Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary data

Contribution of Substrate Reorganization Energies of Electron Transfer to Laccase Activity

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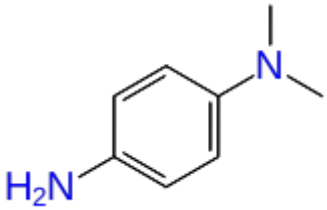
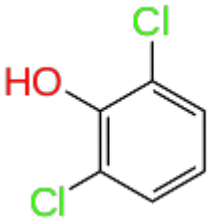
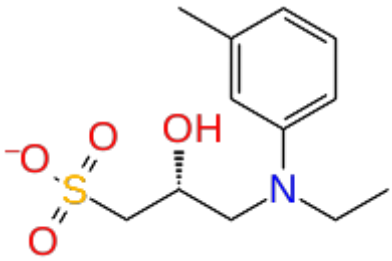
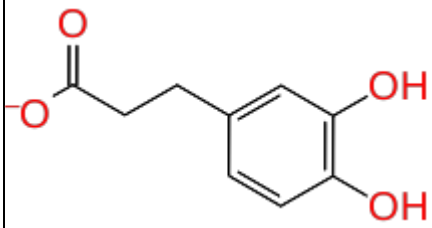
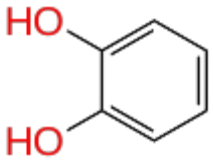
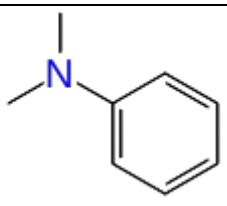
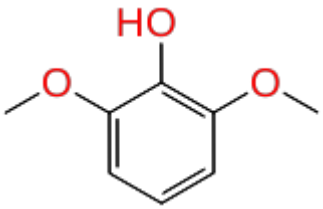
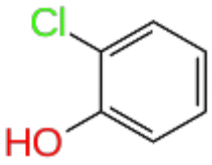
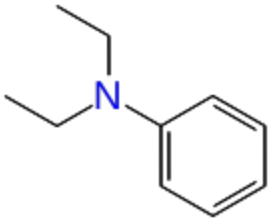
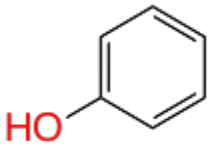
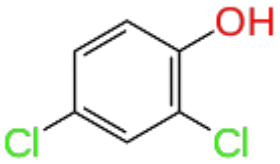
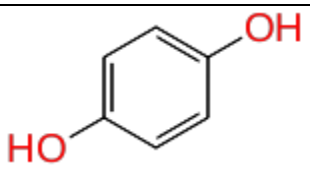
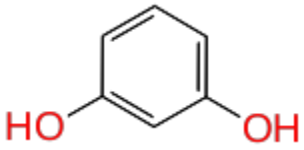
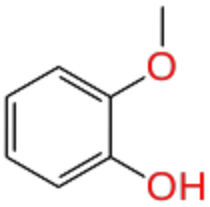
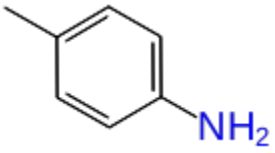
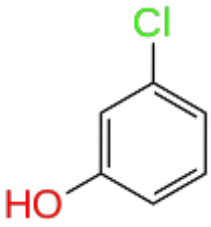
Tables

Table S1. 2D-structures of dataset-A and -B compounds (ordered according to activity).

Dataset A compounds

Compound	**Relative activity**	**log (relative activity)**	**Structure at pH 9 (LigPrep prepared states)**
N,*N*-Dimethyl-*p*-phenylenediamine	377	2.58	
2,6-Dichlorophenol	258	2.41	
TOOS	198	2.30	
Hydrocaffeic acid	185	2.27	
Catechol	176	2.25	
Dimethylaniline	165	2.22	
2,6-Dimethoxyphenol	159	2.20	

o-Chlorophenol	150	2.18	
Diethylaniline	103	2.01	
Phenol	100	2.00	
2,4-Dichlorophenol	93	1.97	
Hydroquinone	89	1.95	
Resorcinol	73	1.86	
Guaiacol	61	1.79	
p-Toulidine	51	1.71	
m-Chlorophenol	50	1.70	

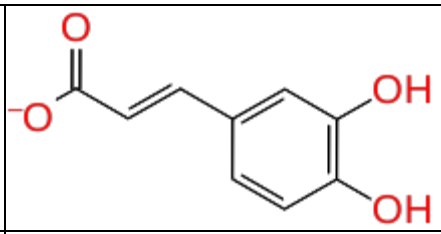
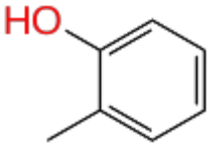
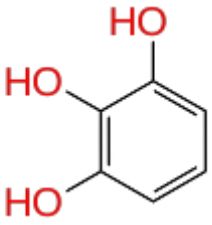
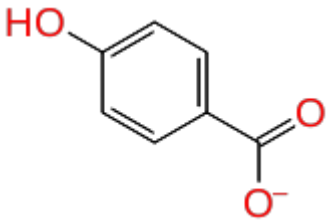
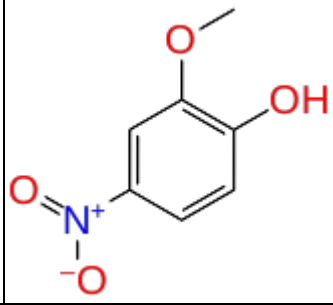
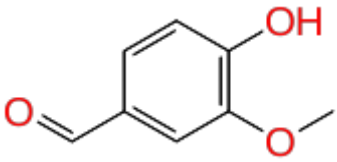
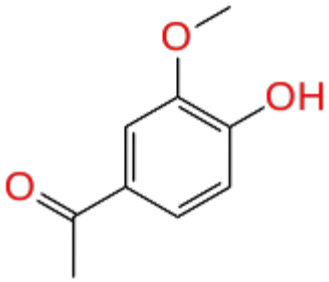
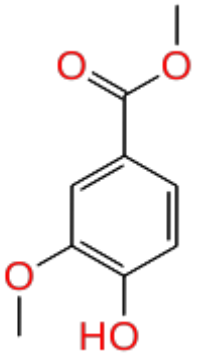
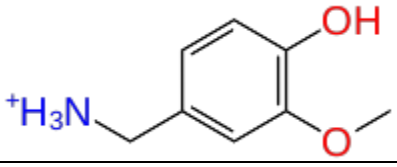
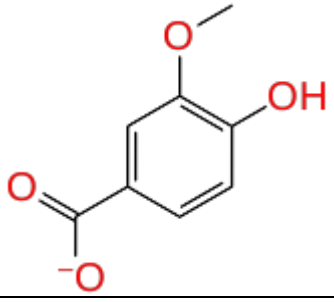
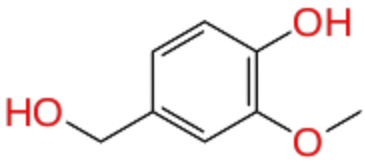
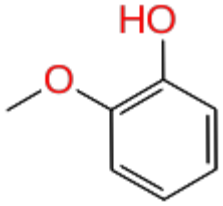
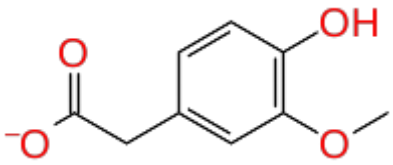
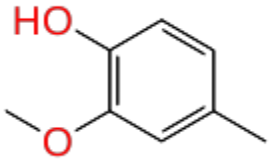
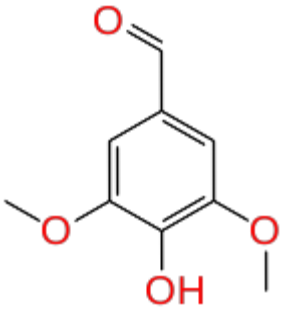
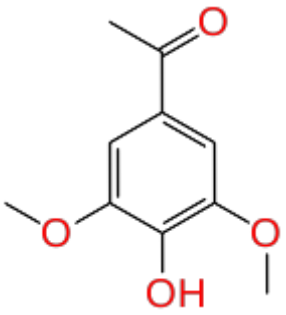
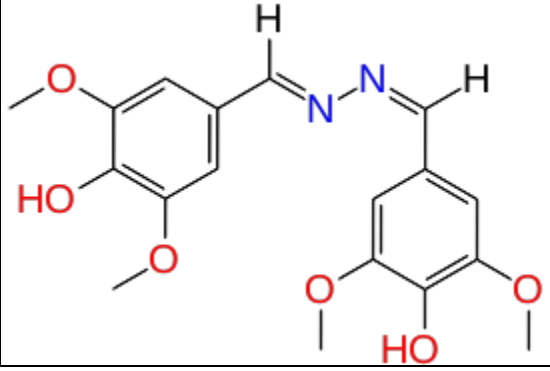
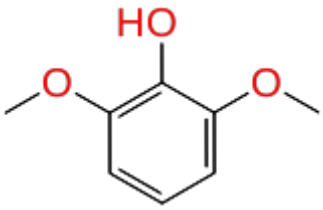
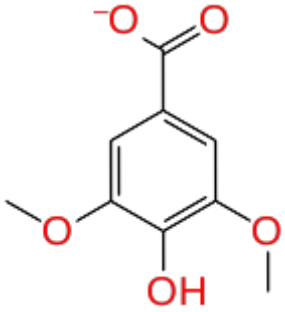
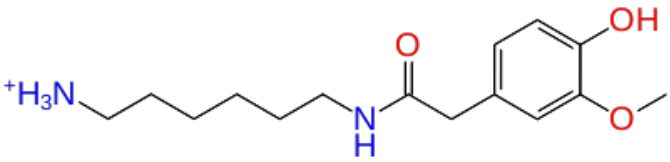
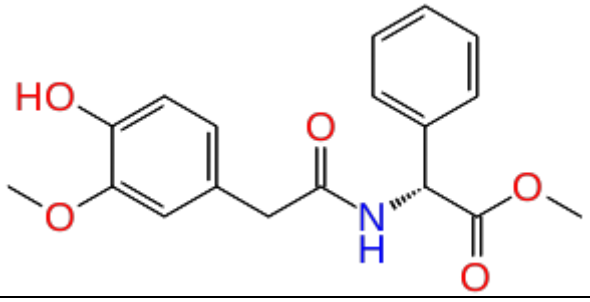
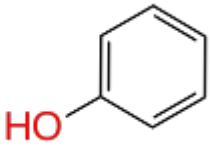
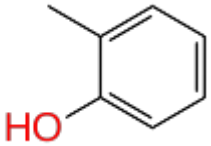
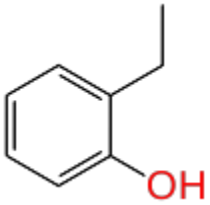
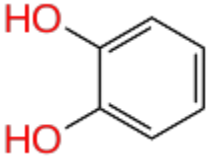
Caffeic acid	39	1.59	
o-Cresol	39	1.59	
Pyrogallol	10	1.00	
p-Hydroxybenzoic acid	3	0.48	

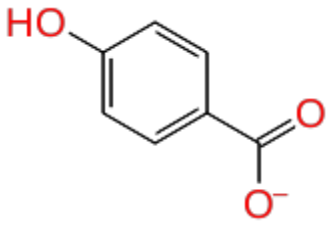
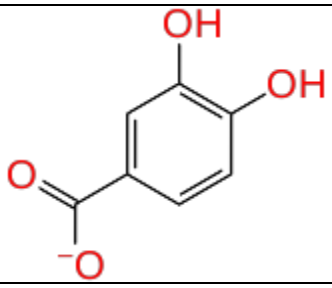
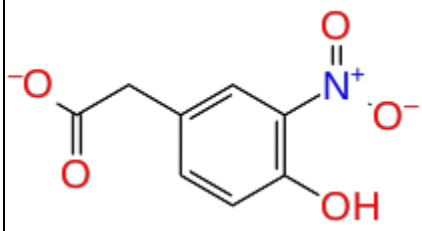
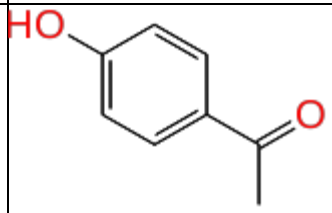
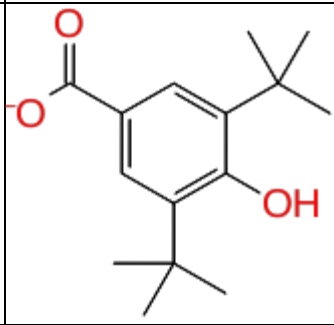
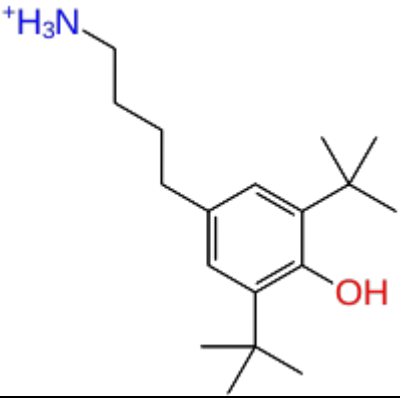
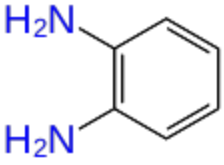
Table S1, continued.

2D-structures of the dataset-B compounds (named as in original article).

Compound	k_{cat} (min^{-1})	log(k_{cat})	Structure at pH 5 (LigPrep prepared states)
1	320	2.51	
2	1300	3.11	
3	1100	3.04	
4	1200	3.08	
5	2300	3.36	
6	2500	3.40	

7	2600	3.41	
8	2400	3.38	
9	2200	3.34	
10	3600	3.56	
11	2200	3.34	
12	1800	3.26	
13	2900	3.46	

14	3100	3.49	
15	3100	3.49	
16	1700	3.23	
17	2100	3.32	
20	1600	3.20	
21	1300	3.11	
22	3500	3.54	
23	3300	3.52	

24	120	2.08	
25	3000	3.48	
26	340	2.53	
27	40	1.60	
28	40	1.60	
29	40	1.60	
30	2100	3.32	

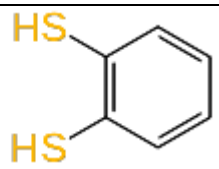
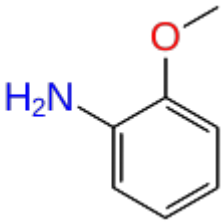
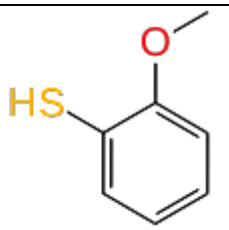
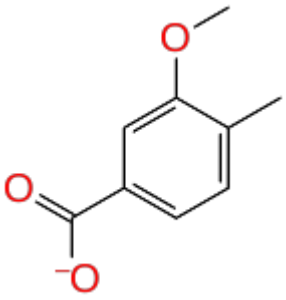
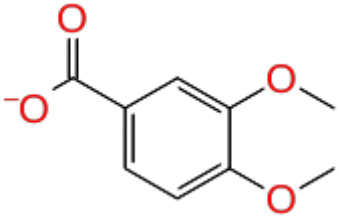
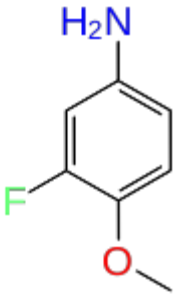
31	45000	4.65	
32	970	2.99	
33	2900	3.46	
34	40	1.60	
35	40	1.60	
36	240	2.38	

Table S2. Sensitivity test of conformation change for most flexible molecules (λ calculated using total internal energy and M06 functional). Energies in kcal/mol.

Substrates	**λ for freely optimized substrates**	**λ for protein-docked (1GYC) states after optimization**
p-Hydroxybenzoic acid	23.9	23.8
Hydrocaffeic acid	9.9	10.8
2,6-Dimethoxyphenol	10.8	10.8
Dimethylaniline	4.2	4.2
Diethylaniline	4.7	8.0
TOOS	2.3	6.3

Table S3. Total internal energies (in Hartree) of dataset-A reported using B3LYP.

Compound	**$E_x(x)$**	**$E_{x^+}(x)$**	**$E_{x^+}(x^+)$**	**$E_x(x^+)$**
N,*N*-Dimethyl-*p*-phenylenediamine	-421.3865	-421.2065	-421.2097	-421.3827
2,6-Dichlorophenol	-1226.5758	-1226.3438	-1226.3510	-1226.5693
TOOS	-1221.7832	-1221.6051	-1221.6092	-1221.7865
Hydrocaffeic acid	-649.2782	-649.0789	-649.0853	-649.2687
Catechol	-382.5974	-382.3911	-382.3994	-382.5889
Dimethylaniline	-366.0389	-365.8541	-365.8582	-366.0353
2,6-Dimethoxyphenol	-536.3518	-536.1513	-536.1599	-536.3426
o-Chlorophenol	-766.9784	-766.6606	-766.6636	-766.9670
Diethylaniline	-444.6292	-444.4523	-444.4547	-444.6257
Phenol	-307.3775	-307.0505	-307.0656	-307.3636
2,4-Dichlorophenol	-1226.5790	-1226.3514	-1226.3591	-1226.5714
Hydroquinone	-382.5994	-382.2741	-382.2818	-382.5840
Resorcinol	-382.6024	-382.2623	-382.2754	-382.5879
Guaiacol	-421.8641	-421.6593	-421.6677	-421.8555
p-Toulidine	-326.7915	-326.6108	-326.6147	-326.7861
m-Chlorophenol	-766.9802	-766.6576	-766.6587	-766.9750
Caffeic acid	-648.0790	-647.8584	-647.8698	-648.0552
o-Cresol	-346.6687	-346.3478	-346.3617	-346.6512
Pyrogallol	-457.8185	-457.6145	-457.6236	-457.8089
p-Hydroxybenzoic acid	-495.4904	-495.2666	-495.2787	-495.4679

Table S4. Total internal energies (in Hartree) of dataset-A reported using the M06 functional.

Compound	$E_x(x)$	$E_{x^+}(x)$	$E_{x^+}(x^+)$	$E_x(x^+)$
N,*N*-Dimethyl-*p*-phenylenediamine	-421.0696	-420.8840	-420.8873	-421.0662
2,6-Dichlorophenol	-1226.3131	-1226.0775	-1226.0849	-1226.3053
TOOS	-1221.2478	-1221.0614	-1221.0665	-1221.2493
Hydrocaffeic acid	-648.9007	-648.6976	-648.7051	-648.8924
Catechol	-382.3577	-382.1483	-382.1570	-382.3490
Dimethylaniline	-365.7514	-365.5605	-365.5644	-365.7487
2,6-Dimethoxyphenol	-536.0185	-535.8148	-535.8229	-536.0094
o-Chlorophenol	-766.7386	-766.4198	-766.4205	-766.7309
Diethylaniline	-444.2808	-444.0960	-444.0985	-444.2758
Phenol	-307.1618	-306.8391	-306.8498	-307.1461
2,4-Dichlorophenol	-1226.3146	-1226.0847	-1226.0925	-1226.3067
Hydroquinone	-382.3595	-382.0338	-382.0472	-382.3425
Resorcinol	-382.3627	-382.0069	-382.0288	-382.3477
Guaiacol	-421.5895	-421.3820	-421.3898	-421.5808
p-Toulidine	-326.5392	-326.3540	-326.3594	-326.5343
m-Chlorophenol	-766.7399	-766.4162	-766.4210	-766.7301
Caffeic acid	-647.7034	-647.4717	-647.4847	-647.6794
o-Cresol	-346.4212	-346.1044	-346.1137	-346.4034
Pyrogallol	-457.5551	-457.3479	-457.3572	-457.5454
p-Hydroxybenzoic acid	-495.2022	-494.9659	-494.9810	-495.1793

Table S5. Total internal energies (in Hartree) of dataset-A reported using the PBE functional.

Compound	$\mathbf{E_x(x)}$	$\mathbf{E_{x^+}(x)}$	$\mathbf{E_{x^+}(x^+)}$	$\mathbf{E_x(x^+)}$
N,*N*-Dimethyl-*p*-phenylenediamine	-420.8420	-420.6655	-420.6684	-420.8376
2,6-Dichlorophenol	-1225.8137	-1225.5873	-1225.5936	-1225.8081
TOOS	-1220.6238	-1220.4482	-1220.4529	-1220.6227
Hydrocaffeic acid	-648.5303	-648.3453	-648.3511	-648.5245
Catechol	-382.1482	-381.9489	-381.9551	-382.1408
Dimethylaniline	-365.5528	-365.3740	-365.3770	-365.5495
2,6-Dimethoxyphenol	-535.7184	-535.5274	-535.5327	-535.7109
o-Chlorophenol	-766.4065	-766.1031	-766.1088	-766.4008
Diethylaniline	-444.0330	-443.8584	-443.8609	-444.0306
Phenol	-306.9972	-306.6906	-306.7052	-306.9841
2,4-Dichlorophenol	-1225.8149	-1225.5957	-1225.6017	-1225.8093
Hydroquinone	-382.1500	-381.8473	-381.8550	-382.1358
Resorcinol	-382.1531	-381.8376	-381.8468	-382.1360
Guaiacol	-421.3572	-421.1594	-421.1654	-421.3501
p-Toulidine	-326.3635	-326.1880	-326.1911	-326.3602
m-Chlorophenol	-766.4081	-766.1027	-766.1100	-766.4005
Caffeic acid	-647.3428	-647.1333	-647.1467	-647.3210
o-Cresol	-346.2323	-345.9306	-345.9451	-346.2193
Pyrogallol	-457.3005	-457.1052	-457.1120	-457.2919
p-Hydroxybenzoic acid	-494.9255	-494.7118	-494.7250	-494.9047

Table S6. Total internal energies (in Hartree) of dataset-B reported using B3LYP.

Compound	**$E_x(x)$**	**$E_{x^+}(x)$**	**$E_{x^+}(x^+)$**	**$E_x(x^+)$**
1	-626.3662	-626.1429	-626.1507	-626.3574
2	-535.1864	-534.9297	-534.9362	-535.1789
3	-574.4805	-574.2299	-574.2356	-574.4720
4	-649.7055	-649.4263	-649.4333	-649.6935
5	-516.9498	-516.7405	-516.7475	-516.9398
6	-609.9770	-609.7526	-609.7653	-609.9544
7	-536.3633	-536.1620	-536.1706	-536.3546
8	-421.8641	-421.6593	-421.6677	-421.8555
9	-649.2535	-649.0619	-649.0633	-649.2473
10	-461.1554	-460.9557	-460.9641	-461.1467
11	-649.6738	-649.4169	-649.4221	-649.6651
12	-688.9687	-688.7175	-688.7231	-688.9586
13	-1258.3631	-1258.1359	-1258.1616	-1258.3325
14	-536.3518	-536.1513	-536.1599	-536.3426
15	-724.4654	-724.2220	-724.2745	-724.4558
16	-921.3458	-921.1299	-921.1600	-921.3451
17	-1127.9226	-1127.7199	-1127.7293	-1127.9165
20	-307.3775	-307.0505	-307.0656	-307.3636
21	-346.6687	-346.3478	-346.3617	-346.6512
22	-385.9534	-385.7394	-385.7466	-385.9469
23	-382.5972	-382.3908	-382.3993	-382.5888
24	-495.4904	-495.2666	-495.2787	-495.4679
25	-570.7103	-570.4854	-570.4981	-570.6880
26	-739.2633	-739.0466	-739.0537	-739.2471
27	-459.9944	-459.7456	-459.7494	-459.9866
28	-809.7707	-809.5486	-809.5611	-809.7483
29	-834.6063	-834.4042	-834.4088	-834.5996
30	-342.8402	-342.6757	-342.6825	-342.8340
31	-1028.5272	-1028.3169	-1028.3224	-1028.5233
32	-401.9884	-401.8103	-401.8157	-401.9824
33	-744.8323	-744.6263	-744.6329	-744.8271
34	-574.0472	-573.8242	-573.8344	-574.0253
35	-649.2433	-649.0192	-649.0317	-649.2206
36	-501.2233	-501.0443	-501.0511	-501.2145

Table S7. Total internal energies (in Hartree) of dataset-B reported using M06.

Compound	**$E_x(x)$**	**$E_{x^+}(x)$**	**$E_{x^+}(x^+)$**	**$E_x(x^+)$**
1	-626.0077	-625.7798	-625.7880	-625.9994
2	-534.8583	-534.5951	-534.6000	-534.8510
3	-574.1207	-573.8630	-573.8687	-574.1120
4	-649.3192	-649.0309	-649.0389	-649.3059
5	-516.6077	-516.3954	-516.4019	-516.5973
6	-609.6278	-609.3897	-609.4086	-609.6141
7	-536.0323	-535.8272	-535.8362	-536.0229
8	-421.5895	-421.3820	-421.3898	-421.5808
9	-648.8778	-648.6788	-648.6874	-648.8674
10	-460.8486	-460.6468	-460.6544	-460.8397
11	-649.2871	-649.0240	-649.0280	-649.2784
12	-688.5499	-688.2925	-688.2969	-688.5399
13	-1257.5898	-1257.3571	-1257.3825	-1257.5609
14	-536.0185	-535.8148	-535.8229	-536.0094
15	-724.0596	-723.8247	-723.8648	-724.0500
16	-920.7351	-920.5152	-920.5364	-920.7236
17	-1127.2152	-1127.0066	-1127.0174	-1127.2063
20	-307.1618	-306.8391	-306.8498	-307.1461
21	-346.4212	-346.1044	-346.1136	-346.4036
22	-385.6732	-385.4577	-385.4641	-385.6666
23	-382.3575	-382.1481	-382.1569	-382.3489
24	-495.2003	-494.9529	-494.9809	-495.1866
25	-570.3960	-570.1547	-570.1764	-570.3825
26	-738.8585	-738.6333	-738.6377	-738.8442
27	-459.6935	-459.4374	-459.4415	-459.6856
28	-809.2308	-808.9821	-809.0141	-809.2178
29	-833.9760	-833.7712	-833.7760	-833.9698
30	-342.5923	-342.4217	-342.4288	-342.5854
31	-1028.2806	-1028.0679	-1028.0733	-1028.2764
32	-401.7097	-401.5263	-401.5322	-401.7033
33	-744.5543	-744.3471	-744.3521	-744.5479
34	-573.6904	-573.4521	-573.4698	-573.6764
35	-648.8588	-648.6190	-648.6395	-648.8450
36	-500.9236	-500.7391	-500.7461	-500.9145

Table S8. Total internal energies (in Hartree) of dataset-B reported using PBE.

Compound	**$E_x(x)$**	**$E_{x^+}(x)$**	**$E_{x^+}(x^+)$**	**$E_x(x^+)$**
1	-625.6865	-625.4709	-625.4764	-625.6797
2	-534.5649	-534.3193	-534.3222	-534.5606
3	-573.8025	-573.5630	-573.5674	-573.7961
4	-648.9561	-648.6941	-648.6960	-648.9506
5	-516.3274	-516.1232	-516.1293	-516.3196
6	-609.2855	-609.0724	-609.0856	-609.2650
7	-535.7286	-535.5361	-535.5413	-535.7226
8	-421.3572	-421.1594	-421.1654	-421.3501
9	-648.5086	-648.3261	-648.3343	-648.4987
10	-460.5912	-460.4004	-460.4057	-460.5840
11	-648.9263	-648.6827	-648.6842	-648.9218
12	-688.1646	-687.9259	-687.9296	-688.1579
13	-1256.9066	-1256.6941	-1256.7155	-1256.8784
14	-535.7184	-535.5273	-535.5327	-535.7110
15	-723.6471	-723.4341	-723.4468	-723.6263
16	-920.2122	-920.0229	-920.0244	-920.2038
17	-1126.5914	-1126.3987	-1126.4007	-1126.5816
20	-306.9972	-306.6905	-306.7052	-306.9841
21	-346.2323	-345.9303	-345.9451	-346.2191
22	-385.4595	-385.2514	-385.2565	-385.4526
23	-382.1480	-381.9487	-381.9549	-382.1407
24	-494.9255	-494.7118	-494.7251	-494.9047
25	-570.0767	-569.8630	-569.8763	-570.0561
26	-738.4691	-738.2693	-738.2758	-738.4560
27	-459.4427	-459.2011	-459.2049	-459.4347
28	-808.7569	-808.5465	-808.5587	-808.7366
29	-833.4872	-833.2894	-833.2943	-833.4810
30	-342.4111	-342.2535	-342.2568	-342.4050
31	-1027.8564	-1027.6524	-1027.6561	-1027.8529
32	-401.4923	-401.3181	-401.3227	-401.4862
33	-744.2147	-744.0156	-744.0196	-744.2097
34	-573.3684	-573.1543	-573.1668	-573.3486
35	-648.4939	-648.2810	-648.2939	-648.4732
36	-500.6429	-500.4704	-500.4760	-500.6369

Table S9. Reorganization energies (in kcal/mol; based on internal energies) of dataset-A calculated using B3LYP, M06 and PBE functionals (arranged according to decreasing activity).

Compound	**Relative activity**	**log (relative activity)**	**Reorganization energy (λ in kcal/mol)**		
			B3LYP	**M06**	**PBE**
N,*N*-Dimethyl-*p*-phenylenediamine	377	2.58	4.35	4.21	4.55
2,6-Dichlorophenol	258	2.41	8.66	9.52	7.45
TOOS	198	2.30	0.48	2.26	3.59
Hydrocaffeic acid	185	2.27	9.92	9.92	7.28
Catechol	176	2.25	10.59	10.93	8.51
Dimethylaniline	165	2.22	4.86	4.09	3.90
2,6-Dimethoxyphenol	159	2.20	11.13	10.80	8.03
o-Chlorophenol	150	2.18	9.08	5.34	7.15
Diethylaniline	103	2.01	3.72	4.72	3.11
Phenol	100	2.00	18.23	16.56	17.43
2,4-Dichlorophenol	93	1.97	9.52	9.92	7.29
Hydroquinone	89	1.95	14.45	19.12	13.76
Resorcinol	73	1.86	17.32	23.17	16.50
Guaiacol	61	1.79	10.67	10.37	8.23
p-Toulidine	51	1.71	5.81	6.47	4.03
m-Chlorophenol	50	1.70	3.93	9.13	9.31
Caffeic acid	39	1.59	22.11	23.22	22.10
o-Cresol	39	1.59	19.68	17.01	17.29
Pyrogallol	10	1.00	11.72	11.90	9.65
p-Hydroxybenzoic acid	3	0.48	21.77	23.87	21.36

Table S10. Reorganization energies (in kcal/mol; based on internal energies) of dataset-B calculated using B3LYP, M06 and PBE functionals (arranged according to decreasing k_{cat}).

Compound	**k_{cat} (min^{-1})**	**$log(k_{cat})$**	**Reorganization energy (λ in kcal/mol)**		
			B3LYP	**M06**	**PBE**
31	45000	4.65	5.90	6.00	4.51
10	3600	3.56	10.69	10.38	7.83
22	3500	3.54	8.53	8.15	7.60
23	3300	3.52	10.60	10.95	8.51
14	3100	3.49	11.11	10.78	8.02
15	3100	3.49	38.95	31.19	21.05
25	3000	3.48	21.98	22.12	21.32
13	2900	3.46	35.32	34.09	31.10
33	2900	3.46	7.46	7.18	5.66
7	2600	3.41	10.88	11.52	7.05
6	2500	3.40	22.10	20.46	21.10
8	2400	3.38	10.67	10.33	8.23
5	2300	3.36	10.73	10.63	8.71
9	2200	3.34	4.81	11.97	11.38
11	2200	3.34	8.74	7.96	3.72
17	2100	3.32	9.74	12.42	7.43
30	2100	3.32	8.18	8.74	5.89
12	1800	3.26	9.78	9.02	6.55
16	1700	3.23	19.31	20.55	6.25
20	1600	3.20	18.23	16.57	17.43
2	1300	3.11	8.72	7.69	4.51
21	1300	3.11	19.68	16.84	17.53
4	1200	3.08	11.90	13.34	4.56
3	1100	3.04	8.93	8.98	6.79
32	970	2.99	7.20	7.78	6.68
26	340	2.53	14.61	11.70	12.29
1	320	2.51	10.40	10.36	7.75
36	240	2.38	9.78	10.04	7.27
24	120	2.08	21.75	26.22	21.32
27	40	1.60	7.27	7.60	7.43
28	40	1.60	21.94	28.24	20.43
29	40	1.60	7.08	6.92	6.94
34	40	1.60	20.14	19.88	20.26
35	40	1.60	22.12	21.55	21.11

Table S11. Total free energies (in Hartree) of dataset-A reported using the B3LYP functional.

Compound	$E_x(x)$	$E_{x^+}(x)$	$E_{x^+}(x^+)$	$E_x(x^+)$
N,*N*-Dimethyl-*p*-phenylenediamine	-421.4277	-421.2490	-421.2521	-421.4239
2,6-Dichlorophenol	-1226.6168	-1226.3857	-1226.3928	-1226.6105
TOOS	-1221.8513	-1221.6690	-1221.6773	-1221.8497
Hydrocaffeic acid	-649.3266	-649.1267	-649.1347	-649.3188
Catechol	-382.6340	-382.4282	-382.4363	-382.6254
Dimethylaniline	-366.0787	-365.8945	-365.8972	-366.0762
2,6-Dimethoxyphenol	-536.3985	-536.1991	-536.2070	-536.3898
o-Chlorophenol	-767.0159	-766.6996	-766.7020	-767.0042
Diethylaniline	-444.6771	-444.4990	-444.5012	-444.6733
Phenol	-307.4120	-307.0853	-307.1015	-307.3984
2,4-Dichlorophenol	-1226.6203	-1226.3934	-1226.4009	-1226.6135
Hydroquinone	-382.6361	-382.3102	-382.3191	-382.6225
Resorcinol	-382.6397	-382.2992	-382.3121	-382.6247
Guaiacol	-421.9046	-421.7018	-421.7090	-421.8964
p-Toulidine	-326.8285	-326.6490	-326.6560	-326.8264
m-Chlorophenol	-767.0178	-766.6967	-766.6971	-767.0125
Caffeic acid	-648.1260	-647.9058	-647.9194	-648.1009
o-Cresol	-346.7069	-346.3853	-346.4016	-346.6891
Pyrogallol	-457.8588	-457.6551	-457.6636	-457.8490
p-Hydroxybenzoic acid	-495.5302	-495.3074	-495.3204	-495.5065

Table S12. Total free energies (in Hartree) of dataset-A reported using the M06 functional.

Compound	**$E_x(x)$**	**$E_x^+(x)$**	**$E_x^+(x^+)$**	**$E_x(x^+)$**
N,*N*-Dimethyl-*p*-phenylenediamine	-421.1129	-420.9263	-420.9295	-421.1096
2,6-Dichlorophenol	-1226.3541	-1226.1196	-1226.1267	-1226.3465
TOOS	-1221.3093	-1221.1250	-1221.1348	-1221.3087
Hydrocaffeic acid	-648.9492	-648.7456	-648.7548	-648.9391
Catechol	-382.3943	-382.1856	-382.1939	-382.3854
Dimethylaniline	-365.7915	-365.6013	-365.6036	-365.7883
2,6-Dimethoxyphenol	-536.0652	-535.8600	-535.8700	-536.0565
o-Chlorophenol	-766.7765	-766.4585	-766.4592	-766.7684
Diethylaniline	-444.3264	-444.1421	-444.1470	-444.3242
Phenol	-307.1963	-306.8739	-306.8853	-307.1808
2,4-Dichlorophenol	-1226.3559	-1226.1268	-1226.1344	-1226.3494
Hydroquinone	-382.3963	-382.0699	-382.0842	-382.3801
Resorcinol	-382.3999	-382.0441	-382.0671	-382.3841
Guaiacol	-421.6300	-421.4214	-421.4311	-421.6215
p-Toulidine	-326.5764	-326.3923	-326.3975	-326.5713
m-Chlorophenol	-766.7779	-766.4567	-766.4595	-766.7680
Caffeic acid	-647.7504	-647.5207	-647.5340	-647.7251
o-Cresol	-346.4593	-346.1421	-346.1529	-346.4412
Pyrogallol	-457.5952	-457.3887	-457.3972	-457.5854
p-Hydroxybenzoic acid	-495.2420	-495.0072	-495.0226	-495.2179

Table S13. Total free energies (in Hartree) of dataset-A reported using PBE.

Compound	**$E_x(x)$**	**$E_{x^+}(x)$**	**$E_{x^+}(x^+)$**	**$E_x(x^+)$**
N,*N*-Dimethyl-*p*-phenylenediamine	-420.8835	-420.7094	-420.7122	-420.8818
2,6-Dichlorophenol	-1225.8548	-1225.6303	-1225.6363	-1225.8495
TOOS	-1220.6892	-1220.5130	-1220.5203	-1220.6883
Hydrocaffeic acid	-648.5795	-648.3938	-648.4012	-648.5738
Catechol	-382.1843	-381.9863	-381.9922	-382.1770
Dimethylaniline	-365.5921	-365.4126	-365.4157	-365.5891
2,6-Dimethoxyphenol	-535.7651	-535.5731	-535.5811	-535.7579
o-Chlorophenol	-766.4442	-766.1422	-766.1480	-766.4384
Diethylaniline	-444.0812	-443.9054	-443.9078	-444.0786
Phenol	-307.0316	-306.7255	-306.7406	-307.0186
2,4-Dichlorophenol	-1225.8562	-1225.6383	-1225.6442	-1225.8512
Hydroquinone	-382.1861	-381.8856	-381.8918	-382.1724
Resorcinol	-382.1898	-381.8751	-381.8847	-382.1733
Guaiacol	-421.3974	-421.2020	-421.2070	-421.3905
p-Toulidine	-326.4049	-326.2263	-326.2312	-326.3995
m-Chlorophenol	-766.4459	-766.1426	-766.1488	-766.4383
Caffeic acid	-647.3903	-647.1820	-647.1951	-647.3672
o-Cresol	-346.2702	-345.9681	-345.9849	-346.2570
Pyrogallol	-457.3397	-457.1456	-457.1521	-457.3314
p-Hydroxybenzoic acid	-494.9657	-494.7536	-494.7665	-494.9438

Table S14. Total free energies (in Hartree) of dataset-B reported using B3LYP.

Compound	**$E_x(x)$**	**$E_{x^+}(x)$**	**$E_{x^+}(x^+)$**	**$E_x(x^+)$**
1	-626.4126	-626.1910	-626.1989	-626.4055
2	-535.2316	-534.9766	-534.9810	-535.2242
3	-574.5285	-574.2790	-574.2841	-574.5192
4	-649.7562	-649.4761	-649.4866	-649.7418
5	-516.9975	-516.7900	-516.7963	-516.9885
6	-610.0224	-609.7988	-609.8129	-609.9986
7	-536.4110	-536.2103	-536.2167	-536.4006
8	-421.9046	-421.7018	-421.7089	-421.8963
9	-649.3050	-649.1124	-649.1155	-649.2948
10	-461.1984	-461.0024	-461.0093	-461.1903
11	-649.7252	-649.4707	-649.4739	-649.7166
12	-689.0227	-688.7734	-688.7773	-689.0120
13	-1258.4433	-1258.2157	-1258.2426	-1258.4115
14	-536.3985	-536.1991	-536.2071	-536.3898
15	-724.5171	-724.2759	-724.3282	-724.5084
16	-921.4170	-921.1986	-921.2380	-921.4169
17	-1128.0024	-1127.7931	-1127.8080	-1127.9915
20	-307.4120	-307.0853	-307.1015	-307.3984
21	-346.7069	-346.3853	-346.4016	-346.6890
22	-385.9947	-385.7829	-385.7889	-385.9882
23	-382.6338	-382.4280	-382.4361	-382.6253
24	-495.5302	-495.3075	-495.3204	-495.5065
25	-570.7522	-570.5280	-570.5422	-570.7288
26	-739.3126	-739.0972	-739.1048	-739.2979
27	-460.0364	-459.7877	-459.7918	-460.0280
28	-809.8325	-809.6116	-809.6254	-809.8091
29	-834.6823	-834.4768	-834.4863	-834.6728
30	-342.8765	-342.7140	-342.7197	-342.8712
31	-1028.5675	-1028.3572	-1028.3622	-1028.5632
32	-402.0290	-401.8501	-401.8571	-402.0230
33	-744.8746	-744.6699	-744.6757	-744.8694
34	-574.0940	-573.8715	-573.8832	-574.0708
35	-649.2924	-649.0693	-649.0834	-649.2684
36	-501.2663	-501.0884	-501.0948	-501.2588

Table S15. Total free energies (in Hartree) of dataset-B reported using M06.

Compound	**$E_x(x)$**	**$E_{x^+}(x)$**	**$E_{x^+}(x^+)$**	**$E_x(x^+)$**
1	-626.0541	-625.8284	-625.8363	-626.0446
2	-534.9035	-534.6421	-534.6461	-534.8963
3	-574.1687	-573.9123	-573.9171	-574.1592
4	-649.3698	-649.0804	-649.0919	-649.3538
5	-516.6553	-516.4424	-516.4508	-516.6466
6	-609.6753	-609.4373	-609.4572	-609.6598
7	-536.0776	-535.8764	-535.8822	-536.0688
8	-421.6300	-421.4214	-421.4311	-421.6216
9	-648.9261	-648.7267	-648.7372	-648.9165
10	-460.8916	-460.6917	-460.6998	-460.8832
11	-649.3384	-649.0747	-649.0797	-649.3299
12	-688.6040	-688.3454	-688.3509	-688.5932
13	-1257.6668	-1257.4363	-1257.4600	-1257.6364
14	-536.0652	-535.8600	-535.8700	-536.0565
15	-724.1112	-723.8781	-723.9187	-724.1024
16	-920.8039	-920.5831	-920.6115	-920.7962
17	-1127.2871	-1127.0797	-1127.0924	-1127.2814
20	-307.1963	-306.8739	-306.8853	-307.1808
21	-346.4593	-346.1420	-346.1528	-346.4414
22	-385.7147	-385.4988	-385.5066	-385.7080
23	-382.3941	-382.1854	-382.1938	-382.3853
24	-495.2418	-494.9952	-495.0234	-495.2264
25	-570.4402	-570.1992	-570.2217	-570.4249
26	-738.9084	-738.6840	-738.6917	-738.8935
27	-459.7355	-459.4783	-459.4839	-459.7270
28	-809.2954	-809.0469	-809.0797	-809.2808
29	-834.0519	-833.8439	-833.8537	-834.0430
30	-342.6286	-342.4600	-342.4661	-342.6225
31	-1028.3208	-1028.1083	-1028.1131	-1028.3163
32	-401.7502	-401.5661	-401.5737	-401.7438
33	-744.5962	-744.3884	-744.3951	-744.5898
34	-573.7387	-573.5001	-573.5193	-573.7232
35	-648.9096	-648.6709	-648.6914	-648.8939
36	-500.9665	-500.7836	-500.7898	-500.9584

Table S16. Total free energies (in Hartree) of dataset-B reported using PBE.

Compound	**$E_x(x)$**	**$E_{x^+}(x)$**	**$E_{x^+}(x^+)$**	**$E_x(x^+)$**
1	-625.7333	-625.5197	-625.5253	-625.7282
2	-534.6098	-534.3658	-534.3688	-534.6062
3	-573.8500	-573.6128	-573.6142	-573.8427
4	-649.0074	-648.7433	-648.7494	-649.0000
5	-516.3724	-516.1705	-516.1769	-516.3656
6	-609.3314	-609.1201	-609.1341	-609.3096
7	-535.7752	-535.5842	-535.5894	-535.7675
8	-421.3974	-421.2020	-421.2070	-421.3905
9	-648.5573	-648.3767	-648.3845	-648.5480
10	-460.6360	-460.4448	-460.4514	-460.6286
11	-648.9777	-648.7334	-648.7378	-648.9737
12	-688.2185	-687.9803	-687.9833	-688.2109
13	-1256.9856	-1256.7726	-1256.7944	-1256.9562
14	-535.7650	-535.5730	-535.5810	-535.7579
15	-723.6994	-723.4892	-723.5007	-723.6771
16	-920.2826	-920.0893	-920.0936	-920.2711
17	-1126.6687	-1126.4717	-1126.4719	-1126.6579
20	-307.0316	-306.7254	-306.7406	-307.0186
21	-346.2703	-345.9678	-345.9849	-346.2569
22	-385.5014	-385.2929	-385.2974	-385.4948
23	-382.1841	-381.9860	-381.9921	-382.1769
24	-494.9657	-494.7536	-494.7665	-494.9438
25	-570.1191	-569.9071	-569.9211	-570.0973
26	-738.5191	-738.3205	-738.3276	-738.5073
27	-459.4843	-459.2446	-459.2481	-459.4780
28	-808.8195	-808.6113	-808.6235	-808.7981
29	-833.5569	-833.3576	-833.3684	-833.5509
30	-342.4474	-342.2907	-342.2960	-342.4427
31	-1027.8963	-1027.6938	-1027.6968	-1027.8927
32	-401.5325	-401.3607	-401.3644	-401.5274
33	-744.2570	-744.0599	-744.0630	-744.2519
34	-573.4155	-573.2034	-573.2165	-573.3945
35	-648.5434	-648.3326	-648.3461	-648.5215
36	-500.6853	-500.5148	-500.5203	-500.6793

Table S17. Solution phase energies (in Hartree) of dataset-A reported using B3LYP.

Compound	**$E_x(x)$**	**$E_{x^+}(x)$**	**$E_{x^+}(x^+)$**	**$E_x(x^+)$**
N,*N*-Dimethyl-*p*-phenylenediamine	-421.5827	-421.4008	-421.4048	-421.5792
2,6-Dichlorophenol	-1226.6697	-1226.4370	-1226.4447	-1226.6630
TOOS	-1222.0973	-1221.9173	-1221.9227	-1222.0989
Hydrocaffeic acid	-649.4585	-649.2574	-649.2653	-649.4491
Catechol	-382.7132	-382.5072	-382.5159	-382.7046
Dimethylaniline	-366.2184	-366.0326	-366.0363	-366.2150
2,6-Dimethoxyphenol	-536.5329	-536.3324	-536.3416	-536.5236
o-Chlorophenol	-767.0806	-766.7577	-766.7622	-767.0689
Diethylaniline	-444.8715	-444.6936	-444.6961	-444.8680
Phenol	-307.4880	-307.1529	-307.1674	-307.4733
2,4-Dichlorophenol	-1226.6727	-1226.4451	-1226.4530	-1226.6651
Hydroquinone	-382.7150	-382.3793	-382.3935	-382.6991
Resorcinol	-382.7182	-382.3677	-382.3846	-382.7015
Guaiacol	-422.0098	-421.8053	-421.8140	-422.0009
p-Toulidine	-326.9417	-326.7624	-326.7675	-326.9371
m-Chlorophenol	-767.0823	-766.7577	-766.7605	-767.0768
Caffeic acid	-648.2359	-648.0100	-648.0259	-648.2118
o-Cresol	-346.8085	-346.4789	-346.4940	-346.7903
Pyrogallol	-457.9397	-457.7356	-457.7455	-457.9302
p-Hydroxybenzoic acid	-495.6060	-495.3780	-495.3936	-495.5832

Table S18. Solution phase energies (in Hartree) of dataset-A reported using M06.

Compound	$E_x(x)$	$E_{x^+}(x)$	$E_{x^+}(x^+)$	$E_x(x^+)$
N,*N*-Dimethyl-*p*-phenylenediamine	-421.2660	-421.0776	-421.0815	-421.2628
2,6-Dichlorophenol	-1226.4070	-1226.1705	-1226.1784	-1226.3990
TOOS	-1221.5594	-1221.3726	-1221.3788	-1221.5599
Hydrocaffeic acid	-649.0811	-648.8760	-648.8851	-649.0719
Catechol	-382.4737	-382.2643	-382.2734	-382.4649
Dimethylaniline	-365.9300	-365.7378	-365.7413	-365.9266
2,6-Dimethoxyphenol	-536.1994	-535.9945	-536.0040	-536.1901
o-Chlorophenol	-766.8407	-766.5151	-766.5186	-766.8328
Diethylaniline	-444.5207	-444.3361	-444.3396	-444.5166
Phenol	-307.2721	-306.9371	-306.9518	-307.2558
2,4-Dichlorophenol	-1226.4084	-1226.1783	-1226.1865	-1226.4004
Hydroquinone	-382.4753	-382.1395	-382.1543	-382.4577
Resorcinol	-382.4786	-382.1229	-382.1398	-382.4617
Guaiacol	-421.7350	-421.5266	-421.5356	-421.7260
p-Toulidine	-326.6889	-326.5048	-326.5105	-326.6837
m-Chlorophenol	-766.8419	-766.5151	-766.5178	-766.8319
Caffeic acid	-647.8605	-647.6250	-647.6408	-647.8363
o-Cresol	-346.5607	-346.2301	-346.2459	-346.5423
Pyrogallol	-457.6768	-457.4691	-457.4793	-457.6672
p-Hydroxybenzoic acid	-495.3180	-495.0795	-495.0957	-495.2948

Table S19. Solution phase energies (in Hartree) of dataset-A reported using PBE.

Compound	**$E_x(x)$**	**$E_{x^+}(x)$**	**$E_{x^+}(x^+)$**	**$E_x(x^+)$**
N,*N*-Dimethyl-*p*-phenylenediamine	-421.0335	-420.8568	-420.8603	-421.0304
2,6-Dichlorophenol	-1225.9053	-1225.6782	-1225.6846	-1225.8994
TOOS	-1220.9305	-1220.7530	-1220.7590	-1220.9294
Hydrocaffeic acid	-648.7063	-648.5188	-648.5264	-648.7007
Catechol	-382.2616	-382.0619	-382.0683	-382.2540
Dimethylaniline	-365.7279	-365.5467	-365.5502	-365.7249
2,6-Dimethoxyphenol	-535.8950	-535.7024	-535.7093	-535.8876
o-Chlorophenol	-766.5063	-766.1981	-766.2026	-766.5004
Diethylaniline	-444.2696	-444.0938	-444.0963	-444.2669
Phenol	-307.1052	-306.7939	-306.8056	-307.0913
2,4-Dichlorophenol	-1225.9066	-1225.6869	-1225.6932	-1225.9008
Hydroquinone	-382.2632	-381.9529	-381.9645	-382.2484
Resorcinol	-382.2664	-381.9384	-381.9543	-382.2480
Guaiacol	-421.4995	-421.3012	-421.3076	-421.4923
p-Toulidine	-326.5122	-326.3356	-326.3398	-326.5089
m-Chlorophenol	-766.5078	-766.1989	-766.2038	-766.5000
Caffeic acid	-647.4957	-647.2836	-647.2984	-647.4737
o-Cresol	-346.3690	-346.0620	-346.0739	-346.3554
Pyrogallol	-457.4191	-457.2231	-457.2304	-457.4105
p-Hydroxybenzoic acid	-495.0384	-494.8232	-494.8376	-495.0173

Table S20. Solution phase energies (in Hartree) of dataset-B reported using B3LYP.

Compound	**$E_x(x)$**	**$E_{x^+}(x)$**	**$E_{x^+}(x^+)$**	**$E_x(x^+)$**
1	-626.5170	-626.2929	-626.3010	-626.5080
2	-535.3435	-535.0849	-535.0909	-535.3362
3	-574.6663	-574.4141	-574.4203	-574.6579
4	-649.8985	-649.6146	-649.6248	-649.8854
5	-517.1585	-516.9496	-516.9567	-517.1479
6	-610.1278	-609.8998	-609.9153	-610.1051
7	-536.5443	-536.3429	-536.3509	-536.5345
8	-422.0098	-421.8052	-421.8139	-422.0009
9	-649.4325	-649.2381	-649.2424	-649.4249
10	-461.3293	-461.1307	-461.1394	-461.3205
11	-649.8663	-649.6074	-649.6137	-649.8578
12	-689.1899	-688.9369	-688.9435	-689.1800
13	-1258.7526	-1258.5248	-1258.5500	-1258.7201
14	-536.5329	-536.3324	-536.3416	-536.5236
15	-724.6514	-724.4098	-724.4603	-724.6420
16	-921.7650	-921.5461	-921.5792	-921.7617
17	-1128.2916	-1128.0861	-1128.0985	-1128.2845
20	-307.4879	-307.1528	-307.1674	-307.4733
21	-346.8085	-346.4788	-346.4940	-346.7903
22	-386.1233	-385.9090	-385.9165	-386.1165
23	-382.7130	-382.5069	-382.5158	-382.7045
24	-495.6060	-495.3780	-495.3936	-495.5832
25	-570.8314	-570.6028	-570.6184	-570.8088
26	-739.4133	-739.1931	-739.2028	-739.3973
27	-460.1450	-459.8926	-459.8990	-460.1373
28	-810.1228	-809.8970	-809.9124	-810.1001
29	-835.1063	-834.9021	-834.9089	-835.0983
30	-342.9781	-342.8163	-342.8235	-342.9726
31	-1028.6329	-1028.4228	-1028.4283	-1028.6287
32	-402.1457	-401.9682	-401.9750	-402.1394
33	-744.9736	-744.7679	-744.7745	-744.9680
34	-574.2219	-573.9932	-574.0082	-574.1997
35	-649.4238	-649.1960	-649.2115	-649.4009
36	-501.3731	-501.1957	-501.2031	-501.3643

Table S21. Solution phase energies (in Hartree) of dataset-B reported using M06.

Compound	**$E_x(x)$**	**$E_{x^+}(x)$**	**$E_{x^+}(x^+)$**	**$E_x(x^+)$**
1	-626.1587	-625.9298	-625.9383	-626.1492
2	-535.0154	-534.7500	-534.7557	-535.0082
3	-574.3063	-574.0468	-574.0529	-574.2978
4	-649.5121	-649.2188	-649.2303	-649.4977
5	-516.8158	-516.6027	-516.6101	-516.8048
6	-609.7778	-609.5365	-609.5582	-609.7639
7	-536.2124	-536.0078	-536.0161	-536.2028
8	-421.7350	-421.5266	-421.5356	-421.7260
9	-649.0584	-648.8573	-648.8671	-649.0476
10	-461.0222	-460.8203	-460.8291	-461.0131
11	-649.4795	-649.2131	-649.2191	-649.4709
12	-688.7709	-688.5104	-688.5168	-688.7610
13	-1257.9778	-1257.7446	-1257.7691	-1257.9470
14	-536.1994	-535.9945	-536.0040	-536.1901
15	-724.2457	-724.0065	-724.0504	-724.2362
16	-921.1527	-920.9304	-920.9527	-921.1384
17	-1127.5817	-1127.3723	-1127.3847	-1127.5735
20	-307.2721	-306.9371	-306.9519	-307.2558
21	-346.5607	-346.2300	-346.2457	-346.5425
22	-385.8426	-385.6254	-385.6332	-385.8357
23	-382.4736	-382.2641	-382.2733	-382.4647
24	-495.3150	-495.0729	-495.0952	-495.3011
25	-570.5165	-570.2749	-570.2965	-570.5029
26	-739.0091	-738.7803	-738.7864	-738.9946
27	-459.8439	-459.5845	-459.5906	-459.8361
28	-809.5806	-809.3413	-809.3636	-809.5675
29	-834.4735	-834.2663	-834.2731	-834.4658
30	-342.7299	-342.5618	-342.5693	-342.7238
31	-1028.3860	-1028.1735	-1028.1788	-1028.3815
32	-401.8666	-401.6836	-401.6909	-401.8599
33	-744.6951	-744.4865	-744.4926	-744.6885
34	-573.8638	-573.6221	-573.6427	-573.8496
35	-649.0381	-648.7966	-648.8185	-649.0242
36	-501.0732	-500.8902	-500.8978	-501.0640

Table S22. Solution phase energies (in Hartree) of dataset-B reported using PBE.

Compound	**$E_x(x)$**	**$E_{x^+}(x)$**	**$E_{x^+}(x^+)$**	**$E_x(x^+)$**
1	-625.8336	-625.6170	-625.6229	-625.8267
2	-534.7183	-534.4701	-534.4734	-534.7140
3	-573.9837	-573.7416	-573.7457	-573.9776
4	-649.1445	-648.8748	-648.8801	-649.1380
5	-516.5290	-516.3243	-516.3305	-516.5209
6	-609.4327	-609.2180	-609.2323	-609.4119
7	-535.9055	-535.7118	-535.7173	-535.8984
8	-421.4995	-421.3012	-421.3076	-421.4923
9	-648.6848	-648.5008	-648.5097	-648.6749
10	-460.7620	-460.5696	-460.5763	-460.7549
11	-649.1139	-648.8666	-648.8695	-649.1096
12	-688.3801	-688.1377	-688.1422	-688.3737
13	-1257.2862	-1257.0712	-1257.0949	-1257.2562
14	-535.8950	-535.7024	-535.7093	-535.8876
15	-723.8286	-723.6139	-723.6280	-723.8075
16	-920.6170	-920.4251	-920.4278	-920.6075
17	-1126.9499	-1126.7546	-1126.7571	-1126.9401
20	-307.1052	-306.7939	-306.8056	-307.0913
21	-346.3690	-346.0620	-346.0738	-346.3552
22	-385.6256	-385.4156	-385.4208	-385.6184
23	-382.2613	-382.0617	-382.0682	-382.2539
24	-495.0383	-494.8232	-494.8377	-495.0173
25	-570.1950	-569.9797	-569.9941	-570.1740
26	-738.6154	-738.4121	-738.4214	-738.6025
27	-459.5896	-459.3457	-459.3502	-459.5827
28	-809.1005	-808.8880	-808.9018	-809.0799
29	-833.9715	-833.7707	-833.7777	-833.9649
30	-342.5467	-342.3904	-342.3951	-342.5416
31	-1027.9594	-1027.7552	-1027.7590	-1027.9557
32	-401.6458	-401.4727	-401.4776	-401.6407
33	-744.3525	-744.1530	-744.1572	-744.3474
34	-573.5388	-573.3231	-573.3367	-573.5186
35	-648.6700	-648.4555	-648.4696	-648.6490
36	-500.7891	-500.6176	-500.6237	-500.7833

Table S23. Gas phase energies (in Hartree) of dataset-A reported using B3LYP.

Compound	**$E_x(x)$**	**$E_{x^+}(x)$**	**$E_{x^+}(x^+)$**	**$E_x(x^+)$**
N,*N*-Dimethyl-*p*-phenylenediamine	-421.5739	-421.3159	-421.3200	-421.5701
2,6-Dichlorophenol	-1226.6643	-1226.3516	-1226.3594	-1226.6567
TOOS	-1221.9933	-1221.8521	-1221.8594	-1221.9951
Hydrocaffeic acid	-649.3252	-649.2125	-649.2283	-649.3111
Catechol	-382.6923	-382.4080	-382.4168	-382.6831
Dimethylaniline	-366.2174	-365.9489	-365.9522	-366.2138
2,6-Dimethoxyphenol	-536.5232	-536.2564	-536.2662	-536.5130
o-Chlorophenol	-767.0695	-766.6696	-766.6747	-767.0575
Diethylaniline	-444.8662	-444.6190	-444.6220	-444.8625
Phenol	-307.4782	-307.0587	-307.0733	-307.4629
2,4-Dichlorophenol	-1226.6618	-1226.3566	-1226.3646	-1226.6540
Hydroquinone	-382.6952	-382.2777	-382.2927	-382.6789
Resorcinol	-382.6978	-382.2680	-382.2834	-382.6792
Guaiacol	-421.9973	-421.7204	-421.7294	-421.9877
p-Toulidine	-326.9341	-326.6755	-326.6806	-326.9289
m-Chlorophenol	-767.0725	-766.6666	-766.6714	-767.0663
Caffeic acid	-648.0978	-647.9889	-648.0013	-648.0567
o-Cresol	-346.7993	-346.3902	-346.4052	-346.7805
Pyrogallol	-457.9129	-457.6333	-457.6434	-457.9027
p-Hydroxybenzoic acid	-495.4818	-495.3700	-495.3821	-495.4429

Table S24. Gas phase energies (in Hartree) of dataset-A reported using M06.

Compound	**$E_x(x)$**	**$E_{x^+}(x)$**	**$E_{x^+}(x^+)$**	**$E_x(x^+)$**
N,*N*-Dimethyl-*p*-phenylenediamine	-421.2568	-420.9923	-420.9963	-421.2532
2,6-Dichlorophenol	-1226.4004	-1226.0852	-1226.0933	-1226.3924
TOOS	-1221.4554	-1221.3036	-1221.3110	-1221.4561
Hydrocaffeic acid	-648.9461	-648.8235	-648.8410	-648.9313
Catechol	-382.4521	-382.1646	-382.1737	-382.4426
Dimethylaniline	-365.9287	-365.6540	-365.6573	-365.9253
2,6-Dimethoxyphenol	-536.1894	-535.9179	-535.9280	-536.1791
o-Chlorophenol	-766.8293	-766.4264	-766.4307	-766.8211
Diethylaniline	-444.5153	-444.2615	-444.2656	-444.5110
Phenol	-307.2618	-306.8420	-306.8570	-307.2449
2,4-Dichlorophenol	-1226.3973	-1226.0899	-1226.0982	-1226.3892
Hydroquinone	-382.4548	-382.0365	-382.0525	-382.4369
Resorcinol	-382.4576	-382.0226	-382.0381	-382.4388
Guaiacol	-421.7221	-421.4411	-421.4505	-421.7123
p-Toulidine	-326.6809	-326.4182	-326.4238	-326.6751
m-Chlorophenol	-766.8317	-766.4228	-766.4283	-766.8212
Caffeic acid	-647.7214	-647.6020	-647.6152	-647.6792
o-Cresol	-346.5511	-346.1404	-346.1560	-346.5320
Pyrogallol	-457.6492	-457.3660	-457.3764	-457.6386
p-Hydroxybenzoic acid	-495.1927	-495.0709	-495.0836	-495.1528

Table S25. Gas phase energies (in Hartree) of dataset-A reported using the PBE functional.

Compound	**$E_x(x)$**	**$E_{x^+}(x)$**	**$E_{x^+}(x^+)$**	**$E_x(x^+)$**
N,*N*-Dimethyl-*p*-phenylenediamine	-421.0239	-420.7723	-420.7760	-421.0205
2,6-Dichlorophenol	-1225.8994	-1225.5940	-1225.6008	-1225.8928
TOOS	-1220.8266	-1220.7058	-1220.7122	-1220.8259
Hydrocaffeic acid	-648.5776	-648.4849	-648.4941	-648.5695
Catechol	-382.2415	-381.9635	-381.9705	-382.2328
Dimethylaniline	-365.7266	-365.4635	-365.4665	-365.7235
2,6-Dimethoxyphenol	-535.8858	-535.6271	-535.6346	-535.8771
o-Chlorophenol	-766.4955	-766.1115	-766.1165	-766.4891
Diethylaniline	-444.2636	-444.0193	-444.0217	-444.2609
Phenol	-307.0956	-306.7001	-306.7118	-307.0805
2,4-Dichlorophenol	-1225.8961	-1225.5996	-1225.6061	-1225.8897
Hydroquinone	-382.2439	-381.8522	-381.8647	-382.2281
Resorcinol	-382.2465	-381.8354	-381.8537	-382.2255
Guaiacol	-421.4877	-421.2170	-421.2241	-421.4793
p-Toulidine	-326.5037	-326.2486	-326.2529	-326.4997
m-Chlorophenol	-766.4982	-766.1117	-766.1165	-766.4896
Caffeic acid	-647.3622	-647.2639	-647.2755	-647.3242
o-Cresol	-346.3597	-345.9732	-345.9851	-346.3449
Pyrogallol	-457.3932	-457.1214	-457.1298	-457.3827
p-Hydroxybenzoic acid	-494.9180	-494.8160	-494.8274	-494.8823

Table S26. Gas phase energies (in Hartree) of dataset-B reported using B3LYP.

Compound	**$E_x(x)$**	**$E_{x^+}(x)$**	**$E_{x^+}(x^+)$**	**$E_x(x^+)$**
1	-626.5011	-626.1971	-626.2065	-626.4908
2	-535.3257	-534.9963	-535.0045	-535.3149
3	-574.6470	-574.3289	-574.3370	-574.6361
4	-649.8820	-649.5355	-649.5465	-649.8640
5	-517.0426	-516.6371	-516.6470	-517.0321
6	-610.0022	-609.8896	-609.9022	-609.9629
7	-536.5232	-536.2546	-536.2636	-536.5127
8	-421.9973	-421.7204	-421.7294	-421.9877
9	-649.3134	-649.2063	-649.2140	-649.2907
10	-461.3170	-461.0487	-461.0577	-461.3075
11	-649.8520	-649.5263	-649.5355	-649.8401
12	-689.1743	-688.8587	-688.8680	-689.1619
13	-1258.7283	-1258.4528	-1258.4805	-1258.6949
14	-536.5232	-536.2564	-536.2662	-536.5130
15	-724.5302	-724.4016	-724.4129	-724.5146
16	-921.6656	-921.2743	-921.3269	-921.6199
17	-1128.2699	-1128.0048	-1128.0178	-1128.2598
20	-307.4782	-307.0587	-307.0733	-307.4629
21	-346.7993	-346.3902	-346.4052	-346.7805
22	-386.1152	-385.8234	-385.8308	-386.1078
23	-382.6923	-382.4080	-382.4168	-382.6831
24	-495.4818	-495.3700	-495.3821	-495.4429
25	-570.6985	-570.5841	-570.5966	-570.6589
26	-739.2980	-739.1701	-739.1806	-739.2746
27	-460.1283	-459.8059	-459.8135	-460.1182
28	-810.0057	-809.8946	-809.9068	-809.9660
29	-834.9904	-834.6475	-834.6550	-834.9831
30	-342.9621	-342.7215	-342.7279	-342.9555
31	-1028.6288	-1028.3416	-1028.3467	-1028.6245
32	-402.1392	-401.8870	-401.8941	-402.1318
33	-744.9698	-744.6927	-744.6996	-744.9634
34	-574.1085	-573.9953	-574.0073	-574.0713
35	-649.3064	-649.1950	-649.2074	-649.2667
36	-501.3633	-501.1100	-501.1188	-501.3542

Table S27. Gas phase energies (in Hartree) of dataset-B reported using the M06 functional.

Compound	**$E_x(x)$**	**$E_{x^+}(x)$**	**$E_{x^+}(x^+)$**	**$E_x(x^+)$**
1	-626.1423	-625.8334	-625.8432	-626.1315
2	-534.9970	-534.6603	-534.6683	-534.9865
3	-574.2862	-573.9608	-573.9689	-574.2752
4	-649.4949	-649.1388	-649.1514	-649.4758
5	-516.6996	-516.2883	-516.2992	-516.6883
6	-609.6543	-609.5240	-609.5448	-609.6230
7	-536.1905	-535.9189	-535.9281	-536.1801
8	-421.7221	-421.4411	-421.4505	-421.7123
9	-648.9327	-648.8138	-648.8245	-648.9134
10	-461.0093	-460.7377	-460.7469	-460.9996
11	-649.4647	-649.1310	-649.1399	-649.4527
12	-688.7546	-688.4312	-688.4405	-688.7421
13	-1257.9529	-1257.6712	-1257.6977	-1257.9209
14	-536.1894	-535.9179	-535.9280	-536.1791
15	-724.1237	-723.9993	-723.9978	-724.1080
16	-921.0526	-920.6558	-920.6976	-920.9986
17	-1127.5585	-1127.2887	-1127.3038	-1127.5485
20	-307.2618	-306.8420	-306.8570	-307.2449
21	-346.5511	-346.1404	-346.1560	-346.5323
22	-385.8341	-385.5399	-385.5474	-385.8264
23	-382.4521	-382.1646	-382.1737	-382.4426
24	-495.1927	-495.0633	-495.0836	-495.1620
25	-570.3855	-570.2534	-570.2741	-570.3541
26	-738.8925	-738.7528	-738.7652	-738.8624
27	-459.8263	-459.4970	-459.5045	-459.8160
28	-809.4662	-809.3375	-809.3580	-809.4351
29	-834.3574	-834.0105	-834.0185	-834.3502
30	-342.7134	-342.4673	-342.4739	-342.7062
31	-1028.3821	-1028.0934	-1028.0986	-1028.3776
32	-401.8598	-401.6024	-401.6099	-401.8520
33	-744.6912	-744.4112	-744.4181	-744.6837
34	-573.7526	-573.6224	-573.6418	-573.7223
35	-648.9238	-648.7941	-648.8148	-648.8921
36	-501.0631	-500.8042	-500.8133	-501.0536

Table S28. Gas phase energies (in Hartree) of dataset-B reported using the PBE functional.

Compound	**$E_x(x)$**	**$E_x^+(x)$**	**$E_x^+(x^+)$**	**$E_x(x^+)$**
1	-625.8188	-625.5233	-625.5304	-625.8104
2	-534.7014	-534.3847	-534.3891	-534.6949
3	-573.9654	-573.6591	-573.6643	-573.9575
4	-649.1291	-648.7997	-648.8056	-649.1193
5	-516.4151	-516.0144	-516.0232	-516.4046
6	-609.3111	-609.2090	-609.2207	-609.2749
7	-535.8853	-535.6250	-535.6316	-535.8765
8	-421.4877	-421.2170	-421.2241	-421.4793
9	-648.5660	-648.4714	-648.4811	-648.5466
10	-460.7502	-460.4883	-460.4957	-460.7420
11	-649.1004	-648.7890	-648.7933	-649.0936
12	-688.3653	-688.0623	-688.0679	-688.3568
13	-1257.2624	-1257.0017	-1257.0278	-1257.2305
14	-535.8858	-535.6271	-535.6346	-535.8772
15	-723.7112	-723.6083	-723.6201	-723.6741
16	-920.4800	-920.1783	-920.1834	-920.4654
17	-1126.9297	-1126.6776	-1126.6855	-1126.9125
20	-307.0956	-306.7001	-306.7118	-307.0805
21	-346.3597	-345.9732	-345.9851	-346.3447
22	-385.6179	-385.3307	-385.3371	-385.6086
23	-382.2415	-381.9635	-381.9705	-382.2328
24	-494.9180	-494.8160	-494.8274	-494.8822
25	-570.0660	-569.9623	-569.9740	-570.0292
26	-738.5074	-738.3844	-738.3990	-738.4828
27	-459.5734	-459.2601	-459.2655	-459.5649
28	-808.9868	-808.8856	-808.8969	-808.9506
29	-833.8606	-833.5187	-833.5294	-833.8484
30	-342.5293	-342.2945	-342.2988	-342.5229
31	-1027.9549	-1027.6743	-1027.6782	-1027.9507
32	-401.6385	-401.3913	-401.3967	-401.6321
33	-744.3481	-744.0778	-744.0829	-744.3425
34	-573.4291	-573.3256	-573.3368	-573.3952
35	-648.5566	-648.4555	-648.4669	-648.5202
36	-500.7791	-500.5329	-500.5403	-500.7725

Table S29. Reorganization energies (in kcal/mol; based on total free energies) of dataset-A calculated using B3LYP, M06 and PBE functionals (arranged according to decreasing activity).

Compound	**Relative activity**	**log (relative activity)**	**Reorganization energy (λ in kcal/mol)**		
			B3LYP	**M06**	**PBE**
N,*N*-Dimethyl-*p*-phenylenediamine	377	2.58	4.35	4.13	2.85
2,6-Dichlorophenol	258	2.41	8.37	9.14	7.13
TOOS	198	2.30	6.19	6.59	5.15
Hydrocaffeic acid	185	2.27	9.92	12.18	8.21
Catechol	176	2.25	10.47	10.75	8.27
Dimethylaniline	165	2.22	3.27	3.47	3.78
2,6-Dimethoxyphenol	159	2.20	10.43	11.78	9.55
o-Chlorophenol	150	2.18	8.85	5.55	7.28
Diethylaniline	103	2.01	3.80	4.50	3.12
Phenol	100	2.00	18.73	16.86	17.67
2,4-Dichlorophenol	93	1.97	8.93	8.89	6.80
Hydroquinone	89	1.95	14.14	19.08	12.53
Resorcinol	73	1.86	17.48	24.35	16.35
Guaiacol	61	1.79	9.69	11.36	7.47
p-Toulidine	51	1.71	5.77	6.46	6.46
m-Chlorophenol	50	1.70	3.59	7.95	8.67
Caffeic acid	39	1.59	24.23	24.29	22.75
o-Cresol	39	1.59	21.40	18.14	18.84
Pyrogallol	10	1.00	11.47	11.49	9.28
p-Hydroxybenzoic acid	3	0.48	22.94	24.75	21.85

Table S30. Reorganization energies (in kcal/mol; based on total free energies) of dataset-B calculated using B3LYP, M06 and PBE functionals (arranged according to decreasing k_{cat}).

Compound	**k_{cat} (min^{-1})**	**log(k_{cat})**	**Reorganization energy (λ in kcal/mol)**		
			B3LYP	**M06**	**PBE**
31	45000	4.65	5.78	5.86	4.22
10	3600	3.56	9.43	10.37	8.71
22	3500	3.54	7.84	9.07	6.89
23	3300	3.52	10.49	10.77	8.28
14	3100	3.49	10.41	11.78	9.53
15	3100	3.49	38.33	31.02	21.16
25	3000	3.48	23.57	23.70	22.48
13	2900	3.46	36.87	33.89	32.11
33	2900	3.46	6.89	8.25	5.09
7	2600	3.41	10.55	9.13	8.09
6	2500	3.40	23.77	22.21	22.41
8	2400	3.38	9.69	11.32	7.46
5	2300	3.36	9.65	10.79	8.30
9	2200	3.34	8.35	12.61	10.76
11	2200	3.34	7.48	8.47	5.25
17	2100	3.32	16.19	11.54	6.87
30	2100	3.32	6.95	7.63	6.32
12	1800	3.26	9.18	10.22	6.69
16	1700	3.23	24.81	22.73	9.88
20	1600	3.20	18.73	16.87	17.67
2	1300	3.11	7.48	7.06	4.18
21	1300	3.11	21.40	17.98	19.14
4	1200	3.08	15.63	17.18	8.47
3	1100	3.04	9.00	9.00	5.46
32	970	2.99	8.14	8.80	5.54
26	340	2.53	13.97	14.21	11.90
1	320	2.51	9.38	10.98	6.73
36	240	2.38	8.75	8.99	7.20
24	120	2.08	22.93	27.39	21.81
27	40	1.60	7.80	8.87	6.14
28	40	1.60	23.36	29.72	21.05
29	40	1.60	11.88	11.70	10.60
34	40	1.60	21.90	21.79	21.44
35	40	1.60	23.90	22.69	22.25

Table S31. Reorganization energies (in kcal/mol; based on solution phase energies) of dataset-A calculated using B3LYP, M06 and PBE (arranged according to decreasing activity).

Compound	**Relative activity**	**log (relative activity)**	**Reorganization energy (λ in kcal/mol)**		
			B3LYP	**M06**	**PBE**
N,*N*-Dimethyl-*p*-phenylenediamine	377	2.58	4.69	4.41	4.16
2,6-Dichlorophenol	258	2.41	9.01	9.95	7.78
TOOS	198	2.30	2.41	3.59	4.50
Hydrocaffeic acid	185	2.27	10.87	11.49	8.30
Catechol	176	2.25	10.89	11.26	8.76
Dimethylaniline	165	2.22	4.47	4.27	4.08
2,6-Dimethoxyphenol	159	2.20	11.55	11.84	8.96
o-Chlorophenol	150	2.18	10.16	7.21	6.57
Diethylaniline	103	2.01	3.82	4.85	3.19
Phenol	100	2.00	18.36	19.47	16.07
2,4-Dichlorophenol	93	1.97	9.72	10.14	7.54
Hydroquinone	89	1.95	18.85	20.35	16.56
Resorcinol	73	1.86	21.02	21.24	21.46
Guaiacol	61	1.79	11.01	11.32	8.52
p-Toulidine	51	1.71	6.13	6.79	4.71
m-Chlorophenol	50	1.70	5.30	8.01	7.97
Caffeic acid	39	1.59	25.06	25.07	23.14
o-Cresol	39	1.59	20.86	21.46	15.99
Pyrogallol	10	1.00	12.19	12.42	10.02
p-Hydroxybenzoic acid	3	0.48	24.08	24.70	22.29

Table S32. Reorganization energies (in kcal/mol; based on solution phase energies) of dataset-B calculated using B3LYP, M06 and PBE (arranged according to decreasing k_{cat}).

Compound	k_{cat} (min^{-1})	$log(k_{cat})$	Reorganization energy (λ in kcal/mol)		
			B3LYP	M06	PBE
31	45000	4.65	6.06	6.16	4.61
10	3600	3.56	11.02	11.31	8.70
22	3500	3.54	8.95	9.20	7.79
23	3300	3.52	10.90	11.27	8.76
14	3100	3.49	11.53	11.82	8.96
15	3100	3.49	37.57	33.57	22.10
25	3000	3.48	23.95	22.10	22.20
13	2900	3.46	36.18	34.73	33.72
33	2900	3.46	7.69	8.00	5.84
7	2600	3.41	11.19	11.25	7.93
6	2500	3.40	24.02	22.28	22.00
8	2400	3.38	11.01	11.29	8.52
5	2300	3.36	11.07	11.58	8.98
9	2200	3.34	7.49	12.89	11.81
11	2200	3.34	9.32	9.14	4.59
17	2100	3.32	12.25	12.99	7.74
30	2100	3.32	7.99	8.55	6.19
12	1800	3.26	10.30	10.26	6.88
16	1700	3.23	22.87	22.96	7.69
20	1600	3.20	18.36	19.48	16.08
2	1300	3.11	8.35	8.05	4.71
21	1300	3.11	20.89	21.27	16.11
4	1200	3.08	14.62	16.24	7.40
3	1100	3.04	9.16	9.16	6.45
32	970	2.99	8.20	8.78	6.28
26	340	2.53	16.15	12.93	13.90
1	320	2.51	10.73	11.32	8.04
36	240	2.38	10.20	10.47	7.48
24	120	2.08	24.07	22.73	22.25
27	40	1.60	8.85	8.80	7.15
28	40	1.60	23.84	22.22	21.59
29	40	1.60	9.25	9.11	8.50
34	40	1.60	23.30	21.77	21.20
35	40	1.60	24.06	22.53	22.01

Table S33. Reorganization energies (in kcal/mol; based on gas phase energies) of dataset-A calculated using B3LYP, M06 and PBE (arranged according to decreasing activity).

Compound	**Relative activity**	**log (relative activity)**	**Reorganization energy (λ in kcal/mol)**		
			B3LYP	**M06**	**PBE**
N,*N*-Dimethyl-*p*-phenylenediamine	377	2.58	4.97	4.70	4.43
2,6-Dichlorophenol	258	2.41	9.67	10.10	8.39
TOOS	198	2.30	3.41	4.15	4.44
Hydrocaffeic acid	185	2.27	18.77	20.31	10.87
Catechol	176	2.25	11.29	11.68	9.91
Dimethylaniline	165	2.22	4.37	4.21	3.80
2,6-Dimethoxyphenol	159	2.20	12.49	12.80	10.20
o-Chlorophenol	150	2.18	10.72	7.90	7.19
Diethylaniline	103	2.01	4.20	5.21	3.18
Phenol	100	2.00	18.75	19.98	16.83
2,4-Dichlorophenol	93	1.97	9.89	10.33	8.15
Hydroquinone	89	1.95	19.65	21.25	17.75
Resorcinol	73	1.86	21.38	21.58	24.65
Guaiacol	61	1.79	11.68	12.06	9.69
p-Toulidine	51	1.71	6.55	7.14	5.31
m-Chlorophenol	50	1.70	6.87	10.08	8.39
Caffeic acid	39	1.59	33.60	34.77	31.09
o-Cresol	39	1.59	21.24	21.75	16.77
Pyrogallol	10	1.00	12.77	13.20	11.90
p-Hydroxybenzoic acid	3	0.48	32.06	33.01	29.58

Table S34. Reorganization energies (in kcal/mol; based on gas phase energies) of dataset-B calculated using B3LYP, M06 and PBE (arranged according to decreasing k_{cat}).

Compound	k_{cat} (min^{-1})	$log(k_{cat})$	Reorganization energy (λ in kcal/mol)		
			B3LYP	M06	PBE
31	45000	4.65	5.87	6.10	5.15
10	3600	3.56	11.56	11.85	9.73
22	3500	3.54	9.28	9.55	9.81
23	3300	3.52	11.28	11.68	9.88
14	3100	3.49	12.49	12.79	10.17
15	3100	3.49	16.89	8.86	30.73
25	3000	3.48	32.66	32.67	30.41
13	2900	3.46	38.36	36.64	36.38
33	2900	3.46	8.29	9.07	6.69
7	2600	3.41	12.22	12.31	9.66
6	2500	3.40	32.60	32.73	30.00
8	2400	3.38	11.68	12.06	9.70
5	2300	3.36	12.86	13.87	12.11
9	2200	3.34	19.11	18.85	18.28
11	2200	3.34	13.26	13.07	6.93
17	2100	3.32	14.55	15.81	15.73
30	2100	3.32	8.14	8.60	6.74
12	1800	3.26	13.66	13.73	8.81
16	1700	3.23	61.63	60.13	12.35
20	1600	3.20	18.75	19.98	16.81
2	1300	3.11	11.85	11.58	6.81
21	1300	3.11	21.28	21.64	16.92
4	1200	3.08	18.21	19.90	9.87
3	1100	3.04	11.92	11.98	8.16
32	970	2.99	9.08	9.54	7.40
26	340	2.53	21.33	26.64	24.63
1	320	2.51	12.36	12.96	9.73
36	240	2.38	11.24	11.74	8.77
24	120	2.08	32.06	32.03	29.58
27	40	1.60	11.11	11.13	8.70
28	40	1.60	32.57	32.46	29.75
29	40	1.60	9.25	9.51	14.38
34	40	1.60	30.89	31.17	28.21
35	40	1.60	32.63	32.85	29.94

Table S35. X- and Y-intersects of correlation plot of dataset-A (after leaving one compound out; using 19 dataset compounds).

	X-intersect	**Y-intersect**
B3LYP	3.39	25.80
M06	3.28	26.24
PBE	3.19	23.75

Table S36. X- and Y-intersects of correlation plot of dataset-B (after leaving two compounds out; using 32 dataset compounds).

	X-intersect	**Y-intersect**
B3LYP	7.72	20.38
M06	7.07	22.26
PBE	6.06	20.37

Figures

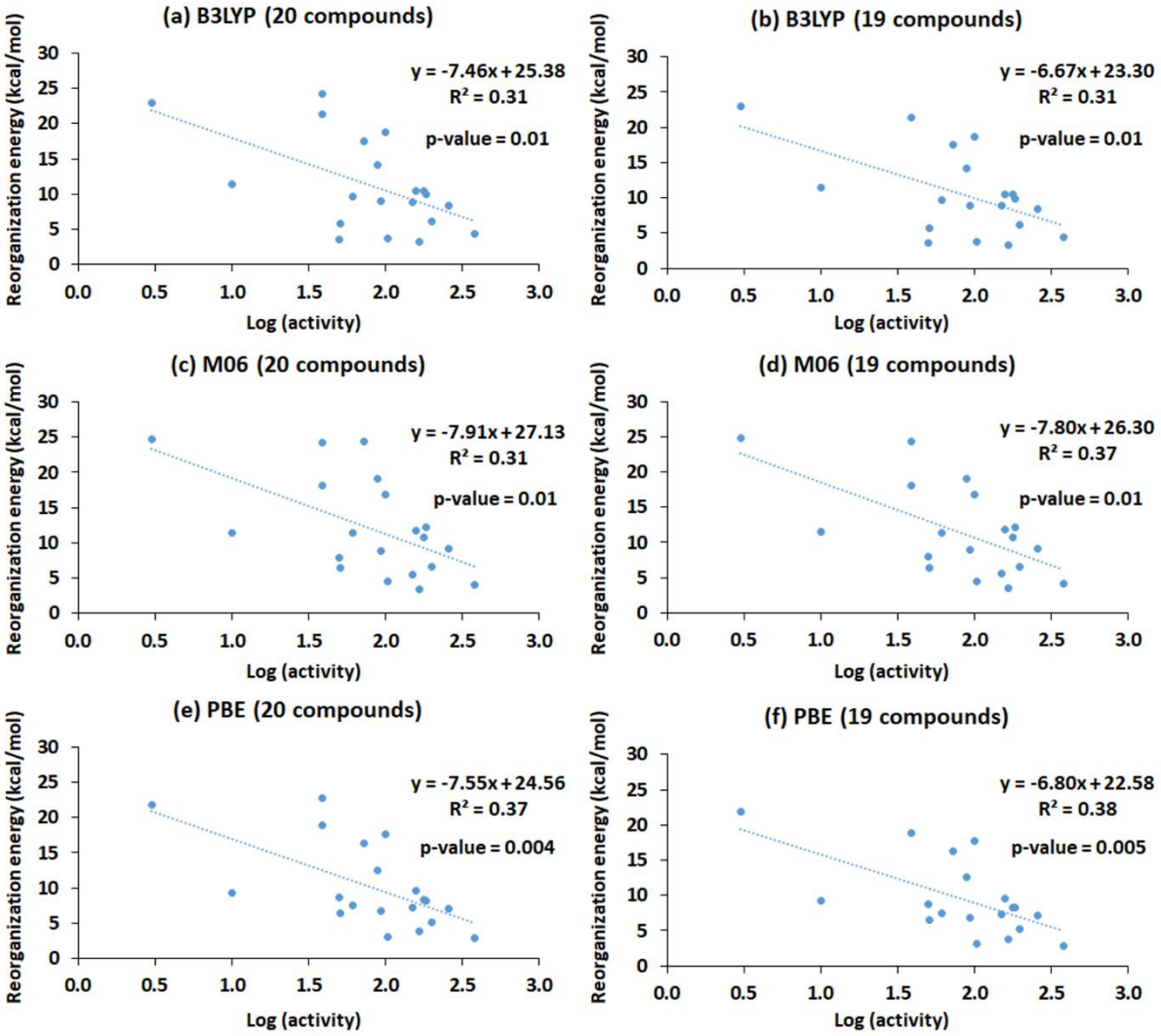
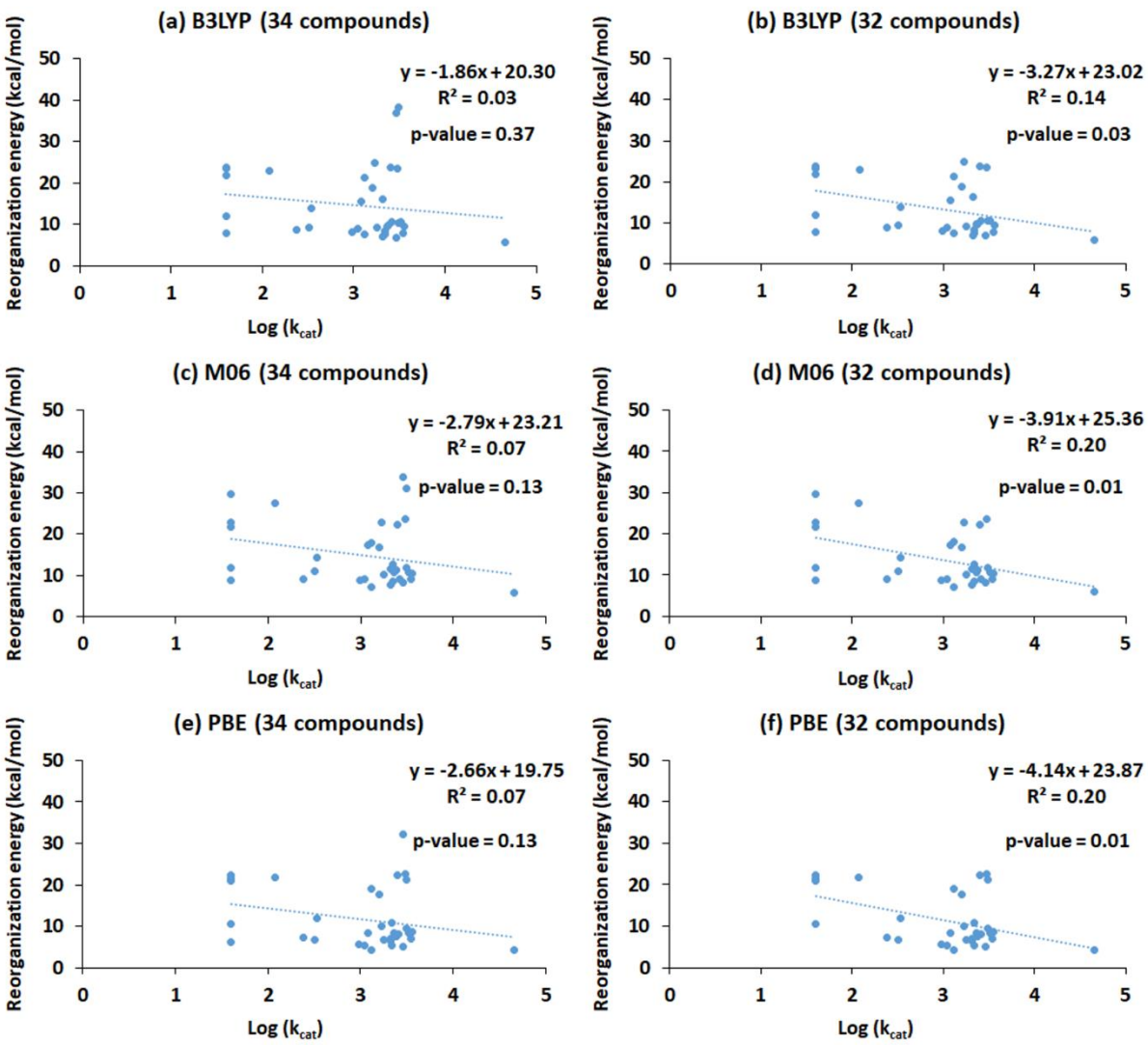


Figure S1. Correlation between log (relative activity) and reorganization energies (computed using total free energies) of dataset-A. **(a)** Correlation with energies calculated using B3LYP. **(b)** Correlation with energies calculated using B3LYP when caffeic acid was left out. **(c)** Correlation with energies calculated using M06. **(d)** Correlation with energies calculated using M06 when resorcinol was left out. **(e)** Correlation with energies calculated using PBE. **(f)** Correlation with energies calculated using PBE when caffeic acid was left out.



Figures S2. Correlation between log (k_{cat}) and reorganization energy (computed using total free energies) of dataset-B. **(a)** Correlation with energies calculated using the B3LYP functional. **(b)** Correlation with energies using B3LYP when compounds 13 and 15 were left out. **(c)** Correlation with energies calculated using M06. **(d)** Correlation with energies using M06 when compounds 13 and 15 were left out. **(e)** Correlation with energies calculated using PBE. **(f)** Correlation with energies using PBE when compounds 13 and 27 were left out.

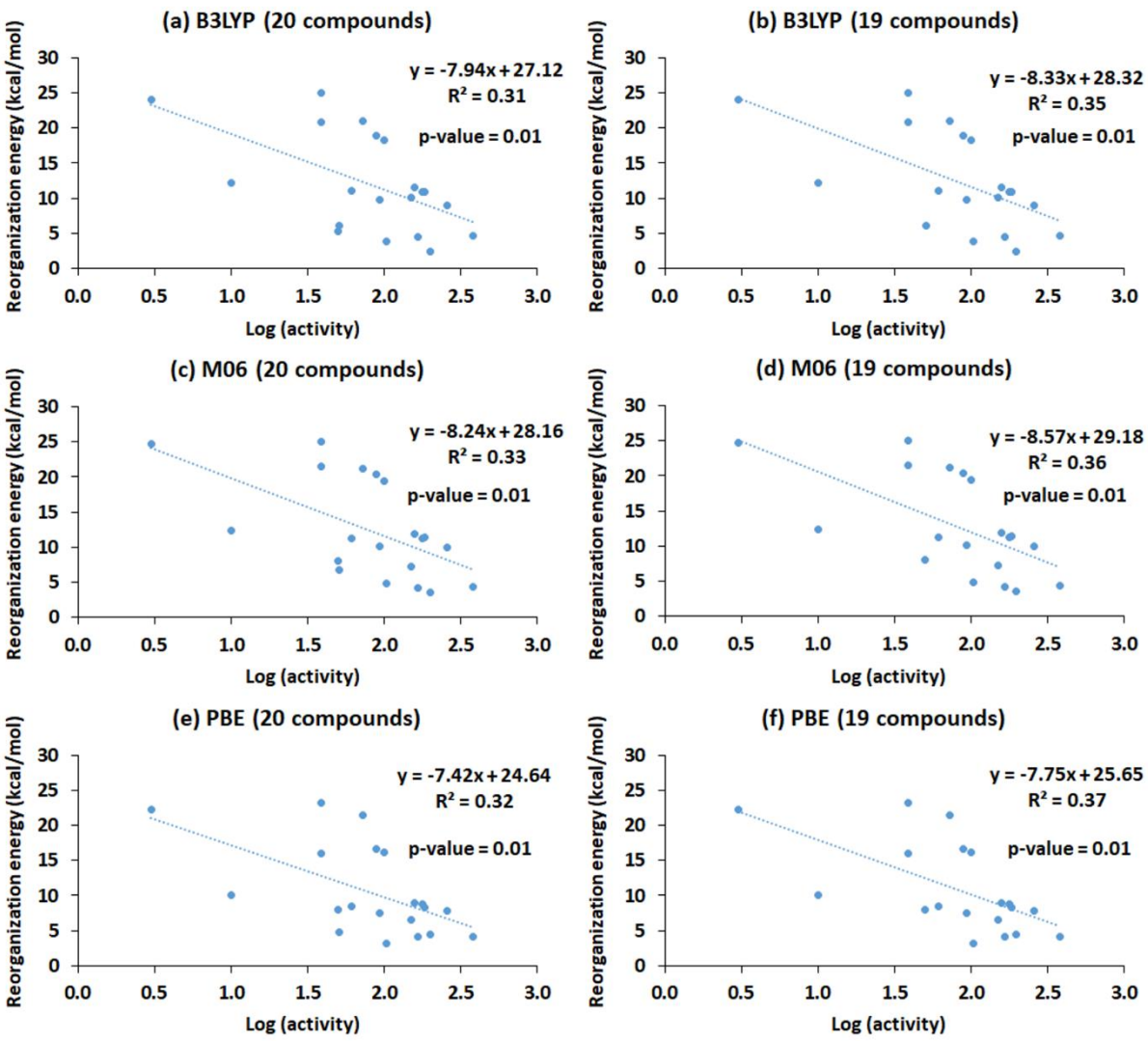


Figure S3. Correlation between log (relative activity) and reorganization energies (computed using solution phase energies) of dataset-A. **(a)** Correlation with energies calculated using B3LYP. **(b)** Correlation with energies calculated using B3LYP when *m*-chlorophenol was left out. **(c)** Correlation with energies using M06. **(d)** Correlation with energies calculated using M06 when *p*-toulidine was left out. **(e)** Correlation with energies using PBE. **(f)** Correlation with energies calculated using PBE when *p*-toulidine was left out.

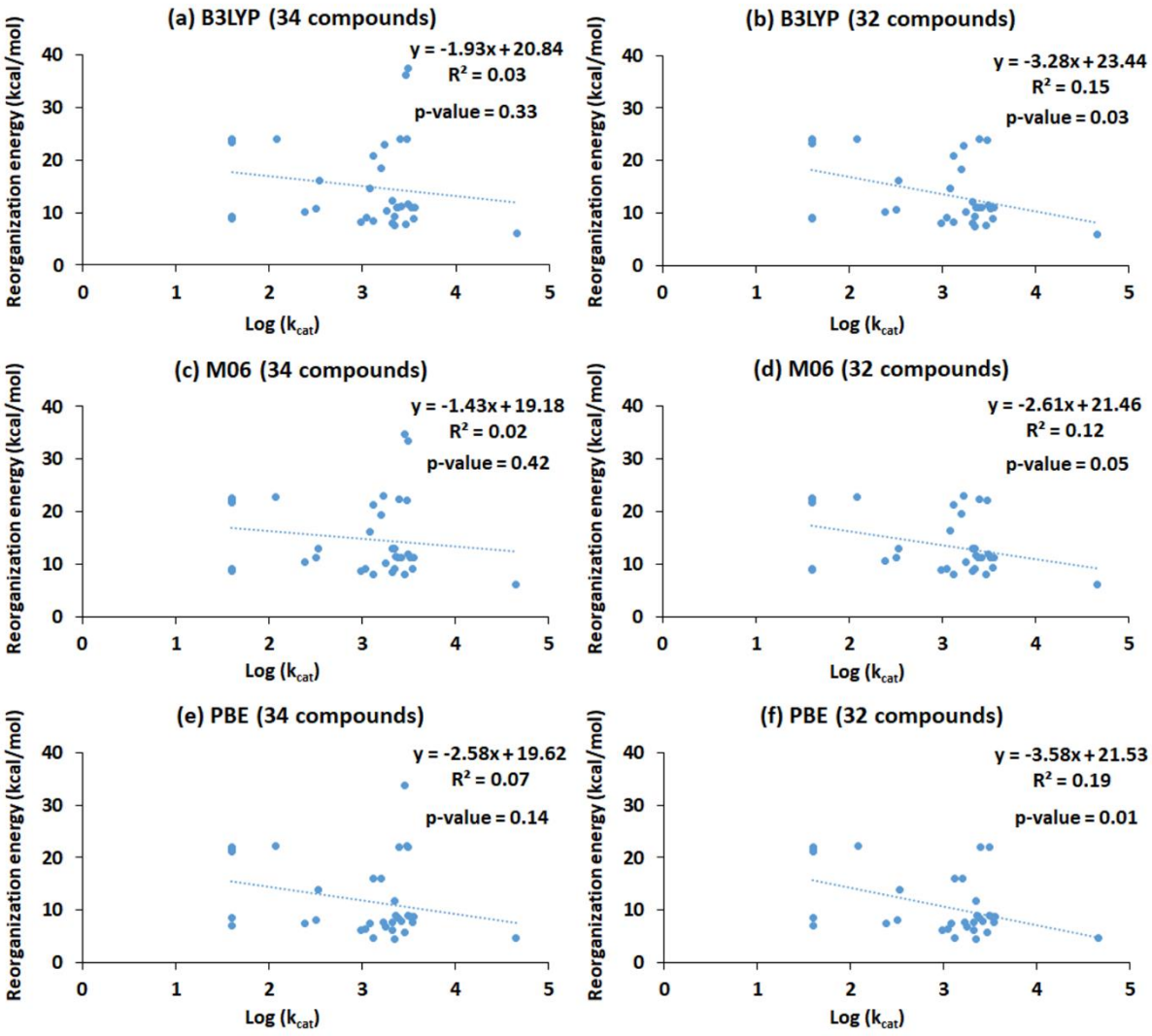


Figure S4. Correlation between log (k_{cat}) and reorganization energies (computed using solution phase energies) of dataset-B. **(a)** Correlation with energies calculated using B3LYP functional. **(b)** Correlation with energies using B3LYP functional when compounds 13 and 15 were left out. **(c)** Correlation with energies using M06 functional. **(d)** Correlation with energies calculated using M06 functional when outliers compounds 13 and 15 were left out. **(e)** Correlation with energies calculated using PBE. **(f)** Correlation with energies using PBE when compounds 13 and 25 were left out.

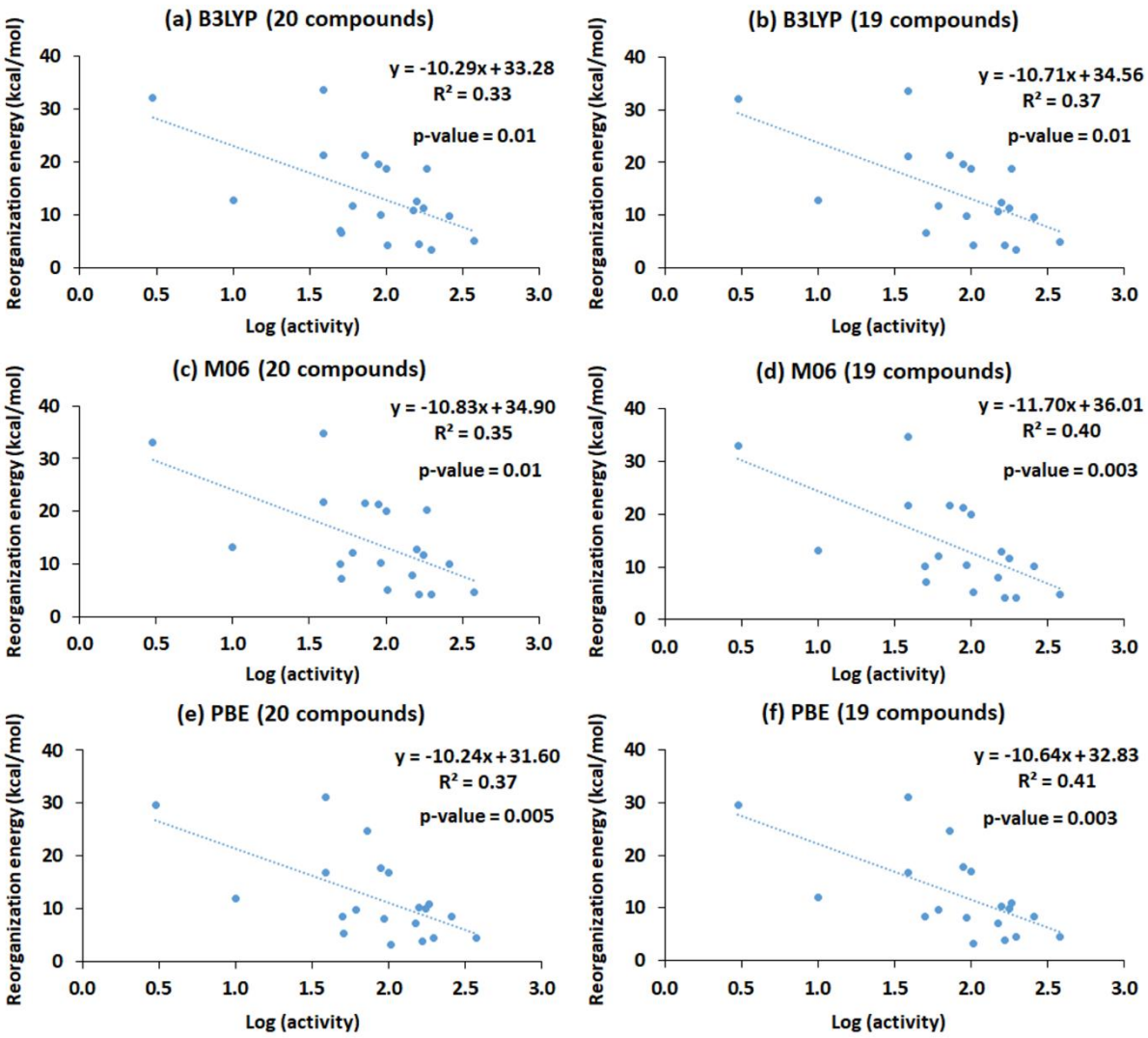


Figure S5. Correlation between log (relative activity) and reorganization energies (computed using gas phase energies) of dataset-A. **(a)** Correlation with energies calculated using B3LYP. **(b)** Correlation with energies using B3LYP when *m*-chlorophenol was left out. **(c)** Correlation with energies calculated using M06. **(d)** Correlation with energies using M06 functional when hydrocaffeic acid was left out. **(e)** Correlation with energies using PBE. **(f)** Correlation with energies calculated using PBE when *p*-toulidine was left out.

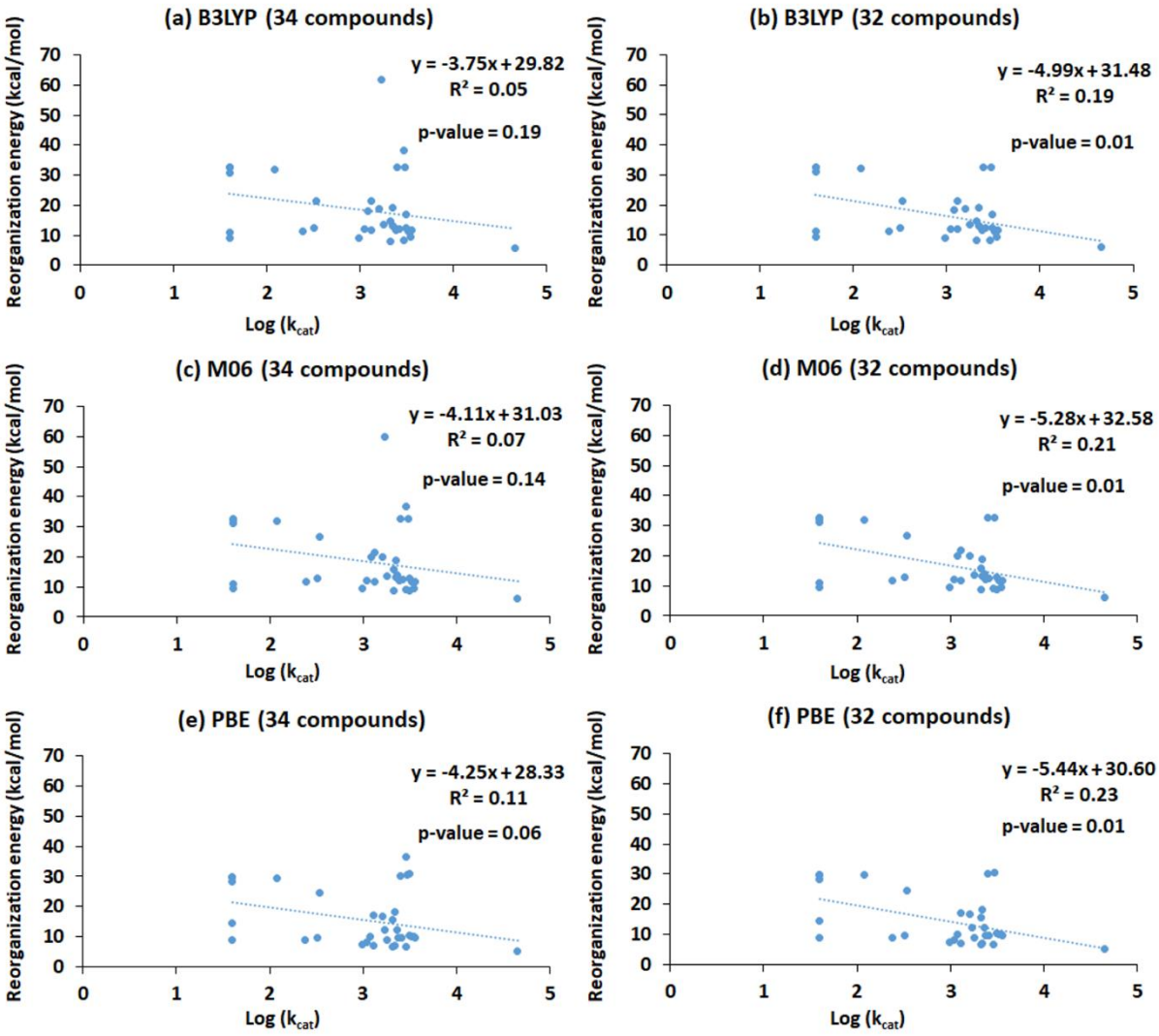
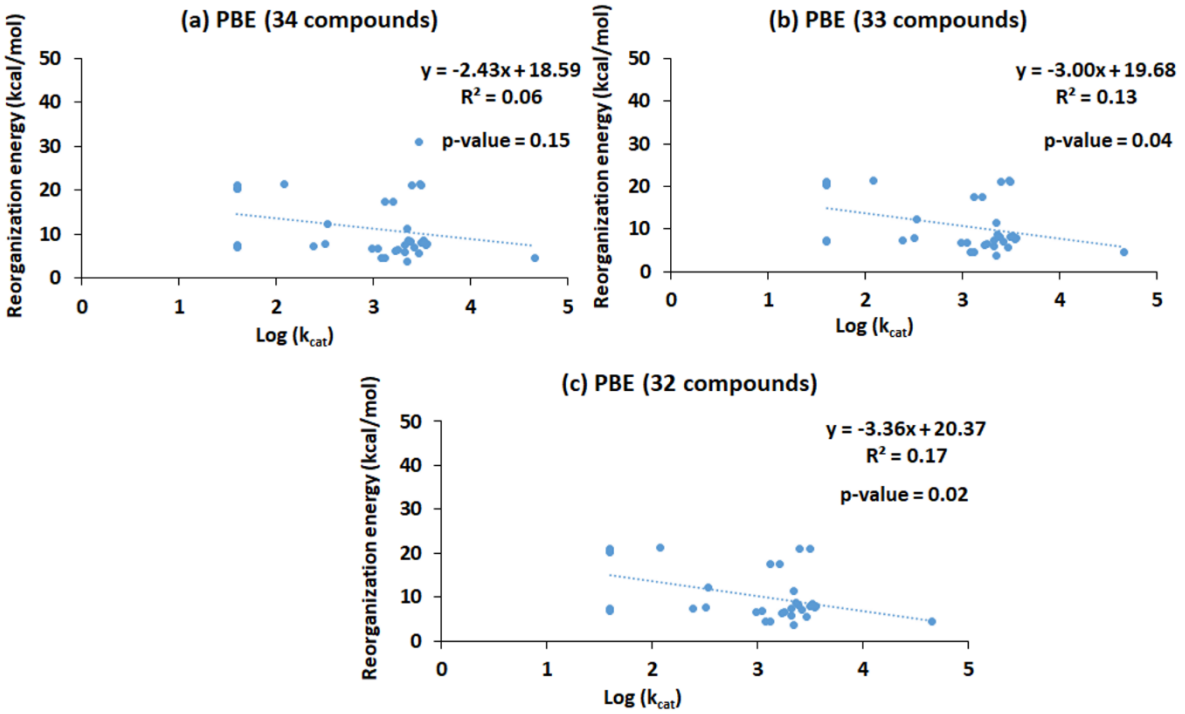
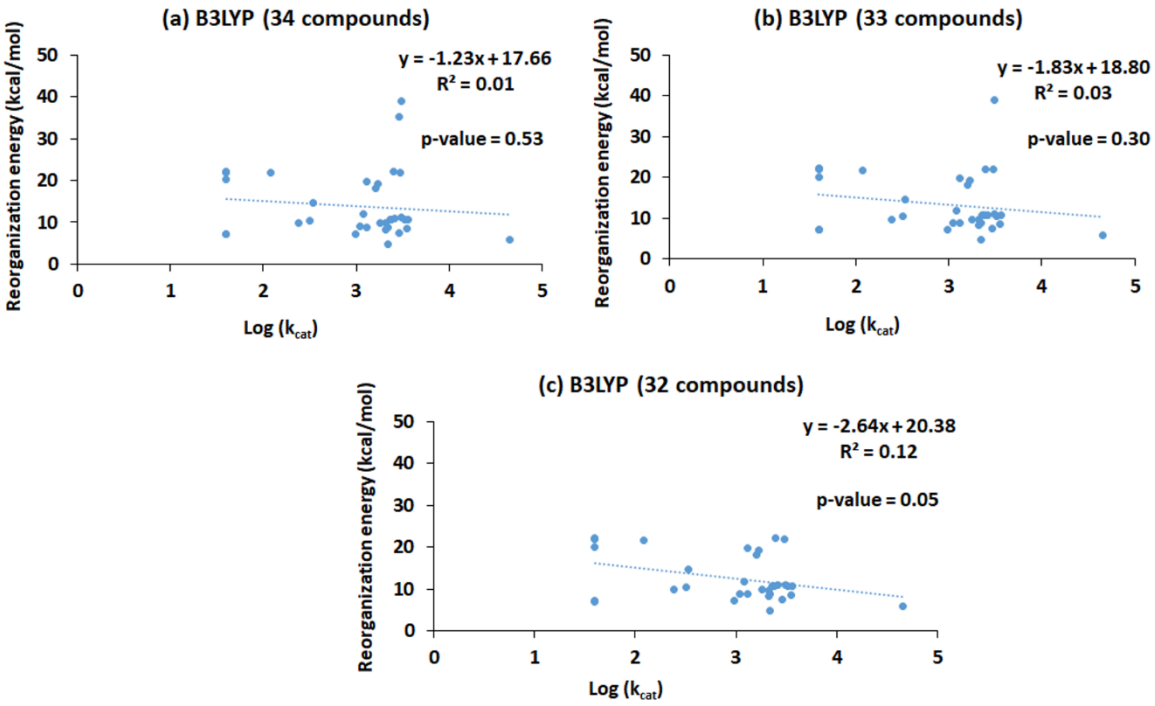


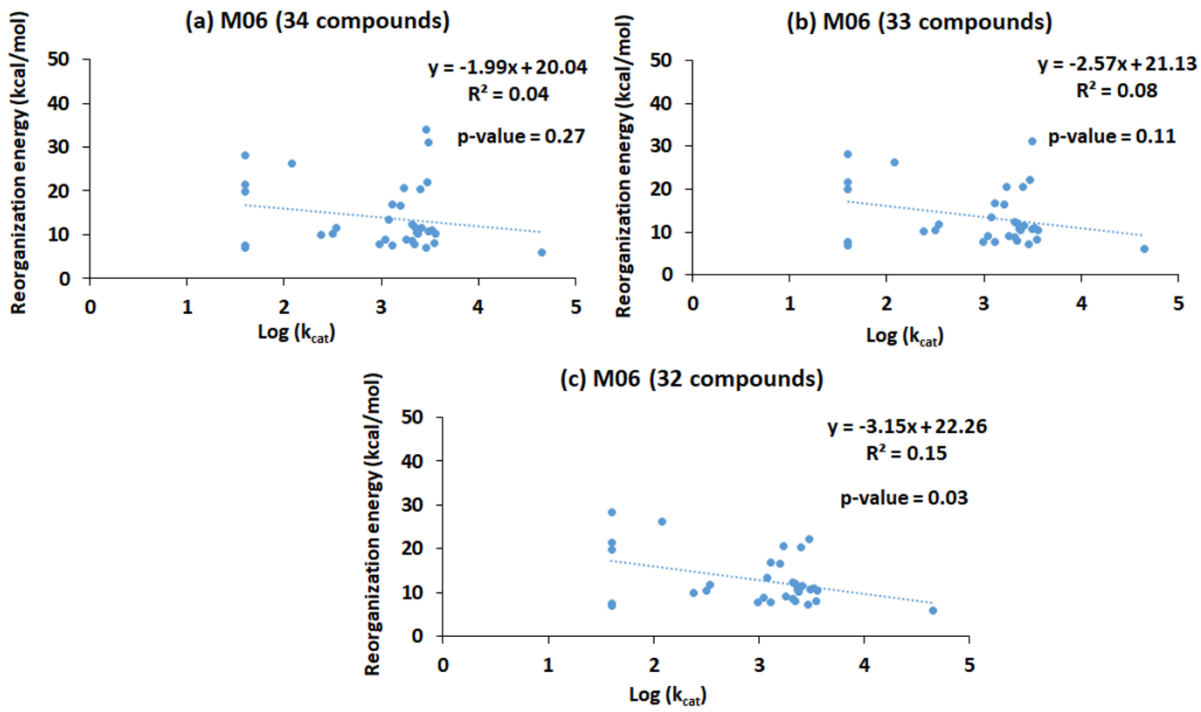
Figure S6. Correlation between log (k_{cat}) and reorganization energies (computed using gas phase energies) of dataset-B. **(a)** Correlation with energies calculated using the B3LYP functional. **(b)** Correlation with energies using B3LYP when compounds 13 and 16 were left out. **(c)** Correlation with energies using M06. **(d)** Correlation with energies using M06 when compounds 13 and 16 were left out. **(e)** Correlation with energies using PBE. **(f)** Correlation with energies using PBE when compounds 13 and 15 were left out.



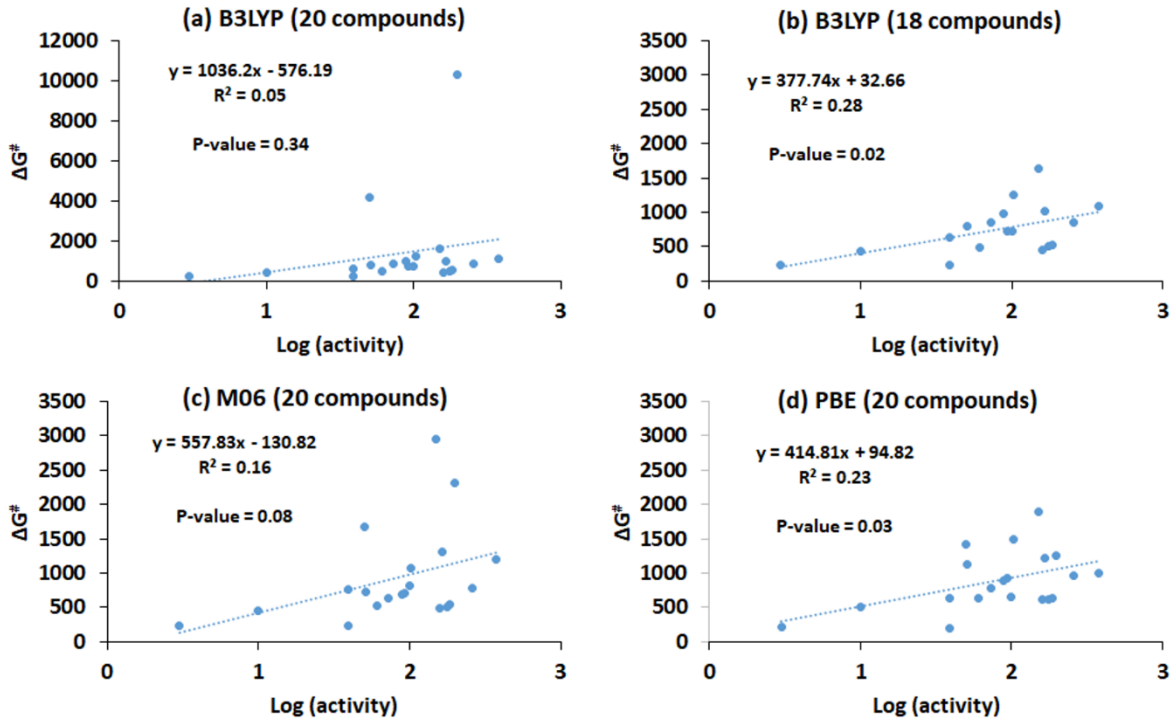
Figures S7. Correlation between log (k_{cat}) and reorganization energy (kcal/mol; computed using total internal energies) of dataset-B compounds calculated using PBE functional. **(a)** Correlation using full dataset. **(b)** Correlation with energies when an outlier compound 13 was removed. **(c)** Correlation with energies when another compound 25 was left out.



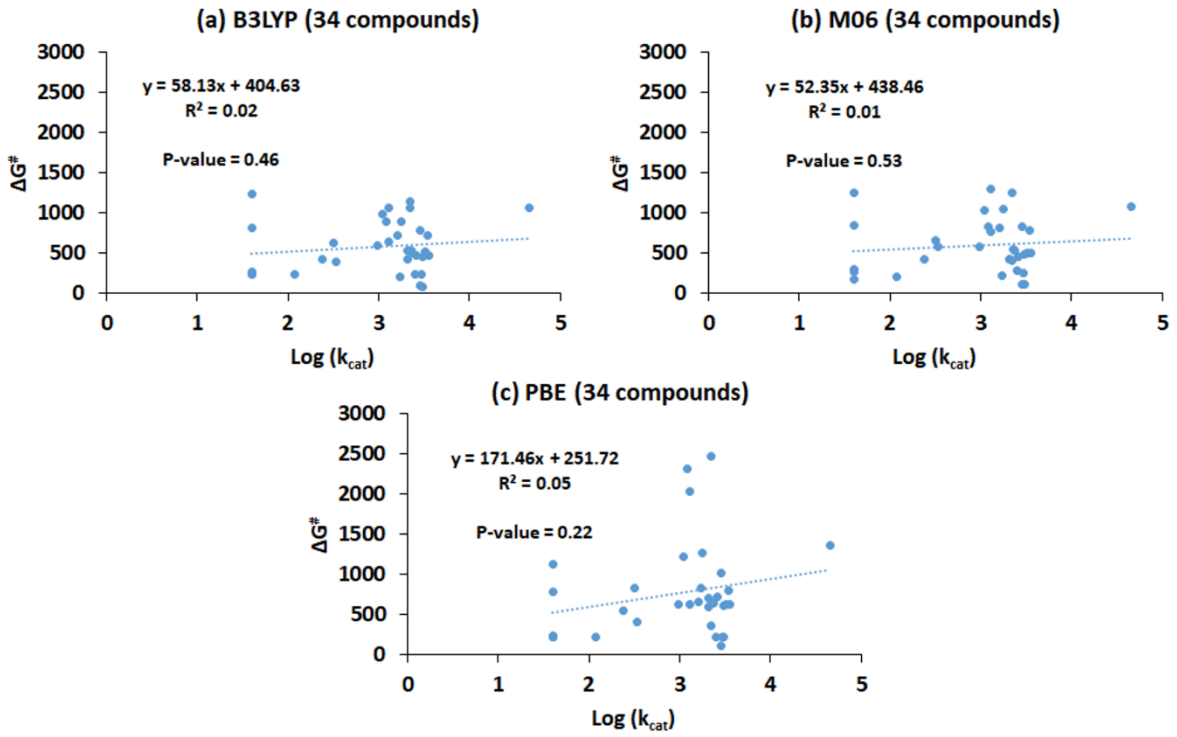
Figures S8. Correlation between log (k_{cat}) and reorganization energy (kcal/mol; computed using total internal energies) of dataset-B compounds calculated using B3LYP functional. **(a)** Correlation using full dataset. **(b)** Correlation with energies when an outlier compound 13 was removed. **(c)** Correlation with energies when another compound 15 was left out.



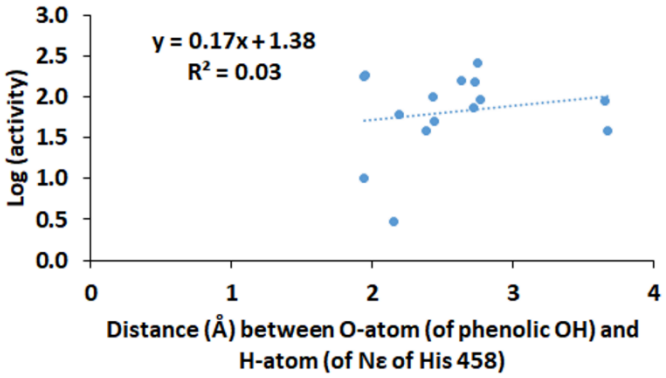
Figures S9. Correlation between log (k_{cat}) and reorganization energy (kcal/mol; computed using total internal energies) of dataset-B compounds calculated using M06 functional. **(a)** Correlation using full dataset. **(b)** Correlation with energies when an outlier compound 13 was removed. **(c)** Correlation with energies when another compound 15 was left out.



Figures S10. Correlation between log (activity) and activation energy $\Delta G^{\#} = (E^0 + \lambda)^2 / 4\lambda RT$ (in kcal/mol) of dataset A (20 compounds). **(a)** Using B3LYP functional that includes the full dataset. **(b)** Correlation improved significantly after removing two outliers (TOOS and *m*-chlorophenol). **(c)** Using M06 functional. **(d)** Using PBE functional.



Figures S11. Correlation between log (k_{cat}) and activation energy $\Delta G^{\#} = (E^0 + \lambda)^2 / 4\lambda RT$ (in kcal/mol) of dataset B (34 compounds). **(a)** Using B3LYP functional. **(c)** Using M06 functional. **(d)** Using PBE functional. The standard potential E^0 was estimated as the computed ionization energy in solution (the oxidation potential) of the substrate, since the contribution from the protein T1 site is constant for all substrates.



Figures S12. Correlation between distance and log (activity) for the 15 phenols found in the dataset A.