Supporting Information

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**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 '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.
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.
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-ethylenenbenzoate 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).
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 $[\text{C}_{8}\text{H}_{96}\text{N}_{8}\text{O}_{16}+\text{Ag}]^+$. ($m/z$) calculated for $[\text{C}_{8}\text{H}_{96}\text{N}_{8}\text{O}_{16}+\text{Ag}]^+$, 1627.6; found, 1627.6.
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.
Figure SI-8: MALDI-ToF-MS analysis showing the recorded isotopic pattern for poly(PNI) terminated with termer 4, and the isotopic pattern for [C\textsubscript{169}H\textsubscript{185}N\textsubscript{15}O\textsubscript{29}+Ag]\textsuperscript{+} (u). (m/z) calculated for [C\textsubscript{169}H\textsubscript{185}N\textsubscript{15}O\textsubscript{29}+Ag]\textsuperscript{+}, 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)stanannane ($cis/trans = 75/25$) 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.