Supporting Information

Stereoselective Synthesis of the Macrolactone Core of (+)-Neopeltolide.

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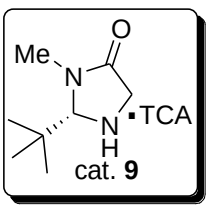
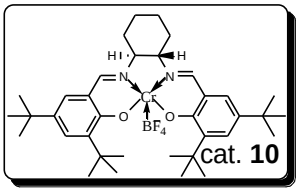
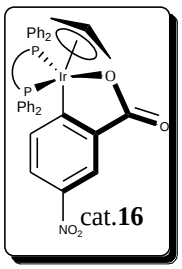
Table of Contents

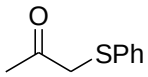
General Information

All materials were used as received from a commercial supplier without further purification. All anhydrous reactions were performed using oven-dried or flame dried glassware, which was then cooled under nitrogen or argon gas. Tetrahydrofuran (THF), toluene was distilled over Na/Ph_2CO under nitrogen or argon atmosphere. Dichloromethane (CH_2Cl_2), tertiary butyl methyl ether (TBME), benzene, pentane, acetonitrile, dimethylsulfoxide, triethylamine (TEA) and diethyl ether (Et_2O) were dried over CaH_2 and distilled prior to use. 4 Å molecular sieves were flame dried and then cooled under high vacuum prior to use. All reactions were monitored by E. Merck analytical thin layer chromatography (TLC) plates (AL SIL G/UV, aluminum back) and analyzed with 254 nm UV light and / or anisaldehyde – sulfuric acid or potassium permanganate or PMA treatment. Silica gel for column chromatography was purchased from acme's (Silica Gel 60-120, 100-200 mesh). All ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using Gemini 200, Avance 300, Inova 400, Inova 500 spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual $CHCl_3$ as an internal reference (^{1}H: δ 7.26 ppm, ^{13}C: δ 77.00 ppm). Coupling constants (*J*) are reported in Hertz (Hz). Peak multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), br (broad), and m (multiplet). Enantiomeric excess were recorded by Waters and Agilent HPLC instruments. For the preparation of Danishefsky diene an inert atmosphere filtration setup was employed. Sealed tube was purchased from Aldrich Company. Mass spectra were recorded using Waters Mass spectrometers. High resolution spectroscopies (HRMS) were recorded using Applied Bio-Sciences HRMS spectrometers. All IR- spectra were recorded using Nexus 870-FT-IR Thermo Nicolet spectrometer.



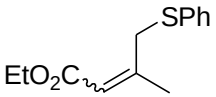






27

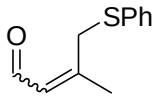
Compound (27): To a solution of chloroacetone (5.81 g, 62 mmol, 1 eq) in acetonitrile (310 mL) cooled at 0 ^{o}C in a two necked rb flask , was added anhydrous triethyl ammine (10.3 mL, 75.3 mmol, 1.2 eq) followed by the dropwise addition of thiophenol (7 mL, 68.2 mmol, 1.1 eq) over a period of 10 min and the reaction mixture was stirred further for a period of 20 min under a nitrogen atmosphere. The reaction mixture was diluted with CH_2Cl_2, washed with water, brine and dried over Na_2SO_4 and filtered. The organic layer was evaporated under reduced pressure to furnish the crude product which was purified by flash column chromatography using 5% EtOAc/hexane (v/v) to afforded **27** as a brown colour oil (9.6 g, 57.8 mmol) in 97% yield. TLC (SiO_2): R_f = 0.2 (ethyl acetate: hexanes, 0.5:9.5); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34-7.15 (m, 5H), 3.57 (s, 2H), 2.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.4, 134.6, 129.4, 129.1, 126.8, 44.6, 27.9; IR (neat) ν_{max}: 2924, 1710, 741 cm^{-1}; MS (ESI): 205 $[M+K]^+$; HRMS (ESI) : *m/z* $[M+K]^+$ Calcd. for $C_9H_{10}OKS$: 205.2435, found 205.2433.



28

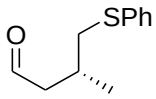
Compound (28): To a solution of ketone **27** (9.5 g, 57.2 mmol, 1 eq) in benzene (173 mL, 0.2 M) was added ethyl(triphenylphosphoranylidene)acetate (22.6 g, 65.8 mmol, 1.15 eq) and the reaction mixture was heated to reflux for 12 h. The reaction mixture was cooled to rt and benzene was evaporated under reduced pressure. The residue was cooled to 0 ^{o}C, diluted with ether and the precipitated solids were removed by filtration through a sintered funnel. The filtrate was evaporated under reduced pressure to afford the crude product which was purified by column chromatography using 5% EtOAc/hexane (v/v) as the eluent to give **28** as a light yellow colour oil (13.24 g, 56.1 mmol) in 98% yield. TLC (SiO_2): R_f = 0.66 (ethyl acetate: hexane, 1:9); ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.50-7.21 (m, 10H), 5.71 (s, 1H), 5.69 (s, 1H), 4.27-4.01 (m, 4H), 3.55 (s, 4H), 2.29 (s, 3H), 2.01 (s, 3H), 1.32-1.17 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.1, 165.8, 153.8, 153.4, 135.2, 135.0, 131.4, 131.1, 130.7, 128.8, 128.6, 126.9, 126.7, 118.6, 118.1, 59.6, 58.9, 44.5, 35.8, 23.9, 21.8, 17.8, 14.1; IR (neat) ν_{max}: 2981, 1713, 1152, 742 cm^{-1}; MS (ESI): 275 $[M+K]^+$; HRMS (ESI): *m/z* $[M+K]^+$

Calcd. for $C_{13}H_{16}O_2SK$ 275.2105, found 275.2120. Note: The proton count has been doubled since a equimolar diastereomeric mixture, differing at the doublebond, was obtained.



8

Compound (8): To a solution of copmound **28** (17.7 g, 75 mmol, 1 eq) in anhydrous CH_2Cl_2 (250 ml) cooled at -78 ^oC, was maintained under nitrogen atmosphere slowly added DIBAL-H (56.3 mL, 78.8 mmol, 1.4 M in Toluene, 1.05 eq) dropwise during 30 min and the mixture stirred further for a period of 20 min. The reaction mixture was quenched using saturated aqueous solution of sodium, potassium tartarate and extracted with CH_2Cl_2 (150 mL x 3). The combined organic layers were washed with brine solution and dried over Na_2SO_4 and filterd. Evaporation of the solvent under reduced pressure afforded the crude product which was purified by flash column chromatography using 5% EtOAc/hexane (v/v) as the eluent to afford **8** as a yellow colour oil (12.67 g, 66 mmol) in 88% yield. TLC (SiO_2): R_f = 0.56 (ethyl acetate: hexane, 1:9). ^1H NMR (300 MHz, $CDCl_3$): δ 9.85 (d, *J* = 7.5 Hz, 1H), 9.66 (d, *J* = 7.5 Hz, 1H), 7.32-7.15 (m, 10H), 5.65 (d, *J* = 7.5 Hz, 1H), 5.59 (d, *J* = 7.5 Hz, 1H), 3.53 (s, 4H), 2.24 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.9, 133.5, 131.3, 129.2, 129.0, 128.7, 127.4, 44.4, 24.0; IR (neat) ν_{max}: 2981, 1722, 1232, 1106 cm^{-1}; MS (EI): 192 $[M]^+$; HRMS (ESI): *m/z* $[M+Na]^+$ Calcd. for $C_{11}H_{12}ONaS$: 215.0609, found 215.0615. Note: The proton count has been doubled since a equimolar diastereomeric mixture, differing at the doublebond, was obtained.

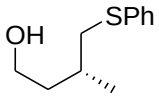


7

Compound (7): A solution of compound **8** (192 mg, 1 mmol, 1eq) dissolved in chloroform (5 mL) was cooled to -30 ^oC. To this solution was added the trichloroacetic acid salt of *(S)*-2-*tert*-butyl-3-methylimidazolidin-4-one (64 mg, 0.2 mmol, 20 mol%) and

Hantzsch ester (304 mg, 1.2 mmol, 1.2 eq). The resulting yellow suspension was stirred at -30 ^{o}C for 72 h, by which time the mixture was a light yellow homogeneous solution. The cold reaction mixture was poured into an aq. 4 N HCl solution and diluted with diethyl ether. The organic layer was separated, washed four times with aq. 4 N HCl solution, and once with a saturated aqueous solution of $NaHCO_3$. The organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash chromatography on silicagel using 4% EtOAc/hexane (v/v) as the eluent to provide the title compound **7** as a colorless oil (146 mg, 0.75 mmol), in 75% yield. TLC (SiO_2): R_f = 0.5 (ethyl acetate: hexanes, 1:9); $[\alpha]^{25}_{D}$ = +3.8° (*c* = 3.0 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.84 (s, 1H), 7.4-7.2 (m, 5H), 2.8 (d, *J* = 8.1 Hz, 2H), 2.6 (dd, *J* = 13.6, 8.3 Hz, 1H), 2.25 (dd, *J* = 13.6, 5.8 Hz, 1H), 1.52-1.36 (m, 1H), 1.23 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.5, 136.1, 129.1, 128.8, 125.9, 49.5, 40.3, 28.0, 19.6; IR (neat) ν_{max}: 2961, 1630, 1478, 741 cm^{-1}; MS (EI): 194 $[M]^{+}$; HRMS (ESI): *m/z* $[M+Na]^{+}$ Calcd. for $C_{11}H_{14}ONaS$: 217.0765, found 217.0770.

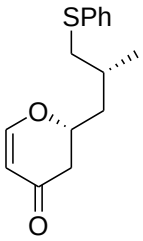
Note: The enantiomeric excess in the organocatalytic conjugate addition reaction (95% ee) was determined in the benzoate ester of the alcohol obtained by a sodium borohydride reduction of aldehyde **7**. Eurocel® (250 x 4.6 mm), isocratic 5% isopropyl alcohol, 95% hexane, flow rate:1.0 mL/min, 25 ^{o}C; *(S)* isomer t_r = 7.6 min and *(R)* isomer t_r = 12.0 min.



Alcohol

Alcohol: To a solution of the aldehyde **7** (97 mg, 0.5 mmol, 1 eq) in MeOH (2.5 mL) cooled at -10 ^{o}C, was added sodium borohydride (21 mg, 0.55 mmol, 1.1 eq). After 5 min the reaction mixture was quenched by adding an aq. saturated ammonium chloride solution. The organic layer was separated and the aq. layer extracted with EtOAc (10 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and the solvent evaporated under reduced pressure to afford the crude product. Purification by flash column chromatography using 20% EtOAc/hexane (v/v) as the eluent afforded **alcohol**[1] as a light yellow colour oil (78.4 mg, 0.4 mmol) in 80% yield. TLC (SiO_2): R_f = 0.1 (ethyl acetate: hexanes, 3:7); $[\alpha]^{25}_{D}$ = -9.23° (*c* = 0.81 in CH_3OH); ^{1}H NMR (300 MHz , $CDCl_3$): δ 7.37-7.08 (m, 5H), 3.87-3.58 (m, 2H), 2.95 (dd, *J* = 12.5, 5.8 Hz, 1H), 2.75 (dd, *J* = 12.5, 7.6 Hz, 1H), 1.95-1.82 (m, 1H), 1.81-1.67 (m, 1H), 1.55-1.33 (m, 1H), 1.03 (d, *J* = 7.0 Hz , 3H); MS

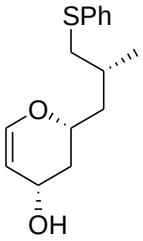
(ESI): 197 $[M+H]^+$ HRMS (ESI): *m/z* $[M+H]^+$ Calcd. for $C_{11}H_{17}SO$ 197.1232 , found 197.1230.



11

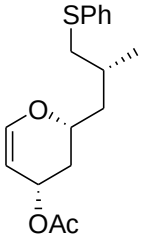
Compound (11): To a solution of the aldehyde **7** (3.9 g, 20 mmol, 1 eq) in *tert*-butyl methyl ether (40 mL)cooled at 0 °C, was added 4 Å molecular sieves (6.24 g, 0.3 g/mmol of **7**) and stirred for 30 min at 0 °C. The white slurry was cooled to -78 °C for 20 min. *(S,S)*-Cr-salen-BF_4^+ catalyst (520 mg, 0.8 mmol, 0.04 eq) was added to the reaction mixture and stirring continued for 5 min at -78 °C. The reaction mixture had become red-orange in colour and very difficult to stir. After rapid addition of the neat Danishefsky's diene **6** (5.2 g, 30 mmol, 1.5 eq), the reaction mixture was stirred for 2 h at -78 °C. The reaction mixture was warmed to -30 °C and stirred further for a period of 18 h. The reaction mixture was cooled to -78 °C and treated sequentially with CH_2Cl_2 (50 ml) and TFA (0.6 ml). The reaction mixture was warmed to room temperature and stirred for 1 h. The reaction mixture was filtered through silica and the pad was washed with EtOAc (100 mL x 5). The organic layers were washed sequentially with saturated aqueous $NaHCO_3$ and brine. The organic layer was separated, dried over anhydrous Na_2SO_4, filtered, and evaporated *in vacuo* to afford a red-colored oil. The crude product was purified by flash column chromatography using 20% EtOAc/hexane (v/v) to furnish **11** as a dark yellow colour oil (3.93 g, 15 mmol) in 75% yield. TLC (SiO_2): R_f = 0.4 [ethyl acetate: hexanes, 2:8 (two times elution)]; $[\alpha]^{25}_D$ = +89.2° (*c* = 2.75 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 (d, *J* = 6.8 Hz, 1H), 7.36-7.21 (m, 4H), 7.16 (t, *J* = 6.8 Hz, 1H), 5.38 (d, *J* = 6.8 Hz, 1H), 4.56 (ddt, *J* = 10.8, 9.8, 3.8 Hz, 1H), 2.90 (dd, *J* = 12.8, 6.8 Hz, 1H), 2.83 (dd, *J* = 12.8, 6.0 Hz, 1H), 2.50 (dd, *J* = 16.6, 12.8 Hz, 1H), 2.50 (dd, *J* = 16.6, 3.8 Hz, 1H), 2.20-1.93 (m, 1H), 2.19-1.94 (m, 2H), 1.40 (ddd, *J* = 12.8, 9.8, 3.8 Hz, 1H), 1.06 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.5, 163.1, 136.7,

129.2, 129.0, 126.0, 107.1, 76.7, 42.4, 41.5, 40.6, 29.2, 19.2; IR (neat) ν_{max}: 3449, 2924, 1675, 1593, 1274, 1035, 741 cm^{-1}; MS (ESI): 263 $[M+H]^+$, HRMS (ESI): *m/z* $[M+H]^+$ Calcd. for $C_{15}H_{19}O_2$ 263.1105, found 263.1095.



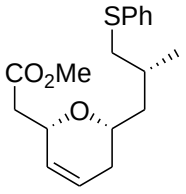
12

Compound (12): To a solution of the enone **11** (2.2 g, 8.4 mmol, 1 eq) in MeOH (42 mL) cooled at -10 ^oC, was added $CeCl_3.7H_2O$ (3.5 g, 9.24 mmol, 1.1 eq) followed by portionwise addition of sodium borohydride (352 mg, 9.24 mmol, 1.1 eq). After 5 min the reaction mixture was quenched by adding an aq. saturated ammonium chloride solution. The organic layer was separated and the aq. layer extracted with EtOAc (50 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and the solvent evaporated under reduced pressure to afford the crude product. Purification by flash column chromatography using 20% EtOAc/hexane (v/v) as the eluent afforded allylic alcohol **12** as a yellow colour oil (2.1 g, 8.1 mmol) in 96% yield. TLC (SiO_2): R_f = 0.2 (ethyl acetate: hexanes, 3:7); $[\alpha]^{25}_D$ = +13.3° (*c* = 1.9 in $CHCl_3$); ^1H NMR (300 MHz , $CDCl_3$): δ 7.32-7.19 (m, 4H), 7.16-7.07 (m, 1H), 6.28 (d, *J* = 6.8 Hz , 1H), 4.68 (dd, *J* = 6.8, 1.1 Hz, 1H), 4.36 (ddd, *J* = 8.5, 7.5, 1.1 Hz , 1H), 3.98 (tt, *J* = 10.2, 2.1 Hz, 1H), 2.91 (dd, *J* = 12.6, 6.0 Hz, 1H), 2.76 (dd, *J* = 12.6, 6.9 Hz, 1H), 2.12-1.98 (m, 2H), 1.95-1.86 (m, 1H), 1.68-1.49 (m, 2H), 1.31 (ddd, J = 12.8, 9.2, 3.4 Hz, 1H), 1.05 (d, *J* = 6.4 Hz , 3H); ^{13}C NMR (75 MHz , $CDCl_3$) : δ 145.0 , 137.3 , 129.2, 128.8, 125.8, 105.6, 72.6, 63.0, 41.8, 41.6, 39.0, 29.5, 19.4; IR (neat) ν_{max}: 3422, 2925, 1112, 1042, 968, 740, 692 cm^{-1}; MS (ESI): 265 $[M+H]^+$ HRMS (ESI): *m/z* $[M+H]^+$ Calcd. for $C_{15}H_{21}SO_2$ 265.1262 , found 265.1252.

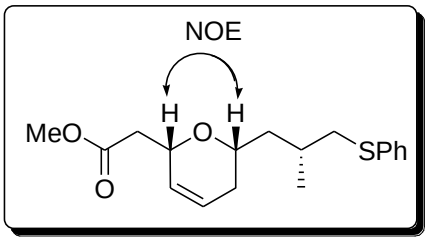


13

Compound (13): To a solution of the allylic alcohol **12** (1 g, 3.8 mmol, 1 eq) in anhydrous dichloromethane (19 mL) cooled at 0 ^{o}C was added anhydrous TEA (1.03 mL, 7.6 mmol, 2 eq) followed by DMAP (5 mol%). Acetic anhydride (0.54 mL, 5.7 mmol, 1.5 eq)was added dropwise and the reaction mixture was stirred at the same temperature for 5 min. The reaction mixture was diluted with dichloromethane (40 mL) and washed with water (2 x 10 mL), brine and dried over anhydrous Na_2SO_4 and filtered. Evaporation of the solvent under reduced pressure yielded the crude product which was purified by flash column chromatography on silica gel using 5% EtOAc/hexane (v/v) as the eluent afforded allylic acetate **13** as a yellow colour oil (1.1 g, 3.6 mmol) in 95% yield. TLC (SiO_2): R_f = 0.80 (ethyl acetate: hexane, 3:7); $[\alpha]^{25}_{D}$ = -4.7° (*c* = 0.35 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 7.9 Hz, 2H), 7.26 (t, *J* = 7.9 Hz, 2H), 7.15 (t, *J* = 7.9 Hz, 1H), 6.39 (d, *J* = 6.9 Hz, 1H), 5.35 (ddd, *J* = 11.9, 9.9, 7.9 Hz, 1H), 4.71 (d, *J* = 6.9 Hz, 1H), 4.08 (tt, *J* = 9.9, 2.9, Hz, 1H), 2.94 (dd, *J* = 12.9, 5.9 Hz, 1H), 2.81 (dd, *J* = 12.9 , 6.9 Hz, 1H) , 2.19 (ddd, *J* = 11.9, 9.9, 7.9 Hz, 1H), 2.12-1.95 (m , 4H), 1.35 (ddd, *J* = 13.8 , 11.9, 3.9 Hz, 1H), 1.32-1.18 (m , 1H), 1.1 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.8, 146.4, 137.0, 128.9, 128.7, 125.7, 100.8, 72.1, 65.5, 41.4, 40.9, 37.0, 29.3, 21.2, 19.0; IR (neat) ν_{max}: 2923, 1738, 1240, 1049, 960, 740, 692 cm^{-1}; MS (ESI): 307 $[M+H]^+$; HRMS (ESI): *m/z* $[M+H]^+$ Calcd. for $C_{17}H_{23}O_3S$ 307.1367, found 307.1362.

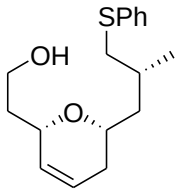


14



Compound (14): To a solution of diisopropyl amine (0.2 mL, 1.44 mmol, 3.6 eq) in anhydrous THF (1.4 mL) cooled at 0 ^{o}C, *n*-butyllithium (0.9 mL, 1.6 M in hexane, 3.5 eq) was added slowly by syringe. This mixture was stirred for 5 min at 0 ^{o}C and subsequently cooled to -78 ^{o}C. Allylic acetate **13** (122 mg, 0.4 mmol, 1 eq) dissolved in anhydrous THF (1 mL) was added via syringe over a two min time period under intensive stirring. After 20 min,

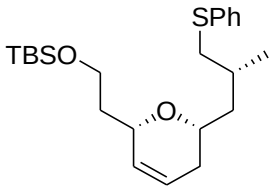
neat TMS-Cl (0.2 mL, 1.6 mmol, 4 eq) was added. The reaction mixture was stirred for an additional 5 min at -78 ^{o}C and subsequently allowed to warm to rt. After 16 h the reaction mixture was quenched with 2 N aqueous HCl (0.5 mL) and diluted with of cold pentane (100 mL). The layers were separated and the aq. layer extracted with dichloromethane (50 mL x 5). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to furnish the crude acid. The crude compound was dissolved in ether (5 mL) cooled to 0 ^{o}C and treated with ethereal CH_2N_2. Ether was removed under reduced pressure to provide a dark red oil. Purification of the crude ester via flash chromatography on silica gel using 15% EtOAc/hexane (v/v) as the eluent afforded unsaturated ester **14** as a colourless oil (114.82 mg, 0.36 mmol) in 90% yield. TLC (SiO_2): R_f = 0.60 (ethyl acetate: hexane, 3:7); $[\alpha]^{25}_{D}$ = -35° (*c* = 2.25 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (d, *J* = 7.9 Hz, 2H), 7.26 (t, *J* = 7.9 Hz, 2H), 7.15 (t, *J* = 7.9 Hz, 1H), 5.82 (ddt, *J* = 10.1, 4.5, 2.2 Hz, 1H), 5.63 (dd, *J* = 10.1, 1.1 Hz, 1H), 4.54-4.48 (br m, 1H), 3.67-3.61 (m , 4H), 3.05 (dd, *J* = 12.4, 5.6 Hz, 1H), 2.72 (dd, *J* = 12.4 , 7.9 Hz, 1H) , 2.53 (dd, *J* = 14.6, 7.9 Hz, 1H), 2.42 (dd, *J* = 14.6, 5.6 Hz, 1H), 2.05-1.95 (m, 2H), 1.91-1.86 (m, 1H), 1.75-1.69 (m, 1H), 1.38-1.23 (m, 1H), 1.04 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.2, 137.1, 129.1, 129.0, 128.8, 125.7, 124.0, 70.6, 65.9, 60.9, 42.0, 41.7, 36.9, 30.5, 29.2, 19.2; IR (neat) ν_{max}: 2959, 2934, 1745, 1588, 1446, 1053, 741, 695 cm^{-1}; MS (ESI): 321 $[M+H]^+$; HRMS (ESI): *m/z* $[M+H]^+$ Calcd. for $C_{18}H_{25}O_3S$ 321.1524, found 321.1517.



15

Compound (15): To a suspension of LAH (37.4 mg, 1 mmol, 1 eq) in anhydrous THF (5 mL) cooled at 0 ^{0}C was added a solution of unsaturated ester **14** (320 mg, 1 mmol, 1 eq) in anhydrous THF (1.5 mL) dropwise during 10 min, the reaction mixture was stirred for an additional 15 min at 0 ^{o}C and allowed to warm to rt. After 3 h the reaction mixture was diluted with ether (20 mL) and quenched with ice picces. The resulting reaction mixture was filterd through a Celite® pad. The filtrate was dried over anhydrous Na_2SO_4, filtered and

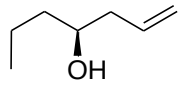
concentrated under reduced pressure to yield a colourless crude product. Purification of the crude residue via flash chromatography on silica gel using 30% EtOAc/hexane (v/v) as the eluent afforded alcohol **15** as a colourless oil (263 mg, 0.90 mmol) in 90% yield. TLC (SiO_2): R_f = 0.1 (ethyl acetate: hexane, 3:7); $[\alpha]^{25}_D$ = -24.2° (*c* = 1.55 in $CHCl_3$); ^{1}H NMR (500 MHz , $CDCl_3$): δ 7.30 (d, *J* = 6.7 Hz, 2H), 7.24 (t, *J* = 6.8 Hz, 2H), 7.12 (t, *J* = 6.8 Hz, 1H), 5.78 (ddt, *J* = 10.1, 4.5, 2.2 Hz, 1H), 5.61 (dd, *J* = 10.1, 2.2 Hz, 1H), 4.27 (ddd, *J* = 9.0, 4.5, 2.2 Hz, 1H), 3.86-3.78 (m , 1H), 3.68 (dt, *J* = 11.3, 6.8 Hz , 1H), 3.63 (dt, *J* = 11.3, 6.8 Hz, 1H) , 2.87 (dd, *J* = 12.4, 6.7 Hz , 1H), 2.81 (dd, *J* = 12.4, 6.8 Hz, 1H), 2.08 (ddd, *J* = 16.9, 4.5, 2.2 Hz, 1H), 2.00-1.94 (m, 1H), 1.92 (t, *J* = 5.5 Hz, 1H), 1.90-1.82 (m, 1H), 1.81-1.74 (m, 1H), 1.64-1.56 (m, 1H), 1.23-1.16 (m, 1H), 1.07 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.2, 129.2, 129.1, 128.9, 125.7, 124.0, 70.6, 65.9, 60.9, 41.8, 40.9, 35.9, 30.6, 29.3, 19.3; IR (neat) ν_{max}: 3422, 2923, 1476, 1436, 1063, 740 cm^{-1}; MS (ESI): 315 $[M+Na]^+$; HRMS (ESI): *m/z* $[M+Na]^+$ Calcd. for $C_{17}H_{24}O_2SNa$ 315.1394, found 315.1401.



4

TBS Ether (4): To a solution of alcohol **15** (292 mg, 1 mmol, 1 eq) in anhydrous CH_2Cl_2 (5 mL) cooled at 0 ^oC was added imidazole (204 mg, 3 mmol, 3 eq) followed by subsequently *t*-butyldimethylchlorosilane (227 mg, 1.5 mmol, 1.5 eq). The reaction mixture was stirred and gradually allowing it to warm to rt over a period of 1 h. The reaction mixture was quenched with a saturated ammnium chloride (5 mL). The layers were separated and the aq. layer extracted with dichloromethane (20 mL x 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to furnish the crude product. Purification of the crude residue via flash chromatography on silica gel using 5% EtOAc/hexane (v/v) as the eluent afforded silyl ether **4** as a colourless oil (386 mg, 0.95 mmol) in 95% yield. TLC (SiO_2): R_f = 0.6 (ethyl acetate: hexane, 1:9); $[\alpha]^{25}_D$ = -34.1° (*c* = 1.25 in $CHCl_3$); ^{1}H NMR (300 MHz , $CDCl_3$): δ 7.43-7.09 (m, 5H), 5.89-5.63 (m, 2H), 4.42-4.23 (m, 1H), 3.86-3.56 (m , 3H), 2.98 (dd, *J* = 12.8, 6.0 Hz, 1H), 2.79 (dd, *J* = 12.8, 6.8 Hz, 1H), 2.23-1.94 (m, 2H), 1.90-1.50 (m, 2H), 1.46-1.39 (m, 1H), 1.38-1.23 (m, 2H), 1.07 (d, *J* = 6.8 Hz, 3H), 0.91 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (75

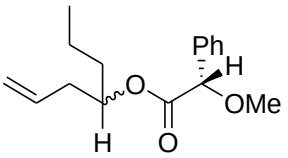
MHz, $CDCl_3$): δ 137.4, 129.9, 128.8, 128.7, 125.5, 123.8, 69.2, 65.0, 59.8, 42.0, 41.8, 36.8, 31.3, 29.3, 26.0, 19.0, 18.25, -3.7, -5.3; IR (neat) ν_{max}: 2954, 2929, 2857, 1466, 1253, 1094, 837, 776 cm^{-1}; MS (ESI): 429 $[M+Na]^+$; HRMS (ESI): *m/z* $[M+Na]^+$ Calcd. for $C_{23}H_{38}SiSO_2Na$ 429.2259, found 429.2265.



17

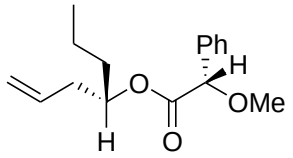
Compound (17): To a sealed tube charged with *n*-butanol (74 mg, 1 mmol, 1 eq), $[Ir(cod)Cl]_2$ (17 mg, 0.025mmol, 2.5 mol%), *(R)*-BINAP (31.1 mg, 0.05 mmol, 5 mol%), Cs_2CO_3 (65.0 mg, 0.2 mmol, 0.2 eq), *m*-nitrobenzoic acid (16.5 mg, 0.1 mmol, 0.1 eq) was added anhydrous THF (5.0 mL, 0.2 M) followed by allyl acetate (1.1 mL, 10 mmol, 10 eq). The reaction mixture was stirred at 110 ^oC for 24 h. The reaction mixture was allowed to cool to rt and filtered through a small pad of silica gel. The organic layer was evaporated under reduced to afford the crude product which was purified via column chromatography on silica gel using 10% EtOAc/hexane (v/v) as the eluent to afford homoallyl alcohol **17** as a pale yellow oil (96.9 mg, 0.85 mmol) in 85% yield. TLC (SiO_2): R_f = 0.6 (ethyl acetate:hexane, 2:8); $[\alpha]^{25}_D$ = +23° (*c* = 2.25 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 5.89-5.70 (m, 1H), 5.16-5.09 (m, 1H), 5.08-5.03 (m, 1H), 3.70-3.55 (m, 1H), 2.33-2.20 (m, 1H), 2.18-2.05 (m, 1H), 1.55-1.32 (m, 2H), 1.30-1.21 (m, 2H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.1, 118.3, 70.2, 39.3, 34.4, 19.1, 14.4; IR (neat) ν_{max}: 3427, 2961, 2933, 1711, 1461, 1189 cm^{-1}; MS (ESI): 137 $[M+Na]^+$; HRMS (ESI): *m/z* $[M+Na]^+$ Calcd. for $C_7H_{14}ONa$ 137.1855, found 137.1850.

HPLC: The enantiomeric excess of the alcohol **17** was determined by HPLC analysis of the 4-nitrobenzoate derivative (Chiralcel® OD-H column (4.6 mm x 250 mm), isocratic 1% *i*-PrOH in hexane, 0.5 mL/min, 254 nm), t_{major} = 8.3 min, t_{minor} = 10.1 min; *ee* = 97 %.



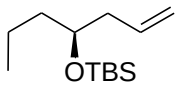
Mandelate ester of racemic alcohol: To a solution of the racemic alcohol **17** (30 mg, 0.26 mmol, 1 eq) in anhydrous CH_2Cl_2 (2.5 mL) (*S*)-O-methyl mandelic acid (43.2 mg, 0.26 mmol, 1 eq), DCC (64.4 mg, 0.31 mmol, 1.2 eq), and a few crystals of DMAP were added, and the mixture was stirred for 45 min. The solvent was removed under vacuum, and the

residue was purified by flash column chromatography on silicagel using pet ether as the eluent to afford a diastereomeric mixture of ester (58.4 mg, 0.21 mmol) 81% yield as a pale yellow colour oil. TLC (SiO_2): R_f = 0.5 (ethyl acetate:hexane, 0.5:9.5); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.18 (m, 10H), 5.68-5.51 (m, 1H), 5.44-5.29 (m, 1H), 4.98-4.93 (m, 1H), 4.92-4.81 (m , 1H), 4.76 (s, 2H), 4.75-4.73 (m, 2H), 4.61-4.58 (m, 2H), 3.33 (s, 6H), 2.60-2.55 (m, 2H), 2.25-1.96 (m, 2H), 2.13-1.95 (m, 2H), 1.50-1.32 (m , 3H), 1.28-1.11 (m , 3H), 1.02 (t, *J* = 7.3 Hz, 3H), 0.82 (t, *J* = 7.3 Hz, 3H**).** MS (ESI): 285 $[M+Na]^+$.



Mandelate ester of alcohol 17: The mandelate ester was prepared following the procedure detailed using (*S*)-O-methyl mandelic acid to afforded single diastereomer in 80% yield. TLC (SiO_2): R_f = 0.5 (ethyl acetate: hexanes, 0.5:9.5); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.18 (m, 5H), 5.44-5.29 (m, 1H), 4.92-4.81 (m, 1H), 4.76 (s, 1H), 4.75-4.73 (m, 1H), 4.61-4.58 (m, 1H), 3.33 (s, 3H), 2.30-2.19 (m, 1H), 2.18-2.07 (m , 2H), 2.06-1.89 (m, 1H), 1.50-1.32 (m, 2H), 0.82 (t, 3H, *J* = 7.3 Hz). MS (ESI): 285 $[M+Na]^+$; HRMS (ESI): *m/z* $[M+Na]^+$ Calcd. for $C_{16}H_{22}O_3Na$ 285.3441, found 285.3432.

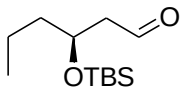
A comparison of the ^{1}H nmr of the diastereomeric mixture of ester with that of the ester prepared from alcohol **17** helped to unambiguously assign the configuration at the carbinol stereogenic centre is '*S*'.



18

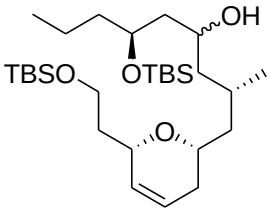
Compound (18): To a solution of homoallylic alcohol **17** (1.31 g, 11.5 mmol, 1 eq) in anhydrous CH_2Cl_2 (58 mL) cooled at 0 ^oC, was added imidazole (2.35 g, 34.5 mmol, 3 eq), followed by *t*-butyldimethylchlorosilane (2.61 g, 17.25 mmol, 1.5 eq). The reaction was stirred at rt for 1 h. The reaction mixture was quenched with a saturated ammnium chloride (5 mL). The layers were separated and the aq. layer extracted with dichloromethane (50 mL x 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to furnish the crude product. Purification of the crude residue via flash chromatography on silica gel using hexane as the eluent afforded

TBS-protected homoallyl alcohol **18** as a pale yellow colour oil (2.5 g, 10.94 mmol) in 95% yield. TLC (SiO_2): R_f = 0.70 (ethyl acetate:hexane, 0.5:9.5). $[\alpha]^{25}_D$ = +8° (*c* = 2.0 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.86-5.69 (m, 1H), 5.06-4.92 (m, 2H), 3.67 (tdd, *J* = 10.6, 5.3, 1.5 Hz, 1H), 2.25-2.12 (m, 2H), 1.47-1.21 (m, 4H), 1.00-0.79 (m, 12H), 0.04 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.4, 116.6, 71.9, 42.1, 39.2, 26.0, 25.8, 18.7, 14.4, -4.3, -4.4; IR (Neat) ν_{max}: 2923, 1640, 1640, 1466, 1254, 1044, 835, 774 cm^{-1}; MS (ESI): 251 $[M+Na]^+$; HRMS (ESI): *m/z* $[M+Na]^+$ Calcd. for $C_{13}H_{28}OSiNa$ 251.4463, found 251.4443.



5

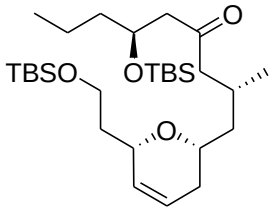
Compound (5): A mixture of oxygen and ozone were bubbled through a solution of the silyl ether **18** (228.5 mg, 1 mmol, 1 eq) in anhydrous CH_2Cl_2 (5 mL) cooled at -78 °C for 20 min or until the blue colour was persisted. Dimethyl sulfide (310 mg, 5 mmol, 5 eq) was dropwise during 10 min and the reaction mixture stirred allowing it to attain rt gradually over a period of 16 h. The solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel using hexane afforded aldehyde **5**[2] as a pale yellow colour oil (200 mg, 0.87 mmol) in 87% yield. TLC (SiO_2): R_f = 0.5 (ethyl acetate: hexane, 0.5:9.5); $[\alpha]^{25}_D$ = +1.6° (*c* = 1.3 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.81 (t, *J* = 3.0 Hz, 1H), 4.18 (ddd, *J* = 11.0, 6.0, 5.0 Hz, 1H), 2.54-2.42 (m, 2H), 1.58-1.43 (m, 2H), 1.40-1.30 (m, 2H), 0.94 (t, *J* = 7.0 Hz, 3H), 0.87 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.5, 68.3, 50.0, 40.5, 25.8, 18.1, 18.0, 14.1, -4.6, -4.7; MS (ESI): 253 $[M+Na]^+$; HRMS (ESI): *m/z* $[M+Na]^+$ Calcd. for $C_{12}H_{26}O_2SiNa$ 253.1702, found 253.1720.



19

Compound (19): To a stirred solution of sulphide **4** (812 mg, 2 mmol, 1 eq) in anhydrous THF (10 mL), cooled at -78 °C, was added a freshly prepared solution of LiDBB (~4.4 mL, 1M in THF) dropwise until dark blue colour persisted. This solution was stirred for another 10 min at -78 °C and followed by addition of aldehyde **5** (506 mg, 2.2 mmol, 1.1 eq) in anhydrous THF (1 mL), cooled at -78 °C resulting in a dark yellow solution. The reaction

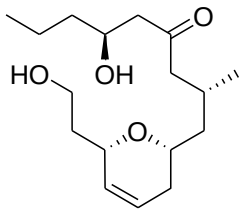
mixture was stirred for another 30 min at -78 °C, and subsequently quenched with aq saturated NH_4Cl solution (10 mL). The layers were separated. After the ensuing extraction of the aqueous layer with EtOAc (20 mL x 3), the organic layers were combined, washed with water, brine, dried over Na_2SO_4, filtered and concentrated under vacuum. Purification of the crude residue via flash chromatography on silica gel using 7% EtOAc/hexane (v/v) as the eluent afforded a equimolar mixture of epimeric alcohols **19** as a yellow colour oil (633.6 mg, 1.2 mmol) in 60% yield. TLC (SiO_2): R_f = 0.5 (ethyl acetate:hexane, 1.5:8.5); $[\alpha]^{25}_D$ = +12° (*c* = 1.20 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.76 (ddt, *J* = 9.6, 5.6, 2.0 Hz, 2H), 5.66 (dd, *J* = 9.6, 2.0 Hz, 2H), 4.32-4.21 (m, 2H), 3.81-3.54 (m, 10H), 2.45-2.22 (m, 2H), 2.11 (t, *J* = 5.5 Hz, 4H), 2.29-2.10 (m, 2H), 1.96-1.85 (m, 4H), 1.82-1.70 (m, 2H), 1.68-1.51 (m, 4H), 1.43-1.18 (m, 14H), 0.99 (d, *J* = 6.6 Hz, 6H), 0.94-0.86 (m, 42H), 0.06 (s, 12H), 0.03 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 129.98, 123.9, 123.5, 71.5, 71.3, 69.3, 69.1, 68.4, 68.2, 65.1, 65.0, 59.1, 59.0, 42.9, 42.8, 40.8, 40.7, 39.1, 39.2, 36.9, 36.7, 32.5, 30.8, 30.7, 29.9, 29.7, 25.0, 24.9, 20.2, 20.0, 18.5, 18.3, 14.3, 14.2, -4.3, -4.5, -5.3; IR (neat) ν_{max}: 3454, 2931, 1463, 1253, 1145, 1089, 836, 775 cm^{-1}; MS (ESI): 551 $[M+Na]^+$; HRMS (ESI): *m/z* $[M+Na]^+$ Calcd. for $C_{29}H_{60}O_4Si_2Na$ 551.3553, found 551.3564. Note: The proton count has been doubled since an equimolar epimeric mixture, differing at the C-11 carbinol bearing stereogenic center, was obtained.



20

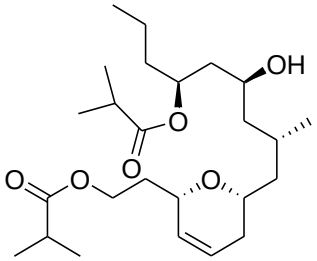
Compound (20): To a solution of 2-iodoxy benzoic acid (569.2 mg, 2.04 mmol, 1.2 eq) in DMSO (2 mL) was added a solution of the mixture of epimeric alcohols **19** (898 mg, 1.7 mmol, 1 eq) in CH_2Cl_2 (10 mL) at rt and the mixture was stirred for 2 h. The precipitated solid filtered, and the filtrte was diluted with ether, washed with water, brine solution, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude residue via flash chromatography on silica gel using 5% EtOAc/hexane (v/v) as the eluent afforded ketone **20** as a yellow colour oil (762.1 mg, 1.45 mmol) in 85% yield. TLC (SiO_2): R_f = 0.6 (ethyl acetate:hexane, 1.5:8.5); $[\alpha]^{25}_D$ = +45° (*c* = 1.28 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.76 (ddt, *J* = 9.8, 5.5, 2.6 Hz, 1H), 5.66 (dd, *J* = 9.8, 2.6 Hz, 1H), 4.30 (dt, *J* = 5.5, 2.6 Hz, 1H), 4.15 (dddd, *J*= 11.9, 11.1, 6.0, 5.5 Hz, 1H), 3.81-3.53 (m, 3H), 2.54

(dd, *J* = 15.7, 6.8 Hz, 1H), 2.46-2.33 (m, 2H), 2.30-2.21 (m, 1H), 2.20-2.14 (m, 1H), 1.95-1.87 (m, 2H), 1.85-1.71 (m, 1H), 1.70-1.59 (m, 1H), 1.53 (ddd, *J* = 13.8, 9.8, 4.1 Hz, 1H), 1.45-1.35 (m, 2H), 1.34-1.28 (m, 1H), 1.27-1.23 (m, 2H), 1.00-0.90 (m, 15H), 0.86 (s, 9H), 0.05 (s, 9H), 0.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.1, 130.3, 123.9, 69.1, 68.6, 65.0, 59.8, 52.6, 50.4, 42.85, 40.1, 36.5, 31.5, 29.8, 26.1, 25.6, 19.8, 18.5, 14.4, -4.4, -5.1; IR (neat) ν_{max}: 2931, 2859, 1719, 1463, 1314, 1253, 1145, 1089, 836, 775 cm^{-1}; MS (ESI): 549 $[M+Na]^+$; HRMS (ESI): *m/z* $[M+Na]^+$ Calcd. for $C_{29}H_{58}O_4Si_2Na$ 549.3771, found 549.3780.



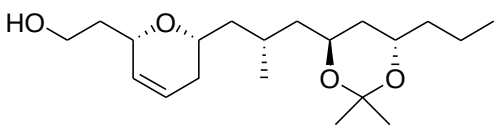
21

Compound (21): To a solution of ketone **20** (1.05 g, 2 mmol, 1 eq) in anhydrous THF (10 mL) cooled at 0 ºC was added a premixed solution of TBAF (5 mL, 5 mmol, 2.5 eq) and AcOH (0.35 mL, 5 mmol, 2.5 eq), drop wise over 5 min. The resulting solution was allowed to stir at room temperature for 6 h. The reaction was then diluted with ethyl acetate (100 mL) and the combined organic layers were washed with water (25 mL x 2) and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo to furnish the crude product. Purification of the crude product by flash column chromatography on silica gel using 30% EtOAc/hexane (v/v) as the eluent afforded diol **21** as a yellow colour oil (566.2 mg, 1.9 mmol) in 95% yield. TLC (SiO_2): R_f = 0.1 (ethyl acetate:hexane, 3:7); $[\alpha]^{25}_D$ = +37° (*c* = 1.26 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.76 (ddt, *J* = 9.8, 5.5, 2.6 Hz, 1H), 5.62 (dd, *J* = 9.8, 2.6 Hz, 1H), 4.36 (dt, *J* = 9.2, 2.6 Hz, 1H), 4.04 (dddd, *J* = 12.1, 11.3, 8.3, 4.5 Hz, 1H), 3.81-3.68 (m, 3H), 2.49 (d, *J* = 7.5 Hz, 2H), 2.36 (dd, *J* = 15.0, 4.5 Hz, 1H), 2.33-2.13 (m, 2H), 2.03 (dd, *J* = 15.7, 8.3 Hz, 1H), 1.93-1.74 (m, 2H), 1.70-1.56 (m, 2H), 1.53-1.50 (m, 2H), 1.39-1.25 (m, 4H), 1.15 (ddd, *J* = 13.6, 8.3, 3.0 Hz, 1H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.95 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.1, 130.3, 123.9, 69.1, 68.6, 65.0, 59.8, 52.6, 50.4, 42.9, 40.1, 36.5, 31.5, 29.8, 19.8, 18.5, 14.4; IR (neat) ν_{max}: 3439, 2924, 1701, 1633, 1374, 1063, 767 cm^{-1}; MS (ESI): 321 $[M+Na]^+$; HRMS (ESI): *m/z* $[M+Na]^+$ Calcd. for $C_{17}H_{30}O_4Na$ 321.2041, found 321.2053.



22

Compound (22): To a solution of ketone **21** (65.6 mg, 0.22 mmol, 1 eq), and isobutyraldehyde (80 µL, 0.87 mmol, 4 eq) anhydrous PhMe[3] (1.1 m L) cooled at –78 °C, under nitrogen atmosphere neat Zr(O*t*-Bu)$_4$ (43 µL, 0.11 mmol, 0.5 eq) was added dropwise, and the resulting mixture was stirred at –55 °C for 6 h. Aqueous saturated $NaHCO_3$ (1 mL) and water (1 mL) were introduced into the reaction flask at –55 °C, the cooling bath was removed and the reaction mixture was allowed to warm to room temperature. The layers were separated and the aqueous phase was extracted with Et_2O (10 mL x 3). The combined organic layers were washed with brine (10 mL x 1), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude product by flash column chromatography on silica gel using 5% EtOAc/hexane (v/v) as the eluent furnished hydroxy ester **22** as yellow colour oil (82.44 mg, 0.187 mmol) in 85% yield. TLC (SiO_2): R_f = 0.75 (ethyl acetate:hexane, 3:7); $[\alpha]^{25}_D$ = +17° (*c* = 0.48 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.81 (ddt, *J* = 9.8, 5.5, 2.0 Hz, 1H), 5.66 (dd, *J* = 9.8, 2.0 Hz, 1H), 5.17-4.98 (m, 1H), 4.36-4.10 (m, 3H), 3.78-3.62 (m, 1H), 3.59-3.45 (m, 1H), 2.71-2.41 (m, 2H), 2.32 (dd, *J* = 14.3, 6.8 Hz, 1H), 2.11-1.74 (m, 4H), 1.73-1.45 (m, 5H), 1.28-1.13 (m, 8H), 1.05-0.83 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 175.0, 175.3, 129.2, 124.3, 76.5, 75.3, 72.6, 70.5, 69.7, 43.1, 41.2, 40.7, 39.4, 37.2, 33.0, 31.2, 29.6, 29.1, 26.4, 26.3, 20.6, 18.1, 14.3; IR (neat) ν_{max}: 3437, 2965, 2931, 2877, 1713, 1469, 1387, 1106, 1025, 996 cm^{-1}; MS (ESI): 463 $[M+Na]^+$; HRMS (ESI): *m/z* $[M+Na]^+$ Calcd. for $C_{25}H_{44}O_6Na$ 463.3035, found 463.3014.

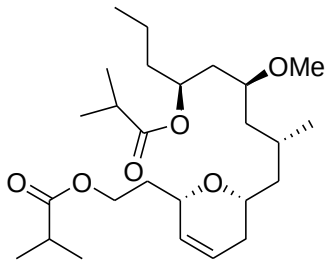


Acetonide of 22

Acetonide of 22: To a suspension of K_2CO_3 (167 mg, 1.2 mmol, 4 eq) in MeOH (2 mL) cooled at 0 ^{o}C, maintained under N_2 atmosphere was added the solution of compound **22** (132

mg, 0.3 mmol, 1 eq) in MeOH (0.2 mL) dropwise. The reaction mixture was stirred at room temperature for 30 min, during which time a large amount of white turbid precipitate had formed. The reaction mixture was diluted with EtOAc (50 ml), and quenched with ice pieces, washed with H_2O, brine and dried over anhydrous Na_2SO_4, filtered. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel using 30% EtOAc/hexane (v/v) as the eluent to afford triol as a colourless oil. Without further characterisation the triol taken ahead to the next step.

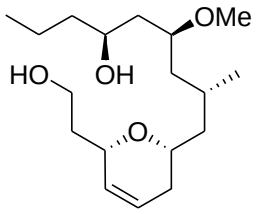
To a solution of the triol (75 mg, 0.25 mmol, 1 eq) in anhydrous CH_2Cl_2 (1.3 mL) cooled at 0 ^oC, maintain under N_2 atmosphere was added neat 2,2-dimethoxypropane (2,2-DMP) (46 µL, 0.375 mmol, 1.5 eq) and consequently catalytic amounts of camphorsulphonic acid (3 mg, 0.0125 mmol, 5 mol%). The reaction mixture was stirred at room temperature for 2 h. The reaction mixture was diluted with CH_2Cl_2 (50 ml), washed with H_2O, brine and dried over anhydrous Na_2SO_4 and filtered. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel using 12% EtOAc/hexane (v/v) as the eluent furnished title compound **acetonide of 22** as colourless oil (76.5 mg, 0.22 mmol) in 88% yield. TLC (SiO_2): R_f = 0.5 (ethyl acetate:hexane, 3:7); $[\alpha]^{25}_D$ = +32° (*c* = 1.3 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.77 (ddt, *J* = 9.6, 5.6, 2.0 Hz, 1H), 5.62 (dd, *J* = 9.6, 2.0 Hz, 1H), 4.35 (dt, *J* = 9.2, 5.6 Hz, 1H), 4.10-3.95 (m, 1H), 3.81-3.55 (m, 4H), 2.55-2.32 (m, 2H), 2.30-2.15 (m, 1H), 2.20-1.95 (m, 1H), 1.96-1.75 (m, 2H), 1.69-1.55 (m, 2H), 1.54-1.21 (m, 8H), 1.15 (ddd, *J* = 12.8, 11.2, 1.6 Hz, 1H), 0.99-0.85 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 130.3, 123.9, 101.6, 73.1, 69.1, 68.6, 65.0, 59.8, 43.4, 42.8, 41.8, 40.1, 31.5, 29.8, 26.2, 24.7, 24.6, 19.8, 18.46, 14.4; IR (neat) ν_{max}: 3449, 2924, 2854, 1460, 1373, 1259, 1086, 1022, 800 cm^{-1}; MS (ESI): 363 $[M+Na]^+$; HRMS (ESI): *m/z* $[M+Na]^+$ Calcd. for $C_{20}H_{36}O_4Na$ 363.2614, found 363.2625.



23

Compound (23): To a suspension of NaH (20 mg, 60% in Nujol, 0.5 mmol, 1.1 eq) suspension in anhydrous THF (2.3 mL) cooled at 0 ^oC maintained under N_2 atmosphere was

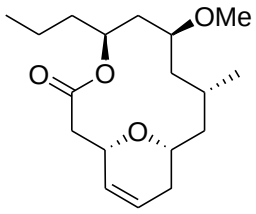
added a solution of the compound **22** (200 mg, 0.45 mmol, 1 eq) in THF (0.5 mL) dropwise. The reaction mixture was stirred at room temperature for 45 min, during which time a large amount of opaque white had formed. Distilled MeI (129 mg, 0.91 mmol, 2 eq) was added dropwise at 0 ^{o}C and the stirring continued for an additional 45 min. The reaction mixture was diluted with EtOAc (100 ml), quenched with ice pieces, washed with H_2O, brine and dried with Na_2SO_4, filtered. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel using 5% EtOAc/hexane (v/v) as the eluent to afford title compound **23** as a colourless oil (181.6 mg, 0.40 mmol) in 88% yield. TLC (SiO_2): R_f = 0.55 (ethyl acetate: hexane, 2:8); $[\alpha]^{25}_{D}$ = +12° (*c* = 0.37 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.81 (ddt, *J* = 9.8, 5.5, 2.0 Hz, 1H), 5.66 (dd, *J* = 9.8, 2.0 Hz, 1H), 5.17-4.98 (m, 1H), 4.36-4.10 (m, 3H), 3.78-3.62 (m, 1H), 3.59-3.45 (m, 1H), 3.19 (s, 3H), 2.71-2.41 (m, 2H), 2.32 (dd, *J* = 14.3, 6.8 Hz, 1H), 2.11-1.74 (m, 4H), 1.73-1.45 (m, 5H), 1.35-1.00 (m, 8H), 1.05-0.83 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.4, 174.3, 128.8, 123.9, 76.2, 75.0, 72.2, 70.4, 69.0, 56.1, 43.0, 42.3, 41.1, 39.1, 36.2, 32.5, 30.2, 29.2, 28.9, 25.9, 25.8, 18.3, 18.1, 13.9; IR (Neat) ν_{max}: 2924, 2859, 2848, 1728, 1725, 1461, 1375, 1259, 1157, 1109, 767 cm^{-1}; MS (ESI): 477 $[M+Na]^+$; HRMS (ESI): *m/z* $[M+Na]^+$ Calcd. for $C_{26}H_{46}O_6Na$ 477.3192, found 477.3183.



24

Compound (24): To a suspension of K_2CO_3 (227.3 mg, 1.64 mmol, 4 eq) in MeOH (2 mL) cooled at 0 ^{o}C, maintained under N_2 atmosphere was added the solution of compound **23** (188 mg, 0.41 mmol, 1 eq) in MeOH (0.2 mL) dropwise. The reaction mixture was stirred at room temperature for 30 min, during which time a large amount of white turbid precipitate had formed. The reaction mixture was diluted with EtOAc (50 ml), and quenched with ice pieces, washed with H_2O, brine and dried over anhydrous Na_2SO_4, filtered. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel using 20% EtOAc/hexane (v/v) as the eluent to afford title compound **24** as a colourless oil (116.4 mg, 0.37 mmol) in 90% yield. TLC (SiO_2): R_f = 0.35 (ethyl acetate:hexane, 3:7); $[\alpha]^{25}_{D}$ = +22° (*c* = 1.45 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.77 (ddt, *J* = 9.6, 5.6, 2.0 Hz, 1H),

5.62 (dd, *J* = 9.6, 2.0 Hz, 1H), 4.35 (dt, *J* = 9.2, 5.6 Hz, 1H), 4.10-3.95 (m, 1H), 3.81-3.55 (m, 4H), 3.28 (s, 3H), 2.55-2.32 (m, 2H), 2.30-2.15 (m, 1H), 2.12-1.85 (m, 1H), 1.96-1.75 (m, 3H), 1.69-1.55 (m, 3H), 1.54-1.21 (m, 5H), 1.15 (ddd, *J* = 12.8, 11.2, 1.6 Hz, 1H), 0.99-0.85 (m, 7H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 130.6, 124.4, 73.6, 69.2, 68.2, 65.5, 59.8, 56.7, 43.6, 42.6, 41.8, 40.0, 36.8, 31.3, 29.3, 20.2, 18.3, 14.0; IR (neat) ν_{max}: 3449, 2924, 2856, 1460, 1374, 1253, 1157, 1090, 765 cm^{-1}; MS (ESI): 337 $[M+Na]^+$; HRMS (ESI): *m/z* $[M+Na]^+$ Calcd. for $C_{18}H_{34}O_4Na$ 337.2340, found 337.2330.



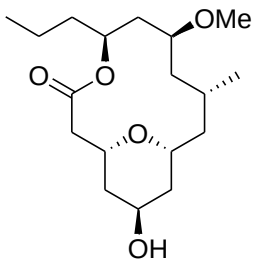
26

Compound (26): To a solution of well stirred diol **24** (157 mg, 0.5 mmol, 1 eq) in anhydrous CH_2Cl_2 (2.5 mL) was consequently added $PhI(OAc)_2$ (177.10 mg, 0.55 mmol, 1.1 eq) and TEMPO (15.62 mg, 0.1 mmol, 0.2 eq) under nitrogen atmosphere. The reaction mixture was stirred for 2 h. The solvent was evaporated under reduced pressure to afford the crude product which was passed through a short pad silica gel, the solvent was removed under reduced pressure to afford aldehyde **25** as light yellow colour oil (143.5 mg, 0.46 mmol) in 92% crude yield. Without further characterisation of the aldehyde **25** taken ahead to the next step.

To a solution of aldehyde **25** (140.4 mg, 0.45 mmol, 1 eq) in *t*-butyl alcohol (1.25 mL) and H_2O (0.1 mL) cooled at 0 ^oC was added cyclohexene (92 µL, 0.9 mmol, 2 eq) in one portion. A freshly prepared solution of $NaClO_2$ (122.1 mg, 1.35 mmol, 3 eq) and NaH_2PO_4 (245.7 mg, 1.57 mmol, 3.5 eq) in *t*-butyl alcohol (1 mL) and H_2O (0.1 mL) were added dropwise. The reaction mixture was stirred at rt for 3 h. The reaction mixture was quenched by the addition of an aq. saturated solution of NH_4Cl (15 mL).The layers were separated and the aq. layer was extracted with EtOAc (10 mL x 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (30 mL) basified with aqueous saturated $NaHCO_3$ solution at P^H = 9. The layers were separated and aqueous layer was adjusted to P^H = 3-4 using aqueous 1N HCl. The acid was extracted with CH_2Cl_2 (15 mL x 4), washed with brine and dried with anhydrous Na_2SO_4, filtered. The

solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel using 20% EtOAc/hexane (v/v) as the eluent to afford compound **3** as colourless viscous oil (125.6 mg, 0.38 mmol) in 85% yield. TLC (SiO_2): R_f = 0.15 (ethyl acetate: hexane, 3:7); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.78 (ddt, *J* = 9.6, 5.5, 2.0 Hz, 1H), 5.70-5.62 (m, 1H), 4.32-4.23 (m, 1H), 4.03 (tt, *J* = 10.3, 3.2 Hz, 1H), 3.81-3.60 (m, 2H), 3.29 (s, 3H), 2.51 (dd, *J* = 14.3, 4.1, Hz, 1H), 2.32-2.12 (m, 2H), 1.98-1.86 (m, 2H), 1.85-1.70 (m, 1H), 1.69-1.60 (m, 1H), 1.58-1.47 (m, 1H), 1.45-1.15 (m, 5H), 1.01-0.85 (m, 8H). The *seco* acid **3** was taken ahead to next step Yamaguchi macrolactonisation.

To a stirred solution of acid **3** (63 mg, 0.19 mmol, 1 eq) in THF (2 mL) at 0^{o}C under nitrogen atmosphere was added Hunig's base (0.24 mL, 1.2 mmol, 6 eq) followed by 2,4,6-trichlorobenzoyl chloride (0.16 mL,1 mmol, 5 eq). The reaction mixture was stirred at rt for 2 h, after which time toluene was added (5 mL). This solution was added over 24 h by syringe pump to a refluxing solution of DMAP (600 mg, 4.88 mmol, 25 eq) in toluene (152 mL). Stirring was continued for an additional 10 h. The mixture was then allowed to cool to ambient temperature and concentrated in vacuo. The residue was purified by flash chromatography on silica gel using 10% EtOAc/hexane (v/v) as the eluent to afford the compound **26**[4] as a colourless oil (33.34 mg, 0.11 mmol) in 56% yield. TLC (SiO_2): R_f = 0.4 (ethyl acetate: hexane, 2:8); $[\alpha]^{25}_D$ = -50.0° (*c* = 1.0 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.79 (ddt, *J* = 9.6, 5.6, 2.0 Hz, 1H), 5.56 (m, 1H**)**, 5.31 (dt, *J* = 9.2, 4.4 Hz, 1H), 4.08-4.41 (m, 1H), 3.56 (dt, *J* = 11.2, 2.0 Hz, 1H), 3.35 (dt, *J* = 10.4, 3.2 Hz, 1H), 3.30 (s, 3H), 2.64 (dd, *J* = 14.4, 4.0 Hz, 1H), 2.33 (dd, *J* = 14.4, 12.0 Hz, 1H), 1.98-1.80 (m, 2H), 1.75 (dd, *J* = 14.4, 10.8 Hz, 1H), 1.64-1.30 (m , 9H), 1.06 (ddd, *J* = 12.8, 11.2, 1.6 Hz, 1H), 0.97 (d, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, CDCl3): δ 170.9, 128.4, 125.9, 76.1, 75.5, 72.2, 71.9, 56.4, 43.8, 42.6, 41.8, 41.2, 37.1, 31.5, 30.4, 25.3, 18.9, 14.0; IR (neat) ν_{max}: 3031, 2956, 2921, 2870, 2845, 1731, 1599, 1462, 1369, 1273, 1186, 1092 cm^{-1}; MS (ESI): 311 $[M+H]^+$; HRMS (ESI): *m/z* $[M+H]^+$ Calcd. for $C_{18}H_{31}O_4$ 311.2144, found 311.2154.



2

Compound (2): To a solution of macrolactone **26** (40 mg, 0.13 mmol, 1 eq) in a mixture of anhydrous THF (1 mL) and water (0.8 mL) was added with mercuric trifluoroacetate (274.8 mg, 0.64 mmol, 5 eq). The mixture was stirred for 24 h at ambient teperature before NaOH solution (3 N, 0.8 mL) and sodium borohydride (12 mg in 0.11 mL, 3 N NaOH solution) were added. The mixture was stirred for 10 min and diluted with EtOAc (10 ml), quenched with ice pieces, washed with H_2O, brine and dried with Na_2SO_4, filtered. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel using 25% EtOAc/hexane (v/v) as the eluent to afford title compound **2**[3] as colourless clear oil (25.39 mg, 0.08 mmol) in 60% yield. TLC (SiO_2): R_f = 0.3 (ethyl acetate:hexane, 3:7); $[\alpha]^{25}_D$ = +28.0° (*c* = 1.10 in $CHCl_3$)[Lit. $[\alpha]^{20}_D$ = +30.0° (*c* = 1.13 in $CHCl_3$)]; IR (neat) ν_{max}: 3436, 2917, 1732, 1462, 1385, 1277, 1080, 986 cm^{-1}; MS (ESI): 329 $[M+H]^+$; HRMS (ESI): *m/z* $[M+H]^+$ Calcd. For $C_{18}H_{33}O_5$ 329.2328, found 329.2325.

Comparison with the literature data reported for macrolactone **2** (i) Youngsaye, W.; Lowe, J. T.; Pohlki, F.; Ralifo, P.; Panek, J. S. *Angew. Chem., Int. Ed*. **2007**, 46, 9211. (ii) Kartika, R.; Gruffi, T. R.; Taylor, R. E. *Org. Lett.* **2008**, 10, 5047.

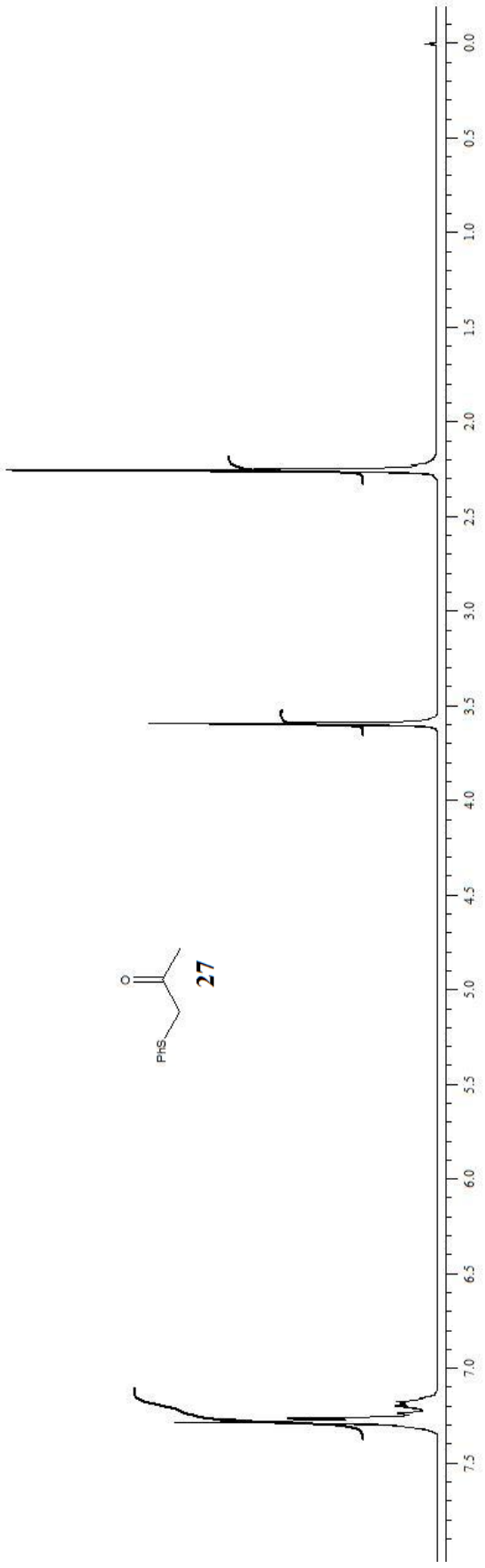
Observed data for compound **2**	Literature data for compound **2**
^{1}H NMR (500 MHz, $CDCl_3$): δ =	^{1}H NMR (600 MHz, $CDCl_3$): δ =
5.17 (tdd, *J* = 9.6, 4.8, 0.6 Hz, 1H)	5.17 (dddd, *J* = 9.6, 9.6, 4.8, 0.6 Hz, 1H)
4.22 (br, 1H)	4.22 (b, 1H)
4.17 (tdd, *J* = 11.4, 4.8, 2.4 Hz, 1H)	4.17 (dddd, *J* = 11.4, 11.4, 4.8, 2.4 Hz, 1H)
3.66 (ddd, *J* = 11.4, 9.0, 2.4 Hz, 1H)	3.66 (ddd, *J* = 11.4, 9.0, 2.4 Hz, 1H)
3.58 (dddd, *J* = 10.8, 9.6, 2.4, 1.2 Hz, 1H)	3.58 (dddd, *J* = 10.8, 9.6, 2.4, 1.2 Hz, 1H)
3.29 (s, 3H)	3.29 (s, 3H)
2.56 (dd, *J* = 14.4, 4.2 Hz, 1H)	2.56 (dd, *J* = 14.4, 4.2 Hz, 1H)
2.32 (dd, *J* =15.0, 11.4 Hz, 1H)	2.32 (dd, *J* = 15.0, 11.4 Hz, 1H)
1.86 (br, 1H)	1.86 (b, 1H)
1.83 (ddd, *J* = 15.0, 10.8, 1.8 Hz,1H)	1.83 (ddd, *J* = 15.0, 10.8, 1.8 Hz, 1H),
1.69 – 1.62 (m, 2H)	1.69 – 1.62 (m, 2H)
1.55 (ddd, *J* = 13.2, 11.4, 2.4 Hz, 1H)	1.55 (ddd, *J* = 13.2, 11.4, 2.4 Hz, 1H)
1.55 –1.44 (m, 5H)	1.55 – 1.44 (5H, m)
1.39 (ddd, *J* = 15.0, 9.0, 5.4 Hz, 1H)	1.39 (ddd, *J* = 15.0, 9.0, 5.4 Hz, 1H)
1.37 – 1.29 (m, 3H)	1.37 – 1.29 (m, 3H)
1.21 (dd, *J* = 15.6, 1.8 Hz, 1H)	1.21 (dd, *J* = 15.6, 1.8 Hz, 1H)
1.12 (ddd, *J* = 13.2, 10.8, 2.4 Hz, 1H)	1.12 (ddd, *J* = 13.2, 10.8, 2.4 Hz, 1H)
0.95 (d, *J* = 7.2 Hz, 3H)	0.95 (d, *J* = 7.2 Hz, 3H)
0.89 (t, *J* = 7.8 Hz, 3H)	0.89 (t, *J* = 7.8 Hz, 3H)

Observed data for compound **2**	Literature data for compound **2**
^{13}C NMR (75 MHz, $CDCl_3$): δ	^{13}C NMR (125 MHz, $CDCl_3$): δ
171.2	171.11
75.5	75.59
74.9	74.85
72.7	72.74
69.1	69.09
65.0	64.74
56.2	56.15
44.2	44.12
42.4	42.43
42.2	42.27
40.1	40.09
39.4	39.32
38.2	38.21
36.9	36.89
31.5	31.37
25.6	25.65
18.4	18.87
13.8	13.86

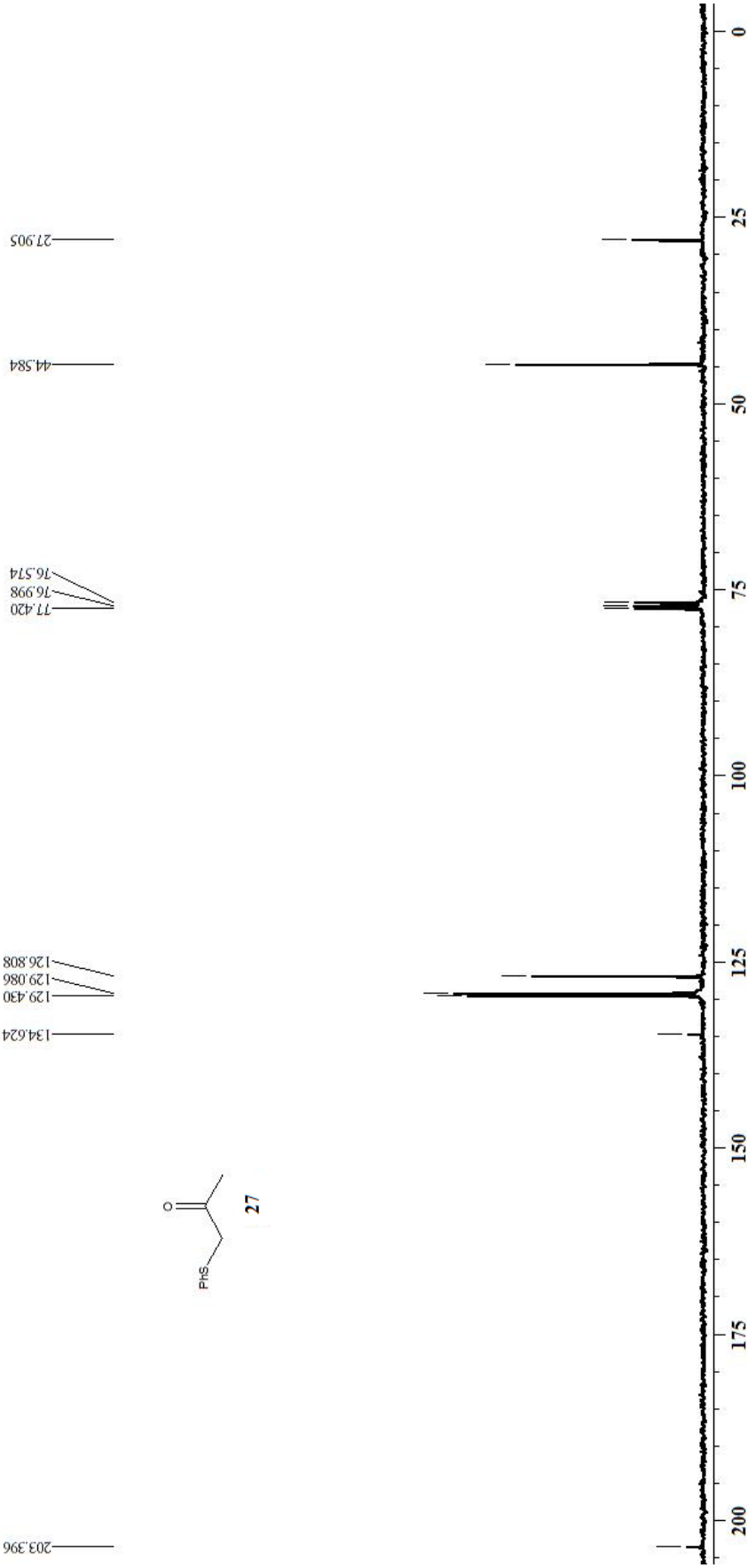
Reference:

1. Sato, T.; Hanayama, K.; Fujisawa, T. *Tetrahedron Letters*, **1988**, 29, 2197.
2. Deng, L. S.; Huang, X. P.; Zhao, G. *J. Org. Chem.*, 2006, 71, 4625.
3. Toluene used in this reaction was purified via distillation over Na/Ph_2CO under argon atmosphere.
4. (i)Youngsaye, W.; Lowe, J. T.; Pohlki, F.; Ralifo, P.; Panek, J. S. *Angew. Chem., Int. Ed*. **2007**, 46, 9211. (ii) Kartika, R.; Gruffi, T. R.; Taylor, R. E. *Org. Lett.* **2008**, 10, 5047.

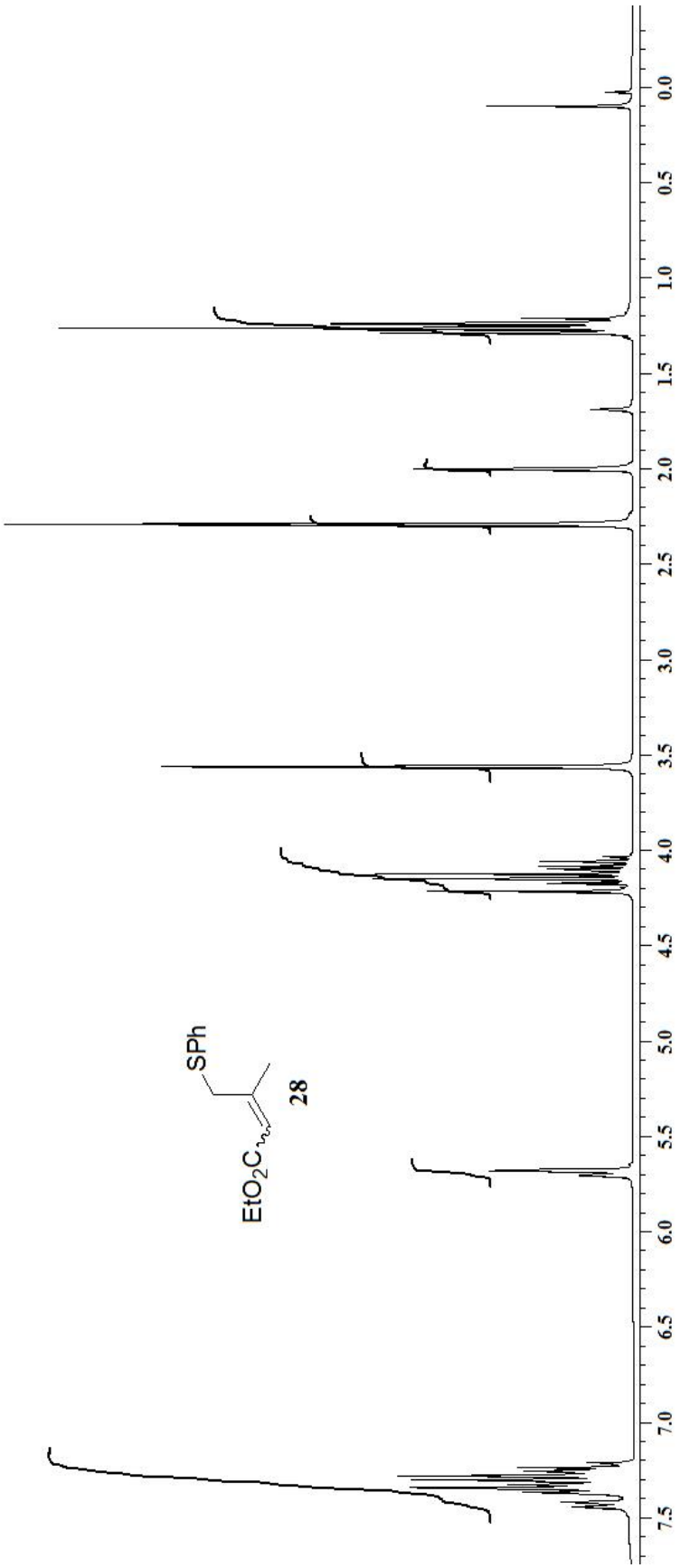
^{1}H NMR Spectrum of Compound 27



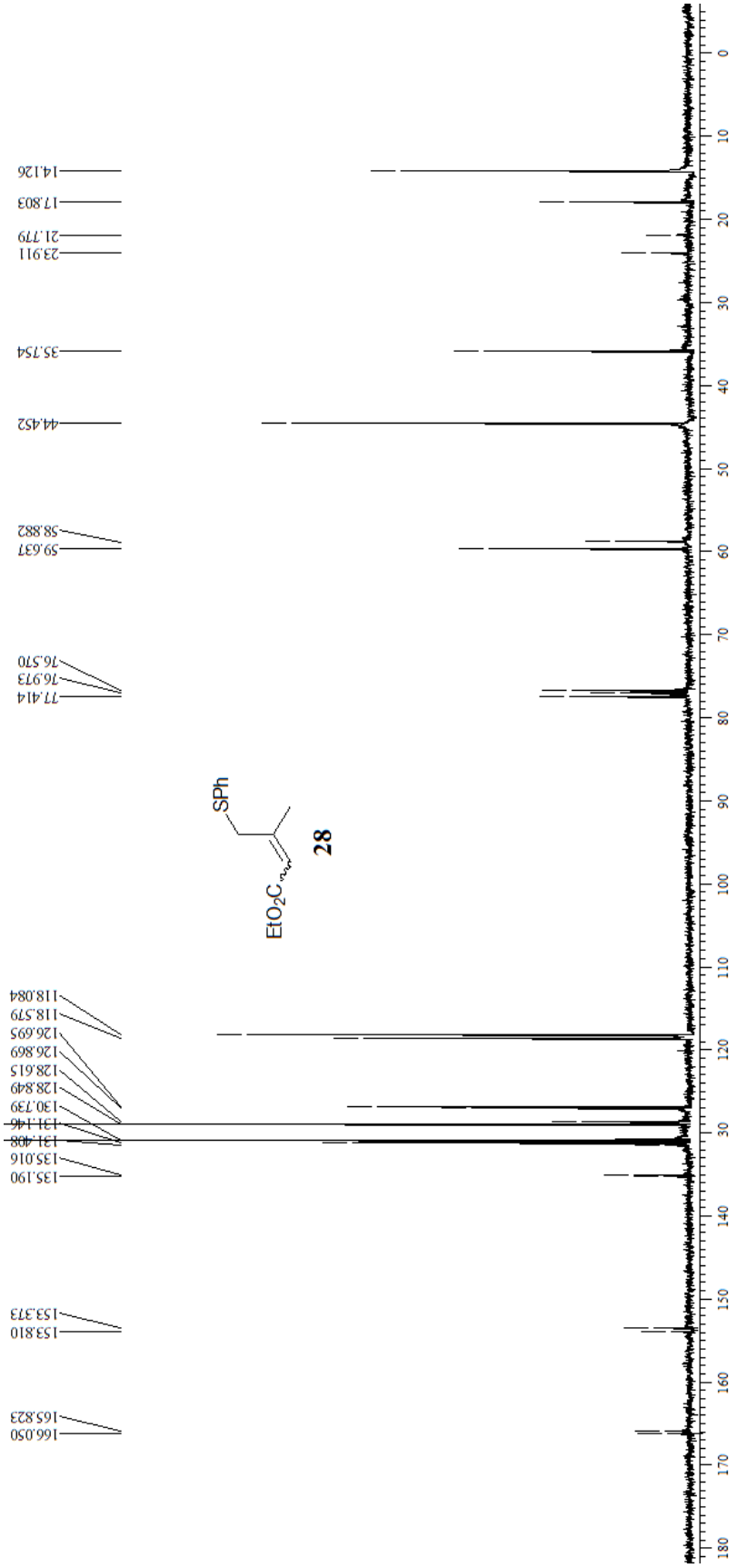
^{13}C NMR Spectrum of Compound 27



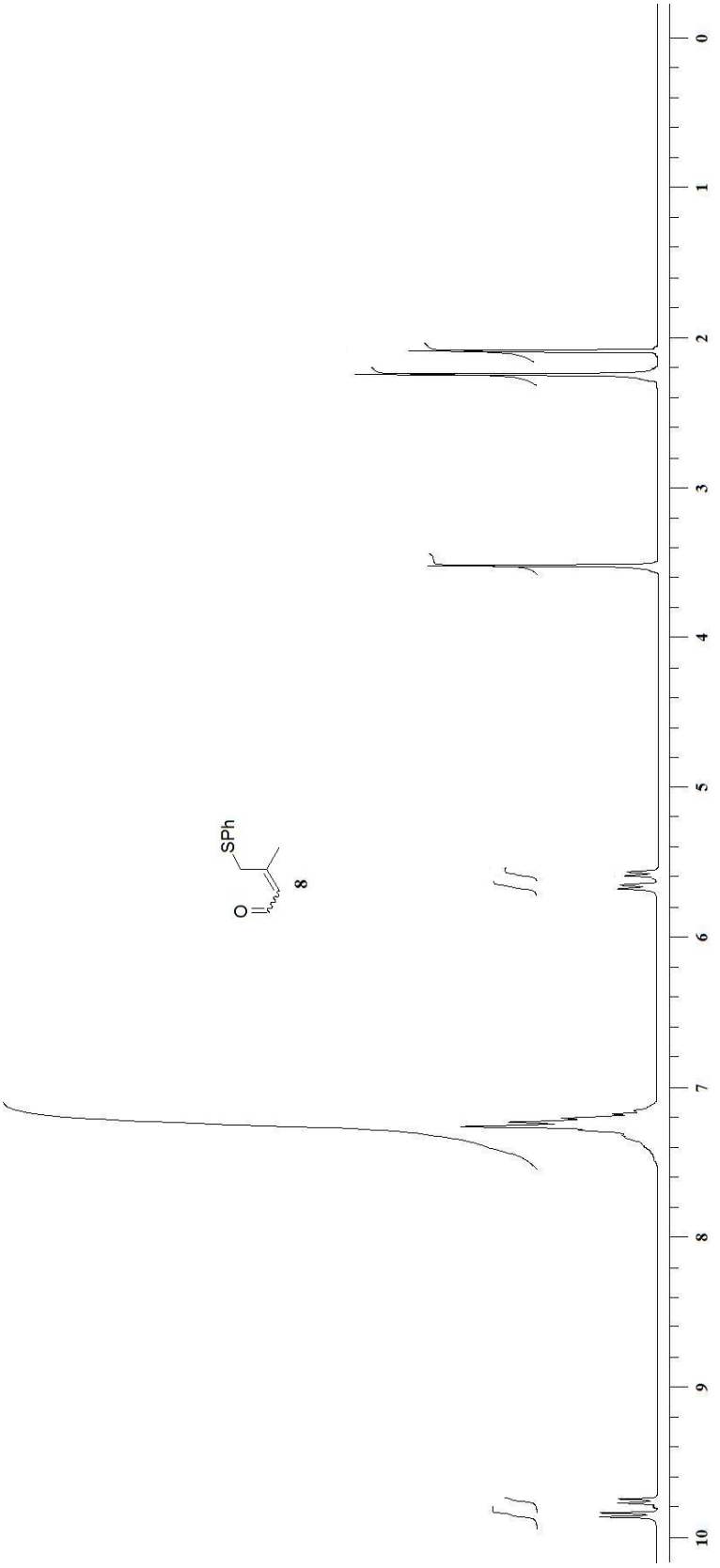
^{1}H NMR Spectrum of Compound 28(*E* & *Z* mixture)



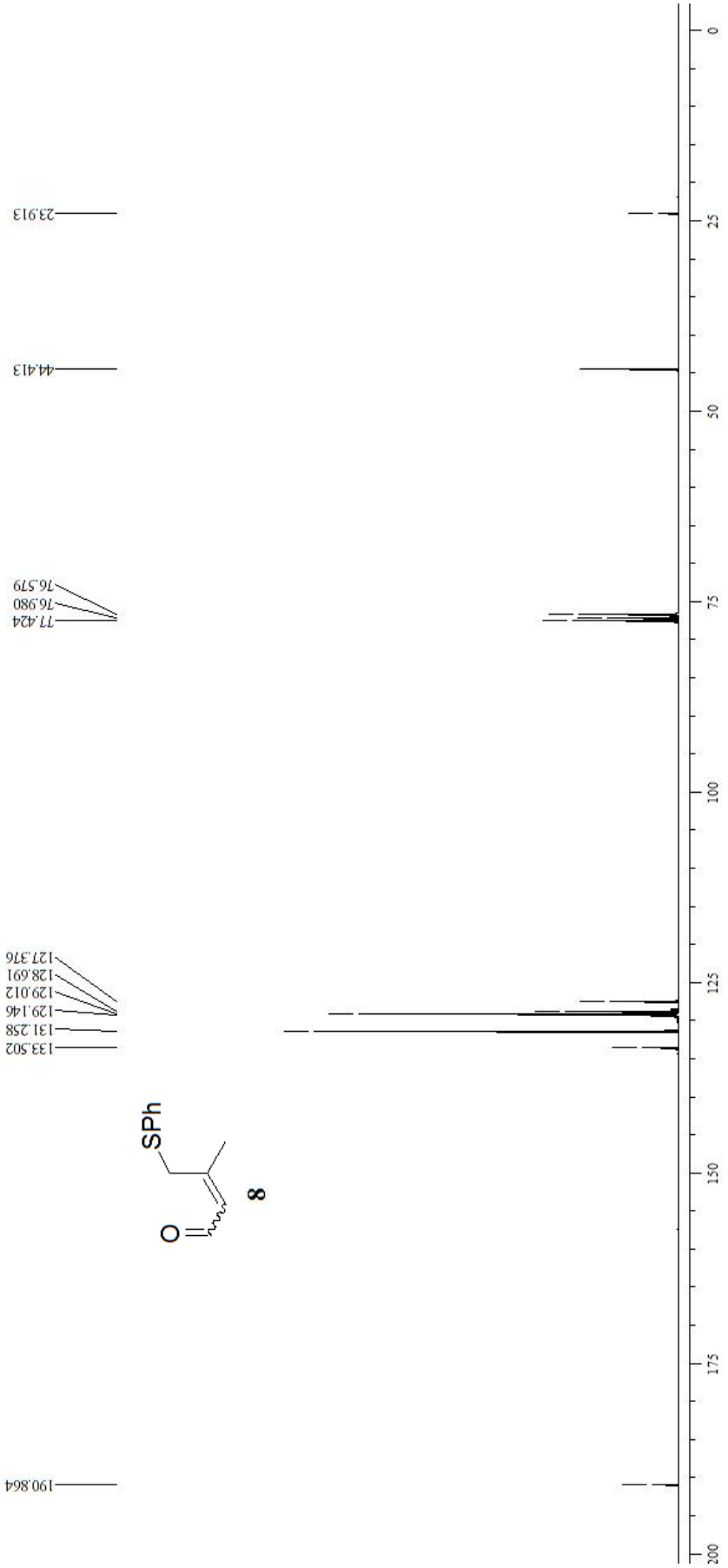
^{13}C NMR Spectrum of Compound 28 (*E* & *Z* mixture)



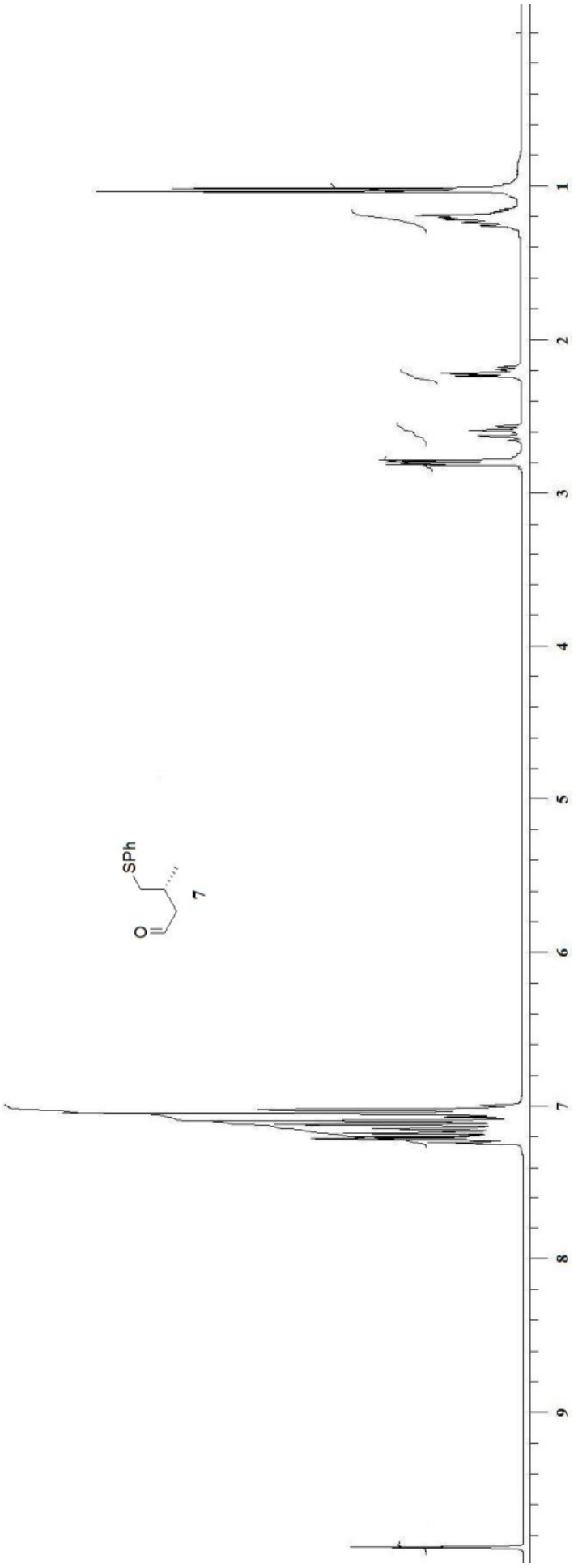
^{1}H NMR Spectrum of Compound 8 (*E* & *Z* mixture)



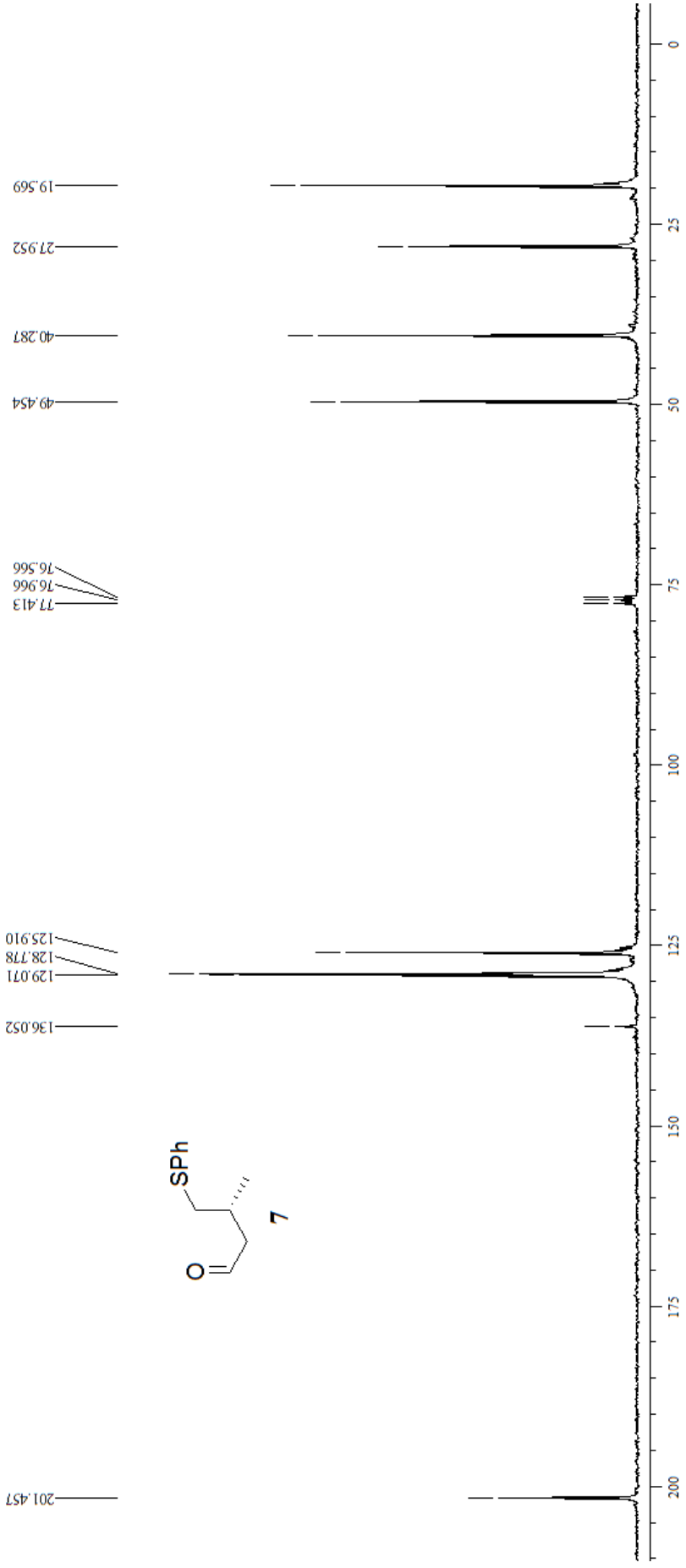
^{13}C NMR Spectrum of Compound 8 (*E* & *Z* mixture)



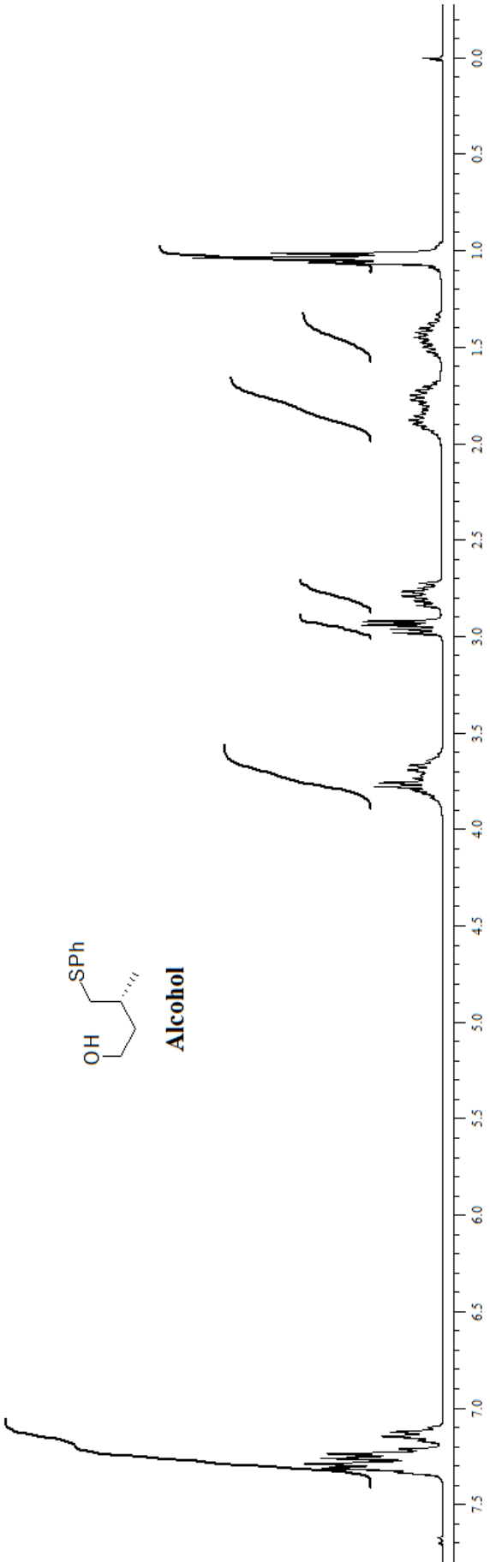
^{1}H NMR Spectrum of Compound 7



^{13}C NMR Spectrum of Compound 7

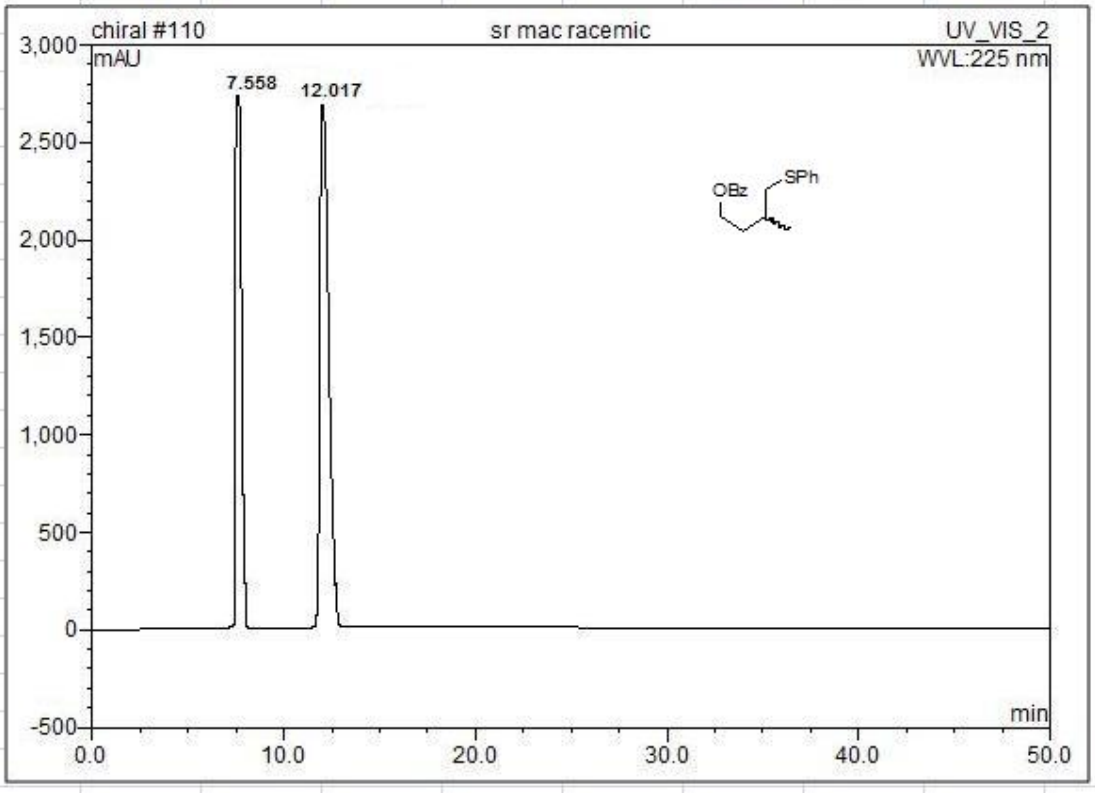


^{1}H NMR Spectrum of Alcohol



Indian Institute of Chemial Technology,Hyderabad

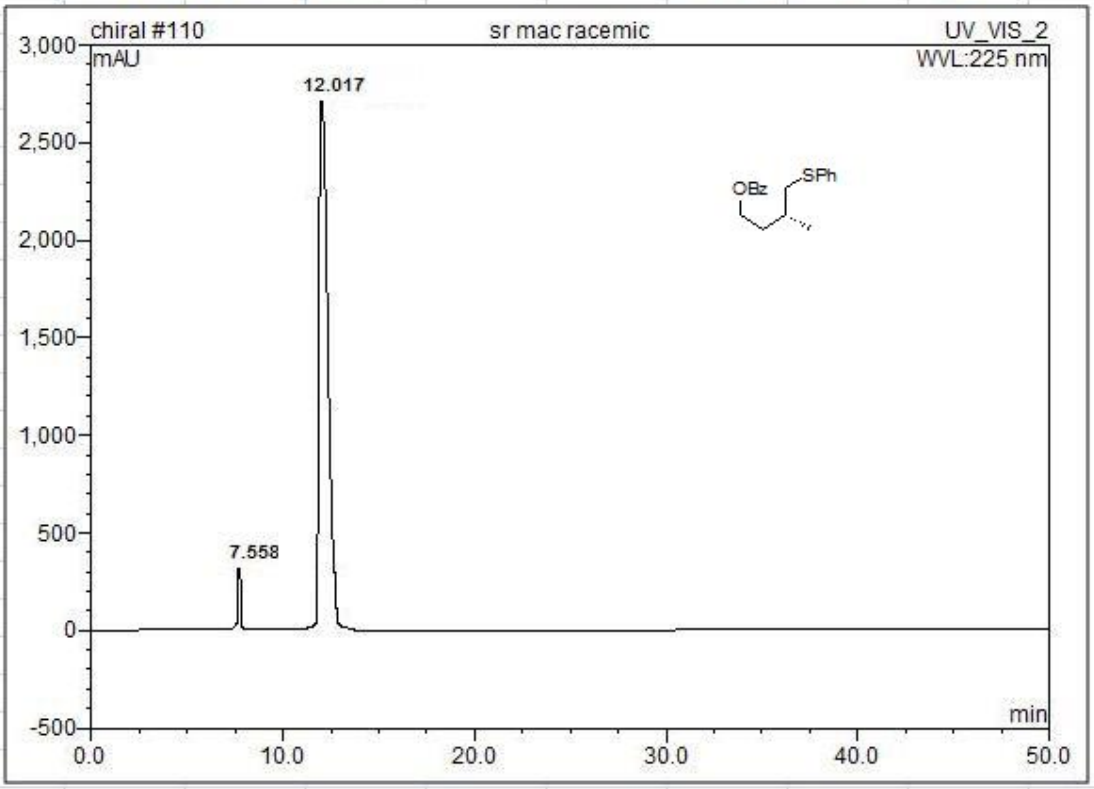
Sample Name:	**sr mac racemic**	*Injection Volume:*	**10.0**
Vial Number:	**RB6**	*Channel:*	**UV_VIS_2**
Sample Type:	**unknown**	*Wavelength:*	**n.a.**
Control Program:	**rama**	*Bandwidth:*	**n.a.**
Quantif. Method:	**rama**	*Dilution Factor:*	**1.0000**
Recording Time:	**########**	*Sample Weight:*	**1.0000**
Run Time (min):	**50.00**	*Sample Amount:*	**1.0000**



No.	Ret.Time	Peak Name	Height	Area	Rel.Area	Amount	Type
	min		mAU	mAU*min	%		
1	7.56	n.a.	2718.106	1462.968	50.35	n.a.	Mb
2	12.02	n.a.	2676.347	1442.629	49.65	n.a.	MB
Total:			5394.453	2905.597	100.00	0.000	

Indian Institute of Chemial Technology,Hyderabad

Sample Name:	**sr mac chiral**	*Injection Volume:*	**10.0**
Vial Number:	**RB6**	*Channel:*	**UV_VIS_2**
Sample Type:	**unknown**	*Wavelength:*	**n.a.**
Control Program:	**rama**	*Bandwidth:*	**n.a.**
Quantif. Method:	**rama**	*Dilution Factor:*	**1.0000**
Recording Time:	**########**	*Sample Weight:*	**1.0000**
Run Time (min):	**50.00**	*Sample Amount:*	**1.0000**



No.	Ret.Time	Peak Name	Height	Area	Rel.Area	Amount	Type
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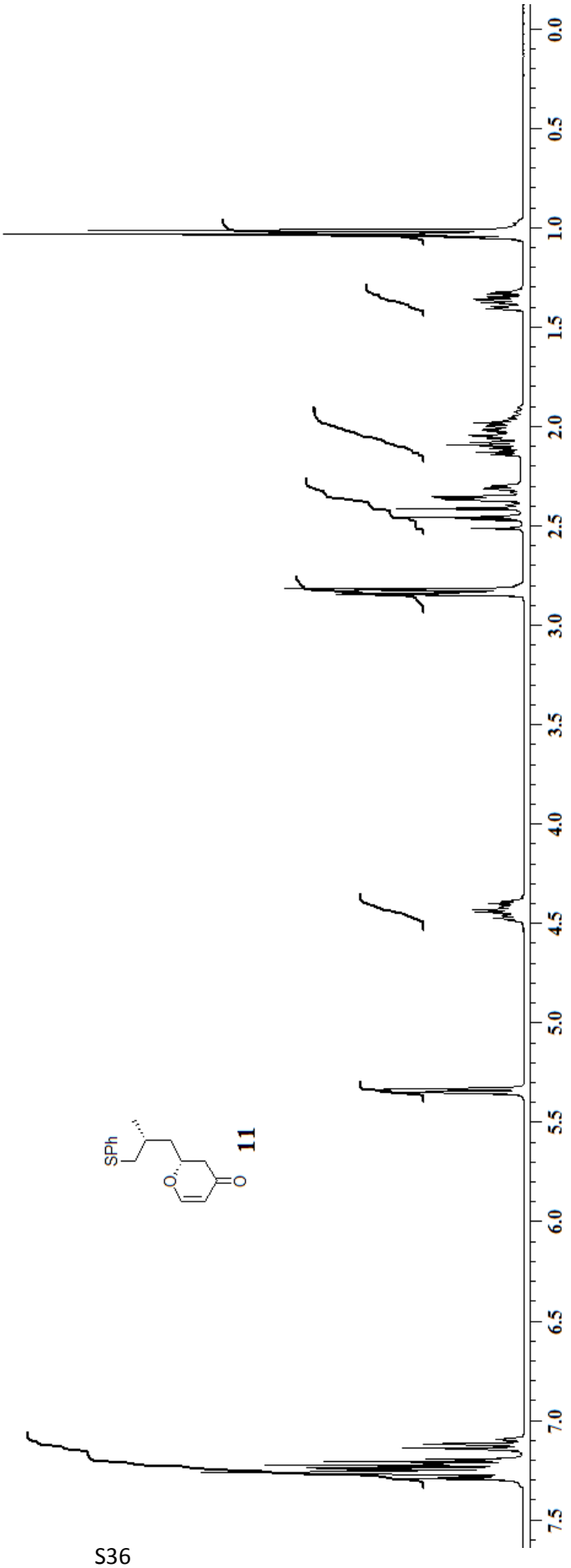
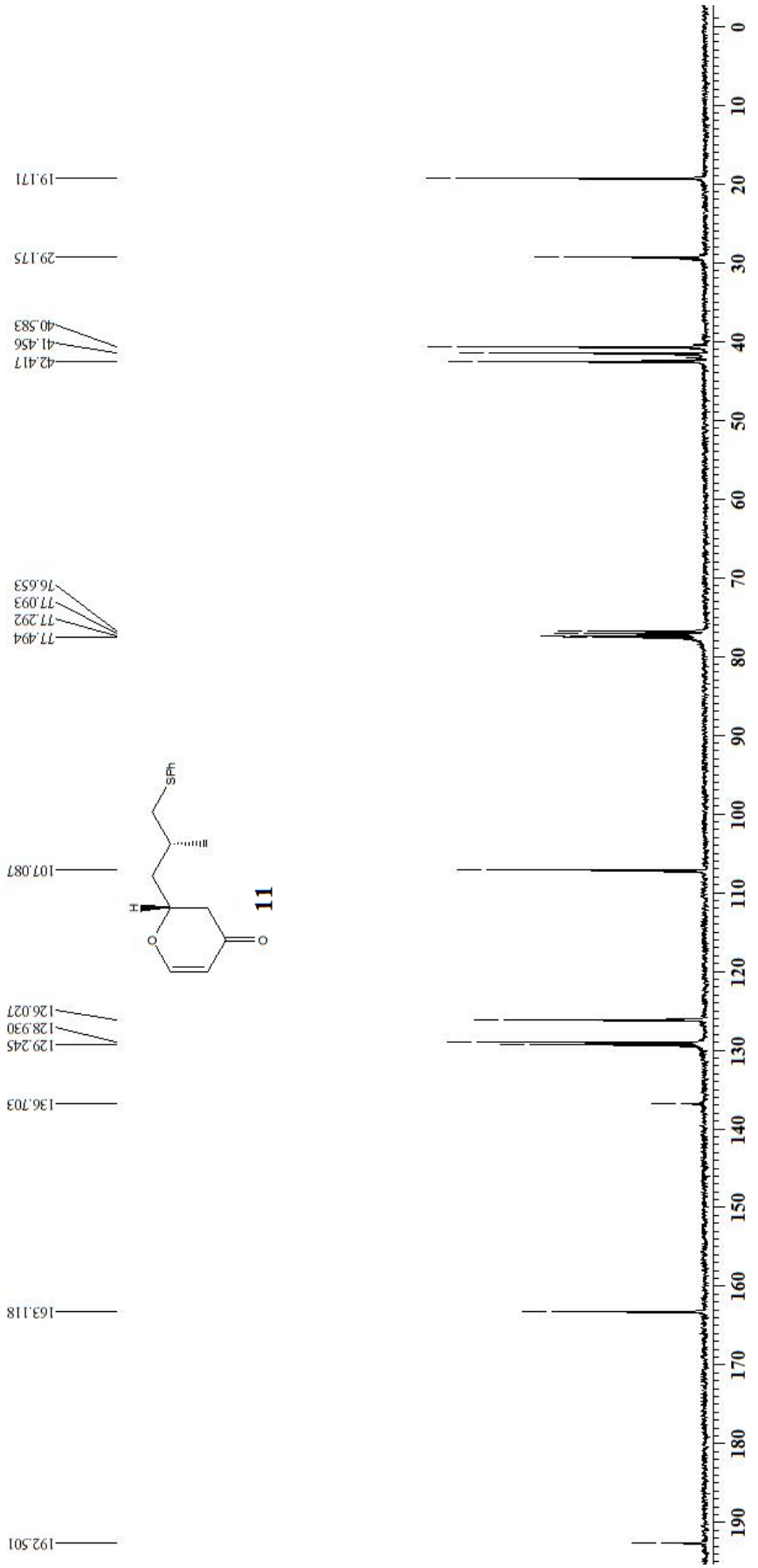
2	12.02	n.a.	2676.347	1442.629	97.52	n.a.	MB
Total:			2992.083	1479.316	100.00	0.000	

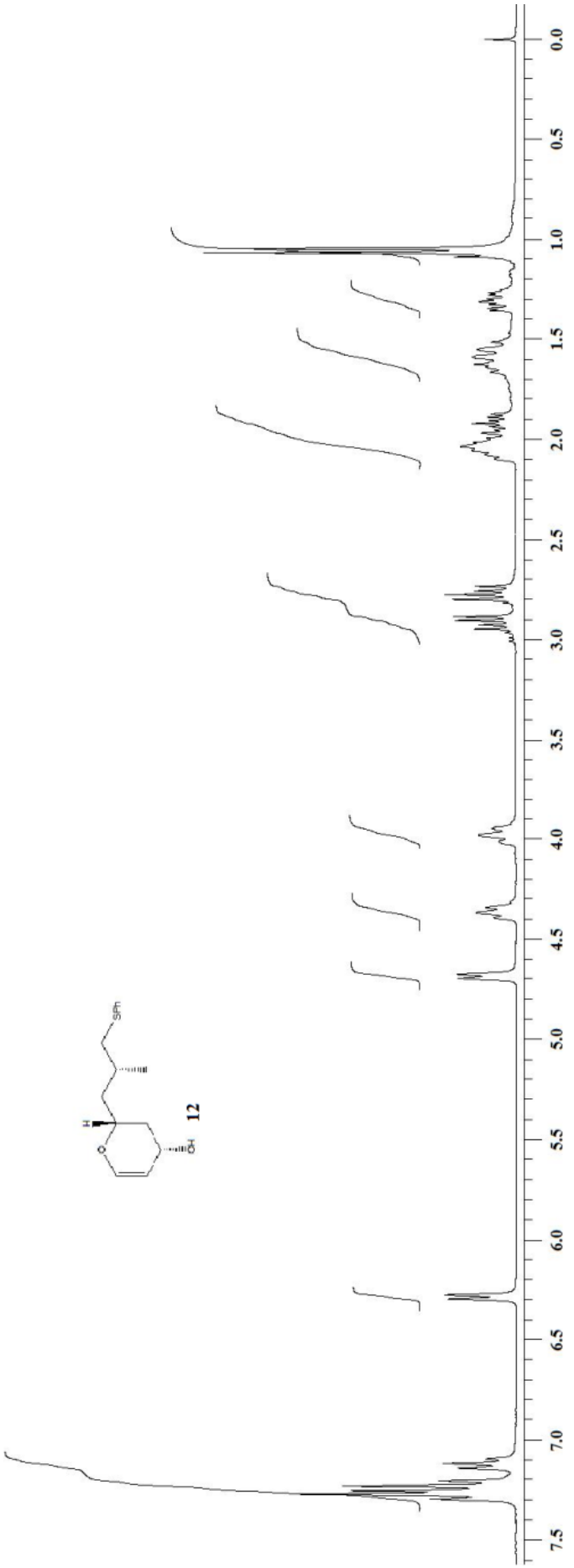
^{1}H NMR Spectrum of Compound 11



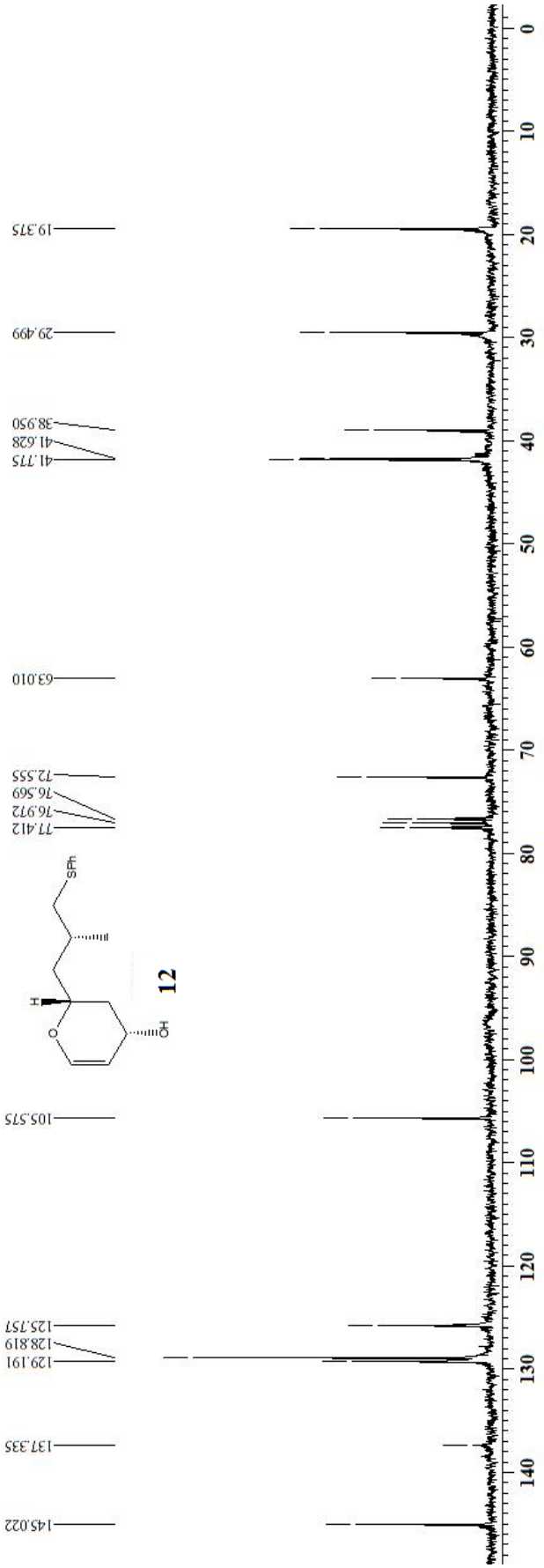
^{13}C NMR Spectrum of Compound 11



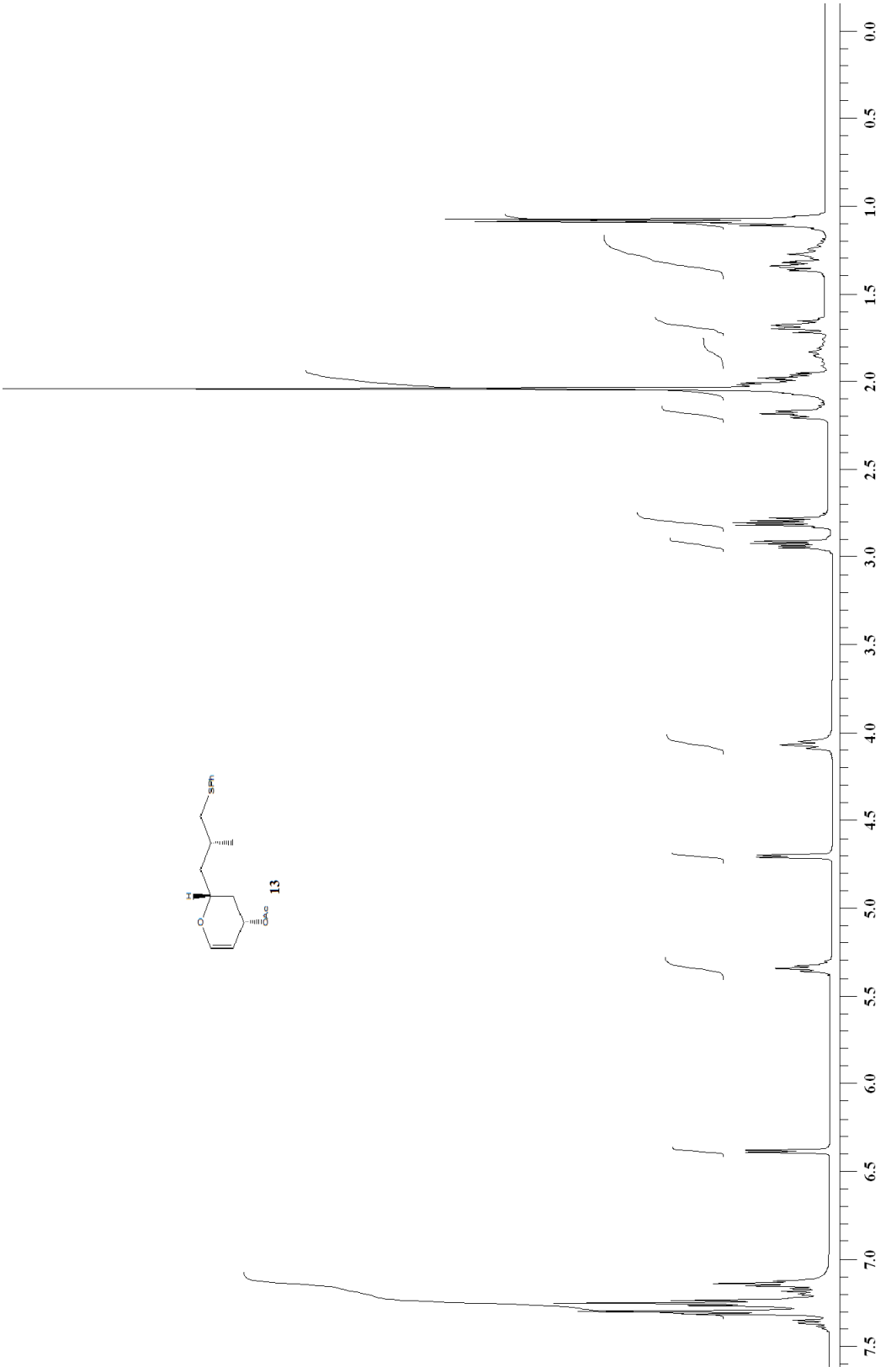
^{1}H NMR Spectrum of Compound 12



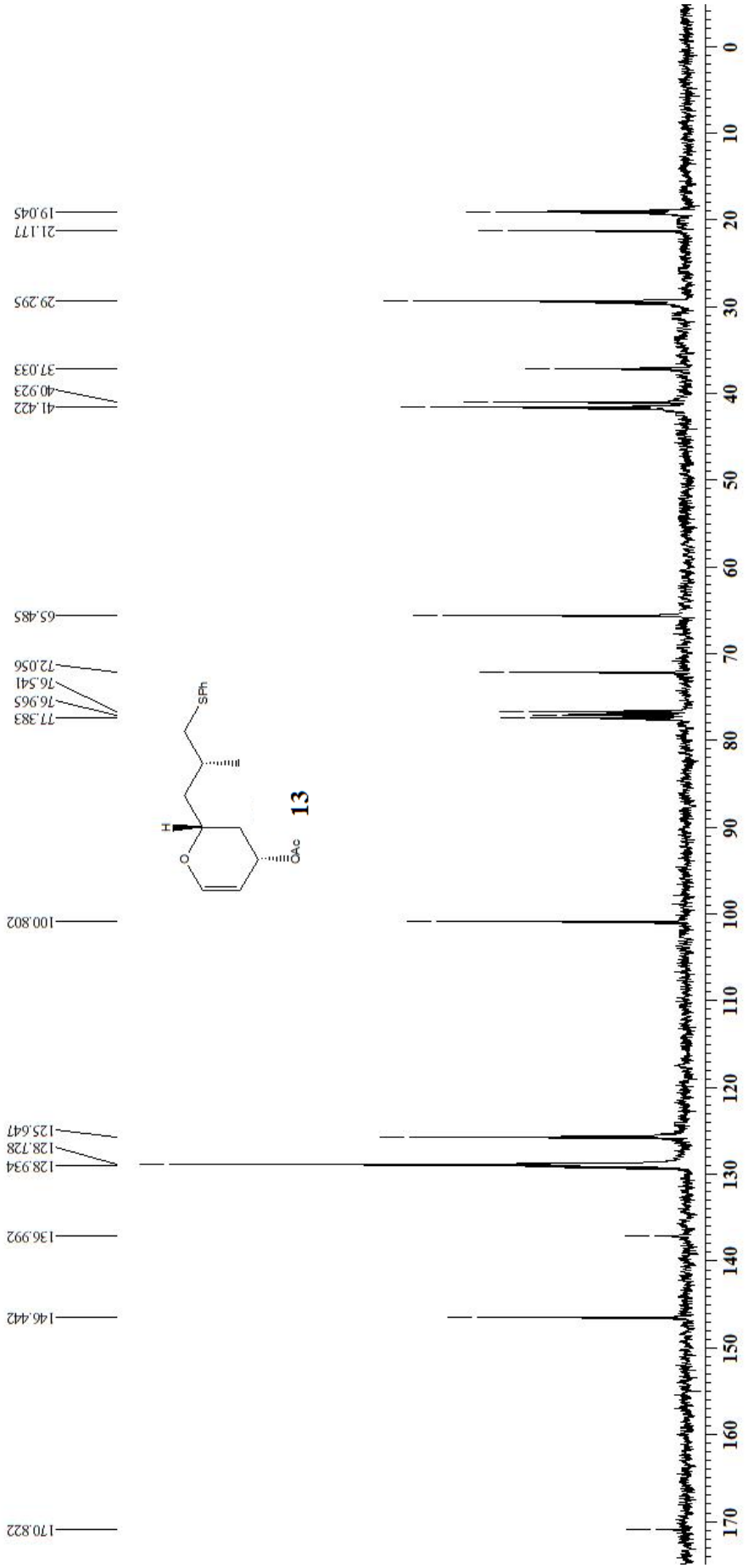
^{13}C NMR Spectrum of Compound 12



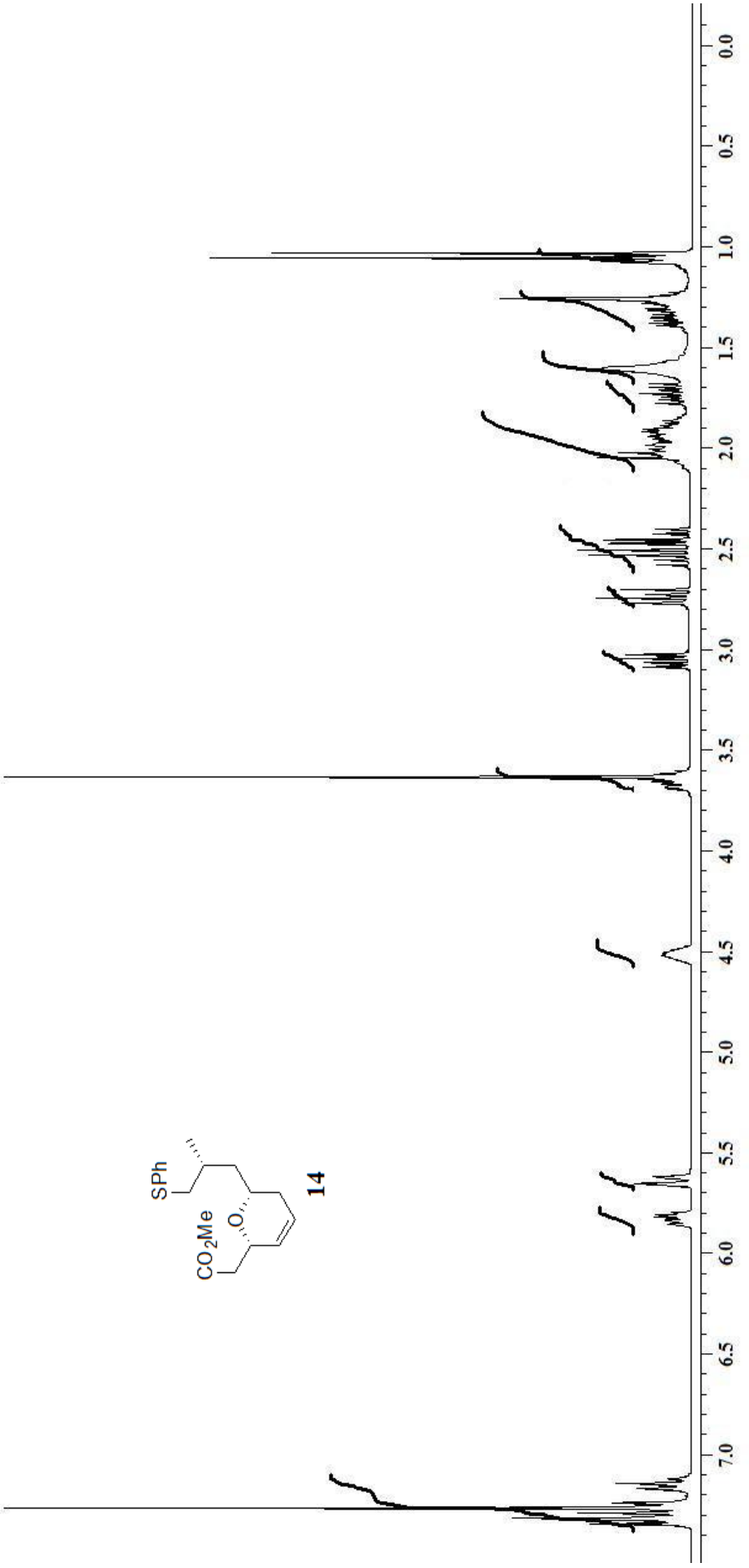
^{1}H NMR Spectrum of Compound 13



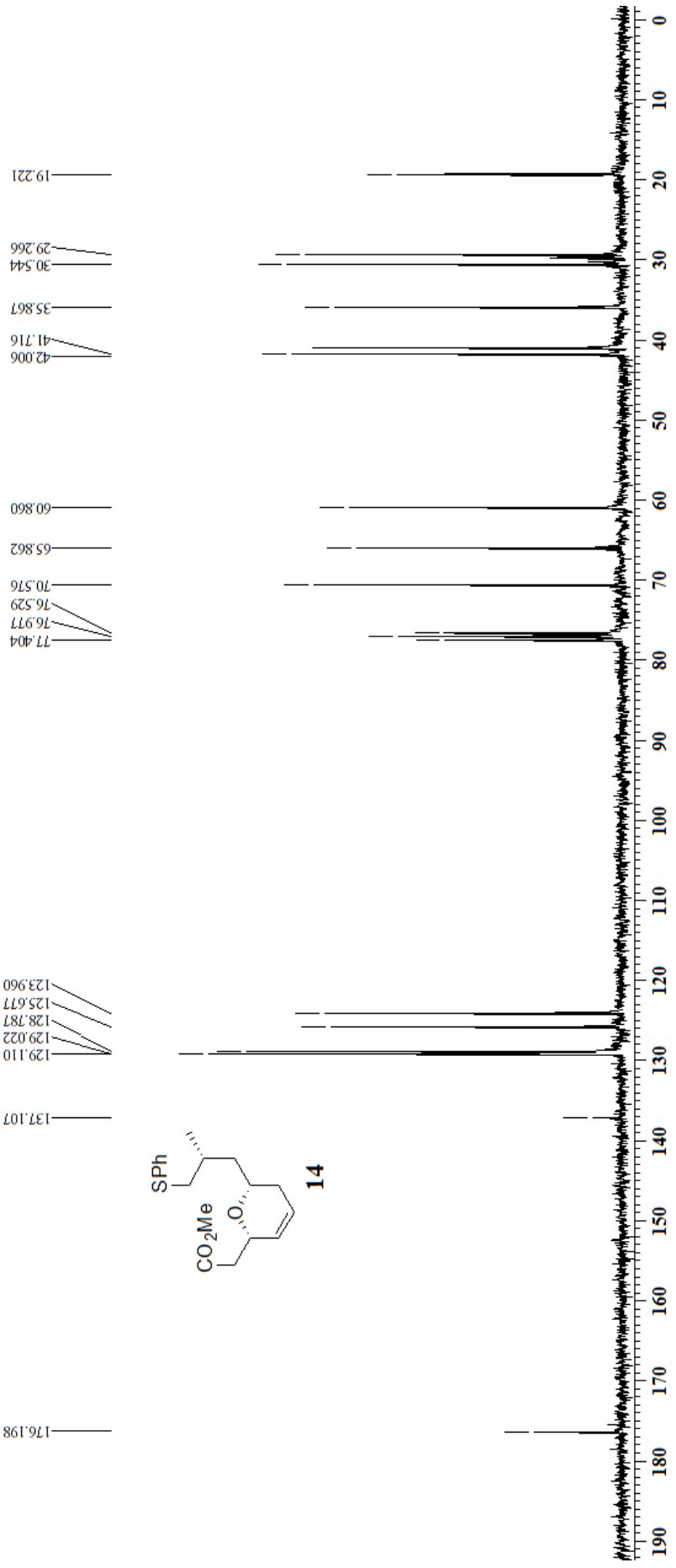
^{13}C NMR Spectrum of Compound 13



^{1}H NMR Spectrum of Compound 14

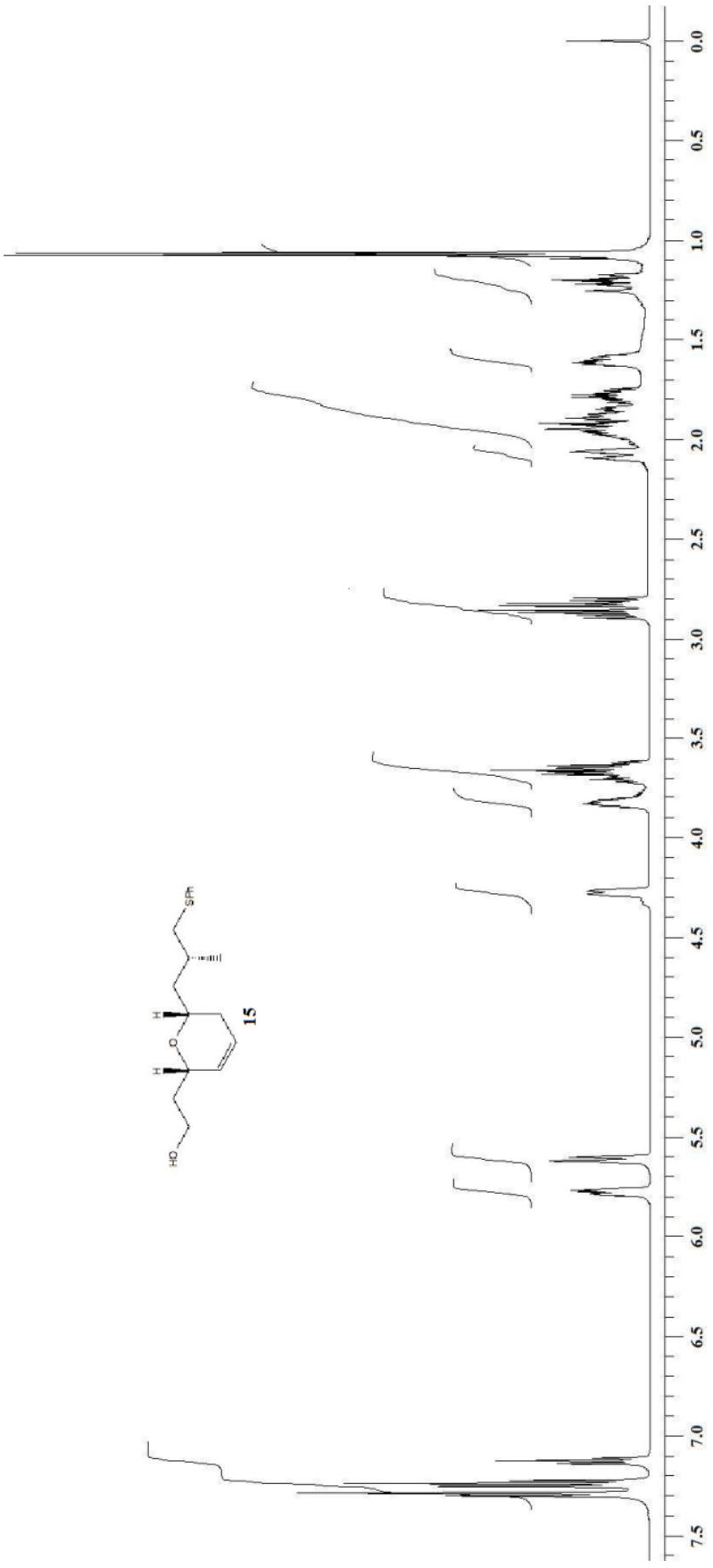


^{13}C NMR Spectrum of Compound 14

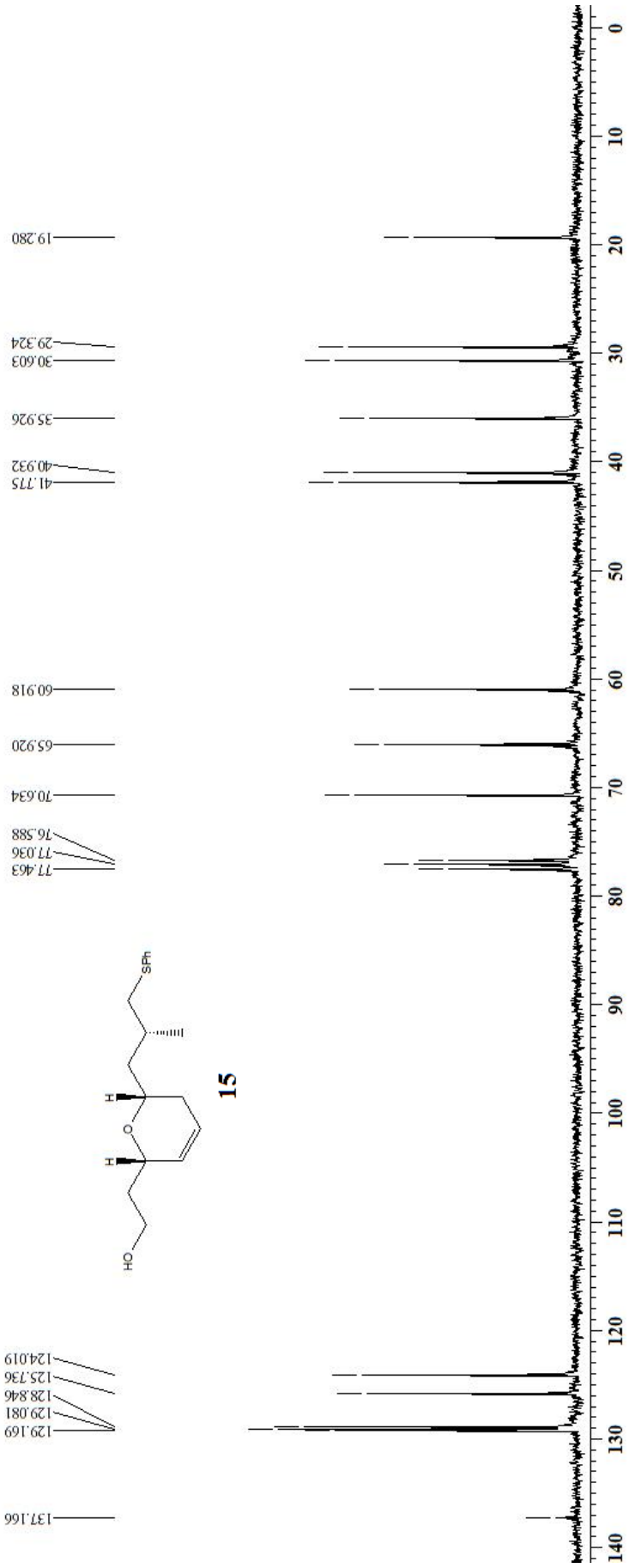


1D-NMR Spectrum of Compound 14

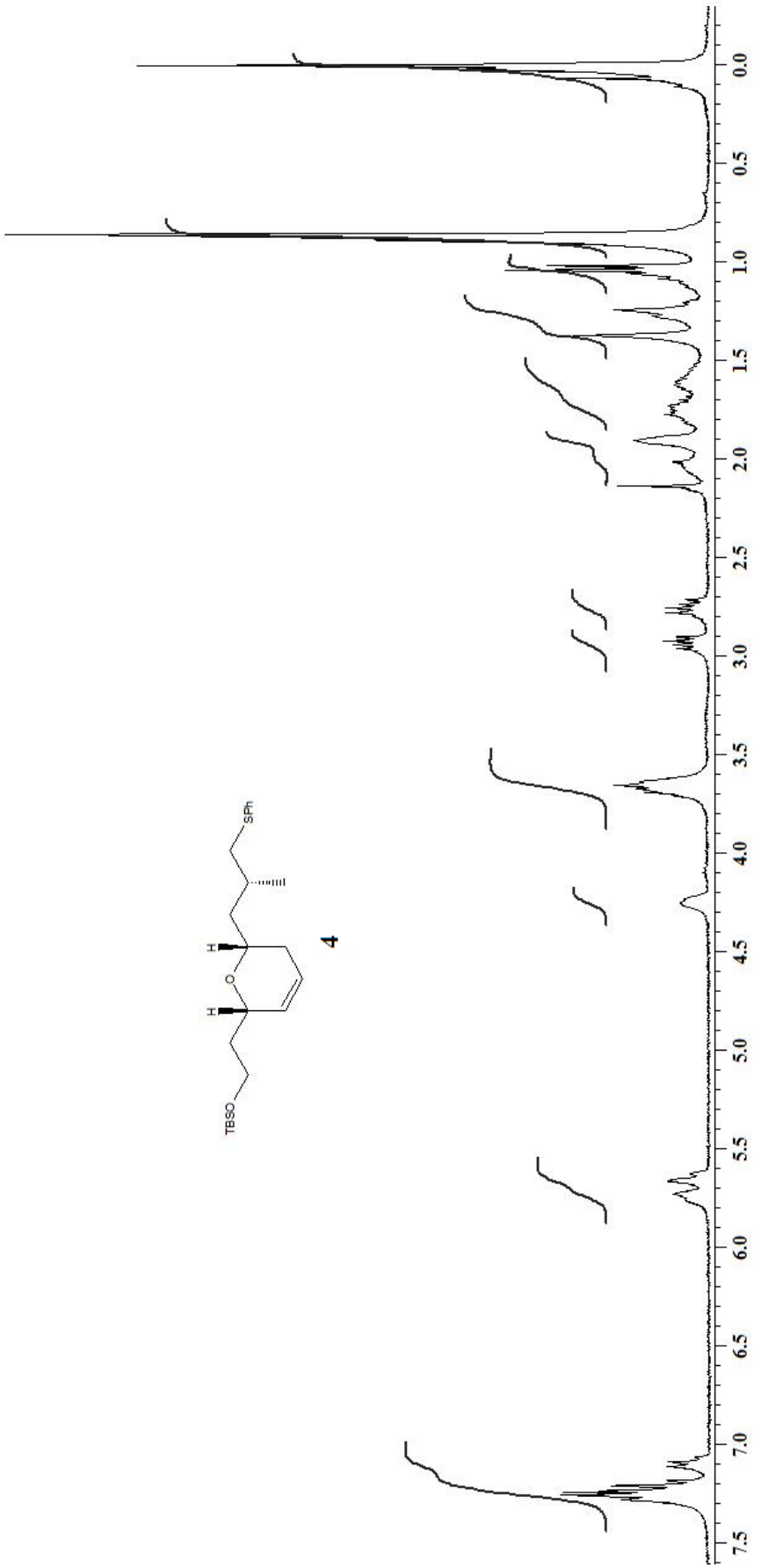
^{1}H NMR Spectrum of Compound 15



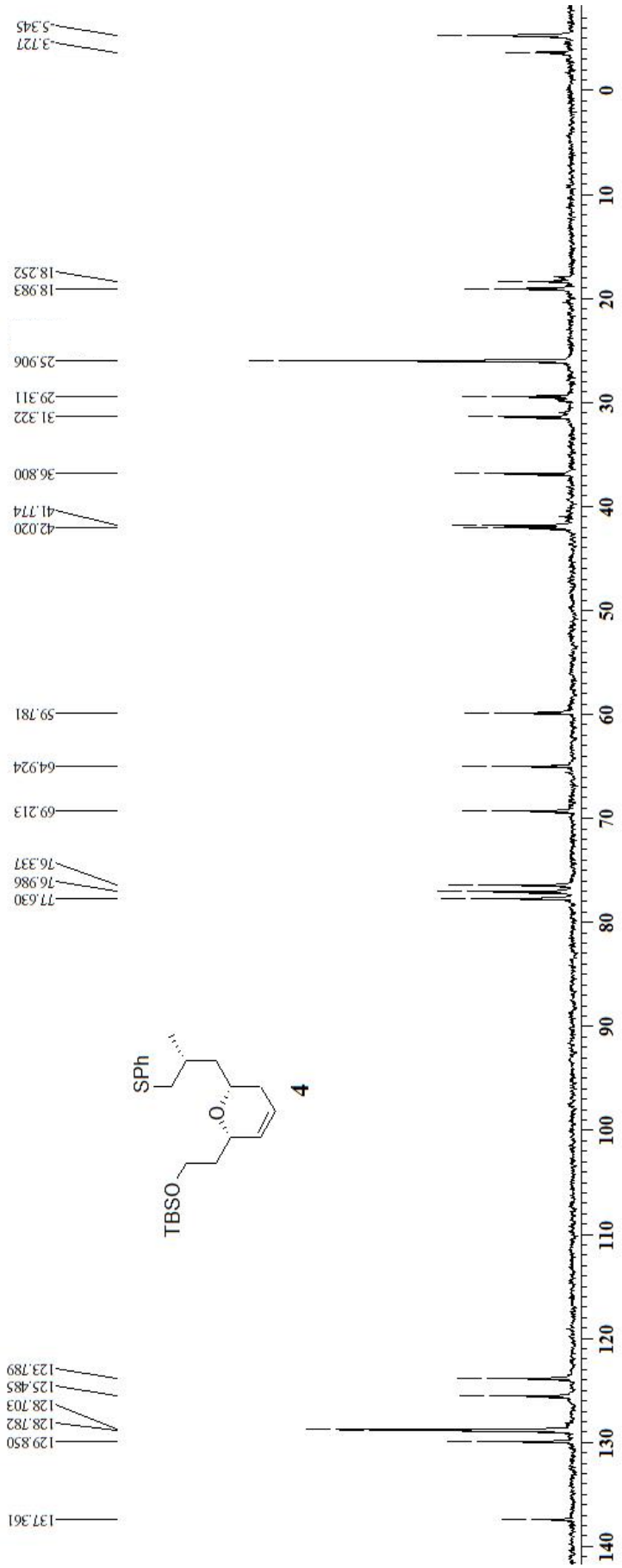
^{13}C NMR Spectrum of Compound 15



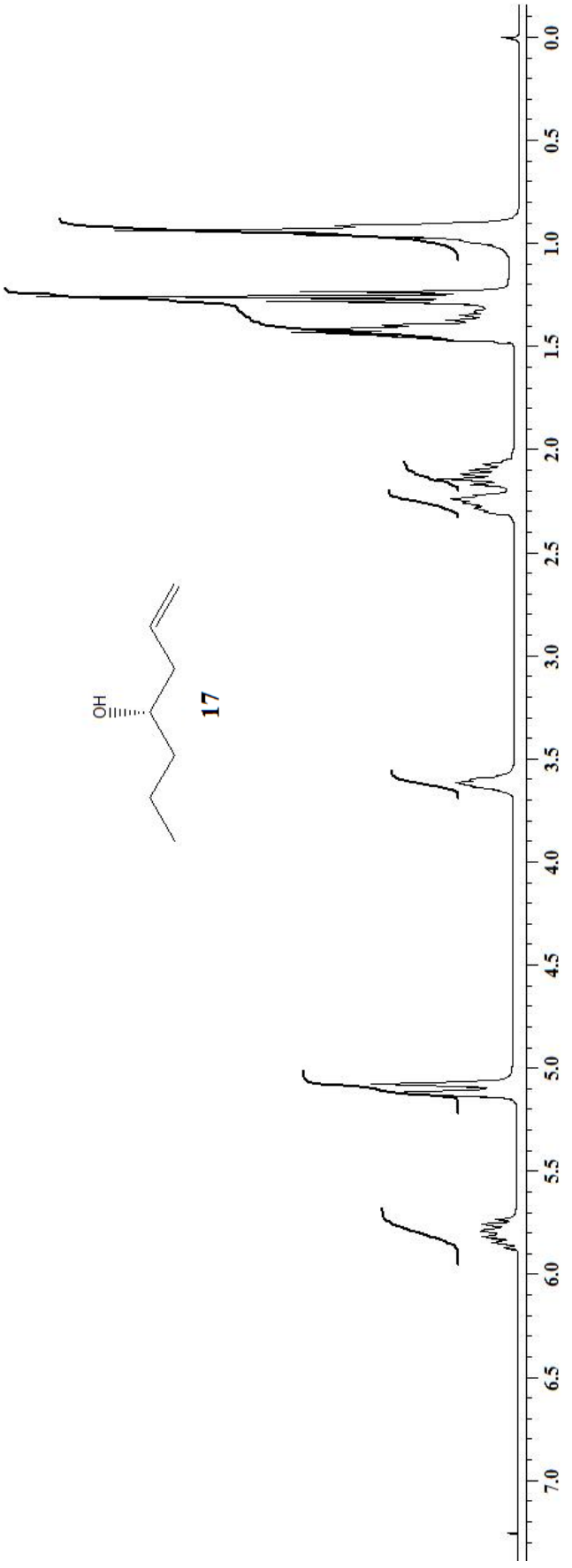
^{1}H NMR Spectrum of Compound 4



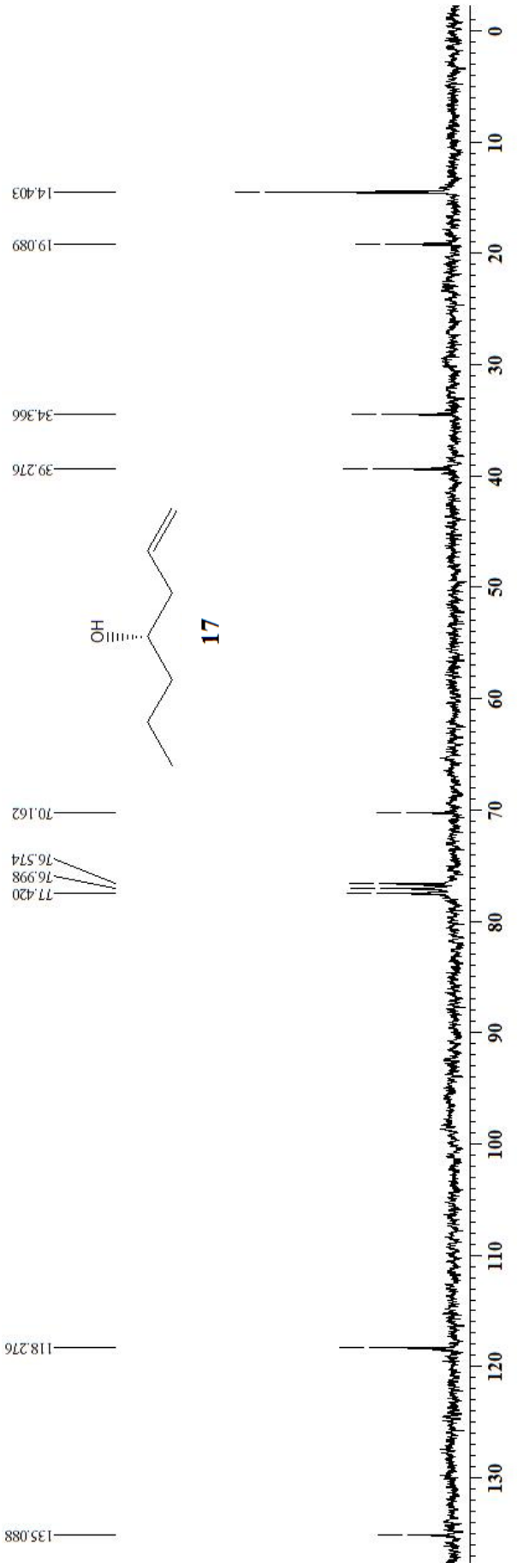
^{13}C NMR Spectrum of Compound 4



^{1}H NMR Spectrum of Compound 17



^{13}C NMR Spectrum of Compound 17



Empower 2 software

Default Individual Report

SAMPLE INFORMATION

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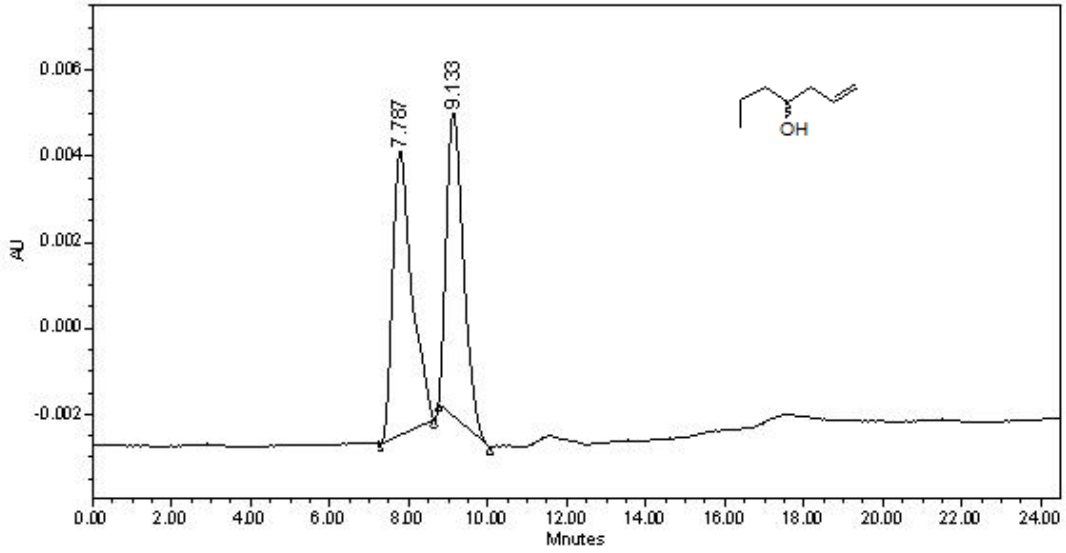
Sample Type:	Unknown	Sample Set Name:	
Vial:	1	Acq. Method Set:	1%IPA
Injection #:	2	Processing Method:	Default
Injection Volume:	10.00 ul	Channel Name:	254.0nm@1
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	PDA 254.0 nm
Date Acquired:	10/15/2009 8:29:44 PM IST		
Date Processed:	11/5/2011 3:32:55 PM IST		



	RT	Area	% Area	Height
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2	9.133	212260	48.82	7056

Empower 2 software

Default Individual Report

SAMPLE INFORMATION

Sample Name:	sr-pk-kris1	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	
Vial:	1	Acq. Method Set:	1%IPA
Injection #:	1	Processing Method:	Default1
Injection Volume:	10.00 ul	Channel Name:	254.0nm
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	PDA 254.0 nm
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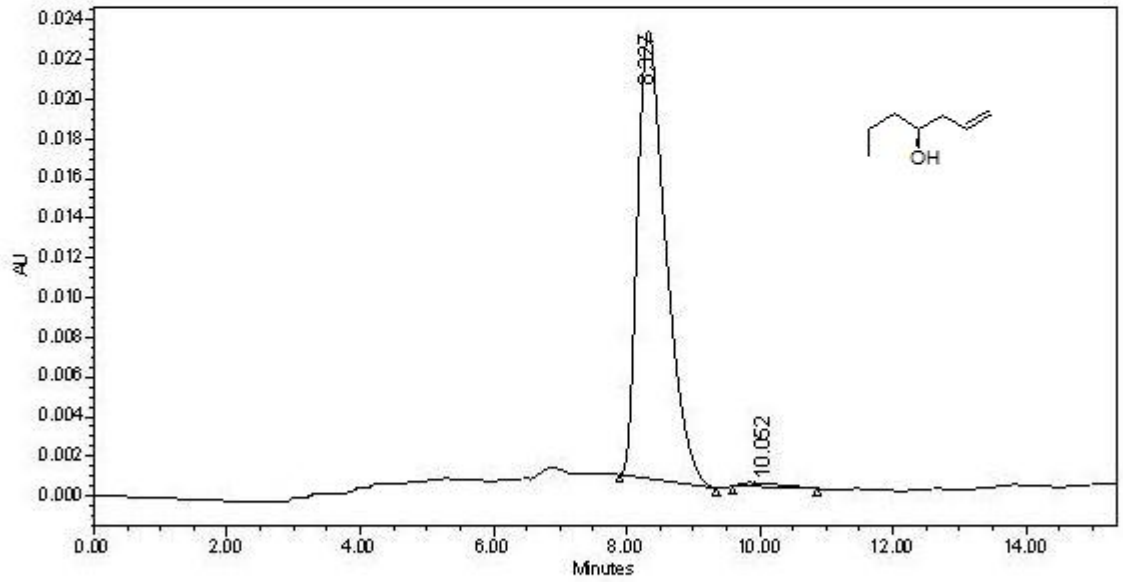

	RT	Area	% Area	Height
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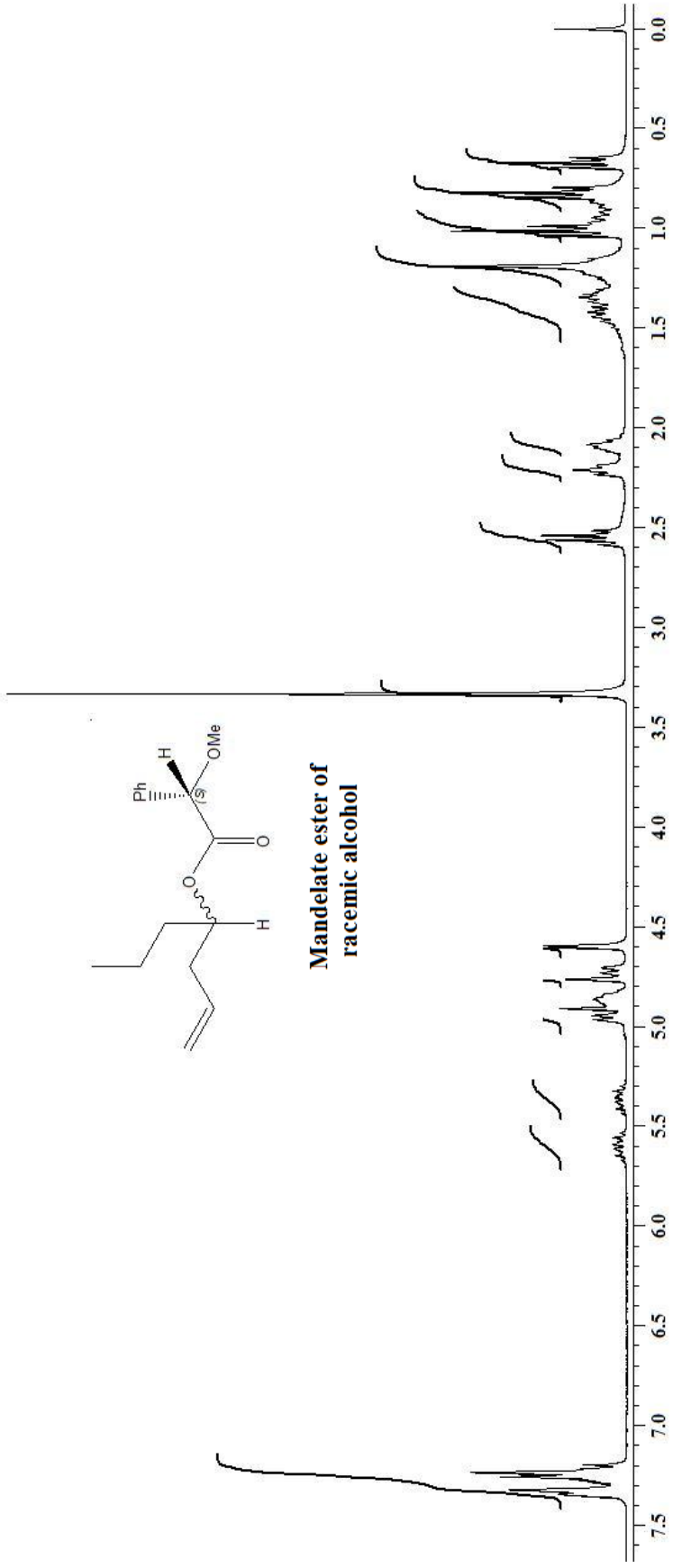
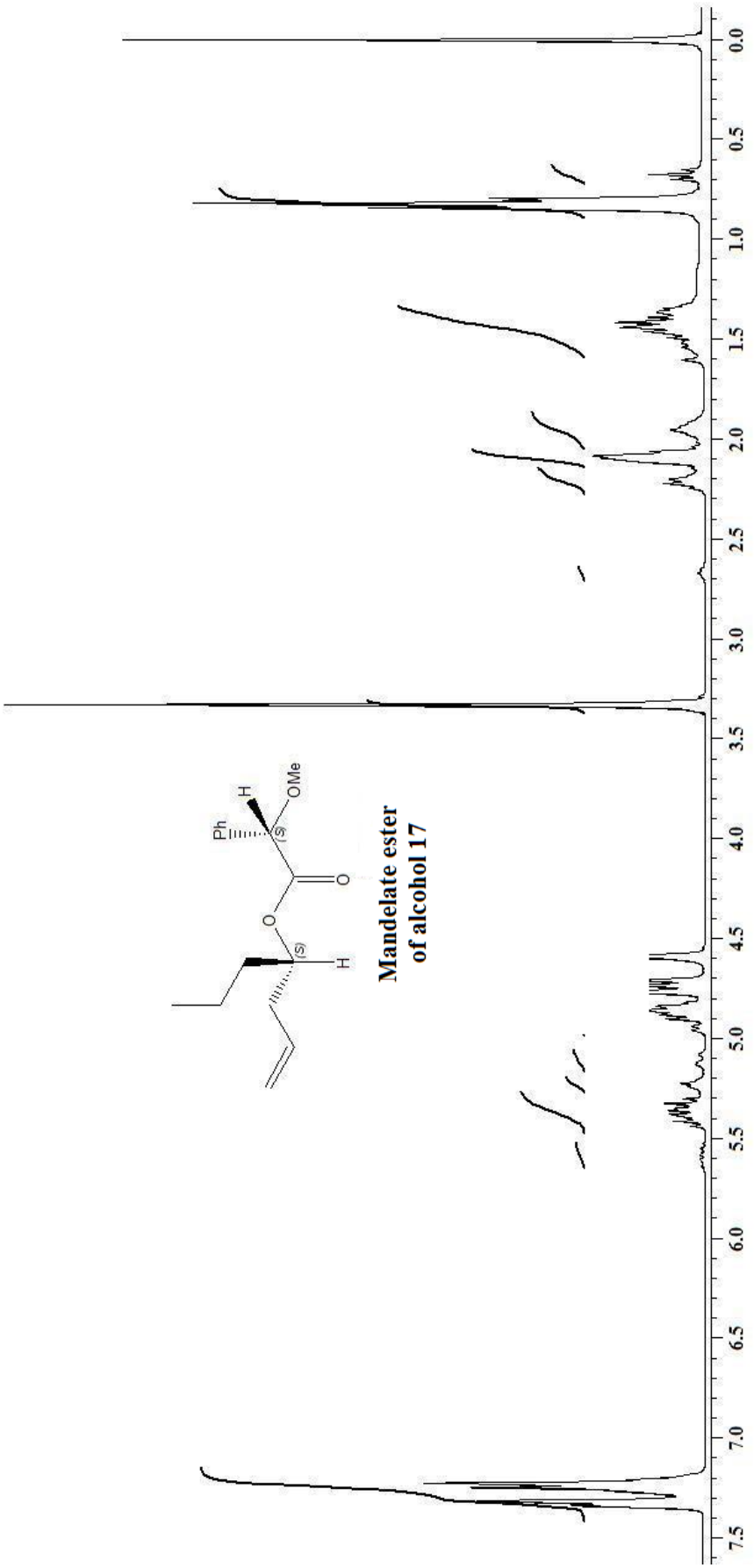
2	10.052	8355	1.23	221

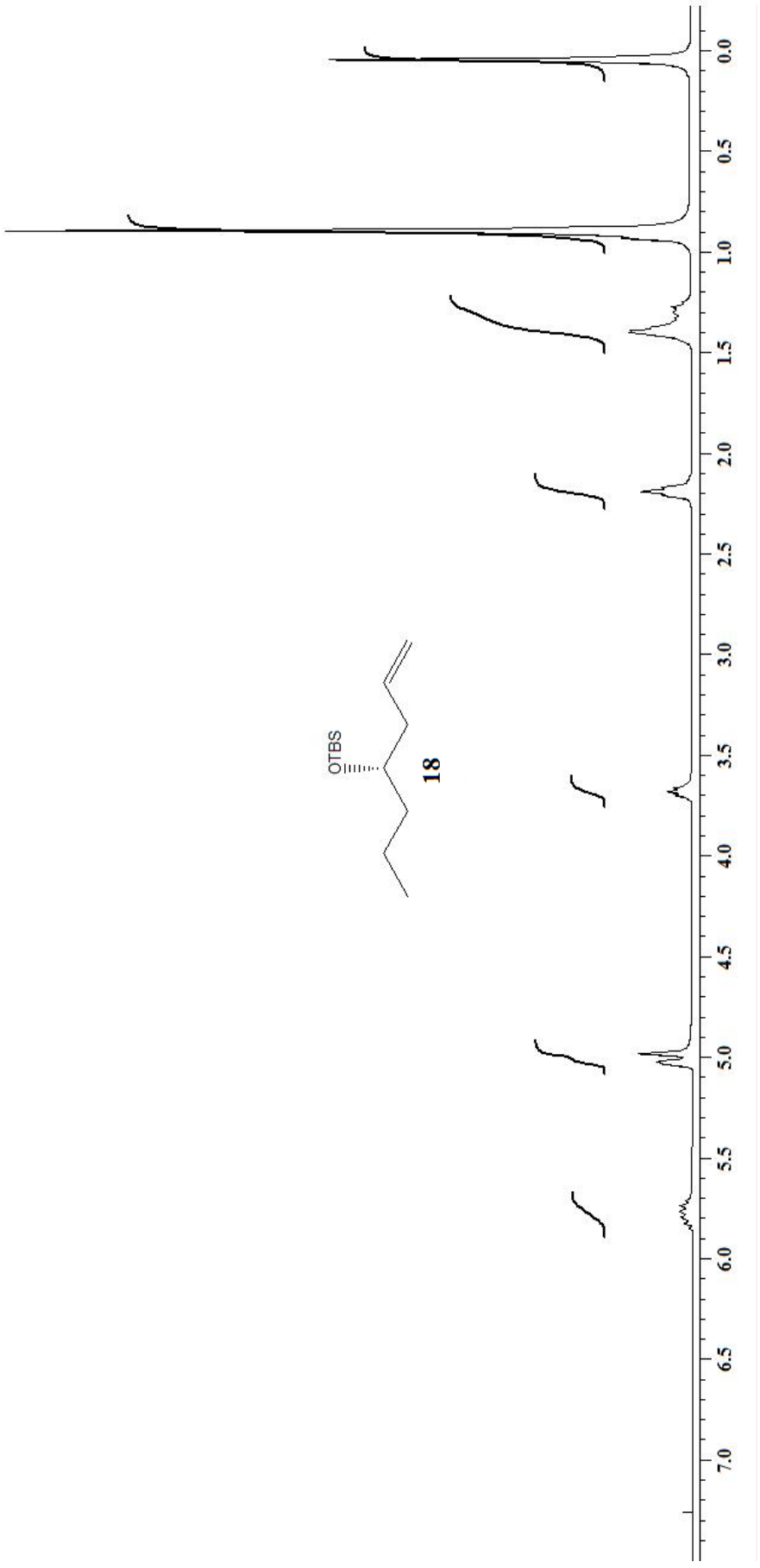
^{1}H NMR Spectrum of Mandelate ester of racemic alcohol



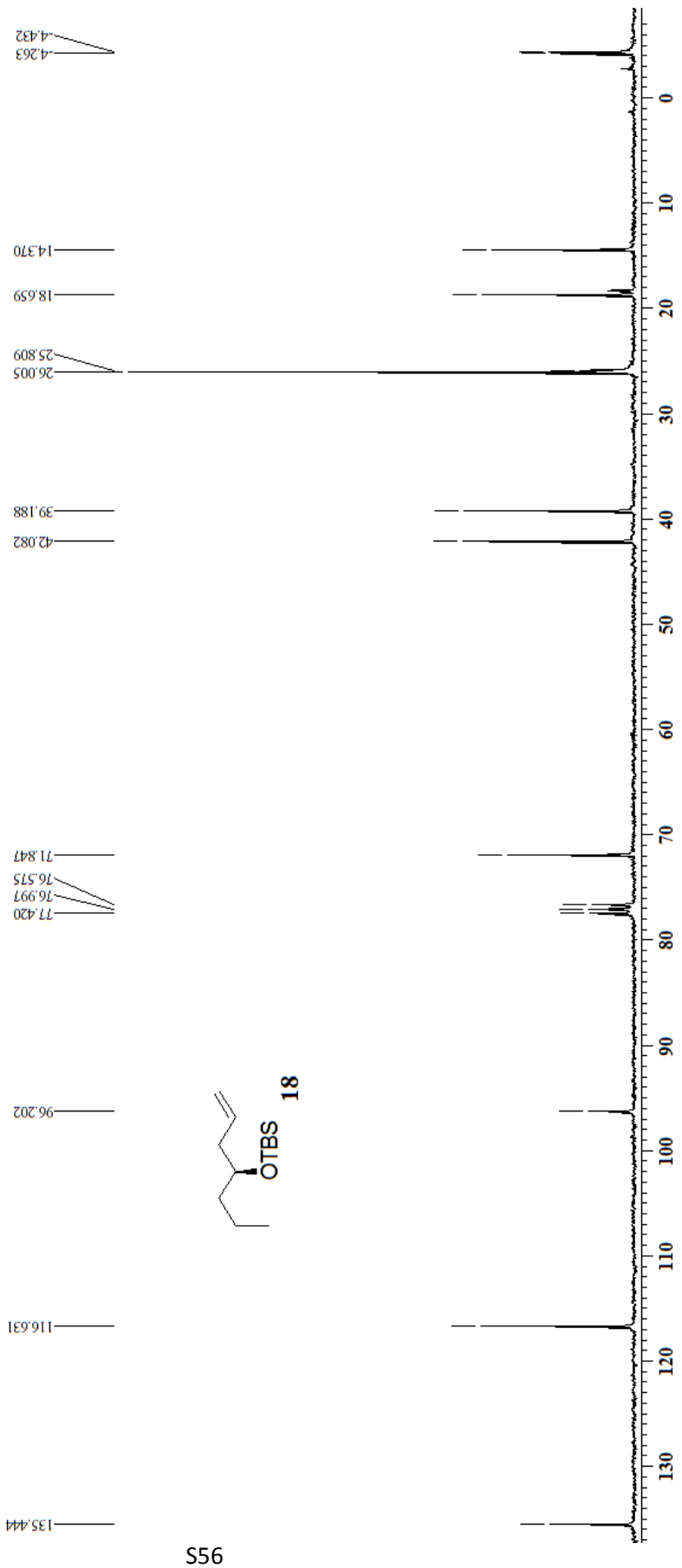
^{1}H NMR Spectrum of Mandelate ester of alcohol 17



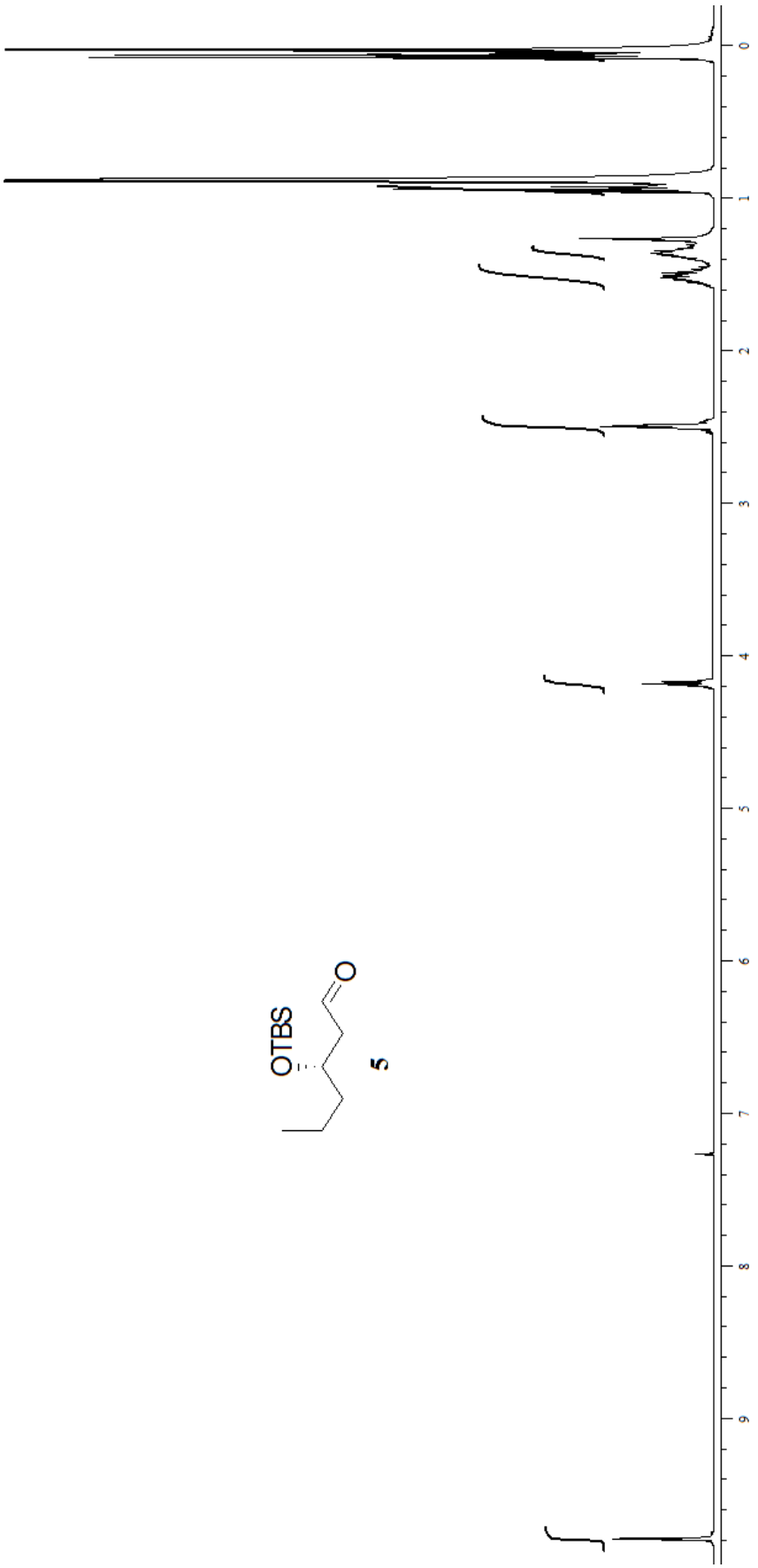
^{1}H NMR Spectrum of Compound 18



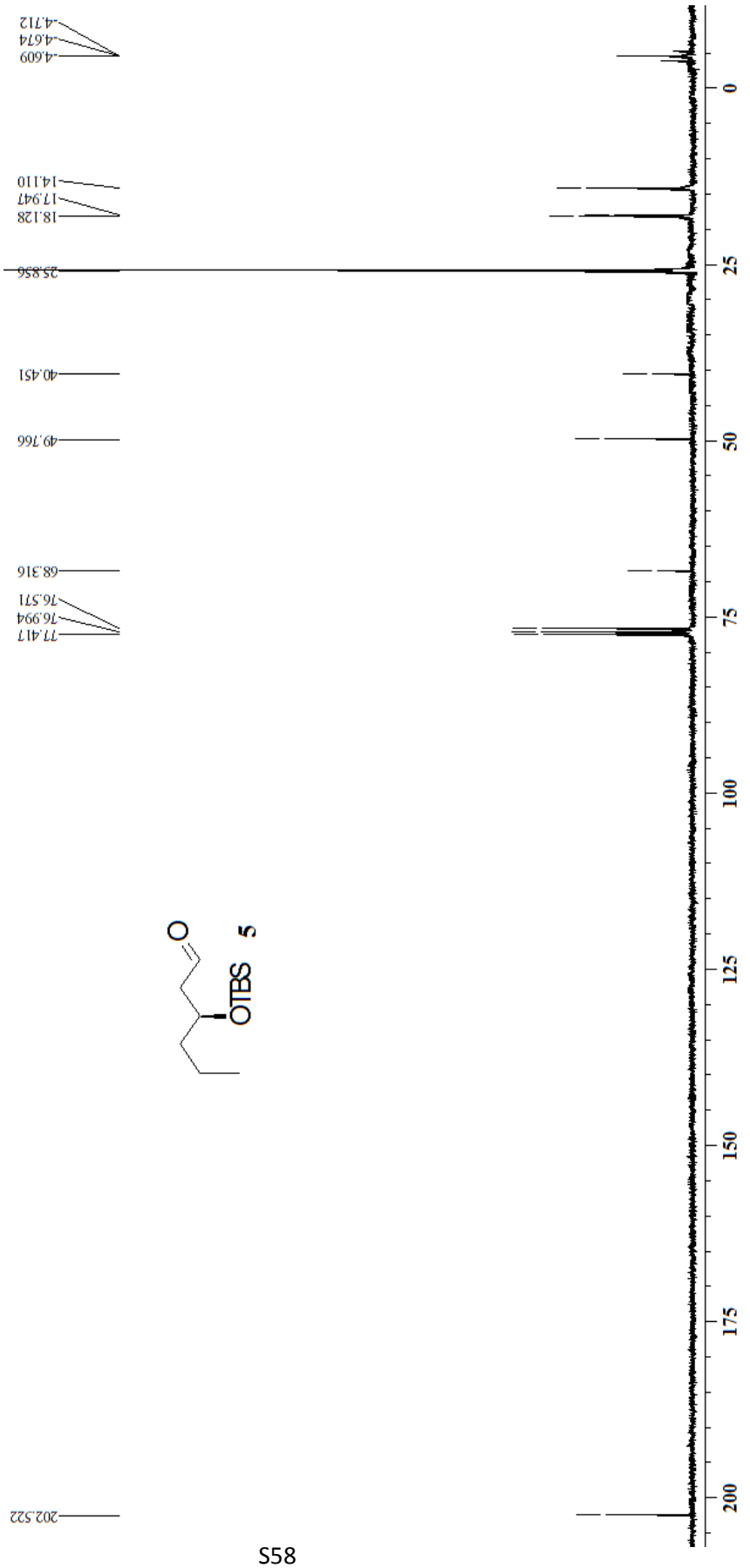
^{13}C NMR Spectrum of Compound 18



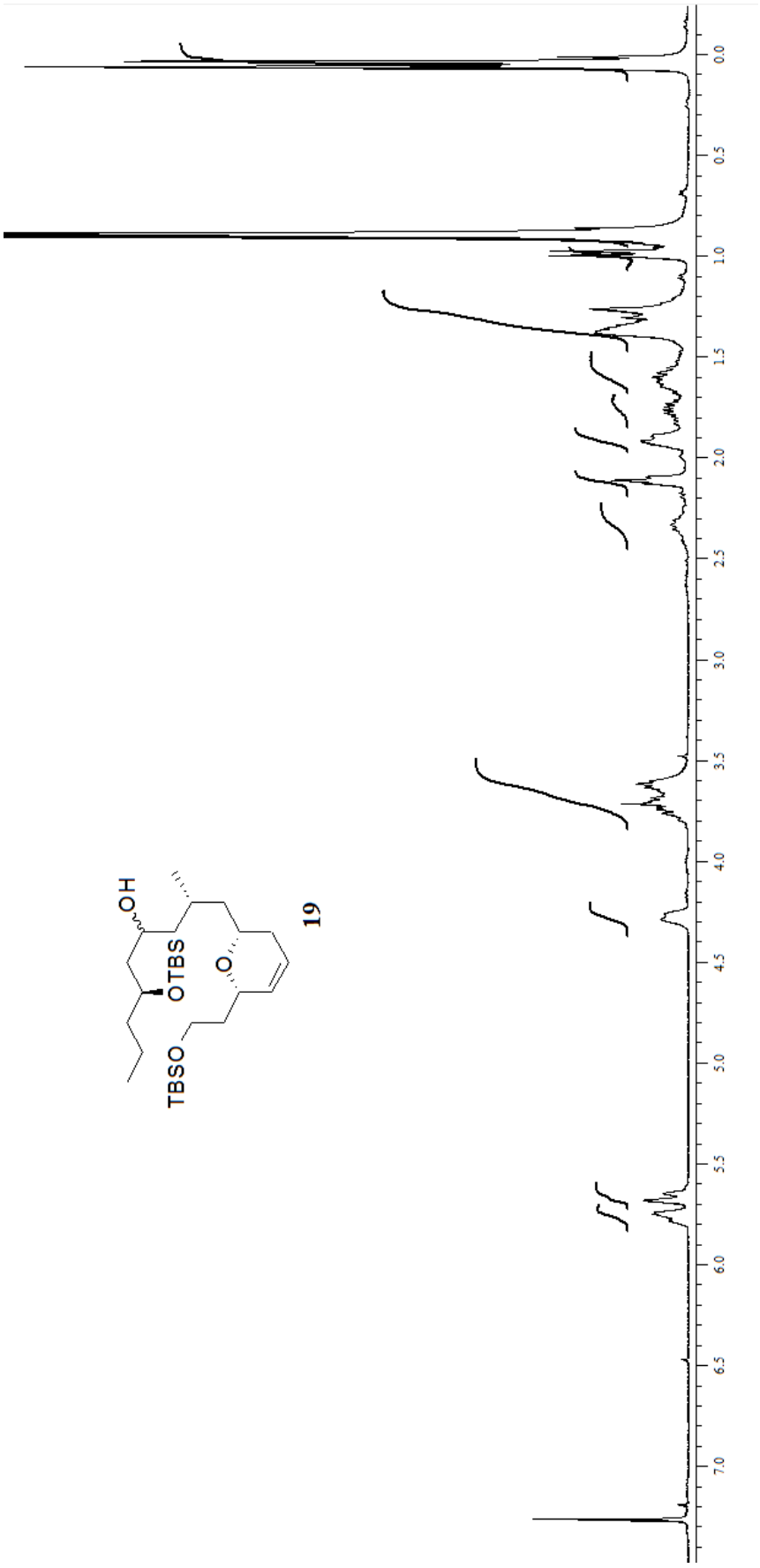
^{1}H NMR Spectrum of Compound 5



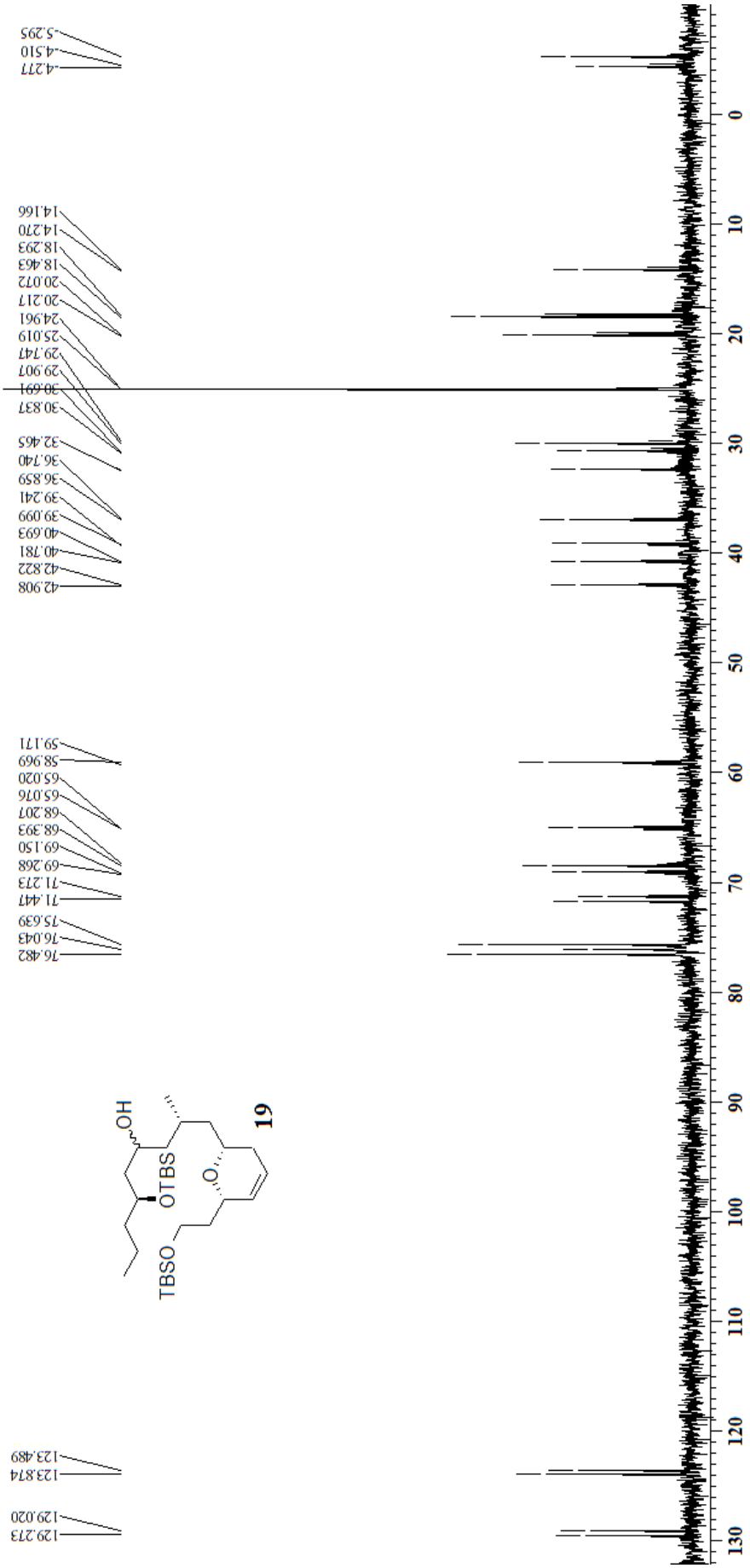
^{13}C NMR Spectrum of Compound 5



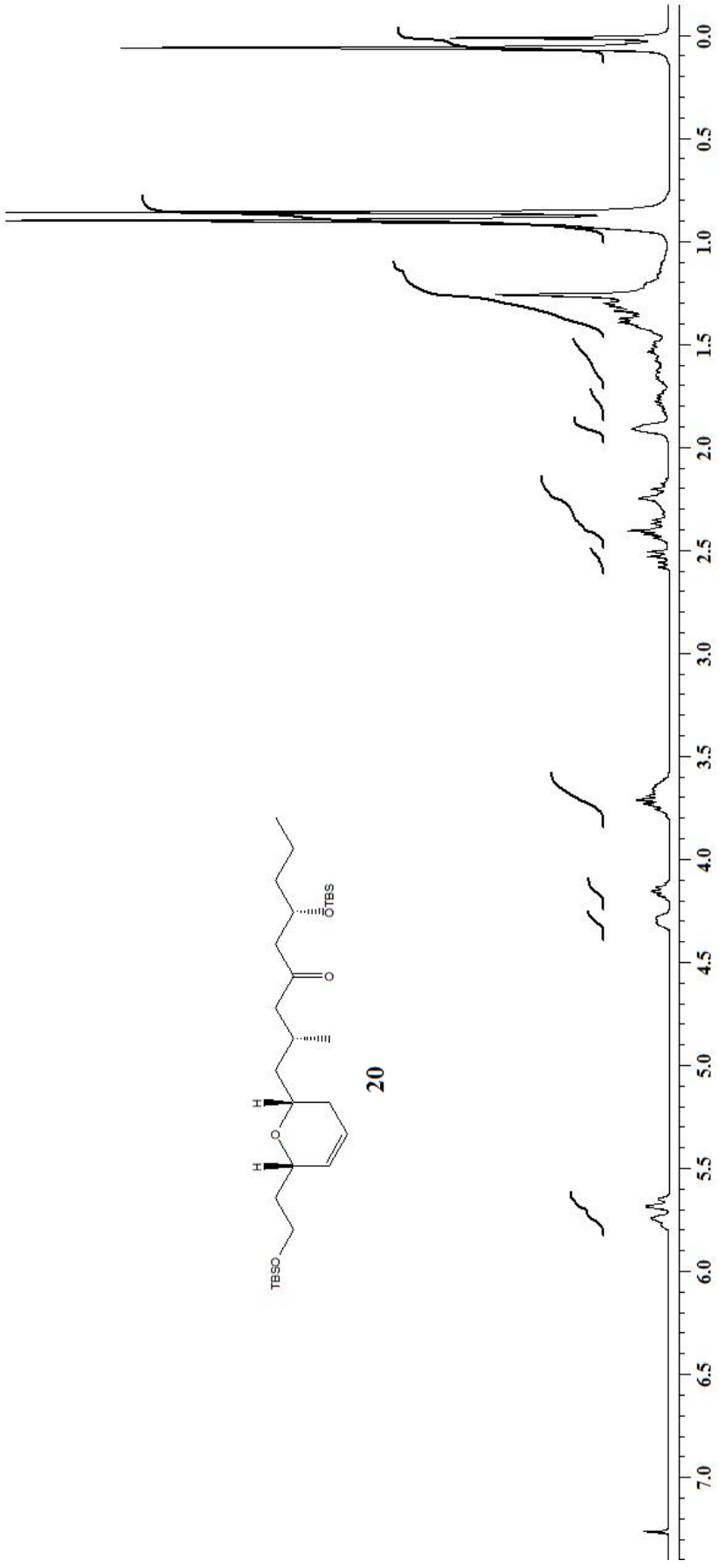
^{1}H NMR Spectrum of Compound 19



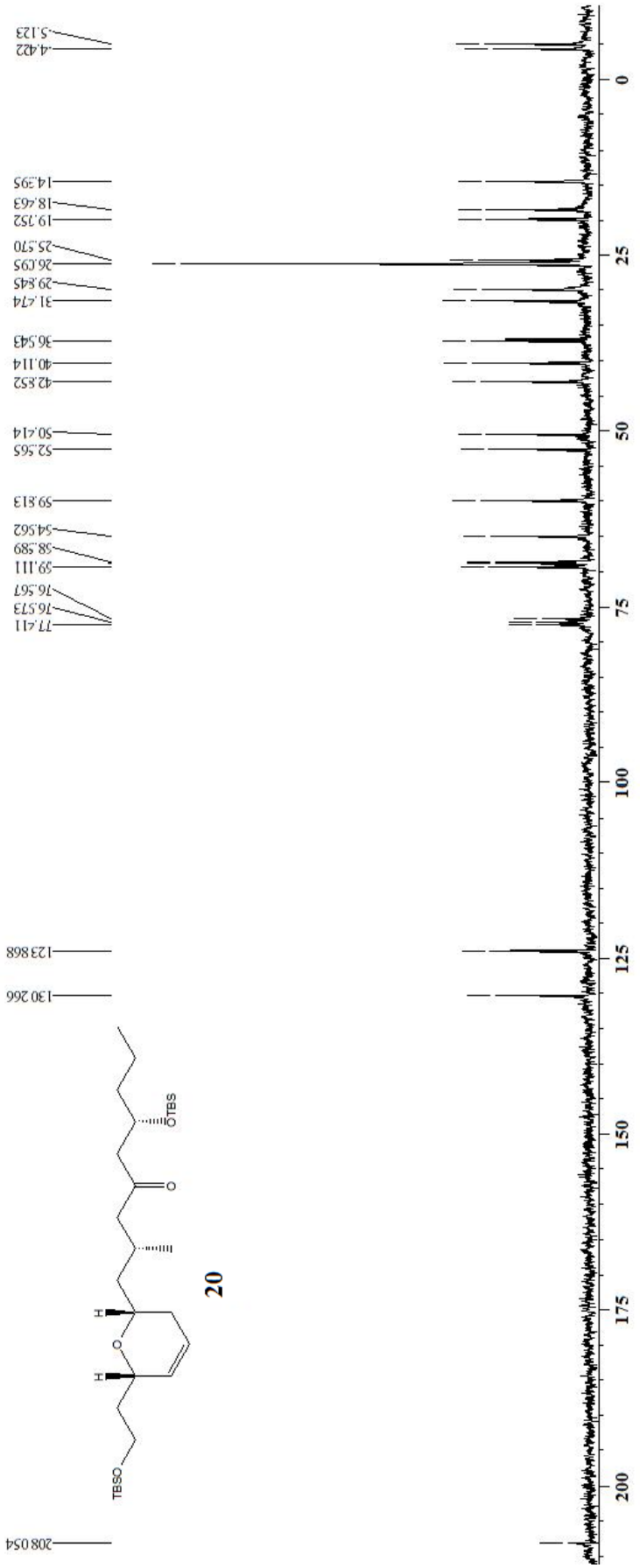
^{13}C NMR Spectrum of Compound 19



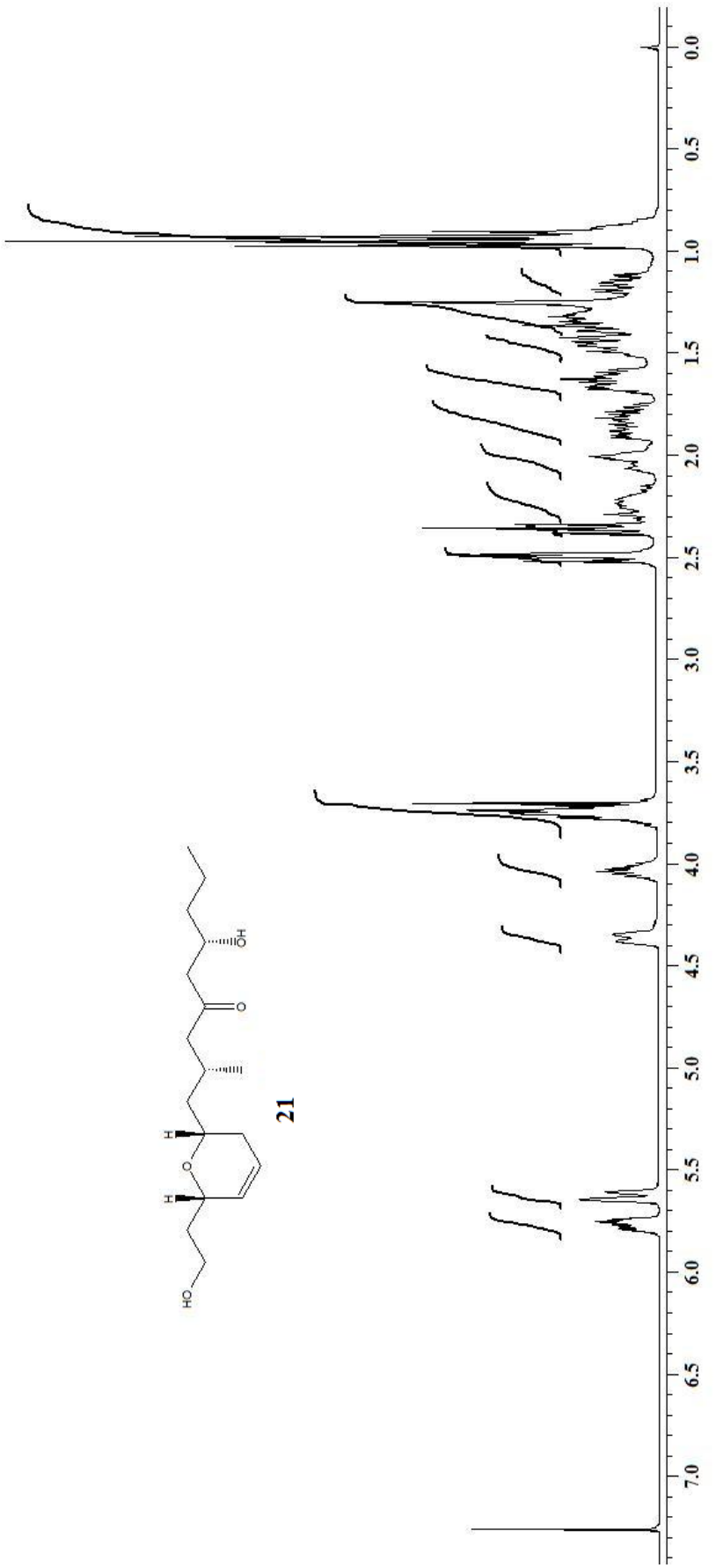
^{1}H NMR Spectrum of Compound 20



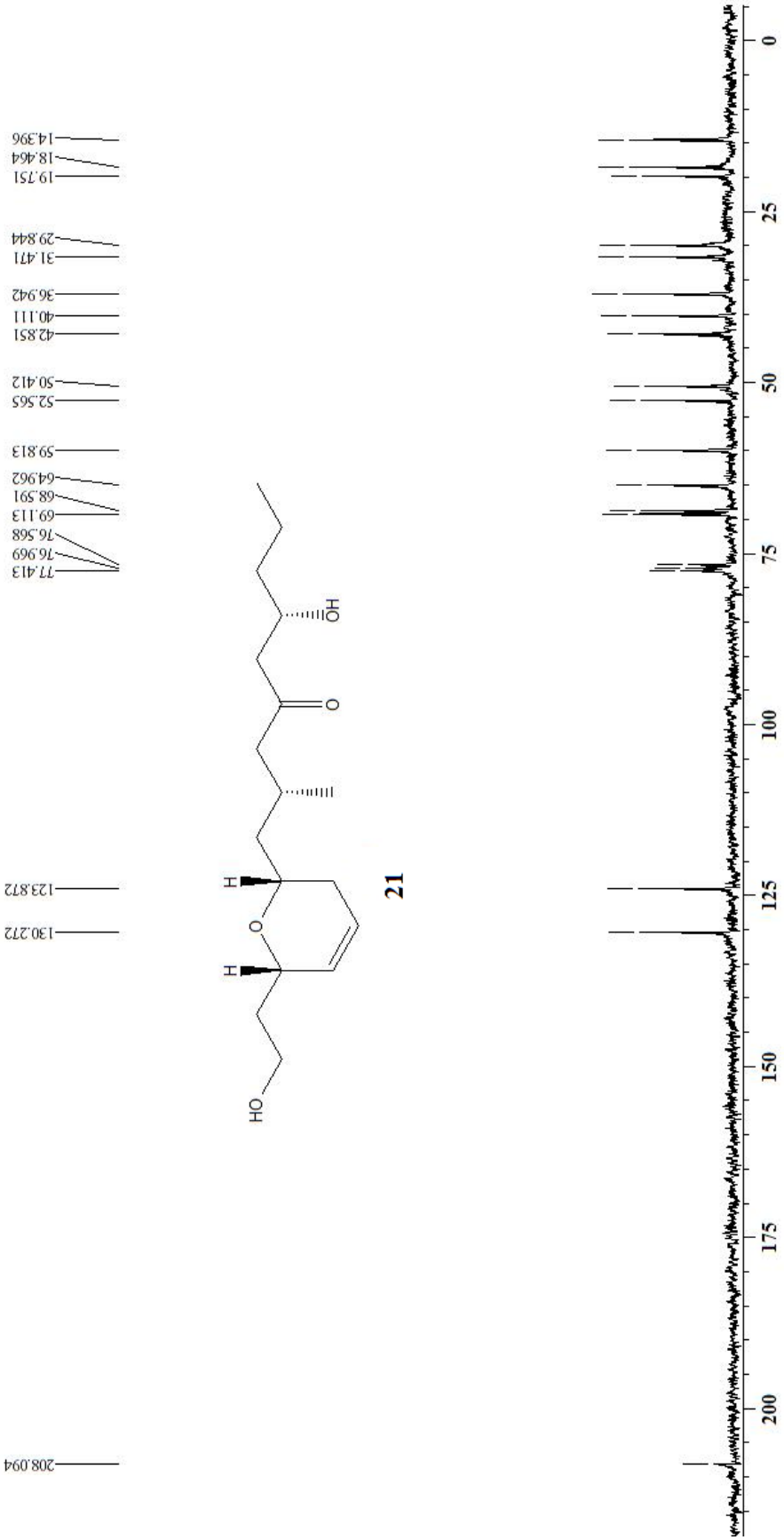
^{13}C NMR Spectrum of Compound 20



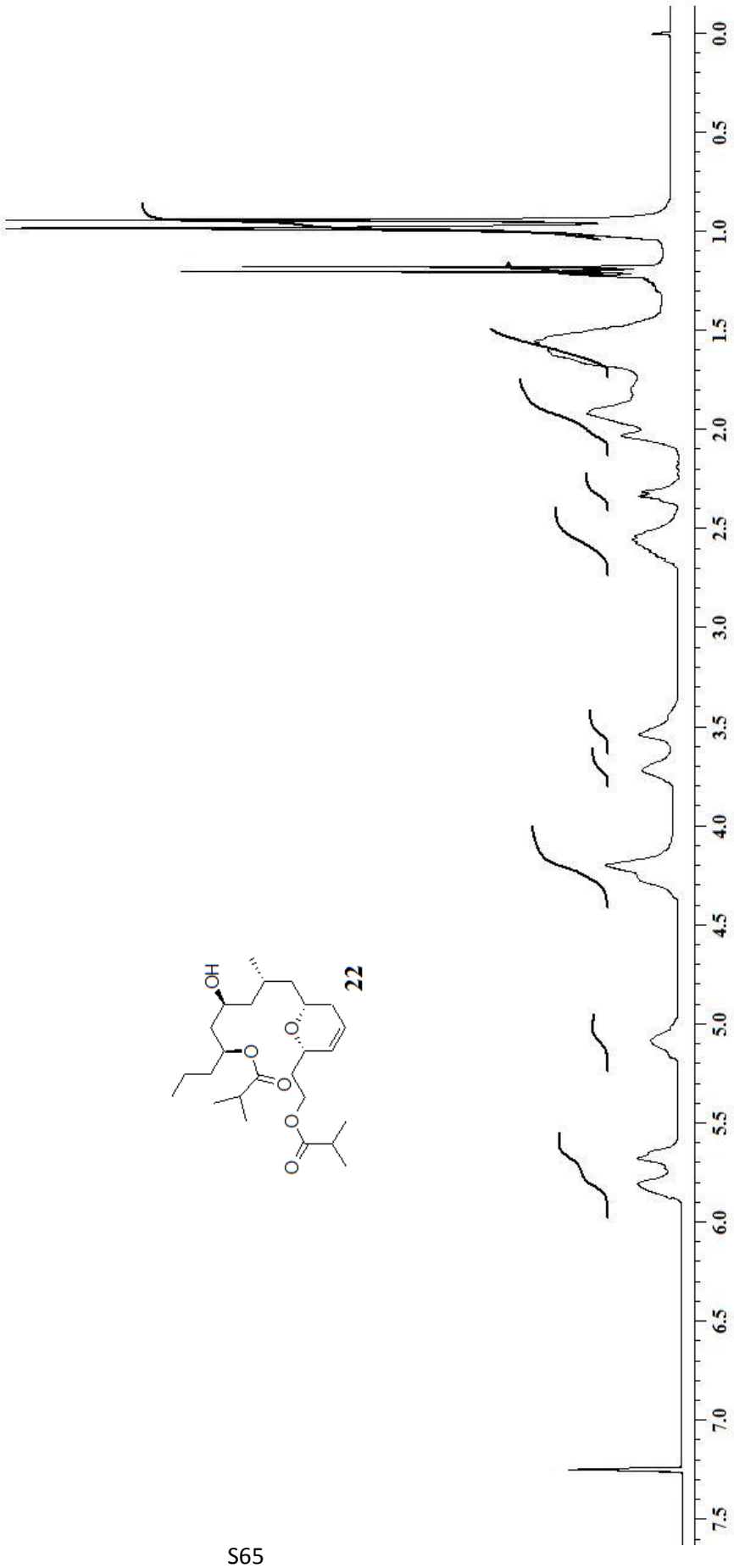
^{1}H NMR Spectrum of Compound 21



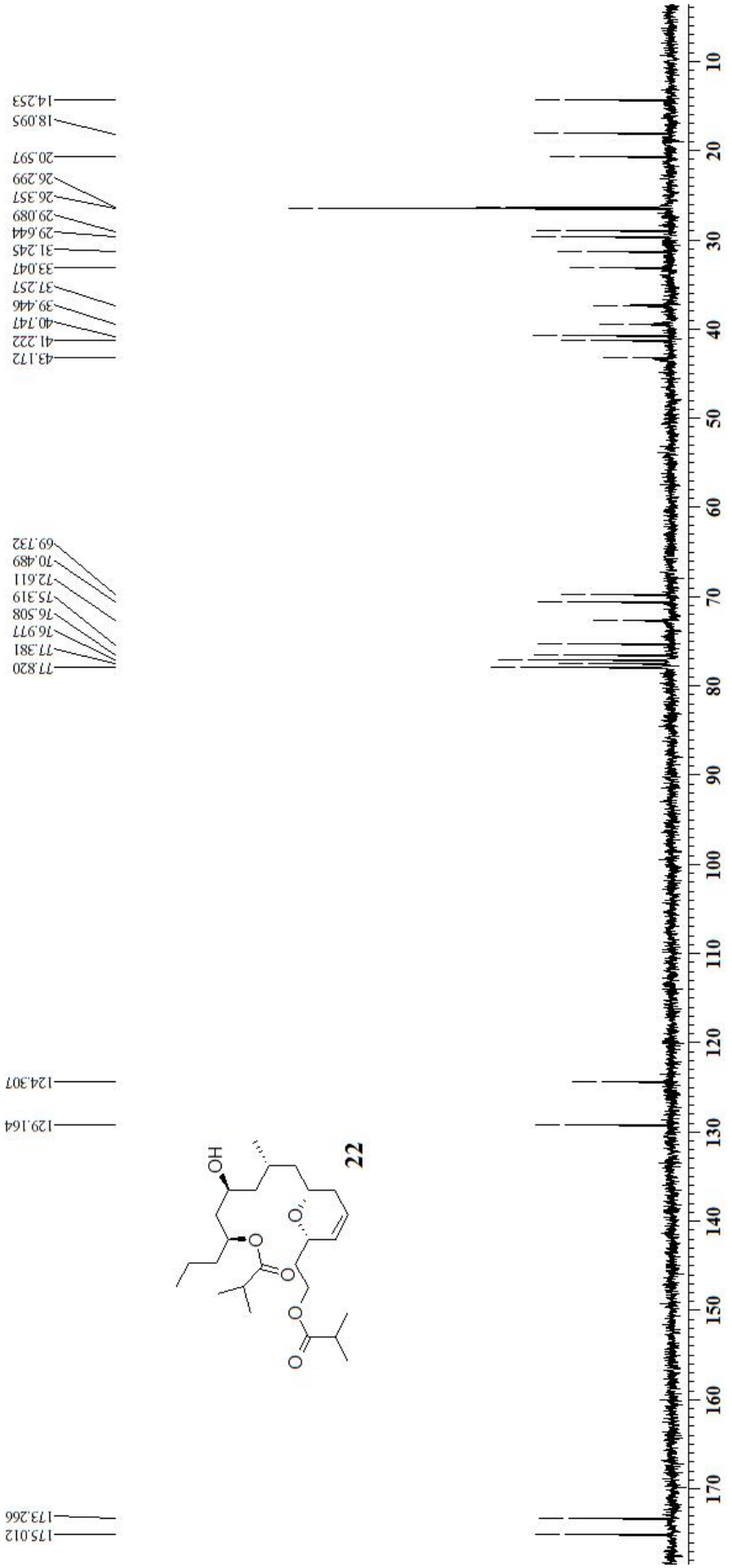
^{13}C NMR Spectrum of Compound 21



^{1}H NMR Spectrum of Compound 22



^{13}C NMR Spectrum of Compound 22



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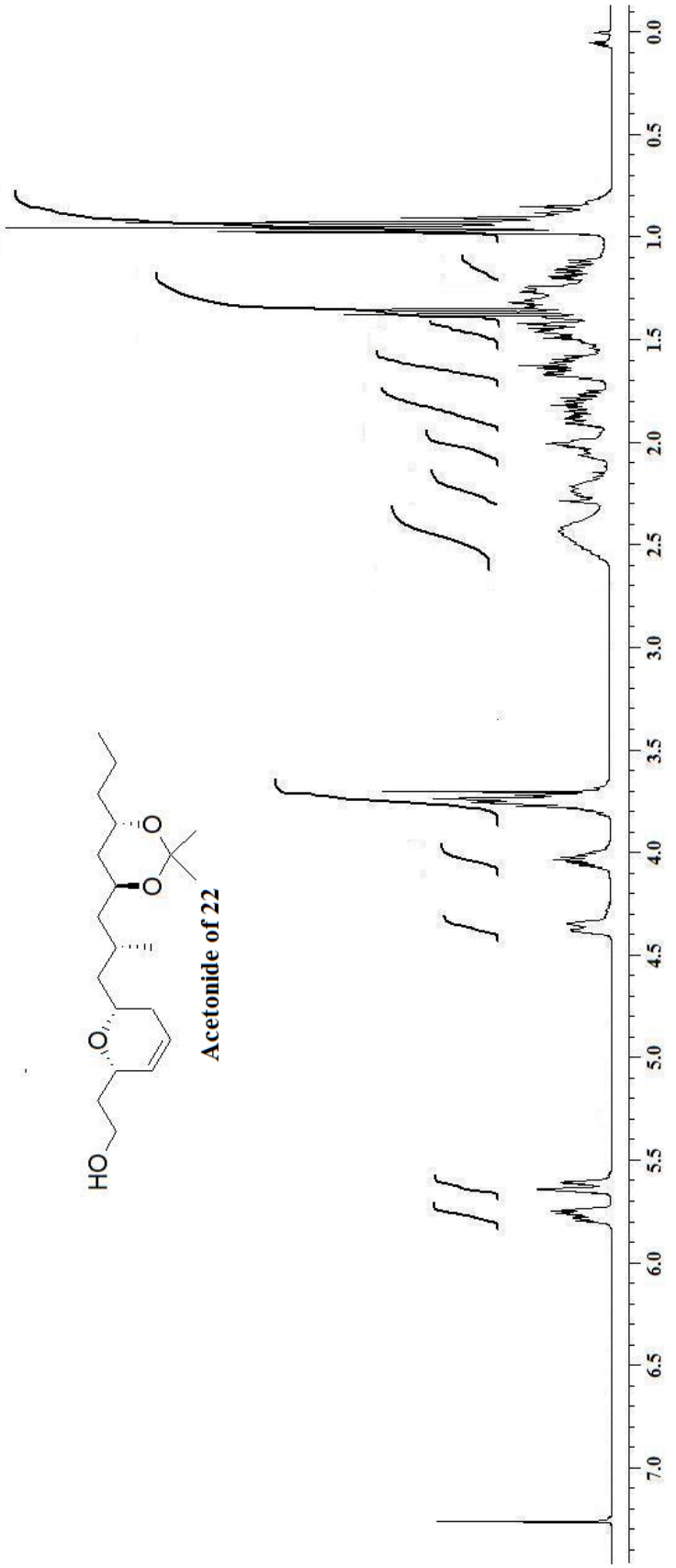
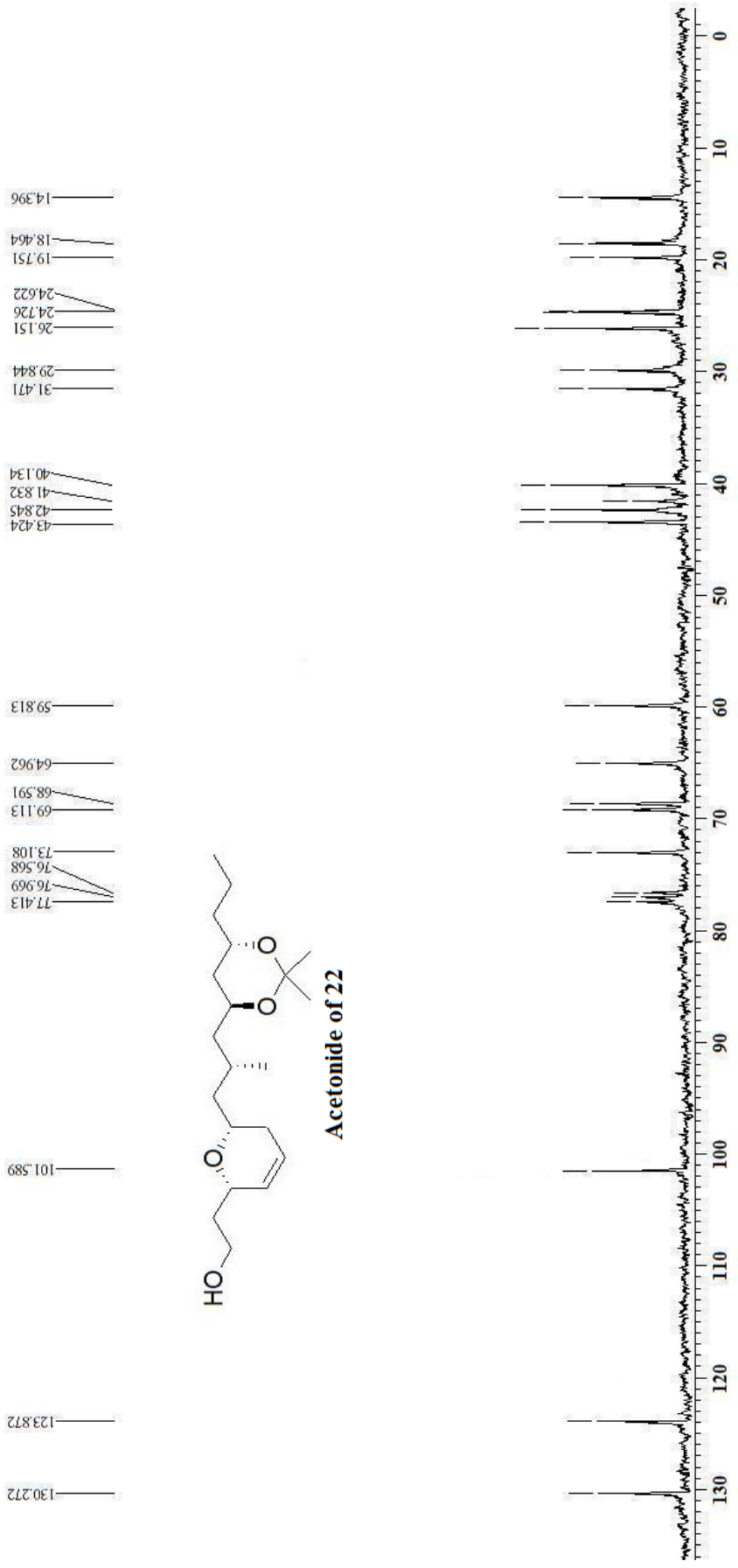
^{1}H NMR Spectrum for acetonide of 22

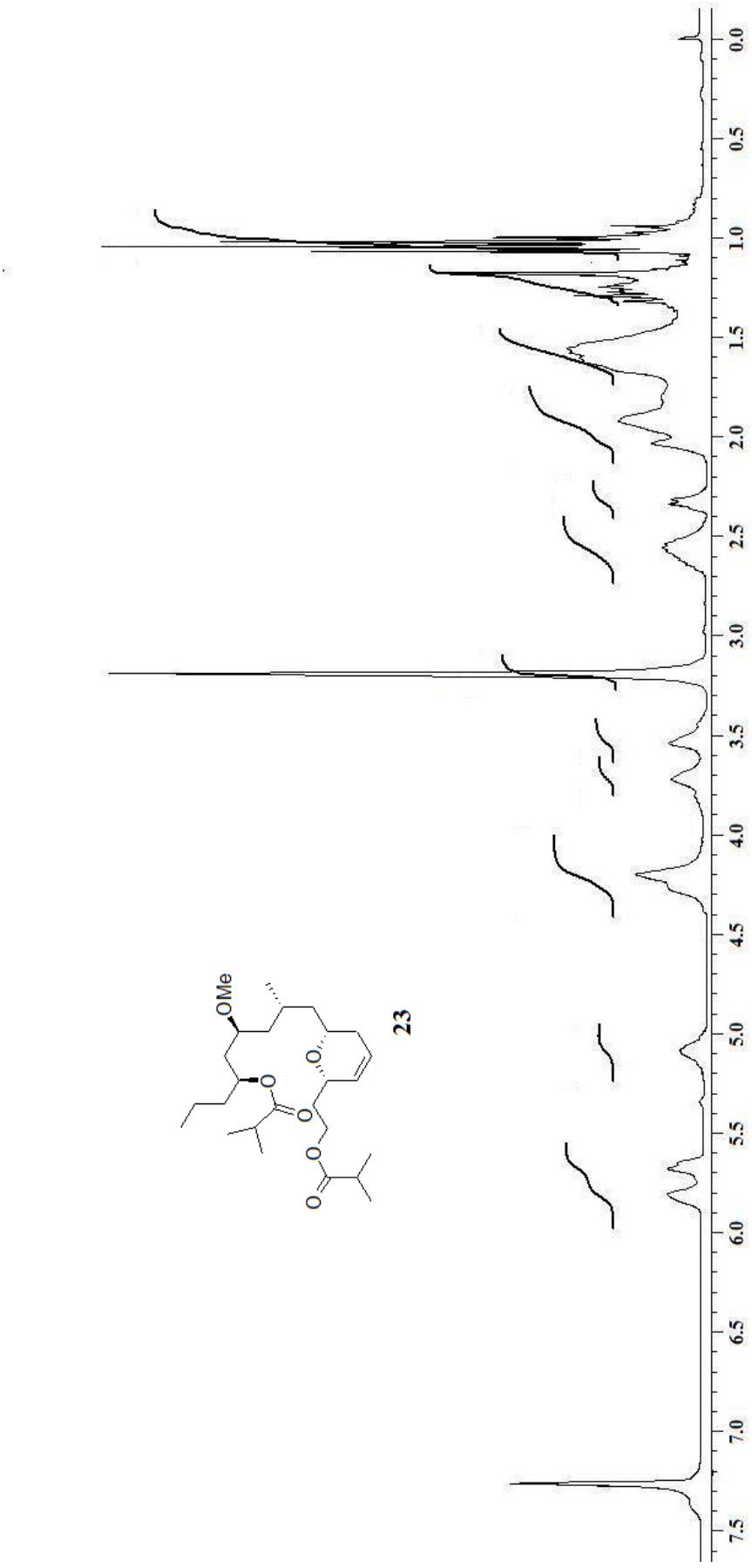


^{13}C NMR Spectrum for acetonide of 22

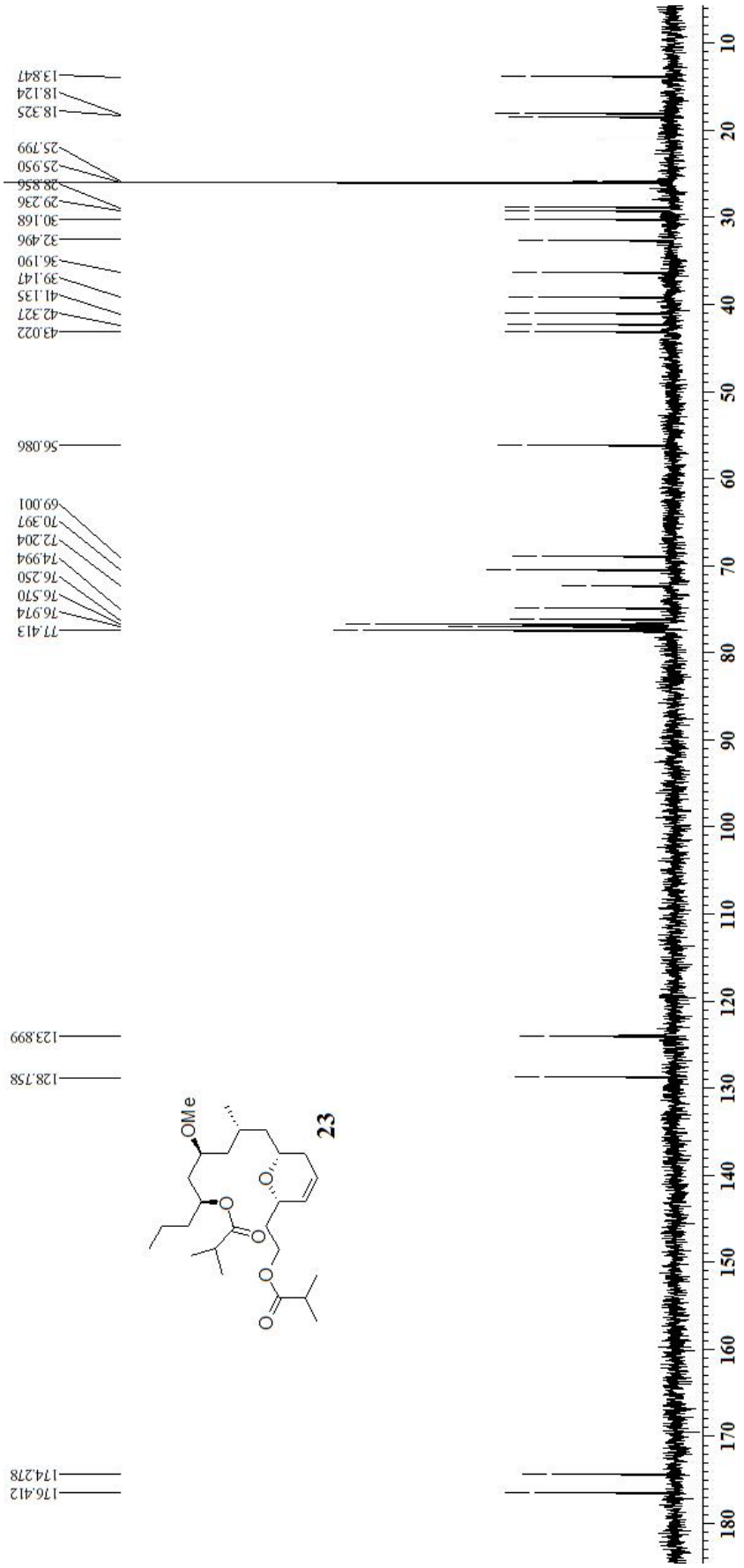


Acetonide of 22

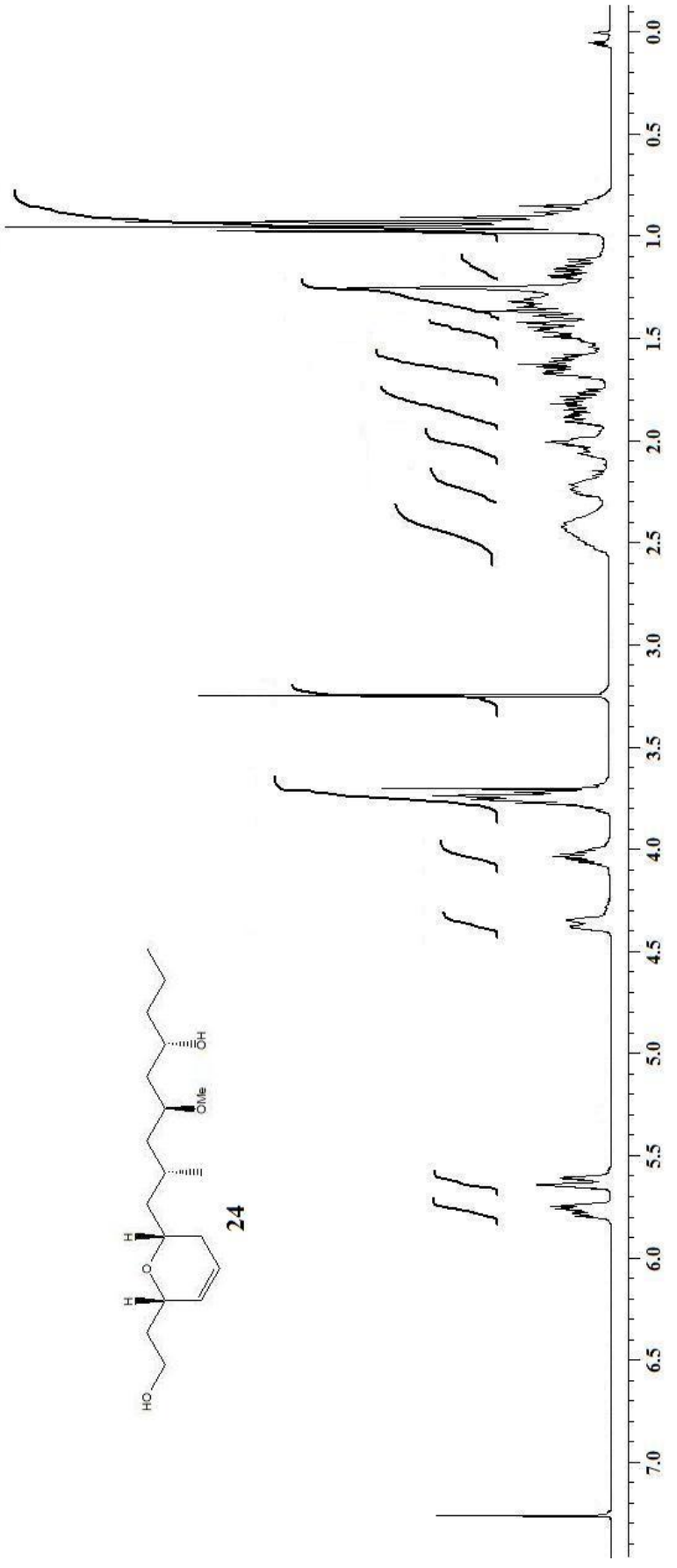
^{1}H NMR Spectrum of Compound 23



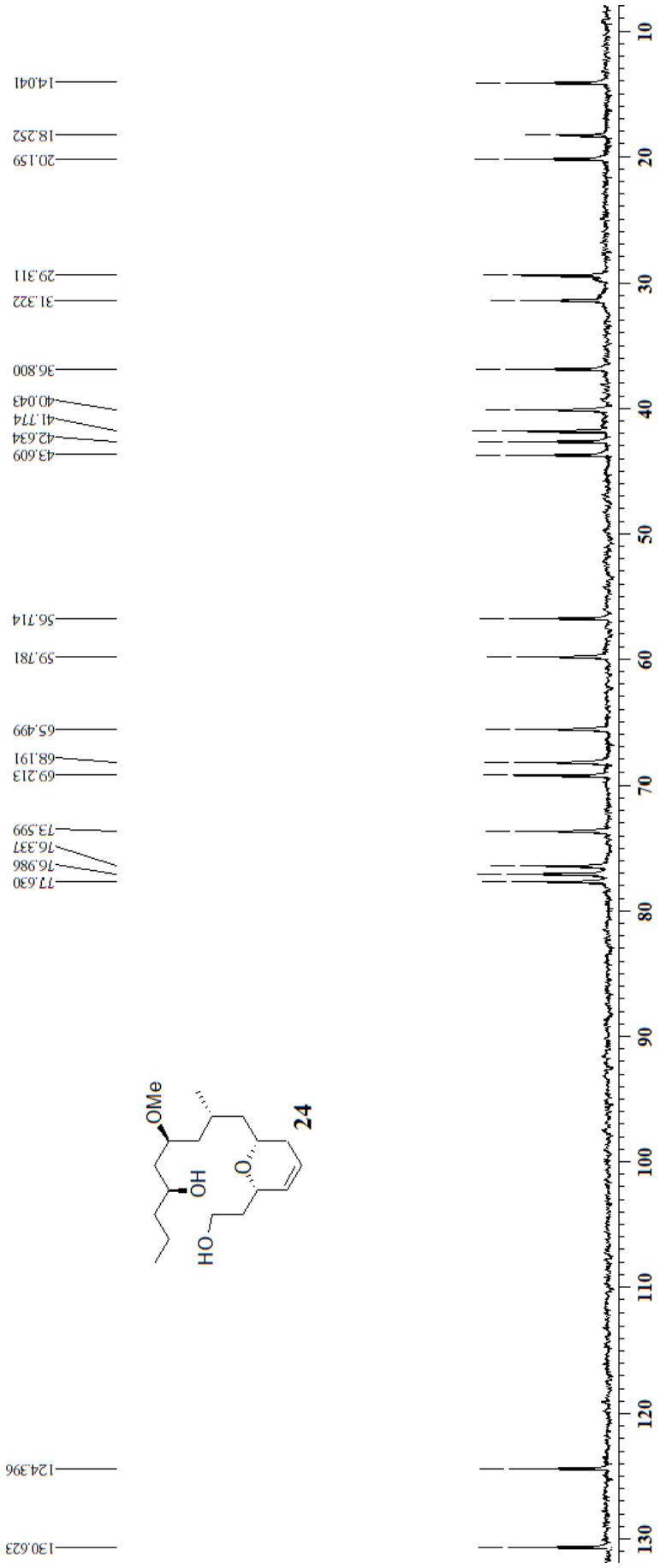
^{13}C NMR Spectrum of Compound 23



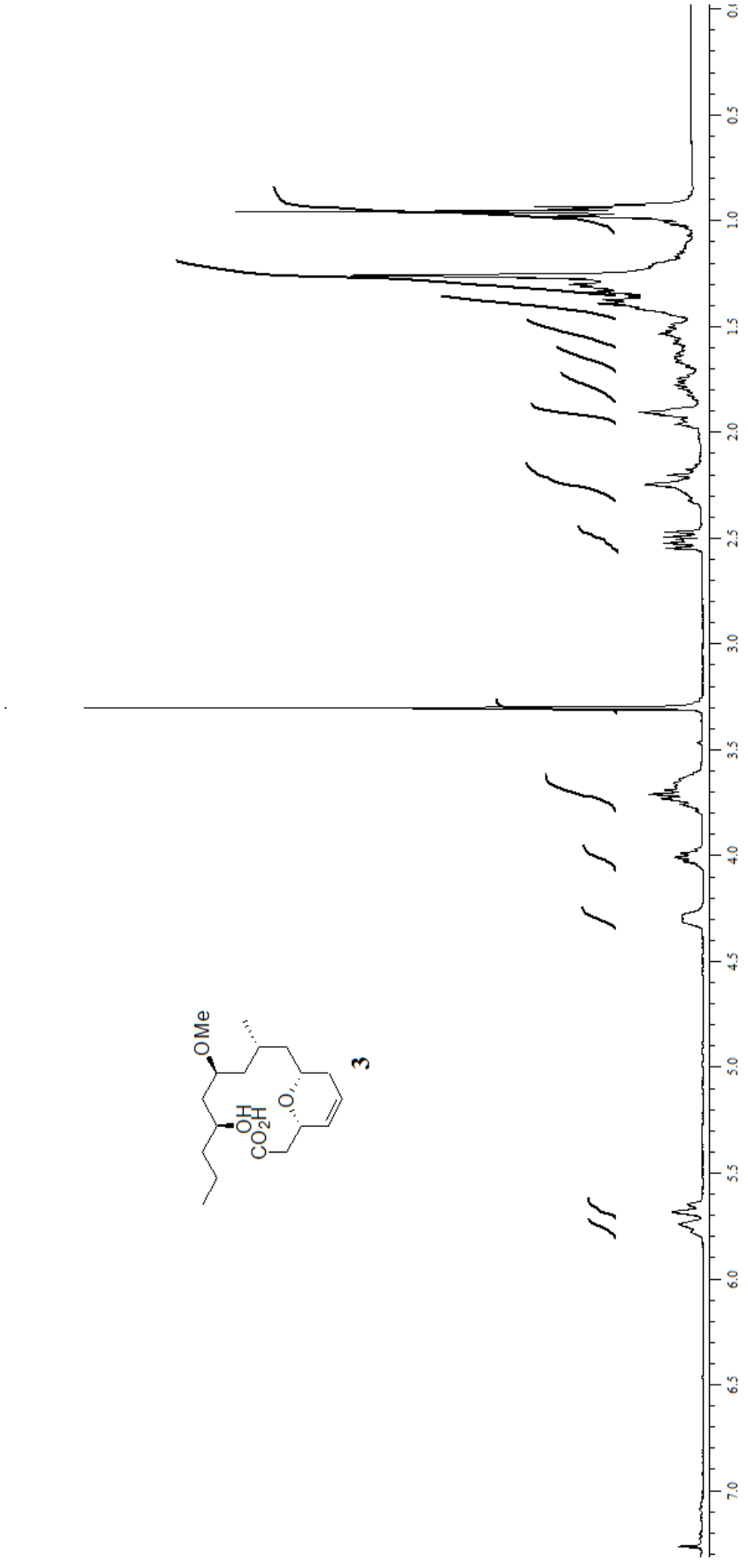
^{1}H NMR Spectrum of Compound 24



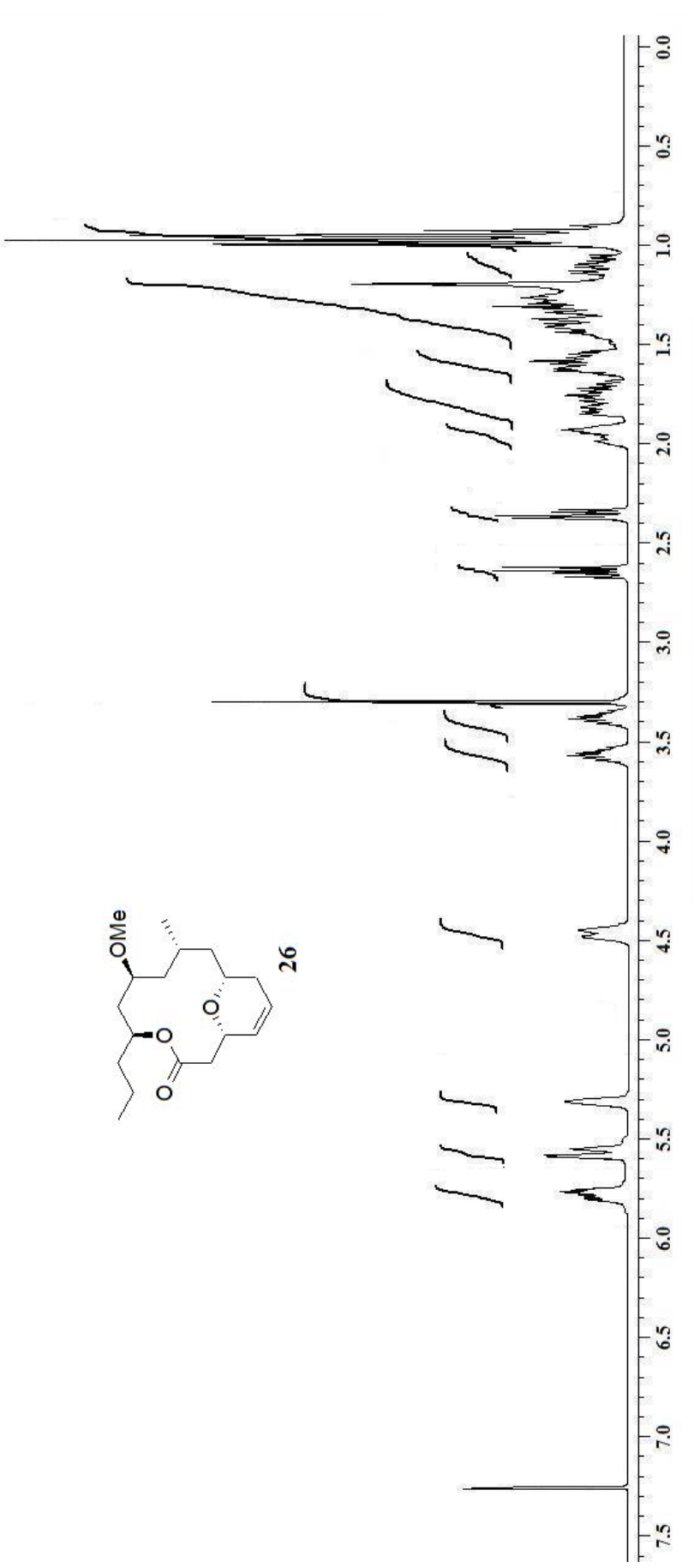
^{13}C NMR Spectrum of Compound 24



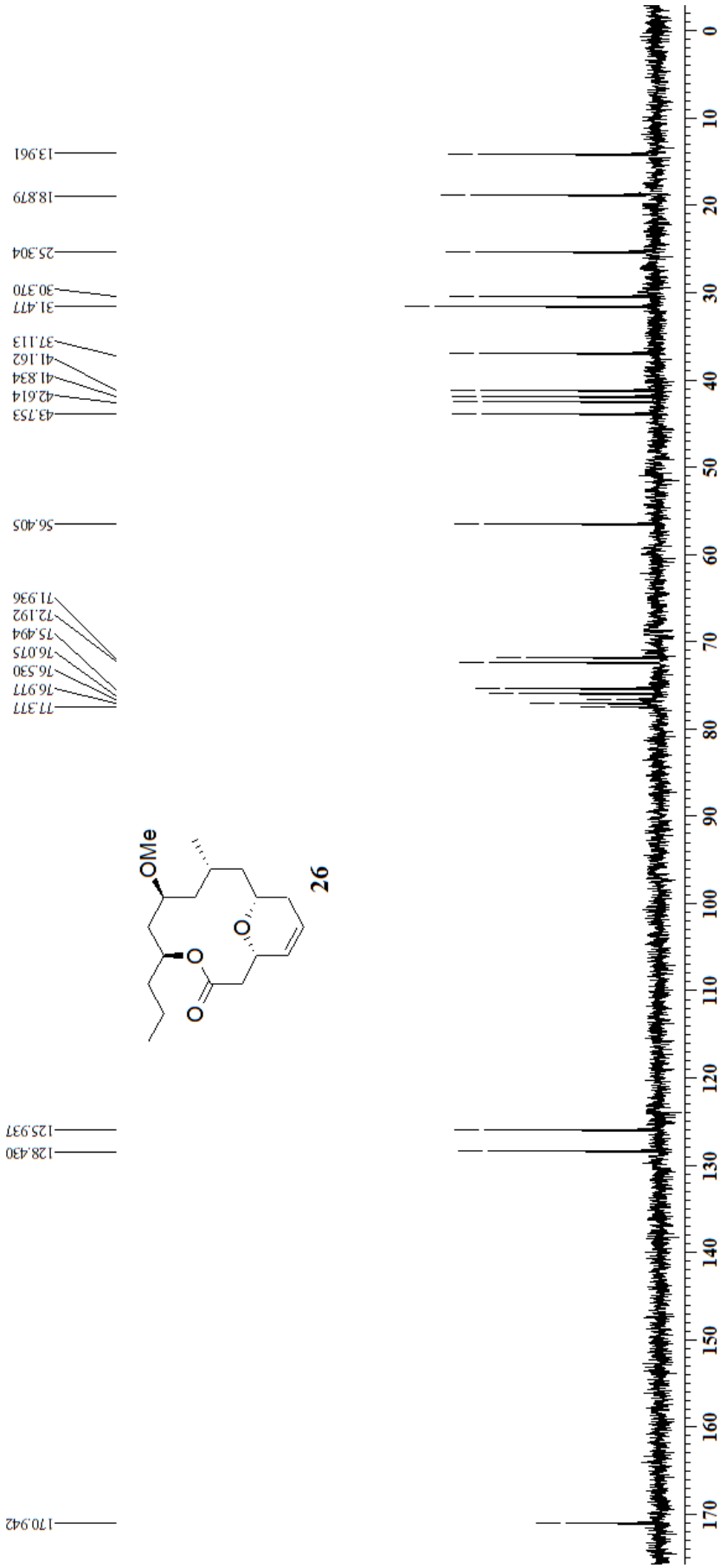
^{1}H NMR Spectrum of Compound 3



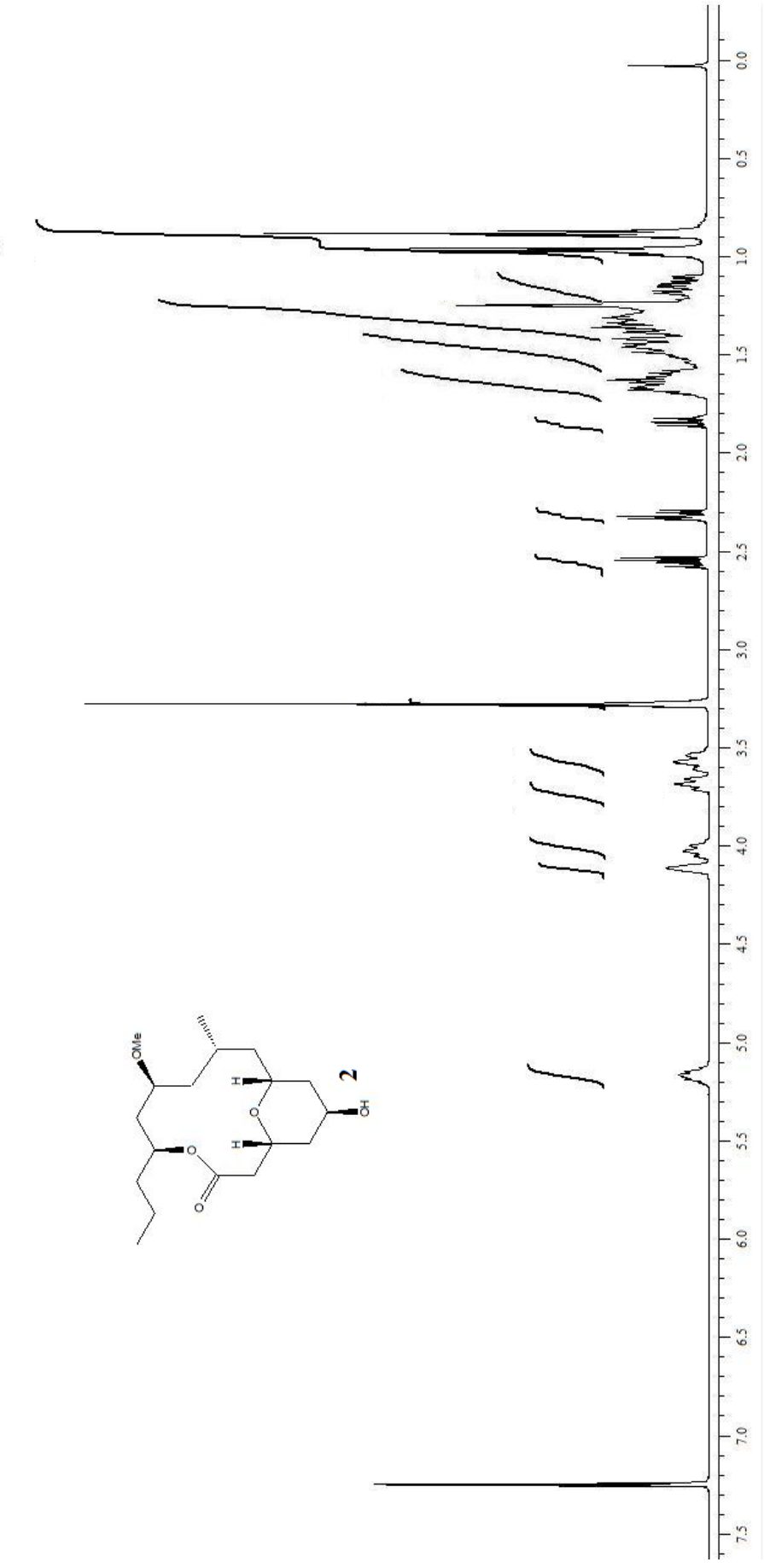
^{1}H NMR Spectrum of Compound 26



^{13}C NMR Spectrum of Compound 26



^{1}H NMR Spectrum of Compound 2



^{13}C NMR Spectrum of Compound 2