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Stereochemically enriched extractants for the extraction of actinides

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Experimental section

S1: Materials and methods

All chemicals were analytically pure (Sigma-Aldrich, Acros or ABCR) and used without further purification, anhydrous solvents (AcroSeal) were obtained from Acros.

All intermediate and final products were characterised by NMR (Nuclear Magnetic Resonance) analysis. The NMR experiments achieved in this study were ^{1}H, ^{13}C, DEPT135 and HSQC spectroscopy recorded in deuterated chloroform ($CDCl_3$) at room temperature on a Bruker AVANCE III 400Hz apparatus. Signal of chloroform ($CDCl_3$) at 7.26 ppm and at 77.16 ppm were taken as reference in ^{1}H and ^{13}C NMR experiments, respectively.

Flash-chromatography purifications were carried out on prepacked irregular 40µm silica gel cartridges connected to a BUCHI Grace RevelerisX2 device. Detection was monitored by UV-VIS absorption and by light scattering (evaporative light scattering detector). Thin layer chromatography (TLC) was performed on silica (40-63 µm) plate $60F_{254}$ adsorbed onto alumina sheet from Carlo Erba. Stains were revealed by UV fluorescence (254 nm) or/and after aspersion of TLC plates with a w:w 10 % ethanolic solution of phosphomolybdic acid followed by heating at 150°C.

Polarimetry measurements were realized with an Anton Paar MCP150, at 20°C with dichloromethane used as solvent.

The purity of compounds was assessed by Gas Chromatography coupled to mass spectrometry (Waters GCT high-resolution time-of-flight (TOF) mass spectrometer). Runs were performed on a nonpolar column containing a 100% dimethylpolysiloxane (PDMS), CP-Sil 5 CB (LxID: 25m x 0.25 mm, df 0.25 µm) from Agilent.
Experimental conditions: For the analysis of the final molecule, the monoamide was reacted with DIAZALD® in ethyl acetate, allowing the methylation of the functions such as carboxylic acid or acidic alcohol (*i.e.* phenol) in order to observe them more easily by the GC analysis. The following time–temperature program was used for the analysis: 60°C (1 min); 60–150 °C at 10°C/min, 150-175°C at 5°C/min, 175°C (10 min) 175-250°C at 20°C/min, 250°C (5 min) using Helium as the carrier gas.

The enantiomeric excess was determined after separation of enantiomers by GC-MS (Shimadzu GC-2010- Shimadzu GCS-QP2010S), on a chiral stationary phase Supelco β-DEX120 from SUPELCO. This chiral column (LxID: 30m x 0.25 mm, df 0.25 µm) contains permethylated β-cyclodextrin (20 %) embedded in an intermediate polarity stationary phase (SPB-35 poly: 35 % diphenyle / 65 % dimethylesiloxane).
Experimental conditions: The analyses were performed at a constant temperature (80°C) for 45 min using Helium as the carrier gas.

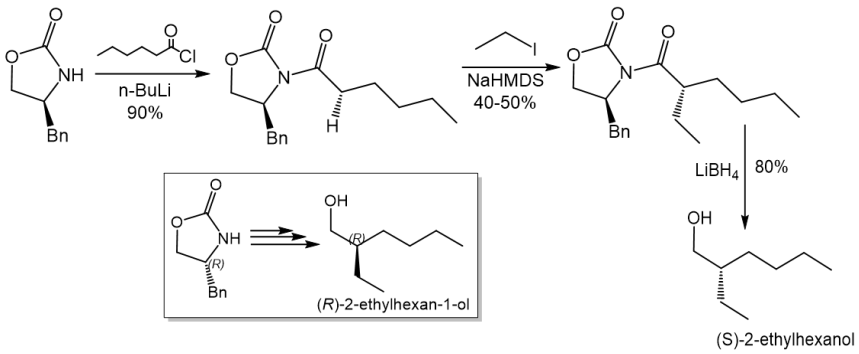
The titration of the ligand concentration was done using perchloric acid (0.1 mol L^{-1}) in acetic anhydride with a Metrohm titroprocessor. The titration of nitric acid concentration was realized with 0.1 mol L^{-1} sodium hydroxide (NaOH) in ammonium oxalate.

The concentrations of the metals were determined using ICP-AES (Bruker Optiva 3000DV) for Uranium in the aqueous phases and by α-spectrometer (CANBERRA) for Plutonium in both aqueous and organic phases.

S2: Synthesis and characterization of intermediate chemical compounds and DEHBA extractants

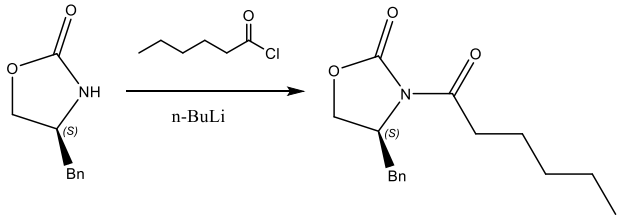
S2.1: Synthesis of (*S*) and (*R*)-2-ethylhexanol using Evans's chiral auxiliary

The synthesis of both configurations was adapted from literature method as described by *Zerdan et al.*[1] according to the Scheme S1.



Scheme S1. Synthesis of (S) and (R)-2-ethylhexanol using Evans's chiral auxiliary.

- *Synthesis of (S)-4-benzyl-3-hexanoyloxazolidin-2-one*



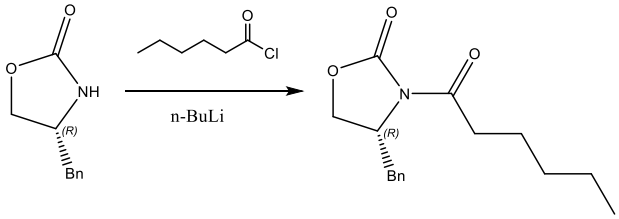
Yield : 94 %

^{1}H NMR (400 MHz, CDCl3, δ) : 7.39-7.32 (m, 2H); 7.32-7.28 (m, 1H); 7.26-7.21 (m, 2H); 4.70 (m, 1H); 4.26–4.16 (m, 2H); 3.32 (dd, 1H, J=13,32Hz); 3.05–2.86 (m, 2H); 2.79 (dd, 1H, J=13.32Hz); 1.80–1.65 (m, 2H); 1.42-1.34 (m, 4H); 0.94 (t, 3H, J=6.98Hz)

^{13}C NMR (100 MHz, CDCl3, δ) : 173.48; 153.48; 135.35; 129.44; 128.96; 127.35; 66.16; 55.18; 37.95; 35.51; 31.29; 23.97; 22.45; 13.94

Polarimeter : $[\alpha]^{20°C}$ = +90.93 (° g-1 mL dm-1) in DCM; $[\alpha]_{literature}$ = +100 (° g^{-1} mL dm^{-1}) [1]

- *Synthesis of (R)-4-benzyl-3-hexanoyloxazolidin-2-one*



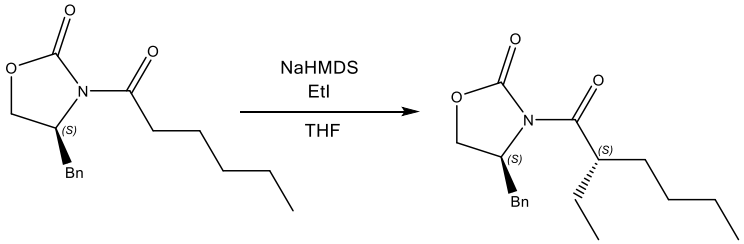
Yield : 94 %

^{1}H NMR (400 MHz, $CDCl_3$, δ) : 7.39–7.32 (m, 2H); 7.32–7.27 (m, 1H); 7.26–7.21 (m, 2H); 4.74-4.65 (m, 1H); 4.26–4.14 (m, 2H); 3.32 (dd, 1H, J=13.32Hz); 3.06–2.86 (m, 2H); 2.79 (dd, 1H, J=13.32Hz); 1.79– 1.64 (m, 2H); 1.43–1.31 (m, 4H); 0.94 (t, 3H, J=6.98Hz)

^{13}C NMR (100 MHz, $CDCl_3$, δ) : 173.54; 153.48; 135.35; 129.44; 128.96; 127.35; 66.16; 55.17; 37.95; 35.51; 31.29 ;23.97; 22.45; 13.94

Polarimeter : $[\alpha]^{20°C}$ = -93.98 (° g^{-1} mL dm^{-1}) in DCM; $[\alpha]_{literature}$ = -95.3 (° g^{-1} mL dm^{-1})[1]

- *Synthesis of (S)-4-benzyl-3-((S)-2-ethylhexanoyl) oxazolidin-2-one*



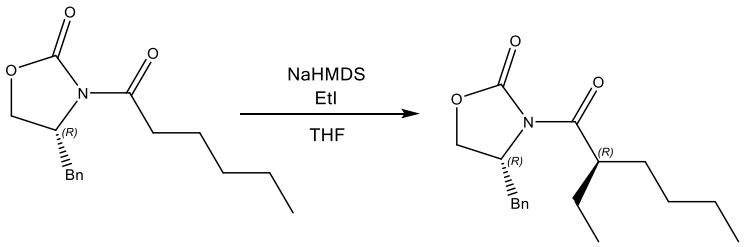
Yield : 50 %

^{1}H NMR (400 MHz, $CDCl^3$, δ) : 7.38-7.33 (m, 2H) ; 7.33-7.28 (m, 1H) ; 7.28-7.23 (m, 2H) ; 4.77–4.68 (m, 1H) ; 4.24– 4.15 (m, 2H) ; 3.80-3.71 (m, 1H) ; 3.37 (dd, 1H) ; 2.73 (dd, 1H) ; 1.85–1.69 (m, 2H) ; 1.69–1.58 (m, 1H) ; 1.57–1.46 (m, 1H) ; 1.39–1.23 (m, 4H) ; 0.98 (t, 3H) ; 0.91 (t, 3H)

^{13}C NMR (100 MHz, $CDCl^3$, δ) : 176.8 ; 153.19 ; 135.47 ; 129.41 ; 128.96 ; 127.32 ; 65.91 ; 55.52 ; 44.07 ; 38.15 ; 31.19 ; 29.55 ; 25.48 ; 22.83 ; 13.97 ; 11.44

Polarimeter : $[\alpha]^{20°C}$ = -55.72 (° g^{-1} mL dm^{-1}) in DCM; $[\alpha]_{literature}$ = -63.2 (° g^{-1} mL dm^{-1}) [1]

- *Synthesis of (R)-4-benzyl-3-((R)-2-ethylhexanoyl) oxazolidin-2-one*



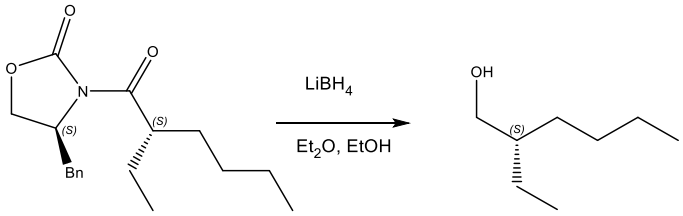
Yield : 50 %

^{1}H NMR (400 MHz, CDCl^{3}, δ) : 7.39–7.33 (m, 2H) ; 7.33–7.28 (m, 1H) ; 7.28–7.23 (m, 2H) ; 4.77-4.69 (m, 1H) ; 4.23–4.15 (m, 2H) ; 3.76 (tt, 1H) ; 3.37 (dd, 1H, J=13,24Hz) ; 2.73 (dd, 1H, J=13,23Hz) ; 1.85–1.69 (m, 2H) ; 1.69-1.58 (m, 1H) ; 1.57–1.46 (m, 1H) ; 1.39-1.23 (m, 4H) ; 0.98 (t, 3H, J=7,44z) ; 0.91 (t, 3H, J=7,02Hz)

^{13}C NMR (100 MHz, CDCl^{3}, δ) : 176.91 ; 153.21 ; 135.48 ; 129.43 ; 128.99 ; 127.34 ; 65.91 ; 55.52 ; 44.07 ; 38.17 ; 31.19 ; 29.56 ; 25.48 ; 22.86 ; 13.97 ; 11.48.

Polarimeter : $[\alpha]^{20°C}$ = +54.73 (° g^{-1} mL dm^{-1}) in DCM; $[\alpha]_{literature}$ = +55.8 (° g^{-1} mL dm^{-1})[1]

- *Synthesis of (S)-2-ethylhexanol*



Yield : 80 %

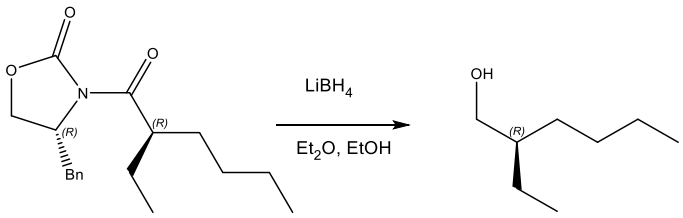
^{1}H NMR (400 MHz, CDCl^{3}, δ) : 3.57 (d, 2H, J=4.12Hz) ; 1.47–1.28 (m, 9H) ; 0.92 (t, 6H ; J=7.14Hz)

^{13}C NMR (100 MHz, CDCl^{3}, δ) : 65.35 ; 42.00 ; 30.14 ; 29.13 ; 23.36 ; 23.10 ; 14.10 ; 11.11

EE% (GC-MS) : 98.8 %

Polarimeter : $[\alpha]^{20°C}$ = -2.48 (° g^{-1} mL dm^{-1}) in DCM; $[\alpha]_{literature}$ = -3.4 (° g^{-1} mL dm^{-1})[1]

- *Synthesis of (R)-2-ethylhexanol*



Yield : 80 %

^{1}H NMR (400 MHz, CDCl^{3}, δ) : 3.57 (d, 2H, J=4.95Hz) ; 1.47–1.26 (m, 9H) ; 0.92 (t, 6H, J=7.05Hz)

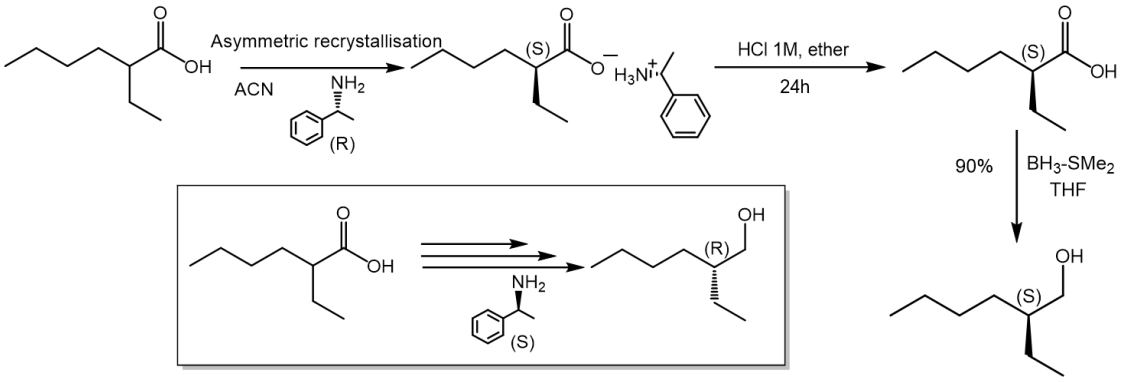
^{13}C NMR (100 MHz, CDCl^{3}, δ) : 65.35 ; 41.99 ; 30.14 ; 29.13 ; 23.36 ; 23.10 ; 14.10 ; 11.12

EE% (GC-MS) : 98.2 %

Polarimeter : $[\alpha]^{20°C}$ = +2.87 (° g^{-1} mL dm^{-1}) in DCM; $[\alpha]_{literature}$ = +3.4 (° g^{-1} mL dm^{-1})[1]

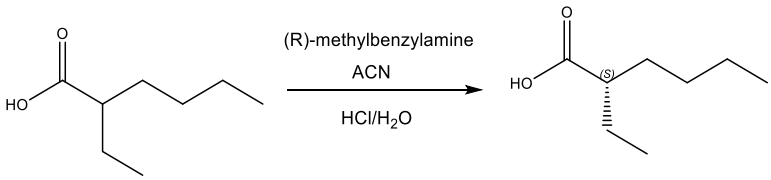
S2.2: Synthesis of (*S*) and (*R*)-2-ethylhexanol using chiral resolution by precipitation

This synthesis path is described by *Larpent et al.*[2] however, this study describes only the synthesis of the (*S*)-2-ethylhexanol from the (*S*)-2-ethyhexanoic acid. Based on this work, the same reactions conditions were used for the synthesis of (*R*)-ethylhexanoic acid using (*S*)-methylbenzylamine and the (*R*)-2-ethylhexanol after reduction of the carboxylic acid (Scheme S2).



Scheme S2. Synthesis of (*S*) and (*R*)-2-ethylhexanol using chiral resolution by precipitation

- *Synthesis of (S) -2-ethylhexanoic acid*



Yield: 30 %

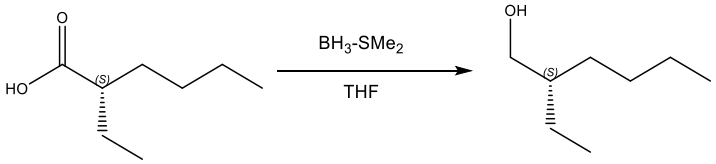
^{1}H NMR (400 MHz. $CDCl_3$. δ): 2.31 (m, 1H) ; 1.74-1.44 (m, 4H) ; 1.41-1.27 (m, 4H) ; 1.00-0.87 (m, 6H)

^{13}C NMR (100 MHz. $CDCl_3$. δ): 182.9 ; 47.1 ; 31.5 ; 29.5 ; 25.2 ; 22.6 ; 13.9 ; 11.7

EE% (GC-MS): 97.9 % (*S*)

Polarimeter: $[\alpha]^{20°C}$ = +8.46 (° g^{-1} mL dm^{-1}) in DCM ; $[\alpha]_{literature}$ = +8.2 (° g^{-1} mL dm^{-1})[2]

- *Synthesis of (S)-2-ethylhexanol*



Yield : 90 %

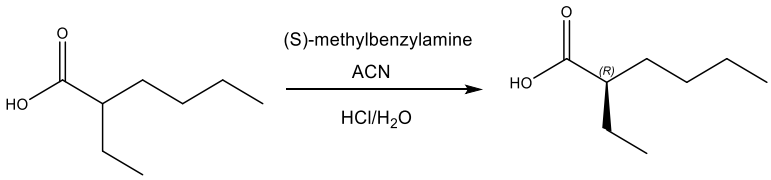
^{1}H NMR (400 MHz. $CDCl_3$. δ): 3.57 (d, *J*=4.9Hz, 2H). 1.48-1.26 (m, 9H). 0.98-0.87 (t, 6H, *J*=7. Hz)

^{13}C NMR (100 MHz. $CDCl_3$. δ): 65.3 ; 42; 30.1 ; 29.1 ; 23.4 ; 23.1 ; 14.1 ; 11.1

EE% (GC-MS): 97.4 % (S)

Polarimeter: $[\alpha]^{20°C}$ = +3.26(° g^{-1} mL dm^{-1}) in DCM; $[\alpha]_{literature}$ = +3.4 (° g^{-1} mL dm^{-1})[1]

- *Synthesis of (R) -2-ethylhexanoic acid*



Yield: 30 %

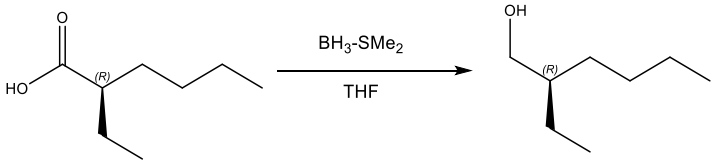
^{1}H NMR (400 MHz. $CDCl_3$. δ): 2.31 (m, 1H) ; 1.74-1.44 (m, 4H) ; 1.41-1.26 (m, 4H) ; 1.00-0.89 (m, 6H)

^{13}C NMR (100 MHz. $CDCl_3$. δ): 182.5; 47.0 ; 31.5 ; 29.5 ; 25.2 ; 22.6 ; 13.9 ; 11.8

EE% (GC-MS): 97.2 % (R)

Polarimeter: $[\alpha]^{20°C}$ = -8.25 (° g^{-1} mL dm^{-1}) in DCM ; $[\alpha]_{literature}$ = not described

- *Synthesis of (R)-2-ethylhexanol*



Yield : 90 %

^{1}H NMR (400 MHz. $CDCl_3$. δ): 3.57 (d, *J*=5.01Hz, 2H). 1.48-1.27 (m, 9H). 0.98-0.87 (t, 6H, *J*=6.96 Hz)

^{13}C NMR (100 MHz. $CDCl_3$. δ): 65.4 ; 42.0; 30.1 ; 29.1 ; 23.4 ; 23.1 ; 14.1 ; 11.1

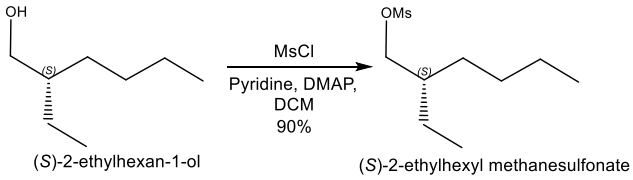
EE% (GC-MS): 96.4 % (R)

Polarimeter: $[\alpha]^{20°C}$ = -3.25(° g^{-1} mL dm^{-1}) in DCM; $[\alpha]_{literature}$ = -3.4 (° g^{-1} mL dm^{-1})[1]

S2.3: Synthesis of brominated and amine compounds from alcohol derivative

Mesylation

- *Synthesis of (S)-2-ethylhexyl methanesulfonate*



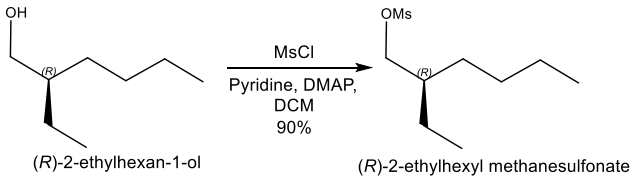
A solution of **(*S*)-2-ethyhexanol** (0.3734 g ; 2.87 mmol), **pyridine** (0.88 mL ; 10.9 mmol), **DMAP** (0.0016g ; 0.013 mmol) and **dichloromethane** (25 mL) was prepared. The **mesylate chloride** (0.411 g ; 3.59 mmol) was added dropwise and stirred overnight. The reaction was stopped by addition of water, the mixture was poured into a separating funnel containing HCl 3 mol L^{-1}. Successive washings were done with HCl 1 mol L^{-1} (x2), water (x2),$NaHCO_3$ (x2) and brine (x2). Organic phase was dried with $MgSO_4$ and concentrated under vacuum. The product was purified by distillation at 100°C for 1h under vacuum (10^{-2} mBar). The final product was obtained with a 90% yield and a purity higher than 99%.

^{1}H NMR (400 MHz. $CDCl_3$. δ): 4.20–4.10(m, 2H). 3.02 (s, 3H). 1.74-1.63 (m, 1H). 1.50–1.25 (m, 8H). 0.99-0.88 (m, 6H)

^{13}C NMR (100 MHz. $CDCl_3$. δ): 72.14 ; 39.19 ; 37.19 ; 29.85 ; 28.77 ; 23.27 ; 22.88 ; 14.01 ; 10.83

Polarimeter: $[\alpha]^{20°C}$ = +4.25(° g^{-1} mL dm^{-1}) in DCM; $[\alpha]_{literature}$ = not described

- *Synthesis of (R)-2-ethylhexyl methanesulfonate*



Synthesis performed according to the same procedure as previously described.

Yield: 90 %

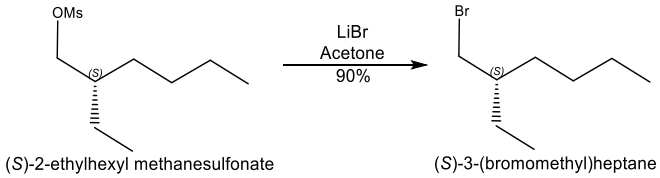
^{1}H NMR (400 MHz. $CDCl_3$. δ): 4.22–4.11(m, 2H); 3.02 (s, 3H); 1.74-1.63 (m, 1H); 1.50–1.26 (m, 8H); 1.00-0.87 (m, 6H)

^{13}C NMR (100 MHz. $CDCl_3$. δ): 72.1 ; 39.2 ; 37.2 ; 29.8 ; 28.8 ; 23.3 ; 22.9 ; 14 ; 10.8

Polarimeter : $[\alpha]^{20°C}$ = -4.16 (° g^{-1} mL dm^{-1}) in DCM; $[\alpha]_{literature}$ = not described

Bromination

- *Synthesis of (S)-3-(bromoethyl)heptane*



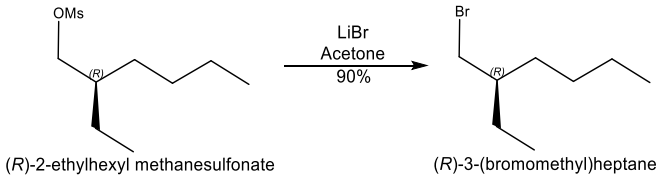
A solution of **(S)-2-ethylhexyl methanesulfonate** (1.5708 g ; 7.54 mmol), **acetone** (30 mL) and **LiBr** (0.982 g ; 11.3 mmol) was prepared and heated at 80°C (reflux) for 24h. The reaction mixture was concentrated under vacuum and the product was subsequently dissolved in pentane. The organic phase was washed with water, dried over $MgSO_4$ and concentrated under vacuum. No further purification was required. The final product was obtained with a 90 % yield and a purity higher than 99 %.

^{1}H NMR (400 MHz. $CDCl_3$. δ): 3.53–3.43(m, 2H); 1.60-1.51 (m, 1H); 1.50–1.22 (m, 8H); 0.97-0.88 (m, 6H)

^{13}C NMR (100 MHz. $CDCl_3$. δ): 41 ; 39.2 ; 31.9 ; 28.8 ; 25.2 ; 22.8 ; 14.1 ; 10.9

Polarimeter: $[\alpha]^{20°C}$ = +5.77 (° g^{-1} mL dm^{-1}) in DCM; $[\alpha]_{literature}$ = +5.30 (° g^{-1} mL dm^{-1})[1]

- *Synthesis of (R)-3-(bromoethyl)heptane*



Synthesis performed according to the same procedure as that previously described.

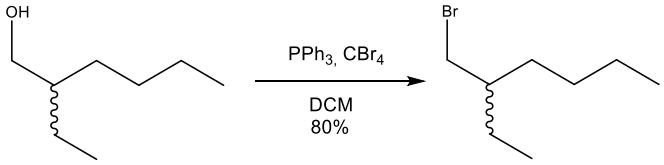
Yield: 90 %

^{1}H NMR (400 MHz. $CDCl_3$. δ): 3.54–3.44(m, 2H) ; 1.61-1.51 (m, 1H) ; 1.48–1.20 (m, 8H) ; 0.97-0.87 (m, 6H)

^{13}C NMR (100 MHz. $CDCl_3$. δ): 41.1 ; 39.2 ; 31.9 ; 28.8 ; 25.2 ; 22.8 ; 14.1 ; 10.9

Polarimeter: $[\alpha]^{20°C}$ = -5.39 (° g^{-1} mL dm^{-1}) in DCM; $[\alpha]_{literature}$ = -11.2 (° g^{-1} mL dm^{-1})[1]

- *Synthesis du 3-(bromoethyl)heptane*



A solution of **2-ethylhexanol** (1 g ; 7.68 mmol), **dichloromethane** (20 mL) and **triphenylphosphine** (2.503 g ; 9.54 mmol) was prepared. **Carbon tetrabromide** (2.84 g ; 8.55 mmol) was added and the reaction was stirred for 3h at room temperature. The reaction mixture was washed with water and the aqueous phase was extracted with DCM. The combined organic phases were dried over $MgSO_4$ and concentrated under vacuum. The crude product was dissolved in pentane, filtered and concentrated under vacuum. The final product was obtained with a 90 % yield.

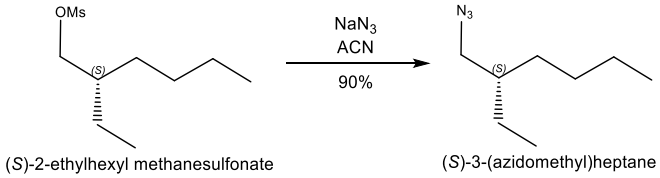
Yield: 90 %

^{1}H NMR (400 MHz. $CDCl_3$. δ): 3.53–3.43(m, 2H); 1.61-1.51 (m, 1H); 1.49–1.20 (m, 8H); 0.97-0.88 (m, 6H)

^{13}C NMR (100 MHz. $CDCl_3$. δ): 41.0 ; 39.2 ; 31.9 ; 28.8 ; 25.2 ; 22.8 ; 14.1 ; 10.9

Azidation

- *Synthesis of (S)-3-(azidomethyl)heptane from (S)-2-ethylhexyl methanesulfonate*

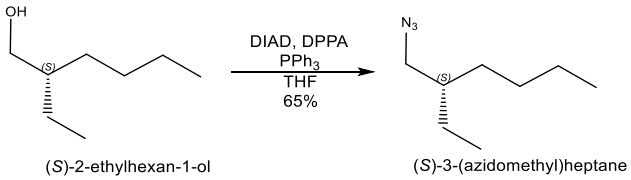


In a microwave reactor, the **(R)-2-ethylhexyl methanesulfonate** (0.4224 g ; 2 mmol), **NaN_3** (0.4 g ; 6 mmol) and **acetonitrile** (8 mL) were placed. The reactor was placed in the microwave and heated up to 130 °C for 18h. Diethyl ether was added to the reaction mixture and the organic phase was washed with water (x3). The organic phase was dried over $MgSO_4$ and concentrated under vacuum. The final product was obtained with a 90 % yield and a purity higher than 99 %.

Yield: 90 %

^{1}H NMR (400 MHz. $CDCl_3$. δ): 3.26 (d, *J*=5.9Hz, 2H); 1.57-1.47 (m, 1H); 1.47–1.25 (m, 8H); 0.97-0.87 (m, 6H)

- *Synthesis of (S)-3-(azidomethyl)heptane from (S)-2-ethylhexan-1-ol*



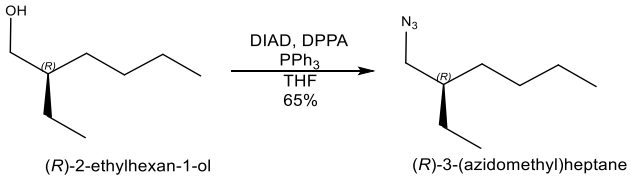
A solution of **(S)-2-ethylhexanol** (1.9596 g ; 15.06 mmol) and **THF** (100 mL) was prepared. **DIAD** (5.82 mL ; 29.67 mmol), **PPh_3** (7.9 g ; 30.12 mmol) and **DPPA** (6.47 mL ; 30.12 mmol) were successively added. The reacting mixture was stirred overnight, then concentrated under vacuum. The organic phase was extracted with EtOAc (3x), the combined organic phases were washed with brine (3x). The organic phase was dried over $MgSO_4$ and concentrated under vacuum. The obtained product was dissolved in pentane and stirred for a couple hours and then filtered. The obtained filtrate was concentrated under vacuum and purified on a silica gel column (DCM: cyclohexane / 10 : 90). The final product was obtained as a colourless oil, with a 65 % yield and a purity higher than 99 %.

^{1}H NMR (400 MHz. $CDCl_3$. δ): 3.26 (d, *J*=5.9Hz, 2H); 1.57-1.47 (m, 1H); 1.46–1.25 (m, 8H); 0.96-0.88 (m, 6H)

^{13}C NMR (100 MHz. $CDCl_3$. δ): 54.9 ; 39.6 ; 31 ; 28.8 ; 24.3 ; 22.9 ; 14 ; 10.9

Polarimeter: $[\alpha]^{20°C}$ = -0.31 (° g^{-1} mL dm^{-1}) in DCM; $[\alpha]_{literature}$ = not described

- *Synthesis of (R)-3-(azidomethyl)heptane from (R)-2-ethylhexan-1-ol*



Synthesis performed according to the same procedure as that previously described.

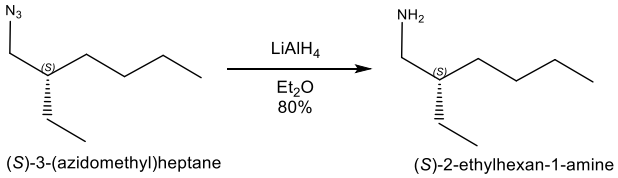
^{1}H NMR (400 MHz. $CDCl_3$. δ): 3.26 (d, *J*=5.9Hz, 2H) ; 1.57-1.48 (m, 1H) ; 1.46-1.24 (m, 8H) ; 0.97-0.88 (m, 6H)

^{13}C NMR (100 MHz. $CDCl_3$. δ): 54.9; 39.6 ; 31 ; 28.8 ; 24.3 ; 22.9 ; 14; 10.9

Polarimeter : $[\alpha]^{20°C}$ = +0.24 (° g^{-1} mL dm^{-1}) in DCM; $[\alpha]_{literature}$ = not described

Amination

- *Synthesis of (S)-2-ethylhexylamine*



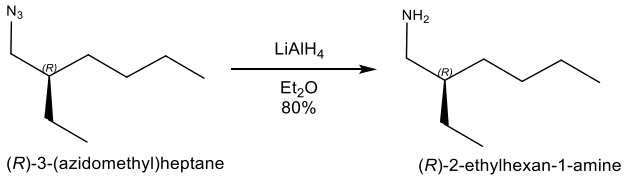
A solution of **$LiAlH_4$** (3.79 g ; 99.94 mmol) in **Et_2O** (160 mL) was prepared under argon and stirred for 10 min at 0°C. A solution of **(R)-3-(azidomethyl)heptane** (2.5843 g ; 16.37 mmol) and **Et_2O** (80 mL) was added dropwise and the reaction was stirred for 4h. 3.79 mL of water, 3.79 mL of NaOH 2 mol L^{-1} and three times 3.79 mL of water were successively added to the reaction mixture, the reaction was stirred for 20 min and filtered. The filtrate was washed with water (3x). The organic phase was dried over $MgSO_4$ and concentrated under vacuum. The final product was obtained as a colourless oil with an 80% yield and a purity higher than 99 %.

^{1}H NMR (400 MHz. $CDCl_3$. δ): 2.62 (d, *J*=4.7Hz, 2H,); 1.41–1.22 (m, 9H); 0.96-0.87 (m, 6H)

^{13}C NMR (100 MHz. $CDCl_3$. δ): 44.8 ; 42.4 ; 30.8 ; 29.1 ; 23.9 ; 23.1 ; 14.1 ; 11

Polarimeter: $[\alpha]^{20°C}$ = +1.12 (° g^{-1} mL dm^{-1}) in DCM ; $[\alpha]_{literature}$ = not described

- *Synthesis of (R)-2-ethylhexylamine*



Synthesis performed according to the same procedure as that previously described.

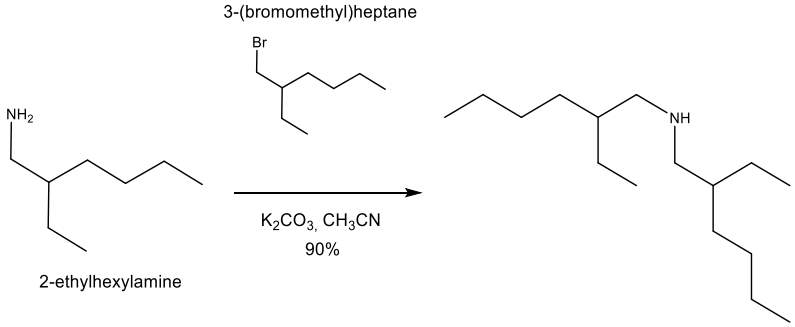
^{1}H NMR (400 MHz. $CDCl_3$. δ): 2.63 (d, *J*=4.7Hz, 2H); 1.41–1.21 (m, 9H); 0.96-0.87 (m, 6H)

^{13}C NMR (100 MHz. $CDCl_3$. δ): 44.7 ; 42.2 ; 30.8 ; 29 ; 23.8 ; 23.1 ; 14.1 ; 10.9

Polarimeter: $[\alpha]^{20°C}$ = -1.02 (° g^{-1} mL dm^{-1}) in DCM ; $[\alpha]_{literature}$ = not described

S2.4: Synthesis of bis (2-ethylhexyl)amine compounds

- *Synthesis of bis (2-ethylhexyl)amine*

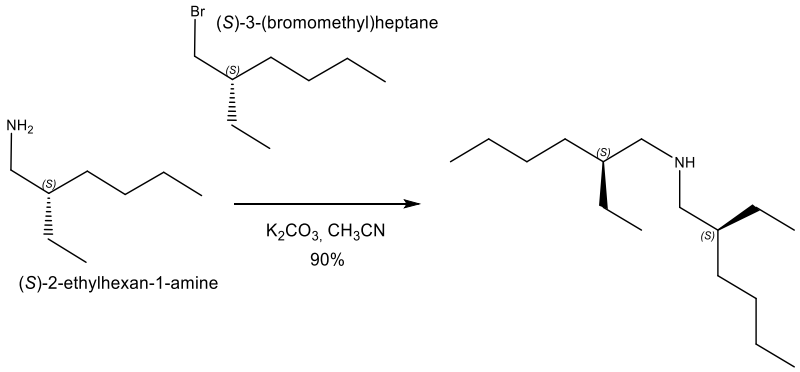


A solution of **2-ethylhexylamine** (0.7692 g ; 5.95 mmol), **3-(bromoethyl)heptane** (1.1495 g ; 5.95 mmol). **K_2CO_3** (0.822 g ; 5.95 mmol) and **acetonitrile** (10 mL) was prepared and placed in a microwave reactor. The mixture was heated at 120°C for 5h in the microwave. Diethyl ether was added to the reaction mixture and washed with brine, the organic phase was dried over $MgSO_4$ and concentrated under vacuum. The crude product was then purified on a silica gel column. The final product was obtained as a light yellow oil with 90% yield and a purity higher than 97%.

^{1}H NMR (400 MHz. $CDCl_3$. δ): 2.50 (d, *J*=6.26Hz, 4H); 1.50-1.41 (m, 2H); 1.41–1.21 (m, 16H); 0.97-0.85 (m, 12H)

^{13}C NMR (100 MHz. $CDCl_3$. δ): 53.6 ; 39.3 ; 31.4 ; 29 ; 24.5 ; 23.1 ; 14.1 ; 10.9

- *Synthesis of (S,S)- bis (2-ethylhexyl)amine*



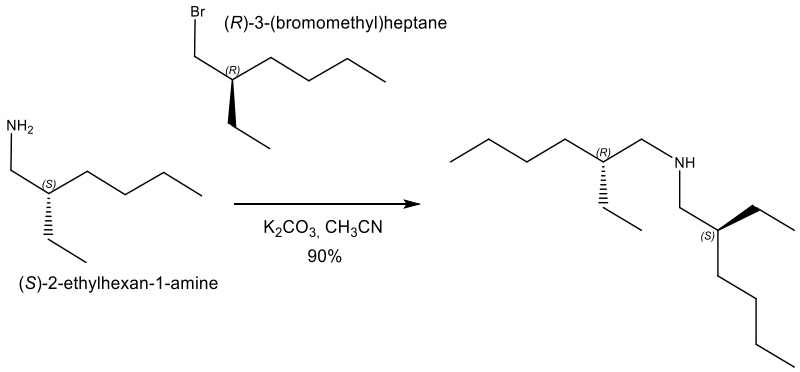
Synthesis performed according to the same procedure as that previously described.

^{1}H NMR (400 MHz. $CDCl_3$. δ): 2.50 (d, *J*=6.3Hz, 4H,); 1.51-1.41 (m, 2H); 1.41–1.24 (m, 16H); 0.96-0.85 (m, 12H)

^{13}C NMR (100 MHz. $CDCl_3$. δ): 53.5 ; 39.2 ; 31.4 ; 29 ; 24.5 ; 23.1 ; 14.1 ; 10.9

Polarimeter: $[\alpha]^{20°C}$ = +0.84 (° g^{-1} mL dm^{-1}) in DCM ; $[\alpha]_{literature}$ = not described

- *Synthesis of (R,S)- bis (2-ethylhexyl)amine*



Synthesis performed according to the same procedure as that previously described.

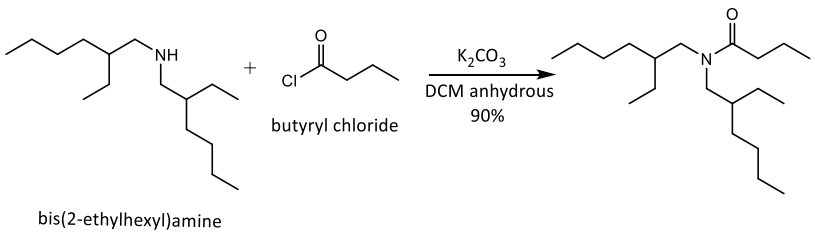
^{1}H NMR (400 MHz. $CDCl_3$. δ): 2.49 (d, *J*=6.2Hz, 4H,); 1.49-1.40 (m, 2H); 1.41–1.22 (m, 16H); 0.96-0.83 (m, 12H)

^{13}C NMR (100 MHz. $CDCl_3$. δ): 53.5 ; 39.2 ; 31.4 ; 29 ; 24.5 ; 23.1 ; 14.1 ; 10.9

Polarimeter: $[\alpha]^{20°C}$ = +0.04 (° g^{-1} mL dm^{-1}) ; $[\alpha]_{literature}$ = not described

S2.5: Synthesis of di-2-ethylhexylbutyramide (DEHBA) compounds

- *Synthesis of DEHBA*



A solution of **bis(2-ethylhexyl)amine** (1.4003 g ; 5.80 mmol), **K_2CO_3** (1.603 g ; 11.6 mmol) and **dichloromethane** (50 mL) was prepared and cooled to 0°C. **Butyryl chloride** (0.73 mL ; 6.96 mmol) was added dropwise and the reaction was stirred for 20h. The reaction was quenched by addition of water, the organic phase was washed with NaOH 2 mol L^{-1} (x2) and water (x2) successively. The organic phase was dried over MgSO4 and concentrated under vacuum. The crude product was purified on a silica gel column (cyclohexane : EtOAc / 97 : 3). The final product was obtained as a light yellow oil with 90% yield and a purity higher than 97%.

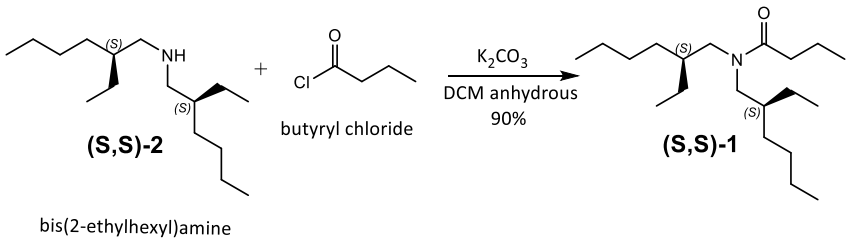
^{1}H NMR (400 MHz. $CDCl_3$. δ): 3.37-3.21 (m, 2H); 3.16 (d, *J*=7.5Hz, 2H,); 2.31 (t, *J*=15Hz, 2H); 1.75-1.65 (m, 3H); 1.64-1.55 (m, 1H); 1.40-1.16 (m, 16H); 1.00-0.85 (m, 15H)

^{13}C NMR (100 MHz. $CDCl_3$. δ) : 173.5 ; 51.4 ; 48.7 ; 38.6 ; 37 ; 35.5 ; 30.6 ; 30.5 ; 28.8 ; 28.7 ; 23.9 ; 23.8 ; 23.1 ; 23 ; 19.1 ; 14.1 ; 14 ; 13.9 ; 10.9 ; 10.7

Purity (GC-MS (TOF MS EI+)) : 98.8 %

GC-HRMS (TOF MS EI+) : Calc. for $C_{20}H_{42}NO$: 312.3266; found: 312.3268

- *Synthesis of (S,S)-DEHBA*



Synthesis performed according to the same procedure as that previously described.

Yield: 90 %

^{1}H NMR (400 MHz. $CDCl_3$. δ): 3.35-3.23 (m, 2H); 3.16 (d, *J*=7.4Hz, 2H,); 2.31 (t, *J*=14.9Hz, 2H,); 1.75-1.65 (m, 3H); 1.64-1.55 (m, 1H); 1.40-1.15 (m, 16H); 1.00-0.85 (m, 15H)

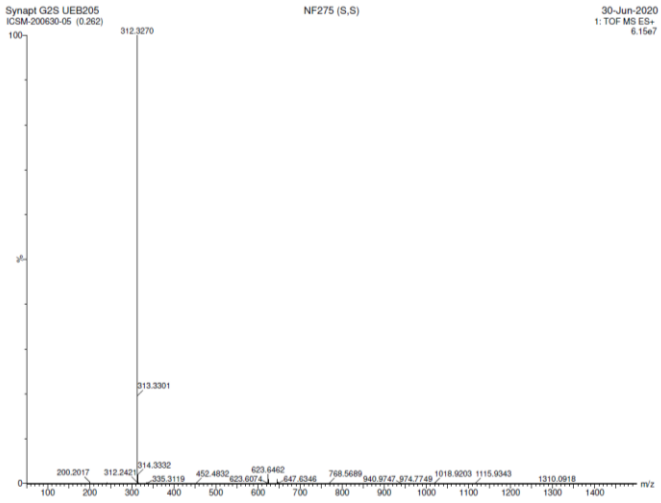
^{13}C NMR (100 MHz. $CDCl_3$. δ): 173.5 ; 51.4 ; 48.7 ; 38.5 ; 37; 35.5 ; 30.6 ; 30.5 ; 28.8 ; 28.7 ; 23.9 ; 23.8 ; 23.1 ; 23; 19.1 ; 14.1 ; 14; 10.9 ; 10.7

Polarimeter: $[\alpha]^{20°C}$ = -0.44 (° g^{-1} mL dm^{-1}) in DCM ; $[\alpha]_{literature}$ = not described

Purity (GC-MS (TOF MS EI+)): 99.0 %

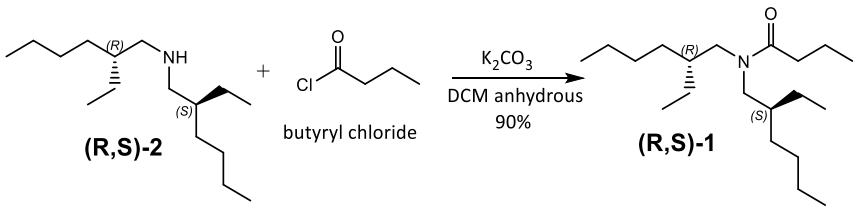
EE%(GC-MS) : >90% (based on the optical purity of the starting materials)

GC-HRMS (TOF MS EI+): Calc. for $C_{20}H_{42}NO$: 312.3266; found: 312.3270



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
312.3270	312.3266	0.4	1.3	0.5	1657.4	0.000	100.00	C20 H42 N O
	312.3271	-0.1	-0.3	-6.5	1672.1	14.645	0.00	C5 H38 N13 O2

- *Synthesis of (R,S)-DEHBA*



bis(2-ethylhexyl)amine

Synthesis performed according to the same procedure as that previously described.

Yield: 90 %

^{1}H NMR (400 MHz. $CDCl_3$. δ): 3.37-3.22 (m, 2H); 3.16 (d, *J*=7.5Hz, 2H,); 2.31 (t, *J*=14.9Hz, 2H,); 1.75-1.65 (m, 3H); 1.64-1.56 (m, 1H); 1.40-1.17 (m, 16H); 1.00-0.84 (m, 15H)

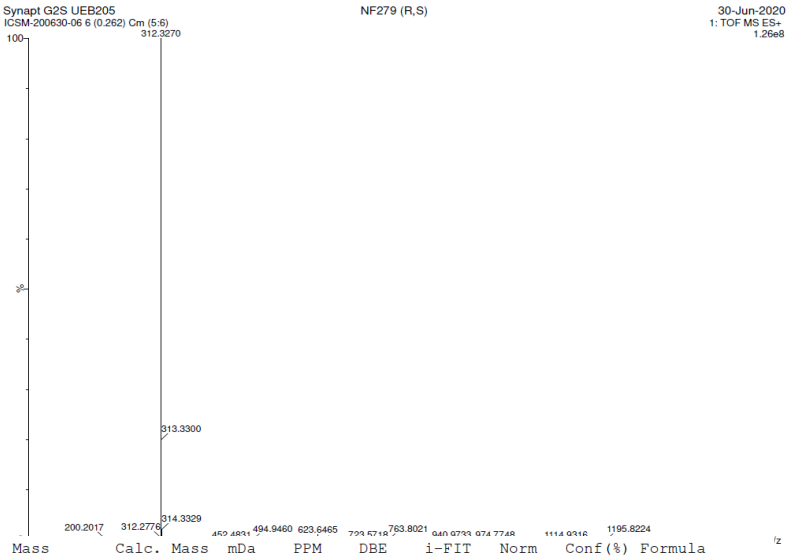
^{13}C NMR (100 MHz. $CDCl_3$. δ): 173.5 ; 51.4 ; 48.7 ; 38.5 ; 37 ; 35.5 ; 30.6 ; 30.5 ; 28.8 ; 28.7 ; 23.9 ; 23.8 ; 23.1 ; 23; 19.1 ; 14.1 ; 14; 13.9 ; 11 ; 10.7

Polarimeter: $[\alpha]^{20°C}$ = -0.08 (° g^{-1} mL dm^{-1}) in DCM; $[\alpha]_{literature}$ = not described

Purity (GC-MS (TOF MS EI+)): 98.5 %

EE%(GC-MS) : >90% (based on the optical purity of the starting materials)

HRMS (TOF MS EI+): Calc. for $C_{20}H_{42}NO$: 312.3266; found: 312.3270



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
312.3270	312.3266	0.4	1.3	0.5	1817.9	0.000	100.00	C20 H42 N O
	312.3271	-0.1	-0.3	-6.5	1834.6	16.695	0.00	C5 H38 N13 O2

S3: Extraction procedure

The extraction experiments were performed in ATALANTE facility (CEA Marcoule, France) in laboratory equipped for the handling of radioactive elements. The extraction experiments were repeated three times to verify the repeatability of the results. In addition, a reference extractant was used during the extractions confirming the reliability of the results obtained.

Organic Phases.

The organic phases at 1.2 mol L^{-1} of extractant in TPH were prepared starting from extractant molecules with a purity higher than 97% (estimated by GC-MS) and for the stereochemically enriched compounds with a stereoisomeric excess higher than 90%.

Aqueous Phases.

The aqueous phases were prepared as follows: 6 µL of Pu(IV) stock solution was added in 450 µL of stock solution of U(VI) at 10.3 g L^{-1} with 4 M or 0.5 mol L^{-1} HNO_3.
Preparation of the U(VI) solution: The solution of U(VI) was prepared from a solution at 323 g L^{-1} in water. The solution was diluted 32 times and 15.4 mol L^{-1} nitric acid was added to reach the desired concentration. ICP-OES was used to check U(VI) concentration, which was found at 10.3 g L^{-1}.

Stock solution of Pu(IV): The solution contains 0.06 mol.L^{-1} of Pu (3.4 ×10^{10} Bq.L^{-1} of $^{239+240}$Pu) and a negligible residual concentration of ^{241}Am. UV absorption bands of Pu(IV) were observed.

General extraction procedure

Pre-equilibrium: The organic phase was contacted with a solution of nitric acid 0.5 mol L^{-1} or 4 mol L^{-1} with a ratio of aqueous phase over the organic phase of 2 (A/O = 2). The combined phases were mechanically stirred for 5 min at 25°C and decanted after centrifugation (2 min at 8000 rpm). The contact with nitric acid was done twice.

Liquid-liquid extraction experiments: The aqueous phase containing U(VI) in nitric acid at 0.5 or 4 mol L^{-1} was contacted with an equal volume of pre-equilibrated organic phase (A/O=1) stirred for 30 min at 25°C. The phases were centrifuged for 2 min, separated and a volume of each phase was diluted and used in α-spectrometry analysis. Acidity of the aqueous phase after extraction was controlled by potentiometry using NaOH 0.1 mol L^{-1} as titrant in saturated ammonium oxalate as medium.

Back-extraction of the organic phase was done by contacting a 0.01 mol L^{-1} nitric acid solution (A/O=5) for 15 min at 25°C. The phases were separated by centrifugation and the aqueous phase was diluted in order to be analysed by ICP-AES allowing to measure U concentration in the organic phase ($C_U^{org,eq}$).

The distribution ratio (D_M) of the metals were determined from the concentrations (uranium) or activities (plutonium) in aqueous and organic phases.

- The distribution ratio of uranium D_U from ICP-AES analyses (analytical uncertainty: ± 5%) was determined using the following equation :

$$D_U = \frac{C_U^{org,eq}}{C_U^{aq,eq}}$$

- The results yielded after α-spectrometry analysis of the different phases allowed the calculation of the distribution ratios of plutonium D_{Pu} (analytical uncertainty: ± 10%) that were determined by using the following equation:

$$D_{Pu} = \frac{A_{Pu}^{org,eq}}{A_{Pu}^{aq,eq}}$$

- Mass balance was verified (100% ± 5%) for each cation using the following equation:

$$Balance\ (\%) = \frac{\left(C_M^{org,eq} + C_M^{aq,eq}\right)}{C_M^{aq,ini}} \times 100$$

where $[M]_{aq,ini}$ represents the M metal concentration in the initial aqueous phase; $[M]_{aq,eq}$ and $[M]_{org,eq}$ correspond to the metal concentration reached at equilibrium in the aqueous and the organic phases, respectively.

- The separation factor ($SF_{U/Pu}$) is given by the following equation :

$$SF_{U/Pu} = \frac{D_U}{D_{Pu}}$$

using respectively the distribution ratio of uranium (D_U) and plutonium (D_{Pu}).

Reference:

[1] R. B. Zerdan, N. T. Shewmon, Y. Zhu, J. P. Mudrick, K. J. Chesney, J. Xue and R. K. Castellano, *Adv. Funct. Mater.*, 2014, **24**, 5993–6004.

[2] C. Larpent and X. Chasseray, *Tetrahedron*, 1992, **48**, 3903–3914.