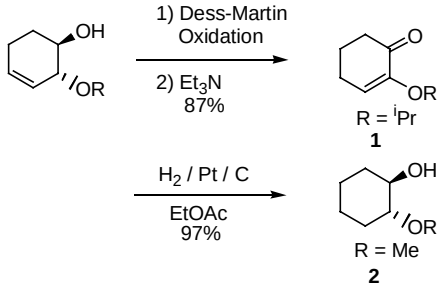
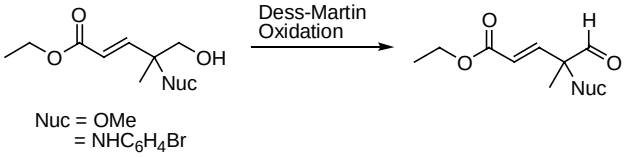
The regiochemistry of the ring opened product was determined by oxidation and isomerisation to enone **1**.[1] The relative stereochemistry was determined by hydrogenation of the olefin to give the known *trans*-methoxyalcohol **2** (Scheme 1).[2]

Scheme 1: Proof of Regoichemistry and Relative Stereochemistry



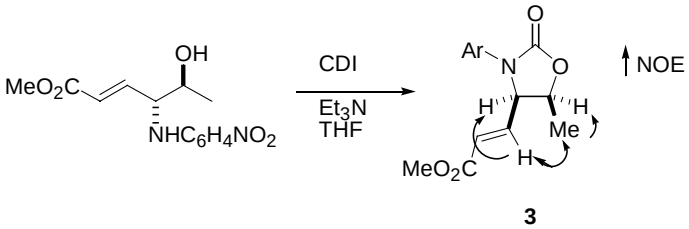
The regiochemistry for linear vinyl epoxides was determined for both alcohol and aromatic amine nucleophiles by oxidation of the primary alcohol resulting from the ring opening step. In both cases, generation of the aldehyde proved that nucleophilic attack had occurred at the more sterically hindered allylic carbon atom (Scheme 2).

Scheme 2: Proof of Regioselectivity for Linear Vinyl Epoxide Ring Opening



The relative stereochemistry was established by formation of the oxazolidinone **3** and NOE analysis.

Scheme 3: Proof of Regioselectivity for Linear Vinyl Epoxide Ring Opening



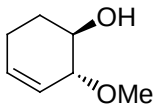
[1] Ponaras, A.A.; Meah, M.Y. *Tetrahedron Lett.***1986**, *27*, 4953.
[2] Shibata, I.; Yoshida, T.; Kawakami, T.; Baba, A.; Matsuda, H. *J. Org. Chem.* **1992**, *57*, 4049.

General Procedure (A): For reaction of cyclic substrates with alcohol nucleophiles. A round bottom flask was charged with cyclohexadiene monoxide (50mg, 0.52mmol) and $[Rh(CO)_2Cl]_2$ (2mg, 0.005mmol). THF (0.5mL) and MeOH (0.5mL) were then added producing a light yellow solution which was stirred at room temperature for one hour. After one hour the solvents were removed *in vacuo* and the resulting oil chromatographed (30% ethyl acetate:hexanes) to give **1** a colourless oil (62mg, 93%).

General Procedure (B): For reaction of cyclic substrates with phenol nucleophiles. A round bottom flask was charged with cyclohexadiene monoxide (50mg, 0.52mmol) and phenol (244mg, 2.6mmol) and THF (1mL). $[Rh(CO)_2Cl]_2$ (2mg, 0.005mmol) was then added producing a light yellow solution which was stirred at room temperature for two hours. After the reaction was completed, the reaction was poured into ether and washed three times with 5% aqueous NaOH. The aqueous layers were combined and back extracted with ether. The organic layers were combined, washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The resulting oil was then chromatographed (20% ethyl acetate:hexanes) to give **4** a white crystalline solid (83mg, 84%).

General Procedure (C): For reaction of cyclic or acyclic substrates with aniline nucleophiles. A round bottom flask was charged with cyclohexadiene monoxide (50mg, 0.52mmol), N-methylaniline (278mg, 2.6mmol) and $[Rh(CO)_2Cl]_2$ (2mg, 0.005mmol). THF (1mL) was then added producing a light yellow solution which was stirred at room temperature for one hour. After one hour the THF was removed *in vacuo* and the resulting oil chromatographed (10% ethyl acetate:hexanes) to give **5** a colourless oil (96mg, 91%).

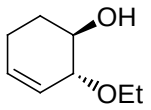
General Procedure (D): For reaction of acyclic substrates with alcohol nucleophiles. A round bottom flask was charged with 2-styryl-oxirane (50mg, 0.34mmol) and $[Rh(CO)_2Cl]_2$ (2mg, 0.005mmol). MeOH (1mL) was then added producing a light yellow solution which was stirred at room temperature for one hour. After one hour the solvents were removed *in vacuo* and the resulting oil chromatographed (30% ethyl acetate:hexanes) to give **7** a colourless oil (62mg, 93%).



1

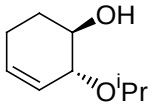
2-Methoxy-cyclohex-3-enol (1): Following general procedure (A), cyclohexadiene monoxide (50mg, 0.52mmol) and $[Rh(CO)_2Cl]_2$ (2mg, 0.005mmol) were reacted in THF (0.5mL) and MeOH (0.5mL) for one hour. Concentration and chromatography (30% ethyl acetate:hexanes) gave **1** a colourless oil (62mg, 93%). R_f = 0.13 on silica gel (30% ethyl acetate:hexanes); IR (neat, cm^{-1}) 3421, 3027, 2926, 1652, 1391, 1086. ^1H NMR

(400MHz, $CDCl_3$) δ 5.74-5.81(1H, m), 5.68-5.73 (1H, m), 3.68-3.78 (2H, m), 3.45 (3H, s), 2.58 (1H, s (br)), 2.16-2.22 (2H, m), 1.92-2.00 (1H, m), 1.60-1.72 (1H, m); ^{13}C NMR (400MHz, $CDCl_3$) δ 129.6, 124.6, 82.1, 70.5, 56.2, 28.0, 24.4; HRMS calcd for $C_7H_{12}O_2$ (M^+): 128.0837 Found: 128.0835.



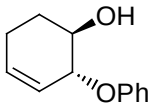
2

2-Ethoxy-cyclohex-3-enol (2): Following general procedure (A), cyclohexadiene monoxide (50mg, 0.52mmol) and $[Rh(CO)_2Cl]_2$ (2mg, 0.005mmol) were reacted in THF (0.5mL) and EtOH (0.5mL) for one hour. Concentration and chromatography (30% ethyl acetate:hexanes) gave **2** a colourless oil (68mg, 92%). R_f= 0.17 on silica gel (30% ethyl acetate:hexanes); IR (neat, cm^{-1}) 3421, 3027, 2972, 1651, 1440, 1090. ^1H NMR (400MHz, $CDCl_3$) δ 5.65-5.79 (2H, m), 3.68-3.80 (3H, m), 3.50-3.60 (1H, m), 2.40 (1H, s (br)), 2.12-2.22 (1H, m), 1.92-2.02 (1H, m), 1.58-1.72 (1H, m), 1.24 (3H, t, *J*= 7.0 Hz); ^{13}C NMR (400MHz, $CDCl_3$) δ 129.3, 125.5, 80.7, 70.8, 64.2, 27.9, 24.4, 15.7; HRMS calcd for $C_8H_{14}O_2$ (M^+): 142.0994 Found: 142.0997.



3

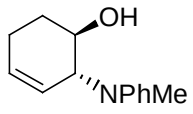
2-Isopropoxy-cyclohex-3-enol (3): Following general procedure (A), cyclohexadiene monoxide (50mg, 0.52mmol) and $[Rh(CO)_2Cl]_2$ (2mg, 0.005mmol) were reacted in THF (0.5mL) and ^{i}PrOH (0.5mL) for 90 minutes. Concentration and chromatography (20% ethyl acetate:hexanes) gave **3** a colourless oil (76mg, 94%). R_f= 0.19 on silica gel (20% ethyl acetate:hexanes); IR (neat, cm^{-1}) 3408, 3028, 2929, 1648, 1394, 1088. ^1H NMR (400MHz, $CDCl_3$) δ 5.69-5.75 (1H, m), 5.61 (1H, ddd, *J*= 10.1, 4.0, 2.0 Hz), 3.78-3.85 (2H, m), 3.64-3.71 (1H, m), 2.39 (1H, s), 2.12-2.18 (2H, m), 1.94-2.02 (1H, m), 1.60-1.70 (1H, m), 1.21 (6H, dd, *J*= 6.2, 2.2 Hz); ^{13}C NMR (400MHz, $CDCl_3$) δ 1298.9, 126.6, 78.4, 71.1, 70.3, 27.8, 24.4, 23.4, 22.4; HRMS calcd for $C_9H_{16}O_2$ (M^+): 156.1150 Found: 156.1149.



4

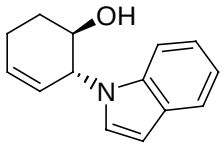
2-Phenoxy-cyclohex-3-enol (4): Following general procedure (B), cyclohexadiene monoxide (50mg, 0.52mmol), phenol (244mg, 2.6mmol) and $[Rh(CO)_2Cl]_2$ (2mg, 0.005mmol) were reacted in THF (1mL) for two hours. Extraction and chromatography (30% ethyl acetate:hexanes) gave **4** a colourless oil (83mg, 84%). R_f= 0.26 on silica gel

(20% ethyl acetate:hexanes); IR (CH_2Cl_2, cm^{-1}) 3410, 3030, 2997, 1648, 1390, 1090. ^1H NMR (400MHz, $CDCl_3$) δ 7.26-7.31 (2H, m), 6.93-6.99 (3H, m), 4.70 (1H, ddd, *J*= 6.8, 2.1, 2.1 Hz), 3.95-4.03 (1H, m), 2.41 (1H, s), 2.20-2.28 (2H, m), 2.02-2.12 (1H, m), 1.70-1.84 (1H, m); ^{13}C NMR (400MHz, $CDCl_3$) δ 157.7, 130.5, 129.6, 124.2, 121.2, 115.8, 78.8, 70.6, 27.8, 24.4; HRMS calcd for $C_{12}H_{14}O_2$ (M^+): 190.0994 Found: 190.0997.



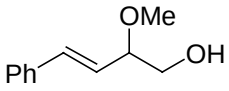
5

2-(Methyl-phenyl-amino)-cyclohex-3-enol (5): Following general procedure (C), cyclohexadiene monoxide (50mg, 0.52mmol), N-methylaniline (278mg, 2.6mmol) and $[Rh(CO)_2Cl]_2$ (2mg, 0.005mmol) were reacted in THF (0.5mL) for 1 hour. Concentration and chromatography (10% ethyl acetate:hexanes) gave **5** a colourless oil (96mg, 91%). R_f= 0.22 on silica gel (20% ethyl acetate:hexanes); IR (neat, cm^{-1}) 3408, 3014, 2929, 1644, 1595, 1500, 1356, 1205, 1067, 898. ^1H NMR (400MHz, $CDCl_3$) δ 7.20-7.26 (2H, m), 6.90 (2H, d, *J*= 8.1 Hz), 6.75 (1H, t, *J*= 7.1 Hz), 5.75-5.85 (1H, m), 5.45 (1H, dd, *J*= 9.9, 1.5 Hz), 4.26-4.34 (1H, m), 3.83-3.93 (1H, m), 2.76 (3H, s), 2.41 (1H, s), 2.16-2.23 (1H, m), 2.03-2.10 (1H, m), 1.70-1.81 (1H, m); ^{13}C NMR (400MHz, $CDCl_3$) δ 150.8, 130.2, 129.1, 126.5, 117.2, 114.2, 68.6, 64.2, 32.3, 29.2, 24.7; HRMS calcd for $C_{13}H_{17}NO$ (M^+): 203.1310 Found: 203.1308.



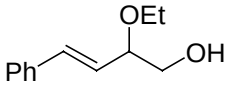
6

2-Indol-1-yl-cyclohex-3-enol (6): Following general procedure (C), cyclohexadiene monoxide (50mg, 0.52mmol), indole (278mg, 2.6mmol) and $[Rh(CO)_2Cl]_2$ (2mg, 0.005mmol) were reacted in THF (0.5mL) for 2 hours. Concentration and chromatography (10% ethyl acetate:hexanes) gave **6** a colourless oil (96mg, 91%). R_f=0.20 on silica gel (20% ethyl acetate:hexanes); IR (neat, cm^{-1}) ^1H NMR (400MHz, $CDCl_3$) δ 8.13 (1H, s), 7.67 (1H, d, *J*= 7.9 Hz), 7.33 (1H, d, *J*= 8.1 Hz), 7.23-7.16 (1H, m), 7.12-7.06 (1H, m), 7.01 (1H, d, *J*= 2.4 Hz), 5.86-5.79 (1H, m), 5.74-5.68 (1H, m), 4.01-3.94 (1H, m), 3.59-3.53 (1H, m), 2.33-2.26 (2H, m), 2.08-1.99 (2H, m), 1.80-1.67 (1H, m); ^{13}C NMR (400MHz, $CDCl_3$) δ 136.7, 128.6, 126.9, 126.6, 122.5, 122.2, 119.6, 119.4, 116.8, 111.3, 71.9, 43.0, 29.1, 24.4; HRMS calcd for $C_{14}H_{15}NO$ (M^+): 213.1154 Found: 213.1155.



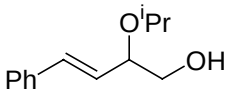
7

2-Methoxy-4-phenyl-but-3-en-1-ol (7): Following general procedure (D), 2-styryl-oxirane (50mg, 0.34mmol) and $[Rh(CO)_2Cl]_2$ (2mg, 0.005mmol) were reacted in MeOH (0.5mL) for 30 minutes. Concentration and chromatography (40% ethyl acetate:hexanes) gave **7** a colourless oil (65mg, 92%). R_f=0.19 on silica gel (30% ethyl acetate:hexanes); IR (neat, cm^{-1}) 3429, 3021, 2936, 1493, 1447, 1106, 1067, 913. ^1H NMR (400MHz, $CDCl_3$) δ 7.38-7.42 (2H, m), 7.31-7.36 (2H, m), 7.24-7.29 (1H, m), 6.65 (1H, d, *J*= 16.1 Hz), 6.05 (1H, dd, *J*= 16.1, 8.8 Hz), 3.86-3.92 (1H, m), 3.61-3.68 (2H, m), 3.40 (3H, s), 2.20 (1H, s); ^{13}C NMR (400MHz, $CDCl_3$) δ 136.1, 134.3, 128.6, 128.0, 126.5, 125.8, 83.0, 65.5, 56.6; HRMS calcd for $C_{11}H_{14}O_2$ (M^+): 178.0994 Found: 178.0990.



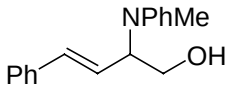
8

2-Ethoxy-4-phenyl-but-3-en-1-ol (8): Following general procedure (D), 2-styryl-oxirane (50mg, 0.34mmol) and $[Rh(CO)_2Cl]_2$ (2mg, 0.005mmol) were reacted in EtOH (0.5mL) for 30 minutes. Concentration and chromatography (20% ethyl acetate:hexanes) gave **8** a colourless oil (67mg, 89%). R_f=0.27 on silica gel (30% ethyl acetate:hexanes); IR (neat, cm^{-1}) 3422, 2971, 1493, 1447, 1085, 969. ^1H NMR (400MHz, $CDCl_3$) δ 7.37-7.41 (2H, m), 7.30-7.35 (2H, m), 7.23-7.28 (1H, m), 6.63 (1H, d, *J*= 15.9 Hz), 6.07 (1H, ddd, *J*= 15.9, 7.7, 0.9 Hz), 3.97-4.03 (1H, m), 3.57-3.72 (3H, m), 3.41-3.49 (1H, m), 2.29 (1H, dd, *J*= 6.8, 6.8 Hz), 1.24 (3H, dt, *J*= 6.8, 1.1 Hz); ^{13}C NMR (400MHz, $CDCl_3$) δ 136.2, 133.6, 128.6, 127.9, 126.6, 126.5, 81.2, 65.5, 64.2, 15.3; HRMS calcd for $C_{12}H_{16}O_2$ (M^+): 192.1150 Found: 192.1153.



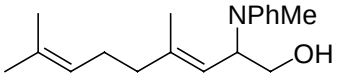
9

2-Isopropoxy-4-phenyl-but-3-en-1-ol (9): Following general procedure (D), 2-styryl-oxirane (50mg, 0.34mmol) and $[Rh(CO)_2Cl]_2$ (2mg, 0.005mmol) were reacted in ^{i}PrOH (0.5mL) for 45 minutes. Concentration and chromatography (20% ethyl acetate:hexanes) gave **9** a colourless oil (72mg, 90%). R_f=0.2 on silica gel (20% ethyl acetate:hexanes); IR (neat, cm^{-1}) 3422, 2975, 1490, 1447, 1080. ^1H NMR (400MHz, $CDCl_3$) δ 7.37-7.41 (2H, m), 7.30-7.34 (2H, m), 7.23-7.27 (1H, m), 6.62 (1H, d, *J*= 16.1 Hz), 6.08 (1H, dd, *J*= 16.1, 7.5 Hz), 4.08-4.14 (1H, m), 3.76 (1H, h, *J*= 6.0 Hz), 3.54-3.65 (2H, m), 2.22 (1H, dd, *J*= 8.0, 4.4 Hz), 1.19 (6H, dd, *J*= 6.0, 3.1 Hz); ^{13}C NMR (400MHz, $CDCl_3$) δ 136.3, 133.0, 128.6, 127.9, 127.4, 126.5, 78.6, 69.3, 65.6, 23.5, 21.6; HRMS calcd for $C_{13}H_{18}O_2$ (M^+): 206.1307 Found: 206.1307.



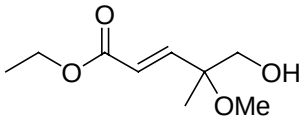
10

2-(Methyl-phenyl-amino)-4-phenyl-but-3-en-1-ol (10): Following general procedure (C), 2-styryl-oxirane (50mg, 0.34mmol), N-methylaniline (182mg, 1.7mmol) and $[Rh(CO)_2Cl]_2$ (2mg, 0.005mmol) were reacted in THF (0.5mL) for 1 hour. Concentration and chromatography (10% increasing to 30% ethyl acetate:hexanes) gave **10** a colourless oil (80mg, 93%). R_f= on silica gel (% ethyl acetate:hexanes); IR (neat, cm^{-1}) 3394, 3021, 2887, 1595, 1496, 1384, 1032, 747. ^1H NMR (400MHz, $CDCl_3$) δ 7.17-7.33 (7H, m), 6.93 (2H, d, *J*= 0.9 Hz), 6.80 (1H, ddd, *J*= 0.9, 1.9, 8.3 Hz), 6.46 (1H, dd, *J*= 1.3, 16.2 Hz), 6.12 (1H, dd, *J*= 5.9, 16.2 Hz), 4.50-4.60 (1H, m), 3.76-3.89 (2H, m), 2.82 (3H, s), 2.25 (1H, s); ^{13}C NMR (400MHz, $CDCl_3$) δ 150.8, 136.2, 132.7, 129.1, 128.5, 127.7, 126.3, 124.5, 118.4, 115.0, 63.2, 62.1, 31.9. HRMS calcd for $C_{17}H_{19}NO$ (M^+): 253.1467, Found: 253.1466.



11

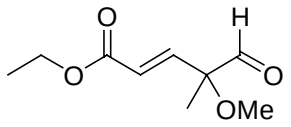
4,8-Dimethyl-2-(methyl-phenyl-amino)-nona-3,7-dien-1-ol (11): Following general procedure (C), 2-(2,6-dimethyl-hepta-1,5-dienyl)-oxirane (50mg, 0.30mmol), N-methylaniline (182mg, 1.7mmol) and $[Rh(CO)_2Cl]_2$ (2mg, 0.005mmol) were reacted in THF (0.5mL) for 1 hour. Concentration and chromatography (10% increasing to 30% ethyl acetate:hexanes) gave **11** a colourless oil (71mg, 87%). R_f=0.15 on silica gel (15% ethyl acetate:hexanes); IR (neat, cm^{-1}) 3401, 2915, 1658, 1598, 1500, 1447, 1103, 1025, 747. ^1H NMR (400MHz, $CDCl_3$) δ 7.22 (2H, d, *J*= 8.0 Hz), 6.92 (2H, d, *J*= 8.1 Hz), 6.79 (1H, d, *J*= 7.1 Hz), 5.08 (1H, d, *J*= 8.1 Hz), 5.02-5.00 (1H, m), 4.58-4.50 (1H, m), 3.67 (1H, t, *J*= 11.8 Hz), 3.60-3.52 (1H, m), 1.67 (3H, s), 1.57 (3H, s), 1.48 (3H, s); ^{13}C NMR (400MHz, $CDCl_3$) δ 151.4, 142.0, 131.7, 129.0, 123.8, 119.1, 118.4, 115.3, 62.5, 60.1, 39.7, 31.5, 26.3, 25.7, 17.7, 17.1; HRMS calcd for $C_{18}H_{27}NO$ (M^+): 273.2093 Found: 273.2090.



12

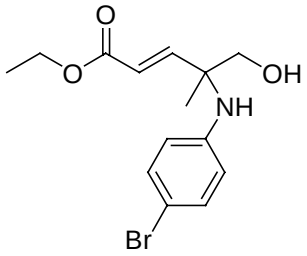
5-Hydroxy-4-methoxy-4-methyl-pent-2-enoic acid ethyl ester (12): Following general procedure (D), 3-(2-methyl-oxiranyl)-acrylic acid ethyl ester (50mg, 0.32mmol) and $[Rh(CO)_2Cl]_2$ (2mg, 0.005mmol) were reacted in MeOH (0.5mL) for 5 hrs. Concentration and chromatography (50% ethyl acetate:hexanes) gave **12** a colourless oil (57mg, 94%). R_f =0.34 on silica gel (50% ethyl acetate:hexanes); IR (neat, cm^{-1}) 3464,

2936, 1715, 1655, 1461, 1366, 1292, 1176, 1064. ^{1}H NMR (400MHz, $CDCl_3$) δ 6.86 (1H, d, *J*= 16.1Hz), 5.99 (1H, d, *J*= 16.1Hz), 4.21 (2H, q, *J*= 7.1Hz), 3.51 (2H, d, *J*= 6.2Hz), 3.24 (3H, s), 2.52 (1H, t, *J*= 6.3Hz), 1.32 (3H, s), 1.31 (3H, t, *J*= 7.1Hz); ^{13}C NMR (400MHz, $CDCl_3$) δ 166.0, 148.7, 122.6, 77.6, 68.3, 60.5, 50.7, 18.2, 14.1. HRMS calcd for $C_9H_{16}O_4$ (M^+): 188.1049 Found: 188.1042 .



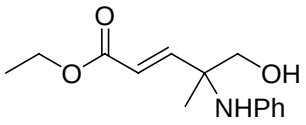
13

4-Methoxy-4-methyl-5-oxo-pent-2-enoic acid ethyl ester (13): To a round bottom flask was dissolved **12** (30mg, 0.16mmol) and Dess-Martin periodinane (64mg, 0.18mmol) in 1mL dichloromethane. The reaction was stirred for 1 hr at room temperature. The mixture was the concentrated and chromatographed (10% ethyl acetate:hexanes) gave **13** a colourless oil (28mg, 94%). R_f =0.27 on silica gel (10% ethyl acetate:hexanes); IR (neat, cm^{-1}) 2985, 1729, 1451, 1370, 1303, 1180. ^{1}H NMR (400MHz, $CDCl_3$) δ 9.48 (1H, s), 6.78 (1H, d, *J*= 16.0Hz), 6.15 (1H, d, *J*= 16.0Hz), 4.22 (2H, q, *J*= 7.0Hz), 3.36 (3H, s), 1.43 (3H, s), 1.30 (3H, t, *J*= 7.0Hz); ^{13}C NMR (400MHz, $CDCl_3$) δ 165.5, 143.7, 124.3, 83.1, 60.7, 52.2, 18.4, 14.1, 12.7. HRMS calcd for $C_9H_{14}O_4$ (M^+): 186.0892 Found: 186.0895.



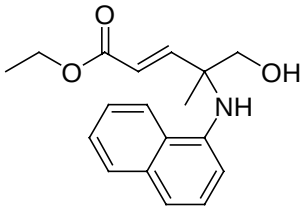
14

4-(4-Bromo-phenylamino)-5-hydroxy-4-methyl-pent-2-enoic acid ethyl ester (14): Following general procedure (C), 3-(2-methyl-oxiranyl)-acrylic acid ethyl ester (50mg, 0.32mmol), 4-bromoaniline (172mg, 1.6mmol) and $[Rh(CO)_2Cl]_2$ (2mg, 0.005mmol) were reacted in THF (0.5mL) for 8 hours. Concentration and chromatography (10% increasing to 30% ethyl acetate:hexanes) gave **14** a colourless oil (97mg, 93%). R_f=0.11 on silica gel (30% ethyl acetate:hexanes); IR (neat, cm^{-1}) 3401, 2971, 1704, 1655, 1496, 1363, 1303, 1180, 1036, 909. ^{1}H NMR (400MHz, $CDCl_3$) δ 7.20 (2H, d, *J*= 8.8Hz), 6.97 (1H, d, *J*= 15.9Hz), 6.50 (2H, d, *J*= 8.8Hz), 5.98 (1H, d, *J*= 15.9Hz), 4.30 (1H, s), 4.18 (2H, q, *J*= 7.1Hz), 3.64 (1H, d, AB, *J*= 11.0 Hz), 3.52 (1H, d, AB, *J*= 11.0 Hz), 2.47 (1H, s), 1.40 (3H, s), 1.28 (3H, t, *J*= 7.1Hz); ^{13}C NMR (400MHz, $CDCl_3$) δ 166.3, 150.4, 144.3, 131.6, 122.5, 117.5, 110.1, 68.2, 60.7, 58.3, 21.4, 14.1. HRMS calcd for $C_{14}H_{18}BrNO_3$ (M^+): 327.0470 Found: 327.0472.



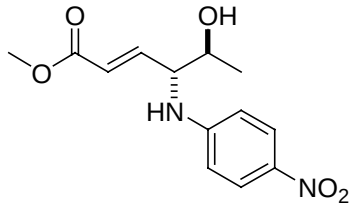
15

5-Hydroxy-4-methyl-4-phenylamino-pent-2-enoic acid ethyl ester (15): Following general procedure (C), 3-(2-methyl-oxiranyl)-acrylic acid ethyl ester (50mg, 0.34mmol), N-methylaniline (182mg, 1.7mmol) and $[Rh(CO)_2Cl]_2$ (2mg, 0.005mmol) were reacted in THF (0.5mL) for 9 hours. Concentration and chromatography (10% increasing to 30% ethyl acetate:hexanes) gave **15** a colourless oil (80mg, 93%). R_f=0.40 on silica gel (50% ethyl acetate:hexanes); IR (neat, cm^{-1}) 3300(br), 2980, 3007, 1715, 1655, 1450; ^1H NMR (400MHz, $CDCl_3$) δ 7.10-7.15 (2H, m), 7.02 (1H, d, *J*= 16.0Hz), 6.72-6.76 (1H, m), 6.63 (1H, d, *J*= 8.6Hz), 6.00 (1H, d, *J*= 16.0Hz), 4.18 (2H, q, *J*= 7.1Hz), 3.69 (1H, d, AB, *J*= 11.0 Hz), 3.53 (1H, d, AB, *J*= 11.0 Hz), 2.34 (1H, s), 1.41 (3H, s), 1.28 (3H, t, *J*= 7.1Hz); ^{13}C NMR (400MHz, $CDCl_3$) δ 166.4, 151.0, 145.2, 128.9, 122.1, 118.5, 116.2, 68.1, 60.6, 58.3, 2.8, 14.1. HRMS calcd for $C_{14}H_{19}NO_3$ (M^+): 249.1365 Found: 249.1362.



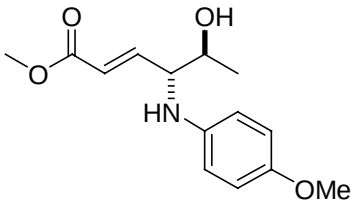
16

5-Hydroxy-4-methyl-4-(naphthalen-1-ylamino)-pent-2-enoic acid ethyl ester (16): Following general procedure (C), 3-(2-methyl-oxiranyl)-acrylic acid ethyl ester (50mg, 0.32mmol), 1-aminonaphthalene (228mg, 1.6mmol) and $[Rh(CO)_2Cl]_2$ (2mg, 0.005mmol) were reacted in THF (0.5mL) for 10 hours. Concentration and chromatography (10% increasing to 30% ethyl acetate:hexanes) gave **16** a colourless oil (80mg, 87%). R_f=0.20 on silica gel (30% ethyl acetate:hexanes); IR (neat, cm^{-1}) 3400(br), 3010, 2990, 1715, 1660, 1460; ^1H NMR (400MHz, $CDCl_3$) δ 7.87-7.91 (1H, m), 7.76-7.79 (1H, m), 7.41-7.46 (2H, m), 7.23-7.26 (2H, m), 7.08 (1H, d, *J*= 16.0Hz), 6.59-6.63 (1H, m), 6.02 (1H, d, *J*= 16.0Hz), 5.04 (1H, s), 4.16 (2H, q, *J*= 7.1Hz), 3.79 (1H, d, AB, *J*= 10.8 Hz), 3.63 (1H, d, AB, *J*= 10.8 Hz), 2.40 (1H, s), 1.51 (3H, s), 1.25 (3H, t, *J*= 7.1Hz); ^{13}C NMR (400MHz, $CDCl_3$) δ 166.4, 150.8, 139.9, 134.4, 128.7, 125.9, 125.6, 124.9, 122.4, 122.4, 120.0, 118.2, 109.2, 68.8, 60.6, 58.3, 21.2, 14.1. HRMS calcd for $C_{18}H_{21}NO_3$ (M^+): 299.1521 Found: 299.1526.



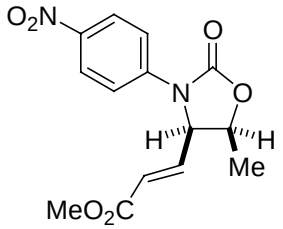
17

5-Hydroxy-4-(4-nitro-phenylamino)-hex-2-enoic acid methyl ester (17): Following general procedure (C), 3-(3-methyl-oxiranyl)-acrylic acid methyl ester (50mg, 0.35mmol), 4-nitroaniline (243mg, 1.76mmol) and $[Rh(CO)_2Cl]_2$ (2mg, 0.005mmol) were reacted in THF (0.5mL) for 6 hours. Concentration and chromatography (10% increasing to 30% ethyl acetate:hexanes) gave **17** a colourless oil (80mg, 93%). R_f=0.15 on silica gel (50% ethyl acetate:hexanes); IR (neat, cm^{-1}) 3400(br), 3011, 2970, 1720, 1660, 1441; ^1H NMR (400MHz, $CDCl_3$) δ 8.03 (2H, d, *J*= 9.2 Hz), 6.96 (1H, dd, *J*= 9.7, 15.8 Hz), 6,52 (2H, d, *J*= 9.2 Hz), 6.04 (1H, dd, *J*= 1.2, 15.8 Hz), 5.44 (1H, d, *J*= 7.7 Hz), 4.04-4.42 (2H, m), 3.72 (3H, s), 2.65 (1H, s), 1.32 (3H, d, *J*= 6.4 Hz); ^{13}C NMR (400MHz, $CDCl_3$) δ 166.2, 152.1, 143.2, 138.1, 126.3, 124.2, 111.8, 69.1, 59.0, 51.8, 20.0; HRMS calcd for $C_{13}H_{16}N_2O_5$ (M^+): 280.1059; Found: 280.1057.



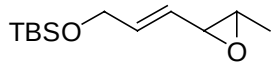
18

5-Hydroxy-4-(4-methoxy-phenylamino)-hex-2-enoic acid methyl ester (17): Following general procedure (C), 3-(3-methyl-oxiranyl)-acrylic acid methyl ester (50mg, 0.35mmol), p-anisidine (216mg, 1.76mmol) and $[Rh(CO)_2Cl]_2$ (2mg, 0.005mmol) were reacted in THF (0.5mL) for 1 hour. Concentration and chromatography (10% increasing to 30% ethyl acetate:hexanes) gave **18** a colourless oil (80mg, 93%). R_f=0.10 on silica gel (40% ethyl acetate:hexanes); IR (neat, cm^{-1}) 3300(br), 2940, 1720, 1660, 1470; ^1H NMR (400MHz, $CDCl_3$) δ 6.93 (1H, dd, *J*= 6.4, 15.8 Hz), 6.77 (2H, d, *J*= 9.0 Hz), 6.57 (2H, d, *J*= 9.0 Hz), 6.02 (1H, dd, *J*= 1.0, 15.8 Hz), 4.05-4.12 (1H, m), 3.90-3.95 (1H, m), 3.73 (3H, s), 3.71 (3H, s), 1.80-2.20 (1H, br s), 1.24 (3H, d, *J*= 6.6 Hz); ^{13}C NMR (400MHz, $CDCl_3$) δ 166.4, 152.6, 145.6, 140.5, 123.5, 115.3, 114.9, 69.2, 61.0, 55.7, 51.6, 19.7; HRMS calcd for $C_{14}H_{19}NO_4$ (M^+): 265.1314; Found: 265.1310.



19

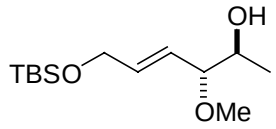
3-[5-Methyl-3-(4-nitro-phenyl)-2-oxo-oxazolidin-4-yl] acrylic acid methyl ester (19): To a round bottom flask was added **17** (30mg, 0.1mmol), 200μL triethylamine and 1mL THF. Carbonyldiimidazole (20mg, 0.125mmol) was then added and the reaction stirred at room temperature for 2 hours. The solution was then concentrated and chromatographed (50% ethyl acetate:hexanes) to give **19** (28mg, 90%). R_f=0.15 on silica gel (40% ethyl acetate:hexanes); mp 155°; IR (CCl_4, cm^{-1}) 3010, 2940, 1770, 1660, 1450; ^{1}H NMR (300MHz, $CDCl_3$) δ 8.21 (2H, d, *J*= 9.2Hz), 7.68 (2H, d, *J*= 9.2Hz), 6.86 (1H, dd, *J*= 6.6, 15.8Hz), 6.05 (1H, dd, *J*= 0.8, 15.8Hz), 5.08-4.93 (2H, m), 3.75 (3H, s), 1.44 (3H, d, *J*= 6.4Hz); ^{13}C NMR (400MHz, $CDCl_3$) δ 164.8, 153.8, 143.5, 142.8, 139.4, 126.6, 124.9, 118.7, 73.5, 60.4, 52.1, 15.8. HRMS calcd for $C_{14}H_{14}N_2O_4$ (M^+): 306.0852; Found: 306.0850.



20

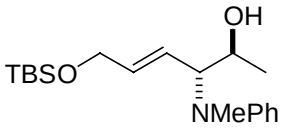
***tert*-Butyl-dimethyl-[3-(3-methyl-oxiranyl)-allyloxy]-silane (20):** To a flame dried round bottom flask was added TBSCl (595mg, 3.95mmol), imidazole (410mg, 6.0mmol), DMAP (10mg), and 300mg 3-(3-methyl-oxiranyl)-prop-2-en-1-ol[3] (300mg, 2.63mmol). DCM (3mL) was then added and the reaction was stirred at room temperature for 30 minutes. The solution was then concentrated and chromatographed (2.5% ethyl acetate:hexanes) to give **20** a colourless oil (475mg, 80%). R_f=0.5 on silica gel (5% ethyl acetate:hexanes); IR (neat, cm^{-1}) 3010, 2985, 1565, 1275; ^{1}H NMR (400MHz, $CDCl_3$) δ 5.96 (1H, ddd, *J*= 4.6, 4.6, 15.5Hz), 5.44 (1H, dddd, *J*= 1.8, 1.8, 7.9, 15.5Hz), 4.17 (2H, dd, *J*= 1.8, 4.6Hz), 3.06 (1H, dd, *J*= 2.1, 7.9Hz), 2.90 (1H, ddd, *J*= 2.1, 5.2, 10.4Hz), 1.32 (3H, d, *J*= 5.2Hz), 0.89 (9H, s), 0.06 (6H, s); ^{13}C NMR (400MHz, $CDCl_3$) δ 134.4, 127.2, 62.9, 59.1, 56.4, 25.9, 18.4, 17.5, -5.3. HRMS calcd for $C_{12}H_{24}O_2Si$ (M^+): 228.1546 Found: 228.1544.

[3] Ley, S.V.; Bruckhart, S.; Cox, L.R.; Meek, G. *JCS Perkin 1*, **1997**, 3327.



21

5-(*tert*-Butyl-dimethyl-silanoxy)-2-methoxy-pent-3-en-1-ol (21): Following general procedure (D), **20** (50mg, 0.22mmol) and $[Rh(CO)_2Cl]_2$ (2mg, 0.005mmol) were reacted in MeOH (0.5mL) for 15 minutes. Concentration and chromatography (30% ethyl acetate:hexanes) gave **21** a colourless oil (51mg, 90%). R_f=0.15 on silica gel (30% ethyl acetate:hexanes); IR (neat, cm^{-1}) 3400(br), 3010, 2990, 1565, 1275; ^1H NMR (400MHz, $CDCl_3$) δ 5.81 (1H, ddd, *J*= 4.6, 4.6, 15.6Hz), 5.53-5.64 (1H, m), 4.22 (2H, d, *J*= 3.2Hz), 3.78-3.87 (1H, m), 3.51 (1H, dd, *J*= 3.8, 8.0Hz), 3.30 (3H, s), 2.19 (1H, s), 1.11 (3H, d, *J*= 6.6Hz), 0.90 (9H, s), 0.07 (6H, s); ^{13}C NMR (400MHz, $CDCl_3$) δ 135.5, 125.7, 85.7, 69.4, 63.0, 56.4, 25.9, 18.4, 17.8, -5.2. HRMS calcd for $C_{13}H_{28}O_3Si$ (M^+): 260.1808 Found: 260.1801.



22

5-(*tert*-Butyl-dimethyl-silanoxy)-2-(methyl-phenyl-amino)-pent-3-en-1-ol (22): Following general procedure (C), **20** (50mg, 0.34mmol), N-methylaniline (182mg, 1.7mmol) and $[Rh(CO)_2Cl]_2$ (2mg, 0.005mmol) were reacted in THF (0.5mL) for 1 hour. Concentration and chromatography (10% increasing to 30% ethyl acetate:hexanes) gave **22** a colourless oil (80mg, 93%). R_f=0.40 on silica gel (20% ethyl acetate:hexanes); IR (neat, cm^{-1}) 3400(br), 3014, 2930, 1644, 1590, 1210; ^1H NMR (400MHz, $CDCl_3$) δ 7.22 (2H, dd, *J*= 7.4, 8.8Hz), 6.79 (2H, d, *J*= 7.9Hz), 6.72 (1H, t, *J*= 7.2Hz), 5.90 (1H, dddd, *J*= 1.4, 1.4, 6.1, 15.6Hz), 5.78 (1H, ddd, *J*= 4.1, 4.1, 15.6Hz), 4.19 (2H, d, *J*= 4.1Hz), 3.95-4.16 (2H, m), 2.80 (3H, s), 1.77 (1H, s), 1.21 (3H, d, *J*= 5.7Hz), 0.89 (9H, s), 0.05 (6H, s); ^{13}C NMR (400MHz, $CDCl_3$) δ 150.3, 134.2, 129.1, 124.9, 117.1, 113.5, 68.5, 66.5, 63.2, 33.2, 25.9, 20.4, 18.4, -5.2. HRMS calcd for $C_{19}H_{33}NO_2Si$ (M^+): 335.2281 Found: 335.2278.