Carbocationic polymerization of isoprene initiated by dimethylallyl derivatives associated to B(C₆F₅)₃

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**Figure S1.** $^1$H NMR spectra of 3,3-DMAOH (a) and 3,3-DMAOAc (b)
Figure S2. $^1$H NMR spectra of 3,3-DMAOAc/$\text{B(C}_6\text{F}_5\text{)}_3$ at ratio 1/2 over time in CD$_2$Cl$_2$ at 20°C.
Figure S3. $^1$H NMR spectra of 3,3-DMABr/B(C$_6$F$_5$)$_3$ at ratio 1/2 over time in CD$_2$Cl$_2$ at 20°C.
Figure S4. $^1$H NMR spectra of 3,3-DMACl/B(C$_6$F$_5$)$_3$ at ratio 1/2 over time in CD$_2$Cl$_2$ at 20°C.
**Figure S5.** $^1$H NMR spectra superimposition of PIs obtained with the system IP/3,3-DMA MAX/B(C₆F₅)$_3$/DtBp 75/1/2/0 in CH₂Cl₂ at 20 °C (case X = OH, Cl). Normalization based on the olefinic peaks characteristic of a *trans*-1,4 unit at 5.1 ppm.

**Figure S6.** SEC chromatograms of PIPs obtained in presence of IP/3,3-DMA MAX/B(C₆F₅)$_3$ in 75/1/2 proportions in CH₂Cl₂ at 20°C (PIPs obtained with 3,3-DMABr were insoluble in THF).
**Figure S7.** Zoom of Maldi-TOF spectrum of polyisoprenes obtained with IP/3,3-DMAOAc/B(C_6F_5)_3d/BP (75/1/2/0.26) in dichloromethane at 20°C (ionized by Ag).