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Supporting Information for

Thermodynamics regulated organic hydride/acid pairs as novel organic hydrogen reductants

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Table S1. The Gibbs free energies changes of XH releasing hydrides [$\Delta G_{H\text{-}D}$(XH)], the Gibbs free energies of XH/$HClO_4$ pairs releasing two hydrogen ions [ΔG_{PH}-(XH/$HClO_4$)], the Gibbs free energies of XH/PhOH pairs releasing two hydrogen ions[ΔG_{PH}-(XH/PhOH)], the Gibbs free energies of XH/TsOH pairs releasing two hydrogen ions [ΔG_{PH}-(XH/TsOH)], the pK_a of HB_S [pK_a(HB_S)] to make XH/HB_S pairs be the thermodynamically equivalent organic hydrogen reductants of HEH

XH	G or R	$\Delta G_{H\text{-}D}$ (XH)[S1,a]	ΔG_{PH}-(XH/$HClO_4$)[b]	ΔG_{PH}-(XH/PhOH)[c]	ΔG_{PH}-(XH/TsOH)[d]	pK_a(HB_S)[e]
1H	*p*-CH_3O	61.9[S2]	60.9	101.9	73.5	15.5
2H	*p*-CH_3	63.0[S2]	62.0	103.0	74.6	14.7
3H	*p*-H	64.6[S2]	63.6	104.6	76.2	13.5
4H	*p*-Cl	66.4[S2]	65.4	106.4	78.0	12.2
5H	*p*-Br	66.0[S2]	65.0	106.0	77.6	12.5
6H	*p*-CH_3O	63.4[S2]	62.4	103.4	75.0	14.4
7H	*p*-CH_3	64.5[S2]	63.5	104.5	76.1	13.6
8H	*p*-H	66.1[S2]	65.1	106.1	77.7	12.4
9H	*p*-Cl	67.6[S2]	66.6	107.6	79.2	11.3
10H	*p*-Br	67.3[S2]	66.3	107.3	78.9	11.5
11H	*p*-CF_3	67.7[S2]	66.7	107.7	79.3	11.2
12H	*p*-CH_3O	58.2[S3]	57.2	98.2	69.8	18.2
13H	*p*-CH_3	58.7[S3]	57.7	98.7	70.3	17.8
14H	*p*-F	59.4[S3]	58.4	99.4	71.0	17.3
15H	*p*-Cl	60.1[S3]	59.1	100.1	71.7	16.8
16H	*p*-CN	61.4[S3]	60.4	101.4	73.0	15.8
17H	-	59.3[S2]	58.3	99.3	70.9	17.4
18H	-	69.7[S4]	68.7	109.7	81.3	9.8
19H	*p*-CH_3O	61.3[S3]	60.3	101.3	72.9	15.9
20H	*p*-CH_3	61.6[S3]	60.6	101.6	73.2	15.7
21H	*p*-H	62.2[S3]	61.2	102.2	73.8	15.3
22H	*p*-F	62.3[S3]	61.3	102.3	73.9	15.2
23H	*p*-Cl	62.7[S3]	61.7	102.7	74.3	14.9
24H	*p*-CN	64.1[S3]	63.1	104.1	75.7	13.9
25H	*p*-CH_3O	60.0[S3]	59.0	100.0	71.6	16.9
26H	*p*-CH_3	60.3[S3]	59.3	100.3	71.9	16.6
27H	*p*-H	60.9[S3]	59.9	100.9	72.5	16.2
28H	*p*-F	61.0[S3]	60.0	101.0	72.6	16.1
29H	*p*-Cl	61.7[S3]	60.7	101.7	73.3	15.6
30H	*p*-CN	63.0[S3]	62.0	103.0	74.6	14.7
31H	*p*-CH_3O	64.8[S3]	63.8	104.8	76.4	13.4
32H	*p*-CH_3	65.2[S3]	64.2	105.2	76.8	13.1
33H	*p*-H	65.6[S3]	64.6	105.6	77.2	12.8
34H	*p*-F	65.7[S3]	64.7	105.7	77.3	12.7
35H	*p*-CN	67.7[S3]	66.7	107.7	79.3	11.2
36H	*p*-CH_3O	65.3[S3]	64.3	105.3	76.9	13.0
37H	*p*-CH_3	65.7[S3]	64.7	105.7	77.3	12.7

XH	G or R	ΔG_{H-D} (XH)[S1,a]	ΔG_{PH} (XH/$HClO_4$)[b]	ΔG_{PH} (XH/PhOH)[c]	ΔG_{PH} (XH/TsOH)[d]	pK_a(HB_S)[e]
38H	*p*-H	66.4[S3]	65.4	106.4	78.0	12.2
39H	*p*-F	66.5[S3]	65.5	106.5	78.1	12.1
40H	*p*-Cl	67.5[S3]	66.5	107.5	79.1	11.4
41H	*p*-CN	69.0[S3]	68.0	109.0	80.6	10.3
42H	-	62.6[S3]	61.6	102.6	74.2	15.0
43H	-	58.9[S3]	57.9	98.9	70.5	17.7
44H	-	61.0[S3]	60.0	101.0	72.6	16.1
45H	-	48.1[S3]	47.1	88.1	59.7	25.5
46H	-	43.1[S3]	42.1	83.1	54.7	29.2
47H	-	56.6[S3]	55.6	96.6	68.2	19.3
48H	-	63.3[S3]	62.3	103.3	74.9	14.5
49H	CH_3	55.8[S3]	54.8	95.8	67.4	19.9
50H	Et	56.6[S3]	55.6	96.6	68.2	19.3
51H	*p*r	55.9[S3]	54.9	95.9	67.5	19.9
52H	i-*p*r	56.4[S3]	55.4	96.4	68.0	19.5
53H	n-Bu	56.5[S3]	55.5	96.5	68.1	19.4
54H	*p*-CH_3O	63.5[S5]	62.5	103.5	75.1	14.3
55H	*p*-CH_3	64.0[S5]	63.0	104.0	75.6	13.9
56H	*p*-H	64.6[S5]	63.6	104.6	76.2	13.5
57H	*p*-Br	65.2[S5]	64.2	105.2	76.8	13.1
58H	*p*-CN	66.4[S5]	65.4	106.4	78.0	12.2
59H	*p*-CH_3O	63.3[S5]	62.3	103.3	74.9	14.5
60H	*p*-CH_3	63.7[S5]	62.7	103.7	75.3	14.2
61H	*p*-H	64.2[S5]	63.2	104.2	75.8	13.8
62H	*p*-Br	64.9[S5]	63.9	104.9	76.5	13.3
63H	*p*-CN	66.1[S5]	65.1	106.1	77.7	12.4
64H	*p*-CH_3O	62.6[S5]	61.6	102.6	74.2	15.0
65H	*p*-CH_3	63.0[S5]	62.0	103.0	74.6	14.7
66H	*p*-H	63.6[S5]	62.6	103.6	75.2	14.2
67H	*p*-Br	64.2[S5]	63.2	104.2	75.8	13.8
68H	*p*-CN	65.5[S5]	64.5	105.5	77.1	12.8
69H	*p*-CH_3O	65.9[S5]	64.9	105.9	77.5	12.6
70H	*p*-CH_3	66.4[S5]	65.4	106.4	78.0	12.2
71H	*p*-H	66.7[S5]	65.7	106.7	78.3	12.0
72H	*p*-Br	67.2[S5]	66.2	107.2	78.8	11.6
73H	*p*-CN	68.0[S5]	67.0	108.0	79.6	11.0
74H	-	66.4[S5]	65.4	106.4	78.0	12.2
75H	Bz	65.3[S5]	64.3	105.3	76.9	13.0
76H	CH_3	61.6[S5]	60.6	101.6	73.2	15.7
77H	-	78.0[S5]	77.0	118.0	89.6	3.7
78H	-	65.0[S6]	64.0	105.0	76.6	13.2
79H	-	64.4[S7]	63.4	104.4	76.0	13.6

XH	G or R	ΔG_{H-D} (XH)[S1,a]	ΔG_{PH}-(XH/$HClO_4$)[b]	ΔG_{PH}-(XH/PhOH)[c]	ΔG_{PH}-(XH/TsOH)[d]	pK_a(HB_S)[e]
80H	-	44.6[S8]	43.6	84.6	56.2	28.1
81H	(CH_3O, H)	44.8[S8]	43.8	84.8	56.4	28.0
82H	(CH_3, H)	46.1[S8]	45.1	86.1	57.7	27.0
83H	(Cl, H)	53.3[S8]	52.3	93.3	64.9	21.8
84H	(CF_3, H)	57.0[S8]	56.0	97.0	68.6	19.1
85H	(CH_3, CH_3)	44.1[S8]	43.1	84.1	55.7	28.5
86H	*p*-$N(CH_3)_2$	45.7[S8]	44.7	85.7	57.3	27.3
87H	*p*-OH	47.7[S8]	46.7	87.7	59.3	25.8
88H	*p*-CH_3O	48.0[S8]	47.0	88.0	59.6	25.6
89H	*p*-CH_3	48.5[S8]	47.5	88.5	60.1	25.3
90H	*p*-H	49.2[S8]	48.2	89.2	60.8	24.7
91H	*p*-Cl	50.3[S8]	49.3	90.3	61.9	23.9
92H	*p*-Br	50.3[S8]	49.3	90.3	61.9	23.9
93H	*p*-CF_3	51.6[S8]	50.6	91.6	63.2	23.0
94H	*p*-CN	51.8[S8]	50.8	91.8	63.4	22.8
95H	*p*-NO_2	52.2[S8]	51.2	92.2	63.8	22.6
96H	*m*-CH_3O	49.7[S8]	48.7	89.7	61.3	24.4
97H	*m*-CH_3	48.9[S8]	47.9	88.9	60.5	25.0
98H	*m*-Cl	50.7[S8]	49.7	90.7	62.3	23.6
99H	*m*-Br	50.8[S8]	49.8	90.8	62.4	23.6
100H	*m*-NO_2	52.0[S8]	51.0	92.0	63.6	22.7
101H	o-CH_3	46.5[S8]	45.5	86.5	58.1	26.7
102H	o-Cl	48.3[S8]	47.3	88.3	59.9	25.4
103H	o-OH	48.9[S8]	47.9	88.9	60.5	25.0
104H	(NO_2, CH_3O)	51.0[S8]	50.0	91.0	62.6	23.4
105H	(Br, CH_3O)	49.7[S8]	48.7	89.7	61.3	24.4
106H	(CH_3O,CH_3O)	48.6[S8]	47.6	88.6	60.2	25.2
107H	(CH_3, CH_3)	48.2[S8]	47.2	88.2	59.8	25.5
108H	(F, F)	50.8[S8]	49.8	90.8	62.4	23.6
109H	(Br, F)	51.1[S8]	50.1	91.1	62.7	23.4
110H	(F, Cl)	51.5[S8]	50.5	91.5	63.1	23.1
111H	(Cl, Cl)	51.7[S8]	50.7	91.7	63.3	22.9
112H	-	49.1[S8]	48.1	89.1	60.7	24.8
113H	*p*-CH_3O	65.0[S8]	64.0	105.0	76.6	13.2
114H	*p*-CH_3	66.1[S8]	65.1	106.1	77.7	12.4
115H	*p*-H	68.1[S8]	67.1	108.1	79.7	10.9
116H	*p*-F	68.8[S8]	67.8	108.8	80.4	10.4
117H	*p*-Cl	70.7[S8]	69.7	110.7	82.3	9.1
118H	*p*-Br	70.8[S8]	69.8	110.8	82.4	9.0
119H	*m*-CH_3O	69.5[S8]	68.5	109.5	81.1	9.9
120H	*m*-CH_3	67.2[S8]	66.2	107.2	78.8	11.6
121H	*m*-Cl	72.0[S8]	71.0	112.0	83.6	8.1

XH	G or R	ΔG_{H-D} (XH)[SI,a]	ΔG_{PH}-(XH/$HClO_4$)[b]	ΔG_{PH}-(XH/PhOH)[c]	ΔG_{PH}-(XH/TsOH)[d]	pK_a(HB_S)[e]
122H	-	52.7[S9]	51.7	92.7	64.3	22.2
123H	*p*-CH_3O	83.4[S8]	82.4	123.4	95.0	-0.2
124H	*p*-CH_3	84.4[S8]	83.4	124.4	96.0	-0.9
125H	*p*-H	86.3[S8]	85.3	126.3	97.9	-2.3
126H	*p*-Cl	88.5[S8]	87.5	128.5	100.1	-3.9
127H	*p*-Br	88.3[S8]	87.3	128.3	99.9	-3.8
128H	-	48.8[S10]	47.8	88.8	60.4	25.0
129H	-	50.8[S10]	49.8	90.8	62.4	23.6
130H	-	52.7[S10]	51.7	92.7	64.3	22.2
131H	-	50.2[S10]	49.2	90.2	61.8	24.0
132H	*p*-CH_3O	52.9[S10]	51.9	92.9	64.5	22.0
133H	*p*-CH_3	53.2[S10]	52.2	93.2	64.8	21.8
134H	*p*-H	53.7[S10]	52.7	93.7	65.3	21.5
135H	*p*-Br	54.5[S10]	53.5	94.5	66.1	20.9
136H	*p*-CF_3	55.5[S10]	54.5	95.5	67.1	20.1
137H	*m*-CH_3O	54.2[S10]	53.2	94.2	65.8	21.1
138H	*m*-CH_3	53.5[S10]	52.5	93.5	65.1	21.6
139H	*m*-Br	55.0[S10]	54.0	95.0	66.6	20.5
140H	*m*-CF_3	55.2[S10]	54.2	95.2	66.8	20.4
141H	-	55.7[S10]	54.7	95.7	67.3	20.0
142H	*p*-CH_3O	79.8[S10]	78.8	119.8	91.4	2.4
143H	*p*-CH_3	80.4[S10]	79.4	120.4	92.0	2.0
144H	*p*-H	81.5[S10]	80.5	121.5	93.1	1.2
145H	*p*-Cl	83.1[S10]	82.1	123.1	94.7	0.0
146H	*p*-CF_3	84.9[S10]	83.9	124.9	96.5	-1.3
147H	*p*-CH_3O	70.1[S11]	69.1	110.1	81.7	9.5
148H	*p*-CH_3	70.2[S11]	69.2	110.2	81.8	9.4
149H	*p*-H	70.5[S11]	69.5	110.5	82.1	9.2
150H	*p*-Cl	70.8[S11]	69.8	110.8	82.4	9.0
151H	*p*-NO_2	71.6[S11]	70.6	111.6	83.2	8.4
152H	*p*-CH_3O	70.9[S11]	69.9	110.9	82.5	8.9
153H	*p*-CH_3	71.1[S11]	70.1	111.1	82.7	8.8
154H	*p*-H	71.3[S11]	70.3	111.3	82.9	8.6
155H	*p*-Cl	71.7[S11]	70.7	111.7	83.3	8.3
156H	*p*-NO_2	72.5[S11]	71.5	112.5	84.1	7.7
157H	*p*-CH_3O	71.8[S11]	70.8	111.8	83.4	8.2
158H	*p*-CH_3	71.9[S11]	70.9	111.9	83.5	8.2
159H	*p*-H	72.0[S11]	71.0	112.0	83.6	8.1
160H	*p*-Cl	72.1[S11]	71.1	112.1	83.7	8.0
161H	*p*-NO_2	72.5[S11]	71.5	112.5	84.1	7.7
162H	*p*-CH_3O	73.1[S11]	72.1	113.1	84.7	7.3
163H	*p*-CH_3	73.2[S11]	72.2	113.2	84.8	7.2

XH	G or R	$\Delta G_{H\text{-}D}$ (XH)[SI,a]	ΔG_{PH}-(XH/$HClO_4$)[b]	ΔG_{PH}-(XH/PhOH)[c]	ΔG_{PH}-(XH/TsOH)[d]	pK_a(HB_S)[e]
164H	*p*-H	73.4[S11]	72.4	113.4	85.0	7.1
165H	*p*-Cl	73.5[S11]	72.5	113.5	85.1	7.0
166H	*p*-NO_2	74.1[S11]	73.1	114.1	85.7	6.6
167H	*p*-CH_3O	72.0[S11]	71.0	112.0	83.6	8.1
168H	*p*-CH_3	72.0[S11]	71.0	112.0	83.6	8.1
169H	*p*-H	72.2[S11]	71.2	112.2	83.8	8.0
170H	*p*-Cl	72.4[S11]	71.4	112.4	84.0	7.8
171H	*p*-NO_2	72.9[S11]	71.9	112.9	84.5	7.4
172H	*p*-CH_3O	66.4[S12]	65.4	106.4	78.0	12.2
173H	*p*-CH_3	67.5[S12]	66.5	107.5	79.1	11.4
174H	*p*-H	68.1[S12]	67.1	108.1	79.7	10.9
175H	*p*-Cl	69.2[S12]	68.2	109.2	80.8	10.1
176H	*p*-CF_3	70.9[S12]	69.9	110.9	82.5	8.9
177H	*m*-CH_3O	69.0[S12]	68.0	109.0	80.6	10.3
178H	(H, H)	71.8[S13]	70.8	111.8	83.4	8.2
179H	(CH_3O, H)	72.1[S13]	71.1	112.1	83.7	8.0
180H	(CH_3, H)	70.9[S13]	69.9	110.9	82.5	8.9
181H	(Cl, H)	74.9[S13]	73.9	114.9	86.5	6.0
182H	(F, H)	74.5[S13]	73.5	114.5	86.1	6.3
183H	(Br, H)	74.3[S13]	73.3	114.3	85.9	6.4
184H	(CH_3O, CH_3)	69.3[S13]	68.3	109.3	80.9	10.1
185H	(H, CH_3)	71.1[S13]	70.1	111.1	82.7	8.8
186H	(H, Cl)	74.3[S13]	73.3	114.3	85.9	6.4
187H	(H, F)	72.5[S13]	71.5	112.5	84.1	7.7
188H	(H, Br)	73.1[S13]	72.1	113.1	84.7	7.3
189H	-	76.2[S14]	75.2	116.2	87.8	5.0
190H	-	95.6[S14]	94.6	135.6	107.2	-9.1
191H	-	91.3[S14]	90.3	131.3	102.9	-6.0
192H	*p*-CH_3O	90.2[S14]	89.2	130.2	101.8	-5.2
193H	*p*-CH_3	90.6[S14]	89.6	130.6	102.2	-5.5
194H	*p*-H	91.6[S14]	90.6	131.6	103.2	-6.2
195H	*p*-Cl	92.5[S14]	91.5	132.5	104.1	-6.9
196H	*p*-Br	92.7[S14]	91.7	132.7	104.3	-7.0
197H	*p*-CF_3	93.5[S14]	92.5	133.5	105.1	-7.6
198H	*m*-CH_3O	91.8[S14]	90.8	131.8	103.4	-6.4
199H	*m*-CH_3	91.3[S14]	90.3	131.3	102.9	-6.0
200H	*m*-CF_3	93.1[S14]	92.1	133.1	104.7	-7.3
201H	$N(CH_3)_2$	90.2[S14]	89.2	130.2	101.8	-5.2
202H	*p*-CH_3O	99.6[S14]	98.6	139.6	111.2	-12.0
203H	*p*-CH_3	102.4[S14]	101.4	142.4	114.0	-14.1
204H	*p*-H	104.8[S14]	103.8	144.8	116.4	-15.8
205H	*p*-Cl	106.4[S14]	105.4	146.4	118.0	-17.0

XH	G or R	ΔG_{H^-D} (XH)[S1,a]	ΔG_{PH^-} (XH/$HClO_4$)[b]	ΔG_{PH^-} (XH/PhOH)[c]	ΔG_{PH^-} (XH/TsOH)[d]	pK_a(HB_S)[e]
206H	*p*-Br	107.0[S14]	106.0	147.0	118.6	-17.4
207H	*p*-CH_3O	102.2[S14]	101.2	142.2	113.8	-13.9
208H	*p*-CH_3	103.4[S14]	102.4	143.4	115.0	-14.8
209H	*p*-Cl	106.5[S14]	105.5	146.5	118.1	-17.1
210H	$N(CH_3)_2$	79.5[S14]	78.5	119.5	91.1	2.6
211H	*p*-CH_3O	94.6[S14]	93.6	134.6	106.2	-8.4
212H	*p*-CH_3	100.2[S14]	99.2	140.2	111.8	-12.5
213H	*p*-Cl	108.5[S14]	107.5	148.5	120.1	-18.5
214H	*p*-Br	109.3[S14]	108.3	149.3	120.9	-19.1
215H	-	103.4[S14]	102.4	143.4	115.0	-14.8
216H	-	86.2[S14]	85.2	126.2	97.8	-2.3

Note: [a] Most ΔG_{H^-D}(XH) are from *ref. S1(a)* and all the ΔH_{H^-D}(XH) are available from our recent review *ref. S1(b)*. ΔG_{H^-D}(XH) = ΔH_{H^-D}(XH) - 4.9 kcal/mol; [b] ΔG_{PH^-}(XH/$HClO_4$) = ΔG_{H^-D}(XH) + 1.37pK_a($HClO_4$); [c] ΔG_{PH^-}(XH/PhOH) = ΔG_{H^-D}(XH) + 1.37pK_a(PhOH); [d] ΔG_{PH^-}(XH/TsOH) = ΔG_{H^-D}(XH) + 1.37 pK_a(TsOH); [e] pK_a(HB_S) = [ΔG_{PH^-}(HEH) - ΔG_{H^-D}(XH)]/1.37. The unit of ΔG_{H^-D}(XH), ΔG_{PH^-}(XH/$HClO_4$), ΔG_{PH^-}(XH/PhOH), ΔG_{PH^-}(XH/TsOH) is kcal/mol.

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