Electronic Supporting Information

Crystallization-based downstream processing of ω-transaminase- and amine dehydrogenase-catalyzed reactions

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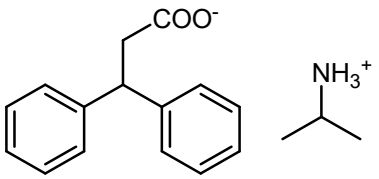
1. General Information

^{1}H and ^{13}C NMRs were recorded on Bruker AVANCE 250 or 300 spectrometers. All salt samples were dissolved in DMSO-d_6 for better solubility and heated prior to measurement (if necessary, temperature is noted if applied). All dry solvents were used as received.

2. NMR spectra for prepared IPA-salts for the solubility screening

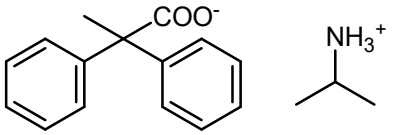
IPA-3DPPA (Isopropylammonium-3,3-diphenylpropionate)



^{1}H NMR: (250.13 MHz; DMSO-d6; 80°C): δ[ppm]: 1.03-1.05 (d, J = 6.37 Hz, 6H, CH_3), 2.85-2.88 (d, J = 7.79 Hz, 2H, CH_2), 2.98-3.13 (m/sept, J = 6.42 Hz, 1H, CH), 4.44-4.50 (t, J = 7.56, 1H, CH^{3DPPA}), 5.10 (s, 3H, NH_3^+), 7.09-7.28 (m, 10H, CH^{Aryl}).

^{13}C NMR: (63 MHz; DMSO-d6; 80 °C): δ[ppm]: 23.86 (2C, CH_3), 41.91 (1C, CH_2^{3DPPA}), 42.21 (1C, CH^{IPA}), 47.27 (1C, CH^{3DPPA}), 125.73 (2C, CH^{Aryl}), 127.59-128.08 (8C, CH^{Aryl}), 145.04 (2C, CH^{Aryl}), 173.11 (1C, COO^-).

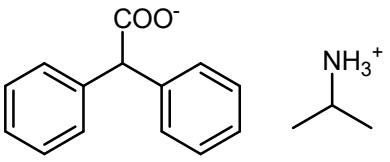
IPA-2DPPA (Isopropylammonium-2,2-diphenylpropionate)



^{1}H NMR: (250.13 MHz; DMSO-d6; 80°C): δ[ppm]: 1.08-1.11 (d, J = 6.53 Hz, 6H, CH_3), 1.77 (s, 3H, CH_3^{2DPPA}), 3.05-3.21 (m/sept, J = 6.52 Hz, 1H, CH), 5.66 (s, 3H, NH_3^+), 7.09-7.29 (m, 10H, CH^{Aryl}).

^{13}C NMR: (63 MHz; DMSO-d6; 80 °C): δ[ppm]: 22.41 (2C, CH_3), 27.79 (1C, CH_3^{2DPPA}), 42.29 (1C, CH^{IPA}), 57.07 (1C, CR_4^{2DPPA}), 125.18 (2C, CH^{Aryl}), 127.12-128.07 (8C, CH^{Aryl}), 147.69 (2C, CH^{Aryl}), 176.21 (1C, COO^-).

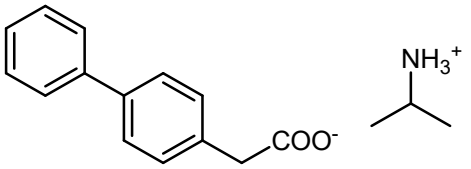
IPA-DPAA (Isopropylammoniumdiphenylacetate)



^{1}H NMR: (250.13 MHz; DMSO-d6): δ[ppm]: 1.07-1.1 (d, J = 6.57 Hz, 6H, CH_3), 3.05-3.21 (m/sept, J = 6.5 Hz, 1H, CH), 4.7 (s, 1H, CH^{DPAA}), 7.08-7.15 (m, J = 1.49, 2.41 , 2H, CH^{Aryl}), 7.18-7.25 (m, J = 1.21, 1.60, 1.89, 2.16 Hz, 4H, CH^{Aryl}), 7.31-7.36 (m, J = 1.54, 1.89, 2.10, 3.10 Hz, 4H, CH^{Aryl}).

^{13}C NMR: (63 MHz; DMSO-d6): δ[ppm]: 20.91 (2C, CH_3), 42.25 (1C, CH^{IPA}), 61.05 (1C, CH^{DPAA}), 125.45 (2C, CH^{Aryl}), 127.62 (4C, CH^{Aryl}), 128.62 (4C, CH^{Aryl}), 143.10 (2C, CH^{Aryl}), 174.51 (1C, COO^-).

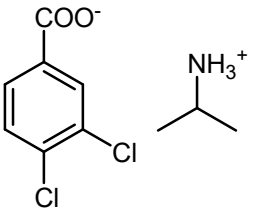
IPA-4BPA (Isopropylammonium-4-biphenylacetate)



^{1}H NMR: (250.13 MHz; DMSO-d6; 50°C): δ[ppm]: 1.14-1.16 (d, J = 6.42 Hz, 6H, CH_3), 3.11-3.26 (m/sept, J = 6.28 Hz, 1H, CH), 3.44 (s, 2H, CH_2), 6.47 (s, 3H, NH_3^+), 7.33-7.68 (m, 10H, CH^{Aryl}).

^{13}C NMR: (63 MHz; DMSO-d6; 50 °C): δ[ppm]: 21.94 (2C, CH_3), 42.29 (1C, CH^{IPA}), 44.05 (1C, CH_2), 126.02-129.70 (9C, CH^{Aryl}), 137.43 (1C, CH^{Aryl}), 137.68 (1C, CH^{Aryl}), 140.34 (1C, CH^{Aryl}), 173.70 (1C, COO^-).

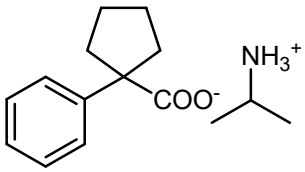
IPA-34CA (Isopropylammonium-3,4-dichlorobenzoate)



^{1}H NMR: (250.13 MHz; DMSO-d6): δ[ppm]: 1.18-1.20 (d, J = 6.37 Hz, 6H, CH_3), 3.21-3.37 (m/sept, J = 6.46 Hz, 1H, CH), 7.52-7.55 (ds, J = 8.21 Hz, 1H, CH^{Aryl}), 7.76-7.80 (dd, J = 1.80, 8.24 Hz, 1H, CH^{Aryl}), 7.96-7.97 (d, J =1.79, CH^{Aryl}).

^{13}C NMR: (63 MHz; DMSO-d6): δ[ppm]: 20.59 (2C, CH_3), 42.50 (1C, CH^{IPA}), 128.93 (1C, CH^{Aryl}), 129.62 (1C, CH^{Aryl}), 130.07 (1C, CH^{Aryl}), 130.69 (1C, CH^{Aryl}), 131.60 (1C, CH^{Aryl}), 140.45 (1C, CH^{Aryl}), 167.09 (1C, COO^-).

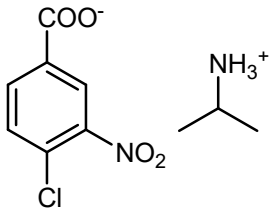
IPA-PCPA (Isopropylammonium-1-phenylcyclopentanecarboxylate)



^{1}H NMR: (250.13 MHz; DMSO-d6; 70°C): δ[ppm]: 1.04-1.06 (d, J = 6.38 Hz, 6H, CH_3), 1.56-1.76 (m, 6H), 2.54-2.61 (m, 2H), 2.99-3.15 (m/sept, J = 6.36 Hz, 1H, CH), 5.45 (s, 3H, NH_3^+), 7.09-7.16 (m, 1H, CH^{Aryl}), 7.20-7.26 (m, 2H, CH^{Aryl}), 7.32-7.37 (m, 2H, CH^{Aryl}).

^{13}C NMR: (63 MHz; DMSO-d6; 70°C): δ[ppm]: 23.16 (2C, CH_2), 23.63 (2C, CH_3), 36.26 (2C, CH_2), 42.17 (1C, CH^{IPA}), 59.54 (1C, CR_4^{PCPA}), 125.28 (1C, CH^{Aryl}), 126.58-127.48 (4C, CH^{Aryl}), 146.17 (1C, CH^{Aryl}), 177.16 (1C, COO^-).

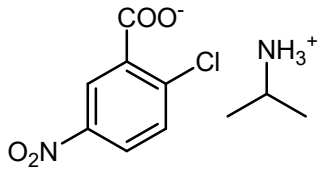
IPA-43CNA (Isopropylammonium-4-chloro-3-nitrobenzoate)



^{1}H NMR: (250.13 MHz; DMSO-d6): δ[ppm]: 1.18-1.20 (d, J = 6.53 Hz, 6H, CH_3), 3.23-3.38 (m/sept, J = 6.47 Hz, 1H, CH), 7.67-7.70 (ds, J = 8.18 Hz, 1H, CH^{Aryl}), 8.07-8.11 (dd, J = 1.90, 8.20 Hz, 1H, CH^{Aryl}), 8.34-8.35 (d, J =1.86, CH^{Aryl}), 8.38 (s, 3H, NH_3^+).

^{13}C NMR: (63 MHz; DMSO-d6): δ[ppm]: 20.51 (2C, CH_3), 42.57 (1C, CH^{IPA}), 125.43 (1C, CH^{Aryl}), 125.50 (1C, CH^{Aryl}), 130.85 (1C, CH^{Aryl}), 133.79 (1C, CH^{Aryl}), 140.43 (1C, CH^{Aryl}), 146.82 (1C, CH^{Aryl}), 166.02 (1C, COO^-).

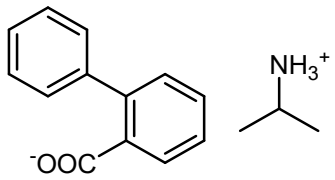
IPA-25CNA (Isopropylammonium-2-chloro-5-nitrobenzoate)



^{1}H NMR: (250.13 MHz; DMSO-d6): δ[ppm]: 1.18-1.20 (d, J = 6.62 Hz, 6H, CH_3), 3.21-3.36 (m/sept, J = 6.54 Hz, 1H, CH), 7.59-7.63 (ds, J = 8.71 Hz, 1H, CH^{Aryl}), 8.02-8.09 (dd, J = 2.87, 8.64 Hz, 1H, CH^{Aryl}), 8.17-8.18 (d, J =2.88, CH^{Aryl}), 8.27 (s, 3H, NH_3^+).

^{13}C NMR: (63 MHz; DMSO-d6): δ[ppm]: 20.42 (2C, CH_3), 42.67 (1C, CH^{IPA}), 122.83 (1C, CH^{Aryl}), 123.34 (1C, CH^{Aryl}), 130.89 (1C, CH^{Aryl}), 136.59 (1C, CH^{Aryl}), 142.49 (1C, CH^{Aryl}), 145.84 (1C, CH^{Aryl}), 166.85 (1C, COO^-).

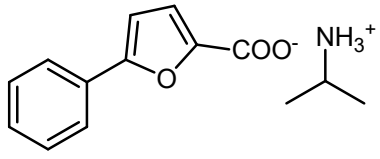
IPA-2BPA (Isopropylammonium-2-biphenylcarboxylate)



^{1}H NMR: (250.13 MHz; DMSO-d6): δ[ppm]: 1.05-1.07 (d, J = 6.60 Hz, 6H, CH_3), 3.00-3.16 (m/sept, J = 6.67 Hz, 1H, CH), 7.19-7.48 (m, 10H, CH^{Aryl}), 8.15 (s, 3H, NH_3^+).

^{13}C NMR: (63 MHz; DMSO-d6): δ[ppm]: 20.70 (2C, CH_3), 42.28 (1C, CH^{IPA}), 126.21-129.15 (9C, CH^{Aryl}), 137.51 (1C, CH^{Aryl}), 142.10 (1C, CH^{Aryl}), 142.55 (1C, CH^{Aryl}), 173.70 (1C, COO^-).

IPA-PFA (Isopropylammonium-5-phenyl-2-furoate)

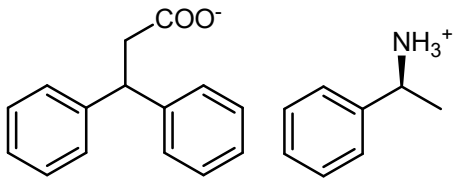


^{1}H NMR: (250.13 MHz; DMSO-d6; 70°C): δ[ppm]: 1.19-1.22 (d, J = 6.49 Hz, 6H, CH_3), 3.22-3.37 (m/sept, J = 6.60 Hz, 1H, CH), 6.75-6.89 (dd, J = 3.34, 33.66 Hz, 2H), 7.24-7.31 (m, 1H, CH^{Aryl}), 7.35-7.48 (m, 2H, CH^{Aryl}), 7.68-7.73 (m, 2H, CH^{Aryl}), 8.15 (s, 3H, NH_3^+).

^{13}C NMR: (63 MHz; DMSO-d6; 70°C): δ[ppm]: 20.64 (2C, CH_3), 42.54 (1C, CH^{IPA}), 106.92 (1C, CH), 113.65 (1C, CH), 123.6 (1C, CH^{Aryl}), 126.99-130.51 (5C, CH^{Aryl}), 152.29 (1C, CR_4), 152.62 (1C, CR_4), 162.38 (1C, COO^-).

3. NMR spectra for prepared (*S*)-1PEA-salts for the solubility screening

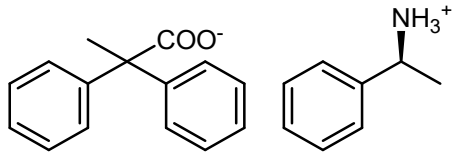
(*S*)-1PEA-3DPPA ((*S*)-1-phenylethylammonium-3,3-diphenylpropionate)



^{1}H NMR: (250.13 MHz; DMSO-d6; 70°C): δ [ppm]: 1.29-1.31 (d, J = 6.62 Hz, 3H, CH_3), 2.93-2.96 (d, J = 7.80 Hz, 2H, CH_2), 4.01-4.09 (q, J = 6.67 Hz, 1H, CH^{1PEA}), 4.43-4.49 (t, J = 7.78, 1H, CH^{3DPPA}), 5.43 (s, 3H, NH_3^+), 7.11-7.40 (m, 15H, CH^{Aryl}).

^{13}C NMR: (63 MHz; DMSO-d6; 70 °C): δ [ppm]: 25.13 (1C, CH_3), 40.84 (1C, $CH_2{}^{3DPPA}$), 46.96 (1C, CH^{3DPPA}), 50.41 (1C, CH^{IPA}), 125.81 (2C, CH^{Aryl}), 125.94 (1C, CH^{Aryl}), 126.37-128.19 (12C, CH^{Aryl}), 144.54 (2C, CH^{Aryl}), 147.23 (1C, CH^{Aryl}), 172.71 (1C, COO^-).

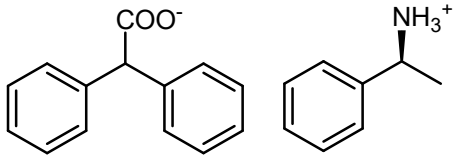
(*S*)-1PEA-2DPPA ((*S*)-1-phenylethylammonium-2,2-diphenylpropionate)



^{1}H NMR: (250.13 MHz; DMSO-d6; 70°C): δ [ppm]: 1.34-1.36 (d, J = 6.84 Hz, 3H, CH_3), 1.80 (s, 3H, $CH_3{}^{2DPPA}$), 4.08-4.15 (q, J = 6.67 Hz, 1H, CH), 6.19 (s, 3H, NH_3^+), 7.14-7.42 (m, 15H, CH^{Aryl}).

^{13}C NMR: (63 MHz; DMSO-d6; 70 °C): δ [ppm]: 24.08 (1C, CH_3), 27.37 (1C, $CH_3{}^{2DPPA}$), 50.24 (1C, CH^{1PEA}), 56.54 (1C, $CR_4{}^{2DPPA}$), 125.68 (2C, CH^{Aryl}), 126.03 (1C, CH^{Aryl}), 126.72-128.10 (12C, CH^{Aryl}), 145.53 (1C, CH^{Aryl}), 146.45 (2C, CH^{Aryl}), 176.02 (1C, COO^-).

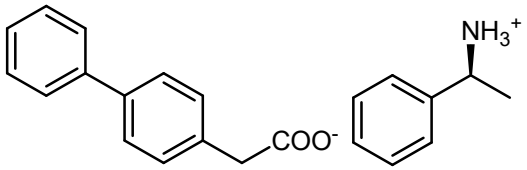
(*S*)-1PEA-DPAA ((*S*)-1-phenylethylammonium-diphenylacetate)



^{1}H NMR: (250.13 MHz; DMSO-d6, 60 °C): δ [ppm]: 1.35-1.37 (d, J = 6.67 Hz, 3H, CH_3), 4.09-4.17 (q, J = 6.88 Hz, 1H, CH^{1PEA}), 4.90 (s, 1H, CH^{DPAA}), 6.49 (s, 3H, NH_3^+), 7.14-7.43 (m, 15H, CH^{Aryl}).

^{13}C NMR: (63 MHz; DMSO-d6, 60 °C): δ [ppm]: 23.71 (1C, CH_3), 50.19 (1C, CH^{1PEA}), 58.81 (1C, CH^{DPAA}), 125.45 (2C, CH^{Aryl}), 126.11 (1C, CH^{Aryl}), 126.90-128.58 (12C, CH^{Aryl}), 141.48 (2C, CH^{Aryl}), 144.84 (1C, CH^{Aryl}), 173.75 (1C, COO^-).

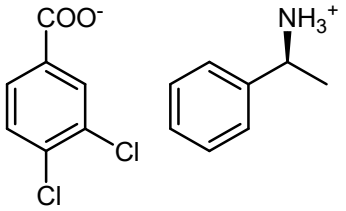
(*S*)-1PEA-4BPA ((*S*)-1-phenylethylammonium-4-biphenylacetic)



^{1}H NMR: (250.13 MHz; DMSO-d6): δ [ppm]: 1.35-1.37 (d, J = 6.67 Hz, 3H, CH_3), 3.44 (s, 2H, CH_2), 4.11-4.19 (q, J = 6.82 Hz, 1H, CH), 7.17 (s, 3H, NH_3^+), 7.22-7.65 (m, 15H, CH^{Aryl}).

^{13}C NMR: (63 MHz; DMSO-d6): δ [ppm]: 23.28 (1C, CH_3), 43.21 (1C, CH_2), 50.03 (1C, CH^{1PEA}), 126.15-129.81 (14C, CH^{Aryl}), 136.93 (1C, CH^{Aryl}), 137.60 (1C, CH^{Aryl}), 140.19 (1C, CH^{Aryl}), 143.94 (1C, CH^{Aryl}), 173.66 (1C, COO^-).

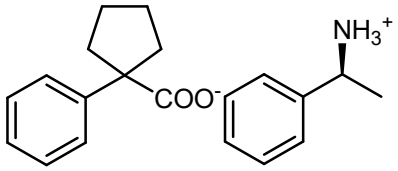
(*S*)-1PEA-34CA ((*S*)-1-phenylethylammonium-3,4-dichlorobenzoate)



^{1}H NMR: (250.13 MHz; DMSO-d6): δ [ppm]: 1.49-1.52 (d, J = 6.79 Hz, 3H, CH_3), 4.33-4.41 (q, J = 6.82 Hz, 1H, CH), 7.27-7.57 (m, 6H, CH^{Aryl}), 7.77-7.81 (dd, J = 1.83, 8.25 Hz, 1H, CH^{Aryl}), 7.97-7.98 (d, J =1.83, CH^{Aryl}).

^{13}C NMR: (63 MHz; DMSO-d6): δ [ppm]: 21.36 (1C, CH_3), 49.79 (1C, CH^{1PEA}), 126.63-128.49 (5C, CH^{Aryl}), 128.97 (1C, CH^{Aryl}), 129.72 (1C, CH^{Aryl}), 130.15 (1C, CH^{Aryl}), 130.72 (1C, CH^{Aryl}), 131.84 (1C, CH^{Aryl}), 139.93 (1C, CH^{Aryl}), 140.65 (1C, CH^{Aryl}), 167.07 (1C, COO^-).

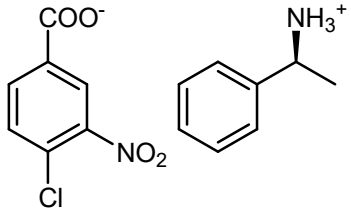
(*S*)-1PEA-PCPA ((*S*)-1-phenylethylammonium-1-phenylcyclopentanecarboxylate)



^{1}H NMR: (250.13 MHz; DMSO-d6; 60°C): δ [ppm]: 1.29-1.32 (d, J = 7.01 Hz, 3H, CH_3), 1.62-1.83 (m, 6H), 2.52-2.61 (m, 2H, H6&H13), 4.02-4.10 (q, J = 6.65 Hz, 1H, CH), 5.66 (s, 3H, NH_3^+), 7.13-7.40 (m, 10H, CH^{Aryl}).

^{13}C NMR: (63 MHz; DMSO-d6; 60°C): δ [ppm]: 23.46 (2C, CH_2), 23.68 (2C, CH_3), 36.00 (2C, CH_2), 50.30 (1C, CH^{1PEA}), 59.01 (1C, CR_4^{PCPA}), 125.79 (1C, CH^{Aryl}), 125.92-128.05 (9C, CH^{Aryl}), 144.95 (1C, CH^{Aryl}), 146.52 (1C, CH^{Aryl}), 176.86 (1C, COO^-).

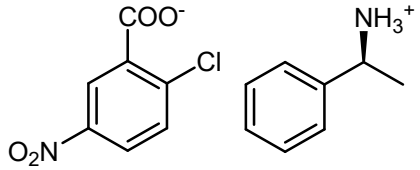
(*S*)-1PEA-43CNA ((*S*)-1-phenylethylammonium-4-Chloro-3-nitrobenzoate)



^{1}H NMR: (250.13 MHz; DMSO-d6): δ [ppm]: 1.50-1.53 (d, J = 6.76 Hz, 3H, CH_3), 4.36-4.44 (q, J = 6.80 Hz, 1H, CH), 7.27-7.53 (m, 5H, CH^{Aryl}), 7.68-7.71 (ds, J = 8.35 Hz, 1H, CH^{Aryl}), 8.07-8.11 (dd, J = 1.92, 8.27 Hz, 1H, CH^{Aryl}), 8.34-8.35 (d, J =1.84, CH^{Aryl}), 8.78 (s, 3H, NH_3^+).

^{13}C NMR: (63 MHz; DMSO-d6): δ [ppm]: 21.16 (1C, CH_3), 49.80 (1C, CH^{1PEA}), 125.54 (2C, CH^{Aryl}), 126.65-128.53 (5C, CH^{Aryl}), 130.89 (1C, CH^{Aryl}), 133.80 (1C, CH^{Aryl}), 140.16 (1C, CH^{Aryl}), 140.25 (1C, CH^{Aryl}), 146.84 (1C, CH^{Aryl}), 166.06 (1C, COO^-).

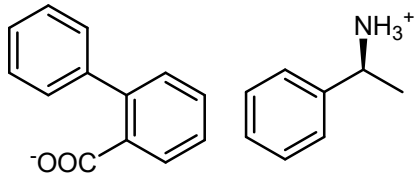
(*S*)-1PEA-25CNA ((*S*)-1-phenylethylammonium-2-chloro-5-nitrobenzoate)



^{1}H NMR: (250.13 MHz; DMSO-d6): δ [ppm]: 1.50-1.53 (d, J = 6.89 Hz, 3H, CH_3), 4.34-4.42 (q, J = 6.87 Hz, 1H, CH), 7.29-7.53 (m, 5H, CH^{Aryl}), 7.58-7.62 (ds, J = 8.70 Hz, 1H, CH^{Aryl}), 8.01-8.06 (dd, J = 2.89, 8.70 Hz, 1H, CH^{Aryl}), 8.14-8.15 (d, J =2.88, CH^{Aryl}), 8.76 (s, 3H, NH_3^+).

^{13}C NMR: (63 MHz; DMSO-d6): δ [ppm]: 20.97 (1C, CH_3), 49.85 (1C, CH^{1PEA}), 122.58 (1C, CH^{Aryl}), 123.23 (1C, CH^{Aryl}),126.67-128.54 (5C, CH^{Aryl}), 130.80 (1C, CH^{Aryl}), 136.49 (1C, CH^{Aryl}), 139.88 (1C, CH^{Aryl}), 142.13 (1C, CH^{Aryl}), 145.83 (1C, CH^{Aryl}), 166.95 (1C, COO^-).

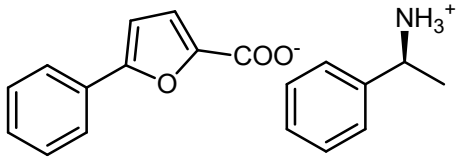
(*S*)-1PEA-2BPA ((*S*)-1-phenylethylammonium-2-biphenylcarboxylate)



^{1}H NMR: (250.13 MHz; DMSO-d6): δ [ppm]: 1.36-1.38 (d, J = 6.46 Hz, 3H, CH_3), 4.12-4.20 (q, J = 6.78 Hz, 1H, CH), 7.23-7.46 (m, 15H, CH^{Aryl}).

^{13}C NMR: (63 MHz; DMSO-d6): δ [ppm]: 22.03 (1C, CH_3), 49.81 (1C, CH^{1PEA}), 126.34-129.37 (14C, CH^{Aryl}), 138.15 (1C, CH^{Aryl}), 140.80 (1C, CH^{Aryl}), 141.92 (1C, CH^{Aryl}), 141.95 (1C, CH^{Aryl}), 172.63 (1C, COO^-).

(*S*)-1PEA-PFA ((*S*)-1-phenylethylammonium-5-phenyl-2-furoate)

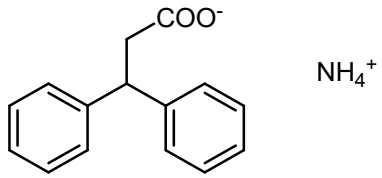


^{1}H NMR: (250.13 MHz; DMSO-d6): δ [ppm]: 1.49-1.52 (d, J = 6.84 Hz, 3H, CH_3), 4.32-4.40 (q, J = 6.78 Hz, 1H, CH), 6.79-6.92 (dd, J = 3.31, 28.94 Hz, 2H), 7.25-7.74 (m, 12H, CH^{Aryl}), 8.38 (s, 3H, NH_3^+).

^{13}C NMR: (63 MHz; DMSO-d6): δ [ppm]: 21.53 (1C, CH_3), 49.85 (1C, CH^{1PEA}), 106.99 (1C, CH), 114.12 (1C, CH), 123.64 (1C, CH^{Aryl}), 126.62-130.42 (10C, CH^{Aryl}), 140.96 (1C, CH^{Aryl}), 152.00 (1C, CR_4), 152.57 (1C, CR_4), 162.17 (1C, COO^-).

4. NMR spectra for prepared ammonium salts for the solubility screening

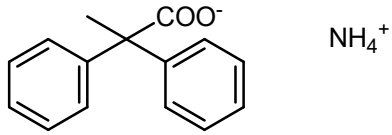
NH_4^+-3DPPA$^-$ (Ammonium-3,3-diphenylpropionate)



^{1}H NMR: (250.13 MHz; DMSO-d6; 80°C): δ [ppm]: 2.93-2.96 (d, J = 7.84 Hz, 2H, CH_2), 4.42-4.48 (t, J = 7.77, 1H, CH^{3DPPA}), 7.11-7.31 (m, 10H, CH^{Aryl}), 7.68 (s, 4H, NH_4^+).

^{13}C NMR: (63 MHz; DMSO-d6; 80 °C): δ [ppm]: 40.76 (1C, CH_2^{3DPPA}), 46.91 (1C, CH^{3DPPA}), 125.96 (2C, CH^{Aryl}), 127.52-128.22 (8C, CH^{Aryl}), 144.56 (2C, CH^{Aryl}), 172.86 (1C, COO^-).

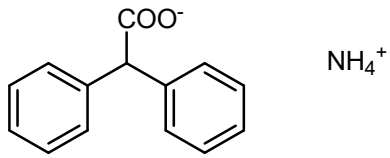
NH_4^+-2DPPA$^-$ (Ammonium-2,2-diphenylpropionate)



^{1}H NMR: (250.13 MHz; DMSO-d6; 50°C): δ [ppm]: 1.75 (s, 3H, CH_3^{2DPPA}), 5.89 (s, 4H, NH_4^+), 7.09-7.26 (m, 10H, CH^{Aryl}).

^{13}C NMR: (63 MHz; DMSO-d6; 50 °C): δ [ppm]: 27.74 (1C, CH_3^{2DPPA}), 56.91 (1C, CR_4^{2DPPA}), 125.35 (2C, CH^{Aryl}), 127.26-128.04 (8C, CH^{Aryl}), 147.38 (2C, CH^{Aryl}), 176.33 (1C, COO^-).

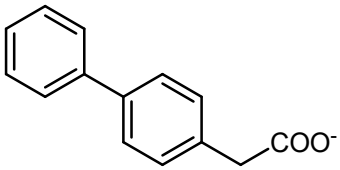
NH_4^+-DPAA$^-$ (Ammoniumdiphenylacetate)



^{1}H NMR: (300.13 MHz; DMSO-d6): δ [ppm]: 4.83 (s, 1H, CH^{DPAA}), 5.89 (s, 4H, NH_4^+), 7.12-7.18 (m, 2H, CH^{Aryl}), 7.21-7.27 (m, 4H, CH^{Aryl}), 7.31-7.35 (m, 4H, CH^{Aryl}).

^{13}C NMR: (75 MHz; DMSO-d6): δ [ppm]: 59.79 (1C, CH^{DPAA}), 125.78 (2C, CH^{Aryl}), 127.80 (4C, CH^{Aryl}), 128.61 (4C, CH^{Aryl}), 142.22 (2C, CH^{Aryl}), 174.28 (1C, COO^-).

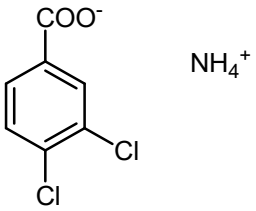
NH_4^+-4BPA$^-$ (Ammonium-4-biphenylacetate)



^{1}H NMR: (300.13 MHz; DMSO-d6): δ [ppm]: 3.46 (s, 2H, CH_2), 7.31-7.65 (m, 10H, CH^{Aryl}).

^{13}C NMR: (75 MHz; DMSO-d6): δ [ppm]: 43.08 (1C, CH_2), 126.19-129.82 (9C, CH^{Aryl}), 136.77 (1C, CH^{Aryl}), 137.66 (1C, CH^{Aryl}), 140.19 (1C, CH^{Aryl}), 173.65 (1C, COO^-).

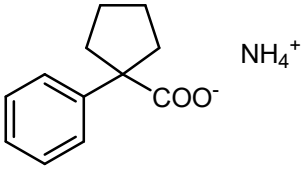
NH_4^+-34CA$^-$ (Ammonium-3,4-dichlorobenzoate)



^{1}H NMR: (300.13 MHz; DMSO-d6): δ [ppm]: 7.64-7.67 (ds, J = 8.32 Hz, 1H, CH^{Aryl}), 7.82-7.86 (dd, J = 1.89, 8.26 Hz, 1H, CH^{Aryl}), 8.01-8.02 (d, J =1.85, CH^{Aryl}).

^{13}C NMR: (75 MHz; DMSO-d6): δ [ppm]: 128.37 (1C, CH^{Aryl}), 130.33 (1C, CH^{Aryl}), 130.80 (2C, CH^{Aryl}), 133.72 (1C, CH^{Aryl}), 135.80 (1C, CH^{Aryl}), 166.23 (1C, COO^-).

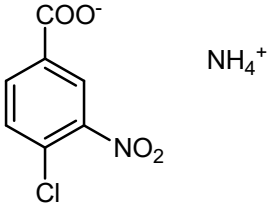
NH_4^+-PCPA$^-$ (Ammonium-1-phenylcyclopentanecarboxylate)



^{1}H NMR: (300.13 MHz; DMSO-d6): δ [ppm]: 1.64-1.82 (m, 6H), 2.51-2.57 (m, 2H), 7.19-7.25 (m, 1H, CH^{Aryl}), 7.28-7.37 (m, 4H, CH^{Aryl}).

^{13}C NMR: (63 MHz; DMSO-d6): δ [ppm]: 23.18 (2C, CH_2), 35.59 (2C, CH_2), 58.44 (1C, CR_4^{PCPA}), 126.39 (1C, CH^{Aryl}), 126.57-128.09 (4C, CH^{Aryl}), 143.61 (1C, CH^{Aryl}), 176.61 (1C, COO^-).

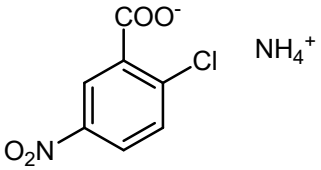
NH_4^+-43CNA$^-$ (Ammonium-4-chloro-3-nitrobenzoate)



^{1}H NMR: (300.13 MHz; DMSO-d6): δ [ppm]: 7.56 (s, 4H, NH_4^+), 7.58-7.72 (ds, J = 8.71 Hz, 1H, CH^{Aryl}), 8.01-8.11 (dd, J = 3.00, 8.75 Hz, 1H, CH^{Aryl}), 8.16-8.35 (d, J =2.88, CH^{Aryl}).

^{13}C NMR: (75 MHz; DMSO-d6): δ [ppm]: 122.60 (1C, CH^{Aryl}), 123.27 (1C, CH^{Aryl}), 130.81 (1C, CH^{Aryl}), 136.50 (1C, CH^{Aryl}), 143.07 (1C, CH^{Aryl}), 145.85 (1C, CH^{Aryl}), 166.87 (1C, COO^-).

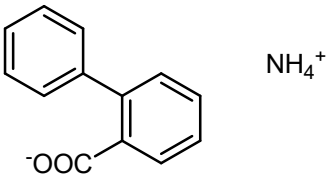
NH_4^+-25CNA$^-$ (Ammonium-2-Chloro-5-nitrobenzoate)



^{1}H NMR: (300.13 MHz; DMSO-d6): δ [ppm]: 7.53 (s, 4H, NH_4^+), 7.58-7.61 (ds, J = 8.66 Hz, 1H, CH^{Aryl}), 8.01-8.05 (dd, J = 2.90, 8.74 Hz, 1H, CH^{Aryl}), 8.16-8.17 (d, J =2.88, CH^{Aryl}).

^{13}C NMR: (75 MHz; DMSO-d6): δ [ppm]: 122.54 (1C, CH^{Aryl}), 123.24 (1C, CH^{Aryl}), 130.80 (1C, CH^{Aryl}), 136.47 (1C, CH^{Aryl}), 143.21 (1C, CH^{Aryl}), 145.85 (1C, CH^{Aryl}), 166.85 (1C, COO^-).

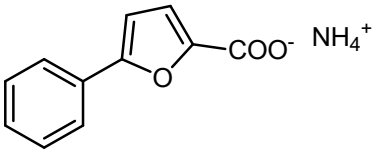
NH_4^+-2BPA$^-$ (Ammonium-2-biphenylcarboxylate)



^{1}H NMR: (300.13 MHz; DMSO-d6): δ [ppm]: 7.22-7.46 (m, 10H, CH^{Aryl}).

^{13}C NMR: (75 MHz; DMSO-d6): δ [ppm]: 126.30-129.30 (9C, CH^{Aryl}), 137.91 (1C, CH^{Aryl}), 141.57 (1C, CH^{Aryl}), 141.99 (1C, CH^{Aryl}), 172.81 (1C, COO^-).

NH_4^+-PFA$^-$ (Ammonium-5-phenyl-2-furoate)



^{1}H NMR: (300.13 MHz; DMSO-d6): δ [ppm]: 6.76-6.90 (dd, J = 3.16, 35.64 Hz, 2H), 7.25-7.31 (m, 1H, CH^{Aryl}), 7.35-7.48 (m, 2H, CH^{Aryl}), 7.61 (s, 4H, NH_4^+), 7.68-7.83 (m, 2H, CH^{Aryl}).

^{13}C NMR: (75 MHz; DMSO-d6): δ [ppm]: 106.95 (1C, CH), 113.82 (1C, CH), 123.64 (1C, CH^{Aryl}), 127.49-130.46 (5C, CH^{Aryl}), 152.39 (1C, CR_4), 152.43 (1C, CR_4), 162.25 (1C, COO^-).

5. Calibration curve for (*S*)-1PEA quantification via GC

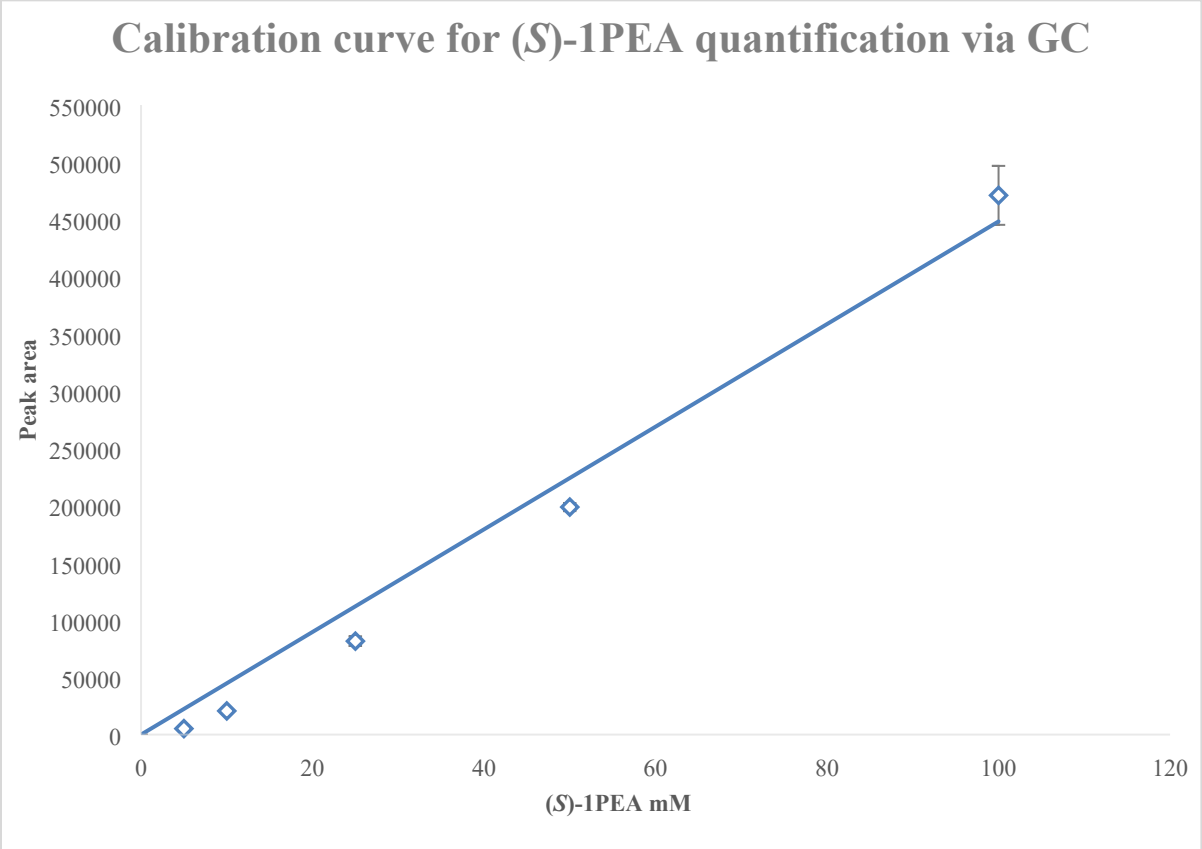
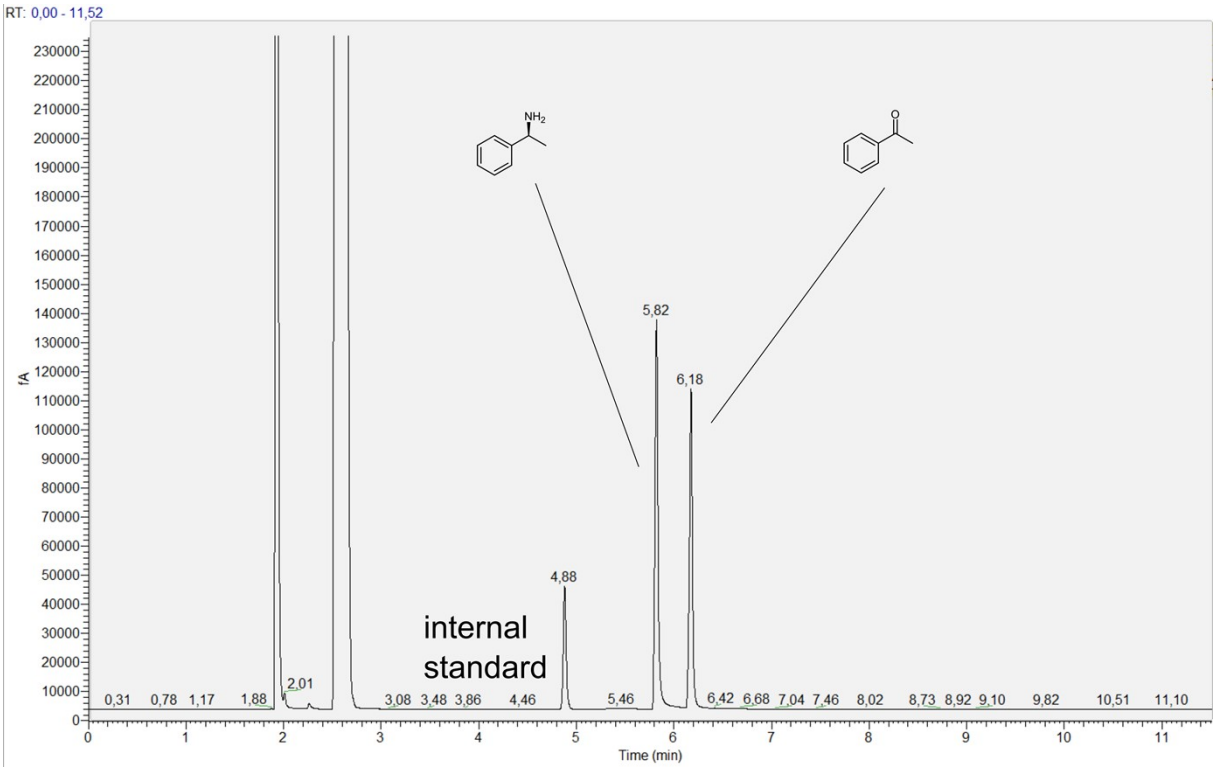


Figure SI1: Calibration curve for (*S*)-1PEA determination

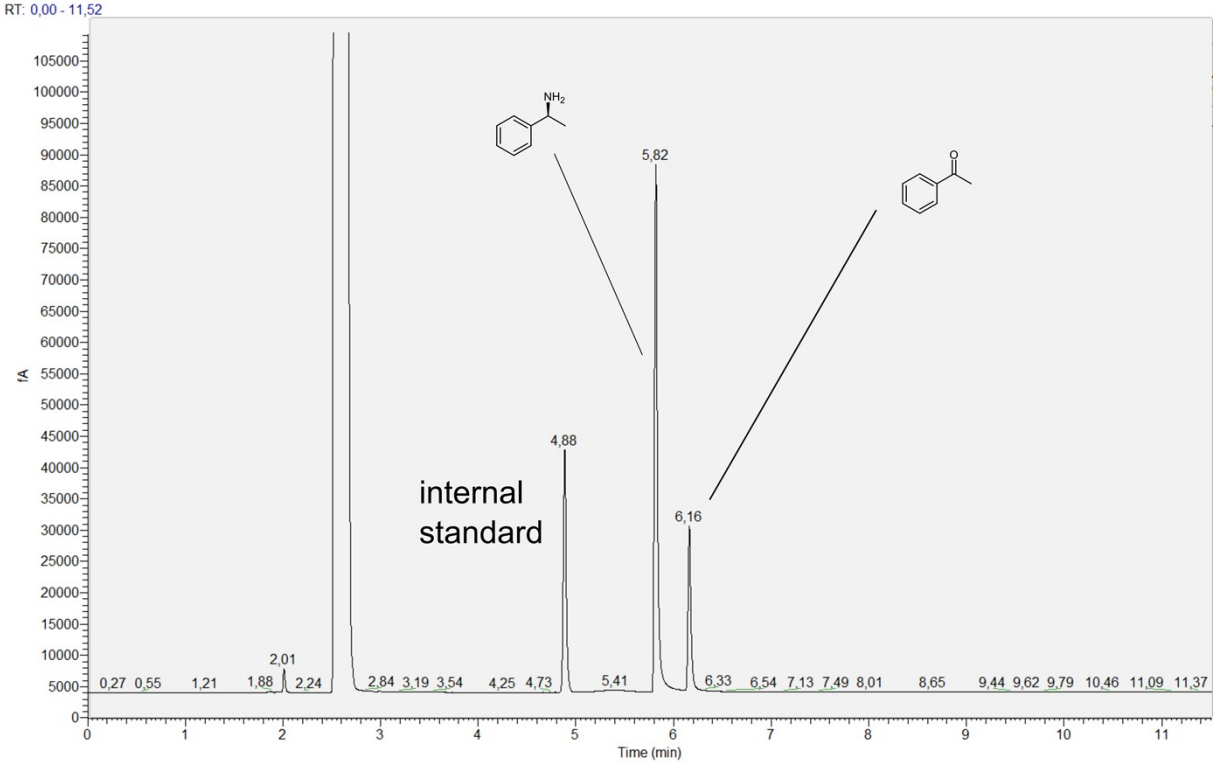
Note: This calibration curve was prepared accordingly to the GC sample preparation protocol, as it can be found in the Experimental section. (*S*)-1PEA was dissolved in the concentrations of 5, 10, 25, 50 and 100 mM in 50 mM aqueous Na-phosphate buffer in triplicates and extracted with CPME for GC-sample preparation. The measured (*S*)-1PEA values were normalized with the help of the internal standard ($\frac{amine\ peak\ area}{internal\ standard\ peak\ area} \times 100000$) and the mean values of the triplicate were plotted and fitted, resulting in this curve (4477.1 squ of the amine peak equal 1 mM of amine in the reaction mixture).

6. Exemplary GC-chromatograms for the transaminase and amine dehydrogenase reactions

Transaminase-catalyzed reaction: exemplary 96h chromatogram



LE-AMDH-v1-catalyzed reaction: exemplary 72h chromatogram



7. Ternary phase diagram preparation procedure

As described briefly in the Experimental section, the preparation of the phase diagrams consisted of several steps.
In the first step, the two salts of each salt pair (for example IPA/(*S*)-1PEA-43CNA) were mixed in 9 different proportions (with additionally each pure salt as a control) and dissolved in 0.01 M phosphate buffer (pH 7.5) until a saturated solution was formed. To compensate for the dissolved parts, the same salt proportion mixture was added to each sample individually. The salts were left to equilibrate at 25 °C and 150 rpm for 6 days (or until no further pH changes occurred) to reach solution saturation. Additional salt mixture was added on the second day to ensure sufficient saturation and the pH was readjusted every 2 days.
In the second step, the salt solutions were centrifuged at 10000 xg for 5 min and the supernatant was filtered through 0.2 µm filters to remove all residual salt crystals. Afterwards, solution samples of approx. 1 ml were evaporated in a *Thermo Scientific Pierce ReactiTherm I & ReactiVap I* heating and evaporation unit under a constant dry argon stream. Prior to evaporation, the vials were weighed empty. After filling the evaporation samples, the vials were weighed again. After evaporation, the samples were weighed a third time. All weights were noted.
Approximately 10-20 mg of the evaporated salt samples were dissolved in DMSO-d6 and 1H-NMR spectra were measured for each evaporated sample. This allowed the determination of the salt ratios, in which the two salts remained in solution. For the IPA/(*S*)-1PEA-43CNA salt pair, two $\underline{CH}R_3$ signals, one belonging to IPA and the other to (*S*)-1PEA were integrated and their integration sum was normalized to 100, resulting in the ratio between the salts (see Figure SI4 for example). Alternatively, the RCH_3 signals of both compounds (1.1 to 1.7 ppm) could be compared, normalized by their respective number of protons.

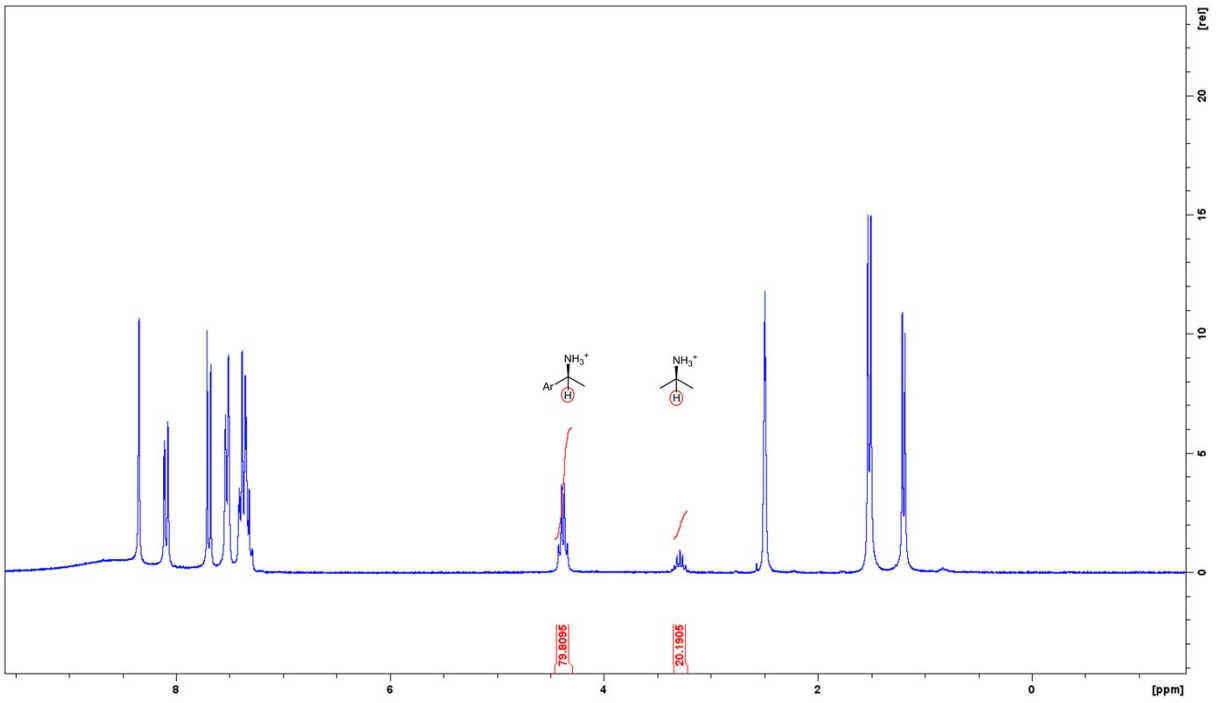


Figure SI4: exemplary NMR of a IPA/(*S*)-1PEA-43CNA salt mixture (here – from *Rpo*-TA catalyzed reaction after crystallization before washing steps).

For the ammonium/(*S*)-1PEA-DPAA salt pair, a $\underline{CH}R_3$ signal belonging to DPAA and a $\underline{CH}R_3$ signal belonging to (*S*)-1PEA were compared. Here, the DPAA signal was normalized to the value of 1.0, thus allowing to determine the percentage of (*S*)-1PEA salt in the mixture by simply integrating the (*S*)-1PEA signal (see Figure SI5). Alternatively, the DPAA signal could be compared to the RCH_3 signal of (*S*)-1PEA (1.5-1.7 ppm), normalized by their respective number of protons.

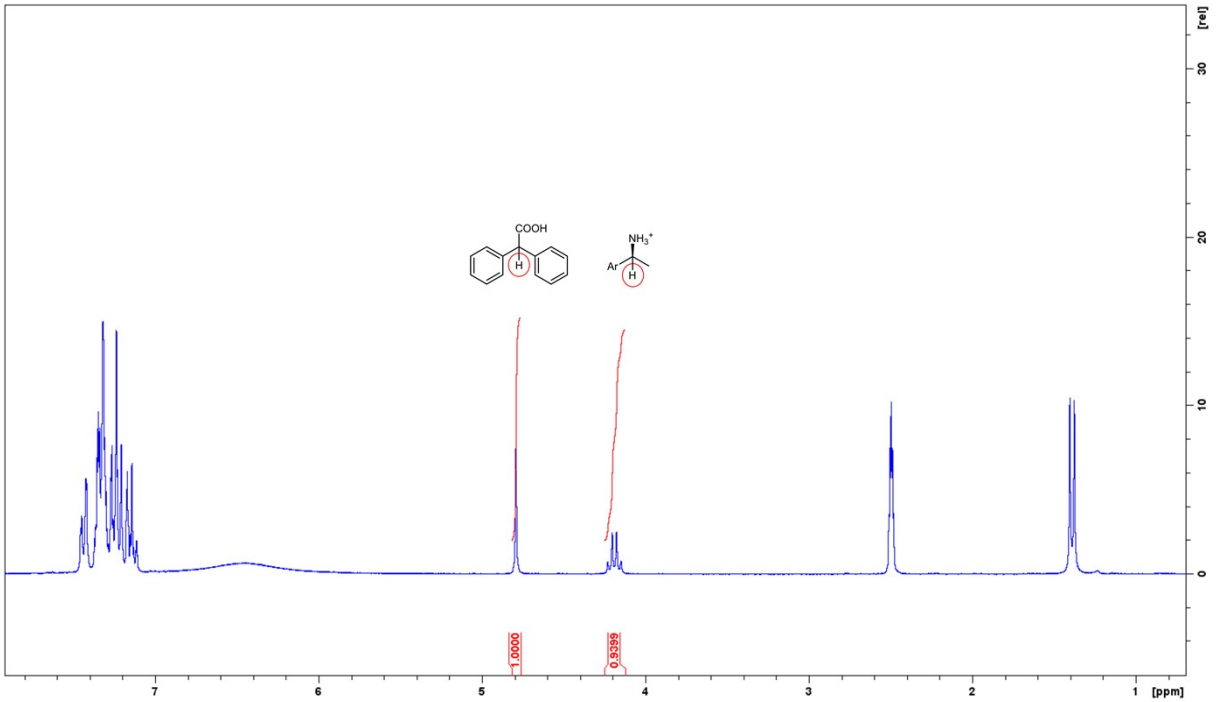


Figure SI5: exemplary NMR of an ammonium/(*S*)-1PEA-DPAA salt mixture (here – from LE-AMDH-v1 catalyzed reaction after crystallization before washing steps).

In the final step, the obtained data was summarized. From the difference between the full (with liquid sample) and the evaporated vials, the exact mass of the solvent in the sample (water) was obtained. From the difference between the evaporated and empty vials, the exact mass of the dissolved salts was obtained. With this obtained salt mixture mass, the molar amount of the salt mixture was calculated, utilizing the measured (NMR) percentages of the salts in the salt mixture:

$$n(salt\ mixture) = \frac{m(salt\ mixture)}{(ratio(salt\ 1) \times M(salt\ 1)\ +\ ratio(salt\ 2) \times M(salt\ 2)}$$

The amount of solvent (water) was also calculated from its mass. Finally, the mole fractions of the components were determined. For water:

$$x(solvent) = \frac{n(solvent)}{n(solvent) + n(salt\ mixture)}$$

and for each salt:

$$x(salt) = (1 - x(solvent)) \times ratio\ (salt)$$

Those mole fractions were plotted as a ternary plot to obtain the phase diagram.