Photocatalysis
in alkylation of unsaturated boronic acid MIDA esters

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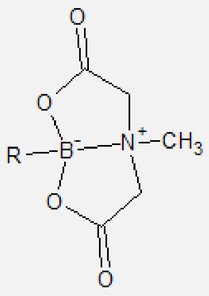
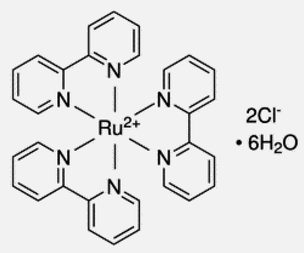
Reaction description

Photocatalytic synthesies is a quickly developed method which allows to attach perflurinatedalkyls to unsaturated boronic acids. It would be impossible without protecing group like MIDA to conduct such reaction. In our reaserch used boronic acid MIDA esters and perfuloriantedalkyl iodine in a radcial reactions. The Reaction requires photocatalyst in a catalytic amount and also 10 mol% of sodium ascorbate, which is not necessary but increases the efficiency. The sample has to be irradiated with blue light to initiate the reaction. Solvent is also impormant, we used deoxygenated DMSO.



Boronic acid MIDA ester

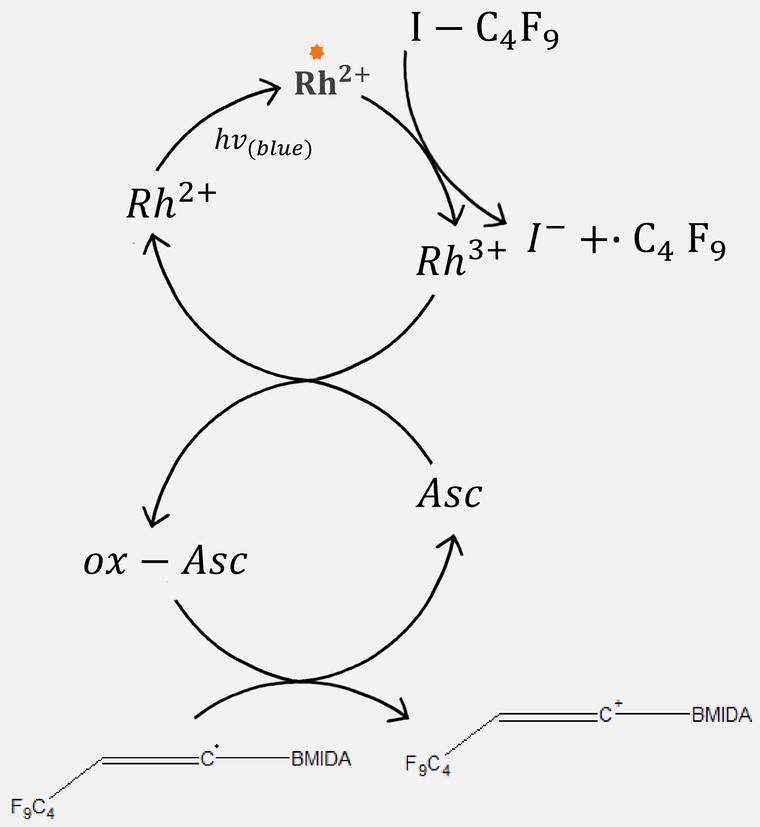


tris(bipirydyno)ruthenium(ii) chloride

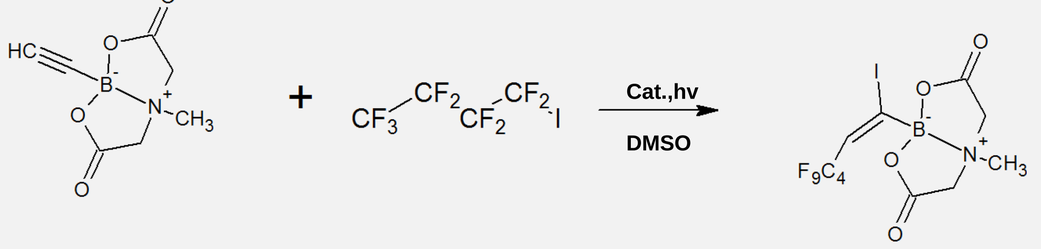
Abstract

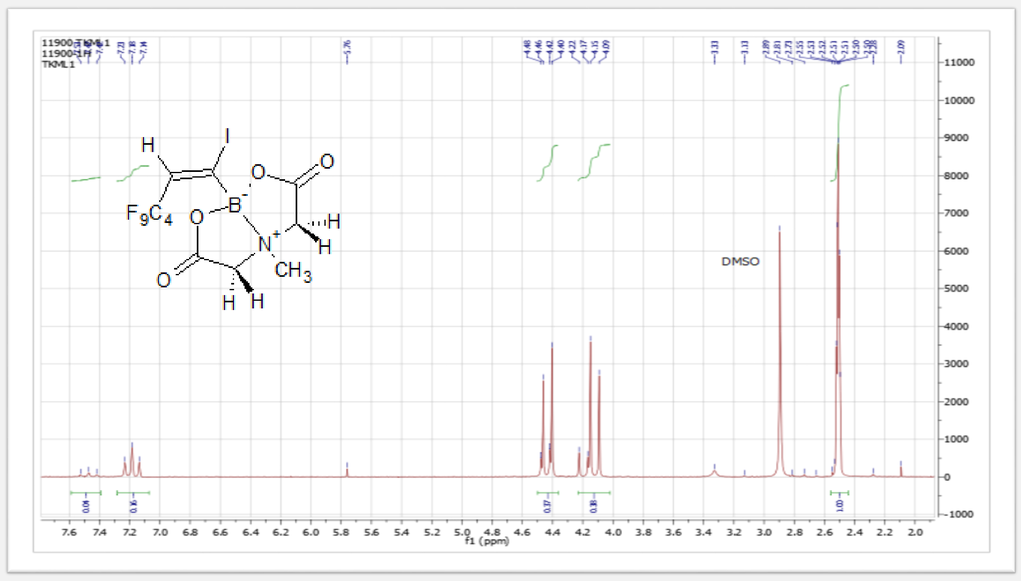
Boronic organic compounds are widely used as substrates in many chemical synthesis. However there are only few publications about using photo-redox reactions to synthesise them. Furthermore C-B bound can be easily broken by too thought conditions and that exclude metalorganic alkylation because it can destroy electrophilic groups. Therefore it is really important, while planning photocatalytic syntheses, to secure this fragile bound. In our research we focused on unsaturated boronic acid MIDA esters. Attached MIDA makes the C-B bound resistant to photocatalytic reaction conditions. We have tried to attach perfluorinatedalkyl halides to unsaturated bound in radical reaction. Radicals have been generated in ATRA process, using tris(bipyridine)ruthenium(II) chloride as a photocatalyst. Our research team has also verified iridium catalyst. We have used perfuorinatedalkyl iodide with different length of carbon chain and got satisfying results; NMR spectre confirms that expected products really occur in post-reaction mixture and the results are repetitive. We have measured the efficiency of the conducted reactions and influence of factors like water and oxygen presence. Compounds with perfulorinated carbon chain are used in medicine, automotive, aeronautics and cosmetic industry. Therefore finding good way to synthesise this substances is worth effort.

Catalytic cycle



Photocatlytic addition to multiple bound



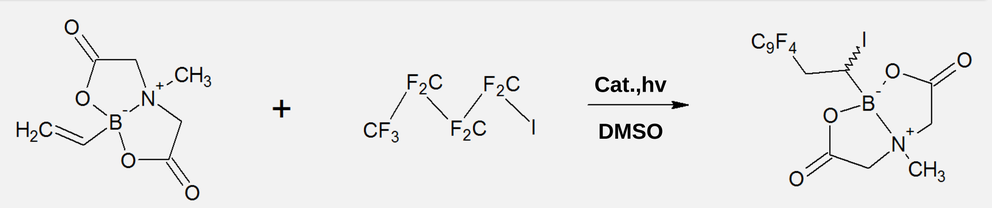


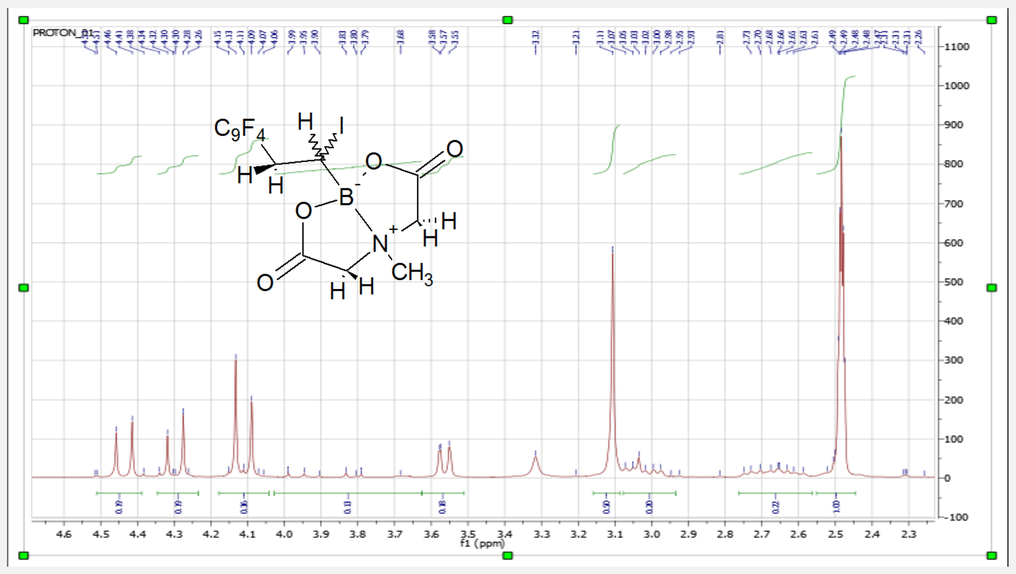
H NMR spectrum confirms that the reaction produces expected product and the efficiency is quite satisfying. Measured efficiency equals about 49%. However two diasteroisomers are obtained in much diffrent ratios. We get only a smal fraction of cis isomer. The trans isomer is more stable and the transitional state leading from longitiual radical, which is the temporary product, to final product can be achived easier due to sterodial factors.

Reaction yield

To research how does the presence of water and oxygan affects the course of the reaction, we comapred products and yields from three samples. The products and effcinecy from both (clean and water containing) samples were similar. Oxygen molecule is a double radical so it interrupts reaction mechanizm and expected products do not occure in post-reaction mixture.

Factor	Yield
Clean sample	49%
Non-deoxygenated solvent	n/a
Water addition	45%





The final product of addition to double bound has a stereogenic center. In this reaction both enantiomers are produced in the same ratio. However the peaks from both enantiomers overlapa and the specter is quite complicated because of the disateroptopic hydrogen atoms.

44	77
Ru	Ir
101.07	192.22

Other photocatalysts containing iridium also give despired compounds. The course of the reaction is not changed dramaticly.