Nucleophilically-Assisted and Cationic Ring-Opening Polymerization (ROP) of Tin-Bridged \([1\)]\text{Ferrocenophanes}

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Supporting Material

Experimental Section

The compounds Me\textsubscript{3}SiCl, HCl, MeOTf, HCl (1M in Et\textsubscript{2}O), SiCl\textsubscript{4}, Me\textsubscript{3}SnCl, Bu\textsubscript{3}SnH, Bu\textsubscript{3}SnOTf, HOTf, AlMe\textsubscript{3} (2M in toluene), Al'Bu\textsubscript{3} (1M in toluene), NEt\textsubscript{3}, TMEDA (N,N,N',N'-tetramethylethlenediamine), pyridine, 4-dimethylaminopyrididine, 2,6-di-\textit{t}-butylpyridine, 1,4-diazabicyclo[2.2.2]octane, Galvinoxyl (2,6-di-\textit{t}-butyl-\(\alpha\)-(3,5-di-\textit{t}-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-\(p\)-tolyloxy, free radical), TEMPO (2,2,5,5-tetramethyl-1-piperidinyloxy), BzSSBz, BHT (2,6-di-\textit{t}-butyl-4-methylphenol), 1,4-cyclohexadiene, AIBN (2,2'-azobisisobutyronitrile) and DBO (dibenzoyl peroxide) were purchased from Aldrich. The compounds C\textsubscript{6}D\textsubscript{6}, NEt\textsubscript{3}, THF and TMEDA were distilled...
from Na, CH₂Cl₂ and pyridine were distilled twice from CaH₂ prior to use. Compounds
3a and 3b were synthesized as described previously and purified by repeated
crystallization.¹⁷,¹⁸ Both compounds were spectroscopically pure, however compound 3b
contained small amounts of hexanes and Et₂O (< 3%), which could not be removed in
high vacuum. All reactions and manipulations were carried out under an atmosphere of
prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glove-box
(Vacuum Atmospheres) except for the molecular weight determination of the resulting
polymers, which was carried out in air. 200, 300 or 400 MHz ¹H NMR spectra and 50.3,
75.5 or 100.5 MHz ¹³C NMR spectra were recorded either on a Varian XL200, Varian
XL300 or a Unity 400 spectrometer, respectively. The 111.8 MHz and 186.3 MHz ¹¹⁹Sn
NMR spectra were recorded on a Varian XL 300 and a Unity 500 spectrometer,
respectively. All solution ¹H and ¹³C NMR spectra were referenced externally to TMS
and ¹¹⁹Sn NMR spectra were referenced externally to SnMe₄. Mass spectra were
obtained with the use of a VG 70-250S mass spectrometer operating in an Electron
Impact (EI) mode. The molecular weight of the polymers was estimated by gel
permeation chromatography (GPC) using a Waters Associates 2690 Separations Module
equipped with a column heater, ultrastyragel columns with a pore size between 10³-10⁵
Å, in-line degasser and a Waters 410 differential refractometer. A flow rate of 1.0 ml
min⁻¹ was used and the sample was dissolved in a solution of 0.1% [nBu₄N]Br in THF or
pure THF. Polystyrene standards purchased from American Polymer Standards were
used for calibration purposes. For irradiation experiments, the mixtures were irradiated
with monochromatic light (λ = 365 nm; Rayonette bulbs) at ca. 35 °C, and kept within a
Suntest CPS Solar Simulator, respectively, and the conversion and polymer composition
was compared with those of samples, which were kept in the dark.
Mechanistic Studies and Trapping Experiments. All experiments were carried out in 5 mm NMR tubes. In an inert atmosphere glove-box, 20 mg (48 µmol) of the [1]stannaferrocenophane 3a were placed in the NMR tube which was then sealed with a septum. The reagent of choice to be reacted with 3a was dissolved in the deuterated solvent (0.5 ml C$_6$D$_6$), and the reaction solution was injected by syringe into the NMR tube containing 3a at the start of the NMR experiment. Crystalline 3a dissolved immediately and the reaction was monitored by $^1$H NMR spectroscopy. In the case of 3b (20 mg; 37 µmol), first dissolving the monomer inside the NMR tube and then adding the reagent was more practical because of the much higher stability and the decreased solubility of 3b in C$_6$D$_6$.

Reaction of 3b with excess Bu$_3$SnH and 1 Equiv. of Radicals Derived From AIBN:

Synthesis of 6. Neat Bu$_3$SnH (50 µl; 0.19 mmol) was added in a glove-box to a solution of 3b (20 mg; 37 µmol) and AIBN (3 mg; 18 µmol) in 0.5 ml C$_6$D$_6$ and the reaction solution was transferred with a pipette to a 5 mm NMR tube. The reaction mixture was kept at 60 °C and was followed by $^1$H NMR spectroscopy until conversion of 3b was complete (ca. 2 d). The crude product was analyzed by multinuclear NMR spectroscopy and by mass spectrometry indicating the formation of 6 (spectroscopic purity: ca. 90%). Excess Bu$_3$SnH was distilled off in high vacuum (ca. 100 °C; trap to trap). In order to further purify compound 6, it was taken up in acetonitrile / toluene (4.5 mL / 0.5 mL), a small amount of insoluble material was filtered off to give an orange solution, which was kept at –30 °C for 7 d. A light yellow supernatant was decanted form an orange oil which was dried in high vacuum (26 mg; 84%). For 6: $^1$H NMR (400 MHz, C$_6$D$_6$, 20 °C): $\delta$ = 6.97 (s/d, $J$ (H-117/119Sn) = 1787, 1870 Hz, 1H, Sn-H), 6.78 (s/d, $J$ (H-117/119Sn) = 19 Hz, 4H, meta-Mes), 4.36 (ps. t, $J$ = 2 Hz, 2H, Cp), 4.29 (ps. t, $J$ = 2 Hz, 2H, Cp), 4.26 (ps. t, $J$
\( = 2 \text{ Hz, 2H, Cp}) \), 4.07 (ps. t, \( J = 2 \text{ Hz, 2H, Cp}) \), 2.50 (s/d, \( J (\text{H-}^{117/119}\text{Sn}) = 6 \text{ Hz, 12H, ortho-Me}) \), 2.12 (s, 6H, para-Me), 1.7-1.3 (m, 12H, Sn-Bu), 1.11 (t, \( J (\text{H-H}) = 8 \text{ Hz, 6H, Sn-CH}_2 \)), 0.93 (q. \( J (\text{H-H}) = 8 \text{ Hz, 9H, CH}_3 \)); \( ^{13}\text{C NMR (100.4 MHz, C}_6\text{D}_6, 20 ^{\circ}\text{C): } \delta = 144.7 \text{ (s/d, } J (\text{C-}^{117/119}\text{Sn}) = 34 \text{ Hz, ortho-Mes}), 138.5 \text{ (s/d, } J (\text{C-}^{117/119}\text{Sn}) = 10 \text{ Hz, para-Mes}), 137.7 \text{ (ips-o-Mes}), 128.5 \text{ (s/d, } J (\text{C-}^{117/119}\text{Sn}) = 44 \text{ Hz, meta-Mes}), 75.4 \text{ (s/d, } J (\text{C-}^{117/119}\text{Sn}) = 41 \text{ Hz, Cp}), 75.4 \text{ (s/d, } J (\text{C-}^{117/119}\text{Sn}) = 58 \text{ Hz, Cp}), 71.9 \text{ (s/d, } J (\text{C-}^{117/119}\text{Sn}) = 34 \text{ Hz, Cp}), 71.4 \text{ (s/d, } J (\text{C-}^{117/119}\text{Sn}) = 44 \text{ Hz, Cp}), 70.7 \text{ (ips-o-Cp), 69.4 \text{ (ips-o-Cp), 29.6 \text{ (s/d, } J (\text{C-}^{117/119}\text{Sn}) = 20 \text{ Hz, Sn-Bu}), 27.8 \text{ (s/d, } J (\text{C-}^{117/119}\text{Sn}) = 57, 60 \text{ Hz, Sn-Bu}), 25.9 \text{ (s/d, } J (\text{C-}^{117/119}\text{Sn}) = 40 \text{ Hz, ortho-Me}), 21.0 \text{ (para-Me), 13.9 \text{ (Me), 10.5 \text{ (s/d, } J (\text{C-}^{117/119}\text{Sn}) = 331, 346 \text{ Hz, Sn-CH}_2 \)); } ^{119}\text{Sn NMR (186.3 MHz, C}_6\text{D}_6, 20 ^{\circ}\text{C): } \delta = -16.9 \text{ (SnBu}_3\text{), -213.5 \text{ (d, } J (\text{H-}^{119}\text{Sn}) = 1870 \text{ Hz, SnMes}_2\text{H}); MS (EI): 832 } [\text{M}^{+}] (100). \)

**Attempted Reaction of 3a and 3b with the cyclic dimer 5a.** a) A 1:1 mixture of 3a and 5a in C\(_6\)D\(_6\) was found to form high molecular weight polymer 4a without consuming detectable quantities of 5a by \(^1\text{H NMR spectroscopy. b) A 1:1 mixture of 3b and 5a in C}_6\text{D}_6/pyridine (0.5 mL/ 0.1 mL) afforded homopolymer 4b and no copolymer whereas 5a remained unchanged by \(^1\text{H NMR spectroscopy. For this reaction pyridine was added so an appreciable reaction rate was detected.**

**Reaction of 3a and 3b with excess Me\(_3\)SiCl.** Neat Me\(_3\)SiCl (50 µl; 0.39 mmol) was added in a glove-box to a solution of 3a (20 mg; 48 µmol) and 3b (20 mg; 37 µmol) in 0.5 ml C\(_6\)D\(_6\), respectively, and the reaction solution was transferred with a pipette to a 5 mm NMR tube. The reaction mixture was kept at ambient temperature and the reaction was followed by \(^1\text{H NMR spectroscopy until conversion was complete. The crude
product was analyzed by multinuclear NMR spectroscopy, gel permeation chromatography and by mass spectrometry confirming the formation of polymeric material 4a and 4b and of small amounts of the dimers 5a and 5b without any indication of Me$_3$SiCl incorporation. The reaction rate did not significantly differ from the one observed in a control experiment without Me$_3$SiCl addition (see Tables 1 and 2). GPC for 4a: bimodal; $M_n = 1,300,000$, $PDI = 4.7$ and $M_n = 15,000$, $PDI = 1.5$ (approx. ratio 30:70); GPC for 4b: $M_n = 29,000$, $PDI = 2.4$.

**Polymerization of 3a in different solvents.** In an inert atmosphere glove-box, 20 mg (48 $\mu$mol) of the [1]stannaferrocenophane 3a were placed in an NMR tube, the solvent of choice was added (C$_6$D$_6$, THF, chlorobenzene, CH$_2$Cl$_2$), and the NMR tube was then sealed with a septum. Crystalline 3a dissolved immediately and the reaction was monitored by $^1$H NMR spectroscopy (D$_2$O insert). Only in the case of THF as a solvent was a significant increase of the relative rate of polymerization in comparison to benzene observed (ca. 10 fold increase). In CH$_2$Cl$_2$ solution a substantial amount of cyclic dimer 5a was observed in addition to high molecular weight polymer 4a as determined by gel permeation chromatography and $^1$H NMR spectroscopy (Table 1S).
Table 1S. Representative NMR experiments with 3a (20 mg; 48 µmol; 0.1 M) in a variety of solvents; rates are given in comparison to reaction of 3a in neat benzene (rate = 1) and are based on 50% conversion; molecular weights are estimated by GPC of the crude reaction mixture.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Relative Rate</th>
<th>$M_w (10^3)$</th>
<th>PDI</th>
<th>% 4a</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_6$D$_6$</td>
<td>1</td>
<td>480</td>
<td>1.3</td>
<td>&gt;90</td>
</tr>
<tr>
<td>C$_6$H$_5$Cl</td>
<td>0.5</td>
<td>267</td>
<td>3.4</td>
<td>&gt;90</td>
</tr>
<tr>
<td>THF</td>
<td>10</td>
<td>178</td>
<td>3.9</td>
<td>&gt;97</td>
</tr>
<tr>
<td>CD$_2$Cl$_2$</td>
<td>50</td>
<td>13.3</td>
<td>4.1</td>
<td>ca. 35$^a$</td>
</tr>
</tbody>
</table>

$^a$ A large amount of cyclic dimer 5a was also detected.

Irradiation of 3b in the presence of pyridine. A solution of 3b (60 mg, 111 µmol) in a mixture of 1.5 ml ml C$_6$D$_6$ and 0.3 ml pyridine was quickly mixed and divided into three portions (A, B, C). Sample A was kept in the dark for 7 h, sample B was irradiated with monochromatic light ($\lambda = 365$ nm) and sample C was kept inside a sunlight simulator for the same time. An $^1$H NMR spectroscopic investigation revealed similar reaction rates in the case of A, B and C (70%, 90% and 95% estimated conversion). GPC analysis was performed on the resulting polymers. For A: $M_n = 27,000$, $PDI = 3.0$; B: $M_n = 39,000$, $PDI = 2.9$; C: $M_n = 55,000$, $PDI = 5.2$.

Reaction of 3a and 3b with excess Me$_3$SiCl/pyridine: A mixture of neat Me$_3$SiCl (50 µl; 0.39 mmol) and pyridine (50 µl; 0.62 mmol) was added in a glove-box to a solution of 3a (20 mg; 48 µmol) and 3b (20 mg; 37 µmol) in 0.5 ml C$_6$D$_6$, respectively, and the
reaction solution was transferred with a pipette to a 5 mm NMR tube. The reaction mixture was kept at ambient temperature and the reaction was followed by $^1$H NMR spectroscopy until conversion was complete. The crude product was analyzed by multinuclear NMR spectroscopy, gel permeation chromatography and by mass spectrometry confirming the formation of polymeric material 4a and 4b without any indication of Me$_3$SiCl incorporation. The reaction rate did not significantly differ from the one of a control experiment without Me$_3$SiCl addition. GPC for 4a: bimodal; $M_n = 2,400,000$, $PDI = 3.0$ and $M_n = 10,000$, $PDI = 2.0$ (approx. ratio 30:70); GPC for 4b: $M_n = 17,000$, $PDI = 2.5$.

**Reaction of 3b with 0.1 equiv. BuLi.** To a solution of 3b (0.27 g; 0.5 mmol) in THF was added BuLi (31 µl, 0.05 mmol; 1.6M in hexanes) at ambient temperature. The reaction mixture was stirred for 1 h, treated with Me$_3$SiCl (0.05 mmol, 7 µl) and subsequently analyzed by $^1$H NMR spectroscopy and GPC. The analysis indicated the presence of a small amount of oligomeric material (ca. 5%) in addition to a large amount of unreacted 3b.

**Reaction of 3b with 1 equiv. MeLi.** A solution of MeLi in diethylether (1.4 M; 140 µl; 0.19 mmol) was added drowise to a frozen solution of 3b (0.10 g; 0.19 mmol) in d$^8$-THF (1 ml) in an NMR tube at $-196$ °C via syringe. The NMR tube was sealed under vacuum, the mixture was allowed to warm up to $-78$ °C and the reaction was monitored by low temperature $^1$H and $^{119}$Sn NMR spectroscopy. At $-60$ °C reaction occurred to give 7a. At this temperature broad signals were observed particularly in the ferrocene region of the $^1$H NMR spectrum. Warming the sample up to -20 °C led to sharp signals in both, the $^1$H and $^{119}$Sn NMR spectra. At ambient temperature fast decomposition to a range of
unknown products occurred. For 7a; ¹H NMR (499.9 MHz, d⁸-THF/Et₂O, -20 °C): δ = 6.74 (s/d, J (H-¹¹⁷/¹¹⁹Sn) = 16 Hz, 4H, meta-Mes), 4.04, 3.93, 3.79, 3.62 (4 x s, 2H, Cp), 2.31 (s, 12H, ortho-Me), 2.19 (s, 6H, para-Me), 0.87 (s/d, J (H-¹¹⁷/¹¹⁹Sn) = 53 Hz, 3H, Sn-Me); ¹¹⁹Sn NMR (186.4 MHz, d⁸-THF/Et₂O, -20 °C): δ = -103.5.

Synthesis of 7b: A solution of MeLi in diethylether (1.4 M; 140 µl; 0.19 mmol) was added dropwise to a solution of 3b (0.10 g; 0.19 mmol) in THF (5 ml) at -60 °C via syringe. The mixture was allowed to warm up to -20 °C and treated first with 100 µl MeOH and subsequently with a few drops of aqueous NH₄Cl. All volatile material was removed under vacuum, the product was redissolved in a minimal amount of hexanes / toluene and passed through a short column with neutral alumina. Evaporation of the solvent gave 7b as an orange oil (yield: 64 mg; 61%). For 7b; ¹H NMR (400 MHz, C₆D₆, 20 °C): δ = 6.75 (s/d, J (H-¹¹⁷/¹¹⁹Sn) = 18 Hz, 4H, meta-Mes), 4.24, 4.17 (2 x ps.t, J = 2 Hz, 4H, Cp), 3.94 (s, 5H, Cp), 2.41 (s/d, J (H-¹¹⁷/¹¹⁹Sn) = 6 Hz, 12H, ortho-Me), 2.11 (s, 6H, para-Me), 0.90 (s/d, J (H-¹¹⁷/¹¹⁹Sn) = 54 Hz, 3H, Sn-Me); ¹³C NMR (100.4 MHz, C₆D₆, 20 °C): δ = 144.3 (s/d, J (C-¹¹⁷/¹¹⁹Sn) = 34 Hz, ortho-Mes), 140.1 (ipso-Mes), 138.1 (s/d, J (C-¹¹⁷/¹¹⁹Sn) = 7 Hz, para-Mes), 128.6 (s/d, J (C-¹¹⁷/¹¹⁹Sn) = 44 Hz, meta-Mes), 74.6 (s/d, J (C-¹¹⁷/¹¹⁹Sn) = 52 Hz, Cp), 71.1 (s/d, J (C-¹¹⁷/¹¹⁹Sn) = 40 Hz, Cp), 68.6 (CpH), not observed (ipso-Cp), 25.8 (s/d, J (C-¹¹⁷/¹¹⁹Sn) = 33 Hz, ortho-Me), 21.0 (para-Me), -1.5 (s/d, J (C-¹¹⁷/¹¹⁹Sn) = 351, 368 Hz, SnMe); ¹¹⁹Sn NMR (111.8 MHz, C₆D₆, -20 °C): δ = -109.0; MS (EI): m/z (%) 558 [M⁺] (100), 543 [M⁺ - Me] (10), 439 [M⁺ - Mes] (33), 373 [M⁺ - Fc] (33), 305 [FcSn⁺] (37); high resolution MS: 558.104753 (calcd 558.103190).
**Reaction of 3b with 0.1 equiv. MeLi.** A solution of MeLi in diethylether (0.1 equiv.; 1.4 M; 46 µl; 65 µmol) was added quickly via syringe to a solution of 3b (0.35 g; 0.65 mmol) in THF (5 ml) at –78 °C.

a) The reaction mixture was stirred at this temperature for 2 h and then gradually warmed up to ambient temperature over a period of 2 h and stirred for 1h at room temperature. All volatile material was removed in high vacuum subsequently. \(^1\)H NMR analysis indicated the formation of a small amount of decomposition products in addition to a large amount of unreacted 3b.

b) The reaction mixture was stirred at this temperature for 2 h and then gradually warmed up to –50 °C over a period of 1 h. MeOH (20 µl) was added via syringe, the reaction mixture was allowed to slowly warm up to ambient temperature and all volatile material was removed in high vacuum. \(^1\)H and \(^{119}\)Sn NMR analysis indicated the formation of a small amount of FcSnMes\(_2\)Me (7b) in addition to a large amount of unreacted 3b.

**Reaction of 3b with excess AlMe\(_3\).** A solution of 100 mg (0.18 mmol) 3b in hexanes (3 mL) was treated with AlMe\(_3\) (1 mL, 2 mmol; 2M solution in toluene) and the resulting orange solution was stirred at ambient temperature for 2 d. All volatile material was evaporated in high vacuum leaving an orange oil. An NMR spectroscopic investigation showed that the starting material 3b was completely consumed, and that the major product was 8a (spectroscopic purity: 90-95%). The weakly bound AlMe\(_3\) could be removed in high vacuum at 60 °C over a period of 12 h to give the dimer 8b. Reaction of 8b with 2 equivalents of pyridine (0.32 mmol, 19 µL) at room temperature afforded the monomeric adduct 8c.
For **8a**: $^1$H NMR (300 MHz, C$_6$D$_6$, 20 °C): $\delta = 6.73$ (s/d, $J$ (H-$^{117/119}$Sn) = 17 Hz, 4H, meta-Mes), 4.38 (m, 4H, Cp), 4.31 (br., 2H, Cp), 4.14 (ps. t, $J = 2$ Hz, 2H, Cp), 2.32 (s, 12H, ortho-Me), 2.11 (s, 6H, para-Me), 0.82 (s/d, $J$ (H-$^{117/119}$Sn) = 54 Hz, 3H, CH$_3$), -0.32 (br., 15H, AlMe); $^{13}$C NMR (100.4 MHz, C$_6$D$_6$, 20 °C): $\delta = 144.1$ (s/d, $J$ (C-$^{117/119}$Sn) = 34 Hz, ortho-Mes), 139.3 (s/d, $J$ (C-$^{117/119}$Sn) = 523, 549 Hz, ipso-Mes), 138.4 (para-Mes), 128.5 (s/d, $J$ (C-$^{117/119}$Sn) = 46 Hz, meta-Me), 86.1, 77.3 (br., br., Cp-Al), 75.7 (s/d, $J$ (C-$^{117/119}$Sn) = 44 Hz, Cp-Sn), 73.7 (br., Cp-Sn), 25.7 (s/d, $J$ (C-$^{117/119}$Sn) = 5 Hz, para-Me), -1.8 (s/d, $J$ (C-$^{117/119}$Sn) = 356, 367 Hz, Sn-Me), -5.8 (br., Al-Me); $^{119}$Sn NMR (111.8 MHz, C$_6$D$_6$, 20 °C): $\delta = -111.6$ (br.); $^{27}$Al NMR (78.2 MHz, C$_6$D$_6$, 20 °C): $\delta = 152$ (h$_{1/2}$ = 2400 Hz).

For **8b**: $^1$H NMR (300 MHz, C$_6$D$_6$, 20 °C): $\delta = 6.75$ (s/d, $J$ (H-$^{117/119}$Sn) = 18 Hz, 4H, meta-Mes), 4.42 (s, 2H, Cp), 4.39 (m, 4H, Cp), 4.14 (s, 2H, Cp), 2.34 (s, 12H, ortho-Me), 2.12 (s, 6H, para-Me), 0.86 (s/d, $J$ (H-$^{117/119}$Sn) = 53 Hz, 3H, CH$_3$), -0.38 (br., 6H, AlMe); $^{13}$C NMR (100.4 MHz, C$_6$D$_6$, 20 °C): $\delta = 144.1$ (s/d, $J$ (C-$^{117/119}$Sn) = 34 Hz, ortho-Mes), 139.3 (s/d, $J$ (C-$^{117/119}$Sn) = 523, 549 Hz, ipso-Mes), 138.4 (para-Mes), 128.5 (s/d, $J$ (C-$^{117/119}$Sn) = 46 Hz, meta-Mes), 85.9, 76.8 (br., br., Cp-Al), 75.5 (s/d, $J$ (C-$^{117/119}$Sn) = 49 Hz, Cp-Sn), 73.4 (br., Cp-Sn), 25.8 (s/d, $J$ (C-$^{117/119}$Sn) = 34 Hz, ortho-Me), 21.0 (s/d, $J$ (C-$^{117/119}$Sn) = 6 Hz, para-Me), -1.6 (s/d, $J$ (C-$^{117/119}$Sn) = 356, 366 Hz, Sn-Me), -4.5 (br., Al-Me); $^{119}$Sn NMR (111.8 MHz, C$_6$D$_6$, 20 °C): $\delta = -113.2$ (br.); $^{27}$Al NMR (78.2 MHz, C$_6$D$_6$, 20 °C): $\delta = 154$ (h$_{1/2}$ = 4050 Hz).

For **8c**: $^1$H NMR (300 MHz, C$_6$D$_6$, 20 °C): $\delta = 8.26$ (d, 2H, ortho-py), 6.78 (s/d, $J$ (H-$^{117/119}$Sn) = 11 Hz, 4H, meta-Mes), 6.72 (t, 1H, para-py), 6.37 (t, 2H, meta-py), 4.65 (br., 2H, Cp), 4.40 (br., 4H, Cp), 4.23 (br., 2H, Cp), 2.50 (s, 12H, ortho-Me), 2.13 (s, 6H, para-Me), 1.07 (s/d, $J$ (H-$^{117/119}$Sn) = 57 Hz, 3H, CH$_3$), -0.12 (br., 6H, AlMe); $^{13}$C NMR
(75.2 MHz, C\text{\textsubscript{6}}D\text{\textsubscript{6}}, 20 °C): δ = 147.9 (s, ortho-Mes), 144.5 (s, para-Mes), 140.6 (s, para-py), 138.3 (s, ortho-py), 137.8 (s, meta-py), 128.5 (s/d, J (C-\textsuperscript{117}/\textsuperscript{119}Sn) = 44.5 Hz, ipso-Mes), 124.4 (s, meta-Mes), 76.7, 74.2, 74.1, 72.1, 71.1, 68.6 (br., Cp), 25.9 (s/d, J (C-\textsuperscript{117}/\textsuperscript{119}Sn) = 32 Hz, ortho-Me), 21.1 (s, para-Me), -1.4 (Sn-Me), -8.9 (br., Al-Me); \textsuperscript{119}Sn NMR (111.8 MHz, C\text{\textsubscript{6}}D\text{\textsubscript{6}}, 20 °C): δ = -109.4; \textsuperscript{27}Al NMR (78.2 MHz, C\text{\textsubscript{6}}D\text{\textsubscript{6}}, 20 °C): δ = 167 (\textsuperscript{1/2} = 4700 Hz).

Reaction of 3b with excess Al\textsubscript{i}Bu\textsubscript{3}. A solution of 105 mg (0.19 mmol) of 3b in toluene (5 mL) was treated with Al\textsubscript{i}Bu\textsubscript{3} (2 mL, 1M solution in toluene, 2 mmol) and the resulting orange solution was stirred at r.t. for 1 d. All volatile material was evaporated in high vacuum leaving an orange oil. An NMR spectroscopic investigation showed that the starting material 3b was completely consumed, and suggested that the major product was Fc(Al\textsubscript{i}Bu\textsubscript{2})SnMes\textsubscript{2}iBu·Al\textsubscript{i}Bu\textsubscript{3} (spectroscopic purity: 70%). For the reaction mixture containing Fc(Al\textsubscript{i}Bu\textsubscript{2})SnMes\textsubscript{2}iBu·Al\textsubscript{i}Bu\textsubscript{3} and excess Al\textsubscript{i}Bu\textsubscript{3}: \textsuperscript{1}H NMR (300 MHz, C\text{\textsubscript{6}}D\text{\textsubscript{6}}, 20 °C): δ = 6.72 (br., 4H, meta-Mes), 4.45, 4.41, 4.33, 4.09 (4 x s, 4 x 2H, Cp), 2.31 (s, 12H, ortho-Me), 2.12 (s, 6H, para-Me), the signals for the iBu groups are overlapping with those for Al\textsubscript{i}Bu\textsubscript{3}; \textsuperscript{119}Sn NMR (111.8 MHz, C\text{\textsubscript{6}}D\text{\textsubscript{6}}, 20 °C): δ = -113.9 (br.).

Reaction of 3b with 2 equiv. Me\textsubscript{3}SnCl: Synthesis of 9a. A mixture of 0.50 g (0.92 mmol) 3b and 0.36 g (1.81 mmol) Me\textsubscript{3}SnCl was dissolved in 50 ml toluene and the resulting orange solution was stirred at r.t. until no more 3b could be detected by \textsuperscript{1}H-NMR spectroscopy (1 d). All volatile material was evaporated in high vacuum at 50 °C leaving behind 9a as an orange oil (spectroscopic purity greater 95%). For 7; \textsuperscript{1}H NMR
(300 MHz, C$_6$D$_6$, 20 °C): δ = 6.67 (s/d, J (H-$_{117/119}$Sn) = 25 Hz, 4H, meta-Mes), 4.47 (ps. t, J = 2 Hz, 2H, Cp), 4.42 (ps. t, J = 2 Hz, 2H, Cp), 4.30 (ps. t, J = 2 Hz, 2H, Cp), 4.11 (ps. t, J = 2 Hz, 2H, Cp), 2.54 (s/d, J (H-$_{117/119}$Sn) = 7 Hz, 12H, ortho-Me), 2.05 (s, 6H, para-Me), 0.19 (s/d, J (H-$_{117/119}$Sn) = 53, 55 Hz, 9H, Sn-Me); $^{13}$C NMR (50.3 MHz, C$_6$D$_6$, 20 °C): δ = 144.0 (J (C-$_{117/119}$Sn) = 45 Hz, ortho-Mes), 140.0 (ipso-Mes), 139.6 (para-Mes), 129.3 (J (C-$_{117/119}$Sn) = 57 Hz, meta-Mes), 77.6 (ipso-Cp), 75.4 (J (C-$_{117/119}$Sn) = 48 Hz, Cp), 73.9 (J (C-$_{117/119}$Sn) = 81 Hz, Cp), 72.3 (J (C-$_{117/119}$Sn) = 38 Hz, Cp), 71.6 (J (C-$_{117/119}$Sn) = 55 Hz, Cp), 70.3 (ipso-Cp), 25.1 (J (C-$_{117/119}$Sn) = 41 Hz, ortho-Me), 21.0 (para-Me), -9.0 (J (C-$^{119}$Sn) = 1229 Hz, J (C-$^{117}$Sn) = 1175 Hz, SnMe); $^{119}$Sn NMR (111.8 MHz, C$_6$D$_6$, 20 °C): δ = -6.2 (SnMe$_3$), -27.9 (SnMes$_2$Cl); MS (EI): m/z (%) 742 [M$^+$] (100), 727 [M$^+$ - Me] (10), 423 [Fe(η-C$_5$H$_4$)$_2$SnMes$^+$] (33), 304 [Fe(η-C$_5$H$_4$)$_2$Sn$^+$] (37).

**Reaction of 3b with 1 equiv. Me$_3$SnCl.** A mixture of 0.50 g (0.92 mmol) 3b and 0.18 g (0.90 mmol) Me$_3$SnCl was dissolved in 50 ml toluene and the resulting orange solution was stirred at r.t. until no more 3b could be detected by $^1$H NMR spectroscopy (1 d). An NMR spectroscopic investigation ($^1$H, $^{13}$C, $^{119}$Sn NMR) of the crude product revealed that a mixture of the Me$_3$SnCl addition product 9a (80%) and the higher homologue 10$_1$ consisting of two ferrocenylstannane units (20%) had formed. After evaporation of the solvent at r.t., a substantial amount of unreacted Me$_3$SnCl could be recovered by sublimation. In order to obtain an enriched sample of the higher homologue, the resulting orange oil was redissolved in a mixture of Et$_2$O and CH$_3$CN and kept at -55 °C for 10 d. An orange oil formed, which consisted of a 1:1 mixture of 9a and 10$_1$. For 10$_1$: $^1$H NMR (300 MHz, C$_6$D$_6$, 20 °C): δ = 6.75, 6.67 (s/d, s/d, J (H-$_{117/119}$Sn) = 18 Hz, J (H-$_{117/119}$Sn) =
25 Hz, 4H, 4H, _meta_-Mes), 4.73, 4.72, 4.61, 4.43, 4.34, 4.27, 4.27, 3.94 (8 x m, 8 x 2H, Cp), 2.50, 2.42 (s/d, s/d, J (H-117/119Sn) = 6 Hz, 12H, 12H, _ortho_-Me), 2.10, 2.05 (s, s, 6H, 6H, _para_-Me), 0.21 (s/d, J (H-117/119Sn) = 53, 55 Hz, 9H, Sn-Me); 119Sn NMR (111.8 MHz, C6D6, 20 °C): δ = -6.0 (SnMe3), -27.9 (SnMes2Cl), -128.1 (fc-Sn-fc); MS (EI): m/z (%) 1282 [M+](40).

**Reaction of 3b with Varying Amounts of Me3SnCl.** A solution of the selected amount of Me3SnCl (Me3SnCl/3b: 1:2, 1:4, 1:10, 1:100) in 1.2 ml C6D6 was added in a glove-box to 3b (40 mg; 74 µmol) under stirring, and the reaction solution was transferred with a pipette to a 5 mm NMR tube. The reaction was followed by 1H NMR spectroscopy and GPC, showing oligomeric species and varying amounts of 4b depending on the ratio Me3SnCl/3b. GPC: Mn = 423,000; PDI = 1.9 (1:2); Mn = 627,000; PDI = 1.5 (1:4); Mn = 974,000; PDI = 1.3 (1:10); Mn = 892,000; PDI = 1.3 + Mn = 15,000; PDI = 1.5 (1:100, bimodal);

**Reaction of 3b with 9a.** (a) A solution of 9a (0.17 g; 0.23 mmol) in 1.2 ml C6D6 was added in a glove-box to 3b (0.12 g; 0.22 mmol) with stirring, and the reaction solution was transferred with a pipette to a 5 mm NMR tube. The reaction was followed by 1H NMR spectroscopy until 3b was completely consumed (ca. 14 d). At this time, a considerable amount of compound 9a was still present, and the formation of higher homolog 101 and of other species was observed, which were assigned as the analogous higher oligomers 10x (x > 1). (b) A similar reaction of 3b and 9a in a mixture of 1.0 mL C6D6 and 0.2 mL pyridine resulted mainly in the formation of polymer 4b in addition to unreacted 9a. GPC for 4b: Mn = 34,000, PDI = 2.1.
Reaction of 3b with 0.1 equiv. HCl. To a solution of 54 mg (0.1 mmol) of 3b in 0.6 mL of CD$_2$Cl$_2$ or C$_6$D$_6$ were added dropwise 10 µL (1.0 µmol) HCl (1M in Et$_2$O) at room temperature. $^1$H NMR spectroscopy (after 2h) revealed the formation of 10% 9b together with 90% of unreacted 3b. $^1$H NMR for 9b (300 MHz, CD$_2$Cl$_2$, 20 °C): δ = 6.91 (s/d, $J$ (H-117/119Sn) = 18 Hz, 4H, meta-Mes), 4.48 (ps. t, $J$ = 1.6 Hz, 2H, Cp), 4.33 (ps. t, $J$ = 1.6 Hz, 2H, Cp), 4.12 (s, 5H, Cp), 2.46 (s/d, $J$ (H-117/119Sn) = 6.4 Hz, 12H, ortho-Me), 2.28 (s, 6H, para-Me); $^{13}$C NMR (75.5 MHz, C$_6$D$_6$, 20 °C): δ = 143.8 (ortho-Mes), 139.5 (ipso-Mes), 137.4 (para-Mes), 129.4 (meta-Mes), 77.6 (ipso-Cp), 73.9 (Cp), 71.4 (Cp), 69.2 (Cp), 70.3 (ipso-Cp), 25.0 (ortho-Me), 20.8 (para-Me).

Reaction of 3a with 0.1 equiv. HCl. To a solution of 42 mg (0.1 mmol) of 3a in 0.6 mL of C$_6$D$_6$ were added dropwise 10 µL (1.0 µmol) HCl (1M in Et$_2$O) at room temperature. $^1$H NMR spectroscopy (after 15 min) revealed the formation of 10% ring-opened FcSnBu$_2$Cl in addition to 90% of unreacted 3a. Formation of oligomeric/polymeric products was confirmed by $^1$H NMR spectroscopy and size exclusion chromatography after 2 d. GPC: $M_n$ = 6,450, PDI = 1.4.

$^1$H NMR for FcSnBu$_2$Cl (300 MHz, C$_6$D$_6$, 20 °C): δ = 4.48 (s br., 5H, Cp), 4.23 (ps. t, $J$ = 1.2 Hz, 2H, Cp), 4.06 (ps. t, $J$ = 1.2 Hz, 2H, Cp), 1.31 (s/d, $J$ (H-117Sn) = 84.4 Hz, $J$ (H-119Sn) = 81.6 Hz, 18H, t-Bu).

Reaction of 3b with 1 equiv. HOTf: Synthesis of 11a. Neat HOTf (46 µl; 0.52 mmol) was added dropwise to a solution of 3b (0.295 g; 0.55 mmol) in CH$_2$Cl$_2$ (10 ml) at –78 °C via syringe. Upon addition the color of the solution turned from orange to yellow. After stirring the reaction mixture for 30 min at –78 °C, the solution was allowed to slowly warm up to ambient temperature. All volatile material was removed under vacuum, the
orange-brownish residue was taken up in toluene/hexanes (2 mL/8 mL) and filtered from a small amount of insoluble material. Evaporation of all volatile material in high vacuum gave 11a as an orange oil (yield: 0.345 g (96%); spectroscopic purity ca. 90%). For 11a: \(^1\)H NMR (300 MHz, C\(_6\)D\(_6\), 20 °C): \(\delta = 6.66\) (s/d, \(J (\text{H}^{117/119}\text{Sn}) = 19\) Hz, 4H, meta-Mes), 4.41 (s, 2H, Cp), 4.20 (s, 2H, Cp), 4.13 (s, 5H, CpH), 2.41 (s, 12H, ortho-Me), 2.01 (s, 6H, para-Me); \(^{13}\)C NMR (100.4 MHz, C\(_6\)D\(_6\), 20 °C): \(\delta = 143.7\) (s/d, \(J (\text{C}^{117/119}\text{Sn}) = 48\) Hz, ortho-Mes), 140.9 (s/d, \(J (\text{C}^{117/119}\text{Sn}) = 12\) Hz, para-Mes), 139.3 (ipso-Mes), 129.5 (s/d, \(J (\text{C}^{117/119}\text{Sn}) = 59\) Hz, meta-Mes), 119.6 (q, \(J (\text{C}^{19}\text{F}) = 318\) Hz, CF\(_3\)), 75.5 (ipso-Cp), 74.7 (s/d, \(J (\text{C}^{117/119}\text{Sn}) = 77\) Hz, Cp), 72.4 (s/d, \(J (\text{C}^{117/119}\text{Sn}) = 60\) Hz, Cp), 69.5 (CpH), 24.7 (s/d, \(J (\text{C}^{117/119}\text{Sn}) = 7\) Hz, para-Me); \(^{19}\)Sn NMR (111.8 MHz, C\(_6\)D\(_6\), 20 °C): \(\delta = 36.9\); \(^{19}\)F NMR (375.7 MHz, C\(_6\)D\(_6\), 20 °C): \(\delta = -77.8\).

**Reaction of 11a with pyridine: Synthesis of 12.** Neat HOTf (16 µl; 0.18 mmol) was added dropwise to a solution of 3b (0.10 g; 0.19 mmol) in CH\(_2\)Cl\(_2\) (5 ml) at –78 °C via syringe. Upon addition the color of the solution turns from orange to yellow. After stirring the reaction mixture for 30 min at –78 °C neat pyridine (2 equiv.; 30 µl; 0.37 mmol) was added, and the solution was allowed to slowly warm up to ambient temperature. All volatile material was removed under vacuum and the orange residue was taken up in C\(_6\)D\(_6\) (1 ml). Orange X-ray quality crystals of 12·C\(_6\)D\(_6\) formed over a period of 2 days and were isolated by decanting the solvent. Yield: 60 mg (39%). For 12·C\(_6\)D\(_6\): \(^1\)H NMR (399.3 MHz, C\(_6\)D\(_6\), 20 °C): \(\delta = 8.42\) (d, \(J = 4\) Hz, 2H, ortho-py), 6.95 (tr, \(J = 7\) Hz, 1H, para-py), 6.65 (s/d, \(J (\text{H}^{117/119}\text{Sn}) = 19\) Hz, 4H, meta-Mes), 6.59 (ps.t., \(J = 6\) Hz, 2H, meta-py), 4.41 (br., 2H, Cp), 4.23 (br., 2H, Cp), 4.07 (br., 5H, CpH), 2.42 (s, 12H, ortho-Me), 2.05 (s, 6H, para-Me); \(^{13}\)C NMR (100.4 MHz, C\(_6\)D\(_6\), 20 °C): \(\delta = 149.4\)
(ortho-py), 144.2 (s/d, J (C-^{117/119}Sn) = 49 Hz, ortho-Mes), 140.6 (para-Mes), 139.8 (ipso-Mes), 136.4 (para-py), 129.5 (s/d, J (C-^{117/119}Sn) = 62 Hz, meta-Mes), 123.8 (meta-py), 120.2 (q, J (C-^{19}F) = 319 Hz, CF₃), 78.2 (ipso-Cp), 75.5 (br., Cp), 72.1 (br., Cp), 69.7 (br., CpH), 25.1 (s/d, J (C-^{117/119}Sn) = 40 Hz, ortho-Me), 21.0 (para-Me);

^{119}Sn NMR (111.8 MHz, C₆D₆, 20 °C): δ = -66.1; MS (EI): m/z (%) 692 [M⁺ - py] (100).

**Reaction of 3b with 0.05 equiv. of HOTf.** Neat HOTf (0.05 equiv.; 2 µl; 23 µmol) was added dropwise to a solution of 3b (0.25 g; 0.46 mmol) in CH₂Cl₂ (5 ml) at −78 °C via syringe. In contrast to the equimolar reaction, the color of the solution remained orange indicating the presence of unreacted 3b. After stirring the reaction mixture for 30 min at −78 °C it was allowed to slowly warm to ambient temperature. A yellow precipitate gradually formed over a period of 3h. The supernatant was decanted, and the solid was washed with hexanes (2 x 5 ml) and dried in vacuum. ^1H and ^{119}Sn NMR analysis indicated the formation of high molecular weight polymer 4b, which was characterized by size exclusion chromatography. GPC (Mₙ = 385,000; PDI = 2.2). Yield: 0.21 g (84%).

**Reaction of 3b with 0.001 Equiv. of 11a.** (a) 0.1 ml of a solution of 11a (0.1 µmol, 1.0 mM in CD₂Cl₂) was added in a glove-box to a solution of 3b (54 mg; 0.1 mmol) in 0.6 mL of CD₂Cl₂ in a 5 mm NMR tube. A yellow precipitate formed gradually over a period of 3h. ^1H NMR spectroscopy revealed the formation of polymer 4b in addition to a small amount (ca.15%) of unreacted 3b. GPC for 4b: Mₙ = 470,200, PDI = 2.1.

**Reaction of 3b with excess MeOH: Synthesis of 13.** Neat MeOH (100 µl; 2.5 mmol) was added to a solution of 3b (40 mg; 74 µmol) in C₆D₆ (0.5 ml) via syringe and the
solution stirred at 40-50 °C. The reaction was followed by \(^1\)H NMR spectroscopy and the mixture was heated until \(3b\) was completely consumed (6 d). All volatile material was removed under vacuum to give \(13\) as an orange solid in ca 95% purity. \(^1\)H NMR (300 MHz, \(\text{C}_6\text{D}_6\), 20 °C): \(\delta = 6.73\) (s/d, \(J (\text{H}^{117/119}\text{Sn}) = 21\) Hz, meta-Mes), 4.23 (br., 2H, Cp), 4.20 (br., 2H, Cp), 4.09 (br., 5H, CpH), 3.73 (s/d, \(J (\text{H}^{117/119}\text{Sn}) = 42\) Hz, 3H, OMe), 2.47 (s/d, 12H, ortho-Me), 2.10 (s, 6H, para-Me); \(^{13}\)C NMR (100.4 MHz, \(\text{C}_6\text{D}_6\), 20°C): \(\delta = 144.6\) (s/d, \(J (\text{C}^{117/119}\text{Sn}) = 43\) Hz, ortho-Mes), 139.5 (s/d, \(J (\text{C}^{117/119}\text{Sn}) = 11\) Hz, para-Mes), 139.2 (ipso-Mes), 128.9 (s/d, \(J (\text{C}^{117/119}\text{Sn}) = 56\) Hz, meta-Mes), 74.4 (s/d, \(J (\text{C}^{117/119}\text{Sn}) = 64/66\) Hz, Cp), 71.2 (s/d, \(J (\text{C}^{117/119}\text{Sn}) = 51\) Hz, Cp), 69.1 (s, CpH), 53.9 (s/d, \(J (\text{C}^{117/119}\text{Sn}) = 22\) Hz, OMe), 24.8 (s/d, \(J (\text{C}^{117/119}\text{Sn}) = 35\) Hz, ortho-Me), 21.0 (para-Me), not observed (ipso-Cp); \(^{119}\)Sn NMR (111.8 MHz, \(\text{C}_6\text{D}_6\)): \(\delta = -35.5\); MS (EI): m/z (%): 574 \([\text{M}^+]\) (100), 543 \([\text{M}^+ - \text{OMe}]\) (10), 455 \([\text{M}^+ - \text{Mes}]\) (15). High resolution MS: 574.097408 (calcd: 574.098104 for C\(_{29}\)H\(_{34}\)OFeSn).

**Reaction of 3b with 1 equiv. MeOTf.** Neat MeOTf (31 µl; 0.28 mmol) was added dropwise to a solution of \(3b\) (0.15 g; 0.28 mmol) in \(\text{CH}_2\text{Cl}_2\) (5 ml) at ambient temperature via syringe. A yellow precipitate gradually formed over a period of 1 h. The supernatant was decanted, and the solid was washed with hexanes (2 x 5 ml) and dried in vacuum. \(^1\)H and \(^{119}\)Sn NMR analysis indicated the formation of high molecular weight polymer \(4b\), which was characterized by size exclusion chromatography. Yield: 0.12 g (80%). GPC: \(M_n = 116,900, PDI = 2.4\).

**Reaction of 3b with 1 equiv. MeOTf in the presence of 2,6-di-t-Bu-l-pyridine.** in a similar reaction neat 2,6-di-t-Bu-pyridine (0.019g, 0.1 mmol) was added to a solution of 10µl (0.1 mmol) of MeOTf in 3 ml of \(\text{CH}_2\text{Cl}_2\). After 16h, 54 mg of \(3b\) (0.1 mmol) were
added. A yellow precipitate gradually formed over a period of 10-12 h. The supernatant was decanted, and the solid was washed with hexanes (2 x 5 ml) and dried in vacuum. $^1$H NMR spectroscopy and GPC indicated the formation of high molecular weight polymer 4b. Yield 0.040 g (74%). GPC: $M_n = 145,400$, $PDI = 2.2$.

**Reaction of 3b with 0.1 equiv. MeOTf.** Neat MeOTf (1.3 μl; 0.01 mmol) was added dropwise to a solution of 3b (60 mg; 0.11 mmol) in CH$_2$Cl$_2$ (5 ml) at ambient temperature via syringe. A yellow precipitate gradually formed over a period of 5 h. The supernatant was decanted, and the solid was washed with hexanes (2 x 5 ml) and dried in vacuum. $^1$H NMR analysis indicated the formation of high molecular weight polymer 4b, which was characterized by size exclusion chromatography. Yield: 45 mg (75%). GPC: $M_n = 222,700$, $PDI = 3.0$.

**Reaction of 3b with 1 equiv. nBu$_3$SnOTf.** Neat Bu$_3$SnOTf (41 mg; 93 μmol) was added to a solution of 3b (50 mg; 92 μmol) in C$_6$D$_6$ (1 ml) at ambient temperature. Complete conversion of 3b was observed within 1 d as shown by $^1$H NMR analysis. The spectrum reveals the formation of the addition product 11b in ca. 80% purity. The major impurity was identified as compound 11a, the formation of which can be attribute to HOTf impurities in the sample of Bu$_3$SnOTf used.

For 11b: $^1$H NMR (300 MHz, C$_6$D$_6$, 20 °C): $\delta = 6.66$ (s/d, $J$ (H-117/119Sn) = 27 Hz, 4H, meta-Mes), 4.62, 4.56, 4.42, 4.13 (4 x ps. t, $J = 2$ Hz, 8H, Cp), 2.42 (s/d, $J$ (H-117/119Sn) = 7 Hz, 12H, ortho-Me), 2.02 (s, 6H, para-Me), 1.6-0.9 (m, 27H, Bu); $^{13}$C NMR (75.5 MHz, C$_6$D$_6$, 20 °C): $\delta = 143.7$ (s/d, $J$ (C-117/119Sn) = 49 Hz, ortho-Mes), 140.9 (s/d, $J$ (C-117/119Sn) = 12 Hz, para-Mes), 139.3 (ipso-Mes), 129.5 (s/d, $J$ (C-117/119Sn) = 61 Hz, meta-Mes), 119.6 (q, $J$ (C-19F) = 319 Hz, CF$_3$), 75.9 (ipso-Cp), 75.8 (s/d, $J$ (C-117/119Sn)
$= 40 \text{ Hz, Cp}$), 74.4 (s/d, $J (\text{C}^{-117/119}\text{Sn}) = 79 \text{ Hz, Cp}$), 72.6 (s/d, $J (\text{C}^{-117/119}\text{Sn}) = 60 \text{ Hz, Cp}$), 72.3 (s/d, $J (\text{C}^{-117/119}\text{Sn}) = 34 \text{ Hz, Cp}$), 70.9 (ipso-Cp), 29.5 (s/d, $J (\text{C}^{-117/119}\text{Sn}) = 20 \text{ Hz, Sn-Bu}$), 27.7 (s/d, $J (\text{C}^{-117/119}\text{Sn}) = 54, 57 \text{ Hz, Sn-Bu}$), 24.8 (s/d, $J (\text{C}^{-117/119}\text{Sn}) = 42 \text{ Hz}$, ortho-Me), 21.0 (s/d, $J (\text{C}^{-117/119}\text{Sn}) = 6 \text{ Hz, para-Me}$), 13.9 (Me), 10.4 (s/d, $J (\text{C}^{-117/119}\text{Sn}) = 20 \text{ Hz, Sn-CH}_2$); $^{119}\text{Sn NMR}$ (111.8 MHz, C$_6$D$_6$, 20 °C): $\delta = 34.7$ (SnMes$_2$OTf), -20.5 (SnBu$_3$); $^{19}$F NMR (375.7 MHz, C$_6$D$_6$, 20 °C): $\delta = -77.9$.

**Reaction of 3b with 0.3 equiv. $n$Bu$_3$SnOTf in C$_6$D$_6$.** Neat Bu$_3$SnOTf (12 mg; 27 µmol) was added to a solution of 3b (50 mg; 92 µmol) in C$_6$D$_6$ (1 ml) at ambient temperature. Complete conversion of $n$Bu$_3$SnOTf to form 11b and no formation of polymer 4b was observed within 1 d as shown by $^1$H NMR analysis. Complete conversion of unreacted 3b to polymer 4b was observed after 14 d. $^{119}\text{Sn NMR}$ (111.9 MHz, C$_6$D$_6$, 20 °C): $\delta = 34.2$ (SnMes$_2$OTf), -20.1(SnBu$_3$), -127.6 (-SnMes$_2$-); $^{19}$F NMR (375.7 MHz, C$_6$D$_6$, 20 °C): $\delta = -78.1$. GPC: $M_n = 58,100$; $PDI = 2.2$.

**Reaction of 3b with 0.3 equiv. $n$Bu$_3$SnOTf in CD$_2$Cl$_2$.** Neat Bu$_3$SnOTf (13 mg; 30 µmol) was added to a solution of 3b (54 mg; 0.1 mmol) in CD$_2$Cl$_2$ (1 ml) at ambient temperature. Complete conversion of $n$Bu$_3$SnOTf to form 11b and formation of 4b was observed within 1 d as shown by $^1$H NMR analysis. Complete conversion of unreacted 3b to polymer 4b was observed within 3d at ambient temperature. GPC: $M_n = 244,000$; $PDI = 2.3$.

**Reaction of 3b with 1 equiv. MeOTf and excess [NBu$_4$]OTf.**

a) 4 equiv. of [NBu$_4$][OTf]: Neat MeOTf (16.5 µL, 0.15 mmol) and neat [NBu$_4$][OTf] (250 mg, 0.64 mmol) were added to a solution of 3b (80 mg; 0.15 mmol) in CH$_2$Cl$_2$
(3 mL) at ambient temperature. After stirring for 19 h the formation of a yellow precipitate was observed. The supernatant was decanted and the solid washed with hexanes (2 x 5 mL) and dried in vacuum. $^1$H NMR indicated the formation of high molecular weight polymer 4b, which was characterized by size exclusion chromatography. Yield: 65 mg (81%). GPC: $M_n = 53,800$, $PDI = 2.4$.

b) 100 equiv. of [NBu$_4$]OTf: Neat MeOTf (12.5 µL, 0.10 mmol) and neat [NBu$_4$]OTf (3.91g, 10 mmol) were added to a solution of 3b (54 mg; 0.10 mmol) in CH$_2$Cl$_2$ (6 mL) at ambient temperature. After stirring for 19 h the yellow solution was evaporated to dryness and the residue extracted with hexanes. After filtration, the yellow hexanes solution was then evaporated to dryness again. $^1$H NMR indicated the formation of mono/oligomeric ring-opened species, which were characterized by size exclusion chromatography. ($M_n < 1000$). Yield: 30 mg (55%).

**Reaction of 3b with 0.3 equiv. Bu$_3$SnOTf and 100 equiv. [NBu$_4$]OTf.** Neat Bu$_3$SnOTf (13 mg; 30 µmol) and neat [NBu$_4$]OTf (3.91g, 10 mmol) were added to a solution of 3b (54 mg; 0.10 mmol) in CH$_2$Cl$_2$ (6 mL) at ambient temperature. After stirring for 19 h the yellow solution was evaporated to dryness and the residue extracted with ether. After filtration, the yellow ether solution was then evaporated to dryness again. $^1$H NMR indicated the formation of mono/oligomeric ring-opened species, which were characterized by size exclusion chromatography. ($M_n < 1000$). Yield: 35 mg (65%).