Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

for

The Living Anionic Polymerization of Activated Aziridines: Systematic Study of Reaction Conditions and Kinetics

*Elisabeth Rieger, Tassilo Gleede, Katja Weber, Angelika Manhart, Manfred Wagner, Frederik R. Wurm**

Max-Planck-Institut für Polymerforschung (MPI-P), Ackermannweg 10, D-55128 Mainz, Germany

wurm@mpip-mainz.mpg.de

Temperature (MsMAz (1))

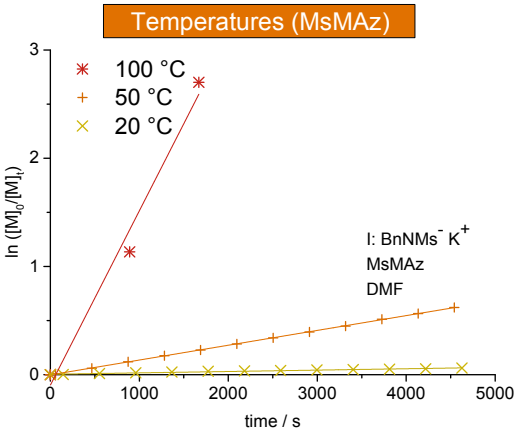


Figure S1. Kinetic Plots of $\ln([M]_0/[M]_t)$ vs. time for the azaanionic polymerization of MsMAz (1), BnNKMs (4, initiator) in DMF-d_7 at different temperatures. (also compare Table 1).

Counter Ion (MsMAz (1))

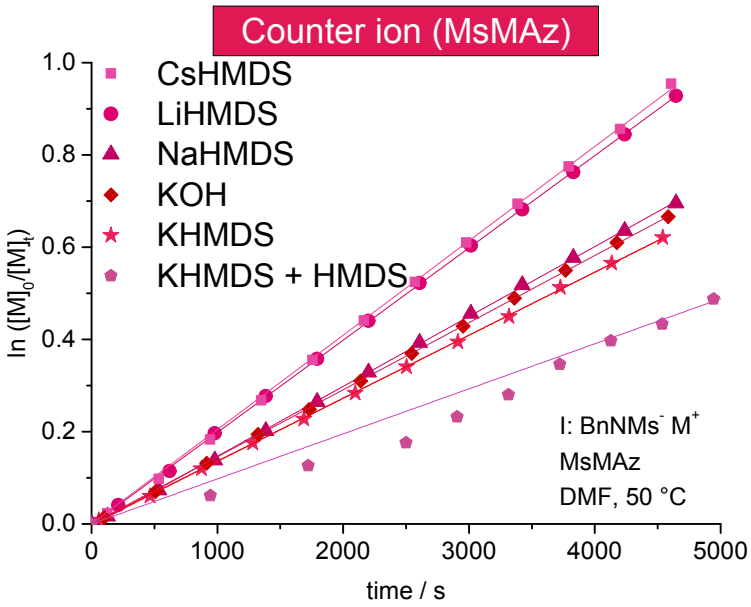


Figure S2. Kinetic Plots of $\ln([M]_0/[M]_t)$ vs. time for the azaanionic polymerization of MsMAz (1), BnNHMs (3, initiator) in DMF-d_7 at 50 °C with different counter ions (also compare Table 5).

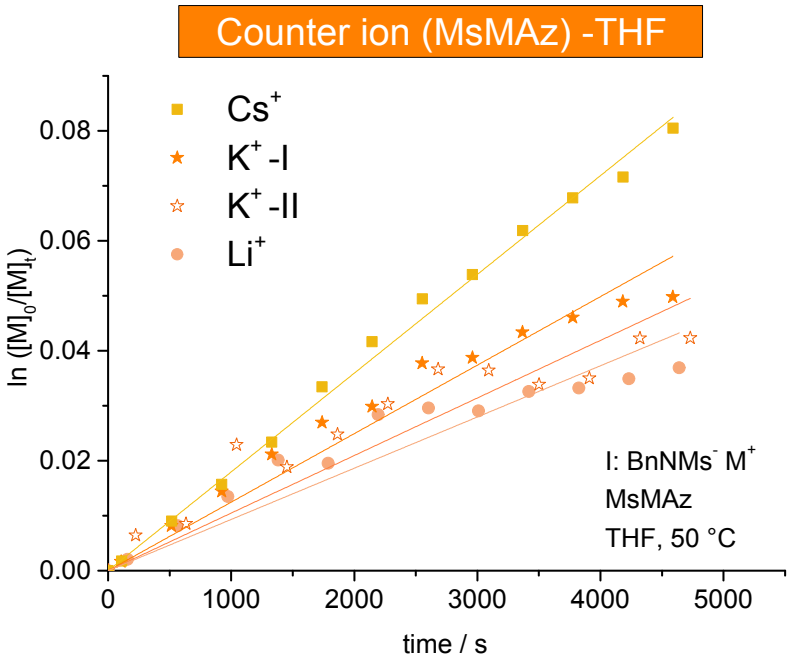


Figure S3. Kinetic Plots of $\ln([M]_0/[M]_t)$ vs. time for the azaanionic polymerization of MsMAz (1), BnNHMs (3, initiator) in DMF-d_7 at 50 °C with different counter ions. All data are listed in Table 6. In case potassium the measurements were repeated and are marked with I, respectively II.

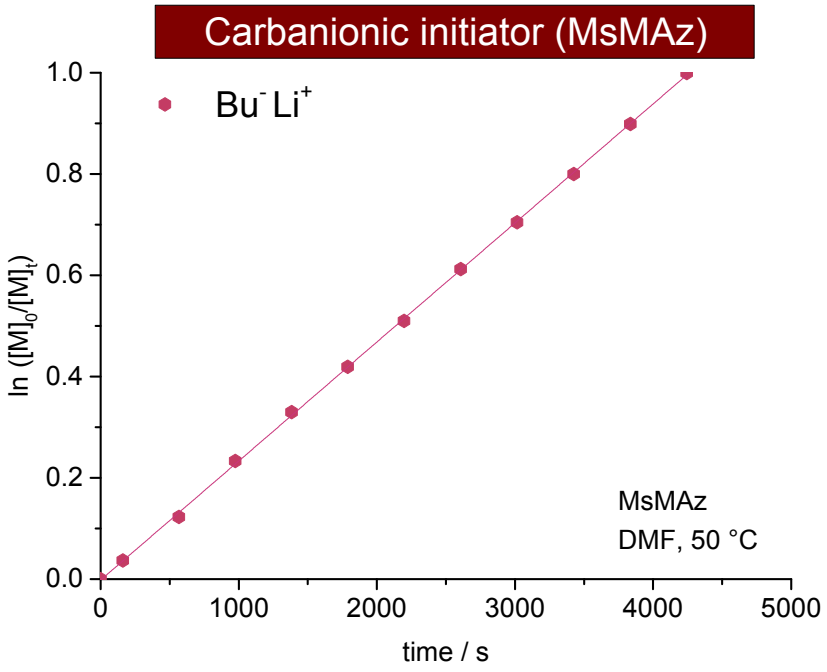
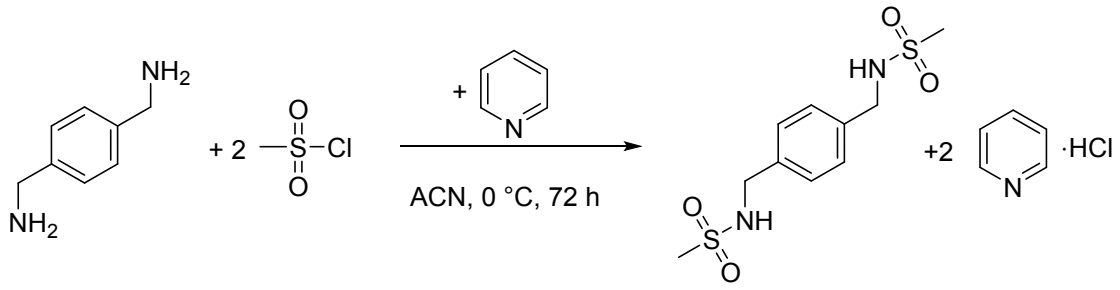


Figure S4. Kinetic Plots of $\ln([M]_0/[M]_t)$ vs. time for the azaanionic polymerization of MsMAz (1) with *n*-butyllithium in DMF-d_7 at 50 °C. All data are listed in Table 3.

Initiators

N,N'-(1,4-phenylenebis(methylene))dimethanesulfonamide (BnBi(NHMs),5)



Scheme S1. Synthesis of *N,N'*-(1,4-phenylenebis(methylene))dimethanesulfonamide.

The compound was synthesized following to literature procedures.[1] 1,4-bis(amino-methyl)-benzene (4.50 g, 33.0 mmol) and pyridine (13.3 mL, 165 mmol) were dissolved in anhydrous ACN (100 mL). The solution was cooled down to 0 °C and methanesulfonylchloride (5.1 mL, 66.1 mmol) was added dropwise over ten minutes. The reaction mixture turned yellow and was stirred for 72 h. The precipitation was filtered and the solvent was removed at reduced pressure. The residue was recrystallized twice from H_2O/EtOH (1:1) and yielded the product as yellowish, needle-shaped crystals (1.32 g, 4.51 mmol, 14 %) ^{1}H NMR (250 MHz, 297 K, DMSO-d_6): δ [ppm] = 7.55 (t, 2H, b), 7.32 (s, 4H, b), 4.14 (d, 4H, c), 2.73 (s, 6H, d). ^{13}C NMR (176 MHz, 297 K, DMSO-d_6): δ [ppm] = 137.25, 127.70, 45.77, 39.96. Analysis (calcd., found for $C_{10}H_{16}N_2O_4S_2$): C (41.05, 41.27), H (5.43, 5,66), N (9.45, 9,70), S (21.81, 21.99).

Polymers prepared in the NMR-kinetic experiments

Bn-P(MsMAz)

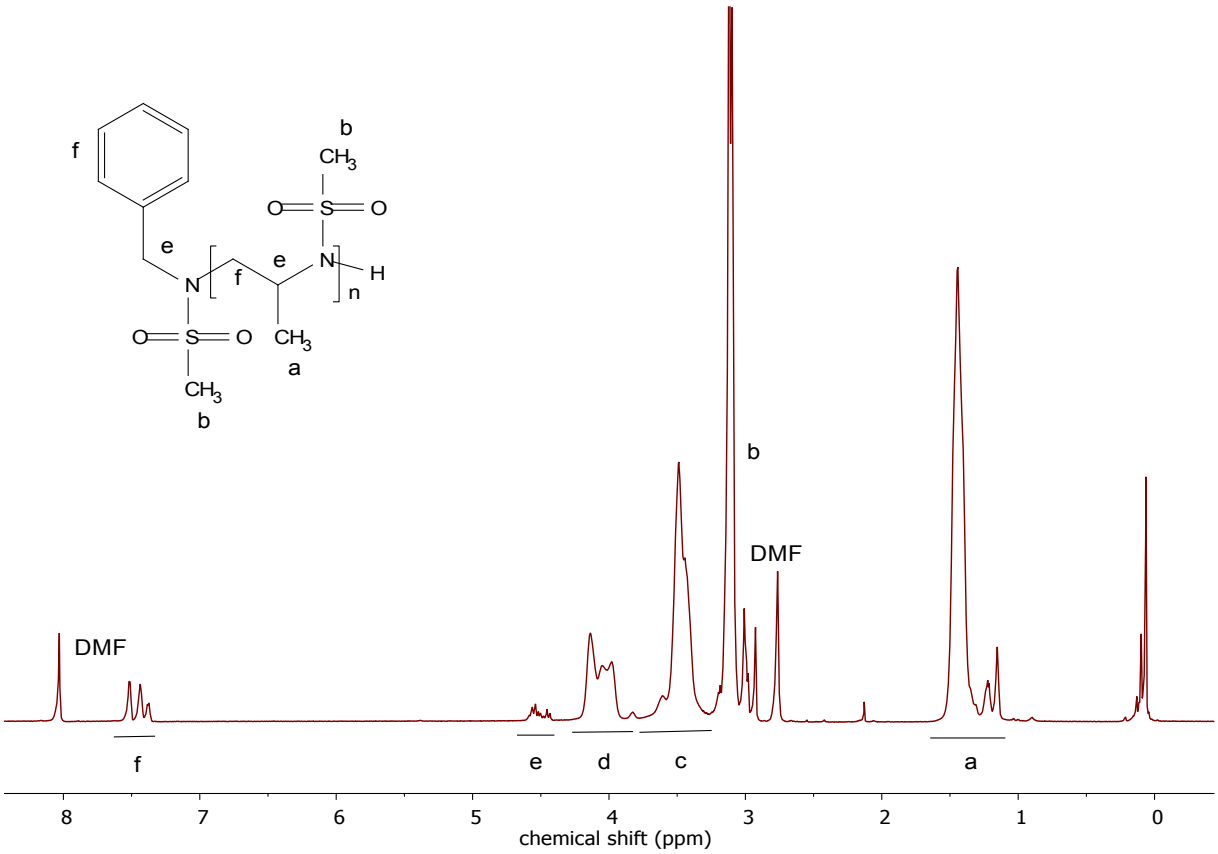


Figure S5: ^{1}H NMR (700 MHz, 323 K, DMF-d_7) of Bn-P(MsMAz).

BiBn-P(MsMAz)

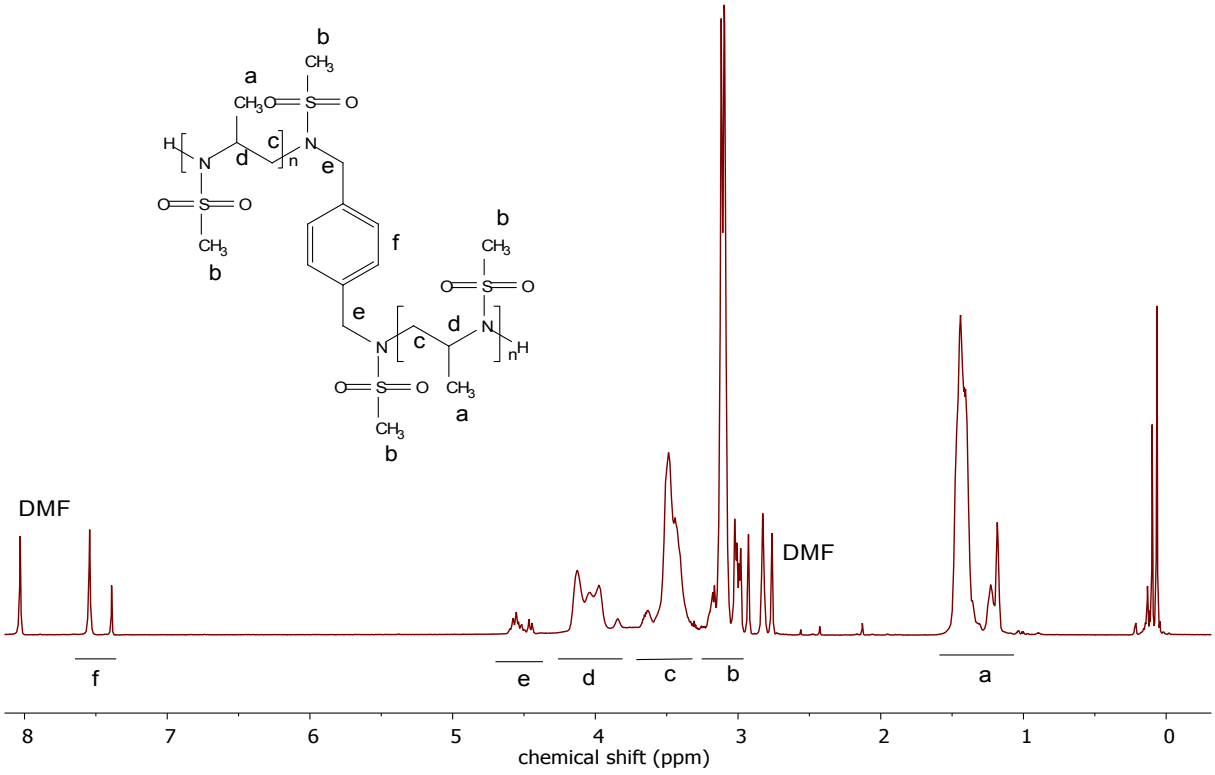


Figure S6: ^{1}H NMR (700 MHz, 323 K, DMF-d_7) of BiBn-P(MsMAz).

Bu-P(MsMAz)

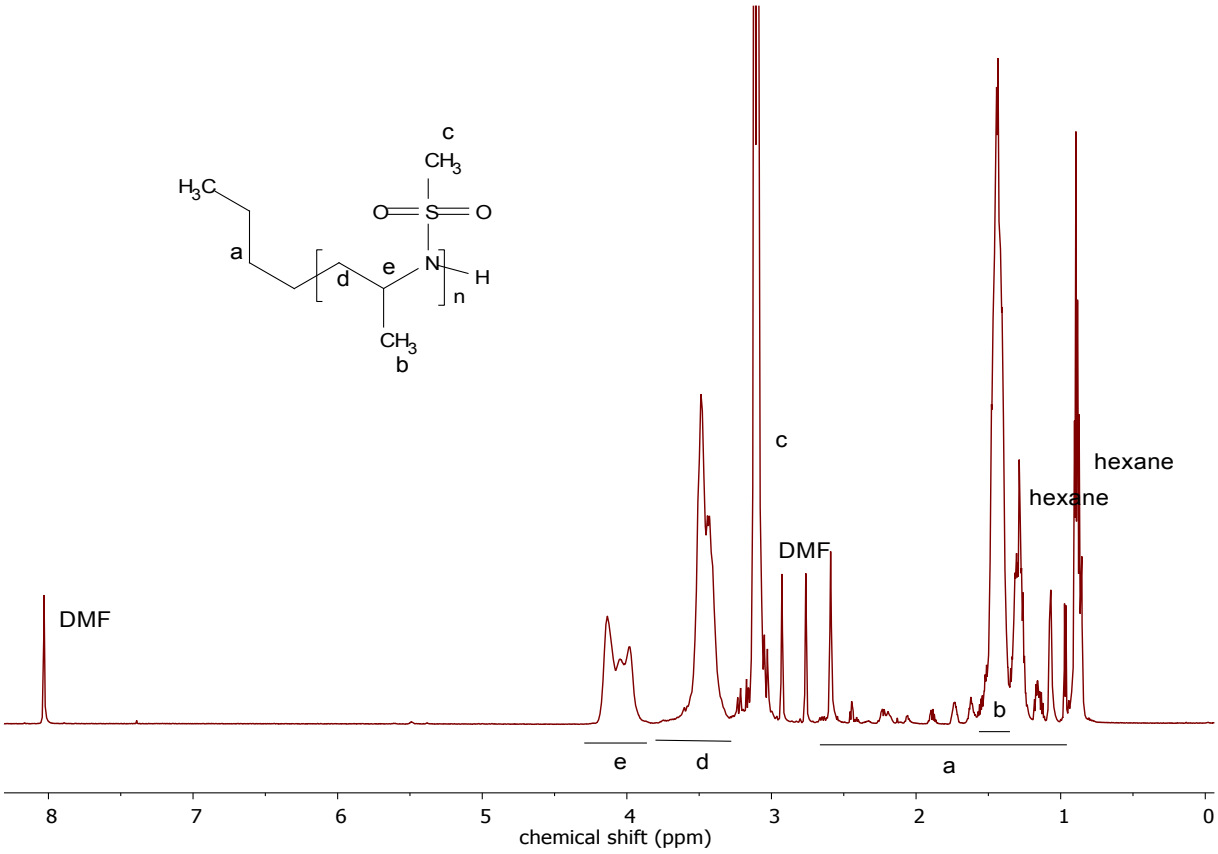


Figure S7: ^{1}H NMR (700 MHz, 323 K, DMF-d_7) of Bu-P(MsMAz).

Bn-P(TsMAz)

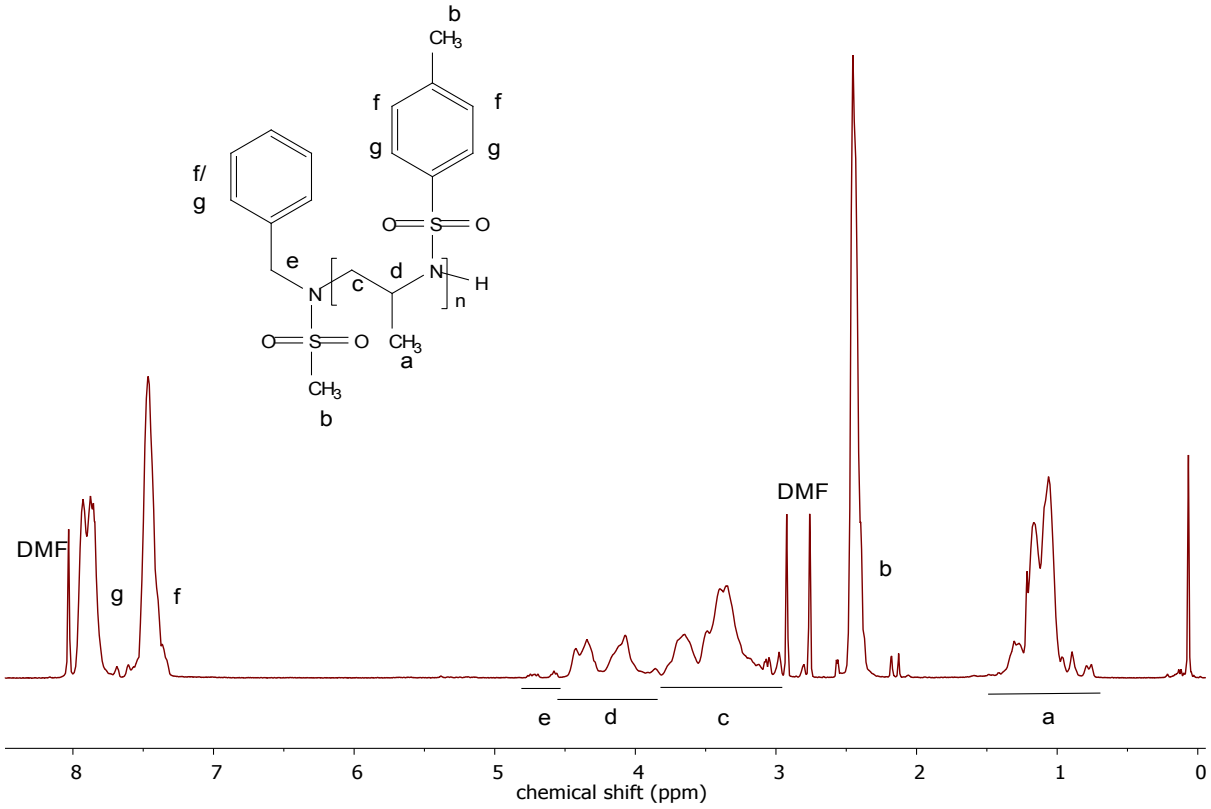


Figure S8: ^{1}H NMR (700 MHz, 323 K, DMF-d_7) of Bn-P(TsMAz).

Bu-P(TsMAz)

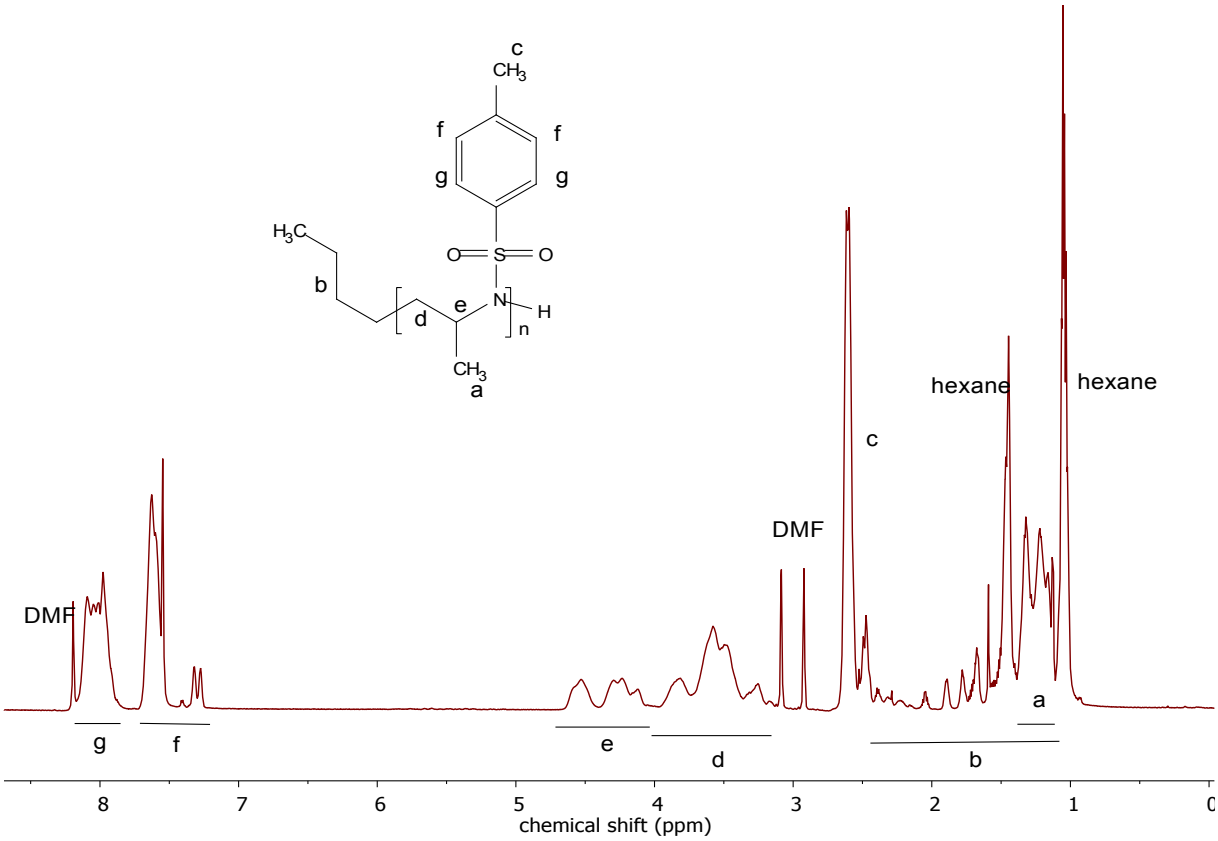


Figure S9: ^{1}H NMR (700 MHz, 323 K, DMF-d_7) of Bu-P(TsMAz).

MALDI ToF mass spectra

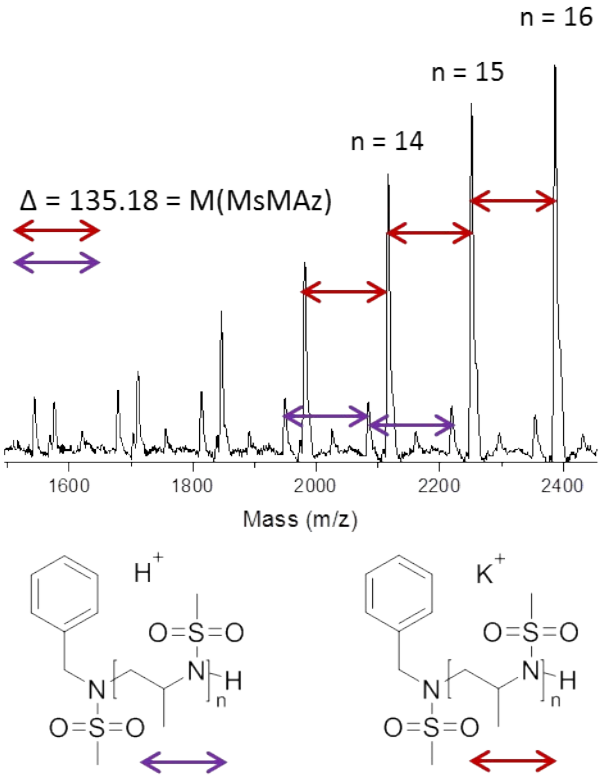


Figure S10: Zoom into the MALDI ToF mass spectrum of Bn-P(MsMAz).

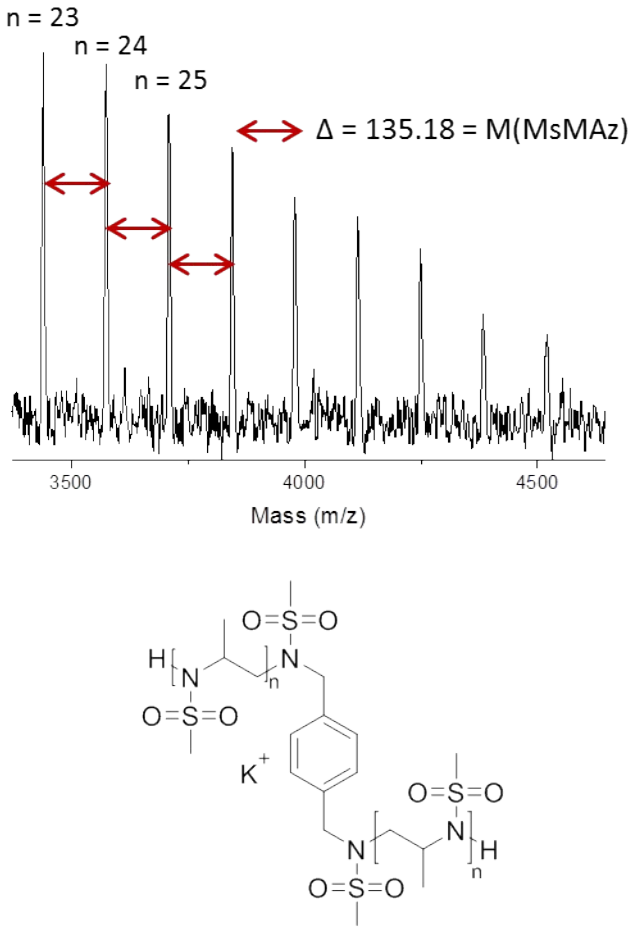


Figure S11: Zoom into the MALDI ToF mass spectrum of BiBn-P(MsMAz).

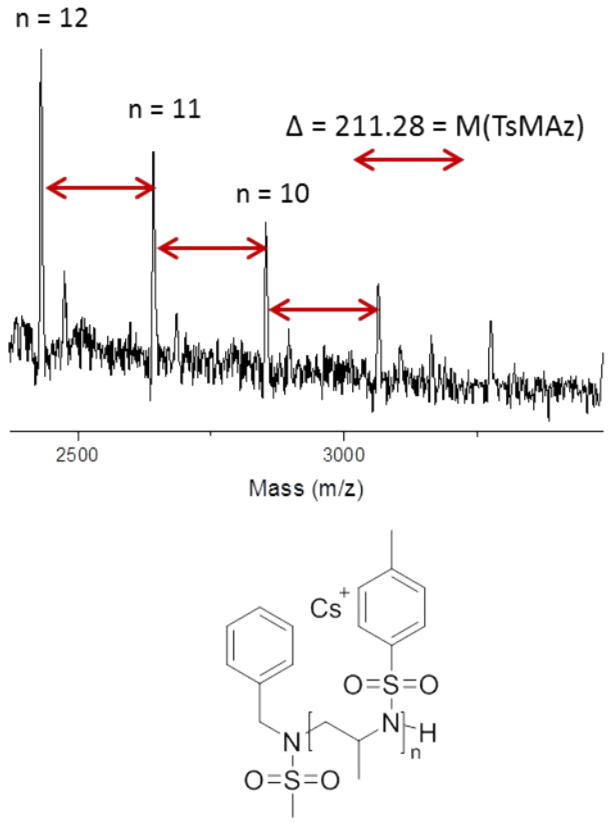


Figure S12: Zoom into the MALDI ToF mass spectrum of Bn-P(TsMAz).

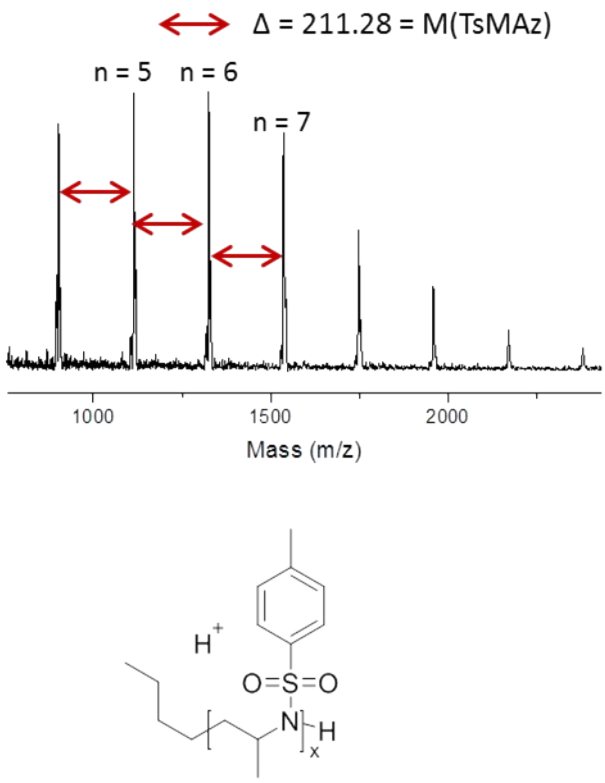


Figure S13: Zoom into the MALDI ToF mass spectrum of Bu-P(TsMAz).

SEC kinetics

All polymerizations were carried out in analogy to the conventional procedure in a Schlenk-flask. 100 µL-samples were taken in specific time intervals and analyzed by SEC and ^{1}H NMR.

LiMDS

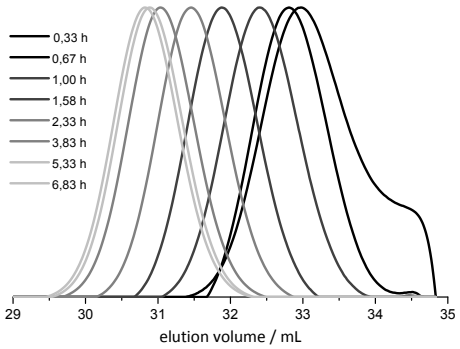


Figure S14: SEC-kinetics of MsMAz (1) (monomer), BnN**Li**Ms (4) (initiator) at 50 °C in DMF (RI-signal, PEO-standard).

NaMDS

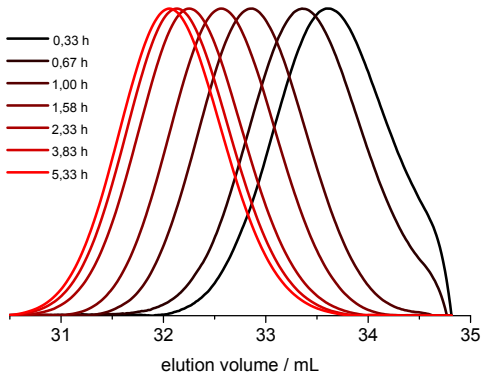
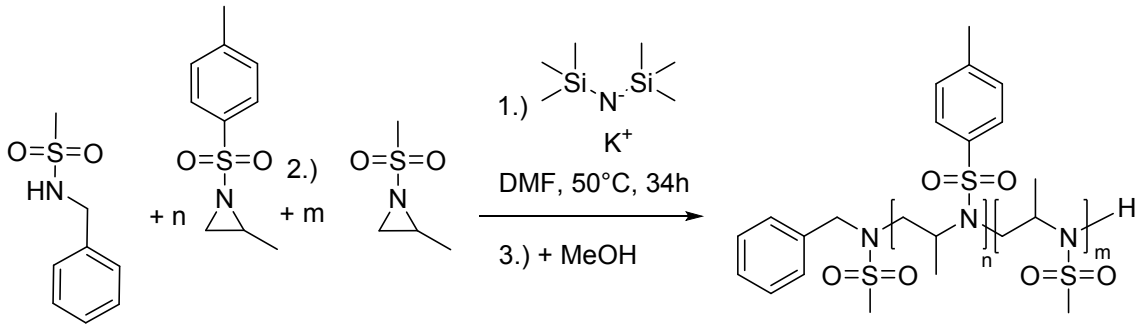


Figure S15: SEC-kinetics of MsMAz (1) (monomer), BnN**Na**Ms (4) (initiator) at 50 °C in DMF (RI-signal, PEO-standard).

Chain extension experiments

All polymerizations were carried out in analogy to the conventional procedure in a Schlenk-flask. The first monomer and the initiator were dissolved in 2 mL anhydrous *N,N*-dimethylformamide (DMF) each. A stock solution of the initiator system was prepared and only the appropriate volume extracted and added to the monomer solution. After stirring the mixture for 10 h at the respective temperature, the second monomer, in 1 mL DMF, was added and stirred for further 24 h at the same temperature. To terminate the polymerization, 0.5 mL degassed methanol were added and the reaction mixture was precipitated in ca. 30 mL methanol.

P(TsMAz-*block*-MsMAz) at 50 °C



P(TsMAz$_{50(theo)}$-*block*-MsMAz$_{50(theo)}$): [1.) TsMAz (100.0 mg, 0.47 mmol), 2.) MsMAz (63.9 mg, 0.47 mmol), BnNHMs (1.8 mg, 9.5 µmol), KMDS (1.9 mg, 9.5 µmol)].

1. block: SEC (RID, DMF, PEO): M_n = 3200; $Đ$ = 1.13

2. block: SEC (RID, DMF, PEO): M_n = 4800; $Đ$ = 1.11

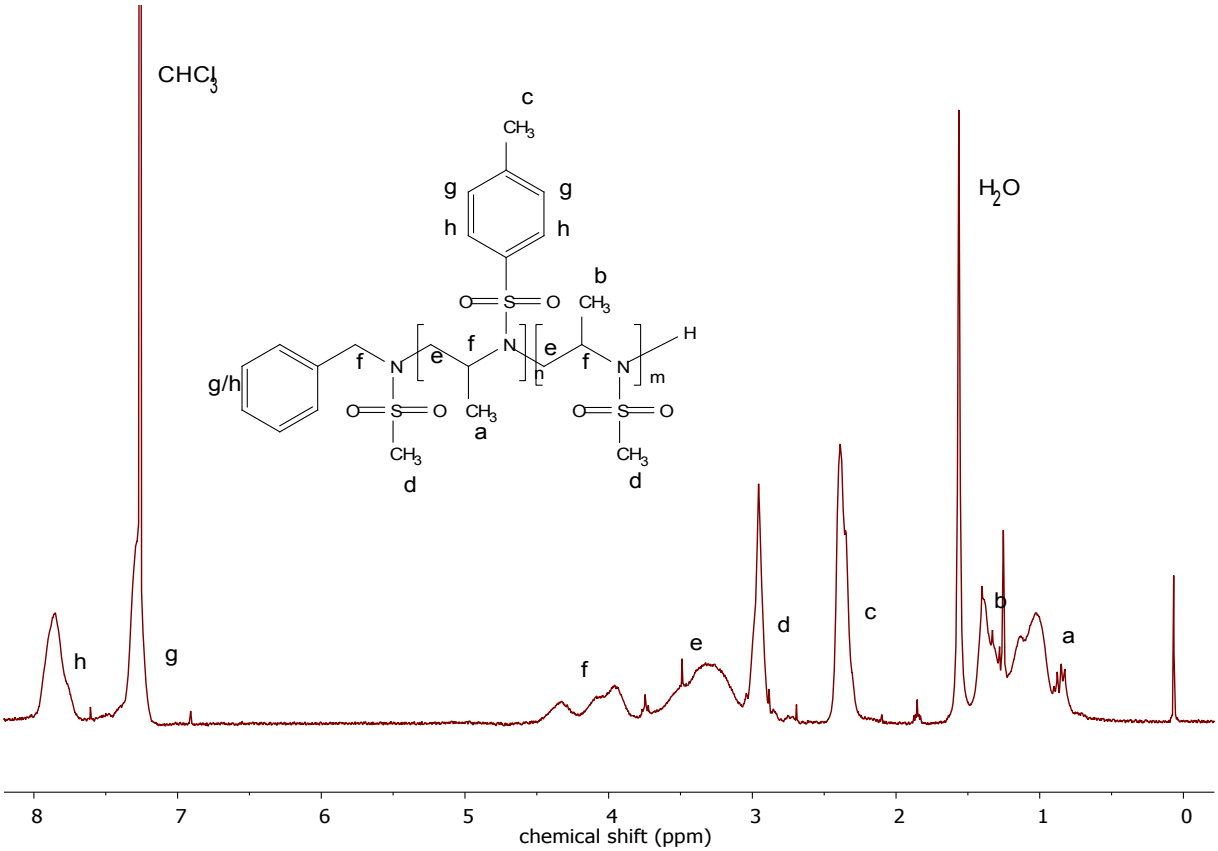


Figure S16: ^{1}H NMR ($CDCl_3$, 300 MHz, 298K) of P(TsMAz-*block*-MsMAz).

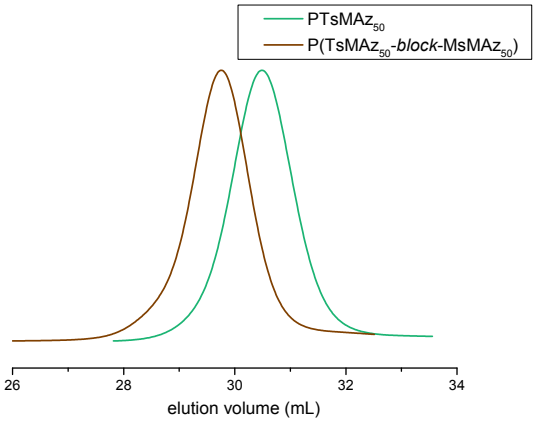
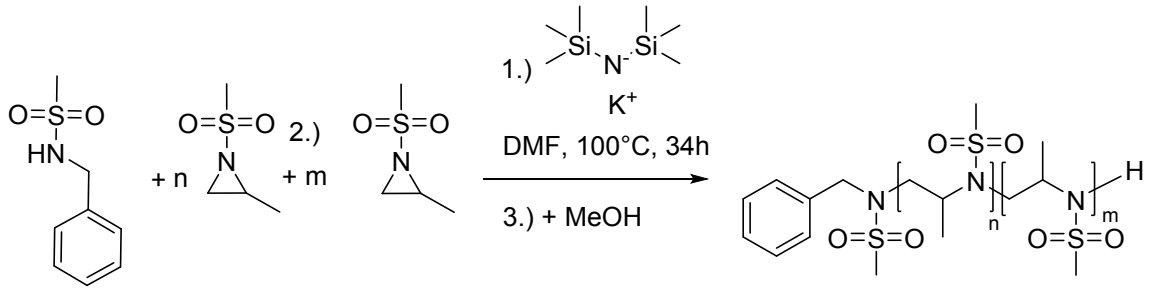


Figure S17: SEC traces of P(TsMAz-*block*-MsMAz) in DMF (RI signal).

P(MsMAz-*block*-MsMAz) at 100 °C



P(MsMAz$_{30(theo)}$-*block*-MsMAz$_{30(theo)}$): [1.) MsMAz (100.0 mg, 0.74 mmol), 2.) MsMAz (100.0 mg, 0.74 mmol), BnNHMs (4.6 mg, 24.7 µmol), KMDS (4.9 mg, 24.7 µmol)].

1. block: SEC (RID, DMF, PEO): M_n = 700; $Đ$ = 1.14

2. block: SEC (RID, DMF, PEO): M_n = 1200; $Đ$ = 1.13

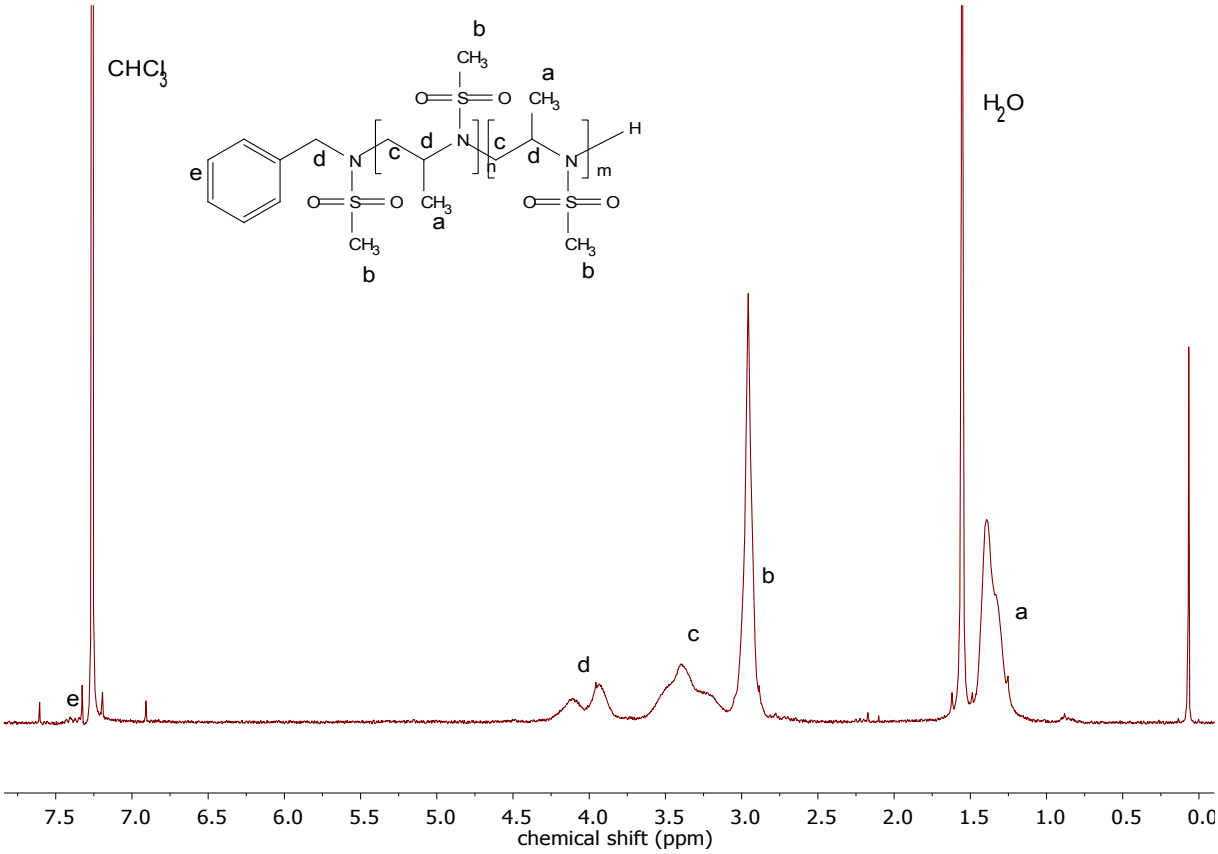


Figure S18: ^{1}H NMR ($CDCl_3$, 300 MHz, 298K) of P(MsMAz-*block*-MsMAz).

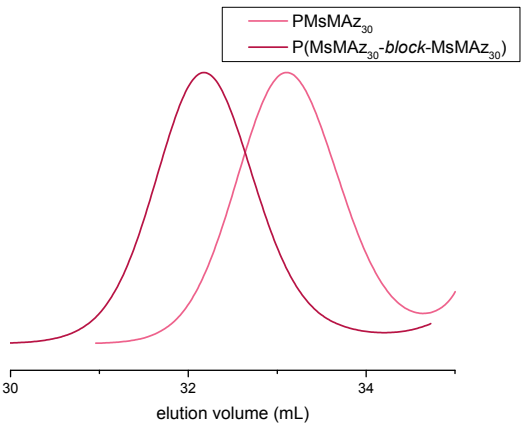


Figure S19: SEC traces of P(MsMAz-*block*-MsMAz) in DMF (RI signal).

References

1. Johnson, D. C.; Widlanski, T. S. Cerium(III) Chloride-Mediated Reactions of Sulfonamide Dianions. *J. Org. Chem.* **2003,** 68, 5300-5309.