Hydroarylation reactions involving electrophilic alkyne activation catalyzed by Brønsted superacids

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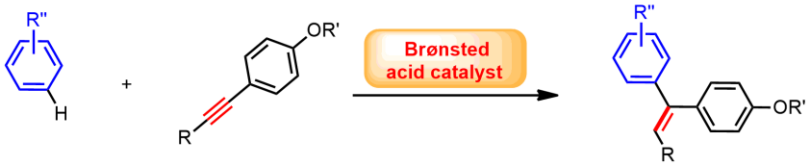
So far, the activation of an alkyne function towards nucleophilic attack was mainly described in the presence of late transition metal complexes exhibiting carbophilic Lewis acid properties, such as platinum gold, or mercury[1,2], characterized either by their rarity and high cost, or by their toxicity. The possibility to offer a metal-free alternative[3,4,5] involving a catalytic system of higher activity and selectivity represents an economic and environmental interest. The use of Brønsted superacids organocatalysts allows the selective protonation of the alkyne carbon-carbon triple bond in the presence of a directing group that induces (*i*) an increase of the electron density of the alkyne function, increasing its reactivity and promoting chemoselectivity, (*ii*) its polarization leading to enhanced regioselectivity for the formation of the vinyl cation intermediate, (*iii*) a conformational restriction by hydrogen bonding which could result in asymmetric induction if the conjugated base of the acid is chiral during the enantiodeterminent step of the reaction.



The scope of the inter- and intramolecular hydroarylation reaction of alkynes catalyzed by Brønsted superacids, including an asymmetric variant leading to atropisomeric alkenes and phenanthrenes, will be presented. A mechanistic rationale will also be discussed.

References

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