Supplementary Material (ESI) for Chemical Communications
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SUPPORTING INFORMATION
Rh(II)-Catalysed Room Temperature Aziridination of Homoallyl-Carbamates

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General Procedures
Reactions were performed in flame-dried glassware under an atmosphere of argon. Starting materials were obtained from commercial suppliers and used without further purification. \(\text{C}_6\text{H}_6\) was distilled from \(\text{CaH}_2\) and stored over 3 Å MS before use. Molecular sieves were activated by heating over a Bunsen flame under reduced pressure. Thin layer chromatography was carried out on Merck silica 60 gel glass-backed plates. Plates were visualised by exposure to UV light followed by staining with basic potassium permanganate solution. Flash chromatography was carried out using Merck silica gel 60 as the stationary phase. Melting points were recorded on Gallenkamp MPD350.BM2.5 apparatus and are uncorrected. Microanalytical data were obtained using an Exeter Analytical CE-440 elemental analyser. Proton NMR spectra were recorded using either a Bruker DRX500 or AV400 MHz spectrometer at 298 K. Data are expressed as chemical shifts in parts per million (p.p.m.) relative to residual chloroform (\(\delta 7.27\)) as internal standard on the \(\delta\) scale. The multiplicity of each signal is designated by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; app, apparent; b, broad. All coupling constants are quoted in Hertz (Hz). Carbon NMR spectra were recorded using Bruker DRX500 or AV400 MHz spectrometers at 298 K. Data are expressed as chemical shifts in p.p.m. relative to D-chloroform (\(\delta 77.16\)) as internal standard on the \(\delta\) scale. Infra-red spectra were recorded using a Nicolet Avatar 320 FT-IR spectrophotometer.
using liquid films or ATR for solids. High-resolution mass spectra were acquired on VG micromass 70E and MM70E instruments using electron ionisation (EI), chemical ionisation (CI) and electrospray ionisation (ES). All carbamates were prepared from the corresponding alcohol following the general procedure of Kocovsky.\(^1\) Iodosylbenzene, PhIO, was prepared according to the procedure of Sharefkin and Saltzman.\(^2\) Enantiomeric excesses (e.e.) were determined by integration of the specified peaks in the \(^1\)H-NMR spectrum, using the given mass of compound in solvent (1.5 mL), with the specified loading of europium tris[3-(heptafluoropropylhydroxymethylene)-(+)camphorate], Eu(hfc)$_3$, chiral shift reagent.

**General Procedure A**

Carbamate, iodobenzene diacetate, PhI(OAc)$_2$, (2.0 eq.), MgO (3.3 eq.), and rhodium(II) acetate dimer, Rh$_2$(OAc)$_4$, (0.05 eq.) were stirred at 23 °C in CH$_2$Cl$_2$ (0.1 M solution of carbamate) for 24 h. The reaction mixture was then filtered through Celite\(^\circledR\) and the filter cake washed with CH$_2$Cl$_2$. The filtrate was concentrated under reduced pressure and the resulting crude oil was purified by flash column chromatography over silica, SiO$_2$.

**General Procedure B**

Carbamate, PhIO (2.0 eq.) and rhodium dimer catalyst (0.05 eq.) were stirred at 23 °C in benzene (0.1 M solution of carbamate) for 24 h. over activated 3 Å molecular sieves. The reaction mixture was then filtered through Celite\(^\circledR\) and the filter cake washed with

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\(^1\) Kocovsky, P. *Tetrahedron Lett.* 1986, **27**, 5521-5524.

CH$_2$Cl$_2$. The filtrate was concentrated under reduced pressure and the resulting crude oil was purified by flash column chromatography over SiO$_2$.

**Trans-7-ethyl-3-oxa-1-aza-bicyclo[4.1.0]heptan-2-one (2a) & ((E)-4-but-1-enyloxa-2-one (2b)**

Prepared following General Procedure A with carbamic acid (E)-hex-3-enyl ester 1 (201.7 mg, 1.41 mmol), PhI(OAc)$_2$ (0.907 g, 2.82 mmol), MgO (0.187 g, 4.65 mmol) and Rh$_2$(OAc)$_4$ (31.1 mg, 0.071 mmol) and CH$_2$Cl$_2$ (14.1 mL). Purification was by flash column chromatography over SiO$_2$ (petroleum ether 40-60/Et$_2$O (1:4)) to afford recovered 1 (27.2 mg, 13 %). Further elution afforded 2b (52.7 mg, 26 %) as a yellow oil: R$_f$ = 0.21 (petroleum ether 40-60/Et$_2$O (1:4)); $\nu_{\text{max}}$/cm$^{-1}$ (film) 3286, 2966, 2934, 1754; $\delta_{\text{H}}$ (400 MHz, CDCl$_3$) 5.78 (1H, dtd, $J$ 15.3, 6.3, 0.5), 5.41 (2H, bs & ddt, $J$ 15.3, 8.0, 1.6), 4.51 (1H, appt, $J$ 8.5), 4.38 – 4.33 (1H, m), 4.04 (1H, dd, $J$ 8.5, 7.0), 2.11 – 2.04 (2H, m), 1.01 (3H, t, $J$ 7.5); $\delta_{\text{C}}$ (400 MHz, CDCl$_3$) 159.5 (C), 137.7 (CH), 126.6 (CH), 70.5 (CH$_2$), 55.2 (CH), 25.2 (CH$_2$), 13.2 (CH$_3$); m/z (ES+) 142.0867 (M+H, C$_7$H$_{12}$NO$_2$ requires 142.0868), 174 (100 %, M+MeOH+H), 164 (20, M+Na) 142 (98, M+H). Further elution afforded 2a (90.6 mg, 46 %) as a yellow oil: R$_f$ = 0.12 (petroleum ether 40-60/Et$_2$O (1:4)); $\nu_{\text{max}}$/cm$^{-1}$ (film) 2968, 2933, 2877, 1720, 1464; $\delta_{\text{H}}$ (400 MHz, CDCl$_3$) 4.40 (1H, ddd, $J$ 12.5, 10.6, 1.9), 4.29 (1H, ddd, $J$ 10.6, 4.2, 1.9), 2.60 (1H, ddd, $J$ 9.0, 6.2, 3.3), 2.35 (1H, ddt, $J$ 14.6, 6.2, 1.9), 2.23 (1H, apptd, $J$ 6.0, 3.3), 1.66 – 1.59 (2H, m),
1.44 – 1.34 (1H, m), 1.06 (3H, t, J 7.4); δC (400 MHz, CDCl3) 161.0 (C), 68.2 (CH2), 50.1 (CH), 40.0 (CH), 25.2 (CH2), 25.1 (CH2), 10.6 (CH3); m/z (ES+) 142.0874 (M+H, C7H12NO2 requires 142.0868), 164 (100 %, M+Na), 142 (31, M+H).

Prepared following General Procedure B with carbamic acid (E)-hex-3-enyl ester 1 (200.2 mg, 1.40 mmol), PhIO (0.615 g, 2.80 mmol), Rh2(OAc)4 (30.9 mg, 0.070 mmol) and benzene (14.0 mL). Purification was by flash column chromatography (petroleum ether 40-60/Et2O (1:4)) yielding 2b (27.6 mg, 14 %). The data were identical with those reported previously (vide supra). Further elution afforded 2a (134.2 mg, 68 %). The data were identical with those reported previously (vide supra).

Prepared following General Procedure B with carbamic acid (E)-hex-3-enyl ester 1 (205.1 mg, 1.43 mmol), PhIO (0.630 g, 2.86 mmol), Rh2(Oct)4 (55.8 mg, 0.072 mmol) and benzene (14.3 mL). Purification was by flash column chromatography (petroleum ether 40-60/Et2O (1:4)) yielding 2b (11.4 mg, 6 %). The data were identical with those reported previously (vide supra). Further elution afforded 2a (143.5 mg, 71 %). The data were identical with those reported previously (vide supra).

Prepared following General Procedure B with carbamic acid (E)-hex-3-enyl ester 1 (208.3 mg, 1.46 mmol), PhIO (0.640 g, 2.92 mmol), Rh2(S-TBSP)4 (105.3 mg, 0.073 mmol) and benzene (14.5 mL). Purification was by flash column chromatography (petroleum ether 40-60/Et2O (1:4)) yielding 2b (25.4 mg, 12 %). The data were identical with those reported previously (vide supra). Further elution afforded 2a (135.6 mg, 66
The data were identical with those reported previously (*vide supra*); *e.e.* 6% (2a (7.7 mg), 10 mol% Eu(hfc)$_3$, $C_6D_6$, CH$_3$, 1.01/1.06 p.p.m. 1:0.88).

((E)-4-But-1-enyl)-oxazolidin-2-one (2b)

Prepared following General Procedure B with carbamic acid (E)-hex-3-enyl ester 1 (40.9 mg, 0.29 mmol), PhIO (0.126 g, 0.58 mmol), Rh$_2$(S-MeOX)$_4$ (12.3 mg, 0.015 mmol) and benzene (2.9 mL). Purification was by flash column chromatography (petroleum ether 40-60/Et$_2$O (1:4)) yielding 2b (16.4 mg, 40%). The data were identical with those reported previously (*vide supra*); *e.e.* 23% (2b (3.1 mg), 5 mol% Eu(hfc)$_3$, CDCl$_3$, CH$_3$, 0.90/0.94 p.p.m. 1:0.62).

Cis-7-ethyl-3-oxa-1-aza-bicyclo[4.1.0]heptan-2-one (4a) & ((Z)-4-but-1-enyl)-oxazolidin-2-one (4b)

Prepared following General Procedure A with carbamic acid (Z)-hex-3-enyl ester 3 (201.0 mg, 1.40 mmol), PhI(OAc)$_2$ (0.904 g, 2.80 mmol), MgO (0.187 g, 4.62 mmol) and Rh$_2$(OAc)$_4$ (31.0 mg, 0.070 mmol) and CH$_2$Cl$_2$ (14.0 mL). Purification was by flash
column chromatography over SiO₂ (petroleum ether 40-60/Et₂O (1:4)) to afford recovered 3 (39.6 mg, 20 %). Further elution afforded 4b (37.1 mg, 19 %) as a yellow oil: Rf = 0.24 (petroleum ether 40-60/Et₂O (1:4)); \( \nu_{\text{max}}/\text{cm}^{-1} \) (film) 3280, 2967, 2935, 1752; \( \delta_H \) (400 MHz, CDCl₃) 5.76 (1H, bs), 5.64 (1H, dtd, \( J \) 10.8, 7.6, 1.0), 5.38 (1H, ddt, \( J \) 10.8, 9.0, 1.5), 4.77 – 4.71 (1H, m), 4.52 (1H, appt, \( J \) 8.5), 4.00 (1H, dd, \( J \) 8.5, 7.4), 2.17 – 2.00 (2H, m), 0.99 (3H, t, \( J \) 7.5); \( \delta_C \) (400 MHz, CDCl₃) 159.9 (C), 137.3 (CH), 126.9 (CH), 70.5 (CH₂), 49.6 (CH), 21.0 (CH₂), 14.4 (CH₃); \( m/z \) (ES⁺) 164.0682 (M+Na, C₇H₁₁NNaO₂ requires 164.0682), 305 (24 %, 2M+Na), 164 (100, M+Na). Further elution afforded 4a (88.6 mg, 45 %) as a yellow oil: Rf = 0.12 (petroleum ether 40-60/Et₂O (1:4)); \( \nu_{\text{max}}/\text{cm}^{-1} \) (film) 2969, 2939, 2907, 2879, 1720, 1469; \( \delta_H \) (400 MHz, CDCl₃) 4.39 (1H, ddd, \( J \) 12.0, 10.5, 1.9), 4.33 (1H, ddd, \( J \) 10.5, 4.9, 1.9), 2.89 (1H, ddd, \( J \) 9.0, 6.9, 5.0), 2.60 (1H, ddd, \( J \) 8.3, 5.3, 5.0), 2.18 (1H, appddt, \( J \) 14.7, 6.9, 1.9), 1.86 (1H, ddq, \( J \) 14.8, 7.3, 5.3), 1.47 (1H, ddd, \( J \) 14.7, 12.0, 9.0, 4.9), 1.23 (1H, m), 1.10 (3H, appt, \( J \) 7.3); \( \delta_C \) (400 MHz, CDCl₃) 158.8 (C), 68.0 (CH₂), 44.1 (CH), 37.3 (CH), 19.1 (CH₂), 19.1 (CH₂), 10.9 (CH₃); \( m/z \) (EI⁺) 142.0867 (M+H, C₇H₁₂NO₂ requires 142.0868), 142 (19 %, M+H), 112 (4, M-C₂H₅), 96 (9, M-CHO₂), 82 (40, M-CO₂-CH₃), 68 (100, M-C₃H₅O₂).

Prepared following General Procedure B with carbamic acid (Z)-hex-3-enyl ester 3 (199.5 mg, 1.39 mmol), PhIO (0.613 g, 2.78 mmol), Rh₂(OAc)₄ (30.8 mg, 0.070 mmol) and benzene (13.9 mL). Purification was by flash column chromatography (petroleum ether 40-60/Et₂O (1:2)) yielding 4b and 2b (34.6 mg, 18 %) in a 21:1 (Z:E) ratio as a yellow oil. The data recorded were identical with those reported previously (vide supra).
Further elution afforded 4a (114.0 mg, 58 %). The data recorded were identical with those reported previously (vide supra).

Prepared following General Procedure B with carbamic acid (Z)-hex-3-enyl ester 3 (218.6 mg, 1.53 mmol), PhIO (0.672 g, 3.06 mmol), Rh2(Oct)4 (59.4 mg, 0.077 mmol) and benzene (15.3 mL). Purification was by flash column chromatography (petroleum ether 40-60/Et2O (1:4)) yielding 2b (27.0 mg, 13 %). The data were identical with those reported previously (vide supra). Further elution afforded 2a (151.0 mg, 70 %). The data were identical with those reported previously (vide supra).

Prepared following General Procedure B with carbamic acid (Z)-hex-3-enyl ester 3 (41.7 mg, 0.29 mmol), PhIO (0.128 g, 0.58 mmol), Rh2(S-TBSP)4 (21.1 mg, 0.015 mmol) and benzene (2.9 mL). Purification was by flash column chromatography (petroleum ether 40-60/Et2O (1:4)) yielding 4b (5.3 mg, 13 %). The data recorded were identical to those reported previously (vide supra); e.e. 3 % (4b (5.3 mg), 25 mol% Eu(hfc)3, C6D6, CH3, 0.78/0.74 p.p.m. 1:0.95). Further elution afforded 4a (29.2 mg, 71 %). The data recorded were identical to those reported previously (vide supra); e.e. 23% (4a (3.9 mg), 5 mol% Eu(hfc)3, C6D6, CH3, 0.86/0.92 p.p.m. 1:0.63).

Prepared following General Procedure B with carbamic acid (Z)-hex-3-enyl ester 3 (41.7 mg, 0.29 mmol), PhIO (0.128 g, 0.58 mmol), Rh2(S-MeOX)4 (12.6 mg, 0.015 mmol) and benzene (2.9 mL). Purification was by flash column chromatography (petroleum ether 40-60/Et2O (1:4)) yielding 4b (12.5 mg, 30 %). The data recorded were identical to those
reported previously (*vide supra*); e.e. 10 % (4b (1.6 mg), 50 mol% Eu(hfc)₃, C₆D₆, CH₃, 0.70/0.74 p.p.m. 1:0.81). Further elution afforded 4a (13.0 mg, 31 %). The data recorded were identical to those reported previously (*vide supra*); e.e. 11% (4a (4.8 mg), 10 mol% Eu(hfc)₃, C₆D₆, CH₃, 0.99/1.06 p.p.m. 1:0.80).

*Trans*-7-(acetyloxymethyl)-3-oxa-1-aza-bicyclo[4.1.0]heptan-2-one (5a) & (*E*)-3-(2-oxo-oxazolidin-4-yl)-allyl acetate (5b)

![Chemical structures](image)

Prepared following General Procedure B with acetic acid (*E*)-5-carbamoyloxy-pent-2-enyl ester 13 (108.2 mg, 0.58 mmol), PhIO (0.254 g, 1.16 mmol), Rh₂(OAc)₄ (12.8 mg, 0.029 mmol) and benzene (5.8 mL). Purification was by flash column chromatography (petroleum ether 40-60/EtOAc (1:3)) yielding 5b (18.2 mg, 17 %) as a yellow oil: R₇ = 0.27 (petroleum ether 40-60/EtOAc (1:4)); \( \nu_{\text{max}}/\text{cm}^{-1} \) (film) 3307, 2941, 1738, 1733, 1682; \( \delta_H \) (400 MHz, CDCl₃) 5.86 (1H, dt, \( J = 15.5, 5.4 \)), 5.75 (1H, dd, \( J = 15.5, 7.3 \)), 5.61 (1H, bs), 4.58 (2H, d, \( J = 5.4 \)), 4.55 (1H, appt, \( J = 8.5 \)), 4.46 – 4.40 (1H), 4.08 (1H, dd, \( J = 18.5, 6.5 \)), 2.10 (3H, s); \( \delta_C \) (400 MHz, CDCl₃) 170.7(C), 159.3 (C), 131.2 (CH), 128.8 (CH), 70.0 (CH₂), 63.4 (CH₂), 54.3 (CH), 21.0 (CH₃); \( m/z \) (EI+) 186.0774 (M+H, C₈H₁₂NO₄ requires 186.0766), 186 (6 %, M+H), 125 (100, M – C₂H₄O₂), 67 (26). Further elution afforded 5a (41.7 mg, 39 %) as a yellow oil: R₇ = 0.24 (petroleum ether 40-60/EtOAc (1:4)); \( \nu_{\text{max}}/\text{cm}^{-1} \) (film) 2960, 1733; \( \delta_H \) (400 MHz, CDCl₃) 4.44 (1H, ddd, \( J = 12.3, 10.7, 3.8 \)), 4.42 (1H, dd, \( J = 15.5, 8.5 \)).
1.9), 4.34 (1H, ddd, J 10.7, 4.2, 1.9), 4.20 (2H, appd, J 5.5), 2.79, (1H, ddd, J 8.6, 6.3, 3.1), 2.58 (1H, apptd, J 5.5, 3.1), 2.41 (1H, appddt, J 14.7, 6.3, 1.9), 2.12 (3H, s), 1.45 (1H, ddd, J 14.7, 12.3, 8.6, 4.2); δC (400 MHz, CDCl3) 170.8 (C), 159.9 (C), 68.2 (CH2), 63.8 (CH2), 44.9 (CH), 38.6 (CH), 24.8 (CH2), 20.9 (CH3); m/z (ES+) 186.0745 (M +H, C8H12NO4 requires 186.0766), 186 (42 %, M+ H), 142 (24, M – CO2 + H), 126 (14, M – OAc), 100 (100), 68 (86, M – CO2 – AcOCH2).

*Trans*-7-(acetyloxymethyl)-3-oxa-1-aza-bicyclo[4.1.0]heptan-2-one (5a)

Prepared following General Procedure B with acetic acid (*E*)-5-carbamoyloxypent-2-enyl ester 13 (50.1 mg, 0.27 mmol), PhIO (0.118 g, 0.54 mmol), Rh2(S-TBSP)4 (19.4 mg, 0.014 mmol) and benzene (2.7 mL). Purification was by flash column chromatography (petroleum ether 40-60/EtOAc (1:4)) yielding 5a (38.6 mg, 78 %). The data recorded were identical with those reported previously (*vide supra*); e.e. 12% (5a (4.0 mg), 10 mol% Eu(hfc)3, C6D6, CH3, 1.79/1.80 p.p.m. 1:0.79).

(*E*)-3-(2-oxo-oxazolidin-4-yl)-allyl acetate (5b)

S9
Prepared following General Procedure B with acetic acid (E)-5-carbamoyloxy-pent-2-enyl ester 13 (53.4 mg, 0.29 mmol), PhIO (0.126 g, 0.58 mmol), Rh$_2$(S-MeOX)$_4$ (12.3 mg, 0.015 mmol) and benzene (2.9 mL). Purification was by flash column chromatography (petroleum ether 40-60/EtOAc (1:4)) yielding recovered 13 (9.8 mg, 18 %). Further elution afforded 5b (17.4 mg, 33 %). The data recorded were identical with those reported previously (vide supra); e.e. 16% (5b (3.3 mg), 10 mol% Eu(hfc)$_3$, C$_6$D$_6$, CH$_3$, 1.65/1.67 p.p.m. 1:0.73).

**Trans-7-(benzyloxymethyl)-3-oxa-1-aza-bicyclo[4.1.0]heptan-2-one (6a) & 4-((E)-3-benzyloxy-propenyl)-oxazolidin-2-one (6b)**

Prepared following General Procedure B with carbamic acid (E)-5-benzyloxy-pent-3-enyl ester 14 (224.9 mg, 0.96 mmol), PhIO (0.421 g, 1.92 mmol), Rh$_2$(OAc)$_4$ (21.1 mg, 0.048 mmol) and benzene (9.6 mL). Purification was by flash column chromatography (petroleum ether 40-60/Et$_2$O (1:4) to neat Et$_2$O) yielding recovered 14 (30.2 mg, 13 %). Further elution yielded 6b (17.8 mg, 8 %) as a yellow oil: R$_f$ = 0.22 (Et$_2$O); $\nu_{\text{max}}$/cm$^{-1}$ (film) 3300, 2915, 2856, 1750, 1651; $\delta_{\text{H}}$ (400 MHz, CDCl$_3$) 7.37 – 7.30 (5H, m), 5.88 (1H, dt, $J$ 15.5, 5.1), 5.76 (1H, dd, $J$ 15.5, 7.6), 4.99 (1H, bs), 4.55 (2H, s), 4.54 (1H, app, $J$ 8.5), 4.44 – 4.39 (1H, m), 4.07 (1H, dd, $J$ 8.5, 6.7), 4.04 (2H, dd, $J$ 5.1, 1.0); $\delta_{\text{C}}$ (500 MHz, CDCl$_3$) 159.0 (C), 137.9 (C), 131.6 (CH), 129.6 (CH), 128.6 (2 $\times$ CH), 128.0 (CH), 127.9 (2 $\times$ CH), 73.0 (CH$_2$), 70.2 (CH$_2$), 69.4 (CH$_2$), 54.6 (CH); m/z (EI+)
142.0510 (M-Bn, C₆H₈NO₃ requires 142.0504), 234 (4 %, M+H), 127 (32, M-OBn+H), 91 (100, Bn). Further elution afforded 6a (69.1 mg, 31 %) as a yellow oil: R_f = 0.29 (petroleum ether 40-60/EtOAc (1:2)); \nu_{\text{max}}/\text{cm}^{-1} (\text{film}) 3030, 2904, 2861, 1725; \delta_{\text{H}} (500 MHz, CDCl₃) 7.49 – 7.29 (5H, m), 4.65 (1H, d, J 11.9), 4.60 (1H, d, J 11.9), 4.42 (1H, ddd, J 12.4, 10.6, 1.9), 4.32 (1H, ddd, J 10.6, 4.2, 1.9), 3.80 (1H, ddd, J 11.1, 4.7), 3.53 (1H, dd, J 11.1, 5.3), 2.78 (1H, ddd, J 8.7, 6.3, 3.2), 2.52 (1H, ddd, J 5.3, 4.7, 3.2), 2.37 (1H, appddt, J 14.7, 6.3, 1.9), 1.42 (1H, dddd, J 14.7, 12.4, 8.7, 4.2); \delta_{\text{C}} (500 MHz, CDCl₃) 160.5 (C), 137.7 (C), 128.6 (2 × CH), 128.1 (3 × ArCH), 73.5 (CH₂), 69.3 (CH₂), 68.3 (CH₂), 46.4 (CH), 38.3 (CH), 24.9 (CH₂); m/z (ES+) 256.0953 (M + Na, C₁₃H₁₅NNaO₃ requires 256.0950), 489 (54 %, 2M + Na), 256 (100, M + Na), 190 (2, M – CO₂ + H).

**Trans-7-(benzyloxymethyl)-3-oxa-1-aza-bicyclo[4.1.0]heptan-2-one (6a)**

\[
\begin{align*}
\text{BnO} & \quad \text{O} \\
\text{O} & \quad \text{NH}_2 \\
\text{14} & \quad \text{6a}
\end{align*}
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Prepared following General Procedure B with carbamic acid (E)-5-benzyloxy-pent-3-enyl ester 14 (66.0 mg, 0.28 mmol), PhIO (0.123 g, 0.56 mmol), Rh₂(S-TBSP)₄ (20.3 mg, 0.014 mmol) and benzene (2.8 mL). Purification was by flash column chromatography (petroleum ether 40-60/EtOAc (1:2)) yielding 6a (43.3 mg, 66 %). The data recorded were identical to those reported previously (vide supra); e.e. 18% (6a (4.4 mg), 10 mol% Eu(hfc)₂, C₆D₆, NCH, 2.32/2.39 p.p.m. 1:0.70).
Spirocyclic aziridine (7a), 4-cyclohex-1-enyl-oxazolidin-2-one (7b) & carbamic acid 2-(7-oxa-bicyclo[4.1.0]hept-1-yl)-ethyl ester (16)

Prepared following General Procedure B with carbamic acid 2-cyclohex-1-enyl-ethyl ester 15 (210.9 mg, 1.15 mmol), PhIO (0.548 g, 2.30 mmol), Rh₂(OAc)₄ (27.5 mg, 0.058 mmol) and benzene (12.5 mL). Purification was by flash column chromatography (petroleum ether 40-60/Et₂O (1:4)) yielding recovered 15 (30.9 mg, 15 %), and an impure orange oil containing 7b and 16. Further elution afforded 7a (53.8 mg, 26 %) as a white solid: mp 75.0 – 76.5 °C; Rₚ = 0.14 (petroleum ether 40-60/Et₂O (1:4)); ν_max/cm⁻¹ (ATR) 2935, 2866, 1705; δ_H (400 MHz, CDCl₃) 4.42 (1H, ddd, J 12.4, 10.7, 1.9), 4.27 (1H, ddd, J 10.7, 4.0, 2.0), 2.56 (1H, appd, J 5.0), 2.18 – 2.06 (3H, m), 1.96 – 1.91 (1H, m), 1.67 (1H, ddd, J 14.1, 8.6, 5.5), 1.56 – 1.47 (3H, m), 1.40 – 1.39 (1H, m), 1.29 – 1.25 (1H, m); δ_C (500 MHz, CDCl₃) 162.1, (C), 67.0 (CH₂), 49.0 (CH), 42.9 (C), 32.7 (CH₂), 29.5 (CH₂), 24.0 (CH₂), 20.0 (CH₂), 19.6 (CH₂); m/z (EI+) 167.0945 (M, C₉H₁₃NO₂ requires 167.0946), 167 (22 %, M), 94 (100, M-H-CH₂OC(O)NH₂), 67 (59, M-C₄H₆NO₂). The mixture of 7b and 16 was purified by flash column chromatography over SiO₂ (2 % MeOH/CH₂Cl₂) to yield 7b (9.3 mg, 5 %) as a white solid: mp 53.0-55.0 °C; Rₚ = 0.20 (petroleum ether 40-60/Et₂O (1:4)); ν_max/cm⁻¹ (ATR) 3249, 2932, 2856, 1727, 1707; δ_H (CDCl₃, 400 MHz) 5.74 – 5.73 (1H, m), 5.14 (1H, bs), 4.49 (1H, appd, J 8.5), 4.31 (1H, dd, J 8.5, 6.1), 4.11 (1H, dd, J 8.5, 6.1), 2.04 – 2.02 (2H, m, CH₂), 1.99 – 1.94 (2H, m CH₂), 1.71 – 1.55 (4H, m, 2 × CH₂); δ_C (CDCl₃, 400 MHz) 159.7 (C), 135.0 (C), 126.1
Spirocyclic aziridine (7a)

Prepared following General Procedure B with carbamic acid 2-cyclohex-1-enyl-ethyl-ester 15 (102.4 mg, 0.61 mmol), PhIO (0.266 g, 1.22 mmol), Rh2(S-TBSP)4 (36.9 mg, 0.026 mmol) and benzene (6.05 mL). Purification was by flash column chromatography (petroleum ether 40-60/Et2O (1:7)) yielding 7a as a white solid (60.4 mg, 60 %). The data recorded were identical to those reported previously (vide supra); e.e. 8% (7a (2.0 mg), 20 mol% Eu(hfc)3, C6D6, CHHO, 4.11/4.25 p.p.m. 1:0.86).
6-Methyl-3-oxa-1-aza-bicyclo[4.1.0]heptan-2-one (8a) & 4-isopropenyl-oxazolidin-2-one (8b)

Prepared following General Procedure B with carbamic acid 3-methyl-but-3-enyl ester 17 (271 mg, 2.10 mmol), PhIO (0.924 g, 4.20 mmol), Rh$_2$(OAc)$_4$ (46.4 mg, 0.105 mmol) and benzene (21.0 mL). Purification was by flash column chromatography (petroleum ether 40-60/Et$_2$O (1:1)) yielding recovered starting material (77.5 mg, 29 %). Further elution afforded 8b (15.4 mg, 5 %) as a white solid: mp 48.0 – 49.5 °C; R$_f$ = 0.15 (petroleum ether 40-60/Et$_2$O (1:4)); $\nu_{\text{max}}$/cm$^{-1}$ (ATR) 3234, 3136, 1730, 1656; $\delta_{\text{H}}$ (400 MHz, CDCl$_3$) 5.04 (1H, bd, $J$ 0.8 & 1H, bs), 4.97 (1H, bs), 4.55 (1H, appt, $J$ 8.7), 4.38 (1H, dd, $J$ 8.8, 6.1), 4.11 (1H, dd, $J$ 8.5, 6.1), 1.78 (3H, s); $\delta_{\text{C}}$ (500 MHz, CDCl$_3$) 159.3 (C), 142.4 (C), 113.9 (CH$_2$), 69.3 (CH$_2$), 57.7 (CH), 17.3 (CH$_3$); m/z (ES+) M+Na (150.0525, C$_6$H$_9$NNaO$_2$ requires 150.0525), 150 (100 %, M+Na), 128 (22, M+H). Further elution afforded 8a (92.7 mg, 35 %) as a yellow oil; R$_f$ = 0.12 (Et$_2$O); $\nu_{\text{max}}$/cm$^{-1}$ (ATR) 2969, 1698; $\delta_{\text{H}}$ (400 MHz, CDCl$_3$) 4.45 (1H, ddd, $J$ 12.4, 10.7, 1.9), 4.31 (1H, ddd, $J$ 10.7, 4.0, 2.0), 2.40 (1H, s), 2.20 (1H, s), 2.12 (1H, appdt, $J$ 14.5, 1.9), 1.48 (1H, ddd, $J$ 14.5, 12.4, 4.0), 1.39 (3H, s); $\delta_{\text{C}}$ (400 MHz, CDCl$_3$) 161.8 (C), 66.8 (CH$_2$), 42.6 (CH$_2$), 39.6 (C), 30.9 (CH$_2$), 22.1 (CH$_3$); m/z (EI+) 128.0707 (M+H, C$_6$H$_9$NO$_2$ requires 128.0712), 128 (20 %, M+H), 82 (46, C$_3$H$_8$N), 68 (17, M-C$_2$H$_3$O$_2$), 55 (100).
Glacial AcOH (2.0 eq., 0.09 mL, 1.54 mmol) was added dropwise to a stirring ice-cooled solution of trans-7-ethyl-3-oxa-1-aza-bicyclo[4.1.0]heptan-2-one 2a (108.7 mg, 0.77 mmol) in THF (2.0 mL). The reaction mixture was then allowed to attain 23 °C, and after complete consumption of starting material (48 h.) the reaction mixture was taken up with water (5 mL) and CHCl₃ (5 mL). The aqueous layer was neutralised by addition of sat. aq. NaCO₃. The aqueous layer was extracted with CHCl₃ (3 × 5 mL), dried (MgSO₄) and concentrated by evaporation under reduced pressure to yield a yellow oil. This was purified by flash column chromatography over SiO₂ (NH₃-saturated petroleum ether 40-60/EtOAc (1:3)) to yield 9 (122.4 mg, 88 %) as a white solid: mp 77.0 – 78.5 °C; Rᶠ = 0.15 (petroleum ether 40-60/EtOAc (1:3)); υmax/cm⁻¹ (ATR) 3237, 3127, 2976, 1727; δH (400 MHz, CDCl₃) 5.36 (1H, bs), 4.92 (1H, td, J 6.6, 4.3), 4.37 (1H, dt, J 11.2, 4.3), 4.20 (1H, ddd, J 11.2, 9.8, 3.5), 3.67 (1H, dddd, J 9.9, 5.4, 4.3, 1.1), 2.11 (3H, s), 1.99 – 1.85 (2H, m), 1.67 – 1.60 (2H, m), 0.95 (3H, t, J 7.4); δC (400 MHz, CDCl₃) 171.0 (C), 154.0 (C), 75.0 (CH), 65.3 (CH₂), 53.5 (CH), 22.6 (CH₂), 22.4 (CH₂), 21.1 (CH₃), 10.0 (CH₃); m/z (ES+) 224.0898 (M+Na, C₉H₁₅NNaO₄ requires 224.0893), 425 (44 %, 224 (100, M+Na).
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SUPPORTING INFORMATION

**Syn-1-(2-oxo-[1,3]-oxazinan-4-yl)-propyl acetate (10)**

Glacial AcOH (2.0 eq., 0.09 mL, 1.54 mmol) was added dropwise to a stirring ice-cooled solution of cis-7-ethyl-3-oxa-1-aza-bicyclo[4.1.0]heptan-2-one 4a (108.7 mg, 0.77 mmol) in THF (2.0 mL). The reaction mixture was then allowed to attain 23 °C and was stirred for 48 h. The reaction mixture was diluted with CHCl₃ (5 mL) and water (5 mL), and the aq. layer neutralised with sat. aq. NaHCO₃ solution. The aq. layer was extracted with CHCl₃ (3 × 5 mL), dried (MgSO₄) and concentrated by evaporation under reduced pressure to afford a yellow oil. This was purified by flash column chromatography over SiO₂ (NH₃-saturated petroleum ether 40-60/EtOAc (1:3)) to yield 10 (115.1 mg, 74 %) a white solid: mp 104.0 – 106.0 °C; R₇ = 0.13 (petroleum ether 40-60/EtOAc (1:3)); v_max/cm⁻¹ (ATR) 3246, 3127, 2936, 1721, 1700; δ_H (400 MHz, CDCl₃) 5.50 (1H, bs, NH), 4.77 (1H, td, J 7.3, 4.3), 4.36 (1H, dt, J 11.1, 4.2), 4.22 (1H, td, J 11.1, 2.8), 3.65 – 3.60 (1H, m), 2.14 (3H, s), 2.03 – 1.96 (1H, m), 1.84 – 1.69 (2H, m), 1.63 – 1.52 (1H, m), 0.93 (3H, t, J 7.5); δ_C (400 MHz, CDCl₃) 170.7 (C), 153.8 (C), 76.6 (CH), 65.2 (CH₂), 52.5 (CH), 24.2 (CH₂), 23.6 (CH₂), 21.1 (CH₃), 9.2 (CH₃); m/z (ES+) 202.1080 (M+H, C₉H₁₆NO₄ requires 202.1074), 425 (42 %, 2M+Na), 403 (20, 2M+H), 224 (81, M+Na), 202 (100, M+H), 142 (10, M+H).

**Anti-4-(1-chloro-propyl)-[1,3]oxazinan-2-one (11)**
HCl (1N, 0.25 mL) was added to a solution of \textit{trans}-7-ethyl-3-oxa-1-aza-bicyclo[4.1.0]heptan-2-one 2a (35.3 mg, 0.25 mmol) in 1,4-dioxane (0.5 mL) and water (0.5 mL) at 23 °C for 24 h. The reaction mixture was extracted with CH$_2$Cl$_2$ (10 mL) and the aq. layer neutralised with aq. K$_2$CO$_3$. The aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 10 mL) and the combined organic layers dried (MgSO$_4$) and concentrated under reduced pressure to afford a white solid. This was purified by flash column chromatography over SiO$_2$ (5 % MeOH/CH$_2$Cl$_2$) to yield 11 (27.7 mg, 62 %) as a white solid: (found: C, 46.92; H, 6.69; N, 7.49; C$_7$H$_{12}$ClNO$_2$ requires C, 47.33; H, 6.81; N, 7.89); mp 81.0 – 82.0 °C; $R_f$ = 0.32 (5 % MeOH/CH$_2$Cl$_2$); $\nu_{\text{max}}$/cm$^{-1}$ (ATR) 3230, 3125, 2675, 1686, 1494; $\delta_H$ (400 MHz, CDCl$_3$) 6.06 (1H, bs), 4.36 (1H, ddd, $J$ 11.3, 5.0, 4.3), 4.25 (1H, ddd, $J$ 11.3, 9.0, 3.7), 3.83 (1H, ddd, $J$ 9.5, 6.0, 3.2), 3.71 (1H, apptdd, $J$ 6.6, 6.0, 1.4), 2.16 – 2.02 (2H, m), 1.91 (1H, dqq, $J$ 14.5, 7.3, 3.2), 1.71 (1H, ddq, $J$ 14.5, 9.5, 7.3), 1.11 (3H, t, $J$ 7.3); $\delta_C$ (400 MHz, CDCl$_3$) 154.3 (C), 66.1 (CH), 64.9 (CH$_2$), 55.2 (CH), 26.6 (CH$_2$), 23.7 (CH$_2$), 11.1 (CH$_3$); $m/z$ (EI+) 177.0548 (M, C$_7$H$_{12}$ClNO$_2$ requires 177.0557), 177 (5 %, M), 100 (100, M-C$_3$H$_6$Cl), 56 (95).

\textit{Syn-4-(1-phenylsulfanyl-propyl)}-[1,3]oxazinan-2-one (12)
PhSH (1.2 eq., 88 μL, 0.86 mmol) was added to a solution of cis-7-ethyl-3-oxa-1-aza-bicyclo[4.1.0]heptan-2-one 4a (101 mg, 0.72 mmol) in CH₂Cl₂ (1.0 mL) at 23 °C. After stirring at 23 °C for 14 h, the reaction mixture was concentrated by evaporation under reduced pressure, and the resulting white/brown solid was purified by flash column chromatography over SiO₂ (NH₃-saturated petroleum ether 40-60/EtOAc (1:1)) to afford 12 (163.4 mg, 91 %) as a white solid: mp 124.0 – 126.0 °C; Rf = 0.08 (NH₃-saturated petroleum ether 40-60/EtOAc (1:1)); νmax/cm⁻¹ (ATR) 3255, 3132, 2968, 1689; δH (400 MHz, CDCl₃) 7.47 – 7.43 (2H, m), 7.36 – 7.32 (3H, m), 6.00 (1H, bs), 4.37 (1H, ddd, J 11.2, 4.2, 2.9), 4.17 (1H, apptd, J 11.6, 2.3), 3.39 (1H, ddd, J 10.5, 8.5, 4.8), 2.73 (1H, ddd, J 9.5, 8.5, 3.5), 2.12 – 2.06 (1H, m), 1.85 – 1.72 (2H, m), 1.42 (1H, ddq, J 14.5, 9.5, 7.3), 1.17 (3H, t, J 7.3); δC (400 MHz, CDCl₃) 153.8 (C), 133.8 (2 × CH), 132.2 (C), 129.4 (2 × CH), 128.4 (CH), 65.7 (CH₂), 57.6 (CH), 53.2 (CH), 25.9 (CH₂), 23.2 (CH₂), 11.5 (CH₃); m/z (ES+) 252.1046 (M+H, C₁₃H₁₃NO₂S requires 252.1064) 525 (63 %, 2M+Na), 503 (20, 2M+H), 274 (60, M+Na), 252 (100, M+H).