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# Synthesis of new 4,6-disubstituted-1,3-oxazinan-2-one analogues

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**Abstract.** 1,3-Oxazinan-2-one analogues are important heterocyclic compounds having significant biological activities. This study reports the synthesis of eight new 4,6-disubstituted -1,3-oxazinan-2-one analogues from corresponding homoallylic carbamates. Homoallylic carbamates were synthesized via a three-component reaction of aldehyde, allyltrimethylsilane and benzyl carbamate in presence of iodine as catalyst. In the next step, homoallylic carbamates were subjected to Sharpless dihydroxylation (racemic) to produce 3,4-dihydroxybutylcarbamate derivatives. This product was then treated with NaH in tetrahydrofuran (THF) to produce the desired 6-(hydroxymethyl)-1,3-oxazinan-2-one in high yield.

**Keywords.** 1,3-Oxazinan-2-one; homoallylic carbamates; Sharpless dihydroxylation; iodine; heterocyclic compound.

## 1. Introduction

Heterocyclic compounds containing nitrogen and oxygen in the skeleton are important building blocks in the synthesis of biologically active compounds.[1] 1,3-Oxazinan-2-one skeleton is one of such important compounds, used as building block for the synthesis of new heterocycles of biological significance. These 6-memebered cyclic carbamates derivatives are found in many biologically important natural products such as maystansine, maystanprine, colubrinol and maytanbutine.[2–4] 1, 3-Oxazinan-2-one derivatives exhibit a variety of biological activities such as antibacterial,[5] anti-inflammatory[6] and antithrombotic[7] properties. These molecules are used in treating asthma, allergies, ulcers, arthritis and diabetes.[4b] In addition, they are also being used as anticonvulsant,[8] penetration enhancer,[9] sedative,[10] and analgesic.[11] Some 6-phenyl-1, 3-oxazinan-2-one derivatives have phosphodiesterase IV inhibitor property and are used as remedies for inflammatory diseases and anti-asthmatics.[12] 1,3-Oxazinan-2-one derivatives have also been used as key intermediates in the synthesis of several biologically important compounds such as L-ristosamine, L-daunosamine,[13] (±)-negamycin[14] erythromycin A[15] and thrombolytics.[7] Besides being important bulding blocks in the preparation of complex synthetic targets, they are also used for the synthesis of amino alcohols[16,17] and liquid crystal devices.[18]

There are very limited approaches to the synthesis of 1, 3-oxazinan-2-one in literature. Lohray[19] developed a method for enantiospecific synthesis of 6-substituted *N*-aryl-1,3-oxazinan-2-ones using aspartic acid as starting material. A quicker synthesis of the same was carried out by reductive amination of 2-deoxy-D-ribose followed by cyclization of aryl chloroformate derivatized amine.[20] Other methods include halogen-mediated cyclization reactions,[15b,c,21–30] rearrangement from cyclic sulphates,[31] selenium-mediated cyclization of amino alcohols with carbon monoxide,[32] asymmetric dihydroxylation of homoallylic amine,[33] tethered aminohydroxylation,[34] Hofmann rearrangement of primary amide[35] and intramolecular Michael addition.[36] Cyclization of 1, 3-aminoalcohol is one of the versatile methods in the synthesis of cyclic carbamate.[20,37–40] A method used for the synthesis of oxazinanones via intramolecular diazocarbonyl insertion reaction of activated diazoketone catalysed by metal triflates was reported by Avery *et al*.[41]

## 2. Experimental

### 2.1 *Synthesis of homoallylic carbamate (**1**)*[42]

Benzyl carbamate (2.55 mmol, 1.05 equiv) and allyltrimethylsilane (2.5 mmol, 1 equiv) were added to a solution of aldehyde (2.5 mmol, 1 equiv) and iodine (10 mol%) in acetonitrile at room temperature. The reaction was completed within 10–20 min. After completion of the reaction thin layer chromatography

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(TLC), sodium thiosulphate was added to reaction mixture. The mixture was extracted with EtOAc. The organic extract was washed with brine and dried over anhydrous sodium sulphate. Evaporation of solvent and purification of the crude product using flash chromatography on silica gel (230–400 mesh) with petroleum ether-EtOAc (10–20%) as eluent gave the pure product (yield 50–82%).

2.1a *Benzyl 1-(4-chlorophenyl)but-3-enylcarbamate* ***1a***: Yield: 70% (colourless solid); mp: 68–70°C; IR (KBr, $cm^{-1}$): 3342, 3064, 2950, 1678, 1534, 1489, 1346, 1263, 1119, 1035, 752; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.35–7.19 (m, 9H), 5.72–5.57 (m, 1H), 5.15–5.02 (m, 5H), 4.71 (br, 1H), 2.50 (br, 2H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 155.6, 140.5, 136.2, 133.2, 133.0, 128.7, 128.5, 128.2, 127.6, 118.9, 66.9, 53.9, 40.9.

2.1b *Benzyl 1-(4-bromophenyl)but-3-enylcarbamate* ***1b***: Yield: 75% (colourless solid); mp: 87–88°C; IR (KBr, $cm^{-1}$): 3345, 3087, 2950, 1684, 1592, 1533, 1455, 1347, 1264, 1119, 1034, 751; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.44 (d, $J$ = 8.1Hz, 2H), 7.40–7.25 (m, 5H), 7.13 (d, $J$ = 7.7 Hz, 2H), 5.72–5.54 (m, 1H), 5.22–4.96 (m, 5H), 4.82–4.65 (m, 1H), 2.60–2.36 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 155.6, 141.0, 136.2, 133.2, 131.6, 128.5, 128.2, 127.9, 121.1, 118.9, 66.9, 53.9, 40.8.

2.1c *Benzyl 1-p-tolylbut-3-enylcarbamate* ***1c***: Yield: 72% (colourless solid); mp: 70–71°C; IR (KBr, $cm^{-1}$): 3357, 3058, 2958, 1692, 1590, 1526, 1457, 1350, 1263, 1143, 1044, 732; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.35–7.16 (m, 9H), 5.75–5.62 (m, 1H), 5.14–5.07 (m, 5H), 4.78 (m, 1H), 2.56–2.62 (m, 2H), 2.34 (s, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 155.6, 138.8, 136.9, 136.4, 133.8, 129.2, 128.4, 128.1, 126.1, 118.2, 66.6, 54.2, 40.9, 30.9.

2.1d *Benzyl 1-(4-methoxyphenyl)but-3-enylcarbamate* ***1d***: Yield: 75% (colourless solid); mp: 70–71°C; IR (KBr, $cm^{-1}$): 3362, 3067, 2950, 1685, 1597, 1528, 1454, 1346, 1243, 1116, 1032, 748; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.41–7.29 (m, 5H), 7.19 (d, $J$ = 7.8 Hz, 2H), 6.86 (d, $J$ = 8.6 Hz, 2H), 5.77–5.58 (m, 1H), 5.20–5.00 (m, 5H), 4.80–4.70 (m, 1H), 3.79 (s, 3H), 2.60–2.54 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 158.7, 155.6, 136.4, 133.9, 128.4, 128.0, 127.3, 118.2, 113.8, 86.7, 55.2, 53.9, 40.9.

2.1e *Benzyl 1-(naphthalene-6-yl)but-3-enylcarbamate* ***1e***: Yield: 65% (colourless solid); mp: 73–75°C; IR (KBr, $cm^{-1}$): 3365, 3049, 2970, 1686, 1528, 1323, 1250, 1122, 1036, 751; $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 7.86–7.27 (m, 12H), 5.79–5.65 (m, 1H), 5.30 (m, 1H), 5.18–5.01 (m, 5H), 2.65 (br, 2H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 155.6, 139.2, 136.3, 133.6, 133.2, 132.7, 128.4, 128.4, 128.1, 127.8, 127.5, 126.1, 125.7, 124.8, 124.4, 118.5, 66.8, 54.5, 40.9.

2.1f *Benzyl 1-(4-flurophenyl)but-3-enylcarbamate* ***1f***: Yield: 71% (yellowish liquid); IR (KBr, $cm^{-1}$): 3445, 1697, 1604, 1540, 1349, 1224, 1159, 1041, 736; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.33–7.00 (m, 9H), 5.66–5.63 (m, 1H), 5.12–5.05 (m, 5H), 4.77 (br, 1H), 2.50 (br, s, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 163.1, 160.7, 155.6, 137.1, 136.3, 133.4, 128.5, 128.1, 127.8, 127.8, 118.7, 115.4, 115.2, 66.8, 53.8, 41.3.

2.1g *Benzyl (1-phenylhex-5-en-3-yl)carbamate* ***1g***: Yield: 70% (colourless solid); mp: 70–71°C; IR (Nujol, $cm^{-1}$): 3065, 1696, 1534, 1451, 1243, 1045, 739; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.32–7.16 (m, 7H), 7.13–7.06 (m, 3H), 5.77–5.60 (m, 1H), 5.10–4.95 (m, 4H), 4.54 (d, $J$ = 7.8 Hz, 1H), 3.79–3.63 (m, 1H), 2.68–2.50 (m, 2H), 2.29–2.09 (m, 2H), 1.83–1.70 (m, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 156.2, 141.7, 136.6, 133.9, 128.5, 128.4, 128.3, 128.1, 125.9, 118.1, 66.6, 50.5, 39.5, 36.5, 32.3.

2.1h *Benzyl 1-(2-methoxyphenyl)but-3-enylcarbamate* ***1h***: Yield: 80% (colourless solid); mp: 88–90°C; IR (KBr, $cm^{-1}$): 3333, 3060, 2942, 1685, 1600, 1537, 1468, 1352, 1264, 1121, 1035,754; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.30–6.83 (m, 9H), 5.63–5.61 (m, 2H), 5.04–4.98 (m, 5H), 3.80 (s, 3H), 2.52 ( br, s, 2H); $^{13}$C NMR ($CDCl_3$,100 MHz): $\delta$ 156.8, 155.6, 136.5, 134.7, 129.3, 128.4, 128.3, 128.2, 128.1, 120.5, 117.4, 110.8, 66.6, 55.2, 52.8, 39.7.

### 2.2 *Synthesis of 3,4-dihydroxybutylcarbamate derivative (**2**)*[43]

A flask was charged with $K_2CO_3$ (4.5 mmol) and $K_3Fe(CN)_6$ (4.5 mmol) in a mixture of $^t$BuOH and water (1:1). The mixture was stirred for 5–10 min and a drop of pyridine and $K_2OsO_2(OH)_4$ (0.006 mmol) was added to the mixture and stirred for another 5 min. Thereafter, homoalylic carbamate, **1** (1.5 mmol) was added to the reaction mixture and stirred for 24 h. The reaction was then quenched with sodium sulphite and

the reaction mixture was stirred for another half an hour. The reaction mixture was then extracted with EtOAc. The organic extract was washed with brine and dried over anhydrous sodium sulphate. The solvent was evaporated under reduced pressure to get the crude mixture. The crude product was purified by flash column chromatography using petroleum ether and ethyl acetate (1:1) as eluent to get the desired diol as a inseparable mixture of two diastereomers (yield: 70–95%).

2.2a *Benzyl 1-(4-chlorophenyl)-3, 4-dihydroxybutylcarbamate* ***2a***: Yield: 72% (colourless solid); mp: 103–105°C; IR (KBr, $cm^{-1}$): 3429 (br), 2930, 1684, 1593, 1539, 1454, 1350, 1261, 1094, 1013,758; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.27–7.13 (m, 18H), 5.54 (d, $J$ = 8 Hz, 2H), 5.06–4.94 (m, 4H), 3.68 (br, s, 2H), 3.56–3.48 (m, 2H), 3.42–3.31 (m, 2H), 2.36 (br, s, 2H), 1.84–1.75 (m, 2H), 1.68–1.63 (m, 2H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 156.6, 155.9, 140.1, 136.1, 135.9, 133.1, 128.8, 128.5, 128.4, 128.2, 128.1, 127.9, 127.7, 127.6, 69.8, 69.8, 68.6, 67.1, 66.9, 66.4, 51.6, 39.5, 39.2; MS ($m/z$): 372.1 ($M^+$+ Na), 373.1; Anal. calcd. for $C_{18}H_{20}ClNO_4$ (%): C, 61.80; H, 5.76; N, 4.00; Found: C, 61.75; H, 5.90; N, 4.10.

2.2b *Benzyl 1-(4-bromophenyl)-3, 4-dihydroxybutylcarbamate* ***2b***: Yield: 74% (colourless solid); mp: 123–125°C; IR (KBr, $cm^{-1}$): 3362, 3058, 2950, 1686, 1593, 1525, 1455, 1346, 1269, 1097, 1049, 754; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.41–7.09 (m, 18H), 5.52–5.46 (m, 2H), 5.07–4.91 (m, 4H), 3.69 (br, 1H), 3.57–3.51 (m, 3H), 3.44–3.32 (m, 2H), 2.07–2.04 (m, 1H), 1.95–1.93 (m, 1H), 1.86–1.77 (m, 2H), 1.70–1.59 (m, 2H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 156.7,155.8, 140.3, 136.1, 135.9, 131.8, 131.8, 128.5, 128.5, 128.3, 128.2, 128.1, 127.9, 124.3, 121.4, 121.3, 69.9, 68.5, 67.2, 66.9, 66.5, 66.4, 53.5, 51.7, 39.5, 39.2 ; MS ($m/z$): 416.1 ($M^+$+ Na), 418.0 ($M^+$ +2+ Na); Anal. calcd. for $C_{18}H_{20}BrNO_4$ (%): C, 54.84; H, 5.11; N, 3.55; Found: C, 54.90; H, 5.15; N, 3.55.

2.2c *Benzyl 3, 4-dihydroxy-1-p-tolylbutylcarbamate* ***2c***: Yield: 84% (colourless solid); mp: 102–104°C; IR (KBr, $cm^{-1}$): 3345, 3283, 3055, 2928, 1697, 1538, 1456, 1350, 1257, 1100, 1014, 737; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.57–7.35 (m, 18H), 5.68–5.59 (m, 2H), 5.33–5.18 (m, 4H), 4.05–4.00 (m, 1H), 3.89–3.78 (m, 3H), 3.74–3.61 (m, 2H), 2.82 (br, s, 2H), 2.55 (s, 6H), 2.20–1.95 (m, 4H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 156.8, 155.9, 138.4, 137.2, 136.2, 135.9, 129.4, 128.4, 128.4, 128.2, 128.1, 126.2, 126.1, 69.9, 68.7, 67.1, 66.7, 66.5, 66.4, 53.3, 51.8, 39.7, 39.7, 21.1, 20.9; MS ($m/z$): 338.2 (8) ($M^+$+ Na), 339.0 (15), 179.5 (55); Anal. calcd. for $C_{19}H_{23}NO_4$ (%): C, 69.28; H, 7.04; N, 4.25; Found: C, 69.18; H, 6.95; N, 4.20.

2.2d *Benzyl-3, 4-dihydroxy-1-(4-methoxyphenyl)butylcarbamate* ***2d***: Yield: 75% (colourless solid); mp: 67–70°C; IR (KBr, $cm^{-1}$): 3421, 3352, 3038, 2940, 1690, 1606, 1528, 1459, 1346, 1243, 1096, 1047, 753; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.27–6.79 (m, 18H), 5.22 (m, 2H), 5.07–4.94 (m, 4H), 4.90–4.85 (m, 1H), 4.77–4.67 (m, 1H), 3.72 (s, 6H), 3.57–3.50 (m, 2H), 3.46–3.33 (m, 2H), 2.10–2.08 (br, 2H), 1.92–1.66 (m, 4H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 158.9, 156.9, 156.1, 136.2, 136.1, 133.4, 128.5, 128.4, 128.2, 128.1, 127.9, 127.6, 127.4, 114.1, 69.9, 68.7, 67.1, 66.8, 66.5, 66.4, 55.2, 55.2, 51.5, 51.5, 39.7; MS ($m/z$): 368.1 ($M^+$+ Na, 100), 369.1 (15); Anal. calcd. for $C_{19}H_{23}NO_5$ (%): C, 66.07; H, 6.71; N, 4.06; Found: C, 66.10; H, 6.80; N, 4.10.

2.2e *Benzyl-3, 4-dihydroxy-1-(naphthalene-6-yl)butylcarbamate* ***2e***: Yield: 93% (colourless solid); mp: 87–89°C; IR (KBr, $cm^{-1}$): 3336, 3054, 2944, 1684, 1601, 1631, 1455, 1331, 1258, 1097, 1045, 742; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.78–7.27 (m, 24H), 5.75 (d, $J$ = 8 Hz, 2H), 5.17–5.01 (m, 4H), 4.09–4.04 (m, 1H), 3.77 (br, 1H), 3.52–3.46 (m, 4H), 2.96–2.80 (m, 2H), 2.15–1.81 (m, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 156.9, 156.1, 133.2, 128.6, 128.5, 128.4, 128,2, 128.1, 127.6, 126.2, 67.2, 66.9, 66.6, 66.5, 53.8, 52.3, 39.7, 39.4, 30.9; MS ($m/z$): 388.2 ($M^+$+Na, 39), 372.2 (8); Anal. calcd. for $C_{22}H_{23}NO_4$ (%): C, 72.31; H, 6.34; N, 3.83; Found: C, 72.25; H, 6.30; N, 3.87.

2.2f *Benzyl 1-(4-flurophenyl)-3, 4-dihydroxybutylcarbamate* ***2f***: Yield: 95% (colourless solid); mp: 79–82°C; IR (KBr, $cm^{-1}$): 3445, 2925, 1697, 1593, 1350, 1226, 1054, 735; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.28–6.93 (m, 18H), 5.43–5.34 (m, 2H), 5.04–4.94 (m, 4H), 4.76 (br, 1H), 3.71 (br, s, 1H), 3.59–3.52 (m, 2H), 3.45–3.34 (m, 2H), 2.00–1.66 (m, 6H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 163.6, 160.3, 156.7, 155.9, 137.7, 137.2, 136.1, 135.9, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 115.7, 115.4, 69.9, 68.6, 67.2, 66.9, 66.5, 66.4, 53.1, 51.5, 39.7, 39.5 MS ($m/z$): 356.1 ($M^+$+ Na, 100), 338.2 (10); Anal. calcd. for $C_{18}H_{20}FNO_4$ (%): C, 64.85; H, 6.05; N, 4.20; Found: C, 64.80; H, 6.10; N, 4.25.

2.2g *Benzyl (5,6-dihydroxy-1-phenylhexan-3-yl)carbamate* ***2g***: Yield: 75% (colourless solid); mp: 73–76°C; IR ( KBr, $cm^{-1}$): 3426, 3335, 2924, 1687, 1599,

1541, 1454, 1352, 1253, 1051, 750; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.32–7.05 (m, 20 H), 5.06–5.04 (m, 4H), 4.74 (br, 1H), 4.61 (d, $J$ = 12 Hz, 1H), 3.86–3.68 (m, 4H), 3.59–3.57 (m, 1H), 3.51–3.48 (m, 1H), 3.42–3.38 (m, 2H), 2.70–2.55 (m, 4H), 1.81–1.64 (m, 4H), 1.60–1.51 (m, 2H), 1.27–1.19 (m, 2H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ 157.6, 156.5, 141.3, 141.1, 136.3, 136.1, 128.6, 128.5, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 126.0, 125.9, 70.1, 68.3, 67.2, 66.8, 66.5, 66.4, 49.3, 47.9, 39.8, 38.9, 37.5, 37.4, 32.6, 32.1; MS ($m/z$): 366.0 ($M^+$+ Na); Anal. calcd. for $C_{20}H_{25}NO_4$ (%): C, 69.95; H, 7.34; N, 4.08; Found: C, 69.90; H, 7.30; N, 4.12.

2.2h *Benzyl-3, 4-dihydroxy-1-(2-methoxyphenyl)butyl-carbamate* ***2h***: Yield: 70% (colourless solid); mp: 110–113°C; IR (KBr, cm$^{-1}$): 3430, 3338, 2927, 1686, 1597, 1543, 1469, 1351, 1259, 1101, 1051, 755; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.30–6.81 (m, 18H), 5.98 (d, $J$ = 8 Hz, 1H), 5.81 (br, s, 1H), 5.04–4.96 (m, 6H), 3.78 (s, 6H), 3.53–3.50 (m, 2H), 3.44–3.37 (m, 2H), 2.25 (br, 2H), 1.93–1.81 (m, 3H), 1.61–1.54 (m, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 157.4, 156.9, 156.7, 156.0, 136.4, 136.2, 128.9, 128.8, 128.7, 128.6, 128.5, 128.3, 128.1, 121.1, 120.9, 111.1, 111.0, 70.2, 68.7, 67.2, 66.8, 66.7, 66.4, 55.4, 55.3, 51.3, 51.1, 39.3, 39.0; MS ($m/z$): 368.1 ($M^+$+ Na, 100), 369.1($M^+$+1+ Na ,18); Anal. calcd. for $C_{19}H_{23}NO_5$ (%): C, 66.07; H, 6.71; N, 4.06; Found: C, 66.10; H, 6.75; N, 4.10.

## 2.3 *Synthesis of 1, 3-oxazinan-2-one (**3**)*[44]

The diol (**2,** 1 mmol, 1 equiv) was dissolved in dry THF (3–4 mL) under $N_2$ atmosphere. The mixture was then cooled in an ice water bath and NaH (1.4 mmol, 1.4 equiv) was added to the mixture. The reaction mixture was then allowed to stir at 0–5°C for appropriate time (TLC). The reaction was then quenched with aq. $NH_4Cl$ solution and extracted with EtOAc. The organic extract was then dried over anhydrous sodium sulphate. The solvent was evaporated under reduced pressure to get the crude reaction mixture. The crude product was purified by flash column chromatography to get the 1, 3-oxazinan-2-one as a inseparable diastereomeric mixture (yield 70–85%).

2.3a *4-(4-Chlorophenyl)-6-(hydroxymethyl)-1, 3-oxazinan-2-one (**3a** + **4a**)*: Yield: 75% (colourless solid); mp: 158–160°C; IR (KBr, cm$^{-1}$): 3515, 3283, 3058, 2938, 1714, 1541, 1492, 1340, 1291, 1087, 1056, 766; $^1$H NMR (DMSO, 400 MHz) $\delta$ 7.73 (br, m, 1H), 7.61 (br, s, 1H), 7.46–7.42 (m, 4H), 7.36–7.33 (m, 4H), 5.00–4.93 (m, 2H), 4.70–4.69 (m, 1H), 4.60 (dd, $J$ = 12 Hz, 4 Hz, 1H), 4.34–4.30 (m, 1H), 3.97–3.92 (m, 1H), 3.52–3.44 (m, 2H), 2.13–2.05 (m, 2H), 1.89–1.86 (br, m, 1H), 1.59–1.50 (m, 1H); $^{13}$C NMR (DMSO,100 MHz): $\delta$ 153.2, 152.9, 142.3, 141.3, 132.0, 131.7, 128.5, 128.4, 128.1, 128.0, 76.7, 73.4, 62.8, 62.7, 53.1, 50.5, 32.9, 30.4; MS ($m/z$): 264.1 ($M^+$+Na), 266.1 ($M^+$ +2+ Na); Anal. calcd. for $C_{11}H_{12}ClNO_3$(%): C, 54.67; H, 5.00; N, 5.80; Found: C, 54.60; H, 4.95; N, 5.70.

2.3b *4-(4-Bromophenyl)-6-(hydroxymethyl)-1, 3-oxazinan-2-one (**3b** + **4b**)*: Yield: 82% (colourless solid); mp: 173–175°C; IR (KBr, cm$^{-1}$): 3418, 3293, 3126, 2936, 1710, 1592, 1538, 1459, 1341, 1292, 1086, 1057, 768; $^1$H NMR (DMSO, 400 MHz): $\delta$ 7.72 (d, $J$ = 4 Hz, 1H), 7.61–7.55 (m, 5H), 7.29–7.26 (m, 4H), 4.98–4.94 (m, 2H), 4.68–4.66 (m, 1H), 4.58 (dd, $J$ = 12 Hz, 4Hz, 1H), 4.33–4.30 (m, 1H), 3.96–3.92 (m, 1H), 3.50–3.45 (m, 2H), 2.12–2.04 (m, 2H), 1.88–1.85 (br, m, 1H), 1.58–1.49 (m, 1H); $^{13}$C NMR (DMSO, 100 MHz): $\delta$ 153.2, 152.9, 142.7, 141.7, 131.4, 131.3, 128.5, 128.3, 120.5, 120.2, 76.7, 73.3, 62.8, 62.7, 53.2, 50.6, 32.9, 30.3; MS ($m/z$): 308.0 ($M^+$+ Na), 310.0 ($M^+$ +2+ Na); Anal. calcd. for $C_{11}H_{12}BrNO_3$(%): C, 46.18; H, 4.23; N, 4.90; Found: C, 46.25; H, 4.30; N, 4.85.

2.3c *6-(Hydroxymethyl)-4-p-tolyl-1, 3-oxazinan-2-one (**3c** + **4c**)*: Yield: 73% (colourless solid); mp: 124–125°C; IR (KBr, cm$^{-1}$): 3372, 3272, 2969, 2917, 1707, 1592, 1538, 1464, 1353, 1294, 1090, 1052; $^1$H NMR (DMSO, 400 MHz): $\delta$ 7.66 (m, 1H), 7.50 (br, s, 1H), 7.20–7.15 (m, 8H), 4.97–4.91 (m, 2H), 4.63 (m, 1H), 4.52 (dd, $J$ = 12 Hz, 4Hz, 1H), 4.32–4.29 (m, 1H), 3.96–3.94 (m, 1H), 3.50–3.43 (m, 2H), 2.29 (s, 6H), 2.08–2.02 (m, 2H), 1.86–1.83 (m, 1H), 1.59–1.49 (m, 1H); $^{13}$C NMR (DMSO,100 MHz): $\delta$ 153.5, 153.3, 140.3, 139.3, 136.9, 136.4, 129.2, 129.1, 126.1, 125.9, 76.9, 73.5, 63.0, 62.8, 53.7, 50.9, 40.1, 39.9, 33.2, 30.7, 20.7, 20.7; MS ($m/z$): 244.1 ($M^+$+ Na, 100), 245.2 ($M^+$ + 1+ Na, 28); Anal. calcd. for $C_{12}H_{15}CNO_3$(%): C, 65.14; H, 6.83; N, 6.33; Found: C, 65.10; H, 6.88; N, 6.29.

2.3d *6-(Hydroxymethyl)-4-(4-methoxyphenyl)-1, 3-oxazinan-2-one (**4d**)*: Yield: 70% (light brown solid); mp: 132–135°C; IR (KBr, cm$^{-1}$): 3450, 3254, 3097, 2930, 1655, 1587, 1508, 1459, 1351, 1297, 1253, 1081, 1023, 767; $^1$H NMR (DMSO, 400 MHz): $\delta$ 7.65 (m, 1H), 7.20 (d, $J$ = 12 Hz, 2H), 6.94 (d, $J$ = 8 Hz, 2H),

4.93 (br, m. 1H), 4.62 (br, m, 1H), 3.99–3.96 (m, 1H), 3.74 (s, 3H), 3.45–3.44 (m, 1H), 2.08–2.00 (m, 1H), 1.86–1.82 (br, m, 1H); $^{13}$C NMR (DMSO,100 MHz): $\delta$ 158.4, 153.0, 135.1, 127.1, 113.3, 73.4, 62.8, 55.1, 50.5, 30.8; MS ($m/z$) 260.8 ($M^+$+ Na, 100); Anal. calcd. for $C_{12}H_{15}NO_4$(%): C, 60.75; H, 6.37; N, 5.90; Found: C, 60.71; H, 6.34; N, 5.85.

2.3e *6-(Hydroxymethyl)-4-(naphthalene-6-yl)-1, 3-oxazinan-2-one (**3e** + **4e**)*: Yield: 76% (colourless solid); mp: 170–172°C; IR (KBr, cm$^{-1}$): 3443, 3249, 3129, 2931, 1702, 1507, 1425, 1336, 1155, 1073, 762; $^1$H NMR (DMSO, 400 MHz): $\delta$ 7.95–7.46 (m, 16H), 5.00–4.93 (br, m, 2H), 4.85 (br, m, 1H), 4.77–4.73 (m, 1H), 4.41–4.38 (m, 1H), 4.03–4.01 (m, 1H), 3.53–3.46 (m, 2H), 2.20–2.12 (m, 2H), 2.01–1.98 (m, 1H), 1.74–1.63 (m, 1H); $^{13}$C NMR (DMSO, 75 MHz): $\delta$ 153.3, 153.1, 140.9, 139.7, 132.8, 132.7, 132.5, 132.2, 128.2, 127.8, 127.7, 127.5, 127.5, 126.4, 126.3, 126.0, 124.7, 124.6, 124.5, 125.4, 76.8, 73.3, 62.9, 62.7, 53.9, 51.2, 33.0, 30.3; MS ($m/z$): 280.1 ($M^+$+ Na, 100), 279.2 (12), 264.0 (5); Anal. calcd. for $C_{15}H_{15}NO_3$(%): C, 70.02; H, 5.88; N, 5.44; Found: C, 69.98; H, 5.91; N, 5.41.

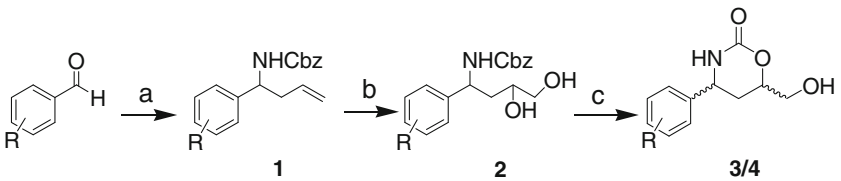
2.3f *4-(4-Flurophenyl)-6-(hydroxymethyl)-1, 3-oxazinan-2-one (**4f**)*: Yield:70% (colourless solid); mp: 102–105°C; IR (KBr, cm$^{-1}$): 3298, 2919, 1708, 1603, 1509, 1433, 1351, 1293, 1156, 1052, 767; $^1$H NMR (DMSO, 400 MHz): $\delta$ 7.71 (m, 1H), 7.36–7.32 (m, 2H), 7.23–7.19 (m, 2H), 4.97 (br, 1H), 4.70–4.67 (m, 1H), 3.99–3.93 (m, 1H), 3.46–3.45 (m, 1H), 2.11–2.04 (m, 1H), 1.89–1.85 (m, 1H); $^{13}$CNMR (DMSO, 100 MHz): $\delta$ 162.5, 153.0,139.4, 128.0, 127.9, 115.2, 115.0, 73.4, 62.7, 50.5, 30.6; MS ($m/z$): 248.1 ($M^+$+Na, 100); Anal. calcd. for $C_{11}H_{12}FNO_3$(%): C, 58.66; H, 5.37; N, 6.22; Found: C, 58.63; H, 5.34; N, 6.19.

2.3g *6-(Hydroxymethyl)-4-(2-phenylethyl)-1, 3-oxazinan-2-one (**3g** + **4g**)*: Yield: 85% (yellowish oily liquid); IR (KBr, cm$^{-1}$): 3445, 1701, 1593, 1351, 1455, 1335, 1092, 677; $^1$H NMR (DMSO, 400 MHz): $\delta$ 7.38–7.37 (m, 1H), 7.30 (m, 1H), 7.28–7.15 (m, 10 H), 4.98 (br, 2H), 4.30–4.24 (m, 1H), 4.19–4.13 (m, 1H), 3.49–3.48 (m, 4H), 2.67–2.54 (m, 4H), 2.04–2.00 (m, 1H), 1.87–1.74 (m, 4H), 1.72–1.59 (m, 2H), 1.41–1.32 (m, 1H); $^{13}$C NMR (DMSO, 100 MHz): $\delta$ 153.2, 152.9, 141.6, 141.6, 128.3, 128.3, 128.3, 128.3, 125.8, 125.8, 76.9, 74.2, 63.1, 62.8, 49.4, 47.1, 37.9, 37.4, 31.1, 30.3, 29.1, 26.8; MS ($m/z$): 258.0 ($M^+$+ Na, 21), 241.6 (41); Anal. calcd. for $C_{13}H_{17}NO_3$(%): C, 66.36; H, 7.28; N, 5.95; Found: C, 66.38; H, 7.31; N, 5.92.

2.3h *6-(Hydroxymethyl)-4-(2-methoxyphenyl)-1, 3-oxazinan-2-one (**3h** + **4h**)*: Yield: 71% (colourless solid); mp: 154–155°C; IR (KBr, cm$^{-1}$): 3373, 3244, 3107, 2939, 1690, 1597, 1344, 1294, 1246, 1106, 1081, 759; $^1$H NMR (DMSO, 300 MHz): $\delta$ 7.55–7.54 (m, 1H), 7.43 (br, s, 1H), 7.32–7.18 (m, 4H), 7.04–6.96 (m, 4H), 4.93–4.87 (m, 2H), 4.85–4.82 (m, 2H), 4.34–4.30 (m, 1H), 3.94–3.87 (m, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.49–3.48 (m, 2H), 2.15 (dd, $J$ = 15 Hz, 6 Hz, 1H), 2.05–1.96 (m, 1H), 1.88–1.83 (br, m, 1H), 1.51–1.39 (m, 1H); $^{13}$C NMR (DMSO, 75 MHz): $\delta$ 156.1, 155.5, 153.7, 153.4, 130.5, 129.8, 128.5, 128.5, 126.6, 125.9, 120.6, 120.1, 110.9, 110.9, 76.7, 73.5, 62.9, 55.5, 55.4, 47.8, 46.7, 31.0, 28.3; MS ($m/z$): 260.8 ($M^+$+ Na, 100); Anal. calcd. for $C_{12}H_{15}NO_4$(%): C, 60.75; H, 6.37; N, 5.90; Found: C, 60.78; H, 6.40; N, 5.92.

## 3. Results and discussion

Although a number of methods are available for the synthesis of 1,3-oxazinan-2-one, development of new simple and efficient synthetic pathways for preparation of such compounds are quite interesting for a synthetic chemist. Due to the wide biological activity of oxazinanones, synthesis of new analogues and a study of their biological properties is essential. We report the synthesis of some new analogues of 1,3-oxazinan-2-ones starting from homoallylic carbamate (scheme 1).



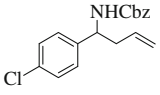
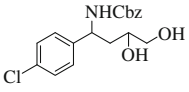
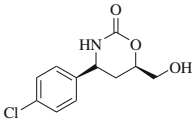
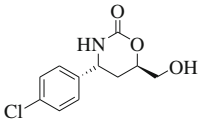
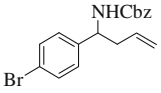
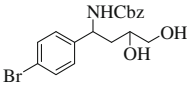
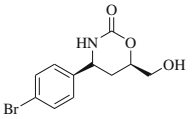
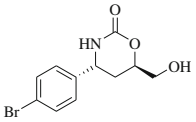
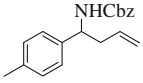
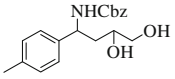
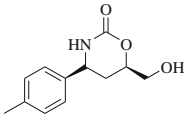
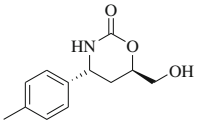
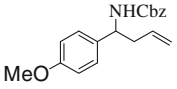
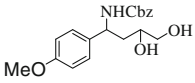
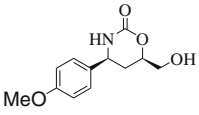
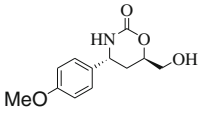
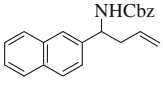
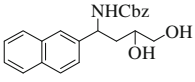
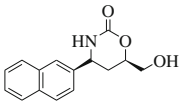
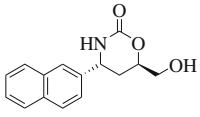
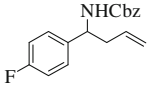
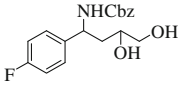
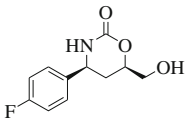
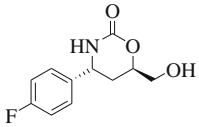
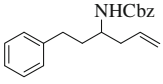
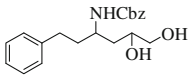
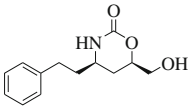
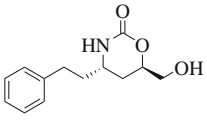
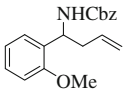
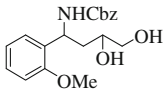
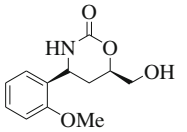
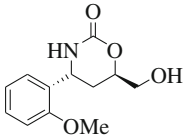

R = Cl, Br, F, Me, OMe, etc.

Reagent and condition: (a) Allyltrimethylsilane, benzyl carbamate, $I_2$, $CH_3CN$, rt; (b) $K_2OsO_2(OH)_4$, $K_3Fe(CN)_6$, $K_2CO_3$, pyridine, tBuOH:$H_2O$ (1:1); (c) NaH, THF, 0°C

**Scheme 1.** Synthetic pathway for 1,3-oxazinan-2-one.

We have synthesized some new 4,6-disubstituted 1,3-oxazinan-2-one using homoallyl amine via Sharpless dihydroxylation and cyclization strategy. In our approach, we have used Cbz-protected homoallyl amine **1** as the staring material which was prepared by a three-component condensation reaction of aromatic aldehyde, benzyl carbamate and allyltrimethylsilane, developed in our laboratory.[42] Initially, the synthesis (scheme 1) was carried out with homoallylic carbamate **1a**, prepared from 4-chloro benzaldehyde. The compound **1a** was prepared by adding benzyl carbamate (1.05 equiv) and allyltrimethylsilane (1 equiv) to a solution of 4-chloro benzaldehyde (1 equiv) and iodine (10 mol%) in acetonitrile at room temperature.[42a] The protected homoallyl amine **1a** was then subjected to Sharpless dihydroxylation.[43] The reaction was carried out using standard dihydroxylation reaction condition in presence of a small

**Table 1.** Synthesis of 4,6-disubstituted 1,3-oxazinan-2-one derivatives.

| Sl. No. | Homoallylic carbamate **1** | 3,4-dihydroxybutylcarbamate **2** | Yield[a] | 1,3-oxazinan-2-one **3** (*cis*) | **4** (*trans*) | Yield[a] | dr (**4**/**3**)[a] |
|---|---|---|---|---|---|---|---|
| 1 |  (**1a**) |  (**2a**) | 72 |  (**3a**) |  (**4a**) | 75 | 2:1 |
| 2 |  (**1b**) |  (**2b**) | 74 |  (**3b**) |  (**4b**) | 82 | 2:1 |
| 3 |  (**1c**) |  (**2c**) | 84 |  (**3c**) |  (**4c**) | 73 | 2:3 |
| 4 |  (**1d**) |  (**2d**) | 75 |  (**3d**) |  (**4d**) | 70 | >99 |
| 5 |  (**1e**) |  (**2e**) | 93 |  (**3e**) |  (**4e**) | 76 | 2:3 |
| 6 |  (**1f**) |  (**2f**) | 95 |  (**3f**) |  (**4f**) | 70 | >99 |
| 7 |  (**1g**) |  (**2g**) | 75 |  (**3g**) |  (**4g**) | 85 | 3:2 |
| 8 |  (**1h**) |  (**2h**) | 70 |  (**3h**) |  (**4h**) | 71 | 2:1 |

[a]isolated yield after chromatographic purifications

amount of pyridine to produce corresponding 3,4-dihydroxybutylcarbamate derivative **2a**. The product was found to be an inseparable mixture of two diastereomers. The 3,4-dihydroxybutylcarbamate derivative **2a** was then treated with NaH in THF at 0°C. This base-induced intramolecular cyclization reaction[44] resulted in the formation of a diastereomeric mixture of 6-membered 1, 3-oxazinan-2-one (**3a** + **4a**) in 75% yield. The nuclear magnetic resonance (NMR) studies indicate the presence of two diastereomers in the final product. In this case also, it was not possible to separate the diastereomers using column chromatography and was isolated as a mixture of *cis* and *trans* products. Relative stereochemistry of the products has been assigned by comparison of the chemical shifts of $-\mathbf{CH_2}$OH protons with data on similar skeleton already reported in literature.[30] Diastereomeric ratio (*cis* : *trans*) was calculated using $^1$H NMR and found to be 1:2. In the $^1$H NMR spectrum, one of the $-\mathbf{CH_2}$OH protons appear as two different multiplets at 4.34–4.30 $\delta$ (for *cis* isomer) and 3.97–3.92 $\delta$ (for *trans* isomer) with a ratio of 1:2. The other proton in the same group, appears at 3.52–3.44 $\delta$ as multiplet (for both diastereomers). In a similar way, one proton of 5-$\mathbf{CH_2}$ group appears as a multiplet at 1.89–1.86 $\delta$ (*trans* isomer), while the same proton in the other diastereomer appears at 1.59–1.50 $\delta$ (*cis* isomer) with a ratio of 2:1 (*trans*:*cis*). The other proton for both diastereomers comes at 2.13–2.05 $\delta$ as multiplet.

After optimizing the synthetic strategy, we have expanded the scope of the process using a number of homoallylic carbamates prepared with different aromatic aldehydes. Results are presented in table 1.

In general, this strategy works well for a variety of aldehydes to produce the corresponding 4,6-disubstituted-1,3-oxazinan-2-one derivatives in high yield. All the products were characterized through IR, NMR and mass apectral data. Integration ratio of proton in $^1$H NMR spectra of the cyclic carbamate reveals the formation of diastereomers in a 1:2 ratio (*cis* : *trans*) for the entries (1, 2, 8); while 1:1.5 (*cis* : *trans*) selectivity was observed for entry 7. However for the entries 3 and 5, the *cis*-isomer was found to be dominant over the *trans*-isomer with diasteromeric ratio 1.5:1 (*cis* : *trans*). Interestingly for the entries 4 and 6 (table 1), only *trans*-isomers **4d** and **4f**, respectively, were formed predominantly. This may be due to strong resonance effect of substituents on the aromatic ring.

## 4. Conclusion

In conclusion, we have developed an efficient synthetic strategy for the synthesis of 4,6-disubstituted 1,3-oxazinan-2-one derivatives starting from a homoallylic amine. Although, in most of the cases, a mixture of diostereomers is formed, 6-(hydroxymethyl)-4-(4-methoxyphenyl)-1,3-oxazinan-2-one and 4-(4-fluorophenyl)-6-(hydroxymethyl)-1,3-oxazinan-2-one were formed predominantly with only *trans* diastereomer.

## Supplementary information

For $^1$H NMR and $^{13}$NMR spectra as supporting information see www.ias.ac.in/chemschi: website.

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## References

1. (a) Wang G, Ella-Menye J R and Sharma V 2006 *Bioorg. Med. Chem. Lett.* **16** 2177; (b) Ullrich T, Baumann K, Welzenbach K, Schmutz S, Camenisch, G, Meingassner J G and Weitz-Schmidt G 2004 *Bioorg. Med. Chem. Lett.* **14** 2483; (c) Zanatta N, Borchhardt D M, Alves S H, Coelho H S, Squizani A M C, Marchi T M, Bonacorso H G and Martins M A P 2006 *Bioorg. Med. Chem. Lett.* **14** 3174; (d) Zhang P, Terefenko E A, Fensome A, Wrobel J, Winneker R and Zhang Z 2003 *Bioorg. Med. Chem. Lett.* **13** 1313; (e) Roller S G, Dieckhaus C M, Santos W L, Sofia R D and MacDonald T L 2002 *Chem. Res. Toxicol.* **15** 815
2. Corey E J and Cheng X–M 1989 *The logic of chemical synthesis* (New York: John Wiley & Sons) p. 423
3. Gormley Jr G, Chan Y Y and Fried J 1980 *J. Org. Chem.* **45** 1447
4. (a) Larson G M, Schaneberg B T and Sneden A T 1999 *J. Nat. Prod.* **62** 361; (b) Cassady J M, Chan K K, Floss H G and Leistner E 2004 *Chem. Pharm. Bull.* **52** 1; (c) Widdison W C, Wilhelm S D, Cavanagh E E, Whiteman K R, Leece B A, Kovtun Y, Goldmacher V S, Xie H, Steeves R M, Lutz R J, Zhao R, Wang L, Blattler A and Chari R V J 2006 *J. Med. Chem.* **49** 4392
5. (a) Wang G 2008 *Anti-Infect. Agents Med. Chem.* **7** 32; (b) Wang G, Ella-Menye J-R and Sharma V 2006 *Bioorg. Med. Chem. Lett.* **16** 2177
6. Ullrich T, Baumann K, Welzenbach K, Schmutz S, Camenisch G, Meingassner J G and Weitz-Schmidt G 2004 *Bioorg. Med. Chem. Lett.* **14** 2483
7. Jin F 2000 Confalone P N PCT Int. Appl. WO0000481, 119; *Chem. Abstr.* **132** 78560

8. Engel J, Emig P, Nickel B and Szelenyi I 1990 Ger. Often DE 3.915.184: *Chem. Abstr.* **112** 2352861
9. Rajadhyaksha V J 1990 PCT Int. Appl. WO 90,00407: *Chem. Abstr.* **113** 59177
10. Testa E, Fontanella L, Cristiani G and Gallo G 1959 *J. Org. Chem.* **24** 1928
11. Franran C P, Douzon C, Raynaud G M and Serganl M Y 1975 U.S. 3.821.215: *Chem. Abstr.* **82** 49951
12. Yamana K, Suzuki N and Takahama A 2002 Ine, S. Jpn. Kokai Tokkyo Koho JP 2002179572; *Chem. Abstr.* **137** 57555
13. Hirama M, Shigemoto T and Ito S 1987 *J. Org. Chem.* **52** 3342
14. Wang Y-F, Izawa T, Kobayashi S and Ohno M 1982 *J. Am. Chem. Soc.* **104** 6465
15. Woodward R B, Logusch E, Nambiar K P, Sakan K, Ward D E, Au-Yeung B-W, Balaram P, Browne L J, Card P J, Chen C H, Chenevert R B, Fliri A and Frobel K *et al.* 1981 *J. Am. Chem. Soc.* **103** 3213
16. (a) Hirama M, Shigemoto T, Yamazaki Y and Ito S 1985 *J. Am. Chem. Soc.* **107** 1797; (b) González-Rosende M E, Jordá-Gregori J M, Sepúlveda-Arques J and Orena M 2004 *Tetrahedron: Asymm.* **15** 419; (c) Bongini A, Cardillo G and Orena M 1988 *Chem. Lett.* **87**
17. (a) Abbas T R, Cadogan J I G, Doyle A A, Gosney I, Hodgson P K G, Howells G E, Hulme A N, Parsons S and Sadler I H 1997 *Tetrahedron Lett.* **38** 4917; (b) Banks M R, Cadogan J I G, Gosney I, Gould R O, Hodgson K G, and McDougall D 1998 *Tetrahedron* **54** 9765; (c) Osa Y, Hikima Y, Sato Y, Takino K, Ida Y, Hirono S and Nagase H 2005 *J. Org. Chem.* **70** 5737; (d) Takahata H, Saito Y and Ichinose M 2006 *Org. Biomol. Chem.* **4** 1587; (e) Wang C and Tunge J A 2006 *Org. Lett.* **8** 3211; (f) Perch N S and Widenhoefer R A 1999 *J. Am. Chem. Soc.* **121** 6960; (g) Perry M C, Powell M T, Cui X, Hou D-R, Reibenspies J H and Burgess K 2003 *J. Am. Chem. Soc.* **125** 113
18. Takiguchi T, Iwaki T, Tokanou G, Kosaka Y and Nakamura S JP9151179 1997; *Chem. Abstr.* **127** 42427
19. Lohray B B, Baskaran S, Reddy B Y and Rao K S 1998 *Tetrahedron Lett.* **39** 6555
20. Ross B C 1977 U.S. Patent 4107435, *Chem. Abstr.* **88** 7304
21. Fujita M, Kitagawa O, Suzuki T and Taguchi T 1997 *J. Org. Chem.* **62** 7330
22. Jorda-Gregori J M, Gonzalez-Rosende M E, Cava-Montesinos P, Sepulveda-Arques J, Galeazzi R and Orena M 2000 *Tetrahedron: Asymm.* **11** 3769
23. Muehlstaedt M, Meusinger R, Olk B, Weber L and Widera R 1986 *J. Prakt. Chem.* **328** 309
24. Davies S G, Haggitt J R, Ichihara O, Kelly R J, Leech M A, Price Mortimer A J, Roberts P M and Smith A D 2004 *Org. Biomol. Chem.* **2** 2630
25. Takahata H, Ouchi H, Ichinose M and Nemoto H 2002 *Org. Lett.* **4** 3459
26. Jung J-W, Shin D-Y, Seo S-Y, Kim S-H, Paek S-M, Jung J-K and Suh Y-G 2005 *Tetrahedron Lett.* **46** 573
27. Puigbó G, Diaba F and Bonjoch J 2003 *Tetrahedron* **59** 2657
28. Davies S G and Ichihara O 1999 *Tetrahedron Lett.* **40** 9313
29. (a) Yamamoto Y, Komatsu T and Muruyama K 1985 *J. Org. Chem.* **50** 3115; (b) Yamamoto Y, Nishii S, Muruyama K, Komatsu T and Ito W 1986 *J. Am. Chem. Soc.* **108** 7778; (c) David M, Dhimane H, Vanucci-Bacqué C, Lhommet G 1999 *J. Org. Chem.* **64** 8402; (d) Jones A D, Knight D W and Hibbs D E 2001 *J. Chem. Soc. Perkin Trans.* **1** 1182
30. Mangelimckx S, Nural Y, Dondas H A, Denolf B, Sillanpää R and Kimpe N D 2010 *Tetrahedron* **66** 4115
31. Kemp S J, Bao J G and Pedersen S F 1996 *J. Org. Chem.* **61** 7162
32. Sonoda N, Yamamoto G, Natsukawa K, Kondo K and Murai S 1975 *Tetrahedron Lett.* **16** 1969
33. Walsh P J, Bennani Y L and Sharpless K B 1993 *Tetrahedron Lett.* **34** 5545
34. Donohoe T J, Bataille C R R, Gattrell W, Kloesges J and Rossignol E 2007 *Org. Lett.* **9** 1725
35. Hilborn J W, Lu Z-H, Jurgens A R, Fang Q K, Byers P, Wald S A and Senanayake C H 2001 *Tetrahedron Lett.* **42** 8919
36. Hirama M, Nishizaki I, Shigemoto T and Ito S 1986 *J. Chem. Soc. Chem. Commun.* 393
37. Ella-Menye J-R, Sharma V and Wang G 2005 *J. Org. Chem.* **70** 463
38. Davies S G, Garner A C, Roberts P M, Smith A D, Sweet M J and Thomson J E 2006 *Org. Biomol. Chem.* **4** 2753
39. Ella-Menye J-R and Wang G 2007 *Tetrahedron* **63** 10034
40. Murakami M, Suginome M, Fujimoto K, Nakamura H, Andersson P G and Ito Y 1993 *J. Am. Chem. Soc.* **115** 6487
41. Jung J-C and Avery M A 2006 *Tetrahedron Lett.* **47** 7969
42. (a) Phukan P 2004 *J. Org. Chem.* **69** 4005; (b) Kalita H R and Phukan P 2005 *Synth. Commun.* **35** 485
43. Kolb H C, van Nieuwenhze M S and Sharpless K B 1994 *Chem. Rev.* **94** 2483
44. Ager D J, Prakash I and Schaad D R 1996 *Chem. Rev.* **96** 835