Electronic Supplementary Material (ESI) for Chemical Communications

Formal Asymmetric Enone Aminohydroxylation: Organocatalytic One-pot Synthesis of 4,5-Disubstituted Oxazolidinones

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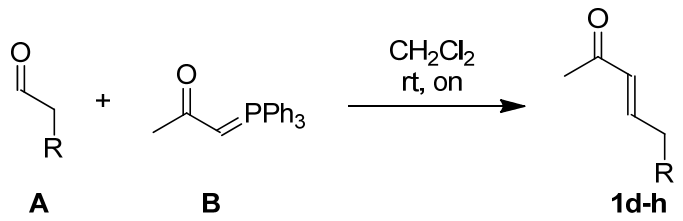
Supporting Information

1. General methods

NMR spectra were acquired on a Varian AS 400 spectrometer, running at 400 MHz for ^{1}H and 100 MHz for ^{13}C, respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CHCl_3$, 7.26 ppm for ^{1}H NMR, $CDCl_3$, 77.0 ppm for ^{13}C NMR). The following abbreviations are used to indicate the multiplicity in NMR spectra: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; bs, broad signal. ^{13}C NMR spectra were acquired on a broad band decoupled mode. Mass spectra were recorded on micromass LCT spectrometer using electrospray (ES^+) ionization techniques. Analytical thin layer chromatography (TLC) was performed using pre-coated aluminium-backed plates (Merck Kieselgel 60 F254) and visualized by ultraviolet irradiation or $KMnO_4$ dip. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. The melting points (mp) were measured in a Büchi Melting Point B-540 apparatus and the data were not normalized. The enantiomeric excess (*ee*) of the products was determined by chiral stationary phase HPLC (Chiralpack IB column). Unless otherwise noted, analytical grade solvents and commercially available reagents were used without further purification. For flash chromatography (FC) silica gel (SiO_2 60, 230-400 mesh, Fluka) was used.

2. Synthesis of the non-commercial enones 1d-h

To access to the noncommercial enones **1d-h** a methylenation reaction of the precursor aldehyde was carried out using the commercial Wittig reagent 1-(triphenylphosphoranylidene)acetone **B** (Scheme S1)

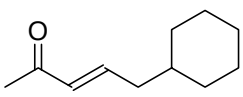


Scheme S1

General procedure.

To a solution of the commercial aldehyde **A** (2.00 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) the ylide **B** (955 mg, 3 mmol, 1.5 equiv) was added in one portion. The mixture was stirred at rt. After stirring for 12 h, the mixture was concentrated *in vacuo* and directly purified by FC on silica gel.

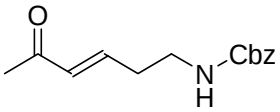
1d *E*-5-Cyclohexylpent-3-en-2-one



Following the general procedure and starting from cyclohexylacetaldehyde was isolated by FC on silica gel (pentane:AcOEt 20:1-10:1) in 75% yield as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 6.72 (td, *J* = 7.6, 16 Hz, 1H), 5.98 (td, *J* = 1.2, 16 Hz,

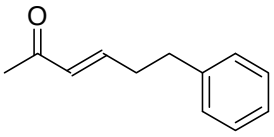
1H), 2.18 (s, 3H), 2.07-2.03 (m, 2H), 1.65-1.56 (m, 5H), 1.43-1.31 (m, 1H), 1.22-1.02 (m, 3H), 0.91-0.82 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 198.5, 147.3, 132.2, 40.4, 37.3, 33.1, 26.8, 26.3, 26.1. HRMS calc. for $C_{11}H_{19}O^+$ 167.1430 $[M+H]^+$, found 167.1429.

1e *E*-6-(Benzyloxycarbonyl)amino-hex-3-en-2-one



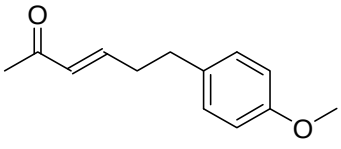
Following the general procedure and starting from 3-(benzyloxycarbonyl)aminopropenal was isolated by FC on silica gel (CH_2Cl_2:AcOEt 2:1) in 80% yield as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.32-7.24 (m, 5H), 6.66 (td, *J* = 6.4, 16 Hz, 1H), 6.05 (d, *J* = 16 Hz, 1H), 5.03 (s, 2H), 4.74 (bs, 1H), 3.30 (dd, *J* = 6.4, 13.2 Hz, 2H), 2.38 (dd, *J* = 6.4, 14.4 Hz, 2H), 2.17 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 198.6, 156.6, 144.5, 136.7, 128.7, 128.4, 128.3, 66.9, 39.7, 33.2, 27.2. HRMS calc. for $C_{14}H_{17}NO_3Na^+$ 270.1101 $[M+Na]^+$, found 270.1112.

1f *E*-6-Phenylhex-3-en-2-one



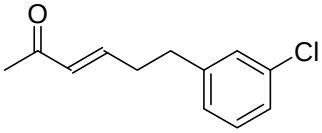
Following the general procedure and starting from 3-phenylpropionaldehyde was isolated by FC on silica gel (pentane:AcOEt 5:1) in 79% yield as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.32-7.29 (m, 2H), 7.24-7.18 (m, 3H), 6.83 (td, *J* = 6.8, 16 Hz, 1H), 6.10 (td, *J* = 1.6, 16 Hz, 1H), 2.79 (t, *J* = 6.8, 2H), 2.58-2.52 (m, 2H), 2.23 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 198.6, 147.1, 140.6, 131.7, 128.5, 128.3, 126.2, 34.4, 34.1, 26.9. HRMS calc. for $C_{12}H_{14}ONa^+$ 197.0937 $[M+Na]^+$, found 197.0937.

1g *E*-6-(4-Methoxyphenyl)hex-3-en-2-one



Following the general procedure and starting from 3-(4-methoxyphenyl)-propionaldehyde was isolated by FC on silica gel (pentane:AcOEt 6:1) in 65% yield as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 6.96 AA´BB´system (4H), 6.82-6.77 (m, 1H), 6.08 (td, *J* = 1.6, 16 Hz, 1H), 3.79 (s, 3H), 2.73 (t, *J* = 7.2 Hz, 2H), 2.54-2.48 (m, 2H), 2.23 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 198.5, 158.0, 147.2, 132.7, 131.6, 129.2, 113.9, 55.2, 34.4, 33.5, 26.8. HRMS calc. for $C_{13}H_{16}O_2Na^+$ 227.1042 $[M+Na]^+$, found 227.1046.

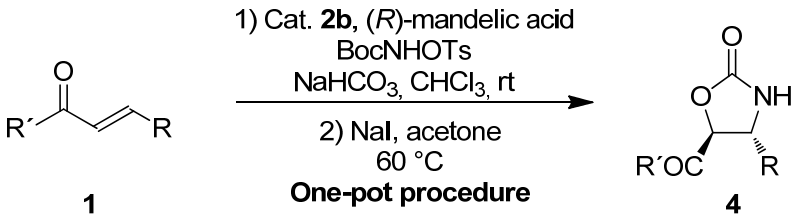
1h *E*-6-(3-Chlorophenyl)hex-3-en-2-one



Following the general procedure and starting from 3-(3-chlorophenyl)-propionaldehyde was isolated by FC on silica gel (pentane:AcOEt 5:1) in 61% yield as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.25-7.18 (m, 3H), 7.07-7.04 (m, 1H), 6.79 (td, *J* = 6.8, 16 Hz, 1H), 6.09 (td, *J* = 1.6, 16 Hz, 1H), 2.79

(t, *J* = 7.2 Hz, 2H), 2.57-2.51 (m, 2H), 2.24 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 198.4, 146.3, 142.6, 134.2, 131.8, 129.8, 128.4, 126.5, 126.4, 34.0, 33.7, 27.0. HRMS calc. for $C_{12}H_{14}ClO^+$ 209.0728 [M+H$^+$], found 209.0730.

3. Organocatalytic asymmetric formal *trans*-aminohydroxylation of α,β-unsaturated ketones

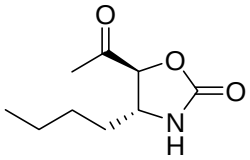


1 **4**

General procedure.

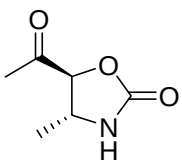
A normal glass vial equipped with a magnetic stirring bar was charged with the catalyst **2b** (6.47 mg, 0.02 mmol, 10 mol%) *R*-mandelic acid (4.53 mg, 0.03 mmol, 15 mol%) and $CHCl_3$ (0.35 mL). After 10 min stirring at rt, the enone **1** (0.20 mmol, 1.0 equiv) was added and the mixture stirred for another 10 min at rt. Then BocNHOTs (68.96 mg, 0.24 mmol, 1.2 equiv) and $NaHCO_3$ (33.6 mg, 0.40 mmol, 2.0 equiv) was added at one time. After stirring 24 h at 50 °C, NaI (60 mg, 0.40 mmol, 2.0 equiv) and acetone (2 mL) was added and stirred 48 h at 60 °C. The crude reaction was concentrated *in vacuo* and purified by FC on silica gel. Only the major diastereomer was characterized.

4a (4*R*,5*S*)-5-Acetyl-4-butyloxazolidin-2-one (Table 1, entry 1).



Following the general procedure **4a** was isolated by FC on silica gel (Et_2O) as a colorless oil in 64% global yield (dr >20:1; only one diasteromer is observed by ^{1}H-NMR in the crude) and 98% ee (HPLC analysis on a Chiralpak IB column after derivatization 90/10 hexane/i-PrOH, flow rate 1.00 mL/min, λ = 220 nm τ_{major} = 5.85 min, τ_{minor} = 6.83 min). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 6.50 (bs, 1H), 4.41 (d, *J* = 5.1 Hz, 1H), 3.83 (dt, *J* = 5.7, 5.1 Hz, 1H), 2.35 (s, 3H), 1.75-1.49 (m, *2*H), 1.42-1.28 (m, 4H), 0.92 (t, *J* = 6.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 206.1, 158.2, 84.1, 55.2, 35.6, 27.0, 26.4, 22.2, 13.8. HRMS calc. for $C_9H_{15}NO_3$ 185.1052; found 185.1052. $[\alpha]_D^{20}$: +8.0 (c=0.93, $CHCl_3$).

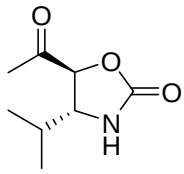
4b (4*R*,5*S*)-5-Acetyl-4-methyloxazolidin-2-one (Table , entry 2).



Following the general procedure **4b** was isolated by FC on silica gel (Et_2O:AcOEt 2:1) as a white solid in 78% global yield (dr >20:1; only one diasteromer is observed by ^{1}H-NMR in the crude) and 99% ee (HPLC analysis on a Chiralpak IB column after derivatization 90/10 hexane/i-PrOH, flow rate 1.00 mL/min, λ = 220 nm τ_{major} = 7.61 min, τ_{minor} = 10.34 min) mp: 107-109 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 5.31 (bs, 1H), 4.35 (d, *J* = 5.8 Hz, 1H), 3.95 (p, *J* = 6.2 Hz, 1H),

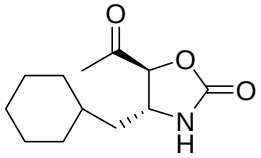
2.33 (s, 3H), 1.40 (d, *J* = 6.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 205.6, 157.9, 85.5, 51.0, 26.4, 21.6. HRMS calc. for $C_6H_9NO_3$ 143.0582; found 143.0582. $[\alpha]_D^{20}$: -21.6 (c=1.12, $CHCl_3$).

4c (4*R*,5*S*)-5-Acetyl-4-isopropyloxazolidin-2-one (Table 1, entry 3).



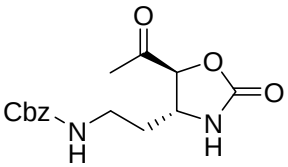
Following the general procedure **4c** was isolated by FC on silica gel (Et_2O) as a white solid in 51% global yield (dr >20:1; only one diasteromer is observed by ^{1}H-NMR in the crude) and 98% ee (HPLC analysis on a Chiralpak IB column after derivatization 90/10 hexane/i-PrOH, flow rate 1.00 mL/min, λ = 220 nm τ_{major} = 5.80 min, τ_{minor} = 7.11 min). mp: 76 °C ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 5.86 (bs, 1H), 4.47 (d, *J* = 4.3 Hz, 1H), 3.62 (t, *J* = 5.2 Hz, 1H), 2.32 (s, 3H), 1.81 (hex, *J* = 6.5 Hz 1H), 0.99-0.94 (m, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 206.8, 158.6, 82.1, 60.5, 32.7, 26.3, 17.7, 17.1. HRMS calc. for $C_8H_{13}NO_3$ 171.0895; found 171.0895. $[\alpha]_D^{20}$: -8.6 (c=1.16, $CHCl_3$).

4d (4*R*,5*S*)-5-Acetyl-4-cyclohexylmethyloxazolidin-2-one (Table 1, entry 4).



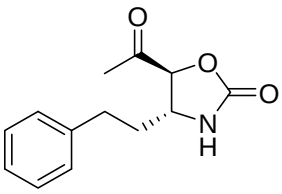
Following the general procedure **4d** was isolated by FC on silica gel (Et_2O) as a white solid in 81% global yield (dr >20:1; only one diasteromer is observed by ^{1}H-NMR in the crude) and 97% ee (HPLC analysis on a Chiralpak IB column after derivatization 95/5 hexane/i-PrOH, flow rate 1.00 mL/min, λ = 220 nm τ_{major} = 6.98 min, τ_{minor} = 8.12 min). mp: 71-73 °C ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 6.62 (bs, 1H), 4.36 (d, *J* = 5.2 Hz, 1H), 3.91 (ddd, *J* = 0.8, 5.2, 13.6 Hz, 1H), 2.32 (s, 3H), 1.82-1.62 (m, 5H), 1.41-1.10 (m, 4H), 1.53 (dd, *J* = 0.8, 7.2, 2H) 0.98-0.874 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 206.0, 158.3, 84.5, 52.9, 43.7, 34.0, 33.4, 32.6, 26.5, 26.2, 25.9, 25.8. HRMS calc. for $C_{12}H_{19}NO_3Na^+$ 248.1257 $[M+Na]^+$; found 248.1261. $[\alpha]_D^{20}$: -12.2 (c=1.65, $CHCl_3$).

4e (4*R*,5*S*)-4-(2´-Benzyloxycarbonyl-aminoethanyl)-5-acyloxazolidin-2-one (Table 1, entry 5).



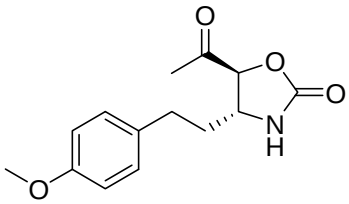
Following the general procedure **4e** was isolated by FC on silica gel (AcOEt:Et_2O 2:1) as a colorless oil in 56% global yield (dr >20:1; only one diasteromer is observed by ^{1}H-NMR in the crude) and 94% ee (HPLC analysis on a Chiralpak IB column after derivatization 80/20 hexane/i-PrOH, flow rate 1.00 mL/min, λ = 220 nm τ_{major} = 13.31 min, τ_{minor} = 15.45 min). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.29-7.25 (m, 5H), 6.29 (bs, 1H), 5.02 (dd, *J* = 12.4, 15.2 Hz, 2H), 4.28 (d, *J* = 5.6 Hz, 1H), 3.76-3.72 (m, 1H), 3.50-3.39 (m, 1H), 3.16-3.08 (m, 1H), 2.27 (s, 3H), 1.83-1.75 (m, 1H), 1.72-1.64 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 206.3, 157.4, 157.1, 136.1, 128.5, 128.2, 128.0, 83.7, 67.0, 52.6, 37.0, 36.4, 26.5. HRMS calc. for $C_{15}H_{18}N_2O_5$ 306.1216; found 306.1216. $[\alpha]_D^{20}$: +25.7 (c=1.9, $CHCl_3$).

4f (4*R*,5*S*)-5-Acetyl-4-phenethyl-oxazolidin-2-one (Table 1, entry 6).



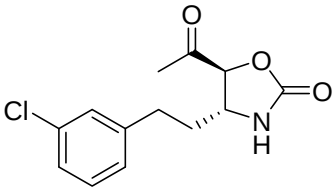
Following the general procedure **4f** was isolated by FC on silica gel (Et_2O) as a colorless oil in 73% global yield (dr >20:1; only one diasteromer is observed by ^{1}H-NMR in the crude) and 98% ee (HPLC analysis on a Chiralpak IB column after derivatization 90/10 hexane/i-PrOH, flow rate 1.00 mL/min, λ = 220 nm τ_{major} = 8.43 min, τ_{minor} = 12.46 min). mp: 69-70 °C ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.27-7.11 (m, 5H), 5.27 (bs, 1H), 4.35 (d, *J* = 5.6 Hz, 1H), 3.81-3.77 (m, 1H), 2.71-2.60 (m, 2H), 2.27 (s, 3H), 2.05-1.85 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 205.8, 158.2, 139.9, 128.7, 128.3, 126.5, 84.1, 54.8, 37.5, 31.4, 26.5. HRMS calc. for $C_{13}H_{15}NO_3Na^+$ 256.0944 $[M+Na]^+$; found 256.0947. $[\alpha]_D^{20}$: +30.7 (c=0.9, $CHCl_3$).

4g (4*R*,5*S*)-5-Acetyl-4-[2-(4-methoxyphenyl)-ethyl]-oxazolidin-2-one (Table 1, entry 7).



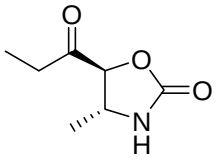
Following the general procedure **4g** was isolated by FC on silica gel (Et_2O) as a colorless oil in 93% global yield (dr >20:1; only one diasteromer is observed by ^{1}H-NMR in the crude) and 98% ee (HPLC analysis on a Chiralpak IB column after derivatization 90/10 hexane/i-PrOH, flow rate 1.00 mL/min, λ = 220 nm τ_{major} = 10.48 min, τ_{minor} = 17.32 min). ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 6.96 AA´BB´ (4H), 6.12 (bs, 1H), 4.42 (d, *J* = 5.2 Hz, 1H), 3.85-3.80 (m, 1H), 3.78 (s, 3H) 2.66 (t, *J* = 7.6 2H), 2.32 (s, 3H), 2.06-1.87 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 205.9, 158.2, 157.9, 131.7, 129.3, 114.1, 84.1, 55.2, 54.7, 37.7, 30.6, 26.5. HRMS calc. for $C_{14}H_{17}NO_4Na^+$ 286.1050 $[M+Na]^+$; found 286.1053. $[\alpha]_D^{20}$: +33.6 (c=2.37, $CHCl_3$).

4h (4*R*,5*S*)-5-Acetyl-4-[2-(3-chlorophenyl)-ethyl]-oxazolidin-2-one (Table 1, entry 8).



Following the general procedure **4h** was isolated by FC on silica gel (Et_2O) as a colorless oil in 53% global yield (dr 17:1; determinated by integration of one set of ^{1}H-NMR signal: δ_{major} 4.38 ppm, δ_{minor} 4.63) and 99% ee (HPLC analysis on a Chiralpak IB column after derivatization 90/10 hexane/i-PrOH, flow rate 1.00 mL/min, λ = 220 nm τ_{major} = 8.85 min, τ_{minor} = 12.51 min). mp: 62-63 °C ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.17-7.12 (m, 3H), 7.02-6.99 (m, 1H), 5.84 (bs, 1H), 4.37 (d, *J* = 5.2 Hz, 1H), 3.79 (ddd, *J* = 0.8, 5.2, 12.4, 1H), 2.63 (t, *J* = 7.6 2H), 2.28 (s, 3H), 2.02-1.84 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 205.8, 158.1, 141.9, 134.4, 129.9, 128.5, 126.7, 126.5, 84.0, 54.6, 37.3, 31.0, 26.5. HRMS calc. for $C_{13}H_{14}ClNO_3Na^+$ 290.0554 $[M+Na]^+$; found 290.0557. $[\alpha]_D^{20}$: +25.7 (c=0.76, $CHCl_3$).

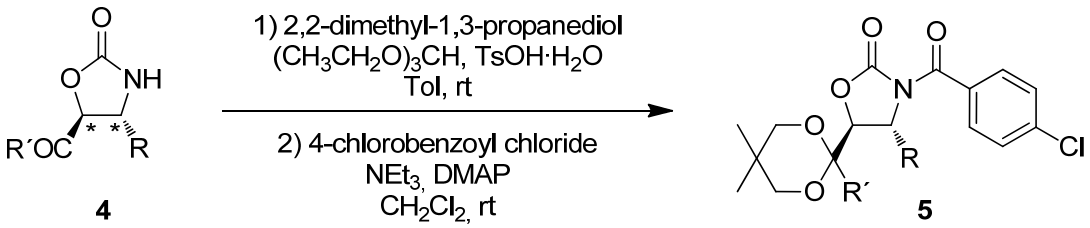
4i (4*R*,5*S*)-4-Methyl-5-propionyl-oxazolidin-2-one (Table 1, entry 9).



Following the general procedure **4b** was isolated by FC on silica gel (Et_2O) as a white solid in 57% global yield (dr 15:1; determinated by integration of one set of ^{1}H-NMR signal: δ_{major} 4.36 ppm, δ_{minor} 4.68) and 99% ee (HPLC analysis on a Chiralpak IC column

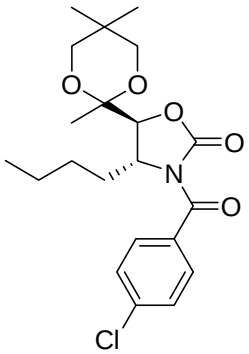
after derivatization 95/5 hexane/i-PrOH, flow rate 1.00 mL/min, λ = 220 nm τ_{major} = 15.08 min, τ_{minor} = 14.00 min) mp: 89 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 5.58 (bs, 1H), 4.37 (d, *J* = 5.8 Hz, 1H), 3.93 (m, 1H), 2.68 (q, *J* = 7.2 Hz, 2H), 1.39 (d, *J* = 6.2 Hz, 3H), 1.07 (t, *J* = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 208.3, 157.9, 85.3, 51.2, 32.2, 21.6, 6.7. HRMS calc. for $C_7H_{11}NO_3$ 157.0739; found 157.0739. $[\alpha]_D^{20}$: -21.4 (c=0.56, $CHCl_3$).

4. Derivatization of oxazolidin-2-ones 4a-4i



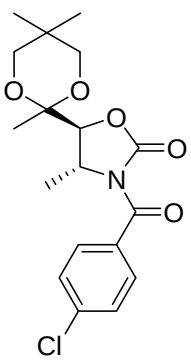
General procedure: A normal glass vial equipped with magnetic stirring bar was charged with the corresponding oxazolidin-2-one **4** (0.10 mmol, 1.0 equiv), 2,2-dimethyl-1,3-propanediol (31.25 mg, 0.30 mmol, 3.0 equiv), triethylorthoformate (29.64 mg, 0.20 mmol, 2.0 equiv), $TsOH·H_2O$ (0.95 mg, 5.00 μmol, 50.0 mequiv) and toluene (0.5 mL). After stirring 24 h at rt (60 °C for **4i**) the crude reaction was directly added to a short-pad of silica gel (Et_2O) to remove side products, then the solvent was removed and was added 4-chlorobenzoyl chloride (26.25 mg, 0.15 mmol, 1.5 equiv), Et_3N (15.17 mg, 0.15 mmol, 1.5 equiv), DMAP (3.66 mg, 0.03 mmol, 0.3 equiv) and CH_2Cl_2 (0.5 mL). After 1 h stirring at rt, the product was directly purified by FC on silica gel.

5a (4*R*,5*S*)-4-Butyl-3-(4-chlorobenzoyl)-5-(2,5,5-trimethyl-[1,3]dioxan-2-yl)-oxazolidin-2-one



Following the general procedure **5a** was isolated by FC on silica gel (pentane:AcOEt 8:1) as a white solid in 60% global yield. mp: 83-85 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.45 AA´BB´ system (4H), 4.87 (ddd, *J* = 2.4, 3.6, 8.4 Hz, 1H), 4.06 (d, *J* = 2.4 Hz, 1H), 3.71 (dd, *J* = 11.6, 21.2 Hz, 2H), 3.44-3.38 (m, 2H), 1.96-1.78 (m, 2H), 1.51 (s, 3H), 1.43-1.32 (m, 4H), 1.18 (s, 3H) 0.93 (t, *J* = 7.2 Hz, 3H), 0.77 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 168.2, 153.2, 138.0, 132.0, 130.0, 128.1, 97.6, 82.2, 70.3, 70.2, 55.4, 32.6, 30.2, 26.2, 23.3, 22.3, 22.2, 14.3, 13.9. HRMS calc. for $C_{21}H_{28}ClNO_5Na^+$ 432.1548 $[M+Na]^+$; found 432.1555. $[\alpha]_D^{20}$: -58.1 (c=0.9, $CHCl_3$).

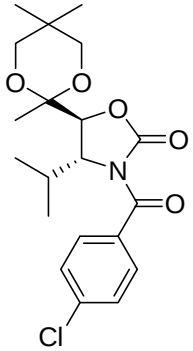
5b (4*R*,5*S*)-3-(4-Chlorobenzoyl)-4-methyl-5-(2,5,5-trimethyl-[1,3]dioxan-2-yl)-oxazolidin-2-one



Following the general procedure **5b** was isolated by FC on silica gel (pentane:AcOEt 5:1) as a white solid in 76% global yield. mp: 142-144 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.45 AA´BB´ system (4H), 4.93 (dq, *J* = 3.6, 6.8 Hz, 1H), 3.99 (d, *J* = 3.6 Hz, 1H), 3.71 (dd, *J* =

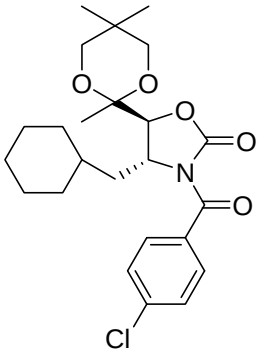
11.6, 18 Hz, 2H), 3.41 (ddd, *J* = 2.4, 4.4, 11.6 Hz, 2H), 1.54 (d, *J* = 6.8 Hz, 3H), 1.51 (s, 3H), 1.17 (s, 3H), 0.77 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 168.3, 152.9, 138.2, 132.0, 130.1, 128.2, 97.6, 84.1, 70.3, 70.2, 51.8, 30.2, 23.3, 22.2, 19.9, 14.4. HRMS calc. for $C_{18}H_{22}ClNO_5Na^+$ 390.1079 $[M+Na]^+$; found 390.1111. $[\alpha]_D^{20}$: -68.4 (c=1.31, $CHCl_3$).

5c (4*R*,5*S*)-3-(4-Chlorobenzoyl)-4-isopropyl-5-(2,5,5-trimethyl-[1,3]dioxan-2-yl)-oxazolidin-2-one



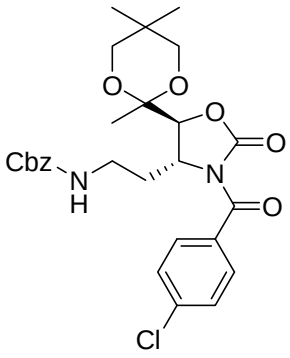
Following the general procedure **5c** was isolated by FC on silica gel (pentane:AcOEt 7:1) as a white solid in 34% global yield. mp: 149-151 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.45 AA´BB´ system (4H), 4.84 (dd, *J* = 2.4, 4.4 Hz, 1H), 4.10 (d, *J* = 2.4 Hz, 1H), 3.70 (dd, *J* = 11.6, 21.6 Hz, 2H), 3.44-3.38 (m, 2H), 2.39 (dhex, *J* = 4.4, 6.4 Hz, 1H), 1.50 (s, 3H), 1.19 (s, 3H), 0.99 (d, *J* = 6.4 Hz, 3H), 0.98 (d, *J* = 6.4 Hz, 3H) 0.76 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 168.4, 153.6, 138.0, 132.1, 130.1, 128.1, 97.7, 78.9, 70.4, 70.3, 59.6, 30.2, 29.8, 23.3, 22.2, 18.0, 16.0, 14.2. HRMS calc. for $C_{20}H_{26}ClNO_5Na^+$ 418.1392 $[M+Na]^+$; found 418.1398. $[\alpha]_D^{20}$: -58.0 (c=0.89, $CHCl_3$).

5d (4*R*,5*S*)-3-(4-Chlorobenzoyl)-4-cyclohexylmethyl-5-(2,5,5-trimethyl-[1,3]dioxan-2-yl)-oxazolidin-2-one



Following the general procedure **5d** was isolated by FC on silica gel (pentane:AcOEt 10:1) as a white solid in 35% global yield. mp: 148-150 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.43 AA´BB´ system (4H), 4.96 (ddd, *J* = 2.0, 3.6, 10.4 Hz, 1H), 4.05 (d, *J* = 2.0 Hz, 1H), 3.71 (dd, *J* = 11.6, 26.0 Hz, 2H), 3.43-3.37 (m, 2H), 1.95-1.84 (m, 2H), 1.75-1.54 (m, 5H) 1.51 (s, 3H), 1.42-1.12 (m, 4H), 1.18 (s, 3H), 1.07-0.96 (m, 2H), 0.77 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 167.0, 152.2, 136.9, 131.1, 129.0, 127.1, 96.6, 81.8, 69.4, 69.2, 52.6, 39.9, 33.0, 32.6, 31.1, 29.2, 25.4, 25.2, 24.9, 22.3, 21.2, 13.3. HRMS calc. for $C_{24}H_{32}ClNO_5Na^+$ 472.1861 $[M+Na]^+$; found 472.1874. $[\alpha]_D^{20}$: -50.8 (c=1.37, $CHCl_3$).

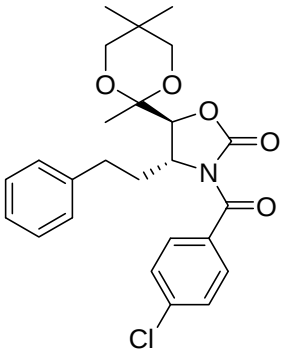
5e (4*R*,5*S*)-{2-[3-(4-Chlorobenzoyl)-2-oxo-5-(2,5,5-trimethyl-[1,3]dioxan-2-yl)-oxazolidin-4-yl]-ethyl}-carbamic acid benzyl ester



Following the general procedure **5e** was isolated by FC on silica gel (pentane:AcOEt 2:1) as a colorless oil in 81% global yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.37 AA´BB´ system (4H), 7.28-7.23 (m, 5H), 5.27 (bs, 1H), 5.03 (s, 2H), 4.91 (ddd, *J* = 2.4, 6.0, 8.0 Hz, 1H), 4.04 (d, *J* = 2.4 Hz, 1H), 3.63 (dd, *J* = 12.0, 23.6 Hz, 2H), 3.41-3.30 (m, 3H), 3.22-3.14 (m, 1H), 2.13-2.03 (m, 1H), 1.95-1.87 (m, 1H), 1.43 (s, 3H), 1.06 (s, 3H), 0.68 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 168.7, 156.3, 152.8, 138.3, 136.6, 131.6, 130.1, 128.5, 128.2, 128.1, 97.7, 82.6, 70.3, 70.2, 66.6, 60.3, 53.2, 37.2, 34.0, 30.2, 23.2, 22.2, 14.3. HRMS calc. for

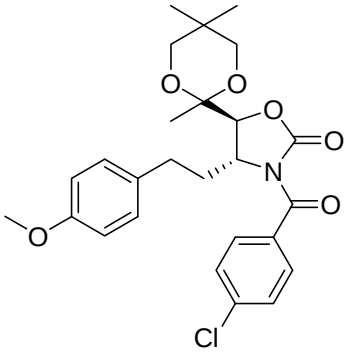
$C_{27}H_{31}ClN_2O_7Na^+$ 553.1712 $[M+Na]^+$; found 553.1730. $[\alpha]_D^{20}$: -22.7 (c=1.05, $CHCl_3$).

5f (4*R*,5*S*)-3-(4-Chlorobenzoyl)-4-phenethyl-5-(2,5,5-trimethyl-[1,3]dioxan-2-yl)-oxazolidin-2-one



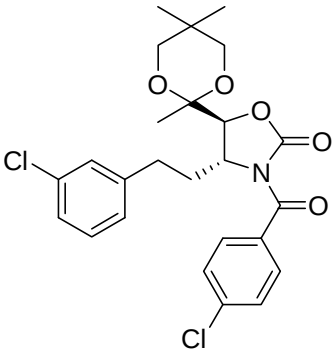
Following the general procedure **5f** was isolated by FC on silica gel (pentane:AcOEt 6:1) as a colorless oil in 31% global yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.42 AA´BB´ system (4H), 7.31-7.18 (m, 5H) 4.94 (ddd, *J* = 2.8, 3.6, 8.8 Hz, 1H), 4.16 (d, *J* = 2.8 Hz, 1H), 3.71 (dd, *J* = 11.2, 23.6 Hz, 2H), 3.43-3.37 (m, 2H), 2.81-2.66 (m, 2H), 2.37-2.29 (m, 1H), 2.18-2.09 (m, 1H), 1.53 (s, 3H), 1.10 (s, 3H), 0.76 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 168.2, 153.0, 140.3, 138.1, 131.9, 130.0, 128.5, 128.3, 128.1, 126.2, 97.6, 82.2, 70.3, 55.1, 34.3, 30.9, 30.5, 30.2, 23.3, 22.2, 14.3. HRMS calc. for $C_{25}H_{28}ClNO_5Na^+$ 480.1548 $[M+Na]^+$; found 480.1571. $[\alpha]_D^{20}$: -32.7 (c=0.4, $CHCl_3$).

5g (4*R*,5*S*)-3-(4-Chlorobenzoyl)-4-[2-(4-methoxy-phenyl)-ethyl]-5-(2,5,5-trimethyl-[1,3]dioxan-2-yl)-oxazolidin-2-one



Following the general procedure **5g** was isolated by FC on silica gel (pentane:AcOEt 4:1) as a colorless oil in 67% global yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.42 AA´BB´ system (4H), 6.98 AA´BB´ system (4H), 4.92 (ddd, *J* = 2.4, 3.2, 8.8 Hz, 1H), 4.15 (d, *J* = 2.4 Hz, 1H), 3.78 (s, 3H), 3.74 (dd, *J* = 11.2, 23.6 Hz, 2H), 3.43-3.37 (m, 2H), 2.76-2.61 (m, 2H), 2.33-2.25 (m, 1H), 2.15-2.06 (m, 1H), 1.52 (s, 3H), 1.10 (s, 3H), 0.76 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 168.2, 158.0, 153.0, 138.1, 132.3, 131.9, 130.0, 129.3, 128.1, 113.9, 97.6, 82.2, 70.3, 55.2, 55.1, 34.4, 30.2, 29.6, 23.3, 22.2, 14.4. HRMS calc. for $C_{26}H_{30}ClNO_6Na^+$ 510.1654 $[M+Na]^+$; found 510.1668. $[\alpha]_D^{20}$: -32.5 (c=1.94, $CHCl_3$).

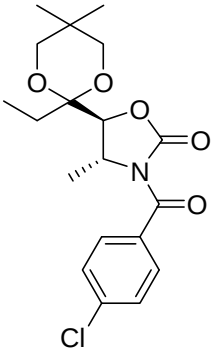
5h (4*R*,5*S*)-3-(4-Chlorobenzoyl)-4-[2-(3-chloro-phenyl)-ethyl]-5-(2,5,5-trimethyl-[1,3]dioxan-2-yl)-oxazolidin-2-one



Following the general procedure **5h** was isolated by FC on silica gel (pentane:AcOEt 5:1) as a colorless oil in 74% global yield. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.42 AA´BB´ system (4H), 7.25-7.12 (m, 4H), 4.89 (ddd, *J* = 2.4, 3.2, 9.2 Hz, 1H), 4.12 (d, *J* = 2.4 Hz, 1H), 3.71 (dd, *J* = 11.6, 28.0 Hz, 2H), 3.40 (ddd, *J* = 2.4, 11.6, 26.0 Hz, 2H), 2.82-2.62 (m, 2H), 2.39-2.31 (m, 1H), 2.14-2.06 (m, 1H), 1.53 (s, 3H), 1.06 (s, 3H), 0.76 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 167.2, 152.0, 141.2, 137.1, 133.1, 130.8, 129.0, 128.7, 127.8, 127.2, 125.5, 124.4, 96.6, 81.2, 69.3, 69.2, 53.9, 32.9, 29.2, 29.1, 22.1, 21.2, 13.4. HRMS calc. for $C_{25}H_{27}Cl_2NO_6Na^+$ 514.1158 $[M+Na]^+$; found 514.1170. $[\alpha]_D^{20}$: -

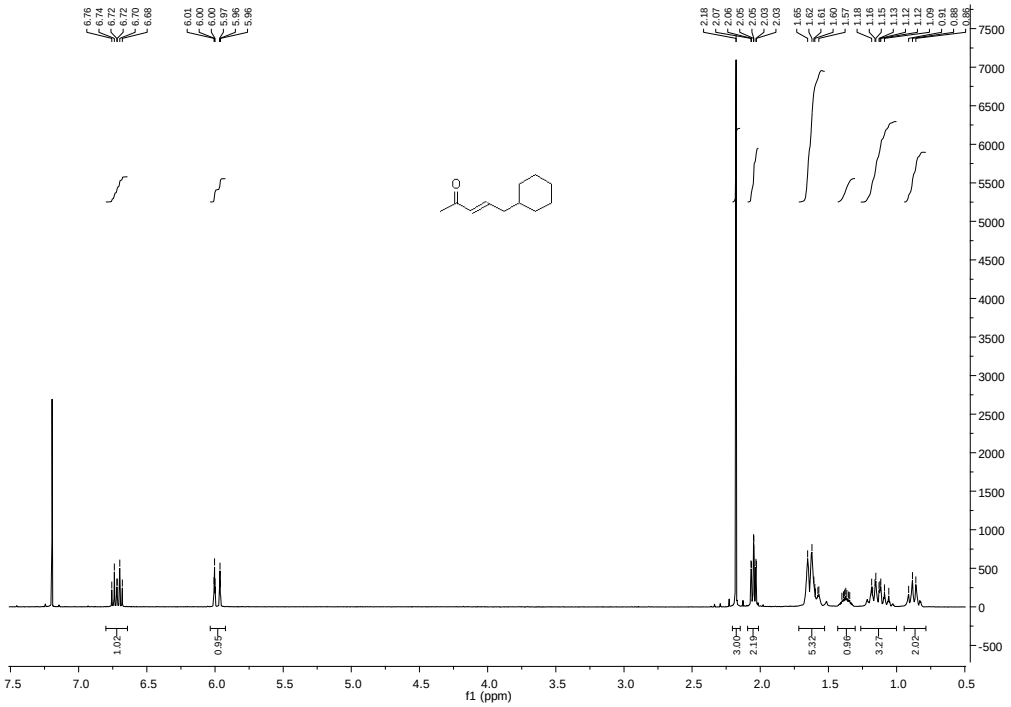
24.0 (c=0.85, $CHCl_3$).

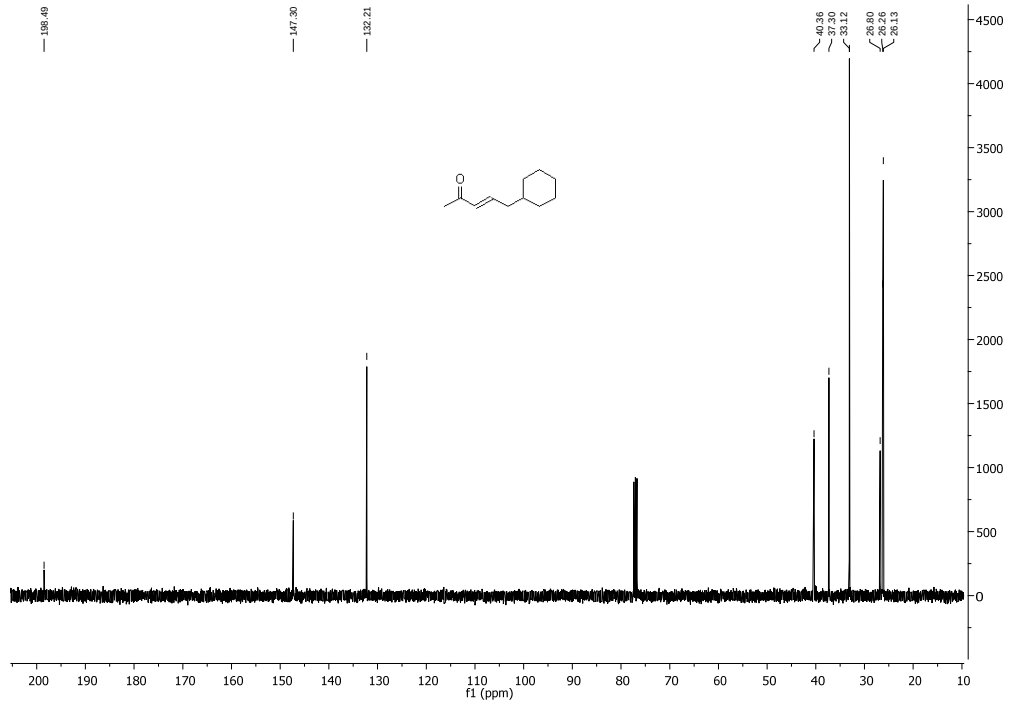
5i (4*R*,5*S*)- 3-(4-Chlorobenzoyl)-5-(2-ethyl-5,5-dimethyl-[1,3]dioxan-2-yl)-4-methyl-oxazolidin-2-one



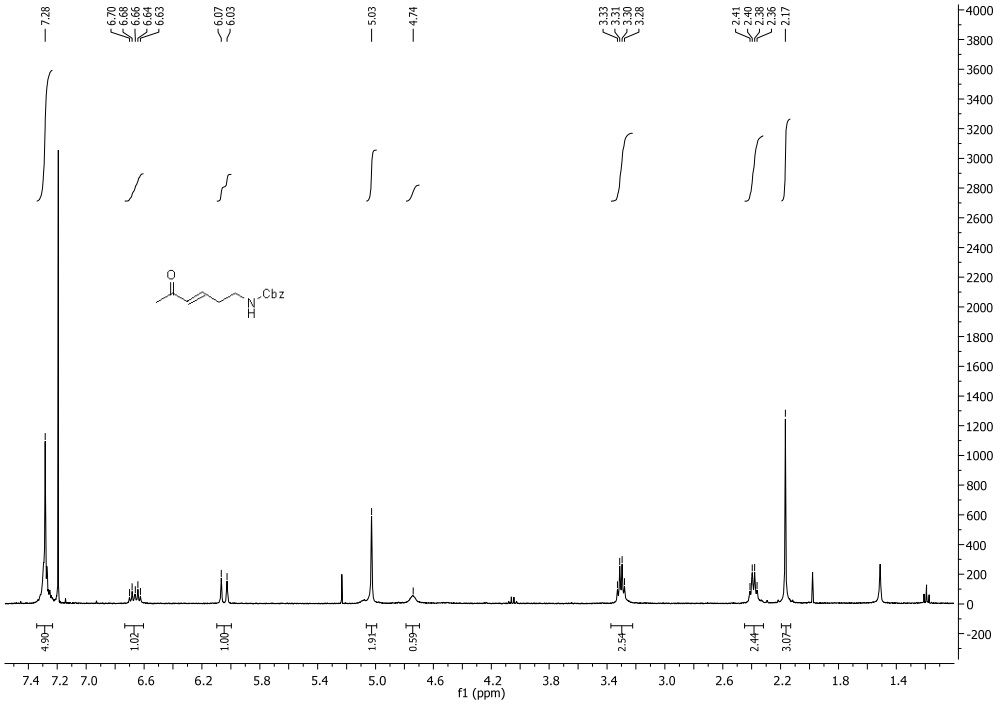
Following the general procedure **5i** was isolated by FC on silica gel (pentane:AcOEt 6:1) as a white solid in 37% global yield. mp: 149-150 °C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ ppm 7.45 AA´BB´ system (4H), 4.91 (dq, *J* = 3.6, 6.4 Hz, 1H), 4.06 (d, *J* = 3.6 Hz, 1H), 3.61 (dd, *J* = 11.6, 33.6 Hz, 2H), 3.32 (d, *J* = 11.6 Hz, 2H), 2.21 (qd, *J* = 7.2, 14.8, Hz, 1H), 1.70 (qd, *J* = 7.6, 14.8 Hz, 1H), 1.48 (d, *J* = 6.4 Hz, 3H), 1.11 (s, 3H), 0.86 (t, *J* = 6.4 Hz, 3H) 0.70 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ ppm 168.3, 152.9, 138.1, 132.0, 130.1, 128.2, 99.2, 80.4, 70.0, 69.9, 51.8, 29.8, 23.5, 22.3, 19.9, 18.6, 7.4. HRMS calc. for $C_{19}H_{24}ClNO_5K^+$ 420.0975 $[M+K]^+$; found 420.0978. $[\alpha]_D^{20}$: -58.5 (c=0.49, $CHCl_3$).

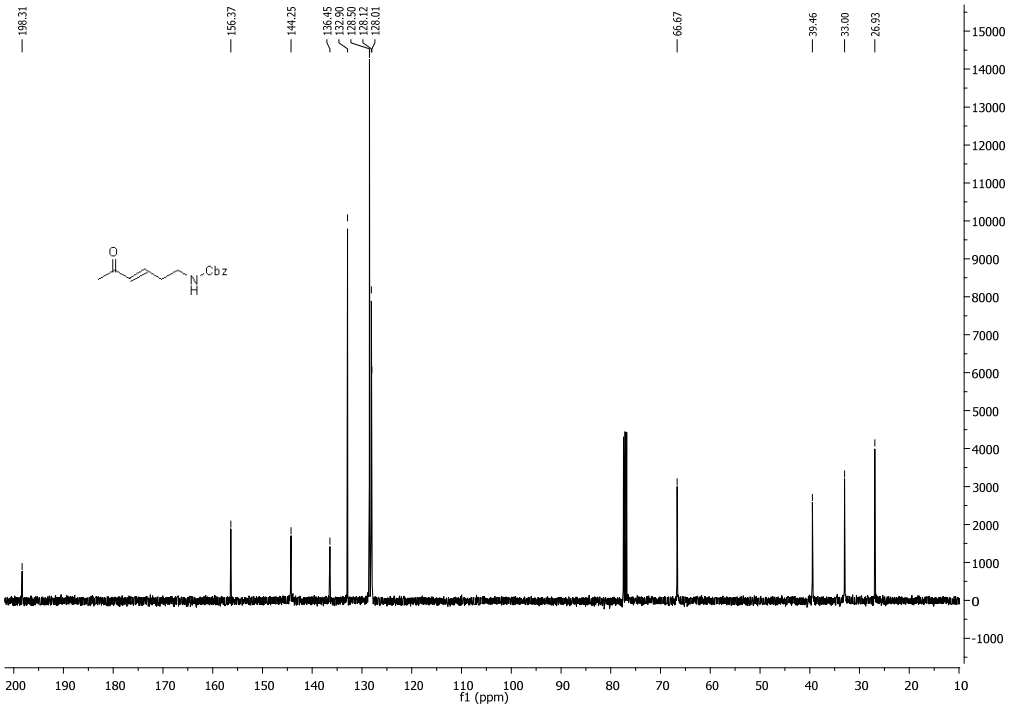
1d: ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz



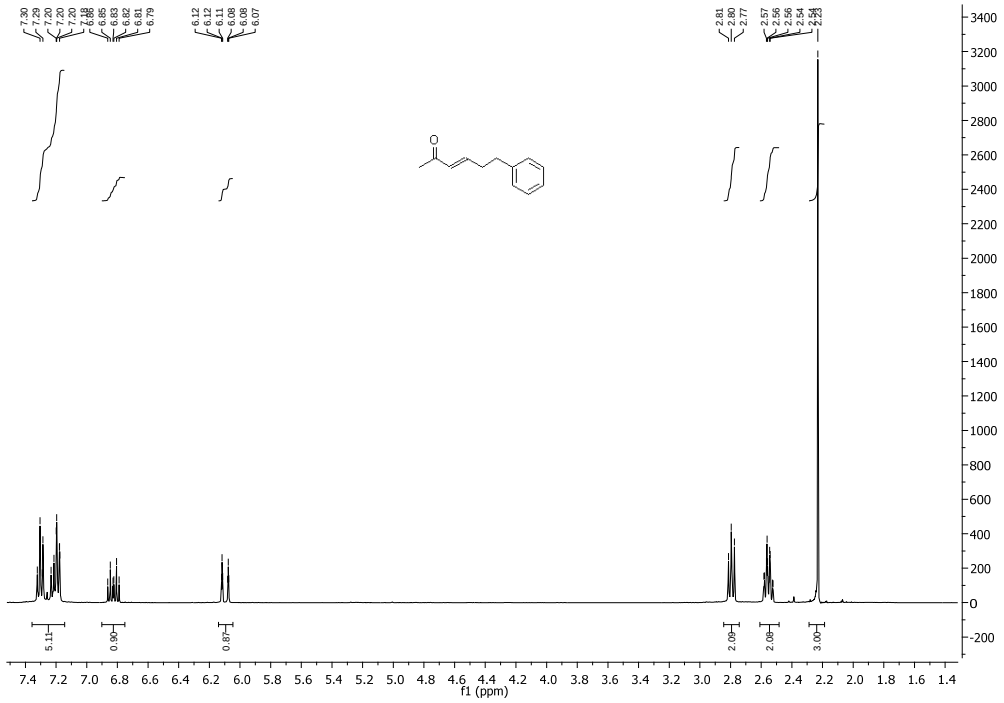


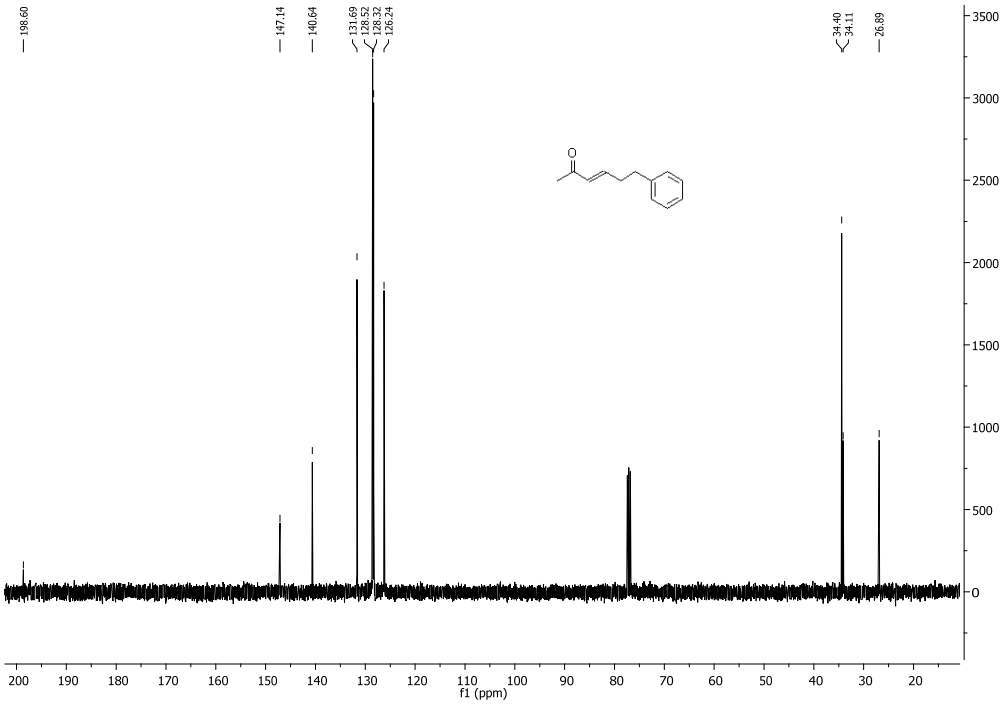
1e: ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz



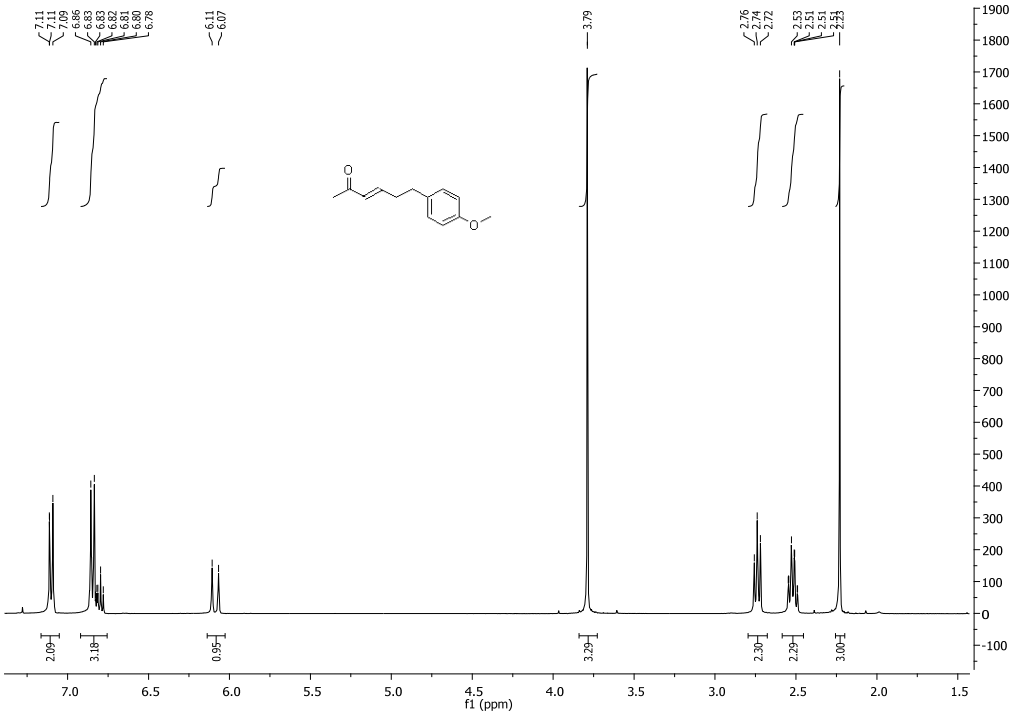


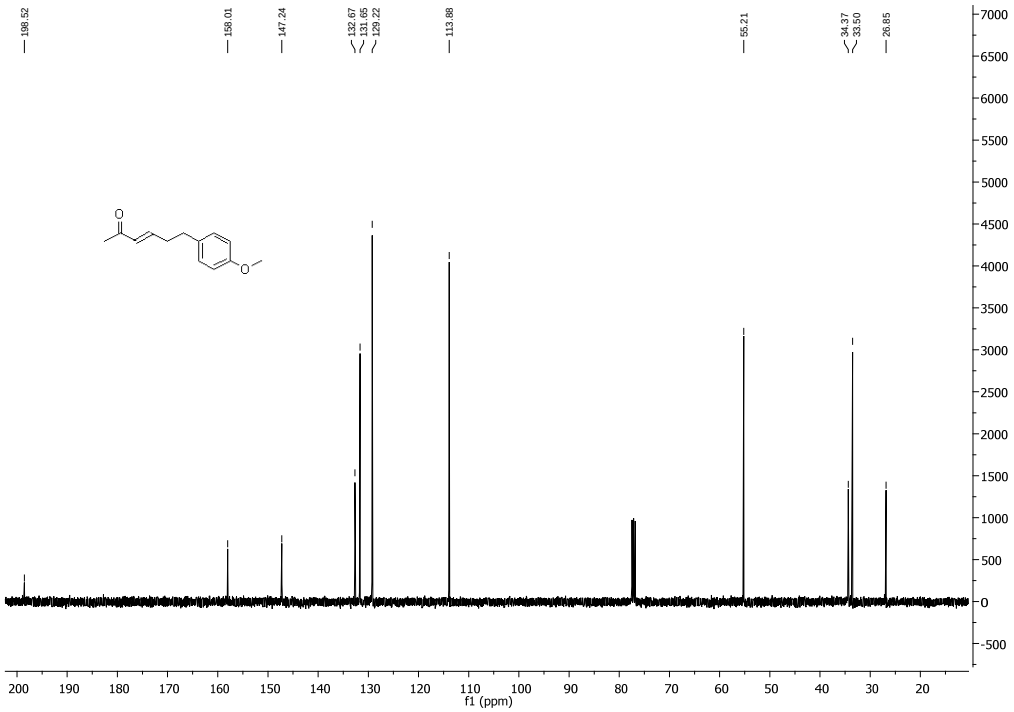
1f: ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz



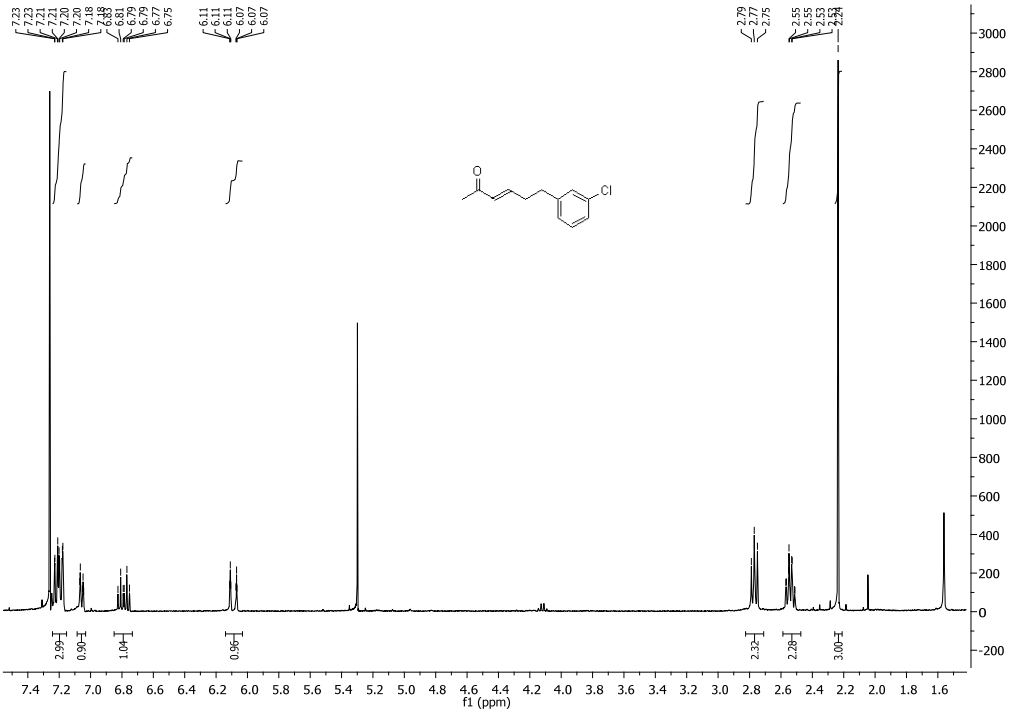


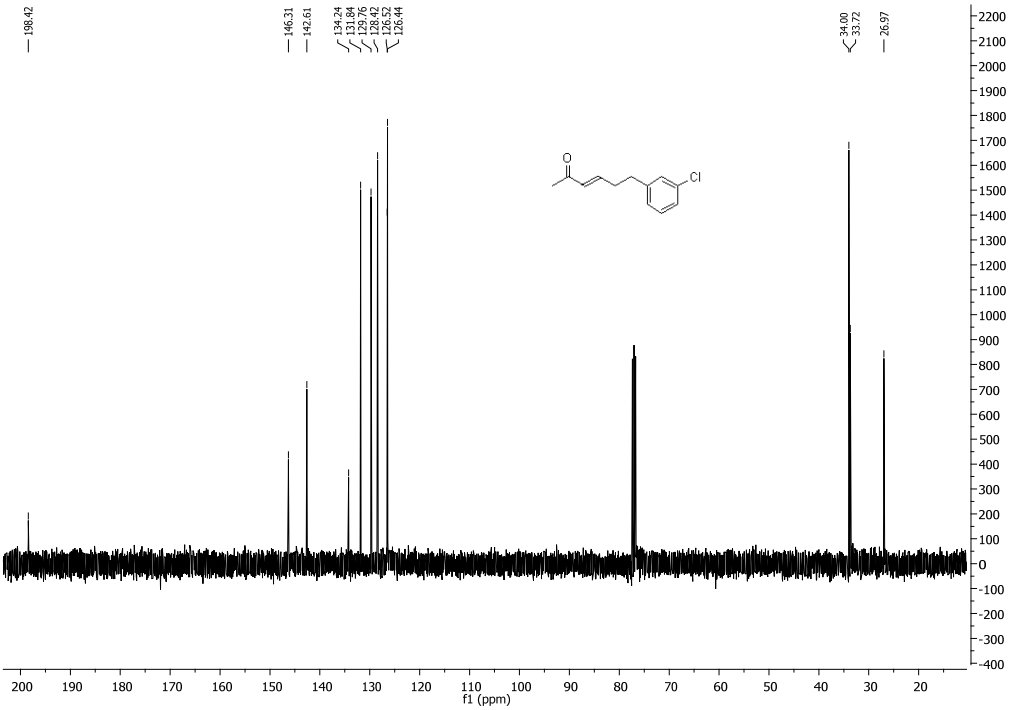
1g: ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz



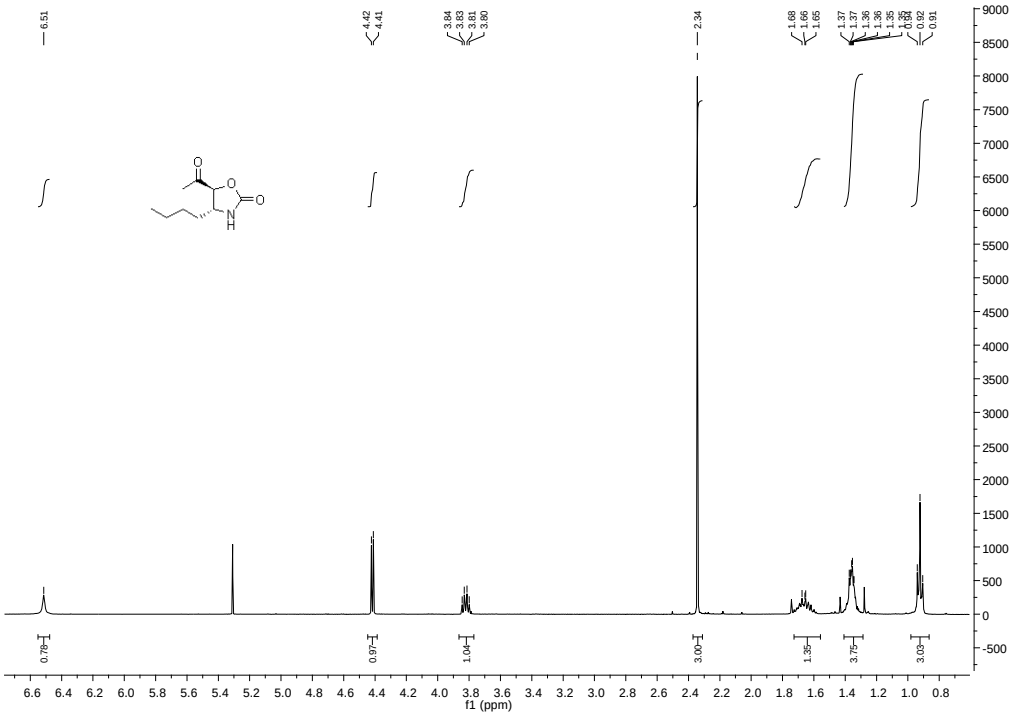


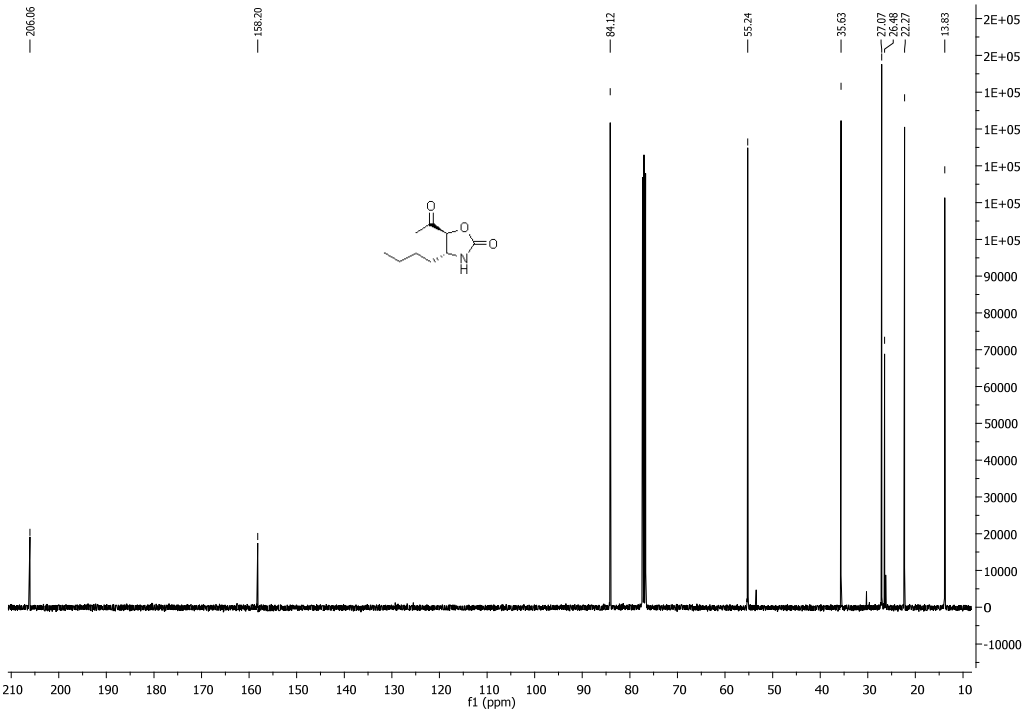
1h: ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz



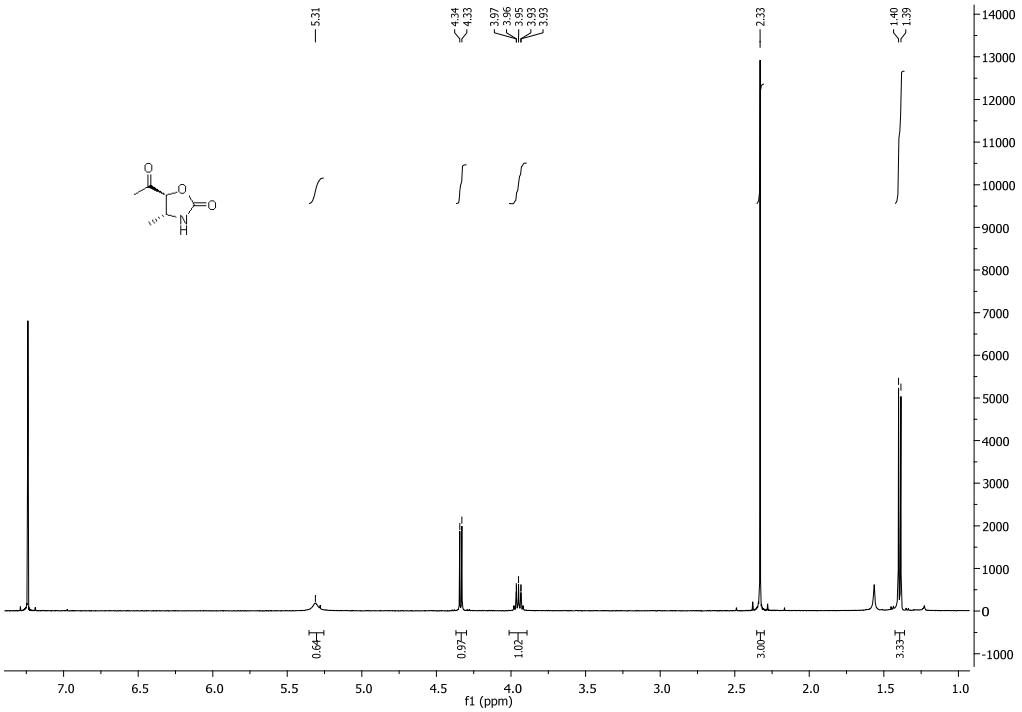


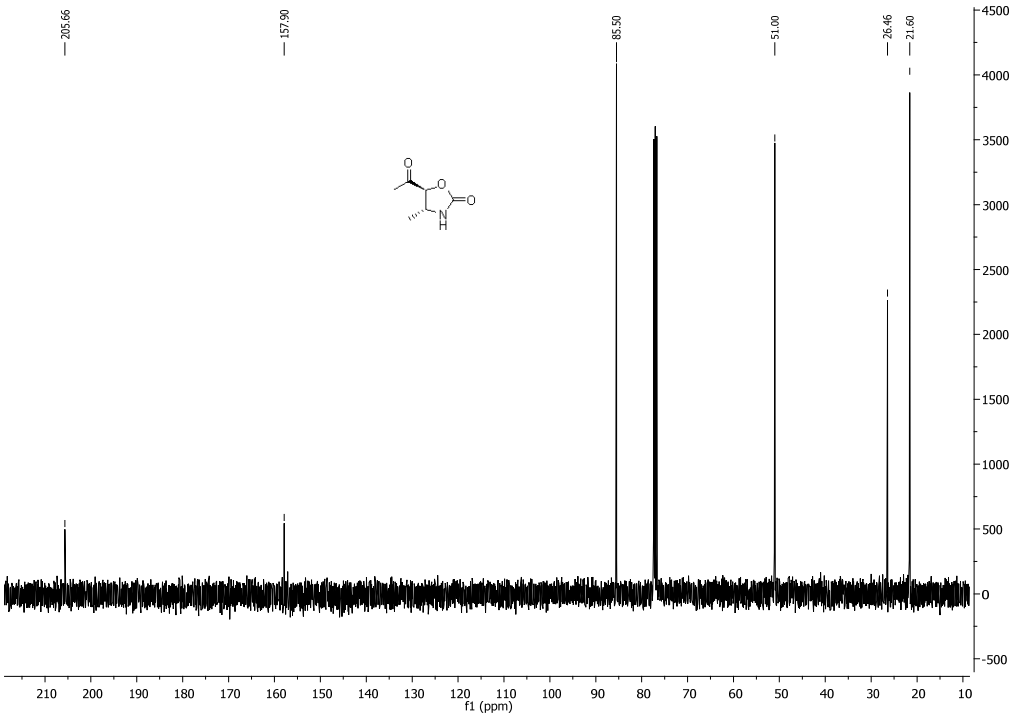
4a: ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz



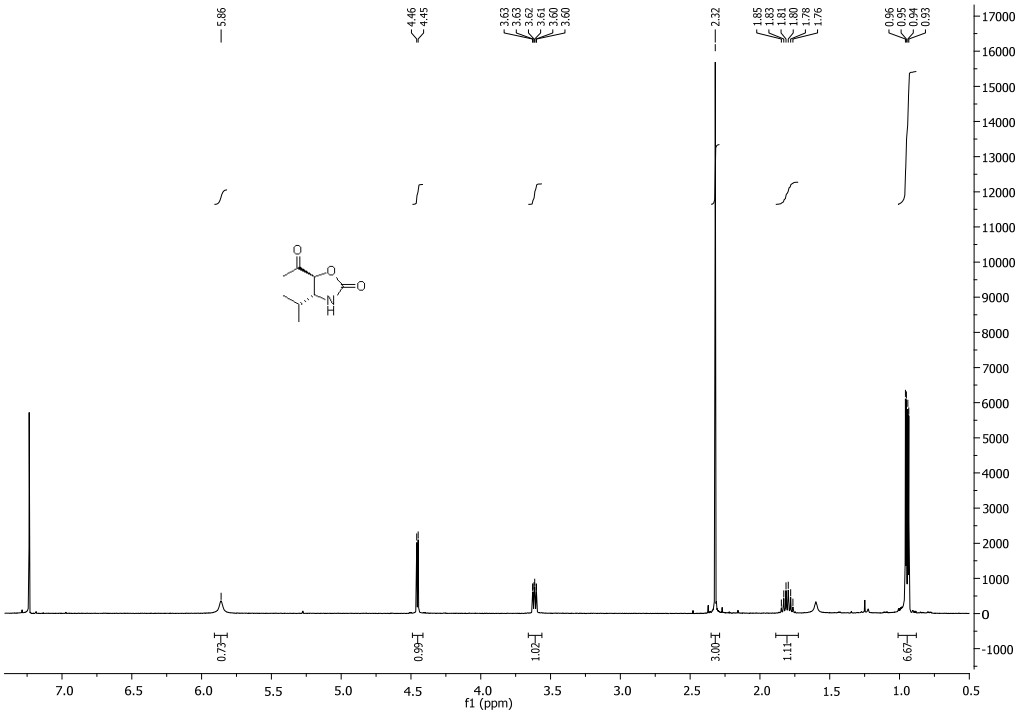


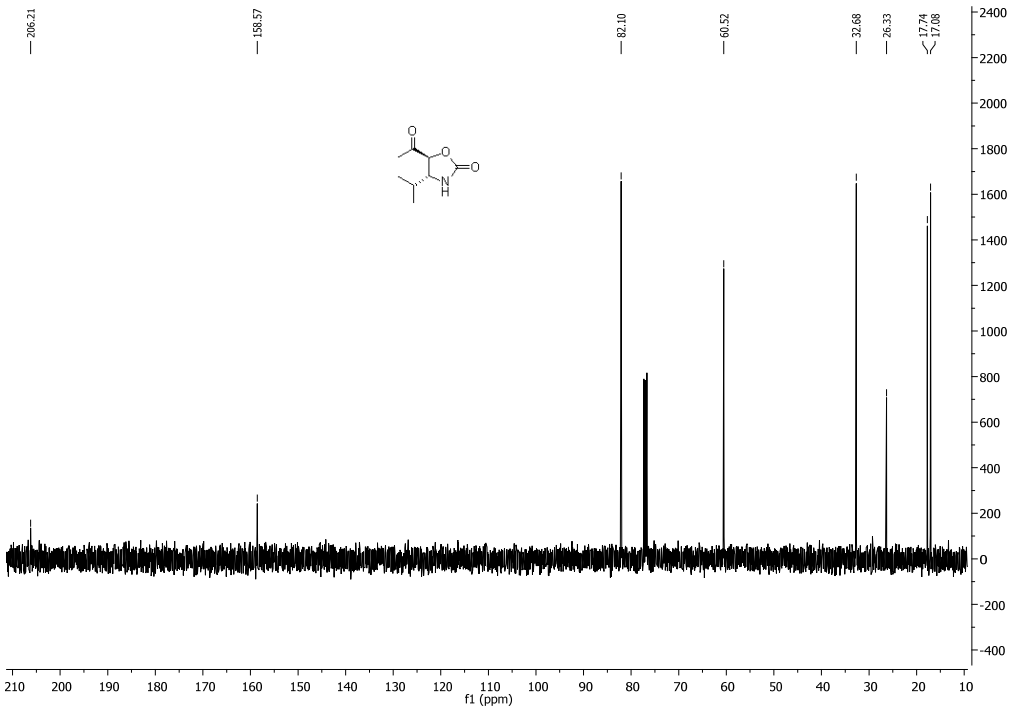
4b: ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz



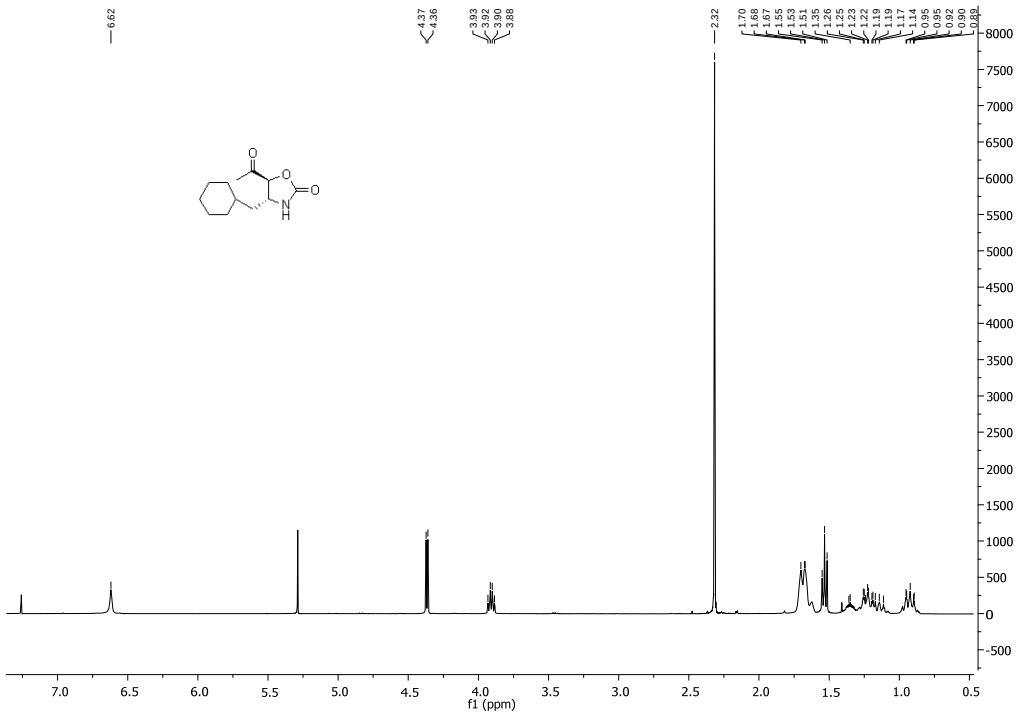


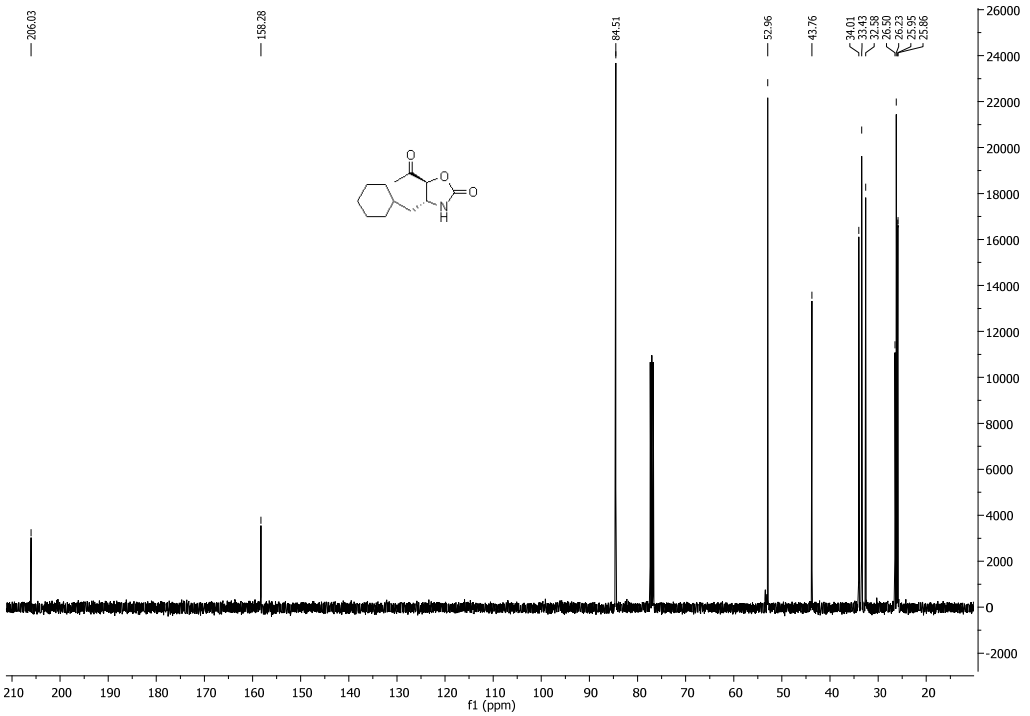
4c: ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz



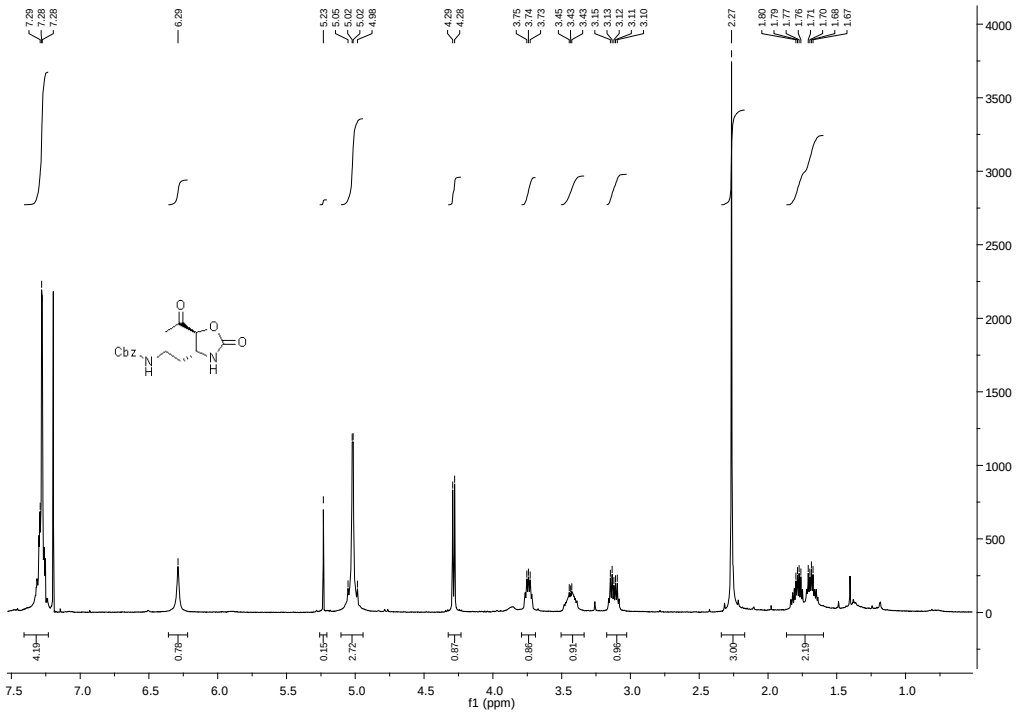


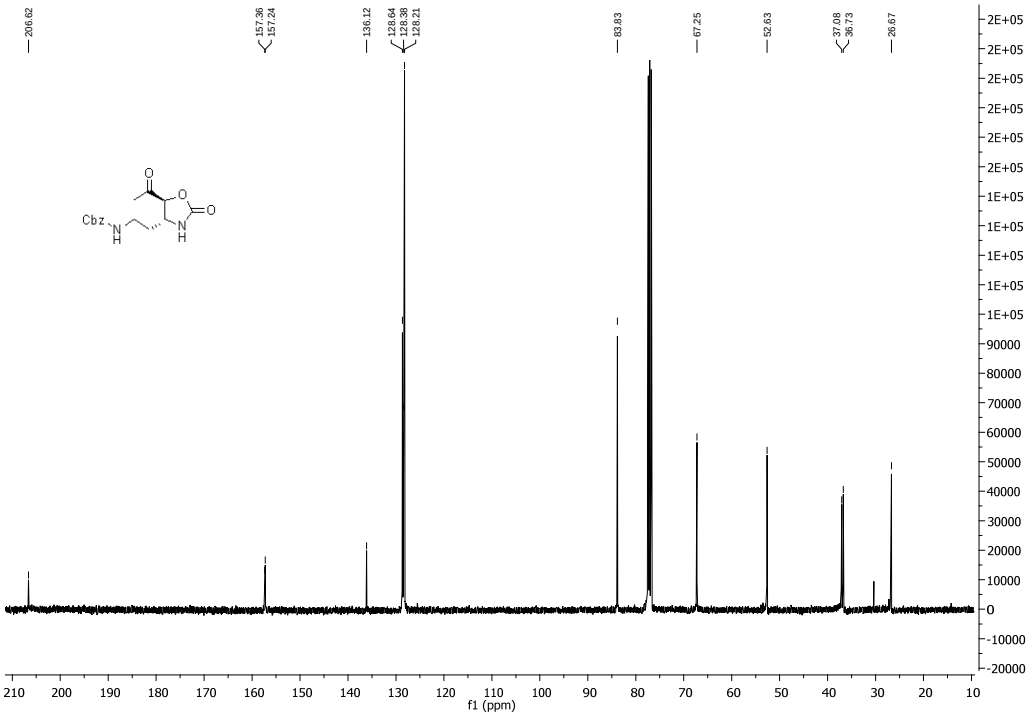
4d: ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz



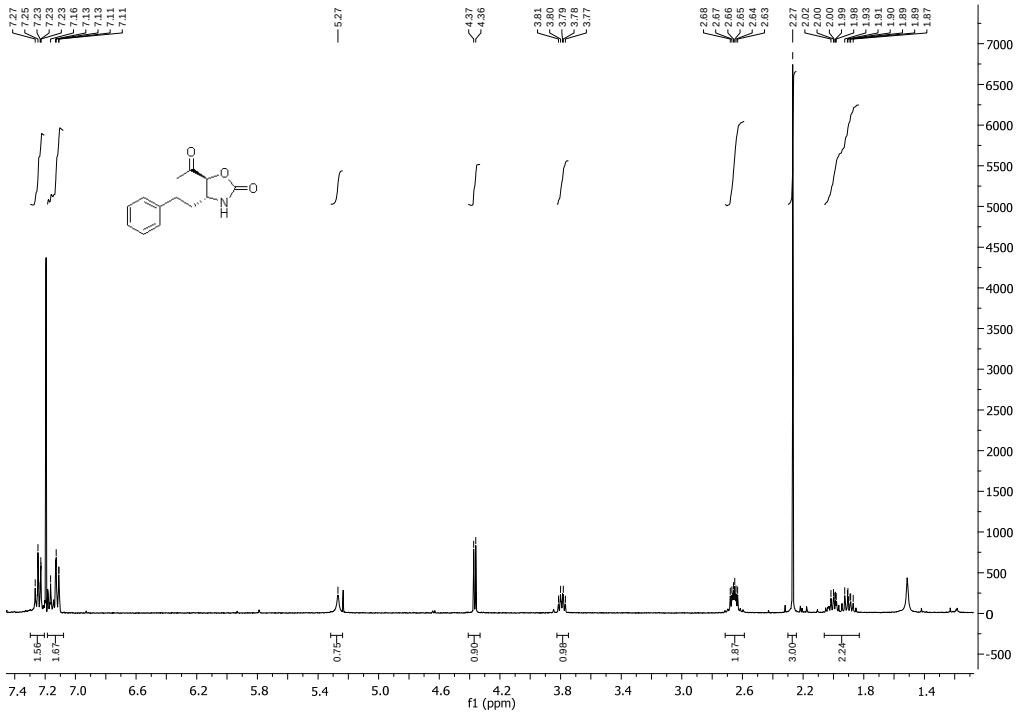


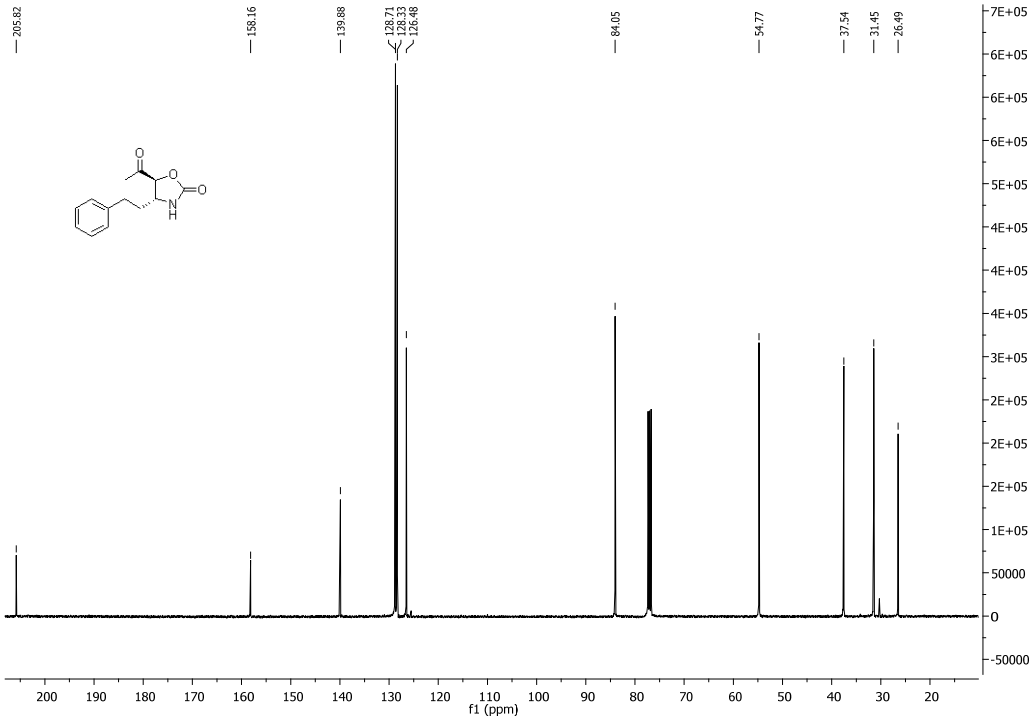
4e: ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz



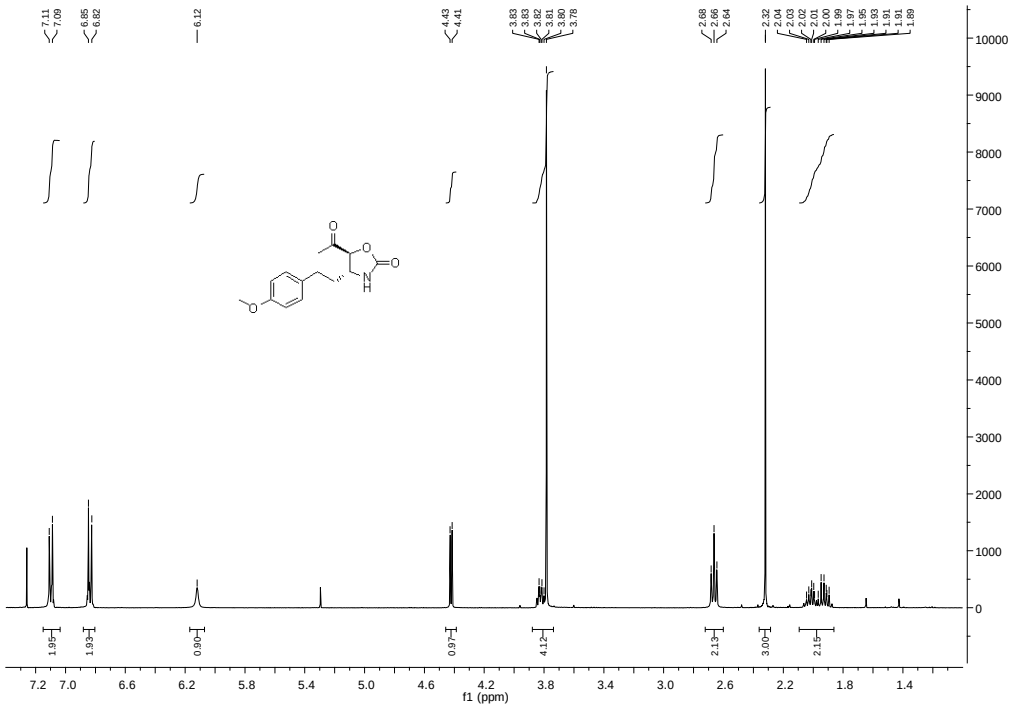


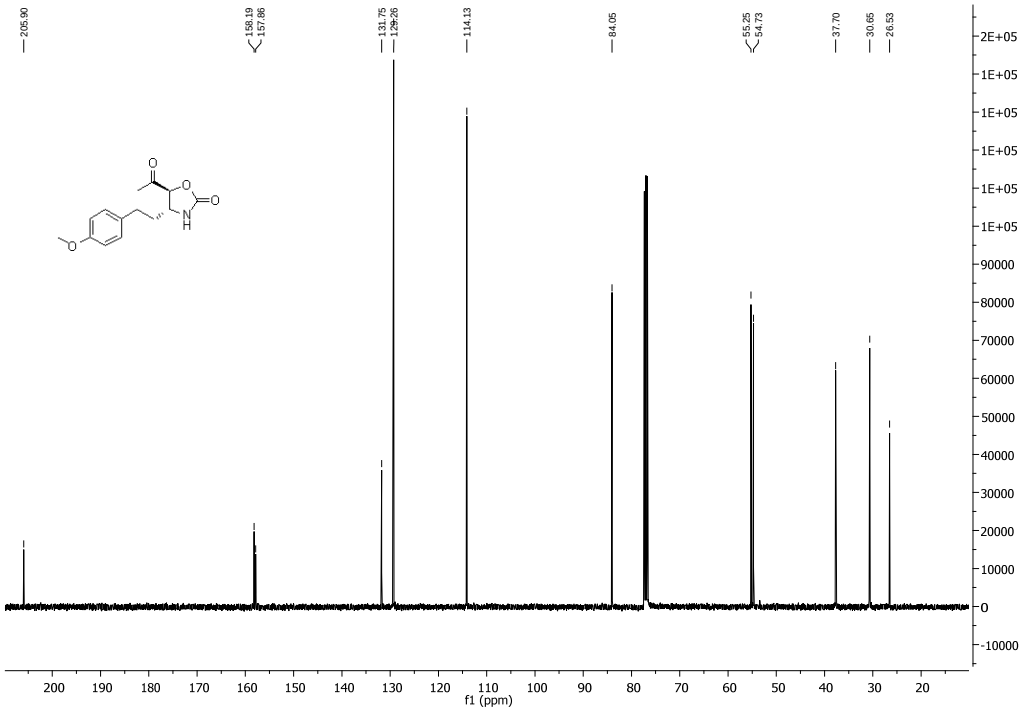
4f: ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz



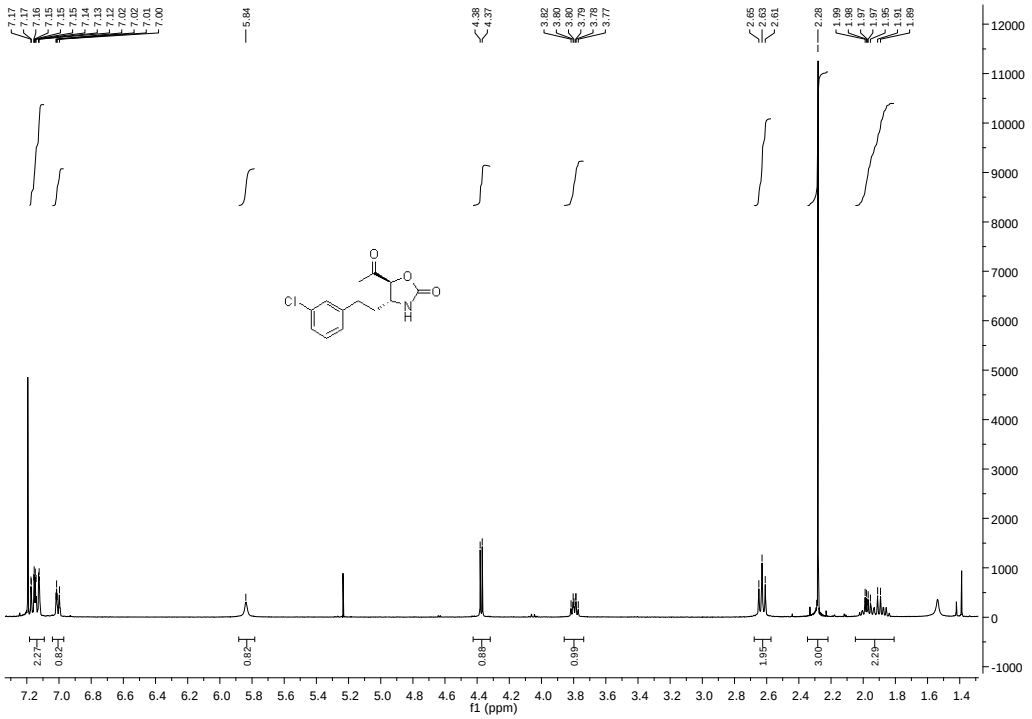


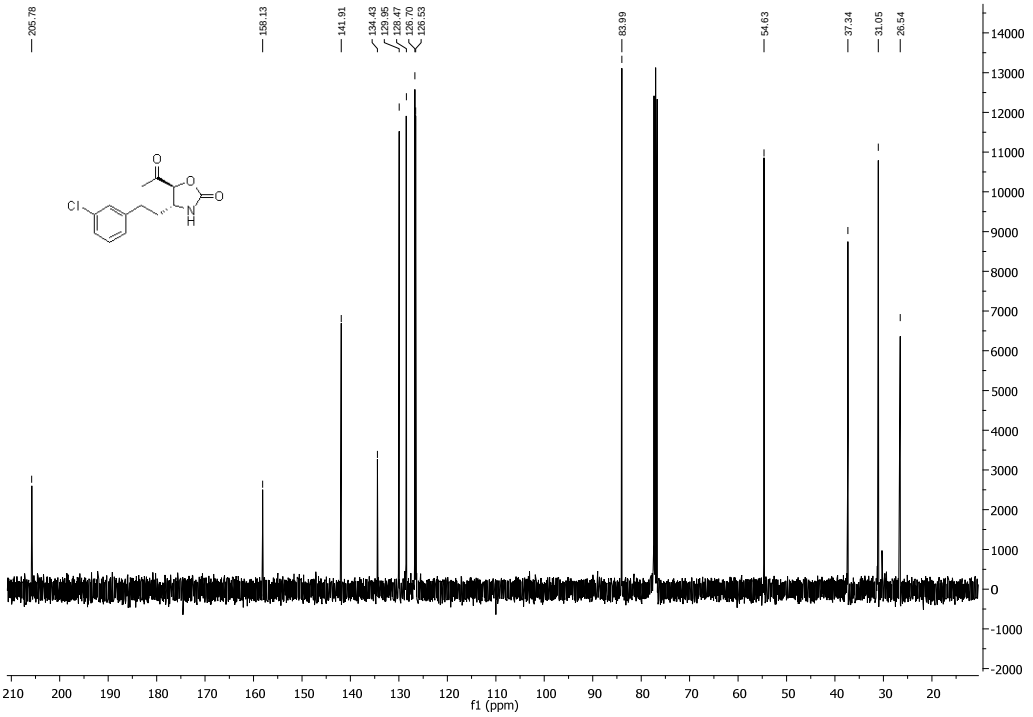
4g: ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz



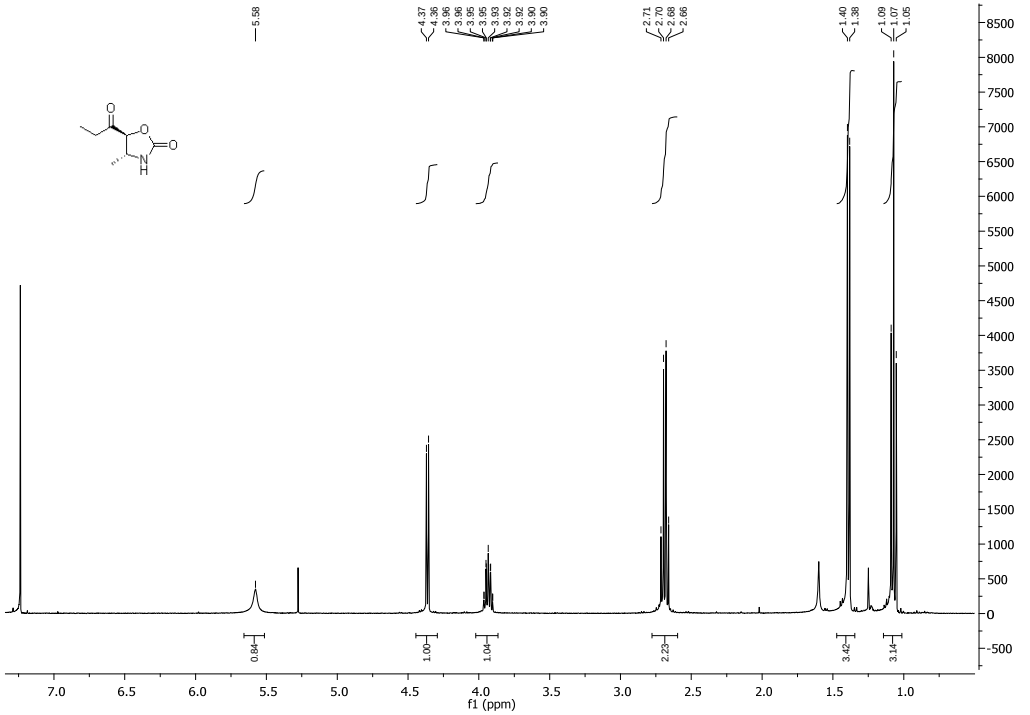


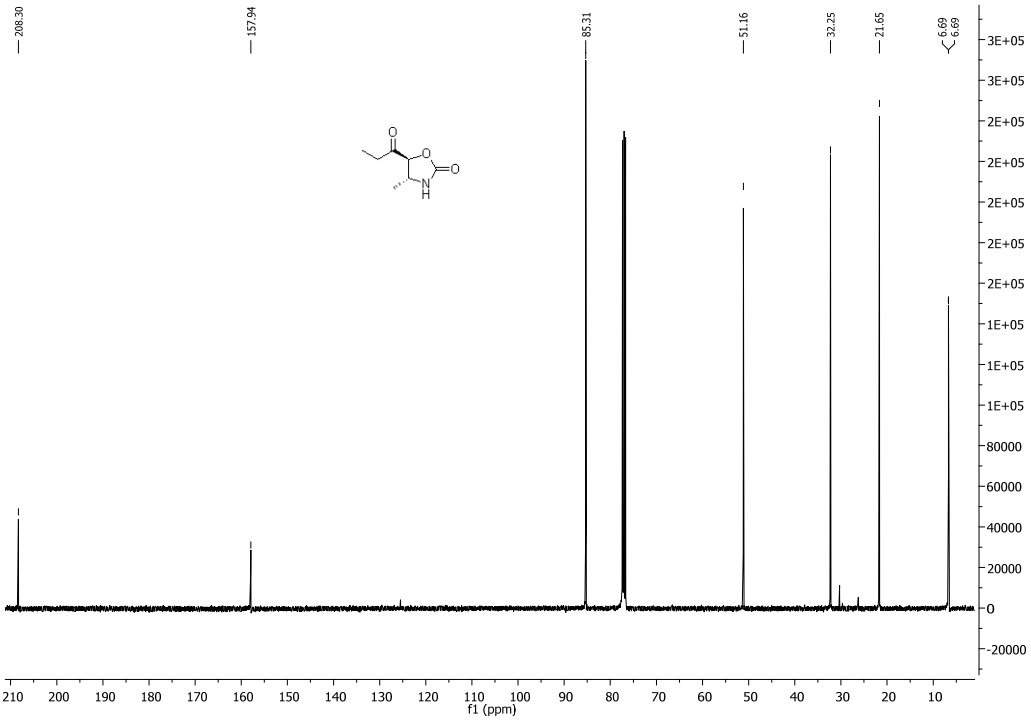
4h: ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz



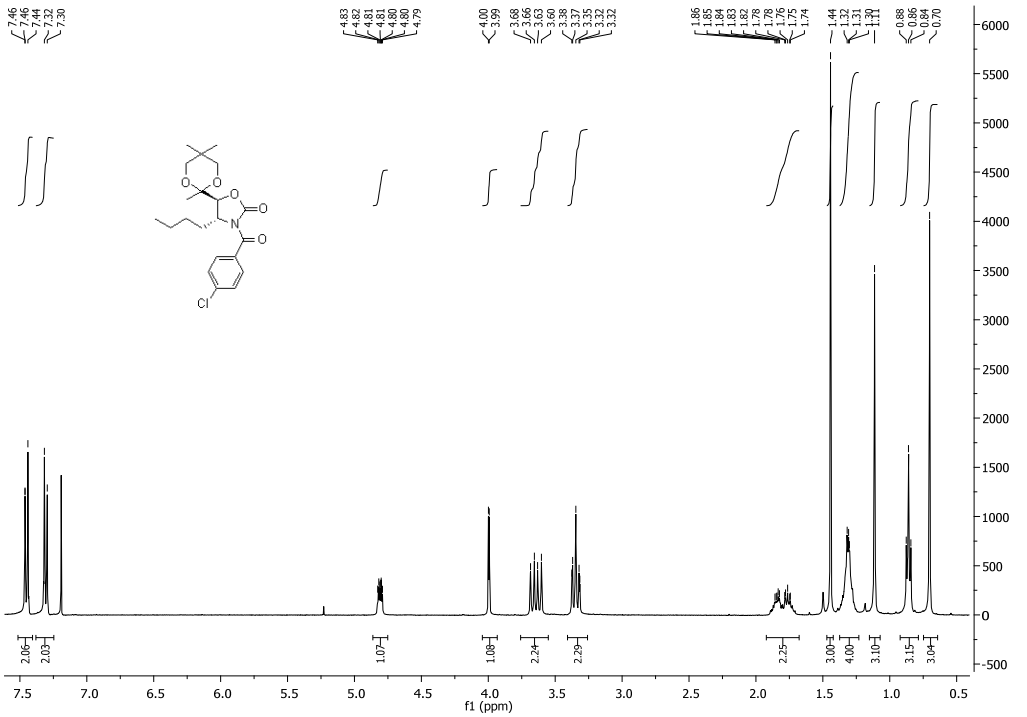


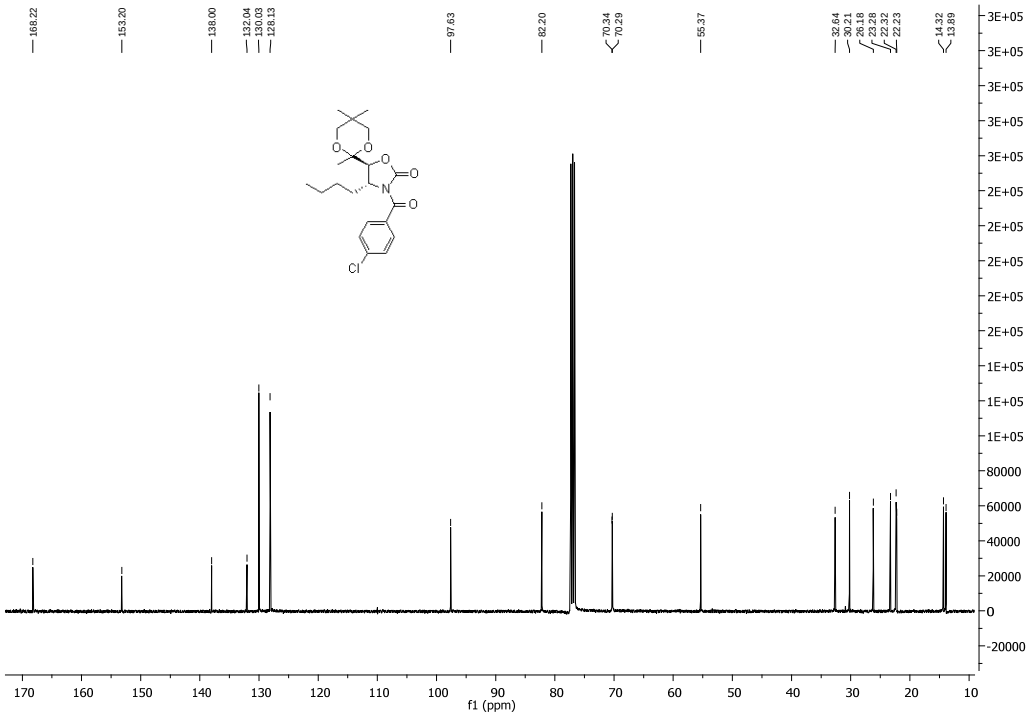
4i: ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz



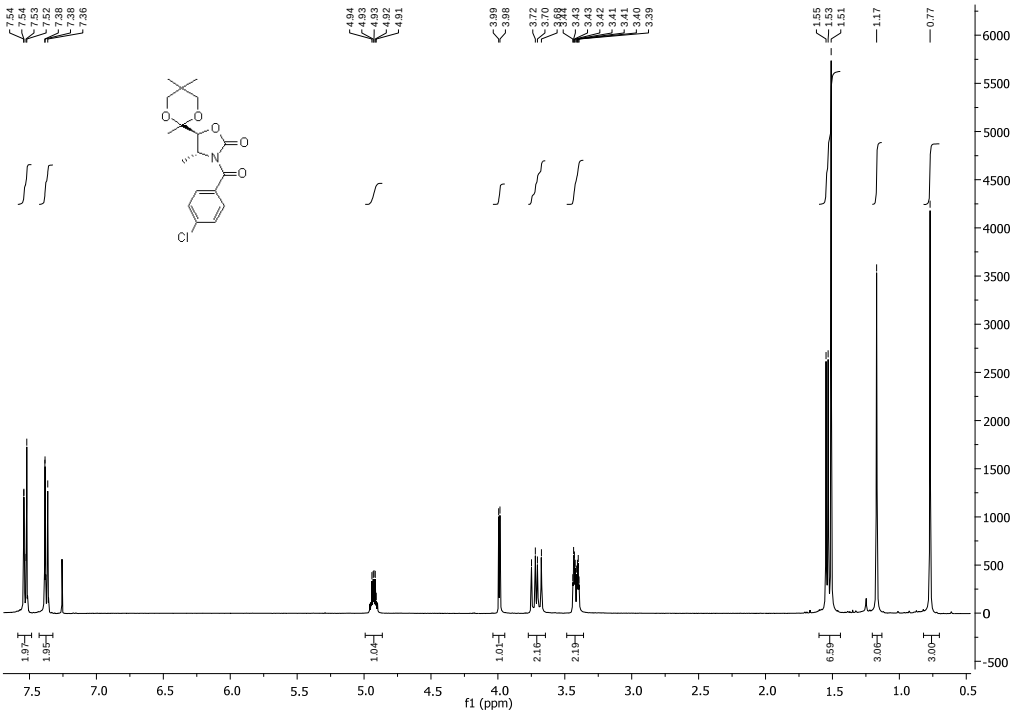


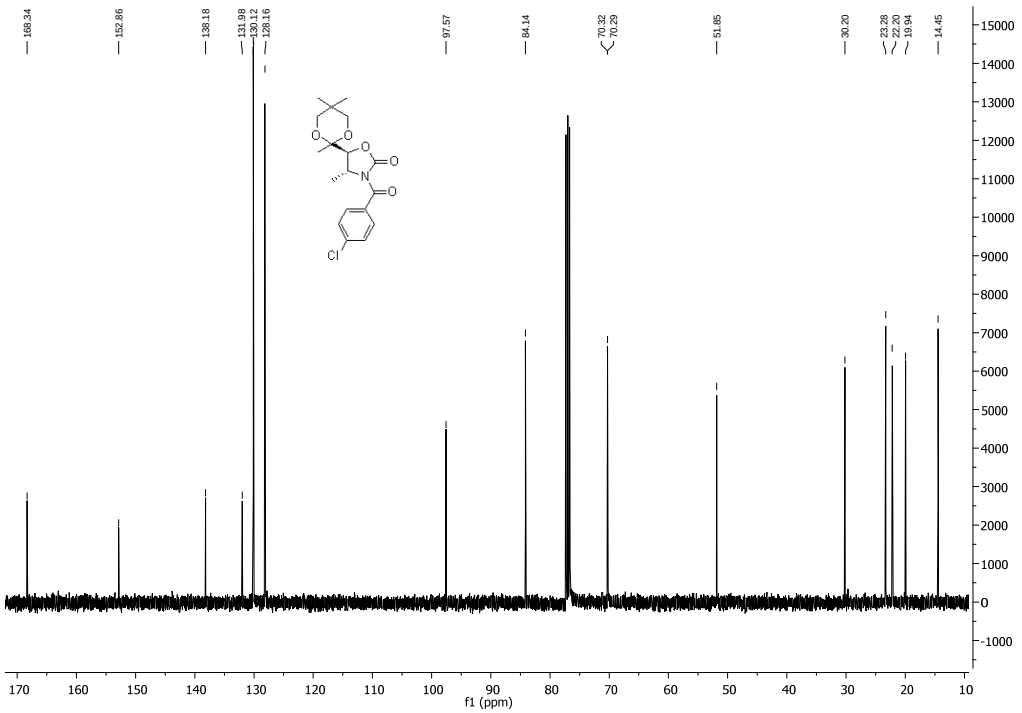
5a: ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz



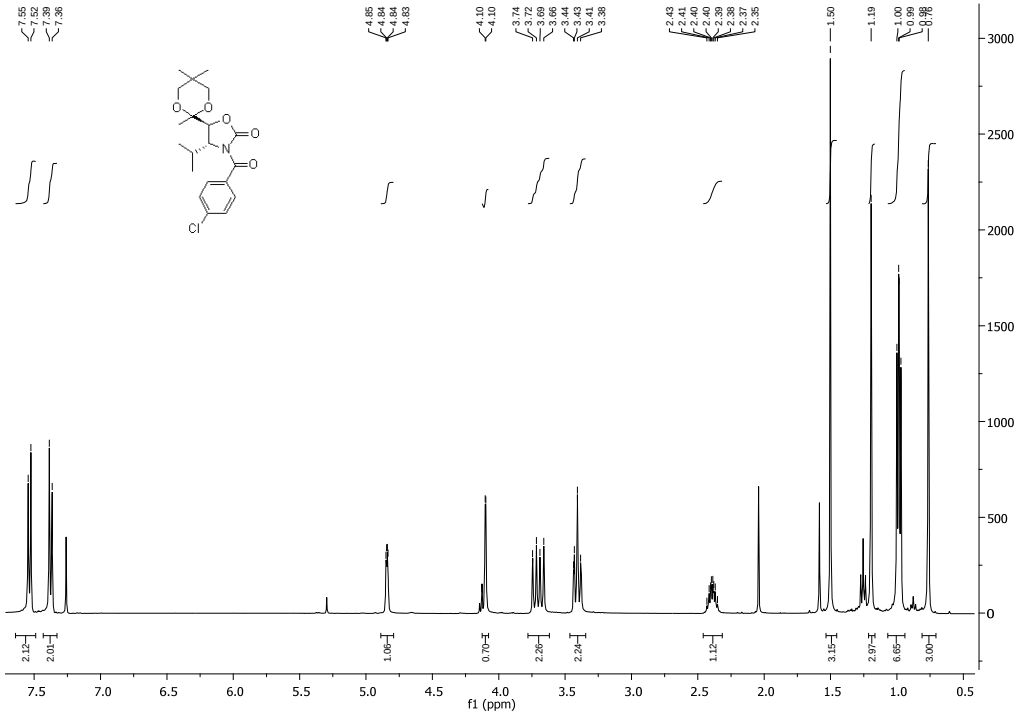


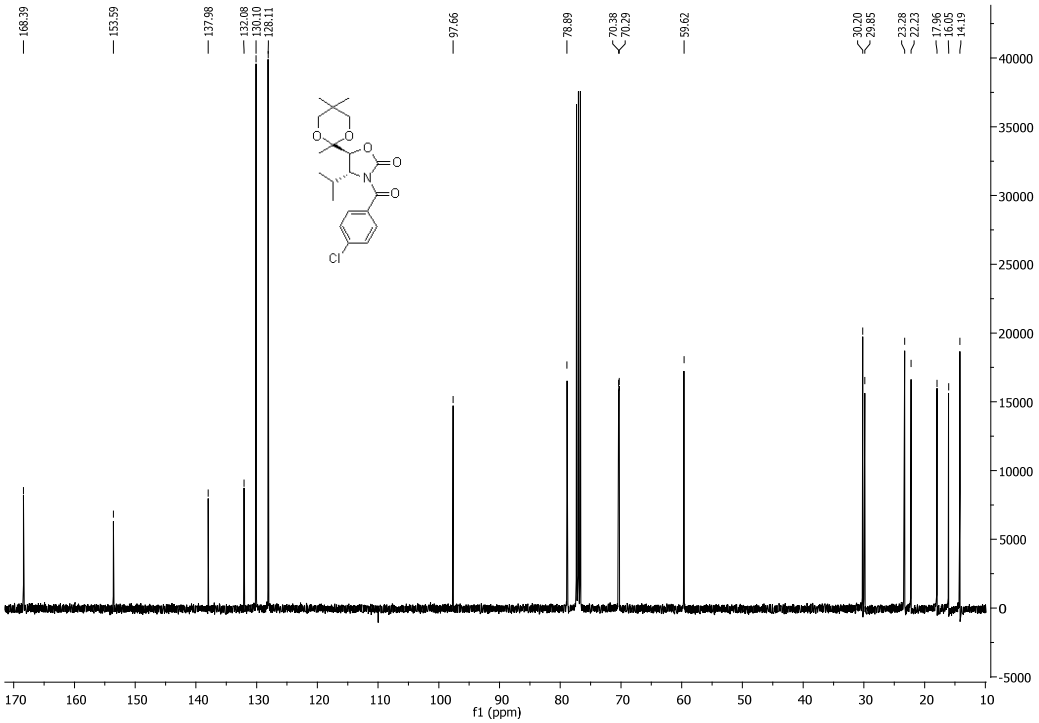
5b: ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz



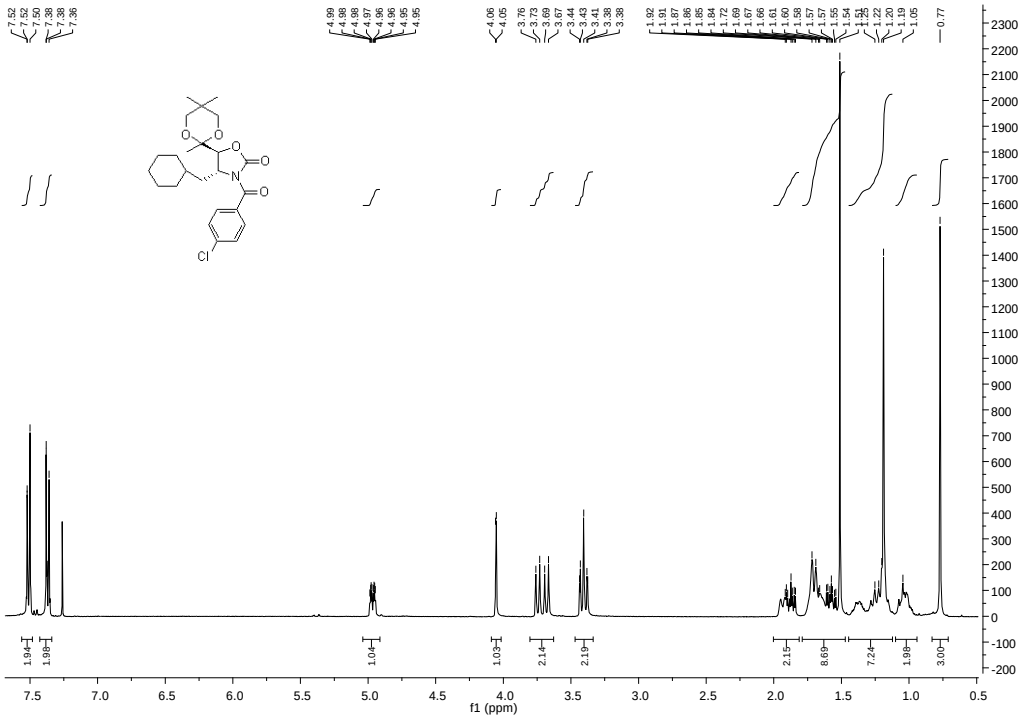


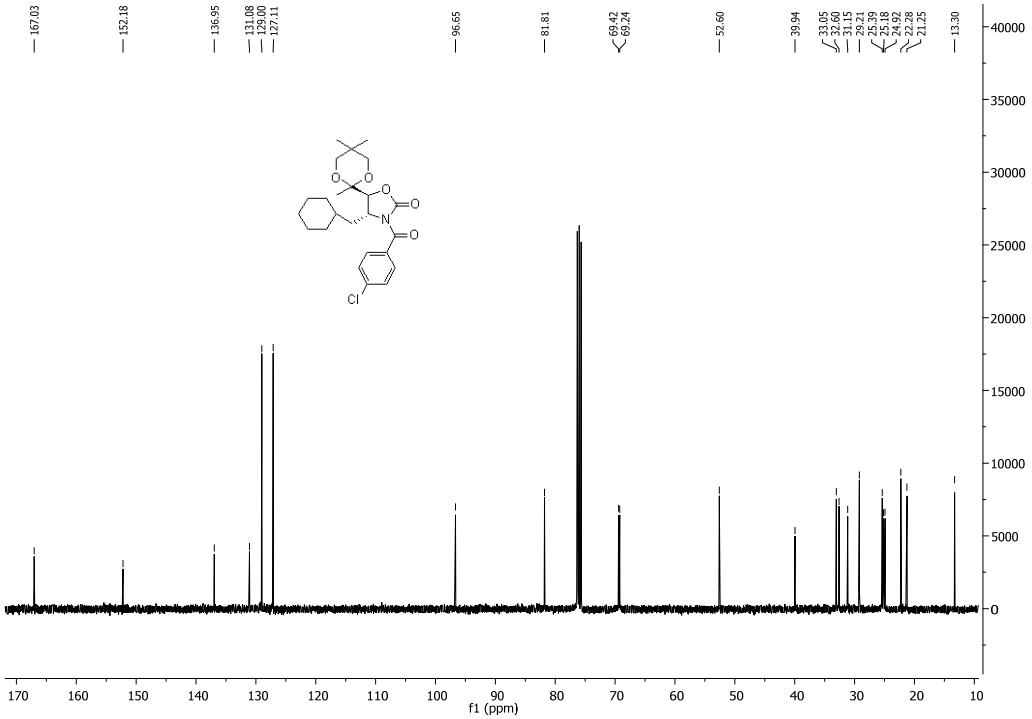
5c: ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz



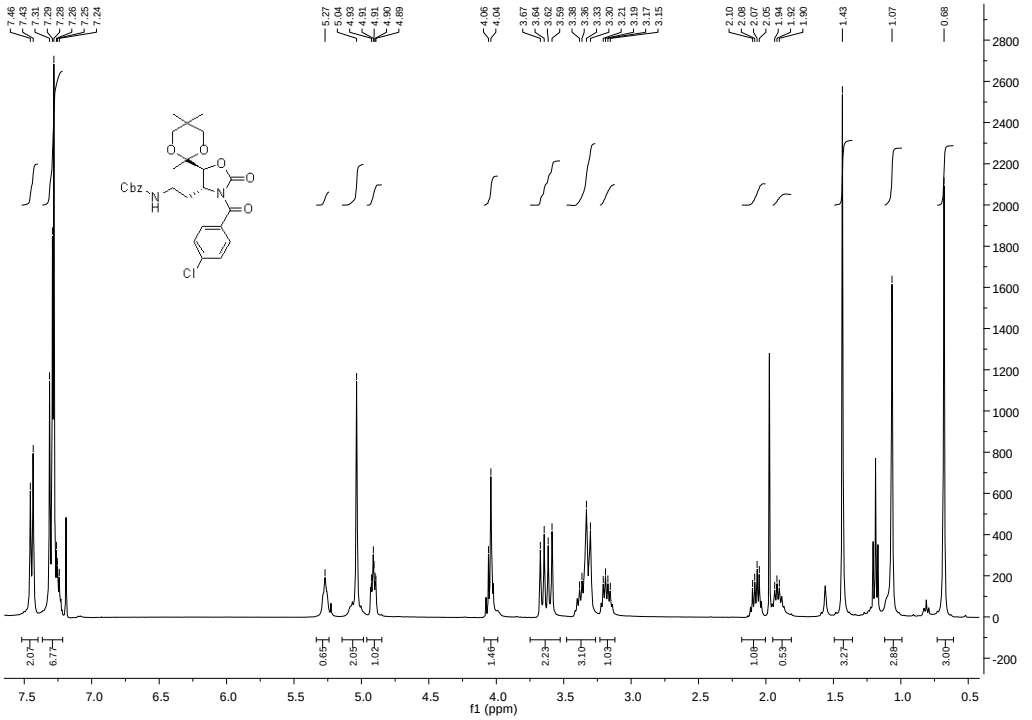


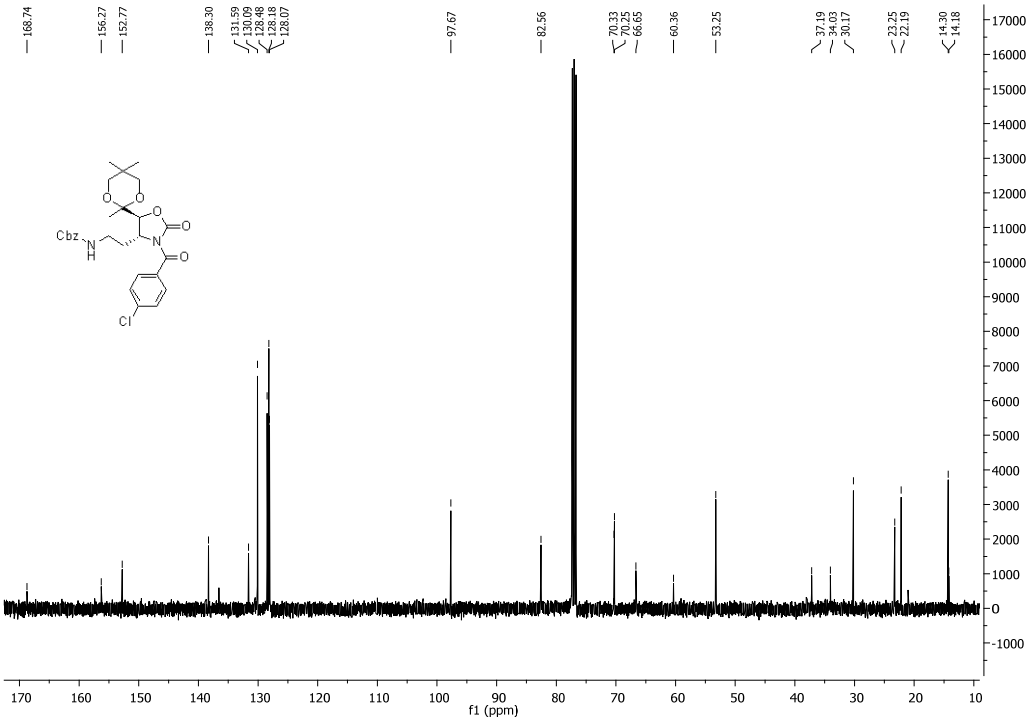
5d: ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz



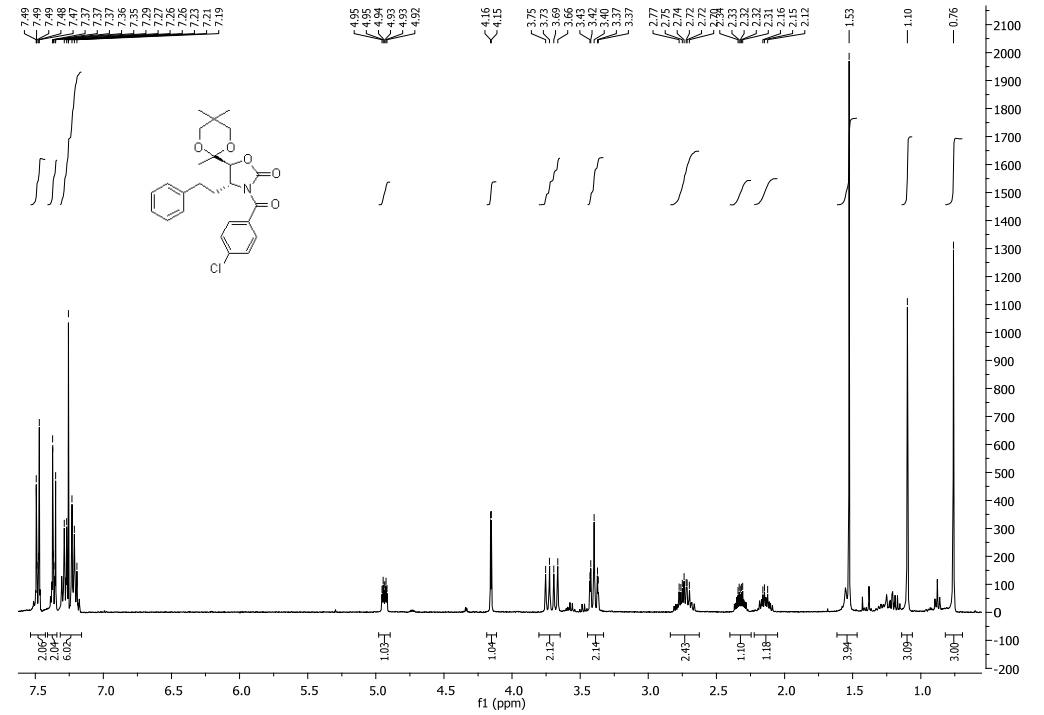


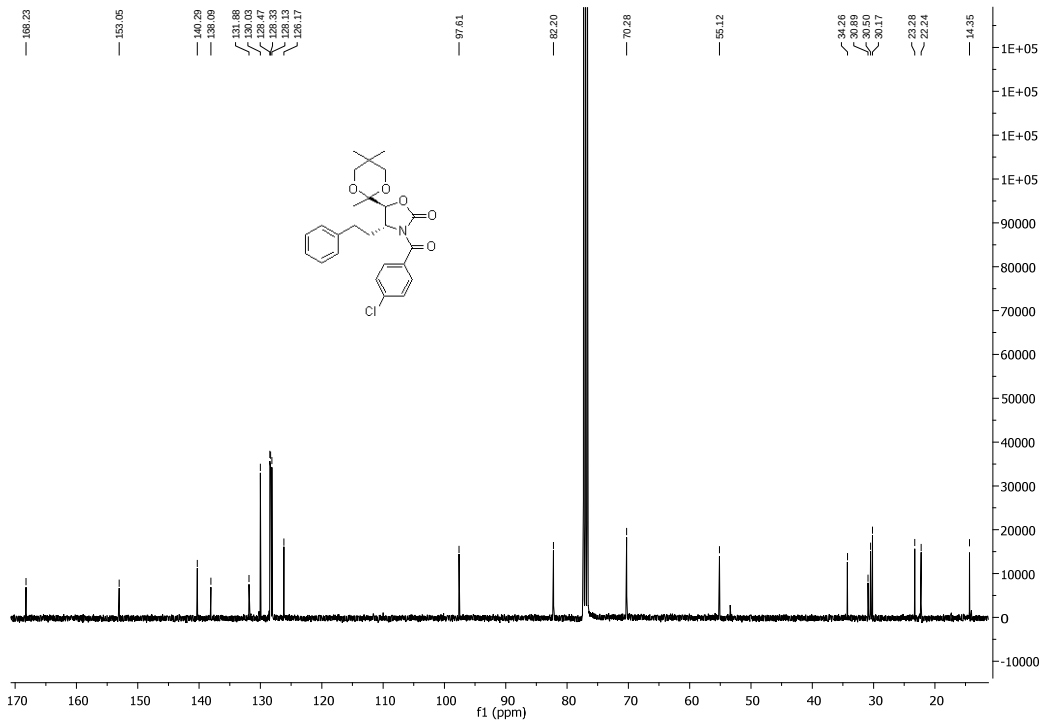
5e: ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz



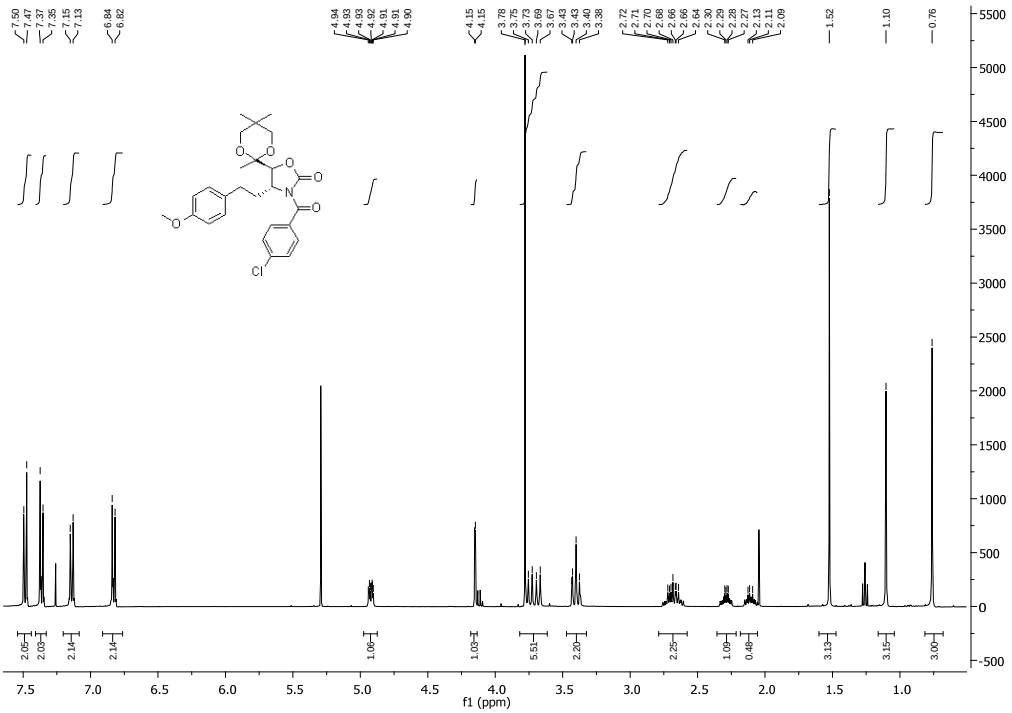


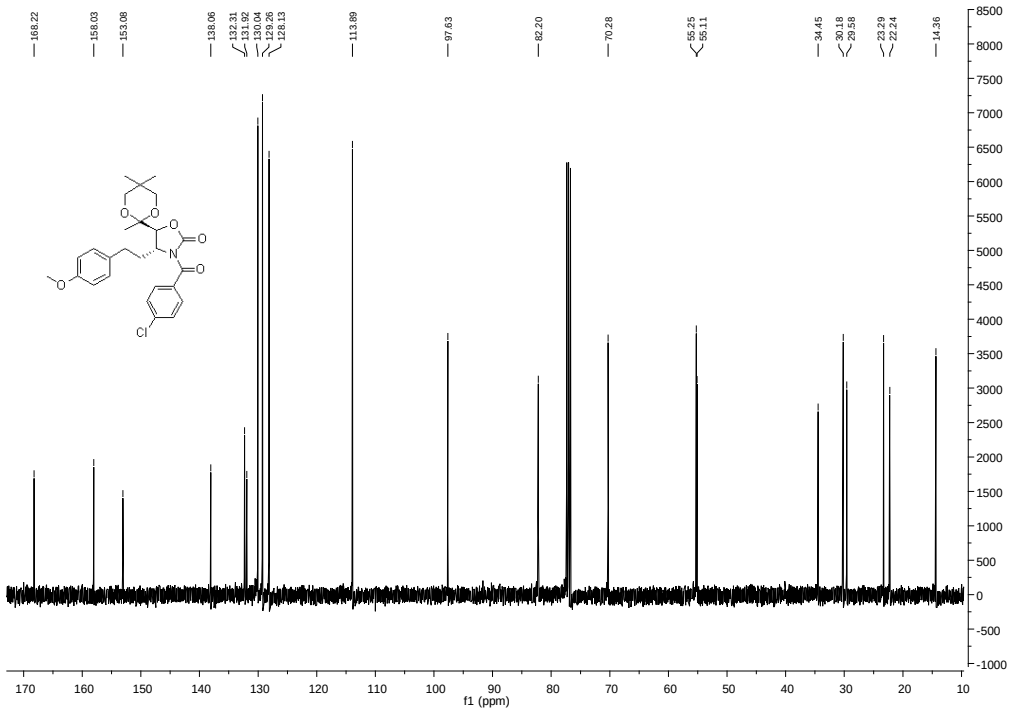
5f: ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz



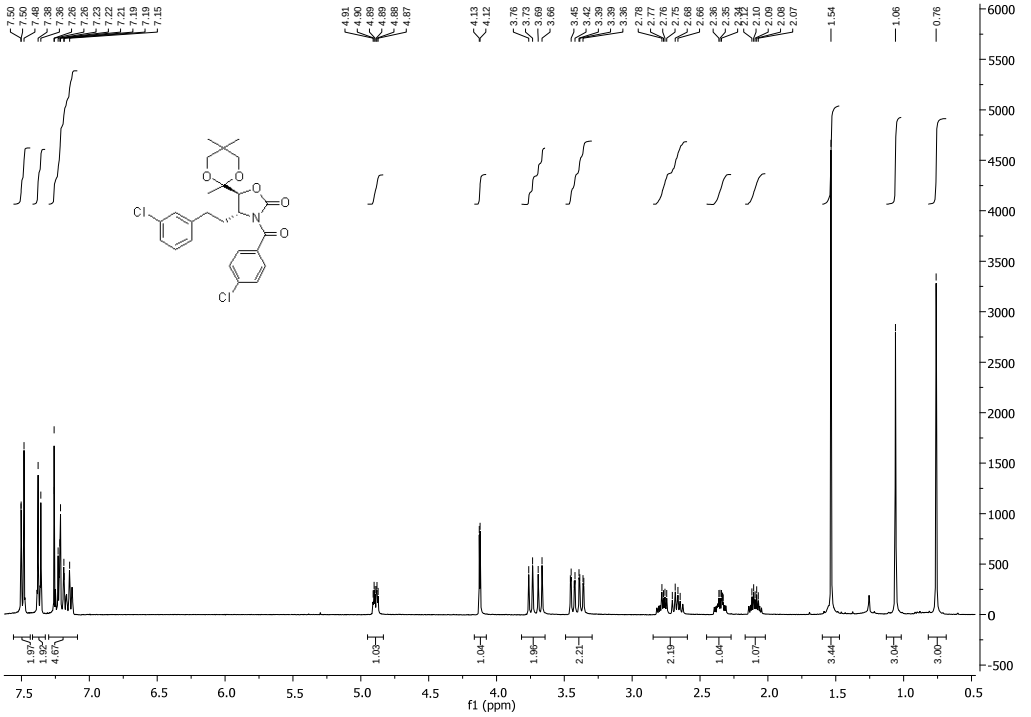


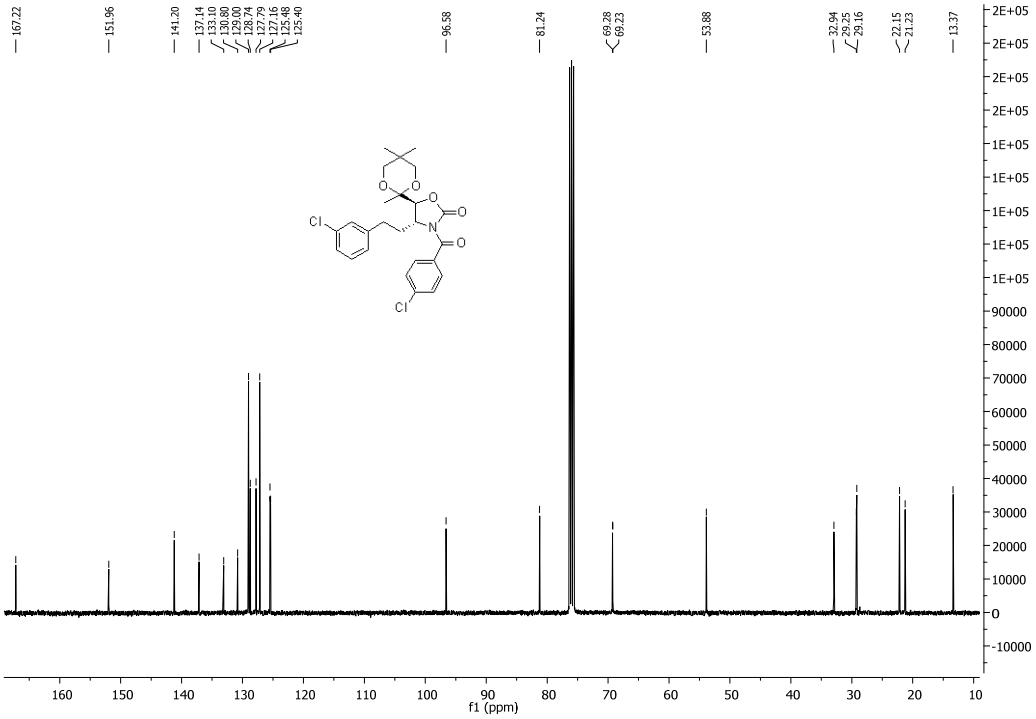
5g: ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz





5h: ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz





5i: ^{1}H-NMR: 400 MHz, ^{13}C-NMR: 100 MHz