(S)-(-)-Fluorenylethylchloroformate (FLEC); preparation using asymmetric transfer hydrogenation and applications to the analysis and resolution of amines.

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NMR Spectra S2
HPLC Spectra S21
NMR spectra

(S)-1-(9H-Fluoren-9-yl)ethan-1-ol (S)-3

\[ ^1H \text{NMR (400 MHz, CDCl}_3) \]
$^{13}$C NMR (101 MHz, CDCl$_3$)
(S)-1-(9H-Fluoren-9-yl)ethyl carbonochloridate [(S)-FLEC] (S)-4.

\[\text{OCl}\]

\[^1\text{H}\text{ NMR (400 MHz, CDCl}_3\text{)}\]
$^{13}$C NMR (101 MHz, CDCl$_3$).
(S)-1-(9H-Fluoren-9-yl)ethyl-2-methyl-3,4-dihydroquinoline-1(2H)-carboxylate 7

(S,S)-7:

\[^1\text{H} \text{NMR (400 MHz, CDCl}_3\)]
$^{13}$C NMR (101 MHz, CDCl$_3$)
\((S,R)-7:\)

\[ \text{Feoc} \]

\(^1\text{H NMR (400 MHz, CDCl}_3\)
$^{13}$C NMR (101 MHz, CDCl$_3$)
(S)-2-Methyl-1,2,3,4-tetrahydroquinoline, (S)-6.

^1^H NMR (400 MHz, CDCl\textsubscript{3})
$^{13}$C NMR (101 MHz, CDCl$_3$)
(S)-1-(2-Methyl-3,4-dihydroquinolin-1(2H)-yl)ethan-1-one (S)-8.

\[\text{H NMR (400 MHz, CDCl}_3\text{)}\]
$^{13}$C NMR (101 MHz, CDCl$_3$).
6-Bromo-2-methyl-1,2,3,4-tetrahydroquinoline 10.

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (101 MHz, CDCl$_3$) Matching free base:

HBr salt:
(S)-1-(9H-Fluoren-9-yl)ethyl 6-bromo-2-methyl-3,4-dihydroquinoline-1(2H)-carboxylate 11 as mixture of (S,S) and (S,R) diastereomers.

\[ \text{ON} \]

\( ^1H \) NMR (400 MHz, CDCl\(_3\))
(S)-1-(9H-Fluoren-9-yl)ethyl-2-methyl-6-nitro-3,4-dihydroquinoline-1(2H)-carboxylate 12

\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl}_3\text{)} \]
13 as mixture of (S,S) and (S,R) diastereomers. $^1$H NMR (400 MHz, CDCl$_3$).
2-Methyl-6-nitro-1,2,3,4-tetrahydroquinoline 14

1H NMR (400 MHz, CDCl₃)
$^{13}$C NMR (101 MHz, CDCl$_3$).
HPLC spectra.

1) Chiral HPLC of enantiomers of 3 and reference samples.

Analytical and semi-preparative chiral-HPLC were conducted on an Agilent Infinity 1260 system fitted with Lux 5µ Cellulose-1 columns 150 × 4.60 mm. Isocratic elution of 10% ethanol and 90% petroleum spirit at a flow rate of 1 mL/min was used with UV detection at 254 nm.

racemic 3

(S)-3

after column chromatography
after recrystallisation

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2) **RP-HPLC of mixture of diastereomers of 7.**

Analytical Reverse-Phase High Performance Liquid Chromatography (RP-HPLC) was conducted on an Agilent Infinity 1260 system fitted with Zorbax Eclipse Plus C-8 Rapid Resolution 4.6 × 100 mm, 3.5 μm column (Agilent Technologies, Palo Alto, CA) using a binary solvent system (solvent A: 0.1% TFA, 99.9% H2O; solvent B: 0.1% TFA, 99.9% acetonitrile (ACN), with ultraviolet (UV) detection at 254 nm. Linear gradient of 20-80% solvent B, 5 minutes.

\[
\begin{align*}
(\text{S})-7 & \quad + \quad (\text{R})-7 \\
\end{align*}
\]

Diastereomers after column chromatography purification. Linear gradient of 60-100% solvent B, 5 minutes.

\[
(\text{S})-7
\]
Co-injection of above samples:

(S)-7 + (R)-7
3) **Chiral HPLC of enantiomers of (RS)-8 and reference samples.**

Analytical and semi-preparative chiral-HPLC were conducted on an Agilent Infinity 1260 system fitted with a Lux 5µ Amylose-2 column 150 × 4.60 mm (Phenomonex). Isocratic elution of 10% ethanol and 90% petroleum spirit at a flow rate of 1 mL/min was used with UV detection at 254 nm.
4) **RP-HPLC of mixture of diastereomers of 11.**

Analytical Reverse-Phase High Performance Liquid Chromatography (RP-HPLC) was conducted on an Agilent Infinity 1260 system fitted with Zorbax Eclipse Plus C-8 Rapid Resolution 4.6 × 100 mm, 3.5 μm column (Agilent Technologies, Palo Alto, CA) using a binary solvent system (solvent A: 0.1% TFA, 99.9% H₂O; solvent B: 0.1% TFA, 99.9% acetonitrile (ACN), with ultraviolet (UV) detection at 254 nm. Linear gradient of 80-100% solvent B, 9 minutes.

Re-run: Linear gradient of 60-100% solvent B, 5 minutes.
5) RP-HPLC of crude mixture of regioisomers and diastereomers 12 and 13.

Analytical RP-HPLC: 20-100% CH$_3$CN in 0.05% TFA at a flow rate of 0.2 mL/min over 10 min on a C8, 100 Å, 5 μm, (150 × 4.6 mm I.D.) column (Phenomenex) with ultraviolet (UV) detection at 214 nm.

![Diagram of compounds 12 and 13](image-url)