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Supporting Information

Electrosynthesis of Amino Acids from Biomass-Derivable Acids on Titanium Dioxide

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1. Materials and Methods

1-1. Materials

Pyruvic acid, glyoxylic acid, α-ketoglutaric acid, 4-methyl-2-oxovaleric acid, phenylpyruvic acid, 4-hydroxyphenylpyruvic acid, and hydroxylamine sulfate were purchased from Tokyo Chemical Industry Co., Ltd. (TCI). $H_2IrCl_6 \bullet nH_2O$, Na_2SO_4, NaOH, 28% NH_3 aqueous solution, and $(NH_4)_2SO_4$ were purchased from FUJIFILM Wako Pure Chemical Corporation. Ti mesh (100 mesh) and Ti felt (WB/Ti/20/150, 150 g m^{-2}) were purchased from Manabe Industry Co., Ltd and NIKKO TECHNO, Ltd., respectively. Ti paper, WEBTi-K (0.025 mm thickness), was purchased from Toho Technical Service, Co., Ltd. Nafion NRE-212, Nafion 117 membranes, and Nafion solution (5 wt%) were purchased from Sigma-Aldrich Co. Lab-designed Ti current collectors with flow channels (4 cm^2, serpentine flow) were used for the polymer electrolyte amino acid electrosynthesis cell (AAEC). All chemicals were used without further purification.

1-2. Spectroscopic measurements

^{1}H NMR spectra were recorded on a Bruker Avance III (600 MHz) spectrometer at 25 ºC. The obtained spectra were analyzed by using JEOL Delta NMR Processing and Control Software v5.3. The ^{1}H NMR chemical shifts were reported to be δ values (ppm) relative to methyl proton of 4,4-dimethyl-4-silapentane-1-sulfonic acid.

1-3. Preparation of Ti mesh and Ti felt covered with anatase-TiO_2 layer (TiO_2/Ti mesh and TiO_2/Ti felt)

TiO_2/Ti mesh and TiO_2/Ti felt (2.5 × 2 cm^2) were prepared from Ti mesh and Ti felt, respectively, through a two-step hydrothermal reaction that we reported previously [1]. A Ti substrate, i.e., Ti mesh or Ti felt, was cut into 2.5 × 2 cm^2 pieces, washed with hexane and ethanol and dried in air. Subsequently, 3 pieces of Ti substrate were placed into a 50 mL Teflon-lined autoclave filled with 30 mL of 1 M NaOH aq. The autoclave was then sealed and heated at 220 ºC for 12 h. After cooling to room temperature, the Ti substrate covered with sodium titanate was removed from the autoclave and immersed in 0.1 M HCl aq. for 10 min to replace Na^+ with H^+. Then, the mesh was washed with water and ethanol and dried in air. After that, the 3 pieces of titanate covered Ti substrate was placed in a 50 mL Teflon-lined autoclave containing 40 mL of water. The autoclave was then sealed and heated at 200 ºC for 24 h. After

cooling to room temperature, the TiO_2/Ti substrate was removed from the autoclave, washed with water and ethanol and dried in air.

1-4. Preparation of IrO_2 nanoparticles

Nanosized IrO_2 particles for the anode catalyst of the AAEC were prepared from H_2IrCl_6•$n$$H_2O$ as the starting material according to a reported procedure [2, 3]. An aqueous solution containing H_2IrCl_6•$n$$H_2O$ (97.0 mM, 200 mL) was stirred for 45 min. at 100 ºC. An aqueous solution of NaOH (1 M, 200 mL) was added to promote the formation of Ir-hydroxide, and the solution was stirred for another 45 min. at 100 ºC. Afterwards, the solution was centrifuged for 15 min and filtered. The prepared nonstoichiometric hydroxide ($Ir(OH)_x$) was dried for 5 h at 80 ºC and calcined in air at 400 ºC for 1 h. to obtain IrO_2 powder.

1-5. Electrochemical studies with typical glass cells

Electrochemical experiments were conducted using a 3-electrode system connected to a VersaSTAT 4 potentiostat (Princeton Applied Research). TiO_2/Ti mesh, a coiled Pt wire (length of 230 mm, diameter of 0.5 mm, BAS Inc.) and an Ag/AgCl reference electrode (3 M NaCl, RE-1B, BAS Inc.) were used as a working electrode, counter electrode and reference electrode, respectively. Potentials applied to the working electrode were measured against a reference electrode and converted to the reversible hydrogen electrode (RHE) reference scale using:

$$E \text{ (vs RHE)} = E \text{ (vs Ag/AgCl)} + 0.196 \text{ V} + 0.059 \text{ V} \times \text{pH} \qquad (1)$$

1-5-1. Cyclic voltammetry (CV) measurements

CV measurements were conducted in a glass three-electrode electrochemical cell (100 mL in volume) sealed to be gas-tight with Teflon caps. An aqueous electrolyte aqueous solution (40 mL) was introduced into the glass cell. After the glass cell was tightly sealed with a Teflon cap, Ar gas was bubbled through the solution for 30 min. in order to purge the air from the inside of the cell. The current value was recorded against the applied potential at a scan rate of 10 mV/s with 3 scan cycles. A 1.5 M NH_3/$(NH_4)_2SO_4$ buffer containing 30 mM pyruvic acid (pH 10) was used as the electrolyte solution for CV measurements in the presence of NH_3. This electrolyte solution was prepared by mixing 1.5 M NH_3 (aq.) containing 30 mM pyruvic acid and 0.75 M $(NH_4)_2SO_4$ aq. containing 30 mM pyruvic acid to adjust the pH to 10. For CV measurements in the presence of NH_2OH, 0.2 M H_2SO_4 (aq.) containing 160 mM pyruvic acid and 80 mM $(NH_2OH)_2$•H_2SO_4 (pH 0.53) was used as the electrolyte solution for CV

measurements in the presence of NH_2OH. In both cases (employing NH_3 and NH_2OH), blank CV measurements were conducted with the electrolyte solution without pyruvic acid.

1-5-2. Chronoamperometry (CA) experiments

The electrosynthesis of amino acids at a constant potential, i.e., CA, was performed in a two-compartment electrochemical cell sealed to be gas-tight with Teflon caps. A piece of proton-conducting membrane (Nafion NRE-212) was used as a separator. A typical procedure is as follows. A 6.0 M $NH_3/(NH_4)_2SO_4$ buffer containing 160 mM pyruvic acid (pH 10, 35 mL) was introduced into a cathodic cell (75 mL in volume) into which the working and reference electrode were subsequently immersed. A counter electrode was placed in an anodic cell (75 mL in volume) containing a 6.0 M $NH_3/(NH_4)_2SO_4$ buffer (pH 10, 35 mL). After the Teflon caps were tightly closed, Ar gas was bubbled through both the cathodic and anodic cells for 30 min. to purge the air from the cells. The electrosynthesis of alanine was conducted at –0.32 V vs RHE and 40 ºC for 2 h, during which the potential was controlled using a VersaSTAT 4 potentiostat. The reaction solution collected from the cathodic cell was analyzed using a high-performance liquid chromatograph (HPLC, Prominence, Shimadzu) system equipped with a refractive index detector (RID-10A, Shimadzu). α-Keto acids and α-hydroxyl acids were quantified on a Shodex KC-811 column using a 50 mM $HClO_4$ (aq.) as the mobile phase. The reaction solution was also analyzed by ^{1}H NMR spectroscopy (Avance III, Bruker). A ^{1}H NMR spectrum of the reaction solution diluted 5 times with D_2O was measured, and amino acids were quantified by the signal appearing in the area of approximately 3.4 – 3.8 ppm assignable to the proton on the α-carbon of the amino acids.

$NH_3/(NH_4)_2SO_4$ buffers with and without α-keto acids were used as the cathodic and anodic electrolyte solutions, respectively, for the electrosynthesis of amino acids employing NH_3 as the nitrogen source. A H_2SO_4 (aq.) containing α-keto acids and $(NH_2OH)_2{\bullet}H_2SO_4$ and a H_2SO_4 (aq.) were used as cathodic and anodic electrolyte solutions, respectively, for the electrosynthesis of amino acids employing NH_2OH as a nitrogen source. The electrolyte solution with a pH of 1.2 – 9 was prepared with 0.2 M Na_2SO_4 as the supporting electrolyte instead of H_2SO_4 and the pH of the solution was adjusted by adding aqueous H_2SO_4 or NaOH.

The Faradaic efficiency (FE) for each product was determined as follows:

$$\text{Faradaic efficiency} = \frac{n \times m_{\text{products}} \times F}{Q} \times 100 \quad (2)$$

where n represents the number of electrons required for the formation of products via α-keto acid reduction (n = 2 for the formation of amino acids and α-hydroxy acids in the presence of NH_3, n = 4 for formation of amino acids in the presence of NH_2OH); $m_{products}$ is the moles of products; F is the Faraday constant (96,485 C mol^{-1}); and Q is the total charge (in Coulombs) passed across the electrode during the electroreduction.

1-6. Electrosynthesis of alanine using the AAEC

1-6-1. Preparation of the membrane electrode assembly (MEA)

A MEA composed of a Nafion 117 membrane, an IrO_2 anode catalyst layer, and a porous Ti paper was prepared as follows. IrO_2 was deposited on the Nafion membrane using the airbrush technique [4, 5]. Catalyst ink containing 12 mg of IrO_2 powder, 62 μL of Nafion solution (5 wt%), 50 μL of 2-propanol and 50 μL of water was dispersed on the Nafion membrane (IrO_2: 3 mg cm^{-2}) using an airbrush and naturally dried in the atmosphere. Ti paper (2 × 2 cm^2) was placed on the deposited IrO_2 layer on the Nafion membrane. Then, the Nafion membrane with the IrO_2 layer and the Ti paper was inserted into a hot press machine (H400-15, AS ONE Corporation) and pressed at 120 ºC for 4 minutes. After cooling to room temperature, the MEA was extracted from the press machine.

1-6-2. Fabrication of the AAEC

Fig. S1 illustrates a schematic view of the AAEC equipped with a TiO_2/Ti felt cathode and the prepared MEA between two current collectors having sample flow channels. Lab-made titanium blocks having serpentine flow patterns were utilized as current collectors (reaction area is 4 cm^2). The MEA and TiO_2/Ti felt were placed between the current collectors. Silicon rubber was used as a gasket. These components were stacked and fastened with nuts and bolts.

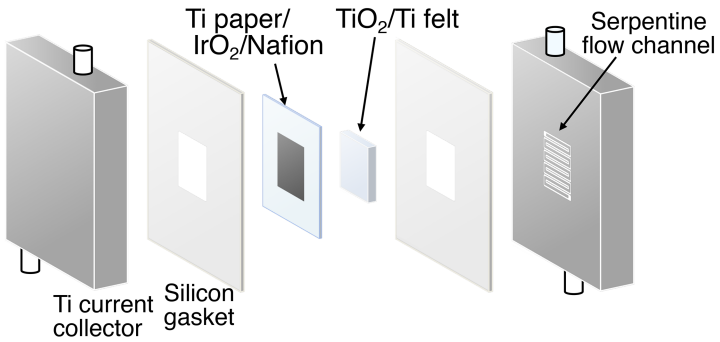


Fig. S1 A schematic view of the AAEC.

1-6-3. Operation of the AAEC

An aqueous solution containing 160 mM pyruvic acid, 96 mM $(NH_2OH)\cdot H_2SO_4$, and 0.2 M H_2SO_4 (pH 0.53) and a deionized water were used as the reaction solutions for the cathode and anode, respectively. To avoid the influence of the O_2 reduction reaction during the electrolysis, the solution was bubbled once with argon and degassed using a degasser (Gastorr BG-34, FLOM Co.) before being flowed into the AACE. The reaction solution was introduced using a flow controller (PCS Pump SP-21, FLOM Co.) on the cathode and anode side at low rates of 1.0 and 0.5 mL min^{-1}, respectively. The operation temperature of the AAEC was kept at 25ºC.

The reduction current was monitored under the application of a constant voltage in the range from 2.2 to 2.8 V between the electrodes using a potentiogalvanostat (1280 C, Solartron). After waiting for 3 min to reach a steady state, the solution from the cathode outlet was collected for 116 min under each applied voltage. The collected solution was analyzed using an HPLC system (Prominence, Shimadzu) equipped with a refractive index detector (RID-10A, Shimadzu). Pyruvic oxime was quantified on a Shodex KC-811 column using a 50 mM $HClO_4$ (aq.) as the mobile phase. The collected solution was also analyzed by ^1H NMR spectroscopy (Avance III, Bruker). A ^1H NMR spectrum of the collected solution diluted 5 times with D_2O was measured, and alanine was quantified by the signal appearing in the area of approximately

4.4 ppm assignable to the proton on the α-carbon of alanine. The FE for alanine production was determined with equation (2) as mentioned above.

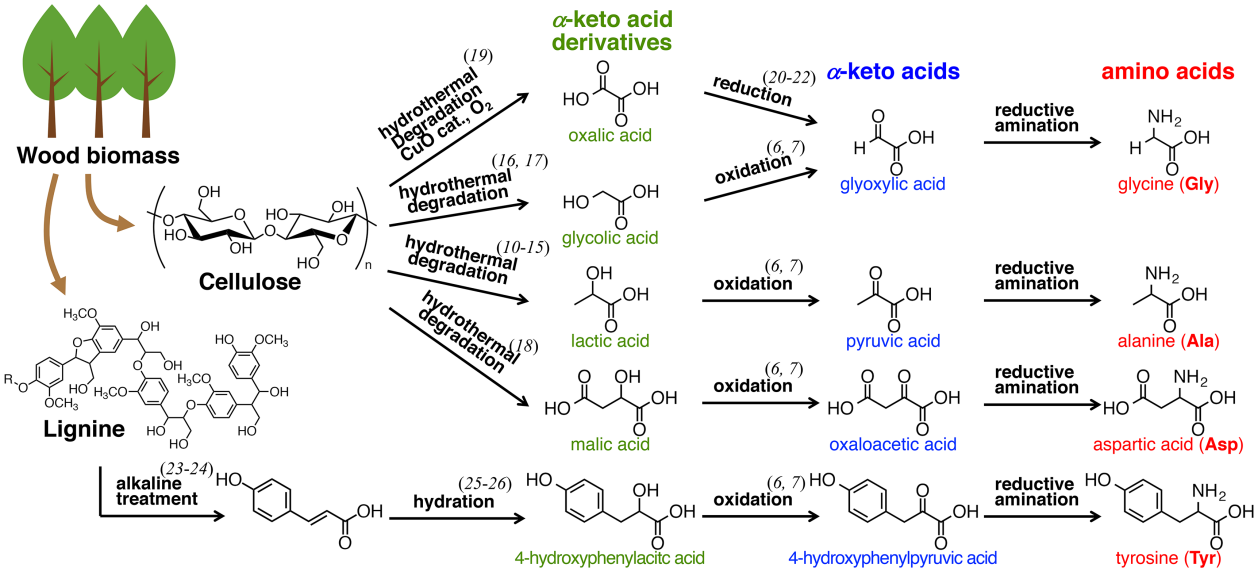


Fig. S2 Possible routes for the preparation of α-keto acids from wood biomass. Representative references[6-26] for the each chemical process are given in the figure. Amino acids that can be synthesized from the α-keto acids by reductive amination reaction are also provided in the figure.

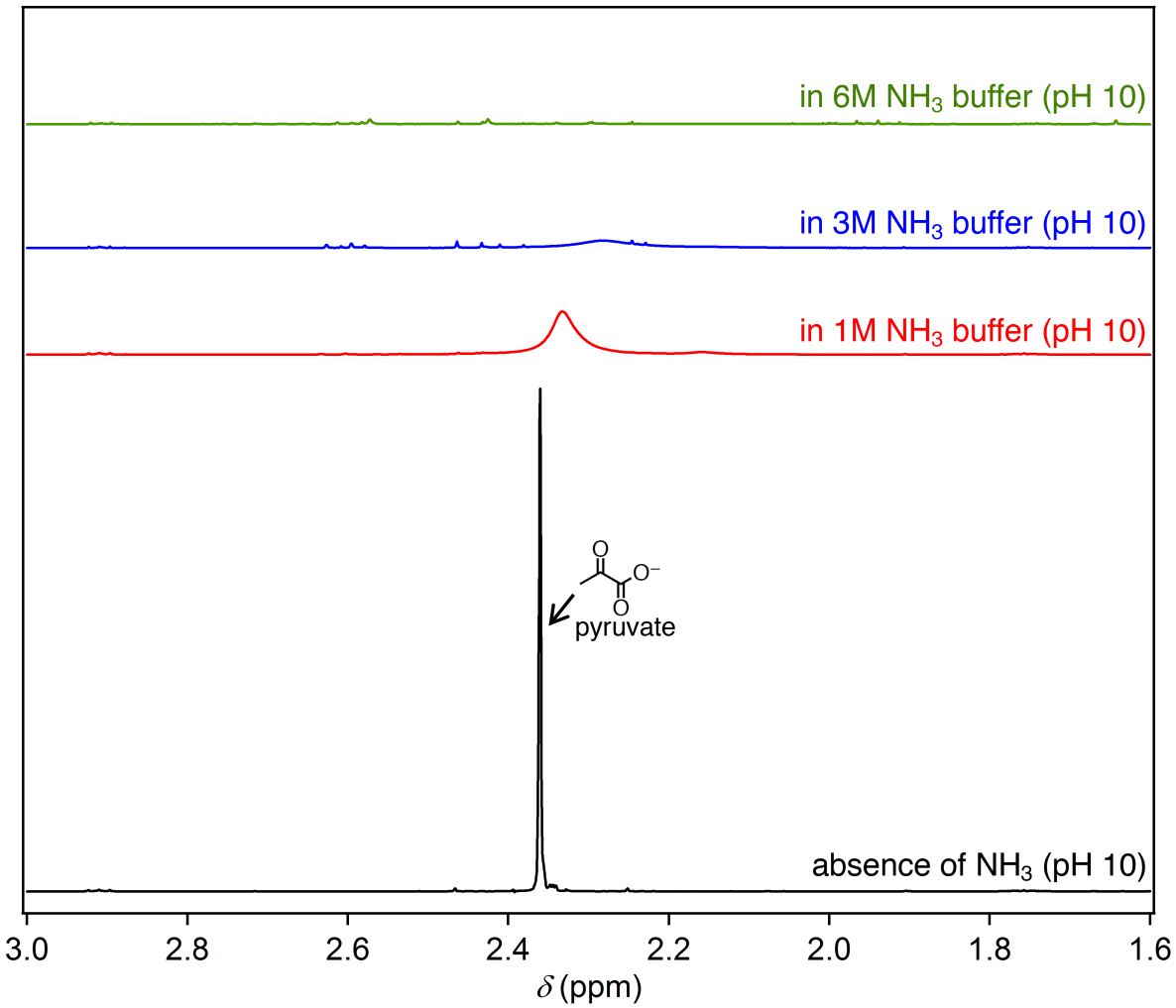


Fig. S3 ^{1}H NMR spectra for 160 mM pyruvic acid in (black line) D_2O, and in D_2O buffered with (red line) 1 M, (blue line) 3 M, and (green line) 6 M $NH_3/(NH_4)_2SO_4$. The signal at 2.3 ppm assignable to methyl proton of pyruvate becomes broader with increasing NH_3 concentration. Even in 6 M NH_3 buffer, no distinguishable signal is observed around 2.1 ppm where the signal attributable to methyl proton of pyruvate imine is expected to appear.

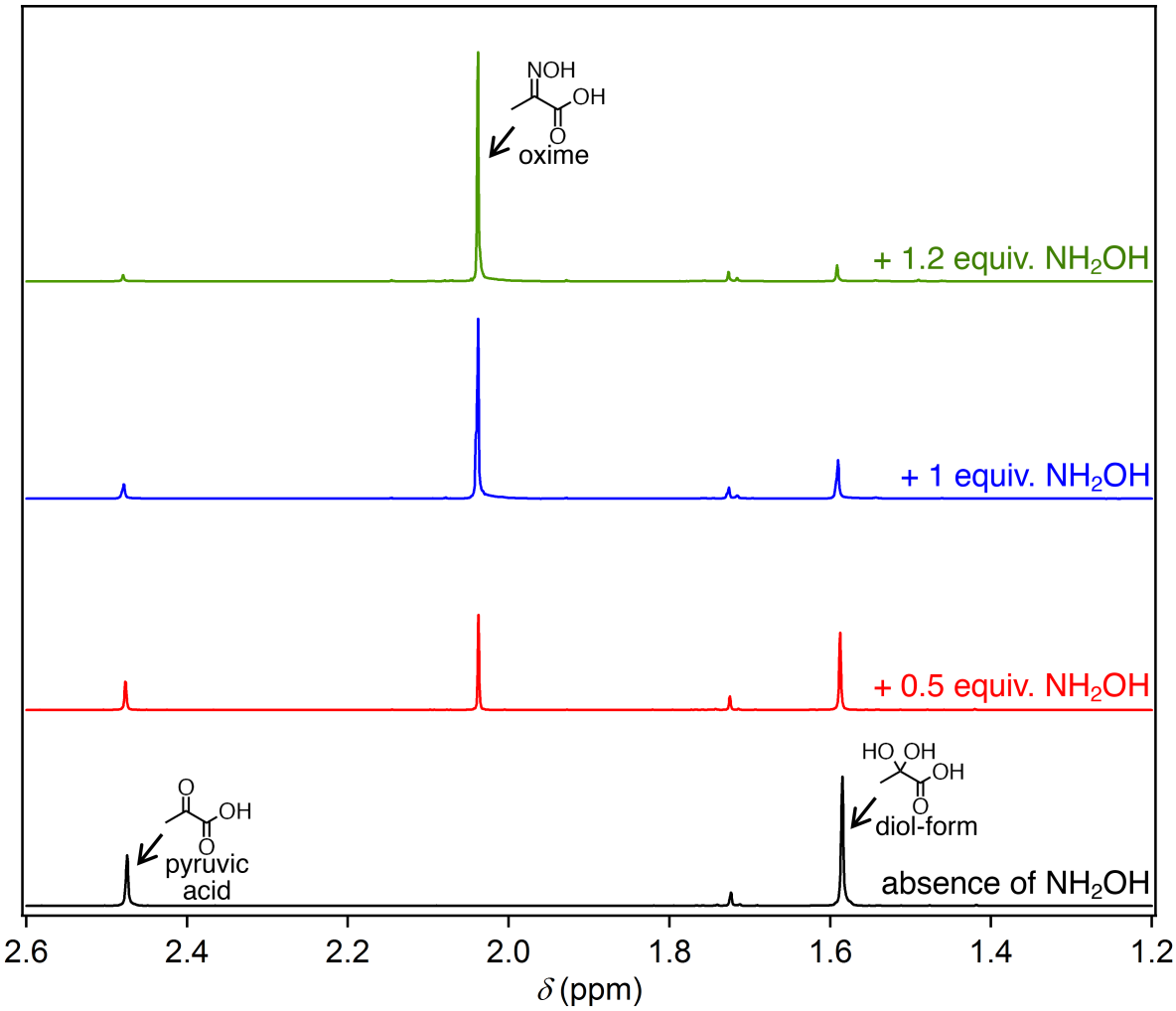


Fig. S4 ^{1}H NMR spectra for 160 mM pyruvic acid with (red line) 40 mM, (blue line) 80 mM, and (green line) 96 mM $(NH_2OH)_2 \cdot H_2SO_4$ and (black line) without $(NH_2OH)_2 \cdot H_2SO_4$ in 0.5 M H_2SO_4 D_2O solution. The signals at 2.5 and 1.6 ppm assignable to pyruvic acid and its hydrated diol-form, respectively, decrease with increasing NH_2OH concentration, and almost disappear in the presence of 1.2 equivalent of NH_2OH.

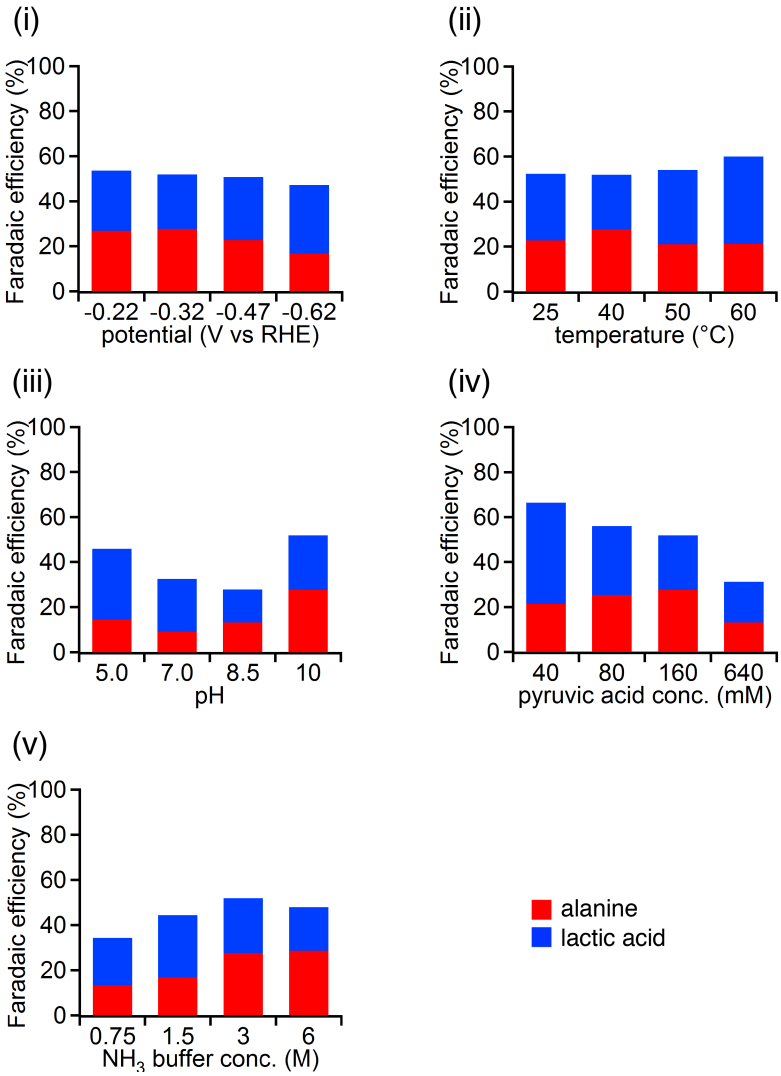


Fig. S5 FEs for alanine (red bar) and lactic acid (blue bar) productions in the presence of NH_3 at various (i) applied potentials, (ii) temperatures, (iii) pH values, (iv) pyruvic acid concentrations, and (v) NH_3 buffer concentrations. Detailed conditions for each electrochemical run are summarized in Table S1.

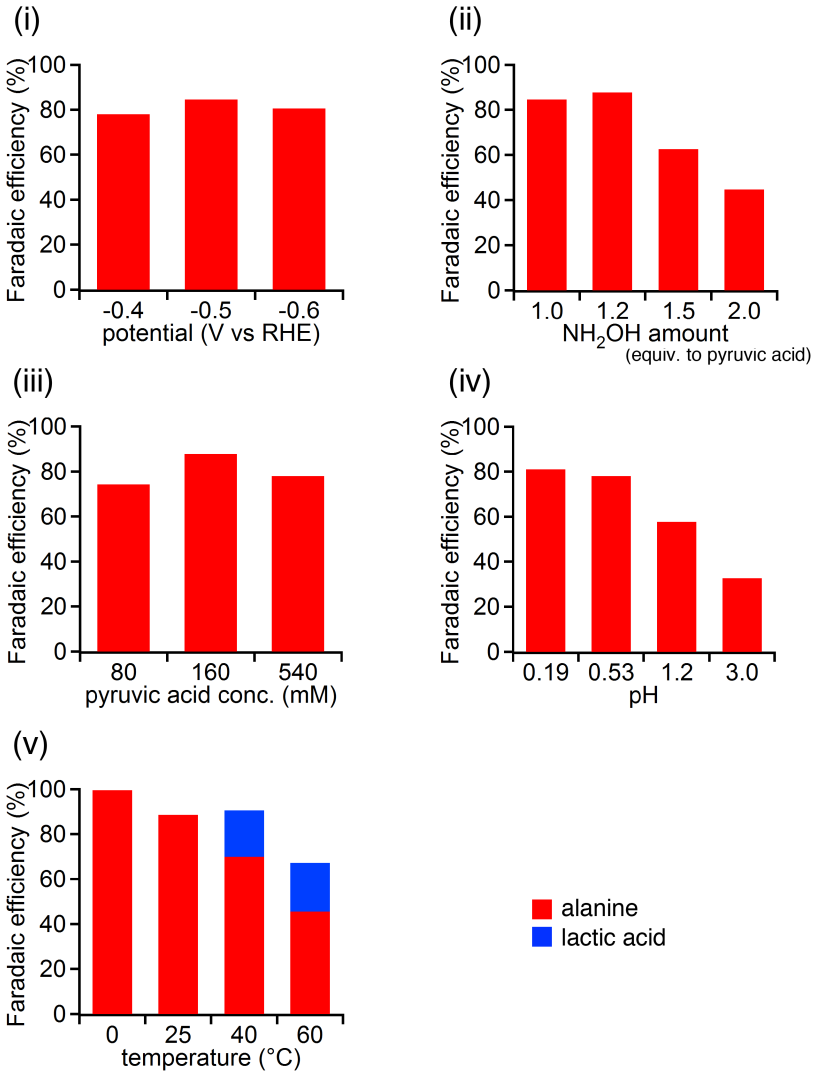


Fig. S6 FEs for alanine (red bar) and lactic acid (blue bar) production in the presence of NH_2OH at various (i) applied potentials, (ii) NH_2OH amounts, (iii) pyruvic acid concentrations, (iv) pH values, and (v) temperatures. Detailed conditions for each electrochemical run are summarized in Table S2.

Table S1 Electrochemical reduction of pyruvic acid under various (i) potentials, (ii) temperatures, (iii) pH values, (iv) pyruvic acid concentrations, and (v) NH_3 buffer concentrations.

	Reaction conditions					FE (%) for products	
	Potential (V vs RHE)	Temp. (C°)	pH	Pyruvic acid conc. (mM)	NH_3 buffer conc. (M)	Alanine	Lactic acid
(i)	**-0.22**	40	10	160	3.0	26.8	26.8
(i)	**-0.32**	40	10	160	3.0	27.7	24.2
(i)	**-0.47**	40	10	160	3.0	22.7	28.1
(i)	**-0.62**	40	10	160	3.0	16.8	30.5
(ii)	-0.32	**25**	10	160	3.0	22.8	29.6
(ii)	-0.32	**40**	10	160	3.0	27.7	24.2
(ii)	-0.32	**50**	10	160	3.0	21.0	33.1
(ii)	-0.32	**60**	10	160	3.0	21.2	38.8
(iii)	-0.32	40	**5.0**	160	3.0	14.5	31.5
(iii)	-0.32	40	**7.0**	160	3.0	9.16	23.3
(iii)	-0.32	40	**8.5**	160	3.0	13.3	14.6
(iii)	-0.32	40	**10**	160	3.0	27.7	24.2
(iv)	-0.32	40	10	**40**	3.0	21.4	45.0
(iv)	-0.32	40	10	**80**	3.0	25.5	30.6
(iv)	-0.32	40	10	**160**	3.0	27.7	24.2
(iv)	-0.32	40	10	**640**	3.0	13.1	18.2
(v)	-0.32	40	10	160	**0.75**	13.4	21.0
(v)	-0.32	40	10	160	**1.5**	16.8	27.6
(v)	-0.32	40	10	160	**3.0**	27.7	24.2
(v)	-0.32	40	10	160	**6.0**	28.7	19.3

Table S2 Electrochemical reduction of pyruvic acid at various (i) potentials, (ii) NH_2OH amounts, (iii) pyruvic acid concentrations, (iv) pH values, and (v) temperatures.

	Reaction conditions					FE (%) for products	
	Potential (V vs RHE)	NH_2OH amount (equiv. to pyruvic acid)	Pyruvic acid conc. (mM)	pH	Temp. (C°)	alanine	lactic acid
(i)	**-0.4**	1.0	160	0.53	25	78.0	–
(i)	**-0.5**	1.0	160	0.53	25	84.5	–
(i)	**-0.6**	1.0	160	0.53	25	80.6	–
(ii)	-0.5	**1.0**	160	0.53	25	84.5	–
(ii)	-0.5	**1.2**	160	0.53	25	87.8	–
(ii)	-0.5	**1.5**	160	0.53	25	62.6	–
(ii)	-0.5	**2.0**	160	0.53	25	44.7	–
(iii)	-0.5	1.2	**80**	0.53	25	74.3	–
(iii)	-0.5	1.2	**160**	0.53	25	87.8	–
(iii)	-0.5	1.2	**540**	0.53	25	78.0	–
(iv)	-0.4	1.2	160	**0.19**	25	81.0	–
(iv)	-0.4	1.2	160	**0.53**	25	78.0	–
(iv)	-0.4	1.2	160	**1.23**	25	57.7	–
(iv)	-0.4	1.2	160	**3**	25	32.7	–
(v)	-0.5	1.2	160	0.19	**0**	99.5	–
(v)	-0.5	1.2	160	0.19	**25**	88.5	–
(v)	-0.5	1.2	160	0.19	**40**	69.9	20.6
(v)	-0.5	1.2	160	0.19	**60**	45.5	21.8

Table S3 Electrosynthesis of various amino acids from corresponding α-keto acids and NH_2OH. The following conditions are identical for all the electrochemical reactions; 1.2 equiv. to α-keto acid for NH_2OH amount, 0 ºC of reaction temperature, pH = 0.19. Every experiment was conducted 3 times, and averages and errors were calculated for the obtained FE values.

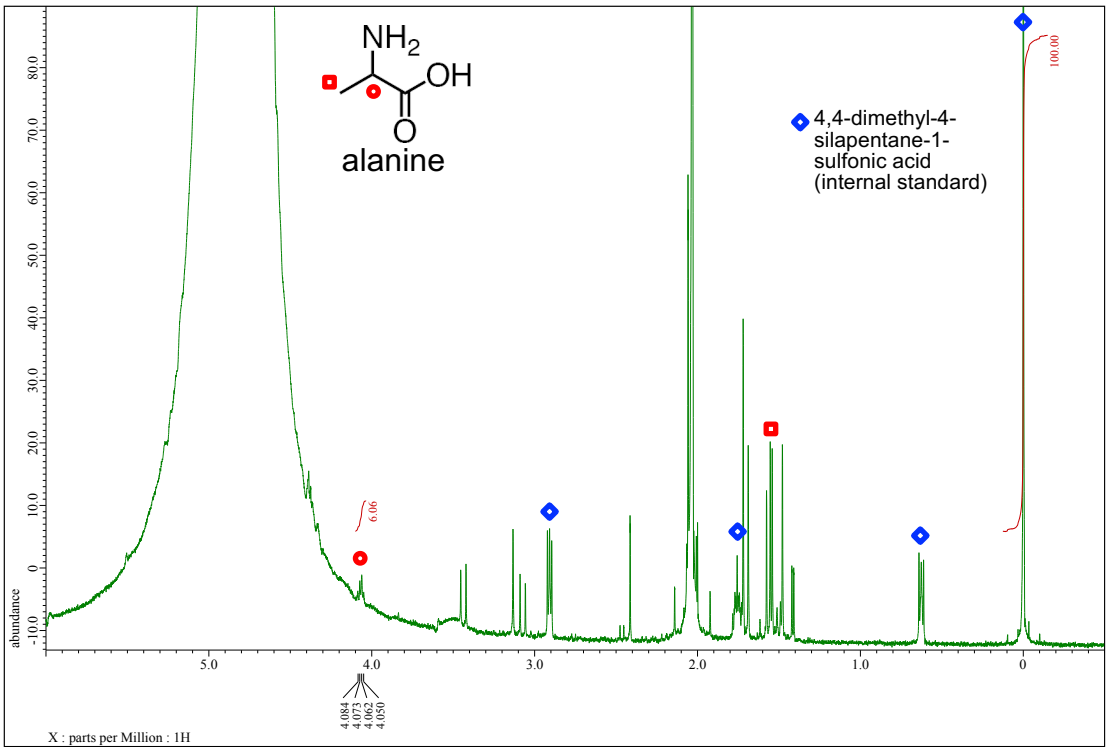
Reaction conditions				Products		
α-Keto acids and its concentration	Potential vs RHE	Reaction time	Electrolyte	Amino acid	FE	Ave. and error of FE
pyruvic acid 160 mM	– 0.5 V	2 h.	0.5 M H_2SO_4 aq.	alanine	1st 99.5% 2nd 98.9% 3rd 100%	99.5±0.5%
glyoxylic acid 160 mM	– 0.5 V	2 h.	0.5 M H_2SO_4 aq.	glycine	1st 96.4% 2nd 97.9% 3rd 99.2%	97.8±1.4%
oxaloacetic acid 160 mM	– 0.5 V	2 h.	0.5 M H_2SO_4 aq.	aspartic acid	1st 95.8% 2nd 98.1% 3rd 95.5%	96.5±1.4%
α-ketoglutaric acid 160 mM	– 0.5 V	2 h.	0.5 M H_2SO_4 aq.	glutamic acid	1st 95.4% 2nd 96.5% 3rd 98.2%	96.7±1.4%
4-methyl-2-oxovaleric acid 80 mM	– 0.5 V	2 h.	0.5 M H_2SO_4 aq.	leucine	1st 90.7% 2nd 88.7% 3rd 92.7%	90.7±2.0%
phenylpyruvic acid 20 mM	– 0.6 V	5 h.	0.5 M H_2SO_4 aq. contains 33% DMSO	phenylalanine	1st 87.0% 2nd 86.3% 3rd 87.7%	87.0±0.7%
4-hydroxyphenyl-pyruvic acid 30 mM	– 0.6 V	5 h.	0.5 M H_2SO_4 aq. contains 25% DMSO	tyrosine	1st 75.3% 2nd 77.0% 3rd 78.5%	77.0±1.6%

Table S4 Comparison of the reaction conditions and FE values for amino acid electrosynthesis

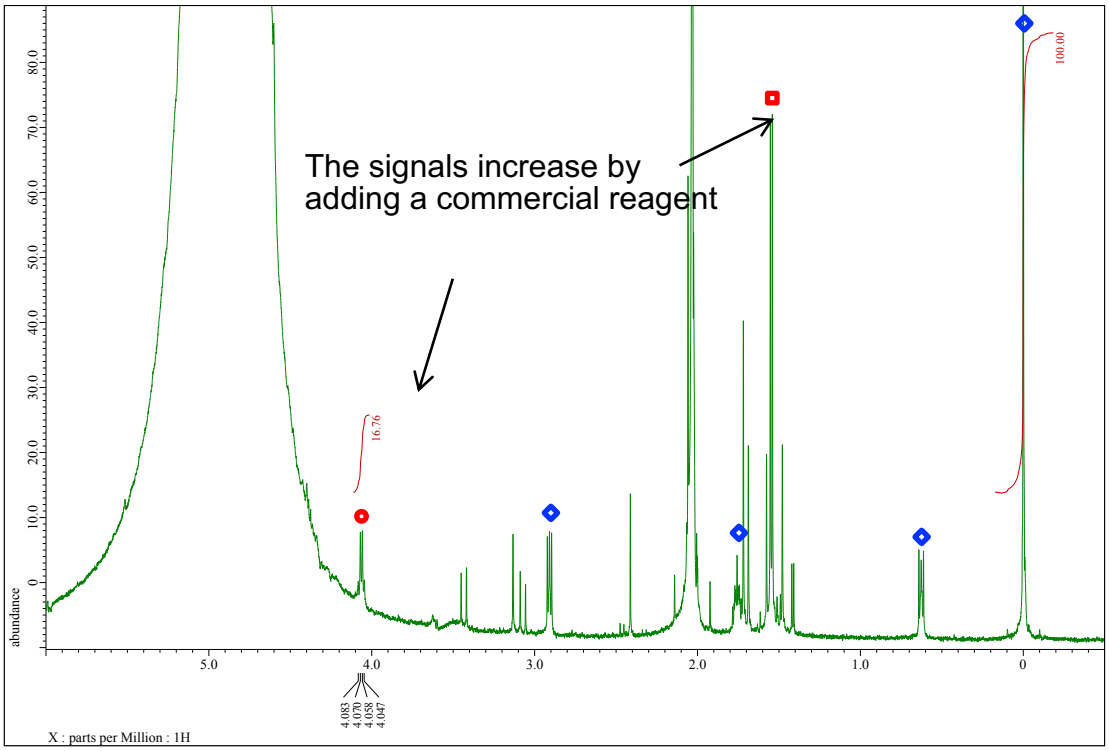
Reaction conditions			Amino acids and FE (%)		References
α-Keto acids	Electrodes	Nitrogen sources			
pyruvic acid	TiO_2/Ti mesh	$(NH_2OH)_2 \cdot H_2SO_4$	alanine	99	This work
glyoxylic acid	TiO_2/Ti mesh	$(NH_2OH)_2 \cdot H_2SO_4$	glycine	96	This work
oxaloacetic acid	TiO_2/Ti mesh	$(NH_2OH)_2 \cdot H_2SO_4$	aspartic acid	96	This work
α-ketoglutaric acid	TiO_2/Ti mesh	$(NH_2OH)_2 \cdot H_2SO_4$	glutamic acid	95	This work
4-methyl-2-oxovaleric acid	TiO_2/Ti mesh	$(NH_2OH)_2 \cdot H_2SO_4$	leucine	91	This work
phenylpyruvic acid	TiO_2/Ti mesh	$(NH_2OH)_2 \cdot H_2SO_4$	phenylalanine	87	This work
4-hydroxyphenyl-pyruvic acid	TiO_2/Ti mesh	$(NH_2OH)_2 \cdot H_2SO_4$	tyrosine	75	This work
pyruvic acid	Hg	NH_3/NH_4Cl	alanine	58	[27]
α-ketoglutaric acid	Hg	NH_3/NH_4Cl	glutamic acid	63	[27]
pyruvic acid	Pt black	NH_3/NH_4Cl	alanine	64	[28]
α-ketoglutaric acid	Pt black	NH_3/NH_4Cl	glutamic acid	83	[28]
α-ketoglutaric acid	Hg	$NH_3/(NH_4)_2SO_4$	glutamic acid	–[1]	[29]
4-methyl-2-oxovaleric acid	carbon felt	$NH_3/(NH_4)_2SO_4$	leucine	–[1]	[30]
oxalic acid[2]	Pb	$(NH_2OH)_2 \cdot H_2SO_4$	glycine	–[1]	[31]

[1] Not reported, [2] Not α-keto acid

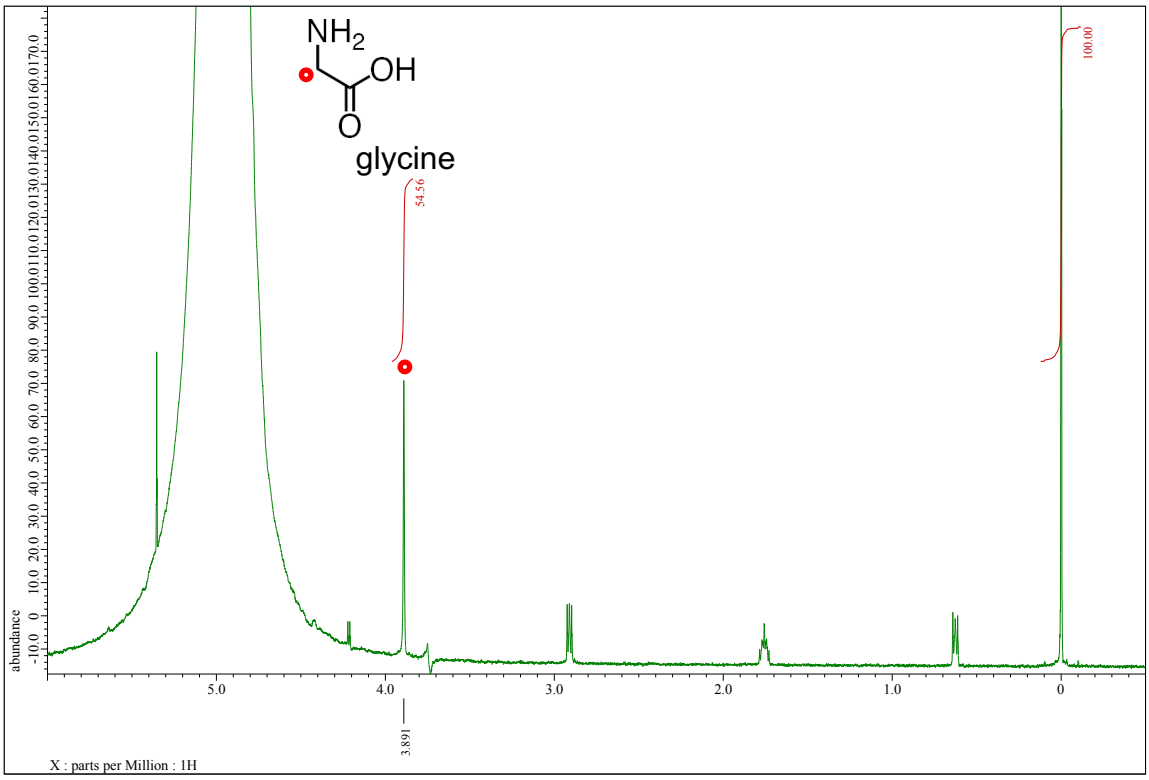
^{1}H NMR spectrum of the reaction solution diluted 5 times with D_2O



Addition of approximately 10 mM commercial alanine

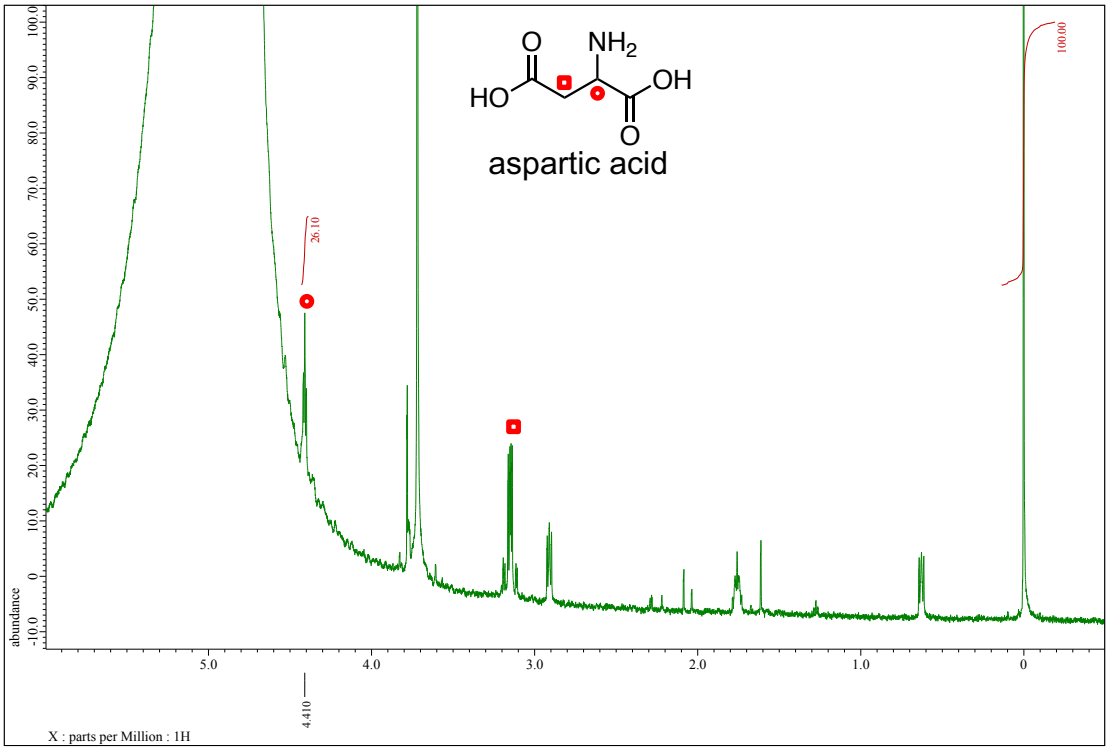


^{1}H NMR spectrum of the reaction solution diluted 5 times with D_2O

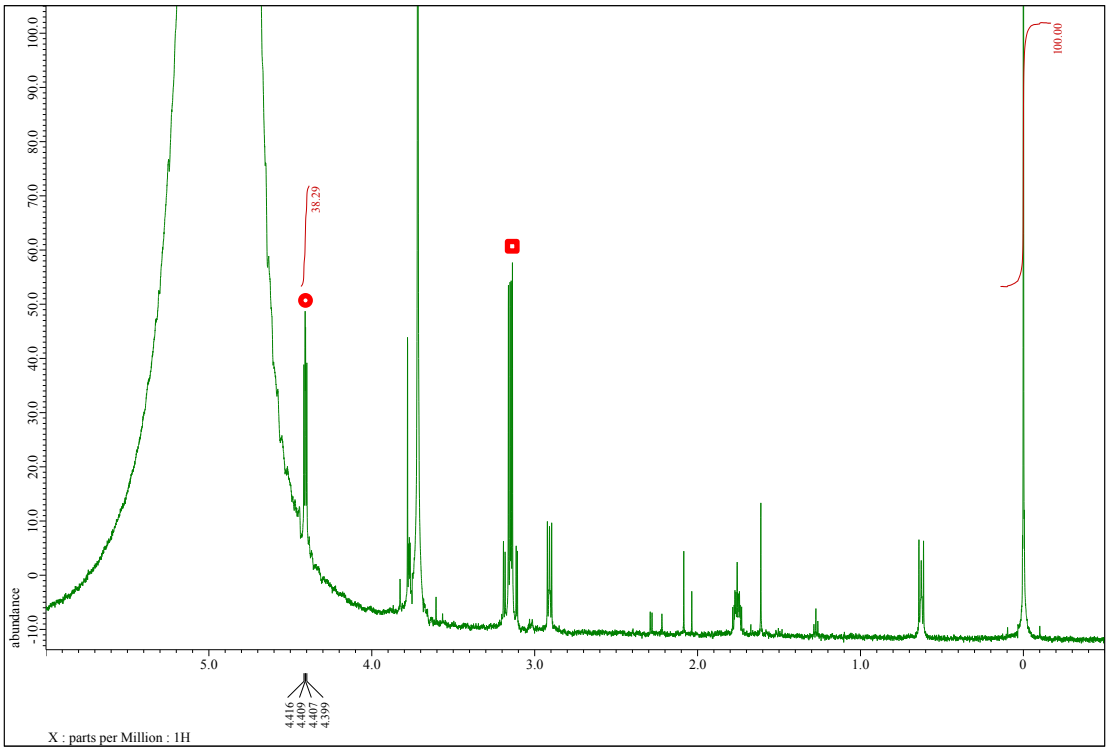


^{1}H NMR spectrum with additional commercial glycine was not measured.

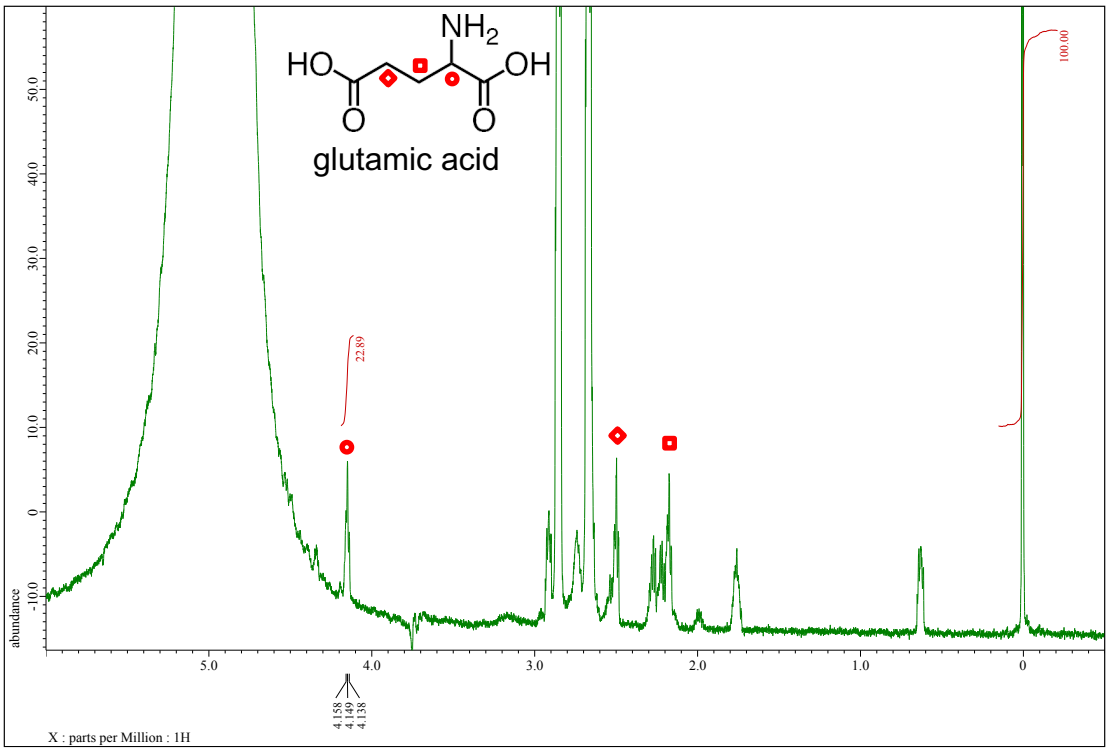
^{1}H NMR spectrum of the reaction solution diluted 5 times with D_2O



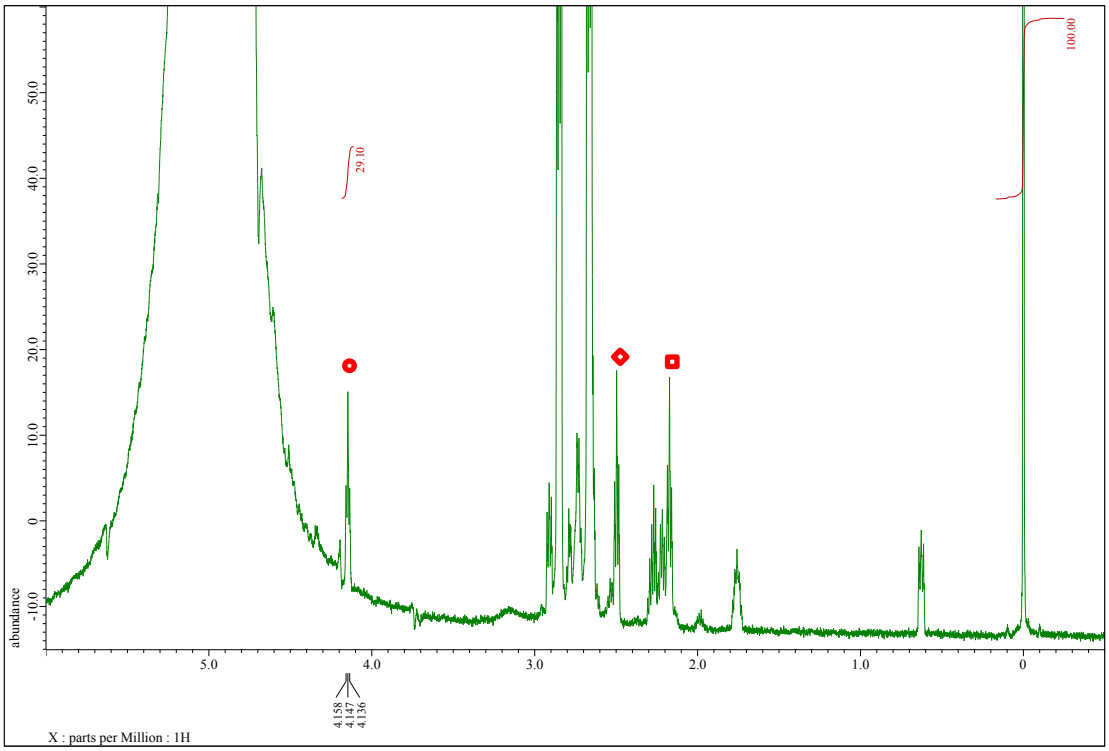
Addition of approximately
10 mM commercial aspartic acid



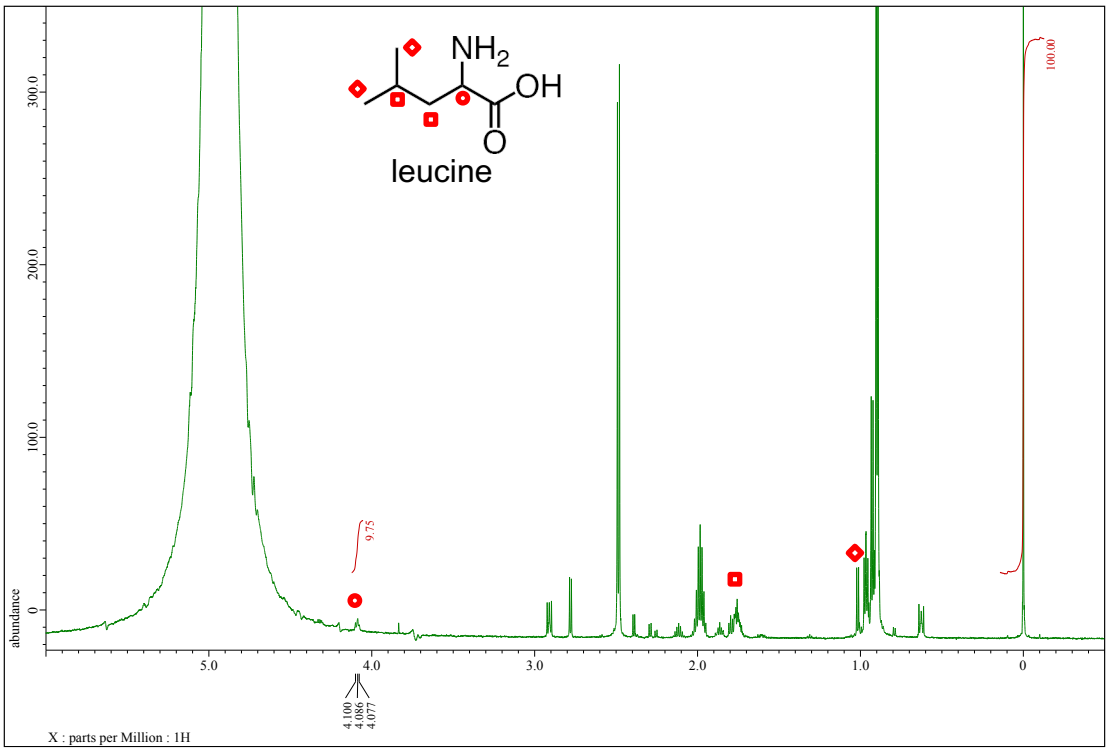
^{1}H NMR spectrum of the reaction solution diluted 5 times with D_2O



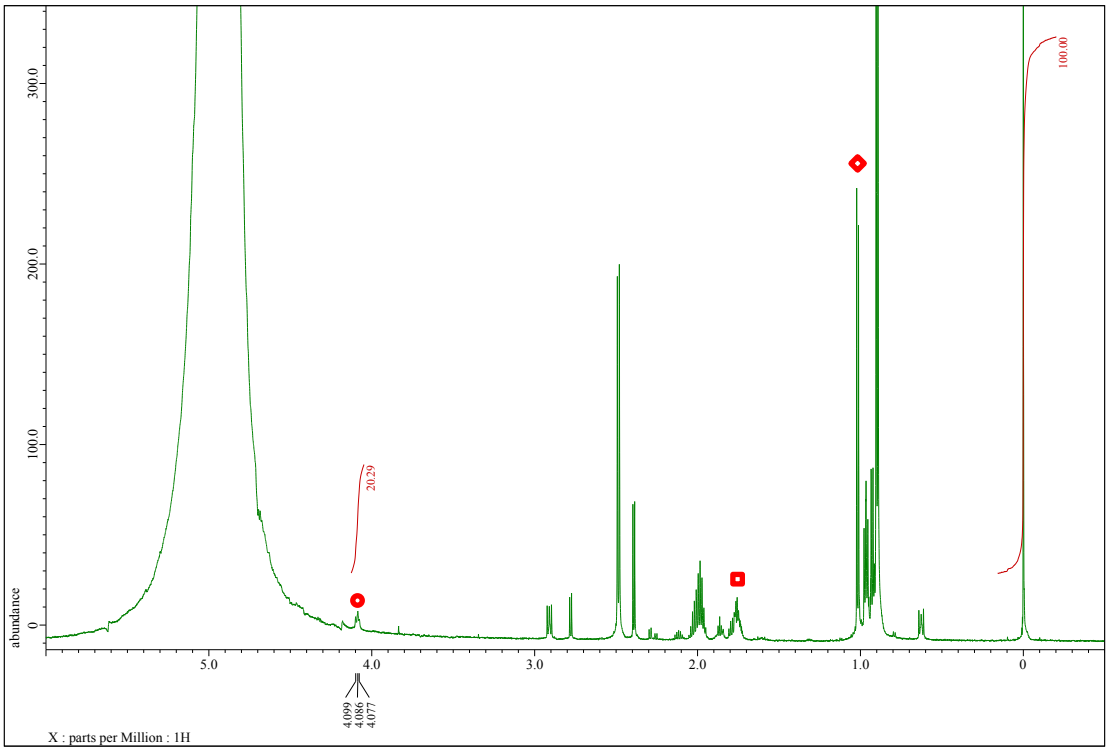
Addition of approximately
10 mM commercial glutamic acid



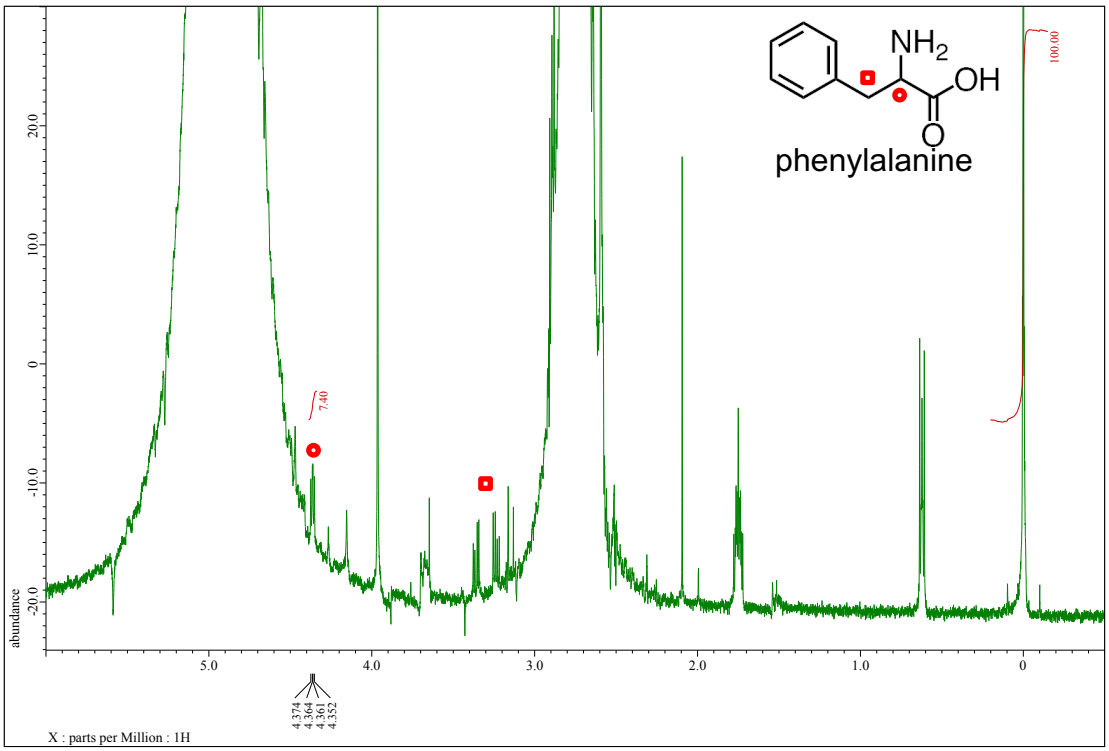
^{1}H NMR spectrum of the reaction solution diluted 5 times with D_2O



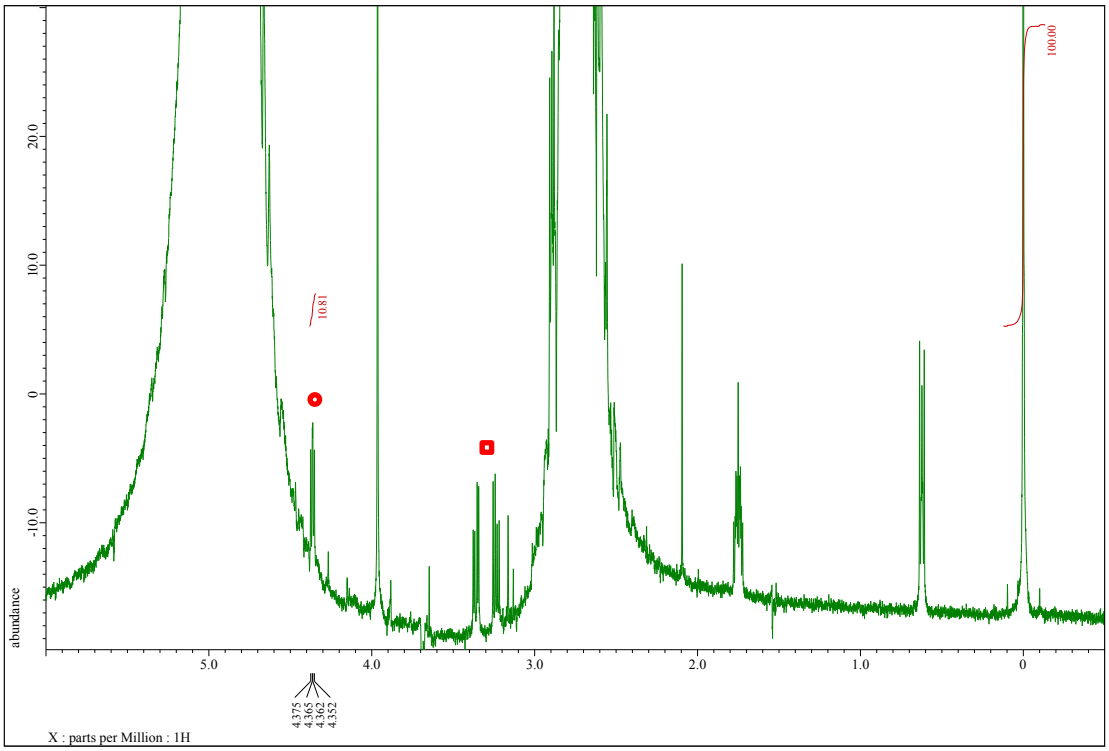
Addition of approximately
10 mM commercial leucine



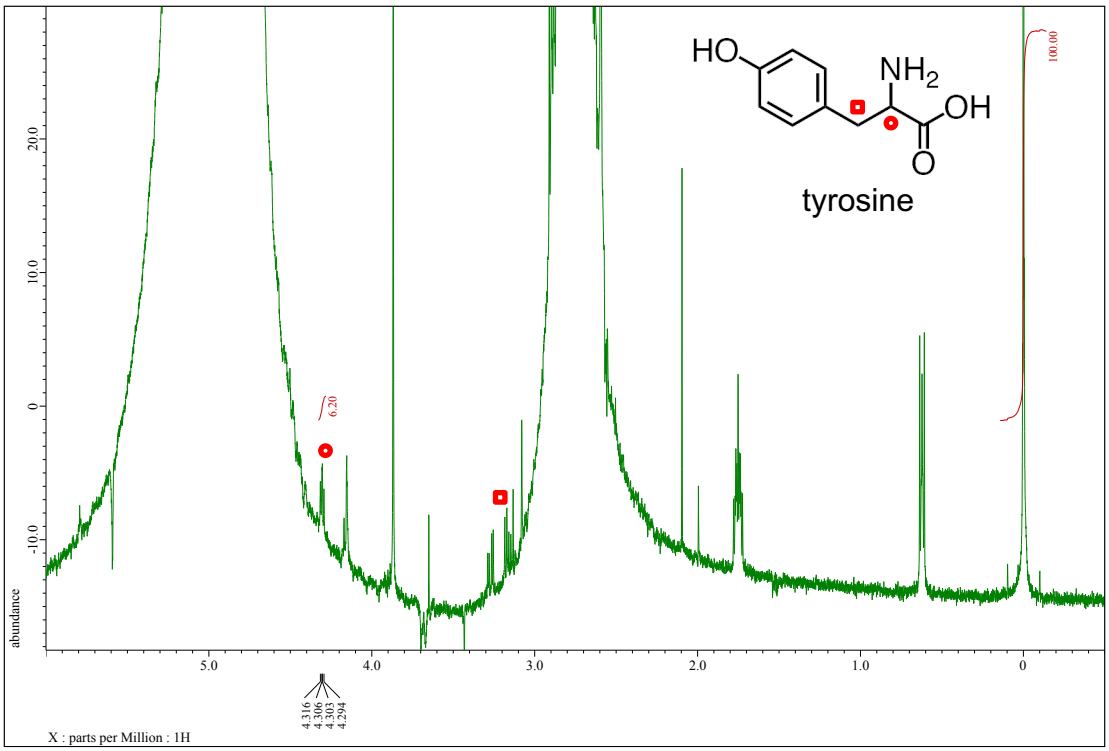
^{1}H NMR spectrum of the reaction solution diluted 5 times with D_2O



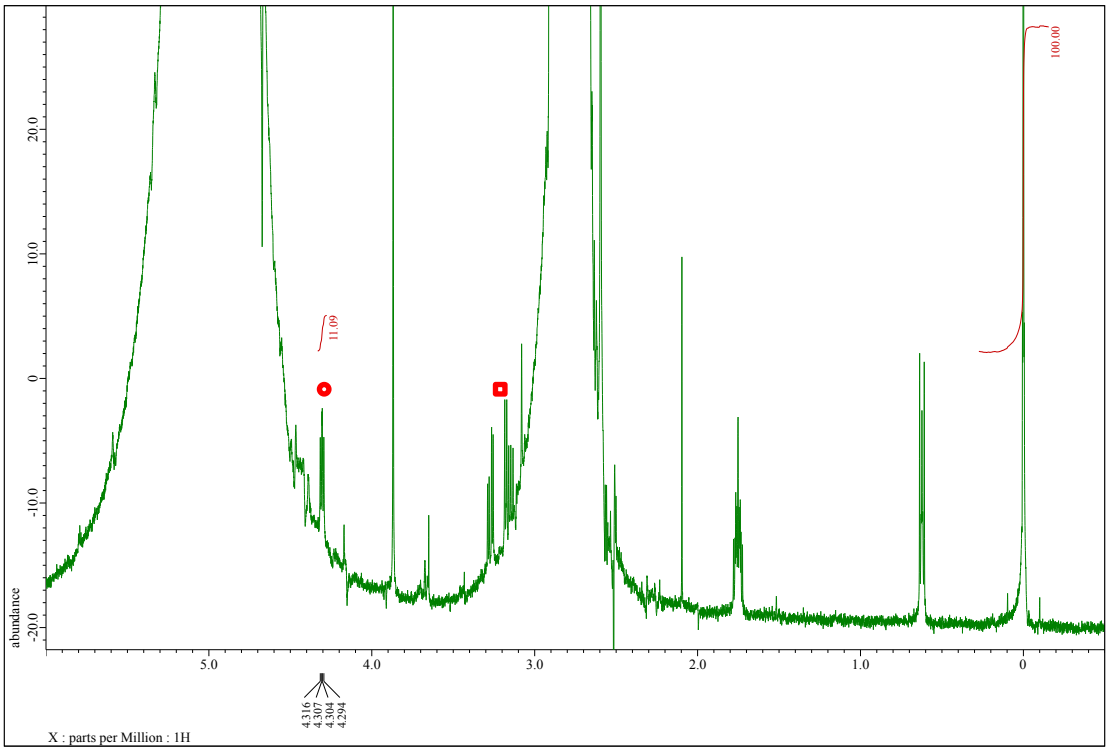
Addition of approximately
5 mM commercial phenylalanine



^{1}H NMR spectrum of the reaction solution diluted 5 times with D_2O



Addition of approximately
5 mM commercial tyrosine



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