Electronic Supplementary Material (ESI) for Polymer Chemistry.

Thermal and photo RAFT Polymerization of 2,2,2-trifluoroethyl α-fluoroacrylate

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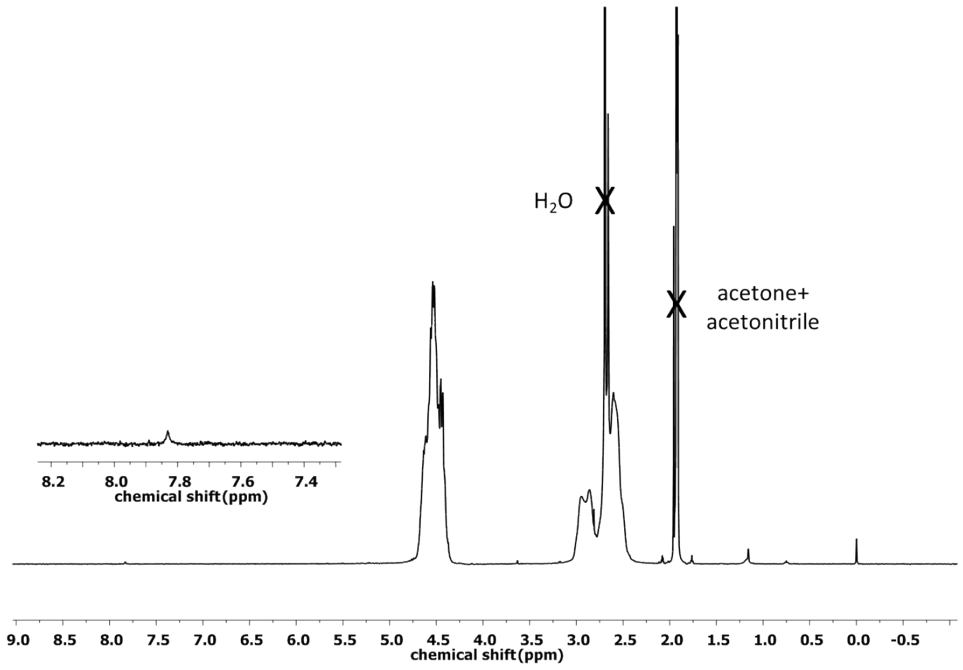

Figure S1. ^{1}H NMR spectrum of purified poly(FATRIFE) using CTA_1 as the chain transfer agent (recorded in acetone-d_6).

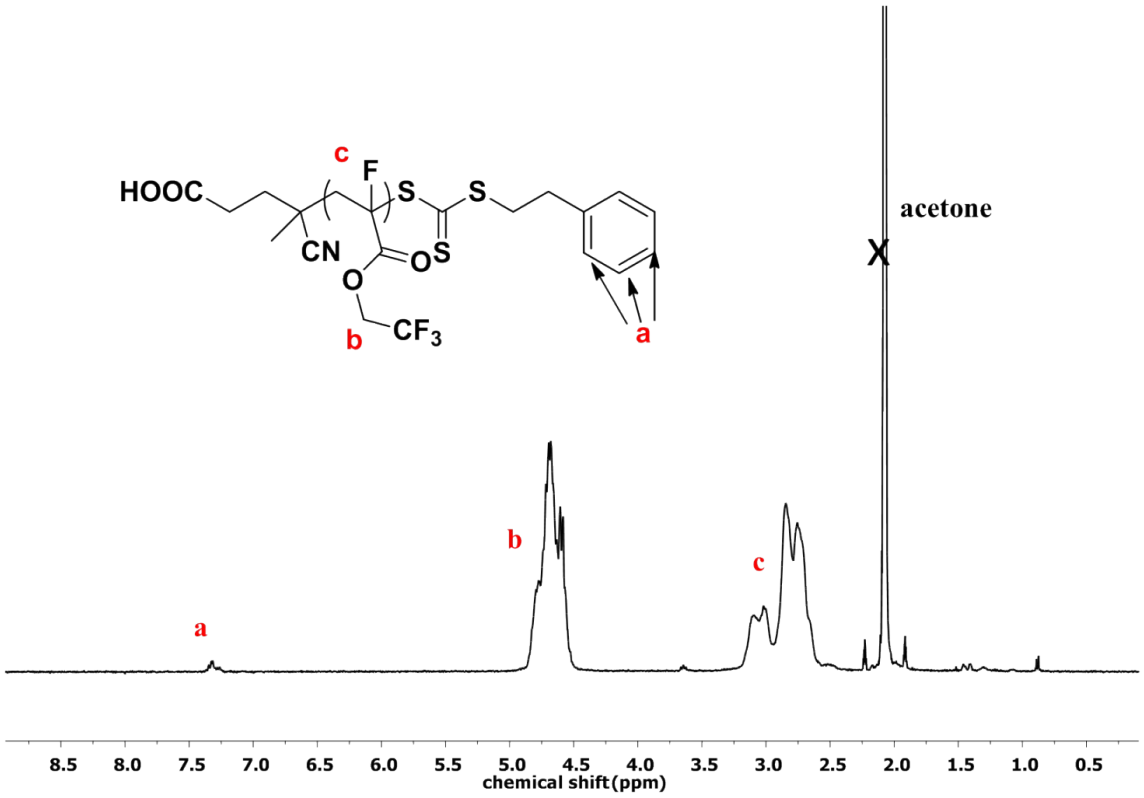

Figure S2. ^{1}H NMR spectrum of purified Poly(FATRIFE) synthesized by thermal RAFT (**Table 1**, Entry 2, recorded in acetone-d_6).

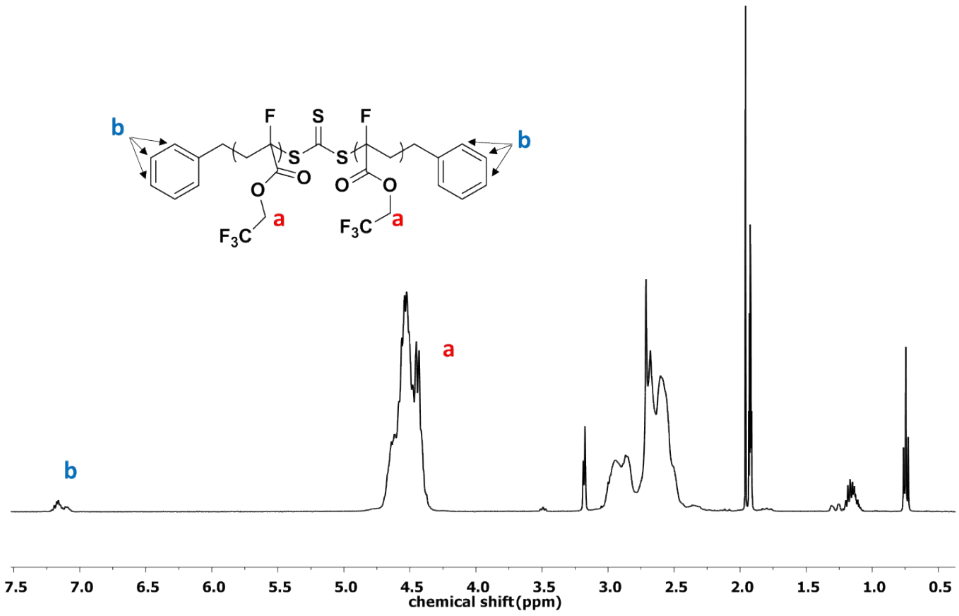

Figure S3. 1H NMR spectrum of purified poly(FATRIFE) using CTA_3 as chain transfer agent (recorded in acetone-d_6, **Table 1**, Entry 3). The ratio of FATRIFE unit and aromatic chain ends enables to calculate the degree of polymerization as follows:

Degree of polymerization = $(I_a/2)/(I_b/10)$,

where I_a and I_b represent the integrals of protons **a** and **b**, respectively.

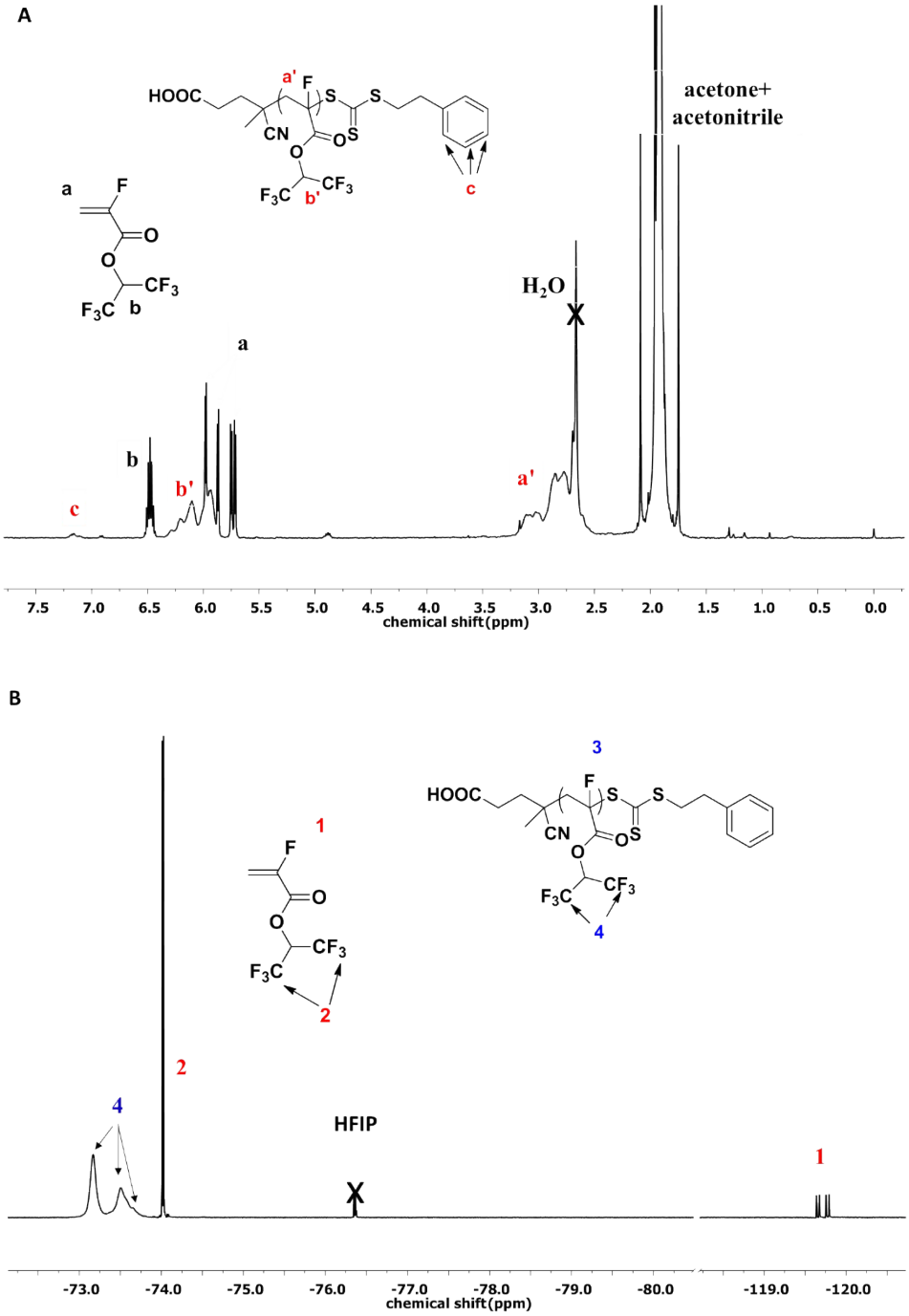

Figure S4. NMR spectra of crude product obtained in the photoRAFT polymerization of FAHFiP using CTA2 as the chain transfer agent (recorded in acetone-d_6, **Table 2**, Entry 5). A: ^{1}H NMR spectrum; B ^{19}F NMR spectrum (expansion from -72 ppm to -121 ppm). Converision of FATRIFE and MAF-TBE were calculated from the ^{19}F NMR spectrum. $Conv_{FAHFiP} = I_4/(I_2+I_4)\times100\%$. $[FAHFiP]_0/[CTA_2]_0=100/1$. I_2 and I_4 stand for the integrals of fluorine atoms **2** and **4**, respectively. Two white LED lamps were used as light source. Polymerization was carried out in acetonitrile at room temperature.

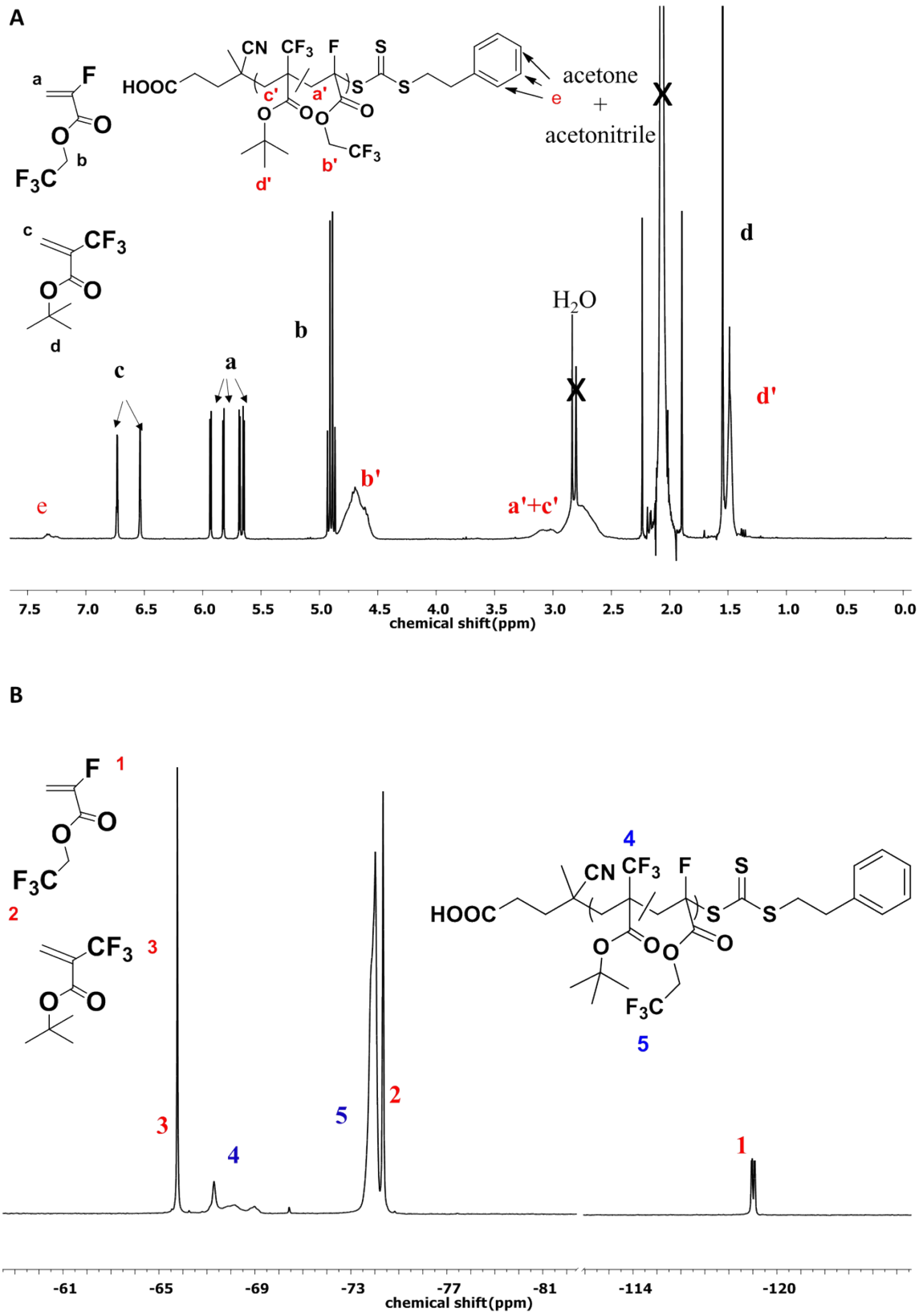

Figure S5. NMR spectra of crude product obtained in the photoRAFT copolymerization of FATRIFE and MAF-TBE using CTA_2 as the chain transfer agent (in acetone-d_6, **Table 2**, Entry 6). A) ^{1}H NMR spectrum; B) ^{19}F NMR spectrum. Conversions of FATRIFE and MAF-TBE were calculated from ^{19}F NMR

spectrum. $Conv_{FATRIFE}$ $=I_6/(I_6+I_2)\times100\%$, $conv_{MAF\text{-}TBE}=I_4/(I_3+I_4)\times100\%$.$[FATRIFE]_0/[MAF\text{-}TBE]_0/[CTA_2]_0$=80/20/1. Two white LED lamps were used as light source. Polymerization was carried out in acetonitrile at room temperature.

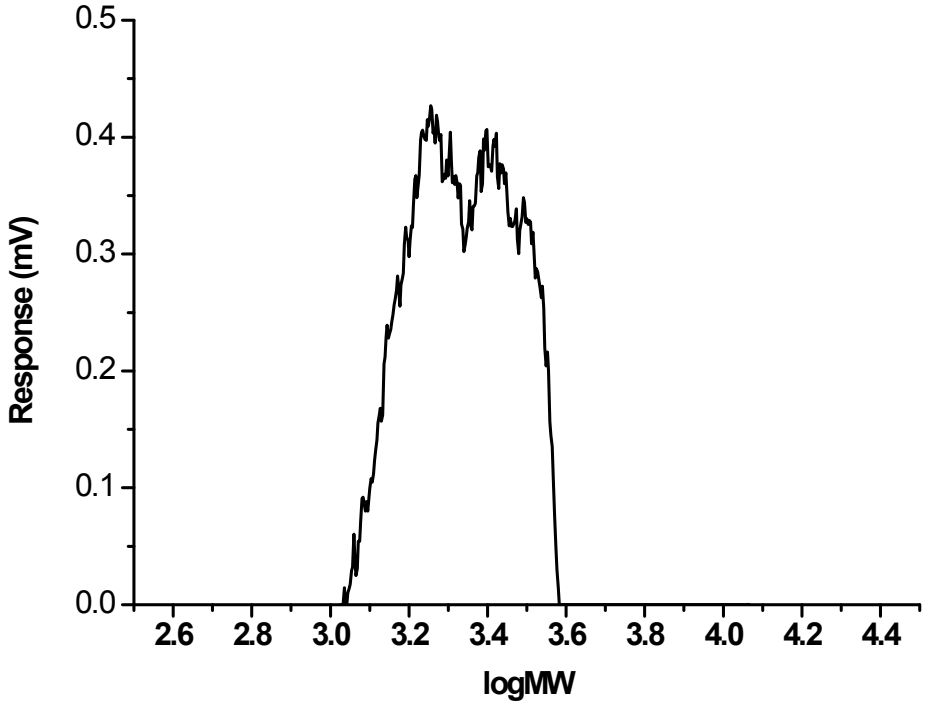

Figure S6. Chromatogram (RI signal) of polymer sample obtained by photoRAFT in the kinetics experiment at t = 2h.

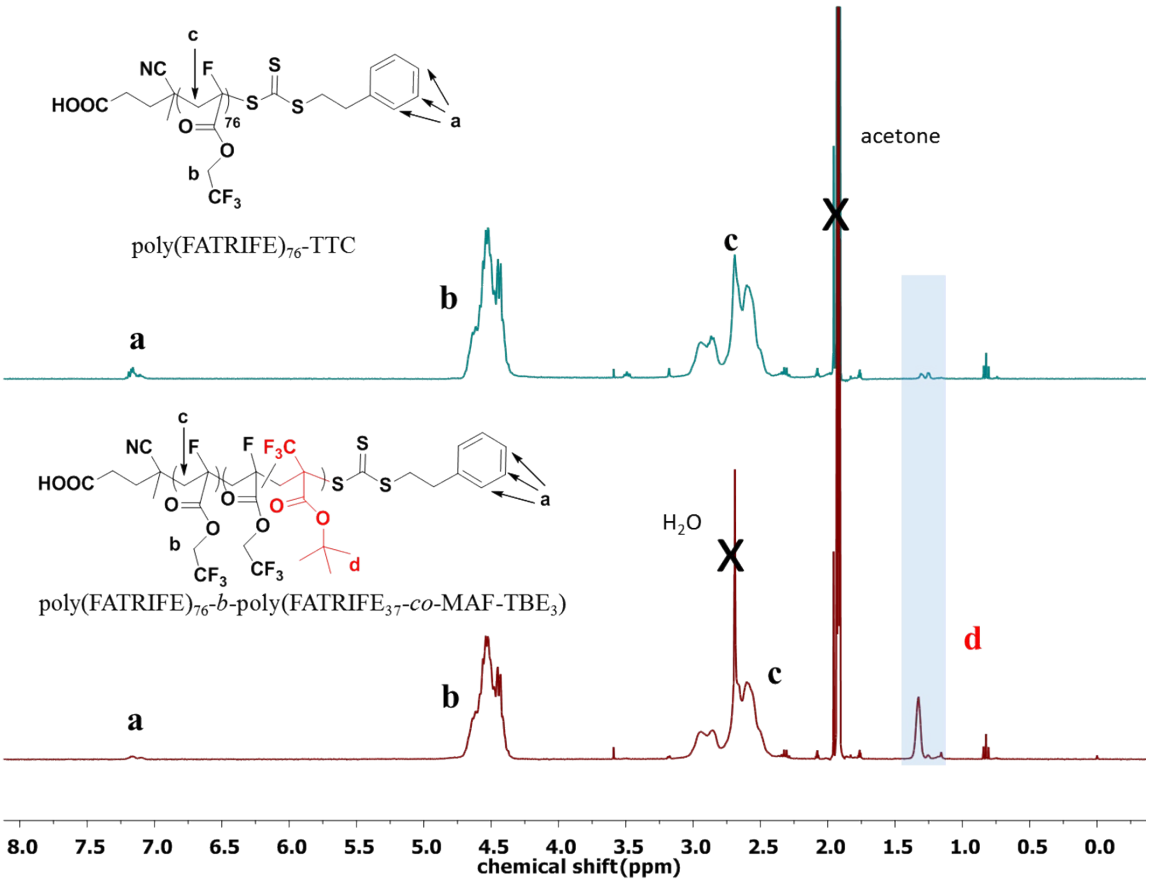

Figure S7. ^{1}H NMR spectra (recorded in acetone-d_6) of the polymers before (blue, poly(FATRIFE)$_{76}$-TTC) and after (red-brown, poly(FATRIFE)$_{76}$-*b*-poly(FATRIFE$_{37}$-*co*-MAF-TBE$_3$) in situ chain extension. The MAF-TBE molar content in the diblock copolymer was 2.6%.

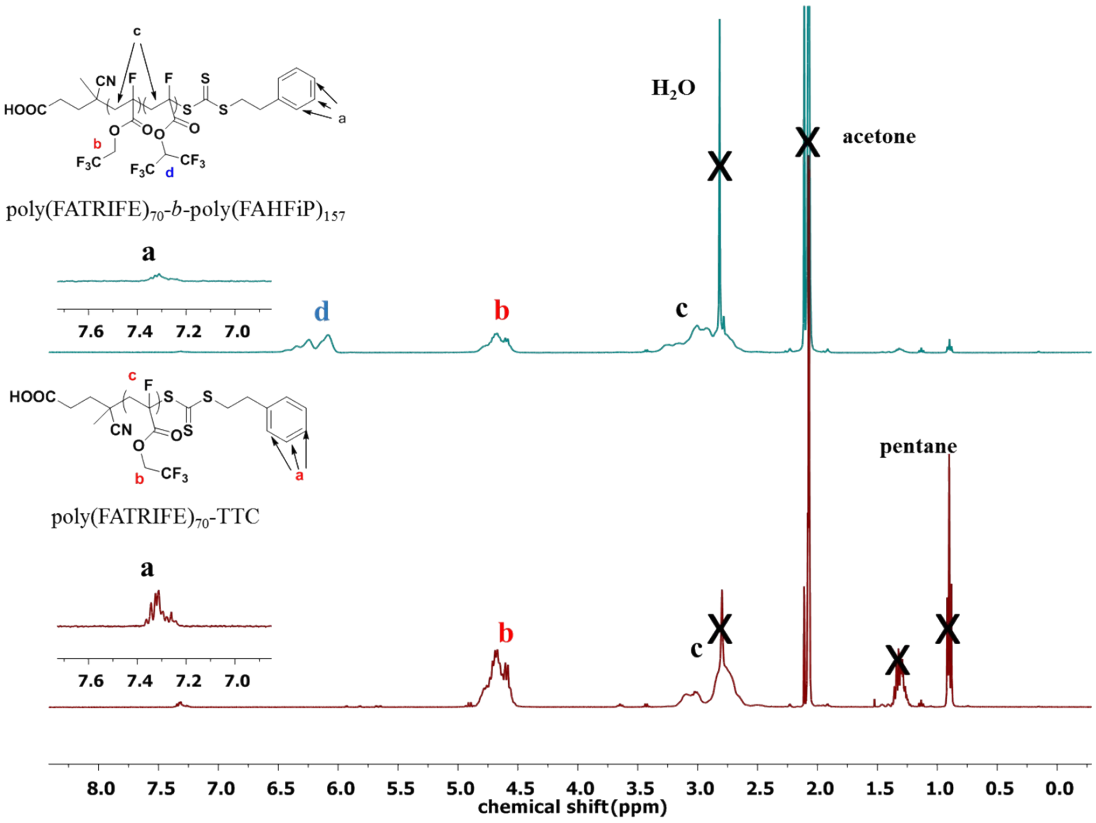

Figure S8. ^{1}H NMR spectra (recorded in acetone-d_6) of the poly(FATRIFE)$_{70}$-*b*-poly(FAHFiP)$_{157}$ block copolymer and macro chain transfer agent (poly(FATRIFE)$_{70}$-TTC) in the chain extension experiment. Purified poly(FATRIFE)$_{70}$-TTC was synthesized by photoRAFT polymerization method and used as macro chain transfer agent.

Equations used in the calculation of the conversions of different monomers:

FATRIFE: supplied in equations 1 and 2 in main manuscript

FAHFiP:

From ^{1}H NMR spectroscopy,

$$Conv_{(FAHFiP)}\,(\%) = 100 - \frac{\int_{5.61}^{5.90} CH = \ of\ FAHFiP}{\left(\int_{6.48}^{5.96} (CH(CF_3) of\ FAHFiP\ unit\ in\ polymer + CH = \ of\ FAHFiP\ unit) + \int_{6.69}^{6.49} H(CF_3) of\ F\right.} \times 100$$

(**Equation S1**)

From ^{19}F NMR spectroscopy,

$$Conv_{(FAHFiP)}\,(\%) = 100 - \frac{\int_{-73.90}^{-74.17} CF_3\ of\ FAHFiP\ monomer}{\left(\int_{-72.89}^{-73.90} CF_3\ of\ FAHFiP\ unit\ in\ the\ polymer + \int_{-73.90}^{-74.17} CF_3\ of\ FATRIFE\ monomer\right)} \times 100$$

(**Equation S2**)

MAF-TBE:

From ^{1}H NMR:

$$Conv_{(MAF-TBE)}\,(\%) = 100 - \frac{(\int_{6.44}^{6.88} CH_2\ of\ MAF-TBE\ monomer)/2}{\left(\int_{1.41}^{1.52} CH_3\ of\ MAF-TBE\ unit\ in\ polymer + \int_{1.52}^{1.62} CH_3\ of\ MAF-TBE\ monomer\right)/9} \times 100$$

(**Equation S3**)

From ^{19}F NMR spectroscopy:

$$Conv_{(MAF-TBE)}\,(\%) = 100 - \frac{\int_{-65.5}^{-66.8} CF_3\ of\ MAF-TBE\ monomer}{\left(\int_{-65.5}^{-66.8} CF_3\ of\ MAF-TBE\ monomer + \int_{-66.80}^{-69.80} CF_3\ of\ MAF-TBE\ unit\ in\ polymer\right)} \times 100$$

(**Equation S4**)

Calculation of MAF-TBE content in the polymer:

Content of MAF-TBE mol% =

$$\frac{\int_{-66.80}^{-69.80} CF_3\ of\ MAF-TBE\ unit\ in\ polymer}{\left(\int_{-66.80}^{-69.80} CF_3\ of\ MAF-TBE\ unit\ in\ the\ polymer + \int_{-73.43}^{-74.76} CF_3\ of\ FATRIFE\ unit\ in\ polymer\right)}$$ (**Equation S5**)