Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information for

Accessing Libraries of Bifunctional Block Copolymers Using Two Distinct Pentafluorophenyl Moieties

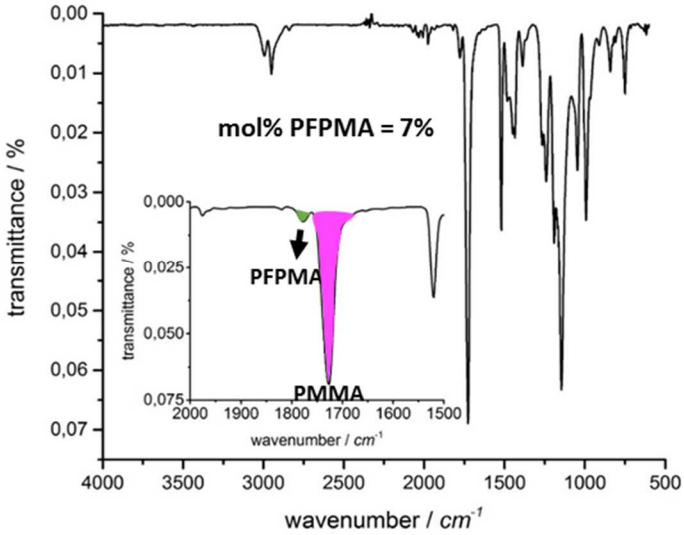
Divya Varadharajan,[a,b] Guillaume Delaittre [a,b,*]

[a]*Institute of Toxicology and Genetics, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*

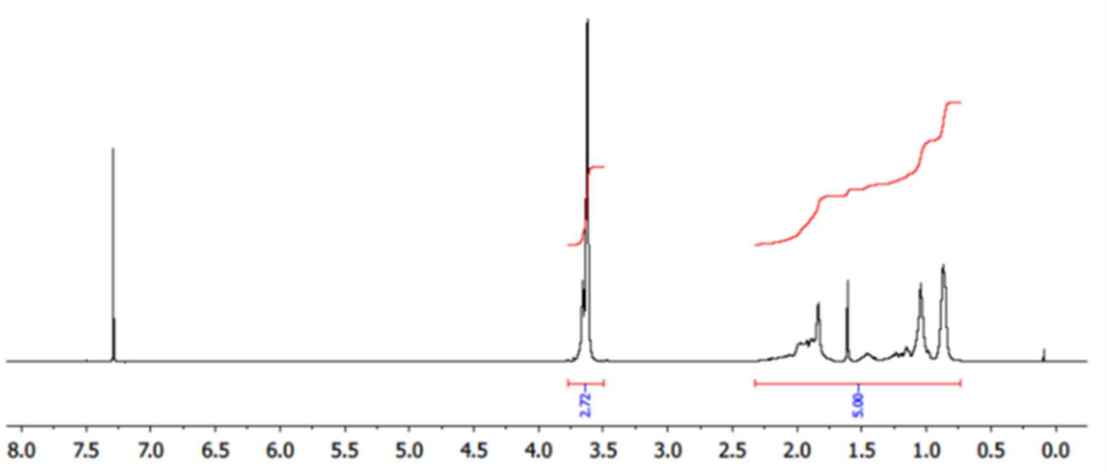
[b]*Preparative Macromolecular Chemistry, Institute for Technical Chemistry and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), Engesserstrasse 15, 76131 Karlsruhe, Germany*

guillaume.delaittre@kit.edu

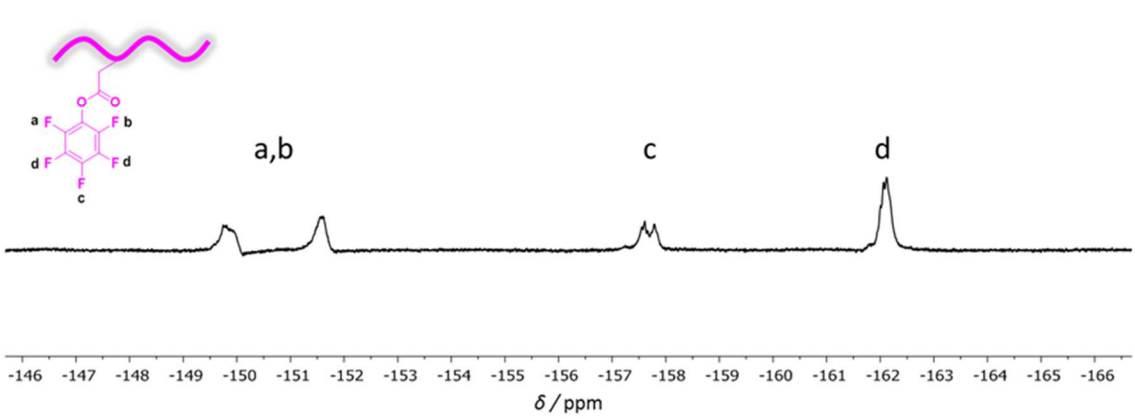
A


mol% PFPMA = 7%
transmittance / %
wavenumber / cm-1
PFPMA
PMMA

B



C


a,b
c
d
δ / ppm

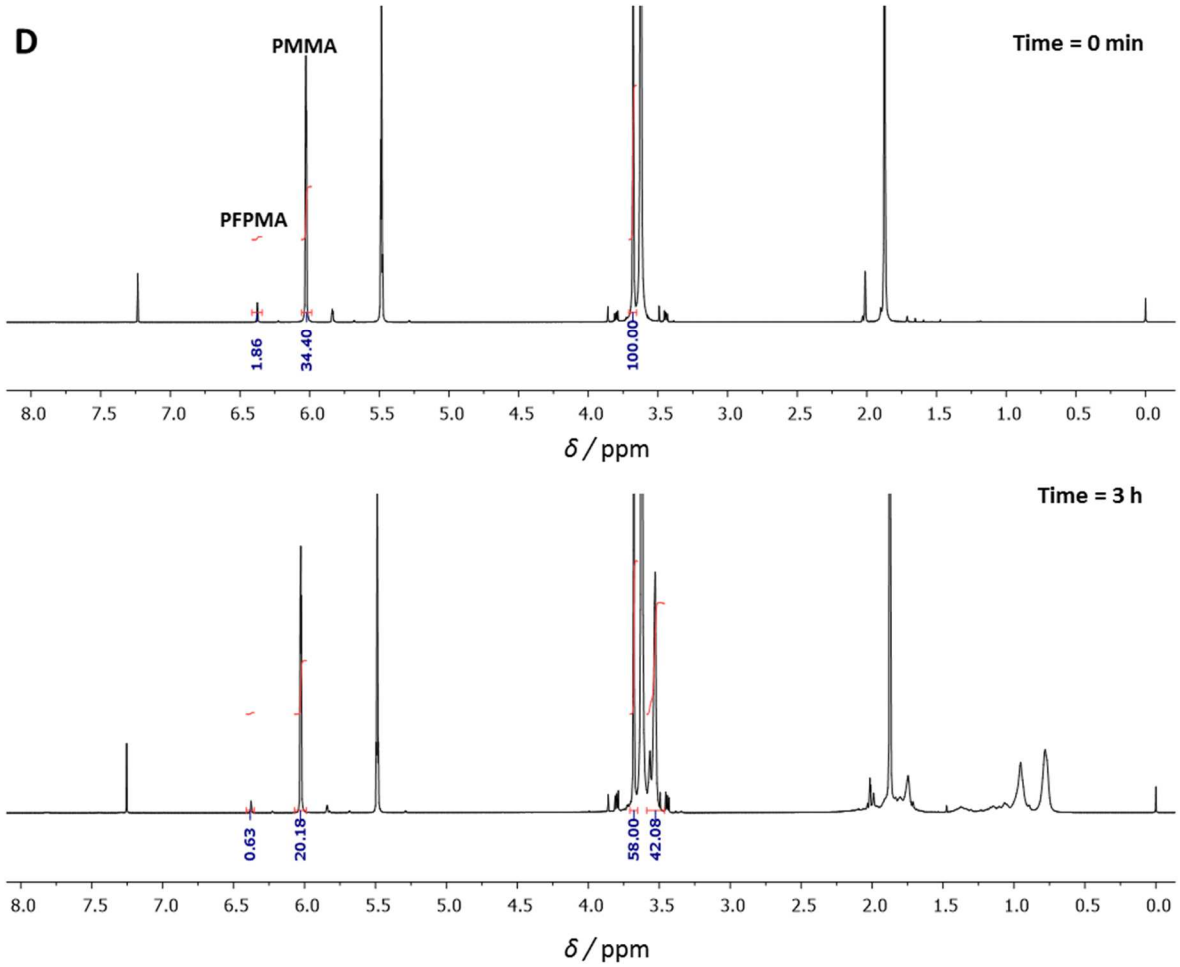


Figure S1. (A) IR spectrum of **1** showing the characteristic absorptions of –C=O stretches of PMMA and PFPMA. (B) ^{1}H NMR and (C) ^{19}F NMR spectra of **1** (purified). (D) ^{1}H NMR spectrum of the crude synthesis mixture of **1** at 0 min (top) and 3 h (bottom).

Calculation of PFPMA content in the macroRAFT agent P(MMA-*stat*-PFPMA) 1

The amount of PFPMA incorporated in macroRAFT agent **1** was obtained as an average of the values calculated from NMR and IR data as previously reported by Zhang *et al*.[1] Below are the calculations for data obtained from IR and NMR.

From IR spectroscopy: On integrating the areas of PFPMA (0.164) and PMMA (2.346) absorption bands in green and pink, respectively, the amount of incorporated PFPMA was determined to be **7 mol%** (Figure S1a).

From NMR: Two methods of calculation based on NMR spectroscopy were employed: (i) from the NMR spectrum of the crude polymerization mixture, allowing us to determine the respective conversions in PFPMA and MMA (Figure S1d) and (ii) from the NMR spectrum of the purified macroRAFT **1** by comparing the integral values of the methyl ester peak of MMA units to those of the backbone (Figure S1b), respectively.

Method (i)

Conversion of PFPMA = (1.86-0.63)/1.87 = 66%

Conversion of PMMA = (34.40-20.18)/34.40 = 41.3%

Ratio of PFPMA to MMA introduced into the reaction mixture = 5:95

Therefore, mol% PFPMA incorporated = (0.66×0.05)/[(0.66×0.05)+(0.413×0.95)] = **7.8 mol%**

Method (ii)

Mol% PFPMA = $1 - [\frac{2.72}{3.0}] \times 100$ = **9.3 mol%**

As stated by Zhang et al., IR spectroscopy provides an overestimated value and NMR an underestimated value due to their noise reductions and baseline corrections. Therefore an average of **8 mol%** was considered as a plausible fraction of PFPMA in the macroRAFT agent.

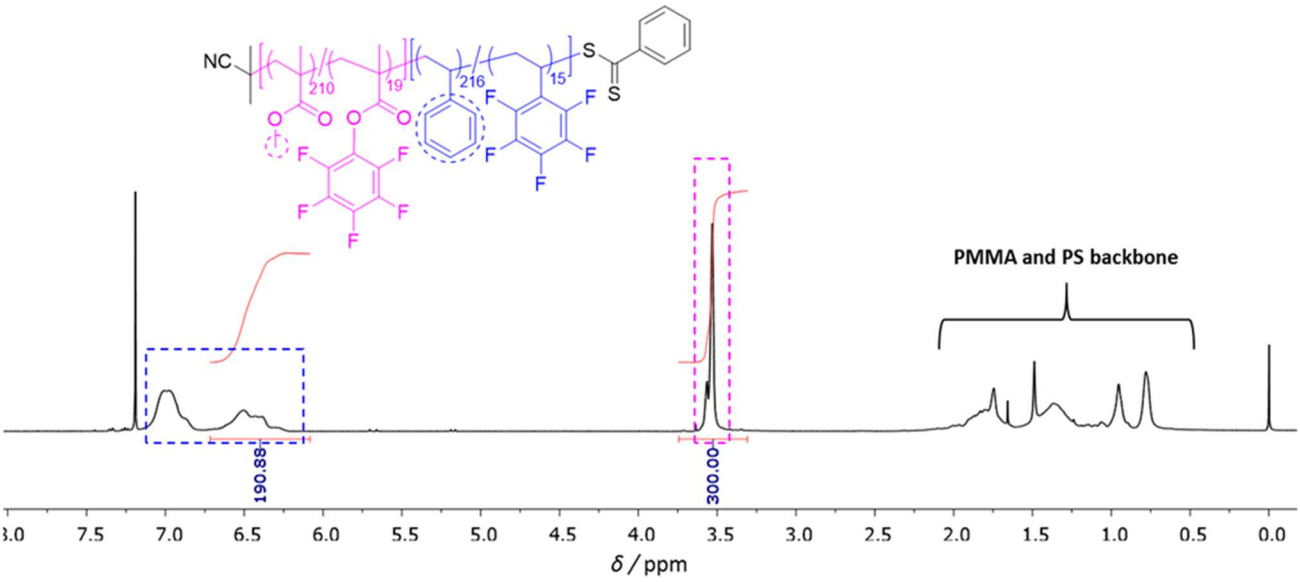


Figure S2. ^{1}H NMR spectrum of block copolymer **2**.

Calculation of the number-average molar mass of 2 using NMR ($M_{n,NMR}$)

From Figure S2: For 1 MMA unit, block copolymer **2** contains 0.954 styrene units.

Molar mass of the PS block = $(\frac{M_{n,SEC}(PMMA\ \mathbf{1}) - MW(end\ groups)}{MW(MMA)} \times \frac{styrene}{MMA} ratio \times MW(styrene)$

$= (\frac{(26000 - 221.34)}{100.12}) \times 0.954 \times 104.15$ = 25800 g/mol;

Hence, $M_{n,NMR}$**(2)** = 25800 + 26000 = 51800 g mol^{-1} = ~ 52,000 g mol^{-1}

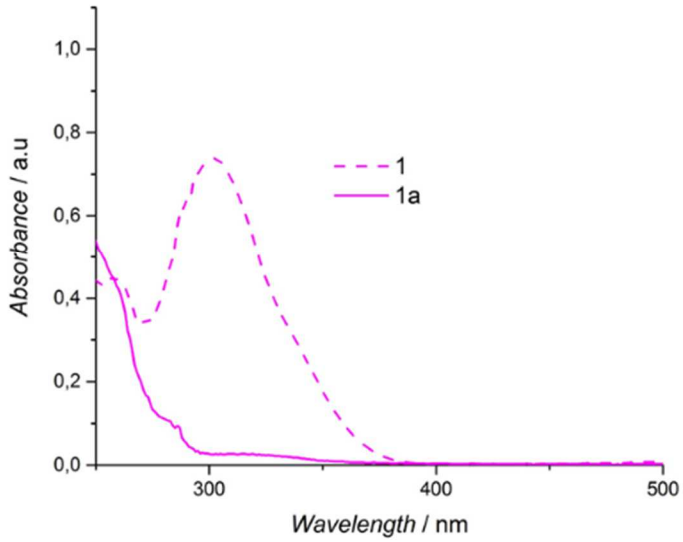


Figure S3. UV–Vis spectra of **1** before (dashed line) and after (solid line, **1a**) end group capping with 2-methoxy-6-methylbenzaldehyde.

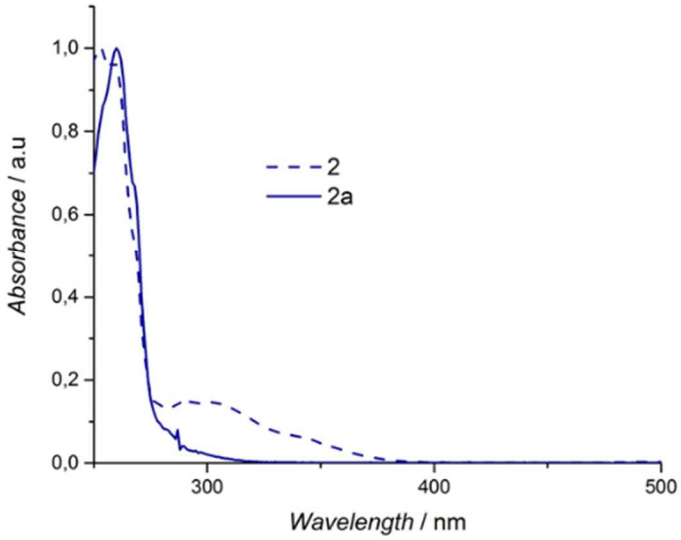


Figure S4. UV–Vis spectra of **2** before (dashed line) and after (dashed line, **2a**) end group capping with 2-methoxy-6-methylbenzaldehyde.

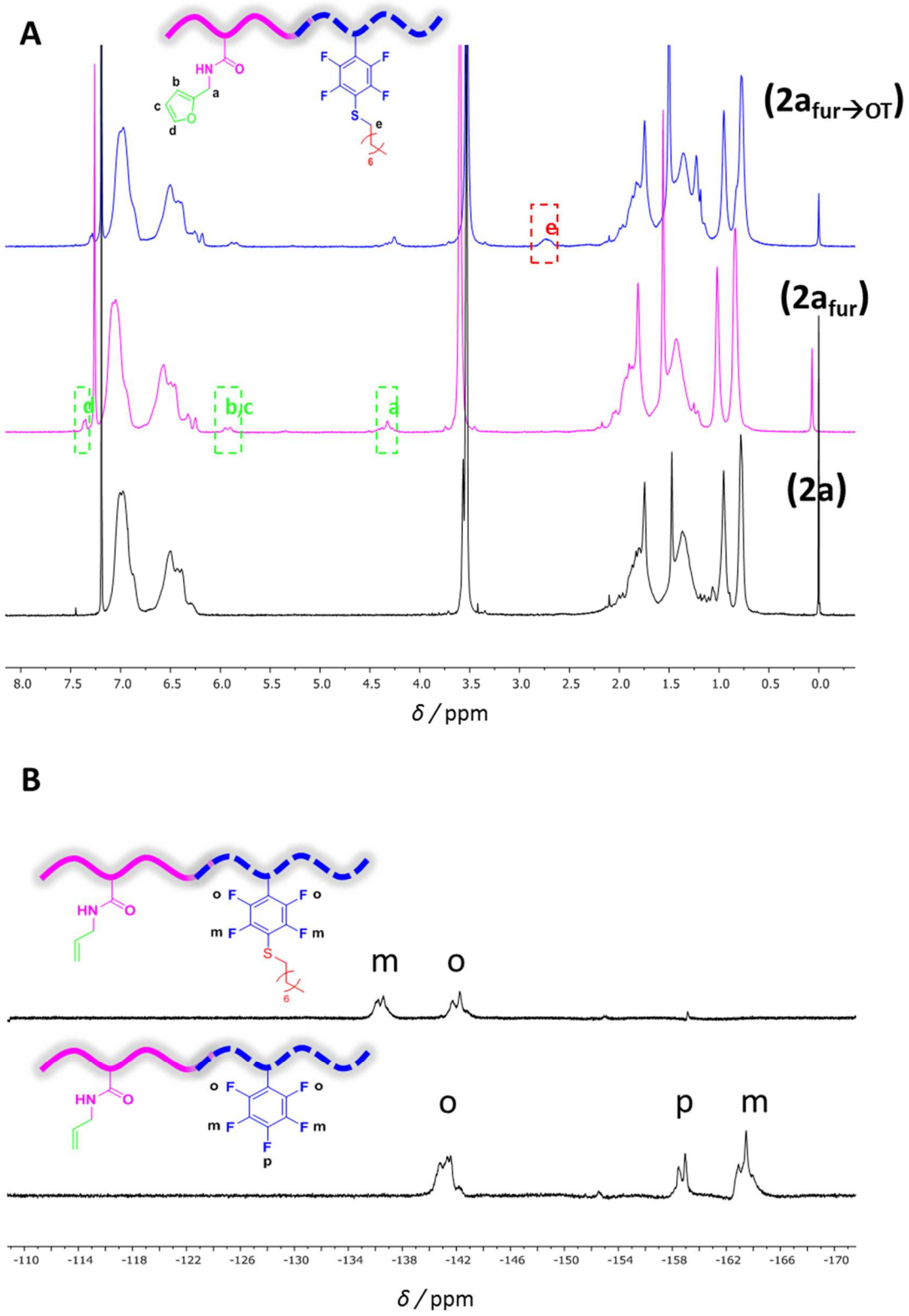


Figure S5. (A) ^{1}H NMR spectra of block copolymers **2a** (black), **2a$_{fur}$** (pink), and **2a$_{fur→OT}$** (blue). (B) ^{19}F NMR spectra of block copolymers **2a$_{fur}$** (bottom) and **2a$_{fur→OT}$** (top).

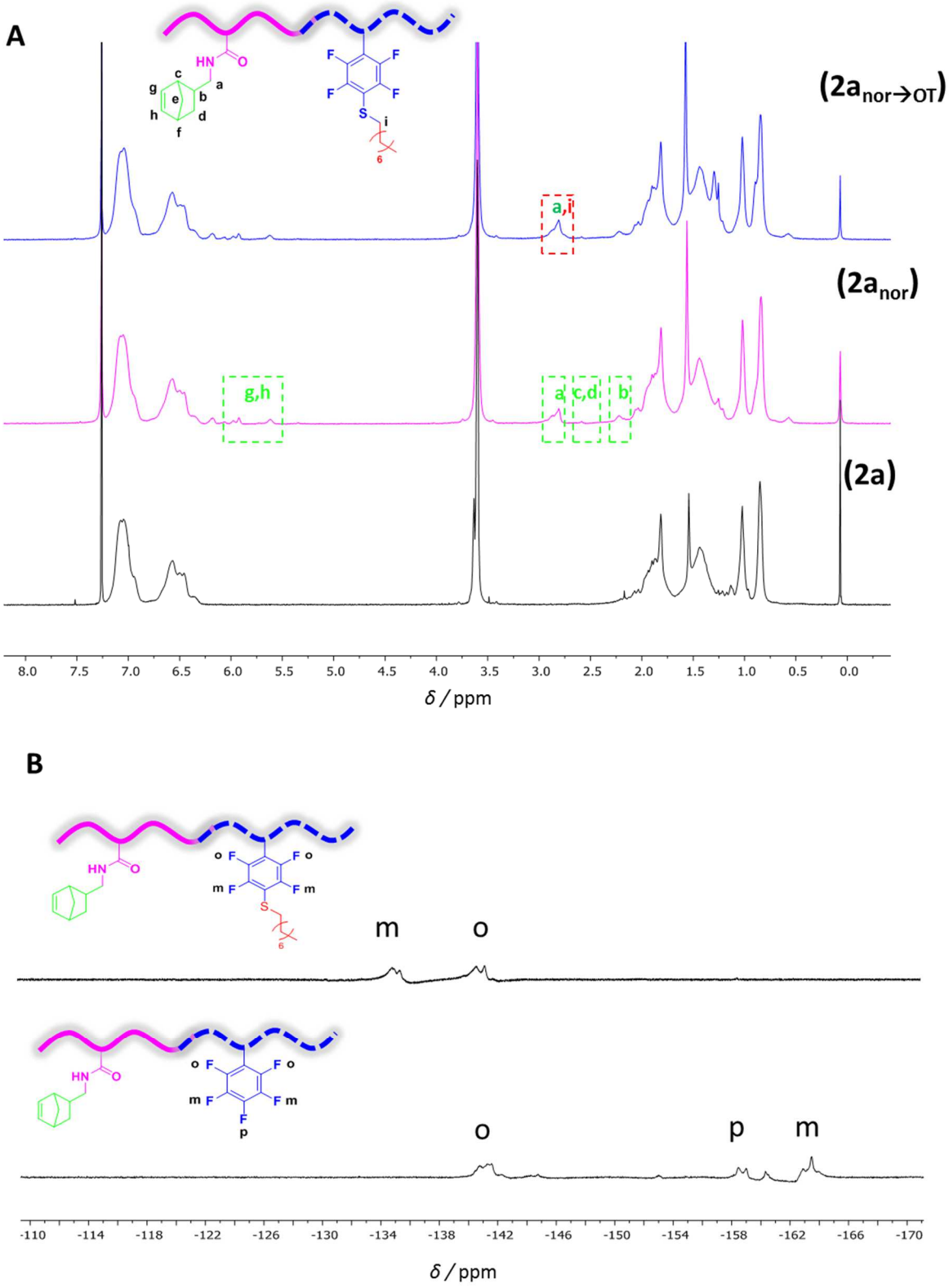


Figure S6. (A) ^{1}H NMR spectra of block copolymers **2a** (black), **2a**$_{nor}$ (pink), and **2a**$_{nor→OT}$ (blue). (B) ^{19}F NMR spectra of block copolymers **2a**$_{nor}$ (bottom) and **2a**$_{nor→OT}$ (top).

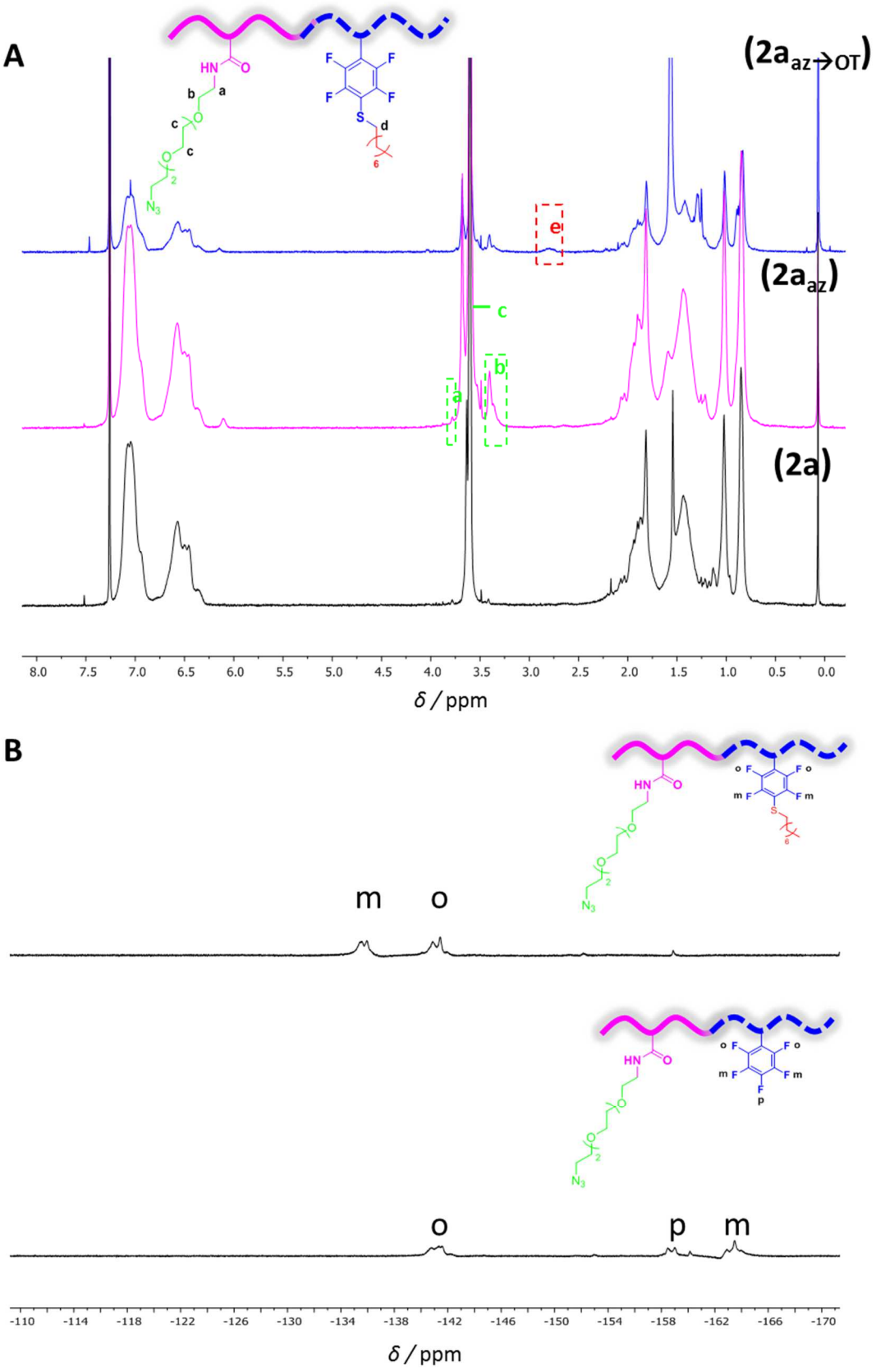


Figure S7. (A) ^{1}H NMR spectra of block copolymers **2a** (black), **2a$_{az}$** (pink), and **2a$_{az\rightarrow OT}$** (blue). (B) ^{19}F NMR spectra of block copolymers **2a$_{az}$** (bottom) and **2a$_{az\rightarrow OT}$** (top).

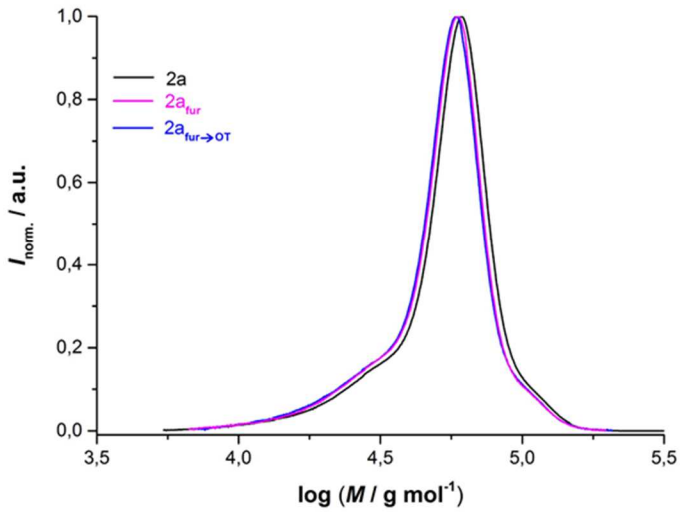


Figure S8. SEC traces of block copolymers **2a** (black), **2a**$_{fur}$ (pink), and **2a**$_{fur\rightarrow OT}$ (blue).

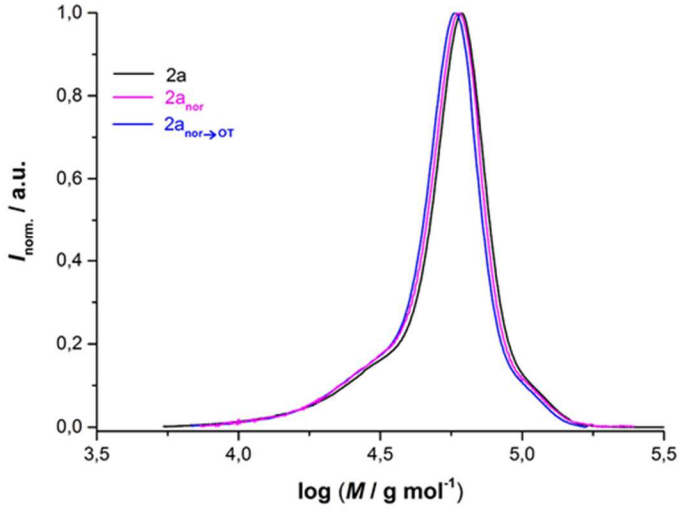


Figure S9. SEC traces of block copolymers **2a** (black), **2a**$_{nor}$ (pink), and **2a**$_{nor\rightarrow OT}$ (blue).

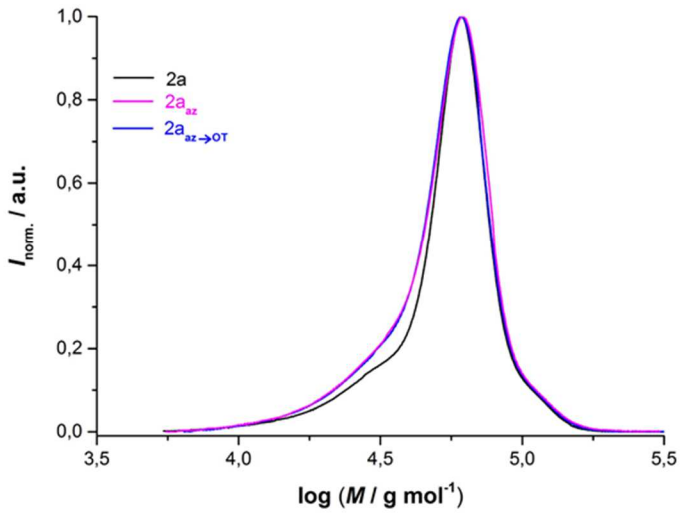


Figure S10. SEC traces of block copolymers **2a** (black), **2a$_{az}$** (pink), and **2a$_{az\rightarrow OT}$** (blue).

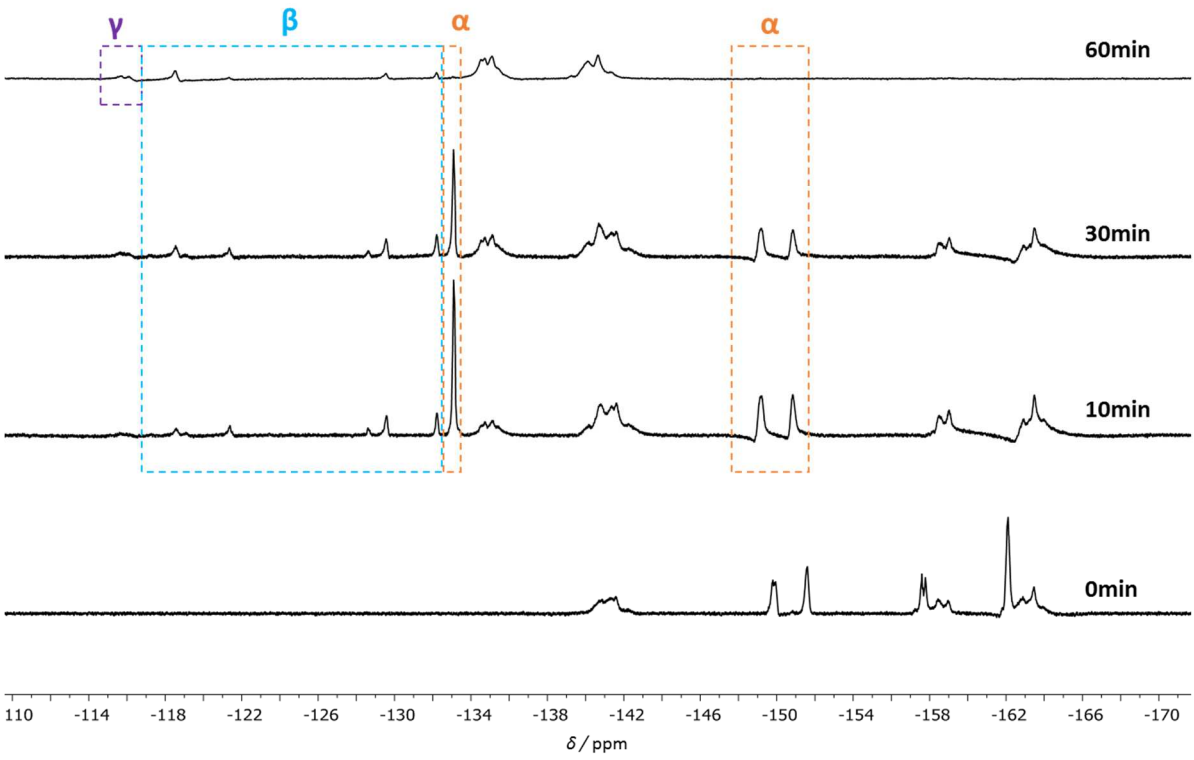


Figure S11. ^{19}F NMR of **2a** at various time intervals in the presence of 5 eq. mercaptoethanol and 1 eq. DBU at RT. α represents the PFPMA *para*-substituted species while β represents that of mono *meta*-substituted and γ that of *meta* disubstituted.

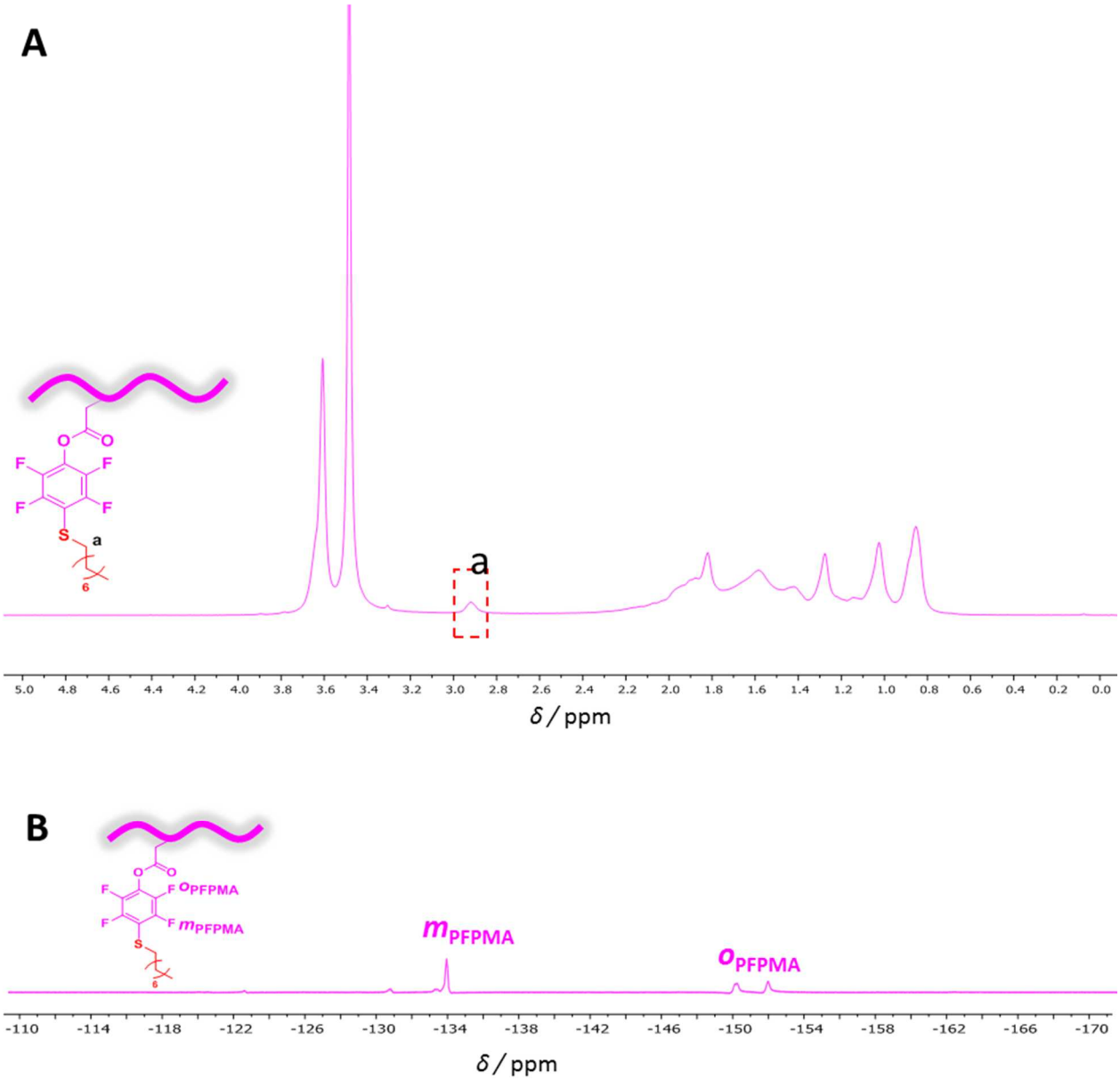


Figure S12. ^{1}H (A) and ^{19}F (B) NMR spectra of **1a** after reaction with 1 eq. of OT per unit of PFPMA under PFTR standard conditions.

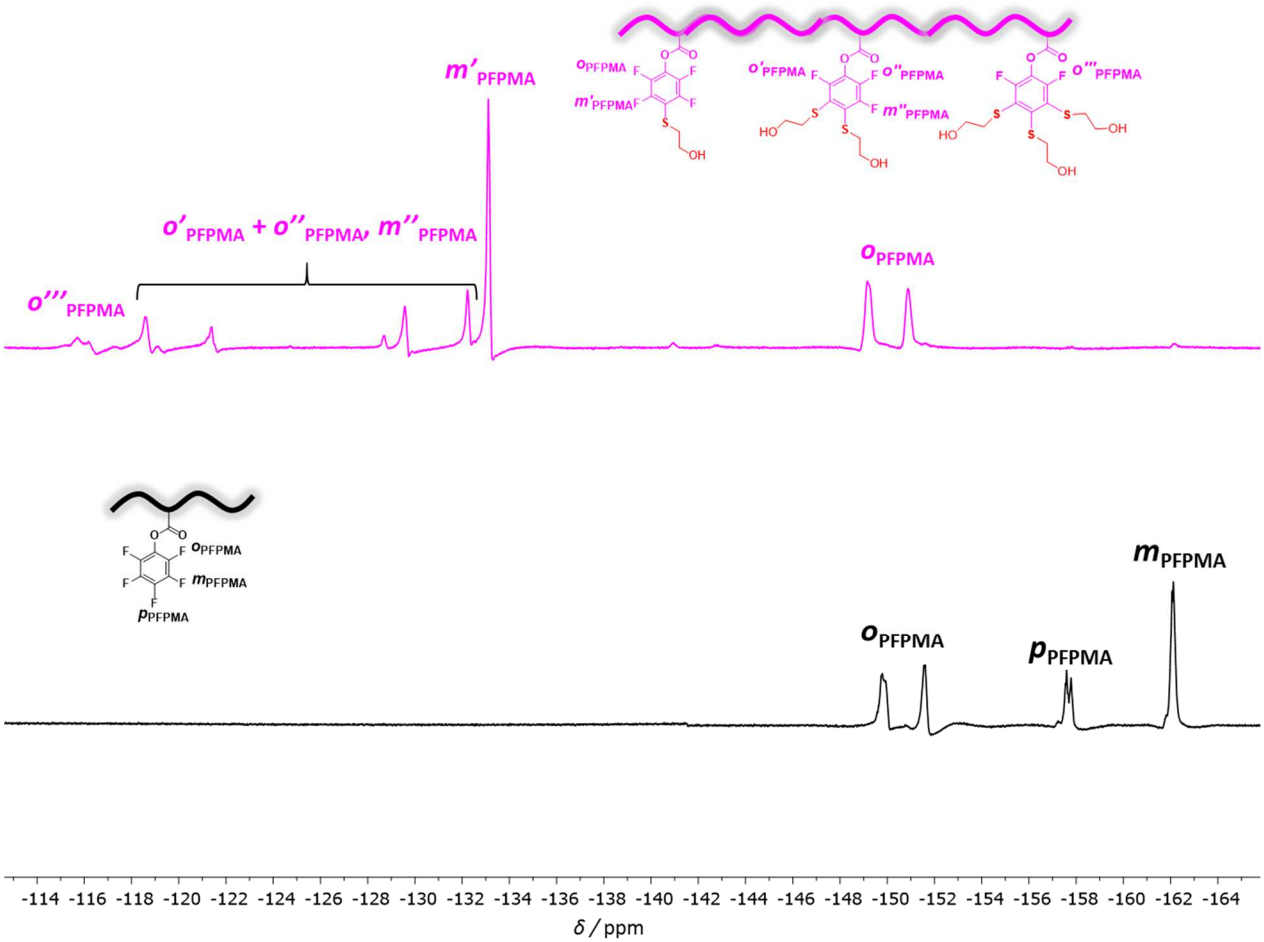


Figure 13. ^{19}F NMR of **1a** before (bottom) and after (top) reaction with 5 eq. mercaptoethanol under PFTR standard conditions.

References

1. Q. Zhang, P. Schattling, P. Theato and R. Hoogenboom, *Polym. Chem.*, 2012, **3** , 1418-1426.