Electronic Supplementary Information

for

Thermodynamic and Kinetic Hydricity of Transition Metal Hydrides

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Deriving the reduction potential of proton to hydride in organic solvents

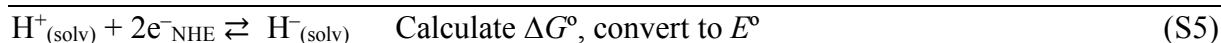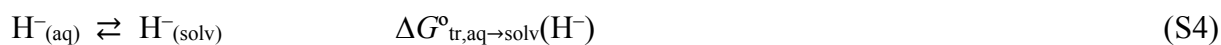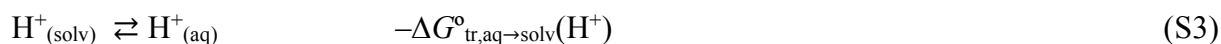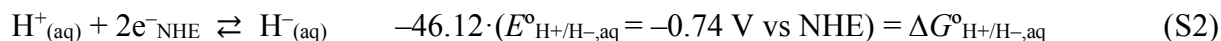The reduction potential of a proton to a hydride in an organic solvent (solv) is denoted $E^{\circ}_{H+/H-,solv}$ and reported in V vs $Fc^{+/0}$, eq S1.

$$H^+_{(solv)} + 2e^- \rightleftarrows H^-_{(solv)} \qquad E^{\circ}_{H+/H-,solv} \text{ in V vs } Fc^{+/0} \qquad (S1)$$

Parker, Bruno, and DuBois derived the reduction potential in acetonitrile, $E^{\circ}_{H+/H-,MeCN}$ in V vs $Fc^{+/0}$ according to Scheme S1.[1–3] The free energy associated with the aqueous reduction potential ($E^{\circ}_{H+/H-,aq}$) is combined with the free energy to transfer H^+ from the organic solvent to water ($-\Delta G^{\circ}_{tr,aq\rightarrow solv}(H^+)$) and the free energy to transfer H^- from water to the organic solvent ($\Delta G^{\circ}_{tr,aq\rightarrow solv}(H^-)$). The resulting free energy is referenced to NHE in water, so a correction ($\Delta E^{\circ solv}_{NHE\rightarrow Fc}$) must be applied to convert the reference electrode from NHE in water to ferrocenium/ferrocene (Fc^+/Fc) in the organic solvent. When the acetonitrile scale was derived, the value of $E^{\circ}_{H+/H-,aq}$ came from Parker.[4] A new value for the reduction potential $E^{\circ}_{H+/H-,aq}$ was recently reported, based on the best available experimentally derived estimates in 2015, which gives $\Delta G^{\circ}_{H+/H-} = 34.2$ kcal/mol.[5] Because this value has been widely adopted for aqueous hydricity measurements, we now adopt this value to construct hydricity scales in other solvents to enable self-consistent cross-solvent comparisons.

Scheme S1.

$H^+_{(aq)} + 2e^-_{NHE} \rightleftarrows H^-_{(aq)}$	$-46.12 \cdot (E^{\circ}_{H+/H-,aq} = -0.74 \text{ V vs NHE}) = \Delta G^{\circ}_{H+/H-,aq}$	(S2)
$H^+_{(solv)} \rightleftarrows H^+_{(aq)}$	$-\Delta G^{\circ}_{tr,aq\rightarrow solv}(H^+)$	(S3)
$H^-_{(aq)} \rightleftarrows H^-_{(solv)}$	$\Delta G^{\circ}_{tr,aq\rightarrow solv}(H^-)$	(S4)
$H^+_{(solv)} + 2e^-_{NHE} \rightleftarrows H^-_{(solv)}$	Calculate ΔG°, convert to E°	(S5)
$H^+_{(solv)} + 2e^-_{Fc} \rightleftarrows H^-_{(solv)}$	Reference electrode correct $\Delta E^{\circ solv}_{NHE\rightarrow Fc}$, convert to $\Delta G^{\circ}_{H+/H-}$ (S6)
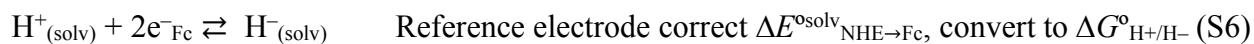
To generalize the approach of Scheme S1, the following values are needed for each organic solvent: $\Delta G^{\circ}_{tr,aq\rightarrow solv}(H^+)$, $\Delta G^{\circ}_{tr,aq\rightarrow solv}(H^-)$, and $\Delta E^{\circ solv}_{NHE\rightarrow Fc}$. We have previously calculated the first two values for several organic solvents.[6] Here we adopt the method of Savéant[7] and Gennaro[8] for obtaining $\Delta E^{\circ solv}_{NHE\rightarrow Fc}$, eq S7, which is then used for converting reference potentials.

$$\Delta E^{\circ solv}_{NHE\rightarrow Fc} = E^{\circ Fc,solv}_{Ag+/Ag,S} - [(\Delta G^{\circ}_{tr,aq\rightarrow solv}(Ag^+))/F] - E^{\circ NHE,aq}_{Ag+/Ag,aq} \quad (S7)$$

Given that $E^{\circ\text{NHE,aq}}_{\text{Ag+/Ag,aq}} = 0.799$ V, we obtain the following equation, where F is the Faraday constant:

$$\Delta E^{\circ\text{solv}}_{\text{NHE}\to\text{Fc}} = E^{\circ\text{Fc,solv}}_{\text{Ag+/Ag,S}} - [(\Delta G^{\circ}_{\text{tr,aq}\to\text{solv}}(\text{Ag}^+))/F] - 0.799 \qquad \text{(S8)}$$

$E^{\circ\text{Fc,solv}}_{\text{Ag+/Ag,solv}}$, the reduction potential of Ag^+ to Ag^0 in an organic solvent vs. $\text{Fc}^{+/0}$ in the same organic solvent, was obtained from Gritzner's tables of $\text{Ag}^{+/0}$ and $\text{Fc}^{+/0}$ reduction potentials relative to the same organometallic reference system.[9,10] $\Delta G^{\circ}_{\text{tr,aq}\to\text{solv}}(\text{Ag}^+)$ was obtained from either Gritzner's or Marcus's tables.[9–11] The transfer free energies require an extrathermodynamic assumption (often called the tetraphenylborate assumption) that an electrolyte composed of large, inert cations and anions with the same volume and charge enables analysis of a single ion transfer.[12,13] The experimental uncertainty in transfer free energies can be substantial, with $\Delta G^{\circ}_{\text{tr,aq}\to\text{solv}}$ values sometimes varying by several kcal/mol. Where possible, data was sourced from critical reviews of experimental reports that recommend a reliable value. We have made every effort to provide the most accurate possible values here, but it is most important for the scientific community to adhere to a value of $E^{\circ}_{\text{H+/H–,solv}}$ once it is established, because this allows for comparisons between studies. Having perfectly accurate values is less important for experimental studies than the community adopting the same set of solvent-specific constants, which enables a self-consistent relative scale.

The $\Delta G^{\circ}_{\text{H+/H–}}$ values derived from Scheme S1 for eight organic solvents are shown in Table S1 (reproduced from Table 1 in the main text). The individual thermodynamic parameters utilized are given in Table S2. The approach of Scheme S1 is favored because (a) it follows the approach already in use for the acetonitrile scale; (b) it relies on a single set of estimated aqueous reduction potentials; and (c) a wealth of transfer free energy data is available that enables estimates for many organic solvents. The value of $\Delta E^{\circ\text{solv}}_{\text{NHE}\to\text{Fc}}$ for acetonitrile derived using this method is –0.46 V, a 68 mV (3.1 kcal/mol) difference from the value –0.528 V that was derived using a different methods and utilized in constructing the original acetonitrile scale.[1]

An alternative approach is shown in Scheme S2. The free energy of H_2 heterolysis in the organic solvent of interest ($\Delta G^{\circ}_{\text{H2}}$) can be summed with the free energy associated with reduction of protons to H_2 in the solvent of interest ($\Delta G^{\circ}_{\text{H+/H2}}$). This approach seems ideal, because there are experimental methods to directly measure to $E^{\circ}_{\text{H+/H2}}$ potential. Values for $E^{\circ}_{\text{H+/H2}}$ have only been reported for MeCN (–0.028 V vs Fc^+/Fc)[14] and DMF (–0.662 V vs Fc^+/Fc),[15] however, which

drastically limits the applicability of this approach. A THF value, $E^{\circ}_{H+/H2} = -0.339$ V vs Fc$^+$/Fc, was recently reported by Mayer and coworkers.[16] The experimental error associated with this method is expected to be smaller than that of Scheme 1, because this approach relies more directly on experimentally measurable parameters. We therefore favor its utilization when data is available. The $\Delta G^{\circ}_{H+/H-}$ values calculated using Scheme S2 for MeCN and DMF are also presented in Table S1.
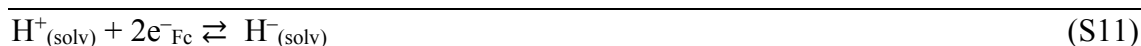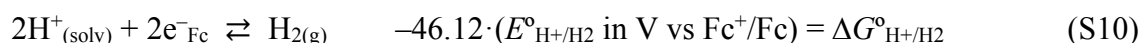
Scheme S2.

$H_{2(g)} \rightleftarrows H^+_{(solv)} + H^-_{(solv)}$	ΔG°_{H2}	(S9)
$2H^+_{(solv)} + 2e^-_{Fc} \rightleftarrows H_{2(g)}$	$-46.12 \cdot (E^{\circ}_{H+/H2}$ in V vs Fc$^+$/Fc$) = \Delta G^{\circ}_{H+/H2}$	(S10)
$H^+_{(solv)} + 2e^-_{Fc} \rightleftarrows H^-_{(solv)}$		(S11)

Table S1. Free energies of H$_2$ heterolysis $(\Delta G^{\circ}_{H2})^6$ and H$^+$ reduction to H$^-$ $(\Delta G^{\circ}_{H+/H-})$ in various solvents.

Reaction	$H_2 \rightleftarrows H^+ + H^-$ ΔG°_{H2} (kcal/mol)	$H^+ + 2e^- \rightleftarrows H^-$ $\Delta G^{\circ}_{H+/H-}$ (kcal/mol)
Water	34.2	34.2
Acetonitrile	76.0[a]	79.6[a]
N,N-Dimethylformamide	55.4	90.2[b] **86.1**[c]
Dimethylsulfoxide	48.1 (60.7)[a]	71.4
Ethanol	45.4	85.6
Ethylene glycol	41.6	76.9
Methanol	43.3	89.4
N-methyl-2-pyrrolidone	—	74.6
Tetrahydrofuran	68.7	74.7[b] **84.3**[c]

[a] Value derived using Parker's original aqueous reduction potential value, $E^{\circ}_{H\bullet/H-}$ = 0.18 V vs NHE.
[b] Based on Scheme S1.
[c] Based on Scheme S2. This value is recommended when available.

Table S2. Values used in deriving $E^{\circ}_{H+/H-}$ in organic solvents.

Solvent	$E^{\circ}(Ag^{+/0})$ (V vs BCr)[a]	$E^{\circ}(Fc^{+/0})$ (V vs BCr)[a]	$E^{\circ Fc,solv}_{Ag+/Ag,S}$ (V vs Fc$^{+/0}$)[b]	$\Delta G^{\circ}_{tr,Ag+}{}^{aq/solv}/F$ (eV)	$\Delta E^{\circ solv}_{NHE \to Fc}$
MeCN	1.03	1.119	0.089	-0.25[c]	-0.46
DMF	1.112	1.127	0.015	-0.18[c]	-0.61
DMSO	0.958	1.123	0.165	-0.33[c]	-0.30
PC	1.514	1.114	-0.4	0.24[c]	-1.44
MeOH	1.337	1.134	-0.203	0.09[c]	-1.09
EtOH	1.275	1.134	-0.141	0.05[c]	-0.99
HO(CH$_2$)$_2$OH	1.217	1.132	-0.085	-0.05[d]	-0.83
NMPy	1.032	1.126	0.094	-0.19[d]	-0.51
THF	1.297	1.209	-0.088	0.03[d]	-0.92

[a] Data from references 9,10. [b] Obtained from the differences of $E^{\circ}(Ag^{+/0})$ and $E^{\circ}(Fc^{+/0})$. [c] Data from reference 11. [d] Data from reference 17.

Correlations between thermochemical parameters and solvent parameters

The two thermodynamic parameters used to determine hydricity, ΔG^{o}_{H2} and $\Delta G^{o}_{H+/H-}$, require two other thermodynamic parameters to convert values from aqueous solvent to organic solvent, $\Delta G^{o}_{tr}(H^+)$ and $\Delta G^{o}_{tr}(H^-)$. To understand how these four quantities are related to solvent properties, correlations were sought with (a) the dielectric constant, (b) donor number, (c) acceptor number, and (d) the Dimroth-Reichart parameter, ET_{30}.[18–21] These were chosen based on the large data sets available for these parameters and their origins in solvation as it relates to charge, Lewis acidity, and Lewis basicity. Interestingly, these four thermodynamic parameters each exhibit the strongest correlation with a *different* solvent parameter.
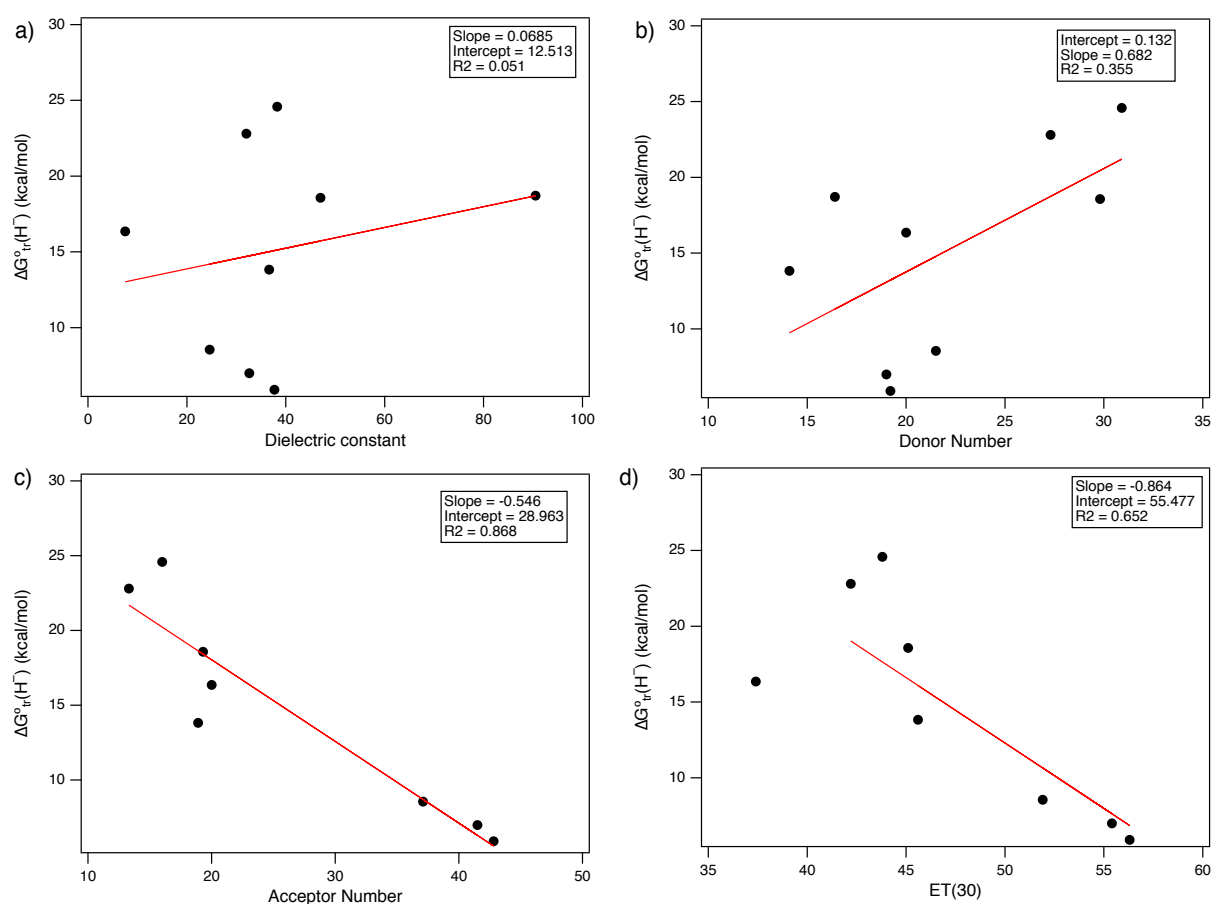

Figure S1. Correlations between $\Delta G^{o}_{tr}(H^-)$ and four solvent parameters.

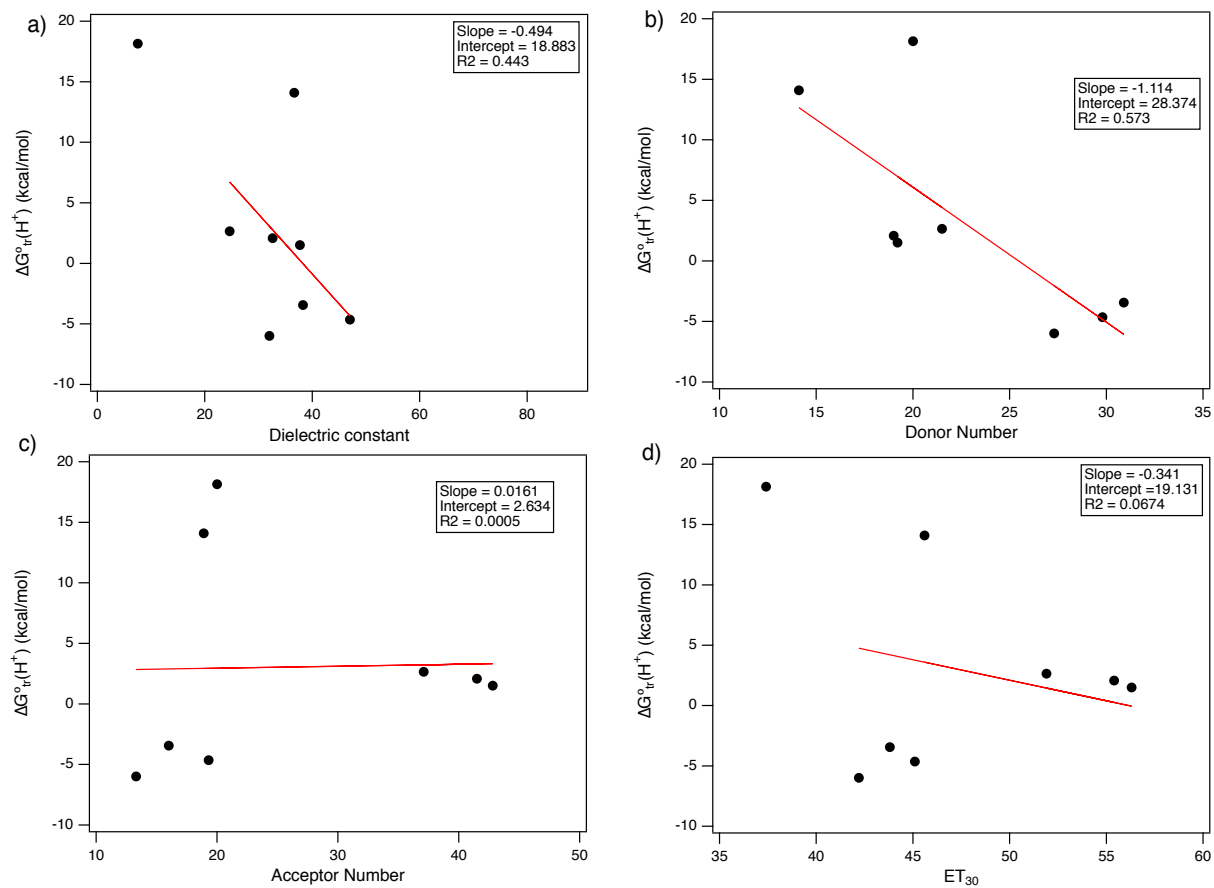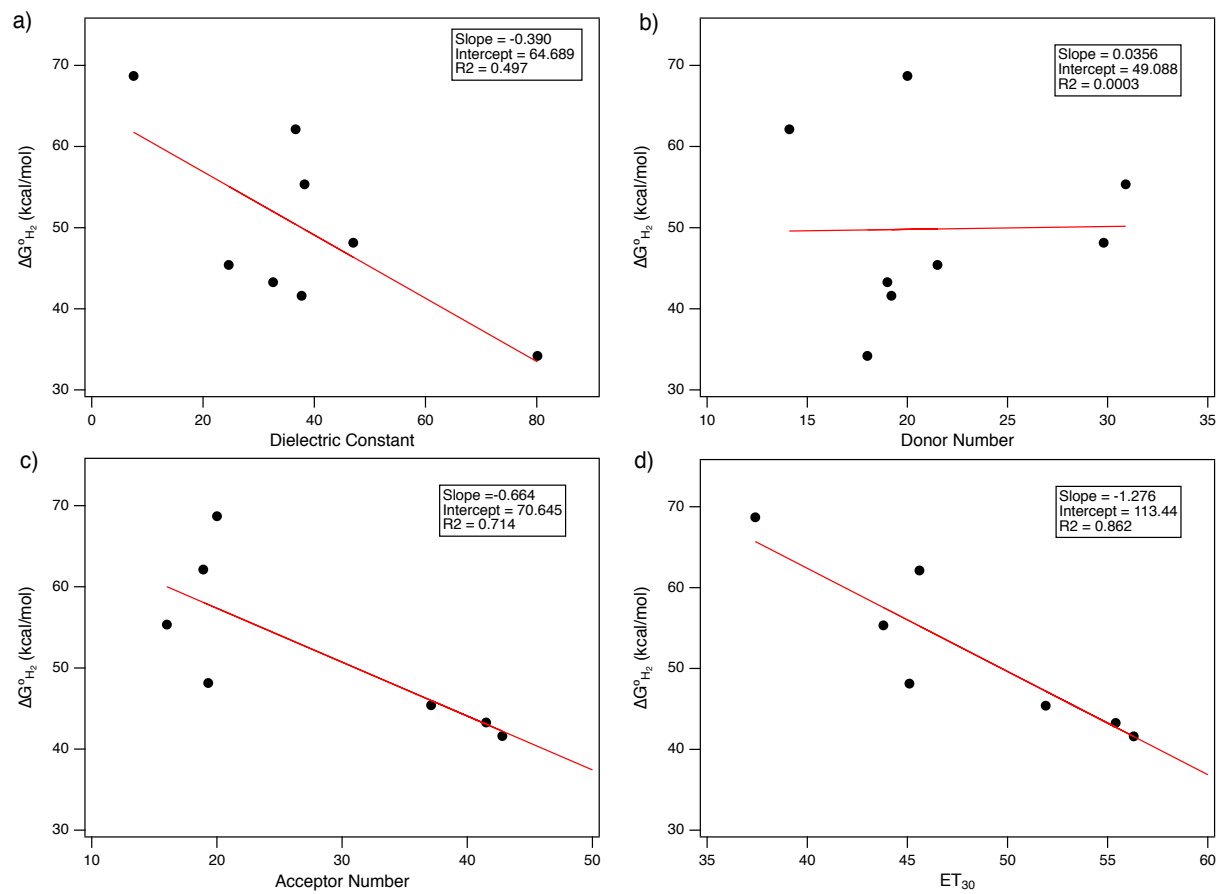Figure S2. Correlations between $\Delta G^{\circ}_{tr}(H^+)$ and four solvent parameters.

Figure S3. Correlations between ΔG^o_{H2} and four solvent parameters.
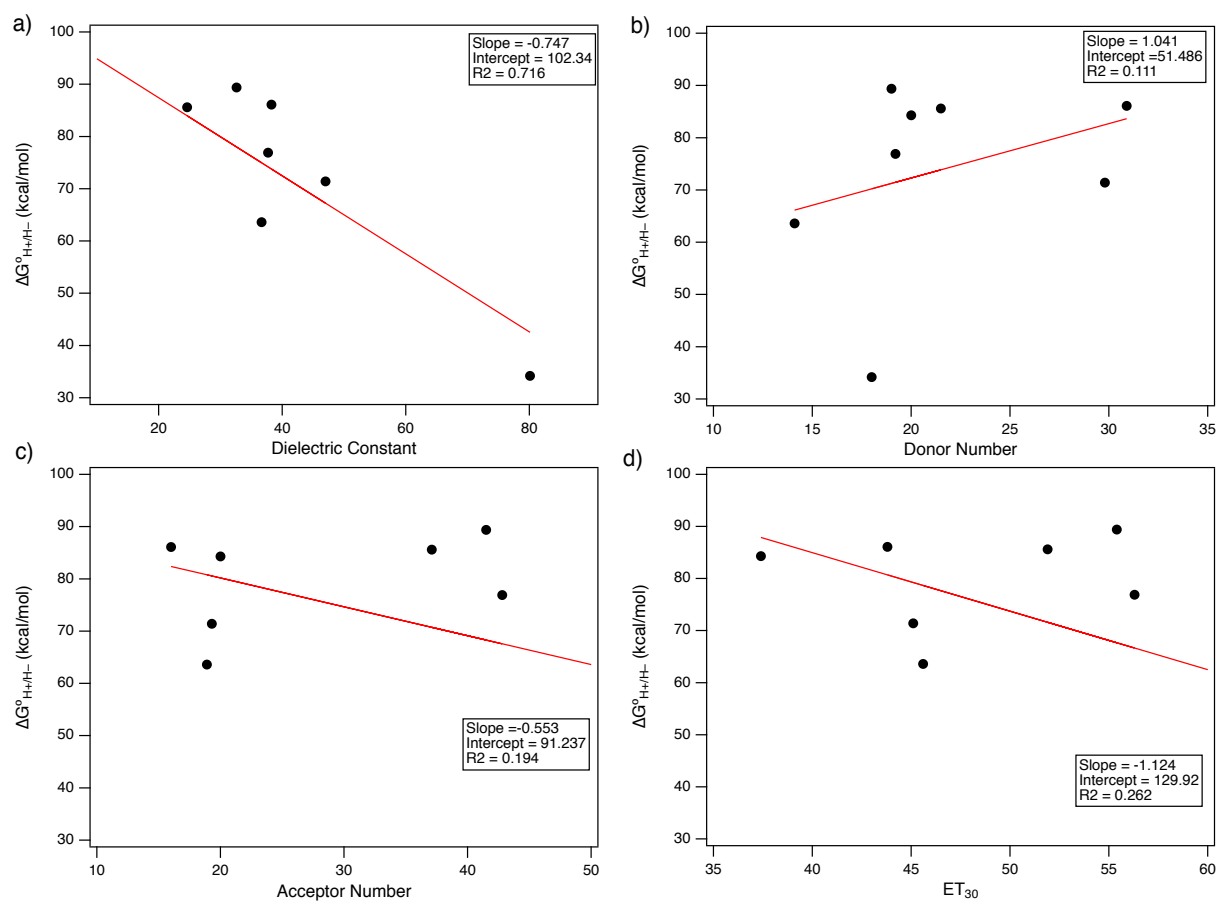
Figure S4. Correlations between $\Delta G^{\circ}_{H+/H-}$ and four solvent parameters.

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