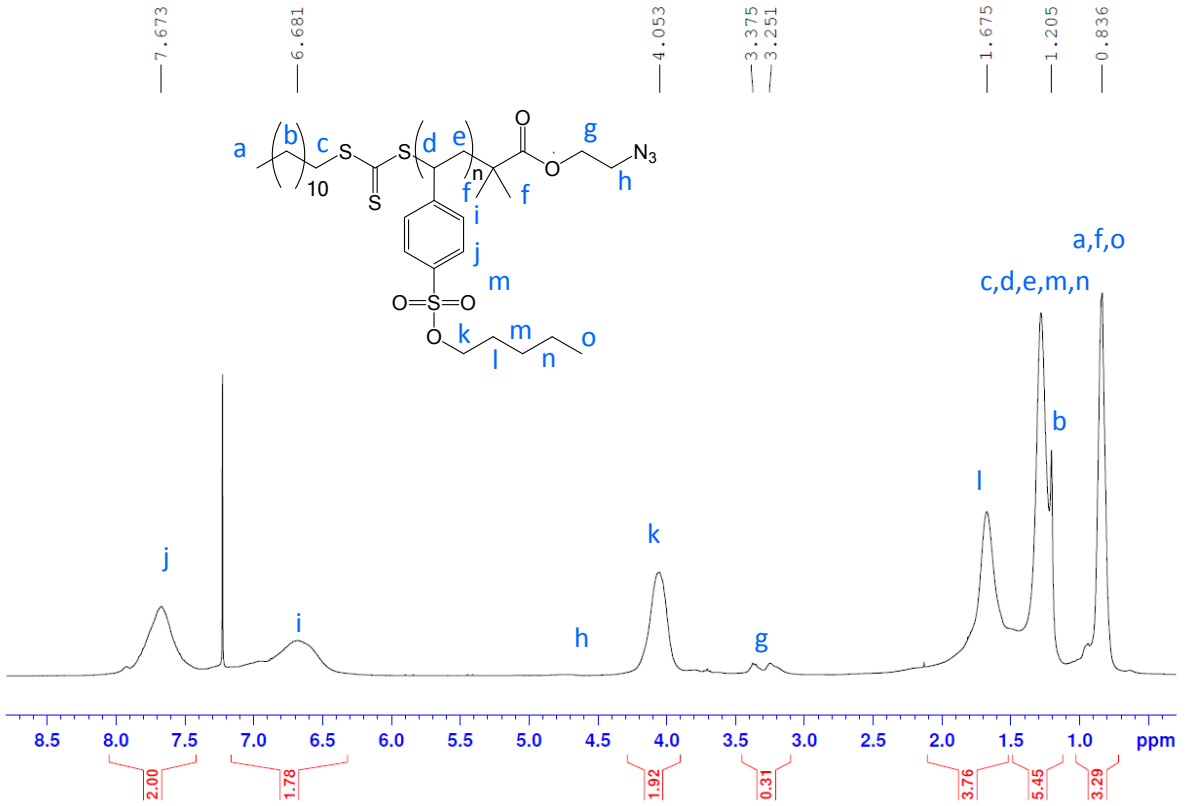

Figure S12. ^{1}H NMR spectrum of poly(*n*-pentyl styrene sulfonate), **12**.

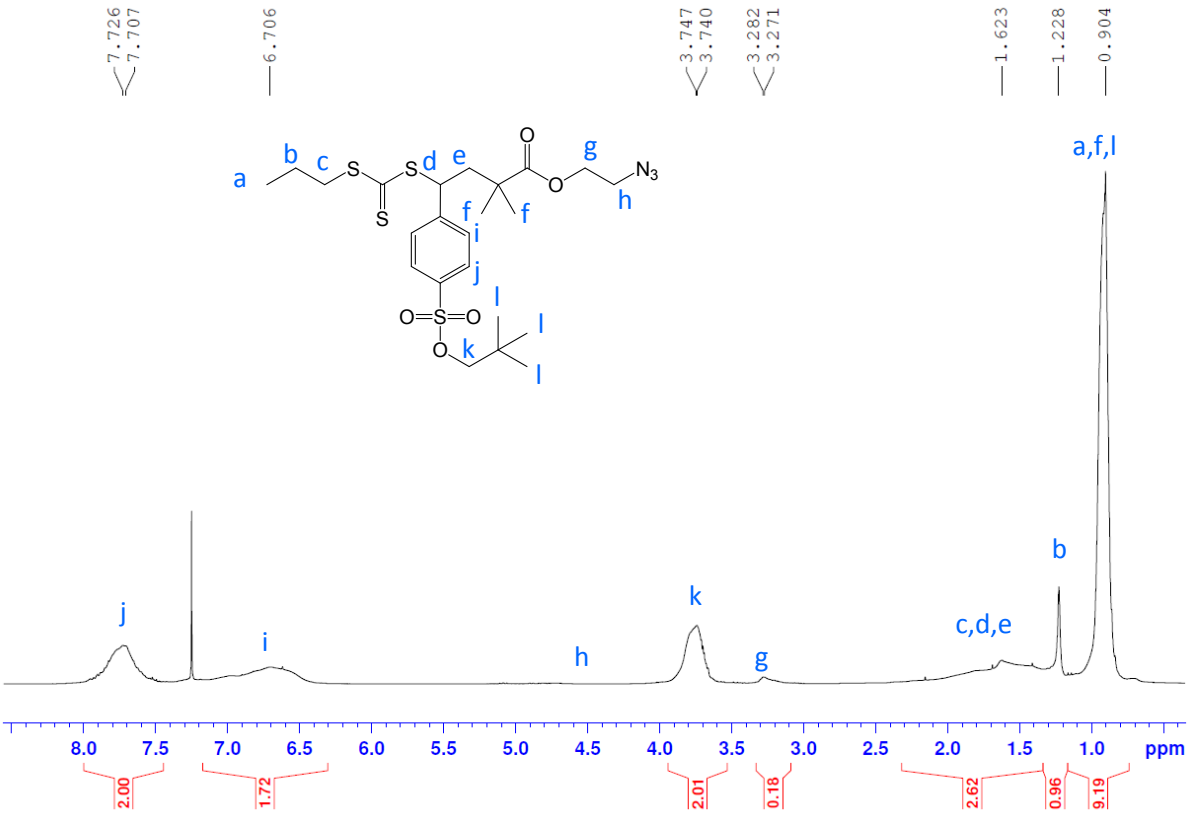

Figure S13. ^{1}H NMR spectrum of poly(neopentyl styrene sulfonate), **13**.

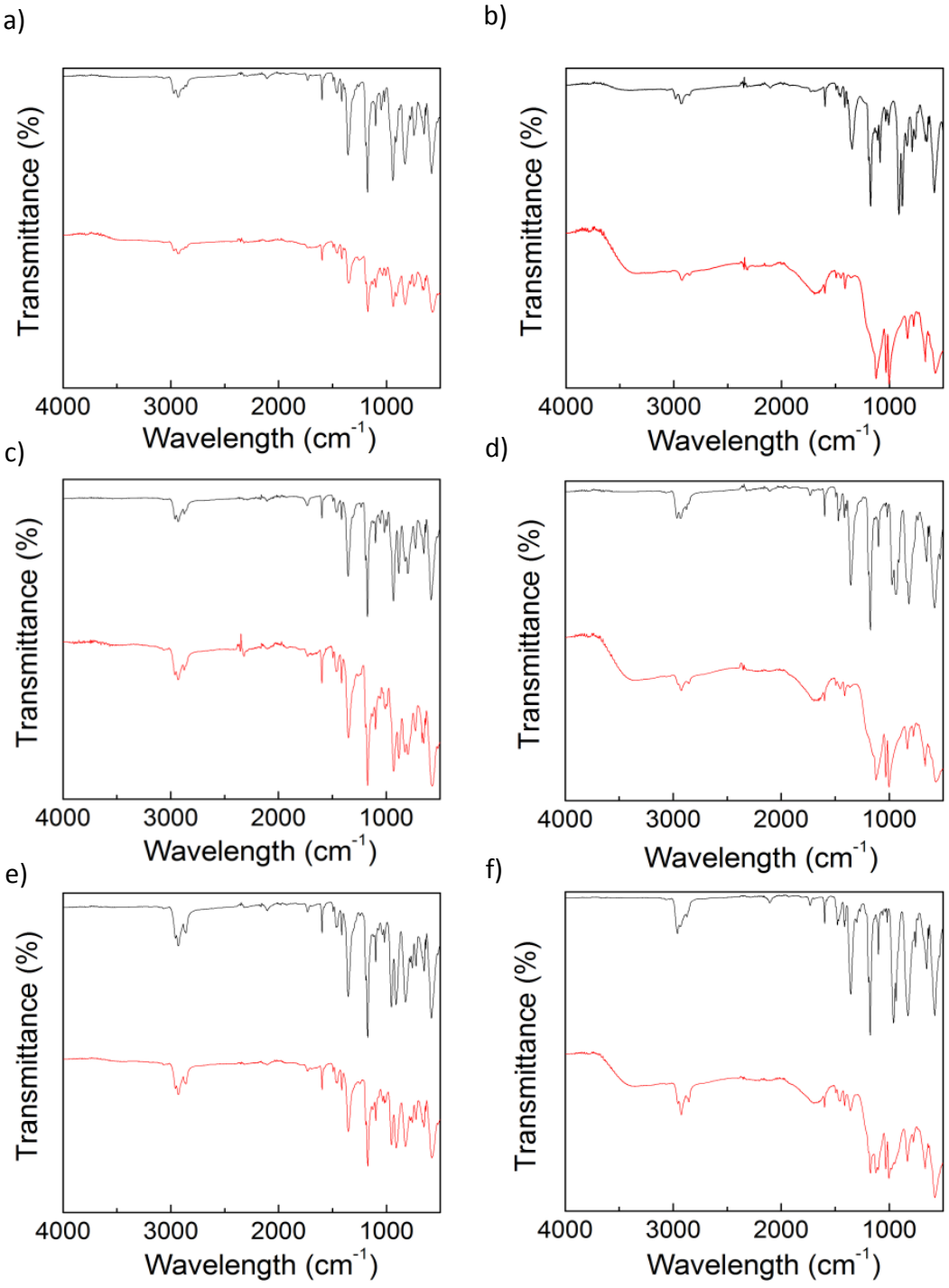

Figure S14. FTIR spectra of R-protected styrene sulfonate before (top) and after deprotection (bottom), (a) R = *n*-propyl, (b) R = isopropyl, (c) R = *n*-butyl, (d) R = isobutyl, (e) R = *n*-pentyl, (f) R = neopentyl.

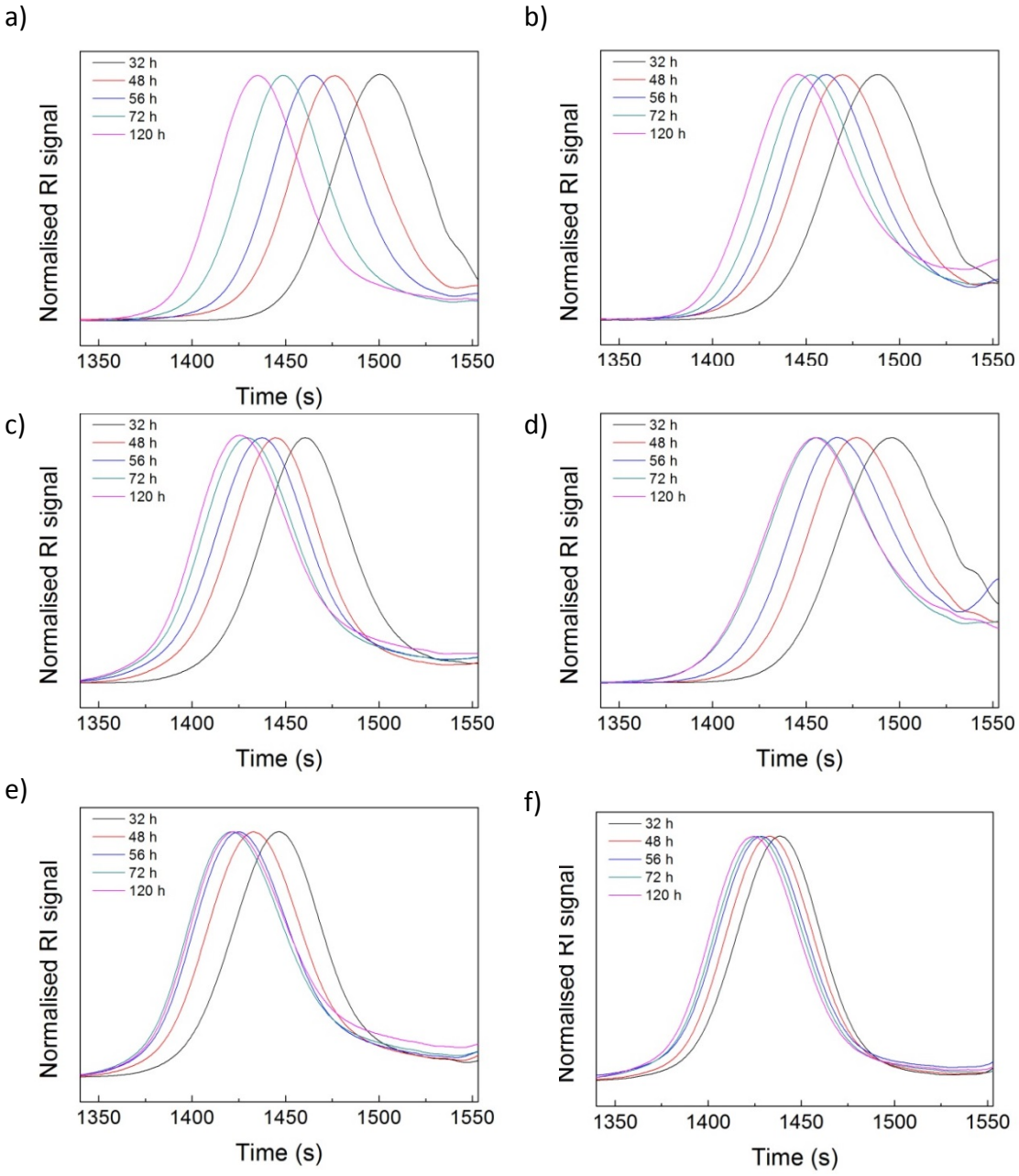

Figure S15. GPC traces of R-protected styrene sulfonate M_n evolution for T = 32-120 h, (a) R = *n*-propyl, (b) R = isopropyl, (c) R = *n*-butyl, (d) R = isobutyl, (e) R = *n*-pentyl, (f) R = neopentyl.

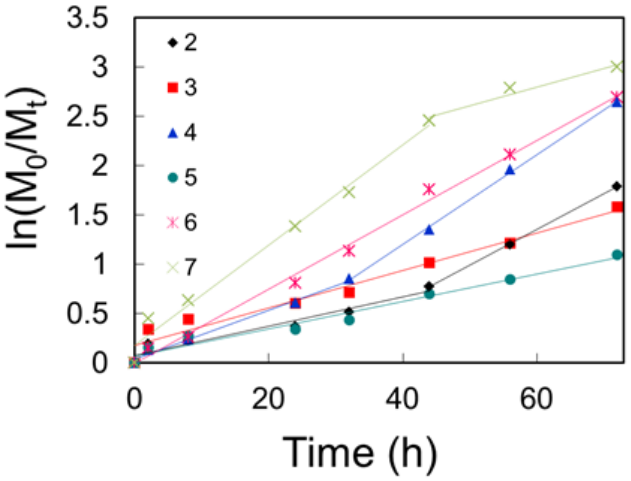

Figure S16. *Pseudo* first-order kinetic plots for the polymerisation of monomers (**2-7**).

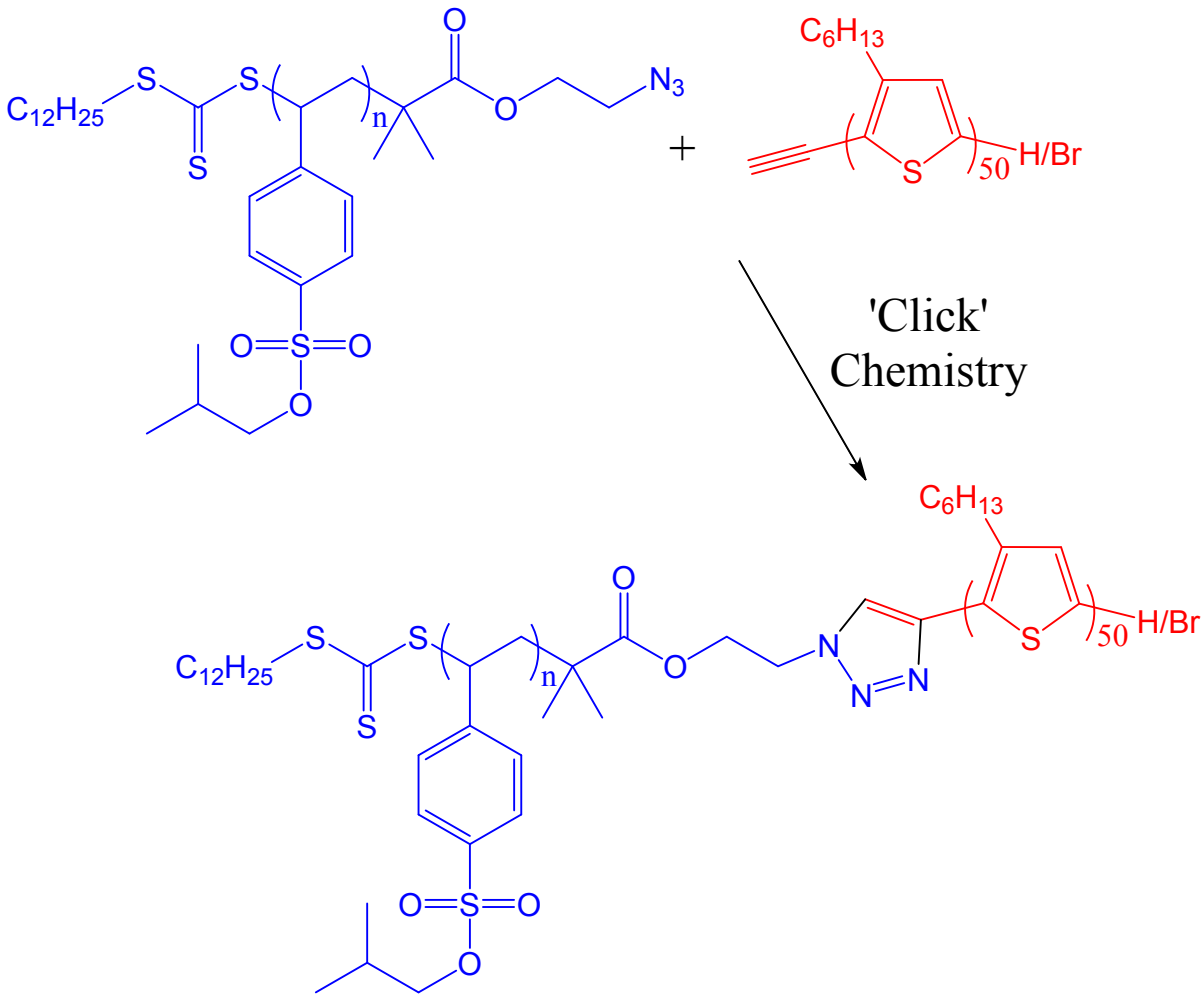

Figure S17. Synthesis of P3HT-*b*-PiBSS.

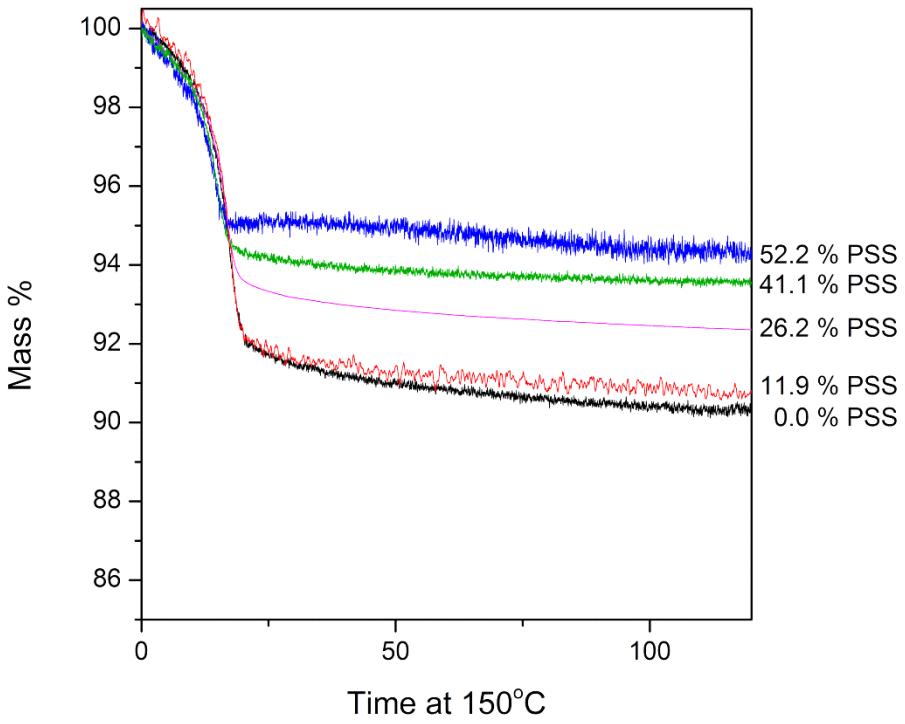

Figure S18. Thermograms obtained for isothermal TGA (150°C, 2 h) experiments using PSS-doped PiBSS.

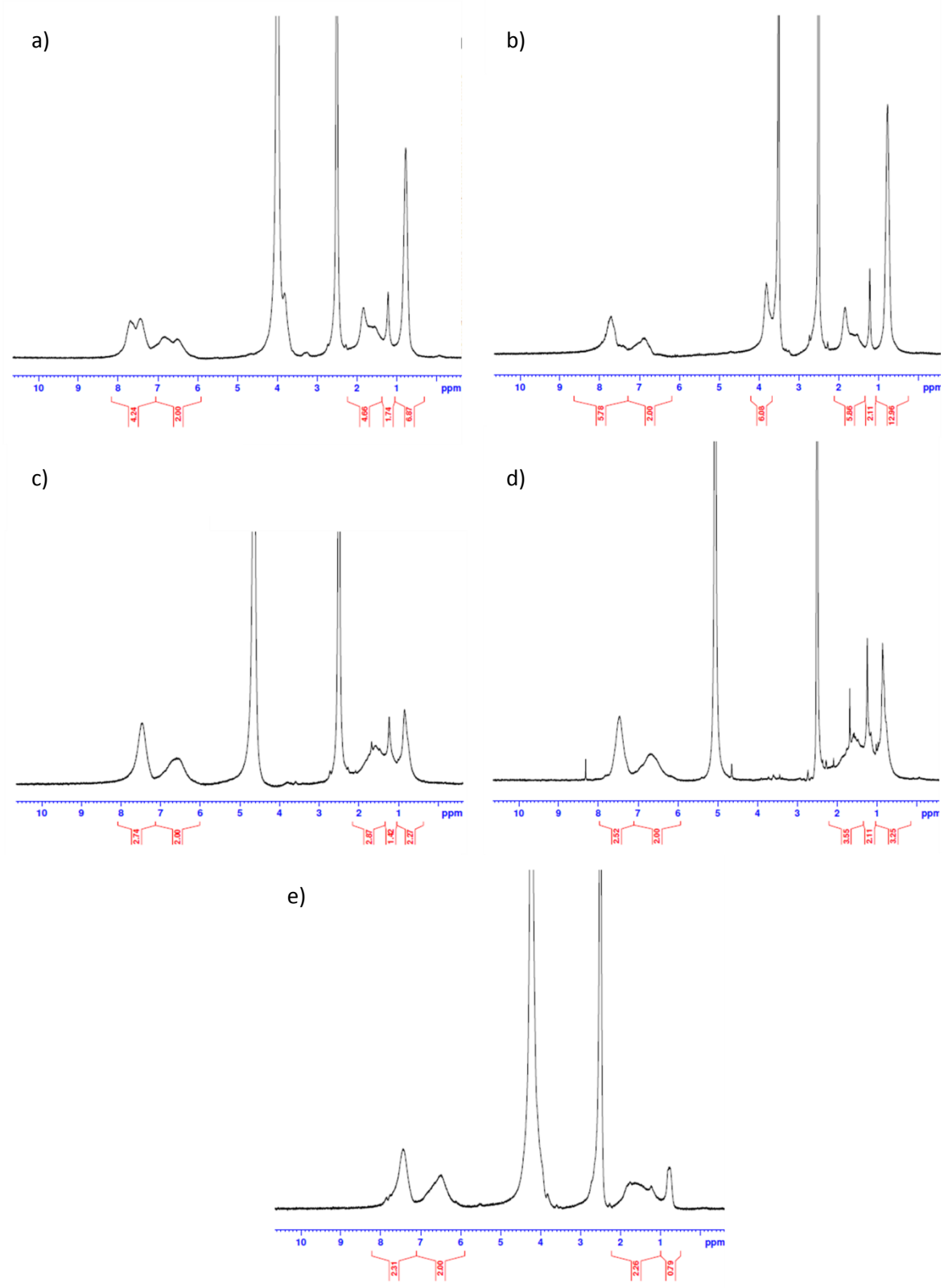

Figure S19. ^{1}H NMR spectra obtained for (a) PSS doped PiBSS containing 41.1 % added PSS, (b) PSS doped PiBSS containing 11.9 % added PSS PSS, (c) thermally treated (2 h at 150 °C) PSS doped PiBSS containing 41.1 % added PSS, (d) thermally treated (2 h at 150 °C) PSS doped PiBSS containing 11.9 % added PSS, (e) commercial PSS (M_w = 75000 g mol^{-1}) in d_6-DMSO.

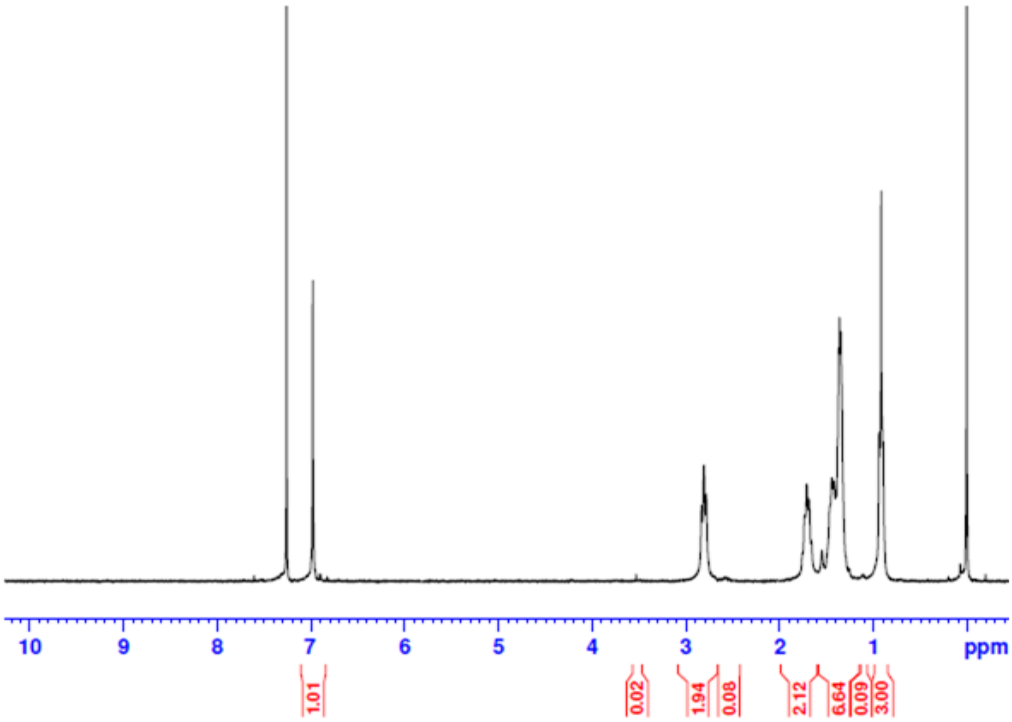

Figure S20. ^{1}H NMR spectrum for P3HT-ethynyl in $CDCl_3$.

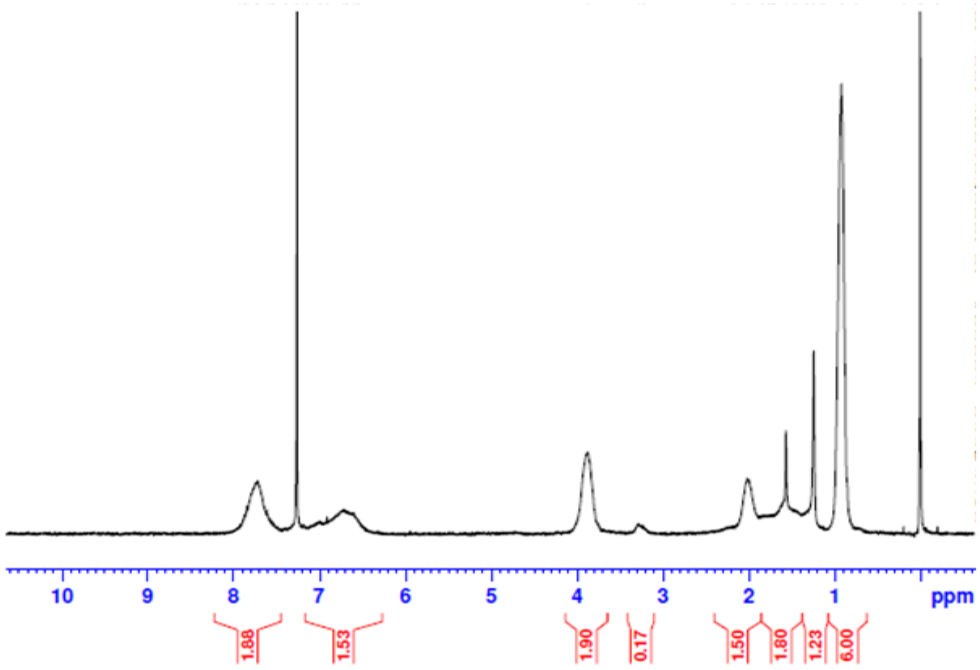

Figure S21. ^{1}H NMR spectrum for PiBSS-N_3 in $CDCl_3$.

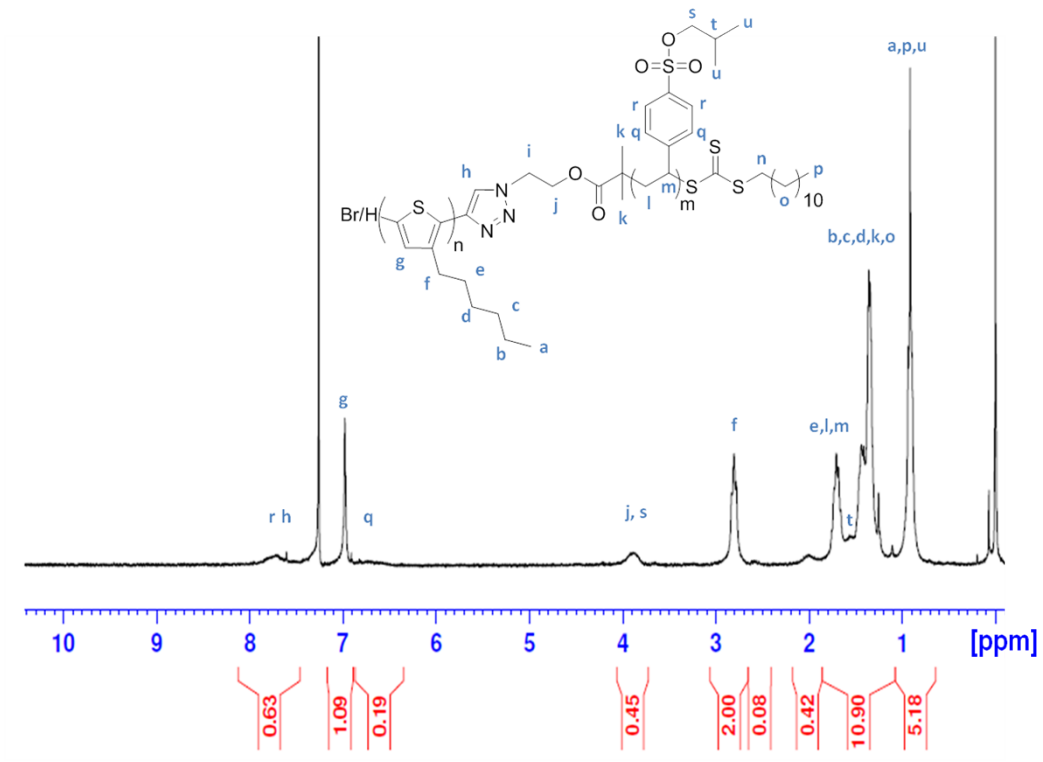

Figure S22. ^{1}H NMR spectrum and assignment for PiBSS-*b*-P3HT in $CDCl_3$.