Supporting Information for

Asymmetric Synthesis of Trisubstituted Oxazolidinones by the Thiourea-Catalyzed Aldol Reaction of 2-Isocyanatomalonate Diester

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1. General information

All non-aqueous reactions were carried out under a positive atmosphere of argon in dried glassware. Analytical thin-layer chromatography was performed with Silica gel 60 (Merck). Silica gel column chromatography was performed with Kanto silica gel 60 (particle size, 63–210 mm) and Fuji silysia Chromatorex BW-300. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a JEOL JNM-ECA 500 at 500 MHz. Chemical shifts are reported relative to Me_4Si (d 0.00) in $CDCl_3$ and internal residual solvent (methanol-d_4 d 3.31). Multiplicity is indicated by one or more of the following: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); br (broad). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a JEOL JNM-ECA 500 at 125 MHz. Chemical shifts are reported relative to $CDCl_3$ (d 77.0) and methanol-d_3 (d 49.0). Infrared spectra were recorded on a JASCO FT/IR-4100 Fourier-transform infrared spectrometer ATR (attenuated total reflectance). Low and High resolution mass spectra were recorded on JEOL JMS-700 MStation mass spectrometer (FAB) and SHIMADZU LC-IT-TOF (ESI).

2. Material

Anhydrous CH_2Cl_2, THF, DMF, and methanol were purchased from KANTO Chemical Co and Wako chemicals. Materials were obtained from Tokyo Chemical Industry Co., Ltd. Aldrich Inc., Wako chemicals and other commercial suppliers, and used without further purification.

3. Typical procedures for the synthesis of isocyanatomalonate diester 1a–d and these spectra data

We initially prepared four 2-isocyanatomalonate diesters **1a–d** by the treatment of the corresponding 2-aminomalonate diesters with triphosgene. Dimethyl 2-isocyanatomalonate (**1a**) was found to be relatively unstable and had to be purified by Kugelrohr distillation. Diethyl isocyanatomalonate (**1b**) could be isolated by distillation or an aqueous work-up. The two other isocyanates **1c** and **1d** were relatively stable with high boiling points, and were consequently isolated by following an aqueous work-up. Although the distilled isocyanates **1a** and **1b** could be stored for a few weeks without any discernible decrease in their purity, the isocyanates purified by an aqueous work-up were used immediately in the next reaction because they contained small amounts of water which accelerated their polymerization.

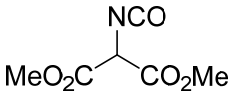
Typical procedure A for the synthesis of isocyanatomalonate diester (1a and b)

To a mixture of diethyl aminomalonate hydrochloride (3.48 g, 16.5 mmol) in 1,4-dioxane (12 mL) were added activated charcoal (12.1 mg) and triphosgene (3.93 g, 13.4 mmol) at 0 °C. The reaction mixture was stirred at 80 °C for 1 h and then refluxed overnight. The reaction mixture was cooled to room temperature and filtered through ceilte. The filtrate was concentrated under reduced pressure. The resultant oil was distilled by using Kugelrohr (110 °C, 0.5 mmHg) to give the diethyl 2-isocyanatomalonate **1b** (1.95 g, 59%) as a colorless oil.

Typical procedure B for the synthesis of isocyanatomalonate (1b-d)

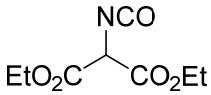
To a mixture of diethyl aminomalonate hydrochloride (422 mg, 2 mmol) in THF (10 mL) were added Et_3N (0.55 mL, 4 mmol) and triphosgene (653 mg, 2.2 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 1 h. The reaction was quenched with 10% HCl aq. and extracted with EtOAc. The extract was washed with sat. aq. $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4, and concentrated in vacuo to give the crude product **1b** (412 mg, 78%, containing an urea).

Dimethyl 2-isocyanatomalonate (1a)



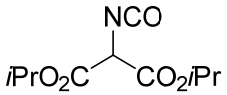
Using the typical procedure A, **1a** was obtained colorless oil. (Kugelrohr distillation, 100 °C, 0.5 mmHg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.58 (s, 1H), 3.87-3.86 (m, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.4, 43.3, 37.6 ppm; **1a** was too unstable to measure IR and MS under the measurement conditions.

Diethyl 2-isocyanatomalonate (1b)



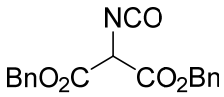
Using the typical procedure A, **1b** was obtained colorless oil. (Kugelrohr distillation, 110 °C, 0.5 mmHg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.55 (s, 1H), 4.34-4.30 (m, 4H), 1.33 (t, J = 7.1 Hz, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 129.7, 63.5, 60.2, 14.1 ppm; IR (ATR) 2253, 1759 cm^{-1}; LRMS (FAB^{+}) 202 ([M+H]$^{+}$); HRMS (FAB^{+}): Calcd for $C_8H_{12}O_5N$ ([M+H]$^{+}$) 202.0715, Found: 202.0717.

Diisopropyl 2-isocyanatomalonate (1c).



Using the typical procedure B, **1c** was obtained colorless oil (containing small amount of an urea); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.48 (s, 1H), 4.35-4.28 (m, 2H), 1.34-1.28 (m, 12H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.0, 129.7, 71.6, 63.3, 21.5 ppm; IR (ATR) 2387, 1732 cm^{-1}; LRMS (FAB^{+}) 230 ([M+H]$^{+}$); HRMS (FAB^{+}): Calcd for $C_{10}H_{16}O_5N$ ([M+H]$^{+}$) 230.0977, Found: 230.0972.

Dibenzyl 2-isocyanatomalonate (1d)



Using the typical procedure B, **1d** was obtained as a colorless oil (containing small amount of an urea); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.19 (m, 10H), 5.13 (s, 4H), 4.54 (s, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2, 134.2, 129.6, 128.8, 128.7, 128.4, 68.9, 60.1 ppm; IR (ATR) 2253, 1761 cm^{-1}; LRMS (FAB^{+}) 326 (MH^{+}); HRMS (FAB^{+}): Calcd for $C_{18}H_{16}O_5N$ ([M+H)$^{+}$) 326.1271, Found: 326.1281.

4. Typical procedures for asymmetric aldol reaction using thiourea and spectra data of the oxazolidinones 3

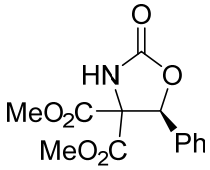
Typical procedure A for asymmetric aldol reaction using thiourea 4a (Table 1, entry 8)

To a mixture of isocyanatomalonate **1b** (25.5 mg, 0.126 mmol) in toluene (1.2 mL) were added thiourea **4a** (4.8 mg, 0.0116 mmol) and benzaldehyde (11.8 μl, 0.115 mmol) at ‐60 ° C. After being stirred at the same temperature for 72 h, the reaction mixture was concentrated *in vacuo*. The resulting residue was purified by silica gel chromatography (25–33% EtOAc/hexanes) to give **3b** (31.7 mg, 90%).

Typical procedure B for asymmetric aldol reaction using thiourea 4b (Table 1, entry 10)

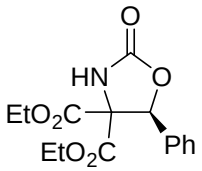
To a mixture of isocyanatomalonate **1b** (30.0 mg, 0.144 mmol) in toluene (1.3 mL) were added thiourea **4b** (7.1 mg, 0.0135 mmol) and benzaldehyde (17.2 μl, 0.131 mmol) at –60 °C. After being stirred at the same temperature for 72 h, the reaction mixture was concentrated *in vacuo*. The resulting residue was purified by silica gel chromatography (25–33% EtOAc/hexanes) to give **3e** (28.8mg, 66%).

(*S*)-Dimethyl 2-oxo-5-phenyloxazolidine-4,4-dicarboxylate (3a)



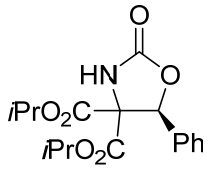
Using the typical procedure A , **3a** was obtained (87%) as a white solid ; $[\alpha]^{28}_{D}$ –59.4 (*c* 1.55, $CHCl_3$, 88%ee) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.36 (m, 5H), 6.21 (s, 1H), 6.04 (brs, 1H), 3.99 (d, *J* = 1.1 Hz, 3H), 3.22 (d, *J* = 1.1 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 166.1, 157.1, 133.9, 129.6, 128.5, 126.9, 80.8, 71.7, 63.3, 62.9, 14.0, 13.4 ppm; IR (ATR) 3254, 1776, 1747, 1268, 1023 $cm^{-1;}$ HRMS (ESI^+): Calcd for $C_{13}H_{13}O_6N$ ($[M+H]^+$) 280.0816, Found: 280.0815; HPLC [CHIRALPAK AD, hexane/2-propanol = 90/10, 0.5 mL/min, λ = 254 nm, retention times: (major) 25.1 min, (minor) 28.6 min]

(*S*)-Diethyl 2-oxo-5-phenyloxazolidine-4,4-dicarboxylate (3b)



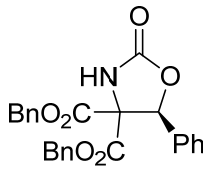
Using the typical procedure A, **3b** was obtained (90%) as a white solid; $[\alpha]^{28}_{D}$ –45.6 (*c* 1.51, $CHCl_3$, 88%ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.41 (m, 2H), 7.36-7.33 (m, 3H), 6.22 (s, 1H), 6.20 (brs, 1H), 4.41-4.32 (m, 2H), 3.81-3.59 (m, 1H), 3.61-3.56 (m, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.80 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 166.1, 157.1, 133.9, 129.6, 128.5, 126.9, 80.8, 71.7, 63.3, 62.9, 14.0, 13.4 ppm; IR (ATR) 3333, 1766, 1741, 1114, 1060 cm^{-1}; LRMS (FAB^+) 308 ($[M+H]^+$); HRMS (FAB^+): Calcd for $C_{15}H_{18}O_6N$ ($[M+H]^+$) 308.1314, Found: 308.1310; HPLC [CHIRALCEL OJ-3, hexane/2-propanol = 90/10, 0.5 mL/min, λ = 254 nm, retention times: (major) 28.7 min, (minor) 33.5 min].

(*S*)-Diisopropyl 2-oxo-5-phenyloxazolidine-4,4-dicarboxylate (3c)



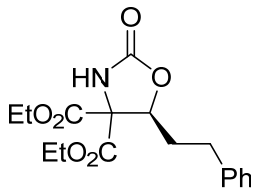
Using the typical procedure A, **3c** was obtained (88%) as a colorless oil; $[\alpha]^{25}_{D}$ –22.0 (*c* 0.57, $CHCl_3$, 61%ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.35 (m, 5H), 6.19 (s, 1H), 5.95 (s, 1H), 5.21-5.16 (m, 1H), 4.59-4.54 (m, 1H), 1.33 (d, *J* = 6.2 Hz, 3H), 1.29 (d, *J* = 6.2 Hz, 3H), 0.99 (t, *J* = 6.2 Hz, 3H), 0.55 (t, *J* = 6.2 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1, 165.6, 156.6, 133.8, 129.4, 128.4, 127.1, 80.6, 71.3 (x3), 21.5, 21.4, 21.2, 20.5 ppm; IR (ATR) 1776, 1740, 1220, 1107, 1070 cm^{-1}; LRMS (FAB$^+$) 336 ([M+H]$^+$); HRMS (FAB$^+$): Calcd for $C_{17}H_{22}NO_6$ ([M+H]$^+$) 336.1447, Found: 336.1454; HPLC [CHIRALPAK AD, hexane/2-propanol = 90/10, 0.5 mL/min, λ = 254 nm, retention times: (major) 19.5 min, (minor) 21.3 min].

(*S*)-Dibenzyl 2-oxo-5-phenyloxazolidine-4,4-dicarboxylate (3d)



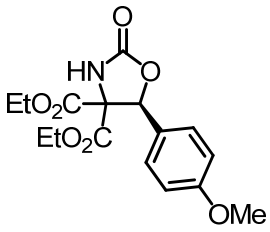
Using the typical procedure A, **3d** was obtained (80%) as a colorless oil; $[\alpha]^{25}_{D}$ –4.63 (*c* 0.92, $CHCl_3$, 78%ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.21 (m, 15H), 6.89 (s, 1H), 6.21 (s, 1H), 5.24 (d, *J* = 12.0 Hz, 1H), 5.18 (d, *J* = 12.0 Hz, 1H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.33 (d, *J* = 12.0 Hz, 1H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 165.8, 156.4, 134.0, 133.6, 133.4, 129.6, 128.9, 128.7, 128.6, 128.53, 128.49, 128.3, 128.2, 126.7, 80.7, 71.7, 68.9, 68.4 ppm; IR (ATR) 1752 cm^{-1}; LRMS (FAB$^+$) 432 ([M+H]$^+$); HRMS (FAB$^+$): Calcd for $C_{25}H_{22}NO_6$ ([M+H]$^+$) 432.1447, Found: 432.1445; HPLC [CHIRALPAK IB, hexane/2-propanol = 90/10, 0.5 mL/min, λ = 254 nm, retention times: (major) 28.2 min, (minor) 27.2 min].

(*S*)-Diethyl 2-oxo-5-phenethyloxazolidine-4,4-dicarboxylate (3e)



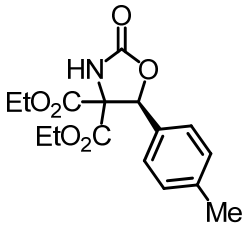
Using the typical procedure B, **3e** was obtained (66%) as a colorless oil; $[\alpha]^{28}_{D}$ –54.1 (*c* 0.98, $CHCl_3$, 78%ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.20 (m, 5H), 5.90 (brs, 1H), 5.01 (dd, *J* = 12.0, 4.0 Hz, 1H), 4.35-4.22 (m, 4H), 2.98-2.93 (m, 1H), 2.80-2.74 (m, 1H), 2.08-2.03 (m, 1H), 1.90-1.83 (m, 1H), 1.30-1.26 (m, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 166.5, 156.9, 140.1, 128.7, 128.6, 126.5, 79.0, 69.9, 63.3, 63.2, 32.7, 31.8, 14.1, 14.0 ppm; IR (ATR) 1771, 1742, 1219 cm^{-1}; LRMS (FAB$^+$) 336 ([M+H]$^+$); HRMS (FAB$^+$): Calcd for $C_{17}H_{22}NO_6$ ([M+H]$^+$) 336.1447, Found: 336.1452; HPLC [CHIRALPAK AD, hexane/2-propanol = 90/10, 0.5 mL/min, λ = 254 nm, or 210 nm, retention times: (major) 24.5 min, (minor) 33.6 min].

(*S*)-Diethyl 5-(4-methoxyphenyl)-2-oxooxazolidine-4,4-dicarboxylate (**3f**).



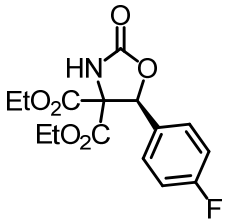
Using the typical procedure B, **3f** was obtained (92%) as a colorless oil; $[\alpha]^{27}_{D}$ –46.4 (*c* 1.70, $CHCl_3$, 91%ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.16 (s, 1H), 5.88 (brs, 1H), 4.37-4.31 (m, 2H), 3.84-3.80 (m, 1H), 3.80 (s, 3H), 3.68-3.64 (m, 1H), 1.32 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 166.0, 160.3, 157.1, 128.1, 125.7, 113.6, 80.5, 71.6, 63.0, 62.6, 55.2, 13.8, 13.3 ppm; IR (ATR) 3338, 1778, 1746, 1115, 1063 cm^{-1}; LRMS (FAB$^+$) 338 ([M+H]$^+$); HRMS (FAB$^+$): Calcd for $C_{16}H_{20}O_7N$ ([M+H]$^+$) 338.1240, Found: 338.1229; HPLC [CHIRALCEL OJ-3, hexane/2-propanol = 90/10, 0.5 mL/min, λ= 254 nm, retention times: (major) 26.5 min, (minor) 30.8 min].

(*S*)-Diethyl 2-oxo-5-(p-tolyl)oxazolidine-4,4-dicarboxylate (**3g**)



Using the typical procedure B, **3g** was obtained (94%) as a colorless oil; $[\alpha]^{27}_{D}$ –59.1 (*c* 2.11 $CHCl_3$, 89%ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.34 (s, 1H), 6.18 (s, 1H), 4.40-4.31 (m, 2H), 3.82-3.76 (m, 1H), 3.66-3.60 (m, 1H), 2.34 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 0.83 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 166.1, 157.1, 139.5, 130.8, 129.1, 126.8, 80.7, 71.5, 63.1, 62.7, 21.2, 13.9, 13.2 ppm; IR (ATR) 1778, 1746, 1223 cm^{-1}; LRMS (FAB$^+$) 322 ([M+H]$^+$); HRMS (FAB$^+$): Calcd for $C_{16}H_{20}NO_6$ ([M+H]$^+$) 322.1291, Found: 322.1287; HPLC [CHIRALCEL OJ-3, hexane/2-propanol = 90/10, 0.5 mL/min, λ = 254 nm, retention times: (major) 16.5. min, (minor) 18.0 min].

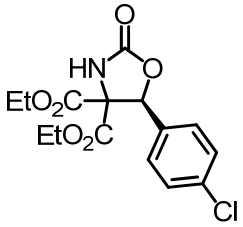
(*S*)-Diethyl 5-(4-fluorophenyl)-2-oxooxazolidine-4,4-dicarboxylate (**3h**)



Using the typical procedure B, **3h** was obtained (85%) as a white solid; $[\alpha]^{27}_{D}$ –41.0 (*c* 4.00, $CHCl_3$, 88%ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 8.8, 5.2 Hz, 2H), 7.06 (t, *J* = 8.8 Hz, 2H), 6.19 (s, 1H), 6.00 (brs, 1H), 4.41-4.30 (m, 2H), 3.86-3.80 (m, 1H), 3.69-3.62 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.86 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.5, 165.9, 163.2 (d, *J* = 250 Hz), 156.7, 129.5 (d, *J* = 2.4 Hz), 128.7 (d, *J* = 8.4 Hz), 115.4 (d, *J* = 21.6 Hz), 80.0, 71.5, 63.3, 62.9, 13.9, 13.4 ppm; IR (ATR) 3315, 1774, 1746, 1216, 771 cm^{-1}; LRMS (FAB$^+$) 326 ([M+H]$^+$); HRMS (FAB$^+$): Calcd for $C_{15}H_{17}FO_6N$ ([M+H]$^+$) 326.1040, Found: 326.1041; HPLC [CHIRALCEL OJ-3, hexane/2-propanol = 90/10, 0.5

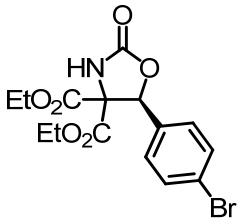
mL/min, λ = 254 nm, retention times: (major) 18.5 min, (minor) 20.6 min]

(*S*)-Diethyl 5-(4-chlorophenyl)-2-oxooxazolidine-4,4-dicarboxylate (**3i**)



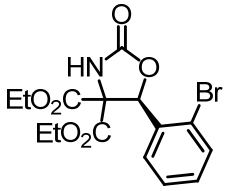
Using the typical procedure B, **3i** was obtained (88%) as a white solid; $[\alpha]^{27}_{D}$ –28.9 (*c* 3.2, $CHCl_3$, 89%ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 6.27 (brs, 1H), 6.17 (s, 1H), 4.41-4.30 (m, 2H), 3.85-3.80 (m, 1H), 3.70-3.64 (m, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 165.9, 156.5, 135.5, 132.2, 128.9, 128.2, 79.9, 71.4, 63.3, 63.0, 13.9, 13.4 ppm; IR (ATR) 1782, 1744, 1220 cm^{-1}; LRMS (FAB^+) 342 ($[M+H]^+$); HRMS (FAB^+) Calcd for $C_{15}H_{17}ClO_6N$ ($[M+H]^+$) 342.0744, Found: 342.0728; HPLC [CHIRALCEL OJ-3, hexane/2-propanol = 90/10, 0.5 mL/min, λ = 254 nm, retention times: (major) 18.5 min, (minor) 20.6 min].

(*S*)-Diethyl 5-(4-bromophenyl)-2-oxooxazolidine-4,4-dicarboxylate (**3j**)



Using the typical procedure A, **3j** was obtained (91%) as a colorless oil; $[\alpha]^{27}_{D}$ –55.2 (*c* 0.95, $CHCl_3$, 89%ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.20 (brs, 1H), 6.14 (s, 1H), 4.40-4.29 (m, 2H), 3.79-3.73 (m, 1H), 3.61-3.54 (m, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 165.9, 156.5, 135.5, 132.2, 128.2, 79.9, 71.4, 63.3, 63.0, 13.9, 13.4 ppm; IR (ATR) 1786, 1739, 1220, 772 cm^{-1}; LRMS (FAB^+) 386 ($[M+H]^+$); HRMS (FAB^+): Calcd for $C_{15}H_{17}BrNO_6$ ($[M+H]^+$) 386.0239, Found: 386.0237; HPLC [CHIRALCEL OJ-3, hexane/2-propanol = 90/10, 0.5 mL/min, λ = 254 nm, retention times: (major) 19.6 min, (minor) 21.7 min].

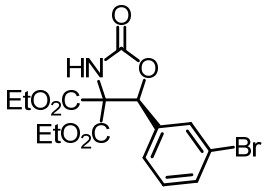
(*S*)-Diethyl 5-(2-bromophenyl)-2-oxooxazolidine-4,4-dicarboxylate (**3k**).



Using the typical procedure B, **3k** was obtained (quant.) as a white solid; $[\alpha]^{26}_{D}$ –37.0 (*c* 1.97., $CHCl_3$, 92%ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 11.0 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.27-7.20 (m, 1H), 6.85 (s, 1H), 6.52 (s, 1H), 4.40-4.30 (m, 2H), 3.86-3.80 (m, 1H), 3.68-3.61 (m, 1H), 1.33 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 165.4, 156.6, 134.3, 132.9, 131.0, 128.3, 127.8, 123.5, 79.1, 71.2, 63.4, 62.8, 13.9, 13.3 ppm; IR (ATR) 3315, 1778, 1748, 1219, 771 cm^{-1}; LRMS (FAB^+) 386 ($[M+H]^+$); HRMS (FAB^+): Calcd for

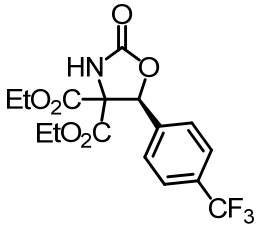
$C_{15}H_{17}BrNO_6$ ([M+H]$^+$) 386.0239, Found: 386.0237; HPLC [CHIRALCEL OJ-3, hexane/2-propanol = 90/10, 0.5 mL/min, λ = 254 nm, retention times: (major) 17.3 min, (minor) 26.2 min].

(*S*)-Diethyl 5-(3-bromophenyl)-2-oxooxazolidine-4,4-dicarboxylate (**3l**).



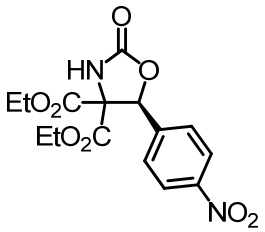
Using the typical procedure B, **3l** was obtained (97%) as a colorless oil; $[\alpha]^{26}_D$ –60.7. (*c* 1.20, $CHCl_3$, 91%ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 1.7 Hz, 1H), 7.50 (d, *J* = 6.9 Hz, 1H), 7.39 (d, *J* = 6.9 Hz, 1H), 7.26 (q, *J* = 6.9 Hz, 1H), 6.75 (s, 1H), 6.16 (s, 1H), 6.07 (s, 1H), 4.42-4.32 (m, 2H), 3.87-3.80 (m, 1H), 3.73-3.66 (m, 1H), 1.34 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 165.8, 156.7, 135.9, 132.5, 130.1, 129.8, 125.4, 122.3, 79.6, 71.4, 63.3, 63.0, 13.8, 13.3 ppm; IR (ATR) 3283, 1777, 1742, 1206, 1106, 1073 cm^{-1}; LRMS (FAB$^+$) 386([M+H]$^+$); HRMS (FAB$^+$): Calcd for $C_{15}H_{17}BrNO_6$ ([M+H]$^+$)386.0239, Found: 386.0237; HPLC [CHIRALCEL OJ-3, hexane/2-propanol = 90/10, 0.5 mL/min, λ = 254 nm, retention times: (major) 19.4 min, (minor) 21.3 min].

(*S*)-Diethyl 2-oxo-5-[4-(trifluoromethyl)phenyl]oxazolidine-4,4-dicarboxylate (**3m**).



Using the typical procedure A, **3m** was obtained (94%) as a white solid; $[\alpha]^{25}_D$ –25.7 (*c* 2.36, $CHCl_3$, 90%ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 6.62 (brs, 1H), 6.25 (s, 1H), 4.43-4.32 (m, 2H), 3.82-3.75 (m, 1H), 3.66-3.60 (m, 1H), 1.34 (t, *J* = 7.1 Hz, 3H), 0.78 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 165.8, 156.8, 137.7 131.6 (q, *J* = 33.6 Hz), 127.3, 125.4 (d, *J* = 2.4 Hz), 123.7 (q, *J* = 273 Hz), 79.8, 71.4, 63.4, 62.9, 13.8, 13.1 ppm; IR (ATR) 3311, 1782, 1747, 1327, 1114, 1069 cm^{-1}; LRMS (FAB$^+$) 376 ([M+H]$^+$); HRMS (FAB$^+$): Calcd for $C_{16}H_{17}F_3O_6N$ ([M+H]$^+$) 376.1008, Found: 376.0999; HPLC [CHIRALPAK AD, hexane/2-propanol = 90/10, 0.5 mL/min, λ = 254 nm, retention times: (major) 18.3 min, (minor) 15.0 min].

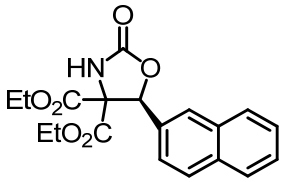
(*S*)-Diethyl 5-(4-Nitrophenyl)-2-oxooxazolidine-4,4-dicarboxylate (**3n**).



Using the typical procedure A, **3n** was obtained (89%) as a white solid ; $[\alpha]^{26}_D$ –20.7 (*c* 2.1, $CHCl_3$, 91%ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 8.8 Hz, 2H), 6.48 (brs, 1H), 6.28 (s, 1H), 4.45-4.36 (m, 2H), 3.87-3.80 (m, 1H), 3.69-3.62 (m, 1H), 1.35 (t, *J* = 7.1 Hz, 3H), 0.86 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1,

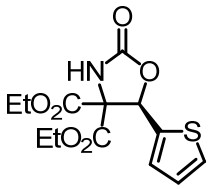
165.6, 156.0, 148.5, 140.5, 127.9, 123.5, 79.4, 71.2, 63.6, 63.2, 13.9, 13.4 ppm; IR (ATR) 1783, 1747, 1525, 1353, 1220 cm^{-1}; LRMS (FAB^+) 353 ($[M+H]^+$); *Anal*. Calcd for $C_{15}H_{16}N_2O_8$ C: 51.14, H: 4.58, N: 7.95, Found C: 50.71, H: 4.48, N: 8.02.; HPLC [CHIRALPAK AD, hexane/2-propanol = 90/10, 0.5 mL/min, λ = 254 nm, retention times: (major) 39.8 min, (minor) 33.4 min].

(*S*)-Diethyl 5-(naphthalen-2-yl)-2-oxooxazolidine-4,4-dicarboxylate (3o)



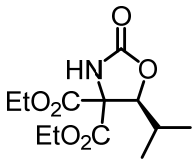
Using the typical procedure B, **3o** was obtained (quant.) as a white solid ; $[\alpha]^{26}_D$ –49.0 (*c* 1.68, $CHCl_3$, 95%ee); ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.84 (m, 3H), 7.51 (m 3H), 6.82 (s, 1H), 6.40 (s, 1H), 4.42-4.30 (m, 2H), 3.68-3.63 (m, 1H), 3.47-3.40 (m, 1H), 1.34 (t, *J* = 7.2 Hz, 3H), 0.58 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 166.0, 157.1, 133.5, 132.6, 131.0, 128.2, 128.1, 127.6, 126.8, 126.5 (2C), 123.7, 80.8, 71.6, 63.2, 62.7, 13.8, 13.0 ppm; IR (ATR) 3339, 1774, 1744, 1263, 1216 cm^{-1}; LRMS (FAB^+) 358 ($[M+H]^+$); HRMS (FAB^+): Calcd for $C_{19}H_{20}NO_6$ ($[M+H]^+$) 358.1291, Found: 358.1292; HPLC [CHIRALCEL OJ-3, hexane/2-propanol = 90/10, 0.5 mL/min, λ = 254 nm, retention times: (major) 24.4 min, (minor) 30.2 min].

(*R*)-Diethyl 2-oxo-5-(thiophen-2-yl)oxazolidine-4,4-dicarboxylate (3p)



Using the typical procedure A, **3p** was obtained (79%) as a colorless oil; $[\alpha]^{23}_D$ –66.4 (*c* 1.63, $CHCl_3$, 87%ee); ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.20-7.19 (m, 1H), 7.00 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.41 (s, 1H), 6.29 (brs, 1H), 4.41-4.31 (m, 2H), 3.96-3.91 (m, 1H), 3.85-3.80 (m, 1H), 1.34 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 165.6, 156.5, 135.4, 127.4, 126.8, 126.7, 77.3, 71.6, 63.3, 62.9, 13.8, 13.3 ppm; IR (ATR) 3303, 1776, 1742, 1218, 1177 cm^{-1}; LRMS (FAB^+) 314 ($[M+H]^+$); *Anal.* Calcd for $C_{13}H_{15}NO_6S$ C: 49.83, H: 4.83, N: 4.47. Found C: 49.83, H: 4.83, N: 4.47; HPLC [CHIRALCEL OJ-3, hexane/2-propanol = 90/10, 0.5 mL/min, λ = 254 nm, retention times: (major) 24.9 min, (minor) 30.1 min].

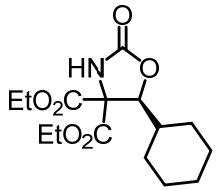
(*S*)-diethyl 5-isopropyl-2-oxooxazolidine-4,4-dicarboxylate (3q)



Using the typical procedure A, **3q** was obtained (72%) as a colorless oil; $[\alpha]^{26}_D$ –115.1 (c =1.0, $CHCl_3$, 92 %ee); ^1H NMR (500 MHz, $CDCl_3$) δ 6.28 (s, 1H), 4.91 (d, *J* = 5.4 Hz, 1H), 4.38-4.25 (m, 4H), 2.05-1.99 (m, 1H), 1.33-1.29(q, *J* =7.3 Hz, 6H), 1.09 (d, *J* =6.9 Hz, 3H), 0.99 (d, *J* = 6.6 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 166.6, 156.8, 84.4, 69.6, 63.10, 63.08, 29.6, 19.9, 16.7, 13.9, 13.8 ppm; IR (ATR) 3353, 2982, 1777, 1370, 1263, 1097, 1028 cm-1; HRMS (ESI):

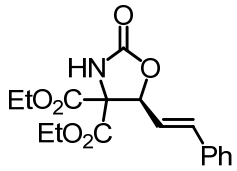
Calcd for $C_{12}H_{19}NO_6$ ([M+H]$^+$) 274.1285, found: 274.1455; HPLC [CHIRALPAK AD, λ = 235 nm, hexane 2-propanol = 90/10, 0.5 ml/min, (major) 19.3 min, (minor) 25.5 min]

(*S*)-Diethyl 5-cyclohexyl-2-oxooxazolidine-4,4-dicarboxylate(3r)



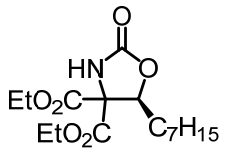
Using the typical procedure A, **3r** was obtained (66%) as a colorless oil; $[\alpha]^{27}_D$ –103 (c = 2.0, $CHCl_3$, 91 %ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.12 (brs, 1H), 4.89 (d, *J* = 5.7 Hz, 1H), 4.34-4.24 (m, 4H), 1.76 (m, 4H), 1.34-1.24 (m, 8H), 1.25-1.16 (m, 5H) ppm; ^{13}C NMR, (126 MHz, $CDCl_3$) δ 166.9, 166.7, 157.0, 83.8, 69.6, 63.04, 63.00, 39.1, 29.9, 26.9, 25.8, 25.4, 13.9, 13.8 ppm; IR (ATR) 3278, 2930, 2856, 1773, 1745, 1368, 1257, 1213, 1016 cm-1; HRMS (ESI): Calcd for $C_{15}H_{23}NO_6$ ([M+H]$^+$) 314.1598, found: 314.1599; HPLC [CHIRALPAK AD, λ = 235 nm, hexane 2-propanol = 90/10, 0.5 ml/min, retention times, (major) 18.6, (minor) 21.8]

(*S*,*E*)-Diethyl 2-oxo-5-styryloxazolidine-4,4-dicarboxylate (3s)



Using the typical procedure B, **3s** was obtained (93%) as a colorless oil; $[\alpha]^{26}_D$ –90.2 (*c* 0.77, $CHCl_3$, 82%ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.27 (m, 5H), 6.78 (d, *J* = 16.0 Hz, 1H), 6.04 (dd, *J* = 16.0, 7.8 Hz, 1H), 5.98 (s, 1H), 5.67 (d, *J* = 7.8 Hz, 1H), 4.33-4.24 (m, 2H), 4.11-4.06 (m, 2H), 1.26 (t, *J* = 7.8 Hz, 3H), 1.06 (t, *J* = 7.8 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 166.0, 156.3, 135.8, 135.1, 128.8, 128.7, 126.8, 120.1, 79.7, 70.5, 63.21, 63.16, 14.0, 13.9 ppm; IR (ATR) 3257, 1771, 1745, 1220 cm^{-1}; LRMS (FAB$^+$) 334 ([M+H]$^+$); HRMS (FAB$^+$): Calcd for $C_{17}H_{20}O_6N$ ([M+H]$^+$) 334.1291, Found: 334.1316; HPLC [CHIRALPAK AD-3, hexane/2-propanol = 90/10, 0.5 mL/min, λ = 254 nm, retention times: (major) 35.2 min, (minor) 40.3 min].

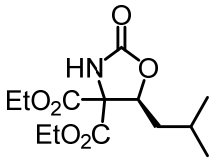
(*S*)-Diethyl 5-heptyl-2-oxooxazolidine-4,4-dicarboxylate (3t)



Using the typical procedure B, **3t** was obtained (86%) as a colorless oil; $[\alpha]^{26}_D$ –59.5 (c 2.26, $CHCl_3$, 65%ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.36 (brs, 1H), . (dd, *J* = 2.9, 10.6 Hz, 1H), 4.35-4.25 (m, 4H), 1.74-1.69 (m, 1H), 1.60-1.50(m, 2H), 1.48-1.44 (m, 1H), 1.32-1.28 (m, 14H), 0.88 (t, *J* = 6,0 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 166.5, 156.9, 79.0, 69.9, 63.0, 62.9, 31.6, 30.9, 29.0, 28.9, 25.6, 22.5, 14.0, 13.8 ppm; IR (ATR), 3267, 2932, 2858, 1777, 1750, 1468, 1370, 1265, 1098 cm-^{1}; HRMS (ESI): Calcd for $C_{16}H_{27}NO_6$ ([M+H]$^+$) 330.1911, found: 330.1905; HPLC [CHIRALPAK IB,

λ = 235 nm, hexane 2-propanol = 90/10, 0.5 ml/min, retention times (major) 16.0 min, (minor) 21.5 min]

(*S*)-Diethyl 5-isobutyl-2-oxooxazolidine-4,4-dicarboxylate (3u)

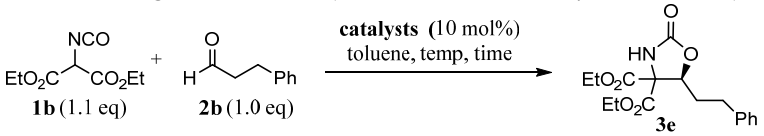


Using the typical procedure B, **3u** was obtained (98%) as a colorless oil; $[\alpha]^{26}_{D}$ -68.8 (c 3.11, $CHCl_3$, 70 %ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.44 (brs, 1H), 5.10 (dd, *J* = 2.9, 10.6 Hz, 1H), 4.36-4.25 (m, 4H), 1.96-1.88 (m, 1H), 1.56-1.44 (m, 2H), 1.33 (dt, *J* = 2.6, 7.5 Hz, 6H), 0.98 (t, *J* = 6,9 Hz, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 166.5, 157.1, 78.3, 69.9, 63.0, 62.9, 39.4, 24.7, 23.3, 21.1, 14.0, 13.8 ppm; IR (ATR), 3271, 2962, 2874, 1776, 1750, 1469, 1370, 1265, 1098, 1047, 863 cm^{-1}; HRMS (ESI): Calcd for $C_{13}H_{21}NO_6$ ($[M+H]^+$) 284.1442, found: 288.1444; HPLC [CHIRALPAK IB, λ = 235 nm, hexane 2-propanol = 90/10, 0.5 ml/min, retention times (major) 12.8 min, (minor) 13.9 min]

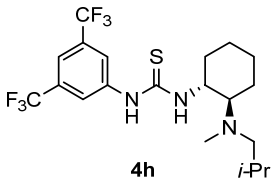
5. TUC-catalyzed Asymmetric Aldol reaction of aldehyde 2 with 2-isocyanatomalonate diester 1b

The aldol reaction of 3-phenylpropanal (**2b**) with diethyl 2-isocyanatomalonate **1b** and 10 mol% of other TUC catalysts **4** were investigated (Table S1). Use of TUC catalysts **4h** and **4i** having benzyl (Bn) and CH_2iPr side chains resulted in medium ee, probably because of an unfavorable steric interaction (entries 1 and 2). The imidazole and pyridine units (**4j-l**) were introduced to TUC catalysts expecting the control of the transition state through hydrogen bonds, but the low ee was only observed (entries 3-5). Thus, we thought the steric factor is more important for this reaction. Several bulky amines were introduced to TUC catalyst instead of the dimethyl amine moiety. While the introduction of $–NBn_2$ and $–N(CH_2iPr)_2$ was not effective (entries 6 and 7), TUC **4o** having $–N(CH_2iPr)_2$ improved an enantioselectivities (entry 8). Bis-thioure, ether side chains and carbocyclic structure (**4p-r**) were not effective (entries 9-11). The aldol reaction with other organocatalysts including benzothiadiazine **4s-u** and squaramide **4v** proceeded, but the obtained ee was not satisfied (entries 12-15).

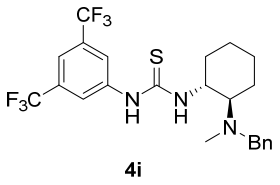
Table S1. Investigation of TUC catalysts for the reaction of isocyanate and aldehyde.



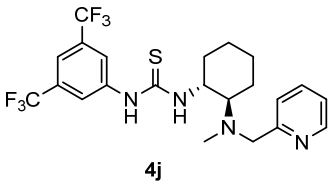
entry	cat	temp (°C)	time (h)	yield (%)	ee (%)
1	**4h**	0	24	89	59
2	**4i**	0	6	59	49
3	**4j**	0	3	84	29
4	**4k**	0	4	86	13
5	**4l**	0	6	88	2
6	**4m**	rt	24	73	3
7	**4n**	0	6	94	0
8	**4o**	rt	6	58	76
9	**4p**	0	21	41	0
10	**4q**	-60	72	38	0
11	**4r**	-60	72	58	28
12	**4s**	rt	24	20	42
13	**4t**	rt	24	76	50
14	**4u**	rt	24	68	50
15	**4v**	rt	24	33	41



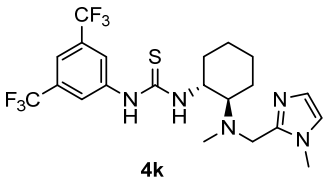
4h



4i



4j



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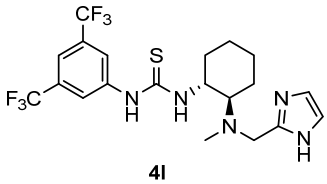

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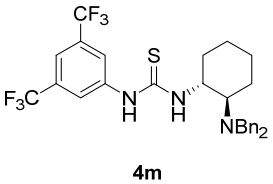

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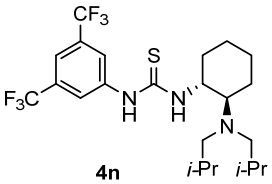

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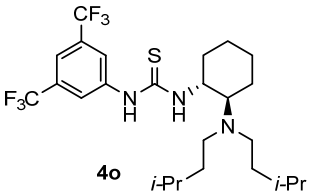

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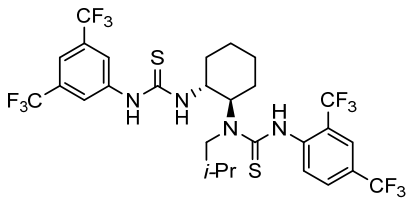

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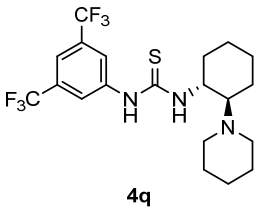

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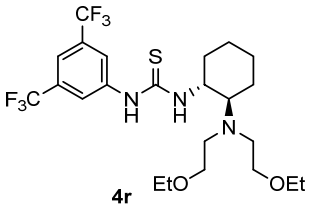

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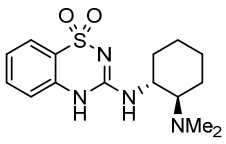

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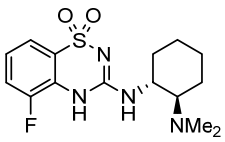

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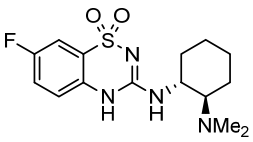
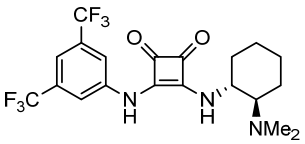
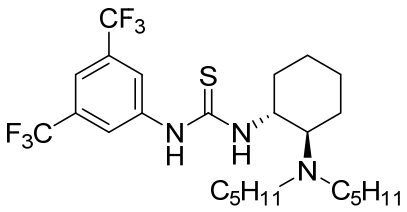


4u



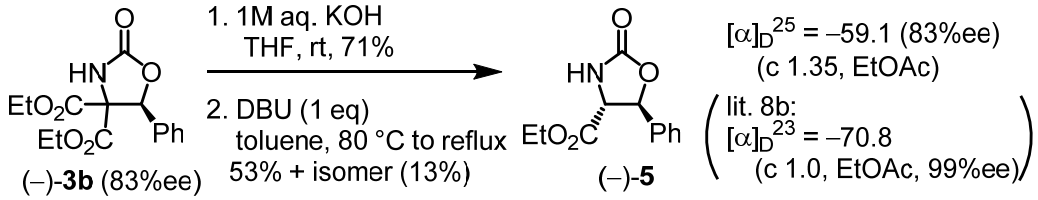
4v

Thiourea 4b



White solide; $[\alpha]^{25}_{D}$ –68.8 (c 1.09, $CHCl_3$, 99 %ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (s, 2H), 7.67 (s, 1H), 3.69 (br, 1H), 2.76 (br, 2H), 2.28 (br, 2H), 1.88 (d, *J* = 11.7 Hz, 1H), 1.83 (d, *J* = 11.5 Hz, 1H), 1.74 (d, *J* = 13.2 Hz, 1H), 1.33-1.11 (m, 15H), 0.82 (t, *J* = 7.2 Hz, 6H), ppm ; ^{13}C NMR, (126 MHz, $CDCl_3$) δ 180.5, 139.7, 132.6, 132.3, 125.9, 129.1, 123.7, 121.6, 118.3, 63.5, 55.9, 49.6, 32.3, 29.3, 28.1, 25.2, 24.2, 23.2, 22.1, 13.5 ppm; IR (ATR) 3260, 2933, 2860, 1751, 1507, 1385, 1279, 1179, 1140, cm^{-1}; LRMS (FAB^+) 526, HRMS (ESI): Calcd for $C_{25}H_{37}F_6N_3S$ ($[M–H]^-$) 524.2540, found: 524.2541.

6. Synthesis of (4*R*,5*S*)-Ethyl 2-oxo-5-phenyloxazolidine-4-carboxylate (5).



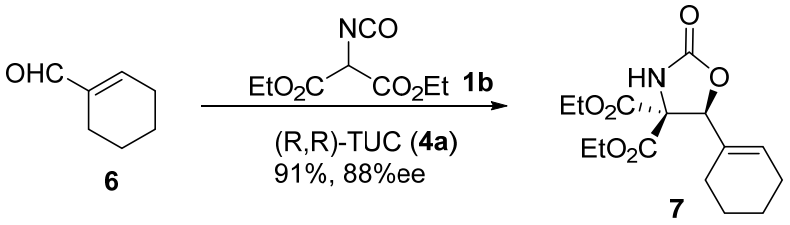
To a solution of **3b** (77.1 mg, 0.253 mmol) in THF (2.5 mL) was added 0.2 M aq. KOH (1.52 mL, 0.303 mmol) at 0 °C. The resultant mixture was stirred at 0 °C for 7.5 h. Then the reaction was quenched with 1M aq. HCl (3 mL) and extracted with EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure to give a crude carboxylic acid (51.4 mg, 71%) as a white solid:

The above carboxylic acid (18.5 mg, 0.0662 mmol) was dissolved in toluene (1 mL), and DBU (0.010 mL, 0.0669 mmol) was added. The resultant solution was stirred at 80 °C for 2 h and then refluxed for 1 h. Then the reaction mixture was concentrated under reduced pressure. The resulting residue was purified by silica gel chromatography (20-33%EtOAc/hexane) to give **5** (8.3 mg, 53%) as a colorless oil and its isomer (2.1 mg, 13%) as a white solid.

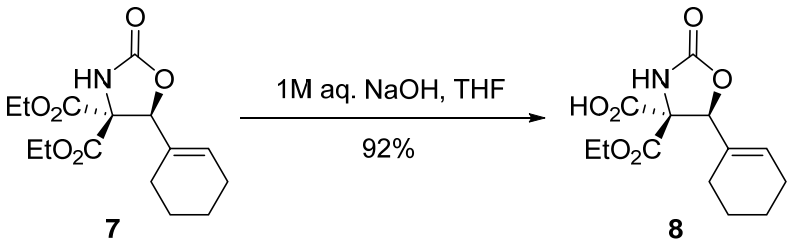
5: $[\alpha]^{25}_{D}$ –59.1 (*c* 1.35, $CHCl_3$, 83%ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.39 (m, 5H), 6.16 (s, 1H), 5.66 (d, *J* = 5.0 Hz, 1H), 4.36-4.29 (m, 2H), 4.27 (d, *J* = 5.2 Hz, 1H), 1.35 (t, *J* = 7.2 Hz) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.6, 158.1, 138.1, 129.1, 129.0, 125.3, 79.4, 62.5, 61.3, 14.1 ppm; IR (ATR) 3303, 1760, 1219 cm^{-1}; LRMS (FAB^+) 236 (MH^+); HRMS (FAB^+): Calcd for $C_{12}H_{14}NO_4$ ($[M+H]^+$) 236.1025, Found: 236.1027.

lit. 8b: Lu, Z.; Zang, Y.; Wulff, W. D.; *J. Am. Chem. Soc.* **2007**, *129*, 7185.

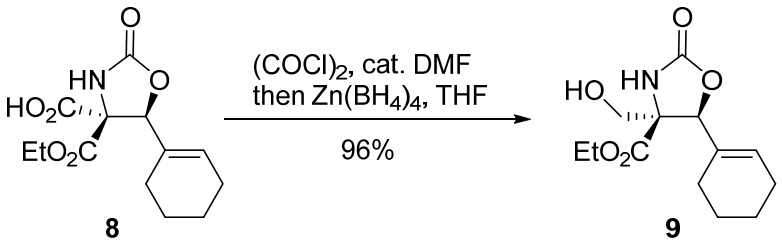
7. Total synthesis of mycestericin C



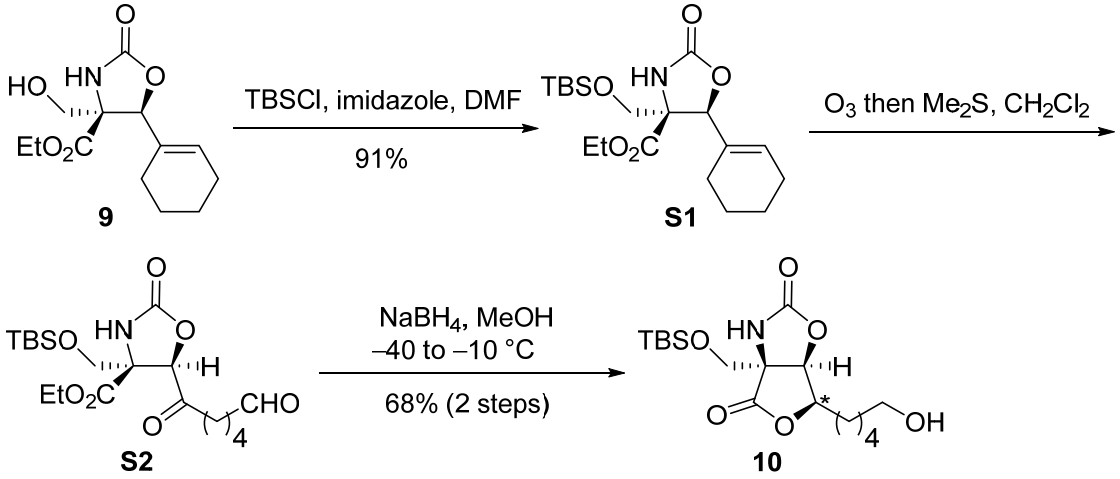
Diethyl (S)-5-(cyclohex-1-en-1-yl)-2-oxooxazolidine-4,4-dicarboxylate 7 : To a mixture of isocyanatomalonate **1b** (250.0 mg, 1.24 mmol) in toluene (1.2 mL) were added thiourea (101.4 mg, 0.245 mmol) and 1-Cyclohexene-1-carboxyaldehyde (125 µl, 1.09 mmol) at ‑78 °C. After being stirred at –78 °C for 72 h, the reaction mixture was concentrated *in vacuo*. The resulting residue was purified by silica gel chromatography (25% The EtOAc/hexanes) to give **7** (308.9. mg, 91%) as a white solid: $[\alpha]^{27}_{D}$ -93.7 (c 2.60, $CHCl_3$, 88 %ee) ; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.94 (s, 1H), 5.72 (brs, 1H), 5.52 (s, 1H) 4.36-4.24 (m, 4H), 4.18-4.10 (m, 1H), 2.13-2.05 (m, 3H), 1.93-1.90 (m, 1H), 1.57-1.52 (m, 4H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 6.5 Hz, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 166,8, 166.3, 156.8, 131.4, 129.1, 82.5, 70.7, 63.0, 62.9, 25.0, 24.0, 22.1, 21.8, 14.0, 13.8 ppm; IR (ATR) 3249, 2986, 2935, 1771, 1742, 1446, 1300, 1219, 1017, 771 cm^{-1}; HRMS (ESI): Calcd for $C_{15}H_{21}NO_6$ ($[M+H]^+$) 312.1442, found: 312.1438; HPLC [CHIRALPAK AD, hexane 2-propanol = 90/10, 0.5 ml/min, retention times (major) 19.0 min, (minor) 25.9 min]



Carboxylic acid 8: To a solution of compound 7 (300.0 mg, 0.964 mmol) in THF (4.8 mL) was added 1 M aq. NaOH (1.5 mL, 1.5 mmol) at 0 °C. The resultant mixture was stirred at 0 °C for 3.5 h. The mixture was acidified with 1 M aq. HCl (5 mL) and extracted with EtOAc three times. The combined organic layers were washed with water, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (0–10% MeOH/$CHCl_3$) to give carboxylic acid **8** (250.6 mg, 92%) as a white solid: $[\alpha]^{28}_{D}$ -132.6 (c 0.99, MeOH); ^{1}HNMR (500 MHz, CD_3OD) δ 5.87 (s, 1H), 5.46 (s, 1H), 4.23-4.11 (m, 2H) 2.09-2.05 (m, 3H), 1.93 (m, 1H), 1.61-1.55 (m, 4H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, CD_3OD) δ 170.6, 169.1, 160.7, 134.3, 130.4 84.8, 73.4, 65.5, 26.8, 26.0, 24.2, 24.0, 15.2 ppm; IR (ATR), 3328, 2938, 2858, 2480, 1725, 1367, 1247, 1158, 771 cm^{-1}; HRMS (ESI): Calcd for $C_{13}H_{17}NO_6$ ($[M+H]^+$) 284.1129, found: 284.1125



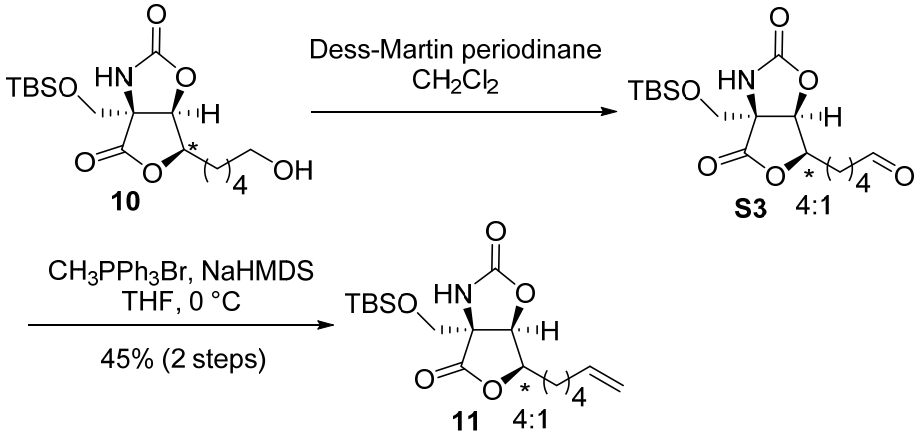
Alcohol **9**: To a solution of carboxylic acid **8** (65.8 mg, 0.232 mmol) in THF (2.3 mL) were added catalytic amount of DMF (30 mL) and $(COCl)_2$ (0.323 mL, 0.349 mmol) at 0 °C. The resultant solution was stirred at room temperature for 2 h. After complete consumption of the starting material (TLC analysis), a freshly prepared $Zn(BH_4)_4$ solution (0.2 M Et_2O solution, 1.75 mL, 0.35 mmol) was added to the reaction solution at 0 °C. The resultant solution was stirred at 0 C for 15 min, and then the reaction was quenched with 1 M aq. HCl (3 ml). The mixture was diluted with EtOAc, and washed with water. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (50–67% EtOAc/hexanes) to give alcohol **9** (59.8 mg, 96%) as a colorless oil: $[\alpha]^{27}_D$ –31.3 (c 1.02, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.59 (brs, 1H), 5.78 (s, 1H), 4.71 (s, 1H) 4.17-4.12. (m, 2H), 3.94 (dd, *J* = 5.7, 11.5 Hz, 1H), 3.76 (d, *J* = 7.2, 11.5 Hz,1H), 3.64 (brs, 1H), 1.97 (s, 3H), 1.86- 1.77 (m, 1H), 1.51-1.44 (m, 4H), 1.21 (t, *J* = 7.2 Hz) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.4, 159.2, 131.6, 128.6, 83.7, 70.1, 66.2, 62.4, 24.9, 24.1, 22.1, 21.9, 14.0 ppm; IR (ATR), 3339, 2933, 1736, 1369, 1304, 1039, 754 cm^{-1}; HRMS (ESI): Calcd for $C_{13}H_{19}NO_5$ ($[M+H]^+$) 270.1336, found: 270.1324.



Lactone 10: To a solution of alcohol **9** (1.05 g, 3.90 mmol) in DMF (26 mL) were added imidazole (398 mg, 5.85 mmol) and TBSCl (705 mg, 4.68 mmol) at room temperature. The resultant solution was stirred at room temperature for 5 h. The reaction was quenched with water, and extracted with Et_2O. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (20-25% EtOAc/hexanes) to give alcohol **S1** (1.36 g, 91%) as a colorless oil: $[\alpha]^{28}_D$ –38.0 (c 0.97, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.81 (s, 1H), 5.69 (s, 1H), 4.58 (s, 1H) 4.20-4.10 (m, 2H), 4.09 (d, *J* = 9.5 Hz, 1H), 3.73 (d, *J* =9.5 Hz, 1H), 2.08-2.05 (m, 3H), 1.86-1.83 (m, 1H), 1.61-1.51 (m, 4H), 1.27 (t, *J* = 7.2 Hz, 3H), 0.86 (s, 9H), 0.06 (s, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2, 157.5, 132.0, 128.7, 83.4, 70.3, 68.3, 62.0, 25.6, 25.0, 23.9, 22.1, 21.9, 18.1, 14.1, -5.46, -5.71 ppm; IR (ATR), 3297, 2929, 2858, 1767, 1471, 1251, 1120, 838 cm^{-1}; HRMS (ESI): Calcd for $C_{19}H_{33}NO_5Si$ ($[M+H]^+$) 384.2201, found: 384.2197

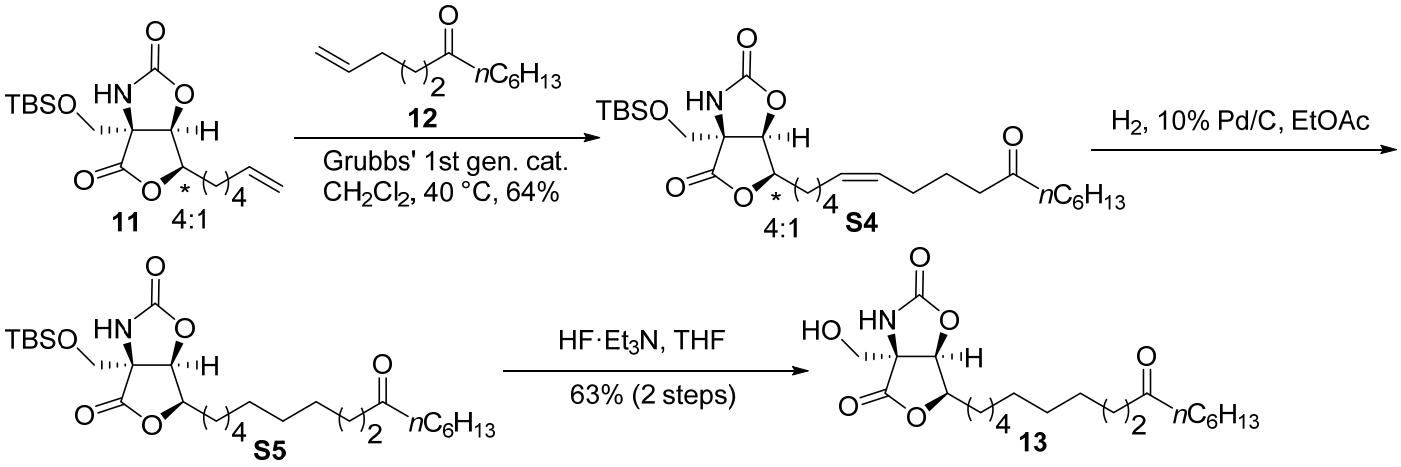
Ozone was bubbled through a solution of the above alcohol **S1** (300 mg, 0.783 mmol) in CH_2Cl_2 (15.6 mL) at -78 °C until a pale blue color persisted for 5 min. After oxygen was bubbled through the solution for 5 min, Me_2S (0.290 mL, 3.92 mmol) was added to the solution at -78 °C. The resultant solution was allowed to warm to room temperature, and then stirred for 2.5 h. The solution was diluted with CH_2Cl_2, and washed with water. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure to give crude aldehyde **S2** (330 mg) as a colorless oil, which was used for the next reaction without further purification.

To a solution of the above crude aldehyde **S2** (330 mg) in MeOH (16 mL) was added $NaBH_4$ (30.0 mg, 0.793 mmol) at –20 °C. The resultant solution was stirred at –20 °C for 1.5 h, and then stirred at –10 °C for 1 h. The mixture was diluted with EtOAc, and washed with water. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (50-66% EtOAc/hexanes) to give lactone **10** (200 mg, 68% (2 steps), dr = 4:1) as a colorless oil: $[\alpha]^{28}_D$ +24.1 (c 1.07, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.21 (brs, 0.2H), 6.17 (brs, 0.8H), 4.96 (d, *J* = 4.87 Hz, 0.8H) 4.70 (d, *J* = 2.3 Hz 0.2H), 4.54-4.49 (m, 0.2H), 4.48-4.44 (m, 0.8H), 4.01 (d, *J* = 9.7 Hz, 0.8H), 3.96 (d, *J* = 9.7Hz, 0.2H), 3.75 (d, *J* = 9.7 Hz, 0.8H), 3.69 (d, *J* = 9.7 Hz, 0.2H) , 3.56 (t, *J* = 6,3 Hz, 2H), 1.87-1.73 (m, 2H), 1.70-1.63 (m, 1H), 1.60-1.38(m, 7H), 0.83 (s, 9H), 0.45 (t, *J* = 5.4 Hz, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.6, 173.2, 156.6, 132.0, 85.0, 82.4, 81.9, 80.7, 66.1, 65.1, 63.2, 62.6, 62.5, 33.2, 32.31, 32.28, 31.6, 28.7, 25.7, 25.6, 25.4, 25.2, 24.9, 24.6, 22.6, 18.2, 18.0, 14.2, 14.1, -5.67, -5.82 ppm; IR (ATR); 3304, 2930, 2858, 1764, 1464, 1463, 1254, 1212, 1101, 838, 782 cm^{-1} HRMS (ESI): Calcd for $C_{17}H_{31}NO_6Si$ ($[M+H]^+$) 374.1993, found: 374.1993



Olefine **11**: To a solution of lactone **10** (120 mg, 0321 mmol) in CH_2Cl_2 (4.0 mL) was added Dess-Martine periodinane (204 mg, 0.481 mmol) at room temperature. The resultant solution was stirred at room temperature for 30 min. The solution was diluted with EtOAc, and washed with water. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was filtered through a plug of silica gel (33% EtOAc/hexanes) to give crude aldehyde **S3** (118 mg) as a colorless oil, which was used for the next reaction without further purification: $[\alpha]^{29}_D$ +22.3 (c 0.74, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.79 (s, 1H), 5.52 (s, 1H), 5.05 (d, *J* = 4.6 Hz, 0.8H) 4.79 (d, *J* = 2.3 Hz, 0.2H), 4.61-4.52 (m, 1H), 4.10 (d, *J* = 9.4 Hz, 0.8H), 4.50 (d, *J* = 10.0 Hz, 0.2H), 3.84 (d, *J* = 9.7 Hz, 0.8H), 3.79. (d, *J* = 10.0 Hz, 0.2H), 2.52-2.49 (m, 2H), 1.97-1.82 (m, 2H), 1.76-1.69 (m, 2H), 1.62-1.48 (m, 8H) 0.813 (s, 9H), 0.1 ppm;

To a suspension of methyl triphenylphosphonium bromide (281 mg, 0.787 mmol) in THF (10 mL) at 0 °C was added NaHMDS (1.0 M in THF solution, 0.950 mL, 0.950 mmol). The reaction mixture was stirred at 0 °C for 10 min, and then treated with a solution of the above crude aldehyde S3 (118 mg) in THF (6.0 mL). The resultant solution was stirred at 0 °C for 30 min. After the reaction was quenched with water, the resultant mixture was diluted with EtOAc, and washed with water. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (20-25% EtOAc/hexanes) to give olefin **11** (53.0 mg, 45%, (2 steps) dr = 4:1) as a colorless oil: $[\alpha]^{28}_D$ +18.4 (c 1.07, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.92 (brs, 0.2H), 5.90 (brs, 0.8H), 5.84-5.75 (m, 1H), 5.05 (s, 0.2H), 5.04 (s, 0,8H), 5.05-4.96 (m, 1.6H), 4.79-4.78 (m, 1H), 4.60-4.57 (m, 0.2H), 4.57-4.52 (m, 0.8H), 4.10 (d, *J* = 9.5 Hz, 0.8H), 4.05 (d, *J* = 10.0 Hz, 0.2H), 3.84 (d, *J* = 9.6 Hz, 0.8H), 3.78 (d, *J* = 9.9 Hz, 0.2H), 2.10-2.05 (m, 2H), 1.93-1.82 (m, 2H), 1.55-1.47 (m, 4H), 0.89-0.87 (m, 9H), 0.10-0.07 (m, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.5, 156.2, 138.3, 138.1, 115.0, 114.8, 85.1, 82.4, 81.9, 80.7, 66.0, 65.0, 63.4, 63.3, 33.4, 33.1, 28.6, 28.4, 28.2, 25.7, 25.6, 24.6, 24.2, 18.2, 18.0, -5.7, -5.8 ppm; IR (ATR) 3288, 2930, 2858, 1789, 1471, 1362, 1257, 1210, 1102, 842, 785; HRMS (ESI): Calcd for $C_{18}H_{31}NO_5Si$ ($[M+H]^+$) 370.2044, found: 370.2499.

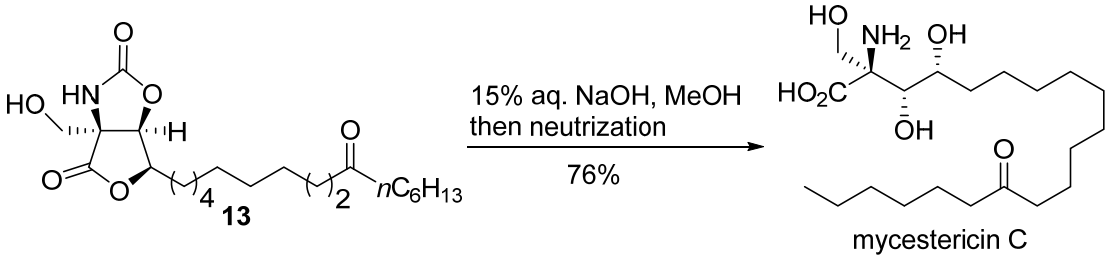


Protected mycestericin C (**13**): To a solution of olefin **11** (30.8 mg, 0.0834 mmol) and compound **12** (45.6 mg, 0.250 mmol) in CH_2Cl_2 (2.0 mL) was added Grubbs catalyst 1st generation (13.7 mg, 0.0166 mmol) at room temperature. The resultant solution was stirred at 40 °C for 5 h. The solution was directly concentrated under reduced pressure. The residue was purified by silica gel column chlomatography (0-5% EtOAc/hexanes) to give coupling product **S4** (28.0 mg, 64%) as a colorless oil: $[\alpha]^{28}_D$ +0.48 (c 1.03, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.38 (brs, 1H), 5.85 (m, 0.2H), 5.43-5.34 (m, 1.6H), 5.04 (d, *J* = 4.9 Hz, 0.8H), 4.78 (d, *J* = 1.4 Hz, 0.2H), 4.52-4.60 (m, 1H), 4.13 (d, *J* = 9.5 Hz, 0.8H), 4.05 (d, *J* = 9.7 Hz, 0.2H), 3.85 (d, *J* = 9.7 Hz, 0.8H), 3.78 (d, *J* = 9.7 Hz, 0.2H), 2.39 (t, *J* = 7.7 Hz, 2H), 2.10-1.97 (m, 4H), 1.90-1.81 (m, 2H), 1.66-1.60 (m, 2H), 1.57-1.40 (m, 6H), 1.32-1.27 (m, 4H), 0.89-0.87 (m, 11H), 0.1-0.07 (m, 6H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.7, 174.6, 173.2, 156.5, 138.3, 138.1, 130.5, 130.4, 130.0, 129.8, 114.9, 114.8, 85.0, 82.4, 82.3, 81.9, 80.7, 66.1, 65.1, 63.6, 63.2, 42.9, 42.1, 42.0, 33.4, 33.10, 33.08, 21.2, 31.9, 31.6, 29.2, 29.1, 28.9, 28.64, 28.57, 28.41, 28.2, 26.9, 26.6, 25.6, 24.8, 24.63, 24.60, 24.2, 24.1, 23.8, 23.7, 23.5, 22.4, 18,2, 18.0, 14.0, -5.70, -5.82 ppm; IR (ATR), 2961, 2932, 2872, 1705, 1381, 1129, 1093, 987 $cm^{-1;}$ HRMS (FAB^+): Calcd for $C_{28}H_{50}NO_6Si$ ($[M+H]^+$) 524.3407, found: 524.3431.

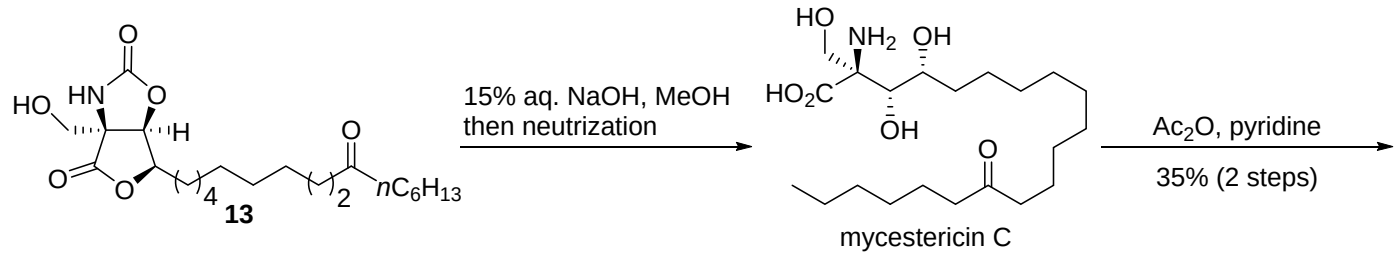
To a solution of the above coupling product (28.0 mg, 0.0535 mmol) in EtOAc (1.0 mL) was added 10% Pd/C (7.4 mg). The resultant mixture was stirred at room temperature under hydrogen atmosphere for 1.5 h. The catalyst was removed by filtering through a plug of Celite with EtOAc, and the filtrate was concentrated under reduced pressure to give a crude compound **S5** (27.0 mg) as a colorless oil, which was used for the next reaction without further purification.

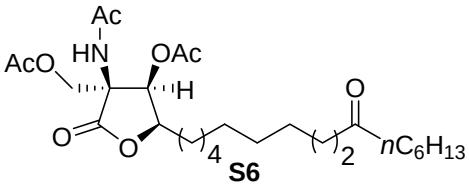
To a solution of the above crude compound **S5** (27.0 mg) in CH_3CN (4.0 mL) was added $3HF{\cdot}Et_3N$ (42 μL, 0.257 mmol) at room temperature. The resultant solution was stirred at 50 ° C for 2 h, and then $3HF{\cdot}Et_3N$ (208 μL, 1.29 mmol) was added. The resultant solution was stirred at 50 ° C for 6 h. After the reaction was quenched with satd. aq. $NaHCO_3$ (5 mL), the solution was extracted with EtOAc three times, and washed with water. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (40-66% EtOAc/hexanes) to give the protected mycestericin C (**13**) (13.8 mg, 63% (2 steps)) and the protected 4-epi mycestericin (3.6 mg, 16% (2 stpes)) as a colorless oil: $[\alpha]^{28}_D$ +17.2 (c 0.77, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.57 (brs, 1H), 5.13 (d, *J* = 10.9 Hz, 1H), 4.68-4.64 (m, 1H), 4.02 (d, *J* = 10.6 Hz, 1H), 3.93 (d, *J* = 10.6 Hz, 1H), 3.24 (brs, 1H), 2.93 (t, *J* = 10.9 Hz, 2H), 1.89-1.77(m, 4H), 1.57-1.44(m, 4H), 1.41-1.23(m, 18H), 0.91-0.87(m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.3, 174.7, 156.9, 82.65, 82.58, 80.1, 66.4, 61.7, 42.8, 31.6, 31.5, 29.2, 29.16, 28.9, 28.8, 28.7, 25.1, 25.05, 23.84, 23.80, 22.5, 14.0 ppm ; IR (ATR) 3331, 2929, 2857, 1774, 1459 cm^{-1}; HRMS (ESI): Calcd for $C_{22}H_{37}NO_6$ ($[M+H]^+$) 412.2694, found: 412.2675.

4-*Epi* protected mycestericin C (**13'**): $[\alpha]^{28}_D$ –2.4 (c 0.68, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.70 (brs, 1H), 4.83 (dd, *J* = 2.3Hz, 8.0Hz, 1H), 4.67-4.63 (m, 1H), 4.04-3.99 (m, 1H), 3.89 (d, *J* = 11.2 Hz, 1H), 2.67 (brs, 1H), 2.39 (t, *J* =8.3 Hz, 4H), 1.85-1.70 (m, 2H), 1.58-1.44 (m, 4H), 1.39-1.19(m, 18H), 0.91-0.87(m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.4, 173.4, 156.6, 85.5, 81.5, 81.5, 65.3, 61.9, 42.9, 42.8, 31.6, 31.5, 29.2, 29.05, 29.00, 28.63, 24.7, 24.5, 23.8, 23.7, 22.49, 14.0 ppm; IR (ATR) 3306, 2956, 2929, 2857, 1783, 1460, 1281, 1107, 1062, 805; HRMS (ESI) Calcd for $C_{22}H_{37}NO_6$ ($[M+H]^+$) 412.2694, found: 412.2694



Mycestericin C: To a solution of the protected mycestericin C (**13**) (3.5 mg, 0.0085 mmol) in MeOH (1.5 mL) was added 15% aq. NaOH (0.75 mL, 2.8 mmol) at room temperature. The resultant solution was stirred at room temperature for 1 h and then allowed to 50 °C, and stirred for additional 20 h. After cooling, the resultant solution was neutralized with Amberlite IRC-85 H^+ form (pH 7), washed with MeOH, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (0-50% MeOH/$CHCl_3$) to give mycestericin C (2.6 mg, 76%) as a white solid: $[\alpha]^{30}_D$ +6.6 (c 0.24, MeOH); ^{1}H NMR (500 MHz, CD_3OD) δ 4.01 (d, *J* = 10.9 Hz, 1H), 3.92 (d, *J* = 10.9 Hz, 1H), 3.79-3.67 (m, 1H), 3.80-3.76 (m, 1H), 3.73-3.70 (m, 1H), 3.66 (brs, 3H), 2.43 (t, *J* = 7.2 Hz, 2H), 1.60-1.59 (br, 2H), 1.54-1.51(m, 4H) 1.33-1.28 (m, 20H), 0.89 (t, *J* = 6.9 Hz, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 214.4, 154.6, 73.8, 71.0, 70.8, 65.2, 43.5, 35.2, 33.1, 33.0, 32.8, 30.8, 30.6, 30.5, 30.4, 30.3, 26.6, 24.9, 23.8, 23.7, 14.4ppm; IR (ATR), 3369, 2925, 2852, 1723, 1641, 1631, 1384, 1033, 768 cm^{-1} ; HRMS (ESI): Calcd for $C_{21}H_{41}NO_6$ ($[M–H]^-$) 402.2861, found: 402.2861.



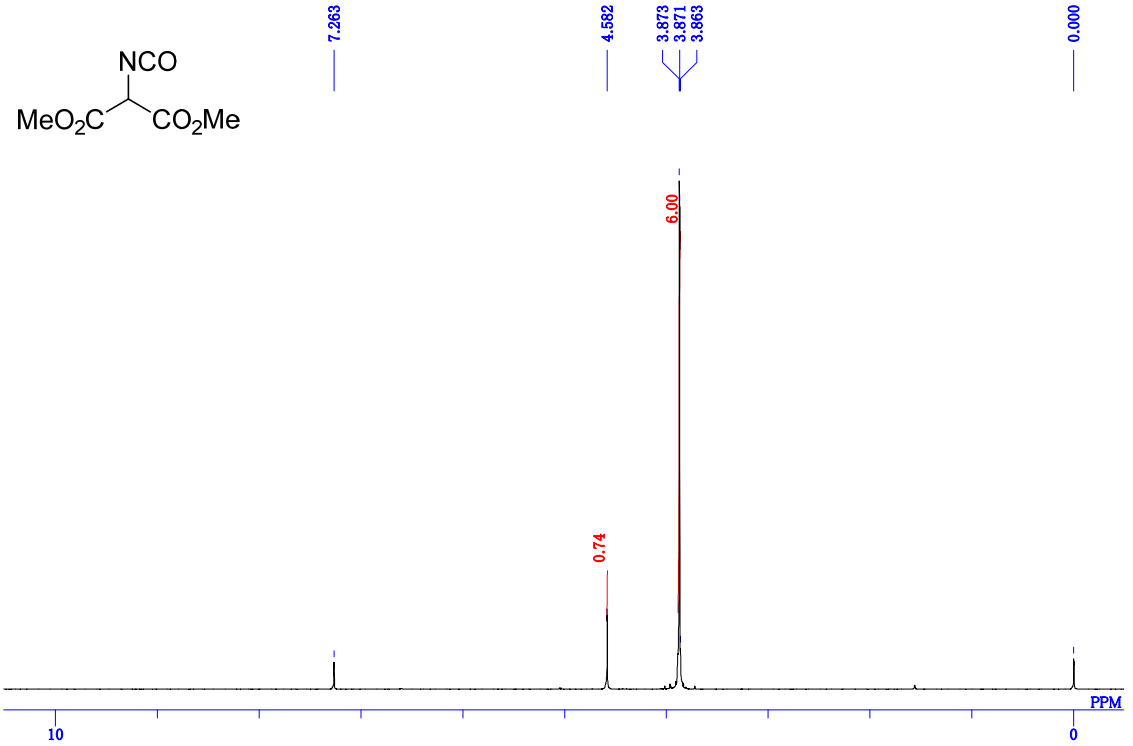


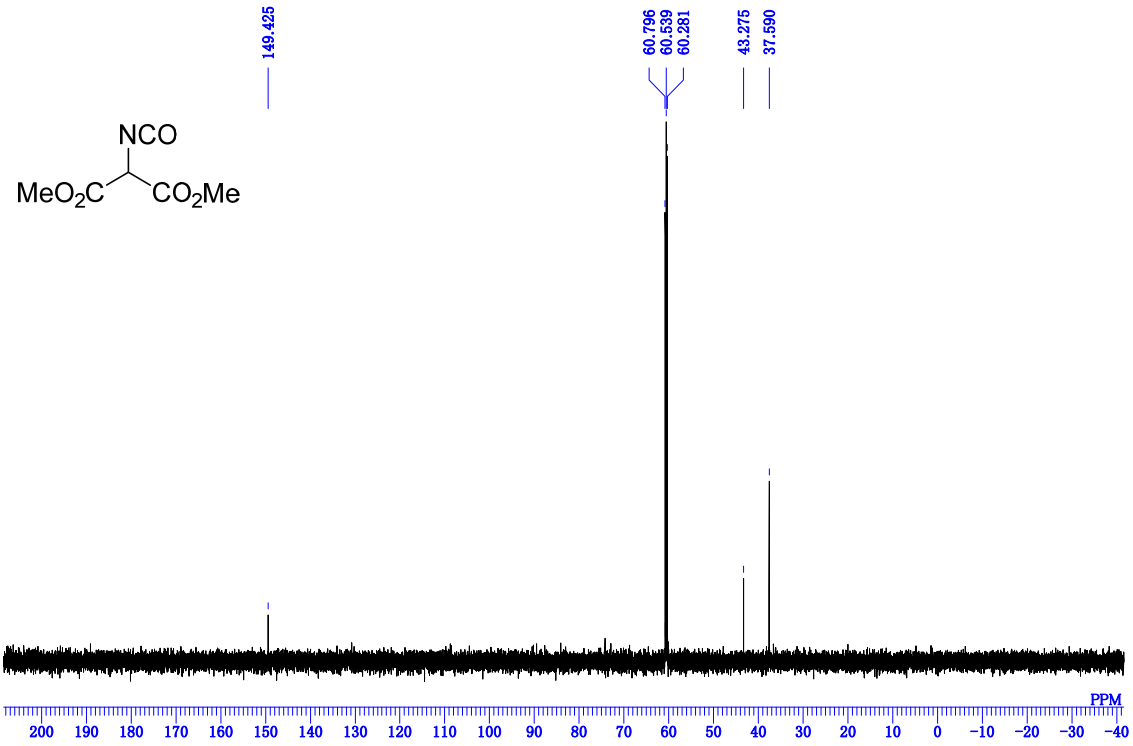
Triacetylmycestericin C γ-lactione (S6): To a solution of the protected mycestericin C (**13**) (2.0 mg, 0.00486 mmol) in MeOH (1.0 mL) was added 15% aq. NaOH (0.5 mL, 1.88 mmol) at room temperature. The resultant solution was stirred at room temperature for 15 min and then allowed to 50 °C, and stirred for additional 23 h. After cooling, the resultant solution was neutralized with 1M aq. HCl (1.69 ml, 1.69mmol). Amberlite IRC-86 H^+ form (pH 7), washed with MeOH, and concentrated under reduced pressure. The residue was concentrated under reduced pressure to give a crude mycestericin C (79.1 mg) as a white solid, which was used for the next reaction without further purification.

To a solution of the above crude mycestericin C (79.1 mg) in pyridine (1.2 mL, 0.00497) was added Ac_2O (0.4 mL, 0.00423 mmol) at room temperature, and stirred for additional 1 h. The solution was directly concentrated under reduced pressure. The residue was purified by silica gel column chromatography (40-50% EtOAc/hexanes) to give **S6** (0.9. mg, 35% (2 steps)) as a colorless oil: $[\alpha]^{26}_{D}$ +34.8 (*c* 0.11, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.92 (brs, 1H), 5.73 (s, 1H), 4.67-4.63 (m, 1H), 4.46 (s, 2H), 2.32 (t, *J*= 7.4 Hz), 2.03 (s, 3H), 1.99 (s, 3H), 1.96 (s, 3H), 1.66-1.60 (m, 1H), 1.55-1.49 (m, 5H), 1.25-1.16 (18H, m), 0.82-0.80(m, 3H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.3, 172.6, 170.2, 169.4, 168.9, 72.2, 82.1, 62.7, 62.5, 42.83, 42.77, 31.6, 31.5, 29.33, 29.28, 29.2, 28.9, 28.7, 25.7, 25.6, 23.8, 22.8, 22.5, 20.6, 20.3, 14.03 14.01 ppm; IR (ATR) 3340, 2930, 1783, 1756, 1230 cm^{-1} ; HRMS (FAB^+) Calcd for $C_{27}H_{46}NO_8$ ($[M+H]^+$) 512.3229, found: 512.3226

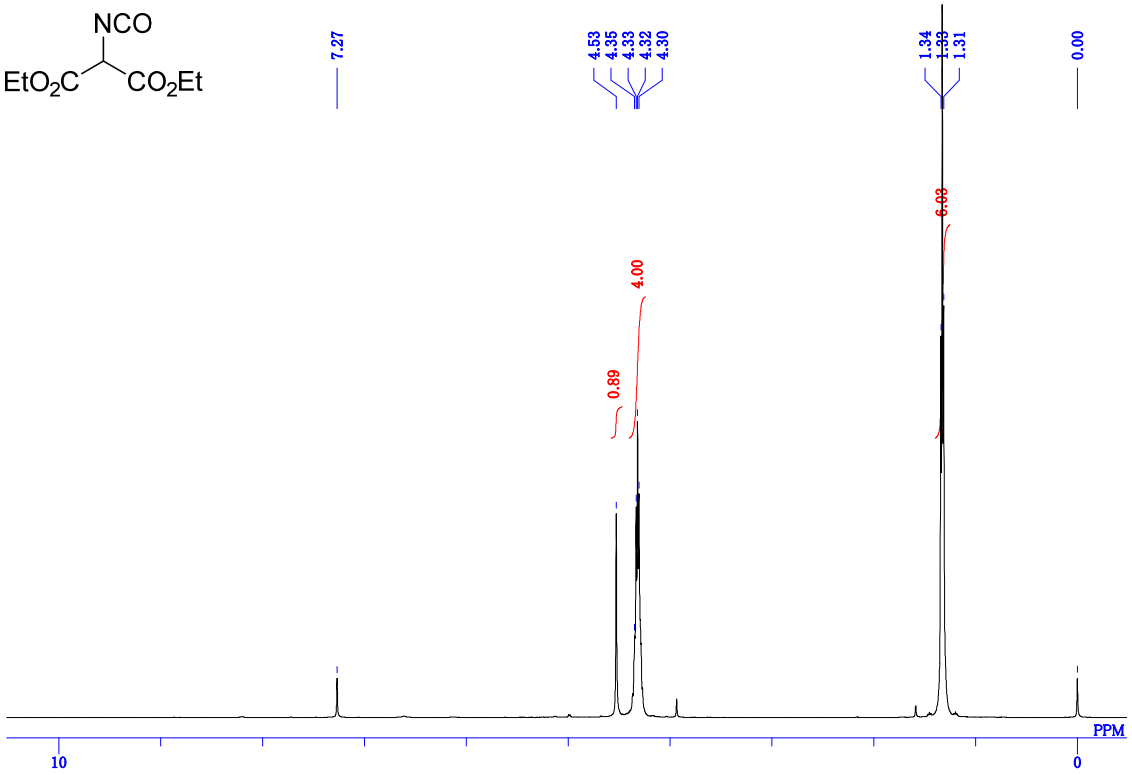
8. Copy of ^{1}H and ^{13}C NMR spectra of new substrates and products

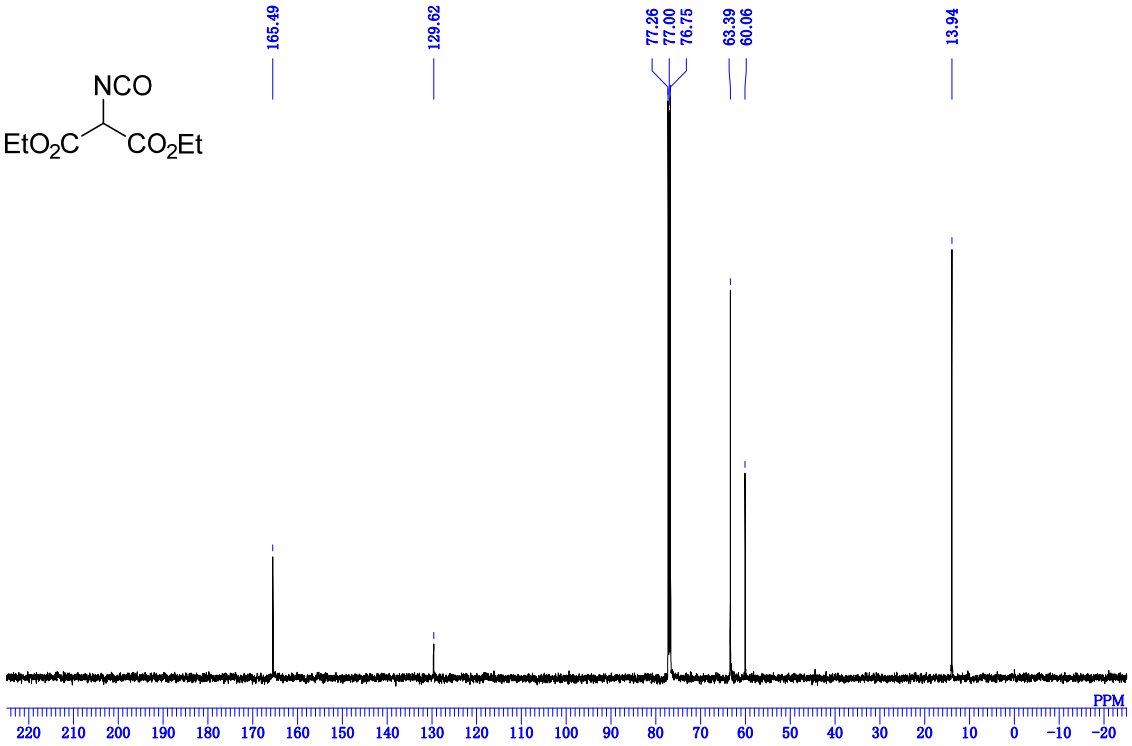
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **1a**



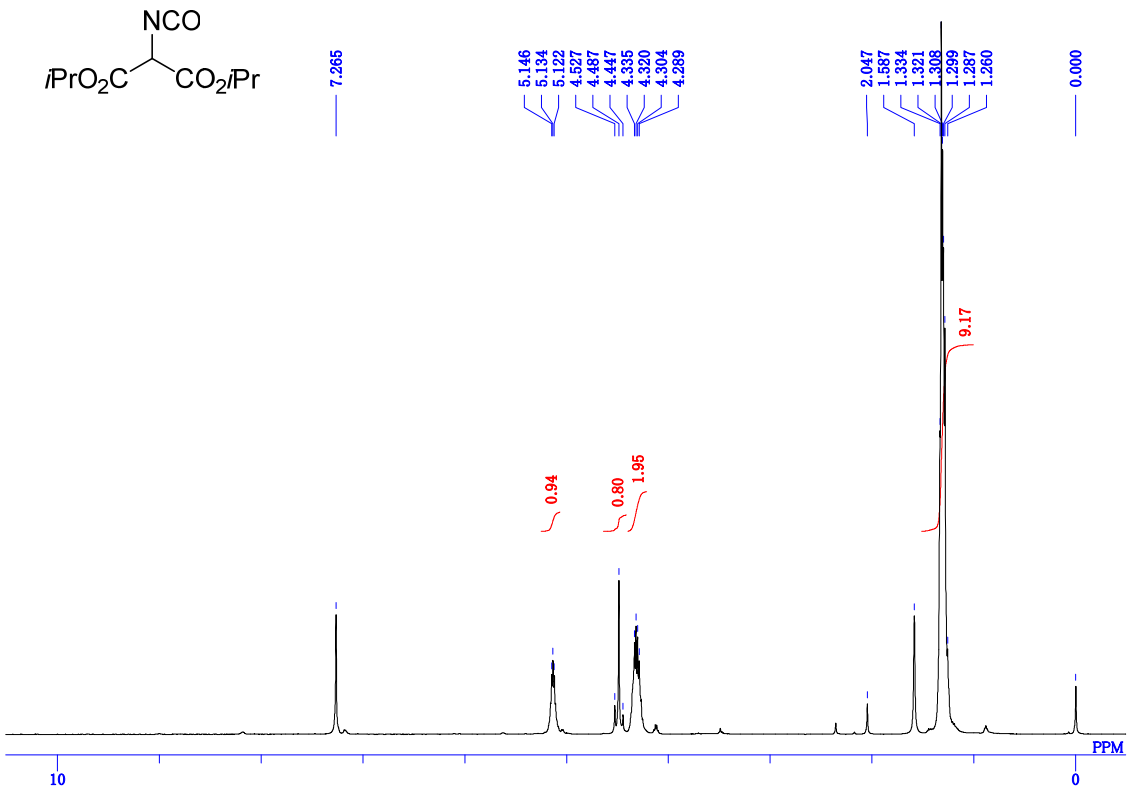


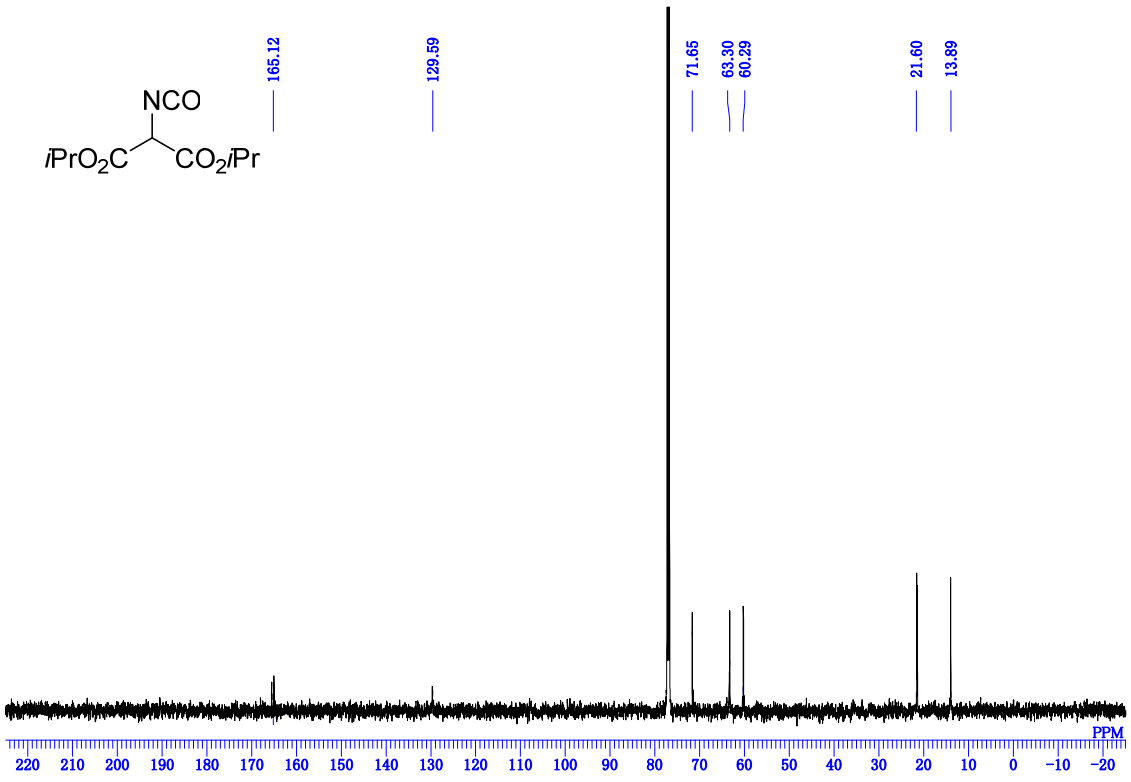
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **1b**



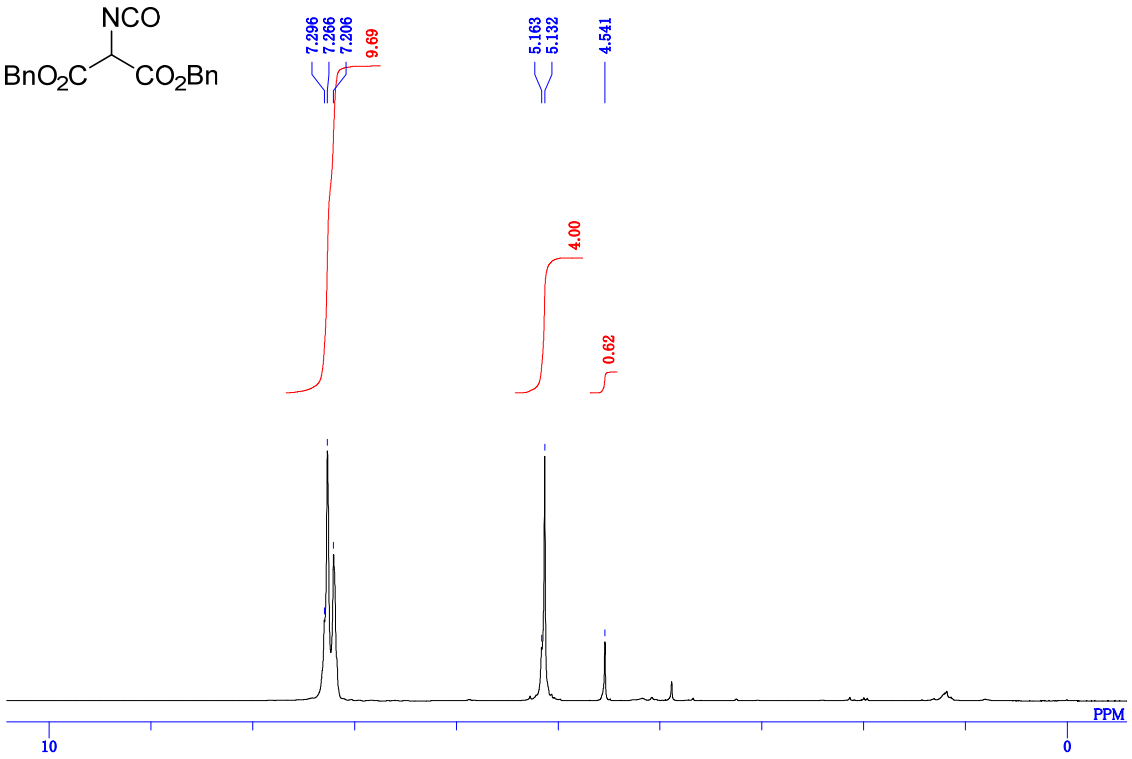


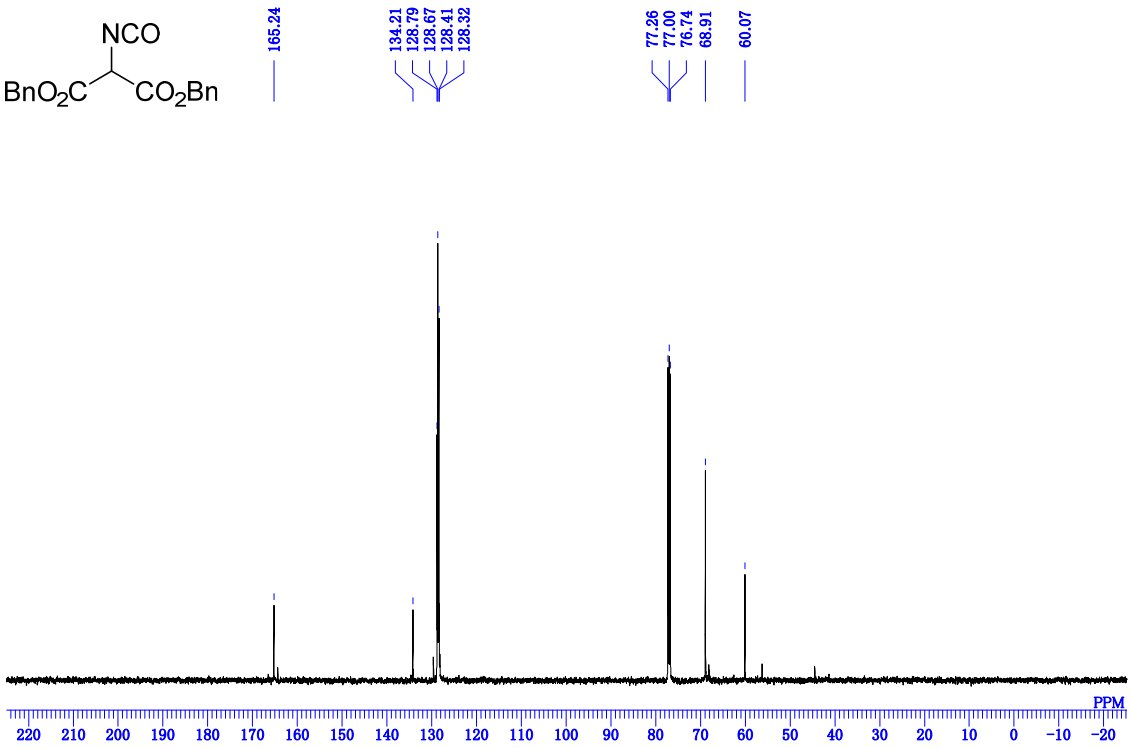
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **1c**.



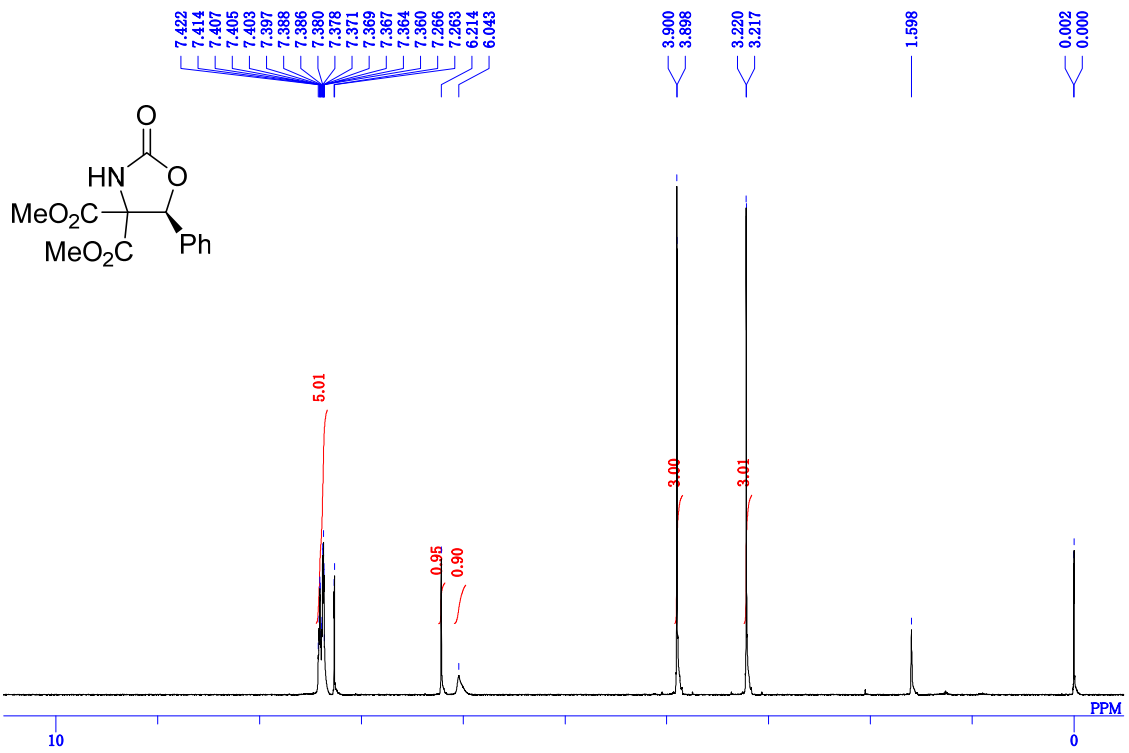


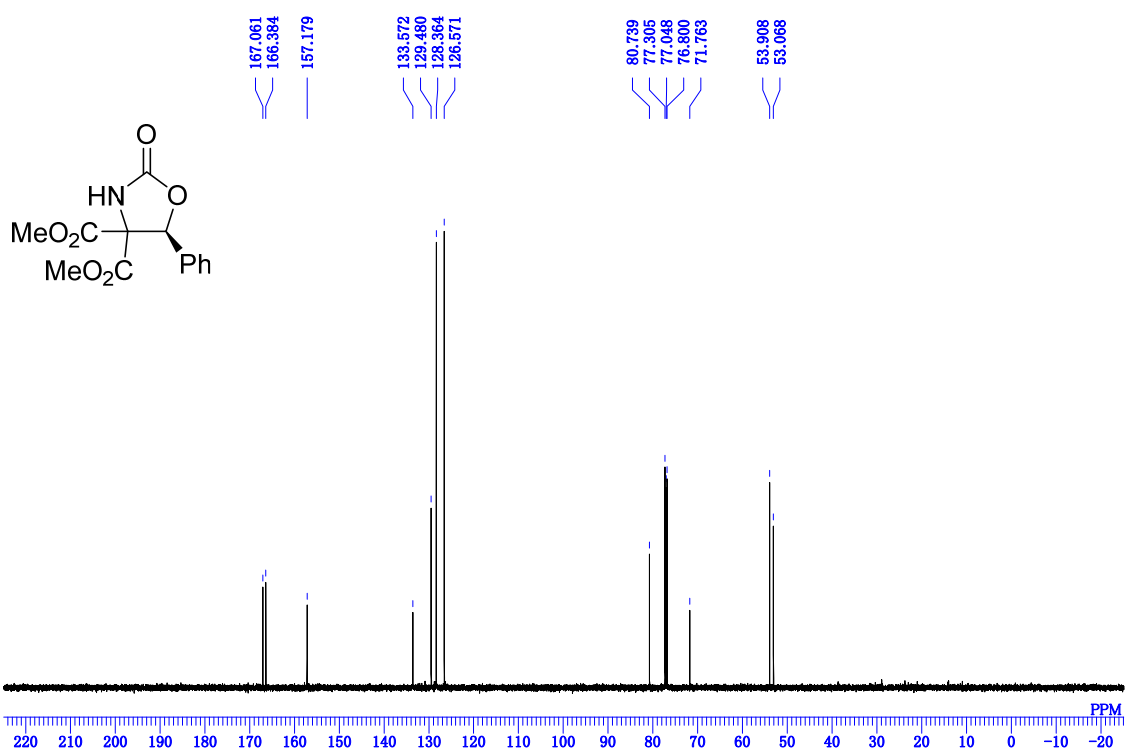
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **1d**.



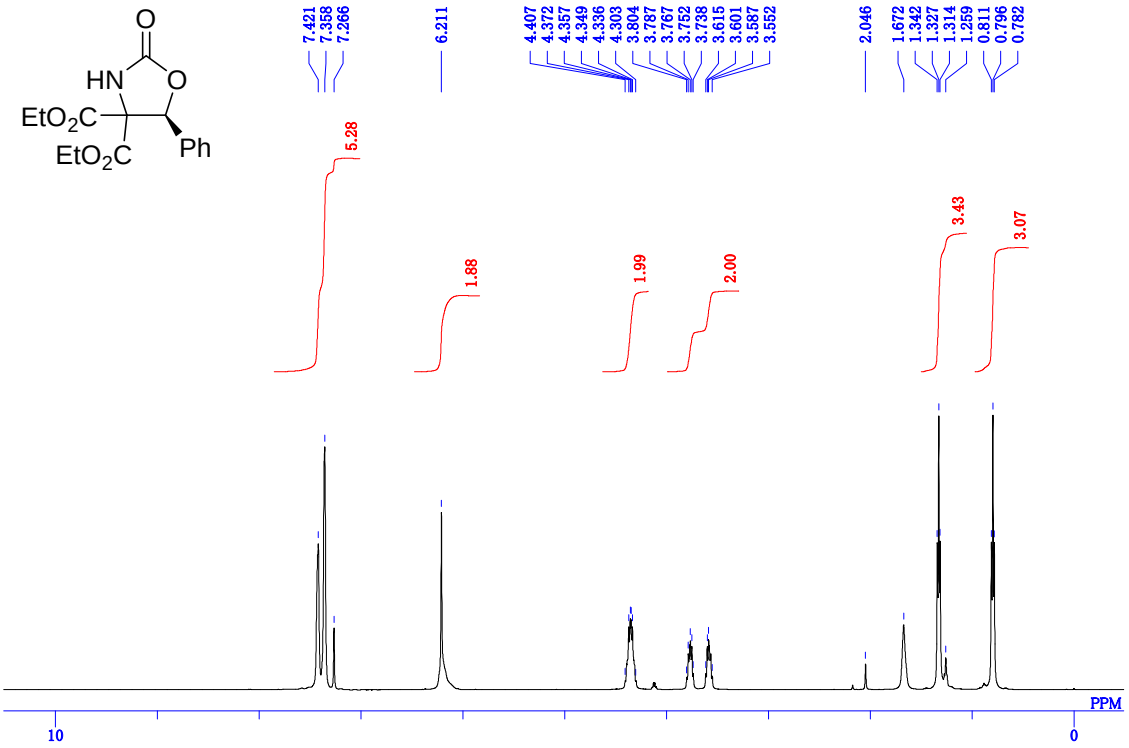


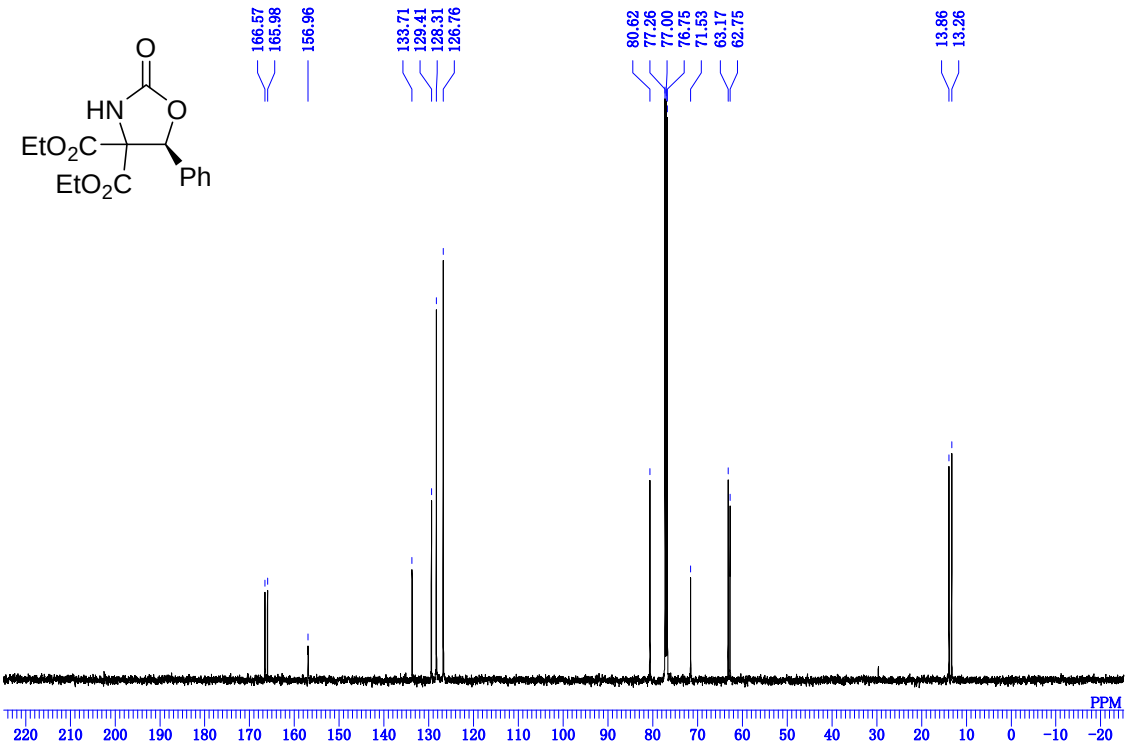
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **3a**.



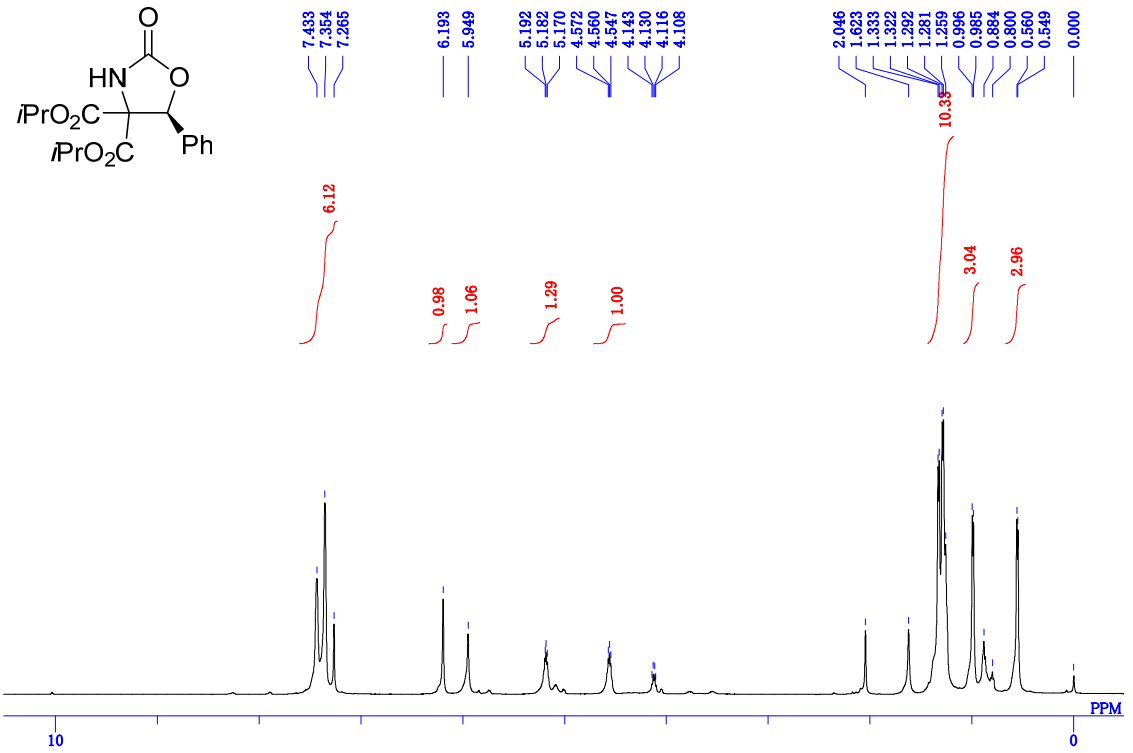


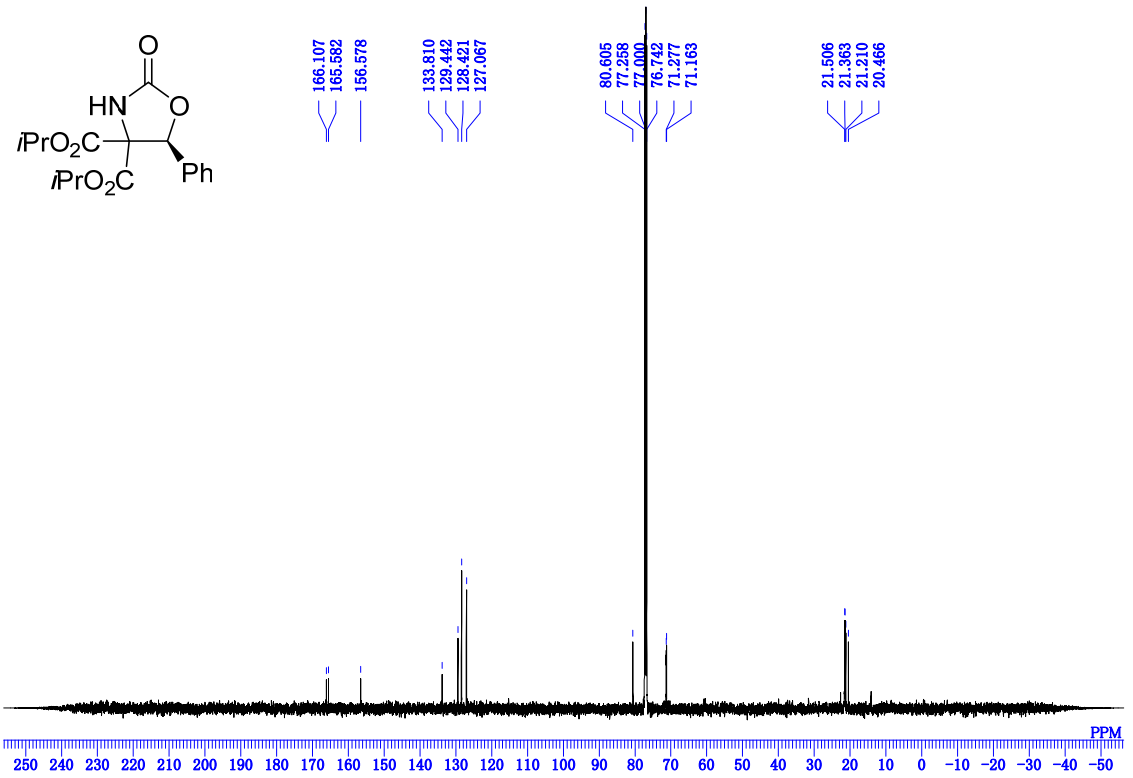
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **3b**.



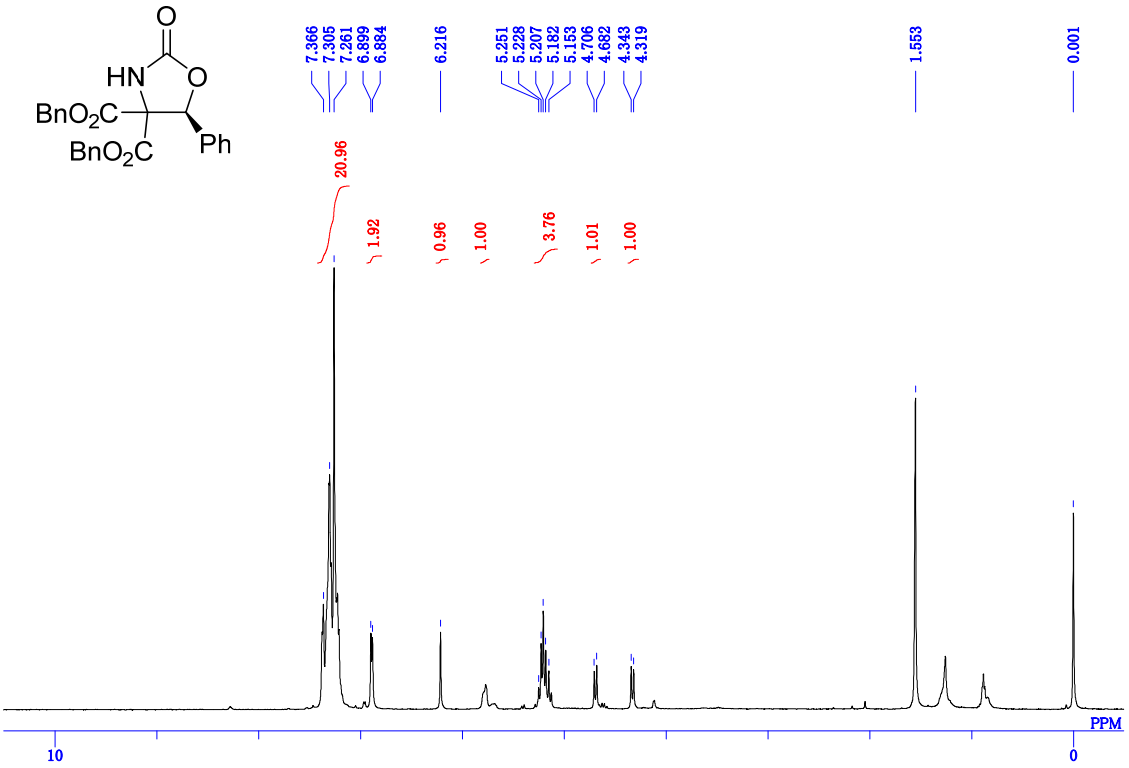


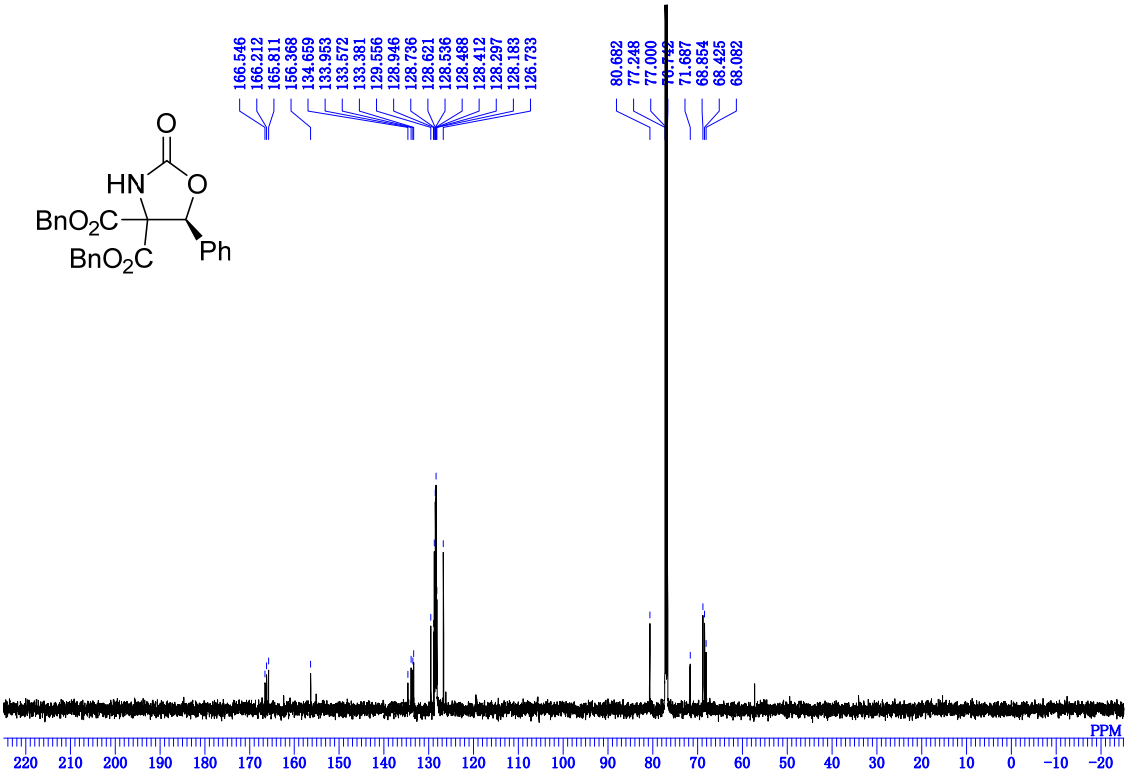
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **3c**.



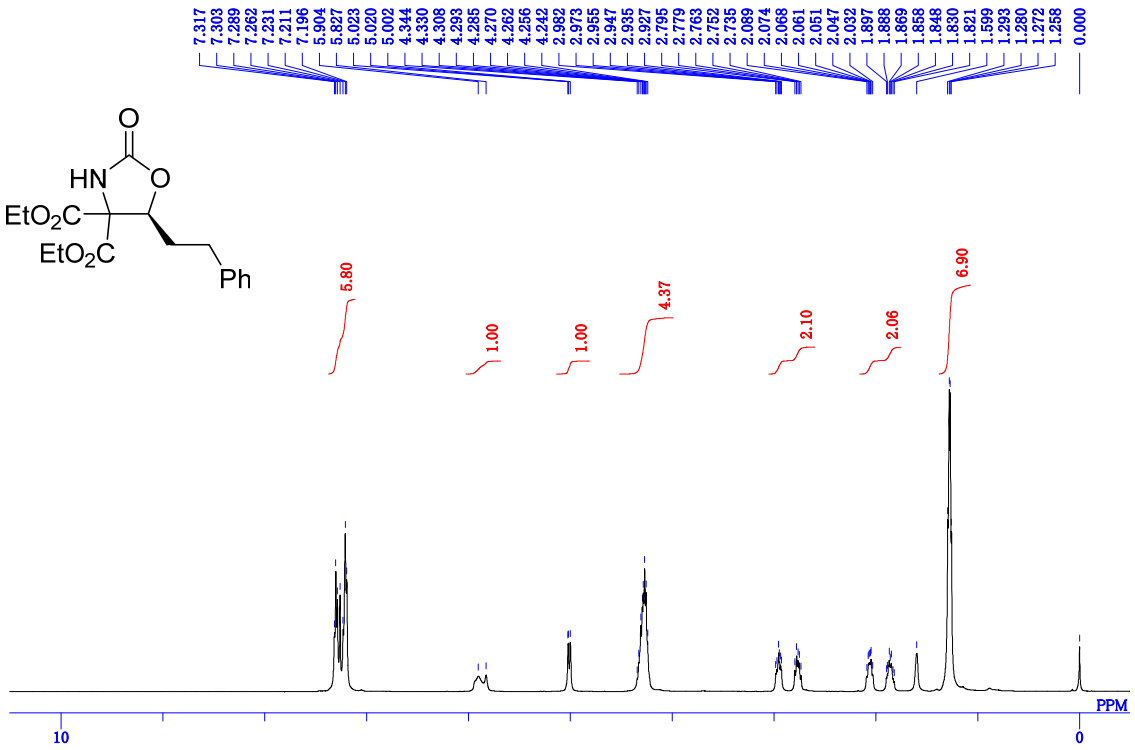


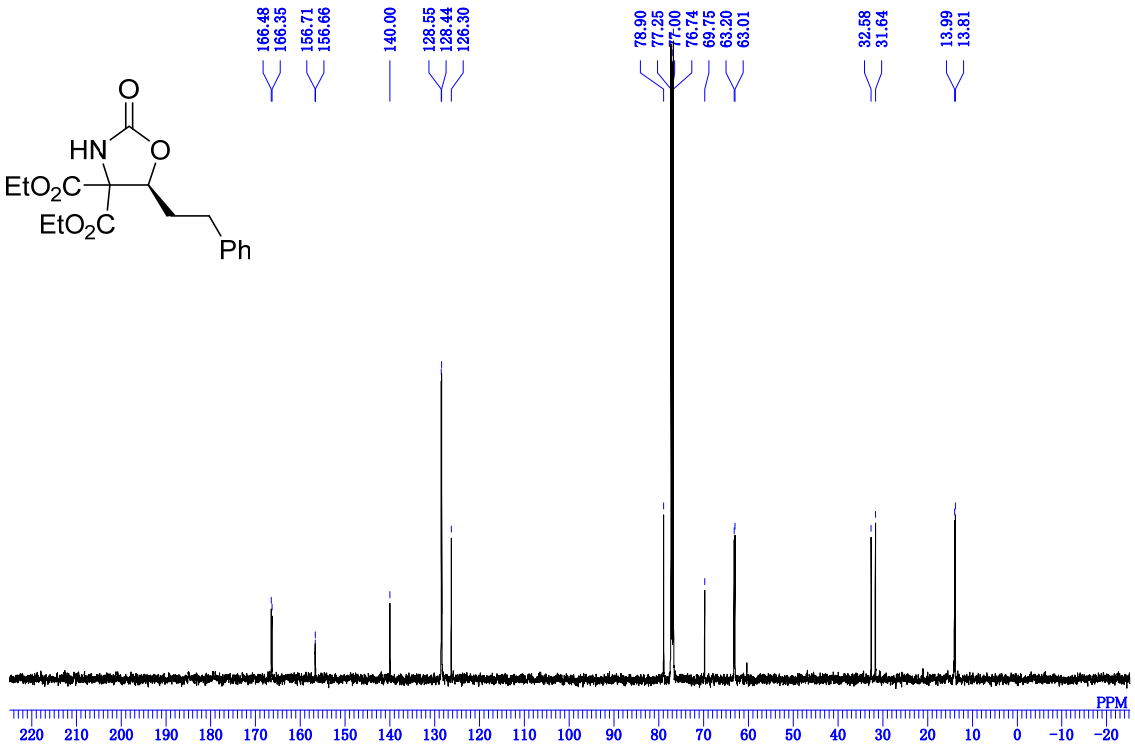
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **3d**.



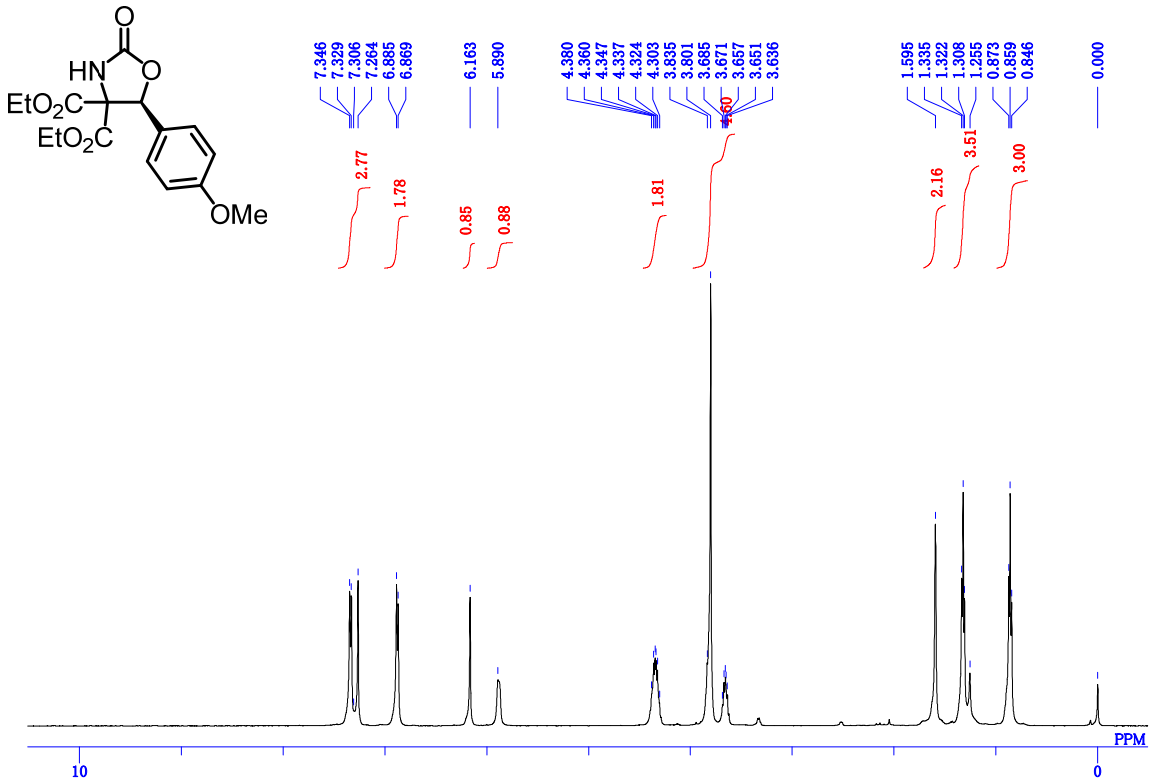


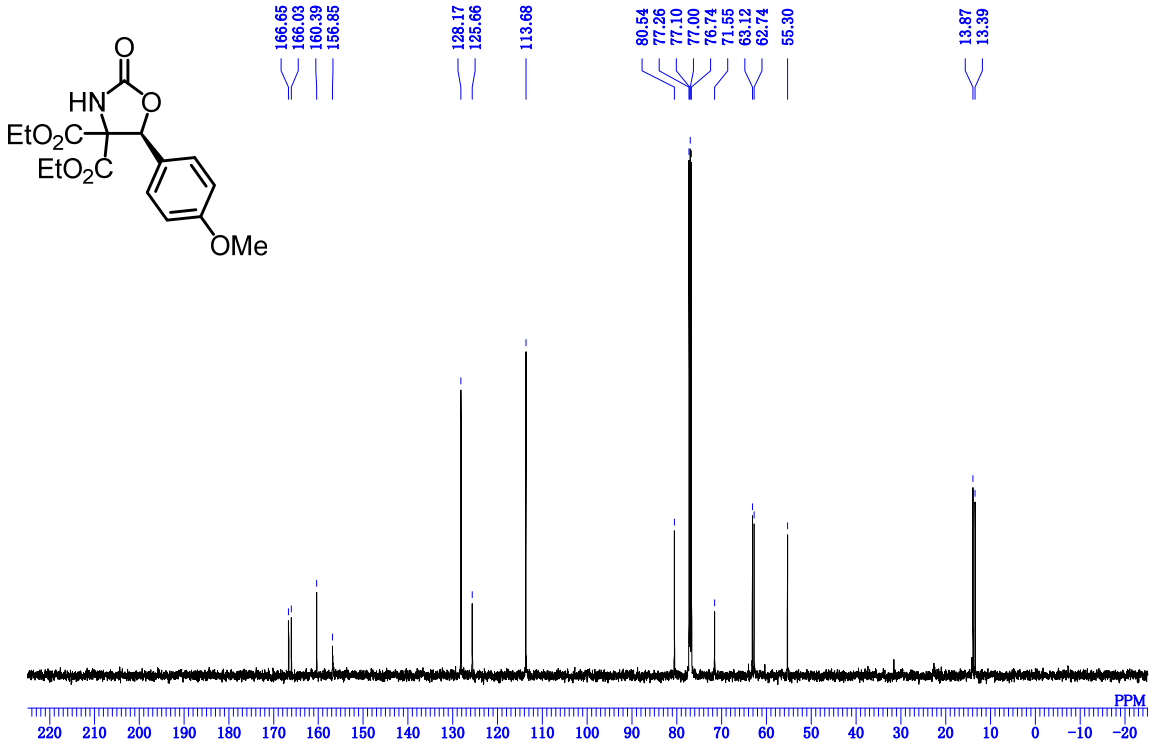
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **3e**.



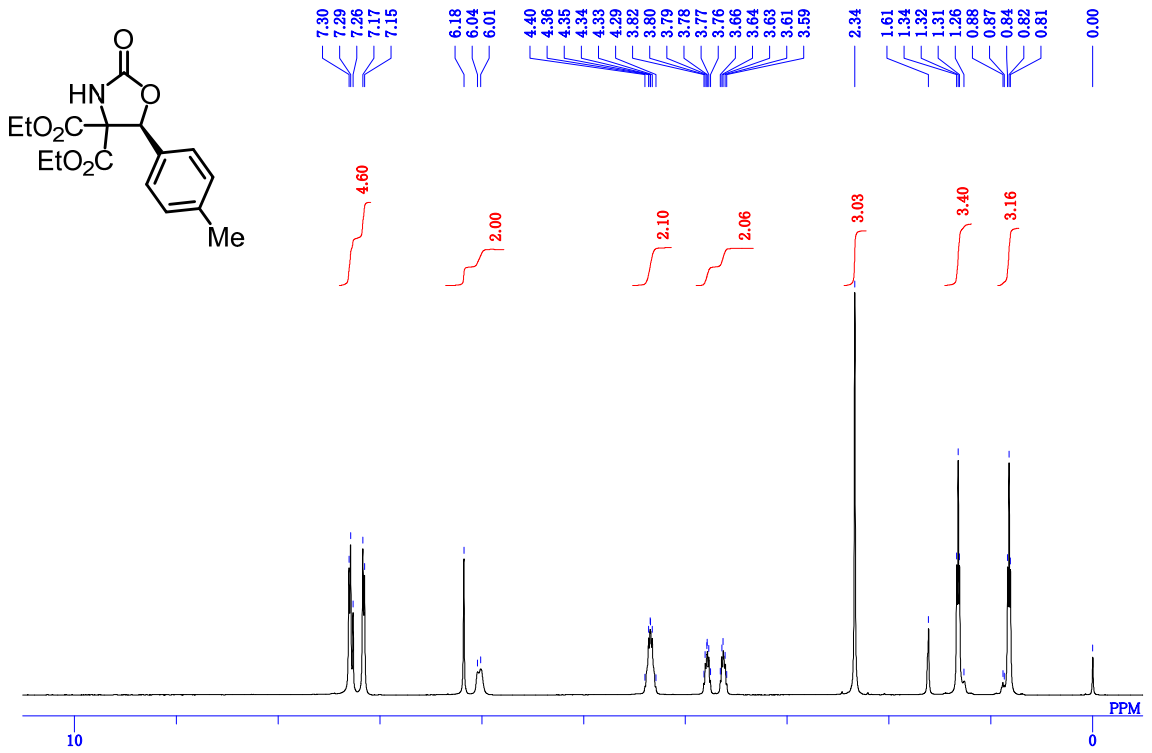


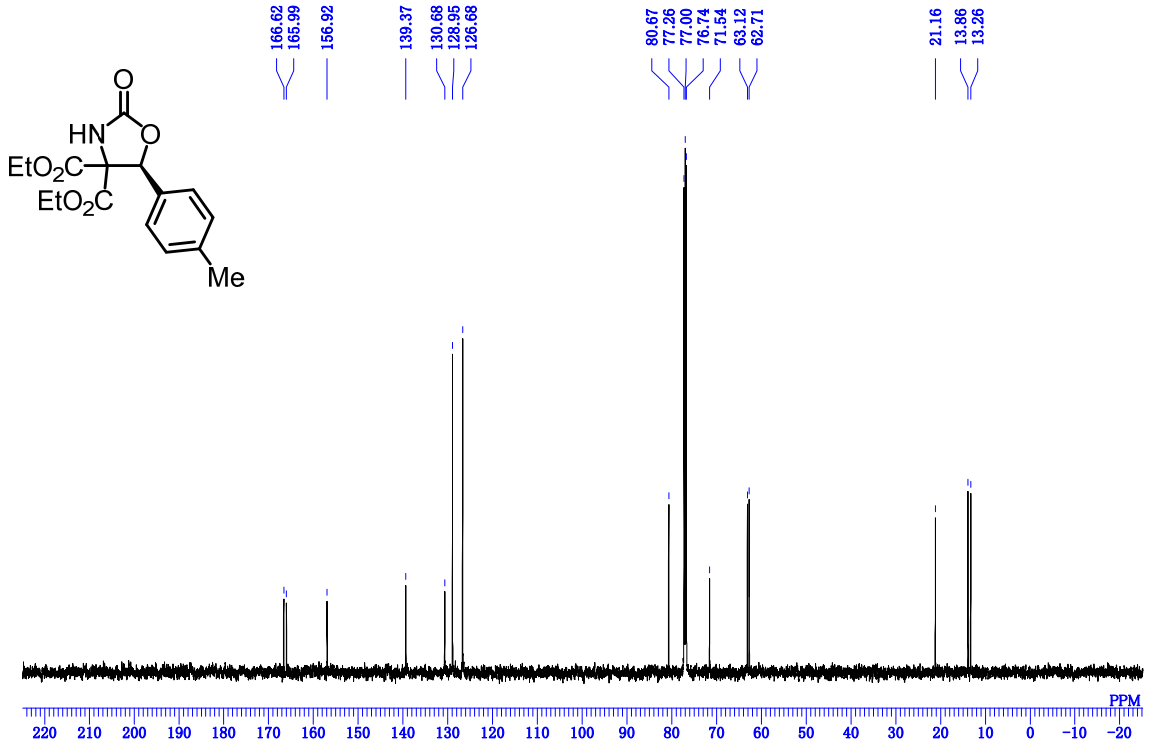
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **3f**.



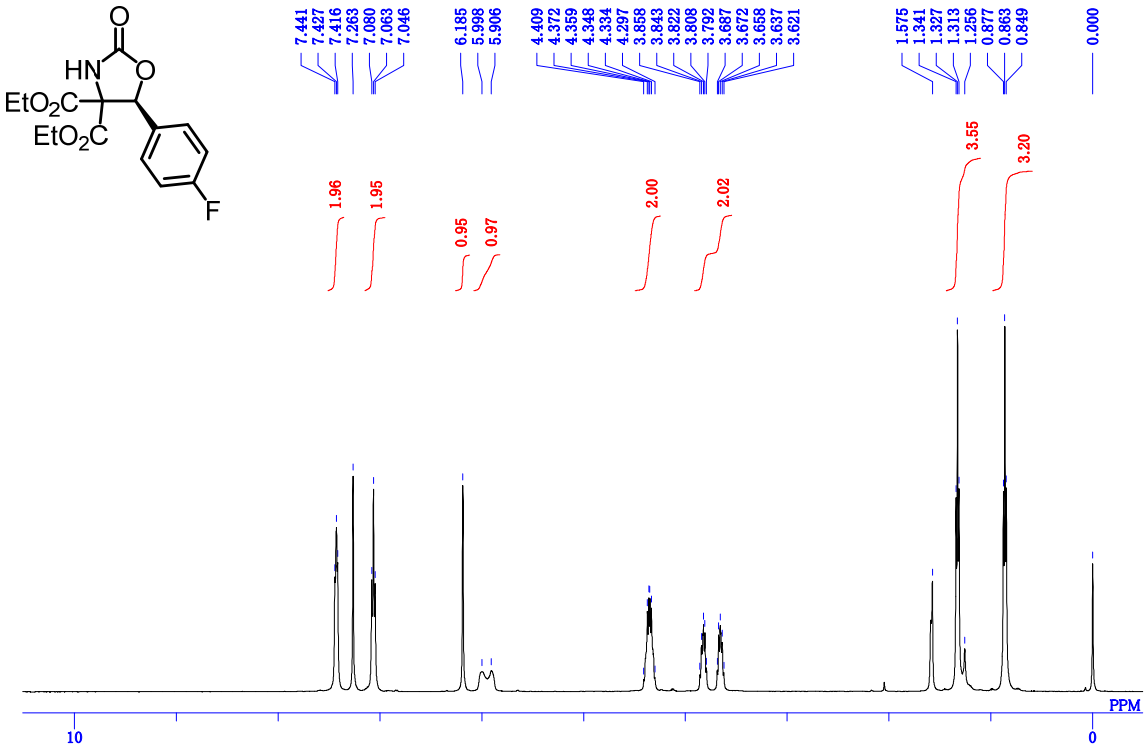


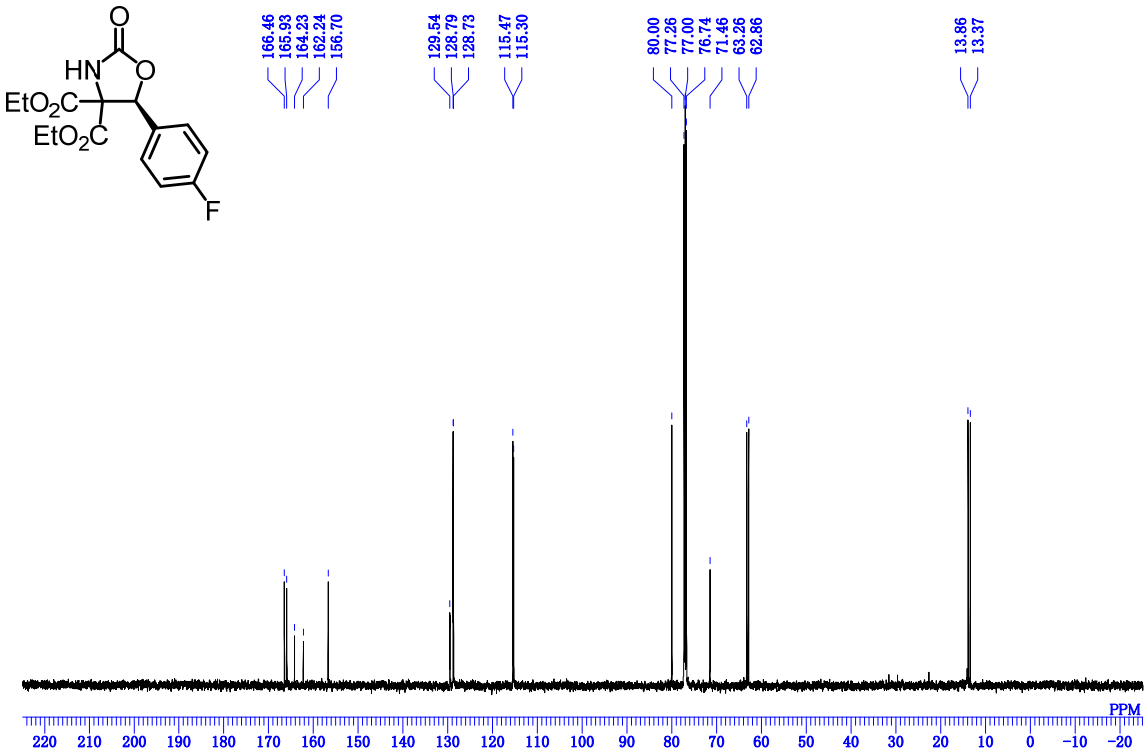
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **3g**.



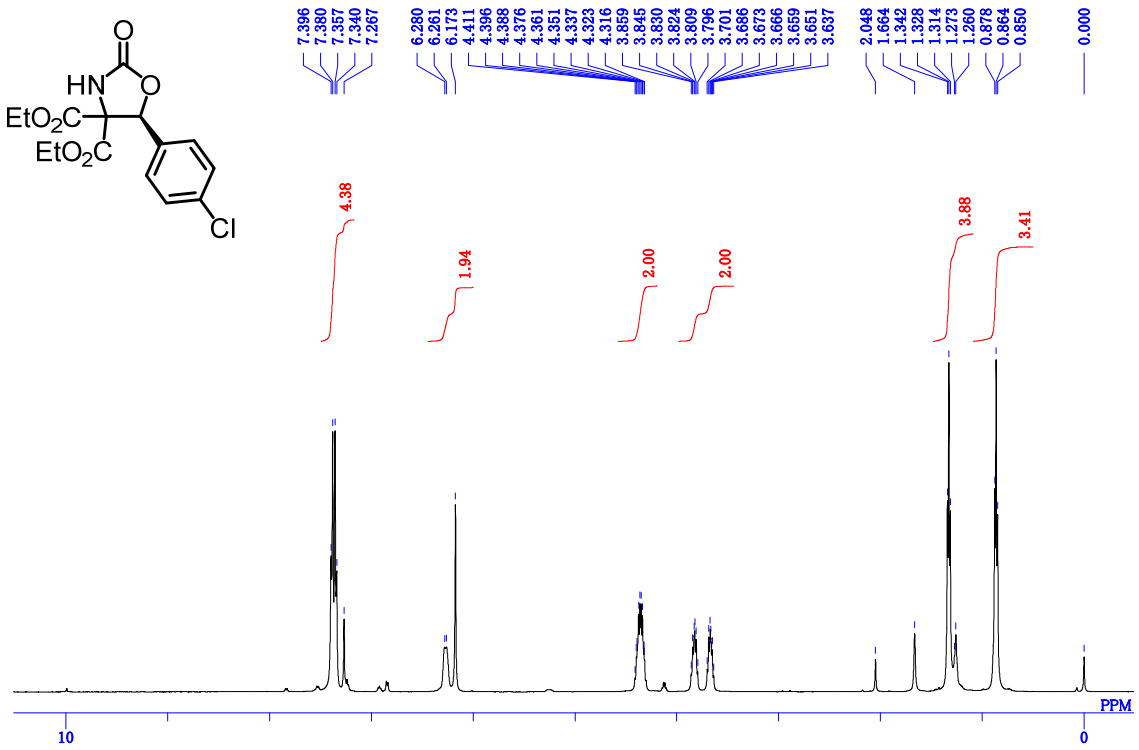


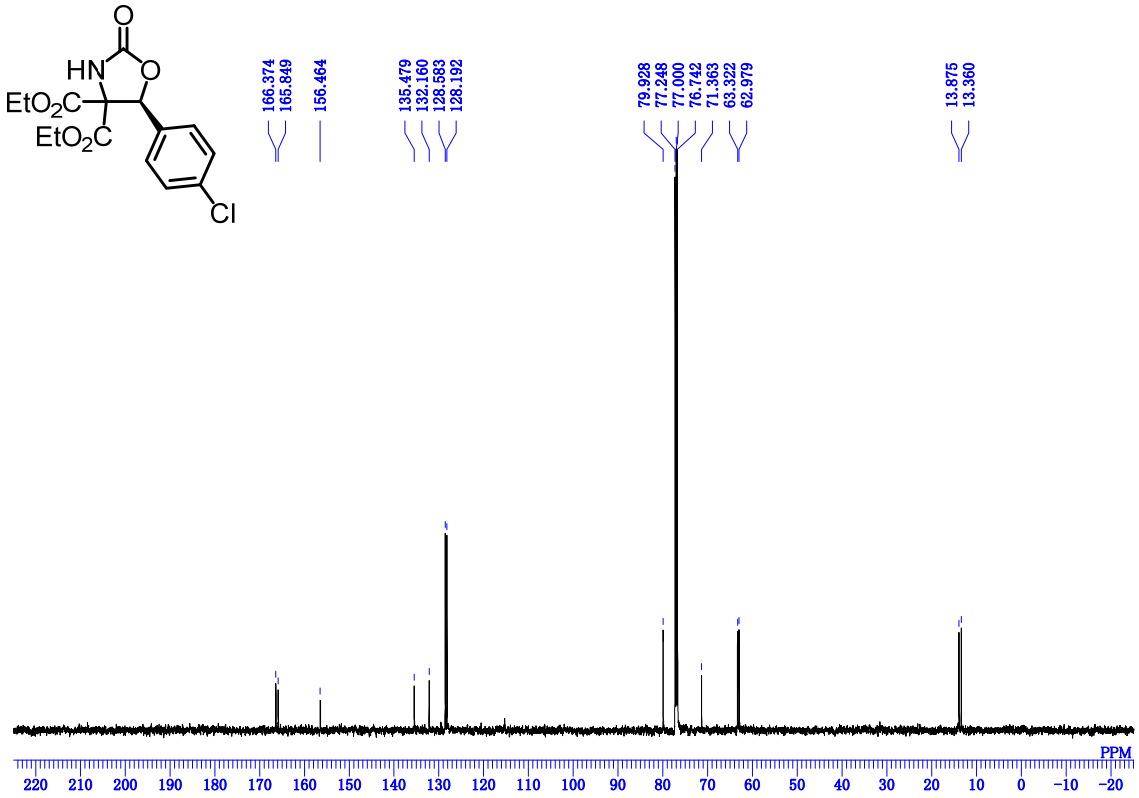
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **3h**.



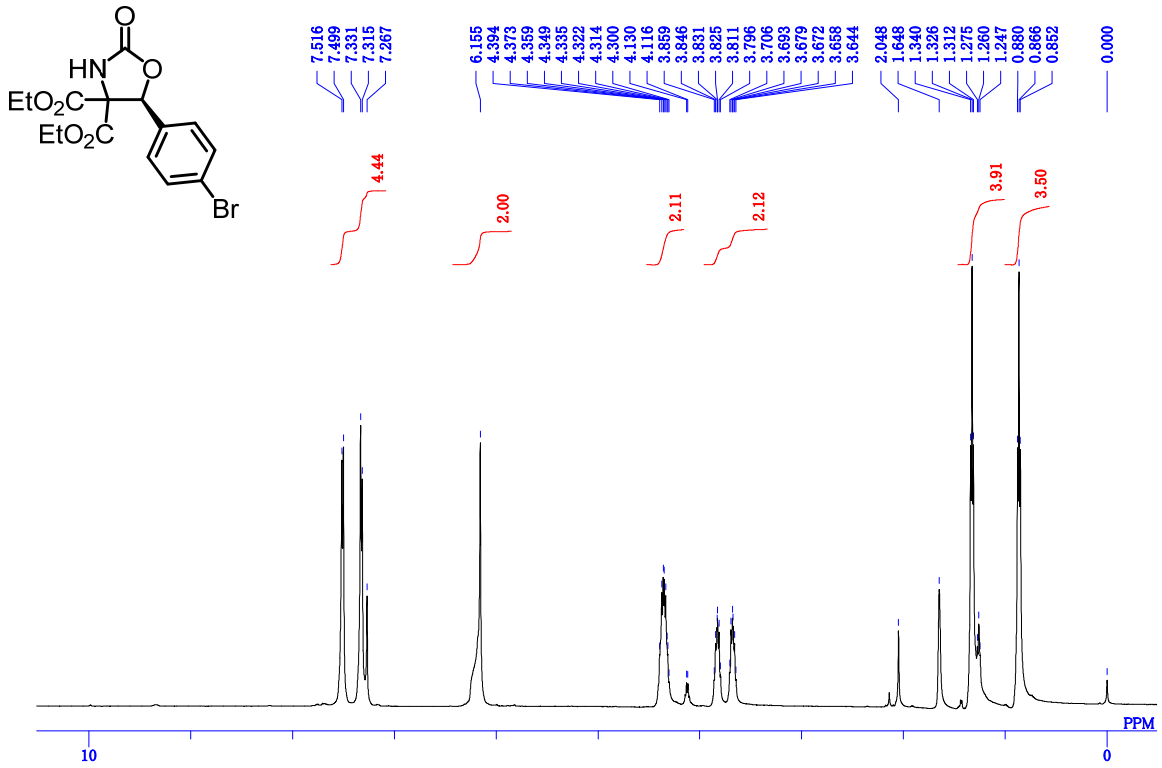


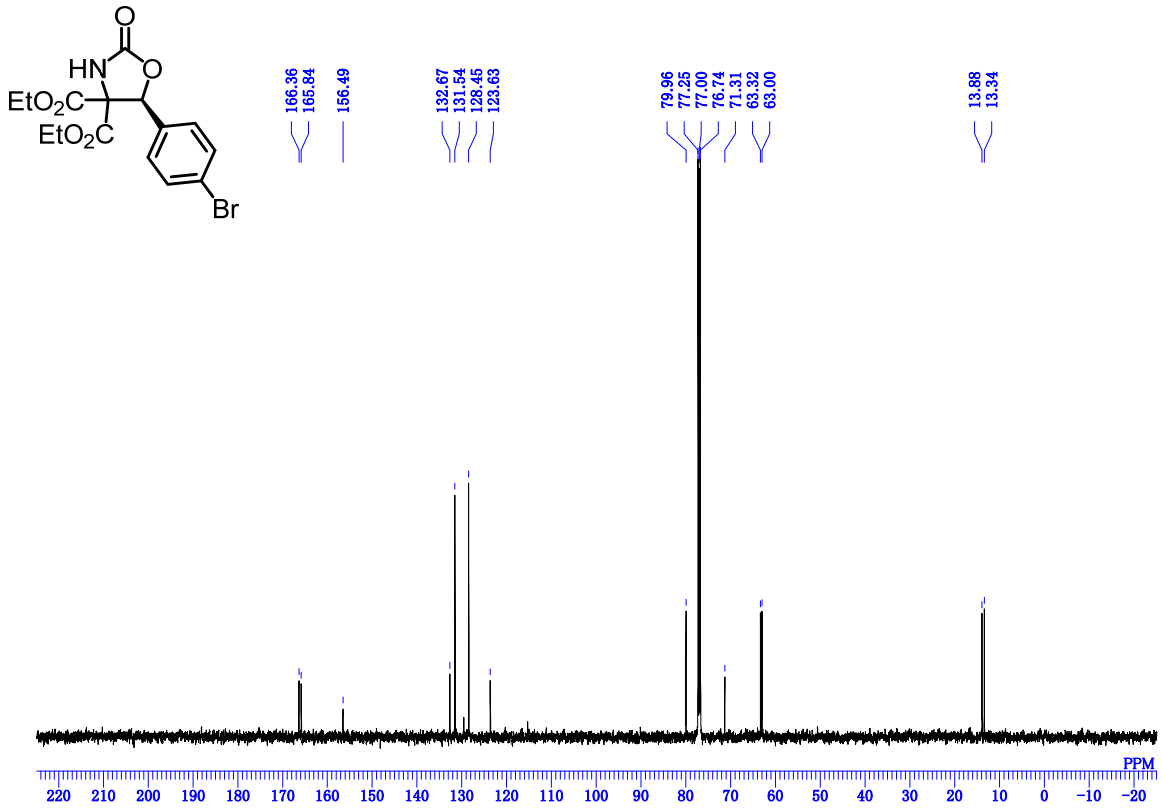
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **3i**.



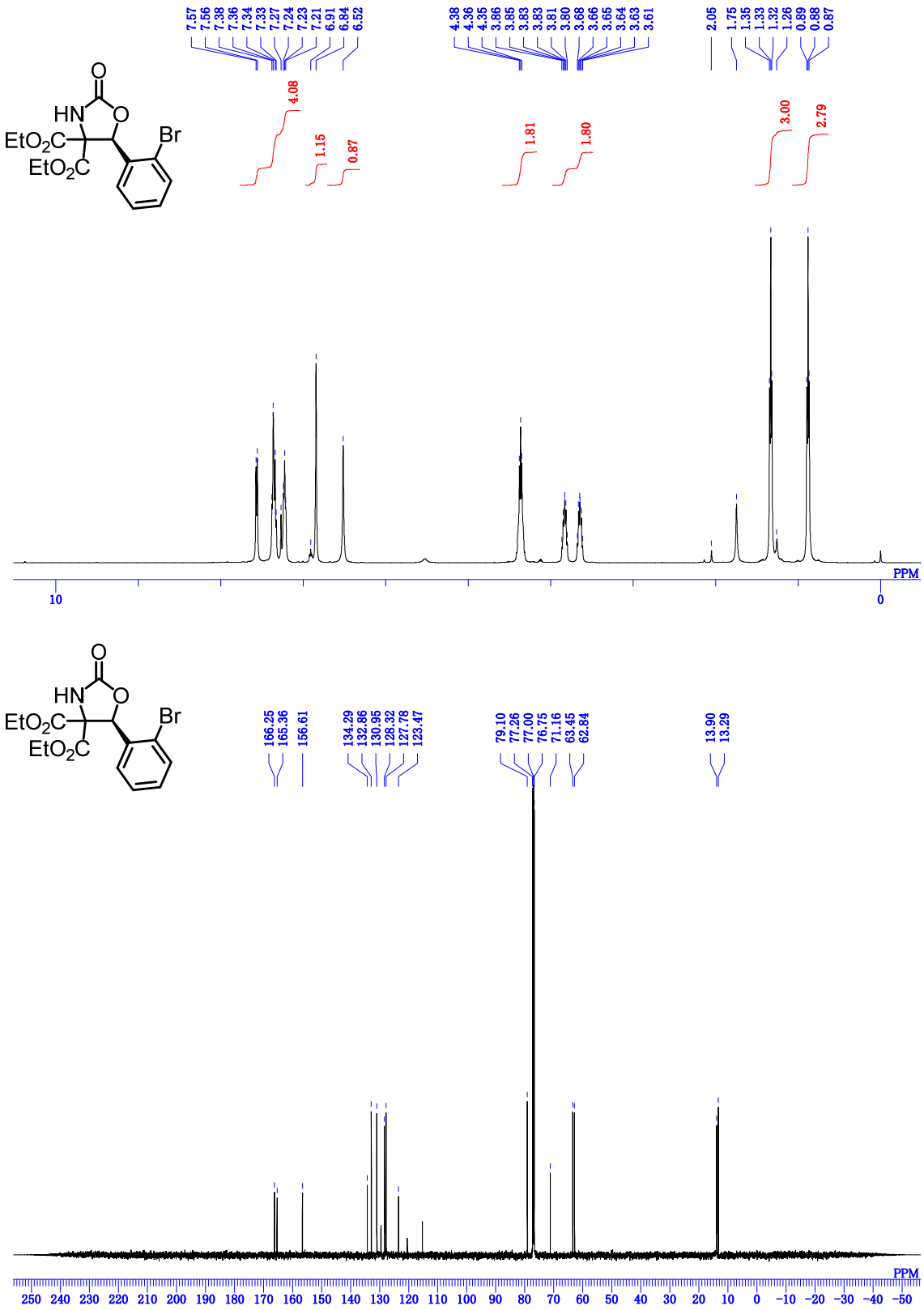


^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **3j**.

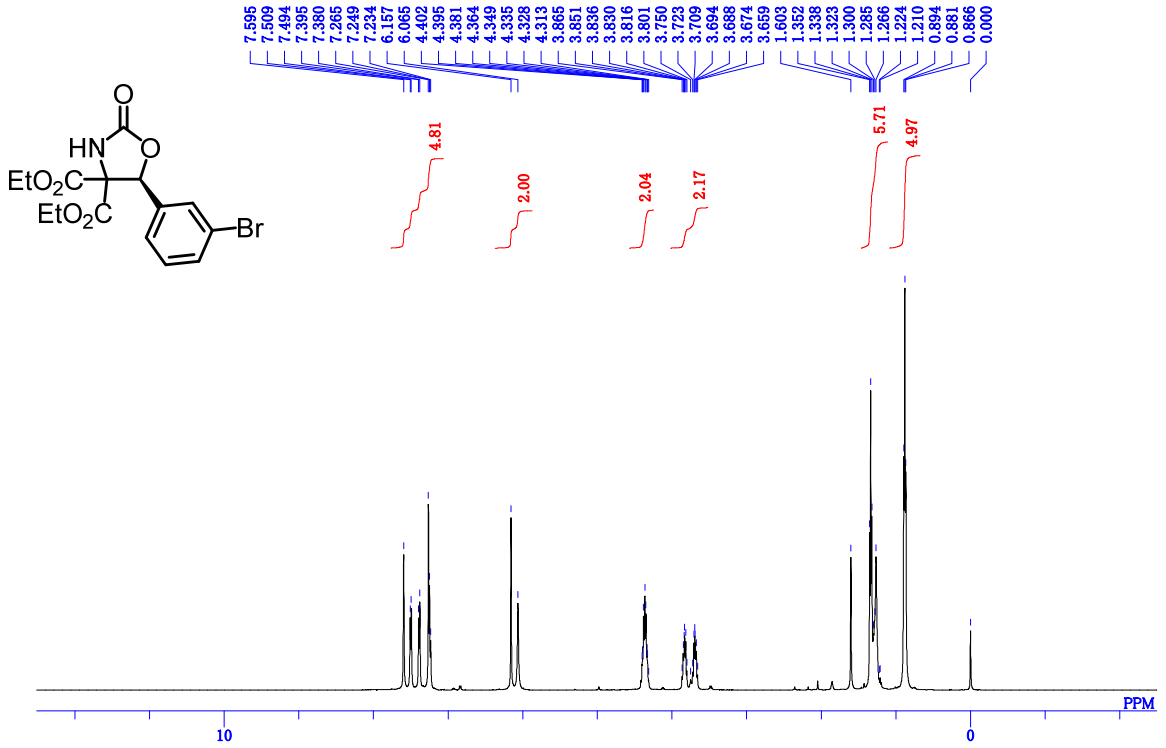


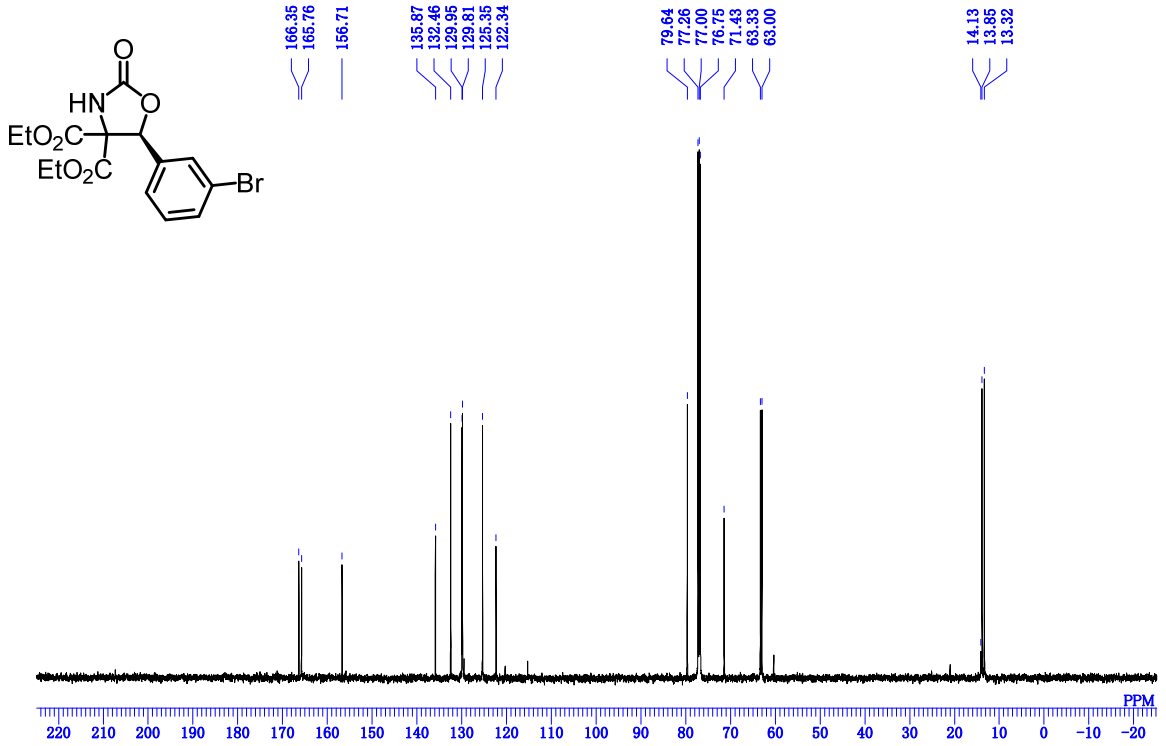


^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **3k**.

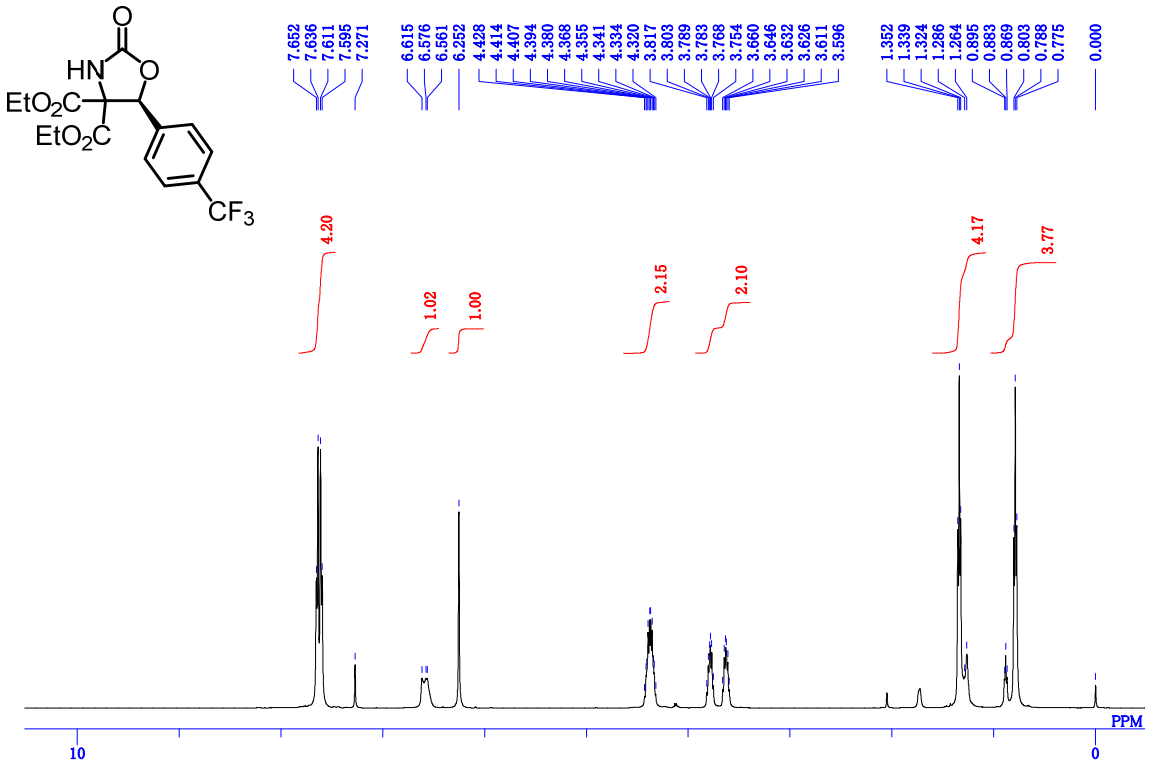


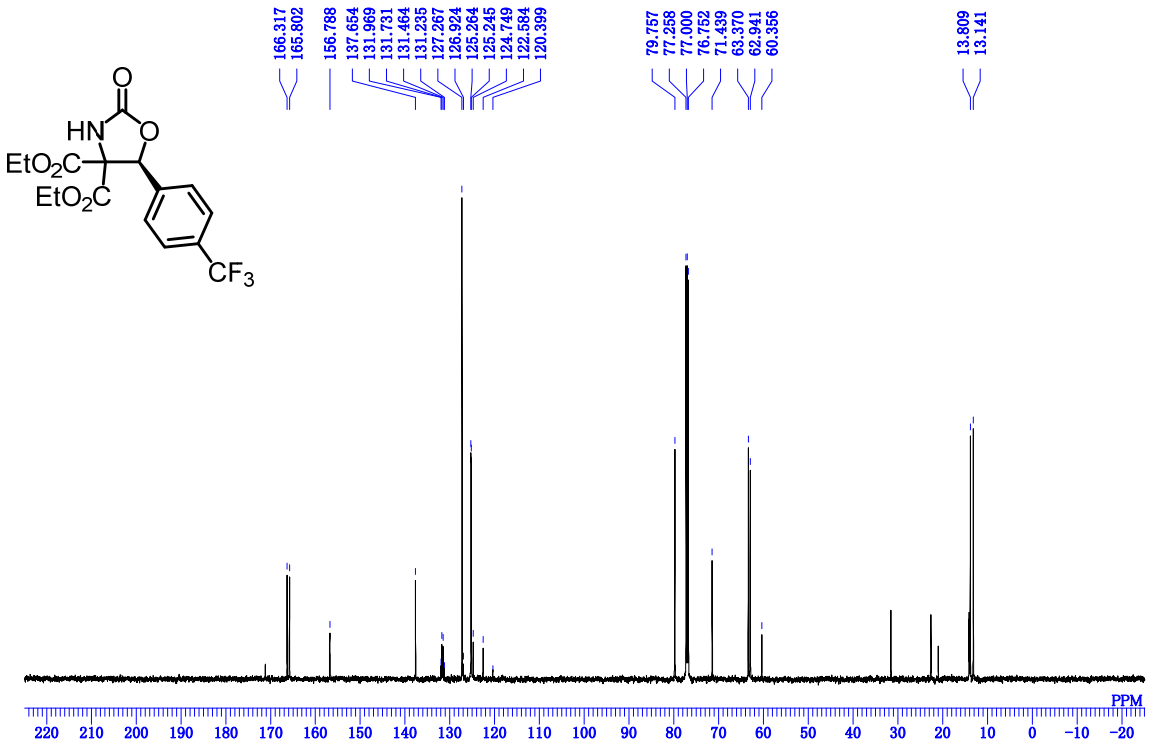
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **3l**.



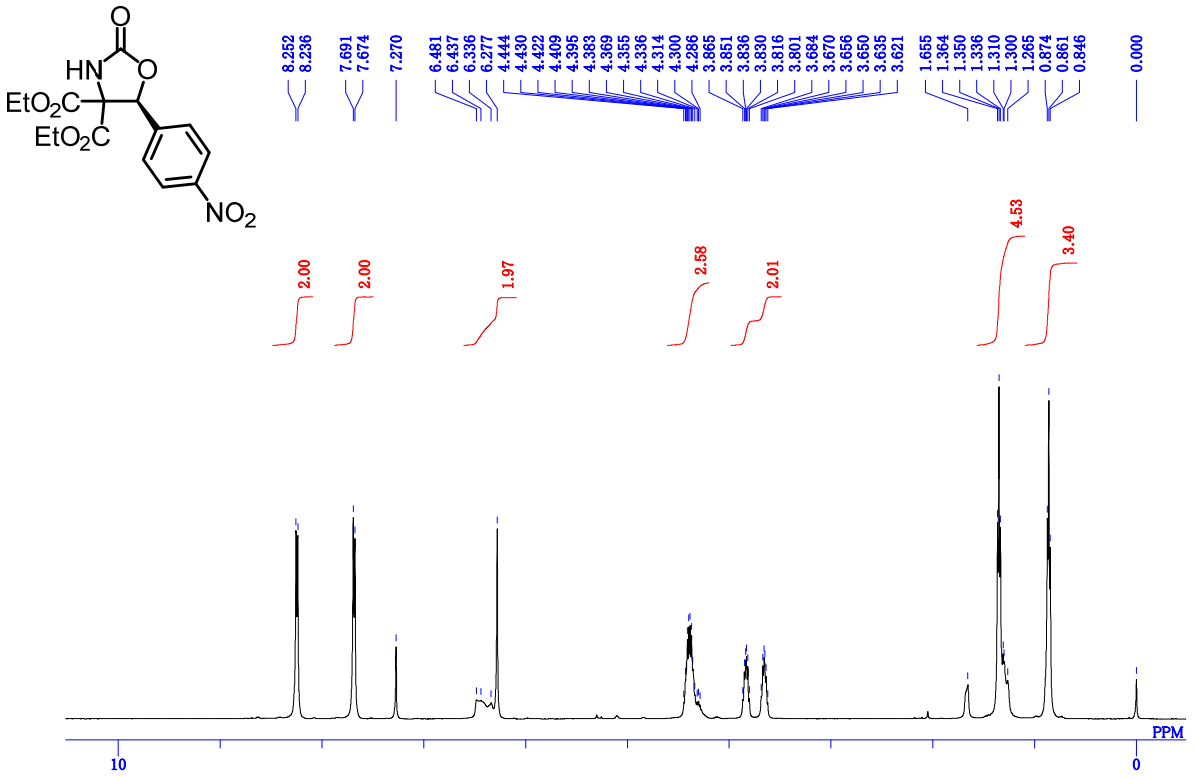


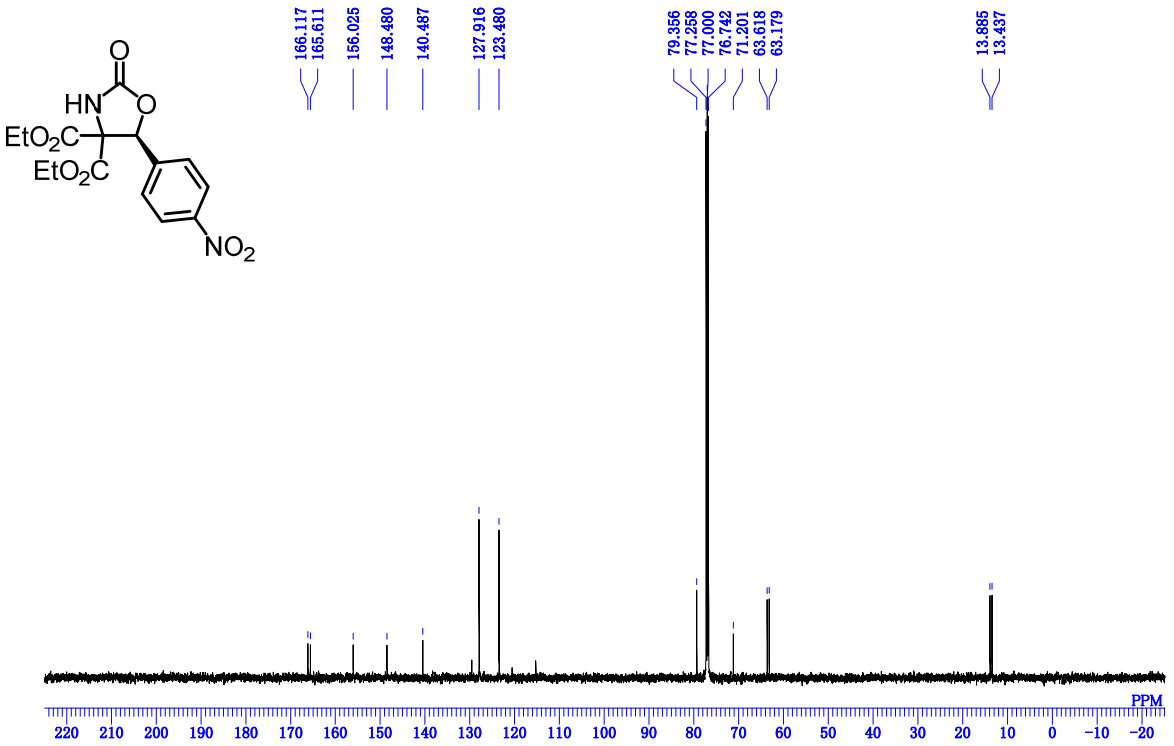
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **3m**.



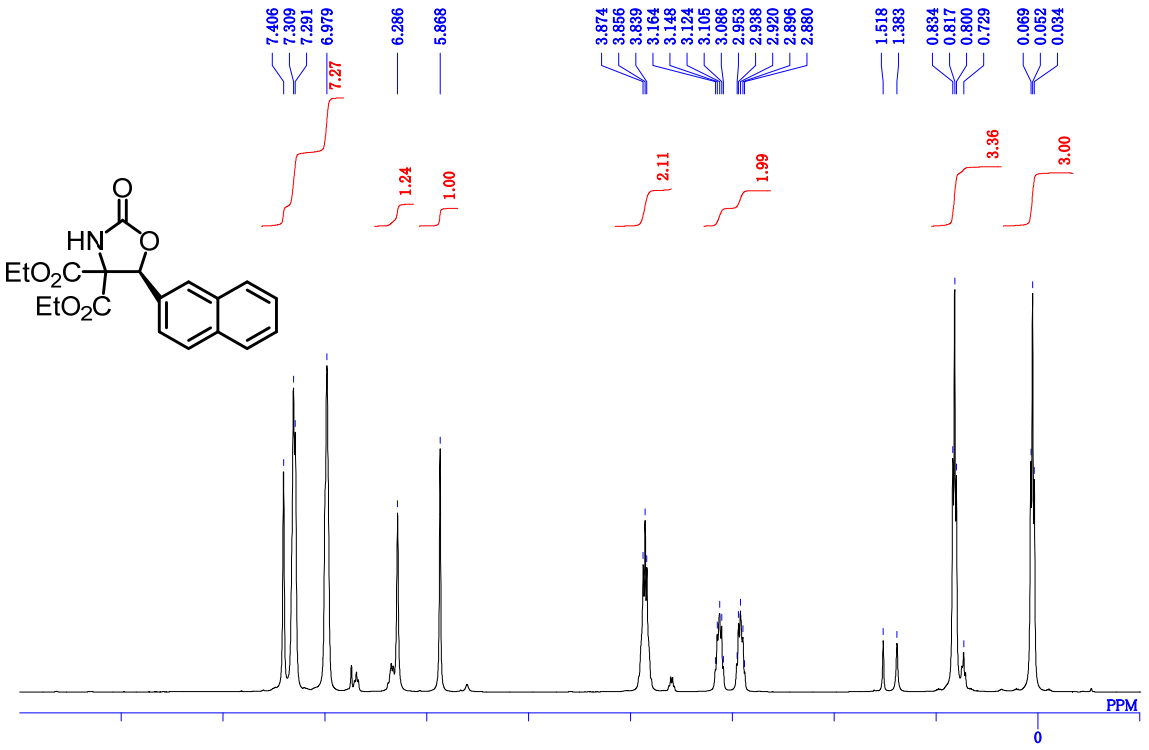


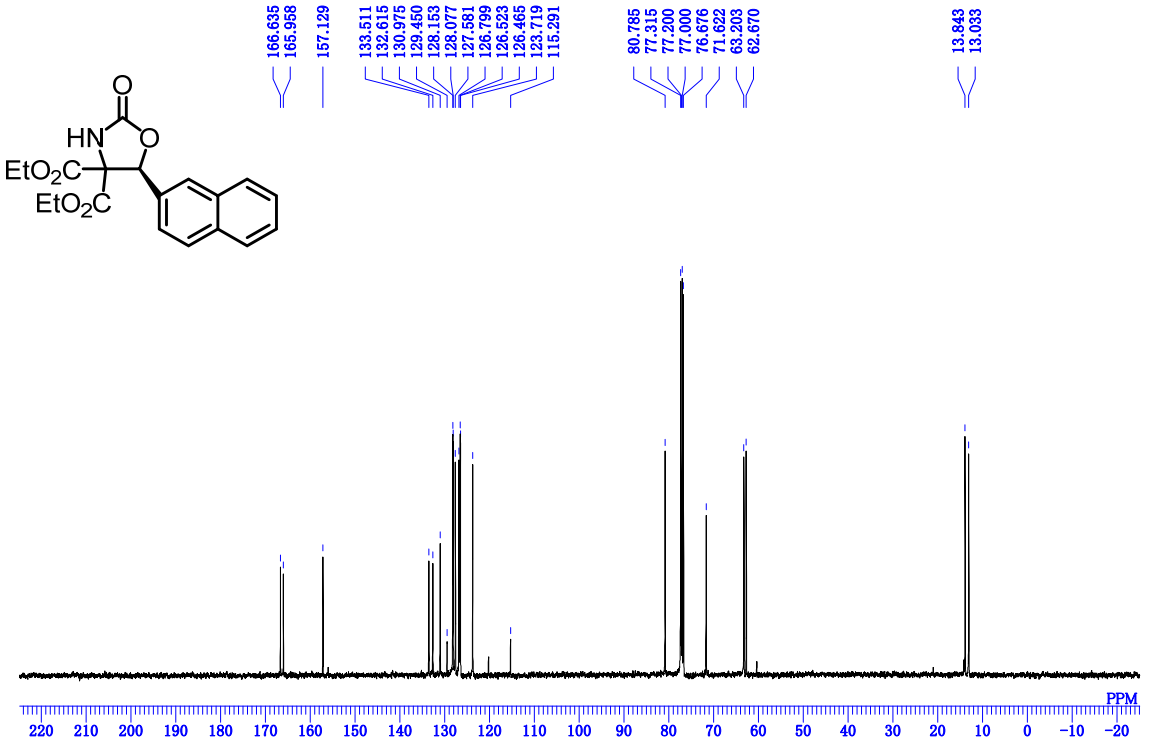
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **3n**.



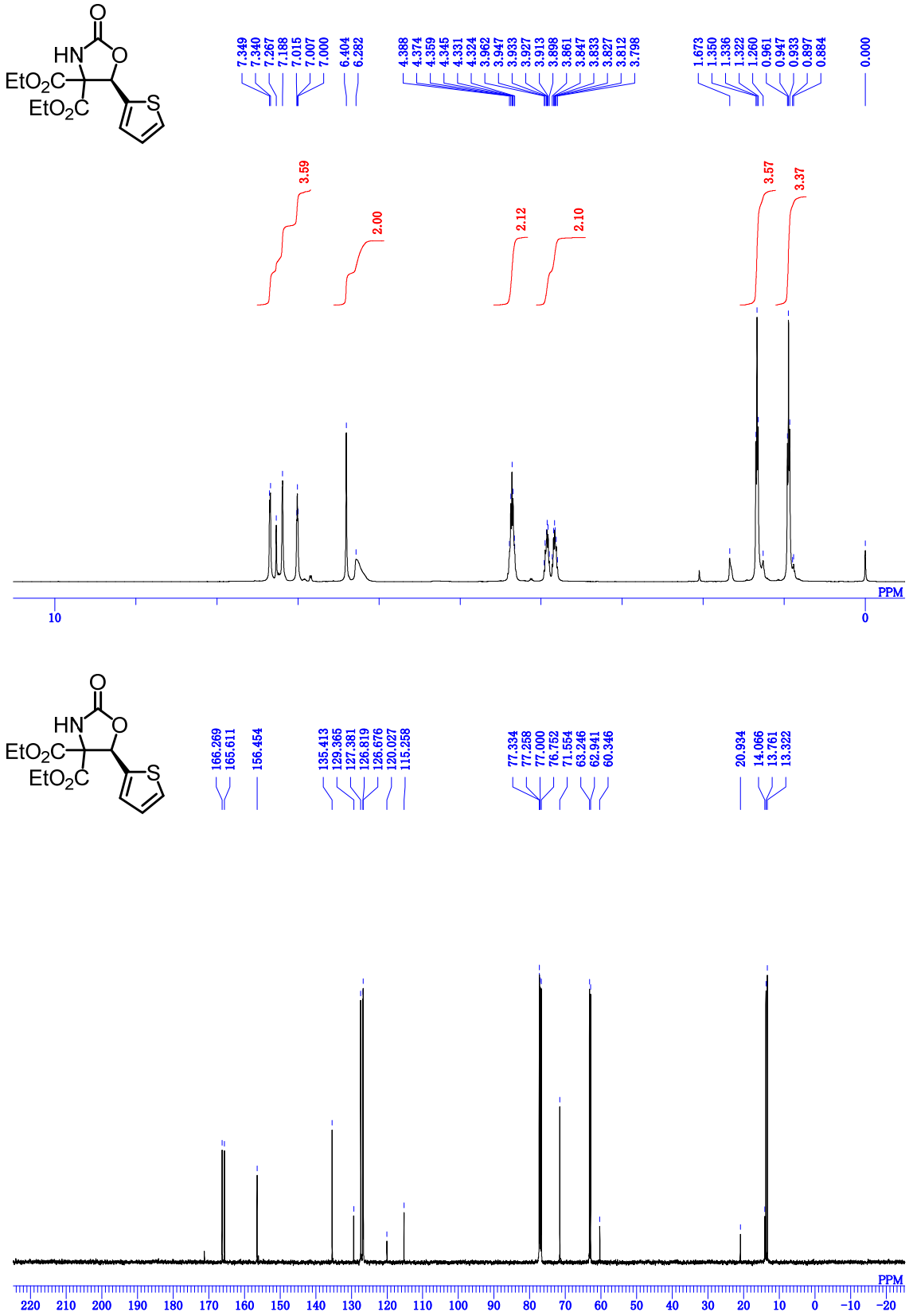


^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **3o**.

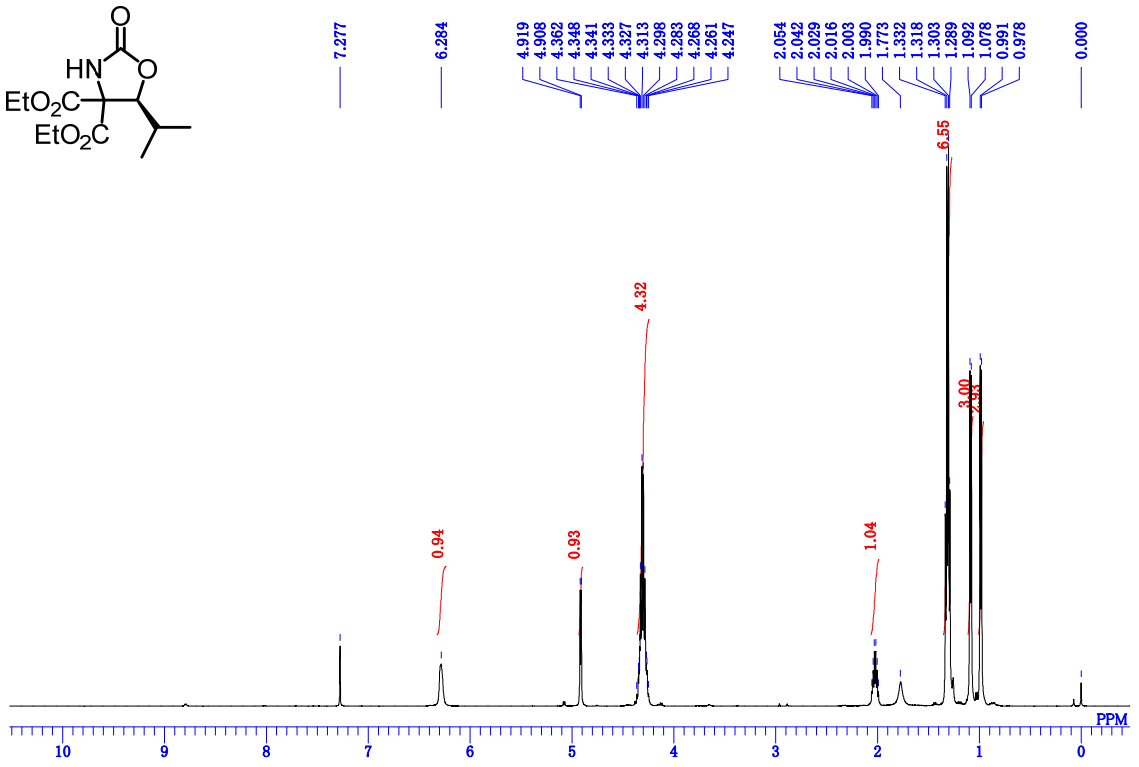


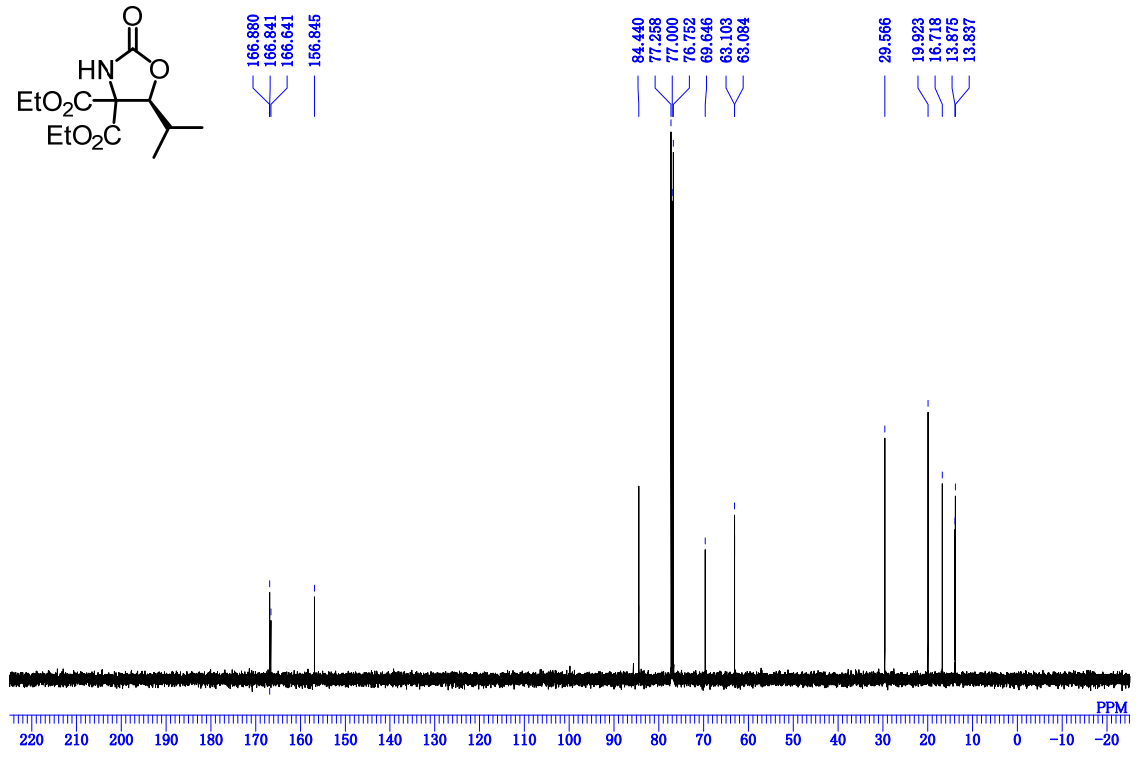


^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **3p**.

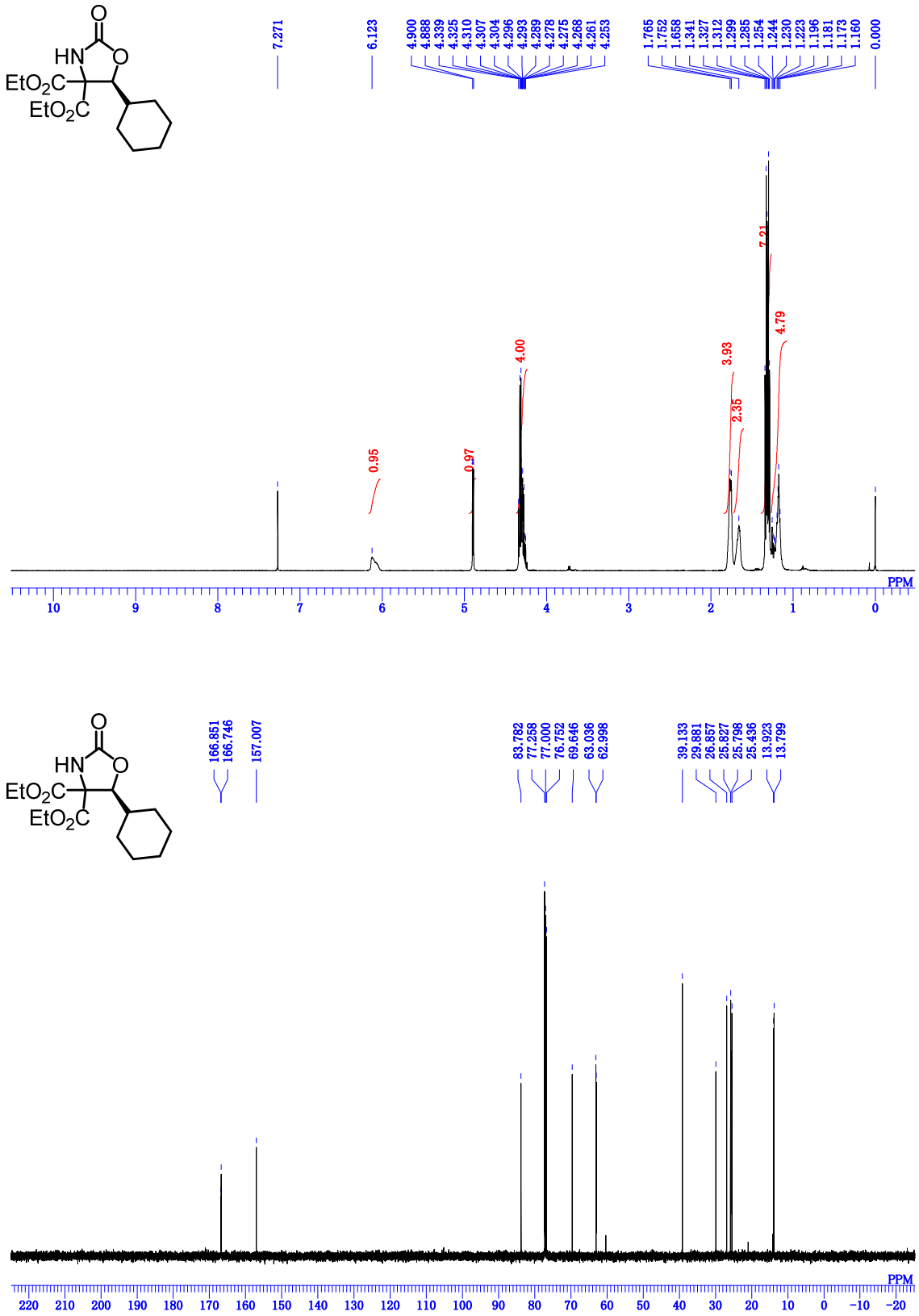


^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **3q**.

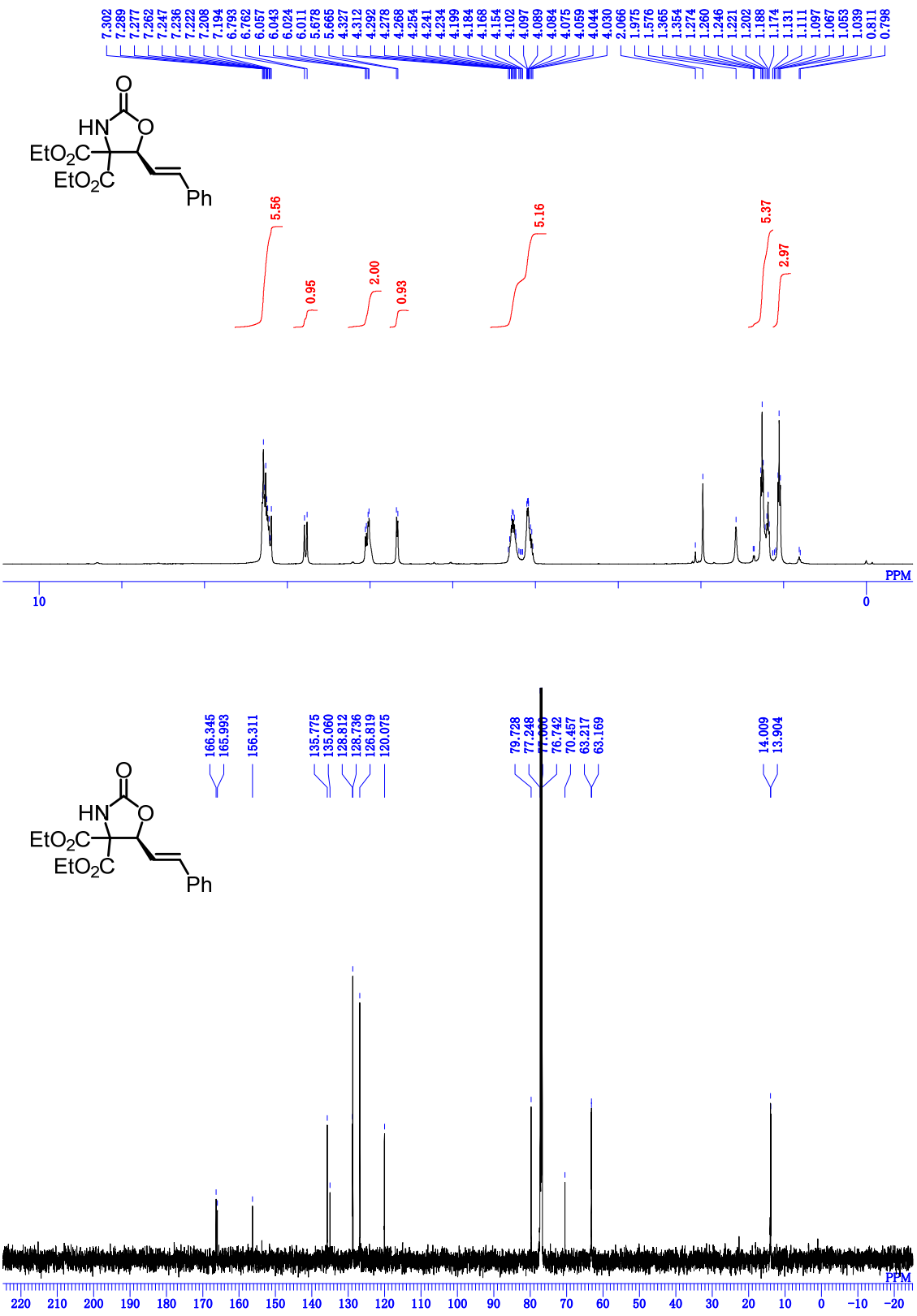




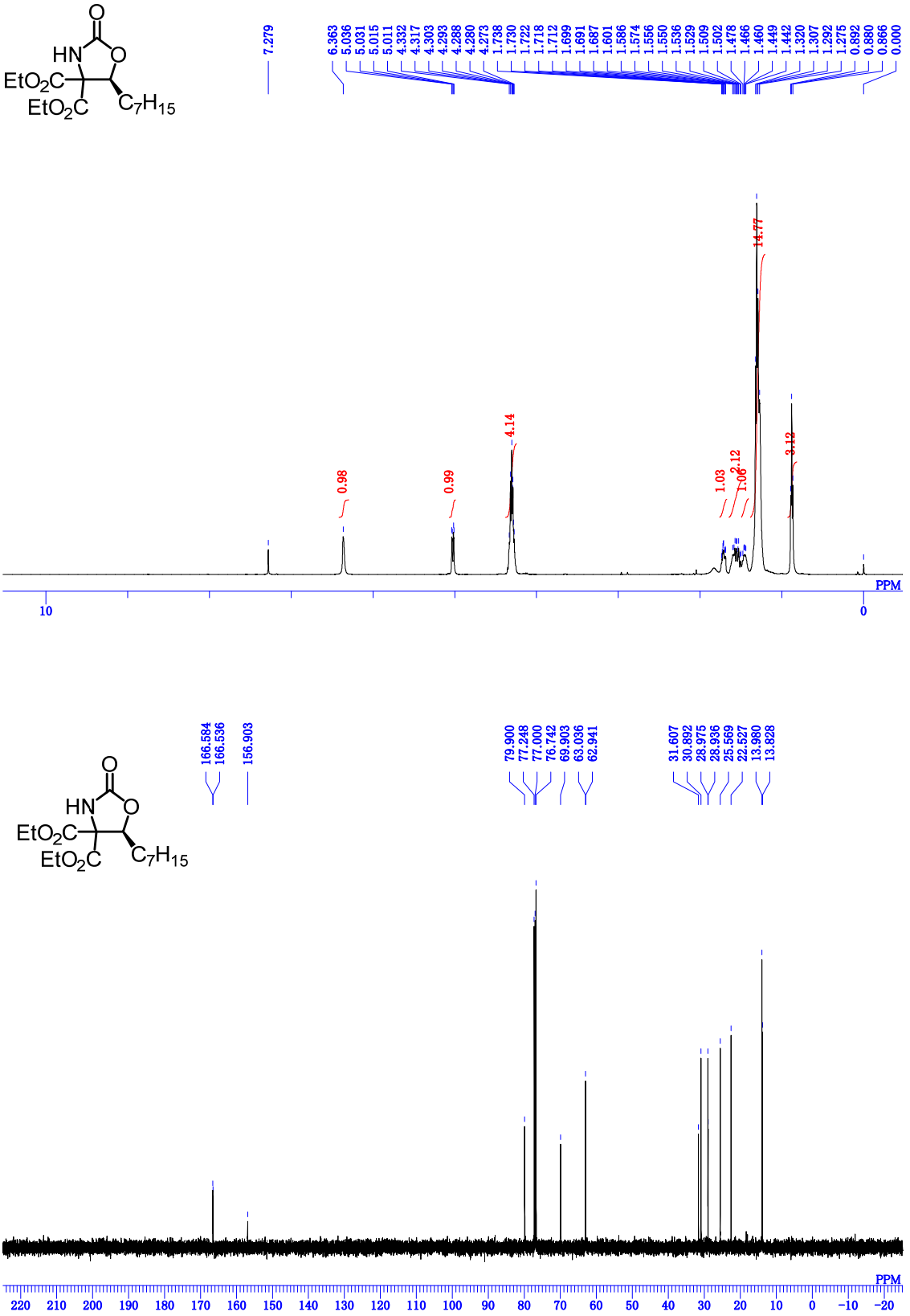
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **3r**.



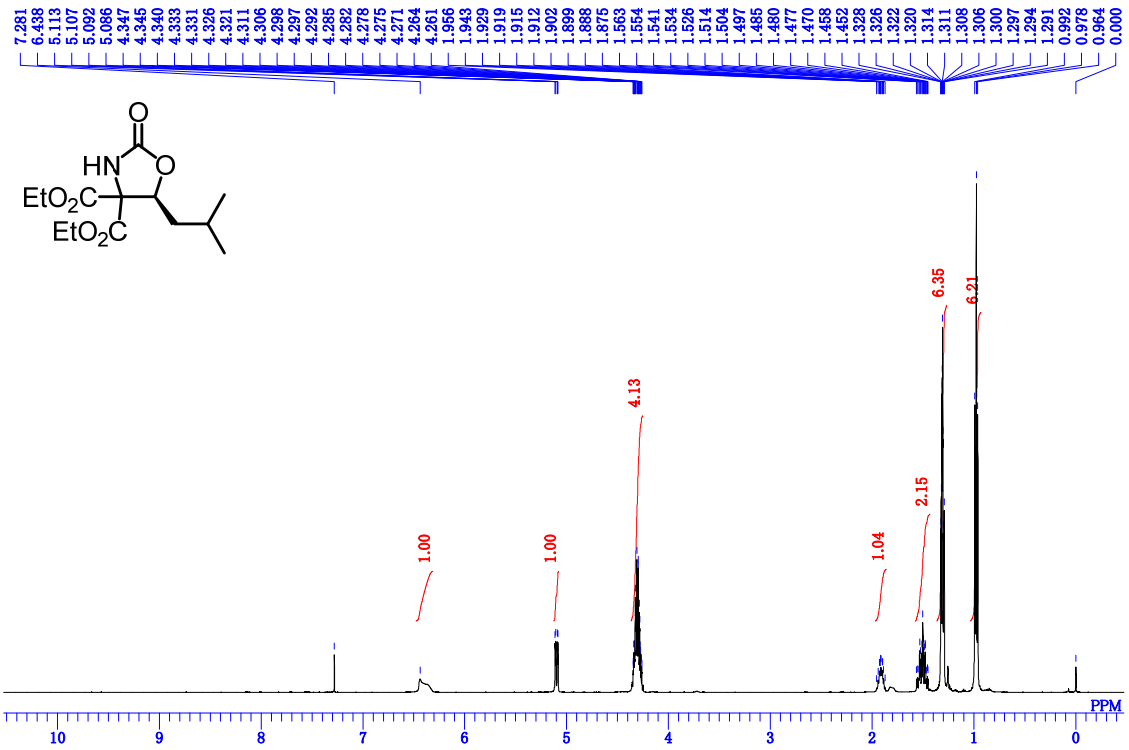
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **3s**.

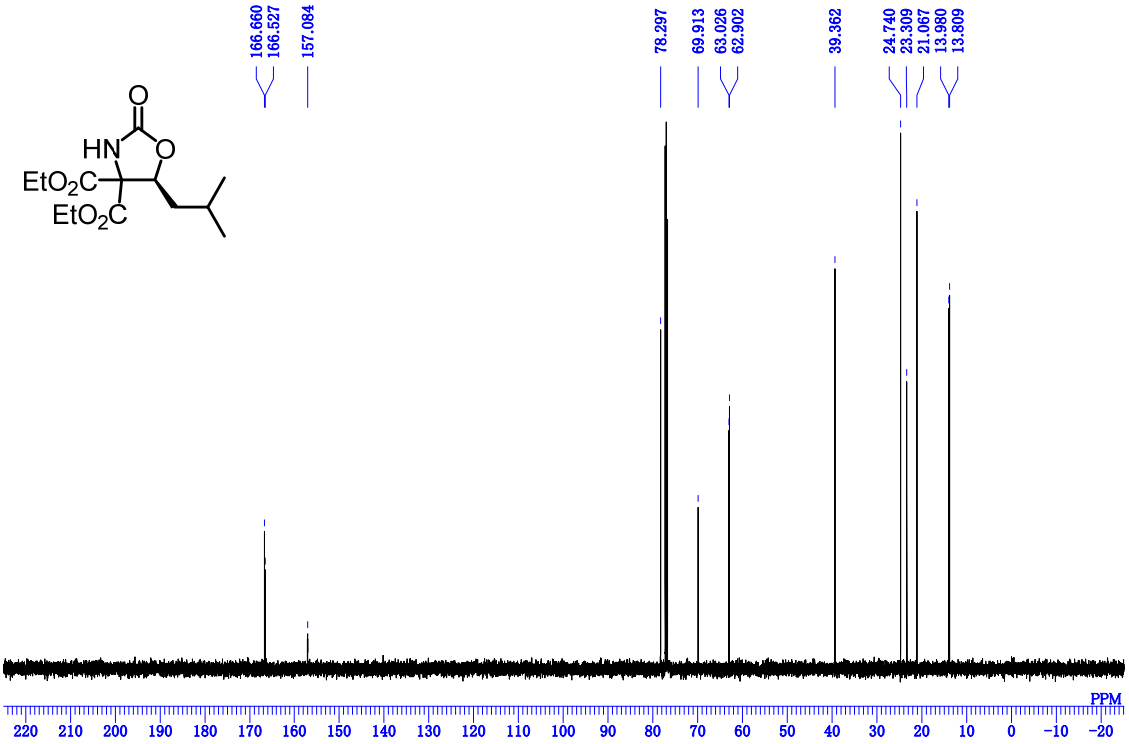


^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **3t**.

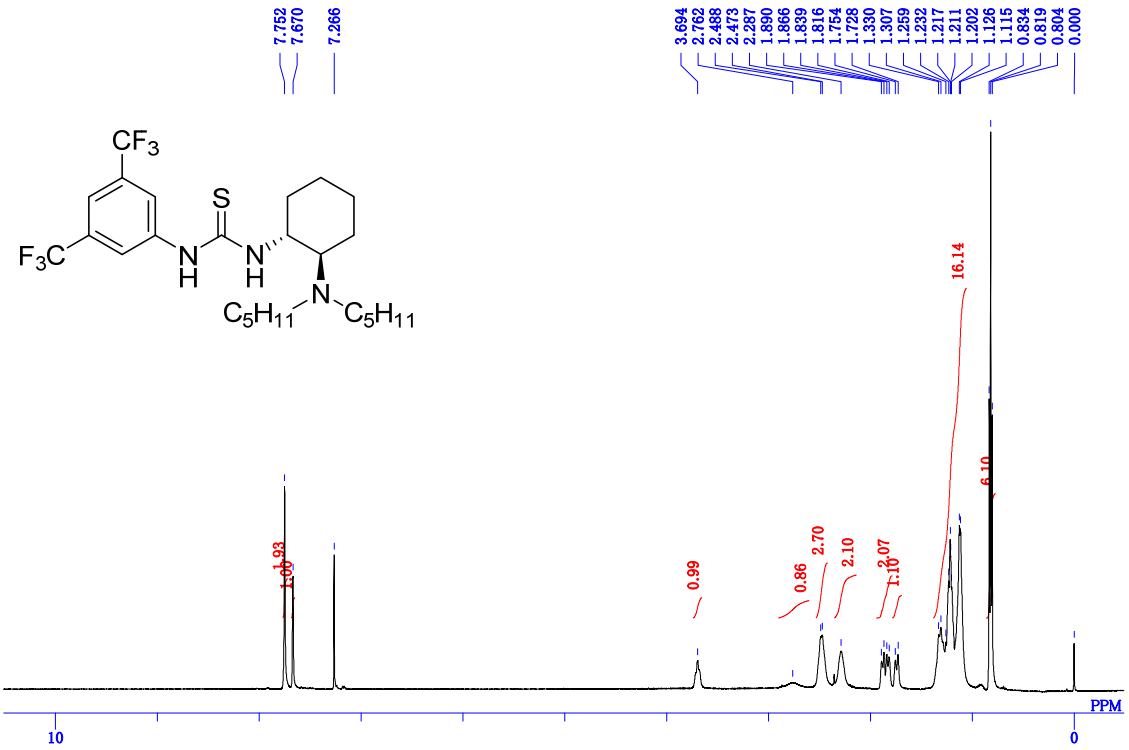


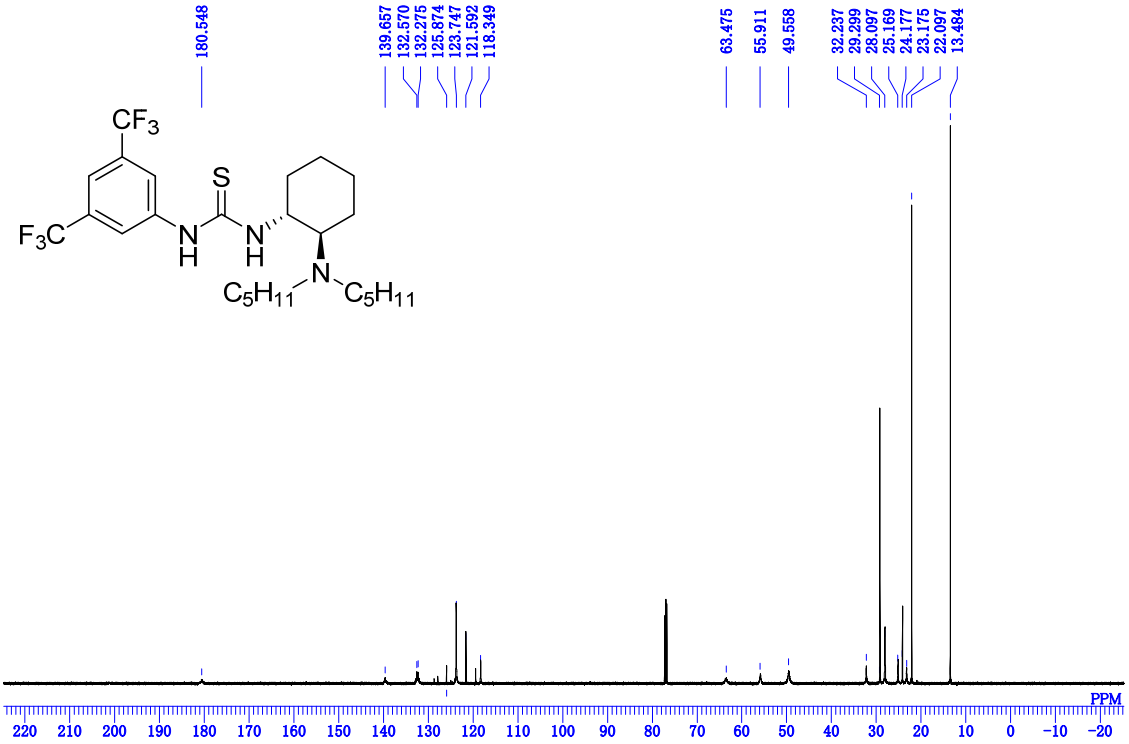
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **3u**



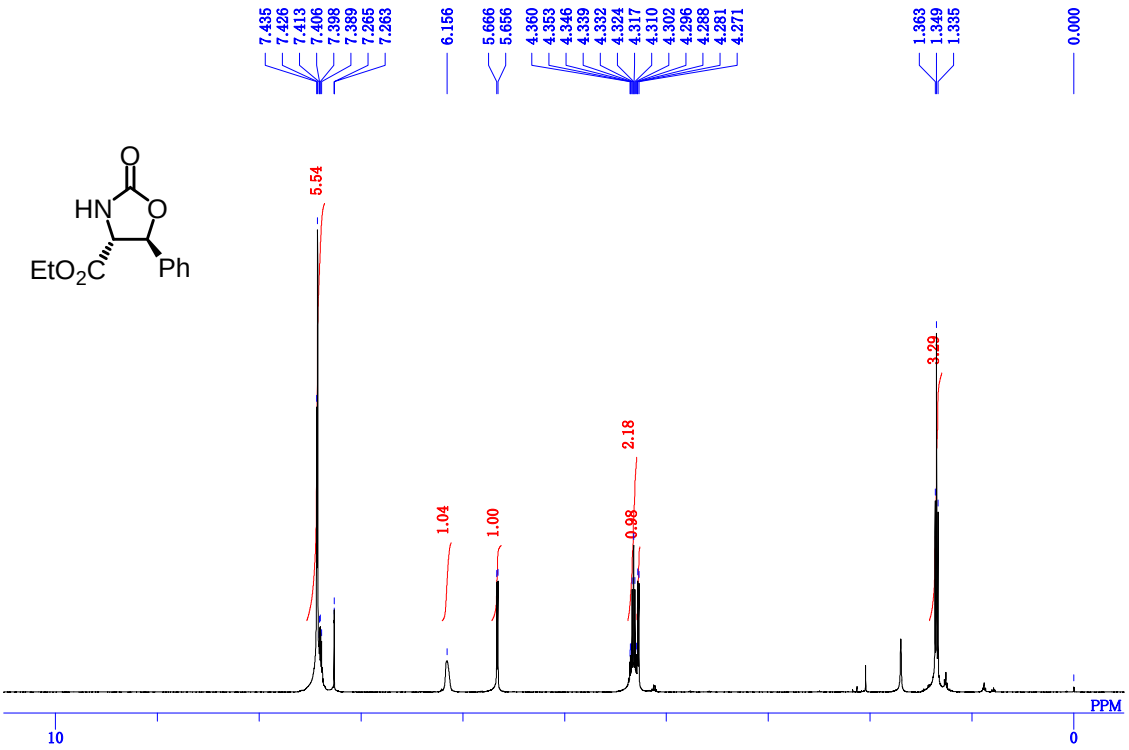


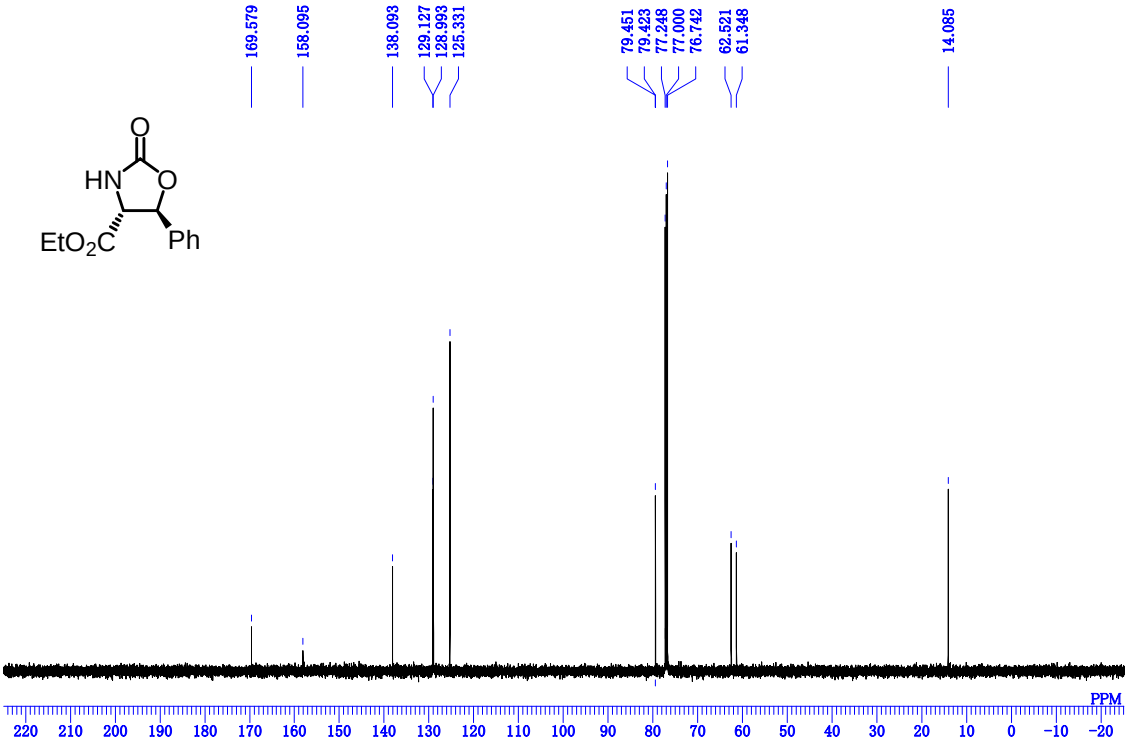
^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **4b.**



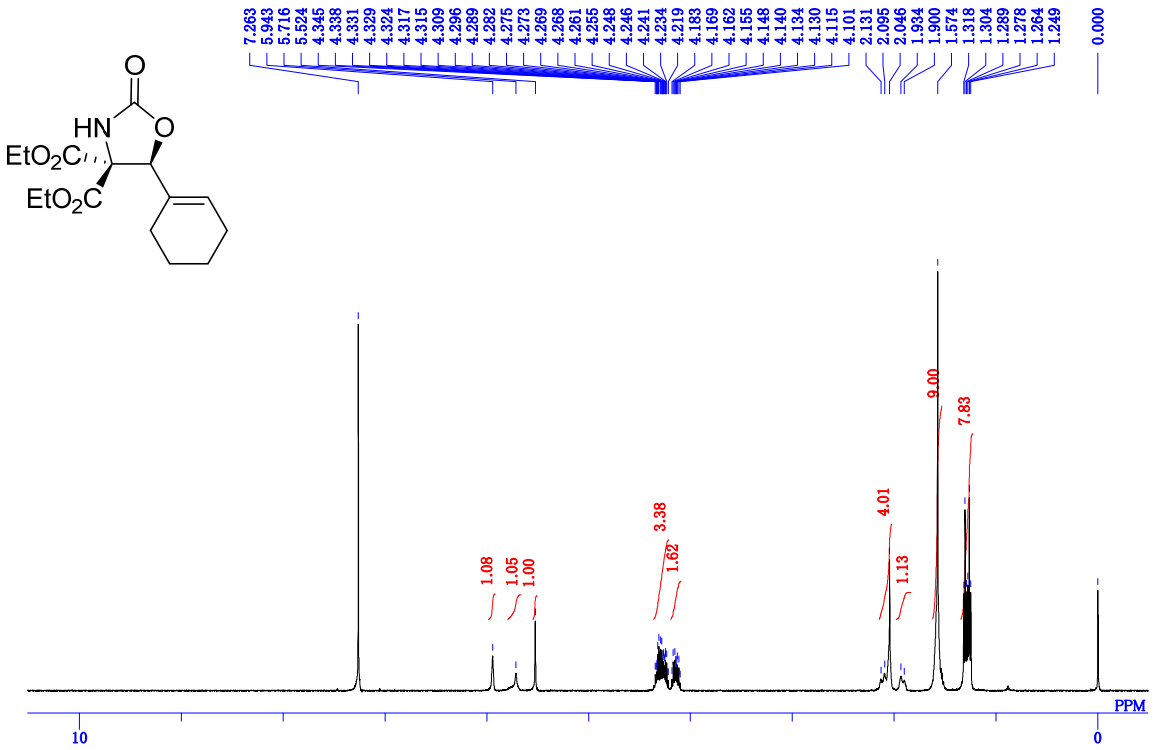


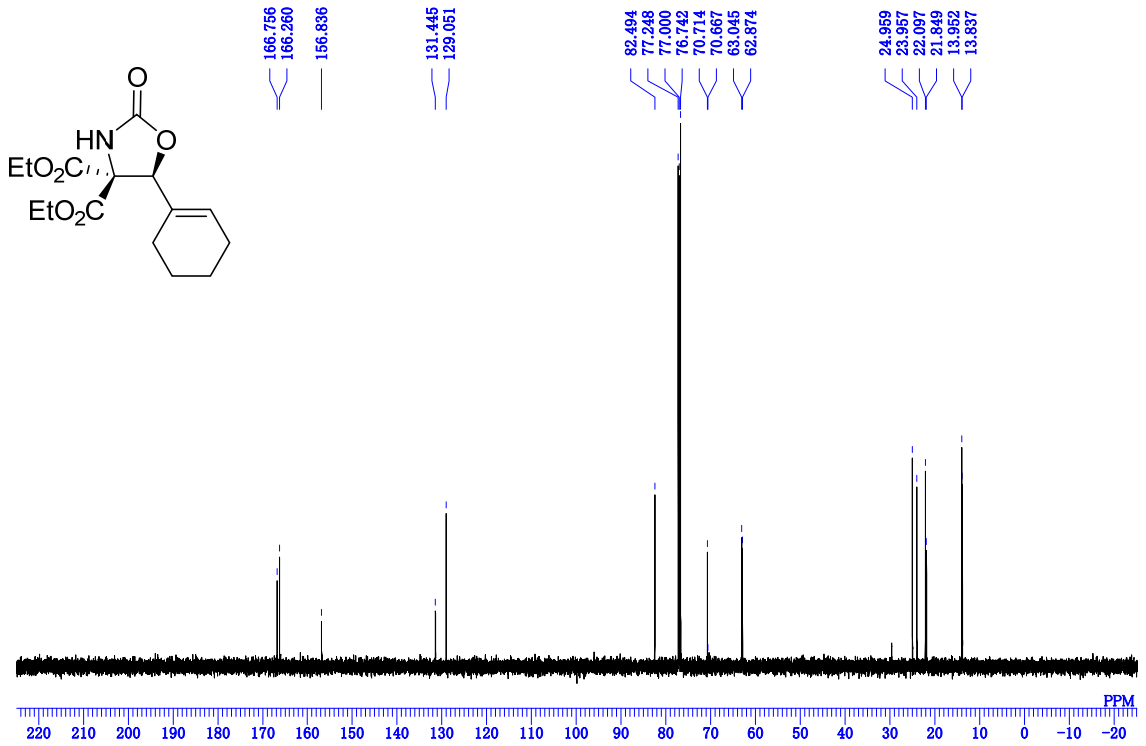
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **5**



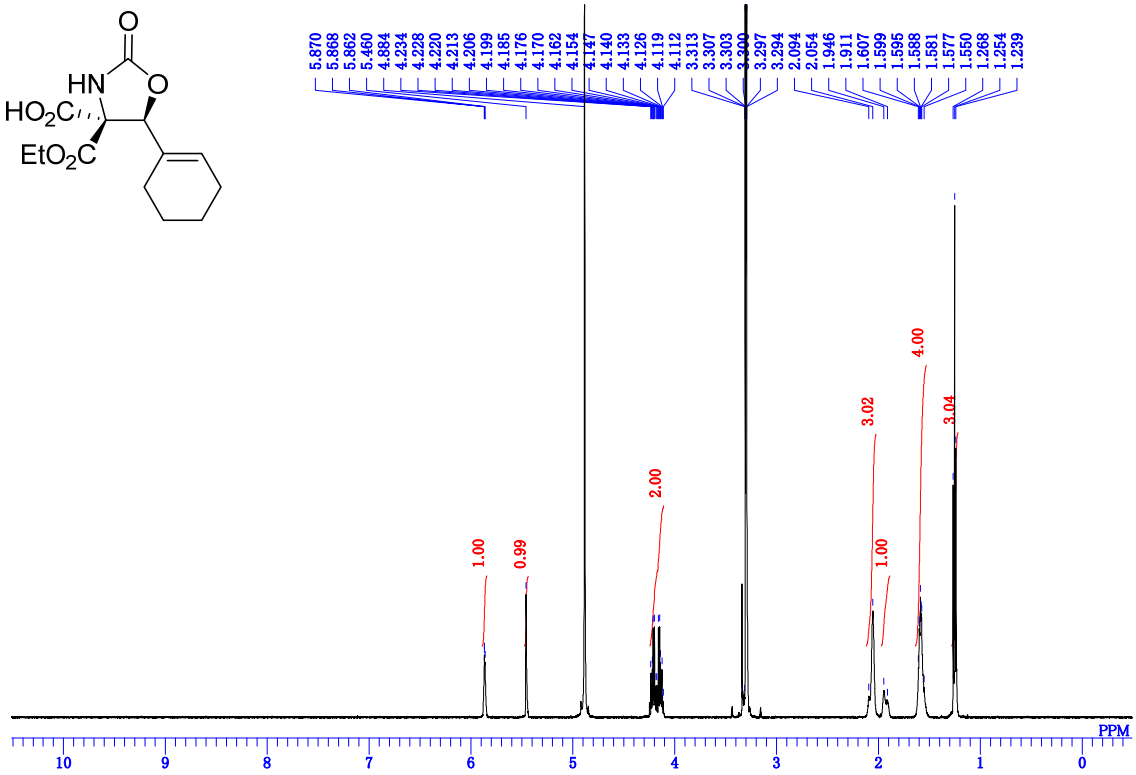


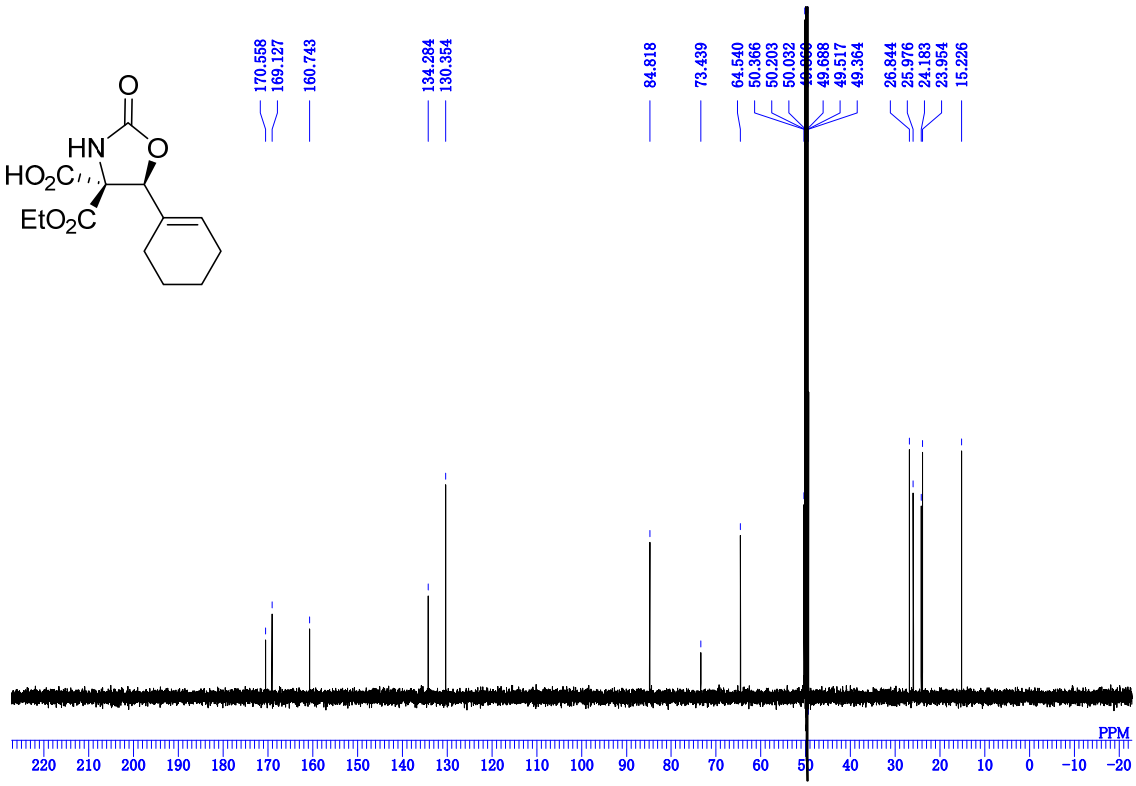
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **5**



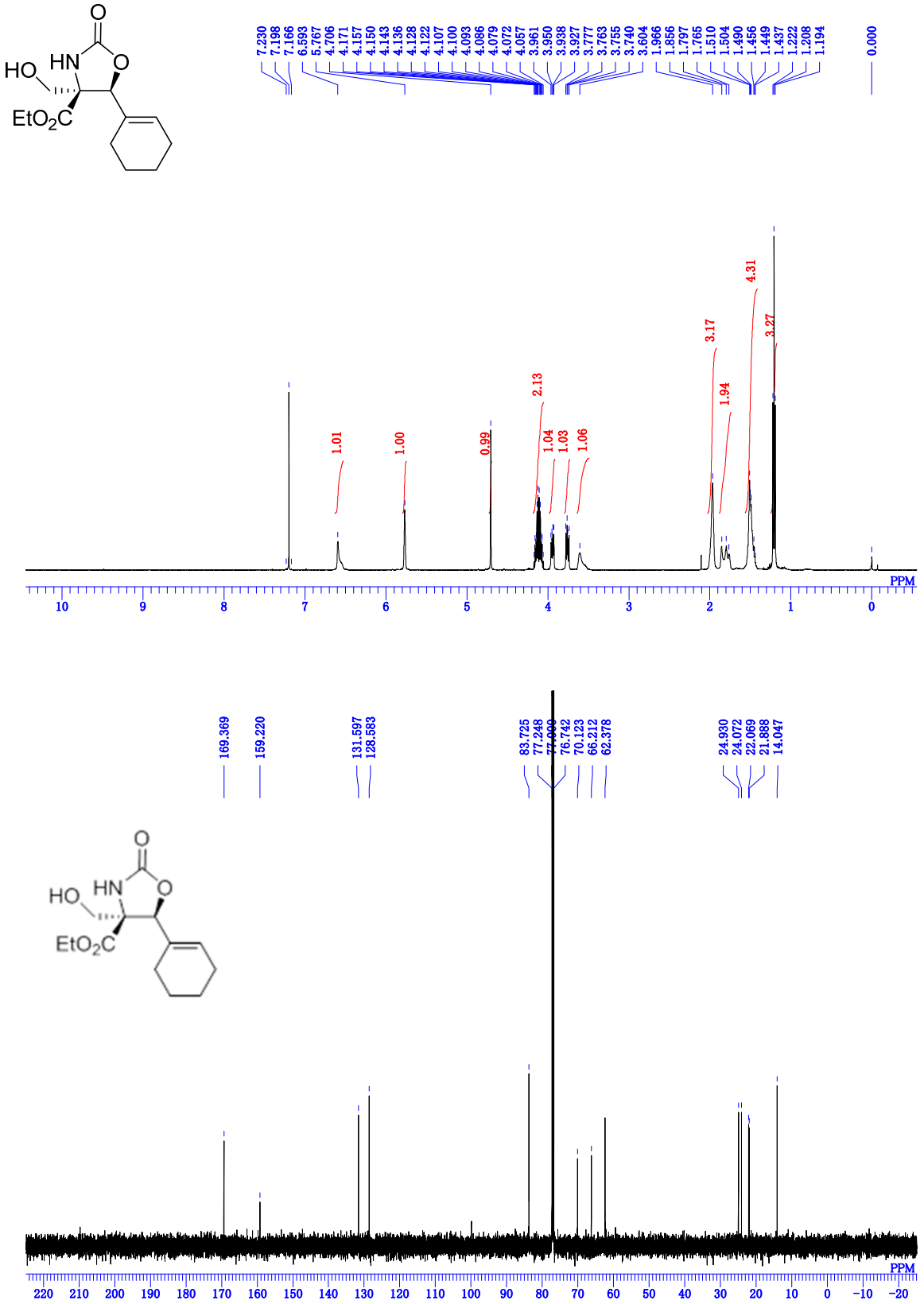


^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **8**.

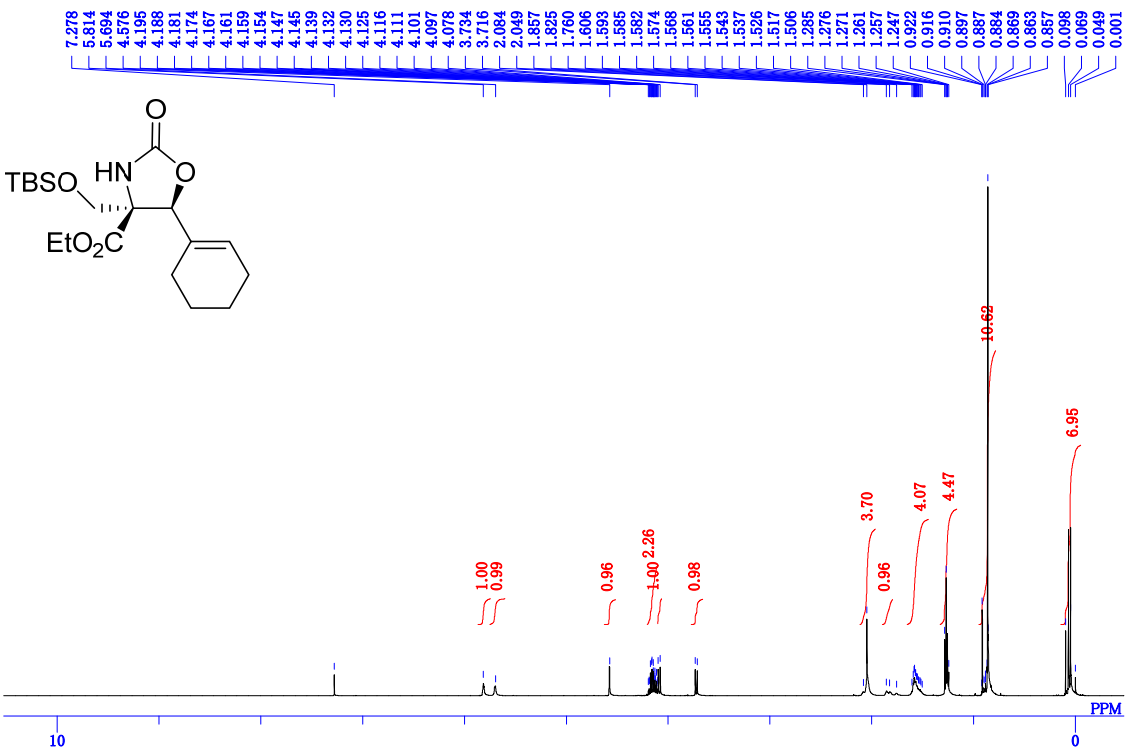


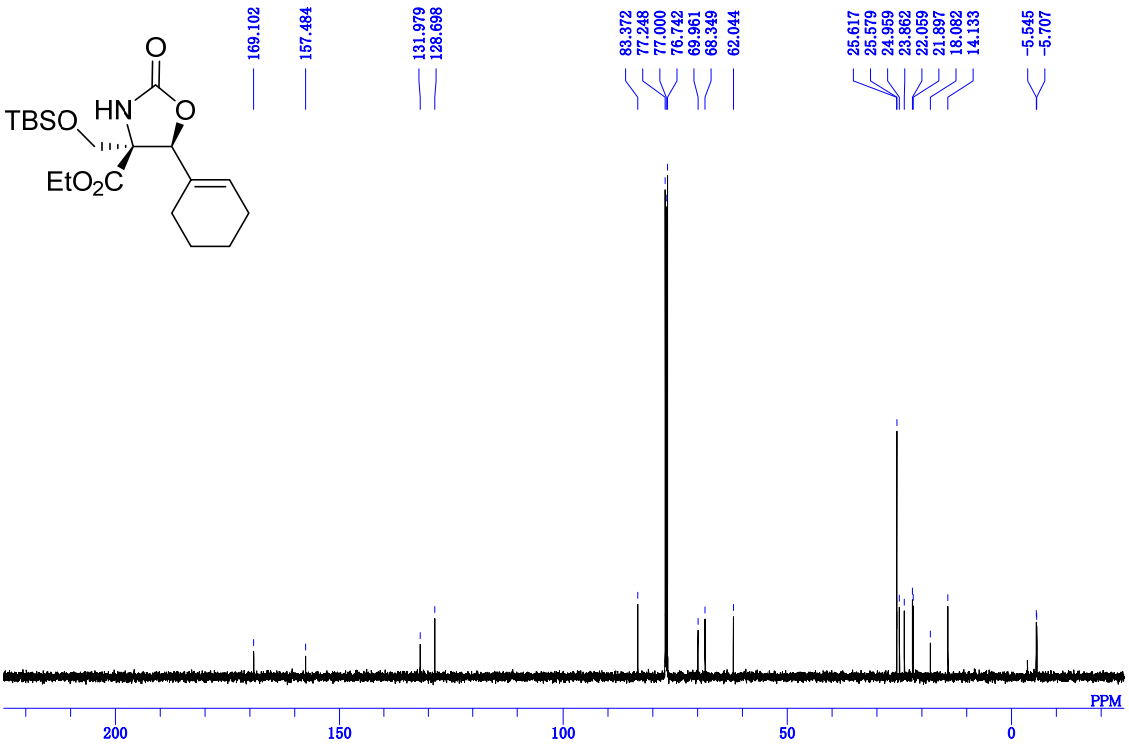


^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **9**.

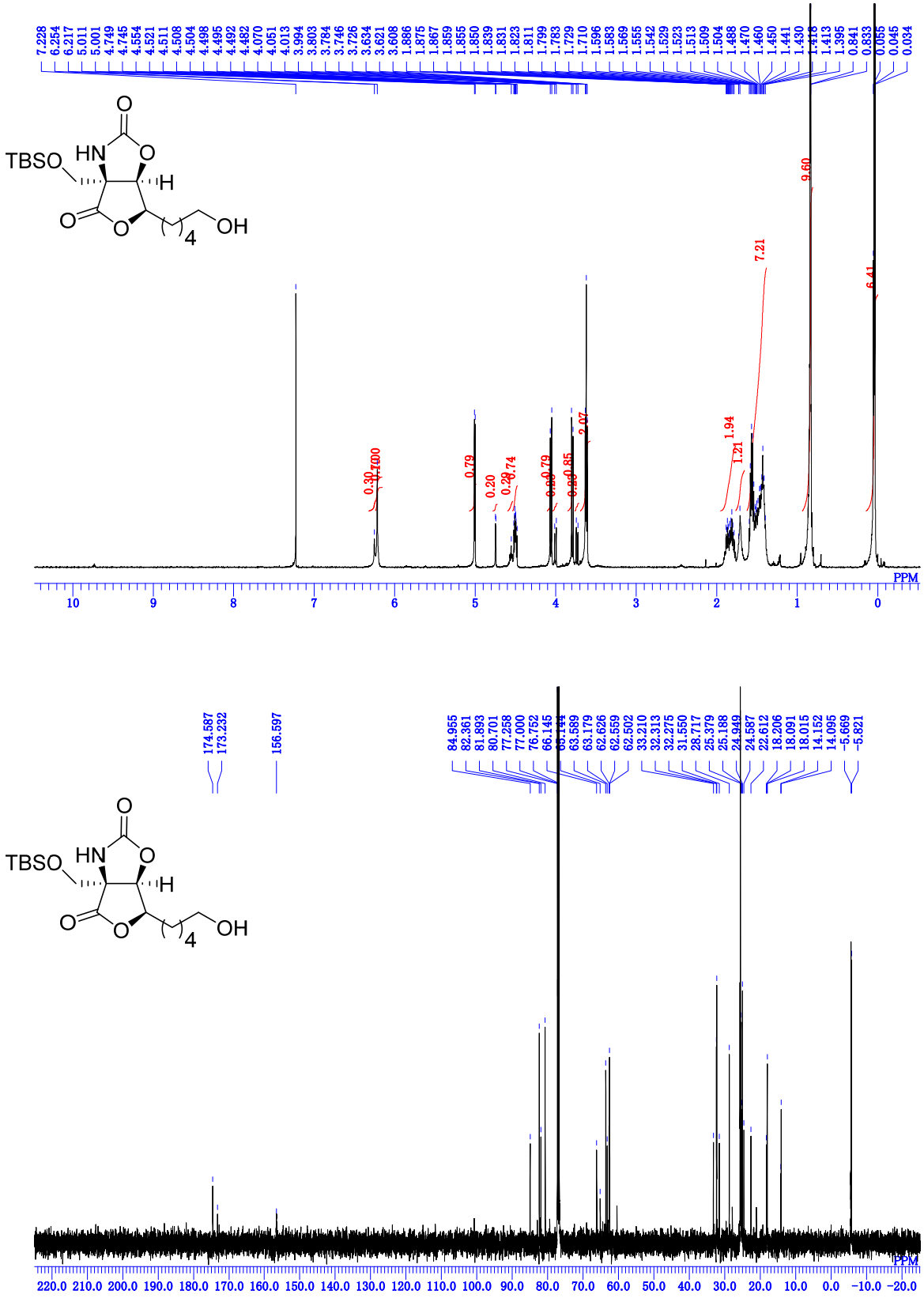


^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **S1**.

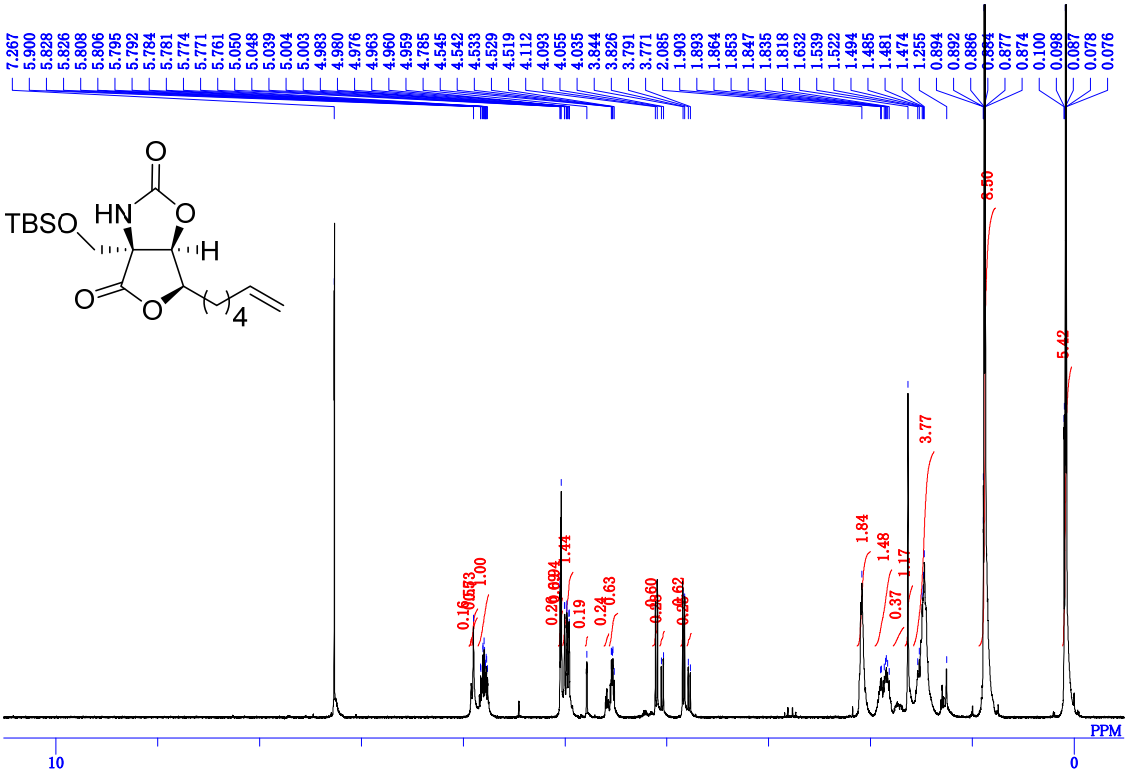


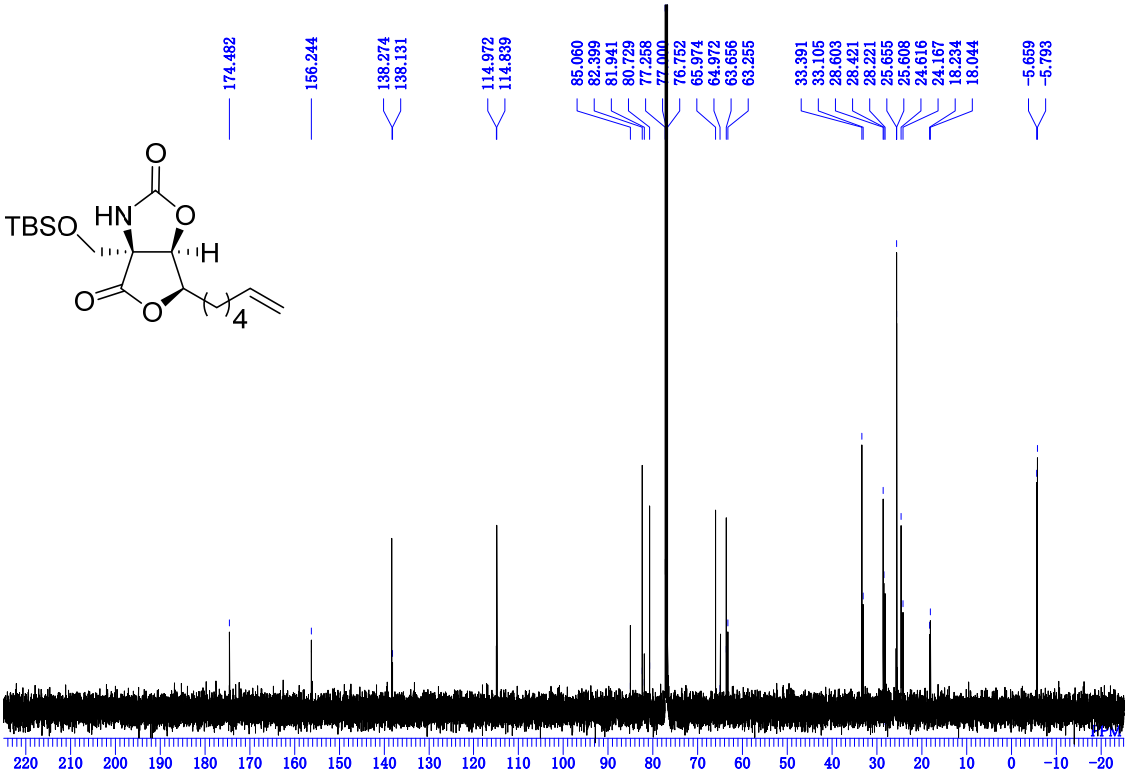


^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **10**.

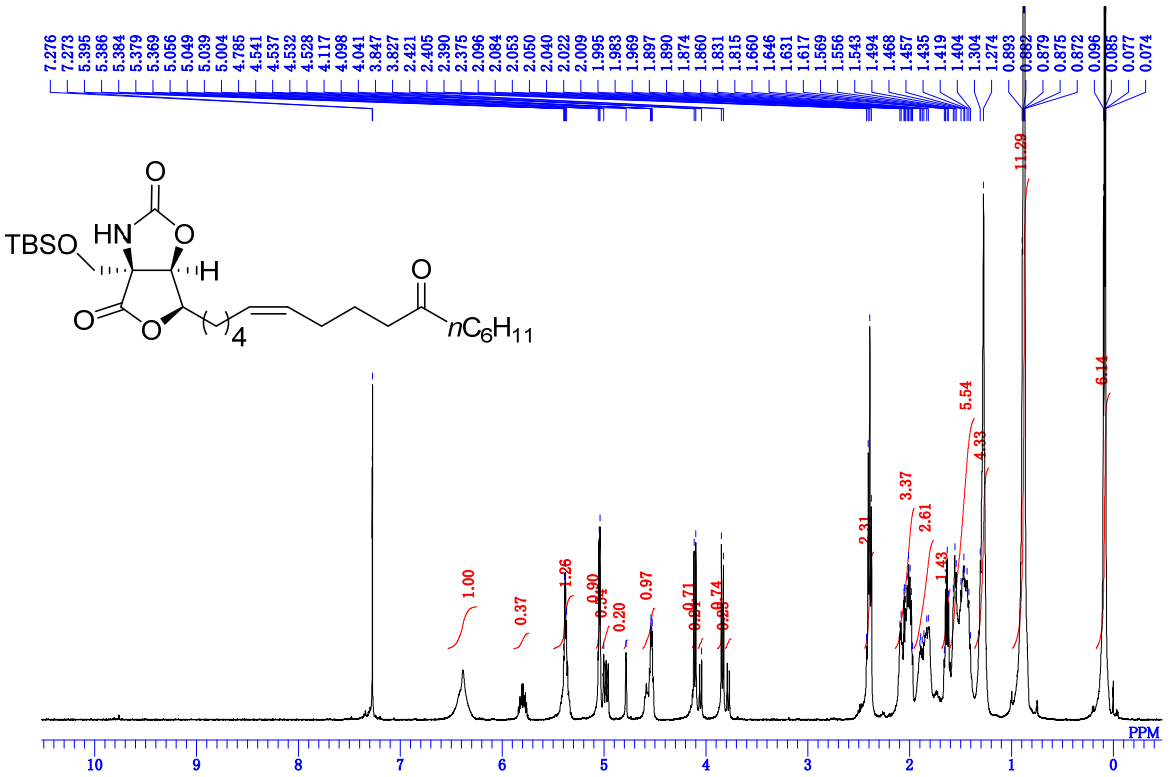


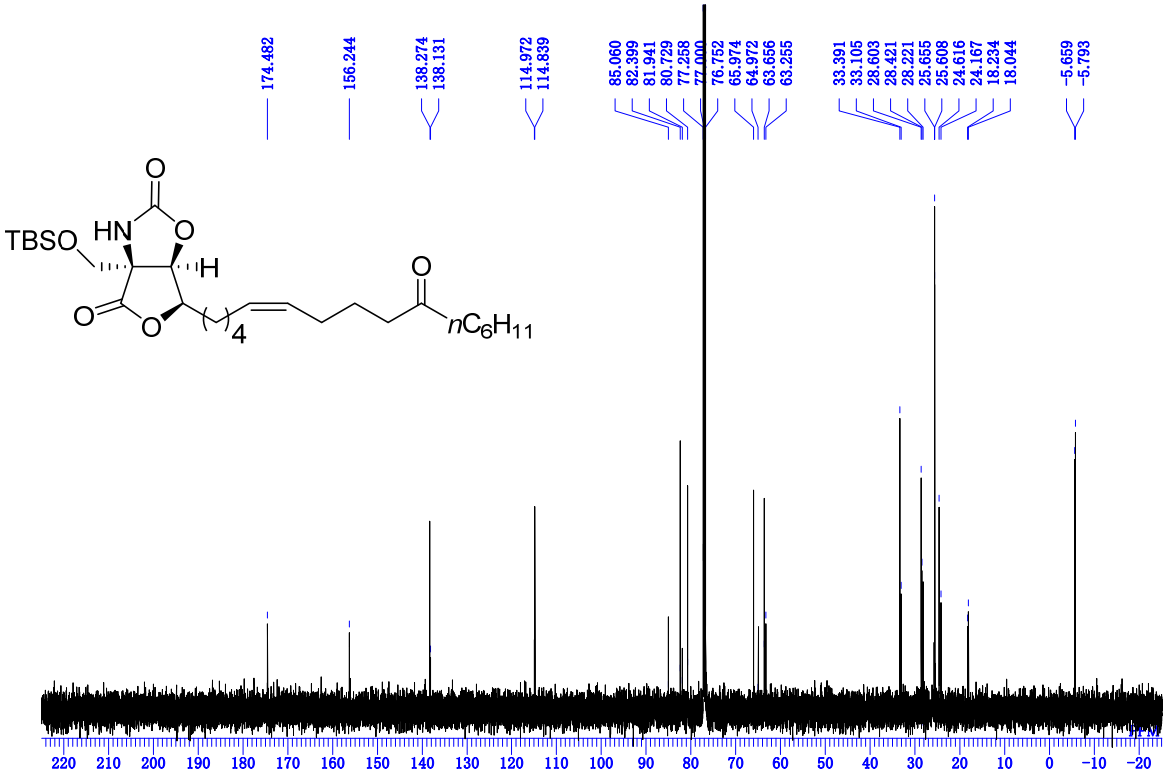
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **11**.



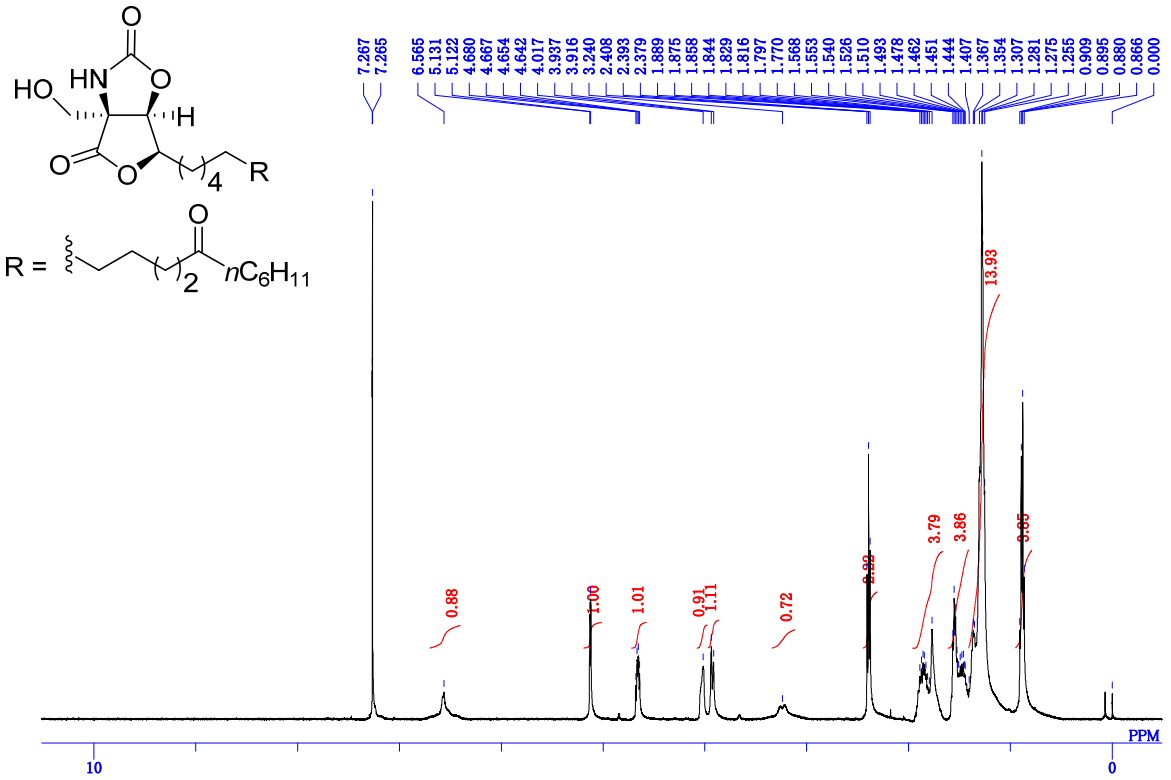


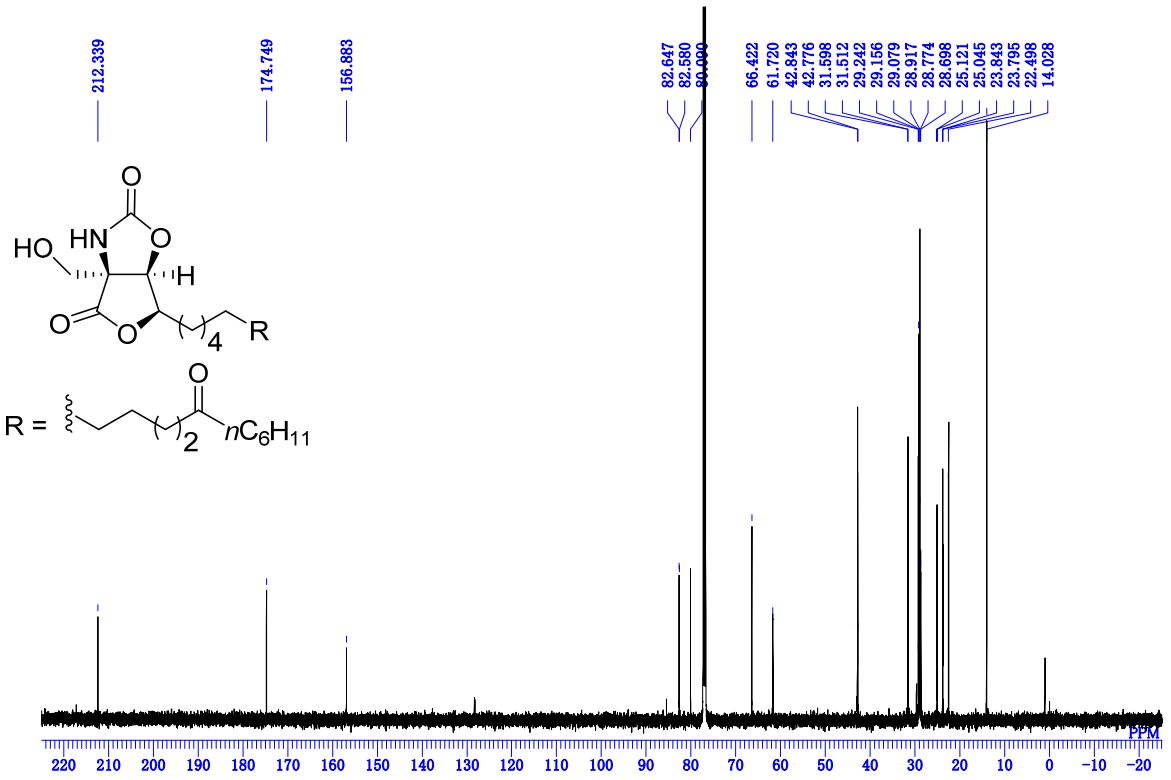
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **S4**.



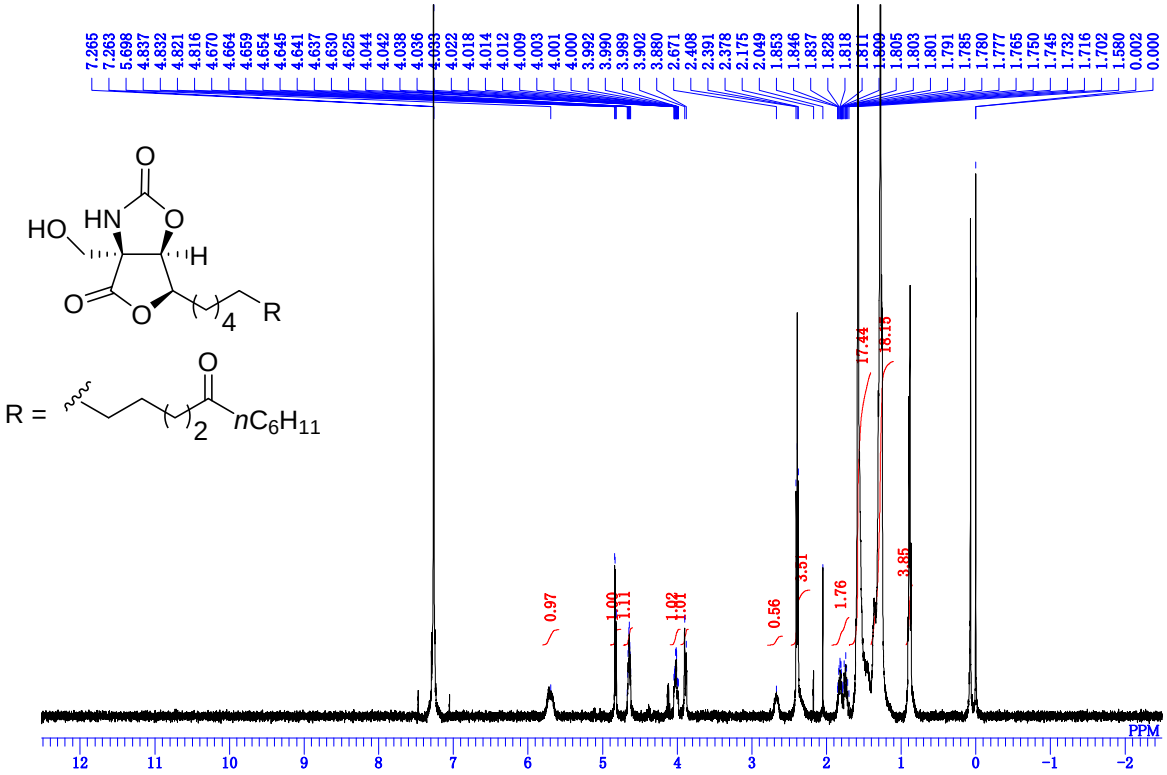


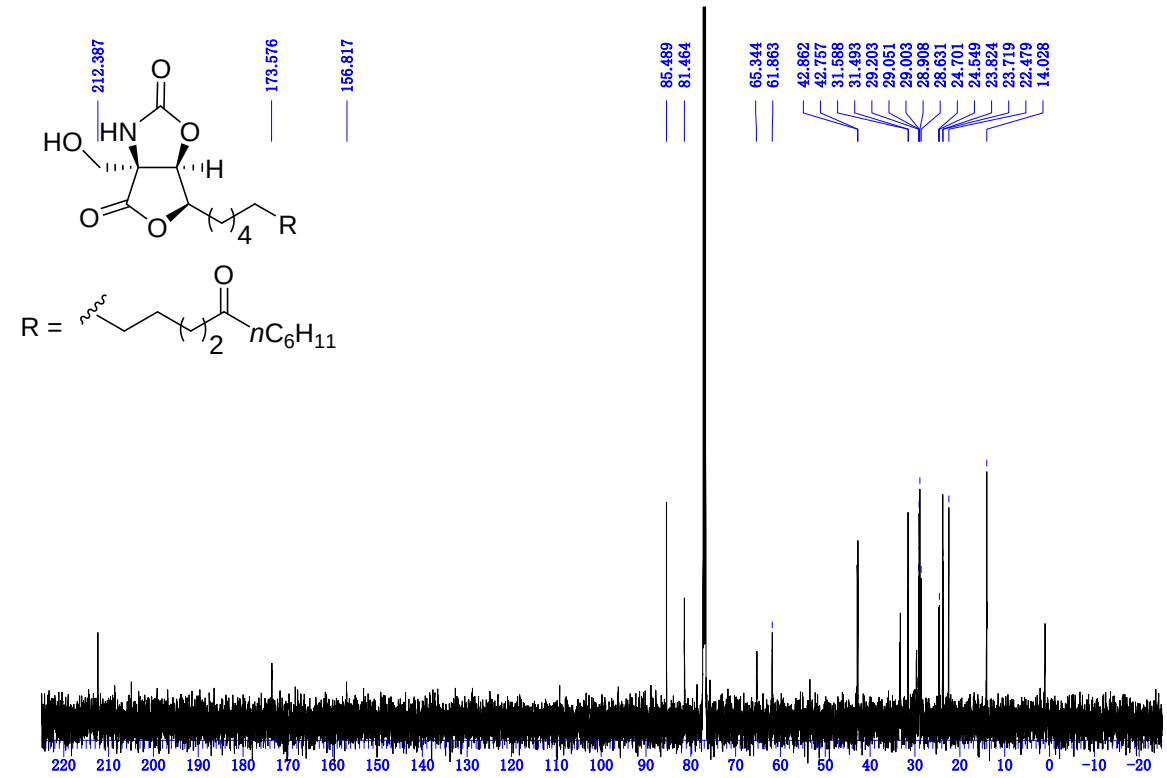
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **13**.



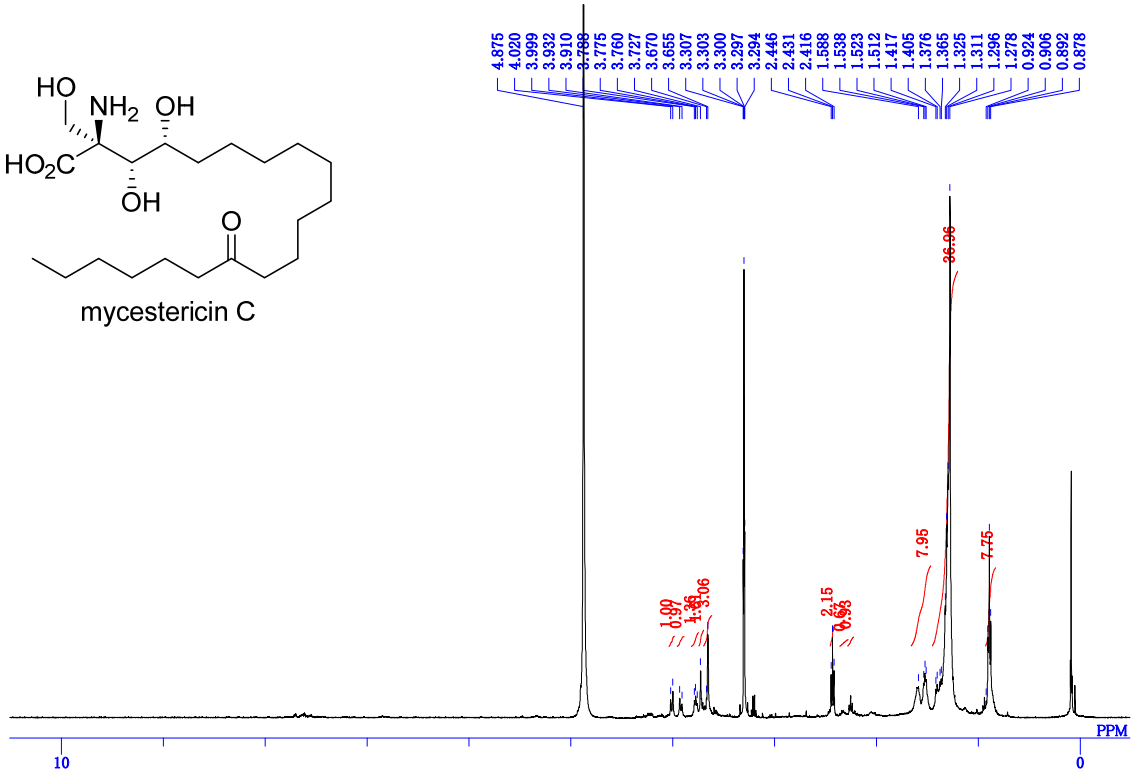


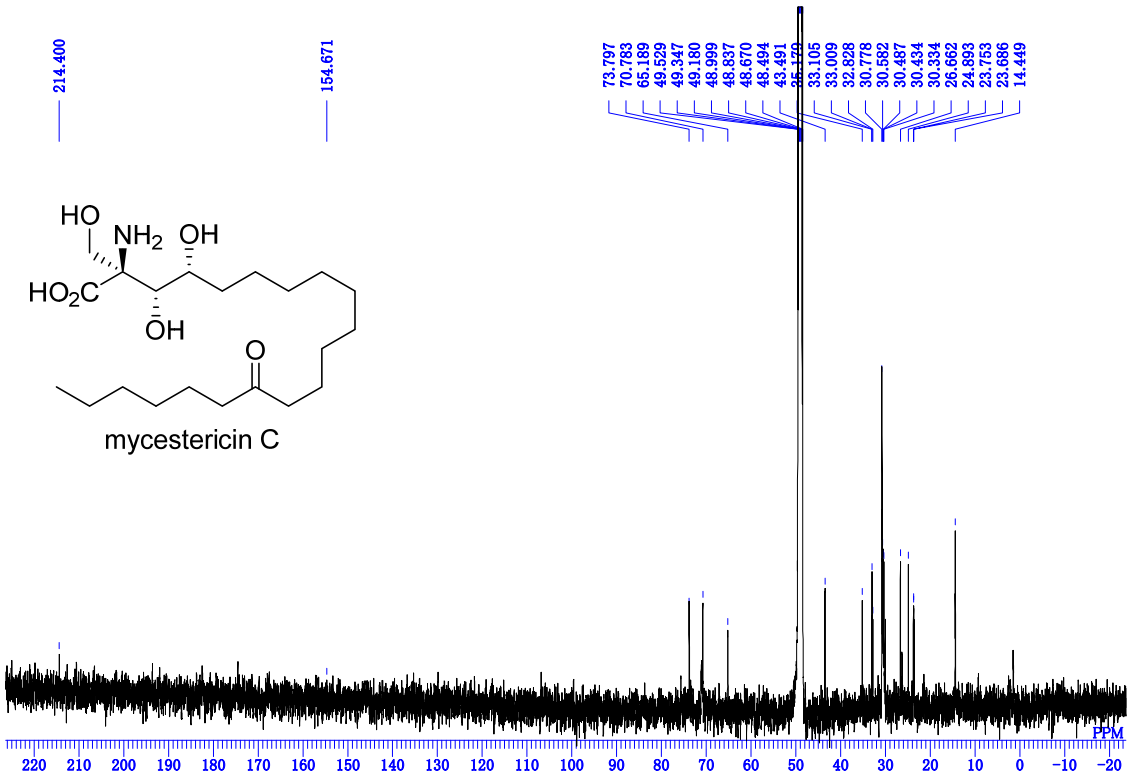
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **13'**.



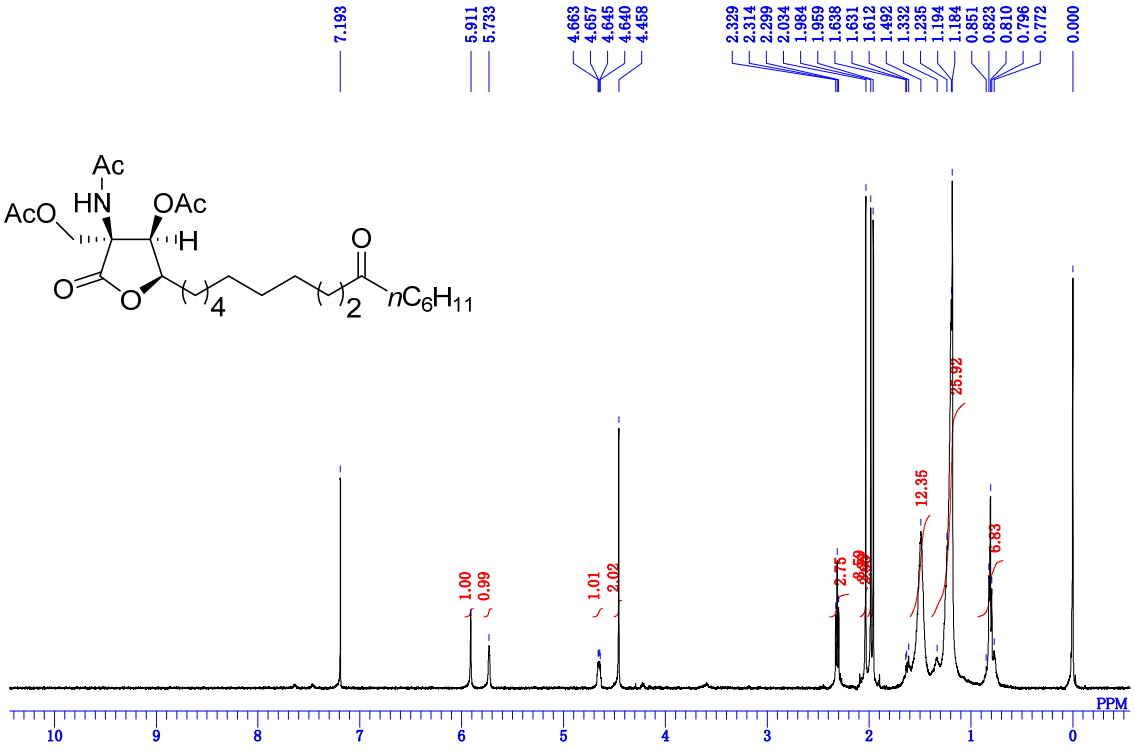


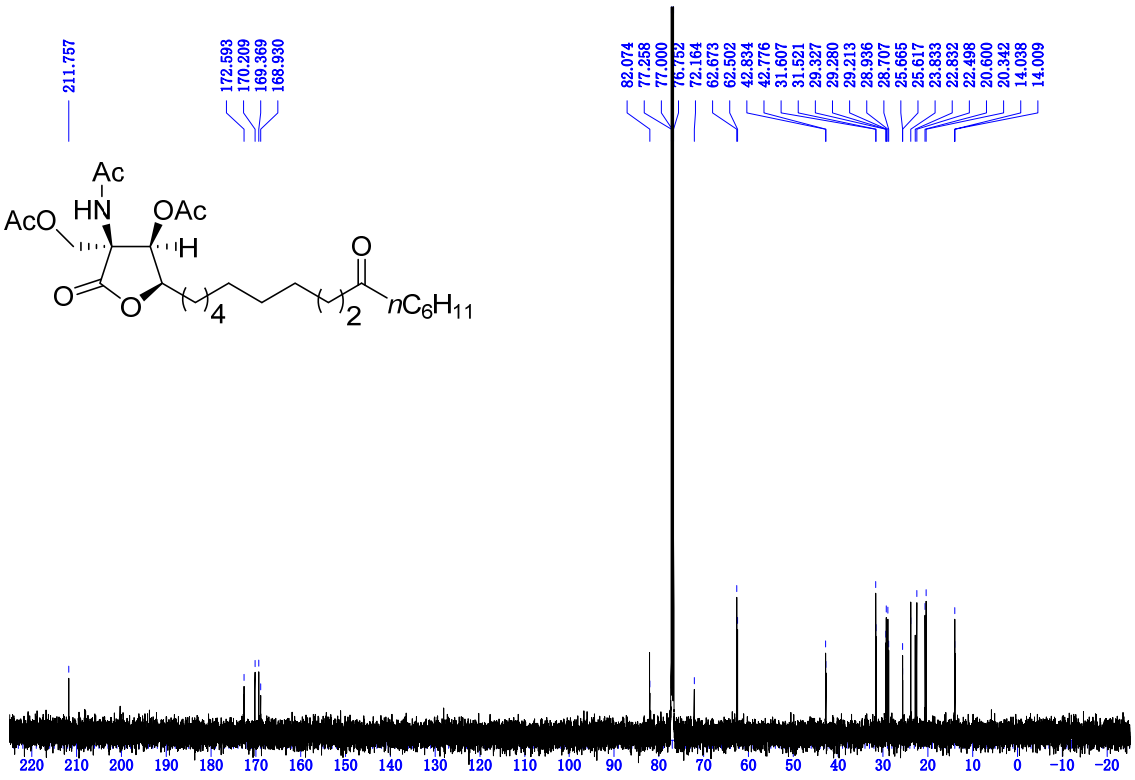
^{1}H NMR(500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of Mycestericin C.





^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR(125 MHz, $CDCl_3$) of **S6** .





9. Copy of HPLC chart of the oxazolidinones 3 and 7

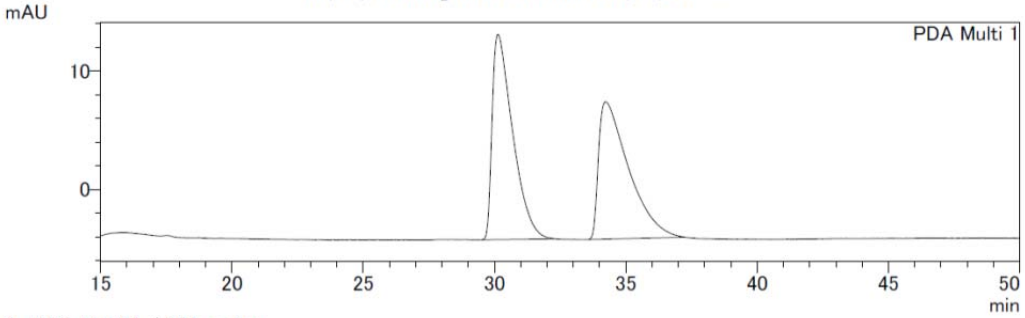
==== Shimadzu LCsolution Analysis Report ====

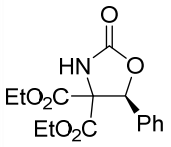
C:¥data_131217¥Kazumi¥3b (rac)002.lcd

sample ID : 3b (rac)
method name : 0.5-iPrOH5-NO3-wash10.lcm
acquisition date : 2014/06/03 20:33:14
modified date : 2014/07/19 9:24:31

<Chromatogram>

chromatogram
3b (rac) C:¥data_131217¥Kazumi¥3b (rac)002.lcd





3b (racemic)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥3b (rac)002.lcd

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	30.127	938185	50.553
2	34.224	917666	49.447

==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3b, table 1, entry 8.lcd

sample ID : 750 table 1, 3b entry 8
method name : 0.5-iPrOH5-NO3-wash10.lcm
acquisition date : 2014/02/10 23:55:18
modified date : 2014/06/03 22:11:38

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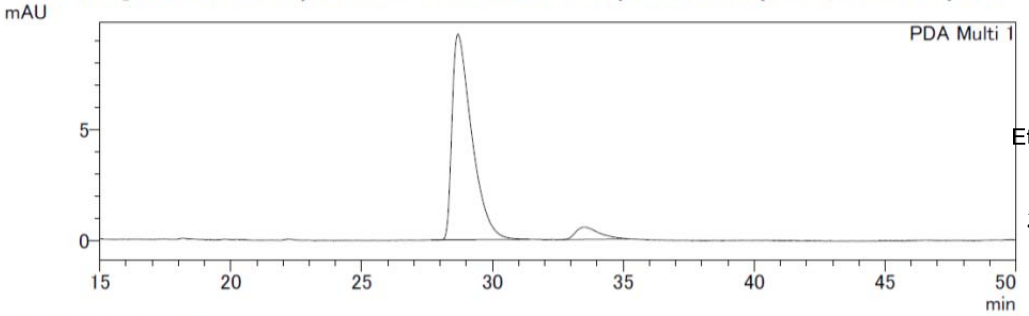
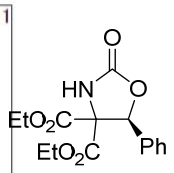
chromatogram
750 C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3b, table 1, entry 8.lcd





3b (87%ee)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥...¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3b, table 1, entry 8.lcd

PDA Ch1 254nm 4nm

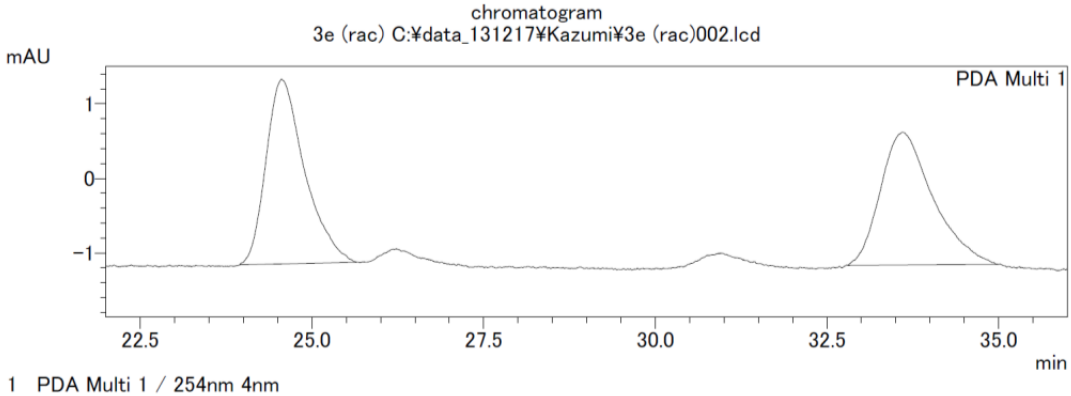
peak#	retention time (min)	area	area (%)
1	28.682	484014	93.337
2	33.544	34554	6.663

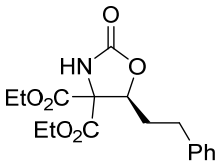
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥3e (rac)002.lcd

sample ID : 3e (rac)
method name : 0.5-iPrOH10-NO2-wash10.lcm
acquisition date : 2014/06/03 14:12:20
modified date : 2014/06/03 19:40:34

<Chromatogram>





3e (racemic)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥3e (rac)002.lcd

PDA Ch1 254nm 4nm

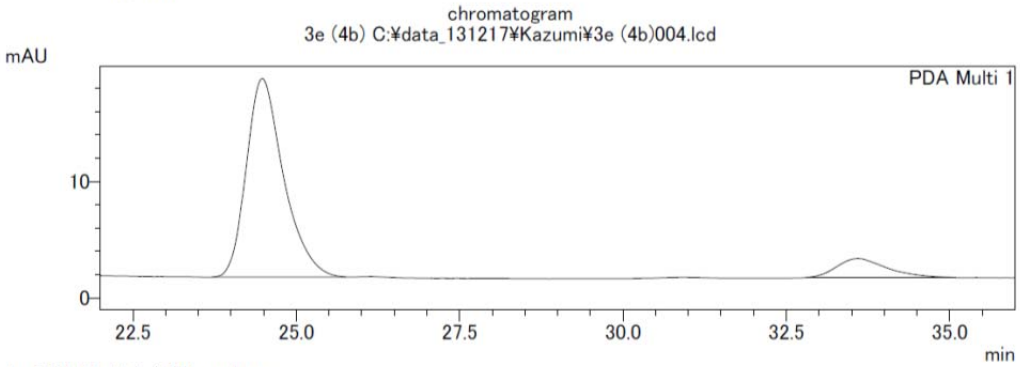
peak#	retention time (min)	area	area (%)
1	24.553	96818	50.611
2	33.595	94482	49.389

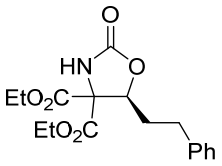
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥3e (4b)004.lcd

sample ID : 3e (4b)
method name : 0.5-iPrOH10-NO2-wash10.lcm
acquisition date : 2014/06/04 16:11:55
modified date : 2014/06/04 17:11:59

<Chromatogram>





3e (78%ee)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥3e (4b)004.lcd

PDA Ch1 254nm 4nm

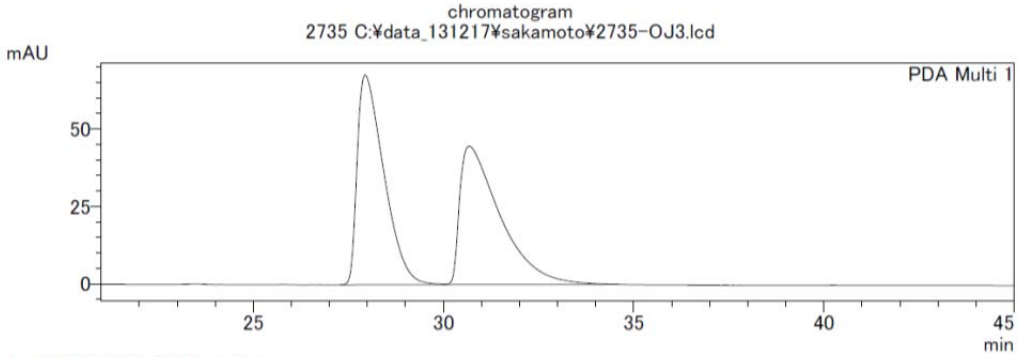
peak#	retention time (min)	area	area (%)
1	24.474	676164	88.888
2	33.582	84528	11.112

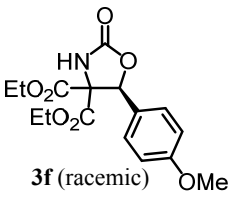
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥sakamoto¥2735-OJ3.lcd

sample ID : 2735
method name : 90.0.5.IPA 3.lcm
acquisition date : 2012/10/29 23:29:49
modified date : 2012/10/30 0:29:51

<Chromatogram>





3f (racemic)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥sakamoto¥2735-OJ3.lcd

PDA Ch1 254nm 4nm

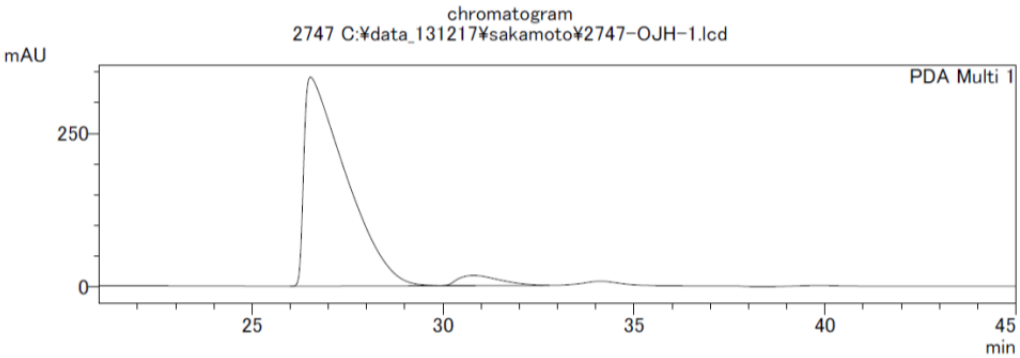
peak#	retention time (min)	area	area (%)
1	27.934	3301696	50.068
2	30.672	3292717	49.932

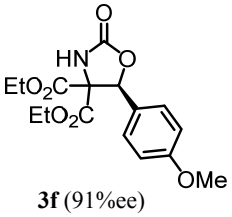
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥sakamoto¥2747-OJH-1.lcd

sample ID : 2747 3f (4a)
method name : 90.0.5.IPA 3.lcm
acquisition date : 2012/11/05 14:42:55
modified date : 2014/06/02 18:31:42

<Chromatogram>





3f (91%ee)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥sakamoto¥2747-OJH-1.lcd

PDA Ch1 254nm 4nm

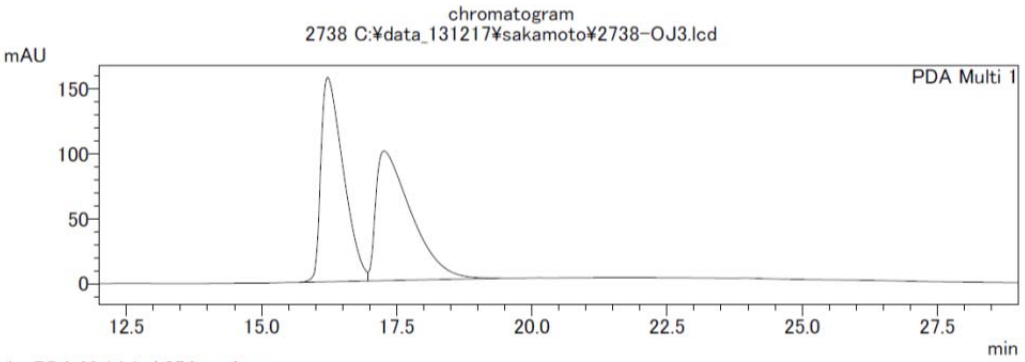
peak#	retention time (min)	area	area (%)
1	26.525	25927238	95.436
2	30.791	1239772	4.564

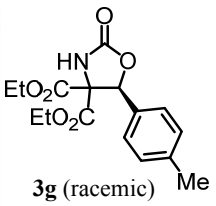
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥sakamoto¥2738-OJ3.lcd

sample ID : 2738
method name : 90.0.5.IPA 3.lcm
acquisition date : 2012/10/30 23:36:00
modified date : 2012/10/31 0:36:08

<Chromatogram>





3g (racemic)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥sakamoto¥2738-OJ3.lcd

PDA Ch1 254nm 4nm

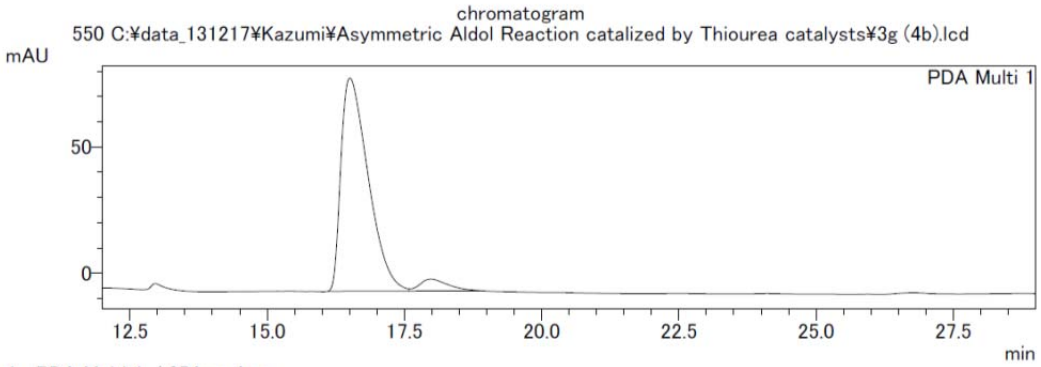
peak#	retention time (min)	area	area (%)
1	16.218	4529589	49.935
2	17.263	4541390	50.065

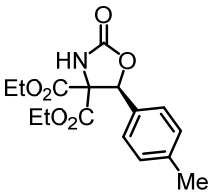
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3g (4b).lcd

sample ID : 550 table 2, 3g (4b)
method name : 0.5-iPrOH10-NO3-wash10_2.lcm
acquisition date : 2013/10/01 21:53:01
modified date : 2014/07/19 9:36:50

<Chromatogram>





3g (89%ee)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3g (4b).lcd

PDA Ch1 254nm 4nm

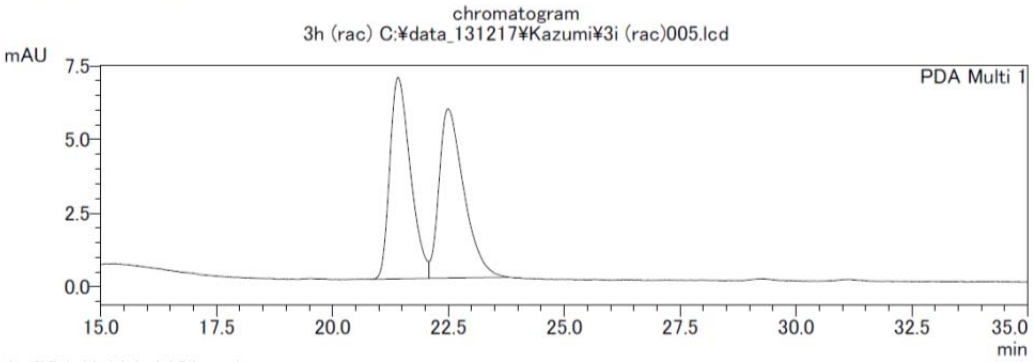
peak#	retention time (min)	area	area (%)
1	16.502	2910717	94.623
2	17.970	165390	5.377

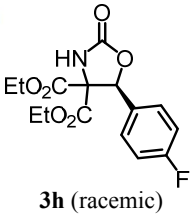
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥3i (rac)005.lcd

sample ID : 3h (rac)
method name : 0.5-iPrOH10-NO3-wash10_2.lcm
acquisition date : 2014/06/05 11:29:07
modified date : 2014/06/05 12:29:14

<Chromatogram>





3h (racemic)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥3i (rac)005.lcd

PDA Ch1 254nm 4nm

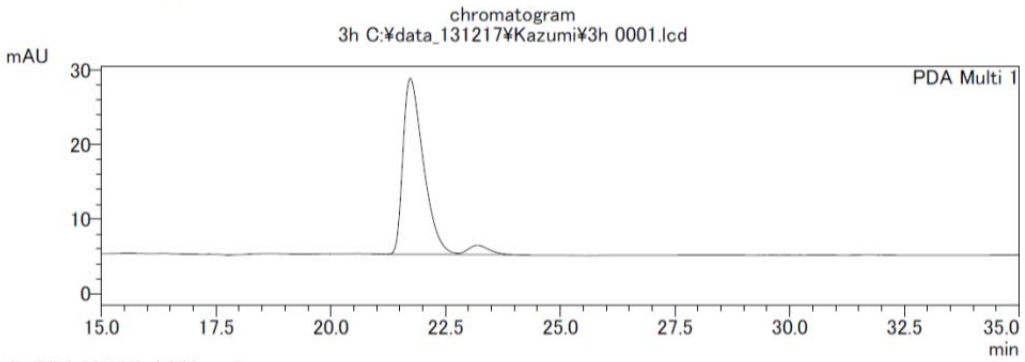
peak#	retention time (min)	area	area (%)
1	21.411	211135	49.690
2	22.490	213772	50.310

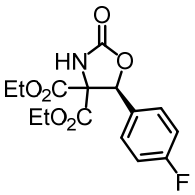
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥3h 0001.lcd

sample ID : 3h
method name : 0.5-iPrOH10-NO3-wash10_2.lcm
acquisition date : 2014/07/24 15:20:49
modified date : 2014/07/24 16:00:42

<Chromatogram>





3h (90%ee)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥3h 0001.lcd

PDA Ch1 254nm 4nm

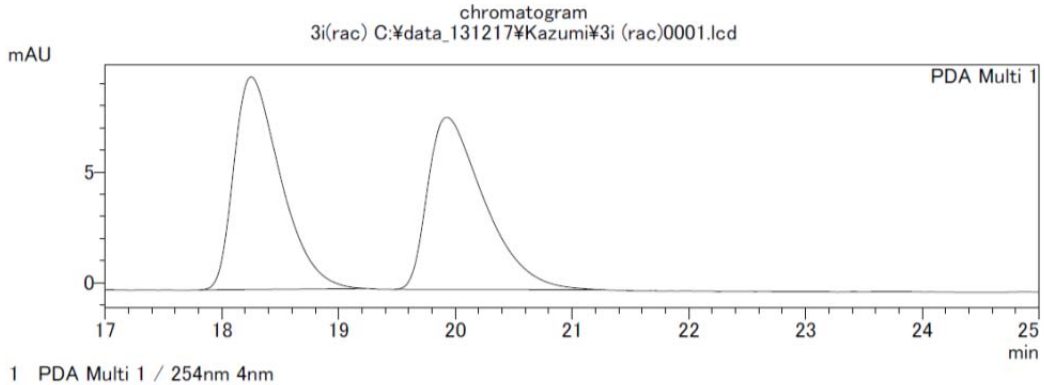
peak#	retention time (min)	area	area (%)
1	21.726	729326	94.800
2	23.186	40009	5.200

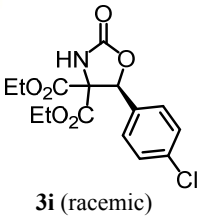
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥3i (rac)0001.lcd

sample ID : 3i(rac)
method name : 0.5-iPrOH10-NO3-wash10_2.lcm
acquisition date : 2014/07/24 16:01:06
modified date : 2014/07/24 16:48:05

<Chromatogram>





3i (racemic)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥3i (rac)0001.lcd

PDA Ch1 254nm 4nm

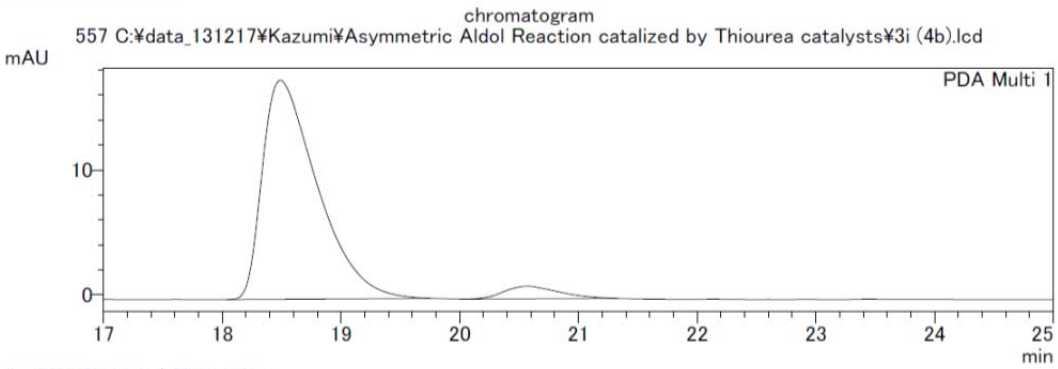
peak#	retention time (min)	area	area (%)
1	18.247	268020	50.549
2	19.925	262201	49.451

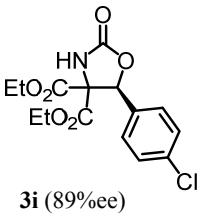
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3i (4b).lcd

sample ID : 557 table 2, 3i (4b)
method name : 0.5-iPrOH10-NO3-wash10_2.lcm
acquisition date : 2013/10/03 14:15:04
modified date : 2014/05/31 3:20:52

<Chromatogram>





3i (89%ee)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3i (4b).lcd

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	18.485	563850	94.585
2	20.562	32278	5.415

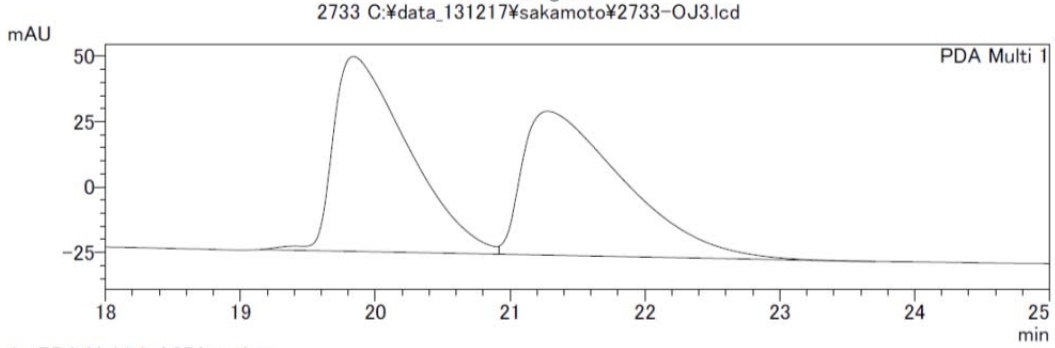
==== Shimadzu LCsolution Analysis Report ====

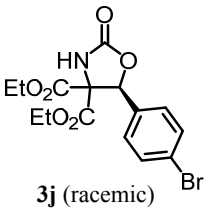
C:¥data_131217¥sakamoto¥2733-OJ3.lcd

sample ID : 27333j rac
method name : 90.0.5.IPA 3.lcm
acquisition date : 2012/10/29 22:05:46
modified date : 2012/10/29 23:05:49

<Chromatogram>

chromatogram
2733 C:¥data_131217¥sakamoto¥2733-OJ3.lcd





3j (racemic)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥sakamoto¥2733-OJ3.lcd

PDA Ch1 254nm 4nm

peak#	retention time (min)	area	area (%)
1	19.832	2885363	50.111
2	21.274	2872566	49.889

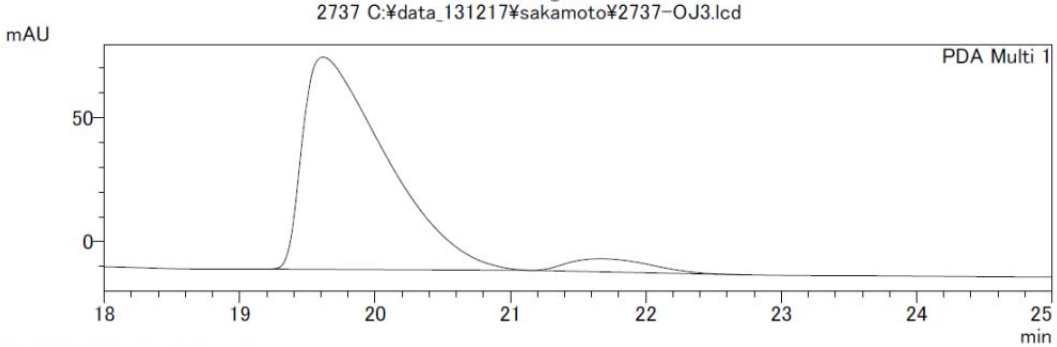
==== Shimadzu LCsolution Analysis Report ====

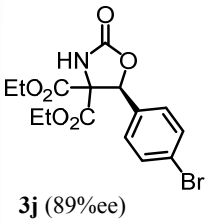
C:¥data_131217¥sakamoto¥2737-OJ3.lcd

sample ID : 2737
method name : 90.0.5.IPA 3.lcm
acquisition date : 2012/10/31 14:32:45
modified date : 2012/10/31 15:32:48

<Chromatogram>

chromatogram
2737 C:¥data_131217¥sakamoto¥2737-OJ3.lcd





3j (89%ee)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥sakamoto¥2737-OJ3.lcd

PDA Ch1 254nm 4nm

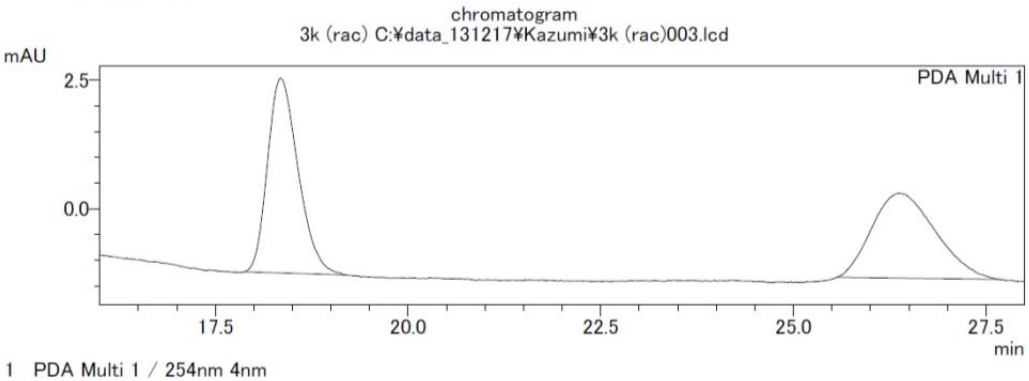
peak#	retention time (min)	area	area (%)
1	19.609	3648336	94.235
2	21.660	223180	5.765

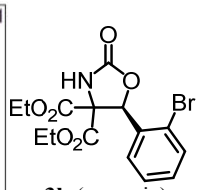
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥3k (rac)003.lcd

sample ID : 3k (rac)
method name : 0.5-iPrOH10-NO3-wash10_2.lcm
acquisition date : 2014/06/03 21:57:30
modified date : 2014/06/03 22:57:33

<Chromatogram>





3k (racemic)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥3k (rac)003.lcd

PDA Ch1 254nm 4nm

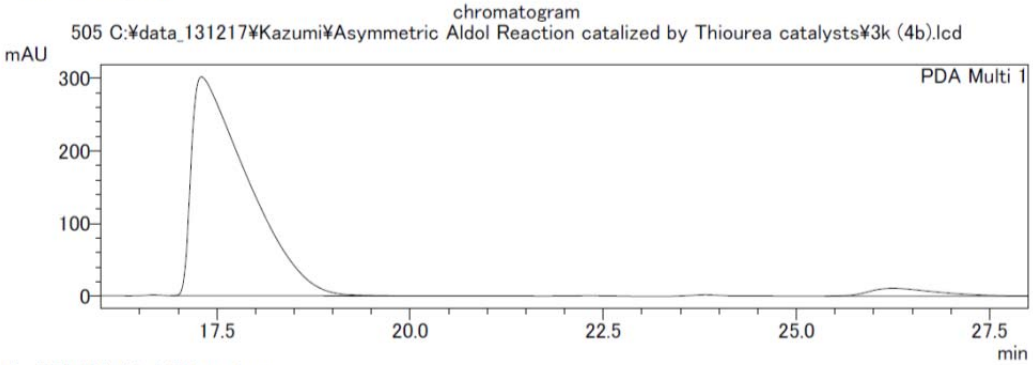
peak#	retention time (min)	area	area (%)
1	18.341	104515	52.519
2	26.370	94491	47.481

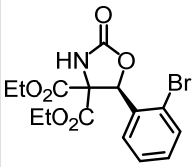
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3k (4b).lcd

sample ID : 505 table 2, 3k (4b)
method name : 0.5-iPrOH10-NO3-wash10_2.lcm
acquisition date : 2013/08/30 18:10:18
modified date : 2014/06/02 16:40:02

<Chromatogram>





3k (92%ee)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3k (4b).lcd

PDA Ch1 254nm 4nm

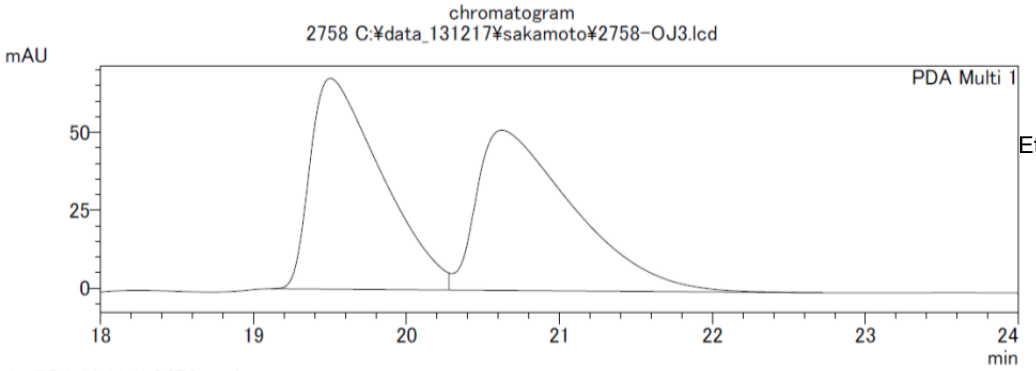
peak#	retention time (min)	area	area (%)
1	17.296	15299241	95.978
2	26.241	641069	4.022

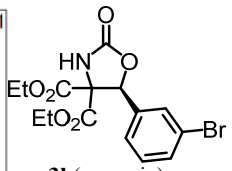
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥sakamoto¥2758-OJ3.lcd

sample ID : 27583I rac
method name : 90.0.5.IPA 3.lcm
acquisition date : 2012/11/08 19:27:39
modified date : 2012/11/08 20:27:42

<Chromatogram>





3l (racemic)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥sakamoto¥2758-OJ3.lcd

PDA Ch1 254nm 4nm

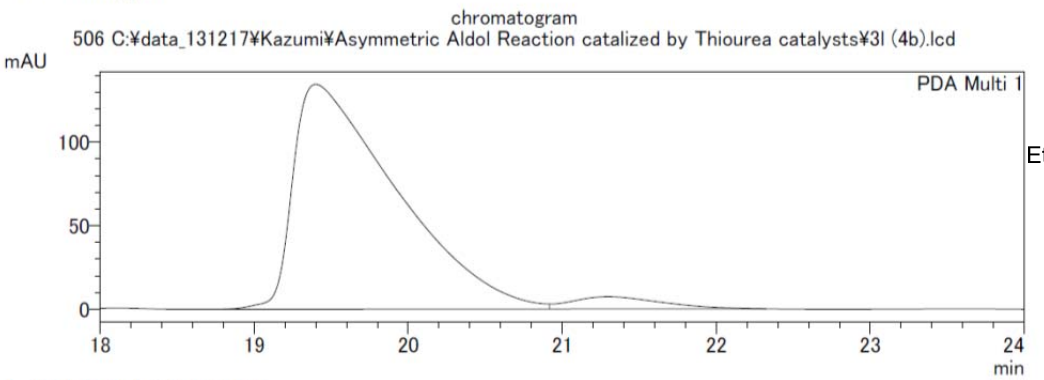
peak#	retention time (min)	area	area (%)
1	19.497	2197940	49.346
2	20.617	2256237	50.654

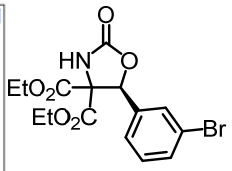
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3l (4b).lcd

sample ID : 506 table 2, 3l (4b)
method name : 0.5-iPrOH10-NO3-wash10_2.lcm
acquisition date : 2013/08/31 13:25:43
modified date : 2014/05/31 3:14:49

<Chromatogram>





3l (91%ee)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3l (4b).lcd

PDA Ch1 254nm 4nm

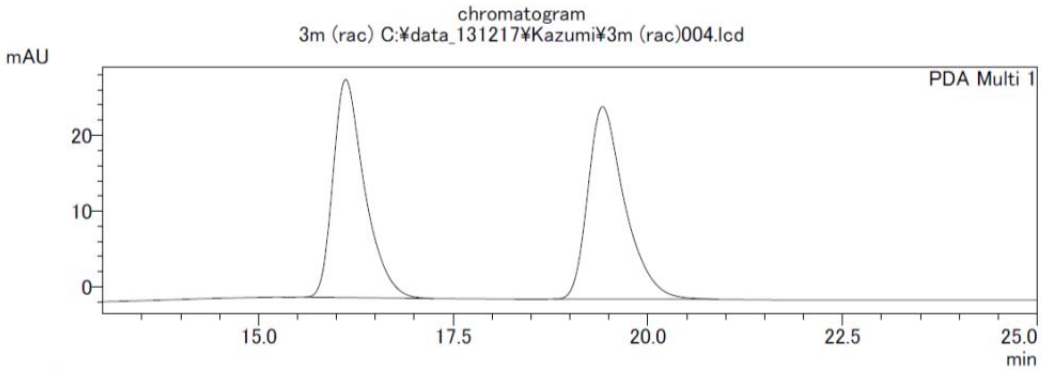
peak#	retention time (min)	area	area (%)
1	19.393	6281302	95.514
2	21.295	294982	4.486

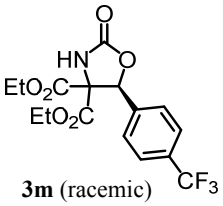
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥3m (rac)004.lcd

sample ID : 3m (rac)
method name : 0.5-iPrOH10-NO2-wash10.lcm
acquisition date : 2014/06/04 18:55:09
modified date : 2014/06/04 19:55:13

<Chromatogram>





3m (racemic)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥3m (rac)004.lcd

PDA Ch1 254nm 4nm

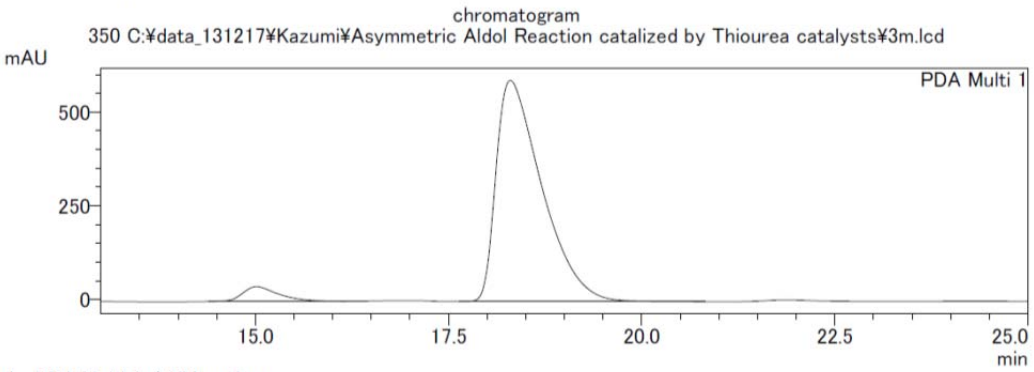
peak#	retention time (min)	area	area (%)
1	16.114	810511	49.205
2	19.414	836714	50.795

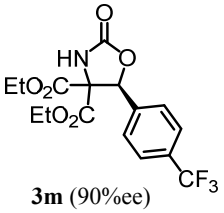
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3m.lcd

sample ID : 350 table 2, 3m
method name : 0.5-iPrOH10-NO2-wash10.lcm
acquisition date : 2013/04/20 10:12:29
modified date : 2014/06/02 16:42:47

<Chromatogram>





3m (90%ee)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3m.lcd

PDA Ch1 254nm 4nm

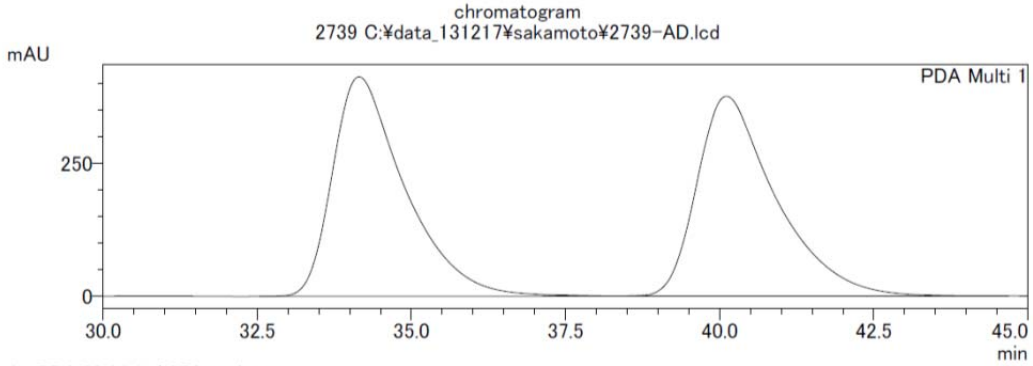
peak#	retention time (min)	area	area (%)
1	15.011	1253381	4.920
2	18.294	24220544	95.080

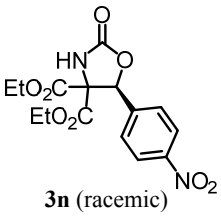
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥sakamoto¥2739-AD.lcd

sample ID : 2739 3n rac
method name : 90.0.5.IPA 2.lcm
acquisition date : 2012/11/08 22:15:57
modified date : 2012/11/08 23:16:03

<Chromatogram>





3n (racemic)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥sakamoto¥2739-AD.lcd

PDA Ch1 254nm 4nm

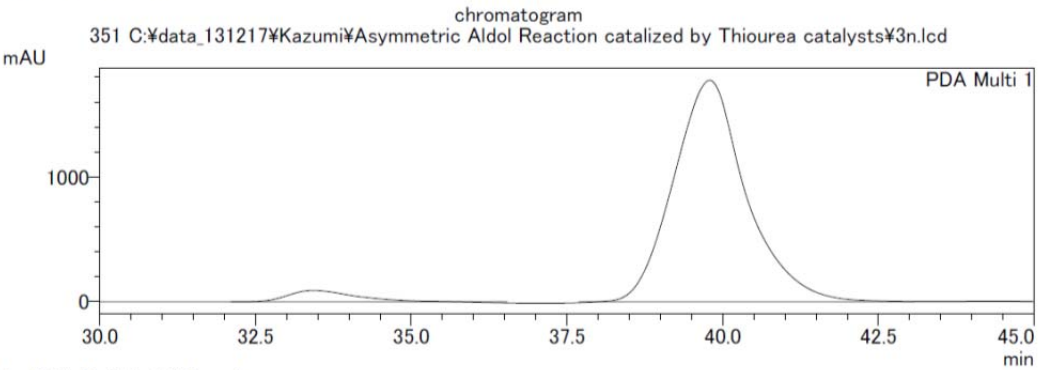
peak#	retention time (min)	area	area (%)
1	34.147	33688616	50.144
2	40.106	33494770	49.856

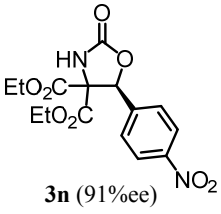
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3n.lcd

sample ID : 351 table 2, 3n
method name : 0.5-iPrOH10-NO2-wash10.lcm
acquisition date : 2013/04/20 11:26:46
modified date : 2014/05/31 3:09:53

<Chromatogram>





3n (91%ee)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3n.lcd

PDA Ch1 254nm 4nm

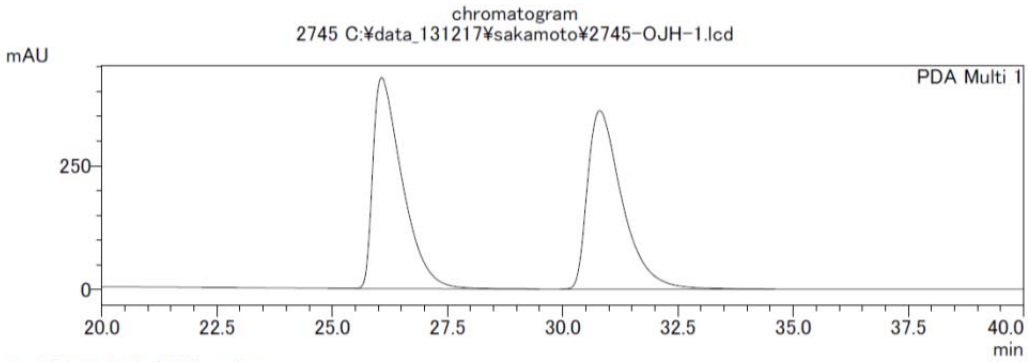
peak#	retention time (min)	area	area (%)
1	33.426	6924565	4.577
2	39.788	144363632	95.423

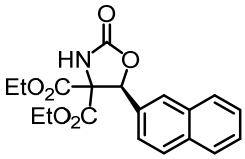
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥sakamoto¥2745-OJH-1.lcd

sample ID : 2745
method name : 90.0.5.IPA 3.lcm
acquisition date : 2012/11/01 12:13:23
modified date : 2014/06/01 16:17:46

<Chromatogram>





3o (racemic)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥sakamoto¥2745-OJH-1.lcd

PDA Ch1 254nm 4nm

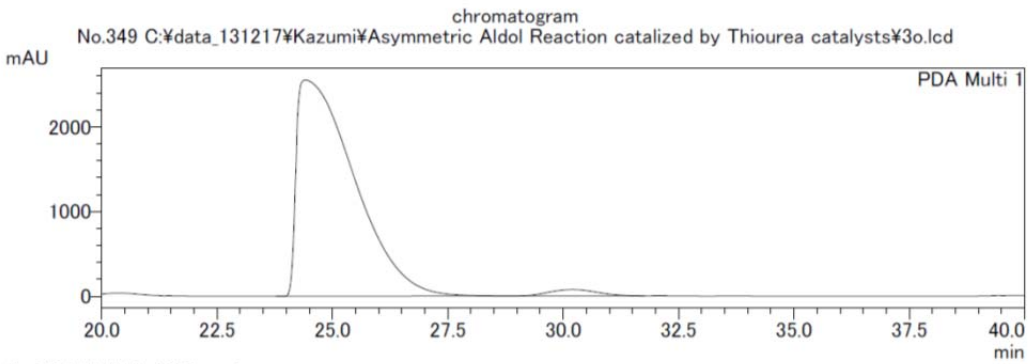
peak#	retention time (min)	area	area (%)
1	26.066	18844697	49.961
2	30.800	18874055	50.039

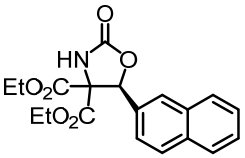
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3o.lcd

sample ID : No.349 table 2, 3o
method name : 0.5-iPrOH10-NO3-wash10.lcm
acquisition date : 2013/04/16 18:46:09
modified date : 2014/06/02 16:45:54

<Chromatogram>





3o (95%ee)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3o.lcd

PDA Ch1 254nm 4nm

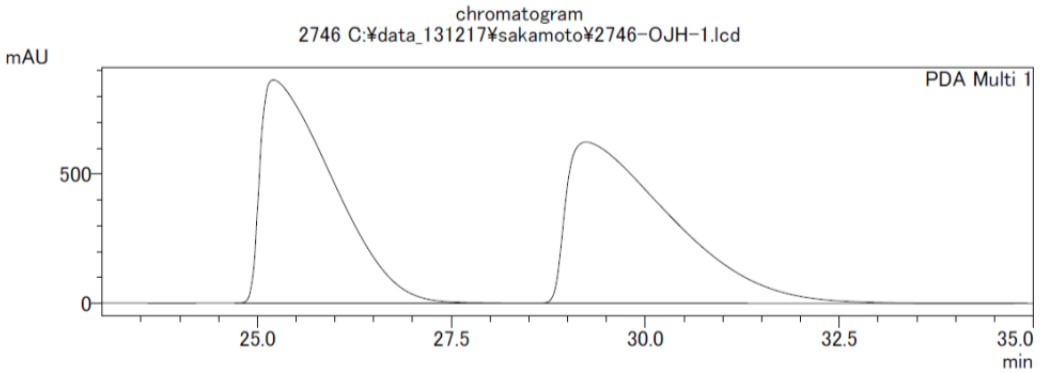
peak#	retention time (min)	area	area (%)
1	24.406	221502537	97.605
2	30.196	5434830	2.395

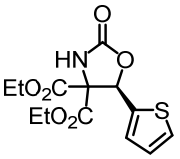
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥sakamoto¥2746-OJH-1.lcd

sample ID : 2746
method name : 90.0.5.IPA 3.lcm
acquisition date : 2012/11/01 21:00:00
modified date : 2012/11/01 21:37:22

<Chromatogram>





3p (racemic)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥sakamoto¥2746-OJH-1.lcd

PDA Ch1 254nm 4nm

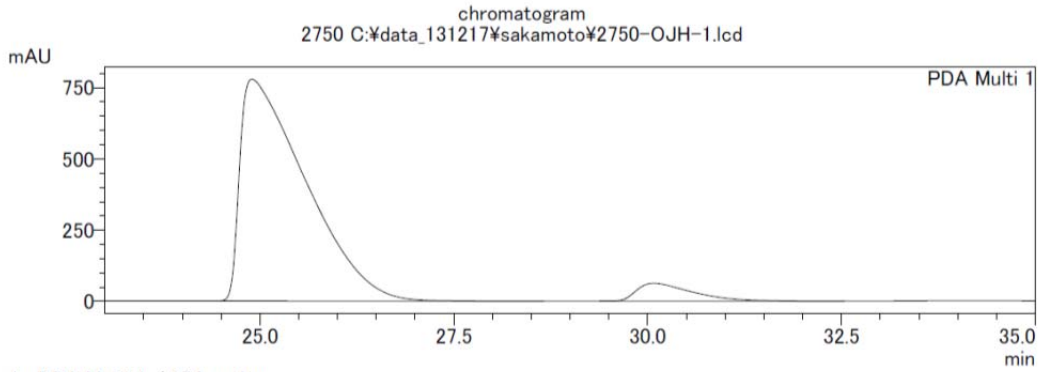
peak#	retention time (min)	area	area (%)
1	25.203	55698208	48.693
2	29.234	58689429	51.307

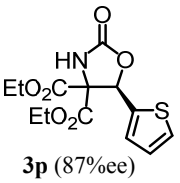
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥sakamoto¥2750-OJH-1.lcd

sample ID : 2750 3p (4a)
method name : 90.0.5.IPA 3.lcm
acquisition date : 2012/11/07 10:09:57
modified date : 2012/11/07 10:46:53

<Chromatogram>





3p (87%ee)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥sakamoto¥2750-OJH-1.lcd

PDA Ch1 254nm 4nm

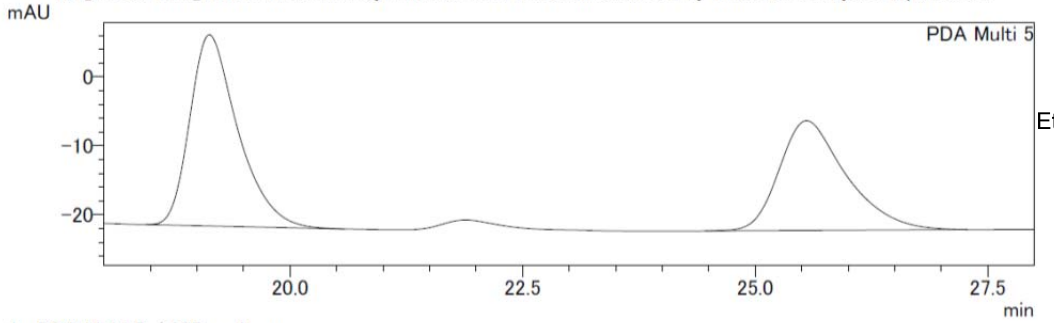
peak#	retention time (min)	area	area (%)
1	24.891	45829320	93.522
2	30.075	3174706	6.478

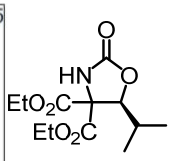
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3q (rac).lcd
sample ID : 481_AD table 2, 3o (rac)
method name : 0.5-iPrOH10-NO2-wash10.lcm
acquisition date : 2013/07/22 13:19:52
modified date : 2014/06/02 16:52:49

<Chromatogram>

chromatogram
481_AD C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3q (rac).lcd





3q (racemic)

1 PDA Multi 5 / 235nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3q (rac).lcd
PDA Ch5 235nm 4nm

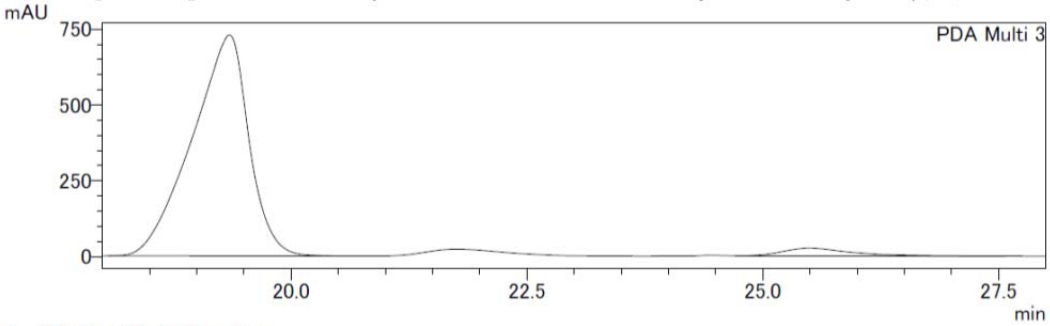
peak#	retention time (min)	area	area (%)
1	19.128	996132	55.622
2	25.546	794776	44.378

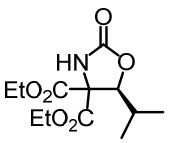
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3q (4a).lcd
sample ID : 483_2 table 2, 3q (4a)
method name : 0.5-iPrOH10-NO2-wash10.lcm
acquisition date : 2013/07/29 16:45:11
modified date : 2014/05/31 2:48:41

<Chromatogram>

chromatogram
483_2 C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3q (4a).lcd





3q (92%ee)

1 PDA Multi 3 / 235nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3q (4a).lcd
PDA Ch3 235nm 4nm

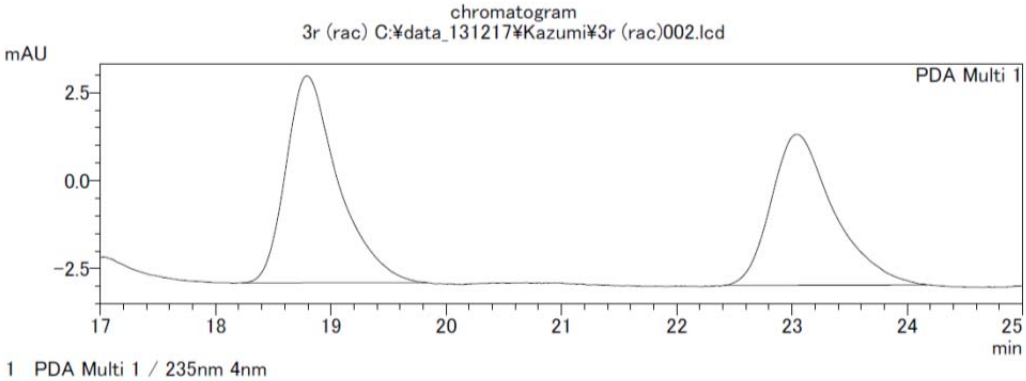
peak#	retention time (min)	area	area (%)
1	19.341	30534079	95.848
2	25.491	1322835	4.152

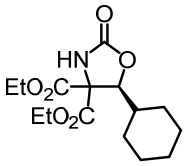
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥3r (rac)002.lcd

sample ID : 3r (rac)
method name : 0.5-iPrOH10-NO2-wash10.lcm
acquisition date : 2014/06/03 16:42:07
modified date : 2014/06/03 17:25:22

<Chromatogram>





3r (racemic)

1 PDA Multi 1 / 235nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥3r (rac)002.lcd

PDA Ch1 235nm 4nm

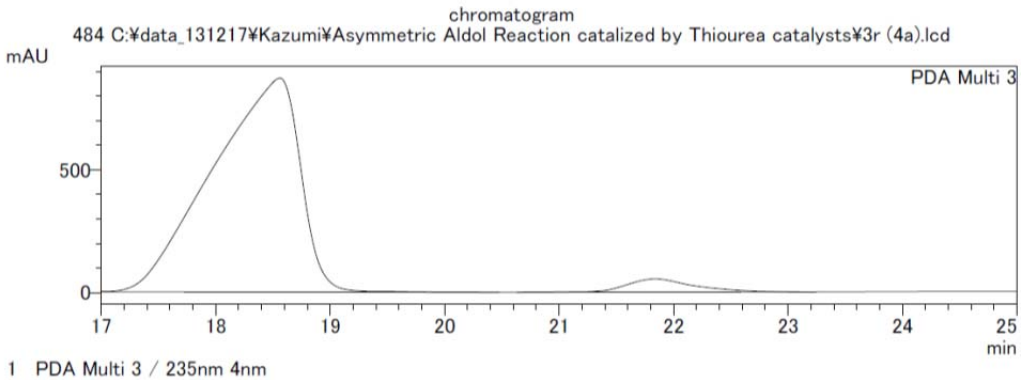
peak#	retention time (min)	area	area (%)
1	18.788	185363	53.433
2	23.035	161542	46.567

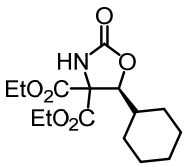
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3r (4a).lcd

sample ID : 484 table 2, 3r (4a)
method name : 0.5-iPrOH10-NO2-wash10.lcm
acquisition date : 2013/07/30 16:09:33
modified date : 2014/06/03 17:25:39

<Chromatogram>





3r (91%ee)

1 PDA Multi 3 / 235nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3r (4a).lcd

PDA Ch3 235nm 4nm

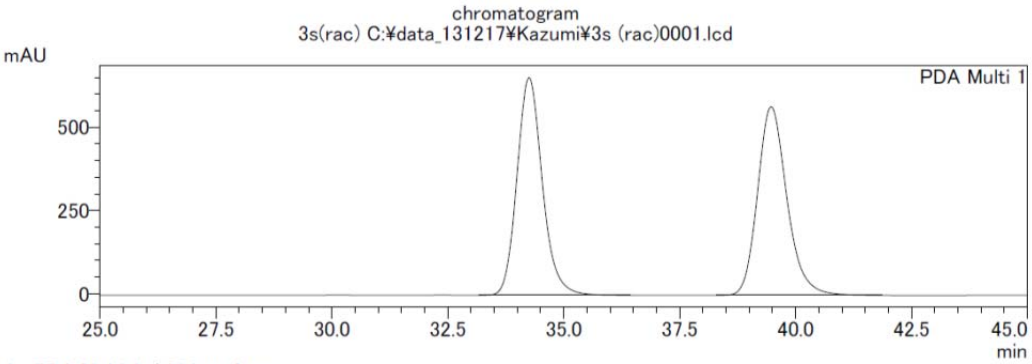
peak#	retention time (min)	area	area (%)
1	18.554	46472178	95.534
2	21.832	2172547	4.466

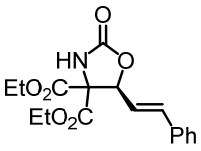
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥3s (rac)0001.lcd

sample ID : 3s(rac)
method name : 0.5-iPrOH10-NO5-wash10.lcm
acquisition date : 2014/07/24 17:47:55
modified date : 2014/07/24 18:47:59

<Chromatogram>





3s (racemic)

1 PDA Multi 1 / 254nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥3s (rac)0001.lcd

PDA Ch1 254nm 4nm

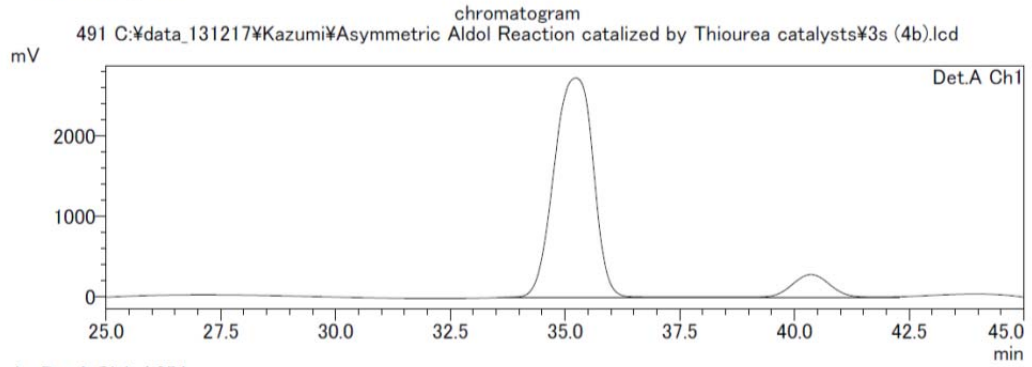
peak#	retention time (min)	area	area (%)
1	34.248	24885784	49.987
2	39.468	24899025	50.013

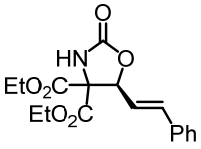
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3s (4b).lcd

sample ID : 491 table 2, 3s (4b)
method name : 254nm-0.5mL-90%.lcm
acquisition date : 2013/08/08 22:12:15
modified date : 2014/06/04 15:56:52

<Chromatogram>





3s (82%ee)

1 Det.A Ch1 / 254nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3s (4b).lcd

検出器A Ch1 254nm

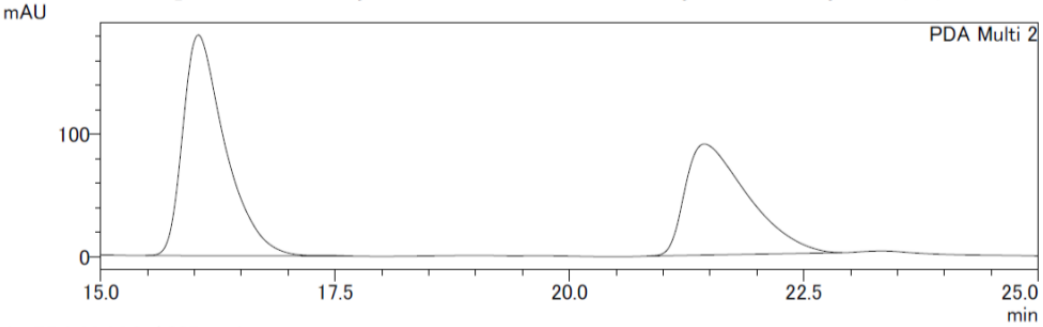
peak#	retention time (min)	area	area (%)
1	35.231	161158635	91.096
2	40.357	15752382	8.904

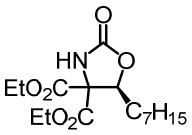
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3t (rac).lcd
sample ID : 475 table 2, 3t (rac)
method name : 0.5-iPrOH10-NO2-wash10.lcm
acquisition date : 2013/07/17 9:19:49
modified date : 2014/05/31 2:56:15

<Chromatogram>

chromatogram
475 C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3t (rac).lcd





3t (racemic)

1 PDA Multi 2 / 235nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3t (rac).lcd
PDA Ch2 235nm 4nm

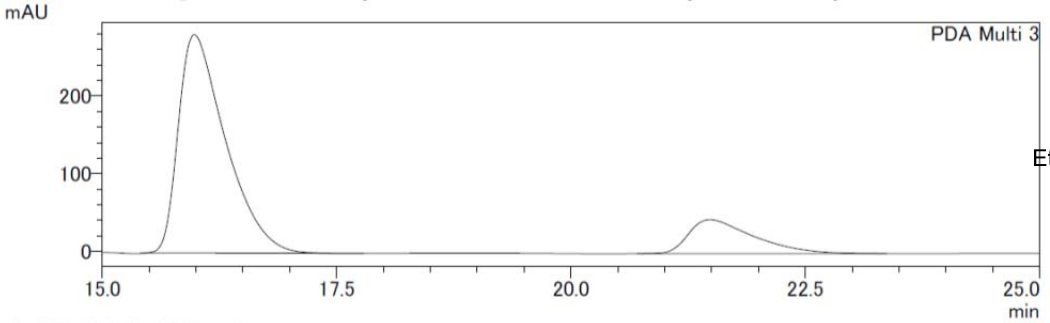
peak#	retention time (min)	area	area (%)
1	16.036	5648111	57.337
2	21.437	4202538	42.663

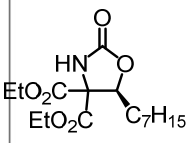
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3t (4b).lcd
sample ID : 498 table 2, 3t (4b)
method name : 0.5-iPrOH10-NO2-wash10.lcm
acquisition date : 2013/08/06 20:21:42
modified date : 2014/05/31 2:55:18

<Chromatogram>

chromatogram
498 C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3t (4b).lcd





3t (65%ee)

1 PDA Multi 3 / 235nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3t (4b).lcd
PDA Ch3 235nm 4nm

peak#	retention time (min)	area	area (%)
1	15.977	9842188	82.486
2	21.477	2089807	17.514

==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3u (rac).lcd
sample ID : 532 table 2, 3u (rac)
method name : 0.5-iPrOH5-NO4-wash10.lcm
acquisition date : 2013/09/10 23:30:32
modified date : 2014/07/19 9:54:34

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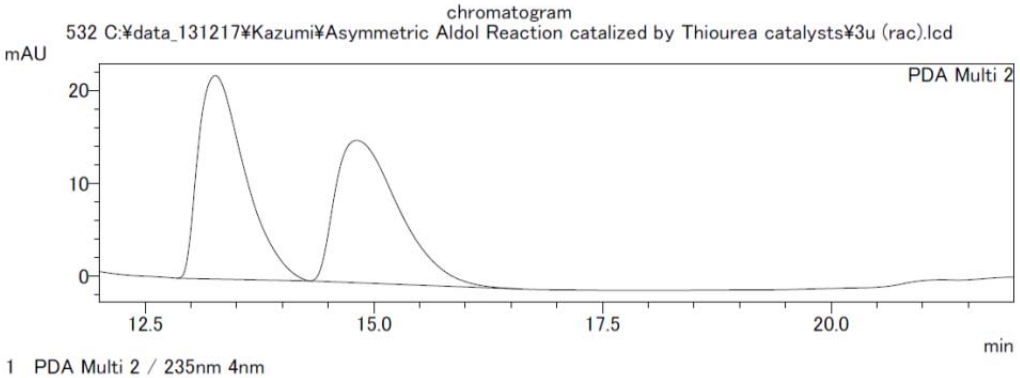
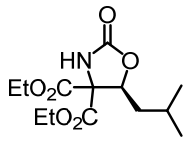




3u (racemic)

1 PDA Multi 2 / 235nm 4nm

<Peak Report>

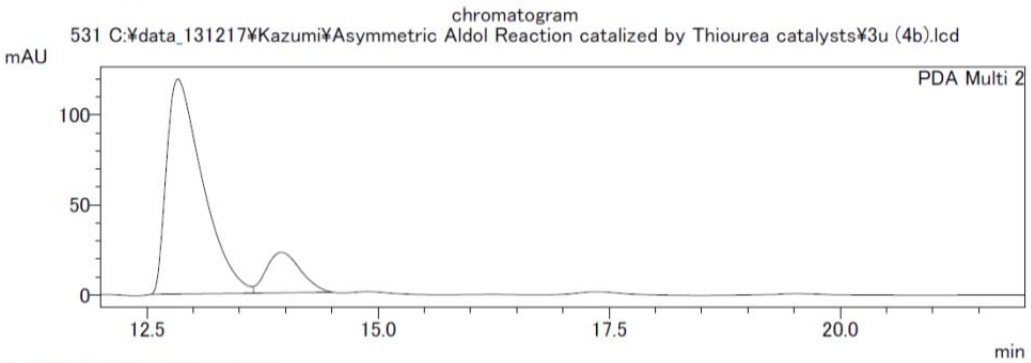
peak table C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3u (rac).lcd
PDA Ch2 235nm 4nm

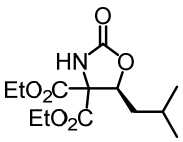
peak#	retention time (min)	area	area (%)
1	13.262	777679	51.168
2	14.807	742172	48.832

==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3u (4b).lcd
sample ID : 531 table 2, 3u (4b)
method name : 0.5-iPrOH10-NO4-wash10.lcm
acquisition date : 2013/09/18 13:01:10
modified date : 2014/07/19 9:55:15

<Chromatogram>





3u (70%ee)

1 PDA Multi 2 / 235nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥3u (4b).lcd
PDA Ch2 235nm 4nm

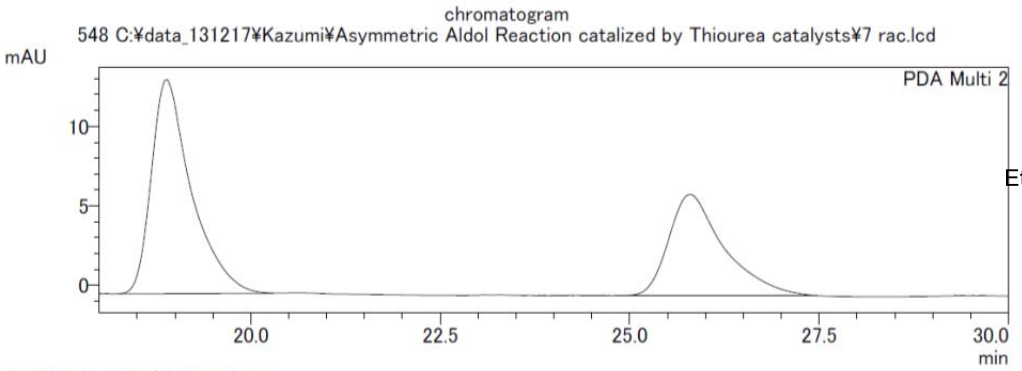
peak#	retention time (min)	area	area (%)
1	12.828	3268313	84.993
2	13.948	577090	15.007

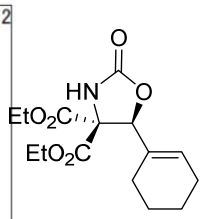
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥7 rac.lcd

sample ID : 548 scheme 2, 7 (rac)
method name : 0.5-iPrOH10-NO2-wash10.lcm
acquisition date : 2013/09/24 16:46:23
modified date : 2014/06/02 17:18:47

<Chromatogram>





7 (racemic)

1 PDA Multi 2 / 235nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥Asymmetric Aldol Reaction catalized by Thiourea catalysts¥7 rac.lcd

PDA Ch2 235nm 4nm

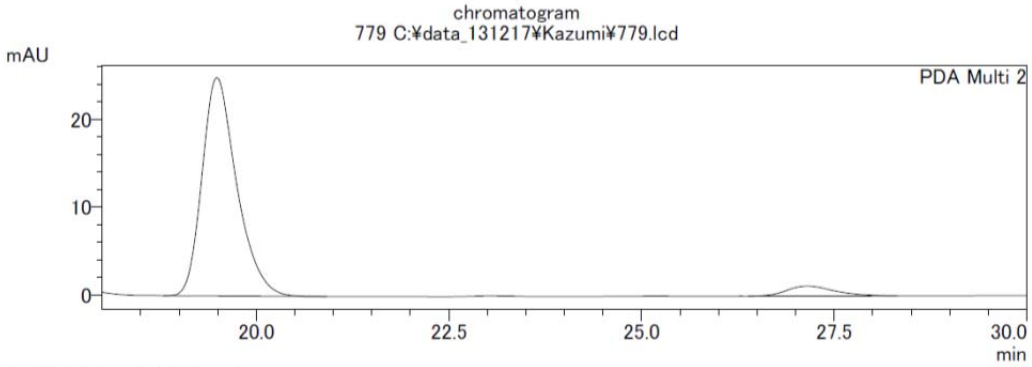
peak#	retention time (min)	area	area (%)
1	18.879	494312	60.614
2	25.783	321201	39.386

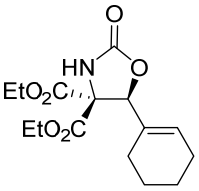
==== Shimadzu LCsolution Analysis Report ====

C:¥data_131217¥Kazumi¥779.lcd

sample ID : 779 scheme 2, 7 (4a)
method name : 0.5-iPrOH10-NO2-wash10.lcm
acquisition date : 2014/03/11 11:03:06
modified date : 2014/05/31 12:00:54

<Chromatogram>





7 (88%ee)

1 PDA Multi 2 / 235nm 4nm

<Peak Report>

peak table C:¥data_131217¥Kazumi¥779.lcd

PDA Ch2 235nm 4nm

peak#	retention time (min)	area	area (%)
1	19.484	777775	94.092
2	27.143	48836	5.908