Supplementary Information

Relative kinetic reactivity of boronic acid to boronate ion toward Tiron, 2,2-biphenol, and propyleneglycol

Eisuke Watanabe,[a] Chiaki Miyamoto,[a] Asumi Tanaka,[a] Kenzo Iizuka,[a] Satoshi Iwatsuki,[b] Masahiko Inamo,[c] Hideo D. Takagi,[d] and Koji Ishihara[a]*

Figs S1 – S8
Tables S1 – S4

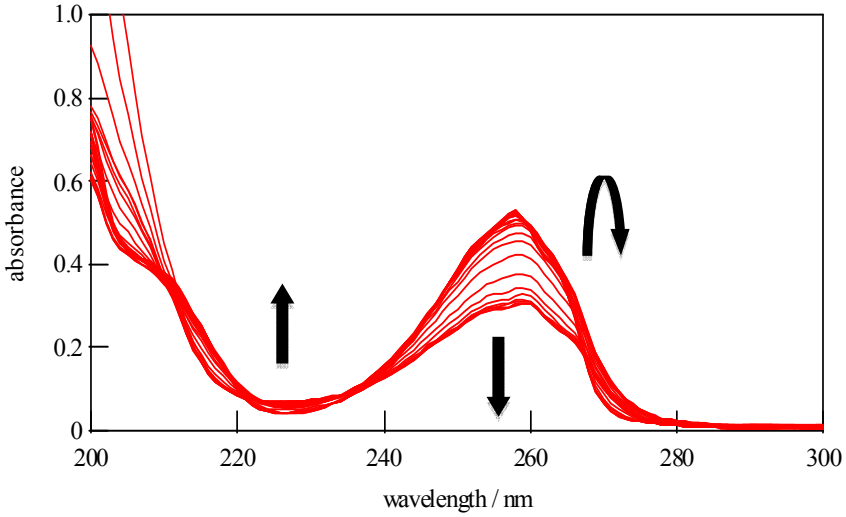

Fig. S1 Change in UV-Vis spectra of 3-Pyridylboronicacid with pH in aqueous solution at 25 ºC and I = 1.0 M. $C_B = 1.0 \times 10^{-4}$ M. pH 2.69–10.14

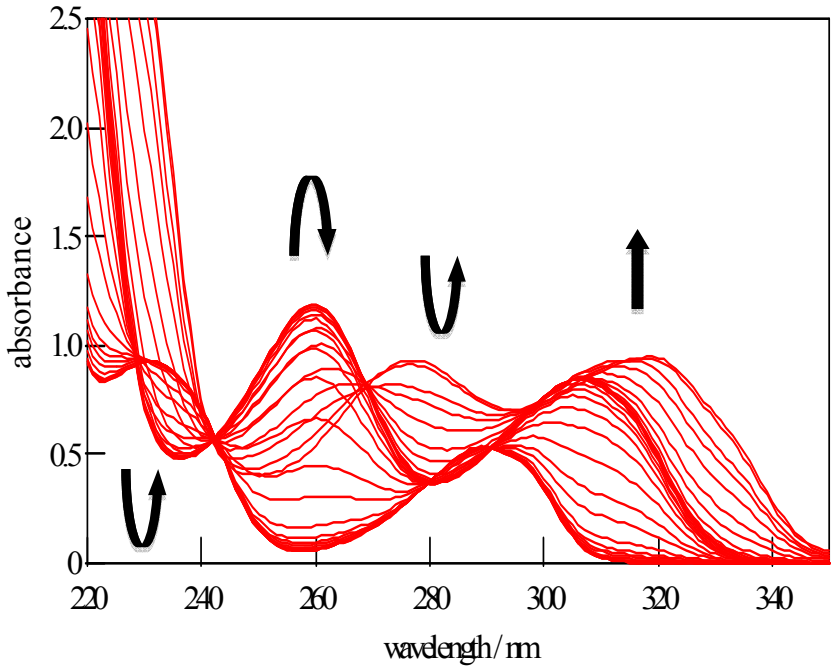

Fig. S2 Change in UV-Vis spectra of Tiron with pH in aqueous solution at 25 ºC and I = 1.0 M. $C_L = 1.47 \times 10^{-4}$ M. pH 2.25–12.42

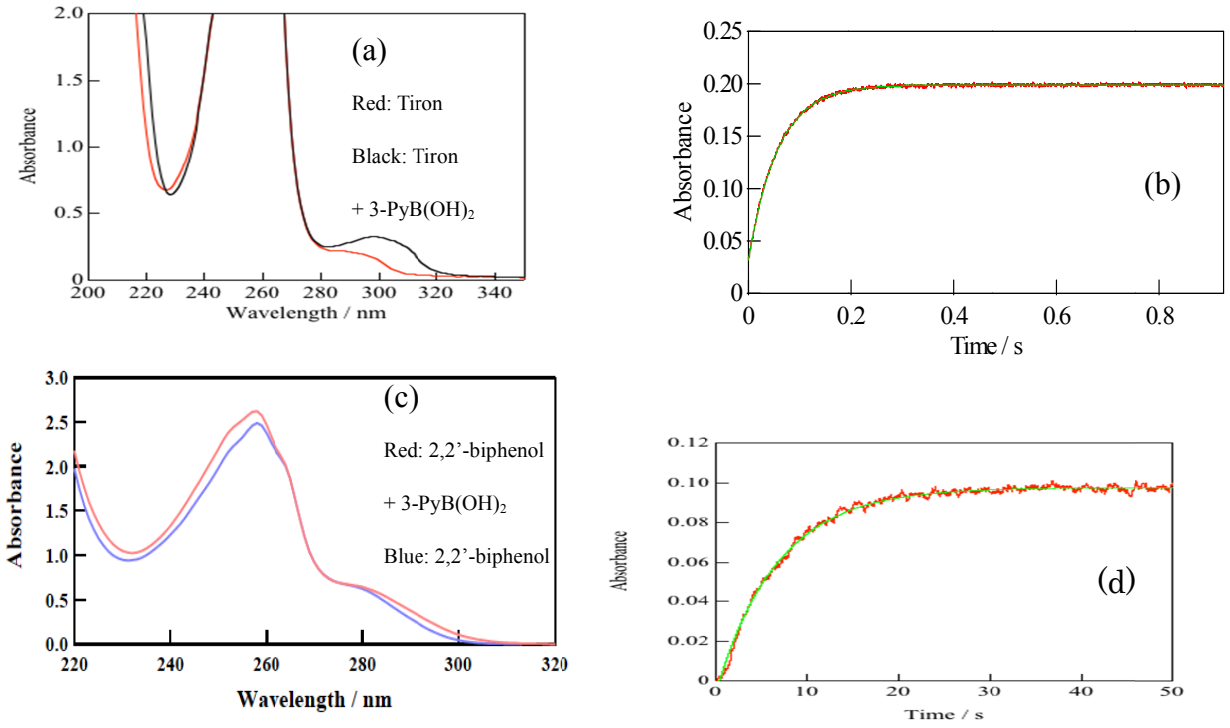

Fig. S3 (a) Change in UV-Vis spectra of 3-PyB(OH)$_2$ with Tiron in acidic aqueous solution at 25 ºC and I = 1.0 M. C_B = 1.0 x 10^{-3} M, C_L = 5.0 x 10^{-5} M, and [H^+] = 1.0 x 10^{-4} M; (b) time course measurements (at 309 nm) for the reaction of Tiron with 3-PyB(OH)$_2$ in acidic aqueous solution at 25.0 ºC and I = 1.0 M. C_B = 6.0 x 10^{-4} M, C_L = 5.00 x 10^{-5} M, and pH = 6.07; (c) Change in UV-Vis spectra of 3-PyB(OH)$_2$ with 2,2'-biphenol in acidic aqueous solution at 25 ºC and I = 1.0 M. C_B = 3.00 x 10^{-3} M, C_L = 1.45 x 10^{-4} M, and pH = 4.40; (d) time course measurements (at 294 nm) for the reaction of 2,2'-biphenol with 3-PyB(OH)$_2$ in acidic aqueous solution at 15.0 ºC and I = 1.0 M. C_B = 3.0 x 10^{-3} M, C_L = 6.0 x 10^{-5} M, and pH = 4.80.

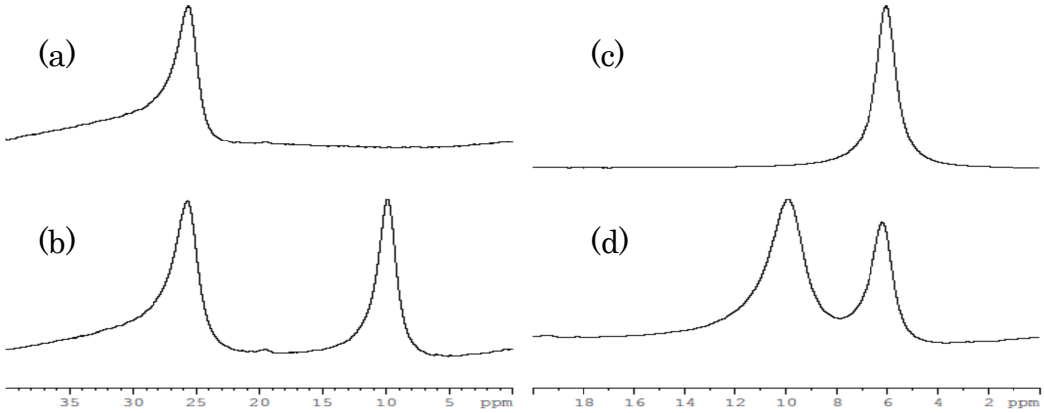

Fig. S4 ^{11}B NMR spectra of (a) 3-PyB(OH)$_2$ at pD = 2.6, (b) 3-PyB(OH)$_2$ + Tiron at pD = 2.6, (c) 3-PyB(OH)$_2$ at pD = 6.0, and (d) 3-PyB(OH)$_2$ + Tiron at pD = 6.0. (a) C_B = 7.1 x 10^{-2} M; (b) C_B = 1.0 x 10^{-2} M, C_L = 4.8 x 10^{-2} M; (c) C_B = 6.9 x 10^{-2} M; (d) C_B = 6.9 x 10^{-2} M, C_L = 4.6 x 10^{-2} M.

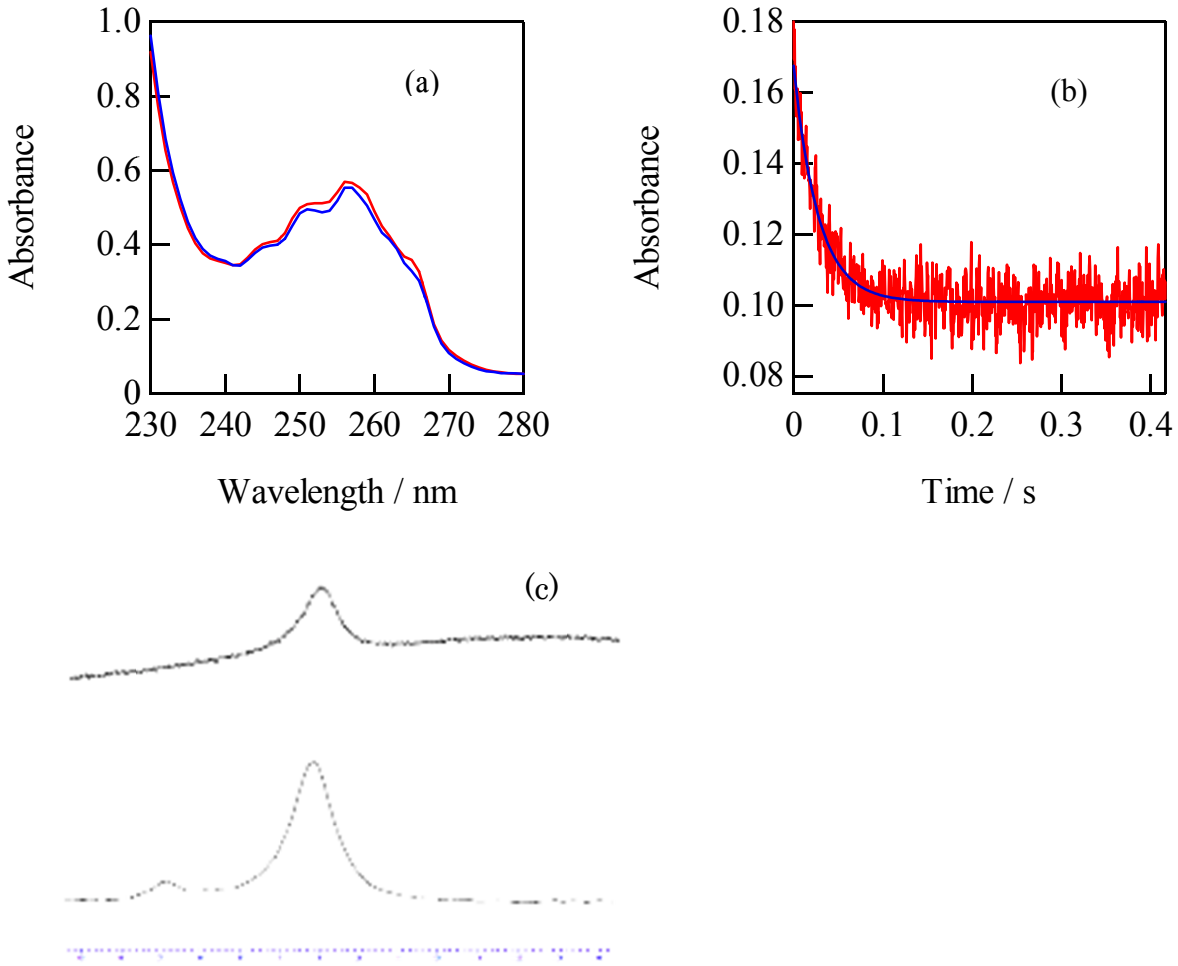

Fig. S5 (a) UV-Vis spectra of $PhB(OH)_2$ (red) and the mixture of $PhB(OH)_2$ and propylene glycol (PG) (blue) at 25 ºC and I = 0.10 M; (b) change in absorbance with time for the reaction of $PhB(OH)_2$ with PG at 270 nm; (c) ^{11}B NMR spectra of $PhB(OH)_2$ (i) and the mixture of $PhB(OH)_2$ and PG (ii) in D_2O. (a) $C_B = 3.5 \times 10^{-3}$ M, $C_L = 9.9 \times 10^{-1}$ M, $C_{CAPS} = 0.10$ M, pH = 11.0; (b) $C_B = 3.3$ mM, $C_{PG} = 1.00$ M, $C_{CAPS} = 0.10$ M, pH = 10.40; (c) (i) $C_B = 1.0 \times 10^{-2}$ M, pD = 11.6, (ii) $C_B = 1.0 \times 10^{-2}$ M, $C_{PG} = 2.6 \times 10^{-2}$ M, pD = 11.6.

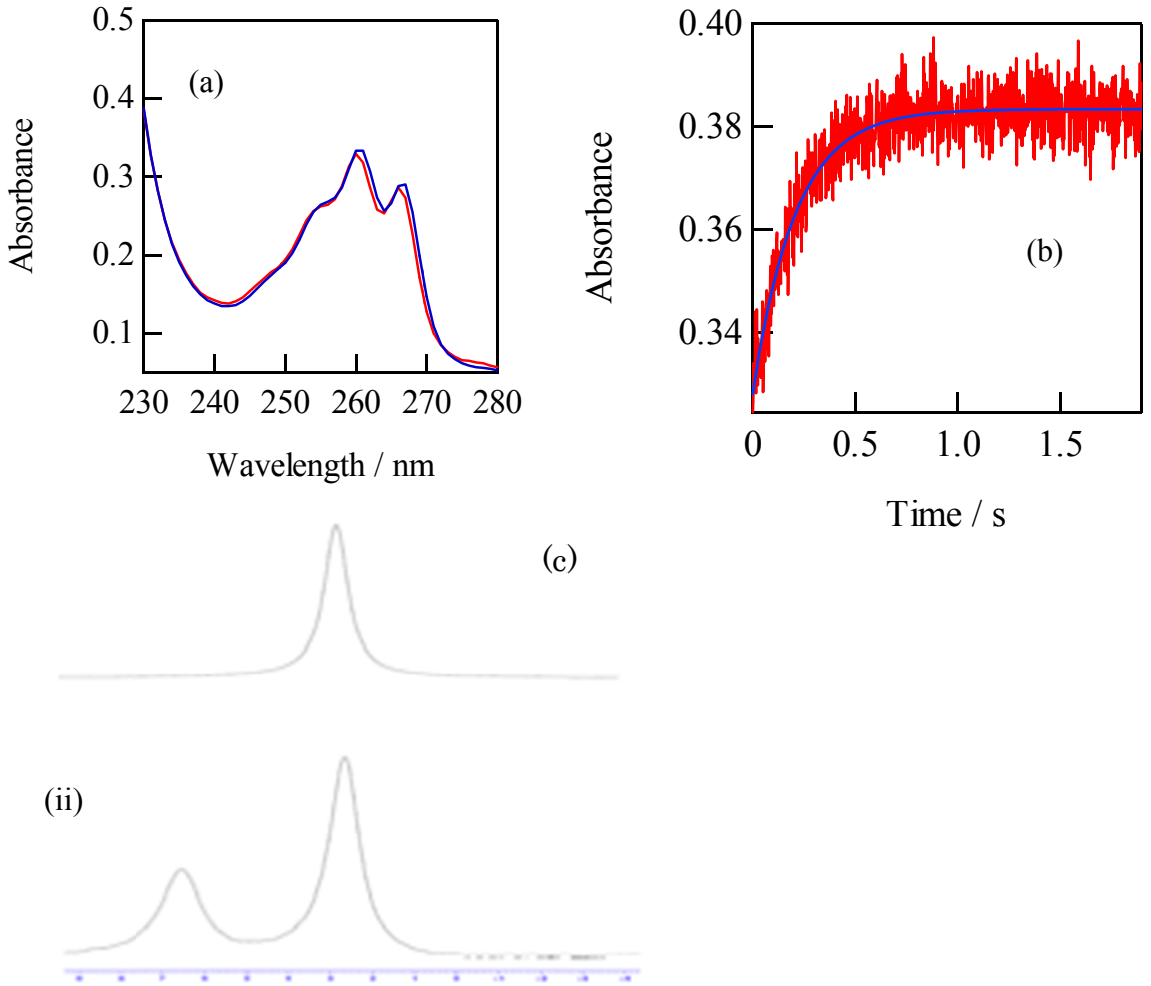

Fig. S6 (a) UV-Vis spectra of 3-$FPhB(OH)_2$ (red) and the mixture of 3-$FPhB(OH)_2$ and propylene glycol (blue) at 25 ºC and I = 0.10 M; (b) change in absorbance with time for the reaction of 3-$FPhB(OH)_2$ with PG at 268 nm; (c) ^{11}B NMR spectra of 3-$FPhB(OH)_2$ (i) and the mixture of 3-$FPhB(OH)_2$ and PG (ii) in D_2O. (a) $C_B = 6.1 \times 10^{-4}$ M, $C_L = 1.1$ M, $C_{CAPS} = 0.10$ M, pH = 10.4; (b) $C_B = 2.4$ mM, $C_{PG} = 2.50 \times 10^{-1}$ M, $C_{CAPS} = 0.10$ M, pH = 10.30; (c) (i) $C_B = 3.4 \times 10^{-2}$ M, pD = 11.0, (ii) $C_B = 1.7 \times 10^{-2}$ M, $C_{PG} = 3.3 \times 10^{-1}$ M, pD = 11.0.

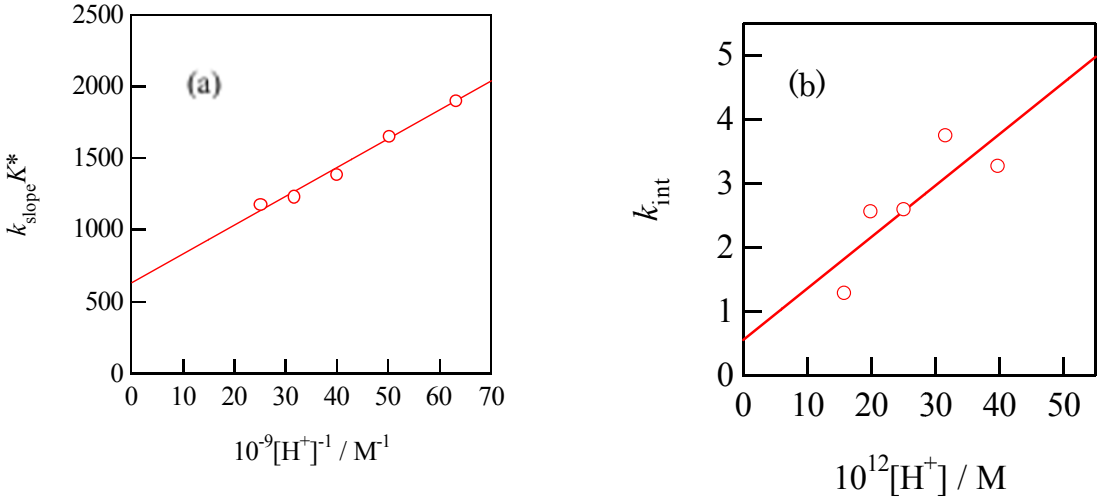

Fig. S7 Dependence of (a) k_{slope} on $[H^+]^{-1}$, (b) k_{int} vs $[H^+]$ for the reactions of $PhB(OH)_2$ with PG at 25 ºC and I = 0.10 M.

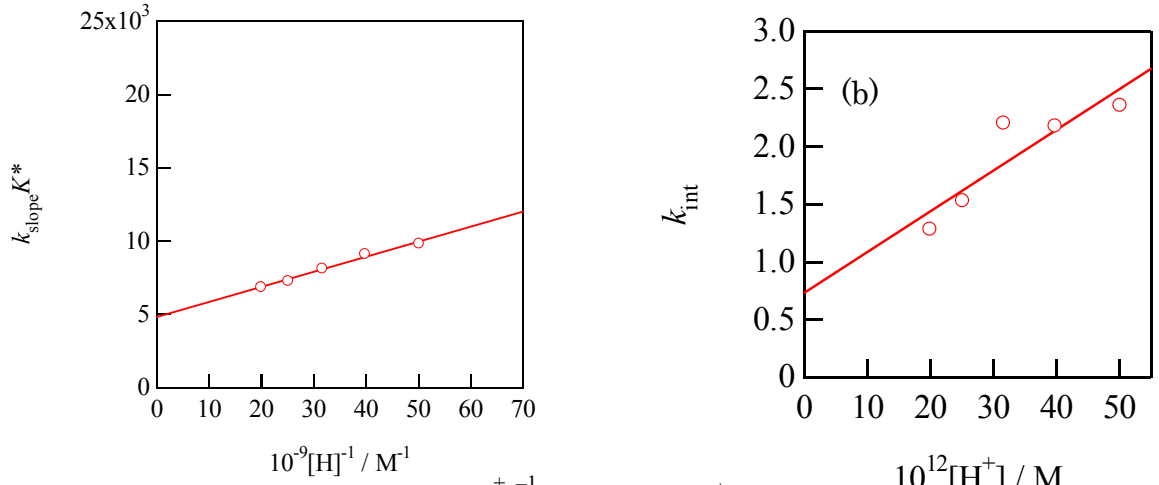

Fig. S8 Dependence of (a) k_{slope} on $[H^+]^{-1}$, (b) k_{int} vs $[H^+]$ for the reactions of 3-$FPhB(OH)_2$ with PG at 25 ºC and I = 0.10 M.

Table S1 Rate constants (25 ºC, I = 0.10 M) for the reaction of phenylboronic acid with propyleneglycol in alkaline solution. C_B = 3.3 x 10^{-3} M, CAPS buffer (0.10 M) was used

pH	C_B / M	k_{obs}(average)	k_{obs} / s^{-1}									
10.4	0.25	9.49	9.85	9.08	8.62	9.24	9.27	9.28	9.09	9.19	10.1	9.91
			10.6	9.60	9.53							
	0.5	15.0	17.5	14.3	14.1	13.3	14.4	15.9	17.1	16.2	14.5	15.1
			13.7	15.4	13.7							
	0.75	21.3	23.2	23.1	22.0	21.0	17.8	23.4	22.0	19.7	23.9	19.7
			21.6	18.5	22.1	19.6						
	1.00	27.5	30.8	26.7	27.3	30.6	30.0	34.0	33.0	21.1	25.6	30.2
			23.1	26.6	25.6	25.7	22.3					
10.5	0.25	8.91	9.19	8.27	9.54	9.72	9.57	8.07	8.83	8.78	8.56	9.26
			8.69	8.86	8.90	9.55	7.97	8.85				
	0.5	13.9	14.3	14.7	15.8	13.2	13.8	15.1	14.1	12.2	15.0	12.7
			15.7	13.3	13.9	14.5	12.1	12.3	12.6	14.8		
	0.751	18.2	20.5	15.2	15.7	19.5	18.2	20.2	18.9	16.8	18.1	16.6
			19.1	19.5	18.6	18.5	19.0	17.1				
	1.00	24.2	24.7	25.2	24.6	24.2	20.6	22.7	23.4	25.1	25.0	25.4
			26.6	23.1								
10.6	0.25	7.08	6.96	6.94	7.76	7.42	6.26	6.63	6.86	7.24	7.62	6.81
			7.53	6.71	7.31	7.26	7.19	6.59	7.43	6.97		
	0.499	11.7	10.1	11.8	11.5	11.2	11.2	13.2	11.7	11.5	13.8	10.7
			12.7	10.9	11.6	11.4	12.3					
	0.75	15.9	12.2	18.9	17.9	15.5	13.5	12.3	14.7	19.9	15.5	14.1
			17.9	15.6	16.8	18.0	15.7	17.5	14.8	16.6	15.5	
	1.00	20.7	17.8	15.4	16.3	19.3	19.8	23.0	21.7	22.2	22.3	23.6
			20.0	23.5	25.3	19.8						
10.7	0.25	7.08	7.97	7.42	7.01	6.35	7.05	8.04	6.94	7.15	7.02	6.97
			6.82	7.47	6.05	7.14	7.66	6.02	8.33	6.55	6.62	
	0.501	10.6	9.09	9.80	12.7	10.3	9.15	11.3	11.0	12.4	10.9	10.1
			11.1	11.1	11.5	10.7	10.1	11.9	9.68	9.23	10.7	10.8
			8.80									
	0.75	15.8	14.4	15.1	21.1	15.2	14.2	13.4	16.7	14.4	15.1	14.3
			15.1	20.6	14.3	15.1	13.4	14.1	14.5	16.6	18.8	15.5
			20.2									
	0.998	19.6	19.1	22.9	22.6	22.7	17.1	19.2	20.8	16.2	19.5	18.2
			17.3									
10.8	0.251	5.54	5.77	4.71	5.84	5.93	5.43	5.27	5.61	4.72	5.83	5.68
			5.43	5.56	5.43	6.02	5.69	5.74	5.56	5.85	4.68	5.95
	0.501	8.83	9.24	7.03	11.1	10.3	10.1	9.01	6.91	7.54	9.65	11.5
			7.67	6.14	7.91	8.51	9.00	8.39	9.41	9.23	9.95	7.86
			10.6	8.47	9.05	6.99	8.86	9.23				
	0.75	12.7	9.49	11.5	12.7	16.8	14.8	12.5	12.2	13.6	14.8	12.4
			13.4	12.2	9.76	12.7	15.7	10.8	11.6	11.2		
	1.00	17.3	16.2	13.0	15.7	15.5	19.8	16.4	16.9	18.6	16.1	13.4
			19.3	16.8	20.4	18.8	20.9	19.2	17.6			

Table S2 Rate constants (25 ºC, I = 0.10 M) for the reaction of 3-F-phenylboronic acid with propyleneglycol in alkaline solution. $C_B = 2.4 \times 10^{-3}$ M, CAPS buffer (0.10 M) was used.

pH	C_B / M	k_{obs}(average)	k_{obs} / s^{-1}									
10.3	0.250	5.10	5.08	4.93	5.18	4.87	5.14	5.36	5.00	5.08	5.27	4.83
			5.29	4.95	5.06	4.93	4.98	5.28	5.17	5.30	5.13	
	0.501	7.73	7.63	8.00	8.09	7.50	7.56	7.51	7.78	7.74	7.86	7.77
			7.64	7.94	7.42	7.63	7.75	7.78				
	0.750	10.5	9.56	10.1	11.6	11.8	9.87	12.00	9.86	10.60	9.81	9.34
			9.55	10.9	10.2	10.4	12.1	11.0	11.6	10.2	9.57	
	1.00	13.2	14.1	12.4	11.7	16.0	13.1	12.5	11.9	12.4	15.5	14.2
			13.0	11.6	12.6	15.7	12.9	12.1	12.8	13.0		
10.4	0.250	4.51	4.49	4.77	4.83	4.44	4.47	4.36	4.67	4.48	4.50	4.34
			4.46	4.66	4.51	4.52	4.57	4.52	4.40	4.37	4.34	
	0.500	6.78	6.78	6.86	6.40	6.78	6.31	6.13	6.09	7.18	6.56	7.23
			6.86	6.71	6.75	6.94	6.98	7.10	6.75	7.16	6.85	6.36
			7.13	6.71	7.31							
	0.750	8.79	9.10	8.82	8.19	8.69	8.84	8.40	9.04	9.02	8.79	8.77
			8.68	8.46	9.60	8.30	8.86	8.81	8.69	9.78	8.15	8.53
			8.15									
	1.00	11.4	10.7	11.4	12.1	10.7	11.6	11.8	10.9	12.2	12.0	11.6
			11.7	11.3	10.2	11.0	11.4	10.7	12.7	12.3		
10.5	0.250	4.06	4.19	4.07	3.84	3.98	3.53	4.30	3.66	3.96	3.97	4.22
			4.33	4.03	4.37	3.82	4.03	4.16	4.23	4.38		
	0.500	6.33	6.11	6.35	5.98	6.18	6.24	6.58	6.28	6.33	6.36	6.55
			6.07	6.44	6.56	6.28	6.53	6.27	6.44	6.34		
	0.750	8.64	8.48	8.97	8.26	8.54	8.64	8.48	7.87	8.44	8.59	9.10
			9.33	9.27	9.12	8.59	8.83	8.17	8.46	8.42		
	0.998	10.0	11.3	9.98	9.79	9.20	9.14	9.89	9.81	9.36	10.0	11.1
			9.95	9.54	10.2	10.6	9.28	9.23	11.1	9.36	11.7	
10.6	0.250	3.24	3.07	3.38	3.08	3.25	3.42	3.10	3.30	3.16	3.23	3.13
			3.28	3.22	3.28	3.31	3.29	3.32				
	0.500	5.35	5.55	5.45	5.51	5.23	5.17	5.49	5.29	5.35	5.27	5.27
			5.32	5.29								
	0.750	6.83	6.75	7.49	6.83	7.05	6.77	7.38	7.30	6.43	6.79	6.49
			6.90	6.13	6.99	6.57	6.55	6.29	7.28	7.04	6.62	6.77
			7.10									
	1.00	8.76	9.31	8.72	8.52	9.91	8.62	8.91	8.18	9.89	8.88	8.22
			7.58	7.97	7.92	8.58	8.71	9.68	9.24	8.56	9.11	
10.7	0.25	2.86	2.97	2.77	2.97	2.86	2.85	2.69	2.98	2.88	2.85	2.93
			2.83	2.90	2.93	2.87	2.64	2.80				
	0.5	4.23	4.34	4.95	4.05	4.15	4.74	4.49	3.78	4.22	4.22	4.10
			4.40	4.24	4.12	4.20	4.10	4.19	3.85	4.07	4.15	
	0.75	6.14	6.42	6.02	5.94	6.21	5.94	6.08	6.30	6.35	6.17	6.16
			5.83	6.30	6.22	6.22	5.93	6.07	6.24			
	1.00	7.38	7.40	7.35	7.24	7.38	7.36	7.18	7.32	7.17	7.37	7.33
			7.48	7.60	7.55	7.40	7.60					

Table S3 Rate constants (25 ºC, I = 1.0 M) for the reaction of 3-pyridylboronic acid with Tiron in acidic aqueous solution. C_L = 5.0 x 10^{-5} M.

pH	C_B / mM	k_{obs}(average)	k_{obs} / s^{-1}									
2.40	1.00	26.9	27.3,	27.6	26.5	26.4	25.6	27.9	27.4	27.5	26.1	26.1
			27.4,	27.1	27.5	27.8	26.4	27.5	27.4	27.3	27.2	26.8
			26.2,	26.9	25.6	25.5	27.8	25.8	27.1	26.5	27.3	27.8
	1.50	30.1	30.5,	30.7	29.3	30.4	29.9	30.2	30.4	31.4	30.6	29.3
			30.2,	29.5	29.1	29.4	29.1	29.7	30.4	29.2	29.7	31.1
			29.8,	30.2	29.1	31.3	29.7	30.1	31.1	31.4	29.9	29.5
			30.1									
	2.00	33.0	33.4,	33.0	33.1	32.9	32.8	32.9	32.8	33.4	33.1	33.0
			33.2,	33.0	32.7,	33.1,	33.1,	32.9,	32.8,	32.8,	32.8,	33.1,
			33.4,	32.5								
	2.50	35.7	38.0,	35.7,	35.9,	35.8,	35.6,	35.3,	34.7,	35.6,	35.2,	35.4,
			36.0,	35.6								
2.60	1.00	22.0	22.1,	21.3,	21.8,	21.8,	21.6,	21.9,	22.3,	20.9,	21.0,	21.1,
			22.9,	23.6,	21.8,	22.4,	23.1,	22.5,	22.5,	22.1,	21.3,	21.1,
			23.7,	21.6								
	1.50	25.0	26.0,	25.1,	25.7,	24.7,	24.8,	25.4,	24.7,	24.8,	24.9,	24.6,
			25.0,	24.5,	25.5,	25.1,	25.1,	25.8,	25.3,	24.5,	24.4,	24.3,
			25.0,	25.0								
	2.00	28.3	28.0,	28.4,	28.1,	28.4,	28.9,	27.9,	28.7,	28.2,	28.1,	27.7,
			28.7,	28.2,	28.6,	28.6,	28.0,	28.4,	28.3			
	2.50	31.3	32.5,	31.5,	31.4,	31.4,	31.1,	30.6,	30.9,	31.2,	32.6,	30.5,
			31.8,	31.1,	30.4,	31.1,	30.6,	30.6,	31.3,	32.1,	32.1,	31.5,
			31.0									
2.80	1.00	18.9	18.8,	19.4,	18.5,	19.1,	19.1,	19.7,	18.6,	19.1,	18.6,	18.4,
			19.3,	18.7,	19.5,	19.2,	18.2,	18.4,	18.7,	18.7		
	1.50	22.7	23.5,	22.4,	23.2,	22.3,	23.0,	22.6,	23.2,	22.3,	22.8,	22.1,
			22.2,	23.2,	22.3,	23.2,	22.9,	22.7,	22.9,	22.0		
	2.00	27.4	26.3,	26.1,	25.6,	27.0,	27.0,	27.4,	26.8,	27.2,	26.3,	26.1,
			27.2,	25.9,	25.9,	26.6,	26.8,	27.0,	26.1,	25.7,	31.1,	28.8,
			29.0,	32.2,	28.5,	29.1,	29.1	31.1,	28.8			
	2.50	30.6	30.7,	29.5,	30.8,	30.0,	31.5,	32.4,	30.3,	30.0,	29.0,	29.7,
			31.9,	30.4,	32.0,	29.8,	31.7,	31.8,	29.6,	31.2,	29.5	
3.20	1.00	17.1	17.1,	16.7,	17.3,	16.8,	17.5,	17.0,	17.6,	16.8,	17.2,	16.8,
			16.9,	17.5,	17.1,	16.9,	17.7,	16.9,	16.9			
	1.50	22.4	21.5,	23.1,	22.2,	23.0,	23.2,	21.8,	23.0,	22.3,	21.7,	22.0,

			21.8,	22.5,	22.8,	22.5,	21.9,	23.4,	22.0,	22.1,	22.5,	22.3
3.20	2.00	28.0	27.9,	26.9,	28.6,	26.9,	29.1,	28.4,	28.9,	27.7,	27.6,	26.9,
			27.4,	28.8,	28.8,	27.7,	28.4,	28.8,	27.1,	27.6		
	2.50	32.7	34.6,	33.5,	33.8,	32.0,	33.2,	32.2,	34.9,	32.4,	32.0,	31.9,
			32.0,	32.4,	31.9,	32.8,	31.9,	32.6,	32.9			
3.40	1.00	17.1	16.7,	17.5,	16.7,	17.4,	18.1,	17.4,	17.2,	16.6,	16.8,	17.2,
			17.0									
	1.50	23.1	22.9,	23.0,	23.8,	22.6,	24.4,	23.2,	23.7,	23.1,	22.1,	21.8,
			22.9,	23.4,	23.3,	23.0						
	2.00	29.3	28.9,	29.3,	30.3,	29.5,	29.1,	29.0,	29.0,	29.9,	29.7,	29.2,
			29.0,	28.4								
	2.50	36.1	35.2,	36.5,	35.9,	37.3,	35.5,	36.6,	36.1,	35.1,	36.5,	35.8,
			35.2,	37.3,	35.5,	37.6,	35.5,	35.7,	35.8			
3.60	1.00	17.6	17.4,	18.0,	17.6,	17.6,	17.6,	17.5,	17.5,	17.7,	17.3,	18.0,
			17.5,	17.8,	17.8							
	1.50	24.4	25.0,	23.6,	24.8,	24.4,	23.4,	24.9,	25.0,	23.8,	24.4,	24.7,
			24.6,	24.1								
	2.00	31.8	31.4,	31.6,	31.8,	32.2,	31.9,	31.8,	31.0,	32.1,	31.9,	32.2,
			32.2,	31.5,	31.3,	32.2						
	2.50	38.3	38.3,	37.8,	38.3,	38.7,	38.0,	38.0,	39.2,	37.4,	38.2,	38.0,
			38.9,	38.9,	38.2							
4.00	1.00	17.4	17.4,	17.5,	17.5,	17.4,	17.4,	17.4,	17.4,	17.4,	17.4,	17.5
	1.50	25.1	24.4,	24.6,	24.8,	24.4,	25.5,	24.8,	25.4,	25.2,	24.6,	24.3,
			24.8,	25.9,	25.9,	25.1,	25.3,	25.2,	25.8			
			25.3,	24.8,	25.2,	24.9						
	2.00	32.9	33.4,	33.2,	32.4,	33.6,	33.2,	32.6,	33.7,	32.8,	32.4,	32.0,
			33.5,	33.0,	33.4,	32.8,	33.2,	32.3,	31.8			
	2.50	40.1	39.0,	39.5,	39.0,	40.7,	38.8,	39.9,	39.7,	39.8,	41.8,	39.4,
			41.5,	40.6,	41.6,	38.7,	40.6,	42.0,	40.0,	40.7,	39.9,	40.5,
			40.5,	39.5,	38.9,	40.4						
4.20	1.00	15.9	15.8,	16.1,	15.9,	15.7,	16.0,	15.9,	16.1,	15.6,	15.8,	15.8,
			16.0,	15.7,	16.1,	16.1,	15.9,	15.6,	15.9,	16.0		
	1.50	23.1	22.9,	23.1,	23.1,	22.6,	23.6,	23.5,	23.1,	22.8,	22.7,	22.9,
			23.1,	23.0,	23.4,	22.9,	23.4					
	2.00	30.0	29.7,	29.7,	30.8,	29.3,	30.5,	29.8,	30.0,	29.7,	29.5,	29.8,
			30.1,	29.7,	30.6,	30.0,	29.6,	30.3,	30.4,	29.9		

	2.50	37.6	36.9,	37.4,	38.3,	38.4,	38.0,	37.7,	37.1,	38.1,	36.3,	36.8,
			37.8,	38.1								
4.40	1.00	14.5	14.5,	14.3,	14.4,	14.5,	14.5,	14.5,	14.3,	14.6,	14.6,	14.5
	1.50	20.8	20.4,	21.0,	20.8,	20.9,	20.4,	21.1,	21.0,	21.0,	20.5,	20.5,
			20.5,	21.0,	20.8,	20.8						
4.40	2.00	27.5	27.6,	27.5,	27.2,	27.8,	27.3,	27.4,	27.3,	27.9,	27.5,	27.5,
			27.4,	27.6								
	2.50	34.0	33.6,	33.0,	35.5,	33.0,	33.7,	34.3,	35.3,	34.2,	33.9,	33.9,
			34.7,	33.8,	34.1,	33.4,	34.0,	33.9				
4.50	1.00	13.0	13.0,	12.9,	12.9,	13.0,	13.2,	13.0,	13.0,	13.0,	13.3,	13.1,
			13.0,	12.9								
	1.50	19.5	19.7,	19.2,	19.8,	19.5,	19.4,	19.6,	19.5,	19.4,	19.4,	19.5,
			19.6,	19.8								
	2.00	25.9	25.7,	25.6,	25.2,	25.8,	25.7,	26.5,	25.8,	25.8,	25.8,	25.8,
			25.7,	25.6,	26.2,	25.7,	26.1,	25.6,	26.3,	26.1,	26.6,	26.0
	2.50	31.8	31.7,	31.8,	31.0,	32.1,	31.4,	32.3,	32.4,	31.0,	31.1,	31.1,
			31.4,	32.6,	31.9,	32.8,	32.8,	31.7,	31.6,	32.0,	32.0,	31.8
4.60	1.00	11.8	11.7,	11.9,	11.8,	11.8,	11.6,	11.7,	11.7,	11.8,	12.0,	11.8,
			11.8,	11.8,	12.0,	12.0,	11.9,	11.9,	11.9,	11.9,	12.1,	11.9
	1.50	17.0	16.9,	17.2,	17.2,	16.8,	16.9,	17.2,	16.9,	17.1,	17.3,	16.7,
			16.9,	17.2,	16.9,	17.2,	16.6,	17.4,	17.1,	17.1,	17.0,	17.0
	2.00	23.6	23.8,	23.4,	23.5,	23.1,	23.4,	24.3,	23.7,	23.4,	23.0,	22.9,
			24.1,	24.0,	23.5,	23.5,	23.8,	23.3,	23.9,	24.1,	23.3,	23.3,
			23.6									
	2.50	29.3	29.2,	29.2,	29.5,	29.4,	28.4,	29.2,	30.1,	29.2,	28.9,	29.0,
			29.1,	29.8,	29.2,	30.0,	29.3,	28.8,	29.8,	29.8,	29.4,	28.7,
			29.0									
4.70	1.00	10.6	10.6,	10.8,	10.5,	10.6						
	1.50	15.6	15.5,	15.6,	15.3,	15.5,	15.4,	15.7,	15.6,	15.9,	15.5,	15.5,
			16.0,	15.4								
	2.00	21.2	20.8,	21.3,	21.6,	21.0,	21.2					
	2.50	26.6	26.1,	27.0,	26.8,	26.8,	25.9,	26.7,	26.6,	26.7,	26.8,	26.8,
			27.0,	26.3,	26.9,	26.9,	26.9,	26.3,	26.2,	26.1		
4.80	1.00	9.78	9.84,	9.73,	9.77,	9.83,	9.65,	9.71,	9.91,	9.78		
	1.50	14.3	14.2,	14.2,	14.4,	14.4,	14.2,	14.5,	14.1,	14.3,	14.2,	14.4,
			14.2,	14.4,	14.4							

	2.00	19.1	19.2, 18.9,	19.1, 19.1,	19.1, 19.3,	19.2, 19.2,	19.0, 18.8,	19.1, 19.2	19.4,	19.2,	19.1,	19.1,
	2.50	23.9	23.8, 23.7,	24.2, 23.9,	24.2, 23.8	23.9,	23.9,	24.0,	24.2,	23.7,	23.8,	23.8,
4.90	1.00	8.78	8.94, 8.71,	8.76, 8.74	8.76,	8.72,	8.83,	8.75,	8.72,	8.83,	8.75,	8.82,
	1.50	13.3	13.3, 13.3,	13.4, 13.3	13.2,	13.2,	13.2,	13.4,	13.3,	13.4,	13.1,	13.2,
	2.00	17.1	17.2, 17.1,	17.2, 17.0,	17.0, 17.2,	16.9, 17.0	17.1,	17.1,	17.0,	17.2,	17.1,	17.1,
	2.50	21.4	21.5, 21.1,	21.1, 21.4,	21.8, 21.0,	21.7, 21.1,	21.1, 21.7,	20.9, 21.4,	21.8, 21.6	21.6,	21.5,	21.4,
5.00	1.00	7.98	7.87, 8.12,	8.09, 8.06,	8.00, 8.05,	7.96, 8.00,	8.01, 7.89,	8.08, 7.96,	8.04, 7.94,	7.84, 7.93,	7.96, 8.00	7.84,
	1.50	11.6	11.5, 11.6,	11.4, 11.7,	11.6, 11.8,	11.4, 11.7,	11.7, 11.5,	11.5, 11.6,	11.8, 11.6,	11.5, 11.5,	11.5, 11.6	11.4,
	2.00	15.8	15.6, 15.8,	15.8, 15.7,	15.6, 15.7,	16.0, 16.0,	15.6, 15.9,	15.8, 15.5,	15.8, 15.9,	15.4, 15.9,	15.7, 16.1,	15.7, 15.7
	2.50	19.3	19.6, 19.3, 19.1,	19.2, 19.4, 19.3	19.6, 19.2,	19.2, 19.5,	19.5, 19.5,	19.1, 19.2,	19.4, 19.3,	18.7, 19.0,	19.2, 19.1,	19.3, 19.7,
5.10	1.00	7.03	6.93, 7.02,	7.04, 7.03,	7.08, 7.03,	7.11, 7.02,	7.02, 7.02,	7.02, 6.98	7.00,	6.99,	7.06,	7.09,
	1.50	10.3	10.1, 10.5,	10.4, 10.4,	10.5, 10.4,	10.3, 10.3,	10.4, 10.3,	10.3, 10.2,	10.2, 10.3,	10.1, 10.2,	10.1, 10.2,	10.1, 10.2
	2.00	13.5	13.6, 13.5,	13.8, 13.6,	13.6, 13.6,	13.5, 13.7,	13.6, 13.4,	13.5, 13.7,	13.4, 13.5,	13.3, 13.3	13.3,	13.4,
	2.50	17.1	17.0, 17.1, 17.2	17.7, 16.8,	17.3, 17.3,	17.3, 17.2,	17.1, 17.4,	17.0, 17.4,	17.3, 17.3,	16.7, 17.0,	16.8, 16.9,	17.0, 17.4,
5.30	1.00	5.44	5.31, 5.48,	5.44, 5.52	5.38,	5.46,	5.46,	5.40,	5.46,	5.47,	5.45,	5.46,
	1.50	8.05	8.05, 8.12,	8.06, 8.09	7.99,	8.13,	8.19,	8.05,	7.96,	8.03,	7.96,	8.01,
	2.00	10.4	10.5, 10.5,	10.3, 10.4	10.4,	10.4,	10.5,	10.5,	10.5,	10.3,	10.2,	10.3,

	2.50	13.4	13.4, 13.5,	13.6, 13.4	13.3,	13.5,	13.4,	13.2,	13.7,	13.4,	13.3,	13.3,
5.60	1.00	4.14	4.05, 4.18,	4.13, 4.17,	4.10, 4.18,	4.13, 4.18	4.12,	4.13,	4.14,	4.14,	4.16,	4.18,
	1.50	6.24	6.20, 6.27	6.20,	6.24,	6.22,	6.28,	6.25,	6.27,	6.23,	6.22,	6.19,
	2.00	8.29	8.20, 8.38,	8.31, 8.38	8.40,	8.16,	8.32,	8.31,	8.27,	8.17,	8.34,	8.30,
	2.50	10.3	10.2, 10.3,	10.2, 10.3	10.3,	10.3,	10.3,	10.4,	10.4,	10.4,	10.4,	10.4,

Table S4 Rate constants (15 ºC, I = 1.0 M) for the reaction of 3-pyridylboronic acid with 2,2'-biphenol in acidic aqueous solution ($C_B >> C_L$). $C_L = 6.0 \times 10^{-5}$ M.

pH	C_B / mM	k_{obs} (average)	k_{obs} / s^{-1}									
4.00	1.20	147	134,	136,	151,	146,	149,	146,	136,	154,	155,	147,
			150,	146,	147,	143,	146,	152,	142,	161		
	1.80	170	172,	153,	166,	163,	167,	173,	176,	179,	164,	173,
			170,	181,	166,	168,	187,	180,	174,	181,	166,	155,
			152									
	2.40	193	192,	194,	187,	192,	199,	205,	198,	193,	184,	188,
			195,	190								
	3.00	210	211,	217,	201,	206,	228,	215,	195,	219,	196,	208,
			204,	218						,		
4.20	1.20	123	117,	130,	115,	127,	131,	134,	125,	124,	112,	120,
			118									
	1.80	146	154,	131,	137,	150,	154,	143,	144,	154,	150,	148,
			143,	135,	141,	152,	145,	146,	152,	132,	153,	146,
			141,	134,	150,	141,	141,	146,	163,	152,	150,	131,
			147,	150,	143,	139,	150,	156,	144,	143,	160,	150,
			149,	150,	139,	145,	142,	137,	147,	149,	135,	144,
			141,	135,	131,	136,	123,	158,	127,	146,	147,	168,
			161,	147,	137,	169,	139,	154,	152,	168		
	2.40	166	161,	165,	173,	169,	170,	165,	165,	164,	172,	186,
			154,	165,	165,	167,	160,	166,	173,	175,	169,	162,
			160,	165,	161,	155,	171,	150,	147,	159,	157,	167,
			170,	154,	172,	189,	183,	165,	155,	158,	172,	163,
			165,	172,	170,	178,	171,	168,	161,	153,	179	
	3.00	183	171,	182,	190,	192,	183,	178,	174,	188,	178,	191,
			175,	201,	181,	187,	176,	197,	188,	174,	183,	176,
			180,	185,	184,	185,	188,	171,	185			
4.40	1.20	107	89.5,	101,	107,	104,	106,	102,	106,	112,	111,	110,
			116,	118,	116,	103,	102					
	1.80	126	123,	133,	131,	134,	127,	130,	119,	124,	124,	120,
			127,	126,	125,	131,	121					
	2.40	145	144,	146,	147,	141,	139,	140,	144,	139,	142,	153,
			150,	142,	144,	148,	143,	143,	143,	141,	136,	151,
			147,	140,	144,	147,	157,	157,	146,	146,	147,	167,
			155,	148,	148,	128,	148,	147,	144,	146,	143,	132,
			145,	142,	135,	135,	138,	150,	141,	139		

	3.00	167	169,	151,	144,	179,	176,	162,	166,	159,	166,	171,
			160,	171,	181,	163,	167,	166,	166,	167,	187,	159,
			168,	163,	168,	169						
4.60	1.20	93	104,	92.6,	86.1,	97.6,	94.4,	93.4,	91.9,	91.7,	88.3,	85.1,
			89.8,	94.0,	89.7,	96.8,	99.7,	90.7,	95.9,	91.8,	87.2,	92.3,
			88.9,	97.1,	96.8,	95.7,	94.8,	93.9,	97.3,	91.3,	98.1,	101,
			88.9,	94.0								
	1.80	114	120,	112,	116,	112,	112,	110,	113,	115		
	2.40	131	125,	131,	130,	126,	129,	129,	127,	129,	125,	129,
			126,	127,	126,	129,	139,	140,	138,	133,	129,	129,
			135,	133,	130,	133,	137,	137,	134,	137,	132,	130,
			131,	127,	127,	135,	127,	134,	131			
	3.00	150	149,	158,	146,	145,	152,	153,	145,	143,	149,	154,
			144,	147,	153,	151,	146,	152,	145,	148,	165,	169,
			151,	150,	153,	151,	155,	154,	144,	146,	153,	145,
			143,	148,	148,	144,	146,	149,	143,	148,	148,	148,
			148,	155,	148,	152						
4.80	1.20	87	87.2,	88.3,	85.6,	87.3,	90.0,	87.9,	92.7,	90.8,	89.3,	86.5,
			91.7,	90.2,	87.0,	90.6,	85.2,	85.5,	90.3,	92.0,	78.3,	83.1,
			78.6,	80.3,	82.9,	84.5,	86.7,	88.7,	90.1,	84.0,	80.4,	86.5,
			87.5,	87.4,	92.8,	90.0,	86.0,	87.5,	80.5			
	1.80	102	109,	100,	100,	105,	104,	107,	104,	105,	104,	100,
			97.2,	100,	102,	107,	101,	99.3,	95.2,	93.5,	98.2,	106,
			108,	107,	104,	99.1						
	2.40	122	127,	116,	122,	117,	120,	122,	123,	120,	125,	124,
			125,	123								
	3.00	141	147,	146,	148,	146,	129,	132,	136,	141		