

Supporting Information

for

Controlling sequence in the ring-opening metathesis polymerization of functional norbornenes

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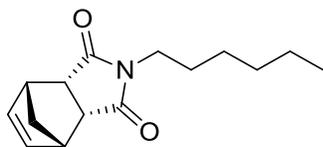
Materials and methods

cis-5-norbornene-*endo*-2,3-dicarboxylic anhydride was purchased from VWR International. All other reagents were purchased from Sigma-Aldrich and were used without further purification.

Nuclear magnetic resonance (^1H , ^{13}C and ^{19}F NMR) spectra were recorded at 250, 300, 400 or 700 MHz in CDCl_3 solution at room temperature on a Bruker AC-250, a Bruker DPX-300, a Bruker AV-400 or a Bruker DPX-400 and a Bruker AV II-700 spectrometer at 293 K, respectively. Chemical shifts are reported as δ in parts per million (ppm) and referenced to the chemical shift of the residual solvent resonances (CDCl_3 ^1H : $\delta=7.26$ ppm; ^{13}C : $\delta=77.16$ ppm). Tetrahydrofuran (THF) SEC analyses were performed in HPLC grade THF containing 2% triethylamine (TEA) at 303 K, at a flow rate of 1.0 mL/min on a set of two PLgel 5 μm Mixed-D columns. *N,N*-dimethylacetamide (DMAc) SEC analyses were performed in DMAc containing LiBr (0.42g/mL) at 308 K, at a flow rate of 0.8 mL/min on a set of two PLgel 5 μm Mixed-D columns. High resolution mass spectra (HRMS) were collected using a Bruker MaXis UHR-ESI-TOF. UV/vis spectroscopy was carried out on a Perkin Elmer Lambda 35 UV/vis spectrometer. Quartz cuvettes transparent above 230 nm were used for all experiments, and recorded

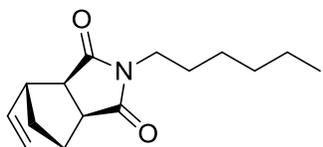
absorbance values corrected for background and solvent absorbance.

Synthesis of *N*-hexyl-*endo*-norbornene-5,6-dicarboximide (*endoHexNb*)



In a round bottom flask equipped with a magnetic stirrer bar, 10g (60.92 mmol, 1 eq.) *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride were dissolved in 200 mL toluene before addition of 8.21 mL (62.13 mmol, 1.02 eq.) hexylamine. The reaction mixture was stirred under reflux overnight. The solvent was then removed under reduced pressure and the crude product was dissolved in DCM and passed from a short silica plug to remove unreacted amines. The pure product was collected as off-yellow viscous oil (73% isolated yield). ^1H NMR (400 MHz, CDCl_3): δ 6.09 (app t, $J = 2.0$ Hz, 2H, CH=CH), 3.39 (m, 2H, =CH-CH), 3.31 (t, $J = 7.5$ Hz, 2H, N-CH₂), 3.24 (dd, $J = 1.3, 1.5$ Hz, 2H, -CH-CH), 1.55-1.74 (m, 2H, CH₂ bridge), 1.42 (tt, $J = 8.3, 6.5$ Hz, 2H, N-CH₂-CH₂), 1.26 (m, 6H, (CH₂)₃), 0.87 (t, $J = 6.8$ Hz, 3H, CH₃); ^{13}C NMR (400 MHz, CDCl_3): $\delta = 177.70, 134.36, 52.17, 45.67, 44.86, 38.40, 31.28, 27.71, 26.50, 22.45, 13.96$. HRMS (m/z): expected, 270.1470; found, 270.1468 [$\text{M}+\text{Na}$]⁺

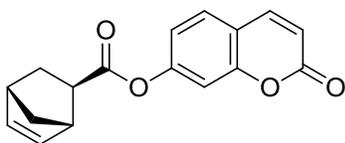
Synthesis of *N*-hexyl-*exo*-norbornene-5,6-dicarboximide (*exoHexNb*)¹



exoHexNb was synthesized using the same procedure followed for the synthesis of *endoHexNb* using *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride as a starting material. ^1H

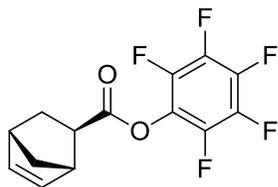
NMR (250 MHz, CDCl₃): δ 6.28 (app t, J = 2.0 Hz, 2H, CH=CH), 3.44 (m, 2H, =CH-CH), 3.26 (t, J = 1.9, 2H, N-CH₂), 2.65 (d, J = 1.1 Hz, 2H, =CH-CH-CH), 1.52 (m, 2H, N-CH₂-CH₂), 1.24-1.47 (m, 2H, CH₂ bridge), 1.24-1.37 (m, 6H, (CH₂)₃), 0.86 (t, J = 6.6 Hz, 3H, CH₃). ¹³C NMR (300 MHz, CDCl₃): δ = 177.46, 137.18, 17.15, 44.51, 42.06, 38.11, 30.67, 27.08, 25.97, 21.82, 13.35. HRMS (m/z): expected, 270.1470; found, 270.1467 [M+Na]⁺

Synthesis of 7-coumarinyl-*exo*-5-norbornene-2-carboxylate (*exo*CoumNb)²



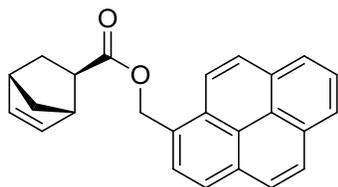
In an ice cold round bottom flask 0.785 g *exo*-5-norbornene-2-carboxylic acid (5.68 mmol, 1 eq.), 1.5 g umbelliferone (9.25 mmol, 1.63 eq.) and 1.4 g *N,N'*-dicyclohexylcarbodiimide (6.816 mmol, 1.2 eq.) were dissolved in 20 mL dichloromethane before the addition of 45 mg 4-(dimethylamino)pyridine (0.37 mmol, 0.065 eq.). The reaction was allowed to warm to room temperature and was stirred overnight. Subsequently, the formed precipitate was removed by filtration and the pure product was collected as a white powder after recrystallization in hexane/methanol (1.2 g, 75% isolated yield). ¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, J = 9.6 Hz, 1H, CH-CH-C=O), 7.48 (d, J = 8.4 Hz, 1H, CH-CH-CO), 7.12 (d, J = 2.2 Hz, 1H, CH-CO), 7.06 (dd, J = 2.2, 8.4 Hz, 1H, CH-CH-CO), 6.41 (d, J = 9.5 Hz, 1H, CH-CH-C=O), 6.19-6.22 (m, 2H, CH=CH), 3.24 (m, 1H, =CH-CH-CH), 3.02 (s, 1H, =CH-CH-CH₂), 2.50 (m, 1H, CH₂-CH-C=O), 1.55-2.05 (m, 2H, CH₂), 1.48-1.53 (m, 2H, CH₂ bridge). ¹³C NMR (300 MHz, CDCl₃): δ 173.63, 159.79, 154.10, 152.90, 142.28, 137.84, 134.90, 127.91, 117.82, 115.93, 115.37, 109.78, 46.23, 45.78, 42.76, 41.16, 30.01. HRMS (m/z): expected, 305.0790; found, 305.0783 [M+Na]⁺

Synthesis of pentafluorophenyl *exo*-5-norbornene-2-carboxylate (*exo*PFPNb)³



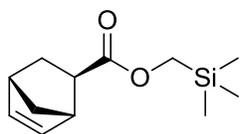
In an ice cold round bottom flask 0.5 g *exo*-5-norbornene-2-carboxylic acid (3.619 mmol, 1.02 eq.), 0.653 g pentafluorophenol (3.548 mmol, 1 eq.) and 0.878 g *N,N'*-dicyclohexylcarbodiimide (4.258 mmol, 1.2 eq.) were dissolved in 10 mL dichloromethane before the addition of 28 mg 4-(dimethylamino)pyridine (0.23 mmol, 0.065 eq.). The reaction was allowed to warm to room temperature and was stirred overnight. Subsequently, the formed precipitate was removed by filtration and the product was isolated by flash chromatography (30% isolated yield). TLC (DCM): $R_f = 0.67$; ^1H NMR (300 MHz, CDCl_3): δ 6.19-6.23 (m, 2H, CH=CH), 3.28 (m, 1H, =CH-CH-CH), 3.03 (m, 1H, =CH-CH-CH₂), 2.57-2.61 (m, 1H, CH-C=O), 1.55-2.13 (m, 2H, CH₂), 1.49-1.55 (m, 2H, CH₂ bridge). ^{13}C NMR (300 MHz, CDCl_3): $\delta = 171.73, 141.90, 138.30, 137.84, 137.30, 134.90, 125.53, 46.23, 45.78, 42.76, 41.16, 30.01$. ^{19}F NMR (300 MHz, CDCl_3): δ -153.75 (d, $J = 17.6$ Hz, 2F, *ortho*), -159.04 (t, $J = 21.8$ Hz, 1F, *para*), -163.17 (dd, $J = 17.9, 21.8$ Hz, 2F, *meta*); analysis (calcd., found for $\text{C}_{14}\text{H}_9\text{F}_5\text{O}_2$): C (54.11, 54.02), H (2.98, 2.93), F (31.23, 30.80)

Synthesis of (1-pyrenyl)methyl *exo*-5-norbornene-2-carboxylate (*exo*PyrNb)⁴



In an ice cold round bottom flask 0.372 g *exo*-5-norbornene-2-carboxylic acid (2.7 mmol, 1 eq.), 1 g 1-pyrenemethanol (4.3 mmol, 1.6 eq.) and 0.665 g *N,N'*-dicyclohexylcarbodiimide (3.2 mmol, 1.2 eq.) were dissolved in 10 mL dichloromethane before the addition of 21 mg 4-(dimethylamino)pyridine (0.18 mmol, 0.065 eq.). The reaction was allowed to warm to room temperature and was stirred overnight. Then, the formed precipitate was removed by filtration and the product was isolated by flash chromatography (74% isolated yield). TLC (DCM): $R_f = 0.85$; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.96-8.22 (m, 9H, Ar), 6.02-6.07 (m, 2H, CH=CH), 5.80 (dd, $J = 12.4, 18.4$ Hz, 2H, O-CH₂), 3.06 (m, 1H, CH-CH-CH₂), 2.88 (m, 1H, CH-CH-CH), 2.29 (m, 1H, CH-CH-CH), 1.54-1.97 (m, 2H, =CH-CH-CH₂), 1.33-1.35 (app d, 2H, CH₂ bridge); $^{13}\text{C NMR}$ (400 MHz, CDCl_3): δ 176.23, 138.11, 135.76, 131.68, 131.22, 130.71, 129.49, 129.20, 128.13, 127.77, 127.69, 127.38, 126.08, 125.50, 125.43, 124.88, 124.63, 122.95, 64.84, 53.51, 46.75, 46.48, 43.34, 41.73, 30.48. HRMS (m/z): expected, 375.1361; found, 375.1356 [$\text{M}+\text{Na}$]⁺

Synthesis of (trimethylsilyl)methyl *exo*-5-norbornene-2-carboxylate (*exo*TMSNb)⁵



In an ice cold round bottom flask 0.5 g *exo*-5-norbornene-2-carboxylic acid (3.62 mmol, 1.02 eq.), 448 μL trimethylsilyl methanol (3.55 mmol, 1 eq.) and 0.878 g *N,N'*-

dicyclohexylcarbodiimide (4.26 mmol, 1.2 eq.) were dissolved in 10 mL dichloromethane before the addition of 28 mg 4-(dimethylamino)pyridine (0.23 mmol, 0.065 eq.). The reaction was allowed to warm to room temperature and was stirred overnight. After filtration to remove the precipitates, the product was isolated by flash chromatography (50% isolated yield). TLC (DCM): $R_f = 0.83$; $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 6.07 (m, 2H, CH=CH), 3.75 (app d, 2H, Si-CH₂), 2.97 (m, 1H, CH-CH-CH₂), 2.87 (m, 1H, CH-CH-CH), 2.19 (m, 1H, CH-CH-CH₂), 1.46-1.89 (m, 2H, CH-CH₂-CH), 1.32 (m, 2H, CH₂ bridge), 0.04 (s, 9H, Si-(CH₃)₃); $^{13}\text{C NMR}$ (300 MHz, CDCl_3): δ 164.51, 137.32, 135.14, 57.09, 45.98, 45.76, 42.54, 40.98, 29.75, -3.64. HRMS (m/z): expected, 247.1130; found, 247.1121 $[\text{M}+\text{Na}]^+$

Homopolymerizations

For comparison of the polymerization rates of *endo* and *exo* norbornenes three homopolymerizations were carried out, employing *endo*HexNb, *exo*HexNb and *exo*CoumNb respectively as the monomers. For a typical polymerization 0.1 g (0.40 mmol, 50 eq.) of *exo*HexNb was added in an NMR glass tube together with 6.6 mg Grubbs catalyst 1st generation (0.008 mmol, 1 eq.) dissolved in 1 mL CDCl_3 . The monomer conversion was followed by $^1\text{H NMR}$ spectroscopy. From the slope of the best fit line of $\ln([\text{M}]_0/[\text{M}])$ vs. reaction time (s), k_p was calculated. For the homopolymerization of *endo*HexNb this was found to be $1.37 \times 10^{-6} \text{ s}^{-1}$. The k_p values for homopolymerizations of *exo*HexNb and *exo*CoumNb were not calculated because the absence of monomer peaks in the first spectrum suggest the polymerization had reached full conversion within the 10 minutes required to acquire the spectrum.

Block copolymers: P(HexNb-*b*-CoumNb)

To assess the effect of the presence of an *exo* norbornene on the polymerization rate of an *endo* norbornene and *vice versa*, 1 g *endo*HexNb (4.04 mmol, 50 eq.) and 66.4 mg Grubbs catalyst 1st generation (0.08 mmol, 1 eq.) were dissolved in 5 mL CDCl₃. The solution was degassed by three freeze-pump-thaw cycles before allowing the reaction to proceed under a nitrogen blanket. After ~29 h, 1 mL of the polymerization mixture was collected and 22.8 mg *exo*CoumNb (0.08 mmol, 5 eq.) were added to it. The sample was then added to an NMR glass tube and flushed with nitrogen before monitoring the reaction by ¹H NMR spectroscopy. This process was repeated after ~73 h and ~124 h, in order to monitor the reactivity of the monomers at different *endo* norbornene conversions.

Controlled monomer addition: P(HexNb-*co*-CoumNb)

For the sequential addition polymerization, in an ampule equipped with a magnetic stirrer bar 1 g *endo*HexNb (4.04 mmol, 100 eq.) and 33.2 mg Grubbs Catalyst 1st generation (0.04 mmol, 1 eq.) were dissolved in 10 mL CHCl₃. The solution was degassed by three freeze-pump-thaw cycles before filling the ampule with nitrogen. The polymerization was allowed to proceed at room temperature. Before each addition of an *exo* monomer, 1 mL of the polymerization mixture was removed for analysis. 57 mg *exo*CoumNb (0.2 mmol, 5 eq.) were dissolved in 2.5 mL chloroform and degassed by three freeze-pump-thaw cycles and stored at 4 °C under nitrogen. For each addition to the polymerization mixture, the right amount of solution was calculated each time in order to add 1 eq. of *exo*CoumNb. The reaction was allowed to proceed for 1-2 hours before removing a sample for analysis. Each sample was first characterized by ¹H NMR spectroscopy in order to determine the monomer conversions (Figure S1) before quenching by

the addition of 100 mL ethyl vinyl ether. Further purification was achieved by the addition of potassium cyanoacetate⁶ (10 eq.) and stirring for 1 hour before removing the precipitate by filtration. The polymers were isolated by precipitation in cold hexane and analyzed by SEC (Figure S2).

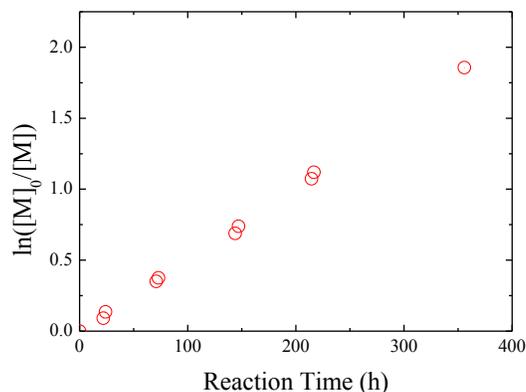


Figure S1. First order linear plot of $\ln([M]_0/[M])$ vs polymerization time for the *endoHexNb* with *exoCounNb*. Apparent overall $k_p = 1.44 \times 10^{-6} \text{ s}^{-1}$.

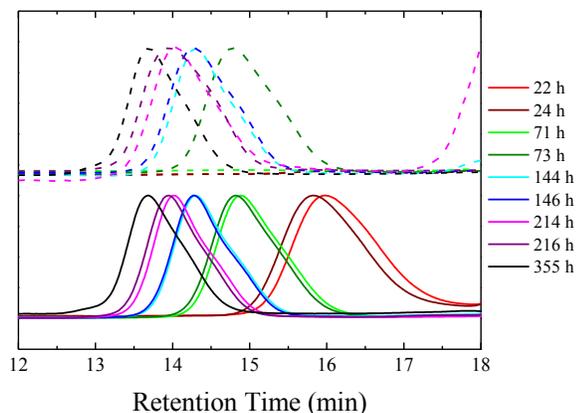


Figure S2. SEC traces from a UV detector at 309 (top) and an RI detector (bottom) of the samples collected from the polymerization of *endoHexNb* with the addition of *exoCounNb* after 22, 71, 144 and 214 h.

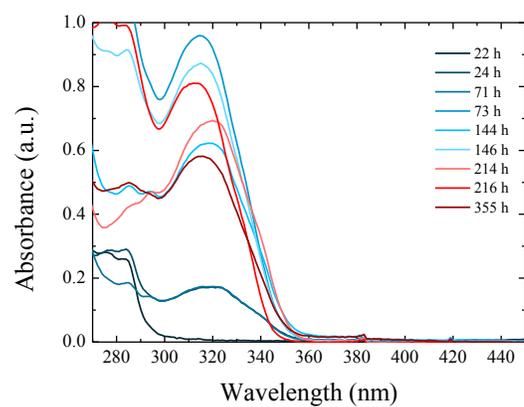


Figure S3. Absorption spectra of the purified products from the polymerization of endoHexNb with the addition of exoCoumNb after 22, 71, 144 and 214 h.

$$A = \epsilon l c, \quad C_{\text{polymer}} = \frac{m_{\text{polymer}}}{M_n V}$$

$$\frac{\#_{\text{coumarins}}}{\text{polymer chain}} = \frac{A}{\epsilon l C_{\text{polymer}}}$$

Equation S1. The amount of coumarin moieties per polymer chain were calculated based on the known absorption (A), polymer concentration (C_{polymer}) and polymer molecular weight (M_n).

Multifunctional polynorbornene: P(HexNb-*co*-PFPNb-*co*-TMSNb-*co*-PyrNb-*co*-CoumNb)

0.06 g *endo*HexNb (0.243 mmol, 20 eq.) and 10 mg Grubbs catalyst 1st generation (0.012 mmol, 1 eq.) were dissolved in 0.6 mL CDCl₃ in an NMR glass tube. The solution was degassed by three freeze-pump-thaw cycles before allowing the reaction to proceed under a nitrogen blanket while being monitored by ¹H NMR spectroscopy. After 24.5 h, 7.4 mg *exo*PFPNb (0.024 mmol, 2 eq.) was added and the polymerization was monitored for a further 5 h. Then, 5.5 mg *exo*TMSNb (0.024 mmol, 2 eq.) were added and the reaction was followed for 5 h before the addition of 8.5 mg *exo*PyrNb (0.024 mmol, 2 eq.) and further monitoring for 5 h. Last, 6.8 mg *exo*CoumNb (0.024 mmol, 2 eq.) were added and the reaction was followed by ¹H NMR spectroscopy until all *exo* norbornene signals had disappeared. The final polymer was isolated by precipitation in cold hexane and characterized by ¹H NMR, ¹⁹F NMR and diffusion-ordered NMR spectroscopy (DOSY).

Figure S4 shows the ¹H NMR spectra of the polymerization mixture before and after the addition of *exo*PFPNb. The appearance of peaks at ~6.15 ppm in the middle spectrum is attributed to the alkene protons of the *exo* norbornene. Their disappearance after 3 h into the polymerization indicates complete consumption of the monomer. In addition to that, the relative

integration of the poly(norbornene) alkene peak at ~5.65 ppm increases with time, confirming the propagation of the polymerization. Figure S5 shows the ^{19}F NMR of the pentafluorophenyl-containing monomer and the copolymer. While relative integration is not possible due to the absence of a reference peak, the broadening of the peaks is consistent with polymer signals.

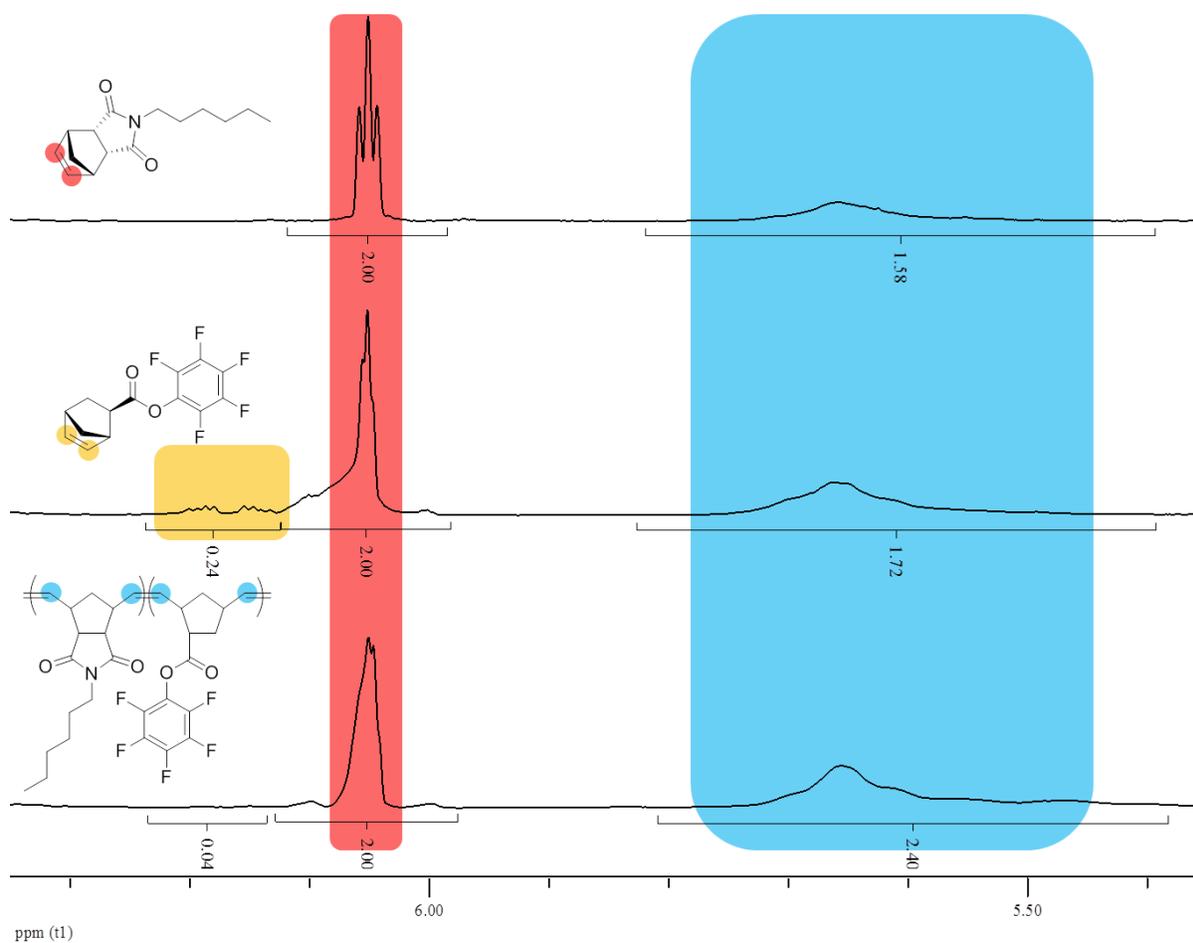


Figure S4. ^1H NMR spectra of the polymerization of *endo*HexNb before (top), 12 minutes after (middle) and 2 hours after (bottom) the addition of *exo*PFPNb in the reaction mixture.

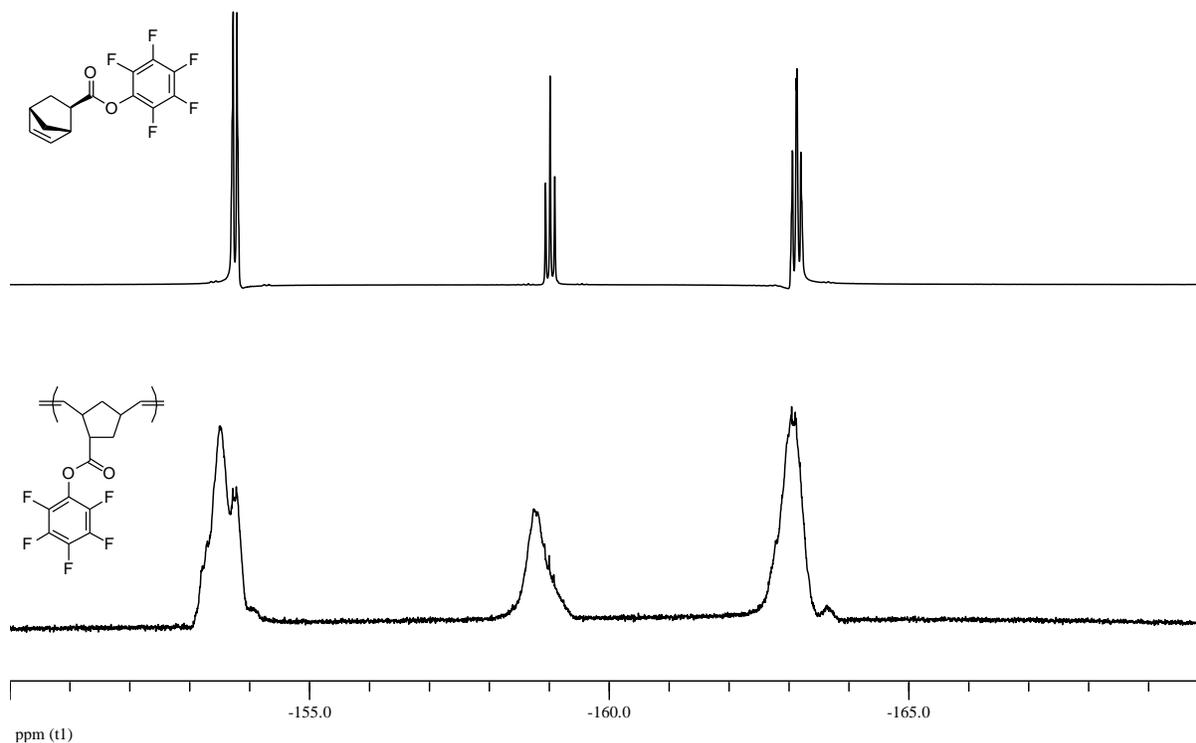


Figure S5. ^{19}F NMR spectrum of *exo*PFPNb (top) and the P(HexNb-*co*-PFPNb) copolymer after 3 h.

Upon addition of the second functional monomer, *exo*TMSNb, a sharp doublet at ~ 3.7 ppm corresponding to the TMS linker protons appears, as shown in Figure S6. As a result of the polymerization, the peak appears significantly broader 2 hours after the addition. Similarly, when examining the upfield region of the spectrum (Figure S7), a sharp peak at ~ 0.05 ppm appears upon addition of the monomer attributed to the methyl protons of the TMS group. A broad overlapping peak can be observed which is attributed to the polymerized *exo*TMSNb. 2 hours after the addition, the sharp peak corresponding to the monomer has disappeared and the broader peak has dominated, thus signifying the consumption of the monomer.

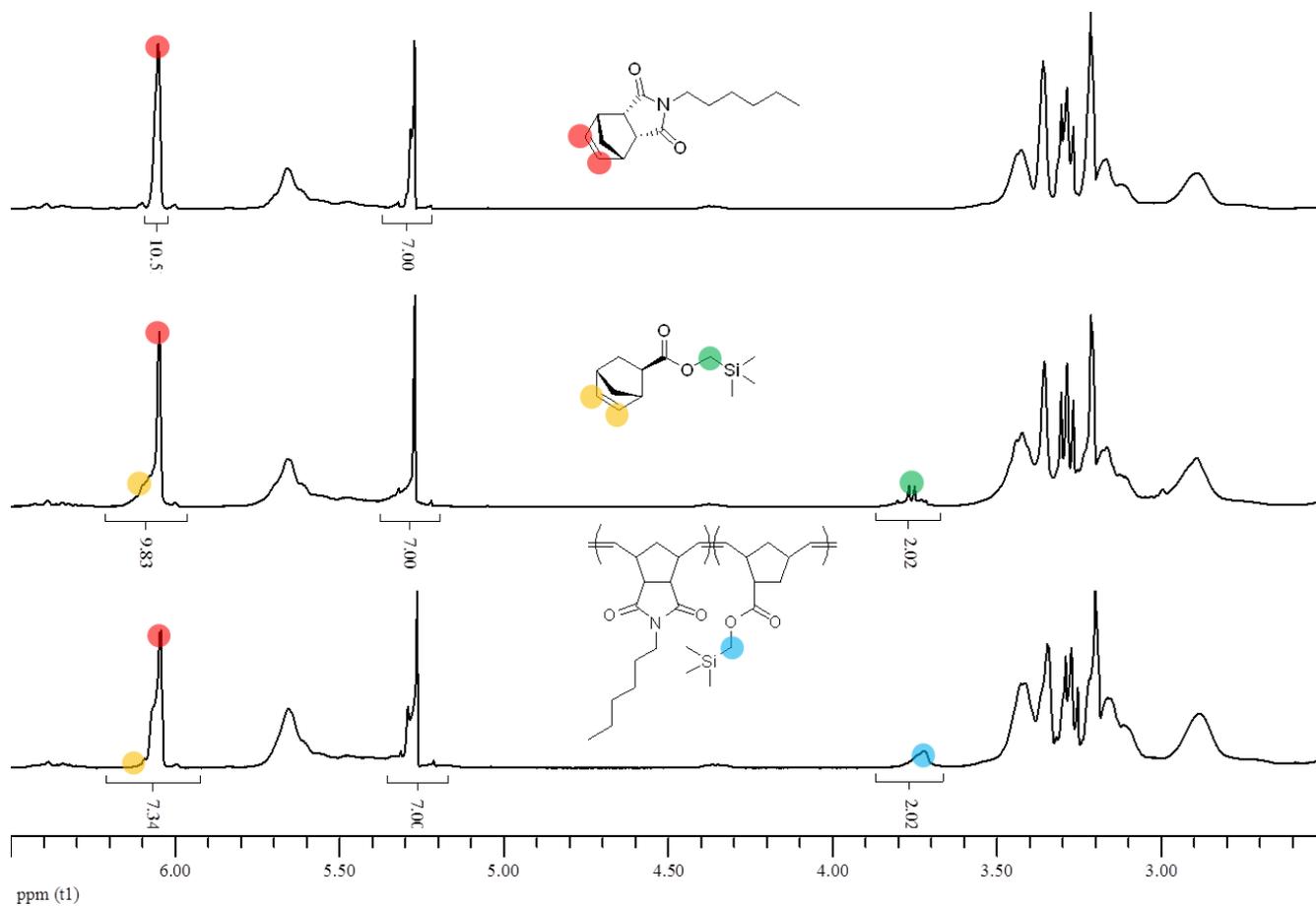


Figure S6. ^1H NMR spectra of the polymerization mixture before (top), 15 minutes after (middle) and 2 hours after (bottom) the addition of *exo*TMSNb.

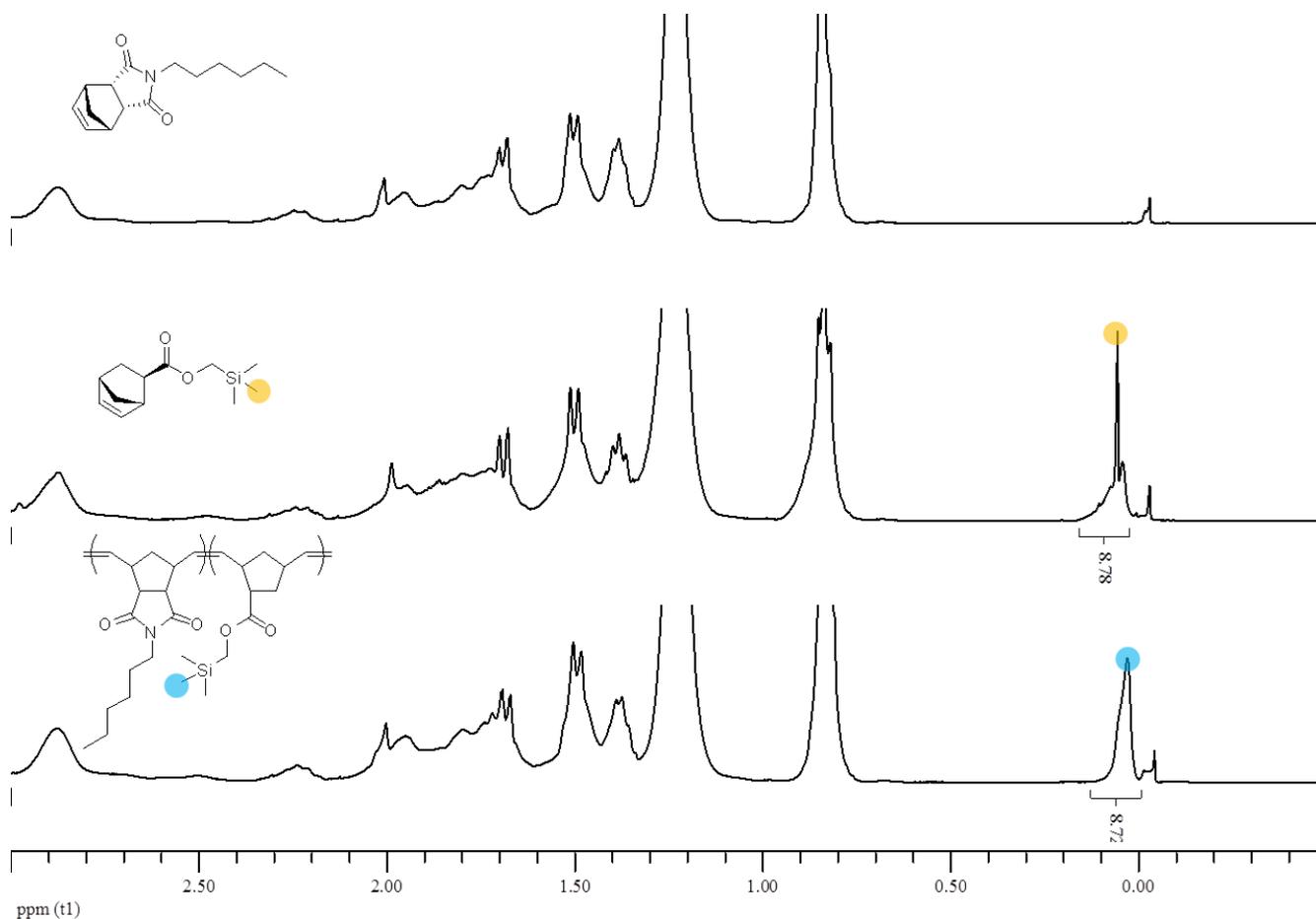


Figure S7. ¹H NMR spectra of the polymerization mixture before (top), 15 minutes after (middle) and 2 hours after (bottom) the addition of *exo*TMSNb.

Prior to the addition of *exo*PyrNb to the reaction mixture, the downfield region of the ¹H NMR spectrum (Figure S8) is free of peaks and upon addition of the monomer, multiple peaks attributed to the pyrene group of the molecule appear at ~8.00-8.25 ppm. In addition to that, two peaks corresponding to the linker protons appear at ~5.7 ppm. 3 hours after the monomer addition, all sharp peaks have disappeared and broader ones consistent with polymer proton peaks have appeared, thus signifying the consumption of the monomer.

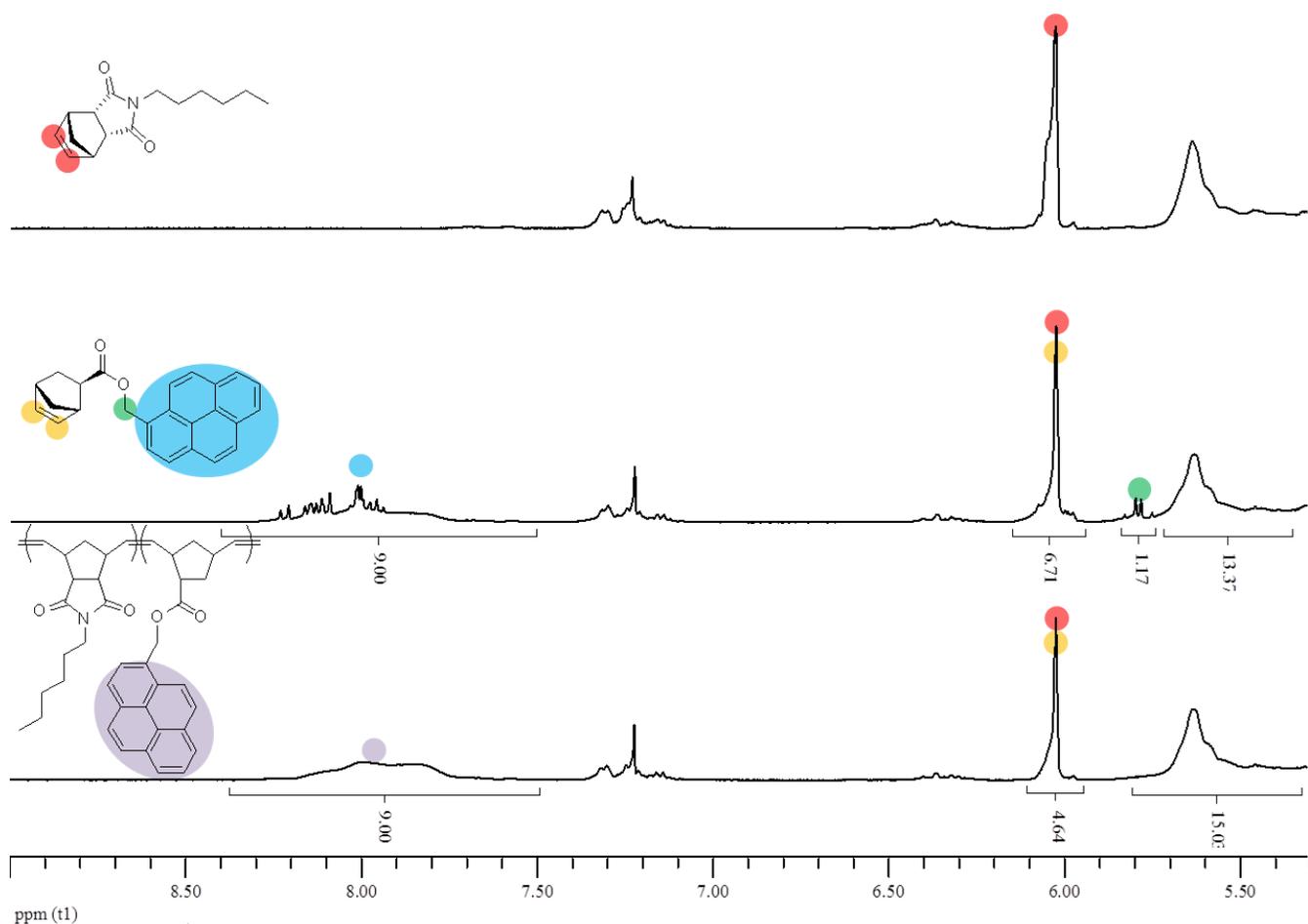


Figure S8. ^1H NMR spectra of the polymerization mixture before (top), 15 minutes after (middle) and 3 hours after (bottom) the addition of *exoPyrNb*.

Figure S9 shows the ^1H NMR spectrum of the polymerization mixture before and after the addition of *exoCouvNb* in the reaction upon which the monomer alkene peaks at ~ 6.15 ppm appear. Also, some of the coumarin peaks appear which - upon completion of the polymerization after 3 hours - disappear and the corresponding polymer peaks appear. This is accompanied by the complete disappearance of the aforementioned monomer alkene peaks.

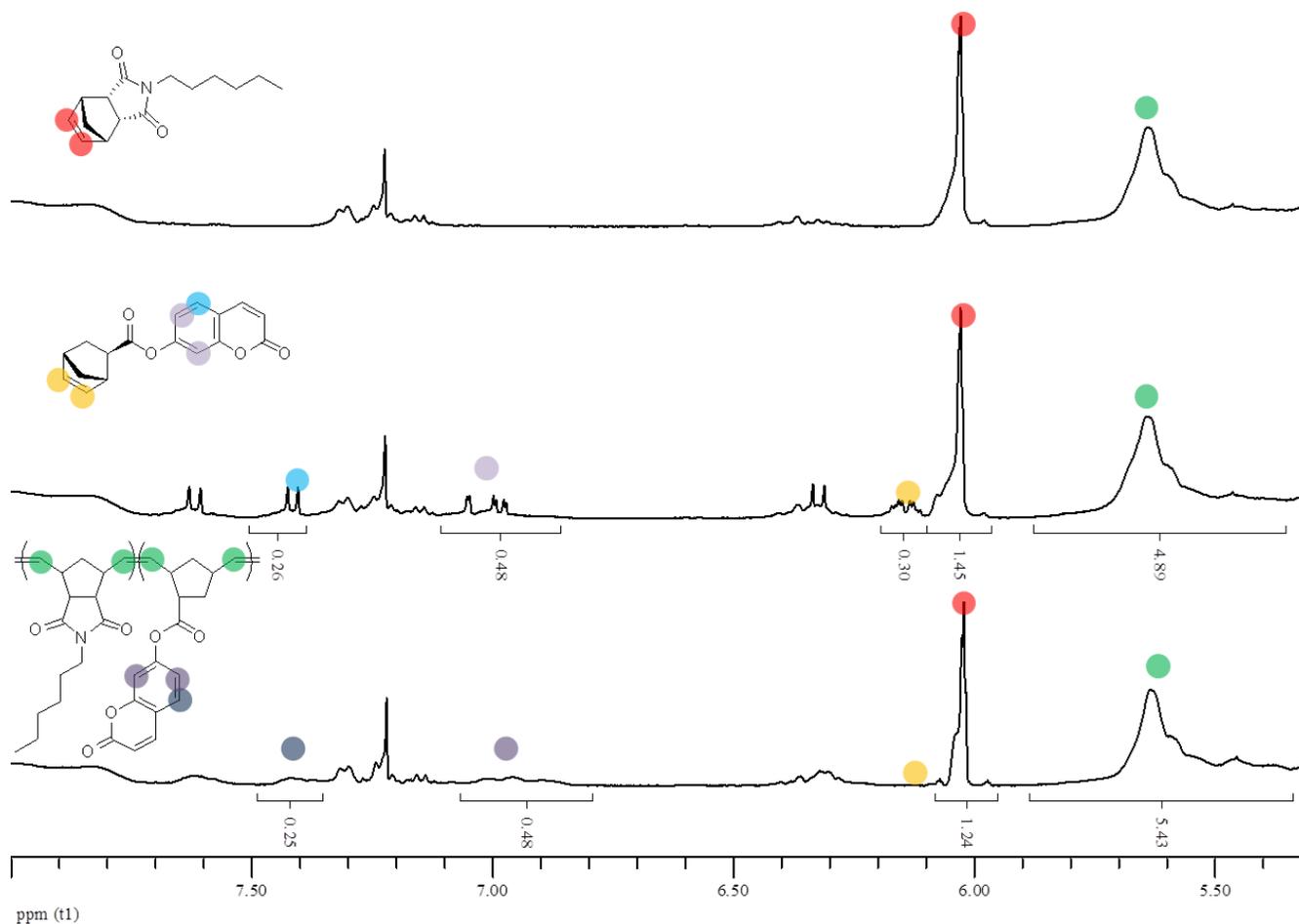


Figure S9. ^1H NMR spectra of the polymerization mixture before (top), 12 minutes after (middle) and 3 hours after (bottom) the addition of *exoCouvNb*.

After isolation of the polymer by precipitation in cold hexane in order to remove unreacted *endoHexNb*, the product was characterized by ^1H NMR and ^{19}F NMR spectroscopy (Figure S10). All signals corresponding to the inserted functional groups were found present in the respective spectra, thus suggesting successful incorporation of all monomers onto the growing polymer chain.

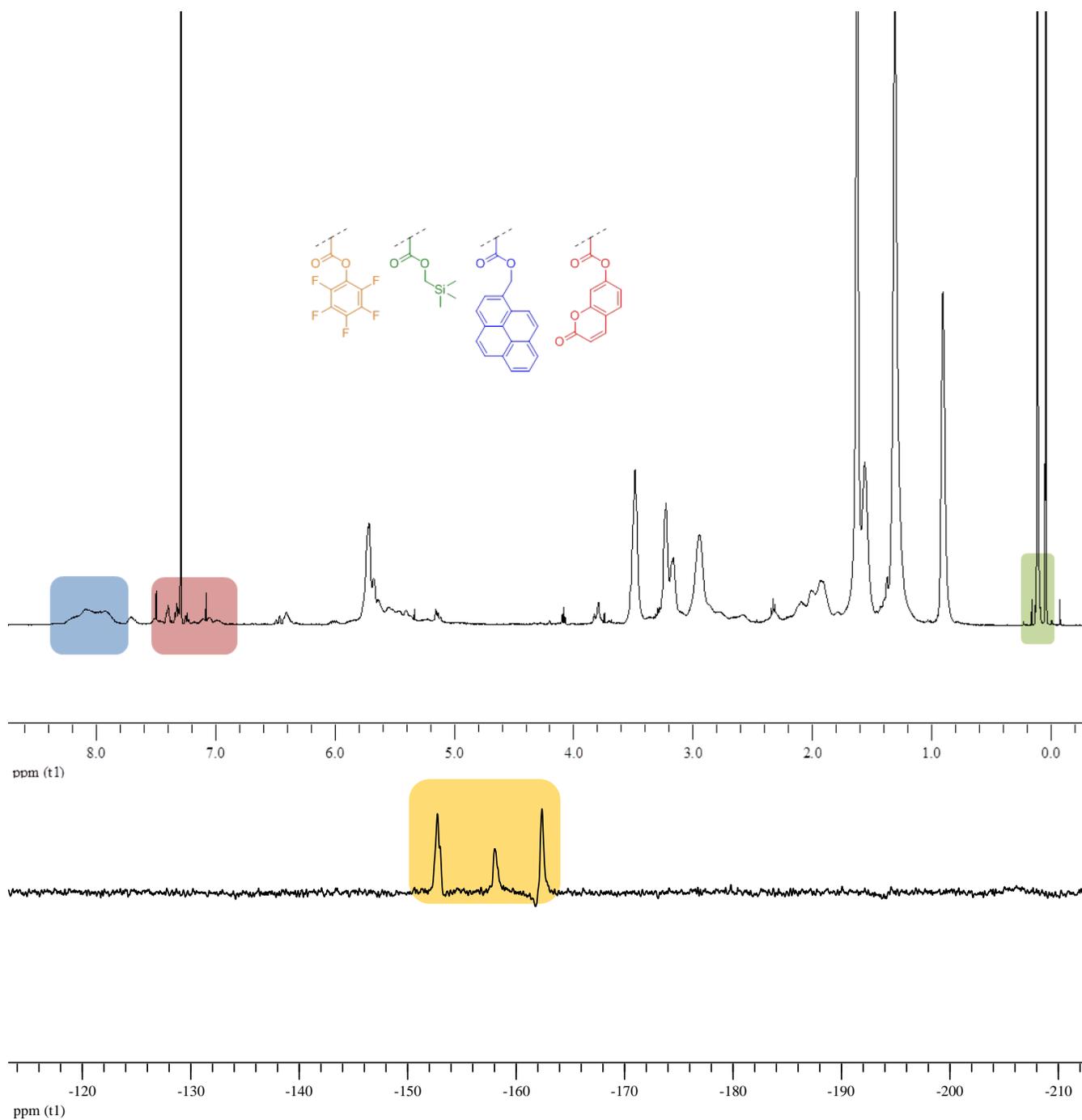


Figure S10. ^1H NMR (top) and ^{19}F NMR (bottom) spectra of the precipitated polymer exhibiting all the characteristic peaks of the introduced functional monomers.

Analysis of the final copolymer by DOSY (Figure S 11) revealed a single diffusion coefficient verifying that all functional groups are indeed attached to the same polymer backbone.

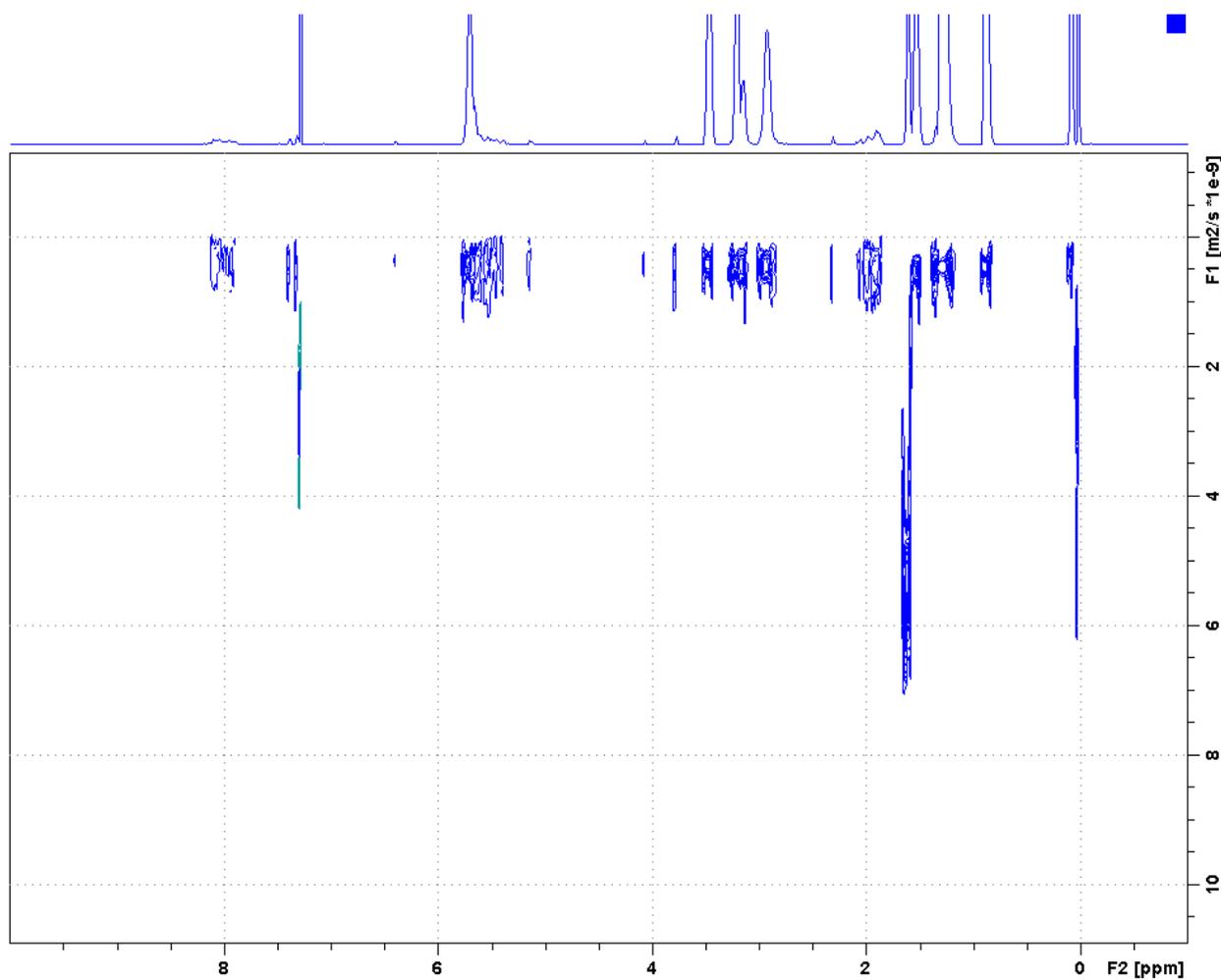


Figure S 11. DOSY of the final copolymer showing a single diffusion coefficient for all peaks corresponding to the functional groups.

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