Supplementary Material for Organic & Biomolecular Chemistry

The dihydrofuran template approach to furofuran synthesis

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3-(3',4'-Methylenedioxyphenyl)prop-2-en-1-ol[1] **7b**

A solution of carboethoxytriphenylphosphorane (30 g, 84 mmol) in benzene (5 mL) was added to a solution of piperonal (7.2 g, 48 mmol) under N_2. The reaction mixture was then heated under reflux for 60 hours. The mixture was then concentrated and the residue suspended in ether : petrol (1 : 1). Filtration through a bed of silica and Celite removed the insoluble phosphorus by-products and afforded *ethyl 3-(3',4'-methylenedioxyphenyl)prop-2-enoate*[2] (9.3 g, 88%). Mp 68–70 °C (lit.[2] 68–69 °C); found: C, 65.35%; H, 5.49%; calc. for $C_{12}H_{12}O_4$: C, 65.45%; H, 5.49%; ν_{max} 1709, 1603, 1174 cm^{-1}; δ_H (300 MHz): 7.59 (1 H, d, *J* = 15.9 Hz, 3-*H*), 7.03 (1 H, s, Ar-*H*), 7.00 (1 H, d, *J* = 7.8 Hz, Ar-*H*), 6.80 (1 H, d, *J* = 7.8 Hz, Ar-*H*), 6.26 (1 H, d, *J* = 15.9 Hz, 2-*H*), 6.00 (2 H, s, OCH_2O), 4.25 (2 H, q, *J* = 7.2 Hz, OCH_2CH$_3$), 1.32 (3 H, t, *J* = 7.2 Hz, CH_3); δ_C (63 MHz): 167.2 (C-1), 149.5, 148.3, 144.2, 128.9, 124.3, 116.2, 108.5 (C-2), 106.4 (C-3), 101.5 (O*C*H$_2$O), 60.3 (*C*H$_2$CH$_3$), 14.3 (*C*H$_3$); *m/z* (EI): 220 (100%, M^+), 175 (90), 148 (55), 145 (70), 89 (57).

A solution of DIBAL-H 1 M in hexanes (106 mL, 106 mmol) was added slowly to a solution of ethyl 3-(3',4'-methylenedioxyphenyl)prop-2-enoate (9 g, 41 mmol) in THF (150 mL) under argon and the resultant mixture was stirred at –80 °C for 4 hours. The reaction was quenched with MeOH (30 mL) at –80 °C, stirred for 1 hour then water (14 mL) was added. Celite was added and the resulting granular suspension was filtered through a celite plug and the residue washed with ethyl acetate. The filtrate was then concentrated to yield the alcohol **7b** (5.8g, 80%). Mp 77–79 °C (lit.[1] 78–79 °C); found: C, 67.44%; H, 5.69%; calc. for $C_{10}H_{10}O_3$: C, 67.41%; H, 5.66%; ν_{max} 3400–3300 cm^{-1}; δ_H (300 MHz): 6.93 (1 H, s, Ar-*H*), 6.82 (1 H, d, *J* = 6.9 Hz, Ar-*H*), 6.75 (1 H, d, *J* = 6.9 Hz, Ar-*H*), 6.52 (1 H, d, *J* = 15.6 Hz, 3-*H*), 6.20 (1 H, dt, *J* =

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5.7, 15.6 Hz, 2-*H*), 5.95 (2 H, s, OCH_2O), 4.29 (2 H, d, *J* = 5.7 Hz, 1-*H*), 1.46 (1 H, broad s, O*H*); δ_C (63 MHz): 148.0, 147.3, 131.1, 130.9, 126.7, 121.1, 108.3 (*C-2*), 105.7 (*C-3*); 101.4 (O*C*H_2O), 63.7 (*C-1*); *m/z* (EI): 178 (100%, $M^{+\cdot}$), 135 (95), 122 (78), 91 (88), 77 (65).

***3-(3',4'-Methylenedioxyphenyl)prop-2-enal*[1] 8b**

Manganese dioxide 90% (325 mg, 3.4 mmol) was added slowly to the solution of the vinylic alcohol **7b** (100 mg, 0.56 mmol) in DCM (7.5 mL). The reaction mixture was stirred for 24 hours at rt, filtered through a Celite plug and washed with DCM. The solvent was removed under reduced pressure to yield the aldehyde **8b** (94 mg, 95%). Mp 84.7–85.8 °C (lit.[1] 85–86.5 °C); found: C, 68.20%; H, 4.59%; calc. for $C_{10}H_8O_3$: C, 68.18%; H, 4.58%; ν_{max} 1666, 1600 cm^{-1}; δ_H (200 MHz): 9.64 (1 H, d, *J* = 7.6 Hz, 1-*H*), 7.38 (1 H, d, *J* = 15.6 Hz, 3-*H*), 7.2–6.8 (3 H, m, Ar-*H*), 6.56 (1 H, dd, *J* = 7.5, 15.6 Hz, 2-*H*), 6.05 (2 H, s, OCH_2O); δ_C (63 MHz): 193.5 (1-*C*), 152.5, 150.5, 148.5, 128.5, 126.8, 125.2, 108.7 (3-*C*), 106.7 (2-*C*), 101.8 (O*C*H_2O); *m/z* (EI): 176 (100%, $M^{+\cdot}$), 147 (60), 89 (60), 63 (41).

***3-Phenyloxirane-2-carboxaldehyde*[3] 10a**.

A solution of cinnamaldehyde (132 g, 1 mol) in methanol (400 ml) was added dropwise over 60 minutes to a stirred solution of *tert*-butyl hydroperoxide (154ml, 108 g in a 70% (w/v) aqueous solution, 1.2 mol) in methanol (500ml) maintained at pH 10.5 by the addition of 1 M sodium hydroxide (NaOH) (*ca.* 30ml), at 35–40 °C. After stirring for 4 hours, a second portion of *tert*-butyl hydroperoxide (103 ml, 72 g in a 70% (w/v) aqueous solution, 0.8 mol) was added. The pH was again maintained at 10.5 by addition of NaOH (20 ml). After stirring for a further 48 hours, water (500 ml) was added, and the reaction mixture was extracted with DCM (3 x 200 ml). The organic extracts were combined and dried ($MgSO_4$) and concentrated. Vacuum distillation, yielded the title compound **10a** as a colourless oil (127.4 g, 86%). (Epoxide isomer ratio by ^{1}H NMR *trans* : *cis* 6.5 : 1), bp 70–75°C, 0.5 mbar (lit.[3] 66–68°C, 0.2 mmHg). ν_{max} (LF) 2820, 1723, 1459 cm^{-1}. *m/z* (CI/NH_3): 149 (100%, MH^+), 119, 106, 91; *trans*: δ_H (200 MHz): 9.18 (1 H, d, *J* = 6 Hz, 1-*H*), 7.5–7.2 (5 H, m, Ar-*H*), 4.16 (1 H, d, *J* = 1.8 Hz, 3-*H*), 3.44 (1 H, dd, *J* = 6Hz, 1.8 Hz, C2-*H*); δ_C (50 MHz): 199 (*C*-1), 131, 130, 130, 128, 65 (*C*-3), 59 (*C*-2); *cis*: δ_H (200 MHz): 9.09 (1 H, d, *J* = 6 Hz, 1-*H*), 7.5–7.2 (5 H, m, Ar-*H*), 4.38 (1 H, d, *J* = 5 Hz, 3-*H*), 3.53 (1 H, dd, *J* = 6, 5 Hz, 2-*H*); δ_C (63 MHz): 197 (*C*-1), 130, 129, 128, 126, 63 (*C*-3), 57 (*C*-2).

Ethyl 3-(3'-phenyloxirin-2'-yl)propenoate **11a**.

A solution of triethyl phosphonoacetate (98 g, 0.44 mol) in toluene (300 ml) was added over 1 hour to a stirred suspension of NaH (13.6 g, 0.55 mol) in toluene (400 ml) at –10 °C after which the mixture was warmed to room temperature. The mixture was then cooled to –10 °C and a solution of epoxy aldehyde (**32**) (50.0 g, 0.338 mol) in toluene (300 ml) was added dropwise over 45 minutes. The reaction was warmed to room temperature after which water (500 ml) was added. The organic layer was separated and combined with ether extracts (2 x 300 ml) of the aqueous layer. The combined organic extracts were dried ($MgSO_4$) and concentrated. Vacuum distillation (86–95 °C, 0.3 mbar) gave the title compound **11** as a colourless oil (58.2 g, 79%). At this stage *cis* and *trans* epoxide isomers are separable by flash chromatography eluting with 12% ethyl acetate in petrol. *Trans*-epoxide found: C, 71.23; H, 6.62; $C_{13}H_{14}O_3$ requires: C, 71.54; H, 6.46%; ν_{max} (LF) 2983, 1713, 1655, 1094, 1038 cm^{-1}; δ_H (200 MHz): 7.5–7.2 (5 H, m, Ar-*H*), 6.81 (1 H, dd, *J* = 7, 15 Hz, 3-*H*), 6.18 (1 H, d, *J* = 15 Hz, 2-*H*), 4.23 (2 H, q, *J* = 7 Hz, C*H*$_2$CH$_3$), 3.83 (1 H, d, *J* = 1.5 Hz, 5-*H*), 3.47 (1 H, dd, *J* = 7, 1.5 Hz, 4-*H*), 1.30 (3 H, t, *J* = 7 Hz, CH$_2$C*H*$_3$); δ_C (50 MHz): 160 (*C*-1), 144 (*C*-3), 139, 136, 129, 127, 124 (*C*-2), 62, 61, 60, 15 (*C*H$_3$); *m/z* (CI/NH_3): 236 (92%, MNH_4^+), 219 (79, MH^+), 203, 190, 173, 145, 116 (100). c*is*-epoxide δ_H (200 MHz): 7.2–7.5 (5 H, m, Ar-*H*), 6.46 (1 H, dd, *J* = 7, 15Hz, 3-*H*), 5.95 (1 H, d, *J* = 15 Hz, 2-*H*), 4.23 (2 H, q, *J* = 7 Hz, C*H*$_2$CH$_3$), 4.32 (1 H, d, *J* = 5 Hz, 5-*H*), 3.83 (1 H, dd, *J* = 7, 5 Hz, 4-*H*), 1.30 (3 H, t, *J* = 7 Hz, C*H*$_3$).

5-phenyl-4,5-epoxypent-2-enoic acid

A solution of $LiOH{\cdot}H_2O$ (250 mg, 6 mmol) in water (3 mL) was added at 0 °C to a solution of methyl ester **11a** (800 mg, 3.67 mmol) in methanol (10 mL). The reaction mixture was stirred at rt for 2 hours. The methanol was removed and the residue was treated with a saturated solution of citric acid in water until pH 3 at 0 °C then extracted with ether. The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography (ether : petrol 1 : 1) to give the title acid (580 mg, 83%). Mp = 84.5–89 °C. Recrystallisation from ether–petrol yielded the pure *trans*, *trans* isomer as a white solid; mp 86–88°C; found C, 69.31%; H, 5.38%; calc. for $C_{11}H_{10}O_3$: C, 69.31%; H, 5.26%; ν_{max} 1286 cm^{-1}; δ_H (200 MHz): 7.45–7.20 (5 H, m, Ar-*H*), 6.95 (1 H, dd, *J* = 6.8, 15.8 Hz, 3-*H*), 6.20 (1 H, d, *J* = 15.8 Hz, 2-*H*), 3.86 (1 H, d, *J* = 1.6 Hz, 5-*H*), 3.51 (1 H, dd, *J* = 1.6, 6.8 Hz, 4-*H*); δ_C (63 MHz): 171.0 (*C*-1), 146.4 (*C*-2), 135.8, 128.7, 128.6, 125.5, 123.1 (*C*-3), 61.2 (*C*-5), 60.3 (*C*-4); *m/z* (CI, NH_3): 208 (10%, M + NH_4), 190 (100, M).

General procedure for the preparation of modified vinyl epoxides from *5-phenyl-4,5-epoxypent-2-enoic acid*

Triethylamine (300 μL, 2 mmol, 4 eq.) was slowly added to a solution of 5-phenyl-4,5-epoxypent-2-enoic acid (95 mg, 0.5 mmol, 1 eq.) in THF (5 mL) at –30 °C under argon. Then, pivaloyl chloride (62 μL, 0.5 mmol, 1 eq.) was added dropwise to the mixture at –30 °C under argon. The reaction mixture was stirred for 3 hours under argon, and warmed up to –20 °C before adding lithium chloride (21 mg, 0.5 mmol, 1 eq.) and the amine or alcohol (0.6 mmol, 1.2 eq.). The reaction mixture was then warmed up to rt and stirred for 12 hours. After quenching with sat. $NaHCO_3$ solution (3 mL), water (5 mL) and ether (5 mL) were then added and the layers were separated. The aqueous layer was extracted with ether (3 x 5 mL) and the combined organic layers were washed with brine (3 x 5 mL), dried ($MgSO_4$) and concentrated. The residue was purified by Kügelrohr distillation (typically *P* = 0.2–1 mbar; *T* = 100–180 °C, the distillate contained the pivalamide) and/or flash chromatography.

2'-Hydroxyethyl 5-phenyl-4,5-epoxy-pent-2-enoate 19

Obtained in 47% yield after flash chromatography (ether : petrol 2 : 1); ν_{max} 3083, 1719 cm^{-1}; δ_H (300 MHz): 7.38–7.28 (5 H, m, Ar-*H*), 6.87 (1 H, dd, *J* = 6.9, 15.9 Hz, 3-*H*), 6.23 (1 H, d, *J* = 15.9 Hz, 2-*H*), 4.33–4.30 (2 H, m, 1'-H_a, 2'-H_a), 3.90–3.86 (2 H, m, 1'-H_b, 2'-H_b), 3.84 (1 H, d, *J* = 1.8 Hz, 5-*H*), 3.48 (1 H, dd, *J* = 1.8, 6.9 Hz, 4-*H*); *m/z* (ES^+): 235.1 (MH^+), 257.1 (MNa^+), 491.2 ($2MNa^+$).

***N-^{n}Butyl 5-phenyl-4,5-epoxypent-2-enamide* 20**

Obtained in 78% yield after flash chromatography (ether : petrol 2 : 1). Mp_{syn} = 107–110 °C; mp_{anti} = 121–122 °C; ν_{max} 3286, 3086 (NH), 2958, 2931, 2871 (CH, aromatics), 1667, 1629 (CONH); *Syn epoxide isomer* δ_H (400 MHz): 7.35–7.28 (5 H, m, Ar-*H*), 6.36 (1 H, dd, 7.9, 15.3 Hz, 3-*H*), 6.12 (1 H, dd, 0.7, 15.3 Hz, 2-*H*), 5.42 (1 H, broad s, NH), 4.32 (1 H, d, 4.3 Hz, 5-*H*), 3.76 (1 H, ddd, 0.7, 4.7, 7.9 Hz, 4-*H*), 3.28–3.22 (2 H, m, 1'-H_2), 1.50–1.42 (2 H, m, 2'H_2), 1.36–1.26 (2 H, m, 3'-H_2), 0.90 (3 H, t, 7.3 Hz, 4'-H_3); δ_C (100 MHz): 164.2 (C-1), 136.4 (C-2), 134.0, 129.3 (*C*-3), 128.3, 128.1, 126.4, 59.5 (*C*-5), 58.1 (*C*-4), 39.3 (*C*-1'), 31.5 (*C*-2'), 20.0 (*C*-3'), 13.7 (*C*-4'); *m*/*z* (ES^+): 268.2 (MNa^+), 513.3 ($2MNa^+$); HRMS (ES^+) found MNa^+, 268.1319; $C_{15}H_{19}NNaO_2$ requires *M*, 268.1313. *Anti epoxide isomer*: found: C, 73.39%; H,

7.83%; N, 7.83%; calc. for $C_{15}H_{19}NO_2$: C, 73.44%; H, 7.81%; N, 5.71%; δ_H (400 MHz): 7.36–7.25 (5 H, m, Ar-*H*), 6.76 (1 H, dd, *J* = 6.5, 15.2 Hz, 3-*H*), 6.14 (1 H, d, *J* = 15.2 Hz, 2-*H*), 5.71 (1 H, broad s, N*H*), 3.79 (1 H, d, *J* = 1.8 Hz, 5-*H*), 3.46 (1 H, dd, *J* = 1.8, 6.6 Hz, 4-*H*), 3.36–3.31 (2 H, m, 1'-H_2), 1.58–1.48 (2 H, m, 2'H_2), 1.41–1.31 (2 H, m, 3'-H_2), 0.93 (3 H, t, *J* = 7.3 Hz, 4'-H_3); δ_C (100 MHz): 164.6 (*C*-1), 139.3 (*C*-2), 136.2, 128.6, 128.5, 126.0 (*C*-3), 125.4, 61.2 (*C*-5), 60.7 (*C*-4), 39.4 (*C*-1'), 31.6 (*C*-2'), 20.0 (*C*-3'), 13.7 (*C*-4').

N-Prop-2-enyl 4,5-epoxy-5-phenylpent-2-enamide 21

Obtained in 65% yield after flash chromatography (ether : petrol 2 : 1). Mp 105–106 °C; found: C, 73.50%; H, 6.64%; N, 6.04%; calc. for $C_{14}H_{15}NO_2$: C, 73.34%; H, 6.59%; N, 6.11%; ν_{max} 3226, 2953, 2923, 2853, 1663, 1560 cm^{-1} (CONH); δ_H (300 MHz): 7.36–7.28 (5 H, m, Ar-*H*), 6.80 (1 H, dd, *J* = 6.6, 15.3 Hz, 3-*H*), 617 (1 H, dd, *J* = 0.6, 15.3 Hz, 2-*H*), 5.94–5.78 (1 H, m, 2'-*H*), 5.78–5.66 (1 H, bs, NH), 5.25–5.13 (2 H, m, 3'-H_2), 4.00–3.94 (2 H, m, 1'-H_2), 3.80 (1 H, d, *J* = 1.8 Hz, 5-*H*), 3.47 (1 H, ddd, *J* = 0.6, 1.8, 6.6 Hz, 4-*H*); δ_C (50 MHz): 164.5 (*C*-1), 139.8 (*C*-3), 136.2 (*C*-2'), 133.8 (*C*-3), 128.6, 125.6, 125.5, 116.7, 101.8 (*C*-3'), 61.3 (*C*-5), 60.7 (*C*-4), 42.05 (*C*-2'); *m/z* (ES^+): 284.1 (MNa^+), 481.2 ($2MNa^+$).

***N-oxazolidinone 5-phenyl-4,5-epoxy-pent-2-enamide* 22**

Obtained in 35% yield following recrystallisation from ethyl acetate; mp = 139–141 °C; ν_{max} 1773, 1683, 1635, 1362 cm^{-1}; δ_H (300 MHz): 7.53 (1 H, d, *J* = 15.5 Hz, 2-*H*), 7.35–7.10 (5 H, m, Ar-*H*), 6.84 (1 H, dd, *J* = 7.5, 15.5, 3-*H*), 4.36 (2 H, t, *J* = 7.5 Hz, NCH_2), 4.00 (2 H, t, *J* = 7.5 Hz, OCH_2), 3.80 (1 H, s, 5-*H*), 3.49 (1 H, d, *J* = 7.5 Hz, 4-*H*); δ_C (100 MHz): 164.1 (O*C*ON), 153.3 (*C*-1), 145.6 (2-*C*), 135.9, 128.7, 128.6, 125.5, 122.8 (*C*-3), 62.1 (*C*-5), 61.0 (*C*-4), 60.9 (O*C*H_2), 42.6 (N*C*H_2); *m/z* (EI): 259 (0.4%, $M^{+\cdot}$), 172 (16), 153 (100), 77 (44).

***N-(5-Phenyl-4,5-epoxypent-2-enoyl)-3'-phenyloxazolidinone* 23 (mixture of 2 diastereoisomers)**

Mp 60.5–62.8 °C. Found: C, 71.19%; H, 5.13%; N, 4.03%; calc. for $C_{20}H_{17}NO_4$: C, 71.63%; H, 5.11%; N, 4.18%; ν_{max} 3055, 2985, 1781, 1689, 1637, 1385, 1355, 1330, 1273, 1201 cm^{-1}; δ_H (400 MHz, $CDCl_3$): 3.56 (1 H, dd, *J* = 1.8, 7.8 Hz), 3.84 (0.5 H, d, *J* = 1.8 Hz), 3.86 (0.5 H, d, *J* = 1.8 Hz), 4.31 (1 H, dd, *J* = 4.0, 8.8 Hz), 4.72 (0.5 H, t, *J* = 8.8 Hz), 4.73 (0.5 H, apparent t, *J* = 8.8 Hz), 5.50 (1 H, dd, *J* = 4.0, 8.8 Hz), 6.86 (0.5 H, dd, *J* = 7.8, 15.4 Hz), 6.87 (0.5 H, dd, *J* = 7.8, 15.4 Hz), 7.22–7.50 (10 H,

m, Ph), 7.64 (1 H, d, *J* = 15.4 Hz). δC (100 MHz, $CDCl_3$): 57.67, 60.86, 60.96, 69.99, 122.83, 122.94, 125.45, 125.89, 125.93, 128.56, 128.72, 129.14, 135.85, 135.90, 138.65, 145.74, 145.92, 153.47, 163.40, 163.44; *m/z* (CI, NH_3): 353 (MNH_4^+), 336 $(M)^+$; HRMS (EI) found MH^+, 336.1236; $C_{20}H_{18}NO_4$ requires *M*, 336.1236.

***4,5-Epoxy-5-phenylpent-2-enoyl-2',5'-trans-diphenylpyrrolidinyl amide* 24**

Obtained as a light brown solid (55%). Found C, 81.92; H, 6.23; N, 3.62%; calc. for $C_{27}H_{25}NO_2$: C, 82.00; H, 6.37; N, 3.54%; ν_{max} (ATR) 3063, 3029, 1661, 1617, 1399 cm^{-1}; δ_H (300 MHz): 7.5–7.0 (15 H, m, Ar-*H*), 6.81–6.64 (1 H, m, 3-*H*), 6.38–6.21 (1 H, m, 2-*H*), 5.69–5.43 (2 H, m, 2'-*H*, 5'-*H*), 3.75 (1 H, s, 5-*H*), 3.33 (1 H, d, 4-*H*), 2.80–2.17 (2 H, m), 1.94–1.67 (2 H, m); δ_C (75 MHz): 164 (*C*-1), 143, 142, 141, 136, 129, 128, 127, 126, 125, 124, 62, 61 (*C*-4*, C*-5), 61 (*C*-2'*, C*-5'), 33; *m/z* (CI, NH_3): 395 (100%, M^+), 318, 241, 222, 173, 145, 119, 77.

2'-Hydroxyethyl 2,3-dihydro-2-phenylfuran-3-carboxylate 27

Following general procedure D (500 °C and 0.04 mbar) 2-hydroxyethyl vinyl epoxide ester **19** was rearranged to afford a crude mixture of dihydrofurans **27** (*cis : trans* 8.8 : 1). Filtration on silica afforded the *cis*-dihydrofuran **27c** (60%). δ_H (300 MHz): 7.37–7.34 (5 H, m, Ar-*H*), 6.72 (1 H, t, *J* = 2.1 Hz, 5-*H*), 5.77 (1 H, d, *J* = 11.1 Hz, 2-*H*), 5.08 (1 H, t, *J* = 2.1 Hz, 4-*H*), 4.13 (1 H, dt, *J* = 2.1, 11.1 Hz, 3-*H*), 3.75–3.71 (2 H, m), 3.37–3.17 (2 H, m).

N-^{n}Butylamino 2,3-dihydro-2-phenylfuran-3-carboxamide 28

Following general procedure C (500 °C and 0.04 mbar) *n*-butyl amide **20** (550 mg) was converted to the title dihydrofurans (60% 8 : 1 *cis* : *trans)*. Flash chromatography (ether : petrol 3 : 7) afforded the *cis*-dihydrofuran **28c** (45%). ν_{max} 3301, 3075, 2984, 1652 cm^{-1}; δ_H (300 MHz): 7.32–7.28 (5 H, m, Ar-*H*), 6.79 (1 H, t, *J* = 2.3 Hz, 5-*H*), 5.82 (1 H, d, *J* = 11.1 Hz, 2-*H*), 5.50 (1 H, broad s, N*H*), 5.06 (1 H, t, *J* = 2.7 Hz, 4-*H*), 3.96 (1 H, dt, *J* = 2.1, 11.1 Hz, 3-*H*), 2.85–2.75 (2 H, m, 1'-H_2), 1.20–1.00 (4 H, m, 2'-H_2, 3'-H_2), 0.79 (3 H, t, 6.7 Hz, 4'-H_3).

***N-Prop-2-enyl 2,3-dihydro-2-phenylfuran-3-carboxamide* 29**

Following general procedure C (500 °C and 0.05 mbar) *n*-allyl amide **21** was converted to the title dihydrofurans (9 : 1 *cis* : *trans)*. Flash chromatography (ether : petrol 3 : 7) afforded unreacted starting vinyl epoxide (~20%) and *cis*-*N*-allyl

dihydrofuryl amide **29c** (48%). Mp = 78–81 °C; ν_{max} 3303, 2927, 1643 cm^{-1}; δ_H (300 MHz): 7.28–7.20 (5 H, m, Ar-*H*), 6.75 (1 H, dd, *J* = 1.8, 2.7 Hz, 5-*H*), 5.77 (1 H, d, *J* = 11.1 Hz, 2-*H*), 5.55 (1 H, bs, N*H*), 5.35–5.22 (1 H, m, *2'-H*), 5.02 (1 H, t, *J* = 2.7 Hz, 4-*H*), 4.92–4.81 (2 H, m, 3'-*H*), 3.93 (1 H, dt, *J* = 1.8, 11.1 Hz, 3-*H*), 3.44 (2 H, t, *J* = 5.7 Hz, 1'-*H*); δ_C (75 MHz): 169.5 (CO), 149.9 (*C*-5), 136.6, 133.7 (*C*-2'), 128.0, 127.9, 126.0, 116.4 (*C*-3'), 100.1 (*C*-4), 85.2 (*C*-2), 55.0 (*C*-3), 41.8 (*C*-1'); *m/z* (ES^+): 252.0 (MNa^+), 481.1 ($2MNa^+$); HRMS (ES) found MNa^+, 252.0997; $C_{14}H_{15}NNaO_2$ requires *M*, 252.1000.

***N-(2,3-Dihydro-2-phenylfuran-3-carboxy)oxazolidin-2'-one* 30**

Following general procedure D, *(*500 °C and 0.05 mbar) oxazolidinone vinyl epoxide **22** was rearranged to afford a crude mixture of dihydrofurans (*cis* : *trans* 11 : 1). Filtration on silica afforded the *cis*-dihydrofuran **30c** (70%). δ_H (300 MHz): 7.32–7.22 (5 H, m, Ar-*H*), 6.68 (1 H, t, *J* = 2.4 Hz, 5-*H*), 5.82 (1 H, d, *J* = 11.7 Hz, 2-*H*), 5.28 (1 H, dt, *J* = 2.4, 11.7 Hz, 3-*H*), 5.00 (1 H, t, *J* = 2.4 Hz, 4-*H*), 4.14–4.02 (1 H, m), 3.63–3.57 (2 H, m), 3.05–2.95 (1 H, m); *m/z* (EI): 259.1 (8%, $M^{+\cdot}$), 172 (100), 144 (31), 115 (94).

***(2R,3S,4'S)-3'-(2,3-dihydro-2-phenylfuran-3-oyl)-4'-phenyloxazolidin-2'-one* 31**

Following general procedure D (500 °C, 0.04 mbar) the vinyl epoxide **23** was rearranged to afford a crude mixture of dihydrofurans (conversion 67%). The ratio of the individual diastereoisomers was determined by ^1H NMR spectroscopy to be 50 : 36 : 8 : 6. Data for the major isomer *(2R,3S,4'S)-3'-(2,3-dihydro-2-phenylfuran-3-oyl)-4'phenyloxazolidin-2'-one*; Mp 142–143.5°C. $[\alpha]_D^{21}$ = +87 (*c* = 2.9, $CHCl_3$); ν_{max} 3054, 2918, 1777, 1703, 1631, 1494, 1456, 1381, 1347, 1239, 1195, 1045, 701 cm^{-1}. δ_H (400 MHz, $CDCl_3$): 7.46–7.22 (8 H, m, Ar-*H*), 7.18–7.10 (2 H, m, Ar-*H*), 6.68 (1 H, t, *J* = 2.5 Hz, 5-*H*), 5.85 (1 H, d, *J* = 11.6 Hz, 2-*H*), 5.34 (1 H, dt, *J* = 11.6, 2.2 Hz, 3-*H*), 4.97 (1 H, t, *J* = 2.5 Hz, 4-*H*), 4.47 (1 H, dd, *J* = 8.6, 2.5 Hz, 4'-*H*), 3.98 (1 H, dd, *J* = 8.6, 2.5 Hz, 5'-H_b), 3.71 (1 H, t, *J* = 8.6 Hz, 5'-H_a); δ_C (100 MHz, $CDCl_3$): 170.84, 153.35, 148.49, 138.77, 137.51, 129.01, 128.64, 128.61, 128.14, 127.22, 125.85, 98.32, 84.14, 69.89, 57.59, 52.87; *m/z* (CI, NH_3): 353 (MNH_4^+), 336 (MH^+); HRMS (EI) found MH^+, 336.1236. $C_{20}H_{17}NO_4$ requires *M*, 336.1236.

***2-phenyl-2,3-dihydrofuran-3-carboxylic acid (2',5'-diphenylpyrrolidine)amide* 32**

Following general procedure C (500 °C, 0.04 mbar) the vinyl epoxide **24** (35 mg) was rearranged to afford a crude mixture of dihydrofurans **32** (43%). The ratio of individual diastereoisomers (54 : 34) : (7 : 5) (*cis)* : *(trans*) was determined by HPLC. No attempt was made to separate the individual isomers.

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