Supporting Information

Noncovalent Organocatalytic Synthesis of Enantioenriched Terminal Aziridines with a Quaternary Stereogenic Center

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**General Methods**

All reactions requiring dry or inert conditions were conducted in flame dried glassware under a positive pressure of nitrogen. THF was freshly distilled before use from LiAlH₄, chloroform was dried over molecular sieves. Molecular sieves (Aldrich Molecular Sieves, 3 Å, 1.6 mm pellets) were activated under vacuum at 200°C overnight. Reactions were monitored by thin layer chromatography (TLC) on Merck silica gel plates (0.25 mm) and visualised by UV light. Flash chromatography was performed on Merck silica gel (60, particle size: 0.040–0.063 mm). ^1^H NMR and ^1^C NMR spectra were recorded on Bruker DRX 400 spectrometer at room temperature in CDCl₃ as solvent. Chemical shifts for protons are reported using residual CHCl₃ as internal reference (δ = 7.26 ppm). Carbon spectra were referenced to the shift of the ^1^C signal of residual CDCl₃ (δ = 77.0 ppm). Optical rotation of compounds 3a-q, 9b, 10a, 11a and 12a was performed on a Jasco Dip-1000 digital polarimeter using the Na lamp (582 nm). FTIR spectra were recorded as thin films on KBr plates using Bruker Vertex 70 spectrometer and absorption maxima are reported in wavenumber (cm⁻¹). ESI-MS was performed using a Bio-Q triple quadrupole mass spectrometer (Micromass, Manchester, UK) equipped with an electrospray ion source. Melting points were measured on a digital Electrothermal 9100 apparatus.

Petrol ether (PE) refers to light petroleum ether (boiling point 40-60°C). Anhydrous toluene and all starting materials (unless otherwise noted) were purchased from Aldrich and used as received. Catalysts 4-9 were synthetized as reported in the literature. Enantiomeric excess of aziridines 3a-q and compound 12a was determined by HPLC (Waters-Breeze 2487, UV dual λ, absorbance detector and 1525 Binary HPLC Pump) using Chiralpak and Phenomenex chiral columns.

**Experimental Procedures and Compounds Characterization**

Alkenes 1 were synthesized using a modified protocol reported in the literature. In a screw capped vial containing freshly distilled THF (40 mL), β-ketoesters (4.0 mmol), p-formaldehyde (360 mg, 12 mmol) and CF₃COONH₂iPr₂ salt (861 mg, 4 mmol) were added. CF₃COOH (31 µL, 0.40 mmol) was added and the mixture was warmed to 60°C and stirred overnight. The reaction mixture was then extracted with AcOEt/water and the organic layer dried over Na₂SO₄. The solvent was then

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removed under vacuum. The residue was loaded onto silica gel and purified by flash chromatography (mixtures of EP/AcOEt as eluent) to obtain the alkenes.\(^3\)

Starting amines 2a-e were synthesized according to the literature.\(^4\) As an example, the N-Boc-protected amine is prepared as follows: to a solution of the Boc-hydroxyamine (1 mmol) in dry CH\(_2\)Cl\(_2\) (2 mL), pyridine is added (2.4 mmol). The solution is cooled at -20°C followed by a portion-wise addition of TsCl (1 mmol). The mixture is allowed to warm to room temperature and after completion, monitored by TLC (eluent EP/ethyl acetate 60:40, diluted with CHCl\(_3\) and washed with water. The organic layers were concentrated in vacuo and the product was isolated by flash chromatography (eluents EP/ethyl acetate 80:20).

**Ethyl 2-benzoylacrylate (1a)**\(^3\)

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{Et} & \quad \text{Et}
\end{align*}
\]

Purified by flash chromatography (EP/AcOEt 98:2 as eluent), 800.5 mg, 98% yield. Pale yellow oil.  
**FTIR** \(\nu_{\text{max}}\) (KBr)/cm\(^{-1}\) 2982, 1728, 1665, 1241, 772.  
**\(^1\)H NMR** (CDCl\(_3\), 400 MHz): \(\delta\) 7.84-7.82 (m, 2H), 7.56 (t, 1H, \(J = 7.3\) Hz), 7.44 (t, 2H, \(J = 7.8\) Hz), 6.66 (s, 1H), 6.04 (s, 1H), 4.19 (q, 2H, \(J = 7.1\) Hz), 1.16 (t, 3H, \(J = 7.1\) Hz).  
**\(^{13}\)C NMR** (CDCl\(_3\), 100 MHz): \(\delta\) 193.0, 164.2, 141.3, 136.1, 133.5, 131.2, 129.3, 128.6, 128.4, 61.4, 13.8.  
**MS** (ESI m/z) 205.10 [MH\(^+\), 100%], 227.09 [MNa\(^+\), 35%].

**Methyl 2-benzoylacrylate (1d)**

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{OMe} & \quad \text{OMe}
\end{align*}
\]

Purified by flash chromatography (EP/AcOEt 98:2 as eluent), 608.6 mg, 80% yield. Pale yellow oil.  
**FTIR** \(\nu_{\text{max}}\) (KBr)/cm\(^{-1}\) 2980, 1725, 1673, 1223, 772.  
**\(^1\)H NMR** (CDCl\(_3\), 400 MHz): \(\delta\) 7.85 (dd, 2H, \(J_1 = 7.1\) Hz, \(J_2 = 1.1\) Hz), 7.61-7.57 (m, 1H), 7.48-7.44 (m, 2H), 6.71 (s, 1H), 6.05 (s, 1H), 3.75 (s, 3H).  
**\(^{13}\)C NMR** (CDCl\(_3\), 100 MHz): \(\delta\) 193.0, 164.7, 140.8, 136.0, 133.6, 131.5, 129.4, 128.6, 52.4.  
**MS** (ESI m/z) 191.08 [MH\(^+\), 100%].

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\(^3\) Alkenes 1a-n have been used freshly prepared, because they are prone to spontaneous polymerization on standing.  
**tert-Butyl 2-benzoylacrylate (1e)**

![tert-Butyl 2-benzoylacrylate](image)

Purified by flash chromatography (EP/AcOEt 98:2 as eluent), 278.5 mg, 30% yield. Pale yellow oil.

**FTIR** $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 2979, 1725, 1678, 1248, 1148, 772. **$^1$H NMR** (CDCl$_3$, 400 MHz): $\delta$ 7.83 (d, 2H, $J = 7.3$ Hz), 7.60-7.55 (m, 1H), 7.48-7.42 (m, 2H), 6.58 (s, 1H), 6.05 (s, 1H), 1.34 (s, 9H). **$^{13}$C NMR** (CDCl$_3$, 100 MHz): $\delta$ 193.7, 163.4, 143.3, 136.7, 133.3, 130.7, 129.0, 128.4, 82.3, 27.7. **MS** (ESI $m/z$) 234.50 [MH$^+$, 40%], 255.46 [MNa$^+$, 100%].

**Benzyl 2-benzoylacrylate (1f)**

![Benzyl 2-benzoylacrylate](image)

Purified by flash chromatography (EP/AcOEt 95:5 as eluent), 319.5 mg, 30% yield. Pale yellow oil.

**FTIR** $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 3033, 1729, 1674, 1221, 772. **$^1$H NMR** (CDCl$_3$, 400 MHz): $\delta$ 7.85-7.82 (m, 2H), 7.62-7.55 (m, 1H), 7.47-7.41 (m, 2H), 7.31-7.27 (m, 2H), 7.21-7.16 (m, 2H), 6.73 (s, 1H), 5.20 (s, 2H). **$^{13}$C NMR** (CDCl$_3$, 100 MHz): $\delta$ 192.9, 164.1, 141.2, 136.2, 135.1, 133.5, 132.0, 129.3, 128.5, 128.4, 128.2, 127.9, 67.0. **MS** (ESI $m/z$) 289.42 [MNa$^+$, 100%].

**Ethyl 2-(4-methylbenzoyl)acrylate (1g)**

![Ethyl 2-(4-methylbenzoyl)acrylate](image)

Purified by flash chromatography (EP/AcOEt 98:2 as eluent), 523.8 mg, 60% yield. Pale yellow oil.

**FTIR** $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 2983, 1727, 1671, 1237, 771. **$^1$H NMR** (CDCl$_3$, 400 MHz): $\delta$ 7.76 (d, 2H, $J = 8.2$ Hz), 7.26 (d, 2H, $J = 8.1$ Hz), 6.67 (s, 1H), 6.03 (s, 1H), 4.22 (q, 2H, $J = 7.1$ Hz), 2.42 (s, 3H), 1.20 (t, 3H, $J = 7.1$ Hz). **$^{13}$C NMR** (CDCl$_3$, 100 MHz): $\delta$ 192.9, 164.4, 144.6, 141.5, 133.7, 131.0, 129.6, 129.2, 61.5, 21.7, 14.0. **MS** (ESI $m/z$) 219.25 [MH$^+$, 10%], 256.39 [MNa$^+$, 60%].
Ethyl 2-(3-methylbenzoyl)acrylate (1h)

Purified by flash chromatography (EP/AcOEt 98:2 as eluent), 488.9 mg, 56% yield. Pale yellow oil.

**FTIR** $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 2982, 1728, 1675, 1251, 763. **$^{1}$H NMR** (CDCl$_3$, 400 MHz): $\delta$ 7.65 (s, 1H), 7.63-7.58 (m, 1H), 7.58-7.27 (m, 2H), 6.64 (s, 1H), 6.01 (s, 1H), 4.19 (q, 2H, $J = 7.1$ Hz), 2.36 (s, 3H), 1.16 (t, 3H, $J = 7.1$ Hz). **$^{13}$C NMR** (CDCl$_3$, 100 MHz): $\delta$ 193.2, 164.2, 141.3, 138.3, 136.1, 134.3, 131.0, 129.6, 128.3, 126.6, 61.3, 21.1, 13.8. **MS** (ESI m/z) 219.37 [MH$^+$, 10%], 256.41 [MK$^+$, 70%].

Ethyl 2-(2-methylbenzoyl)acrylate (1i)

Purified by flash chromatography (EP/AcOEt 98:2 as eluent), 371.2 mg, 45% yield. Pale yellow oil.

**FTIR** $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 2867, 1718, 1636, 1219, 771. **$^{1}$H NMR** (CDCl$_3$, 400 MHz): $\delta$ 7.51-7.42 (m, 1H), 7.41-7.35 (m, 1H), 7.28-7.19 (m 2H), 6.63 (s, 1H), 6.12 (s, 1H), 4.19 (q, 2H, $J = 7.2$ Hz), 2.51 (s, 3H), 1.17 (t, 3H, $J = 7.2$ Hz). **$^{13}$C NMR** (CDCl$_3$, 100 MHz): $\delta$ 195.2, 164.6, 143.0, 138.6, 136.7, 132.4, 131.7, 129.8, 125.4, 61.4, 20.7, 13.9. **MS** (ESI m/z) 219.44 [MH$^+$, 15%], 256.39 [MK$^+$, 90%].

Ethyl 2-(4-methoxybenzoyl)acrylate (1j)

Purified by flash chromatography (EP/AcOEt 97:3 as eluent), 805.8 mg, 86% yield. Pale yellow oil.

**FTIR** $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 2982, 1725, 1666, 1600, 1263, 772. **$^{1}$H NMR** (CDCl$_3$, 400 MHz): $\delta$ 7.85 (d, 2H, $J = 8.8$ Hz), 6.94 (d, 2H, $J = 8.8$ Hz), 6.66 (s, 1H), 6.00 (s, 1H), 4.23 (q, 2H, $J = 7.1$ Hz), 3.88 (s, 3H), 1.22 (t, 3H, $J = 7.1$ Hz). **$^{13}$C NMR** (CDCl$_3$, 100 MHz): $\delta$ 191.8, 164.5, 164.0, 141.5, 131.9, 130.5, 129.2, 113.8, 61.5, 55.5, 14.0. **MS** (ESI m/z) 235.24 [MH$^+$, 5%], 257.19 [MNa$^+$, 100%].
Ethyl 2-(4-chlorobenzoyl)acrylate (1k)

[Chemical structure image]

Purified by flash chromatography (EP/AcOEt 98:2 as eluent), 486.9 mg, 51% yield. Pale yellow oil.

**FTIR** $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 2984, 1732, 1683, 1588, 1220, 772. **$^1$H NMR** (CDCl$_3$, 400 MHz): $\delta$ 7.79 (d, 2H, $J = 8.6$ Hz), 7.44 (d, 2H, $J = 8.5$ Hz), 6.70 (s, 1H), 6.07 (s, 1H), 4.22 (q, 2H, $J = 7.1$ Hz), 1.20 (t, 3H, $J = 7.1$ Hz). **$^{13}$C NMR** (CDCl$_3$, 100 MHz): $\delta$ 192.0, 164.1, 141.0, 140.1, 134.6, 131.7, 130.7, 128.9, 61.6, 13.9. **MS** (ESI $m/z$) 239.34 [M$^+$H$^+$, 55%], 261.37 [M$^{+}$Na$^+$, 85%], 268.38 [M$^{+}$K$^+$, 45%].

Ethyl 2-(3-bromobenzoyl)acrylate (1l)

[Chemical structure image]

Purified by flash chromatography (EP/AcOEt 98:2 as eluent), 509.6 mg, 45% yield. Pale yellow oil.

**FTIR** $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 2984, 1733, 1687, 1565, 1233, 772. **$^1$H NMR** (CDCl$_3$, 400 MHz): $\delta$ 7.98 (s, 1H), 7.77-7.53 (m, 2H), 7.34 (t, 1H, $J = 7.8$ Hz), 6.71 (d, 1H, $J = 0.7$ Hz), 6.09 (d, 1H, $J = 0.6$ Hz), 4.26-4.18 (m, 2H), 1.20 (t, 3H, $J = 7.1$ Hz). **$^{13}$C NMR** (CDCl$_3$, 100 MHz): $\delta$ 191.7, 164.0, 140.8, 138.0, 136.4, 132.1, 132.1, 130.1, 127.9, 122.8, 61.6, 13.9. **MS** (ESI $m/z$) 305.19 [M$^+$Na$^+$, 100%].

Ethyl 2-(2-naphthoyl)acrylate (1m)

[Chemical structure image]

Purified by flash chromatography (EP/AcOEt 98:2 as eluent), 640.8 mg, 63% yield. Pale yellow oil.

**FTIR** $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 2981, 1727, 1673, 1222, 771. **$^1$H NMR** (CDCl$_3$, 400 MHz): $\delta$ 8.33 (s, 1H), 8.01-7.89 (m, 4H), 7.65-7.53 (m, 2H), 6.77 (d, 1H, $J = 0.6$ Hz), 6.12 (d, 1H, $J = 0.6$ Hz), 4.24 (q, 2H, $J = 7.1$ Hz), 1.19 (t, 3H, $J = 7.1$ Hz). **$^{13}$C NMR** (CDCl$_3$, 100 MHz): $\delta$ 193.2, 164.4, 141.4, 135.8, 133.6, 132.3, 131.9, 131.4, 129.6, 128.8, 128.6, 127.8, 126.9, 124.4, 61.6, 14.0. **MS** (ESI $m/z$) 255.47 [M$^+$H$^+$, 10%], 277.37 [M$^{+}$Na$^+$, 100%].
Ethyl 2-(furan-2-carbonyl)acrylate (1n)

Purified by flash chromatography (EP/AcOEt 90:10 as eluent), 435.0 mg, 56% yield. Pale yellow oil. FTIR $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 3134, 2984, 1726, 1661, 1465, 1255, 771. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.64-7.61 (m, 1H), 7.17-7.15 (m, 1H), 6.62 (s, 1H), 6.54 (dd, 1H, $J_1 = 3.6$ Hz, $J_2 = 1.7$ Hz), 6.17 (s, 1H), 4.23 (q, 2H, $J = 7.1$ Hz), 1.23 (t, 3H, $J = 7.1$ Hz). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 179.8, 164.0, 151.8, 147.5, 140.5, 131.7, 120.1, 112.4, 61.5, 13.9. MS (ESI $m/z$) 195.26 [MH$^+$, 15%], 217.26 [MNa$^+$, 100%], 233.19 [MK$^+$, 10%].

Ethyl 2-(cyclohex-1-enecarbonyl)acrylate (1o)

Purified by flash chromatography (EP/AcOEt 98:2 as eluent), 658.1 mg, 79% yield. Pale yellow oil. FTIR $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 2941, 1724, 1658, 1634, 1220, 772. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 6.76 (t, 1H, $J = 3.9$ Hz), 6.49 (s, 1H), 5.81 (s, 1H), 4.23 (q, 2H, $J = 7.2$ Hz), 2.35-2.19 (m, 4H), 1.70-1.56 (m, 4H), 1.27 (t, 3H, $J = 7.2$ Hz). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 194.6, 164.5, 145.4, 141.2, 139.2, 129.2, 61.3, 26.3, 22.8, 21.7, 21.5, 14.0. MS (ESI $m/z$) 231.31 [MNa$^+$, 100%].

Ethyl 2-(benzylcarbamoyl)acrylate (1p)

Purified by flash chromatography (EP/AcOEt 90:10 as eluent), 780.4 mg, 56% yield. Pale yellow oil. FTIR $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 2982, 1714, 1663, 1534, 1143, 772. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.79 (bs, 1H), 7.34-7.17 (m, 5H), 7.17 (s, 1H), 6.79 (s, 1H), 4.57 (d, 2H, $J = 5.7$ Hz), 4.26 (q, 2H, $J = 7.1$ Hz), 1.34 (t, 3H, $J = 7.1$ Hz). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 166.2, 162.1, 138.4, 137.9, 132.4, 128.6, 127.6, 127.3, 61.7, 43.6. MS (ESI $m/z$) 256.13 [MNa$^+$, 100%].
Diethyl 3-oxo-3-phenylprop-1-en-2-ylphosphonate (1q)

Purified by flash chromatography (EP/AcOEt 50:50 as eluent), 870.2 mg, 76% yield. Colourless oil, FTIR ν\textsubscript{max} (KBr)/cm\textsuperscript{-1} 2985, 1667, 1251, 1023, 772. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): δ 7.85 (d, 2H, J = 7.4 Hz), 7.62-7.53 (m, 1H), 7.49-7.43 (m, 2H), 6.81 (d, 1H, J = 23.5 Hz), 6.28 (d, 1H, J = 45.0 Hz), 4.22-4.13 (m, 4H), 1.31 (t, 6H, J = 7.1 Hz). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): δ 193.9, 139.6, 138.3, 136.1, 133.5, 129.8, 128.5, 62.8 (d, J = 5.0 Hz), 16.2 (d, J = 6.0 Hz). MS (ESI m/z) 269.27 [MH\textsuperscript{+}, 30%], 291.24 [MNa\textsuperscript{+}, 100%], 307.20 [MK\textsuperscript{+}, 40%].

Catalyst 9b was synthesized according to literature procedure.\textsuperscript{1}

4-methyl-N-((1R, 2R)-2-(pyrrolidin-1-yl)cyclohexyl)benzenesulfonamide (9b)

Purified by flash chromatography (EP/AcOEt 50:50 as eluent), 80% yield for the alkylation step. Yellow oil, FTIR ν\textsubscript{max} (KBr)/cm\textsuperscript{-1} 2933, 1219, 1164, 772. [\textgreek{a}]\textsubscript{D}\textsuperscript{19} = -64.0 (c 0.98, CHCl\textsubscript{3}). \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): δ 7.74 (d, 2H, J = 8.1 Hz), 7.29 (d, 2H, J = 8.0 Hz), 2.69-2.58 (m, 1H), 2.51-2.34 (m, 7H), 2.19-2.05 (m, 2H), 1.80-1.72 (m, 2H), 1.64-1.52 (m, 5H), 1.28-1.04 (m, 6H), 0.93-0.79 (m, 1H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): δ 143.1, 137.0, 129.4, 127.2, 61.4, 55.2, 46.6, 32.7, 24.9, 24.2, 23.4, 21.8, 21.5. MS (ESI m/z) 323.14 [MH\textsuperscript{+}, 100%].

General procedure for the synthesis of racemic aziridines 3

A sample vial was charged with compound 1 (0.20 mmol) and amine 2 (0.20 mmol) in anhydrous toluene (4.0 mL). Triethylamine (0.20 mmol) was added and the solution was stirred at room temperature until completion (1-3 hours), monitored by TLC (eluent EP/CHCl\textsubscript{3} 30:70) Purification of the crude mixture by flash chromatography (PE/ diethyl ether 95:5 as eluent) gave racemic aziridines 3.
Procedure for the asymmetric aziridination of compounds 1

To a sample vial charged with the appropriate catalyst (0.02 mmol), K$_2$CO$_3$ (0.1 mmol) and the amine (0.1 mmol) a solution of the alkene (0.1 mmol) in anhydrous toluene (2 mL), cooled at 0°C for 10 minutes, was added and the reaction mixture stirred at 0°C. After completion, monitored by TLC (eluent EP/CHCl$_3$ 30:70), the reaction mixture was directly loaded onto silica gel and purified by flash chromatography (eluting with solvent mixtures of PE/diethyl ether) to give the corresponding chiral aziridines 3a-q.

Table 1S. Aziridination of alkene 1a with phase transfer catalysts.

<table>
<thead>
<tr>
<th>entry</th>
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<th>time (h)</th>
<th>yield (%)$^a$</th>
<th>er (%)$^b$</th>
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<td>26</td>
<td>50</td>
<td>57/43</td>
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<tr>
<td>2</td>
<td>PTC2</td>
<td>27</td>
<td>39</td>
<td>-55/44</td>
</tr>
</tbody>
</table>

$^a$Isolated yield after chromatography. $^b$Determined by chiral HPLC analysis.

(R)-1-tert-butyl 2-ethyl 2-benzoyleziridine-1,2-dicarboxylate (3a)

Purified by flash chromatography (PE/diethyl ether 95:5 as eluent), 30.3 mg, 95% yield. Colourless oil. $[\alpha]_D^{13}$ = -79.2 (c 0.9, CHCl$_3$), er 89/11. **FTIR** $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 2981, 1747, 1733, 1688, 1369, 1249, 1156, 772. **H NMR** (CDCl$_3$, 400 MHz): $\delta$ 8.24 (d, 2H, $J = 8.2$ Hz), 7.63-7.58 (m, 1H), 7.52-
7.43 (m, 2H), 4.31-4.20 (m, 1H), 2.95 (s, 1H), 2.70 (s, 1H), 1.52 (s, 9H), 1.11 (t, 3H, J = 7.2 Hz). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 190.7, 166.6, 158.0, 134.7, 133.7, 129.6, 128.4, 82.9, 62.8, 48.6, 36.4, 27.9, 13.9. MS (ESI m/z) 342.40 [MNa$^+$, 80%]. HPLC analysis with Chiralpak AS-H column, 95:5 n-hexane:2-propanol, 0.6 mL/min, detection at 254 nm; minor enantiomer $t_R = 13.3$ min, major enantiomer $t_R = 10.1$ min.

1-Benzyl 2-ethyl 2-benzoylaziridine-1,2-dicarboxylate (3b)

![Chemical Structure](image)

Purified by flash chromatography (PE/ diethyl ether 95:5 as eluent), 20.8 mg, 59% yield. Colourless oil. $[\alpha]_D^{20} = -57.4$ (c 0.7, CHCl$_3$), er 86/14. FTIR $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 2923, 1744, 1730, 1685, 1219, 772. $^1$H NMR (CDCl$_3$, 400 MHz): δ 8.22-8.16 (m, 2H), 7.62-7.52 (m, 2H), 7.48-7.36 (m, 6H), 5.25 (s, 2H), 4.24-4.04 (m, 2H), 3.04 (d, 1 H, $J = 1.28$ Hz), 2.77 (d, 1 H, 1.28 Hz), 1.06 (t, 3H, $J = 7.2$ Hz). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 190.3, 166.4, 159.4, 135.0, 134.5, 133.8, 129.5, 128.6, 128.5, 69.0, 63.0, 48.5, 36.5, 13.8. MS (ESI m/z) 376.41 [MNa$^+$, 100%]. HPLC analysis with Chiralpak AS-H column, 80:20 n-hexane:2-propanol, 1 mL/min, detection at 220 nm; minor enantiomer $t_R = 13.8$ min, major enantiomer $t_R = 10.7$ min.

Ethyl 2-benzoyl-1-tosylaziridine-2-carboxylate (3c)

![Chemical Structure](image)

Purified by flash chromatography (PE/ diethyl ether 95:5 as eluent), 22.8 mg, 61% yield. Colourless oil. $[\alpha]_D^{18} = 8.6$ (c 0.9, CHCl$_3$), er 68/32. FTIR $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 2977, 1751, 1733, 1691, 1220, 1166, 772. $^1$H NMR (CDCl$_3$, 400 MHz): δ 8.10 (d, 2H, $J = 8.2$ Hz), 7.89-7.68 (m, 2H), 7.63-7.55 (m, 1H), 7.51-7.41 (m, 2H), 7.33-7.27 (m, 2H), 4.34-4.16 (m, 2H), 3.37 (s, 1H), 2.94 (s, 1H), 2.42 (s, 3H), 1.17 (t, 3H, $J = 7.1$ Hz). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 188.9, 164.9, 144.8, 136.2, 134.3, 134.0, 129.7, 129.6, 128.5, 127.8, 63.2, 53.6, 37.3, 21.6, 13.6. MS (ESI m/z) 396.36 [MNa$^+$, 100%].
HPLC analysis with Chiralpak AS-H column, 70:30 n-hexane:2-propanol, 0.8 mL/min, detection at 220 nm; minor enantiomer $t_R = 19.3$ min, major enantiomer $t_R = 14.9$ min.

(R)-1-tert-butyl 2-methyl 2-benzoylaziridine-1,2-dicarboxylate (3d)

Purified by flash chromatography (PE/ diethyl ether 95:5 as eluent), 24.1 mg, 79% yield. Colourless oil. $[\alpha]_D^{13} = -65.8$ (c 0.9, CHCl$_3$), $er$ 89/11. FTIR $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 2979, 1751, 1733, 1688, 1370, 1251, 1156, 802. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.27-8.21 (m, 2H), 7.63-7.58 (m, 1H), 7.51-7.46 (m, 2H), 3.74 (s, 3H), 2.97 (d, 1H, $J = 1.4$ Hz), 2.70 (d, 1H, $J = 1.4$ Hz), 1.53 (s, 9H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 190.6, 167.1, 157.9, 134.5, 133.9, 129.7, 128.5, 83.0, 53.4, 48.4, 36.6, 27.9. MS (ESI m/z) 328.30 [MNa$^+$, 100%], 344.15 [MK$^+$, 5%]. HPLC analysis with Chiralpak AS-H column, 95:5 n-hexane:2-propanol, 0.6 mL/min, detection at 254 nm; minor enantiomer $t_R = 14.4$ min, major enantiomer $t_R = 10.5$ min.

(R)-di-tert-butyl 2-benzoylaziridine-1,2-dicarboxylate (3e)

Purified by flash chromatography (PE/ diethyl ether 95:5 as eluent), 28.8 mg, 83% yield. Colourless oil. $[\alpha]_D^{22} = -55.1$ (c 0.6, CHCl$_3$), $er$ 88/12. FTIR $\nu_{\text{max}}$ (KBr)/cm$^{-1}$ 2979, 2933, 1725, 1678, 1248, 1148, 772. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.24 (d, 2H, $J = 7.4$ Hz), 7.59 (t, 1H, $J = 7.4$ Hz), 7.49-7.42 (m, 2H), 2.89 (d, 1H, $J = 1.0$ Hz), 2.68 (d, 1H, $J = 1.0$ Hz), 1.54 (s, 9H), 1.30 (s, 9H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 191.0, 165.3, 158.3, 135.1, 133.4, 129.4, 128.2, 84.4, 82.7, 49.3, 35.8, 27.9, 27.6. MS (ESI m/z) 370.42 [MNa$^+$, 100%]. HPLC analysis with Chiralpak AS-H column, 95:5 n-hexane:2-propanol, 0.6 mL/min, detection at 254 nm; minor enantiomer $t_R = 9.1$ min, major enantiomer $t_R = 8.3$ min.
**(R)-2-benzyl 1-tert-butyl 2-benzoylaziridine-1,2-dicarboxylate (3f)**

Purified by flash chromatography (PE/ diethyl ether 95:5 as eluent), 30.1 mg, 79% yield. Colourless oil. $[\alpha]_D^{20} = -73.2$ ($c$ 0.5, CHCl$_3$), $er$ 86/14%. **FTIR** $\nu_{max}$ (KBr)/cm$^{-1}$ 3032, 2347, 1735, 1685, 1220, 772. **$^1$H NMR** (CDCl$_3$, 400 MHz): $\delta$ 8.19 (d, 2H, $J = 1.2$ Hz), 7.61-7.53 (m, 1H), 7.46-7.38 (m, 2H), 7.32-7.18 (m, 3H), 7.07-7.01 (m, 2H), 5.26 (d, 1H, $J = 12.3$ Hz), 5.05 (d, 1H, $J = 12.3$ Hz), 2.96 (d, 1H, $J = 1.5$ Hz), 2.75 (d, 1H, $J = 1.4$ Hz), 1.45 (s, 9H). **$^{13}$C NMR** (CDCl$_3$, 100 MHz): $\delta$ 190.4, 166.5, 157.9, 134.7, 134.4, 133.7, 129.6, 128.4, 128.1, 82.9, 68.1, 48.6, 36.4, 27.8. **MS** (ESI $m/z$) 404.27 [MNa$^+$, 100%]. HPLC analysis with Phenomenex Lux column, 90:10 $n$-hexane:2-propanol, 1.0 mL/min, detection at 254 nm; minor enantiomer $t_R = 13.8$ min, major enantiomer $t_R = 11.2$ min.

**(R)-1-tert-butyl 2-ethyl 2-(4-methylbenzoyl)aziridine-1,2-dicarboxylate (3g)**

Purified by flash chromatography (PE/ diethyl ether 95:5 as eluent), 28 mg, 84% yield. Colourless oil. $[\alpha]_D^{22} = -73.6$ ($c$ 0.5, CHCl$_3$), $er$ 89/11. **FTIR** $\nu_{max}$ (KBr)/cm$^{-1}$ 2979, 1746, 1685, 1249, 1156, 772. **$^1$H NMR** (CDCl$_3$, 400 MHz): $\delta$ 8.14 (d, 2H, $J = 8.1$ Hz), 7.27 (d, 2H, $J = 8.2$ Hz), 4.30-4.21 (m, 1H), 4.20-4.09 (m, 1H), 2.94 (s, 1H), 2.68 (s, 1H), 2.42 (s, 3H), 1.52 (s, 9H), 1.13 (t, 3H, $J = 7.1$ Hz). **$^{13}$C NMR** (CDCl$_3$, 100 MHz): $\delta$ 190.3, 166.7, 158.0, 144.8, 132.2, 129.8, 129.1, 82.8, 62.7, 48.6, 36.4, 27.9, 21.8, 13.9. **MS** (ESI $m/z$) 356.37 [MNa$^+$, 100%]. HPLC analysis with Chiralpak AS-H column, 95:5 $n$-hexane:2-propanol, 0.6 mL/min, detection at 254 nm; minor enantiomer $t_R = 14.0$ min, major enantiomer $t_R = 11.2$ min.
(R)-1-tert-butyl 2-ethyl 2-(3-methylbenzoyl)aziridine-1,2-dicarboxylate (3h)

Purified by flash chromatography (PE/ diethyl ether 95:5 as eluent), 26.7 mg, 80% yield. Colourless oil. \([\alpha]_D^{22} = -69.7 (c 0.5, \text{CHCl}_3), \text{er} 91/9\) FTIR \(v_{\text{max}}\) (KBr)/cm\(^{-1}\) 2981, 1747, 1732, 1686, 1250, 1156, 772. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 8.07 (d, 1H, \(J = 7.5\) Hz), 7.98 (s, 1H), 7.42-7.32 (m, 2H), 4.31-4.09 (m, 2H), 2.94 (d, 1H, \(J = 1.4\) Hz), 2.68 (d, 1H, \(J = 1.4\) Hz), 2.42 (s, 3H), 1.52 (s, 9H), 1.13 (t, 3H, \(J = 7.1\) Hz). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 191.0, 166.6, 158.0, 138.3, 134.7, 134.6, 129.7, 128.3, 127.1, 82.8, 62.7, 48.7, 36.5, 27.9, 21.3, 13.9. MS (ESI \(m/z\)) 334.28 [MH\(^+\), 10%], 356.43 [MNa\(^+\), 100%]. HPLC analysis with Chiralpak AS-H column, 95:5 n-hexane:2-propanol, 0.6 mL/min, detection at 254 nm; minor enantiomer \(t_R = 12.8\) min, major enantiomer \(t_R = 9.4\) min.

(R)-1-tert-butyl 2-ethyl 2-(2-methylbenzoyl)aziridine-1,2-dicarboxylate (3i)

Purified by flash chromatography (PE/ diethyl ether 95:5 as eluent), 30.3 mg, 91% yield. Colourless oil. \([\alpha]_D^{23} = -24.0 (c 0.6, \text{CHCl}_3), \text{er} 75/25\) FTIR \(v_{\text{max}}\) (KBr)/cm\(^{-1}\) 2979, 1746, 1688, 1248, 1156, 772. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 8.19-8.11 (m, 1H), 7.45-7.38 (m, 1H), 7.29- 7.27 (m, 2H), 4.25-4.13 (m, 1H), 4.12-4.05 (m, 1H), 2.90 (d, 1H, \(J = 1.6\) Hz), 2.77 (d, 1H, \(J = 1.6\) Hz), 2.54 (s, 3H), 1.49 (s, 9H), 1.06 (t, 3H, \(J = 7.1\) Hz). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 193.1, 166.7, 157.9, 139.8, 134.8, 132.2, 131.8, 130.5, 125.4, 82.8, 62.5, 49.8, 36.6, 27.9, 21.2, 13.7. MS (ESI \(m/z\)) 334.34 [MH\(^+\), 10%], 356.45 [MNa\(^+\), 100%]. HPLC analysis with Chiralpak IC column, 90:10 n-hexane:2-propanol, 1 mL/min, detection at 254 nm; minor enantiomer \(t_R = 13.6\) min, major enantiomer \(t_R = 12.5\) min.
(R)-1-tert-butyl 2-ethyl 2-(4-methoxybenzoyl)aziridine-1,2-dicarboxylate (3j)

Purified by flash chromatography (PE/ diethyl ether 95:5 as eluent), 32.5 mg, 93% yield. Colourless oil. [α]D23 = -56.6 (c 0.8, CHCl3), er 90/10. FTIR νmax (KBr)/cm⁻¹ 2982, 1746, 1678, 1251, 1156, 772. ¹H NMR (CDCl3, 400 MHz): δ 8.24 (d, 2H, J = 8.8 Hz), 6.95 (d, 2H, J = 8.8 Hz), 4.29-4.25 (m, 1H), 4.24-4.11 (m, 1H), 3.88 (s, 3H), 2.93 (d, 1H, J = 1.0 Hz), 2.66 (d, 1H, J = 1.0 Hz). ¹³C NMR (CDCl3, 100 MHz): δ 189.2, 166.8, 158.1, 132.2, 127.8, 113.7, 82.8, 62.7, 55.5, 48.6, 36.5, 27.9, 13.9. MS (ESI m/z) 372.18 [MNa⁺, 100%]. HPLC analysis with Chiralpak AS-H column, 80:20 n-hexane:2-propanol, 0.6 mL/min, detection at 254 nm; minor enantiomer tR = 12.5 min, major enantiomer tR = 10.4 min.

(R)-1-tert-butyl 2-ethyl 2-(4-chlorobenzoyl)aziridine-1,2-dicarboxylate (3k)

Purified by flash chromatography (PE/ diethyl ether 95:5 as eluent), 34.7 mg, 98% yield. Colourless oil. [α]D19 = -59.0 (c 0.6, CHCl3), er 89/11. FTIR νmax (KBr)/cm⁻¹ 2981, 1749, 1735, 1690, 1250, 1156, 772. ¹H NMR (CDCl3, 400 MHz): δ 8.22 (d, 2H, J = 8.4 Hz), 7.45 (d, 2H, J = 8.5 Hz), 4.32-4.21 (m, 1H), 4.20-4.07 (m, 1H), 2.95 (s, 1H), 2.68 (s, 1H), 1.53 (s, 9H), 1.14 (t, 3H, J = 7.1 Hz). ¹³C NMR (CDCl3, 100 MHz): δ 189.7, 166.3, 157.8, 140.3, 133.0, 131.0, 128.8, 83.1, 62.9, 48.4, 36.5, 27.9, 13.9. MS (ESI m/z) 376.19 [MNa⁺, 100%]. HPLC analysis with Chiralpak AS-H column, 98:2 n-hexane:2-propanol, 0.6 mL/min, detection at 254 nm; minor enantiomer tR = 13.5 min, major enantiomer tR = 11.5 min.
(R)-1-tert-butyl 2-ethyl 2-(3-bromobenzoyl)aziridine-1,2-dicarboxylate (3l)

Purified by flash chromatography (PE/ diethyl ether 95:5 as eluent), 34.6 mg, 87% yield. Colourless oil. [α]D24 = -52.1 (c 0.6, CHCl₃), er 85/15. FTIR νmax (KBr)/cm⁻¹ 2978, 1749, 1733, 1693, 1567, 1370, 1248, 1155, 772. ¹H NMR (CDCl₃, 400 MHz): δ 8.35 (s, 1H), 8.22 (d, 1H, J = 7.8 Hz), 7.72 (dd, 1H, J₁ = 7.9 Hz, J₂ = 0.84 Hz), 7.36 (t, 1H, J = 7.9 Hz), 4.35-4.22 (m, 1H), 4.21-4.09 (m, 1H), 2.97 (d, 1H, J = 0.6 Hz), 2.67 (d, 1H, J = 0.6 Hz), 1.54 (s, 9H), 1.15 (t, 3H, J = 7.1 Hz). ¹³C NMR (CDCl₃, 100 MHz): δ 189.7, 166.2, 157.8, 136.6, 136.5, 132.3, 130.0, 128.4, 122.8, 83.3, 62.9, 48.4, 36.5, 28.0, 13.9. MS (ESI m/z) 422.10 [MNa⁺, 100%]

(R)-1-tert-butyl 2-ethyl 2-(2-naphthoyl)aziridine-1,2-dicarboxylate (3m)

Purified by flash chromatography (PE/ diethyl ether 95:5 as eluent), 34.4 mg, 93% yield. White solid. Mp 72.5-74.0 °C. [α]D22 = -55.23 (c 0.7, CHCl₃), er 87/13. FTIR νmax (KBr)/cm⁻¹ 2980, 1746, 1733, 1683, 1250, 1156, 772. ¹H NMR (CDCl₃, 400 MHz): δ 8.90 (s, 1H), 8.23-8.18 (m, 1H), 8.01 (d, 1H, J = 8.0 Hz), 7.93-7.85 (m, 2H), 7.63-7.57 (m, 1H), 7.56-7.49 (m, 1H), 4.30-4.05 (m, 2H), 3.02 (s, 1H), 2.75 (s, 1H), 1.57 (s, 9H), 1.10 (t, 3H, J = 7.1 Hz). ¹³C NMR (CDCl₃, 100 MHz): δ 190.8, 166.7, 158.1, 135.8, 132.4, 132.2, 132.0, 129.9, 128.9, 128.2, 127.8, 126.7, 124.6, 83.0, 62.8, 48.8, 36.7, 28.0, 13.9. MS (ESI m/z) 392.16 [MNa⁺, 100%], 408.11 [MK⁺, 20%]. HPLC analysis with Chiralpak AS-H column, 95:5 n-hexane:2-propanol, 0.6 mL/min, detection at 254 nm; minor enantiomer tᵣ = 15.0 min, major enantiomer tᵣ = 12.3 min.
(R)-1-tert-butyl 2-ethyl 2-(furan-2-carbonyl)aziridine-1,2-dicarboxylate (3n)

Purified by flash chromatography (PE/ diethyl ether 95:5 as eluent), 26.6 mg, 86% yield. Colourless oil. $[\alpha]_D^{20} = -94.4$ (c 0.6, CHCl$_3$), $er$ 87/13. FTIR $\nu_{\text{max}}$ (KBr)/cm$^{-1}$: 2983, 1748, 1733, 1678, 1252, 1219, 772. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.76 (d, 1H, $J = 3.2$ Hz), 7.66 (s, 1H), 6.59-6.54 (m, 1H), 4.32-4.11 (m, 2H), 2.94 (s, 1H), 2.64 (s, 1H), 1.49 (s, 9H), 1.49-1.11 (m, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 178.6, 166.0, 157.8, 150.6, 147.7, 121.7, 112.5, 82.9, 62.8, 48.1, 36.1, 27.9, 14.0. MS (ESI m/z) 332.18 [MNa$^+$, 100%], 348.14 [MK$^+$, 20%]. HPLC analysis with Chiralpak AS-H column, 90:10 n-hexane:2-propanol, 1 mL/min, detection at 254 nm; minor enantiomer $t_R = 8.9$ min, major enantiomer $t_R = 7.9$ min.

1-tert-butyl 2-ethyl 2-(cyclohex-1-enecarbonyl)aziridine-1,2-dicarboxylate (3o)

Purified by flash chromatography (PE/ diethyl ether 95:5 as eluent), 21.7 mg, 67% yield. Colourless oil. $[\alpha]_D^{22} = -57.14$ (c 0.4, CHCl$_3$), $er$ 86/14. FTIR $\nu_{\text{max}}$ (KBr)/cm$^{-1}$: 2938, 1746, 1673, 1369, 1220, 1158, 772. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.52-7.47 (m, 1H), 4.36-4.23 (m, 1H), 4.21-4.09 (m, 1H), 2.79 (d, 1H, $J = 1.4$ Hz), 2.54 (d, 1H, $J = 1.4$ Hz), 2.38-2.12 (m, 4H), 1.73-1.58 (m, 4H), 1.49 (s, 9H), 1.24 (t, 3H, $J = 7.1$ Hz). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 191.3, 167.0, 158.1, 145.6, 137.1, 82.5, 62.5, 48.2, 36.2, 27.9, 26.3, 22.9, 21.7, 21.4, 14.0. MS (ESI m/z) 346.20 [MNa$^+$, 100%], 362.18 [MK$^+$, 25%]. HPLC analysis with Chiralpak AD-H column, 98:2 n-hexane:2-propanol, 0.6 mL/min, detection at 220 nm; minor enantiomer $t_R = 14.9$ min, major enantiomer $t_R = 13.4$ min.
1-tert-butyl 2-ethyl 2-(benzylcarbamoyl)aziridine-1,2-dicarboxylate (3p)

Purified by flash chromatography (PE/diethyl ether 95:5 as eluent), 28.6 mg, 82% yield. Colourless oil. [α]_D^{20} = -20.8 (c 0.9, CHCl_3), [α]_D^{20} = 86/14. **FTIR** ν_{max} (KBr)/cm^{-1} 2981, 1734, 1676, 1531, 1370, 1249, 1157, 772. **^1H NMR** (CDCl_3, 400 MHz): δ 7.68 (bs, 1H), 7.40-7.19 (m, 5H), 4.51 (d, 2H, J = 5.8 Hz), 4.38-4.15 (m, 2H), 2.94 (d, 1H, J = 1.1 Hz), 2.72 (d, 1H, J = 1.1 Hz), 1.43 (s, 9H), 1.31 (t, 3H, J = 7.2 Hz). **^13C NMR** (CDCl_3, 100 MHz): δ 167.0, 164.0, 157.5, 137.6, 128.7, 127.6, 82.7, 62.8, 44.7, 43.5, 37.6, 27.8, 13.9. **MS** (ESI m/z) 371.25 [MNa^+], 100%. HPLC analysis with Chiralpak AD-H column, 95:5 n-hexane:2-propanol, 1 mL/min, detection at 220 nm; minor enantiomer t_R = 17.6 min, major enantiomer t_R = 16.2 min.

tert-butyl 2-benzoyl-2-(diethoxyphosphoryl)aziridine-1-carboxylate (3q)

Purified by flash chromatography (PE/diethyl ether 95:5 as eluent), 27.6 mg, 72% yield. Colourless oil. [α]_D^{24} = 46.3 (c 0.5, CHCl_3), [α]_D^{24} = 75/25. **FTIR** ν_{max} (KBr)/cm^{-1} 2982, 1729, 1679, 1271, 1159, 1023, 772. **^1H NMR** (CDCl_3, 400 MHz): δ 8.41-8.34 (m, 2H), 7.62-7.54 (m, 1H), 7.49-7.42 (m, 2H), 4.28-4.10 (m, 4H), 3.02 (dd, 1H, J_1 = 9.4 Hz, J_2 = 0.9 Hz), 2.50 (dd, 1H, J_1 = 3.9 Hz, J_2 = 1.0 Hz), 1.56 (s, 9H), 1.33 (t, 3H, J = 7.1 Hz), 1.20 (t, 3H, J = 7.1 Hz). **^13C NMR** (CDCl_3, 100 MHz): δ 192.4 (d, J = 11 Hz), 158.3 (d, J = 9 Hz), 134.6, 133.8, 130.5, 128.1, 82.8, 63.9 (d, J = 7 Hz), 63.5 (d, J = 6 Hz), 45.8, 44.1, 33.7, 27.9, 16.1. **MS** (ESI m/z) 406. 25 [MNa^+], 100%. HPLC analysis with Chiralpak AS-H column, 95:5 n-hexane:2-propanol, 0.6 mL/min, detection at 254 nm; minor enantiomer t_R = 9.3 min, major enantiomer t_R = 12.2 min.
Enantiomerically enriched aziridine 3a (0.2 mmol, 88.5/11.5 er) dissolved in dry THF (1 mL) was treated with tetrabutylammonium fluoride (0.2 mmol, 1 M solution in THF) at 60°C. After completion of reaction, monitored by TLC (eluent EP/Ethyl acetate 60:40), the reaction was quenched with saturated NaHCO$_3$ aqueous solution and extracted with ethyl acetate (3 x 50 mL). Anhydrous Na$_2$SO$_4$ was added to the combined organic phases. After filtration of the salt, the organic phase was evaporated under reduced pressure. The residue was purified by flash chromatography (eluting with EP/ethyl ether 8:2) and isolated in 98% yield.

Deprotected aziridine 10a was dissolved in dry THF (4 mL) and at 0°C a solution of HCl·Et$_2$O (0.2 mmol) diluted in THF (0.14 M) was added dropwise. After 2 hours, the reaction mixture was treated with 5% aqueous NaHCO$_3$ solution and extracted with CH$_2$Cl$_2$ (3 x 50 mL). Anhydrous Na$_2$SO$_4$ was added to the combined organic phases. After filtration of the salt, the organic phase was evaporated under reduced pressure. The residue was directly treated with a solution of benzyl dicarbonate (1.4 equivalents) in dry THF (800 µL) at 0°C. After 2 hours, the mixture was diluted with ethyl acetate and washed with water. The aqueous phase was extracted (2 x 50 mL) with ethyl acetate. Anhydrous Na$_2$SO$_4$ was added to the combined organic phases. After filtration of the salt, the organic phase was evaporated under reduced pressure and after purification by flash chromatography (eluent EP/ethyl acetate 98:2) compound 12a was obtained in 38% yield (88.4/11.6 er).

(R)-Ethyl 2-benzyiaziridine-2-dicarboxylate (10a)
Purified by flash chromatography (EP/ethyl ether 80:20 as eluent), 43.0 mg, 98% yield. Colourless oil. \([\alpha]_D^{20} = -12.3 (c \ 0.5, \text{CHCl}_3)\). \textbf{FTIR} \(\nu_{\text{max}}\) (KBr)/cm\(^{-1}\) 2924, 2854, 1733, 1688, 1220, 772. \(^1\text{H} \textbf{NMR}\) (CDCl\(_3\), 400 MHz): \(\delta\) 7.94 (d, 2H, \(J = 7.7\) Hz), 7.88 (d, 1H, \(J = 7.7\) Hz), 7.58-7.52 (m, 2H), 7.50-7.32 (m, 3H), 4.30-3.98 (m, 6H), 2.64 (d, 1H, \(J = 9.2\) Hz), 2.47 (t, 1H, \(J = 9.6\) Hz), 2.39 (d, 1H, \(J = 10.9\) Hz), 2.33 (d, 1H, \(J = 9.0\) Hz), 2.12 (d, 1H, \(J = 10.0\) Hz), 2.06 (t, 1H, \(J = 9.5\) Hz), 1.05 (t, 3H, \(J = 7.1\) Hz), 0.99 (t, 3H, \(J = 7.0\) Hz). \(^{13}\text{C} \textbf{NMR}\) (CDCl\(_3\), 100 MHz): \(\delta\) 194.3, 191.9, 170.9, 168.9, 135.6, 135.3, 133.6, 133.5, 128.8, 128.6, 128.5, 128.3, 62.7, 62.0, 44.7, 43.1, 33.4, 32.7, 13.8, 13.6 \textbf{MS} (ESI \(m/z\)) 220.45 [MH\(^+\), 25%], 242.44 [MNa\(^+\), 100%].

\((R)-\text{Ethyl 2-amino-2-(chloromethyl)-3-oxo-3-phenylpropanoate (11a)}\)

\[
\begin{align*}
\text{Cl} & \quad \text{O} \\
\text{EtO} & \quad \text{O} \\
\text{NH}_2 & \quad \text{Ph}
\end{align*}
\]

Colourless oil. \([\alpha]_D^{22} = +15.1 (c \ 0.5, \text{CHCl}_3)\). \textbf{FTIR} \(\nu_{\text{max}}\) (KBr)/cm\(^{-1}\) 2360, 1729, 1692, 1219, 772. \(^1\text{H} \textbf{NMR}\) (CDCl\(_3\), 400 MHz): \(\delta\) 7.98 (d, 2H, \(J = 8.1\) Hz), 7.62-7.52 (m, 1H), 7.49-7.37 (m, 2H), 4.45-4.15 (m, 3H), 4.11 (d, 1H, \(J = 11.6\) Hz), 1.15 (t, 3H, \(J = 7.0\) Hz). \(^{13}\text{C} \textbf{NMR}\) (CDCl\(_3\), 100 MHz): \(\delta\) 193.4, 169.4, 134.2, 133.5, 129.0, 128.6, 69.4, 63.0, 49.2, 13.7. \textbf{MS} (ESI \(m/z\)) 256.24 [MH\(^+\), 100%].

\((R)-\text{Ethyl 2-(benzoylcarbonylamino)-2-(chloromethyl)-3-oxo-3-phenylpropanoate (12a)}\)

\[
\begin{align*}
\text{Cl} & \quad \text{O} \\
\text{EtO} & \quad \text{O} \\
\text{NH} & \quad \text{Cbz} \\
& \quad \text{Ph}
\end{align*}
\]

Purified by flash chromatography (EP/ethyl acetate 98:2 as eluent), 29.6 mg, 0.080 mmol, 38% yield over 2 steps. Colourless oil. \([\alpha]_D^{22} = +8.8 (c \ 0.5, \text{CHCl}_3)\), \(er\ 88.4/11.6\). \textbf{FTIR} \(\nu_{\text{max}}\) (KBr)/cm\(^{-1}\) 2360, 1729, 1497, 1289, 1219, 1038, 772. \(^1\text{H} \textbf{NMR}\) (CDCl\(_3\), 400 MHz): \(\delta\) 7.91 (d, 2H, \(J = 8.0\) Hz), 7.59-7.49 (m, 1H), 7.47-7.41 (m, 2H), 7.32-7.21 (m, 3H), 7.12-7.03 (m, 2H), 6.64 (s, 1H), 5.01 (d, 1H, \(J = 12.4\) Hz), 4.91 (d, 1H, \(J = 12.4\) Hz), 4.53 (d, 1H, \(J = 11.6\) Hz), 4.43 (d, 1H, \(J = 11.7\) Hz), 4.38-4.18 (m, 2H), 1.20 (t, 3H, \(J = 7.1\) Hz). \(^{13}\text{C} \textbf{NMR}\) (CDCl\(_3\), 100 MHz): \(\delta\) 190.5, 166.9, 153.9, 153.8, 135.8, 134.2, 133.4, 128.5, 128.4, 128.1, 127.7, 70.5, 67.0, 63.8, 46.6, 13.8. HPLC analysis with
Chiralpak IC column, 95:05 n-hexane:2-propanol, 0.8 mL/min, detection at 220 nm; minor enantiomer $t_R = 15.0$ min, major enantiomer $t_R = 15.6$ min.

**X-Ray Data for the Absolute Configuration Assignment of Compound 3m**

Single crystal diffraction data were collected on an Oxford Xcalibur CCD area detector diffractometer, using graphite monochromatic Mo Kα ($\lambda = 0.71069\text{Å}$) radiation. Data reduction and absorption correction were performed using CrysAlisPRO 171.34.44 (Oxford Diffraction). The structure was solved by direct methods using SIR2011 and refined by full-matrix least squares using SHELX-97. Hydrogen atoms were generated in calculated position using SHELX-97. The absolute structure of the title compound was determined on the basis of the Flack x parameter and Bayesian statistics on Bijvoet differences.

Details of data collections and refinements are given in table below.

**ORTEP plot of (3m)** with 30% probability ellipsoids (for seek of brevity H atoms are not shown).

![ORTEP plot of (3m)](image)

**Crystal data for (3m)**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C21 N1 O5 H23</td>
</tr>
<tr>
<td>Formula weight</td>
<td>369.40</td>
</tr>
<tr>
<td>Temperature</td>
<td>293(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P 21</td>
</tr>
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</table>

---

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a = 5.852(5) Å</td>
<td>α = 90°.</td>
</tr>
<tr>
<td>b = 11.039(5) Å</td>
<td>β = 96.987(5)°.</td>
</tr>
<tr>
<td>c = 15.374(5) Å</td>
<td>γ = 90°.</td>
</tr>
<tr>
<td>Volume</td>
<td>985.8(10) Å³</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.245 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.089 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>392</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.8 x 0.6 x 0.3 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>4.14 to 28.20°.</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-7 &lt;= h &lt;= 7, -14 &lt;= k &lt;= 14, -20 &lt;= l &lt;= 20</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>19850</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>4481 [R(int) = 0.0522]</td>
</tr>
<tr>
<td>Completeness to theta = 25.00∞</td>
<td>99.3 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>1.0000 and 0.86524</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>4481 / 1 / 249</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.046</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0703, wR2 = 0.1737</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.1207, wR2 = 0.1962</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.274 and -0.172 e.V.³</td>
</tr>
</tbody>
</table>
NMR Spectra

CDCl$_3$, 400 MHz
CDCl$_3$, 100 MHz
CDCl$_3$, 400 MHz
CDCl₃, 100 MHz
CDCl₃, 100 MHz
CDCl₃, 400 MHz

![NMR Spectrum of Compound](image-url)
CDCl₃, 100 MHz
CDCl₃, 400 MHz
CDCl$_3$, 100 MHz

S31
CDCl$_3$, 400 MHz
CDCl$_3$, 100 MHz
CDCl₃, 100 MHz
CDCl₃, 100 MHz
CDCl$_3$, 100 MHz
CDCl$_3$, 400 MHz
CDCl₃, 100 MHz
CDCl₃, 400 MHz
CDCl$_3$, 100 MHz
CDCl₃, 400 MHz
CDCl$_3$, 100 MHz
CDCl₃, 100 MHz
CDCl₃, 400 MHz
CDCl₃, 400 MHz
CDCl₃, 100 MHz
CDCl₃, 400 MHz
CDCl₃, 100 MHz
CDCl₃, 400 MHz
CDCl$_3$, 100 MHz

S55
CDCl₃, 400 MHz
CDCl₃, 100 MHz
CDCl₃, 400 MHz
CDCl₃, 100 MHz
CDCl₃, 400 MHz
CDCl₃, 400 MHz
CDCl₃, 100 MHz
CDCl₃, 400 MHz
CDCl₃, 100 MHz
CDCl₃, 400 MHz
CDCl$_3$, 100 MHz
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CDCl$_3$, 400 MHz
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CDCl₃, 400 MHz
CDCl$_3$, 100 MHz
CDCl$_3$, 400 MHz
CDCl$_3$, 100 MHz
CDCl$_3$, 400 MHz
CDCl₃, 100 MHz
CDCl₃, 400 MHz
CDCl$_3$, 100 MHz

S81
CDCl₃, 400 MHz
CDCl₃, 100 MHz
CDCl$_3$, 400 MHz
CDCl₃, 100 MHz
CDCl₃, 100 MHz
CDCl₃, 100 MHz
CDCl₃, 400 MHz
CDCl₃, 100 MHz
CDCl₃, 100 MHz
CDCl₃, 400 MHz
CDCl₃, 100 MHz

S94
CDCl₃, 100 MHz
HPLC chromatograms:

<table>
<thead>
<tr>
<th>Peak Name</th>
<th>RT (min)</th>
<th>Area (V*sec)</th>
<th>% Area</th>
<th>Height (V)</th>
<th>% Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak1</td>
<td>9.986</td>
<td>25133725</td>
<td>48.10</td>
<td>1302294</td>
<td>63.85</td>
</tr>
<tr>
<td>Peak2</td>
<td>13.211</td>
<td>27123847</td>
<td>51.90</td>
<td>737264</td>
<td>36.15</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Peak Name</th>
<th>RT (min)</th>
<th>Area (V*sec)</th>
<th>% Area</th>
<th>Height (V)</th>
<th>% Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak1</td>
<td>10.085</td>
<td>7536961</td>
<td>89.19</td>
<td>491760</td>
<td>92.72</td>
</tr>
<tr>
<td>Peak2</td>
<td>13.315</td>
<td>913404</td>
<td>10.81</td>
<td>38591</td>
<td>7.28</td>
</tr>
</tbody>
</table>
### Peak 1

<table>
<thead>
<tr>
<th>Peak Name</th>
<th>RT (min)</th>
<th>Area (V*sec)</th>
<th>% Area</th>
<th>Height (V)</th>
<th>% Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak1</td>
<td>12.565</td>
<td>6264943</td>
<td>49.97</td>
<td>321801</td>
<td>52.96</td>
</tr>
<tr>
<td>Peak2</td>
<td>13.661</td>
<td>6272114</td>
<td>50.03</td>
<td>285832</td>
<td>47.04</td>
</tr>
</tbody>
</table>

### Peak 2

<table>
<thead>
<tr>
<th>Peak Name</th>
<th>RT (min)</th>
<th>Area (V*sec)</th>
<th>% Area</th>
<th>Height (V)</th>
<th>% Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak1</td>
<td>12.497</td>
<td>2376444</td>
<td>74.57</td>
<td>124306</td>
<td>77.00</td>
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<tr>
<td>Peak2</td>
<td>13.608</td>
<td>810470</td>
<td>25.43</td>
<td>37129</td>
<td>23.00</td>
</tr>
</tbody>
</table>
### Peak 1
- **RT (min):** 6.166
- **Area (V*sec):** 14183540
- **% Area:** 49.43
- **Height (V):** 1325006
- **% Height:** 63.54

### Peak 2
- **RT (min):** 7.499
- **Area (V*sec):** 14510924
- **% Area:** 50.57
- **Height (V):** 760224
- **% Height:** 36.46

### Peak 1
- **RT (min):** 7.436
- **Area (V*sec):** 857060
- **% Area:** 15.30
- **Height (V):** 51341
- **% Height:** 9.78
### Peak 1:
- RT (min): 9.369
- Area (\(\text{V}^*\text{sec}\)): 5604775
- % Area: 50.00
- Height (\(\text{V}\)): 242490
- % Height: 57.63

### Peak 2:
- RT (min): 12.314
- Area (\(\text{V}^*\text{sec}\)): 5604248
- % Area: 50.00
- Height (\(\text{V}\)): 179065
- % Height: 42.47

### Peak 1:
- RT (min): 9.346
- Area (\(\text{V}^*\text{sec}\)): 11543546
- % Area: 25.36
- Height (\(\text{V}\)): 496584
- % Height: 31.70

### Peak 2:
- RT (min): 12.150
- Area (\(\text{V}^*\text{sec}\)): 33967575
- % Area: 74.64
- Height (\(\text{V}\)): 1070001
- % Height: 68.30