Structural modifications of cobalamin and their catalytic properties

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Research presented in the dissertation picture synthetic modifications of vitamin B_{12} „nucleotide loop", natural compound possessing a cobalt ion in the macrocyclic ring and their influence on catalytic properties of the obtained derivatives.

I have found an effective method for axial nitrogen quaternisation leading to a **new, stable *base-off* cobalamin** and proved that the cleavage of strongly binding ligands is possible.

Moreover, a less time-consuming, **new synthetic method for the preparation of cobinamide and its *c*-lactone** derivative was developed. Further modifications of the aforementioned compound with coupling agent - CDT - allowed to synthesize cobalamin derivatives bearing non-natural "loops". Derivatives possessing other than DMBI intramolecular bases proved less efficiant catalysts than the cobalamin itself. Furthermore DFT calculations allowed me to justify the synthetic complications that were observed during the preparation of these compounds.

Catalytic properties of the obtained compounds were examined in model reactions: dimerisation of benzyl bromide, alkylation of olefins with ethyldiazoacetate and the most adequate for the purpose of my research - dimerisation of 1,1-diphenylethene.

A series of heptamethylester derivatives was synthesized and subjected to the reaction of 1,1-diphenylethene and ethyldiazoacetate proving that the **reaction yield**, since there is not intramolecular coordination, is **directly proportional to minimum of the electron density localized on the central atom**. The best yields were obtained for *c*-amides and the DFT calculations suggest that for the conditions used no more than 80% of yield is achievable.