Diethylamino substituted silyllithium compounds have been prepared in situ from the corresponding phenylchlorosilanes and lithium. These reagents undergo coupling reactions with triflate derivatives of silanes and oligosilanes. Exchange processes analogous to metal halogen exchange and Si-Si bond cleavage, which are side reactions with chlorosilanes, were not observed. Based on the coupling reaction and the amino-to-triflate transformation, functionalized tri-, tetra-, penta- and hexasilanes have been synthesized. α,ω-Triflate substituted oligosilanes containing π-systems have also been obtained. These compounds are useful building blocks for new organosilicon polymers. The formation of the silicon polymers at low temperatures, in short reaction times, and with high yields is reported. The $^{29}$Si NMR spectra indicate a regular, alternating arrangement of the building blocks in the polymer backbone.

**Key words:** Aminosilanes, Oligosilanes, Silyl Triflates