Synthesis of oxazolidinones initiated by regio- and diastereo-controlled crotylation of α-dicarbonyl compounds

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5d: CCDC 729634
6d: CCDC 729636
7: CCDC 729635
8: CCDC 729637
9: CCDC 729638
Experimental

**Analysis.** IR spectra were recorded as thin film on a Horiba FT-720 spectrometer. All $^1$H and $^{13}$C NMR spectra were recorded with a JEOL JMTC-400/54/SS (400 and 100 MHz, respectively) in deuteriochloroform (CDCl$_3$) containing 0.03% (w/v) of tetramethylsilane as internal standard. Mass spectra were recorded on a JEOL JMS-DS-303 spectrometer. Column chromatography was performed by using MERCK Silica gel 60. Purification of products by recycle GPC system was performed by JAPAN ANALYTICAL INDUSTRY CO., LTD. LC-908. Preparative TLC was carried out on Wakogel B-5F silica gel.

**Materials.** Allyl-tri-n-butyltin was prepared by the reaction of tri-n-butyltin chloride ($n$Bu$_3$SnCl) with the corresponding Grignard reagents. Crotyl-tri-n-butyltin were prepared by hydrostannation of butadiene as known method. Substrates 1a, 1b and 1c were commercially available. All reactions were carried out under dry nitrogen.


Representative procedure for the preparation of 2-oxazolidinone initiated by allylation. To a dry nitrogen-filled 10-mL round-bottomed flask containing allyltri-n-butyltin (0.331 g, 1 mmol) in THF (1 mL) was added di-n-butyltin diiodide (0.487 g, 1 mmol) at rt. After stirring at rt for 10 min, to the resulting solution of allyliododi-n-butyltin (1 mmol) was added 2,3-butanedione (1a) (0.086 g, 1 mmol), and stirred at rt for 1 h. The reaction mixture was cooled to rt. To this mixture was added tosyl isocyanate (0.592 g, 3 mmol) and stirred for 1 h. The IR absorption band of NCO (2200 cm$^{-1}$) disappeared, which indicated the formation of stannylcarbamate adduct (II). The mixture was heated to 80 ºC and stirred for 5 h. The reaction was quenched by H$_2$O (0.5 mL), and the residue was chromatographed on silica-gel column (FL100-DX (Fuji silysia)). By-products such as organotin compounds were removed by eluting with hexane. Subsequent elution with Hexane/EtOAc=85/15 gave 2-oxazolidinone 3a (0.221 g, 72%).

Representative procedure for the preparation of 2-oxazolidinone (5a) initiated by crotylation. To a dry nitrogen-filled 10-mL round-bottomed flask containing crotyltri-n-butyltin (0.345 g, 1 mmol), carbonyl substrate (1a) (0.086 g, 1 mmol) in THF (1 mL) were added di-n-butyltin diiodide (0.487 g, 1 mmol) at rt. After stirring for 4 h, the reaction mixture was cooled to 0 ºC. To this mixture was added tosyl isocyanate (0.592 g, 3 mmol) and stirred for 1 h. The mixture was warmed to 80 ºC and stirred for 5 h. The reaction was quenched by H$_2$O (0.5 mL), and the residue was chromatographed on silica-gel column (FL100-DX (Fuji silysia)). By-products such as organotin compounds were removed by eluting with hexane. Subsequent elution with Hexane/EtOAc=85/15 gave 5-(Z)-crotyl substituted 2-oxazolidinone 5a (0.212 g, 66%). Reactions using other substrates was performed in a similar manner. Spectral data of products obtained are listed in the following pages. Further purification of 5d was performed by recrystallization. The structure of crystalline product 5d was indicated by X-ray analysis.

Representative procedure for the preparation of 2-oxazolidinone (6a) initiated by 1-methylallylation. To a dry nitrogen-filled 10-mL round-bottomed flask containing crotyl-n-butyltin (0.345 g, 1 mmol) in THF
(1 mL) was added di-n-butyltin dichloride (0.608 g, 2 mmol) at rt. After stirring at 60 °C for 2 h, the reaction mixture was cooled to 40 °C and carbonyl substrate (1a) (0.086 g, 1 mmol) was added. To this mixture was added tosyl isocyanate (0.592 g, 3 mmol). The mixture was warmed to 80°C and stirring was continued for 5 h. The reaction was quenched by H₂O, and the residue was chromatographed on silica-gel column (FL100-DX (Fuji silysia)). Removal of by-products such as organotin compounds was performed by eluting with hexane. Subsequent elution with Hexane/EtOAc= 85/15 gave 2-oxazolidone 6a (0.231 g, 72%). Diastereomer ratio was determined by ¹H-NMR. Further purification of the main diastereoisomer of 6d was performed by recrystallization. The structure of the crystalline product was indicated by X-ray analysis. 1-Methylallylation using other substrates was performed in a similar manner. Spectral data of products obtained are listed in the following pages.
5-Allyl-5-methyl-4-methylene-3-(toluene-4-sulfonyl)-oxazolidin-2-one (3a)

Colorless wax
IR (neat) 1790 cm\(^{-1}\) (C=O)
\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.93 (d, \(J = 8.2\) Hz, 2H, Ts \(o\)), 7.36 (d, \(J = 8.2\) Hz, 2H, Ts \(m\)), 5.57 (d, \(J = 3.0\) Hz, 1H, g C=CH\(_2\)), 5.49-5.38 (m, 1H, b C=CH), 5.05 (d, \(J = 17.2, 1.3\) Hz, 1H, a C=CH\(_2\)), 4.92 (d, \(J = 10.1, 1.3\) Hz, 1H, a C=CH\(_2\)), 4.43 (d, \(J = 3.0\) Hz, 1H, g C=CH\(_2\)), 2.46 (s, 3H, Ts CH\(_3\)), 2.33 (dd, \(J = 14.0, 7.7\) Hz, 1H, c CH\(_2\)), 2.43 (dd, \(J = 14.0, 7.0\) Hz, 1H, c CH\(_2\)), 1.46 (s, 3H, e CH\(_3\))
\(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 150.3 (h), 146.0 (Ts \(i\)), 143.2 (f), 134.4 (Ts \(p\)), 129.7 (Ts \(m\)), 129.4 (b), 128.1 (Ts \(o\)), 121.2 (a), 90.5 (g), 84.5 (d), 45.3 (c), 81.7 (g), 45.0 (c), 26.2 (e), 21.7 (Ts CH\(_3\))
MS (EI, 70 eV) m/z 307 (M\(^+\), 9.4), 266 (M\(^+\) - CH\(_2\)CH=CH\(_2\), 1.3), 155 (Ts, 52), 152 (24), 91 (100), 43 (30)
HRMS calcd for C\(_{15}\)H\(_{17}\)NO\(_4\)S 307.0878, found m/z 307.0887 (EI, (M\(^+\)), + 0.9 mmu)
Anal calcd for C\(_{15}\)H\(_{17}\)NO\(_4\)S C 58.61, H 5.57, N 4.56, S 10.43, found C 58.67, H 5.50, N 4.42, S 10.23

5-Allyl-5-methyl-4-methylene-3-phenyl-oxazolidin-2-one (3b)

Colorless wax
IR (neat) 1770 cm\(^{-1}\) (C=O)
\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.47 (dd, \(J = 7.7, 7.5\) Hz, 2H, Ph \(m\)), 7.38 (t, \(J = 7.5\) Hz, 1H, Ph \(p\)), 7.31 (d, \(J = 7.5\) Hz, 2H, Ph \(o\)), 5.90-5.80 (m, 1H, b C=CH), 5.27-5.21 (m, 2H, a C=CH\(_2\)), 4.18 (d, \(J = 2.9\) Hz, 1H, g C=CH\(_2\)), 4.04 (d, \(J = 2.9\) Hz, 1H, g C=CH\(_2\)), 2.64 (dd, \(J = 14.0, 7.7\) Hz, 1H, c CH\(_2\)), 2.51 (dd, \(J = 14.0, 7.0\) Hz, 1H, c CH\(_2\)), 1.62 (s, 3H, e CH\(_3\))
\(^13\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 154.6 (h), 150.0 (f), 134.0 (Ph \(i\)), 130.5 (b), 129.5 (Ph \(m\)), 128.3 (Ph \(p\)), 127.0 (Ph \(o\)), 120.6 (a), 84.9 (d), 81.7 (g), 45.3 (c), 26.2 (e)
MS (EI, 70 eV) m/z 229 (M\(^+\), 35), 188 (M\(^+\) - CH\(_2\)CH=CH\(_2\), 100), 104 (31), 77 (Ph, 28)
HRMS calcd for C\(_{14}\)H\(_{13}\)NO\(_2\) 229.0887, found m/z 229.1112 (EI, (M\(^+\)), + 1.0 mmu)
Anal calcd for C\(_{14}\)H\(_{13}\)NO\(_2\) C 73.34, H 6.59, N 6.11, found C 73.41, H 6.52, N 6.12

5-Allyl-3-(4-methoxy-phenyl)-5-methyl-4-methylene-oxazolidin-2-one (3c)

White solid
mp 58˚C
IR (KBr) 1750 cm\(^{-1}\) (C=O)
H NMR (CDCl₃, 400 MHz) δ 7.21 (d, J = 8.9 Hz, 2H, j), 6.97 (d, J = 8.9 Hz, 2H, k), 5.90-5.78 (m, 1H, b C=CH), 5.26-5.20 (m, 2H, a C=CH₂), 4.10 (d, J = 2.7 Hz, 1H, c CH₂), 4.01 (d, J = 2.7 Hz, 1H, g C=CH₂), 3.83 (s, 3H, m CH₃), 2.62 (dd, J = 14.1, 7.6 Hz, 1H, c CH₂), 2.49 (dd, J = 14.1, 7.0 Hz, 1H, e CH₃), 1.61 (s, 3H, e CH₃)

13C NMR (CDCl₃, 100 MHz) δ 159.3 (l), 154.9 (h), 150.5 (f), 130.6 (b), 128.4 (j), 126.5 (i), 120.5 (a), 114.8 (k), 83.8 (d), 81.4 (g), 55.4 (m), 45.3 (c), 26.2 (e)

MS (EI, 70 eV) m/z 259 (M⁺, 54), 218 (M⁺-CH₂CH=CH₂, 100), 134 (28), 133 (23)
HRMS calcd for C₁₅H₁₇NO₃ 259.1208, found m/z 259.1211 (EI, (M⁺), + 0.3 mmu)

Anal calcd for C₁₅H₁₇NO₃ C 69.48, H 6.61, N 5.40, found C 69.21, H 6.34, N 5.44

5-Allyl-5-phenyl-3-(toluene-4-sulfonyl)-oxazolidine-2,4-dione (4a)
White solid
mp 107-108°C
IR (KBr) 1828 cm⁻¹ (C=O), 1774 cm⁻¹ (C=O)

H NMR (CDCl₃, 400 MHz) δ 8.00 (d, J = 8.5 Hz, 2H, Ts o), 7.53-7.49 (m, 2H, Ph o), 7.42-7.37 (m, 5H, Ph p and Ts m), 5.46-5.35 (m, 1H, b C=CH), 5.11 (dd, J = 17.1, 1.3 Hz, 1H, a C=CH₂), 4.89 (dd, J = 10.1, 1.3 Hz, 1H, a C=CH₂), 2.90 (dd, J = 14.4, 7.6 Hz, 1H, c CH₂), 2.78 (dd, J = 14.4, 6.9 Hz, 1H, e CH₃)

13C NMR (CDCl₃, 100 MHz) δ 168.3 (e), 148.1 (f), 147.2 (Ts ᵐ), 134.1 (Ar), 133.7 (Ar), 130.0 (Ts ᵚ), 129.4 (Ph p), 128.9 (Ar), 127.7 (Ar), 124.4 (Ph o), 122.9 (a), 87.4 (d), 43.9 (c), 21.8 (Ts CH₃)

MS (CI, 200 eV) m/z 372 (M⁺+H, 100), 328 (5.5), 218 (22)
HRMS calcd for C₁₉H₁₇NO₅S 372.0906, found m/z 372.0901 (Cl, (M⁺+H), - 0.5 mmu)
Anal calcd for C₁₉H₁₇NO₅S C 61.44, H 4.61, N 3.77, S 8.63, found C 61.35, H 4.47, N 3.75, S 8.62

5-Allyl-5-phenyl-3-phenyl-oxazolidine-2,4-dione (4b)
White solid
mp 97°C
IR (KBr) 1812 cm⁻¹ (C=O), 1731 cm⁻¹ (C=O)

H NMR (CDCl₃, 400 MHz) δ 7.71-7.68 (m, 2H, Ph-C o), 7.50-7.34 (m, 8H, Ar), 5.87-5.76 (m, 1H, b C=CH₂), 3.07 (dd, J = 14.4, 7.6 Hz, 1H, c CH₂), 2.96 (dd, J = 14.4, 6.9 Hz, 1H, e CH₃)

13C NMR (CDCl₃, 100 MHz) δ 172.0 (e), 153.3 (f), 135.4 (Ph-C ᵐ), 130.7 (Ph-N ᵐ), 129.3, 129.2, 129.0, 128.9, 128.7, 125.7, 124.7, 122.6 (a), 87.5 (d), 43.3 (c)

MS (EI, 70 eV) m/z 293 (M⁺, 0.72), 252 (M⁺ - CH₂CH=CH₂, 39), 105 (100), 77 (Ph, 18)
HRMS calcd for C₁₈H₁₅NO₃ 293.1052, found m/z 293.1050 (El, (M⁺), + 0.2 mmu)
Anal calcd for C₁₈H₁₅NO₃ C 73.71, H 5.15, N 4.78, found C 73.47, H 5.07, N 4.78
5-Allyl-3-(4-methoxy-phenyl)-5-phenyl-oxazolidine-2,4-dione (4c)

White solid
mp 79°C
IR (KBr) 1813 cm$^{-1}$ (C=O), 1741 cm$^{-1}$ (C=O)
$^1$H NMR (CDCl$_3$, 400 MHz) δ 7.70-7.67 (m, 2H, Ph $o$), 7.46-7.37 (m, 3H, Ph $m$ p), 7.24 (d, $J = 9.1$ Hz, 2H, h), 6.95 (d, $J = 9.1$ Hz, 2H, i), 5.86-5.74 (m, 2H, a C=CH), 3.79 (s, 3H, k CH$_3$), 3.05 (dd, $J = 14.3$, 7.6 Hz, 1H, c CH$_2$), 2.94 (dd, $J = 14.3$, 6.8 Hz, 1H, c CH$_2$) 
$^{13}$C NMR (CDCl$_3$, 100 MHz) δ 172.2 (e), 159.7 (j), 153.6 (f), 135.4 (Ph $i$), 129.0, 128.8, 128.8, 127.1 (h), 124.6 (Ph o), 123.2 (g), 114.5 (i), 87.4 (d), 55.4 (k), 43.2 (c)
MS (EI, 70 eV) m/z 323 (M$^+$, 67), 282 (M$^+$ - CH$_2$CH=CH$_2$, 5.8), 210 (96), 149 (34), 129 (22), 105 (100), 77 (Ph, 27)
HRMS calcd for C$_{19}$H$_{17}$NO$_3$ 323.1158, found m/z 323.1153 (EI, (M$^+$), - 0.5 mmu)
Anal calcd for C$_{19}$H$_{17}$NO$_3$ C 70.58, H 5.30, N 4.33, found C 70.48, H 5.21, N 4.33

5-((Z)-But-2-enyl)-5-methyl-4-methylene-3-(toluene-4-sulfonyl)-oxazolidin-2-one (5a)

Colorless wax
IR (neat) 1793 cm$^{-1}$ (C=O)
$^1$H NMR (CDCl$_3$, 400 MHz) δ 7.93 (d, $J = 8.3$ Hz, 2H, Ts $o$), 7.35 (d, $J = 8.3$ Hz, 2H, Ts $m$), 5.54 (d, $J = 2.9$ Hz, 1H, h C=CH$_2$), 5.40 (qd, $J = 10.9$, 6.8 Hz, 1H, b C=CH), 5.10-5.01 (m, 1H, c C=CH), 4.44 (d, $J = 2.9$ Hz, 1H, h C=CH$_2$), 2.51 (dd, $J = 14.5$, 8.7 Hz, 1H, d CH$_2$), 2.46 (s, 3H, Ts CH$_3$), 2.30 (dd, $J = 14.5$, 7.1 Hz, 1H, d CH$_2$), 1.53 (d, $J = 6.8$ Hz, 3H, a CH$_3$), 1.48 (s, 3H, f CH$_3$) 
$^{13}$C NMR (CDCl$_3$, 100 MHz) δ 150.3 (i), 146.0 (Ts $i$), 143.6 (g), 134.6 (Ts $p$), 129.9 (b), 129.7 (Ts $m$), 128.2 (Ts $o$), 121.1 (c), 90.3 (h), 85.1 (e), 38.1 (d), 26.2 (f), 21.7 (Ts CH$_3$), 13.1 (a)
MS (Cl, 200 eV) m/z 322 (M$^+$ + 1, 100), 278 (5.1)
HRMS calcd for C$_{16}$H$_{15}$NO$_3$ 322.1113, found m/z 322.1153 (EI, (M$^+$), - 0.5 mmu)
Anal calcd for C$_{16}$H$_{15}$NO$_3$ C 59.79, H 5.30, N 4.33, found C 59.48, H 5.21, N 4.33

5-((Z)-But-2-enyl)-5-methyl-4-methylene-3-phenyl-oxazolidin-2-one (5b)

Colorless wax
IR (neat) 1770 cm$^{-1}$ (C=O)
$^1$H NMR (CDCl$_3$, 400 MHz) δ 7.50-7.45 (m, 2H, Ph $m$), 7.38 (t, $J = 7.5$ Hz, 1H, Ph $o$), 7.33-7.30 (m, 2H, Ph $o$), 5.75 (qd, $J = 6.8$, 10.9 Hz, 1H, b C=CH), 5.53-5.45 (m, 1H, c C=CH), 4.15 (d, $J =
2.9 Hz, 1H, h C=CH), 4.05 (d, J = 2.9 Hz, 1H, h C=CH), 2.69 (dd, J = 14.5, 8.0 Hz, 1H, d CH2), 2.51 (dd, J = 14.5, 7.2 Hz, 1H, d CH2), 1.68 (d, J = 6.8 Hz, 3H, a CH3), 1.64 (s, 3H, f CH3)

13C NMR (CDCl3, 100 MHz) δ 154.7 (i), 150.3 (g), 134.1 (Ph i), 129.5 (Ph m), 129.3 (b), 128.3 (Ph p), 127.1 (Ph o), 122.2 (c), 84.5 (e), 81.5 (h), 38.3 (d), 26.3 (f), 13.3 (a)

MS (EI, 70 eV) m/z 243 (M⁺, 14), 189 (32), 188 (M⁺ - CH₂CH=CHCH₃, 100), 104 (24), 77 (Ph, 16)

HRMS calcd for C₁₅H₁₇NO₂ 243.1259, found m/z 243.1255 (EI, (M⁺), - 0.4 mmu)

Anal calcd for C₁₅H₁₇NO₂ C 74.05, H 7.04, N 5.76, found C 73.77, H 6.94, N 5.79

5-((Z)-But-2-enyl)-3-(4-methoxy-phenyl)-5-methyl-4-methylene-oxazolidin-2-one (5c)

White solid
mp 71°C
IR (KBr) 1755 cm⁻¹ (C=O)

1H NMR (CDCl3, 400 MHz) δ 7.21 (d, J = 8.8 Hz, 2H, k), 6.97 (d, J = 8.8 Hz, 2H, l), 5.74 (qd, J = 6.8,11.0 Hz, 1H, b C=CH), 5.53-5.44 (m, 1H, c C=CH), 4.07 (d, J = 2.7 Hz, 1H, h C=CH), 4.02 (d, J = 2.7 Hz, 1H, h C=CH), 3.83 (s, 3H, n CH3), 2.68 (dd, J = 14.5, 7.9 Hz, 1H, d CH2), 2.50 (dd, J = 14.5, 7.2 Hz, 1H, d CH2), 1.67 (d, J = 6.8 Hz, 3H, a CH3), 1.62 (s, 3H, f CH3)

13C NMR (CDCl3, 100 MHz) δ 159.3 (m), 155.0 (i), 150.8 (g), 129.2 (b), 128.4 (k), 126.6 (j), 122.2 (c), 114.8 (l), 84.4 (e), 81.2 (h), 55.5 (n), 38.3 (d), 26.3 (f), 13.2 (a)

MS (EI, 70 eV) m/z 273 (M⁺, 28), 219 (32), 218 (M⁺ - CH₂CH=CHCH₃, 100), 134 (28)

HRMS calcd for C₁₆H₁₉NO₃ 273.1365, found m/z 273.1369 (EI, (M⁺), + 0.4 mmu)

Anal calcd for C₁₆H₁₉NO₃ C 70.31, H 7.01, N 5.12, found C 70.05, H 7.13, N 5.04

5-((Z)-But-2-enyl)-3-(4-iodo-phenyl)-5-methyl-4-methylene-oxazolidin-2-one (5d)

White solid
mp 73°C
IR (KBr) 1760 cm⁻¹ (C=O)

1H NMR (CDCl3, 400 MHz) δ 7.80 (d, J = 8.7 Hz, 2H, l), 7.08 (d, J = 8.7 Hz, 2H, k), 5.74 (qd, J = 6.8,11.0 Hz, 1H, b C=CH), 5.53-5.44 (m, 1H, c C=CH), 4.16 (d, J = 2.9 Hz, 1H, h C=CH), 4.08 (d, J = 2.9 Hz, 1H, h C=CH), 2.68 (dd, J = 14.5, 8.0 Hz, 1H, d CH2), 2.50 (dd, J = 14.5, 7.2 Hz, 1H, d CH2), 1.67 (d, J = 6.8 Hz, 3H, a CH3), 1.63 (s, 3H, f CH3)

13C NMR (CDCl3, 100 MHz) δ 154.3 (i), 149.7 (g), 138.7 (l), 133.8 (j), 129.5 (b), 128.8 (k), 122.0 (c), 93.5 (m), 84.7 (e), 81.8 (h), 38.3 (d), 26.3 (f), 13.2 (a)

MS (EI, 70 eV) m/z 369 (M⁺, 23), 315 (37), 314 (M⁺ - CH₂CH=CHCH₃, 100), 230 (19)

HRMS calcd for C₁₅H₁₆INO₂ 369.0226, found m/z 369.0233 (EI, (M⁺), + 0.7 mmu)

Anal calcd for C₁₅H₁₆INO₂ C 48.80, H 4.37, I 34.37, N 3.79, found C 48.67, H 4.09, I 34.58, N 3.79

5-((Z)-But-2-enyl)-3-(4-iodo-phenyl)-5-methyl-4-methylene-oxazolidin-2-one (5d)
(S')-5-Methyl-5-((R')-1-methyl-allyl)-4-methylene-3-(toluene-4-sulfonyl)-oxazolidin-2-one (6a)

Colorless wax
IR (neat) 1790 cm\(^{-1}\) (C=O)
\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.95 (d, \(J = 8.5\) Hz, 2H, Ts o), 7.36 (d, \(J = 8.5\) Hz, 2H, Ts m), 5.58 (d, \(J = 2.9\) Hz, 1H, h C=CH\(_2\)), 5.60-5.50 (m, 1H, b C=CH), 5.06 (dd \(J = 17.1, 1.3\) Hz, 1H, a C=CH\(_2\)), 5.00 (dd \(J = 10.1, 1.3\) Hz, 1H, a C=CH\(_2\)), 4.41 (d, \(J = 2.9\) Hz, 1H, h C=CH\(_2\)), 2.46 (s, 3H, Ts CH\(_3\)), 2.28 (qd, \(J = 7.0, 8.9\) Hz, 1H, c CHMe), 1.41 (s, 3H, f CH\(_3\)), 0.85 (d, \(J = 7.0\) Hz, 3H, d CH\(_3\))

\(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 150.6 (i), 146.1 (Ts i), 143.1 (g), 136.5 (b), 134.4 (Ts p), 129.8 (Ts m), 128.1 (Ts o), 118.2 (a), 90.7 (h), 86.6 (e), 25.2 (f), 14.1 (d)

MS (EI, 70 eV) m/z 321 (M\(^+\), 9.8), 266 (M\(^+\)-CH(CH\(_3\))CH=CH\(_2\), 3.2), 166 (20), 155 (Ts, 80), 112 (37), 91 (100), 55 (CH(CH\(_3\))CH=CH\(_2\), 42)

HRMS calcd for C\(_{16}\)H\(_{19}\)NO\(_4\)S 321.1035, found m/z 321.1031 (EI, (M\(^+\)), -0.4 mmu)

Anal calcd for C\(_{16}\)H\(_{19}\)NO\(_4\)S C 59.79, H 5.96, N 4.36, S 9.98, found C 59.51, H 5.70, N 4.28, S 9.72

(5'-5-Methyl-5-((R')-1-methyl-allyl)-4-methylene-3-phenyl-oxazolidin-2-one (6b)

Colorless wax
IR (neat) 1774 cm\(^{-1}\) (C=O)
\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.51-7.45 (m, 2H, ph m), 7.39 (t, \(J = 7.5\) Hz, 1H, Ph p), 7.34-7.30 (m, 2H, Ph o), 5.91-5.80 (m, 1H, b C=CH), 5.22-5.15 (m, 2H, a C=CH\(_2\)), 4.19 (d, \(J = 2.8\) Hz, 1H, h C=CH\(_2\)), 4.03 (d, \(J = 2.8\) Hz, 1H, C=CH\(_2\)), 2.45 (qd, \(J = 6.9, 8.8\) Hz, 1H, c CHMe), 1.57 (s, 3H, f CH\(_3\)), 1.15 (d, \(J = 6.9\) Hz, 3H, d CH\(_3\))

\(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\) 155.0 (i), 149.9 (g), 137.4 (b), 133.9 (Ph i), 129.6 (Ph m), 128.4 (Ph p), 127.1 (Ph o), 117.7 (a), 86.1 (e), 81.9 (h), 48.1 (c), 25.5 (f), 14.4 (d)

MS (EI, 70 eV) m/z 243 (M\(^+\), 20), 188 (M\(^+\)-CH(CH\(_3\))CH=CH\(_2\), 100), 104 (28), 77 (Ph, 19)

HRMS calcd for C\(_{15}\)H\(_{17}\)NO\(_2\) 243.1259, found m/z 243.1261 (EI, (M\(^+\)), + 0.2 mmu)

Anal calcd for C\(_{15}\)H\(_{17}\)NO\(_2\) C 74.05, H 5.96, N 4.36, S 9.98, found C 74.80, H 6.98, N 5.75
(S')-3-(4-Methoxy-phenyl)-5-methyl-5-((R')-1-methyl-allyl)-4-methylene-oxazolidin-2-one (6c)

White solid
mp 102°C
IR (KBr) 1753 cm⁻¹ (C=O)
¹H NMR (CDCl₃, 400 MHz) δ 7.22 (d, J = 8.9 Hz, 2H, k), 6.98 (d, J = 8.9 Hz, 2H, l), 5.90-5.80 (m, 1H, b C=CH), 5.22-5.15 (m, 2H, a C=CH₂), 4.11 (d, J = 2.7 Hz, 1H, h C=CH₂), 4.01 (d, J = 2.7 Hz, 1H, h C=CH₂), 3.84 (s, 3H, n CH₃), 2.43 (qd, J = 6.8, 9.1 Hz, 1H, CMe), 1.56 (s, 3H, f CH₃), 1.14 (d, J = 6.8 Hz, 3H, d CH₃)
¹³C NMR (CDCl₃, 100 MHz) δ 159.4 (m), 155.3 (i), 150.4 (g), 137.3 (b), 128.4 (k), 126.5 (j), 117.7 (a), 114.9 (l), 86.0 (e), 81.7 (h), 55.5 (n), 48.1 (c), 25.5 (f), 14.4 (d)
MS (EI, 70 eV) m/z 273 (M⁺, 29), 218 (M⁺ - CH(CH₃)CH=CH₂, 100), 134 (27)
HRMS calcd for C₁₆H₁₉NO₃ 273.1365, found m/z 273.1373 (EI, (M⁺), + 0.8 mmu)
Anal calcd for C₁₆H₁₉NO₃ C 70.31, H 7.01, N 5.12, found C 70.26, H 6.99, N 4.99

ORTEP Drawing of 6d: CCDC 729636
5-((Z)-But-2-enyl)-5-phenyl-3-(toluene-4-sulfonyl)-oxazolidine-2,4-dione (7)

White solid
mp 104˚C
IR (KBr) 1828 cm⁻¹ (C=O), 1774 cm⁻¹ (C=O)
¹H NMR (CDCl₃, 400 MHz) δ 8.00 (d, J = 8.5 Hz, 2H, Ts o), 7.55-7.51 (m, 2H, Ph o), 7.43-7.37 (m, 5H, Ph m p and Ts m), 5.40 (qd, J = 6.8, 10.9 Hz, 1H, b C=CH), 5.05-4.96 (m, 1H, c C=CH), 2.96 (dd, J = 14.7, 8.0 Hz, 1H, d CH₂), 2.76 (dd, J = 14.7, 7.5 Hz, 1H, d CH₂), 2.48 (s, 3H, Ts CH₃), 1.53 (d, J = 6.8 Hz, 3H, a CH₃)
¹³C NMR (CDCl₃, 100 MHz) δ 168.7 (f), 148.1 (g), 147.1 (Ts i), 134.4 (Ar), 133.9 (Ar), 132.3 (b), 130.0 (Ts m), 129.4 (Ph p), 128.9 (Ar), 128.8 (Ar), 124.5 (Ph o), 119.1 (c), 87.8 (e), 36.9 (d), 21.8 (Ts CH₃), 13.1 (a)
MS (Cl, 200 eV) m/z 386 (M⁺ + 1, 100), 232 (28)
HRMS calcd for C₂₀H₁₉NO₅S 386.1062, found m/z 386.1067 (Cl, (M⁺ + H), + 0.5 mmu)
Anal calcd for C₂₀H₁₉NO₅S C 62.32, H 4.97, N 3.63, S 8.32, found C 62.26, H 4.85, N 3.65, S 8.30

ORTEP Drawing of 7: CCDC 729635

(R')-5-((S')-1-Methyl-allyl)-5-phenyl-3-(toluene-4-sulfonyl)-oxazolidine-2,4-dione (8)

White solid
mp 152-153˚C
IR (KBr) 1824 cm⁻¹ (C=O), 1778 cm⁻¹ (C=O)
¹H NMR (CDCl₃, 400 MHz) δ 8.00 (d, J = 8.5 Hz, 2H, Ts o), 7.54-7.50 (m, 2H, Ph o), 7.43-7.37 (m, 5H, Ph m p and Ts m), 5.43-5.33 (m, 1H, b C=CH), 5.07 (dd, J = 17.1, 1.3 Hz, 1H, a C=CH₂), 4.69 (dd, J = 10.4, 1.3 Hz, 1H, a C=CH₂), 3.02 (qd, J = 7.0, 7.7 Hz, 1H, c CHMe), 2.48 (s, 3H, Ts CH₃), 1.09 (d, J = 7.0 Hz, 3H, d CH₃)
$\text{^13}C \text{ NMR (CDCl}_3, 100 \text{ MHz)} \delta 168.7 (f), 148.4 (g), 147.1 (Ts \ i), 134.1 (b), 133.8 (Ar), 133.0 (Ar), 129.9 (Ts \ m), 129.3 (Ph \ p), 128.9 (Ar), 128.8 (Ar), 124.7 (Ph \ o), 120.3 (a), 89.9 (e), 46.0 (c), 21.8 (Ts \ CH_3), 13.3 (d)$

MS (CI, 200 eV) $m/z$ 386 ($M^+ + 1$, 100), 232 (20)
HRMS calcd for C$_{20}$H$_{19}$NO$_5$S 386.1062, found $m/z$ 386.1064 (CI, ($M^+ + H^+$), + 0.1 mmu)
Anal calcd for C$_{20}$H$_{19}$NO$_5$S C 62.32, H 4.97, N 3.63, S 8.32, found C 62.28, H 4.83, N 3.60, S 8.29

ORTEP Drawing of 8: CCDC 729637

(4$R'$,5$R'$)-4-Hydroxy-3-(4-iodo-phenyl)-5-((S$'$)-1-methyl-allyl)-4,5-diphenyl-oxazolidin-2-one (9)

White solid
mp 220°C
IR (KBr) 3301 cm$^{-1}$ (OH), 1724 cm$^{-1}$ (C=O)
$\text{^1}H \text{ NMR (DMSO-d}_6, 400 \text{ MHz)} \delta 7.91 (s, 1H, OH), 7.66-6.92 (m, 14H, Ar), 6.30-6.17 (m, 1H, b), 5.23-5.13 (m, 2H, a), 3.50 (qd, $J = 6.8$, 6.8 Hz, 1H, c), 0.81 (d, $J = 6.8$ Hz, 3H, d)
$\text{^13}C \text{ NMR (DMSO-d}_6, 100 \text{ MHz)} \delta 153.8, 139.5-120.5$ (Ar mixture), 116.3 (a), 95.3 (e or f or k), 92.0 (e or f or k), 91.1 (e or f or k), 42.1 (c), 15.3 (d)
NMR sample includes non cyclized compound.
MS (EI, 70 eV) m/z 511 ($M^+$, 2.9), 323 (18), 245 (14), 211 (20), 161 (18), 105 (100), 77 (Ph, 16)
HRMS calcd for C$_{23}$H$_{22}$INO$_2$ 511.0644, found m/z 511.0651 (EI, ($M^+$), + 0.6 mmu)

ORTEP Drawing of 9: CCDC 729638
5-Allyl-5-methyl-4-methylene-3-(toluene-4-sulfonyl)-oxazolidin-2-one (3a)
5- Allyl-3-(4-methoxy-phenyl)-5-methyl-4-methylene-oxazolidin-2-one (3c)
5-Allyl-5-phenyl-3-(toluene-4-sulfonyl)-oxazolidine-2,4-dione (4a)
5-Allyl-5-phenyl-3-phenyl-oxazolidine-2,4-dione (4b)
5- Allyl-3-(4-methoxy-phenyl)-5-phenyl-oxazolidine-2,4-dione (4c)
5-((Z)-But-2-enyl)-5-methyl-4-methylene-3-(toluene-4-sulfonyl)-oxazolidin-2-one (5a)
5-((Z)-But-2-enyl)-5-methyl-4-methylene-3-phenyl-oxazolidin-2-one (5b)
5-((Z)-But-2-enyl)-3-(4-methoxy-phenyl)-5-methyl-4-methylene-oxazolidin-2-one (5c)
5-((Z)-But-2-enyl)-3-(4-iodo-phenyl)-5-methyl-4-methylene-oxazolidin-2-one (5d)

\[
\text{\includegraphics{image.png}}
\]
(S’)-5-Methyl-5-((R’)-1-methyl-allyl)-4-methylene-3-(toluene-4-sulfonyl)-oxazolidin-2-one (6a)
(S'')-5-Methyl-5-((R'')-1-methyl-allyl)-4-methylene-3-phenyl-oxazolidin-2-one (6b)
(S')-3-(4-Methoxy-phenyl)-5-methyl-5-((R')-1-methyl-allyl)-4-methylene-oxazolidin-2-one (6c)
(S’)-3-(4-Iodo-phenyl)-5-methyl-5-((R’)-1-methyl-allyl)-4-methylene-oxazolidin-2-one (6d)
5-((Z)-But-2-enyl)-5-phenyl-3-(toluene-4-sulfonyl)-oxazolidine-2,4-dione (7)
(R′)-5-((S′)-1-Methyl-allyl)-5-phenyl-3-(toluene-4-sulfonyl)-oxazolidine-2,4-dione (8)
(4R’,5R’)-4-Hydroxy-3-(4-iodo-phenyl)-5-((S’)-1-methyl-allyl)-4,5-diphenyl-oxazolidin-2-one (9)

![Chemical structure of the compound](image)

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![NMR spectrum](image)

### Chemical Structure

![Chemical structure of the compound](image)
X-ray Structure

X-ray Structure of 5d (CCDC 729634)

X-ray Structure of 6d (CCDC 729636)

X-ray Structure Report of 7 (CCDC 729635)
X-ray Structure Report of 8 (CCDC 729637)

X-ray Structure Report of 9 (CCDC 729638)