

Electronic supporting information

**Carbocationic polymerization of isoprene using cumyl initiators: progress in
understanding side reactions**

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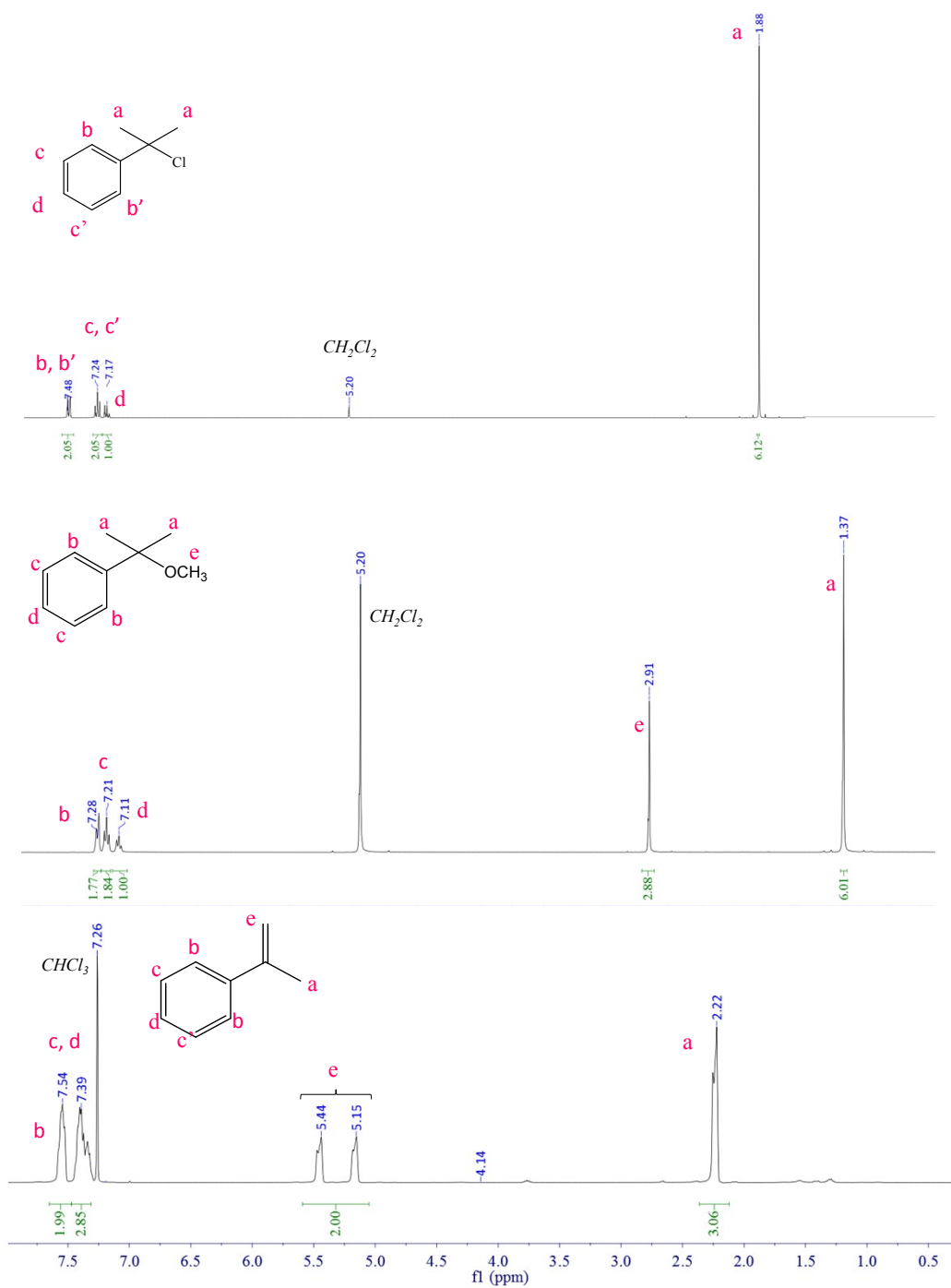
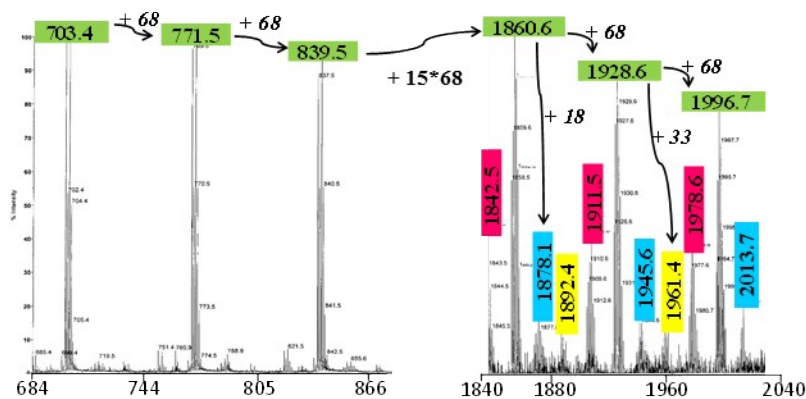
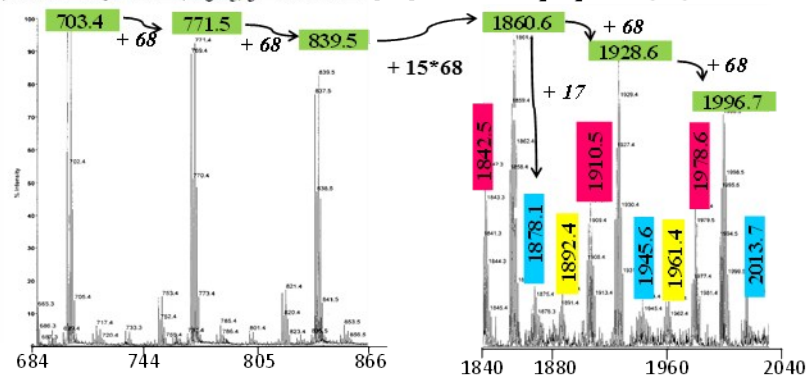


Figure S1: 1H NMR spectra of cumyl chloride, cumyl ether and α -methylstyrene. (from top to bottom)

(a) IP/cumylCl/B(C₆F₅)₃ 75/1/2, [IP] = 2M, CH₂Cl₂/methylcyclohexane 100/0



(b) IP/cumylCl/B(C₆F₅)₃ 150/1/2, [IP] = 4M, CH₂Cl₂/methylcyclohexane 100/0



(c) IP/cumylCl/B(C₆F₅)₃ 75/1/2, [IP] = 2M, CH₂Cl₂/methylcyclohexane 50/50

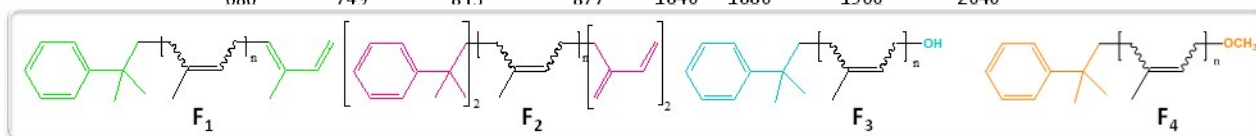
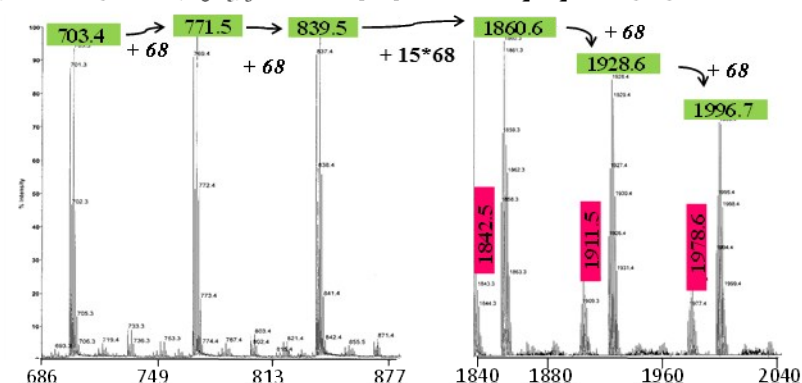


Figure S2: Maldi-TOF MS spectra of oligoisoprenes obtained by the system IP/CumylCl/B(C₆F₅)₃/d^tBP at 20°C.

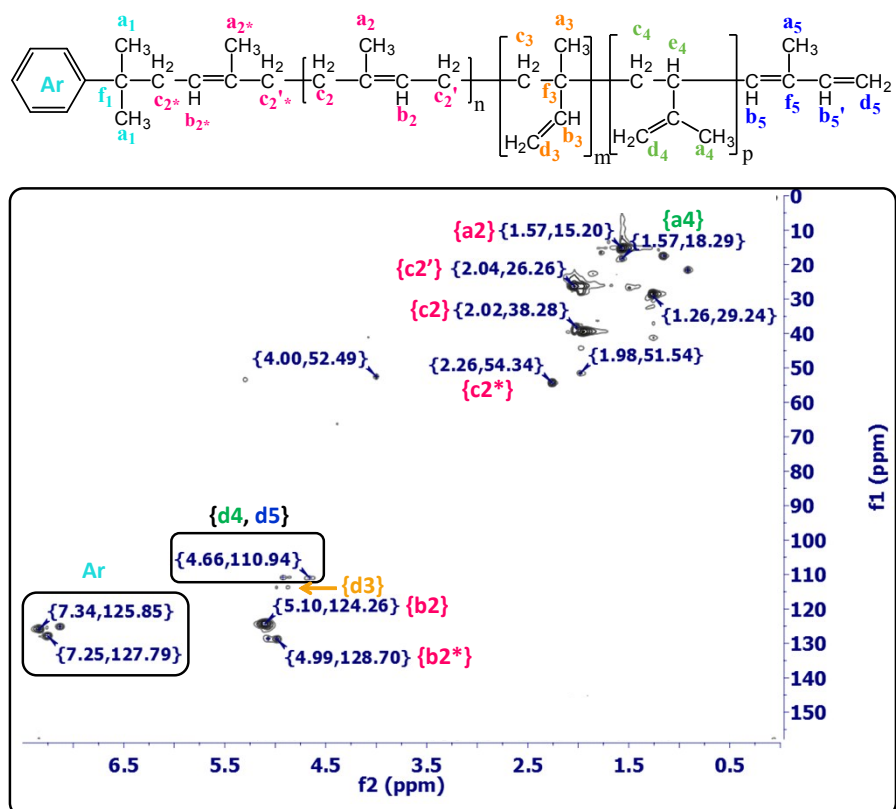


Figure S3: Typical HSQC NMR spectrum of the polyisoprene obtained with IP/CumylOCH₃/TiCl₄/d¹BP system.

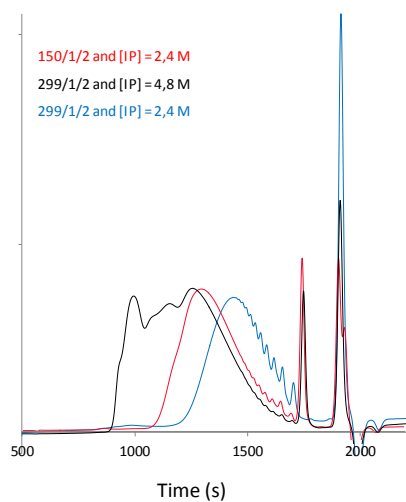


Figure S4: SEC spectra of polyisoprenes obtained varying IP/CumylOCH₃/TiCl₄ ratio.

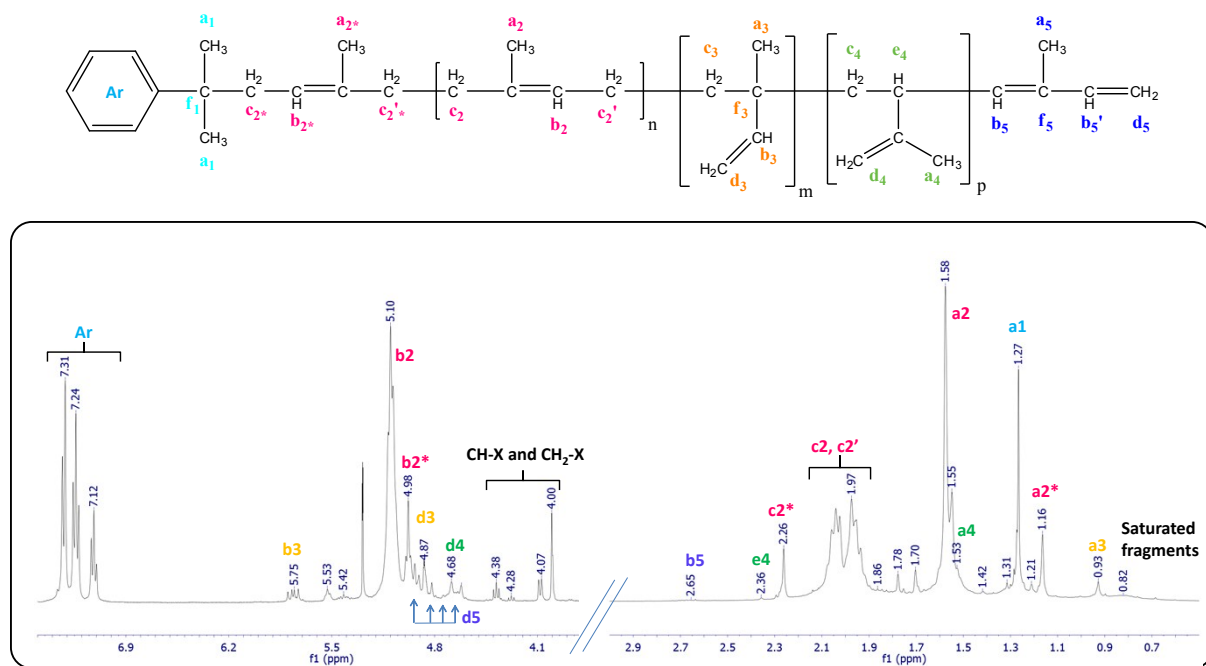


Figure S5: ^1H NMR spectrum of the polyisoprene obtained with IP/cumylOCH₃/TiCl₄/d⁴BP systems.

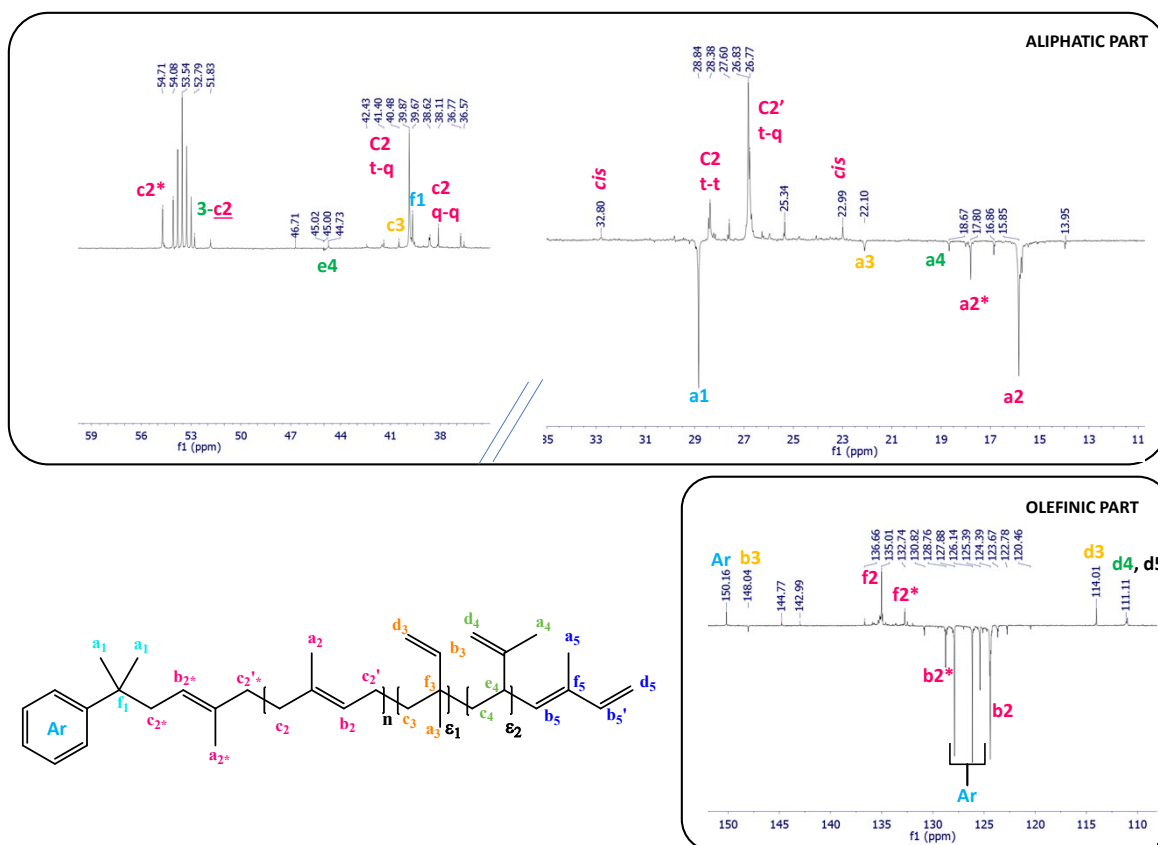


Figure S6: JMOD NMR spectrum of the polyisoprene obtained with IP/cumylOCH₃/TiCl₄/d⁴BP system.

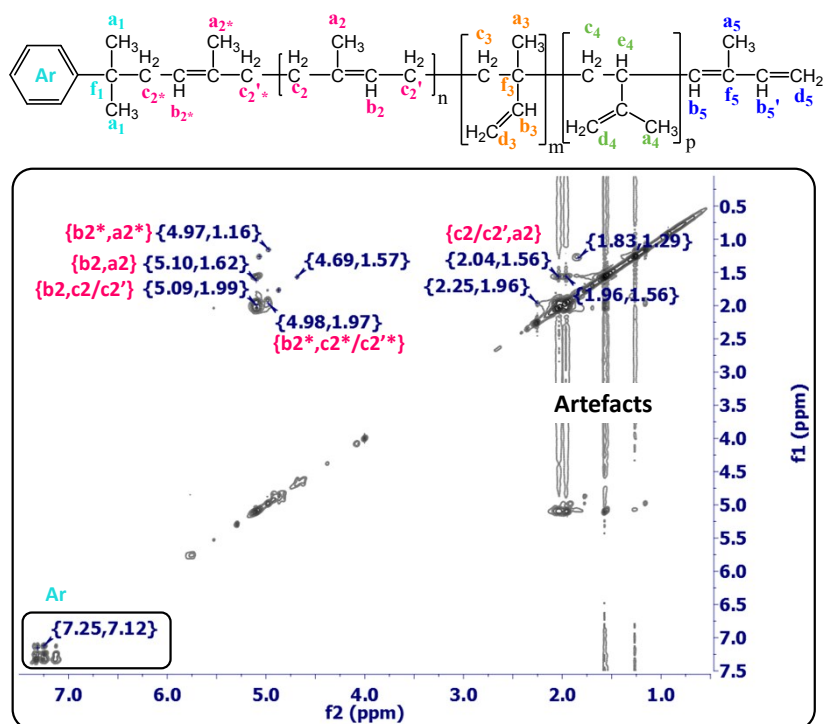


Figure S7: TOCSY NMR spectrum of the polyisoprene obtained with IP/cumylOCH₃/TiCl₄/d⁴BP system.

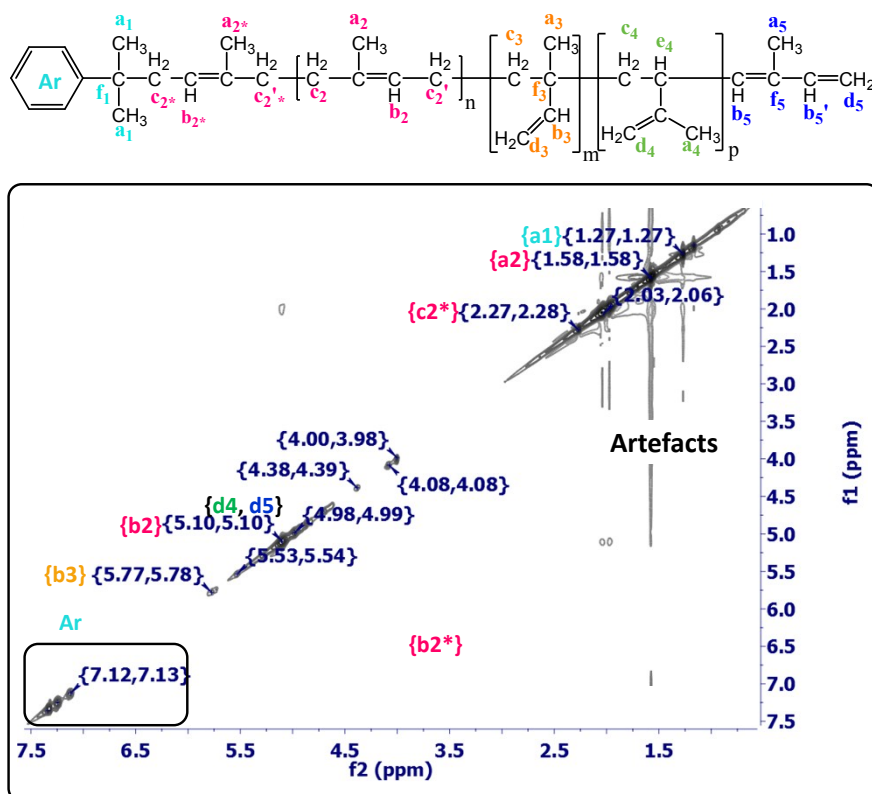


Figure S8: NOESY NMR spectrum of the polyisoprene obtained with IP/cumylOCH₃/TiCl₄/d⁴BP system.

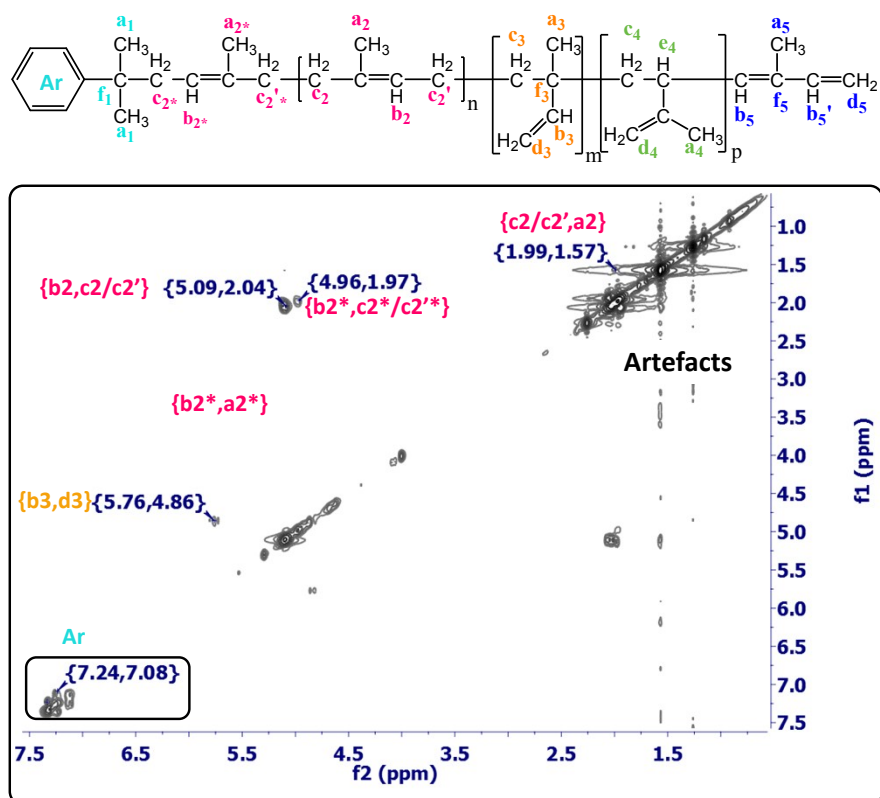


Figure S9: COSY NMR spectrum of the polyisoprene obtained with IP/cumylOCH₃/TiCl₄/d^tBP system.

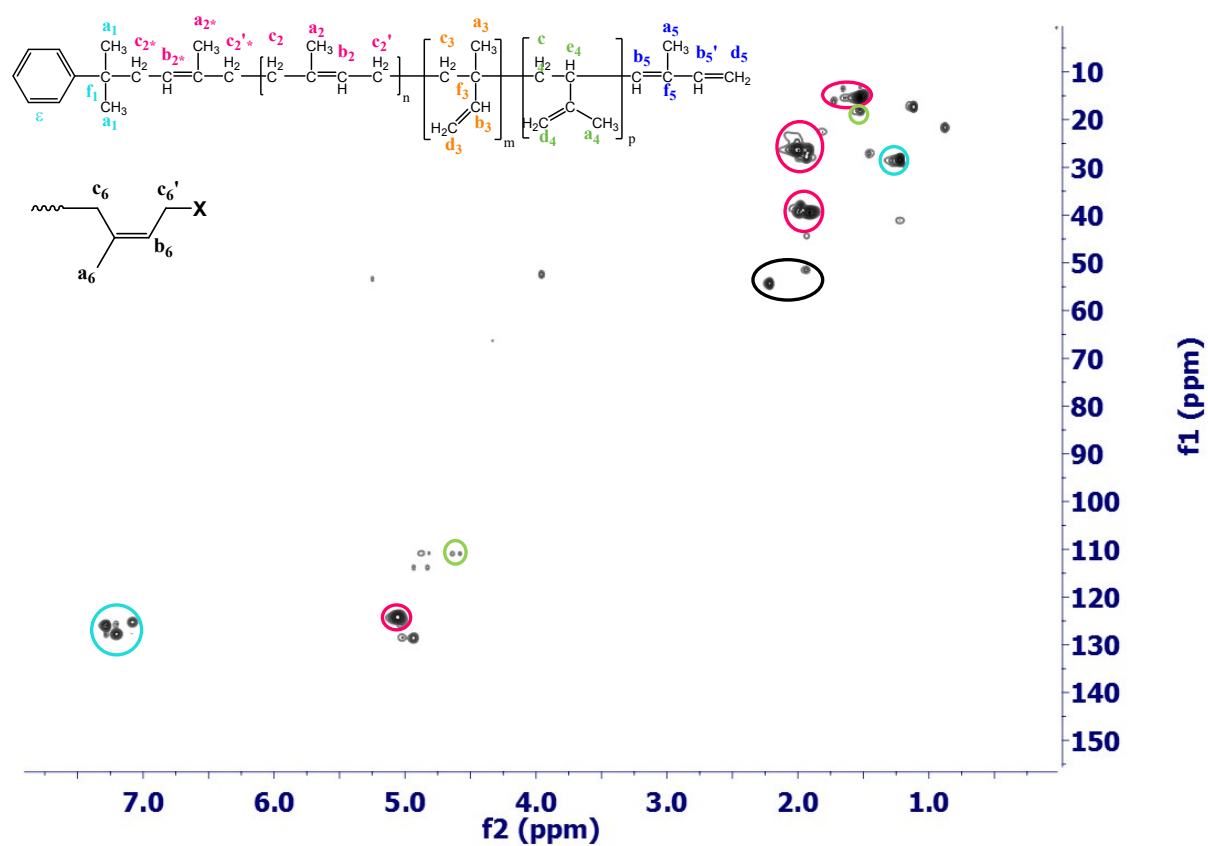


Figure S10: HMBC NMR spectrum of the polyisoprene obtained with IP/cumylOCH₃/TiCl₄/d^tBP system.