This dissertation focuses on the issue of obtaining DCLs (Dynamic Combinatorial Libraries) of TASPs (Template-Assembled Synthetic Proteins) in terms of DCvC (Dynamic Covalent Chemistry), which can be implemented in two ways: 1) by dynamic exchange of peptide chains in a rigid macrocyclic scaffold or 2 ) using reversible reactions to dynamically form a template from properly designed peptide conjugates. Both approaches have been tested before, but they were limited to obtaining systems of a predetermined size (multiplicity of peptide chains). The dissertation presents the results of research, the novelty of which is based on the use of conjugation of peptides with aromatic trithiols by forming a thioether bond with bromoacetylated peptides. The developed conjugates subjected to the oxidative conditions form DCL (Dynamic Combinatorial Libraries) of macrocyclic compounds of various sizes, leading to the creation of TASP libraries that allow obtaining information about preferences regarding the size of the peptide self-assemblies formed. The thioether linkage, thanks to conformational freedom and C-S-C bond geometry, optimizes intramolecular interchain interactions in contrast to the previously used amide linkage, which promotes intermolecular interactions in macrocycle libraries based on 3,5-dimercaptobenzoic acid peptide conjugates. The following new conjugates of this type have been developed: 1) *N*-[S-(3,5-dimercaptophen-1-yl)mercaptoacetyl]peptides (TMB-peptides)150, *N*-{S-[3,5-bis(dimercaptomethyl)phen-1- ylmethyl]mercaptoacetyl}peptides (TMMB-peptides) and *N*-[S-(4,6-dimercapto-1,2,3-triazin-2-yl)mercaptoacetyl]peptides (TMT-peptides). In addition, the investigaton on the stability of TMT-peptides resulted in the development of stable hydrophilic peptide conjugates, N-(4,6-dimercapto-1,3,5-triazin-2-yl)peptides (DMT-peptides) and the discovery of the chemoselective reversible aromatic nucleophilic substitution reaction of thiocyanurates proceeding by transthioestification in the presence of thiols. The new reaction is highly chemoselective, proceeds effectively in mildly alkaline aqueous buffers, and acidification allows to freeze the thermodynamic equilibrium. On the other hand, DMT-peptides are capable of highly reversible formation of metastable TASPs with a hydrophilic matrix, eliminating the influence of hydrophobic interactions between TASP templates and between the template and hydrophobic side chains of amino acid residues, which in the case of TMB- and TMMB peptides have a real impact on the size of the formed self-ssemblies. Disulfide bonds between TMT peptides are partially unstable in mild basic aqueous buffers and even in the presence of oxidants, an equilibrium is formed between the monomer and the cyclic oligomer library, while in an acidic environment these bonds are stable.

The result of the research work presented in the dissertation is primarily 1) development of a set of tools based on a relatively new concept of dynamic formation of oligodisulfide macrocycles guided by peptide interactions and 2) description of a new reversible reaction of sulfanyl ligand exchange in thiocyanuric acid esters and validation of its use in DCvC. The developed solutions can be widely used in research on the association of peptides, the formation of supramolecular structures by interactions between peptides, the search for selective catalysts and molecular receptors.