# Tuning Hydricity of the Benzimidazole Hydride Donors – A Computational Approach

**Zoran Glasovac,[a] Borislav Kovačević[b] and Davor Margetić[a]**

*glasovac@irb.hr*

[a]*Division of organic chemistry and biochemistry, Ruđer Bošković Institute, HR-10000, Zagreb, Croatia*
[b]*Division of physical chemistry, Ruđer Bošković Institute, HR-10000, Zagreb, Croatia*

Hydride donors are essential in modern research, with demand increasing alongside rising atmospheric $CO_2$ levels [1]. Non-metallic hydride donors are particularly compelling because they are more cost-effective, tunable, and easier to recycle than metal-based alternatives. Benzimidazoles (**BIM**) have emerged as a promising group of donors; their hydricity is remarkably close to that of formic acid, meaning properly substituted BIMs can reduce $CO_2$ to formic acid—a process already experimentally confirmed [2].

To enlarge the pool of BIM derivatives capable of transforming $CO_2$ to formic acid, we modelled a pool of *α*- and *β-substituted* 2-methylbenzimidazoles, as well as 4-X-phenyl substituted benzimidazoles (Figure 1) by the CPCM(ACN)/wB97xD/aug-cc-pVTZ//CPCM(ACN)/wB97xD/6-31+G(d,p) calculations. In addition to typical substituents such as $–NMe_2$, –OMe, and halides, superbasic (SB) groups—encompassing guanidine, cyclopropenimine, and phosphazene—were included. The changes in hydricity are interpreted using Hammett and Taft-type analyses of substituent effects. A strong deviation from linearity of amino derivatives was found. The correlation between hydricities and the change in aromaticity upon hydride transfer confirms that aromaticity is a very important property of the electronic structure governing the process.

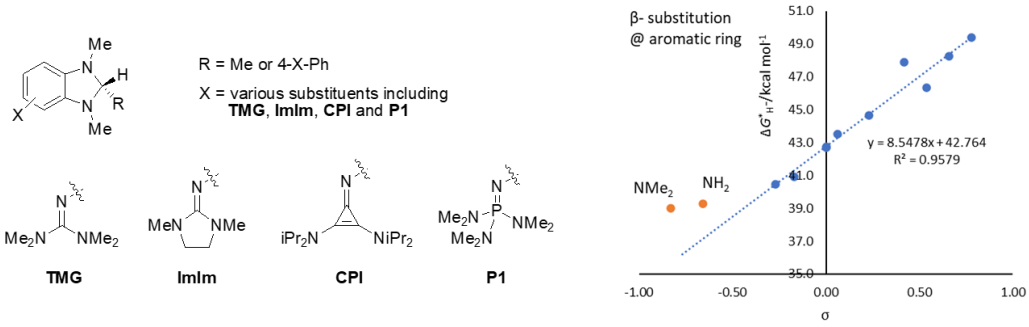


**Figure 1.** Structures of the investigated **BIM** derivatives and the example of the Hammett-type correlation for β-substituted benzimidazole derivatives.

## References:

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[2] C.-H. Lim, S. Ilic, A. Alherz, B. T. Worrell, S. S. Bacon, J. T. Hynes, K. D. Glusac, C. B. Musgrave, *J. Am. Chem. Soc.* **141** (2019) 272–280.