Rh-catalyzed hydrogenation of amino acids to bio-based amino alcohols: tackling challenging substrates and application to protein hydrolysates

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Supplementary Information

Total number of pages: 28

Total number of figures: 9

Total number of tables: 6

EXPERIMENTAL DETAILS

Chemicals

All chemicals were purchased and used without further purification. Rhodium chloride trihydrate (Alfa Aesar, 38.5-45.5% Rh), tetraammineplatinum(II) chloride hydrate (Sigma Aldrich, ≥ 99.99%), ammonium molybdate tetrahydrate (Sigma-Aldrich, 81-83% MoO_3 basis), ruthenium(IV) oxide (Acros, 99.5+%), rhenium(VII) oxide (Aldrich, 99.9+%), silica (Evonik, Aerosil 380, powder), zirconia (Alfa Aesar, catalyst support, 1/8" pellets), titania (Alfa Aesar, anatase, catalyst support, 1/8" pellets), zeolite beta (PQ corporation, CP 811 BL-25, H-form) and alumina (CONDEA Chemie GmbH, Puralox NGa-150, acidic) were used for catalyst synthesis. The commercially available 5 wt% ruthenium on carbon and 5 wt% rhodium on carbon catalysts used in this work were obtained from Alfa Aesar. L-Glutamic acid (Acros, 99%), L-glycine (Sigma-Aldrich, ≥ 99%), L-alanine (Janssen, 99%), L-valine (Acros, 99%), L-leucine (Acros, 99%), L-isoleucine (Fluka, ≥ 99%), L-proline (Sigma-Aldrich, ≥ 99%), L-serine (Sigma-Aldrich, ≥ 99%), L-threonine (Sigma-Aldrich, ≥ 98%), L-lysine (SAFC, 97%), L-ornithine monohydrochloride (Sigma-Aldrich, ≥ 99.5%), L-arginine (Merck, > 99%), L-histidine (Acros, 98%), L-aspartic acid (Acros, 98+%), L-glutamine (Janssen, 99%), L-asparagine (Sigma-Aldrich, ≥ 98%), L-phenylalanine (Acros, 98.5+%), L-tyrosine (Acros, 99+%), L-tryptophan (Avocado, 99%), L-cysteine (Sigma-Aldrich, 97%), L-methionine (Sigma-Aldrich, > 99.5%), L-cysteic acid monohydrate (Acros, 99%), L-methionine sulfone (Acros, 98%), dimethyl sulfoxide (VWR Chemicals, > 99.7%), sulfolane (Sigma-Aldrich, 99%), methanesulfonic acid (Sigma-Aldrich, ≥ 99.5%) and phosphoric acid (VWR Chemicals, 85%) were used as reagents in hydrogenation reactions. Hydrogen peroxide (Alfa Aesar, 29-32 wt% aqueous solution, stabilized) and formic acid (Chem-Lab, 99-100% a.r.) were used in the oxidation of sulfur-containing amino acids. A protein hydrolysate was prepared using bovine serum albumin (Sigma-Aldrich, heat shock fraction, pH 7, ≥ 98%) and hydrochloric acid (VWR Chemicals, 37%). Sodium dihydrogen phosphate monohydrate (Merck, > 99%), sodium hydroxide (Acros, micropearls), *o*-phthalaldehyde (TCI, > 99%), 3-mercaptopropionic acid (TCI, > 98%), 9-fluorenylmethyl chloroformate (TCI, > 97%), methanol (Fischer Scientific, HPLC grade) and acetonitrile (Fischer Scientific, HPLC grade) were used for HPLC analysis. Deuterium oxide (Sigma-Aldrich, 99.9 atom% D) was used to prepare samples for analysis by NMR spectroscopy.

Catalyst synthesis

Supported bimetallic M-MoO_x catalysts (where M = Rh or Pt; support = SiO_2, zeolite beta, TiO_2 or ZrO_2) with 1, 4 or 8 wt% M and a Mo/M molar ratio of 1:8 were synthesized by impregnation according to a procedure reported by Tomishige and coworkers.[1] First, an aqueous solution of $RhCl_3.3H_2O$ or

$Pt(NH_3)_4Cl_2.xH_2O$ (25 or 10.6 mM, 20 ml) was added to the commercial support (1 g). This suspension was stirred at ambient temperature to evaporate water and afterwards the pre-catalyst was dried overnight in an oven at 60 °C. In the second step, the pre-catalyst was contacted with an aqueous solution of $(NH_4)_6Mo_7O_{24}.4H_2O$ (0.35 mM, 20 ml) and dried in a similar manner. Finally, the material was granulated (250-500 μm), calcined at 500 °C (2.5 °C min^{-1}, 100 ml min^{-1} O_2, 3 h) and reduced at 500 °C (2.5 °C min^{-1}, 100 ml min^{-1} H_2, 3 h) in a quartz U-tube.

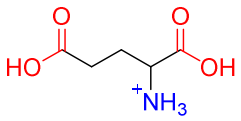
Supported monometallic Rh catalysts (where support = SiO_2, zeolite beta) with 1 wt% Rh were also synthesized by impregnation. To that end, an aqueous solution of $RhCl_3.3H_2O$ (6.2 mM, 20 ml) was added to the commercial support (1 g). This suspension was stirred at ambient temperature to evaporate water and afterwards the catalyst was dried overnight in an oven at 60 °C. Finally, the material was granulated (250-500 μm), calcined at 500 °C (2.5 °C min^{-1}, 100 ml min^{-1} O_2, 3 h) and reduced at 500 °C (2.5 °C min^{-1}, 100 ml min^{-1} H_2, 3 h) in a quartz U-tube.

Supported monometallic Pt catalysts (where support = SiO_2, Al_2O_3) with 5 wt% Pt were synthesized by incipient wetness. An aqueous solution of $Pt(NH_3)_4Cl_2.xH_2O$ (90 mM, 5.7 ml for SiO_2; 0.6 M, 0.85 ml for Al_2O_3) was added to the commercial support (1.9 g). The catalyst was dried overnight in an oven at 60 °C. Finally, the material was granulated (250-500 μm), calcined at 400 °C (2 °C min^{-1}, 100 ml min^{-1} O_2, 30 min) and reduced 400 °C (2 °C min^{-1}, 100 ml min^{-1} H_2, 1 h) in a quartz U-tube.

Product identification

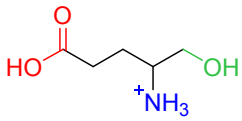
The following abbreviations were used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, quin = quintet, sext = sextet, oct = octet, br = broad, dd = doublet of doublets. Chemical shifts and coupling constants (*J*) were expressed in ppm and in Hz respectively.

Glutamic acid (1a)



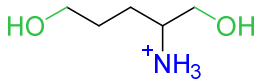
^{1}H NMR (400 MHz, D_2O): δ 3.95 (t, ^3J(H,H) = 6.60 Hz, 1H; -CH_2-C**H**(NH_2)-COOH), 2.51 (t, ^3J(H,H) = 7.19 Hz, 2H; HOOC-C**H$_2$**-CH_2-), 2.10 (m, 2H; -CH_2-C**H$_2$**-CH(NH_2)-) ppm.

4-Amino-5-hydroxypentanoic acid (1b)



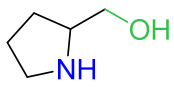
^{1}H NMR (400 MHz, D_2O): δ 3.74 (dd, ^3J(H,H) = 12.40, 3.70 Hz, 1H; -CH(NH_2)-**H**CH-OH), 3.57 (dd, ^3J(H,H) = 12.36, 6.35 Hz, 1H; -CH(NH_2)-HC**H**-OH), 3.31 (br, 1H; -CH_2-C**H**(NH_2)-CH_2OH), 2.47 (t, ^3J(H,H) = 7.59 Hz, 2H; HOOC-C**H$_2$**-CH_2), 1.86 (q, ^3J(H,H) = 7.49 Hz, 2H; -CH_2-C**H$_2$**-CH(NH_2)-) ppm.

Glutamidiol (1d)



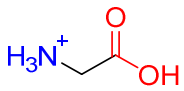
^{1}H NMR (400 MHz, D_2O): δ 3.74 (dd, ^3J(H,H) = 12.40, 3.70 Hz, 1H; -CH(NH_2)-**H**CH-OH), 3.57 (dd, ^3J(H,H) = 12.36, 6.35 Hz, 1H; -CH(NH_2)-HC**H**-OH), 3.57 (t, 2H, ^3J(H,H) could not be determined due to overlap with the -CH(NH_2)-HC**H**-OH signal of 4-amino-5-hydroxypentanoic acid; HO-C**H$_2$**-CH_2-), 3.31 (br, 1H; -CH_2-C**H**(NH_2)-CH_2OH), 1.58 (m, 4H; -CH_2-C**H$_2$**-C**H$_2$**-CH(NH_2)-) ppm.

Prolinol (2c)



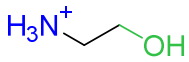
^{1}H NMR (400 MHz, D_2O): δ 3.75 (dd, ^3J(H,H) = 11.79, 3.40 Hz, 1H; -CH(NH-)-**H**CH-OH), 3.63 (br, 1H; -CH_2-C**H**(NH-)-CH_2OH), 3.56 (dd, ^3J(H,H) = 11.83, 7.47 Hz, 1H; -CH(NH-)-HC**H**-OH), 3.21 (m, 2H; -NH-C**H$_2$**-CH_2-), 1.97 (m, 3H; -CH_2-HC**H**-C**H$_2$**-CH(NH-)-), 1.62 (m, 1H; -NH-CH_2-**H**CH-CH_2-) ppm.

Glycine (3a)



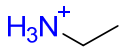
^{1}H NMR (400 MHz, D_2O): δ 3.73 (s, 2H; HOOC-C**H$_2$**-NH_2) ppm.

Ethanolamine (3b)



^{1}H NMR (400 MHz, D_2O): δ 3.70 (t, ^{3}J(H,H) = 5.40 Hz, 2H; HO-C**H$_2$**-CH_2-NH_2), 3.03 (br, 2H; HO-CH_2-C**H$_2$**-NH_2) ppm.

Ethylamine (3c)

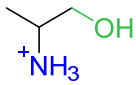


^{1}H NMR (400 MHz, D_2O): δ 2.92 (m, 2H; CH_3-C**H$_2$**-NH_2), 1.15 (t, ^{3}J(H,H) = 7.30 Hz, 3H; C**H$_3$**-CH_2-NH_2) ppm.

Alanine (4a)

^{1}H NMR (400 MHz, D_2O): δ 3.94 (q, ^{3}J(H,H) = 7.32 Hz, 1H; CH_3-C**H**(NH_2)-COOH), 1.42 (d, ^{3}J(H,H) = 7.08 Hz, 3H; C**H$_3$**-CH(NH_2)-) ppm.

Alaninol (4b)

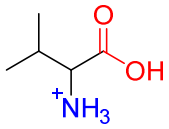


^{1}H NMR (400 MHz, D_2O): δ 3.65 (dd, ^{3}J(H,H) = 12.18, 3.94 Hz, 1H; -CH(NH_2)-**H**CH-OH), 3.44 (dd, ^{3}J(H,H) = 12.25, 7.36 Hz, 1H; -CH(NH_2)-HC**H**-OH), 3.33 (br, 1H; CH_3-C**H**(NH_2)-CH_2OH), 1.14 (d, ^{3}J(H,H) = 6.69 Hz, 3H; C**H$_3$**-CH(NH_2)-) ppm.

Isopropylamine (4c)

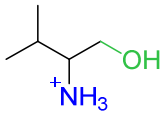
^{1}H NMR (400 MHz, D_2O): δ 3.33 (br, 1H; CH_3-C**H**(NH_2)-CH_3), 1.17 (d, ^{3}J(H,H) = 6.64 Hz, 6H; C**H$_3$**-CH(NH_2)-C**H$_3$**) ppm.

Valine (5a)



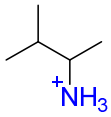
^{1}H NMR (400 MHz, D_2O): δ 3.79 (d, ^3J(H,H) = 4.32 Hz, 1H; -CH_2-C**H**(NH_2)-COOH), 2.23 (m, 1H; (CH_3)$_2$-C**H**-CH(NH_2)-), 0.94 (d, ^3J(H,H) = 7.06 Hz, 3H; C**H$_3$**-CH<), 0.91 (d, ^3J(H,H) = 7.00 Hz, 3H; C**H$_3$**-CH<) ppm.

Valinol (5b)



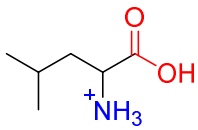
^{1}H NMR (400 MHz, D_2O): δ 3.76 (dd, ^3J(H,H) = 12.37, 3.54 Hz, 1H; -CH(NH_2)-**H**CH-OH), 3.56 (dd, ^3J(H,H) = 12.36, 7.84 Hz, 1H; -CH(NH_2)-HC**H**-OH), 2.99 (br, 1H; >CH-C**H**(NH_2)-CH_2OH), 1.85 (oct, ^3J(H,H) = 6.96 Hz, 1H; (CH_3)$_2$-C**H**-CH(NH_2)-), 0.90 (d, ^3J(H,H) = 6.73 Hz, 3H; C**H$_3$**-CH<), 0.88 (d, ^3J(H,H) = 6.73 Hz, 3H; C**H$_3$**-CH<) ppm.

3-Methyl-2-butanamine (5c)



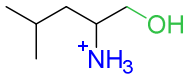
^{1}H NMR (400 MHz, D_2O): δ 3.09 (br, 1H; >CH-C**H**(NH_2)-CH_3), 1.76 (oct, ^3J(H,H) = 6.71 Hz, 1H; (CH_3)$_2$-C**H**-CH(NH_2)-), 1.12 (d, ^3J(H,H) = 6.67 Hz, 3H; -CH(NH_2)-C**H$_3$**), 0.84 (d, ^3J(H,H) = 7.33 Hz, 3H; C**H$_3$**-CH<) ppm. The other C**H$_3$**-CH< signal could not be determined due to overlap with the C**H$_3$**-CH< signal of valinol.

Leucine (6a)



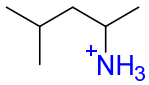
^{1}H NMR (400 MHz, D_2O): δ 3.91 (t, ^3J(H,H) = 6.77 Hz, 1H; -CH_2-C**H**(NH_2)-COOH), 1.67 (m, 3H; (CH_3)$_2$-C**H**-C**H$_2$**-CH(NH_2)-), 0.84 (t, ^3J(H,H) = 5.47 Hz, 6H; (C**H$_3$**)$_2$-CH-) ppm.

Leucinol (6b)



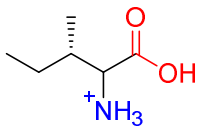
^{1}H NMR (400 MHz, D_2O): δ 3.70 (dd, ^{3}J(H,H) = 12.45, 3.52 Hz, 1H; -CH(NH_2)-**H**CH-OH), 3.48 (dd, ^{3}J(H,H) = 12.39, 7.04 Hz, 1H; -CH(NH_2)-HC**H**-OH), 3.29 (br, 1H; -CH_2-C**H**(NH_2)-CH_2OH), 1.57 (m, 1H; $(CH_3)_2$-C**H**-CH_2-), 1.37 (m, 2H; >CH-C**H$_2$**-CH(NH_2)-), 0.81 (d, ^{3}J(H,H) = 6.65 Hz, 6H; (C**H$_3$**)$_2$-CH-) ppm.

4-Methyl-2-pentanamine (6c)



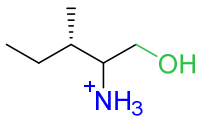
^{1}H NMR (400 MHz, D_2O): δ 3.29 (br, 1H; -CH_2-C**H**(NH_2)-CH_3), 1.57 (m, 1H; $(CH_3)_2$-C**H**-CH_2-), 1.37 (m, 2H; >CH-C**H$_2$**-CH(NH_2)-), 1.16 (d, ^{3}J(H,H) = 6.47 Hz, 3H; C**H$_3$**-CH(NH_2)-), 0.78 (d, ^{3}J(H,H) = 6.64 Hz, 6H; (C**H$_3$**)$_2$-CH-) ppm.

Isoleucine (7a)



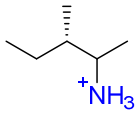
^{1}H NMR (400 MHz, D_2O): δ 3.89 (d, ^{3}J(H,H) = 3.78 Hz, 1H; -CH_2-C**H**(NH_2)-COOH), 1.94 (m, 1H; -CH_2-C**H**(CH_3)-CH(NH_2)-), 1.38 (m, 1H; CH_3-**H**CH-CH<), 1.21 (m, 1H; CH_3-HC**H**-CH<), 0.91 (d, ^{3}J(H,H) = 7.06 Hz, 3H; C**H$_3$**-CH<), 0.82 (t, ^{3}J(H,H) = 7.44 Hz, 3H; C**H$_3$**-CH_2-) ppm.

Isoleucinol (7b)



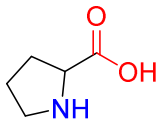
^{1}H NMR (400 MHz, D_2O): δ 3.76 (dd, ^{3}J(H,H) = 12.30, 3.54 Hz, 1H; -CH(NH_2)-**H**CH-OH), 3.56 (dd, ^{3}J(H,H) = 12.52, 8.34 Hz, 1H; -CH(NH_2)-HC**H**-OH), 3.12 (br, 1H; -CH_2-C**H**(NH_2)-CH_2OH), 1.65 (m, 1H; -CH_2-C**H**(CH_3)-CH(NH_2)-), 1.38 (m, 1H; CH_3-**H**CH-CH<), 1.14 (m, 1H; CH_3-HC**H**-CH<), 0.82 (m, 6H; C**H$_3$**-CH_2-CH(C**H$_3$**)-CH(NH_2)-) ppm.

3-Methyl-2-pentanamine (7c)



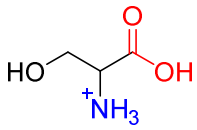
^{1}H NMR (400 MHz, D_2O): δ 3.23 (br, 1H; >CH-C**H**(NH_2)-CH_3), 1.57 (m, 1H; -CH_2-C**H**(CH_3)-CH(NH_2)-), 1.30 (m, 1H; CH_3-**H**CH-CH<), 1.14 (m, 1H; CH_3-HC**H**-CH<), 1.08 (d, ^3J(H,H) = 6.87 Hz, 3H; CH(NH_2)-C**H$_3$**), 0.82 (m, 6H; C**H$_3$**-CH_2-CH(C**H$_3$**)-CH(NH_2)-) ppm.

Proline (8a)



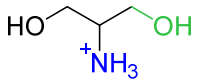
^{1}H NMR (400 MHz, D_2O): δ 4.26 (t, ^3J(H,H) = 7.61 Hz, 1H; -CH_2-C**H**(NH-)-COOH), 3.29 (m, 2H; -NH-C**H$_2$**-CH_2-), 2.30 (m, 1H; -CH_2-**H**CH-CH(NH-)-), 2.04 (m, 1H; -CH_2-HC**H**-CH(NH-)-), 1.93 (quint, ^3J(H,H) = 7.18 Hz, 2H; -NH-CH_2-C**H$_2$**-CH_2-) ppm.

Serine (9a)



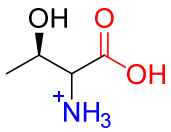
^{1}H NMR (400 MHz, D_2O): δ 4.04 (m, 1H; HOOC-C**H**(NH_2)-CH_2), 3.97 (dd, ^3J(H,H) = 12.33, 3.69 Hz, 1H; HO-**H**CH-), 3.88 (dd, ^3J(H,H) = 12.33, 1.85 Hz, 1H; HO-HC**H**-) ppm.

Serinol (9b)



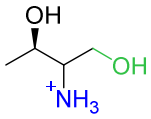
^{1}H NMR (400 MHz, D_2O): δ 3.72 (dd, ^3J(H,H) = 12.32, 4.42 Hz, 2H; HO-**H**CH-CH(NH_2)-**H**CH-OH), 3.61 (dd, ^3J(H,H) = 12.25, 6.69 Hz, 2H; HO-HC**H**-CH(NH_2)-HC**H**-OH), 3.33 (br, 1H; HO-CH_2-C**H**(NH_2)-CH_2OH) ppm.

Threonine (10a)



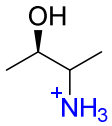
^{1}H NMR (400 MHz, D_2O): δ 4.30 (m, 1H; CH_3-C**H**(OH)-CH(NH_2)-), 3.85 (d, ^3J(H,H) = 3.68 Hz, 1H; -CH(OH)-C**H**(NH_2)-COOH), 1.23 (d, ^3J(H,H) = 6.55 Hz, 3H; C**H$_3$**-CH(OH)-) ppm.

Threoninol (10b)



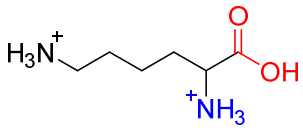
^{1}H NMR (400 MHz, D_2O): δ 3.83 (quint, ^{3}J(H,H) = 6.45 Hz, 1H; CH_3-C**H**(OH)-$CH(NH_2)$-), 3.75 (dd, ^{3}J(H,H) = 12.50, 3.86 Hz, 1H; -$CH(NH_2)$-**H**CH-OH), 3.60 (dd, ^{3}J(H,H) = 12.08, 6.66 Hz, 1H; -$CH(NH_2)$-HC**H**-OH), 3.07 (br, 1H; -CH(OH)-C**H**(NH_2)-CH_2OH), 1.17 (d, ^{3}J(H,H) = 6.65 Hz, 3H; C**H$_3$**-CH(OH)-) ppm.

3-Amino-2-butanol (10c)



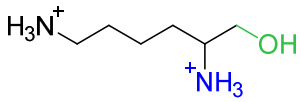
^{1}H NMR (400 MHz, D_2O): δ 3.63 (quint, ^{3}J(H,H) = 7.03 Hz, 1H; CH_3-C**H**(OH)-$CH(NH_2)$-), 3.07 (br, 1H; -CH(OH)-C**H**(NH_2)-CH_3), 1.17 (d, ^{3}J(H,H) = 6.65 Hz, 3H; C**H$_3$**-CH(OH)-), 1.14 (d, ^{3}J(H,H) = 6.55 Hz, 3H; -$CH(NH_2)$-C**H$_3$**) ppm.

Lysine (11a)



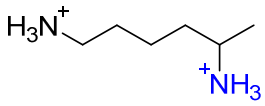
^{1}H NMR (400 MHz, D_2O): δ 3.91 (t, ^{3}J(H,H) = 6.27 Hz, 1H; -CH_2-C**H**(NH_2)-COOH), 2.89 (br, 2H; H_2N-C**H$_2$**-CH_2-) 1.85 (m, 2H; -CH_2-C**H$_2$**-$CH(NH_2)$-), 1.60 (quint, ^{3}J(H,H) = 7.64 Hz, 2H; H_2N-CH_2-C**H$_2$**-CH_2-), 1.39 (m, 2H; H_2N-CH_2-CH_2-C**H$_2$**-CH_2-) ppm.

Lysinol (11b)



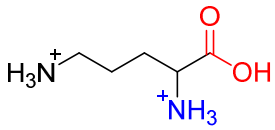
^{1}H NMR (400 MHz, D_2O): δ 3.72 (dd, ^{3}J(H,H) = 12.36, 3.40 Hz, 1H; -$CH(NH_2)$-**H**CH-OH), 3.53 (dd, ^{3}J(H,H) = 12.36, 6.63 Hz, 1H; -$CH(NH_2)$-HC**H**-OH), 3.24 (br, 1H; -CH_2-C**H**(NH_2)-CH_2OH), 2.90 (br, 2H; H_2N-C**H$_2$**-CH_2-), 1.58 (m, 4H; -CH_2-C**H$_2$**-CH_2-C**H$_2$**-$CH(NH_2)$-), 1.36 (m, 2H; H_2N-CH_2-C**H$_2$**-CH_2-) ppm.

1,5-Hexanediamine (11c)



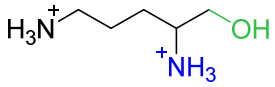
^{1}H NMR (400 MHz, D_2O): δ 3.24 (br, 1H; -CH_2-C**H**(NH_2)-CH_3), 2.90 (br, 2H; H_2N-C**H$_2$**-CH_2-), 1.58 (m, 4H; -CH_2-C**H$_2$**-CH_2-C**H$_2$**-CH(NH_2)-), 1.36 (m, 2H; -CH_2-C**H$_2$**-CH_2-CH(NH_2)-), 1.18 (d, ^3J(H,H) = 6.49 Hz, 3H; -CH(NH_2)-C**H$_3$**) ppm.

Ornithine (12a)



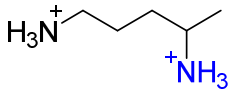
^{1}H NMR (400 MHz, D_2O): δ 3.94 (t, ^3J(H,H) = 6.30 Hz, 1H; HOOC-C**H**(NH_2)-), 2.93 (br, 2H; H_2N-C**H$_2$**-), 1.89 (m, 2H; H_2N-CH_2-C**H$_2$**-), 1.71 (m, 2H; H_2N-CH_2-CH_2-C**H$_2$**-) ppm.

Ornithinol (12b)



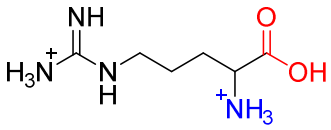
^{1}H NMR (400 MHz, D_2O): δ 3.73 (dd, ^3J(H,H) = 12.40, 3.52 Hz, 1H; -CH(NH_2)-**H**CH-OH), 3.55 (dd, ^3J(H,H) = 12.46, 6.59 Hz, 1H; -CH(NH_2)-HC**H**-OH), 3.27 (br, 1H; -CH_2-C**H**(NH_2)-CH_2OH), 2.93 (br, 2H; H_2N-C**H$_2$**-CH_2-), 1.63 (m, 4H; -CH_2-C**H$_2$**-C**H$_2$**-CH(NH_2)-) ppm.

1,4-Pentanediamine (12c)



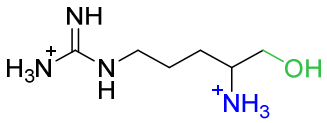
^{1}H NMR (400 MHz, D_2O): δ 3.27 (br, 1H; -CH_2-C**H**(NH_2)-CH_3), 2.93 (br, 2H; H_2N-C**H$_2$**-CH_2-), 1.63 (m, 4H; -CH_2-C**H$_2$**-C**H$_2$**-CH(NH_2)-), 1.20 (d, ^3J(H,H) = 6.66 Hz, 3H; -CH(NH_2)-C**H$_3$**) ppm.

Arginine (13a)



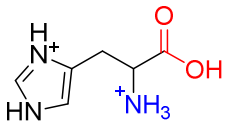
^{1}H NMR (400 MHz, D_2O): δ 3.93 (t, ^3J(H,H) = 6.24 Hz, 1H; -CH_2-C**H**(NH_2)-COOH), 3.13 (t, ^3J(H,H) = 6.45 Hz, 2H; -NH-C**H$_2$**-CH_2-), 1.86 (m, 2H; -CH_2-C**H$_2$**-CH(NH_2)-), 1.60 (m, 2H; -NH-CH_2-C**H$_2$**-CH_2-) ppm.

Argininol (13b)



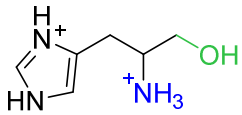
^{1}H NMR (400 MHz, D_2O): δ 3.73 (dd, ^3J(H,H) = 12.45, 3.52 Hz, 1H; -CH(NH_2)-**H**CH-OH), 3.54 (dd, ^3J(H,H) = 12.47, 6.66 Hz, 1H; -CH(NH_2)-HC**H**-OH), 3.25 (br, 1H; -CH_2-C**H**(NH_2)-CH_2OH), 3.13 (m, 2H; -NH-C**H$_2$**-CH_2-), 1.58 (m, 4H; -CH_2-C**H$_2$**-C**H$_2$**-CH(NH_2)-) ppm.

Histidine (14a)



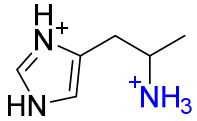
^{1}H NMR (400 MHz, D_2O): δ 8.55 (s, 1H; -NH-C**H**=N-), 7.30 (s, 1H; -NH-C**H**=C(N=)-), 4.14 (t, ^3J(H,H) = 6.46 Hz, 1H; -CH_2-C**H**(NH_2)-COOH), 3.30 (m, 2H; -$C_3H_3N_2$-C**H$_2$**-CH(NH_2)-) ppm.

Histidinol (14b)



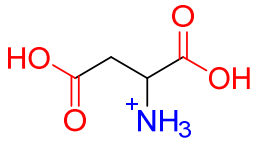
^{1}H NMR (400 MHz, D_2O): δ 8.55 (s, 1H; -NH-C**H**=N-), 7.30 (s, 1H; -NH-C**H**=C(N=)-), 3.73 (m, 1H; -CH_2-C**H**(NH_2)-CH_2OH), 3.57 (m, 2H; -CH(NH_2)-C**H$_2$**-OH), 3.05 (m, 2H; $C_3H_3N_2$-C**H$_2$**-CH(NH_2)-) ppm.

α-Methyl-1*H*-imidazole-5-ethanamine (14c)



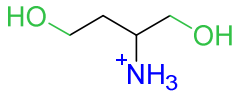
^{1}H NMR (400 MHz, D_2O): δ 8.55 (s, 1H; -NH-C**H**=N-), 7.30 (s, 1H; -NH-C**H**=C(N=)-), 3.73 (m, 1H; -CH_2-C**H**(NH_2)-CH_3), 3.05 (m, 2H; $C_3H_3N_2$-C**H$_2$**-CH(NH_2)-), 1.22 (d, ^3J(H,H) = 6.54 Hz, 3H; -CH(NH_2)-C**H$_3$**) ppm.

Aspartic acid (15a)



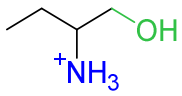
^{1}H NMR (400 MHz, D_2O): δ 4.22 (t, ^{3}J(H,H) = 5.47 Hz, 1H; -CH_2-C**H**(NH_2)-COOH), 3.00 (m, 2H; HOOC-C**H$_2$**-CH(NH_2)-) ppm.

Aspartidiol (15b)



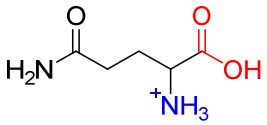
^{1}H NMR (400 MHz, D_2O): δ 3.51-3.76 (m, 4H; HO-C**H$_2$**-CH_2-CH(NH_2)-C**H$_2$**-OH), 3.38 (br, 1H; -CH_2-C**H**(NH_2)-CH_2-), 1.76 (q, ^{3}J(H,H) = 6.40 Hz, 2H; -CH_2-C**H$_2$**-CH(NH_2)-) ppm.

2-Amino-1-butanol (15c)



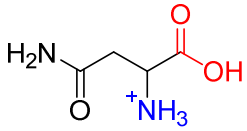
^{1}H NMR (400 MHz, D_2O): δ 3.14 (br, 1H; -CH_2-C**H**(NH_2)-CH_2OH), 1.76 (q, ^{3}J(H,H) = 6.40 Hz, 2H; -CH_2-C**H$_2$**-CH(NH_2)-), 1.55 (m, 2H; CH_3-C**H$_2$**-CH(NH_2)-), 0.87 (t, ^{3}J(H,H) = 7.63 Hz, 3H; C**H$_3$**-CH_2-) ppm.

Glutamine (16a)



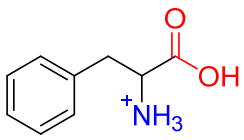
^{1}H NMR (400 MHz, D_2O): δ 3.95 (t, ^{3}J(H,H) = 6.58 Hz, 1H; -CH_2-C**H**(NH_2)-COOH), 2.40 (m, 2H; H_2NOC-C**H$_2$**-CH_2-), 2.09 (m, 2H; -CH_2-C**H$_2$**-CH(NH_2)-) ppm.

Asparagine (17a)



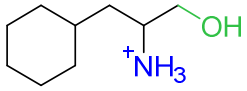
^{1}H NMR (400 MHz, D_2O): δ 4.19 (t, ^{3}J(H,H) = 5.46 Hz, 1H; -CH_2-C**H**(NH_2)-COOH), 2.91 (d, ^{3}J(H,H) = 5.49 Hz, 2H; H_2NOC-C**H$_2$**-CH(NH_2)-) ppm.

Phenylalanine (18a)



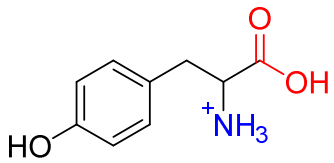
^{1}H NMR (400 MHz, D_2O): δ 7.18-7.35 (m, 5H; $C_6\mathbf{H_5}$-CH_2-), 4.20 (t, ^{3}J(H,H) = 6.80 Hz, 1H; -CH_2-C**H**(NH_2)-COOH), 3.24 (dd, ^{3}J(H,H) = 14.61, 5.59 Hz, 1H; C_6H_5-**H**CH-CH(NH_2)-), 3.10 (dd, ^{3}J(H,H) = 14.61, 7.66 Hz, 1H; C_6H_5-HC**H**-CH(NH_2)-) ppm.

β-Amino-cyclohexanepropanol (18b)



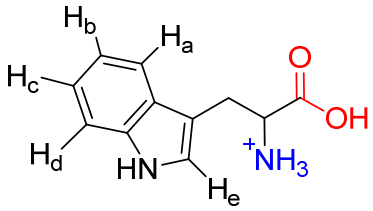
^{1}H NMR (400 MHz, D_2O): δ 3.70 (dd, ^{3}J(H,H) = 12.28, 3.52 Hz, 1H; -CH(NH_2)-**H**CH-OH), 3.48 (dd, ^{3}J(H,H) = 12.28, 7.03 Hz, 1H; -CH(NH_2)-HC**H**-OH), 3.33 (br, 1H; -CH_2-C**H**(NH_2)-CH_2OH), 1.67-0.74 (m, 13H; $C_6\mathbf{H_{11}}$-C$\mathbf{H_2}$-CH(NH_2)-) ppm.

Tyrosine (19a)



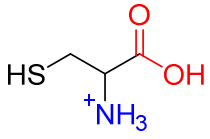
^{1}H NMR (400 MHz, D_2O): δ 7.07 (d, ^{3}J(H,H) = 8.28 Hz, 2H; -C**H**-CH-C(OH)-CH-C**H**-), 6.77 (d, ^{3}J(H,H) = 8.48 Hz, 2H; -CH-C**H**-C(OH)-C**H**-CH-), 4.14 (t, ^{3}J(H,H) = 6.54 Hz, 1H; -CH_2-C**H**(NH_2)-COOH), 3.15 (dd, ^{3}J(H,H) = 14.81, 5.56 Hz, 1H; HO-C_6H_4-**H**CH-CH(NH_2)-), 3.03 (dd, ^{3}J(H,H) = 14.54, 7.59 Hz, 1H; HO-C_6H_4-HC**H**-CH(NH_2)-) ppm.

Tryptophan (20a)



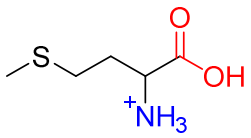
^{1}H NMR (400 MHz, D_2O): δ 7.58 (d, ^{3}J(H,H) = 7.96 Hz, 1H; H_a), 7.42 (d, ^{3}J(H,H) = 8.21 Hz, 1H; H_d), 7.22 (s, 1H; H_e), 7.16 (t, ^{3}J(H,H) = 7.86 Hz, 1H; H_c), 7.07 (t, ^{3}J(H,H) = 7.71 Hz, 1H; H_b), 4.25 (t, ^{3}J(H,H) = 6.20 Hz, 1H; -CH_2-C**H**(NH_2)-COOH), 3.42 (dd, ^{3}J(H,H) = 15.83, 5.28 Hz, 1H; C_8H_6N-**H**CH-CH(NH_2)-), 3.33 (dd, ^{3}J(H,H) = 15.20, 6.93 Hz, 1H; C_8H_6N-HC**H**-CH(NH_2)-) ppm.

Cysteine (21a)



^{1}H NMR (400 MHz, D_2O): δ 4.12 (t, ^{3}J(H,H) = 4.79 Hz, 1H; -CH_2-C**H**(NH_2)-COOH), 3.05 (dd, ^{3}J(H,H) = 15.22, 5.49 Hz, 1H; HS-**H**CH-CH(NH_2)-), 2.97 (dd, ^{3}J(H,H) = 15.17, 4.28 Hz, 1H; HS-HC**H**-CH(NH_2)-) ppm.

Methionine (22a)

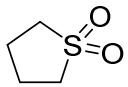


^{1}H NMR (400 MHz, D_2O): δ 4.02 (t, ^{3}J(H,H) = 6.25 Hz, 1H; -CH_2-C**H**(NH_2)-COOH), 2.57 (t, ^{3}J(H,H) = 7.37 Hz, 2H; -S-C**H$_2$**-CH_2-), 2.12 (m, 2H; -CH_2-C**H$_2$**-CH(NH_2)-), 2.01 (s, 3H; C**H$_3$**-S-) ppm.

Dimethyl sulfoxide

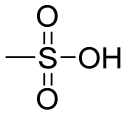
^{1}H NMR (400 MHz, D_2O): δ 2.59 (s, 6H; C**H$_3$**-SO-C**H$_3$**) ppm.

Sulfolane



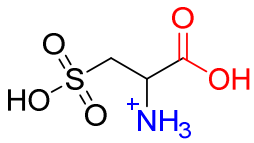
^{1}H NMR (400 MHz, D_2O): δ 3.06 (t, ^{3}J(H,H) = 7.46 Hz, 4H; -C**H$_2$**-SO_2-C**H$_2$**-), 2.13 (m, 4H; -CH_2-C**H$_2$**-C**H$_2$**-CH_2-) ppm.

Methanesulfonic acid



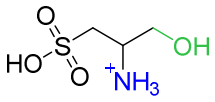
^{1}H NMR (400 MHz, D_2O): δ 2.68 (s, 3H; C**H$_3$**-SO_3H) ppm.

Cysteic acid (24a)



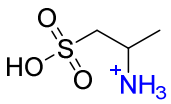
^{1}H NMR (400 MHz, D_2O): δ 4.38 (dd, ^{3}J(H,H) = 8.62, 3.15 Hz, 1H; -CH_2-C**H**(NH_2)-COOH), 3.52 (dd, ^{3}J(H,H) = 15.24, 3.30 Hz, 1H; HO_3S-**H**CH-CH(NH_2)-), 3.38 (dd, ^{3}J(H,H) = 15.33, 8.62 Hz, 1H; HO_3S-HC**H**-CH(NH_2)-) ppm.

2-Amino-3-hydroxy-1-propanesulfonic acid (24b)



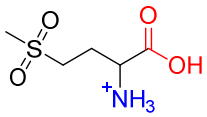
^{1}H NMR (400 MHz, D_2O): δ 3.79 (dd, ^{3}J(H,H) = 16.75, 6.27 Hz, 1H; -CH(NH_2)-**H**CH-OH), 3.65 (dd, 1H, ^{3}J(H,H) could not be determined due to overlap with the -CH_2-C**H**(NH_2)-CH_2OH signal of 2-amino-3-hydroxy-1-propanesulfonic acid and the -CH_2-C**H**(NH_2)-CH_3 signal of 2-amino-1-propanesulfonic acid; -CH(NH_2)-HC**H**-OH), 3.68 (br, 1H; -CH_2-C**H**(NH_2)-CH_2OH), 3.10 (m, 2H; HO_3S-C**H$_2$**-CH(NH_2)-) ppm.

2-Amino-1-propanesulfonic acid (24c)



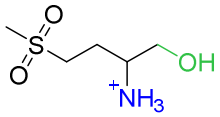
^{1}H NMR (400 MHz, D_2O): δ 3.68 (br, 1H; -CH_2-C**H**(NH_2)-CH_3), 3.10 (m, 2H; HO_3S-C**H$_2$**-CH(NH_2)-), 1.32 (d, ^{3}J(H,H) = 6.85 Hz, 3H; C**H$_3$**-CH(NH_2)-) ppm.

Methionine sulfone (25a)



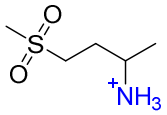
^{1}H NMR (400 MHz, D_2O): δ 3.83 (t, ^{3}J(H,H) = 6.29 Hz, 1H; -CH_2-C**H**(NH_2)-COOH), 3.34 (m, 2H; -SO_2-C**H$_2$**-CH_2-), 3.07 (s, 3H; C**H$_3$**-SO_2-), 2.30 (m, 2H; -CH_2-C**H$_2$**-CH(NH_2)-) ppm.

2-Amino-4-methylsulfonyl-1-butanol (25b)



^{1}H NMR (400 MHz, D_2O): δ 3.74 (dd, ^{3}J(H,H) = 12.45, 3.73 Hz, 1H; -CH(NH_2)-**H**CH-OH), 3.57 (dd, ^{3}J(H,H) = 12.40, 5.86 Hz, 1H; -CH(NH_2)-HC**H**-OH), 3.41 (br, 1H; -CH_2-C**H**(NH_2)-CH_2OH), 3.30 (t, ^{3}J(H,H) = 7.85 Hz, 2H; -SO_2-C**H$_2$**-CH_2-), 3.01 (s, 3H; C**H$_3$**-SO_2-), 2.07 (m, 2H; -CH_2-C**H$_2$**-CH(NH_2)-) ppm.

4-Methylsulfonyl-2-butanamine (25c)



^{1}H NMR (400 MHz, D_2O): δ 3.41 (br, 1H; -CH_2-C**H**(NH_2)-CH_3), 3.30 (t, ^{3}J(H,H) = 7.85 Hz, 2H; -SO_2-C**H$_2$**-CH_2-), 3.01 (s, 3H; C**H$_3$**-SO_2-), 2.07 (m, 2H; -CH_2-C**H$_2$**-CH(NH_2)-), 1.22 (d, ^{3}J(H,H) = 6.64 Hz, 3H; C**H$_3$**-CH(NH_2)-) ppm.

RESULTS AND DISCUSSION

Hydrogenation of glutamic acid: catalyst screening and optimization of reaction parameters

Table S1. Hydrogenation of glutamic acid (**1a**): catalyst screening.[a]

Entry	Catalyst	X_{1a} (%)	$S_{1b\text{-}1c}$ (%)	$S_{1d\text{-}1f}$ (%)	S_{1g} (%)	$S_{2a\text{-}2c}$ (%)
1	-	7	< 1	< 1	< 1	> 99[e]
2[b]	Rh-MoO_x/SiO_2 (4 wt% Rh)	39	70	12	< 1	18
3[b,c]	Pt-MoO_x/SiO_2 (4 wt% Pt)	17	15	< 1	< 1	85[e]
4[b]	Rh-MoO_x/zeolite beta (4 wt% Rh)	36	68	10	< 1	22
5[b]	Rh-MoO_x/TiO_2 (4 wt% Rh)	10	28	< 1	< 1	72
6[b]	Rh-MoO_x/ZrO_2 (4 wt% Rh)	29	65	11	< 1	24
7[b]	Rh-MoO_x/SiO_2 (1 wt% Rh)	29	64	9	< 1	27
8[b]	Rh-MoO_x/SiO_2 (8 wt% Rh)	27	66	8	< 1	26
9	Rh/C (5 wt% Rh)	8	28	< 1	< 1	72
10	Rh/zeolite beta (1 wt% Rh)	10	47	< 1	< 1	53
11[d]	Pt/SiO_2 (5 wt% Pt)	84	< 1	< 1	< 1	> 99[e]
12[d]	Pt/Al_2O_3 (5 wt% Pt)	85	< 1	< 1	< 1	> 99[e]

[a] Conditions: **1a** (0.11 M), catalyst (Rh/**1a** or Pt/**1a** = 1.7 mol%), H_3PO_4 (0.3 M), water (15 ml), H_2 (70 bar), 70 °C, 6 h. Conversion (X) and selectivity (S) were determined by ^{1}H NMR spectroscopy and HPLC. [b] Mo/Rh or Mo/Pt = 1:8. [c] Reaction at 80 °C. [d] Reaction at 140 °C. [e] Selectivity to pyroglutamic acid (**2a**).

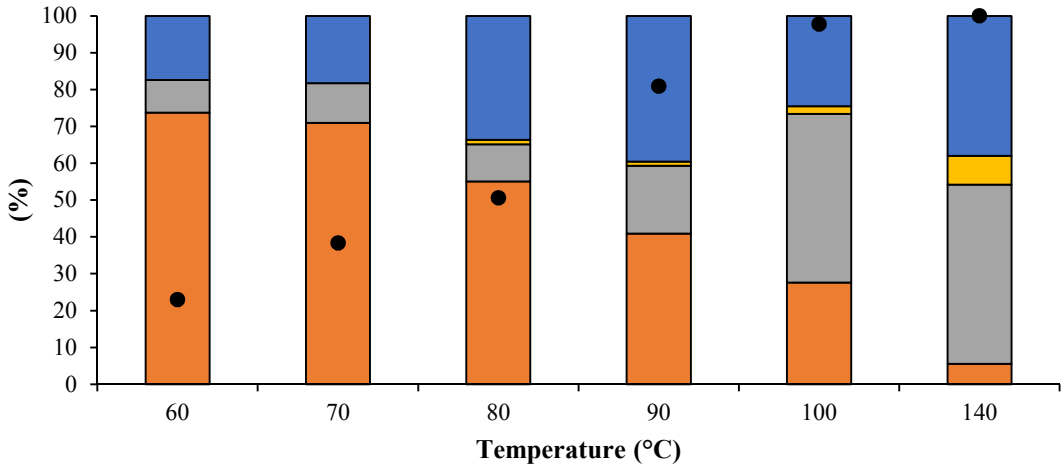


Figure S1. Rh-catalyzed hydrogenation of glutamic acid (**1a**) at various temperatures. Conditions: **1a** (0.11 M), Rh-MoO_x/SiO_2 (4 wt% Rh, Mo/Rh = 1:8, Rh/**1a** = 1.7 mol%), H_3PO_4 (0.3 M), water (15 ml), H_2 (70 bar), 6 h. Legend: conversion of **1a** (●), selectivity to **1b-1c** (orange), selectivity to **1d-1f** (grey), selectivity to **1g** (yellow) and selectivity to **2a-2c** (blue), determined by ^{1}H NMR spectroscopy and HPLC.

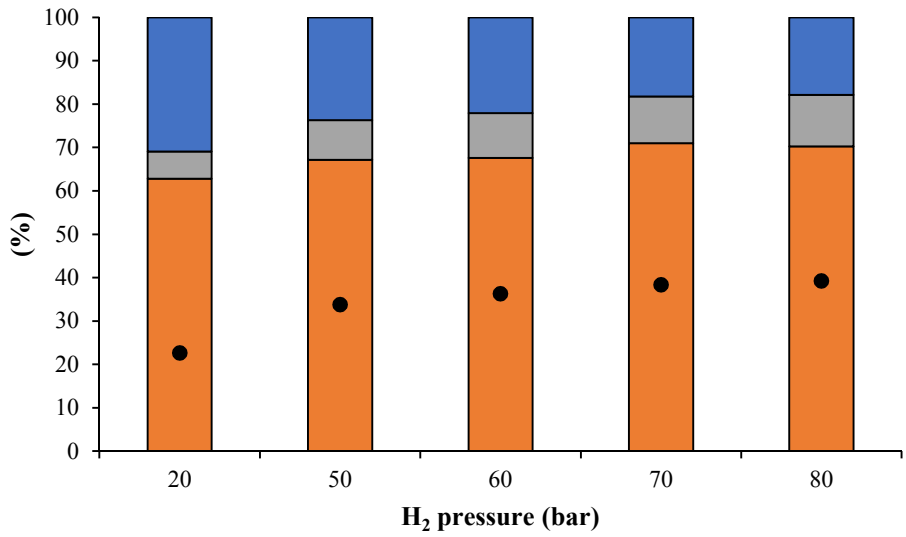


Figure S2. Rh-catalyzed hydrogenation of glutamic acid (**1a**) at various H_2 pressures. Conditions: **1a** (0.11 M), Rh-MoO_x/SiO_2 (4 wt% Rh, Mo/Rh = 1:8, Rh/**1a** = 1.7 mol%), H_3PO_4 (0.3 M), water (15 ml), H_2, 70 °C, 6 h. Legend: conversion of **1a** (●), selectivity to **1b-1c** (orange), selectivity to **1d-1f** (grey) and selectivity to **2a-2c** (blue), determined by ^{1}H NMR spectroscopy and HPLC.

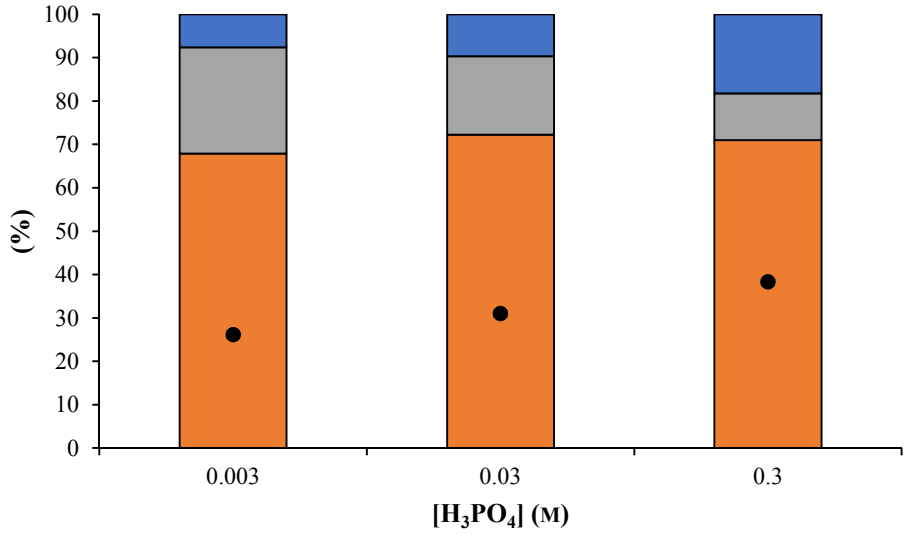


Figure S3. Rh-catalyzed hydrogenation of glutamic acid (**1a**) at various H_3PO_4 concentrations. Conditions: **1a** (0.11 M), Rh-MoO_x/SiO_2 (4 wt% Rh, Mo/Rh = 1:8, Rh/**1a** = 1.7 mol%), H_3PO_4, water (15 ml), H_2 (70 bar), 70 °C, 6 h. Legend: conversion of **1a** (●), selectivity to **1b-1c** (orange), selectivity to **1d-1f** (grey) and selectivity to **2a-2c** (blue), determined by ^{1}H NMR spectroscopy and HPLC.

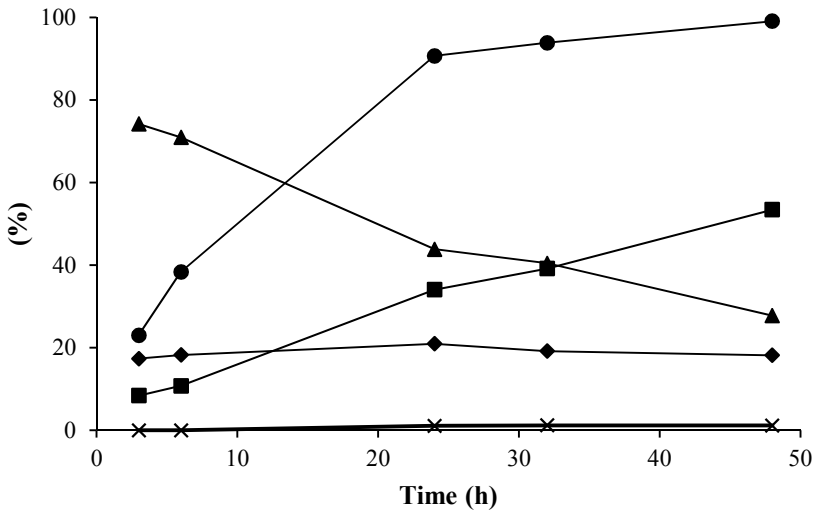


Figure S4. Time course plot for the hydrogenation of glutamic acid (**1a**). Conditions: **1a** (0.11 M), Rh-MoO_x/SiO_2 (4 wt% Rh, Mo/Rh = 1:8, Rh/**1a** = 1.7 mol%), H_3PO_4 (0.3 M), water (15 ml), H_2 (70 bar), 70 °C. Legend: conversion of **1a** (●), selectivity to **1b-1c** (▲), selectivity to **1d-1f** (■), selectivity to **1g** (x) and selectivity to **2a-2c** (◆), determined by ^{1}H NMR spectroscopy and HPLC.

Catalyst recycling

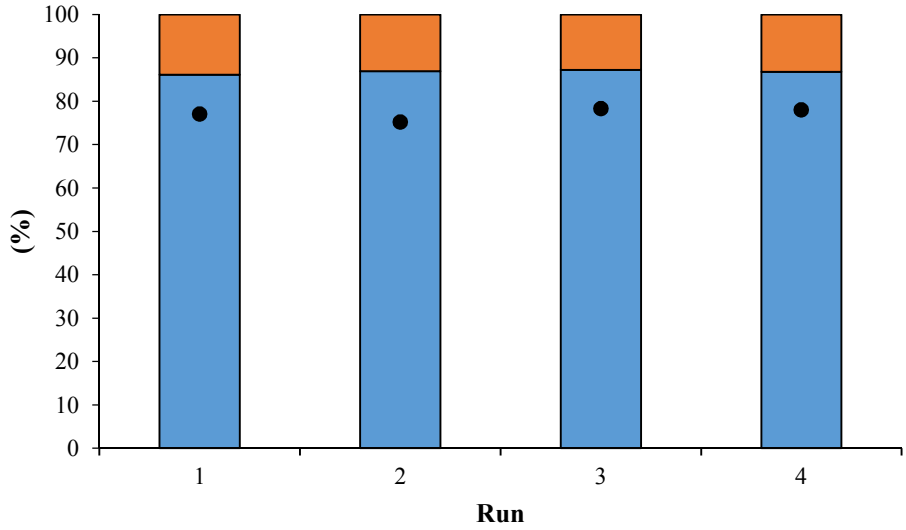


Figure S5. Catalyst recycling in the hydrogenation of isoleucine (**7a**). Conditions: **7a** (0.11 M), Rh-MoO_x/SiO_2 (4 wt% Rh, Mo/Rh = 1:8, Rh/**7a** = 3.5 mol%), H_3PO_4 (0.3 M), water (15 ml), H_2 (70 bar), 80 °C, 6 h. Legend: conversion of **7a** (●), selectivity to **7b** (blue) and selectivity to **7c** (orange), determined by HPLC.

Oxidation of sulfur-containing amino acids

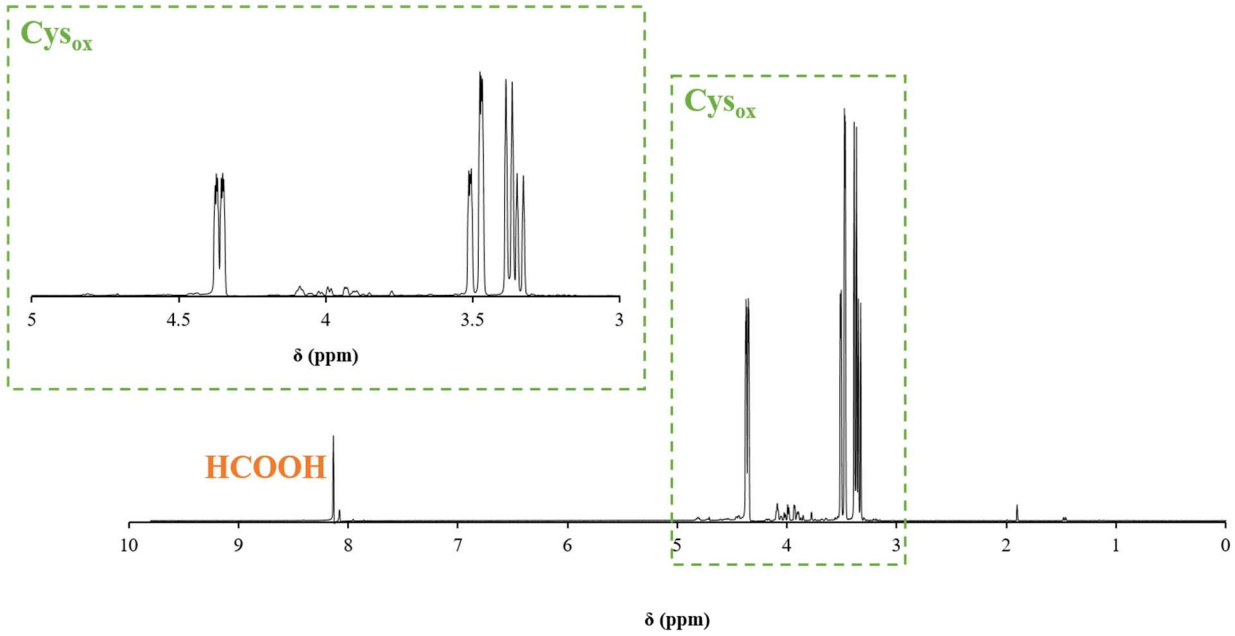


Figure S6. ^{1}H NMR spectrum (400 MHz, D_2O) obtained after oxidation of cysteine with performic acid for 16 h. Other products than cysteic acid and formic acid were not observed.

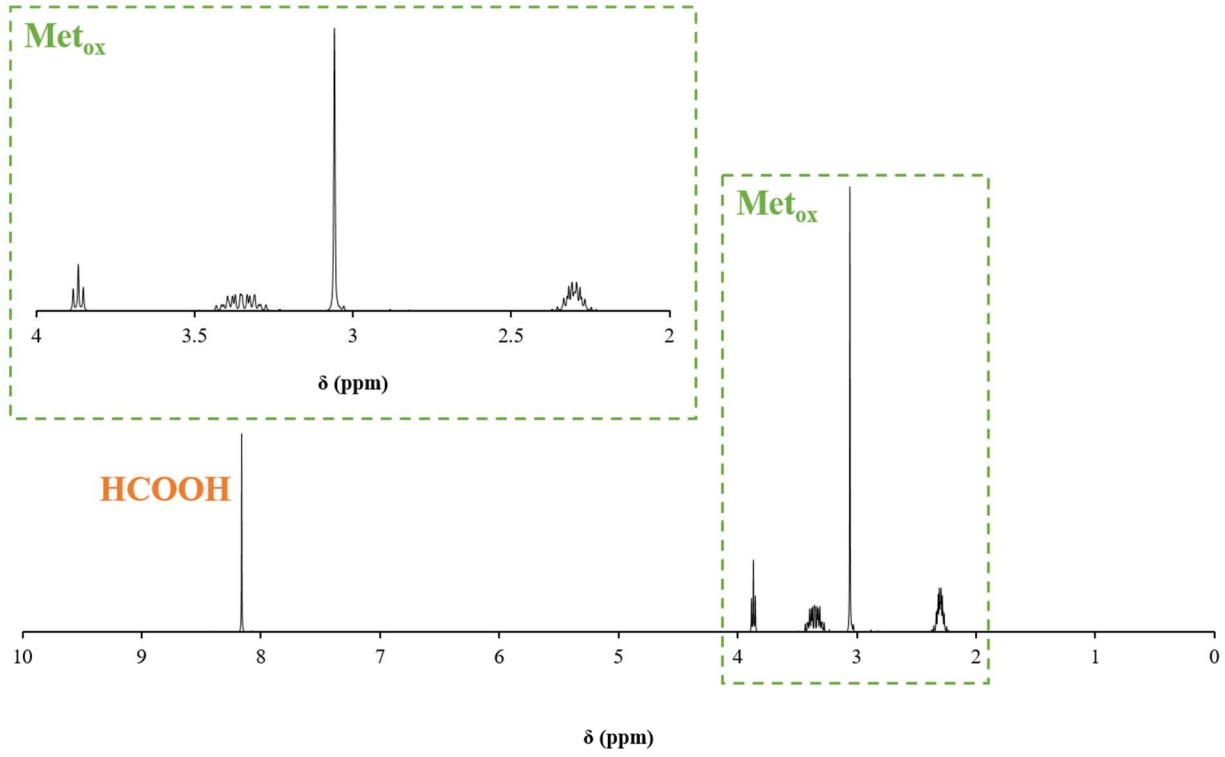


Figure S7. ^{1}H NMR spectrum (400 MHz, D_2O) obtained after oxidation of methionine with performic acid for 16 h. Other products than methionine sulfone and formic acid were not observed.

Protein hydrolysis

Bovine serum albumin (BSA) was hydrolyzed under highly acidic conditions (6 M HCl, 110 °C, 24 h) and the results were generally in line with the expected amino acid composition for this model protein (Table S2).[2–7] However, several side reactions were observed during hydrolysis under these conditions: asparagine and glutamine residues were converted to aspartic acid and glutamic acid, respectively, and tryptophan was degraded completely. Moreover, tyrosine oxidation and the degradation of acid-sensitive amino acids like cysteine, methionine, serine and threonine were more pronounced compared to the literature reference because the hydrolysis was performed for 24 h instead of 16 h.[8] In addition, the reference values for serine and threonine were corrected to account for these losses. On the other hand, the higher levels of valine and isoleucine can also be explained by the prolonged reaction time, which allows to hydrolyze the rather unreactive peptide bonds between these amino acids to a higher extent.[8] Nevertheless, the amino acid composition of this mixture was useful to demonstrate the applicability of our catalytic system in the hydrogenation of amino acid mixtures.

Table S2. Amino acid composition of hydrolyzed bovine serum albumin (BSA).

Amino acid	Mass fraction in BSA (wt%)	
	Experimental[a]	Literature[b]
Ala	6.2	5.0
Arg	5.4	5.3
Asx[c]	10.7	9.4
Cys	5.0[e]	5.5[f]
Glx[d]	11.7	14.5
Gly	2.0	1.4
His	3.8	3.5
Ile	2.64	2.3
Leu	12.0	10.6
Lys	14.3	11.3
Met	0.4[g]	0.7
Phe	6.4	5.8
Pro	6.3	4.0
Ser	2.0	3.5[h]
Thr	3.9	5.0[h]
Trp	-[i]	0.5[j]
Tyr	1.8	4.6
Val	5.8	5.0

[a] Conditions: HCl (6 M), 110 °C, 24 h. [b] Conditions: HCl (6 M), 110 °C, 16 h. [c] Asx = aspartic acid + asparagine. [d] Glx = glutamic acid + glutamine. [e] Determined as cystine + cysteine after oxidation with performic acid. [f] Determined as cystine + cysteine. [g] Determined as methionine sulfone. [h] A correction factor was applied to account for the loss during hydrolysis. [i] Tryptophan was degraded completely under acidic conditions. [j] Determined by hydrolysis under alkaline conditions: NaOH (5 M), 100 °C, 16-30 h.[9,10]

Hydrogenation of protein hydrolysates

The hydrogenation procedure was applied to the BSA hydrolysate. However, the amino acids were not converted at all as a result of catalyst deactivation by the sulfur-containing amino acids (Figure S8). An oxidative pretreatment of the protein with performic acid is therefore recommended.

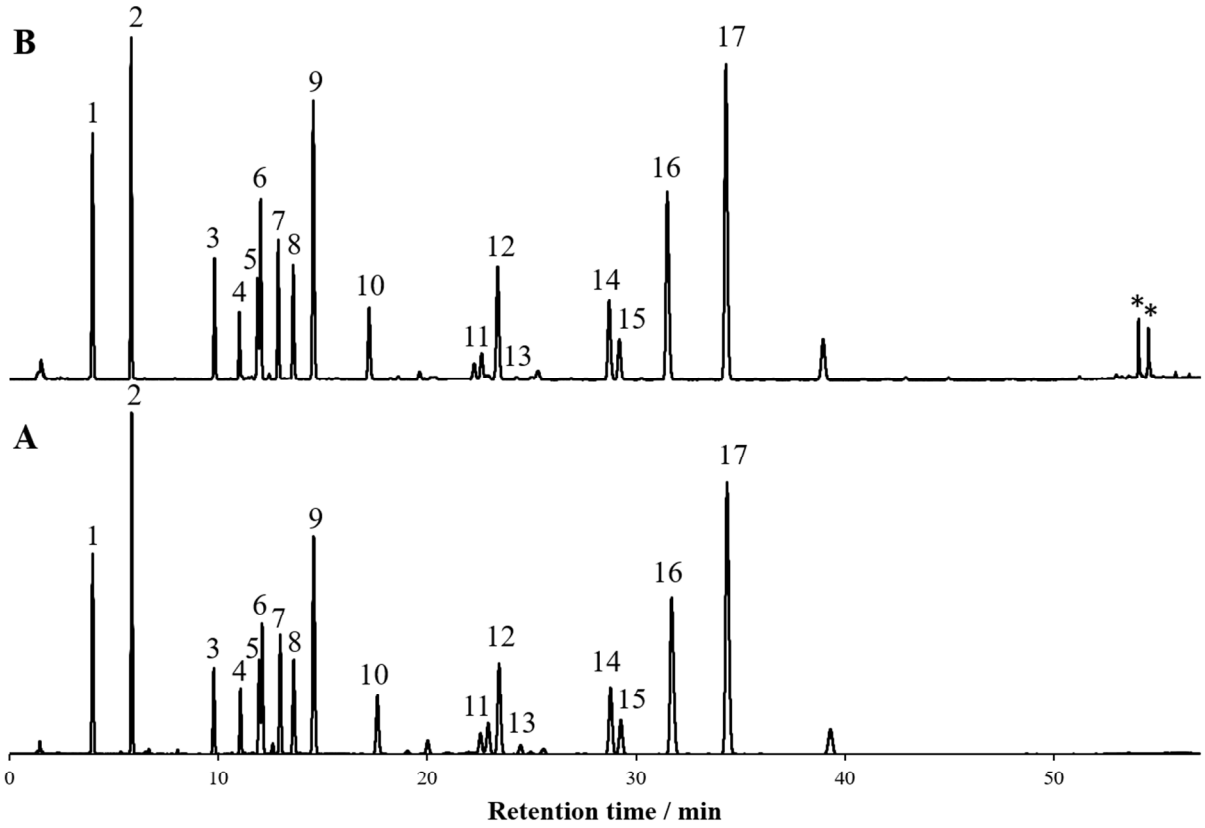


Figure S8. HPLC analysis of amino acids after hydrolysis of BSA (A) and subsequent hydrogenation (B). Conditions A: BSA (0.15 g), 6 M HCl (15 ml), 110 °C, 24 h. Conditions B: amino acids (0.11 M), Rh-MoO_x/SiO_2 (4 wt% Rh, Mo/Rh = 1:8, Rh/amino acids = 3.5 mol%), H_3PO_4 (0.3 M), water (15 ml), H_2 (70 bar), 80 °C, 16 h. [1 = Asx; 2 = Glx; 3 = Ser; 4 = His; 5 = Gly; 6 = Thr; 7 = Arg; 8 = β-alanine, internal standard; 9 = Ala; 10 = Tyr; 11 = Cys + cystine; 12 = Val; 13 = Met; 14 = Phe; 15 = Ile; 16 = Leu; 17 = Lys; * = remaining *o*-phthalaldehyde].

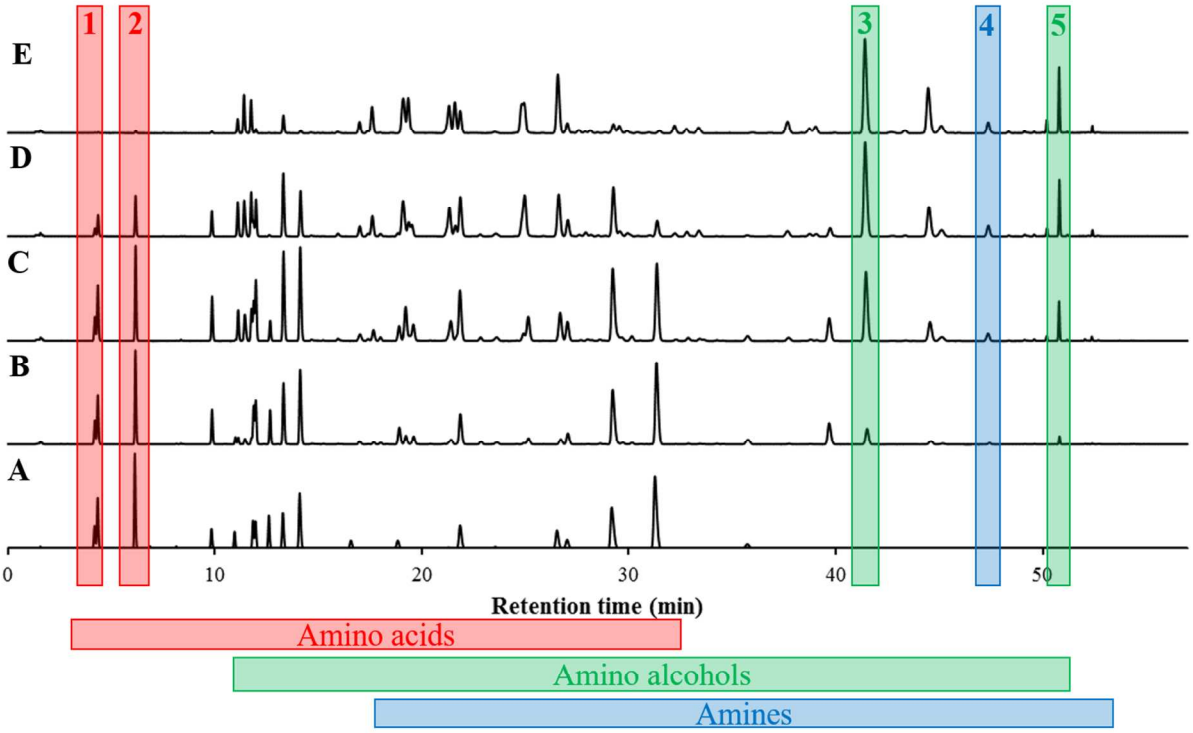


Figure S9. HPLC analysis of amino acids after oxidation and hydrolysis of BSA (**A**), and subsequent hydrogenation for 6 h (**B**), 16 h (**C**), 24 h (**D**) and 48 h (**E**). The elution ranges of amino acids (red), amino alcohols (green) and amines (blue) are highlighted below the chromatograms. Selected compounds: (**1**) cysteic acid and aspartic acid; (**2**) glutamic acid; (**3**) lysinol (from lysine); (**4**) 1,5-hexanediamine (from lysine); (**5**) β-amino-cyclohexanepropanol (from phenylalanine).

Table S3. Identified compounds after oxidation, hydrolysis and hydrogenation of BSA.[a]

Amino acid	Retention time (min)	Product	Retention time (min)
Ala	14.1	Alaninol[f]	27.0
		Isopropylamine	39.1
Arg	12.7	Argininol	21.8
		1-(4-Aminopentyl)guanidine	30.1
Asx[b]	4.4	3-Amino-4-hydroxybutanoic acid	11.1
		Homoserine	11.4
		2-Amino-1,4-butanediol	19.4
		3-Amino-1-butanol	29.7
		2-Amino-1-butanol	33.4
		2-Aminobutane	45.2
Cys_{ox}[c]	4.2	2-Amino-3-hydroxy-1-propanesulfonic acid	11.4
		2-Amino-1-propanesulfonic acid	17.4
Glx[d]	6.2	4-Amino-5-hydroxypentanoic acid	11.8
		5-Hydroxy-norvaline	17.0
		Glutamidiol	21.8
		4-Amino-1-pentanol	31.4
		2-Amino-1-pentanol	39.1
		2-Aminopentane	48.3
		Pyroglutamic acid[h]	2.4
		Pyroglutaminol[h]	2.6
		Prolinol[g,i]	52.1
Gly	11.9	Ethanolamine	21.4
		Ethylamine	32.9
His	11.1	Histidinol	17.0
		α-Methyl-1*H*-imidazole-5-ethanamine	28.1
Ile	29.2	Isoleucinol	43.4
		3-Methyl-2-pentanamine	50.0
Leu	27.0	Leucinol	44.6
		4-Methyl-2-pentanamine	50.2
Lys	31.4	Lysinol	41.5
		1,5-Hexanediamine	47.4

Table S3. Identified compounds after oxidation, hydrolysis and hydrogenation of BSA.[a] (continued)

Amino acid	Retention time (min)	Product	Retention time (min)
Met_{ox}[e]	13.3	2-Amino-4-methylsulfonyl-1-butanol	21.8
		4-Methylsulfonyl-2-butanamine	28.5
Phe	28.7	α-Amino-cyclohexanepropanoic acid	41.5
		β-Amino-cyclohexanepropanol	50.8
		α-Methyl-cyclohexaneethanamine	52.4
Pro[i]	41.7	Prolinol[g,i]	52.1
Ser	9.9	Serinol	17.7
		Alaninol[f]	27.0
Thr	12.0	Threoninol	19.2
		3-Amino-2-butanol	29.2
Tyr	17.6	α-Amino-4-hydroxy-cyclohexanepropanoic acid	22.8
		β-Amino-4-hydroxy-cyclohexanepropanol	29.7
		4-(2-Aminopropyl)-cyclohexanol	33.4
Val	21.8	Valinol	37.7
		3-Methyl-2-butanamine	47.4

[a] Products were detected at 338 nm. [b] Asx = aspartic acid + asparagine. [c] Cys_{ox} = cysteic acid. [d] Glx = glutamic acid + glutamine. [e] Met_{ox} = methionine sulfone. [f] Alaninol can be obtained either by hydrogenation of alanine or by C-O hydrogenolysis of serinol. [g] Prolinol can be obtained either by hydrogenation of proline or by reduction of pyroglutaminol, hence from glutamic acid. [h] Detected at 212 nm. [i] Detected at 262 nm.

Table S4. Rh-catalyzed hydrogenation of amino acids obtained by oxidation and hydrolysis of BSA.[a]

Amino acid	X (%)				$S_{\text{Amino alcohols}}$ (%)				S_{Amines} (%)			
	6 h	16 h	24 h	48 h	6 h	16 h	24 h	48 h	6 h	16 h	24 h	48 h
Ala	11	18	28	90	> 99	96	86	60	< 1	4	14	40
Arg	34	67	96	> 99	80	77	83	82	20	23	17	18
Asx[b]	< 1	22	56	88	> 99	66	63	77	< 1	34	37	23
Cys_{ox}[c]	24	58	85	> 99	94	93	91	92	6	7	9	8
Glx[d]	1	8	23	66	> 99	> 99	93	97	< 1	< 1	7	3
Gly	28	57	86	> 99	> 99	85	84	83	< 1	16	16	17
His	44	36	61	92	> 99	> 99	> 99	77	< 1	< 1	16	23
Ile	< 1	1	4	68	> 99	> 99	> 99	87	< 1	< 1	< 1	13
Leu	46	80	87	> 99	> 99	92	92	90	< 1	8	9	10
Lys	9	37	85	> 99	82	83	83	91	18	17	13	9
Met_{ox}[e]	14	16	88	> 99	> 99	> 99	> 99	76	< 1	< 1	< 1	24
Phe	26	32	41	87	> 99	92	92	91	< 1	8	8	9
Pro	47	85	> 99	> 99	> 99	> 99	> 99	> 99	< 1	< 1	< 1	< 1
Ser	10	28	57	96	> 99	> 99	> 99	> 99	< 1	< 1	< 1	< 1
Thr	33	52	71	95	> 99	> 99	> 99	> 99	< 1	< 1	< 1	< 1
Tyr	44	43	73	> 99	> 99	> 99	> 99	> 99	< 1	< 1	< 1	< 1
Val	4	15	32	67	> 99	90	90	88	< 1	10	11	12
Overall	20	35	63	90	96	90	90	88	4	10	12	12

[a] Conditions: amino acids (0.11 M), Rh-MoO_x/SiO_2 (4 wt% Rh, Mo/Rh = 1:8, Rh/amino acids = 3.5 mol%), H_3PO_4 (0.3 M), water (15 ml), H_2 (70 bar), 80 °C. Conversion (X) and selectivity (S) were determined by HPLC. [b] Asx = aspartic acid + asparagine. [c] Cys_{ox} = cysteic acid. [d] Glx = glutamic acid + glutamine. [e] Met_{ox} = methionine sulfone.

Table S5. Rh-catalyzed hydrogenation of cysteic acid and methionine sulfone obtained either commercially or by oxidation of the corresponding natural amino acid.[a]

Amino acid	Source	X (%)	$Y_{\text{Amino alcohol}}$ (%)	Y_{Amine} (%)
Cysteic acid	Commercial	81	69	12
	Oxidation of cysteine[b]	59	52	7
Methionine sulfone	Commercial	> 99	88	12
	Oxidation of methionine[b]	57	51	6

[a] Conditions: amino acid (0.11 M), Rh-MoO_x/SiO_2 (4 wt% Rh, Mo/Rh = 1:8, Rh/amino acid = 3.5 mol%), H_3PO_4 (0.3 M), water (15 ml), H_2 (70 bar), 80 °C, 6 h. Conversion (X) and yield (Y) were determined by ^{1}H NMR spectroscopy. [b] Oxidation with performic acid performed for 4 h.

Table S6. Rh-catalyzed hydrogenation of two mixtures of amino acids with and without tryptophan.[a]

	Amino acid	X (%)	$Y_{\text{Amino alcohol}}$ (%)	Y_{Amine} (%)
Mixture 1	Glycine	> 99	85	15
	Valine	52	48	4
	Isoleucine	50	38	12
	Leucine	96	93	3
	Cysteic acid (commercial)	94	74	20
Mixture 2	Glycine	83	71	12
	Valine	12	11	1
	Isoleucine	8	8	< 1
	Leucine	43	38	5
	Tryptophan	-	-	-

[a] Conditions: amino acids (0.11 M), Rh-MoO_x/SiO_2 (4 wt% Rh, Mo/Rh = 1:8, Rh/amino acids = 3.5 mol%), H_3PO_4 (0.3 M), water (15 ml), H_2 (70 bar), 80 °C, 6 h. Conversion (X) and yield (Y) were determined by HPLC.

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