

## Supplementary Material

# When a Side Reaction is a Benefit: A Catalyst-Free Route to Obtain High-Molecular Cobaltocenium-Functionalized Polysiloxanes by Hydroamination

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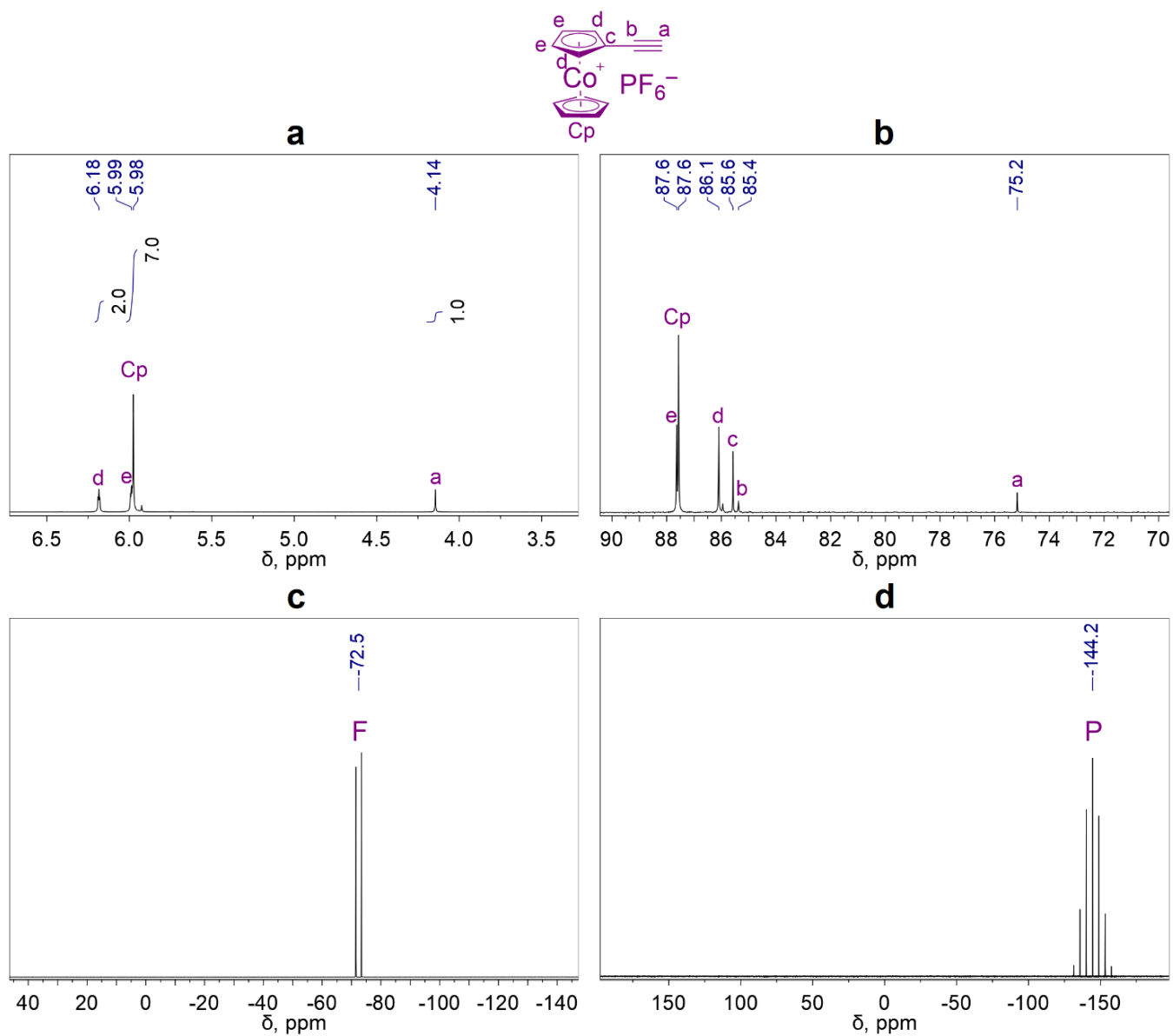
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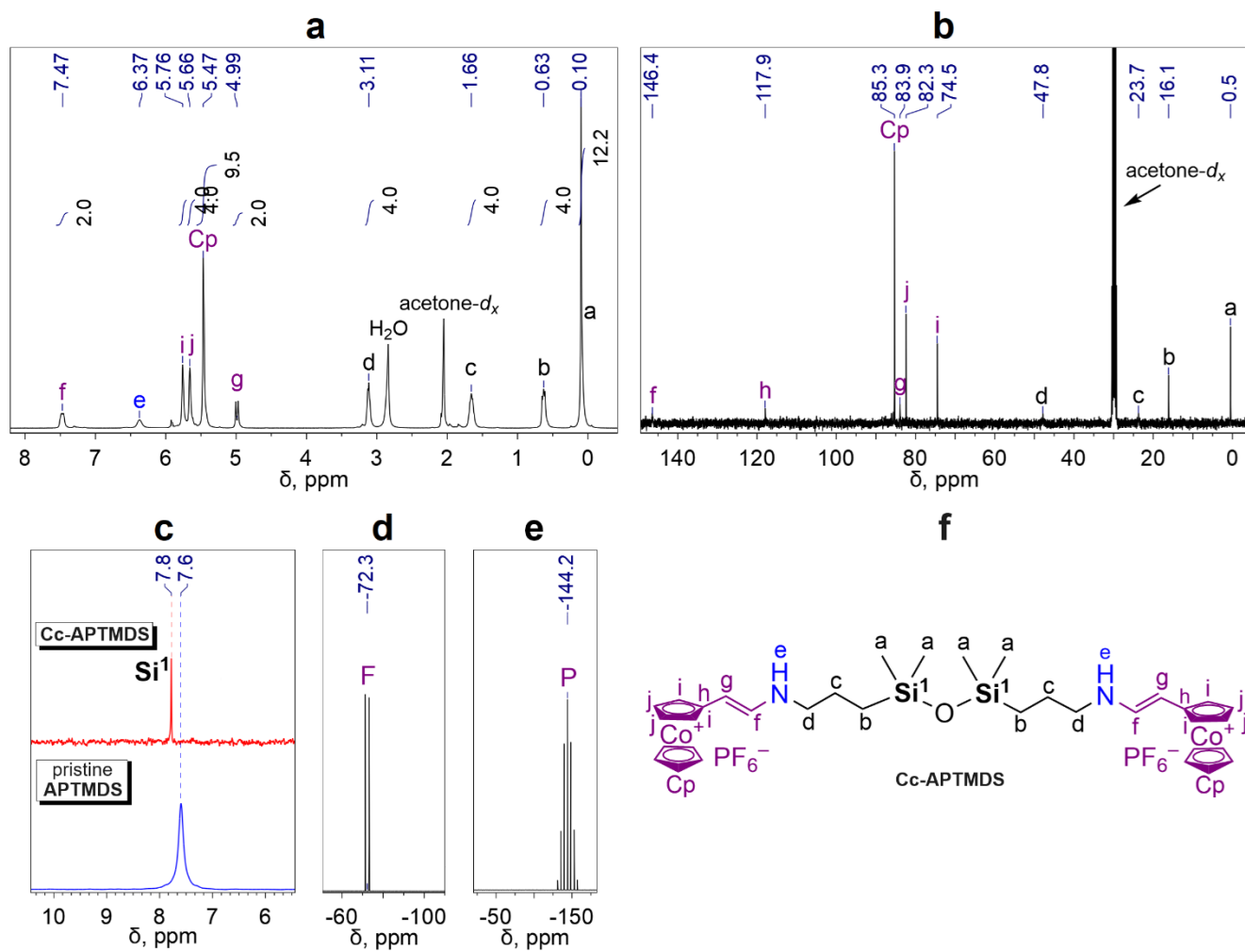
## S1. NMR and mass spectra

### S1.1. NMR spectra of ethynylcobaltocenium hexafluorophosphate

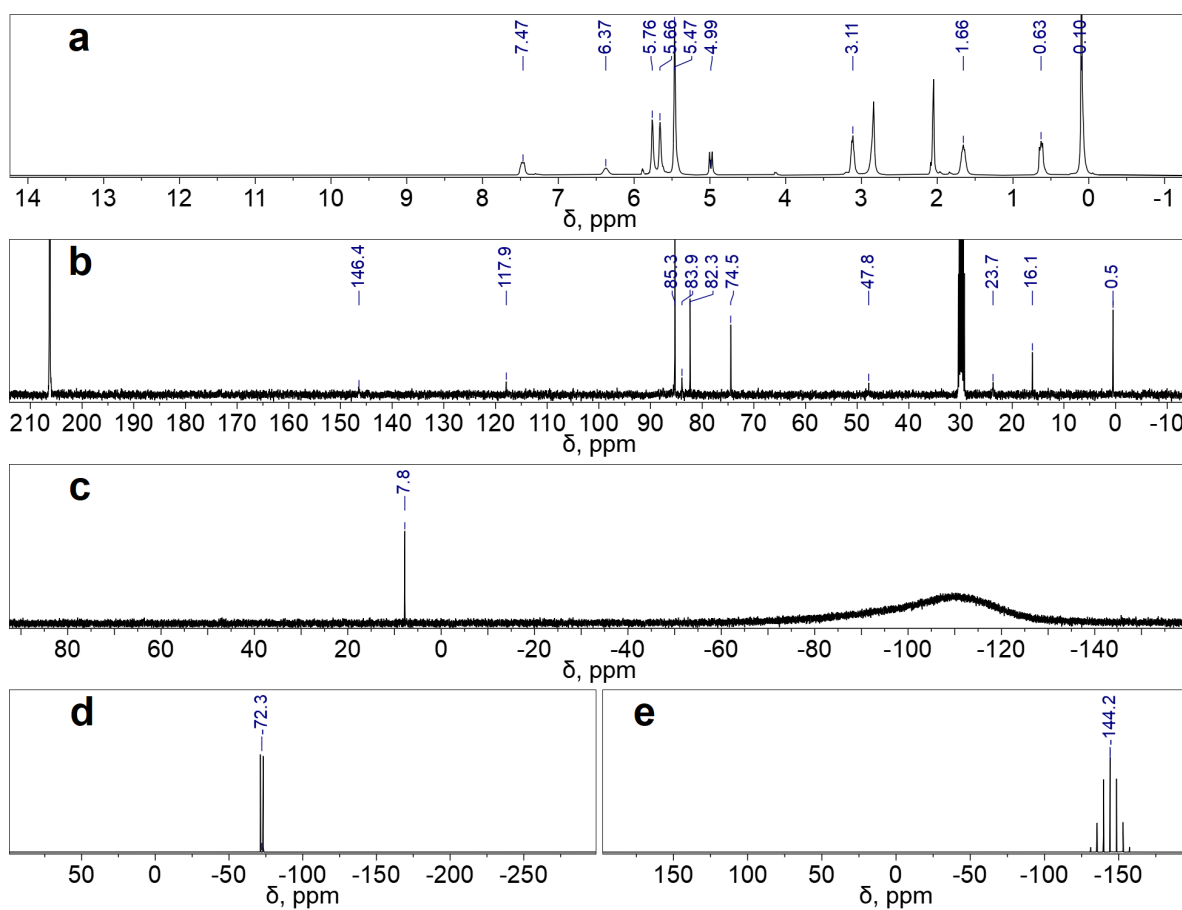


**Figure S1.** Deciphered NMR spectra of ethynylcobaltocenium hexafluorophosphate registered in acetone- $d_6$ :  $^1\text{H}$  (a),  $^{13}\text{C}\{^1\text{H}\}$  (b),  $^{19}\text{F}\{^1\text{H}\}$  (c), and  $^{31}\text{P}\{^1\text{H}\}$  (d).

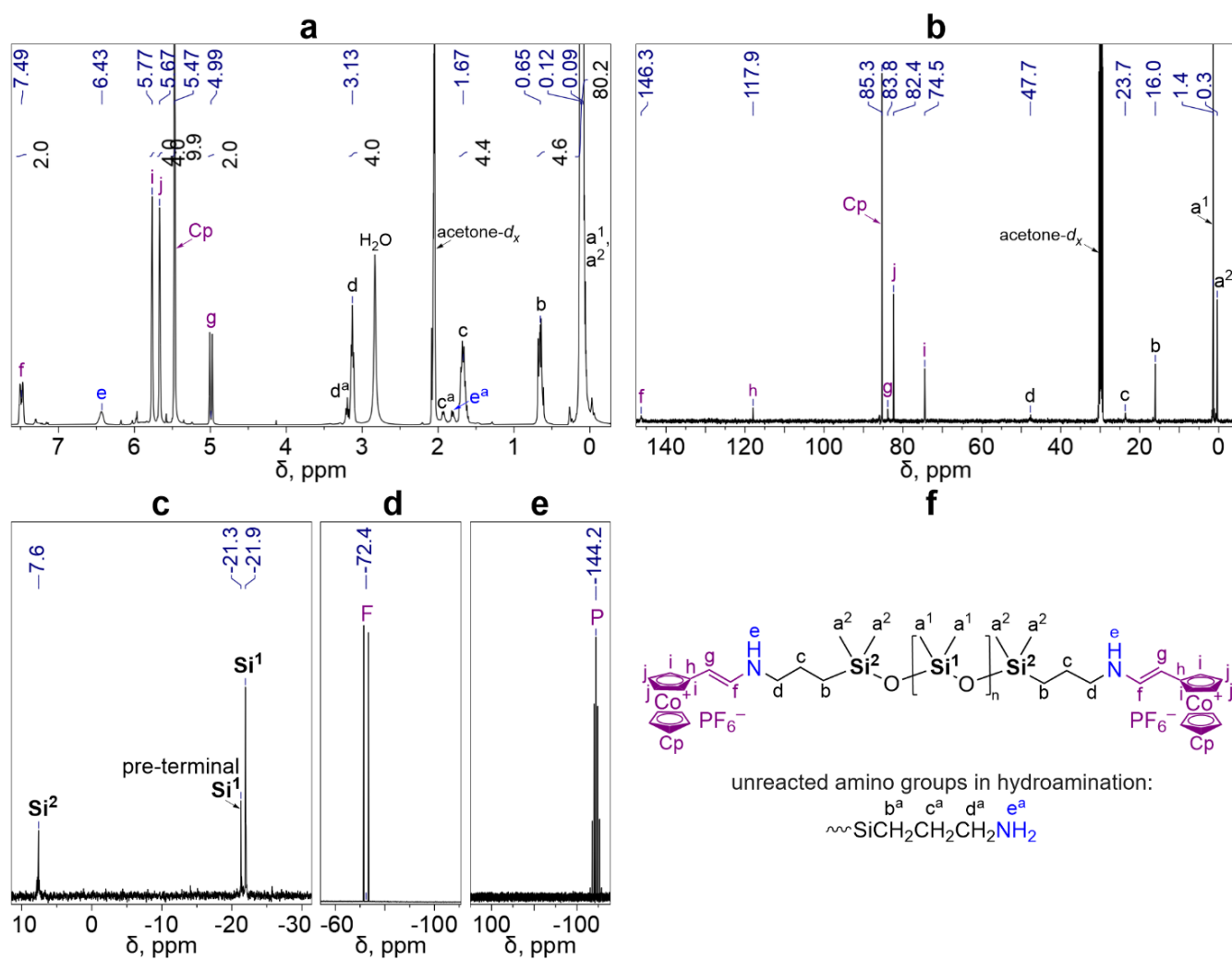
## S1.2. NMR and mass spectra of cobaltocenium-terminated di- and polysiloxanes



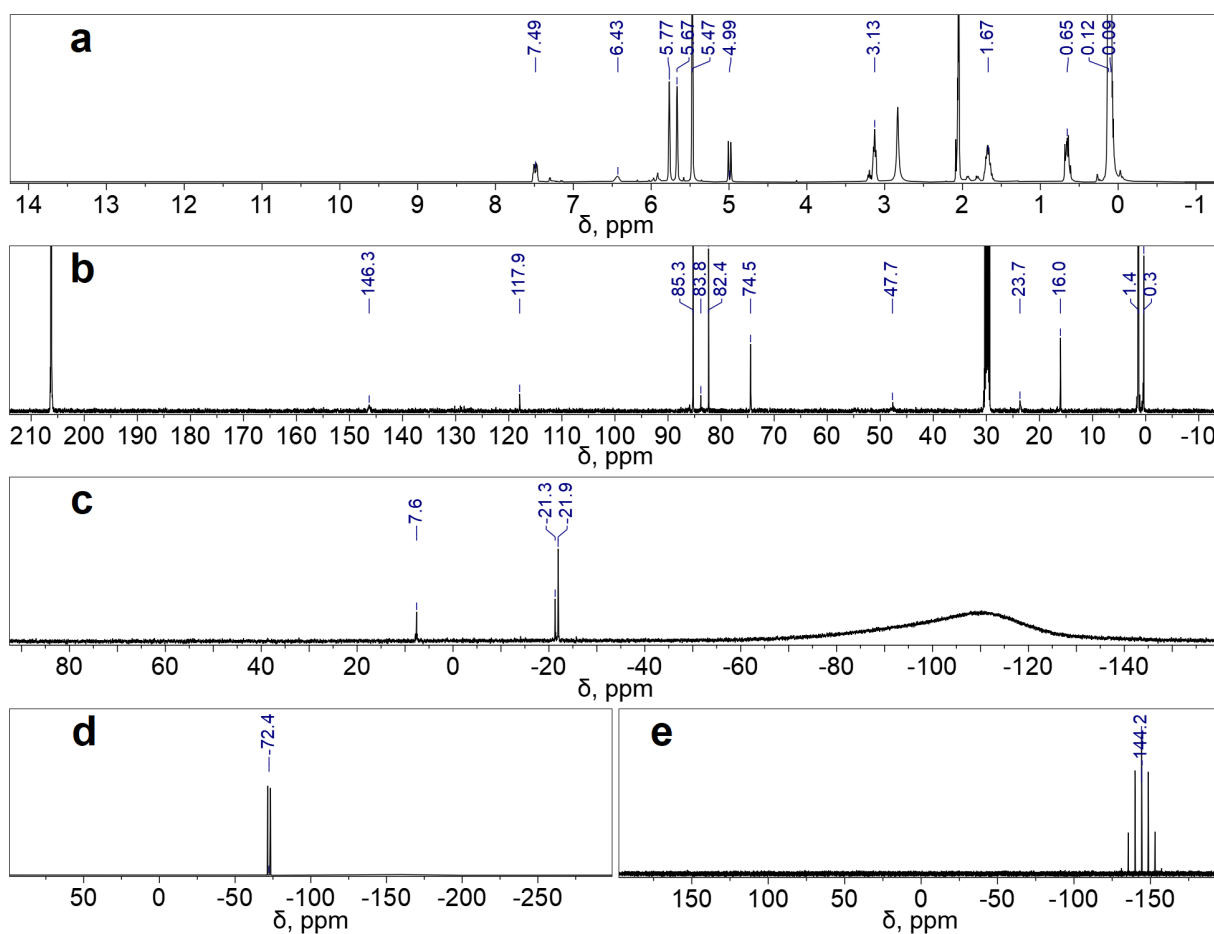
**Figure S2.** Deciphered NMR spectra of Cc-APTMS registered in acetone- $d_6$ :  $^1\text{H}$  (a),  $^{13}\text{C}\{^1\text{H}\}$  (b),  $^{29}\text{Si}\{^1\text{H}\}$  (stacked with pristine APTMS) (c),  $^{19}\text{F}\{^1\text{H}\}$  (d),  $^{31}\text{P}\{^1\text{H}\}$  (e), and its chemical formula (f).



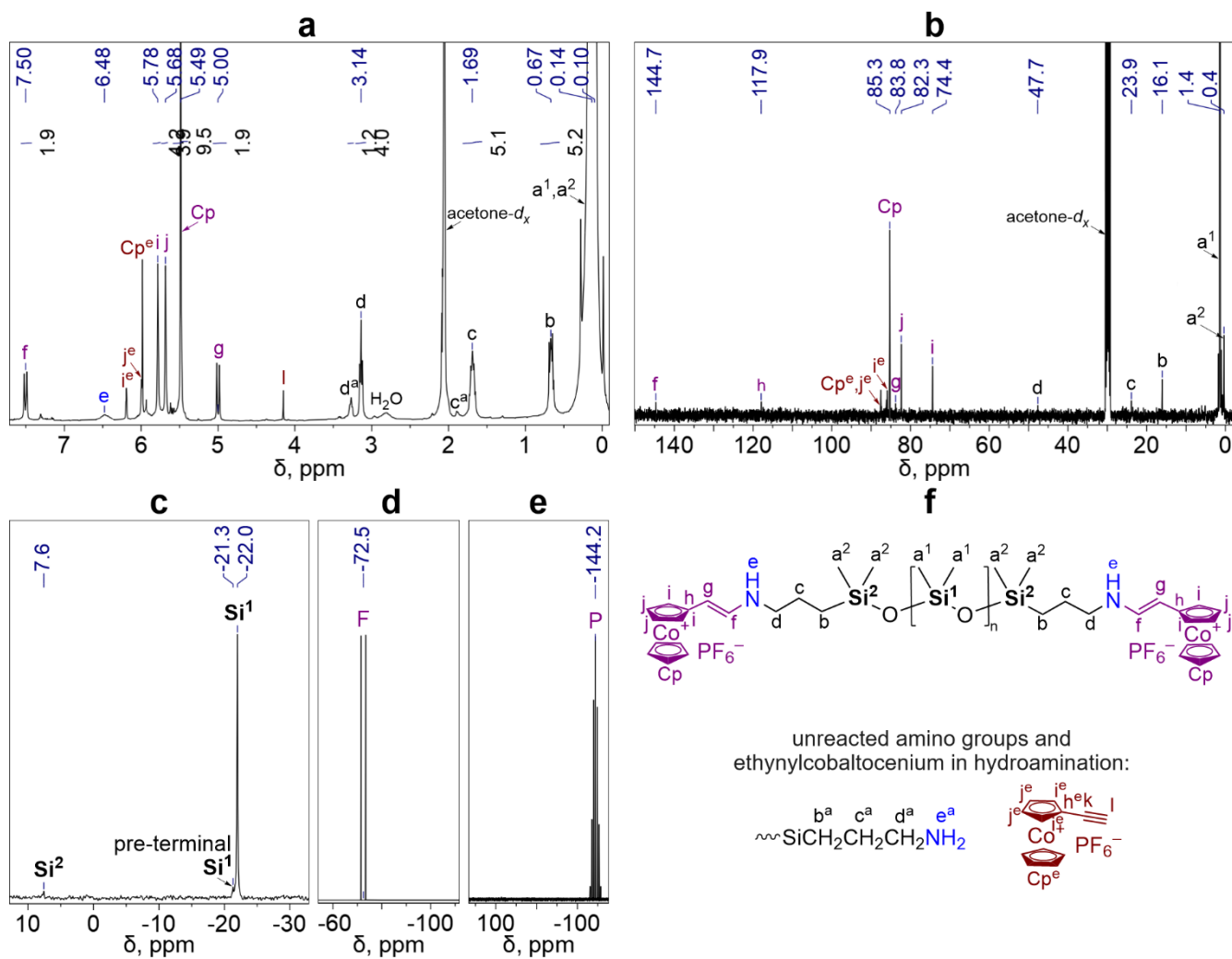
**Figure S3.** Full NMR spectra of Cc-APTMDS registered in acetone- $d_6$ :  $^1\text{H}$  (a),  $^{13}\text{C}\{^1\text{H}\}$  (b),  $^{29}\text{Si}\{^1\text{H}\}$  (c),  $^{19}\text{F}\{^1\text{H}\}$  (d), and  $^{31}\text{P}\{^1\text{H}\}$  (e).



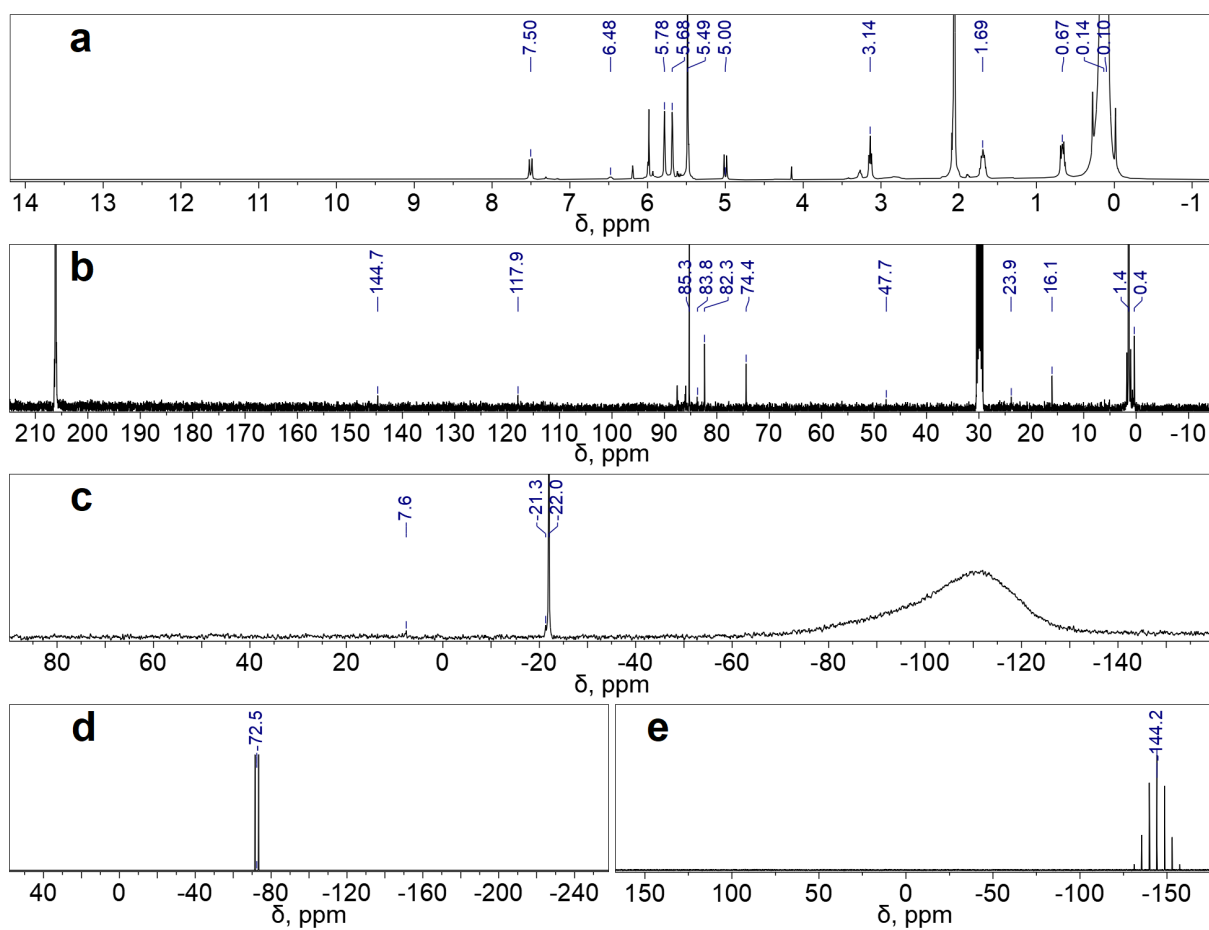
**Figure S4.** Deciphered NMR spectra of Cc-APDMS850 registered in acetone- $d_6$ :  $^1\text{H}$  (a),  $^{13}\text{C}\{^1\text{H}\}$  (b),  $^{29}\text{Si}\{^1\text{H}\}$  (c),  $^{19}\text{F}\{^1\text{H}\}$  (d),  $^{31}\text{P}\{^1\text{H}\}$  (e), and its chemical formula (f).



**Figure S5.** Full NMR spectra of Cc-APDMS850 registered in acetone- $d_6$ :  $^1\text{H}$  (a),  $^{13}\text{C}\{^1\text{H}\}$  (b),  $^{29}\text{Si}\{^1\text{H}\}$  (c),  $^{19}\text{F}\{^1\text{H}\}$  (d), and  $^{31}\text{P}\{^1\text{H}\}$  (e).

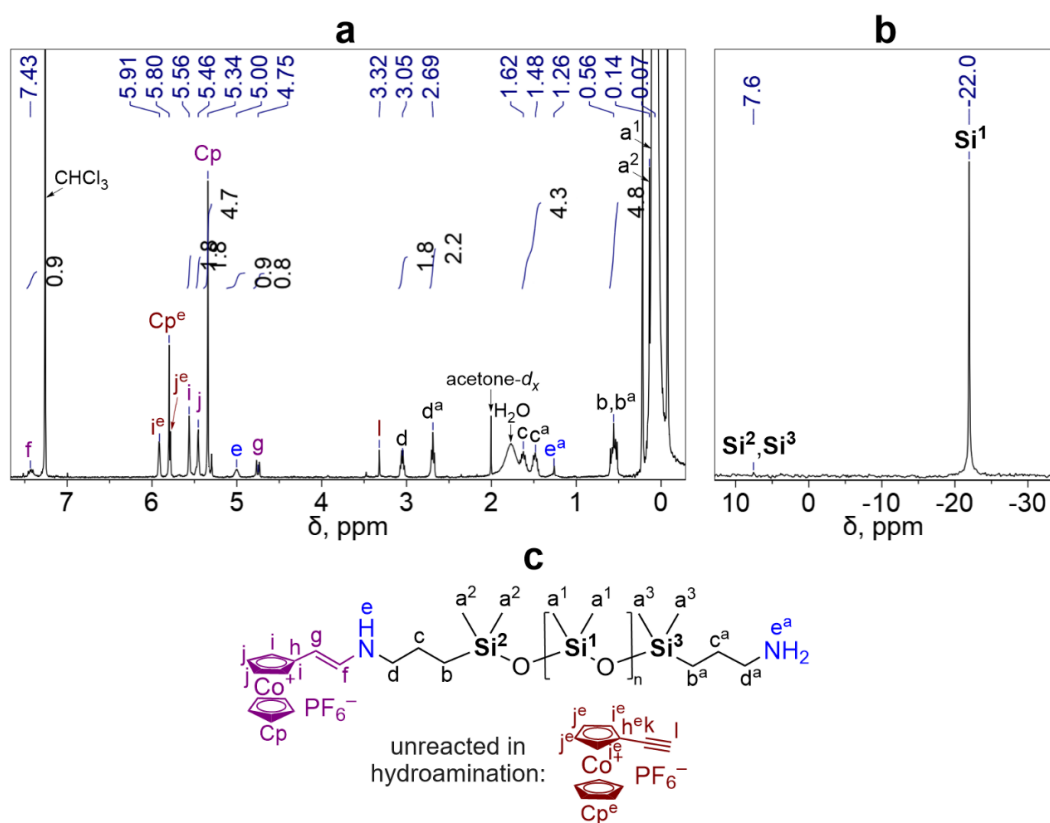


**Figure S6.** Deciphered NMR spectra of Cc-APDMS5000 registered in acetone- $d_6$ :  $^1\text{H}$  (a),  $^{13}\text{C}\{^1\text{H}\}$  (b),  $^{29}\text{Si}\{^1\text{H}\}$  (c),  $^{19}\text{F}\{^1\text{H}\}$  (d),  $^{31}\text{P}\{^1\text{H}\}$  (e), and its chemical formula (f).

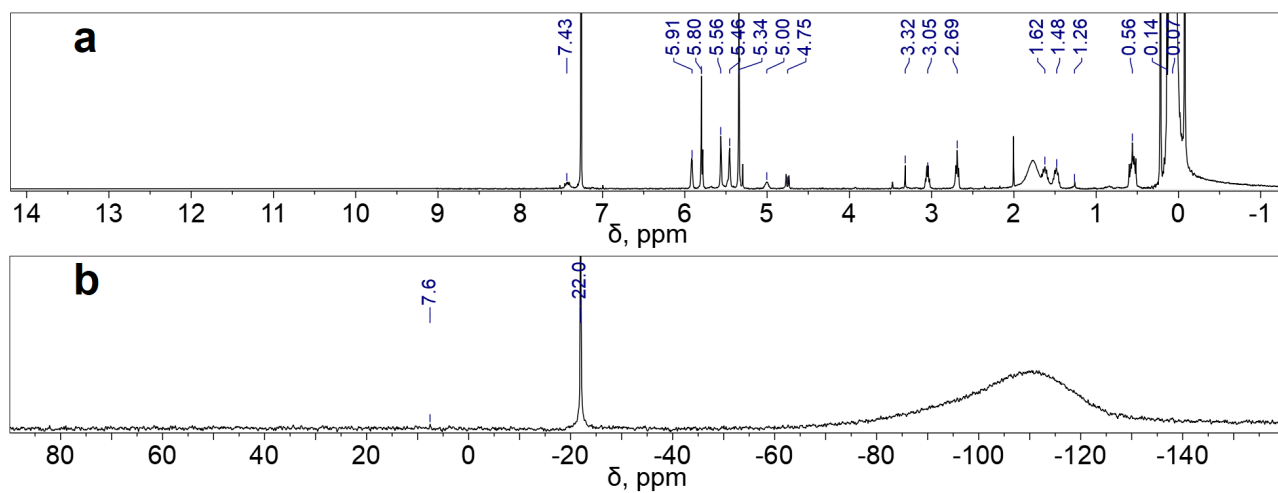


**Figure S7.** Full NMR spectra of Cc-APDMS5000 registered in acetone- $d_6$ :  $^1\text{H}$  (a),  $^{13}\text{C}\{^1\text{H}\}$  (b),  $^{29}\text{Si}\{^1\text{H}\}$  (c),  $^{19}\text{F}\{^1\text{H}\}$  (d), and  $^{31}\text{P}\{^1\text{H}\}$  (e).

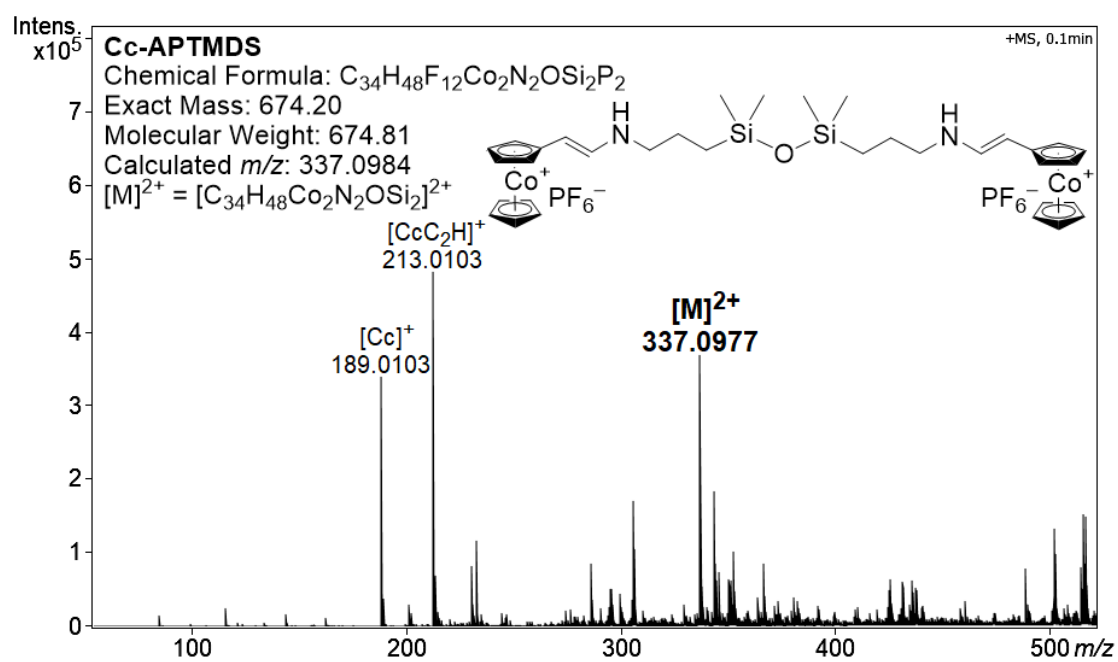




**Figure S8.** Deciphered NMR spectra of Cc-APDMS25000 registered in  $\text{CDCl}_3$ :  $^1\text{H}$  (a),  $^{29}\text{Si}\{^1\text{H}\}$  (b), and its chemical formula (c).

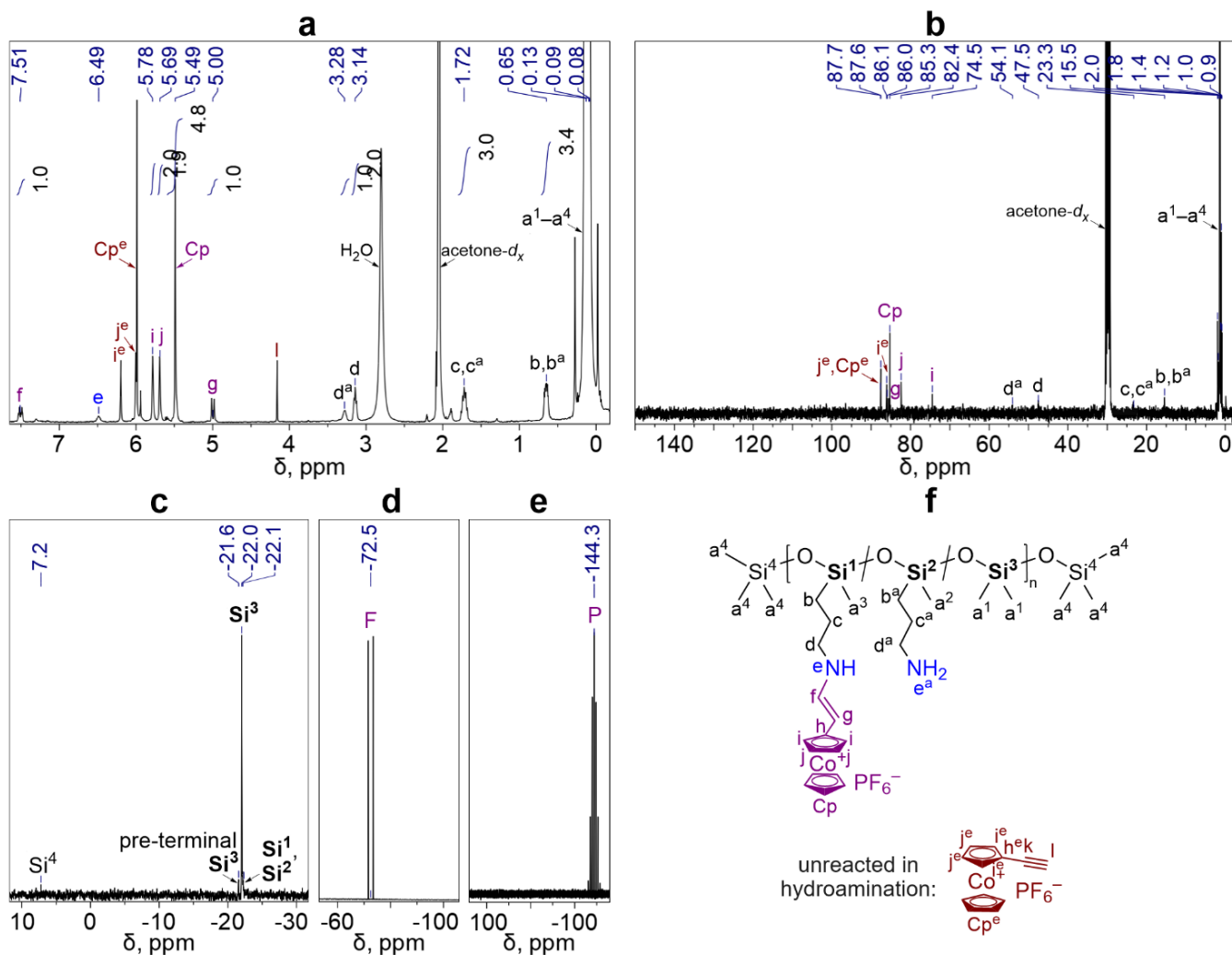


**Figure S9.** Full NMR spectra of Cc-APDMS25000 registered in  $\text{acetone-}d_6$ :  $^1\text{H}$  (a) and  $^{29}\text{Si}\{^1\text{H}\}$  (b).

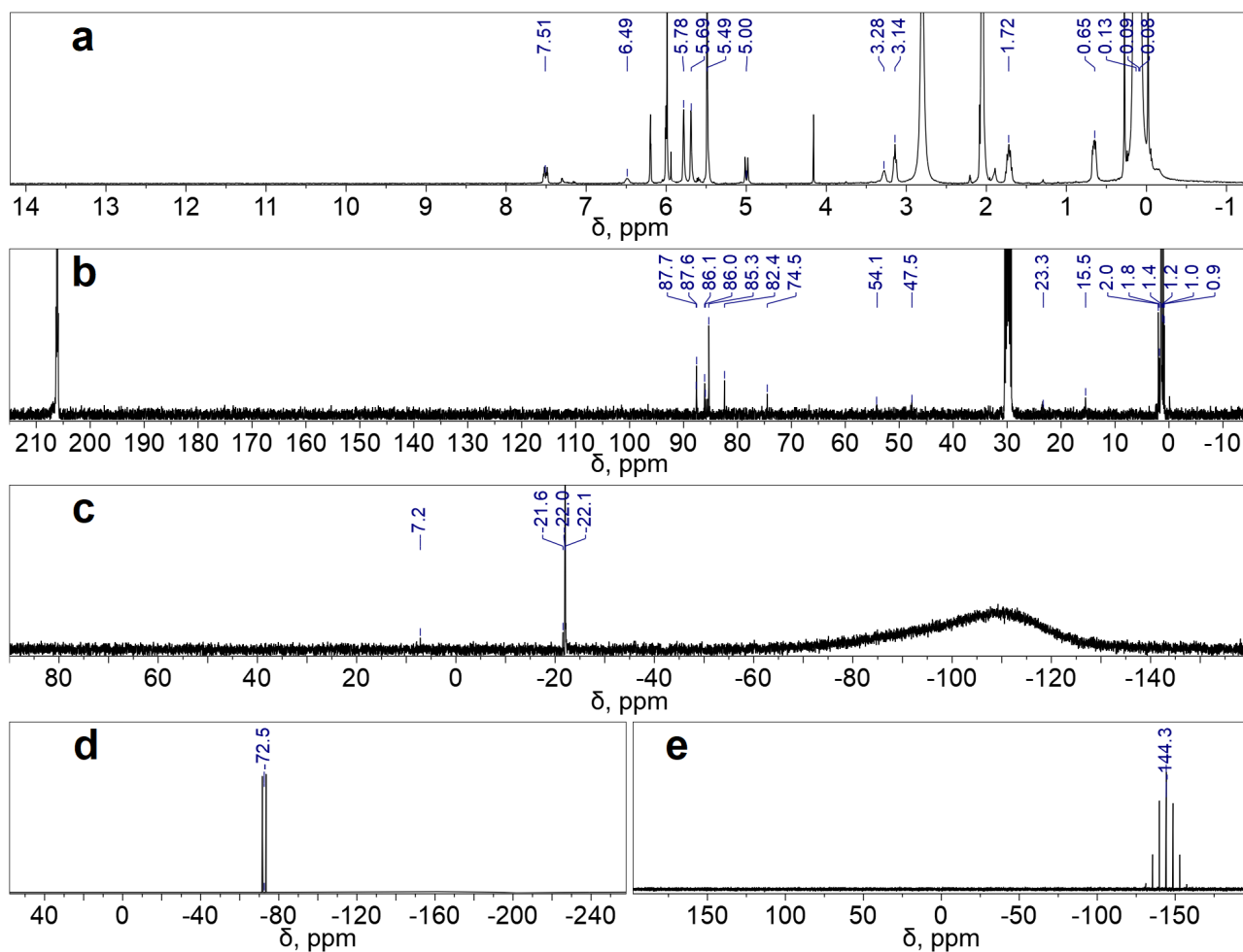


**Figure S10.** HRMS spectrum of Cc-APTMDS recorded in a positive ion mode.

### S1.3. NMR spectra of copolysiloxane containing cobaltocenium as side groups



**Figure S11.** Deciphered NMR spectra of P(Cc-AMS-co-DMS) registered in acetone- $d_6$ :  $^1\text{H}$  (a),  $^{13}\text{C}\{^1\text{H}\}$  (b),  $^{29}\text{Si}\{^1\text{H}\}$  (c),  $^{19}\text{F}\{^1\text{H}\}$  (d),  $^{31}\text{P}\{^1\text{H}\}$  (e), and its chemical formula (f).



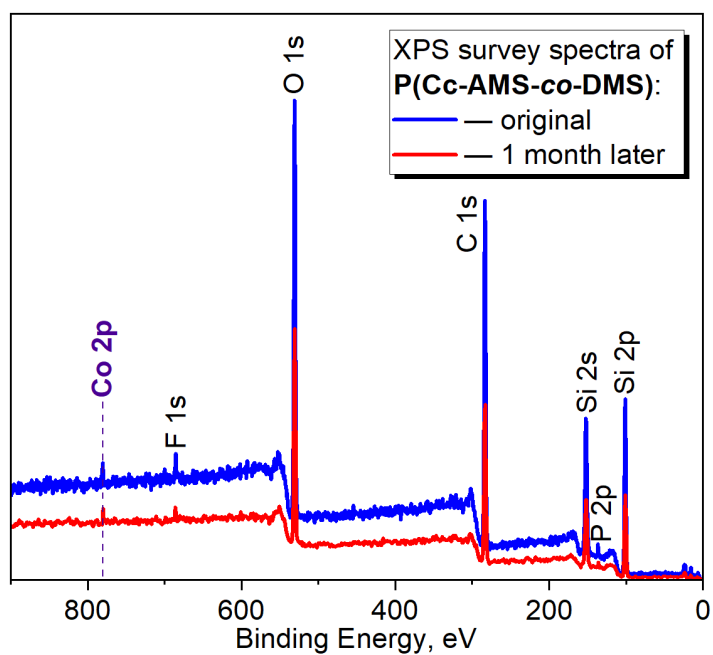
**Figure S12.** Full NMR spectra of P(Cc-AMS-*co*-DMS) registered in acetone-*d*<sub>6</sub>:  $^1\text{H}$  (a),  $^{13}\text{C}\{^1\text{H}\}$  (b),  $^{29}\text{Si}\{^1\text{H}\}$  (c),  $^{19}\text{F}\{^1\text{H}\}$  (d), and  $^{31}\text{P}\{^1\text{H}\}$  (e).

## S2. XPS data

**Table S1.** Concentrations of cobalt in the polymer samples.

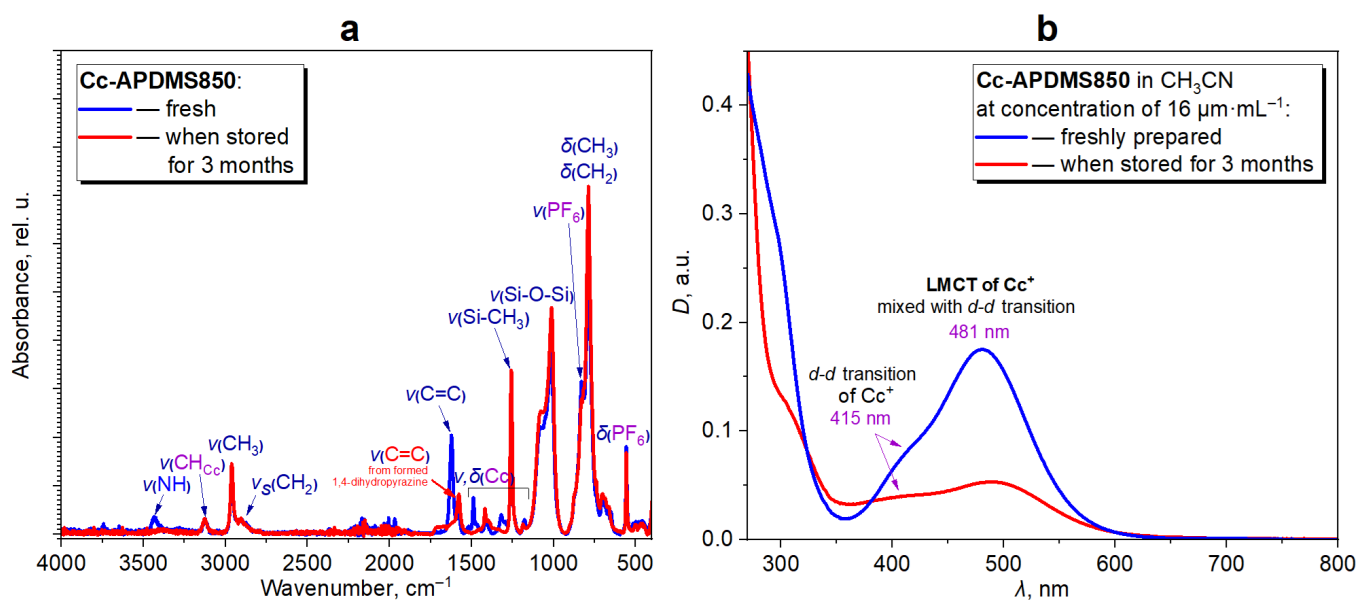
Cobaltocenium-containing (poly)siloxane	Peak BE, <sup>a)</sup> eV	FWHM <sup>b)</sup>	Peak area	Concentration of cobalt		Concentration of cobaltocenium, wt. %
				Atomic %	wt. %	
Cc-APTMS	780.5	1.8	3442	1.4	5.2	15.8
Cc-APDMS850	780.8	1.8	1019	0.6	2.0	6.1
Cc-APDMS5000	779.5	0.3	253	0.2	0.6	1.8
Cc-APDMS25000	780.0	0.2	164	0.1	0.3	0.9
P(Cc-AMS-co-DMS)	779.6	0.7	336	0.2	0.5	1.5

<sup>a)</sup> BE — binding energy; <sup>b)</sup> FWHM — full width at half maximum.

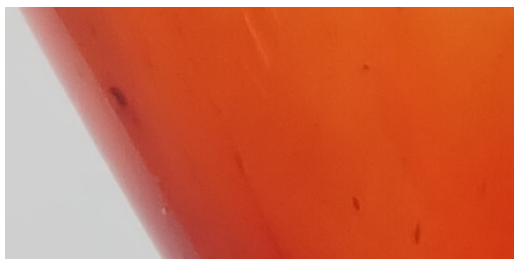


**Figure S13.** XPS survey spectra ranging from 0 to 900 eV of original (freshly synthesized) P(Cc-AMS-co-DMS) and after being stored for 1 month.

### S3. Molecular spectroscopic data and photographs

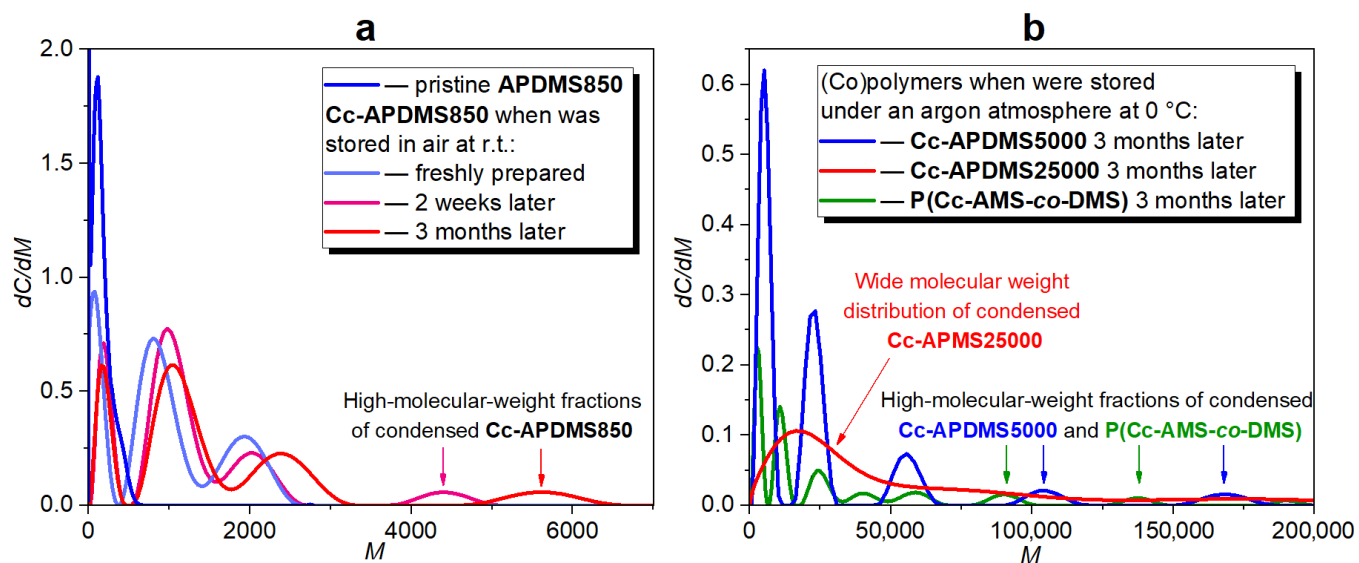


**Figure S14.** Molecular spectra of Cc-APDMS850: FTIR-ATR spectra in the range of 400–4000  $\text{cm}^{-1}$  (a) and UV-vis spectra in  $\text{CH}_3\text{CN}$  solution in the range of 200–800 nm (b).



**Figure S15.** Photograph of Cc-APDMS5000 film on a glassy template after “gelation” during storage for one week.

## S4. Sedimentation velocity data



**Figure S16.** Molecular weight distributions of APDMS850 and Cc-APDMS850 (a) and other Cc-PDMSs (b) obtained by sedimentation velocity experiments of their solutions in acetone at r.t.