

On the Acidity and Reactivity of Highly Effective Chiral Brønsted Acid Catalysts - Establishment of an Acidity Scale**

Karl Kaupmees,^a Nikita Tolstoluzhsky,^b Sadiya Raja,^b Magnus Rueping^{b,*} and Ivo Leito^{a,*}

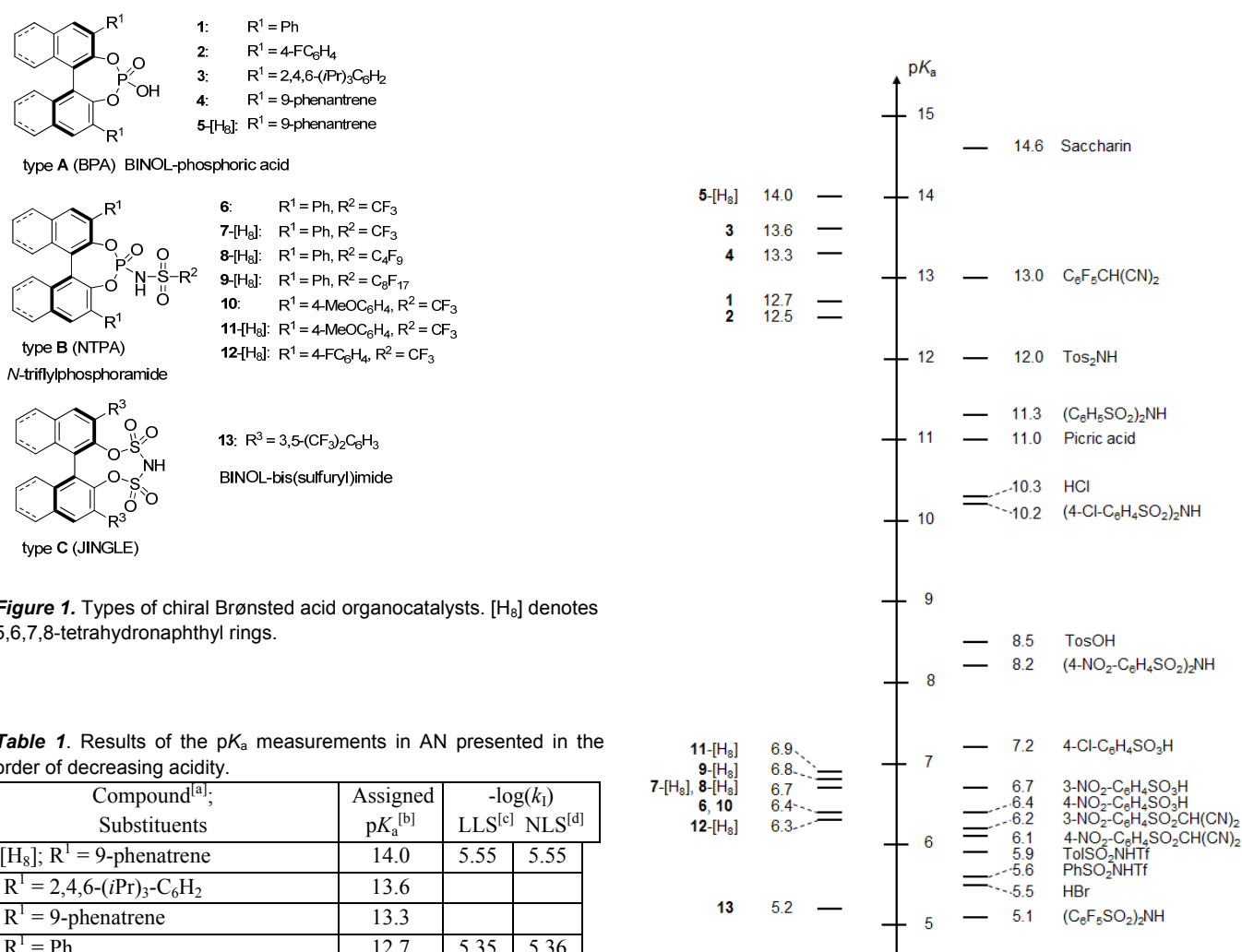


Table 1. Results of the pK_a measurements in AN presented in the order of decreasing acidity.

Compound ^[a] ; Substituents	Assigned pK _a ^[b]	-log(k ₁) LLS ^[c]	-log(k ₁) NLS ^[d]
5-[H ₈]; R ¹ = 9-phenantrene	14.0	5.55	5.55
3; R ¹ = 2,4,6-(iPr) ₃ -C ₆ H ₂	13.6		
4; R ¹ = 9-phenantrene	13.3		
1; R ¹ = Ph	12.7	5.35	5.36
2; R ¹ = 4-F-C ₆ H ₄	12.5		
11-[H ₈]; R ¹ = 4-MeO-C ₆ H ₄ ; R ² = CF ₃	6.9		
9-[H ₈]; R ¹ = Ph; R ² = C ₈ F ₁₇	6.8	3.73	3.72
7-[H ₈]; R ¹ = Ph; R ² = CF ₃	6.7		
8-[H ₈]; R ¹ = Ph; R ² = C ₄ F ₉	6.7	3.60	3.60
10; R ¹ = 4-MeO-C ₆ H ₄ ; R ² = CF ₃	6.4	3.33	3.32
6; R ¹ = Ph; R ² = CF ₃	6.4		
12-[H ₈]; R ¹ = 4-F-C ₆ H ₄ ; R ² = CF ₃	6.3		
13; R ³ = 3,5-(CF ₃) ₂ -C ₆ H ₃	5.2	2.85	2.89

^[a] References describing synthesis are given in Supporting Information; ^[b] pK_a scale in AN anchored to Picric acid pK_a = 11.0; ^[c] LLS - linearized least squares method; ^[d] NLS - nonlinear least squares method.

Figure 2. Comparison of pK_a data^[1,2]. Tos denotes 4-Me-C₆H₄-SO₂-

[1] A. Kütt, I. Leito, I. Kaljurand, L. Sooväli, V. M. Vlasov, L. M. Yagupolskii, I. A. Koppel, *J. Org. Chem.* **2006**, *71*, 2829.

[2] a) I. Leito, E. Raamat, A. Kütt, J. Saame, K. Kipper, I. A. Koppel, I. Koppel, M. Zhang, M. Mishima, L. M. Yagupolskii, S. Yu Garlyauskayte, A. A. Filatov, *J. Phys. Chem. A* **2009**, *113*, 8421; b) F. Eckert, I. Leito, I. Kaljurand, A. Kütt, A. Klamt, M. Diedenhofen, *J. Comput. Chem.* **2009**, *30*, 799; c) A. Kütt, T. Rodima, J. Saame, E. Raamat, V. Mäemets, I. Kaljurand, I. A. Koppel, R. Yu. Garlyauskayte, Y. L. Yagupolskii, L. M. Yagupolskii, E. Bernhardt, H. Willner, I. Leito, *J. Org. Chem.* **2011**, *76*, 391.