Supporting Information to

Intrinsic Relative Scales of Electrophilicity and Nucleophilicity

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Table 1S. Maximum amount of transferred electrons (in water) from the amines (**a-zz**) to benzhydrylium ions (**1-7**), evaluated through Eq. (1) at the B3LYP/6-31G(d) level of theory using the SM8 solvation model

$\Delta N^*_{B\to A}$		**Electrophiles (A)**						
		1	**2**	**3**	**4**	**5**	**6**	**7**
Nucleophiles (B)	**a**	0.148	0.139	0.135	0.130	0.129	0.125	0.114
	b	0.189	0.180	0.176	0.171	0.169	0.165	0.154
	c	0.189	0.180	0.175	0.170	0.169	0.164	0.154
	d	0.186	0.177	0.173	0.167	0.166	0.161	0.151
	e	0.180	0.171	0.166	0.161	0.159	0.155	0.144
	f	0.099	0.089	0.084	0.077	0.075	0.070	0.058
	g	0.098	0.087	0.082	0.075	0.073	0.068	0.055
	h	0.142	0.131	0.127	0.120	0.118	0.114	0.101
	i	0.170	0.161	0.157	0.152	0.150	0.146	0.135
	j	0.195	0.186	0.181	0.176	0.174	0.170	0.159
	k	0.205	0.196	0.191	0.186	0.185	0.180	0.169
	l	0.136	0.126	0.121	0.115	0.113	0.109	0.097
	m	0.129	0.118	0.113	0.107	0.105	0.100	0.088
	n	0.126	0.114	0.108	0.101	0.099	0.093	0.079
	p	0.194	0.181	0.175	0.168	0.166	0.160	0.145
	q	0.208	0.195	0.189	0.182	0.179	0.173	0.158
	r	0.231	0.218	0.211	0.204	0.201	0.195	0.179
	s	0.228	0.219	0.214	0.209	0.208	0.203	0.192
	t	0.229	0.220	0.215	0.210	0.209	0.204	0.193
	u	0.108	0.098	0.093	0.087	0.084	0.079	0.067
	v	0.154	0.144	0.140	0.135	0.133	0.129	0.118
	w	0.225	0.215	0.211	0.205	0.204	0.199	0.188
	x	0.227	0.218	0.213	0.208	0.206	0.202	0.191
	y	0.221	0.211	0.206	0.201	0.199	0.195	0.183
	z	0.214	0.205	0.200	0.195	0.193	0.189	0.178
	zz	0.226	0.216	0.212	0.206	0.205	0.200	0.189

Table 2S. **Maximum stabilization in electronic interaction energy** (in water) for the reaction of amines (**a-zz**) with benzhydrylium ions (**1-7**), evaluated through Eq. (6) at the B3LYP/6-31G(d) level of theory using the SM8 solvation model. All values are reported in **kJ/mol**.

$\Delta E_{AB}\left(\Delta N^{*}_{B\to A}\right)$		**Electrophiles (A)**						
		1	**2**	**3**	**4**	**5**	**6**	**7**
Nucleophiles (B)	**a**	-12.6	-11.2	-10.5	-9.7	-9.4	-8.8	-7.4
	b	-19.5	-17.7	-16.8	-15.8	-15.4	-14.7	-12.8
	c	-19.4	-17.5	-16.7	-15.6	-15.3	-14.5	-12.7
	d	-18.6	-16.7	-15.9	-14.9	-14.5	-13.8	-12.0
	e	-17.0	-15.2	-14.4	-13.4	-13.1	-12.3	-10.6
	f	-4.8	-3.8	-3.4	-2.9	-2.7	-2.4	-1.6
	g	-4.4	-3.5	-3.1	-2.6	-2.4	-2.1	-1.4
	h	-9.7	-8.3	-7.7	-6.9	-6.7	-6.1	-4.9
	i	-16.0	-14.3	-13.6	-12.6	-12.3	-11.6	-10.0
	j	-20.2	-18.3	-17.4	-16.3	-16.0	-15.1	-13.3
	k	-22.1	-20.1	-19.2	-18.1	-17.7	-16.8	-14.8
	l	-9.2	-7.9	-7.3	-6.6	-6.3	-5.8	-4.6
	m	-7.9	-6.6	-6.1	-5.4	-5.2	-4.7	-3.6
	n	-6.6	-5.4	-4.9	-4.2	-4.0	-3.6	-2.6
	p	-14.6	-12.7	-11.8	-10.8	-10.4	-9.7	-7.9
	q	-16.4	-14.4	-13.5	-12.3	-12.0	-11.2	-9.3
	r	-19.3	-17.0	-16.0	-14.7	-14.4	-13.4	-11.3
	s	-27.0	-24.8	-23.7	-22.5	-22.1	-21.1	-18.8
	t	-27.2	-25.0	-23.9	-22.7	-22.3	-21.3	-19.0
	u	-5.6	-4.6	-4.1	-3.6	-3.4	-3.0	-2.1
	v	-12.8	-11.3	-10.6	-9.7	-9.5	-8.8	-7.4
	w	-25.7	-23.6	-22.5	-21.3	-20.9	-20.0	-17.7
	x	-26.5	-24.3	-23.2	-22.0	-21.6	-20.6	-18.4
	y	-24.4	-22.3	-21.3	-20.0	-19.6	-18.7	-16.6
	z	-24.1	-22.0	-21.0	-19.8	-19.4	-18.5	-16.4
	zz	-25.9	-23.7	-22.7	-21.4	-21.0	-20.1	-17.8

Table 3S. Relative electrophilicity (in water) of electrophiles **A** in presence of nucleophile **B**, evaluated through Eq. (7) at the B3LYP/6-31G(d) level of theory using the SM8 solvation model. All values are reported in **kJ/mol**.

$\omega_{A(B)}$		**Electrophiles (A)**						
		1	**2**	**3**	**4**	**5**	**6**	**7**
Nucleophiles (B)	**a**	72.8	69.3	67.7	65.8	65.2	63.7	59.9
	b	76.6	73.0	71.3	69.3	68.7	67.1	63.1
	c	77.1	73.4	71.7	69.7	69.1	67.5	63.5
	d	78.2	74.5	72.8	70.7	70.1	68.5	64.4
	e	80.2	76.3	74.5	72.5	71.9	70.2	66.0
	f	85.7	81.6	79.7	77.5	76.9	75.2	70.6
	g	91.3	87.0	85.0	82.7	82.0	80.2	75.4
	h	86.9	82.8	80.9	78.7	78.0	76.3	71.7
	i	75.6	72.0	70.3	68.3	67.7	66.1	62.2
	j	78.9	75.1	73.4	71.3	70.7	69.1	65.0
	k	79.7	75.9	74.1	72.1	71.4	69.8	65.6
	l	83.7	79.7	77.9	75.7	75.1	73.4	69.0
	m	88.0	83.8	81.9	79.7	79.0	77.2	72.6
	n	100.1	95.3	93.1	90.7	90.0	88.0	82.7
	p	108.3	103.2	100.8	98.2	97.5	95.3	89.6
	q	110.6	105.4	103.0	100.4	99.6	97.5	91.6
	r	116.4	110.9	108.3	105.6	104.9	102.6	96.4
	s	80.9	77.1	75.3	73.2	72.6	70.9	66.7
	t	80.9	77.0	75.2	73.2	72.5	70.9	66.6
	u	87.5	83.4	81.4	79.2	78.6	76.8	72.2
	v	77.4	73.8	72.0	70.0	69.4	67.8	63.8
	w	82.2	78.2	76.4	74.3	73.7	72.0	67.7
	x	81.7	77.8	76.0	73.9	73.3	71.6	67.3
	y	83.5	79.6	77.7	75.6	74.9	73.2	68.8
	z	79.7	75.9	74.1	72.1	71.4	69.8	65.6
	zz	82.5	78.6	76.7	74.6	74.0	72.3	68.0

Table 4S. Relative nucleophilicity slope parameter (in water) of nucleophiles **B** in presence electrophiles **A**, evaluated through Eq. (10) at the B3LYP/6-31g(d) level of theory using the SM8 solvation model. $s_{B(A)}$ is dimensionless.

$s_{B(A)}$		Electrophiles (A)						
		1	**2**	**3**	**4**	**5**	**6**	**7**
Nucleophiles (B)	**a**	-0.218	-0.217	-0.217	-0.212	-0.210	-0.208	-0.209
	b	-0.230	-0.229	-0.228	-0.223	-0.221	-0.219	-0.220
	c	-0.231	-0.230	-0.229	-0.225	-0.223	-0.220	-0.221
	d	-0.234	-0.233	-0.233	-0.228	-0.226	-0.224	-0.225
	e	-0.240	-0.239	-0.239	-0.234	-0.232	-0.229	-0.230
	f	-0.257	-0.256	-0.255	-0.250	-0.248	-0.245	-0.247
	g	-0.274	-0.273	-0.272	-0.267	-0.264	-0.262	-0.263
	h	-0.260	-0.259	-0.259	-0.254	-0.251	-0.249	-0.250
	i	-0.226	-0.225	-0.225	-0.220	-0.218	-0.216	-0.217
	j	-0.236	-0.235	-0.235	-0.230	-0.228	-0.226	-0.227
	k	-0.239	-0.238	-0.237	-0.232	-0.230	-0.228	-0.229
	l	-0.251	-0.250	-0.249	-0.244	-0.242	-0.240	-0.241
	m	-0.264	-0.263	-0.262	-0.257	-0.255	-0.252	-0.253
	n	-0.300	-0.299	-0.298	-0.292	-0.290	-0.287	-0.289
	p	-0.324	-0.323	-0.322	-0.317	-0.314	-0.311	-0.313
	q	-0.331	-0.330	-0.330	-0.324	-0.321	-0.318	-0.320
	r	-0.349	-0.347	-0.347	-0.341	-0.338	-0.335	-0.336
	s	-0.242	-0.241	-0.241	-0.236	-0.234	-0.231	-0.233
	t	-0.242	-0.241	-0.241	-0.236	-0.234	-0.231	-0.233
	u	-0.262	-0.261	-0.261	-0.255	-0.253	-0.251	-0.252
	v	-0.232	-0.231	-0.230	-0.226	-0.224	-0.221	-0.223
	w	-0.246	-0.245	-0.245	-0.240	-0.237	-0.235	-0.236
	x	-0.245	-0.244	-0.243	-0.238	-0.236	-0.234	-0.235
	y	-0.250	-0.249	-0.249	-0.244	-0.241	-0.239	-0.240
	z	-0.239	-0.238	-0.237	-0.232	-0.230	-0.228	-0.229
	zz	-0.247	-0.246	-0.245	-0.241	-0.238	-0.236	-0.237

Table 5S. Relative nucleophilicity (in water) of nucleophile **B** in presence of electrophiles **A**, evaluated through Eq. (11) at the B3LYP/6-31G(d) level of theory using the SM8 solvation model. All values are reported in **kJ/mol**.

$\omega_{B(A)}$		**Electrophiles (A)**						
		1	**2**	**3**	**4**	**5**	**6**	**7**
Nucleophiles (B)	**a**	-276.1	-267.8	-264.0	-264.6	-265.5	-264.0	-250.9
	b	-248.7	-241.8	-238.7	-239.5	-240.5	-239.5	-228.2
	c	-250.0	-243.1	-239.9	-240.7	-241.7	-240.6	-229.3
	d	-254.7	-247.5	-244.2	-245.0	-246.0	-244.9	-233.3
	e	-263.2	-255.6	-252.1	-252.9	-253.9	-252.6	-240.4
	f	-315.3	-304.3	-299.2	-298.6	-299.3	-296.7	-279.9
	g	-317.8	-306.5	-301.2	-300.6	-301.2	-298.5	-281.3
	h	-296.7	-287.2	-282.8	-282.9	-283.8	-281.8	-267.0
	i	-263.2	-255.6	-252.1	-252.9	-253.9	-252.6	-240.4
	j	-248.5	-241.6	-238.4	-239.3	-240.3	-239.3	-228.1
	k	-241.1	-234.5	-231.5	-232.4	-233.4	-232.5	-221.7
	l	-297.1	-287.6	-283.1	-283.2	-284.1	-282.1	-267.3
	m	-304.0	-293.9	-289.3	-289.2	-290.0	-287.8	-272.3
	n	-311.8	-301.1	-296.1	-295.7	-296.5	-294.0	-277.6
	p	-289.0	-280.0	-275.8	-276.1	-277.1	-275.3	-261.1
	q	-284.4	-275.7	-271.6	-272.1	-273.0	-271.3	-257.6
	r	-278.6	-270.3	-266.4	-266.9	-267.8	-266.3	-253.0
	s	-222.5	-216.7	-214.0	-215.0	-216.0	-215.2	-205.6
	t	-221.5	-215.7	-213.1	-214.1	-215.1	-214.3	-204.7
	u	-312.4	-301.7	-296.7	-296.3	-297.0	-294.5	-278.1
	v	-278.9	-270.5	-266.6	-267.1	-268.1	-266.5	-253.2
	w	-229.2	-223.1	-220.3	-221.3	-222.3	-221.5	-211.5
	x	-225.6	-219.7	-216.9	-217.9	-218.9	-218.1	-208.3
	y	-236.3	-229.9	-227.0	-227.9	-228.9	-228.0	-217.6
	z	-233.0	-226.8	-223.9	-224.9	-225.9	-225.0	-214.8
	zz	-229.1	-223.0	-220.2	-221.2	-222.2	-221.4	-211.3

Table 6S. Logarithm of the experimental second order rate constant for the reaction of electrophiles **A** with nucleophiles **B**, taken from Ref. (57), measured in water. Bold-faced numbers correspond to interpolated values from the adjustment of experimental data to the Mayr's regression relationship, Eq. (5).

$\log k_{AB}$		Electrophiles (A)						
		1	**2**	**3**	**4**	**5**	**6**	**7**
Nucleophiles (B)	**a**	2.400	1.281	1.155	0.732	0.378	0.149	-0.390
	b	4.381	3.628	3.236	2.960	2.627	2.307	2.045
	c	4.237	3.378	2.987	2.683	2.373	1.973	1.632
	d	3.645	2.826	2.401	2.127	1.826	1.446	1.105
	e	3.330	2.204	1.779	1.473	0.996	0.672	0.417
	f	3.235	2.340	1.889	1.592	1.253	0.784	0.505
	g	3.946	3.083	2.612	2.310	2.001	1.604	1.231
	h	4.013	3.021	2.622	2.377	1.965	1.679	1.389
	i	4.146	3.215	2.805	2.509	2.227	1.812	1.544
	j	4.577	3.622	3.228	2.938	2.577	2.241	1.956
	k	4.542	3.763	3.358	3.114	2.814	2.436	2.140
	l	4.068	3.079	2.650	2.384	2.037	1.682	1.410
	m	4.161	3.371	2.980	2.697	2.411	2.013	1.743
	n	4.496	3.483	3.111	2.893	2.486	2.260	1.976
	p	5.609	4.230	3.697	3.513	3.104	2.713	2.158
	q	6.025	4.601	4.029	3.866	3.459	2.808	2.340
	r	5.535	4.825	4.448	4.117	3.910	3.563	3.292
	s	5.785	5.021	4.689	4.458	4.079	3.849	3.547
	t	4.899	4.049	3.688	3.453	3.064	2.810	2.500
	u	4.672	3.811	3.375	3.111	2.777	2.373	2.027
	v	4.590	3.688	3.230	2.955	2.605	2.181	1.819
	w	5.748	5.025	4.706	4.418	4.086	3.865	3.533
	x	5.481	4.785	4.566	4.422	3.955	3.844	3.484
	y	5.871	5.204	4.863	4.643	4.328	4.090	3.804
	z	2.400	1.281	1.155	0.732	0.378	0.149	-0.390
	zz	4.381	3.628	3.236	2.960	2.627	2.307	2.045

Table 7S. Summary of the linear adjustment between Maximum electronic interaction energy change ΔE_{AB} and the absolute electrophilicity ω_A for each single nucleophile (B), including standard errors for the parameters and the coefficient of determination R^2. These results indicate that ca. 94-96% of the total variation in ΔE_{AB} can be confidently explained by the linear regression equation $\Delta E_{AB} = s_B\omega_A + s_B\omega_B$ All values in kJ/mol.

	Intercept ($s_B\omega_B$)		Slope (s_B)		Statistics	ω_B
Nucleophile (B)	Value	Standard Error	Value	Standard Error	R^2	Value
a	25.648	3.839	**-0.114**	0.012	0.012	**-33.6**
b	30.105	4.823	**-0.148**	0.015	0.015	**-32.5**
c	30.163	4.814	**-0.148**	0.015	0.015	**-32.5**
d	30.161	4.750	**-0.146**	0.015	0.015	**-32.6**
e	29.946	4.606	**-0.140**	0.015	0.015	**-32.8**
f	18.424	2.573	**-0.069**	0.008	0.008	**-37.2**
g	18.204	2.552	**-0.067**	0.008	0.008	**-37.9**
h	25.858	3.659	**-0.106**	0.012	0.012	**-34.5**
i	28.293	4.368	**-0.132**	0.014	0.014	**-33.0**
j	30.960	4.953	**-0.153**	0.016	0.016	**-32.4**
k	31.835	5.190	**-0.161**	0.017	0.017	**-32.1**
l	24.823	3.517	**-0.102**	0.011	0.011	**-34.6**
m	23.841	3.333	**-0.095**	0.011	0.011	**-35.2**
n	23.462	3.246	**-0.090**	0.010	0.010	**-36.2**
p	34.459	4.885	**-0.146**	0.016	0.016	**-33.4**
q	36.441	5.206	**-0.158**	0.017	0.017	**-33.0**
r	39.698	5.717	**-0.176**	0.018	0.018	**-32.4**
s	33.332	5.706	**-0.180**	0.018	0.018	**-31.6**
t	33.356	5.726	**-0.181**	0.018	0.018	**-31.6**
u	20.260	2.819	**-0.077**	0.009	0.009	**-36.5**
v	26.788	3.969	**-0.118**	0.013	0.013	**-33.6**
w	33.494	5.624	**-0.177**	0.018	0.018	**-31.7**
x	33.493	5.682	**-0.179**	0.018	0.018	**-31.7**
y	33.613	5.531	**-0.174**	0.018	0.018	**-31.9**
z	32.345	5.389	**-0.169**	0.017	0.017	**-31.9**
zz	33.623	5.646	**-0.178**	0.018	0.018	**-31.7**

Full reference for the Spartan'08 program, Ref. (63):

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