

Supporting Information

Polysiloxanes Bearing Pendant Redox-Active Dendritic Wedges Containing Ferrocenyl and (η^6 -Aryl)tricarbonylchromium Moieties

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1.- Structural Characterization of Model Compounds 5–7

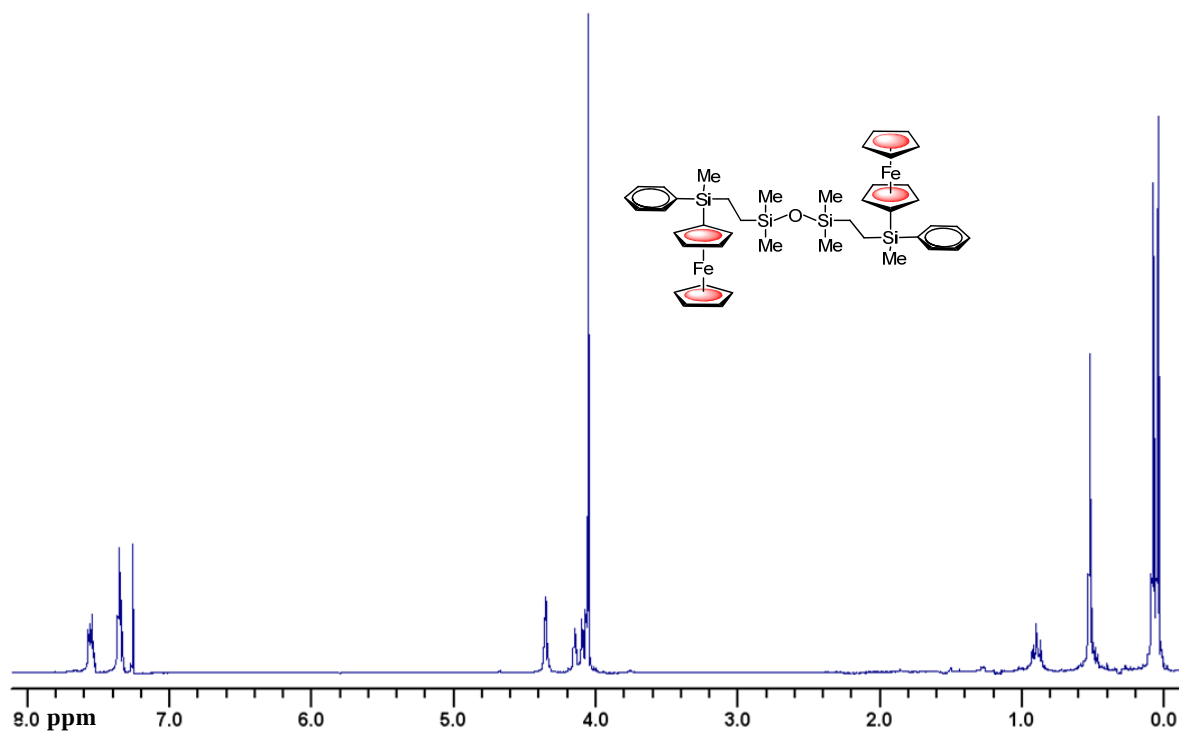


Figure S1. ^1H NMR spectrum (in CDCl_3 , 300 MHz) of compound 5.

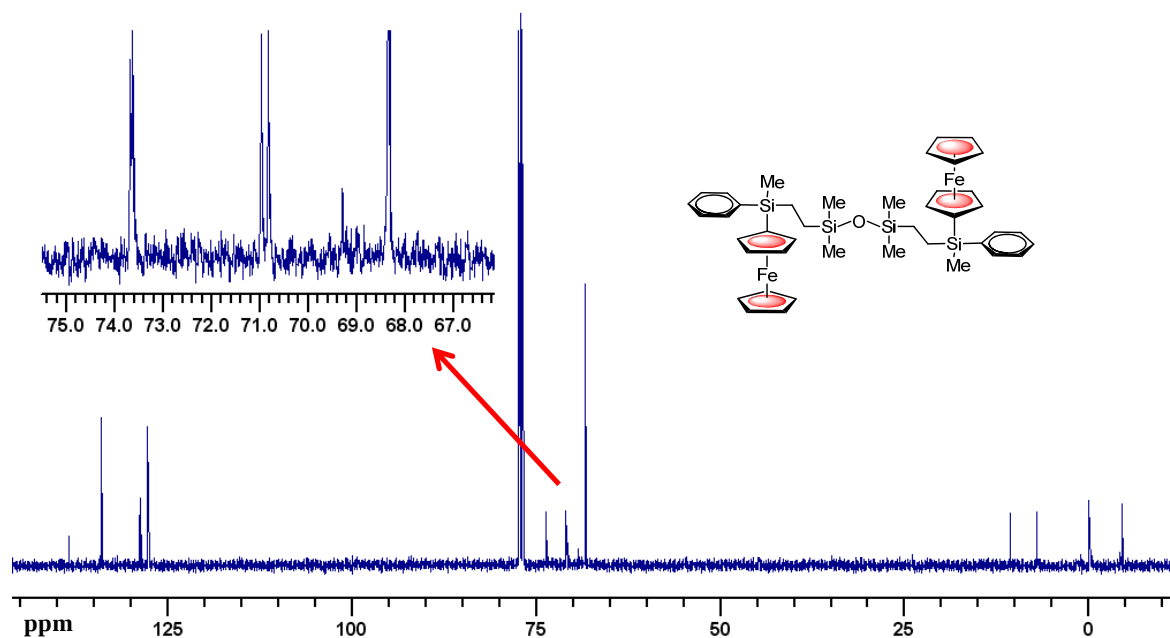


Figure S2. ^{13}C NMR spectrum (in CDCl_3 , 125 MHz) of compound 5 (inset: expanded view of cyclopentadienyl region).

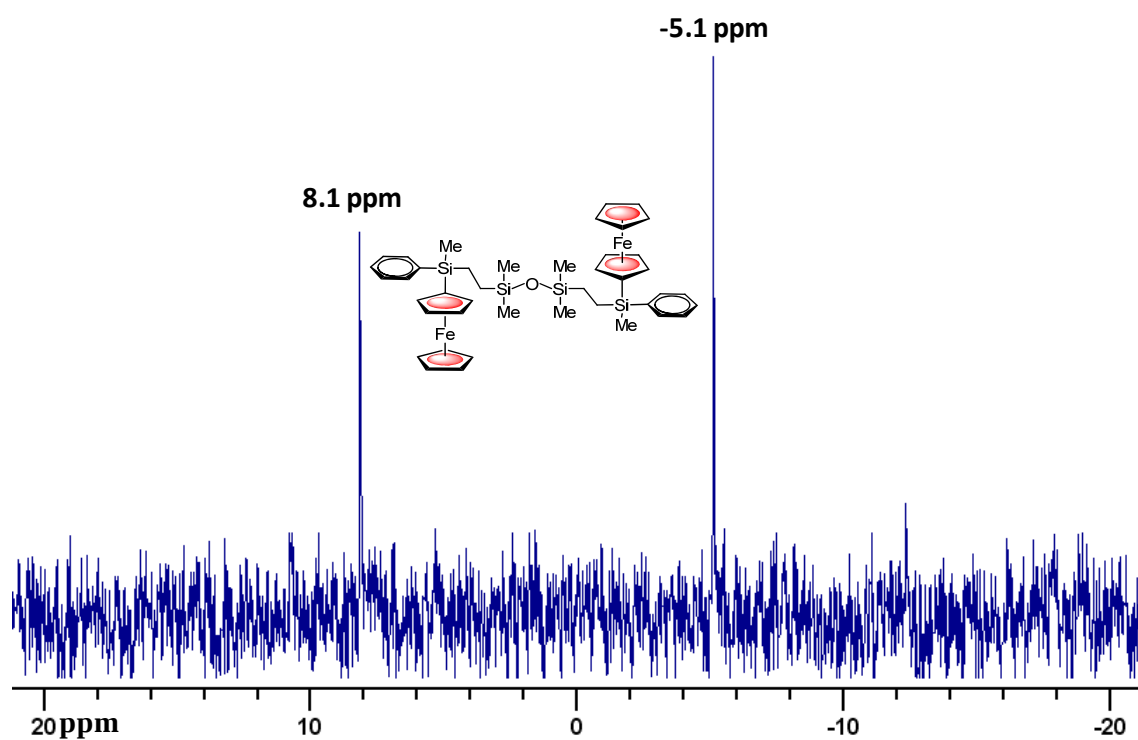


Figure S3. ^{29}Si NMR spectrum (in CDCl_3 , 99 MHz) of compound 5.

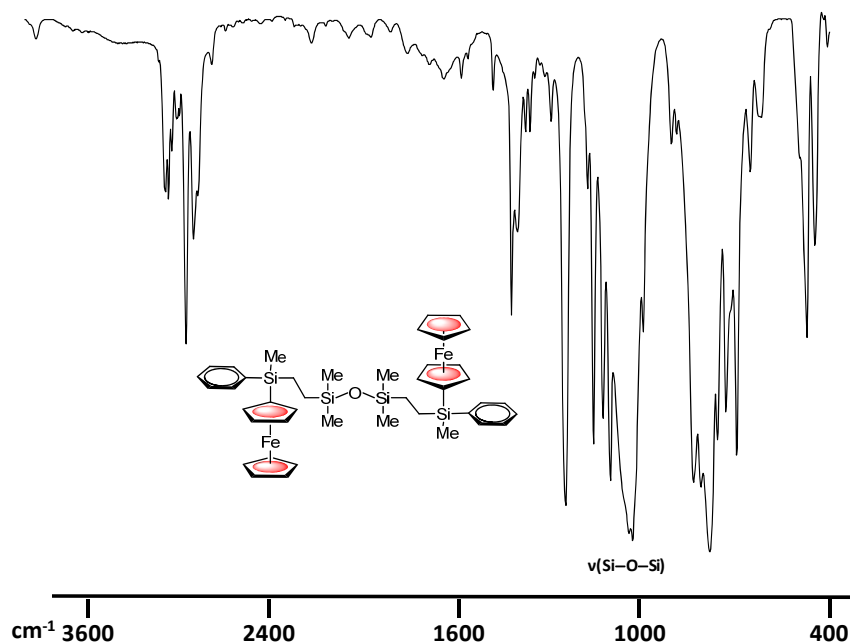


Figure S4. IR spectrum (in KBr windows) of compound 5.

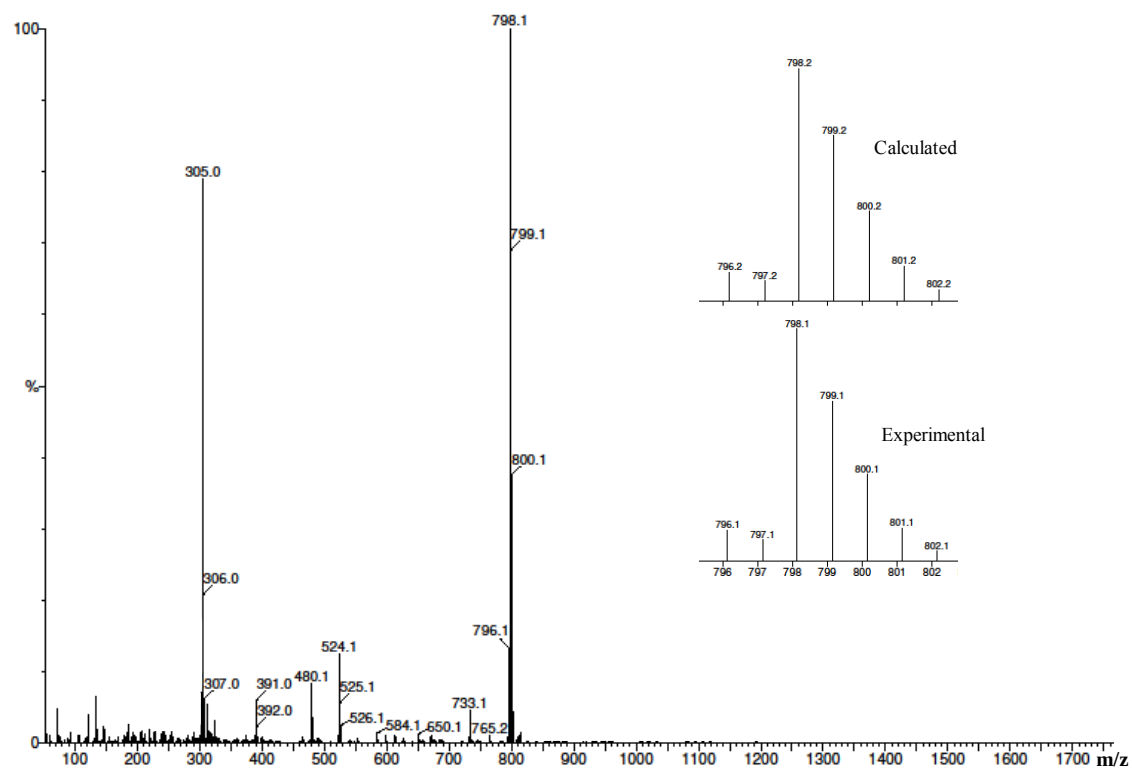


Figure S5. Mass spectrometry characterization by FAB for compound 5. Inset: isotopic distribution of molecular ion peak of 5.

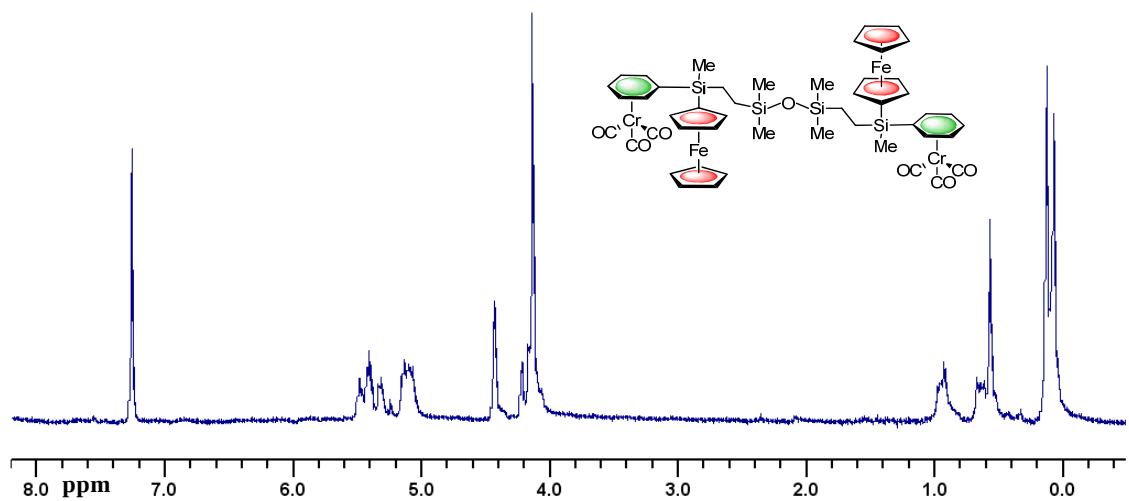


Figure S6. ^1H NMR spectrum (in CDCl_3 , 300 MHz) of compound **6**.

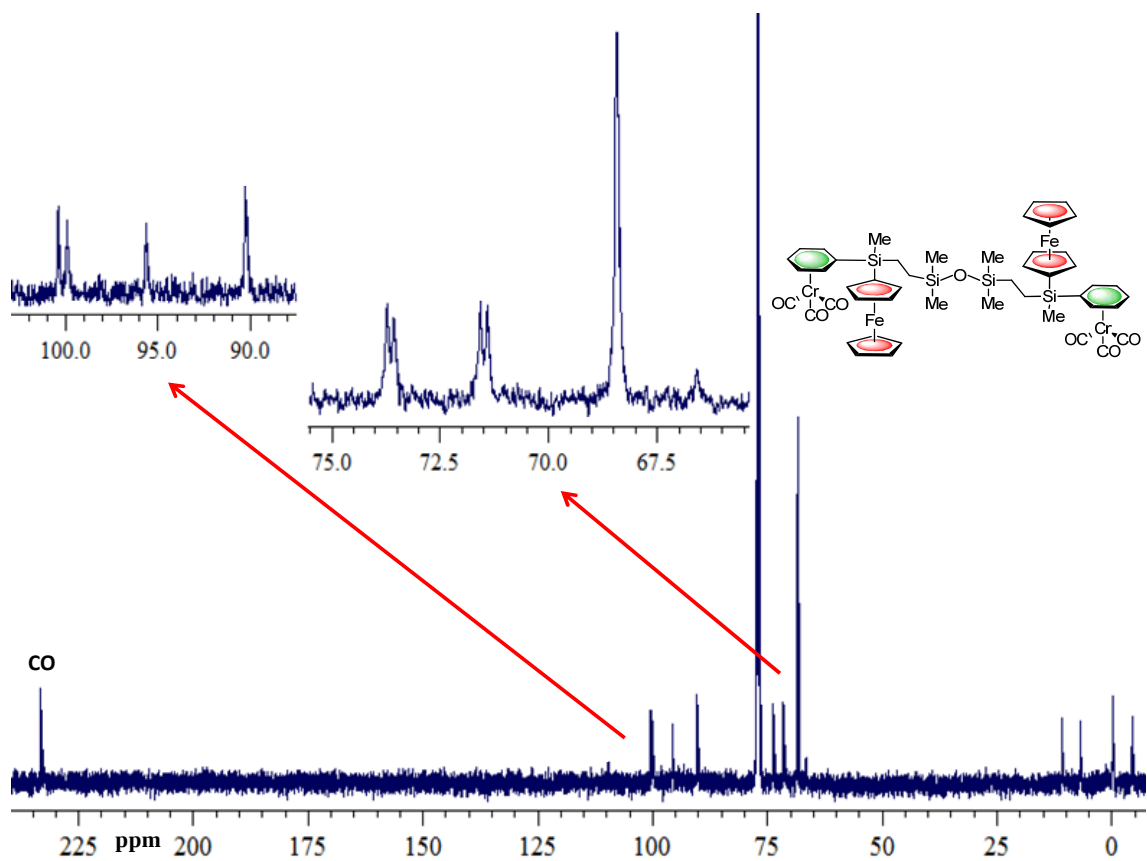


Figure S7. ^{13}C NMR spectrum (in CDCl_3 , 125 MHz) of compound **6**, (inset: expanded view of phenyl and cyclopentadienyl regions).

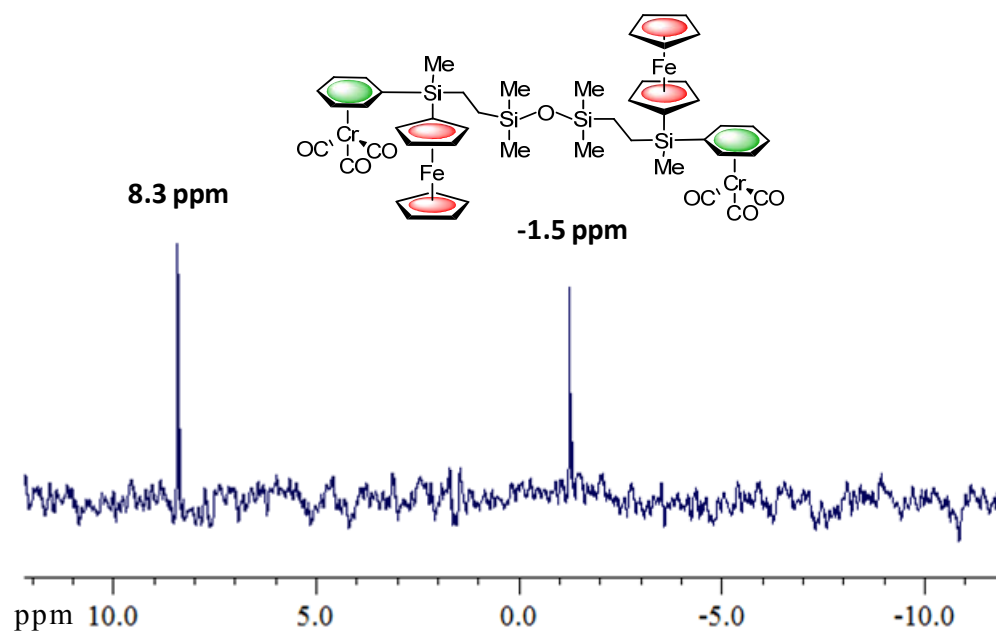


Figure S8. ^{29}Si NMR spectrum (in CDCl_3 , 99 MHz) of compound 6.

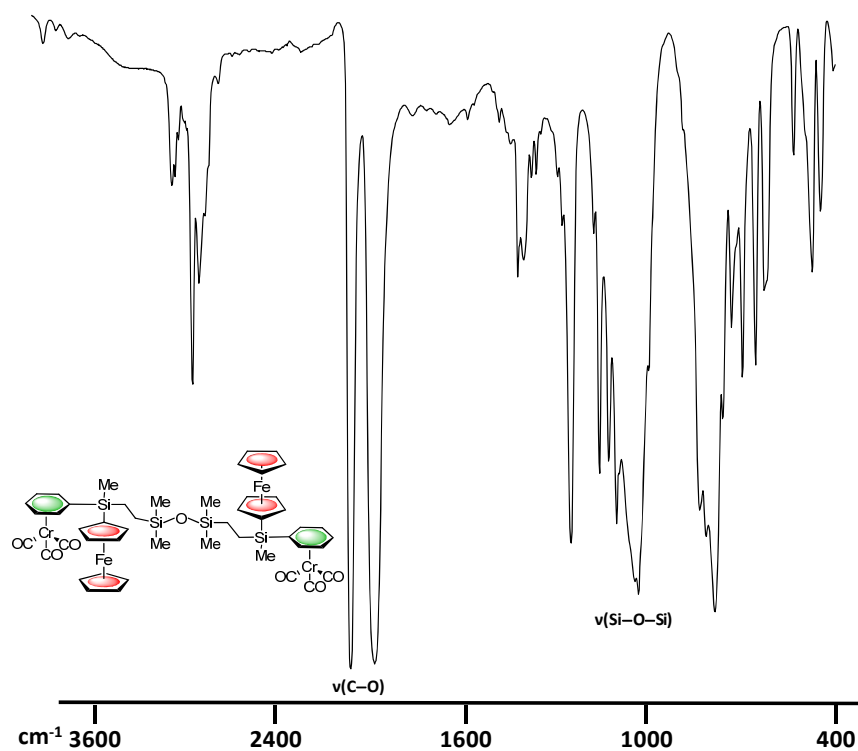


Figure S9. IR spectrum (in KBr windows) of compound 6.

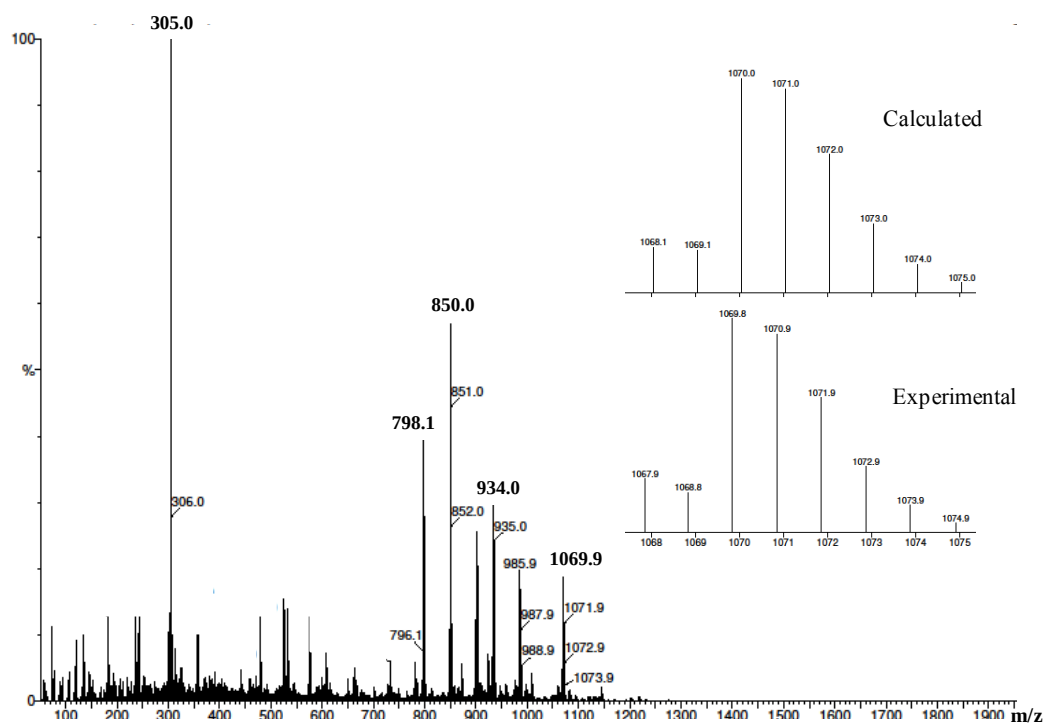


Figure S10. Mass spectrometry characterization by FAB for compound **6**. Inset: isotopic distribution of molecular ion peak of **6**.

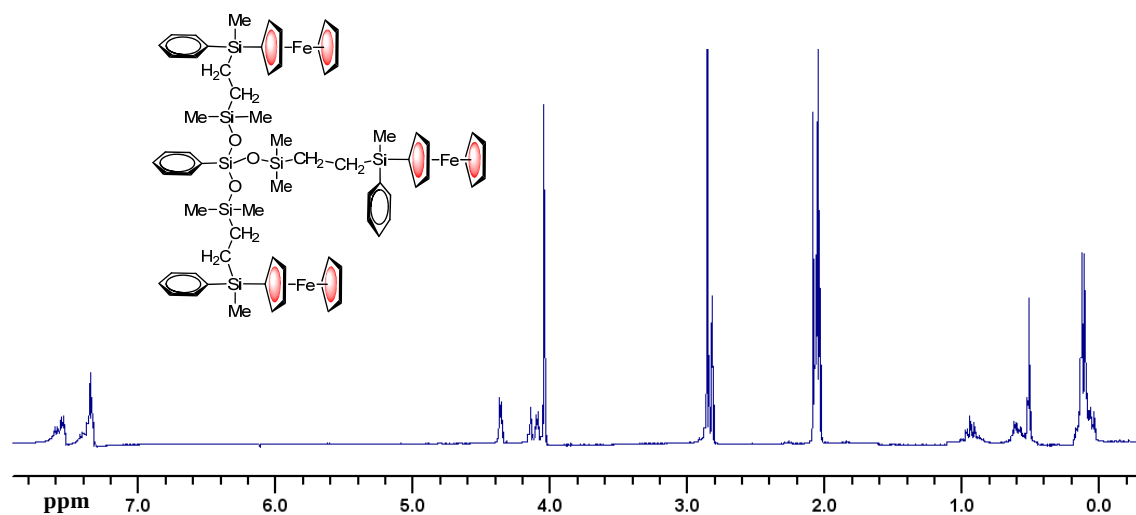


Figure S11. ^1H NMR spectrum (in $(\text{CD}_3)_2\text{CO}$, 300 MHz) of compound 7.

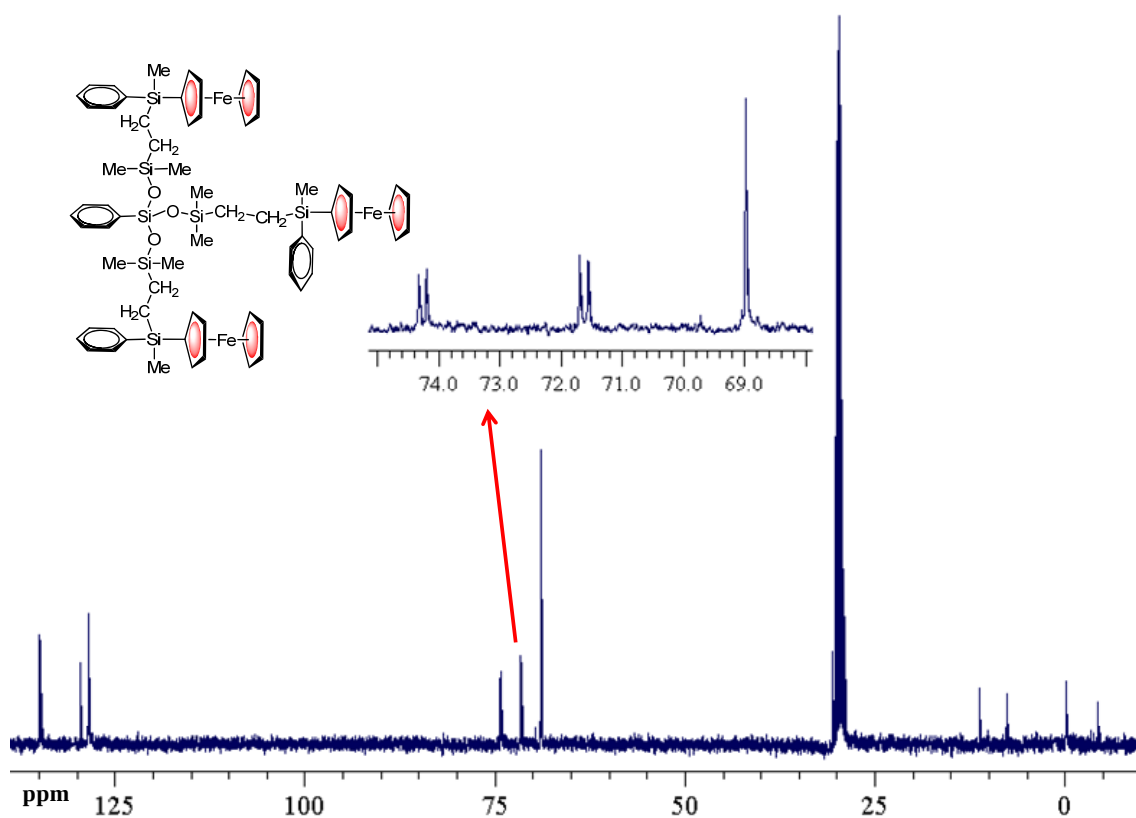


Figure S12. ^{13}C NMR spectrum (in $(\text{CD}_3)_2\text{CO}$, 75 MHz) of compound 7, (inset: expanded view of cyclopentadienyl region).

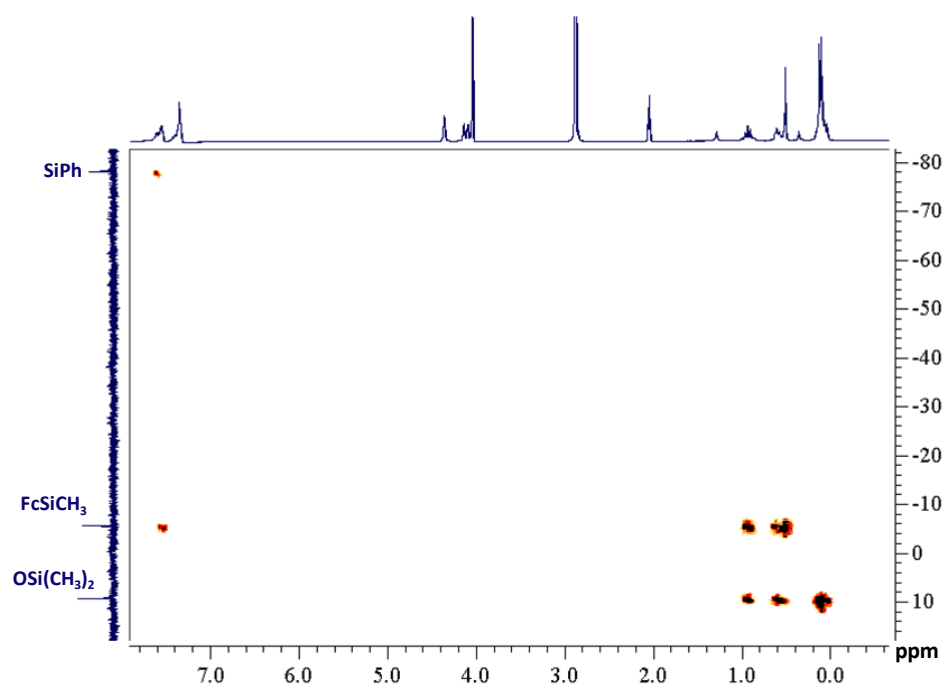


Figure S13. $\{^1\text{H}-^{29}\text{Si}\}$ HMBC spectrum (in $(\text{CD}_3)_2\text{CO}$, 300 MHz) of **7**.

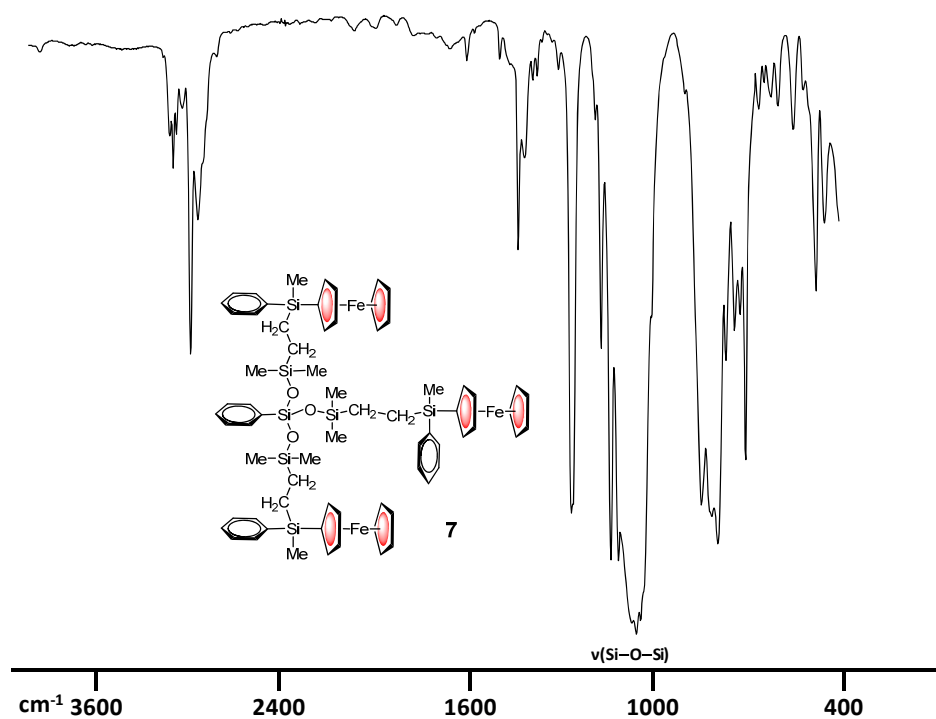


Figure S14. IR spectrum (in KBr windows) of compound **7**.

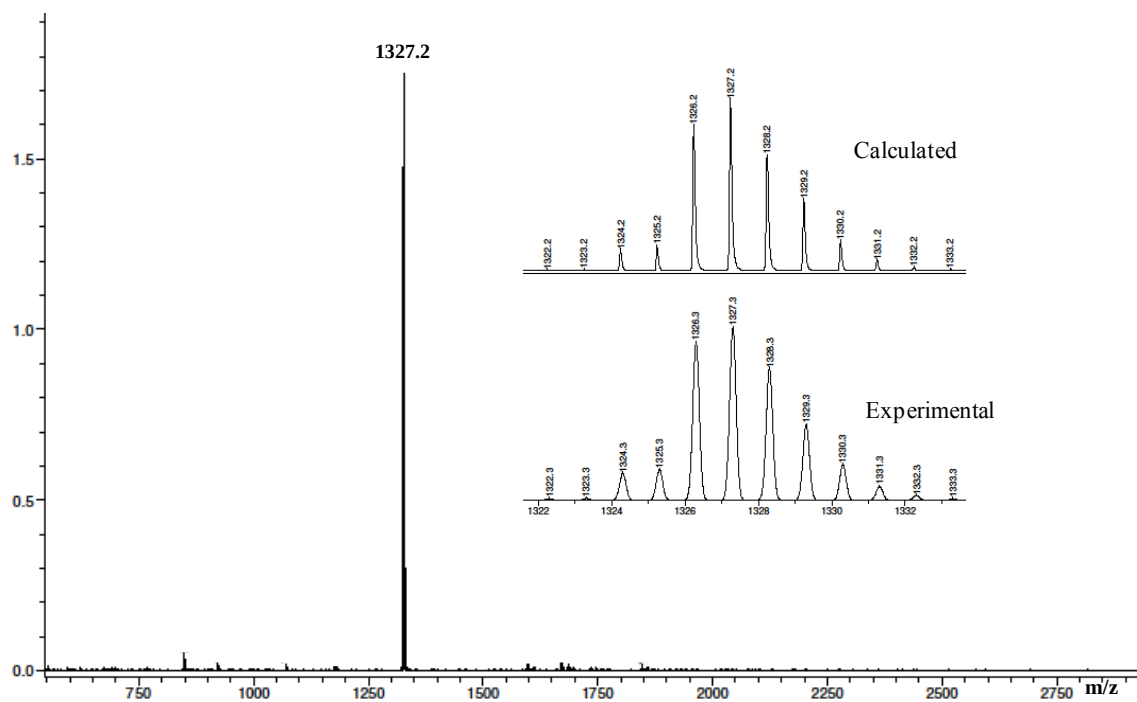


Figure S15. Mass spectrometry characterization by MALDI for compound 7. Inset: isotopic distribution of molecular ion peak of 7.

2.- Structural Characterization of Polymers 8–13

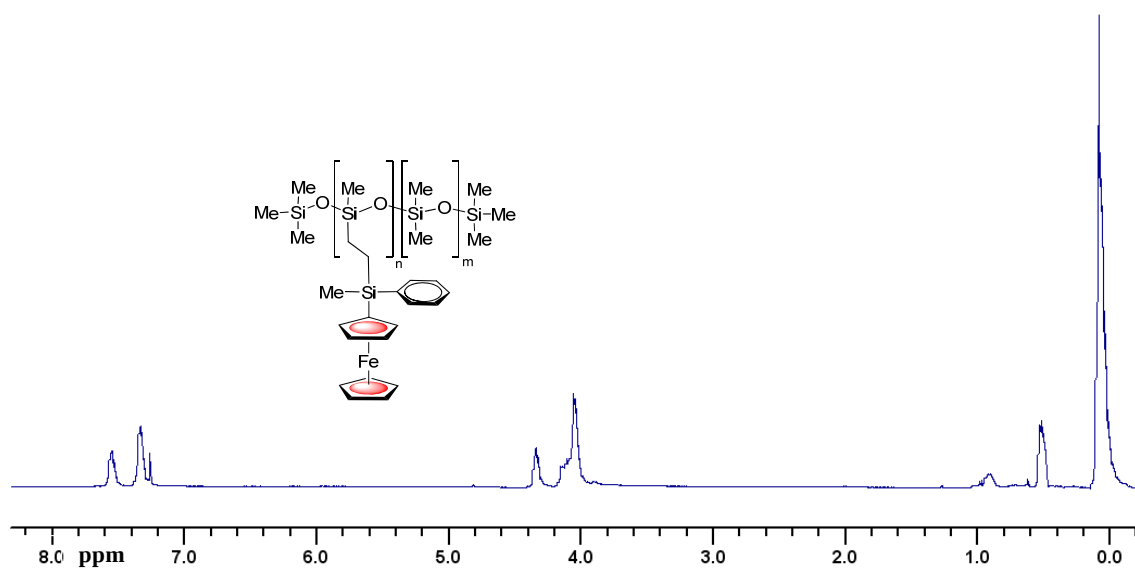


Figure S16. ^1H NMR spectrum (in CDCl_3 , 300 MHz) of compound **8**.

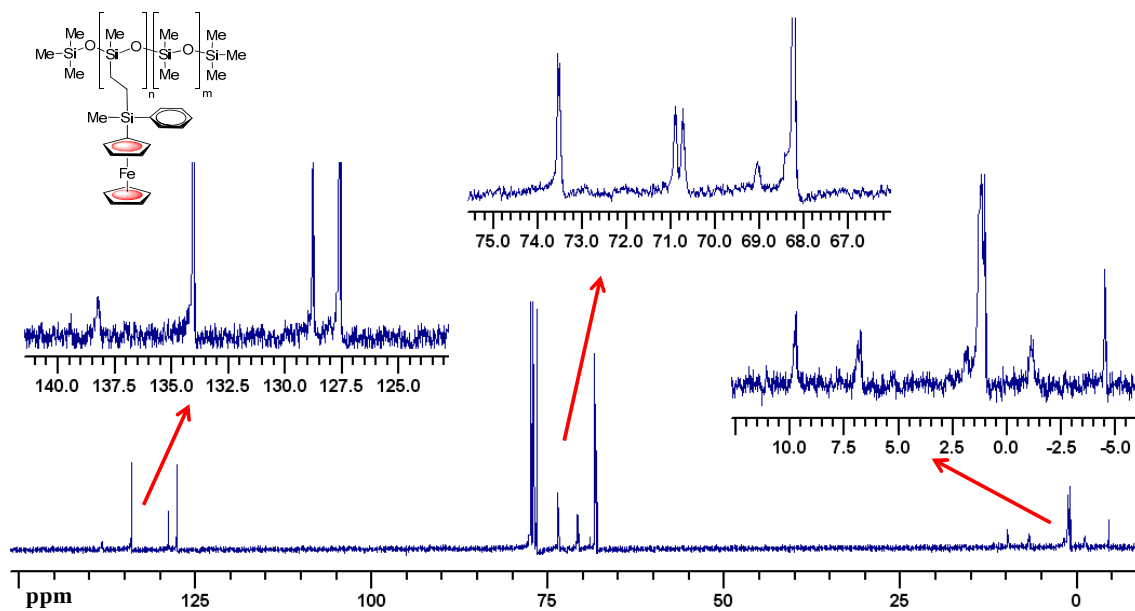


Figure S17. ^{13}C NMR spectrum (in CDCl_3 , 75 MHz) of compound **8**, (inset: expanded view of phenyl, cyclopentadienyl, CH_2 and CH_3 regions).

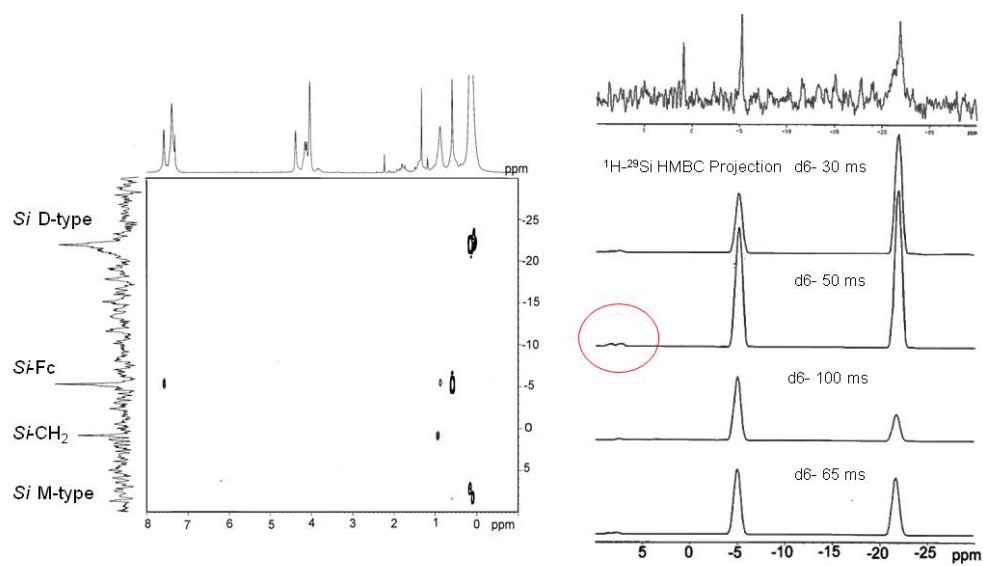


Figure S18. $\{^1\text{H}-^{29}\text{Si}\}$ HMBC spectrum (CDCl₃, 300 MHz) of **8** at $d = 50$ ms (left). Projections of $\{^1\text{H}-^{29}\text{Si}\}$ HMBC experiments at different d values (right).

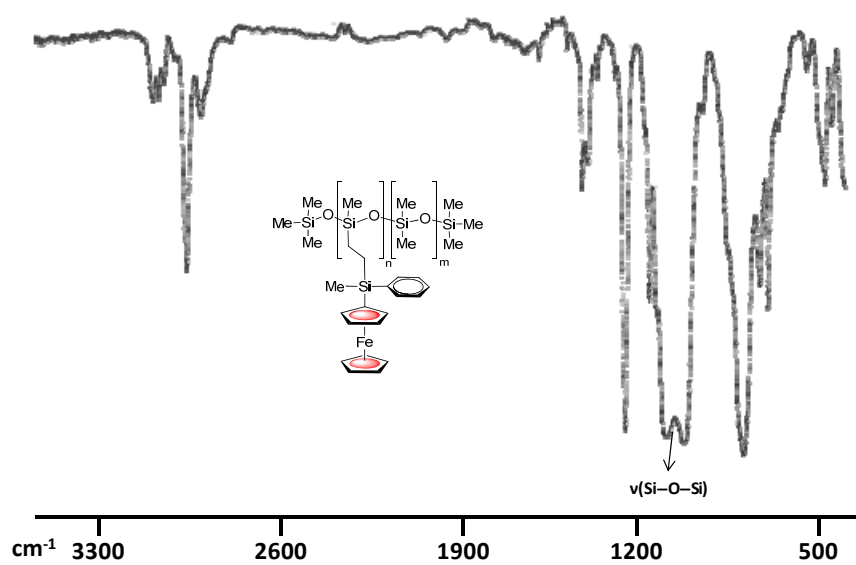


Figure S19. IR spectrum (in KBr windows) of compound **8**.

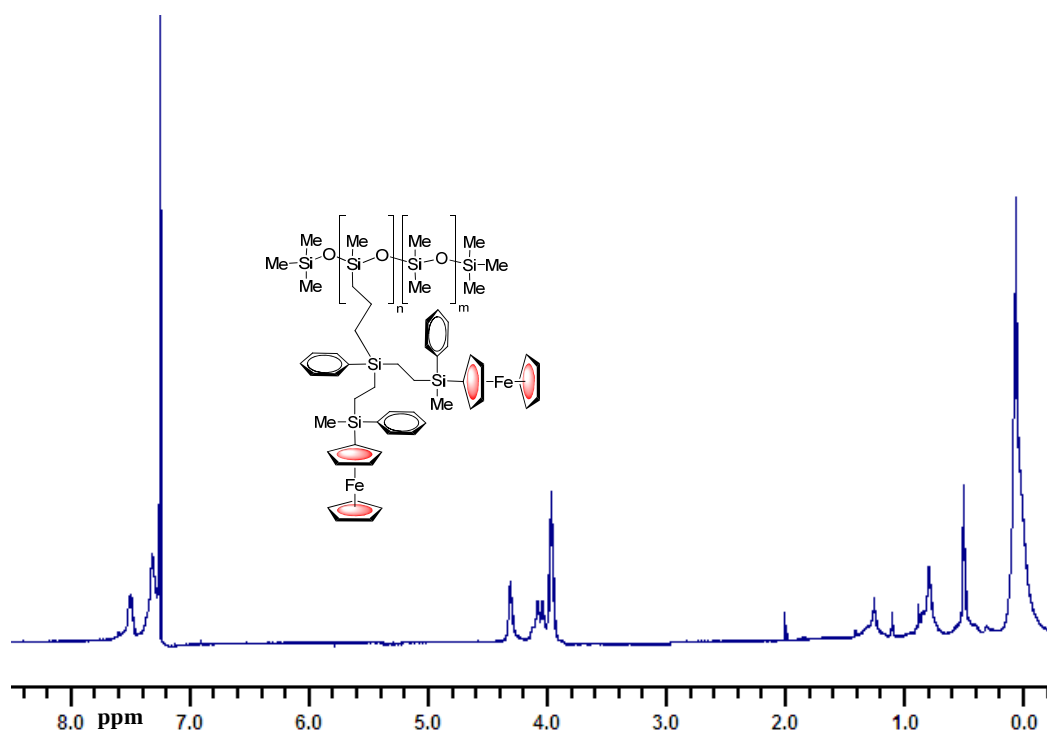


Figure S20. ^1H NMR spectrum (in CDCl_3 , 300 MHz) of compound **9**.

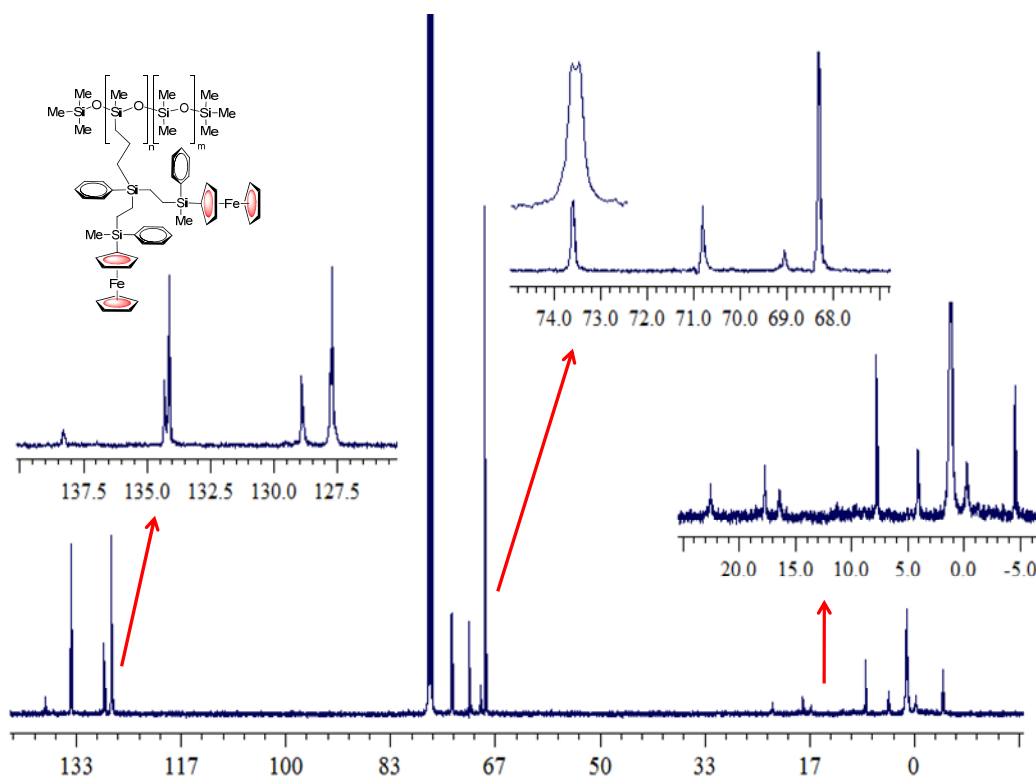


Figure S21. ^{13}C NMR spectrum (in CDCl_3 , 125 MHz) of compound **9**, (inset: expanded view of phenyl, cyclopentadienyl, CH_2 and CH_3 regions).

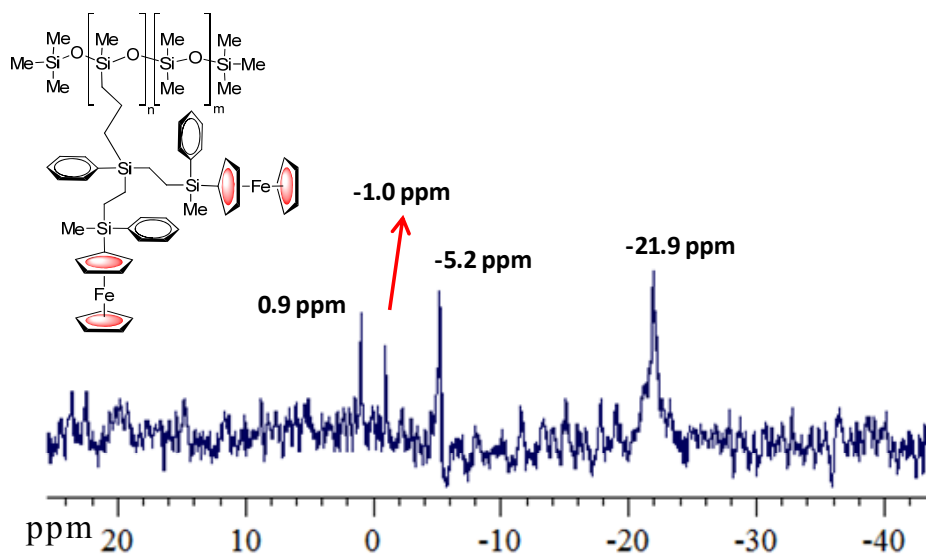


Figure S22. ^{29}Si NMR spectrum (in CDCl_3 , 99 MHz) of compound **9**.

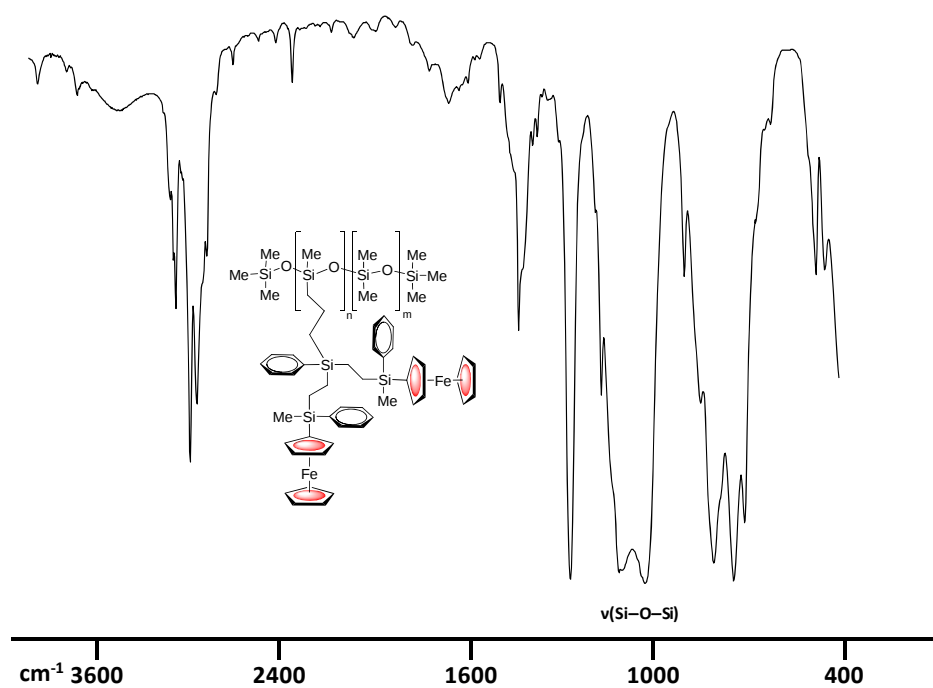


Figure S23. IR spectrum (in KBr windows) of compound **9**.

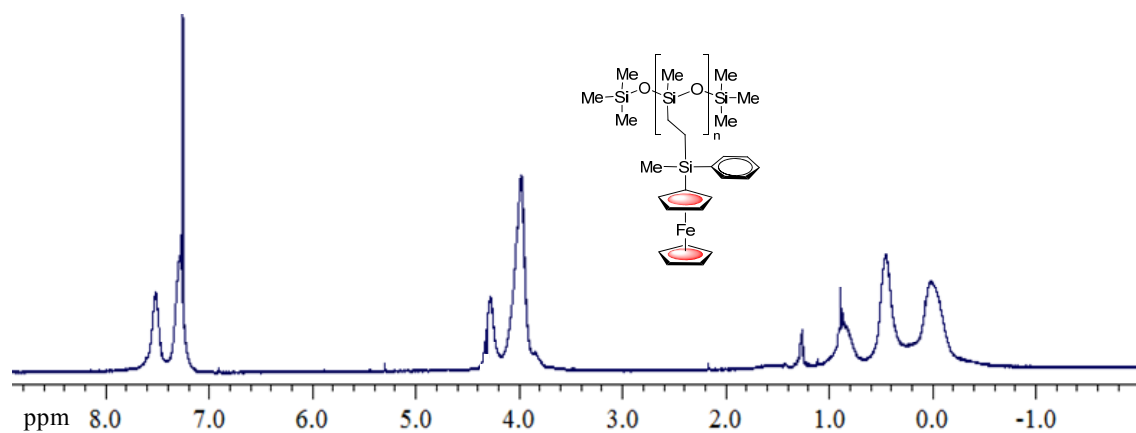


Figure S24. ^1H NMR spectrum (in CDCl_3 , 300 MHz) of compound **10**.

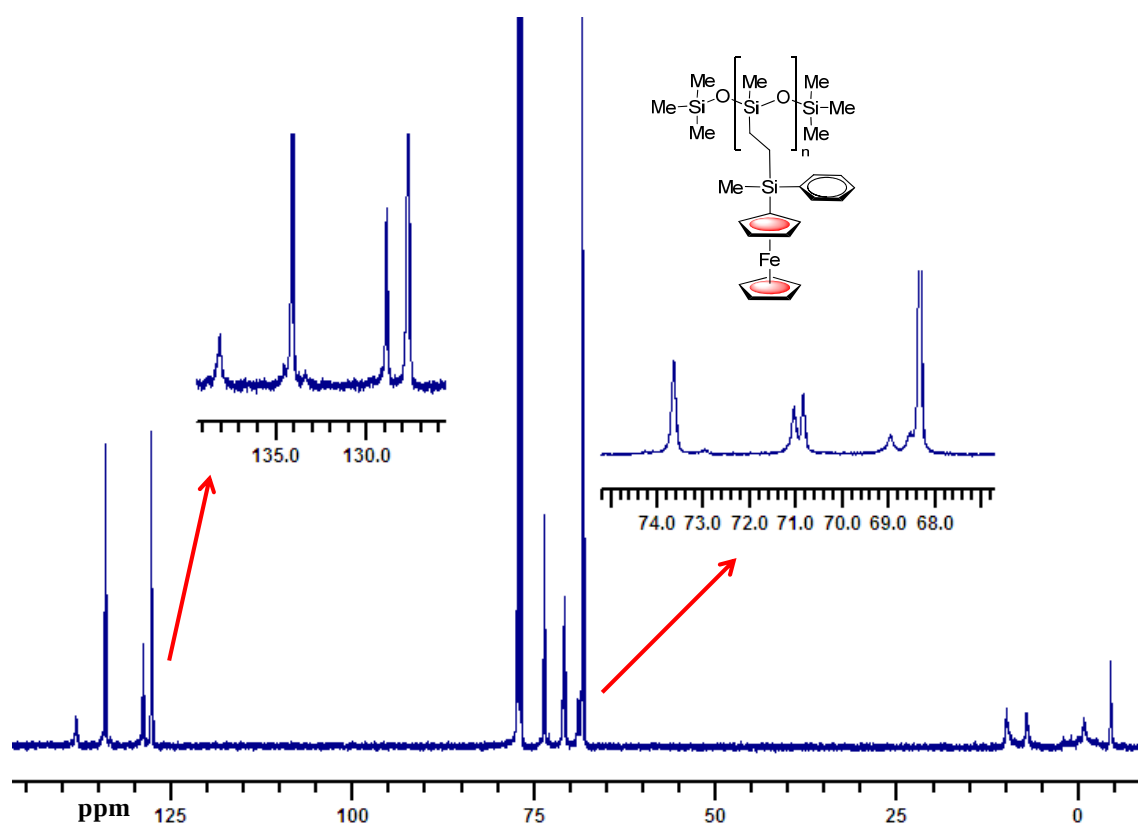


Figure S25. ^{13}C NMR spectrum (in CDCl_3 , 125 MHz) of compound **10**, (inset: expanded view of phenyl and cyclopentadienyl regions).

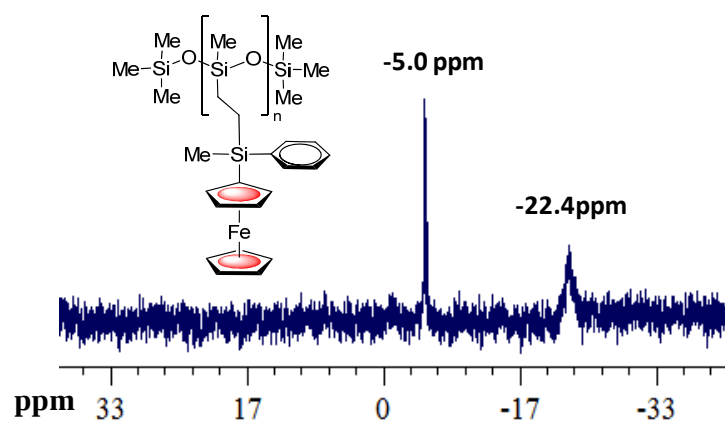


Figure S26. ^{29}Si NMR spectrum (in CDCl_3 , 99 MHz) of compound 10.

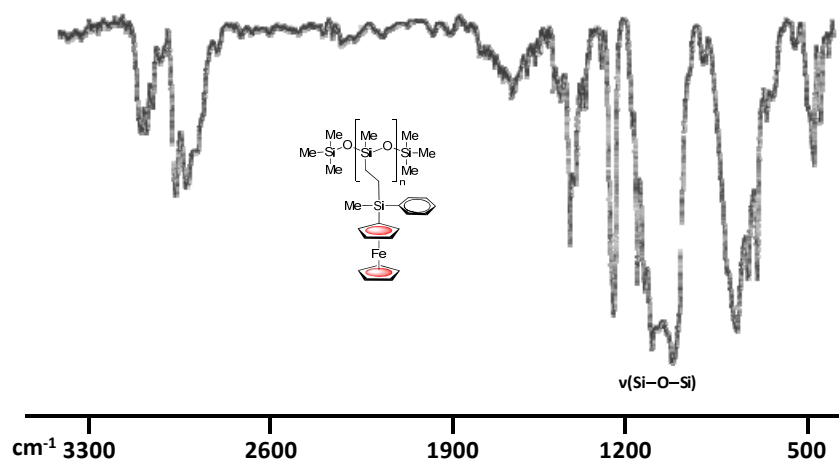


Figure S27. IR spectrum (in KBr windows) of compound 10.

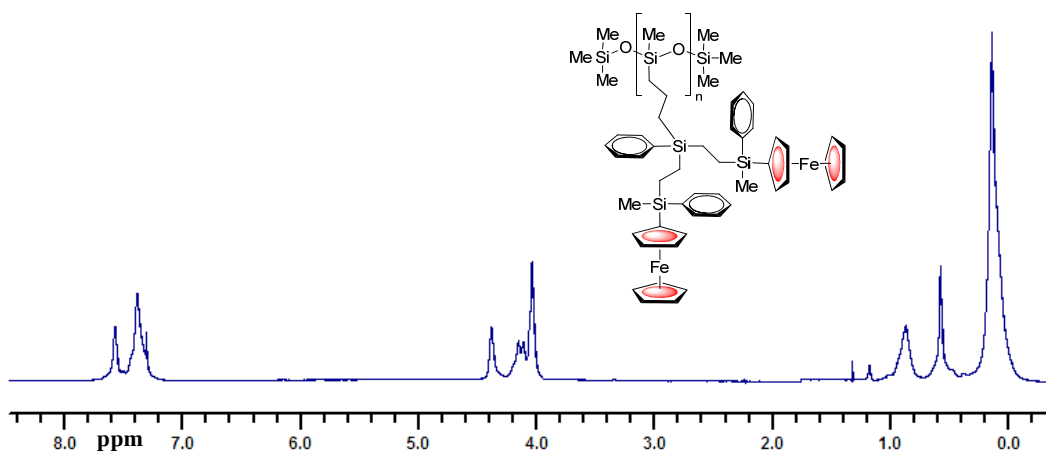


Figure S28. ^1H NMR spectrum (in CDCl_3 , 300 MHz) of compound 11.

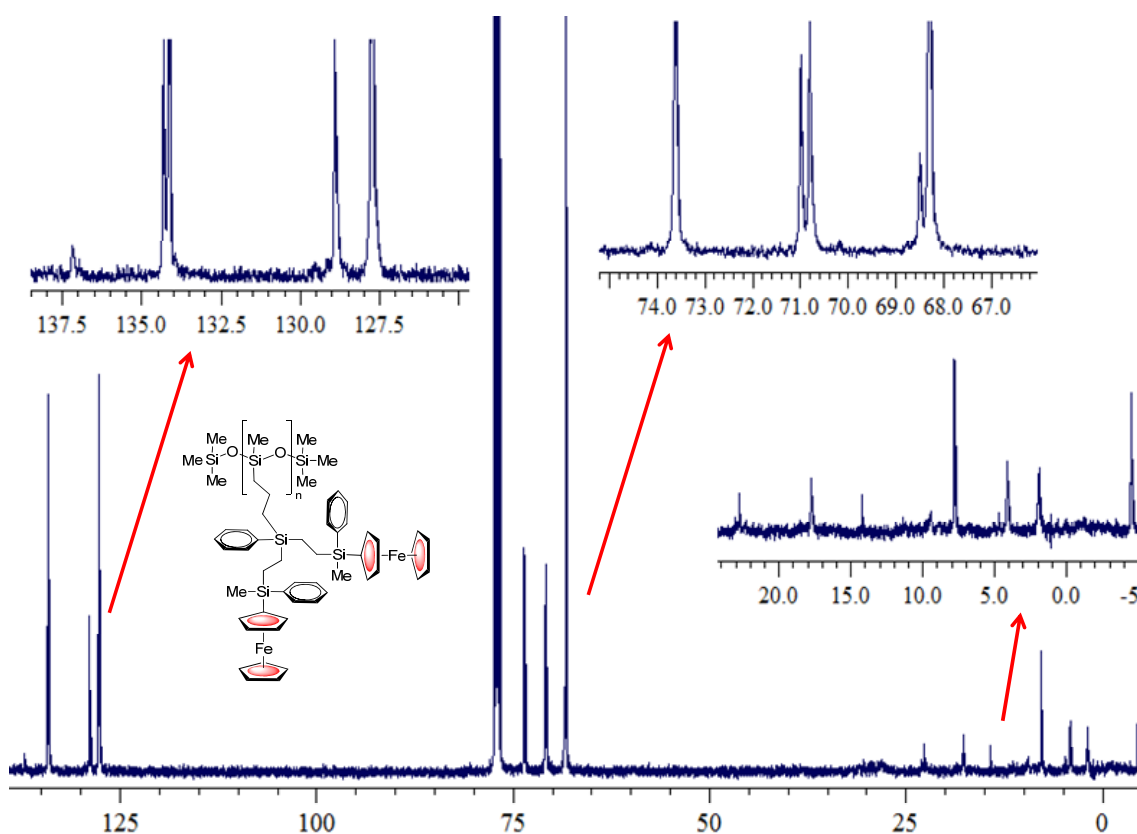


Figure S29. ^{13}C NMR spectrum (in CDCl_3 , 125 MHz) of compound 11, (inset: expanded view of phenyl, cyclopentadienyl, CH_2 and CH_3 regions).

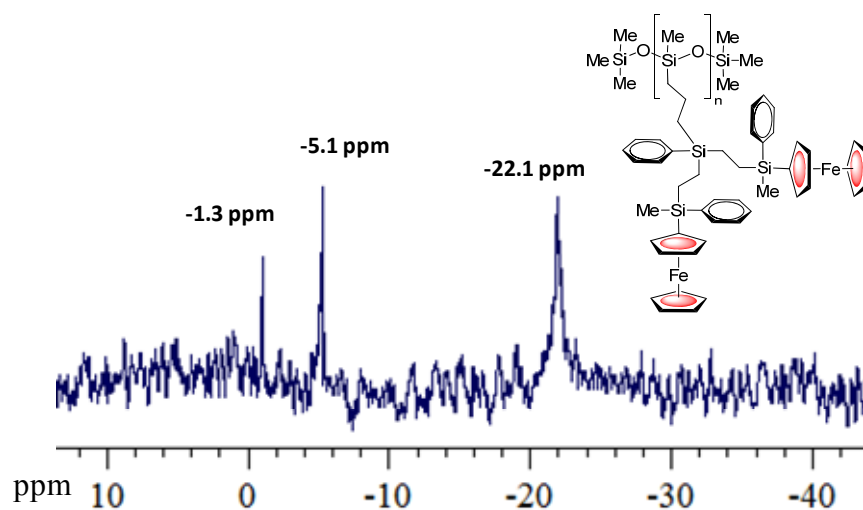


Figure S30. ^{29}Si NMR spectrum (in CDCl_3 , 99 MHz) of compound **11**.

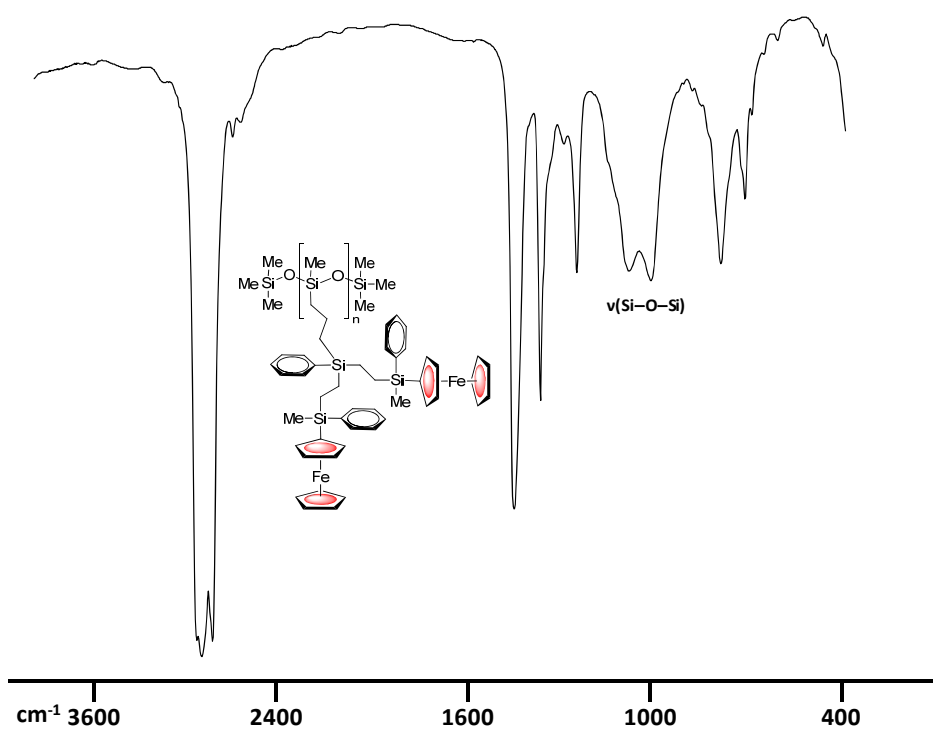


Figure S31. IR spectrum (in Nujol, KBr windows) of compound **11**.

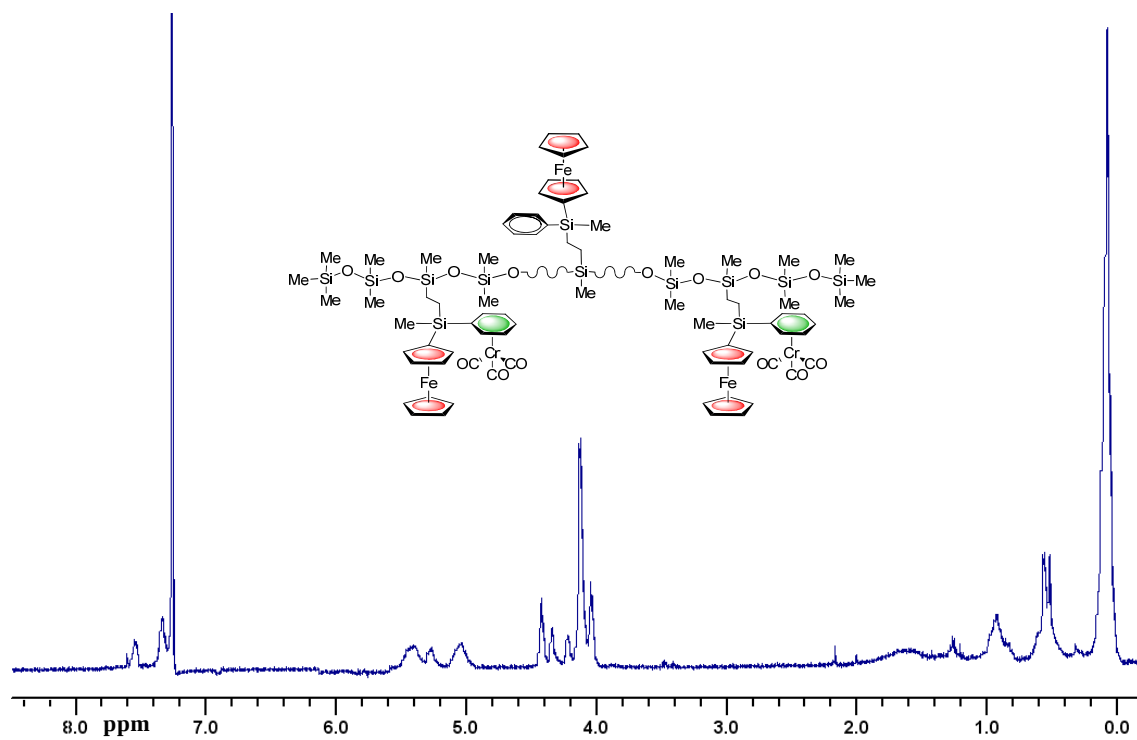


Figure S32. ¹H NMR spectrum (in CDCl₃, 300 MHz) of compound 12.

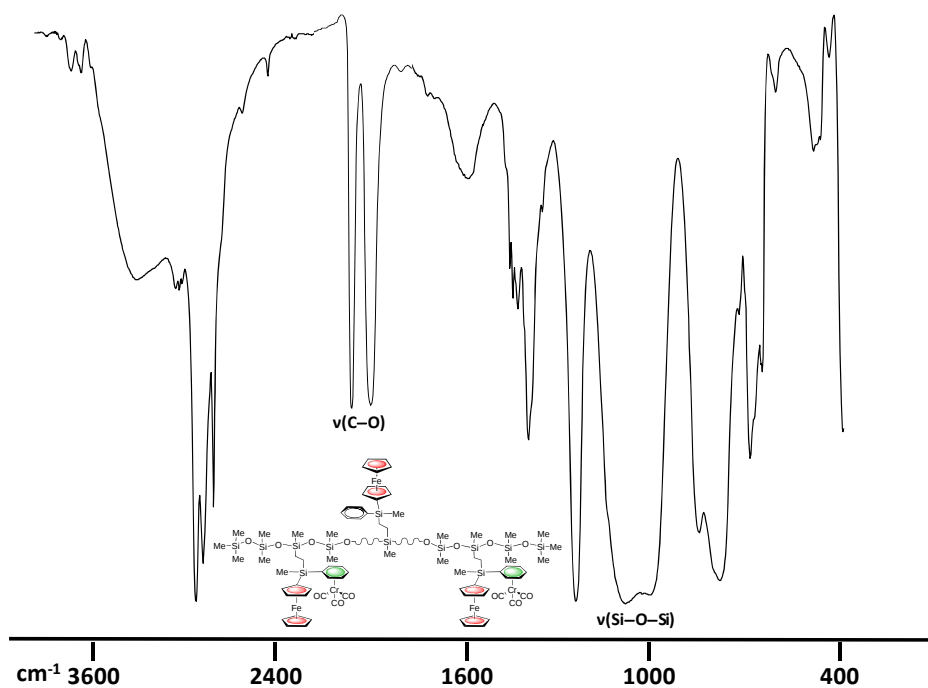


Figure S33. IR spectrum (in KBr windows) of compound 12.

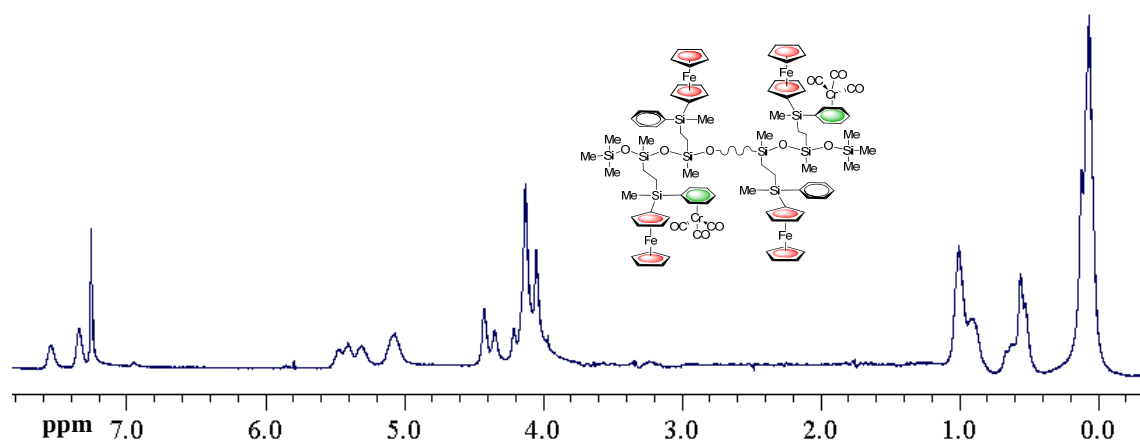


Figure S34. ^1H NMR spectrum (in CDCl_3 , 300 MHz) of compound **13**.

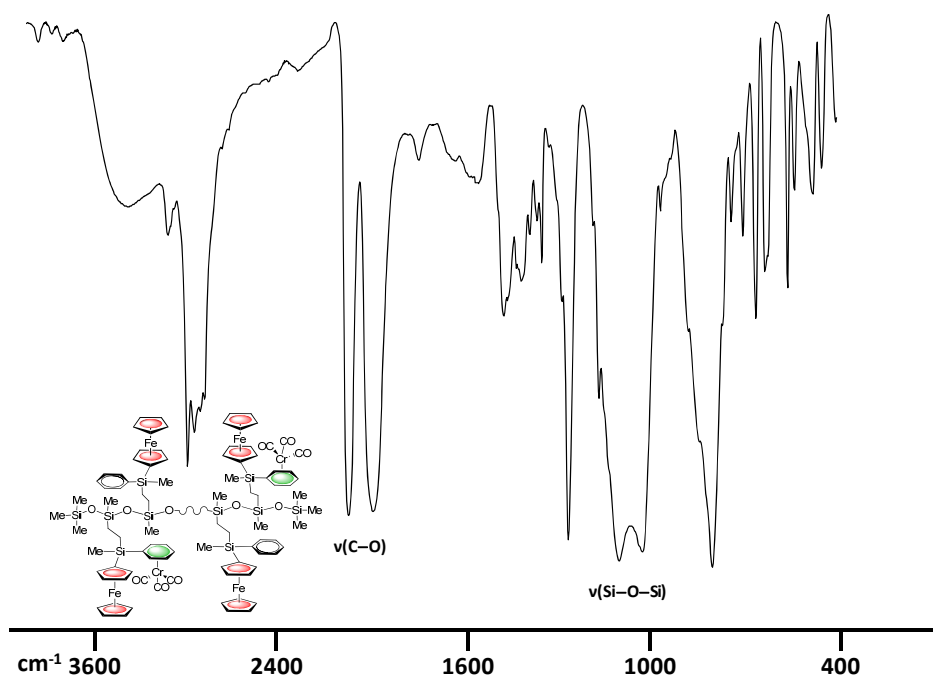


Figure S35. IR spectrum (in KBr windows) of compound **13**.

3.- Electrochemistry of Compounds 5–13.

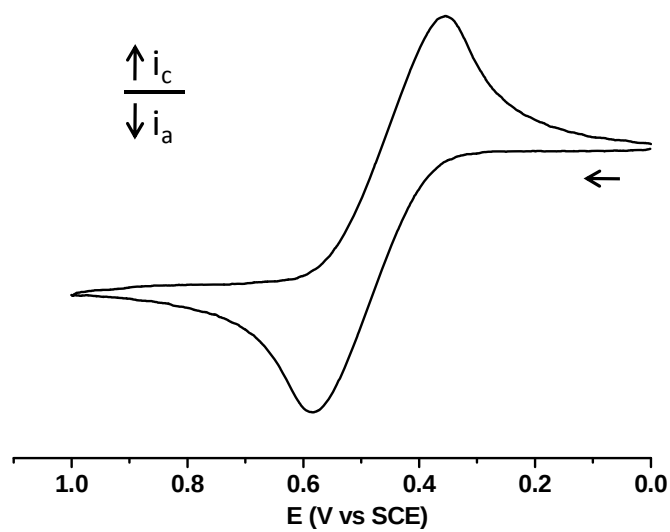


Figure S36. CV response of trimetallic **7** (10^{-3} M) recorded in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 at a scan rate of 0.1 V s^{-1} .

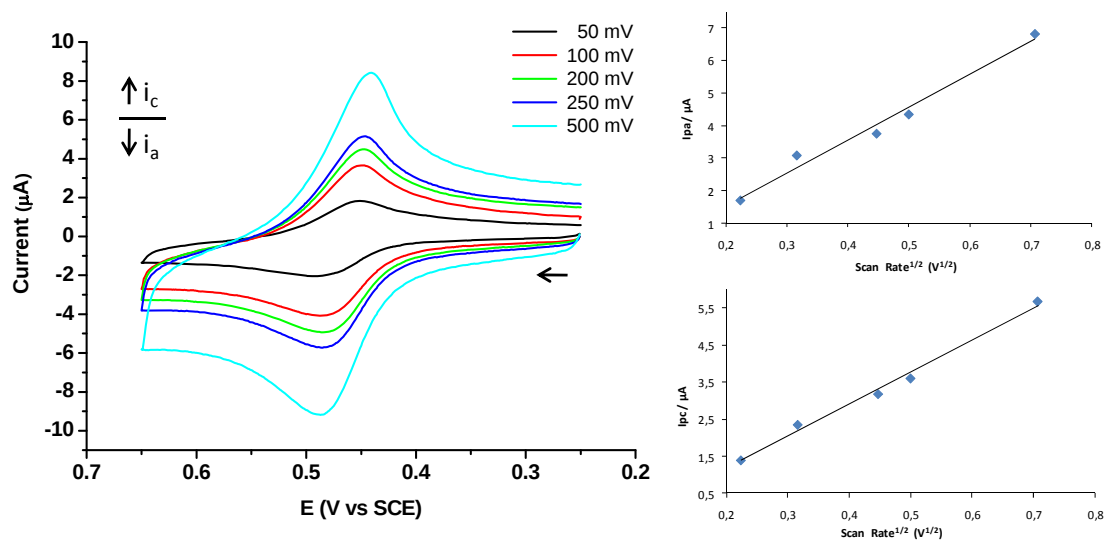


Figure S37. CV responses of ferrocenyl polysiloxane **8** (10^{-3} M) recorded in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 , at different scan rates. Left: plots of I_{pa} and I_{pc} against $\text{scan rate}^{1/2}$.

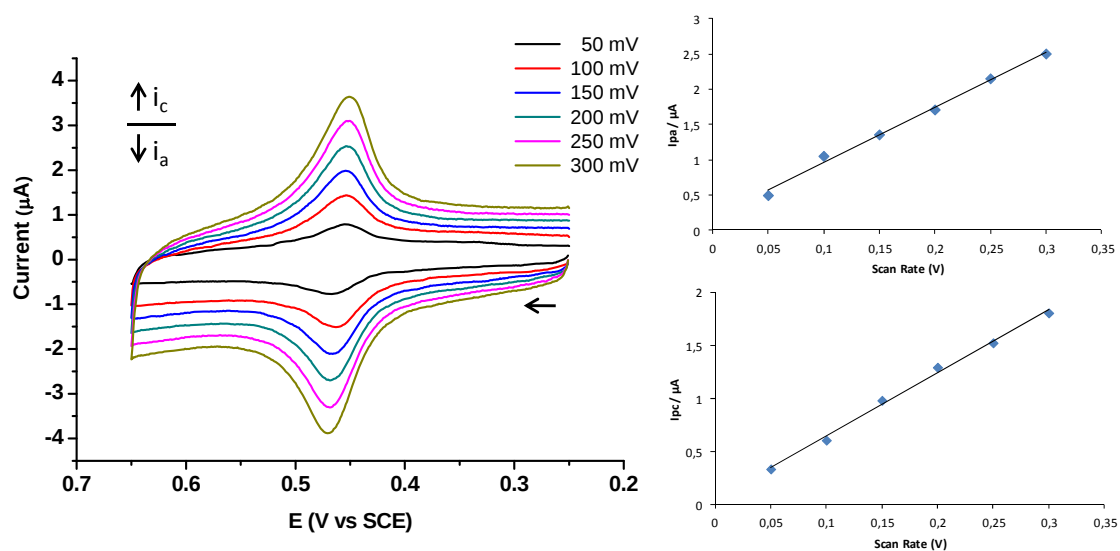


Figure S38. CV responses of a carbon-disk electrode modified with a film of ferrocenyl-containing dimethylsiloxane copolymer **8**, measured in 0.1 M Bu₄NPF₆/CH₂Cl₂ at different potential scan rates (mV s⁻¹). Left: Scan rate dependence upon the anodic and cathodic peak current.

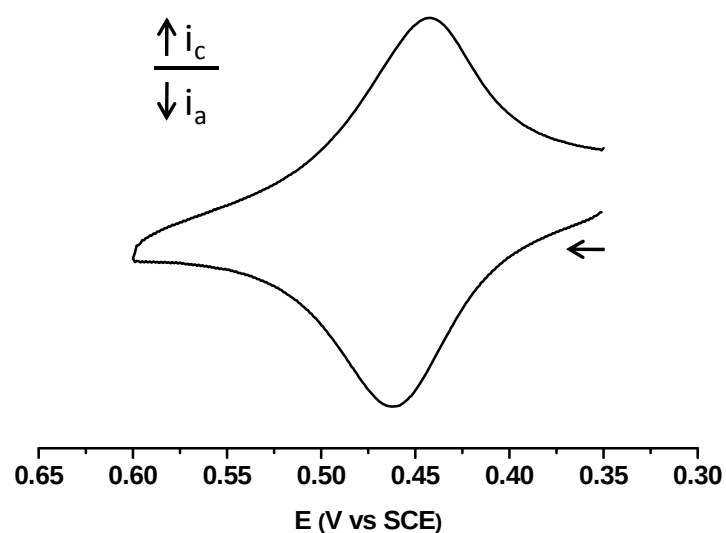


Figure S39. CV response (at 0.1 V s⁻¹) of a platinum-disk electrode modified with a film of ferrocenyl-containing dimethylsiloxane copolymer **9**, measured in 0.1 M Bu₄NPF₆/CH₂Cl₂.

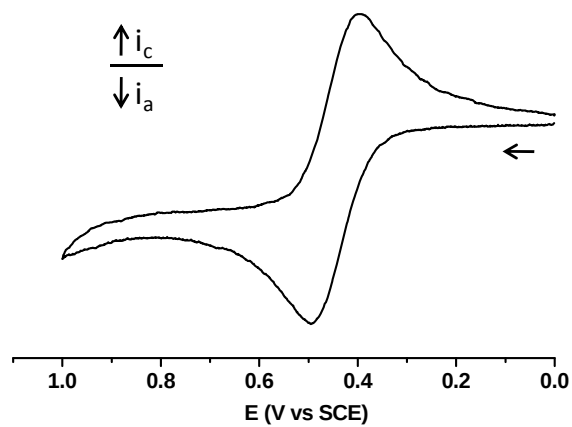


Figure S40. CV response of polysiloxane **11** (10^{-3} M) recorded in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 .

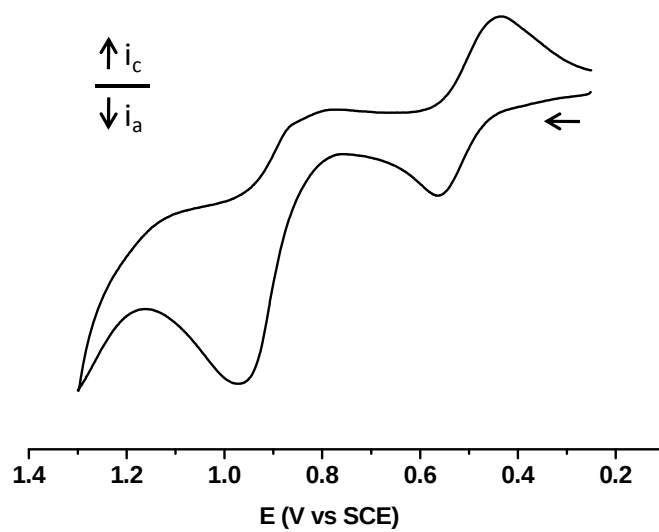
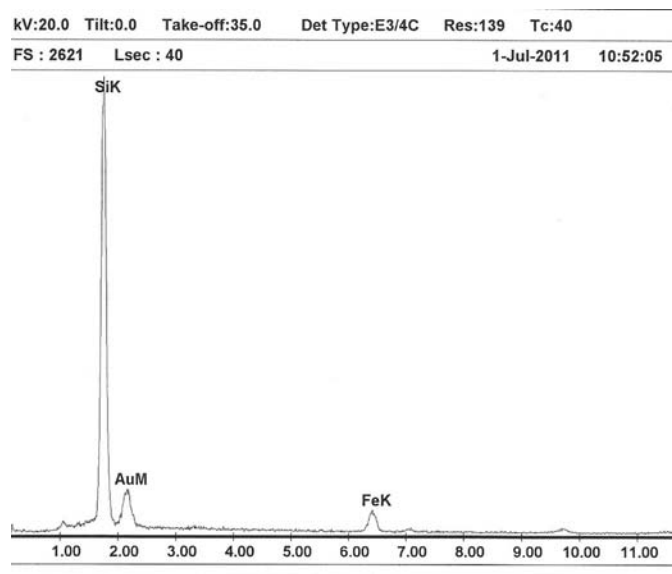


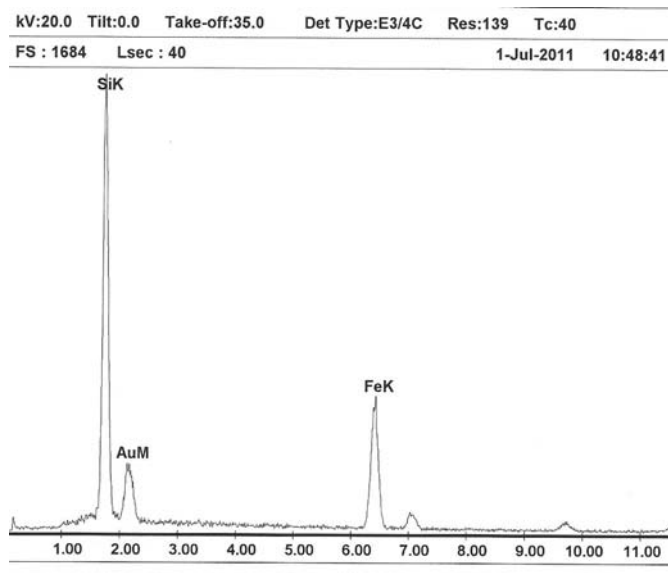
Figure S41. CV response of heterometallic polysiloxane **13** (10^{-3} M) recorded in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 .

4.- Energy-dispersive X-ray (EDX) analyses of ceramic residues.



EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element	Wt %	At %	K-Ratio	Z	A	F
SiK	62.80	87.62	0.5168	1.0641	0.7733	1.0001
AuM	27.28	5.43	0.1476	0.7629	0.7091	1.0000
FeK	9.91	6.96	0.0913	0.9573	0.9516	1.0110
Total	100.00	100.00				



EDAX ZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element	Wt %	At %	K-Ratio	Z	A	F
SiK	43.62	68.53	0.3036	1.0842	0.6418	1.0005
AuM	23.10	5.17	0.1355	0.7782	0.7540	1.0000
FeK	33.28	26.30	0.3148	0.9762	0.9607	1.0083
Total	100.00	100.00				

Figure S42. EDX analyses of the ceramic residue obtained by the pyrolysis of dendronized ferrocenyl polysiloxane **9** (at 1000°C under a nitrogen atmosphere), top: in the bulk; bottom: in the clusters of the surface.