Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Oxidation Potentials of Phenols and Anilines: Correlation Analysis of Electrochemical and Theoretical Values

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Table S1. Rate constants for oxidation of phenols and anilines by MnO_2

No.	IUPAC Name	$\log k_{rel}$ Stone and Morgan [a]	$\log k_{rel}$ Laha and Luthy [b]	$\log k_{rel}$ Klausen et al. [c]	$\log k_{rel}$ Salter-Blanc et al. [d]
1	phenol	−0.244, −0.301			
2	3-methylphenol	0.061			
3	4-methylphenol	0.724, 0.487			
4	4-ethylphenol	0.704			
5	4-nitrophenol	−2.560			
6	2-chlorophenol	−0.195			
7	3-chlorophenol	−1.006			
8	4-chlorophenol	0, 0			
9	4-hydroxyacetophenone	−2.438, −2.495			
10	2-hydroxybenzoic acid	−1.529, −1.921			
11	4-hydroxybenzoic acid	−1.304, −1.228			
12	aniline		−0.626	0.48	-0.100
13	2-methylaniline			0.79	
14	3-methylaniline			0.79	
15	4-methylaniline		0.737	1.6	
16	2-methoxyaniline			1.6	
17	3-methoxyaniline			0.68	
18	4-methoxyaniline		2.862	2.5	
19	3-nitroaniline				−1.34
20	4-nitroaniline		−3.643		~ −4.11 [e]
21	3-chloroaniline			−0.96	
22	4-chloroaniline		0.0	0.0	0.0
23	2-methyl-5-nitroaniline				−1.40
24	4-methyl-3-nitroaniline				−1.20
25	2-methoxy-5-nitroaniline				−0.279
26	4-aminobenzoic acid		−1.107		

a) Sets A and B from Stone (1987) [1] are distinguished with red and blue diamonds, respectively, in Figures 1A, 5, and 6.

b) Calculated from k_{exp} data reported in Laha and Luthy (1990) [2]

c) Calculated from concentration vs. time data in Figure 8 of Klausen et al.(1997) [3]

d) From Salter Blanc et al. (2016). [4]

e) Approximate value because reaction was slow.

Table S2. Substituted phenols used in electrochemical measurements.

No.	Name	CAS-RN	Source (Purity %)	pK_a [a]
1	phenol	108-95-2	Sigma (99)	10.02
2	2-methylphenol (o-cresol)	95-48-7	Sigma	10.37
3	3-methylphenol (m-cresol)	108-39-4	TCI (98)	10.13
4	4-methylphenol (p-cresol)	106-44-5	Matheson, Coleman & Bell	10.36
5	4-ethylphenol	123-07-9	Avocado (97)	10.32
6	2-methoxyphenol (o-guaiacol)	90-05-1	Alfa Aesar (98)	9.98
7	3-methoxyphenol (m-guaiacol)	150-19-6	Acros (97)	9.49
8	4-methoxyphenol (p-guaiacol)	150-76-5	Acros (99)	9.94
9	2-nitrophenol	88-75-5	Acros (99)	6.63
10	3-nitrophenol	554-84-7	Acros (99)	7.89
11	4-nitrophenol	100-02-7	Sigma-Aldrich (99)	7.07
12	2,4-dinitrophenol	51-28-5	Acros (98)	4.35
13	2-methyl-4,6-dinitrophenol (DNOC)	534-52-1	Sigma-Aldrich (99.9)	4.45
14	4-methyl-2,6-dinitrophenol (DNPC)	609-93-8	Combi-Blocks (95)	4.57
15	2-phenylphenol	90-43-7	Aldrich (99)	9.69
16	2-chlorophenol	95-57-8	Acros (98)	7.97
17	3-chlorophenol	108-43-0	Acros (99)	8.79
18	4-chlorophenol	106-48-9	Sigma-Aldrich (99)	8.96
19	2-hydroxyphenol (catechol)	120-80-9	Aldrich (99.5)	9.34, 12.39
20	3-hydroxyphenol (resorcinol)	108-46-3	Aldrich (99)	9.26, 10.73
21	4-hydroxyphenol (hydroquinone)	123-31-9	Aldrich (99)	9.68, 11.55
22	4-cyanophenol	767-00-0	Acros (99)	7.81
23	3-hydroxyacetophenone	121-71-1	TCI (98)	8.92
24	4-hydroxyacetophenone	99-93-4	MP Biomedicals (99.8)	7.79
25	2-hydroxybenzoic acid (o-salicylic acid)	69-72-7	Sigma-Aldrich (99)	13.23
26	3-hydroxybenzoic acid (m-salicylic acid)	99-06-9	Sigma-Aldrich (99)	9.55
27	4-hydroxybenzoic acid (p-salicylic acid)	99-96-7	Aldrich (99)	9.67
28	triclosan	3380-34-5	Sigma-Aldrich (97)	7.68
29	dopamine	51-61-6	Ark Pharm (97)	10.01,12.93
30	bisphenol A	80-05-7	Acros (97)	9.78, 10.39
31	3-aminophenol	591-27-5	Aldrich (98)	9.82
32	4-aminophenol	123-30-8	Sigma-Aldrich (98)	10.4
33	2,5-dimethylphenol	95-87-4	Aldrich (99)	10.47
34	2,6-dimethoxyphenol	91-10-1	Fluka (98)	9.37
35	4-ethyl-2-methoxyphenol	2785-89-9	Alfa Aesar (98)	10.3
36	2-methoxy-4-formylphenol (vanillin)	121-33-5	Aldrich (99)	7.81
37	2,4,6-trimethylphenol	527-60-6	Aldrich (99)	11.07
38	2,4,6-trichlorophenol	88-06-2	Sigma (98)	5.99

a) Estimated using ChemAxon's Instant JChem as described in Salter-Blanc et al. (2016).[4]

Table S3. Substituted anilines used in electrochemical measurements.

No.	**Name**	**CAS-RN**	**Source (Purity %)**	**pK_a [a]**
1	aniline	62-53-3	Aldrich (99.5)	4.64
2	2-methylaniline (o-toluidine)	95-53-4	Alfa Aesar (99)	4.48
3	3-methylaniline (m-toluidine)	108-44-1	Acros (99)	4.86
4	4-methylaniline (p-toluidine)	106-49-0	Alfa Aesar (99)	4.99
5	2-methoxyaniline (o-anisidine)	90-04-0	Acros (99)	4.42
6	3-methoxyaniline (m-anisidine)	536-90-3	Acros (99)	4.01
7	4-methoxyaniline (p-anisidine)	104-94-9	Acros (99)	5.11
8	3-aminobenzoic acid	99-05-8	Sigma	3.27
9	4-aminobenzoic acid	150-13-0	Sigma (99)	2.69
10	2-nitroaniline	88-74-4	Alfa Aesar (98)	0.25
11	3-nitroaniline	99-09-2	Acros (98)	1.72
12	4-nitroaniline	100-01-6	Acros (99)	1.43
13	2-chloroaniline	95-51-2	Alfa Aesar (98)	2.79
14	3-chloroaniline	108-42-9	Acros (99)	3.47
15	4-chloroaniline	106-47-8	Acros (98)	3.49
16	2-methyl-5-nitroaniline	99-55-8	Acros (96)	1.73
17	4-methyl-3-nitroaniline	119-32-4	Acros (97)	2.43
18	2-methoxy-5-nitroaniline	99-59-2	TCI (98)	1.83

a) Estimated using ChemAxon's Instant JChem as described in Salter-Blanc et al. (2016).[4]

Electrochemical Method Development

The experimental methods used by Suatoni et al.[5] were matched as closely as possible and are described in the main text, with deviations elaborated and justified below. The concentration of the IPA was varied from 0% to 75% (v/v in water) to characterize the effects that IPA had on the voltammetry. As illustrated in **Figure S1** for aniline, IPA caused modest changes in peak size and position, but the overall shape of the CVs was equivalent. The effect of IPA on peak resolution varied with compound, and a few phenols/anilines gave notably better resolved peaks with 25% IPA than 50% IPA (Suatoni's conditions). Therefore, we performed most experiments using both 25% and 50% IPA and chose the results with the most pronounced peaks to extract oxidation potentials.

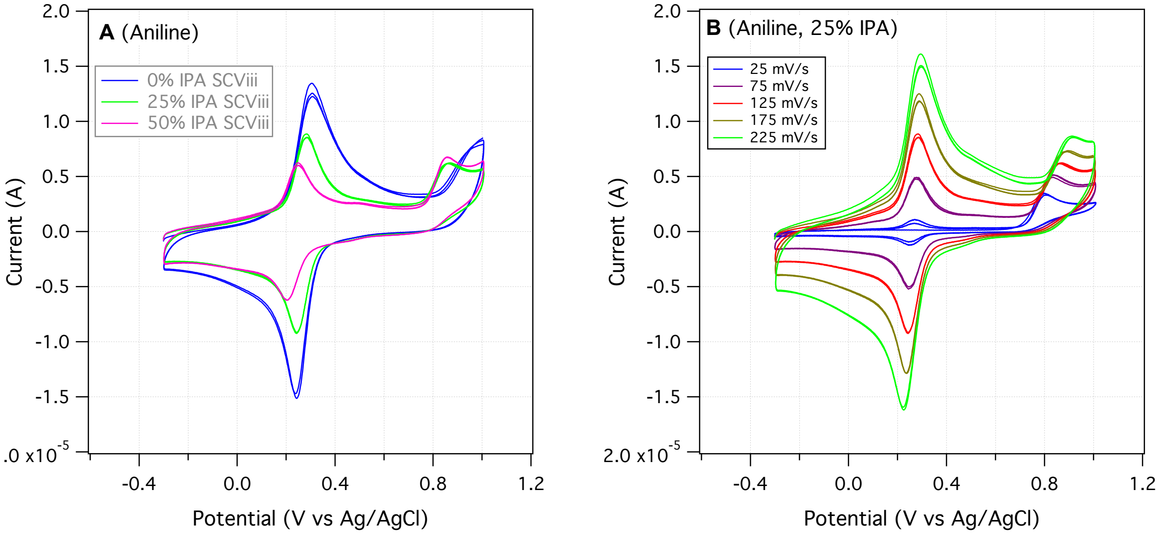

Figure S1. (**A**) SCV of aniline, at three different IPA concentrations, at a scan rate of 125 mV/s. (**B**) SCV of aniline at 25% IPA and varying scan rates. Both voltammograms were done with a glassy carbon working electrode and a step size of 2 mV.

In all cases, peak potential changed slightly with the change in IPA concentration, as can be expected from the slight change in pH, pH at 50% IPA was approximately 5.6, at 25% 5.1 and at 0% 4.7. Theoretically the reduction potentials should increase with decreasing pH, conversely at low pH reduction becomes easier and at high pH oxidation is more facile.[6] Our experimental data however did not reflect this and out of the seventeen phenols and five anilines tested the reverse was true for eleven phenols and four anilines. It was not apparent as to why the phenols and anilines did not follow this expected trend, but possibly due to solvent effects. In comparing the phenol groups 2-nitrophenol oxidation potential decreased as expected (4 mV), but the 4-nitrophenol increased by 12 mV as pH increased. 4-Nitroaniline oxidation potential increased by 6 mV, while the 3-nitroaniline decreased by 12 mV. Both 4-chlorophenol and aniline inreased by 31 and 38 mV, respectively, and 4-chloroaniline increased by 4 mV.

The scan rate was varied for SCVs and an example of the results for aniline can be seen in **Figure S1-B**. The main reason for varying scan rate is to characterize the reversibility of the electrode reactions.[7] For fast reversible reactions, peak potentials do not change with scan rate, as is the case with the large peak at ~ 300 mV in **Figure S1-B**. However, the peak at ~ 900 mV in that figure shifts as a function of scan rate. In general depending on the type of reaction (if there is a chemical step coupled to electron transfer) if the scan rate is slow compared to the chemical reaction then only the chemical reaction will be characterized in the voltammogram, but if the scan rate is fast and the chemical reaction is slow then only the electron transfer step will be present.[8]

For SWV both scan rate and amplitude were varied. SWVi-iv corresponds to varying amplitude from 50 mV (SWVi), 75 mV (SWVii), 100 mV (SWViii), and 125 mV (SWViv) at a constant scan rate of 60 mV/s. SWVv-ix corresponds to a constant 50 mV amplitude and a scan rate of 30 mV/s (SWVv), 60 mV/s (SWVvi), 120 mV/s (SWVvii), 180 mV/s (SWVviii), and 240 mV/s (SWVix). All SWVs had a step size of 2 mV. Varying the amplitude and the scan rate in SWV are used to measure electrode kinetics. Varying the amplitude can be used for species in the solution phase and adsorbed at the electrode, whereas varying the scan rate and the resulting peak to peak separations apply mostly to solution phase species.[9]

In SWV a plot of the forward and reverse currents vs. the potential, as shown in **Figure S2** can be used to show reversibility of the redox couple. In the first scan (SWVi), much like the first pass in the cyclic voltammogram (**Figure S3**), a primary irreversible peak is observed at ~ 800 mV. This irreversibility is evidenced by the absence of a reverse current peak in SWVi and the absence of a cathodic peak in SCV. In SWVii a reverse current peak is still absent at ~800 mV, but a reverse current peak appears at ~350 mV. This reverse current peak is analogous to the reverse cathodic peak in the cyclic voltammogram.

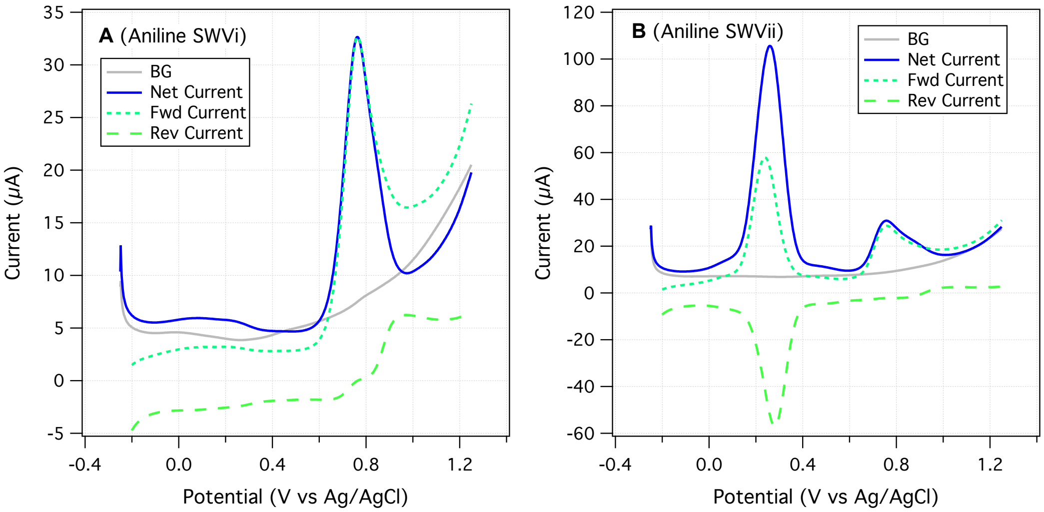

Figure S2. Forward, reverse and net current square wave voltammogram of aniline in 25% IPA/ buffer solution at a scan rate of 60 mV/s and a step size of 2 mV. (**A**) 50 mV amplitude (**B**) 75 mV amplitude.

Classification of Voltammograms

As described in the main text, we classified our voltammograms into four types. For phenols, most compounds were type I or type II, except four phenols that were type III (4-nitrophenol, 4-cyanophenol, DNOC, and 4-hydroxyacetphenone); and two phenols that were type IV (4-aminophenol and dopamine). Almost all of the compounds gave the same type by SCV and SWV, except for 2,4-dinitrophenol (whose current went up and down and therefore could be considered a type II or III), 4-cyanophenol (which fell into a type III for SCV, but whose current went up and down in SWV (type II or III)), and 4-hydroxyacetophenone (which was a type III in SCV, but a type II in SWV). The majority of the anilines were type I except for p-toluidine (type II) and 4-methyl-3-nitroaniline and 2-methoxy-5-nitroaniline (both were type I for SWV, but for SCV fell into type III and type II respectively).

Comparing the voltammograms of SCV and SWV both were in agreement of the four types listed. Type I SCVs main features as described in the main text were a primary anodic peak that decresed with subsequent scans, while after the first pass a secondary reversible peak appeared. This can be seen in **Figure S3-A** and is confirmed by the SWV voltammogram in **Figure S4-A.** For type II SCVs, as can be seen in **Figure S3-B**, there is one prominent anodic peak that decreases, usually drastically with each pass and subsequent scan rates. The same behavior is seen with the SWV voltammogram in **Figure S4-B**, where there is a primary prominent peak that decreased significantly between the first and second scan. At first glance, this is not evident from the voltammogram shown, but the current does decrease with subsequent scans and was verified by obtaining the currents in the peak search function in the Aftermath software. For type III voltammograms where the current response increases with scan rate, the same behavior is seen with SCV, **Figure S3-C** and SWV, **Figure S4-C**. Type IV voltammograms exhibited a reversible or quasi-reversible set of peaks. This can be seen in **Figure S3-D** for dopamine which had an approximate 200 mV separation between the anodic and cathodic peaks. For 4-aminophenol (not shown), the peak seperation was 60 mV denoting a one electron transfer reaction. This reversible peak is verified in SWV **Figure S4-D**. The forward and reverse current peaks have the same potential and the ratio of the peaks for the forward and reverse currents are approximately 0.70, which indicates quasi-reversibility.[10] For 4-aminophenol (not shown) the ratio of currents is closer to 1.0 denoting reversibility.

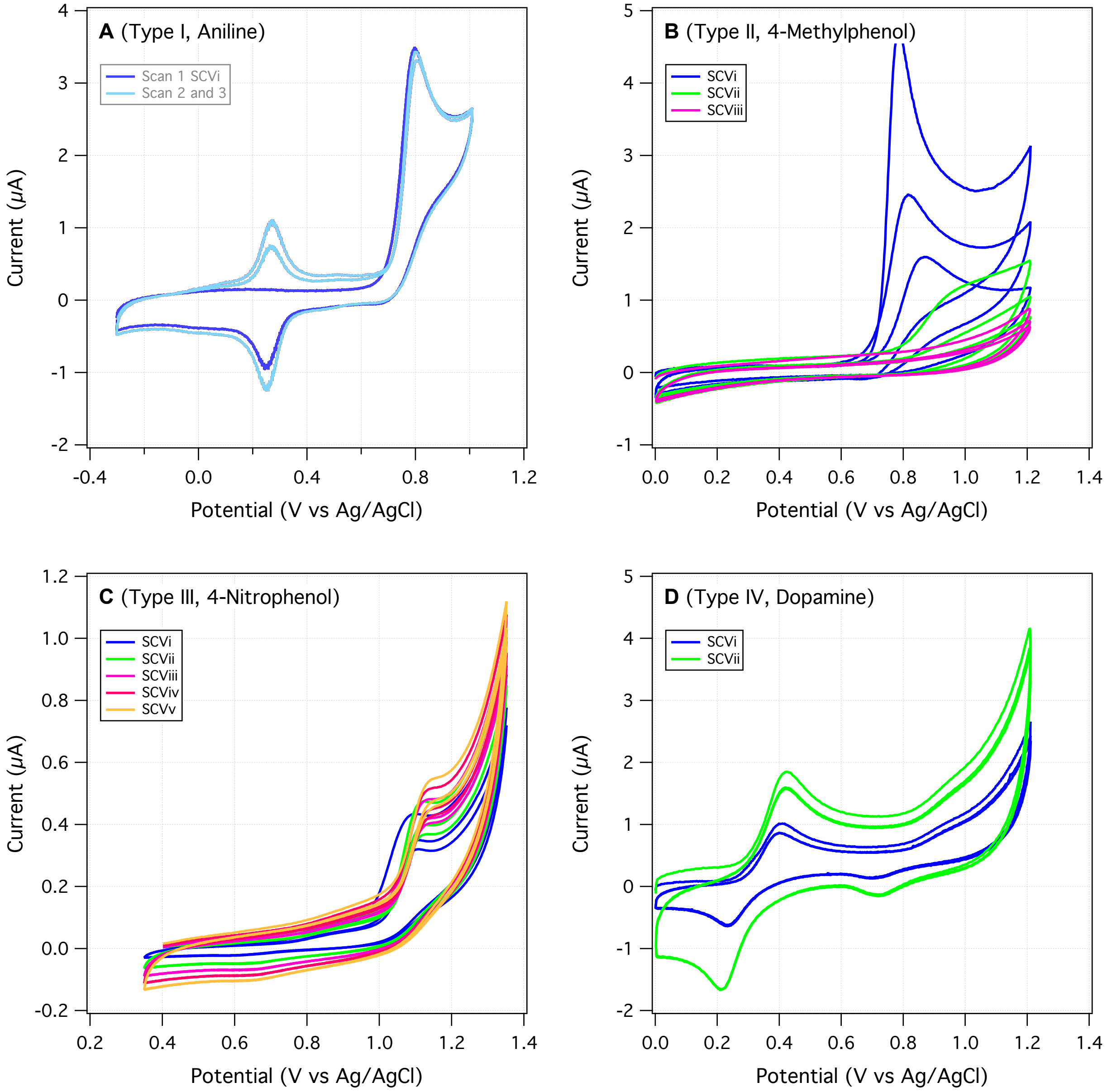

Figure S3. Four types of staircase cyclic voltammograms at varying scan rates. (**A**) Aniline at 25 mV/s, first pass denoted by dark blue. (**B**) 4-methylphenol (**C**) 4-nitrophenol (**D**) Dopamine. (Conditions: All voltammograms were done using a glassy carbon working electrode. Step size 2 mV, scan rates: 25 mV/s (SCVi), 75 mV/s (SCVii), 125 mV/s (SCViii), 175 mV/s (SCViv), and 225 mV/s (SCVv). A, B and D were done in 25% IPA/ Buffer (pH 5.1) C in 50% IPA/Buffer (pH 5.6).

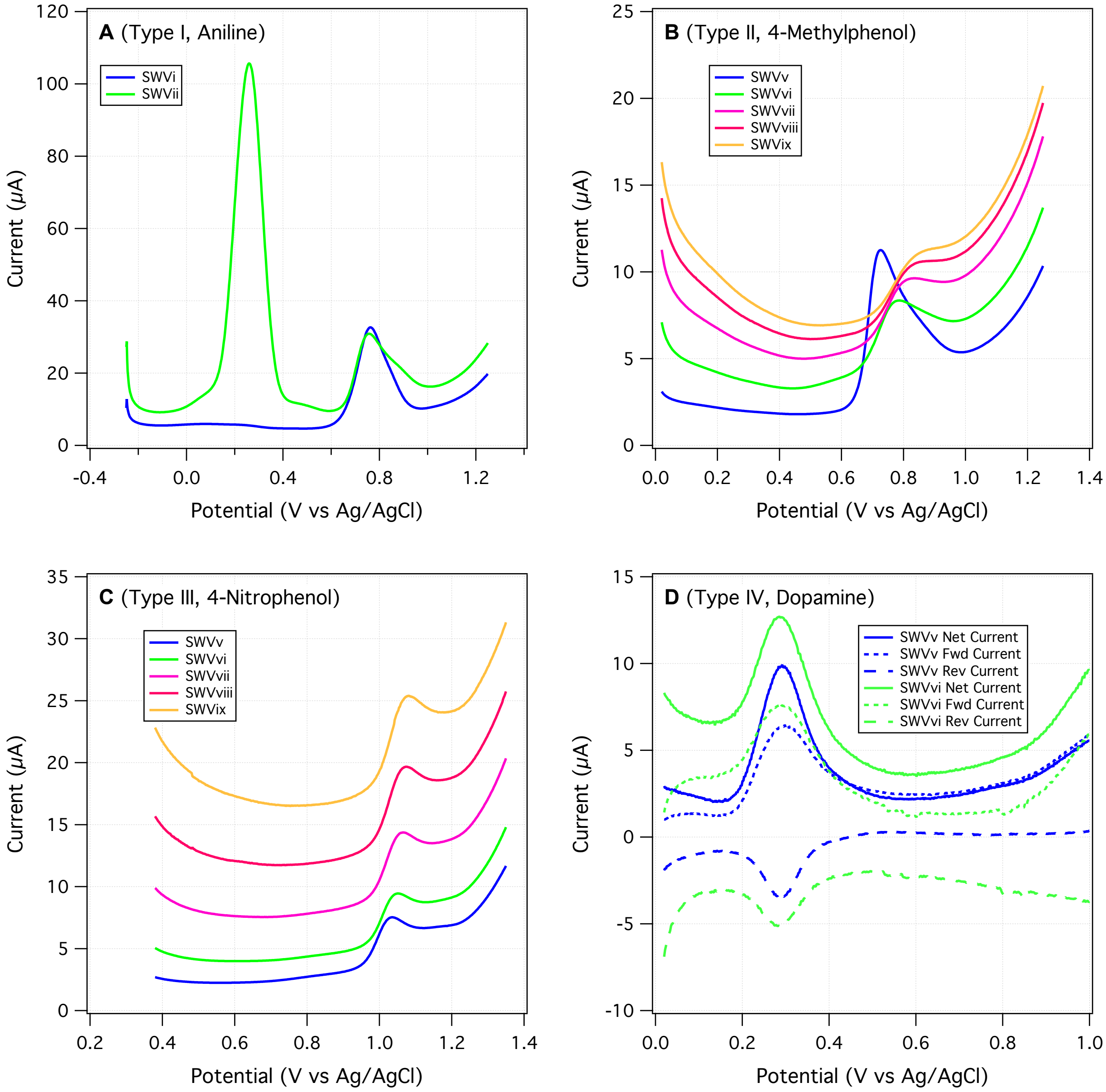

Figure S4. Four types of square wave voltammograms with a step size of 2 mV, amplitude of 50 mV and varying scan rates: 30 mV/s (SWVv), 60 mV/s (SWVvi), 120 mV/s (SWVvii), 180 mV/s (SWVviii), and 240 mV/s (SWVix). (**A**) Aniline step size 2 mV, scan rate 60 mV/s amplitude 50 mV (SWVi) and 75 mV (SWVii), (**B**) 4-methylpheol (**C**), 4-nitrophenol, (**D**) Forward, reverse and net current for Dopamine at 30 mV/s and 60 mV/s.

Electrochemical Data Analysis

To help visualize the overall significance of the variablity in electrochemical oxidation potentials over the range of relevant experimental conditions, **Figure S2** provides a summary all of the primary peak potential data (colored markers) and representative values (black markers).

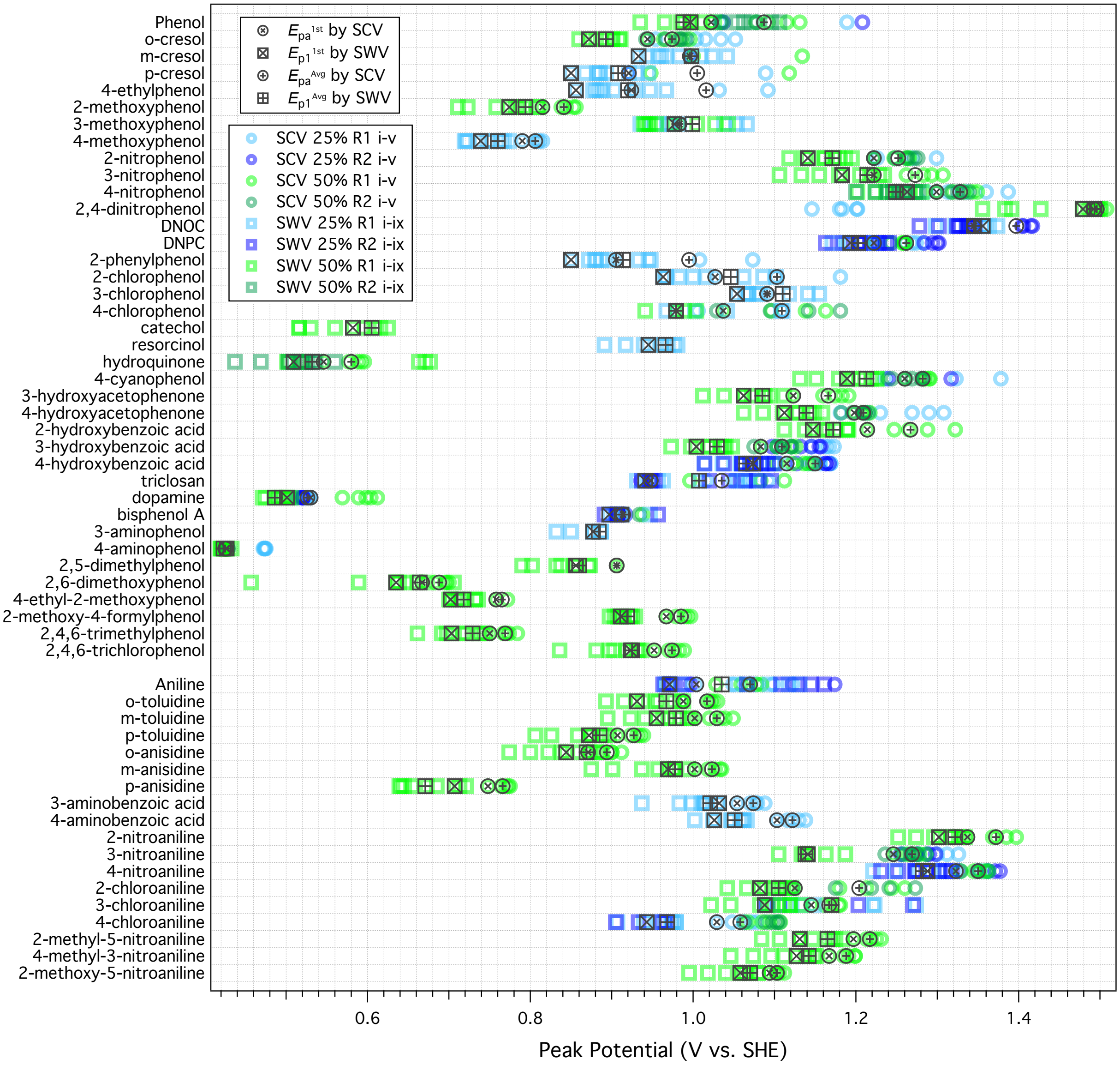

Figure S5. Summary of newly measured peak potentials for phenols and anilines vs. waveform (circles = SCV (E_{pa}), squares = SWV (E_{p1})); scan rate 25 to 330 mV/s; blue denote 25% IPA, green 50% IPA; and replicates (lighter shades are R1 and darker shades R2). Black symbols are 1st scans and average values (calculated over scan rate and replicates), these values are tabulated in Tables S4, S5.

Table S4. Recommended values of new electrochemically measured oxidation potentials for substituted phenols. All values in V vs SHE.

		Suatoni	**E_{pa1} by SCV**		**E_{pa} by SWV**	
No.	**Name**	**$E_{1/2}$** [a]	**1st Scan**	**Avg**	**1st Scan**	**Avg**
1	phenol	0.874	1.022	1.087	0.997	0.988
2	2-methylphenol	0.797	0.944	0.974	0.872	0.893
3	3-methylphenol	0.848	0.996	0.996	0.933	0.998
4	4-methylphenol	0.784	0.921	1.005	0.850	0.908
5	4-ethylphenol	0.808	0.924	1.016	0.856	0.920
6	2-methoxyphenol	0.697	0.815	0.841	0.774	0.794
7	3-methoxyphenol	0.860	0.983	0.983	0.977	0.999
8	4-methoxyphenol	0.647	0.790	0.806	0.739	0.760
9	2-nitrophenol	1.087	1.222	1.252	1.141	1.171
10	3-nitrophenol	1.096	1.222	1.273	1.183	1.214
11	4-nitrophenol	1.165	1.299	1.328	1.263	1.249
12	2,4-dinitrophenol		1.492	1.496	1.479	1.493
13	2-methyl-4,6-dinitrophenol		1.345	1.397	1.356	1.345
14	4-methyl-2,6-dinitrophenol		1.222	1.262	1.193	1.203
15	2-phenylphenol	0.804	0.905	0.995	0.850	0.914
16	2-chlorophenol	0.866	1.027	1.103	0.963	1.046
17	3-chlorophenol	0.975	1.091	1.091	1.054	1.110
18	4-chlorophenol	0.894	1.037	1.109	0.979	0.979
19	2-hydroxyphenol				0.582	0.605
20	3-hydroxyphenol				0.945	0.966
21	4-hydroxyphenol		0.546	0.580	0.509	0.532
22	4-cyanophenol		1.260	1.282	1.189	1.213
23	3-hydroxyacetophenone	0.995	1.123	1.166	1.062	1.085
24	4-hydroxyacetophenone	1.032	1.198	1.209	1.112	1.139
25	2-hydroxybenzoic acid	1.086	1.214	1.267	1.147	1.172
26	3-hydroxybenzoic acid		1.083	1.109	1.004	1.029
27	4-hydroxybenzoic acid	0.957	1.115	1.150	1.074	1.065
28	triclosan		0.948	1.035	0.941	1.007
29	dopamine		0.530	0.526	0.501	0.486
30	bisphenol A		0.914	0.914	0.897	0.912
31	3-aminophenol				0.877	0.884
32	4-aminophenol		0.426	0.425	0.427	0.423
33	2,5-dimethylphenol		0.906	0.906	0.856	0.860
34	2,6-dimethoxyphenol	0.620	0.667	0.688	0.635	0.664
35	4-ethyl-2-methoxyphenol		0.758	0.765	0.702	0.718
36	2-methoxy-4-formylphenol		0.967	0.985	0.911	0.919

37	2,4,6-trimethylphenol	0.750	0.769	0.703	0.729
38	2,4,6-trichlorophenol	0.952	0.974	0.923	0.925

a) Adjusted to SHE from the originally reported values (vs. SCE) by adding 241 mV.

Table S5. Recommended values of new electrochemically measured oxidation potentials for substituted anilines. All values in V vs SHE.

		Suatoni	**E_{pa} by SCV**		**E_{p1} by SWV**	
No.	**Name**	**$E_{1/2}$ [a]**	**1st Scan**	**Avg**	**1st Scan**	**Avg**
1	aniline	0.866	1.004	1.070	0.971	1.035
2	2-methylaniline	0.836	0.988	1.017	0.931	0.967
3	3-methylaniline	0.847	1.002	1.029	0.955	0.979
4	4-methylaniline	0.778	0.907	0.927	0.872	0.885
5	2-methoxyaniline	0.739	0.871	0.894	0.844	0.869
6	3-methoxyaniline	0.856	1.002	1.023	0.969	0.978
7	4-methoxyaniline	0.634	0.748	0.766	0.707	0.671
8	3-aminobenzoic acid	0.909	1.054	1.074	1.032	1.021
9	4-aminobenzoic acid	0.955	1.103	1.122	1.026	1.051
10	2-nitroaniline	1.230	1.337	1.372	1.302	1.322
11	3-nitroaniline	1.095	1.246	1.269	1.141	1.138
12	4-nitroaniline	1.176	1.323	1.350	1.288	1.282
13	2-chloroaniline	0.983	1.125	1.204	1.082	1.105
14	3-chloroaniline	1.015	1.145	1.167	1.088	1.170
15	4-chloroaniline	0.916	1.029	1.058	0.943	0.968
16	2-methyl-5-nitroaniline	1.062	1.197	1.217	1.131	1.165
17	4-methyl-3-nitroaniline		1.167	1.188	1.127	1.142
18	2-methoxy-5-nitroaniline		1.094	1.103	1.058	1.070

a) Adjusted to SHE from the originally reported values (vs. SCE) by adding 241 mV.

Electrochemical Data Comparison

To help visualize the overall agreement between the recommended electrochemical oxidation potentials from this work and previously reported values measured under similar conditions, we have summarized all of our data (from **Table S3, S4**) and selected literature data (not tabulated) in **Figure S3**. The data from Li et al.[6] were anodic peak potentials obtained at pH 12 and Simić et al.[11] listed anodic peak potentials at pH 7. From experimental data for phenol in Li et., we estimated an average decrease of 55.3 mV per pH unit, and that slope was used to calculate potentials adjusted to pH 5.35 (the average of 5.6 and 5.1, the range of pH measured in this work). The same slope was assumed for adjusting the potentials in Simic et al. to pH 5.35. For the anilines, all of which have pK_a's above this pH, no change in potential was assumed. The data from Erickson et al.[12] were for anilines and since all anilines had a pK_a < pH, conditions where potential is not dependent on pH, no adjustment was made.

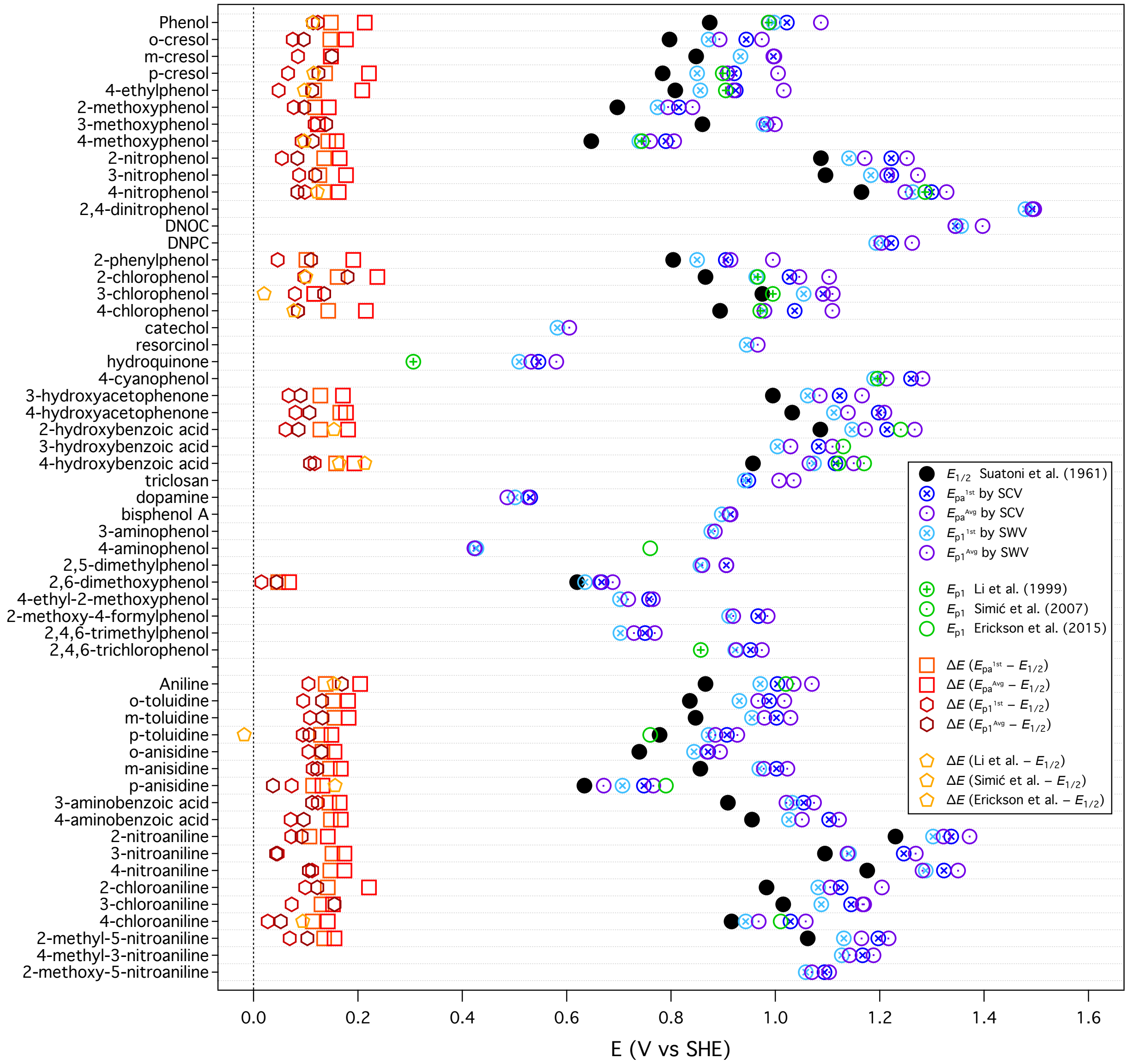

Figure S6. Summary of peak potentials ($E_{pa}{}^{1st}$ and $E_{pa}{}^{Avg}$ from SCV; $E_{p1}{}^{1st}$ and $E_{p1}{}^{Avg}$ from SWV) for phenols and anilines vs. literature data from Suatoni et al.[5] and others.[6, 11, 12] ΔE is the difference between experimental and literature values. The data from Li et al and Simić et al. were adjusted to pH 5.35, as described above.

Computational Methods

For calculation of oxidation potentials (ΔG^0_{ox} and E_{ox}) for the phenols and anilines, we used methods similar to those in our previous work on oxidation of aromatic amines,[4] while adopting some modifications based on (*i*) recent work on similar problems,[13] (*ii*) other work on the general problem of computational electrochemistry,[14-16] and (*iii*) recent advances in the NWChem code (Including bug fixes for the M06-2x functional and porting of COSMO-SMD method. Available in development tree (http://www.nwchem-sw.org/index.php/Developer) and available in release 6.7, February 2017). For both phenols and anilines, only the initial oxidation step was modeled, assuming it involves only the loss of a single electron from the neutral form of the parent compound to give the corresponding radical cation (i.e., equations S1-S2).

$$\mathrm{HOAr}_{(aq)} \rightarrow \mathrm{HOAr}^{\bullet +}_{(aq)} + e^-_{(g)} \tag{S1}$$

$$\mathrm{NH_2Ar}_{(aq)} \rightarrow \mathrm{NH_2Ar}^{\bullet +}_{(aq)} + e^-_{(g)} \tag{S2}$$

For these half-reactions, ΔG^0_{ox} and E_{ox} were calculated from gas phase reaction energy, entropy, and solvation energy differences computed with the NWChem program suite.[17] The electronic structure calculations were carried out using density functional theory (DFT) calculations[18] using the 6-311++G(2d,2p) basis set[19, 20] and the B3LYP,[21, 22] and M06-2X[23] exchange correlation functionals. These functionals were found to produce good correlations for oxidation in our previous work,[4] In these calculations, the geometries of the neutral and radical cation species were optimized first and then the vibrational frequencies were determined by using a finite difference approach. The free energies in the gas phase were determined using the gas-phase optimized structures and frequencies as input for free energy formulae derived from statistical mechanics.[24, 25]

Solvation energies for solutes were approximated as a sum of non-covalent electrostatic, cavitation, and dispersion energies (using the same methods we used in recent work on nitro reduction of energetic compounds[26]). The electrostatic contributions to the solvation energies were estimated by using the self-consistent reaction field theory of Klamt and Schüürmann (COSMO),[27] with the cavity defined by a set of overlapping atomic spheres with radii suggested by Stefanovich and Truong[28] (H– 1.172 Å, C– 2.096 Å, C= 1.635 Å, O– 1.576 Å, and Cl– 1.750 Å). In addition, the solvation energy were estimated using the COSMO-SMD method implemented into NWChem by the Cramer group. The dielectric constant of water used for all of the solvation calculations was 78.4.[27] The cavitation and dispersion contributions to the solvation energy are less straight-forward to handle because the interactions take place at short distances, so several methods have been proposed to do this.[29-36] One of the simplest approaches for estimating these terms is to use empirically derived expressions that depend only on the solvent accessible surface area. In this study, the widely used formula of Sitkoff *et al.*[33] was used to augment the COSMO calculations,

$$\Delta G_{cav+disp} = \gamma A + b \tag{S3}$$

where ɣ and *b* are constants set to 5 cal/mol-Å^2 and 0.86 kcal mol^{-1} respectively. Sitkoff *et al.* parameterized the constants ɣ and *b* to the experimentally determined free energies of solvation of alkanes[37] by using a least-squares fit. The Shrake-Rupley algorithm was used to determine the solvent accessible surface areas.[38] The COSMO-SMD code automatically takes into account atomic sphere radii and the cavitation and dispersion contributions to the solvation energy.

The calculated free energies of reaction was converted to one-electron oxidation potentials (E_{ox}) vs. the standard hydrogen electrode (SHE) using equation S4

$$E_{ox} = -\left(\frac{-\Delta G_{ox}^{0}}{nF} + E_{H}^{0} \right) \tag{S4}$$

where n is the number of electrons transferred (in this case, $n = 1$), F is the Faraday constant (F = 23.061 kcal mol^{-1}), and E^0_{h} (the absolute potential of the SHE) = 98.6 kcal mol^{-1} = 4.28 V.

The EMSL Arrows scientific service was used to carry out and keep track of the large number of calculations (>500 E_{ox} calculations) used in this study. EMSL Arrows is a new scientific service (started in August 2016) that combines NWChem, SQL and NOSQL databases, email, and web APIs that simplifies molecular and materials modeling and can be used carry out and manage large numbers of complex calculations with diverse levels of theories. More information on EMSL Arrows can be found at the www.arrows.emsl.pnl.gov/api and http://www.nwchem-sw.org/index.php/EMSL_Arrows# websites.

Table S6. Calculated potentials (E_1) for the one-electron oxidation of phenols. All data in Volts vs. SHE. The corresponding values corrected by calibration (E_{1c}) are given in Tables S9.

		B3LYP		**M026X**	
No.	**Name**	**COSMO**	**SMD**	**COSMO**	**SMD**
1	phenol	1.5664	1.7382	1.7623	1.9004
2	2-methylphenol	1.469	1.6026	1.6768	1.9621
3	3-methylphenol	1.5367	1.8477	1.7058	1.9029
4	4-methylphenol	1.334	1.6386	1.5477	1.6695
5	2,4-dimethylphenol	1.2309	1.359	1.4122	1.5606
6	2,5-dimethylphenol	1.3419	1.4638	1.5271	1.6459
7	2,4,6-trimethylphenol	1.1395	1.1305	1.428	1.6335
8	2-ethylphenol	1.4533	1.4654	1.6668	1.7985
9	3-ethylphenol	1.4696	1.4907	1.7088	2.0151
10	4-ethylphenol	1.3706	1.4725	1.5898	1.7145
11	2-t-butylphenol	1.4332	1.5678	1.7157	1.7645
12	3-t-butylphenol	1.4285	1.4434	1.6637	1.969
13	4-t-butylphenol	1.3438	1.5009	1.6327	1.8703
14	2-methoxyphenol	1.257	1.2141	1.4984	1.6445
15	3-methoxyphenol	1.3152	1.2365	1.6173	1.7664
16	4-methoxyphenol	1.0197	1.176	1.2455	1.3756
17	2,6-dimethoxyphenol	1.251	1.6515	1.5693	1.7056
18	2-methoxy-4-ethylphenol	1.0576	1.1983	1.2653	1.6607
19	2-methoxy-4-formylphenol	1.3775	1.5171	1.6381	1.4337
20	2-ethoxyphenol	1.2621	1.4159	1.4971	1.8255
21	3-ethoxyphenol	1.2865	1.4346	1.5086	1.9633
22	4-ethoxyphenol	1.0132	1.1668	1.2438	1.3621
23	2-nitrophenol	2.0103	2.6041	2.2212	2.4025
24	3-nitrophenol	1.9082	2.5475	2.1526	2.3624
25	4-nitrophenol	2.1704	2.3792	2.3239	2.5027
26	2,4-dinitrophenol	2.5103	2.1743	2.7433	3.5361
27	2-methyl-4,6-dinitrophenol	2.2734	2.3786	2.5381	2.6395
28	4-methyl-2,6-dinitrophenol	2.2468	2.3852	2.337	2.481
29	2-phenylphenol	1.4069	1.7238	1.7343	2.0495
30	3-phenylphenol	1.4964	1.433	1.8019	2.1329
31	4-phenylphenol	1.2003	1.3526	1.6044	1.6618
32	2-chlorophenol	1.6829	1.8981	1.8768	1.9621
33	3-chlorophenol	1.6487	2.0187	1.9067	2.2325
34	4-chlorophenol	1.5256	1.5859	1.7491	1.7759
35	2,4-dichlorophenol	1.6297	1.8565	1.8649	2.084
36	2,4,6-trichlorophenol	1.7459	1.9267	1.9616	2.1419

37	pentachlorophenol (PCP)	1.8762	2.1674	2.1516	2.4407
38	2-hydroxyphenol	1.2572	1.4419	1.4219	1.6006
39	3-hydroxyphenol	1.3877	1.5898	1.6386	1.8304
40	4-hydroxyphenol	1.065	1.2548	1.2278	1.4097
41	2-cyanophenol	1.8109	2.0866	2.0221	2.282
42	3-cyanophenol	1.7759	2.05	2.0075	2.2788
43	4-cyanophenol	1.8133	2.0726	2.0987	2.3015
44	2-hydroxyacetophenone	1.783	1.9483	1.9862	2.4141
45	3-hydroxyacetophenone	1.7199	2.2134	1.9077	2.3993
46	4-hydroxyacetophenone	1.813	1.6931	2.0712	2.2344
47	2-hydroxybenzoic acid	1.9288	2.1219	2.09	2.7013
48	3-hydroxybenzoic acid	1.7943	1.5741	1.9654	2.2047
49	4-hydroxybenzoic acid	1.9212	2.0784	2.0872	2.7039
50	4-sulfonatophenol [a]	1.3246	2.1543	1.6096	2.4189
51	4-alanylphenol [a]	1.6921	2.0828	1.9513	2.5268
52	triclosan	1.4401	1.6444	1.6857	2.0753
53	dopamine	1.1791	1.5809	1.4789	1.7901
54	p-coumaric acid	1.4431	2.0574	1.6794	2.2915
55	bisphenol A	1.3205	1.7158	1.7178	2.2197

a) IUPAC or common name: 52, 4-hydroxybenzenesulfonate; 53, 2-amino-4'hydroxypropiophenone.

Table S7. Calculated potentials (E_1) for the one-electron oxidation of anilines. All data in Volts vs. SHE. The corresponding values corrected by calibration (E_{1c}) are given in Tables S10.

		B3LYP		**M062X**	
No.	**Name**	**COSMO**	**SMD**	**COSMO**	**SMD**
1	aniline	0.9805	1.0183	1.1785	1.2119
2	2-methylaniline	0.8313	0.9369	1.1173	1.1429
3	3-methylaniline	0.9317	1.0226	1.1221	1.1588
4	4-methylaniline	0.8039	0.8351	0.9915	1.0171
5	2,4-dimethylaniline	0.7374	0.7553	0.9442	0.9369
6	2,5-dimethylaniline	0.8453	0.8693	1.0487	1.1078
7	2,4,6-trimethylaniline	0.6955	0.6753	0.9006	0.8046
8	2-ethylaniline	0.917	0.9957	1.1251	1.1466
9	3-ethylaniline	0.9127	0.8801	1.1699	1.1896
10	4-ethylaniline	0.8368	0.9179	1.0404	1.0468
11	2-t-butylaniline	0.8763	0.8301	1.0055	1.1167
12	3-t-butylaniline	0.8933	0.9265	1.1725	1.2876
13	4-t-butylaniline	0.8681	0.8327	1.0465	1.0131
14	2-methoxyaniline	0.6992	0.7342	0.9036	0.936
15	3-methoxyaniline	0.8778	0.9408	1.1245	1.1797
16	4-methoxyaniline	0.5727	0.6365	0.791	0.8341
17	2,6-dimethoxyaniline	0.618	0.4657	0.834	0.8915
18	4-ethyl-2-methoxyaniline	0.5692	0.6144	0.8259	0.9248
19	2-methoxy-4-formylaniline [a]	1.1	1.14	1.1995	1.3145
20	2-ethoxyaniline	0.7372	0.6548	0.9595	1.1361
21	3-ethoxyaniline	0.8531	0.9374	1.1621	1.2069
22	4-ethoxyaniline	0.5570	0.473	0.7745	0.815
23	2-nitroaniline	1.5473	1.6337	1.6911	2.06
24	3-nitroaniline	1.3237	1.3951	1.5071	1.5805
25	4-nitroaniline	1.5719	1.6412	1.6844	1.7172
26	2,4-dinitroaniline	2.1061	2.1971	2.3424	1.9168
27	4,6-dinitro-2-methylaniline	1.5557	1.6286	1.7708	1.8659
28	2,6-dinitro-4-methylaniline	1.8677	1.9147	2.0529	2.1039
29	2-phenylaniline	0.9411	0.882	1.1762	1.2141
30	3-phenylaniline	0.9749	1.0319	1.2111	1.2448
31	4-phenylaniline	0.7967	0.951	1.1303	1.1752
32	2-chloroaniline	1.1252	1.1379	1.3386	1.3826
33	3-chloroaniline	1.1251	1.1768	1.3333	1.3793
34	4-chloroaniline	0.9966	1.0502	1.2474	1.2615
35	2,4-dichloroaniline	1.129	1.2353	1.3199	1.4207
36	2,4,6-trichloroaniline	1.2614	1.4721	1.4858	1.6926

37	pentachloroaniline	1.4367	1.6959	1.6451	1.8982
38	2-hydroxyaniline [a]	0.9115	0.7316	1.1203	1.1487
39	3-hydroxyaniline [a]	0.9359	0.8228	1.1784	1.2444
40	4-hydroxyaniline [a]	0.6033	0.4921	0.795	0.8627
41	2-cyanoaniline	1.2937	1.41	1.493	1.6046
42	3-cyanoaniline	1.175	1.2807	1.3498	1.4472
43	4-cyanoaniline	1.2328	1.3515	1.4277	1.5235
44	2-acetylaniline	1.2314	1.2774	1.4345	1.6863
45	3-acetylaniline	1.127	0.9587	1.34	1.368
46	4-acetylaniline	1.2386	1.2975	1.4659	1.4827
47	2-aminobenzoic acid	1.3466	1.3814	1.5662	1.5996
48	3-aminobenzoic acid	1.1802	0.8996	1.4011	1.4911
49	4-aminobenzoic acid	1.2981	1.3658	1.4835	1.5299
50	4-sulfonatoaniline [a]	1.0971	1.7675	1.292	1.9484
51	4-alanylaniline [a]	1.4162	1.7355	1.4955	1.3438

a) IUPAC or common name: 20, 4-amino-3-methoxybenzaldehyde; 40-42, aminophenol (2,3, and 4); 52, 4-aminobenzenesulfonate; 53, 2-amino-1-(4-aminophenyl)-1-propanone.

Computational Data Analysis

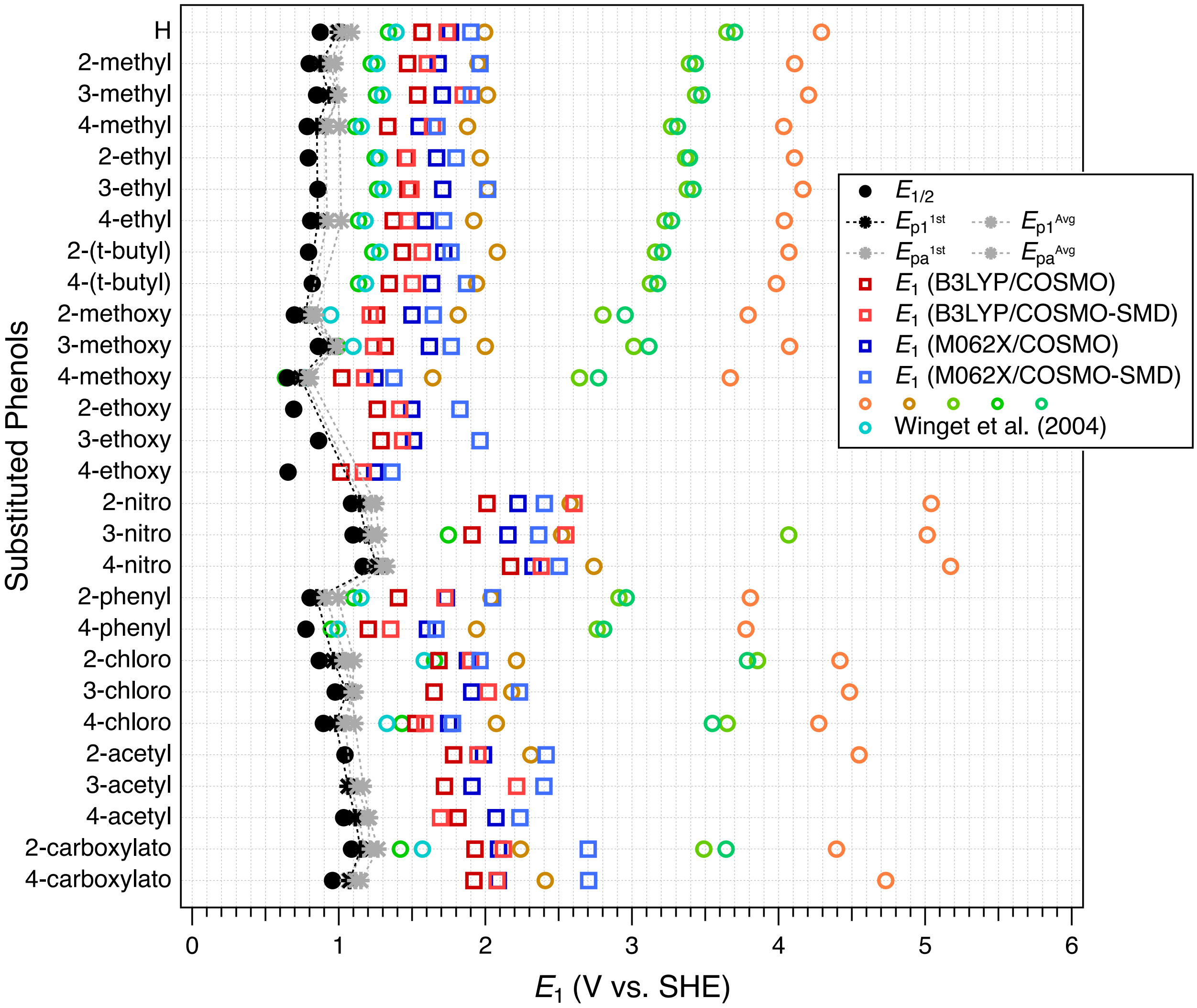

Figure S7. Summary of calculated one-electron oxidation potentials (E_1) for phenols, including values reported in previous work and here (**Table S6**). Color markers represent various computational conditions (squares = this study; circles = Winget et al.). Black symbols are $E_{1/2}$ from Suatoni et al. and $E_{p1}{}^{1st}$ from **Table S4**.

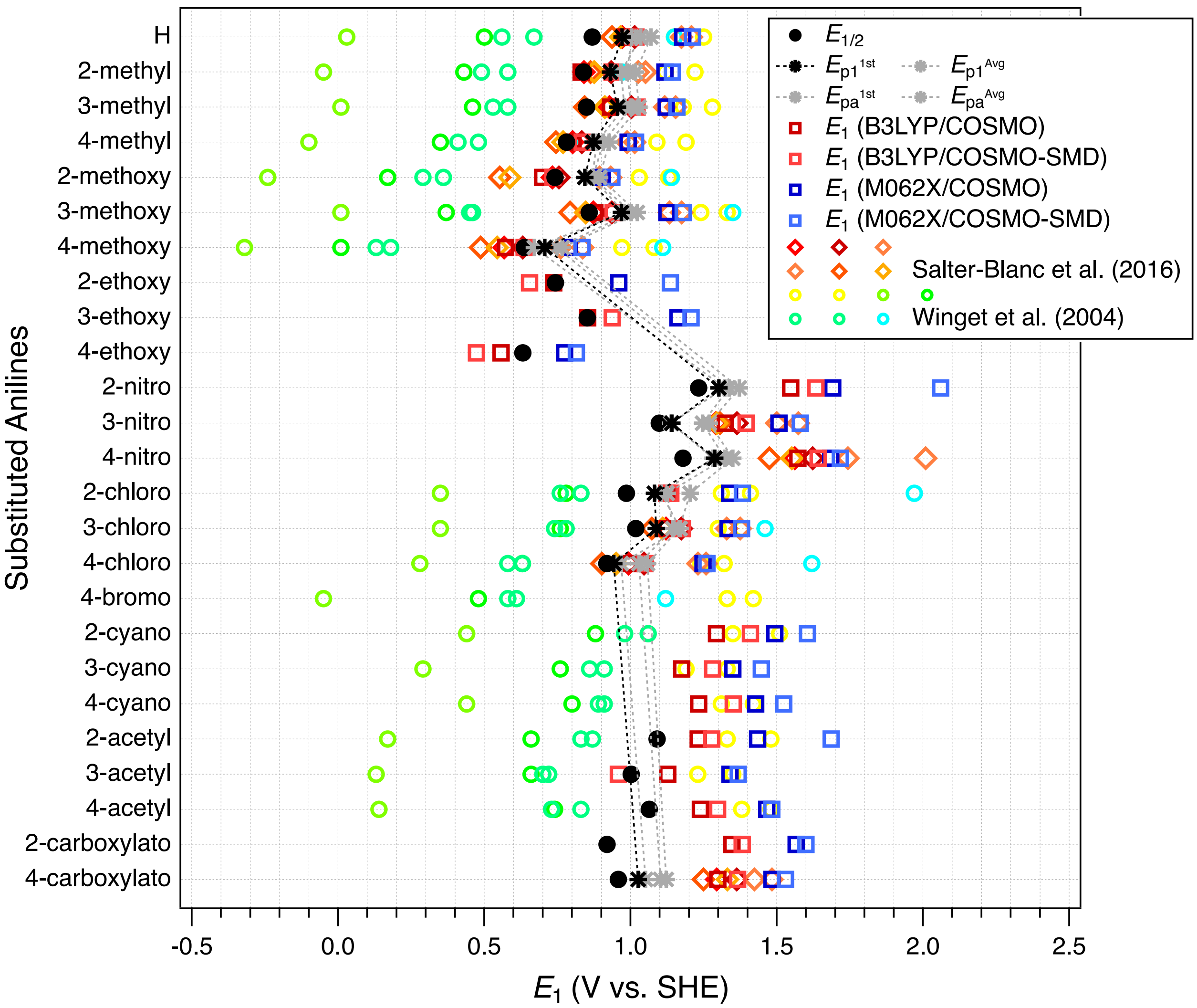

Figure S8. Summary of calculated one-electron oxidation potentials (E_1) for anilines, including values reported in previous work and here (**Table S7**). Color markers represent various computational conditions (squares = this study; circles = Salter et al. and Winget et al.). Black symbols are $E_{1/2}$ from Suatoni et al. and $E_{p1}{}^{1st}$ from **Table S5**.

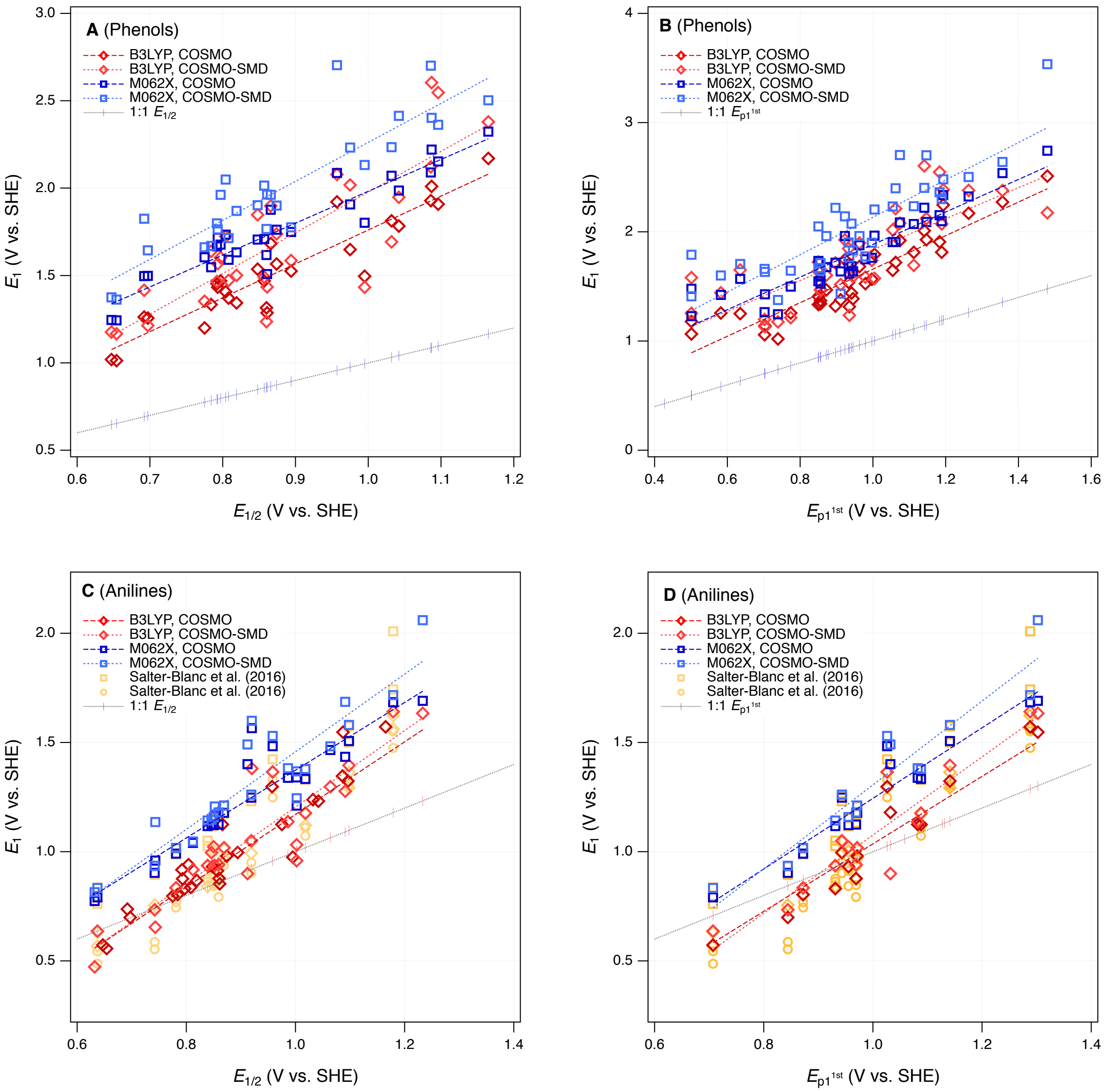

Figure S9. Calibrations of calculated one-electron oxidation potentials (E_1) to experimental potentials from Suatoni et al. ($E_{1/2}$) and this work ($E_{p1}{}^{1st}$). Data are from **Tables S6-S7** and **S4-S5**, respectively. For the anilines, selected E_1's from our prior work are included. Markers and colors represent various conditions used in calculating E_1. The 1:1 line is based on the measured potential on the X axis.

Table S8. Regression equations from calibrations in Figure S9.

Fig	**Calibration Variables**	**Intercept (a)**	**Slope (b)**	r^2	s_{xy}	*n*
		Phenols				
S9a	E_1 (B3LYP/COSMO) vs. $E_{1/2}$	−0.18 ± 0.14	1.94 ± 0.16	0.855	0.113	28
S9a	E_1 (B3LYP/COSMO-SMD) vs. $E_{1/2}$	−0.35 ± 0.27	2.33 ± 0.31	0.689	0.222	28
S9a	E_1 (M062X/COSMO) vs. $E_{1/2}$	0.16 ± 0.11	1.82 ± 0.13	0.883	0.094	28
S9a	E_1 (M062X/COSMO-SMD) vs. $E_{1/2}$	0.03 ± 0.20	2.23 ± 0.23	0.783	0.167	28
S9b	E_1 (B3LYP/COSMO) vs. $E_{p1}{}^{1st}$	0.12 ± 0.11	1.54 ± 0.11	0.849	0.147	36
S9b	E_1 (B3LYP/COSMO-SMD) vs. $E_{p1}{}^{1st}$	0.42 ± 0.19	1.42 ± 0.19	0.611	0.256	36
S9b	E_1 (M062X/COSMO) vs. $E_{p1}{}^{1st}$	0.39 ± 0.10	1.49 ± 0.10	0.866	0.133	36
S9b	E_1 (M062X/COSMO-SMD) vs. $E_{p1}{}^{1st}$	0.42 ± 0.18	1.71 ± 0.18	0.716	0.244	36
		Anilines				
S9c	E_1 (B3LYP/COSMO) vs. $E_{1/2}$	−0.56 ± 0.11	1.77 ± 0.12	0.895	0.086	28
S9c	E_1 (B3LYP/COSMO-SMD) vs. $E_{1/2}$	−0.54 ± 0.15	1.75 ± 0.16	0.835	0.121	25
S9c	E_1 (M062X/COSMO) vs. $E_{1/2}$	−0.18 ± 0.12	1.55 ± 0.13	0.863	0.096	25
S9c	E_1 (M062X/COSMO-SMD) vs. $E_{1/2}$	−0.32 ± 0.14	1.78 ± 0.32	0.806	0.109	10
S9d	E_1 (B3LYP/COSMO) vs. $E_{p1}{}^{1st}$	−0.74 ± 0.15	1.78 ± 0.14	0.922	0.085	15
S9d	E_1 (B3LYP/COSMO-SMD) vs. $E_{p1}{}^{1st}$	−0.71 ± 0.19	1.79 ± 0.19	0.877	0.109	15
S9d	E_1 (M062X/COSMO) vs. $E_{p1}{}^{1st}$	−0.37 ± 0.14	1.62 ± 0.14	0.914	0.081	15
S9d	E_1 (M062X/COSMO-SMD) vs. $E_{p1}{}^{1st}$	−0.61 ± 0.181	1.92 ± 0.18	0.900	0.104	15

Intercept and slope are reported ± 1 standard deviation.
No ad hoc outliers were excluded from the regressions.

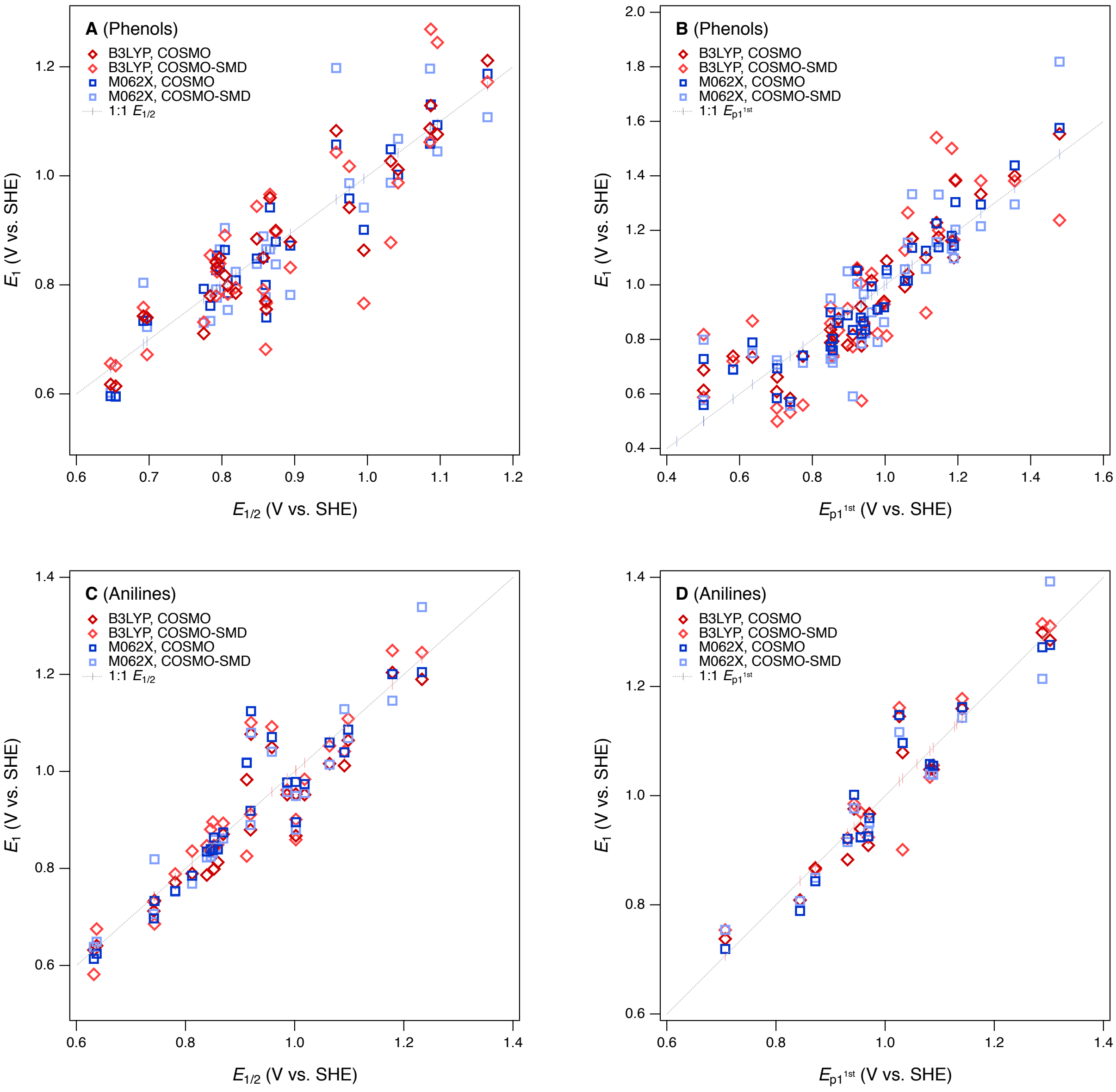

Figure S10. Summary of calibrated calculated one-electron oxidation potentials (E_{1c}) for phenols (**Tables S9, S11**) and anilines (**Tables S10, S12**) vs. measured potentials used in the corresponding calibration. Markers and colors represent various computational conditions. The 1:1 line is based on the measured potential on the X axis.

Table S9. Calculated potentials with correction by calibration ($E_{1\mathrm{c}}$) to $E_{1/2}$ for the one-electron oxidation of phenols. Based on values of E_1 in Table S6. All data in Volts vs. SHE.

		B3LYP		M026X	
No.	**Name**	**COSMO**	**SMD**	**COSMO**	**SMD**
1	phenol	0.900	0.897	0.879	0.838
2	2-methylphenol	0.849	0.839	0.833	0.865
3	3-methylphenol	0.884	0.944	0.848	0.839
4	4-methylphenol	0.780	0.854	0.762	0.734
5	2,4-dimethylphenol	0.727	0.734	0.688	0.685
6	2,5-dimethylphenol	0.784	0.779	0.751	0.724
7	2,4,6-trimethylphenol	0.679	0.636	0.696	0.718
8	2-ethylphenol	0.841	0.780	0.827	0.792
9	3-ethylphenol	0.850	0.791	0.850	0.889
10	4-ethylphenol	0.799	0.783	0.785	0.754
11	2-t-butylphenol	0.831	0.824	0.854	0.777
12	3-t-butylphenol	0.829	0.771	0.825	0.868
13	4-t-butylphenol	0.785	0.795	0.808	0.824
14	2-methoxyphenol	0.740	0.672	0.735	0.723
15	3-methoxyphenol	0.770	0.682	0.800	0.778
16	4-methoxyphenol	0.618	0.656	0.596	0.602
17	2,6-dimethoxyphenol	0.737	0.860	0.774	0.750
18	2-methoxy-4-ethylphenol	0.637	0.665	0.607	0.730
19	2-methoxy-4-formylphenol	0.802	0.802	0.811	0.628
20	2-ethoxyphenol	0.743	0.759	0.734	0.804
21	3-ethoxyphenol	0.755	0.767	0.740	0.866
22	4-ethoxyphenol	0.614	0.652	0.595	0.596
23	2-nitrophenol	1.129	1.269	1.131	1.063
24	3-nitrophenol	1.076	1.245	1.093	1.045
25	4-nitrophenol	1.212	1.172	1.187	1.108
26	2,4-dinitrophenol	1.387	1.084	1.417	1.571
27	2-methyl-4,6-dinitrophenol	1.265	1.172	1.305	1.169
28	4-methyl-2,6-dinitrophenol	1.251	1.175	1.194	1.098
29	2-phenylphenol	0.817	0.891	0.864	0.905
30	3-phenylphenol	0.864	0.766	0.901	0.942
31	4-phenylphenol	0.711	0.732	0.793	0.731
32	2-chlorophenol	0.960	0.966	0.942	0.865
33	3-chlorophenol	0.942	1.018	0.959	0.987
34	4-chlorophenol	0.879	0.832	0.872	0.782
35	2,4-dichlorophenol	0.932	0.948	0.936	0.920
36	2,4,6-trichlorophenol	0.992	0.978	0.989	0.946

37	pentachlorophenol (PCP)	1.060	1.081	1.093	1.080
38	2-hydroxyphenol	0.740	0.770	0.693	0.703
39	3-hydroxyphenol	0.808	0.834	0.812	0.806
40	4-hydroxyphenol	0.641	0.690	0.586	0.618
41	2-cyanophenol	1.026	1.047	1.022	1.009
42	3-cyanophenol	1.008	1.031	1.014	1.007
43	4-cyanophenol	1.027	1.041	1.064	1.018
44	2-hydroxyacetophenone	1.012	0.987	1.002	1.068
45	3-hydroxyacetophenone	0.979	1.101	0.959	1.061
46	4-hydroxyacetophenone	1.027	0.878	1.049	0.987
47	2-hydroxybenzoic acid	1.087	1.062	1.059	1.197
48	3-hydroxybenzoic acid	1.017	0.827	0.991	0.974
49	4-hydroxybenzoic acid	1.083	1.043	1.058	1.198
50	4-sulfonatophenol [a]	0.775	1.076	0.796	1.070
51	4-alanylphenol [a]	0.965	1.045	0.983	1.119
52	triclosan	0.835	0.857	0.837	0.916
53	dopamine	0.700	0.830	0.724	0.788
54	p-coumaric acid	0.836	1.034	0.834	1.013
55	bisphenol A	0.773	0.888	0.855	0.981

a) IUPAC or common name: 52, 4-hydroxybenzenesulfonate; 53, 2-amino-4’hydroxypropiophenone.

Table S10. Calculated potentials with correction by calibration (E_{1c}) to $E_{1/2}$ for the one-electron oxidation of anilines. Based on values of E_1 in Table S7. All data in Volts vs. SHE.

		B3LYP		M062X	
No.	**Name**	**COSMO**	**SMD**	**COSMO**	**SMD**
1	aniline	0.871	0.893	0.874	0.862
2	2-methylaniline	0.787	0.847	0.835	0.823
3	3-methylaniline	0.843	0.896	0.838	0.832
4	4-methylaniline	0.771	0.789	0.754	0.752
5	2,4-dimethylaniline	0.734	0.743	0.723	0.707
6	2,5-dimethylaniline	0.794	0.808	0.791	0.803
7	2,4,6-trimethylaniline	0.710	0.697	0.695	0.632
8	2-ethylaniline	0.835	0.880	0.840	0.825
9	3-ethylaniline	0.832	0.814	0.869	0.849
10	4-ethylaniline	0.790	0.836	0.785	0.769
11	2-t-butylaniline	0.812	0.786	0.763	0.808
12	3-t-butylaniline	0.822	0.841	0.870	0.904
13	4-t-butylaniline	0.807	0.787	0.789	0.750
14	2-methoxyaniline	0.712	0.731	0.697	0.706
15	3-methoxyaniline	0.813	0.849	0.839	0.843
16	4-methoxyaniline	0.641	0.675	0.624	0.649
17	2,6-dimethoxyaniline	0.666	0.578	0.652	0.681
18	4-ethyl-2-methoxyaniline	0.639	0.663	0.647	0.700
19	2-methoxy-4-formylaniline [a]	0.938	0.963	0.888	0.919
20	2-ethoxyaniline	0.734	0.686	0.733	0.819
21	3-ethoxyaniline	0.799	0.847	0.864	0.859
22	4-ethoxyaniline	0.632	0.582	0.614	0.638
23	2-nitroaniline	1.190	1.245	1.205	1.339
24	3-nitroaniline	1.064	1.109	1.086	1.069
25	4-nitroaniline	1.204	1.249	1.200	1.146
26	2,4-dinitroaniline	1.505	1.567	1.625	1.258
27	4,6-dinitro-2-methylaniline	1.195	1.242	1.256	1.230
28	2,6-dinitro-4-methylaniline	1.370	1.406	1.438	1.363
29	2-phenylaniline	0.848	0.815	0.873	0.863
30	3-phenylaniline	0.867	0.901	0.895	0.880
31	4-phenylaniline	0.767	0.855	0.843	0.841
32	2-chloroaniline	0.952	0.962	0.977	0.958
33	3-chloroaniline	0.952	0.984	0.974	0.956
34	4-chloroaniline	0.880	0.912	0.919	0.890
35	2,4-dichloroaniline	0.954	1.017	0.965	0.979
36	2,4,6-trichloroaniline	1.029	1.153	1.072	1.132

37	pentachloroaniline	1.128	1.280	1.175	1.248
38	2-hydroxyaniline [a]	0.832	0.730	0.837	0.826
39	3-hydroxyaniline [a]	0.846	0.782	0.874	0.880
40	4-hydroxyaniline [a]	0.658	0.593	0.627	0.665
41	2-cyanoaniline	1.047	1.117	1.077	1.083
42	3-cyanoaniline	0.980	1.043	0.985	0.994
43	4-cyanoaniline	1.013	1.084	1.035	1.037
44	2-acetylaniline	1.012	1.041	1.039	1.129
45	3-acetylaniline	0.953	0.859	0.978	0.949
46	4-acetylaniline	1.016	1.053	1.060	1.014
47	2-aminobenzoic acid	1.077	1.101	1.124	1.080
48	3-aminobenzoic acid	0.983	0.826	1.018	1.019
49	4-aminobenzoic acid	1.050	1.092	1.071	1.041
50	4-sulfonatoaniline [a]	0.936	1.321	0.947	1.276
51	4-alanylaniline [a]	1.116	1.303	1.079	0.936

a) IUPAC or common name: 20, 4-amino-3-methoxybenzaldehyde; 40-42, aminophenol (2,3,and 4); 52, 4-aminobenzenesulfonate; 53, 2-amino-1-(4-aminophenyl)-1-propanone.

Table S11. Calculated potentials with correction by calibration (E_{1c}) to E_{p1} for the one-electron oxidation of phenols. Based on values of E_1 in Table S6. All data in Volts vs. SHE.

		B3LYP		**M026X**	
No.	**Name**	**COSMO**	**SMD**	**COSMO**	**SMD**
1	phenol	0.940	0.929	0.918	0.864
2	2-methylphenol	0.876	0.834	0.861	0.900
3	3-methylphenol	0.920	1.007	0.880	0.865
4	4-methylphenol	0.789	0.859	0.774	0.729
5	2,4-dimethylphenol	0.721	0.662	0.683	0.665
6	2,5-dimethylphenol	0.794	0.736	0.760	0.715
7	2,4,6-trimethylphenol	0.662	0.500	0.694	0.708
8	2-ethylphenol	0.866	0.737	0.854	0.804
9	3-ethylphenol	0.877	0.755	0.882	0.931
10	4-ethylphenol	0.812	0.742	0.802	0.755
11	2-t-butylphenol	0.853	0.809	0.887	0.784
12	3-t-butylphenol	0.850	0.721	0.852	0.904
13	4-t-butylphenol	0.795	0.762	0.831	0.846
14	2-methoxyphenol	0.738	0.559	0.741	0.714
15	3-methoxyphenol	0.776	0.575	0.821	0.785
16	4-methoxyphenol	0.584	0.532	0.572	0.557
17	2,6-dimethoxyphenol	0.735	0.868	0.789	0.750
18	2-methoxy-4-ethylphenol	0.609	0.548	0.585	0.724
19	2-methoxy-4-formylphenol	0.817	0.773	0.835	0.591
20	2-ethoxyphenol	0.742	0.702	0.740	0.820
21	3-ethoxyphenol	0.758	0.715	0.748	0.900
22	4-ethoxyphenol	0.580	0.526	0.570	0.549
23	2-nitrophenol	1.229	1.541	1.226	1.157
24	3-nitrophenol	1.162	1.501	1.180	1.133
25	4-nitrophenol	1.333	1.382	1.295	1.215
26	2,4-dinitrophenol	1.554	1.237	1.576	1.819
27	2-methyl-4,6-dinitrophenol	1.400	1.382	1.438	1.295
28	4-methyl-2,6-dinitrophenol	1.383	1.386	1.304	1.203
29	2-phenylphenol	0.836	0.919	0.899	0.951
30	3-phenylphenol	0.894	0.714	0.945	0.999
31	4-phenylphenol	0.702	0.657	0.812	0.724
32	2-chlorophenol	1.016	1.042	0.995	0.900
33	3-chlorophenol	0.993	1.127	1.015	1.058
34	4-chlorophenol	0.913	0.822	0.909	0.791
35	2,4-dichlorophenol	0.981	1.013	0.987	0.971
36	2,4,6-trichlorophenol	1.057	1.062	1.052	1.005

37	pentachlorophenol (PCP)	1.141	1.232	1.179	1.179
38	2-hydroxyphenol	0.739	0.720	0.690	0.688
39	3-hydroxyphenol	0.823	0.825	0.835	0.823
40	4-hydroxyphenol	0.613	0.588	0.560	0.577
41	2-cyanophenol	1.099	1.175	1.092	1.086
42	3-cyanophenol	1.076	1.150	1.083	1.085
43	4-cyanophenol	1.100	1.165	1.144	1.098
44	2-hydroxyacetophenone	1.081	1.078	1.068	1.164
45	3-hydroxyacetophenone	1.040	1.265	1.016	1.155
46	4-hydroxyacetophenone	1.100	0.897	1.125	1.059
47	2-hydroxybenzoic acid	1.176	1.200	1.138	1.331
48	3-hydroxybenzoic acid	1.088	0.813	1.054	1.041
49	4-hydroxybenzoic acid	1.171	1.170	1.136	1.333
50	4-sulfonatophenol [a]	0.782	1.223	0.816	1.166
51	4-alanylphenol [a]	1.022	1.173	1.045	1.229
52	triclosan	0.858	0.863	0.867	0.966
53	dopamine	0.688	0.818	0.728	0.799
54	p-coumaric acid	0.860	1.155	0.863	1.092
55	bisphenol A	0.780	0.913	0.888	1.050

a) IUPAC or common name: 52, 4-hydroxybenzenesulfonate; 53, 2-amino-4'hydroxypropiophenone.

Table S12. Calculated potentials with correction by calibration (E_{1c}) to E_{p1} for the one-electron oxidation of anilines. Based on values of E_1 in Table S7. All data in Volts vs. SHE.

		B3LYP		**M062X**	
No.	**Name**	**COSMO**	**SMD**	**COSMO**	**SMD**
1	aniline	0.967	0.967	0.959	0.951
2	2-methylaniline	0.883	0.922	0.921	0.915
3	3-methylaniline	0.939	0.970	0.924	0.923
4	4-methylaniline	0.868	0.865	0.843	0.849
5	2,4-dimethylaniline	0.830	0.820	0.814	0.808
6	2,5-dimethylaniline	0.891	0.884	0.879	0.897
7	2,4,6-trimethylaniline	0.807	0.776	0.787	0.739
8	2-ethylaniline	0.931	0.955	0.926	0.917
9	3-ethylaniline	0.929	0.890	0.954	0.939
10	4-ethylaniline	0.886	0.911	0.874	0.865
11	2-t-butylaniline	0.908	0.862	0.852	0.901
12	3-t-butylaniline	0.918	0.916	0.955	0.990
13	4-t-butylaniline	0.904	0.864	0.877	0.847
14	2-methoxyaniline	0.809	0.809	0.789	0.807
15	3-methoxyaniline	0.909	0.924	0.926	0.934
16	4-methoxyaniline	0.738	0.754	0.719	0.754
17	2,6-dimethoxyaniline	0.763	0.659	0.746	0.784
18	4-ethyl-2-methoxyaniline	0.736	0.742	0.741	0.801
19	2-methoxy-4-formylaniline [a]	1.034	1.035	0.972	1.004
20	2-ethoxyaniline	0.830	0.764	0.824	0.911
21	3-ethoxyaniline	0.895	0.922	0.949	0.948
22	4-ethoxyaniline	0.729	0.663	0.709	0.744
23	2-nitroaniline	1.285	1.311	1.276	1.393
24	3-nitroaniline	1.159	1.178	1.162	1.143
25	4-nitroaniline	1.299	1.315	1.272	1.214
26	2,4-dinitroaniline	1.599	1.626	1.679	1.318
27	4,6-dinitro-2-methylaniline	1.290	1.308	1.325	1.292
28	2,6-dinitro-4-methylaniline	1.465	1.468	1.500	1.415
29	2-phenylaniline	0.945	0.891	0.958	0.952
30	3-phenylaniline	0.964	0.975	0.979	0.968
31	4-phenylaniline	0.864	0.930	0.929	0.932
32	2-chloroaniline	1.048	1.034	1.058	1.040
33	3-chloroaniline	1.048	1.056	1.055	1.038
34	4-chloroaniline	0.976	0.985	1.002	0.977
35	2,4-dichloroaniline	1.050	1.088	1.047	1.060
36	2,4,6-trichloroaniline	1.124	1.221	1.149	1.201

37	pentachloroaniline	1.223	1.346	1.248	1.308
38	2-hydroxyaniline [a]	0.928	0.807	0.923	0.918
39	3-hydroxyaniline [a]	0.942	0.858	0.959	0.968
40	4-hydroxyaniline [a]	0.755	0.673	0.722	0.769
41	2-cyanoaniline	1.143	1.186	1.154	1.155
42	3-cyanoaniline	1.076	1.114	1.065	1.073
43	4-cyanoaniline	1.108	1.153	1.113	1.113
44	2-acetylaniline	1.108	1.112	1.117	1.198
45	3-acetylaniline	1.049	0.934	1.059	1.032
46	4-acetylaniline	1.112	1.123	1.137	1.092
47	2-aminobenzoic acid	1.172	1.170	1.199	1.153
48	3-aminobenzoic acid	1.079	0.901	1.097	1.096
49	4-aminobenzoic acid	1.145	1.161	1.148	1.117
50	4-sulfonatoaniline [a]	1.032	1.386	1.029	1.334
51	4-alanylaniline [a]	1.211	1.368	1.155	1.020

a) IUPAC or common name: 20, 4-amino-3-methoxybenzaldehyde; 40-42, aminophenol (2,3, and 4); 52, 4-aminobenzenesulfonate; 53, 2-amino-1-(4-aminophenyl)-1-propanone

Table S13. Fitting coefficients and statistics for the linear regression of log k_{rel} (literature and newly collected data from Table S1) versus selected sets of oxidation potentials.

Fig	**Descriptor Variable**	**Intercept (a)**	**Slope (b)**	**r²**	**s_{xy}**	***n***
1A	$E_{1/2}$ (from Suatoni et al.)	9.45 ± 0.56	−10.76 ± 0.60	0.903	0.468	36
5A	E_{p1st} (by SWV)	10.19 ± 0.55	−10.60 ± 0.55	0.916	0.436	36
5B	E_1 (M062X/COSMO) Anilines only	7.92 ± 0.53	−6.59 ± 0.43	0.932	0.474	19
5B	E_1 (M062X/COSMO) Phenols only	7.77 ± 0.90	−4.55 ± 0.47	0.869	0.409	16
6A	E_{1c} (M062X/COSMO vs. $E_{1/2}$)	9.08 ± 0.55	−10.29 ± 0.61	0.908	0.470	31
6B	E_{1c} (M062X/COSMO vs. E_{p1st})	10.25 ± 0.59	−10.59 ± 0.59	0.918	0.445	31

Intercept and slope are reported ± 1 standard deviation.
No ad hoc outliers were excluded from the regressions.

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