Total Synthesis of Tetrahydrolipstatin and Stereoisomers via a Highly Regio- and Diastereoselective Carbonylation of Epoxyhomoallylic Alcohols

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Supporting Information

Section A: General Information

Section B: Experiment Procedures

Section C: ^{1}H and ^{13}C NMR Spectra

Section A: General Information

^{1}H and ^{13}C NMR spectra were recorded on a Varian 400 or 500 MHz spectrometer. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or $CDCl_3$ (δ 7.26 ppm) for ^{1}H NMR and $CDCl_3$ (δ 77.2 ppm) for ^{13}C NMR. Infrared (IR) spectra were obtained on a FT-IR spectrometer by preparing neat sample on potassium bromide plates. Optical rotations were measured with a digital polarimeter in the solvent specified. Melting points were determined with a standard melting point apparatus. Flash column chromatography was performed on 60-200 or 230-400 mesh silica gel. Preparative HPLC was performed on a Haisil 100 silica column (5 μm, 250 × 10 mm) with ethyl acetate and hexanes as mobile phase. Analytical thin-layer chromatography was performed with precoated glass-backed plates and visualized by quenching of fluorescence and by charring after treatment with *p*-anisaldehyde or potassium permanganate stain. Retention factors (R_f) were obtained by elution in the stated solvent ratios. Diethyl ether, tetrahydrofuran, methylene dichloride and triethylamine were dried by passing through activated alumina column with argon gas pressure. Commercial reagents were used without purification unless otherwise noted. Air- and/or moisture-sensitive reactions were carried out under an atmosphere of argon/nitrogen using oven- or flame-dried glassware and standard syringe/septa techniques. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained using α-cyano-4-hydroxycinnamic acid (CCA) as the matrix on a MALDI-TOF mass spectrometer.

For carbonylation, anhydrous tetrahydrofuran was purchased from Fischer and purified by passing through two neutral alumina-packed columns and a third column packed with activated 4Å molecular sieves under nitrogen pressure. Tetrahydrofuran was degassed by three freeze-pump-thaw cycles prior to use. All other solvents were reagent grade or better and used as received. Commercial reagents were used without purification unless otherwise noted. Carbon monoxide (Airgas, 99.99% minimum

purity) was used as received. Bis(tetrahydrofuran)-*meso*-tetra(4-chlorophenyl)porphyrinato aluminum tetracarbonyl cobaltate, $[ClTPPAl]^{+}[Co(CO)_4]^{-}$, was synthesized as previously reported.[1] All carbonylation reactions were performed in a custom-designed and -fabricated, six-chamber, stainless steel, high-pressure reactor, which accommodated six 4- or 8-mL glass vials, that has been described previously.[2,3] Because carbon monoxide is a highly toxic gas, all carbonylation reactions were performed in a well-ventilated fume hood equipped with a CO sensor.

[1] Rowley, J. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2007**, *129*, 4948–4960.

[2] Getzler, Y. D. Y. L.; Kundnani, V.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2004**, *126*, 6842–6843.

[3] Schmidt, J. A. R.; Mahadevan, V.; Getzler, Y. D. Y. L.; Coates, G. W. *Org. Lett.* **2004**, *6*, 373–376.

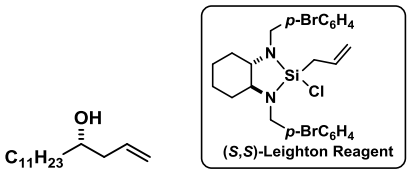
Section B: Experiment Procedures

General Procedure for Carbonylation of Epoxides

In a nitrogen glove box, a 4 mL glass vial equipped with a Teflon-coated magnetic stir bar was charged with the appropriate amount of $[ClTPPAl]^{+}[Co(CO)_4]^{-}$ and tetrahydrofuran. The vial was placed in the glove box freezer at –30 °C along with a custom-made six-well high-pressure reactor (see Section A: General Information) to cool for 30 minutes. (In the absence of CO, isomerization of the epoxide to ketone products[4] can be minimized by keeping the temperature of the reactor below 0 °C.) The appropriate amount of epoxide (also cooled at –30 °C for 30 minutes) was then added to the vial. After adding a cap with a Teflon-coated septum pierced by a 20 G needle (to prevent the reaction solvent from refluxing into the reactor chamber), the vial was placed quickly into the reactor. Subsequently, the reactor was sealed, taken out of the glove box, placed in a well-ventilated hood, and pressurized with carbon monoxide (900 psi). The reactor was then heated to 50 °C and the reaction mixture stirred for the specified time. The reactor was cooled on dry ice for 10 minutes and carefully vented in a fume hood. The crude reaction mixture was concentrated under reduced pressure and then purified via flash column chromatography or preparative HPLC.

[4] Church, T. L.; Getzler, Y. D. Y. L.; Coates, G. W. *J. Am. Chem. Soc.* **2006**, *128*, 10125–10133.

(*S*)-Pentadec-1-en-4-ol (6a)

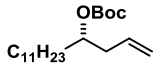


To a stirred solution of dodecanal **7a** (1.91 g, 10.4 mmol) in dichloromethane (30 mL) at 0 °C was added a solution of (*S*,*S*)-Leighton reagent (7.91 g, 14.3 mmol) in dichloromethane (10 mL) via syringe, followed by scandium triflate (128 mg, 0.260 mmol) under N_2. The resulting mixture was stirred at the same temperature for 8 h. The reaction was quenched by adding 1 N hydrochloric acid (20 mL). The formed solid was filtered through a fritted funnel, and the filtrate was extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (2 to 10% EtOAc in hexanes) on silica gel (140 mL) to afford **6a** (1.87 g, 80%, ee = 96%) as a colorless oil.

Data for **6a**: R_f = 0.34 (10% EtOAc in hexanes); $[\alpha]_D^{20}$ = –4.1 (CH_2Cl_2, *c* = 1.05); IR (neat) 3347, 2922, 2853, 1641, 1466, 1275 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.88–5.78 (m, 1H), 5.16–5.12 (m, 2H), 3.67–3.61 (m, 1H), 2.34–2.27 (m, 1H), 2.13 (ddd, *J* = 15.2, 7.6, 7.6 Hz, 1H), 1.56 (s, 1H), 1.49–1.42 (m, 3H), 1.34–1.24 (m, 17H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 118.3, 70.9, 42.1, 37.0, 32.1, 29.85 (2C), 29.82, 29.80 (2C), 29.5, 25.9, 22.9, 14.3.[5]

[5] Aubry, S.; Aubert, G.; Cresteil, T.; Crich, D. *Org. Biomol. Chem.* **2012**, *10*, 2629–2632.

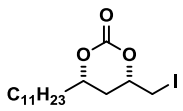
(*S*)-*tert*-Butyl pentadec-1-en-4-yl carbonate (8)



To a stirred solution of **6a** (2.24 g, 9.89 mmol) in tetrahydrofuran (33 mL) at 0 °C was added a solution of *n*-butyllithium (1.8 M, 5.9 mL, 10.6 mmol) in hexane via syringe slowly under N_2. After 15 min, a solution of di-*tert*-butyl dicarbonate (4.32 g, 19.8 mmol) in tetrahydrofuran (10 mL) was added via syringe slowly. The resulting mixture was stirred at 0 °C for 1.5 h, and warmed to room temperature. The stirring was continued for 1.5 h. The reaction was quenched by adding saturated aqueous ammonium chloride (50 mL) and extracted with EtOAc (3 × 80 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (1 to 4% EtOAc in hexanes) on silica gel (60 mL) to afford **8** (3.02 g, 93%) as a colorless oil.

Data for **8**: R_f = 0.22 (hexanes); $[\alpha]_D^{22}$ = –13.7 (CH_2Cl_2, *c* = 1.44); IR (neat) 2923, 2854, 1737, 1466, 1368, 1253, 1164 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.78 (dddd, *J* = 17.0, 10.0, 7.0, 7.0 Hz, 1H), 5.11–5.05 (m, 2H), 4.68 (dddd, *J* = 7.0, 6.0, 6.0, 6.0 Hz, 1H), 2.35–2.32 (m, 2H), 1.60–1.53 (m, 2H), 1.47 (s, 9H), 1.31–1.24 (m, 18H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 133.9, 117.9, 81.8, 76.8, 38.9, 33.9, 32.1, 29.81 (2C), 29.73, 29.70, 29.6, 29.5, 28.0 (3C), 25.5, 22.9, 14.3; HRMS (ESI) calcd for $C_{20}H_{39}O_3$ $[M + H]^+$: 327.2899, found 327.2907.

(4*S*,6*S*)-4-(Iodomethyl)-6-undecyl-1,3-dioxan-2-one (9)

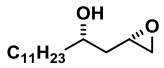


To a stirred solution of **8** (2.59 g, 7.93 mmol) in acetonitrile (25 mL) at –20 °C was added iodine (6.03 g, 23.8 mmol) in one portion under N_2. The resulting mixture was stirred at the same temperature for 2.5

h. The reaction was quenched by adding water (40 mL), and extracted with EtOAc (3 × 60 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (5 to 25% EtOAc in hexanes) on silica gel (60 mL) to afford **9** (2.12 g, 67%) as a white solid.

Data for **9**: mp 65–66 °C; R_f = 0.34 (20% EtOAc in hexanes); $[\alpha]_D^{22}$ = –11.4 (CH_2Cl_2, *c* = 1.07); IR (neat) 3055, 2927, 2855, 1752, 1398, 1265, 1189, 1105 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.48–4.40 (m, 2H), 3.40 (dd, *J* = 10.4, 4.4 Hz, 1H), 3.25 (dd, *J* = 10.4, 7.2 Hz, 1H), 2.38 (ddd, *J* = 14.4, 3.2, 3.2 Hz, 1H), 1.80–1.71 (m, 1H), 1.69–1.59 (m, 2H), 1.55–1.44 (m, 1H), 1.42–1.36 (m, 1H), 1.35–1.25 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 78.7, 77.3, 35.3, 33.4, 32.1, 29.77 (2C), 29.67, 29.57, 29.50, 29.4, 24.6, 22.9, 14.3, 5.5; MALDI-TOF/CCA-HRMS calcd for $C_{16}H_{29}IO_3Na$ $[M + Na]^+$: 419.1054, found 416.1059.

(*S*)-1-((*S*)-Oxiran-2-yl)tridecan-2-ol (10)

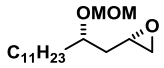


To a stirred solution of **9** (0.58 g, 1.46 mmol) in methanol (20 mL) at room temperature was added potassium carbonate (0.81 g, 5.85 mmol) in one portion. The resulting mixture was stirred at the same temperature for 10 h. The reaction was quenched by adding water, and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (5 to 20% EtOAc in hexanes) on silica gel (30 mL) to afford **10** (0.350 g, 99%) as a colorless oil.

Data for **10**: R_f = 0.32 (20% EtOAc in hexanes); $[\alpha]_D^{23}$ = –8.4 (CH_2Cl_2, *c* = 1.23); IR (neat) 3418, 2921, 2852, 1466, 1260, 1025 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.90–3.85 (m, 1H), 3.08 (dddd, *J* = 7.0, 4.0, 4.0, 3.0 Hz, 1H), 2.78 (dd, *J* = 4.5, 4.5 Hz, 1H), 2.49 (dd, *J* = 5.0, 2.5 Hz, 1H), 1.98 (br s, 1H), 1.84

(ddd, J = 14.5, 4.0, 4.0 Hz, 1H), 1.54–1.47 (m, 3H), 1.44–1.40 (m, 1H), 1.35–1.24 (m, 17H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 70.7, 50.9, 46.8, 39.9, 37.7, 32.1, 29.83, 29.78 (4C), 29.5, 25.7, 22.9, 14.3; MALDI-TOF/CCA-HRMS calcd for $C_{15}H_{30}O_2Na$ $[M + Na]^+$: 265.2138, found 265.2124.

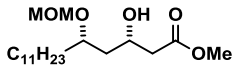
(*S*)-2-((*S*)-2-(Methoxymethoxy)tridecyl)oxirane (5a)



To a stirred solution of **10** (0.36 g, 1.49 mmol) in dichloromethane (7 mL) at 0 °C was added chloromethyl methyl ether (0.17 mL, 2.23 mmol) under N_2, followed by *N*,*N*-diisopropylethylamine (0.61 mL, 3.73 mmol). The resulting mixture was stirred at the same temperature for 24 h. The reaction was quenched by adding water (10 mL), and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (2.5 to 20% EtOAc in hexanes) on silica gel (30 mL) to afford **5a** (0.380 g, 88%) as a colorless oil.

Data for **5a**: R_f = 0.33 (10% EtOAc in hexanes); $[\alpha]_D^{23}$ = +0.2 (CH_2Cl_2, c = 1.18); IR (neat) 2922, 2853, 1466, 1260, 1149, 1098, 1036 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.67 (s, 2H), 3.73 (dddd, J = 6.0, 6.0, 6.0, 6.0 Hz, 1H), 3.38 (s, 3H), 3.05–3.01 (m, 1H), 2.76 (dd, J = 4.5, 4.5 Hz, 1H), 2.47 (dd, J = 5.0, 2.5 Hz, 1H), 1.79–1.70 (m, 2H), 1.64–1.53 (m, 2H), 1.39–1.22 (m, 18H), 0.87 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 95.5, 75.6, 55.8, 49.8, 46.9, 37.6, 34.7, 32.1, 29.89, 29.84, 29.81, 29.80 (2C), 29.5, 25.6, 22.9, 14.3; MALDI-TOF/CCA-HRMS calcd for $C_{17}H_{34}O_3Na$ $[M + Na]^+$: 309.2400, found 309.2410.

Methyl (3*S*,5*S*)-3-hydroxy-5-(methoxymethoxy)hexadecanoate (11)

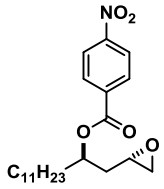


According to a modified literature procedure:[6] In a nitrogen glove box, an 8 mL glass vial equipped with a Teflon-coated magnetic stir bar was charged with dicobalt octacarbonyl ($Co_2(CO)_8$) (35.8 mg, 0.105 mmol, 10 mol %) and 3-hydroxypyridine (20.0 mg, 0.210 mmol, 20 mol %). Tetrahydrofuran (1.0 mL) was added to the vial, followed by (**5a)** (0.301 g, 1.05 mmol). After taking the vial out of the glove box, methanol (1.0 mL) was added to the vial and the vial was placed quickly into a custom-made six-well high-pressure reactor. Subsequently, the reactor was sealed, placed in a well-ventilated hood, purged three times with carbon monoxide, and then pressurized to 900 psi. The reactor was then heated to 60 °C and the reaction mixture was stirred for 16 hours. The reactor was cooled on dry ice for 10 minutes and carefully vented in a fume hood. The crude reaction mixture was concentrated under reduced pressure and then purified via flash column chromatography (10 to 20% EtOAc in hexanes) on silica gel (60 mL) to afford **11** (0.322 g, 89%) as a colorless oil.

Data for **11**: R_f = 0.30 (30% EtOAc in hexanes); $[\alpha]_D^{23}$ = +28.9 (CH_2Cl_2, *c* = 0.51); IR (neat) 3467, 2925, 2854, 1738, 1467, 1439, 1204, 1151, 1099, 1038 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.70 (d, *J* = 7.0 Hz, 1H), 4.63 (d, *J* = 7.0 Hz, 1H), 4.23–4.18 (m, 1H), 3.79 (dddd, *J* = 8.5, 5.5, 5.5, 5.5 Hz, 1H), 3.71 (s, 3H), 3.38 (s, 3H), 2.54–2.46 (m, 2H), 1.76 (ddd, *J* = 14.0, 8.5, 8.5 Hz, 1H), 1.64 (ddd, *J* = 14.0, 4.0, 4.0 Hz, 1H), 1.57–1.52 (m, 2H), 1.32–1.24 (m, 18H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 95.4, 76.8, 67.2, 56.0, 51.9, 41.8, 40.9, 34.4, 32.1, 29.96, 29.82, 29.80, 29.78 (2C), 29.5, 25.1, 22.9, 14.3; MALDI-TOF/CCA-HRMS calcd for $C_{19}H_{38}O_5Na$ $[M + Na]^+$: 369.2611, found 369.2609.

[6] Hinterding, K.; Jacobsen, E. N. *J. Org. Chem.* **1999**, *64*, 2164–2165.

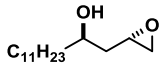
(*R*)-1-((*S*)-Oxiran-2-yl)tridecan-2-yl 4-nitrobenzoate (10a)



To a stirred solution of **10** (0.78 g, 3.22 mmol) in tetrahydrofuran (12 mL) at 0 °C was added triphenylphosphine (1.73 g, 6.60 mmol) and 4-nitrobenzoic acid (1.08 g, 6.44 mmol) under N_2. A solution of diisopropyl azodicarboxylate (1.30 g, 6.44 mmol) in tetrahydrofuran (3 mL) was added slowly via syringe. The resulting mixture was stirred at the same temperature for 1.5 h. The reaction was quenched by adding saturated aqueous sodium bicarbonate (5 mL), and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (5 to 15% EtOAc in hexanes) on silica gel (40 mL) to afford **10a** (1.25 g, 99%) as a colorless oil.

Data for **10a**: R_f = 0.19 (15% Et_2O in hexanes); $[\alpha]_D^{21}$ = –9.2 ($CHCl_3$, *c* = 0.23); IR (neat) 2925, 2854, 1724, 1608, 1529, 1350, 1275, 1103, 1015 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.30 (ddd, *J* = 9.0, 2.0, 2.0 Hz, 2H), 8.21 (ddd, *J* = 9.0, 2.0, 2.0 Hz, 2H), 5.36 (dddd, *J* = 7.5, 7.5, 5.0, 5.0 Hz, 1H), 3.02 (dddd, *J* = 7.0, 4.5, 4.5, 2.5 Hz, 1H), 2.75 (dd, *J* = 4.5, 4.5 Hz, 1H), 2.47 (dd, *J* = 5.0, 2.5 Hz, 1H), 1.99 (ddd, *J* = 14.5, 8.0, 5.0 Hz, 1H), 1.86 (ddd, *J* = 14.5, 7.0, 4.5 Hz, 1H), 1.83–1.72 (m, 2H), 1.43–1.31 (m, 4H), 1.30–1.22 (m, 14H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 150.7, 136.0, 130.9 (2C), 123.8 (2C), 74.2, 49.2, 47.0, 37.6, 34.4, 32.1, 29.78 (2C), 29.70, 29.63, 29.55, 29.51, 25.5, 22.9, 14.3; HRMS (ESI) calcd for $C_{22}H_{34}NO_5$ $[M + H]^+$: 392.2437, found 392.2431.

(*R*)-1-((*S*)-Oxiran-2-yl)tridecan-2-ol (12)

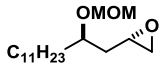


To a stirred solution of **10a** (3.32 g, 8.49 mmol) in methanol (17 mL) at 0 °C was added potassium carbonate (2.35 g, 17.0 mmol). The resulting mixture was stirred at the same temperature for 2 h. The reaction was quenched by adding water (10 mL), and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (10 to 40% EtOAc in hexanes) on silica gel (50 mL) to afford **12** (1.84 g, 90%) as a white solid.

Data for **12**: mp 47–48 °C; R_f = 0.27 (30% EtOAc in hexanes); $[\alpha]_D^{21}$ = –13.3 ($CHCl_3$, *c* = 0.36);

IR (neat) 3396, 2916, 2848, 1464, 1265, 1057 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.84–3.79 (m, 1H), 3.15 (dddd, *J* = 7.0, 4.0, 4.0, 3.0 Hz, 1H), 2.82 (dd, *J* = 4.5, 4.5 Hz, 1H), 2.61 (dd, *J* = 5.0, 3.0 Hz, 1H), 1.95 (br s, 1H), 1.83 (ddd, *J* = 14.5, 8.5, 4.0 Hz, 1H), 1.62 (ddd, *J* = 14.5, 6.0, 3.5 Hz, 1H), 1.53–1.39 (m, 3H), 1.34–1.24 (m, 17H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 69.5, 50.5, 47.0, 39.1, 37.8, 32.1, 29.84, 29.82, 29.78 (3C), 29.54, 25.7, 22.9, 14.3; HRMS (ESI) calcd for $C_{15}H_{30}O_2Na$ $[M + Na]^+$: 265.2144, found 265.2143.

(*S*)-2-((*R*)-2-(Methoxymethoxy)tridecyl)oxirane (13)

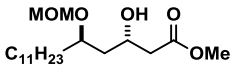


To a stirred solution of **12** (1.73 g, 7.14 mmol) in dichloromethane (15 mL) at 0 °C was added chloromethyl methyl ether (0.81 mL, 10.7 mmol) under N_2, followed by *N*,*N*-diisopropylethylamine (2.95 mL, 17.9 mmol). The resulting mixture was stirred at the same temperature for 20 h. The reaction was quenched by adding water (20 mL), and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced

pressure. The crude residue was purified by flash chromatography (0 to 10% EtOAc in hexanes) on silica gel (50 mL) to afford **13** (1.94 g, 95%) as a colorless oil.

Data for **13**: R_f = 0.22 (15% Et_2O in hexanes); $[\alpha]_D^{21}$ = –18.2 ($CHCl_3$, *c* = 0.48); IR (neat) 2925, 2854, 1467, 1150, 1100, 1041 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.69 (s, 2H), 3.77 (dddd, *J* = 7.0, 6.0, 6.0, 4.5 Hz, 1H), 3.39 (s, 3H), 3.04 (dddd, *J* = 7.0, 4.5, 4.0, 2.5 Hz, 1H), 2.80 (dd, *J* = 4.5, 4.5 Hz, 1H), 2.50 (dd, *J* = 5.0, 3.0 Hz, 1H), 1.76 (ddd, *J* = 14.5, 8.0, 5.0 Hz, 1H), 1.62 (ddd, *J* = 14.5, 7.0, 4.5 Hz, 1H), 1.59–1.50 (m, 2H), 1.38–1.24 (m, 18H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 95.8, 75.6, 55.8, 49.9, 47.7, 38.1, 35.1, 32.1, 29.92, 29.84, 29.82, 29.79 (2C), 29.54, 25.4, 22.9, 14.3; HRMS (ESI) calcd for $C_{17}H_{34}O_3Na$ $[M + Na]^+$: 309.2406, found 309.2400.

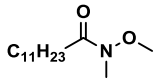
Methyl (3*S*,5*R*)-3-hydroxy-5-(methoxymethoxy)hexadecanoate (14)



According to a modified literature procedure:[6] In a nitrogen glove box, an 8 mL glass vial equipped with a Teflon-coated magnetic stir bar was charged with dicobalt octacarbonyl ($Co_2(CO)_8$) (35.9 mg, 0.105 mmol, 10.1 mol %) and 3-hydroxypyridine (19.5 mg, 0.205 mmol, 19.7 mol %). Tetrahydrofuran (1.2 mL) was added to the vial, followed by (**13)** (0.299 g, 1.04 mmol). After taking the vial out of the glove box, methanol (1.2 mL) was added to the vial and the vial was placed quickly into a custom-made six-well high-pressure reactor. Subsequently, the reactor was sealed, placed in a well-ventilated hood, purged three times with carbon monoxide, and then pressurized to 900 psi. The reactor was then heated to 60 °C and the reaction mixture stirred for 16 hours. The reactor was cooled on dry ice for 10 minutes and carefully vented in a fume hood. The crude reaction mixture was concentrated under reduced pressure and then purified via flash column chromatography (10 to 20% EtOAc in hexanes) on silica gel (60 mL) to afford **14** (0.315 g, 87%) as a colorless oil.

Data for **14**: R_f = 0.31 (30% EtOAc in hexanes); $[\alpha]_D^{24}$ = –29.2 (CH_2Cl_2, *c* = 0.94); IR (neat) 3481, 2925, 2854, 1740, 1466, 1438, 1376, 1205, 1150, 1101, 1039 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.68 (d, *J* = 7.0 Hz, 1H), 4.66 (d, *J* = 7.0 Hz, 1H), 4.29 (dddd, *J* = 10.5, 8.0, 5.0, 3.0 Hz, 1H), 3.81 (dddd, *J* = 9.0, 6.0, 6.0, 3.0 Hz, 1H), 3.70 (s, 3H), 3.04 (s, 3H), 2.52–2.44 (m, 2H), 1.65 (ddd, *J* = 14.5, 9.5, 3.0 Hz, 1H), 1.60–1.55 (m, 1H), 1.56 (ddd, *J* = 14.5, 8.5, 2.5 Hz, 1H), 1.52–1.45 (m, 1H), 1.32–1.22 (m, 18H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 96.5, 75.7, 64.9, 56.0, 51.9, 41.8, 41.2, 35.1, 32.1, 29.94, 29.82, 29.80, 29.77 (2C), 29.5, 25.4, 22.9, 14.3; MALDI-TOF/CCA-HRMS calcd for $C_{19}H_{38}O_5Na$ $[M + Na]^+$: 369.2611, found 369.2600.

_N_-Methoxy-_N_-methyldodecanamide (7c)

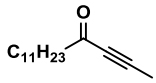


To a stirred solution of ethyl laurate (10.7 g, 46.9 mmol) in tetrahydrofuran (80 mL) at –15 °C was added *N*,*O*-dimethylhydroxylamine hydrochloride (6.85 g, 70.3 mmol), followed by a solution of isopropylmagnesium chloride in tetrahyrofuran (2 M, 47 mL, 94 mmol) via syringe slowly under N_2. The resulting mixture was stirred at the same temperature for 30 min. The reaction was quenched by adding saturated aqueous ammonium chloride (100 mL) and extracted with EtOAc (3 × 120 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (5 to 20% EtOAc in hexanes) on silica gel (200 mL) to afford **7c** (10.2 g, 89%) as a colorless oil.

Data for **7c**: R_f = 0.29 (20% EtOAc in hexanes); IR (neat) 2925, 2854, 1672, 1466, 1414, 1383, 1177, 1119 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.68 (s, 3H), 3.18 (s, 3H), 2.41 (t, *J* = 7.2 Hz, 2H), 1.66–1.58 (m, 3H), 1.34–1.24 (m, 15H), 0.87 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 61.3, 32.0

(2C), 29.75 (3C), 29.64, 29.59, 29.57, 29.47, 24.8, 22.8, 14.2; MALDI-TOF/CCA-HRMS calcd for $C_{14}H_{30}NO_2^+$ $[M + H]^+$: 244.2271, found 244.2285.[7]

Pentadec-2-yn-4-one (7b)

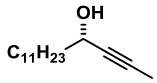


To a stirred solution of **7c** (22.0 g, 90.2 mmol) in tetrahydrofuran (50 mL) at –15 °C was added a solution of 1-propynylmagnesium bromide (0.5 M, 216 mL, 108 mmol) in tetrahydrofuran via syringe slowly under N_2. The resulting mixture was stirred at the same temperature for 0.5 h. The reaction was quenched by adding saturated aqueous ammonium chloride (200 mL) and extracted with EtOAc (3 × 200 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (2 to 5% EtOAc in hexanes) on silica gel (350 mL) to afford **7b** (20.1 g, 99%) as a colorless oil.

Data for **7b**: R_f = 0.44 (10% EtOAc in hexanes); IR (neat) 2922, 2853, 2219, 1673, 1466, 1275, 1164 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.50 (t, J = 7.6 Hz, 2H), 2.00 (s, 3H), 1.67–1.58 (m, 2H), 1.30–1.20 (m, 16H), 0.86 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 89.9, 80.4, 45.6, 32.1, 29.76, 29.75, 29.6, 29.5 (2C), 29.1, 24.2, 22.8, 14.3, 4.2; MALDI-TOF/CCA-HRMS calcd for $C_{15}H_{26}ONa^+$ $[M + Na]^+$: 245.1876, found 245.1864.

[7] Rusch, M.; Zahov, S.; Vetter, I. R.; Lehr, M.; Hedberg, C. *Bioorg. Med. Chem.* **2012**, *20*, 1100–1112.

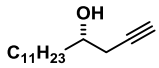
(*S*)-Pentadec-2-yn-4-ol (15)



To a stirred solution of **7b** (7.90 g, 35.5 mmol) in triethylamine (49.5 mL, 355 mmol) at 0 °C was added formic acid (13.4 mL, 355 mmol) slowly under N_2. After the white smoke subsided, (*S*)-RuCl[(1*S*,2*S*)-*p*-TsNCH(C_6H_5)CH(C_6H_5)NH_2](η^6-mesitylene) (110 mg, 178 μmol) was added. The resulting mixture was stirred at room temperature for 12 h. The reaction was quenched by adding water (20 mL), and extracted with EtOAc (3 × 100 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (1 to 15% EtOAc in hexanes) on silica gel (180 mL) to afford **15** (6.60 g, 83%, brsm 93%, ee = 95.5%) as a white solid.

Data for **15**: mp 36.5–37.5 °C; R_f = 0.27 (10% EtOAc in hexanes); $[\alpha]_D^{23}$ = +2.1 (CH_2Cl_2, *c* = 1.37); IR (neat) 3355, 2921, 2853, 1466, 1340, 1266, 1147, 1113, 1031 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.32–4.27 (m, 1H), 2.00 (brs, 1H), 1.82 (d, *J* = 2.5 Hz, 3H), 1.69–1.58 (m, 2H), 1.43–1.37 (m, 2H), 1.30–1.20 (m, 16H), 0.86 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 80.9, 80.7, 62.8, 38.3, 32.1, 29.81, 29.79, 29.74, 29.72, 29.50, 29.47, 25.4, 22.8, 14.3, 3.7; HRMS (EI) calcd for $C_{15}H_{27}O$ [M – 1]$^+$: 223.2062, found 223.2058.

(*S*)-Pentadec-1-yn-4-ol (15a)

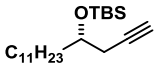


To a flask with oil-free potassium hydride (4.61 g, 115 mmol) at 15 °C was added 1,3-diaminopropane (45 mL) via syringe slowly under N_2. The mixture was stirred at the same temperature for 1.5 h. A solution of **15** (6.45 g, 28.7 mmol) in 1,3-diaminopropane (30 mL) was added to the mixture. The

resulting mixture was warmed to room temperature, and stirred for 18 h. The reaction was quenched by pouring onto ice, and extracted with EtOAc (3 × 80 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (5 to 15% EtOAc in hexanes) on silica gel (200 mL) to afford **15a** (5.16 g, 80%) as a colorless oil.

Data for **15a**: R_f = 0.27 (10% EtOAc in hexanes); $[\alpha]_D^{21}$ = –0.5 (CH_2Cl_2, *c* = 2.26); IR (neat) 3313, 2921, 2852, 1465, 1377, 1275, 1260, 1128, 1066, 1033 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.76–3.70 (m, 1H), 2.40 (ddd, *J* = 16.5, 5.0, 2.5 Hz, 1H), 2.29 (ddd, *J* = 16.5, 6.5, 2.5 Hz, 1H), 2.12 (d, *J* = 4.5 Hz, 1H), 2.03 (t, *J* = 2.5 Hz, 1H), 1.54–1.49 (m, 2H), 1.44–1.37 (m, 1H), 1.33–1.20 (m, 17H), 0.86 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 81.1, 70.9, 70.0, 36.3, 32.1, 29.77, 29.75, 29,71, 29.69, 29.66, 29.5, 27.5, 25.7, 22.8, 14.2.[8]

(*S*)-*tert*-Butyldimethyl(pentadec-1-yn-4-yloxy)silane (16)

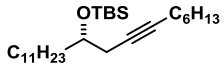


To a stirred solution of **15a** (3.32 g, 14.8 mmol) in dimethylformamide (15 mL) at room temperature was added imidazole (2.52 g, 37.0 mmol), followed by *tert*-butyldimethylsilyl chloride (4.46 g, 29.6 mmol) under N_2. The resulting mixture was stirred at the same temperature for 16 h. The reaction was quenched by adding water (20 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (0 to 1% EtOAc in hexanes) on silica gel (100 mL) to afford **16** (4.83 g, 97%) as a colorless oil.

[8] Ghosh, P.; Chattopadhyay, A. *Tetrahedron Lett.* **2012**, *53*, 5202–5205.

Data for **16**: R_f = 0.25 (hexanes); $[\alpha]_D^{20}$ = –17.5 (CH_2Cl_2, *c* = 1.13); IR (neat) 2955, 2925, 2854, 1463, 1361, 1256, 1099, 1045 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.81–3.76 (m, 1H), 2.32–2.30 (m, 2H), 1.96 (t, *J* = 3.0 Hz, 1H), 1.64–1.57 (m, 1H), 1.54–1.46 (m, 1H), 1.40–1.34 (m, 1H), 1.30–1.20 (m, 17H), 0.89 (s, 9H), 0.88 (t, *J* = 6.5 Hz, 3H), 0.08 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.1, 71.1, 69.9, 36.8, 32.1, 29.84 (3C), 29.79 (2C), 29.5, 27.6, 26.0 (3C), 25.3, 22.9, 18.3, 14.3, –4.3, –4.5; HRMS (EI) calcd for $C_{21}H_{41}OSi$ $[M - 1]^+$: 337.2927, found 337.2930.

(*S*)-*tert*-Butyl(henicos-7-yn-10-yloxy)dimethylsilane (16a)

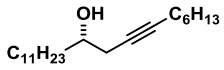


To a stirred solution of **16** (2.75 g, 8.12 mmol) in tetrahydrofuran (9 mL) and hexamethylphosphoramide (6 mL) at –20 °C was added *n*-butyllithium (1.8 M, 5.4 mL, 9.75 mmol) via syringe slowly under N_2. After 1 h at the same temperature, 1-iodohexane was added in one portion. The resulting mixture was stirred at –20 °C for 1 h, warmed slowly to room temperature, and stirred at the temperature for 11 h. The reaction was quenched by adding water (20 mL), and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (0 to 1% EtOAc in hexanes) on silica gel (100 mL) to afford **16a** (3.67 g, 88%) as a colorless oil.

Data for **16a**: R_f = 0.25 (hexanes); $[\alpha]_D^{22}$ = –12.0 (CH_2Cl_2, *c* = 1.23); IR (neat) 2955, 2925, 2854, 1741, 1463, 1361, 1257, 1097, 1046 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.75–3.70 (m, 1H), 2.28–2.24 (m, 2H), 2.15–2.11 (m, 2H), 1.63–1.56 (m, 1H), 1.50–1.44 (m, 2H), 1.40–1.34 (m, 2H), 1.32–1.24 (m, 23H), 0.88 (s, 9H), 0.90–0.87 (m, 6H), 0.07 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.0, 77.6, 71.8, 36.9, 32.1, 31.6, 29.90, 29.88, 29.85, 29.82 (2C), 29.6, 29.2, 28.8, 28.0, 26.1 (3C), 25.3, 22.9, 22.8,

19.0, 18.3, 14.31, 14.26, –4.3, –4.5; HRMS (CI) calcd for $C_{27}H_{53}OSi$ $[M - 1]^+$: 421.3866, found 421.3861.

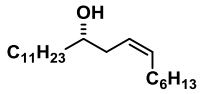
(*S*)-Henicos-7-yn-10-ol (17)



To a flask with **16a** (0.968 g, 2.29 mmol) was added a solution of tetra-*n*-butylammonium fluoride (1 M, 12 mL, 12 mmol) in tetrahydrofuran at room temperature. The resulting mixture was stirred at the same temperature for 14 h. The reaction was quenched by adding saturated aqueous sodium bicarbonate, and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (0 to 4% EtOAc in hexanes) on silica gel (30 mL) to afford **17** (0.678 g, 96%) as a colorless oil.

Data for **17**: R_f = 0.31 (10% EtOAc in hexanes); $[\alpha]_D^{24}$ = +1.5 (CH_2Cl_2, *c* = 3.63); IR (neat) 3373, 2955, 2922, 2853, 1465, 1378, 1275, 1261, 1126, 1085, 1032 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.70–3.66 (m, 1H), 2.40 (dddd, *J* = 16.5, 5.0, 2.5, 2.5 Hz, 1H), 2.26 (dddd, *J* = 16.5, 6.5, 2.5, 2.5 Hz, 1H), 2.17 (m, 2H), 1.92 (s, 1H), 1.53–1.48 (m, 4H), 1.44–1.34 (m, 3H), 1.32–1.25 (m, 21H), 0.89 (t, *J* = 7.0 Hz, 3H), 0.88 (t, *J* = 7.0, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 83.4, 76.3, 70.4, 36.4, 32.1, 31.5, 29.84, 29.81, 29.78 (3C), 29.5, 29.1, 28.7, 27.9, 25.8, 22.9, 22.7, 18.9, 14.3, 14.2; HRMS (EI) calcd for $C_{21}H_{40}O$ $[M]^+$: 308.3079, found 308.3074.

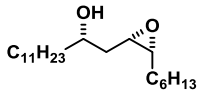
(*S*,*Z*)-Henicos-7-en-10-ol (6b)



To a stirred suspension of palladium/calcium carbonate (5% wt/wt, 30.4 mg, 14.3 μmol) in methanol (5 mL) at room temperature was added quinoline (36.9 mg, 0.286 mmol). The mixture was stirred at the same temperature for 0.5 h. A solution of **17** (0.441 g, 1.43 mmol) in methanol (2 mL) was added to the mixture. The resulting mixture was stirred under H_2 (1 atm) atmosphere. After 18 h, the mixture was concentrated. The crude residue was purified by flash chromatography (2 to 8% EtOAc in hexanes) on silica gel (30 mL) to afford **6b** (0.425 g, 96%) as a colorless oil.

Data for **6b**: R_f = 0.31 (10% EtOAc in hexanes); $[\alpha]_D^{21}$ = –2.0 (CH_2Cl_2, *c* = 1.82); IR (neat) 3341, 2955, 2921, 2853, 1465, 1378, 1275, 1127, 1080, 1030 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.60–5.54 (m, 1H), 5.43–5.37 (m, 1H), 3.61 (dddd, *J* = 6.0, 6.0, 6.0, 6.0 Hz, 1H), 2.23–2.20 (m, 2H), 2.07–2.02 (m, 2H), 1.52 (s, 1H), 1.49–1.42 (m, 3H), 1.37–1.22 (m, 25H), 0.88 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.7, 125.3, 71.7, 37.0, 35.5, 32.1, 31.9, 29.88, 29.85, 29.82 (4C), 29.5, 29.2, 27.6, 26.0, 22.9, 22.8, 14.30, 14.27; HRMS (CI) calcd for $C_{21}H_{41}O$ $[M - 1]^+$: 309.3157, found 309.3153.

(*S*)-1-((2*S*,3*R*)-3-Hexyloxiran-2-yl)tridecan-2-ol (19)

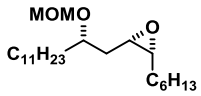


To a stirred solution of **6b** (0.408 g, 1.31 mmol) in dichloromethane (4 mL) at 0 °C was added vanadyl acetylacetonate (6.7 mg, 26 μmol), followed by a solution of *tert*-butyl hydroperoxide (5.5 M, 0.36 mL, 1.97 mmol) in decane slowly via syringe. The resulting mixture was stirred at the same temperature for 2 h, and warmed to room temperature slowly. After 21 h, the reaction was quenched by adding water (10 mL) and sodium sulfite (0.497 g, 3.94 mmol). After 30 min, the mixture was extracted with EtOAc (3 ×

30 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (5 to 10% EtOAc in hexanes) on silica gel (30 mL) to afford **19** (0.403 g, 94%) as a colorless oil.

Data for **19**: R_f = 0.24 (10% EtOAc in hexanes); $[\alpha]_D^{23}$ = –3.2 (CH_2Cl_2, *c* = 1.31); IR (neat) 3427, 2955, 2922, 2853, 1465, 1378, 1275, 1261, 1128, 1110, 1070, 1038 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.93–3.88 (m, 1H), 3.12 (ddd, *J* = 8.0, 4.0, 4.0 Hz, 1H), 2.91 (ddd, *J* = 6.0, 5.0, 5.0 Hz, 1H), 2.28 (s, 1H), 1.80 (ddd, *J* = 14.5, 4.0, 4.0 Hz, 1H), 1.56–1.45 (m, 5H), 1.44–1.39 (m, 1H), 1.37–1.24 (m, 25H), 0.88 (t, *J* = 6.5 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 71.0, 56.5, 55.6, 37.6, 34.8, 32.1, 31.9, 29.81, 29.79 (2C), 29.76 (2C), 29.5, 29.3, 28.1, 26.6, 25.7, 22.8, 22.7, 14.26, 14.20; MALDI-TOF/CCA-HRMS calcd for $C_{21}H_{42}O_2Na$ $[M + Na]^+$: 349.3077, found 349.3070.

(2*R*,3*S*)-2-Hexyl-3-((*S*)-2-(methoxymethoxy)tridecyl)oxirane (5b)

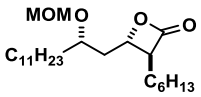


To a stirred solution of **19** (0.211 g, 0.646 mmol) in dichloromethane (4 mL) at room temperature was added chloromethyl methyl ether (98 μL, 1.29 mmol) under N_2, followed by *N*,*N*-diisopropylethylamine (0.267 mL, 1.62 mmol) and 4-dimethylaminopyridine (2 mg). The resulting mixture was stirred at the same temperature for 24 h. The reaction was quenched by adding water (10 mL), and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (3 to 15% EtOAc in hexanes) on silica gel (30 mL) to afford **5b** (0.202 g, 85%) as a colorless oil.

Data for **5b**: R_f = 0.42 (10% EtOAc in hexanes); $[\alpha]_D^{20}$ = +1.3 (CH_2Cl_2, *c* = 0.51); IR (neat) 2925, 2855, 1467, 1378, 1150, 1100, 1041 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.67 (s, 2H), 3.73 (dddd, *J* = 6.0, 6.0.

6.0, 6.0 Hz, 1H), 3.39 (s, 3H), 3.05 (ddd, *J* = 7.0, 4.5, 4.5 Hz, 1H), 2.92–2.88 (m, 1H), 1.78 (ddd, *J* = 15.0, 5.0, 5.0 Hz, 1H), 1.70 (ddd, *J* = 15.0, 6.0, 6.0 Hz, 1H), 1.63–1.55 (m, 2H), 1.52–1.47 (m, 3H), 1.38–1.24 (m, 25H), 0.88 (t, *J* = 6.5 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 95.5, 75.9, 56.7, 55.7, 54.3, 34.7, 33.0, 32.1, 32.0, 29.89, 29.84, 29.80 (3C), 29.5, 29.4, 28.2, 26.8, 25.6, 22.9, 22.8, 14.29, 14.24; MALDI-TOF/CCA-HRMS calcd for $C_{23}H_{46}O_3Na$ $[M + Na]^+$: 393.3339, found 393.3350.

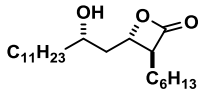
(3*S*,4*S*)-3-Hexyl-4-((*S*)-2-(methoxymethoxy)tridecyl)oxetan-2-one (20)



The general procedure for carbonylation of epoxides was followed using **5b** (99.1 mg 0.267 mmol), $[ClTPPAl]^+[Co(CO)_4]^-$ (2.8 mg, 0.0026 mmol, 0.97 mol %) and tetrahydrofuran (0.53 mL) for 12 hours. The crude residue was purified by flash column chromatography (5 to 15% EtOAc in hexanes) on silica gel (30 mL) to afford **20** (86.0 mg, 81%) as a colorless oil.

Data for **20**: R_f = 0.32 (10% EtOAc in hexanes); $[\alpha]_D^{21}$ = –10.5 (CH_2Cl_2, *c* = 0.44); IR (neat) 2926, 2855, 1825, 1467, 1378, 1151, 1123, 1099, 1039 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.65 (d, *J* = 7.0 Hz, 1H), 4.62 (d, *J* = 7.0 Hz, 1H), 4.42 (ddd, *J* = 6.5, 6.5, 4.0 Hz, 1H), 3.66 (dddd, *J* = 5.5, 5.5, 5.5, 5.5 Hz, 1H), 3.37 (s, 3H), 3.25 (ddd, *J* = 7.5, 7.5, 4.5 Hz, 1H), 2.12 (ddd, *J* = 14.5, 7.0, 6.0 Hz, 1H), 1.94 (ddd, *J* = 14.5, 6.0, 5.5 Hz, 1H), 1.86–1.80 (m, 1H), 1.79–1.71 (m, 1H), 1.62–1.50 (m, 1H), 1.49–1.44 (m, 1H), 1.42–1.36 (m, 1H), 1.35–1.24 (m, 25H), 0.884 (t, *J* = 7.0 Hz, 3H), 0.879 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 95.9, 75.3, 75.0, 57.1, 55.9, 39.1, 34.4, 32.1, 31.7, 29.83 (2C), 29.76, 29.65, 29.56, 29.52, 29.2, 28.0, 26.9, 25.5, 22.9, 22.7, 14.3, 14.2; MALDI-TOF/CCA-HRMS calcd for $C_{24}H_{46}O_4Na$ $[M + Na]^+$: 421.3288, found 421.3268.

(3*S*,4*S*)-3-Hexyl-4-((*S*)-2-hydroxytridecyl)oxetan-2-one (4b)

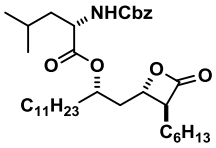


To a stirred solution of **20** (56.6 mg, 0.142 mmol) in dichloromethane (1.5 mL) at 0 °C was added 1,2-ethanedithiol (36 µL, 0.426 mmol), followed by boron trifluoride diethyl etherate (18 µL, 0.142 mmol) under N_2. The resulting mixture was stirred at the same temperature for 30 min. The reaction was quenched by adding saturated aqueous sodium bicarbonate (5 mL), and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (5 to 15% EtOAc in hexanes) on silica gel (35 mL) to afford **4b** (42.0 mg, 83%) as a white solid.

Data for **4b**: mp 60.5–62.0 °C; R_f = 0.39 (20% EtOAc in hexanes); $[\alpha]_D^{22}$ = –10.4 ($CHCl_3$, *c* = 0.42); IR (neat) 3544, 2956, 2922, 2851, 1816, 1726, 1467, 1101 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.47 (ddd, *J* = 6.0, 6.0, 4.5 Hz, 1H), 3.81–3.75 (m, 1H), 3.31 (ddd, *J* = 8.5, 6.5, 4.0 Hz, 1H), 2.01 (ddd, *J* = 14.5, 8.5, 7.5 Hz, 1H), 1.90 (ddd, *J* = 15.5, 6.0, 3.5 Hz, 1H), 1.84 (dddd, *J* = 13.5, 10.0, 6.5, 6.5 Hz, 1H), 1.74 (dddd, *J* = 14.0, 9.0, 9.0, 6.0 Hz, 1H), 1.61 (brs, 1H), 1.53–1.49 (m, 2H), 1.47–1.37 (m, 3H), 1.34–1.24 (m, 23H), 0.883 (t, *J* = 7.0 Hz, 3H), 0.878 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 76.4, 69.5, 57.0, 41.4, 37.9, 32.1, 31.7, 29.83, 29.81, 29.75 (2C), 29.70, 29.5, 29.1, 28.0, 27.0, 25.6, 22.9, 22.7, 14.3, 14.2; MALDI-TOF/CCA-HRMS calcd for $C_{22}H_{42}O_3Na$ $[M + Na]^+$: 377.3026, found 377.3021.[9]

[9] Ghosh, A. K.; Shurrush, K.; Kulkarni, S. *J. Org. Chem.* **2009**, *74*, 4508–4518.

(*S*)-1-((2*S*,3*S*)-3-Hexyl-4-oxooxetan-2-yl)tridecan-2-yl ((benzyloxy)carbonyl)-L-leucinate (21)

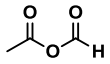


To a stirred solution of **4b** (19.6 mg, 55.3 μmol) in dichloromethane (1 mL) at room temperature was added *N*-Cbz-L-Leu-OH (44.0 mg, 166 μmol), followed by *N*,*N*-dicyclohexylcarbodiimide (45.4 mg, 221 μmol) and 4-dimethylaminopyridine (1 mg). The resulting mixture was stirred at the same temperature for 22 h. The mixture was diluted with hexanes and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The crude residue was purified by flash chromatography (5% EtOAc in hexanes) on silica gel (2 mL) to afford **21** (31.0 mg, 93%) as a colorless oil.

Data for **21**: R_f = 0.24 (10% EtOAc in hexanes); $[\alpha]_D^{23}$ = –24.1 ($CHCl_3$, *c* = 0.56); IR (neat) 3357, 2926, 2855, 1824, 1727, 1524, 1467, 1333, 1262, 1218, 1171, 1121, 1048 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37–7.30 (m, 5H), 5.11 (s, 2H), 5.08 (d, *J* = 8.5 Hz, 1H), 5.02–4.98 (m, 1H), 4.34 (ddd, *J* = 9.0, 9.0, 5.0 Hz, 1H), 4.30–4.26 (m, 1H), 3.20 (ddd, *J* = 7.0, 7.0, 4.0 Hz, 1H), 2.15 (ddd, *J* = 15.0, 7.5, 7.5 Hz, 1H), 1.96 (ddd, *J* = 15.0, 4.5, 4.5 Hz, 1H), 1.82–1.67 (m, 3H), 1.65–1.57 (m, 3H), 1.51 (ddd, *J* = 14.0, 9.5, 5.5 Hz, 1H), 1.46–1.41 (m, 1H), 1.32–1.24 (m, 25H), 0.947 (d, *J* = 6.0 Hz, 3H), 0.939 (d, *J* = 6.0 Hz, 3H), 0.882 (t, *J* = 6.5 Hz, 3H), 0.878 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 171.1, 156.1, 136.4, 128.7 (2C), 128.4, 128.3 (2C), 74.8, 72.5, 67.2, 57.2, 52.9, 41.8, 38.8, 34.2, 32.1, 31.7, 29.82, 29.81, 29.73, 29.63, 29.54, 29.49, 29.2, 27.8, 26.9, 25.3, 25.0, 23.1, 22.9, 22.7, 21.9, 14.3, 14.2; MALDI-TOF/CCA-HRMS calcd for $C_{36}H_{59}NO_6Na$ $[M + Na]^+$: 624.4235, found 624.4238.[9,10]

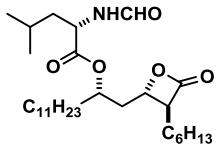
[10] Chadha, N. K.; Batcho, A. D.; Tang, P. C.; Courtney, L. F.; Cook, C. M.; Wovkulich, P. M.; Uskokovic, M. R. *J. Org. Chem.* **1991**, *56*, 4714–4718.

Acetic formic anhydride



To a flask with acetic anhydride (2.0 mL, 21.2 mmol) at room temperature was added formic acid (0.88 mL, 23.3 mmol). The resulting mixture was stirred at reflux for 1.5 h. The mixture was used directly for next step.

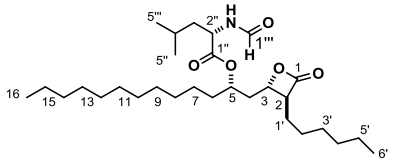
(*S*)-1-((2*S*,3*S*)-3-Hexyl-4-oxooxetan-2-yl)tridecan-2-yl formyl-L-leucinate (1)



To a stirred solution of **21** (20.0 mg, 33.2 μmol) in acetic formic anhydride (1.5 mL) at room temperature was added Pd/C (10% wt/wt, 3.5 mg, 3.3 μmol) under N_2. The resulting mixture was stirred under H_2 (1 atm) for 1h. The mixture was filtered through a pad of Celite, and washed with EtOAc. The filtrate was concentrated under reduced pressure. The crude residue was purified by flash chromatography (30% EtOAc in hexanes) on silica gel (2 mL) to afford **1** (14.7 mg, 80%) as a colorless oil.

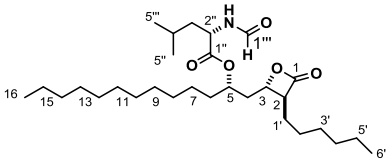
Data for **1**: R_f = 0.27 (30% EtOAc in hexanes); $[\alpha]_D^{23}$ = –33.7 ($CHCl_3$, *c* = 0.48); IR (neat) 3380, 2926, 2854, 1823, 1738, 1666, 1553, 1467, 1378, 1253, 1187, 1123 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 5.91 (d, *J* = 8.0 Hz, 1H), 5.05–5.00 (m, 1H), 4.69 (ddd, *J* = 9.0, 9.0, 5.0 Hz, 1H), 4.29 (ddd, *J* = 7.5, 5.0, 5.0 Hz, 1H), 3.22 (ddd, *J* = 7.5, 7.5, 4.0 Hz, 1H), 2.17 (ddd, *J* = 15.0, 7.5, 7.5 Hz, 1H), 2.00 (ddd, *J* = 15.0, 4.5, 4.5 Hz, 1H), 1.84–1.78 (m, 1H), 1.77–1.63 (m, 4H), 1.61–1.53 (m, 2H), 1.47–1.41 (m, 1H), 1.32–1.24 (m, 25H), 0.972 (d, *J* = 6.5 Hz, 3H), 0.967 (d, *J* = 6.5 Hz, 3H), 0.885 (t, *J* = 6.5 Hz,

3H), 0.878 (t, J = 7.0, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.92, 170.75, 160.60, 74.76, 72.76, 57.03, 49.60, 41.56, 38.70, 34.05, 31.89, 31.47, 29.60 (2C), 29.53, 29.42, 29.33, 29.29, 28.96, 27.61, 26.70, 25.09, 24.88, 22.87, 22.68, 22.51, 21.73, 14.12, 14.01 ($CDCl_3$, δ 77.0 ppm, for comparison with existing papers); MALDI-TOF/CCA-HRMS calcd for $C_{29}H_{53}NO_5Na$ $[M + Na]^+$: 518.3816, found 518.3814.



Position	*J. Antibiot.* **1987**, 1086	**This Work**	*J. Org. Chem.* **2012**, 4885	*Org. Lett.* **2010**, 1556	*J. Org. Chem.* **2009**, 4508	*Synthesis* **2006**, 3888	*Org. Lett.* **2006**, 4497
CHO (1H)	8.21 (s)	8.22 (s)	8.22 (s)	8.22 (s)	8.22 (s)	8.23 (s)	8.23 (s)
	8.07 (d, 12)	8.06 (d, 11.5)					
2''-NH (1H)	6.43 (d, 9)	5.91 (d, 8.5)	5.90 (d, 8.5)	5.96 (d, 8.4)	5.91 (d, 8.1)	6.05 (d, 8.5)	5.92 (d, 8.7)
5 (1H)	5.03 (m)	5.03–5.00 (m)	5.03 (dddd, 7.0, 6.5, 5.5, 4.0)	5.06–4.99 (m, 1H)	5.05–5.00 (m)	5.02 (m, 1H)	5.10–4.98 (m)
2'' (1H)	4.68 (ddd, 9, 9, 5)	4.69 (ddd, 9.0, 9.0, 5.0)	4.69 (ddd, 13.0, 8.5, 4.0)	4.68 (td, 8.7, 4.1)	4.71–4.66 (m)	4.68 (m,1H)	4.70 (dt, 8.4, 4.8)
3 (1H)	4.32 (ddd, 9, 5, 4)	4.29 (ddd, 7.5, 5.0, 5.0)	4.29 (ddd, 8.0, 4.5, 4.5)	4.32–4.27 (m, 1H)	4.29(dt, 7.3, 4.7)	4.28 (m, 1H)	4.23 (ddd, 8.4, 4.2, 3.9)
2 (1H)	3.24 (ddd, 7.5, 7.5, 4)	3.22 (ddd, 7.5, 7.5, 4.0)	3.21 (ddd, 11.5, 4.5, 4.0)	3.22 (ddd, 7.9, 7.2, 4.1)	3.22 (dt, 7.1, 3.2)	3.22 (dt, 7.6, 3.9)	3.28 (dt, 7.2, 3.9)
4, 4a (2H)	1.9–2.25 (m, 2H)	2.17 (ddd, 15.0, 7.5, 7.5)	2.16 (dt, 15.0, 8.0, 7.0)	2.21–2.12 (m, 1H)	2.15–2.10 (m, 1H)	2.25–2.11 (m, 1H)	2.24–1.96 (m, 2H)
		2.00 (ddd, 15.0, 4.5, 4.5)	2.01 (dt, 15.0, 4.5, 4.0)	1.99 (ddd, 14.9, 4.7, 4.1)	2.08–2.00 (m, 1H)	2.02 (m, 1H)	
CH_2 (33H)	1.15–1.85 (m)	1.84–1.78 (m, 1H)	1.85–1.50 (m, 6H)	1.86–1.49 (m, 7H)	1.85–1.51 (m, 7H)	1.80–1.15 (m, 33H)	1.85–1.53 (m, 5H)
		1.77–1.63 (m, 4H)					
		1.61–1.53 (m, 2H)					
		1.47–1.41 (m, 1H)	1.50–1.15 (m, 27H)	1.49–1.03 (m, 26H)	1.41–1.15 (m, 26H)		1.27 (br s, 26H)
		1.32–1.24 (m, 25H)					
5'', 5''' (6H)	0.97 (d, 6, 6H)	0.972 (d, 6.5, 3H)	1.05–0.82 (m, 12H)	0.97 (dd, 6.1, 2.5, 6H)	0.96 (t, 6.3, 6H)	0.95 (d, 5.2, 6H)	0.98 (dd, 6.3, 1.5, 6H)
		0.967 (d, 6.5, 3H)					
16, 6' (6H)	0.89 (t, 7, 6H)	0.885 (t, 6.5, 3H)		0.89 (t, 6.9, 3H)	0.89 (t, 6.5, 6H)	0.87 (distorted t, 6H)	0.89 (t, 6.6, 3H)
		0.878 (t, 7.0, 3H)		0.88 (t, 6.9, 3H)			

Table S1. ^{1}H NMR assignments of THL. *δ_H (multiplicity, coupling constant (*J*) in Hz)

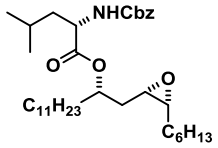


Position	*J. Antibiot.* **1987**, 1086	**This Work**	*J. Org. Chem.* **2012**, 4885	*Org. Lett.* **2010**, 1556	*J. Org. Chem.* **2009**, 4508	*Synthesis* **2006**, 3888	*Org. Lett.* **2006**, 4497
1, 1"	171.93	171.92	171.9	171.9	171.9	171.9	172.2
	170.73	170.75	170.7	170.7	170.7	170.8	171.0
1"'	160.83	160.60	160.6	160.6	160.5	160.7	160.8
3, 5	74.74	74.76	74.7	74.7	74.7	74.8	75.0
	72.63	72.76	72.7	72.7	72.7	72.6	73.0
2, 2"	57.07	57.03	57.0	57.0	57.0	56.9	57.3
	49.76	49.60	49.6	49.6	49.6	49.7	49.9
	41.44	41.56	41.5	41.5	41.5	41.4	41.8
	38.73	38.70	38.7	38.7	38.7	38.7	38.9
	34.07	34.05	34.0	34.0	34.0	34.0	34.3
4, 6, 9	31.93	31.89	31.9	31.9	31.8	31.9	32.1
12, 13,	31.51	31.47	31.4	31.4	31.4	31.2	32.0
14, 1', 2',	29.63	29.60	29.6	29.6	29.6	29.6	29.93
3' 4', 3",	29.63	29.60					29.71
	29.57	29.53	29.5	29.5		29.5	29.65
	29.46	29.42	29.4	29.4	29.4	29.4	29.56
	29.35	29.33	29.3	29.3	29.3	29.3	29.51
	29.35	29.29	29.3	29.2		29.2	29.49
	28.99	28.96	28.9	28.9	28.9	28.8	29.40
7, 8, 10,	27.67	27.61	27.6	27.6	27.6	27.7	27.8
11	26.73	26.70	26.7	26.7	26.6	26.8	27.0
	25.12	25.09	25.1	25.0	25.0	25.2	25.3
4"	24.93	24.88	24.9	24.8	24.8	24.9	25.1
5" or 5"'	22.87	22.87	22.8	22.8	22.8	22.8	23.1
15, 5'	22.69	22.68	22.7	22.6	22.6	22.7	22.89
	22.53	22.51	22.5	22.5	22.5	22.5	22.86
5" or 5"'	21.78	21.73	21.7	21.7	21.7	21.7	22.0
16, 6'	14.10	14.12	14.1	14.1	14.1	14.1	14.3
	14.00	14.01	14.0	14.0	14.0	14.0	
unknown			21.9		25.8		

Table S2. ^{13}C NMR assignments of THL.

Notes: 1) Residual solvent signal was used as reference: $CDCl_3$ δ_c 77.0 ppm. (77.23 ppm for *Org. Lett.* **2006**, 4497)
2) The paper (*J. Org. Chem.* **2012**, 4885) reported one extra peak at 21.9 ppm. The paper (*J. Org. Chem.* **2009**, 4508) reported one extra peak at 25.8 ppm.

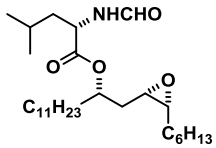
(*S*)-1-((2*S*,3*R*)-3-Hexyloxiran-2-yl)tridecan-2-yl ((benzyloxy)carbonyl)-L-leucinate (24)



To a stirred solution of **19** (100 mg, 0.306 mmol) in dichloromethane (1.5 mL) at room temperature was added *N*-Cbz-L-Leu-OH (122 mg, 0.459 mmol), followed by *N*,*N*-dicyclohexylcarbodiimide (126 mg, 0.612 mmol) and 4-dimethylaminopyridine (4 mg). The resulting mixture was stirred at the same temperature for 20 h. The mixture was diluted with hexanes and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The crude residue was purified by flash chromatography (10% EtOAc in hexanes) on silica gel (2 mL) to afford **24** (175 mg, 99%) as a colorless oil.

Data for **24**: R_f = 0.21 (10% EtOAc in hexanes); $[\alpha]_D^{23}$ = –14.1 (CH_2Cl_2, *c* = 1.06); IR (neat) 3336, 2957, 2926, 2855, 1726, 1527, 1467, 1333, 1262, 1218, 1171, 1048 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36–7.30 (m, 5H), 5.17 (d, *J* = 8.5 Hz, 1H), 5.13–5.06 (m, 1H), 5.10 (s, 2H), 4.38 (ddd, *J* = 9.0, 9.0, 5.0 Hz, 1H), 2.95–2.91 (m, 1H), 2.87–2.84 (m, 1H), 1.83 (ddd, *J* = 15.0, 4.5, 4.5 Hz, 1H), 1.73 (ddd, *J* = 14.0, 7.0, 7.0 Hz, 1H), 1.69–1.60 (m, 3H), 1.55–1.39 (m, 5H), 1.35–1.24 (m, 25H), 0.96 (d, *J* = 6.0 Hz, 3H), 0.94 (d, *J* = 6.0 Hz, 3H), 0.889 (t, *J* = 7.0 Hz, 3H), 0.877 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 156.1, 136.4, 128.7 (2C), 128.32, 128.25 (2C), 74.0, 67.1, 56.4, 53.7, 52.9, 41.9, 34.2, 32.6, 32.1, 31.9, 29.82, 29.80, 29.75, 29.66, 29.56, 29.53, 29.4, 28.1, 26.7, 25.4, 25.0, 23.1, 22.9, 22.7, 22.0, 14.31, 14.25; MALDI-TOF/CCA-HRMS calcd for $C_{35}H_{59}NO_5Na$ $[M + Na]^+$: 596.4285, found 596.4294.

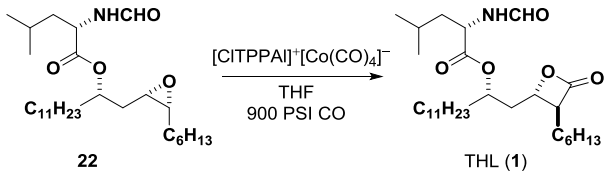
(*S*)-1-((2*S*,3*R*)-3-Hexyloxiran-2-yl)tridecan-2-yl formyl-L-leucinate (22)



To a stirred solution of **24** (175 mg, 0.305 mmol) in tetrahydrofuran (2 mL) at room temperature was added Pd/C (10% wt/wt, 32 mg, 30.6 μmol) under N_2. The resulting mixture was then stirred at the same temperature under H_2 (1 atm) for 2 h. The mixture was filtered through a pad of Celite, and washed with EtOAc. The filtrate was concentrated under reduced pressure. The residue was dissolved in dichloromethane (1 mL). Then a premixed mixture of *N*,*N*-dicyclohexylcarbodiimide (314 mg, 1.53 mmol) and formic acid (35 μL, 0.918 mmol) in dichloromethane (4 mL) was added to the solution. After 5 min, the mixture was diluted with hexanes and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The crude residue was purified by flash chromatography (0 to 20% EtOAc in hexanes) on silica gel (2 mL) to afford **22** (113 mg, 79%) as a colorless oil.

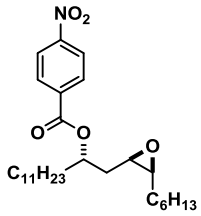
Data for **22**: R_f = 0.32 (30% EtOAc in hexanes); $[\alpha]_D^{23}$ = –21.3 (CH_2Cl_2, *c* = 0.77); IR (neat) 3301, 2957, 2926, 2855, 1740, 1668, 1528, 1467, 1382, 1274, 1253, 1195 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 6.07 (d, *J* = 9.0 Hz, 1H), 5.09 (dddd, *J* = 8.0, 8.0, 5.0, 4.5 Hz, 1H), 4.72 (ddd, *J* = 8.5, 8.5, 5.0 Hz, 1H), 2.93 (ddd, *J* = 7.5, 4.0, 4.0 Hz, 1H), 2.87 (ddd, *J* = 6.0, 6.0, 4.5 Hz, 1H), 1.87 (ddd, *J* = 14.5, 4.5, 4.5 Hz, 1H), 1.74–1.58 (m, 5H), 1.52–1.39 (m, 4H), 1.36–1.24 (m, 25H), 0.96 (d, *J* = 6.0 Hz, 3H), 0.95 (d, *J* = 6.0 Hz, 3H), 0.885 (t, *J* = 6.5 Hz, 3H), 0.871 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 160.8, 74.3, 56.4, 53.8, 49.9, 41.9, 34.3, 32.7, 32.1, 31.9, 29.79, 29.78, 29.74, 29.64, 29.55, 29.52, 29.3, 28.1, 26.7, 25.4, 25.1, 23.0, 22.9, 22.7, 22.1, 14.3, 14.2; MALDI-TOF/CCA-HRMS calcd for $C_{28}H_{53}NO_4Na$ $[M + Na]^+$: 490.3867, found 490.3861.

(*S*)-1-((2*S*,3*S*)-3-Hexyl-4-oxooxetan-2-yl)tridecan-2-yl formyl-L-leucinate (1)



The general procedure for carbonylation of epoxides was followed using **22** (69.8 mg, 0.149 mmol), $[ClTPPAl]^{+}[Co(CO)_4]^{-}$ (3.4 mg, 0.0031 mmol, 2.1 mol %), and tetrahydrofuran (0.30 mL) for 24 hours. The crude residue was purified by preparative HPLC to afford **1** (59.4 mg, 80%) as a colorless oil.

(*S*)-1-((2*R*,3*S*)-3-Hexyloxiran-2-yl)tridecan-2-yl 4-nitrobenzoate (19a)

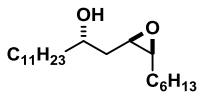


To a stirred solution of *ent*-**19**[11] (1.08 g, 3.31 mmol) in tetrahydrofuran (6 mL) at 0 °C was added triphenylphosphine (1.78 g, 6.78 mmol), followed by *p*-nitrobenzoic acid (1.10 g, 6.62 mmol) under N_2. A solution of diisopropyl azodicarboxylate (94%, 1.42 g, 6.62 mmol) in tetrahydrofuran (4 mL) was added to the solution slowly via syringe. The resulting mixture was stirred at the same temperature for 40 min. The reaction was quenched by adding saturated aqueous sodium bicarbonate (10 mL), and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (2 to 10% Et_2O in hexanes) on silica gel (40 mL) to afford **19a** (1.50 g, 96%) as a colorless oil.

[11] The synthesis of *ent*-**19** was prepared using the same strategy as that for **19**, and will be published in due course.

Data for **19a**: R_f = 0.30 (5% EtOAc in hexanes); $[\alpha]_D^{24}$ = –2.3 (CH_2Cl_2, *c* = 0.69); IR (neat) 2926, 2855, 1725, 1608, 1530, 1467, 1349, 1275, 1102, 1015 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.5 Hz, 2H), 8.21 (d, *J* = 8.5 Hz, 2H), 5.35 (ddd, *J* = 7.5, 7.5, 5.5, 5.5 Hz, 1H), 3.03 (ddd, *J* = 7.0, 4.5, 4.5 Hz, 1H), 2.91 (ddd, *J* = 6.0, 6.0, 4.5 Hz, 1H), 2.01 (ddd, *J* = 14.5, 7.5, 5.0 Hz, 1H), 1.86–1.76 (m, 3H), 1.51–1.45 (m, 3H), 1.40–1.24 (m, 25H), 0.88–0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 150.7, 136.0, 130.9 (2C), 123.7 (2C), 74.6, 57.0, 53.8, 34.5, 32.9, 32.1, 31.9, 29.79 (2C), 29.71, 29.65, 29.57, 29.51, 29.3, 28.1, 26.7, 25.5, 22.9, 22.7, 14.3, 14.2; MALDI-TOF/CCA-HRMS calcd for $C_{28}H_{45}NO_5Na$ $[M + Na]^+$: 498.3190, found 498.3193.

(*S*)-1-((2*R*,3*S*)-3-Hexyloxiran-2-yl)tridecan-2-ol (25)

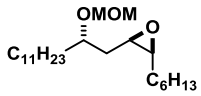


To a stirred solution of **19a** (1.56 g, 3.28 mmol) in methanol (7 mL) at 0 °C was added potassium carbonate (0.91 g, 6.58 mmol). The resulting mixture was stirred at the same temperature for 6 h. The reaction was quenched by adding water (20 mL), and extracted with EtOAc (3 × 40 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (10 to 20% EtOAc in hexanes) on silica gel (40 mL) to afford **25** (0.861 g, 80%) as a colorless oil.

Data for **25**: mp 41–42 °C; R_f = 0.38 (10% EtOAc in hexanes); $[\alpha]_D^{22}$ = +14.4 (CH_2Cl_2, *c* = 1.63); IR (neat) 3459, 2955, 2922, 2853, 1465, 1378, 1275, 1261, 1128, 1110, 1070, 1038 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.87–3.81 (m, 1H), 3.15 (ddd, *J* = 8.8, 4.4, 4.4 Hz, 1H), 2.96 (ddd, *J* = 6.0, 6.0, 4.4 Hz, 1H), 1.81 (brs, 1H), 1.74 (ddd, *J* = 14.4, 8.0, 4.4 Hz, 1H), 1.56 (ddd, *J* = 14.4, 8.0, 4.4 Hz, 1H), 1.55–1.40 (m, 6H), 1.35–1.22 (m, 24H), 0.88 (t, *J* = 6.4 Hz, 3H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 70.4, 57.4, 54.6, 37.9, 35.2, 32.10, 31.95, 29.84, 29.81, 29.78 (3C), 29.5, 29.4, 28.2,

26.7, 25.8, 22.9, 22.8, 14.30, 14.25; MALDI-TOF/CCA-HRMS calcd for $C_{21}H_{42}O_2Na$ $[M + Na]^+$: 349.3077, found 349.3059.

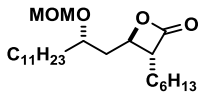
(2*S*,3*R*)-2-Hexyl-3-((*S*)-2-(methoxymethoxy)tridecyl)oxirane (26)



To a stirred solution of **25** (0.325 g, 1.00 mmol) in dichloromethane (3 mL) at room temperature was added chloromethyl methyl ether (0.151 mL, 2.00 mmol) under N_2, followed by *N*,*N*-diisopropyl-ethylamine (0.413 mL, 2.50 mmol) and 4-dimethylaminopyridine (3 mg). The resulting mixture was stirred at the same temperature for 11 h. The reaction was quenched by adding water (10 mL), and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (2 to 8% EtOAc in hexanes) on silica gel (30 mL) to afford **26** (0.309 g, 84%) as a colorless oil.

Data for **26**: R_f = 0.42 (10% EtOAc in hexanes); $[\alpha]_D^{22}$ = +8.9 (CH_2Cl_2, *c* = 1.77); IR (neat) 2922, 2854, 1466, 1275, 1099, 1037 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.68 (s, 2H), 3.75 (dddd, *J* = 7.6, 5.6, 5.6, 5.6 Hz, 1H), 3.38 (s, 3H), 3.05 (ddd, *J* = 7.2, 4.4, 4.4 Hz, 1H), 2.95–2.91 (m, 1H), 1.78 (ddd, *J* = 14.4, 7.2, 4.4 Hz, 1H), 1.60 (ddd, *J* = 14.4, 7.2, 4.8 Hz, 1H), 1.58–1.55 (m, 2H), 1.52–1.47 (m, 3H), 1.38–1.24 (m, 25H), 0.88 (t, *J* = 6.4 Hz, 3H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 95.8, 75.9, 57.4, 55.8, 54.6, 35.1, 33.2, 32.1, 32.0, 29.92, 29.84, 29.81, 29.80 (2C), 29.78, 29.5, 29.4, 28.3, 26.7, 25.4, 22.9, 22.7, 14.30, 14.24; MALDI-TOF/CCA-HRMS calcd for $C_{23}H_{46}O_3Na$ $[M + Na]^+$: 393.3339, found 393.3329.

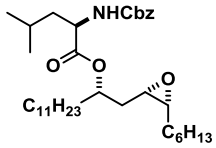
(3*R*,4*R*)-3-Hexyl-4-((*S*)-2-(methoxymethoxy)tridecyl)oxetan-2-one (33)



The general procedure for carbonylation of epoxides was followed using **26** (53.7 mg, 0.145 mmol), $[ClTPPAl]^+[Co(CO)_4]^-$ (1.6 mg, 0.0015 mmol, 1.0 mol %) and tetrahydrofuran (0.30 mL) for 12 hours. The crude residue was purified by preparative HPLC to afford **33** (50.5 mg, 88%) as a colorless oil.

Data for **33**: R_f = 0.31 (10% EtOAc in hexanes); $[\alpha]_D^{23}$ = +45.2 (CH_2Cl_2, *c* = 0.82); IR (neat) 2926, 2855, 1825, 1467, 1390, 1152, 1118, 1101, 1040 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.68 (d, *J* = 7.0 Hz, 1H), 4.64 (d, *J* = 7.0 Hz, 1H), 4.44 (ddd, *J* = 6.5, 6.5, 4.5 Hz, 1H), 3.70 (ddd, *J* = 12.0, 6.0, 6.0 Hz, 1H), 3.38 (s, 3H), 3.21 (ddd, *J* = 8.0, 8.0, 4.5 Hz, 1H), 1.95–1.89 (m, 2H), 1.82 (dddd, *J* = 13.5, 10.5, 6.0, 6.0 Hz, 1H), 1.74 (dddd, *J* = 13.5, 9.0, 9.0, 6.0 Hz, 1H), 1.62–1.56 (m, 1H), 1.52–1.48 (m, 1H), 1.46–1.42 (m, 1H), 1.40–1.35 (m, 1H), 1.34–1.24 (m, 24H), 0.880 (t, *J* = 7.0 Hz, 3H), 0.875 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 96.0, 75.3, 74.6, 56.7, 55.9, 40.1, 34.9, 32.1, 31.7, 29.9, 29.82, 29.80, 29.76 (2C), 29.5, 29.1, 27.9, 27.0, 25.0, 22.9, 22.7, 14.3, 14.2.[12]

(*S*)-1-((2*S*,3*R*)-3-Hexyloxiran-2-yl)tridecan-2-yl ((benzyloxy)carbonyl)-D-leucinate (27)



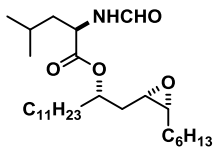
To a stirred solution of **19** (32.0 mg, 98.0 μmol) in dichloromethane (0.8 mL) at room temperature was added *N*-Cbz-D-Leu-OH (39.0 mg, 147 μmol), followed by *N*,*N*-dicyclohexylcarbodiimide (40.2 mg, 196 μmol) and 4-dimethylaminopyridine (1 mg). The resulting mixture was stirred at the same

[12] Yadav, J. S.; Rao, K. V.; Prasad, A. R. *Synthesis* **2006**, 3888–3894.

temperature for 20 h. The mixture was diluted with hexanes and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The crude residue was purified by flash chromatography (5 to 10% EtOAc in hexanes) on silica gel (2 mL) to afford **27** (54.0 mg, 96%) as a colorless oil.

Data for **27**: R_f = 0.21 (10% EtOAc in hexanes); $[\alpha]_D^{21}$ = +2.5 (CH_2Cl_2, *c* = 0.90); IR (neat) 3346, 2956, 2926, 2855, 1727, 1529, 1468, 1334, 1262, 1220, 1200, 1119, 1049 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37–7.29 (m, 5H), 5.20 (d, *J* = 8.5 Hz, 1H), 5.10 (s, 2H), 5.10–5.05 (m, 1H), 4.38 (ddd, *J* = 9.0, 9.0, 5.5 Hz, 1H), 3.00–2.97 (m, 1H), 2.88–2.85 (m, 1H), 1.86 (ddd, *J* = 14.5, 4.5, 4.5 Hz, 1H), 1.74 (ddd, *J* = 14.0, 7.0, 7.0 Hz, 1H), 1.69–1.59 (m, 3H), 1.55–1.39 (m, 5H), 1.37–1.24 (m, 25H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.887 (t, *J* = 6.5 Hz, 3H), 0.875 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 156.1, 136.5, 128.7 (2C), 128.3, 128.2 (2C), 73.9, 67.1, 56.4, 53.5, 52.9, 42.0, 34.0, 32.5, 32.1, 31.9, 29.81, 29.80, 29.71, 29.66, 29.51, 29.50, 29.35, 28.1, 26.7, 25.5, 25.0, 23.1, 22.9, 22.7, 22.0, 14.30, 14.26; MALDI-TOF/CCA-HRMS calcd for $C_{35}H_{59}NO_5Na$ $[M + Na]^+$: 596.4285, found 596.4265.

(*S*)-1-((2*S*,3*R*)-3-Hexyloxiran-2-yl)tridecan-2-yl formyl-D-leucinate (23)

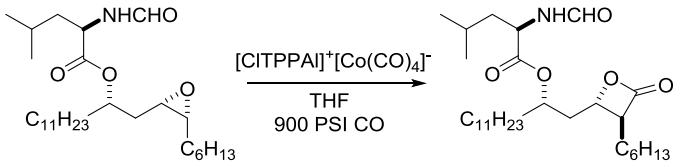


To a stirred solution of **27** (45.5 mg, 79.3 μmol) in tetrahydrofuran (2 mL) at room temperature was added Pd/C (10% wt/wt, 8.4 mg, 7.93 μmol) under N_2. The resulting mixture was then stirred at the same temperature under H_2 (1 atm) for 2 h. The mixture was filtered through a pad of Celite, and washed with EtOAc. The filtrate was concentrated under reduced pressure. The residue was dissolved in dichloromethane (1 mL). Then a premixed mixture of *N*,*N*-dicyclohexylcarbodiimide (65.1 mg, 317

μmol) and formic acid (9.0 μL, 238 μmol) in dichloromethane (2 mL) was added to the solution. After 5 min, the mixture was diluted with hexanes and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The crude residue was purified by flash chromatography (0 to 20% EtOAc in hexanes) on silica gel (2 mL) to afford **23** (30.5 mg, 82%) as a colorless oil.

Data for **23**: R_f = 0.32 (30% EtOAc in hexanes); $[\alpha]_D^{21}$ = +2.9 (CH_2Cl_2, *c* = 1.42); IR (neat) 3296, 2957, 2925, 2855, 1740, 1668, 1529, 1467, 1381, 1273, 1253, 1193, 1144 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 6.11 (d, *J* = 9.0 Hz, 1H), 5.09 (dddd, *J* = 7.5, 7.5, 5.0, 5.0 Hz, 1H), 4.72 (ddd, *J* = 9.0, 9.0, 5.0 Hz, 1H), 2.97 (ddd, *J* = 8.0, 4.0, 4.0 Hz, 1H), 2.89–2.86 (m, 1H), 1.88 (ddd, *J* = 14.5, 5.0, 5.0 Hz, 1H), 1.75–1.58 (m, 5H), 1.49–1.38 (m, 4H), 1.36–1.24 (m, 25H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.877 (t, *J* = 7.0 Hz, 3H), 0.866 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 160.8, 74.3, 56.4, 53.6, 49.7, 41.9, 34.0, 32.6, 32.1, 31.9, 29.79 (2C), 29.70, 29.65, 29.51, 29.47, 29.3, 28.1, 26.7, 25.5, 25.0, 23.0, 22.9, 22.7, 22.0, 14.29, 14.24; HRMS (ESI) calcd for $C_{28}H_{53}NO_4Na$ $[M + Na]^+$: 490.3867, found 490.3853.

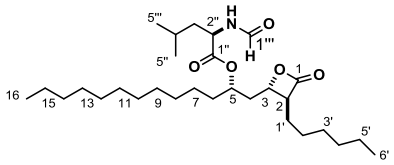
(*S*)-1-((2*S*,3*S*)-3-Hexyl-4-oxooxetan-2-yl)tridecan-2-yl formyl-D-leucinate (34)



The general procedure for carbonylation of epoxides was followed using **23** (20.0 mg, 0.0428 mmol), $[ClTPPAl]^+[Co(CO)_4]^-$ (2.6 mg, 0.0024 mmol, 5.6 mol %) and tetrahydrofuran (0.25) mL for 3 days. The crude residue was purified by flash column chromatography (50% Et_2O in hexanes) on silica gel (30 mL) to afford **34** (16.3 mg, 77%) as a colorless oil.

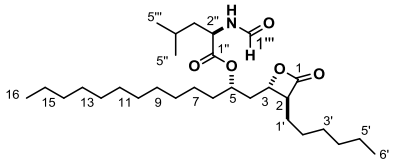
Data for **34**: R_f = 0.27 (30% EtOAc in hexanes); $[\alpha]_D^{22}$ = –5.3 ($CHCl_3$, *c* = 0.17); IR (neat) 3325, 2957, 2927, 2855, 1824, 1740, 1685, 1511, 1467, 1379, 1252, 1188, 1125 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ

8.21 (s, 1H), 5.87 (d, *J* = 8.0 Hz, 1H), 5.03 (dddd, *J* = 7.5, 7.5, 5.0, 5.0 Hz, 1H), 4.66 (ddd, *J* = 8.5, 8.5, 5.5 Hz, 1H), 4.35 (ddd, *J* = 8.0, 5.0, 4.0 Hz, 1H), 3.22 (ddd, *J* = 7.5, 7.5, 4.5 Hz, 1H), 2.18 (ddd, *J* = 15.0, 7.5, 7.5 Hz, 1H), 2.02 (ddd, *J* = 15.0, 5.0, 4.5 Hz, 1H), 1.84–1.77 (m, 1H), 1.76–1.71 (m, 1H), 1.70–1.64 (m, 3H), 1.60–1.53 (m, 2H), 1.47–1.41 (m, 1H), 1.38–1.24 (m, 25H); 0.970 (d, *J* = 6.5 Hz, 3H), 0.967 (d, *J* = 6.5 Hz, 3H), 0.882 (t, *J* = 7.0 Hz, 3H), 0.879 (t, *J* = 7.0, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 171.2, 160.8, 74.8, 72.8, 57.2, 49.8, 41.6, 38.7, 34.0, 32.1, 31.6, 29.8 (2C), 29.7, 29.6, 29.5, 29.4, 29.2, 27.8, 26.9, 25.4, 25.0, 23.0, 22.9, 22.7, 22.0, 14.3, 14.2; MALDI-TOF/CCA-HRMS calcd for $C_{29}H_{53}NO_5Na$ $[M + Na]^+$: 518.3816, found 518.3813.



Position	*Helv. Chim. Acta* **1987**, *70*, 196. (enatiomer)	**This Work**	*J. Med. Chem.* **2008**, *51*, 6970.
CHO (1H)	8.21 (s)	8.21 (s)	8.20 (s)
2"-NH (1H)	5.88 (d, 8)	5.87 (d, 8.0)	6.19 (d, 8.0)
5 (1H)	5.09–4.96 (m)	5.03 (dddd, 7.5, 7.5, 5.0, 5.0)	5.03 (m)
2" (1H)	4.67 (dt, 7.5, 7.5, 4.0)	4.66 (ddd, 8.5, 8.5, 5.5)	4.65 (m)
3 (1H)	4.36–4.25 (m, 1H)	4.35 (ddd, 8.0, 5.0, 4.0)	4.37 (m)
2 (1H)	3.22 (dt, 7.5, 7.5, 4.0)	3.22 (ddd, 7.5, 7.5, 4.5)	3.23 (m)
4, 4a (2H)	2.26–1.97 (m)	2.18 (ddd, 15.0, 7.5, 7.5, 1H)	2.18 (m)
		2.02 (ddd, 15.0, 5.0, 4.5, 1H)	2.00 (m)
CH_2 (33H)	1.50–1.03 (m)	1.84–1.77 (m, 1H)	1.78–1.54 (m)
		1.76–1.71 (m, 1H)	
		1.70–1.53 (m, 5H)	
		1.47–1.24 (m, 1H)	
		1.38–1.24 (m, 25H)	
5", 5'" (6H)	1.03–0.94 (m)	0.970 (d, 6.5, 3H)	0.96 (m)
		0.967 (d, 6.5, 3H)	
16, 6' (6H)	0.94–0.75 (m)	0.882 (t, 7.0, 3H)	0.89 (m)
		0.879 (t, 7.0, 3H)	

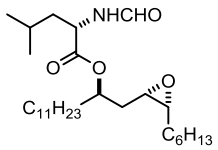
Table S3. ^{1}H NMR assignments of **34**. *δ_H (multiplicity, coupling constant (*J*) in Hz)



Position	*J. Med. Chem.* **2008**, *51*, 6970.	**This Work**
1, 1"	172.27	172.40
	171.07	171.21
1"'	160.77	160.78
3, 5	74.60	74.78
	72.50	72.75
2, 2"	56.99	57.16
	49.69	49.77
	41.36	41.63
	38.53	38.71
	33.83	34.00
	31.91	32.09
4, 6, 9	31.48	31.65
12, 13, 14, 1', 2', 3' 4', 3",	29.63	29.80 (2C)
	29.52	29.70
	29.46	29.63
	29.34	29.53
	29.26	29.42
	28.98	29.16
	27.64	27.79
7, 8, 10, 11	26.68	26.86
	25.21	25.38
	24.87	25.03
4"	22.82	23.01
5" 5"'	22.69	22.88
15, 5'	22.53	22.72
	21.86	22.03
16, 6'	14.12	14.32
	14.03	14.24

Table S4. ^{13}C NMR assignments of **34**.

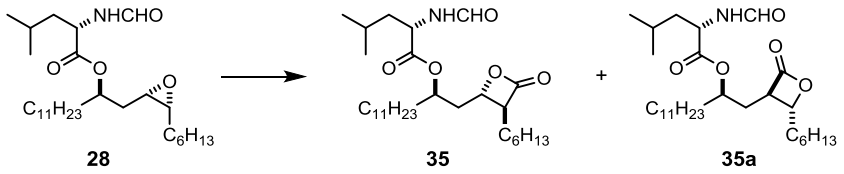
(*R*)-1-((2*S*,3*R*)-3-Hexyloxiran-2-yl)tridecan-2-yl formyl-L-leucinate (28)



To a stirred solution of **19** (65.0 mg, 0.199 mmol) in tetrahydrofuran (1 mL) at 0 °C was added triphenylphosphine (107 mg, 0.408 mmol) and *N*-formyl-L-Leu-OH (63.0 mg, 0.358 mmol) under N_2. A solution of diisopropyl azodicarboxylate (86.0 mg, 0.398 mmol) in tetrahydrofuran (1 mL) was added slowly via syringe. The resulting mixture was stirred at the same temperature for 15 h. The reaction was quenched by adding water (5 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (10 to 30% EtOAc in hexanes) on silica gel (20 mL) to afford **28** (58.0 mg, 61%) as a colorless oil.

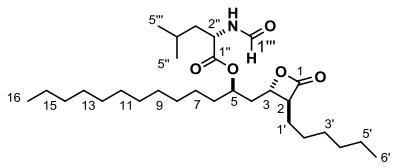
Data for **28**: R_f = 0.32 (30% EtOAc in hexanes); $[\alpha]_D^{22}$ = –2.2 ($CHCl_3$, *c* = 0.47); IR (neat) 3300, 2926, 2857, 1740, 1671, 1523, 1462, 1380, 1269, 1193 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 6.00 (d, *J* = 8.5 Hz, 1H), 5.09 (dddd, *J* = 7.0, 7.0, 5.5, 5.5 Hz, 1H), 4.73 (ddd, *J* = 8.0, 8.0, 4.5 Hz, 1H), 2.96–2.90 (m, 2H), 1.89 (ddd, *J* = 14.5, 8.0, 4.5 Hz, 1H), 1.73–1.63 (m, 5H), 1.59–1.40 (m, 4H), 1.38–1.24 (m, 25H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.95 (d, *J* = 7.0 Hz, 3H), 0.886 (t, *J* = 7.0 Hz, 3H), 0.875 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 160.7, 74.3, 57.1, 53.8, 49.6, 42.1, 34.3, 32.8, 32.1, 31.9, 29.82 (2C), 29.71, 29.66, 29.53, 29.52, 29.4, 28.2, 26.7, 25.4, 25.0, 23.1, 22.9, 22.8, 22.1, 14.32, 14.27; HRMS (ESI) calcd for $C_{28}H_{53}NO_4Na$ $[M + Na]^+$: 490.3867, found 490.3838.

(*R*)-1-((2*S*,3*S*)-3-Hexyl-4-oxooxetan-2-yl)tridecan-2-yl formyl-L-leucinate (35)



The general procedure for carbonylation of epoxides was followed using **28** (61.6 mg, 0.132 mmol), $[ClTPPAl]^{+}[Co(CO)_4]^{-}$ (5.8 mg, 0.0053 mmol, 4.0 mol %) and tetrahydrofuran (0.30) mL for 24 hours. The crude residue was purified by preparative HPLC to afford **35** (46.5 mg, 72%, regioselectivity **35**:**35a** = 6:1; the ratio determined by ^{1}H NMR) as a colorless oil.

Data for **35**: R_f = 0.27 (30% EtOAc in hexanes); $[\alpha]_D^{21}$ = –21.5 ($CHCl_3$, *c* = 0.36); IR (neat) 3353, 2925, 2855, 1822, 1736, 1685, 1461, 1380, 1272, 1187, 1125 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 5.92 (d, *J* = 8.0 Hz, 1H), 5.04 (dddd, *J* = 7.0, 7.0, 5.5, 5.5 Hz, 1H), 4.68 (ddd, *J* = 8.5, 8.5, 5.0 Hz, 1H), 4.29 (ddd, *J* = 9.0, 4.5, 4.5 Hz, 1H), 3.22 (ddd, *J* = 7.5, 7.5, 4.5 Hz, 1H), 2.10–2.00 (m, 2H), 1.85–1.78 (m, 1H), 1.77–1.53 (m, 6H), 1.49–1.42 (m, 1H), 1.38–1.24 (m, 25H), 0.976 (d, *J* = 6.5 Hz, 3H), 0.963 (d, *J* = 6.5 Hz, 3H), 0.89–0.87 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 171.1, 160.8, 74.5, 72.7, 56.9, 49.7, 41.9, 39.3, 34.4, 32.1, 31.7, 29.8 (2C), 29.7, 29.6, 29.5, 29.4, 29.1, 27.8, 27.0, 25.2, 25.0, 23.0, 22.9, 22.7, 22.1, 14.3, 14.2; MALDI-TOF/CCA-HRMS calcd for $C_{29}H_{53}NO_5Na$ $[M + Na]^{+}$: 518.3816, found 518.3798.

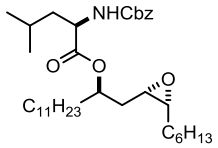


Position	*Helv. Chim. Acta* **1987**, *70*, 196. (enantiomer)	**This Work**
CHO (1H)	8.21 (s)	8.21 (s)
2"-NH (1H)	5.93 (d, 8.5)	5.92 (d, 8.0)
5 (1H)	5.12–5.00 (m)	5.04 (dddd, 7.0, 7.0, 5.5, 5.5)
2" (1H)	4.68 (dt, 8.5, 8.5, 5.0)	4.68 (ddd, 8.5, 8.5, 5.0)
3 (1H)	4.36–4.25 (m)	4.29 (ddd, 9.0, 4.5, 4.5)
2 (1H)	3.32 (dt, 8.0, 8.0, 5.0)	3.22 (ddd, 7.5, 7.5, 4.5)
4, 4a (2H)	2.12–2.01 (m)	2.10–2.00 (m)
CH_2 (33H)	1.90–1.06 (m)	1.85–1.78 (m, 1H)
		1.77–1.53 (m, 6H)
		1.49–1.42 (m, 1H)
		1.38–1.24 (m, 25H)
5", 5"' (6H)	1.06–0.93 (m)	0.976 (d, 6.5, 3H),
		0.963 (d, 6.5, 3H),
16, 6' (6H)	0.93–0.77 (m)	0.89–0.87 (m)

Table S5. ^{1}H NMR assignments of **35**. *δ_H (multiplicity, coupling constant (*J*) in Hz)

Note: No ^{13}C NMR is available for comparison.

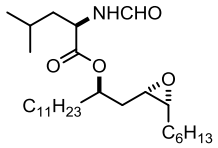
(*R*)-1-((2*S*,3*R*)-3-Hexyloxiran-2-yl)tridecan-2-yl ((benzyloxy)carbonyl)-D-leucinate (29)



To a stirred solution of **19** (32.4 mg, 99.2 μmol) in tetrahydrofuran (0.5 mL) at 0 °C was added triphenylphosphine (53.4 mg, 203 μmol) and *N*-Cbz-D-Leu-OH (52.5 mg, 198 μmol) under N_2. A solution of diisopropyl azodicarboxylate (42.6 mg, 198 μmol) in tetrahydrofuran (0.5 mL) was added slowly via syringe. The resulting mixture was stirred at the same temperature for 0.5 h. The reaction was quenched by adding water (5 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (5 to 15% EtOAc in hexanes) on silica gel (10 mL) to afford **29** (53.0 mg, 93%) as a colorless oil.

Data for **29**: R_f = 0.21 (10% EtOAc in hexanes); $[\alpha]_D^{21}$ = +11.9 ($CHCl_3$, *c* = 0.93); IR (neat) 3338, 2926, 2857, 1729, 1523, 1461, 1335, 1261, 1215, 1119, 1049 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36–7.30 (m, 5H), 5.15 (d, *J* = 9.0 Hz, 1H), 5.09–5.04 (m, 1H), 5.11 (s, 2H), 4.38 (ddd, *J* = 9.0, 9.0, 5.0 Hz, 1H), 2.94–2.88 (m, 2H), 1.86 (ddd, *J* = 15.0, 7.5, 4.5 Hz, 1H), 1.76–1.60 (m, 5H), 1.54–1.42 (m, 4H), 1.36–1.24 (m, 25H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.888 (t, *J* = 7.0 Hz, 3H), 0.876 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 156.1, 136.4, 128.7 (2C), 128.3, 128.2 (2C), 74.1, 67.1, 57.0, 53.7, 52.9, 42.0, 34.3, 32.6, 32.1, 31.9, 29.83, 29.81, 29.76, 29.67, 29.58, 29.54, 29.4, 28.2, 26.7, 25.3, 24.9, 23.1, 22.9, 22.8, 22.0, 14.32, 14.26; MALDI-TOF/CCA-HRMS calcd for $C_{35}H_{59}NO_5Na$ $[M + Na]^+$: 596.4285, found 596.4304.

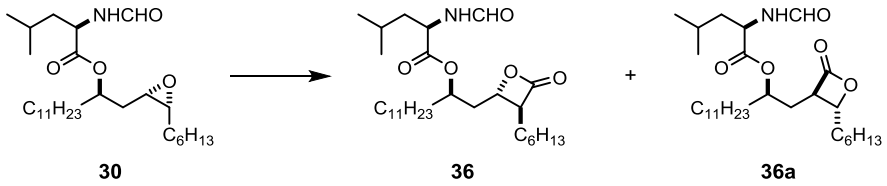
(*R*)-1-((2*S*,3*R*)-3-Hexyloxiran-2-yl)tridecan-2-yl formyl-D-leucinate (30)



To a stirred solution of **29** (47.7 mg, 83.1 μmol) in tetrahydrofuran (1 mL) at room temperature was added Pd/C (10% wt/wt, 17.7 mg, 16.6 μmol) under N_2. The resulting mixture was then stirred at the same temperature under H_2 (1 atm) for 0.5 h. The mixture was filtered through a pad of Celite, and washed with EtOAc. The filtrate was concentrated under reduced pressure. The residue was dissolved in dichloromethane (1 mL). Then a premixed mixture of *N*,*N*-dicyclohexylcarbodiimide (85.3 mg, 416 μmol) and formic acid (9.4 μL, 249 μmol) in dichloromethane (1 mL) was added to the solution. After 5 min, the mixture was diluted with hexanes and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The crude residue was purified by flash chromatography (10 to 30% EtOAc in hexanes) on silica gel (10 mL) to afford **30** (26.0 mg, 67%) as a colorless oil.

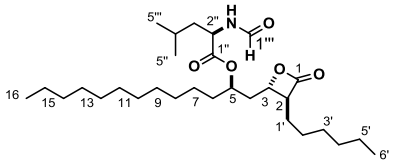
Data for **30**: R_f = 0.32 (30% EtOAc in hexanes); $[\alpha]_D^{22}$ = +12.1 ($CHCl_3$, *c* = 0.62); IR (neat) 3289, 2926, 2856, 1739, 1669, 1523, 1462, 1380, 1267, 1193 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 6.01 (d, *J* = 9.0 Hz, 1H), 5.09 (dddd, *J* = 7.0, 7.0, 5.5, 5.5 Hz, 1H), 4.73 (ddd, *J* = 9.0, 9.0, 4.5 Hz, 1H), 2.95–2.90 (m, 2H), 1.88 (ddd, *J* = 14.5, 7.5, 4.0 Hz, 1H), 1.72–1.60 (m, 5H), 1.59–1.39 (m, 4H), 1.38–1.24 (m, 25H), 0.97 (d, *J* = 6.0 Hz, 3H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.887 (t, *J* = 7.0 Hz, 3H), 0.873 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 160.7, 74.4, 57.0, 53.6, 49.7, 42.0, 34.2, 32.5, 32.1, 31.9, 29.80 (2C), 29.75, 29.65, 29.53, 29.3, 28.1, 26.7, 25.4, 25.0, 23.1, 23.0, 22.9, 22.7, 22.0, 14.30, 14.25; HRMS (ESI) calcd for $C_{28}H_{53}NO_4Na$ $[M + Na]^+$: 490.3867, found 490.3845.

(*R*)-1-((2*S*,3*S*)-3-Hexyl-4-oxooxetan-2-yl)tridecan-2-yl formyl-D-leucinate (36)



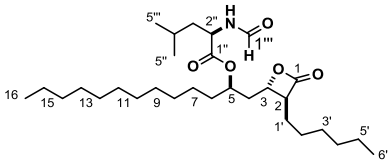
The general procedure for carbonylation of epoxides was followed using **30** (71.1 mg, 0.152 mmol), $[ClTPPAl]^+[Co(CO)_4]^-$ (6.7 mg, 0.0061 mmol, 4.0 mol %) and tetrahydrofuran (0.30) mL for 24 hours. The crude residue was purified by preparative HPLC to afford **36** (58.2 mg, 77%, regioselectivity **36**:**36a** = 5:1; the ratio determined by ^{1}H NMR) as a colorless oil.

Data for **36**: R_f = 0.32 (30% EtOAc in hexanes); $[\alpha]_D^{21}$ = –12.3 ($CHCl_3$, *c* = 0.32); IR (neat) 3324, 2926, 2856, 1823, 1736, 1684, 1461, 1256, 1189, 1123 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 5.90 (d, *J* = 9.0 Hz, 1H), 5.04–4.99 (m, 1H), 4.71 (ddd, *J* = 8.5, 8.5, 4.5 Hz, 1H), 4.26 (ddd, *J* = 8.5, 4.5, 4.5 Hz, 1H), 3.23 (ddd, *J* = 7.0, 7.0, 4.0 Hz, 1H), 2.09–2.00 (m, 2H), 1.86–1.79 (m, 1H), 1.76–1.63 (m, 4H), 1.61–1.54 (m, 2H), 1.47–1.41 (m, 1H), 1.38–1.24 (m, 25H), 0.976 (d, *J* = 6.0 Hz, 3H), 0.964 (d, *J* = 6.0 Hz, 3H), 0.887 (t, *J* = 7.0 Hz, 3H), 0.879 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 170.9, 160.7, 74.4, 72.8, 56.8, 49.8, 41.9, 39.1, 34.2, 32.1, 31.7, 29.8 (2C), 29.7, 29.6, 29.53, 29.51, 29.1, 27.9, 27.0, 25.2, 25.1, 23.0, 22.9, 22.7, 22.1, 14.3, 14.2; MALDI-TOF/CCA-HRMS calcd for $C_{29}H_{53}NO_5Na$ $[M + Na]^+$: 518.3816, found 518.3843.



Position	*Helv. Chim. Acta* **1987**, *70*, 196. (enantiomer)	**This Work**	*Synthesis* **1994**, 1294 (enantiomer)
CHO (1H)	8.25 (s)	8.22 (s)	8.12 (s)
2"-NH (1H)	5.97 (d, 8)	5.90 (d, 9.0)	5.94 (d, 7.7)
5 (1H)	5.06–4.94 (m)	5.04–4.99 (m)	5.02 (m)
2" (1H)	4.71 (dt, 9.0, 9.0, 5.0)	4.71 (ddd, 8.5, 8.5, 4.5)	4.72 (ddd, 8.9. 8.6. 4.3)
3 (1H)	4.33–4.20 (m, 1H)	4.26 (ddd, 8.5, 4.5, 4.5)	4.27 (m)
2 (1H)	3.29–3.20 (m)	3.23 (ddd, *J* = 7.0, 7.0, 4.0)	3.25 (ddd, 5.3, 4.2, 1.4)
4, 4a (2H)	2.09–2.00 (m)	2.09–2.00 (m)	2.05 (m)
CH_2 (33H)	1.87–1.04 (m)	1.86–1.79 (m, 1H)	1.70 (m, 7H)
		1.76–1.63 (m, 4H)	1.30 (m, 26H)
		1.61–1.54 (m, 2H)	
		1.47–1.41 (m, 1H)	
		1.38–1.24 (m, 25H)	
5", 5"' (6H)	1.03–0.93 (m)	0.976 (d, 6.0, 3H)	0.982 (d, 6.2, 3H)
		0.964 (d, 6.0, 3H)	0.968 (d, 6.2, 3H)
16, 6' (6H)	0.93–0.78 (m)	0.887 (t, 7.0, 3H),	0.88 (m)
		0.879 (t, 7.0, 3H);	

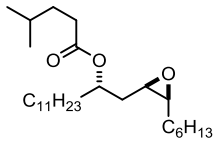
Table S6. ^{1}H NMR assignments of **36**. *δ_H (multiplicity, coupling constant (*J*) in Hz)



Position	*Synthesis* **1994**, 1294	**This Work**
1, 1"	172.2	172.2
	170.8	170.9
1"'	160.7	160.7
3, 5	74.3	74.4
	72.8	72.8
2, 2"	56.8	56.8
	49.8	49.8
	41.9	41.9
	39.1	39.1
	34.2	34.2
	32.1	32.1
4, 6, 9 12, 13, 14, 1', 2', 3' 4', 3",	31.6	31.7
	29.9	29.8 (2C)
	29.8	29.7
	29.7	29.6
	29.6	29.5
	29.5	29.4
	29.1	29.1
	27.8	27.9
	26.9	27.0
7, 8, 10, 11	25.1	25.2, 25.1
	23.0	23.0
4"	22.8	22.9
5" 5"'	22.7	22.7
15, 5'	22.1	22.1
	14.3	14.3
16, 6'	14.1	14.2

Table S7. ^{13}C NMR assignments of **36**.

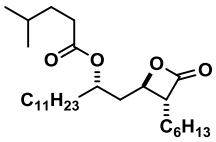
(*S*)-1-((2*R*,3*S*)-3-Hexyloxiran-2-yl)tridecan-2-yl 4-methylpentanoate (31)



To a stirred solution of *ent*-**19** (21.2 mg, 64.9 µmol) in tetrahydrofuran (0.5 mL) at 0 °C was added triphenylphosphine (34.9 mg, 133 µmol) and 2-methylvaleric acid (15.1 mg, 130 µmol) under N_2. A solution of diisopropyl azodicarboxylate (28.0 µL, 130 µmol) in tetrahydrofuran (0.5 mL) was added slowly via syringe. The resulting mixture was stirred at the same temperature for 2 h. The reaction was quenched by adding water (5 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (2.5 to 5% EtOAc in hexanes) on silica gel (20 mL) to afford **31** (20.0 mg, 62%) as a colorless oil.

Data for **31**: R_f = 0.37 (10% Et_2O in hexanes); $[\alpha]_D^{21}$ = –6.2 ($CHCl_3$, *c* = 0.50); IR (neat) 2926, 2857, 1735, 1462, 1378, 1266, 1177, 1107 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 5.05 (ddd, *J* = 13.0, 7.0, 5.5 Hz, 1H), 2.95 (ddd, *J* = 6.5, 4.5, 4.5 Hz, 1H), 2.92–2.88 (m, 1H), 2.31 (d, *J* = 7.0 Hz, 1H), 2.29 (d, *J* = 7.0 Hz, 1H), 1.81 (ddd, *J* = 14.5, 7.5, 5.0 Hz, 1H), 1.71 (ddd, *J* = 14.5, 6.5, 5.0 Hz, 1H), 1.63–1.59 (m, 2H), 1.57–1.40 (m, 5H), 1.38–1.24 (m, 26H), 0.91–0.86 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 72.4, 57.1, 54.2, 34.6, 34.0, 33.0, 32.9, 32.1, 32.0, 29.83 (2C), 29.74, 29.71, 29.61, 29.54, 29.4, 28.2, 27.9, 26.7, 25.4, 22.9, 22.8, 22.4, 22.2, 14.32, 14.26; HRMS (ESI) calcd for $C_{27}H_{53}O_3$ $[M + H]^+$: 425.3995, found 425.3996.

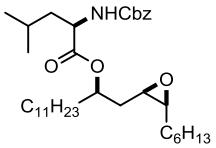
(*S*)-1-((2*R*,3*R*)-3-Hexyl-4-oxooxetan-2-yl)tridecan-2-yl 4-methylpentanoate (37)



The general procedure for carbonylation of epoxides was followed using **31** (12.8 mg, 0.0301 mmol), $[ClTPPAl]^+[Co(CO)_4]^-$ (0.8 mg, 0.0007 mmol, 2 mol %) and tetrahydrofuran (0.10) mL for 24 hours. The crude residue was purified by preparative HPLC to afford **37** (7.2 mg, 53%) as a colorless oil.

Data for **37**: R_f = 0.29 (10% Et_2O in hexanes); $[\alpha]_D^{21}$ = +16.4 ($CHCl_3$, *c* = 0.52); IR (neat) 2925, 2855, 1826, 1736, 1466, 1378, 1269, 1178, 1121 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.96 (dddd, *J* = 7.2, 7.2, 5.2, 5.2 Hz, 1H), 4.26 (ddd, *J* = 8.8, 4.4, 4.4 Hz, 1H), 3.24 (ddd, *J* = 7.6, 7.6, 4.0 Hz, 1H), 2.32–2.28 (m, 2H), 2.10–1.97 (m, 2H), 1.85–1.75 (m, 1H), 1.74–1.67 (m, 1H), 1.61–1.44 (m, 5H), 1.34–1.24 (m, 26H), 0.92–0.86 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 171.2, 74.9, 71.1, 56.9, 39.3, 34.6, 34.0, 32.8, 32.1, 31.7, 29.8 (2C), 29.71, 29.66, 29.54, 29.53, 29.2, 27.92, 27.87, 27.0, 25.2, 22.9, 22.7, 22.4, 22.0, 14.3, 14.2; MALDI-TOF/CCA-HRMS calcd for $C_{28}H_{52}O_4Na$ $[M + Na]^+$: 475.3758, found 475.3733.

(*R*)-1-((2*R*,3*S*)-3-Hexyloxiran-2-yl)tridecan-2-yl ((benzyloxy)carbonyl)-D-leucinate (*ent*-24)

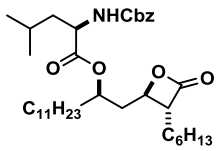


To a stirred solution of *ent*-**19** (47.0 mg, 0.144 mmol) in dichloromethane (1.0 mL) at room temperature was added *N*-Cbz-D-Leu-OH (76.4 mg, 0.288 mmol), followed by *N*,*N*-dicyclohexylcarbodiimide (73.9 mg, 0.360 mmol) and 4-dimethylaminopyridine (2 mg). The resulting mixture was stirred at the same temperature for 22 h. The mixture was diluted with hexanes and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The crude residue was purified by flash

chromatography (5 to 15% EtOAc in hexanes) on silica gel (10 mL) to afford *ent*-**24** (82.0 mg, 99%) as a colorless oil.

Data for *ent*-**24**: R_f = 0.21 (10% EtOAc in hexanes); $[\alpha]_D^{21}$ = +11.9 ($CHCl_3$, *c* = 0.82); IR (neat) 3341, 2926, 2855, 1728, 1526, 1456, 1334, 1264, 1218, 1048 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36–7.30 (m, 5H), 5.17 (d, *J* = 8.5 Hz, 1H), 5.13–5.06 (m, 1H), 5.10 (s, 2H), 4.38 (ddd, *J* = 9.0, 9.0, 5.0 Hz, 1H), 2.95–2.91 (m, 1H), 2.87–2.84 (m, 1H), 1.83 (ddd, *J* = 15.0, 4.5, 4.5 Hz, 1H), 1.73 (ddd, *J* = 14.0, 7.0, 7.0 Hz, 1H), 1.69–1.60 (m, 3H), 1.55–1.39 (m, 5H), 1.35–1.24 (m, 25H), 0.96 (d, *J* = 6.0 Hz, 3H), 0.94 (d, *J* = 6.0 Hz, 3H), 0.890 (t, *J* = 7.0 Hz, 3H), 0.877 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 156.1, 136.5, 128.7 (2C), 128.33, 128.25 (2C), 74.0, 67.1, 56.4, 53.7, 53.0, 41.9, 34.3, 32.7, 32.1, 31.9, 29.82, 29.81, 29.75, 29.66, 29.56, 29.54, 29.4, 28.1, 26.7, 25.4, 25.0, 23.1, 22.9, 22.7, 22.0, 14.31, 14.25; MALDI-TOF/CCA-HRMS calcd for $C_{35}H_{59}NO_5Na$ $[M + Na]^+$: 596.4285, found 596.4283.

(*R*)-1-((2*R*,3*R*)-3-Hexyl-4-oxooxetan-2-yl)tridecan-2-yl ((benzyloxy)carbonyl)-D-leucinate (*ent*-21)

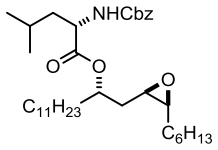


The general procedure for carbonylation of epoxides was followed using *ent*-**24** (76.8 mg, 0.164 mmol), $[ClTPPAl]^+[Co(CO)_4]^-$ (3.0 mg, 0.0027 mmol, 1.6 mol %) and tetrahydrofuran (0.28) mL for 24 hours. The crude residue was purified by preparative HPLC to afford *ent*-**21** (60.3 mg, 75%) as a colorless oil.

Data for *ent*-**21**: R_f = 0.24 (10% EtOAc in hexanes); $[\alpha]_D^{21}$ = +20.3 ($CHCl_3$, *c* = 1.06); IR (neat) 3355, 2923, 2855, 1823, 1731, 1522, 1456, 1369, 1333, 1264, 1219, 1121, 1029 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.30 (m, 5H), 5.11 (s, 2H), 5.08 (d, *J* = 8.5 Hz, 1H), 5.02–4.98 (m, 1H), 4.34 (ddd, *J* = 8.8, 8.8, 5.2 Hz, 1H), 4.30–4.26 (m, 1H), 3.20 (ddd, *J* = 7.2, 7.2, 4.4 Hz, 1H), 2.16 (ddd, *J* = 14.4, 7.2, 7.2 Hz, 1H), 1.96 (ddd, *J* = 14.4, 4.4, 4.4 Hz, 1H), 1.82–1.68 (m, 3H), 1.65–1.57 (m, 3H), 1.55–1.47 (m,

1H), 1.46–1.41 (m, 1H), 1.32–1.24 (m, 25H), 0.97–0.94 (m, 6H), 0.89–0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 171.0, 156.1, 136.4, 128.7 (2C), 128.4, 128.3 (2C), 74.7, 72.5, 67.2, 57.2, 53.0, 41.8, 38.9, 34.2, 32.1, 31.7, 29.81, 29.80, 29.73, 29.62, 29.52, 29.48, 29.2, 27.8, 26.9, 25.3, 25.0, 23.1, 22.9, 22.7, 21.9, 14.3, 14.2; MALDI-TOF/CCA-HRMS calcd for $C_{36}H_{59}NO_6Na$ $[M + Na]^+$: 624.4235, found 624.4242.

(*S*)-1-((2*R*,3*S*)-3-Hexyloxiran-2-yl)tridecan-2-yl ((benzyloxy)carbonyl)-L-leucinate (*ent*-29)

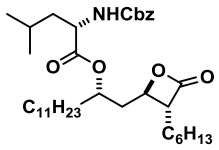


To a stirred solution of *ent*-**19** (43.0 mg, 0.132 mmol) in dichloromethane (1.0 mL) at room temperature was added *N*-Cbz-D-Leu-OH (70.0 mg, 0.264 mmol), followed by *N*,*N*-dicyclohexylcarbodiimide (67.5 mg, 0.329 mmol) and 4-dimethylaminopyridine (2 mg). The resulting mixture was stirred at the same temperature for 22 h. The mixture was diluted with hexanes and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The crude residue was purified by flash chromatography (5 to 15% EtOAc in hexanes) on silica gel (10 mL) to afford *ent*-**29** (70.0 mg, 93%) as a colorless oil.

Data for *ent*-**29**: R_f = 0.21 (10% EtOAc in hexanes); $[\alpha]_D^{22}$ = –15.9 ($CHCl_3$, *c* = 1.58); IR (neat) 3339, 2926, 2857, 1729, 1523, 1461, 1335, 1262, 1216, 1049 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.30 (m, 5H), 5.15 (d, *J* = 9.0 Hz, 1H), 5.09–5.04 (m, 1H), 5.11 (s, 2H), 4.38 (ddd, *J* = 9.0, 9.0, 5.0 Hz, 1H), 2.94–2.88 (m, 2H), 1.86 (ddd, *J* = 14.5, 7.5, 4.5 Hz, 1H), 1.75–1.59 (m, 5H), 1.54–1.42 (m, 4H), 1.36–1.24 (m, 25H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.888 (t, *J* = 7.0 Hz, 3H), 0.876 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 156.1, 136.4, 128.7 (2C), 128.3, 128.2 (2C), 74.1, 67.1, 57.0, 53.7, 52.8, 42.1, 34.3, 32.6, 32.1, 31.9, 29.82, 29.80, 29.76, 29.67, 29.58, 29.54, 29.3, 28.2,

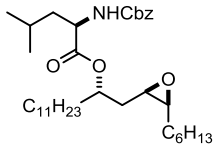
26.7, 25.3, 24.9, 23.1, 22.9, 22.7, 22.0, 14.32, 14.26; MALDI-TOF/CCA-HRMS calcd for $C_{35}H_{59}NO_5Na$ $[M + Na]^+$: 596.4285, found 596.4283.

(*S*)-1-((2*R*,3*R*)-3-Hexyl-4-oxooxetan-2-yl)tridecan-2-yl ((benzyloxy)carbonyl)-L-leucinate (*ent*-38)



The general procedure for carbonylation of epoxides was followed using *ent*-**29** (83.0 mg, 0.145 mmol), $[ClTPPAl]^+[Co(CO)_4]^-$ (3.2 mg, 0.0029 mmol, 2.0 mol %) and tetrahydrofuran (0.30) mL for 24 hours. The crude residue was purified by preparative HPLC to afford *ent*-**38** (70.2mg, 80%) as a colorless oil. Data for *ent*-**38**: R_f = 0.24 (10% EtOAc in hexanes); $[\alpha]_D^{21}$ = +8.2 ($CHCl_3$, *c* = 0.76); IR (neat) 3348, 2926, 2855, 1823, 1729, 1525, 1467, 1336, 1263, 1219, 1171, 1120, 1050 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38–7.31 (m, 5H), 5.11 (s, 2H), 5.09 (d, *J* = 8.4 Hz, 1H), 5.01–4.96 (m, 1H), 4.36 (ddd, *J* = 8.8, 8.8, 4.8 Hz, 1H), 4.27–4.23 (m, 1H), 3.21 (ddd, *J* = 7.2, 7.2, 4.0 Hz, 1H), 2.02–1.99 (m, 2H), 1.83–1.76 (m, 1H), 1.74–1.67 (m, 2H), 1.66–1.57 (m, 3H), 1.55–1.49 (m, 1H), 1.46–1.40 (m, 1H), 1.36–1.24 (m, 25H), 0.97 (m, 6H), 0.89 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 171.0, 156.1, 136.4, 128.7 (2C), 128.4, 128.2 (2C), 74.4, 72.5, 67.2, 56.9, 52.9, 41.9, 39.2, 34.3, 32.1, 31.7, 29.82, 29.80, 29.73, 29.64, 29.52, 29.51, 29.1, 27.8, 26.9, 25.2, 25.0, 23.1, 22.9, 22.7, 22.0, 14.3, 14.2; MALDI-TOF/CCA-HRMS calcd for $C_{36}H_{59}NO_6Na$ $[M + Na]^+$: 624.4235, found 624.4243.

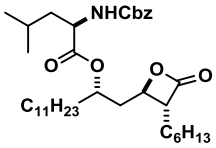
(*S*)-1-((2*R*,3*S*)-3-Hexyloxiran-2-yl)tridecan-2-yl ((benzyloxy)carbonyl)-D-leucinate (32)



To a stirred solution of *ent*-**19** (43.0 mg, 0.132 mmol) in dichloromethane (1.0 mL) at room temperature was added *N*-Cbz-D-Leu-OH (70.0 mg, 0.264 mmol), followed by *N*,*N*-dicyclohexylcarbodiimide (67.5 mg, 0.329 mmol) and 4-dimethylaminopyridine (2 mg). The resulting mixture was stirred at the same temperature for 22 h. The mixture was diluted with hexanes and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The crude residue was purified by flash chromatography (5 to 15% EtOAc in hexanes) on silica gel (10 mL) to afford **32** (74.0 mg, 98%) as a colorless oil.

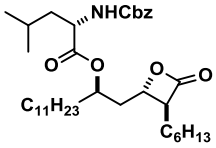
Data for **32**: R_f = 0.21 (10% EtOAc in hexanes); $[\alpha]_D^{22}$ = –2.4 ($CHCl_3$, *c* = 1.50); IR (neat) 3339, 2926, 2857, 1728, 1525, 1461, 1379, 1335, 1262, 1216, 1119, 1049 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37–7.29 (m, 5H), 5.16 (d, *J* = 8.5 Hz, 1H), 5.12–5.06 (m, 1H), 5.10 (s, 2H), 4.36 (ddd, *J* = 8.5, 8.5, 5.0 Hz, 1H), 2.96–2.89 (m, 2H), 1.88 (ddd, *J* = 14.0, 7.5, 5.0 Hz, 1H), 1.76–1.68 (m, 2H), 1.67–1.59 (m, 3H), 1.54–1.41 (m, 4H), 1.37–1.24 (m, 25H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.888 (t, *J* = 7.0 Hz, 3H), 0.875 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 156.1, 136.4, 128.7 (2C), 128.3, 128.2 (2C), 73.9, 67.1, 57.1, 53.9, 52.8, 42.1, 34.4, 32.9, 32.1, 31.9, 29.80 (2C), 29.70, 29.66, 29.51 (2C), 29.4, 28.2, 26.7, 25.3, 24.9, 23.1, 22.9, 22.7, 22.0, 14.30, 14.26; MALDI-TOF/CCA-HRMS calcd for $C_{35}H_{59}NO_5Na$ $[M + Na]^+$: 596.4285, found 596.4316.

(*S*)-1-((2*R*,3*R*)-3-Hexyl-4-oxooxetan-2-yl)tridecan-2-yl ((benzyloxy)carbonyl)-D-leucinate (*ent*-39)



The general procedure for carbonylation of epoxides was followed using **32** (87.3 mg, 0.152 mmol), $[ClTPPAl]^+[Co(CO)_4]^-$ (3.3 mg, 0.0030 mmol, 2.0 mol %) and tetrahydrofuran (0.30) mL for 24 hours. The crude residue was purified by preparative HPLC to afford *ent*-**39** (68.2 mg, 74%) as a colorless oil. Data for *ent*-**39**: R_f = 0.24 (10% EtOAc in hexanes); $[\alpha]_D^{22}$ = +17.3 ($CHCl_3$, *c* = 1.10); IR (neat) 3349, 2926, 2855, 1823, 1725, 1521, 1467, 1336, 1265, 1221, 1199, 1122, 1049 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38–7.30 (m, 5H), 5.12 (d, *J* = 8.4 Hz, 1H), 5.11 (s, 2H), 5.05–5.00 (m, 1H), 4.36–4.29 (m, 2H), 3.21 (ddd, *J* = 7.2, 7.2, 4.0 Hz, 1H), 2.08–1.99 (m, 2H), 1.83–1.68 (m, 3H), 1.64–1.49 (m, 4H), 1.48–1.42 (m, 1H), 1.39–1.24 (m, 25H), 0.97–0.95 (m, 6H), 0.89–0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 171.2, 156.2, 136.4, 128.7 (2C), 128.4, 128.2 (2C), 74.5, 72.4, 67.2, 56.9, 52.9, 41.9, 39.5, 34.4, 32.1, 31.7, 29.80 (2C), 29.68, 29.64, 29.52, 29.46, 29.1, 27.8, 26.9, 25.2, 25.0, 23.1, 22.9, 22.7, 22.0, 14.3, 14.2; MALDI-TOF/CCA-HRMS calcd for $C_{36}H_{59}NO_6Na$ $[M + Na]^+$: 624.4235, found 624.4250.

(*R*)-1-((2*S*,3*S*)-3-Hexyl-4-oxooxetan-2-yl)tridecan-2-yl ((benzyloxy)carbonyl)-L-leucinate (39)

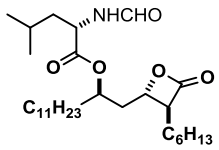


To a stirred solution of **4b** (18.0 mg, 50.8 μmol) in tetrahydrofuran (0.5 mL) at 0 °C was added triphenylphosphine (40.0 mg, 152 μmol) and *N*-Cbz-D-Leu-OH (40.3 mg, 152 μmol) under N_2. A solution of diisopropyl azodicarboxylate (33 μL, 152 μmol) in tetrahydrofuran (0.5 mL) was added

slowly via syringe. The resulting mixture was stirred at the same temperature for 0.5 h. The reaction was quenched by adding water (5 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (5 to 15% EtOAc in hexanes) on silica gel (10 mL) to afford **39** (22.0 mg, 72%) as a colorless oil.

Data for **39**: R_f = 0.24 (10% EtOAc in hexanes); $[\alpha]_D^{21}$ = –26.2 ($CHCl_3$, *c* = 0.51); IR (neat) 3356, 2926, 2855, 1823, 1720, 1523, 1467, 1335, 1263, 1221, 1198, 1171, 1121, 1050 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38–7.30 (m, 5H), 5.12 (d, *J* = 8.5 Hz, 1H), 5.10 (s, 2H), 5.05–5.00 (m, 1H), 4.36–4.29 (m, 2H), 3.21 (ddd, *J* = 8.0, 8.0, 4.0 Hz, 1H), 2.08–1.99 (m, 2H), 1.83–1.68 (m, 3H), 1.63–1.49 (m, 4H), 1.48–1.42 (m, 1H), 1.39–1.24 (m, 25H), 0.97–0.95 (m, 6H), 0.89–0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 171.2, 156.2, 136.4, 128.7 (2C), 128.4, 128.2 (2C), 74.5, 72.4, 67.2, 56.9, 52.9, 41.9, 39.5, 34.4, 32.1, 31.7, 29.81 (2C), 29.69, 29.64, 29.52, 29.47, 29.2, 27.8, 26.9, 25.2, 25.0, 23.1, 22.9, 22.7, 22.0, 14.3, 14.2; MALDI-TOF/CCA-HRMS calcd for $C_{36}H_{59}NO_6Na$ $[M + Na]^+$: 624.4235, found 624.4216.

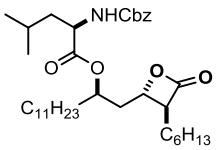
(*R*)-1-((2*S*,3*S*)-3-Hexyl-4-oxooxetan-2-yl)tridecan-2-yl formyl-L-leucinate (35)



To a stirred solution of **39** (10.0 mg, 16.6 μmol) in tetrahydrofuran (1 mL) at room temperature was added Pd/C (10% wt/wt, 3.5 mg, 3.3 μmol) under N_2. The resulting mixture was then stirred at the same temperature under H_2 (1 atm) for 2 h. The mixture was filtered through a pad of Celite, and washed with EtOAc. The filtrate was concentrated under reduced pressure. The residue was dissolved in dichloromethane (0.5 mL). Then a premixed mixture of *N*,*N*-dicyclohexylcarbodiimide (17.0 mg, 83.0

μmol) and formic acid (2.0 μL, 50.4 μmol) in dichloromethane (0.5 mL) was added to the solution. After 5 min, the mixture was diluted with hexanes and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The crude residue was purified by flash chromatography (0 to 20% EtOAc in hexanes) on silica gel (2 mL) to afford **35** (5.2 mg, 63%) as a colorless oil.

(*R*)-1-((2*S*,3*S*)-3-Hexyl-4-oxooxetan-2-yl)tridecan-2-yl ((benzyloxy)carbonyl)-D-leucinate (38)

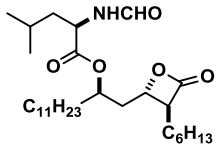


To a stirred solution of **4b** (20.0 mg, 56.4 μmol) in tetrahydrofuran (0.5 mL) at 0 °C was added triphenylphosphine (44.4 mg, 169 μmol) and *N*-Cbz-D-Leu-OH (44.8 mg, 169 μmol) under N_2. A solution of diisopropyl azodicarboxylate (36.3 mg, 169 μmol) in tetrahydrofuran (0.5 mL) was added slowly via syringe. The resulting mixture was stirred at the same temperature for 0.5 h. The reaction was quenched by adding water (5 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (2.5 to 15% EtOAc in hexanes) on silica gel (10 mL) to afford **38** (28.0 mg, 82%) as a colorless oil.

Data for **38**: R_f = 0.24 (10% EtOAc in hexanes); $[\alpha]_D^{21}$ = –10.0 ($CHCl_3$, *c* = 0.79); IR (neat) 3349, 2927, 2857, 1823, 1728, 1524, 1461, 1260, 1217, 1121, 1051 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38–7.31 (m, 5H), 5.11 (s, 2H), 5.09 (d, *J* = 8.5 Hz, 1H), 5.01–4.96 (m, 1H), 4.35 (ddd, *J* = 9.0, 9.0, 5.0 Hz, 1H), 4.27–4.23 (m, 1H), 3.20 (ddd, *J* = 7.5, 7.5, 4.5 Hz, 1H), 2.01–1.99 (m, 2H), 1.83–1.76 (m, 1H), 1.74–1.67 (m, 2H), 1.66–1.57 (m, 3H), 1.55–1.49 (m, 1H), 1.46–1.40 (m, 1H), 1.36–1.24 (m, 25H), 0.963 (d, *J* = 6.0 Hz, 3H), 0.951 (d, *J* = 6.0 Hz, 3H), 0.880 (t, *J* = 7.0 Hz, 3H), 0.877 (t, *J* = 7.0 Hz, 3H);

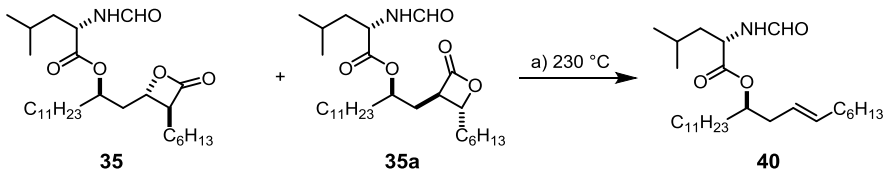
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 171.0, 156.1, 136.4, 128.7 (2C), 128.4, 128.2 (2C), 74.4, 72.5, 67.1, 56.8, 52.9, 41.9, 39.2, 34.3, 32.1, 31.7, 29.82, 29.80, 29.73, 29.64, 29.52, 29.50, 29.1, 27.8, 26.9, 25.2, 25.0, 23.1, 22.9, 22.7, 22.0, 14.3, 14.2; MALDI-TOF/CCA-HRMS calcd for $C_{36}H_{59}NO_6Na$ [M + Na]$^+$: 624.4235, found 624.4250.

(*R*)-1-((2*S*,3*S*)-3-Hexyl-4-oxooxetan-2-yl)tridecan-2-yl formyl-D-leucinate (36)



To a stirred solution of **38** (16.0 mg, 26.6 µmol) in tetrahydrofuran (0.5 mL) at room temperature was added Pd/C (10% wt/wt, 5.6 mg, 2.66 µmol) under N_2. The resulting mixture was then stirred at the same temperature under H_2 (1 atm) for 1 h. The mixture was filtered through a pad of Celite, and washed with EtOAc. The filtrate was concentrated under reduced pressure. The residue was dissolved in dichloromethane (0.5 mL). Then a premixed mixture of *N*,*N*-dicyclohexylcarbodiimide (27.3 mg, 133 µmol) and formic acid (3.0 µL, 79.8 µmol) in dichloromethane (1 mL) was added to the solution. After 5 min, the mixture was diluted with hexanes and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The crude residue was purified by flash chromatography (10 to 30% EtOAc in hexanes) on silica gel (2 mL) to afford **36** (7.9 mg, 60%) as a colorless oil.

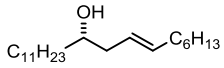
Thermolysis of 35 and 35a



To a resealed tube was added β-lactone **35** and **35a** (as a 2:1 mixture, 5.6 mg, 11.3 μmol). The tube was sealed under Ar, and heated to 230 °C for 1 h. The crude residue was purified by flash chromatography (30% EtOAc in hexanes) on silica gel (3 mL) to afford **40** (2.6 mg, 51%) as a colorless oil.

Data for **40**: ^{1}H NMR (500 MHz, $CDCl_3$) 8.21 (s, 1H), 5.94 (d, *J* = 8.5 Hz, 1H), 5.47 (ddd, *J* = 15.0, 7.0, 7.0 Hz, 1H), 5.31 (ddd, *J* = 15.0, 7.0, 7.0 Hz, 1H); 4.88 (ddd, *J* = 13.0, 6.5, 6.5 Hz, 1H), 4.70 (ddd, *J* = 8.5, 8.5, 5.0 Hz), 2.30–2.21 (m, 2H), 1.99–1.95 (m, 2H), 1.72–1.63 (m, 2H), 1.57–1.51 (m, 3H), 1.33–1.24 (m, 26H), 0.97 (d, *J* = 6.5 Hz, 3H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.89–0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 160.5, 134.6, 124.5, 75.8, 49.8, 42.3, 37.4, 33.4, 32.8, 32.1, 31.9, 29.83 (3C), 29.73, 29.69, 29.54 (2C), 29.0, 25.4, 25.1, 23.0, 22.88, 22.84, 22.2, 14.30, 14.28. (For complete characterization see below)

(*S*,*E*)-Henicos-7-en-10-ol (41)



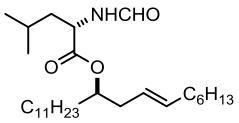
To a stirred solution of **6a** (1.37 g, 6.05 mmol) in dichloromethane at room temperature was added 1-octene (2.18 g, 19.5 mmol), followed by the Grubbs second-generation catalyst[13] (275 mg, 0.32 mmol) under N_2. The resulting mixture was degassed by two freeze−pump−thaw cycles, and then heated to reflux. After 7.5 h, the mixture was concentrated, and the crude residue was purified by flash

[13] Scholl, M.; Trnka, T. M.; Morgan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **1999**, *40*, 2247–2250.

chromatography (5 to 15% EtOAc in hexanes) on silica gel (40 mL) to afford **41** (1.10 g, 59%, *E*:*Z* = 6:1) as a colorless oil.

Data for **41**: R_f = 0.22 (8% Et_2O in hexanes); $[\alpha]_D^{21}$ = –3.0 (CH_2Cl_2, *c* = 0.93); IR (neat) 3396, 2924, 2854, 1719, 1466, 1378, 1263, 1072 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.54 (ddd, *J* = 13.6, 6.8, 6.8 Hz, 1H), 5.40 (ddd, *J* = 13.6, 6.8, 6.8 Hz, 1H), 3.62–3.54 (m, 1H), 2.26–2.19 (m, 1H), 2.08–1.99 (m, 3H), 1.47–1.40 (m, 3H), 1.36–1.24 (m, 25H), 0.89–0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0, 126.0, 71.1, 40.9, 36.9, 32.9, 32.1, 31.9, 29.88, 29.86, 29.81 (3C), 29.6, 29.5, 29.0, 25.9, 22.9, 22.8, 14.32, 14.30; HRMS (EI) calcd for $C_{21}H_{42}O$ $[M]^+$: 310.3236, found 310.3245.

(*R*,*E*)-Henicos-7-en-10-yl formyl-L-leucinate (40)

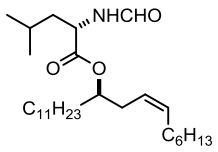


To a stirred solution of **41** (49.0 mg, 158 μmol) in tetrahydrofuran (1 mL) at 0 °C was added triphenylphosphine (82.9 mg, 316 μmol) and *N*-formyl-L-Leu-OH (50.3 mg, 316 μmol) under N_2. A solution of diisopropyl azodicarboxylate (71 μL, 316 μmol) in tetrahydrofuran (1 mL) was added slowly via syringe. The resulting mixture was stirred at the same temperature for 2 h. The reaction was quenched by adding water (5 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (5 to 15% EtOAc in hexanes) on silica gel (15 mL) to afford **40** (49.0 mg, 69%) as a colorless oil.

Data for **40**: R_f = 0.28 (20% EtOAc in hexanes); $[\alpha]_D^{21}$ = +4.0 ($CHCl_3$, *c* = 1.35); IR (neat) 3293, 2925, 2855, 1739, 1666, 1530, 1467, 1380, 1273, 1252, 1195, 1144 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 8.20 (s, 1H), 6.05 (d, *J* = 8.8 Hz, 1H), 5.46 (ddd, *J* = 13.6, 6.8, 6.8 Hz, 1H), 5.30 (ddd, *J* = 13.6, 6.8, 6.8 Hz, 1H),

4.87 (ddd, *J* = 12.4, 6.4, 6.4 Hz, 1H), 4.69 (ddd, *J* = 8.4, 8.4, 6.0 Hz, 1H); 2.62–2.63 (m, 2H), 2.02–1.94 (m, 2H), 1.71–1.61 (m, 2H), 1.59–1.49 (m, 3H), 1.35–1.24 (m, 26H), 0.97–0.93 (m, 6H), 0.89–0.85(m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 160.6, 134.6, 124.4, 75.8, 49.8, 42.3, 37.4, 33.3, 32.7, 32.1, 31.9, 29.80 (3C), 29.70, 29.66, 29.55, 29.51 (2C), 29.0, 25.4, 25.0, 23.0, 22.9, 22.86, 22.82, 22.2, 14.3 (2C); MALDI-TOF/CCA-HRMS $C_{28}H_{53}NO_3Na$ $[M + Na]^+$: 474.3918, found 474.3916.

(*R*,*Z*)-Henicos-7-en-10-yl formyl-L-leucinate (42)



To a stirred solution of **6b** (32.4 mg, 104 μmol) in tetrahydrofuran (0.5 mL) at 0 °C was added triphenylphosphine (54.8 mg, 209 μmol) and *N*-formyl-L-Leu-OH (33.2 mg, 209 μmol) under N_2. A solution of diisopropyl azodicarboxylate (44 μL, 209 μmol) in tetrahydrofuran (0.5 mL) was added slowly via syringe. The resulting mixture was stirred at the same temperature for 2 h. The reaction was quenched by adding water (5 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (5 to 20% EtOAc in hexanes) on silica gel (15 mL) to afford **42** (41.2 mg, 87%) as a colorless oil.

Data for **42**: R_f = 0.28 (20% EtOAc in hexanes); $[\alpha]_D^{22}$ = +12.8 ($CHCl_3$, *c* = 1.26); IR (neat) 3293, 2925, 2855, 1739, 1667, 1530, 1467, 1380, 1332, 1273, 1252, 1195, 1144 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 8.20 (s, 1H), 6.02 (d, *J* = 8.0 Hz, 1H), 5.52–5.45 (m, 1H), 5.33–5.26 (m, 1H), 4.89 (ddd, *J* = 12.0, 6.0, 6.0 Hz, 1H), 4.70 (ddd, *J* = 8.8, 8.8, 4.8 Hz, 1H), 2.38–2.25 (m, 2H), 2.04–1.99 (m, 2H), 1.74–1.62 (m, 2H), 1.58–1.51 (m, 3H), 1.34–1.24 (m, 26H), 0.97–0.93 (m, 6H), 0.89–0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 160.6, 133.3, 123.7, 75.9, 49.8, 42.3, 33.5, 32.1, 31.9, 29.82, 29.81, 29.71, 29.68

(2C), 29.57, 29.52, 29.2, 27.6, 25.5, 25.0, 23.0, 22.9, 22.86, 22.81, 22.2, 14.3 (2C); MALDI-TOF/CCA-HRMS $C_{28}H_{53}NO_3Na$ $[M + Na]^+$: 474.3918, found 474.3903.

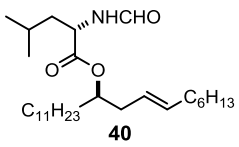
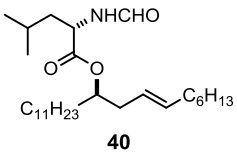
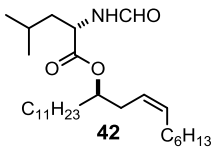
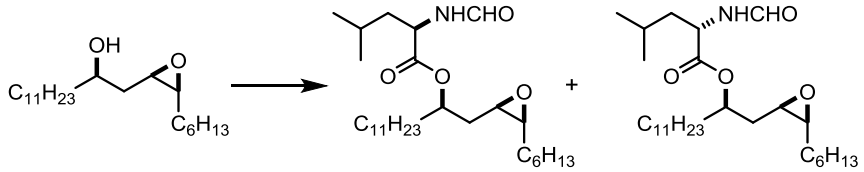
 **40** From synthesis	 **40** From thermolysis	 **42** From synthesis
172.4	172.4	172.5
160.6	160.5	160.6
134.6	134.6	133.3
124.4	124.5	123.7
75.8	75.8	75.9
49.8	49.8	49.8
42.3	42.3	42.3
37.4	37.4	33.5
33.3	33.4	32.1
32.7	32.8	31.9
32.1	32.1	
31.9	31.9	
29.80–29.51	29.83–29.54	29.80–29.52
29.0	29.0	29.2
		27.6
25.4	25.4	25.5
25.0	25.1	25.0
23.0	23.0	23.0
		22.9
22.9	22.88	22.86
22.8	22.84	22.81
22.2	22.2	22.2
14.30	14.30	14.30
14.28	14.28	14.28

Table S8. ^{13}C NMR comparison of **40** and **42**.

(*R*)-1-((2*R*,3*S*)-3-Hexyloxiran-2-yl)tridecan-2-yl formyl-D-leucinate (*ent*-22)

(*R*)-1-((2*R*,3*S*)-3-Hexyloxiran-2-yl)tridecan-2-yl formyl-L-leucinate (*ent*-23)



ent-**19** *ent*-**22** *ent*-**23**

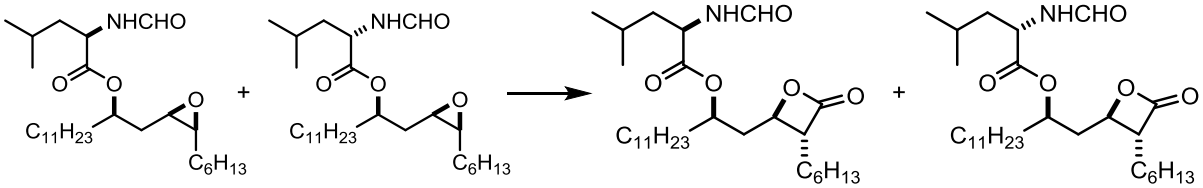
To a stirred solution of *ent*-**19** (0.351 g, 1.08 mmol) in dichloromethane (2 mL) at room temperature was added *N*-formyl-L-Leu-OH (0.189 g, 1.19 mmol), followed by *N*,*N*-dicyclohexyl carbodiimide (0.443 g, 2.16 mmol) and 4-dimethylaminopyridine (5 mg). The resulting mixture was stirred at the same temperature for 24 h. The mixture was diluted with hexanes and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The crude residue was purified by flash chromatography (10 to 30% EtOAc in hexanes) on silica gel (40 mL) to afford a mixture of *ent*-**22** and *ent*-**23** (0.42 g, 86%) as a colorless oil. The product contained two isomers *ent*-**22** and *ent*-**23**, which were separated by HPLC for characterization.

Data for *ent*-**22**: R_f = 0.32 (30% EtOAc in hexanes); $[\alpha]_D^{21}$ = +15.6 ($CHCl_3$, *c* = 0.42); IR (neat) 3296, 2926, 2857, 1739, 1670, 1523, 1462, 1380, 1251, 1195 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 6.07 (d, *J* = 9.0 Hz, 1H), 5.10 (dddd, *J* = 8.0, 8.0, 5.0, 4.5 Hz, 1H), 4.72 (ddd, *J* = 8.5, 8.5, 5.0 Hz, 1H), 2.93 (ddd, *J* = 7.5, 4.0, 4.0 Hz, 1H), 2.87 (ddd, *J* = 6.0, 6.0, 4.5 Hz, 1H), 1.87 (ddd, *J* = 14.5, 4.5, 4.5 Hz, 1H), 1.75–1.55 (m, 5H), 1.53–1.39 (m, 4H), 1.36–1.24 (m, 25H), 0.96 (d, *J* = 6.0 Hz, 3H), 0.95 (d, *J* = 6.0 Hz, 3H), 0.890 (t, *J* = 6.5 Hz, 3H), 0.876 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 160.8, 74.4, 56.4, 53.8, 49.9, 41.9, 34.3, 32.8, 32.1, 31.9, 29.81, 29.76, 29.72, 29.66, 29.55, 29.54, 29.4, 28.1, 26.7, 25.4, 25.1, 23.0, 22.9, 22.8, 22.1, 14.3, 14.2; HRMS (ESI) calcd for $C_{28}H_{53}NO_4Na$ $[M + Na]^+$: 490.3867, found 490.3849.

Data for *ent*-**23**: R_f = 0.32 (30% EtOAc in hexanes); $[\alpha]_D^{21}$ = –2.2 ($CHCl_3$, *c* = 0.54); IR (neat) 3290, 2926, 2857, 1739, 1670, 1523, 1462, 1380, 1269, 1193 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 6.04 (d, *J* = 8.5 Hz, 1H), 5.09 (dddd, *J* = 7.5, 7.5, 5.0, 5.0 Hz, 1H), 4.73 (ddd, *J* = 8.5, 8.5, 5.0 Hz, 1H), 2.98 (ddd, *J* = 8.0, 4.0, 4.0 Hz, 1H), 2.90–2.87 (m, 1H), 1.88 (ddd, *J* = 14.5, 4.5, 4.5 Hz, 1H), 1.74–1.54 (m, 5H), 1.50–1.40 (m, 4H), 1.38–1.24 (m, 25H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.887 (t, *J* = 7.0 Hz, 3H), 0.875 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 160.7, 74.3, 56.4, 53.6, 49.7, 42.0, 34.0, 32.6, 32.1, 31.9, 29.81 (2C), 29.72, 29.66, 29.53, 29.47, 29.4, 28.1, 26.7, 25.5, 25.0, 23.1, 22.9, 22.8, 22.1, 14.30, 14.25; HRMS (ESI) calcd for $C_{28}H_{53}NO_4Na$ $[M + Na]^+$: 490.3867, found 490.3867.

(*R*)-1-((2*R*,3*R*)-3-Hexyl-4-oxooxetan-2-yl)tridecan-2-yl formyl-D-leucinate (*ent*-1)

(*R*)-1-((2*R*,3*R*)-3-Hexyl-4-oxooxetan-2-yl)tridecan-2-yl formyl-L-leucinate (*ent*-34)



ent-**22** *ent*-**23** *ent*-**1** *ent*-**34**

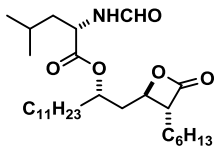
The general procedure for carbonylation of epoxides was followed using 102.7 mg (0.2196 mmol) (*R*)-1-((2*R*,3*S*)-3-hexyloxiran-2-yl)tridecan-2-yl formyl-D,L-leucinate, 12.8 mg (0.0117 mmol, 5.33 mol %) [ClTPPAl][$Co(CO)_4$], and 0.50 mL tetrahydrofuran for 3 days. The crude residue was purified by flash column chromatography (50% Et_2O in hexanes) on silica gel (30 mL) to afford a mixture of *ent*-**1** and *ent*-**34** (90.0 mg, 82%) as a colorless oil. The mixture of *ent*-**1** and *ent*-**34** was separated with HPLC.

Data for *ent*-**1**: R_f = 0.27 (30% EtOAc in hexanes); $[\alpha]_D^{21}$ = +22.3 ($CHCl_3$, *c* = 0.45); IR (neat) 3304, 2956, 2926, 2855, 1823, 1739, 1671, 1523, 1467, 1381, 1252, 1193, 1124 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 5.91 (d, *J* = 8.5 Hz, 1H), 5.05–5.00 (m, 1H), 4.69 (ddd, *J* = 9.0, 9.0, 5.0 Hz, 1H),

4.29 (ddd, *J* = 7.5, 5.0, 5.0 Hz, 1H), 3.22 (ddd, *J* = 7.5, 7.5, 4.0 Hz, 1H), 2.17 (ddd, *J* = 15.0, 7.5, 7.5 Hz, 1H), 2.00 (ddd, *J* = 15.0, 4.5, 4.5 Hz, 1H), 1.84–1.78 (m, 1H), 1.77–1.63 (m, 4H), 1.61–1.53 (m, 2H), 1.47–1.41 (m, 1H), 1.32–1.24 (m, 25H), 0.973 (d, *J* = 6.5 Hz, 3H), 0.965 (d, *J* = 6.5 Hz, 3H), 0.884 (t, *J* = 6.5 Hz, 3H), 0.877 (t, *J* = 7.0, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 170.8, 160.6, 74.8, 72.8, 57.0, 49.6, 41.6, 38.7, 34.1, 31.89, 31.5, 29.6 (2C), 29.5, 29.4, 29.3, 29.3, 29.0, 27.6, 26.7, 25.1, 24.9, 22.9, 22.7, 22.5, 21.7, 14.1, 14.0 ($CDCl_3$, δ 77.0 ppm); MALDI-TOF/CCA-HRMS calcd for $C_{29}H_{53}NO_5Na$ $[M + Na]^+$: 518.3816, found 518.3780.

Data for *ent*-**34**: R_f = 0.27 (30% EtOAc in hexanes); $[\alpha]_D^{22}$ = +4.4 ($CHCl_3$, *c* = 0.81); IR (neat) 3307, 2926, 2855, 1824, 1740, 1687, 1523, 1467, 1380, 1251, 1190, 1125 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 5.92 (d, *J* = 8.5 Hz, 1H), 5.02 (dddd, *J* = 7.5, 7.5, 5.0, 5.0 Hz, 1H), 4.66 (ddd, *J* = 8.5, 8.5, 5.5 Hz, 1H), 4.35 (ddd, *J* = 8.0, 5.0, 4.0 Hz, 1H), 3.22 (ddd, *J* = 7.5, 7.5, 4.5 Hz, 1H), 2.17 (ddd, *J* = 15.0, 7.5, 7.5 Hz, 1H), 2.01 (ddd, *J* = 15.0, 5.0, 4.5 Hz, 1H), 1.84–1.77 (m, 1H), 1.76–1.71 (m, 1H), 1.70–1.64 (m, 3H), 1.60–1.53 (m, 2H), 1.47–1.41 (m, 1H), 1.38–1.24 (m, 25H), 0.970 (d, *J* = 6.5 Hz, 3H), 0.967 (d, *J* = 6.5 Hz, 3H), 0.882 (t, *J* = 7.0 Hz, 3H), 0.879 (t, *J* = 7.0, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 171.2, 160.8, 74.8, 72.7, 57.1, 49.8, 41.6, 38.7, 34.0, 32.1, 31.6, 29.8 (2C), 29.7, 29.6, 29.5, 29.4, 29.1, 27.8, 26.8, 25.4, 25.0, 23.0, 22.9, 22.7, 22.0, 14.3, 14.2; MALDI-TOF/CCA-HRMS calcd for $C_{29}H_{53}NO_5Na$ $[M + Na]^+$: 518.3816, found 518.3813.

(*S*)-1-((2*R*,3*R*)-3-Hexyl-4-oxooxetan-2-yl)tridecan-2-yl formyl-L-leucinate (*ent*-36)

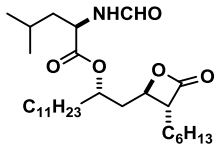


To a stirred solution of *ent*-**38** (10.0 mg, 16.6 μmol) in tetrahydrofuran (1 mL) at room temperature was added Pd/C (10% wt/wt, 3.5 mg, 3.3 μmol) under N_2. The resulting mixture was then stirred at the same

temperature under H_2 (1 atm) for 2 h. The mixture was filtered through a pad of Celite, and washed with EtOAc. The filtrate was concentrated under reduced pressure. The residue was dissolved in dichloromethane (0.5 mL). Then a premixed mixture of *N*,*N*-dicyclohexylcarbodiimide (17.0 mg, 83.0 μmol) and formic acid (2.0 μL, 50.4 μmol) in dichloromethane (0.5 mL) was added to the solution. After 5 min, the mixture was diluted with hexanes and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The crude residue was purified by flash chromatography (0 to 20% EtOAc in hexanes) on silica gel (2 mL) to afford *ent*-**36** (5.8 mg, 70%) as a colorless oil.

Data for *ent*-**36**: R_f = 0.27 (30% EtOAc in hexanes); $[\alpha]_D^{21}$ = +12.6 ($CHCl_3$, *c* = 0.55); IR (neat) 3311, 2926, 2857, 1823, 1739, 1673, 1521, 1462, 1380, 1251, 1193, 1122 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 5.94 (d, *J* = 8.5 Hz, 1H), 5.01(ddd, *J* = 7.0, 7.0, 5.5, 5.5 , 1H), 4.71 (ddd, *J* = 9.0, 9.0, 4.5 Hz, 1H), 4.26 (ddd, *J* = 8.5, 4.5, 4.5 Hz, 1H), 3.24 (ddd, *J* = 7.0, 7.0, 4.0 Hz, 1H), 2.09–2.00 (m, 2H), 1.86–1.79 (m, 1H), 1.76–1.63 (m, 4H), 1.61–1.54 (m, 2H), 1.47–1.41 (m, 1H), 1.38–1.24 (m, 25H), 0.972 (d, *J* = 6.0 Hz, 3H), 0.960 (d, *J* = 6.0 Hz, 3H), 0.883 (t, *J* = 7.0 Hz, 3H), 0.875 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 170.9, 160.8, 74.4, 72.7, 56.8, 49.8, 41.9, 39.1, 34.3, 32.1, 31.7, 29.8 (2C), 29.7, 29.6, 29.52, 29.50, 29.1, 27.9, 27.0, 25.2, 25.1, 23.0, 22.9, 22.7, 22.1, 14.3, 14.2; MALDI-TOF/CCA-HRMS calcd for $C_{29}H_{53}NO_5Na$ $[M + Na]^+$: 518.3816, found 518.3801.

(*S*)-1-((2*R*,3*R*)-3-Hexyl-4-oxooxetan-2-yl)tridecan-2-yl formyl-D-leucinate (*ent*-35)

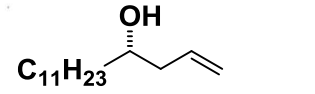


To a stirred solution of *ent*-**39** (10.0 mg, 16.6 μmol) in tetrahydrofuran (1 mL) at room temperature was added Pd/C (10% wt/wt, 3.5 mg, 3.3 μmol) under N_2. The resulting mixture was then stirred at the same temperature under H_2 (1 atm) for 2 h. The mixture was filtered through a pad of Celite, and washed with

EtOAc. The filtrate was concentrated under reduced pressure. The residue was dissolved in dichloromethane (0.5 mL). Then a premixed mixture of *N*,*N*-dicyclohexylcarbodiimide (17.0 mg, 83.0 μmol) and formic acid (2.0 μL, 50.4 μmol) in dichloromethane (0.5 mL) was added to the solution. After 5 min, the mixture was diluted with hexanes and filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The crude residue was purified by flash chromatography (0 to 20% EtOAc in hexanes) on silica gel (2 mL) to afford *ent*-**35** (6.0 mg, 72%) as a colorless oil.

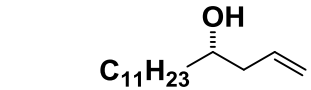
Data for *ent*-**35**: R_f = 0.27 (30% EtOAc in hexanes); $[\alpha]_D^{21}$ = +23.5 ($CHCl_3$, *c* = 0.61); IR (neat) 3353, 2926, 2857, 1822, 1739, 1684, 1462, 1380, 1251, 1189, 1124 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 5.92 (d, *J* = 8.5 Hz, 1H), 5.04 (dddd, *J* = 7.5, 7.5, 5.0, 5.0 Hz, 1H), 4.68 (ddd, *J* = 8.5, 8.5, 5.0 Hz, 1H), 4.29 (ddd, *J* = 9.0, 4.5, 4.5 Hz, 1H), 3.22 (ddd, *J* = 7.5, 7.5, 4.5 Hz, 1H), 2.10–2.00 (m, 2H), 1.85–1.78 (m, 1H), 1.77–1.53 (m, 6H), 1.49–1.42 (m, 1H), 1.38–1.24 (m, 25H), 0.975 (d, *J* = 6.0 Hz, 3H), 0.965 (d, *J* = 6.5 Hz, 3H), 0.89–0.87 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 171.1, 160.8, 74.5, 72.7, 56.9, 49.7, 41.9, 39.3, 34.4, 32.1, 31.7, 29.8 (2C), 29.7, 29.6, 29.5, 29.4, 29.1, 27.8, 27.0, 25.2, 25.1, 23.0, 22.9, 22.7, 22.1, 14.3, 14.2; MALDI-TOF/CCA-HRMS calcd for $C_{29}H_{53}NO_5Na$ $[M + Na]^+$: 518.3816, found 518.3792.

Section C: ^{1}H and ^{13}C NMR Spectra



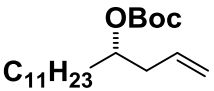
^{1}H NMR (400 MHz, $CDCl_3$)

6a



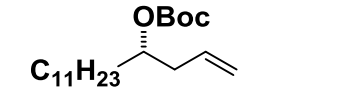
^{13}C NMR (100 MHz, $CDCl_3$)

6a



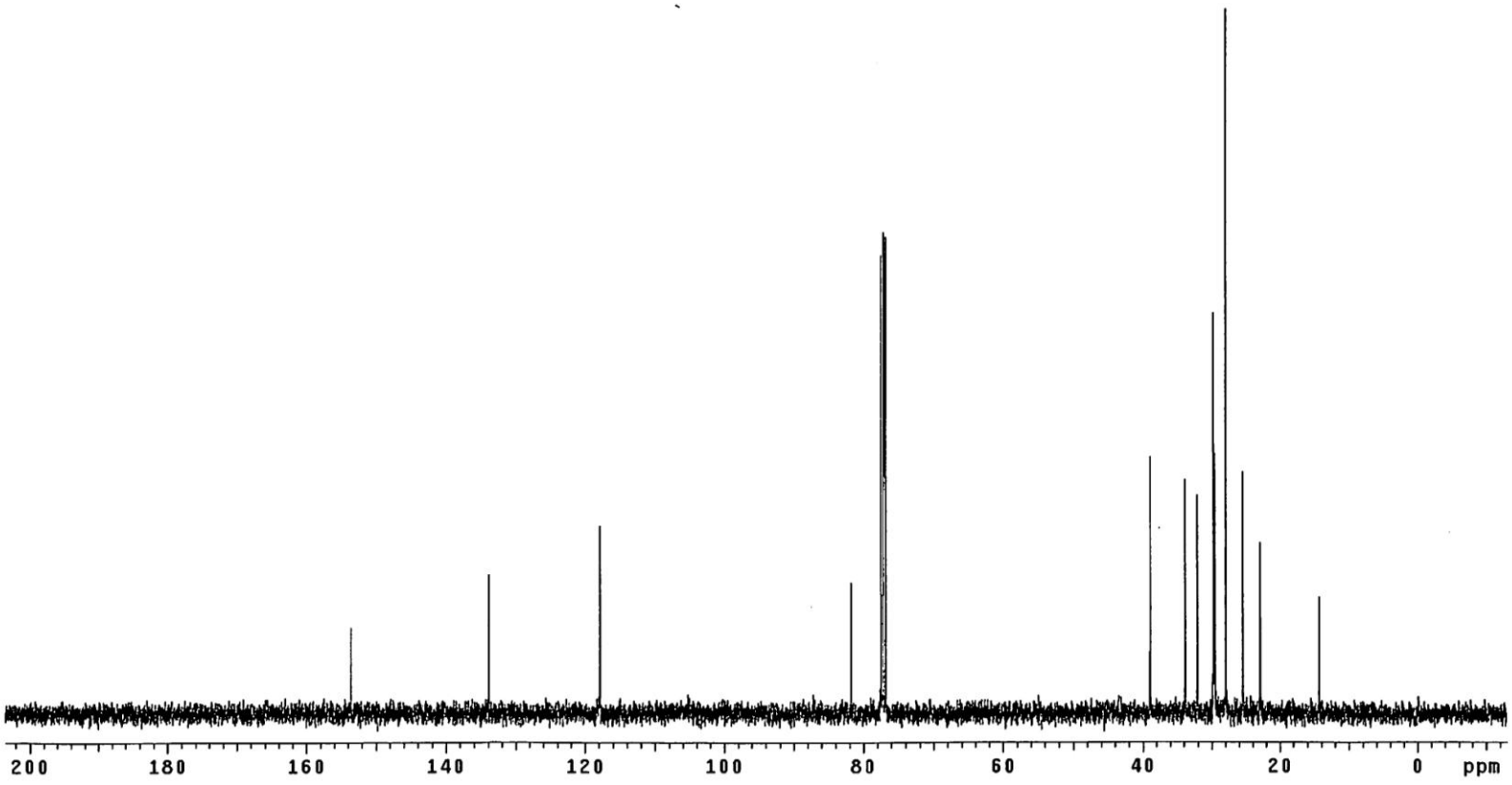
^{1}H NMR (500 MHz, $CDCl_3$)

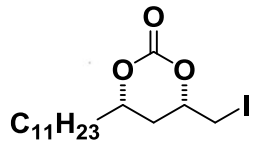
8



^{13}C NMR (100 MHz, $CDCl_3$)

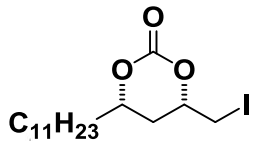
8





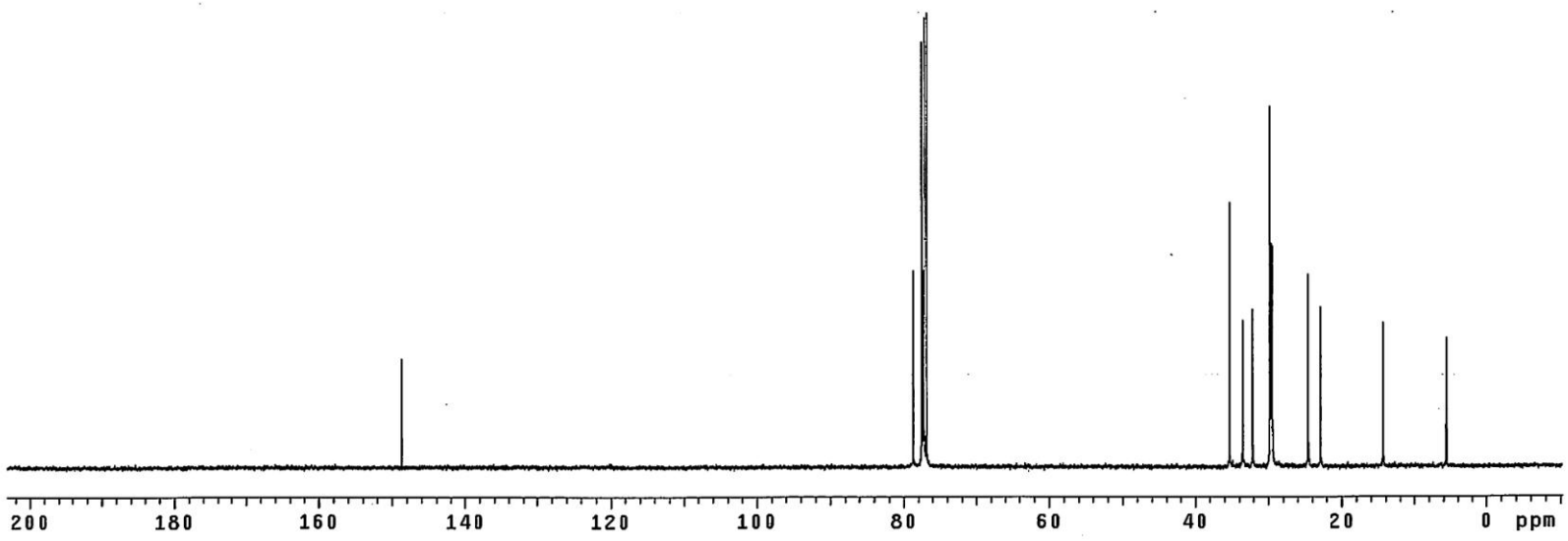
^{1}H NMR (400 MHz, $CDCl_3$)

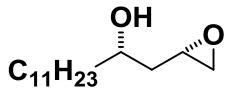
9



^{13}C NMR (100 MHz, $CDCl_3$)

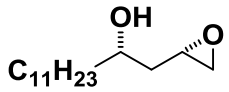
9





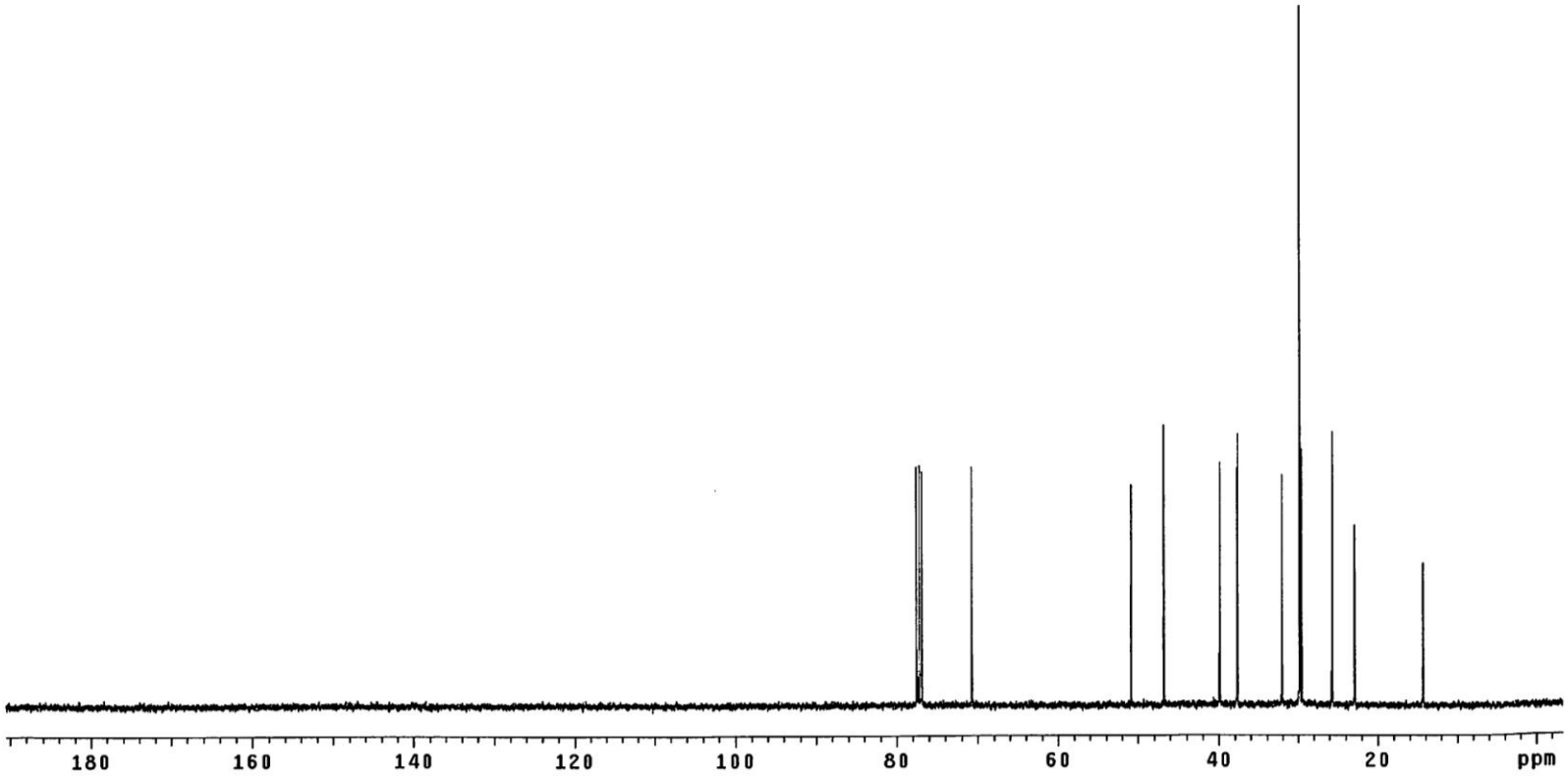
^{1}H NMR (400 MHz, $CDCl_3$)

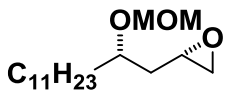
10



^{13}C NMR (100 MHz, $CDCl_3$)

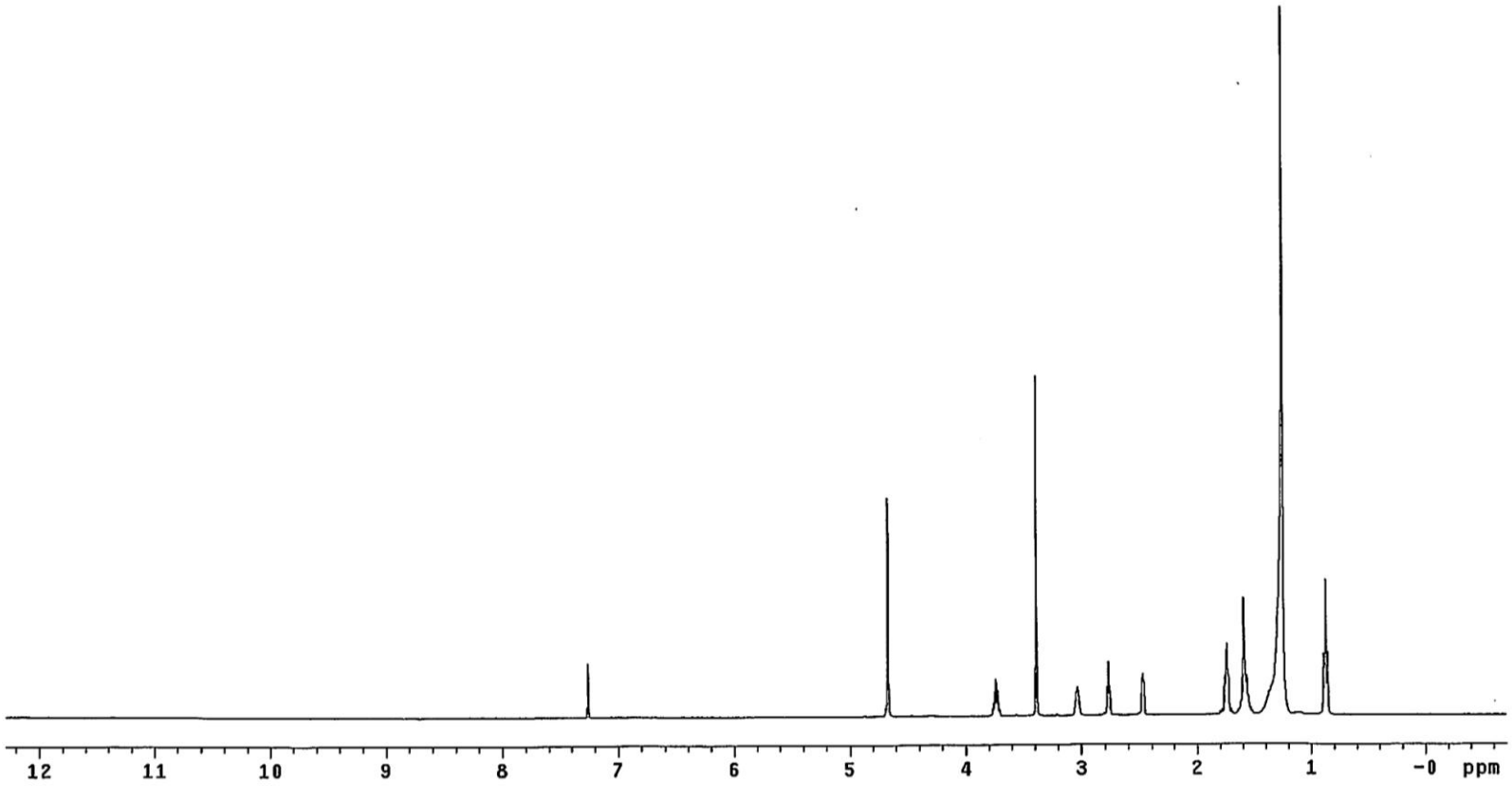
10

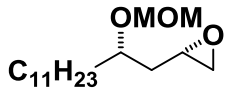




^{1}H NMR (400 MHz, $CDCl_3$)

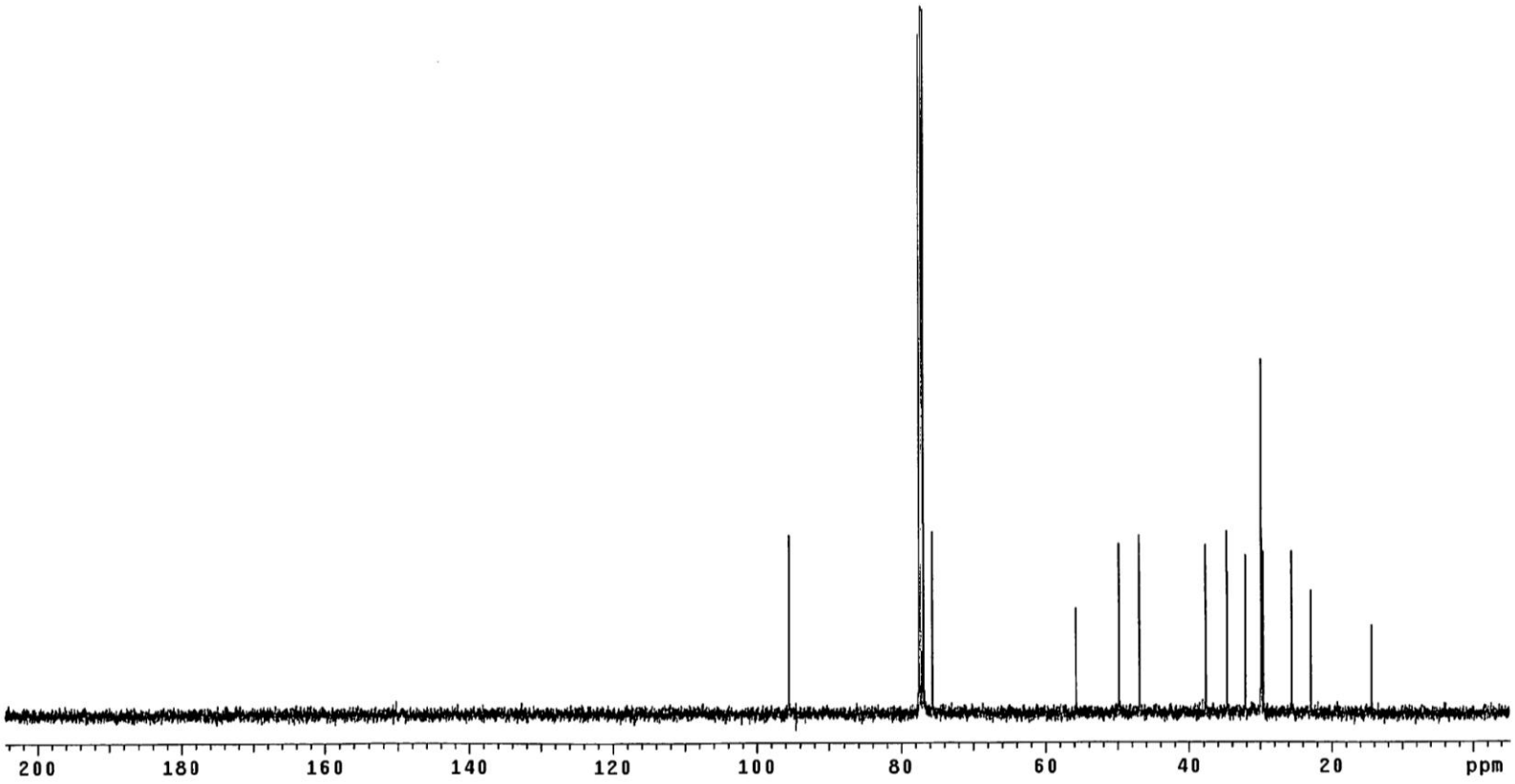
5a

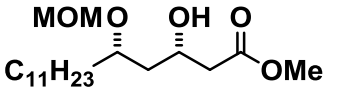




^{13}C NMR (100 MHz, $CDCl_3$)

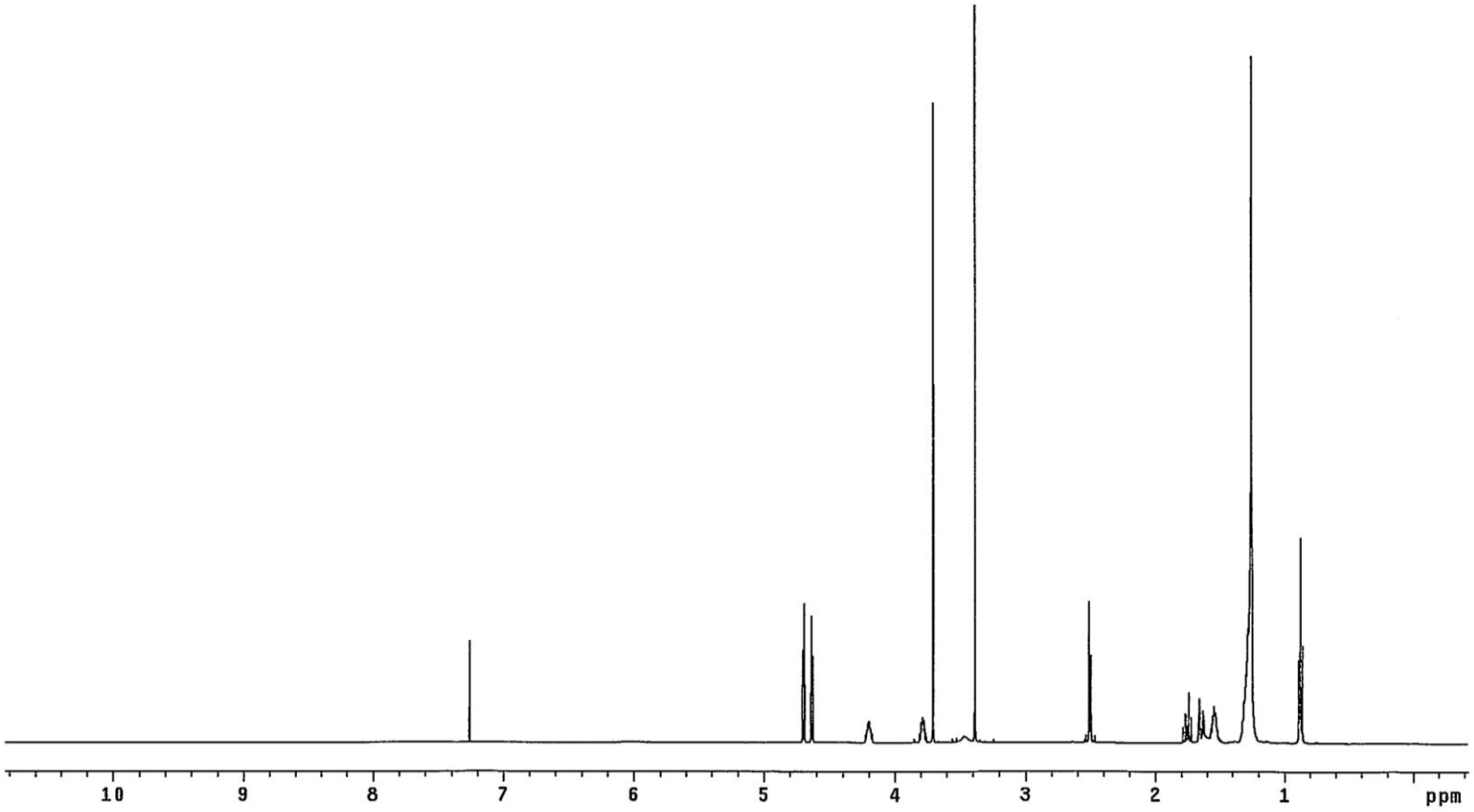
5a

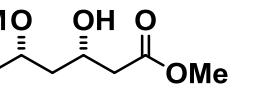




^{1}H NMR (500 MHz, $CDCl_3$)

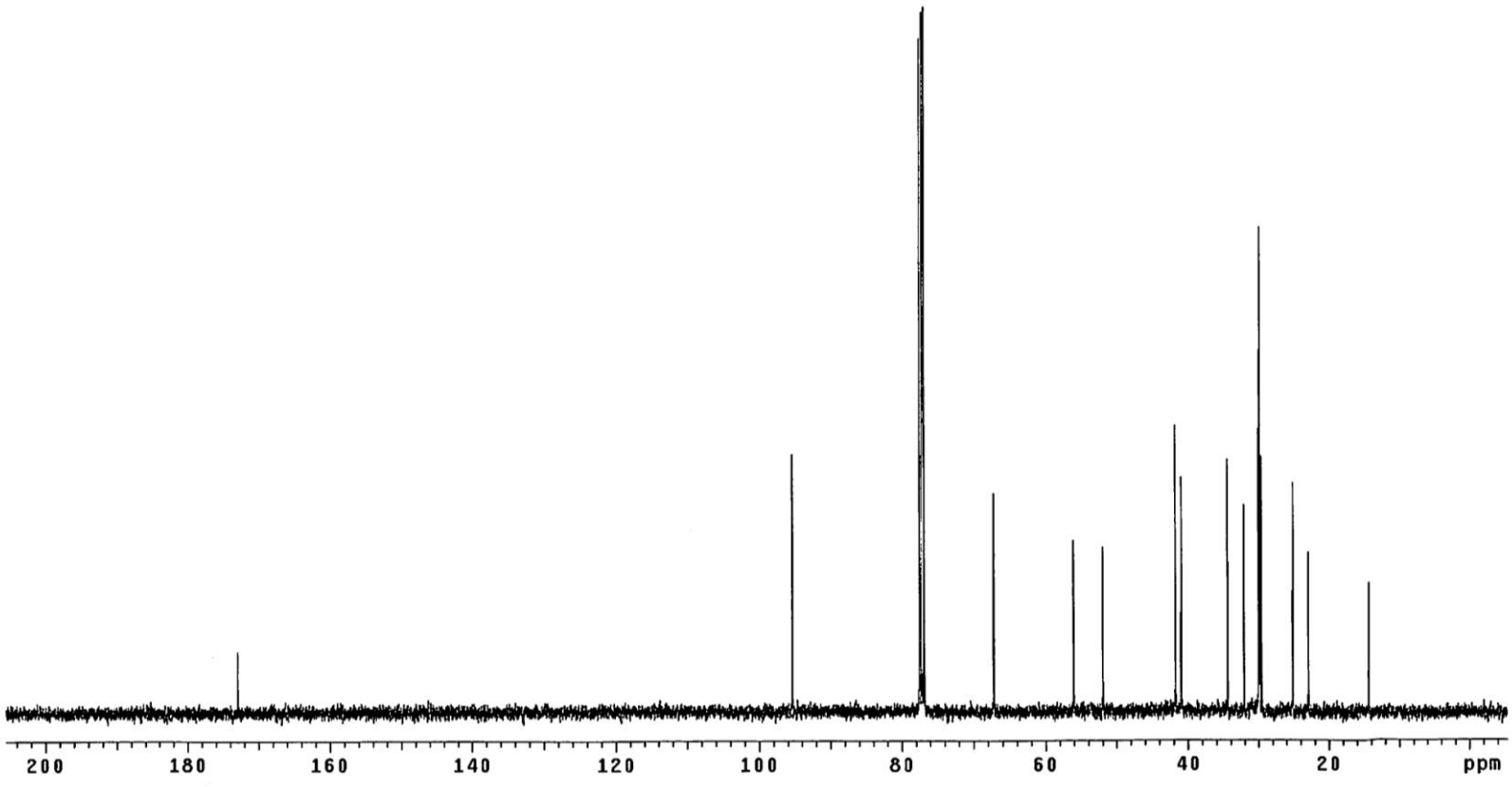
11

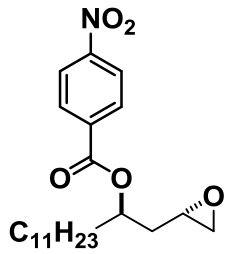




^{13}C NMR (100 MHz, $CDCl_3$)

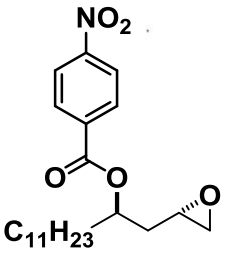
11





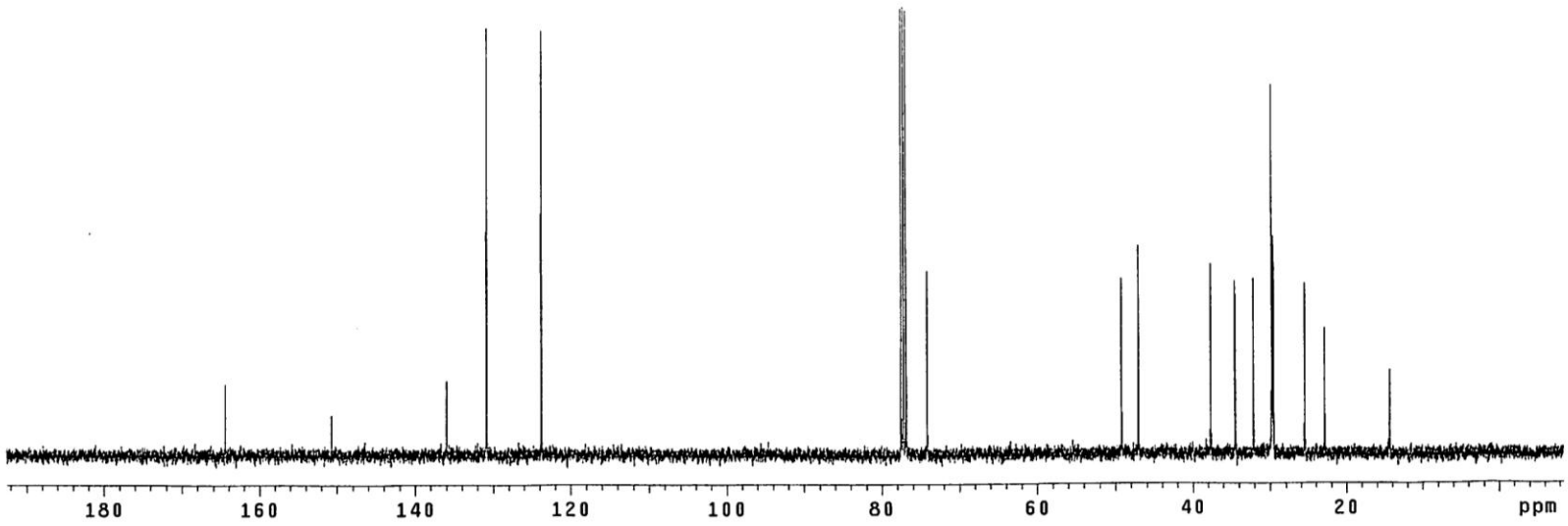
^{1}H NMR (500 MHz, $CDCl_3$)

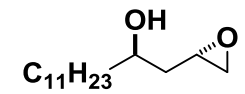
10a



^{13}C NMR (100 MHz, $CDCl_3$)

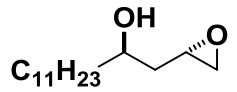
10a





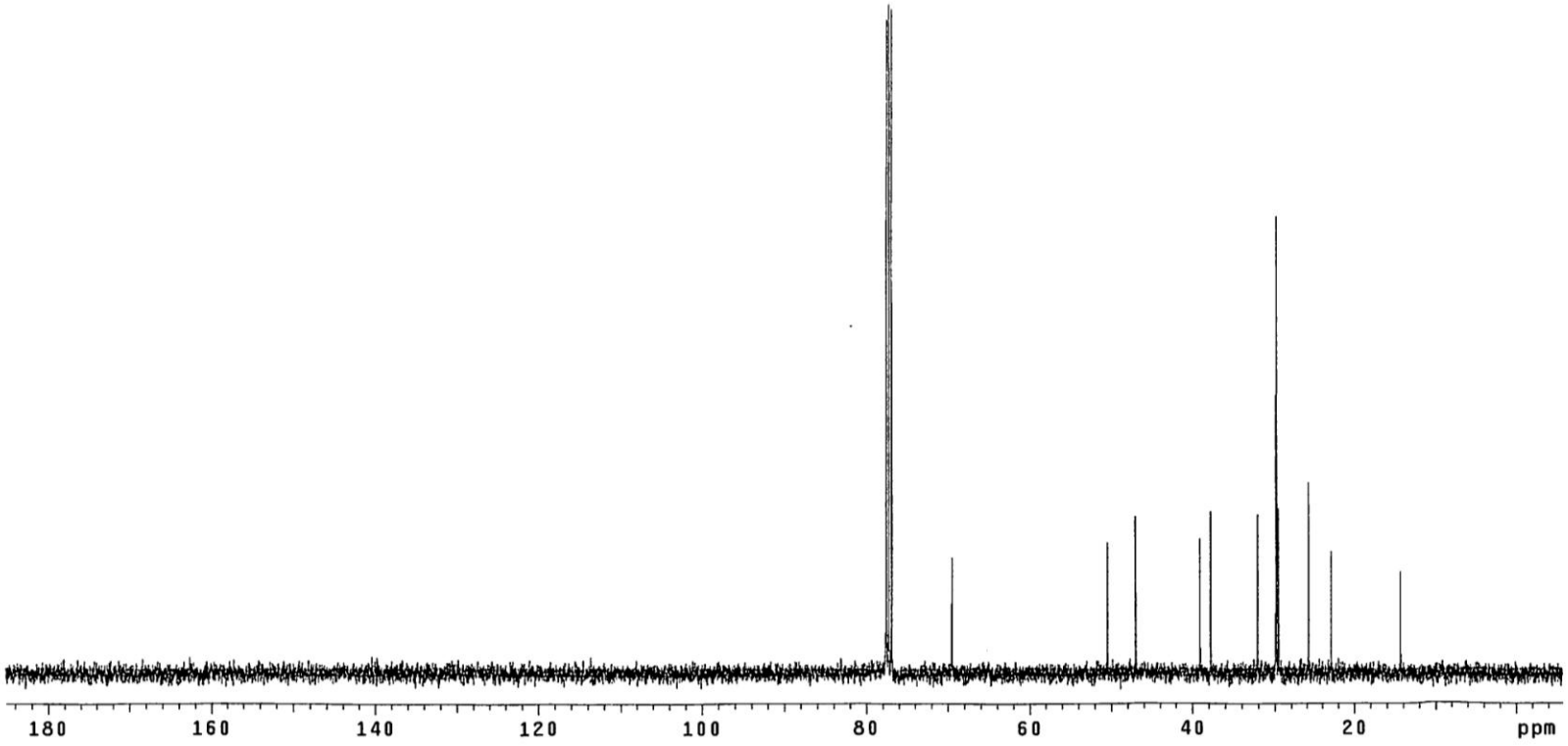
^{1}H NMR (500 MHz, $CDCl_3$)

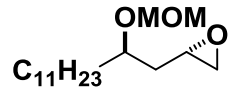
12



^{13}C NMR (100 MHz, $CDCl_3$)

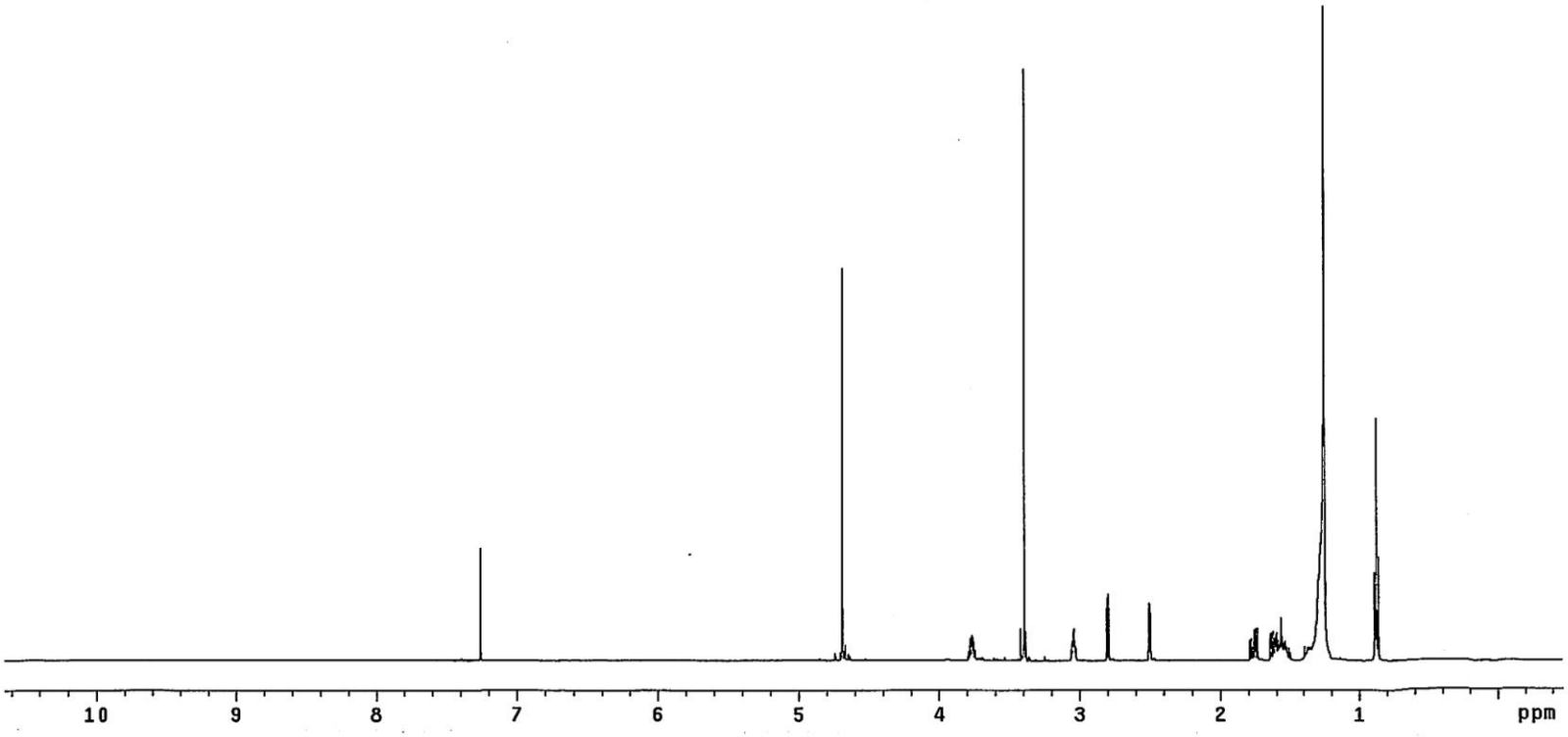
12

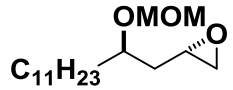




^{1}H NMR (500 MHz, $CDCl_3$)

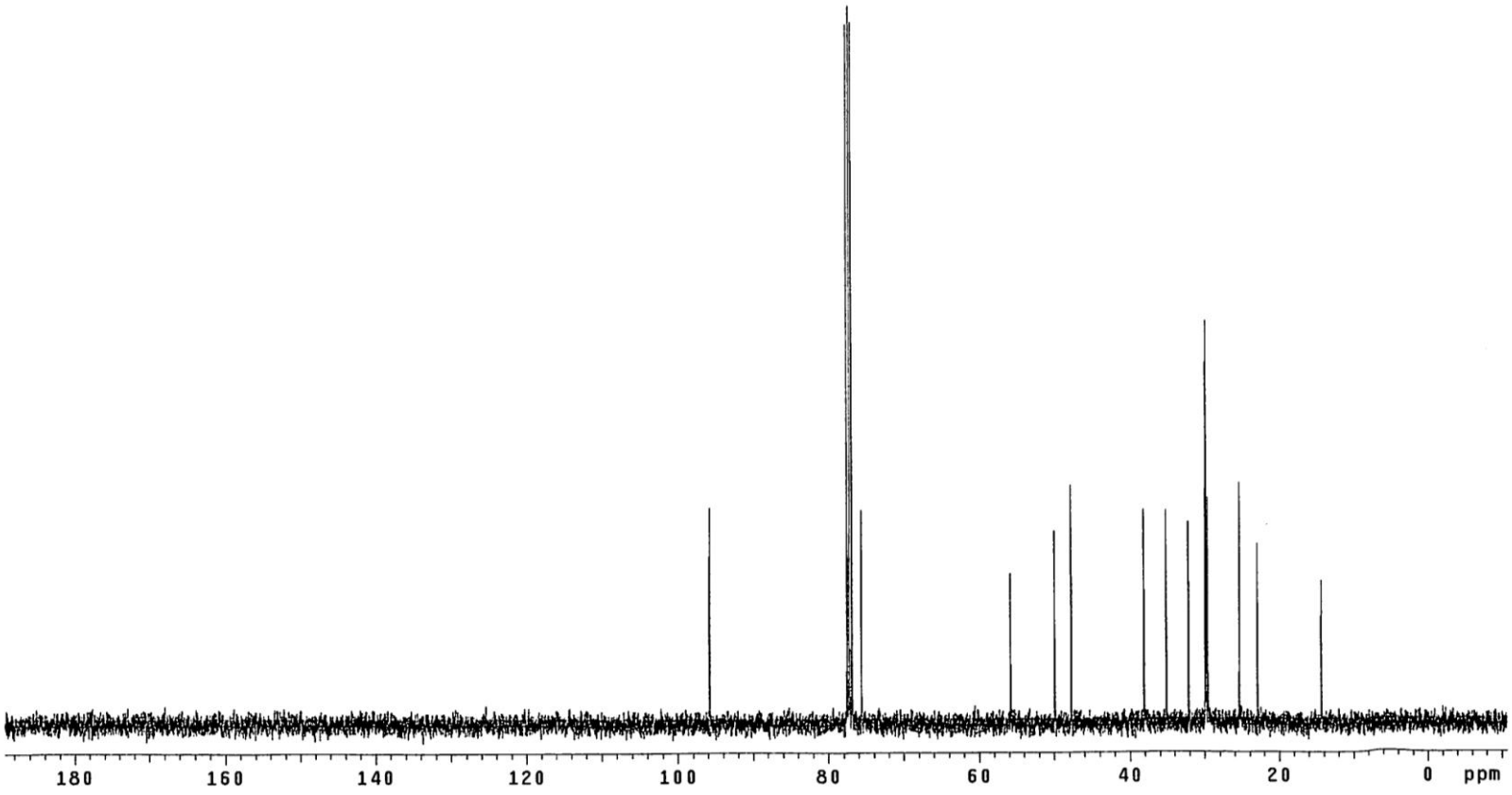
13

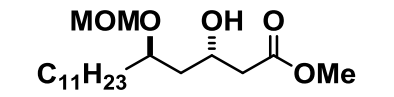




^{13}C NMR (100 MHz, $CDCl_3$)

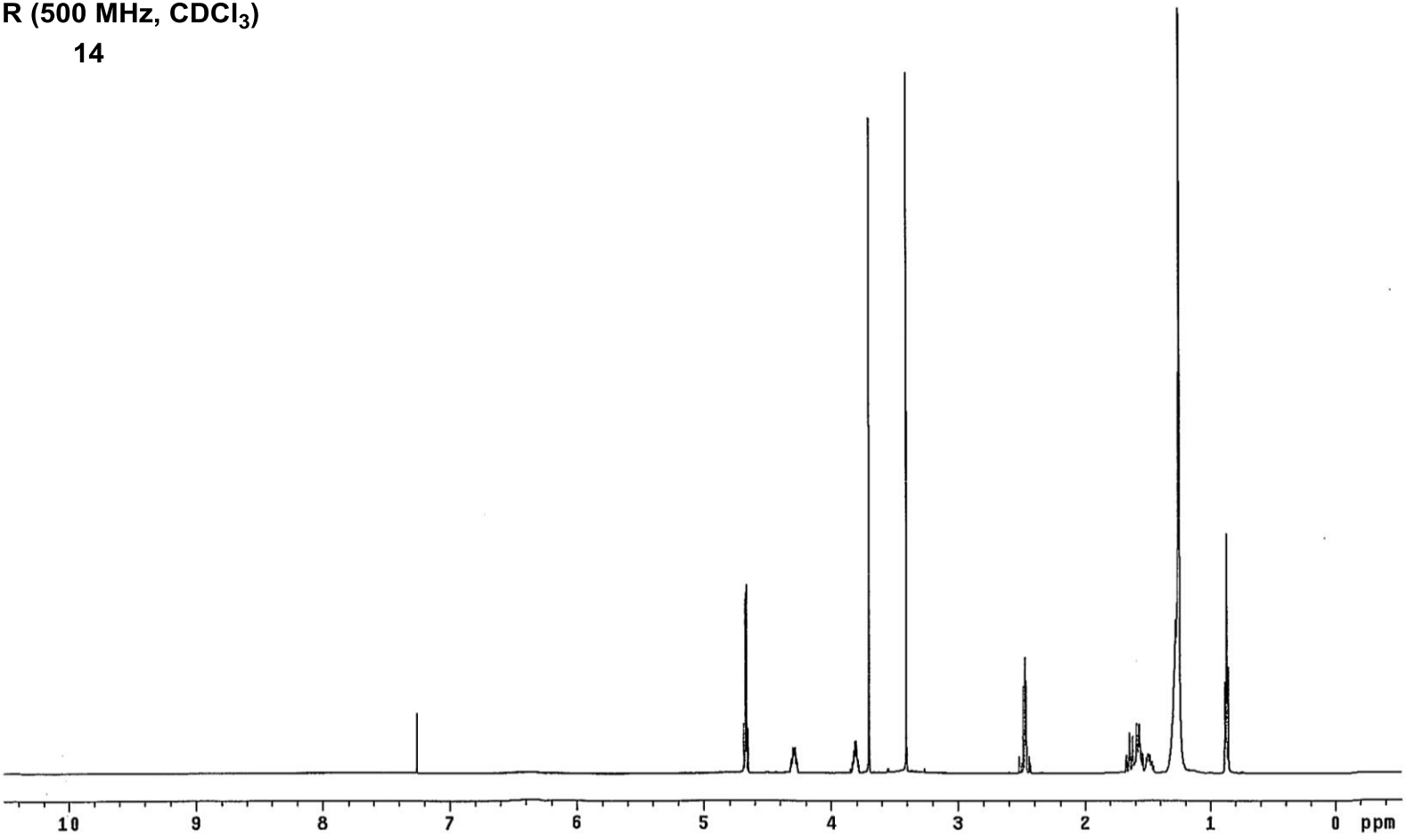
13

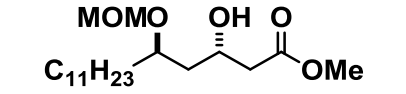




^{1}H NMR (500 MHz, $CDCl_3$)

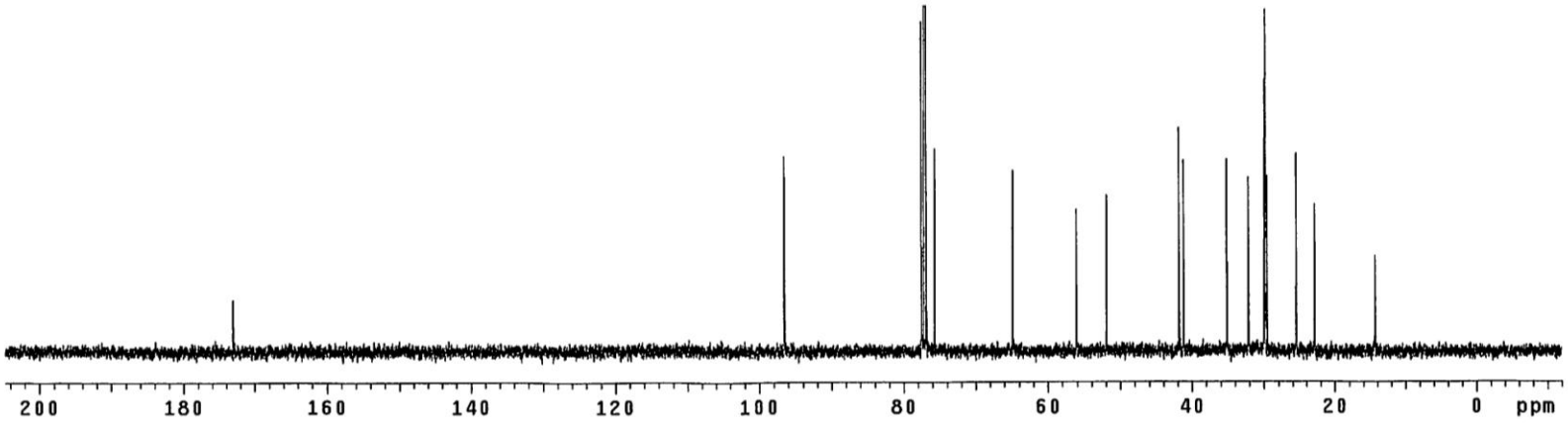
14

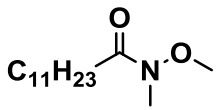




^{13}C NMR (100 MHz, $CDCl_3$)

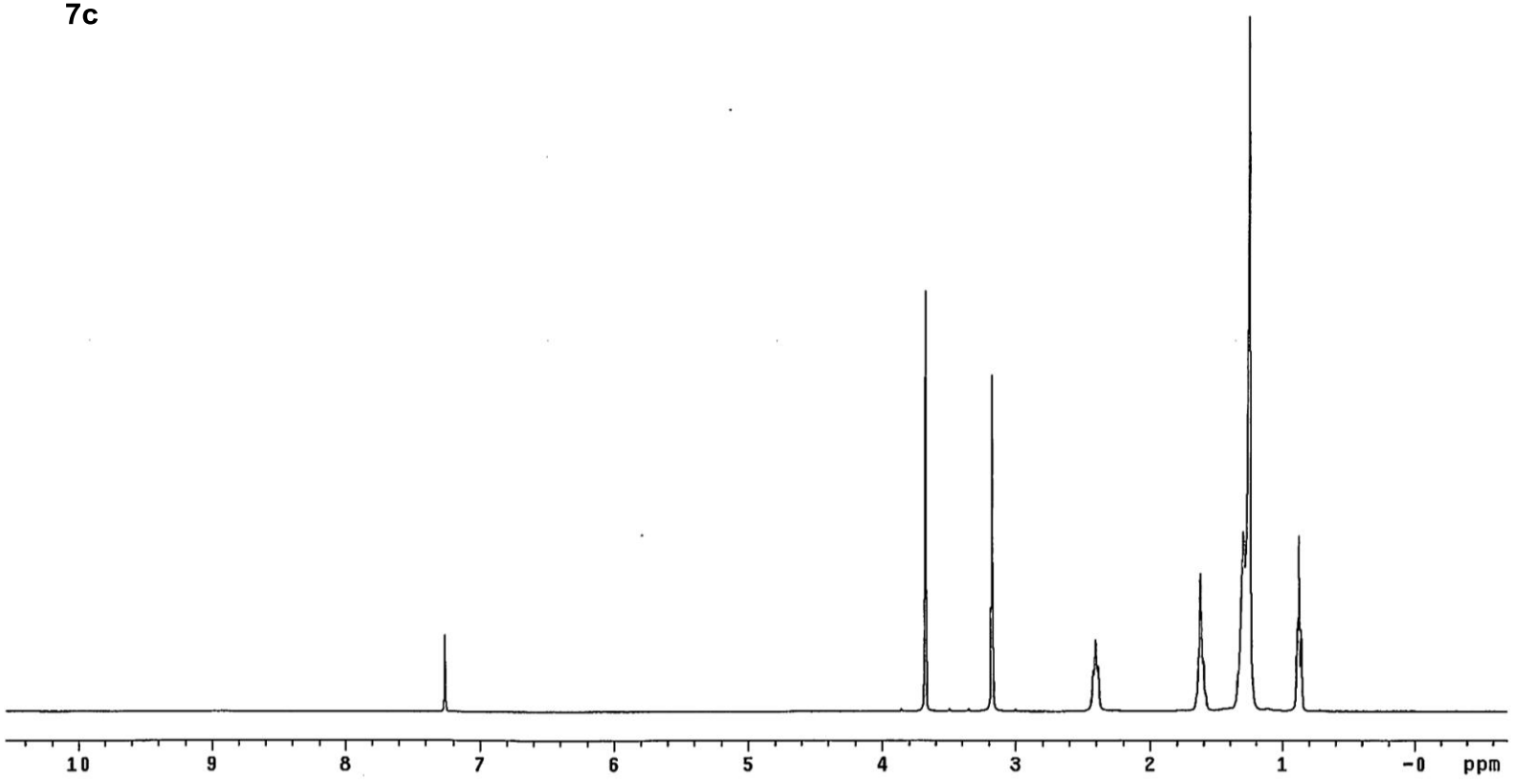
14

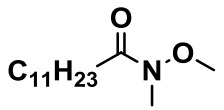




^{1}H NMR (500 MHz, $CDCl_3$)

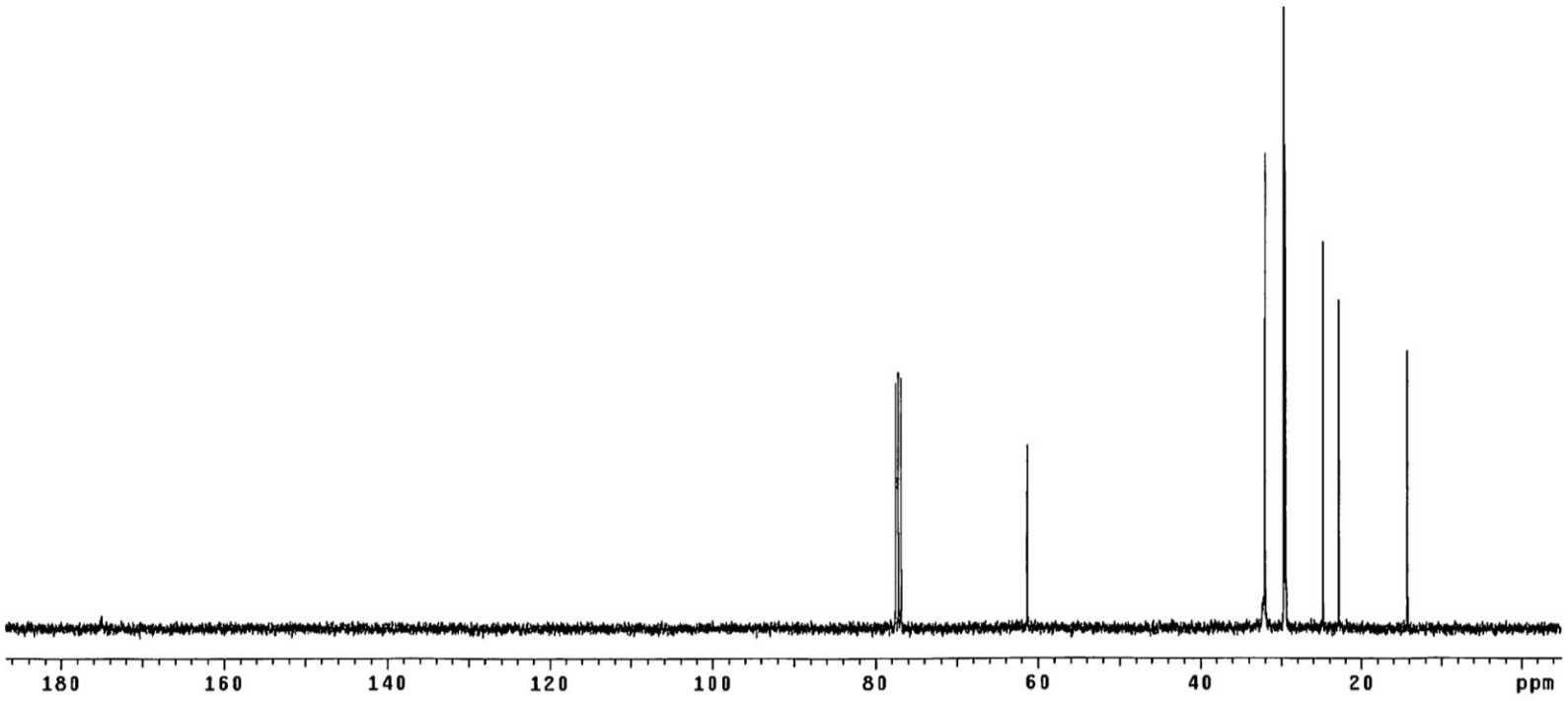
7c

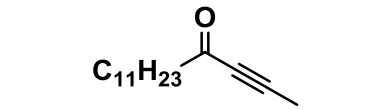




^{13}C NMR (100 MHz, $CDCl_3$)

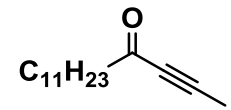
7c





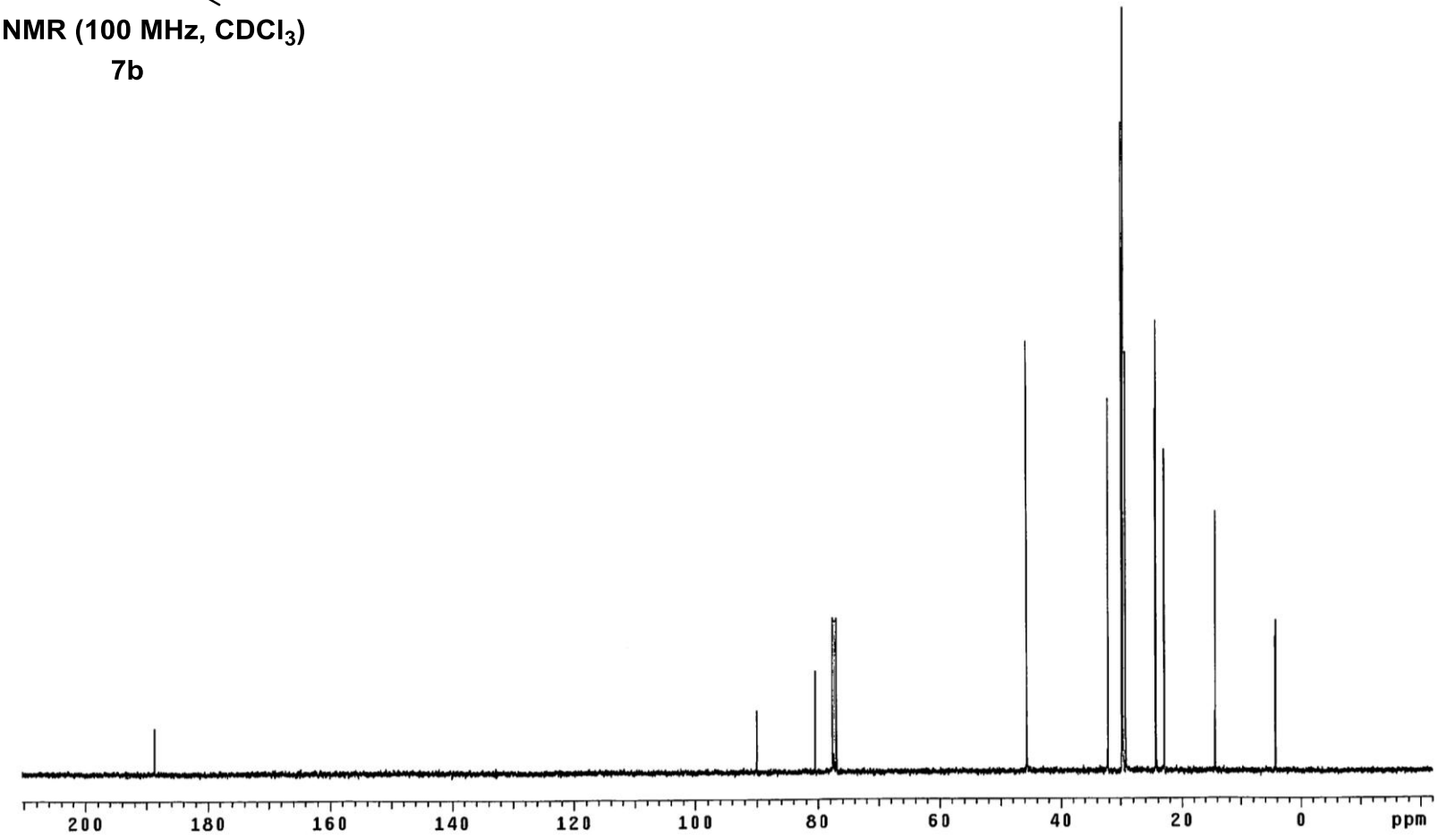
^{1}H NMR (400 MHz, $CDCl_3$)

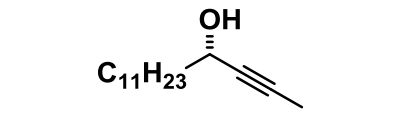
7b



^{13}C NMR (100 MHz, $CDCl_3$)

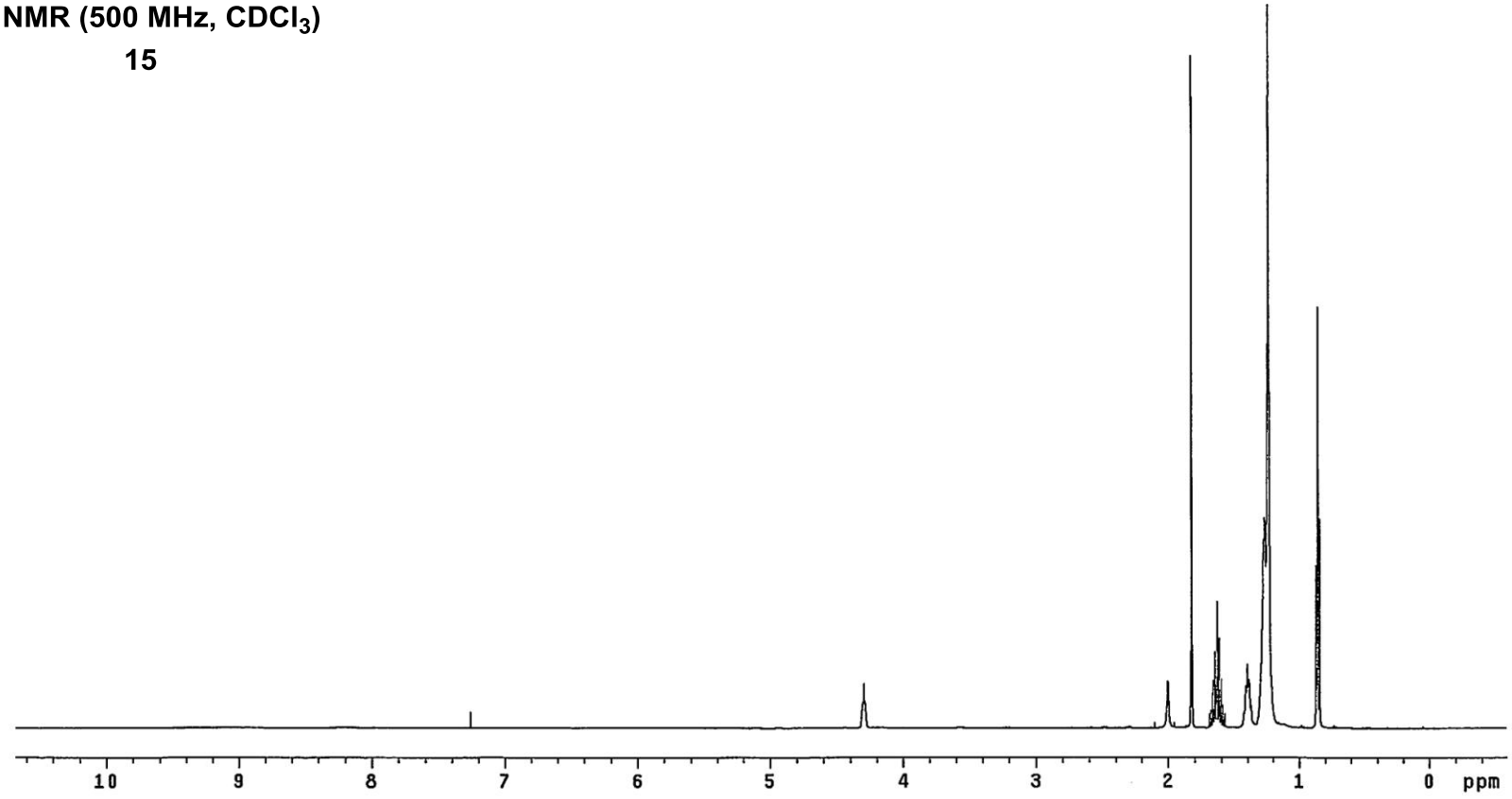
7b

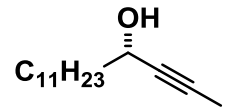




^{1}H NMR (500 MHz, $CDCl_3$)

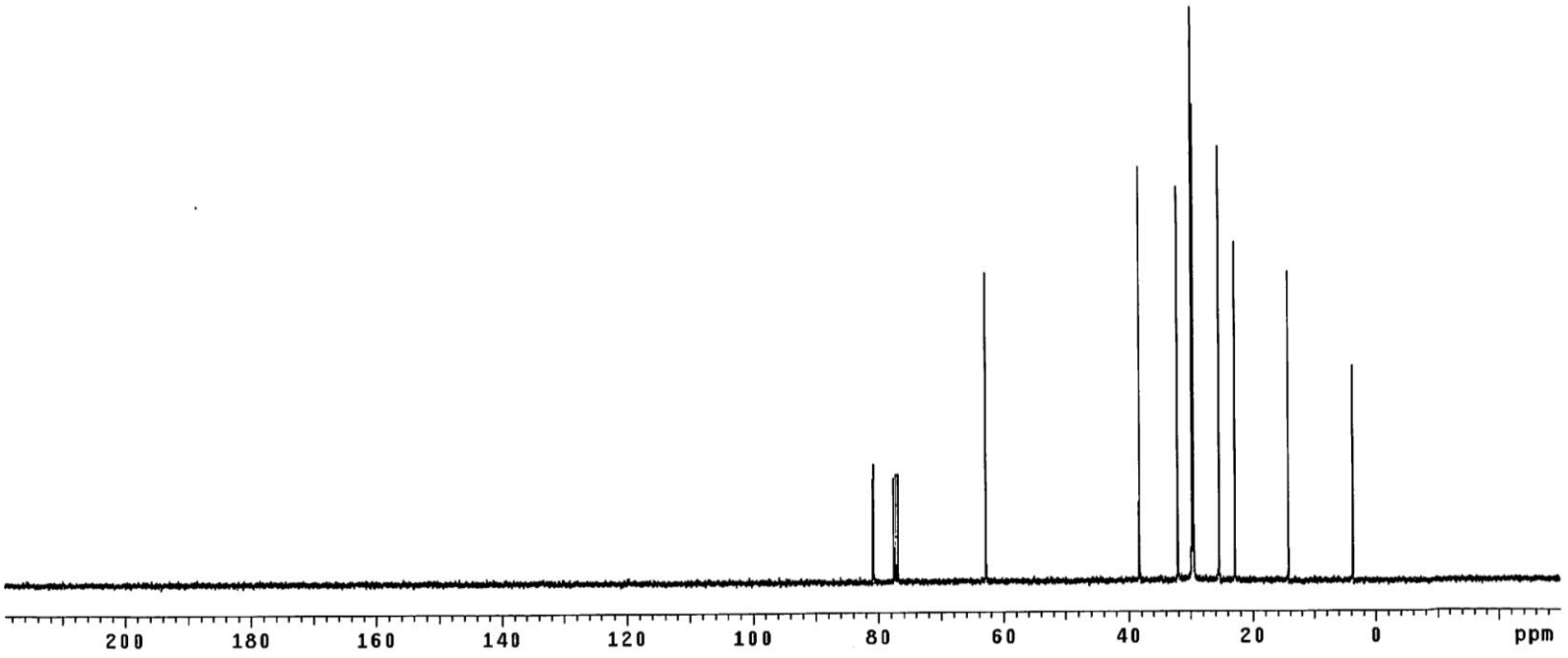
15

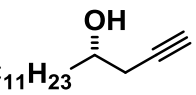




^{13}C NMR (100 MHz, $CDCl_3$)

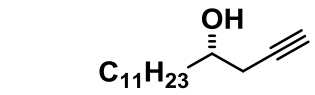
15





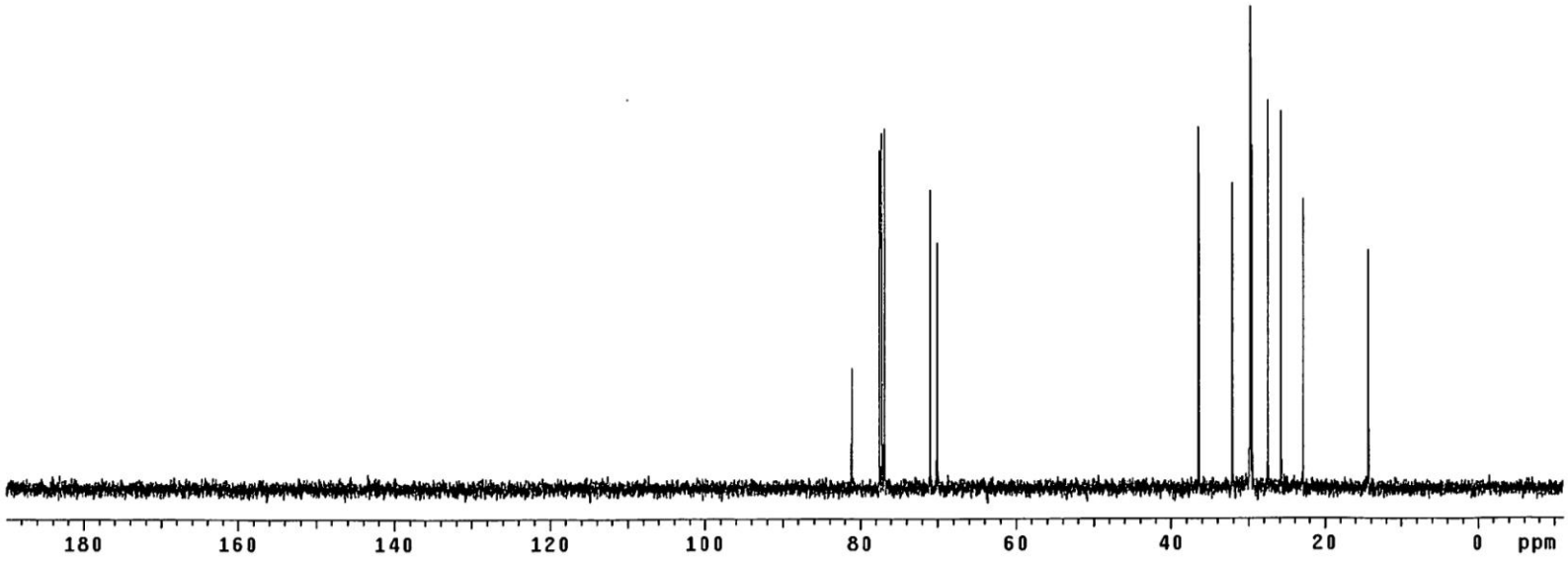
^{1}H NMR (500 MHz, $CDCl_3$)

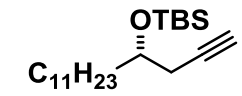
15a



^{13}C NMR (100 MHz, $CDCl_3$)

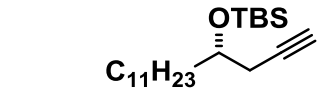
15a





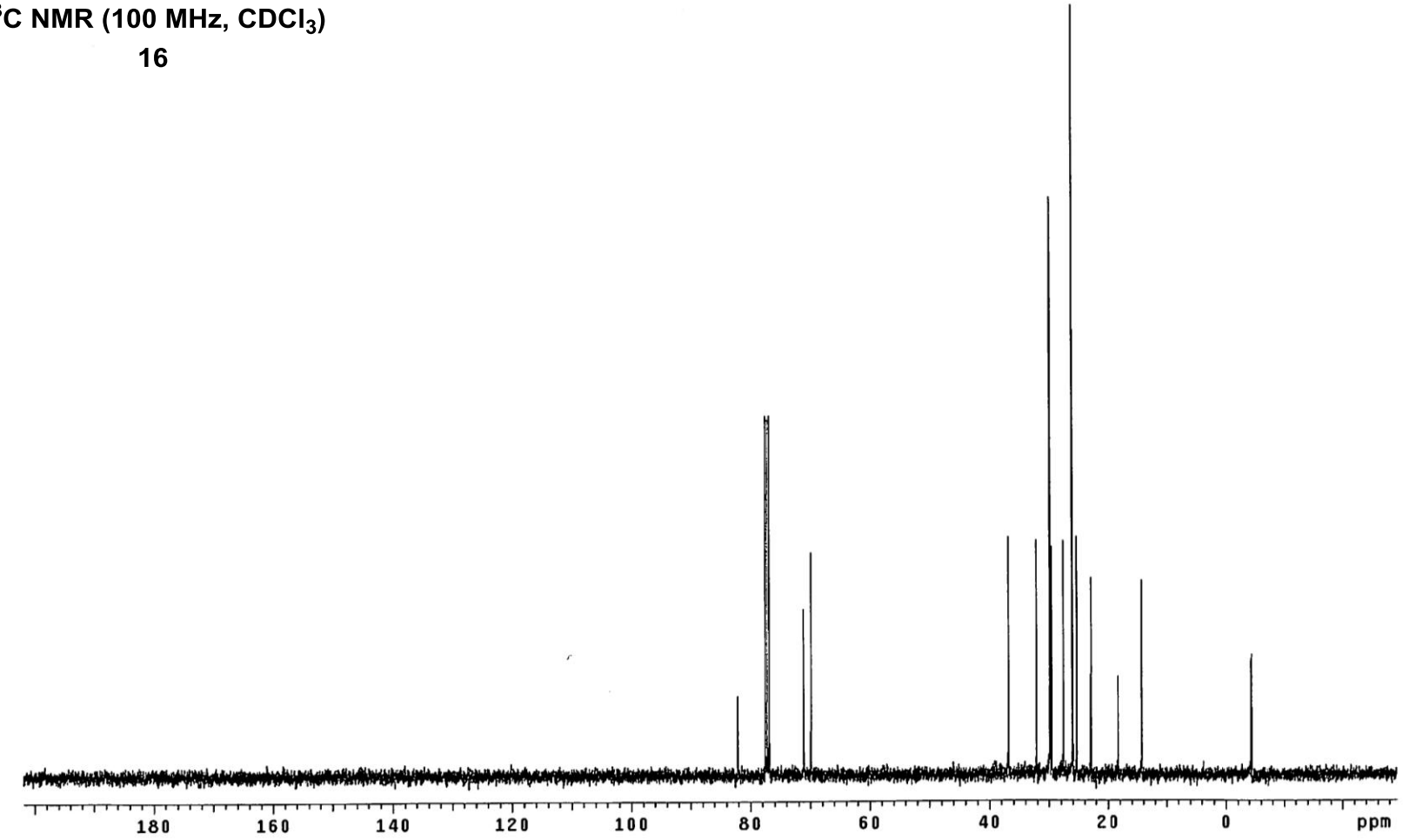
^{1}H NMR (500 MHz, $CDCl_3$)

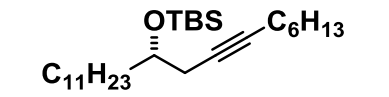
16



^{13}C NMR (100 MHz, $CDCl_3$)

16



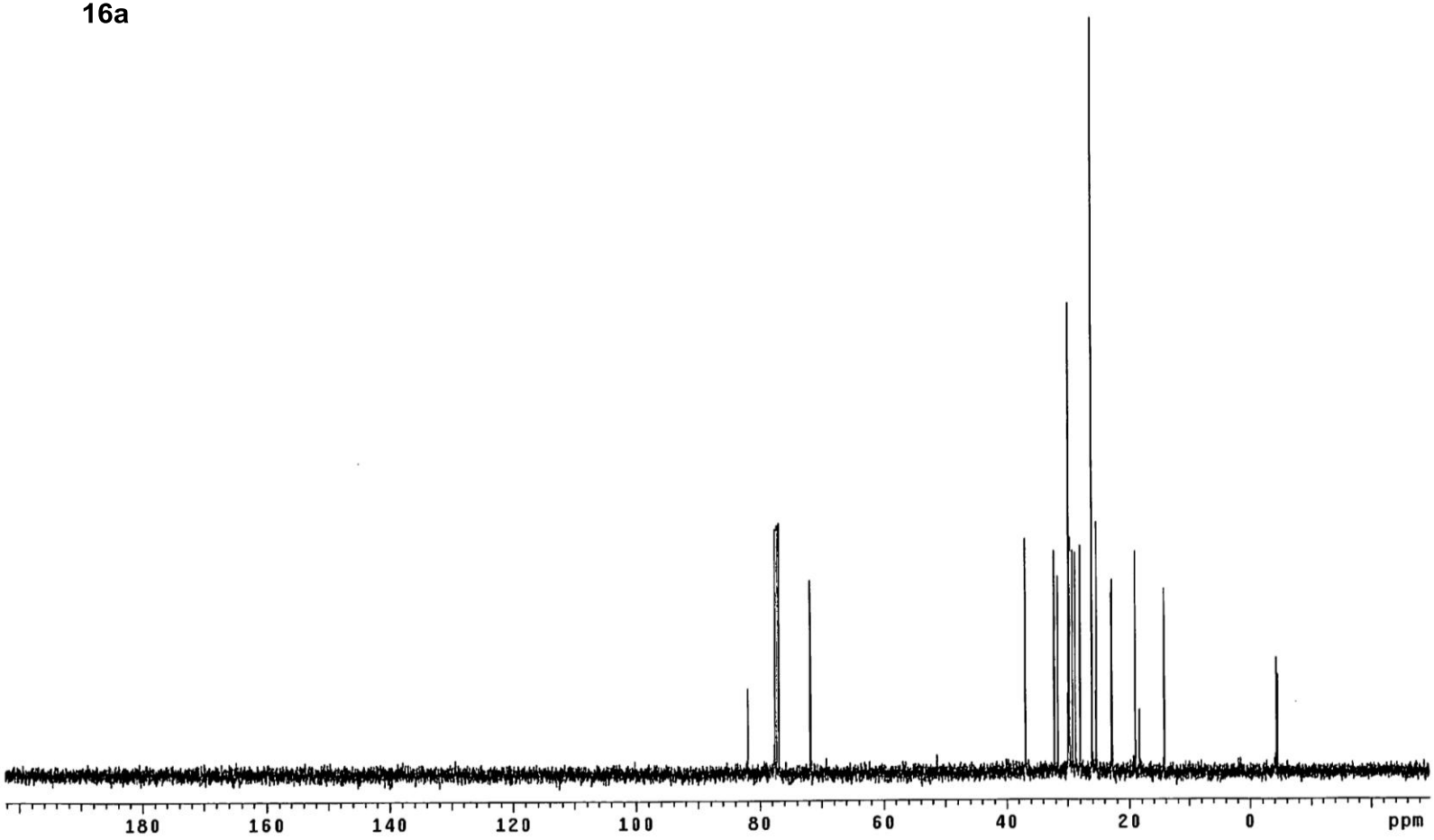


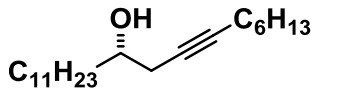
^{1}H NMR (500 MHz, $CDCl_3$)

16a

^{13}C NMR (100 MHz, $CDCl_3$)

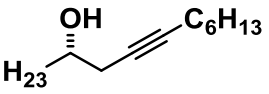
16a





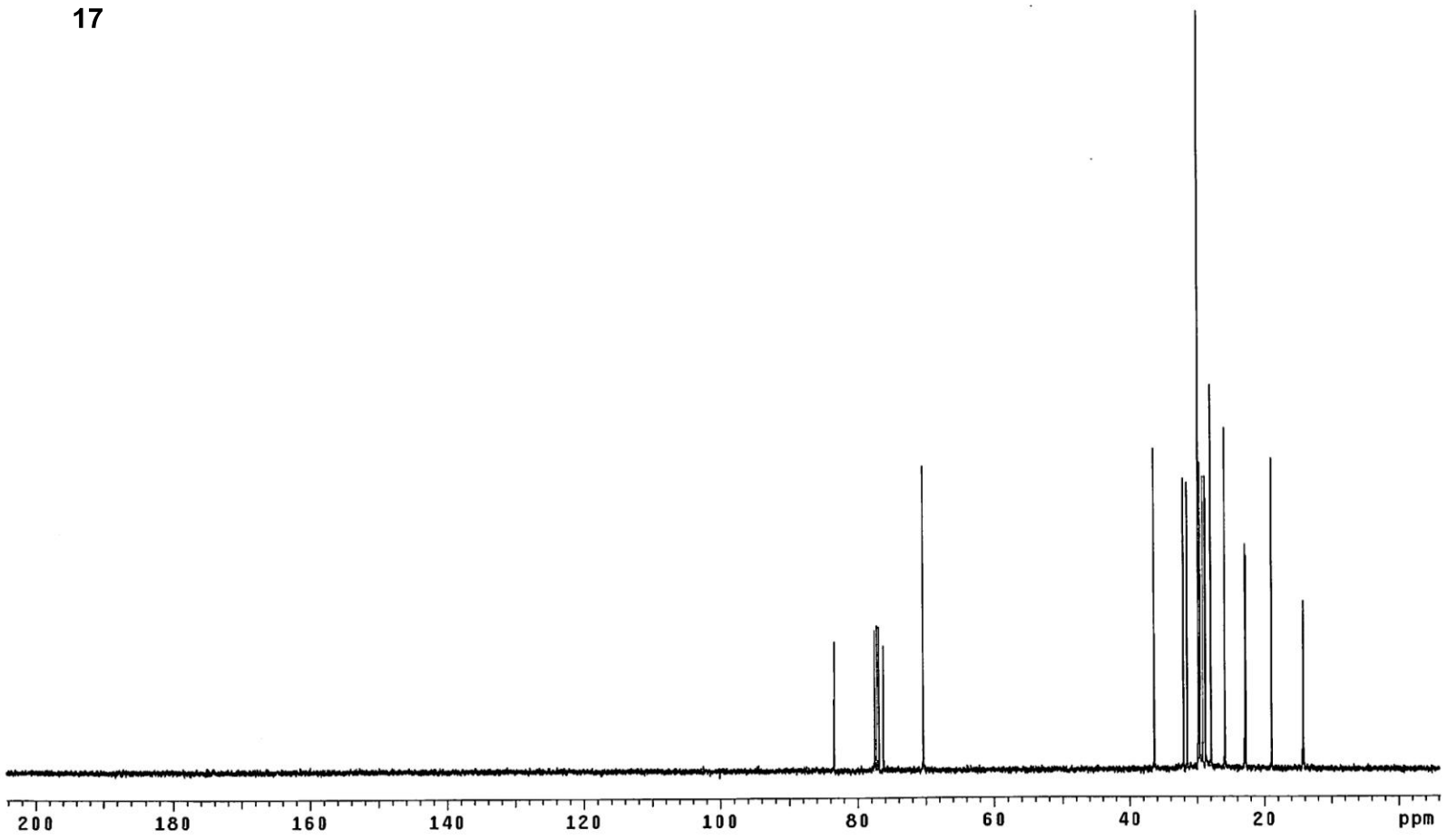
^{1}H NMR (500 MHz, $CDCl_3$)

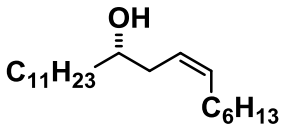
17



^{13}C NMR (100 MHz, $CDCl_3$)

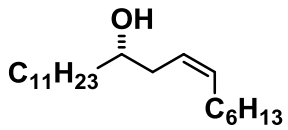
17





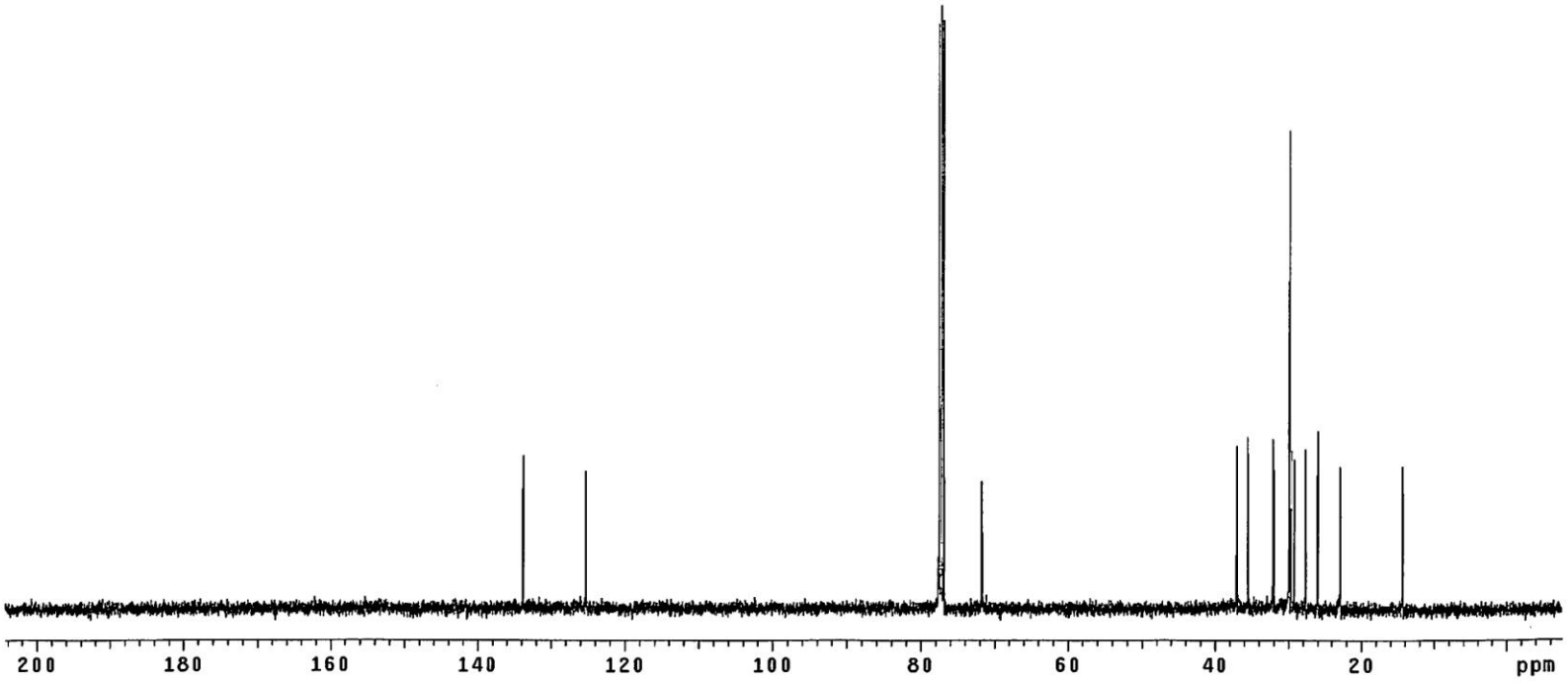
^{1}H NMR (500 MHz, $CDCl_3$)

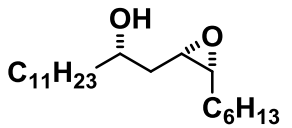
6b



^{13}C NMR (100 MHz, $CDCl_3$)

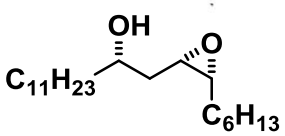
6b





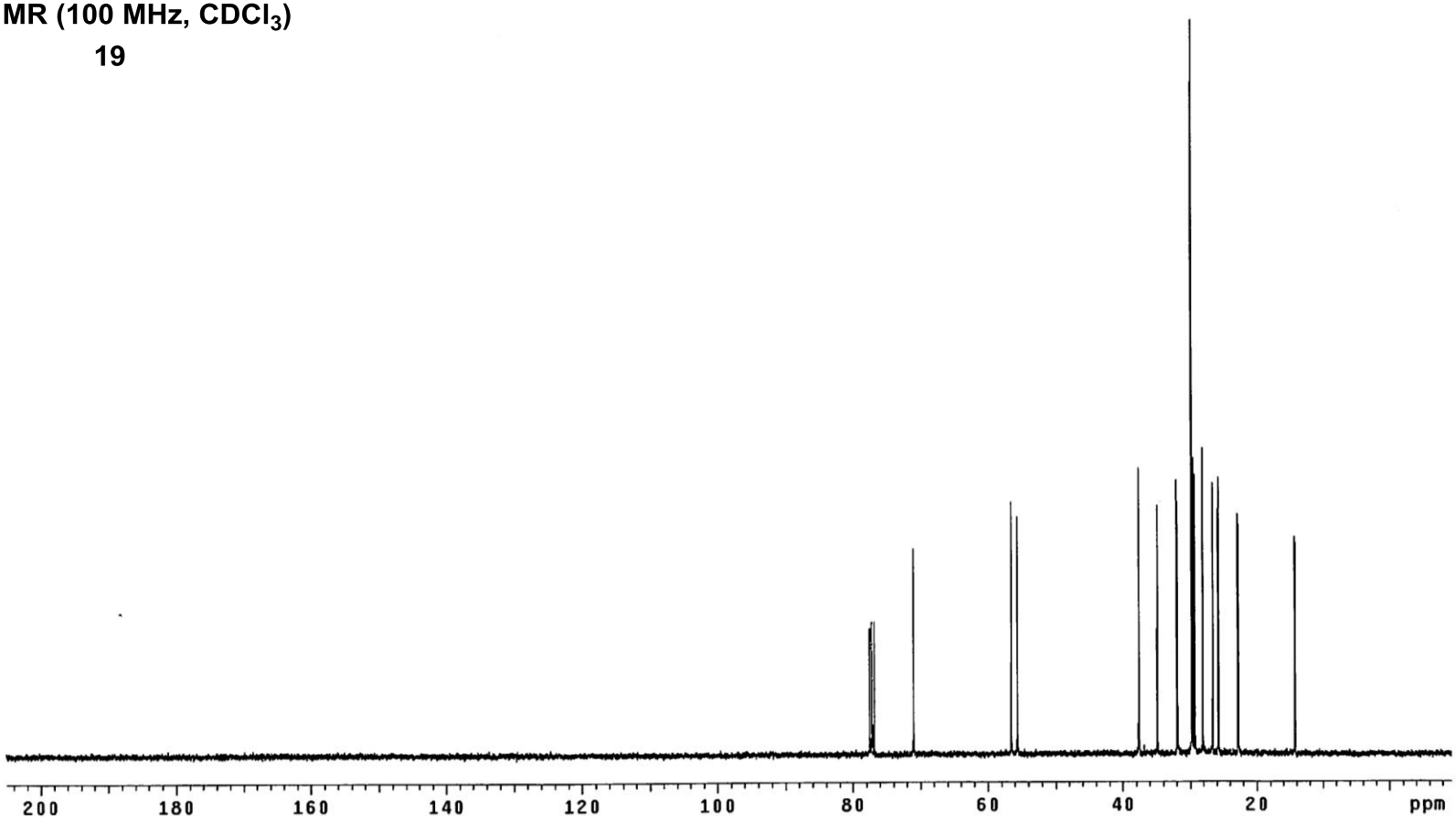
^{1}H NMR (500 MHz, $CDCl_3$)

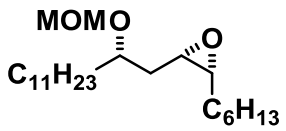
19



^{13}C NMR (100 MHz, $CDCl_3$)

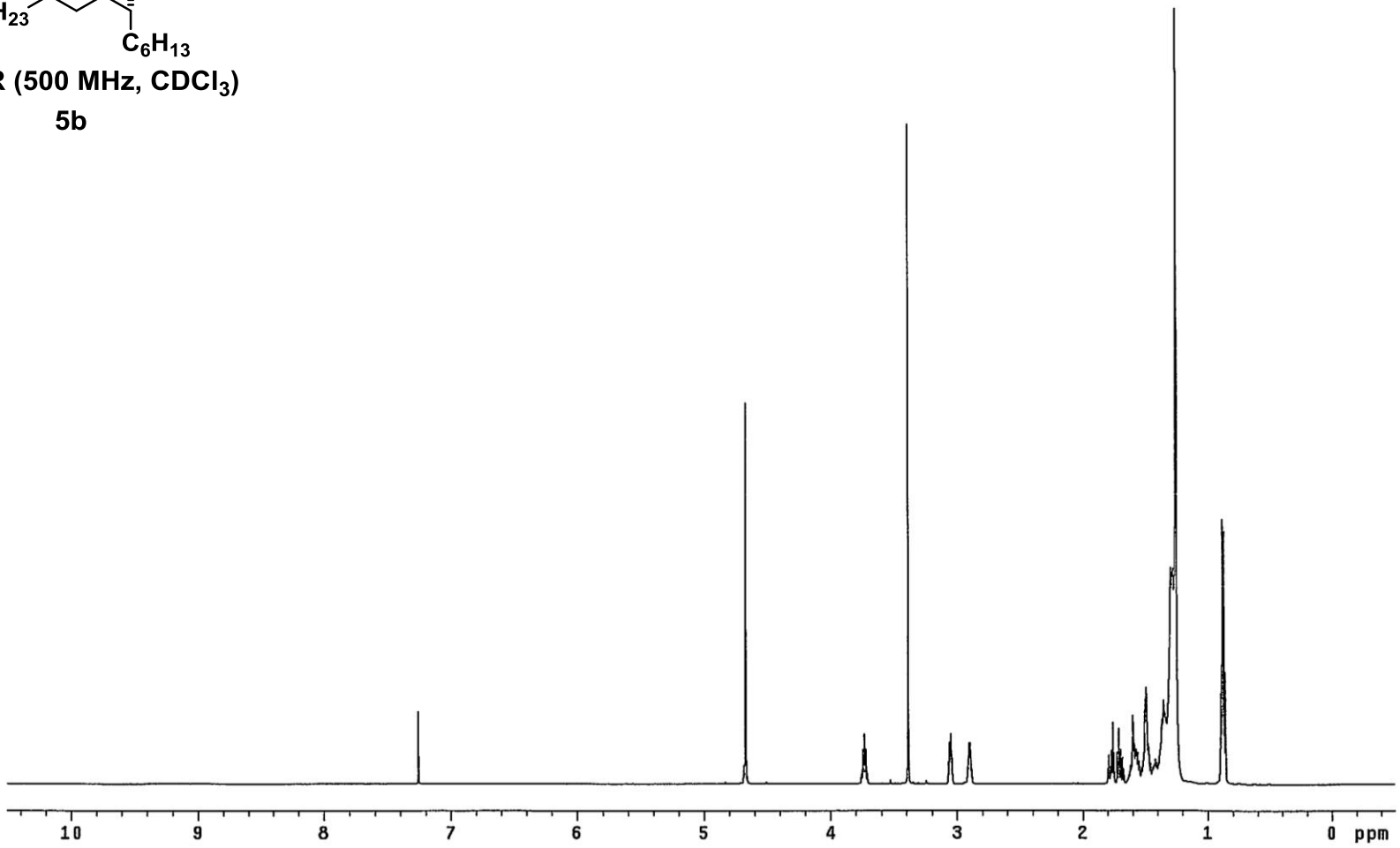
19

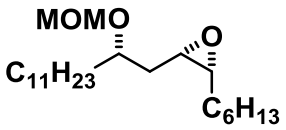




^{1}H NMR (500 MHz, $CDCl_3$)

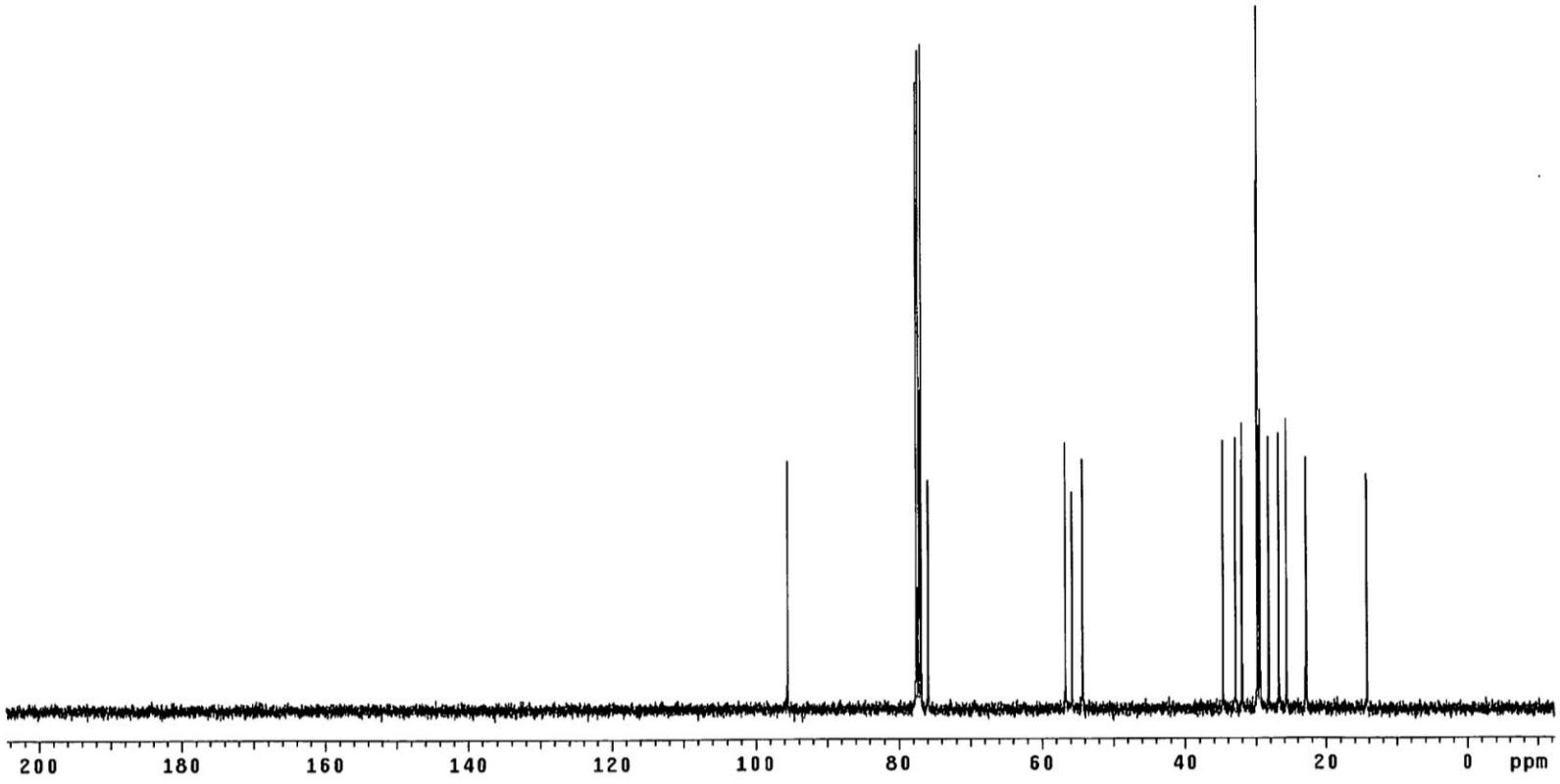
5b

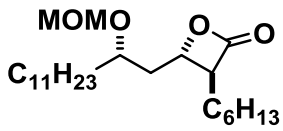




^{13}C NMR (100 MHz, $CDCl_3$)

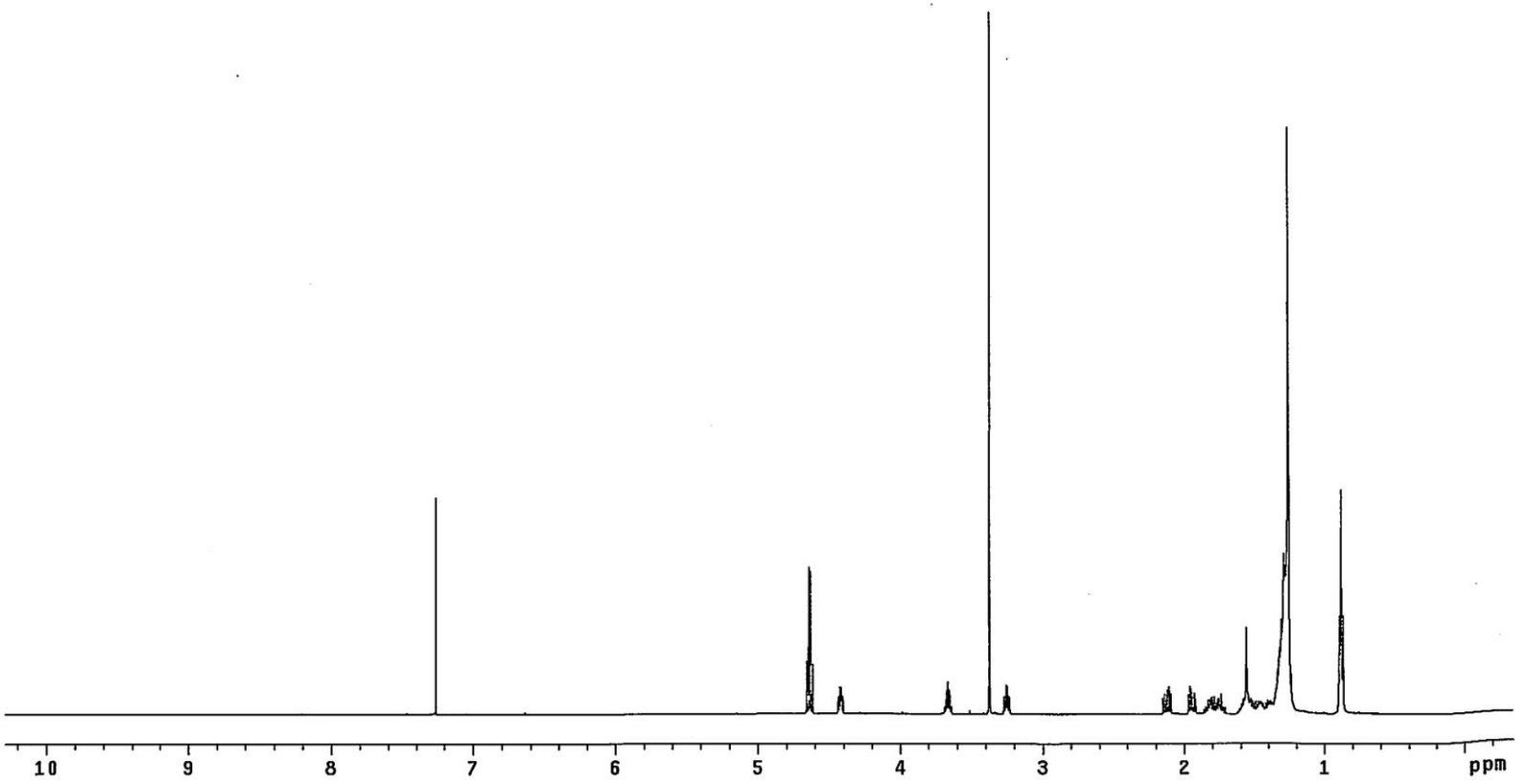
5b

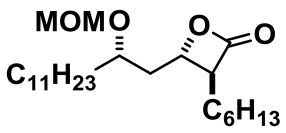




^{1}H NMR (500 MHz, $CDCl_3$)

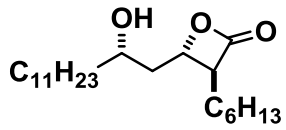
20





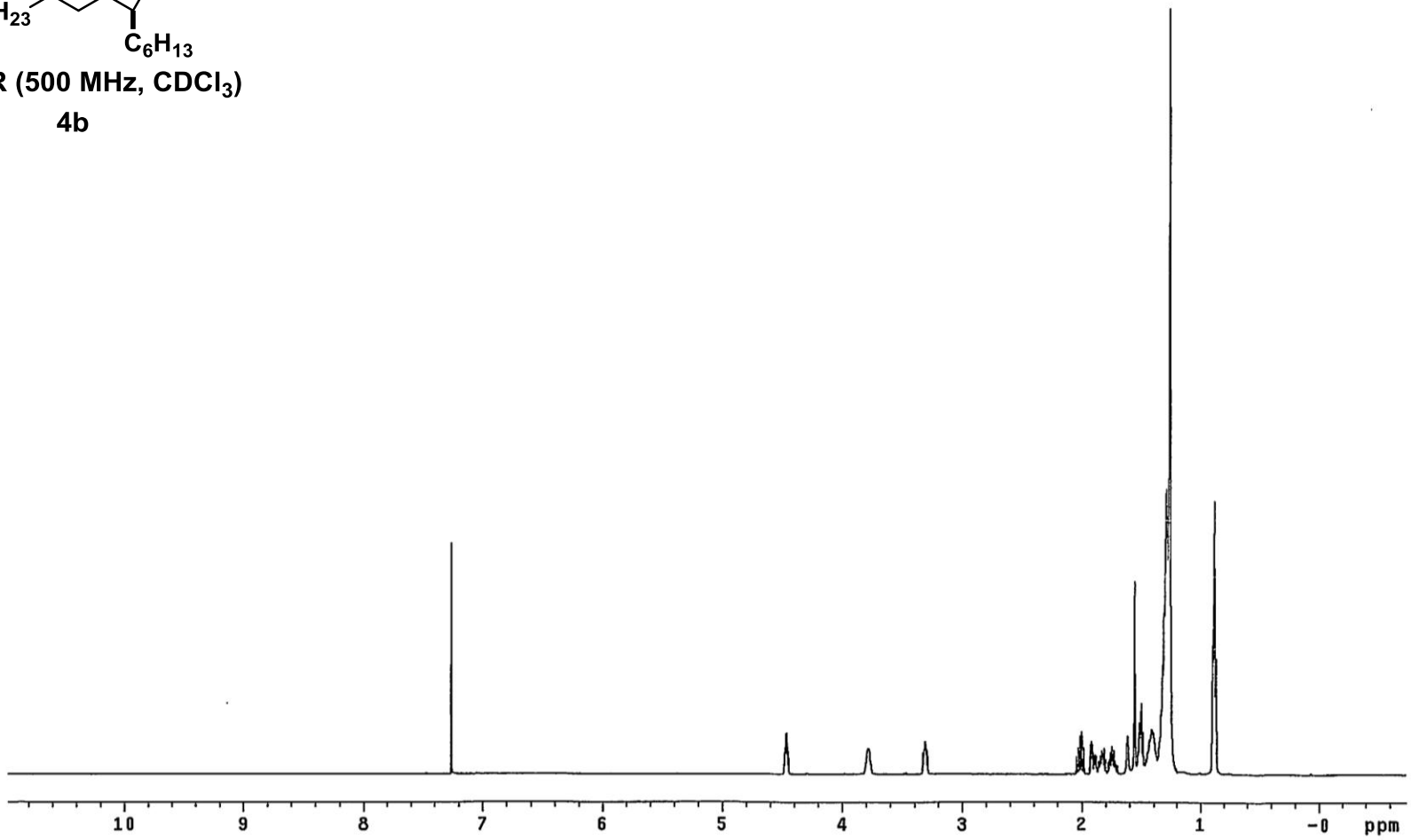
^{13}C NMR (100 MHz, $CDCl_3$)

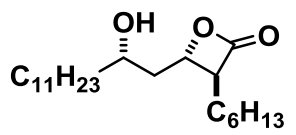
20



^{1}H NMR (500 MHz, $CDCl_3$)

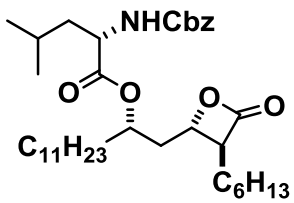
4b





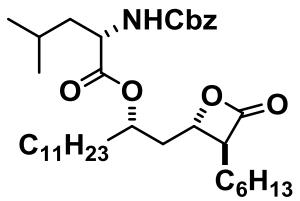
^{13}C NMR (100 MHz, $CDCl_3$)

4b



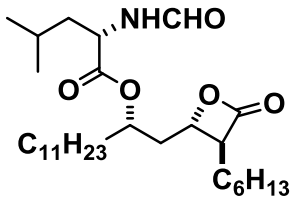
^{1}H NMR (500 MHz, $CDCl_3$)

21



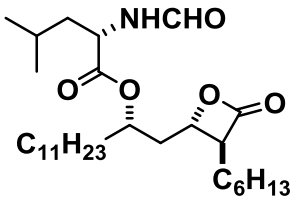
^{13}C NMR (100 MHz, $CDCl_3$)

21



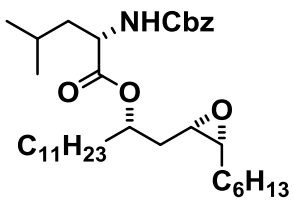
^{1}H NMR (500 MHz, $CDCl_3$)

1



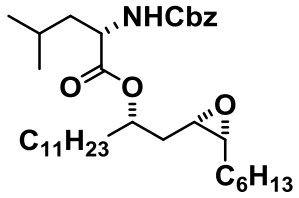
^{13}C NMR (100 MHz, $CDCl_3$)

1



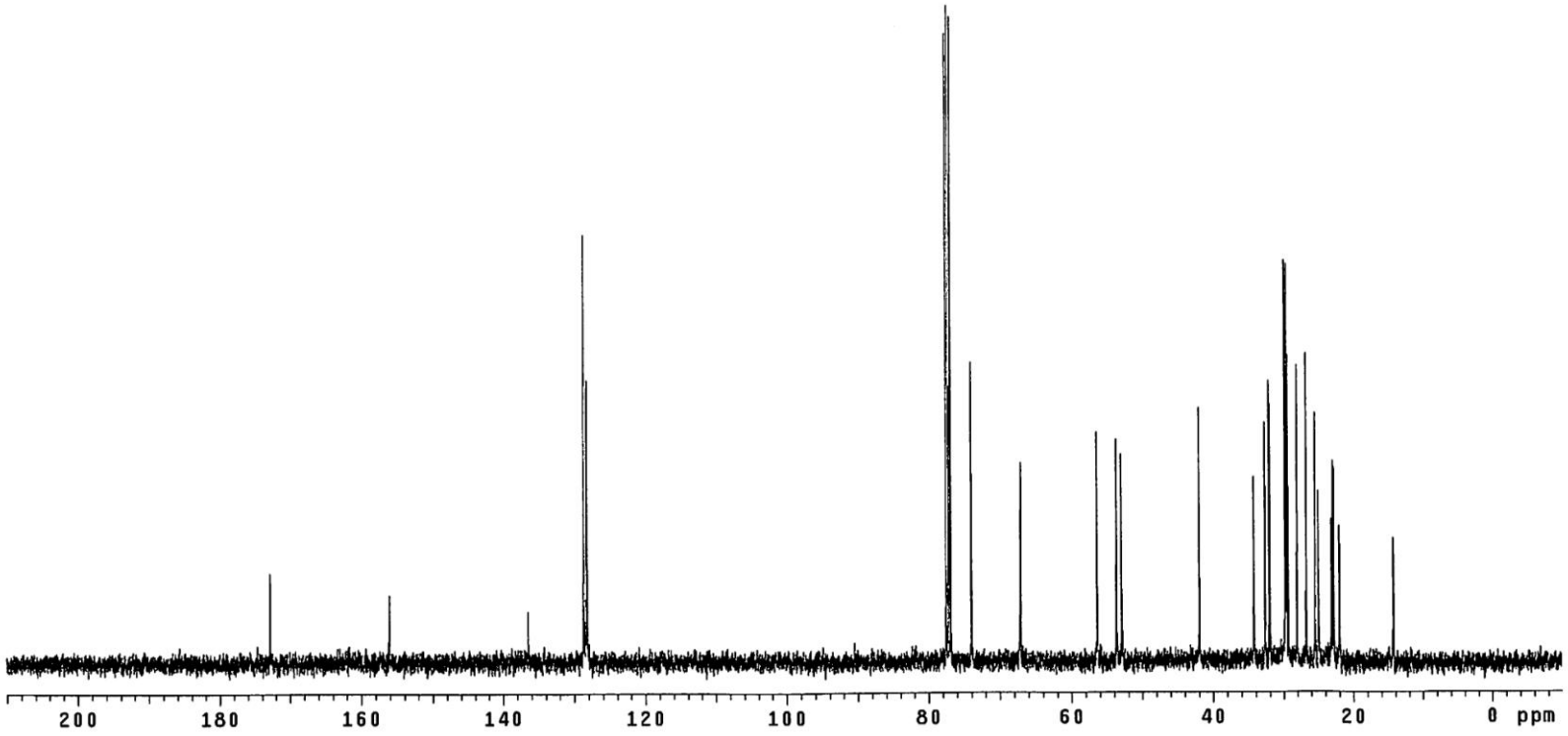
^{1}H NMR (500 MHz, $CDCl_3$)

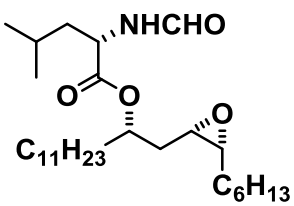
24



^{13}C NMR (100 MHz, $CDCl_3$)

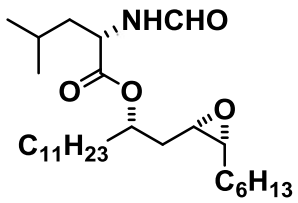
24





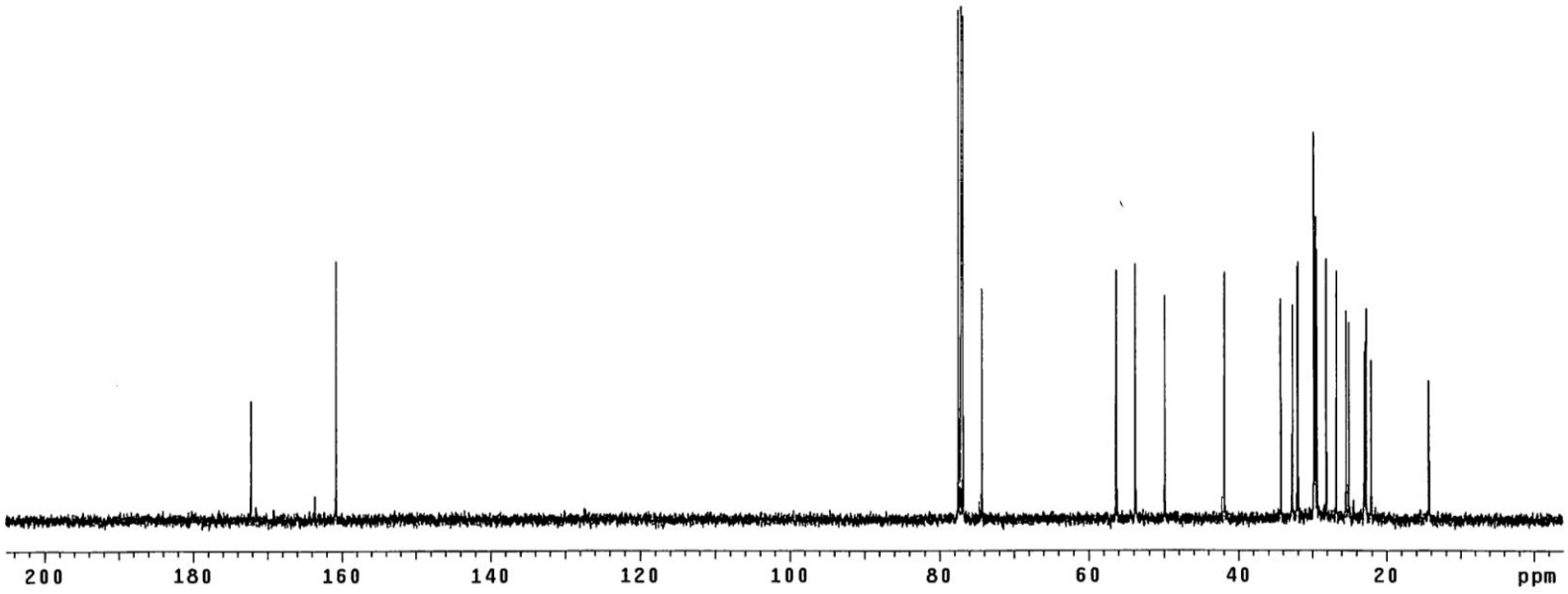
^{1}H NMR (500 MHz, $CDCl_3$)

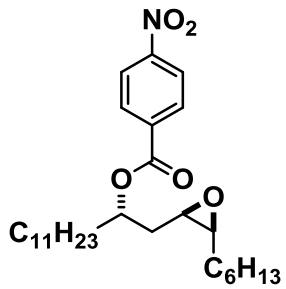
22



^{13}C NMR (100 MHz, $CDCl_3$)

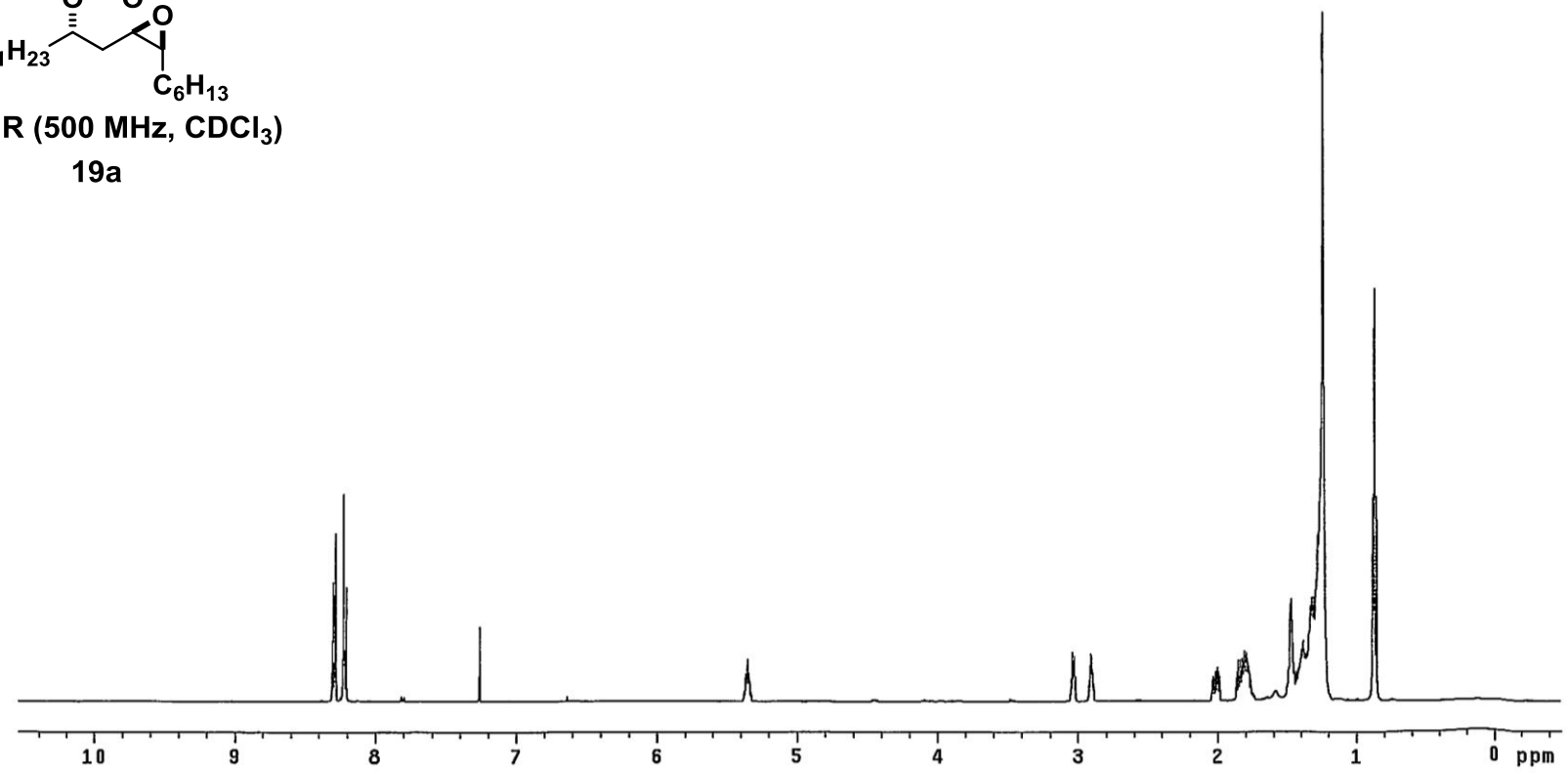
22

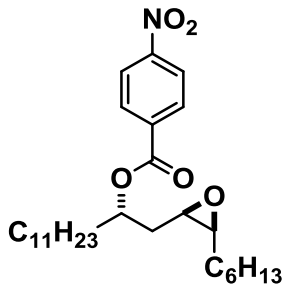




^{1}H NMR (500 MHz, $CDCl_3$)

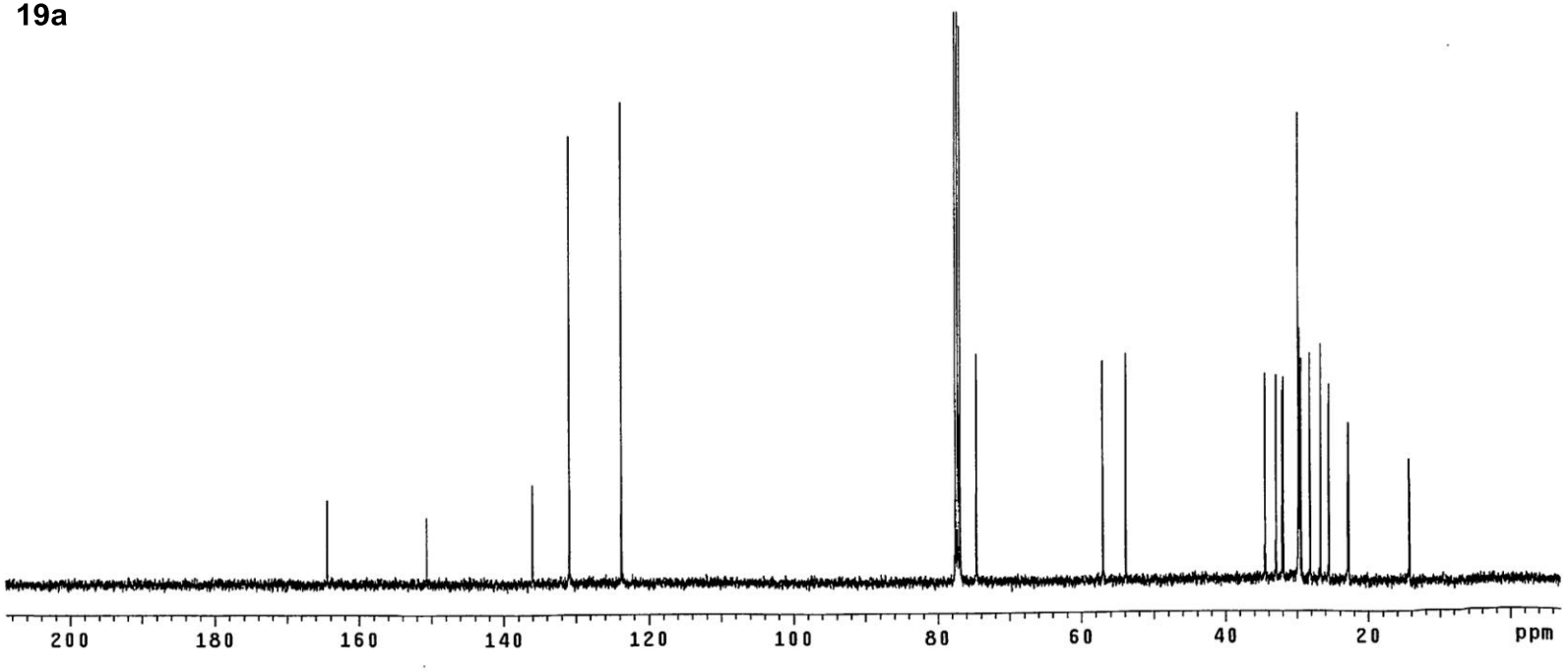
19a

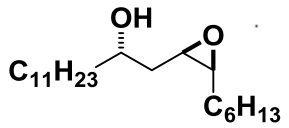




^{13}C NMR (100 MHz, $CDCl_3$)

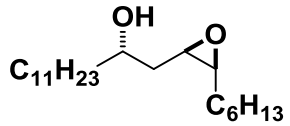
19a





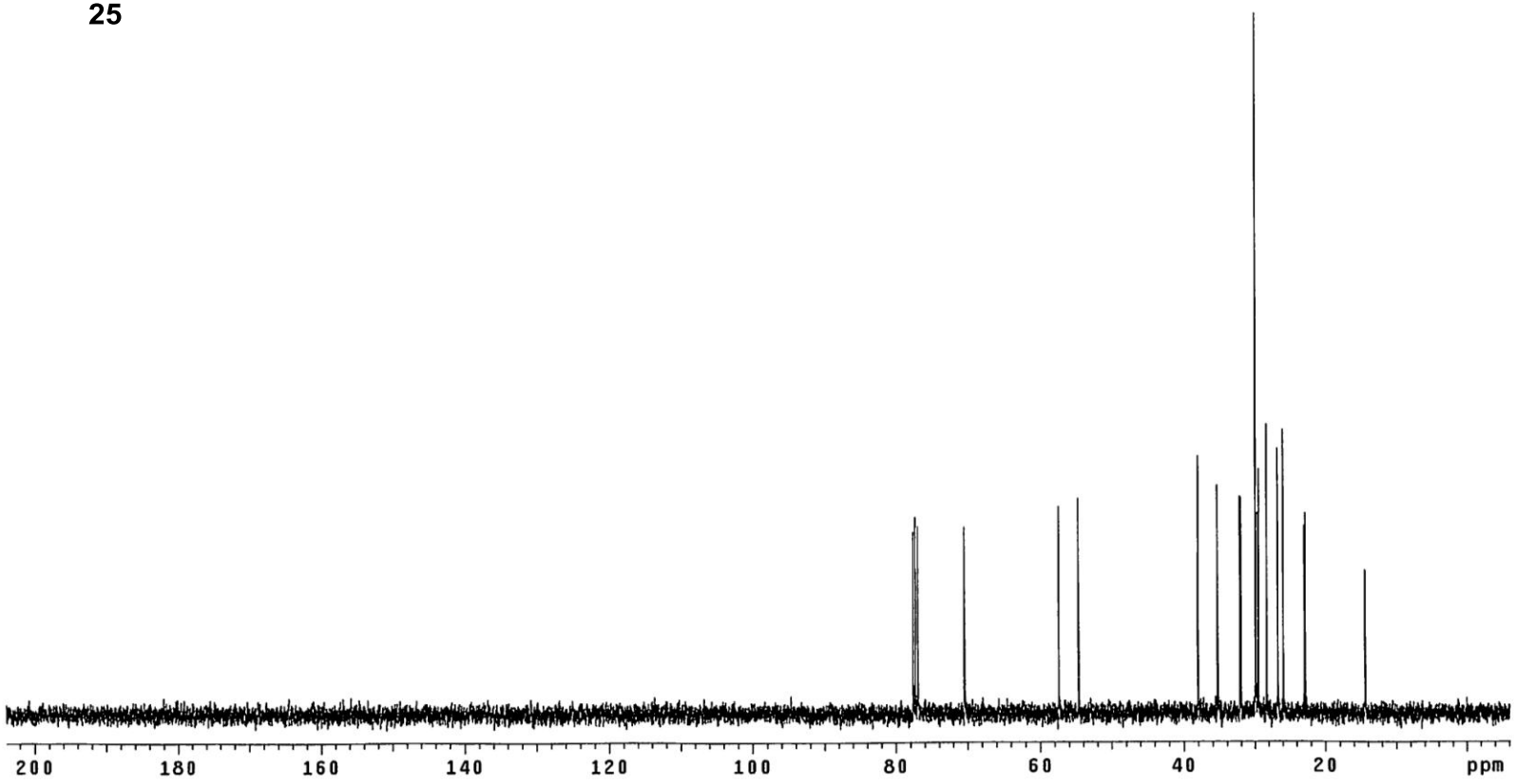
^{1}H NMR (400 MHz, $CDCl_3$)

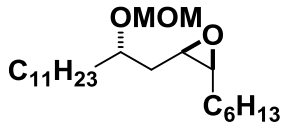
25



^{13}C NMR (100 MHz, $CDCl_3$)

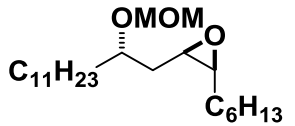
25





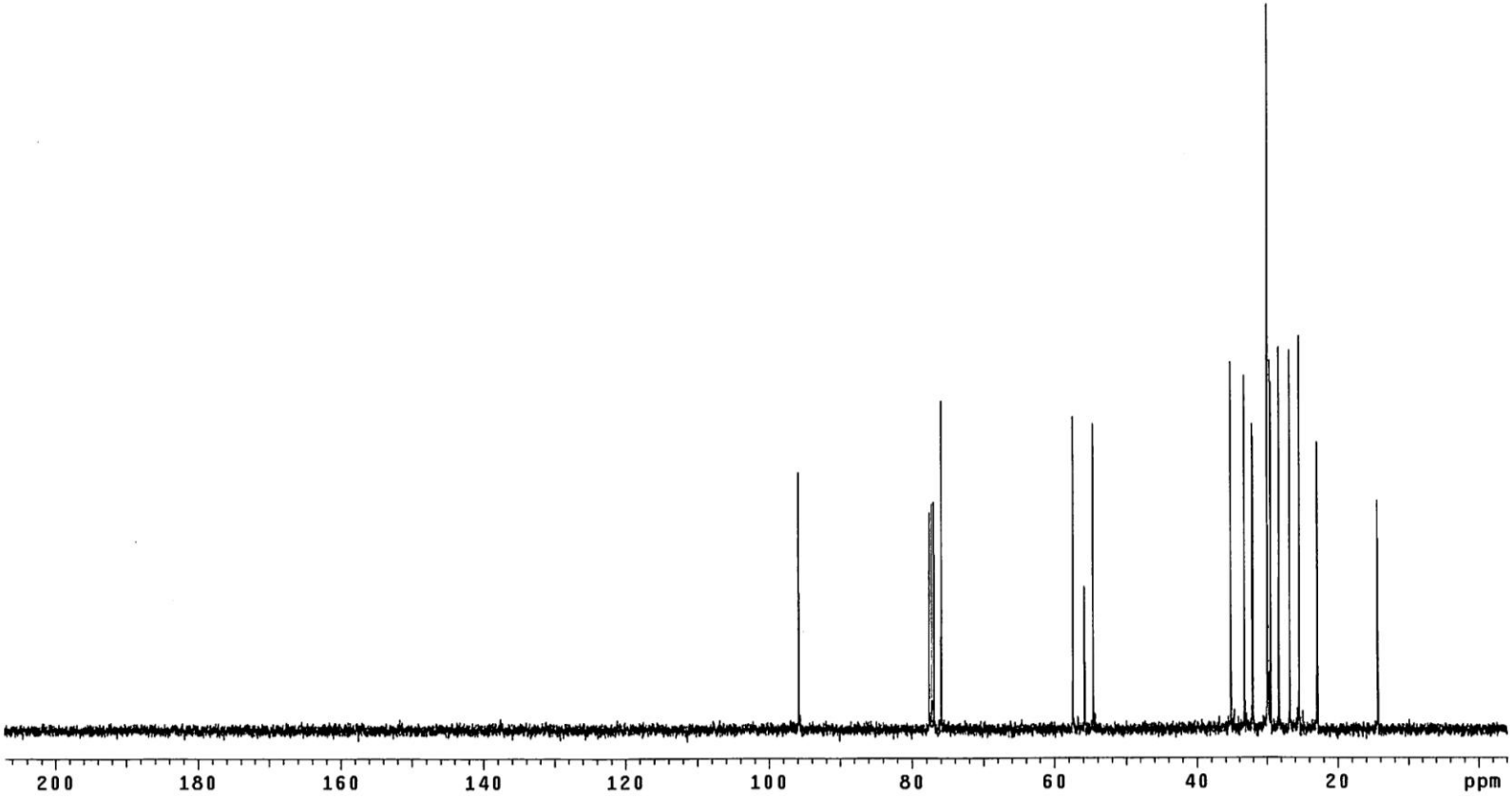
^{1}H NMR (400 MHz, $CDCl_3$)

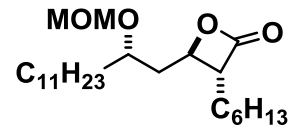
26



^{13}C NMR (100 MHz, $CDCl_3$)

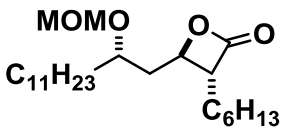
26





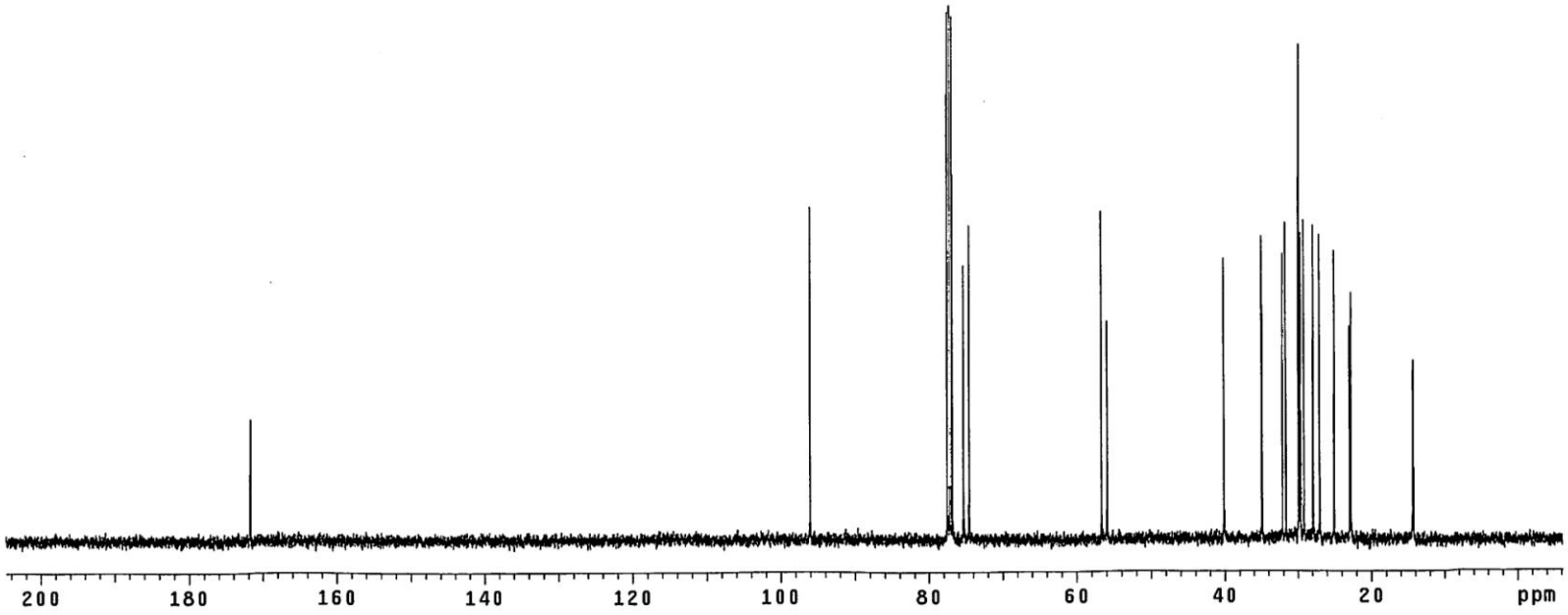
^{1}H NMR (500 MHz, $CDCl_3$)

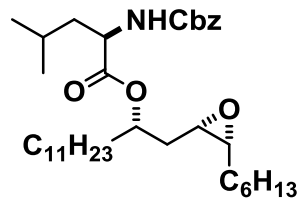
33



^{13}C NMR (100 MHz, $CDCl_3$)

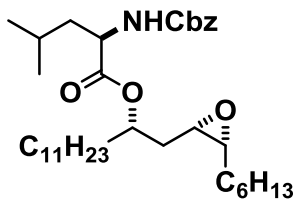
33





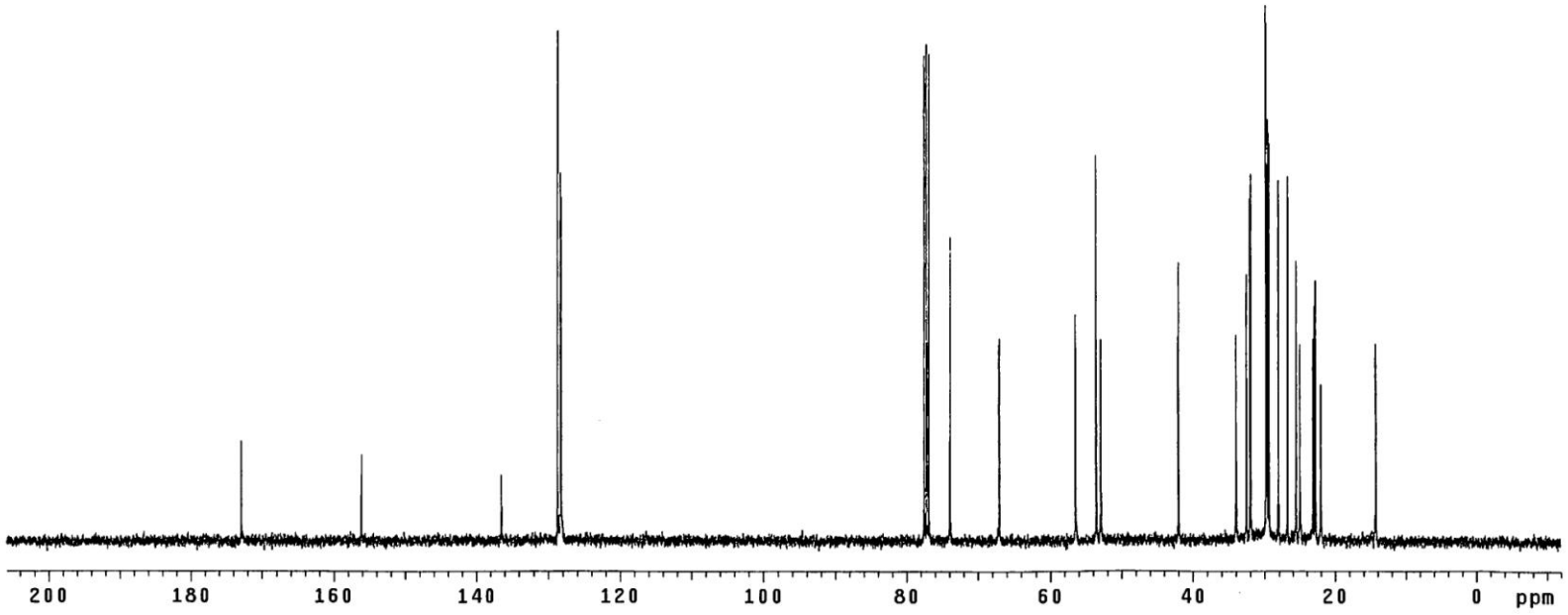
^{1}H NMR (500 MHz, $CDCl_3$)

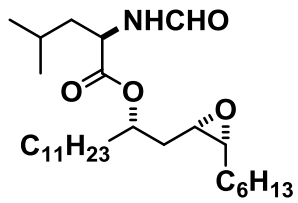
27



^{13}C NMR (100 MHz, $CDCl_3$)

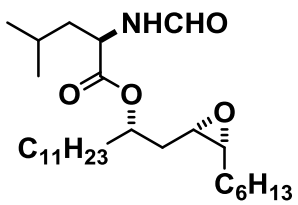
27





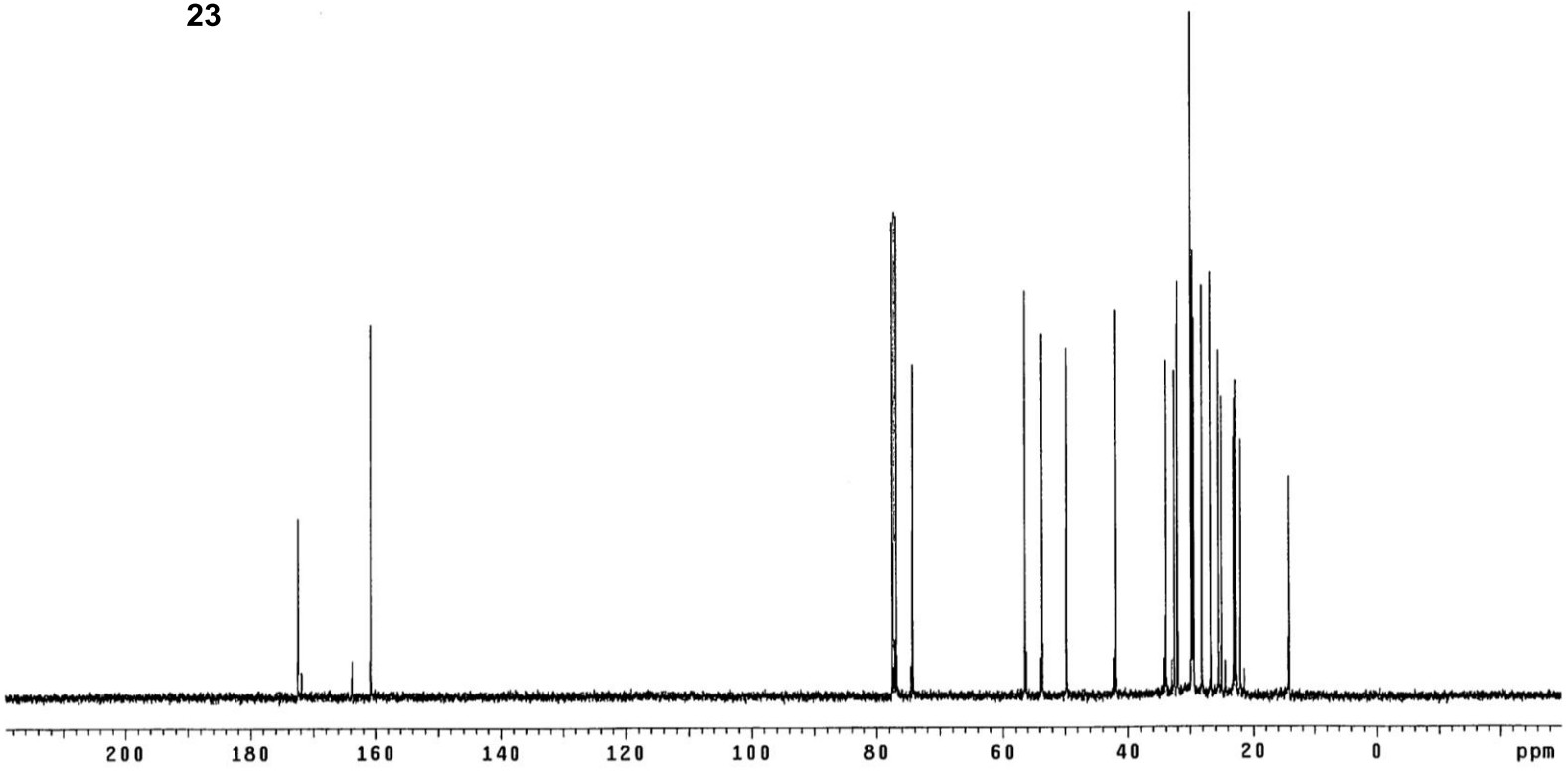
^{1}H NMR (500 MHz, $CDCl_3$)

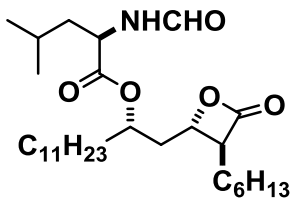
23



^{13}C NMR (100 MHz, $CDCl_3$)

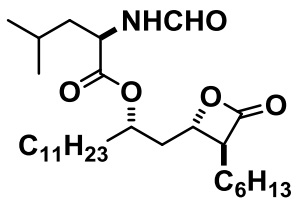
23





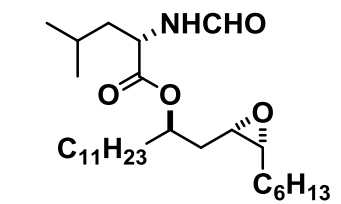
^{1}H NMR (500 MHz, $CDCl_3$)

34



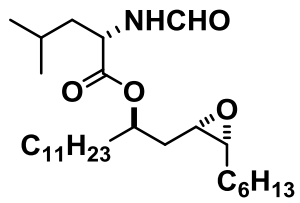
^{13}C NMR (100 MHz, $CDCl_3$)

34



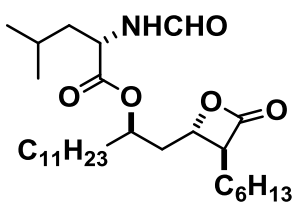
^{1}H NMR (500 MHz, $CDCl_3$)

28



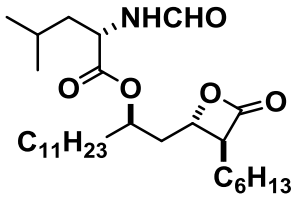
^{13}C NMR (100 MHz, $CDCl_3$)

28



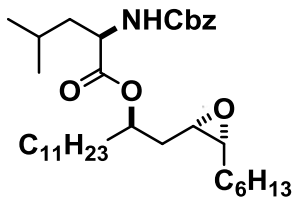
^{1}H NMR (500 MHz, $CDCl_3$)

35



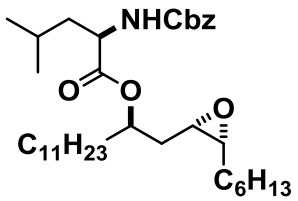
^{13}C NMR (100 MHz, $CDCl_3$)

35



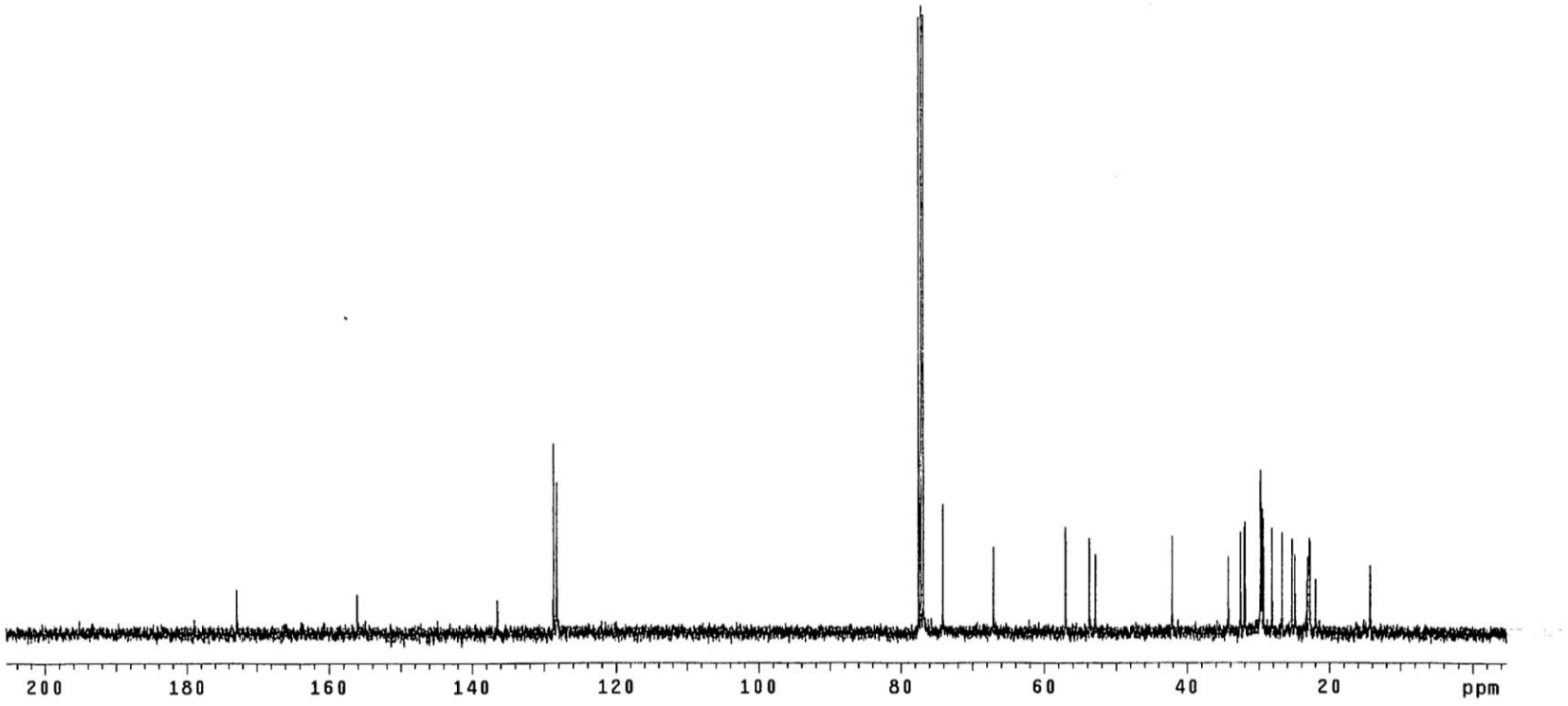
^{1}H NMR (500 MHz, $CDCl_3$)

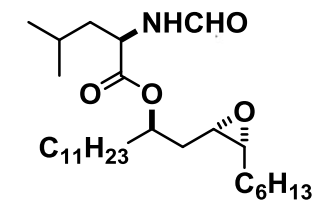
29



^{13}C NMR (100 MHz, $CDCl_3$)

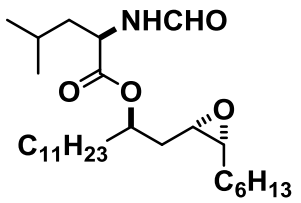
29





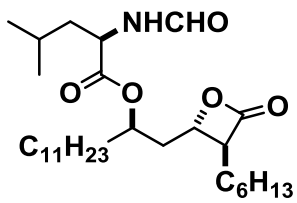
^{1}H NMR (500 MHz, $CDCl_3$)

30



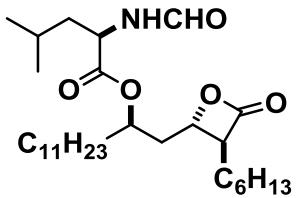
^{13}C NMR (100 MHz, $CDCl_3$)

30



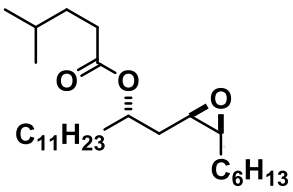
^{1}H NMR (500 MHz, $CDCl_3$)

36



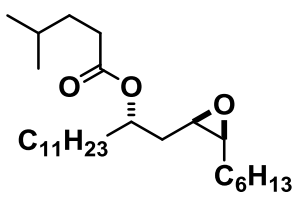
^{13}C NMR (100 MHz, $CDCl_3$)

36



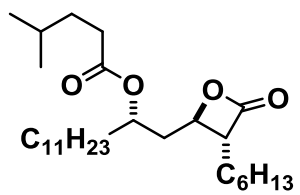
^{1}H NMR (500 MHz, $CDCl_3$)

31



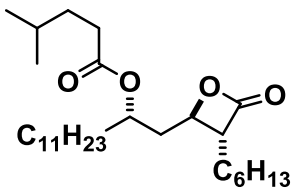
^{13}C NMR (100 MHz, $CDCl_3$)

31



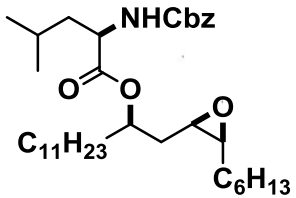
^{1}H NMR (400 MHz, $CDCl_3$)

37



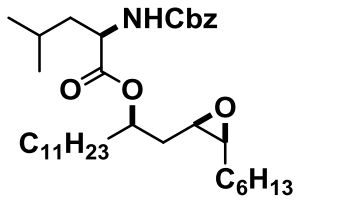
^{13}C NMR (100 MHz, $CDCl_3$)

37



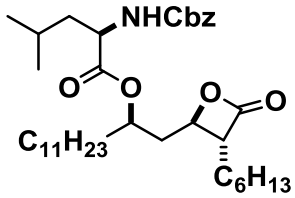
^{1}H NMR (500 MHz, $CDCl_3$)

ent-**24**



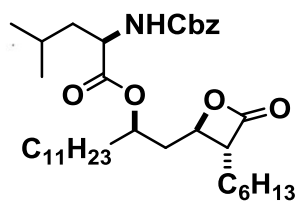
^{13}C NMR (100 MHz, $CDCl_3$)

ent-**24**



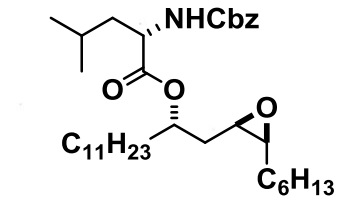
^{1}H NMR (400 MHz, $CDCl_3$)

ent-**21**



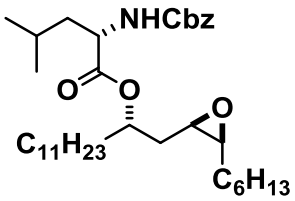
^{13}C NMR (100 MHz, $CDCl_3$)

ent-**21**



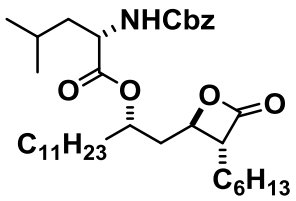
^{1}H NMR (500 MHz, $CDCl_3$)

ent-**29**



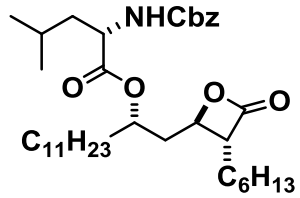
^{13}C NMR (100 MHz, $CDCl_3$)

ent-**29**



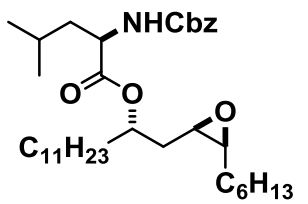
^{1}H NMR (400 MHz, $CDCl_3$)

ent-**38**



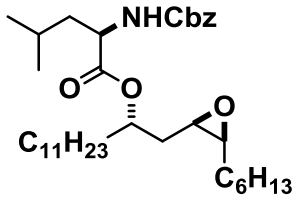
^{13}C NMR (100 MHz, $CDCl_3$)

ent-**38**



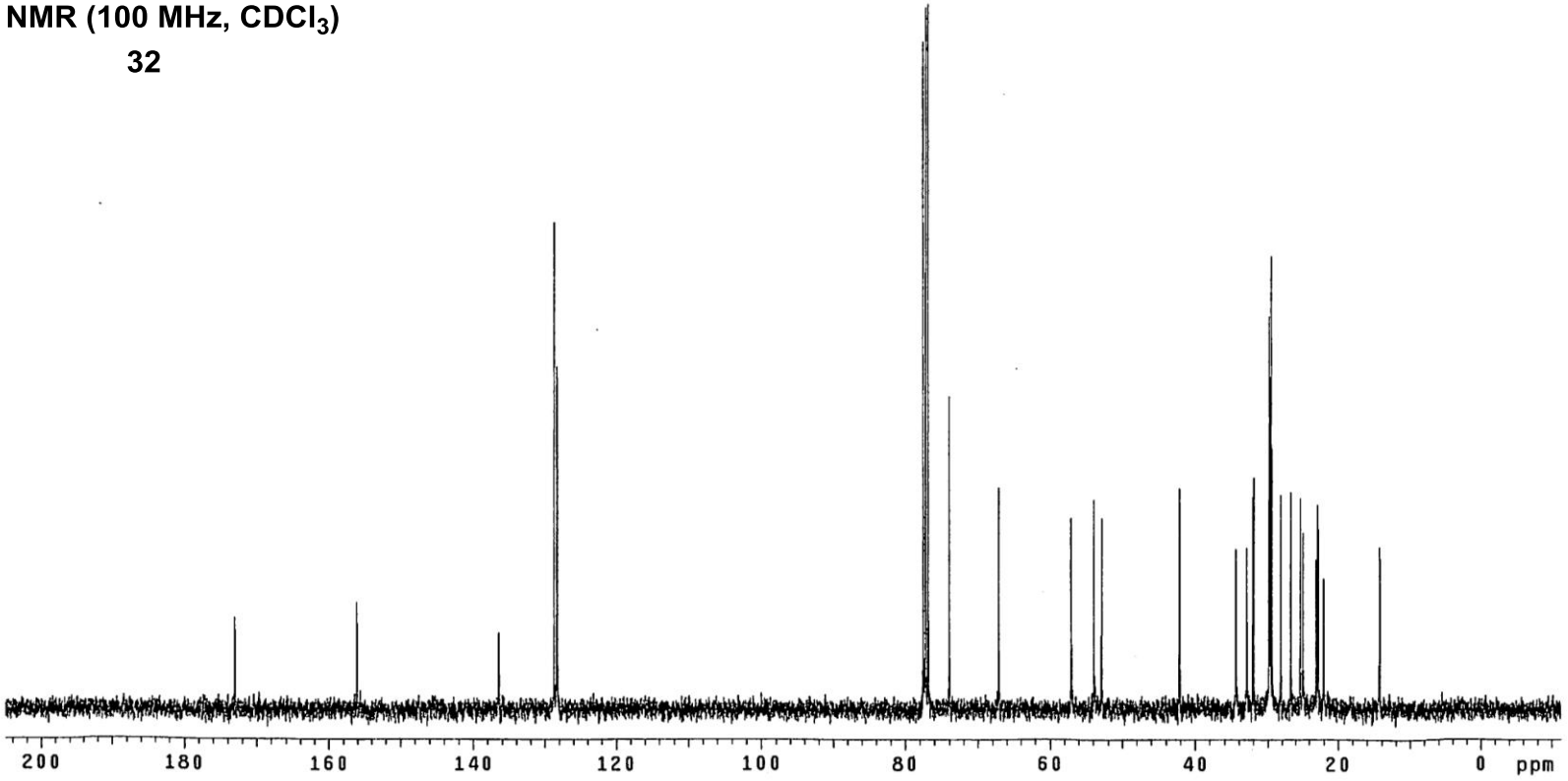
^{1}H NMR (500 MHz, $CDCl_3$)

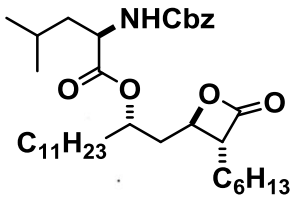
32



^{13}C NMR (100 MHz, $CDCl_3$)

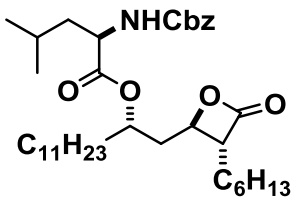
32





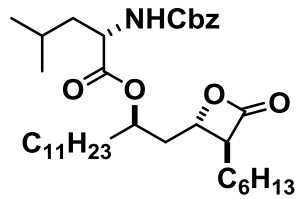
^{1}H NMR (400 MHz, $CDCl_3$)

ent-**39**



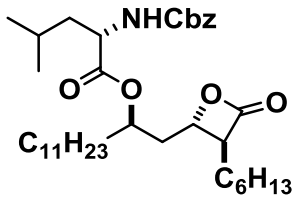
^{13}C NMR (100 MHz, $CDCl_3$)

ent-**39**



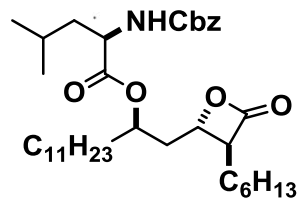
^{1}H NMR (500 MHz, $CDCl_3$)

39



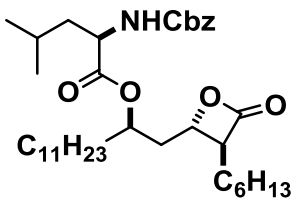
^{13}C NMR (100 MHz, $CDCl_3$)

39



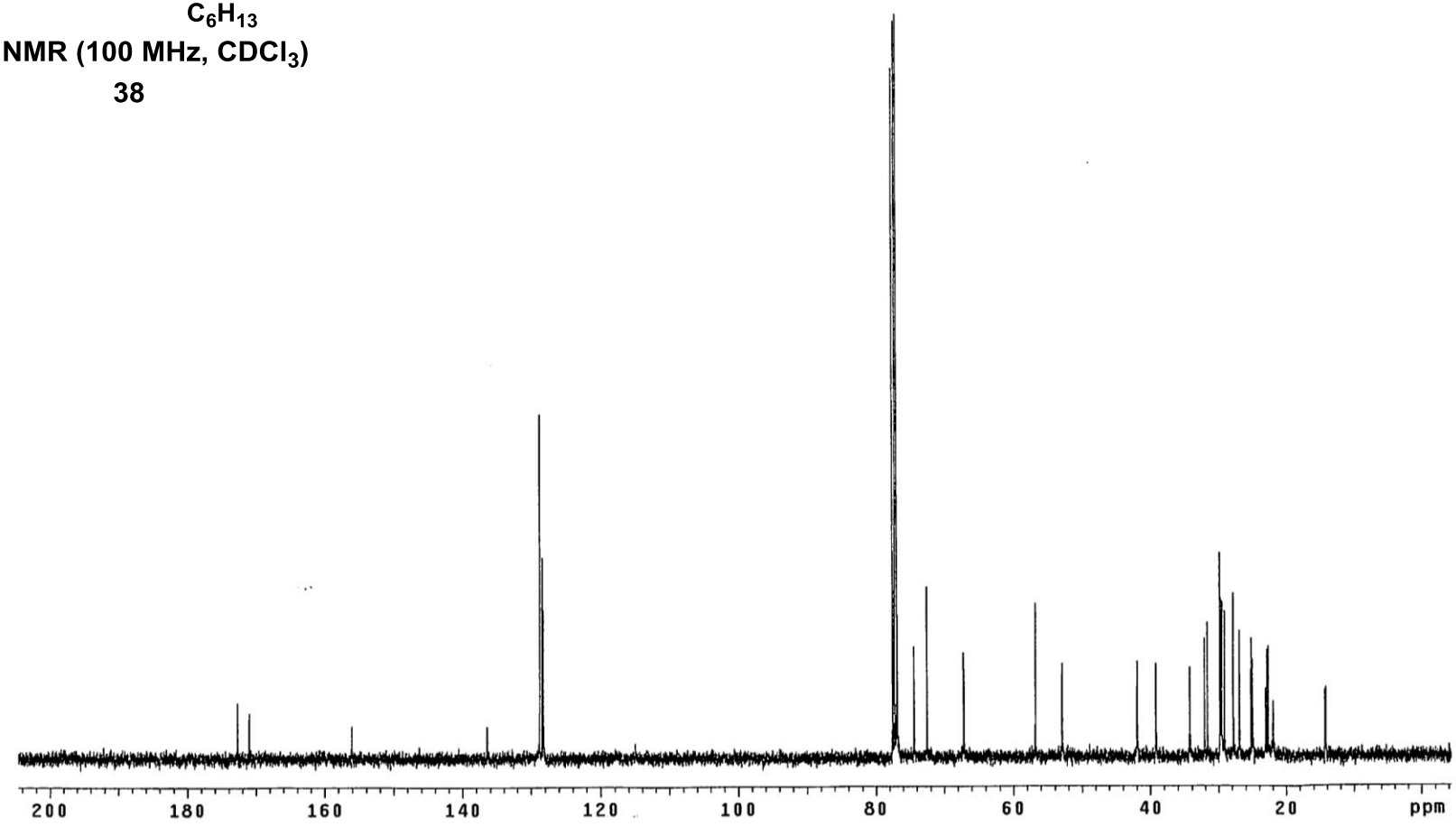
^{1}H NMR (500 MHz, $CDCl_3$)

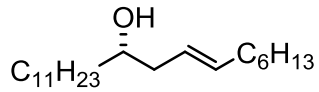
38



^{13}C NMR (100 MHz, $CDCl_3$)

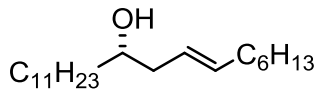
38





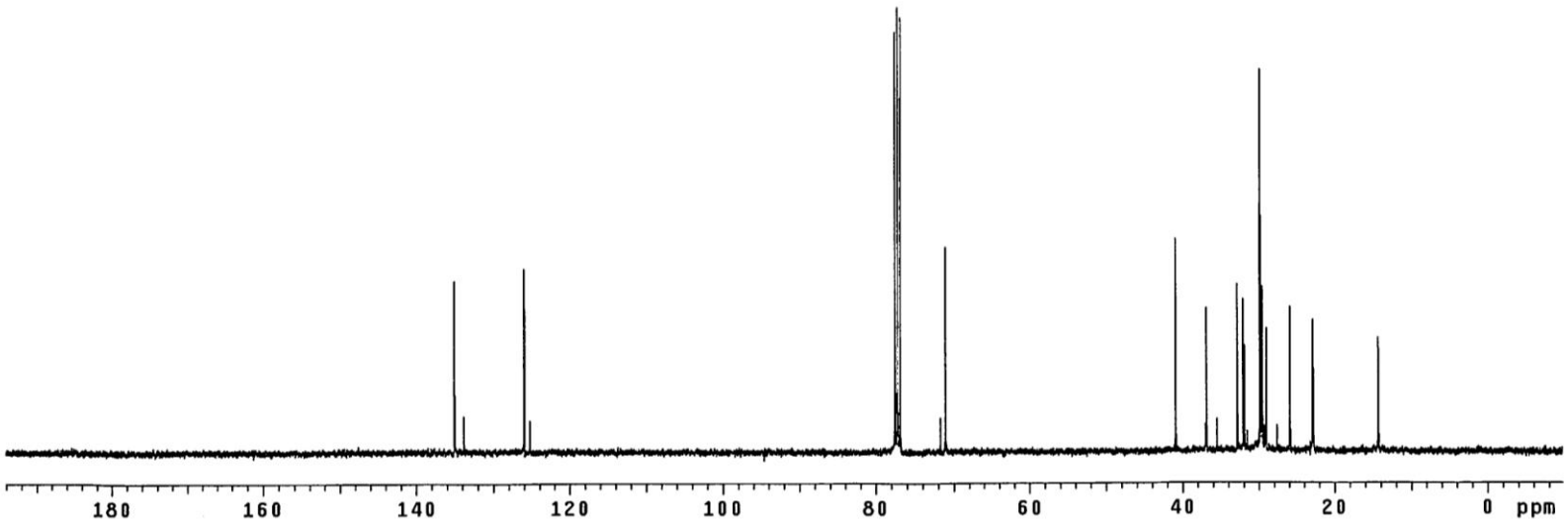
^{1}H NMR (400 MHz, $CDCl_3$)

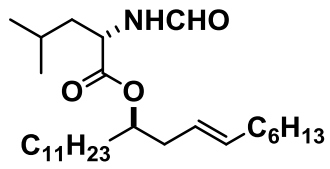
41



^{13}C NMR (100 MHz, $CDCl_3$)

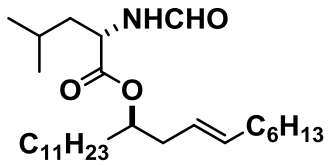
41





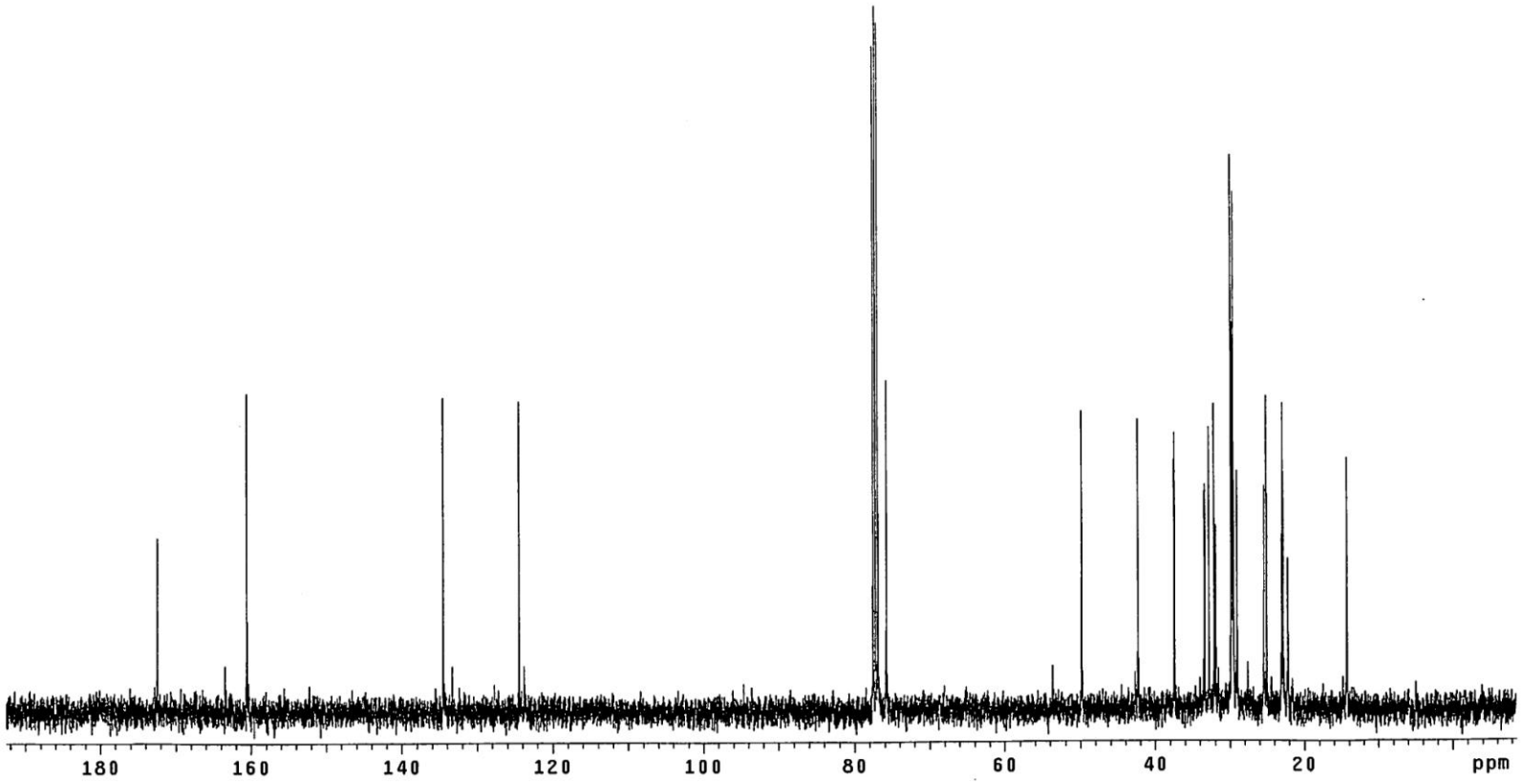
^{1}H NMR (400 MHz, $CDCl_3$)

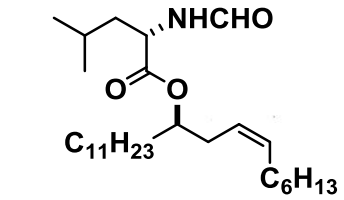
40



^{13}C NMR (100 MHz, $CDCl_3$)

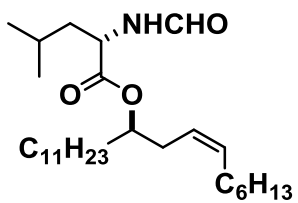
40





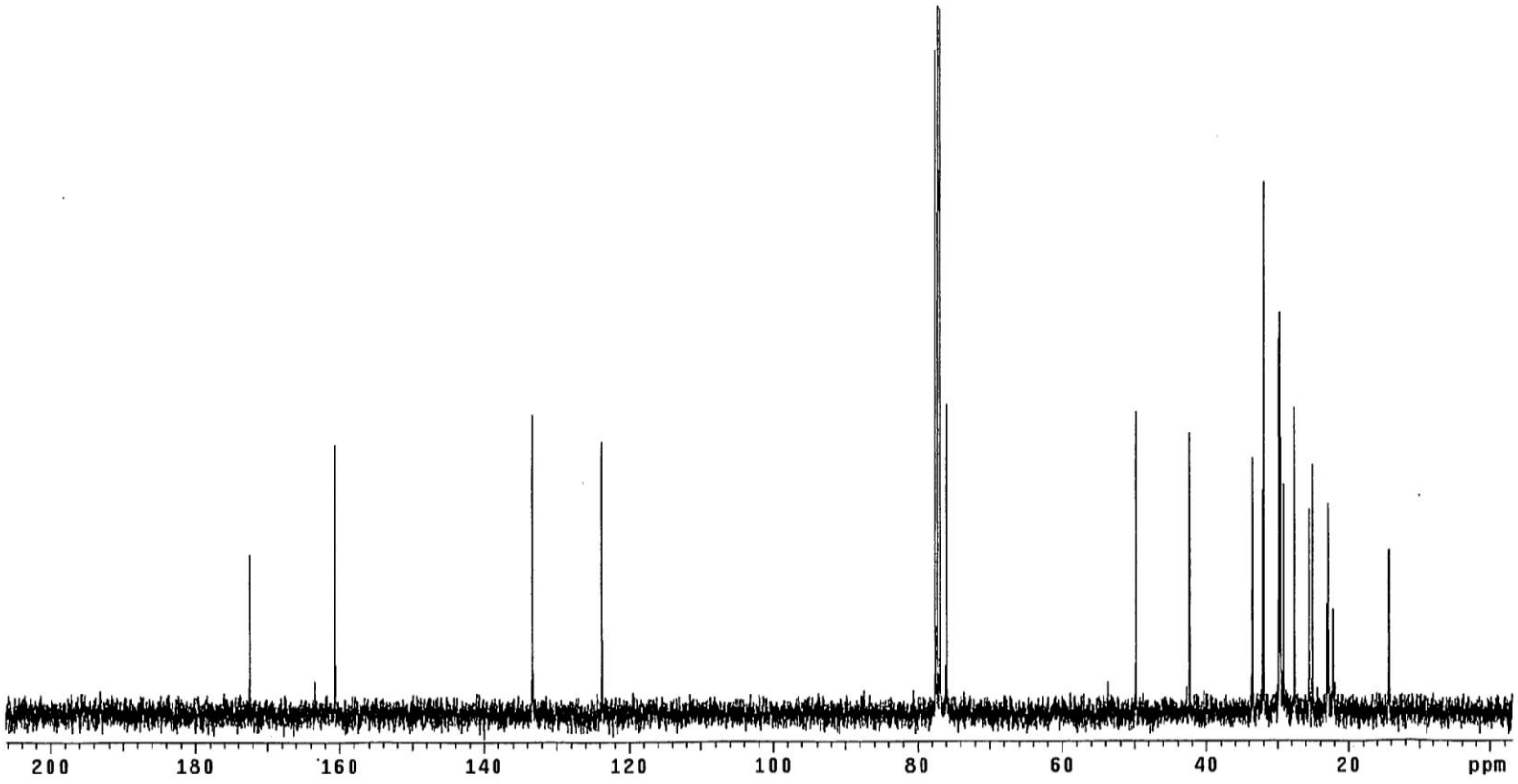
^{1}H NMR (400 MHz, $CDCl_3$)

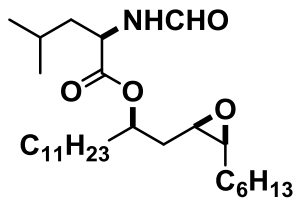
42



^{13}C NMR (100 MHz, $CDCl_3$)

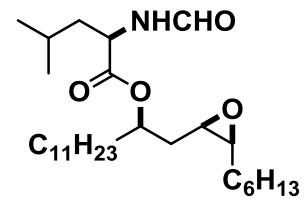
42





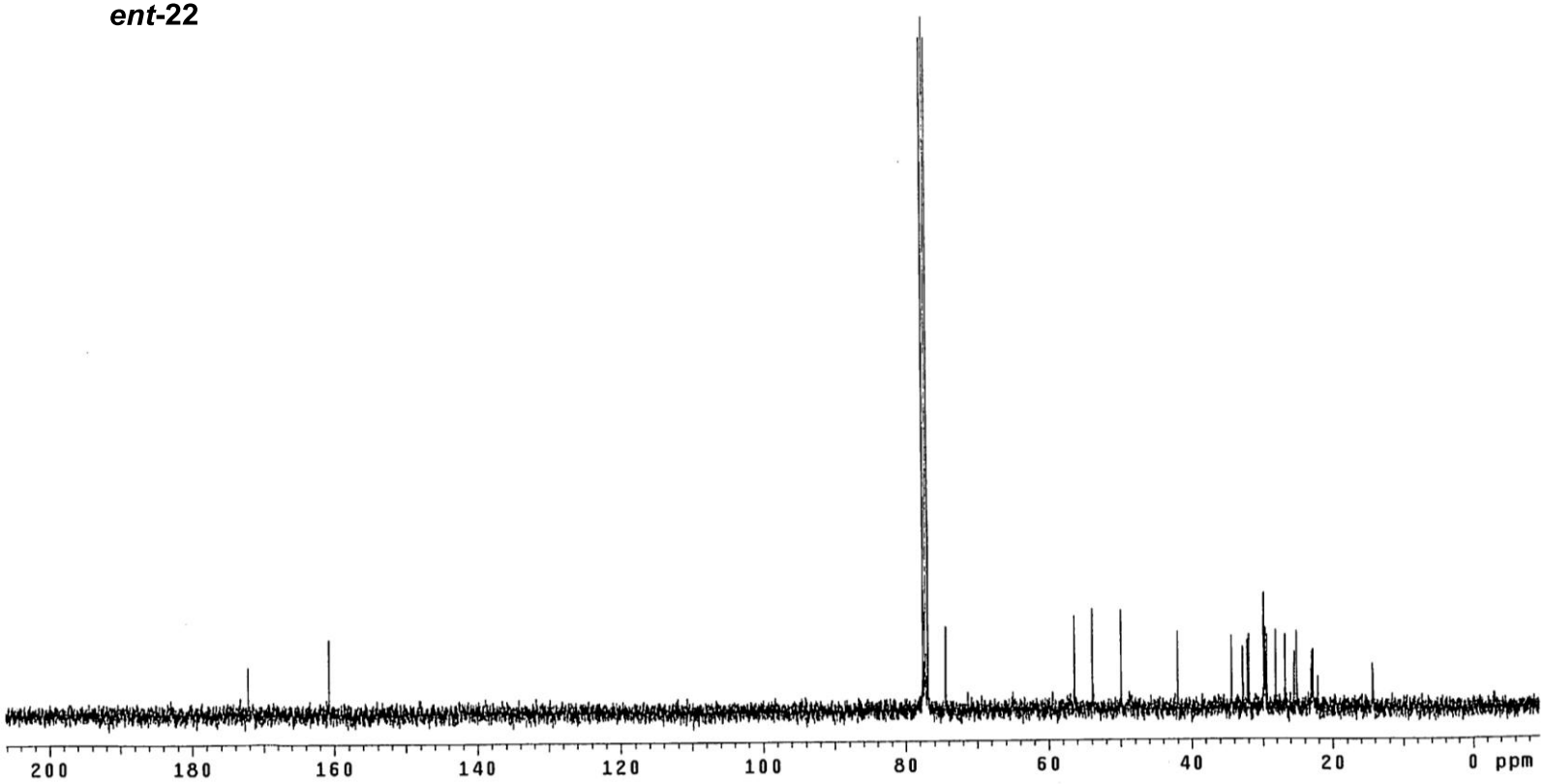
^{1}H NMR (500 MHz, $CDCl_3$)

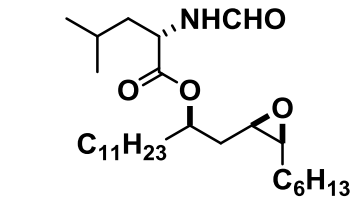
***ent*-22**



^{13}C NMR (100 MHz, $CDCl_3$)

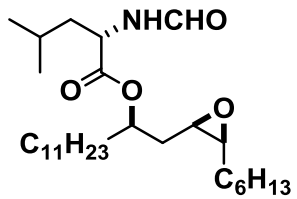
***ent*-22**





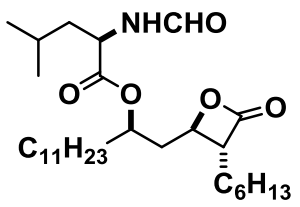
^{1}H NMR (500 MHz, $CDCl_3$)

***ent*-23**



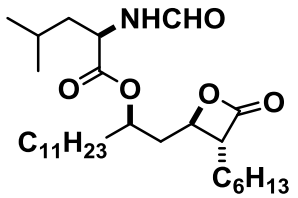
^{13}C NMR (100 MHz, $CDCl_3$)

***ent*-23**



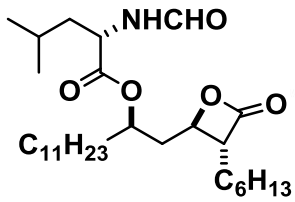
^{1}H NMR (400 MHz, $CDCl_3$)

***ent*-1**



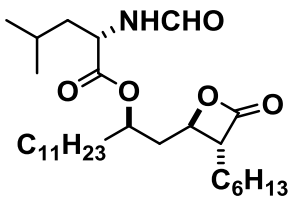
^{13}C NMR (100 MHz, $CDCl_3$)

***ent*-1**



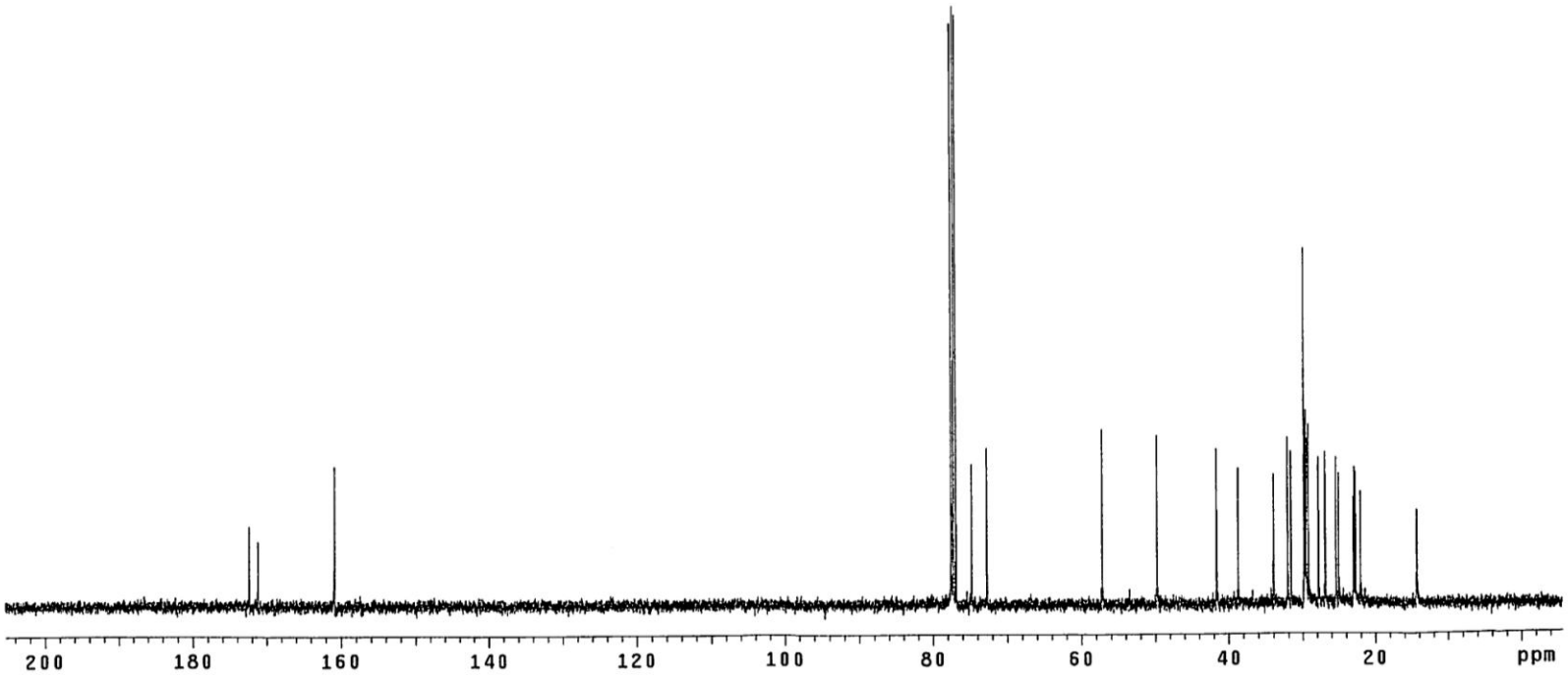
^{1}H NMR (400 MHz, $CDCl_3$)

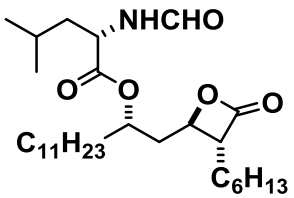
***ent*-34**



^{13}C NMR (100 MHz, $CDCl_3$)

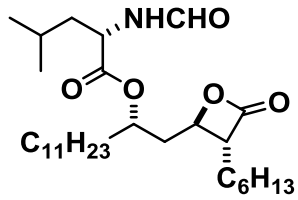
***ent*-34**





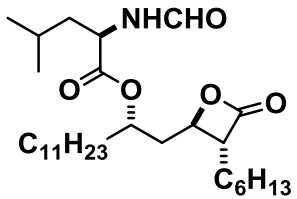
^{1}H NMR (500 MHz, $CDCl_3$)

***ent*-36**



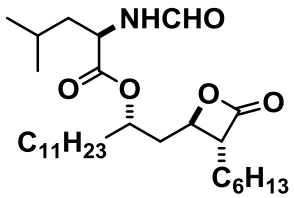
^{13}C NMR (100 MHz, $CDCl_3$)

***ent*-36**



^{1}H NMR (500 MHz, $CDCl_3$)

***ent*-35**



^{13}C NMR (100 MHz, $CDCl_3$)

***ent*-35**