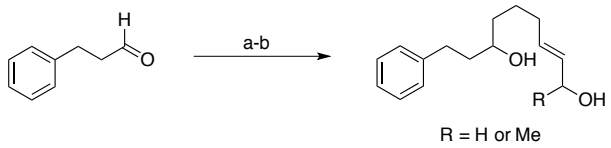
General Experimental Proton (^{1}H NMR) and carbon (^{13}C NMR) nuclear magnetic resonance spectra were taken on a Bruker Avance 300 spectrometer at 300 MHz and 75 MHz respectively, a Bruker Avance 400 spectrometer at 400 MHz and 100 MHz, a Bruker Avance 500 spectrometer at 500 MHz and 125 MHz, or a Bruker Avance 600 spectrometer at 600 MHz and 150 MHz as specified. The chemical shifts are reported in parts per million (ppm) on the delta (δ) scale. The solvent peak was used as a reference value, for ^{1}H NMR: $CDCl_3$ = 7.27 ppm, for ^{13}C NMR: $CDCl_3$ = 77.2 ppm. Data are reported as follows: m = multiplet, s = singlet; d = doublet; t = triplet; q = quartet; p = pentet; s = sextet; dd = doublet of doublets; dt = doublet of triplets; ddq = doublet of doublet of quartets; ddd = doublet of doublet of doublets etc. Peaks listed with an asterisk (*) represent signals from diastereomers. Infrared (IR) spectra were taken on a Nicolet IR200 FT-IR spectrometer with an ATR attachment. Optical rotations were measured at the sodium D line with a 100 mm path length cell, and are reported as follows: $[\alpha]_D^T$, concentration (g/100 mL), and solvent. Methylene chloride was distilled under N_2 from CaH_2. Diethyl Ether was distilled under N_2 from sodium/benzophenone ketyl. Analytical TLC was performed on E. Merck pre-coated (25 mm) silica gel 60 F_{254} plates. Visualization was done under UV (254 nm) or by staining (95mL ethanol, 3mL conc. H_2SO_4, 2mL acetic acid, 5mL anisaldehyde). Flash chromatography was done using SiliCycle SiliaFlash P60 40-63μm 60 Å silica gel. Reagent grade ethyl acetate, diethyl ether, acetone, dichloromethane, methanol, pentane and hexanes (commercial mixture) were purchased from Fisher Scientific and were used as-is for chromatography. All reactions were performed in oven or flame-dried glassware under a positive pressure of N_2 with magnetic stirring unless otherwise noted.

Preparation of Re_2O_7 supported on SiO_2: A slurry of SiO_2 (4.88 g) and of Re_2O_7 (542 mg) in Et_2O (25 mL) was stirred in a round bottom flask at rt for 3 h, then the Et_2O was removed under reduced pressure. The resulting powder was dried under vacuum overnight. The catalyst was transferred to a vial, wrapped in aluminum foil, and stored in a desiccator.

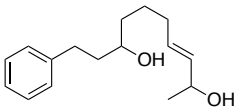
General procedure A for the Re_2O_7-mediated dehydrative cyclizations: To a solution of the substrate in CH_2Cl_2 (0.10 M) was added Re_2O_7 (10% w/w on SiO_2, 0.05 equiv). The reaction mixture was sealed in a 1-dram vial (Chemglass CG-4904-05 with a polypropylene screw cap containing a PTFE faced silicone septum) and stirred at 40 °C for 20 h. The mixture was filtered through a short plug of silica gel (~2 cm) while eluting with CH_2Cl_2 and EtOAc. The solvent was removed under vacuum, and the resulting crude material was purified by silica gel column chromatography. Diastereomeric ratios were determined via ^{1}H NMR analysis of the crude product mixture. Further chromatographic purification was conducted for product characterization purposes if necessary.

General procedure B for the SiO_2•Re_2O_7-mediated cyclization: To a vial of solution of the substrate in CH_2Cl_2 (0.10M) was added SiO_2•Re_2O_7 (10% w/w, 0.05 equiv). The reaction mixture was sealed in a 1-dram vial (Chemglass CG-4904-05 with a polypropylene screw cap containing a PTFE faced silicone septum) and stirred at rt for 0.5h – 1h. The sealed vial was placed into a 40 °C bath for 20 h. The mixture was filtered through a short plug of silica gel (~2 cm) while eluting with CH_2Cl_2 and EtOAc. The solvent was removed under vacuum, and the resulting crude material was purified by silica gel column chromatography. Diastereomeric ratios were determined via ^{1}H NMR analysis of the crude product mixture. Further chromatographic purification was conducted for product characterization purposes if necessary.

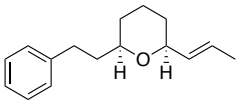


Reagents and conditions
a) Pent-4-en-1-ylmagnesium bromide, Et_2O, 0 °C. b) (*Z*)-But-2-ene-1,4-diol or (*Z*)-hex-3-ene-2,5-diol, Grubbs-Hoveyda 2nd generation metathesis catalyst, CH_2Cl_2, 65%.

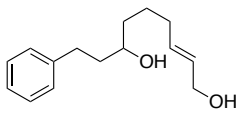
Scheme 1. Synthesis of **1** and **5**.



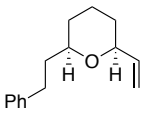
(*E*)-10-Phenyldec-3-ene-2,8-diol (1)
IR (ATR, cm^{-1}) 3346, 3081, 3061, 3026, 2970, 2931, 2859, 1496, 1454, 1369, 1139, 1062, 970, 939, 700
^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 7.24-7.17 (m, 3H), 5.53 (dt, broad, *J* = 15.3, 6.6 Hz, 1H), 5.52 (dd, broad, *J* = 15.4, 6.4 Hz, 1H), 4.27 (dq, *J* = 6.4, 6.3 Hz, 1H), 3.69-3.69 (m, 1H), 2.80 (ddd, *J* = 13.8, 9.5, 5.8 Hz, 1H), 2.68 (ddd, *J* = 13.8, 9.4, 6.8 Hz, 1H), 2.09-2.00 (m, 2H), 1.86-1.69 (m, 2H), 1.60-1.44 (m, 4H), 1.42-1.38 (m, 2H), 1.26 (d, *J* = 6.4 Hz, 3H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 134.7, 130.7, 128.6, 128.56, 126.0, 71.3, 69.1, 39.3, 37.2, 32.2, 32.18, 25.3, 23.6
HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{23}O$ $[M - OH]^+$ 231.1743, found 231.1752



(2*R*,6*S*)-2-Phenethyl-6-((*E*)-prop-1-en-1-yl)tetrahydro-2H-pyran (4): General cyclization protocol A was followed with **1** (41 mg, 0.20 mmol) and Re_2O_7 (10% w/w on SiO_2, 47 mg, 9.8 μmol) in CH_2Cl_2 (2.0 mL). The residue was purified via silica gel flash column chromatography (1% to 10% EtOAc in hexanes) to yield tetrahydropyran **4** as an oil (36.8 mg, 82%, dr > 30:1 cis:trans).
IR (ATR, cm^{-1}) 3084, 3062, 3027, 2933, 2857, 1720, 1496, 1454, 1197, 1078, 1038, 967, 700
^1H NMR (400 MHz, $CDCl_3$) δ 7.31-7.25 (m, 2H), 7.23-7.15 (m, 3H), 5.72 (dqd, *J* = 15.3, 6.4, 1.1 Hz, 1H), 5.55 (ddq, *J* = 15.3, 5.7, 1.5 Hz, 1H), 3.76 (ddd, *J* = 11.2, 5.9, 1.1 Hz, 1H), 3.31 (dddd, *J* = 1.8, 4.9, 7.3, 10.8 Hz, 1H), 2.78 (ddd, *J* = 13.8, 9.4, 5.6 Hz, 1H), 2.70 (ddd, *J* = 13.8, 9.3, 7.0 Hz, 1H), 1.96-1.79 (m, 2H), 1.76-1.67 (m, 1H), 1.72 (dt, broad, *J* = 6.4, 1.2 Hz, 3H), 1.64-1.55 (m, 2H), 1.54-1.44 (m, 1H), 1.38-1.18 (m, 2H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 132.9, 128.6, 128.4, 126.3, 125.7, 78.1, 76.8, 38.2, 31.9, 31.8, 31.4, 23.7, 18.0
HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{23}O$ $[M + H]^+$ 231.1743, found 231.1752



(*E*)-9-Phenylnon-2-ene-1,7-diol (5)
IR (ATR, cm^{-1}) 3342(broad), 3081, 3061, 3026, 2998, 2931, 2860, 1496, 1455, 1090, 1001, 972, 700
^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.27 (m, 2H), 7.24-7.17 (m, 3H), 5.74-5.59 (m, 2H), 4.09 (d, broad, *J* = 4.5 Hz, 2H), 3.69-3.58 (m, 1H), 2.80 (ddd, *J* = 13.9, 9.4, 5.8 Hz, 1H), 2.69 (ddd, *J* = 13.7, 9.4, 6.8 Hz, 1H), 2.15-2.02 (m, 2H), 1.85-1.68 (m, 2H), 1.59-1.30 (m, 6H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 133.0, 129.5, 128.6, 128.5, 126.0, 71.3, 63.9, 39.2, 37.1, 32.3, 32.2, 25.2
HRMS (ESI) *m*/*z* calcd. for $C_{15}H_{23}O_2$ $[M + H]^+$ 235.1693, found 235.1702



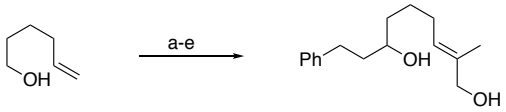
(2*R*,6*S*)-2-Phenethyl-6-((*E*)-prop-1-en-1-yl)tetrahydro-2H-pyran (6): General cyclization protocol A was followed with **5** (46 mg, 0.19 mmol) and Re_2O_7 (10% w/w on SiO_2, 46 mg, 9.5 μmol) in CH_2Cl_2 (1.9 mL). The residue was purified via silica gel flash column chromatography (1% to 10% EtOAc in hexanes) to yield tetrahydropyran **6** as an oil (34 mg, 81%, dr = 1.7:1 cis:trans).

IR (ATR, cm^{-1}) 3084, 3063, 3027, 2934, 2857, 1729, 1496, 1455, 1266, 1202, 1089, 1041, 991, 923, 738, 700

^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.27 (m, 2H), 7.27-7.17 (m, 3H), 6.02-5.87 (m, 1H), 5.30 (dt, *J* = 17.4, 1.6 Hz, 0.60H), 5.25 (dt, *J* = 17.4, 1.7 Hz, 0.40H), 5.21 (dt, *J* = 10.6, 1.7 Hz, 0.40H), 5.13 (dt, *J* = 10.6, 1.5 Hz, 0.60H), 4.43-4.35 (m, 0.40H), 3.86-3.79 (m, 0.60H), 3.76 (dddd, *J* = 2.9, 4.2, 7.9, 7.9 Hz, 0.40H), 3.34 (dddd, *J* = 10.5, 7.8, 4.5, 1.9 Hz, 0.60H), 2.86-2.59 (m, 2H), 2.04-1.90 (m, 1H), 1.90-1.72 (m, 2H), 1.70-1.63 (m, 2H), 1.60-1.54 (m, 1H), 1.44-1.21 (m, 2H)

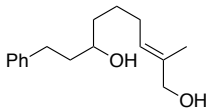
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.48, 142.47, 139.7, 139.0, 128.6, 128.5, 128.3, 128.29, 125.7, 125.6, 115.8, 114.3, 78.1, 76.7, 72.2, 70.5, 38.1, 36.3, 32.0, 31.8, 31.5, 31.3, 30.7, 29.2, 23.6, 18.8

HRMS (ESI) *m/z* calcd. for $C_{15}H_{21}O$ $[M + H]^+$ 217.1587, found 217.1594



Reagents and conditions
a) PCC, Celite, CH_2Cl_2. b) $PhCH_2CH_2MgBr$, THF, reflux. c) TESCl, imidazole, DMAP, CH_2Cl_2, 81%. d) Methacrolein, Grubbs-Hoveyda second generation catalyst, CH_2Cl_2, reflux, 85%. e) $NaBH_4$, MeOH, 0 °C, 48%. f) HF•Py, THF, 64%.

Scheme 2. Synthesis of **7**.



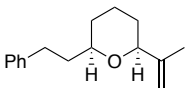
(*E*)-2-Methyl-9-phenylnon-2-ene-1,7-diol (7)

IR (ATR, cm^{-1}) 3323, 3025, 2929, 2858, 1495, 1454, 1011, 911, 731, 699

^1H NMR (500 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 7.23-7.17 (m, 3H), 5.41 (tq, *J* = 7.3, 1.3 Hz, 1H), 4.00 (s, 2H), 3.68-3.60 (m, 1H), 2.81 (ddd, *J* = 13.8, 9.5, 5.6, 1H), 2.68 (ddd, *J* = 13.8, 9.5, 6.7 Hz, 1H), 2.10-2.02 (m, 2H), 1.84-1.70 (m, 2H), 1.66 (s, 3H), 1.56-1.43 (m, 4H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 135.2, 128.6, 128.6, 126.1, 126.0, 71.4, 69.1, 39.3, 37.3, 32.2, 27.7, 25.7, 13.9

HRMS (ESI) *m/z* calcd. for $C_{16}H_{24}O_2Na$ $[M+Na]^+$ 271.1669, found: 271.1648

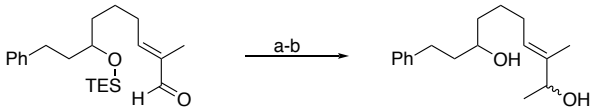


2-Phenethyl-6-(prop-1-en-2-yl)tetrahydro-2*H*-pyran (8): General cyclization procedure B was followed with **7** (87 mg, 0.35 mmol), Re_2O_7 (8.5 mg, 0.017 mmol, 10% on SiO_2) and CH_2Cl_2 (3.5 ml). The reaction crude was directly loaded onto silica gel, then purified by flash chromatography (10% to 20% ethyl acetate in hexane) to give the product diastereomers (66 mg, 81% yield, dr = 2.6:1). The mixture was purified again by flash chromatography (5% to 10% diethyl ether in hexane) to give the pure diastereomers.

Major product (2,6-*cis*-isomer):

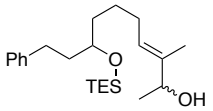
IR (ATR, cm^{-1}) 3026, 2933, 2856, 1652, 1603, 1496, 1454, 1439, 1370, 1311, 1196, 1152, 1087, 1044, 896, 743, 697

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.27 (m, 2H), 7.25-7.17 (m, 3H), 5.03 (s, 1H), 4.86 (s, 1H), 3.71 (d, *J* = 10.8 Hz, 1H), 3.36 (dddd, *J* = 10.7, 8.3, 4.5, 2.1 Hz, 1H), 2.82 (ddd, *J* = 13.8, 9.5, 5.4 Hz, 1H), 2.72 (ddd, *J* = 13.8, 9.5, 7.1 Hz, 1H), 1.96-1.85 (m, 2H), 1.82 (s, 3H), 1.80-1.69 (m, 2H), 1.62-1.48 (m, 2H), 1.42-1.25 (m, 2H)
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 142.7, 128.7, 128.4, 125.7, 110.0. 80.5, 76.9, 38.3, 31.8, 31.5, 30.2, 23.9, 19.6
HRMS (ESI) *m/z* calcd. for $C_{16}H_{22}O$ $[M]^+$ 230.1671, found: 230.1678.
Minor product (2,6-*trans*-isomer):
IR (ATR, cm^{-1}): 3063, 3027, 2938, 2865, 1650, 1603, 1496, 1454, 1373, 1193, 1091, 1042, 897, 699
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2H), 7.24-7.17 (m, 3H), 4.98-4.95 (m, 2H), 4.18 (t, *J* = 4.8 Hz, 1H), 3.74-3.68 (m, 1H), 2.82 (ddd, *J* = 13.8, 10.9, 5.1 Hz, 1H), 2.62 (ddd, *J* = 13.8, 10.9, 6.0 Hz, 1H), 2.02 (dddd, *J* = 14.0, 10.7, 8.8, 5.2 Hz, 1H), 1.79 (s, 3H), 1.77-1.65 (m, 6H), 1.45-1.35 (m, 1H)
^{13}C NMR (125 MHz, $CDCl_3$) δ 145.4, 142.7, 128.5, 128.5, 125.8, 111.7, 73.8, 71.4, 35.7, 32.4, 30.4, 27.9, 20.1, 19.2
HRMS (ESI) *m/z* calcd. for $C_{16}H_{23}O$ $[M+H]^+$ 231.1743, found: 231.1736

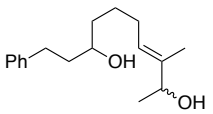


Reagents and conditions
a) MeLi, THF, Et_2O, –78 °C, 65%. b) HF•Py, THF, rt, 72%.

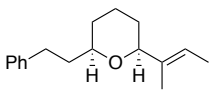
Scheme 3. Synthesis of **9** and **11**.



(*E*)-3-Methyl-10-phenyl-8-((triethylsilyl)oxy)dec-3-en-2-ol (9)
IR (ATR, cm^{-1}) 3363, 3026, 2950, 2875, 1495, 1459, 1414, 1372, 1314, 1238, 1077, 1004, 888, 807, 723, 698
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 2H), 7.21-7.16 (m, 3H), 5.40 (tt, *J* = 7.1, 1.2 Hz, 1H), 4.22 (q, *J* = 6.4 Hz, 1H), 3.73 (p, *J* = 5.7 Hz, 1H), 2.71 (ddd, *J* = 13.7, 10.3, 6.7 Hz, 1H), 2.61 (ddd, *J* = 13.7, 10.3, 6.3 Hz, 1H), 2.02 (dd, *J* = 14.4, 7.2 Hz, 2H), 1.82-1.70 (m, 2H), 1.63 (s, 3H), 1.56-1.32 (m, 4H), 1.26 (d, *J* = 6.4 Hz, 3H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.62 (q, *J* = 7.9 Hz, 6H)
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 138.8, 128.5, 128.5, 125.8, 125.1, 73.6, 72.0, 39.2, 37.0, 31.9, 27.7, 25.4, 21.7, 11.6, 7.1, 5.3
HRMS (ESI) *m/z* calcd. for $C_{23}H_{39}O_2Si$ $[M-H]^+$ 375.2719, found: 375.2739



(*E*)-3-Methyl-10-phenyldec-3-ene-2,8-diol (11)
IR (ATR, cm^{-1}) 3396, 3026, 2929, 2860, 1710, 1665, 1603, 14955, 1453, 1368, 1246, 1179, 1030, 910, 738, 698
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 7.23-7.17 (m, 3H), 5.40 (t, *J* = 7.1 Hz, 1H), 4.21 (q, *J* = 6.4 Hz, 1H), 3.64 (dddd, *J* = 4.0 Hz, 1H), 2.80 (ddd, *J* = 13.7, 9.5, 5.8 Hz, 1H), 2.68 (ddd, *J* = 13.7, 9.5, 6.8 Hz, 1H), 2.07-2.00 (m, 2H), 1.85-1.70 (m, 2H), 1.62 (s, 3H), 1.55-1.40 (m, 4H), 1.26 (d, *J* = 6.4 Hz, 3H)
^{13}C NMR (101 MHz, $CDCl_3$) 142.3, 139.0, 128.6, 128.6, 126.0, 124.9, 73.5, 71.4, 39.3, 37.3, 32.2, 27.6, 25.7, 21.8, 11.7
HRMS (ESI) *m/z* calcd. $C_{17}H_{25}O_2$ $[M-H]^+$ 261.1849, found: 261.1828



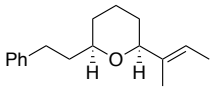
2-((*E*)-But-2-en-2-yl)-6-phenethyltetrahydro-2*H*-pyran (10) (from 9): General cyclization protocol B was followed with **9** (73 mg, 0.34 mmol), Re_2O_7 (4.9 mg, 0.010 mmol, 10% on SiO_2) and CH_2Cl_2 (2.7 ml). The reaction mixture was directly loaded onto silica gel, then purified by flash chromatography (10% to 20% ethyl acetate in hexane) to give the diastereomeric products (34 mg, 71% yield, dr = 38:1). The mixture was purified again by flash chromatography (6% to 12% ethyl acetate in hexane) to give the desired product.

IR (ATR, cm^{-1}) 3026, 2932, 2857, 1496, 1454, 1379, 1311, 1193, 1080, 1040, 908, 697

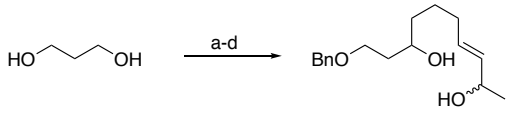
^1H NMR (400 MHz, C_6D_6) δ 7.20-7.05 (m, 5H), 5.62 (qp, *J* = 2.3, 1.3 Hz, 1H), 3.61 (d, *J* = 11.3 Hz, 1H), 3.18 (dddd, *J* = 10.7, 8.6, 4.1, 2.1 Hz, 1H), 2.82 (ddd, *J* = 13.8, 9.2, 5.1 Hz, 1H), 2.71 (ddd, *J* = 13.7, 9.2, 7.3 Hz, 1H), 1,88 (dddd, *J* =13.7, 9.2, 8.4, 5.5 Hz, 1H), 1.70 (t, *J* = 1.1 Hz, 3H), 1.66-1.58 (m, 2H), 1.57 (dt, *J* = 6.7, 0.9 Hz, 3H), 1.48-1.20 (m, 4H), 1.18-1.07 (m, 1H)

^{13}C NMR (101 MHz, C_6D_6) δ 143.5, 138.3, 129.5, 129.2, 126.5, 119.5, 83.4, 77.2, 39.4, 32.7, 32.4, 31.2, 24.8, 13.7, 13.4

HRMS (ESI) *m/z* calcd. for $C_{17}H_{23}O$ $[M-H]^+$ 243.1743, found: 243.1722

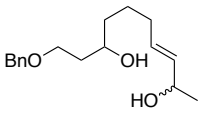


2-((*E*)-But-2-en-2-yl)-6-phenethyltetrahydro-2*H*-pyran (10) (from 11): General cyclization protocol B was followed with **11** (89 mg, 0.34 mmol), Re_2O_7 (8.2 mg, 0.017 mmol, 10% on SiO_2) and CH_2Cl_2 (3.4 ml). The reaction mixture was directly loaded onto silica gel, then purified by flash chromatography (10% to 20% ethyl acetate in hexane) to give the diastereomeric products (72 mg, 86% yield, dr = 33:1). The mixture was purified again by flash chromatography (4% to 10% ethyl acetate in hexane) to give the desired product.



Reagents and conditions
a) NaH, THF, then Bu_4NI, BnBr, 76%. b) PCC, Celite, CH_2Cl_2, 40%.
c) 1-Pentenyl-5-magnesium bromide, THF, reflux, 30%. d) 1-Buten-3-ol, Grubbs-Hoveyda second generation catalyst, CH_2Cl_2, reflux, 30%.

Scheme 4. Synthesis of **12**.



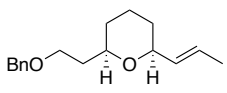
(*E*)-10-(Benzyloxy)dec-3-ene-2,8-diol (12)

IR (ATR, cm^{-1}) 3377, 2923, 2854, 1717, 1553, 1453, 1366, 1285, 1247, 1094, 1071, 1027, 969, 734, 715, 698

^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.28 (m, 5H), 5.64 (dt, *J* = 15.4, 6.5 Hz, 1H), 5.53 (dd, *J* = 15.4, 6.5, 1H), 4.53 (s, 2H), 4.26 (p, *J* = 6.4 Hz, 1H), 3.82 (p, *J* = 5.8 Hz, 1H), 3.74 (dt, *J* = 9.3, 4.9 Hz, 1H), 3.66 (dt, *J* = 9.2, 6.3 Hz, 1H), 2.08-2.01 (m, 2H), 1.77-1.72 (m, 2H), 1.58-1.39 (m, 4H), 1.25 (d, *J* = 6.4 Hz, 3H)

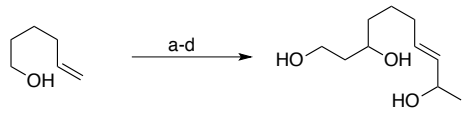
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 134.6, 130.9, 128.6, 127.9, 127.8, 73.5, 71.5, 69.5, 69.1, 37.0, 36.5, 32.2, 25.2, 23.6

HRMS (ESI) *m/z* calcd. for $C_{17}H_{25}O_3$ $[M-H]^+$ 277.1798, found: 277.1777



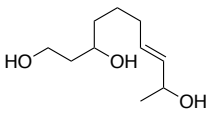
2-(2-(Benzyloxy)ethyl)-6-((*E*)-prop-1-en-1-yl)tetrahydro-2*H*-pyran (13): General cyclization protocol B was followed with **12** (83 mg, 0.30 mmol), Re_2O_7 (7.2 mg, 0.015 mmol, 10% on SiO_2) and CH_2Cl_2 (3.0 ml). The reaction mixture was directly loaded onto silica gel, then was purified by flash chromatography

(10% to 20% ethyl acetate in hexane) to give the diastereomeric products (66 mg, 86% yield, dr = 7.6:1). The mixture was purified again by flash chromatography (6% – 12% diethyl ether in hexanes) for characterization.
IR (ATR cm^{-1}) 2935, 2856, 1557, 1453, 1362, 1266, 1198, 1074, 1035, 965, 732, 697
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.39 (m, 2H), 7.32-7.27 (m, 2H), 7.24-7.16 (m, 1H), 5.77 (dqd, *J* = 15.4, 6.1, 1.0 Hz, 1H), 5.70 (ddq, *J* = 15.4, 5.5, 1.3 Hz, 1H), 4.46 (s, 1H), 4.45 (s, 1H), 3.85-3.80 (m, 1H), 3.76 (ddd, *J* = 9.0, 7.8, 6.1 Hz, 1H), 3.64 (ddd, *J* = 9.1, 6.1, 5.6 Hz, 1H), 3.58-3.64 (m, 1H), 2.07-1.99 (m, 1H), 1.94-1.86 (m, 1H), 1.68 (dt, *J* = 6.2, 1.3 Hz, 3H), 1.56-1.50 (m, 1H), 1.50-1.37 (m, 4H), 1.28-1.18 (m, 1H)
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 132.8, 128.5, 127.7, 127.6, 126.5, 78.2, 74.9, 73.0, 67.1, 36.8, 31.8, 31.6, 23.7, 18.0
HRMS (ESI) *m/z* calcd. for $C_{17}H_{25}O_2$ $[M-H]^+$ 261.1849, found: 261.1830

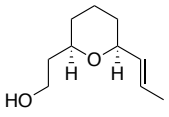


Reagents and conditions
a) PCC, Celite, CH_2Cl_2, 59%. Ethyl diazoacetate, $SnCl_2$, CH_2Cl_2, 0 °C, 76%.
c) (*Z*)-Hex-3-ene-2,5-diol, Grubbs-Hoveyda 2nd generation metathesis catalyst, CH_2Cl_2, 57%. d) $LiAlH_4$, THF, 40%.

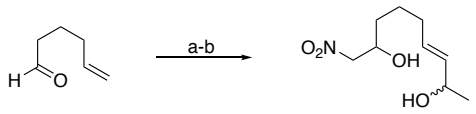
Scheme 5. Synthesis of **14**.



(*E*)-Dec-7-ene-1,3,9-triol (14): IR (ATR, cm^{-1}) 3338(broad), 2931, 2856, 1436, 1369, 1141, 1053, 969, 941, 865
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.67-5.57 (m, 1H), 5.57-5.50 (m, 1H), 4.30-4.21 (m,1H), 3.93-3.84 (m, 2H), 3.84-3.77 (m, 1H), 2.51 (s, broad, 2H), 2.35-2.15 (m, broad, 1H), 2.09-1.98 (m, 2H), 1.74-1.61 (m, 2H), 1.57-1.48 (m, 2H), 1.48-1.37 (m, 2H), 1.25 (d, *J* = 6.3 Hz, 3H)
^{13}C NMR (125 MHz, $CDCl_3$) δ 134.8, 134.7*, 130.63*, 130.62, 72.04*, 72.01, 69.0*, 68.97, 62.0*, 61.8, 38.4, 38.38*, 37.3*, 37.2, 32.1, 31.05*, 25.1, 23.6
HRMS (ESI) *m/z* calcd. for $C_{10}H_{19}O_2$ $[M - OH]^+$ 171.1380, found 171.1379

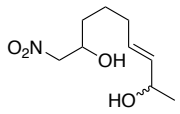


2-((2*R*,6*S*)-6-((*E*)-Prop-1-en-1-yl)tetrahydro-2H-pyran-2-yl)ethan-1-ol (15): General cyclization protocol A was followed with **14** (17 mg, 0.090 mmol) and Re_2O_7 (10% w/w on SiO_2, 22 mg, 4.5 μmol) in CH_2Cl_2 (0.9 mL). The residue was purified via silica gel flash column chromatography (10% to 40% EtOAc in hexanes) to yield alcohol **15** as an oil (13 mg, 85%, dr > 30:1 cis:trans).
IR (ATR, cm^{-1}) 3427 (broad), 2935, 2858, 1721, 1440, 1377, 1308, 1197, 1078, 1036, 967, 935;
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65 (dqd, *J* = 15.4, 6.4, 1.1 Hz, 1H), 5.47 (ddq, *J* = 15.4, 6.0, 1.5 Hz, 1H), 3.85-3.75 (m, 3H), 3.79 (dd, *J* = 6.0, 4.9 Hz, 1H) 3.62 (dddd, *J* = 11.0, 8.7, 3.3, 2.0 Hz, 1H), 2.94 (s, broad, 1H), 1.89-1.81 (m, 1H), 1.81-1.74 (m, 1H), 1.74-1.69 (m, 1H), 1.68 (ddd, *J* = 6.4, 1.4, 0.9 Hz, 3H), 1.64-1.58 (m, 1H), 1.58-1.48 (m, 2H), 1.39-1.24 (m, 2H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 132.4, 126.6, 78.8, 78.5, 61.9, 38.2, 31.7, 31.4, 23.5, 17.9
HRMS (ESI) *m/z* calcd. for $C_{10}H_{19}O_2$ $[M + H]^+$ 171.1380, found 171.1382.



Reagents and conditions
a) CH_3NO_2, KO*t*Bu, THF, *t*BuOH, 54%. b) 2,5-Hex-3-enediol, Grubbs-Hoveyda second generation catalyst, CH_2Cl_2, 63%.

Scheme 6. Synthesis of **16**.



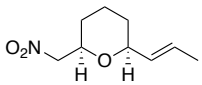
(*E*)-9-Nitronon-3-en-2-ol (16)

IR (ATR, cm^{-1}) 3357, 2925, 1548, 1421, 1382, 1207, 1139, 1058, 967, 935, 886, 723, 684

^1H NMR (500 MHz, $CDCl_3$) δ 5.62 (dt, *J* = 15.4, 6.5 Hz, 1H), 5.54 (dd, *J* =15.4, 6.3 Hz, 1H), 4.44 (dd, *J* = 13.0, 3.0 Hz, 1H), 4.41-4.36 (m, 1H), 4.36-4.30 (m, 1H), 4.27 (p, *J* = 6.3 Hz, 1H), 2.72 (br. s, 1H), 2.13-2.03 (m, 2H), 1.62-1.45 (m, 4H), 1.26 (d, *J* = 6.4 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 135.2, 129.9, 80.8, 68.9, 68.6, 33.2, 31.8, 24.8, 23.6

HRMS (ESI) *m/z* calcd. for $C_9H_{16}O_4N$ $[M-H]^+$ 202.1074, found: 202.1050



(*E*)-2-(Nitromethyl)-6-(prop-1-en-1-yl)tetrahydro-2*H*-pyran (17)

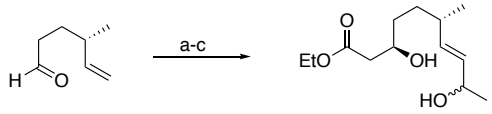
General cyclization protocol B was followed with **16** (105 mg, 0.51 mmol), Re_2O_7 (12.5 mg, 0.026 mmol, 10% on SiO_2) and CH_2Cl_2 (5 ml). The reaction mixture was directly loaded onto silica gel, then purified by flash chromatography (6% to 12% ethyl acetate in hexane) to give the product (81 mg, 84% yield, dr = 13:1) as colorless oil.

IR (ATR, cm^{-1}) 2941, 2861, 1552, 1439, 1377, 1338, 1267, 1223, 1201, 1103, 1073, 1032, 966, 947, 896, 881, 733, 702

^1H NMR (400 MHz, C_6D_6) δ 5.53 (dqd, *J* = 15.4, 6.4, 1.2 Hz, 1H), 5.49 (ddq, *J* = 15.4, 5.4, 1.6 Hz, 1H), 3.90 (dd, *J* = 12.3, 8.8 Hz, 1H), 3.73 (ddt, *J* = 11.4, 8.8, 2.8 Hz, 1H), 3.52-3.46 (m, 1H), 3.45 (dd, *J* = 12.3, 3.4 Hz, 1H), 1.46 (dt, *J* = 6.4, 1.2 Hz, 3H), 1.40-1.33 (m, 1H), 1.26-1.20 (m, 1H), 1.06-0.99 (m, 2H), 0.84-0.77 (m, 1H), 0.71-0.60 (m, 1H)

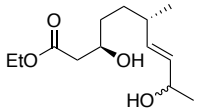
^{13}C NMR (125 MHz, C_6D_6) δ 132.8, 126.5, 80.1, 78.5, 74.6, 31.9, 28.2, 23.5, 18.3

HRMS (ESI) *m/z* calcd. for $C_9H_{14}O_3N$ $[M-H]^+$ 184.0974, found: 184.0973



Reagents and conditions
a) AcCl, *i*Pr_2NEt, trimethylsilyl quinidine, $LiClO_4$, Et_2O, CH_2Cl_2, –78 °C, 60%, dr = 92:8. b) NaOEt, EtOH, 55%. c) 2,5-Hex-3-enediol, Grubbs-Hoveyda second generation catalyst, CH_2Cl_2, 56%.

Scheme 7. Synthesis of **18**.

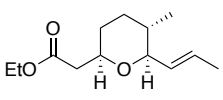


Ethyl (3*R*,6*S*,*E*)-3,9-dihydroxy-6-methyldec-7-enoate (18)

IR (ATR, cm^{-1}) 3396, 2966, 2928, 2871, 1716, 1453, 1371, 1294, 1249, 1164, 1029, 971, 939, 853

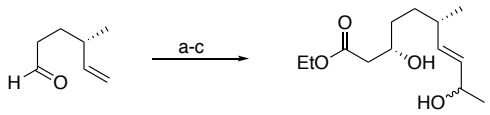
^1H NMR (500 MHz, $CDCl_3$) (including both major diastereomers) δ 5.53-5.45 (m, 2H), 4.30-4.23 (m, 1H), 4.18 (t, *J* = 7.1 Hz, 2H), 4.02-3.94 (m, 1H), 2.96 (d, *J* = 3.6 Hz, 0.51 H), 2.89 (d, *J* = 3.7 Hz, 0.49 H), 2.50 (dd, *J* = 16.4, 3.1 Hz, 1H), 2.42 (dd, *J* = 16.5, 3.1 Hz, 0.51 H), 2.39 (dd, *J* = 16.5, 3.1 Hz, 0.49 H), 2.16-2.08 (m, 1H), 1.53-1.33 (m, 4H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.26 (d, *J* = 6.5 Hz, 0.49 H), 1.26 (d, *J* = 6.5 Hz, 0.51 H), 1.01 (d, *J* = 6.7 Hz, 0.49 H), 1.00 (d, *J* = 6.7 Hz, 0.51H)

^{13}C NMR (125 MHz, $CDCl_3$) (including both diastereomers) δ 173.2, 136.4, 133.2, 133.1, 69.1, 69.1, 68.2, 68.1, 60.9, 41.5, 36.3, 36.3, 34.3, 34.3, 32.6, 32.6, 23.7, 23.6, 20.7, 20.7, 14.3
HRMS (ESI) *m/z* calcd. for $C_{13}H_{24}O_4Na$ $[M+Na]^+$ 267.1567, found: 267.1583
$[\alpha]_D^{22}$ –2.4 (*c* 0.3, $CHCl_3$)



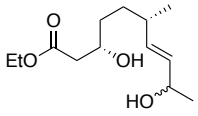
Ethyl 2-((2*R*,5*S*,6*S*)-5-methyl-6-((*E*)-prop-1-en-1-yl)tetrahydro-2*H*-pyran-2-yl)acetate (19)

General cyclization protocol B was followed with **18** (76 mg, 0.31 mmol), Re_2O_7 (7.5 mg, 0.016 mmol, 10% on SiO_2) and CH_2Cl_2 (3.1 ml). The crude mixture was directly loaded onto silica gel, then purified by flash chromatography (10% to 20% ethyl acetate in hexane) to give the product diastereomers (55 mg, 77% yield, dr = 38:1). Then the mixture was purified again by flash chromatography (5% to 10% diethyl ether in hexanes) to give the pure product.
IR (ATR, cm^{-1}) 2927, 2874, 1734, 1450, 1370, 1340, 1300, 1251, 1227, 1190, 1065, 1029, 965, 934, 879
^{1}H NMR (500 MHz, C_6D_6) δ 5.58 (dq, *J* = 15.1, 6.5 Hz, 1H), 5.46 (ddq, *J* = 15.4, 7.3, 1.6 Hz, 1H), 3.95 (dq, *J* = 11.0, 7.1 Hz, 1H), 3.92 (dq, *J* = 10.9, 7.1 Hz, 1H), 3.84 (dddd, *J* = 11.1, 7.5, 5.6, 1.9, 1H), 3.28 (dd, *J* = 9.4, 7.5 Hz, 1H), 2.61 (dd, *J* = 15.1, 7.4 Hz, 1H), 2.28 (dd, *J* = 15.1, 5.7 Hz, 1H), 1.54 (ddd, *J* = 15.1, 12.9, 6.5 Hz, 1H), 1.51 (dd, *J* = 6.4, 1.3 Hz, 3H), 1.49-1.43 (m, 1H), 1.25-1.15 (m ,2H), 1.02-0.93 (m, 1H), 0.93 (t, *J* = 7.1 Hz, 3H), 0.66 (d, *J* = 6.6 Hz, 3H)
^{13}C NMR (125 MHz, C_6D_6) δ 171.4, 132.5, 128.3, 85.6, 74.7, 60.7, 42.5, 36.0, 33.3, 32.6, 18.5, 18.4, 14.8
HRMS (ESI) *m/z* calcd. for $C_{13}H_{23}O_3$ $[M+H]^+$ 227.1642, found: 227.1650
$[\alpha]_D^{22}$ +9.7 (*c* 1.3, $CHCl_3$)



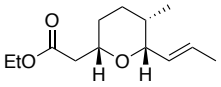
Reagents and conditions
a) AcCl, *i*Pr_2NEt, trimethylsilyl quinine, $LiClO_4$, Et_2O, CH_2Cl_2, –78 °C, 62%, dr = 10:1. b) NaOEt, EtOH, 67%. c) 2,5-Hex-3-enediol, Grubbs-Hoveyda second generation catalyst, CH_2Cl_2, 61%.

Scheme 8. Synthesis of **20**.



Ethyl (3*S*,6*S*,*E*)-3,9-dihydroxy-6-methyldec-7-enoate (20)

IR (ATR, cm^{-1}) 3388, 2966, 2929, 2870, 1716, 1453, 1371, 1291, 1248, 1164, 1028, 971, 938, 852
^{1}H NMR (400 MHz, $CDCl_3$) (a mixture of diastereomers) δ 5.53-5.43 (m, 2H), 4.28-4.21 (m, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.02-3.93 (br. s, 1H), 2.49 (dd, *J* = 16.4, 3,0 Hz, 1H), 2.39 (dd, *J* = 16.3, 8.8, 0.57 H), 2.39 (dd, *J* = 16.5, 9.0 Hz, 0.43 H), 2.16-2.06 (m, 1H), 1.54-1.38 (m, 3H), 1.36-1.29 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.24 (d, *J* = 6.1 Hz, 3H), 0.99 (d, *J* = 6.7 Hz, 0.43 H), 0.98 (d, *J* = 6.7 Hz, 0.57 H)
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 136.3, 133.1, 133.0, 69.0, 68.3, 60.8, 41.4, 36.4, 34.3, 34.3, 32.6, 23.7, 23.6, 20.6, 20.6, 14.1
HRMS(ESI) *m/z* calcd. for $C_{13}H_{24}O_4Na$ $[M+Na]^+$ 267.1567, found: 267.1582
$[\alpha]_D^{22}$ +26.4 (*c* 2.02, $CHCl_3$)



Ethyl 2-((2*S*,5*S*,6*R*)-5-methyl-6-((*E*)-prop-1-en-1-yl)tetrahydro-2*H*-pyran-2-yl)acetate (21)

General cyclization protocol was followed with **20** (27 mg, 0.11 mmol), Re_2O_7 (2.7 mg, 0.006 mmol, 10% on SiO_2) and CH_2Cl_2 (1.1 ml). The reaction mixture was directly loaded onto silica gel, then purified by flash chromatography (10% to 20% ethyl acetate in hexane) to give the crude mixture (14 mg, 55% yield, dr = 2.9:1). The mixture was purified again by flash chromatography (5% to 10% diethyl ether in hexanes) to give separable diastereomers.

Major product (2,6-*cis*-diastereomer):

IR (ATR, cm^{-1}) 2954, 2923, 2854, 1732, 1457, 1378, 1285, 1121, 1072, 1007, 967, 911, 739, 699

^1H NMR (400 MHz, $CDCl_3$) δ 5.66 (dqd, *J* = 15.5, 6.5, 1.2 Hz, 1H), 5.44 (ddq, *J* = 15.4, 5.8, 1.5 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 1H), 3.96 (d, *J* = 5.6 Hz, 1H), 3.81 (dddd, *J* = 10.1, 6.7, 6.7, 3.6 Hz, 1H), 2.61 (dd, *J* = 15.0, 6.7 Hz, 1H), 2.41 (dd, *J* = 15.0, 6.4 Hz, 1H), 1.86-1.75 (m, 1H), 1.69 (dt, *J* = 6.4, 1.3, 3H), 1.73-1.63 (m, 2H), 1.52-1.40 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.94 (d, *J* = 6.9 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 131.1, 126.4, 80.9, 74.9, 60.5, 41.9, 31.9, 30.7, 25.8, 18.0, 14.4, 12.0

HRMS (ESI) *m/z* calcd. for $C_{13}H_{23}O_3$ $[M+H]^+$ 227.1642, found: 227.1650

$[\alpha]_D^{22}$ –8.1 (*c* 1.0, $CHCl_3$)

Minor product (2,6-*trans*-diastereomer)

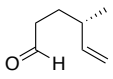
IR (ATR, cm^{-1}) 2927, 2855, 1731, 1459, 1377, 1264, 1179, 1030, 732, 703

^1H NMR (400 MHz, $CDCl_3$) δ 5.68 (dqd, *J* = 15.4, 6.5, 0.8Hz, 1H), 5.44 (ddq, *J* = 15.4, 7.0, 1.5 Hz, 1H), 4.41-4.33 (m, 1H), 4.15 (q, *J* = 7.2 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 1H), 3.70 (t, *J* = 7.4 Hz, 1H), 2.76 (dd, *J* = 14.4, 8.1 Hz, 1H), 2.49 (dd, *J* = 14.4, 6.5 Hz, 1H), 1.84-1.76 (m, 1H), 1.74-1.69 (m, 1H), 1.71 (dd, *J* = 6.4, 1.0 Hz, 3H), 1.57-1.45 (m, 2H), 1.40-1.29 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.89 (d, *J* = 6.7 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 131.2, 129.1, 77.9, 69.2, 60.6, 37.9, 34.1, 27.8, 26.5, 18.3, 18.0, 14.4

HRMS (ESI) *m/z* calcd. for $C_{13}H_{21}O_3$ $[M-H]^+$ 225.1491, found: 225.1514

$[\alpha]_D^{22}$ +35.0 (*c* 0.3, $CHCl_3$)



(*S*)-4-Methylhex-5-enal (24)

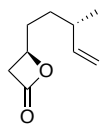
Ozone was bubbled into a solution of (+)-β-citronellene (4.7 g, 34 mmol) in CH_2Cl_2 (200 mL) at –78 °C until starting material was consumed as monitored by TLC (eluent: 100% hexanes, stained with I_2, then anisaldehyde). Me_2S (5 mL) was added, and the resulting solution was warmed to rt slowly, and stirred for 7 h. The reaction mixture was concentrated directly and the residue was purified by flash chromatography (10% to 20% Et_2O in pentane) to afford aldehyde **24** (3.2 g, 84%).

IR (ATR, cm^{-1}) 3078, 2956, 2929, 2867, 1716, 1640, 1456, 1418, 1373, 1127, 994, 909, 681

^1H NMR (300 MHz, $CDCl_3$) δ 9.78 (t, 1H, *J* = 1.7 Hz), 5.64 (ddd, *J* = 16.9, 10.5, 7.8 Hz, 1H), 5.05 – 4.90 (m, 2H), 2.44 (t, *J* = 7.4 Hz, 2H), 2.16 (sep, *J* = 6.0 Hz, 1H), 1.76 – 1.52 (m, 2H), 1.03 (d, *J* = 6.6 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.4, 143.3, 113.8, 41.8, 37.5, 28.5, 20.2

These data match literature values.[1]



(*R*)-4-((*S*)-3-methylpent-4-en-1-yl)oxetan-2-one (25)

A stirred solution of *O*-trimethylsilylquinidine[2] (1.27g, 3.20 mmol) and $LiClO_4$ (1.18g, 11.1 mmol) in CH_2Cl_2 (44.0 mL) and diethyl ether (22.0 mL) was cooled to –78 °C. To this mixture was added *N, N*-diisopropylethylamine (freshly distilled from NaOH, 7.16g, 55.4 mmol) followed by aldehyde **22** (2.49 g, 22.2 mmol). A solution of freshly distilled acetyl chloride (3.48g, 44.3 mmol) in CH_2Cl_2 (11 mL) was then added over 3 hours via syringe pump, taking care to place the tip of the needle in the reaction solution. Following addition of the acyl chloride, the reaction was stirred for 12 h at –78 °C until TLC showed complete consumption of the starting aldehyde. The reaction mixture was diluted with diethyl ether (200 mL) and allowed to warm to rt. The mixture was filtered through a plug of silica gel and concentrated *in vacuo* to give a clear oil. The oil was purified by silica gel column chromatography (0 to 15% EtOAc in hexanes) and concentrated to give β-lactone **23** as a clear colorless oil (2.50 g, 16.2 mmol, dr > 10:1, 73%).

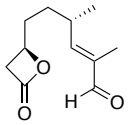
IR (ATR, cm^{-1}) 3076, 2962, 2927, 2870, 1828, 1640, 1457, 1414, 1127, 996, 911

^1H NMR (300 MHz, $CDCl_3$) δ 5.67 (ddd, *J* = 17.4, 10.1, 7.6 Hz, 1H) 5.01 (m, 1H), 4.97 (m, 1H), 4.50 (dddd, *J* = 7.5, 4.3, 5.8, 5.8 Hz, 1H), 3.51 (dd, *J* = 5.8, 16.2 Hz, 1H), 3.07 (dd, *J* = 4.3, 16.2 Hz, 1H), 2.18 (septet, *J* = 6.9 Hz, 1H), 1.87 (dddd, *J* = 13.9, 10.5, 7.6, 5.3 Hz, 1H), 1.74 (dddd, *J* = 14.0, 10.5, 5.8, 5.8 Hz, 1H), 1.42 (m, 2H), 1.04 (d, *J* = 6.7 Hz, 3H)

^{13}C NMR (75 MHz, $CDCl_3$) δ 168.4, 143.6, 113.7, 71.3, 43.0, 37.5, 32.5, 31.5, 20.4

HRMS (ESI) *m/z* calcd. for $C_9H_{15}O_2$ $[M + H]^+$ 155.1067, found 155.1062

$[\alpha]_D^{22}$ +37.7 (*c* 0.56, $CHCl_3$)



(*S*,*E*)-2,4-dimethyl-6-((*R*)-4-oxooxetan-2-yl)hex-2-enal (26)

To a solution of β-lactone **23** (198 mg, 1.28 mmol) in CH_2Cl_2 (4 mL) under a nitrogen atmosphere was added freshly distilled methacrolein (1.79 g, 25.5 mmol, 1% w/w hydroquinone added) followed by Hoveyda Grubbs 2nd generation catalyst (7.9 mg, 0.013 mmol). A reflux condenser was then placed on the flask and the solution was heated to 50 °C with stirring for 18 h. The mixture was concentrated under reduced pressure and purified twice by silica gel flash column chromatography (once with 5% to 30% EtOAc in hexanes to separate the starting material from the product and homodimer, then with 0% to 3% EtOAc in CH_2Cl_2 to separate the product from the homodimer) to give aldehyde **26** as a viscous semi-solid (79 mg, 31%), recovered **25** (91 mg, leading to a 59% BRSM), and the homodimer of **25** (40 mg).

IR (ATR, cm^{-1}) 3060, 2963, 2929, 2858, 2718, 1826, 1684, 1640, 1457, 1414, 1124, 823, 737 cm^{-1}

^1H NMR (300 MHz, $CDCl_3$) δ 9.40 (s, 1H), 6.24 (dd, broad, *J* = 10.0, 1.2 Hz, 1H), 4.49 (dddd, *J* = 6.3, 6.3, 6.1, 4.5 Hz, 1H), 3.53 (dd, *J* = 16.3, 5.8 Hz, 1H), 3.06 (dd, *J* = 16.3, 4.3 Hz, 1H), 2.75 (dddq, *J* = 9.9, 9.9, 6.7, 6.7 Hz, 1H), 1.80-1.76 (m, 2H), 1.75 (d, *J* = 1.3 Hz, 3H), 1.59-1.52 (m, 2H), 1.11 (d, *J* = 6.7 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 195.3, 167.9, 158.5, 138.8, 70.9, 43.0, 33.2, 32.8, 31.9, 19.9, 9.6

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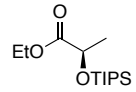
[1] A. Fürstner, F. Feyen, H. Prinz, H. Waldmann, *Tetrahedron* **2004**, *60*, 9543.

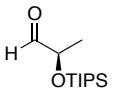
[2] M. A. Calter, *J. Org. Chem.* **1996**, *61*, 8006.

HRMS (ESI) *m*/*z* calcd. for $C_{11}H_{17}O_3$ $[M + H]^+$ 197.1172, found 197.1170
$[\alpha]_D^{22}$ +18.7 (*c* 0.94, $CHCl_3$)



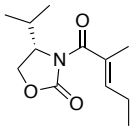
Ethyl (*R*)-2-((triisopropylsilyl)oxy)propanoate (S1)

To a stirred solution of (+)-D-ethyl lactate (7.64 g, 64.7 mmol) in DMF (65 mL) was added imidazole (8.9 g, 130 mmol) and the solution was cooled to 0 °C. To this mixture was added dropwise triisopropylsilyl chloride (13.8 g, 71.5 mmol) and the reaction was stirred for 12 h at rt. The mixture was diluted with water (50 mL) and hexane (300 mL). The organic layer was separated and the aqueous layer was extracted with hexanes (2 x 200mL). The combined organic layers were washed with water (3x) and brine, dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash column chromatography (0% to 10% EtOAc in hexanes) to afford the desired silyl ether **S1** (16.15 g, 91%).
IR (ATR, cm^{-1}) 2942, 2893, 2866, 1756, 1734, 1463, 1371, 1272, 1142, 1061, 970, 881, 677
^1H NMR (500 MHz, $CDCl_3$) δ 4.42 (q, *J* = 6.7 Hz, 1H), 4.21 (dq, *J* = 10.8, 7.1 Hz, 1H), 4.16 (dq, *J* = 10.8, 7.1 Hz, 1H), 1.43 (d, *J* = 6.9 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 1H), 1.16-1.00 (m, 21H)
^{13}C NMR (125 MHz, $CDCl_3$) δ 174.4, 68.7, 60.8, 21.9, 18.0, 17.99, 14.3, 12.3
HRMS (ESI) *m*/*z* calcd. for $C_{14}H_{31}O_3Si$ $[M + H]^+$ 275.2037, found 275.2051
$[\alpha]_D^{21}$ +17.5 (*c* 2.24, $CHCl_3$)
These data match literature values.[3]



(*R*)-2-((Triisopropylsilyl)oxy)propanal (28)

Dry toluene (125 mL) was charged with diisobutylaluminium hydride (1.2 M in toluene, 36.8 mL, 44.2 mmol) and cooled to –78 °C while stirring under a nitrogen atmosphere. A solution of ethyl ester **S1** in toluene (35 mL) was added dropwise over 90 minutes via syringe pump. Following addition, the reaction was allowed to stir for 1 h before quenching with 10 mL MeOH at –78 °C. After 10 minutes sat aq. Rochelle's salt solution (100 mL) was added and the mixture was allowed to warm to rt and stirred until the organic layer was clear. The layers were separated, and the aqueous layer was extracted with Et_2O (2x 50 mL). The combined organic layers were washed with sat. aq. $NaHCO_3$ and brine, dried over Na_2SO_4, filtered and concentrated to yield crude aldehyde **26** as a clear colorless oil (7.60 g, 94%).
^1H NMR (500 MHz, $CDCl_3$) δ 9.66 (d, *J* = 1.7 Hz, 1H), 4.18 (dq, *J* = 6.8, 1.7 Hz, 1H), 1.31 (d, *J* = 6.8 Hz, 3H), 1.16-1.04 (m, 21H)
^{13}C NMR (125 MHz, $CDCl_3$) δ 204.7, 74.0, 19.1, 18.0, 12.3
$[\alpha]_D^{22}$ +9.1 (*c* 2.80, $CHCl_3$)
These data match literature values.[4]



(*S*,*E*)-4-Isopropyl-3-(2-methylpent-2-enoyl)oxazolidin-2-one (S2)

To a stirred solution of (*E*)-methyl-2-pentenoic acid (8.32 g, 72.8 mmol) in THF (350 mL) was added triethylamine (19.66 g, 194.3 mmol) and the mixture was cooled to –78 °C. Trimethyl acetyl chloride (9.15 g, 75.9 mmol) was added slowly

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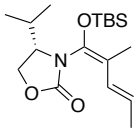
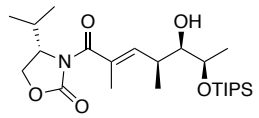
[3] For the enantiomer, see: K. C. Nicolaou, H. J. Mitchell, N. F. Jain, T. Bando, R. Hughes, N. Winssinger, S. Natarajan, A. E. Koumbis, *Chem. Eur. J.* **1999**, *5*, 2648.

[4] E. Richmond, K. B. Ling, N. Duguet, L. B. Manton, N. Celebi-Olcum, Y.-H. Lam, S. Alsancak, A. M. Z. Slawin, K. N. Houk, A. D. Smith, *Org. Biomol. Chem.* **2015**, *13*, 1807.

over ten minutes. The mixture was allowed to warm to rt and was stirred for 60 min. LiCl (3.69 g, 84.99 mmol) and (*S*)-4-isopropyloxazolidin-2-one (7.84 g, 60.70 mmol) were added in a single portion along with additional THF (50 mL). The mixture was stirred until TLC indicated consumption of starting material (65 h) and was quenched with 1:1 water:sat. aq. NH_4Cl. The layers were separated and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash column chromatography (0% to 30% EtOAc in hexanes) to afford the desired oxazolidinone **S2** (12.8 g, 94%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (tq, *J* = 10.7, 1.2 Hz, 1H), 4.55-4.49 (m, 1H), 4.32 (t, *J* = 8.9 Hz, 1H), 4.18 (dd, *J* = 8.9, 5.5 Hz, 1H), 2.43-2.31 (m, 1H), 2.21 (p, *J* = 7.5 Hz, 1H), 1.90 (d, *J* = 0.78 Hz, 3H), 1.06 (t, *J* = 7.5 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.4 Hz, 3H)
^{13}C NMR (125 MHz, $CDCl_3$) δ 172.1, 153.8, 141.3, 130.4, 63.5, 58.4, 28.3, 21.8, 18.0, 15.1, 13.6, 12.9
$[\alpha]_D^{21}$ +75.2 (*c* 5.11, $CHCl_3$)
These data match literature values.[5]



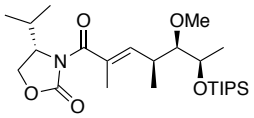
(*S*)-3-((1*E*,3*E*)-1-((*tert*-Butyldimethylsilyl)oxy)-2-methylpenta-1,3-dien-1-yl)-4-isopropyloxazolidin-2-one (27)
To a stirred solution of oxazolidinone **S2** (5.62 g, 25.0 mmol) in THF (166 mL) at –78 °C was added NaHMDS (37.4 mL, 37.4 mmol, 1.0 mol/L in THF) slowly over five minutes. The solution was stirred for 135 min, then TBSCl (freshly distilled, 11.28 g, 74.85 mmol) in THF (20 mL) was added via cannula over ten minutes at –78 °C and the mixture was stirred for an additional 120 min. The reaction was quenched with sat. aq. NH_4Cl and warmed to rt. The layers were separated and the aqueous layer was extracted 2x with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The residue was purified via flash column chromatography (0% to 5% to 10% EtOAc in hexanes). The product co-eluted with unidentified silane impurities, which were removed with a Kugelrohr at 70 to 80 °C under high vacuum (3-5 mmHg) to yield vinylketene silyl *N*,*O*-acetal (**25**) as a viscous clear oil (6.47 g, 76%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.22 (d, broad, *J* = 15.5 Hz, 1H), 5.64 (dq, *J* = 15.5, 6.7 Hz, 1H), 4.32 (t, broad, *J* = 9.0 Hz, 1H), 4.13 (t, broad, *J* = 8.4 Hz, 1H), 4.05-3.95 (m, 1H), 2.01-1.89 (m, 1H), 1.83-1.75 (m, 6H), 0.98 (s, 9H), 0.95-0.92 (m, 6H), 0.20 (s, 3H), 0.15 (s, 3H)
^{13}C NMR (125 MHz, $CDCl_3$) δ 156.0, 134.8, 128.2, 124.4, 115.1, 64.5, 59.5, 29.5, 26.6, 25.8, 18.9,18.4, 16.4, 12.4, -3.5, -4.8
These data match literature values.[5]



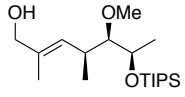
(*S*)-3-((4*S*,5*R*,6*R*,*E*)-5-Hydroxy-2,4-dimethyl-6-((triisopropylsilyl)oxy)hept-2-enoyl)-4-isopropyloxazolidin-2-one (29)
A stirred solution of aldehyde **28** (4.79 g, 20.8 mmol) in CH_2Cl_2 (50 mL) was cooled to –78 °C and $TiCl_4$ (10.4 mL, 10.4 mmol, 1.0 mol/L in CH_2Cl_2) was added dropwise. Vinylketene silyl *N*,*O*-acetal (**27**) (3.52 g, 10.4 mmol) was dissolved in CH_2Cl_2 (50 mL) and cooled to –78 °C. This solution was added dropwise via

[5] C. Jahns, T. Hoffmann, S. Müller, K. Gerth, P. Washausen, G. Höfle, H. Reichenbach, M. Kalesse, R. Müller, *Angew. Chem. Int. Ed.* **2012**, *51*, 5239.

cannula to the aldehyde/$TiCl_4$ solution. The resulting mixture was allowed to warm to –40 °C. After stirring for 20 h, sat. aq. potassium sodium tartrate and sat. aq. $NaHCO_3$ were added in a 1:1 ratio and the mixture was stirred until the organic layer was clear. The layers were separated, and the aqueous layer was extracted 2x with diethyl ether. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified via silica gel flash column chromatography (5% to 20% EtOAc in hexanes) to afford **29** as a clear oil (3.38 g, 71%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.00 (dd, broad, *J* = 9.7, 1.3 Hz, 1H), 4.52 (ddd, *J* = 8.8, 5.2, 4.5 Hz, 1H), 4.31 (t, *J* = 8.9 Hz, 1H), 4.17 (dd, *J* = 9.0, 5.5 Hz, 1H), 4.04 (dq, *J* = 6.1, 4.5 Hz, 1H), 3.20 (ddd, *J* = 6.3, 6.3, 4.3 Hz, 1H), 2.72-2.63 (m, 1H), 2.66 (d, *J* = 6.6 Hz, 1H), 2.36 (dqq, *J* = 7.0, 7.0, 4.5 Hz, 1H), 1.92 (d, *J* = 1.3 Hz, 3H), 1.25 (d, *J* = 6.1 Hz, 3H), 1.11-1.06 (m, 21H), 1.08-1.05 (m, 3H), 0.93 (d, *J* = 7.4 Hz, 3H), 0.91 (d, *J* = 7.4 Hz, 3H)
These data match literature values.[6]



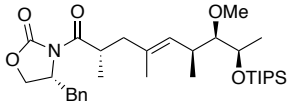
(*S*)-4-Isopropyl-3-((4*S*,5*R*,6*R*,*E*)-5-methoxy-2,4-dimethyl-6-((triisopropylsilyl)oxy)hept-2-enoyl)oxazolidin-2-one (S3)
To a stirred solution of **29** (1.48 g, 3.07 mmol) and 4 Å molecular sieves (2 g) in CH_2Cl_2 (30 mL) was added Proton-sponge® (1.97 g, 9.20 mmol) and Me_3OBF_4 (1.36 g, 9.20 mmol). The reaction was stirred at room temperature while being protected from light for 28 h. Aqueous $NaHCO_3$ was added and the reaction was stirred for 10 min before filtering through Celite. The layers were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with 1 N aq HCl solution and brine, dried over $MgSO_4$, filtered and concentrated. The resulting residue was suspended in EtOAc and filtered through Celite, and concentrated again, and purified via silica gel flash column chromatography (0% to 20% EtOAc in hexanes) to yield methyl ether **S3** as an oil (1.25 g, 87%).
IR (ATR, cm^{-1}) 2963, 2940, 2866, 1784, 1681, 1463, 1365, 1298, 1200, 1093, 1010, 881, 679
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (d, broad, *J* = 9.9, 1.4 Hz, 1H), 4.47 (ddd, *J* = 8.7, 4.4, 4.4 Hz, 1H), 4.30 (dd, *J* = 8.9, 8.9 Hz, 1H), 4.18 (dd, *J* = 8.9, 4.8 Hz, 1H), 4.08 (dq, *J* = 6.2, 6.1 Hz, 1H), 3.46 (s, 3H), 3.03 (dd, *J* = 3.8, 5.3 Hz, 1H), 2.76 (dqd, *J* = 9.6, 6.9, 4.0 Hz, 1H), 2.42 (dqq, *J* = 7.0, 7.0, 4.2 Hz, 1H), 1.92 (d, *J* = 1.4 Hz, 3H), 1.18 (d, *J* = 6.2 Hz, 3H) 1.10-1.05 (m, 21H), 1.03 (d, *J* = 6.9 Hz, 1H), 0.93 (d, *J* = 7.1 Hz, 3H), 0.91 (d, *J* = 7.0 Hz, 3H)
^{13}C NMR (125 MHz, $CDCl_3$) δ 172.1, 153.6, 142.4, 128.7, 87.9, 69.6, 63.5, 60.5, 58.7, 34.1, 28.5, 19.8, 18.4, 18.3, 18.1, 15.1, 14.4, 13.8, 12.8
HRMS (ESI) *m*/*z* calcd. for $C_{25}H_{48}O_5NSi$ $[M + H]^+$ 470.3296, found 470.3301
$[\alpha]_D^{21}$ +31.1 (*c* 0.63, $CHCl_3$)



(4*S*,5*R*,6*R*,*E*)-5-Methoxy-2,4-dimethyl-6-((triisopropylsilyl)oxy)hept-2-en-1-ol (S4)
To a stirred solution of **S3** (3.42 g, 7.27 mmol) in Et_2O (30 mL) was added MeOH (0.35 g, 11 mmol) and the solution was cooled to 0 °C. $LiBH_4$ (5.5 mL, 11 mmol, 2.0 mol/L in THF) was added slowly over five min. The reaction was stirred for 45 min at which

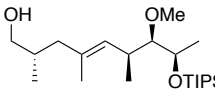
[6] M. Shinoyama, S.-i. Shirokawa, A. Nakazaki, S. Kobayashi, *Org. Lett.* **2009**, *11*, 1277.

time TLC indicated starting material consumption. Sat. aq. NH_4Cl was added along with some water to dissolve any solid. The layers were separated and the aqueous layer was extracted 3x with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The residue was purified via silica gel flash column chromatography (5% EtOAc in hexanes) to yield alcohol (**S4**) as an oil (2.38 g, 95%).
IR (ATR, cm^{-1}) 3420, 2961, 2945, 2859, 1458, 1379, 1263, 1093, 1034, 927, 734, 680
^1H NMR (400 MHz, $CDCl_3$) δ 5.46 (dq, *J* = 9.6, 1.2 Hz, 1H), 4.06 (dq, *J* = 6.3, 4.8 Hz, 1H), 3.99 (d, *J* = 6.2 Hz, 2H), 3.44 (s, 3H), 2.91 (dd, *J* = 6.3, 4.7 Hz, 1H), 2.64 (ddq, *J* = 9.5, 6.7, 6.6 Hz, 1H), 1.69 (d, *J* = 1.2 Hz, 3H), 1.22 (t, *J* = 6.3 Hz, 1H), 1.16 (d, *J* = 6.3 Hz, 3H), 1.11-1.06 (m, 21H), 0.99 (d, *J* = 6.8 Hz, 3H)
^{13}C NMR (125 MHz, $CDCl_3$) δ 132.4, 130.8, 89.2, 69.5, 69.4, 60.1, 33.6, 19.4, 18.3, 18.3, 16.6, 13.8, 12.7
HRMS (ESI) *m*/*z* calcd. for $C_{19}H_{41}O_3Si$ $[M + H]^+$ 345.2820, found 345.2803
$[\alpha]_D^{22}$ +7.4 (*c* 7.87, $CHCl_3$)



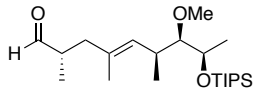
(*R*)-4-Benzyl-3-((2*S*,6*S*,7*R*,8*R*,*E*)-7-methoxy-2,4,6-trimethyl-8-((triisopropylsilyl)oxy)non-4-enoyl)oxazolidin-2-one (S5)
In a round bottom flask, alcohol **S4** (0.900 g, 2.61 mmol) was dissolved in diethyl ether (28 mL) and CH_3CN (7 mL) and cooled to 0 °C. Triphenylphosphine (1.025 g, 3.91 mmol), imidazole (0.266 g, 3.91 mmol) were added and the solution was stirred until all reagents had solubilized. Iodine (0.861 g, 3.39 mmol) was added to the solution in two portions over 10 minutes. The reaction was allowed to warm to rt, and stirred for 45 min, until alcohol **S4** was consumed as determined by TLC. Saturated aqueous $Na_2S_2O_3$ was added and the mixture was stirred for 15 min. The layers were separated and the aqueous layer was extracted twice with EtOAc. The organic layers were combined, washed with sat. aq. NH_4Cl and brine, dried over $MgSO_4$, filtered and concentrated. The crude oil-solid mixture was loaded onto a silica plug and eluted with hexanes:EtOAc (98:2, v:v). The fractions were concentrated and allylic iodide **28** was used immediately in the next reaction.
A solution of NaHMDS (3.9 mL, 3.9 mmol, 1 mol/L in THF) in THF (4 mL) at –78 °C was slowly added via cannula a solution of (*R*)-4-benzyl-3-propionyloxazolidin-2-one (0.913 g, 3.92 mmol) in THF (4 mL) at –78 °C. The solution was stirred for 30 min and then to it was added via cannula a solution of allylic iodide (~2.61 mmol) in THF (5 mL). The solution was stirred at –78 °C for 135 min and then warmed to –40 °C and stirred for an additional 105 min. The reaction was quenched with sat. aq. NH_4Cl and warmed to rt. The layers were separated and the aqueous layer was extracted with EtOAc (3x). The organic layers were washed with sat. aq. $Na_2S_2O_3$ and brine, dried over Na_2SO_4, filtered and concentrated. The resulting residue was purified via silica gel flash column chromatography (0% to 20% EtOAc in hexanes) to yield **S5** as a viscous oil (0.897 g, 61% over two steps).
IR (ATR, cm^{-1}) 2964, 2939, 2866, 1777, 1698, 1455, 1383, 1208, 1090, 882, 734, 701
^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.3 Hz, 2H), 7.28 (t, *J* = 6.7 Hz, 1H), 7.22 (d, *J* = 7.1 Hz, 2H), 5.32 (d, broad, *J* = 9.4 Hz, 1H), 4.69 (dddd, *J* = 9.7, 7.6, 3.3, 2.9 Hz, 1H), 4.23-4.15 (m, 1H), 4.19-4.10 (m, 1H), 4.06-3.99 (m, 1H), 4.02-3.93 (m, 1H), 3.45 (s, 3H), 3.31 (dd, *J* = 13.4, 3.2 Hz, 1H), 2.89 (t, *J* = 5.1 Hz, 1H), 2.70 (dd, *J* = 13.3, 9.9 Hz, 1H), 2.67-2.58 (m, 1H), 2.55 (dd, *J* = 13.1, 6.2 Hz, 1H), 2.01 (dd, *J* = 13.1, 8.2 Hz, 1H), 1.69 (d, *J* = 0.9 Hz, 3H), 1.17 (d, *J* = 6.4 Hz, 3H), 1.14 (d, *J* = 6.8 Hz, 3H), 1.10-1.05 (m, 21H), 0.93 (d, *J* = 6.8 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 177.3, 153.3, 135.6, 132.6, 130.1, 129.6, 129.1, 127.5, 89.7, 69.9, 66.1, 60.5, 55.6, 44.2, 38.3, 35.9, 33.8, 20.0, 18.4, 18.3, 16.6, 16.0, 15.7, 12.8
HRMS (ESI) *m*/*z* calcd. for $C_{32}H_{54}O_5NSi$ $[M + H]^+$ 560.3766, found 560.3744
$[\alpha]_D^{21}$ −20.5 (*c* 8.08, $CHCl_3$)



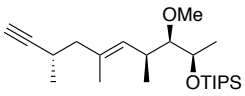
(2*S*,6*S*,7*R*,8*R*,*E*)-7-Methoxy-2,4,6-trimethyl-8-((triisopropylsilyl)oxy)non-4-en-1-ol (**S6**)

To a stirred solution of **S5** (0.897 g, 1.60 mmol) in Et_2O (6.4 mL) was added MeOH (0.076 g, 2.4 mmol). The mixture was cooled to 0 °C then $LiBH_4$ (1.2 mL, 2.4 mmol, 2.0 mol/L in THF) was added slowly over five min. The reaction was stirred for 105 min until TLC indicated consumption of the starting material. NaOH (2.8 mL, 3M) was added and the solution was warmed slowly to rt. The mixture was diluted with EtOAc and water. The layers were separated and the aqueous layer was extracted 3x with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The residue was purified via silica gel flash column chromatography (1% to 10% EtOAc in hexanes) to yield alcohol (**S6**) as an oil (0.55 g, 88%).
IR (ATR, cm^{-1}) 3417, 2943, 2868, 1463, 1382, 1265, 1093, 883, 740
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.25 (d, broad, *J* = 9.4 Hz, 1H), 4.04 (dq, *J* = 6.3, 5.9 Hz, 1H), 3.54-3.48 (m, 1H), 3.45 (s, 3H), 3.45-3.39 (m, 1H), 2.89 (t, *J* = 5.3 Hz, 1H), 2.62 (ddq, *J* = 9.4, 6.7, 6.3 Hz, 1H), 2.05 (dd, *J* = 12.4, 6.4 Hz, 1H), 1.91-1.82 (m, *J* = 6.6 Hz, 1H), 1.83 (dd, *J* = 12.4, 7.1 Hz, 1H), 1.63 (d, *J* = 1.1 Hz, 3H), 1.43-1.37 (m, broad, 1H), 1.17 (d, *J* = 6.4 Hz, 3H), 1.12-1.04 (m, 21H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.5 Hz, 3H)
^{13}C NMR (125 MHz, $CDCl_3$) δ 131.7, 131.1, 89.7, 69.7, 68.7, 60.4, 44.7, 33.9, 33.8, 19.8, 18.4, 18.3, 17.1, 16.3, 16.1, 12.8
HRMS (ESI) *m*/*z* calcd. for $C_{22}H_{47}O_3Si$ $[M + H]^+$ 387.3289, found 387.3291
$[\alpha]_D^{22}$ +6.2 (*c* 4.13, $CHCl_3$)



(2*S*,6*S*,7*R*,8*R*,*E*)-7-methoxy-2,4,6-trimethyl-8-((triisopropylsilyl)oxy)non-4-enal (S7)

To a solution of alcohol **S6** (0.37 g, 1.0 mmol) in CH_2Cl_2 (10 mL) was added $NaHCO_3$ (1.01 g, 12.0 mmol) and the mixture was cooled to 0 °C. Dess-Martin periodinane (0.721 g, 1.70 mmol) was added and the reaction was stirred until TLC showed consumption of the starting alcohol (1.5 h). The mixture was filtered through a silica gel plug eluting with (10% EtOAc in hexanes). The fractions were concentrated to give aldehyde (**S7**) (0.28 g, 76%)
IR (ATR, cm^{-1}) 2936, 2866, 1727, 1459, 1382, 1092, 1000, 911, 882, 732, 677
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.62 (d, *J* = 2.1 Hz, 1H), 5.28 (dq, *J* = 9.3, 1.2 Hz, 1H), 4.04 (dq, *J* = 6.2, 5.3 Hz, 1H), 3.44 (s, 3H), 2.88 (t, *J* = 5.2 Hz, 1H), 2.61 (ddq, *J* = 9.6, 6.7, 6.3 Hz, 1H), 2.53 (dqd, *J* = 13.8, 7.2, 2.1 Hz, 1H), 2.42 (dd, broad, *J* = 13.8, 6.9 Hz, 1H), 1.99 (dd, broad, *J* = 13.8, 7.9 Hz, 1H), 1.63 (d, *J* = 1.2 Hz, 3H), 1.16 (d, *J* = 6.9 Hz, 3H), 1.10-1.07 (m, 21H), 1.06 (d, *J* = 6.9 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H)
^{13}C NMR (125 MHz, $CDCl_3$) δ 205.3, 132.4, 129.3, 89.6, 69.7, 60.4, 44.7, 41.2, 33.9, 19.7, 18.4, 18.3, 16.3, 16.1, 13.5, 12.8
HRMS (ESI) *m*/*z* calcd. for $C_{22}H_{45}O_3Si$ $[M + H]^+$ 385.3133, found 385.3148
$[\alpha]_D^{22}$ +13.2 (*c* 0.82, $CHCl_3$)



Triisopropyl(((2*R*,3*R*,4*S*,8*S*,*E*)-3-methoxy-4,6,8-trimethyldec-5-en-9-yn-2-yl)oxy)silane (31)

The Ohira-Bestmann reagent (dimethyl (1-diazo-2-oxopropyl)phosphonate)[7] (0.56 g, 2.9 mmol) was dissolved in THF (9.6 mL) and cooled to –78 °C.[8] To this solution was added freshly made sodium methoxide (1.95 mL, 2.89 mmol, 1.48 mol/L solution in MeOH). The solution was stirred for 15 min and then aldehyde **S7** (0.28 g, 0.76 mmol) in THF (3.3 mL) was added via cannula at –78 °C. The resulting solution was allowed to slowly warm to –40 °C over 45 min until TLC showed consumption of the aldehyde. The reaction was quenched with sat. aq. NH_4Cl and the layers were separated. The aqueous layer was extracted 3x with EtOAc, and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The resulting residue was purified via silica gel flash column chromatography (0% to 5% EtOAc in hexanes) to yield the desired alkyne **31** (0.268 g, 96%).

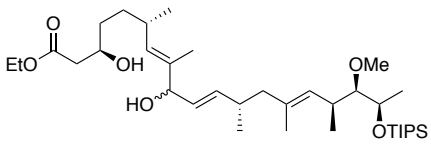
IR (ATR, cm^{-1}) 3313, 2932, 2866, 1460, 1381, 999, 882

^1H NMR (500 MHz, $CDCl_3$) δ 5.28 (dq, *J* =9.4, 1.2 Hz, 1H), 4.04 (dq, *J* = 6.3, 5.3 Hz, 1H), 3.45 (s, 3H), 2.89 (t, *J* = 5.3 Hz, 1H), 2.65-2.58 (m, 1H), 2.63-2.56 (m, 1H), 2.19 (ddd, *J* = 13.4, 7.7, 0.8 Hz, 1H), 2.06 (ddd, *J* = 13.3, 7.2, 0.7 Hz, 1H), 2.03 (d, *J* = 2.4 Hz, 1H), 1.63 (d, *J* = 1.3 Hz, 3H), 1.17 (d, *J* = 6.3 Hz, 3H), 1.16 (d, *J* = 6.9 Hz, 3H), 1.10-1.06 (m, 21H), 0.97 (d, *J* = 6.8 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 132.0, 130.1, 89.7, 89.3, 69.8, 68.4, 60.4, 47.0, 33.8, 24.5, 20.7, 19.8, 18.4, 18.3, 16.3, 16.1, 12.8

HRMS (ESI) *m*/*z* calcd. for $C_{22}H_{45}O_3Si$ $[M + H]^+$ 381.3183, found 381.3163

$[\alpha]_D^{21}$ +4.7 (*c* 0.55, $CHCl_3$)



Ethyl (3*R*,6*S*,7*E*,10*E*,12*S*,14*E*,16*S*,17*R*,18*R*)-3,9-dihydroxy-17-methoxy-6,8,12,14,16-pentamethyl-18-((triisopropylsilyl)oxy)nonadeca-7,10,14-trienoate (32)

To a solution of alkyne **31** (0.248 g, 0.651 mmol) in CH_2Cl_2 (2.2 mL) under argon at rt was added zirconocene hydrochloride (0.192 g, 0.745 mmol). The mixture was stirred at rt for 15 min until a homogenous solution formed, then was placed in a –78 °C bath for 5 min. Dimethyl zinc (0.65 mL, 0.78 mmol, 1.2 M in toluene) was added slowly over 5 min. The reaction mixture was stirred for 20 min and warmed slightly, before being placed back in the –78 °C bath. Aldehyde **26** (0.169 g, 0.861 mmol) in CH_2Cl_2 (2.2 mL) was added and the reaction was placed in a 0 °C ice bath 1 h. The reaction was placed in a –15 °C freezer for 16h, then placed in a 0 °C ice bath for an additional 5.5 h. The reaction mixture was transferred slowly via cannula at 0 °C to a freshly prepared solution of sodium ethoxide (0.045 g Na, 1.95 mmol in 13 mL EtOH). the reaction was allowed to stir for 10 min before being quenched with 10 mL sat. aq. NH_4Cl solution. The mixture was warmed to rt and diluted with 10 mL EtOAc and 3 mL H_2O. The reaction mixture was filtered through silica gel eluting with EtOAc to clear an emulsion, and the layers were separated. The aqueous layer was extracted 3x with EtOAc. The combined organic

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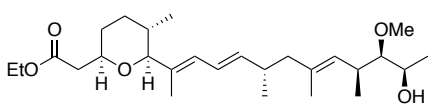
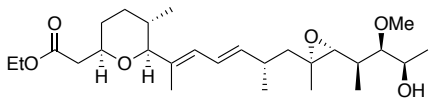
[7] S. Müller, B. Liepold, G. J. Roth, H. J. Bestmann, *Synlett* **1996**, *1996*, 521

[8] Low temperature protocol: B. M. Trost, J. D. Sieber, W. Qian, R. Dhawan, Z. T. Ball, *Angew. Chem. Int. Ed.* **2009**, *48*, 5478-5481.

layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The resulting residue was purified via silica gel column chromatography (0 to 15 to 30% EtOAc in hexanes) to yield as allylic alcohol **32** (0.294 g, 72%) as a mixture of two diastereomers.
IR (ATR, cm^{-1}) 3446, 2961, 2929, 2868, 1720, 1458, 1375, 1216, 1095
^1H NMR (500 MHz, $CDCl_3$) *denotes signals with distinct diastereomer peaks δ 5.59 (dd, broad, *J* = 15.5, 7.3 Hz, 1H), 5.41 (dd, broad, *J* = 15.5, 6.4 Hz, 1H), 5.22 (2* d, broad, *J* = 9.5 Hz, 1H), 5.19 (d, broad, *J* = 9.4 Hz, 1H), 4.42 (d, *J* = 6.3 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.02 (dq, *J* = 5.7, 6.2 Hz, 1H), 4.00-3.94 (m, 1H), 3.44 (s, 3H), 2.93 (m, broad,1H), 2.87 (2* t, *J* = 5.2 Hz, 1H), 2.64-2.54 (m, 1H), 2.52-2.44 (m, 1H), 2.44-2.37 (m, 1H), 2.40-2.29 (m, 2H), 2.04-1.97 (m, 1H), 1.93-1.86 (m, 1H), 1.60-1.56 (m, 6H), 1.54-1.45 (m, 2H), 1.44-1.38 (m, 2H), 1.38-1.34 (m,1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.16 (2* d, *J* = 6.3 Hz, 3H), 1-10-1.05 (m, 21H), 0.99-0.96 (m, 3H), 0.96-0.94 (m, 3H), 0.94-0.92 (m, 3H)
^{13}C NMR (125 MHz, $CDCl_3$) δ 173.2, 138.2*, 138.1, 135.7, 135.6*, 132.1, 131.9*, 131.22, 131.21*, 131.17, 129.16*, 129.0, 89.8, 78.3, 78.2*, 69.8, 68.2, 60.8, 60.4, 47.7, 41.4, 34.6, 34.5, 34.4*, 33.7, 33.3*, 33.2, 32.1*, 32.0, 21.2*, 21.17, 20.16, 20.07*, 19.9*, 19.8, 18.4, 18.3, 16.34*, 16.31, 16.12, 16.10*, 14.3, 12.8, 12.6*, 12.5
HRMS (ESI) *m*/*z* calcd. for $C_{36}H_{68}O_6SiNa$ $[M + Na]^+$ 647.4677, found 647.4663
$[\alpha]_D^{22}$ –4.1 (*c* 0.86, $CHCl_3$)

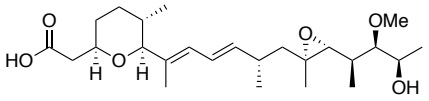


14,15-Desoxy (+)-herboxidiene ethyl ester (33)
To a solution of bis allylic alcohol **30** (0.170 g, .272 mmol) in methylene chloride (5.4 mL) at rt was added Re_2O_7 (13.1 mg, 2.72 μmol, 10% w/w on SiO_2) and the mixture was stirred for 68 h. At the 22 h and 48 h mark, additional portions of Re_2O_7 (13.1 mg 6.56 μmol, 10% w/w on SiO_2) were added to increase the rate of silyl ether cleavage. The mixture was filtered through a short path of silica gel (~2 cm) eluting with DCM. The solvent was removed under vacuum, and the resulting crude material was purified by silica gel column chromatography (5% to 30% EtOAc in hexanes) to yield **33** as a clear oil (0.101 g, 82%).
IR (ATR, cm^{-1}) 3475, 2968, 2927, 2871, 1735, 1455, 1371, 1194, 1091, 1069, 1031, 966, 737
^1H NMR (500 MHz, $CDCl_3$) δ 6.18 (ddd, *J* = 15.1, 10.8, 0.9 Hz, 1H), 5.90 (d, *J* = 10.7 Hz, 1H), 5.53 (dd, *J* = 14.9, 7.3 Hz, 1H), 4.97 (dd, *J* = 9.6, 0.9 Hz, 1H), 4.14 (dq, *J* = 10.9, 7.1, Hz, 1H), 4.11 (dq, *J* = 10.9, 7.1, Hz, 1H), 3.79-3.74 (m, 1H), 3.72 (qd, *J* =6.4, 4.3 Hz, 1H), 3.51 (s, 3H), 3.33 (d, *J* = 9.9 Hz, 1H), 2.71 (dd, *J* = 6.8, 4.1 Hz, 1H), 2.69-2.61 (m, 1H), 2.58 (dd, *J* = 15.1, 6.2 Hz, 1H), 2.43-2.36 (m, 1H), 2.39 (dd, *J* = 15.1, 6.9 Hz, 1H), 2.21-2.06 (s, broad, 1H), 2.02 (dd, *J* = 13.2, 7.3 Hz, 1H), 1.92 (dd, *J* = 13.3, 7.5 Hz, 1H), 1.84 (qd, *J* = 12.8, 3.4 Hz, 1H), 1.71 (d, *J* = 1.0 Hz, 3H), 1.69-1.66 (m, 1H), 1.61 (d, *J* = 1.6 Hz, 3H), 1.59-1.48 (m, 1H), 1.39-1.28 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.24-1.17(m, 1H), 1.20 (d, *J* = 6.5 Hz, 3H), 0.96 (d, *J* = 6.7, 3H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.69 (d, *J* = 6.7 Hz, 3H)
^{13}C NMR (125 MHz, $CDCl_3$) δ 171.6, 140.4, 134.5, 133.8, 129.8, 128.5, 124.2, 90.7, 89.9, 74.08, 68.1, 61.6, 60.4, 47.8, 41.8, 35.1, 35.0, 32.5, 32.3, 31.8, 20.6, 20.2, 17.8, 16.7, 16.4, 14.4, 12.2
HRMS (ESI) *m*/*z* calcd. for $C_{27}H_{47}O_5$ $[M + H]^+$ 451.3418, found 451.3400
$[\alpha]_D^{22}$ +11.9 (*c* 1.23, $CHCl_3$)



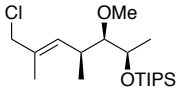
(+)-Herboxidiene ethyl ester (S8)
To a solution of alcohol **33** (0.125 g, 0.276 mmol) in CH_2Cl_2 (2.7 mL) was added $VO(acac)_2$ (0.015 g, 0.055 mmol) and

the mixture was cooled to –78 °C. *t*-BuOOH (0.150 mL, 0.83 mmol, 5.5 mol/L in decane) was added and the mixture was put in a –15 °C freezer for 15 h. The reaction was placed in an ice bath and quenched with 1 mL Me_2S, and was stirred for 1 h. The mixture was concentrated under reduced pressure and the residue was purified via silica gel flash column chromatography (10% to 50% EtOAc in hexanes) to yield herboxidiene ethyl ester as an oil (83 mg, 64%).
IR (ATR, cm^{-1}) 3516, 3051, 2973, 2929, 2872, 2852, 1735, 1456, 1384, 1272, 1195, 1158, 1092, 1068, 1032, 968, 737, 703
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.23 (dd, *J* = 15.0, 10.9 Hz, 1H), 5.88 (d, *J* = 10.8 Hz, 1H), 5.43 (dd, *J* = 15.0, 8.8 Hz, 1H), 4.13 (dq, *J* = 10.9, 7.1 Hz, 1H), 4.10 (dq, *J* = 10.9, 7.1 Hz, 1H), 3.85 (p, *J* = 6.2 Hz, 1H), 3.80-3.72 (m, 1H), 3.53 (s, 3H), 3.32 (d, *J* = 9.8 Hz, 1H), 2.97 (t, *J* = 5.4 Hz, 1H), 2.57 (dd, *J* = 15.2, 6.1 Hz, 1H), 2.55 (d, *J* = 9.7 Hz, 1H), 2.55 (m, OH, 1H), 2.45-2.37 (m, 1H), 2.38 (dd, *J* = 15.1, 6.9 Hz, 1H), 1.89 (dd, *J* = 13.6, 4.7 Hz, 1H), 1.84 (dq, *J* = 13.1, 3.4 Hz, 1H), 1.70 (s, 3H), 1.69-1.66 (m, 1H), 1.60-1.50 (m, 1H), 1.55-1.46 (m, 1H), 1.41-1.28 (m, 1H), 1.28 (s, 3H), 1.27-1.21 (m, 1H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.21-1.19 (m, 1H), 1.18 (d, *J* = 6.5 Hz, 3H), 1.04 (d, *J* = 6.7 Hz, 3H), 0.87 (d, *J* = 6.9 Hz, 3H), 0.66 (d, *J* = 6.6 Hz, 3H)
^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5, 139.3, 135.4, 128.2, 125.3, 90.7, 87.7, 74.0, 68.4, 66.2, 61.4, 61.4, 60.4, 47.0, 41.7, 35.4, 35.2, 32.4, 32.2, 31.8, 22.2, 19.1, 17.7, 16.7, 14.3, 12.0, 12.0
HRMS (ESI) *m*/*z* calcd. for $C_{27}H_{47}O_6$ $[M + H]^+$ 467.3367, found 467.3338
$[\alpha]_D^{22}$ +4.9 (*c* 2.21, $CHCl_3$)



(+)-Herboxidiene (22)

To a solution of herboxidiene ethyl ester (**S8**) (26 mg, 0.055 mmol) in MeOH (4 mL) and water (1 mL) was added powdered potassium carbonate (46 mg, 0.33 mmol). The mixture was heated to reflux for 1.5 h, then cooled to rt. The mixture was diluted with EtOAc and water, and carefully acidified with a few drops of 10% aq. HCl. The layers were separated and the aqueous layer was extracted 3x with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The resulting residue was purified via silica gel column chromatography (gradient elution, 0% to 30% acetone in dichloromethane, then 2% MeOH and 30% acetone in dichloromethane) to yield (+)-herboxidiene as a clear oil (21 mg, 85%).
IR (ATR, cm^{-1}) 3463, 2965, 2927, 2873, 2852, 1715, 1456, 1383, 1309, 1246, 1198, 1154, 1069, 1018, 968, 905, 798, 736
^{1}H NMR (500 MHz, MeOD) δ 6.30 (dd, *J* = 15.0, 10.8 Hz, 1H), 5.92 (d, *J* = 11.0 Hz, 1H), 5.48 (dd, *J* = 15.0, 9.1 Hz, 1H), 3.79 (p, *J* = 6.4 Hz, 1H), 3.79-3.74 (m, 1H), 3.53 (s, 3H), 3.35 (d, *J* = 9.9 Hz, 1H), 2.98 (dd, *J* = 6.3, 4.2 Hz, 1H), 2.66 (d, *J* = 9.5 Hz, 1H), 2.47 (dd, *J* = 15.0, 7.7 Hz, 1H), 2.50-2.42 (m, 1H), 2.39 (dd, *J* = 15.3, 5.6 Hz, 1H), 1.93 (dd, *J* = 13.5, 4.3 Hz, 1H), 1.86 (dq, *J* = 12.3, 3.3 Hz, 1H), 1.75-1.70 (m, 1H), 1.70 (s, 3H), 1.60-1.53 (m, 1H), 1.53-1.45 (m, 1H), 1.41-1.30 (m, 1H), 1.28 (s, 3H), 1.31-1.22 (m, 1H), 1.19 (dd, *J* = 13.4, 10.8 Hz, 1H), 1.11 (d, *J* = 6.5 Hz, 3H), 1.05 (d, *J* = 6.7 Hz, 3H), 0.83 (d, *J* = 7.2 Hz, 3H), 0.83 (d, *J* = 6.7 Hz, 3H)
^{13}C NMR (100 MHz, MeOD) δ 175.2, 140.7, 136.2, 129.6, 126.5, 92.2, 88.5, 75.5, 69.9, 67.9, 62.6, 61.9, 48.1, 42.3, 36.5, 36.4, 33.4, 33.4, 32.8, 22.7, 19.8, 18.1, 16.8, 12.1, 11.6
HRMS (ESI) *m*/*z* calcd. for $C_{25}H_{43}O_6$ $[M + H]^+$ 439.3054, found 439.3047
$[\alpha]_D^{22}$ +4.2 (*c* 0.95, MeOH)



(((2*R*,3*R*,4*S*,*E*)-7-Chloro-3-methoxy-4,6-dimethylhept-5-en-2-yl)oxy)triisopropylsilane (34)

To a solution of alcohol **S6** (0.559 g, 1.62 mmol) in 2,6-lutidine (0.260 g, 2.43 mmol) at 0 °C was added a sonicated solution of dried LiCl (0.096 g, 2.3 mmol) in DMF (2 mL). The reaction was stirred for 20 min, then methanesulfonyl chloride (0.250 g, 2.18 mmol) was added and the mixture was allowed to warm to rt. After 4 h TLC showed incomplete conversion to the desired chloride, and an additional 0.80 mmol of each LiCl, 2,6-lutidine, and $MeSO_2Cl$ were added to the reaction. After an additional 3 h, the reaction was quenched with water and diluted with diethyl ether. The layers were separated and the aqueous layer was extracted 3x with diethyl ether. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The residue was purified via silica gel flash column chromatography (0% to 5% EtOAc in hexanes) to yield allylic chloride (**34**) as an oil (0.54 g, 92%).

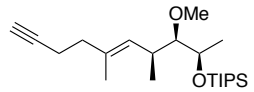
IR (ATR, cm^{-1}) 2943, 2867, 1462, 1383, 1115, 1094, 1014, 883, 682

^1H NMR (400 MHz, $CDCl_3$) δ 5.58 (d, J = 9.8 Hz, 1H), 4.05 (dq, J = 5.1, 6.3 Hz, 1H), 4.01 (s, 2H), 3.44 (2, 3H), 2.91 (dd, J = 4.8, 6.2 Hz, 1H), 2.60 (ddq, J = 9.6, 6.7, 6.6 Hz, 1H), 1.2 (d, J = 1.2 Hz, 3H), 1.15 (d, J = 6.4 Hz, 3H), 1.10-1.05 (m, 21H), 0.99 (d, J = 6.7 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 134.9, 129.2, 89.0, 69.2, 60.2, 53.0, 34.1, 19.3, 18.4, 18.3, 16.2, 14.2, 12.7

HRMS (ESI) m/z calcd. for $C_{19}H_{40}O_2ClSi$ $[M + H]^+$ 363.2481, found 363.2507

$[\alpha]_D^{22}$ +11.1 (*c* 0.55, $CHCl_3$)



Triisopropyl(((2*R*,3*R*,4*S*,*E*)-3-methoxy-4,6-dimethyldec-5-en-9-yn-2-yl)oxy)silane (35)

To a solution of 1-(trimethylsilyl)propyne (0.16 g, 1.46 mmol) in THF (7.0 mL) at –78 °C was added ^{n}BuLi (0.9 mL, 1.44 mmol, 1.6 mol/L in hexanes) via syringe over 1 min. The mixture was stirred for 50 min at –78 °C, removed from the cooling bath for 30 min, then cooled back to –78 °C. A solution of allylic chloride **34** (0.105 g, 0.29 mmol) in THF (1.5 mL) was added via syringe. The reaction was allowed to warm slowly from –78 °C to –5 °C over 3.5 h, after which TLC showed complete consumption of the chloride. Methanol (0.92 g, 29 mmol) was added along with powdered potassium carbonate (0.40 g, 2.9 mmol) and the reaction was concentrated under reduced pressure to remove most of the THF. The resulting residue was dissolved in methanol (5.0 mL) and was stirred at rt for 3.5 h. The reaction was diluted with water (5 mL) and the mixture was extracted 3x with EtOAc, and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified via silica gel flash column chromatography (0% to 5% EtOAc/hexanes) to yield the desired alkyne **35** as an oil (0.101 g, 95%).

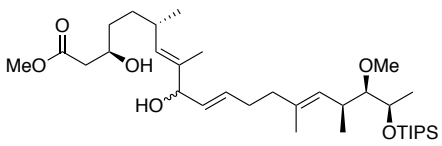
IR (ATR, cm^{-1}) 3314, 2941, 2866, 1462, 1382, 1092, 999, 882, 626

^1H NMR (400 MHz, $CDCl_3$) δ 5.25 (d, broad, J = 9.4 Hz, 1H), 4.03 (dq, J = 6.3, 5.3 Hz, 1H), 3.45 (s, 3H), 2.88 (t, J = 5.3 Hz, 1H), 2.60 (ddq, J = 9.4, 6.6, 6.4 Hz, 1H), 2.32-2.24 (m, 2H), 2.23-2.17 (m, 2H), 1.94 (t, J = 2.5 Hz, 1H), 1.63 (d, J = 0.96 Hz, 3H), 1.16 (d, J = 6.3 Hz, 3H), 1.10-1.05 (m, 21H), 0.96 (d, J = 6.8 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 131.0, 130.5, 89.6, 84.6, 69.7, 68.4, 60.4, 38.7, 33.8, 19.8, 18.4, 18.3, 17.8, 16.4, 16.0, 12.8

HRMS (ESI) m/z calcd. for $C_{22}H_{43}O_2Si$ $[M + H]^+$ 367.3027, found 367.3047

$[\alpha]_D^{22}$ +2.8 (*c* 1.08, $CHCl_3$)



Methyl (3*R*,6*S*,7*E*,10*E*,14*E*,16*S*,17*R*,18*R*)-3,9-dihydroxy-17-methoxy-6,8,14,16-tetramethyl-18-((triisopropylsilyl)oxy)nonadeca-7,10,14-trienoate (S9)

To a solution of alkyne (**35**) (0.377 g, 1.02 mmol) in CH_2Cl_2 (3.0 mL) under argon at rt was added zirconocene hydrochloride (0.289 g, 1.12 mmol). The mixture was stirred at rt for 15 min until a homogenous solution formed, then was placed in a –78 °C bath for 5 min. Dimethyl zinc (1.0 mL, 1.2 mmol, 1.2 mol/L in toluene) was added slowly over 5 min. The reaction mixture was stirred for 30 min and warmed slightly, before being placed back in the –78 °C bath. Aldehyde **26** (0.219 g, 1.12 mmol) in CH_2Cl_2 (3.0 mL) was added and the reaction was placed in a 0 °C ice bath for 5 h. After TLC indicated that no more product formation was occurring, the reaction was transferred slowly via cannula to a freshly prepared 0 °C solution of sodium methoxide (0.070 g Na, 3.06 mmol in 20 mL MeOH). Following cannula transfer, the reaction was allowed to stir for 5 min before being quenched with 12 mL sat. aq. NH_4Cl solution. The mixture was warmed to rt and 4 mL of sat. aq. $NaHCO_3$ was added. The reaction mixture was filtered through silica gel to clear an emulsion and the layers were separated. The aqueous layer was extracted 3x with EtOAc. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The resulting residue was purified via silica gel column chromatography (10% to 40% EtOAc in hexanes) to yield as an oil bis allylic alcohol **S9** (0.391 g, 64%) as a mixture of two diastereomers.

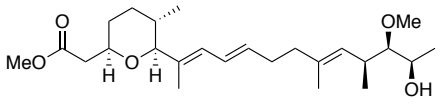
IR (ATR, cm^{-1}) 3428, 2930, 2867, 1740, 1437, 1382, 1292, 1155, 1094, 999, 883, 680 cm^{-1}

^1H NMR (500 MHz, $CDCl_3$) δ 5.68 (dt, broad, *J* = 15.4, 6.6 Hz, 1H), 5.46 (dd, broad, *J* = 15.5, 6.4 Hz, 1H), 5.22 (d, broad, *J* = 9.6 Hz, 1H), 5.19 (d, *J* = 9.6 Hz, 1H), 4.43 (d, broad, *J* = 5.9 Hz, 1H), 4.06-4.00 (m, 1H), 4.01-3.95 (m, 1H), 3.72 (s, 3H), 3.44 (s, 3H), 2.89-2.85 (m, 1H), 2.85-2.83 (m, 1H), 2.64-2.55 (m, 1H), 2.54-2.47 (m, 1H), 2.45-2.39 (m, 1H), 2.42-2.34 (m, 1H), 2.19-2.11 (m, 2H), 2.07-2.00 (m, 2H), 1.61 (s, 3H), 1.59 (s, 3H), 1.57-1.53 (m, 1H), 1.52-1.44 (m, 2H), 1.41-1.35 (m, 2H), 1.16 (d, *J* = 6.3 Hz, 3H), 1.10-1.00 (m, 21H), 0.96 (2, *J* = 6.8 Hz, 3H), 0.94 (d, *J* = 6.7 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$) *denotes signals with distinct diastereomer peaks δ 173.6, 135.7, 135.6*, 132.3, 132.28*, 132.1, 132.0*, 131.2, 131.17, 129.5, 89.8, 78.2, 78.1*, 69.7, 68.2*, 68.2, 60.4, 51.9, 41.2, 39.5, 34.5, 33.8, 33.3*, 33.2, 32.1*, 32.0, 31.1, 21.2, 19.8, 18.4, 18.3, 16.5, 16.22*, 16.21, 12.8, 12.6

HRMS (ESI) *m*/*z* calcd. for $C_{34}H_{63}O_5Si$ $[M - OH]^+$ 579.4439, found 579.4427

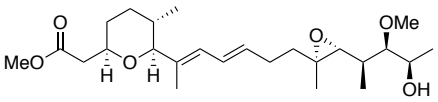
$[\alpha]_D^{22}$ –6.3 (*c* 0.68, $CHCl_3$)



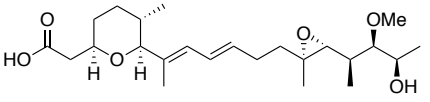
12-Desmethyl-14,15-desoxy (+)-herboxidiene methyl ester (S10)

To a solution of bis allylic alcohol **S9** (0.391 g, 0.656 mmol) in methylene chloride (12 mL) at rt was added Re_2O_7 (31.7 mg, 6.56 μmol, 10% w/w on SiO_2) and the mixture was stirred for 96 h. At the 48 h and 72 h mark, additional portions of Re_2O_7 (31.7 mg 6.56 μmol, 10% w/w on SiO_2) were added to increase the rate of silyl ether cleavage. The reaction was filtered through a short path of silica gel (~2 cm) eluting with DCM. The solvent was removed under vacuum, and the resulting crude material was purified by silica gel column chromatography (0% to 20% EtOAc in hexanes) to yield 12-desmethyl-14,15-desoxy herboxidiene methyl ester **S10** as an oil (0.186 g, 67%).

IR (ATR, cm^{-1}) 3492, 2972, 2930, 2870, 2854, 1741, 1455, 1483, 1365, 1248, 1198, 1160, 1092, 1069, 1020, 993, 967, 890
^1H NMR (500 MHz, $CDCl_3$) δ 6.25 (dd, *J* = 15.0, 10.8 Hz, 1H), 5.91 (d, *J* = 10.8 Hz, 1H), 5.62 (dt, *J* = 15.0, 6.9 Hz, 1H), 5.00 (d, *J* = 9.5 Hz, 1H), 3.82-3.74 (m, 1H), 3.74-3.68 (m, 1H), 3.68 (s, 3H), 3.51 (s, 3H), 3.33 (d, *J* = 9.8 Hz, 1H), 2.71 (dd, *J* = 6.9, 4.3 Hz, 1H), 2.65 (ddq, *J* = 9.4, 6.7, 6.6 Hz, 1H), 2.60 (dd, *J* = 15.3, 6.5 Hz, 1H), 2.40 (dd, *J* = 15.2, 6.8 Hz, 1H), 2.25-2.17 (m, 2H), 2.15 (d, broad, *J* = 6.5Hz, 1H), 2.10-2.05 (m, 2H), 1.85 (dq, *J* = 13.0, 3.3 Hz, 1H), 1.71 (s, 3H), 1.64 (s, 3H), 1.70-1.61 (m, 1H), 1.56-1.48 (m, 1H), 1.38-1.29 (m, 1H), 1.29-1.21 (m, 1H), 1.19 (d, *J* = 6.5 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.69 (d, *J* = 6.7 Hz, 3H)
^{13}C NMR (125 MHz, $CDCl_3$) δ 172.0, 134.8, 134.6, 134.3, 128.4, 128.3, 126.5, 90.6, 89.9, 74.0, 68.1, 61.6, 51.7, 41.5, 39.7, 34.9, 32.5, 32.4, 31.8, 31.6, 20.6, 17.8, 16.7, 16.4, 12.3
HRMS (ESI) *m*/*z* calcd. for $C_{22}H_{43}O_2Si$ $[M + H]^+$ 423.3105 found 423.3069
$[\alpha]_D^{22}$ +5.1 (*c* 2.59, $CHCl_3$)



12-Desmethyl-(+)-herboxidiene methyl ester (S11)
To a solution of **S10** (0.178 g, 0.421 mmol) in CH_2Cl_2 (4.2 mL) was added $VO(acac)_2$ (0.022 g, 0.084 mmol) and the mixture was cooled to –78 °C. *t*-BuOOH (0.23 mL, 1.3 mmol, 5.5 mol/L in decane) was added and the mixture was put in a –15 °C freezer for 15.5 h. The reaction was placed in an ice bath and quenched with 1.5 mL Me_2S, and was stirred for 1 h. The mixture was concentrated under reduced pressure and the residue was purified via silica gel flash column chromatography (10% to 50% EtOAc in hexanes) to yield 12-desmethyl herboxidiene methyl ester as an oil (71 mg, 38%) and recovered starting material (37 mg, 21%, 48% BRSM).
IR (ATR, cm^{-1}) 3485, 3048, 2953, 2930, 2854, 1738, 1456, 1439, 1384, 1268, 1199, 1091, 1071, 1021, 899, 738, 703
^1H NMR (500 MHz, $CDCl_3$) δ 6.28 (dd, *J* = 15.1, 10.8 Hz, 1H), 5.92 (d, *J* = 10.7 Hz, 1H), 5.62 (dt, *J* = 15.1, 7.0 Hz, 1H), 3.93-3.84 (m, 1H), 3.82-3.74 (m, 1H), 3.67 (s, 3H), 3.57 (s, 3H), 3.33 (d, *J* = 9.9 Hz, 1H), 3.01 (t, *J* = 5.4 Hz, 1H), 2.63 (d, *J* = 9.8 Hz, 1H), 2.60 (dd, *J* = 15.1, 6.3 Hz, 1H), 2.54 (d, broad, *J* = 3.5 Hz, 1H), 2.41 (dd, *J* = 15.2, 6.7 Hz, 1H), 2.32-2.22 (m, 1H), 2.24-2.13 (m, 1H), 1.88-1.82 (m, 1H), 1.83-1.76 (m, 1H), 1.71 (s, 3H), 1.70-1.65 (m, 1H), 1.64-1.57 (m, 1H), 1.56-1.50 (m, 1H), 1.53-1.45 (m, 1H), 1.40-1.30 (m, 1H), 1.30 (s, 3H), 1.26-1.20 (m, 1H), 1.21 (d, *J* = 6.5 Hz, 3H), 0.98 (d, *J* = 7.0 Hz, 3H), 0.69 (d, *J* = 6.7 Hz, 3H)
^{13}C NMR (125 MHz, $CDCl_3$) δ 172.0, 135.2, 133.3, 128.0, 126.9, 90.6, 87.7, 74.0, 68.5, 65.6, 61.8, 61.5, 51.7, 41.5, 38.8, 35.3, 32.5, 32.4, 31.8, 29.0, 19.2, 17.8, 16.6, 12.3, 12.0
HRMS (ESI) *m*/*z* calcd. for $C_{22}H_{43}O_2Si$ $[M – H]^+$ 423.3105 found 423.3069
$[\alpha]_D^{22}$ +6.1 (*c* 1.01, $CHCl_3$)



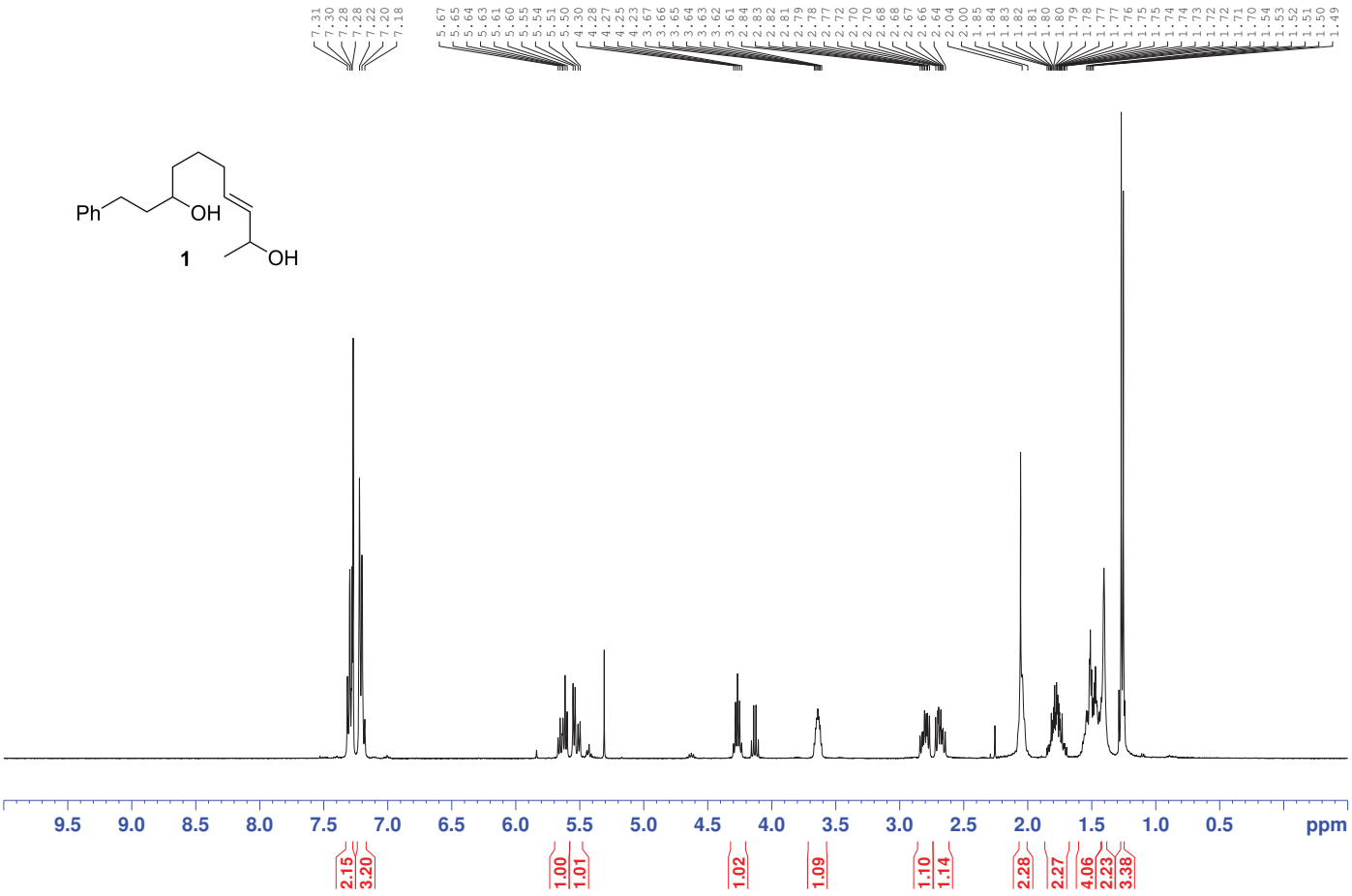
12-Desmethyl-(+)-herboxidiene (36)
To a solution of desmethyl herboxidiene ethyl ester (**S11**) (23.8 mg, 0.053 mmol) in MeOH (4 mL) and water (1 mL) was added powdered potassium carbonate (47 mg, 0.34 mmol). The mixture was heated to reflux for 1 h, then cooled to rt. The mixture was diluted with EtOAc and water, and carefully acidified with a few drops of 10% aq. HCl. The layers were separated and the aqueous layer was extracted 3x with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered and concentrated. The resulting residue was purified via silica gel column chromatography (gradient elution, 0 to

2% to 5% to 10% MeOH in dichloromethane) to yield (+)-desmethyl herboxidiene **34** as a clear semi-solid (15.4 mg, 69%).
IR (ATR, cm^{-1}) 3444, 2962, 2928, 2853, 1715, 1456, 1383, 1262, 1197, 1158, 1092, 1070, 1019, 967, 884, 805, 757, 738
^{1}H NMR (600 MHz, MeOD) δ 6.33 (dd, *J* = 15.0, 10.9 Hz, 1H), 5.93 (d, *J* = 10.8 Hz, 1H), 5.66 (dt, *J* = 14.9, 7.1 Hz, 1H), 3.82 (p, 6.3 Hz, 1H), 3.80-3.74 (m, 1H), 3.55 (s, 3H), 3.35 (d, *J* = 9.8 Hz, 1H), 3.01 (dd, *J* = 6.1, 4.3 Hz, 1H), 2.72 (d, *J* = 9.4 Hz, 1H), 2.46 (dd, *J* = 15.3, 7.3 Hz, 1H), 2.39 (dd, *J* = 15.3, 5.6 Hz, 1H), 2.33-2.25 (m, 1H), 2.25-2.18 (m, 1H), 1.87 (dq, *J* = 12.6, 3.2 Hz, 1H), 1.82 (ddd, *J* = 13.7, 8.3, 5.6 Hz, 1H), 1.74-1.70 (m, 1H), 1.70 (s, 3H), 1.60-1.54 (m, 1H), 1.56-1.51 (m, 1H), 1.48 (dt, *J* = 13.6, 8.1 Hz, 1H), 1.38-1.30 (m, 1H), 1.29 (s, 3H), 1.29-1.22 (m, 1H), 1.14 (d, *J* = 6.4 Hz, 3H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.69 (d, *J* = 6.6 Hz, 3H)
^{13}C NMR (150 MHz, MeOD) δ 175.2, 135.8, 134.8, 129.4, 127.8, 92.1, 88.5, 75.5, 69.9, 67.1, 63.0, 61.9, 42.3, 39.8, 36.2, 33.45, 33.43, 32.8, 30.0, 19.8, 18.0, 16.6, 12.2, 11.2
HRMS (ESI) *m*/*z* calcd. for $C_{24}H_{41}O_6$ $[M + H]^+$ 425.2898, found 425.2892
$[\alpha]_D^{22}$ +6.8 (*c* 0.44, $CHCl_3$)

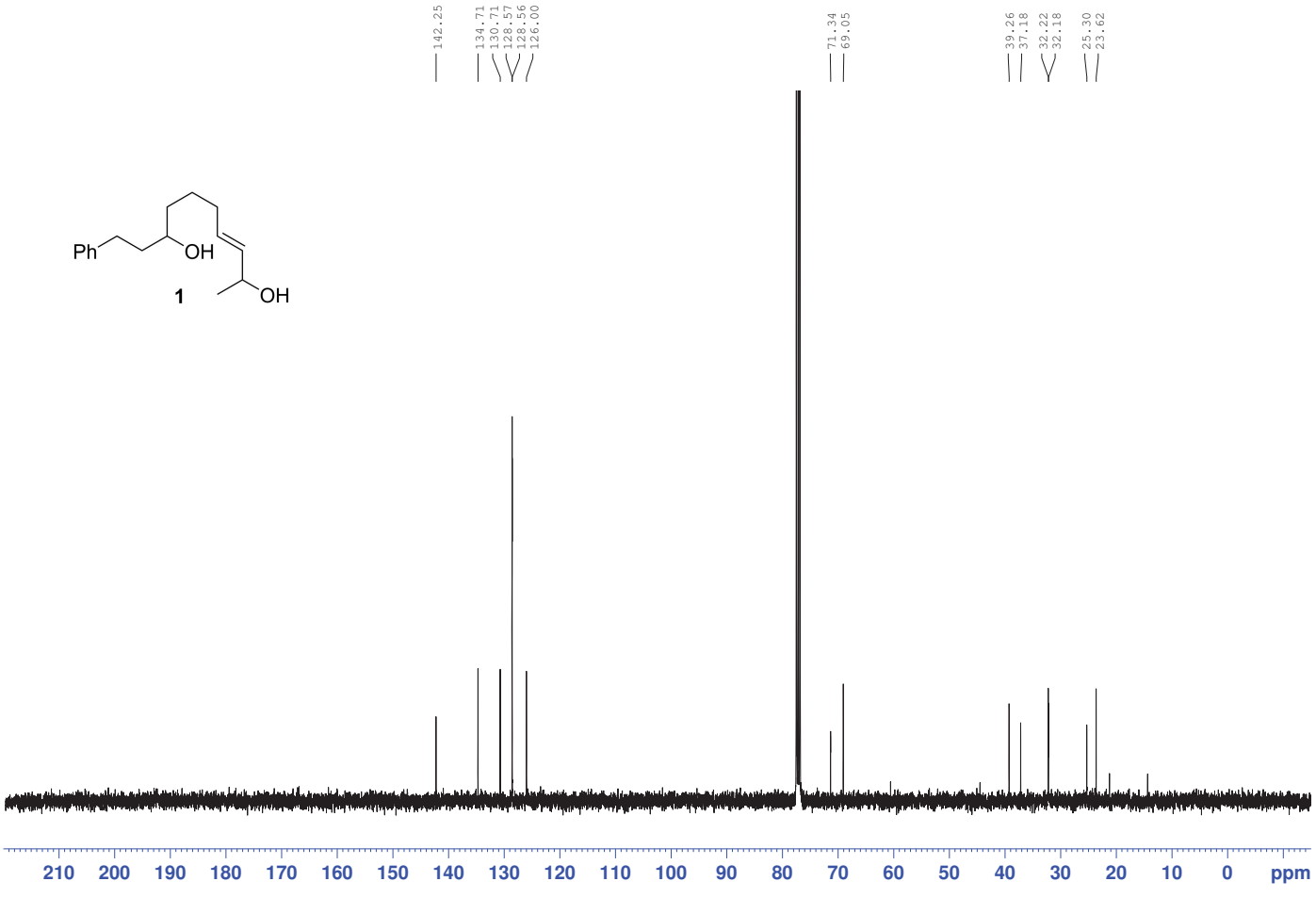
^{13}C NMR data for (+)-herboxidiene and 12-desmethyl analogue			
Position	Synthetic[a] δ	12-Desmethyl[b] δ	Δδ
C1	175.201	175.206	0.005
C2	42.286	42.276	-0.010
C3	75.487	75.489	0.002
C4	32.799	32.797	-0.002
C5	33.454	33.452	-0.002
C6	33.385	33.433	0.048
C6-Me	18.078	18.005	-0.073
C7	92.166	92.069	-0.097
C8	136.196	135.841	-0.355
C8-Me	12.086	12.174	0.088
C9	129.632	129.437	-0.195
C10	126.535	127.844	1.309
C11	140.725	134.792	-5.933
C12	36.525	29.987	-6.538
C12-Me	22.691	—	—
C13	48.108	39.780	-8.328
C14	62.628	62.978	0.350
C14-Me	16.782	16.640	-0.142
C15	67.859	67.117	-0.742
C16	36.437	36.244	-0.193
C16-Me	11.55	11.241	-0.309
C17	88.532	88.498	-0.034
C18	69.914	69.925	0.011
C19	19.822	19.837	0.015
OMe	61.883	61.923	0.040
[a] Recorded in MeOD at 125 MHz. [b] Recorded in MeOD at 150 MHz			

^{1}H NMR data for (+)-herboxidiene and 12-desmethyl analogue						
Position	Synthetic[a] δ	Multiplicity	*J*/Hz	12-Desmethyl[b] δ	Multiplicity	*J*/Hz
H2A	2.47	dd	15.0, 7.7	2.46	dd	15.3, 7.3
H2B	2.39	dd	15.3, 5.6	2.39	dd	15.3, 5.6
H3	3.79-3.74	m	—	3.80-3.74	m	—
H4A	1.75-1.70	m	—	1.74-1.70	m	—
H4B	1.41-1.30	m	—	1.38-1.30	m	—
H5A	1.86	dq	12.3, 3.3	1.89-1.84	dq	12.6, 3.2
H5B	1.31-1.22	m	—	1.29-1.22	m	—
H6	1.60-1.53	m	—	1.60-1.54	m	—
C6-Me	0.83	d	6.7	0.69	d	6.6
H7	3.35	d	9.9	3.35	d	9.8
C8-Me	1.70	s	—	1.70	s	—
H9	5.92	d	11.0	5.93	d	10.8
H10	6.30	dd	15.0, 10.8	6.33	dd	15.0, 10.9
H11	5.48	dd	15.0, 9.1	5.66	dt	14.9, 7.1
H12A	2.50-2.42	m	—	2.33-2.25	m	—
H12B	—	—	—	2.25-2.18	m	—
C12-Me	1.05	d	6.7	—	—	—
H13A	1.93	dd	13.5, 4.3	1.82	ddd	13.7, 8.3, 5.6
H13B	1.19	dd	13.4, 10.8	1.48	dt	13.6, 8.1
C14-Me	1.28	s	—	1.29	s	—
H15	2.66	d	9.5	2.72	d	9.4
H16	1.53-1.45	m	—	1.56-1.51	m	—
C16-Me	0.83	d	7.2	0.92	d	7.0
H17	2.98	dd	6.3, 4.2	3.01	dd	6.1, 4.3
H18	3.79	p	6.4	3.82	p	6.3
H19	1.11	d	6.5	1.14	d	6.4
OMe	3.53	s	—	3.55	s	—
[a] Recorded in MeOD at 500 MHz. [b] Recorded in MeOD at 600 MHz						

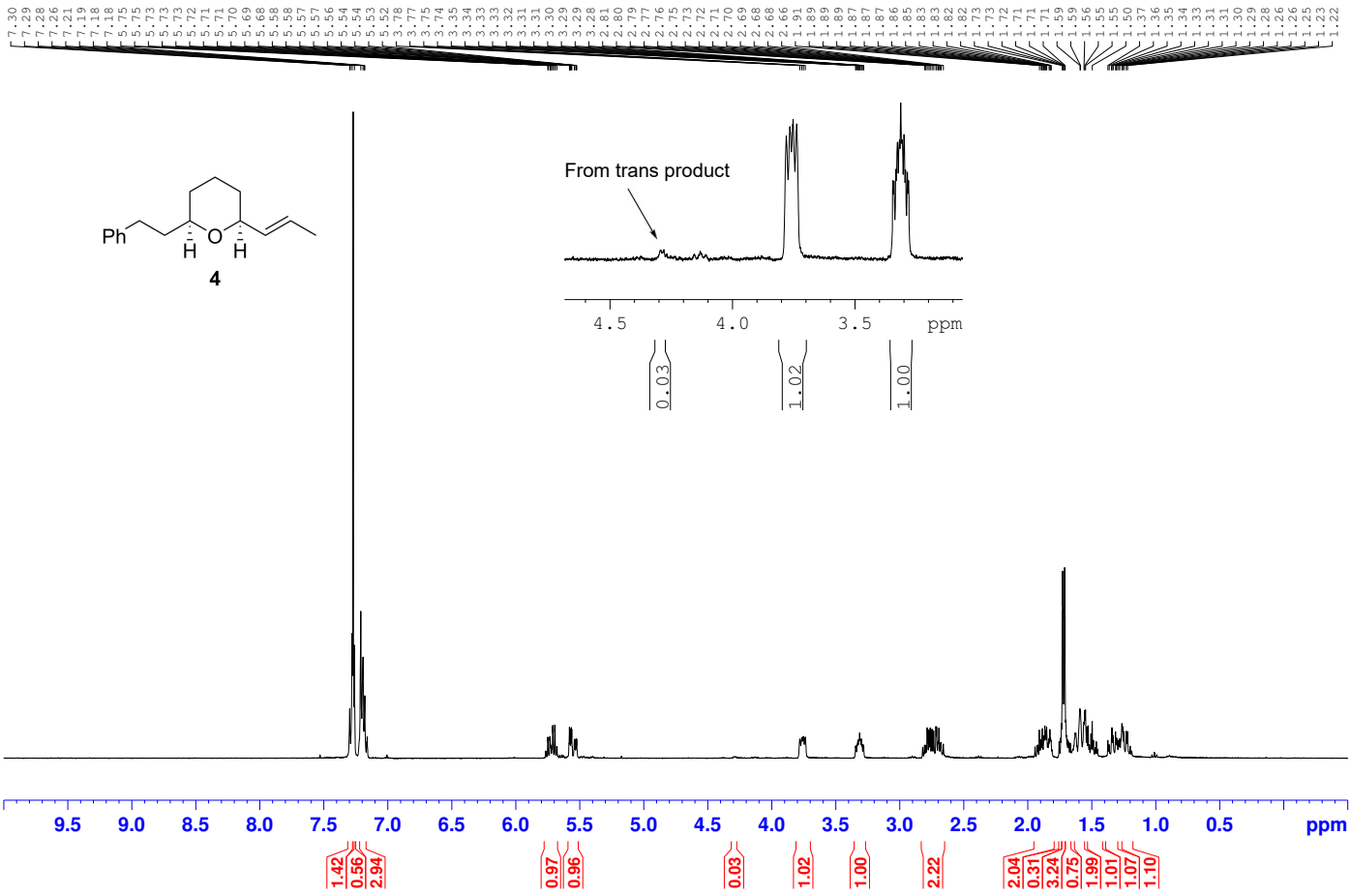
1H NMR (400 MHz, CDCl3)



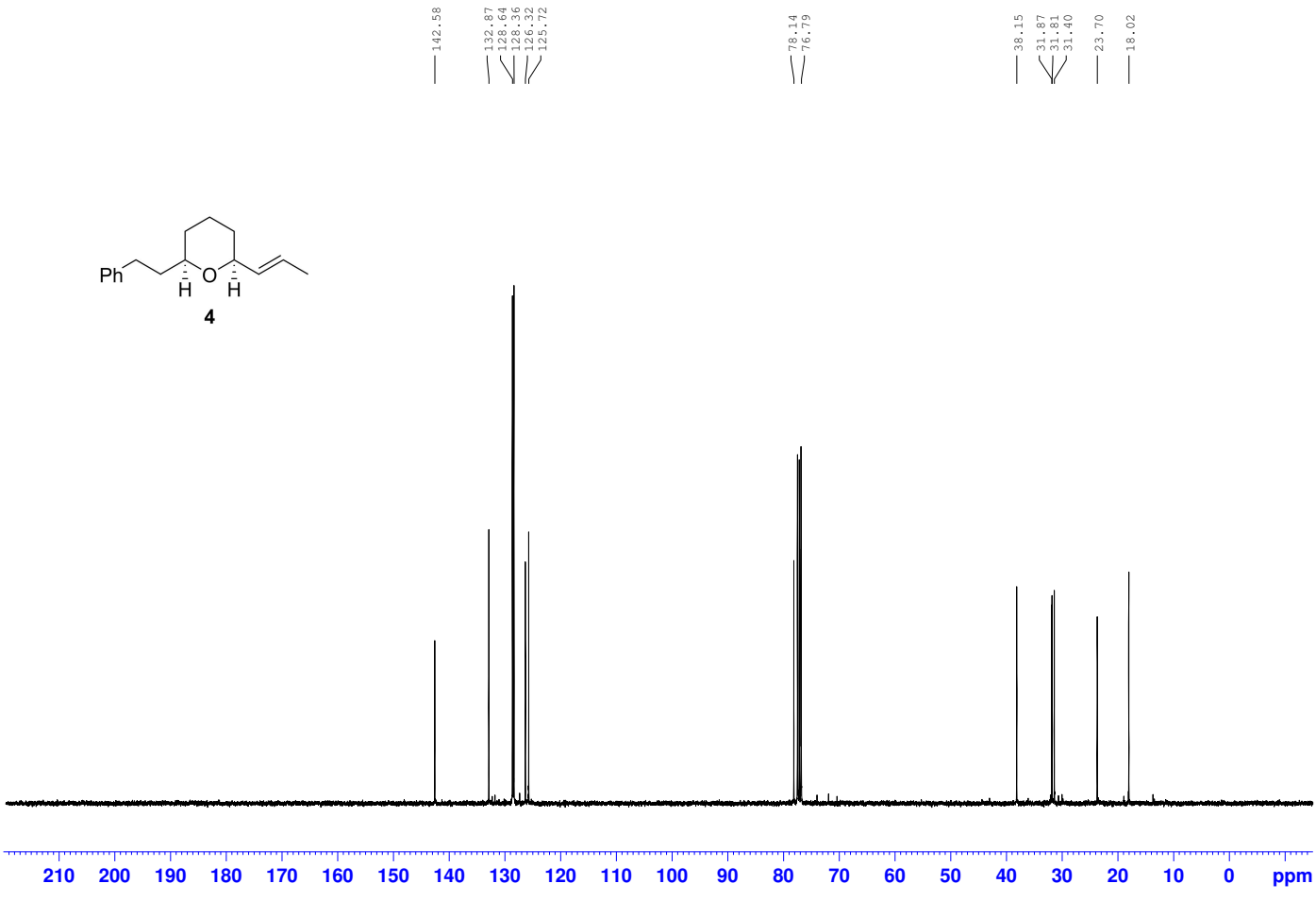
13C NMR (100 MHz, CDCl3)



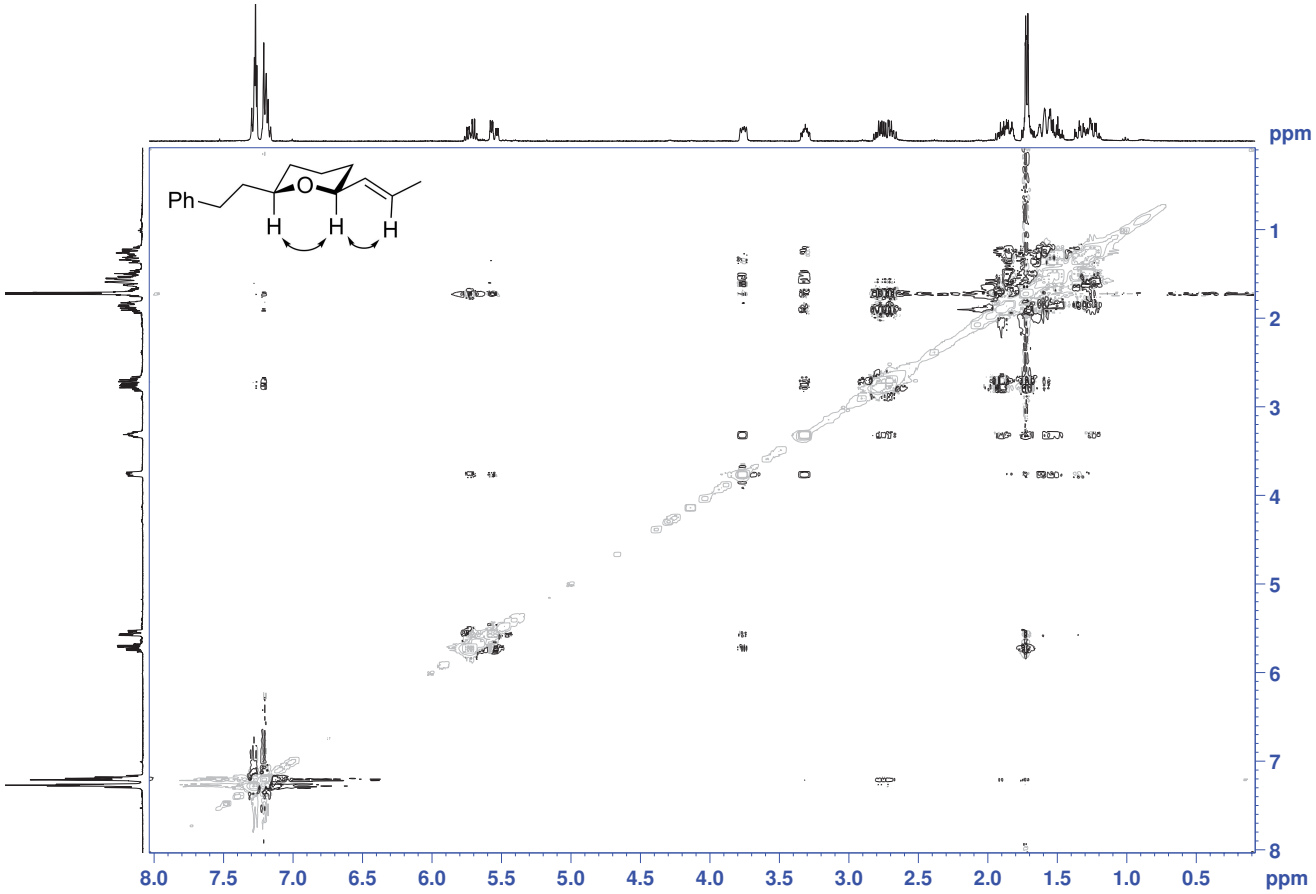
1H NMR (400 MHz, CDCl3)



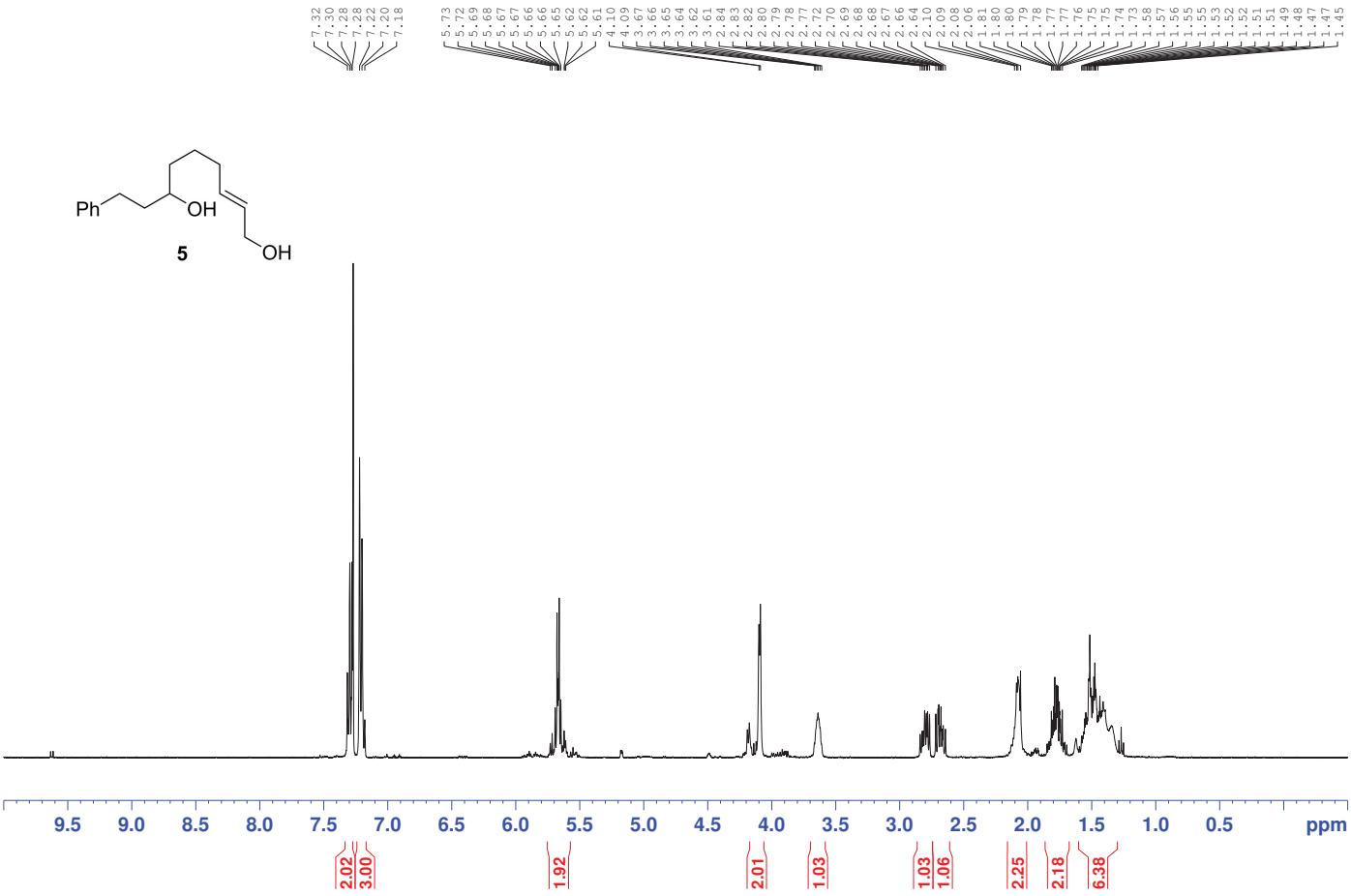
13C NMR (100 MHz, CDCl3)



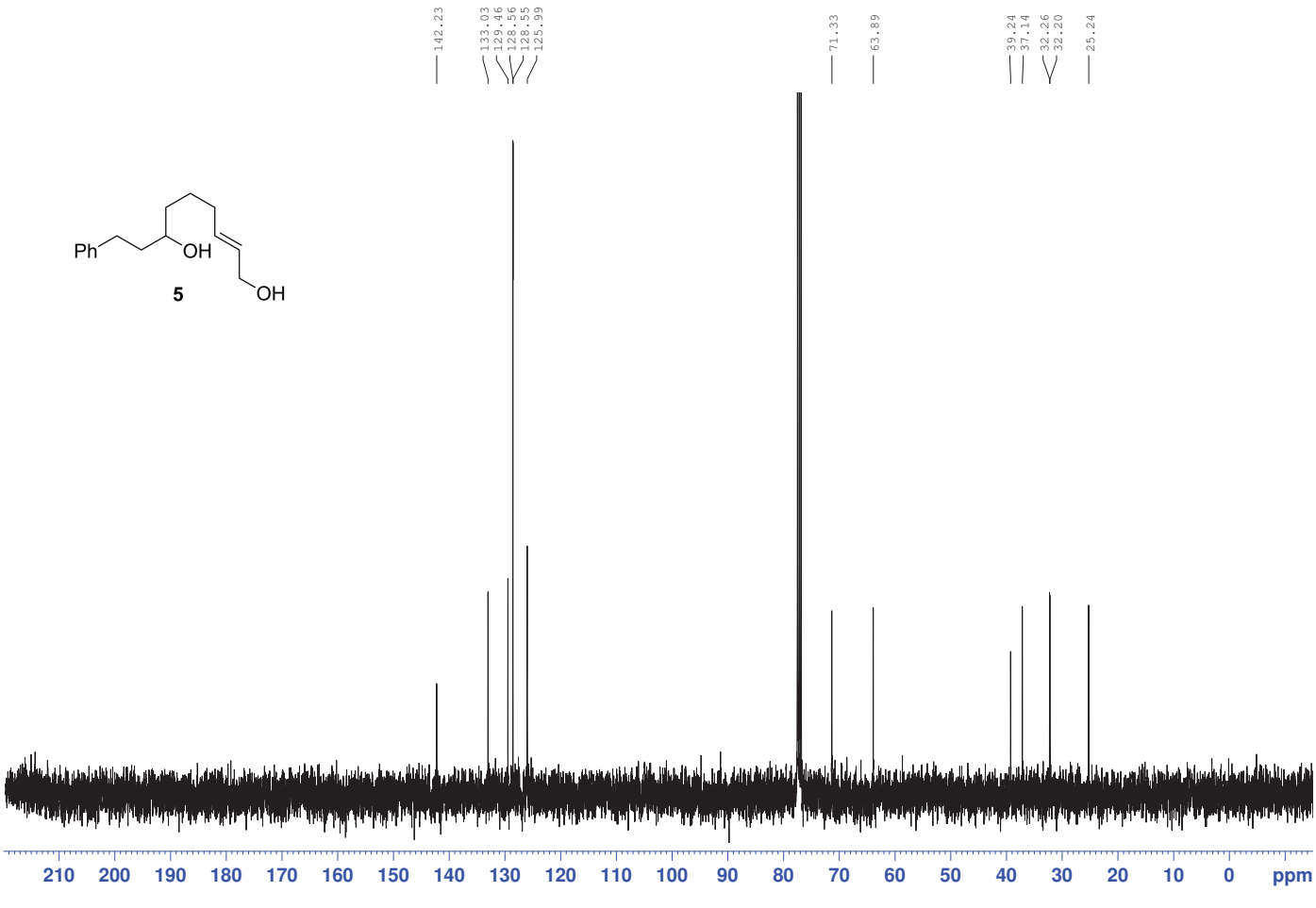
NOESY (400 MHz, CDCl3)



1H NMR (400 MHz, CDCl3)



13C NMR (100 MHz, CDCl3)



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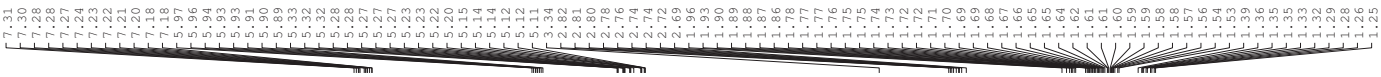

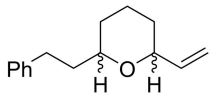

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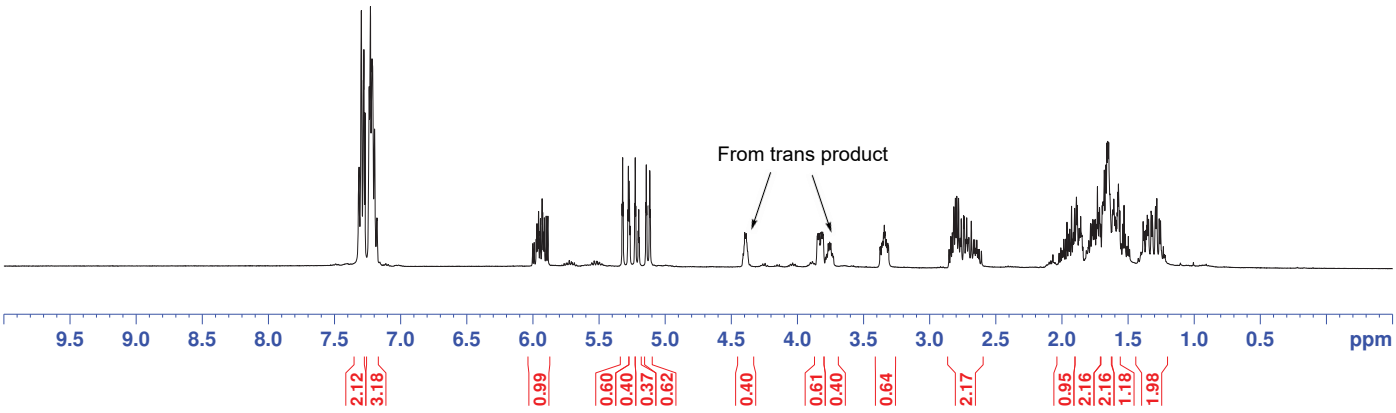
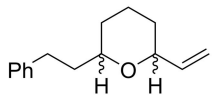


13C NMR (100 MHz, CDCl3)



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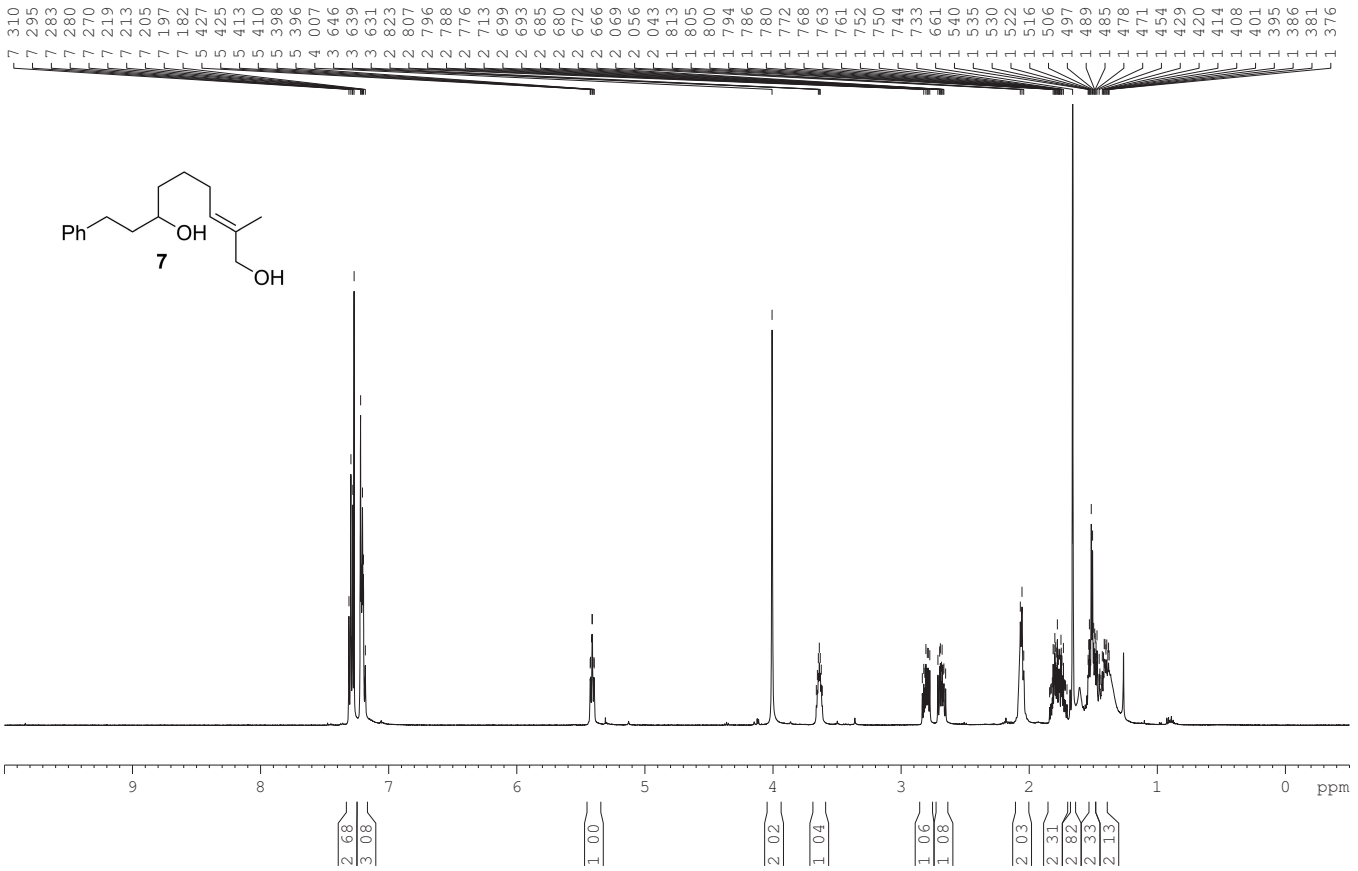
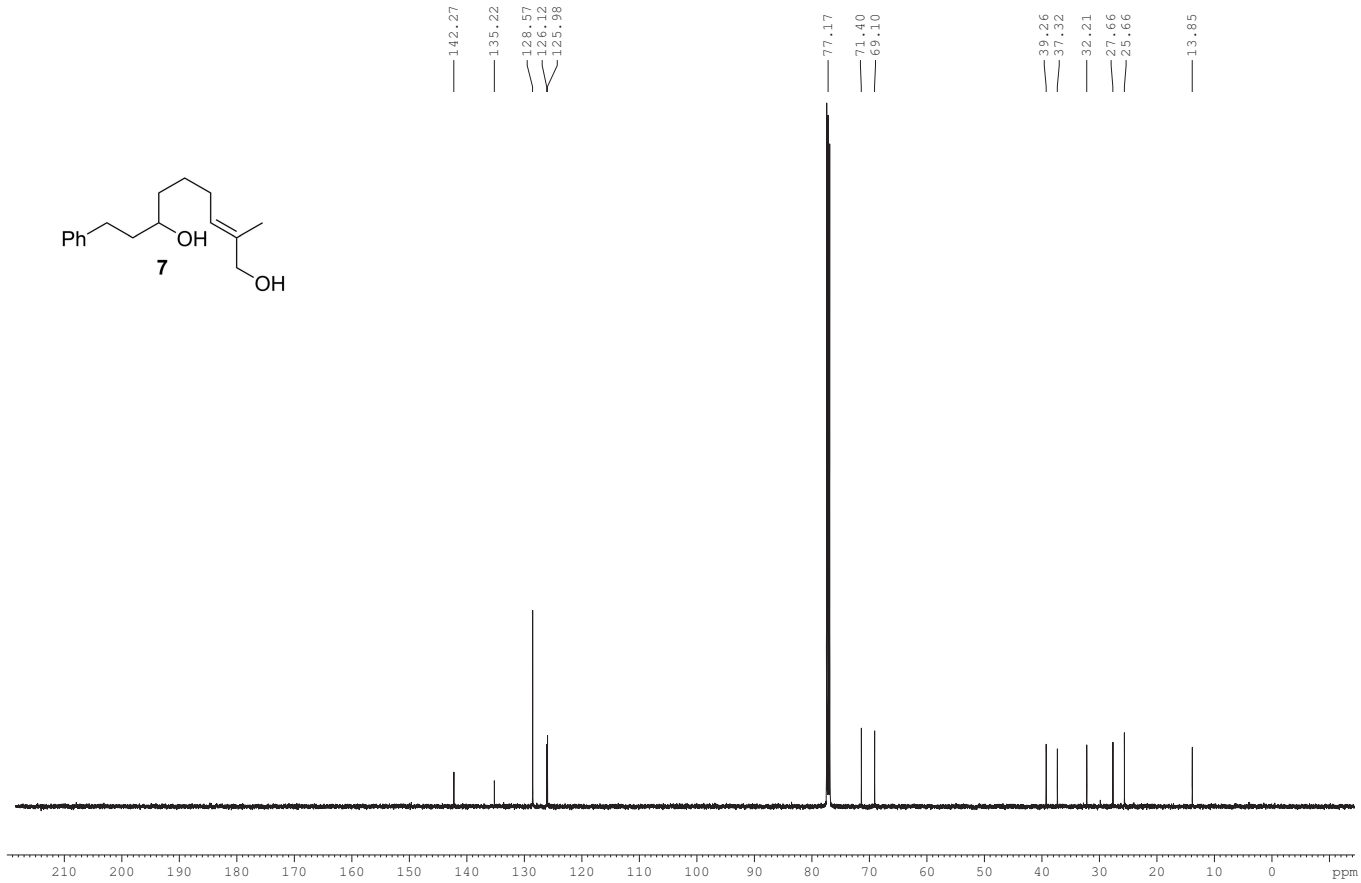
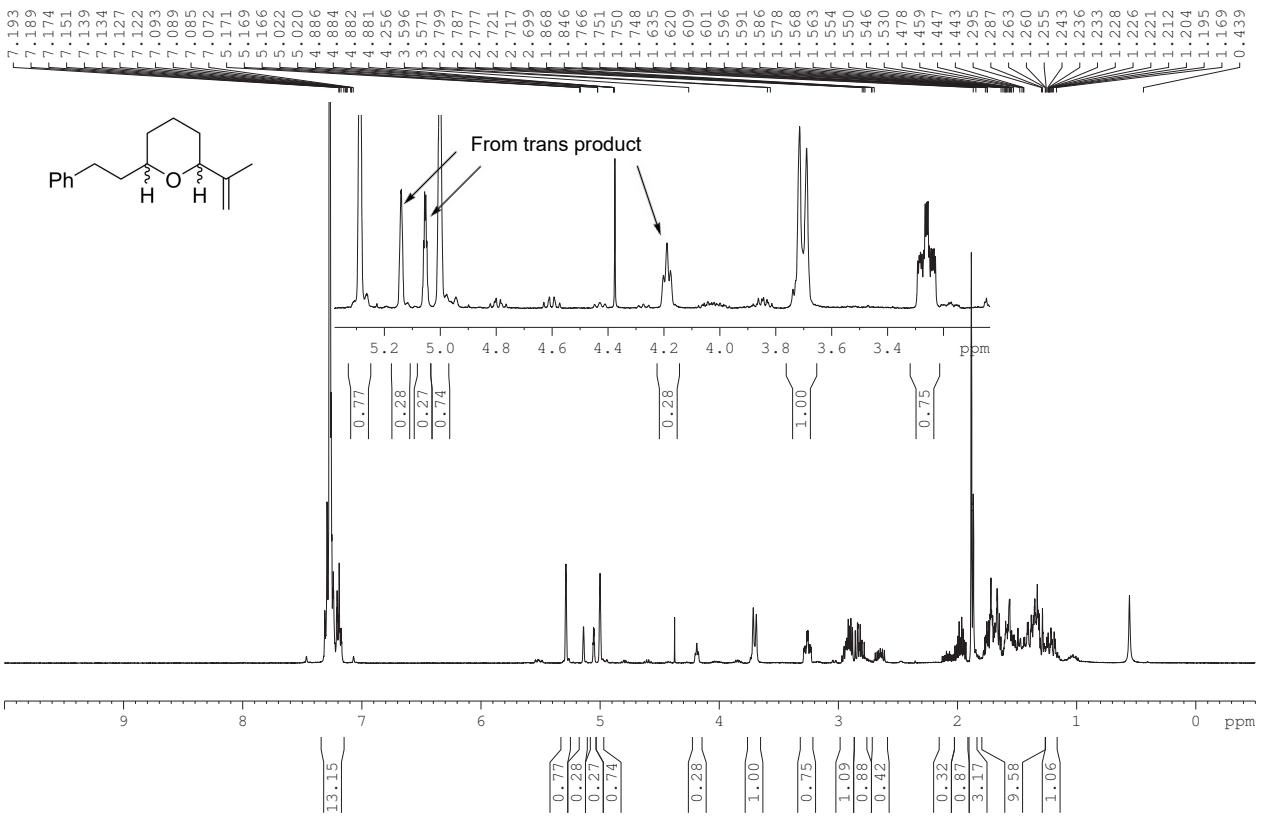
1H NMR (500 MHz, CDCl3)



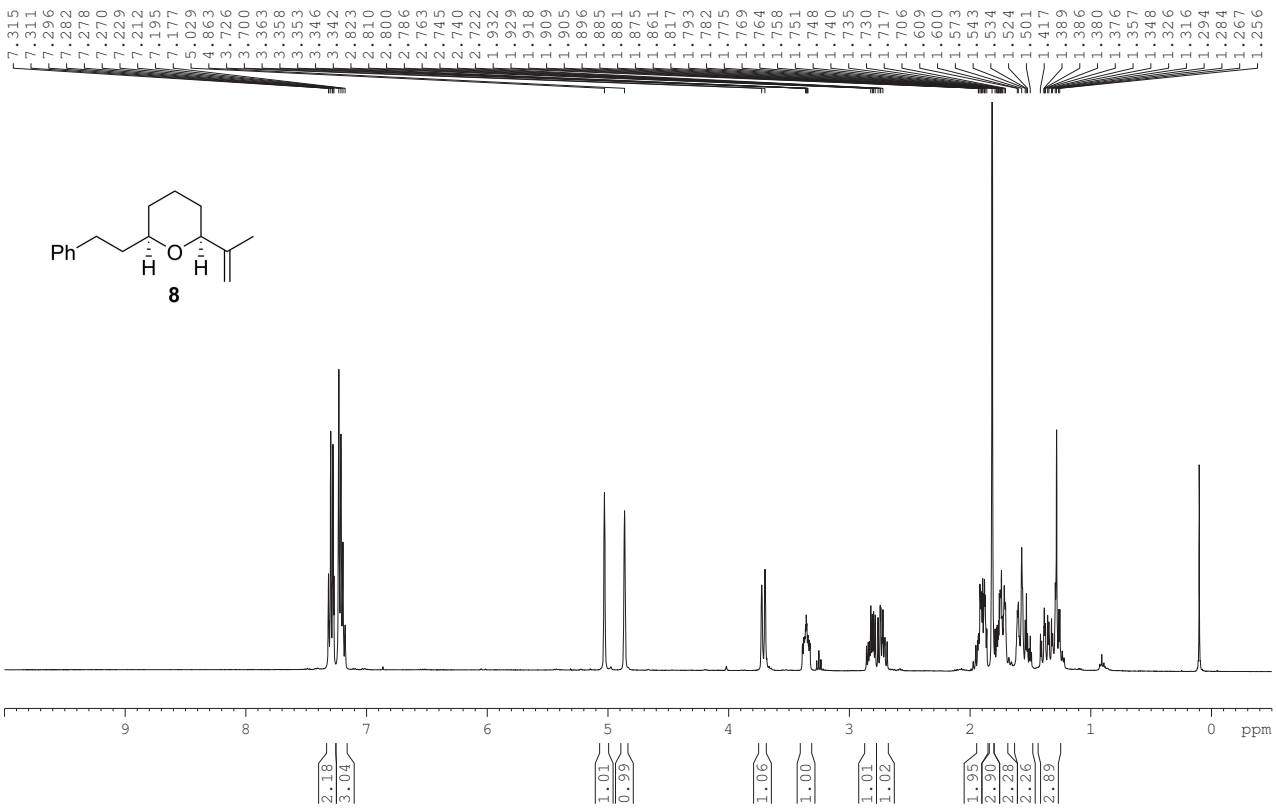
13C NMR (125 MHz, CDCl3)



1H NMR (400 MHz, CDCl3)

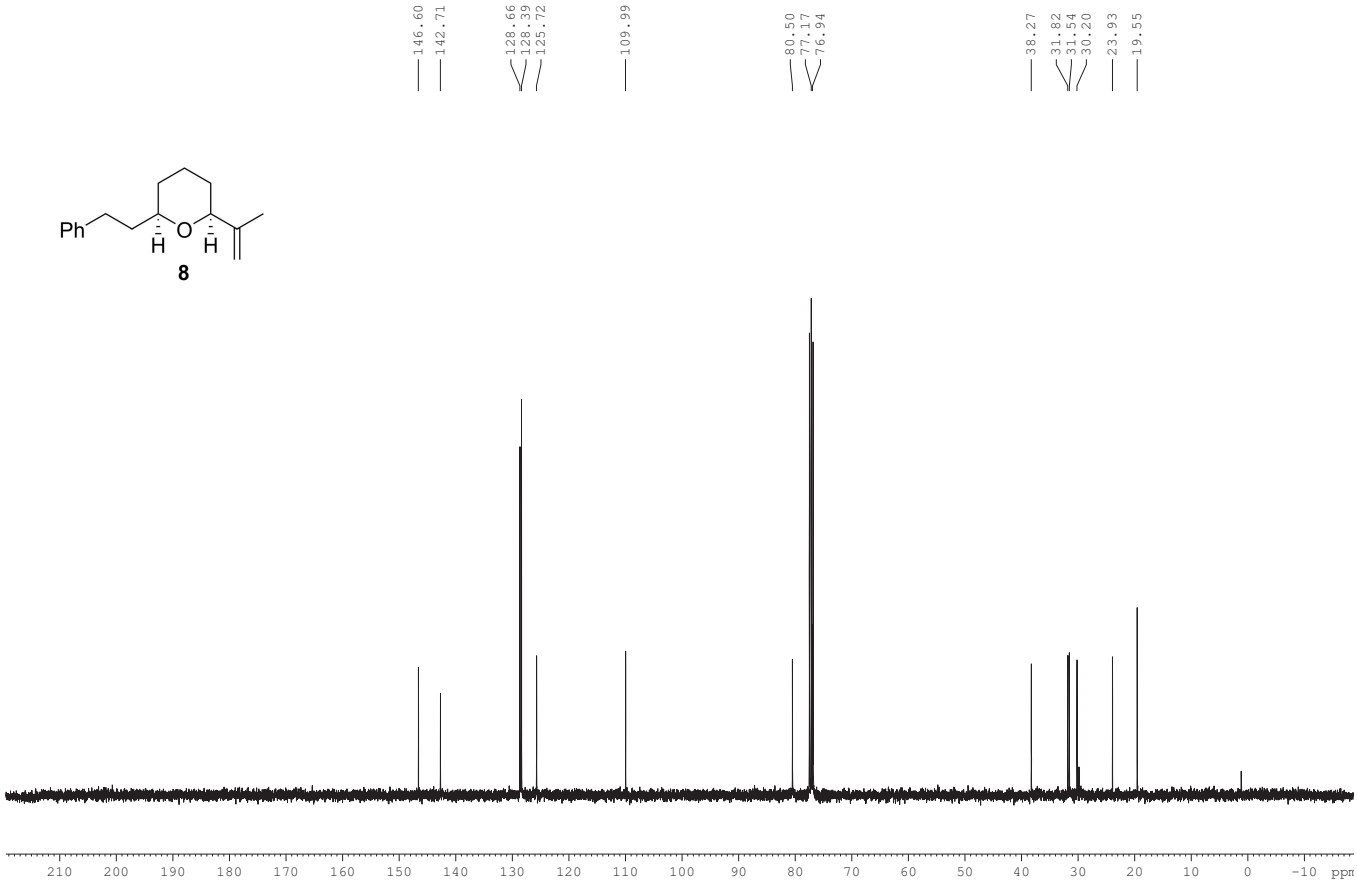


1H NMR (400MHz, CDCl3)

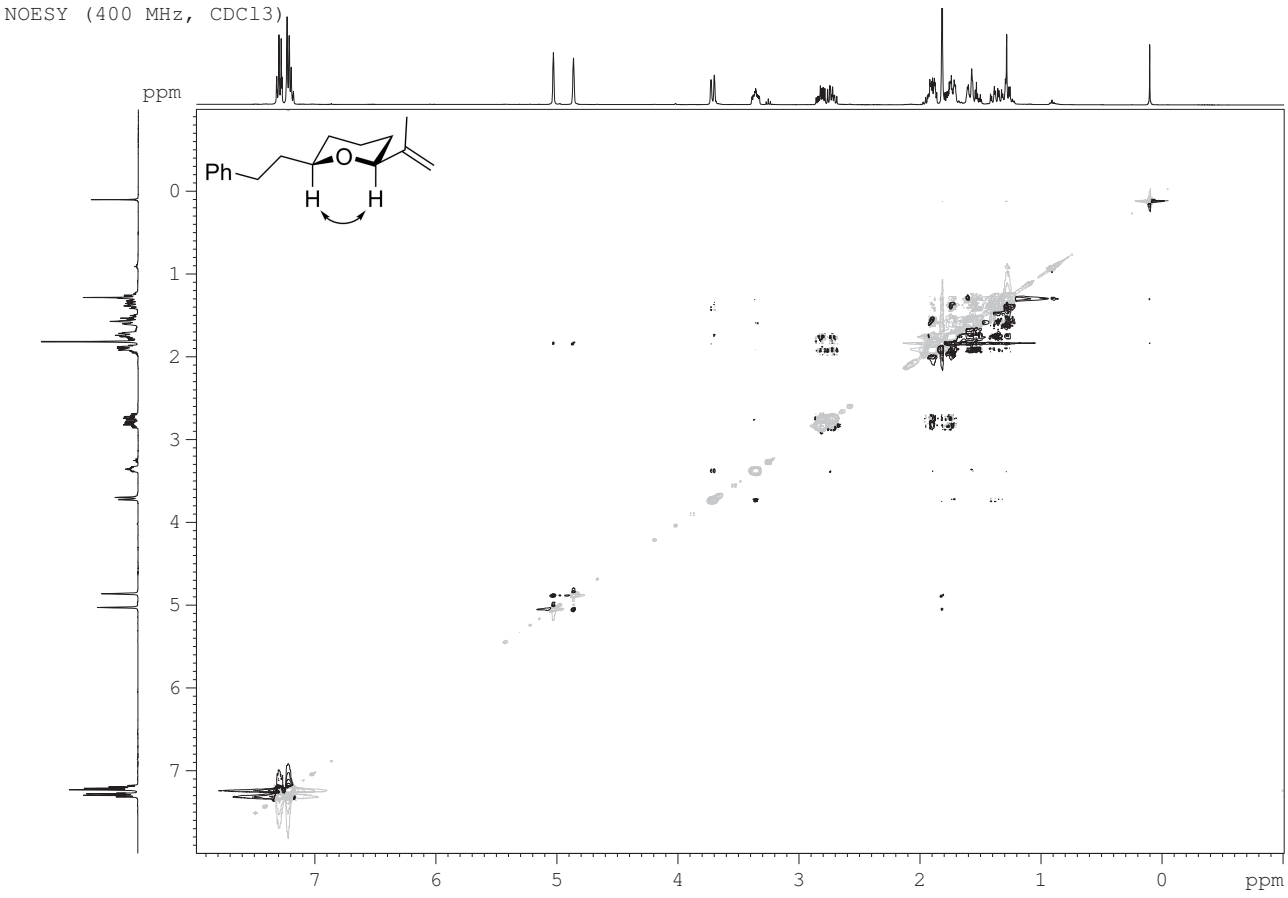


8

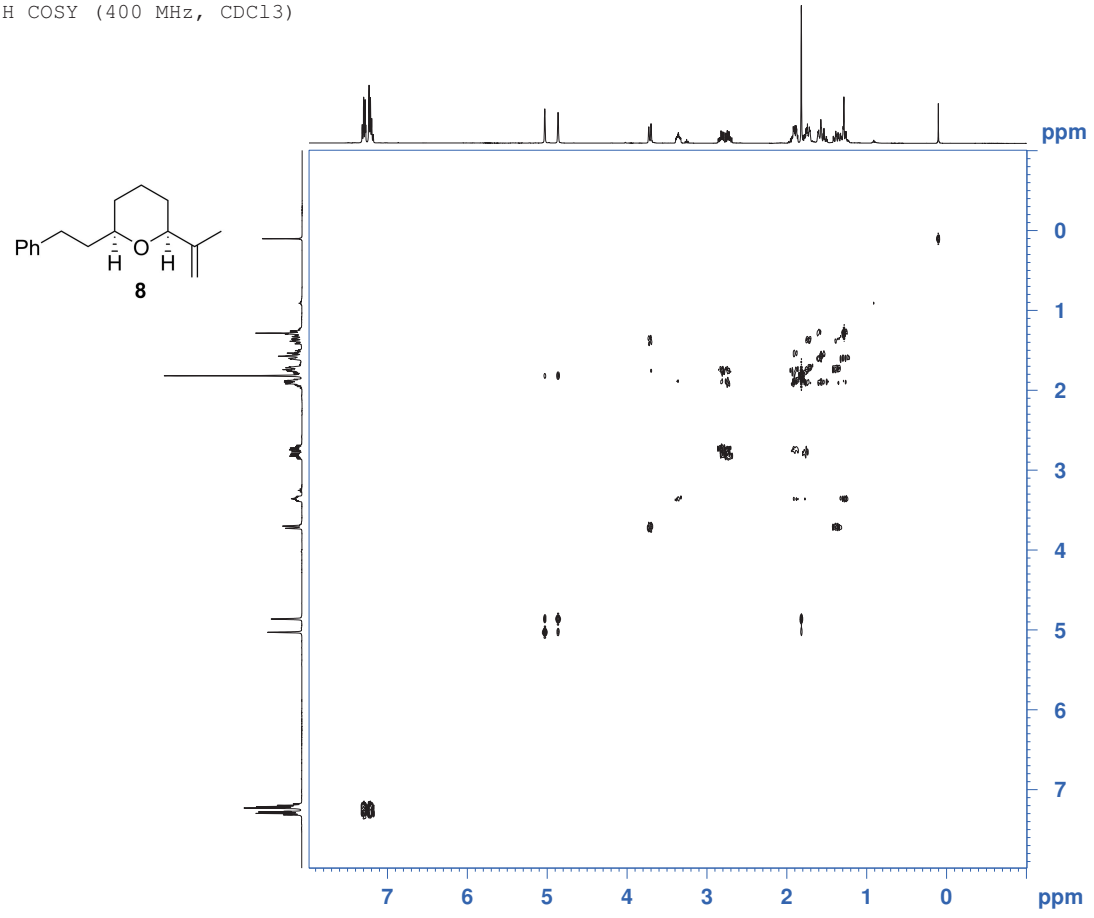
13C NMR (400 MHz, CDCl3)



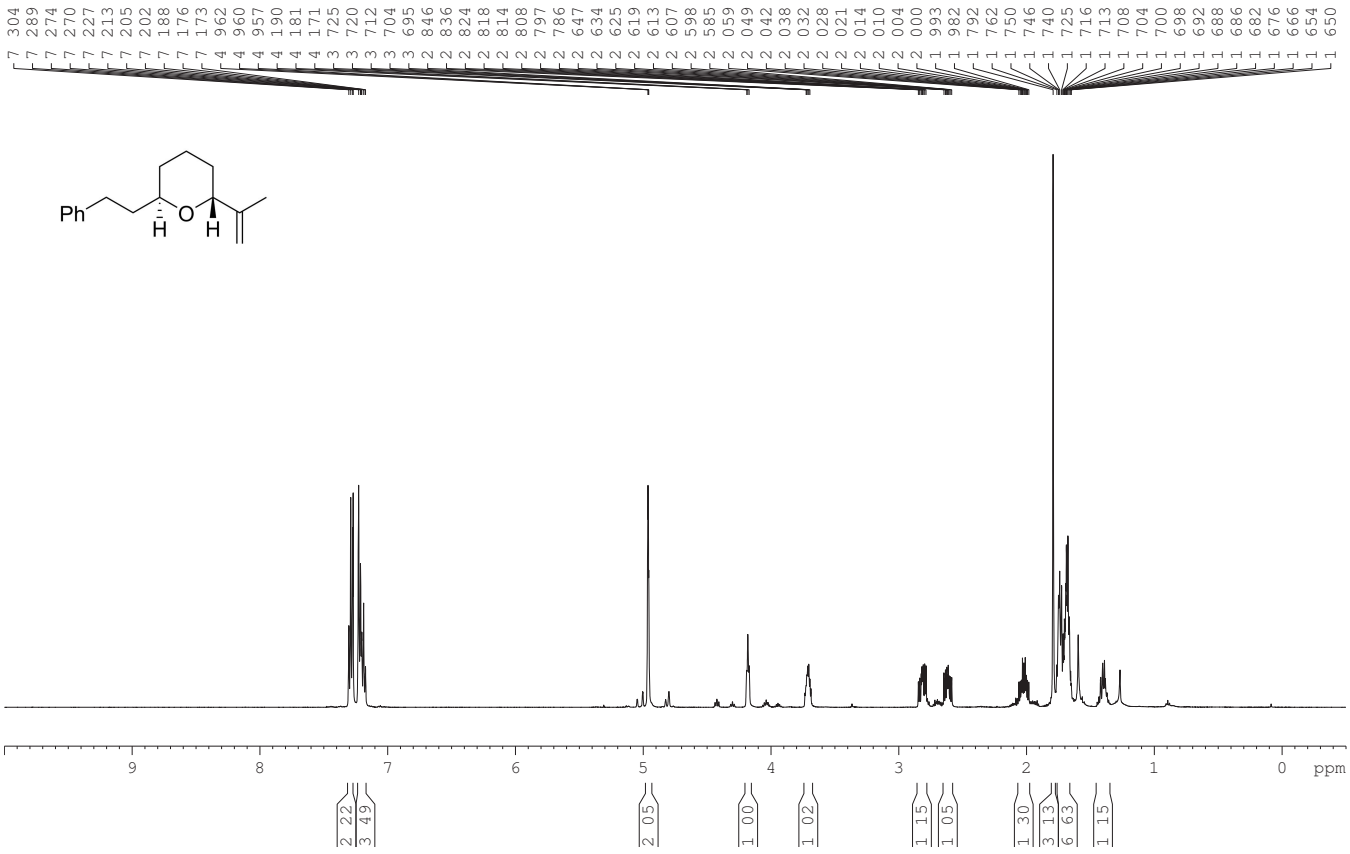
NOESY (400 MHz, CDCl3)



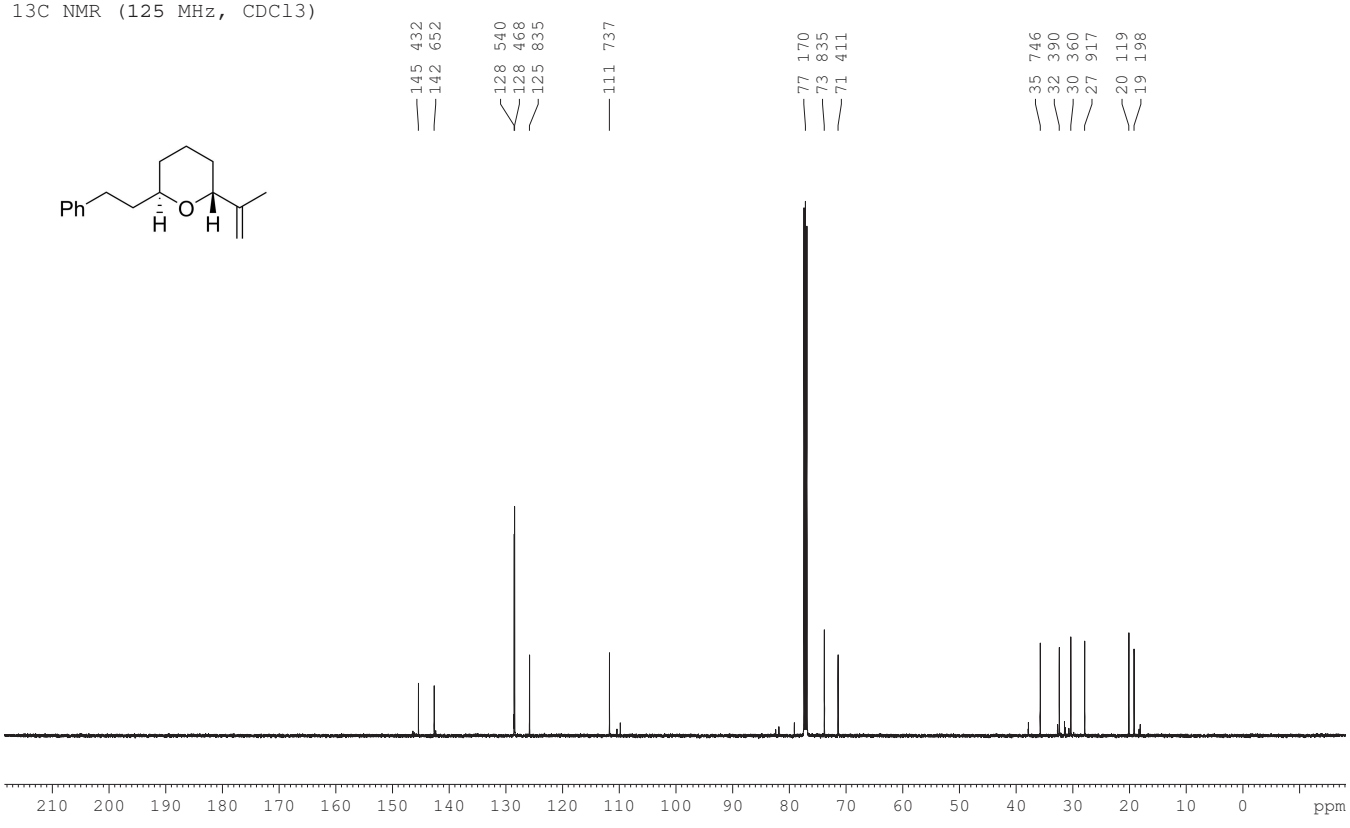
H-H COSY (400 MHz, CDCl3)



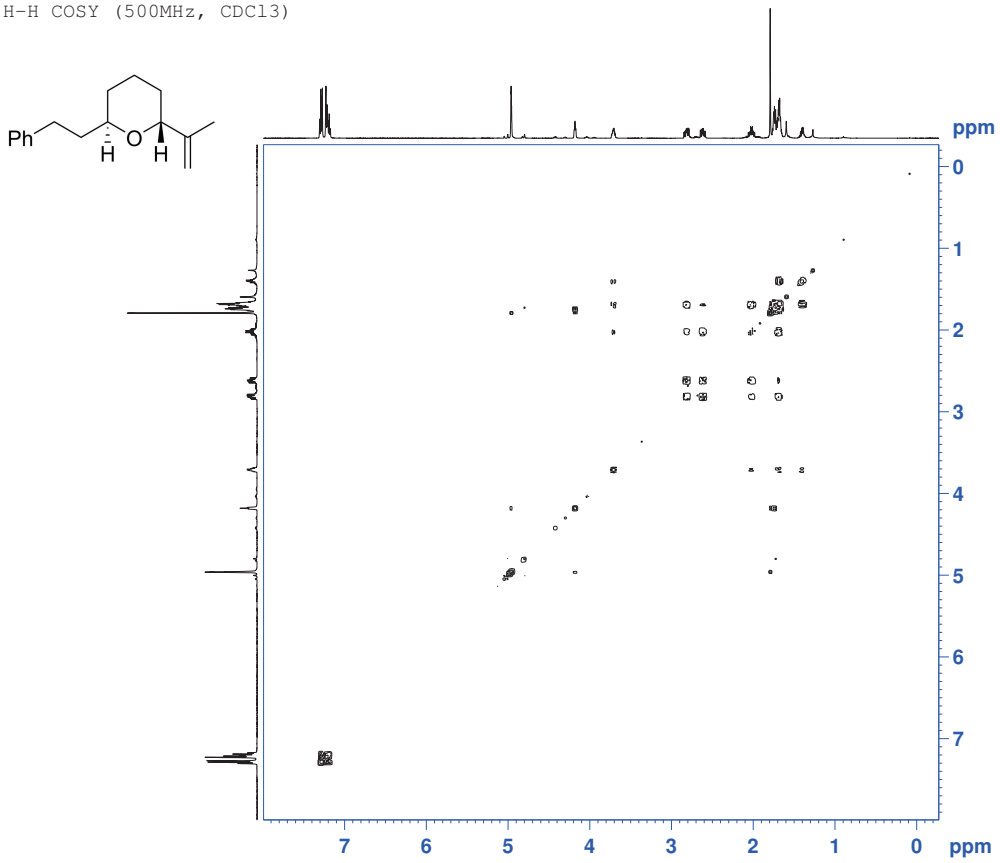
1H NMR (500 MHz, CDCl3)



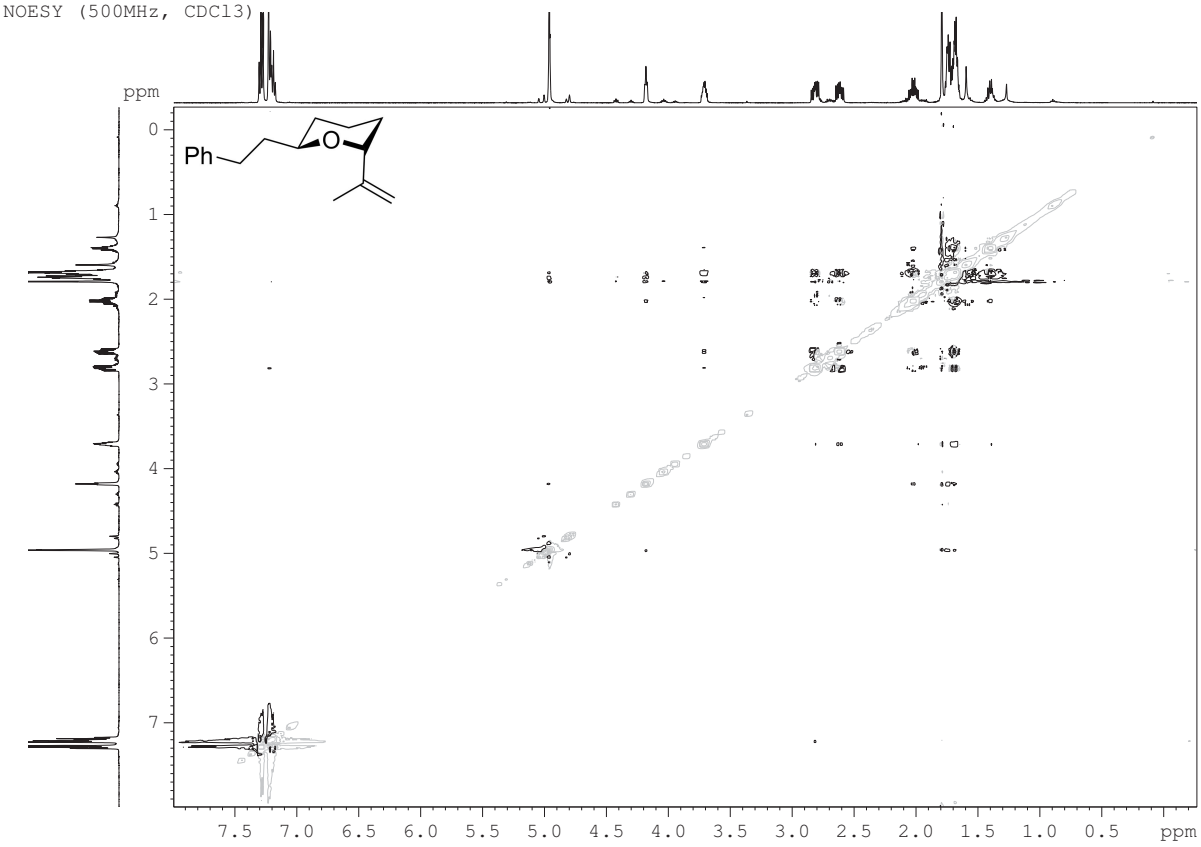
13C NMR (125 MHz, CDCl3)



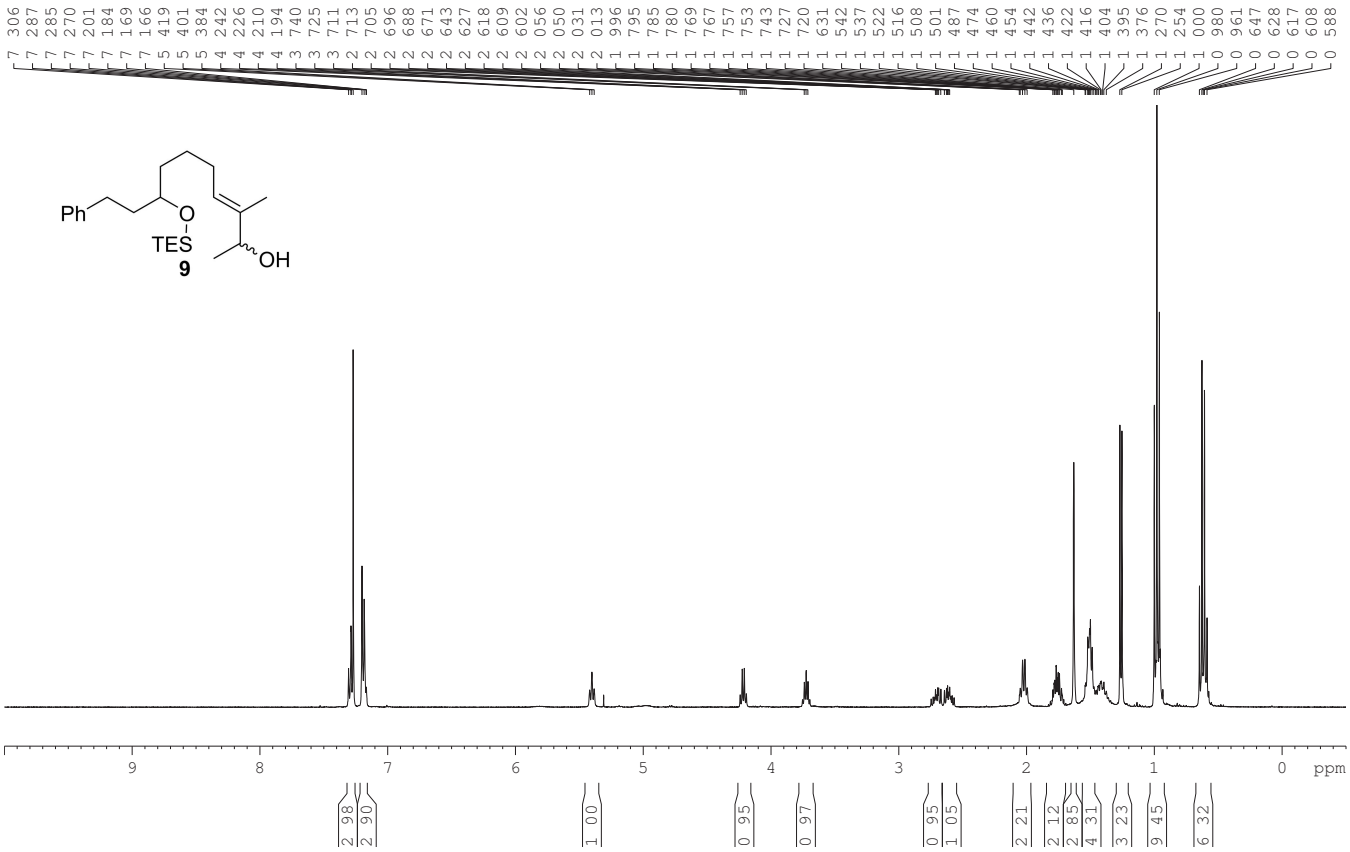
H-H COSY (500MHz, CDCl3)



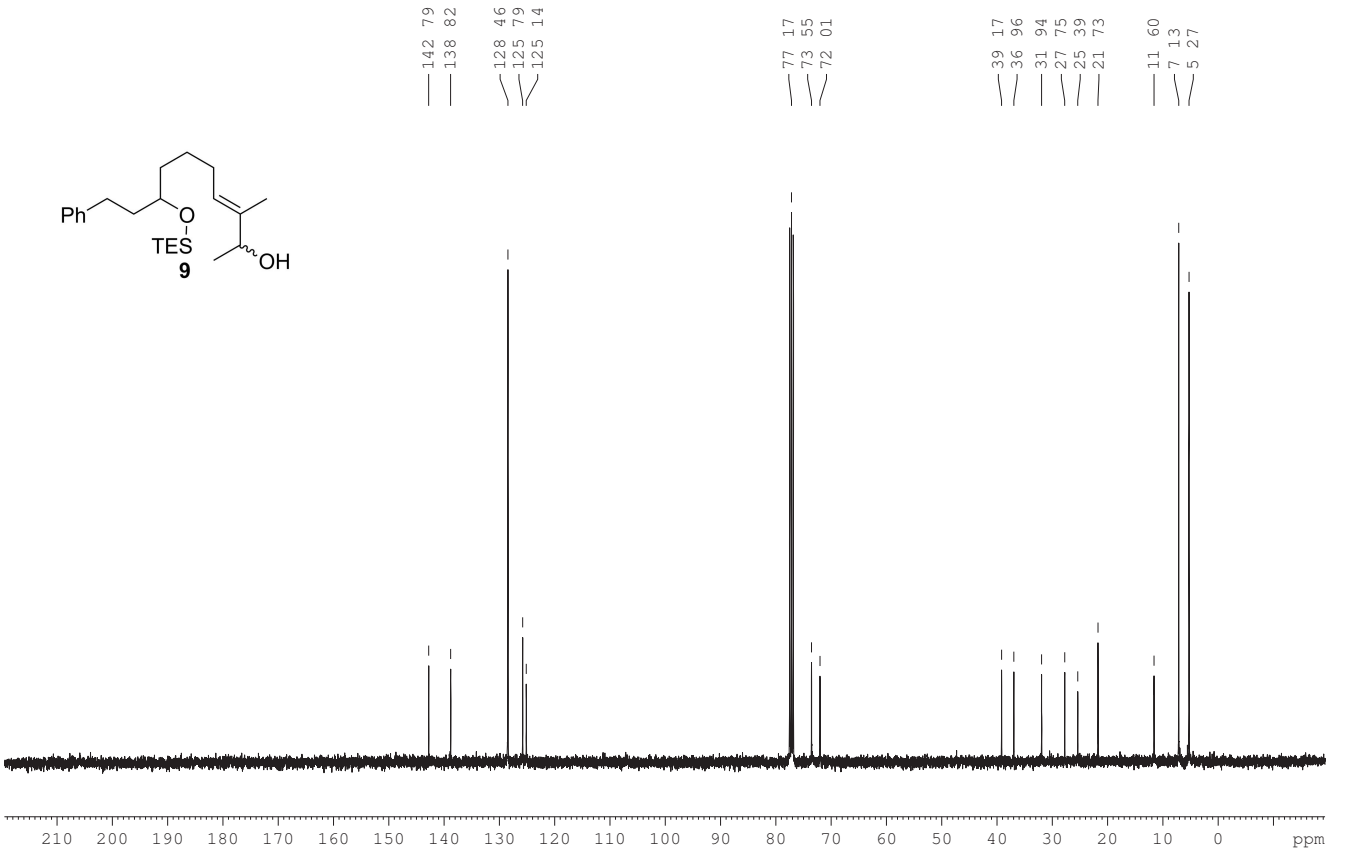
NOESY (500MHz, CDCl3)



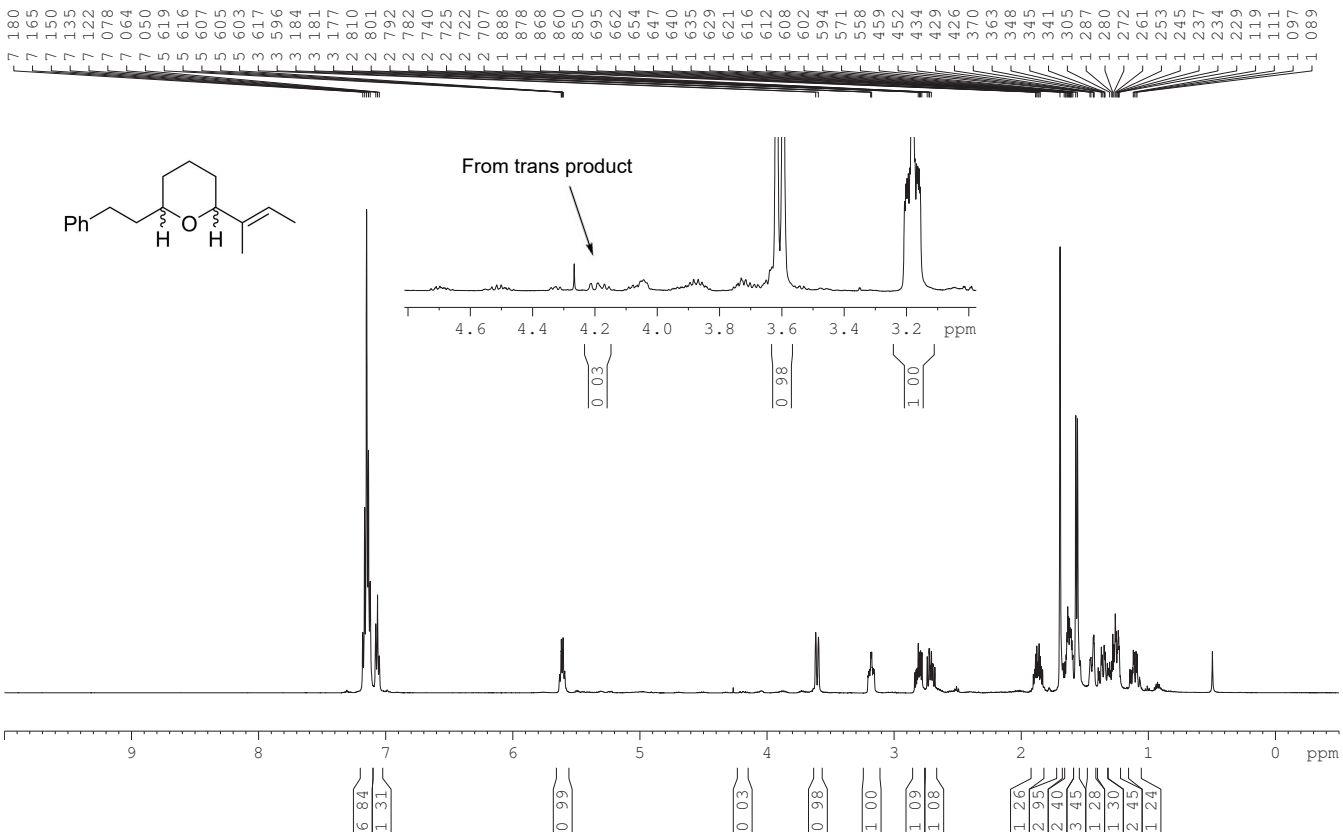
1H NMR (400 MHz, CDCl3)



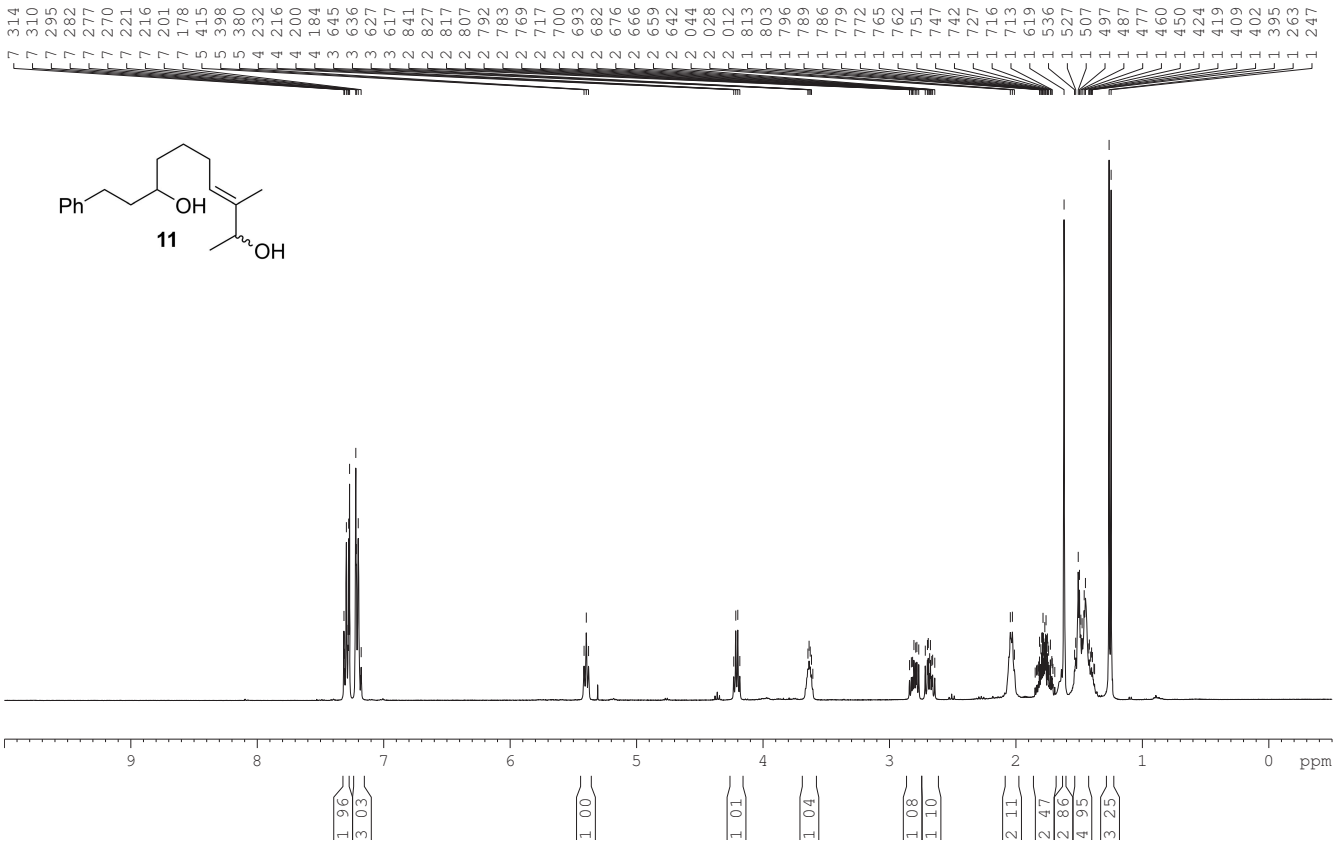
13C NMR (101 MHz, CDCl3)



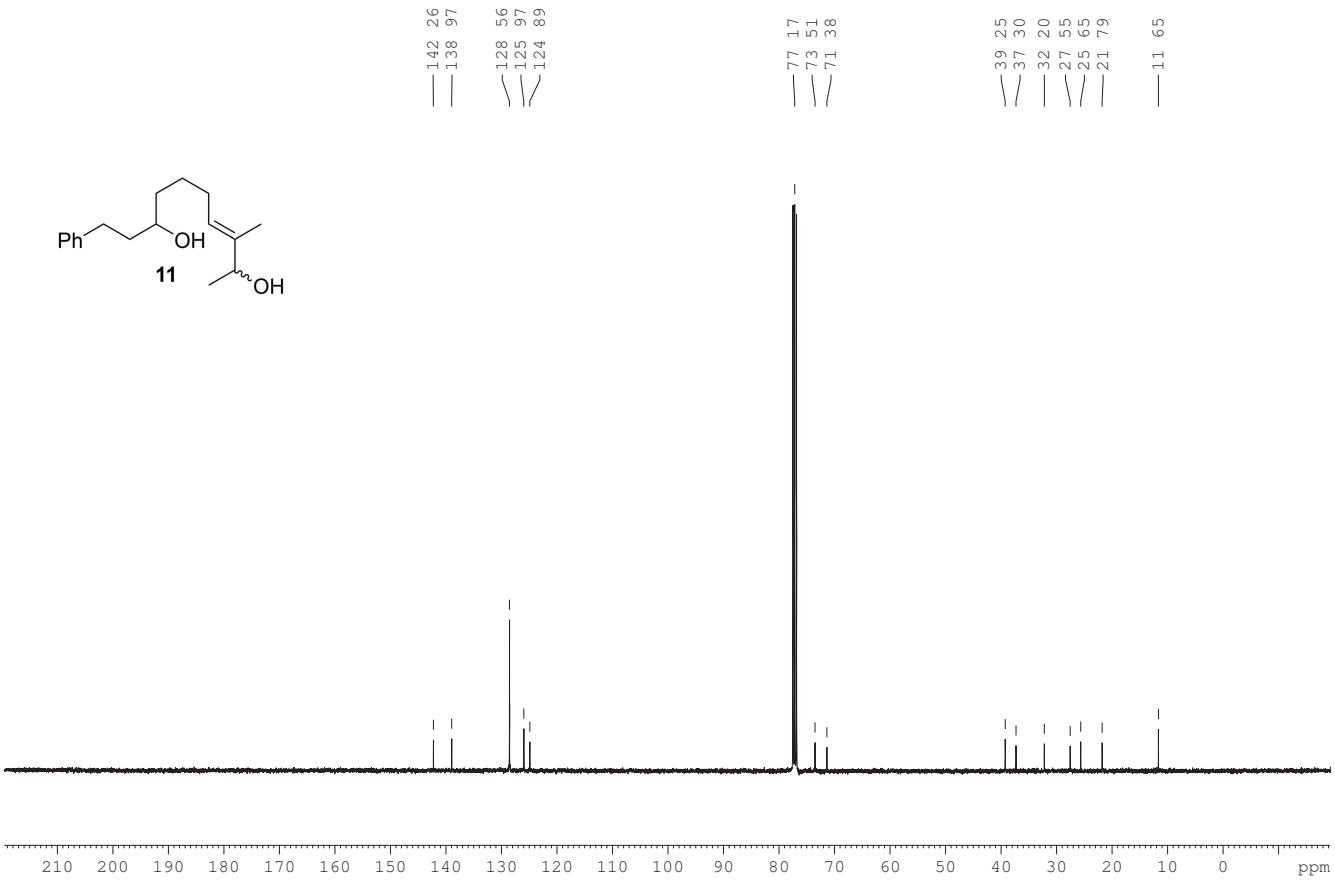
1H NMR (500 MHz, C6D6)



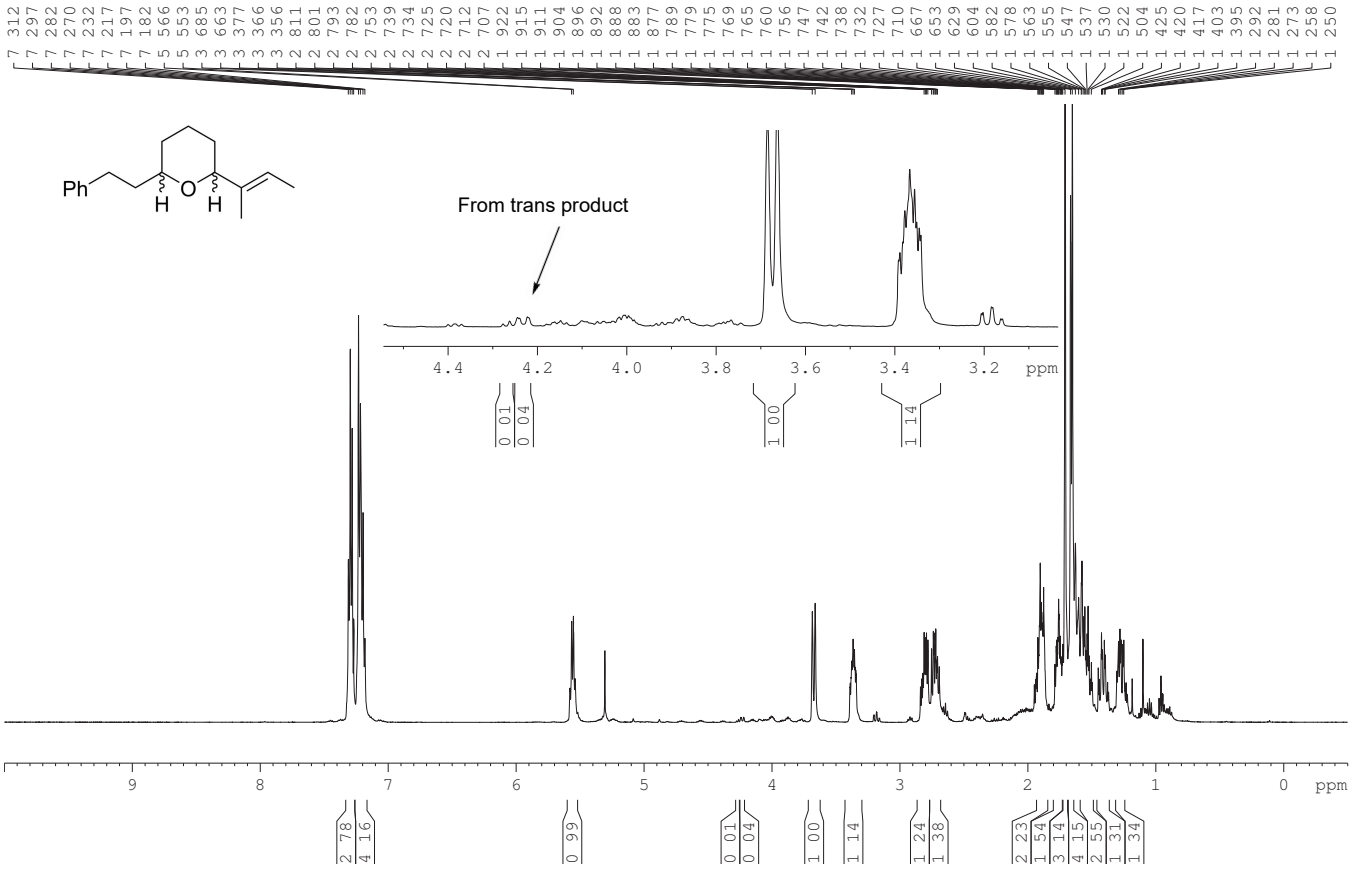
1H NMR (400 MHz, CDCl3)



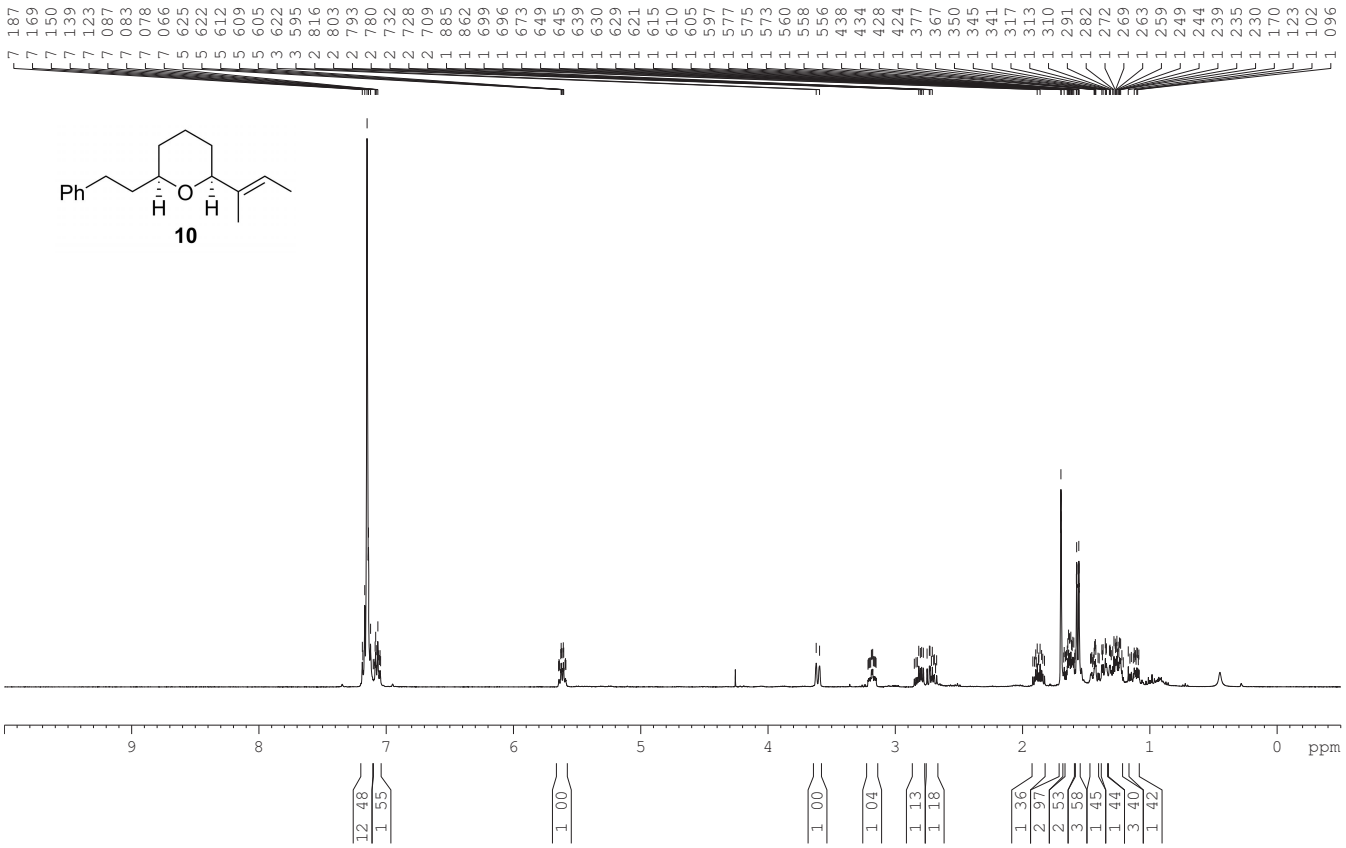
13C NMR (101MHz, CDCl3)



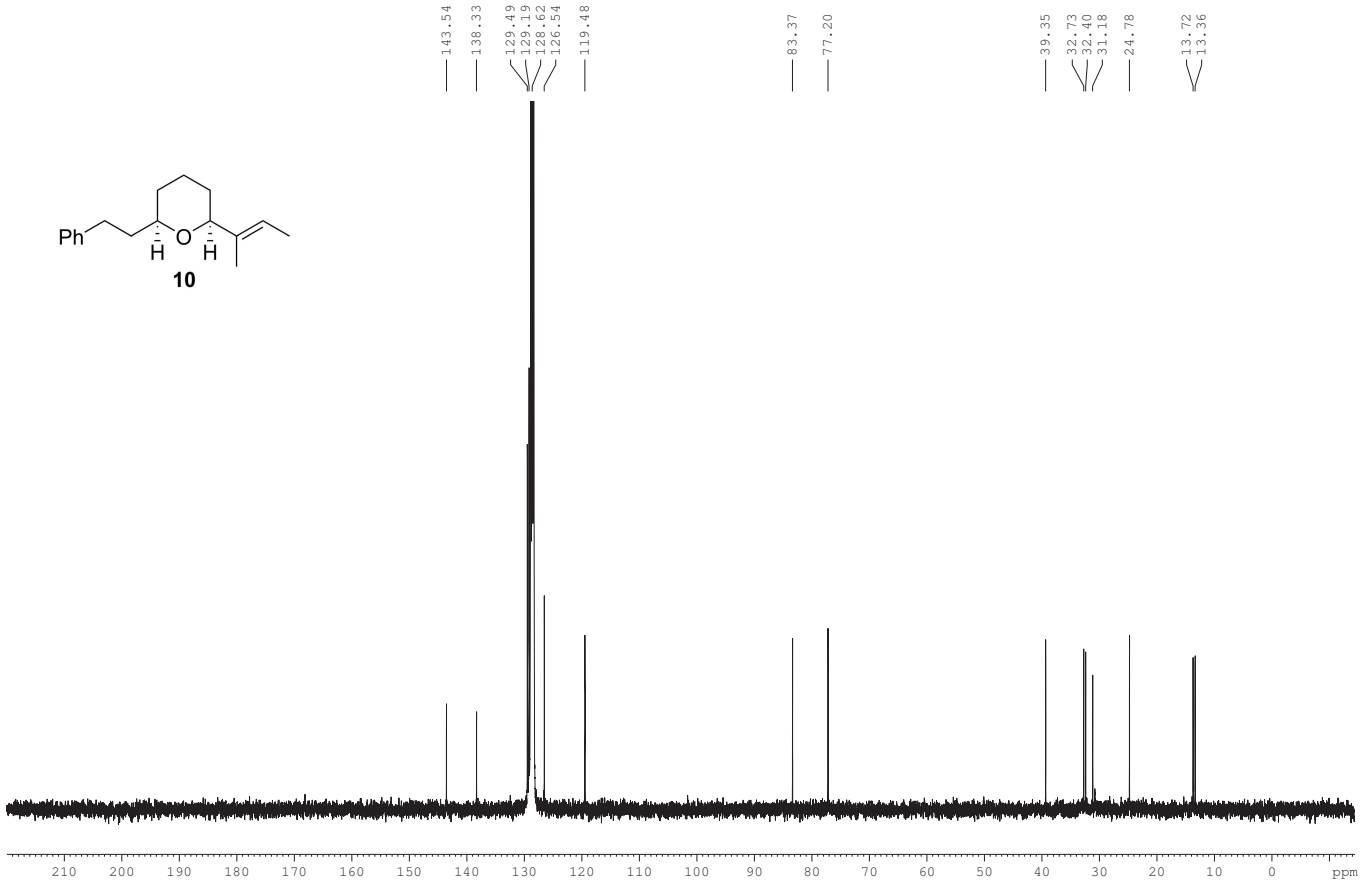
1H NMR (500 MHz, CDCl3)



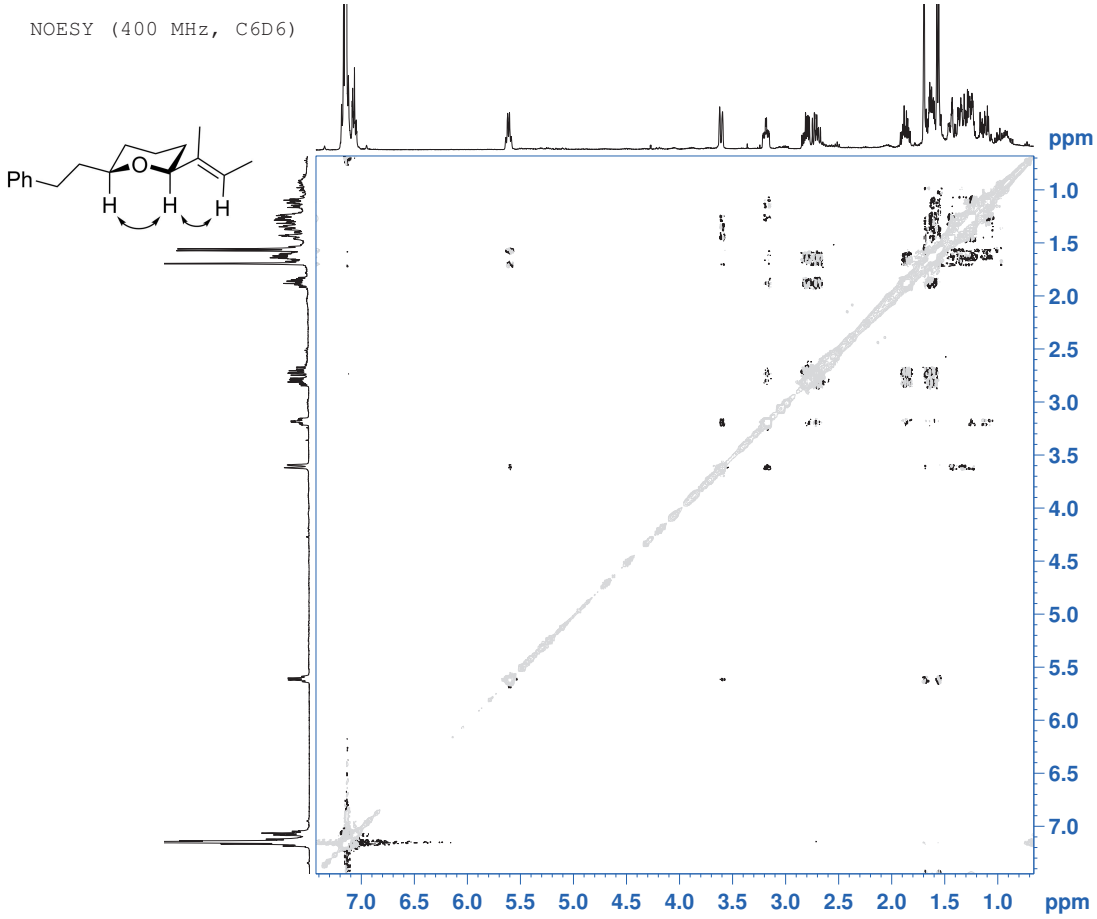
1H NMR (400 MHz, C6D6)



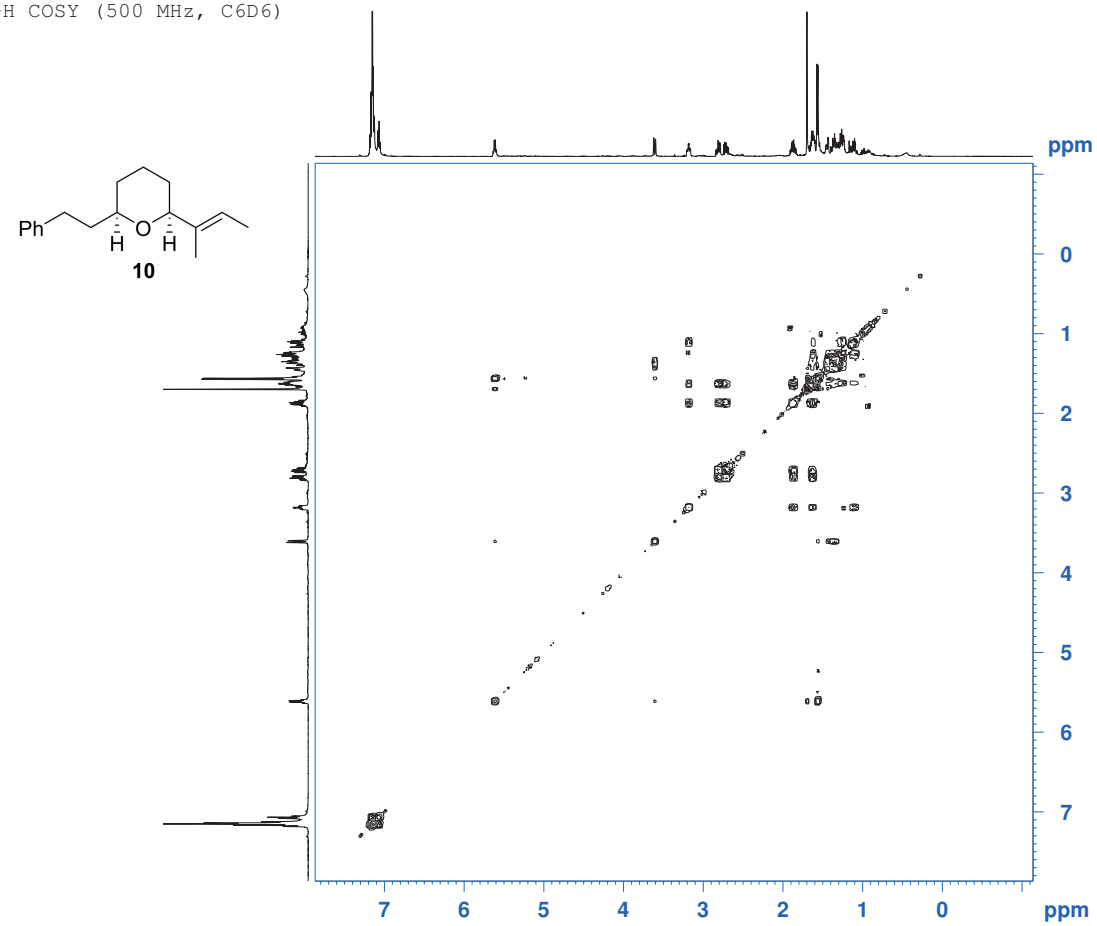
13C NMR (101 MHz, C6D6)



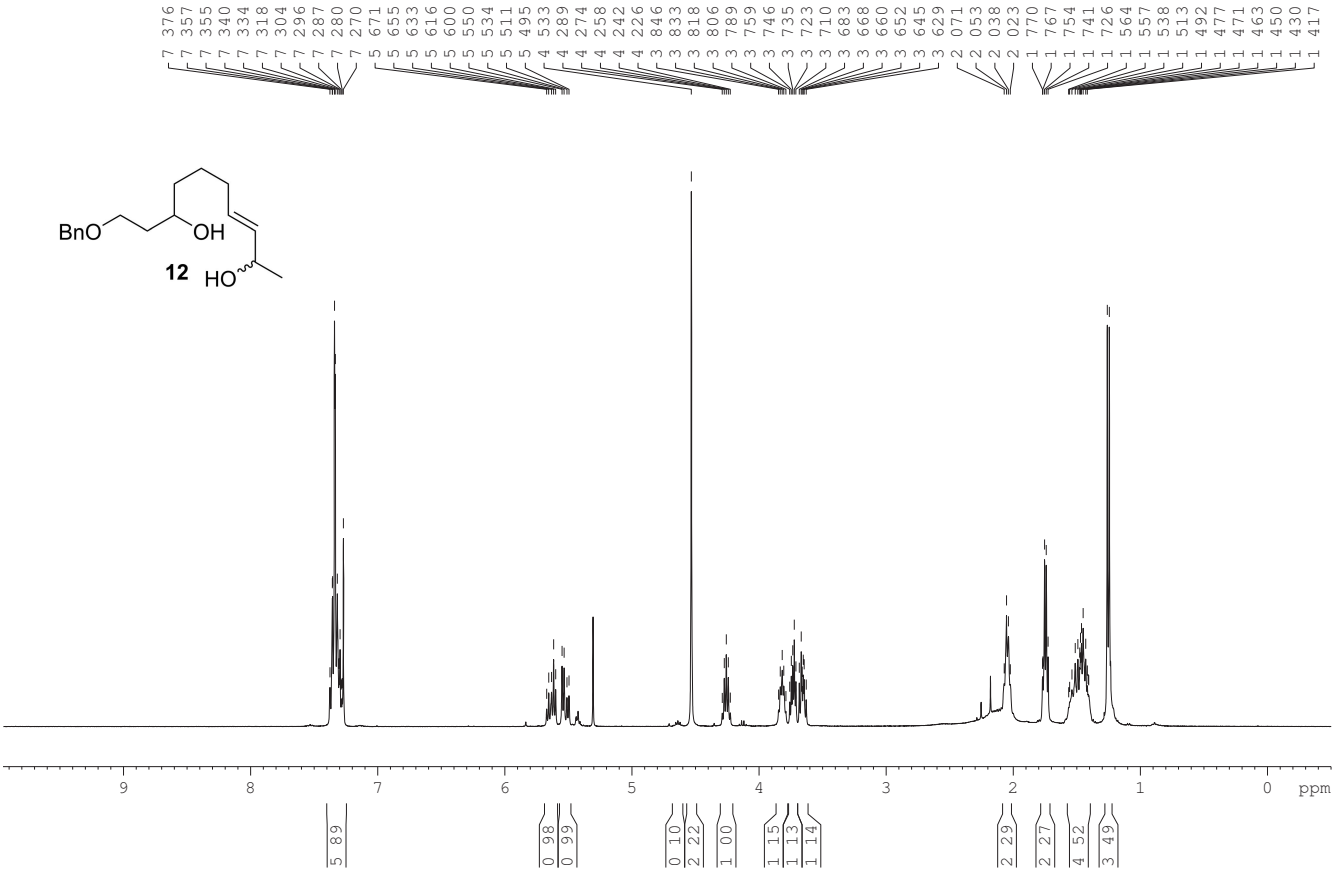
NOESY (400 MHz, C6D6)



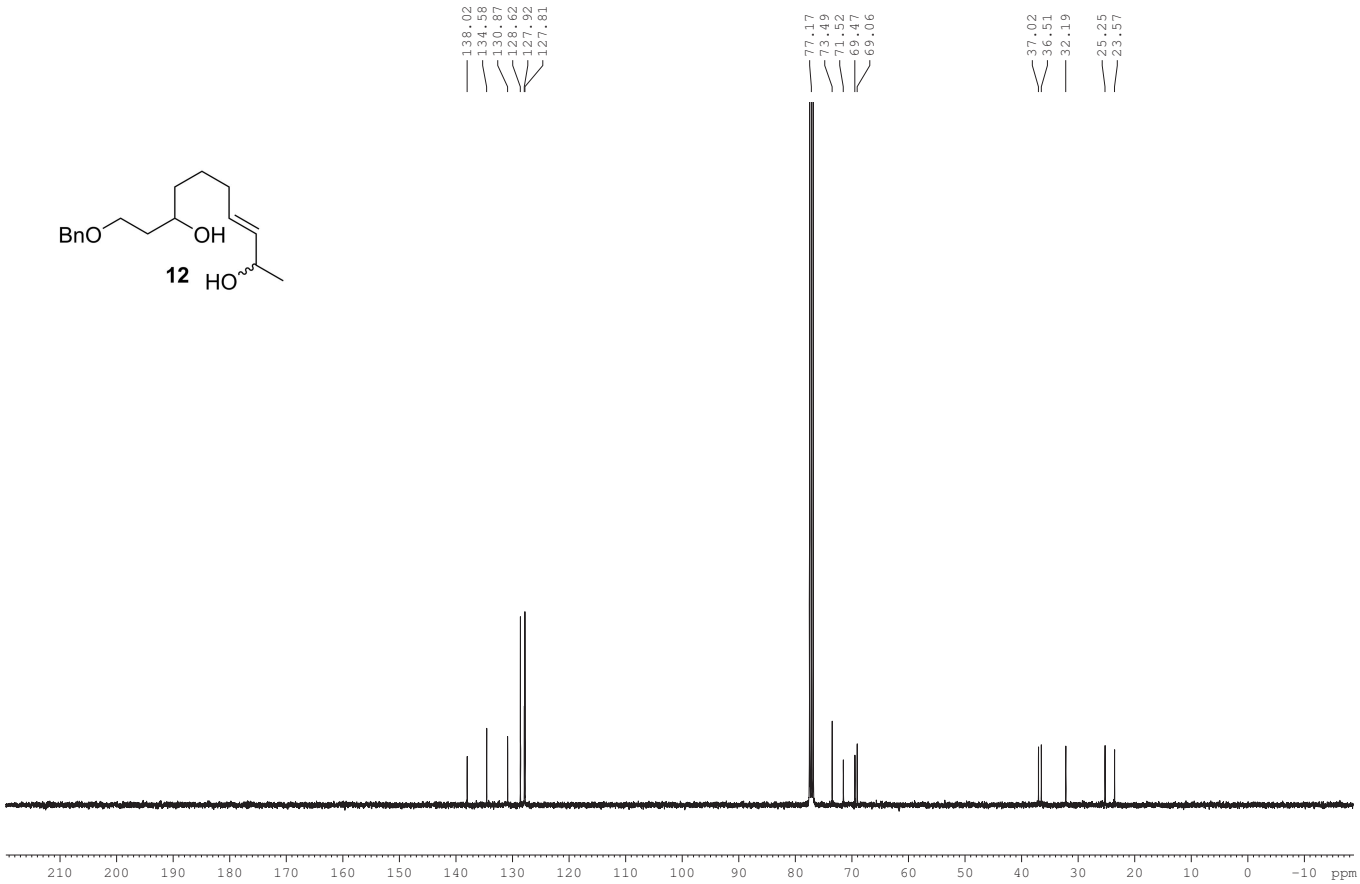
H-H COSY (500 MHz, C6D6)



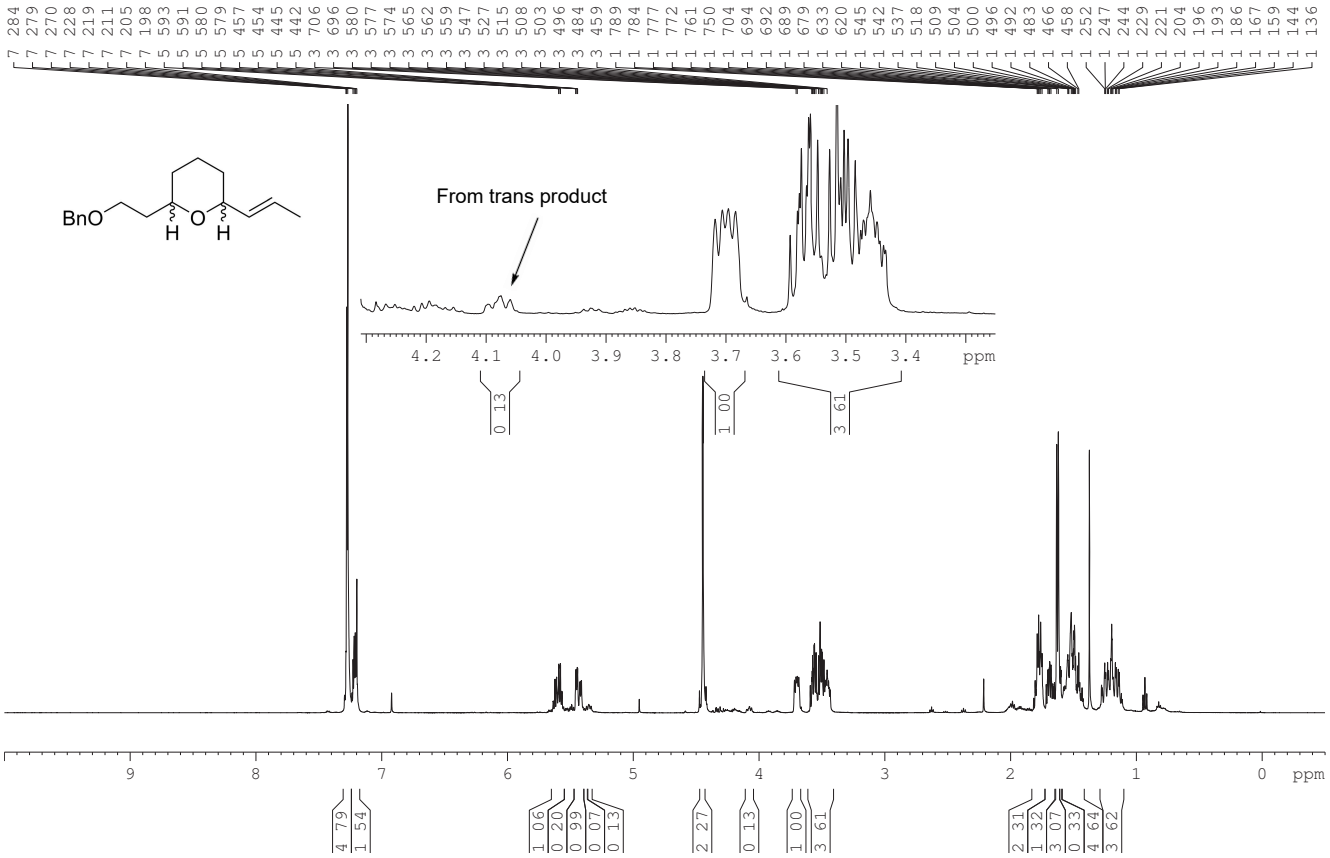
1H NMR (400 MHz, CDCl3)



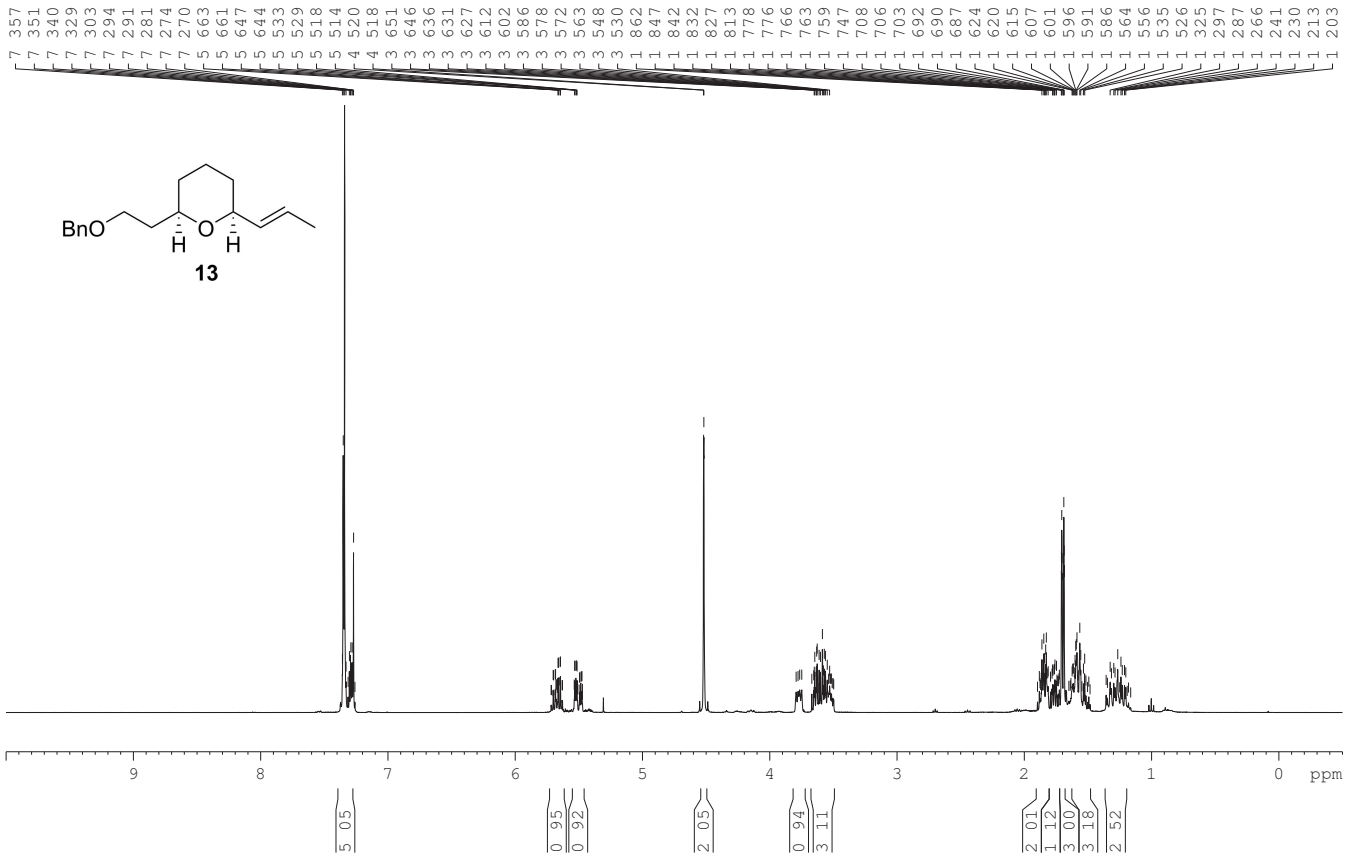
13C NMR (101 MHz, CDCl3)



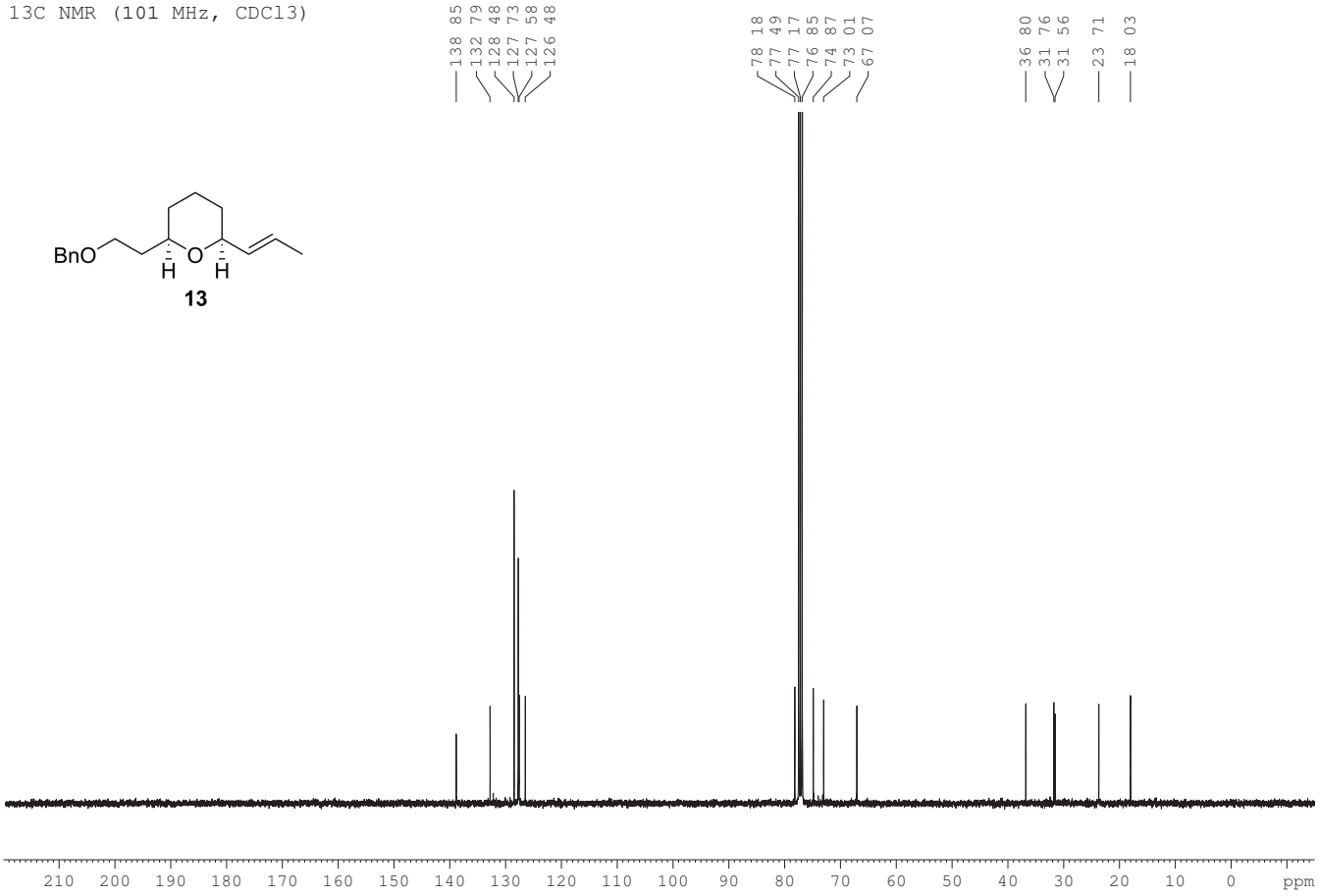
1H NMR (500 MHz, CDCl3)



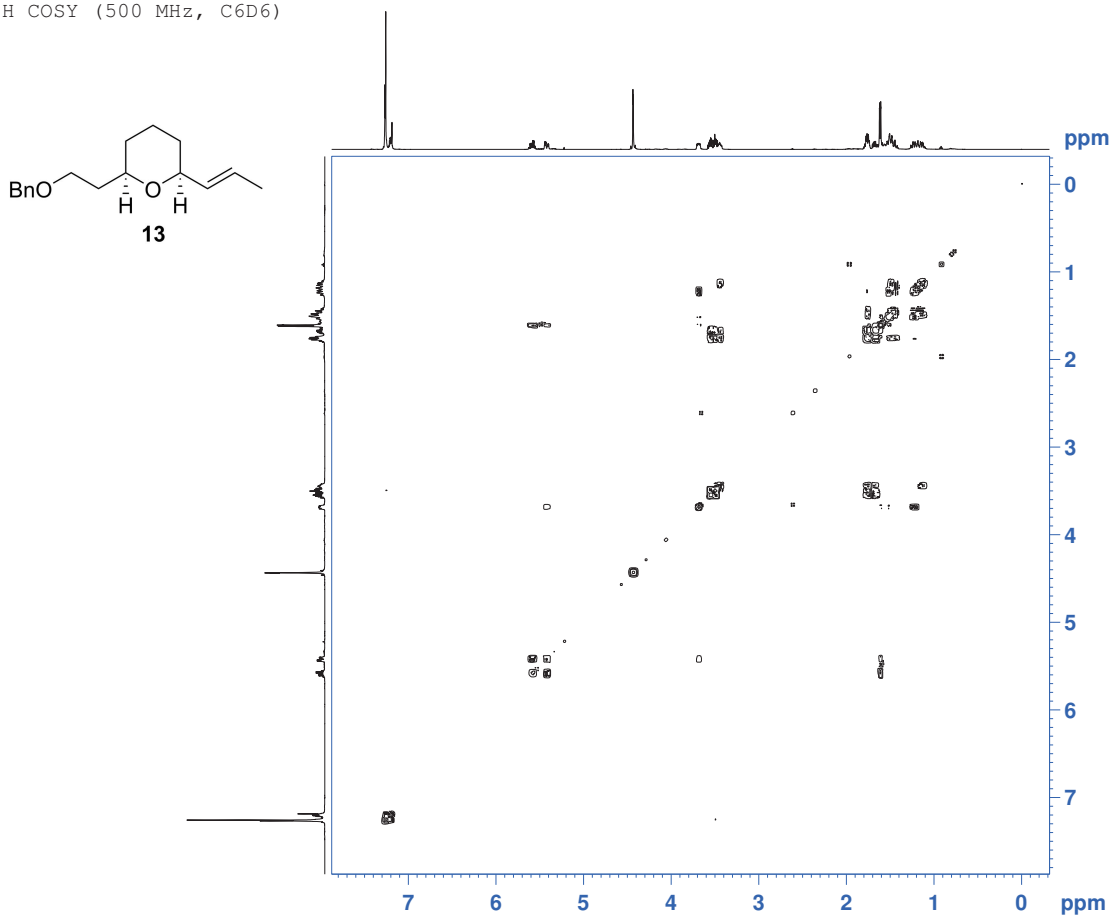
1H NMR (400 MHz, CDCl3)



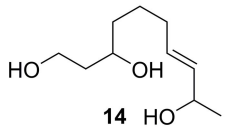
13C NMR (101 MHz, CDCl3)



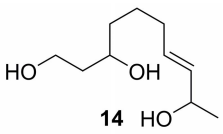
H-H COSY (500 MHz, C6D6)



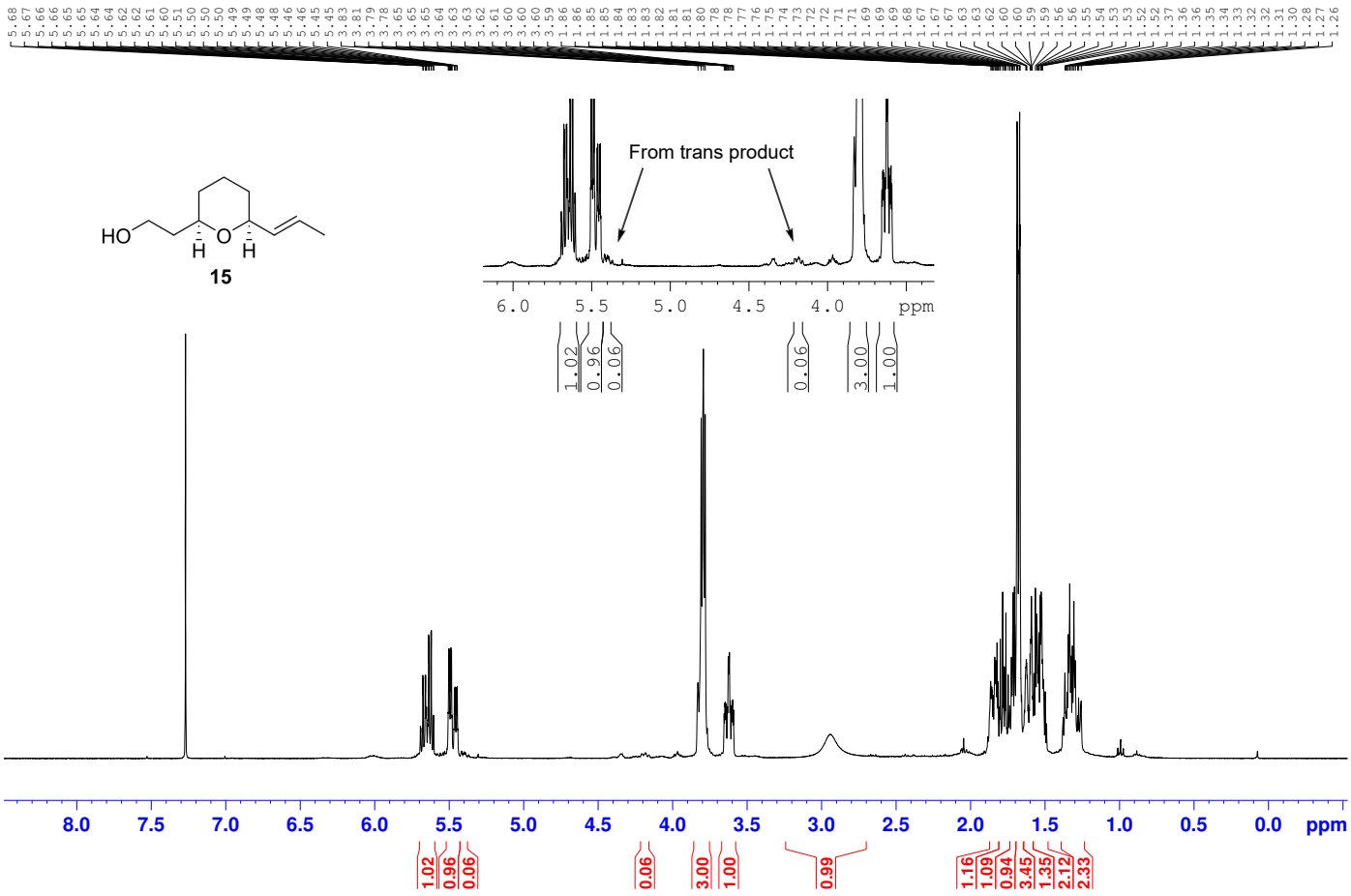
1H NMR (500 MHz, CDCl3)



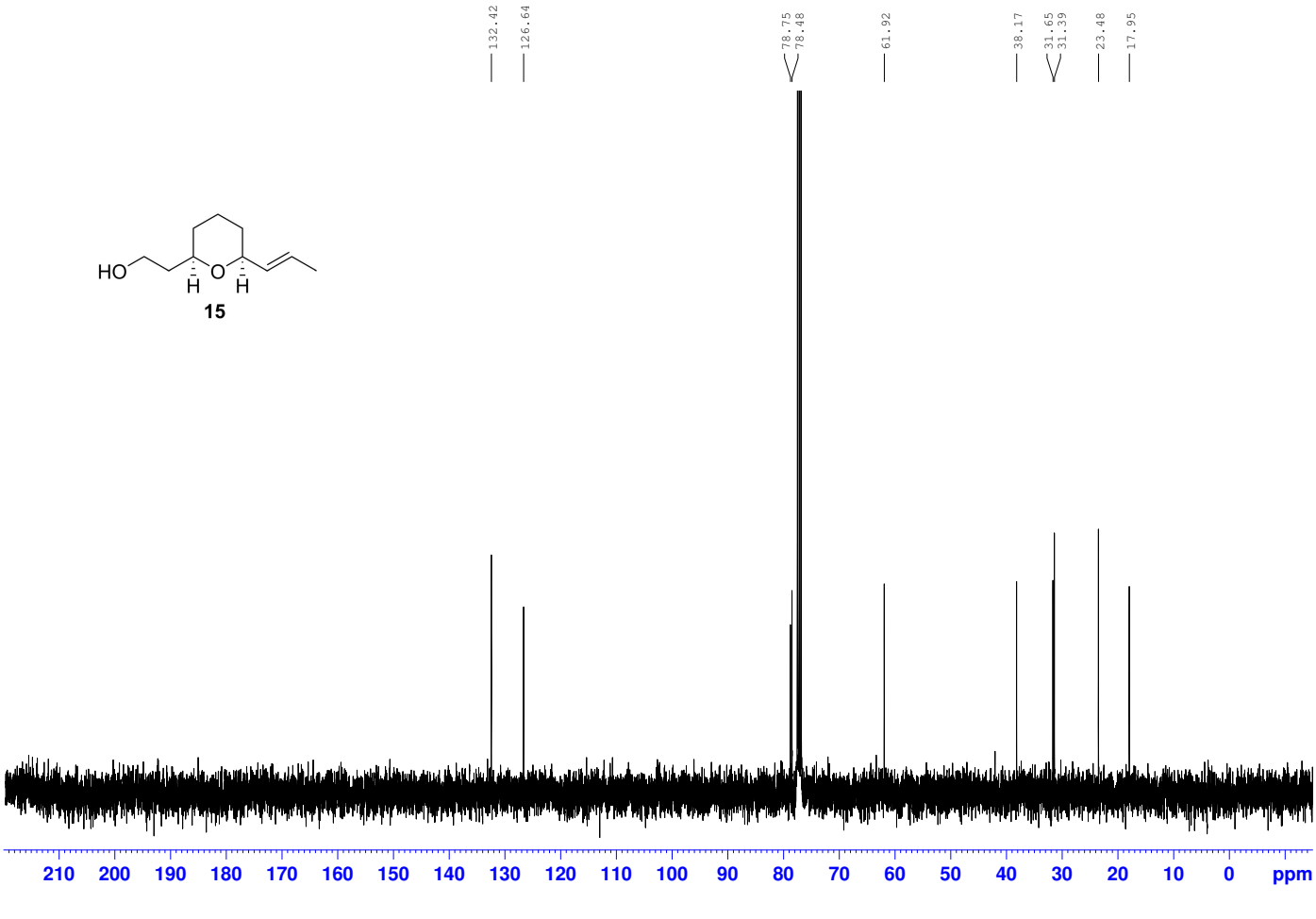
13C NMR (125 MHz, CDCl3)



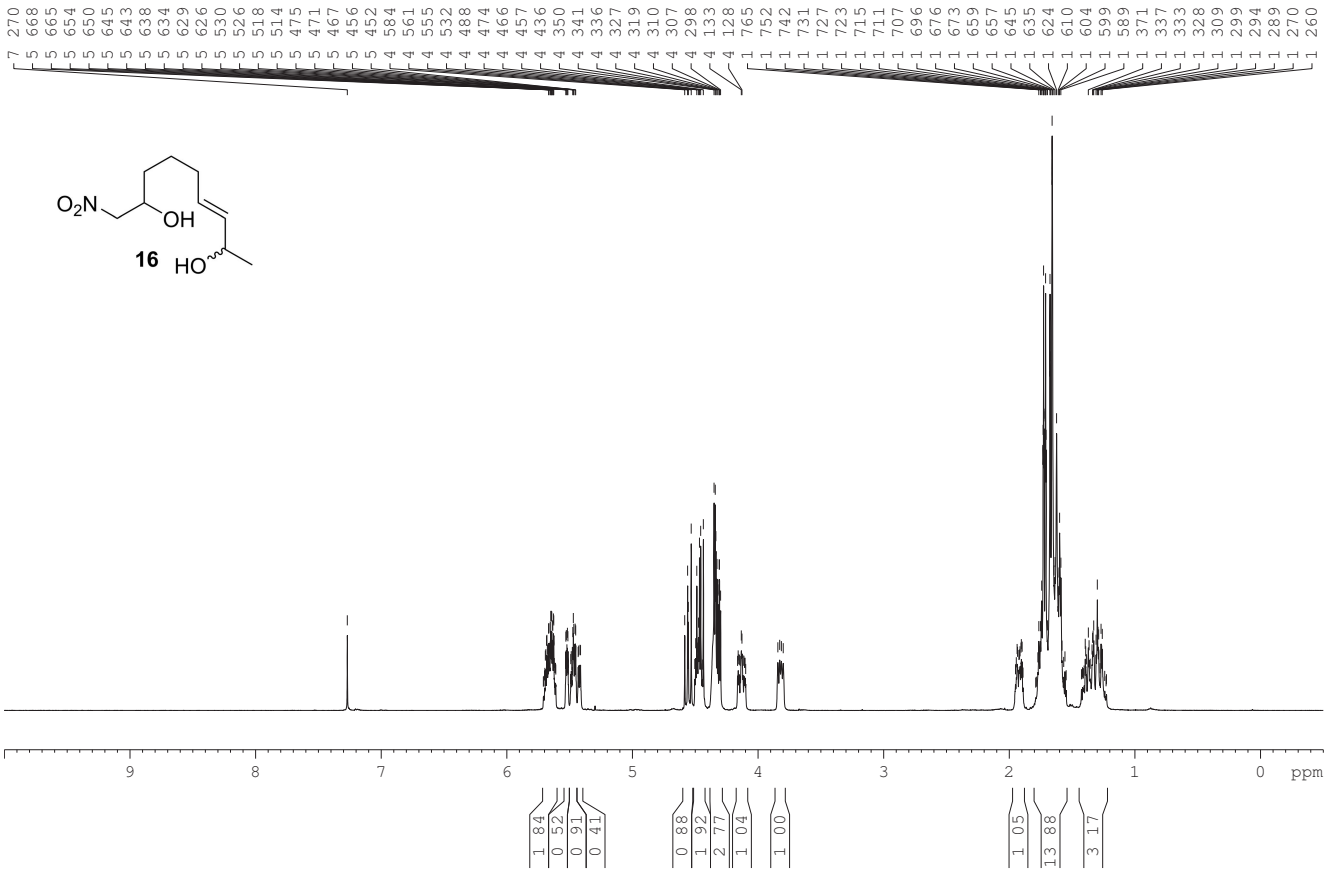
1H NMR (400 MHz, CDCl3)



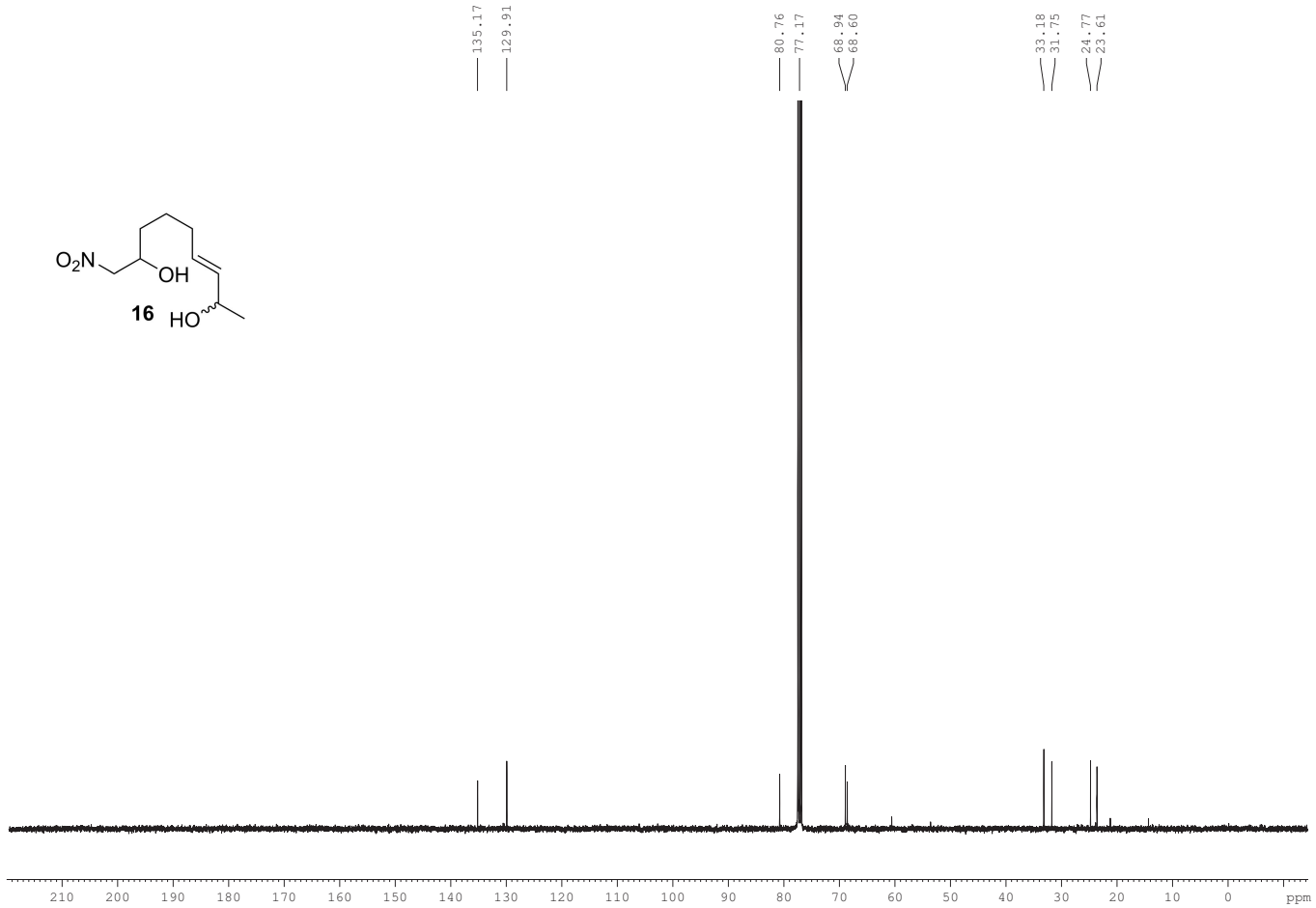
13C NMR (100 MHz, CDCl3)



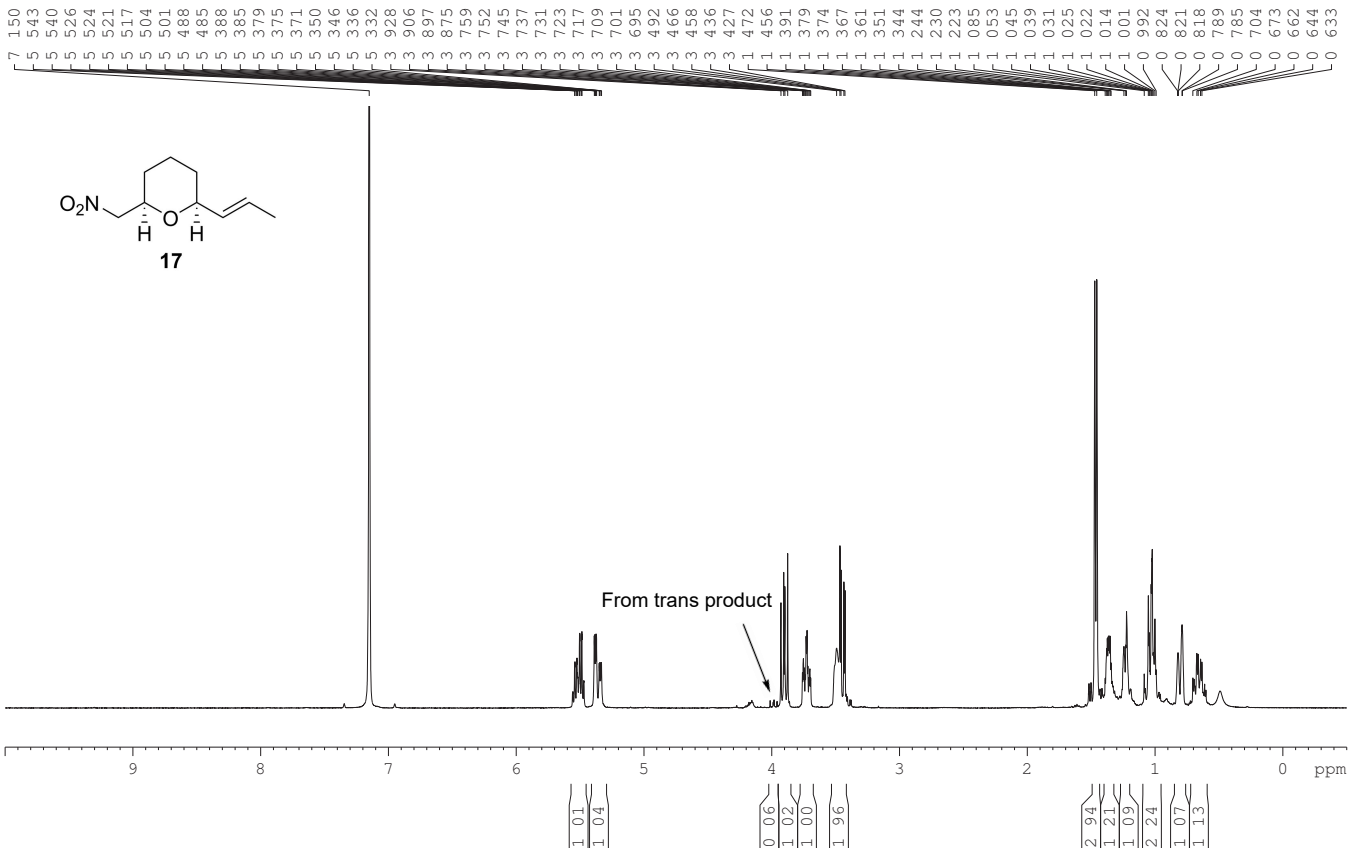
1H NMR (400 MHz, CDCl3)



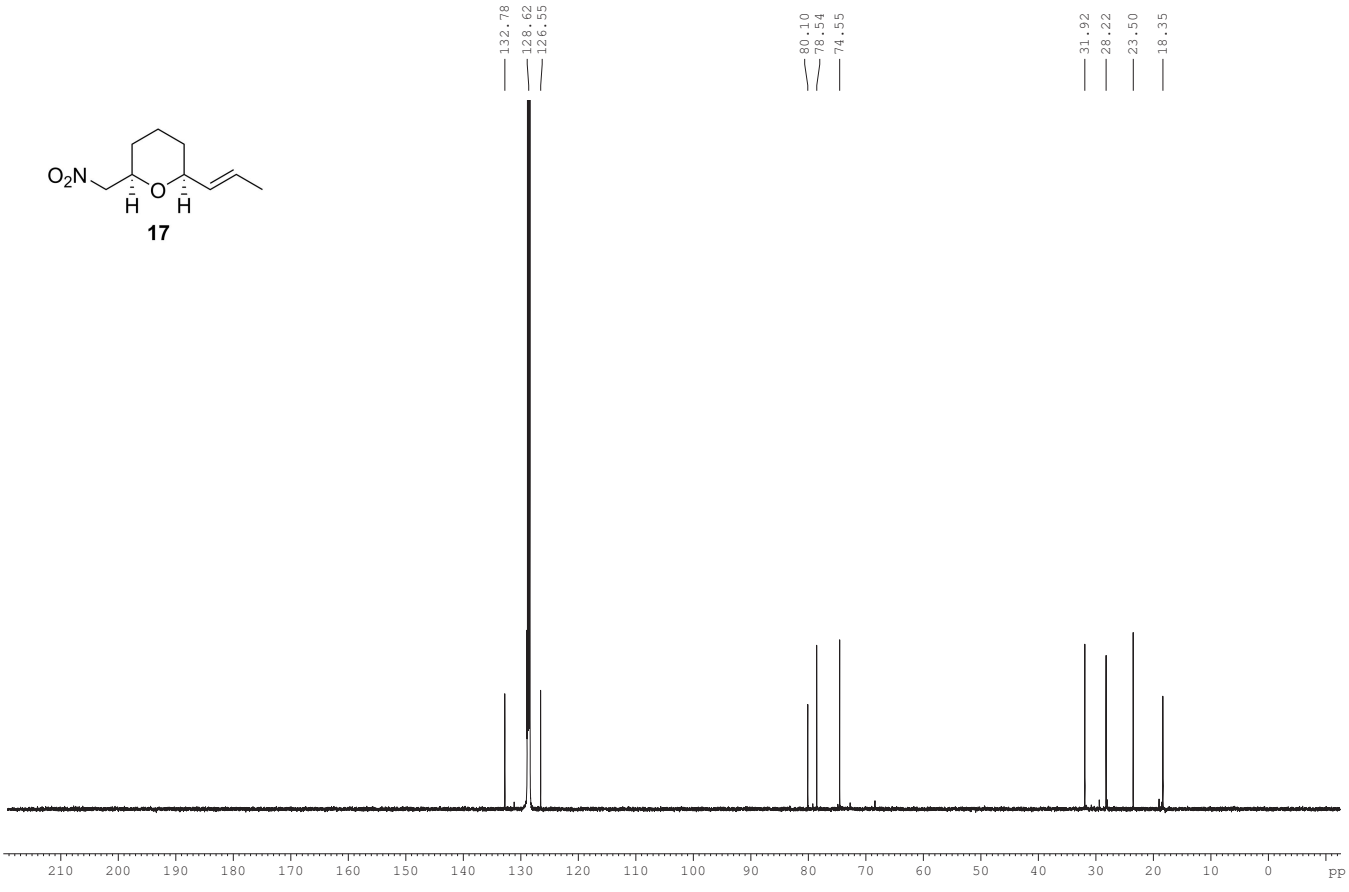
13C NMR (101 MHz, CDCl3)



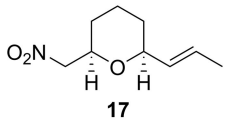
1H NMR (400 MHz, C6D6)



13C NMR (500 MHz, C6D6)



H-H COSY (500 MHz, C6D6)



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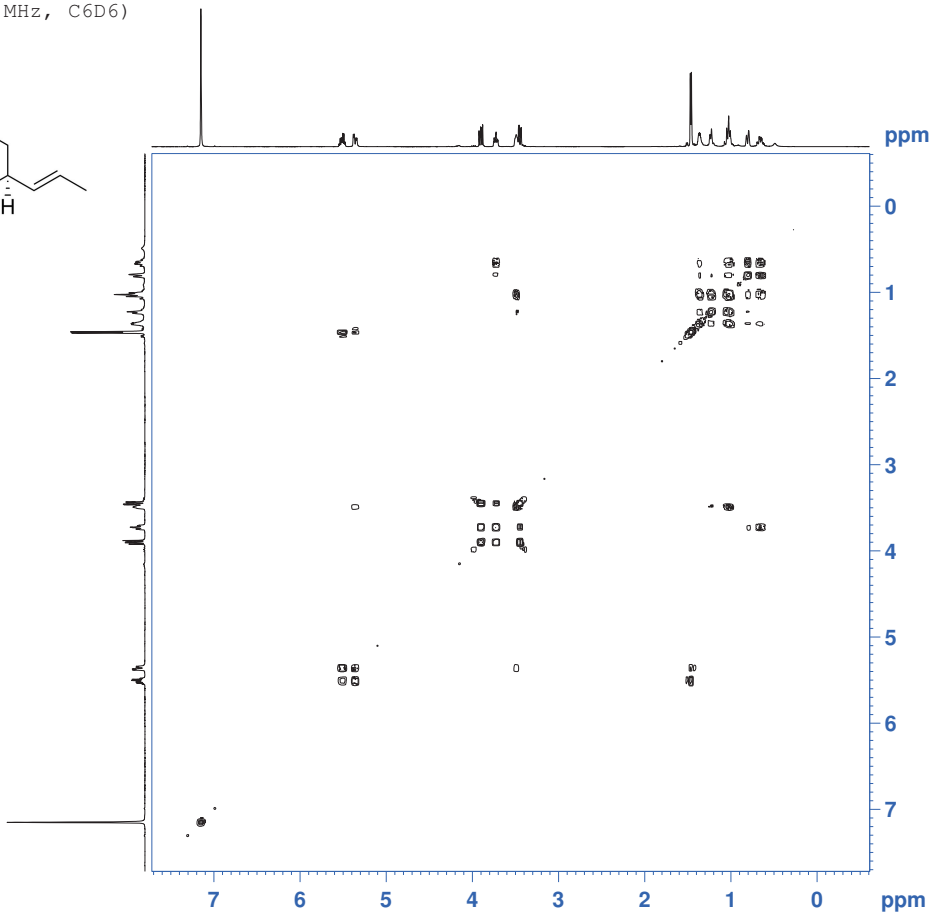
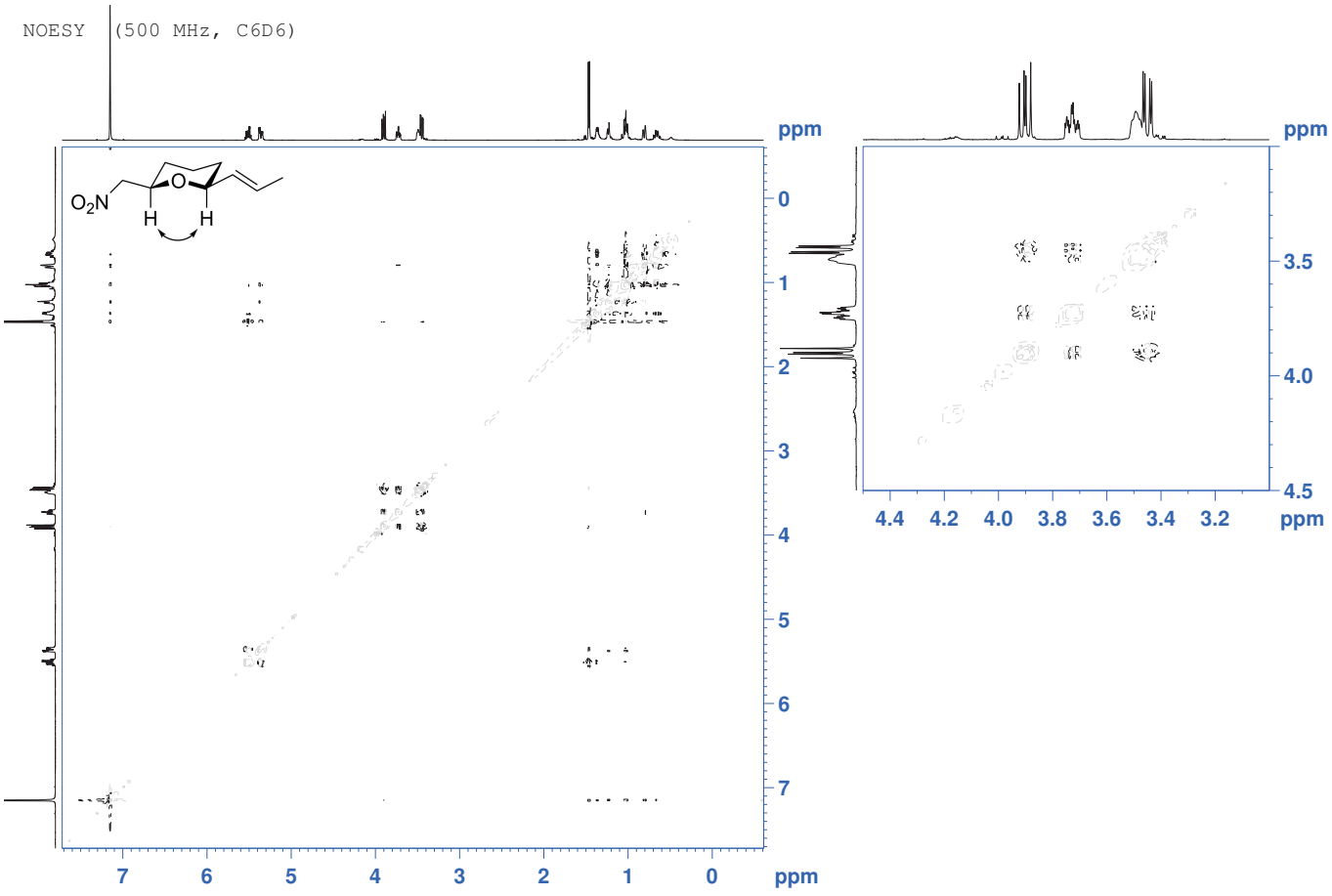
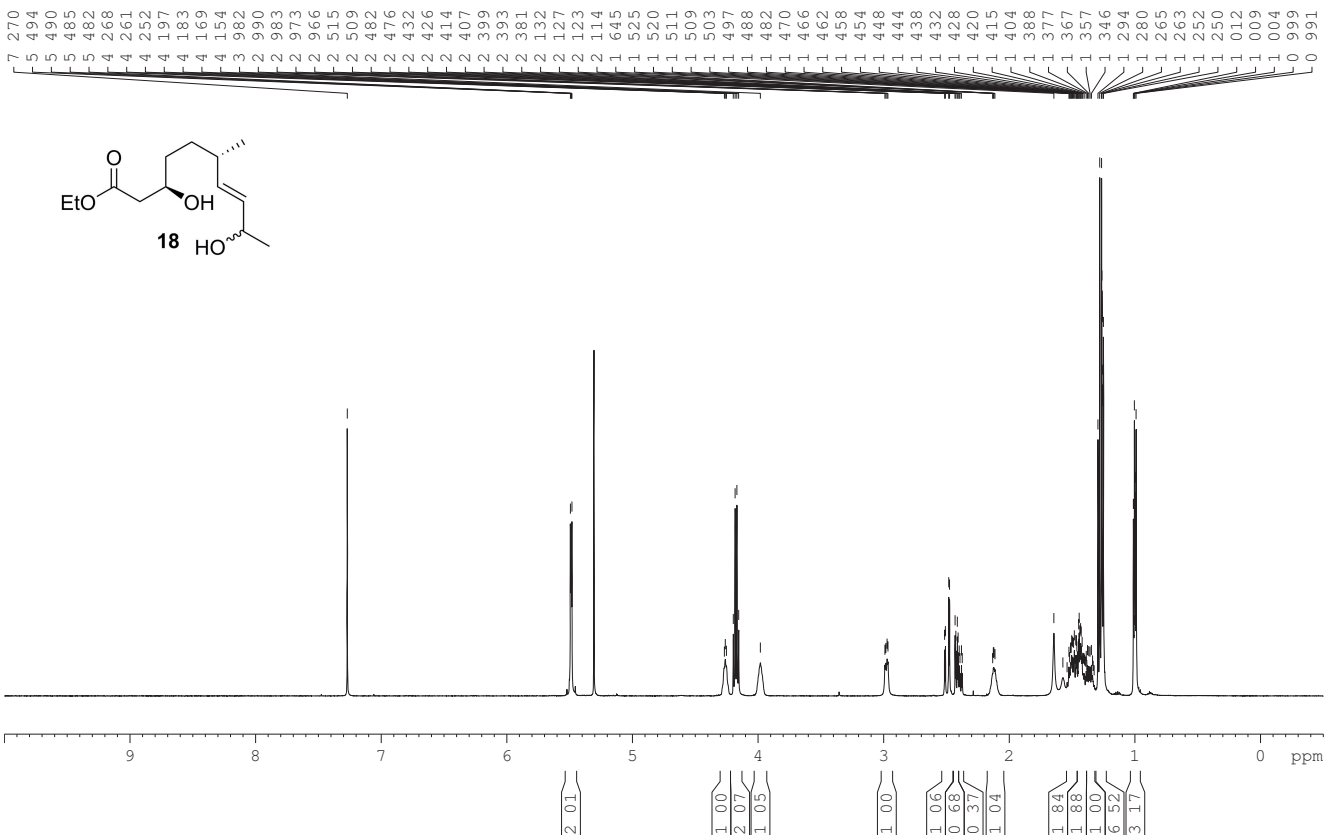


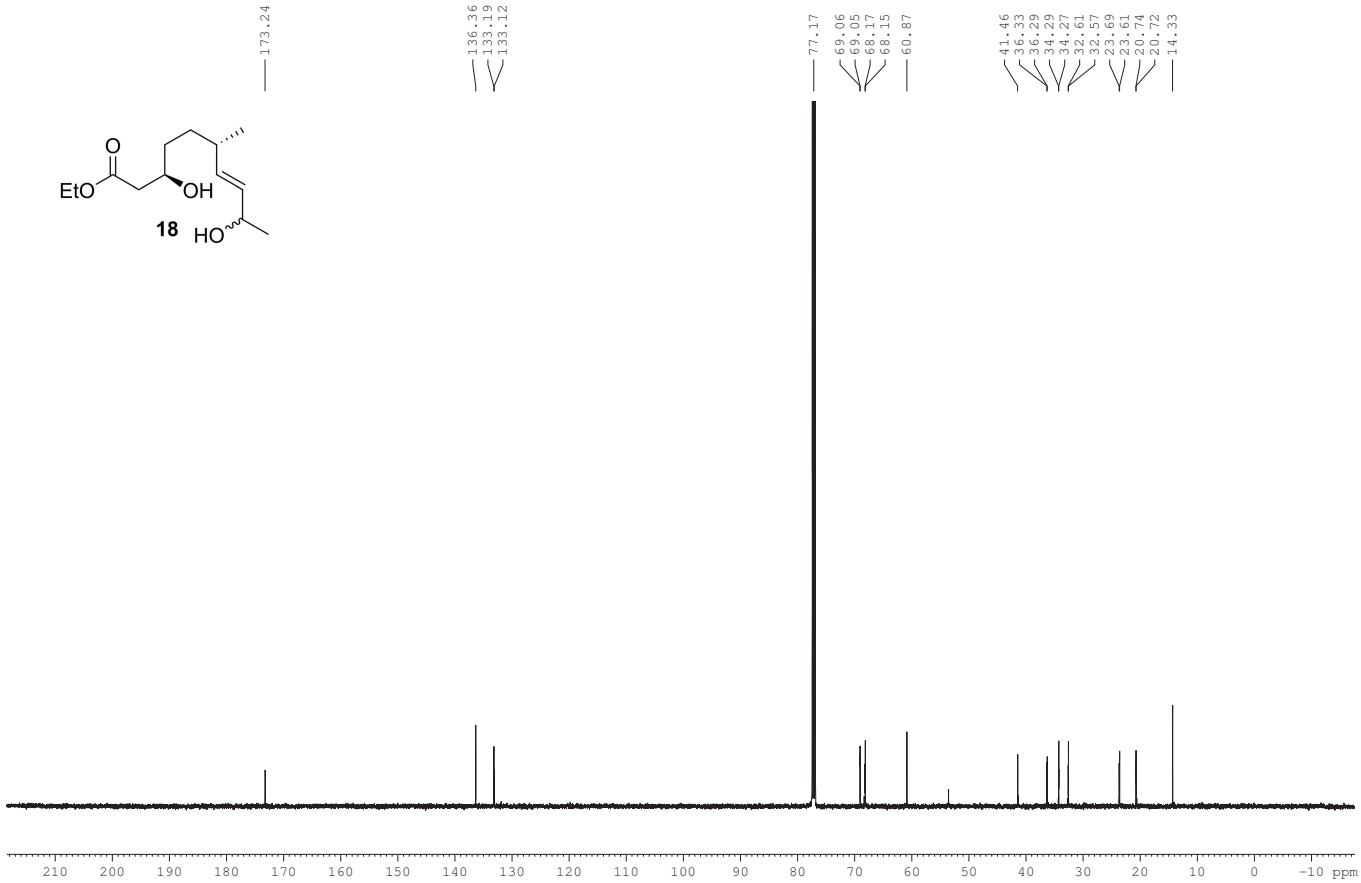
NOESY (500 MHz, C6D6)



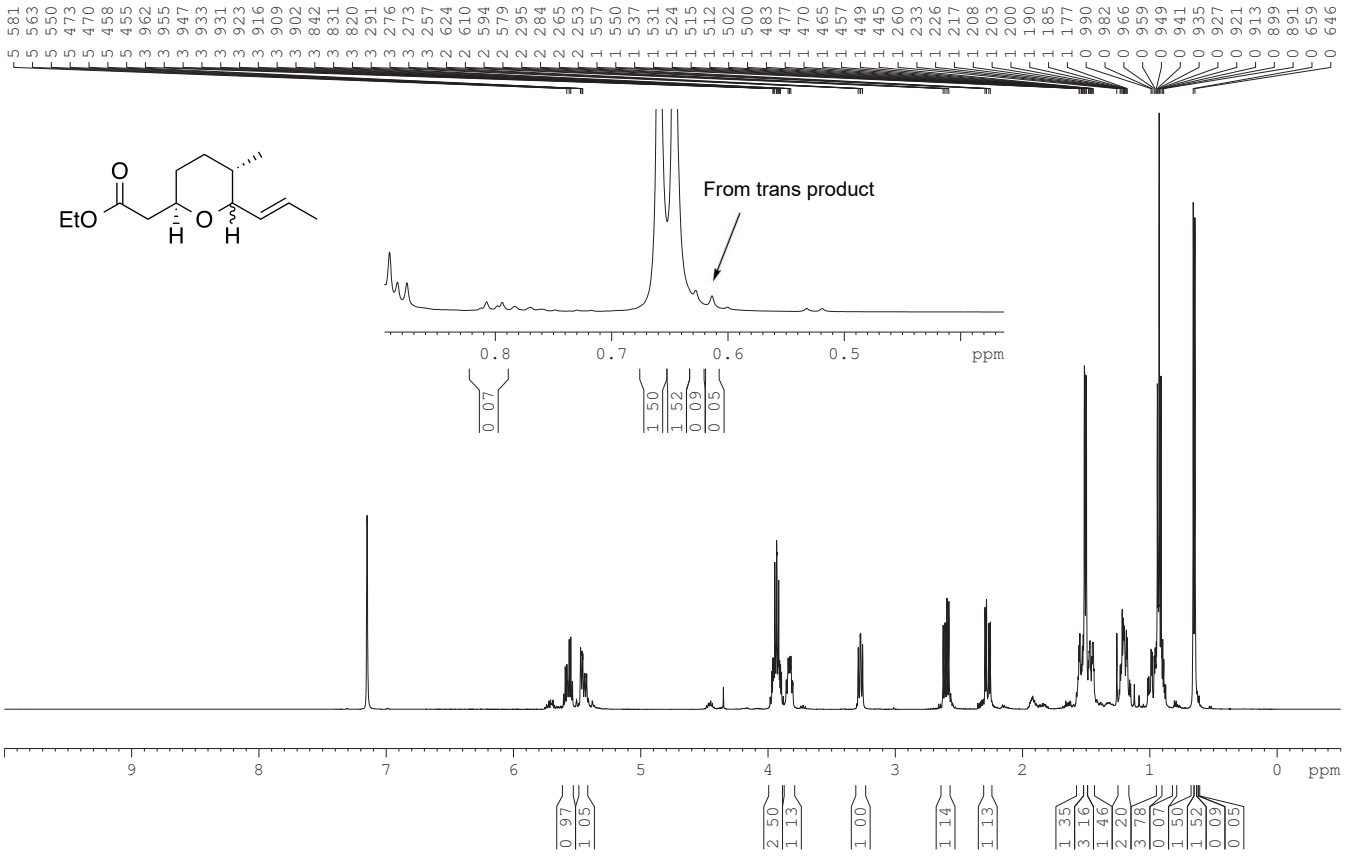
1H NMR (500 MHz, CDCl3)



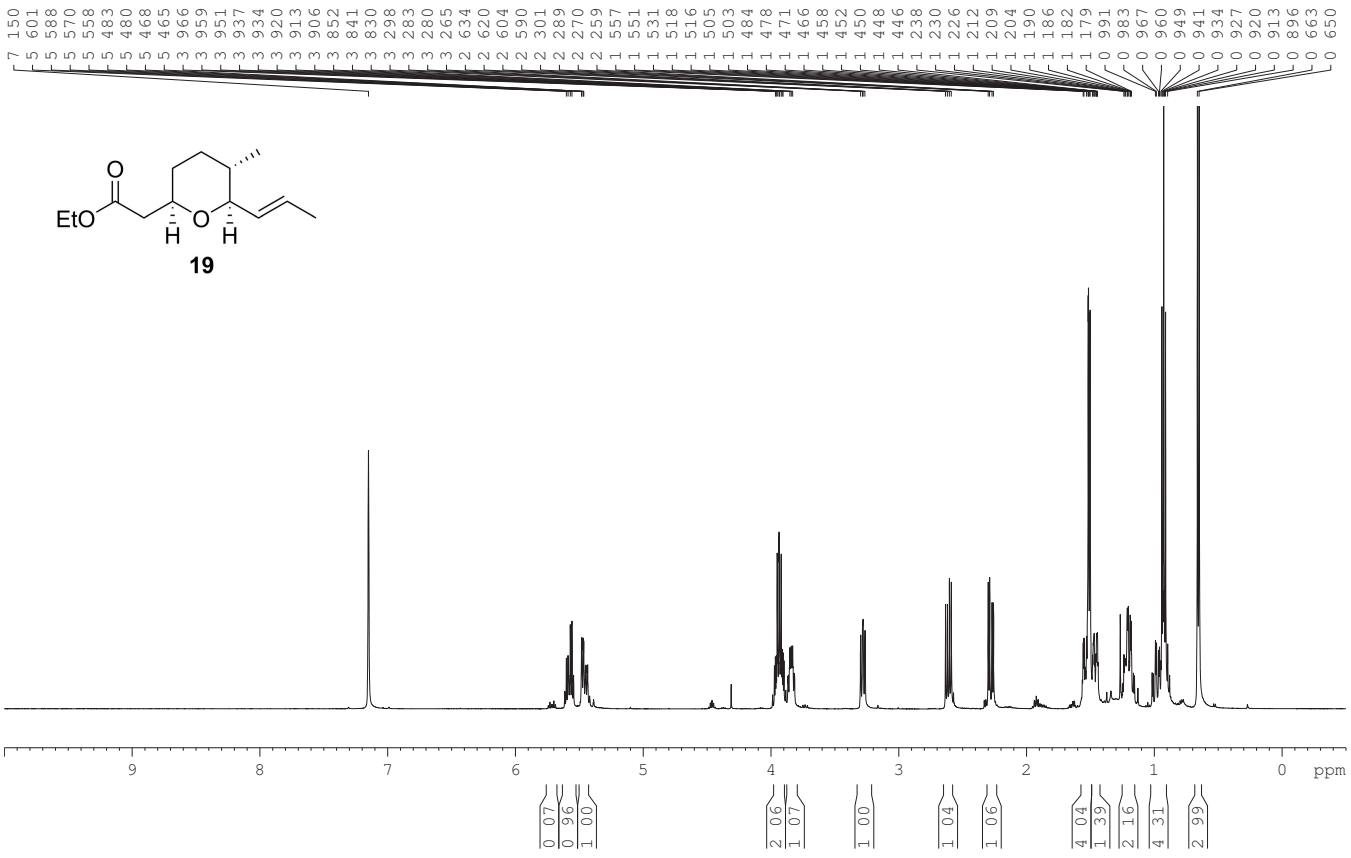
13C NMR (125 MHz, CDCl3)



1H NMR (500MHz, C6D6)

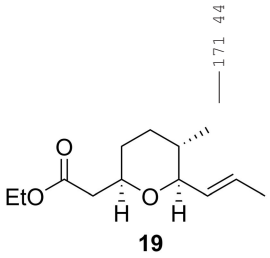


1H NMR (500MHz, C6D6)



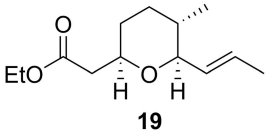
19

13C NMR (500MHz, C6D6)



19

H-H COSY (500MHz, CDCl3)



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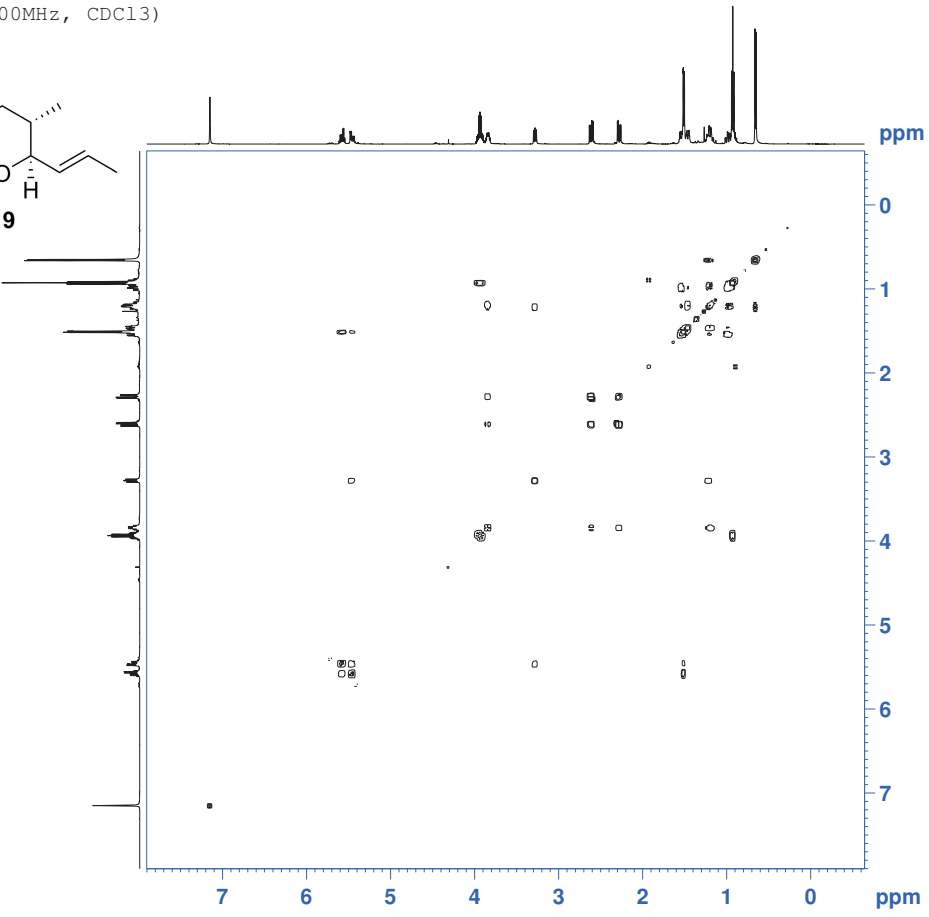
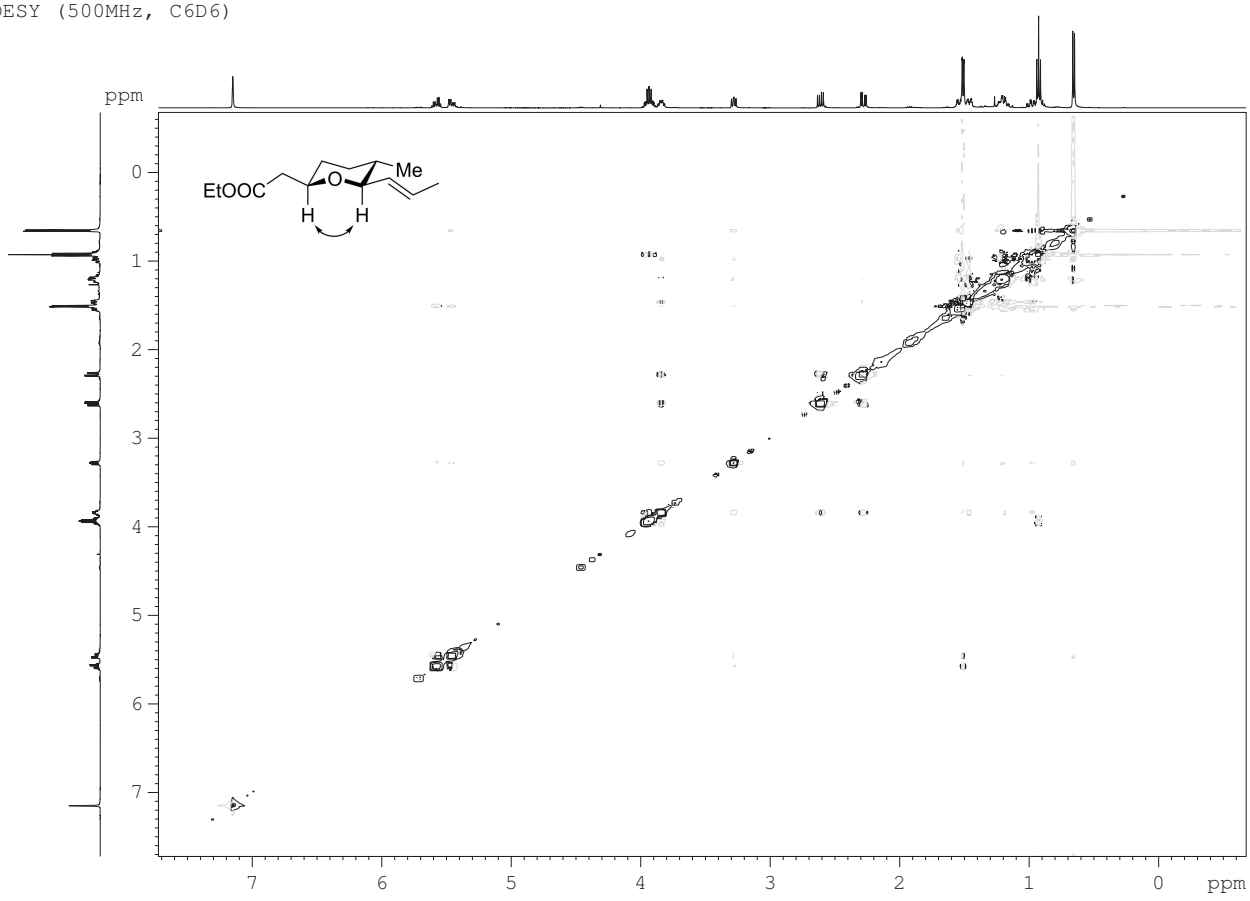
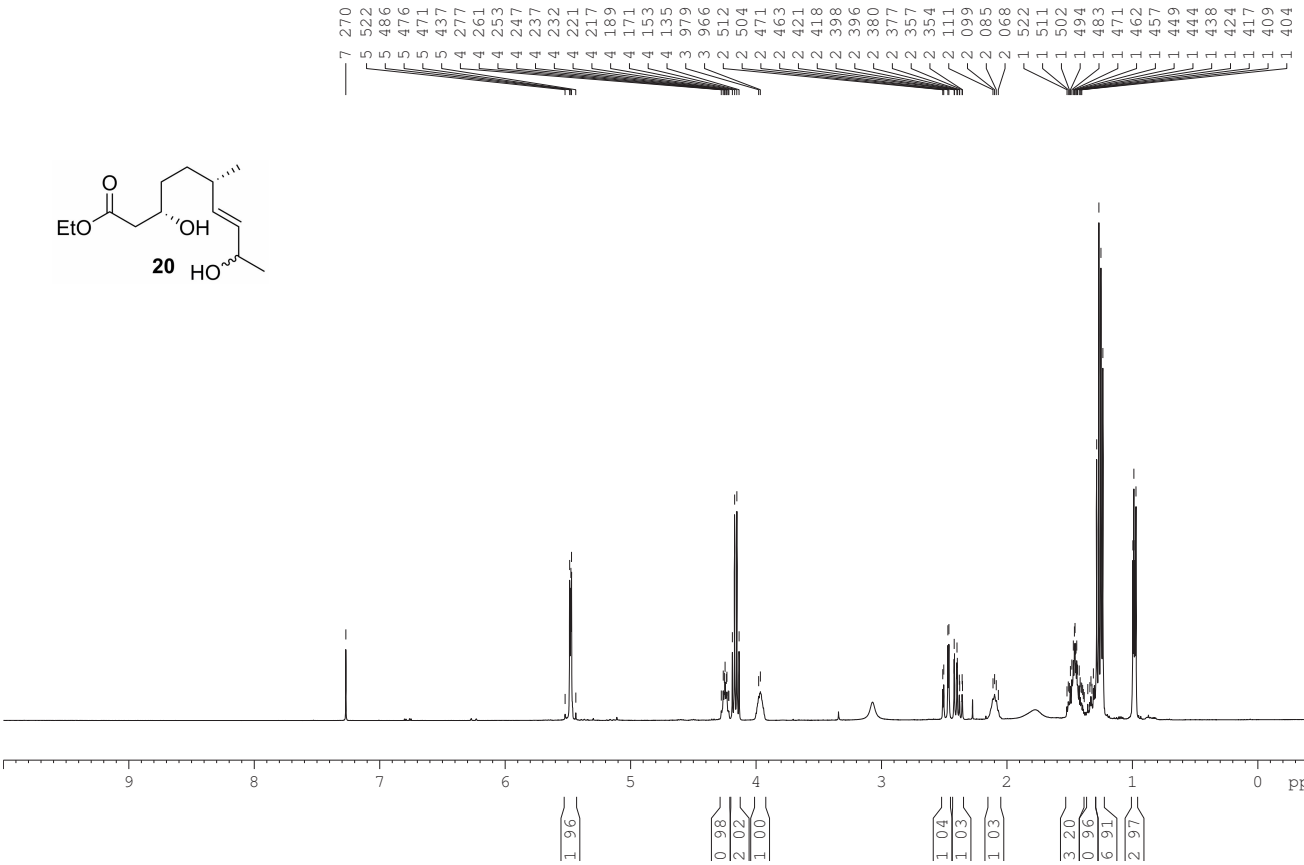


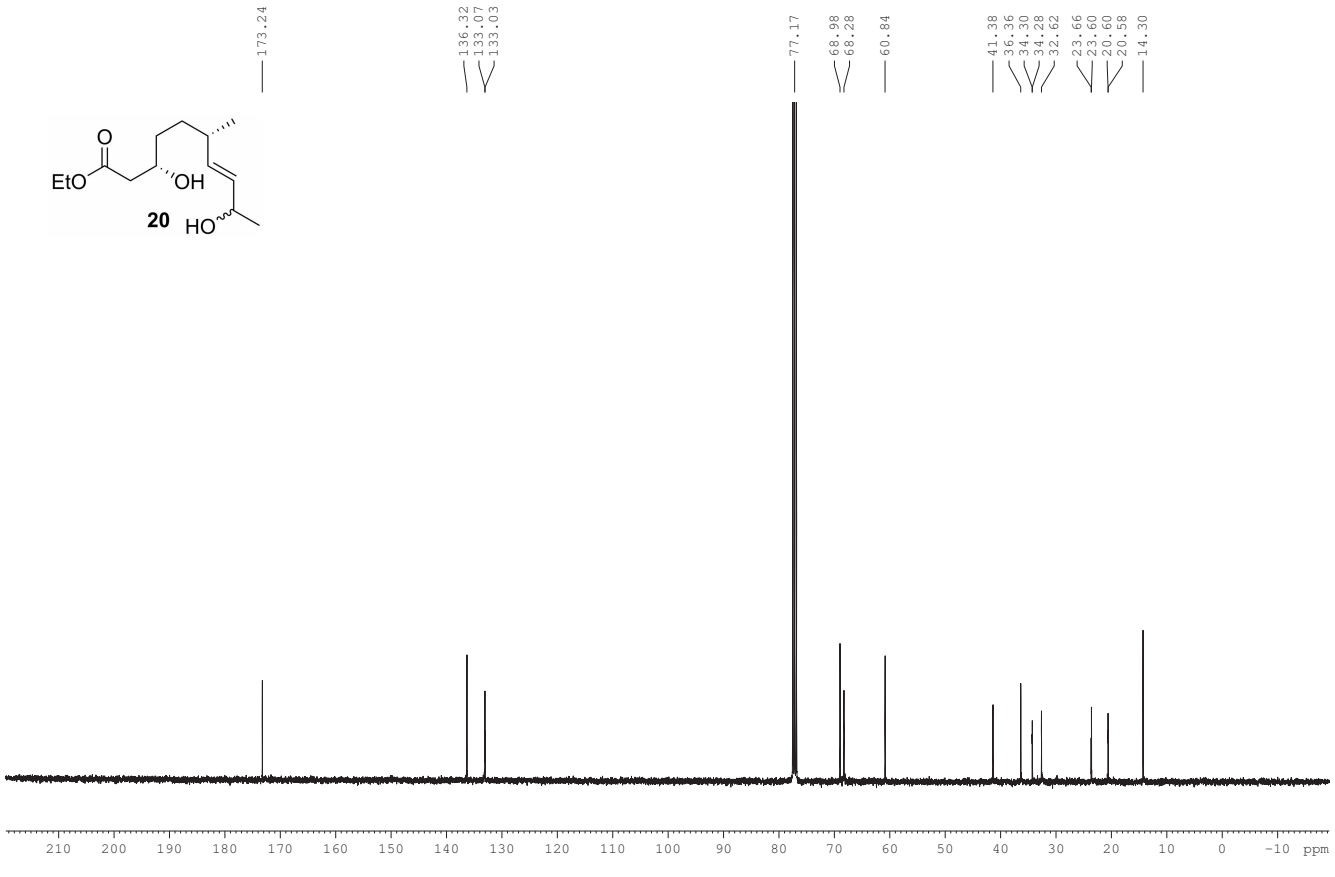
NOESY (500MHz, C6D6)



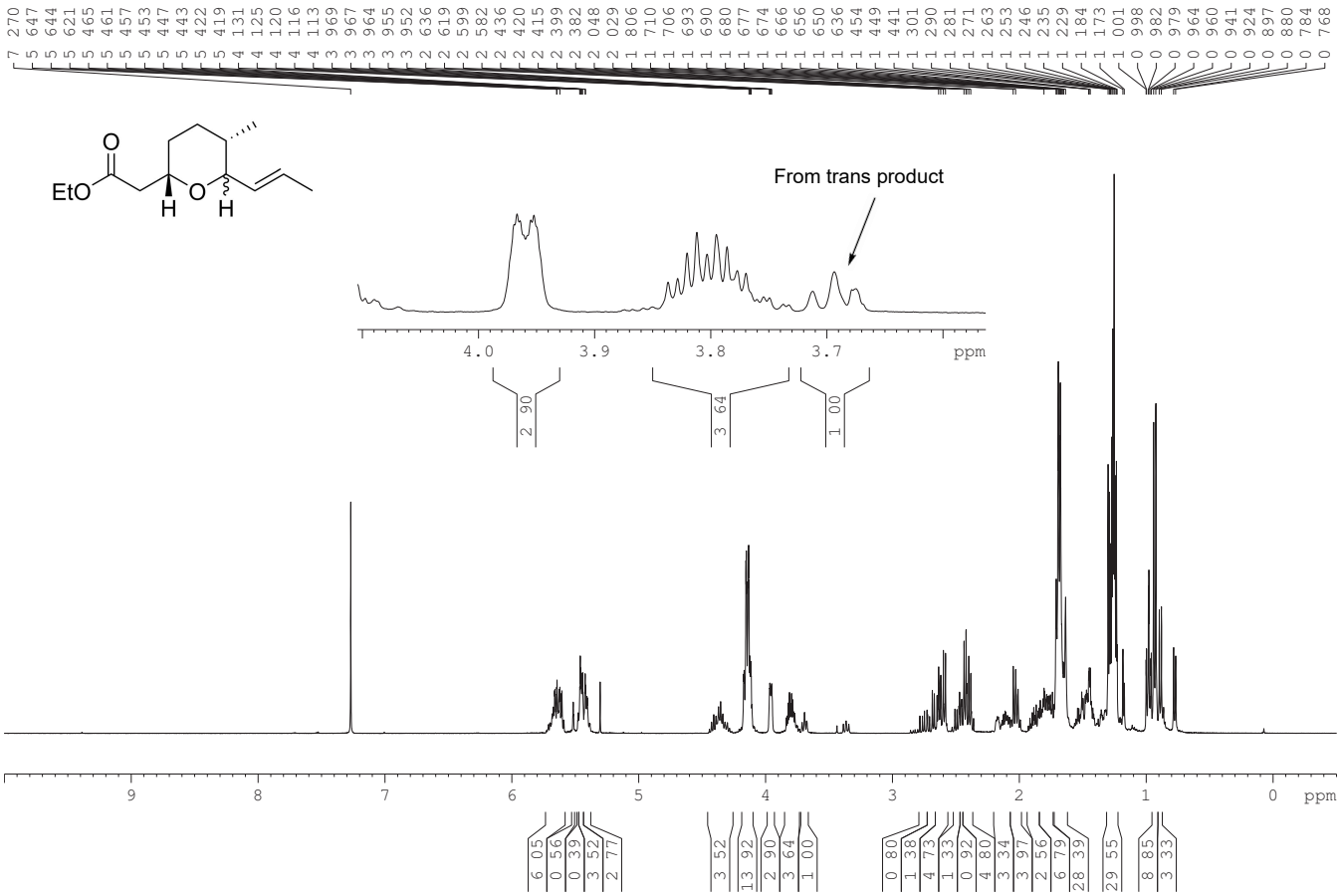
1H NMR (400 MHz, CDCl3)



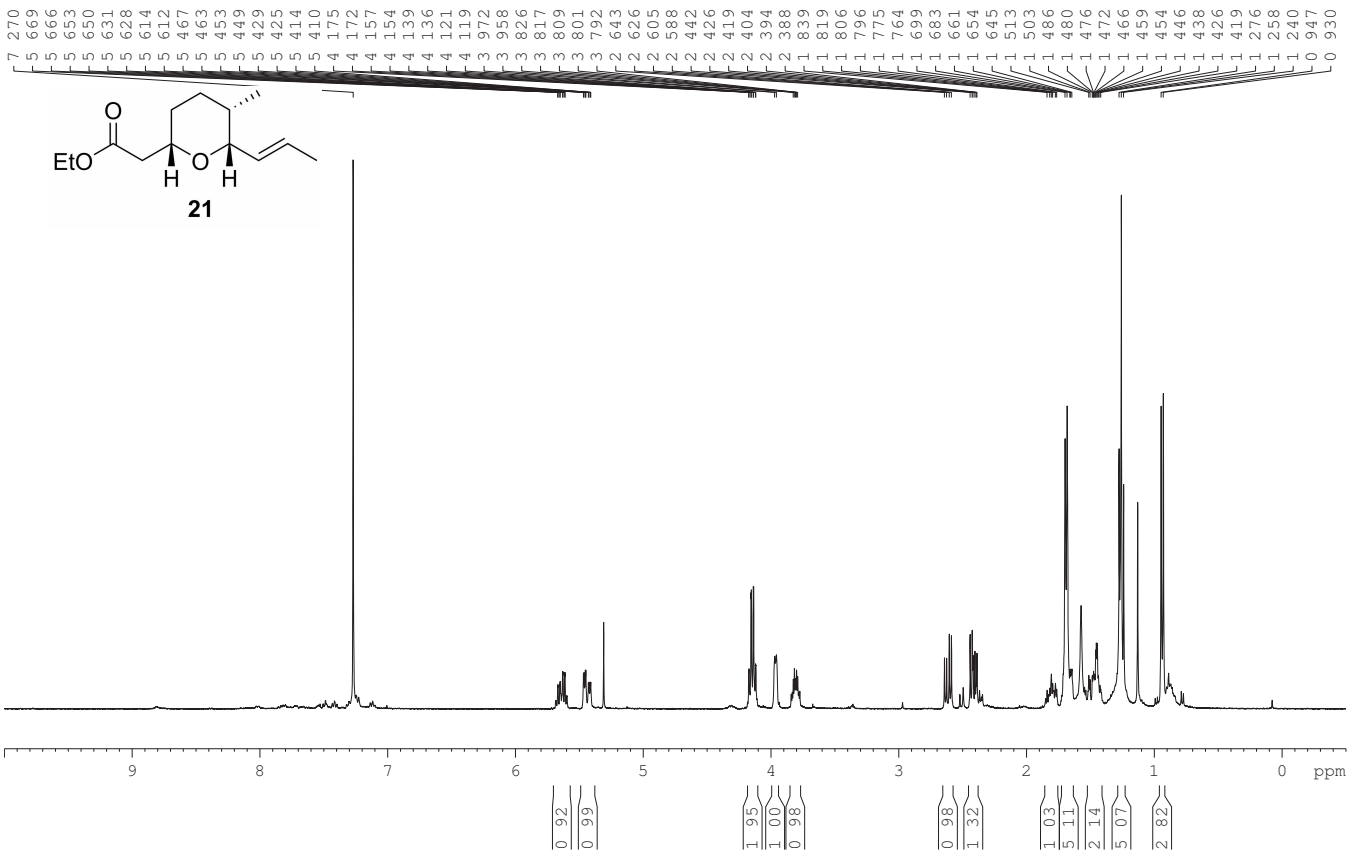
13C NMR (101 MHz, CDCl3)



1H NMR (400 MHz, CDCl3)

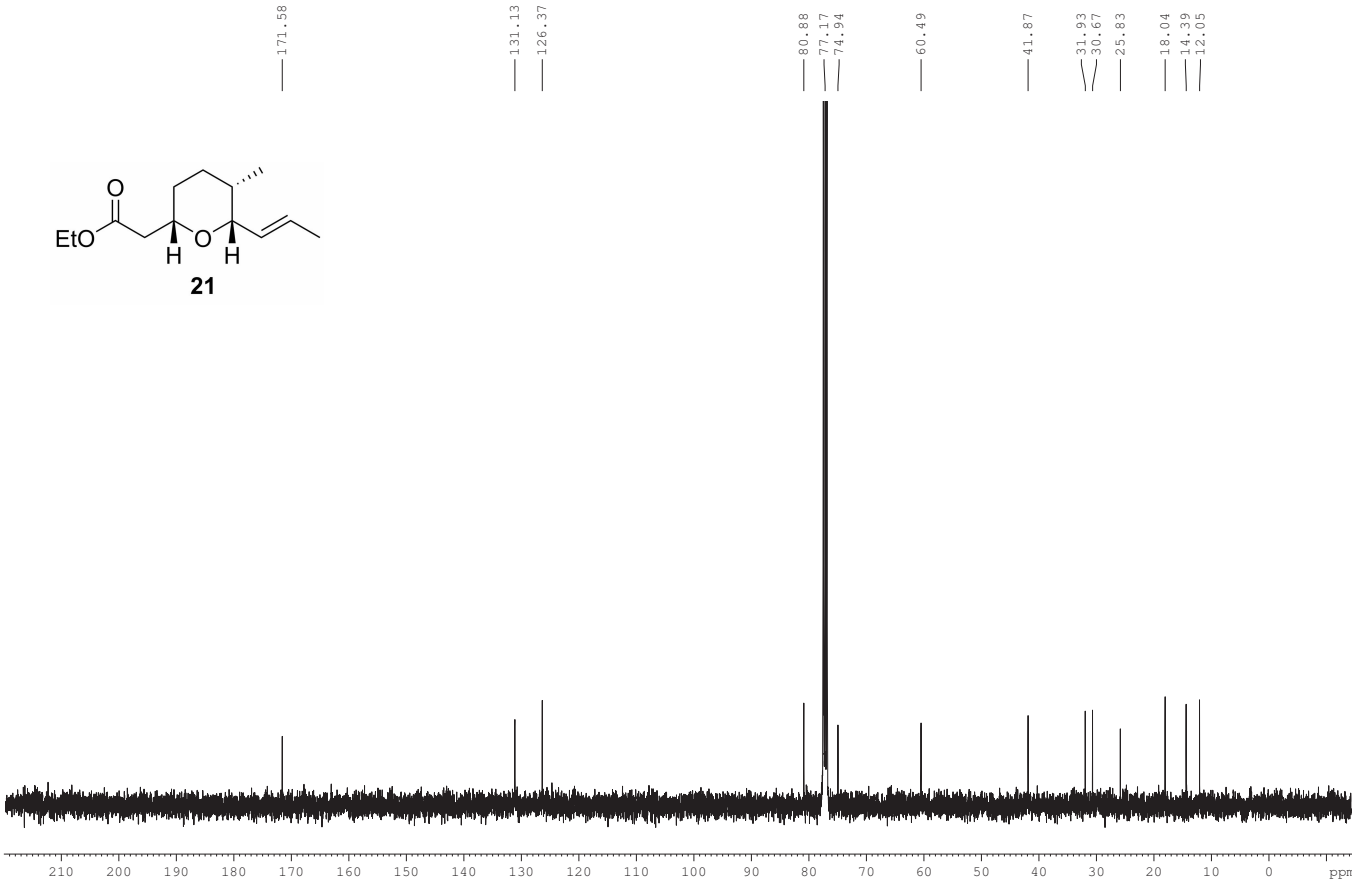


1H NMR (400 MHz, CDCl3)

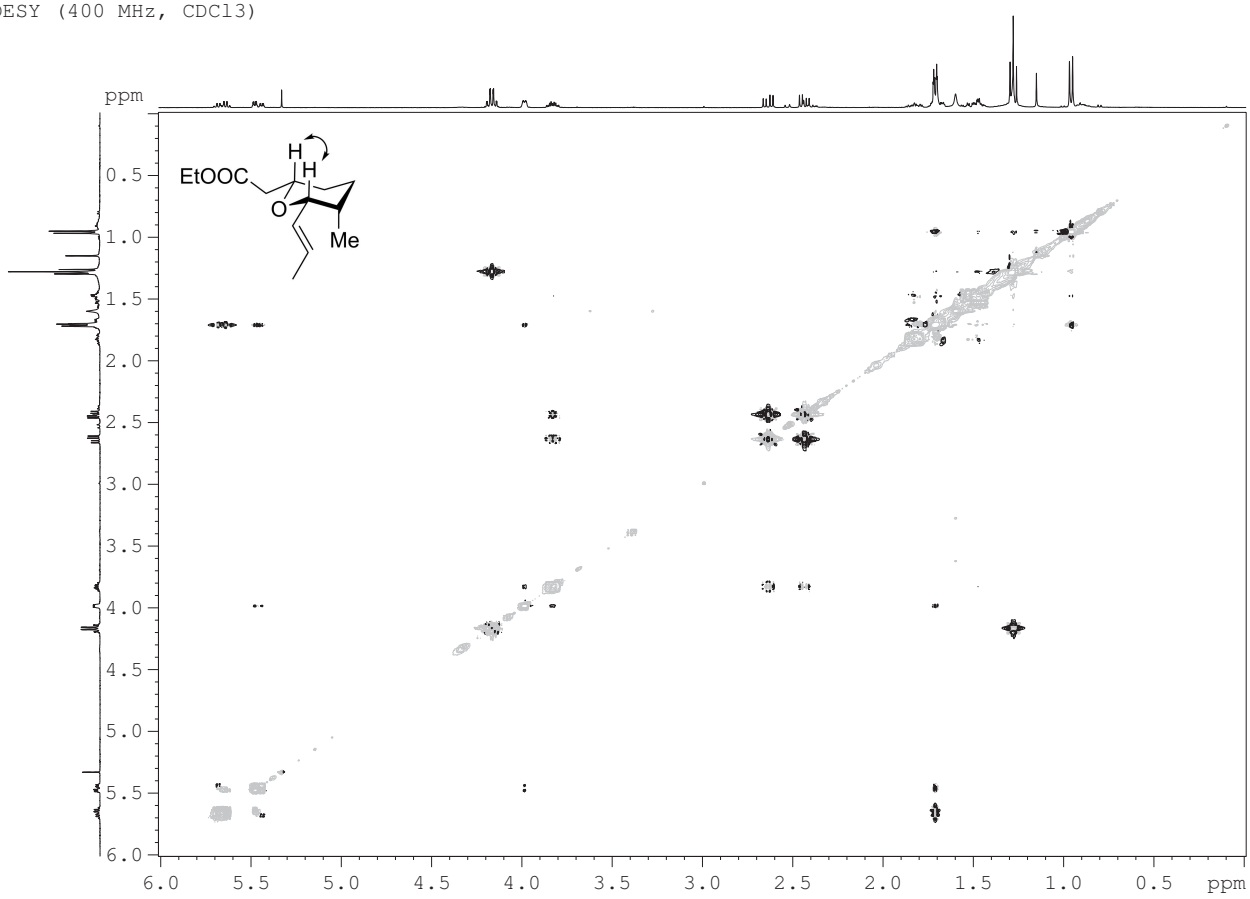


21

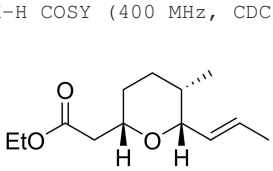
13C NMR (101 MHz, CDCl3)



NOESY (400 MHz, CDCl3)



H-H COSY (400 MHz, CDCl3)



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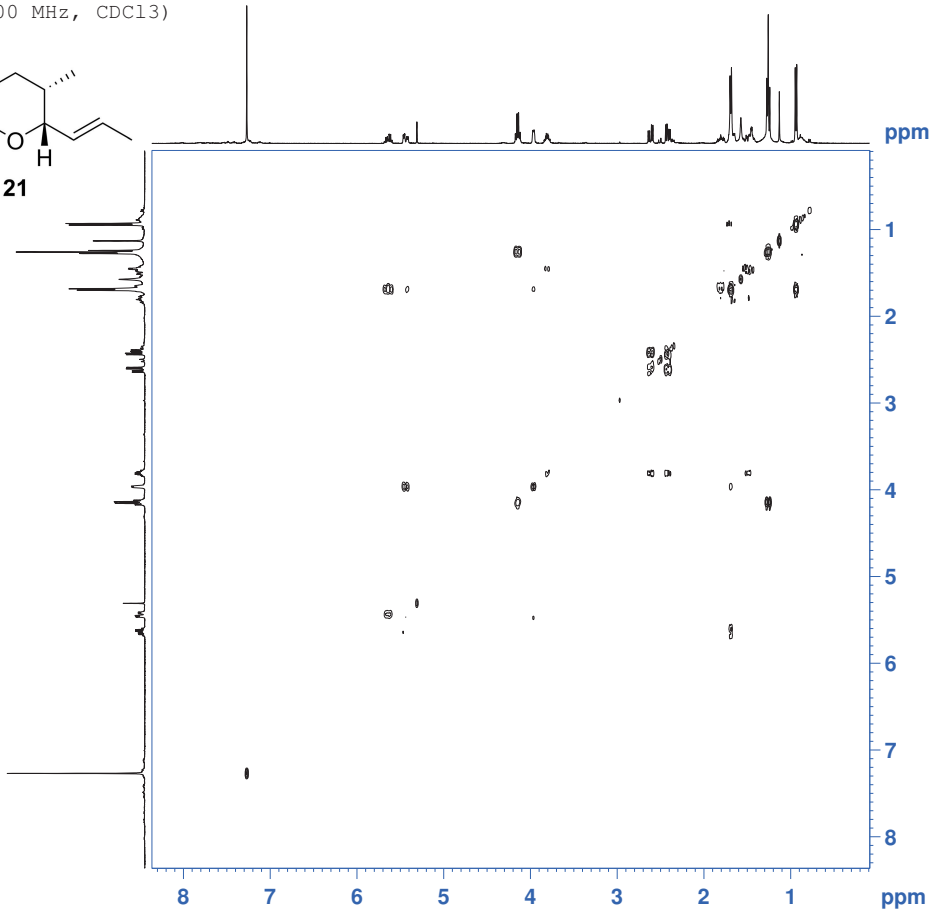
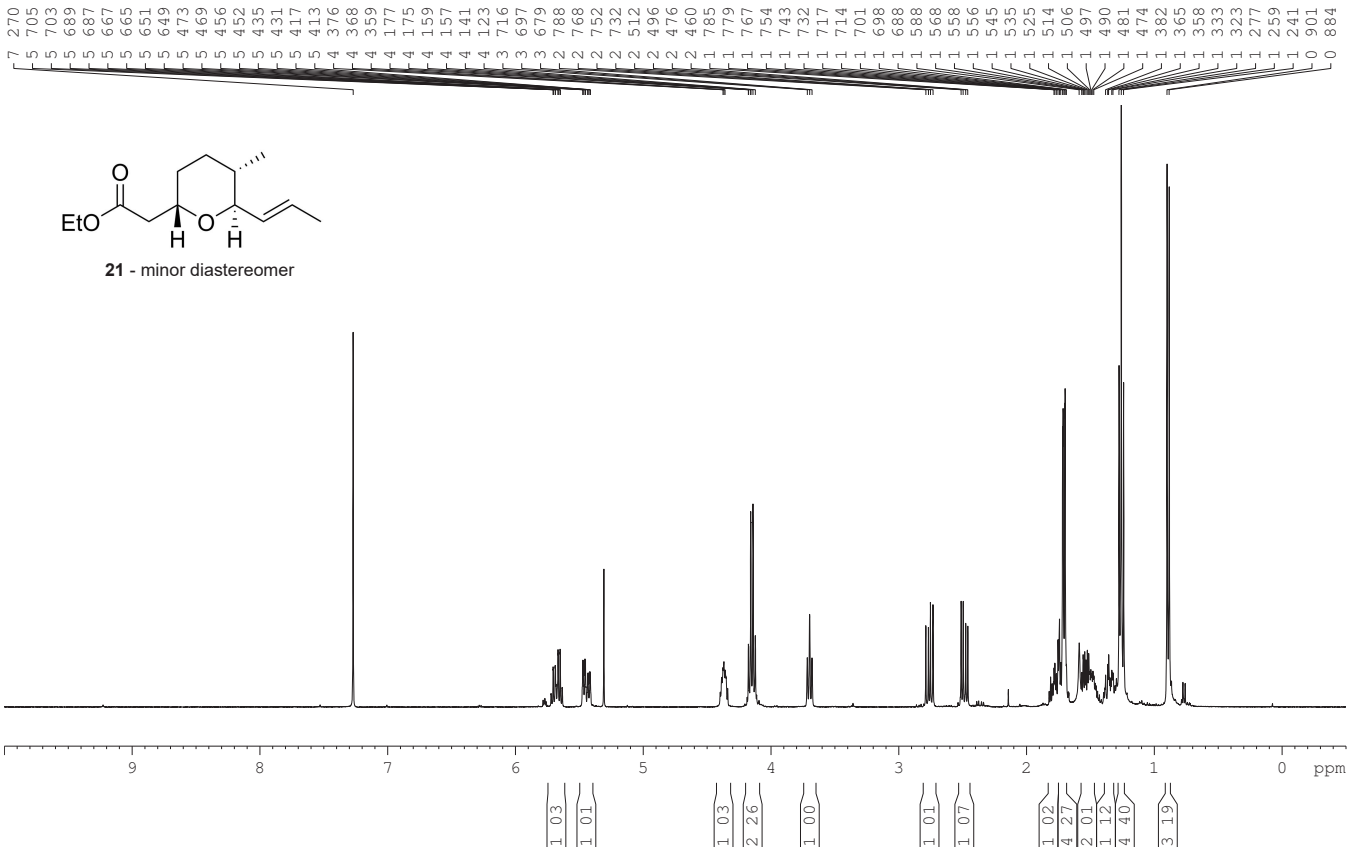
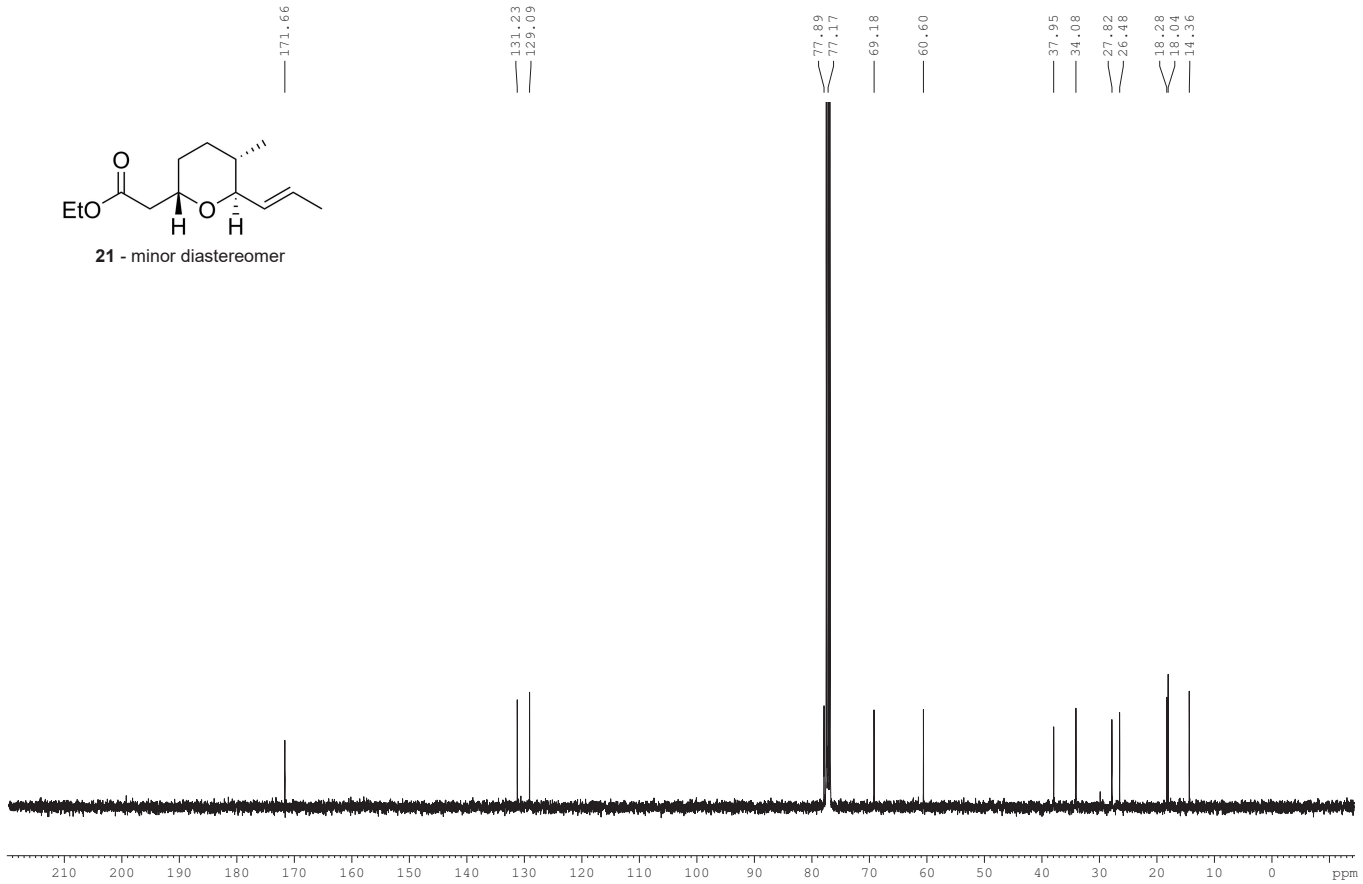


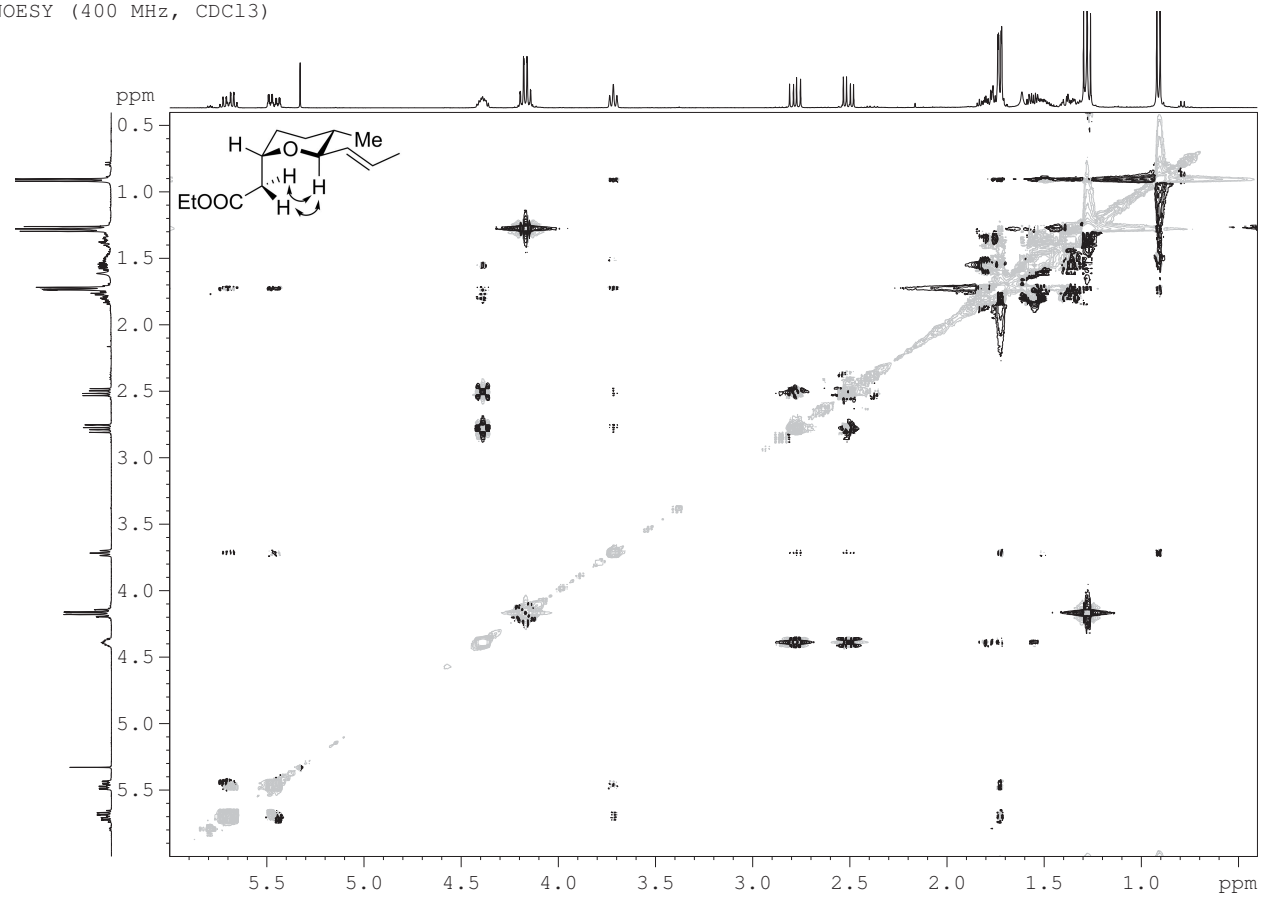
1H NMR (400 MHz, CDCl3)



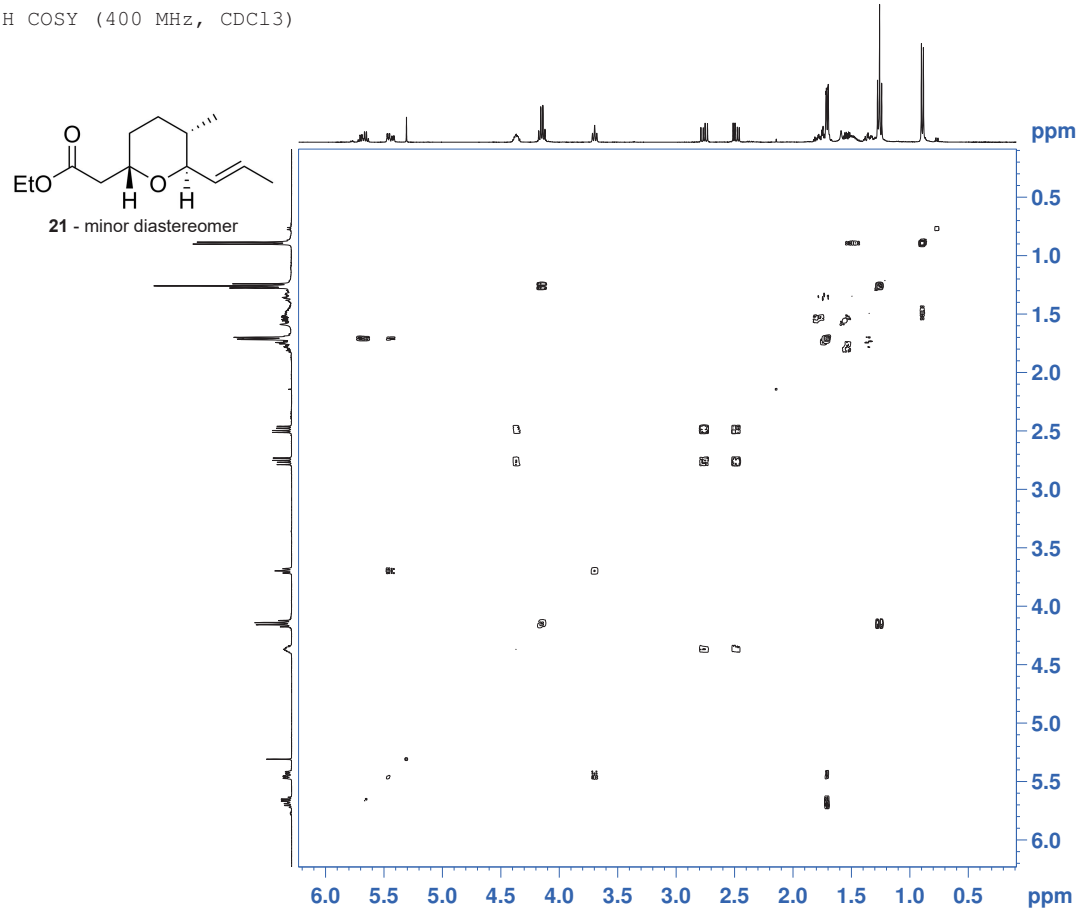
13C NMR (101 MHz, CDCl3)



NOESY (400 MHz, CDCl3)

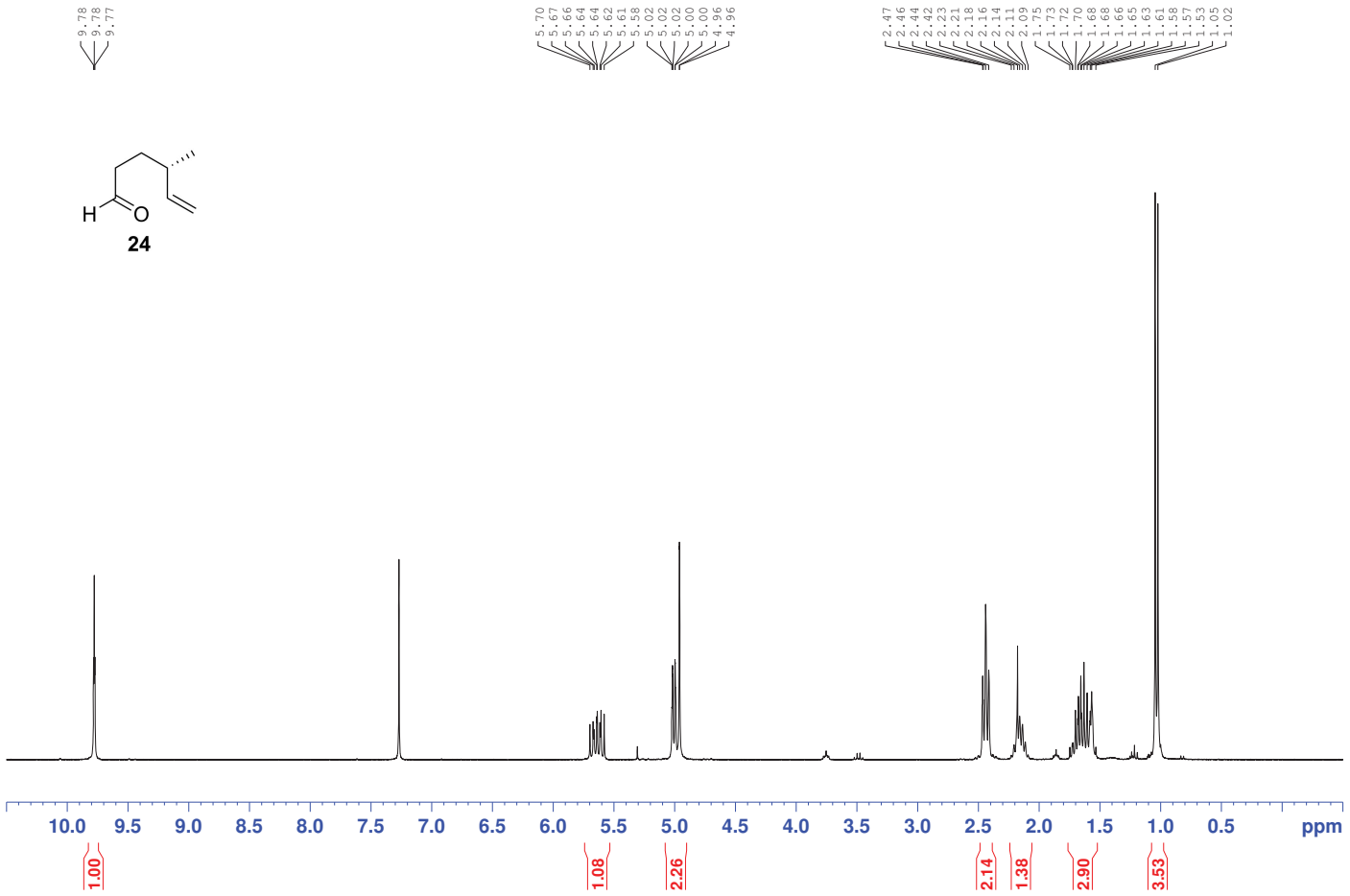


H-H COSY (400 MHz, CDCl3)

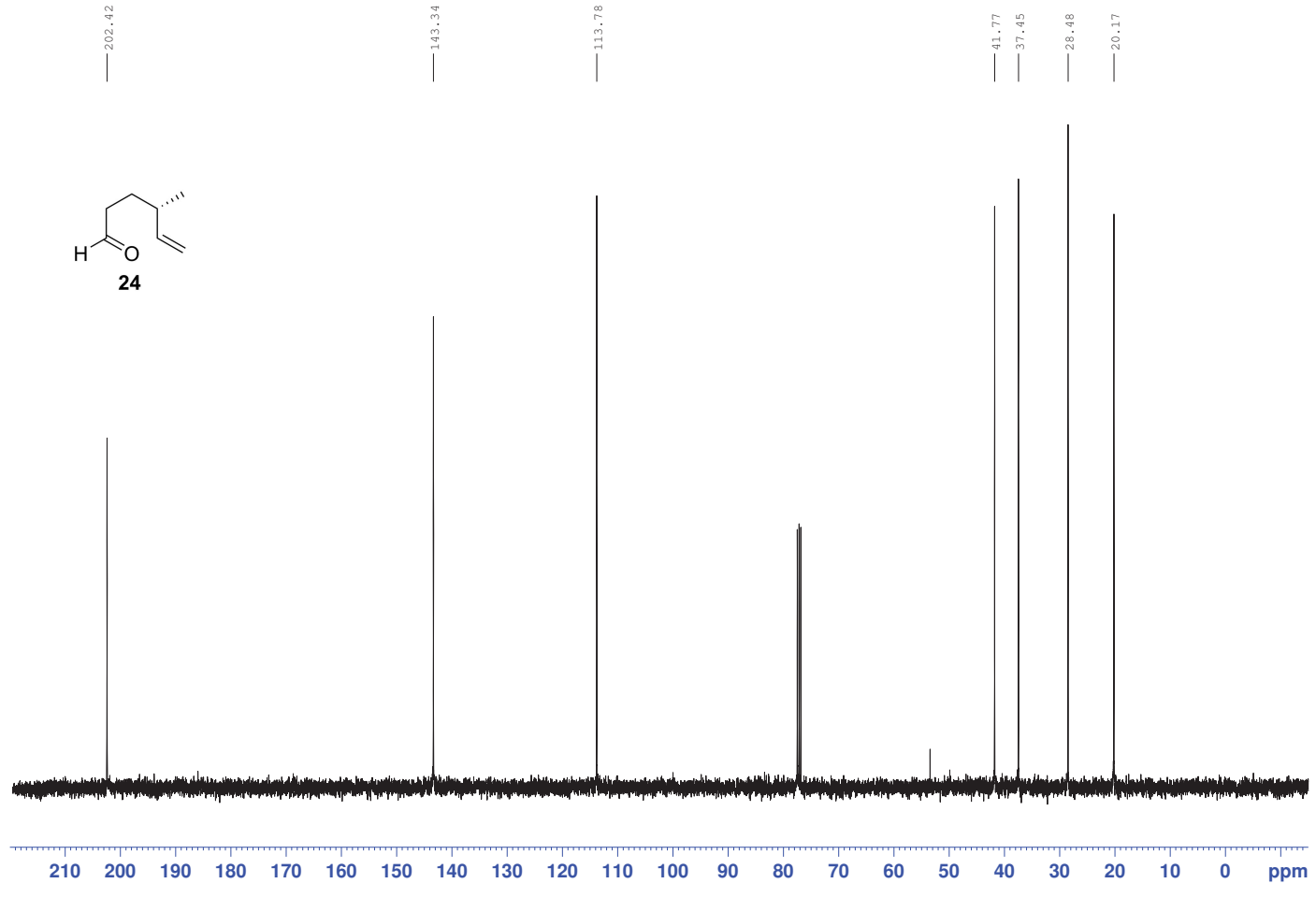


21 - minor diastereomer

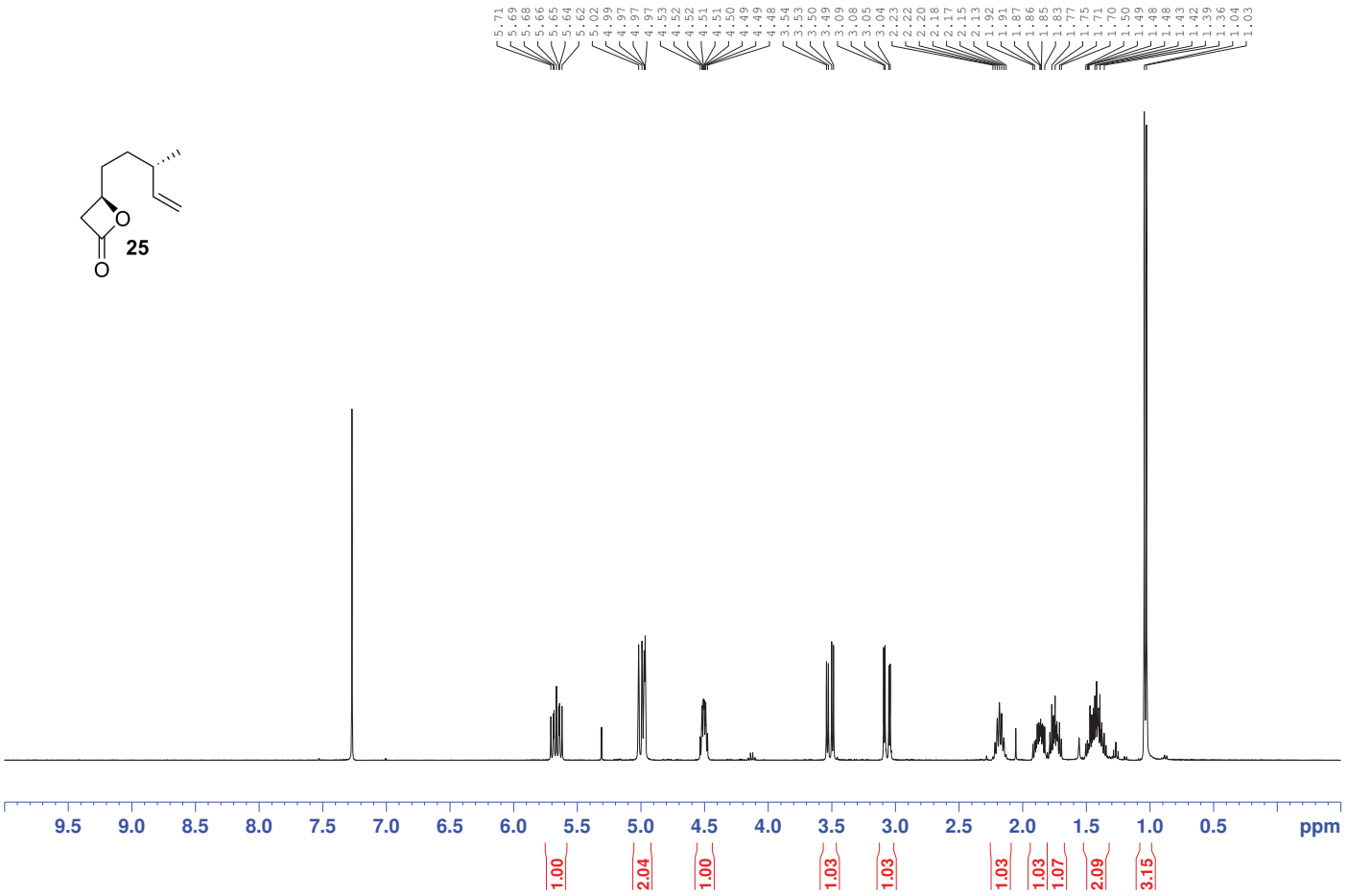
1H NMR (300 MHz, CDCl3)



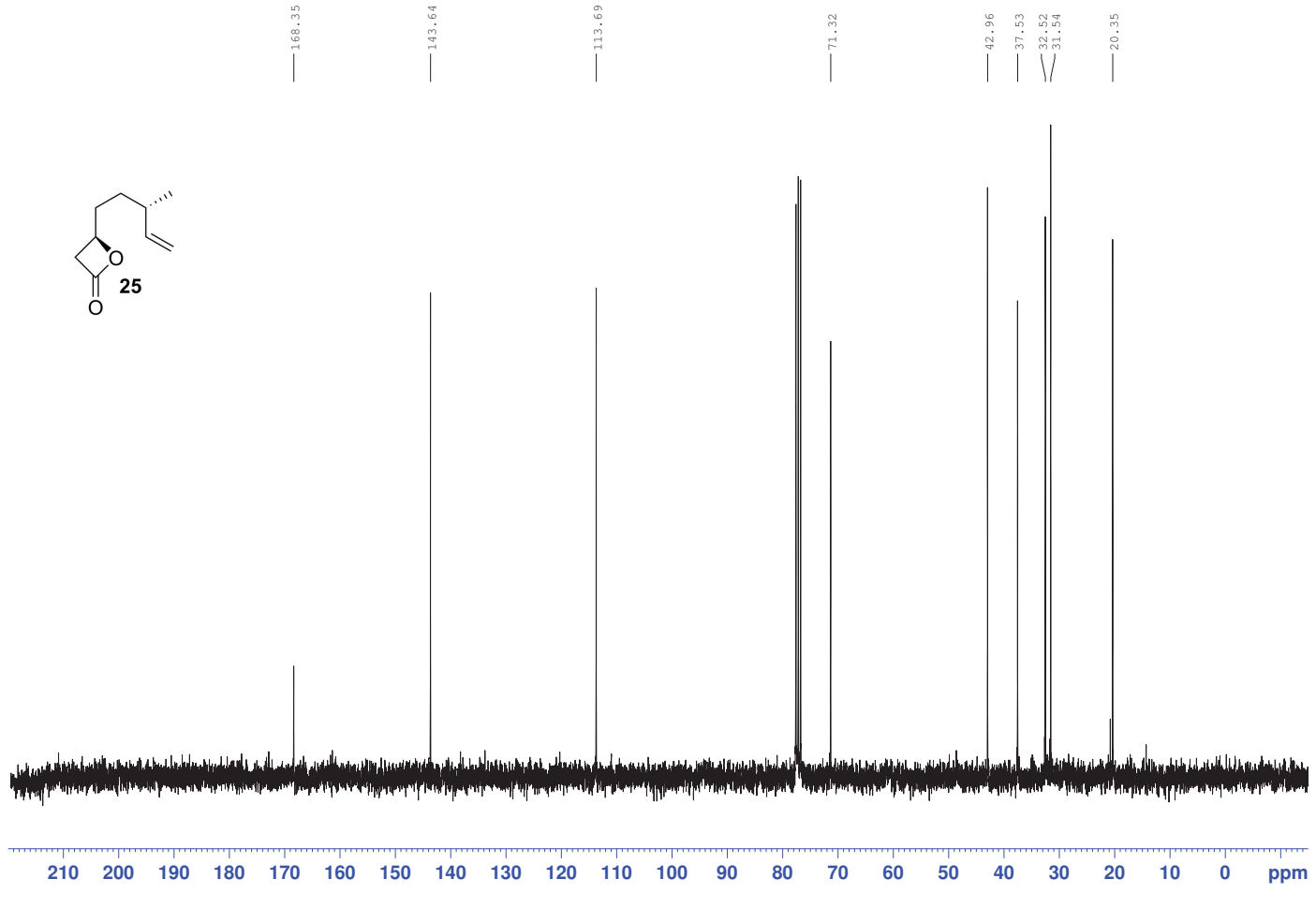
13C NMR (100 MHz, CDCl3)



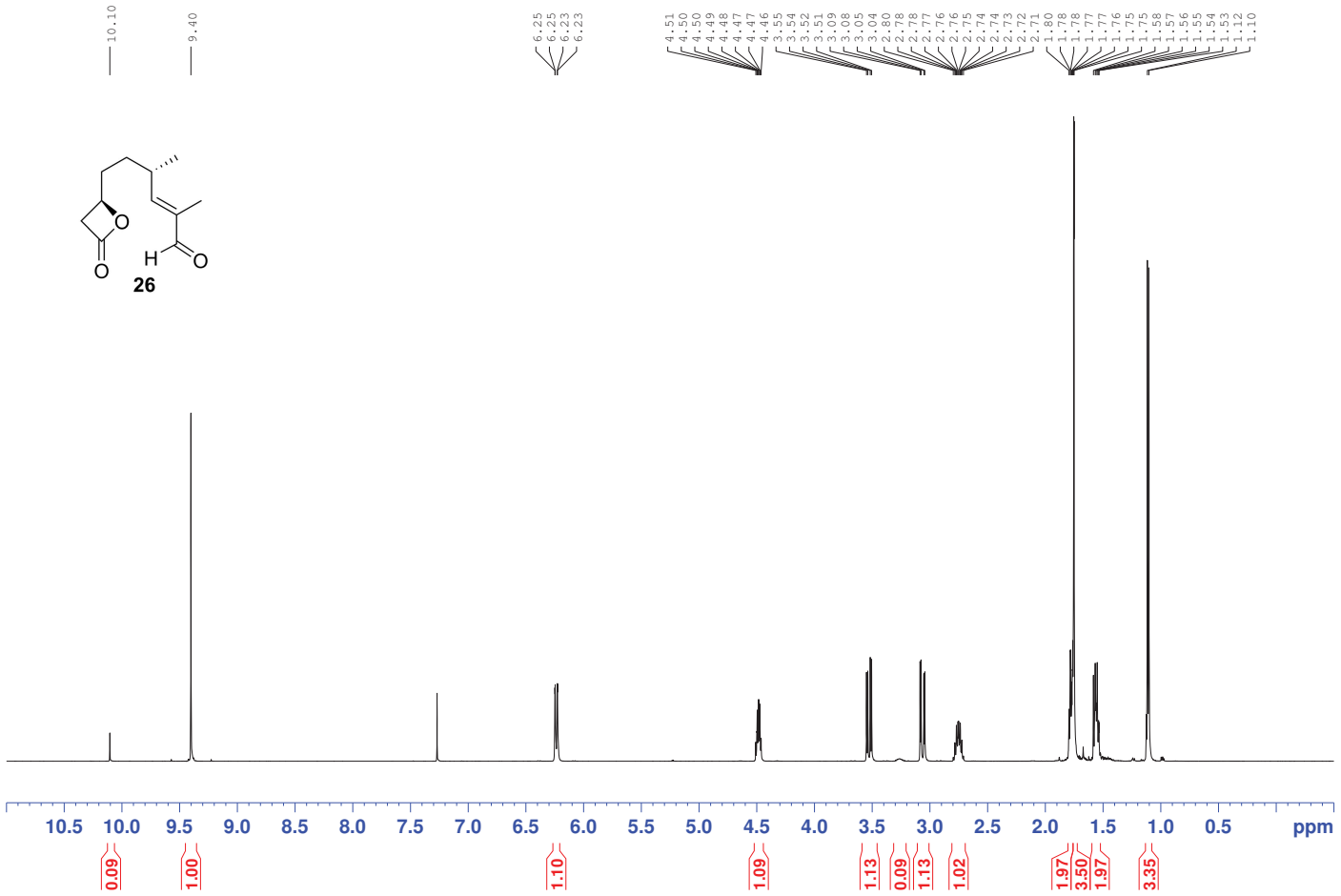
1H NMR (400 MHz, CDCl3)



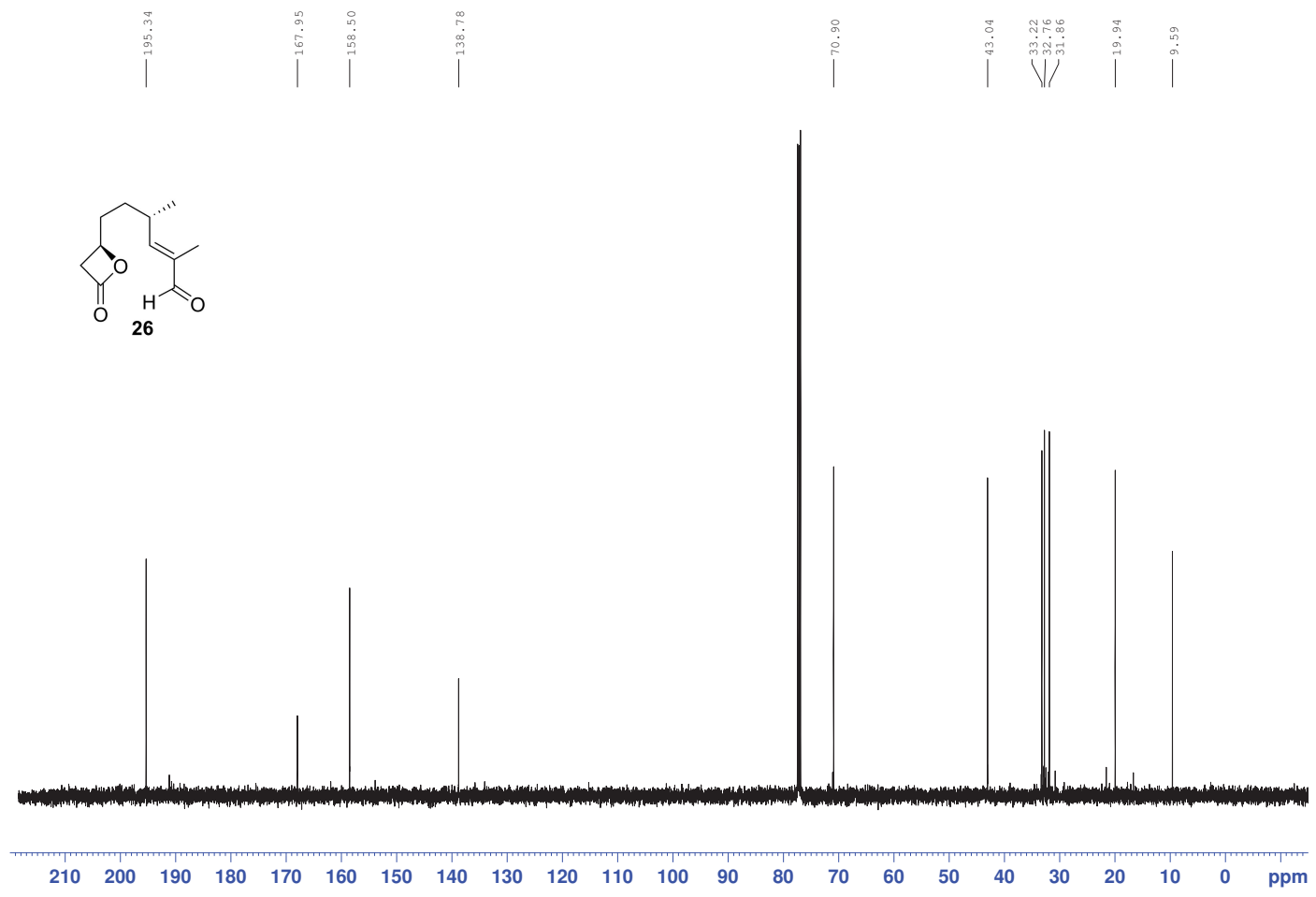
13C NMR (75 MHz, CDCl3)



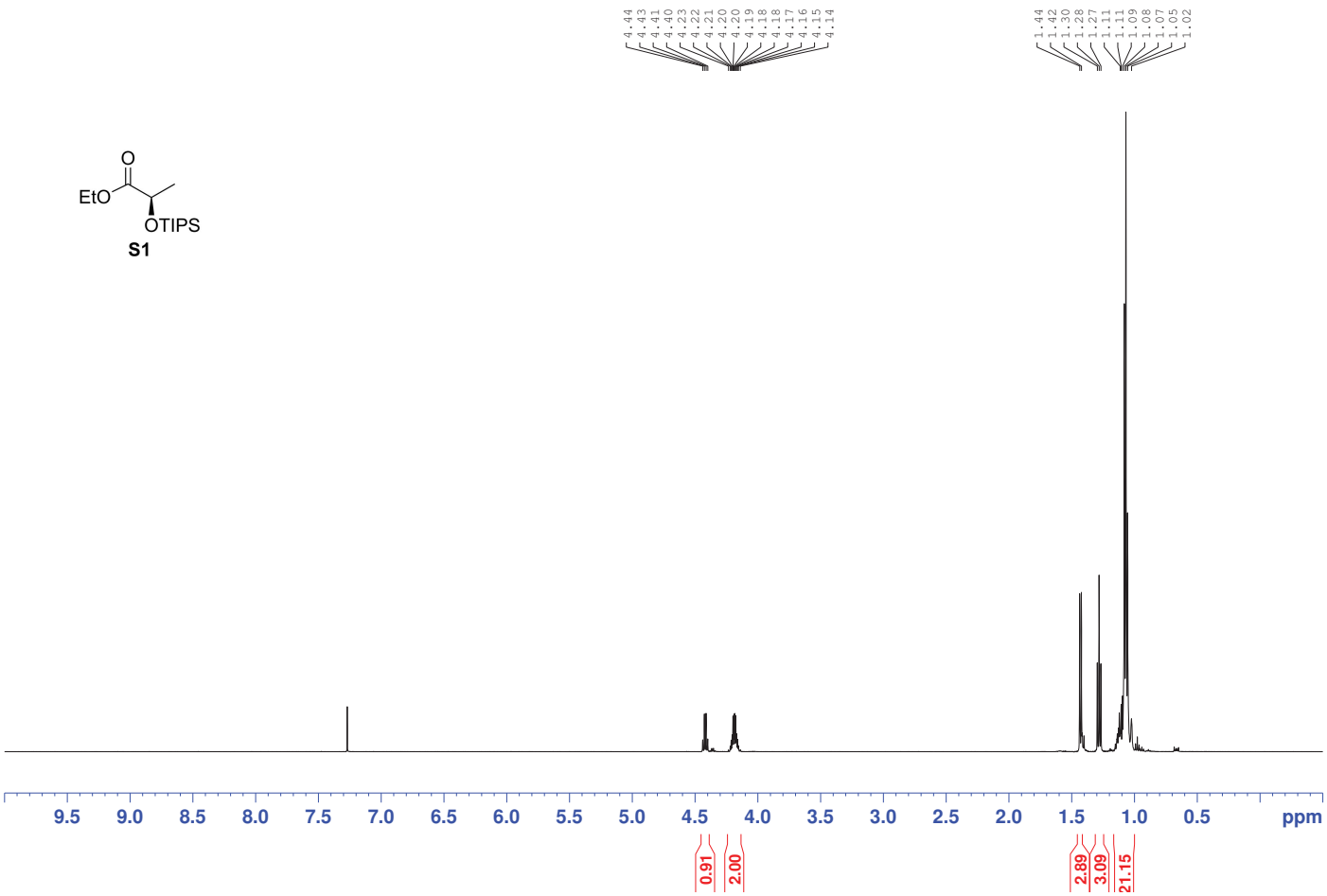
1H NMR (500 MHz, CDCl3)



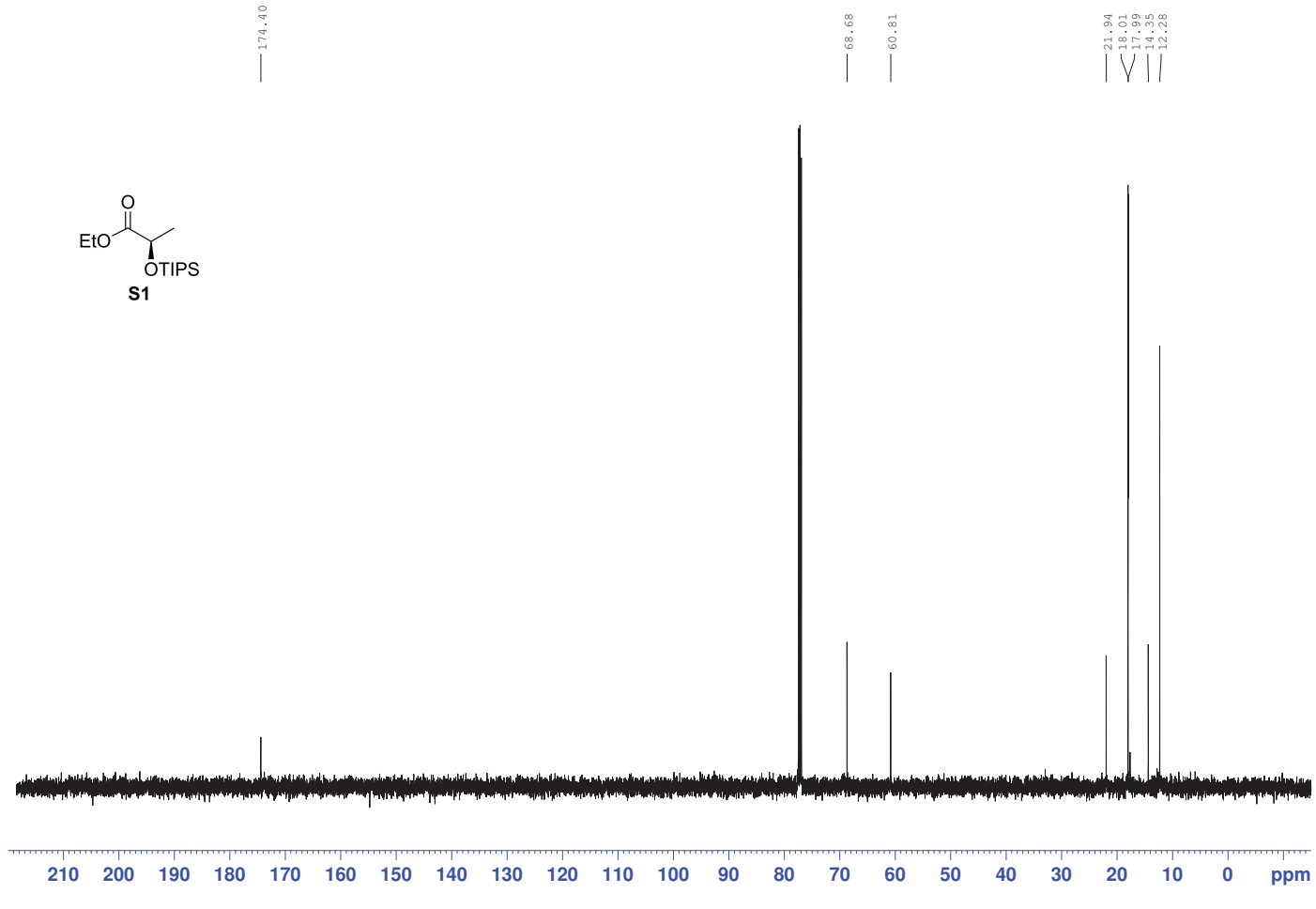
13C NMR (125 MHz, CDCl3)



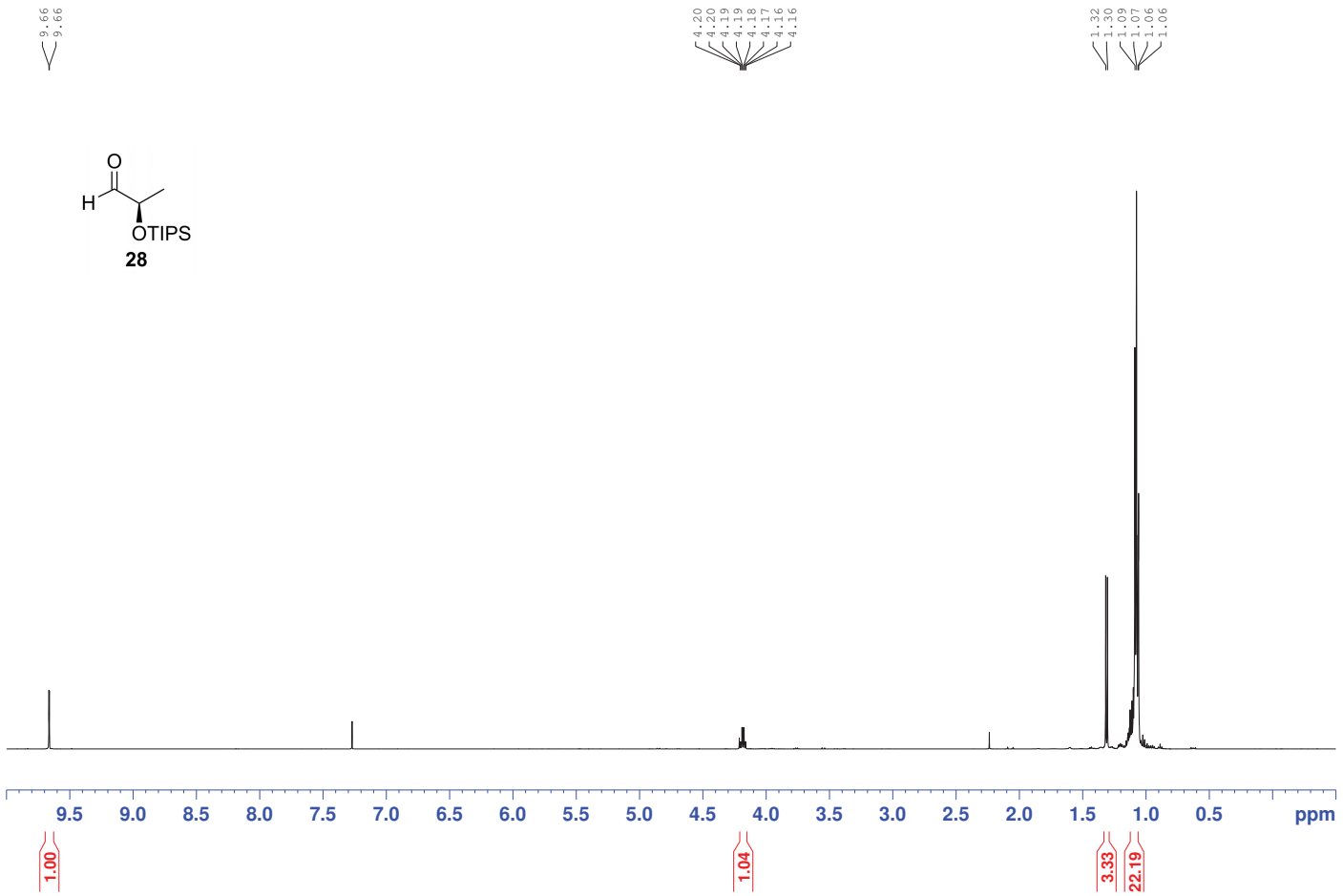
1H NMR (500 MHz, CDCl3)



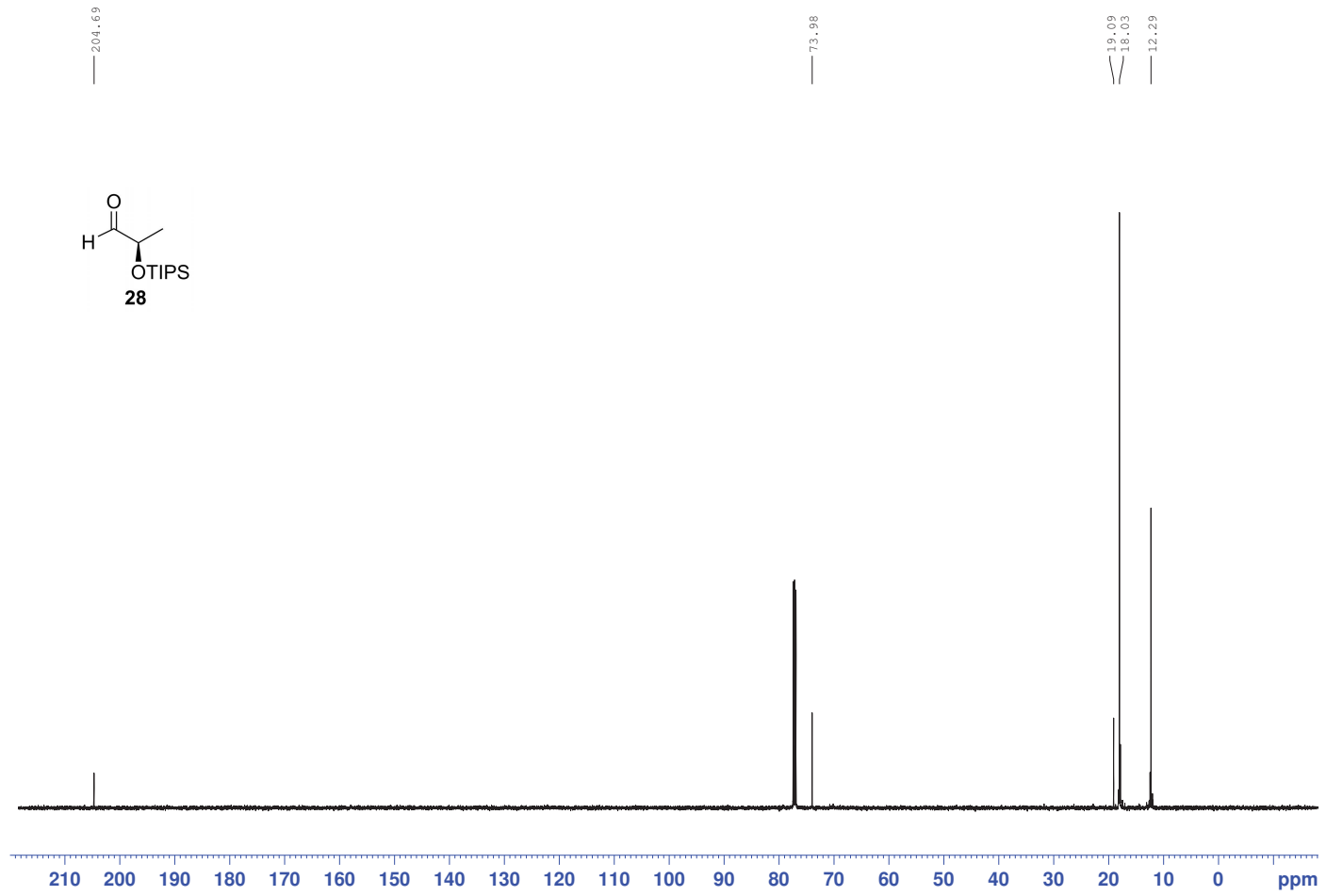
13C NMR (125 MHz, CDCl3)



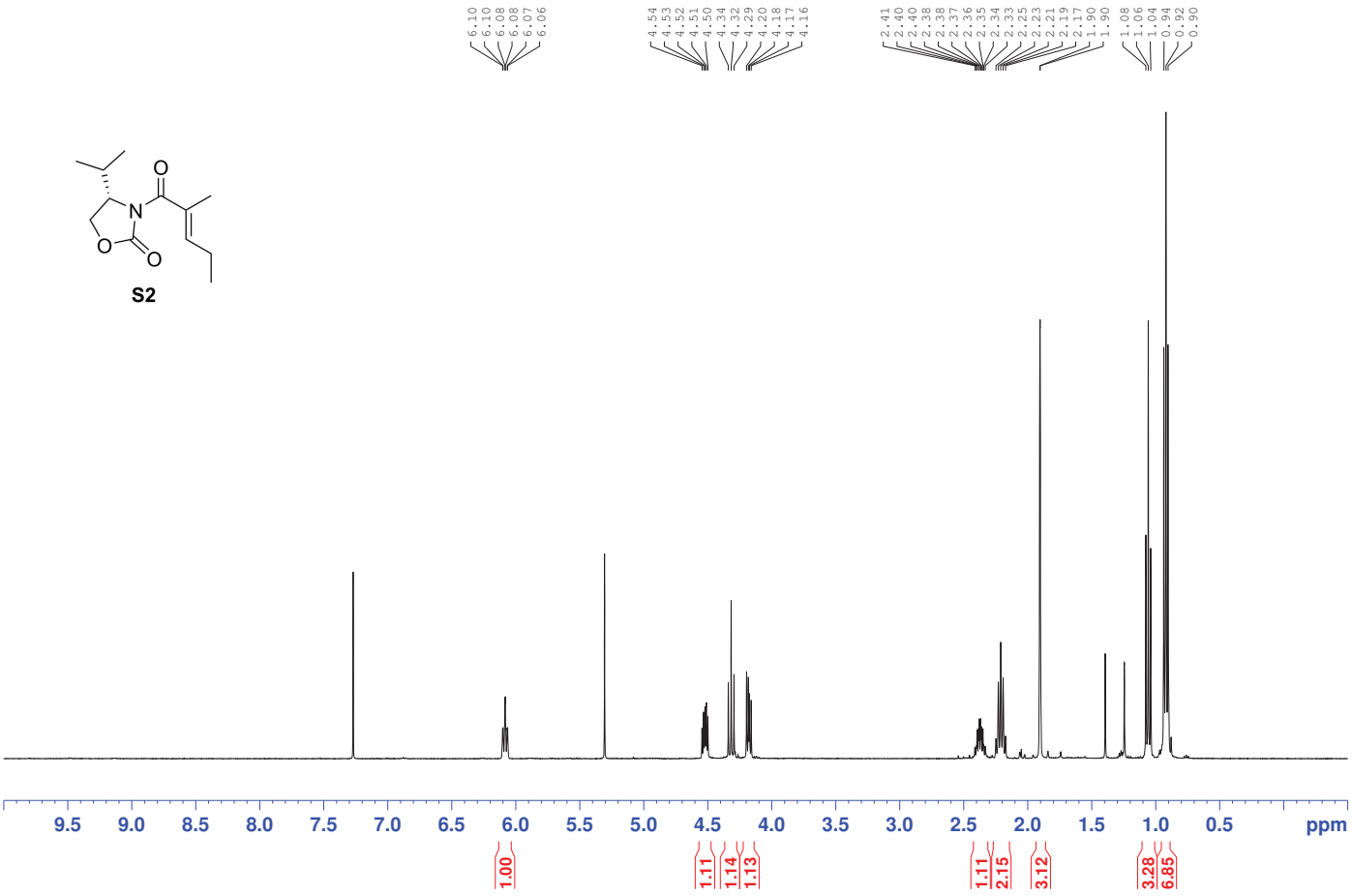
1H NMR (500 MHz, CDCl3)



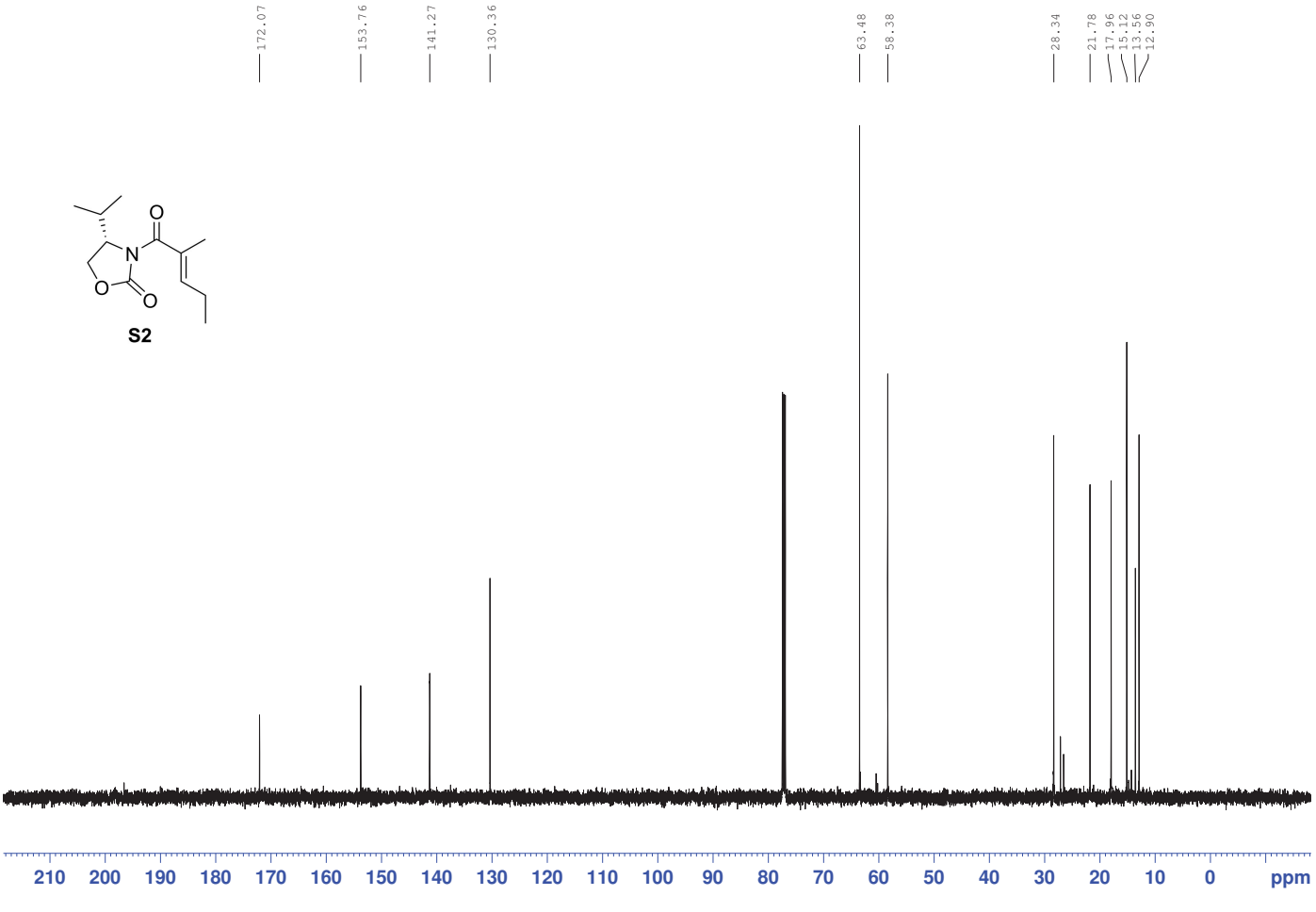
13C NMR (125 MHz, CDCl3)



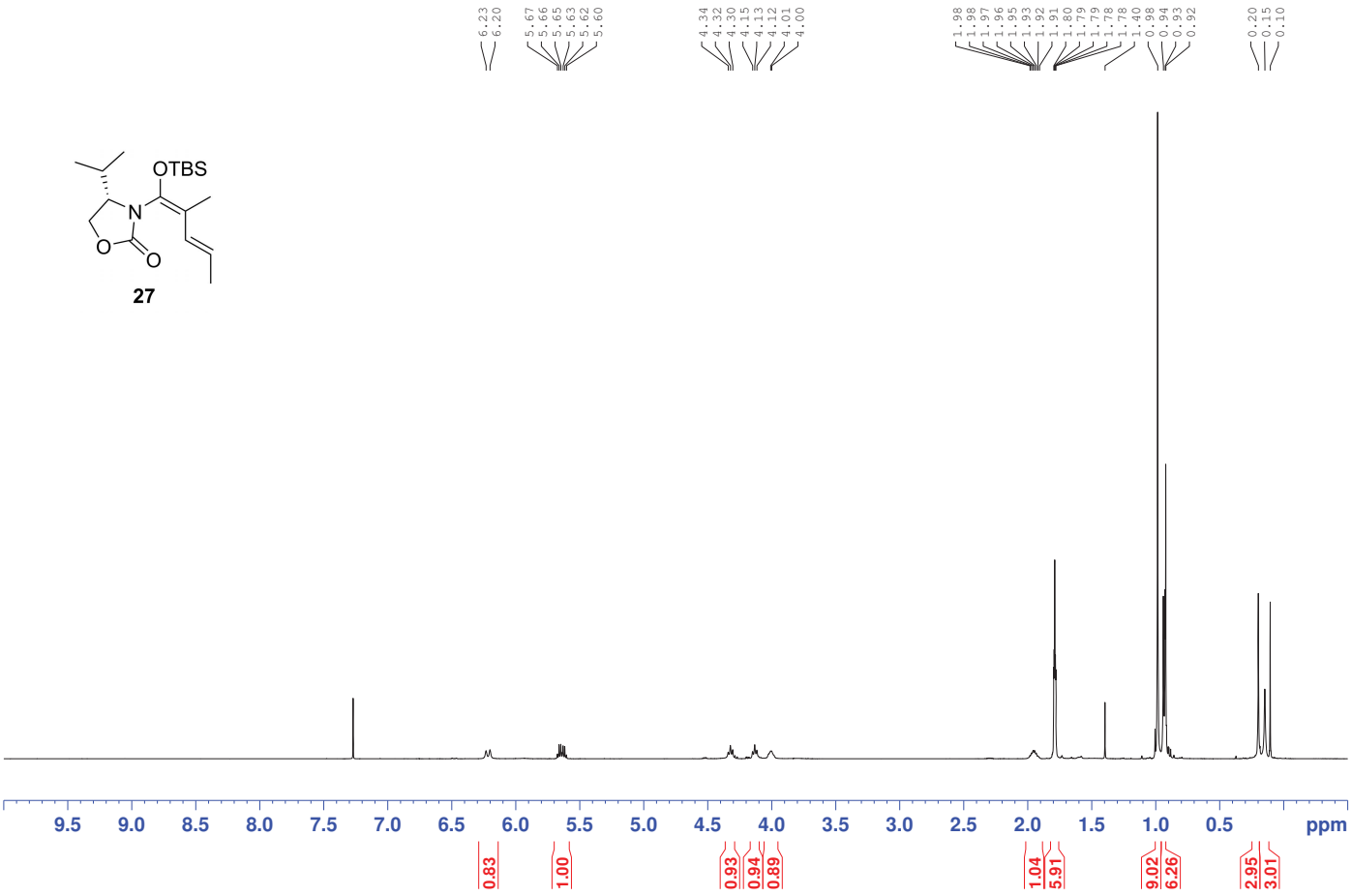
1H NMR (400 MHz, CDCl3)



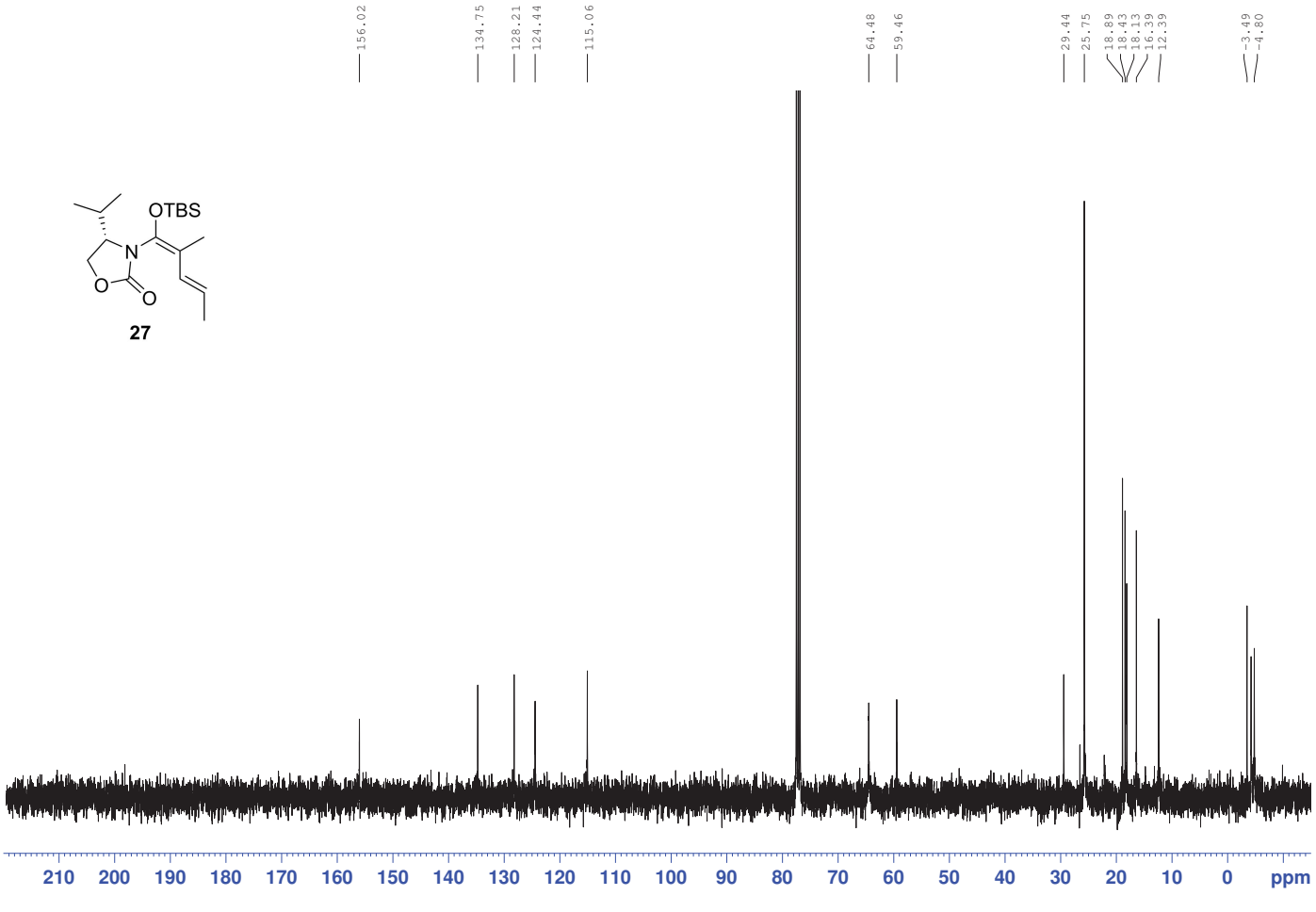
13C NMR (125 MHz, CDCl3)



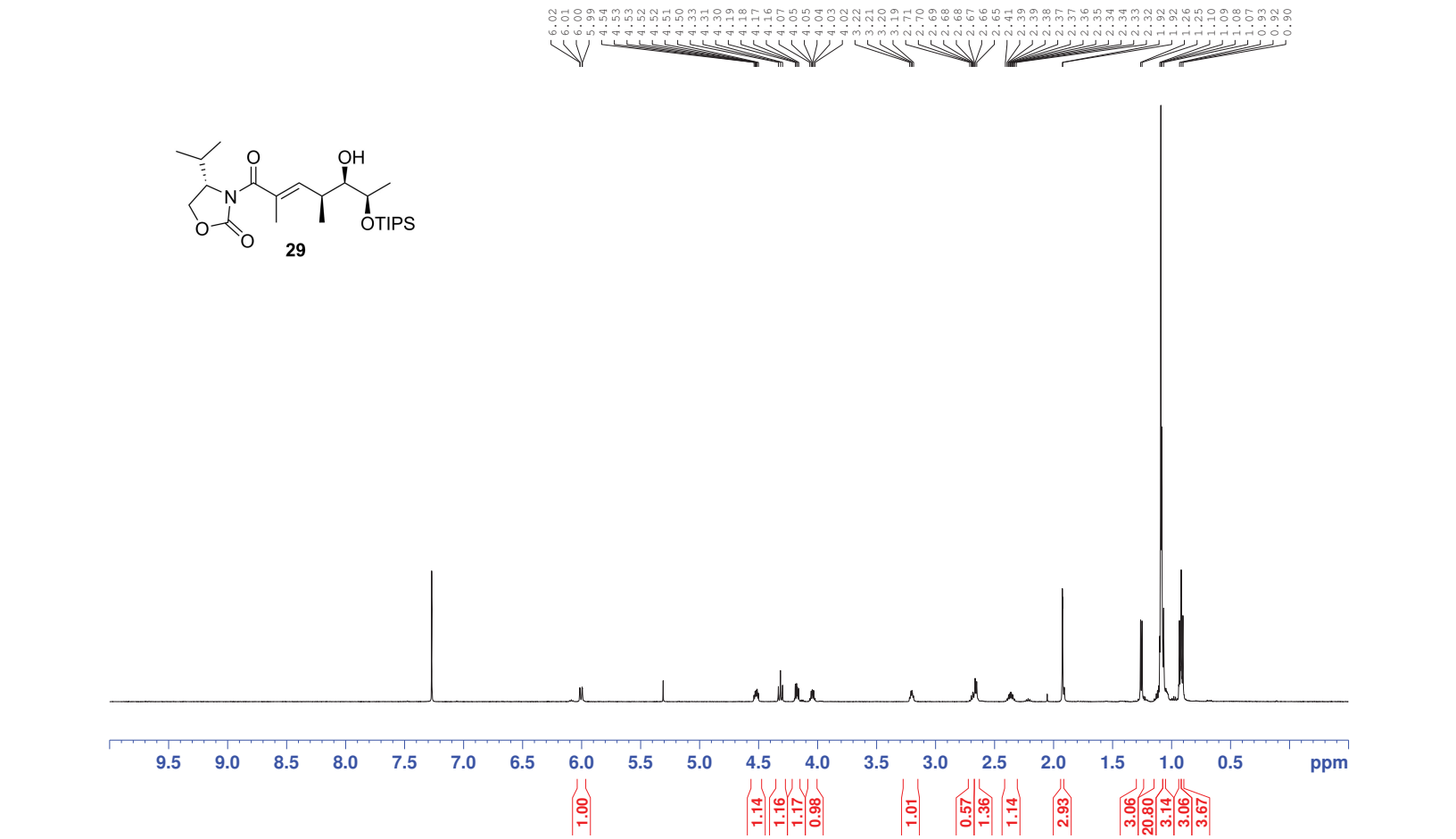
1H NMR (500 MHz, CDCl3)



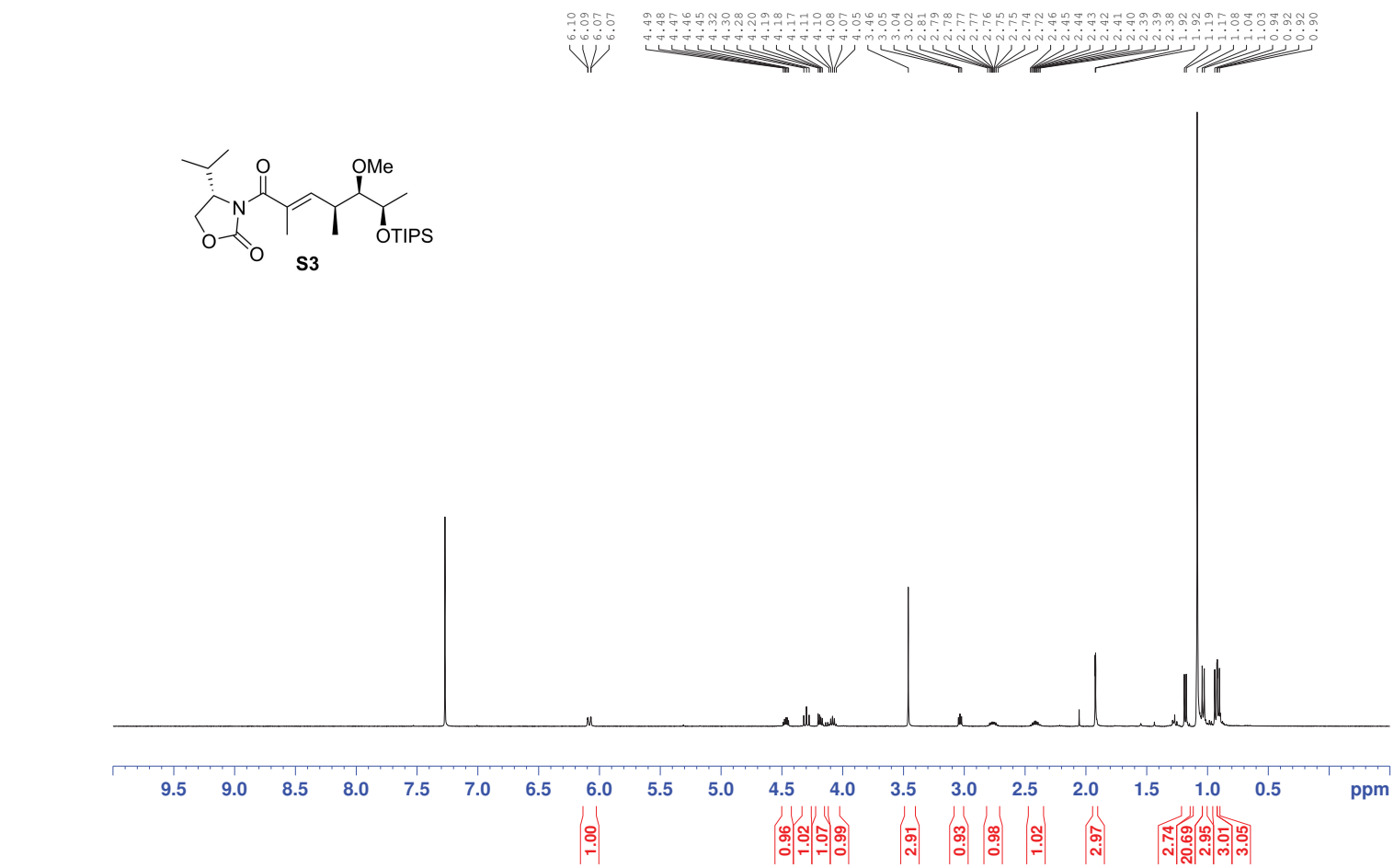
13C NMR (100 MHz, CDCl3)



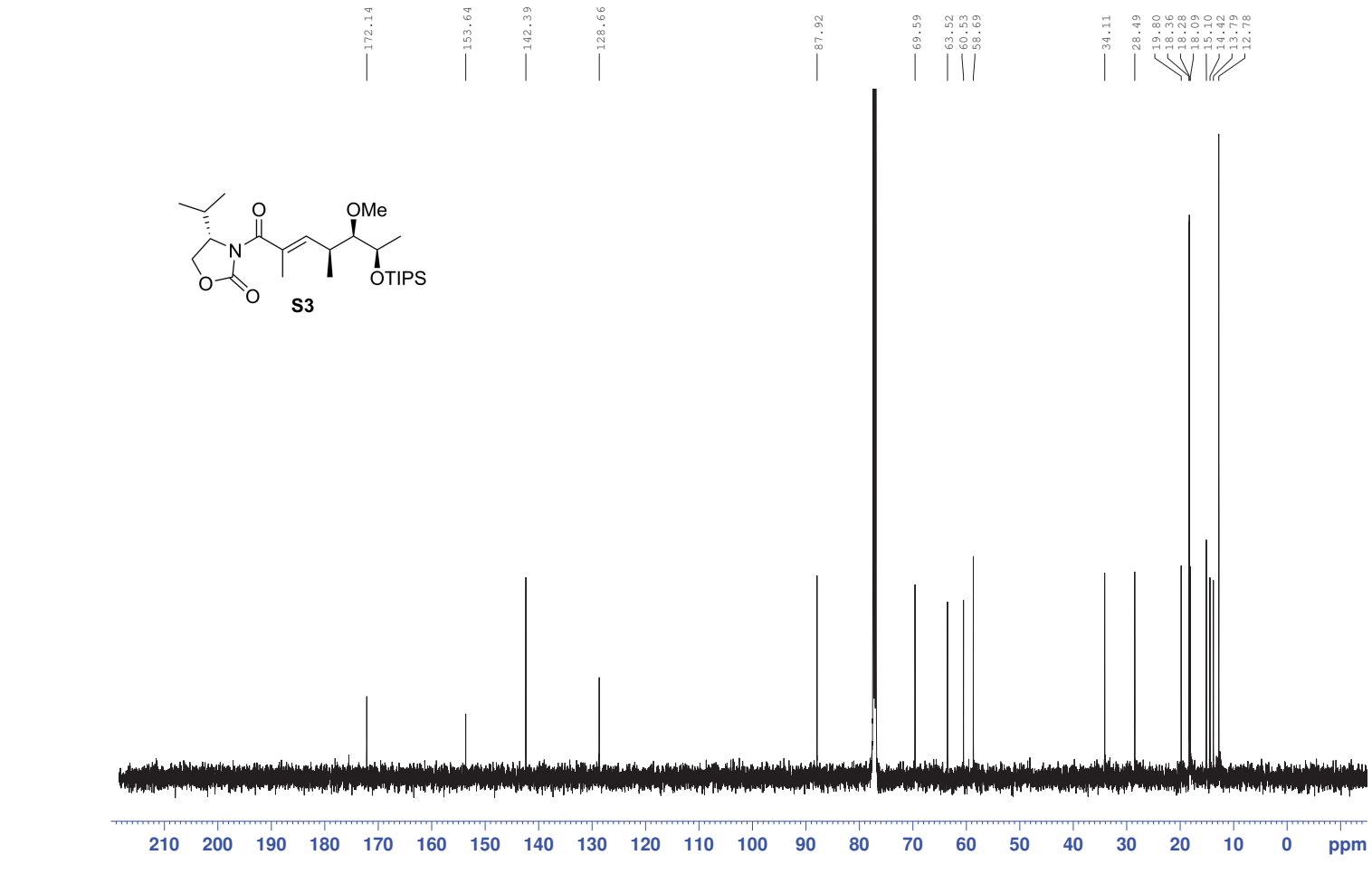
1H NMR (500 MHz, CDCl3)



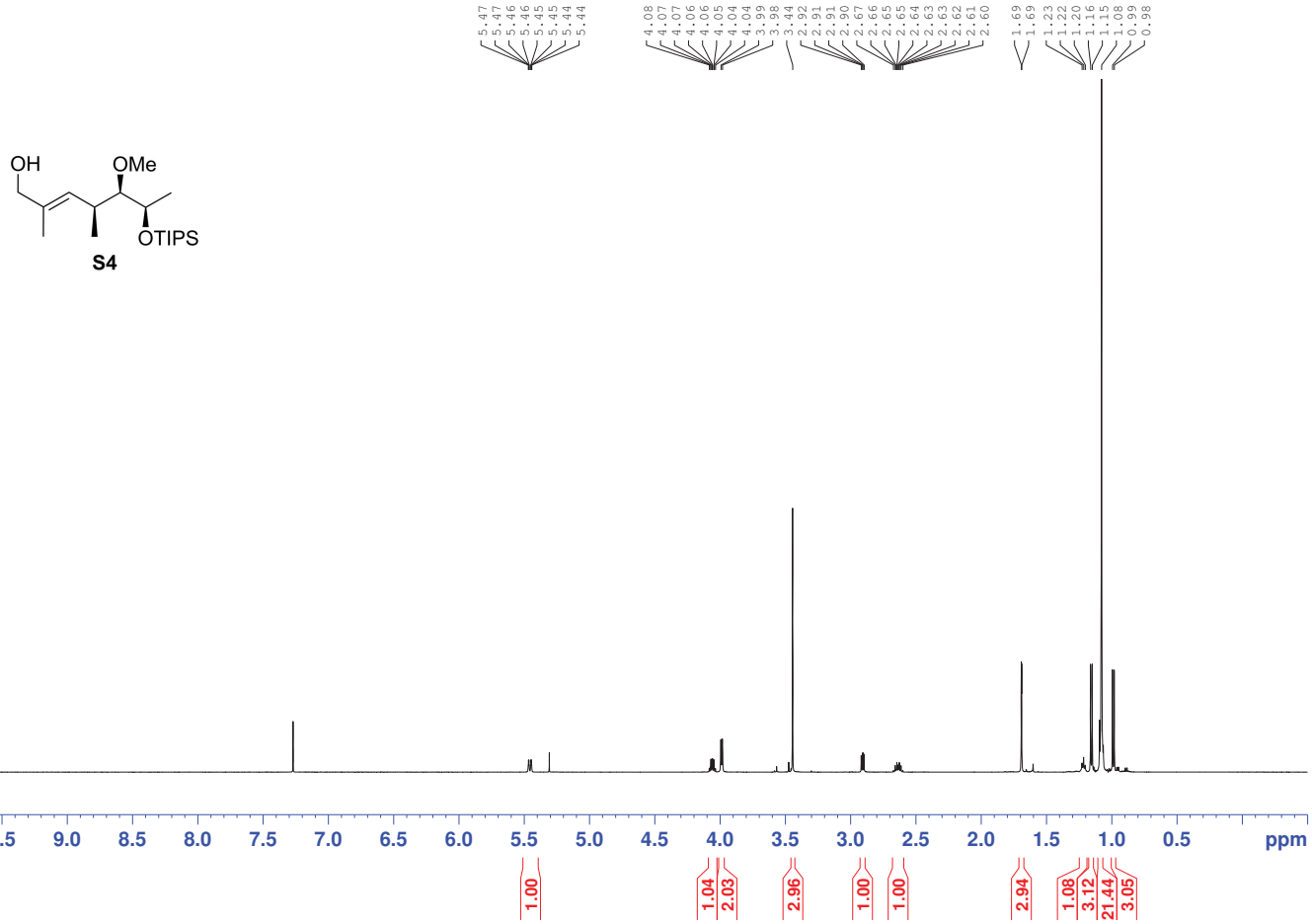
1H NMR (400 MHz, CDCl3)



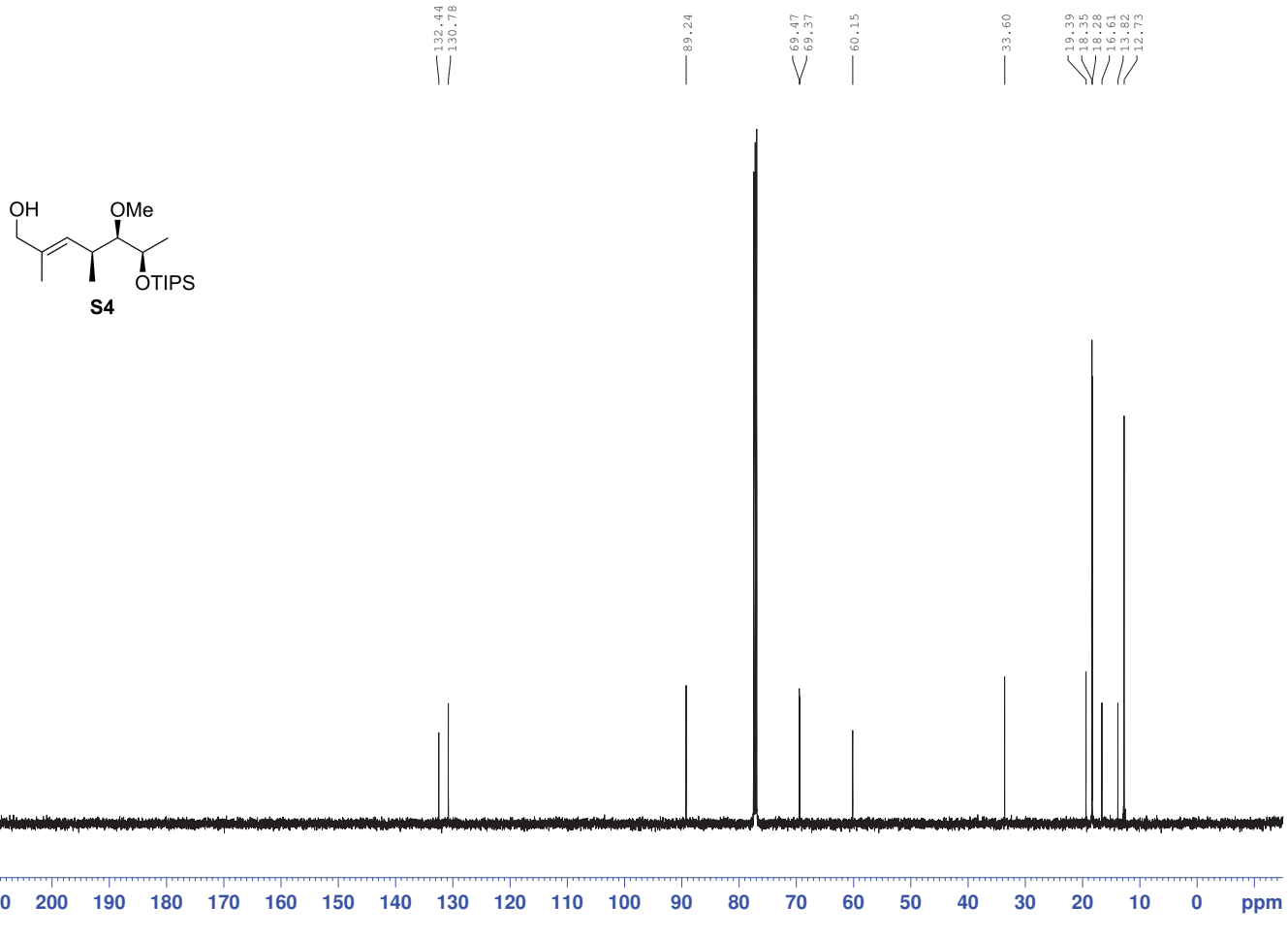
13C NMR (125 MHz, CDCl3)



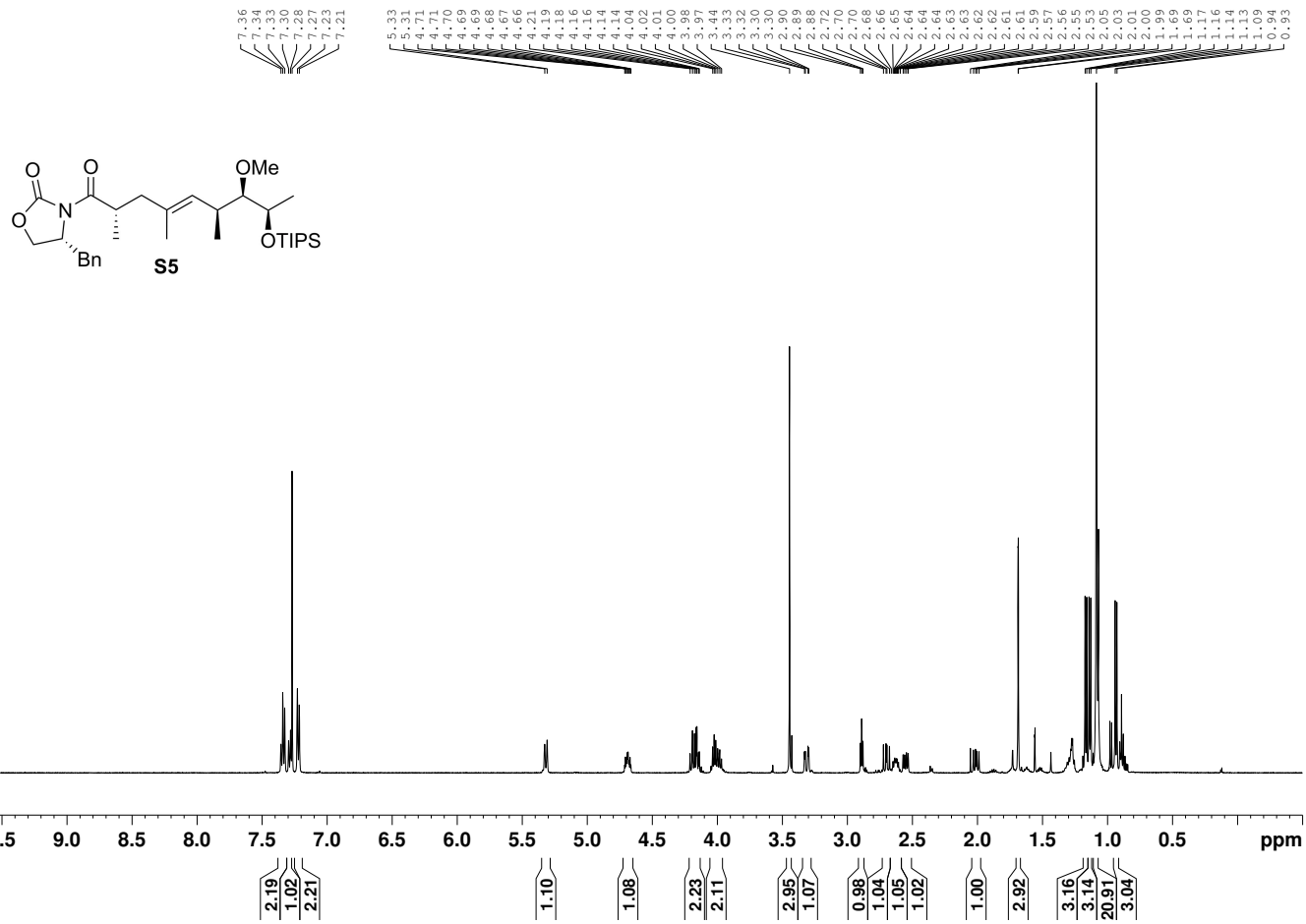
1H NMR (500 MHz, CDCl3)



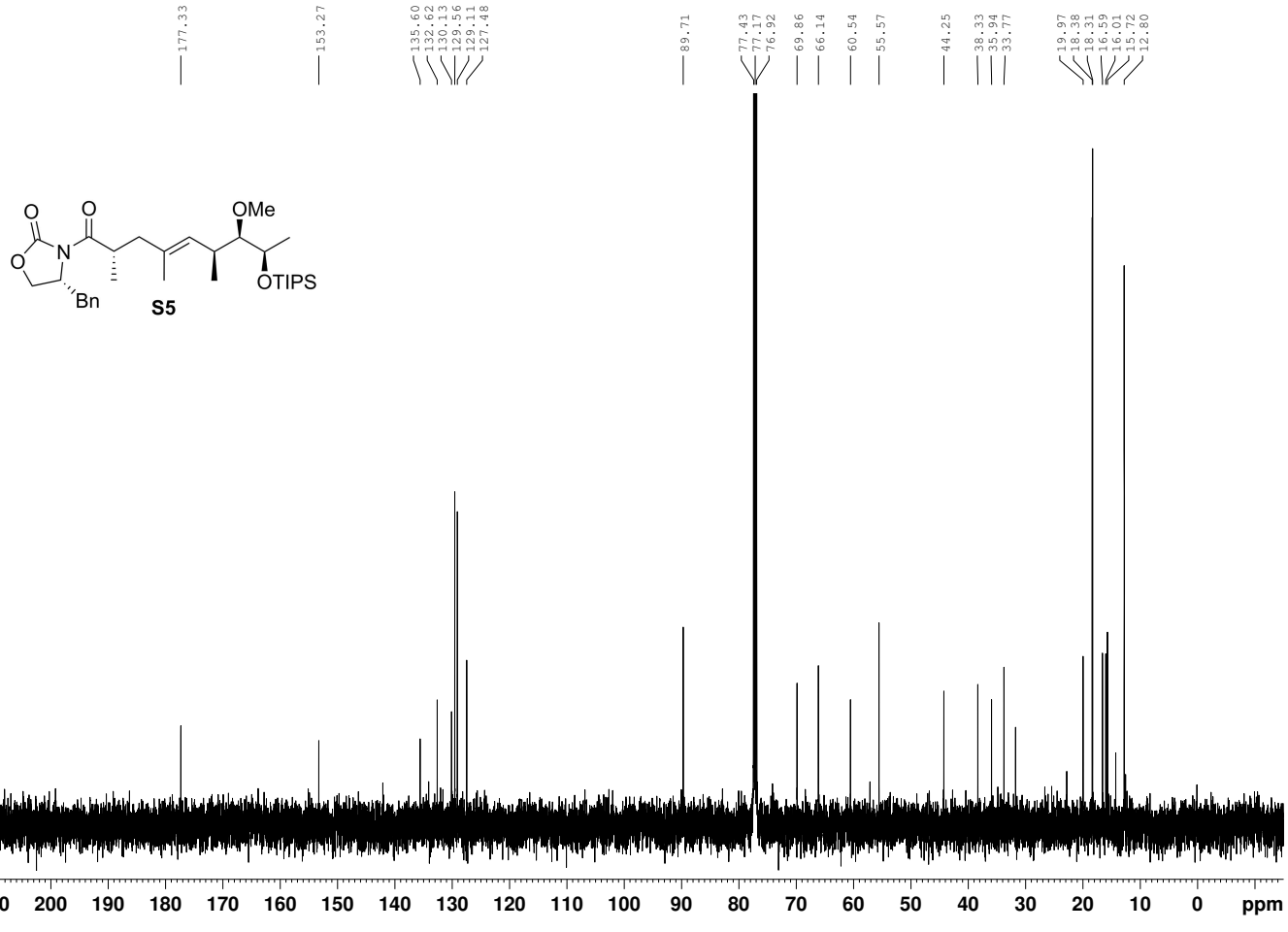
13C NMR (125 MHz, CDCl3)



1H NMR (500 MHz, CDCl3)



13C NMR (125 MHz, CDCl3)



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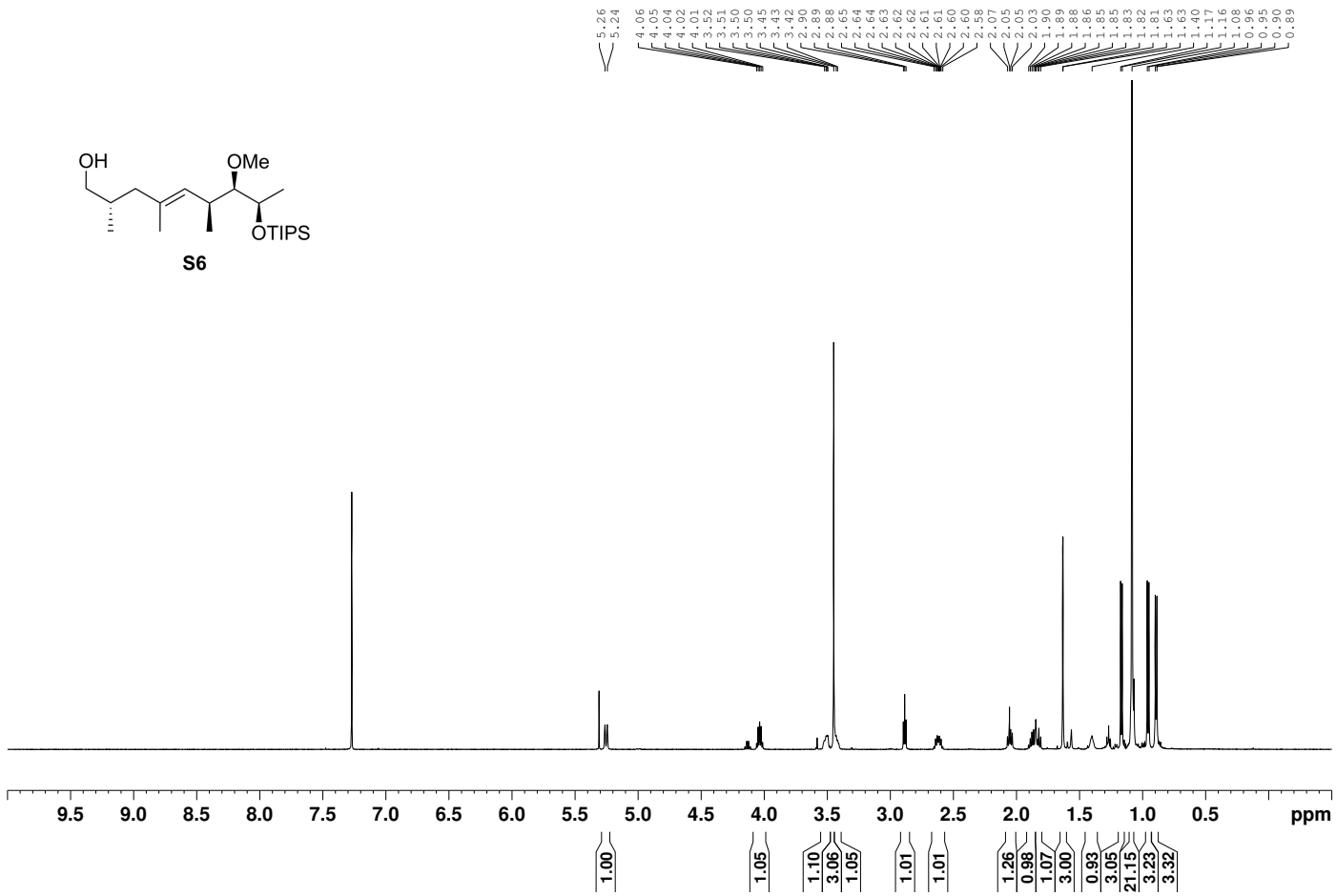
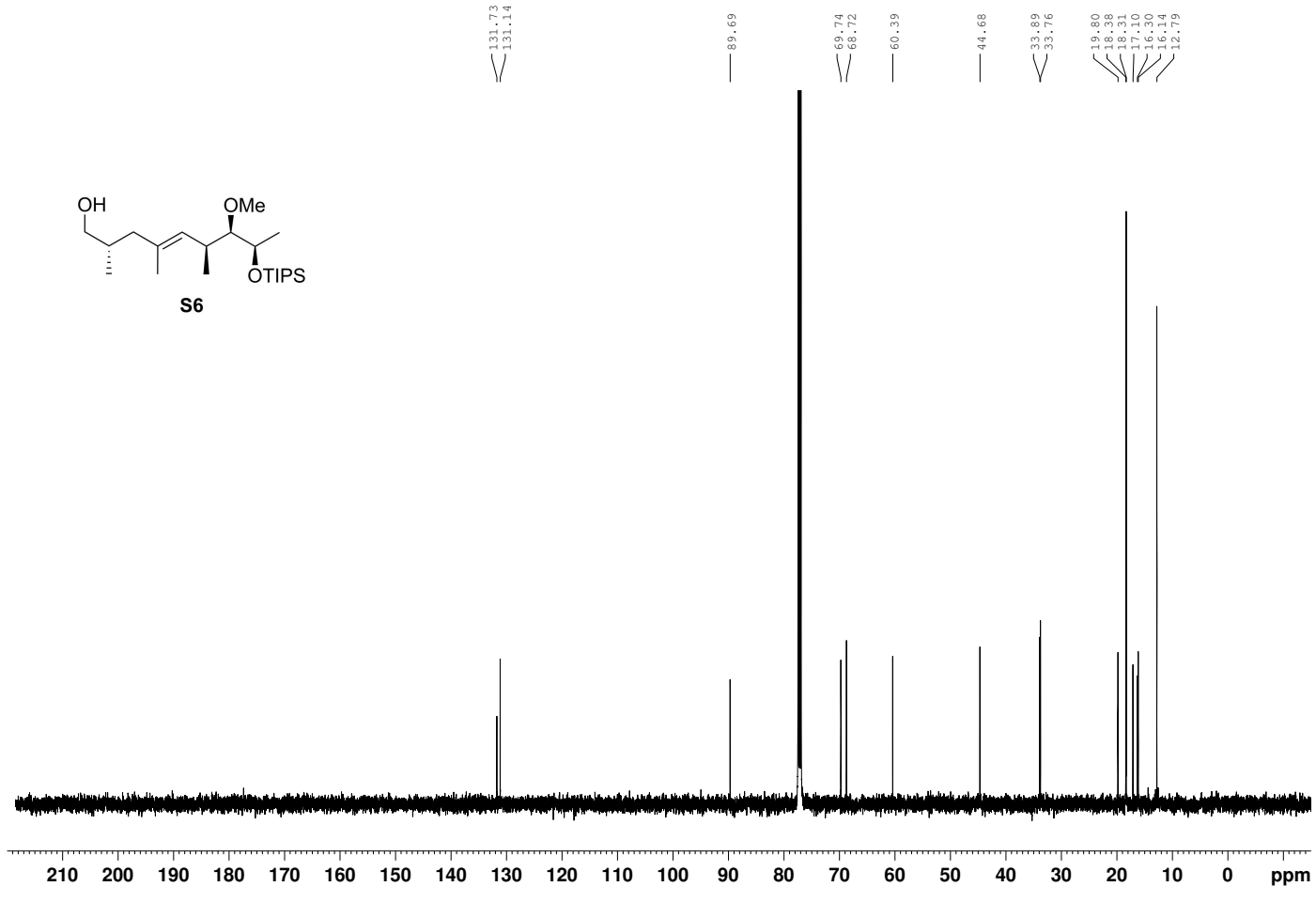
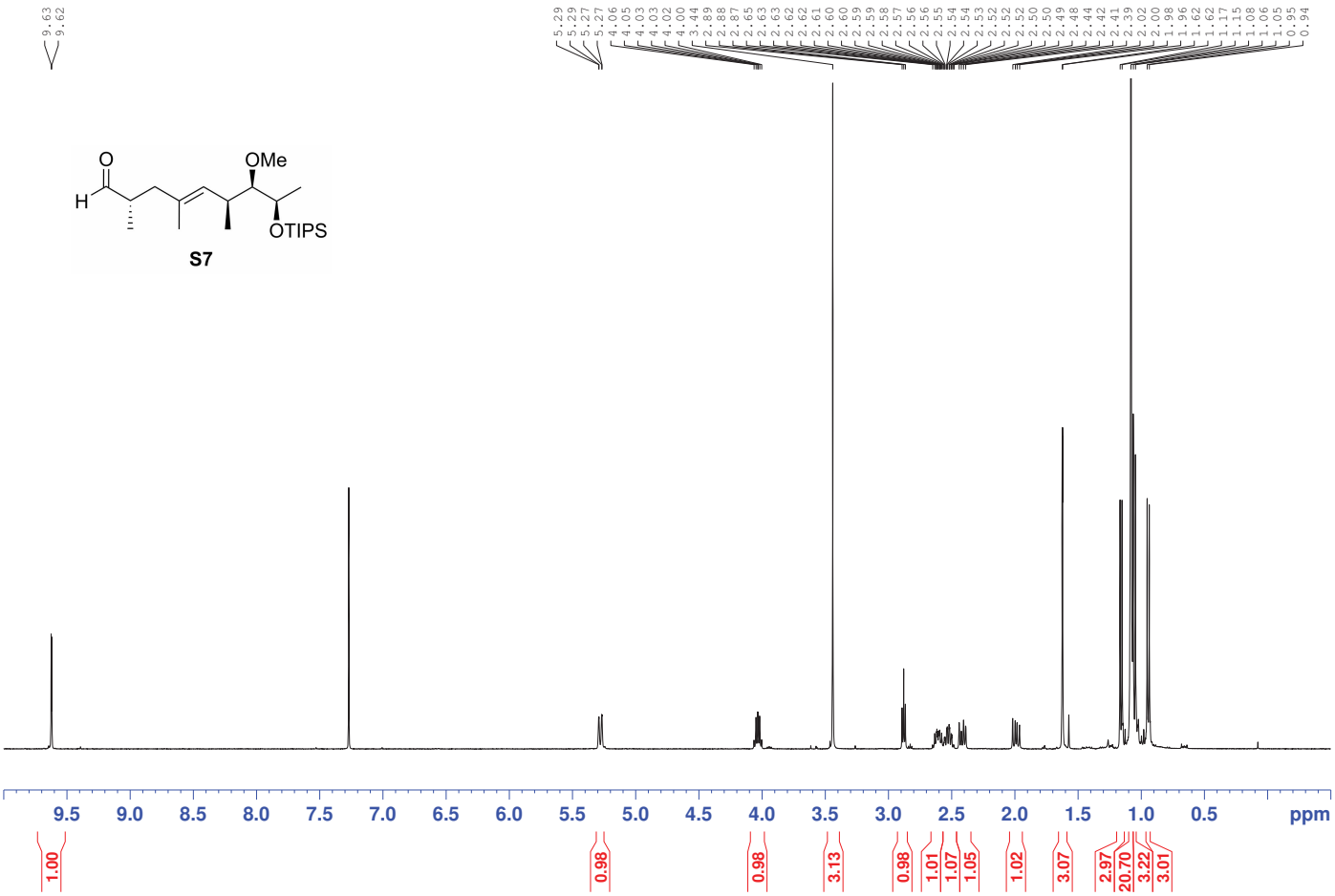


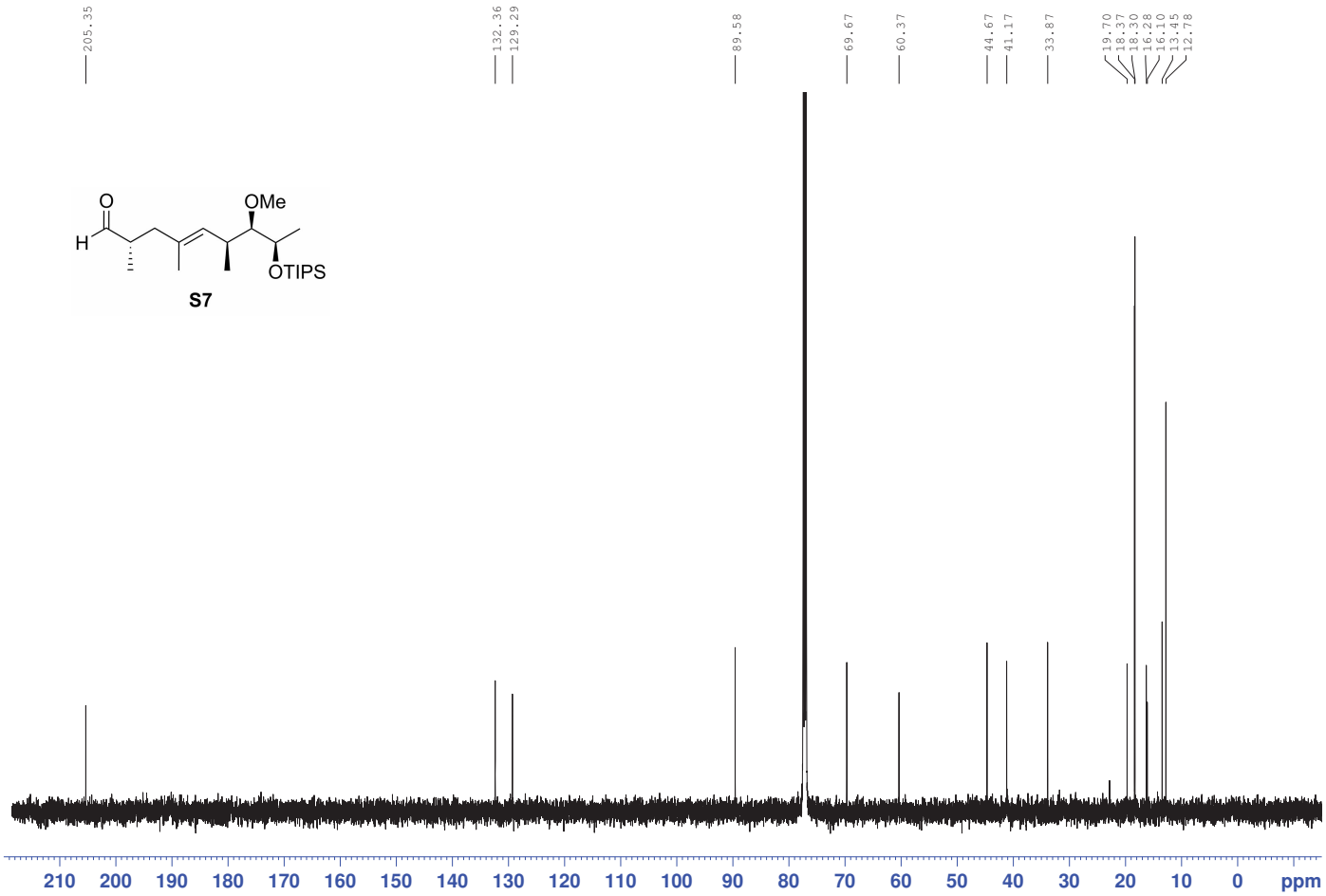
13C NMR (125 MHz, CDCl3)



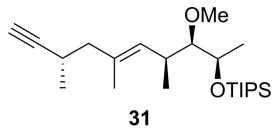
1H NMR (400 MHz, CDCl3)



13C NMR (125 MHz, CDCl3)



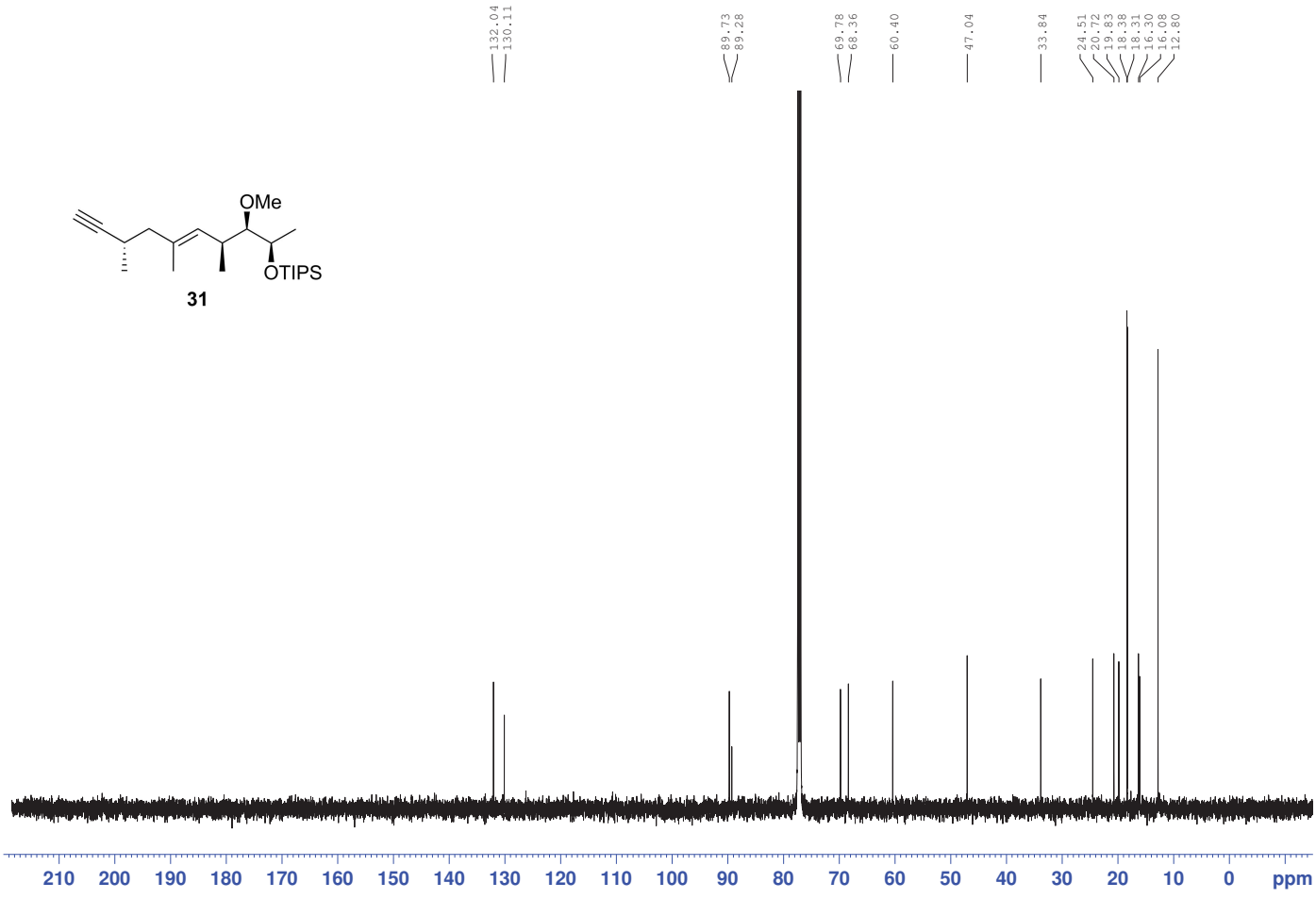
1H NMR (500 MHz, CDCl3)



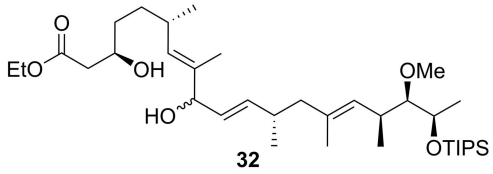
31

13C NMR (125 MHz, CDCl3)

31

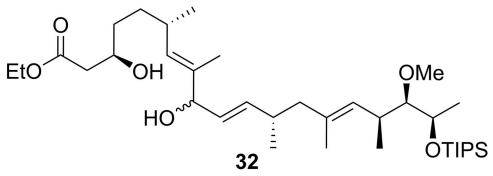


1H NMR (500 MHz, CDCl3)



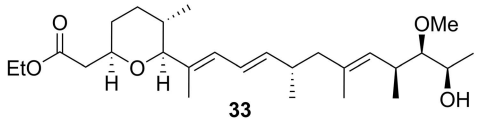
32

13C NMR (125 MHz, CDCl3)



32

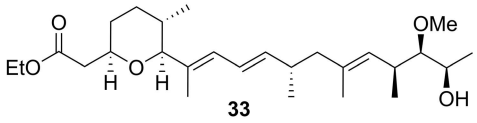
1H NMR (500 MHz, CDCl3)



33

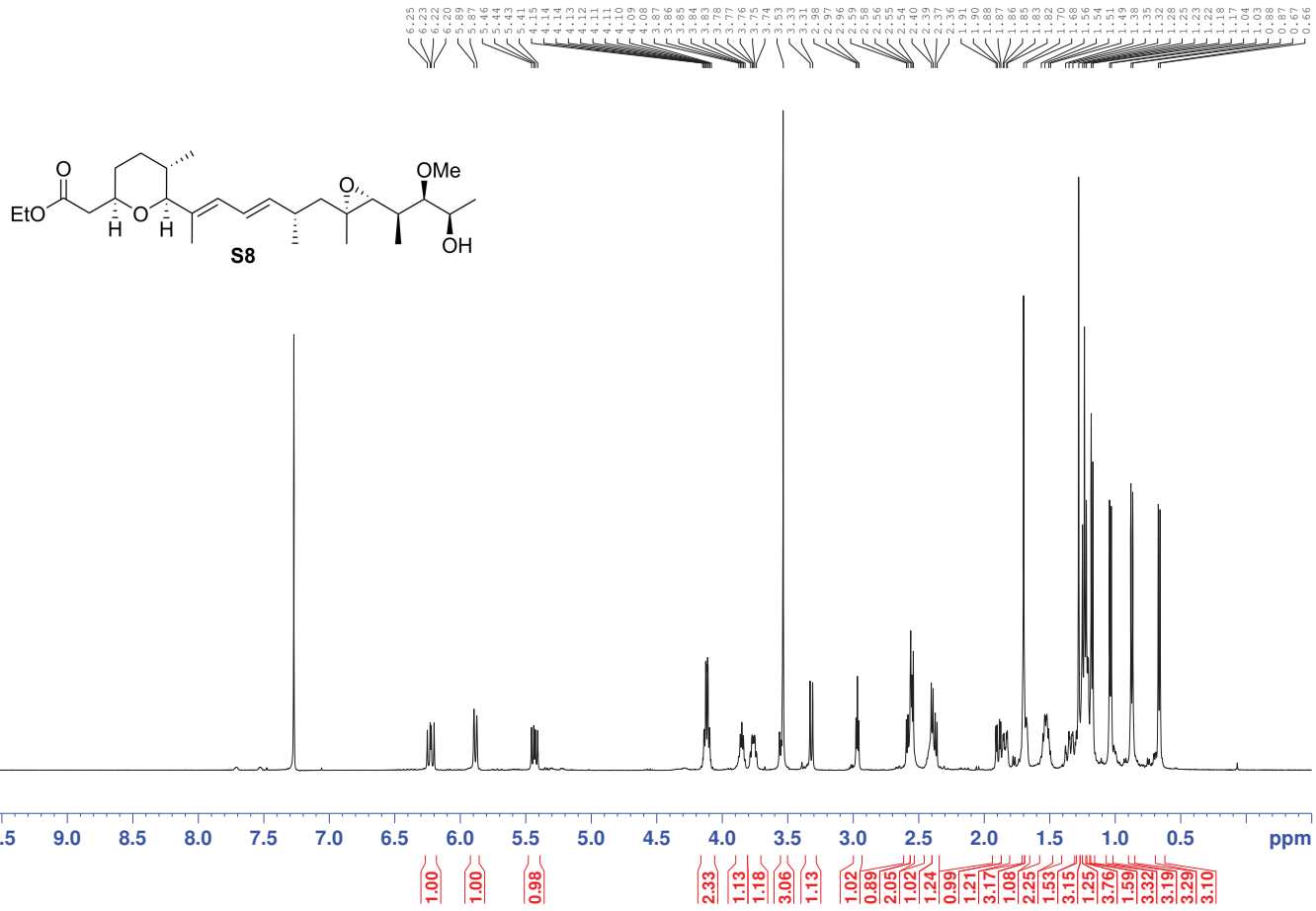
13C NMR (125 MHZ, CDCl3)

171.55 140.42 134.54 133.80 129.84 128.49 124.16 90.70 89.92 74.08 68.08 61.57 60.41 47.76 41.75 35.11 34.96 32.53 32.33 31.81 20.62 20.22 17.80 16.72 16.45 14.36 12.25

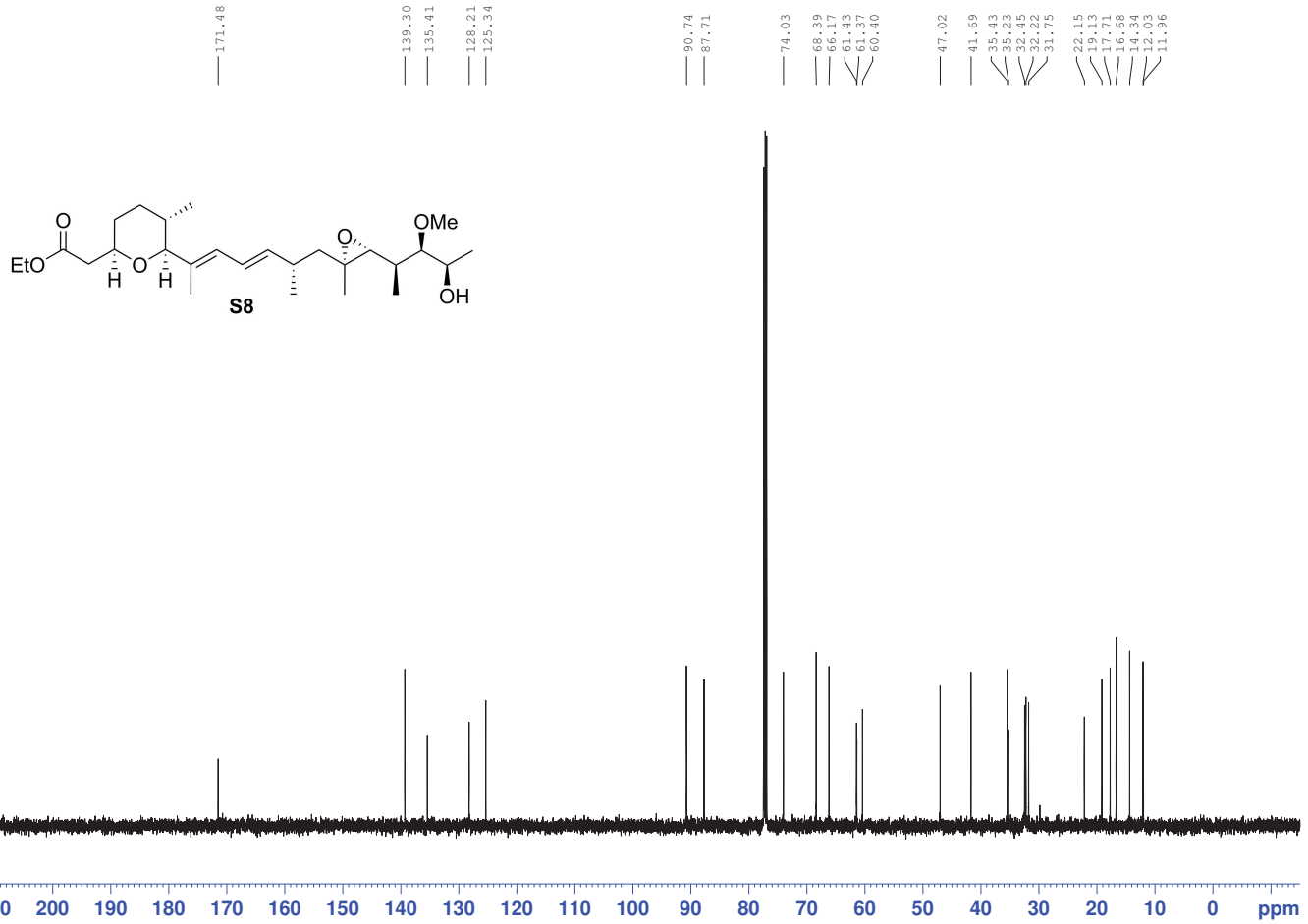


33

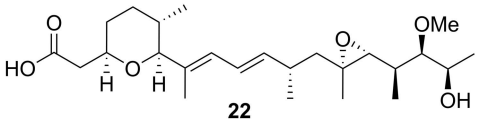
1H NMR (500 MHz, CDCl3)



13C NMR (125 MHz, CDCl3)

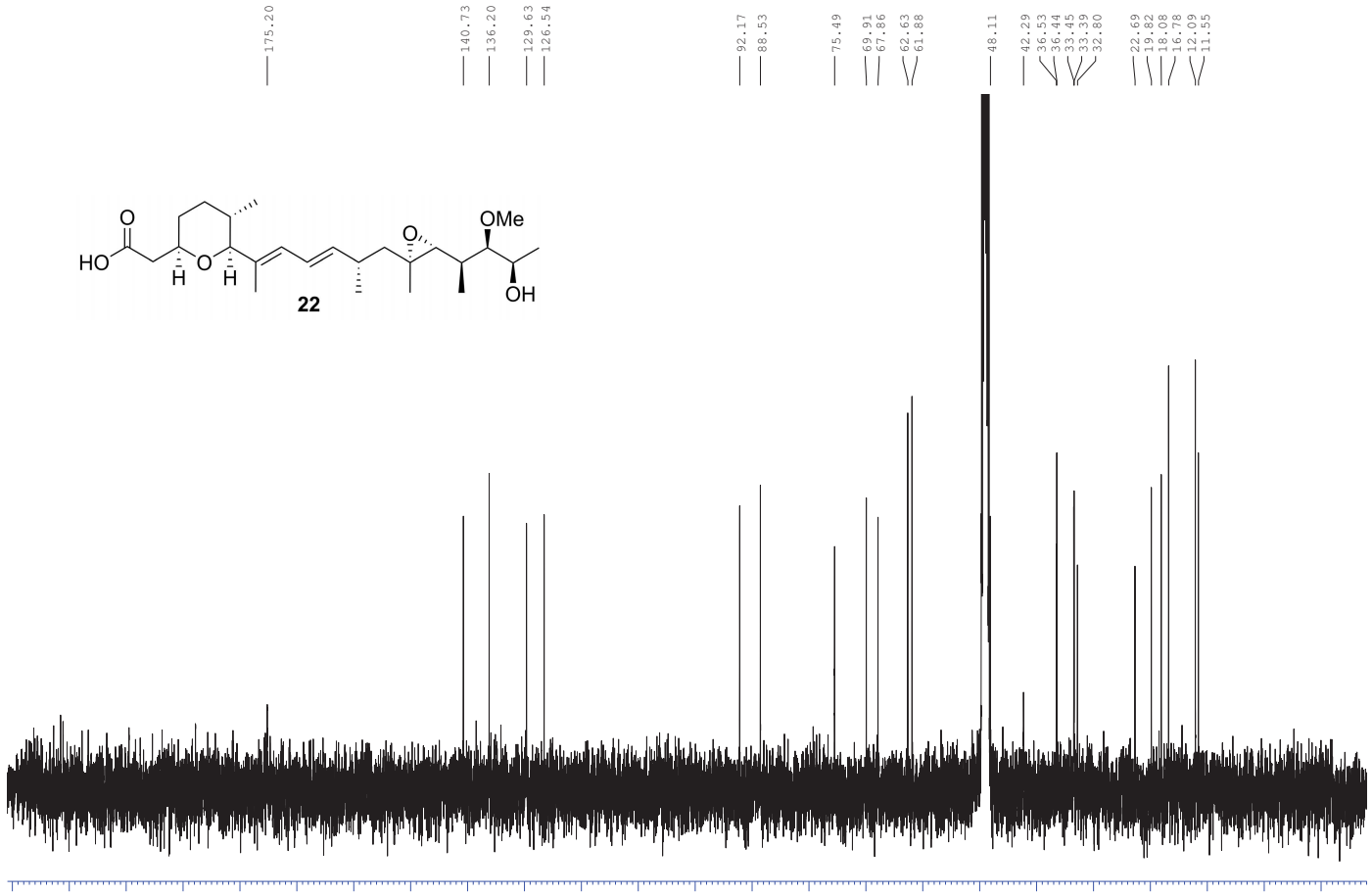


1H NMR (500 MHz, MeOD)



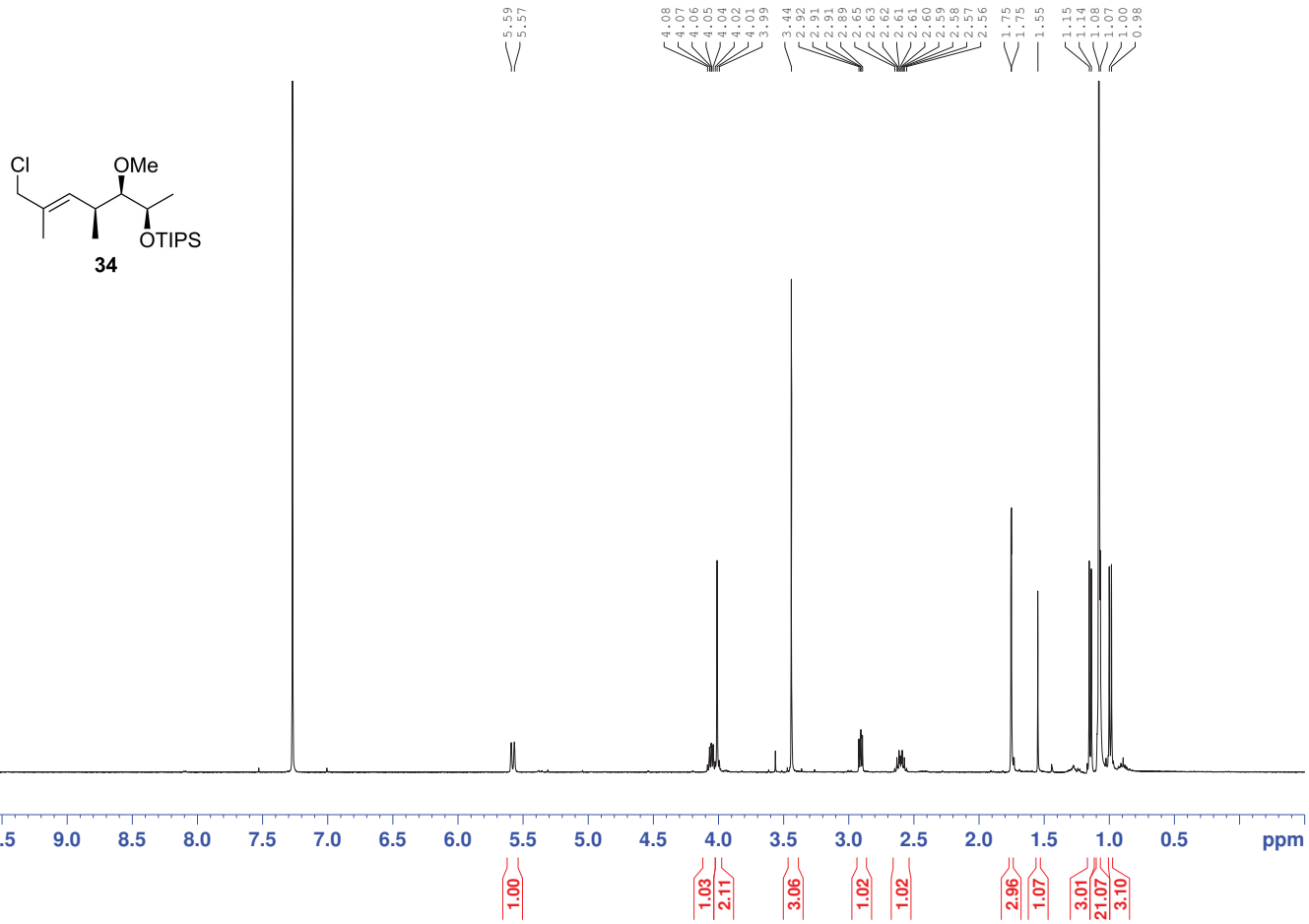
22

13C NMR (100 MHz, MeOD)

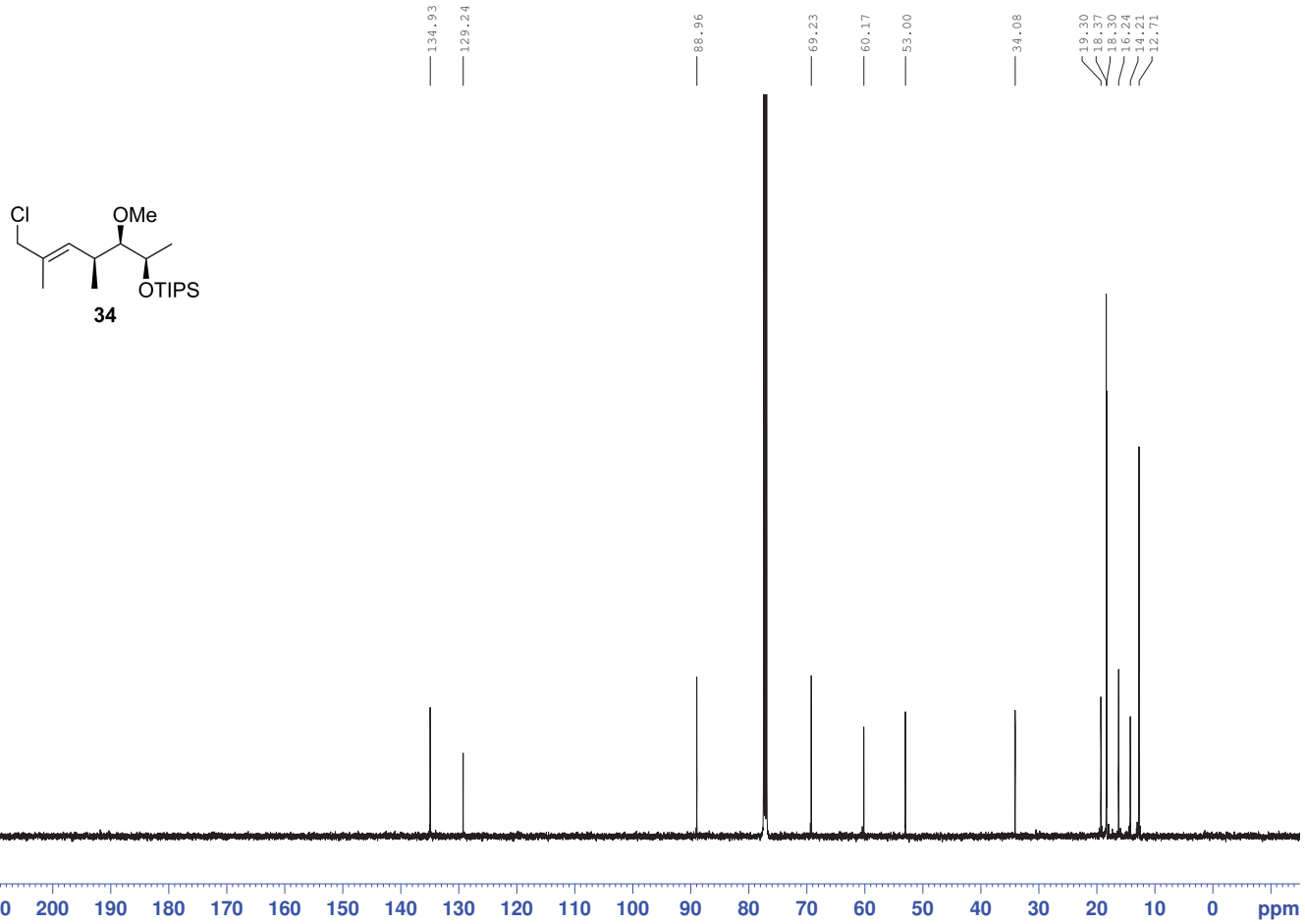


22

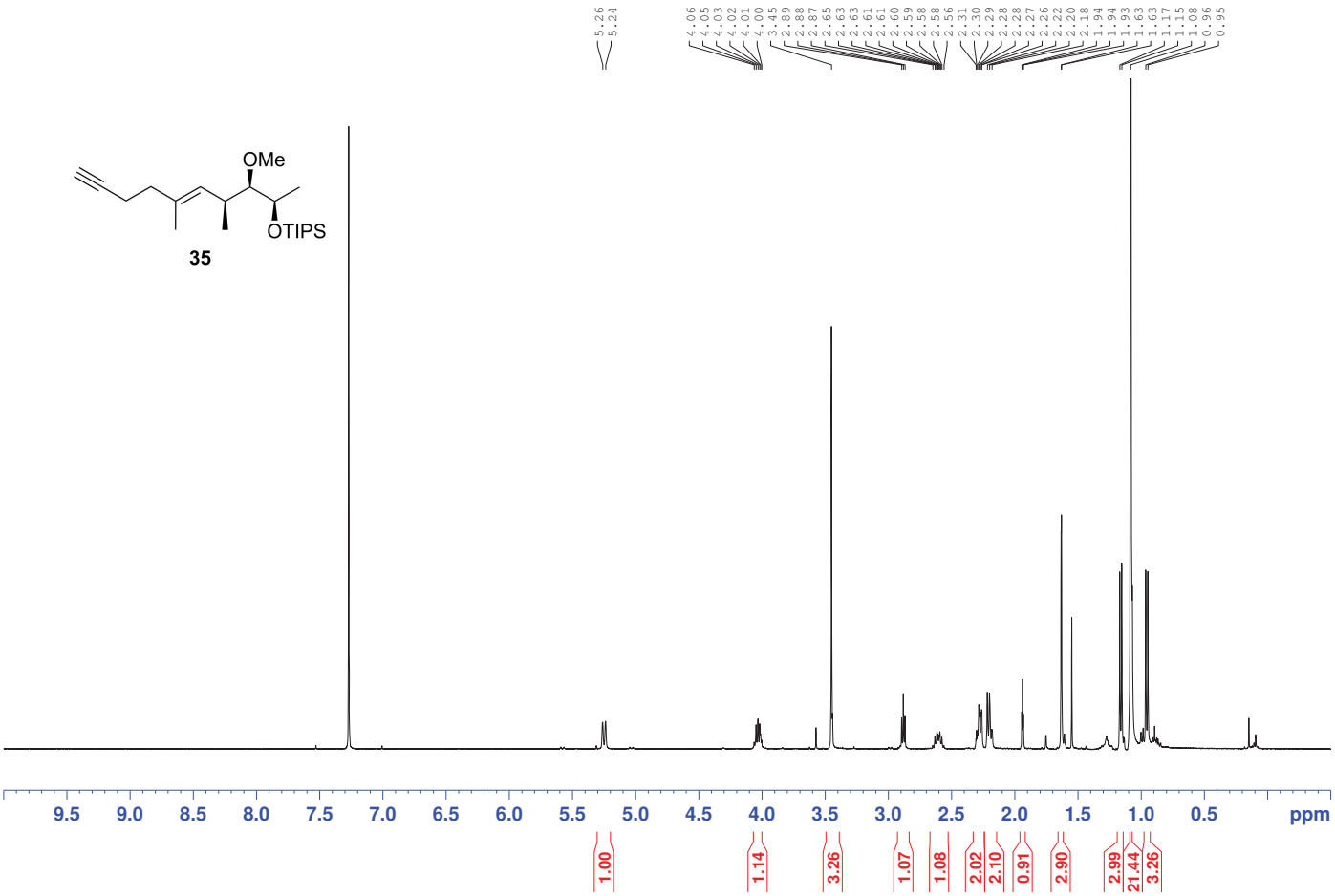
1H NMR (400 MHz, CDCl3)



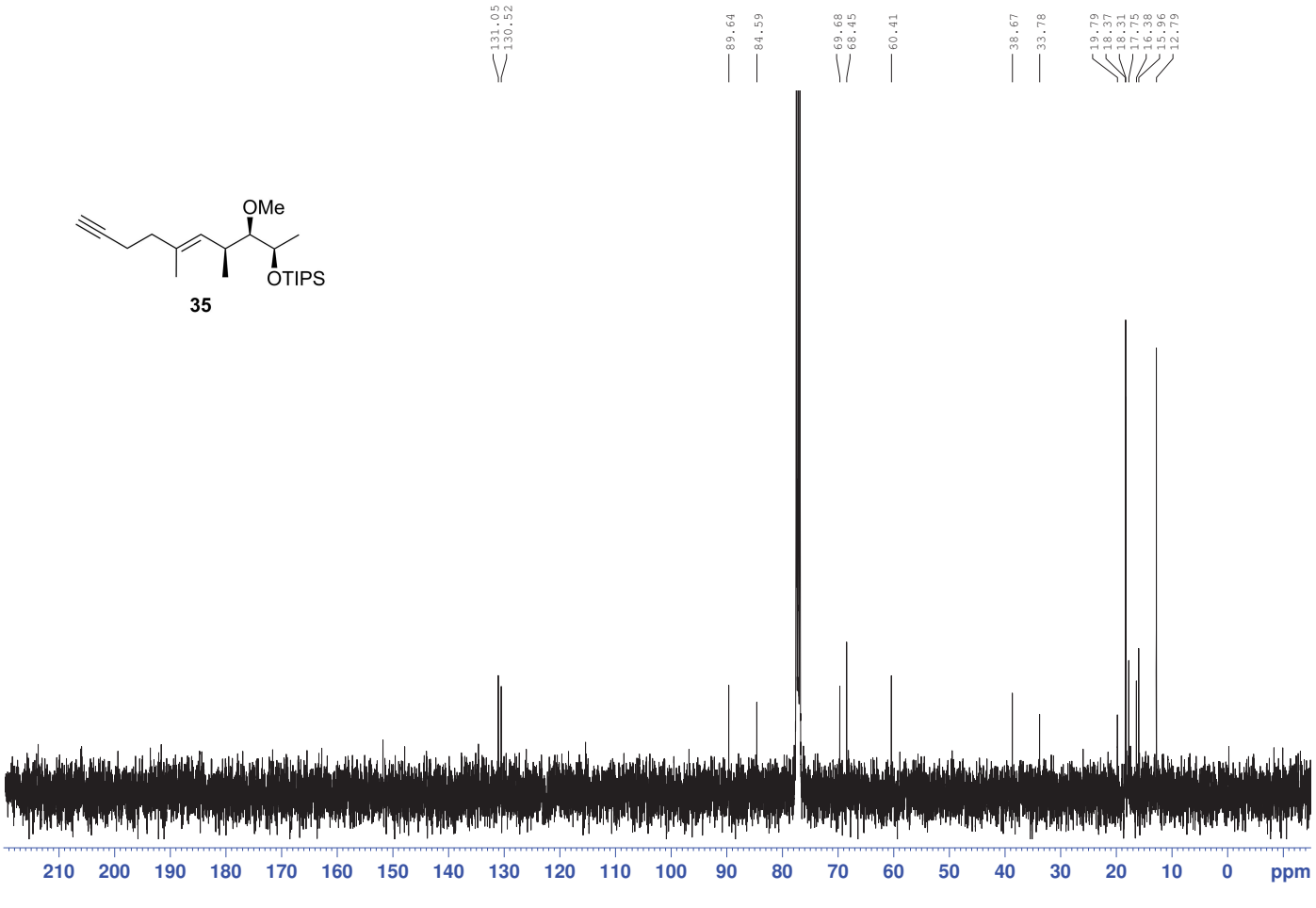
13C NMR (125 MHz, CDCl3)



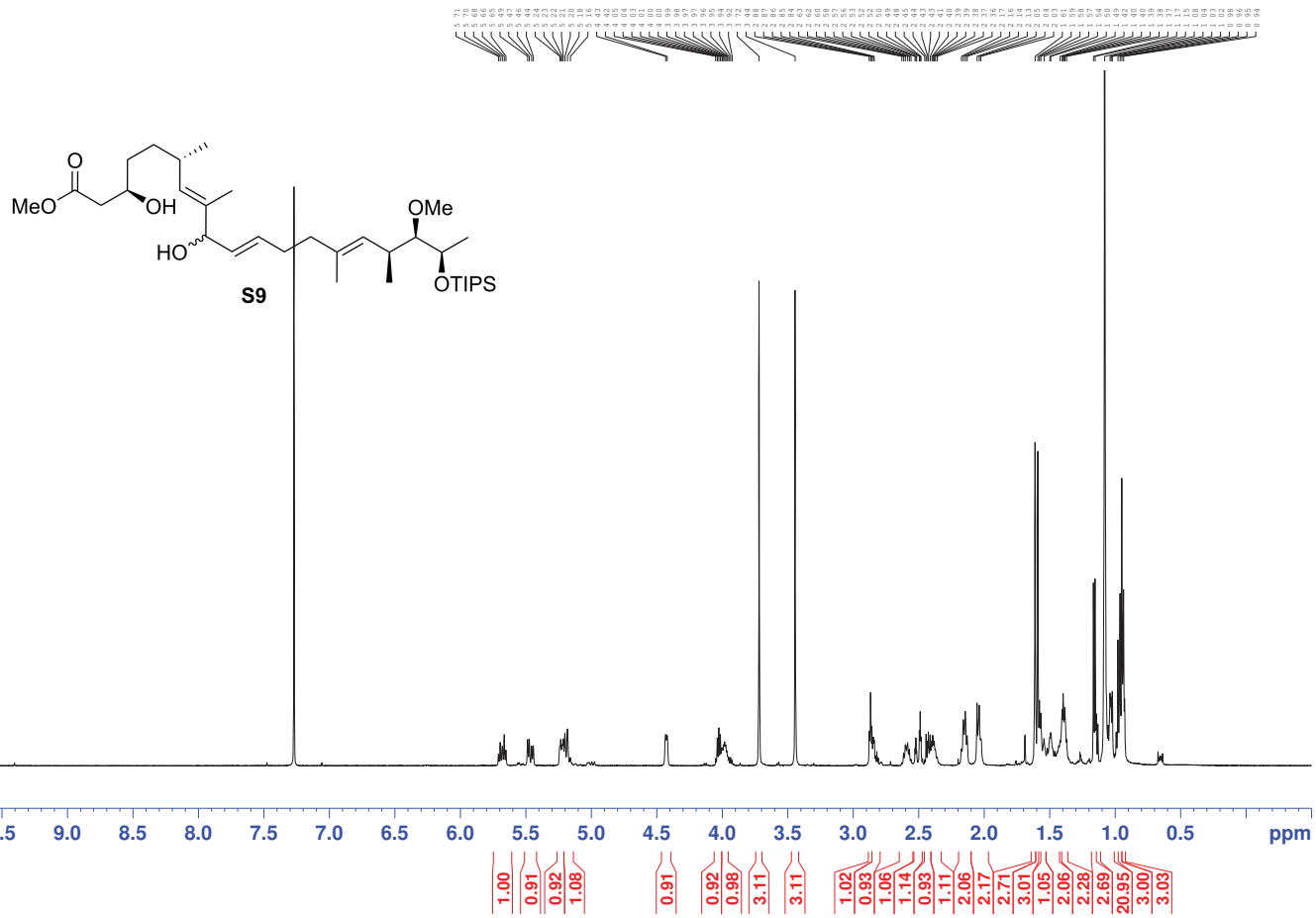
1H 400 CDCl3 10-16-15 TMR-205



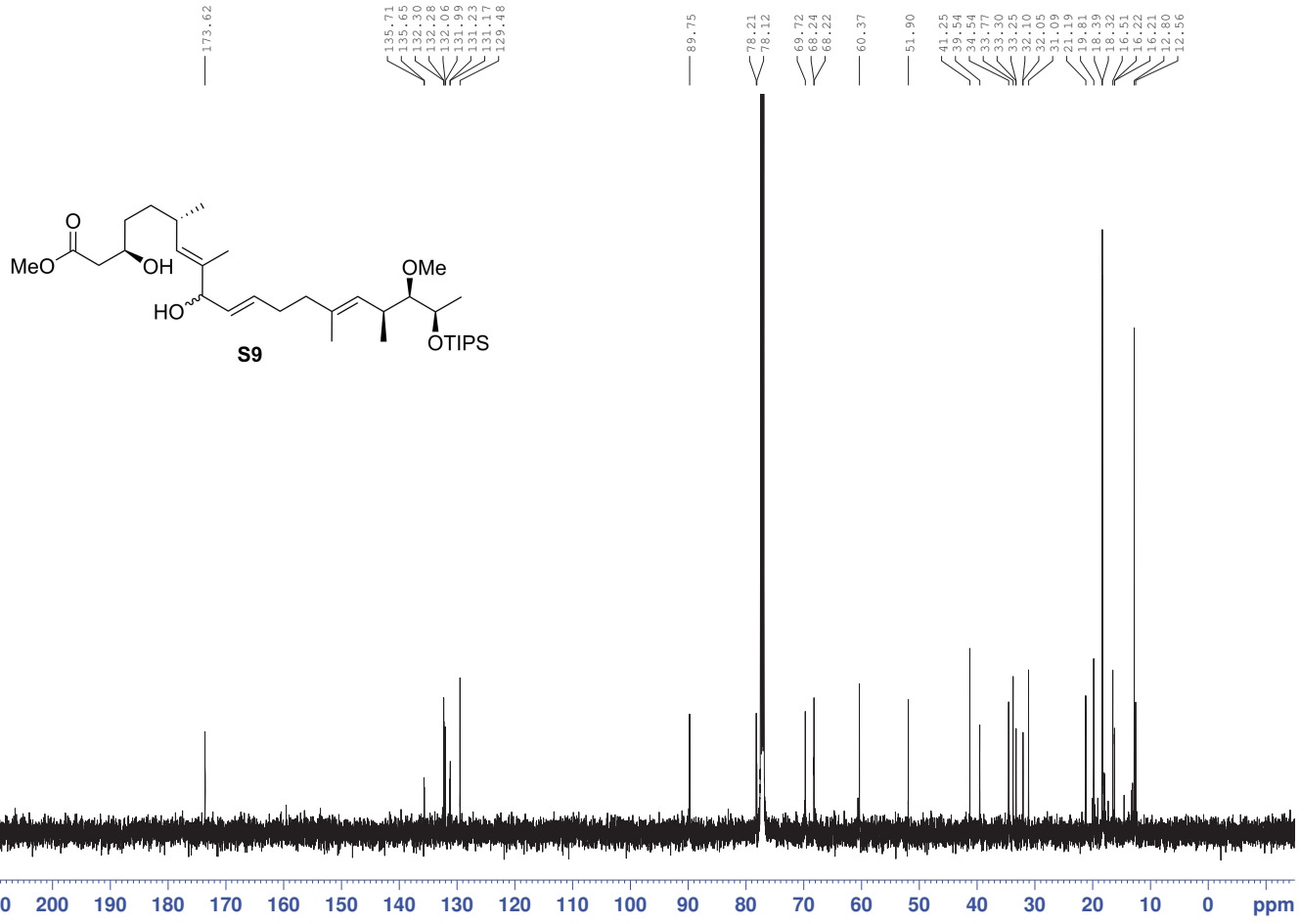
13C NMR (100 MHz, CDCl3)



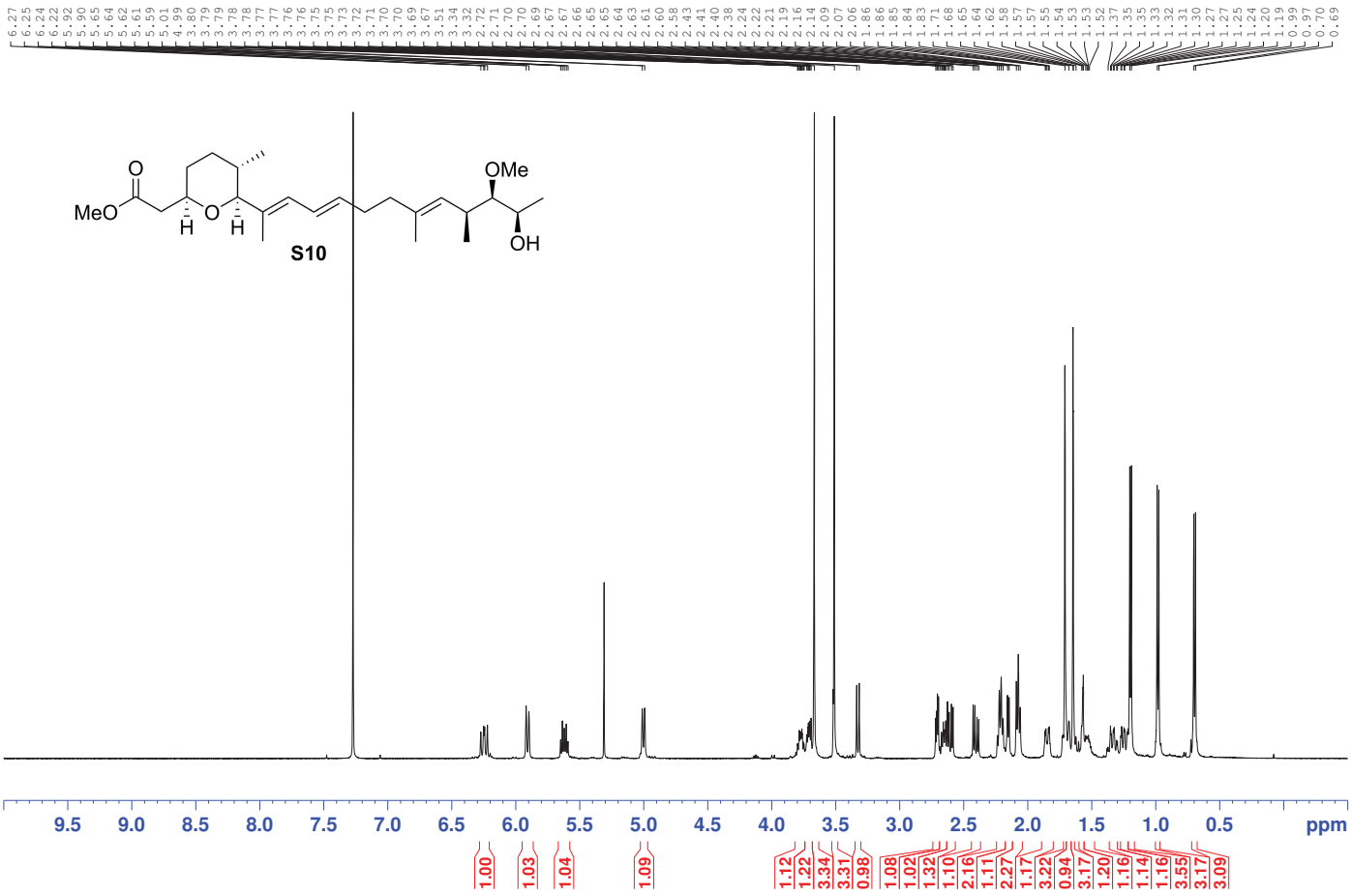
1H NMR (500 MHz, CDCl3)



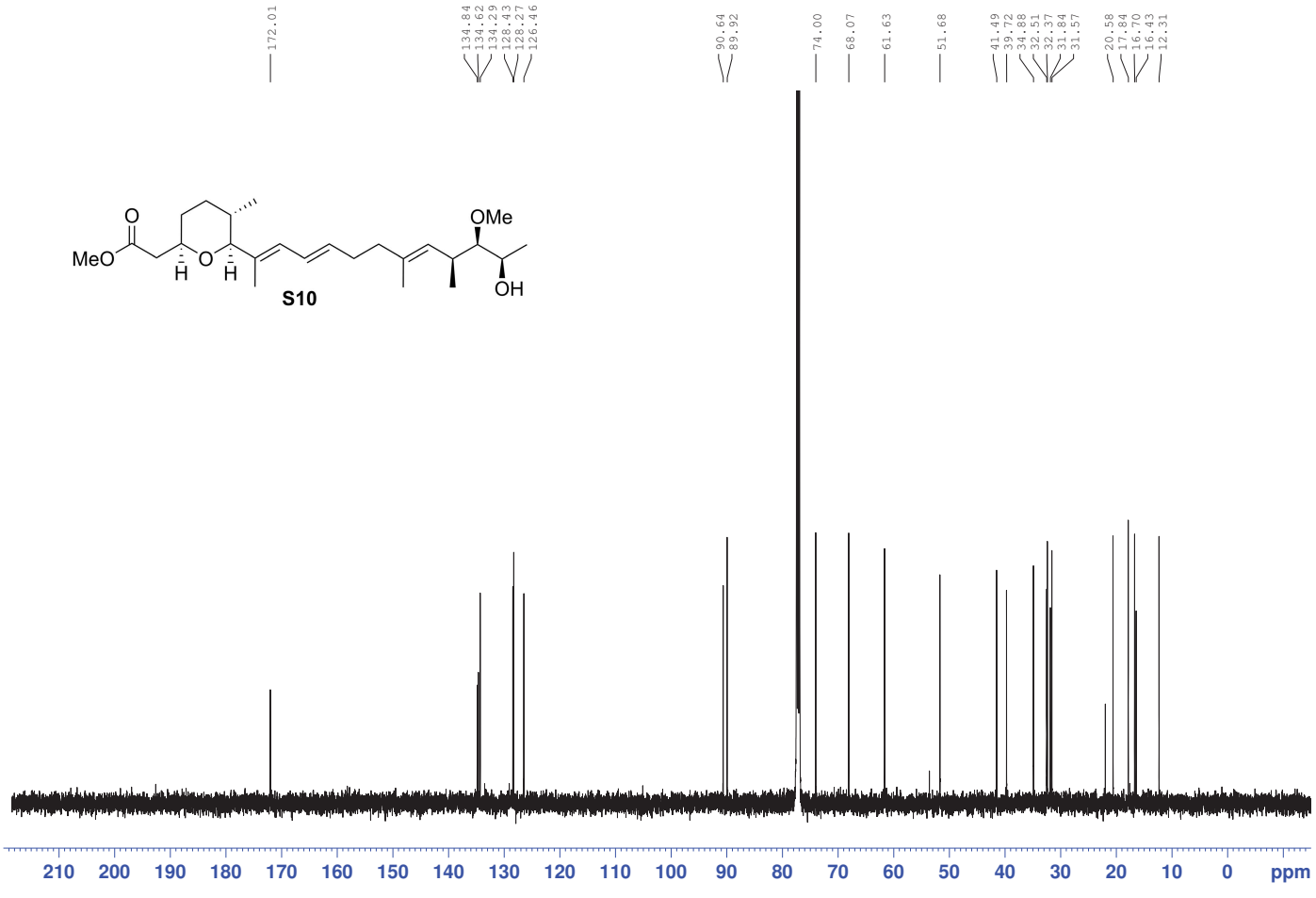
13C NMR (125 MHz, CDCl3)



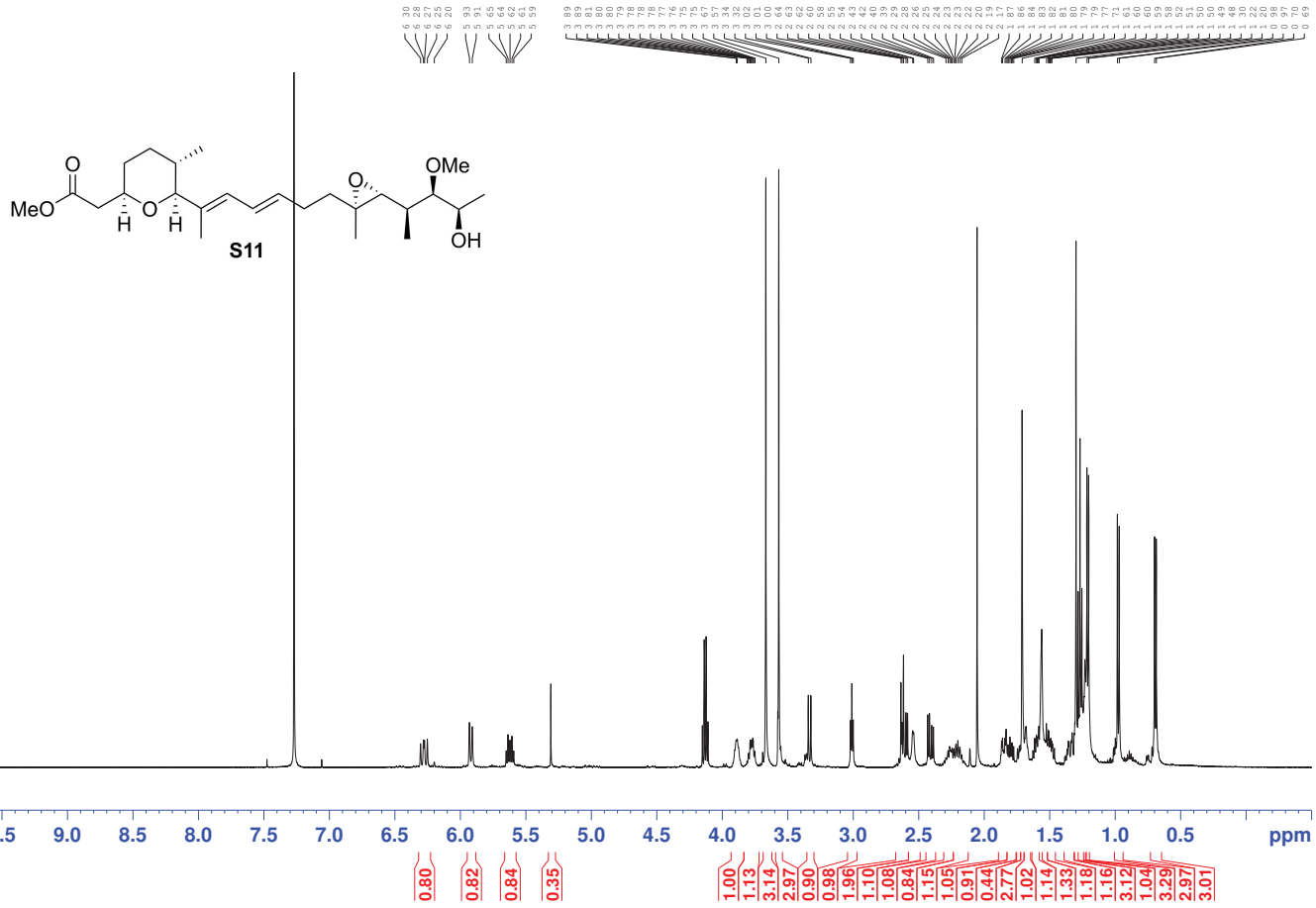
1H NMR (500 MHz, CDCl3)



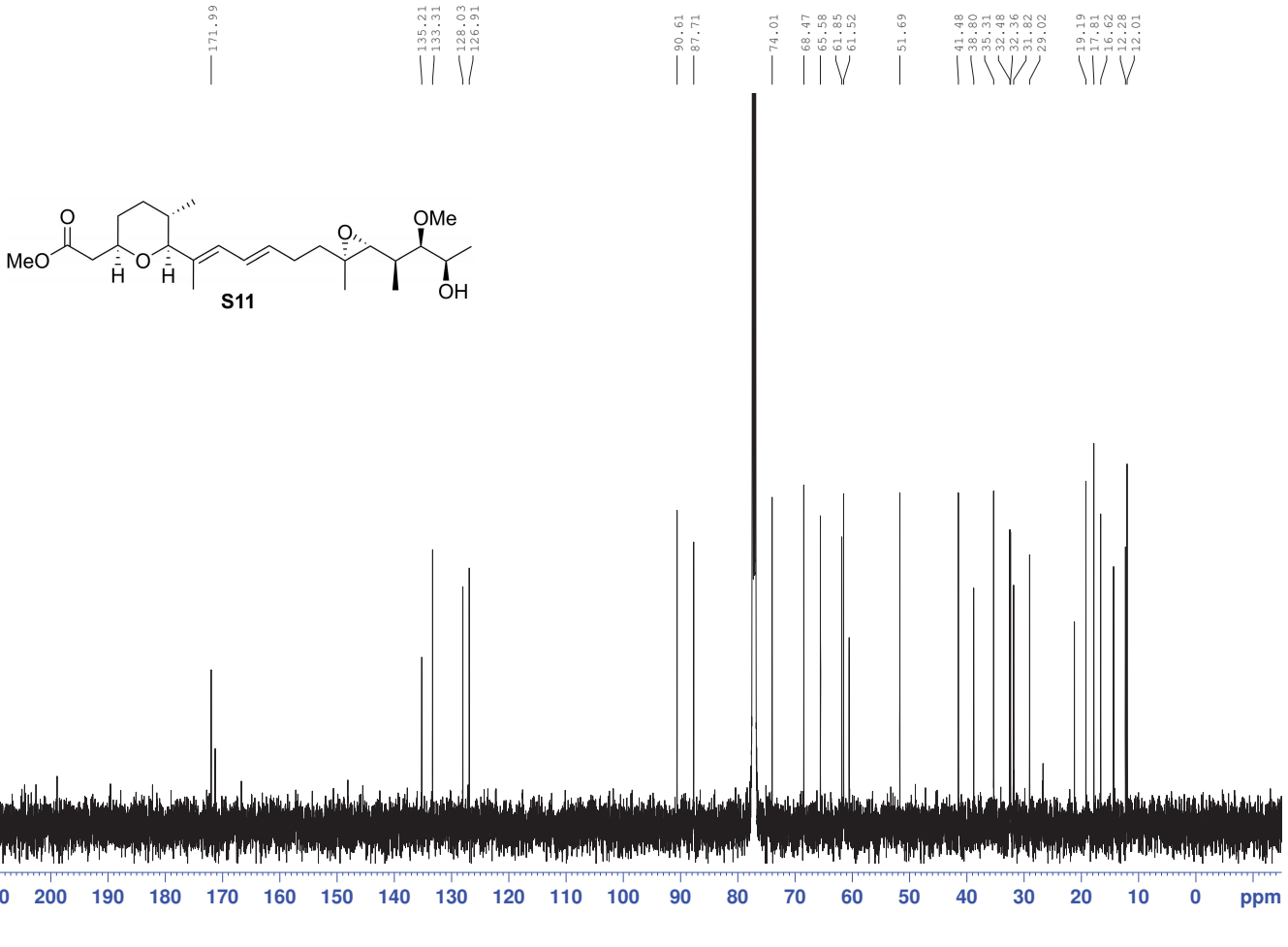
13C NMR (125 MHz, CDCl3)



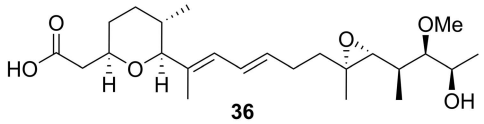
1H NMR (500 MHz, CDCl3)



13C NMR (125 MHz, CDCl3)

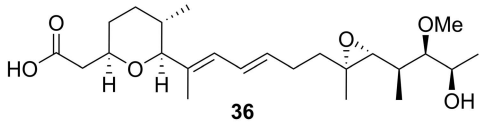


1H NMR (600 MHz, MeOD)



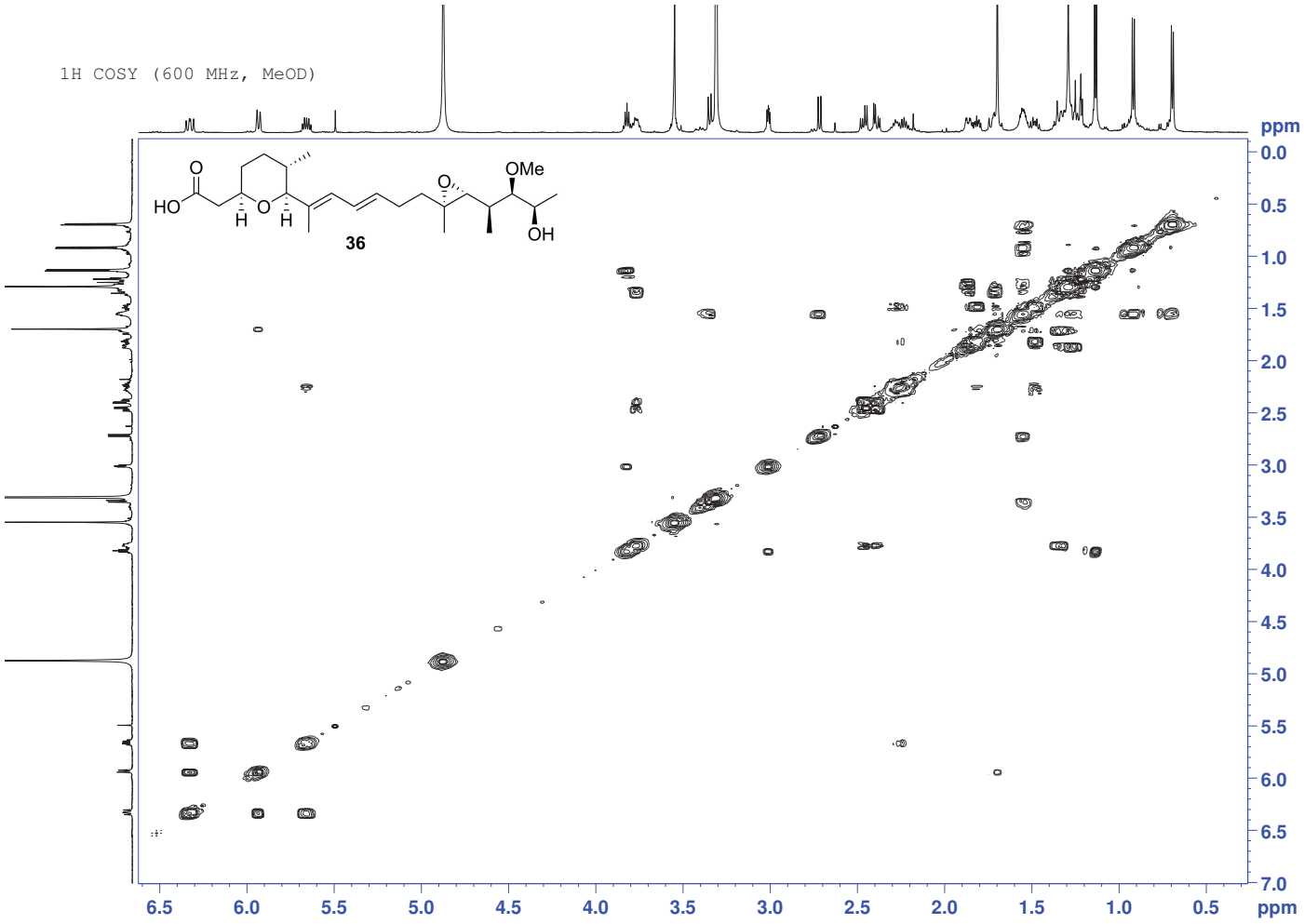
36

13C NMR (150 MHz, MeOD)

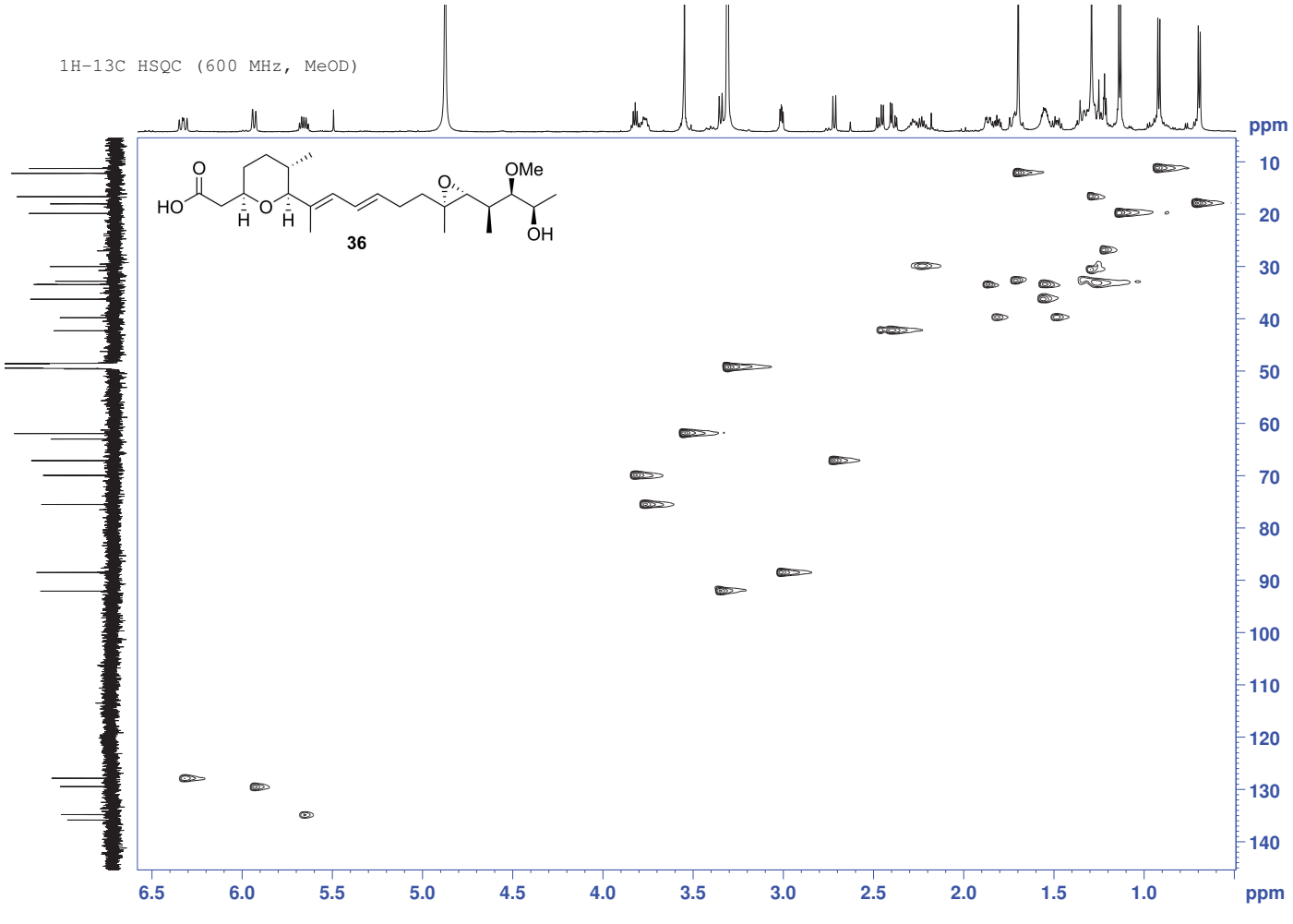


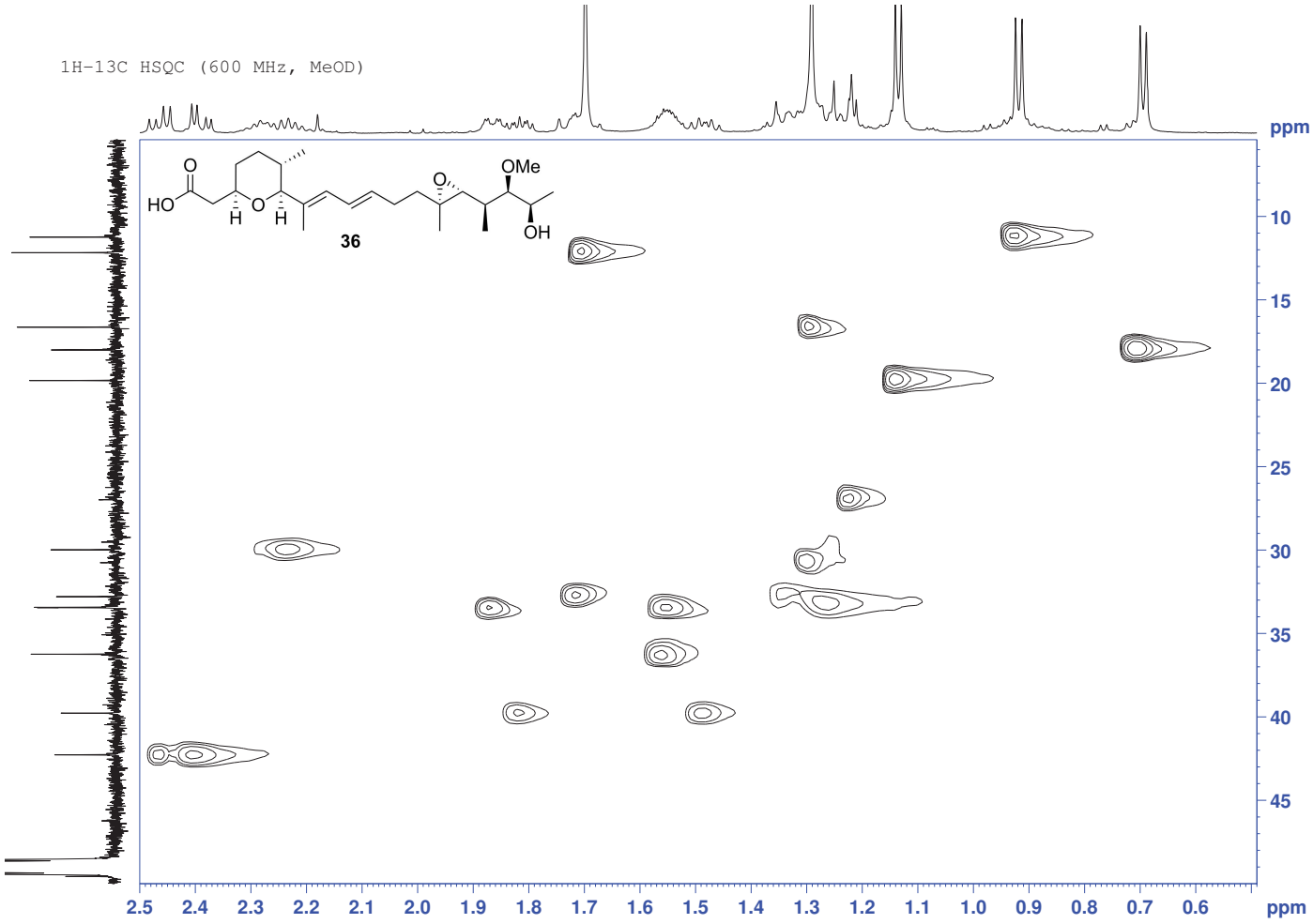
36

1H COSY (600 MHz, MeOD)



1H-13C HSQC (600 MHz, MeOD)




1H-13C HSQC (600 MHz, MeOD)
HO
O
H
O
H
O
OMe
OH
36
ppm
10
15
20
25
30
35
40
45
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
ppm