

**Electronic Supplementary Information**

**Synthesis and Properties of poly(trifluoroethylene) via a persistent radical mediated polymerization of trifluoroethylene**

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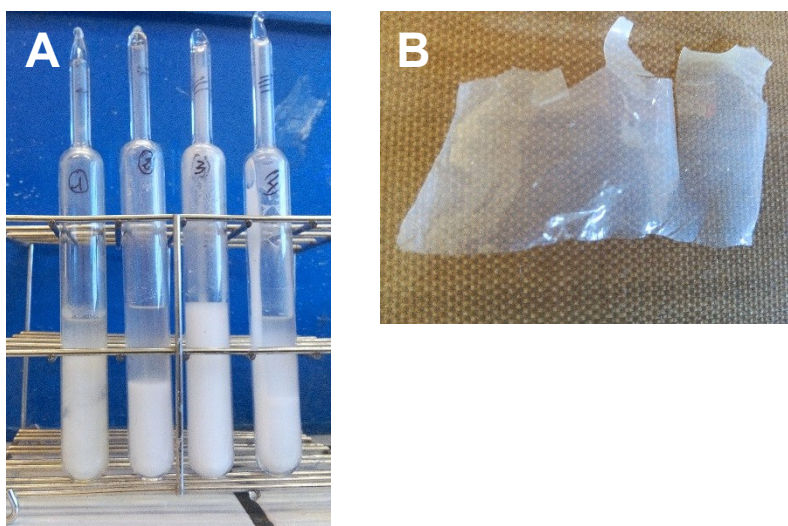
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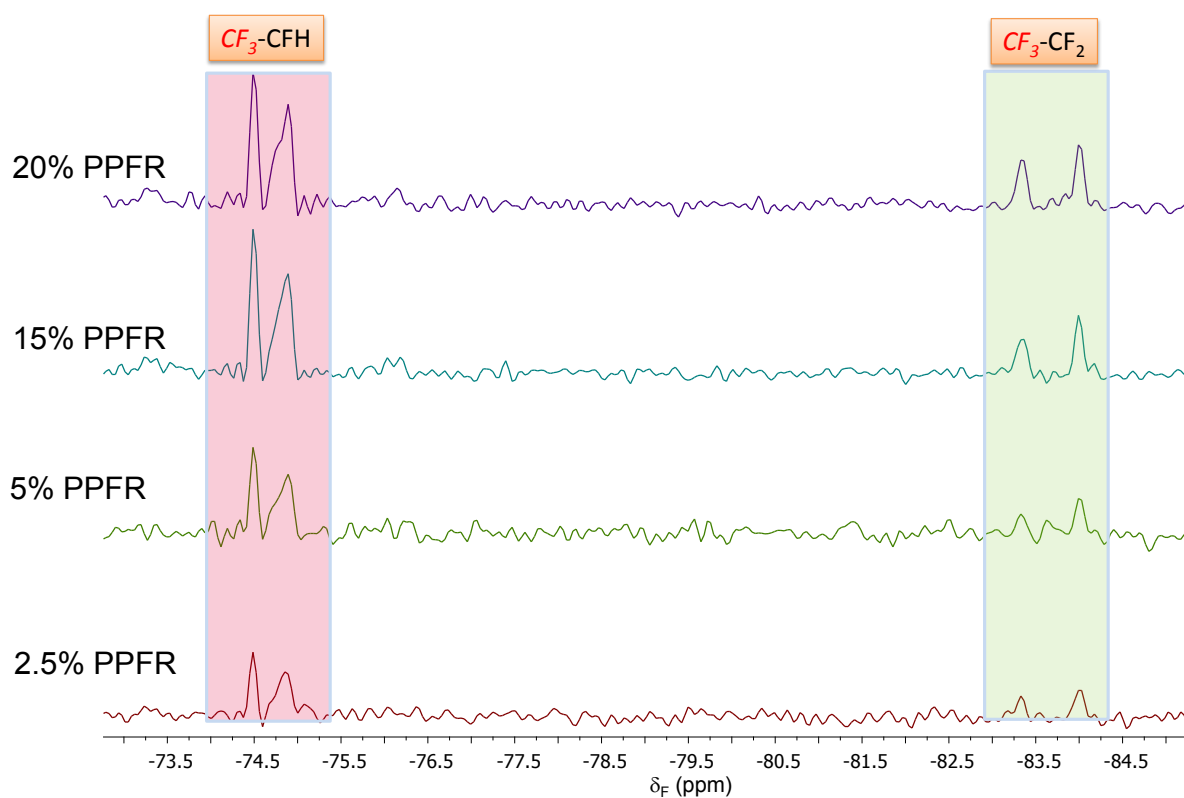
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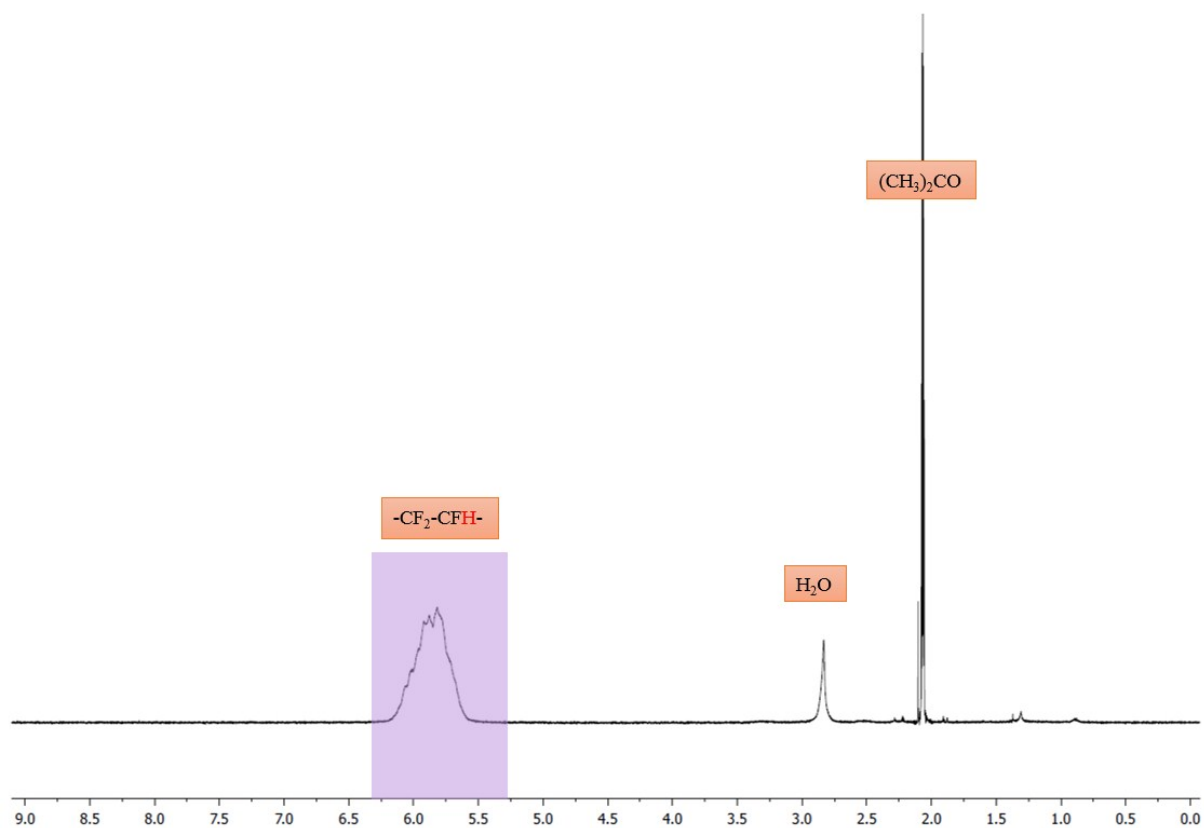
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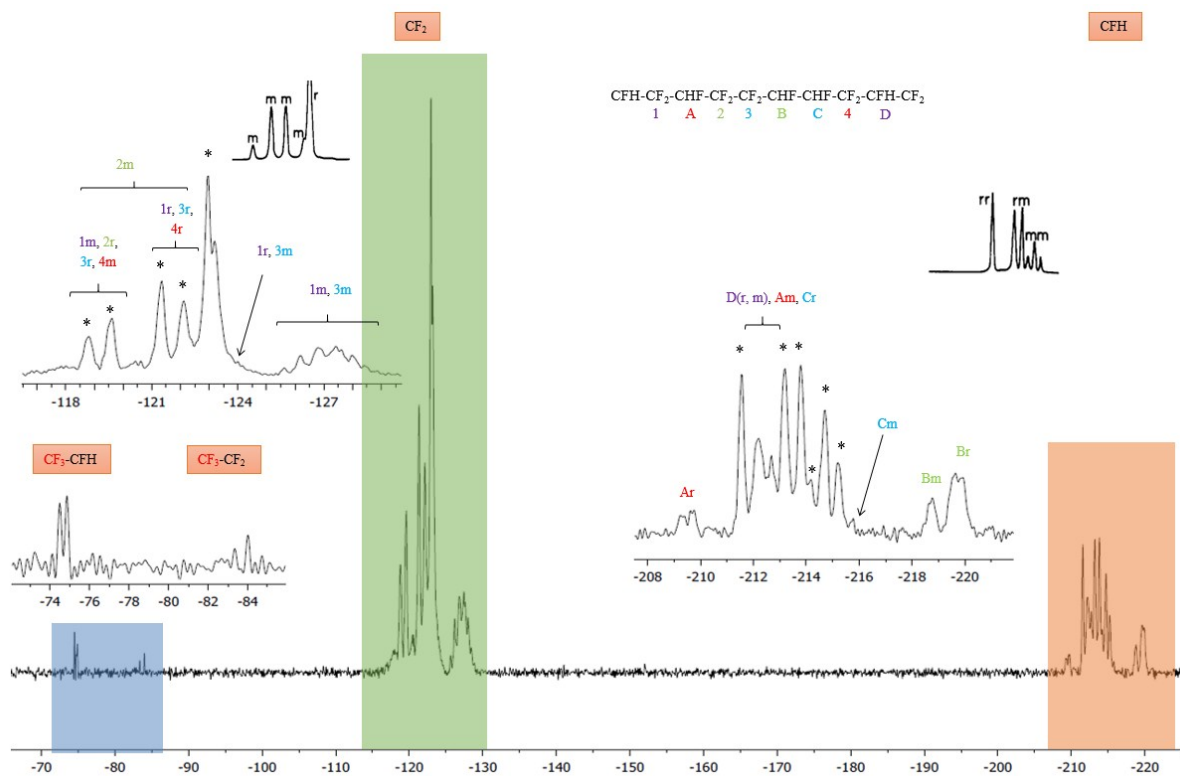
**Fig. S1** A) Pictures of four Carius tubes containing PTrFE samples at the end of the free radical homopolymerization of TrFE initiated by  $\cdot\text{CF}_3$  radical from PPR in 1,1,1,3,3-pentafluorbutane at 83 °C (**P1-P4**, Table 1). B) PTrFE film obtained after purification and casting (**P2**, Table 1)



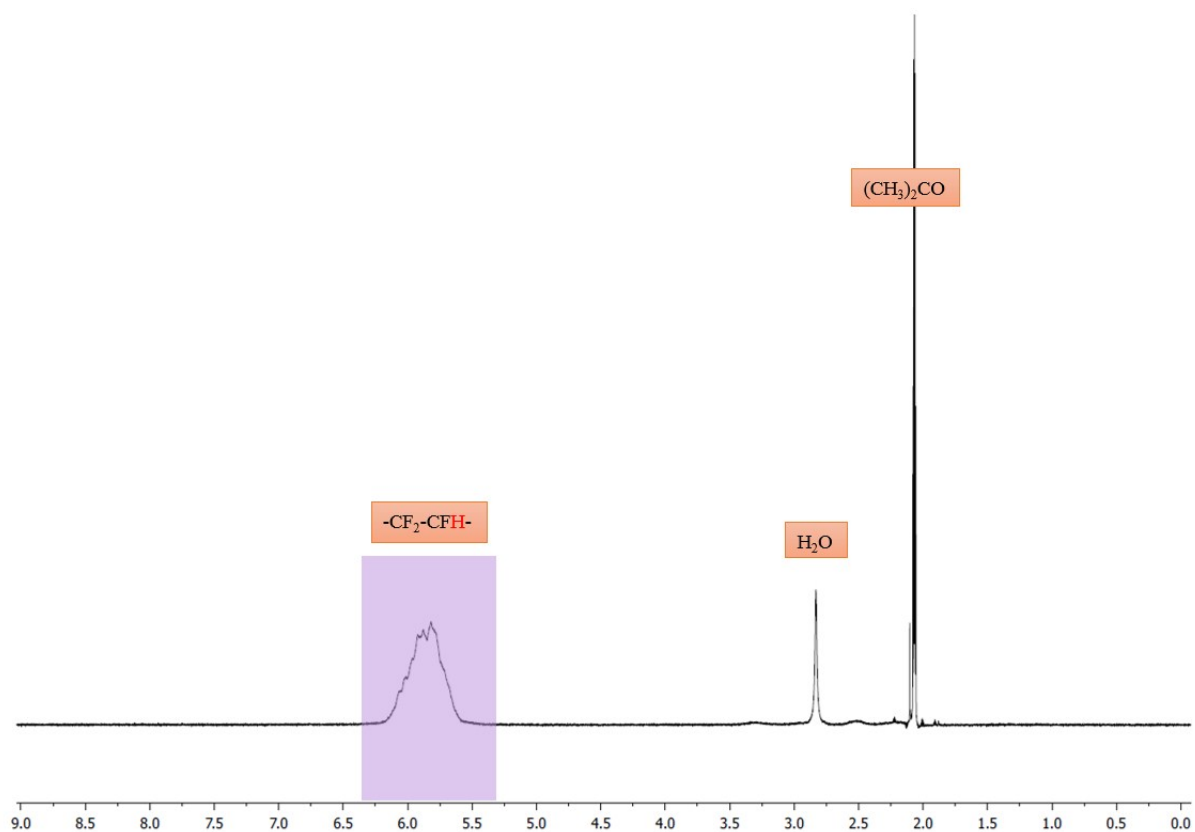
**Fig. S2** Evolution of expansion of -73 to -85 ppm zone in the  $^{19}\text{F}$  NMR spectra of PTrFE prepared by free radical homopolymerization of TrFE initiated by  $\cdot\text{CF}_3$  radical from PPFR in PFB at 83 °C (**P1-P4**, Table 1). The spectra were recorded in acetone- $d_6$ .



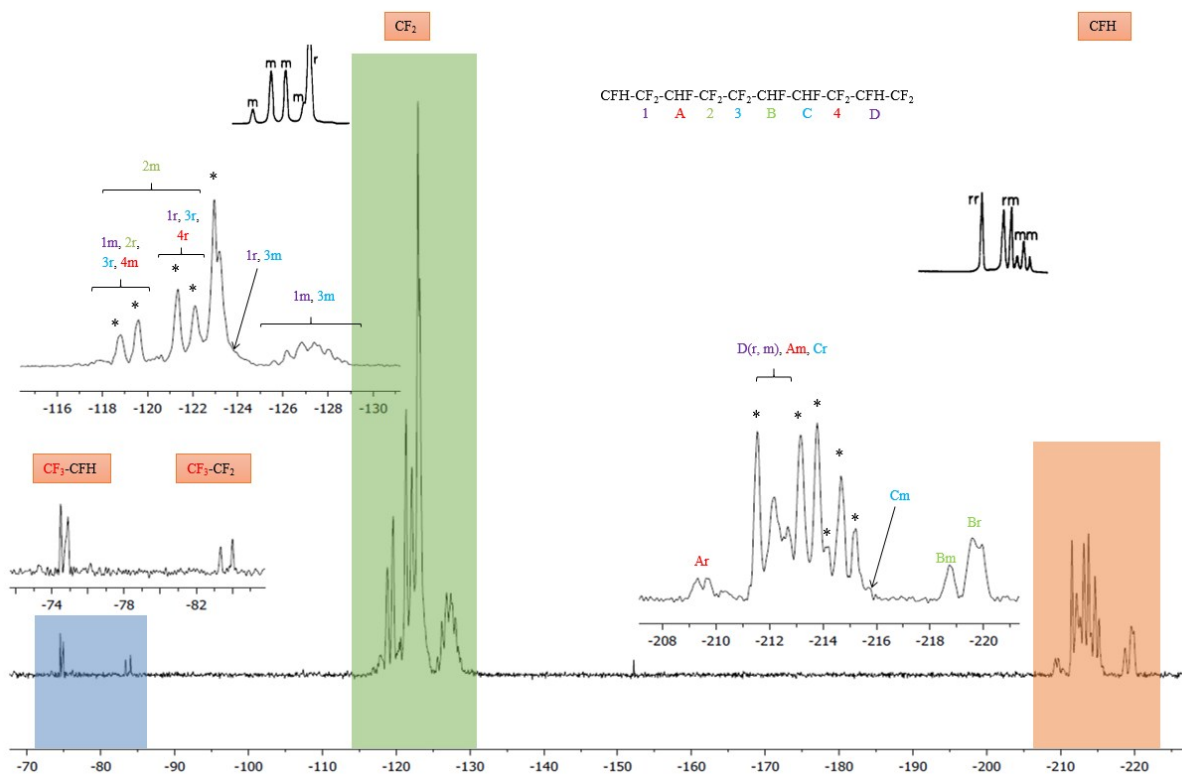
**Fig. S3**  $^1\text{H}$  NMR spectrum of  $\text{CF}_3\text{-PTrFE-CF}_3$  homopolymer prepared by radical polymerization of TrFE initiated by PPFR at  $83\text{ }^\circ\text{C}$  (**P2**, Table 1), recorded in acetone- $d_6$  at  $20\text{ }^\circ\text{C}$ . The signals at 2.05 and 2.84 ppm are assigned to acetone and water, respectively.



**Fig. S4**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of  $\text{CF}_3\text{-PTrFE-CF}_3$  homopolymer prepared by radical polymerization of TrFE initiated by PPFR at  $83\text{ }^\circ\text{C}$  (**P2**, Table 1), recorded in acetone- $d_6$  at  $20\text{ }^\circ\text{C}$ . The expansion in the  $-118$  to  $-129$  ppm range indicates the AB system from the geminal - $\text{CF}_2$ - fluorines in a meso stereochemical dyad.

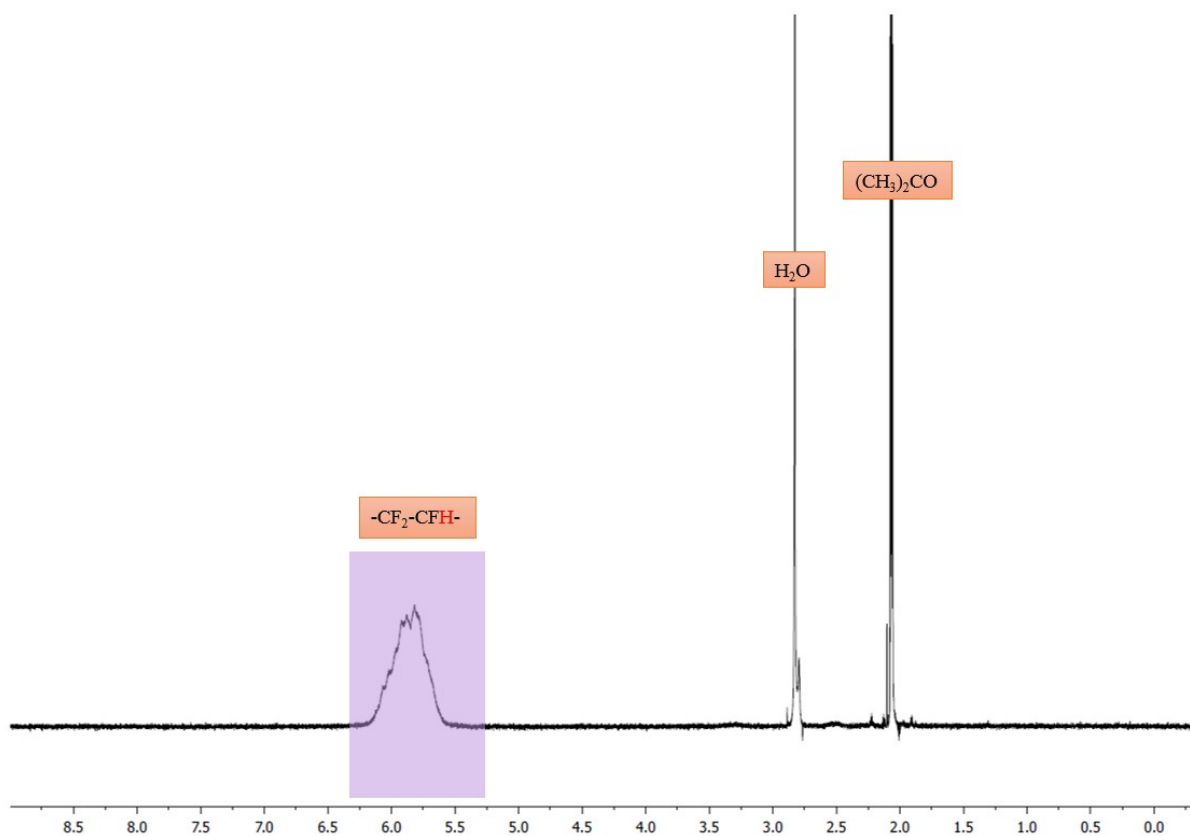


**Fig. S5**  $^1\text{H}$  NMR spectrum of  $\text{CF}_3\text{-PTrFE-CF}_3$  homopolymer prepared by radical polymerization of TrFE initiated by PPFR at  $83\text{ }^\circ\text{C}$  (**P3**, Table 1), recorded in acetone- $d_6$  at  $20\text{ }^\circ\text{C}$ . The signals at 2.05 and 2.84 ppm represent acetone and water, respectively.

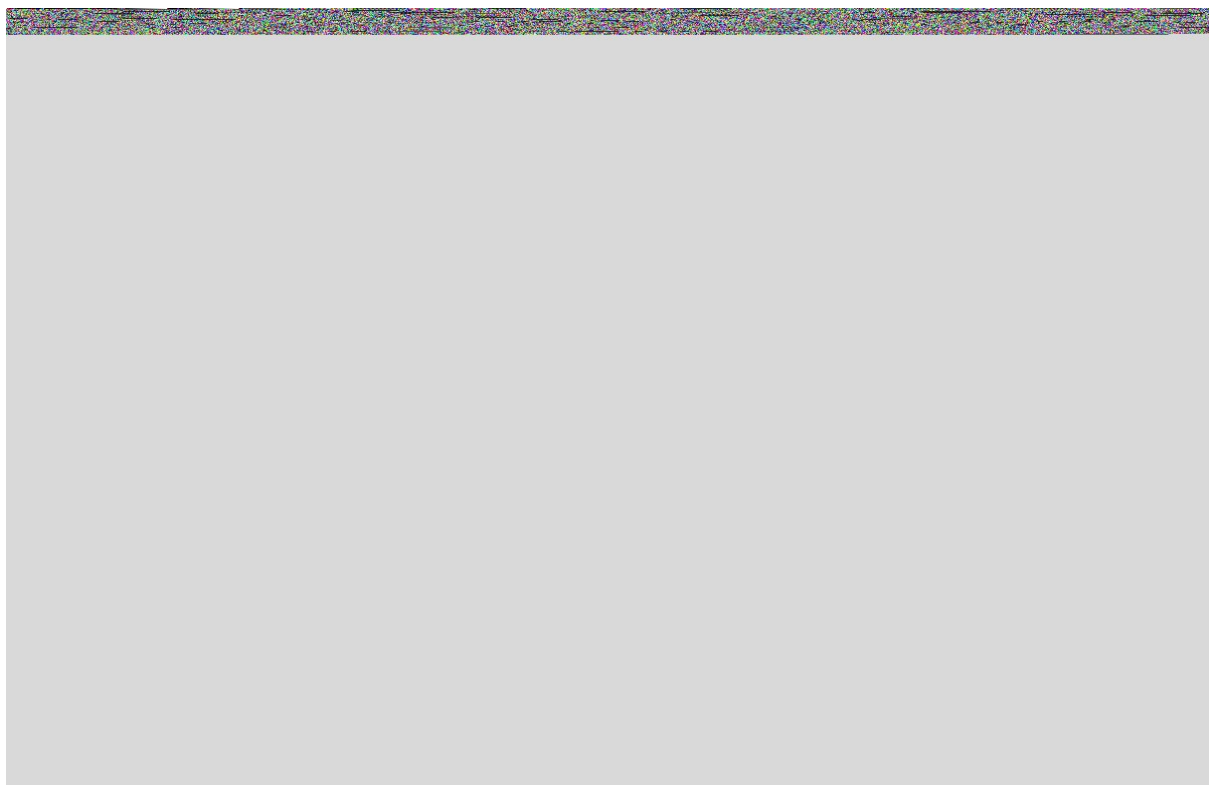


**Fig. S6**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of  $\text{CF}_3\text{-PTrFE-CF}_3$  homopolymer prepared by radical polymerization of TrFE initiated by PPFR at 83 °C (**P3**, Table 1), recorded in acetone- $d_6$  at 20 °C. The expansion in the -118 to -129 ppm range indicates the AB system from the geminal - $\text{CF}_2$ - fluorines in a meso stereochemical dyad.

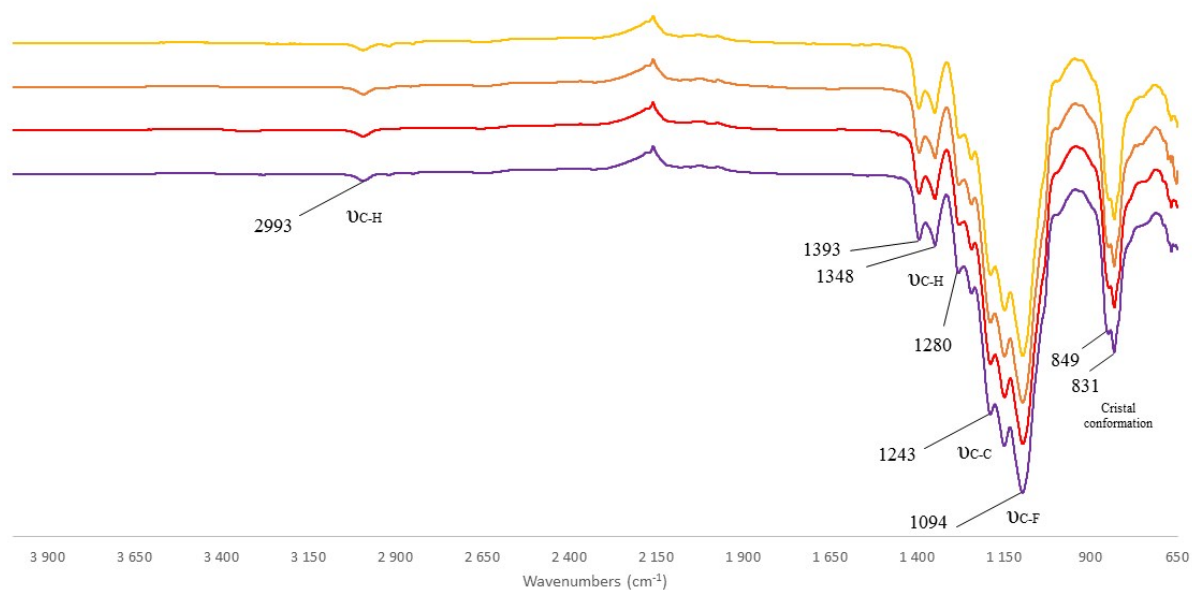




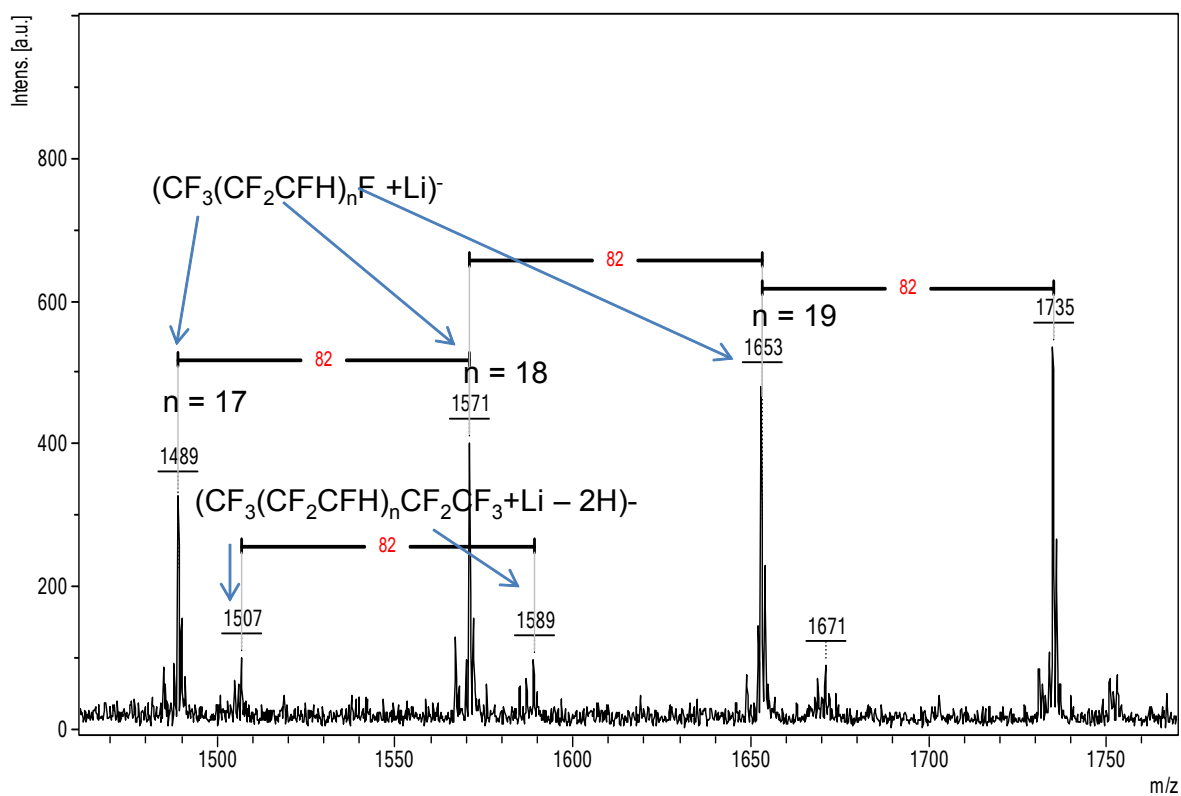
**Fig. S7**  $^1\text{H}$  NMR spectrum of  $\text{CF}_3\text{-PTrFE-CF}_3$  homopolymer prepared by radical polymerization of TrFE initiated by PPFR at  $83\text{ }^\circ\text{C}$  (**P4**, Table 1), recorded in acetone- $d_6$  at  $20\text{ }^\circ\text{C}$ . The signals at 2.05 and 2.84 ppm represent acetone and water, respectively.



**Fig. S8**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of  $\text{CF}_3\text{-PTrFE-CF}_3$  homopolymer prepared by radical polymerization of TrFE initiated by PPFR at 83 °C (**P4**, Table 1), recorded in acetone- $d_6$  at 20 °C. The expansion in the -118 to -129 ppm range indicates the AB system from the geminal - $\text{CF}_2$ - fluorines in a meso stereochemical dyad.



**Fig. S9** ATR-IR spectra of PTrFE prepared by free radical homopolymerization of TrFE initiated by  $\cdot\text{CF}_3$  radical from PPF<sub>6</sub> in PFB at 83 °C (**P1-P4**, Table 1).



**Fig. S10** Magnification of negative ion MALDI-TOF mass spectrum of PTrFE homopolymer prepared by radical polymerization of TrFE initiated by PPR at 83 °C (**P4**, Table 1), with DCTB as matrix and LiCl as cationic agent.  $2063 = (24 \times 82) + 69 + 19 + 7$  (Li+), the interpeak distance of  $m/z = 82$  corresponds to the mass of the TrFE repeat unit.