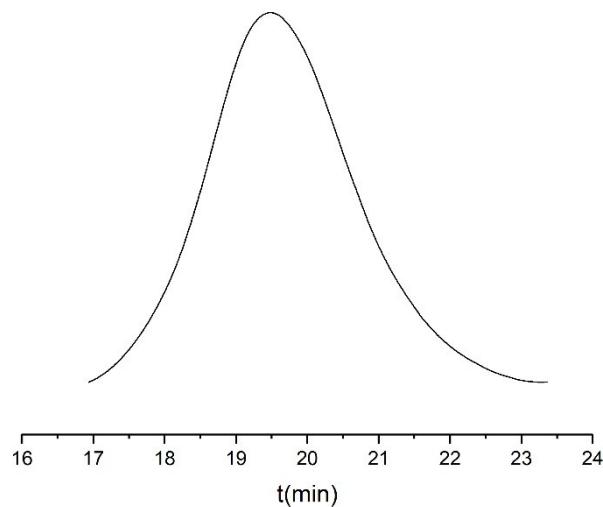


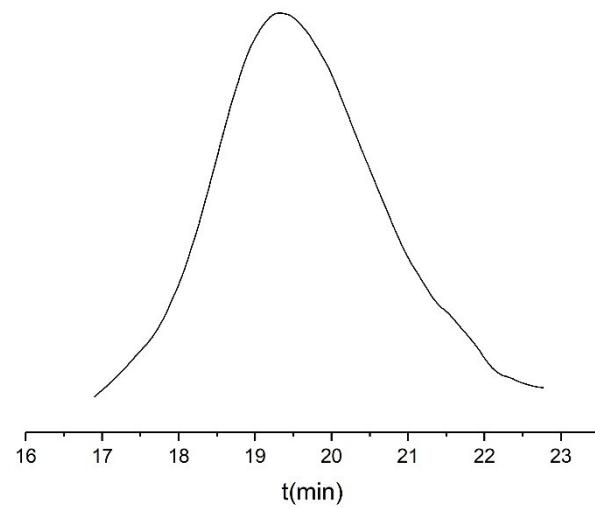
Supporting information

**Highly Syndioselective Coordination (co)Polymerization of Isopropenylstyrene**

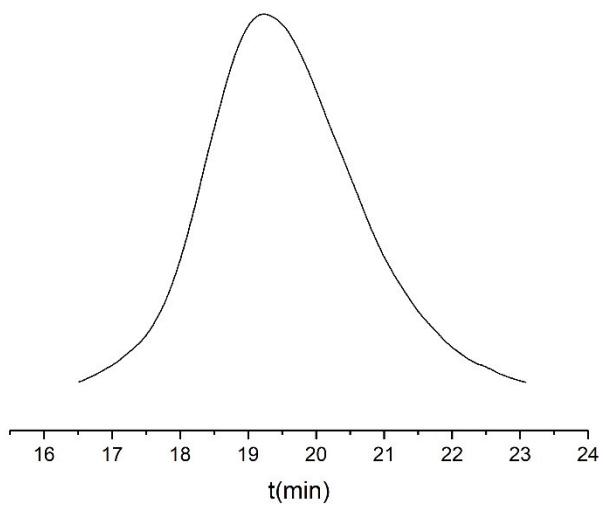
Zhen Zhang<sup>ab</sup>, Yanli Dou<sup>b</sup>, Shihui Li<sup>\*a</sup> and Dongmei Cui<sup>\*a</sup>



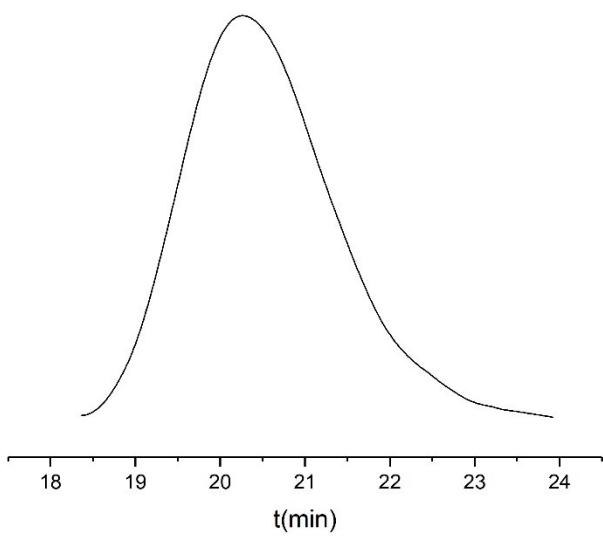
**Fig. S1** GPC trace of poly(pIPSt) (Entry 1, Table 2)



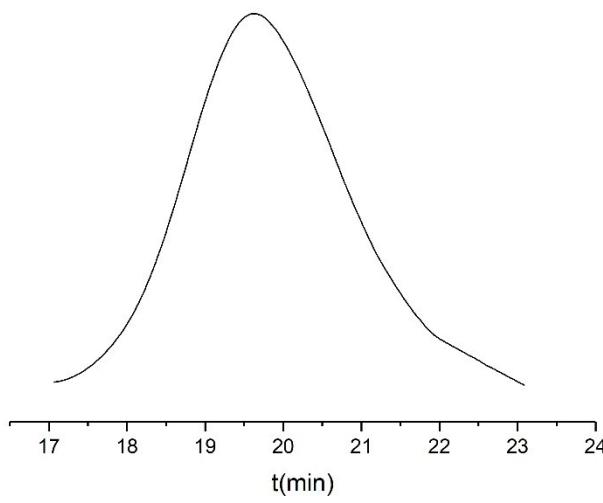
**Fig. S2** GPC trace of poly(pIPSt) (Entry 2, Table 2)



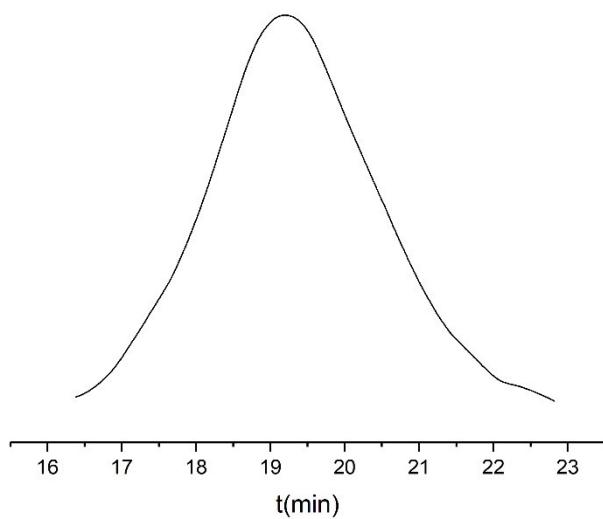
**Fig. S3** GPC trace of poly(pIPSt) (Entry 3, Table 2)



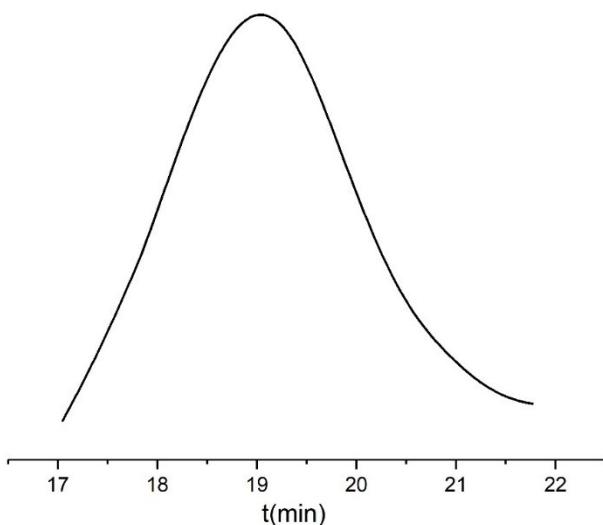
**Fig. S4** GPC trace of poly(pIPSt) (Entry 4, Table 2)



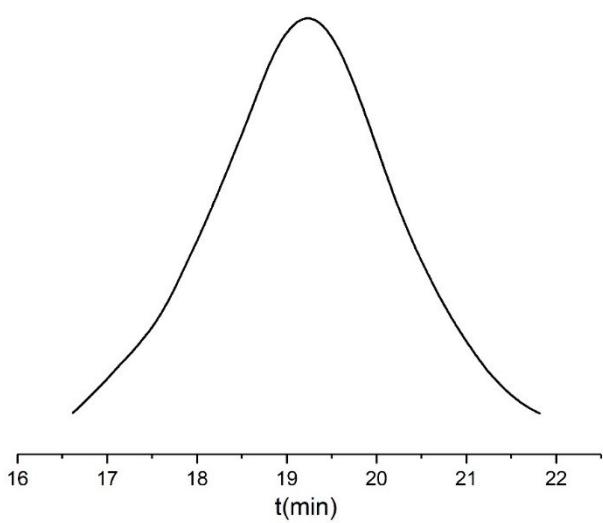
**Fig. S5** GPC trace of poly(pIPSt) (Entry 5, Table 2)



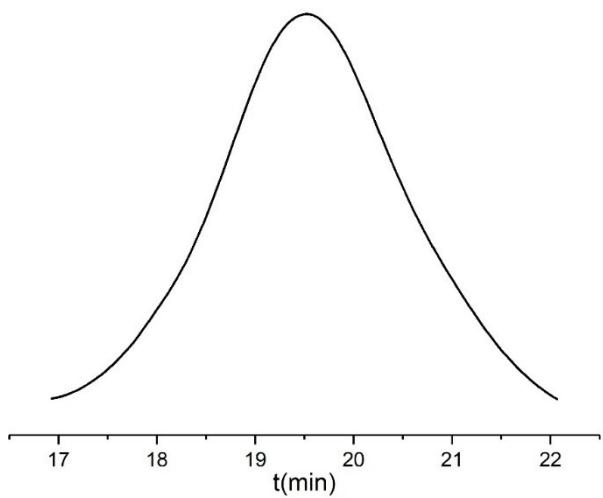
**Fig. S6** GPC trace of poly(pIPSt) (Entry 6, Table 2)



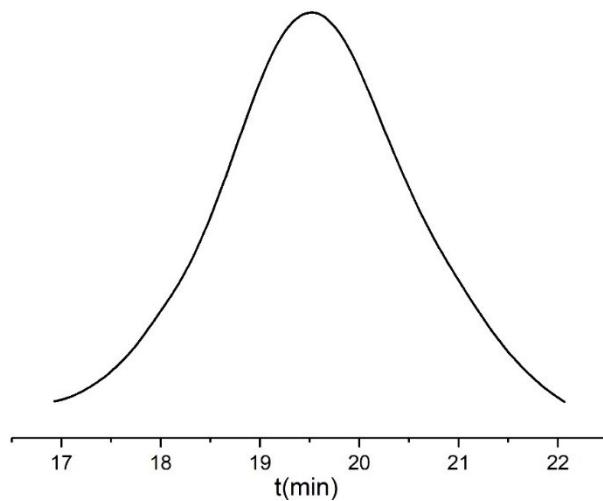
**Fig. S7** GPC trace of a pIPSt-St copolymer with 90% pIPSt units (Entry 1, Table 3)



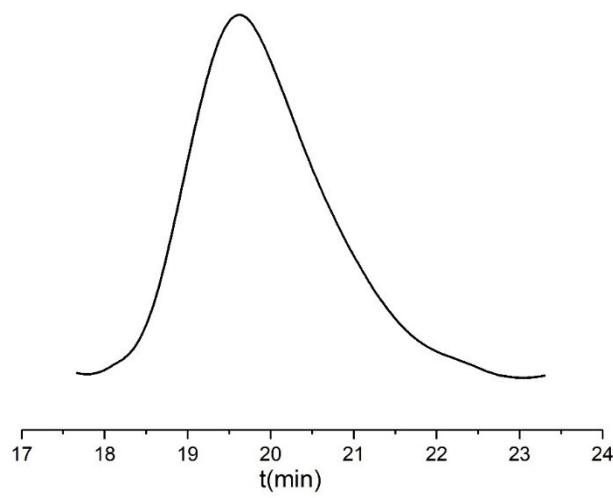
**Fig. S8** GPC trace of a pIPSt-St copolymer with 70% pIPSt units (Entry 2, Table 3)



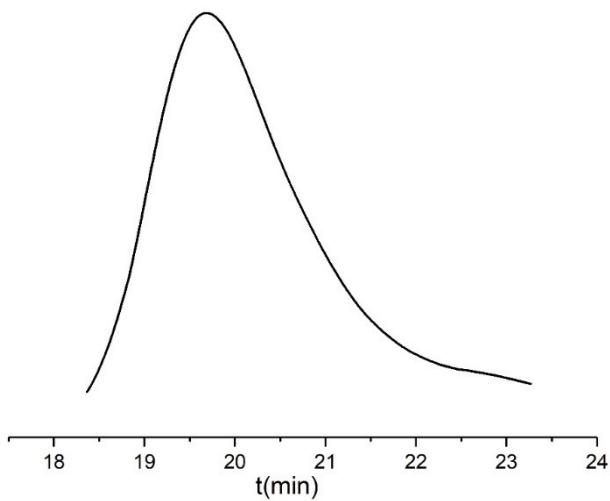
**Fig. S9** GPC trace of a pIPSt-St copolymer with 50% pIPSt units (Entry 3, Table 3)



**Fig. S10** GPC trace of a pIPSt-St copolymer with 30% pIPSt units (Entry 4, Table 3)



**Fig. S11** GPC trace of a pIPSt-St copolymer with 10% pIPSt units (Entry 5, Table 3)



**Fig. S12** GPC trace of a pIPSt-St copolymer with 5% pIPSt units (Entry 6, Table 3)

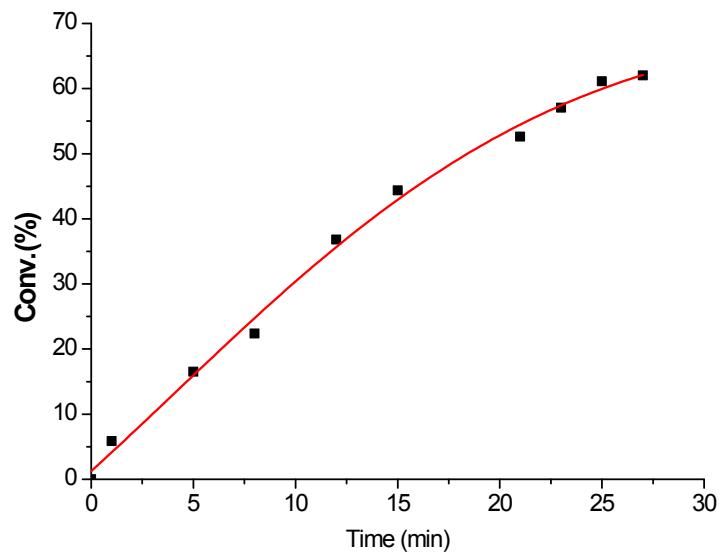


Fig. S13 Kinetic profiles of *p*IPSt polymerization catalyzed by complex 4 ( $[$ styrene]<sub>0</sub>:[Ln] = 500, 0.08mol/L in toluene, 25 °C)

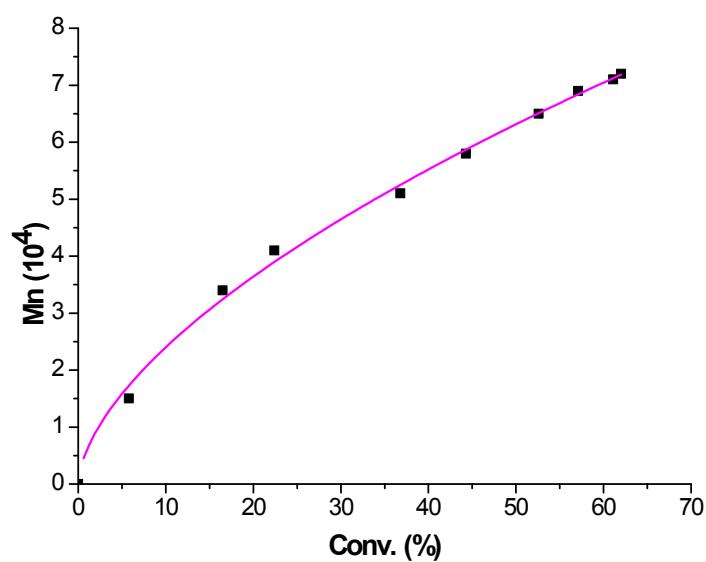


Fig. S14 Dependence of  $M_n$  vs. pIPSt conversion for 4 ( $[$ styrene]<sub>0</sub>:[Ln] = 500, 0.08 mol/L in toluene, 25 °C)

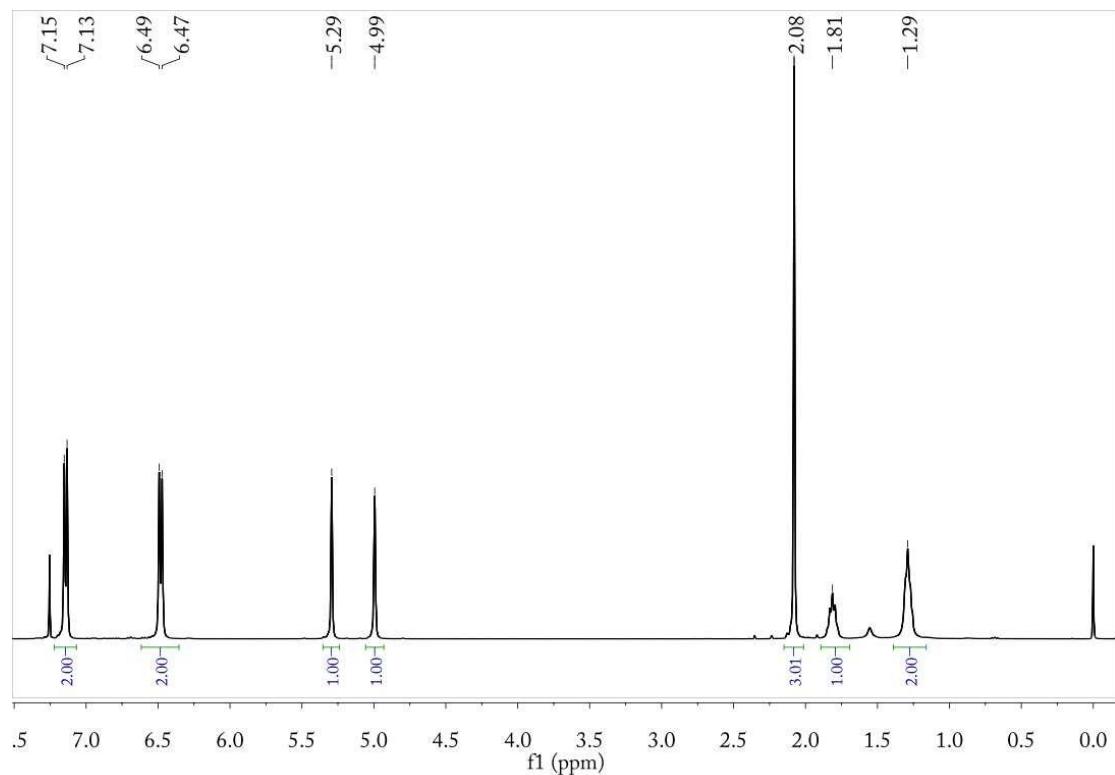


Fig. S15  $^1\text{H}$  NMR spectrum of poly(pIPSt) in  $\text{CDCl}_3$  at 25 °C (Table 1, entry 6)

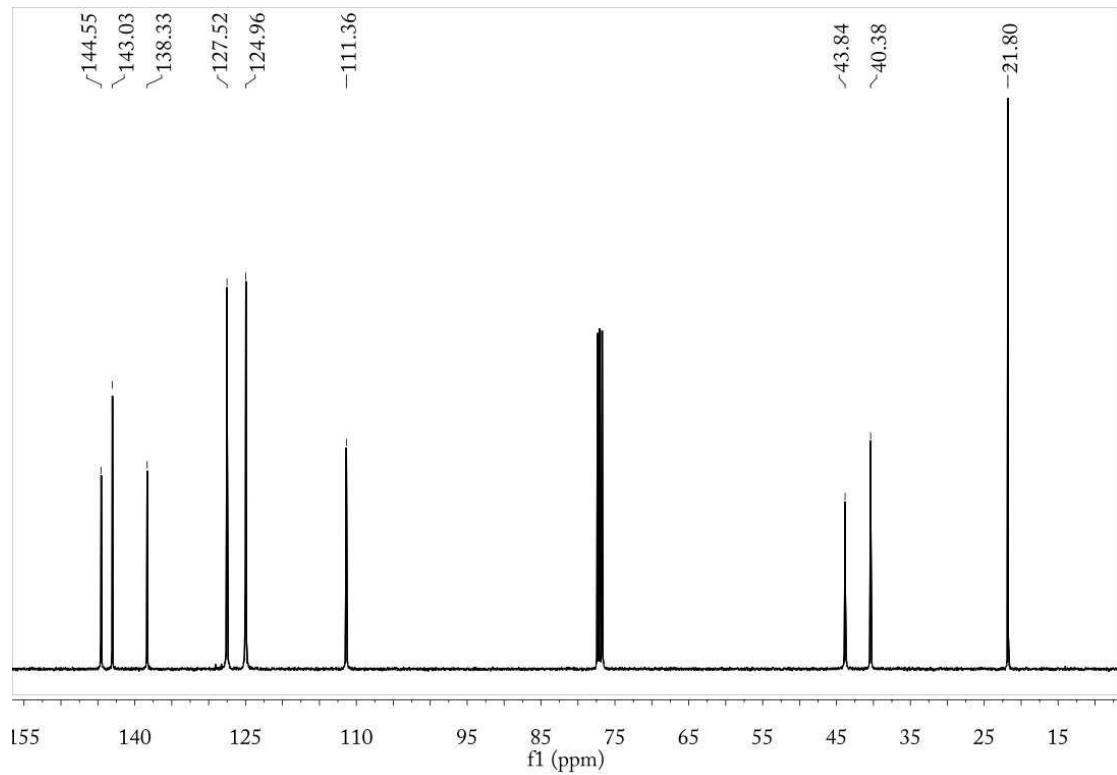


Fig. S16  $^{13}\text{C}$  NMR spectrum of poly(*p*IPSt) in  $\text{CDCl}_3$  at 25 °C. (Table 1, entry 6)

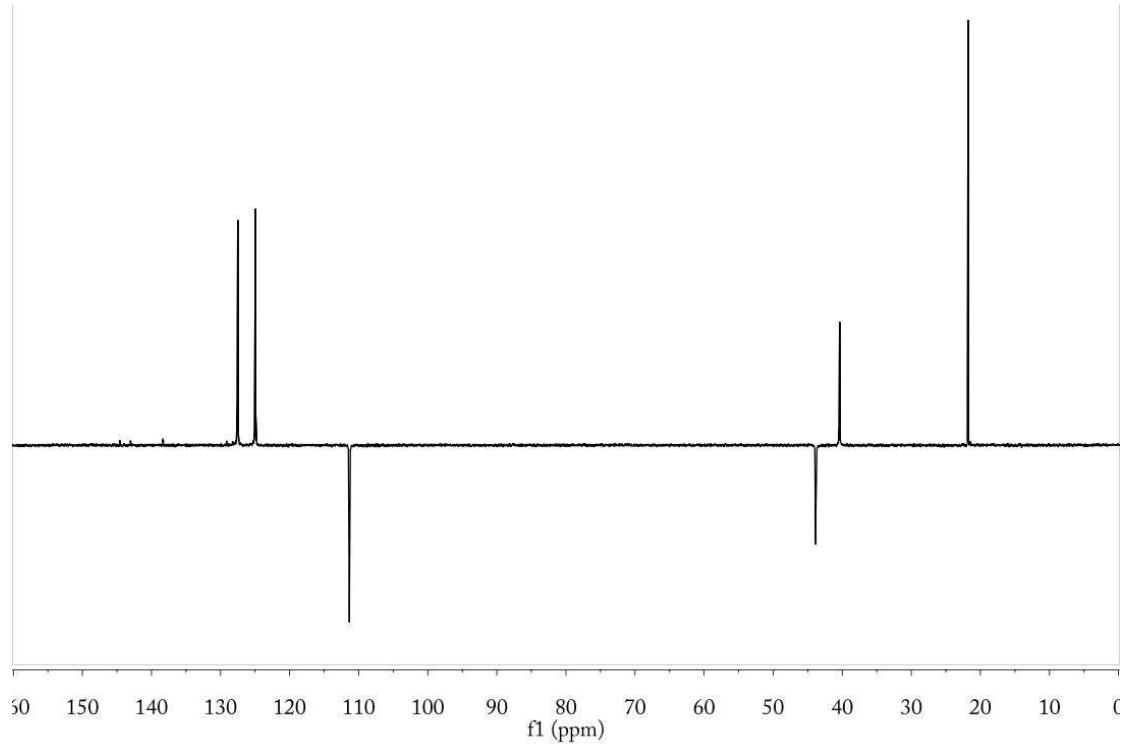


Fig. S17  $\text{dept}135$  NMR spectrum of poly(*p*IPSt) in  $\text{CDCl}_3$  at 25 °C. (Table 1, entry 6)

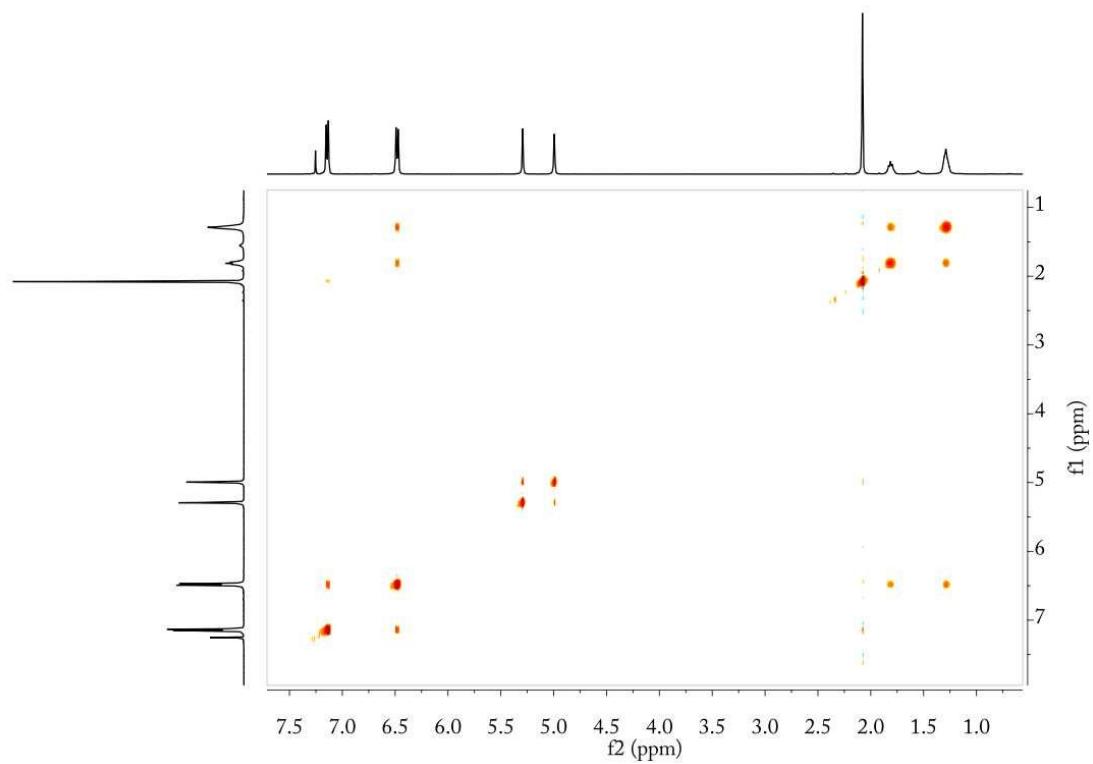
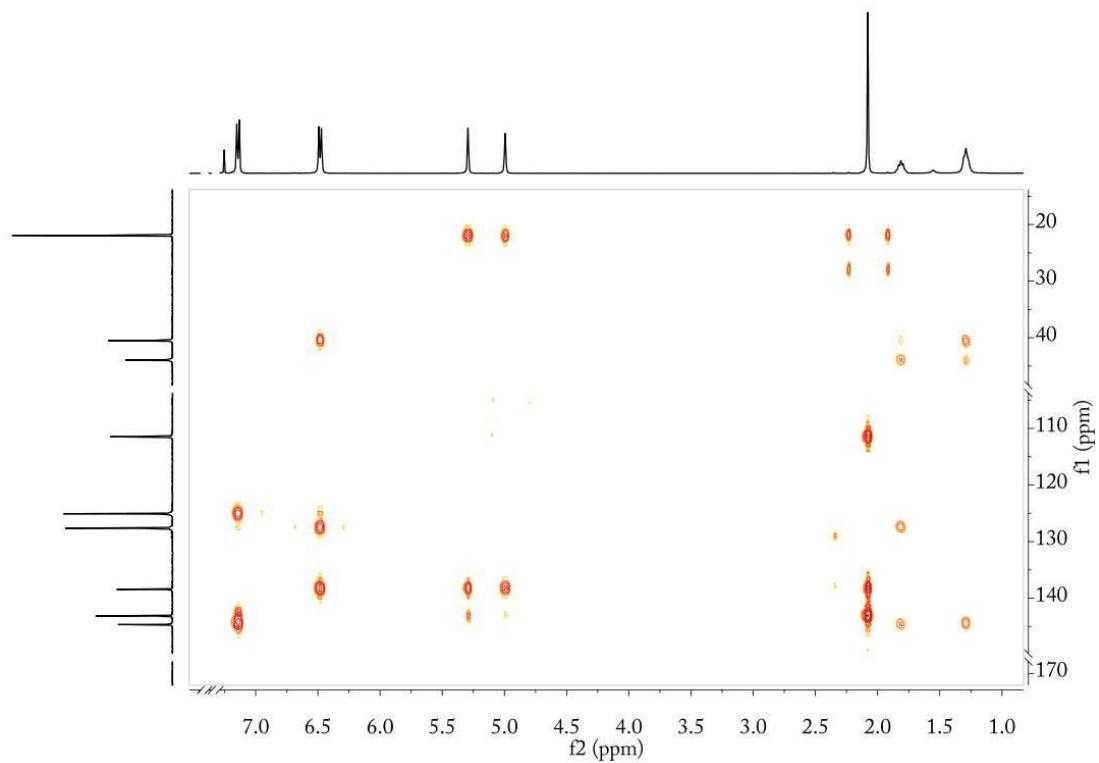


Fig. S18 NOESY spectrum of poly(*p*IPSt) in CDCl<sub>3</sub> at 25 °C. (Table 1, entry 6)



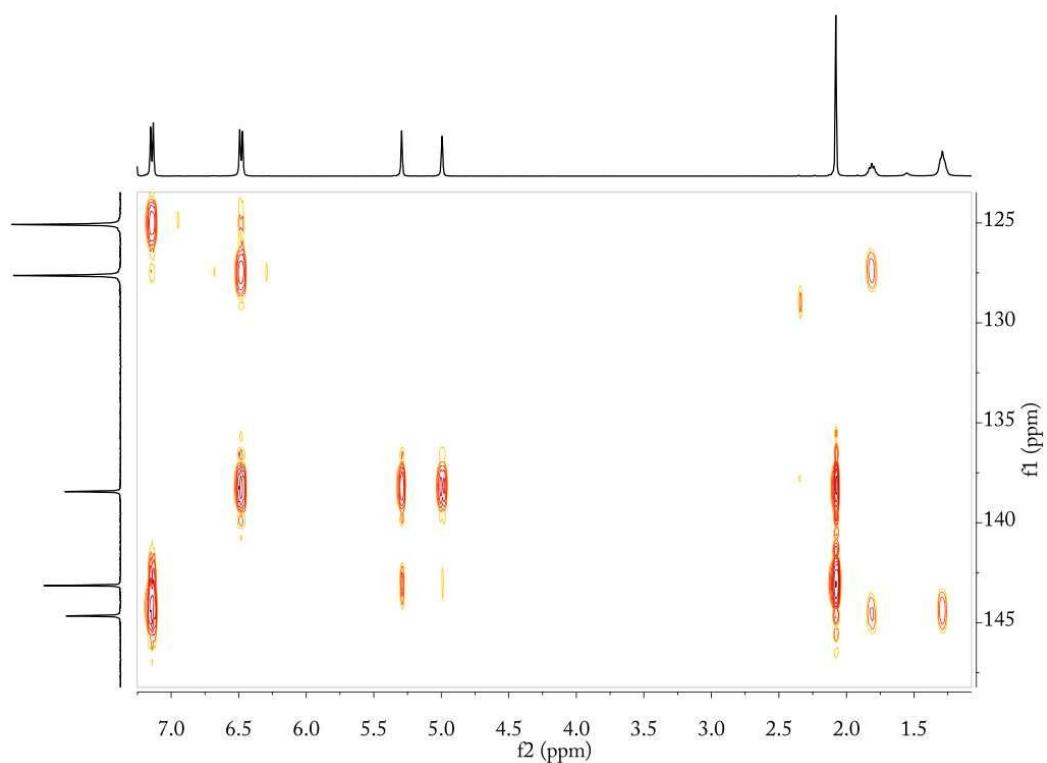


Fig. S19 HMBC spectrum of poly(*p*IPSt) in CDCl<sub>3</sub> at 25 °C. (Table 1, entry 6)

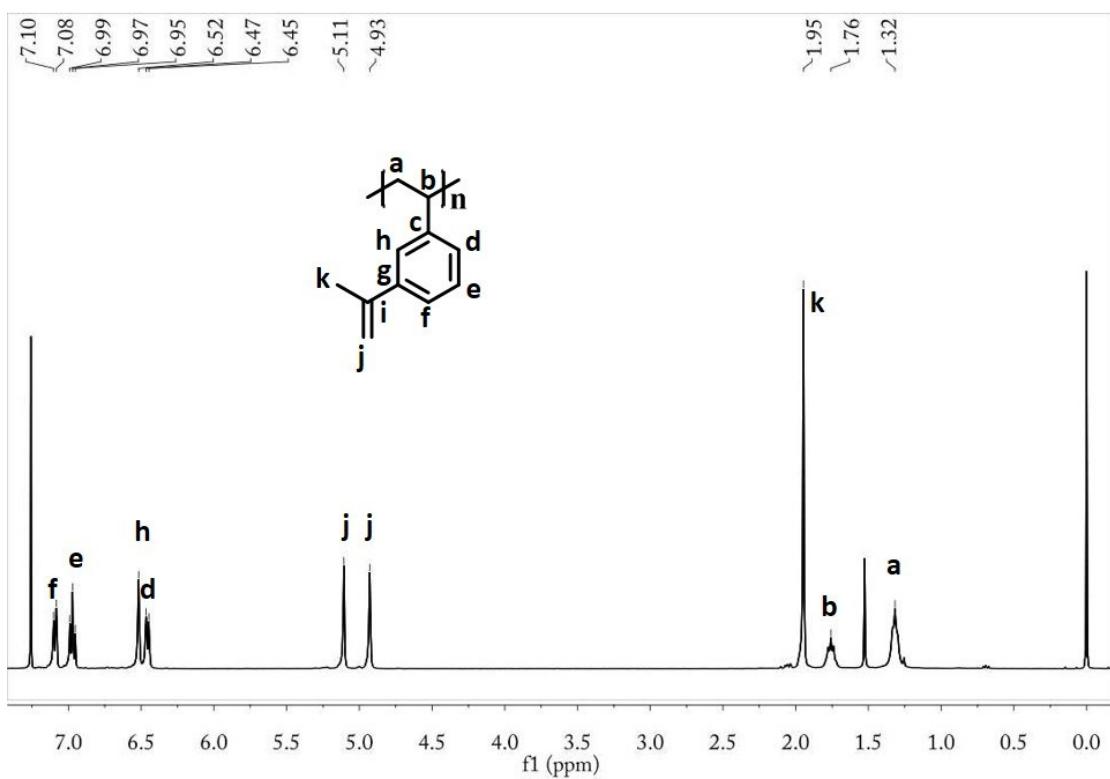


Fig. S20 <sup>1</sup>H NMR spectrum of poly(*m*IPSt) in CDCl<sub>3</sub> at 25 °C (Table 1, entry 8)

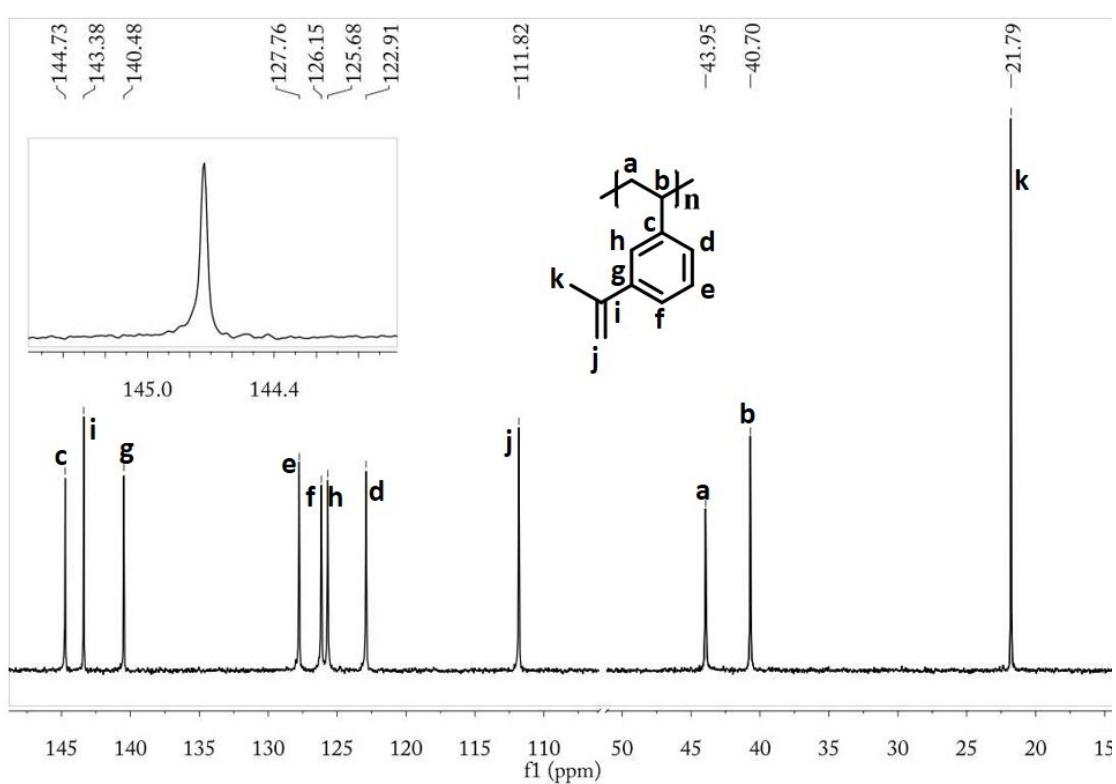


Fig. S21  $^{13}\text{C}$  NMR spectrum of poly(*m*IPSt) in  $\text{CDCl}_3$  at 25 °C (Table 1, entry 8)

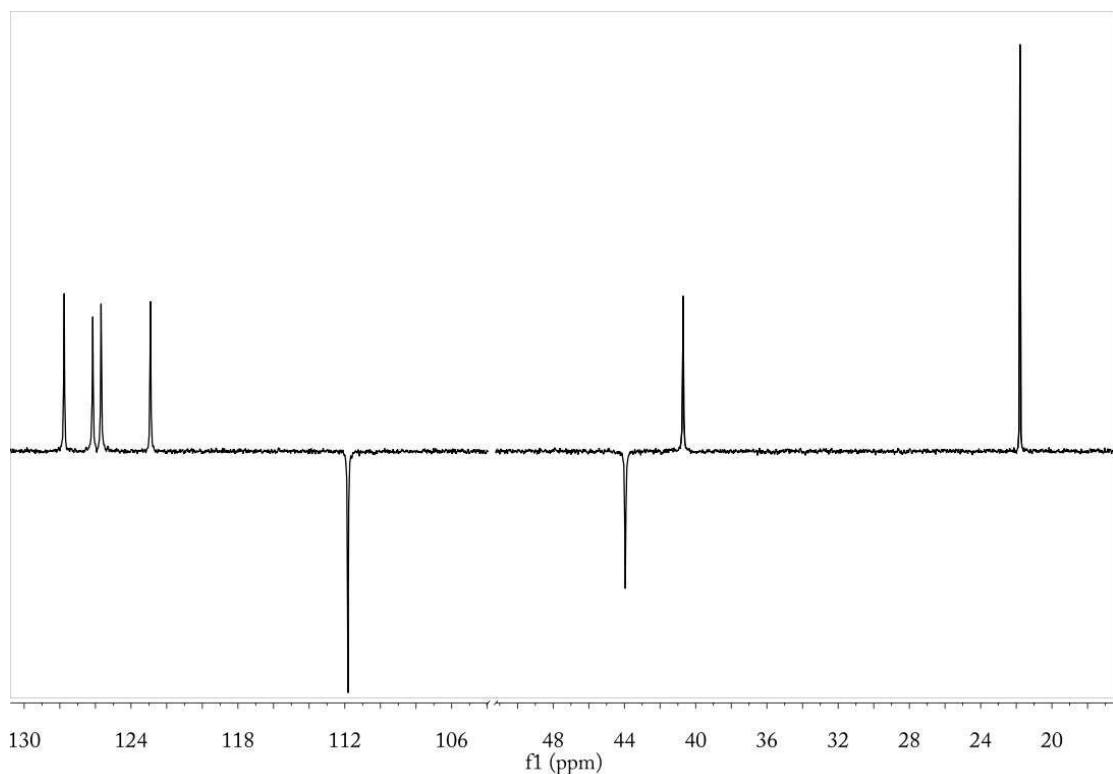


Fig. S22 dept135 NMR spectrum of poly(*m*IPSt) in  $\text{CDCl}_3$  at 25 °C (Table 1, entry 8)

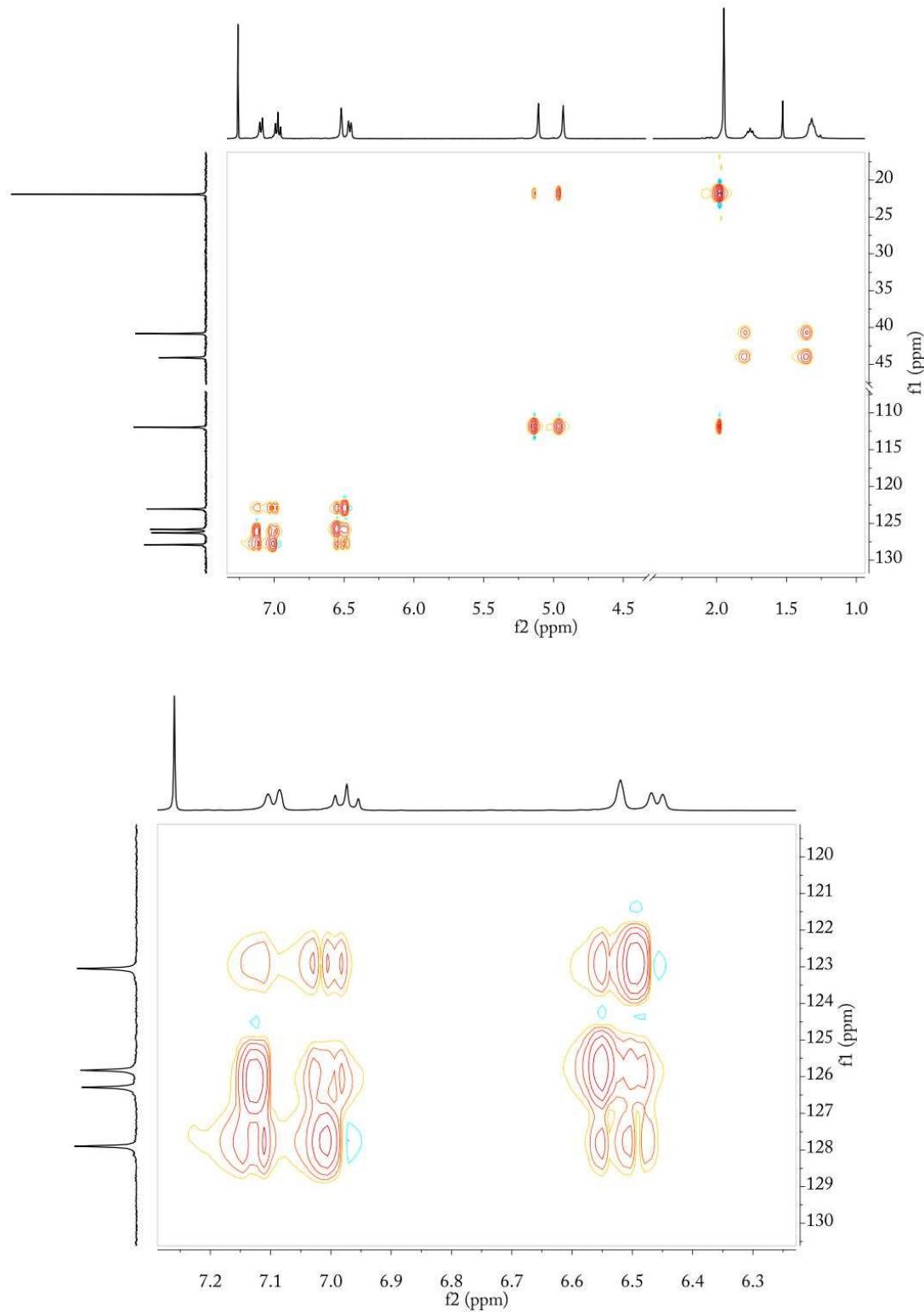


Fig. S23 HMQC spectrum of poly(*m*IPSt) in  $\text{CDCl}_3$  at 25 °C (Table 1, entry 8)

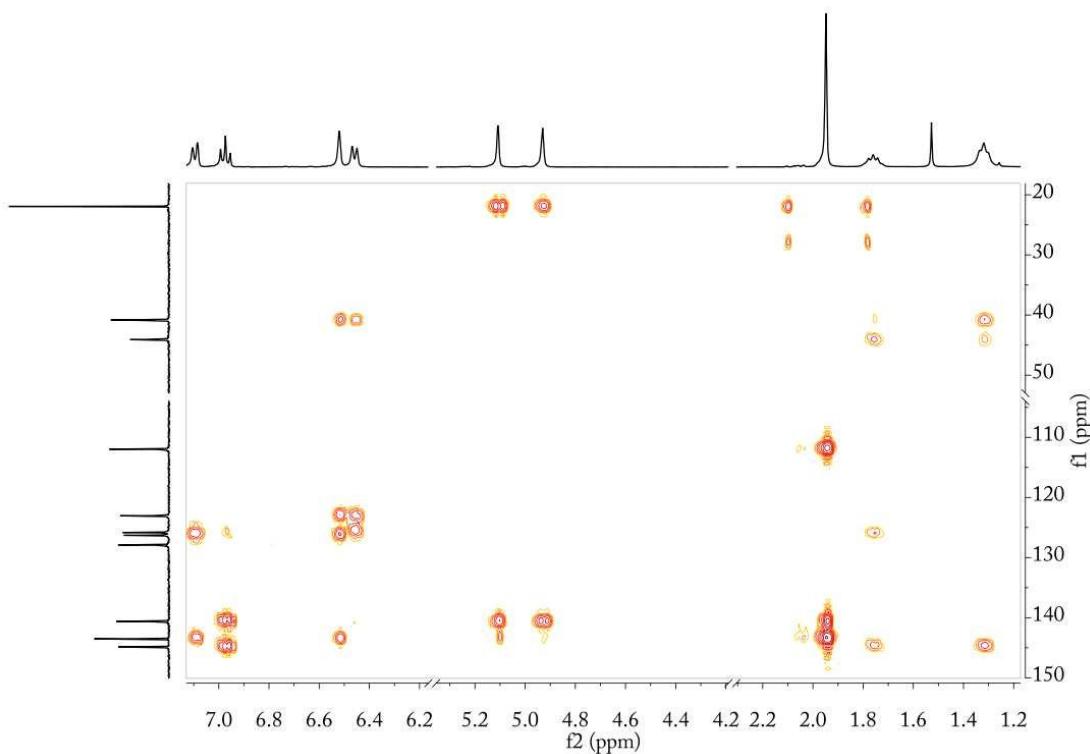


Fig. S24 HMBC NMR spectrum of poly(*m*IPSt) in CDCl<sub>3</sub> at 25 °C (Table 1, entry 8)

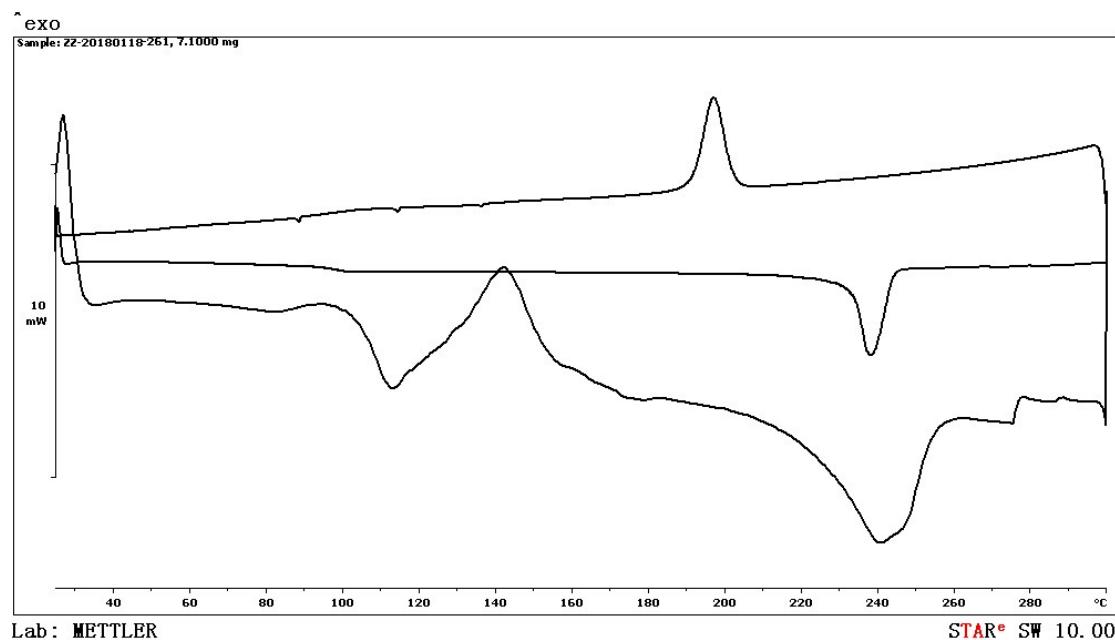


Fig. S25 DSC curve of *p*IPSt-St copolymer containing 5 mol% *p*IPSt units (Table 2, entry 6)

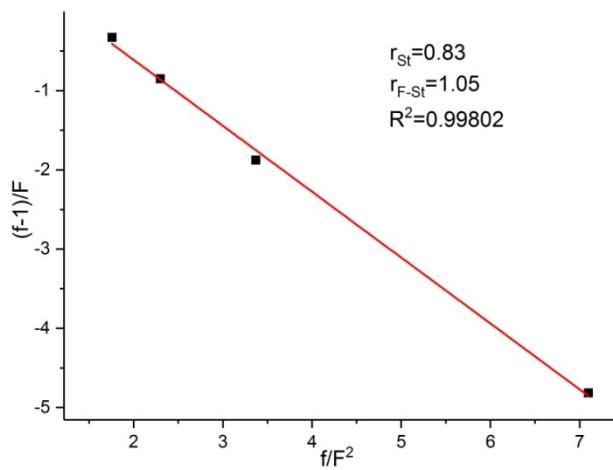


Fig. S26. Fineman and Ross plot for the copolymerization of *p*IPSt and St and least-squares best fit line.

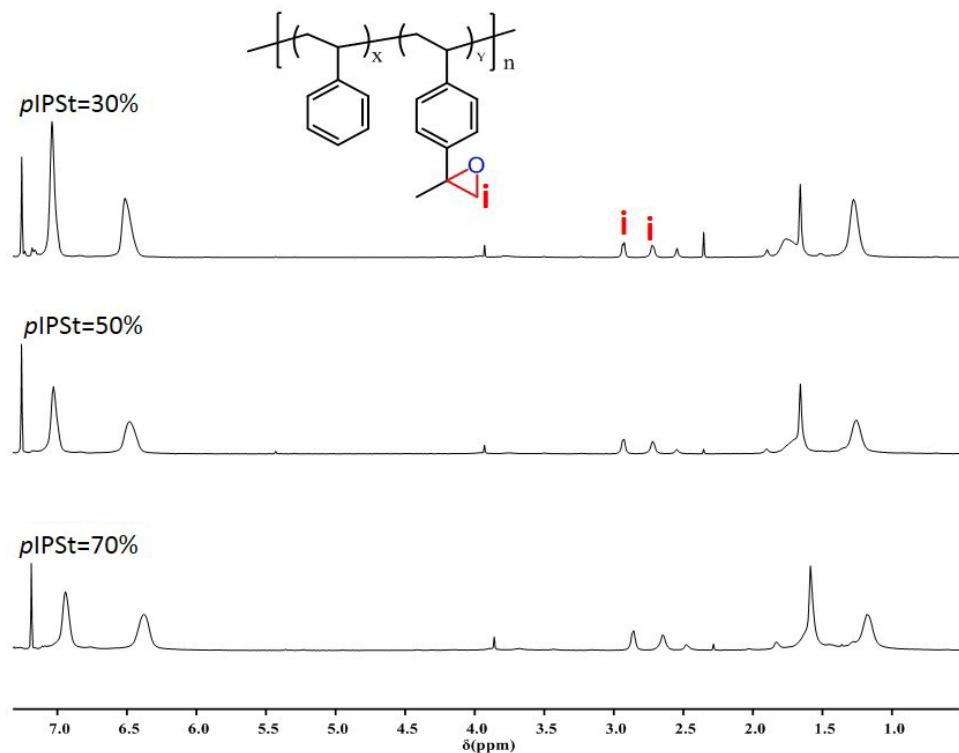


Fig. S27  $^1\text{H}$  NMR spectrum of epoxidized *p*IPSt-St copolymers product in  $\text{CDCl}_3$  at 25 °C

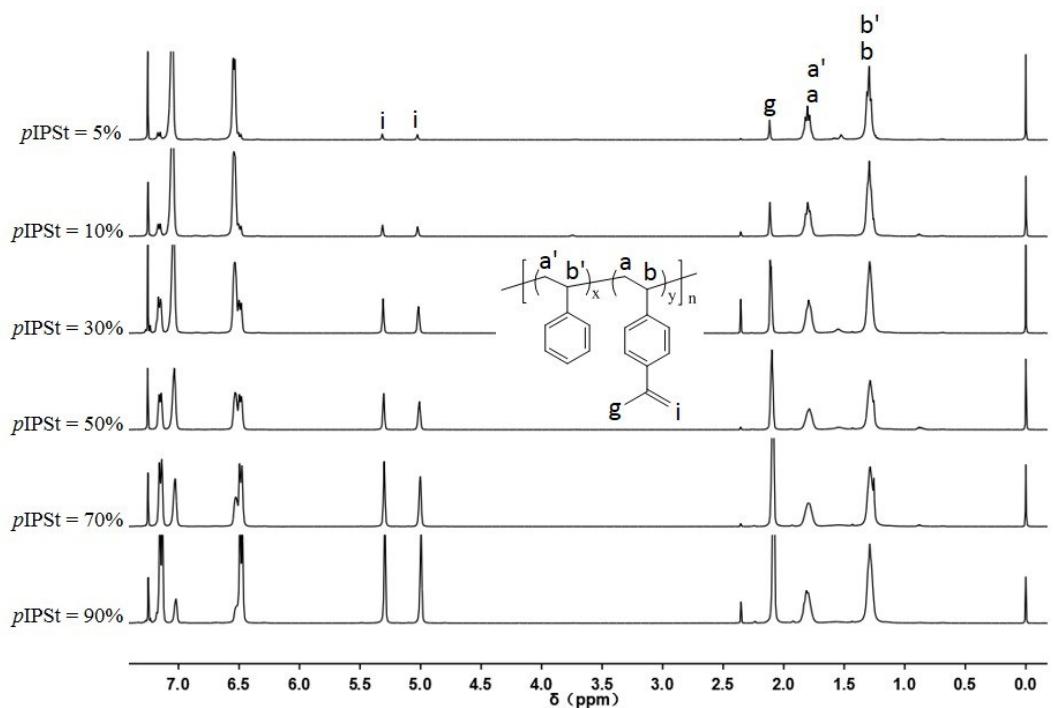


Fig. S28  $^1\text{H}$  NMR spectra of  $p\text{IPSt-St}$  copolymers

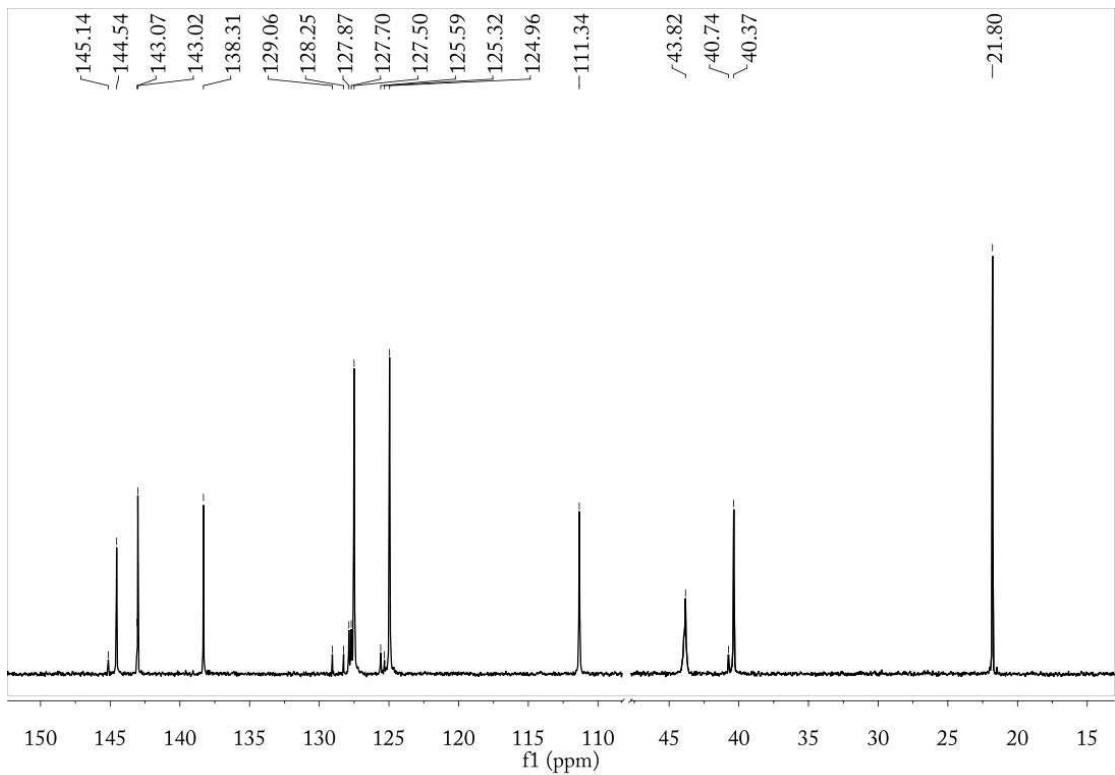


Fig. S29  $^{13}\text{C}$  NMR spectrum of  $p\text{IPSt-St}$  copolymer with 90%  $p\text{IPSt}$  in  $\text{CDCl}_3$  at 25 °C. (Table 3, entry 1)

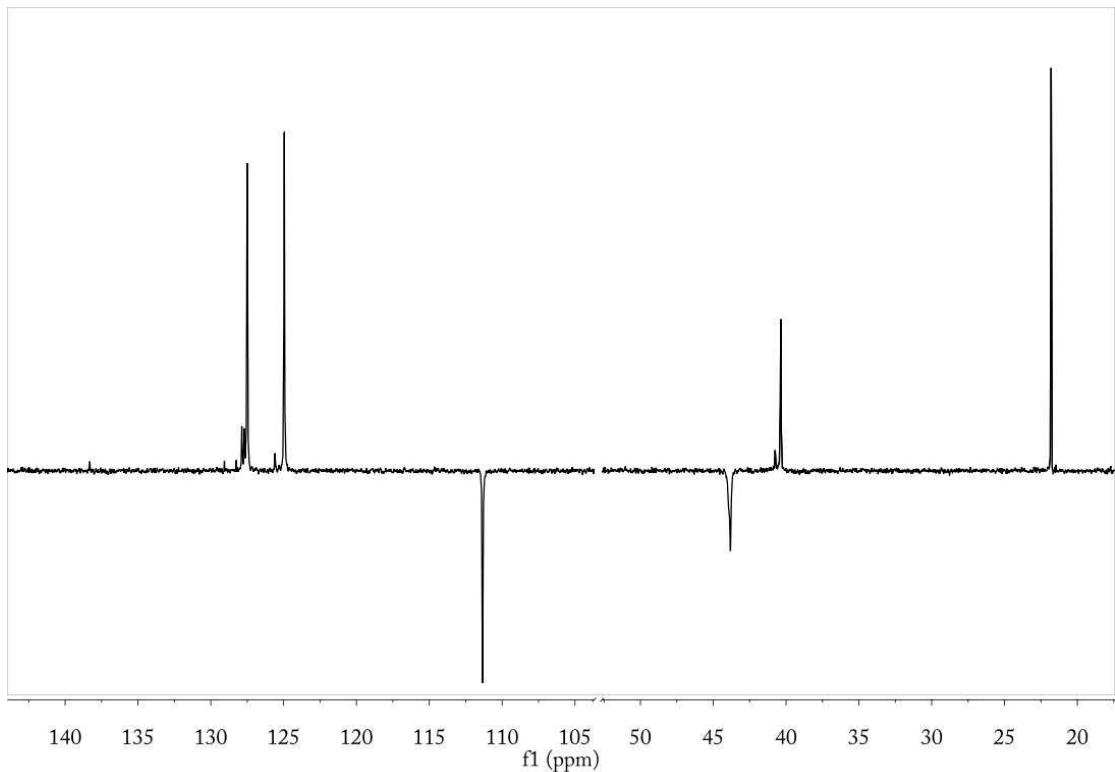


Fig. S30 dept135 NMR spectrum of *p*IPSt-St copolymer with 90% *p*IPSt in  $\text{CDCl}_3$  at 25 °C. (Table 3, entry 1)

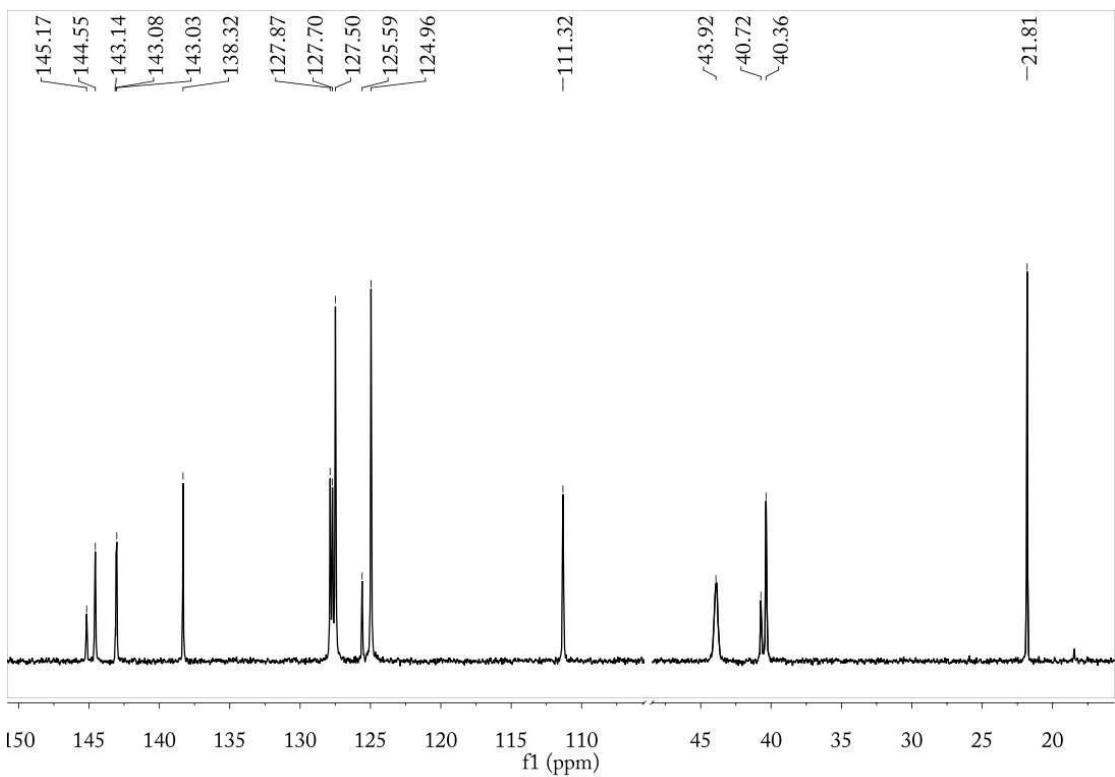


Fig. S31  $^{13}\text{C}$  NMR spectrum of *p*IPSt-St copolymer with 70% *p*IPSt in  $\text{CDCl}_3$  at 25 °C. (Table 3, entry 2)

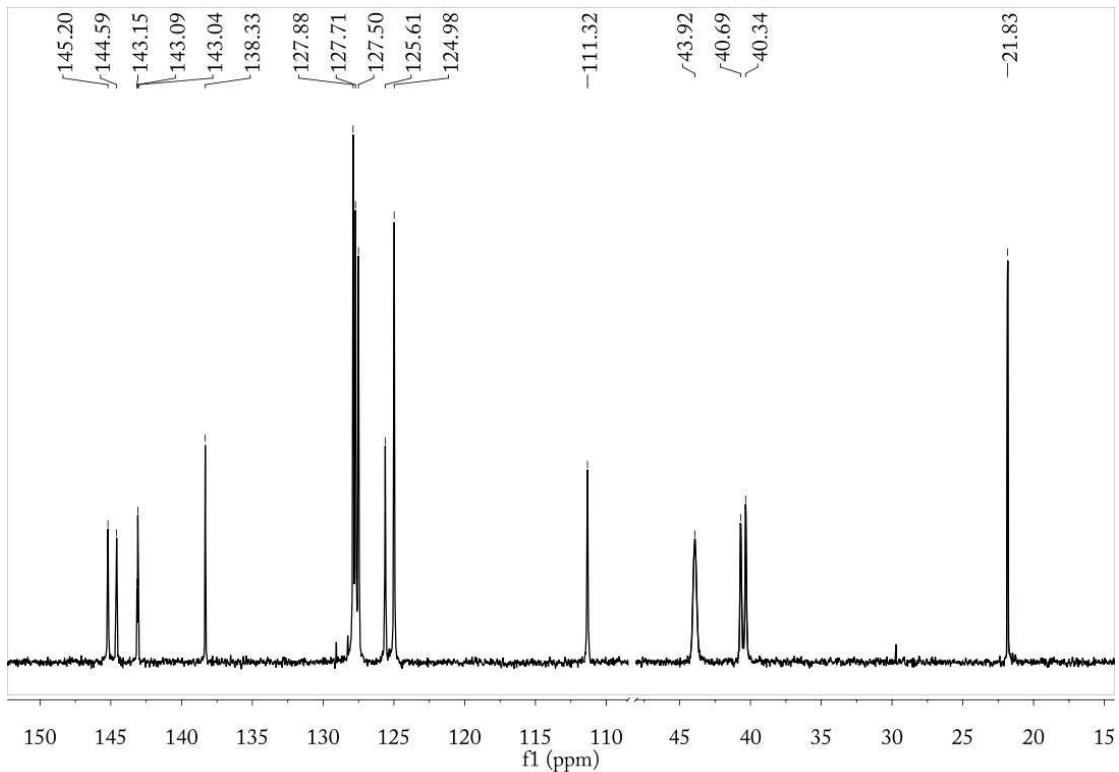


Fig. S32  $^{13}\text{C}$  NMR spectrum of *p*IPSt-St copolymer with 50% *p*IPSt in  $\text{CDCl}_3$  at 25 °C. (Table 3, entry 3)

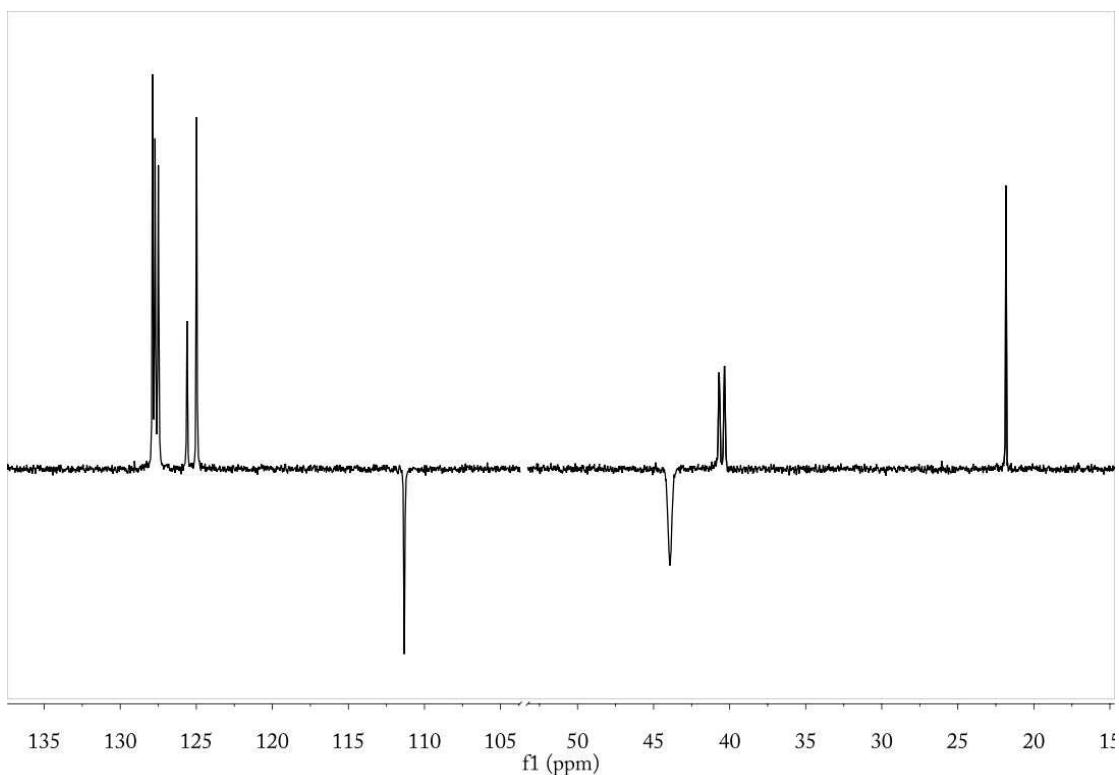


Fig. S33  $\text{dept}135$  NMR spectrum of *p*IPSt-St copolymer with 50% *p*IPSt in  $\text{CDCl}_3$  at 25 °C. (Table 3, entry 3)

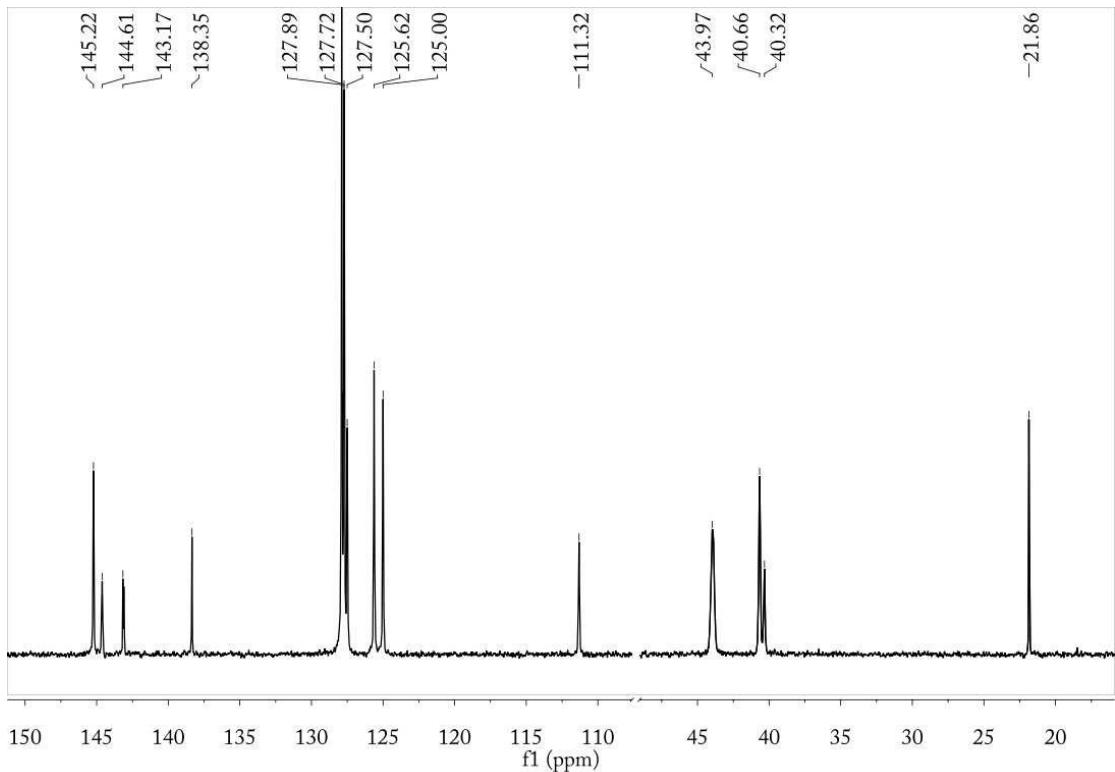


Fig. S34  $^{13}\text{C}$  NMR spectrum of *p*IPSt-St copolymer with 30% *p*IPSt in  $\text{CDCl}_3$  at 25 °C. (Table 3, entry 4)

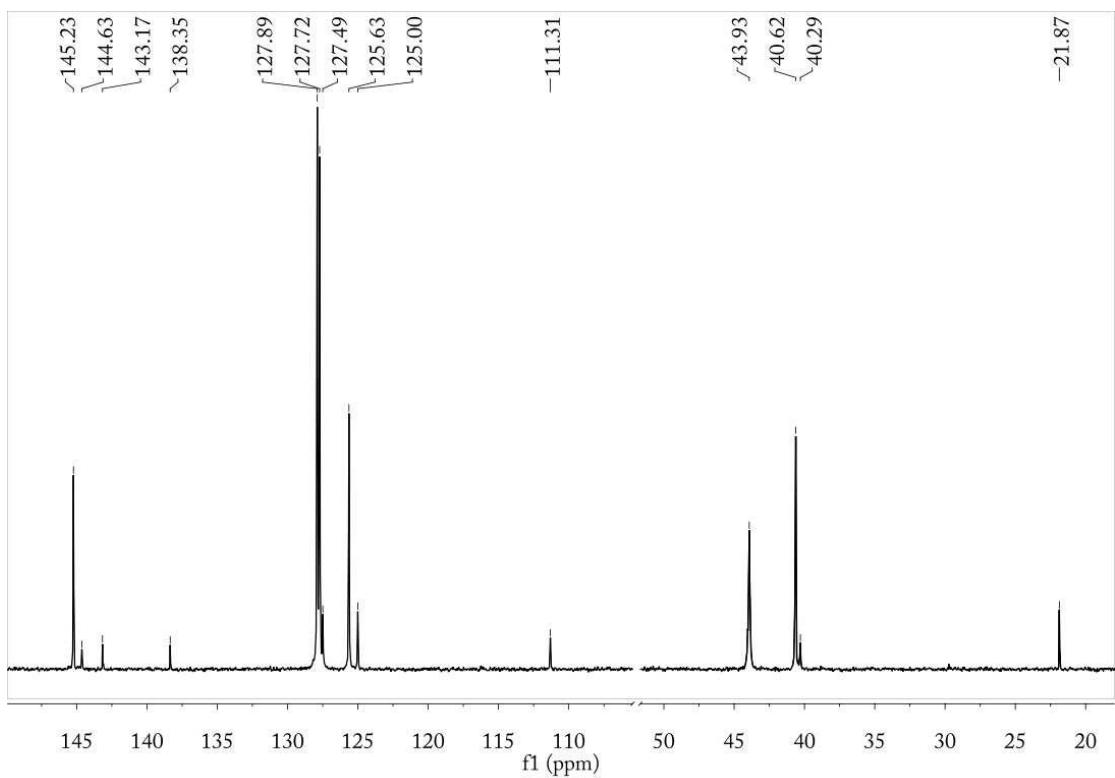


Fig. S35  $^{13}\text{C}$  NMR spectrum of *p*IPSt-St copolymer with 10% *p*IPSt in  $\text{CDCl}_3$  at 25 °C. (Table 3, entry 5)

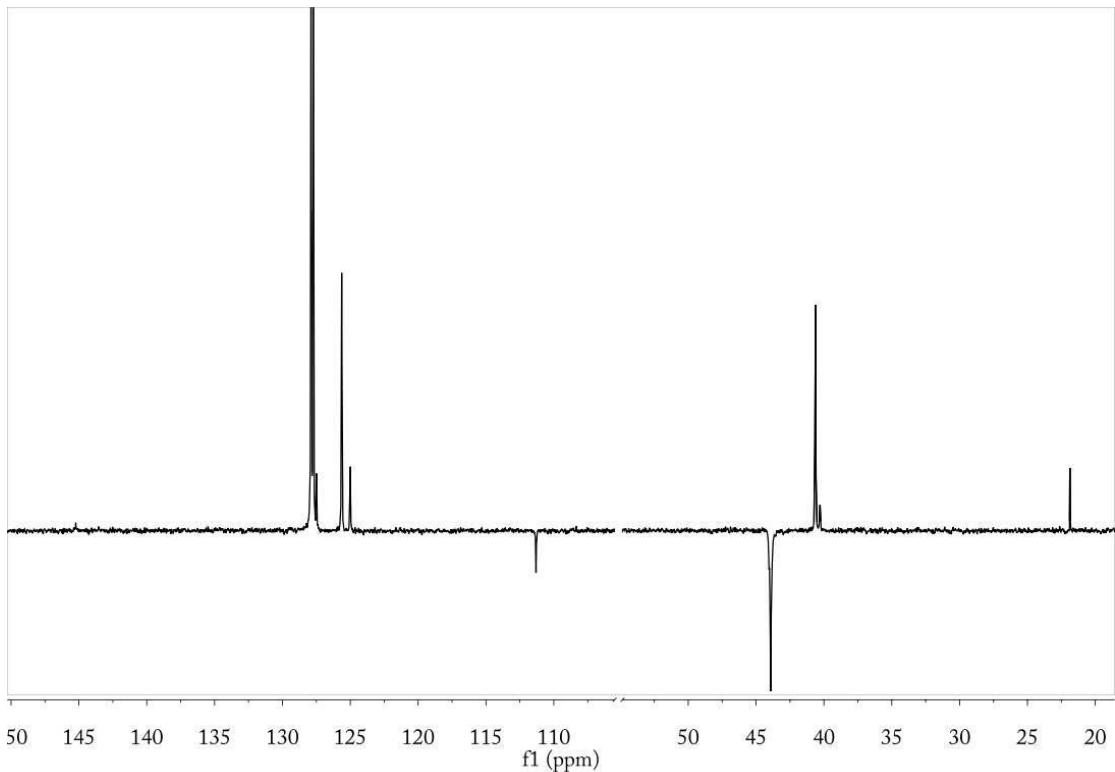


Fig. S36 dept135 NMR spectrum of *p*IPSt-St copolymer with 10% *p*IPSt in CDCl<sub>3</sub> at 25 °C. (Table 3, entry 5)

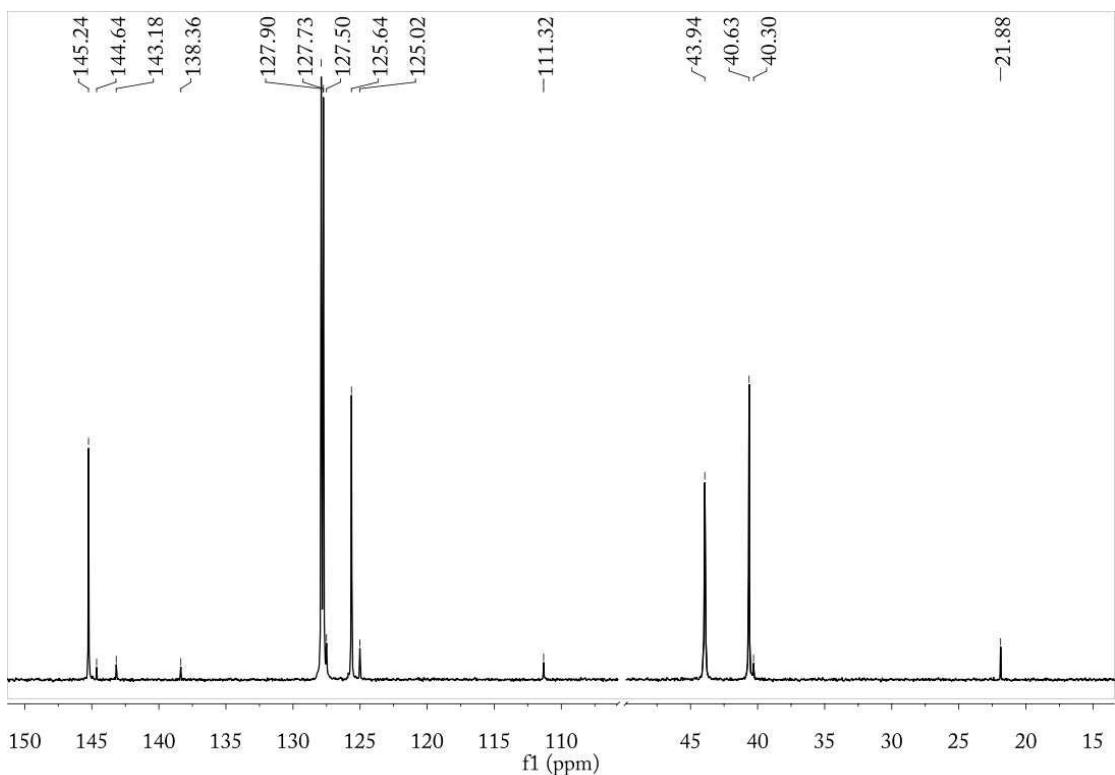


Fig. S37 <sup>13</sup>C NMR spectrum of *p*IPSt-St copolymer with 5% *p*IPSt in CDCl<sub>3</sub> at 25 °C. (Table 3, entry 6)