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Supporting Information

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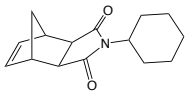
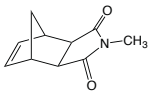
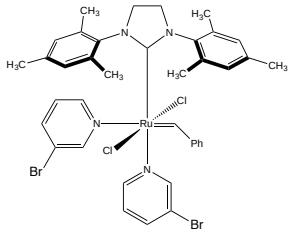


exo-N-cyclohexyl-norbornene-2,3-dicarboximide **5** (CyNI)



exo-*N*-methylnorbornene imide **6** (MNI)



Grubbs' 3rd generation initiator
($(H_2IMes)(3\text{-Br-Py})_2(Cl)_2Ru{=}CHPh$ = **C3**)

Scheme SI-1. Chemical structures of compounds **5**, **6** and **C3**.

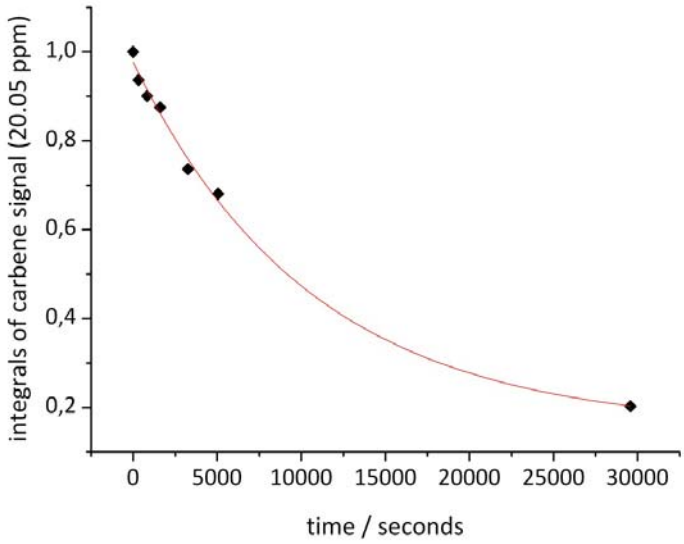


Figure SI-1. Reaction of **C1** with **2** (3 eq). The graph shows the residual carbene signal at 20.05 ppm in time resolved ^{1}H NMR spectroscopy in methylene chloride-d_2, 400 MHz at room temperature. The Integrals were referenced to the residual solvent signal of methylene chloride.

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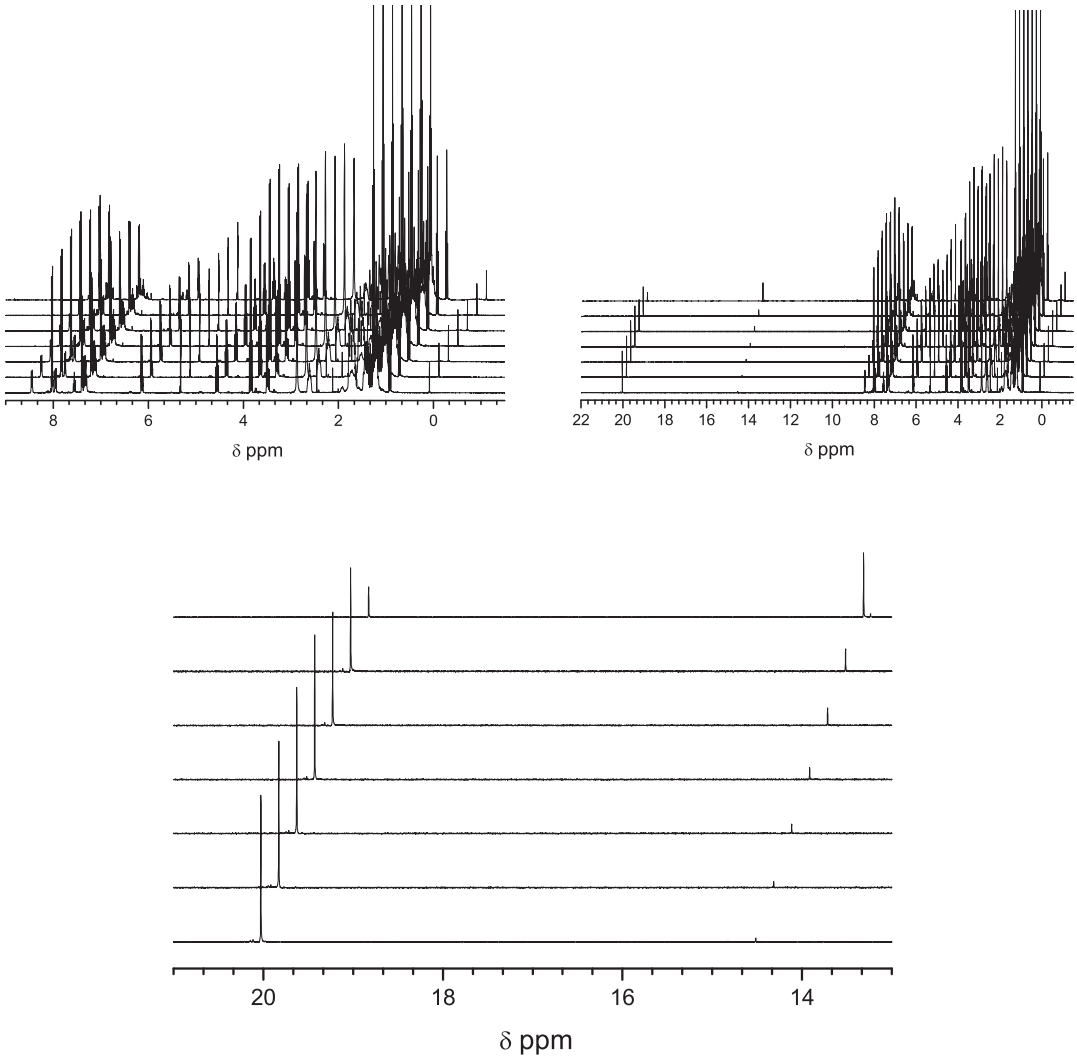

Figure SI-2. Reaction of **C1** with **2** (3 eq). *Top left*, *right* and *bottom*: The graphs show the time resolved ^{1}H NMR spectra corresponding to Figure **SI-1** in methylene chloride-d_2, 400 MHz at room temperature. Different sections of the same NMR spectra are shown.

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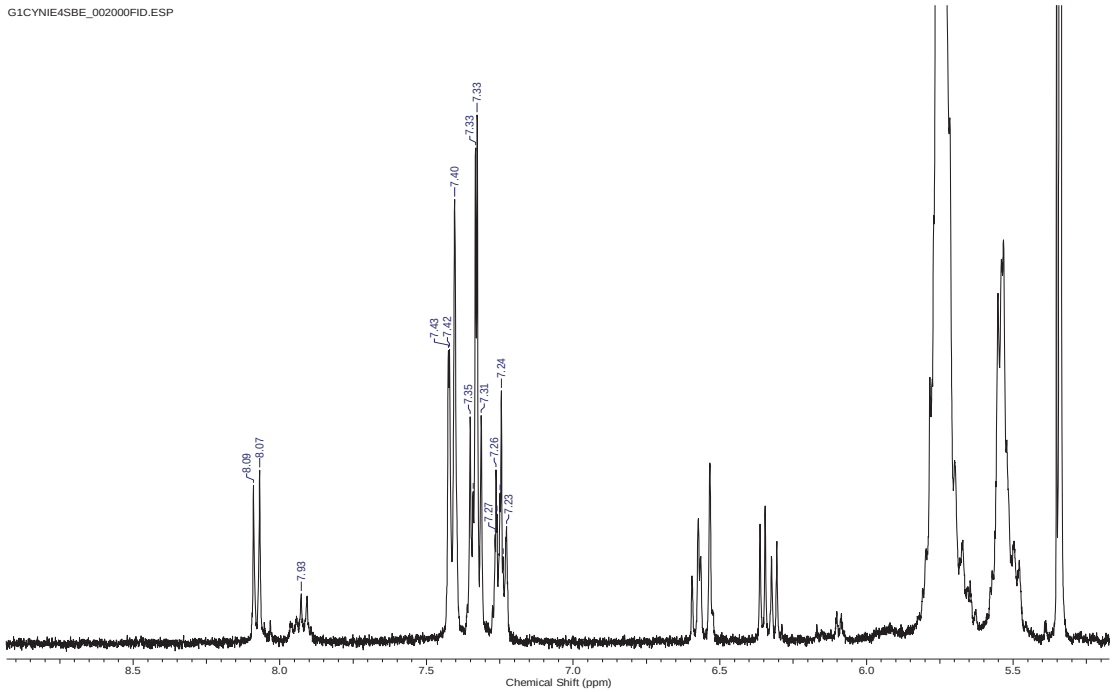

Figure SI-3: ^{1}H NMR analysis (in chloroform-d_1, 400 MHz) of active ester terminated poly(CyNI). Aromatic signals referring to the focal benzylidene unit (also referred to as a styryl unit) and the terminal succinimidyl 4-ethenylenebenzoate unit (7.2-8.2 ppm) transferred during the termination of the propagating ruthenium catalyst **C1** with **2**.

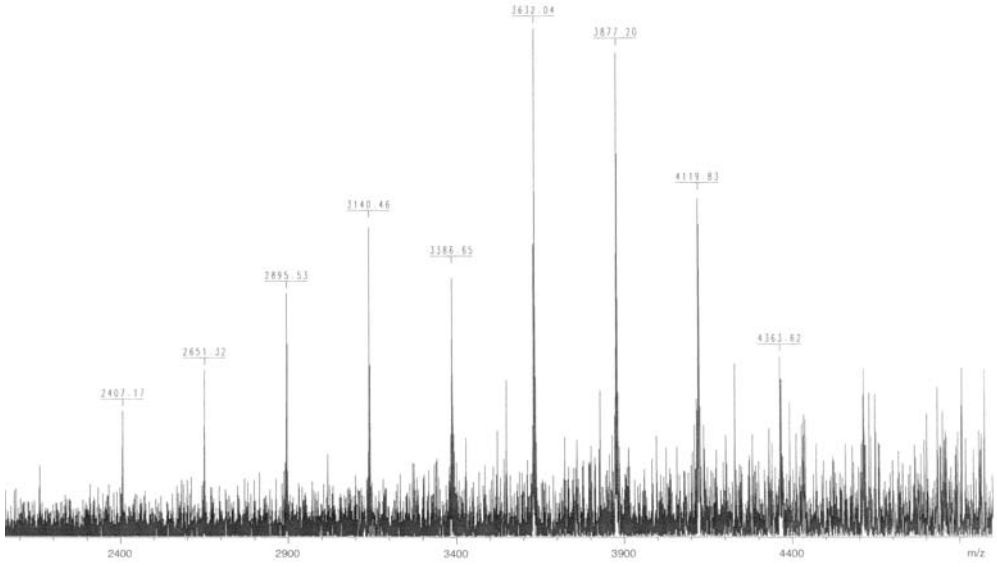

Figure SI-4: MALDI-FT-ICR mass spectrum showing the functionally terminated poly(CyNI) species (DCTB matrix and silver trifluoroacetate for cationization).

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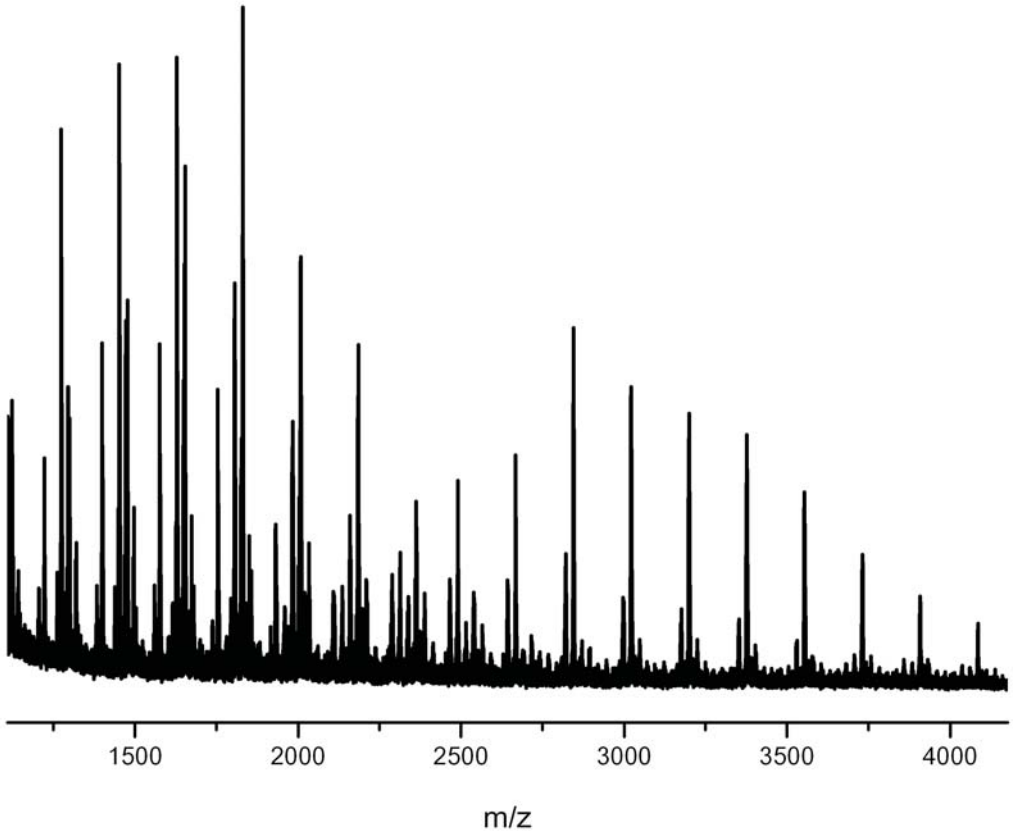

Figure SI-5: MALDI-ToF-MS analysis of the singly-branched poly(PNI). The bimodal molecular weight distribution corresponds well to the observed GPC results. Figures SI-5 - SI-7 show expanded and isotopically resolved peaks from this graph.

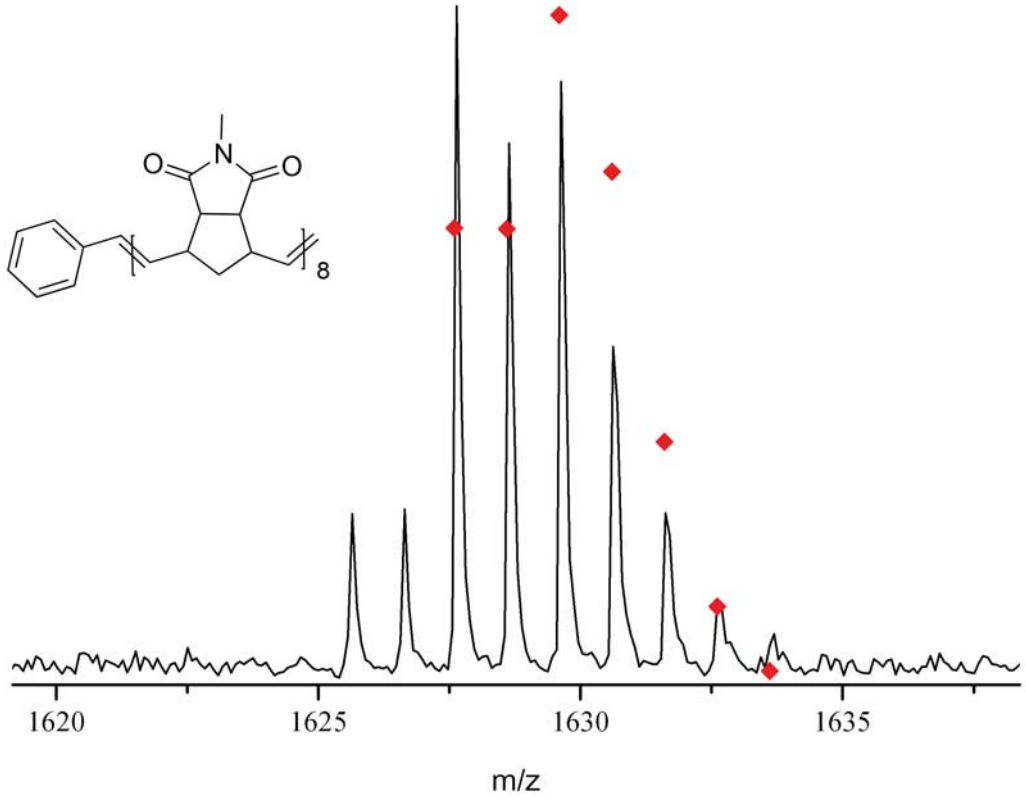

Figure SI-6: MALDI-ToF-MS analysis showing the recorded isotopic pattern for poly(PNI) terminated with ethyl vinyl ether, and the isotopic pattern for $[C_8H_{96}N_8O_{16}+Ag]^+$. *(m/z)* calculated for $[C_8H_{96}N_8O_{16}+Ag]^+$, 1627.6; found, 1627.6.

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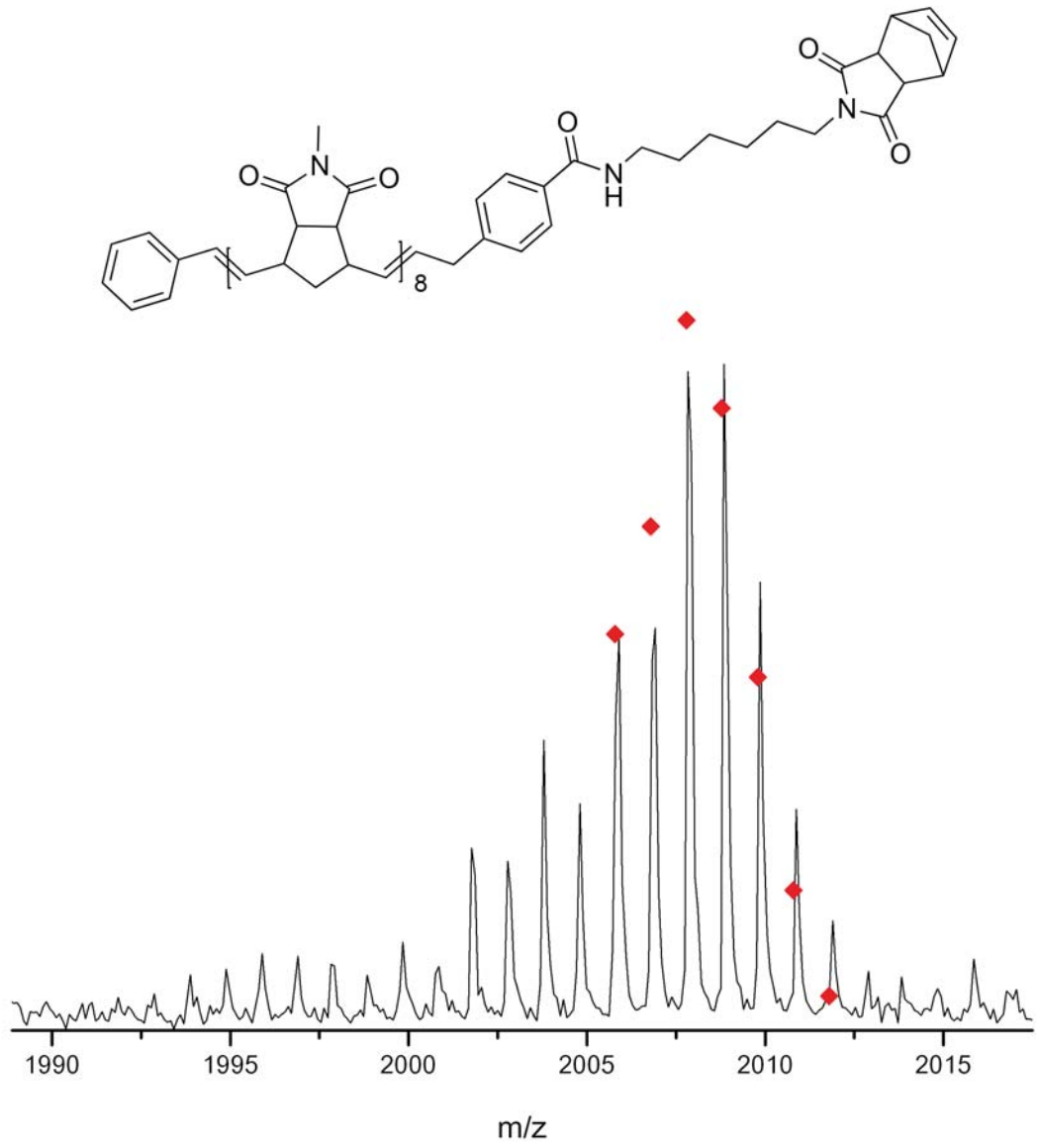

Figure SI-7: MALDI-ToF-MS analysis showing the recorded isotopic pattern for poly(PNI) terminated with termimer **4**, and the isotopic pattern for $[C_{111}H_{122}N_{10}O_{18}+Ag]^+$ (u). *(m/z)* calculated for $[C_{111}H_{122}N_{10}O_{18}+Ag]^+$, 2005.8; found, 2005.9.

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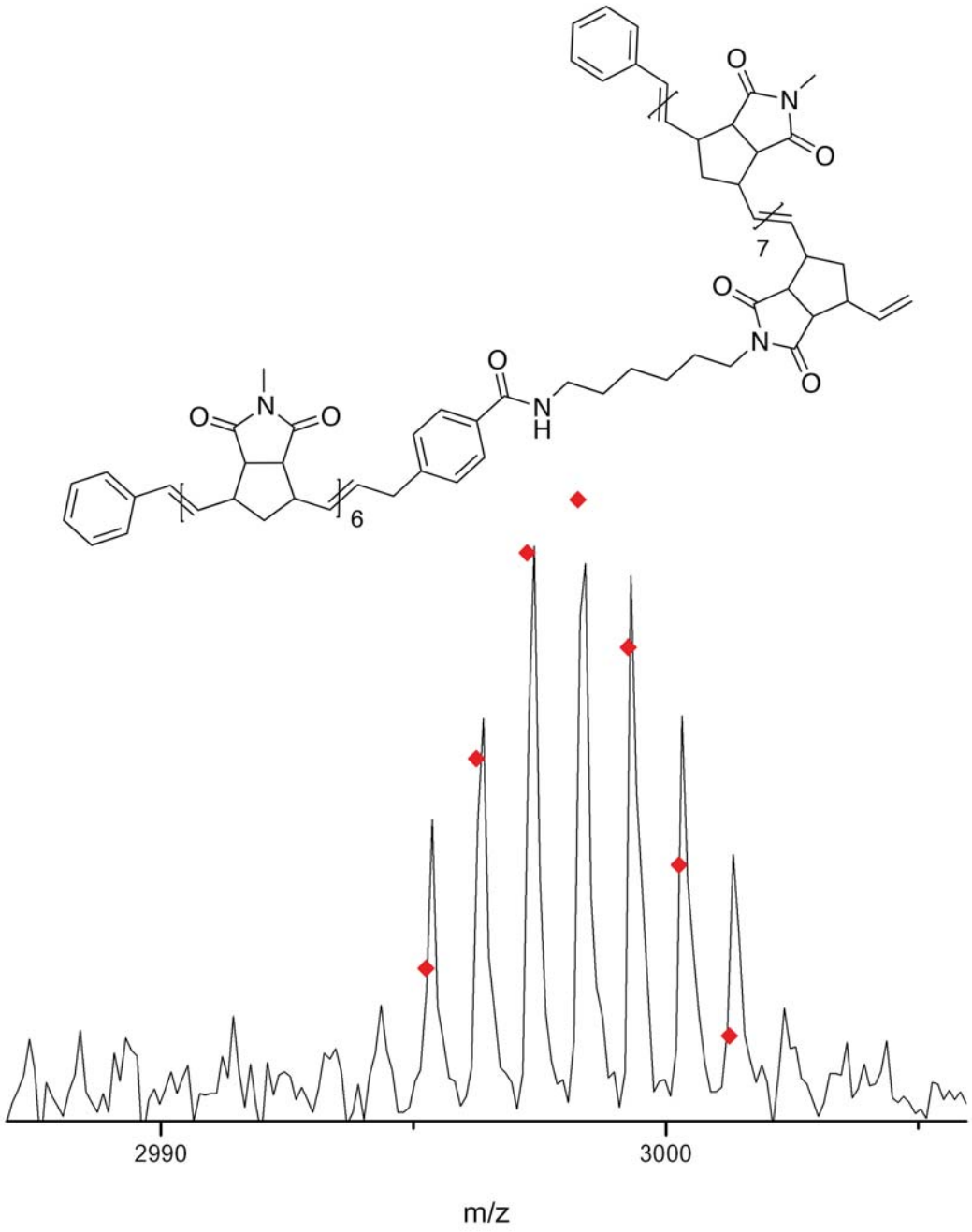

Figure SI-8: MALDI-ToF-MS analysis showing the recorded isotopic pattern for poly(PNI) terminated with termimer **4**, and the isotopic pattern for $[C_{169}H_{185}N_{15}O_{29}+Ag]^+$ (u). *(m/z)* calculated for $[C_{169}H_{185}N_{15}O_{29}+Ag]^+$, 2995.3; found, 2995.4.

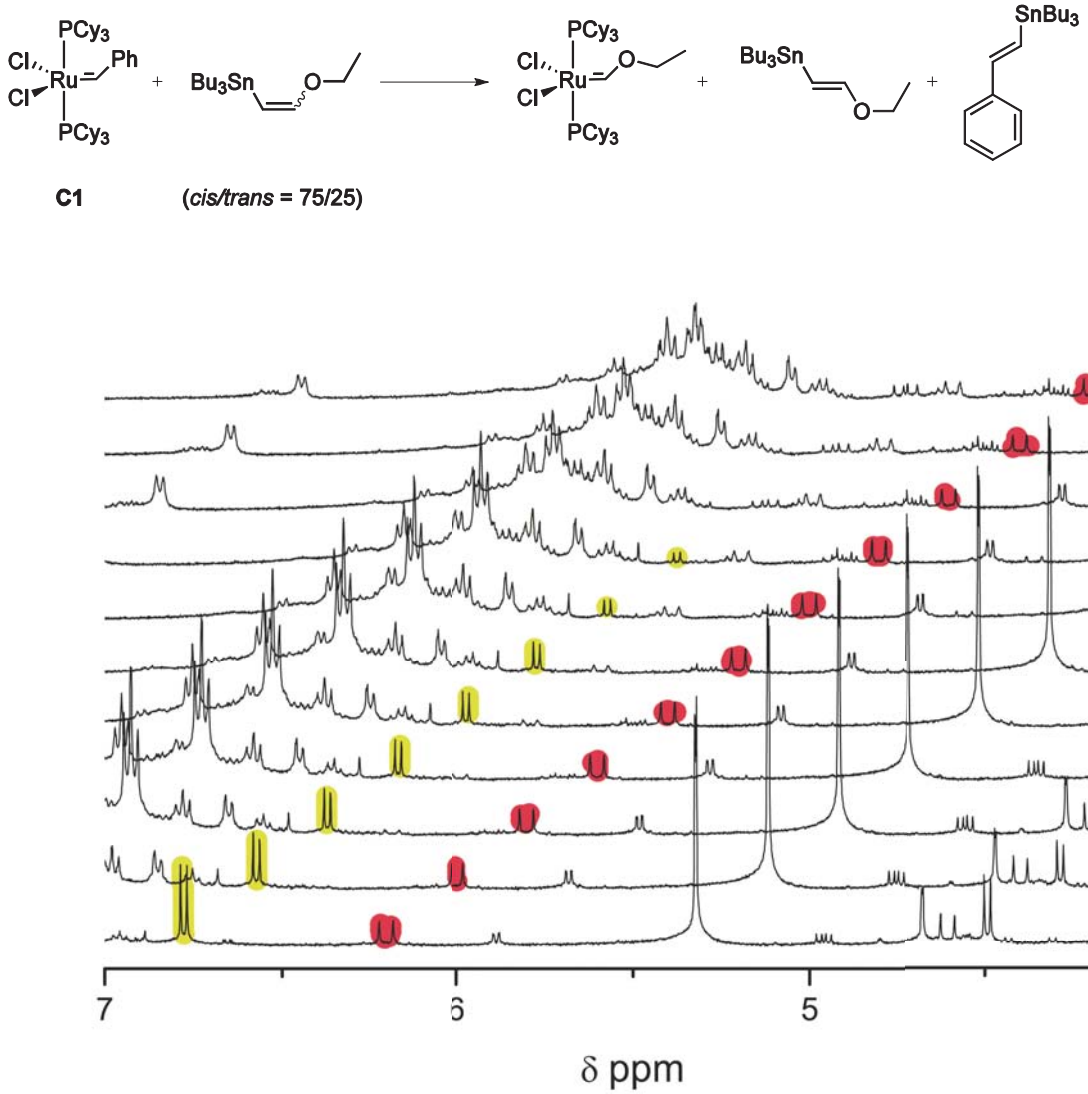

Figure SI-9: *Top*: Model reaction investigated over time by ^{1}H-NMR spectroscopy. *Bottom*: Time resolved ^{1}H NMR spectra (methylene chloride-d_2, 400 MHz). An isomeric mixture of tributyl-(2-ethoxyethenyl)stannane (*cis/trans* = 75/25) was reacted with a 3-fold excess of catalyst **C1** over 21 hours (front to back). The signals of the *cis* (yellow) and *trans* (red) isomer were integrated with respect to TMS as internal standard. The experiment indicates high substrate selectivity towards the *cis*-vinyl ether.

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