

Electronic Supplementary Information for

The connection between Hydride Affinity and Local Electrophilicity: A key factor in designing frustrated Lewis pairs for reversible H₂ activation

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Computational Details

All the electronic structure calculations (geometry optimizations, frequencies calculation and energy evaluations) were carried out using Gaussian 16 software.¹ The energetic parameters studied were computed as:

$$\Delta G_{H2} = (G(\text{FLP-H}^+/\text{H}^-) - G(\text{FLP}) - G(\text{H}_2)) \quad (\text{S1})$$

$$\text{HA} = -(G(\text{FLP-H}^-) - G(\text{FLP}) - G(\text{H}^-)) \quad (\text{S2})$$

$$\text{PA} = -(G(\text{FLP-H}^+) - G(\text{FLP}) - G(\text{H}^+)) \quad (\text{S3})$$

Where $G(X)$ values were obtained as the sum of electronic energy (E) with the Def2-TZVP basis set with SMD(benzene) implicit solvent effect and the thermal corrections obtained with the 6-31G(d,p) basis set at 298 K ($G_{\text{thermal_corr}}$):

$$G = E(\text{SMD(benzene)-M06-2X/def2-TZVP}) + G_{\text{thermal_corr}}(\text{M06-2X/6-31G(d,p)}) \quad (\text{S4})$$

The inclusion of diffuse functions in the HA and CDFT parameters calculation was tested using the Def2-TZVPD basis set. The observed deviations in HA are less than 0.5 kcal/mol compared to the values obtained using the Def2-TZVP basis set.

Table S1. HA and CDFT parameters obtained with Def-2-TVPD basis set.

FLP	HA	ω	f_B^+	ω_B^+
H/H	59.1 (58.8)	1.33 (1.31)	0.194 (0.197)	0.258 (0.259)
H/CF ₃	93.4 (92.9)	1.93 (1.91)	0.215 (0.219)	0.415 (0.418)
H/PFtB	103.2 (103.2)	2.04 (2.05)	0.367 (0.357)	0.749 (0.732)
H/C ₆ F ₅	76.7 (76.2)	2.00 (1.98)	0.175 (0.168)	0.350 (0.333)
H/FMes	70.9 (70.6)	2.02 (2.02)	0.156 (0.151)	0.315 (0.304)

The $G_{\text{thermal_corr}}$ were computed employing the quasi-rotor-rigid-harmonic-oscillator (qRRHO) approximation with the GoodVibes package.^{2,3} This level of theory has been shown to reliably describe small molecule activation by FLPs.⁴ We used a $G(\text{H}^+)$ value of -6.275 kcal/mol, as recommended by Bartmes et al. for a free proton⁵.

The global reactivity indices were computing employing the frontier molecular orbital approximation (FMO), i.e., the ionization potential (I) and electron affinity (A) are approximated to the negative of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies, respectively ($I = -\varepsilon_{\text{HOMO}}$ and $A = -\varepsilon_{\text{LUMO}}$). In this way, the electronic chemical potential (μ) and chemical hardness (η) are defined as:

$$\mu = -\frac{I + A}{2} \approx -\frac{\varepsilon_{\text{HOMO}} + \varepsilon_{\text{LUMO}}}{2} \quad (\text{S5})$$

$$\eta = I - A \approx \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}} \quad (\text{S6})$$

Thus, the electrophilicity can be written as:

$$\omega = \frac{\mu^2}{2\eta} = \frac{(-I - A)^2}{8(I - A)} = \frac{(\varepsilon_{\text{HOMO}} + \varepsilon_{\text{LUMO}})^2}{8(\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}})} \quad (\text{S7})$$

The Fukui function was also computed employing the FMO approach as the square of the HOMO and LUMO:

$$f^+(r) = |\psi_{LUMO}(r)|^2 \quad (S8)$$

$$f^-(r) = |\psi_{HOMO}(r)|^2 \quad (S9)$$

The local electrophilicity is obtained as the product of electrophilicity index and Fukui function:

$$\omega^+(r) = \omega f^+(r) \quad (S10)$$

In the same way, the local philicity when the system donates electrons is defined as:

$$\omega^-(r) = \omega f^-(r) \quad (S11)$$

The condensed-to-atom Fukui function was computed using the “fragment of molecular response” (FMR) approach:⁶⁻⁸

1. First, we perform a topological analysis of the electron density in the reference state of the FLP (neutral species) to obtain the atomic spatial domains as defined by the Quantum Theory of Atoms and Molecules (QTAIM).⁹
2. Then, separately, we compute the Fukui function employing the FMO approximation as described previously.
3. Finally, we integrate the Fukui function over the atomic domains obtained in step 1, obtaining the f_k^+ values.

After obtaining the f_k^+ values, the condensed-to-atom electrophilicity is obtained as: $\omega_k^+ = \omega f_k^+$. The topological analysis of $\rho(\mathbf{r})$ and the integration of $f^+(r)$ over atomic basins was performed in the Multiwfn 3.8 package.¹⁰

We have also computed the electrophilicity employing the definitions of the electroaccepting and electrodonating power:¹¹

$$\omega^+ = \frac{(\mu^+)^2}{2\eta} = \frac{(I + 3A)^2}{16(I - A)} = \frac{(\epsilon_{HOMO} + 3\epsilon_{LUMO})^2}{16(\epsilon_{LUMO} - \epsilon_{HOMO})} \quad (S12)$$

$$\omega^- = \frac{(\mu^-)^2}{2\eta} = \frac{(3I + A)^2}{16(I - A)} = \frac{(3\epsilon_{HOMO} + \epsilon_{LUMO})^2}{16(\epsilon_{LUMO} - \epsilon_{HOMO})} \quad (S13)$$

In this sense the local electrophilicity and philicity of an electrodonating molecule are defined as: $\omega^+(r) = \omega^+ f^+(r)$ and $\omega^-(r) = \omega^- f^-(r)$. The results employing ω^+ and ω^- are presented in Figure S5.

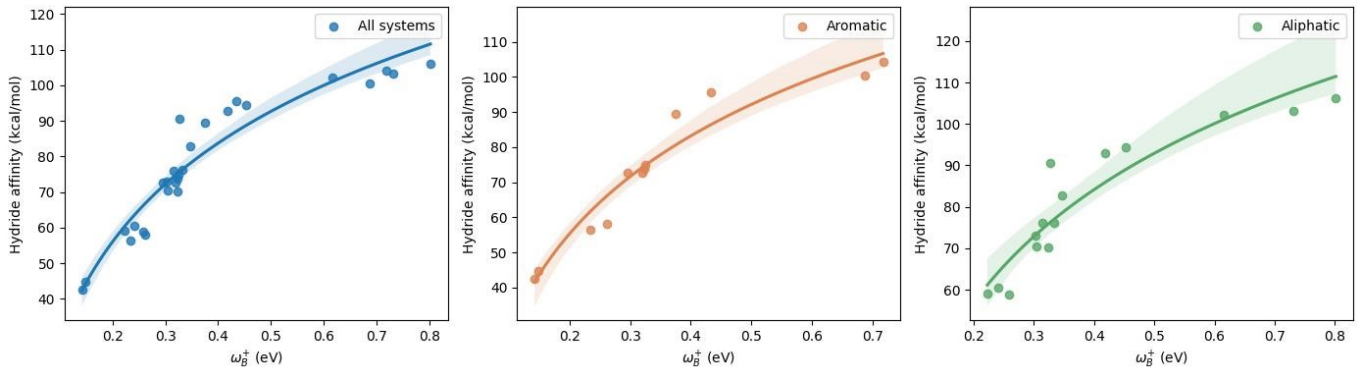


Figure S1. Hydride affinity versus the condensed-to-boron electrophilicity for all systems (left), for aromatic substituents in nitrogen (center) and for aliphatic substituents in nitrogen (right).

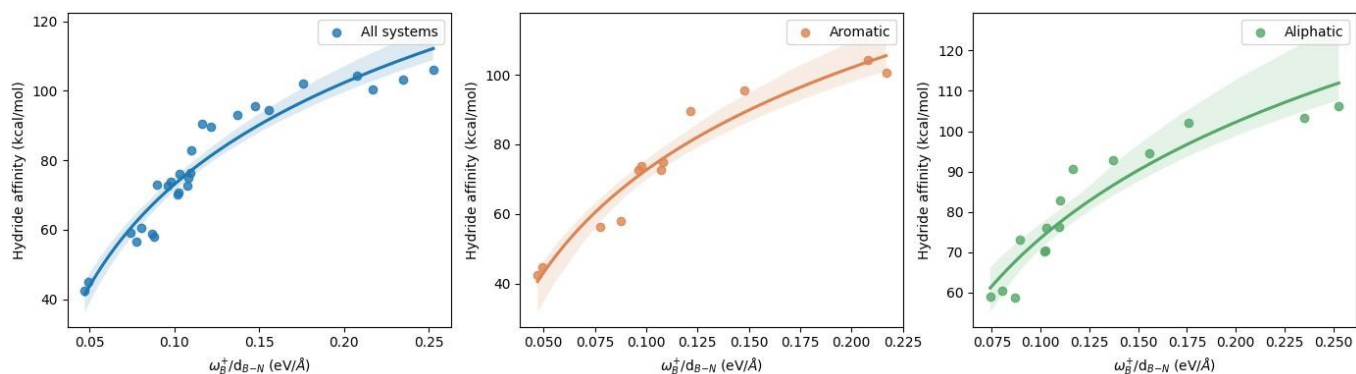


Figure S2. Hydride affinity versus the condensed-to-boron electrophilicity divided by B-N internuclear distance for all systems (left), for aromatic substituents in nitrogen (center) and for aliphatic substituents in nitrogen (right).

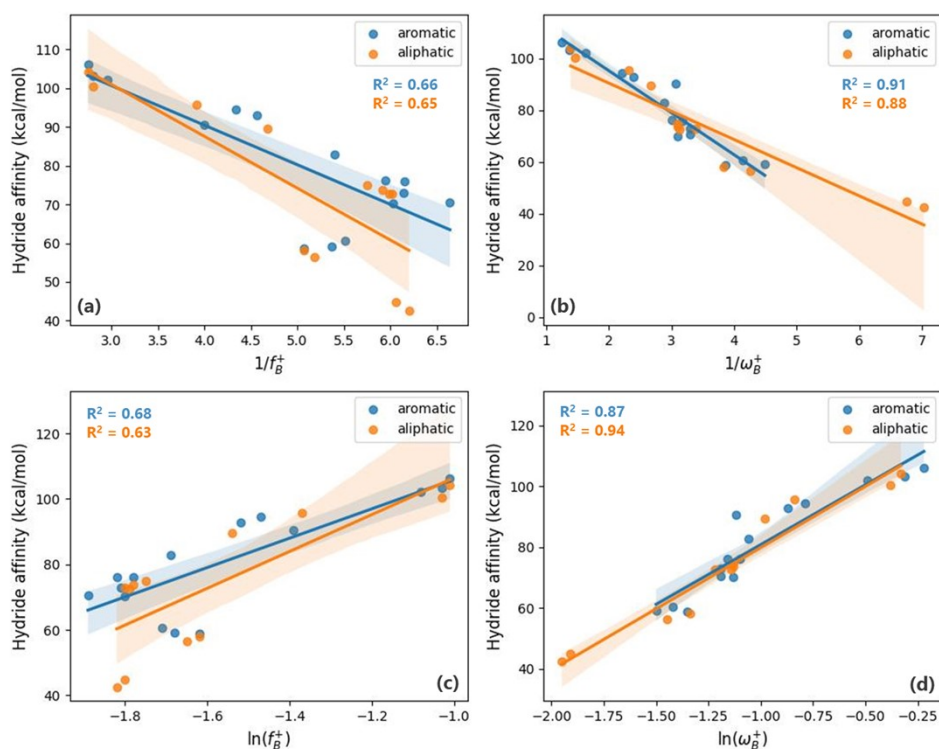


Figure S3. Hydride affinity versus the inverse of condensed-to-boron Fukui function (a), the inverse of condensed-to-boron electrophilicity (b), the logarithm of condensed-to-boron Fukui function (c), and the logarithm of condensed-to-boron electrophilicity (d). The shaded area around the regression line represents the confidence interval for the regression. A narrower confidence interval indicates that the regression line is estimated with more precision.

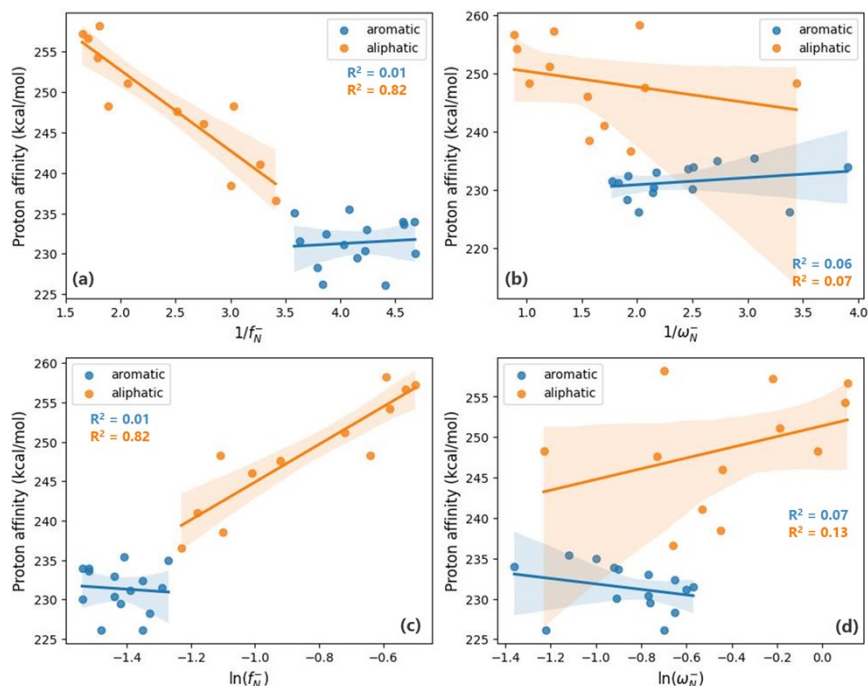


Figure S4. Proton affinity versus the inverse of condensed-to-nitrogen Fukui function (a), the inverse of condensed-to-nitrogen philicity (b), the logarithm of condensed-to-nitrogen Fukui function (c), and the logarithm of condensed-to-nitrogen philicity (d). The shaded area around the regression line represents the confidence interval for the regression. A narrower confidence interval indicates that the regression line is estimated with more precision.

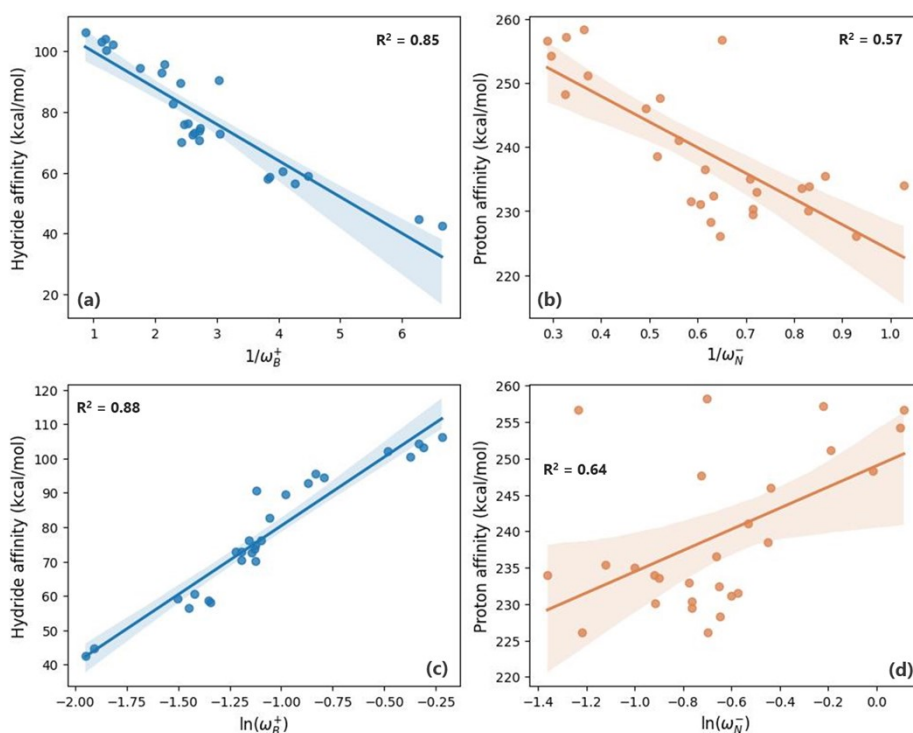


Figure S5. Hydride affinity versus the inverse of condensed-to-boron electrophilicity (a), proton affinity versus the inverse of condensed-to-nitrogen philicity (b), hydride affinity versus the logarithm of condensed-to-boron electrophilicity (c) and proton affinity versus the logarithm of the condensed-to-nitrogen philicity (d). The correlation coefficients are included in each plot. The electrophilicity was computed as defined by Gázquez et al. in the context of the electroaccepting and electrodonating power.¹¹

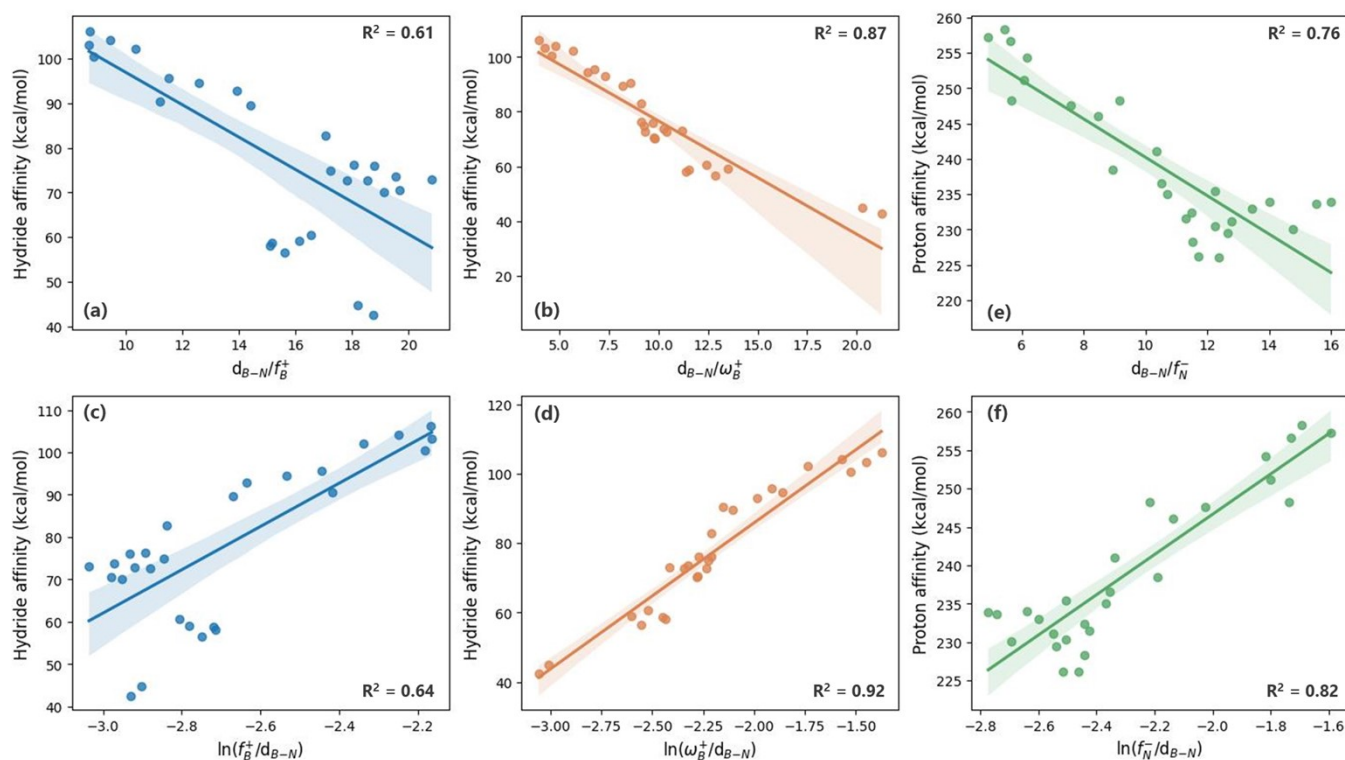


Figure S6. Hydride affinity versus the inverse of condensed-to-boron Fukui function divided by B-N internuclear distance (a), the inverse of condensed-to-boron electrophilicity divided by B-N internuclear distance (b), the logarithm of condensed-to-boron Fukui function divided by B-N internuclear distance (c), and the logarithm of condensed-to-boron electrophilicity divided by B-N internuclear distance (d). Proton affinity versus the inverse of the condensed-to-nitrogen Fukui function divided by B-N internuclear distance (e) and the logarithm of the condensed-to-nitrogen Fukui function divided by B-N internuclear distance (f). The shaded area around the regression line represents the confidence interval for the regression. A narrower confidence interval indicates that the regression line is estimated with more precision.

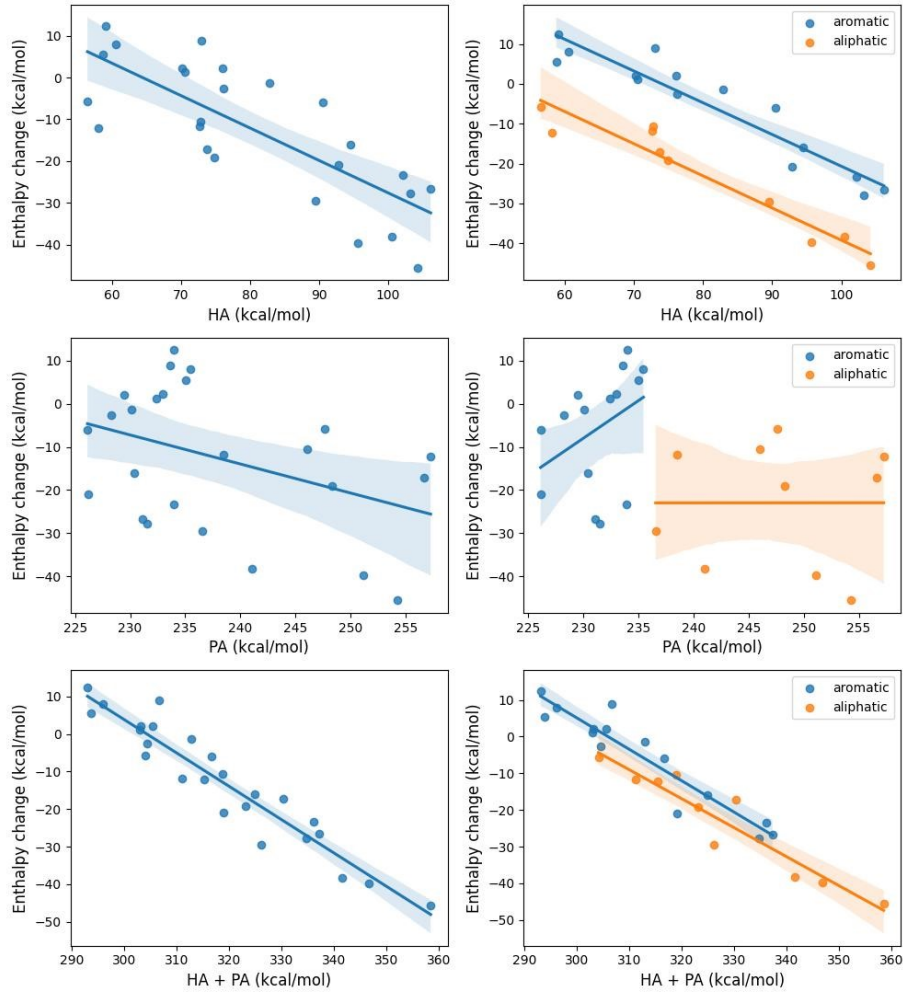


Figure S7. Relationships between energetic parameters shown in Figure 2 of the main text but calculated without the entropic corrections to the energy (only containing enthalpic corrections to the electronic energy).

Aromatic: $\Delta H_{H_2} = -0.80(HA) + 65.082; R^2 = 0.90$ (S14)

Aliphatic: $\Delta H_{H_2} = -0.78(HA) + 44.918; R^2 = 0.94$ (S15)

In the same way, the ω_B^+ relates the HA for all the systems, calculated without the entropic corrections to the energy, as:

$$HA = -12.15 \frac{1}{\omega_B^+} + 123.81; R^2 = 0.86 \quad (S16)$$

$$HA = 39.74 \ln(\omega_B^+) + 127.56; R^2 = 0.91 \quad (S17)$$

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