Supplementary Material (ESI) for Chemical Communications

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. C_6H_6 was distilled from 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 (δ 7.27) as internal standard on the δ 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 (δ 77.16) as internal standard on the δ 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_2Cl_2 (0.1 M solution of carbamate) for 24 h. The reaction mixture was then filtered through Celite® and the filter cake washed with CH_2Cl_2. The filtrate was concentrated under reduced pressure and the resulting crude oil was purified by flash column chromatography over silica, SiO_2.

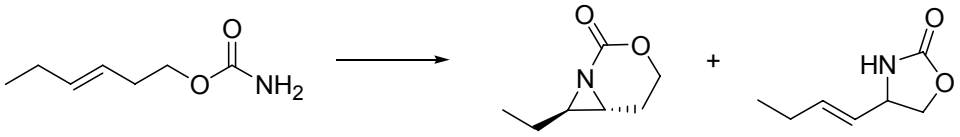
General Procedure B

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® and the filter cake washed with

[1] Kocovsky, P. *Tetrahedron Lett.* 1986, **27**, 5521-5524.
[2] Saltzman, H.; Sharefkin, J. G. *Org. Synth.*, 1973, **5**, 658-659.

CH_2Cl_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-enyl)-oxazolidin-2-one (2b)**



1 **2a** **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_2Cl_2 (14.1 mL). Purification was by flash column chromatography over SiO_2 (petroleum ether 40-60/Et_2O (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_2O (1:4)); υ_{max}/cm^{-1} (film) 3286, 2966, 2934, 1754; δ_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); δ_C (400 MHz, $CDCl_3$) 159.5 (*C*), 137.7 (*C*H), 126.6 (*C*H), 70.5 (CH_2), 55.2 (*C*H), 25.2 (CH_2), 13.2 (CH_3); *m/z* (ES+) 142.0867 (M+H, $C_7H_{12}NO_2$ 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_2O (1:4)); υ_{max}/cm^{-1} (film) 2968, 2933, 2877, 1720, 1464; δ_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); δ_C (400 MHz, $CDCl_3$) 161.0 (*C*), 68.2 (*C*H_2), 50.1 (*C*H), 40.0 (*C*H), 25.2 (*C*H_2), 25.1 (*C*H_2), 10.6 (*C*H_3); *m/z* (ES+) 142.0874 (M+H, $C_7H_{12}NO_2$ requires 142.0868), 164 (100 %, M+Na), 142 (31, M+H).

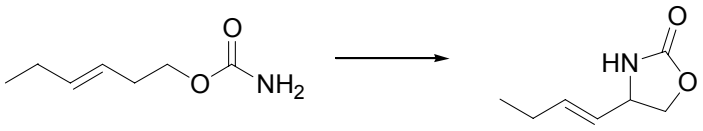
Prepared following General Procedure B with carbamic acid (*E*)-hex-3-enyl ester **1** (200.2 mg, 1.40 mmol), PhIO (0.615 g, 2.80 mmol), $Rh_2(OAc)_4$ (30.9 mg, 0.070 mmol) and benzene (14.0 mL). Purification was by flash column chromatography (petroleum ether 40-60/Et_2O (1:4)) yielding **2b** (27.6 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), $Rh_2(Oct)_4$ (55.8 mg, 0.072 mmol) and benzene (14.3 mL). Purification was by flash column chromatography (petroleum ether 40-60/Et_2O (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), Rh_2(*S*-TBSP)$_4$ (105.3 mg, 0.073 mmol) and benzene (14.5 mL). Purification was by flash column chromatography (petroleum ether 40-60/Et_2O (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).

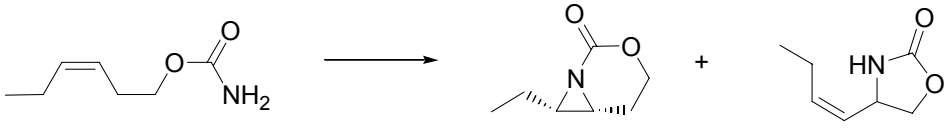
((*E*)-4-But-1-enyl)-oxazolidin-2-one (2b)



1 **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_2O (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)**



3 **4a** **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_2Cl_2 (14.0 mL). Purification was by flash

column chromatography over SiO_2 (petroleum ether 40-60/Et_2O (1:4)) to afford recovered **3** (39.6 mg, 20 %). Further elution afforded **4b** (37.1 mg, 19 %) as a yellow oil: R_f = 0.24 (petroleum ether 40-60/Et_2O (1:4)); υ_{max}/cm^{-1} (film) 3280, 2967, 2935, 1752; δ_H (400 MHz, $CDCl_3$) 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); δ_C (400 MHz, $CDCl_3$) 159.9 (*C*), 137.3 (*C*H), 126.9 (*C*H), 70.5 (*C*H_2), 49.6 (*C*H), 21.0 (*C*H_2), 14.4 (*C*H_3); *m/z* (ES+) 164.0682 (M+Na, $C_7H_{11}NNaO_2$ requires 164.0682), 305 (24 %, 2M+Na), 164 (100, M+Na). Further elution afforded **4a** (88.6 mg, 45 %) as a yellow oil: R_f = 0.12 (petroleum ether 40-60/Et_2O (1:4)); υ_{max}/cm^{-1} (film) 2969, 2939, 2907, 2879, 1720, 1469; δ_H (400 MHz, $CDCl_3$) 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, dddd, *J* 14.7, 12.0, 9.0, 4.9), 1.23 (1H, m), 1.10 (3H, appt, *J* 7.3); δ_C (400 MHz, $CDCl_3$) 158.8 (*C*), 68.0 (*C*H_2), 44.1 (*C*H), 37.3 (*C*H), 19.1 (*C*H_2), 19.1 (*C*H_2), 10.9 (*C*H_3); *m/z* (EI+) 142.0867 (M+H, $C_7H_{12}NO_2$ requires 142.0868), 142 (19 %, M+H), 112 (4, M-C_2H_5), 96 (9, M-CHO_2), 82 (40, M-CO_2-CH_3), 68 (100, M-$C_3H_5O_2$).

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), $Rh_2(OAc)_4$ (30.8 mg, 0.070 mmol) and benzene (13.9 mL). Purification was by flash column chromatography (petroleum ether 40-60/Et_2O (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*).

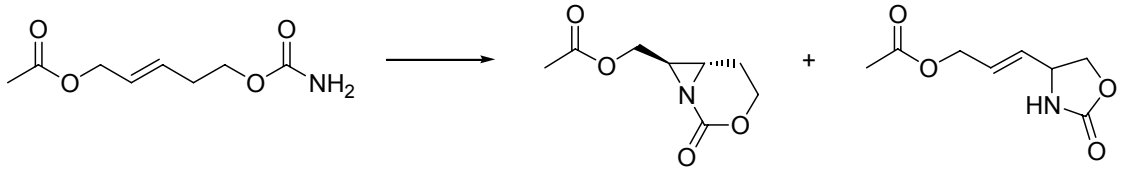
Prepared following General Procedure B with carbamic acid (*Z*)-hex-3-enyl ester **3** (218.6 mg, 1.53 mmol), PhIO (0.672 g, 3.06 mmol), $Rh_2(Oct)_4$ (59.4 mg, 0.077 mmol) and benzene (15.3 mL). Purification was by flash column chromatography (petroleum ether 40-60/Et_2O (1:4)) yielding **2b** (27.0 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), Rh_2(*S*-TBSP)$_4$ (21.1 mg, 0.015 mmol) and benzene (2.9 mL). Purification was by flash column chromatography (petroleum ether 40-60/Et_2O (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)$_3$, C_6D_6, C*H*$_3$, 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)$_3$, C_6D_6, C*H*$_3$, 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), Rh_2(*S*-MeOX)$_4$ (12.6 mg, 0.015 mmol) and benzene (2.9 mL). Purification was by flash column chromatography (petroleum ether 40-60/Et_2O (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)$_3$, C_6D_6, C*H*$_3$, 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)$_3$, C_6D_6, C*H*$_3$, 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)**

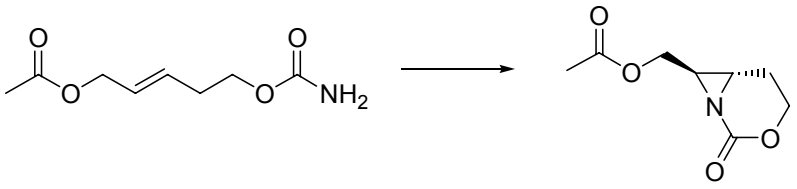


13 **5a** **5b**

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), $Rh_2(OAc)_4$ (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: R_f = 0.27 (petroleum ether 40-60/EtOAc (1:4)); υ_{max}/cm^{-1} (film) 3307, 2941, 1738, 1733, 1682; δ_H (400 MHz, $CDCl_3$) 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* 8.5, 6.5), 2.10 (3H, s); δ_C (400 MHz, $CDCl_3$) 170.7(*C*), 159.3 (*C*), 131.2 (*C*H), 128.8 (*C*H), 70.0 (*C*H_2), 63.4 (*C*H_2), 54.3 (*C*H), 21.0 (*C*H_3); *m/z* (EI+) 186.0774 (M+H, $C_8H_{12}NO_4$ requires 186.0766), 186 (6 %, M+H), 125 (100, M – $C_2H_4O_2$), 67 (26). Further elution afforded **5a** (41.7 mg, 39 %) as a yellow oil: R_f = 0.24 (petroleum ether 40-60/EtOAc (1:4)); υ_{max}/cm^{-1} (film) 2960, 1733; δ_H (400 MHz, $CDCl_3$) 4.44 (1H, ddd, *J* 12.3, 10.7,

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, dddd, *J* 14.7, 12.3, 8.6, 4.2); δ_C (400 MHz, $CDCl_3$) 170.8 (*C*), 159.9 (*C*), 68.2 (*C*H_2), 63.8 (*C*H_2), 44.9 (*C*H), 38.6 (*C*H), 24.8 (*C*H_2), 20.9 (*C*H_3); *m/z* (ES+) 186.0745 (M +H, $C_8H_{12}NO_4$ requires 186.0766), 186 (42 %, M+ H), 142 (24, M – CO_2 + H), 126 (14, M – OAc), 100 (100), 68 (86, M – CO_2 – $AcOCH_2$).

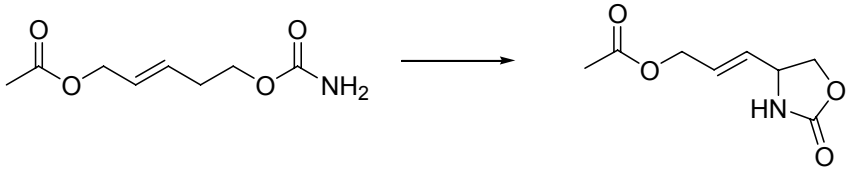
***Trans*-7-(acetyloxymethyl)-3-oxa-1-aza-bicyclo[4.1.0]heptan-2-one (5a)**



13 **5a**

Prepared following General Procedure B with acetic acid (*E*)-5-carbamoyloxy-pent-2-enyl ester **13** (50.1 mg, 0.27 mmol), PhIO (0.118 g, 0.54 mmol), Rh_2(*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)$_3$, C_6D_6, C*H*$_3$, 1.79/1.80 p.p.m. 1:0.79).

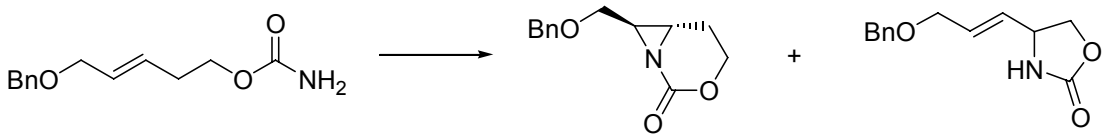
(*E*)-3-(2-oxo-oxazolidin-4-yl)-allyl acetate (5b)



13 **5b**

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_6D_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)**

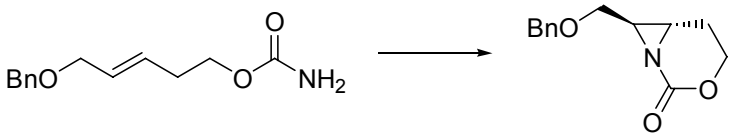


14 **6a** **6b**

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_2O (1:4) to neat Et_2O) yielding recovered **14** (30.2 mg, 13 %). Further elution yielded **6b** (17.8 mg, 8 %) as a yellow oil: R_f = 0.22 (Et_2O); υ_{max}/cm^{-1} (film) 3300, 2915, 2856, 1750, 1651; δ_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, appt, *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); δ_C (500 MHz, $CDCl_3$) 159.0 (*C*), 137.9 (*C*), 131.6 (*C*H), 129.6 (*C*H), 128.6 (2 × *C*H), 128.0 (*C*H), 127.9 (2 × *C*H), 73.0 (*C*H$_2$), 70.2 (*C*H$_2$), 69.4 (*C*H$_2$), 54.6 (*C*H); *m/z* (EI+)

142.0510 (M-Bn, $C_6H_8NO_3$ 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)); υ_{max}/cm^{-1} (film) 3030, 2904, 2861, 1725; δ_H (500 MHz, $CDCl_3$) 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, dd, *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); δ_C (500 MHz, $CDCl_3$) 160.5 (*C*), 137.7 (*C*), 128.6 (2 × *C*H), 128.1 (3 × Ar*C*H), 73.5 (*C*H_2), 69.3 (*C*H_2), 68.3 (*C*H_2), 46.4 (*C*H), 38.3 (*C*H), 24.9 (*C*H_2); *m/z* (ES+) 256.0953 (M + Na, $C_{13}H_{15}NNaO_3$ requires 256.0950), 489 (54 %, 2M + Na), 256 (100, M + Na), 190 (2, M – CO_2 + H).

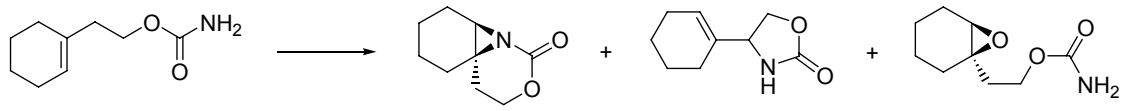
***Trans*-7-(benzyloxymethyl)-3-oxa-1-aza-bicyclo[4.1.0]heptan-2-one (6a)**



14 **6a**

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), Rh_2(*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)$_3$, C_6D_6, NC*H*, 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)

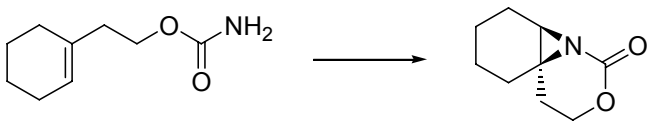


15 **7a** **7b** **16**

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), $Rh_2(OAc)_4$ (27.5 mg, 0.058 mmol) and benzene (12.5 mL). Purification was by flash column chromatography (petroleum ether 40-60/Et_2O (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; R_f = 0.14 (petroleum ether 40-60/Et_2O (1:4)); υ_{max}/cm^{-1} (ATR) 2935, 2866, 1705; δ_H (400 MHz, $CDCl_3$) 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, $CDCl_3$) 162.1, (*C*), 67.0 (*C*H_2), 49.0 (*C*H), 42.9 (*C*), 32.7 (*C*H_2), 29.5 (*C*H_2), 24.0 (*C*H_2), 20.0 (*C*H_2), 19.6 (*C*H_2); *m/z* (EI+) 167.0945 (M, $C_9H_{13}NO_2$ requires 167.0946), 167 (22 %, M), 94 (100, M-H-$CH_2OC(O)NH_2$), 67 (59, M-$C_4H_6NO_2$). The mixture of **7b** and **16** was purified by flash column chromatography over SiO_2 (2 % MeOH/CH_2Cl_2) to yield **7b** (9.3 mg, 5 %) as a white solid: mp 53.0-55.0 °C; R_f = 0.20 (petroleum ether 40-60/Et_2O (1:4)); υ_{max}/cm^{-1} (ATR) 3249, 2932, 2856, 1727, 1707; δ_H ($CDCl_3$, 400 MHz) 5.74 – 5.73 (1H, m), 5.14 (1H, bs), 4.49 (1H, appt, *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, C*H*$_2$), 1.99 – 1.94 (2H, m C*H*$_2$), 1.71 – 1.55 (4H, m, 2 × C*H*$_2$); δ_C ($CDCl_3$, 400 MHz) 159.7 (*C*), 135.0 (*C*), 126.1

(*C*H), 69.4 (*C*H_2), 58.3 (*C*H), 25.0 (*C*H_2), 23.2 (*C*H_2), 22.4 (*C*H_2), 22.3 (*C*H_2); *m/z* (EI+) 167.0950 (M, $C_9H_{13}NO_2$ requires 167.0946), 167 (100 %, M), 138 (39, M-C_2H_5), 108 (25, M-$C_2H_3O_2$). Further elution afforded **16** (5.8 mg, 3 %) as a white solid: mp 68.0 – 69.0 °C; R_f = 0.08 (petroleum ether 40-60/Et_2O (1:1)); υ_{max}/cm^{-1} (ATR) 3375, 3262, 3207, 2940, 2867, 1716, 1622; δ_H (400 MHz, $CDCl_3$) 4.69 (2H, bs), 4.24 (1H, appdt, *J* 11.1, 6.5), 4.16 (1H, appdt, *J* 11.1, 6.5), 3.00 (1H, appd, *J* 3.4), 1.97 – 1.74 (6H, m), 1.50 – 1.38 (2H, m), 1.32 – 1.19 (2H, m); δ_C (500 MHz, $CDCl_3$) 156.7 (*C*), 61.7 (*C*H_2), 58.4 (*C*H), 58.1 (*C*), 37.1 (*C*H_2), 28.1 (*C*H_2), 24.8 (*C*H_2), 20.2 (*C*H_2), 19.6 (*C*H_2); *m/z* (ES+) 208.0941 (M+Na, $C_9H_{15}NO_3$ requires 208.0949), 208 (100 %, M+Na), 125 (26, M-OC(O)NH_2).

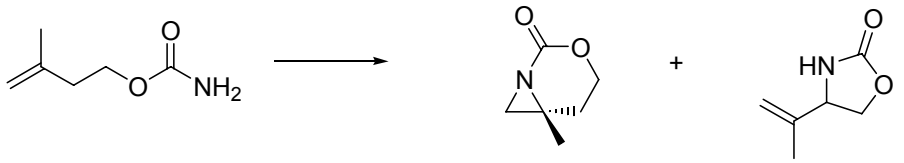
Spirocyclic aziridine (7a)



15 **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), Rh_2(*S*-TBSP)$_4$ (36.9 mg, 0.026 mmol) and benzene (6.05 mL). Purification was by flash column chromatography (petroleum ether 40-60/Et_2O (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)$_3$, C_6D_6, C*H*HO, 4.11/4.25 p.p.m. 1:0.86).

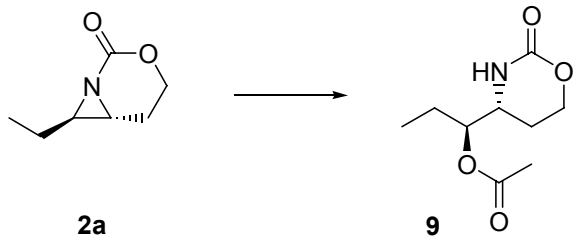
6-Methyl-3-oxa-1-aza-bicyclo[4.1.0]heptan-2-one (8a) & 4-isopropenyl-oxazolidin-2-one (8b)



17 **8a** **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_2O (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_2O (1:4)); υ_{max}/cm^{-1} (ATR) 3234, 3136, 1730, 1656; δ_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); δ_C (500 MHz, $CDCl_3$) 159.3 (*C*), 142.4 (*C*), 113.9 (*C*H_2), 69.3 (*C*H_2), 57.7 (*C*H), 17.3 (*C*H_3); *m/z* (ES+) M+Na (150.0525, $C_6H_9NNaO_2$ 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_2O); υ_{max}/cm^{-1} (ATR) 2969, 1698; δ_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); δ_C (400 MHz, $CDCl_3$) 161.8 (*C*), 66.8 (*C*H_2), 42.6 (*C*H_2), 39.6 (*C*), 30.9 (*C*H_2), 22.1 (*C*H_3); *m/z* (EI+) 128.0707 (M+H, $C_6H_{10}NO_2$ requires 128.0712), 128 (20 %, M+H), 82 (46, C_5H_8N), 68 (17, M-$C_2H_3O_2$), 55 (100).

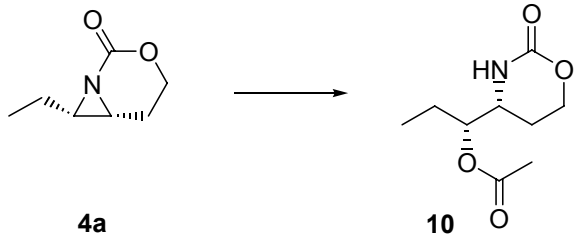
***Anti*-1-(2-oxo-[1,3]-oxazinan-4-yl)-propyl acetate (9)**



2a **9**

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 $CHCl_3$ (5 mL). The aqueous layer was neutralised by addition of sat. aq. $NaCO_3$. The aqueous layer was extracted with $CHCl_3$ (3 × 5 mL), dried ($MgSO_4$) and concentrated by evaporation under reduced pressure to yield a yellow oil. This was purified by flash column chromatography over SiO_2 (NH_3-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; R_f = 0.15 (petroleum ether 40-60/EtOAc (1:3)); υ_{max}/cm^{-1} (ATR) 3237, 3127, 2976, 1727; δ_H (400 MHz, $CDCl_3$) 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); δ_C (400 MHz, $CDCl_3$) 171.0 (*C*), 154.0 (*C*), 75.0 (*C*H), 65.3 (CH_2), 53.5 (*C*H), 22.6 (CH_2), 22.4 (CH_2), 21.1 (CH_3), 10.0 (CH_3); *m/z* (ES+) 224.0898 (M+Na, $C_9H_{15}NNaO_4$ requires 224.0893), 425 (44 %, 224 (100, M+Na).

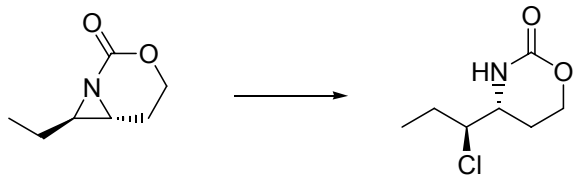
Syn-1-(2-oxo-[1,3]-oxazinan-4-yl)-propyl acetate (10)



4a **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 $CHCl_3$ (5 mL) and water (5 mL), and the aq. layer neutralised with sat. aq. $NaHCO_3$ solution. The aq. layer was extracted with $CHCl_3$ (3 × 5 mL), dried ($MgSO_4$) and concentrated by evaporation under reduced pressure to afford a yellow oil. This was purified by flash column chromatography over SiO_2 (NH_3-saturated petroleum ether 40-60/EtOAc (1:3)) to yield **10** (115.1 mg, 74 %) a white solid: mp 104.0 – 106.0 °C; R_f = 0.13 (petroleum ether 40-60/EtOAc (1:3)); υ_{max}/cm^{-1} (ATR) 3246, 3127, 2936, 1721, 1700; δ_H (400 MHz, $CDCl_3$) 5.50 (1H, bs, N*H*), 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, $CDCl_3$) 170.7 (*C*), 153.8 (*C*), 76.6 (*C*H), 65.2 (CH_2), 52.5 (*C*H), 24.2 (CH_2), 23.6 (CH_2), 21.1 (CH_3), 9.2 (CH_3); *m/z* (ES+) 202.1080 (M+H, $C_9H_{16}NO_4$ requires 202.1074), 425 (42 %, 2M+Na), 403 (20, 2M+H), 224 (81, M+Na), 202 (100, M+H), 142 (10, M+H).

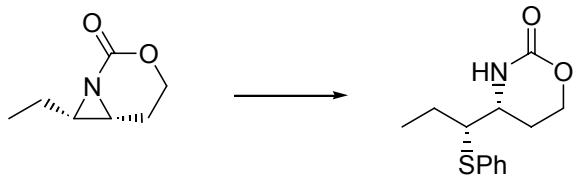
Anti-4-(1-chloro-propyl)-[1,3]oxazinan-2-one (11)



2a **11**

HCl (1N, 0.25 mL) was added to a solution of *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_2Cl_2 (10 mL) and the aq. layer neutralised with aq. K_2CO_3. The aqueous layer was extracted with CH_2Cl_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_2Cl_2) to yield **11** (27.7 mg, 62 %) as a white solid: (found: C, 46.92; H, 6.69; N, 7.49; $C_7H_{12}ClNO_2$ requires C, 47.33; H, 6.81; N, 7.89); mp 81.0 – 82.0 °C; R_f = 0.32 (5 % MeOH/CH_2Cl_2); υ_{max}/cm^{-1} (ATR) 3230, 3125, 2675, 1686, 1494; δ_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, dqd, *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); δ_C (400 MHz, $CDCl_3$) 154.3 (*C*), 66.1 (*C*H), 64.9 (CH_2), 55.2 (*C*H), 26.6 (CH_2), 23.7 (CH_2), 11.1 (CH_3); *m/z* (EI+) 177.0548 (M, $C_7H_{12}{}^{35}ClNO_2$ requires 177.0557), 177 (5 %, M), 100 (100, M-C_3H_6Cl), 56 (95).

Syn-4-(1-phenylsulfanyl-propyl)-[1,3]oxazinan-2-one (12)



4a **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 CH_2Cl_2 (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 SiO_2 (NH_3-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; R_f = 0.08 (NH_3-saturated petroleum ether 40-60/EtOAc (1:1)); υ_{max}/cm^{-1} (ATR) 3255, 3132, 2968, 1689; δ_H (400 MHz, $CDCl_3$) 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); δ_C (400 MHz, $CDCl_3$) 153.8 (*C*), 133.8 (2 × *C*H), 132.2 (*C*), 129.4 (2 × *C*H), 128.4 (*C*H), 65.7 (*C*H_2), 57.6 (*C*H), 53.2 (*C*H), 25.9 (*C*H_2), 23.2 (*C*H_2), 11.5 (*C*H_3); *m/z* (ES+) 252.1046 (M+H, $C_{13}H_{18}NO_2S$ requires 252.1064) 525 (63 %, 2M+Na), 503 (20, 2M+H), 274 (60, M+Na), 252 (100, M+H).