

Supplementary Information

Rapid One-Pot Synthesis of Tapered Star Copolymers via Ultra-Fast Coupling of Polystyryllithium Chain Ends

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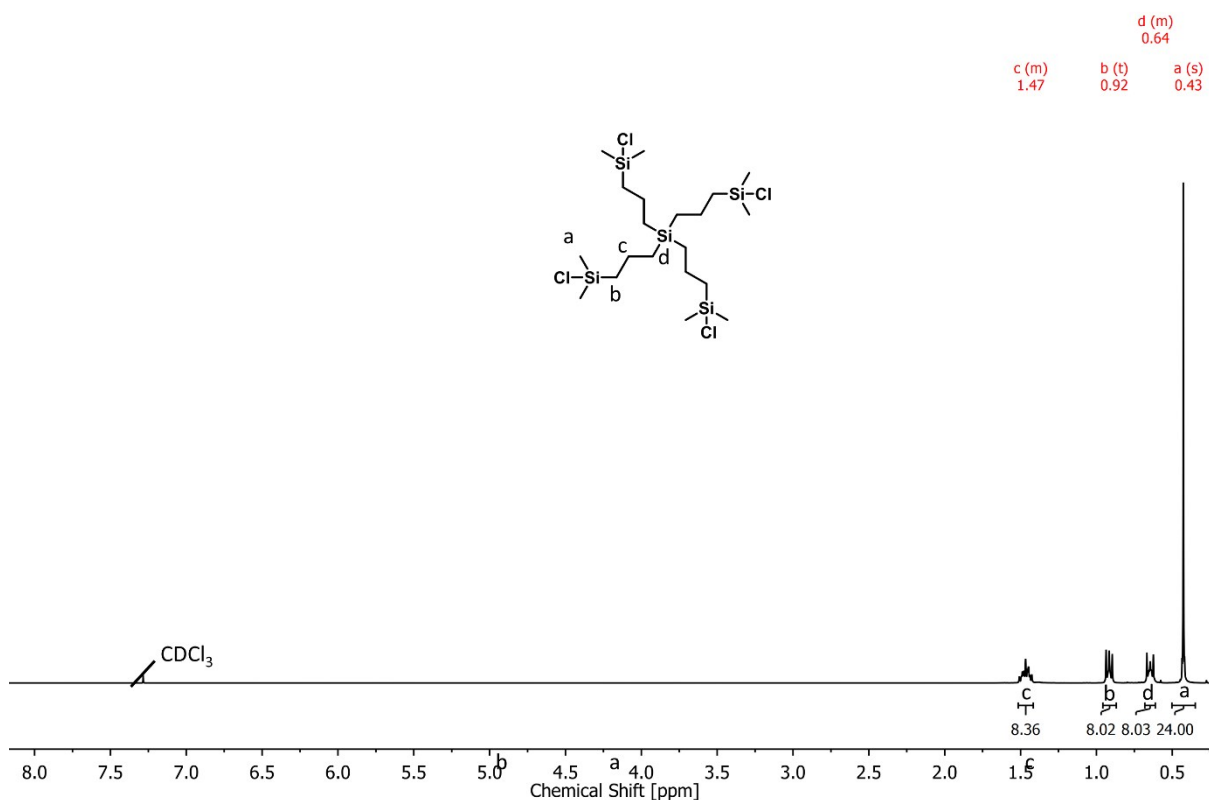


Figure S1: ¹H NMR spectrum of tetra[3-(chloro dimethylsilyl)propyl]silane (400 MHz, CDCl₃).

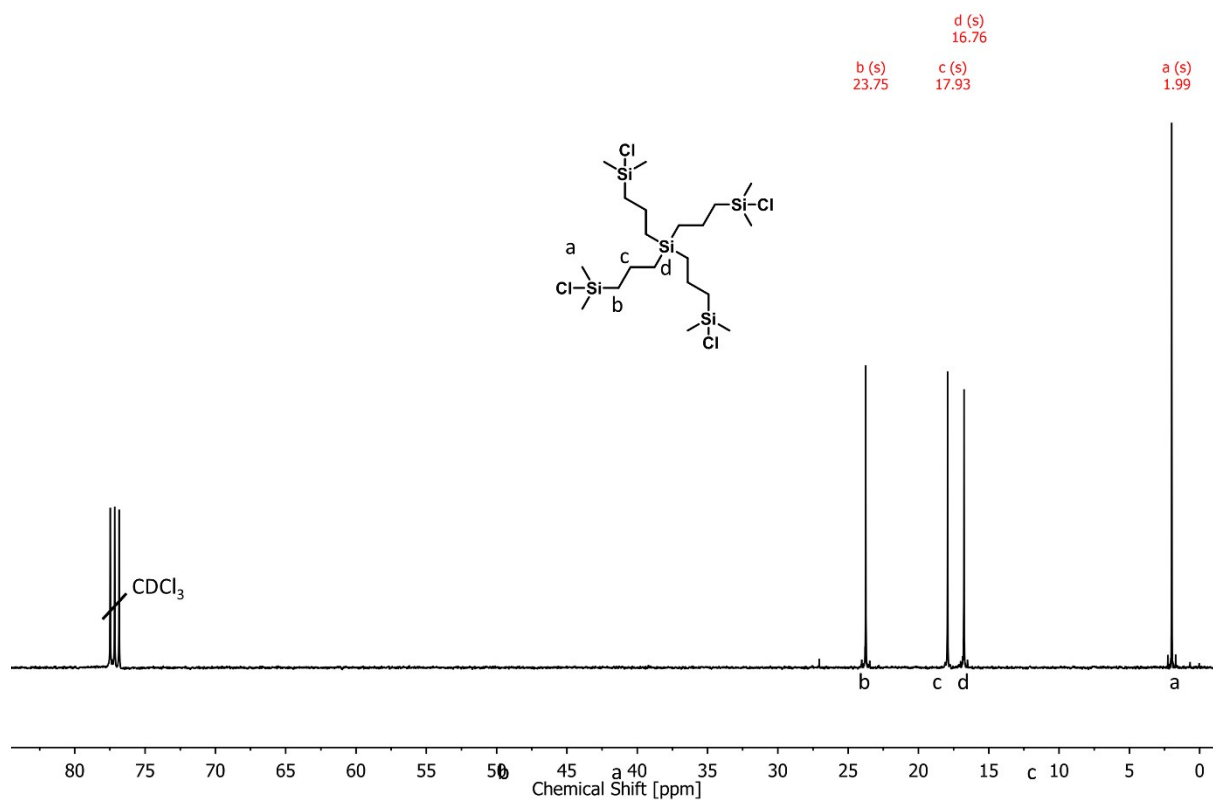


Figure S2: ¹³C NMR spectrum of tetra[3-(chloro dimethylsilyl)propyl]silane (400 MHz, CDCl₃).

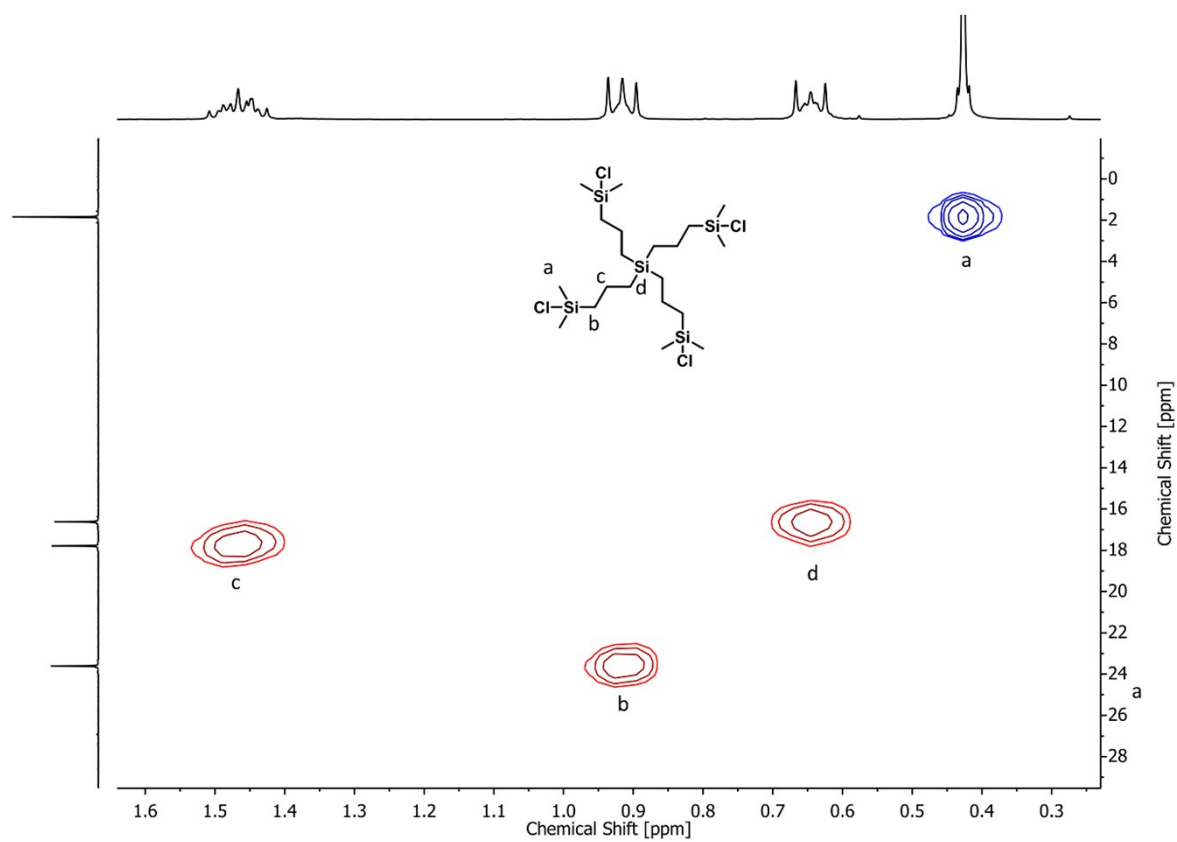


Figure S3: HSQC spectrum of tetra[3-(chloro dimethylsilyl)propyl]silane (400 MHz, CDCl₃).

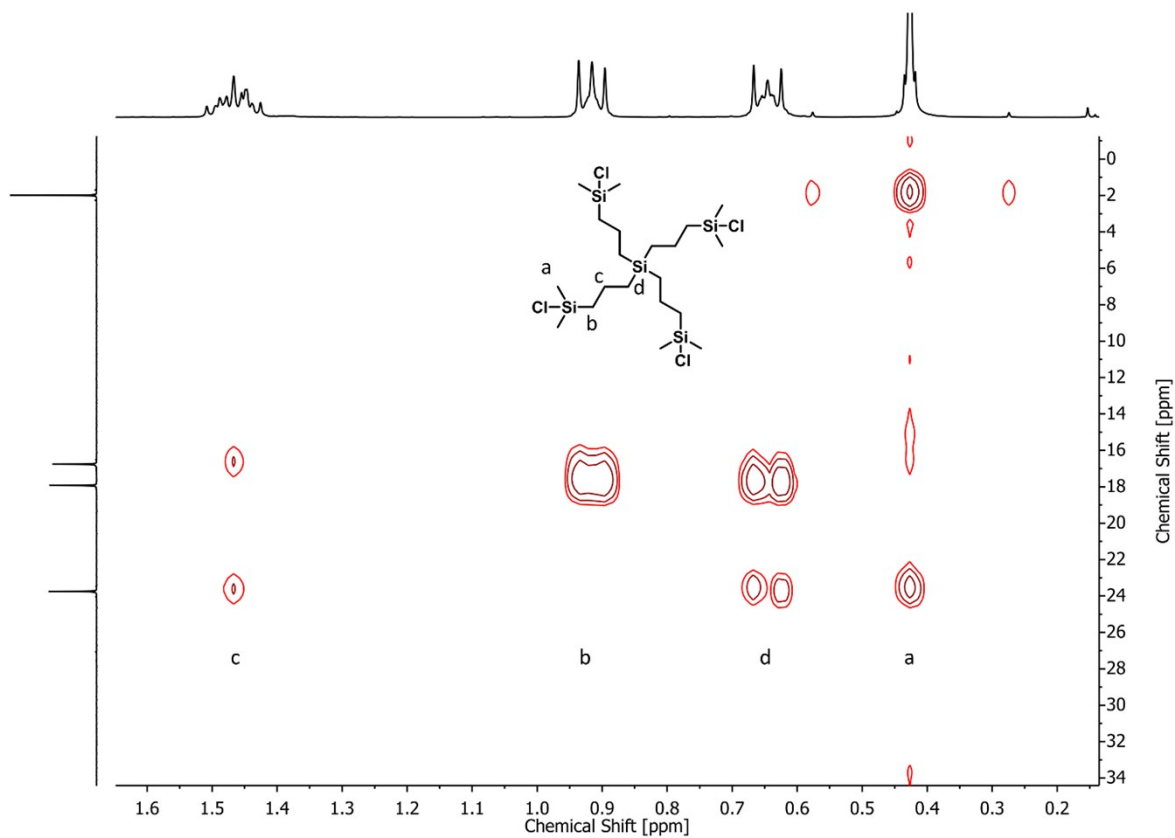


Figure S4: HMBC spectrum of tetra[3-(chloro dimethylsilyl)propyl]silane (400 MHz, $CDCl_3$).

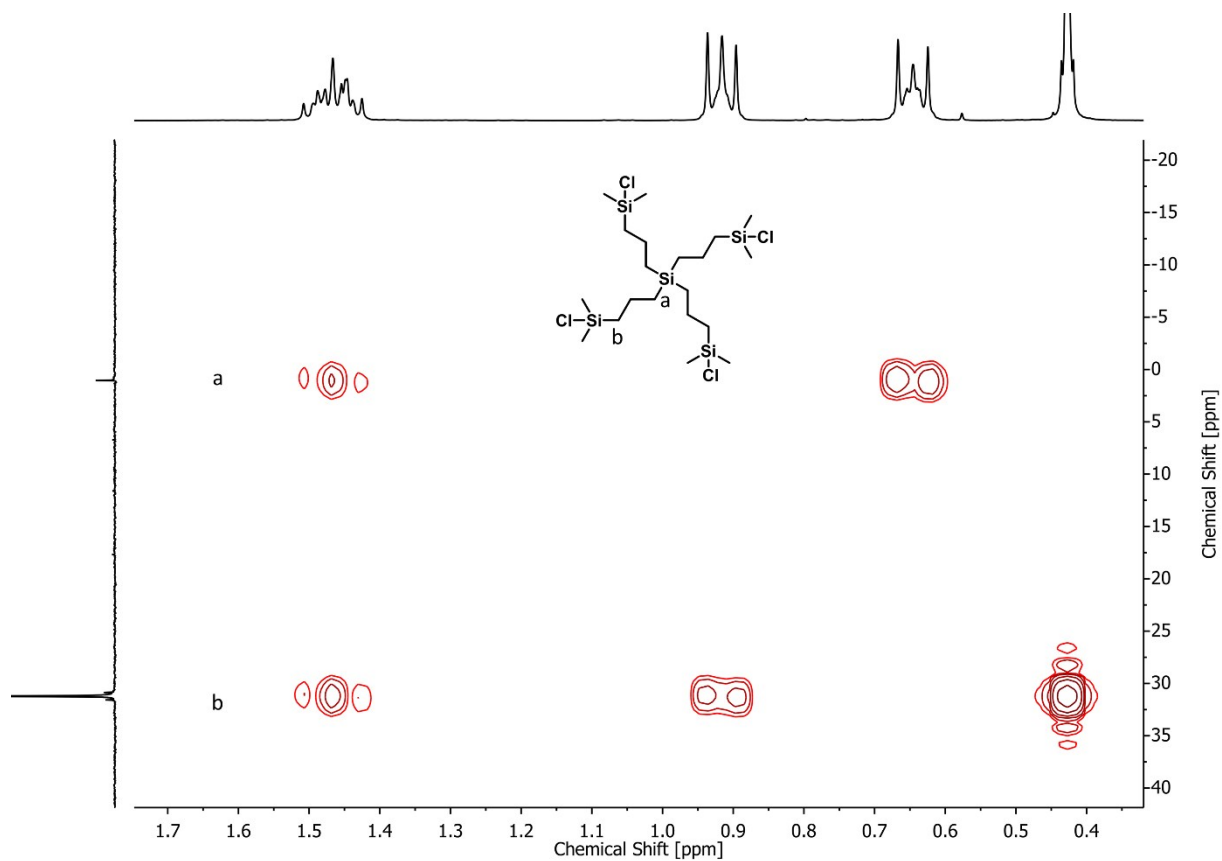


Figure S5: ^{29}Si HMBC/DEPT spectrum of tetra[3-(chloro dimethylsilyl)propyl]silane (400 MHz, $CDCl_3$).

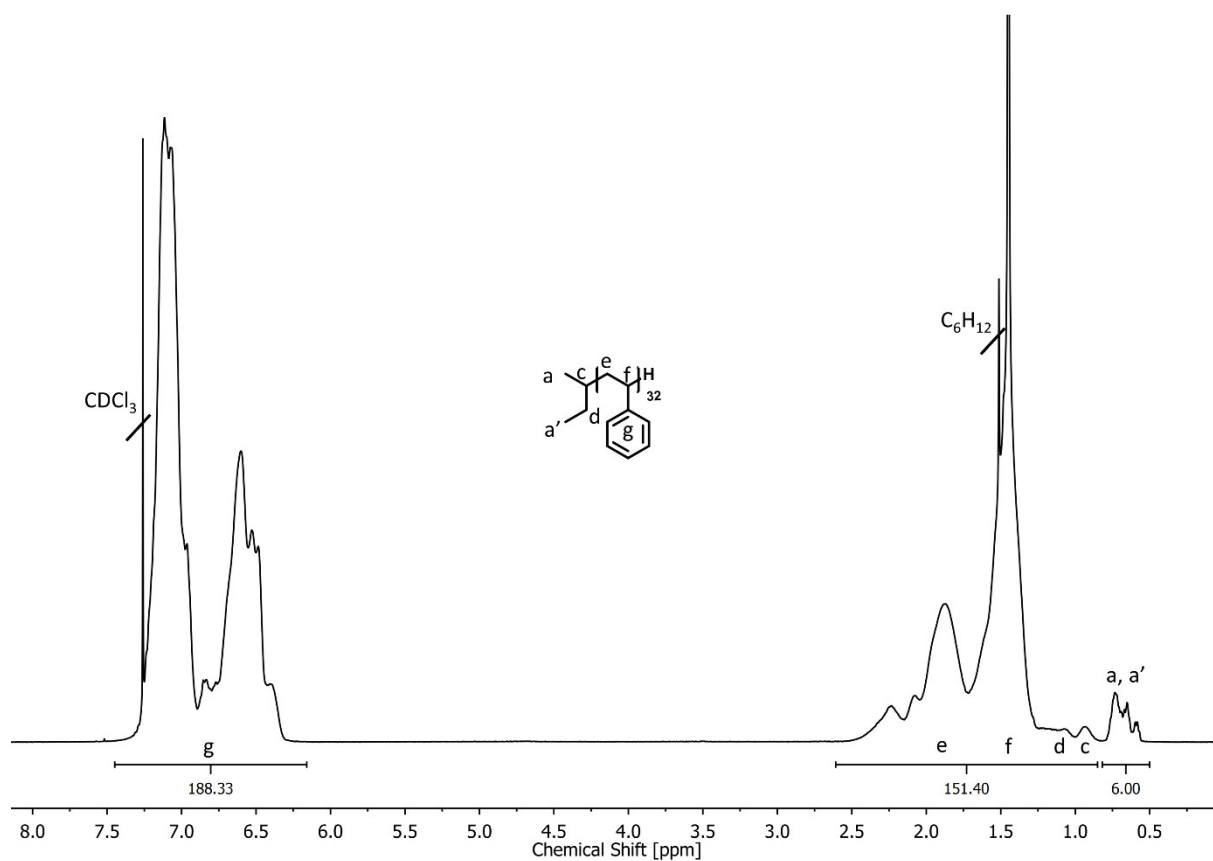


Figure S6: ^1H NMR spectrum of polystyrene star precursor (400 MHz, CDCl_3).

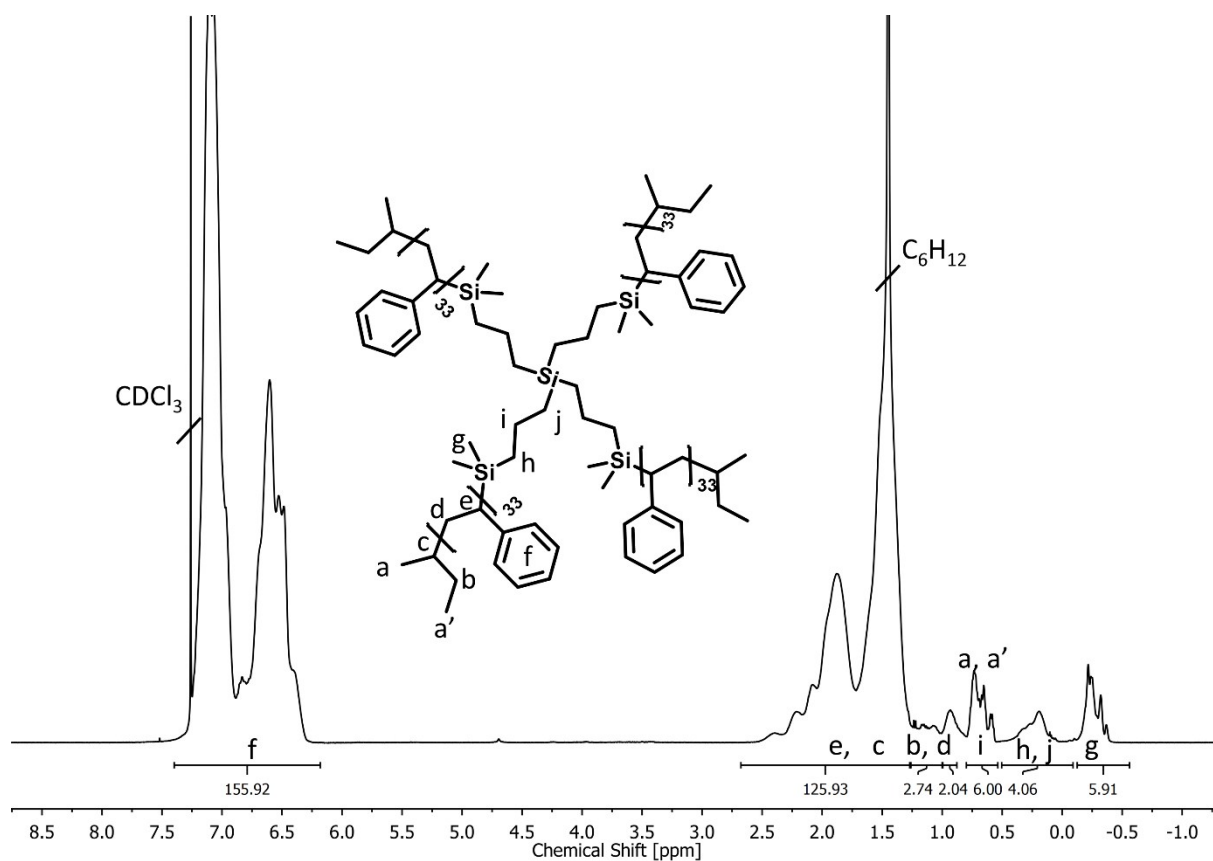


Figure S7. ^1H NMR spectrum of PS 4-arm star polymer targeted 12 kg mol^{-1} (400 MHz, CDCl_3).

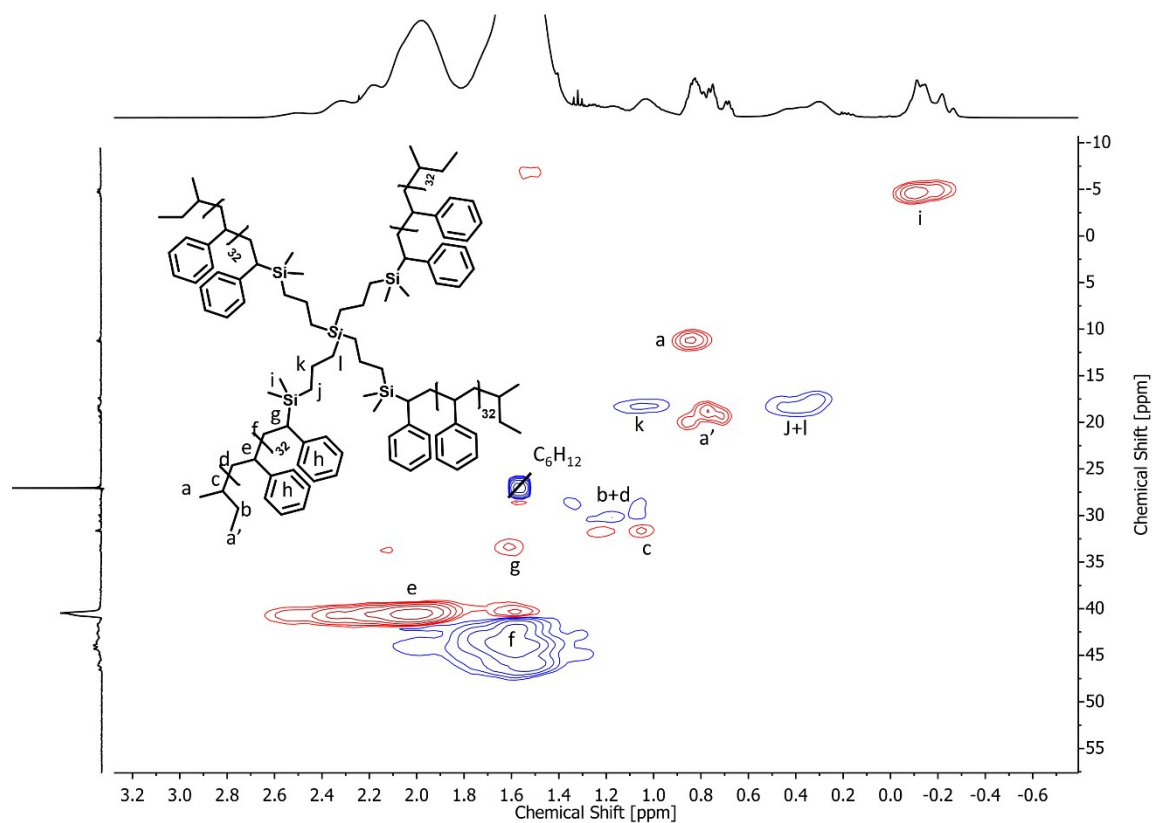


Figure S8: HSQC spectrum of polystyrene 4-arm star (relevant area) 400 MHz, $CDCl_3$).

Table S1 Synthesis results of PS linear and 4-arm star polymers coupled with TCDMSPS

Sample	$M_w^{targeted}$ / kg mol ⁻¹	M_w^a / kg mol ⁻¹	f^b	D^c
1	3	3.7 ± 0.3	-	1.04
2	12	12.4 ± 0.2	3.30 ± 0.1	1.15

^a Determined by SEC (averaged triple inject) viscometry in THF (UV signal) and UC, ^b star functionality calculated by $f = M_{w,star} / M_{w,arm}$, ^c determined by SEC in THF (UV signal).

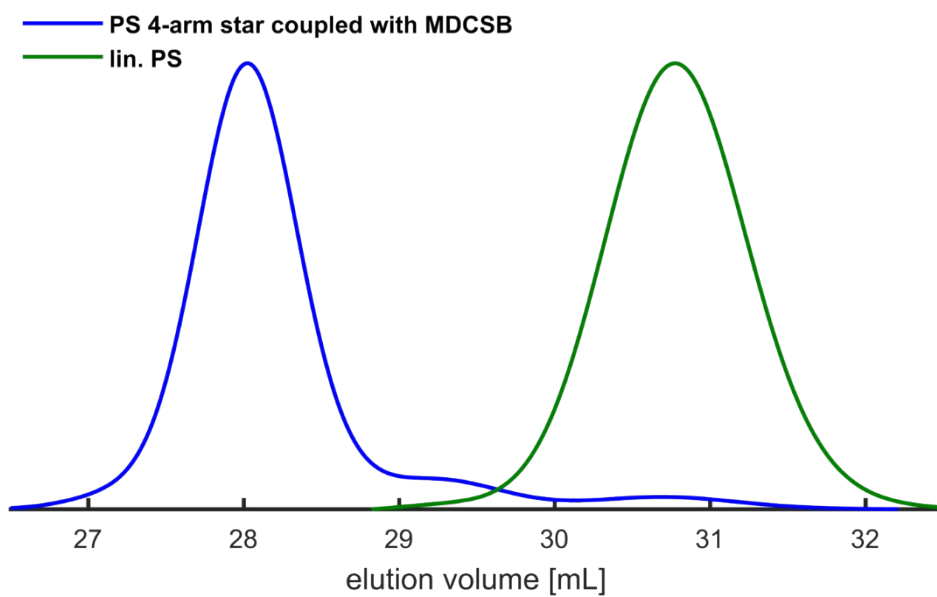


Figure S9: SEC traces (THF, UV signal); blue line PS 4-arm star targeted 12 kg mol^{-1} coupled with MDCSB, green line PS precursor, targeted 3 kg mol^{-1}

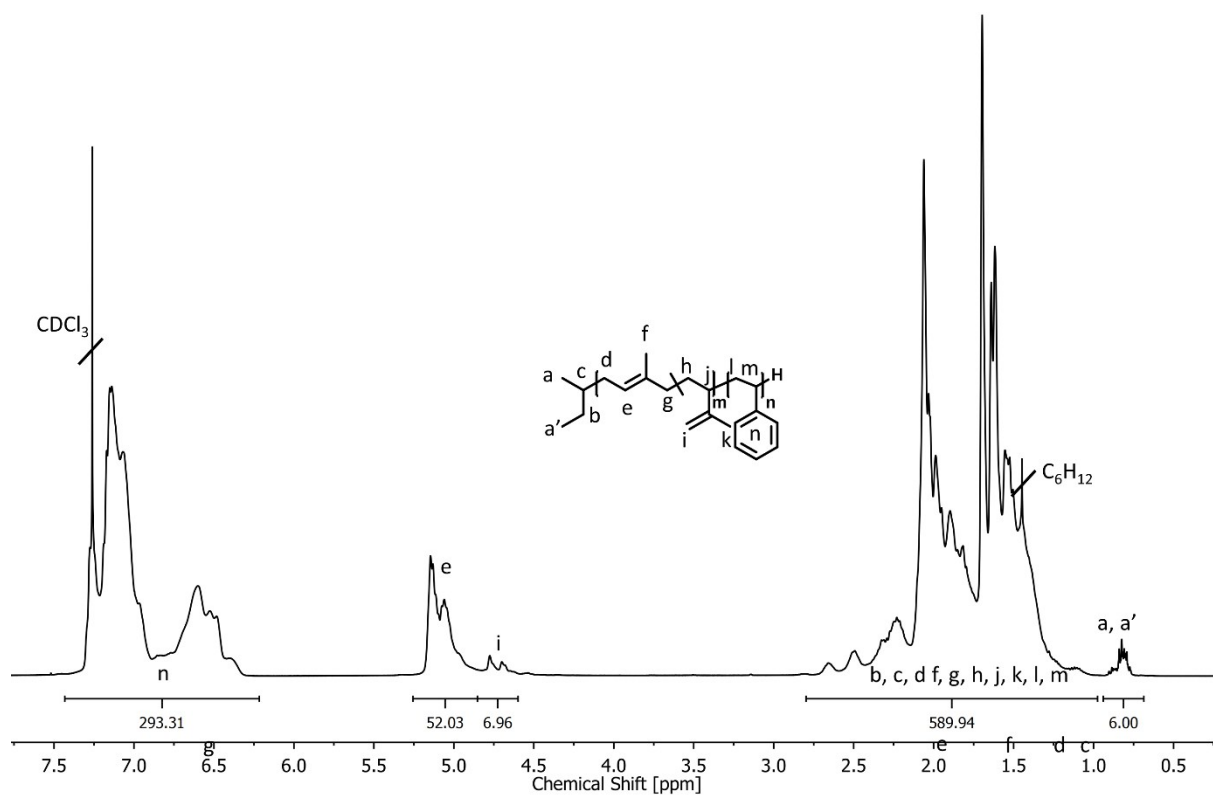


Figure S10: ^1H NMR spectrum of $\text{P}(\text{I}_{0.5}\text{-grad-S}_{0.5})$ star precursor (400 MHz, CDCl_3).

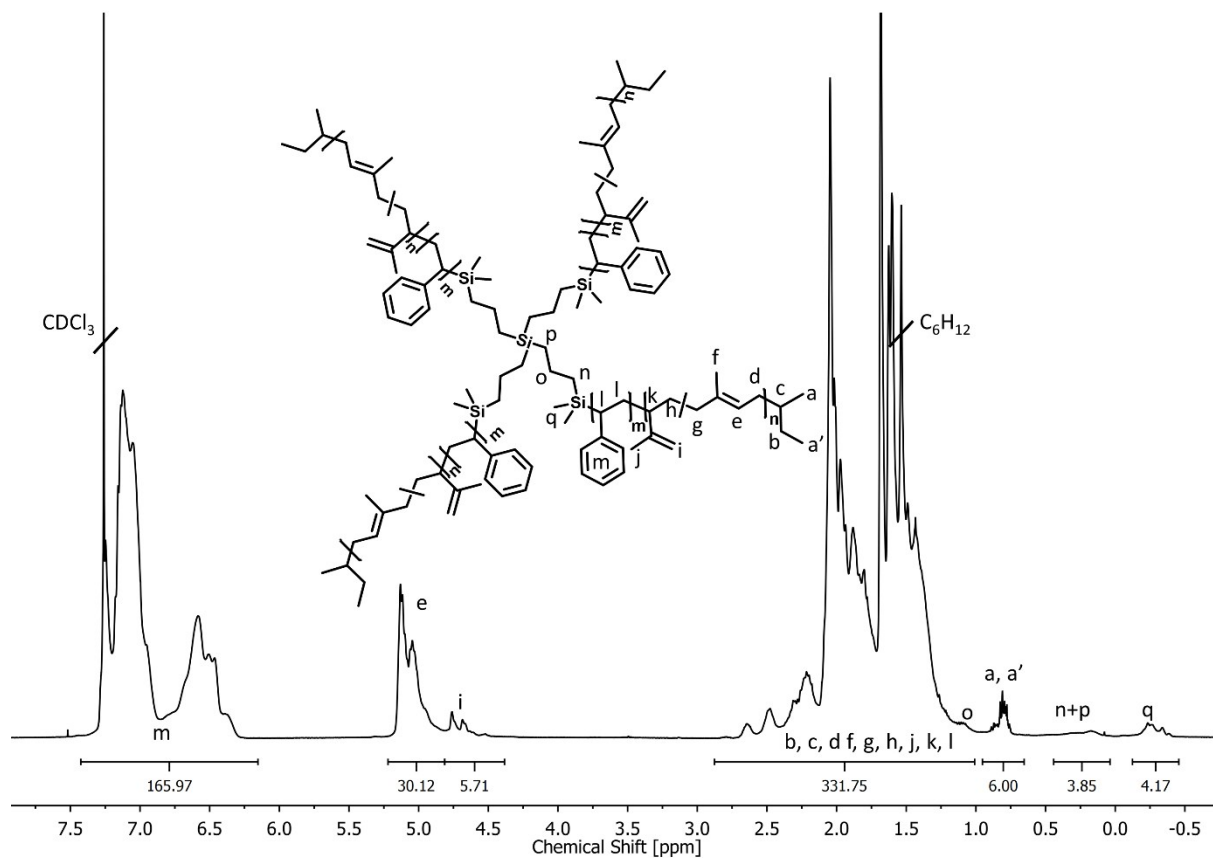


Figure S11: ^1H NMR spectrum of $\text{P}(\text{I}_{0.5}\text{-grad-S}_{0.5})$ 4-arm star tapered copolymer (400 MHz, CDCl_3).

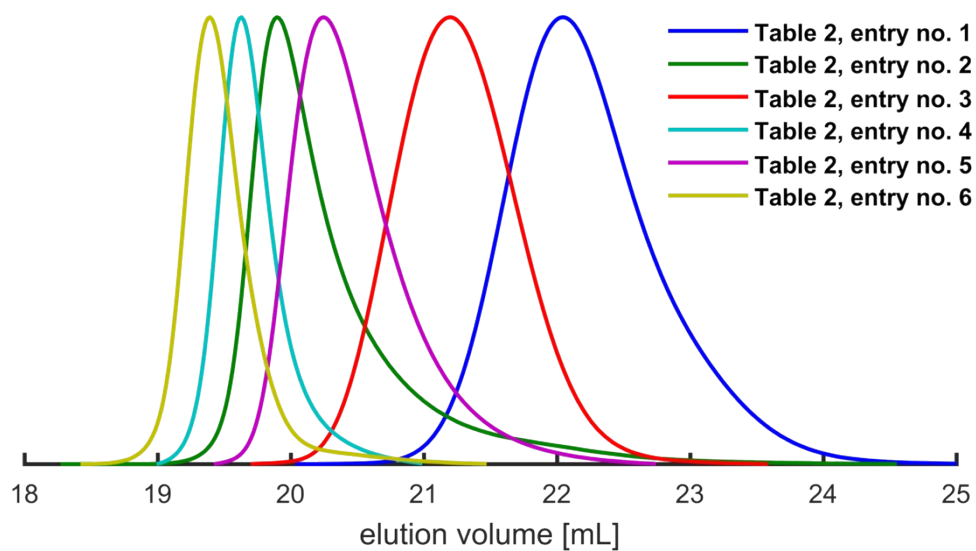


Figure S12. Elution traces from SEC (THF, UV signals) of $\text{P}(\text{I}_{0.5}\text{-grad-S}_{0.5})$ 4 arm star tapered copolymers targeted 40 - 120 kg mol^{-1} (left) and $\text{P}(\text{I}_{0.5}\text{-grad-S}_{0.5})$ linear precursors targeted 10 - 30 kg mol^{-1} (right).

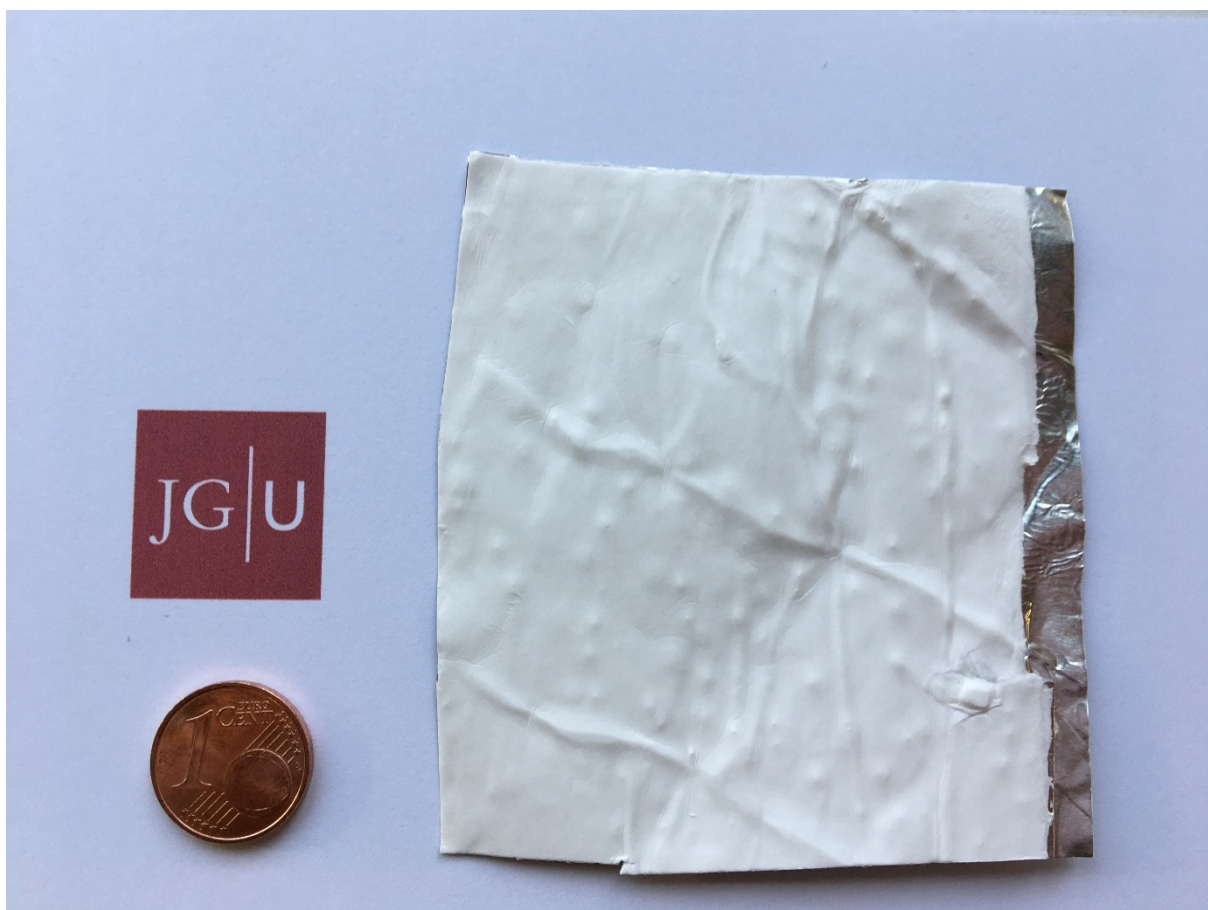


Figure S13. Electrospun P(I_{0.5-grad}-S_{0.5}) 4 arm star tapered copolymer nanofibers, sample 6, $M_w = 118.8 \pm 2.0 \text{ kg mol}^{-1}$)