Electronic Supplementary Material (ESI) for Dalton Transactions

Amino Acid Side Chain Induced Selectivity in the Hydrolysis of Peptides Catalyzed by a Zr(IV)-Substituted Wells-Dawson Type Polyoxometalate

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Supporting Information

Table S1. Fitting indices and hydrolysis yields at the end of the kinetic reaction.

Dipeptide	R^2-value	Hydrolysis yield	Dipeptide	R^2-value	Hydrolysis yield
Gly-Gly	0,998	100%	Gly-Ser	0,99	97%
Gly-Ala	0,999	73%	Ser-Gly	0,986	50%
Ala-Gly	0,982	73%	Gly-Thr	0,997	100%
Gly-Val	0,993	69%	Gly-Tyr	0,974	55%
Gly-Leu	0,997	70%	Leu-Ser	0,997	100%
Gly-Ile	0,993	94%	Ile-Ser	0,966	75%
Gly-Phe	0,996	96%	Gly-Lys	0,996	75%
Gly-Asp	0,994	95%	Gly-Arg	0,996	81%
Gly-Asn	0,972	92%	Gly-His	0,991	94%
Gly-Glu	0,997	56%	His-Gly	0,995	81%
Gly-Gln	0,986	77%			

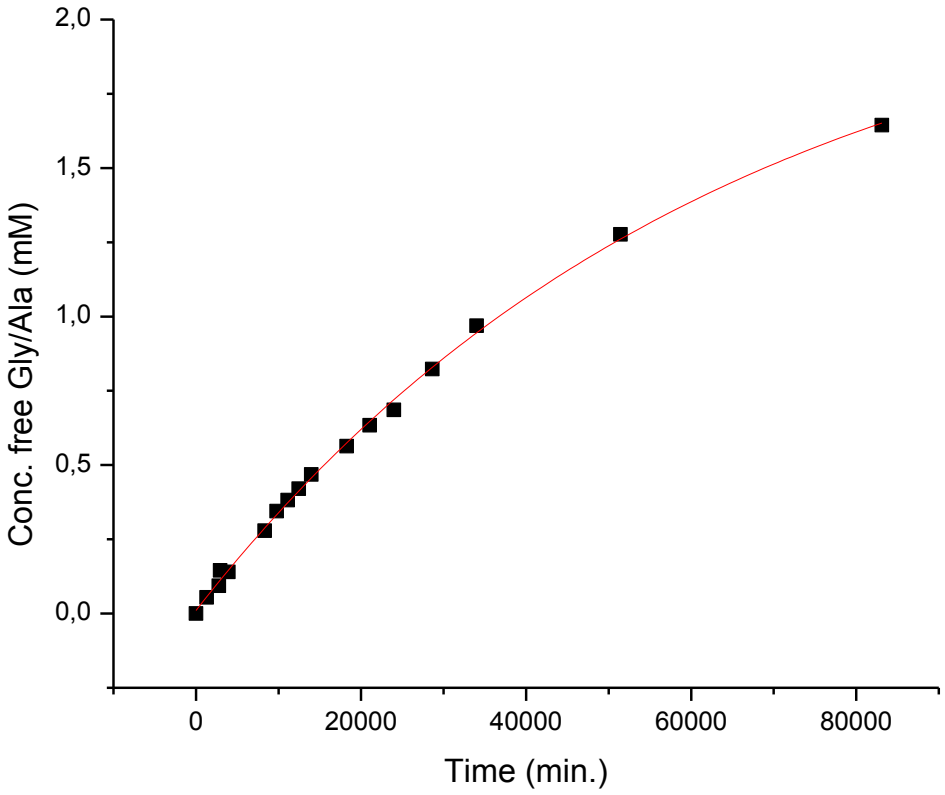


Figure S1. Concentration of the free amino acids Gly/Ala in function of time during the hydrolysis of 2mM Gly-Ala in the presence of 2mM of 1 (pD 5.0, 60 °C). An exponential fit was used to determine the k_{obs} of the hydrolysis reaction.

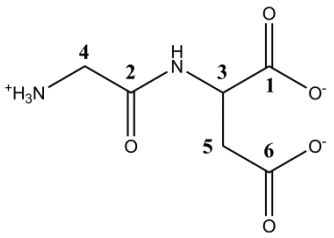
Table S2. Comparison of the reaction behavior of Gly-Ala and Ala-Gly in an equimolar mixture with 1(1:1, 2 mM, pD 5, 60 °C).

Dipeptide start- product	$t_{1/2}$ for glycine formation	Max.% of cyclic product	Max.% of 'inversed' dipeptide
Gly-Ala	30 days	40	10
Ala-Gly	15.9 days	15	4

Table S3. Normalization factors for rate constant for the Gly-Aa dipeptides. (Factor = rate constant of the disappearance of the dipeptide / rate constant of growth free amino acid content)

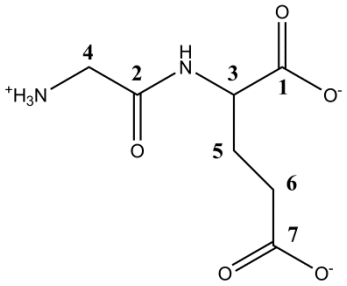
Dipeptide	Normalization factor
Gly-Gly	1.22
Gly-Ala	6.34
Gly-Val	1.0
Gly-Leu	4.58
Gly-Ile	1.29
Gly-Phe	1.58
Gly-Asp	1.99
Gly-Glu	2.94
Gly-Gln	3.87
Gly-Thr	1.26
Gly-Tyr	1.98
Gly-His	1.73

Table S4. Observed ^{13}C NMR chemical shift values for the dipeptide Gly-Asp both in the presence and absence of 1 at pD 5.0.



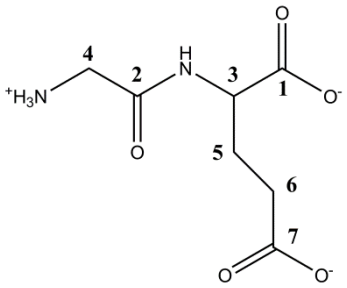
	Gly-Asp (ppm)	Gly-Asp + Zr-WD-POM (ppm)	Δδ (ppm)
C_O Asp (1)	177.52	178.05	**0.53**
C_O Gly (2)	166.45	166.51	**0.06**
C_O Asp (6)	177.35	177.94	**0.58**
C_α Asp (3)	52.44	52.91	**0.46**
C_α Gly (4)	40.54	40.69	**0.14**
C_β Asp (5)	38.38	38.98	**0.60**

Table S5. Observed ^{13}C NMR chemical shift values for the dipeptide Gly-Glu both in the presence and absence of 1 at pD 5.0. Only the 1:2 species is found at these conditions



	16 mM Gly-Glu (ppm)	16 mM Gly-Glu + 4 mM Zr-WD-POM (ppm)	Δδ (ppm)
Co Glu (1)	178.08	178.19	**0.11**
Co Gly (2)	166.48	166.56	**0.08**
Co Glu (7)	179.86	180.23	**0.37**
Cα Glu (3)	54.92	54.94	**0.02**
Cα Gly (4)	40.46	40.56	**0.10**
Cβ Glu (5)	27.51	27.56	**0.05**
Cγ Glu (6)	32.31	32.56	**0.25**

Table S6. Observed ^{13}C NMR chemical shift values for the dipeptide Gly-Glu both in the presence and absence of 1 at pD 5.0. About 83.1 % of 1:1 and 16.9 % of 1:2 species are present at these conditions.



	2 mM Gly-Glu (ppm)	2 mM Gly-Glu + 0.5 mM Zr-WD-POM (ppm)	Δδ (ppm)
Co Glu (1)	178.06	178.33	0.27
Co Gly (2)	166.48	166.46	-0.02
Co Glu (7)	179.84	181.22	1.38
Cα Glu (3)	54.93	55.19	0.26
Cα Gly (4)	40.47	40.52	0.05
Cβ Glu (5)	27.52	27.94	0.42
Cγ Glu (6)	32.3	33.32	1.02

Table S7. ^{1}H shifts of three protons in Gly-His at different pD-values.

pD	α-H Gly Δδ (ppm)	C_7-H Δδ (ppm)	C_8-H Δδ (ppm)
4.0	0.31	0.15	0.29
5.0	0.34	0.15	0.31
6.5	0.33	0.19	0.43
8.0	0.33	0.30	0.75

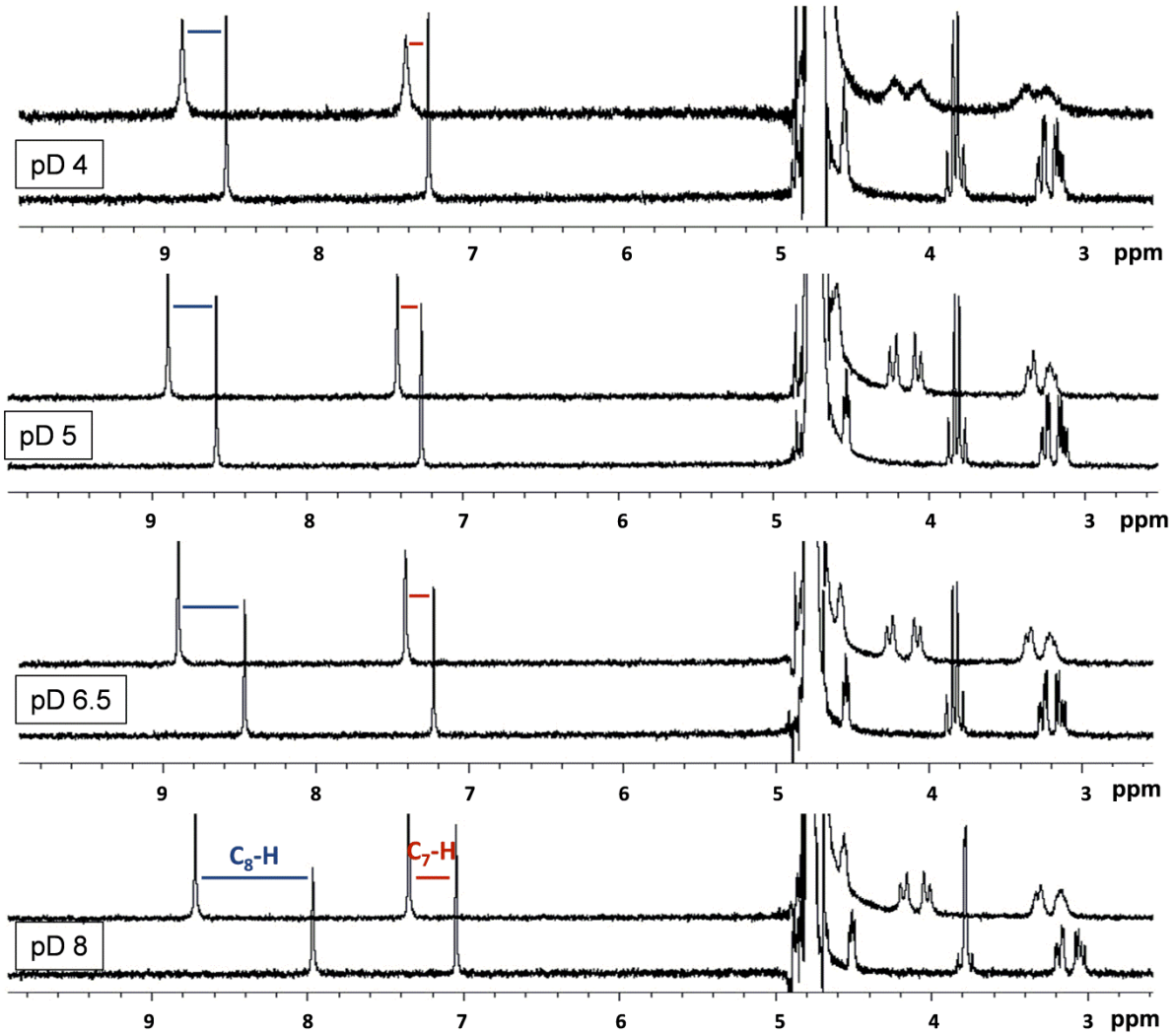


Figure S2. ^{1}H NMR spectrum of Gly-His in the presence (upper) and absence (lower) of 1 at different pD-values.

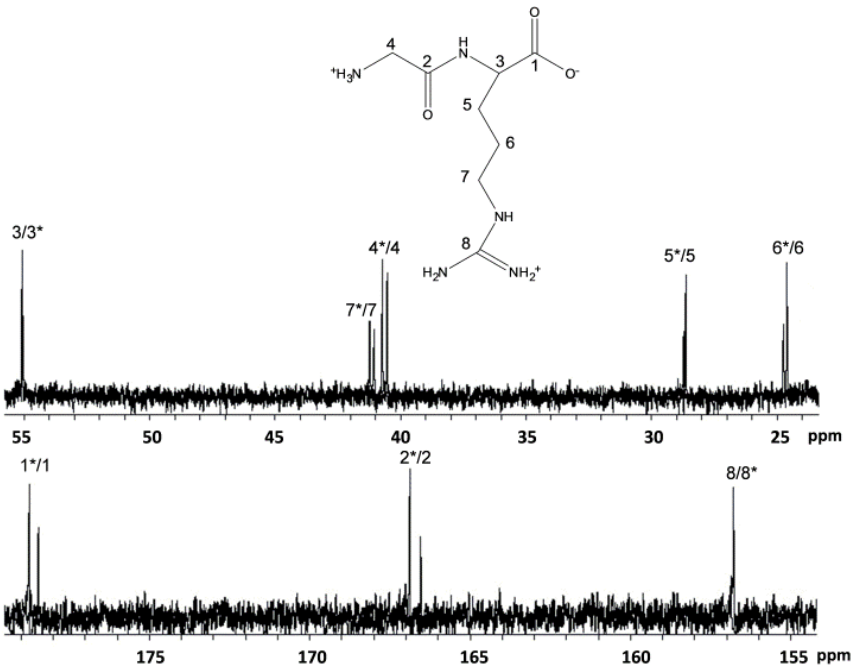


Figure S3. ^{13}C NMR spectrum of Gly-Arg in the presence (*) and absence of 1.

Table S8. Observed ^{13}C NMR chemical shift values for the dipeptide Gly-Arg both in the presence and absence of 1 at pD 5.0.

	30.0 mM Gly-Arg	24.0 mM Gly-Arg + 8.0 mM **1**	Δ(ppm)
C_O Arg (1)	178.43	178.71	0.28
C_O Gly (2)	166.51	166.85	0.34
C_α Arg (3)	55.06	55.02	-0.04
C_α Gly (4)	40.41	41.03	0.52
C_β Arg (5)	28.61	28.69	0.08
C_γ Arg (6)	24.59	24.71	0.13
C_δ Arg (7)	40.71	41.21	0.51
C_N Arg (8)	156.83	156.76	-0.07