# 7 SUMMARY

Besides for an active cellular function of RNA, the investigation of the catalytical potential of ribozymes has important implications for many postulated prebiotic processes. Catalytic nucleic acids also offer new perspectives for the use as tailored enzymes in organic chemistry.

By the use of *in vitro* selection, very large nucleic acid libraries (> $10^{15}$ species) can be screened directly for intermolecular, catalytical activity. To expand the catalysis to reactions between two small organic molecules, oligonucleotide conjugates have to be used with one of the reactants already attached to the nucleic acid.
Towards this end, various multifunctional linkers where synthesized and functionally characterized. They contain a phosphorylated dinucleotide for the ligation to RNA transcripts and a polyethylene glycol spacer ensuring the optimal positioning of the coupled reactants. A photocleavage site further allows a selective partitioning of the desired reaction products. The universal applicability of the dinucleotide analogs was shown by coupling the linker to various potential reactants. With these methods, most reactants of interest are amenable to *in vitro* selection experiments, either activated as phosphoramidites or as NHS esters or via a primary amino group present in the target reactant. The compatibility of the photocleavable linkers with the overall selection scheme was shown by a mock selection cycle. In a selection for photoredox ribozymes, self-cleaving phosphordiesterases were isolated instead of RNAs catalysing the photoreaction.

With the preparation of photocleavable primer-conjugates the strategy of linker-coupled reactants was extended to DNA selection experiments. In a direct comparison of DNA with RNA, no significant acceleration by the conjugated DNA was found within ten selection cycles for the investigated Diels-Alder reaction between anthracene an biotin maleimide. This supports the arguments, that besides structural and chemical limitations DNA is also functionally inferior with respect to RNA.
The development of photocleavable linkers for the first time allows an *in vitro* selection with regioselective control of the reactions.