

*Electronic Supplementary Information*

**Metal-free polycyclotrimerization of trimethylsilyl-protected diynes:  
a facile strategy toward regioregular hyperbranched polyarylenes**

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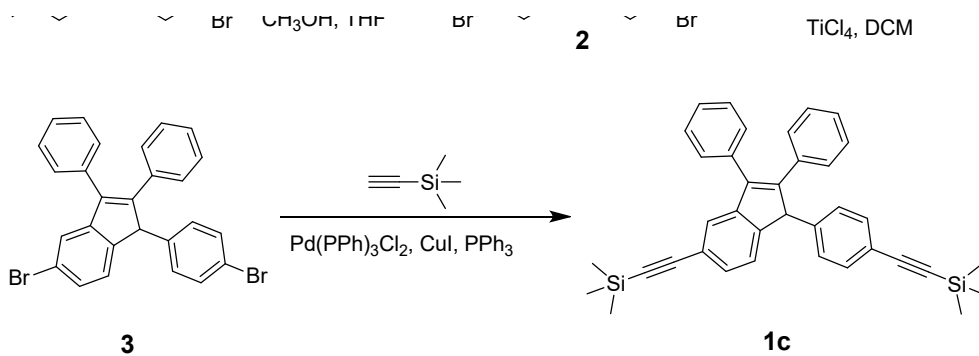
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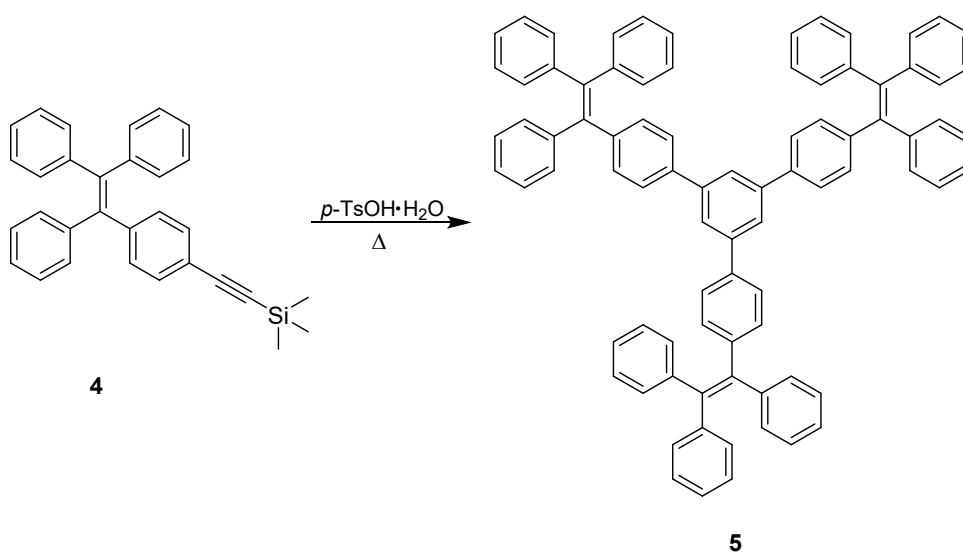
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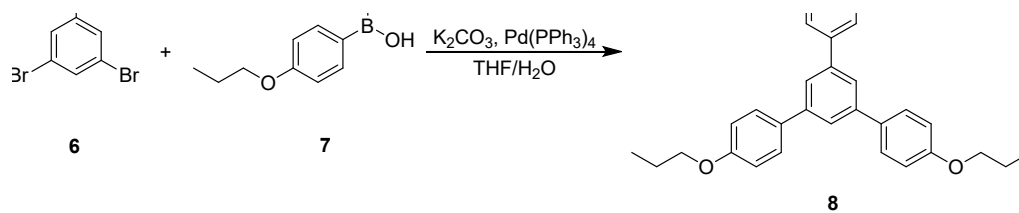
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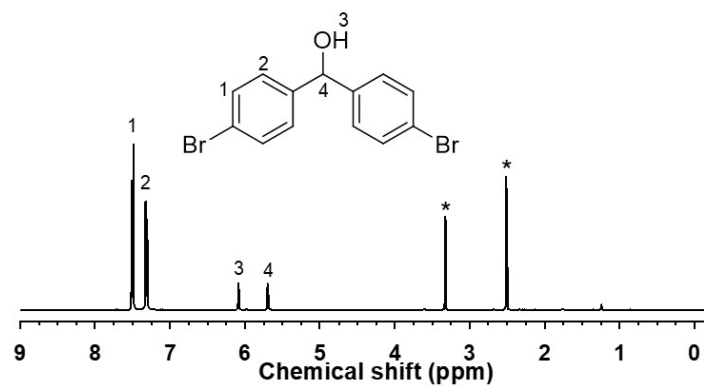
**Scheme S1** Synthetic route to monomer **1c**



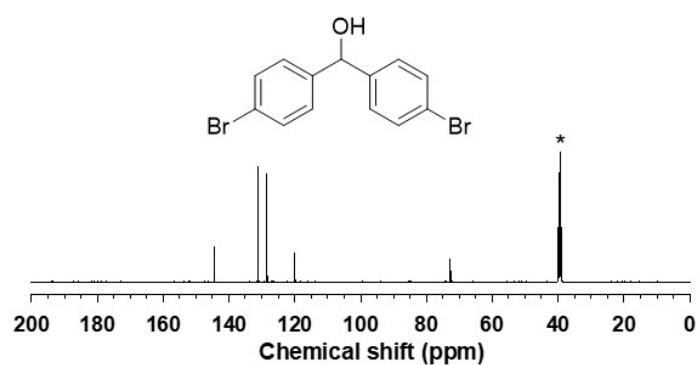
**Scheme S2** Synthetic route to model compound **5**



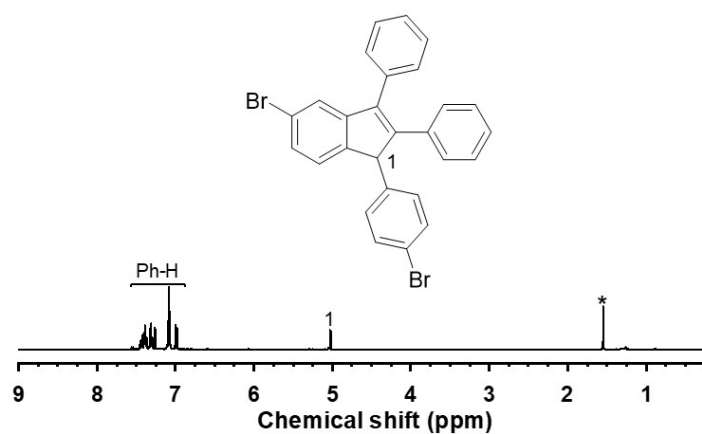
**Scheme S3** Synthetic route to model compound **8**



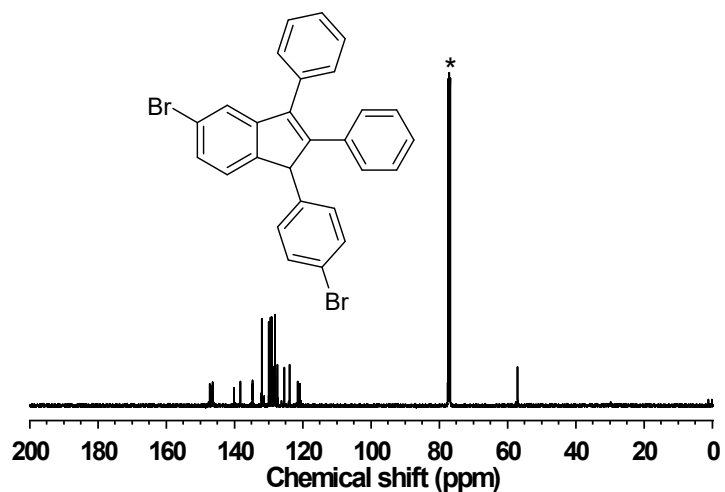
**Fig. S1**  $^1\text{H}$  NMR spectra of intermediate compound **2** in  $\text{DMSO-}d_6$  without TMS. The solvent and water peaks are marked with asterisks.



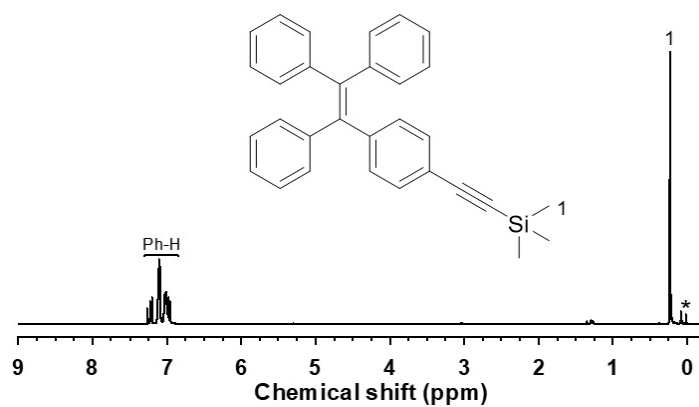
**Fig. S2**  $^{13}\text{C}$  NMR spectra of intermediate compound **2** in  $\text{DMSO-}d_6$  without TMS. The solvent peaks are marked with asterisks.



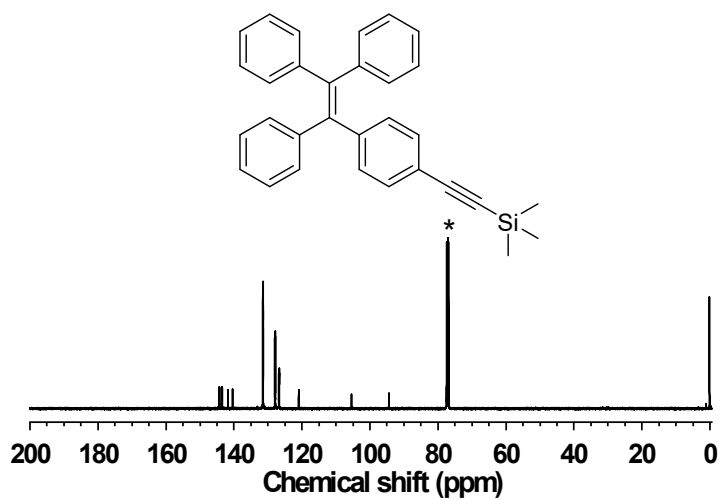
**Fig. S3**  $^1\text{H}$  NMR spectra of intermediate compound **3** in  $\text{CDCl}_3$ . The solvent and water peaks are marked with asterisks.



**Fig. S4**  $^{13}\text{C}$  NMR spectra of intermediate compound **3** in  $\text{CDCl}_3$ . The solvent peaks are marked with asterisks.



**Fig. S5**  $^1\text{H}$  NMR spectra of compound **4** in  $\text{CDCl}_3$ . The solvent and water peaks are marked with asterisks.



**Fig. S6**  $^{13}\text{C}$  NMR spectra of compound **4** in  $\text{CDCl}_3$ . The solvent peaks are marked with asterisks.

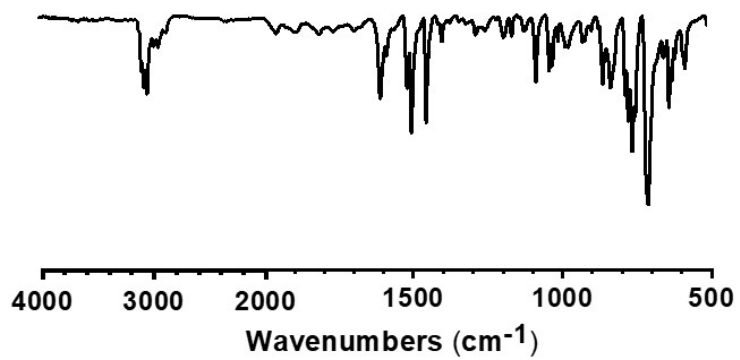


Fig. S7 IR spectra of model compound 5.

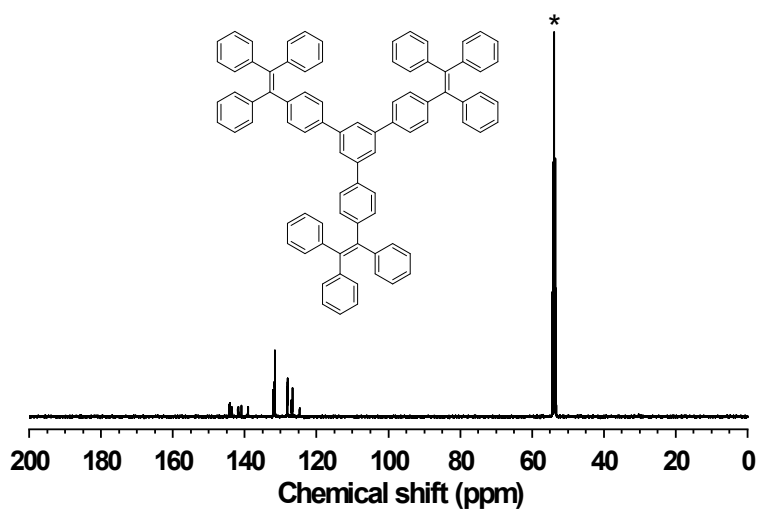


Fig. S8 <sup>13</sup>C NMR spectra of model compound 5 in CD<sub>2</sub>Cl<sub>2</sub> without TMS. The solvent peaks are marked with asterisks.

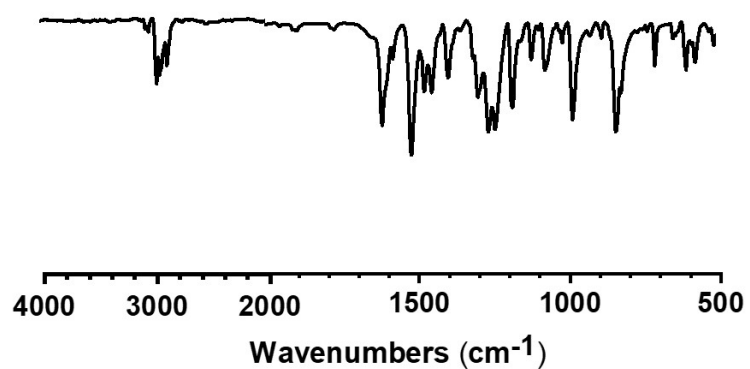


Fig. S9 IR spectra of model compound 8.

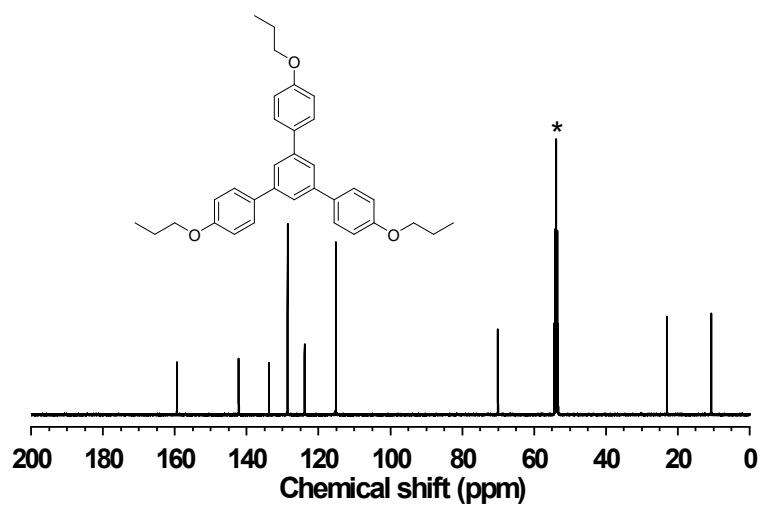


Fig. S10 <sup>13</sup>C NMR spectra of model compound 8 in CD<sub>2</sub>Cl<sub>2</sub> without TMS. The solvent peaks are marked with asterisks.

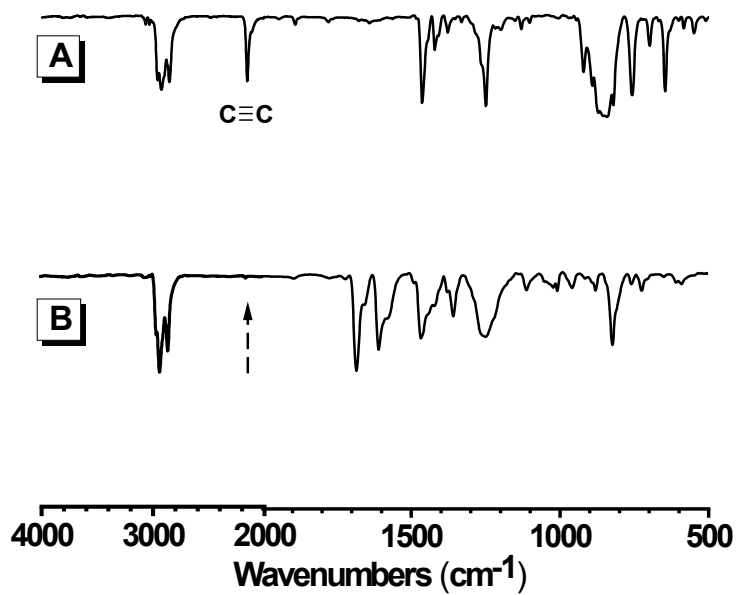


Fig. S11 IR spectra of monomer **1b** (A) and its polymer *hb*-P**1b** (B).

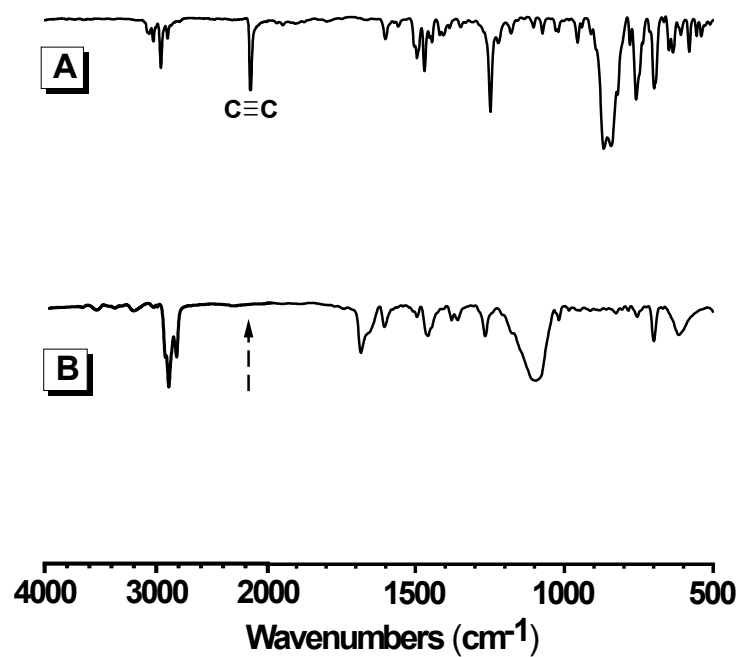


Fig. S12 IR spectra of monomer **1c** (A) and its polymer *hb*-P**1c** (B).



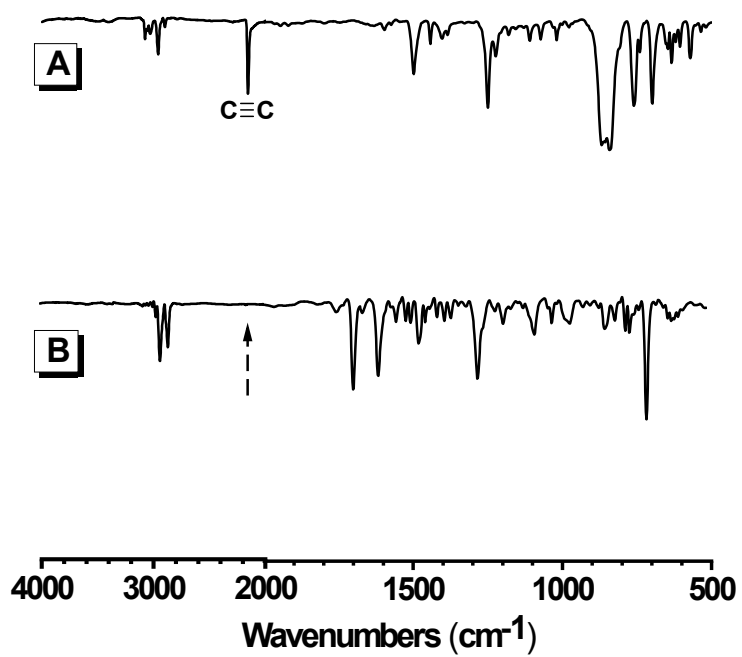


Fig. S13 IR spectra of monomer **1d** (A) and its polymer *hb*-P**1d** (B).

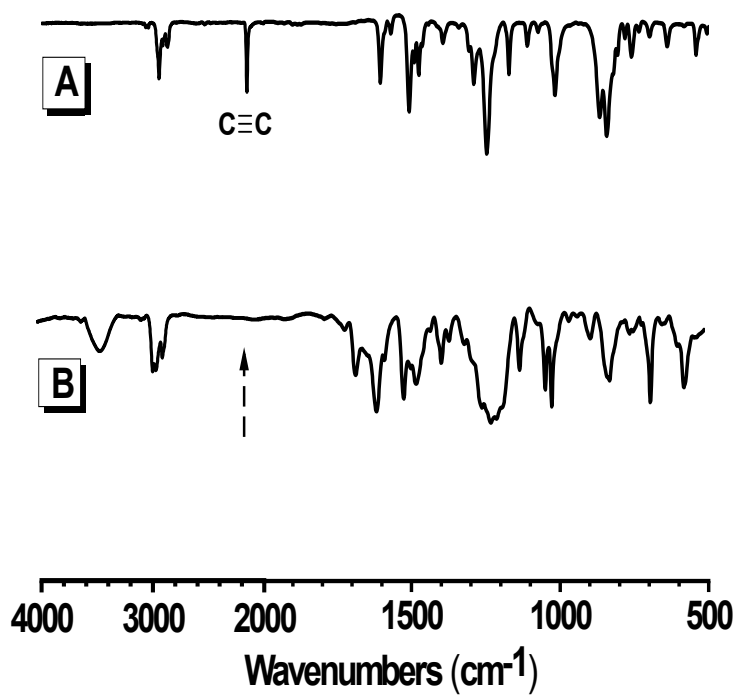
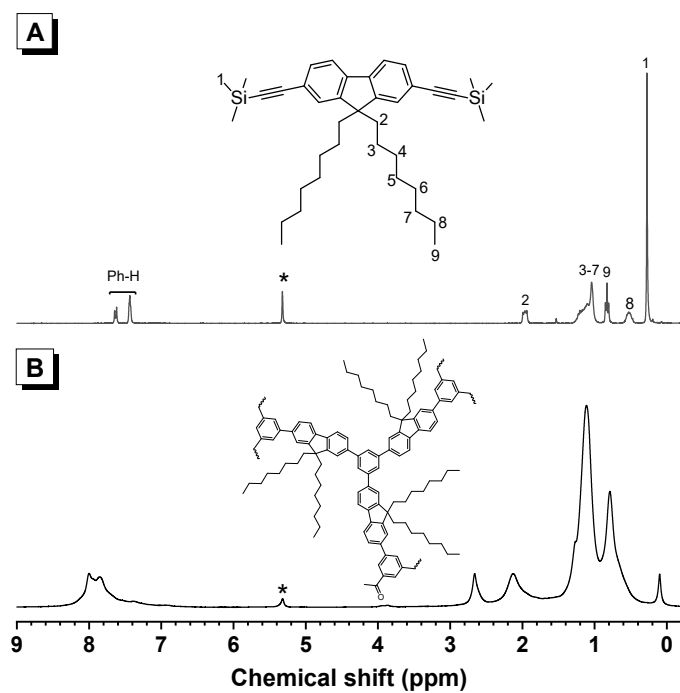
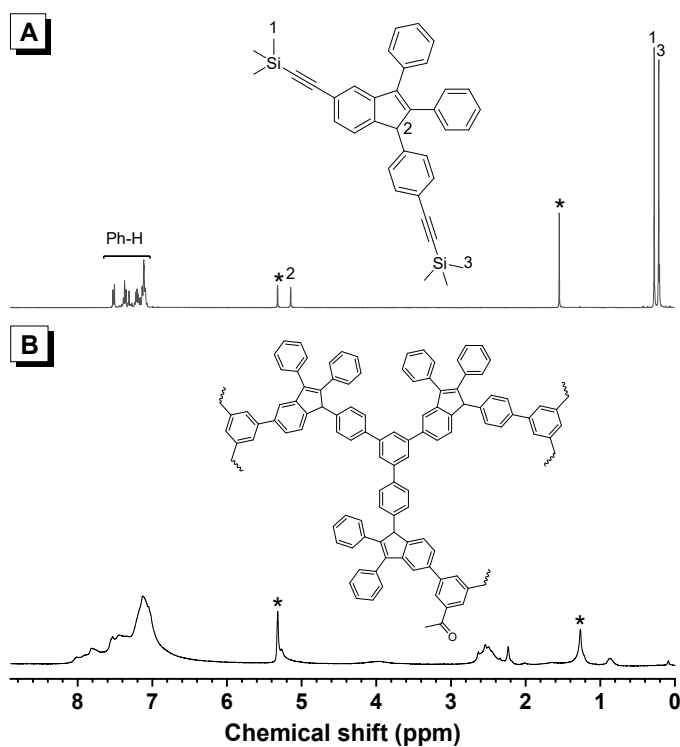


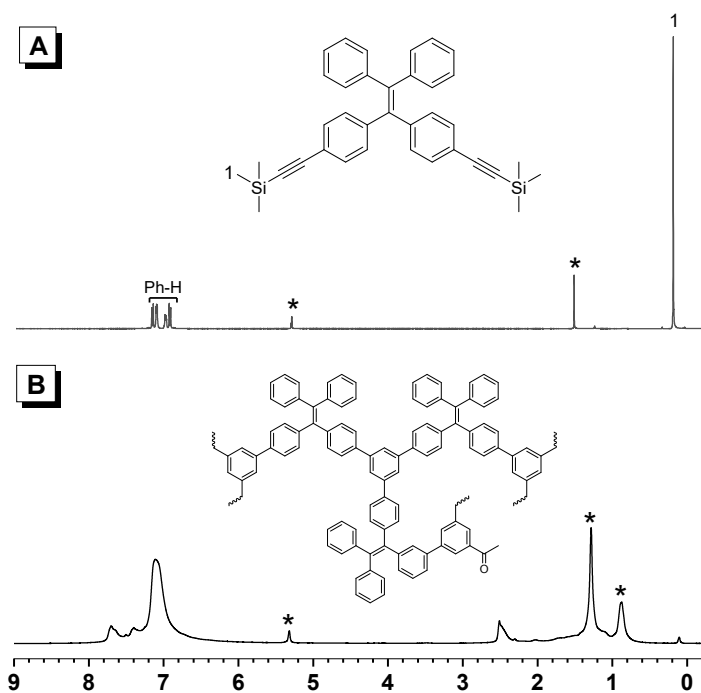
Fig. S14 IR spectra of monomer **1e** (A) and its polymer *hb*-P**1e** (B).



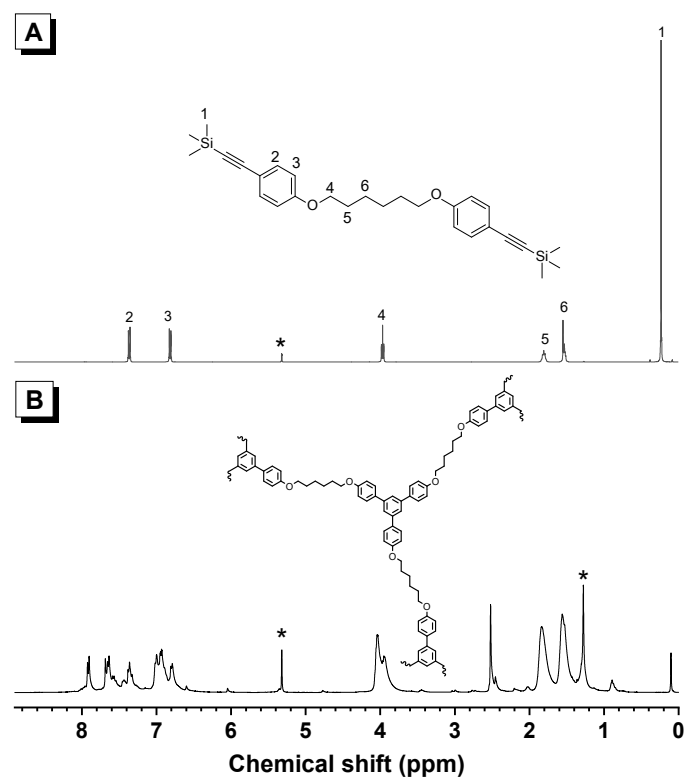
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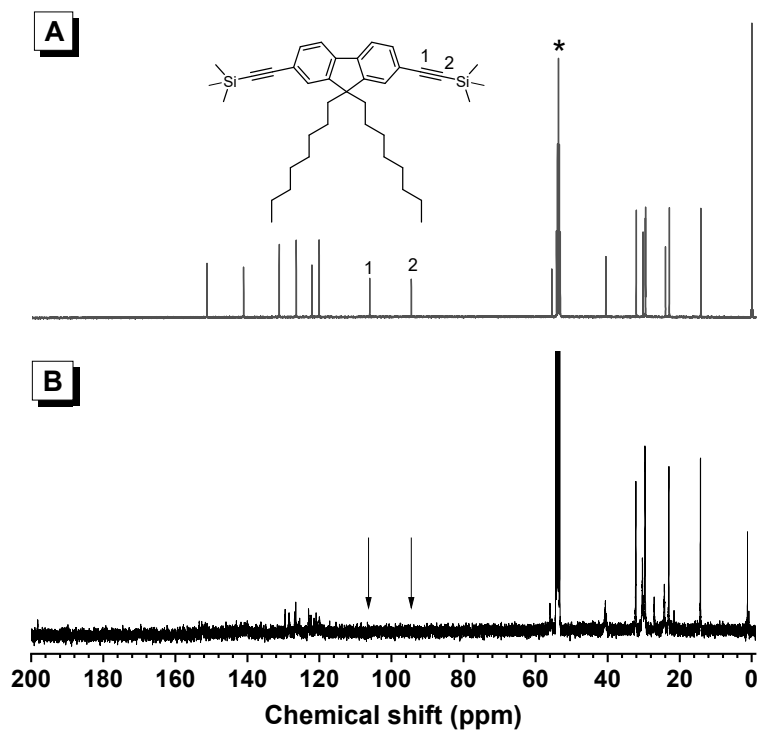
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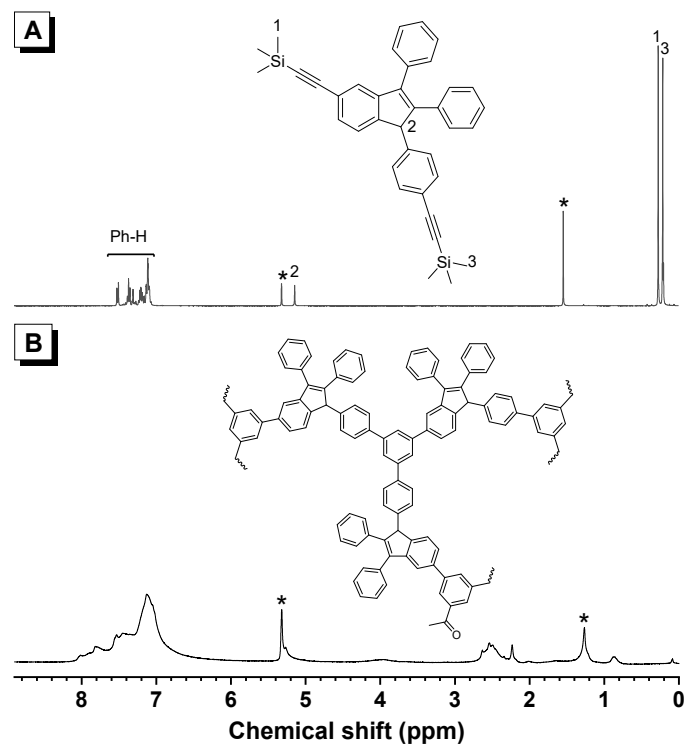
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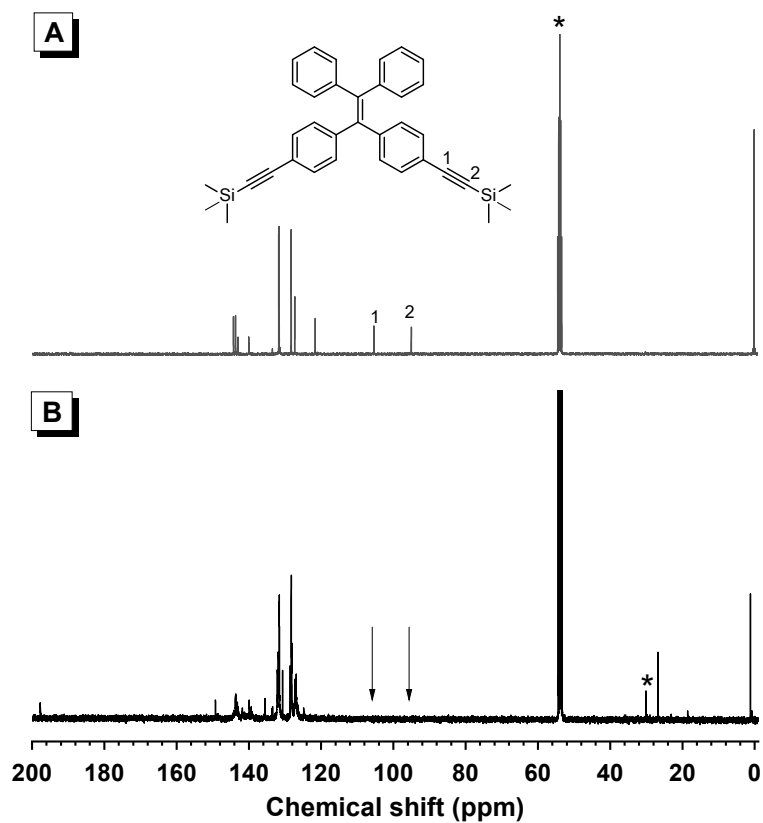
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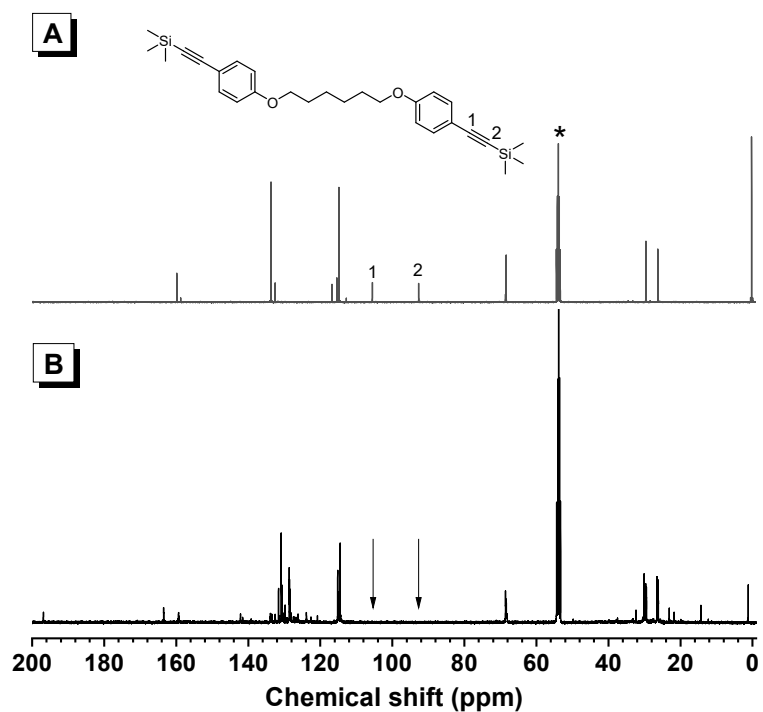
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