Supplementary Information

Redox-responsive organometallic hydrogels for in-situ metal nanoparticle synthesis

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Experimental Part

Materials. (1*R*,8*S*,9*s*)-Bicyclo[6.1.0]non-4-yn-9-ylmethyl succinimidyl carbonate (>95 %), *n*-butyllithium (1.6 M in hexanes), dimethyl sulfoxide (anhydrous), THF (anhydrous, inhibitor-free), phenol (≥99.5 %), triethylamine (>99.5 %), KI (>99 %), NaN_3 (>99.5 %), NaBr (>99 %), DMSO-d_6 (99.9 atom % D), and toluene-d_8 (≥ 99.6 atom % D) were obtained from Aldrich and used as received. THF-d_8 (99.5 atom % D) and $CDCl_3$ (99.8 atom % D) were purchased from Cambridge Isotope Laboratories. 4-Arm PEG amine (pentaerythritol) HCl salt (M_n = 5000 g/mol) was purchased from JenKem Technology USA. Potassium tetrachloropalladate was purchased from Strem Chemicals, Inc. (Newburyport, MA, USA). Methanol, DMSO, THF and diethyl ether were obtained from Biosolve, The Netherlands. Milli-Q water (Millipore) was used in all experiments. Acetone and DMF (extra dry, 99.8%) were purchased from Acros Organics. Isobutyl ethanesulfonate was prepared according to a literature procedure.[37]

Techniques. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz instrument at 400.1 and 100.6 MHz, respectively, in $CDCl_3$, DMSO-d_6, THF-d_8 or toluene-d_8. ^1H and ^{13}C chemical shifts were based on the solvent residual signals (G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176). GPC measurements were carried out in THF (flow rate 2.0 mL/min) at 25 °C, using microstyragel columns (bead size 10 μm) with pore sizes of 10^6, 10^5, 10^4 and 10^3 Å (Waters) and a dual detection system consisting of a differential refractometer (Waters model 410) and a differential viscometer (Viscotek model H502). Molar masses were determined relative to narrow polystyrene standards. Rheological experiments were carried out with an UDS 200 rheometer (Anton Paar) using parallel plates (25 mm diameter) at 25 °C in the oscillatory mode with 0.1 % strain and 1 Hz. Electrochemical measurements were carried out on hydrogels swollen in 0.1 M aqueous $NaClO_4$ using an Autolab, PGSTAT 10 electrochemical workstation. Cyclic voltammograms were recorded between −0.1 and +0.7 V at scan rates between 5 and 100 $mV\cdot s^{-1}$, using a

Ag/AgCl reference electrode, a Pt counter electrode, and a Pt working electrode. FTIR spectra were measured with a Bruker ALPHA on freeze-dried samples. TEM and EDX analyses were performed with a FEI (Philips) CM300ST equipped with a GATAN Tridiem energy filter (2k x 2k CCD camera), extra GATAN Ultrascan 1000 CCD camera (2k x 2k), and a Noran System Six EDX analyzer with a Nanotrace EDX detector. The samples were prepared by sonication of small gel fragments in ethanol and depositing 7.5 μl of the obtained dispersion on a Lacey carbon/Copper grid.

Poly(ferrocenylsilane) 1. PFS **1** was synthesized by Pt-catalyzed ring-opening polymerization of [1](3-chloropropyl)methylsilaferrocenophane (3.05 g, 10.0 mmol), followed by halogen exchange using KI.[28f] At 90% conversion of Cl into I, **1** was isolated by precipitation in MeOH and dried under vacuum. Yield: 3.2 g (81 %) of amber product. ^{1}H NMR (toluene-d$_8$, δ, ppm): 0.52 (SiCH$_3$, s, 3H); 1.00 (1-CH$_2$, m, 2H); 1.82 (2-CH$_2$, m, 2H); 2.95 (3-CH$_2$I, m, 2H); 3.30 (3-CH$_2$Cl, m, 2H); 4.05 + 4.10 + 4.27 + 4.29 (Cp, m, 8H). ^{13}C NMR (toluene-d$_8$, δ, ppm): −2.83 (SiCH$_3$); 12.02 (1-C); 18.52 (2-C); 29.32 (3-CH$_2$I); 48.23 (3-CH$_2$Cl); 70.50 (Cp-Si); 71.96 + 73.95 (Cp). GPC (THF): $M_n = 2.72 \cdot 10^4$ g/mol, $M_w = 4.98 \cdot 10^4$ g/mol, $M_w/M_n = 1.83$.

Poly(ferrocenylsilane) 2. Isobutyl sulfonate side groups were attached to **1** (1.50 g, 3.5 mmol CH$_2$-I units) by alkylation with α-lithio isobutyl ethanesulfonate at −55 °C, using reaction conditions adapted from earlier work.[38] A solution of isobutyl ethanesulfonate (2.49 g, 15.0 mmol) in dry THF (20 mL) was cooled under argon to −80 °C, and *n*-BuLi (7.5 mL, 12 mmol) was added dropwise. After stirring for 60 min, DMSO (7.5 mL) and a solution of **1** (1.50 g, 3.5 mmol CH$_2$-I units) in THF (40 mL) was added dropwise. Stirring was continued at −55 °C for 13 h. The reaction was terminated at −55 °C by adding phenol (0.85 g, 9.0 mmol) in THF (5 mL). Polymer **2** was isolated by repeated precipitation in MeOH and dried under vacuum. Yield: 1.4 g (86 %) of an amber solid. ^{1}H NMR (THF-d$_8$, δ, ppm): 0.51 (SiCH$_3$, s, 3H); 0.96 (1-CH$_2$, m, 2H); 0.96 (CH$_3$, d, J = 6.7 Hz, 6H); 1.31 (ethane CH$_3$, d, J = 6.7 Hz, 3H); 1.49 + 1.60 (2-CH$_2$, m, 2H); 1.60 + 2.02 (3-CH$_2$, m, 2H); 1.97 (CH, m, 1H); 3.18 (4-CH$_2$, m, 1H); 3.54 (3-CH$_2$Cl, m, 2H); 3.93 (SO$_3$CH$_2$, d, J = 6.5 Hz, 2H); 4.01 + 4.04 + 4.08 + 4.23 (Cp, m, 8H). ^{13}C NMR (THF-d$_8$, δ, ppm): −2.86 (SiCH$_3$); 14.73 (ethane CH$_3$); 16.98 (1-C); 19.11 (isobutyl CH$_3$); 22.30 (2-C); 29.45 (CH); 35.26 (3-C); 48.78 (3-CH$_2$Cl); 56.54 (4-C); 71.26 (Cp-Si); 72.0-72.4 + 74.0-74.4 (Cp); 75.46 (SO$_3$CH$_2$). GPC (THF): $M_n = 1.79 \cdot 10^4$ g/mol, $M_w = 4.06 \cdot 10^4$ g/mol, $M_w/M_n = 2.27$. Percentage of CH$_2$Cl moieties: 10 mol%.

Poly(ferrocenylsilane) polyanion 3. The isobutyl sulfonate ester groups of **2** (1.4 g) were deprotected using NaN_3 (2.50 g, 38.5 mmol), initially in THF (150 mL) and methanol (100 mL) at 55 °C. After 24 h, THF and methanol were evaporated, and deprotection was continued in DMSO (60 mL) at 45 °C for 48 h. Simultaneously, in DMSO, the 10 mol% chloride groups of polymer **2** were substituted by azide moieties. PFS **3** was purified by dialysis against Milli-Q containing trace amounts of sodium ascorbate and freeze-dried to yield the amber product. Yield: 1.30 g (100 %). ^1H NMR (DMSO-d_6, δ, ppm): 0.44 ($SiCH_3$, s, 3H); 0.88 (1-CH_2, m, 2H); 1.07 (ethane CH_3, d, J = 6.2 Hz, 3H); 1.32 + 1.50 (2-CH_2, m, 2H); 1.32 + 1.90 (3-CH_2, m, 2H); 2.37 (4-CH_2, m, 2H); 3.31 (3-CH_2N_3); 3.98 + 4.18 (Cp, m, 8H). ^{13}C NMR (DMSO-d_6, δ, ppm): −3.09 ($SiCH_3$); 15.36 (ethane CH_3); 15.70 (1-C); 21.53 (2-C); 35.67 (3-C); 53.88 (4-C); 70.33 (Cp-Si); 70.96 + 73.06 (Cp). ATR-FTIR: 2094 cm^{-1} (azide).

Bicyclononyne (BCN) derivatized tetra-arm PEG 4. (1*R*,8*S*,9*s*)-bicyclo[6.1.0]non-4-yn-9-ylmethyl succinimidyl carbonate (100 mg, 0.343 mmol) was dissolved in DMF (1 mL). Tetra-arm PEG amine 5000 (408 mg, 0.326 mmol) and triethylamine (70 µl, 0.5 mmol) were dissolved in dry DMF (5 mL) and added to the BCN solution. The solution was stirred under argon for 20 h at 20 °C. The product was precipitated in cold diethyl ether, followed by centrifugation (3000 rpm, −20 °C) to isolate the polymer. The product was redissolved in toluene and precipitated in cold diethyl ether, followed by centrifugation (3000 rpm, −20 °C). Yield: 0.45 g of white powder. ^1H NMR ($CDCl_3$, δ, ppm): 0.87 (m, 1H); 1.35 (m, 1H); 1.53 (m, 1H); 2.08-2.28 (m, 6H); 3.03 (m, 2H), BCN; 3.2–3.7 (EO, m); 4.08 ($COOCH_2$, d, J = 8.0 Hz, 2H) 5.25 (NH, bs, 1H). ^{13}C NMR ($CDCl_3$, δ, ppm): 156.81; 98.88; 70.2-70.7; 62.36; 46.13; 41.33; 29.31; 21.59; 18.39.

Hydrogel 5. Polyanion **3** (50 mg) was dissolved in MeOH (0.2 mL) and mixed with a solution of BCN derivatized tetra-arm PEG **4** (18.2 mg) in MeOH (0.1 mL). At this ratio, equimolar amounts of BCN and azide moieties were present in the gel-forming mixture. The viscosity was observed to increase until gel formation was confirmed by the vial tilting method. Typically, gelation was allowed to proceed overnight. In order to completely remove MeOH, the gel was placed in Milli-Q water, replacing the water several times. FTIR analysis of the gel after freeze-drying indicated that the azide signal, originating from polymer **3**, had disappeared.

***In situ* formation of palladium nanoparticles.** The water swollen hydrogel **5** was immersed in a solution of potassium tetrachloropalladate (5 mM). The hydrogel turned from orange to black within minutes after which the reaction was left overnight in the dark. The hydrogel was washed with Milli-Q water to remove unreacted salts and was freeze-dried for analysis.

Table S1. Characteristics of Hydrogel 5.

	Storage modulus (G', Pa)	Loss modulus (G", Pa)	Swelling ratio (by weight)	Effective crosslink density (υ_e, mM)
Hydrogel **5**	370 ± 5	65 ± 5	49	0.6

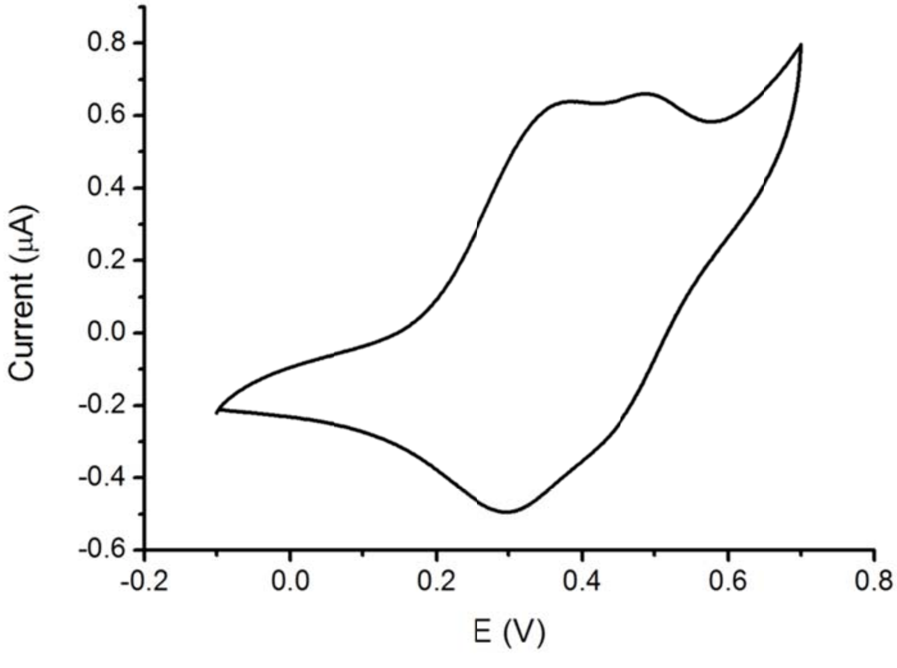


Fig. S1 Cyclic voltammetry curve measured in 0.1 M $NaClO_4$ with a Pt counter electrode and Ag/AgCl reference electrode. For cyclic voltammetry, gels were built up layer-by-layer from PFS **3** and PEG **4** on a gold substrate, which served as working electrode, using an azidobutyl thioacetate self-assembled monolayer (L. Jiang, L. Yuan, L. Cao and C. A. Nijhuis, *J. Am. Chem. Soc.*, 2014, **136**, 1982) for surface anchoring. The CV curve was measured at 5 mV/s on a 5 bilayer sample.

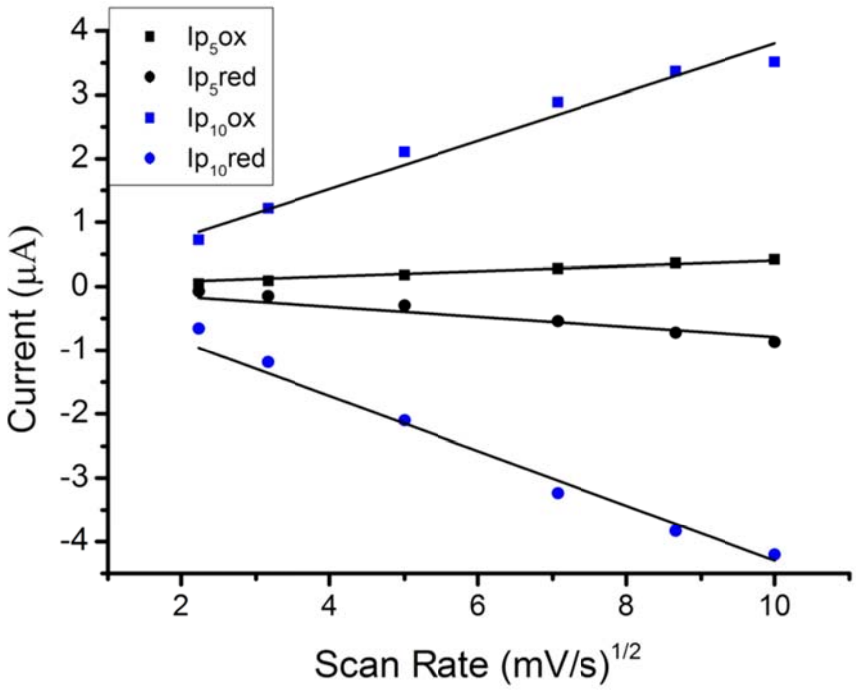


Fig. S2. Peak currents display a square root dependence on scan rate, indicating that the electrochemical processes are diffusion controlled. For these measurements, a 5 bilayer sample was used (Fig. S1).

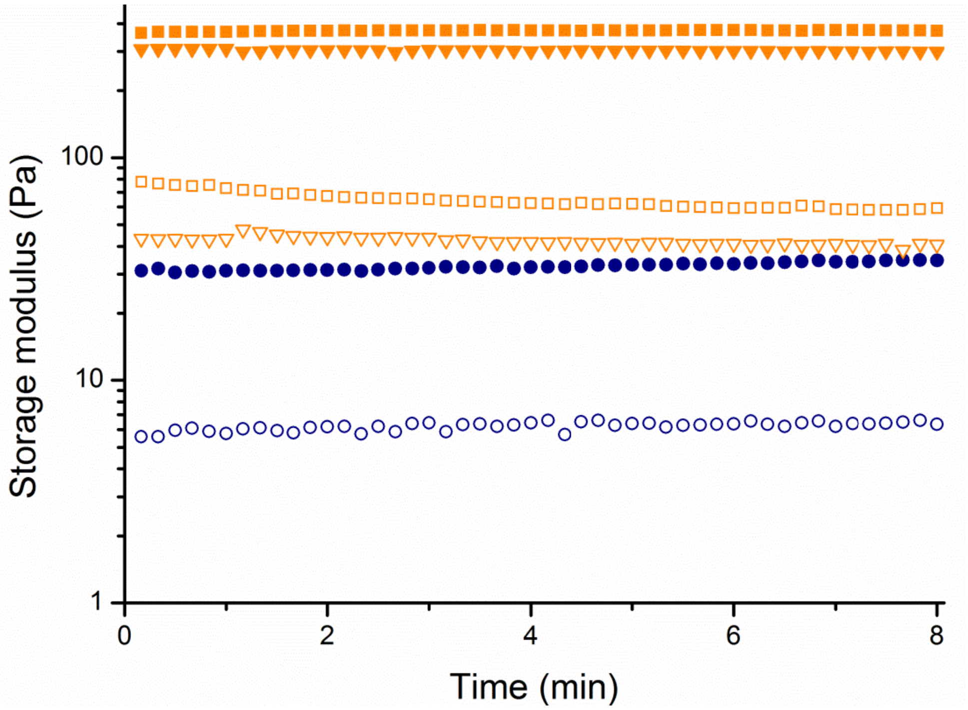


Fig. S3. Storage moduli (closed symbols) and loss moduli (open symbols) of hydrogel **5** in pristine (■), oxidized (●) and reduced state (▼).

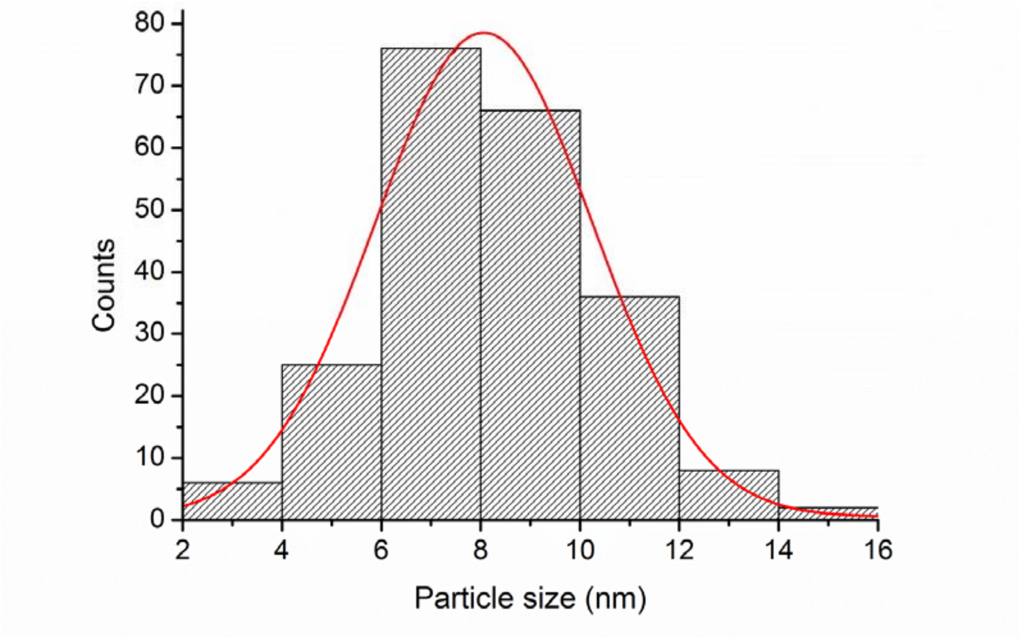


Fig. S4 Pd nanoparticle size distribution histogram. Particle size distribution was obtained by measuring the diameter of 250 Pd particles by TEM.

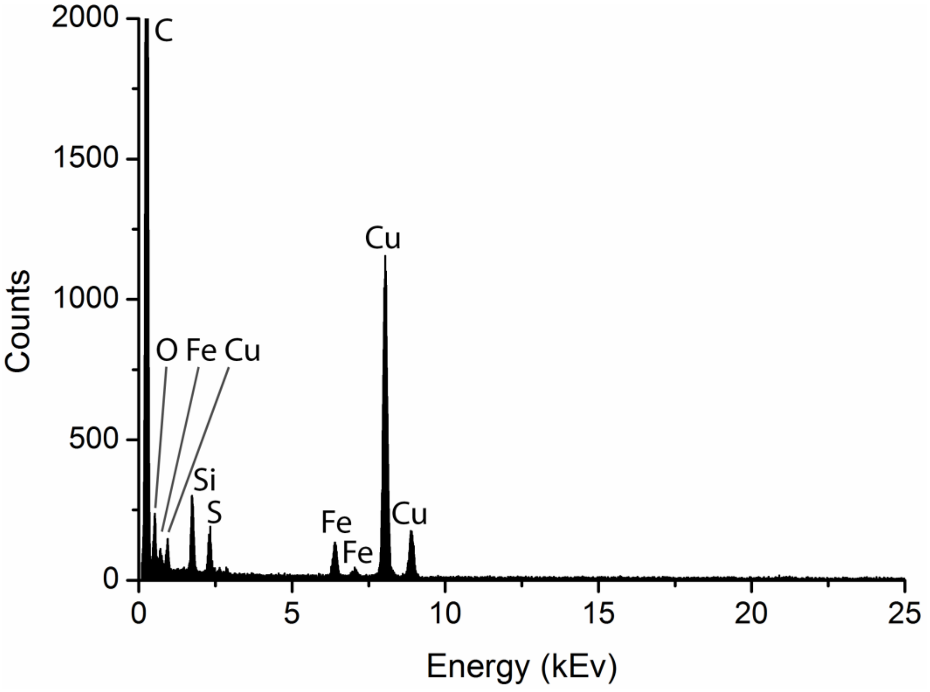
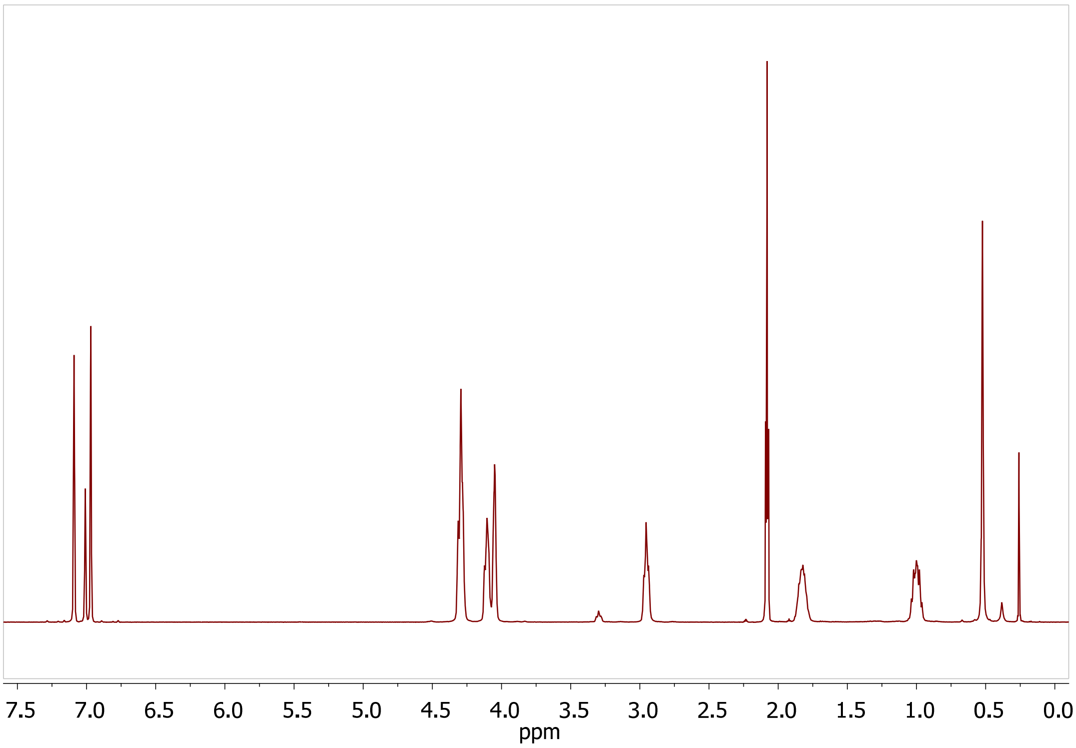
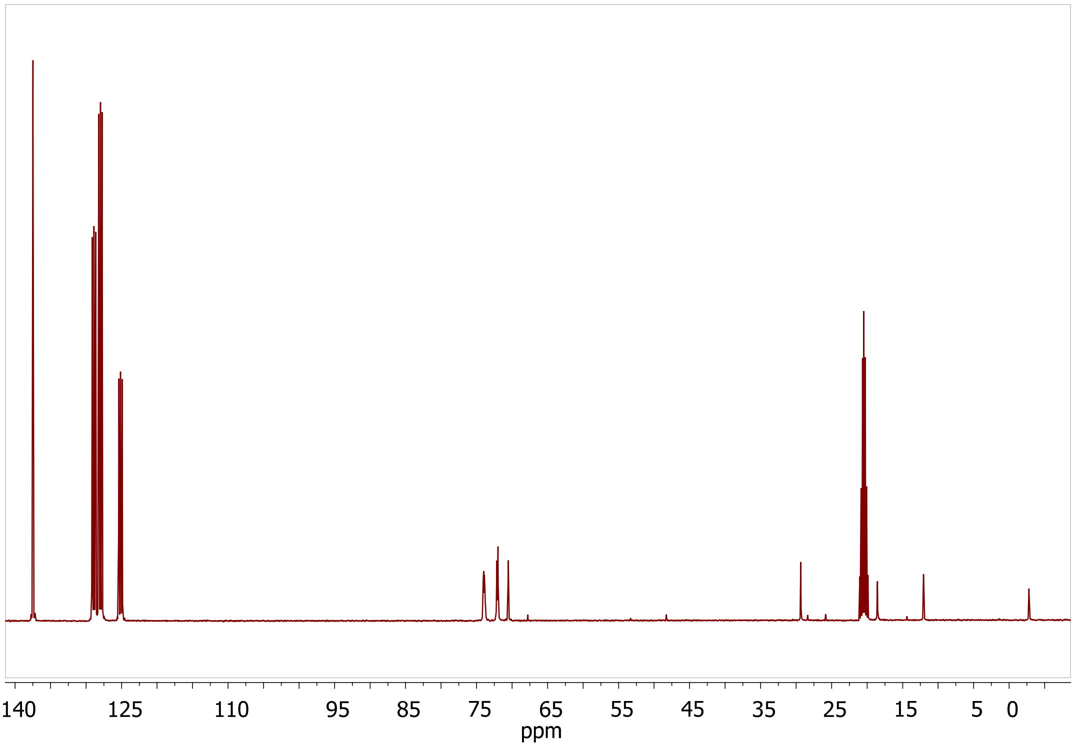


Fig. S5 EDX Spectrum of the poly(ferrocenylsilane) hydrogel.

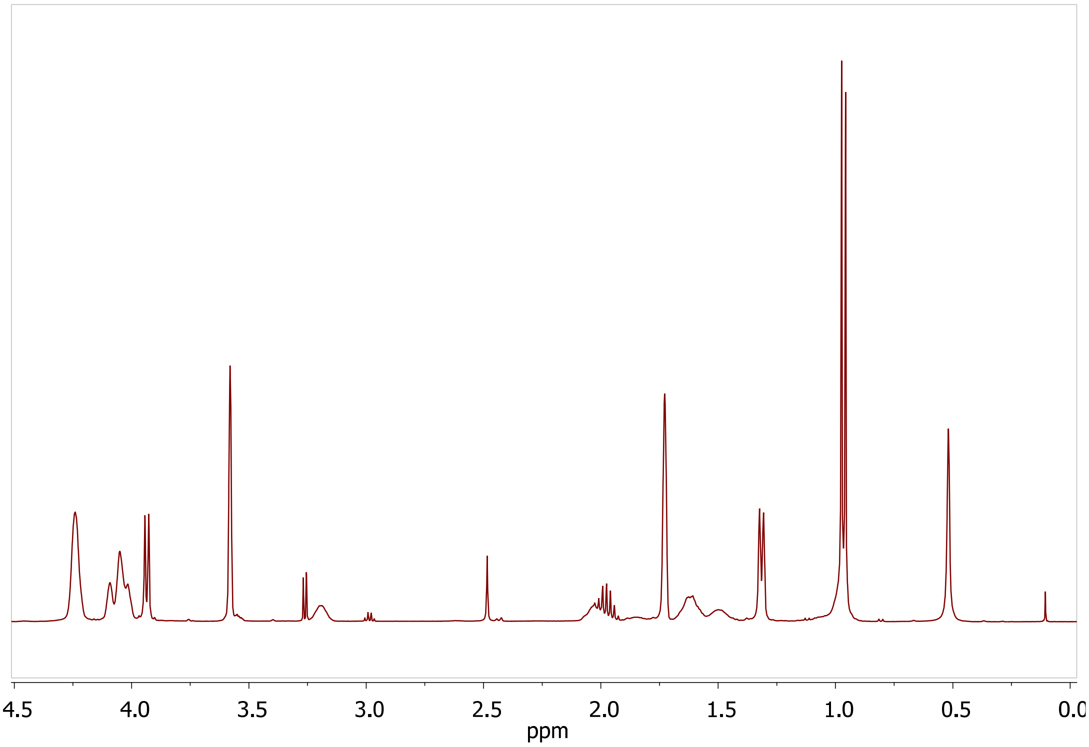
PFS **1** (90 mol% ~CH_2-I, 10 mol% ~CH_2-Cl groups), ^{1}H- and ^{13}C NMR spectra in Toluene-d_8

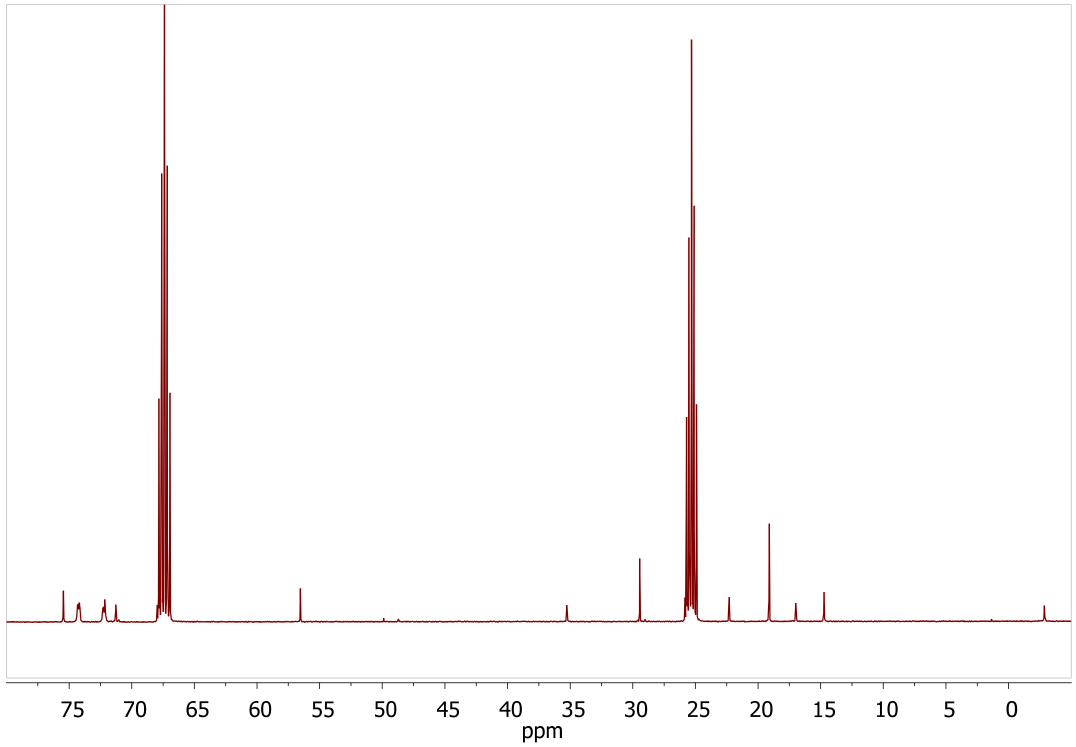




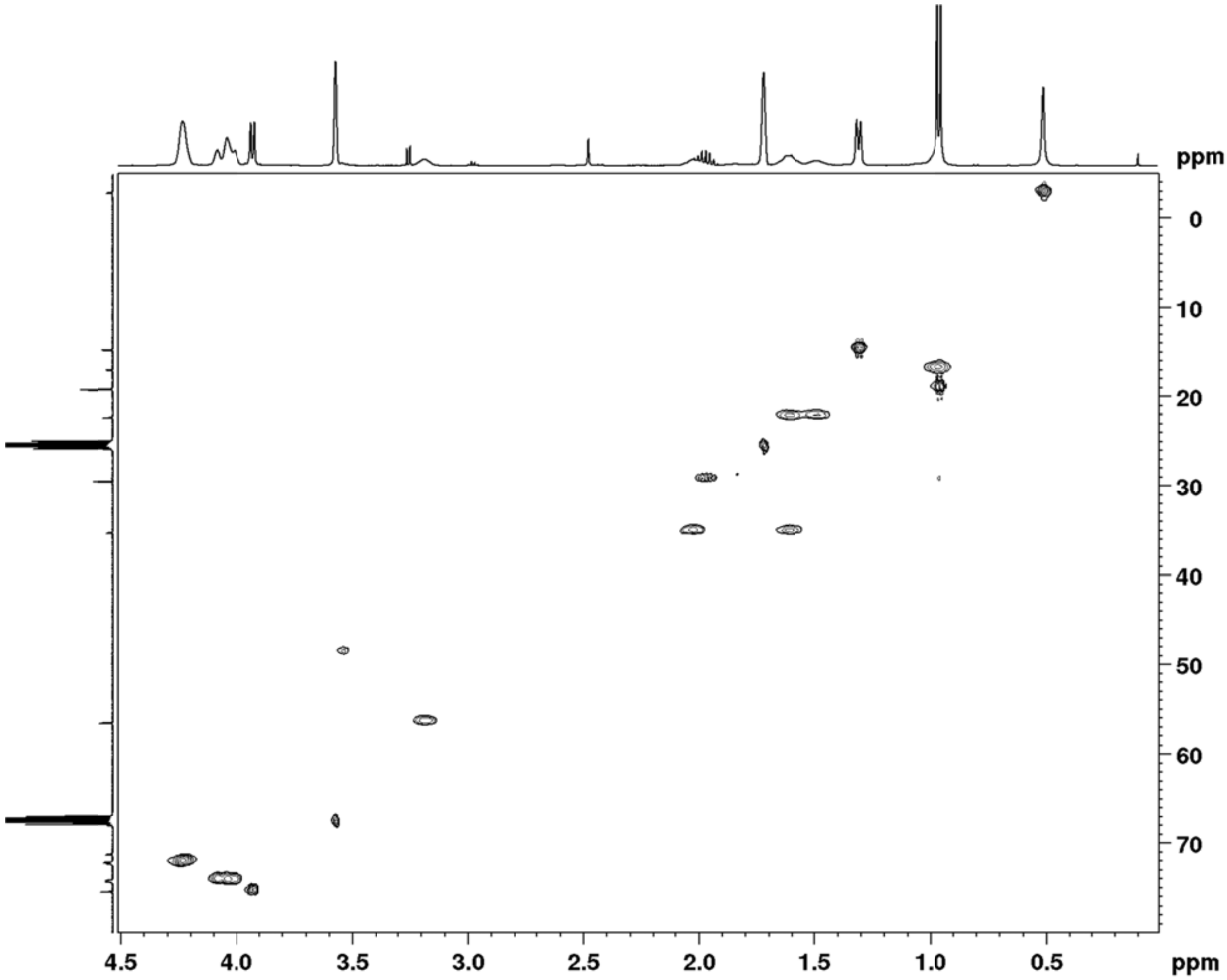
The signal at $\delta = 0.25$ ppm in the ^{1}H NMR spectrum of **1** is ascribed to PDMS (oil bath).

PFS **2** (90 mol% isobutyl sulfonate, 10 mol% ~CH_2-Cl groups), ^{1}H- and ^{13}C NMR spectra in THF-d_8

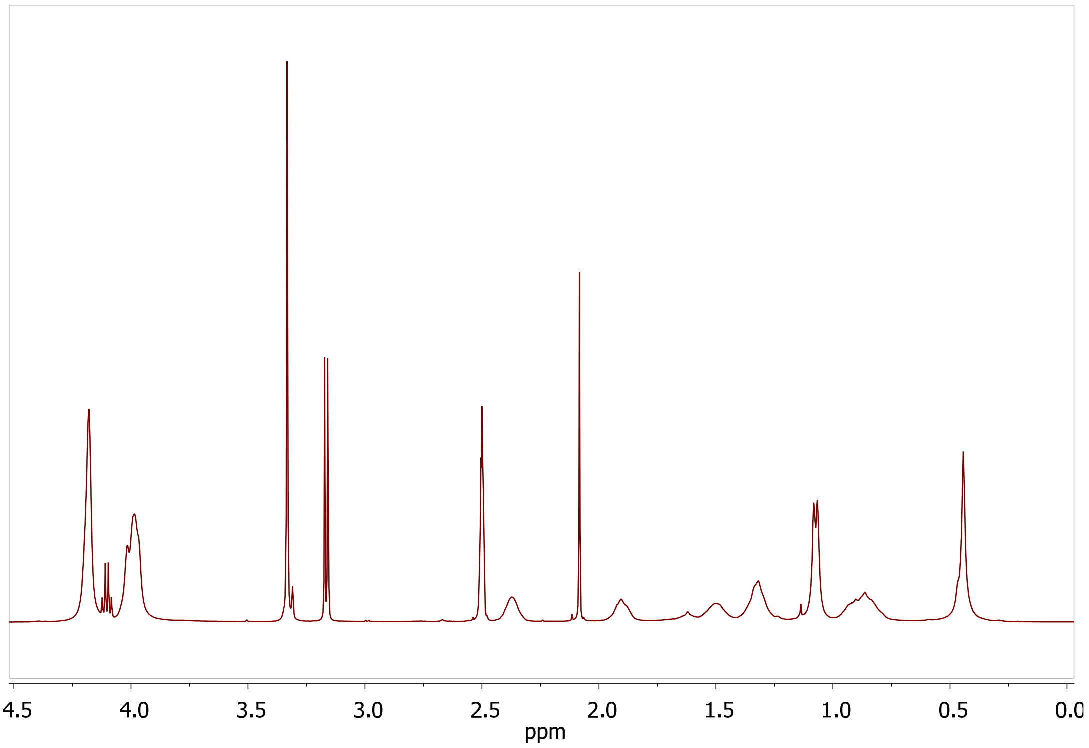


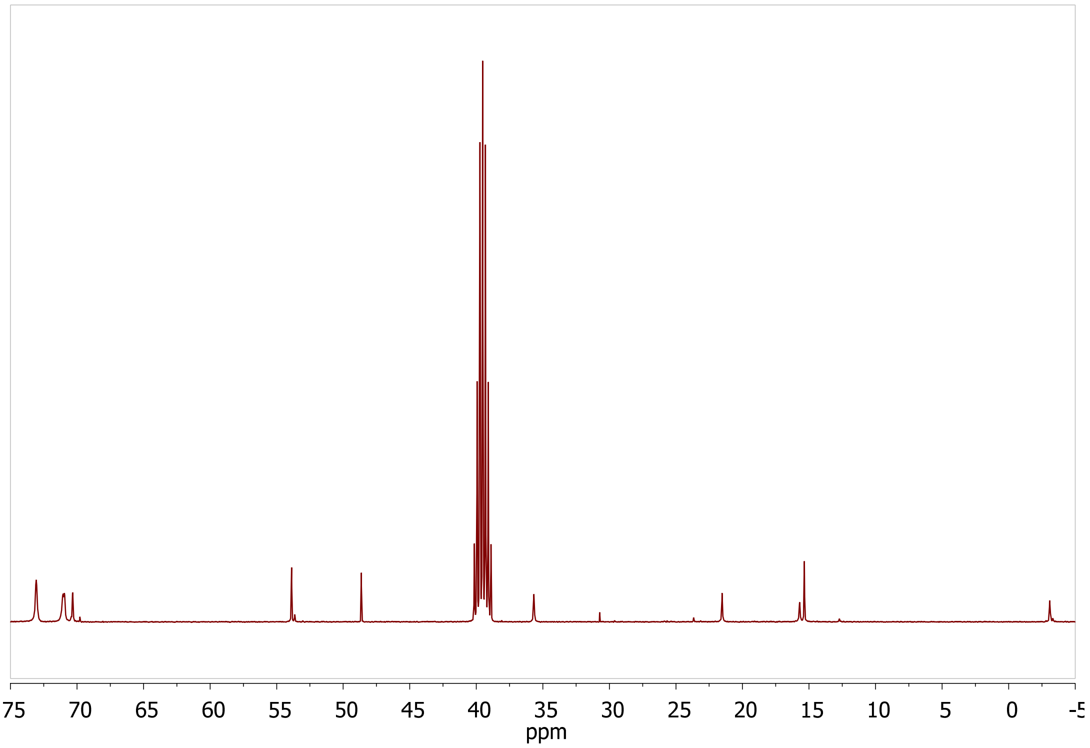


PFS **2**, HSQC-spectrum



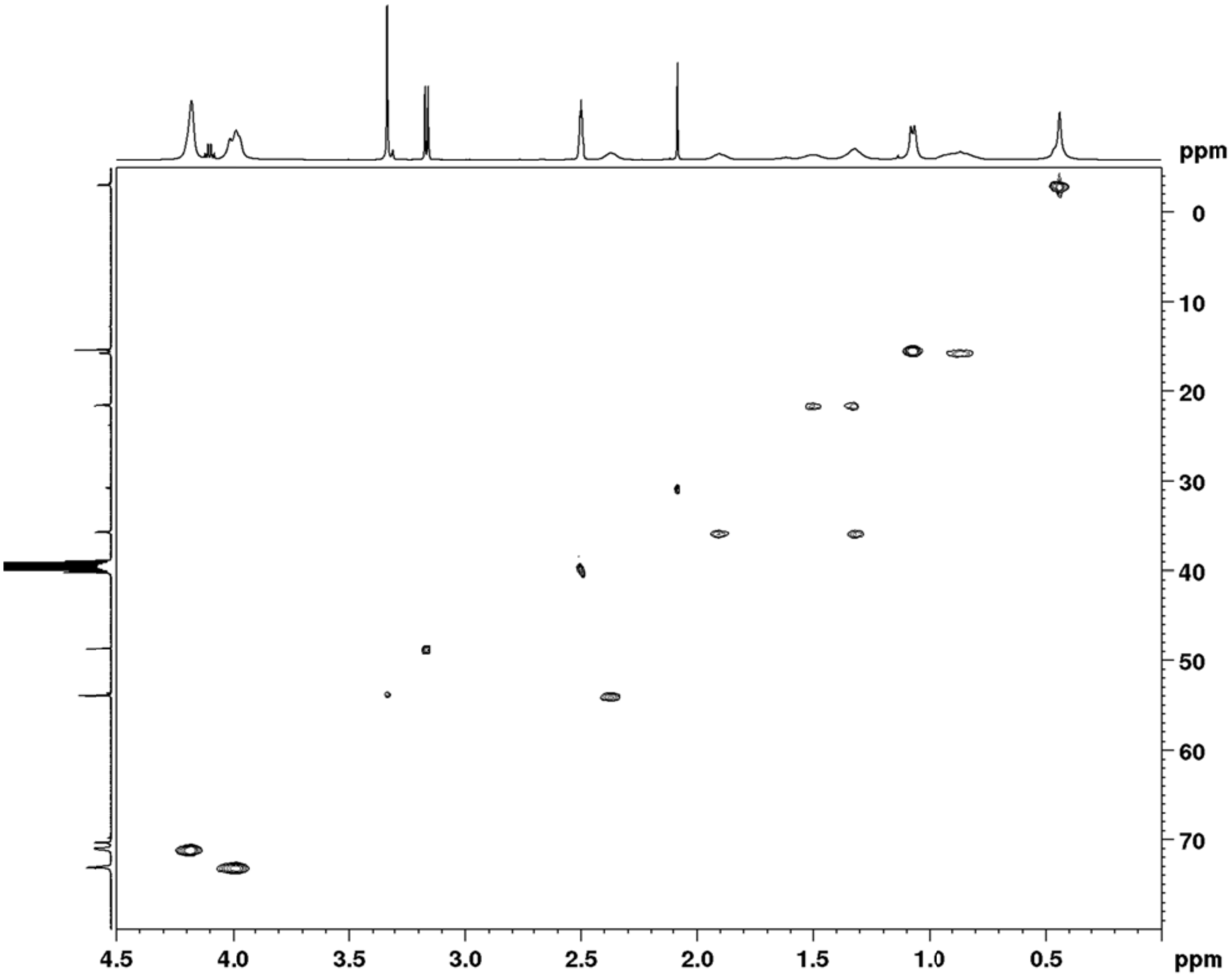
PFS **3**, ^{1}H- and ^{13}C NMR spectra in DMSO-d_6



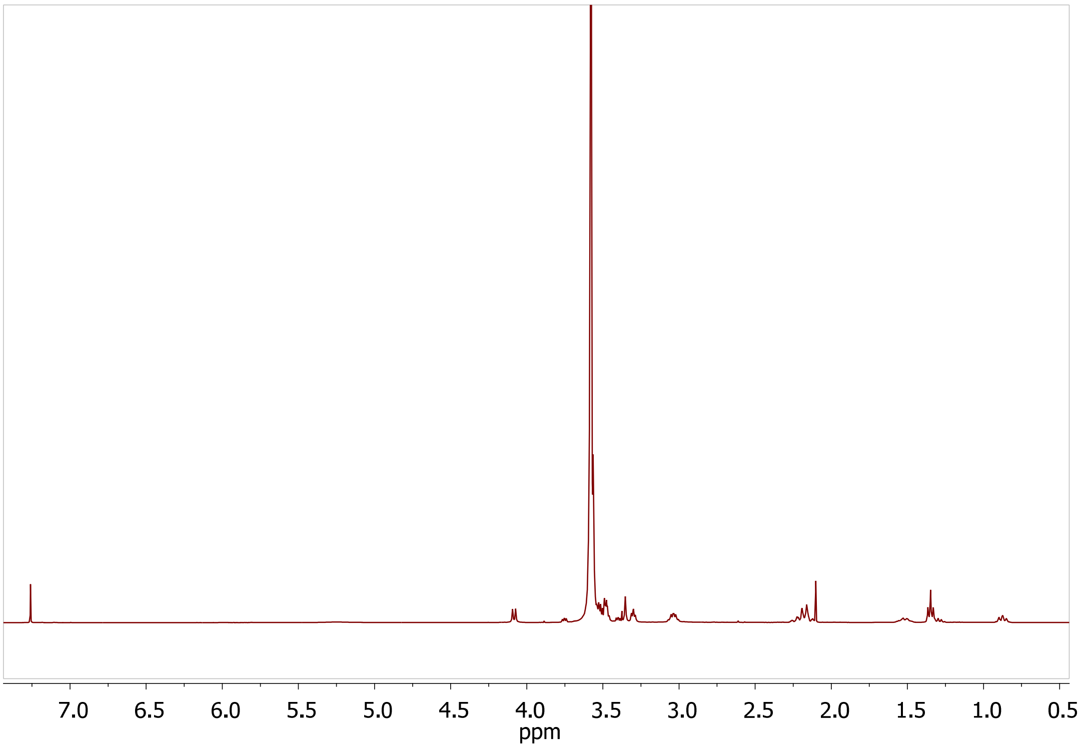


A CH_3OH signal ($\delta = 3.16$ ppm) is present in the ^{1}H NMR spectrum of **3**.

PFS **3**, HSQC-spectrum



PEG-BCN **4**, ^{1}H NMR spectrum in $CDCl_3$



PEG-BCN **4**, ^{13}C-NMR spectrum in Toluene-d_8