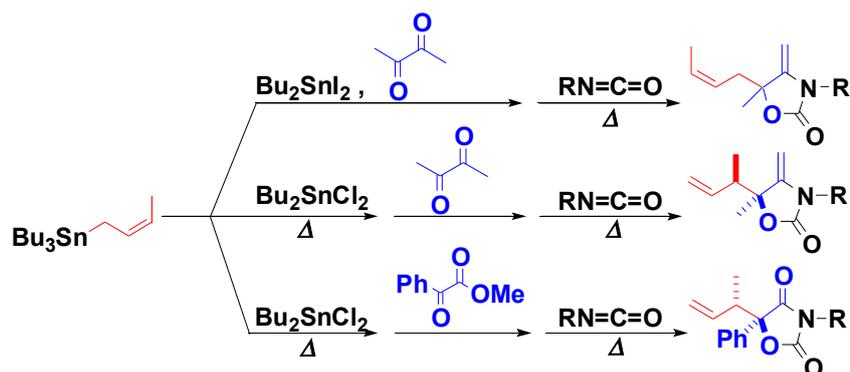


Synthesis of oxazolidinones initiated by regio- and diastereo-controlled crotylation of α -dicarbonyl compounds

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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 ^1H 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 ($^n\text{Bu}_3\text{SnCl}$) with the corresponding Grignard reagents.¹ Crotyl-tri-*n*-butyltin were prepared by hydrostannation of butadiene as known method.² Substrates **1a**, **1b** and **1c** were commercially available. All reactions were carried out under dry nitrogen.

1) Naruta, Y. Nishigaichi, K. Maruyama, *Chem. Lett.* **1986**, 1857.

2) Miyake, K. Yamamura, *Chem. Lett.* **1992**, 507.

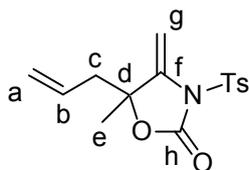
Representative procedure for the preparation of 2-oxazolidinone initiated by allylation. To a dry nitrogen-filled 10-mL round-bottomed flask containing allyltri-*n*-butyltin (0.331 g, 1 mmol) in THF (1 mL) was added di-*n*-butyltin diiodide (0.487 g, 1 mmol) at rt. After stirring at rt for 10 min, to 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 °C and stirred for 5 h. The reaction was quenched by H_2O (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-oxazolidonone **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 °C. To this mixture was added tosyl isocyanate (0.592 g, 3 mmol) and stirred for 1 h. The mixture was warmed to 80 °C and stirred for 5 h. The reaction was quenched by H_2O (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-oxazolidonone **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-oxazolidonone **6a** (0.231 g, 72%). Diastereomer ratio was determined by ¹H-NMR. Further purification of the main diastereo isomer 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)

^1H NMR (CDCl_3 , 400 MHz) δ 7.93 (d, $J = 8.2\text{Hz}$, 2H, Ts *o*), 7.36 (d, $J = 8.2\text{ Hz}$, 2H, Ts *m*), 5.57 (d, $J = 3.0\text{ Hz}$, 1H, g C=CH₂), 5.49-5.38 (m, 1H, b C=CH), 5.05 (d, $J = 17.2, 1.3\text{ Hz}$, 1H, a C=CH₂), 4.92 (d, $J = 10.1, 1.3\text{ Hz}$, 1H, a C=CH₂), 4.43 (d, $J = 3.0\text{ Hz}$, 1H, g C=CH₂), 2.46 (s, 3H, Ts CH₃), 2.43 (dd, $J = 14.0, 7.7\text{ Hz}$, 1H, c CH₂), 2.33 (dd, $J = 14.0, 6.8\text{ Hz}$, 1H, c CH₂), 1.46 (s, 3H, e CH₃)

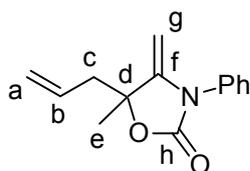
^{13}C NMR (CDCl_3 , 100 MHz) δ 150.3 (h), 146.0 (Ts *i*), 143.2 (f), 134.4 (Ts *p*), 129.7 (Ts *m*), 129.4 (b), 128.1 (Ts *o*), 121.2 (a), 90.5 (g), 84.5 (d), 45.0 (c), 26.1 (e), 21.7 (Ts CH₃)

MS (EI, 70 eV) m/z 307 (M^+ , 9.4), 266 ($\text{M}^+ - \text{CH}_2\text{CH}=\text{CH}_2$, 1.3), 155 (Ts, 52), 152 (24), 91 (100), 43 (30)

HRMS calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_4\text{S}$ 307.0878, found m/z 307.0887 (EI, (M^+), + 0.9 mmu)

Anal calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_4\text{S}$ 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)

^1H NMR (CDCl_3 , 400 MHz) δ 7.47 (dd, $J = 7.7, 7.5\text{ Hz}$, 2H, Ph *m*), 7.38 (t, $J = 7.5\text{ Hz}$, 1H, Ph *p*), 7.31 (d, $J = 7.5\text{ Hz}$, 2H, Ph *o*), 5.90-5.80 (m, 1H, b C=CH), 5.27-5.21 (m, 2H, a C=CH₂), 4.18 (d, $J = 2.9\text{ Hz}$, 1H, g C=CH₂), 4.04 (d, $J = 2.9\text{ Hz}$, 1H, g C=CH₂), 2.64 (dd, $J = 14.0, 7.7\text{ Hz}$, 1H, c CH₂), 2.51 (dd, $J = 14.0, 7.0\text{ Hz}$, 1H, c CH₂), 1.62 (s, 3H, e CH₃)

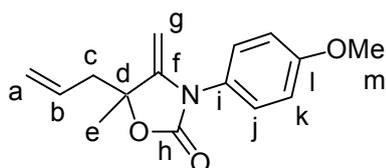
^{13}C NMR (CDCl_3 , 100 MHz) δ 154.6 (h), 150.0 (f), 134.0 (Ph *i*), 130.5 (b), 129.5 (Ph *m*), 128.3 (Ph *p*), 127.0 (Ph *o*), 120.6 (a), 84.9 (d), 81.7 (g), 45.3 (c), 26.2 (e)

MS (EI, 70 eV) m/z 229 (M^+ , 35), 188 ($\text{M}^+ - \text{CH}_2\text{CH}=\text{CH}_2$, 100), 104 (31), 77 (Ph, 28)

HRMS calcd for $\text{C}_{14}\text{H}_{15}\text{NO}_2$ 229.1103, found m/z 229.1112 (EI, (M^+), + 1.0 mmu)

Anal calcd for $\text{C}_{14}\text{H}_{15}\text{NO}_2$ 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)

^1H NMR (CDCl_3 , 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, g 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, c CH₂), 1.61 (s, 3H, e CH₃)

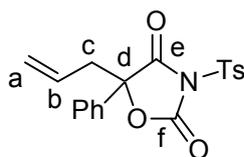
^{13}C NMR (CDCl_3 , 100 MHz) δ 159.3 (l), 154.9 (h), 150.5 (f), 130.6 (b), 128.4 (j), 126.5 (i), 120.5 (a), 114.8 (k), 83.8 (d), 81.4 (g), 55.4 (m), 45.3 (c), 26.2 (e)

MS (EI, 70 eV) m/z 259 (M^+ , 54), 218 ($\text{M}^+ - \text{CH}_2\text{CH}=\text{CH}_2$, 100), 134 (28), 133 (23)

HRMS calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_3$ 259.1208, found m/z 259.1211 (EI, (M^+), + 0.3 mmu)

Anal calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_3$ 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)

^1H NMR (CDCl_3 , 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 *m 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, c CH₂), 2.48 (s, 3H, Ts CH₃)

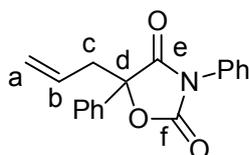
^{13}C NMR (CDCl_3 , 100 MHz) δ 168.3 (e), 148.1 (f), 147.2 (Ts *i*), 134.1 (Ar), 133.7 (Ar), 130.0 (Ts *m*), 129.4 (Ph *p*), 128.9 (Ar), 128.7 (Ar), 127.7 (Ar), 124.4 (Ph *o*), 122.9 (a), 87.4 (d), 43.9 (c), 21.8 (Ts CH₃)

MS (CI, 200 eV) m/z 372 ($\text{M}^+ + 1$, 100), 328 (5.5), 218 (22)

HRMS calcd for $\text{C}_{19}\text{H}_{17}\text{NO}_5\text{S}$ 372.0906, found m/z 372.0901 (CI, ($\text{M}^+ + \text{H}$), - 0.5 mmu)

Anal calcd for $\text{C}_{19}\text{H}_{17}\text{NO}_5\text{S}$ 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)

^1H NMR (CDCl_3 , 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), 5.39-5.29 (m, 2H, a C=CH₂), 3.07 (dd, $J = 14.4, 7.6$ Hz, 1H, c CH₂), 2.96 (dd, $J = 14.4, 6.9$ Hz, 1H, c CH₂)

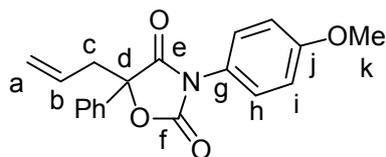
^{13}C NMR (CDCl_3 , 100 MHz) δ 172.0 (e), 153.3 (f), 135.4 (Ph-C *i*), 130.7 (Ph-N *i*), 129.3, 129.2, 129.0, 128.9, 128.7, 125.7, 124.7, 122.6 (a), 87.5 (d), 43.3 (c)

MS (EI, 70 eV) m/z 293 (M^+ , 0.72), 252 ($\text{M}^+ - \text{CH}_2\text{CH}=\text{CH}_2$, 39), 105 (100), 77 (Ph, 18)

HRMS calcd for $\text{C}_{18}\text{H}_{15}\text{NO}_3$ 293.1052, found m/z 293.1050 (EI, (M^+), - 0.2 mmu)

Anal calcd for $\text{C}_{18}\text{H}_{15}\text{NO}_3$ 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)

¹H NMR (CDCl₃, 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, 1H, b C=CH), 5.37-5.28 (m, 2H, a C=CH₂), 3.79 (s, 3H, k CH₃), 3.05 (dd, *J* = 14.3, 7.6 Hz, 1H, c CH₂), 2.94 (dd, *J* = 14.3, 6.8 Hz, 1H, c CH₂)

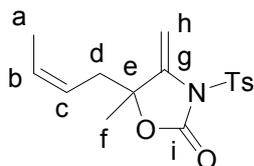
¹³C NMR (CDCl₃, 100 MHz) δ 172.2 (e), 159.7 (j), 153.6 (f), 135.4 (Ph *i*), 129.0, 128.8, 128.8, 127.1 (h), 124.6 (Ph *o*), 123.2 (g), 122.5 (a), 114.5 (i), 87.4 (d), 55.4 (k), 43.2 (c)

MS (EI, 70 eV) *m/z* 323 (M⁺, 67), 282 (M⁺ - CH₂CH=CH₂, 5.8), 210 (96), 149 (34), 129 (22), 105 (100), 77 (Ph, 27)

HRMS calcd for C₁₉H₁₇NO₄ 323.1158, found *m/z* 323.1153 (EI, (M⁺), - 0.5 mmu)

Anal calcd for C₁₉H₁₇NO₄ 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)

¹H NMR (CDCl₃, 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=CH₂), 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=CH₂), 2.51 (dd, *J* = 14.5, 8.7 Hz, 1H, d CH₂), 2.46 (s, 3H, Ts CH₃), 2.30 (dd, *J* = 14.5, 7.1 Hz, 1H, d CH₂), 1.53 (d, *J* = 6.8 Hz, 3H, a CH₃), 1.48 (s, 3H, f CH₃)

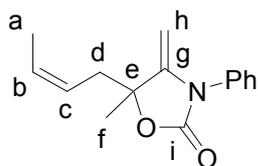
¹³C NMR (CDCl₃, 100 MHz) δ 150.3 (i), 146.0 (Ts *i*), 143.6 (g), 134.6 (Ts *p*), 129.9 (b), 129.7 (Ts *m*), 128.2 (Ts *o*), 121.1 (c), 90.3 (h), 85.1 (e), 38.1 (d), 26.2 (f), 21.7 (Ts CH₃), 13.1 (a)

MS (CI, 200 eV) *m/z* 322 (M⁺ + 1, 100), 278 (5.1)

HRMS calcd for C₁₆H₁₉NO₄ 322.1113, found *m/z* 322.1100 (CI, (M⁺ + H), - 1.3 mmu)

Anal calcd for C₁₆H₁₉NO₄ C 59.79, H 5.96, N 4.36, S 9.98, found C 59.51, H 5.72, N 4.37, S 9.87

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



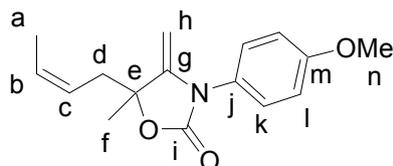
Colorless wax

IR (neat) 1770 cm⁻¹ (C=O)

¹H NMR (CDCl₃, 400 MHz) δ 7.50-7.45 (m, 2H, Ph *m*), 7.38 (t, *J* = 7.5 Hz, 1H, Ph *p*), 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=CH₂), 4.05 (d, *J* = 2.9 Hz, 1H, h C=CH₂), 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=CH₂), 4.02 (d, *J* = 2.7 Hz, 1H, h C=CH₂), 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)

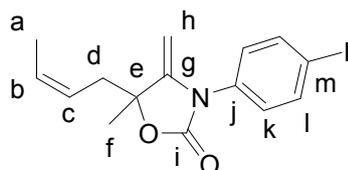
¹³C NMR (CDCl₃, 100 MHz) δ 159.3 (m), 155.0 (i), 150.8 (g), 129.2 (b), 128.4 (k), 126.6 (j), 122.2 (c), 114.8 (l), 84.4 (e), 81.2 (h), 55.5 (n), 38.3 (d), 26.3 (f), 13.2 (a)

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)

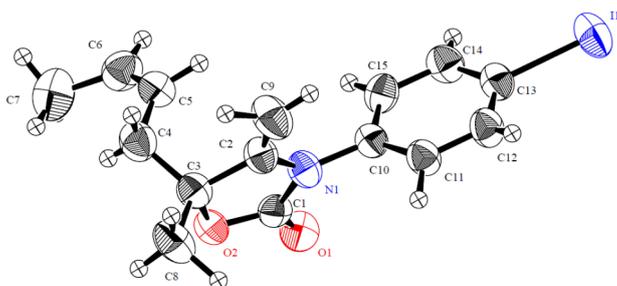
¹H NMR (CDCl₃, 400 MHz) δ 7.80 (d, *J* = 8.7 Hz, 2H, l), 7.08 (d, *J* = 8.7 Hz, 2H, k), 5.74 (qd, *J* = 6.8, 11.0 Hz, 1H, b C=CH), 5.51-5.41 (m, 1H, c C=CH), 4.16 (d, *J* = 2.9 Hz, 1H, h C=CH₂), 4.08 (d, *J* = 2.9 Hz, 1H, h C=CH₂), 2.68 (dd, *J* = 14.5, 8.0 Hz, 1H, d CH₂), 2.50 (dd, *J* = 14.5, 7.2 Hz, 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), 13.3 (a)

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

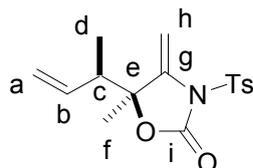
HRMS calcd for C₁₅H₁₆INO₂ 369.0226, found *m/z* 369.0233 (EI, (M⁺), + 0.7 mmu)

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



ORTEP Drawing of **5d**: CCDC 729634

(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)

^1H NMR (CDCl_3 , 400 MHz) δ 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=CH₂), 5.60-5.50 (m, 1H, b C=CH), 5.06 (dd $J = 17.1, 1.3$ Hz, 1H, a C=CH₂), 5.00 (dd $J = 10.1, 1.3$ Hz, 1H, c C=CH₂), 4.41 (d, $J = 2.9$ Hz, 1H, h C=CH₂), 2.46 (s, 3H, Ts CH₃), 2.28 (qd, $J = 7.0, 8.9$ Hz, 1H, c CHMe), 1.41 (s, 3H, f CH₃), 0.85 (d, $J = 7.0$ Hz, 3H, d CH₃)

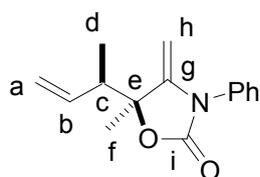
^{13}C NMR (CDCl_3 , 100 MHz) δ 150.6 (i), 146.1 (Ts *i*), 143.1 (g), 136.5 (b), 134.4 (Ts *p*), 129.8 (Ts *m*), 128.1 (Ts *o*), 118.2 (a), 90.7 (h), 86.6 (e), 48.0 (c), 25.2 (f), 21.8 (Ts CH₃), 14.1 (d)

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

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

Anal calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_4\text{S}$ 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

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



Colorless wax

IR (neat) 1774 cm^{-1} (C=O)

^1H NMR (CDCl_3 , 400 MHz) δ 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=CH₂), 4.19 (d, $J = 2.8$ Hz, 1H, h C=CH₂), 4.03 (d, $J = 2.8$ Hz, 1H, h C=CH₂), 2.45 (qd, $J = 6.9, 8.8$ Hz, 1H, c CHMe), 1.57 (s, 3H, f CH₃), 1.15 (d, $J = 6.9$ Hz, 3H, d CH₃)

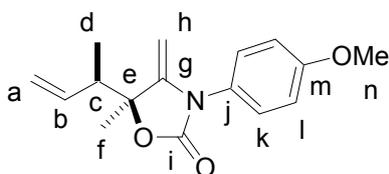
^{13}C NMR (CDCl_3 , 100 MHz) δ 155.0 (i), 149.9 (g) 137.4 (b), 133.9 (Ph *i*), 129.6 (Ph *m*), 128.4 (Ph *p*), 127.1 (Ph *o*), 117.7 (a), 86.1 (e), 81.9 (h), 48.1 (c), 25.5 (f), 14.4 (d)

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

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

Anal calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_2$ C 74.05, H 7.04, N 5.76, found C 74.800, 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, c CHMe), 1.56 (s, 3H, f CH₃), 1.14 (d, *J* = 6.8 Hz, 3H, d CH₃)

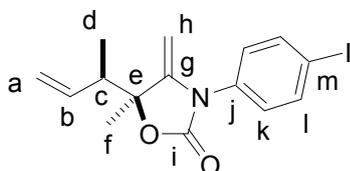
¹³C NMR (CDCl₃, 100 MHz) δ 159.4 (m), 155.3 (i), 150.4 (g), 137.3 (b), 128.4 (k), 126.5 (j), 117.7 (a), 114.9 (l), 86.0 (e), 81.7 (h), 55.5 (n), 48.1 (c), 25.5 (f), 14.4 (d)

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

(S')-3-(4-Iodo-phenyl)-5-methyl-5-((R')-1-methyl-allyl)-4-methylene-oxazolidin-2-one (6d)



White solid

mp 113°C

IR (KBr) 1748 cm⁻¹ (C=O)

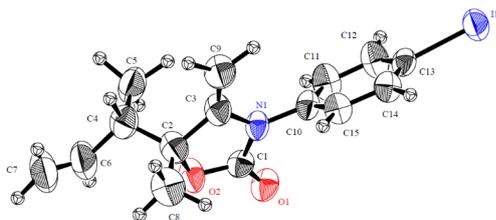
¹H NMR (CDCl₃, 400 MHz) δ 7.81 (d, *J* = 8.7 Hz, 2H, l), 7.08 (d, *J* = 8.7 Hz, 2H, k), 5.88-5.78 (m, 1H, b C=CH), 5.21-5.15 (m, 2H, a C=CH₂), 4.21 (d, *J* = 3.0 Hz, 1H, h C=CH₂), 4.06 (d, *J* = 3.0 Hz, 1H, h C=CH₂), 2.44 (qd, *J* = 6.9, 8.9 Hz, 1H, c CHMe), 1.56 (s, 3H, f CH₃), 1.13 (d, *J* = 6.9 Hz, 3H, d CH₃)

¹³C NMR (CDCl₃, 100 MHz) δ 154.5 (i), 149.3 (g), 138.8 (l), 137.2 (b), 133.7 (j), 128.8 (k), 117.86 (a), 93.6 (m), 86.3 (e), 82.2 (h), 48.0 (c), 25.4 (f), 14.4 (d)

MS (EI, 70 eV) *m/z* 369 (M⁺, 32), 314 (M⁺ - CH(CH₃)CH=CH₂, 100), 230 (19), 43 (20)

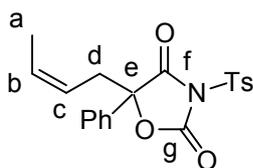
HRMS calcd for C₁₅H₁₆INO₂ 369.0226, found *m/z* 369.0229 (EI, (M⁺), + 0.4 mmu)

Anal calcd for C₁₅H₁₆INO₂ C 48.80, H 4.37, I 34.37, N 3.79, found C 48.78, H 4.10, I 34.32, N 3.92



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)

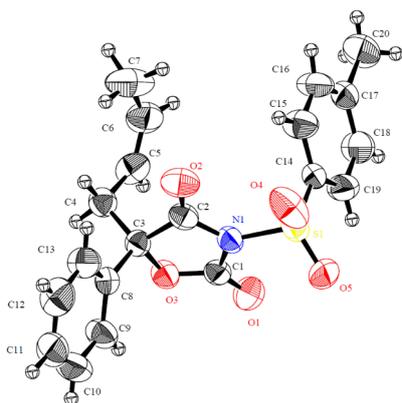
¹H NMR (CDCl₃, 400 MHz) δ 8.00 (d, *J* = 8.5 Hz, 2H, Ts *o*), 7.55-7.51 (m, 2H, Ph *o*), 7.43-7.37 (m, 5H, Ph *m p* and Ts *m*), 5.40 (qd, *J* = 6.8, 10.9 Hz, 1H, b C=CH), 5.05-4.96 (m, 1H, c C=CH), 2.96 (dd, *J* = 14.7, 8.0 Hz, 1H, d CH₂), 2.76 (dd, *J* = 14.7, 7.5 Hz, 1H, d CH₂), 2.48 (s, 3H, Ts CH₃), 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 (CI, 200 eV) *m/z* 386 (M⁺ + 1, 100), 232 (28)

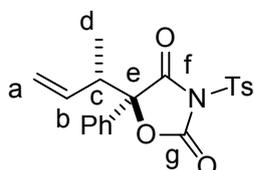
HRMS calcd for C₂₀H₁₉NO₅S 386.1062, found *m/z* 386.1067 (CI, (M⁺ + H), + 0.5 mmu)

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)

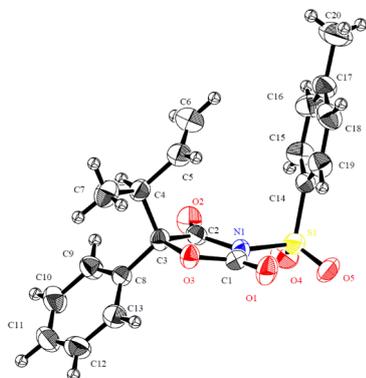
¹H NMR (CDCl₃, 400 MHz) δ 8.00 (d, *J* = 8.5 Hz, 2H, Ts *o*), 7.54-7.50 (m, 2H, Ph *o*), 7.44-7.36 (m, 5H, Ph *m p* and Ts *m*), 5.43-5.33 (m, 1H, b C=CH), 5.07 (dd *J* = 17.1, 1.3 Hz, 1H, a C=CH₂), 4.69 (dd *J* = 10.4, 1.3 Hz, 1H, a C=CH₂), 3.02 (qd, *J* = 7.0, 7.7 Hz, 1H, c CHMe), 2.48 (s, 3H, Ts CH₃), 0.83 (d, *J* = 7.0 Hz, 3H, d CH₃)

^{13}C NMR (CDCl_3 , 100 MHz) δ 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 ($\text{M}^+ + 1$, 100), 232 (20)

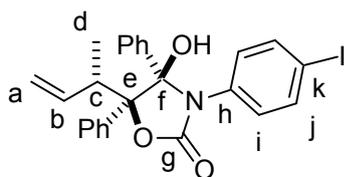
HRMS calcd for $\text{C}_{20}\text{H}_{19}\text{NO}_5\text{S}$ 386.1062, found m/z 386.1064 (CI, ($\text{M}^+ + \text{H}$), + 0.1 mmu)

Anal calcd for $\text{C}_{20}\text{H}_{19}\text{NO}_5\text{S}$ 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



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)

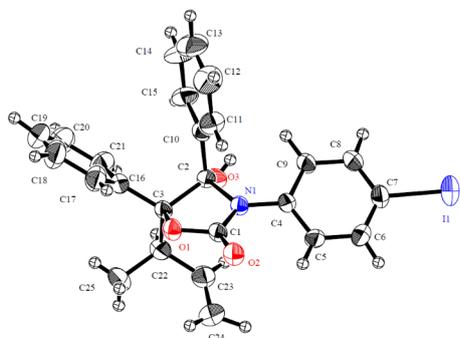
^1H NMR ($\text{DMSO}-d_6$, 400 MHz) δ 7.91 (s, 1H, OH), 7.66-6.92 (m, 14H, Ar), 6.30-6.17 (m, 1H, b), 5.23-5.13 (m, 2H, a), 3.50 (qd, $J = 6.8, 6.8$ Hz, 1H, c), 0.81 (d, $J = 6.8$ Hz, 3H, d)

^{13}C NMR ($\text{DMSO}-d_6$, 100 MHz) δ 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.

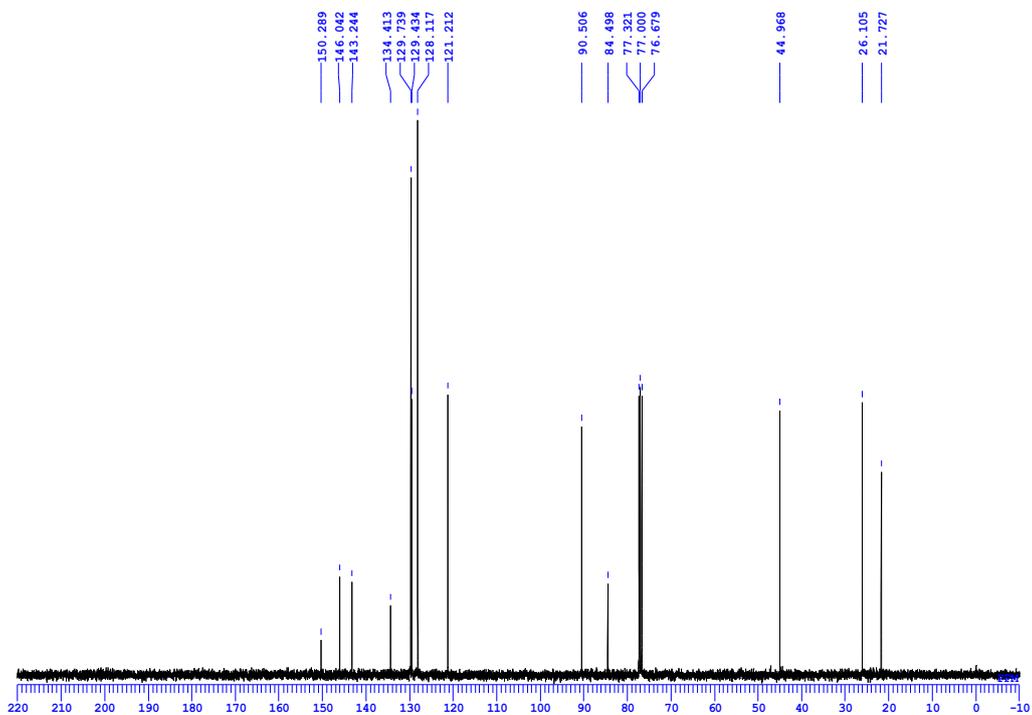
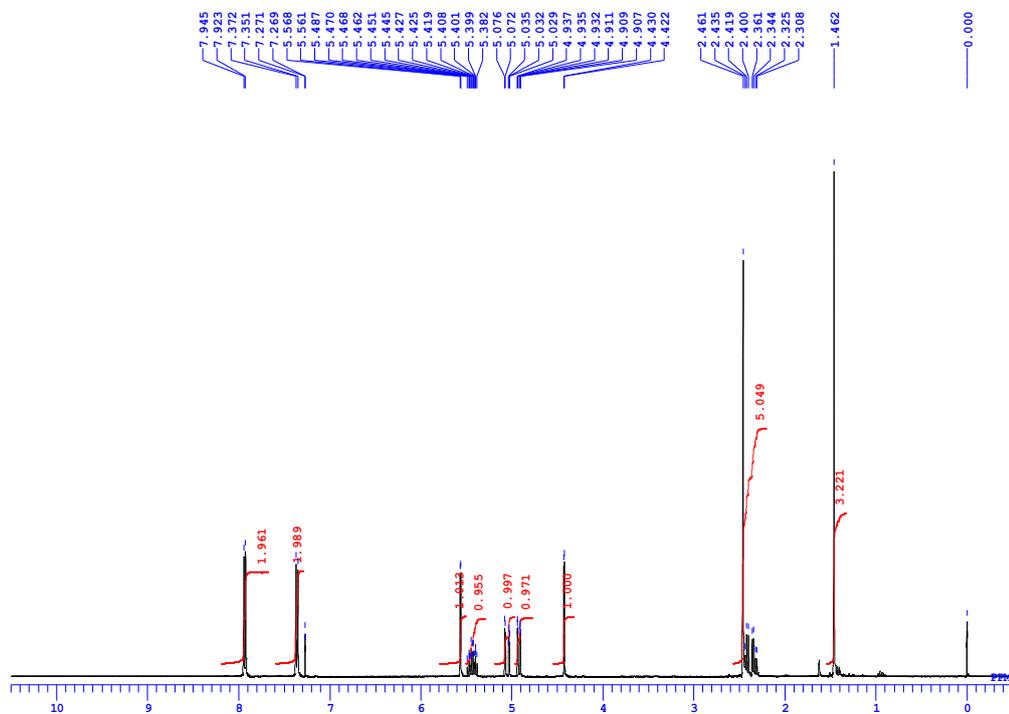
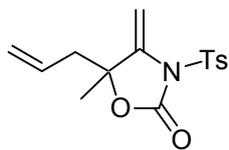
MS (EI, 70 eV) m/z 511 (M^+ , 2.9), 323 (18), 245 (14), 211 (20), 161 (18), 105 (100), 77 (Ph, 16)

HRMS calcd for $\text{C}_{25}\text{H}_{22}\text{INO}_2$ 511.0644, found m/z 511.0651 (EI, (M^+), + 0.6 mmu)

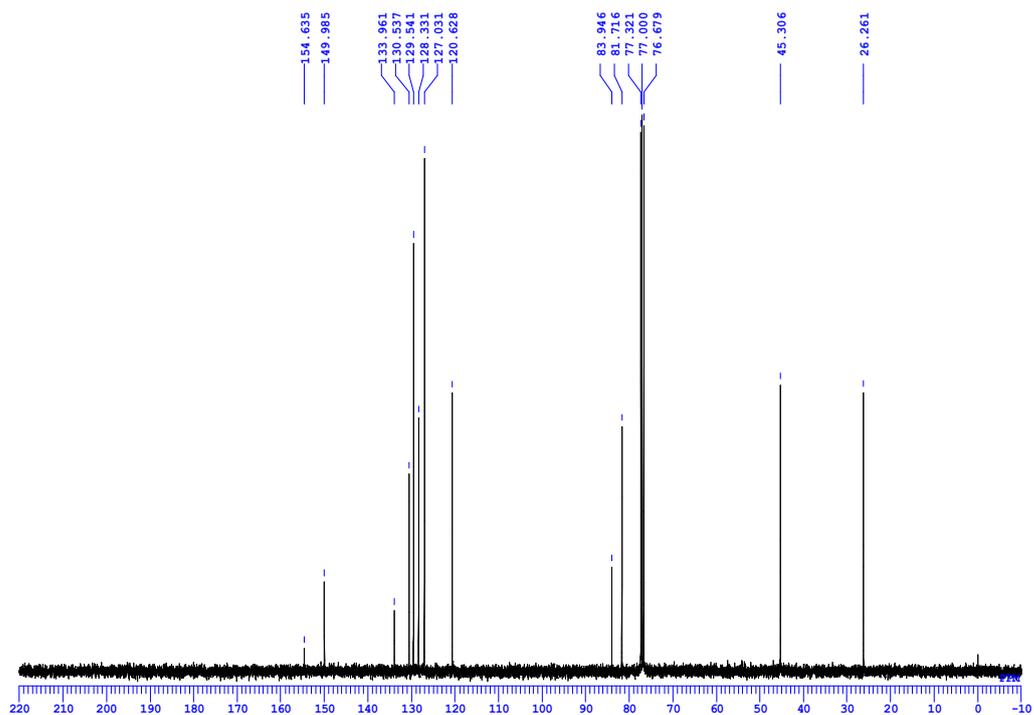
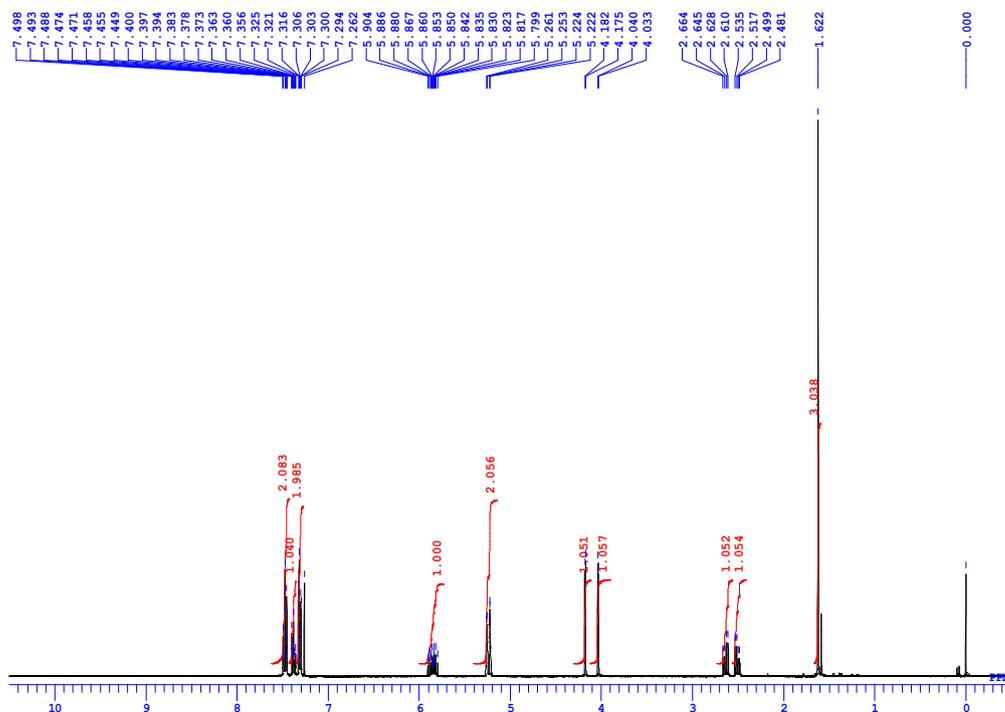
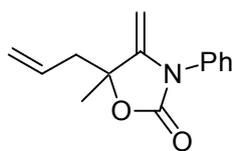


ORTEP Drawing of **9**: CCDC 729638

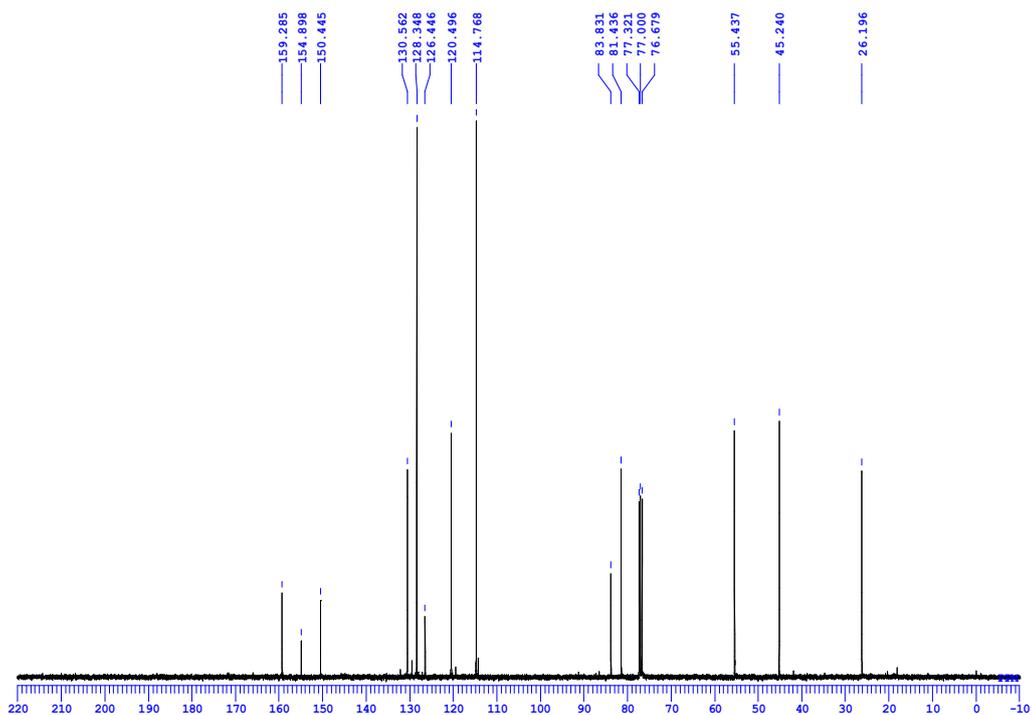
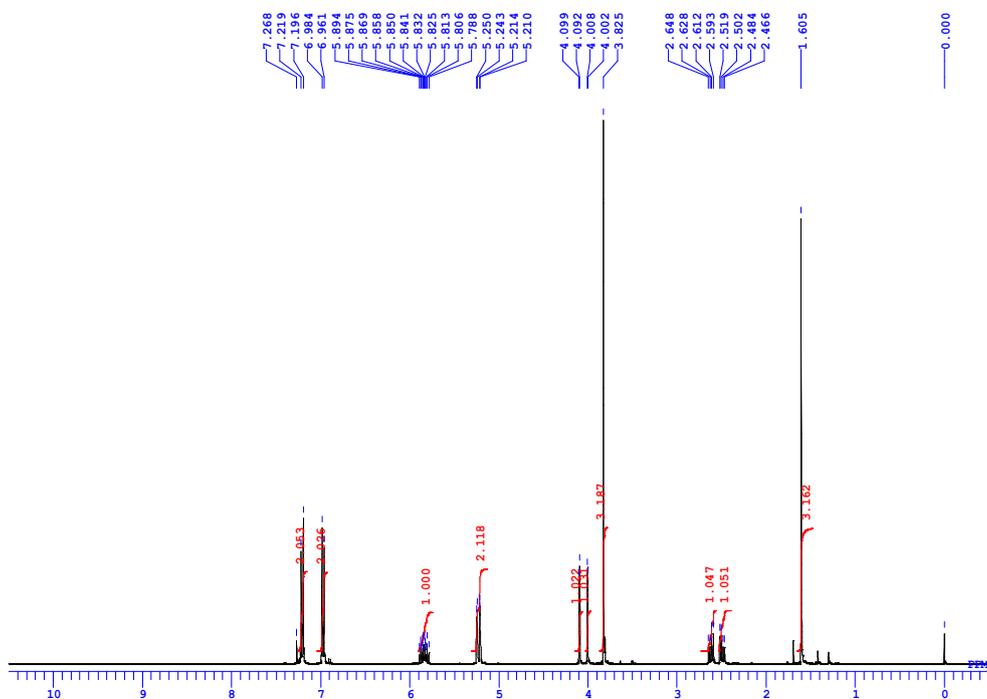
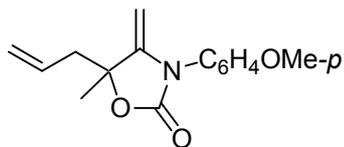
5-Allyl-5-methyl-4-methylene-3-(toluene-4-sulfonyl)-oxazolidin-2-one (3a)



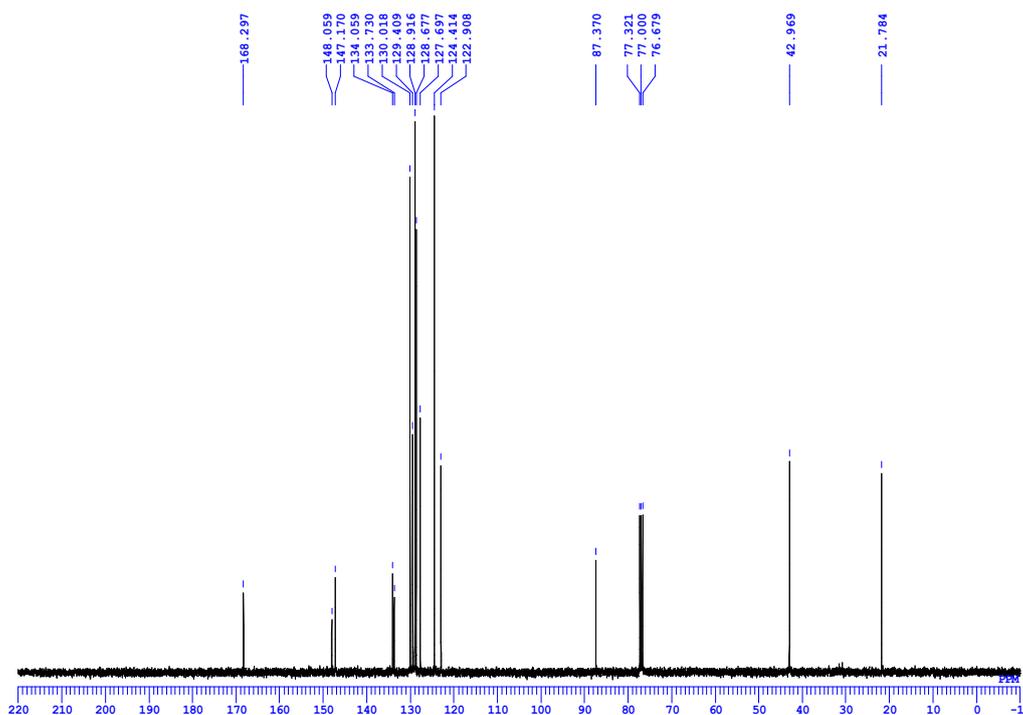
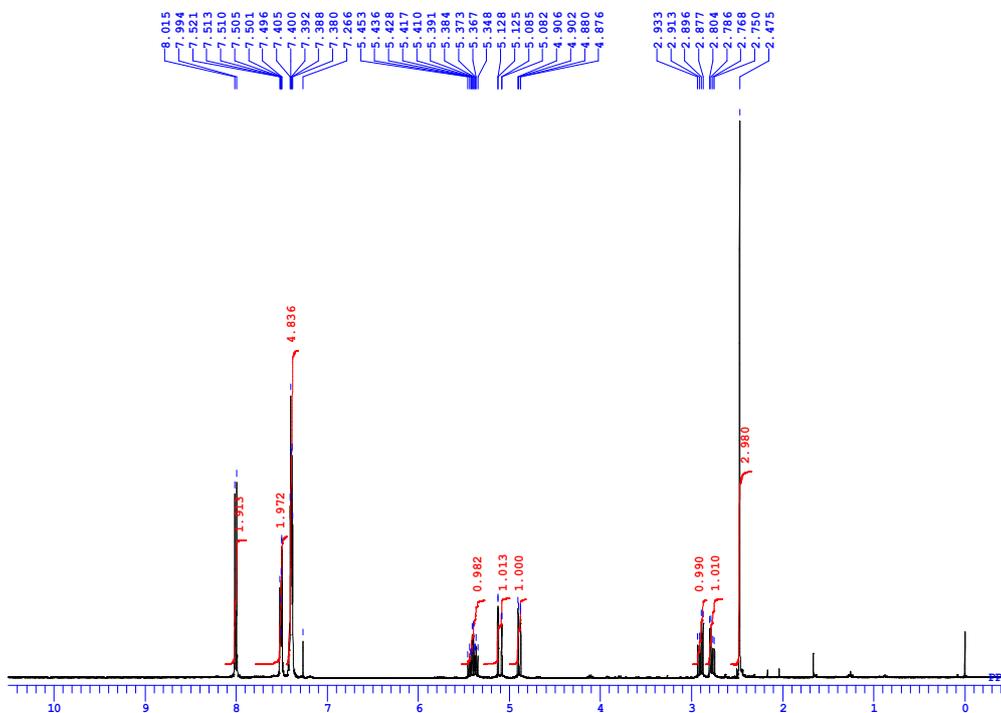
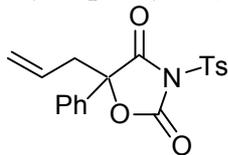
5-Allyl-5-methyl-4-methylene-3-phenyl-oxazolidin-2-one (3b)



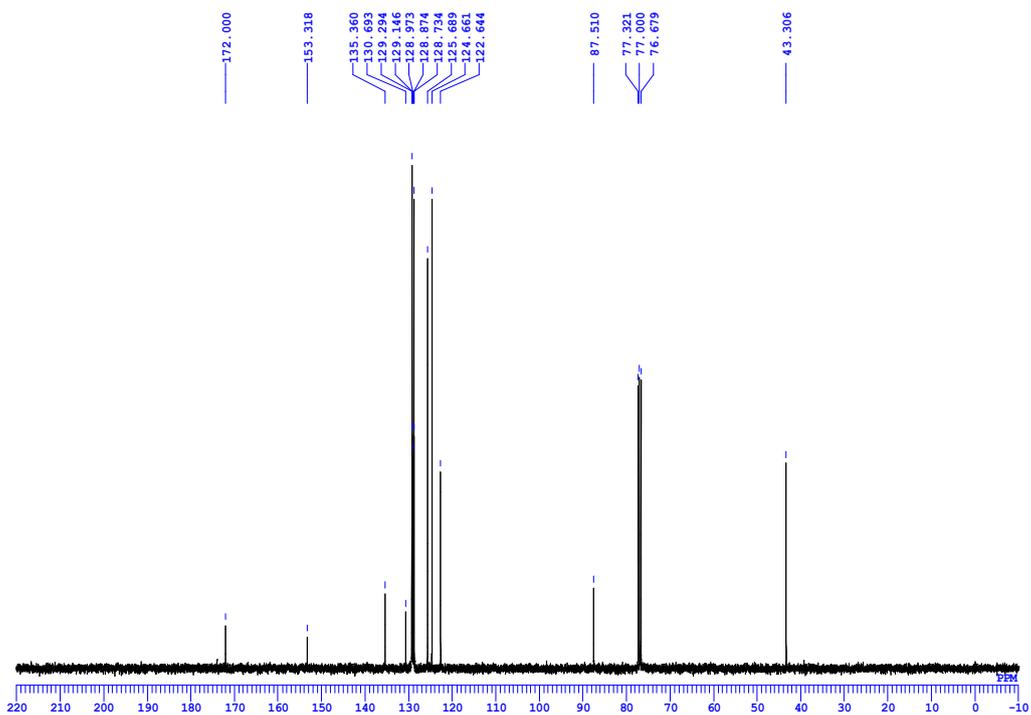
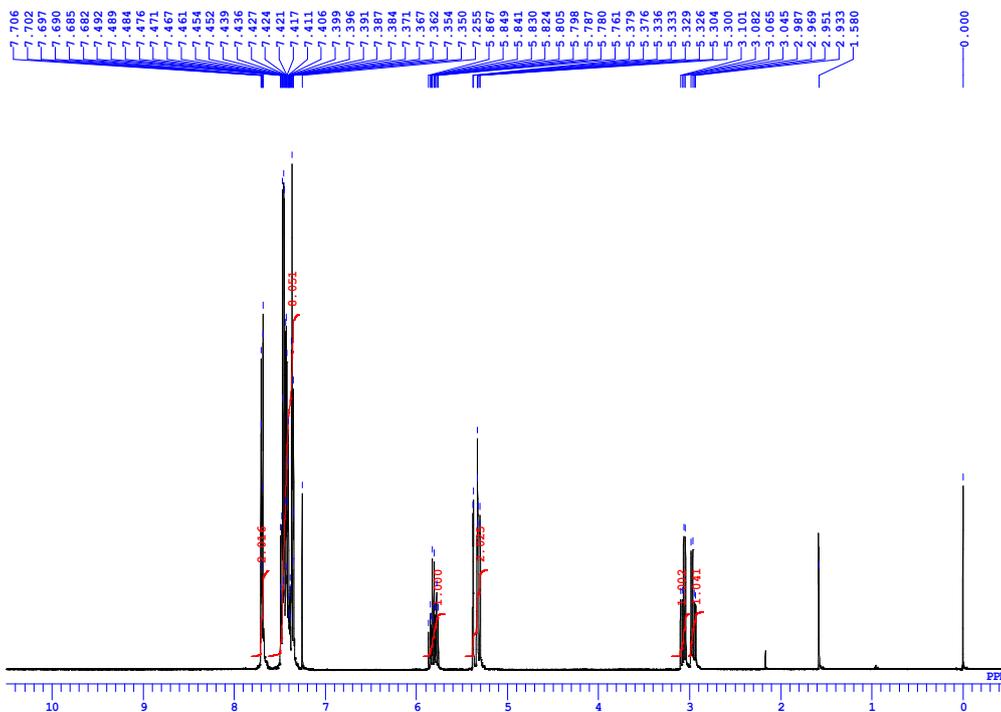
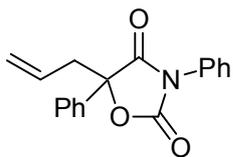
5-Allyl-3-(4-methoxy-phenyl)-5-methyl-4-methylene-oxazolidin-2-one (3c)



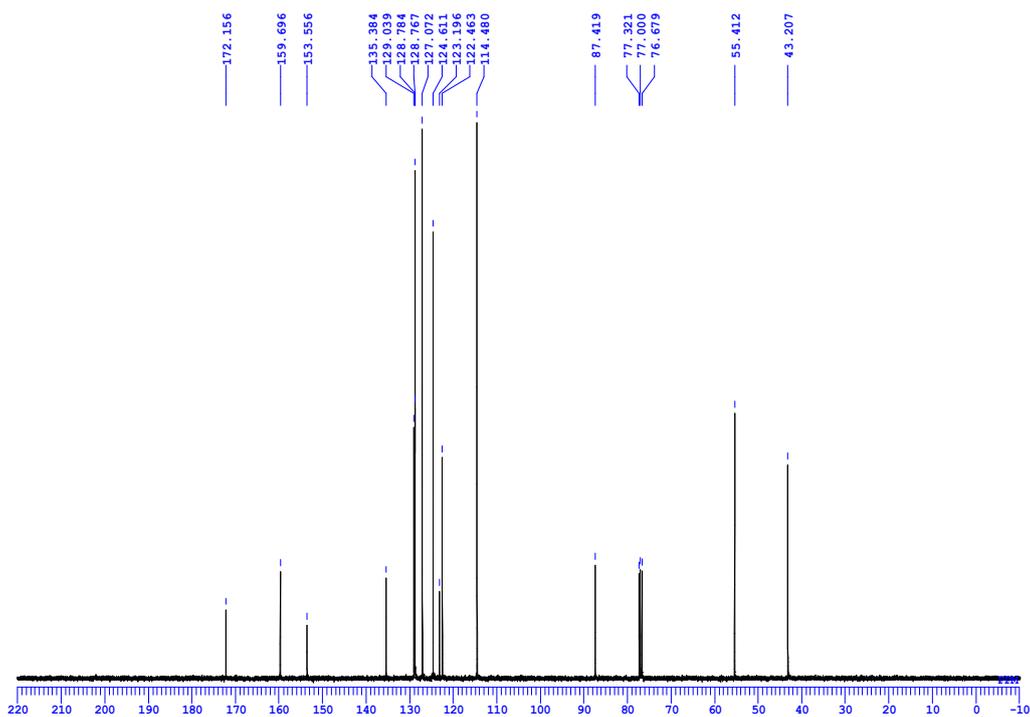
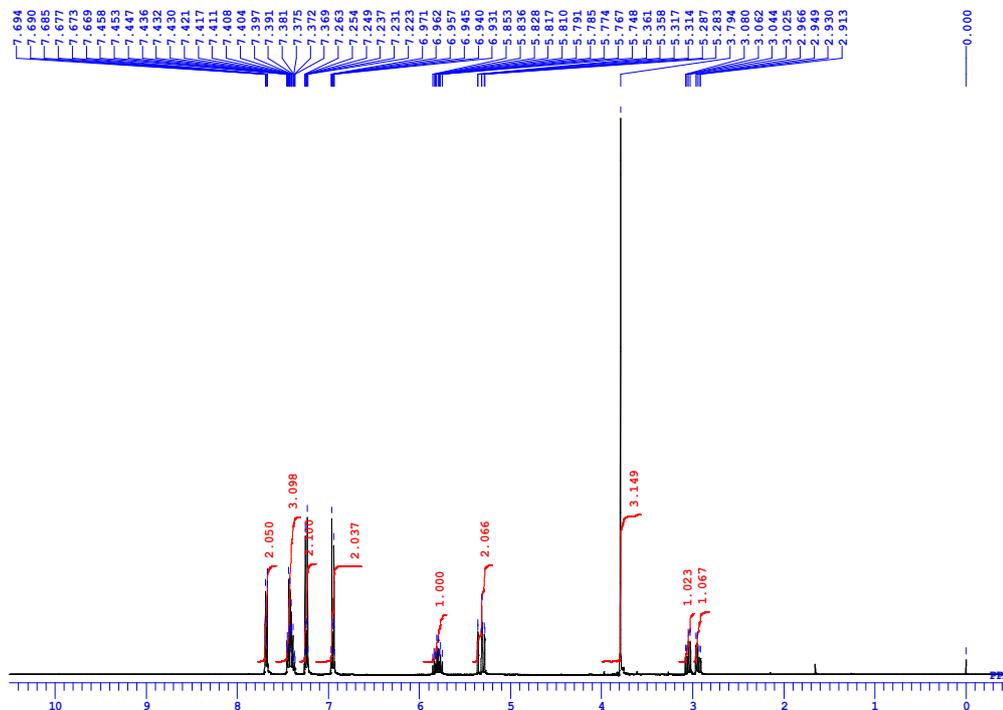
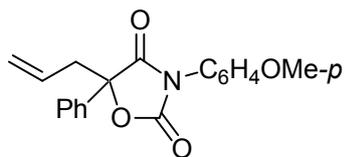
5-Allyl-5-phenyl-3-(toluene-4-sulfonyl)-oxazolidine-2,4-dione (4a)



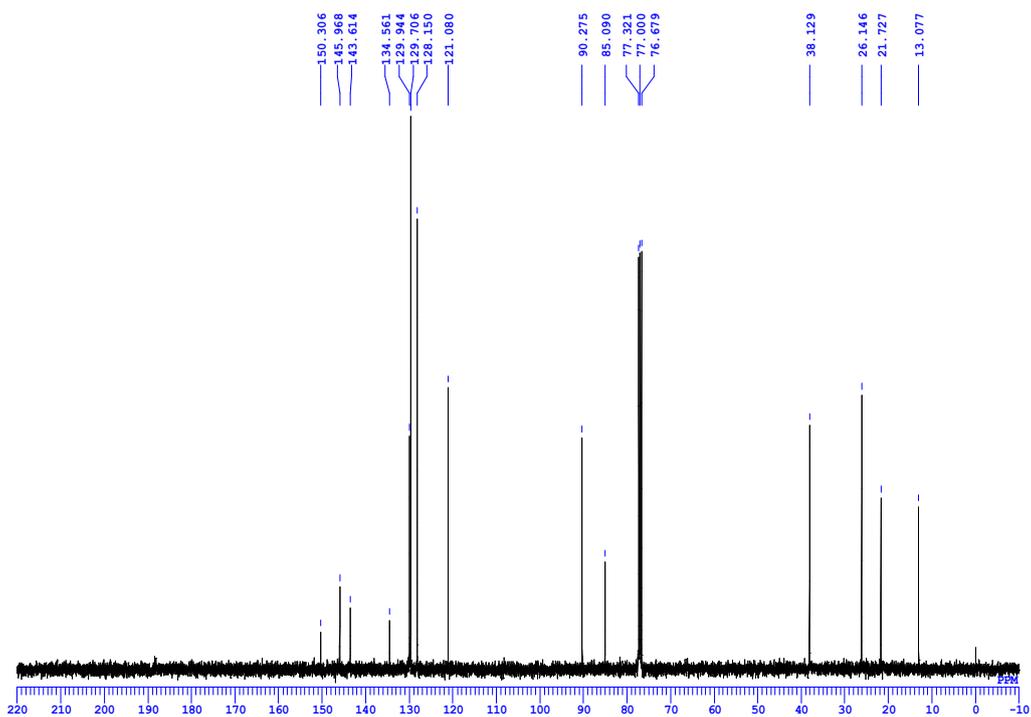
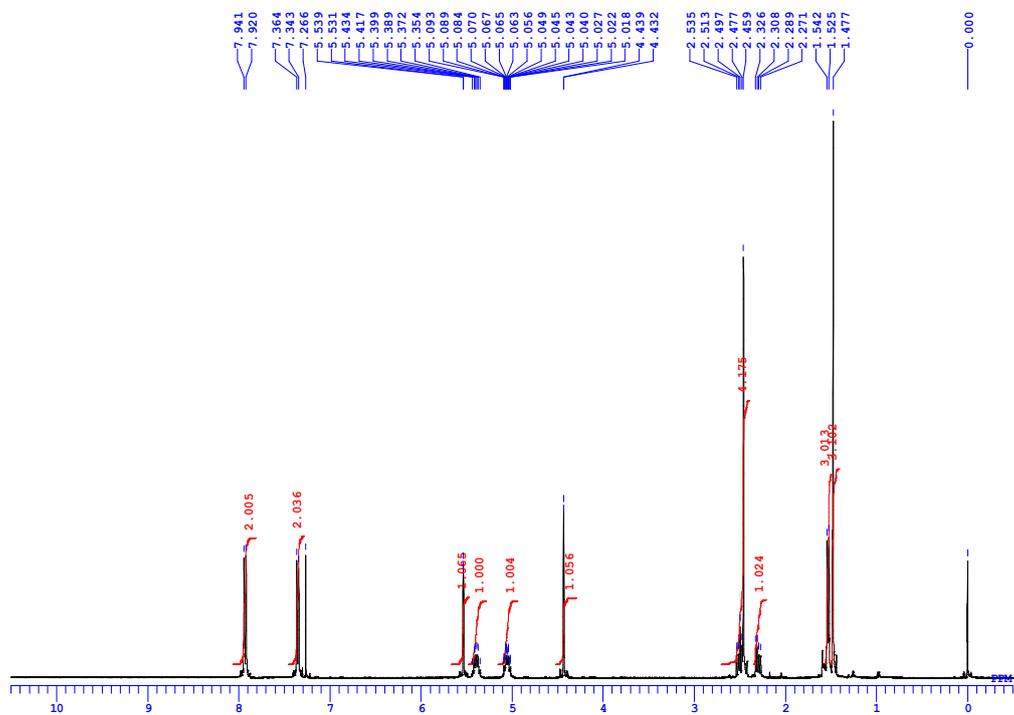
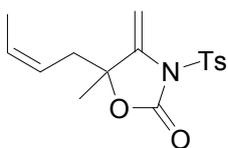
5-Allyl-5-phenyl-3-phenyl-oxazolidine-2,4-dione (4b)



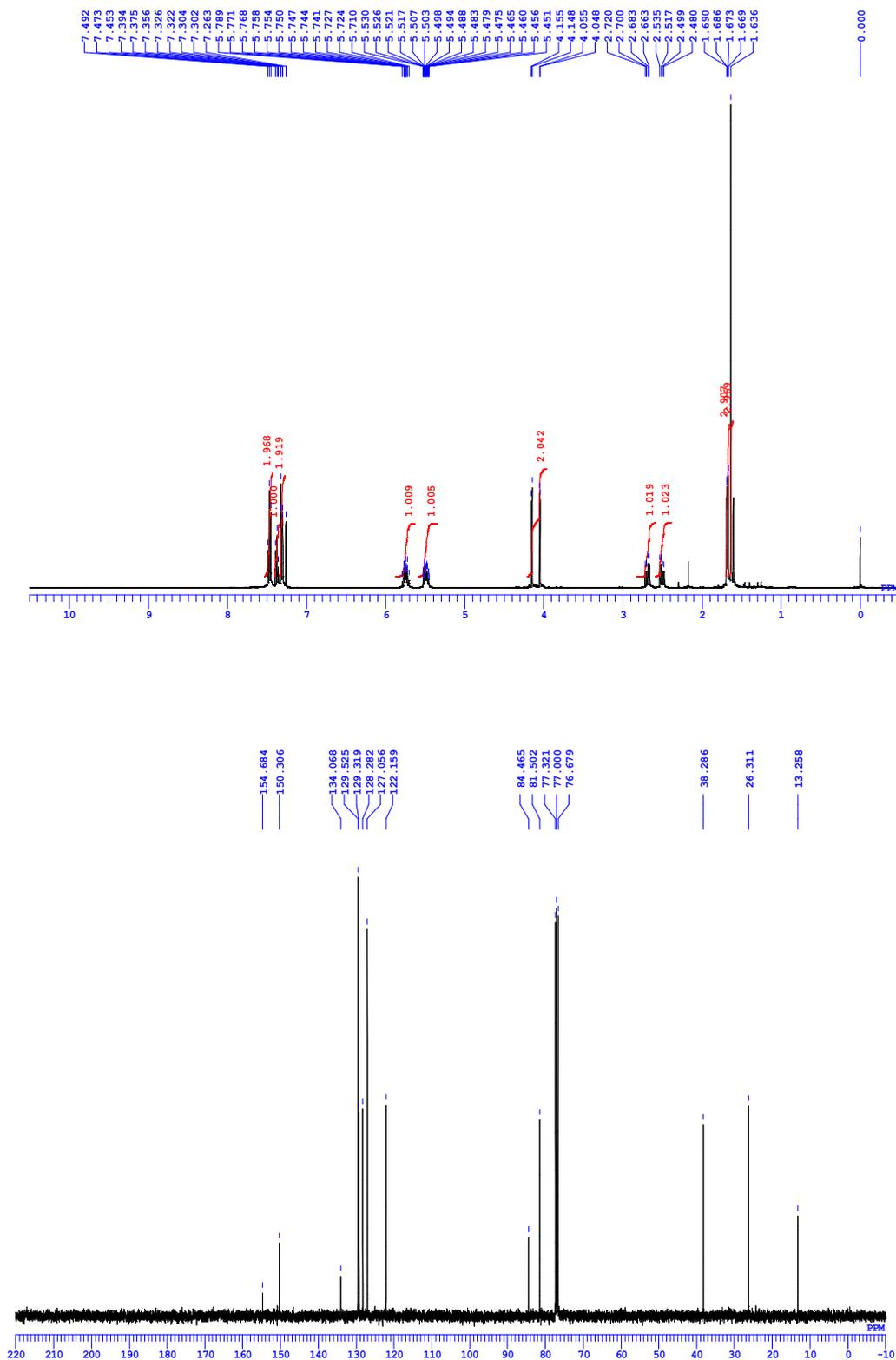
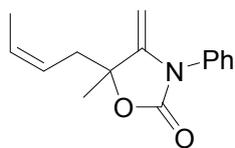
5-Allyl-3-(4-methoxy-phenyl)-5-phenyl-oxazolidine-2,4-dione (4c)



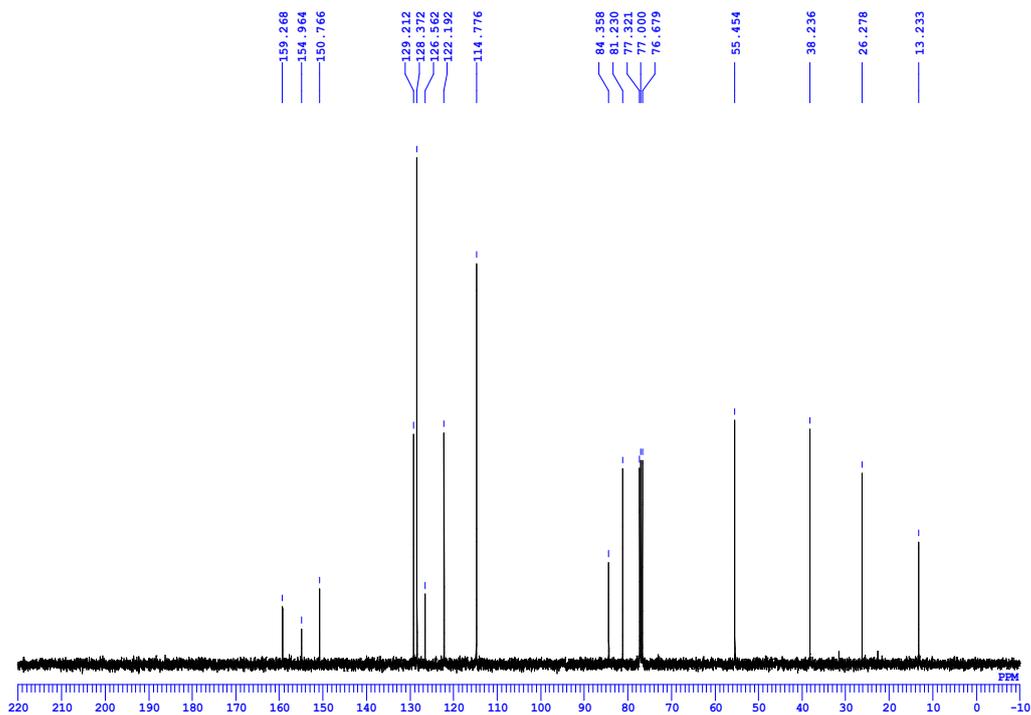
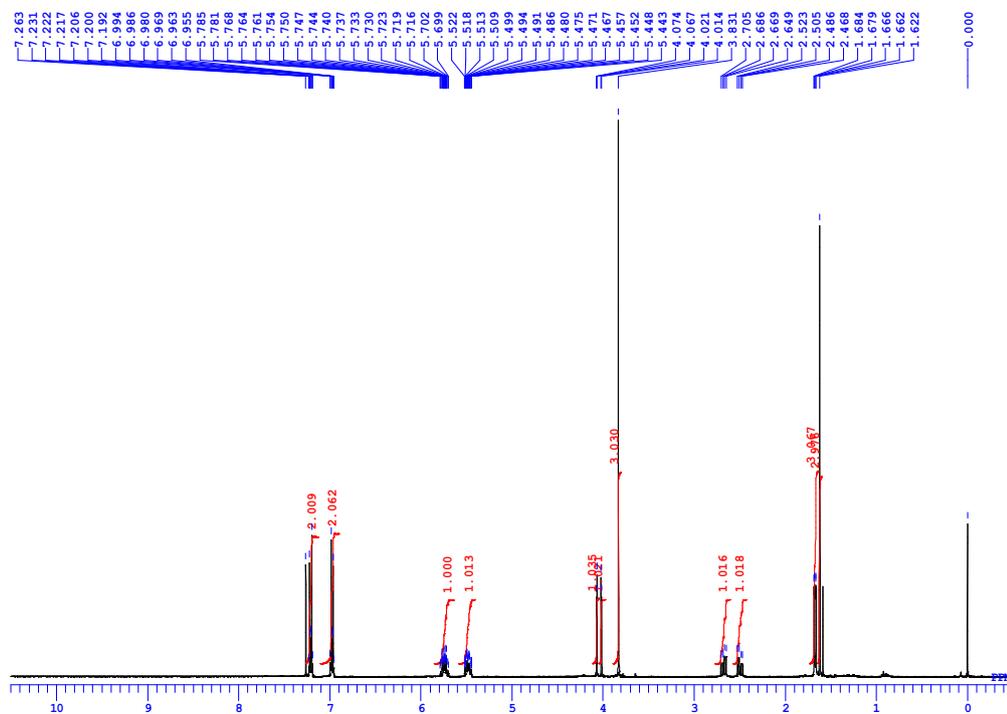
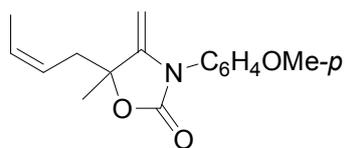
5-((Z)-But-2-enyl)-5-methyl-4-methylene-3-(toluene-4-sulfonyl)-oxazolidin-2-one (5a)



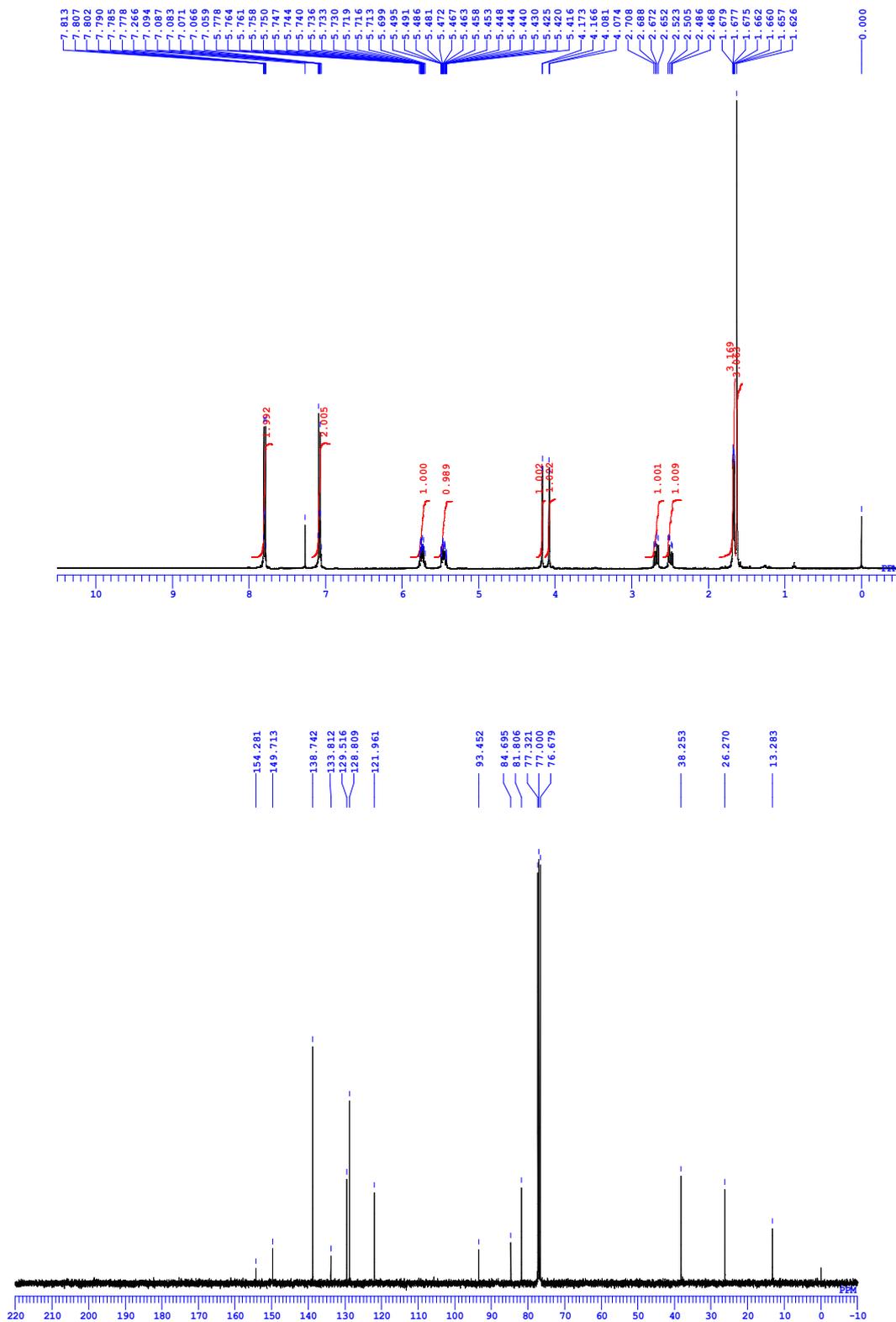
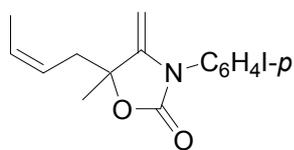
5-((Z)-But-2-enyl)-5-methyl-4-methylene-3-phenyl-oxazolidin-2-one (5b)



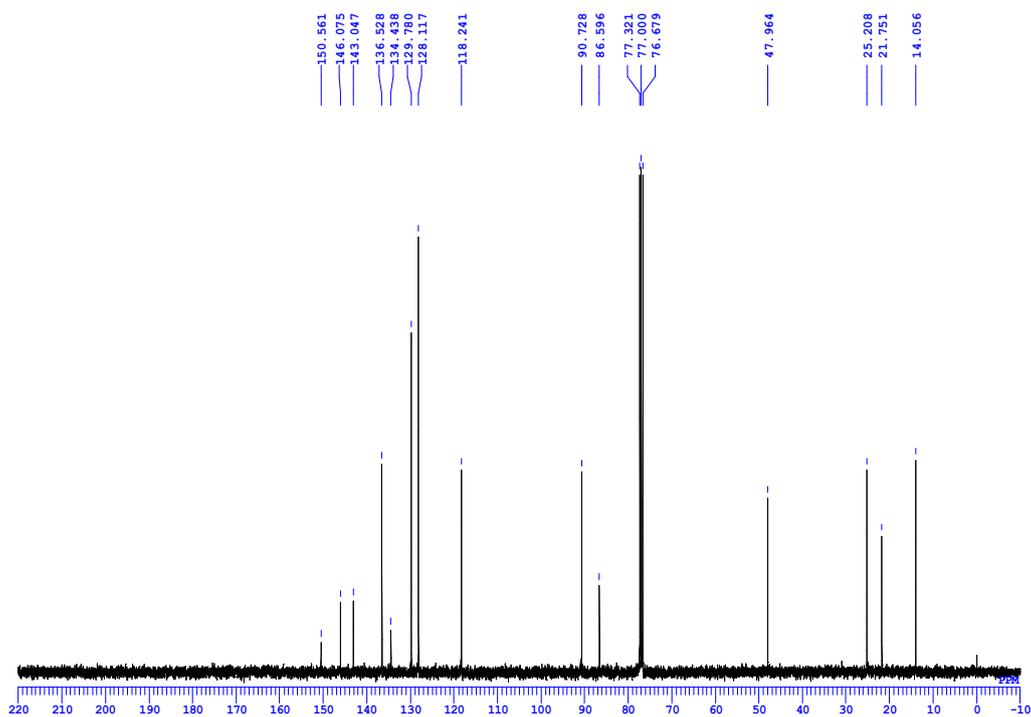
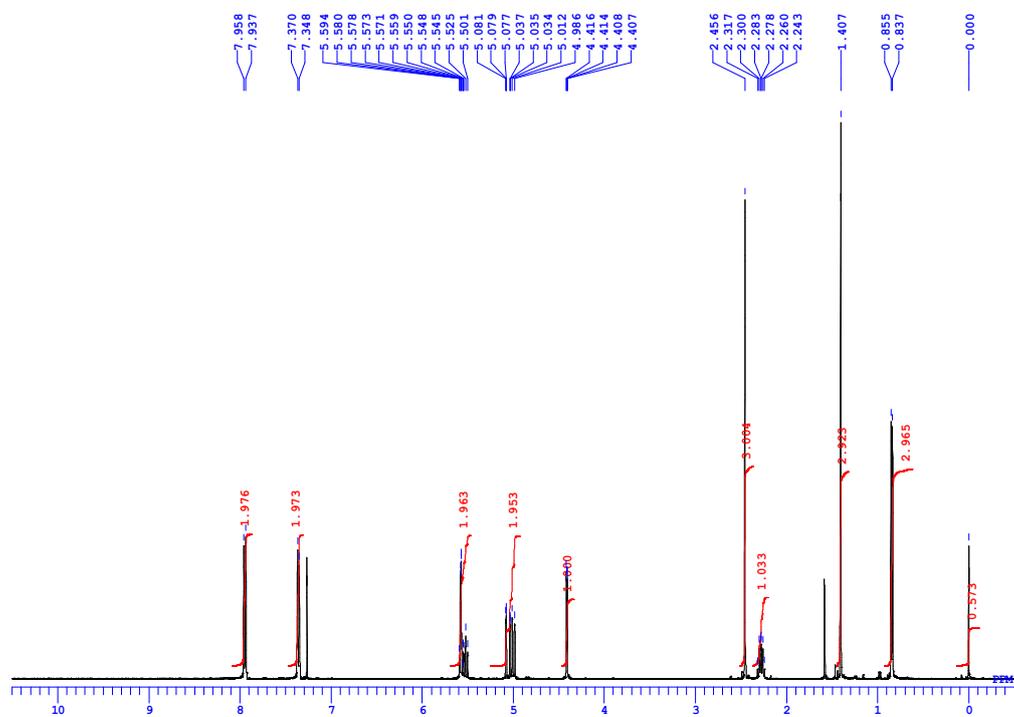
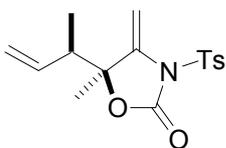
5-((Z)-But-2-enyl)-3-(4-methoxy-phenyl)-5-methyl-4-methylene-oxazolidin-2-one (5c)



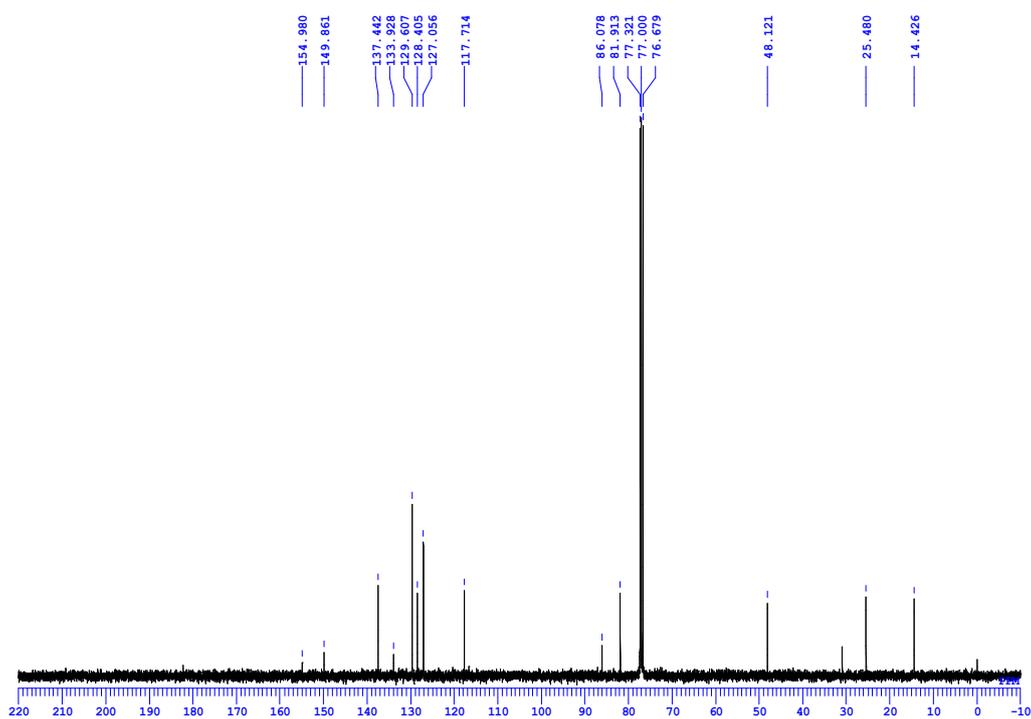
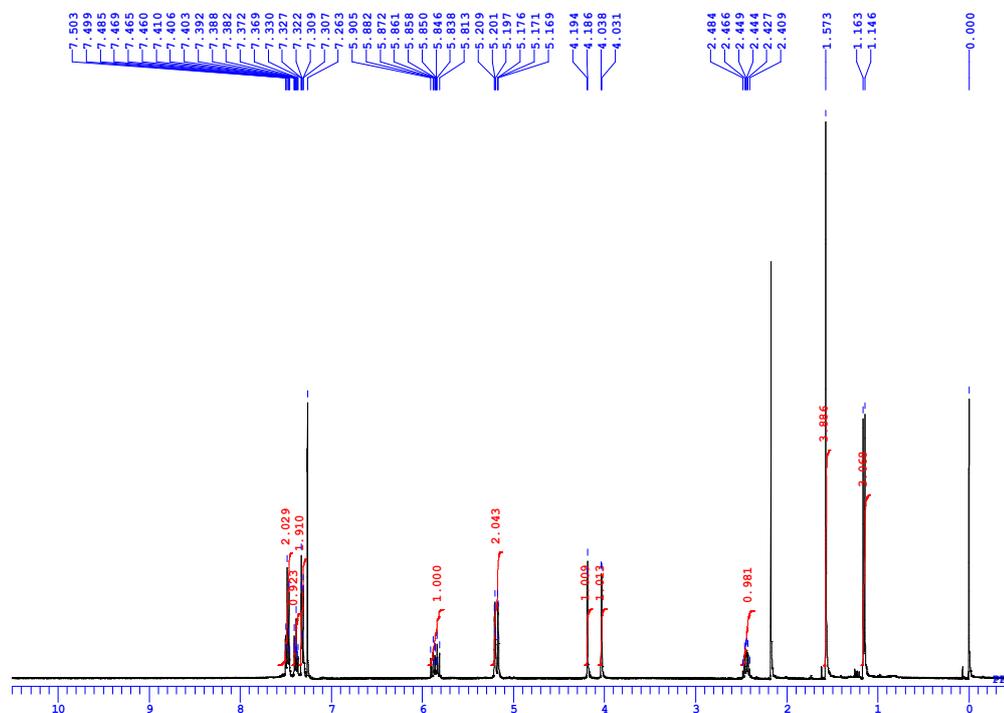
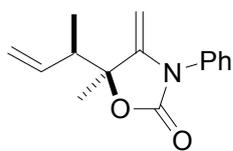
5-((Z)-But-2-enyl)-3-(4-iodo-phenyl)-5-methyl-4-methylene-oxazolidin-2-one (5d)



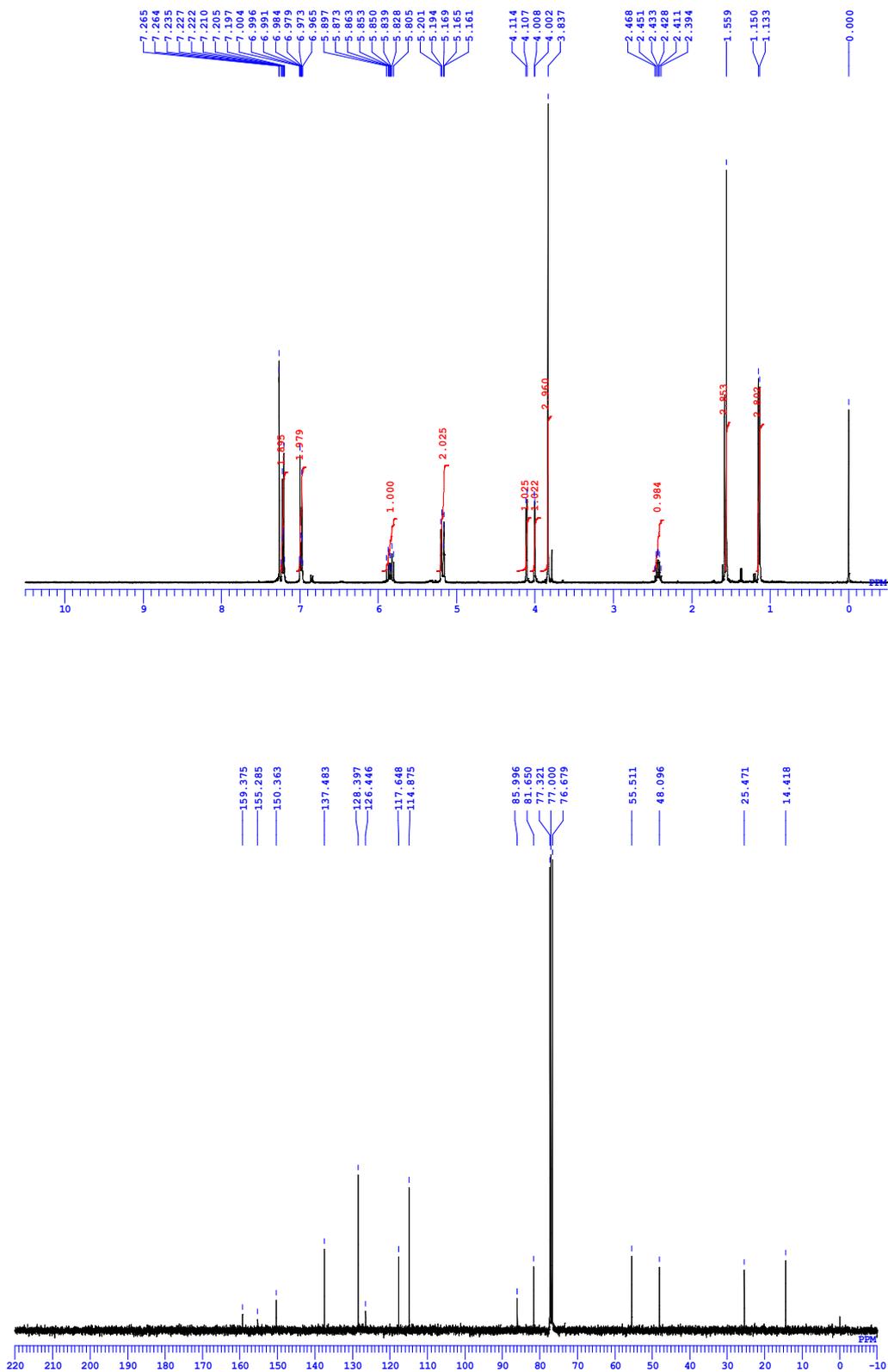
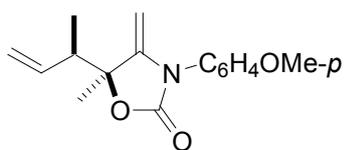
(S')-5-Methyl-5-((R')-1-methyl-allyl)-4-methylene-3-(toluene-4-sulfonyl)-oxazolidin-2-one (6a)



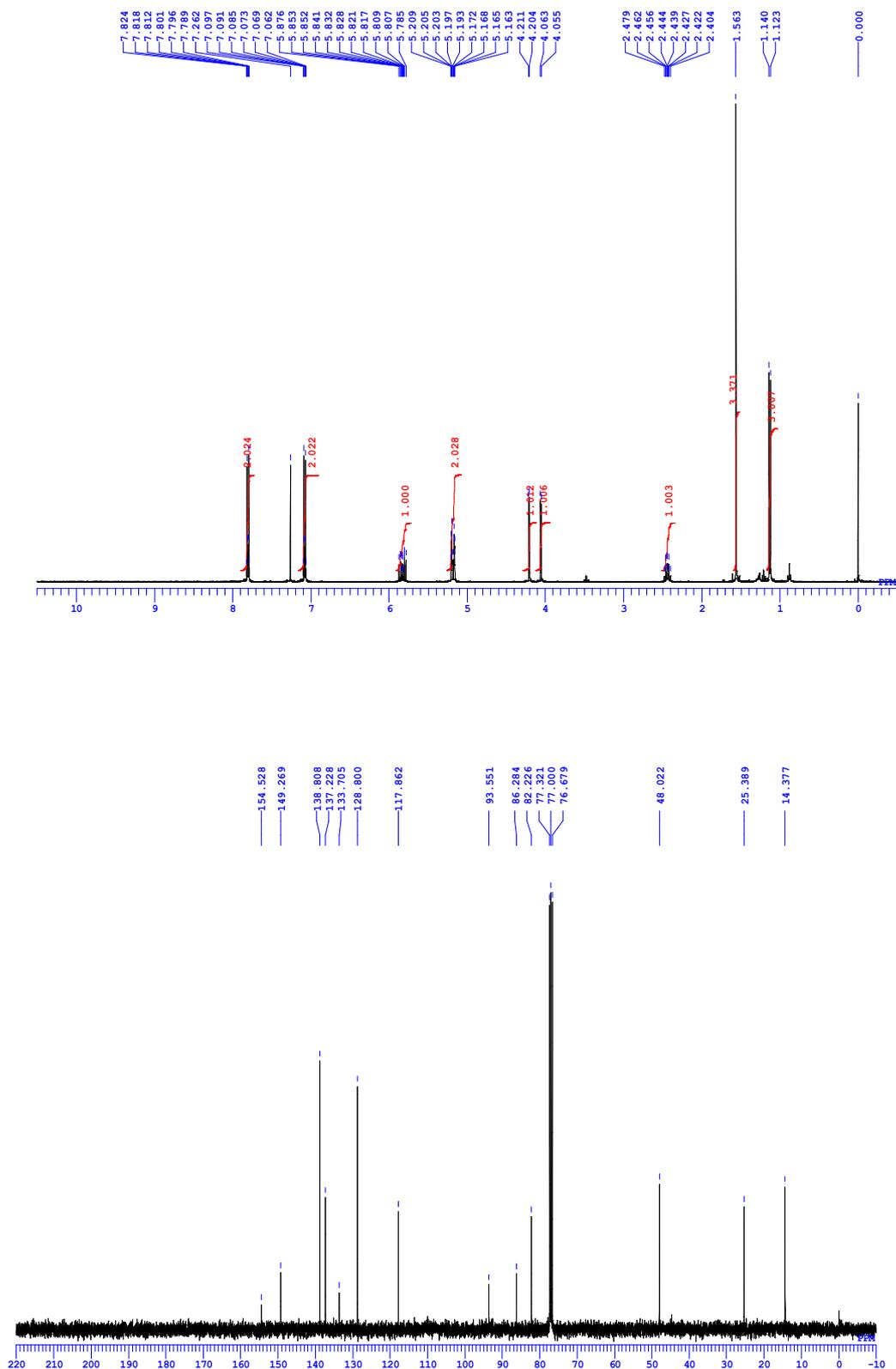
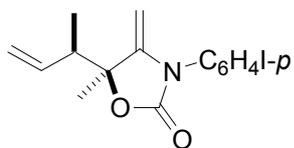
(S')-5-Methyl-5-((R')-1-methyl-allyl)-4-methylene-3-phenyl-oxazolidin-2-one (6b)



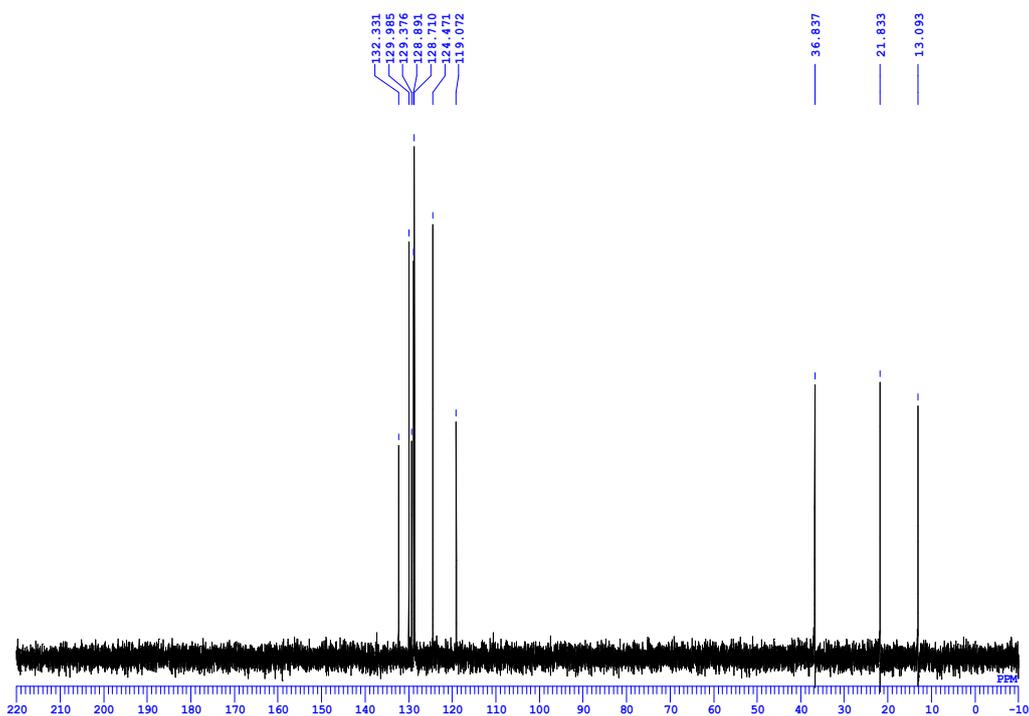
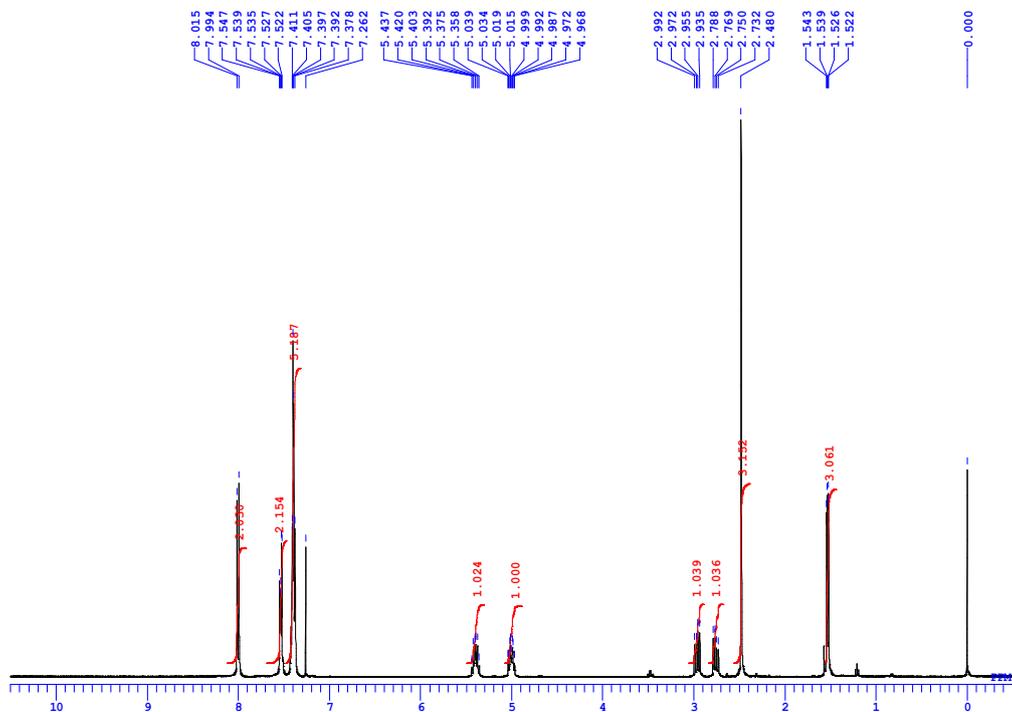
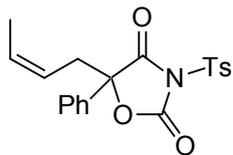
(S')-3-(4-Methoxy-phenyl)-5-methyl-5-((R')-1-methyl-allyl)-4-methylene-oxazolidin-2-one (6c)



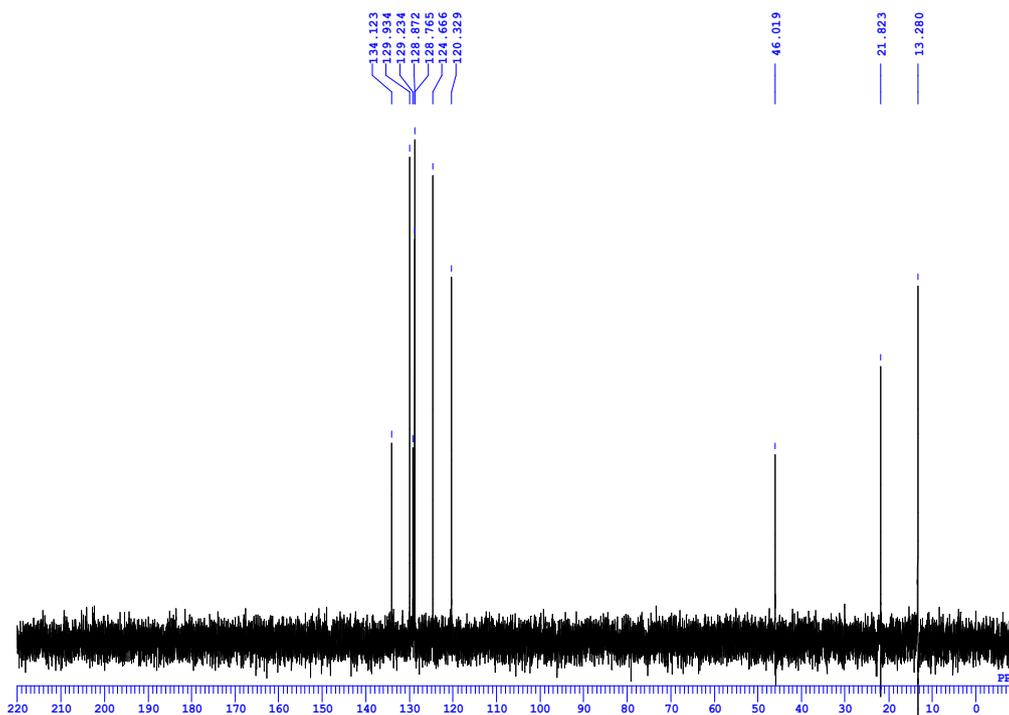
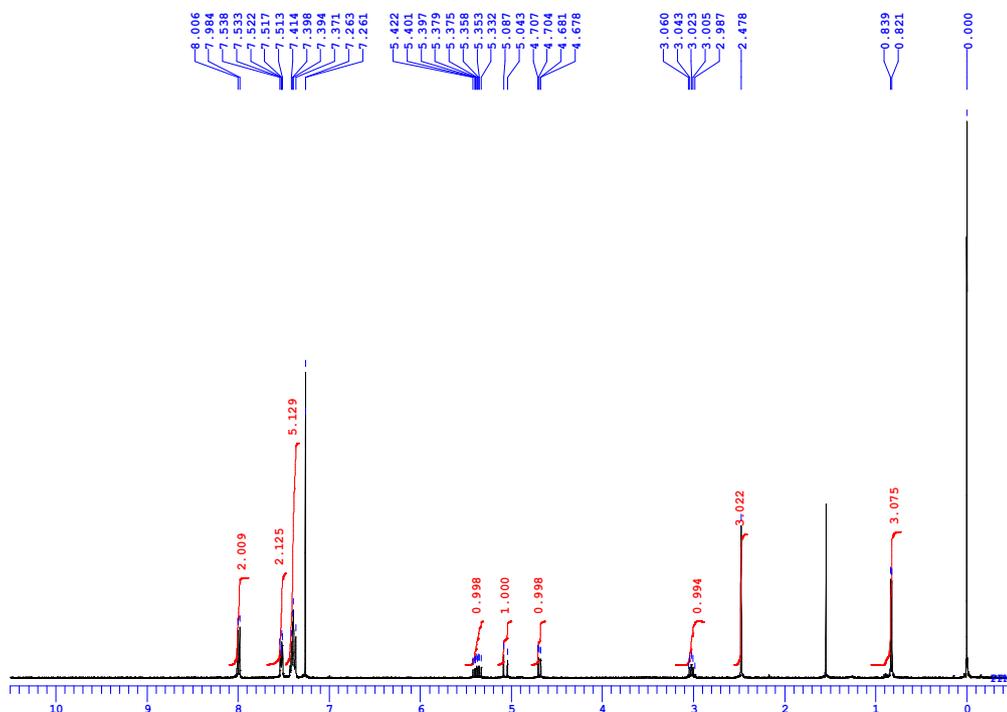
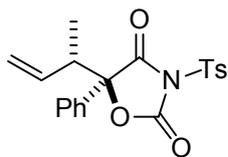
(S')-3-(4-Iodo-phenyl)-5-methyl-5-((R')-1-methyl-allyl)-4-methylene-oxazolidin-2-one (6d)



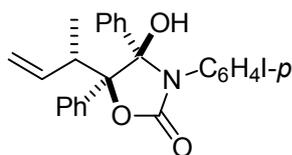
5-((Z)-But-2-enyl)-5-phenyl-3-(toluene-4-sulfonyl)-oxazolidine-2,4-dione (7)



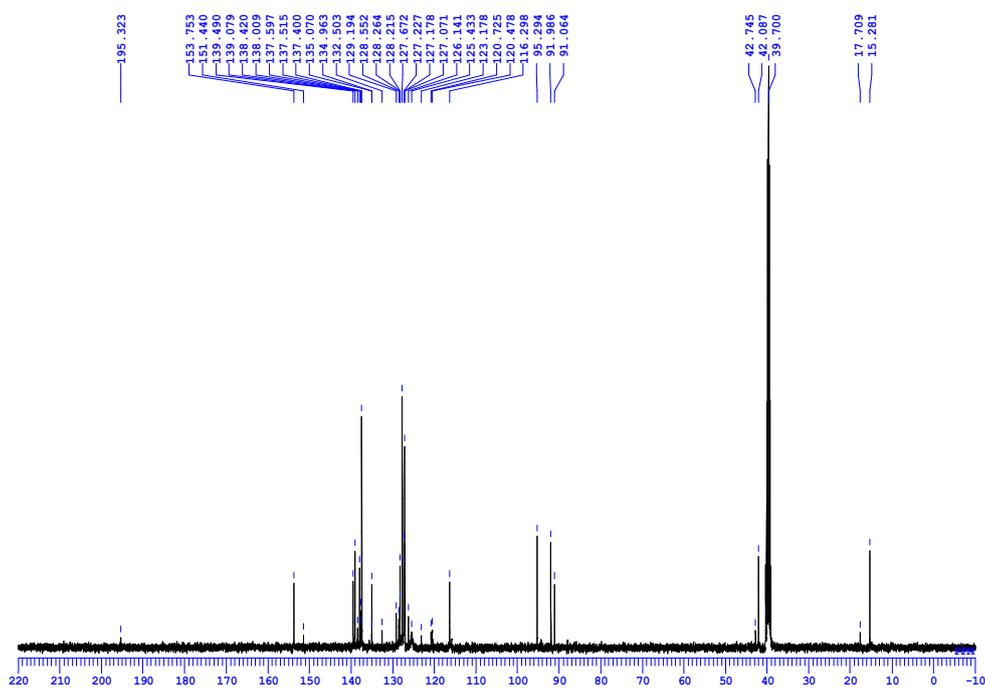
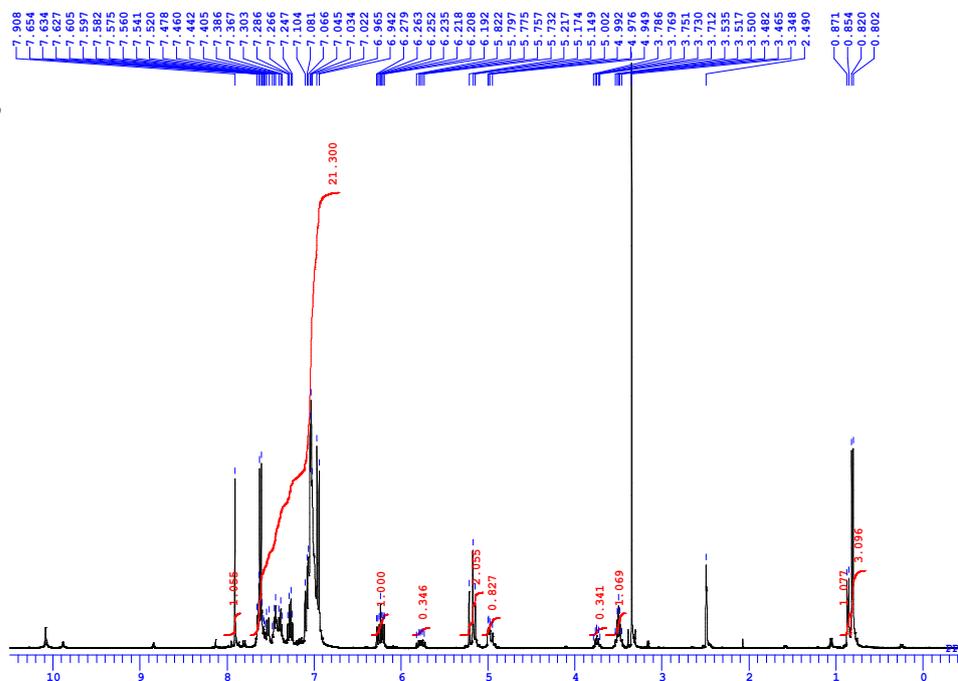
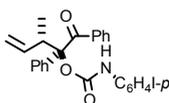
(R²)-5-((S¹)-1-Methyl-allyl)-5-phenyl-3-(toluene-4-sulfonyl)-oxazolidine-2,4-dione (8)



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

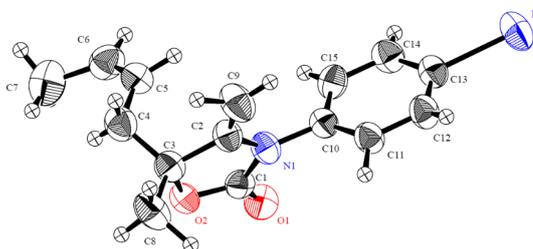
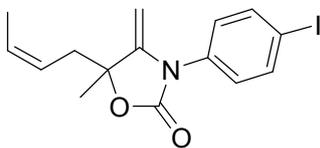


including

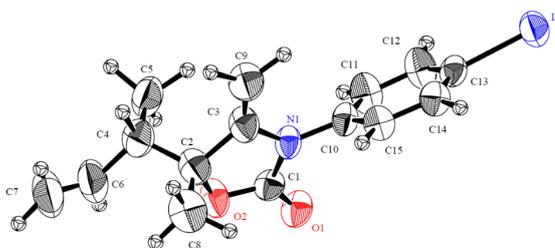
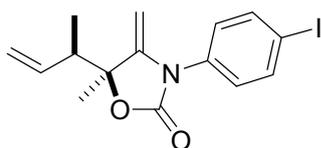


X-ray Structure

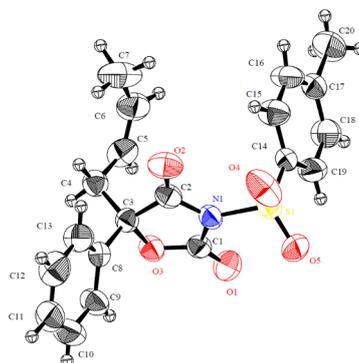
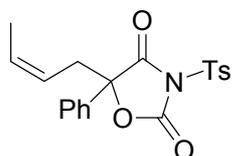
X-ray Structure of **5d** (CCDC 729634)



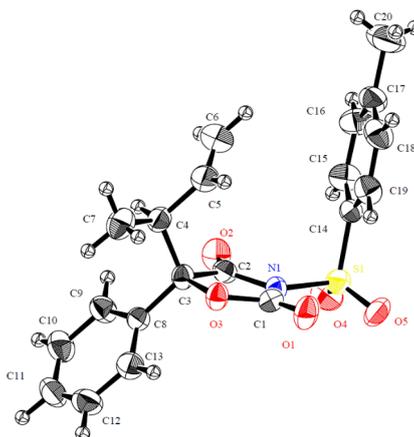
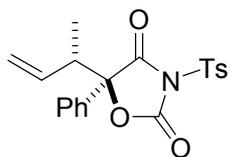
X-ray Structure of **6d** (CCDC 729636)



X-ray Structure Report of **7** (CCDC 729635)



X-ray Structure Report of **8** (CCDC 729637)



X-ray Structure Report of **9** (CCDC 729638)

