A solution of 2.25 g (9.06 mmol) of 119 in 50 ml dry CH2Cl2 was treated with 20 ml (2.0 mmol) of a 1M solution of DIBAL-H in toluene, dispersed and stirred for 30 min at -78°C. The reaction mixture was quenched with H2O (10 ml) and poured into a separatory funnel containing Na2SO4 and 20 ml of water. The combined organic layers were washed with brine, dried over Na2SO4, and evaporated to yield 1.87 g (99%) of 120, an oil, colorless.
Suspension of 358 mg (4.0 mmol) 141 in 30 ml dry DMF was heated with 2 eq. BuLi (2.5 M) and the mixture was cooled to -40°C under N₂. 1H – 35°C, a solution of 404 mg (2.0 mmol) 142 and 657 mg (6.0 mmol) TMSCl in 1 ml was added to the mixture within 10 min. After stirring at room temp. for 1 h, the yellow solution was gradually raised to 4°C (yellow → red = colorless/black) and finally refluxed for 1 h.

The colorless (dark residue) solution was now filtered, evaporated and chromatographed with 15% EA/H₂O to yield 310 mg 143 (60%), 160 mg (40%) 141 (56% NMR).

143: 4 diastereomers, ratio: 2:5:1:0.5:0.3 (NMR)
A solution of 334 mg (1.6 mmol) 194 in 1.5 ml dioxane/1.1 M H₂O was heated at 0° with 70 mg (1.5 mmol) NHOAc and a cat. amount of C₂O₂ and stirring overnight at 0°. Workup with NaCl(aq.) and C₂H₂ followed by chromato- 
graphy with 40% EA/1H₂O led to isolation of 270 mg (80%) 195B (major isomer) and 55 mg (15%) 195A (minor isomer).

58%  

195B: αD = -14.0° (c = 5, CH₃Cl)  
195A: αD = -7.8° (c = 2.3, CH₃Cl)

bp: 100° (0.05 Torr) (Kugelrohr)

same as above, but including 120 mg (0.25 mmol) dihydro-quinidine p-chlorobenzoate: only 60% yield, ratio: 1:2, 1:1.7

0.9 g 194: 72% yield, ratio: 2:1 (A:B) 
2.1 g 194: 69% yield, ratio: 1:4 

Hydroquinine-p-chlorobenzoate: Mix 227 mg 194 in 5 ml acetonitrile/ 
H₂O 1:1 at 0° with 45 mg NMD+ 
4 mg (10 mmol) hydroquinine-p-chlorobenzoate + cat. amount 0.4, 
good yield. Ratio ( crude reaction mixture NMD)

A:B = 1:5

The crude, unvaporized reaction mixture should be immediately 
diluted and chromatographed; otherwise, decrump. -> 
black residue (en. NMD stay decrump.?) -> lower yield.
To a solution of 1.06 g (4.5 mmol) of L-tryptophan in 850 ml of 
water, 15 ml of 0.1 M HCl (15 mmol) was added. After addition was 
complete, the mixture was stirred at rt for 2.5 h.

Solid NaHCO₃ was added and the
layer was separated.

It was vacuum-dried.

$\text{HCl}$

$\text{SO}_2$
To a solution of 30 g (96 mmol) of the spirocycle in 1400 ml of MeOH was added 6.4 g (166 mmol) of NaHCO₃. The mixture was stirred at rt for 7 h. Still spirocycle left so another 4.2 g of NaHCO₃ was added & the mixture stirred at rt for another 15 h.

It was conc in vacuo & taken up in EtOAc & H₂O. The aqueous layer was extracted 1× EtOAc, & the combined org layers washed w/ sat'd NaHCO₃ + brine, dried (MgSO₄), & conc

Giving: 24 g (69 mmol) 72%
To a 0°C solution of 327 mg (0.910 mmol) of the amide in 12 mL of a 5:1 mixture of MeCN/H₂O was added 262 mg (1.37 mmol) of PhSeCl. The reaction was stirred at 0°C for 21 h.

It was quenched with saturated NaHCO₃ and extracted 2×EtOAc, 1×CH₂Cl₂, dried (MgSO₄), concentrated, purified on silica (9:1 → 2:1 → 1:1), hex: EtOAc → Et₂O.

Given: 261 mg (0.534 mmol)
8/8/02

\[
\begin{array}{c}
\text{C} \quad \text{H} \\
\text{O} \\
\text{C} \\
\text{C}
\end{array} \xrightarrow{\text{Pd(dba)}_3 \cdot \text{CHCl}_3} \xrightarrow{\text{PdBr}_3 \cdot \text{TEA/HCOOH}}
\begin{array}{c}
\text{C} \\
\text{H} \\
\text{O} \\
\text{C} \\
\text{C}
\end{array}
\]

451.47 \quad 331.37

S.H.: 23g (51 mmol)

THF: 230 mL

\[
\begin{align*}
\text{Pd(dba)}_3 & : 1.0 g \quad (1.0 \text{ mmol)} \\
\text{PdBr}_3 & : 1.2 g \quad (4.1 \text{ mmol} ) \\
\text{NET}_3 & : 20 mL \quad (153 \text{ mmol}) \\
\text{HCOOH} & : 5.4 mL \quad (153 \text{ mmol})
\end{align*}
\]

The rxn was refluxed for 17 h.

It was conc in vacuo & taken up in EtOAc.

The org layer was washed 3 x sat'd \text{NaHCO}_3

dried \text{MgSO}_4, \text{conc,} \text{ & purified on SiO}_2

\[
\begin{array}{c}
\text{Sn} \\
\text{ex}
\end{array} \quad \xrightarrow{\text{EtOAc}}
\]

(1:1 hex: EtOAc)

\[
\begin{array}{c}
\text{prod}
\end{array}
\]

Anisaldehyde

(Gaunins for Column)

\[
\begin{array}{c}
\text{pink}
\end{array}
\]

\[\text{Gluing} \]

\[
\begin{array}{c}
\text{14.6 g} \quad (44 \text{ mmol})
\end{array}
\]

86%