Palladium-Catalyzed Enantioselective Addition of Two Distinct Nucleophiles across Alkenes Capable of Quinone Methide Formation

Supporting Information

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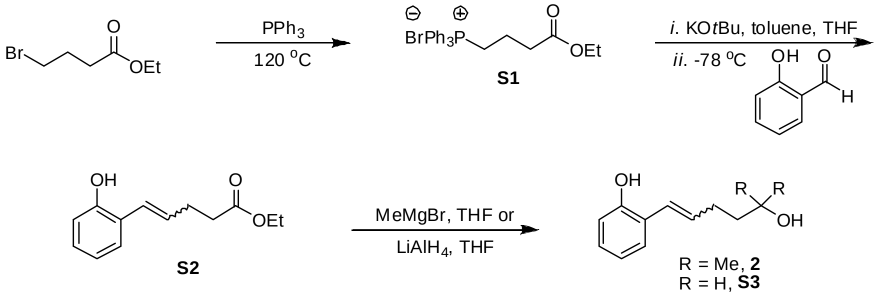
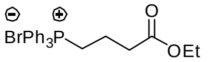
General Information: Unless otherwise noted, all reactions were performed under a nitrogen atmosphere with stirring. Toluene, dichloromethane, dichloroethane and THF were dried before use by passing through a column of activated alumina. Methanol was distilled from magnesium methoxide. Triethylamine was distilled from CaH$_2$. 3Å molecular sieves were powdered and activated by flame heating under vacuum (ca. 3 min). *n*-Butanol, *n*-Butenol and etheleneglycol monomethylether were purified by distillation from MgSO$_4$. All other reagents were purchased from commercial sources and used without further purification. Yields were calculated for material judged homogeneous by thin-layer chromatography and NMR. Thin-layer chromatography was performed with EMD silica gel 60 F254 plates eluting with the solvents indicated, visualized by a 254 nm UV lamp, or stained either with potassium permanganate, *p*-anisaldehyde, phosphomolybdic acid, or ninhydrin. Flash column chromatography was performed with EcoChrom MP Silitech 32-63D 60Å silica gel, or with Brockmann I activated basic alumina (pH 9-10), slurry packed with solvents indicated in glass columns. Nuclear magnetic resonance spectra were acquired at 300, 400, or 500 MHz for ^{1}H, and 75, 100, or 125 MHz for ^{13}C. Chemical shifts for proton nuclear magnetic resonance (^{1}H NMR) spectra are reported in parts per million downfield relative to the line of CHCl$_3$ singlet at 7.26 ppm. Chemical shifts for carbon nuclear magnetic resonance (^{13}C NMR) spectra are reported in parts per million downfield relative to the center-line of the CDCl$_3$ triplet at 77.23 ppm. The abbreviations s, d, t, dd, td, ddd, and m stand for the resonance multiplicities singlet, doublet, triplet, doublet of doublets, triplet of doublets, doublet of doublets of doublets, and multiplet, respectively. Optical rotations were obtained (Na D line) using a Perkin Elmer Model 343 Polarimeter fitted with a micro cell with a 1 dm path length; concentrations are reported in g/100 mL. IR spectra were recorded using a Nicolate FTIR instrument. GC (gas chromatography) analysis was performed using a Hewlett Packard HP 6890 Series GC system fitted with a HP-Chiral permethylated β-cyclodextrin column. HPLC (high pressure liquid chromatography) analysis was performed using a Hewlett Packard Series 1100 instrument fitted with a chiral stationary phase (as indicated). SFC (supercritical fluid chromatography) analysis was performed at 40 °C, using a Thar instrument fitted with a chiral stationary phase (as indicated). HRMS (high resolution mass spectrometry) analysis was performed using Waters LCP Premier XE. Glassware for all reactions was oven-dried at 110 ^{o}C and cooled in a dry atmosphere prior to use.

Substrate Synthesis:

Synthesis of 2 and S3:



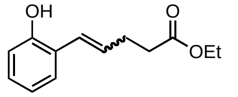
Preparation of (4-ethoxy-4-oxobutyl)triphenylphosphonium bromide (S1):



To a 500 mL oven dried round bottom flask equipped with a stir bar was added 38.0 g of triphenylphosphine (145 mmol, 1.41 equiv.) and 20.0 g of ethyl-4-bromobutanoate (102 mmol, 1.00 equiv.) under a nitrogen atmosphere. The flask was then fitted with condenser and the reaction mixture was heated to 120 °C for 16 h. The reaction mixture was then allowed to cool to room temperature then 20 mL of CH_2Cl_2 was added and it was sonicated for 1 h. To this diethyl ether was added until no further precipitation of product was observed. The precipitate was filtered and rinsed with 100 mL ether to give **2** in quantitative yield. *The product was dried under vacuum at 100 °C for 10 h immediately prior to use.*

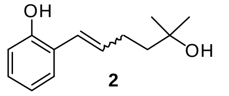
The ^{1}H NMR spectrum matched with previously reported ^{1}H NMR.[1]

Preparation of ethyl 5-(2-hydroxyphenyl)pent-4-enoate (S2):



To an oven-dried 500 mL round bottom flask equipped with a stir bar was added 23.4 g of **S1** (51.0 mmol, 2.30 equiv.) and 200 mL toluene. To this was added a solution of 5.80 g KO^{t}Bu (51.2 mmol, 2.33 equiv.) in 40 mL of THF dropwise *via* cannulation. The reaction mixture slowly turned a deep red color over 4 h. The mixture was cooled to –78 °C and 2.70 g of salicylaldehyde (22.2 mmol, 1.00 equiv.), dissolved in 20 mL of toluene was added dropwise *via* cannulation. The mixture was allowed to slowly warm to ambient temperature and stirred 48 hours then quenched with 50 mL of saturated NH_4Cl solution. The mixture was diluted with 100 mL of diethyl ether and washed with 100 mL (2 x 50 mL) of water and 60 mL of brine. The organic layer was dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*. The crude mixture was purified by flash silica-gel column chromatography with 10%-20% EtOAc/Hexanes as eluent to give 4.15 g of **S2** (85% yield, average of two reactions). Isomeric ratio (E/Z): 10:1, Major isomer: $R_f = 0.52$ w/ 33% EtOAc/Hexane, colorless oil, ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.02-7.28 (m, 2 H), 6.85-6.95 (m, 2 H), 6.38-6.48 (d, *J* = 11.2 Hz, 2 H), 5.89 (s, 1 H), 5.74-5.86 (m, 1 H), 4.08-4.16 (m, 2 H), 2.37-2.48 (m, 4 H), 1.18-1.29 (m, 3 H). ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$) δ = 173.3, 153.1, 134.4, 129.9, 128.8, 125.1, 123.8, 120.5, 116.1, 60.9, 33.9, 24.3, 14.3. IR 3392, 2981, 1705, 1450, 1269, 1195, 1154, 754 cm^{-1}. HRMS $C_{13}H_{16}O_3$ $(M+Na)^+$ calcd. 243.0997, obsvd. 243.0996.

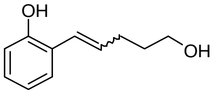
Preparation of 2-(5-hydroxy-5-methylhex-1-enyl)phenol (2):



2

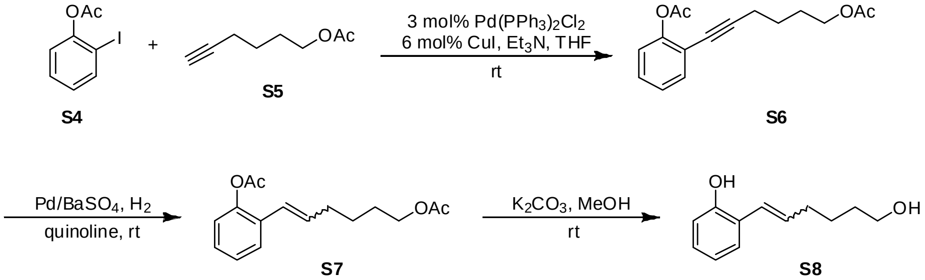
To an oven dried 500 mL round bottom flask equipped with a stir bar was added 4.10 g of **S2** (18.6 mmol, 1.00 equiv.) in 180 mL THF. To this was slowly added a solution of 3.0 M MeMgBr (130 mmol, 7.00 equiv.) at 0 °C. The reaction mixture was then allowed to warm to room temperature and was stirred for 12 h. The reaction was quenched by the slow addition of 20 mL of 1 M HCl solution. The mixture was diluted with 50 mL of diethyl ether and washed with 100 mL (2 x 50 mL) of water and 60 mL of brine. The organic extract was dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The crude mixture was purified by flash silica-gel column chromatography with 1 L of 50% Hexane/EtOAC as eluent to give 3.34 g of **2** in 87% yield. Isomeric ratio (E/Z): 10:1, Major isomer: $R_f = 0.32$ w/ 33% EtOAc/Hexane, colorless solid. MP = 74-75 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.28-7.07 (m, 2 H), 6.95-6.87 (m, 2 H), 6.40-6.37 (*d*, *J* = 10.9 Hz), 5.95-5.88 (m, 1 H), 5.34 (s, 1 H), 2.28-2.19 (m, 2 H), 1.67-1.57 (m, 2 H), 1.19 (s, 6 H). ^{13}C-NMR {^{1}H} (100 MHz, $CDCl_3$): δ 152.9, 137.0, 129.8, 128.8, 123.9, 123.4, 120.4, 115.5, 71.3, 43.3, 29.4, 24.1. IR 3410, 3013, 2971, 1604, 1448, 1377, 1261, 1210, 1147, 1131, 904, 755 cm^{-1}. HRMS $C_{13}H_{18}O_2$ $(M+Na)^+$ calcd. 229.1204, obsvd. 229.1201.

Preparation of (*E*)-2-(5-hydroxypent-1-enyl)phenol (S3):



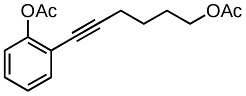
To a 100 mL oven dried round bottom flask equipped with a stir bar was added 1.6 g **S2** (7.27 mmol, 1 equiv.) followed by 40 mL THF under a nitrogen atmosphere. The reaction mixture was cooled to 0 °C. To this was added 544 mg $LiAlH_4$ portion wise (14.5 mmol, 2 equiv.). The reaction mixture was allowed to slowly warm to ambient temperature and stirred overnight. The reaction mixture was cooled to 0 °C, and quenched by the sequential addition of 544 μL of water, 544 μL 15% NaOH, and 1630 μL water. The reaction mixture was warmed to room temperature, $MgSO_4$ was added, and the mixture was stirred for 15 min and then filtered. The filtrate was concentrated *in vacuo* and the crude mixture was purified by silica gel column chromatography with 1:3 EtOAc:Hexanes to give 777 mg of **S3** (60% yield, average of two reactions). Isomeric ratio (E/Z): 10:1, Major isomer: $R_f = 0.20$ w/ 33% EtOAc/Hexanes, white solid. MP = 45-47 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.06-7.21 (m, 2 H), 6.83-6.94 (m, 2 H), 6.38-6.46 (*d*, *J* = 11.2 Hz, 1 H), 5.82-5.95 (m, 1 H), 3.59-3.68 (*t*, *J* = 6.4Hz, 2 H), 2.17-2.25 (m, 2 H), 1.62-1.74 (m, 2 H). ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$) δ = 135.9, 130.0, 128.8, 124.1, 120.4, 115.6, 62.7, 32.1, 25.5. IR 3404, 2938, 2881, 1604, 1448, 1358, 1269, 1225, 1036, 841 cm^{-1}. HRMS $C_{11}H_{14}O_2$ $(M+Na)^+$ calcd. 201.0886, obsvd. 201.0886.

Synthesis of S8:



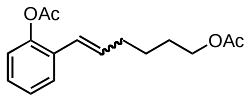
S4,[2] **S5,**[3] and $Pd(PPh_3)_2Cl_2$[4] were prepared according to literature procedure.

Synthesis of 2-(6-acetoxyhex-1-ynyl)phenyl acetate (S6):



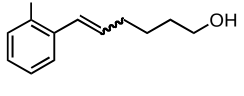
To an oven-dried 100 mL Schlenk flask was added 2.096 g of **S4** (8.000 mmol, 1 equiv.) and 40 mL of triethylamine. The solution was degassed by 2 cycles of freeze-pump-thaw. To a second oven-dried Schlenk flask was added 1.256 g of **S5** (8.96 mmol, 1.120 equiv.), 20 mL of triethylamine and 40 mL of THF. The solution was degassed by 2 cycles of freeze-pump-thaw. To an oven-dried 250 mL round bottom flask equipped with stir bar was added 169 mg of $Pd(PPh_3)_2Cl_2$ (0.240 mmol, 0.0300 equiv.) and 91.4 mg of CuI (0.480 mmol, 0.0600 equiv.). The solutions of **S4** and **S5** were sequentially cannulated into the flask containing the catalysts. The reaction mixture was then stirred at rt overnight. The reaction mixture was diluted with 50 mL of diethyl ether and then 50 mL of 1 M HCl was added and the mixture was allowed to stir for 30 min. The organic layer was washed with 50 mL of 1 M HCl (2 x 25 mL) and 20 mL of brine. The organic extract was dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The crude mixture was purified by flash silica-gel column chromatography with 10% to 20% Hexane/EtOAc as eluent to give 2.0265 g of **S6** (92.3% yield, average of two reactions). $R_f = 0.20$ w/ 20% EtOAc/Hexane, colorless oil, ^{1}H-NMR (300 MHz, $CDCl_3$) $\delta = 7.44$ (dd, $J = 7.6$ Hz, $J = 1.7$ Hz, 1 H), 7.30 (ddd, $J = 8.0$ Hz, $J = 7.6$ Hz, $J = 1.7$ Hz, 1 H), 7.17 (ddd, $J = 7.6$ Hz, $J = 7.6$ Hz, $J = 1.4$ Hz, 1 H), 7.05 (dd, $J = 8.1$ Hz, $J = 1.4$ Hz, 1 H), 4.11 (t, $J = 6.5$ Hz, 2 H), 2.47 (t, $J = 6.9$ Hz, 2 H), 2.33 (s, 3 H), 2.06 (s, 3 H), 1.84-1.76 (m, 2 H), 1.71-1.63 (m, 2 H). ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$) $\delta = 171.4$, 169.1, 151.7, 133.3, 129.0, 126.1, 122.3, 118.0, 94.7, 76.2, 64.1, 28.0, 25.4, 21.2, 21.1, 19.4. IR: 1761, 1733, 1487, 1366, 1237, 1207, 1180, 1037, 907, 755 cm^{-1}. HRMS $C_{16}H_{18}O_4$ $(M+Na)^+$ calcd. 297.1103, obsvd. 297.1097.

Synthesis of (*E*)-2-(6-acetoxyhex-1-enyl)phenyl acetate (S7):



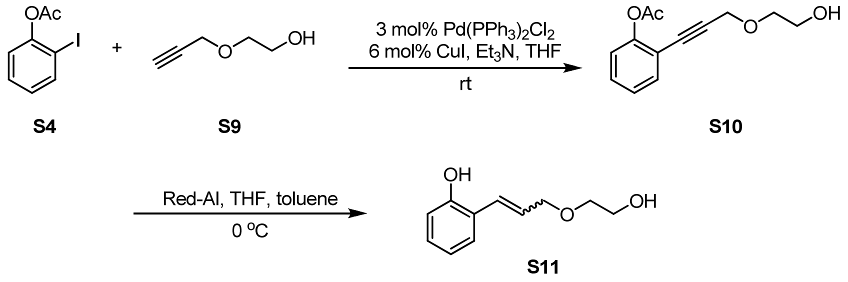
To an oven dried 50 mL Schlenk flask equipped with a stir bar was added 261 mg of 5% Pd/$BaSO_4$, 150 µL of quinoline (1.27 mmol, 0.42 equiv.) and 5 mL of MeOH. A three-way joint fitted with a balloon of H_2 was attached and the flask. To a separate, oven-dried 50 mL round bottom flask was added 823 mg of **S6** (3.00 mmol) and 10 mL MeOH. The solution of **S6** is transferred via cannula to the Schlenk flask. An additional 5 mL of MeOH was used for rinsing. The Schlenk flask was evacuated and refilled with H_2 three times. Upon completion as determined by TLC (four days), the reaction mixture was filtered through plug of celite® using 50 mL of MeOH. The filtrate was concentrated *in vacuo* and dissolved in 100 mL of dichloromethane, washed with 100 mL 0.2 M HCl (2 x 50 mL) and 50 mL brine, dried over Na_2SO_4, filtered, and the solvent was removed *in vacuo*. The crude mixture was purified by flash silica-gel column chromatography with 1:4 EtOAc:Hexanes as eluent to give 576 mg of **S6** as a 10:1 mixture of alkene isomers (75% yield, average of 2 reactions). $R_f = 0.60$ w/ 2:3 EtOAc:Hexanes, colorless oil. Major isomer: ^{1}H-NMR (300 MHz, $CDCl_3$) $\delta = 7.30$-7.15 (m, 3 H), 7.08-6.98 (m, 1 H), 6.30 (d, $J = 11.5$ Hz, 1H), 5.72 (ddd, $J = 14.7$ Hz, $J = 11.5$ Hz, $J = 7.3$ Hz, 1 H), 4.03 (t, $J = 6.6$ Hz, 2 H), 2.27 (s, 3 H), 2.21 (ddd, $J = 14.7$ Hz, $J = 7.4$ Hz, $J = 1.7$ Hz, 2 H), 2.06 (s, 3 H), 1.68-1.40 (m, 4 H). ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$) $\delta = 171.4$, 169.4, 148.6, 134.4, 130.6, 130.5, 128.2, 125.9, 123.9, 122.4, 64.5, 28.4, 28.3, 26.2, 21.2, 21.1. IR: 1762, 1733, 1483, 1448, 1367, 1237, 1197, 1170, 1037, 1010, 912, 760 cm^{-1}. HRMS $C_{12}H_{16}O_2$ $(M+Na)^+$ calcd. 299.1254, obsvd. 299.1257.

Synthesis of (*E*)-2-(6-hydroxyhex-1-enyl)phenol (S8):



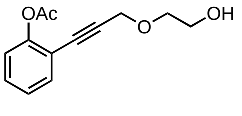
To an oven-dried 50 mL round bottom flask equipped with stir bar was added 300 mg of **S7 (**1.09 mmol, 1 equiv.), 300 mg of K_2CO_3 (2.18 mmol, 2.00 equiv.) and 5 mL of MeOH. The reaction mixture was allowed to stir for 10 h. Upon completion by TLC analysis, the reaction mixture was diluted with 20 mL of dichloromethane and washed with 20 mL of 1 M HCl, 20 mL of water, and 20 mL of brine, dried over Na_2SO_4, filtered, and the solvent was removed *in vacuo*. The crude mixture was purified by flash silica-gel column chromatography with 2:3 EtOAc:Hexanes as eluent to give 188 mg of **S8** as a 10:1 mixture of alkene isomers (83% yield, average of two reactions). $R_f = 0.45$ w/ 1:1 EtOAc:Hexanes, light yellow oil. Major isomer:, ^{1}H-NMR (300 MHz, $CDCl_3$) $\delta = 7.18$-7.08 (m, 2 H), 6.93-6.84 (m, 2 H), 6.41 (d, $J = 11.3$ Hz, 1H), 5.86 (dddd, $J = 11.3$ Hz, $J = 7.3$ Hz, $J = 7.3$ Hz, $J = 1.1$ Hz, 1 H), 5.71 (bs, 1 H), 3.59 (t, $J = 6.3$ Hz, 2 H), 2.15 (ddd, $J = 14.6$ Hz, $J = 7.3$ Hz, $J = 1.6$ Hz, 2 H), 1.85 (bs, 1 H), 1.64-1.36 (m, 4 H). ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$) $\delta = 153.0$, 136.1, 129.9, 128.7, 124.1, 123.8, 120.3, 115.4, 62.8, 32.2, 28.4, 25.7. IR 3303, 2934, 2859, 1604, 1451, 1228, 1037, 753 cm^{-1}. HRMS $C_{12}H_{16}O_2$ $(M+Na)^+$ calcd. 215.1043, obsvd. 215.1058.

Synthesis of S11:



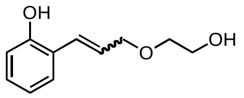
S4,[2] **S9,**[5] and $Pd(PPh_3)_2Cl_2$[4] were prepared according to literature procedure.

Preparation of 2-(3-(2-hydroxyethoxy)prop-1-ynyl)phenyl acetate (S10):



To an oven-dried 100 mL round bottom flask was added 2.90 g of **S4** (11.1 mmol, 1 equiv.), 10 mL of THF, and 10 mL of triethylamine. The solution was degassed by 2 cycles of freeze-pump-thaw. To a second dried round bottom flask was added 1.24 g of **S9** (12.4 mmol, 1.12 equiv.), 10 mL of THF, and 10 mL of triethylamine. The solution was degassed by 2 cycles of freeze-pump-thaw. To an oven-dried round bottom flask equipped with stir bar was added 233 mg of $Pd(PPh_3)_2Cl_2$ (0.332 mmol, 0.0300 equiv.) and 127 mg of CuI (0.664 mmol, 0.0600 equiv.). Solutions of **S4** and **S9** were sequentially cannulated into the flask containing the catalysts. The reaction mixture was stirred at rt for 1 h. The reaction mixture was diluted with 50 mL of dichloromethane and washed with 100 mL (2 x 50 mL) of 1 M HCl, 50 mL of saturated NH_4Cl, and 50 mL of brine. The organic phase was dried over Na_2SO_4, filtered, and the solvent was removed *in vacuo*. The crude mixture was purified by flash silica-gel column chromatography with 1:2 EtOAc:Hexanes to 1:1 EtOAc:Hexanes as eluent to give 1.848 g of **S10** (71.3% yield, average of two reactions). $R_f = 0.20$ w/ 1:1 EtOAc:Hexanes, colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) $\delta = 7.49$ (dd, $J = 7.6$ Hz, $J = 1.7$ Hz, 1 H), 7.36 (ddd, $J = 7.6$ Hz, $J = 7.6$ Hz, $J = 1.7$ Hz, 1 H), 7.20 (ddd, $J = 7.6$ Hz, $J = 7.6$ Hz, $J = 1.2$ Hz, 1 H), 7.09 (dd, $J = 8.1$ Hz, $J = 1.2$ Hz, 1 H), 4.43 (s, 2 H), 3.78 (bdd, $J = 9.1$ Hz, $J = 5.2$ Hz, 2 H), 3.70 (m, 2 H), 2.34 (s, 3 H), 2.07 (bs, 1 H). ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$) $\delta = 169.2$, 151.8, 133.4, 130.0, 126.1, 122.5, 116.8, 90.0, 81.7, 71.3, 62.0, 59.3, 21.1. IR 3426, 2935, 1760, 1486, 1446, 1368, 1180, 1102, 1010, 908, 756, 733 cm^{-1}. HRMS $C_{13}H_{14}O_4$ $(M+Na)^+$ calcd. 257.0784, obsvd. 257.0789.

Preparation of 2-(3-(2-hydroxyethoxy)prop-1-enyl)phenol (S11):



To an oven-dried 50 mL round bottom flask was added 300 mg of **S10** (1.28 mmol, 1 equiv.) and 5 mL THF. The mixture is cooled to 0 °C in an ice bath. In a separate oven-dried round bottom flask 1.6 mL of Red-Al solution (65% by weight in toluene, 5.3 mmol, 4.0 equiv.) was diluted with 5 mL of THF. The solution of Red-Al was transferred dropwise *via* cannula to the reaction mixture. The reaction mixture was stirred at 0 °C for 1 h, and then warmed to rt. To this was slowly added 20 mL of 0.5 M HCl (gas evolution observed) followed by 20 mL of CH_2Cl_2. The phases were separated, and the aqueous phase was extracted with 80 mL of dichloromethane (4 x 20 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and the solvent was removed *in vacuo*. The crude mixture was purified by flash silica-gel column chromatography with 2% MeOH/CH_2Cl_2 as eluent to give 201 mg of **S11** (1:1 mixture of alkene isomers) **(**81% yield, average of two reactions). $R_f = 0.40$ w/ 10% MeOH/CH_2Cl_2, colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.37 (dd, *J* = 7.6 Hz, *J* = 1.7 Hz, 1 H), 7.19 (dddd, *J* = 7.7 Hz, *J* = 7.4 Hz, *J* = 1.6 Hz, *J* = 0.7 Hz, 1 H), 7.13 (ddd, *J* = 8.0 Hz, *J* = 7.4 Hz, *J* = 1.7 Hz, 1 H), 7.05 (ddd, *J* = 8.0 Hz, *J* = 1.9 Hz, *J* = 0.7 Hz, 1 H), 6.93-6.85 (m, 4 H), 6.78 (dd, *J* = 8.0 Hz, *J* = 1.0 Hz, 1 H), 6.65 (d, *J* = 11.4 Hz, 1 H), 6.30 (dt, *J* = 16.1 Hz, *J* = 6.0 Hz, 1 H), 6.07 (dt, *J* = 11.4 Hz, *J* = 7.1 Hz, 1 H), 5.99 (bs, 1 H), 5.61 (bs, 1 H), 4.22 (dd, *J* = 6.0 Hz, *J* = 1.4 Hz, 2 H), 4.07 (dd, *J* = 7.1 Hz, *J* = 1.1 Hz, 2 H), 3.82-3.71 (m, 4 H), 3.64 (ddd, *J* = 4.3 Hz, *J* = 4.3 Hz, *J* = 1.5 Hz, 2 H), 3.57 (ddd, *J* = 3.4 Hz, *J* = 2.1 Hz, *J* = 1.5 Hz, 2 H), 2.38-2.26 (bm, 2 H). ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$) δ = 153.4, 153.1, 130.2, 130.0, 129.4, 129.0, 128.7, 127.8, 127.7, 127.1, 124.0, 123.0, 120.9, 120.6, 116.2, 116.2, 72.2, 72.1, 71.5, 67.7, 62.1, 61.9, IR 3301, 2932, 2867, 1656, 1603, 1455, 1357, 1251, 1093, 1054, 976, 753 cm^{-1}. HRMS $C_{11}H_{14}O_3$ $(M+Na)^+$ calcd. 217.0835, obsvd. 217.0845.

Procedure for Optimization:

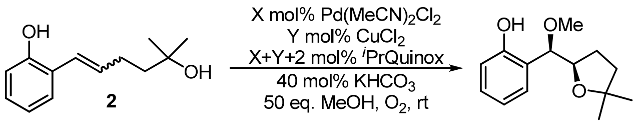
For optimization, four reactions were run simultaneously in separate 5 mL side-arm flasks attached to a four-neck cow.

(*S*)-^{i}PrQuinox was prepared according to literature procedure.[6]

A standard solution was prepared by the addition of 412.6 mg of the substrate **2** and 63.3 mg of the internal standard 2-methoxynaphthalene to a 2 mL volumetric flask, followed by the addition of MeOH. The flask was briefly sonicated to dissolve **2** and stirred to give a solution with [**2**] = 1.00 M and [2-methoxynaphthalene] = 0.20 M.

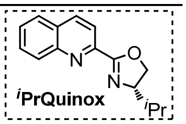
Reaction samples were passed through a short silica plug eluting with 2 mL of EtOAc and analyzed by GC and referenced against a time zero sample containing the standard solution of **2** and 2-methoxynaphthalene. GC yields were calculated based on the ratio of product to internal standard corrected for the response factor. Enantiomeric and diastereomeric ratios were determined using GC with a column equipped with a chiral stationary phase.

Table 1. Optimization of reaction conditions.



entry	X	Y	solvent	time	%conv[a]	%yield[a]	er[b]	dr[b]
1[c]	10	--	MeOH	15 h	100	2	88:12	2.4:1
2	10	--	MeOH	15 h	74	8	92:8	2.7:1
3	10	20	MeOH	10 min	100	95	92:8	9.4:1
4	4	8	MeOH	30 min	100	87	92:8	9.6:1
5	4	8	THF	2 h	79	54	98:2	7.8:1
6	4	8	toluene	2 h	96	68	97:3	5.1:1
7	4	8	1:1 THF:toluene	5 h	100	67	97:3	6.7:1
8[d]	4	8	1:1 THF:toluene	2 h	99	80	98:2	8.9:1

Reactions run on 0.1 mmol scale with [**2**]=0.1 M. [a]Determined by GC analysis using an internal standard. [b]Determined by GC with a column equipped with a chiral stationary phase. [c]With 50 mg 3 Å MS and without $KHCO_3$. [d]CuCl was used in place of $CuCl_2$



^{i}PrQuinox

Entry 1: To a 5 mL side-arm round bottom flask equipped with a stir bar was added 2.6 mg $Pd(MeCN)_2Cl_2$ (0.010 mmol, 0.10 equiv.), 2.9 mg (*S*)-^{i}PrQuinox (0.012 mmol, 0.12 eqiuv), 50 mg of freshly activated 3Å molecular sieves, and 900 μL of MeOH, and the flask was attached to a four-neck cow. A three-way joint fitted with a balloon of O_2 was attached and the apparatus was evacuated (using house vacuum) and refilled with oxygen three times. The mixture was stirred vigorously for 20 minutes at room temperature under O_2. A 100 μL portion of the standard solution of **2** (0.100 mmol, 1 equiv.) and 2-methoxy naphthalene (0.020 mmol, 0.20 equiv.) was added dropwise to the reaction mixture. Aliquots (ca. 50 μL) of the reaction were taken periodically via syringe.

Entry 2: To a 5 mL side-arm round bottom flask equipped with a stir bar was added 2.6 mg $Pd(MeCN)_2Cl_2$ (0.010 mmol, 0.10 equiv.), 2.9 mg (*S*)-^{i}PrQuinox (0.012 mmol, 0.12 eqiuv), 4.0 mg of $KHCO_3$ (0.040 mmol, 0.40 equiv.), and 900 μL of MeOH, and the flask was attached to a four-neck cow. A three-way joint fitted with a balloon of O_2 was attached and the apparatus was evacuated (using house vacuum) and refilled with oxygen three times. The mixture was stirred vigorously for 20 minutes at room temperature under O_2. A 100 μL portion of the standard solution of **2** (0.100 mmol, 1 equiv.) and 2-methoxy naphthalene (0.020 mmol, 0.20 equiv.) was added dropwise to the reaction mixture. Aliquots (ca. 50 μL) of the reaction were taken periodically via syringe.

Entry 3: To a 5 mL side-arm round bottom flask equipped with a stir bar was added 2.6 mg $Pd(MeCN)_2Cl_2$ (0.010 mmol, 0.10 equiv.), 2.7 mg of $CuCl_2$ (0.020 mmol, 0.20 equiv.), 7.7 mg (*S*)-^{i}PrQuinox (0.032 mmol, 0.32 eqiuv), 4.0 mg of $KHCO_3$ (0.040 mmol, 0.40 equiv.), and 900 μL of MeOH, and the flask was attached to a four-neck cow. A three-way joint fitted with a balloon of O_2 was attached and the apparatus was evacuated (using house vacuum) and refilled with oxygen three times. The mixture was stirred vigorously for 20 minutes at room temperature under O_2. A 100 μL portion of the standard solution of **2** (0.100 mmol, 1 equiv.) and 2-methoxy naphthalene (0.020 mmol, 0.20 equiv.) was added dropwise to the reaction mixture. Aliquots (ca. 50 μL) of the reaction were taken periodically via syringe.

Entry 4: To a 5 mL side-arm round bottom flask equipped with a stir bar was added 1.0 mg Pd(MeCN)$_2$Cl$_2$ (0.0040 mmol, 0.040 equiv.), 1.1 mg of CuCl$_2$ (0.0080 mmol, 0.080 equiv.), 3.4 mg (*S*)-^{i}PrQuinox ligand (0.014 mmol, 0.14 eqiuv), 4.0 mg of KHCO$_3$ (0.040 mmol, 0.40 equiv.), and 900 μL of MeOH, and the flask was attached to a four-neck cow. A three-way joint fitted with a balloon of O$_2$ was attached and the apparatus was evacuated (using house vacuum) and refilled with oxygen three times. The mixture was stirred vigorously for 20 minutes at room temperature under O$_2$. A 100 μL portion of the standard solution of **2** (0.100 mmol, 1 equiv.) and 2-methoxy naphthalene (0.020 mmol, 0.20 equiv.) was added dropwise to the reaction mixture. Aliquots (ca. 50 μL) of the reaction were taken periodically via syringe.

Entry 5: To a 5 mL side-arm round bottom flask equipped with a stir bar was added 1.0 mg Pd(MeCN)$_2$Cl$_2$ (0.0040 mmol, 0.040 equiv.), 1.1 mg of CuCl$_2$ (0.0080 mmol, 0.080 equiv.), 3.4 mg (*S*)-^{i}PrQuinox (0.014 mmol, 0.14 eqiuv), 4.0 mg of KHCO$_3$ (0.040 mmol, 0.40 equiv.), 100 μL of MeOH, and 800 μL of THF, and the flask was attached to a four-neck cow. A three-way joint fitted with a balloon of O$_2$ was attached and the apparatus was evacuated (using house vacuum) and refilled with oxygen three times. The mixture was stirred vigorously for 20 minutes at room temperature under O$_2$. A 100 μL portion of the standard solution of **2** (0.100 mmol, 1 equiv.) and 2-methoxy naphthalene (0.020 mmol, 0.20 equiv.) was added dropwise to the reaction mixture. Aliquots (ca. 50 μL) of the reaction were taken periodically via syringe.

Entry 6: To a 5 mL side-arm round bottom flask equipped with a stir bar was added 1.0 mg Pd(MeCN)$_2$Cl$_2$ (0.0040 mmol, 0.040 equiv.), 1.1 mg of CuCl$_2$ (0.0080 mmol, 0.080 equiv.), 3.4 mg (*S*)-^{i}PrQuinox (0.014 mmol, 0.14 eqiuv), 4.0 mg of KHCO$_3$ (0.040 mmol, 0.40 equiv.), 100 μL of MeOH, and 800 μL of toluene, and the flask was attached to a four-neck cow. A three-way joint fitted with a balloon of O$_2$ was attached and the apparatus was evacuated (using house vacuum) and refilled with oxygen three times. The mixture was stirred vigorously for 20 minutes at room temperature under O$_2$. A 100 μL portion of the standard solution of **2** (0.100 mmol, 1 equiv.) and 2-methoxy naphthalene (0.020 mmol, 0.20 equiv.) was added dropwise to the reaction mixture. Aliquots (ca. 50 μL) of the reaction were taken periodically via syringe.

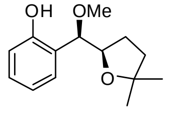
Entry 7: To a 5 mL side-arm round bottom flask equipped with a stir bar was added 1.0 mg Pd(MeCN)$_2$Cl$_2$ (0.0040 mmol, 0.040 equiv.), 1.1 mg of CuCl$_2$ (0.0080 mmol, 0.080 equiv.), 3.4 mg (*S*)-^{i}PrQuinox (0.014 mmol, 0.14 eqiuv), 4.0 mg of KHCO$_3$ (0.040 mmol, 0.40 equiv.), 100 μL of MeOH, 400 μL of toluene, and 400 μL of THF, and the flask was attached to a four-neck cow. A three-way joint fitted with a balloon of O$_2$ was attached and the apparatus was evacuated (using house vacuum) and refilled with oxygen three times. The mixture was stirred vigorously for 20 minutes at room temperature under O$_2$. A 100 μL portion of the standard solution of **2** (0.100 mmol, 1 equiv.) and 2-methoxy naphthalene (0.020 mmol, 0.20 equiv.) was added dropwise to the reaction mixture. Aliquots (ca. 50 μL) of the reaction were taken periodically via syringe.

Entry 8: To a 5 mL side-arm round bottom flask equipped with a stir bar was added 1.0 mg Pd(MeCN)$_2$Cl$_2$ (0.0040 mmol, 0.040 equiv.), 0.8 mg of CuCl (0.0080 mmol, 0.080

equiv.), 3.4 mg (*S*)-^{i}PrQuinox (0.014 mmol, 0.14 eqiuv), 4.0 mg of $KHCO_3$ (0.040 mmol, 0.40 equiv.), 100 μL of MeOH, 400 μL of toluene, and 400 μL of THF, and the flask was attached to a four-neck cow. A three-way joint fitted with a balloon of O_2 was attached and the apparatus was evacuated (using house vacuum) and refilled with oxygen three times. The mixture was stirred vigorously for 20 minutes at room temperature under O_2. A 100 μL portion of the standard solution of **2** (0.100 mmol, 1 equiv.) and 2-methoxy naphthalene (0.020 mmol, 0.20 equiv.) was added dropwise to the reaction mixture. Aliquots (ca. 50 μL) of the reaction were taken periodically via syringe.

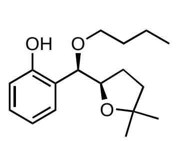
<u>Substrate Scope</u>:

2-((*R*)-((*R*)-5,5-dimethyltetrahydrofuran-2-yl)(methoxy)methyl)phenol (3a):



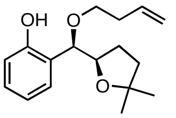
To a 100 mL Schlenk flask equipped with a stir bar was added 5.2 mg $Pd(MeCN)_2Cl_2$ (0.020 mmol, 0.040 equiv.), 4.0 mg of CuCl (0.040 mmol, 0.080 equiv.), 16.8 mg of (*S*)-^{i}PrQuinox (0.700 mmol, 0.140 equiv.), 20.0 mg of $KHCO_3$ (0.200 mmol, 0.400 equiv.), 1 mL of MeOH (25 mmol, 50 equiv.), 2 mL of THF, and 2 mL toluene. A three-way joint fitted with a balloon of O_2 was attached and flask was evacuated and refilled with O_2 three times. The mixture was stirred for 20 minutes at room temperature under an atmosphere of O_2. To the reaction mixture, 103.1 mg of **2** (0.5000 mmol, 1 equiv.) was added. The reaction mixture was stirred for 3 h and diluted with 10 mL of EtOAc. The reaction mixture was then washed with 10 mL 1 M NH_4Cl, 10 mL brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude mixture was purified by flash silica-gel column chromatography with 2% to 10% EtOAc/Hexanes as eluent to give 85.7 mg of product (72% yield, average of two reactions). Diastereomeric ratio: 10:1. R_f = 0.70 w/ 33% EtOAc/Hexane, white solid. Melting point = 81-84 °C. $[\alpha]^{20}_{D} = -31.5°$ (c = 3.53, $CHCl_3$). Major diastereomer: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1 H), 7.20 (ddd, *J* = 8.9, *J* = 7.2, *J* = 1.6, 1 H), 7.09 (dd, *J* = 7.6 Hz, *J* = 1.8 Hz, 1 H), 6.91-6.82 (m, 2 H), 4.42-4.32 (m, 2 H), 3.36 (s, 3 H), 1.83 (ddd, *J* = 14.4 Hz, *J* = 7.0 Hz, *J* = 1.4 Hz, 2 H), 1.72-1.49 (m, 2 H), 1.24 (s, 3 H), 1.22 (s, 3 H). ^{13}C-NMR {^{1}H} (100 MHz, $CDCl_3$): δ 155.8, 129.5, 129.3, 123.5, 119.9, 117.7, 85.5, 82.8, 81.1, 57.9, 38.3, 28.3, 28.2, 27.9, 27.7, IR 3285, 2869, 2930, 1487, 1456, 1367, 1236, 1102, 1056, 754 cm^{-1}. HRMS $C_{14}H_{20}O_3$ $(M+Na)^+$ calcd. 259.1310, obsvd. 259.1308. For x-ray crystal structure data, used to determine relative stereochemistry, see page S31.

2-((*R*)-butoxy((*R*)-5,5-dimethyltetrahydrofuran-2-yl)methyl)phenol (3b):



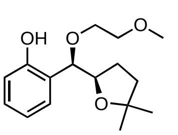
To a 100 mL side-arm round bottom flask equipped with a stir bar was added 5.3 mg $Pd(MeCN)_2Cl_2$ (0.020 mmol, 0.040 equiv.), 4.0 mg of CuCl (0.040 mmol, 0.080 equiv.), 16.8 mg of (*S*)-^{i}PrQuinox (0.700 mmol, 0.140 equiv.), 20 mg of $KHCO_3$ (0.20 mmol, 0.40 equiv.) and 2.6 mL of toluene. A three-way joint fitted with a balloon of O_2 was attached and flask was evacuated and refilled three times with O_2. The mixture was stirred for 20 minutes at room temperature under balloon of O_2. To the reaction mixture, a 2.3 mL of *n*-butanol (25 mmol, 50 equiv.) and 103.1 mg of **2** (0.5000 mmol, 1.000 equiv.) were added. The reaction mixture was stirred for 12 h and diluted with 10 mL of EtOAc. The reaction mixture was then washed with 1 M NH_4Cl (10 mL) followed by brine (10 mL). Organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The crude mixture was purified with flash silica-gel column chromatography with Hexane/EtOAC as eluent to give 87.5 mg of product (63% yield, average of two reactions, *Note: 53% yield in THF:toluene (1:1) as solvent).* Diastereomeric ratio: 5:1, Major diastereomer: R_f = 0.75 w/ 33% EtOAc/Hexane (Silica), colorless liquid, $[\alpha]^{20}_{D} = -8.2°$ (c = 1.0, CHCl_3), ^{1}H-NMR (500 MHz CDCl_3): δ 8.31 (s, 1 H), 7.22 (*dd*, *J* = 1.6 Hz, 8.7 Hz, 1 H), 7.09 (dd, *J* = 1.6 Hz, 7.5 Hz, 1 H), 6.91-6.83 (m, 2 H), 4.43 (d, J = 4.1 Hz, 1 H), 4.3 (ddd, J = &.01, 4.2 Hz, 1 H), 3.47 (ddd, J = 9.3 Hz, 6.7 Hz, 1.0 Hz, 1 H), 3.37 (ddd, J = 9.3 Hz, 6.5 Hz, 1.0 Hz, 1 H), 2.02-1.82 (m, 2 H), 1.70-1.29 (m, 6 H), 1.24 (s, 3 H), 1,21 (s, 3 H), 0.90 (t, *J* = 7.14 Hz, 3 H). ^{13}C-NMR (100 MHz CDCl_3): δ 155.9, 129.2, 124.4, 119.7, 117.7, 83.3, 82.8, 81.7, 70.0, 38.4, 31.9, 28.1, 28.0, 27.9, 19.5, 14.0, IR: 3289, 2962, 2931, 1455, 1367, 1237, 1095 cm^{-1}. HRMS $\text{C}_{17}\text{H}_{26}\text{O}_3$ $(\text{M+Na})^+$ calcd. 301.1780, obsvd. 301.1777.

2-((*R*)-(but-3-enyloxy)((*R*)-5,5-dimethyltetrahydrofuran-2-yl)methyl)phenol (3c):



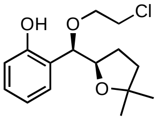
Followed the procedure described for **3b** except 2.9 mL toluene and 2.1 mL of 3-butene-1-ol (25 mmol, 50 equiv.) were used. Yield = 57%, average of two reactions (78.6 mg, *Note: 50% yield in THF:toluene (1:1) as solvent*), Diastereomeric ratio: 4:1, Major diastereomer: R_f = 0.75 w/ 33% EtOAc/Hexane, colorless liquid, $[\alpha]^{20}_{D} = +11.0°$ (c = 0.1, CHCl_3), ^{1}H-NMR (500 MHz CDCl_3) δ 8.28 (s, 1 H), 7.20 (td, *J* = 1.8 Hz, 7.7 Hz, 1 H), 7.04 (dd, *J* = 1.5 Hz, 7.7 Hz, 1 H), 6.90-6.83 (m, 2 H), 5.82 (ddd, *J* = 6.5 Hz, 3.3 Hz, 7.0 Hz, 1 H), 5.02-4.98 (m, 2 H), 4.44 (d, j =3.94, 1 H), 4.38 (ddd, J = 6.9 Hz, 4.1 Hz, 1 H), 3.52 (ddd, J = 9.2 Hz, 6.8 Hz, 1 H), 3.42 (ddd, J = 9.3 Hz, 6.6 Hz, 1 H), 2.38 (dd, *J* = 6.2 Hz, 8.2 Hz, 1 H), 2.09-1.82 (m, 2 H), 1.71-1.4 (m, 2 H), 1.23 (s, 3 H), 1.21 (s, 3 H). ^{13}C-NMR (125 MHz, CDCl_3): δ 155.8, 135.2, 129.3, 129.3, 124.3, 119.7, 117.7, 116.8, 83.3, 82.9, 81.7, 69.3, 38.3, 34.4, 28.1, 28.0, 27.9. IR: 3284, 2971, 1733, 1652, 1558, 1487, 1054 cm^{-1}. HRMS $\text{C}_{17}\text{H}_{24}\text{O}_3$ $(\text{M+Na})^+$ calcd. 299.1623, obsvd. 299.1615.

2-((*R*)-((*R*)-5,5-dimethyltetrahydrofuran-2-yl)(2-methoxyethoxy)methyl)phenol (3d):



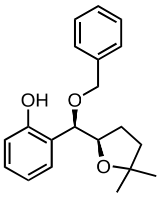
Followed the procedure described for **3a** except 1.5 mL of THF and 1.5 mL toluene (1:1) and 2.0 mL of 2-methoxyethanol (25 mmol, 50 equiv.) were used. Yield = 53%, average of two reactions (74.2 mg, *Note: 40% yield in toluene as solvent*), Diastereomeric ratio: 9:1, Major diastereomer: R_f = 0.35 w/ 33% EtOAc/Hexane, colorless liquid, $[\alpha]^{20}_{D} = -35.0°$ (c = 0.15, CHCl_3), ^{1}H-NMR (400 MHz CDCl_3): δ 8.20 (s, 1 H), 7.20 (dd, *J* = 1.8 Hz, 6.9 Hz, 1 H), 7.11 (dd, *J* = 7.7 Hz, 1 H), 6.91-6.85 (m, 2 H), 4.54 (d, *J* = 4.4 Hz, 1 H), 4,43 (ddd, *J* = 7.0 Hz, 4.3 Hz, 4.3 Hz, 1 H), 3.65-3.51 (m, 4 H), 3.33 (s, 3 H), 2.00-1.83 (m, 2 H), 1.74-1.61 (m, 1 H), 1.56-1.49 (m, 1 H), 1.24 (s, 3 H), 1.20 (s, 3 H). ^{13}C-NMR (100 MHz, CDCl_3): δ 155.9, 129.5, 129.4, 124.3, 119.9, 118.0, 83.3, 82.9, 81.7, 72.1, 69.1, 59.2, 38.4, 28.1, 28.0, 28.0. IR: 3266, 2968, 2872, 1486, 1097, 753 cm^{-1}. HRMS $\text{C}_{16}\text{H}_{24}\text{O}_4$ $(\text{M+Na})^+$ calcd. 303.1572, obsvd. 303.1566.

2-((*R*)-(2-chloroethoxy)((*R*)-5,5-dimethyltetrahydrofuran-2-yl)methyl)phenol (3e):



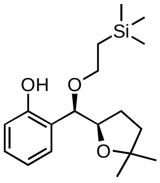
Followed the procedure described for **3b** except 3.3 mL toluene and 1.7 mL of 2-chloroethanol (25 mmol, 50 equiv.) were used. Yield = 61%, average of two reactions (86.6 mg, *Note: 58% yield in THF:toluene (1:1) as solvent*), Diastereomeric ratio: 5:1, Major diastereomer: $[\alpha]^{20}_{D}$ = –38.0° (c = 0.6, $CHCl_3$) R_f = 0.50 w/ 20% EtOAc/Hexane, Colorless liquid, ^{1}H-NMR (400 MHz $CDCl_3$): δ 8.29 (s, 1 H), 7.22 (ddd, J = 7.5 Hz, 0.9 Hz Hz, 1 H), 7.13-7.09 (m, 1 H), 6.93-6.85 (m, 2 H), 4.50 (d, J = 3.4 Hz, 1 H), 4.43 (td, J = 6.98 Hz, 3.45 Hz, 1 H), 3.76-3.55 (m, 4 H), 3.33 (s, 3 H), 2.01 (m, 2 H), 1.74-1.58 (m, 2 H), 1.26 (s, 3 H), 1.24 (s, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.7, 129.8, 129.4, 124.2, 120.0, 118.1, 83.4, 81.9, 69.7, 43.3, 38.3, 28.1, 27.9, 27.8, IR: 3265, 2966, 1490, 1461, 1364, 1190, 1104, 1049, 754 cm^{-1}. HRMS $C_{15}H_{21}ClO_3$ $(M+Na)^+$ calcd. 307.1077, obsvd. 307.1079.

2-((*R*)-benzyloxy((*R*)-5,5-dimethyltetrahydrofuran-2-yl)methyl)phenol (3f):



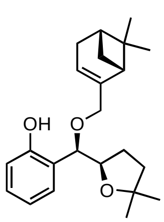
Followed the procedure described for **3a** except 0.7 mL of THF and 0.7 mL toluene (1:1) and 1.6 mL of Benzylalcohol (15 mmol, 50 equiv.) were used. Yield = 51%, average of two reactions (47.7 mg), Diastereomeric ratio: 6:1, Major diastereomer: R_f = 0.50 w/ 20% EtOAc/Hexane, colorless liquid, $[\alpha]^{20}_{D}$ = –49.5° (c = 0.39, $CHCl_3$),^{1}H-NMR (300 MHz $CDCl_3$): δ 8.33 (s, 1 H), 7.36-7.29 (m, 5 H), 7.22 (td, J = 7.7 Hz, 1.4 Hz Hz, 1 H), 7.11 (dd, J = 7.5 Hz, 1.5 Hz, 1 H), 6.94 (dd, J = 8.0. 1.0 Hz, 1 H), 6.88 (td, J = 7.4 Hz, 1.1 Hz, 1 H), 4.64 (d, J = 12.0 Hz, 1 H), 4.54 (d, J = 3.9 Hz, 1 H), 4.43 (td, J = 7.04 Hz, 3.95 Hz, 1 H), 4.34 (d, J = 12.0 Hz, 1 H), 1.99-1.88 (m, 2 H), 1.66 (dt, J = 12.0 Hz, 7.32 Hz, 1 H), 1.59-1.51 (m, 1 H), 1.22 (s, 3 H), 1.20 (s, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 155.9, 137.9, 129.5, 129.4, 128.5, 128.1, 127.9, 124.0, 119.9, 118.0, 83.0, 81.7, 81.6, 71.2, 38.3, 28.0, 27.9, 27.8. IR: 3285, 2970, 2870, 1717, 1615, 1506, 1455, 1180, 1097, 1027, 756 cm^{-1}. HRMS $C_{20}H_{24}O_3$ $(M+Na)^+$ calcd. 335.1623, obsvd. 335.3925.

2-((*R*)-((*R*)-5,5-dimethyltetrahydrofuran-2-yl)(2(trimethylsilyl)ethoxy)methyl) phenol (3g):



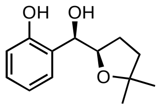
Followed the procedure described for **3b** except 1.9 mL toluene and 1.1 mL of 2-(trimethylsilyl)ethanol (7.5 mmol, 25 equiv.) were used. Yield = 64%, average of two reactions (62.1 mg), Diastereomeric ratio: 5:1, Major diastereomer: R_f = 0.85 w/ 20% EtOAc/Hexane, colorless liquid, $[\alpha]^{20}_{D}$ = –21° (c = 0.25, $CHCl_3$),^{1}H-NMR (300 MHz $CDCl_3$): δ 8.31 (s, 1 H), 7.18 (td, J = 7.7 Hz, 1.1 Hz Hz, 1 H), 7.10 (dd, J = 7.54 Hz, 1.52 Hz, 1 H), 6.89-6.84 (m, 2 H), 4.50 (d, J = 4.5 Hz, 1 H), 4.37 (td, J = 7.08 Hz, 4.58 Hz, 1 H), 3.63-3.57 (m, 1 H), 3.50-3.45 (m, 1 H), 1.91-1.80 (m, 2 H), 1.63 (dt, J = 12.1 Hz, 7.50 Hz, 1 H), 1.46 (ddd, J = 12.08 Hz, 8.20 Hz, 6.25 Hz, 1 H), 1.21 (s, 3 H) 1.16 (s, 3 H), 1.04 (m, 1 H), 0.92 (m, 1 H), -0.02 (s, 9 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 155.9, 129.1, 129.0, 124.3, 119.7, 117.6, 82.6, 82.2, 81.5, 67.6, 38.3, 28.1, 27.8, 27.7, 18.5, 1.2, IR: 3304, 2966, 2894, 1586, 1486, 1384, 1248, 1096, 859, 836, 755 cm^{-1}. HRMS $C_{18}H_{30}O_3Si$ $(M+Na)^+$ calcd. 345.1862, obsvd. 345.1861.

2-((*R*)-(((1*R*,5*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)methoxy)((*R*)-5,5-dimethyltetrahydrofuran-2-yl)methyl)phenol (3h):



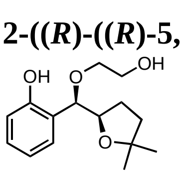
Followed the procedure described for **3b** except 3.0 mL toluene and 2.0 mL of (–)-myrtenol (12.5 mmol, 25.0 equiv.) were used. Yield = 55%, average of two reactions (97.9 mg), Diastereomeric ratio: 9:1, Major diastereomer: $[\alpha]^{20}_{D}$ = –31.3° (c = 0.7, $CHCl_3$) R_f = 0.76 w/ 33% EtOAc/Hexane, colorless liquid, ^{1}H-NMR (400 MHz $CDCl_3$): δ 8.28 (s, 1 H), 7.20-7.16 (m, 1 H), 7.08 (dd, *J* = 7.54 Hz, 1.40 Hz, 1 H), 6.89-6.83 (m, 2 H), 5.46 (dt, *J* = 2.85 Hz, 1.43 Hz, 1 H) 4.51 (d, *J* = 3.94 Hz, 1 H), 4.38 (td, *J* = 5.38 Hz, 3.20 Hz, 1 H), 3.90 (dd, *J* = 12.31 Hz, 1.65 Hz, 1H), 3.75-3.72 (m, 1 H), 2.33 (dt, *J* = 8.62 Hz, 5.61Hz, 1 H), 2.24 (m, 2 H), 2.12 (t, *J* = 5.60 Hz, 1 H), 2.01 (m, 1 H), 1.94-1.88 (m, 2 H), 1.66-1.61 (m, 1 H) 1.54-1.50 (m, 1 H), 1.27 (s, 3 H), 1.21 (s, 3 H), 1.19 (s, 3 H) 1.07 (d, *J* = 8.6 Hz, 1 H), 0.86 (s, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.7, 144.9, 129.1, 129.2, 129.0, 124.1, 120.1, 119.5, 117.5, 82.6, 81.6, 81.5, 81.5, 76.7, 72.4, 43.4, 41.0, 40.8, 38.1, 37.9, 31.5, 31.3, 31.2, 28.0, 27.7, 27.6, 26.2, 21.1, 20.9, IR: 3303, 2969, 2914, 1615, 1486, 1381, 1282, 1126, 1035, 887, 753 cm^{-1}. HRMS $C_{23}H_{32}O_3$ $(M+Na)^+$ calcd. 379.2249, obsvd. 379.2254

2-((*R*)-((*R*)-5,5-dimethyltetrahydrofuran-2-yl)(hydroxy)methyl)phenol (3i):



To a 100 mL side-arm round bottom flask equipped with a stir bar was added 8.3 mg Pd((*S*)-^{i}PrQuinox)Cl_2 (0.020 mmol, 0.040 equiv.), 15.0 mg of Cu((*S*)-^{i}PrQuinox)Cl_2 (0.040 mmol, 0.080 equiv.), 1.2 mg of (*S*)-^{i}PrQuinox (0.0050 mmol, 0.010 equiv.), 4.4 mg of $NaHCO_3$ (0.050 mmol, 0.10 equiv.) and 4.5 mL *t*AmylOH. A three-way joint fitted with a balloon of O_2 was attachedand flask was evacuated and refilled three times with O_2. The mixture was stirred for 20 minutes at room temperature under balloon of O_2. To the reaction mixture, a 450 μL of water (25 mmol, 50 equiv.) and 103.1 mg of **2** (0.5000 mmol, 1.000 equiv.) were added. The reaction mixture was stirred for 24 h and diluted with 10 mL of EtOAc. The reaction mixture was then washed with 1 M NH_4Cl (10 mL) followed by brine (10 mL). Organic layer was dried over Na_2SO_4 and concentrated *in vacuo.* The crude mixture was purified with flash silica-gel column chromatography with EtOAc/ Hexanes (4% to 10%) as eluent to give 69.9 mg of product (63% yield, average of two reactions). Diastereomeric ratio: 5:1, Major diastereomer: R_f = 0.60 w/ 33% EtOAc/Hexane, colorless solid, $[\alpha]^{20}_{D}$ = –17.0° (c = 0.1, $CHCl_3$), ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.40 (s, 1 H), 7.20 (ddd, *J* = 8.1 Hz, 7.4 Hz, 1.7 Hz, 1 H), 7.04 (dd, *J* = 7.6 Hz, 1.7 Hz, 1 H), 6.89 (dd, J = 8.1 Hz, 1.1 Hz, 1 H), 6.84 (td, J = 7.4 Hz, 1.2 Hz, 1 H), 4.58 (d, *J* = 6.8 Hz, 1 H), 4.27 (apparent q, *J* = 6.8 Hz, 1 H), 3.31 (bs, 1 H), 1.95-1.83 (m, 2 H), 1.81-1.75 (m, 2 H), 1.33 (s, 3 H), 1.27 (s, 3 H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 156.1, 129.7, 128.8, 124.4, 119.9, 118.0, 83.3, 81.1, 78.9, 38.5, 29.1, 28.3, 28.2, IR: 3297, 2968, 1237, 752 cm^{-1}, HRMS $C_{13}H_{18}O_3$ $(M+Na)^+$ calcd. 245.1154, obsvd. 245.1146.

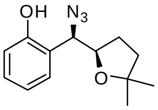
2-((*R*)-((*R*)-5,5-dimethyltetrahydrofuran-2-yl)(2-hydroxyethoxy)methyl)phenol (3j):



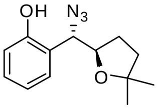
Followed the procedure described for **3i** except 3.6 mL *t*AmylOH and 1.4 mL of ethylene glycol (25 mmol, 50 equiv.) were used. Yield = 59%, average of two reactions (78.5 mg), Diastereomeric ratio: 10:1, Major diastereomer: R_f = 0.30 w/ 66% EtOAc/Hexane, colorless liquid, $[\alpha]^{20}_{D}$ =

–100° (c = 0.1, $CHCl_3$), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 1 H), 7.21 (td, J = 7.7 Hz, 1.2 Hz, 1 H), 7.07 (dd, J = 7.5 Hz, 1.6 Hz, 1 H), 6.91 (dd, J = 8.1 Hz, 0.9 Hz, 1 H), 6.87 (td, J = 7.4 Hz, 1.1 Hz, 1 H), 4.44-4.38 (m, 2 H), 3.81-3.64 (m, 3 H), 3.58 (ddd, J = 10.7 Hz, 5.9 Hz, 3.0 Hz, 1 H), 2.89 (bs, 1 H), 1.93-1.87 (m, 2 H), 1.75-1.65 (m, 2 H), 1.29 (s, 3 H), 1.27 (s, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.9, 129.8, 129.3, 124.1, 118.1, 85.1, 83.1, 81.7, 71.5, 61.9, 38.5, 28.5, 28.3, 28.0, IR: 3263, 2967, 2869, 1454, 1041, 754 cm^{-1}. HRMS $C_{15}H_{22}O_4$ $(M+Na)^+$ calcd. 289.1416, obsvd. 289.1417

2-((*R*)-azido((*R*)-5,5-dimethyltetrahydrofuran-2-yl)methyl)phenol (3k):

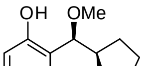


To a 100 mL side-arm round bottom flask equipped with a stir bar was added 8.3 mg Pd((*S*)-^{i}PrQuinox)Cl_2 (0.020 mmol, 0.040 equiv.), 15.0 mg of Cu((*S*)-^{i}PrQuinox)Cl_2 (0.040 mmol, 0.080 equiv.), 1.2 mg of (*S*)-^{i}PrQuinox (0.0050 mmol, 0.010 equiv.), 4.4 mg of $NaHCO_3$ (0.050 mmol, 0.10 equiv.) and 5.0 mL *t*AmylOH. A three-way joint fitted with a balloon of O_2 was attached and flask was emptied and refilled three times with O_2. The mixture was stirred for 20 minutes at room temperature under balloon of O_2. To the reaction mixture, 65 mg of NaN_3 (1.0 mmol, 2.0 equiv.) and 103.1 mg of **2** (0.2000 mmol, 1.000 equiv.) were added. The reaction mixture was stirred for 48 h at 30 °C and diluted with 10 mL of EtOAc. The reaction mixture was then washed with 1.0 M NH_4Cl (10 mL) followed by brine (10 mL). Organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The product was purified with flash silica-gel column chromatography with 2% to 10% EtOAc/Hexanes as eluent to give 62.9 mg of product (50% yield, average of two reactions). $[\alpha]^{20}_D$ = +22.1° (c = 0.25, $CHCl_3$), ^{1}H-NMR for Major Diastereomer (400 MHz $CDCl_3$): δ 8.21 (s, 1 H), 7.28-7.23 (m, 1H), 7.18-7.15 (dd, J = 1.5 Hz, 7.5 Hz, 1 H), 7.01-6.88 (m, 2 H), 4.70-4.65 (d, J = 3.2 Hz, 1 H), 4.35-4.25 (td, J = 3.2 Hz, 6.7 Hz, 1 H), 1.9-1.8 (m, 2 H), 1.78-1.62 (m, 2 H), 1.23 (s, 6 H).^{13}C-NMR (125 MHz, $CDCl_3$): δ 155.3, 130.3, 129.9, 123.3, 120.4, 118.8, 84.3, 81.5, 66.9, 38.1, 28.4, 28.0, 27.8. HRMS $C_{13}H_{17}N_3O_2$ $(M+Na)^+$ calcd. 270.1216, obsvd. 270.1214.



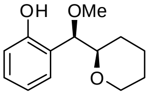
^{1}H-NMR for Minor Diastereomer (400 MHz $CDCl_3$): δ 8.34 (s, 1 H), 7.28-7.23 (m, 1H), 7.18-7.15 (dd, J = 1.5 Hz, 7.5 Hz, 1 H), 7.01-6.88 (m, 2 H), 4.78-4.75 (d, J = 3.2 Hz, 1 H), 4.44-4.38 (td, J = 3.2 Hz, 6.7 Hz, 1 H), 2.1-1.9 (m, 2 H), 1.78-1.62 (m, 2 H), 1.31 (s, 3 H), 1.27 (s, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 155.4, 130.6, 130.5, 120.2, 118.8, 83.9, 81.6, 68.5, 38.1, 28.8, 28.0, 27.8, IR: 3264, 2971, 2100, 1456, 1251, 754 cm^{-1}.

2-((*R*)-methoxy((*R*)-tetrahydrofuran-2-yl)methyl)phenol (3l):



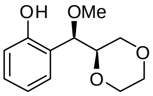
Followed the procedure described for **3a**; 89.0 mg of **S3** (0.500 mmol, 1.00 equiv.) was added**.** Reaction was stirred for 7 h. Yield = 68%, average of two reactions, Diastereomeric ratio: 10:1, Major diastereomer: R_f = 0.40 w/ 33% EtOAc/Hexane, white solid. MP = 64-65 °C. $[\alpha]^{20}_D$ = –62.0° (c = 0.1, $CHCl_3$), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 1 H), 7.22 (dd, J = 1.6 Hz, 8.3 Hz, 1 H), 7.09 (dd, J = 7.5 Hz, 1.9 Hz, 1 H), 6.94-6.84 (m, 2 H), 4.39-4.20 (m, 2 H), 3.98-3.78 (m, 2 H), 3.39 (s, 3 H), 1.89-1.65 (m, 4 H). ^{13}C-NMR {^{1}H} (100 MHz, $CDCl_3$): δ 155.9, 129.7, 129.4, 123.0, 119.9, 117.6, 86.2, 81.5, 69.2, 57.9, 28.2, 26.0, IR 3282, 2933, 2874, 1486, 1456, 1149, 1057, 753 cm^{-1}. HRMS $C_{12}H_{16}O_3$ $(M+Na)^+$ calcd. 231.0997, obsvd. 231.0990.

2-((*R*)-methoxy((*R*)-tetrahydro-2*H*-pyran-2-yl)methyl)phenol (3m):



To a 100 mL side-arm round bottom flask equipped with a stir bar was added 5.2 mg Pd(MeCN)$_2$Cl$_2$ (0.020 mmol, 0.040 equiv.), 4.0 mg of CuCl (0.040 mmol, 0.080 equiv.), 16.8 mg of (*S*)-^{i}PrQuinox (0.070 mmol, 0.140 equiv.), 20.0 mg of KHCO$_3$ (0.200 mmol, 0.400 equiv.), 1 mL of MeOH (25 mmol, 50 equiv.), 1 mL of THF, and 2 mL toluene. A three-way joint fitted with a balloon of O$_2$ was attached, and flask was evacuated and refilled with O$_2$ three times. The mixture was stirred for 20 minutes at room temperature under an atmosphere of O$_2$. To the reaction mixture, 96.1 mg of **S8** (0.5000 mmol, 1 equiv.) in a solution in 1 mL THF was added. The reaction mixture was stirred for 24 h and diluted with 10 mL of EtOAc. The reaction mixture was then washed with 1 M NH$_4$Cl (10 mL) followed by brine (10 mL). Organic layer was dried over Na$_2$SO$_4$ and concentrated *in vacuo*. The crude mixture was purified with flash silica-gel column chromatography with 2% to 10% EtOAc/Hexanes as eluent to give 55.0 mg of product (50% yield, average of two reactions). Diastereomeric ratio: 6:1, Major diastereomer: R$_f$ = 0.66 w/ 1:1 EtOAc:Hexanes, white solid. MP = 98-103 °C. $[\alpha]^{20}_D = -14.0°$ (c = 0.28, CHCl$_3$), ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.97 (s, 1 H), 7.22 (ddd, *J* = 7.7 Hz, *J* = 7.7 Hz, *J* = 1.7 Hz, 1 H), 7.03 (dd, *J* = 7.5 Hz, *J* = 1.7 Hz, 1 H), 6.91-6.83 (m, 2 H), 4.23 (d, *J* = 5.6 Hz, 1 H), 4.16-4.05 (m, 1 H), 3.75-3.68 (m, 1 H), 3.49 (ddd, *J* = 11.5 Hz, *J* = 11.5 Hz, *J* = 2.7, 1 H), 3.38 (s, 3H), 1.85-1.75 (m, 1H), 1.65-1.15 (m, 5 H). ^{13}C-NMR {^{1}H} (75 MHz, CDCl$_3$) δ 155.8, 129.9, 129.7, 122.9, 119.9, 117.6, 87.3, 80.0, 69.1, 57.9, 28.1, 25.9, 23.1. IR 3326, 2937, 2855, 1506, 1457, 1241, 1082, 756 cm^{-1}. HRMS C$_{13}$H$_{18}$O$_3$ (M+Na)$^+$ calcd. 245.1148, obsvd. 245.1152.

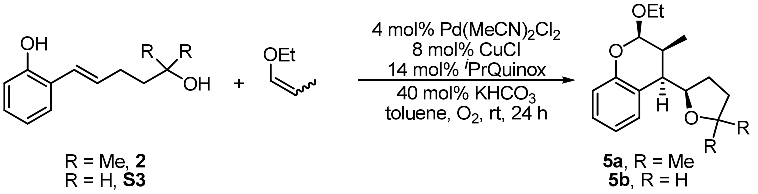
2-((*R*)-((*R*)-1,4-dioxan-2-yl)(methoxy)methyl)phenol (3n):



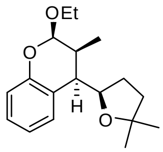
To a 200 mL side-arm round bottom flask equipped with a stir bar was added 5.2 mg Pd(MeCN)$_2$Cl$_2$ (0.020 mmol, 0.040 equiv.), 4.0 mg of CuCl (0.040 mmol, 0.080 equiv.), 16.8 mg of (*S*)-^{i}PrQuinox (0.070 mmol, 0.140 equiv.), 42.0 mg of NaHCO$_3$ (0.500 mmol, 1.00 equiv.), 1 mL of MeOH (25 mmol, 50 equiv.), 1 mL of THF, and 2 mL toluene. A three-way joint fitted with a balloon of O$_2$ was attached, and flask was evacuated and refilled with O$_2$ three times. The mixture was stirred for 20 minutes at room temperature under an atmosphere of O$_2$. To the reaction mixture, 97.1 mg of **S11** (0.5000 mmol, 1 equiv.) in a solution in 1 mL THF was added. The reaction mixture was stirred for 24 h and diluted with 10 mL of CH$_2$Cl$_2$. The reaction mixture was then washed with 1 M NH$_4$Cl (10 mL) followed by brine (10 mL). Organic layer was dried over Na$_2$SO$_4$ and concentrated *in vacuo*. The crude mixture was passed through a plug of alumina with 200 mL of 1:1 EtOAc:hexanes followed by 10% MeOH/EtOAc (to separate the product from ligand, which are inseparable by silica chromatography). The portion eluted with 10% MeOH/EtOAc was concentrated *in vacuo*, then purified with flash silica-gel column chromatography with 1% MeOH/CH$_2$Cl$_2$ as eluent to give 39.5 mg of the product (30% yield, average of two reactions). Diastereomeric ratio: 6:1, Major diastereomer: R$_f$ = 0.60 w/ 10% MeOH/CH$_2$Cl$_2$, clear oil. $[\alpha]^{20}_D = -26.3°$ (c = 1.88, CHCl$_3$), ^{1}H-NMR (300 MHz, CDCl$_3$) δ 7.64 (s, 1 H), 7.23 (dd, *J* = 8.5 Hz, *J* = 1.5 Hz, 1 H), 6.98 (dd, *J* = 7.6 Hz, *J* = 1.8 Hz, 1 H), 6.93-6.83 (m, 2 H), 4.27 (d, *J* = 6.0 Hz, 1 H), 3.97 (ddd, *J* = 9.3 Hz, *J* = 6.1 Hz, *J* = 3.4 Hz, 1 H), 3.90 (bdd, *J* = 9.9 Hz, *J* = 2.1 Hz, 1 H), 3.77 (ddd, *J* = 11.2 Hz, *J* = 11.2 Hz, *J* = 2.8 Hz, 1 H), 3.69 (bdd, *J* = 9.9 Hz, *J* = 2.8 Hz, 1 H), 3.59 (ddd, *J* = 11.2 Hz, *J* = 11.2

Hz, J = 2.8 Hz, 1 H), 3.51-3.41 (m, 2 H), 3.39 (s, 3 H). ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$) δ 155.8, 130.2, 129.2, 121.5, 120.2, 117.6, 84.3, 68.3, 67.1, 66.4, 57.9, 29.9, IR 3363, 3054, 2859, 1489, 1457, 1265, 1242, 1123, 1083, 731, 702 cm^{-1}. HRMS $C_{12}H_{16}O_4$ $(M+Na)^+$ calcd. 247.0941, obsvd. 247.0945.

Inverse Electron Demand Diels Alder Reaction:

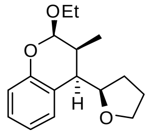


(2*R*,3*S*,4*R*)-4-((*R*)-5,5-dimethyltetrahydrofuran-2-yl)-2-ethoxy-3-methylchroman (5a):



To a 250 mL side-arm round bottom flask equipped with a stir bar was added 5.2 mg $Pd(MeCN)_2Cl_2$ (0.020 mmol, 0.040 equiv.), 4.0 mg of CuCl (0.040 mmol, 0.080 equiv.), 16.8 mg of (*S*)-^{i}PrQuinox (0.070 mmol, 0.140 equiv.), 20.0 mg of $KHCO_3$ (0.200 mmol, 0.40 equiv.), and 2.2 mL toluene. A three-way joint fitted with a balloon of O_2 was attached, and flask was evacuated and refilled with O_2 three times. The mixture was stirred for 20 minutes at room temperature under an atmosphere of O_2. To the reaction mixture, 103.1 mg of **2** (0.5000 mmol, 1 equiv.) as a solution in 2.8 mL of ethyl propenyl ether (25 mmol, 50 equiv., *Z*:*E* = 10:1) was added (*Note*: ethyl propenyl ether was purchased as a 3:1 mixture of isomers and enriched through multiple fractional distillations). The reaction flask was evacuated and refilled with O_2 twice more. The reaction mixture was stirred for 24 h and passed through a plug of silica with 50 mL EtOAc and concentrated *in vacuo*, then purified with flash alumina column chromatography with hexanes followed by 1% EtOAc/hexanes to 2% EtOAc/hexanes as eluent to give 104.1 mg of the product (72% yield). Diastereomeric ratio: 33:5:1, major diastereomer: R_f = 0.60 w/ 1:4 EtOAc:hexanes, clear oil. $[\alpha]^{20}_{D}$ = –30.8° (c = 1.73, $CHCl_3$), ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.31-7.28 (m, 1 H), 7.13 (ddd, J = 7.7 Hz, J = 7.7 Hz, J = 1.7 Hz, 1 H), 6.87-6.81 (m, 2 H), 5.04 (d, J = 2.6 Hz, 1 H), 4.34 (ddd, J = 6.8 Hz, J = 6.8 Hz, J = 4.6 Hz, 1 H), 3.98 (dq, J = 9.5 Hz, J = 7.1 Hz, 1 H), 3.60 (dq, J = 9.5 Hz, J = 7.1 Hz, 1 H), 3.09 (dd, J = 5.0 Hz, J = 5.0 Hz, 1 H), 2.42 (qdd, J = 7.1 Hz, J = 5.5 Hz, J = 2.5 Hz, 1 H), 2.18-2.07 (m, 1 H), 1.71-1.50 (m, 3 H), 1.31 (s, 3 H), 1.23 (t, J = 7.1 Hz, 3 H), 1.20 (s, 3 H), 1.07 (d, J = 7.1 Hz, 3 H). ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$) δ 153.2, 129.4, 127.8, 123.1, 120.3, 116.6, 101.6, 79.7, 77.8, 64.6, 43.4, 39.0, 33.8, 30.7, 29.0, 27.3, 15.3, 10.6, IR 2969, 2879, 1581, 1487, 1454, 1376, 1365, 1222, 1149, 1093, 1040, 978, 932, 752 cm^{-1}. HRMS $C_{18}H_{26}O_3$ $(M+Na)^+$ calcd. 313.1780, obsvd. 313.1775. Relative stereochemistry assigned by a combination of coupling constants, as compared to reported Diels Alder adducts with ethyl propenyl ether and a related quinone methide,[7] and x-ray crystal structure analysis of the lactone derivative (see page S42).

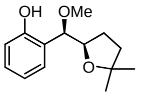
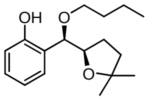
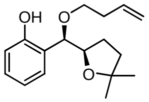
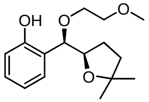
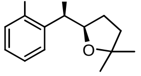
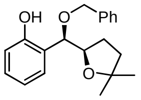
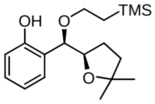
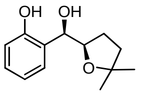
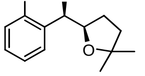
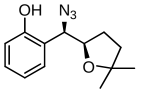
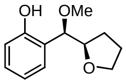
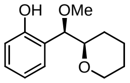
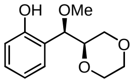
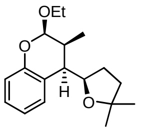
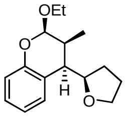
(2*R*,3*S*,4*R*)-2-ethoxy-3-methyl-4-((*R*)-tetrahydrofuran-2-yl)chroman (5b):



To a 250 mL side-arm round bottom flask equipped with a stir bar was added 5.2 mg $Pd(MeCN)_2Cl_2$ (0.020 mmol, 0.040 equiv.), 4.0 mg of CuCl (0.040 mmol, 0.080 equiv.), 16.8 mg of (*S*)-^{i}PrQuinox (0.070 mmol, 0.140 equiv.), 20.0 mg of $KHCO_3$ (0.200 mmol, 0.40 equiv.), and 2.2 mL toluene. A three-way joint fitted with a balloon of O_2 was attached, and flask was evacuated and refilled with O_2 three times. The mixture was stirred for 20 minutes at room temperature under an atmosphere of O_2. To the reaction mixture, 89.1 mg of **S3** (0.5000 mmol, 1 equiv.) as a solution in 2.8 mL of ethyl propenyl ether (25 mmol, 50 equiv., *Z*:*E* = 10:1) was added (*Note*: ethyl propenyl ether was purchased as a 3:1 mixture of isomers and enriched through multiple fractional distillations). The reaction flask was evacuated and refilled with O_2 twice more. The reaction mixture was stirred for 24 h and passed through a plug of silica with 50 mL EtOAc and concentrated *in vacuo*, then purified with flash alumina column chromatography with 1% EtOAc/hexanes to 2% EtOAc/hexanes as eluent to give 88.2 mg of the product (67% yield). Diastereomeric ratio: 33:8:1, major diastereomer: R_f = 0.70 w/ 1:3 EtOAc:hexanes, clear oil. $[\alpha]^{20}_D = -36.1°$ (c = 0.58, $CHCl_3$), ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.26-7.22 (m, 1 H), 7.13 (ddd, *J* = 7.7 Hz, *J* = 7.7 Hz, *J* = 1.7 Hz, 1 H), 6.88-6.81 (m, 2 H), 5.07 (d, *J* = 2.5 Hz, 1 H), 4.22 (ddd, *J* = 7.1 Hz, *J* = 7.1 Hz, *J* = 5.5 Hz, 1 H), 3.98 (dq, *J* = 9.6 Hz, *J* = 7.1 Hz, 1 H), 3.90 (ddd, *J* = 7.3 Hz, *J* = 5.3 Hz, *J* = 5.3 Hz, 1 H), 3.65 (dd, *J* = 7.3 Hz, *J* = 7.1 Hz, 1 H), 3.61 (dq, *J* = 9.6 Hz, *J* = 7.1 Hz, 1 H), 3.15 (dd, *J* = 5.3 Hz, *J* = 5.3 Hz, 1 H), 2.43 (qdd, *J* = 7.0 Hz, *J* = 5.5 Hz, *J* = 2.5 Hz, 1 H), 2.13-2.03 (m, 1 H), 1.94-1.71 (m, 2 H), 1.65-1.53 (m, 1 H), 1.24 (t, *J* = 7.1 Hz, 3 H), 1.06 (d, *J* = 7.0 Hz, 3 H). ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$) δ 153.3, 129.1, 127.9, 122.7, 120.5, 116.7, 101.7, 79.1, 67.4, 64.7, 43.4, 33.7, 30.4, 26.7, 15.3, 10.1, IR 2977, 2875, 1581, 1487, 1454, 1375, 1352, 1237, 1222, 1159, 1064, 1041, 981, 931, 754 cm^{-1}. HRMS $C_{16}H_{22}O_3$ $(M+Na)^+$ calcd. 285.1467, obsvd. 285.1472.

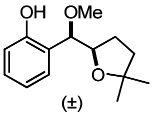
Determination of enantiomeric ratio:

Table 3. Seperation conditions to determine enantiomeric ratio.

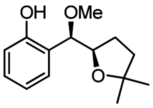
entry	Compound	Conditions	Retention time	er
1		GC, β-cyclodextrin column 120 °C for 20 min, increase to 140 °C at 0.4 °C/min hold at 140 °C for 2 min, increase to 200 °C at 5 °C/min hold at 200 °C for 8 min	56.8 and 57.9 min	97.9:2.1
2		SFC, 1% Methanol, 3 mL/min Whelko chiral column	3.9 and 4.5 min	96.4:3.6[a]
3		SFC, 1% Methanol, 1 mL/min Whelko chiral column	11.6 and 12.7 min	96.0:4.0[a]
4		SFC, 1% Methanol, 3 mL/min 5 μm Cellucoat chiral column	4.9 and 5.7 min	97.7:2.3
5		SFC, 1% Methanol, 3 mL/min Whelko chiral column	3.7 and 4.3 min	94.0:6.0[a]
6		SFC, 1% Methanol, 3 mL/min Whelko chiral column	7.4 and 8.1 min	96.9:3.1[a]
7		HPLC, 0.5% IPA/Hex, 1 mL/min OJ-H chiral column	29.8 and 32.6 min	99.4:0.6[b]
8		HPLC, 0.5% IPA/Hex, 1 mL/min OJ-H chiral column	29.8 and 32.6 min	98.4:1.6
9		SFC, 1% MeCN, 3 mL/min Cellucoat chiral column	2.5 and 3.9 min	94.9:5.1
10		HPLC, 1% IPA:Hex, 1 mL/min OD chiral column	10.0 and 13.7 min for major 18.5 and 32.9 min for minor	91.9:8.1 91.9:8.1
11		SFC, 1% Methanol, 1 mL/min AD-H chiral column	12.2 and 13.7 min	94.8:5.2
12		SFC, 1% Ethanol, 1.5 mL/min Whelko chiral column	12.5 and 14.1 min	94.3:5.7
13		SFC, 1% Methanol, 1.5 mL/min Whelko chiral column	12.3 and 14.1 min	92.0:8.0
14		GC, β-cyclodextrin column 122 °C for 270 min	246.2 and 252.3 min	93.3:6.7
15		GC, β-cyclodextrin column 122 °C for 330 min	276.5 and 286.6 min	95.9:4.1

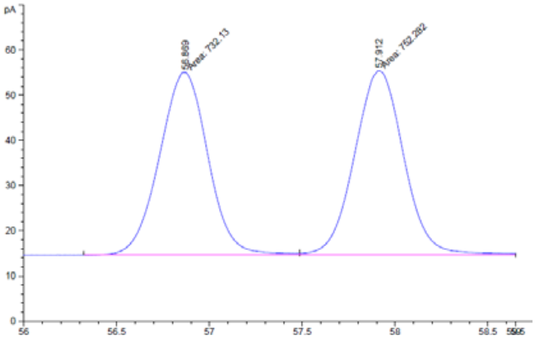
Separations were performed on the major diastereomer of the product. (a) Product was converted to the corresponding methoxy phenol derivative using KOH and MeI. (b) Product was converted to the free alcohol (**3l**) via deprotection using BF$_3$·OEt$_2$.

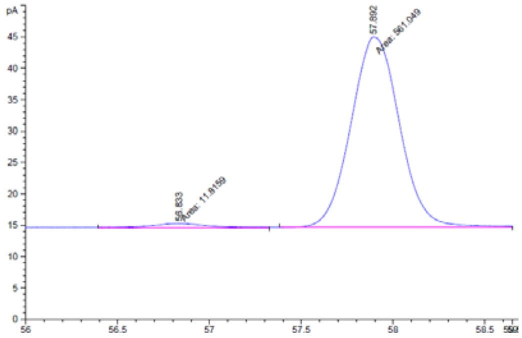
Table 3, Entry 1 (3a):



(±)







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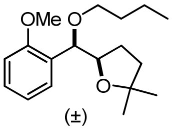
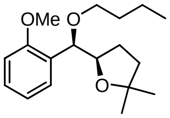
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  56.869 MF    0.3021  732.12994  40.39624  49.3212
   2  57.912 FM    0.3076  752.28223  40.75905  50.6788
```

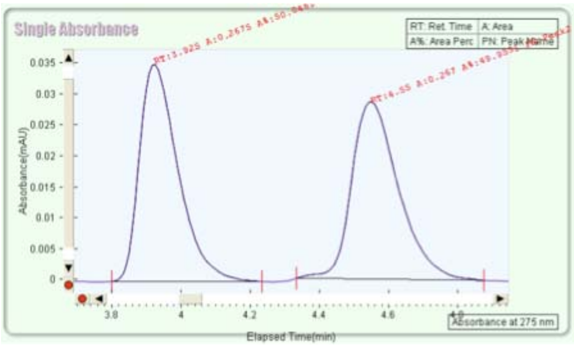
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  56.833 MM    0.3101   11.81586 6.35050e-1   2.0626
   2  57.892 MM    0.3082  561.04932   30.33831  97.9374
```

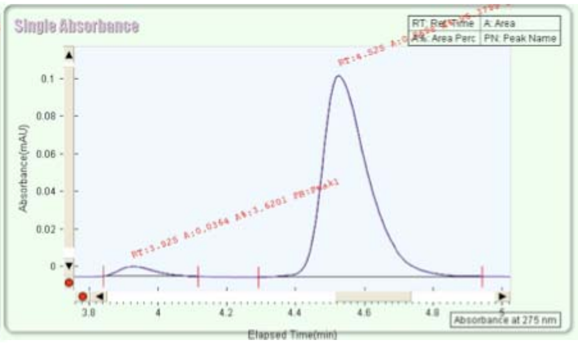
Table 3, Entry 2 (3b):



(±)

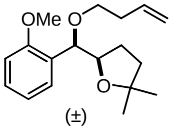


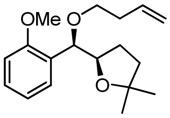


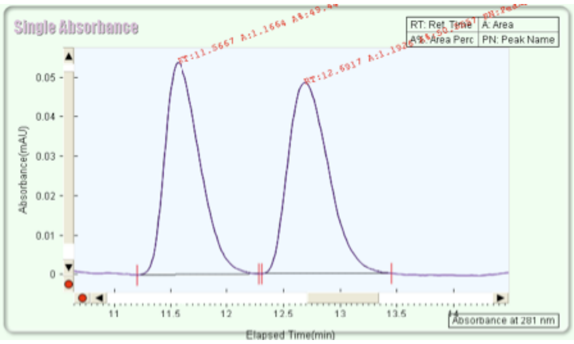


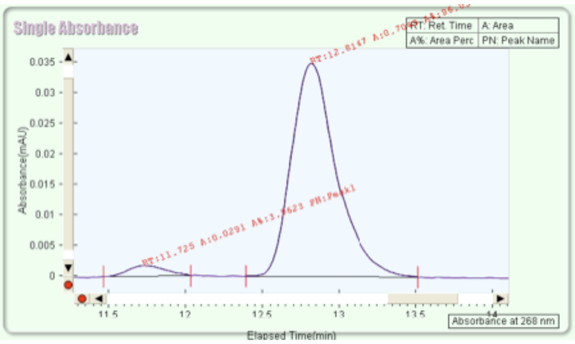
% Peak Area	Retention Time	% Peak Area	Retention Time
50.0469	3.925 min	3.6201	3.925 min
49.9531	4.55 min	96.3799	4.525 min

Table 3, Entry 3 (3c):



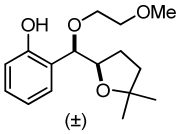


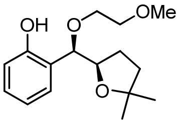


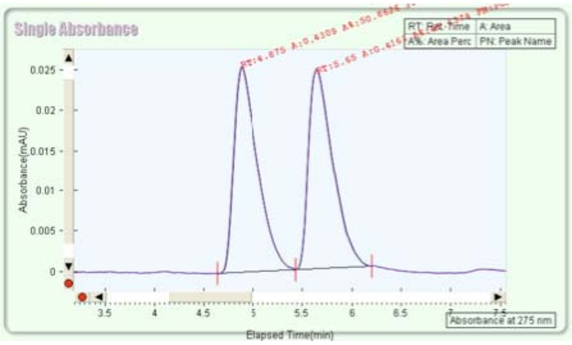


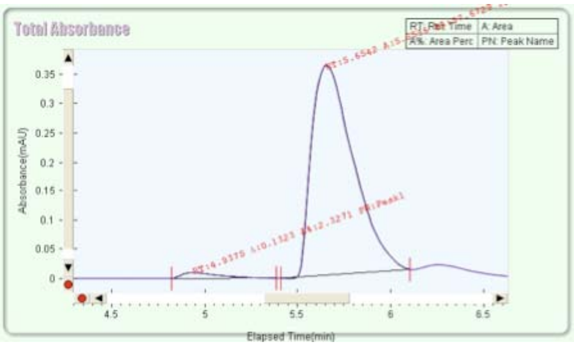
% Peak Area	Retention Time	% Peak Area	Retention Time
49.4443	11.5667 min	3.9623	11.725 min
50.5557	12.6917 min	96.0377	12.8167 min

Table 3, Entry 4 (3d):



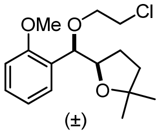


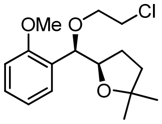


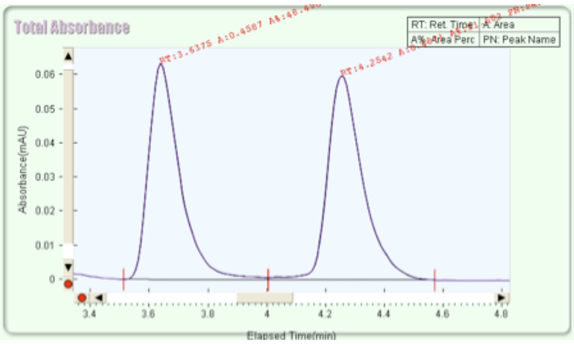


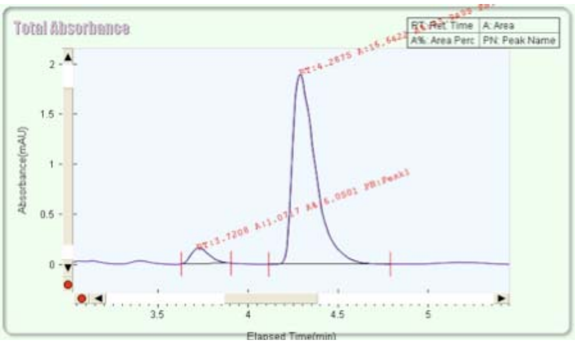
% Peak Area	Retention Time	% Peak Area	Retention Time
50.8626	4.875 min	2.3271	4.9375 min
49.1374	5.65 min	97.6729	5.6542 min

Table 3, Entry 5 (3e):





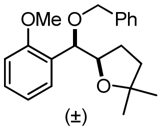


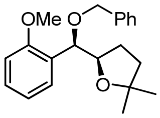


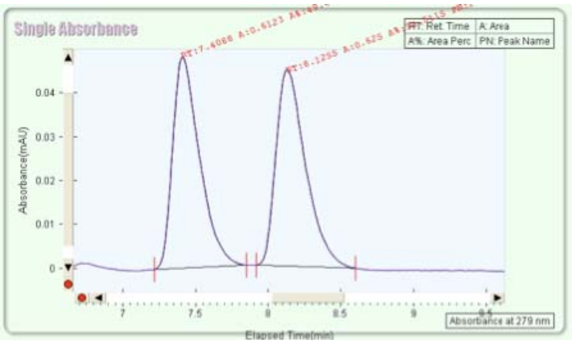
% Peak Area	Retention Time
48.498	3.6375 min
51.502	4.2542 min

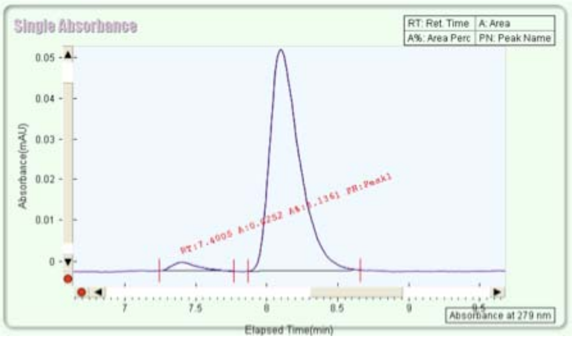
% Peak Area	Retention Time
6.0501	3.7208 min
93.9499	4.2875 min

Table 3, Entry 6 (3f):





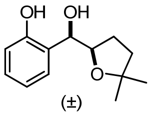


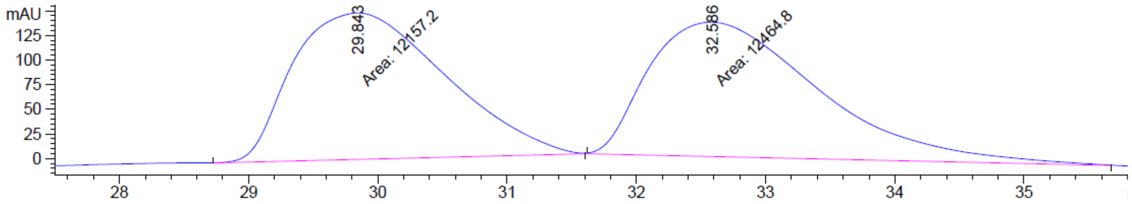


% Peak Area	Retention Time
49.4885	7.4088 min
50.5115	8.1255 min

% Peak Area	Retention Time
3.1361	7.4005 min
96.8639	8.1005 min

Table 3, Entry 7 (3g):





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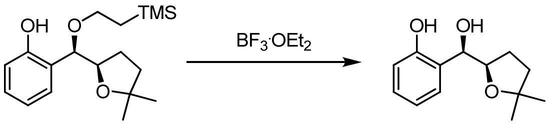
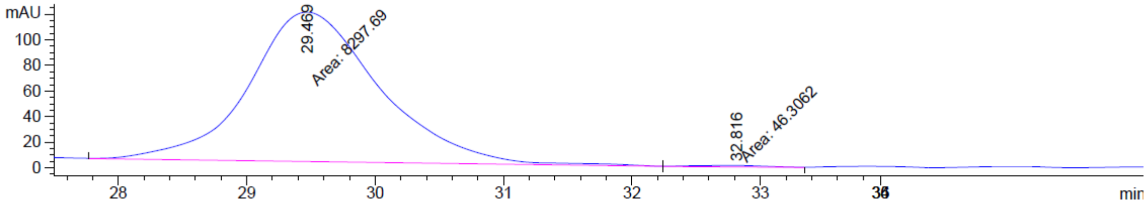
Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  29.843 MM     1.3616 1.21572e4   148.81494  49.3754
   2  32.586 MM     1.5214 1.24648e4   136.54688  50.6246
```





```
Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  29.469 MM     1.1841 8297.69043  116.79210  99.4450
   2  32.816 MM     0.6802   46.30616    1.13460   0.5550
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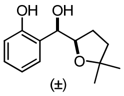
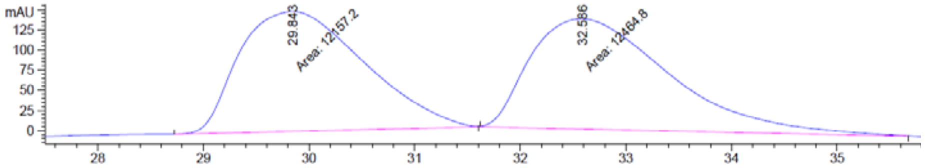
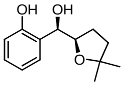
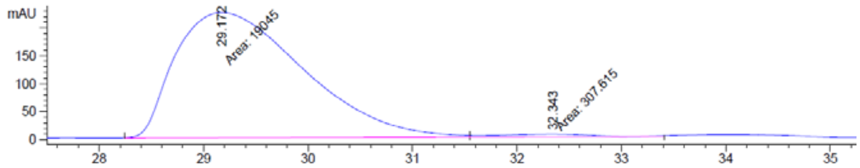
Table 3, Entry 8 (3i):





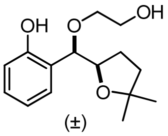
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  29.843 MM     1.3616 1.21572e4  148.81494  49.3754
   2  32.586 MM     1.5214 1.24648e4  136.54688  50.6246
```

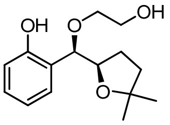


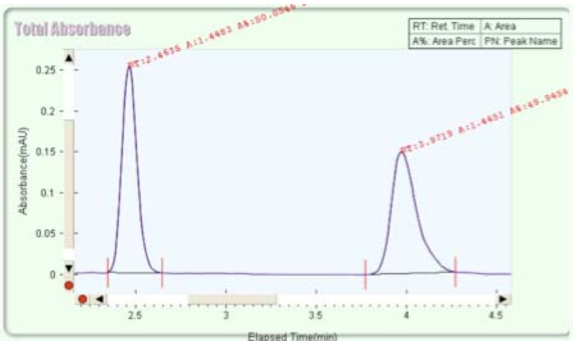


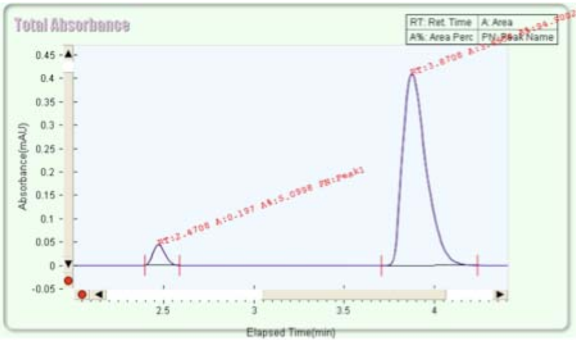
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  29.172 MF     1.4168 1.90450e4  224.04204  98.4105
   2  32.343 FM     1.0120  307.61505   5.06631   1.5895
```

Table 3, Entry 9 (3j):



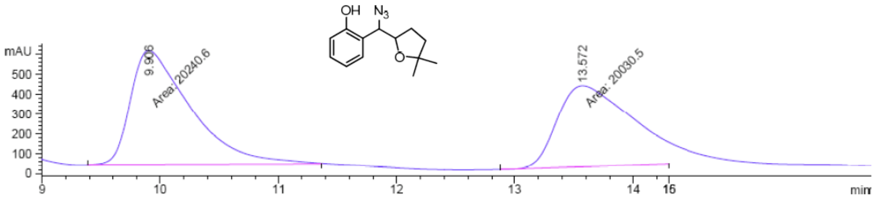






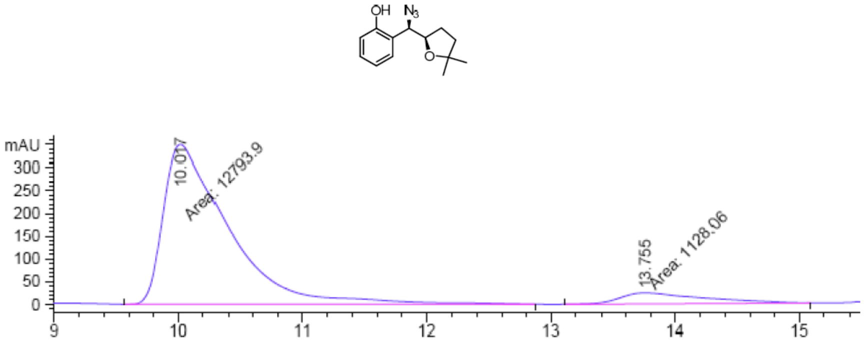
% Peak Area	Retention Time	% Peak Area	Retention Time
50.0546	2.4635 min	5.0998	2.4708 min
49.9454	3.9719 min	94.9002	3.8708 min

Table 3, Entry 10 (3k):



```
Signal 2: DAD1 B, Sig=220,8 Ref=off

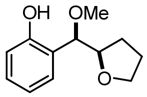
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   9.906 MM    0.5878 2.02406e4  573.88910  50.2609
   2  13.572 MM    0.8089 2.00305e4  412.73068  49.7391
```



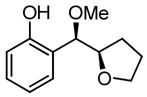
```
Signal 2: DAD1 B, Sig=220,8 Ref=off

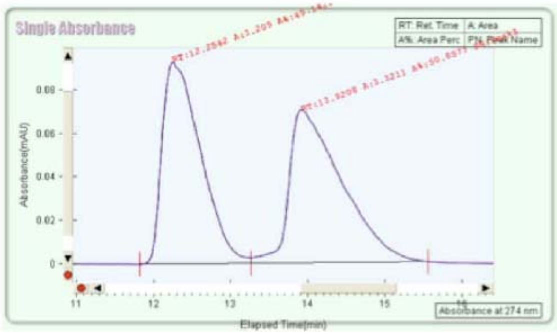
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.017 MM    0.6099 1.27939e4  349.59860  91.8973
   2  13.755 MM    0.7735 1128.05811  24.30574   8.1027
```

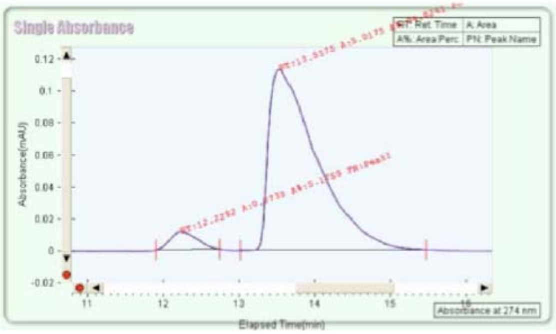
Table 3, Entry 11 (3l):



(±)



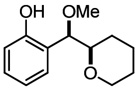




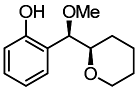
% Peak Area	Retention Time
49.1423	12.2542 min
50.8577	13.9208 min

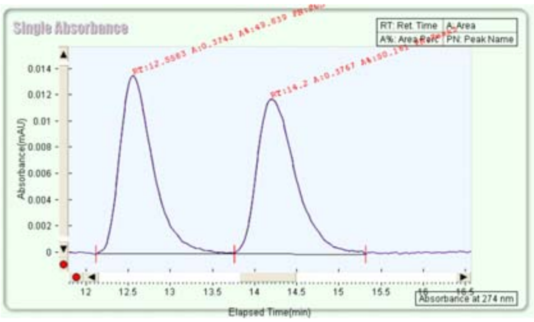
% Peak Area	Retention Time
5.1759	12.2292 min
94.8241	13.5375 min

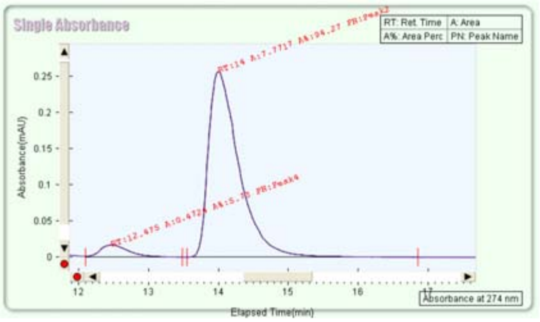
Table 3, Entry 12 (3m):



(±)



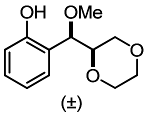


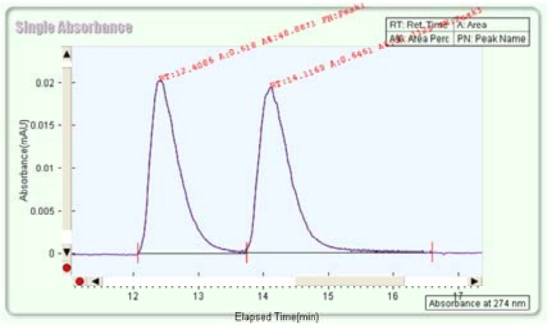


% Peak Area	Retention Time
49.839	12.5583 min
50.161	14.2 min

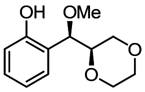
% Peak Area	Retention Time
5.73	12.475 min
94.27	14 min

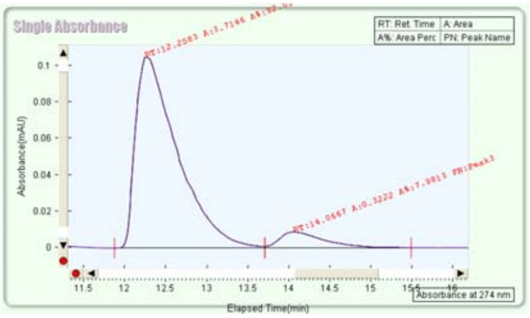
Table 3, Entry 13 (3n):





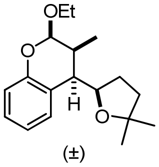
% Peak Area	Retention Time
48.8871	12.4086 min
51.1129	14.1169 min



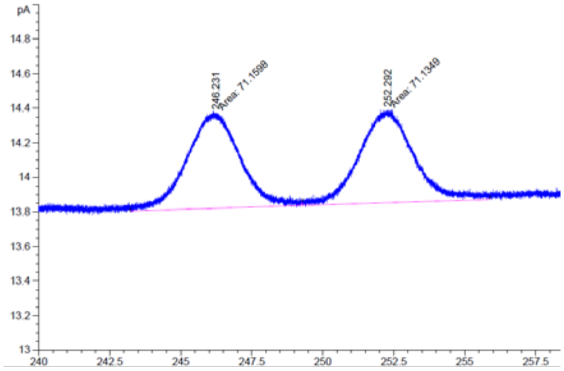


% Peak Area	Retention Time
92.0187	12.2583 min
7.9813	14.0667 min

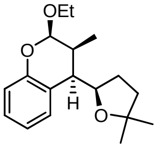
Table 3, Entry 14 (5a):

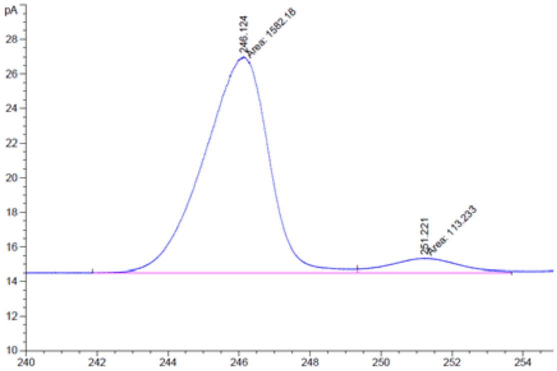


(±)



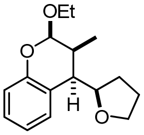
```
Peak RetTime Type  Width      Area      Height      Area
  #   [min]        [min]    [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1 246.231 MF     2.1337   71.15984 5.55828e-1  50.0088
   2 252.292 FM     2.1977   71.13490 5.39465e-1  49.9912
```



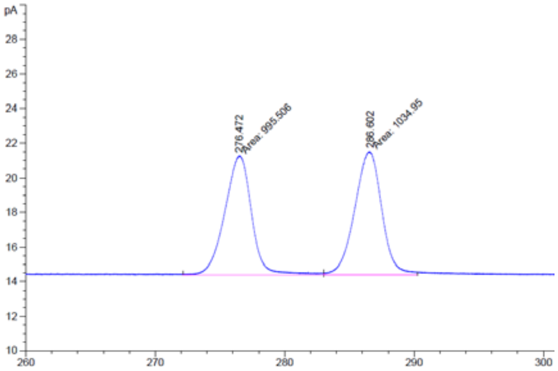


```
Peak RetTime Type  Width      Area      Height      Area
  #   [min]        [min]    [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1 246.124 MF     2.1049 1582.18030   12.52771  93.3212
   2 251.221 FM     2.1976  113.23334 8.58775e-1   6.6788
```

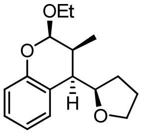
Table 3, Entry 15 (5b):

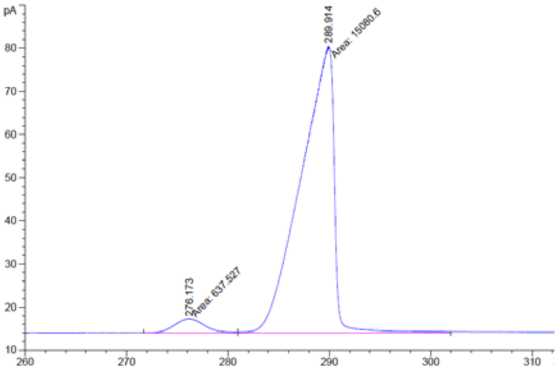


(±)



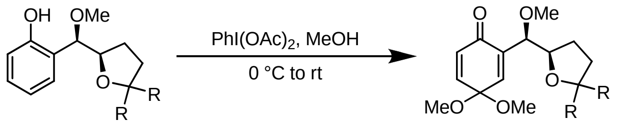
```
Peak RetTime Type  Width      Area      Height      Area
  #   [min]        [min]    [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1 276.472 MF     2.3999  995.50623    6.91358  49.0286
   2 286.602 FM     2.4124 1034.95374    7.15010  50.9714
```





```
Peak RetTime Type  Width      Area      Height      Area
  #   [min]        [min]    [pA*s]      [pA]         %
----|-------|----|-------|----------|----------|--------|
   1 276.173 MF     3.3129  637.52747    3.20726   4.0560
   2 289.914 FM     3.7839 1.50806e4    66.42497  95.9440
```

Dearomatization of Phenol:[8]

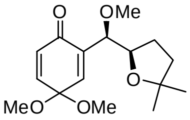


R = Me, **3a**
R = H, **3l**

4a, R = Me, 73% yield
4b, R = H, 71% yield

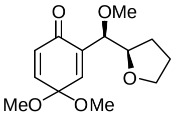
To an oven-dried 50 mL round bottom flask equipped with a stir bar was added 240.0 mg of **3a** (1.010 mmol, 1.000 equiv.) in 7.5 mL MeOH. To the reaction mixture cooled to 0 °C in an ice bath, 720.0 mg of $PhI(OAc)_2$ (2.230 mmol, 2.200 equiv.) in 5 mL of MeOH was added dropwise and warmed to room temperature. After stirring for 90 min, the reaction mixture was then cooled to 0 °C and solution of sat. Na_2CO_3 was added until precipitate was observed. To this 20 mL of EtOAc and 5 mL of water was added. The organic layer was separated and washed with water (5 mL) followed by brine (10 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The product was purified with flash silica-gel column chromatography with 10% to 30% EtOAc/Hexanes as eluent to give 215.5 mg of product (73% yield, average of two reactions).

2-((*R*)-((*R*)-5,5-dimethyltetrahydrofuran-2-yl)(methoxy)methyl)-4,4-dimethoxycyclohexa-2,5-dienone (4a):



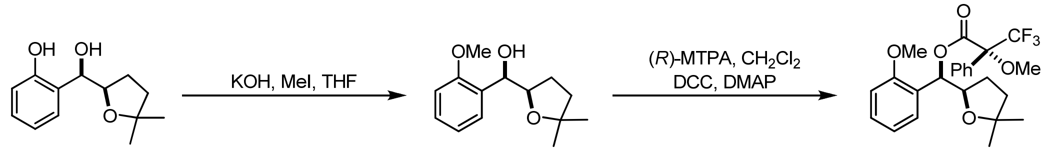
R_f = 0.4 w/ 33% EtOAc/Hexane, colorless liquid, $[\alpha]^{20}_{D}$ = –42.3° (c = 6.3, $CHCl_3$), ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.83 (dd, J = 3.29 Hz, 0.9 Hz, 1 H), 6.76 (dd, J = 10.2 Hz, 3.3 Hz, 1 H), 6.23 (d, J = 10.2 Hz, 1 H), 4.24 (dd, *J* = 6.2, 0.8 Hz, 1 H), 3.90 (q, *J* = 6.5 Hz, 1 H), 3.35 (s, 3 H), 3.33 (s, 3 H), 3.22 (s, 3 H), 1.70 (m, 4 H), 1.20 (s, 3 H), 1.16 (s, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 185.0, 143.1, 140.6, 137.8, 130.0, 93.0, 81.6, 81.0, 79.1, 57.4, 50.5, 50.4, 38.3, 28.8, 28.2, 28.0, IR: 2967, 2936, 1678, 1644, 1458, 1364, 1109, 1038, 962, 843 cm^{-1}. HRMS $C_{16}H_{24}O_5$ $(M+Na)^+$ calcd. 319.1521, obsvd. 319.1526.

4,4-dimethoxy-2-((*R*)-methoxy((*R*)-tetrahydrofuran-2-yl)methyl)cyclohexa-2,5-dienone (4b):



Same procedure as **4a**. 192.4 mg of product (71% yield, average of two reactions). R_f = 0.45 w/ 33% EtOAc/Hexane, colorless liquid, $[\alpha]^{20}_{D}$ = –57.3° (c = 1.4, $CHCl_3$),^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.92 (dd, J = 3.2 Hz, 0.8 Hz, 1 H), 6.82 (dd, J = 10.3 Hz, 3.3 Hz, 1 H), 6.27 (d, J = 10.2 Hz, 1 H), 4.30 (dd, *J* = 5.1 Hz, 0.9 Hz, 1 H), 3.87 (m, 2 H), 3.35 (ddd, J = 4.2 Hz, 1 H), 3.40 (s, 3 H), 3.37 (s, 3 H), 3.30 (s, 3 H), 1.80 (m, 4 H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 185.2, 143.4, 140.5, 137.6, 130.1, 93.2, 80.9, 78.3, 68.7, 57.8, 50.7, 50.5, 27.6, 26.0, IR: 2940, 2830, 1678, 1644, 1461, 1375, 1116, 962, 843 cm^{-1}. HRMS $C_{14}H_{20}O_5$ $(M+Na)^+$ calcd. 291.1208, obsvd. 291.1202.

Determination of absolute configration by Mosher ester analysis:[9]

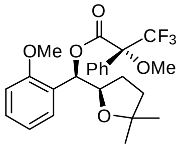


3i **S12** **S13**

To an oven dried 5 mL round bottom flask equipped with a stir bar was added 38.0 mg of **3i** (0.170 mmol, 1.00 equiv.) in 1.7 mL THF. To the reaction mixture, 10.0 mg of KOH (0.170 mmol, 1.00 equiv.) and 21 µL of MeI (0.34 mmol, 2.0 equiv.) were added at room temperature. After 2 h the solution was diluted with EtOAc and washed with water (2 x 5 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The product was used without further purification.

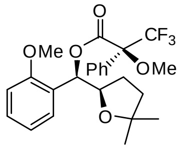
To an oven dried 5 mL round bottom flask equipped with a stir bar was added 20.2 mg of compound **S12** (0.085 mmol, 2.0 equiv.) in 400 µL CH_2Cl_2. To the reaction mixture, a 19.2 mg of DCC (0.0920 mmol, 2.20 equiv.) 1.5 mg of DMAP (0.3 equiv.) and 10 mg of (*R*)-MTPA (0.043 mmol, 1.0 equiv.) was added at room temperature. After 2 days, the solution was diluted with EtOAc and washed with solution of sat. NH_4Cl (2 mL) followed by water (2 x 5 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The product was purified with flash silica-gel column chromatography with EtOAc/Hexanes as eluent to give the product in 40% yield.

(*R*)-((*R*)-((*R*)-5,5-dimethyltetrahydrofuran-2-yl)(2-methoxyphenyl)methyl) 3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (S13):



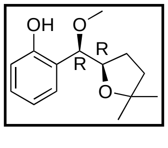
(*R*)-enantiomer of Mosher ester: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.56 (d, 2 H), 7.40-7.31 (m, 4 H), 7.05 (dd, J = 7.6 Hz, J = 1.6 Hz, 1 H), 6.90-6.84 (m, 2 H), 6.32 (d, J = 8.5 Hz, 1 H), 4.32-4.28 (m, 1 H), 3.87 (s, 3 H), 3.63 (s, 3 H), 1.83-1.67 (m, 4 H), 1.30 (s, 3 H), 1.23 (s, 3 H).

(*S*)-((*R*)-((*R*)-5,5-dimethyltetrahydrofuran-2-yl)(2-methoxyphenyl)methyl) 3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (S14)

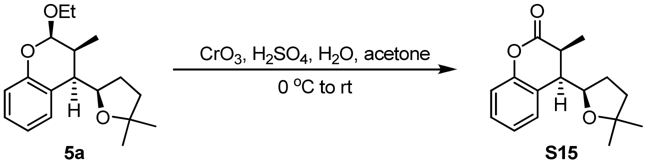


(*S*)- Enantiomer of Mosher ester: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.56 (m, 2 H), 7.40-7.27 (m, 4 H), 6.93 (td, J = 7.5 Hz, J = 1.0 Hz, 1 H), 6.89 (dd, J = 8.3 Hz, 0.9 Hz, 1 H), 6.44 (d, J = 7.3 Hz, 1 H), 4.26 (ddd, J = 7.2 Hz, 6.0 Hz, 1 H), 3.86 (s, 3 H), 3.51 (s, 3 H), 1.82-1.57 (m, 4 H), 1.26 (s, 3 H), 1.14 (s, 3 H).

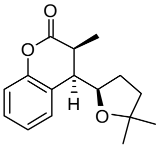
The Mosher ester analysis revealed that absolute configuration of major diastereomer at benzylic position is *R*.



Derivatization of Diels-Alder product via Jones oxidation:[10]



Synthesis of (3*S*,4*R*)-4-((*R*)-5,5-dimethyltetrahydrofuran-2-yl)-3-methylchroman-2-one (S15):



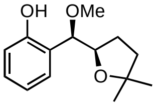
The Jones Reagent was prepared by addition of 2.5 mL of conc. H_2SO_4 to 2.5 g of CrO_3. The solution was cooled to 0 °C and 7.5 mL of cold H_2O was added slowly with rapid stirring. 132 mg of **5a** in a 100 mL round bottom flask was dissolved in 5 mL of acetone under an atmosphere of nitrogen. The reaction flask was cooled to 0 °C and 800 μL of Jones Reagent (2.0 mmol, 4.0 equiv.) was added dropwise. The reaction mixture was slowly warmed to rt and stirred for 3 h. The reaction was quenched by the dropwise addition of isopropanol until the reaction mixture turned from orange to green. Approximately 10 mL of brine was added, and the mixture was extracted with EtOAc (3 x 10 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*, then purified by flash silica-gel column chromatography with 4% EtOAc/hexanes to 10% EtOAc/hexanes as eluent to give 69 mg of product (53% yield). R_f = 0.40 w/ 1:4 EtOAc:hexanes, colorless solid, MP = 79-86 °C. $[\alpha]^{20}_D$ = +43.5° (c = 0.45, $CHCl_3$), ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2 H), 7.08 (ddd, *J* = 7.5 Hz, *J* = 7.5 Hz, *J* = 1.3 Hz, 1 H), 7.04 (dd, *J* = 8.4 Hz, *J* = 1.5 Hz, 1 H), 4.22 (ddd, *J* = 9.4 Hz, *J* = 5.5 Hz, *J* = 4.9 Hz, 1 H), 3.27 (dd, *J* = 6.4 Hz, *J* = 5.0 Hz, 1 H), 3.04 (dq, *J* = 6.9 Hz, *J* = 6.9 Hz, 1 H), 1.80-1.71 (m, 1 H), 1.68-1.59 (m, 1 H), 1.49 (dd, *J* = 7.8 Hz, *J* = 3.0 Hz, 1 H), 1.41 (d, *J* = 7.0 Hz, 3 H), 1.44-1.34 (m, 1 H), 1.22 (s, 3 H), 0.89 (m, 1 H). ^{13}C-NMR {^{1}H} (75 MHz, $CDCl_3$) δ 171.9, 152.0, 130.9, 128.8, 124.1, 123.9, 116.6, 80.6, 77.4, 44.4, 38.7, 37.1, 28.7, 28.6, 27.8, 12.8. IR 2968, 2871, 1767, 1487, 1457, 1379, 1215, 1142, 1083, 1056, 757 cm^{-1}. HRMS $C_{16}H_{20}O_3$ $(M+Na)^+$ calcd. 283.1310, obsvd. 283.1315. X-ray quality single crystals were obtained by recrystallization from cold pentane (see page S42).

Synthesis of Pd((*S*)-^{i}PrQuinox)Cl$_2$: To an oven dried 100 mL round bottom flask equipped with stir bar was added 380.9 mg of Pd(MeCN)$_2$Cl$_2$ (1.470 mmol, 1.000 equiv.), 300 mg of (*S*)-^{i}PrQuinox ligand (1.47 mmol, 1.00 equiv.) and 80 mL of DCE under a nitrogen atmosphere. The reaction mixture was heated at reflux for 10 h. The reaction mixture was then allowed to cool to room temperature and concentrated to ca. 2 mL. To this mixture, 3 mL of CH$_2$Cl$_2$ was added, and precipitation was observed. The remaining solvent was removed *in vacuo* and dried overnight under vacuum to give the desired complex in quantitative yield (680 mg). $[\alpha]^{20}_{D} = -57°$ (c = 0.19, CHCl$_3$), ^{1}H-NMR (400 MHz, CDCl$_3$) δ 9.59 (d, *J* = 8.7 Hz, 1 H), 8.39 (d, *J* = 8.0 Hz, 1 H), 7.83 (d, *J* = 8.4 Hz, 1 H), 7.71 (d, *J* = 8.4 Hz, 1 H), 7.56 (m, 2 H), 5.07 (t, *J* = 10.6 Hz, 1 H), 4.76-4.71 (m, 2 H), 2.89-2.74 (m, 1 H), 0.95 (d, *J* = 6.9 Hz, 3 H), 0.81 (d, *J* = 6.6 Hz, 3 H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ 169.9, 148.7, 145.9, 141.6, 132.3, 131.3, 129.8, 129.5, 127.9, 120.7, 72.1, 67.7, 29.3, 18.8, 14.5. IR: 2958, 1651, 1589, 1371, 923, 839 cm^{-1}.

Synthesis of Cu((*S*)-^{i}PrQuinox)Cl$_2$: To an oven dried 50 mL round bottom flask equipped with stir bar was added 45.3 mg of CuCl$_2$ (0.340 mmol, 1.00 equiv.), 81 mg of (*S*)-^{i}PrQuinox ligand (0.34 mmol, 1.00 equiv.) and 16 mL of MeOH under a nitrogen atmosphere. The reaction mixture was heated at reflux for 10 h. The reaction mixture was then allowed to cool to room temperature and concentrated to ca. 2 mL. 3 mL of CH$_2$Cl$_2$ was added, and precipitation was observed. The remaining solvent was removed *in vacuo* and dried overnight under vacuum to give complex in quantitative yield (126.3 mg). $[\alpha]^{20}_{D} = +229°$ (c = 0.17, CHCl$_3$), IR: 1651, 1590, 1510, 1254, 1165, 758 cm^{-1}, HRMS C$_{16}$H$_{24}$O$_5$ (M+Na)$^+$ calcd. 338.0247, obsvd. 338.0249.

X-Ray crystal structure data for dialkoxylation product 3a:

Crystal Structure Report



Experimental:

A colorless prism shaped crystal 0.35 x 0.33 x 0.20 mm in size was mounted on a glass fiber with traces of viscous oil and then transferred to a Nonius KappaCCD diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å). Ten frames of data were collected at 105(1)K with an oscillation range of *1* deg/frame and an exposure time of 20 sec/frame. [REF1] Indexing and unit cell refinement based on all observed reflection from those ten frames, indicated a hexagonal ***P*** lattice. A total of 3395 reflections (Θ_{max} = 27.45°) were indexed, integrated and corrected for Lorentz, polarization and absorption effects using DENZO-SMN and SCALEPAC. [REF 2] Post refinement of the unit cell gave *a* = 16.7018(5) Å, b = 16.7018(5) Å, c = 9.6419(2) Å, and V = 2329.27(11) Å^3. Axial photographs and systematic absences were consistent with the compound having crystallized in the hexagonal space group ***P***6_2.

The structure was solved by a combination of direct methods and heavy atom using SIR 97. [REF 3]
All of the non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were either located, refined isotropically or assigned isotropic displacement coefficients U(H) = 1.2U(C) or 1.5U(Cmethyl), and their coordinates were allowed to ride on their respective carbons using SHELXL97. [REF 4] The five-member ring carbon atoms (C10, C11) exhibit orientation disorder 50:50. There are also disordered hexanes solvent molecules in the lattice. The weighting scheme employed was $w = 1/[\sigma^2(F_o^2) + (0.0992P)^2 + 1.0242P]$ where $P = (F_o^2 + 2F_c^2)/3$. The refinement converged to R1 = 0.0635, wR2 = 0.1640, and S = 1.036 for 2676 reflections with 1> 2σ (I), and R1 = 0.0861, wR2 = 0.1819, and S = 1.036 for 3395 unique reflections and 257 parameters. [REF 5] The maximum Δ/σ in the final cycle of the least-squares was 0, and the residual peaks on the final difference-Fourier map ranged from -0.196 to 0.393 e/Å^3. Scattering factors were taken from the International Tables for Crystallography, Volume C. [REF 6, REF 7]

REF 1 COLLECT Data Collection Software. Nonius B.V. 1998.

REF 2 Otwinowski, Z.; Minor, W., "Processing of X-ray Diffraction Data Collected in Oscillation Mode", Methods Enzymol. 1997, 276, 307-326.

REF 3 SIR97 (Release 1.02) - A program for automatic solution and refinement of crystal structure. A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G. G. Moliteni, G. Polidori, and R. Spagna.

REF 4 SHELX97 [Includes SHELXS97, SHELXL97, CIFTAB] - Sheldrick, G. M. (1997). Programs for Crystal Structure Analysis (Release 97-2). University of Göttingen, Germany.

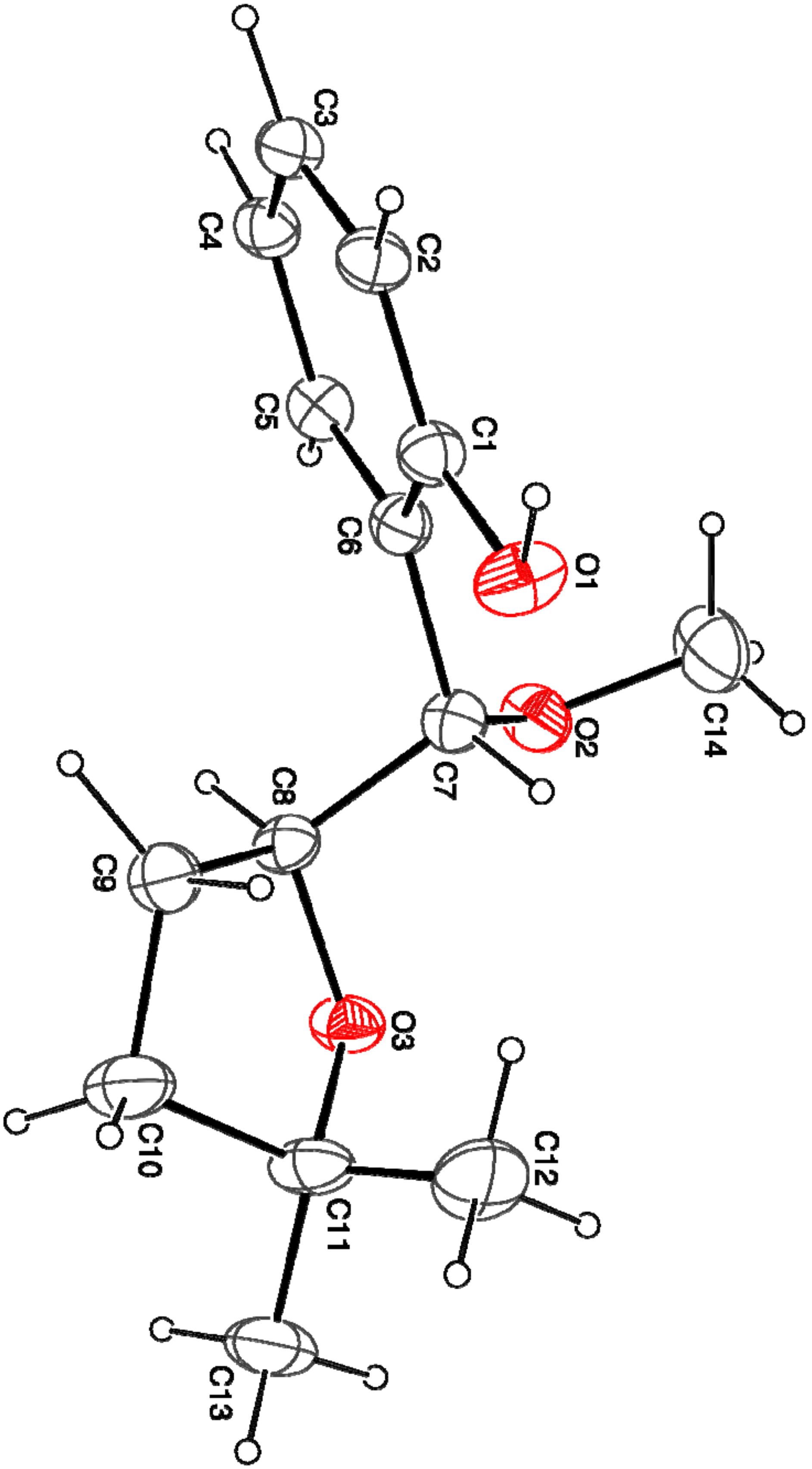
REF 5 $R1 = \Sigma(|| F_o | - |F_c ||) / \Sigma |F_o|$, $wR2 = [\Sigma(w(F_o^2 - F_c^2)2) / \Sigma(F_o^2)^2]^{1/2}$, and S = Goodness-of-fit on $F^2 = [\Sigma(w(F_o^2 - F_c^2)^2 / (n-p)]^{1/2}$, where n is the number of reflections and p is the number of parameters refined.

REF 6 Maslen, E. N.; Fox, A. G.; O'Keefe, M. A., International Tables for Crystallography: Mathemetical, Physical and Chemical Tables, Vol. C, Chapter 6, Wilson, A. J. C., Ed.; Kluwer, Dordrecht, The Netherlands, 1992; pp. 476-516.

REF 7 Creagh, D. C.; McAuley, W. J., International Tables for Crystallography: mathematical, Physical and Chemical tables, Vol. C, Chapter 4 Wilson, A. J. C., Ed.; Kluwer, Dordrecht, The Netherlands, 1992; pp. 206-222.

REF8 ORTEP3 for Windows - L. J. Farrugia, *J. Appl. Crystallogr*. **1997**, *30*, 565.

REF9 WinGX A Windows Program for Crystal Structure Analysis. L. J. Farrugia, University of Glasgow, Glasgow, 1998.


C3
C4
C2
C5
C1
C6
O1
C14
O2
C7
C8
C9
O3
C12
C10
C11
C13

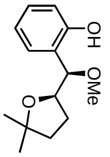

OH
OMe
O

Table 1. Crystal data and structure refinement for mss032.

Identification code	mss032	
Empirical formula	C15.50 H23.50 O3	
Formula weight	257.84	
Temperature	105(1) K	
Wavelength	0.71069 Å	
Crystal system	Hexagonal	
Space group	$\boldsymbol{P}6_2$	
Unit cell dimensions	a = 16.7018(5) Å	〈= 90°.
	b = 16.7018(5) Å	®= 90°.
	c = 9.6419(2) Å	© = 120°.
Volume	2329.27(11) Å^3	
Z	6	
Density (calculated)	1.103 Mg/m^3	
Absorption coefficient	0.075 mm^{-1}	
F(000)	843	
Crystal size	0.35 x 0.33 x 0.20 mm^3	
Theta range for data collection	2.54 to 27.45°.	
Index ranges	-21<=h<=21, -18<=k<=18, -10<=l<=12	
Reflections collected	3395	
Independent reflections	3395 [R(int) = 0.0000]	
Completeness to theta = 27.45°	99.7 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9852 and 0.9743	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3395 / 4 / 257	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0635, wR2 = 0.1640	
R indices (all data)	R1 = 0.0861, wR2 = 0.1819	
Absolute structure parameter	0.1(18)	
Extinction coefficient	0.018(5)	
Largest diff. peak and hole	0.393 and -0.196 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for mss032. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	3818(2)	1488(1)	-421(3)	48(1)
O(2)	3603(2)	3777(2)	3(2)	45(1)
O(3)	3815(2)	3556(2)	2783(2)	42(1)
C(1)	4476(2)	2268(2)	-1069(3)	35(1)
C(2)	5068(2)	2238(2)	-2068(3)	37(1)
C(3)	5726(2)	3040(2)	-2714(3)	37(1)
C(4)	5794(2)	3883(2)	-2361(3)	37(1)
C(5)	5213(2)	3909(2)	-1359(3)	36(1)
C(6)	4550(2)	3112(2)	-700(3)	34(1)
C(7)	3929(2)	3162(2)	411(3)	35(1)
C(8)	4447(2)	3552(2)	1756(3)	35(1)
C(9)	4842(2)	2994(2)	2412(3)	43(1)
C(10)	4577(8)	2857(9)	3884(10)	57(3)
C(11)	3645(6)	2830(7)	3865(8)	47(2)
C(12)	2862(6)	1955(6)	3442(10)	66(3)
C(13)	3481(9)	3168(11)	5216(10)	69(3)
C(10')	4954(7)	3399(8)	3907(9)	53(2)
C(11')	4102(6)	3501(6)	4147(7)	47(2)
C(12')	4348(6)	4403(6)	4877(8)	69(2)
C(13')	3337(9)	2687(8)	4838(14)	72(3)
C(14)	2924(3)	3409(4)	-1044(5)	68(1)
C(15)	1666(4)	845(4)	2063(8)	53(2)
C(16)	1338(4)	743(5)	480(7)	51(2)
C(17)	1546(17)	434(14)	-1036(15)	49(5)
C(18)	1573(7)	951(6)	-2456(9)	43(2)

Table 3. Bond lengths [Å] and angles [°] for mss032.

O(1)-C(1)	1.365(4)
O(2)-C(14)	1.410(4)
O(2)-C(7)	1.436(3)
O(3)-C(11')	1.419(7)
O(3)-C(8)	1.450(3)
O(3)-C(11)	1.515(7)
C(1)-C(6)	1.398(4)
C(1)-C(2)	1.399(4)
C(2)-C(3)	1.385(4)
C(3)-C(4)	1.398(4)
C(4)-C(5)	1.385(4)
C(5)-C(6)	1.390(4)
C(6)-C(7)	1.522(4)
C(7)-C(8)	1.514(4)
C(8)-C(9)	1.522(4)
C(9)-C(10)	1.471(10)
C(9)-C(10')	1.563(9)
C(10)-C(11)	1.535(12)
C(11)-C(12)	1.449(14)
C(11)-C(13)	1.498(14)
C(10')-C(11')	1.533(10)
C(11')-C(13')	1.478(14)
C(11')-C(12')	1.522(11)
C(15)-C(16)	1.602(10)
C(16)-C(17)	1.645(15)
C(17)-C(18)	1.607(15)
C(14)-O(2)-C(7)	113.3(3)
C(11')-O(3)-C(8)	111.2(3)
C(11')-O(3)-C(11)	40.8(4)
C(8)-O(3)-C(11)	108.2(3)
O(1)-C(1)-C(6)	117.9(2)
O(1)-C(1)-C(2)	121.8(2)
C(6)-C(1)-C(2)	120.3(3)
C(3)-C(2)-C(1)	120.5(3)

C(2)-C(3)-C(4)	119.4(3)
C(5)-C(4)-C(3)	119.8(3)
C(4)-C(5)-C(6)	121.6(3)
C(5)-C(6)-C(1)	118.4(3)
C(5)-C(6)-C(7)	120.5(2)
C(1)-C(6)-C(7)	121.1(2)
O(2)-C(7)-C(8)	105.5(2)
O(2)-C(7)-C(6)	111.1(2)
C(8)-C(7)-C(6)	111.6(2)
O(3)-C(8)-C(7)	109.0(2)
O(3)-C(8)-C(9)	105.0(2)
C(7)-C(8)-C(9)	115.0(2)
C(10)-C(9)-C(8)	107.9(5)
C(10)-C(9)-C(10')	30.5(4)
C(8)-C(9)-C(10')	96.5(4)
C(9)-C(10)-C(11)	102.4(7)
C(12)-C(11)-C(13)	112.5(9)
C(12)-C(11)-O(3)	109.0(6)
C(13)-C(11)-O(3)	107.1(8)
C(12)-C(11)-C(10)	115.0(8)
C(13)-C(11)-C(10)	110.7(8)
O(3)-C(11)-C(10)	101.7(6)
C(11')-C(10')-C(9)	105.7(6)
O(3)-C(11')-C(13')	108.2(8)
O(3)-C(11')-C(12')	107.3(5)
C(13')-C(11')-C(12')	112.5(8)
O(3)-C(11')-C(10')	103.3(5)
C(13')-C(11')-C(10')	112.9(7)
C(12')-C(11')-C(10')	111.9(7)
C(16)-C(15)-C(17)#1	86.0(6)
C(15)-C(16)-C(17)	140.0(9)
C(18)-C(17)-C(16)	122.8(12)
C(18)-C(17)-C(15)#2	109.9(11)
C(16)-C(17)-C(15)#2	110.7(10)

Symmetry transformations used to generate equivalent atoms:

#1 x-y,x,z+1/3 #2 y,-x+y,z-1/3

Table 4. Anisotropic displacement parameters (Å^{2}x 10^3)for mss032. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	52(1)	30(1)	56(1)	2(1)	17(1)	17(1)
O(2)	52(1)	59(1)	40(1)	-5(1)	-5(1)	41(1)
O(3)	50(1)	56(1)	32(1)	3(1)	7(1)	37(1)
C(1)	37(2)	33(1)	35(2)	-2(1)	1(1)	17(1)
C(2)	44(2)	34(2)	35(2)	-4(1)	1(1)	21(1)
C(3)	39(2)	45(2)	31(1)	-4(1)	0(1)	23(1)
C(4)	41(2)	40(2)	30(1)	4(1)	0(1)	22(1)
C(5)	43(2)	33(1)	37(2)	-1(1)	-2(1)	24(1)
C(6)	36(1)	38(2)	33(2)	-1(1)	-2(1)	22(1)
C(7)	38(2)	36(2)	37(2)	0(1)	1(1)	24(1)
C(8)	37(2)	40(2)	36(1)	4(1)	6(1)	26(1)
C(9)	46(2)	51(2)	42(2)	7(1)	2(1)	30(2)
C(10)	64(6)	85(7)	43(4)	22(6)	18(4)	51(6)
C(11)	60(5)	61(6)	34(4)	21(4)	16(3)	41(4)
C(12)	67(5)	55(5)	63(5)	28(4)	14(4)	22(4)
C(13)	77(7)	107(10)	32(5)	17(5)	13(4)	53(8)
C(10')	67(6)	85(6)	35(3)	0(4)	-1(4)	58(5)
C(11')	67(4)	59(5)	37(3)	10(3)	6(3)	48(4)
C(12')	97(6)	85(6)	50(4)	-22(4)	-20(4)	66(5)
C(13')	88(7)	75(7)	75(8)	22(6)	11(6)	57(7)
C(14)	66(2)	101(3)	64(2)	-20(2)	-19(2)	61(2)
C(15)	42(3)	23(3)	91(5)	-5(3)	27(3)	15(2)
C(16)	34(3)	42(3)	62(4)	-23(3)	8(3)	8(3)
C(18)	56(5)	36(4)	39(5)	-13(3)	8(4)	23(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for mss032.

	x	y	z	U(eq)
H(10A)	5036	3375	4459	69
H(10B)	4509	2269	4237	69
H(12A)	2979	1791	2518	98
H(12B)	2305	2010	3415	98
H(12C)	2774	1474	4106	98
H(13A)	4031	3754	5466	103
H(13B)	3355	2709	5941	103
H(13C)	2949	3262	5125	103
H(10C)	4979	2975	4600	64
H(10D)	5527	4006	3978	64
H(12D)	4835	4923	4356	103
H(12E)	4568	4397	5816	103
H(12F)	3799	4472	4927	103
H(13D)	3202	2126	4329	108
H(13E)	2785	2751	4853	108
H(13F)	3517	2645	5791	108
H(14A)	2729	3858	-1276	103
H(14B)	2389	2836	-712	103
H(14C)	3180	3278	-1871	103
H(15A)	2345	1188	2191	63
H(15B)	1373	258	2592	63
H(16A)	1432	1366	280	61
H(16B)	660	341	564	61
H(17A)	2191	546	-943	59
H(18A)	1719	665	-3230	65
H(18B)	2048	1605	-2390	65
H(18C)	969	898	-2615	65
H(1)	3870(30)	940(30)	-840(60)	83(15)
H(2)	5040(30)	1680(30)	-2330(50)	55(10)
H(3)	6140(20)	2990(20)	-3360(40)	33(8)
H(4)	6260(30)	4450(30)	-2920(50)	70(12)

H(5)	5230(20)	4460(20)	-1130(30)	30(7)
H(7)	3380(20)	2540(20)	670(40)	41(9)
H(8)	4990(20)	4260(20)	1540(30)	30(7)
H(9A)	5470(20)	3110(20)	1950(30)	36
H(9B)	4360(20)	2290(20)	2220(40)	36

Table 6. Torsion angles [°] for mss032.

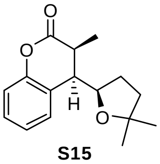
O(1)-C(1)-C(2)-C(3)	179.7(3)
C(6)-C(1)-C(2)-C(3)	-0.7(4)
C(1)-C(2)-C(3)-C(4)	-0.2(4)
C(2)-C(3)-C(4)-C(5)	0.9(4)
C(3)-C(4)-C(5)-C(6)	-0.8(4)
C(4)-C(5)-C(6)-C(1)	0.0(4)
C(4)-C(5)-C(6)-C(7)	179.2(3)
O(1)-C(1)-C(6)-C(5)	-179.6(3)
C(2)-C(1)-C(6)-C(5)	0.7(4)
O(1)-C(1)-C(6)-C(7)	1.2(4)
C(2)-C(1)-C(6)-C(7)	-178.5(3)
C(14)-O(2)-C(7)-C(8)	-165.8(3)
C(14)-O(2)-C(7)-C(6)	73.2(3)
C(5)-C(6)-C(7)-O(2)	43.1(3)
C(1)-C(6)-C(7)-O(2)	-137.7(3)
C(5)-C(6)-C(7)-C(8)	-74.3(3)
C(1)-C(6)-C(7)-C(8)	104.9(3)
C(11')-O(3)-C(8)-C(7)	153.3(4)
C(11)-O(3)-C(8)-C(7)	109.9(5)
C(11')-O(3)-C(8)-C(9)	29.7(5)
C(11)-O(3)-C(8)-C(9)	-13.7(5)
O(2)-C(7)-C(8)-O(3)	61.1(3)
C(6)-C(7)-C(8)-O(3)	-178.2(2)
O(2)-C(7)-C(8)-C(9)	178.6(2)
C(6)-C(7)-C(8)-C(9)	-60.7(3)
O(3)-C(8)-C(9)-C(10)	-11.4(6)
C(7)-C(8)-C(9)-C(10)	-131.1(6)
O(3)-C(8)-C(9)-C(10')	-40.4(5)
C(7)-C(8)-C(9)-C(10')	-160.1(5)

C(8)-C(9)-C(10)-C(11)	31.0(9)
C(10')-C(9)-C(10)-C(11)	102.6(13)
C(11')-O(3)-C(11)-C(12)	168.7(9)
C(8)-O(3)-C(11)-C(12)	-89.6(6)
C(11')-O(3)-C(11)-C(13)	46.8(8)
C(8)-O(3)-C(11)-C(13)	148.5(7)
C(11')-O(3)-C(11)-C(10)	-69.3(8)
C(8)-O(3)-C(11)-C(10)	32.4(7)
C(9)-C(10)-C(11)-C(12)	79.8(9)
C(9)-C(10)-C(11)-C(13)	-151.4(10)
C(9)-C(10)-C(11)-O(3)	-37.9(9)
C(10)-C(9)-C(10')-C(11')	-75.9(12)
C(8)-C(9)-C(10')-C(11')	38.7(7)
C(8)-O(3)-C(11')-C(13')	-123.3(6)
C(11)-O(3)-C(11')-C(13')	-29.8(7)
C(8)-O(3)-C(11')-C(12')	115.0(5)
C(11)-O(3)-C(11')-C(12')	-151.4(9)
C(8)-O(3)-C(11')-C(10')	-3.4(7)
C(11)-O(3)-C(11')-C(10')	90.2(7)
C(9)-C(10')-C(11')-O(3)	-23.3(8)
C(9)-C(10')-C(11')-C(13')	93.3(10)
C(9)-C(10')-C(11')-C(12')	-138.4(7)
C(17)#1-C(15)-C(16)-C(17)	164.1(17)
C(15)-C(16)-C(17)-C(18)	-141.6(12)
C(15)-C(16)-C(17)-C(15)#2	85.8(17)

Symmetry transformations used to generate equivalent atoms:

#1 x-y,x,z+1/3   #2 y,-x+y,z-1/3

X-Ray crystal structure data for Jones oxidation product S15:


S15

Crystal Structure Report

Experimental:

A colorless prism shaped crystal 0.33 x 0.33 x 0.30 mm in size was mounted on a glass fiber with traces of viscous oil and then transferred to a Nonius KappaCCD diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å). Ten frames of data were collected at 150(1) K with an oscillation range of *1* deg/frame and an exposure time of 20 sec/frame. [REF1] Indexing and unit cell refinement based on all observed reflection from those ten frames, indicated a monoclinic ***C*** lattice. A total of 11462 reflections (Θ_{max} = 27.5°) were indexed, integrated and corrected for Lorentz, polarization and absorption effects using DENZO-SMN and SCALEPAC. [REF 2] Post refinement of the unit cell gave *a* = 21.3641(6) Å, b = 10.9638(4) Å, c = 23.4509(5) Å, β =90.8210(17), and V = 5492.4(3) Å^3. Axial photographs and systematic absences were consistent with the compound having crystallized in the monoclinic space group ***C*** 2/*c*.

The structure was solved by a combination of direct methods and heavy atom using SIR 97. [REF 3]

All of the non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were located and refined isotropically using SHELXL97. [REF 4] The weighting scheme employed was $w = 1/[\sigma^2(F_o^2) + (0.0576P)^2 + 1.7804P]$ where $P = (F_o^2 + 2F_c^2)/3$. The refinement converged to R1 = 0.0473, wR2 = 0.1037, and S = 1.0150 for 4096 reflections with 1> 2σ(I), and R1 = 0.0902, wR2 = 0.1225, and S = 1.0150 for 6287 unique reflections and 503 parameters. [REF 5] The maximum Δ/σ in the final cycle of the least-squares was 0, and the residual peaks on the final difference-Fourier map ranged from -0.234 to 0.187 e/Å^3. Scattering factors were taken from the International Tables for Crystallography, Volume C. [REF 6, REF 7]

REF 1 COLLECT Data Collection Software. Nonius B.V. 1998.

REF 2 Otwinowski, Z.; Minor, W., "Processing of X-ray Diffraction Data Collected in Oscillation Mode", Methods Enzymol. 1997, 276, 307-326.

REF 3 SIR97 (Release 1.02) - A program for automatic solution and refinement of crystal structure. A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G. G. Moliteni, G. Polidori, and R. Spagna.

REF 4 SHELX97 [Includes SHELXS97, SHELXL97, CIFTAB] - Sheldrick, G. M. (1997). Programs for Crystal Structure Analysis (Release 97-2). University of Göttingen, Germany.

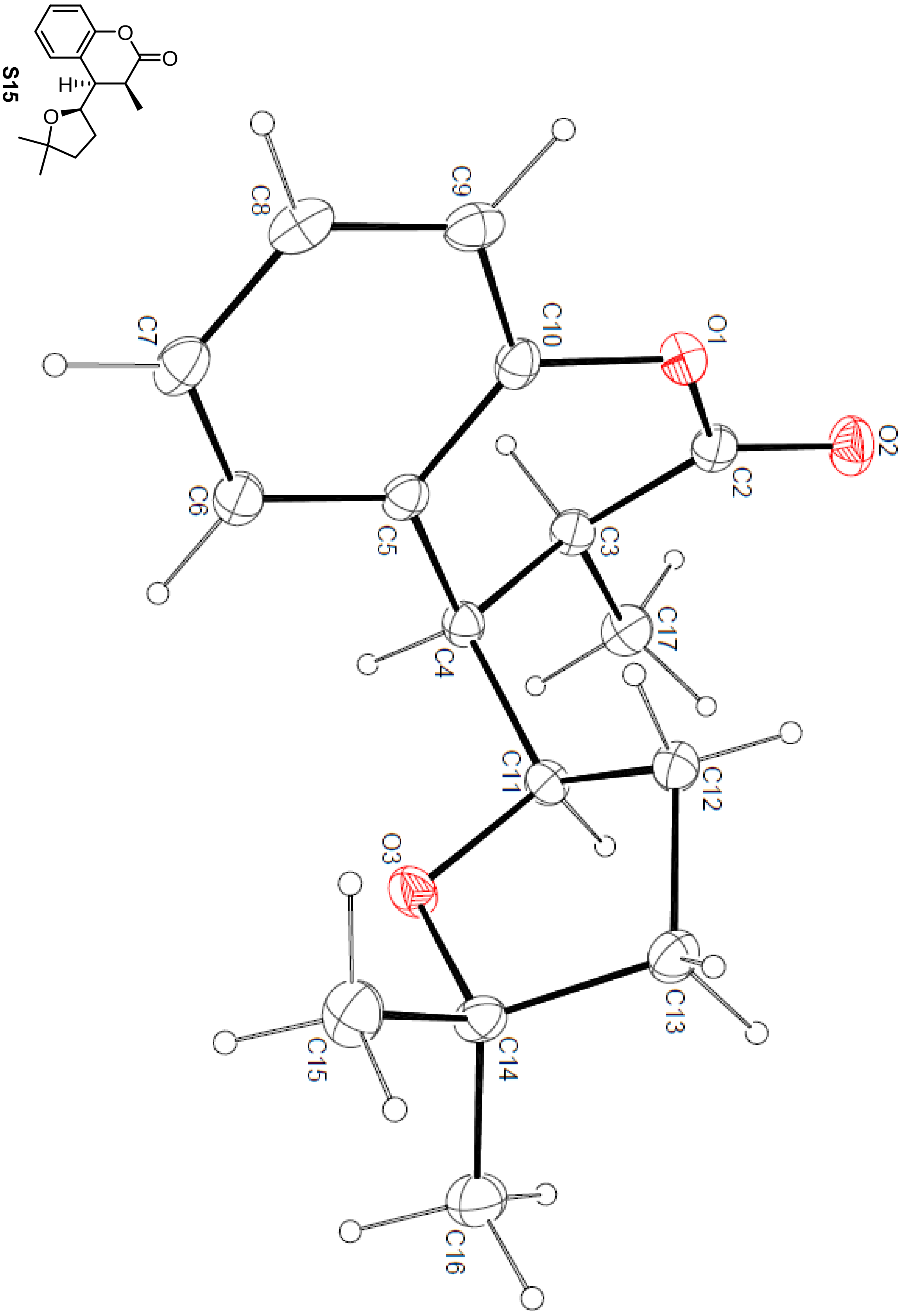
REF 5 $R1 = \Sigma(|| F_o | - |F_c ||) / \Sigma |F_o|$, $wR2 = [\Sigma(w(F_o^2 - F_c^2)2) / \Sigma(F_o^2)^2]^{1/2}$, and S = Goodness-of-fit on $F^2 = [\Sigma(w(F_o^2 - F_c^2)^2 / (n-p)]^{1/2}$, where n is the number of reflections and p is the number of parameters refined.

REF 6 Maslen, E. N.; Fox, A. G.; O'Keefe, M. A., International Tables for Crystallography: Mathemetical, Physical and Chemical Tables, Vol. C, Chapter 6, Wilson, A. J. C., Ed.; Kluwer, Dordrecht, The Netherlands, 1992; pp. 476-516.

REF 7 Creagh, D. C.; McAuley, W. J., International Tables for Crystallography: mathematical, Physical and Chemical tables, Vol. C, Chapter 4 Wilson, A. J. C., Ed.; Kluwer, Dordrecht, The Netherlands, 1992; pp. 206-222.

REF8 ORTEP3 for Windows - L. J. Farrugia, *J. Appl. Crystallogr*. **1997**, *30*, 565.

REF9 WinGX A Windows Program for Crystal Structure Analysis. L. J. Farrugia, University of Glasgow, Glasgow, 1998.


O
O
H
O
C8
C9
C7
C10
O1
O2
C6
C5
C2
C3
C4
C17
C11
C12
O3
C13
C15
C14
C16

S15

Table 1. Crystal data and structure refinement for mss034.

Identification code	mss034	
Empirical formula	C16 H20 O3	
Formula weight	260.32	
Temperature	150(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	***C*** 2/*c*	
Unit cell dimensions	a = 21.3641(6) Å	α= 90°.
	b = 10.9638(4) Å	β= 90.8210(17)°.
	c = 23.4509(5) Å	γ = 90°.
Volume	5492.4(3) $Å^3$	
Z	16	
Density (calculated)	1.259 Mg/m^3	
Absorption coefficient	0.086 mm^{-1}	
F(000)	2240	
Crystal size	0.33 x 0.33 x 0.30 mm^3	
Theta range for data collection	1.91 to 27.50°.	
Index ranges	-27<=h<=27, -14<=k<=14, -30<=l<=30	
Reflections collected	11462	
Independent reflections	6287 [R(int) = 0.0366]	
Completeness to theta = 27.50°	99.3 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9748 and 0.9723	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6287 / 0 / 503	
Goodness-of-fit on F^2	1.015	
Final R indices [I>2sigma(I)]	R1 = 0.0473, wR2 = 0.1037	
R indices (all data)	R1 = 0.0902, wR2 = 0.1225	
Largest diff. peak and hole	0.187 and -0.234 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for mss034. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(2)	152(1)	1308(2)	1829(1)	26(1)
C(2A)	2639(1)	-1115(2)	1928(1)	26(1)
C(3)	711(1)	477(2)	1798(1)	25(1)
C(3A)	3172(1)	-1996(1)	1875(1)	23(1)
C(4)	1168(1)	931(1)	1342(1)	22(1)
C(4A)	3629(1)	-1579(1)	1408(1)	22(1)
C(5)	1331(1)	2231(1)	1486(1)	23(1)
C(5A)	3825(1)	-295(1)	1546(1)	22(1)
C(6)	1918(1)	2740(2)	1398(1)	28(1)
C(6A)	4416(1)	174(2)	1430(1)	27(1)
C(7)	2041(1)	3947(2)	1543(1)	31(1)
C(7A)	4574(1)	1361(2)	1584(1)	33(1)
C(8)	1577(1)	4660(2)	1781(1)	31(1)
C(8A)	4143(1)	2099(2)	1854(1)	34(1)
C(9)	990(1)	4170(2)	1879(1)	29(1)
C(9A)	3550(1)	1658(2)	1970(1)	30(1)
C(10)	879(1)	2966(1)	1731(1)	24(1)
C(10A)	3403(1)	476(1)	1813(1)	24(1)
C(11)	917(1)	779(2)	726(1)	22(1)
C(11A)	3370(1)	-1719(1)	796(1)	23(1)
C(12)	463(1)	1726(2)	491(1)	26(1)
C(12A)	2936(1)	-737(2)	562(1)	26(1)
C(13)	552(1)	1581(2)	-151(1)	28(1)
C(13A)	3027(1)	-873(2)	-81(1)	29(1)
C(14)	1242(1)	1212(1)	-211(1)	24(1)
C(14A)	3709(1)	-1287(1)	-138(1)	25(1)
C(15)	1660(1)	2265(2)	-376(1)	35(1)
C(15A)	4150(1)	-258(2)	-291(1)	37(1)
C(16)	1322(1)	143(2)	-614(1)	36(1)
C(16A)	3776(1)	-2345(2)	-552(1)	38(1)
C(17)	517(1)	-853(2)	1742(1)	32(1)

C(17A)	2948(1)	-3307(2)	1823(1)	32(1)
O(1)	269(1)	2537(1)	1818(1)	28(1)
O(1A)	2787(1)	101(1)	1918(1)	27(1)
O(2)	-385(1)	995(1)	1871(1)	34(1)
O(2A)	2096(1)	-1373(1)	1991(1)	38(1)
O(3)	1444(1)	844(1)	358(1)	28(1)
O(3A)	3899(1)	-1701(1)	427(1)	29(1)

Table 3. Bond lengths [Å] and angles [°] for mss034.

C(2)-O(2)	1.2016(18)
C(2)-O(1)	1.371(2)
C(2)-C(3)	1.506(2)
C(2A)-O(2A)	1.2032(18)
C(2A)-O(1A)	1.3705(19)
C(2A)-C(3A)	1.501(2)
C(3)-C(17)	1.521(2)
C(3)-C(4)	1.5406(19)
C(3)-H(3)	0.993(15)
C(3A)-C(17A)	1.520(2)
C(3A)-C(4A)	1.547(2)
C(3A)-H(3A)	1.007(16)
C(4)-C(5)	1.504(2)
C(4)-C(11)	1.541(2)
C(4)-H(4)	1.003(16)
C(4A)-C(5A)	1.502(2)
C(4A)-C(11A)	1.538(2)
C(4A)-H(4A)	0.985(15)
C(5)-C(10)	1.388(2)
C(5)-C(6)	1.392(2)
C(5A)-C(10A)	1.392(2)
C(5A)-C(6A)	1.394(2)
C(6)-C(7)	1.390(2)
C(6)-H(6)	0.991(17)
C(6A)-C(7A)	1.391(2)
C(6A)-H(6A)	1.013(17)
C(7)-C(8)	1.387(2)
C(7)-H(7)	0.978(17)
C(7A)-C(8A)	1.386(2)
C(7A)-H(7A)	0.981(18)
C(8)-C(9)	1.385(2)
C(8)-H(8)	0.992(19)
C(8A)-C(9A)	1.386(2)
C(8A)-H(8A)	1.002(19)

C(9)-C(10)	1.385(2)
C(9)-H(9)	0.983(17)
C(9A)-C(10A)	1.383(2)
C(9A)-H(9A)	0.953(17)
C(10)-O(1)	1.4020(18)
C(10A)-O(1A)	1.4046(18)
C(11)-O(3)	1.4304(16)
C(11)-C(12)	1.519(2)
C(11)-H(11)	1.041(16)
C(11A)-O(3A)	1.4323(17)
C(11A)-C(12A)	1.519(2)
C(11A)-H(11A)	1.029(16)
C(12)-C(13)	1.527(2)
C(12)-H(12A)	1.032(18)
C(12)-H(12B)	0.968(17)
C(12A)-C(13A)	1.529(2)
C(12A)-H(12C)	1.008(17)
C(12A)-H(12D)	0.984(16)
C(13)-C(14)	1.538(2)
C(13)-H(13A)	0.994(18)
C(13)-H(13B)	1.003(17)
C(13A)-C(14A)	1.533(2)
C(13A)-H(13C)	0.987(19)
C(13A)-H(13D)	1.004(18)
C(14)-O(3)	1.4535(17)
C(14)-C(15)	1.513(2)
C(14)-C(16)	1.518(2)
C(14A)-O(3A)	1.4516(17)
C(14A)-C(15A)	1.516(2)
C(14A)-C(16A)	1.521(2)
C(15)-H(15A)	1.00(2)
C(15)-H(15B)	0.992(19)
C(15)-H(15C)	0.99(2)
C(15A)-H(15D)	1.01(2)
C(15A)-H(15E)	0.99(2)
C(15A)-H(15F)	1.01(2)

C(16)-H(16A)	1.02(2)
C(16)-H(16B)	1.00(2)
C(16)-H(16C)	1.022(19)
C(16A)-H(16D)	1.00(2)
C(16A)-H(16E)	1.042(19)
C(16A)-H(16F)	0.99(2)
C(17)-H(17A)	1.006(18)
C(17)-H(17B)	0.972(17)
C(17)-H(17C)	1.021(19)
C(17A)-H(17D)	0.990(18)
C(17A)-H(17E)	1.013(17)
C(17A)-H(17F)	1.037(19)
O(2)-C(2)-O(1)	117.23(14)
O(2)-C(2)-C(3)	126.16(15)
O(1)-C(2)-C(3)	116.60(13)
O(2A)-C(2A)-O(1A)	116.97(14)
O(2A)-C(2A)-C(3A)	126.36(15)
O(1A)-C(2A)-C(3A)	116.65(13)
C(2)-C(3)-C(17)	111.66(14)
C(2)-C(3)-C(4)	110.46(12)
C(17)-C(3)-C(4)	115.18(13)
C(2)-C(3)-H(3)	105.2(9)
C(17)-C(3)-H(3)	107.9(9)
C(4)-C(3)-H(3)	105.7(8)
C(2A)-C(3A)-C(17A)	112.15(14)
C(2A)-C(3A)-C(4A)	110.90(12)
C(17A)-C(3A)-C(4A)	115.13(13)
C(2A)-C(3A)-H(3A)	105.3(9)
C(17A)-C(3A)-H(3A)	107.8(9)
C(4A)-C(3A)-H(3A)	104.8(9)
C(5)-C(4)-C(3)	107.28(12)
C(5)-C(4)-C(11)	112.93(12)
C(3)-C(4)-C(11)	113.55(12)
C(5)-C(4)-H(4)	110.4(9)
C(3)-C(4)-H(4)	106.6(8)

C(11)-C(4)-H(4)	105.9(9)
C(5A)-C(4A)-C(11A)	112.98(12)
C(5A)-C(4A)-C(3A)	107.53(12)
C(11A)-C(4A)-C(3A)	114.12(12)
C(5A)-C(4A)-H(4A)	108.0(9)
C(11A)-C(4A)-H(4A)	106.7(8)
C(3A)-C(4A)-H(4A)	107.3(8)
C(10)-C(5)-C(6)	117.54(15)
C(10)-C(5)-C(4)	118.88(13)
C(6)-C(5)-C(4)	123.57(14)
C(10A)-C(5A)-C(6A)	117.30(15)
C(10A)-C(5A)-C(4A)	119.06(13)
C(6A)-C(5A)-C(4A)	123.64(14)
C(7)-C(6)-C(5)	120.91(16)
C(7)-C(6)-H(6)	119.9(10)
C(5)-C(6)-H(6)	119.2(10)
C(7A)-C(6A)-C(5A)	120.81(16)
C(7A)-C(6A)-H(6A)	121.0(10)
C(5A)-C(6A)-H(6A)	118.1(10)
C(8)-C(7)-C(6)	120.06(16)
C(8)-C(7)-H(7)	119.5(10)
C(6)-C(7)-H(7)	120.5(10)
C(8A)-C(7A)-C(6A)	120.25(16)
C(8A)-C(7A)-H(7A)	121.7(11)
C(6A)-C(7A)-H(7A)	118.0(11)
C(9)-C(8)-C(7)	120.13(16)
C(9)-C(8)-H(8)	119.6(10)
C(7)-C(8)-H(8)	120.2(10)
C(7A)-C(8A)-C(9A)	120.13(16)
C(7A)-C(8A)-H(8A)	118.6(10)
C(9A)-C(8A)-H(8A)	121.2(10)
C(10)-C(9)-C(8)	118.75(16)
C(10)-C(9)-H(9)	118.3(10)
C(8)-C(9)-H(9)	122.9(10)
C(10A)-C(9A)-C(8A)	118.62(16)
C(10A)-C(9A)-H(9A)	118.9(10)

C(8A)-C(9A)-H(9A)	122.5(10)
C(9)-C(10)-C(5)	122.61(15)
C(9)-C(10)-O(1)	116.10(14)
C(5)-C(10)-O(1)	121.22(14)
C(9A)-C(10A)-C(5A)	122.89(15)
C(9A)-C(10A)-O(1A)	115.99(14)
C(5A)-C(10A)-O(1A)	121.08(14)
O(3)-C(11)-C(12)	104.46(12)
O(3)-C(11)-C(4)	107.07(12)
C(12)-C(11)-C(4)	118.57(13)
O(3)-C(11)-H(11)	107.4(8)
C(12)-C(11)-H(11)	108.5(9)
C(4)-C(11)-H(11)	110.2(8)
O(3A)-C(11A)-C(12A)	104.71(12)
O(3A)-C(11A)-C(4A)	106.65(12)
C(12A)-C(11A)-C(4A)	118.44(13)
O(3A)-C(11A)-H(11A)	107.7(8)
C(12A)-C(11A)-H(11A)	108.8(9)
C(4A)-C(11A)-H(11A)	109.9(8)
C(11)-C(12)-C(13)	101.56(12)
C(11)-C(12)-H(12A)	111.5(9)
C(13)-C(12)-H(12A)	109.5(9)
C(11)-C(12)-H(12B)	113.3(10)
C(13)-C(12)-H(12B)	112.5(10)
H(12A)-C(12)-H(12B)	108.3(14)
C(11A)-C(12A)-C(13A)	101.62(13)
C(11A)-C(12A)-H(12C)	109.5(9)
C(13A)-C(12A)-H(12C)	110.4(9)
C(11A)-C(12A)-H(12D)	112.6(10)
C(13A)-C(12A)-H(12D)	113.7(9)
H(12C)-C(12A)-H(12D)	108.8(14)
C(12)-C(13)-C(14)	104.45(12)
C(12)-C(13)-H(13A)	113.1(10)
C(14)-C(13)-H(13A)	113.1(10)
C(12)-C(13)-H(13B)	110.2(9)
C(14)-C(13)-H(13B)	109.3(9)

H(13A)-C(13)-H(13B)	106.7(13)
C(12A)-C(13A)-C(14A)	104.45(12)
C(12A)-C(13A)-H(13C)	111.8(11)
C(14A)-C(13A)-H(13C)	113.5(10)
C(12A)-C(13A)-H(13D)	109.4(10)
C(14A)-C(13A)-H(13D)	110.4(10)
H(13C)-C(13A)-H(13D)	107.3(14)
O(3)-C(14)-C(15)	106.18(13)
O(3)-C(14)-C(16)	108.84(13)
C(15)-C(14)-C(16)	110.93(14)
O(3)-C(14)-C(13)	105.17(11)
C(15)-C(14)-C(13)	113.16(14)
C(16)-C(14)-C(13)	112.13(13)
O(3A)-C(14A)-C(15A)	106.42(13)
O(3A)-C(14A)-C(16A)	108.46(13)
C(15A)-C(14A)-C(16A)	110.55(14)
O(3A)-C(14A)-C(13A)	105.43(11)
C(15A)-C(14A)-C(13A)	113.25(15)
C(16A)-C(14A)-C(13A)	112.33(14)
C(14)-C(15)-H(15A)	110.4(11)
C(14)-C(15)-H(15B)	110.4(11)
H(15A)-C(15)-H(15B)	106.8(15)
C(14)-C(15)-H(15C)	108.6(11)
H(15A)-C(15)-H(15C)	110.7(16)
H(15B)-C(15)-H(15C)	109.9(15)
C(14A)-C(15A)-H(15D)	111.9(11)
C(14A)-C(15A)-H(15E)	108.7(12)
H(15D)-C(15A)-H(15E)	108.1(15)
C(14A)-C(15A)-H(15F)	111.5(11)
H(15D)-C(15A)-H(15F)	108.6(16)
H(15E)-C(15A)-H(15F)	107.9(15)
C(14)-C(16)-H(16A)	110.0(12)
C(14)-C(16)-H(16B)	110.5(11)
H(16A)-C(16)-H(16B)	107.0(16)
C(14)-C(16)-H(16C)	109.1(10)
H(16A)-C(16)-H(16C)	110.5(15)

H(16B)-C(16)-H(16C)	109.7(15)
C(14A)-C(16A)-H(16D)	110.5(11)
C(14A)-C(16A)-H(16E)	109.7(10)
H(16D)-C(16A)-H(16E)	110.6(15)
C(14A)-C(16A)-H(16F)	111.0(12)
H(16D)-C(16A)-H(16F)	108.2(16)
H(16E)-C(16A)-H(16F)	106.9(15)
C(3)-C(17)-H(17A)	108.7(10)
C(3)-C(17)-H(17B)	111.9(10)
H(17A)-C(17)-H(17B)	106.7(14)
C(3)-C(17)-H(17C)	110.0(11)
H(17A)-C(17)-H(17C)	110.5(14)
H(17B)-C(17)-H(17C)	109.1(14)
C(3A)-C(17A)-H(17D)	110.7(11)
C(3A)-C(17A)-H(17E)	110.7(10)
H(17D)-C(17A)-H(17E)	108.5(14)
C(3A)-C(17A)-H(17F)	109.4(10)
H(17D)-C(17A)-H(17F)	107.4(14)
H(17E)-C(17A)-H(17F)	110.1(14)
C(2)-O(1)-C(10)	120.22(12)
C(2A)-O(1A)-C(10A)	120.36(12)
C(11)-O(3)-C(14)	110.01(11)
C(11A)-O(3A)-C(14A)	110.10(11)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3)for mss034. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(2)	25(1)	36(1)	18(1)	3(1)	1(1)	-3(1)
C(2A)	27(1)	29(1)	23(1)	3(1)	1(1)	-3(1)
C(3)	24(1)	30(1)	20(1)	3(1)	1(1)	-2(1)
C(3A)	26(1)	22(1)	23(1)	2(1)	-1(1)	-2(1)
C(4)	20(1)	24(1)	21(1)	2(1)	1(1)	-1(1)
C(4A)	21(1)	21(1)	23(1)	2(1)	0(1)	0(1)
C(5)	24(1)	26(1)	18(1)	1(1)	-2(1)	-2(1)
C(5A)	23(1)	23(1)	20(1)	1(1)	-2(1)	-1(1)
C(6)	27(1)	34(1)	23(1)	3(1)	0(1)	-4(1)
C(6A)	25(1)	29(1)	28(1)	1(1)	-2(1)	-2(1)
C(7)	32(1)	34(1)	27(1)	2(1)	-3(1)	-12(1)
C(7A)	29(1)	34(1)	35(1)	2(1)	-4(1)	-10(1)
C(8)	41(1)	26(1)	25(1)	1(1)	-7(1)	-6(1)
C(8A)	42(1)	26(1)	34(1)	-1(1)	-5(1)	-9(1)
C(9)	36(1)	28(1)	22(1)	-2(1)	-5(1)	3(1)
C(9A)	40(1)	25(1)	25(1)	-2(1)	0(1)	2(1)
C(10)	23(1)	29(1)	20(1)	3(1)	-3(1)	-2(1)
C(10A)	24(1)	27(1)	21(1)	3(1)	-1(1)	-2(1)
C(11)	21(1)	25(1)	21(1)	0(1)	2(1)	-2(1)
C(11A)	23(1)	22(1)	24(1)	-1(1)	1(1)	-3(1)
C(12)	22(1)	32(1)	24(1)	0(1)	-1(1)	1(1)
C(12A)	23(1)	31(1)	26(1)	-1(1)	-3(1)	0(1)
C(13)	27(1)	33(1)	24(1)	1(1)	-4(1)	-1(1)
C(13A)	31(1)	31(1)	25(1)	1(1)	-5(1)	0(1)
C(14)	28(1)	26(1)	18(1)	1(1)	-1(1)	-2(1)
C(14A)	28(1)	29(1)	20(1)	0(1)	-3(1)	-1(1)
C(15)	35(1)	36(1)	34(1)	6(1)	1(1)	-6(1)
C(15A)	35(1)	38(1)	37(1)	5(1)	-1(1)	-8(1)
C(16)	38(1)	38(1)	34(1)	-9(1)	-3(1)	5(1)
C(16A)	44(1)	39(1)	32(1)	-9(1)	-3(1)	2(1)
C(17)	34(1)	31(1)	30(1)	4(1)	2(1)	-7(1)

C(17A)	36(1)	25(1)	34(1)	2(1)	3(1)	-7(1)
O(1)	23(1)	31(1)	30(1)	-1(1)	2(1)	2(1)
O(1A)	26(1)	25(1)	31(1)	1(1)	4(1)	0(1)
O(2)	23(1)	48(1)	32(1)	6(1)	2(1)	-4(1)
O(2A)	25(1)	40(1)	49(1)	9(1)	4(1)	-3(1)
O(3)	24(1)	41(1)	20(1)	4(1)	2(1)	5(1)
O(3A)	26(1)	40(1)	21(1)	3(1)	2(1)	7(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for mss034.

	x	y	z	U(eq)
H(3)	935(7)	577(14)	2169(6)	21(4)
H(3A)	3418(7)	-1921(15)	2242(7)	28(4)
H(4)	1549(7)	401(15)	1371(6)	25(4)
H(4A)	4002(7)	-2103(14)	1437(6)	18(4)
H(6)	2247(8)	2239(16)	1218(7)	36(5)
H(6A)	4732(8)	-385(16)	1246(7)	32(4)
H(7)	2456(8)	4297(15)	1482(6)	29(4)
H(7A)	5001(8)	1641(17)	1508(7)	39(5)
H(8)	1659(8)	5529(17)	1873(7)	39(5)
H(8A)	4267(8)	2955(18)	1954(7)	45(5)
H(9)	650(8)	4636(16)	2055(7)	33(5)
H(9A)	3242(8)	2138(16)	2156(7)	33(5)
H(11)	717(7)	-80(15)	674(6)	25(4)
H(11A)	3155(7)	-2553(15)	751(6)	24(4)
H(12A)	591(8)	2597(16)	613(7)	33(4)
H(12B)	35(8)	1590(16)	603(7)	33(5)
H(12C)	3085(8)	88(16)	695(7)	31(4)
H(12D)	2500(8)	-851(16)	681(7)	34(5)
H(13A)	441(8)	2328(17)	-370(7)	36(5)
H(13B)	277(7)	909(15)	-302(7)	30(4)
H(13C)	2932(8)	-109(18)	-286(8)	44(5)
H(13D)	2735(8)	-1515(16)	-233(7)	39(5)
H(15A)	1620(8)	2947(18)	-97(8)	46(5)
H(15B)	2105(9)	2008(17)	-367(7)	44(5)
H(15C)	1540(8)	2536(18)	-764(8)	49(5)
H(15D)	4132(8)	432(19)	-7(8)	51(6)
H(15E)	4584(10)	-579(18)	-291(8)	50(6)
H(15F)	4053(9)	77(19)	-683(9)	59(6)
H(16A)	1157(9)	369(19)	-1012(9)	60(6)
H(16B)	1073(9)	-570(20)	-484(8)	55(6)

H(16C)	1785(9)	-85(17)	-629(8)	44(5)
H(16D)	3512(9)	-3051(19)	-431(8)	54(6)
H(16E)	4245(9)	-2600(17)	-574(7)	45(5)
H(16F)	3643(9)	-2102(18)	-944(9)	55(6)
H(17A)	283(8)	-1094(16)	2094(8)	46(5)
H(17B)	235(8)	-984(15)	1420(7)	31(5)
H(17C)	904(9)	-1389(17)	1696(8)	48(5)
H(17D)	2740(8)	-3570(17)	2177(8)	44(5)
H(17E)	2641(8)	-3397(16)	1493(7)	35(5)
H(17F)	3330(9)	-3876(17)	1765(8)	45(5)

Table 6. Torsion angles [°] for mss034.

O(2)-C(2)-C(3)-C(17)	7.9(2)
O(1)-C(2)-C(3)-C(17)	-173.22(12)
O(2)-C(2)-C(3)-C(4)	137.43(15)
O(1)-C(2)-C(3)-C(4)	-43.67(17)
O(2A)-C(2A)-C(3A)-C(17A)	8.1(2)
O(1A)-C(2A)-C(3A)-C(17A)	-173.45(13)
O(2A)-C(2A)-C(3A)-C(4A)	138.41(16)
O(1A)-C(2A)-C(3A)-C(4A)	-43.19(17)
C(2)-C(3)-C(4)-C(5)	55.48(16)
C(17)-C(3)-C(4)-C(5)	-176.89(13)
C(2)-C(3)-C(4)-C(11)	-70.01(17)
C(17)-C(3)-C(4)-C(11)	57.62(18)
C(2A)-C(3A)-C(4A)-C(5A)	54.41(16)
C(17A)-C(3A)-C(4A)-C(5A)	-176.91(13)
C(2A)-C(3A)-C(4A)-C(11A)	-71.74(16)
C(17A)-C(3A)-C(4A)-C(11A)	56.93(18)
C(3)-C(4)-C(5)-C(10)	-33.88(17)
C(11)-C(4)-C(5)-C(10)	91.99(15)
C(3)-C(4)-C(5)-C(6)	144.80(14)
C(11)-C(4)-C(5)-C(6)	-89.33(17)
C(11A)-C(4A)-C(5A)-C(10A)	94.51(16)
C(3A)-C(4A)-C(5A)-C(10A)	-32.32(18)
C(11A)-C(4A)-C(5A)-C(6A)	-86.46(18)
C(3A)-C(4A)-C(5A)-C(6A)	146.71(14)
C(10)-C(5)-C(6)-C(7)	-0.9(2)
C(4)-C(5)-C(6)-C(7)	-179.61(14)
C(10A)-C(5A)-C(6A)-C(7A)	0.9(2)
C(4A)-C(5A)-C(6A)-C(7A)	-178.16(14)
C(5)-C(6)-C(7)-C(8)	0.1(2)
C(5A)-C(6A)-C(7A)-C(8A)	-0.2(2)
C(6)-C(7)-C(8)-C(9)	0.6(2)
C(6A)-C(7A)-C(8A)-C(9A)	-0.3(3)
C(7)-C(8)-C(9)-C(10)	-0.5(2)
C(7A)-C(8A)-C(9A)-C(10A)	0.2(2)

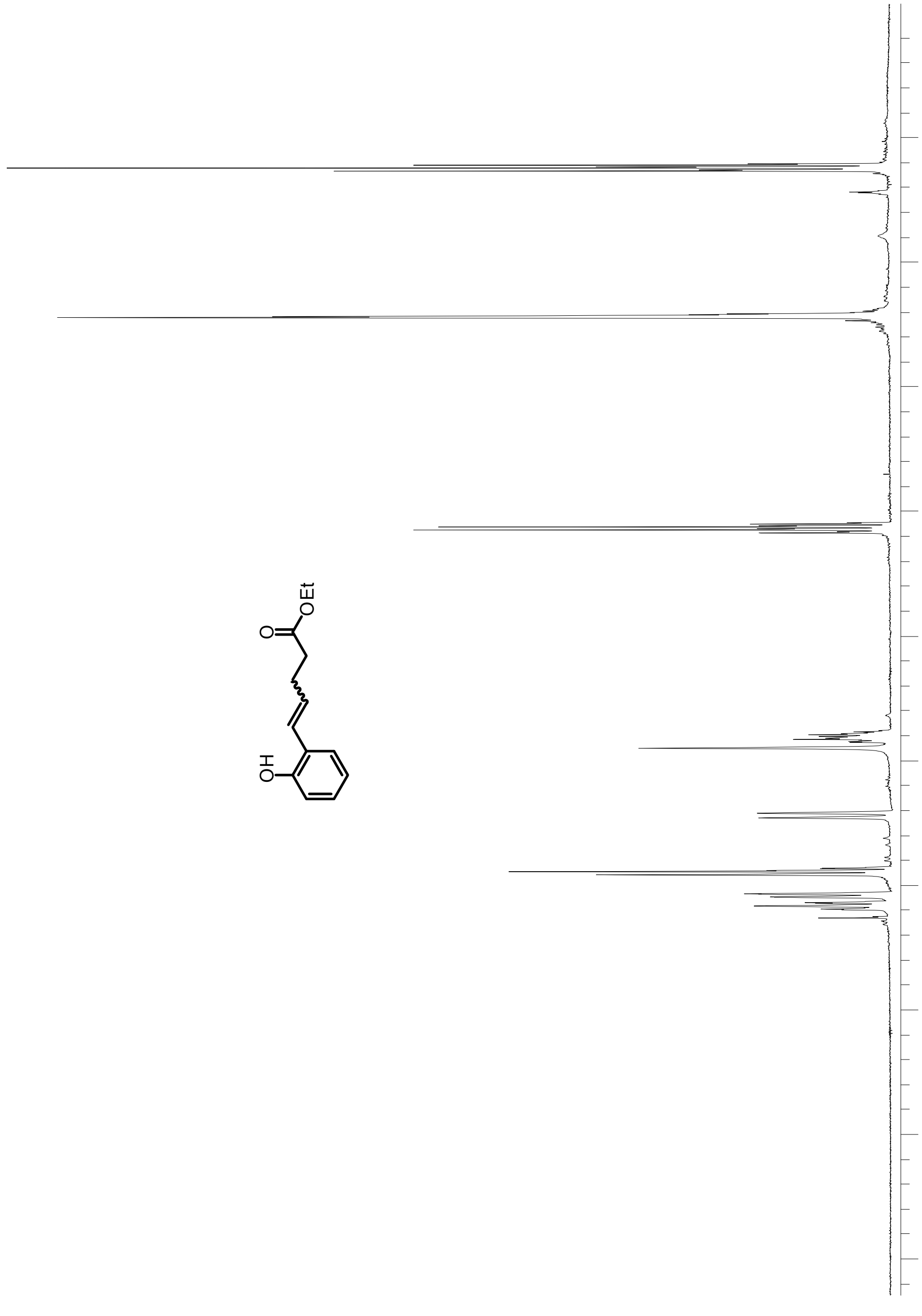
C(8)-C(9)-C(10)-C(5)	-0.3(2)
C(8)-C(9)-C(10)-O(1)	-177.39(13)
C(6)-C(5)-C(10)-C(9)	1.0(2)
C(4)-C(5)-C(10)-C(9)	179.78(13)
C(6)-C(5)-C(10)-O(1)	177.94(12)
C(4)-C(5)-C(10)-O(1)	-3.3(2)
C(8A)-C(9A)-C(10A)-C(5A)	0.6(2)
C(8A)-C(9A)-C(10A)-O(1A)	-177.14(13)
C(6A)-C(5A)-C(10A)-C(9A)	-1.1(2)
C(4A)-C(5A)-C(10A)-C(9A)	178.03(14)
C(6A)-C(5A)-C(10A)-O(1A)	176.51(13)
C(4A)-C(5A)-C(10A)-O(1A)	-4.4(2)
C(5)-C(4)-C(11)-O(3)	76.40(15)
C(3)-C(4)-C(11)-O(3)	-161.17(13)
C(5)-C(4)-C(11)-C(12)	-41.29(18)
C(3)-C(4)-C(11)-C(12)	81.14(17)
C(5A)-C(4A)-C(11A)-O(3A)	75.94(15)
C(3A)-C(4A)-C(11A)-O(3A)	-160.81(12)
C(5A)-C(4A)-C(11A)-C(12A)	-41.67(18)
C(3A)-C(4A)-C(11A)-C(12A)	81.57(17)
O(3)-C(11)-C(12)-C(13)	37.86(15)
C(4)-C(11)-C(12)-C(13)	156.92(13)
O(3A)-C(11A)-C(12A)-C(13A)	36.86(15)
C(4A)-C(11A)-C(12A)-C(13A)	155.49(13)
C(11)-C(12)-C(13)-C(14)	-32.05(16)
C(11A)-C(12A)-C(13A)-C(14A)	-31.97(16)
C(12)-C(13)-C(14)-O(3)	15.36(16)
C(12)-C(13)-C(14)-C(15)	-100.11(15)
C(12)-C(13)-C(14)-C(16)	133.48(14)
C(12A)-C(13A)-C(14A)-O(3A)	16.18(17)
C(12A)-C(13A)-C(14A)-C(15A)	-99.77(16)
C(12A)-C(13A)-C(14A)-C(16A)	134.12(15)
O(2)-C(2)-O(1)-C(10)	-175.66(12)
C(3)-C(2)-O(1)-C(10)	5.34(18)
C(9)-C(10)-O(1)-C(2)	-162.93(13)
C(5)-C(10)-O(1)-C(2)	19.96(19)

O(2A)-C(2A)-O(1A)-C(10A)	-176.20(13)
C(3A)-C(2A)-O(1A)-C(10A)	5.24(19)
C(9A)-C(10A)-O(1A)-C(2A)	-161.87(13)
C(5A)-C(10A)-O(1A)-C(2A)	20.4(2)
C(12)-C(11)-O(3)-C(14)	-29.86(16)
C(4)-C(11)-O(3)-C(14)	-156.43(12)
C(15)-C(14)-O(3)-C(11)	129.14(14)
C(16)-C(14)-O(3)-C(11)	-111.39(14)
C(13)-C(14)-O(3)-C(11)	8.94(16)
C(12A)-C(11A)-O(3A)-C(14A)	-28.29(16)
C(4A)-C(11A)-O(3A)-C(14A)	-154.63(12)
C(15A)-C(14A)-O(3A)-C(11A)	127.96(14)
C(16A)-C(14A)-O(3A)-C(11A)	-113.09(15)
C(13A)-C(14A)-O(3A)-C(11A)	7.42(16)

Symmetry transformations used to generate equivalent atoms:

References:

1) Braddock, D. C.; Cansell, G.; Hermitage, S. A. *Chem. Commun.* **2006**, 2483.
2) Bianco, A.; Cavarischia, C.; Guiso M. *Nat. Prod. Res.,* **2006**, *20*, 93-97
3) Sharma, S.; Oehlschlager, C. A. *J.Org.Chem*. **1989**, *54*, 5064-5073.
4) Hahn, F. E.; von Fehren, T.; Wittenbecher, L.; Frohlich, R. *Z. Naturforsch. B* **2004**, *59*, 541-543
5) Harada, T.; Muramatsu, K.; Mizunashi, K.; Kitano, C.; Imaoka, D.; Fujiwara, T.; Kataoka, H. J. Org. Chem. **2008**, *73*, 249-258
6) Zhang, Y.; Sigman, M. S. *J. Am. Chem. Soc.* **2007**, *129*, 3076.
7) Arduini, A.; Bosi, A.; Pochini, A.; Ungaro, R. *Tetrahedron*, **1985**, *41*, 3095.
8) For a leading reference see: Yu, M.; Danishefsky, S. J.; *J. Am. Chem. Soc.* **2008**, *130*, 2783. For a review see: Magdziak, D.; Meek, S. J.; Pettus, T. R. R. *Chem. Rev.* **2004**, *104*, 1383.
9) Hoye, R. T.; Jefferey, H. C.; Shao, F. *Nature Protocols* **2007**, *2*, 2451-2458
10) Crimmins, M. T.; Jung, D. K.; Gray, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 3146.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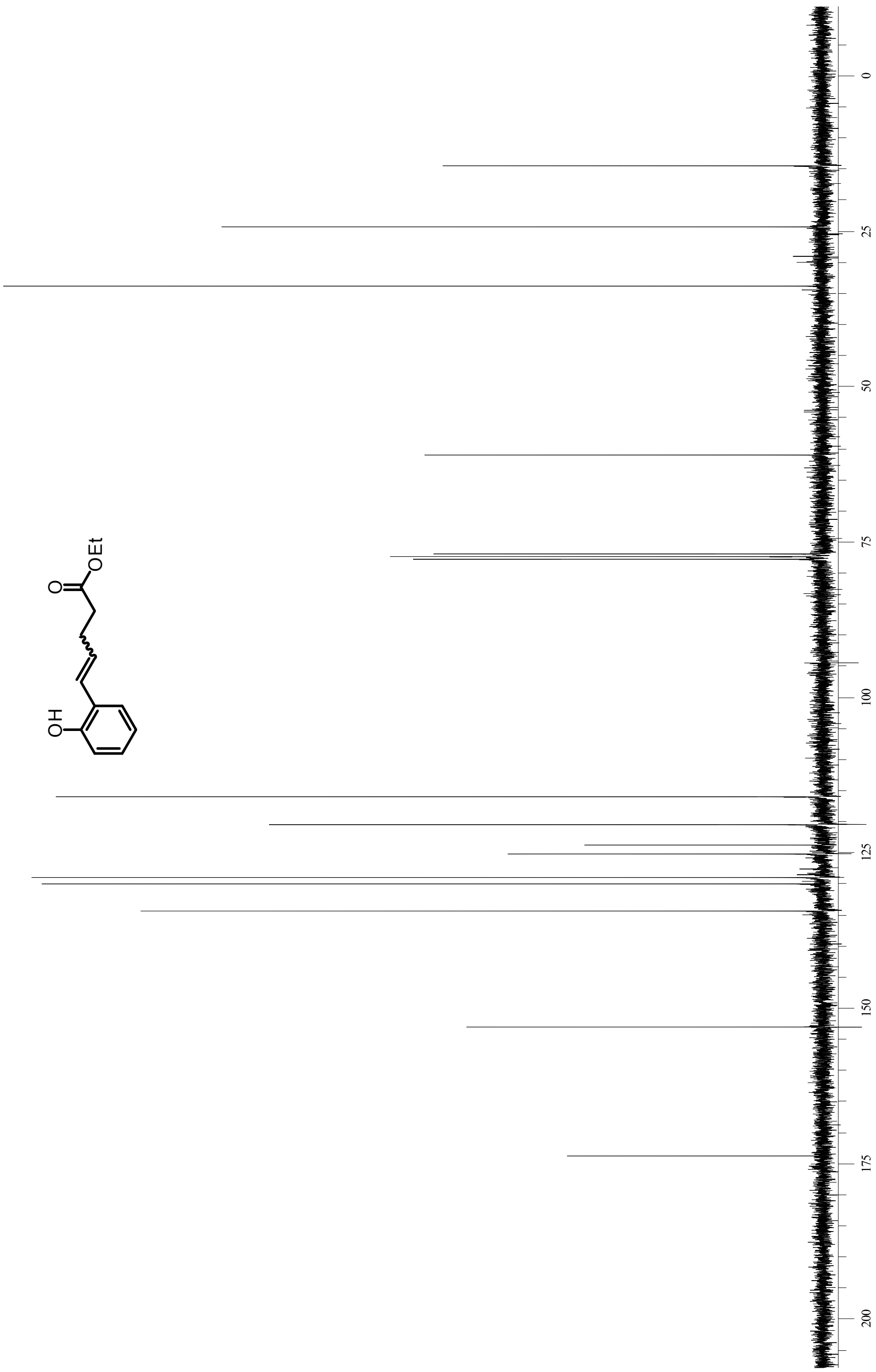

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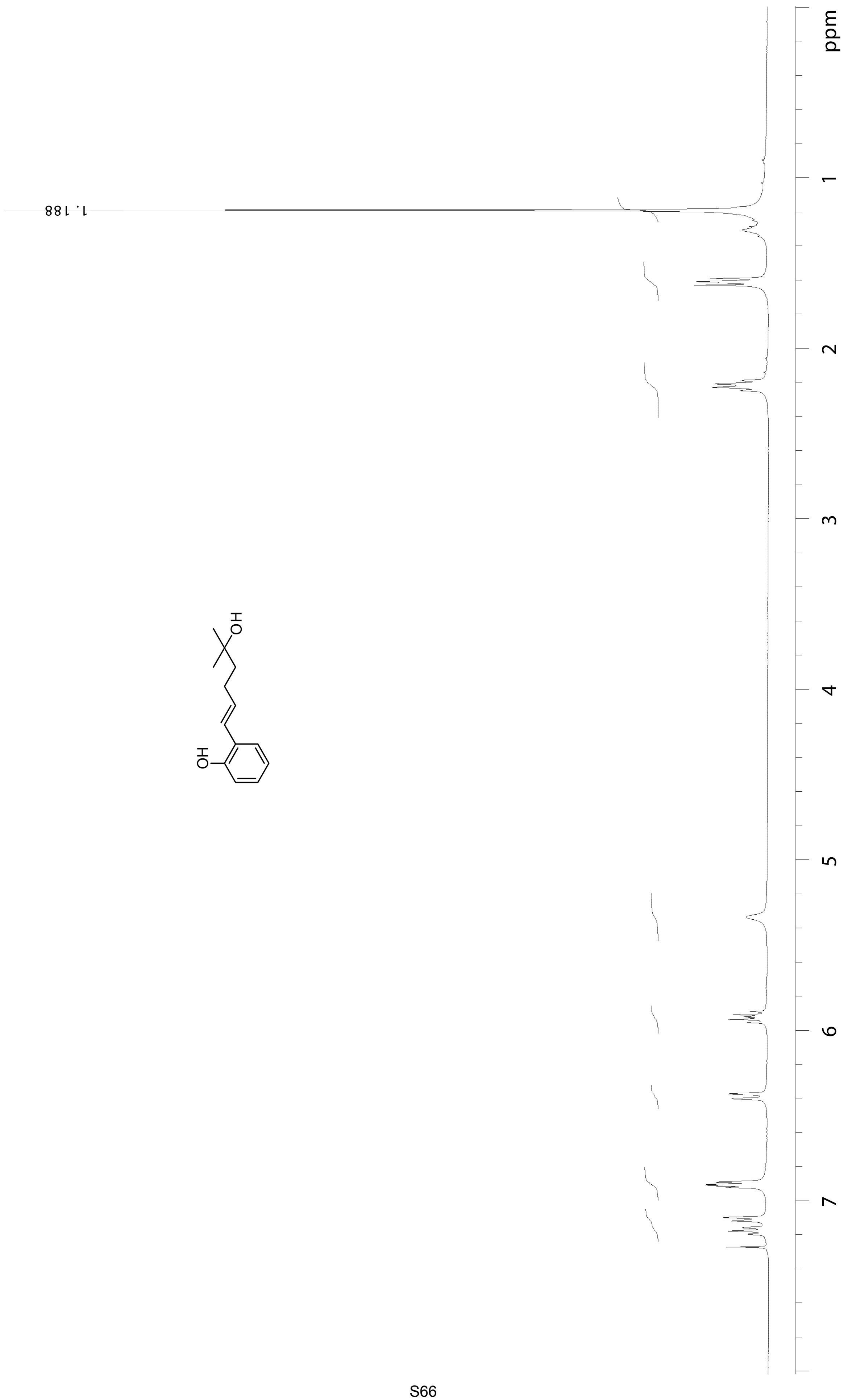
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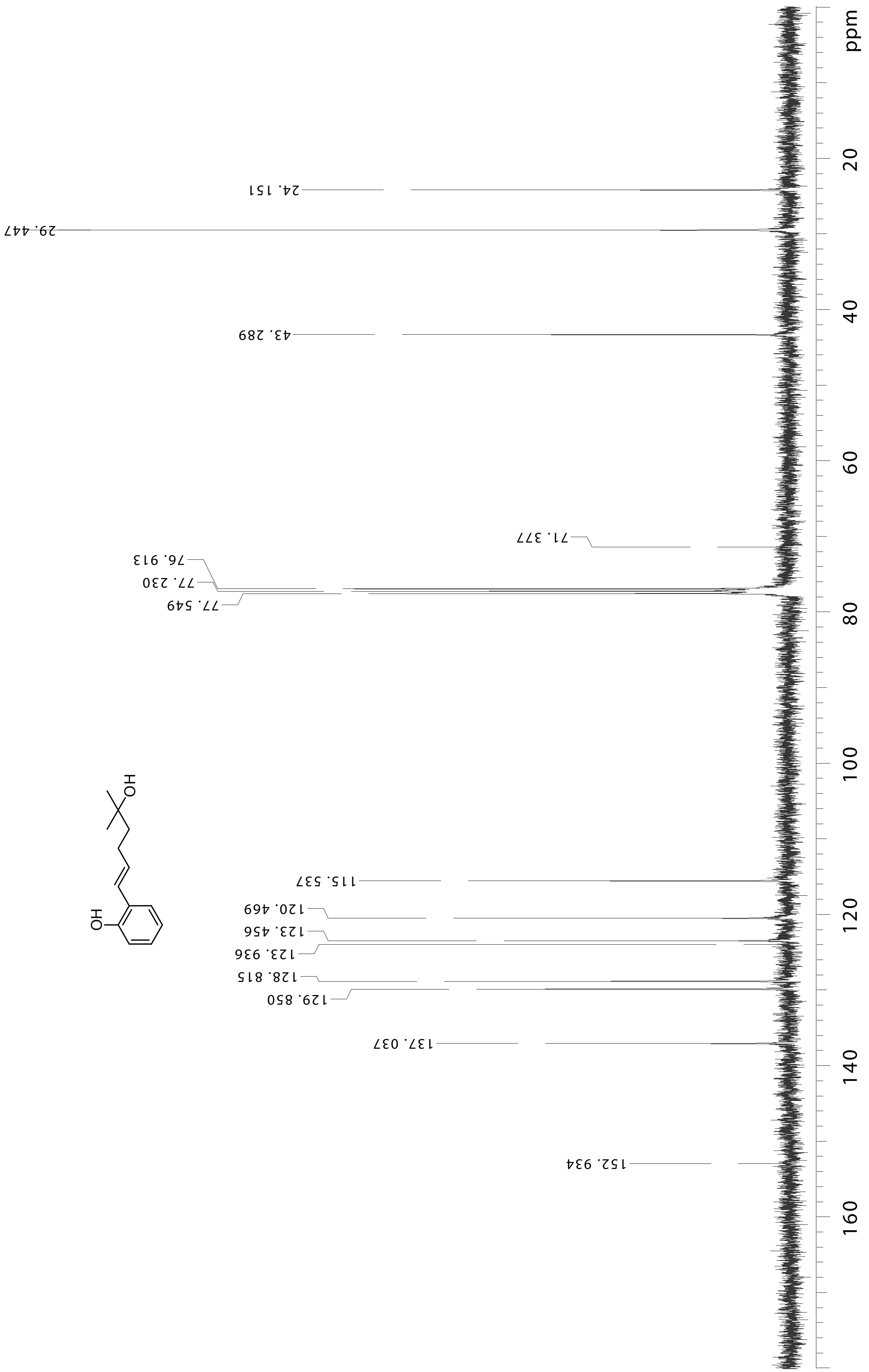
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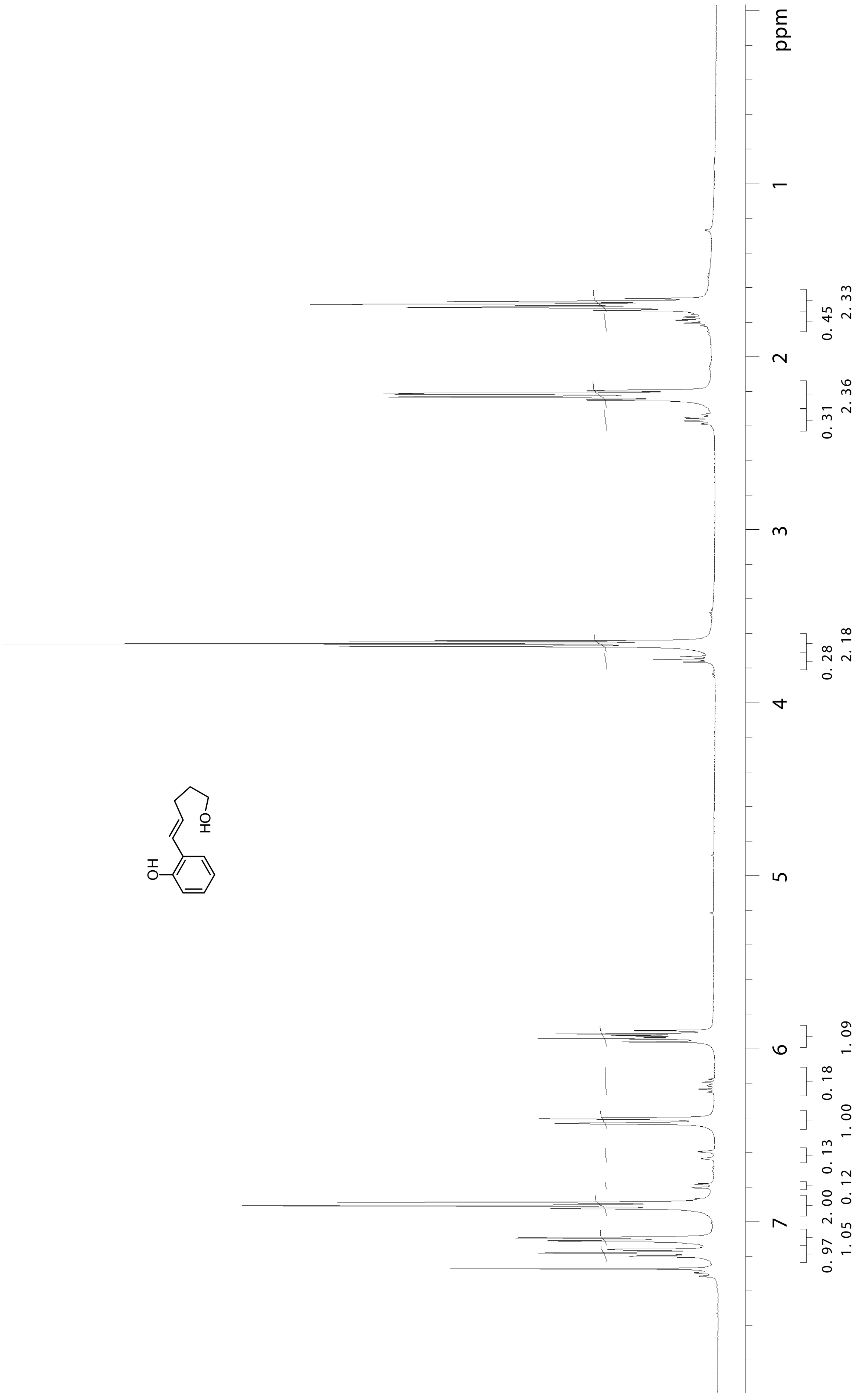

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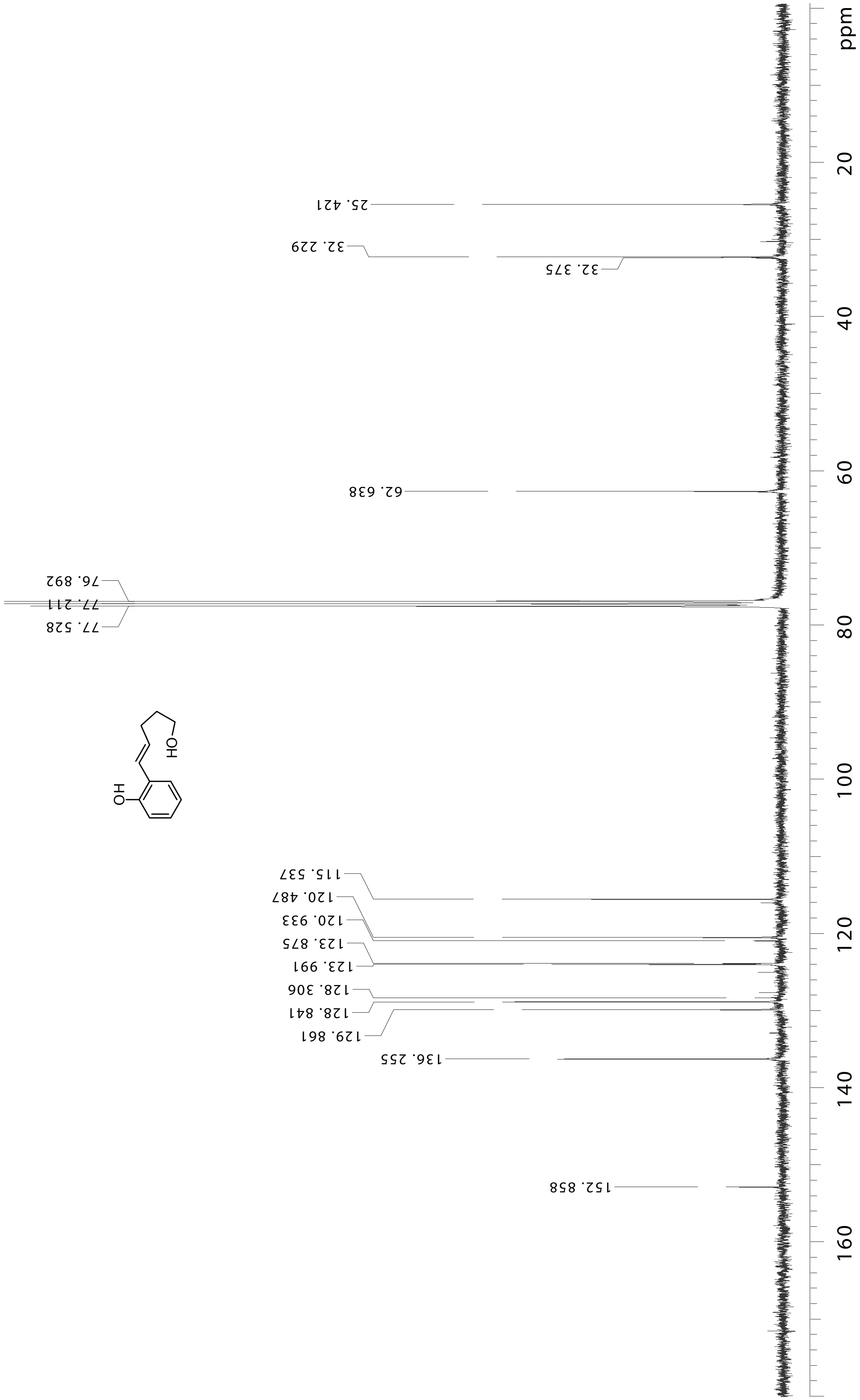
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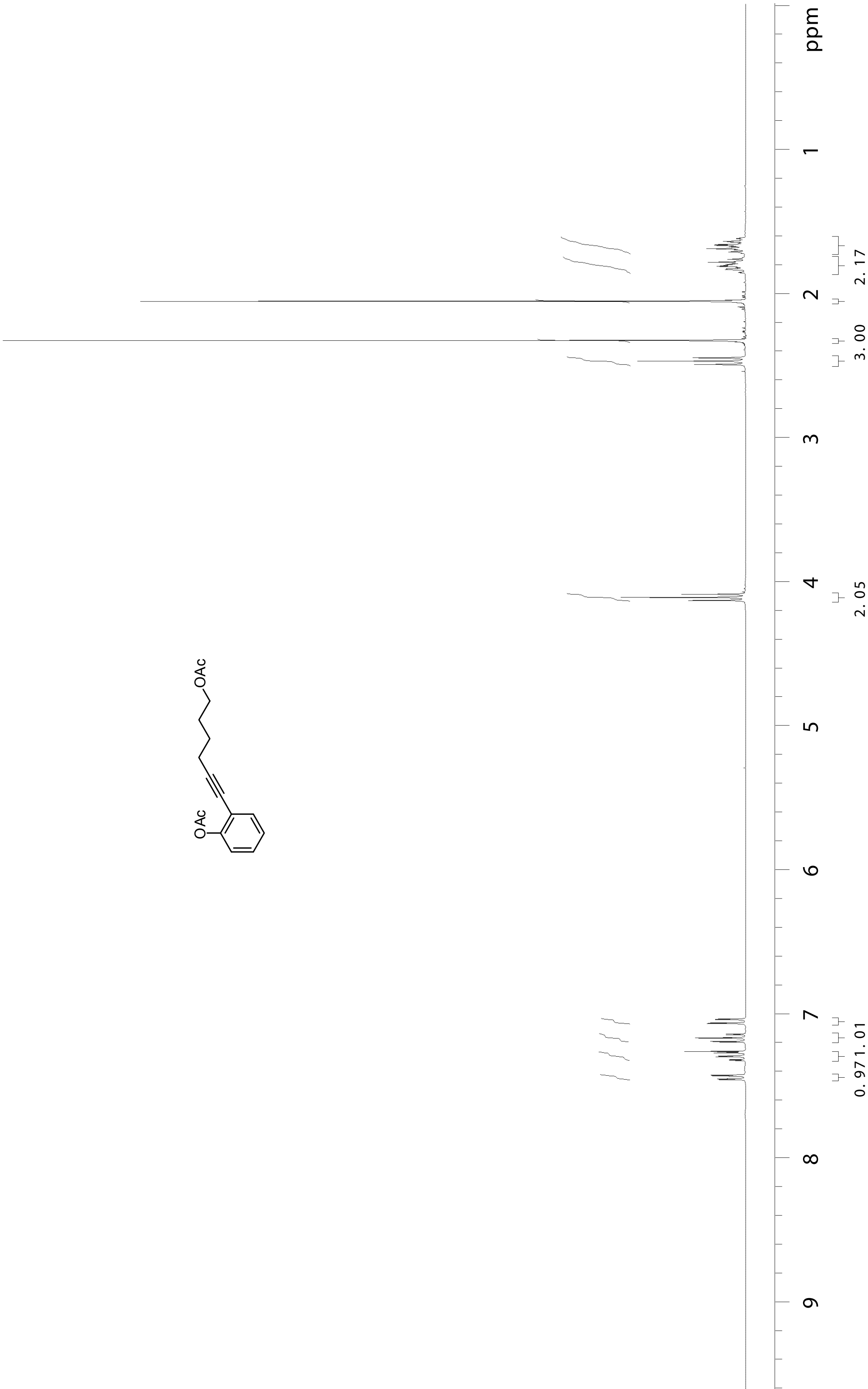
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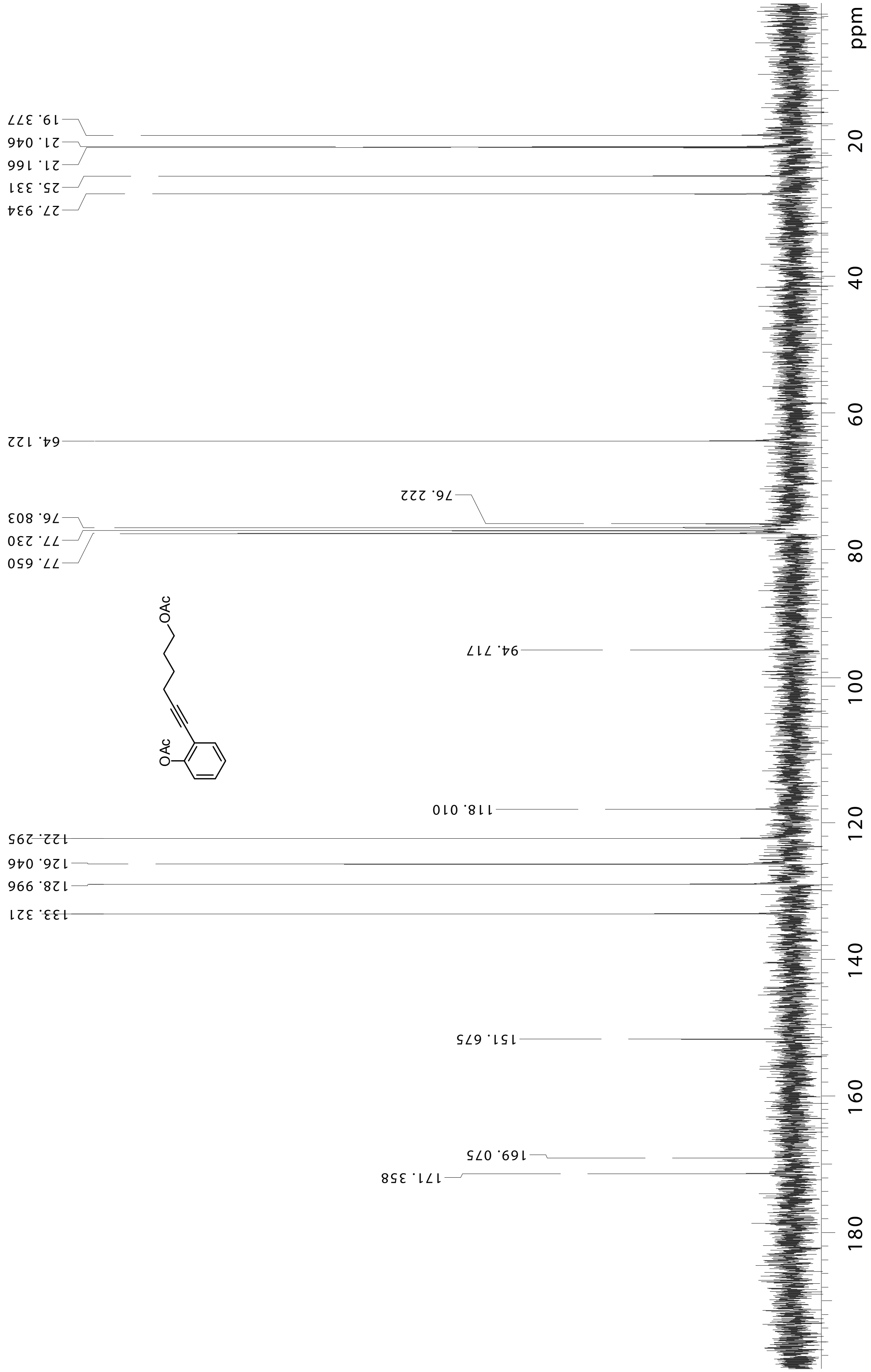
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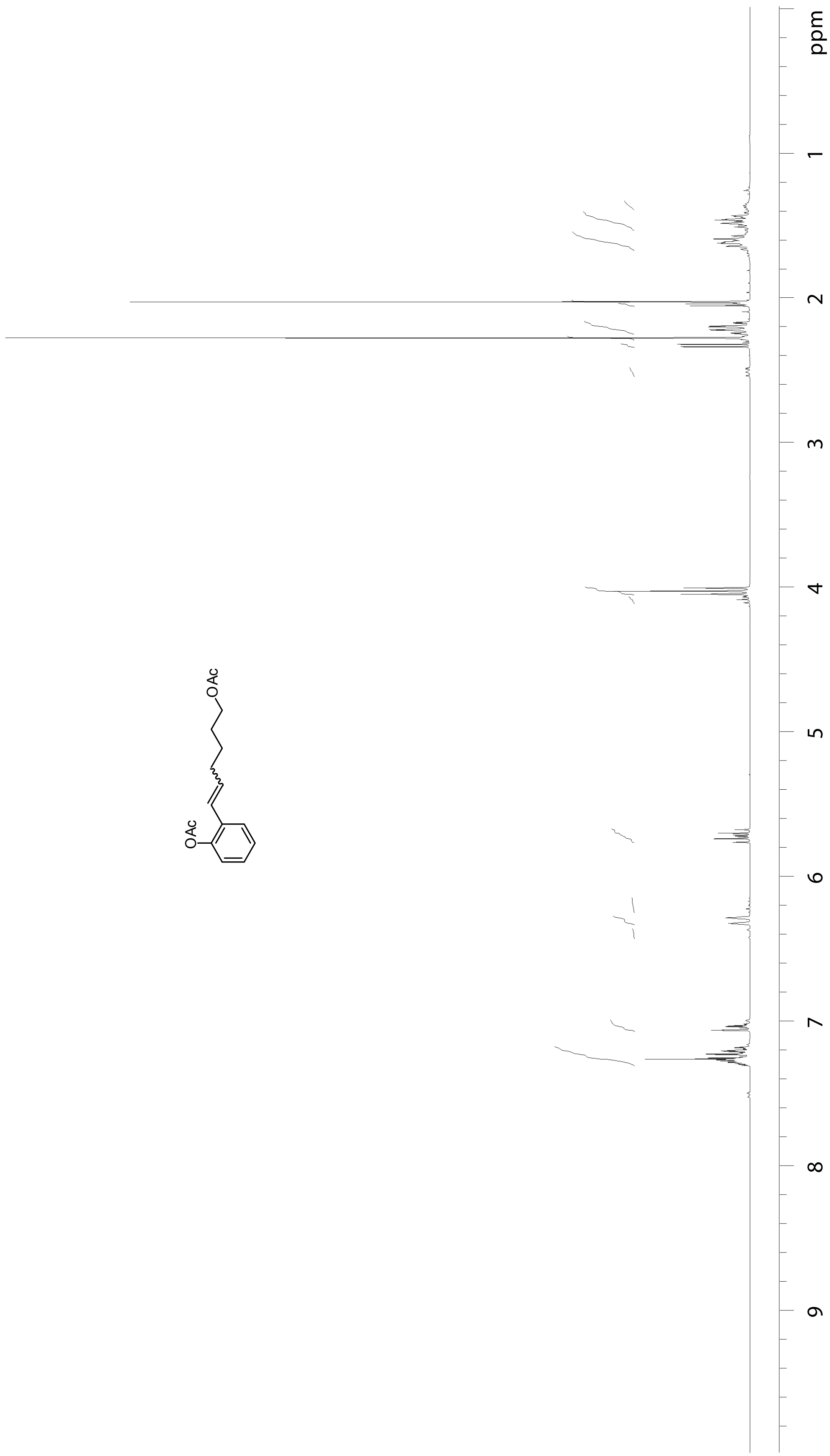
OAc
OAc
ppm
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2
3
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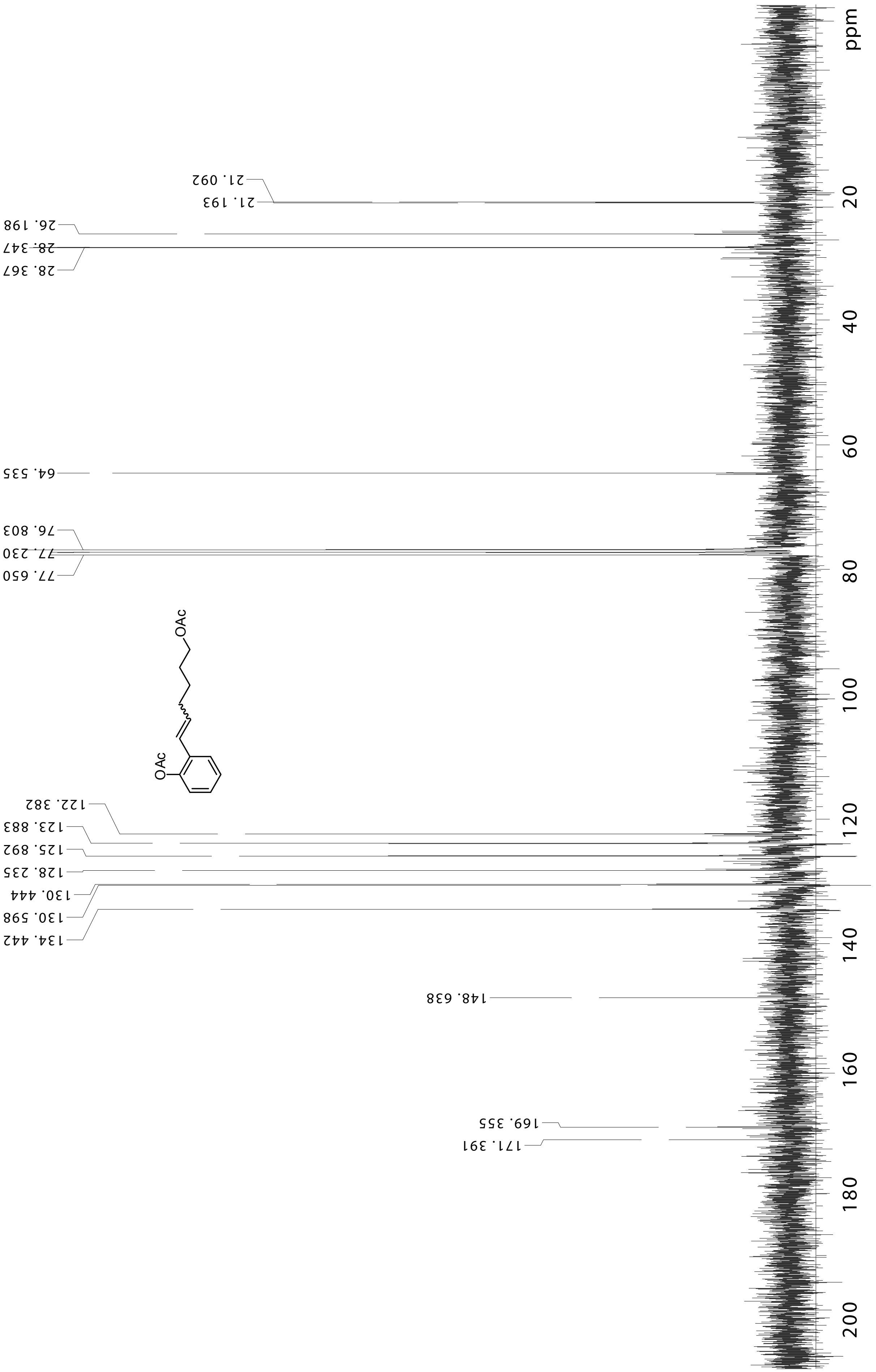
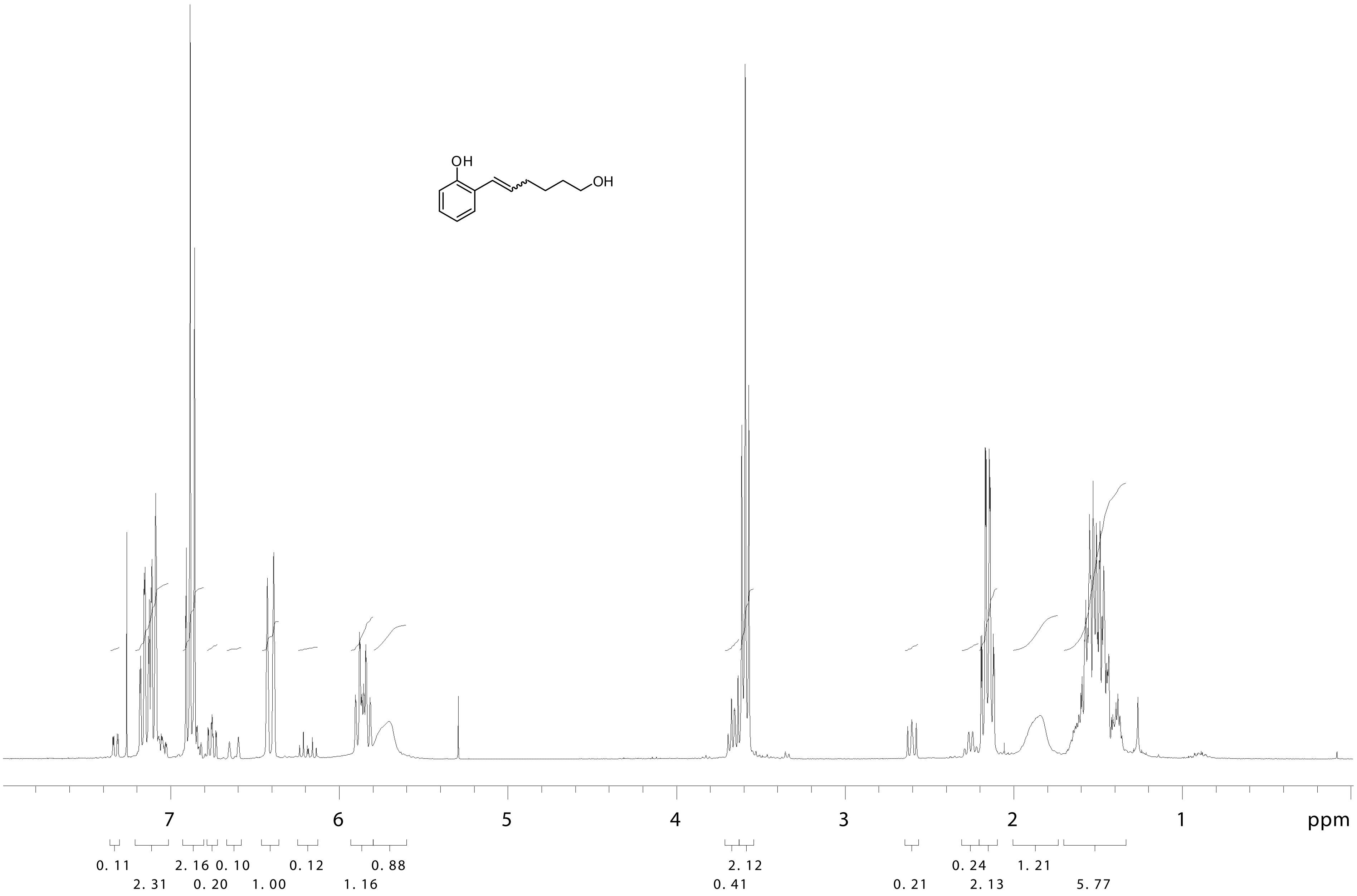
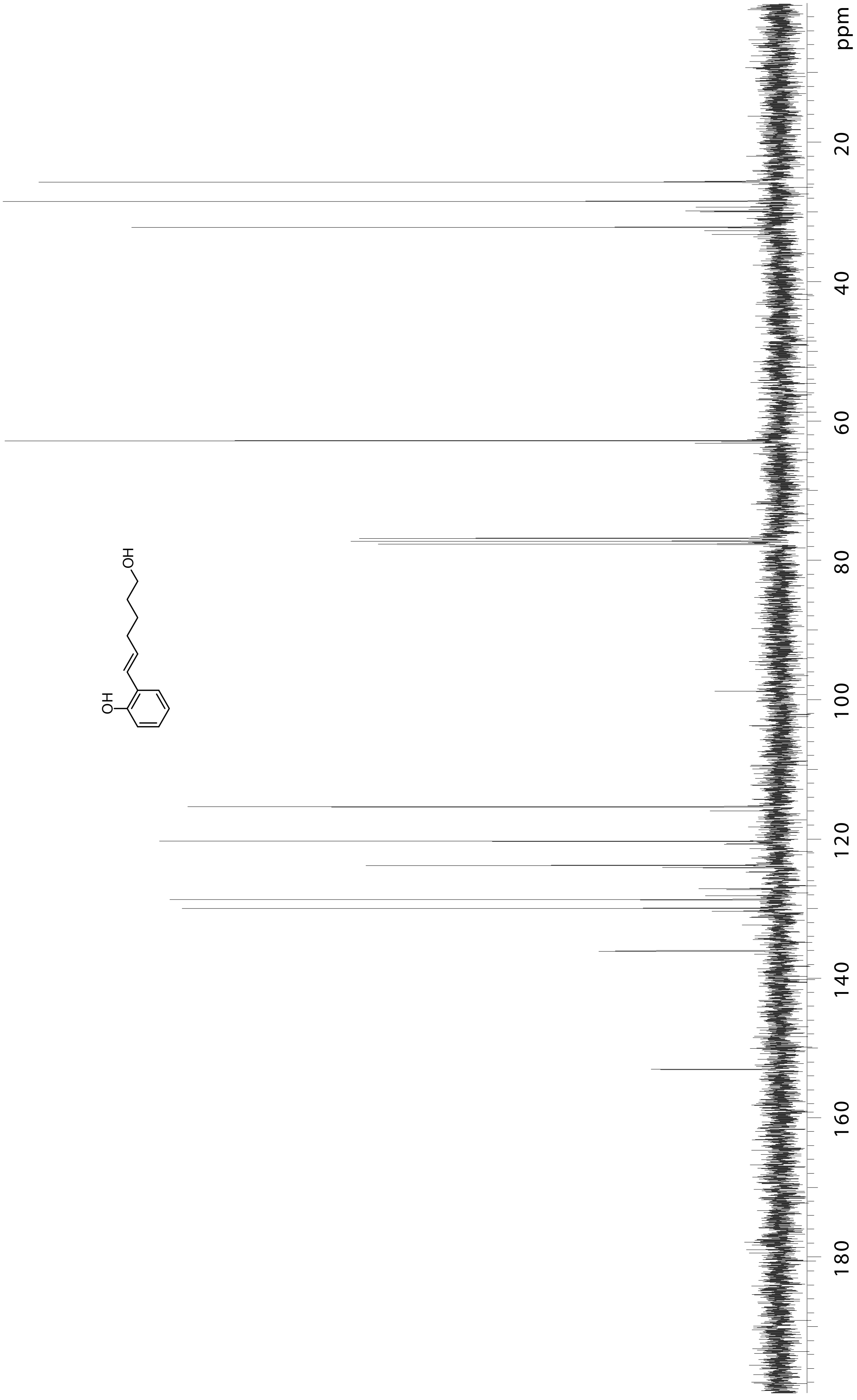
5
6
7
8
9


ppm
20
40
60
80
100
120
140
160
180
200
21.092
21.193
26.198
28.347
28.367
64.535
76.803
77.230
77.650
122.382
123.883
125.892
128.235
130.444
130.598
134.442
148.638
169.355
171.391
OAc
OAc


OH
OH
7
6
5
4
3
2
1
ppm
0. 11
2. 31
2. 16
0. 20
0. 10
1. 00
0. 12
1. 16
0. 88
2. 12
0. 41
0. 21
0. 24
2. 13
1. 21
5. 77


ppm
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40
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80
100
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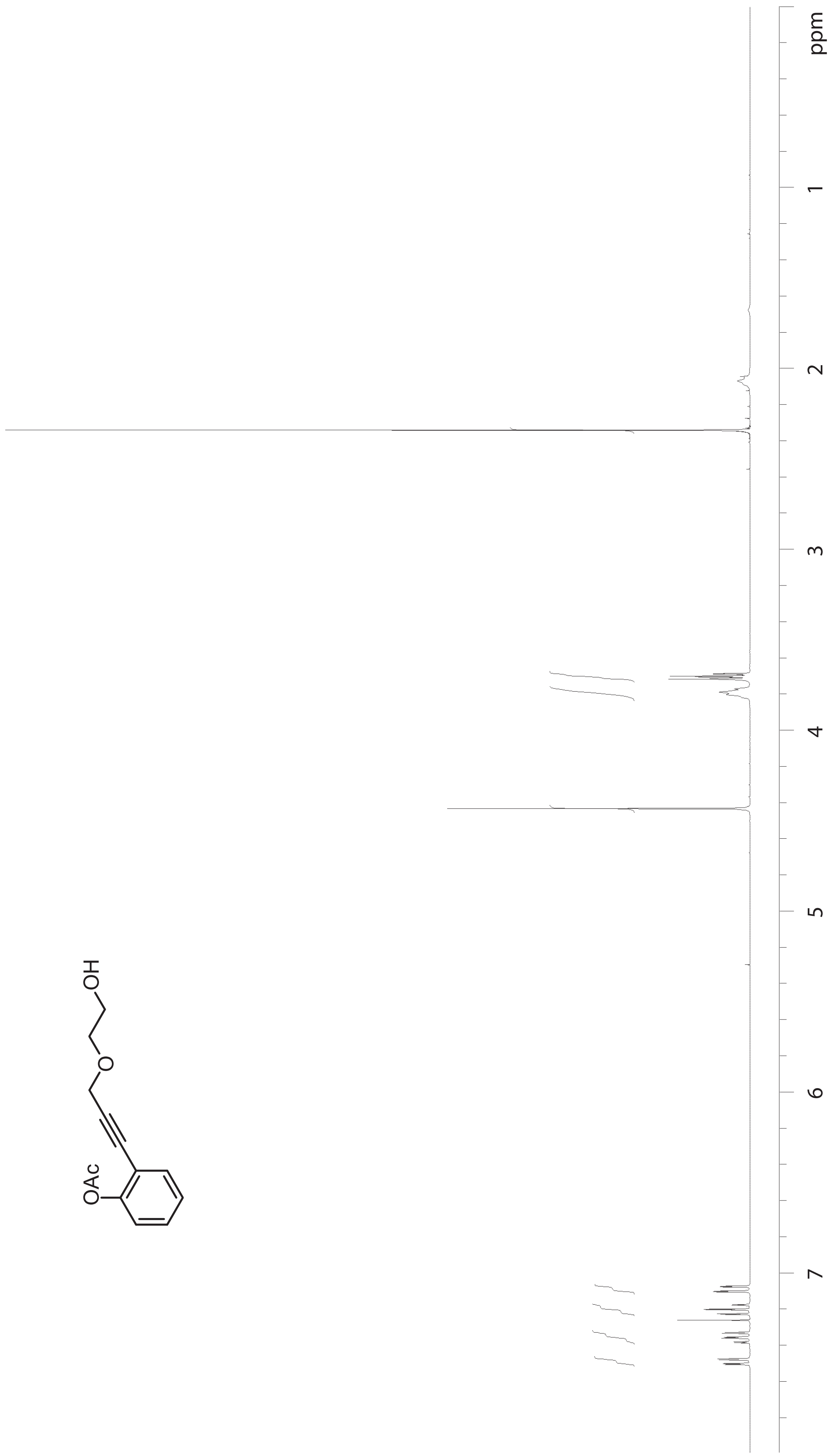
140
160
180
OH
OH


OAc
O
OH
ppm
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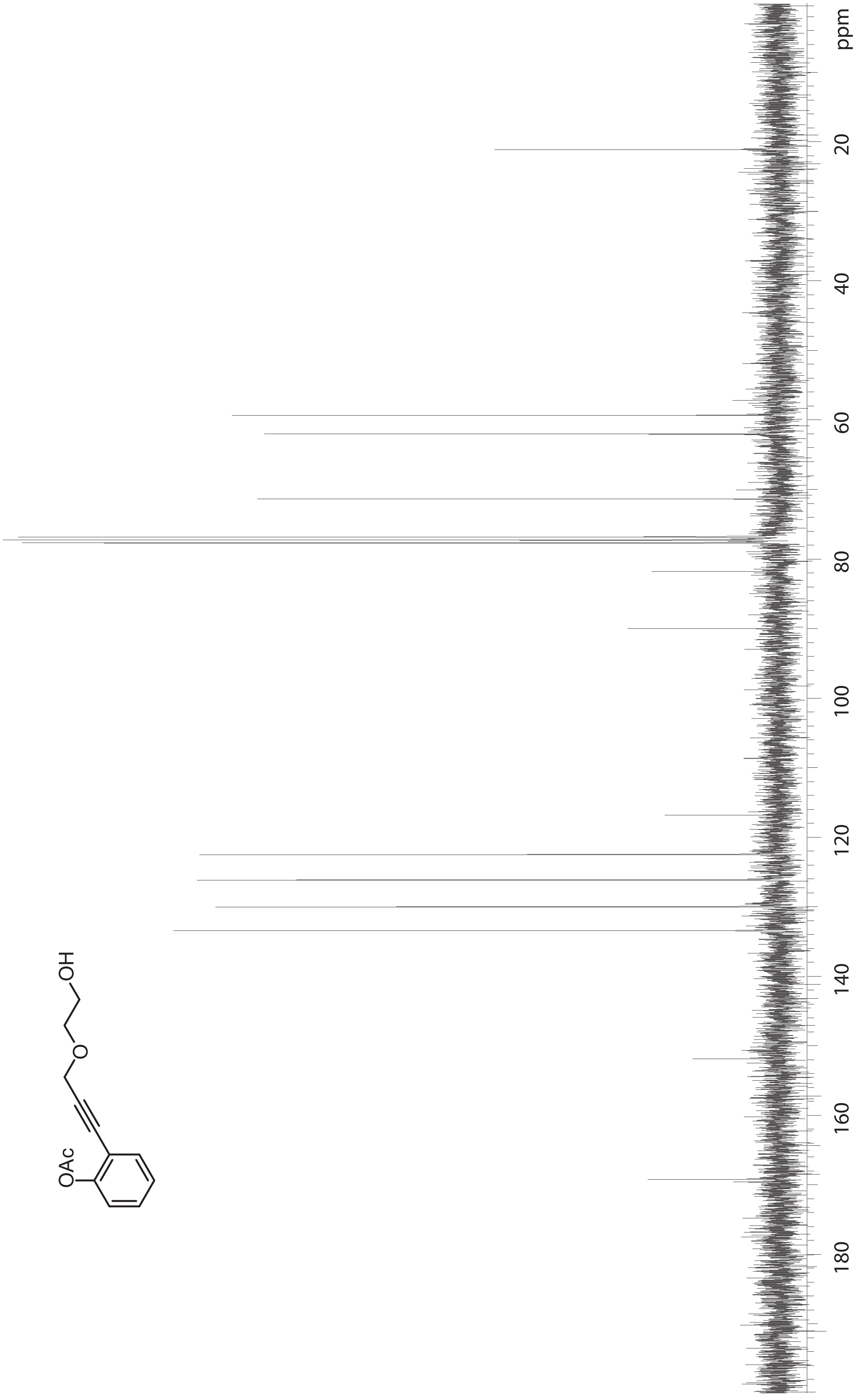
4
5
6
7


OAc
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OH
ppm
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40
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80
100
120
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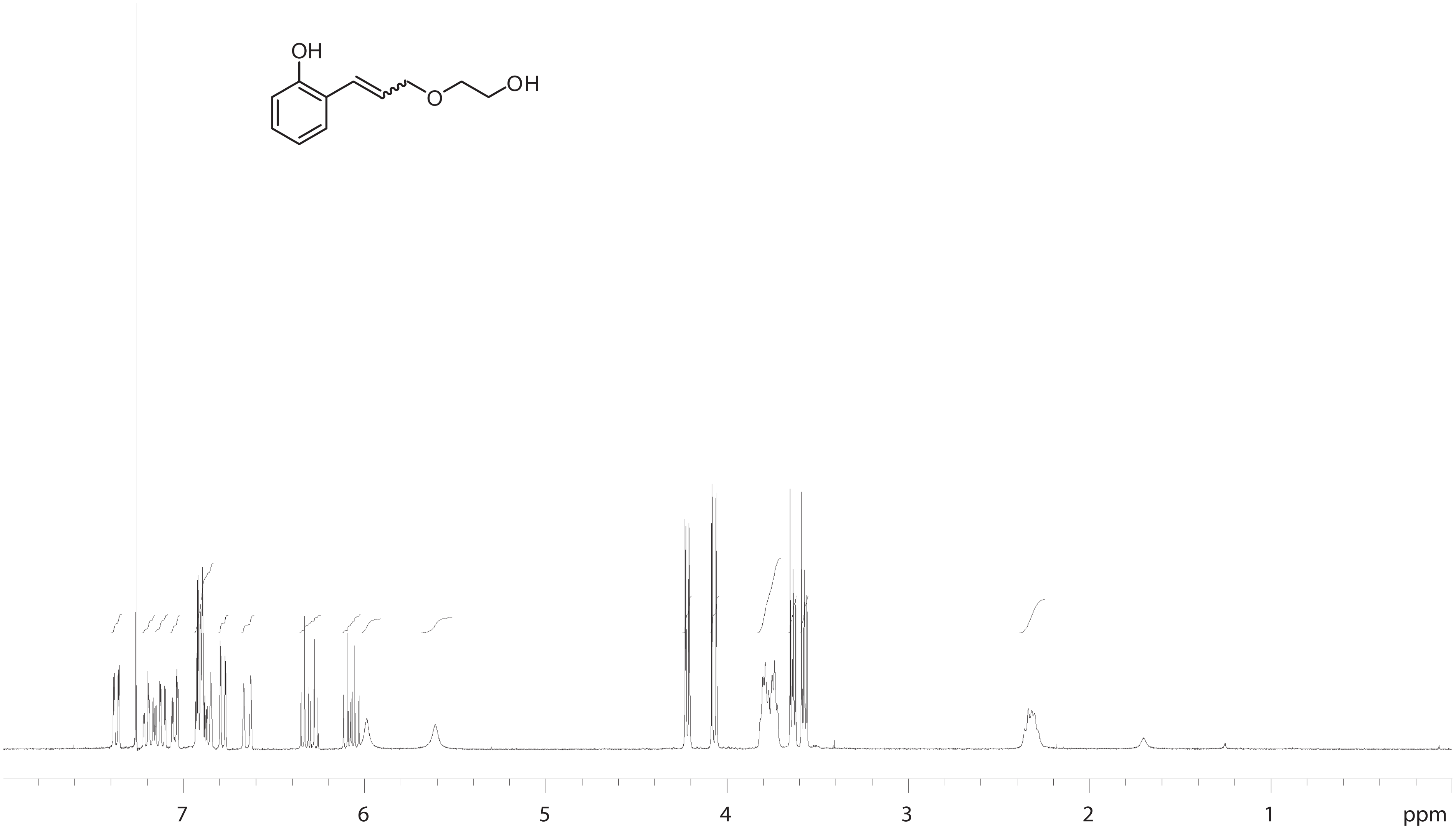
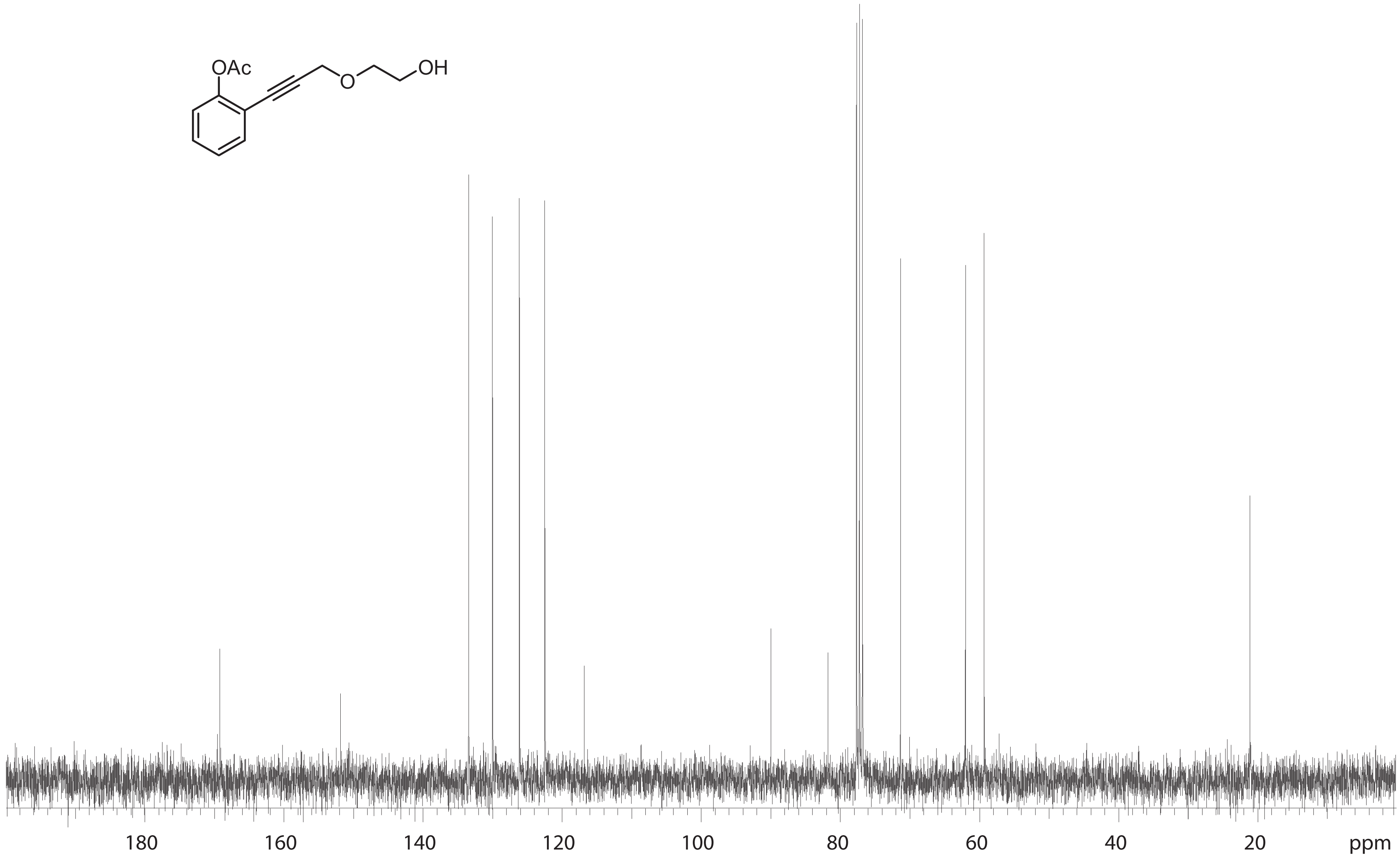
160
180


OH
O
OH
7
6
5
4
3
2
1
ppm


OAc
O
OH
180
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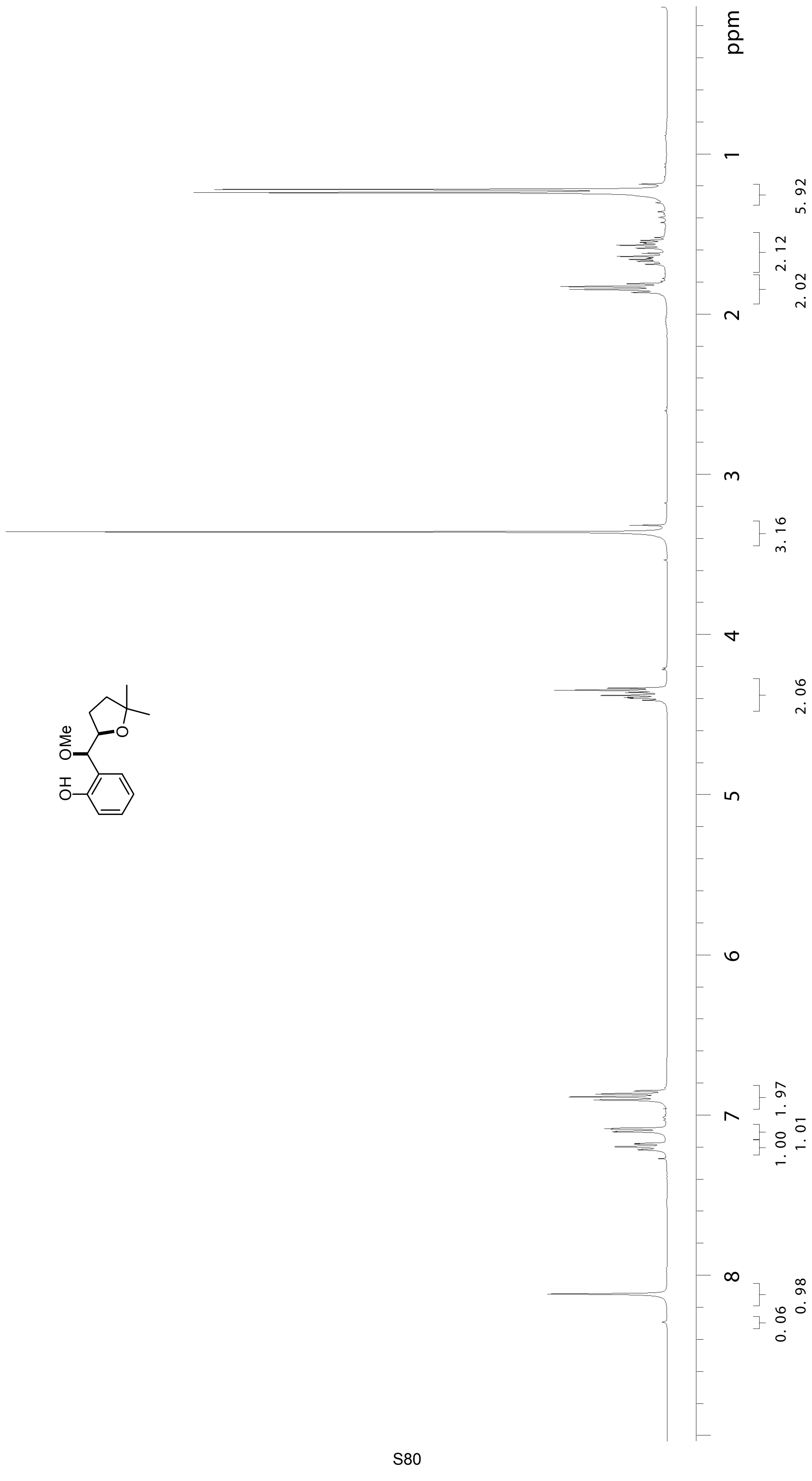
140
120
100
80
60
40
20
ppm


OH
OMe
O
ppm
1
2
3
4
5
6
7
8
5.92
2.12
2.02
3.16
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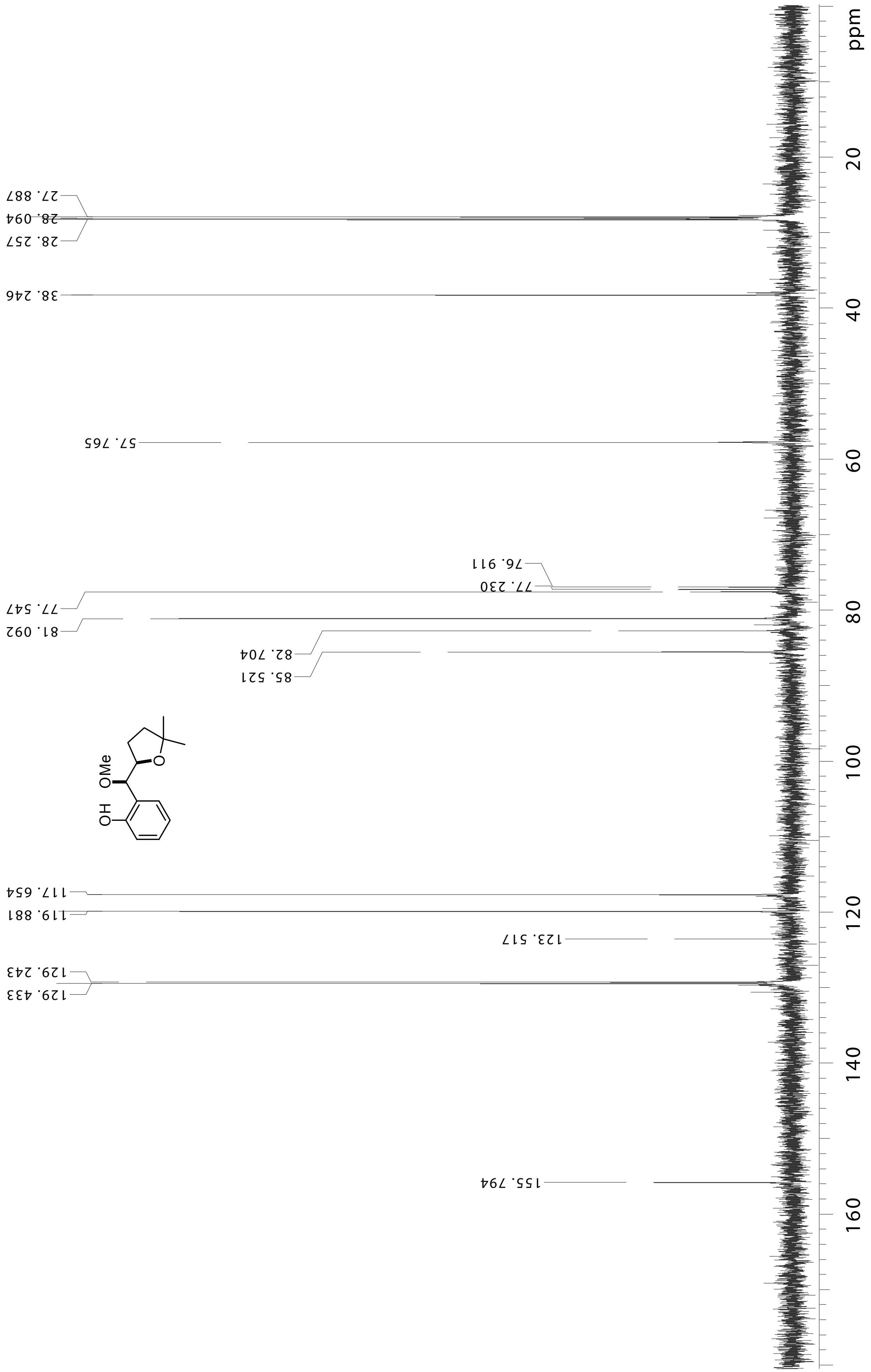
1.00
1.01
0.06
0.98


27.887
28.094
28.257
38.246
57.765
76.911
77.230
77.547
81.092
82.704
85.521
117.654
119.881
123.517
129.243
129.433
155.794
OH
OMe
O
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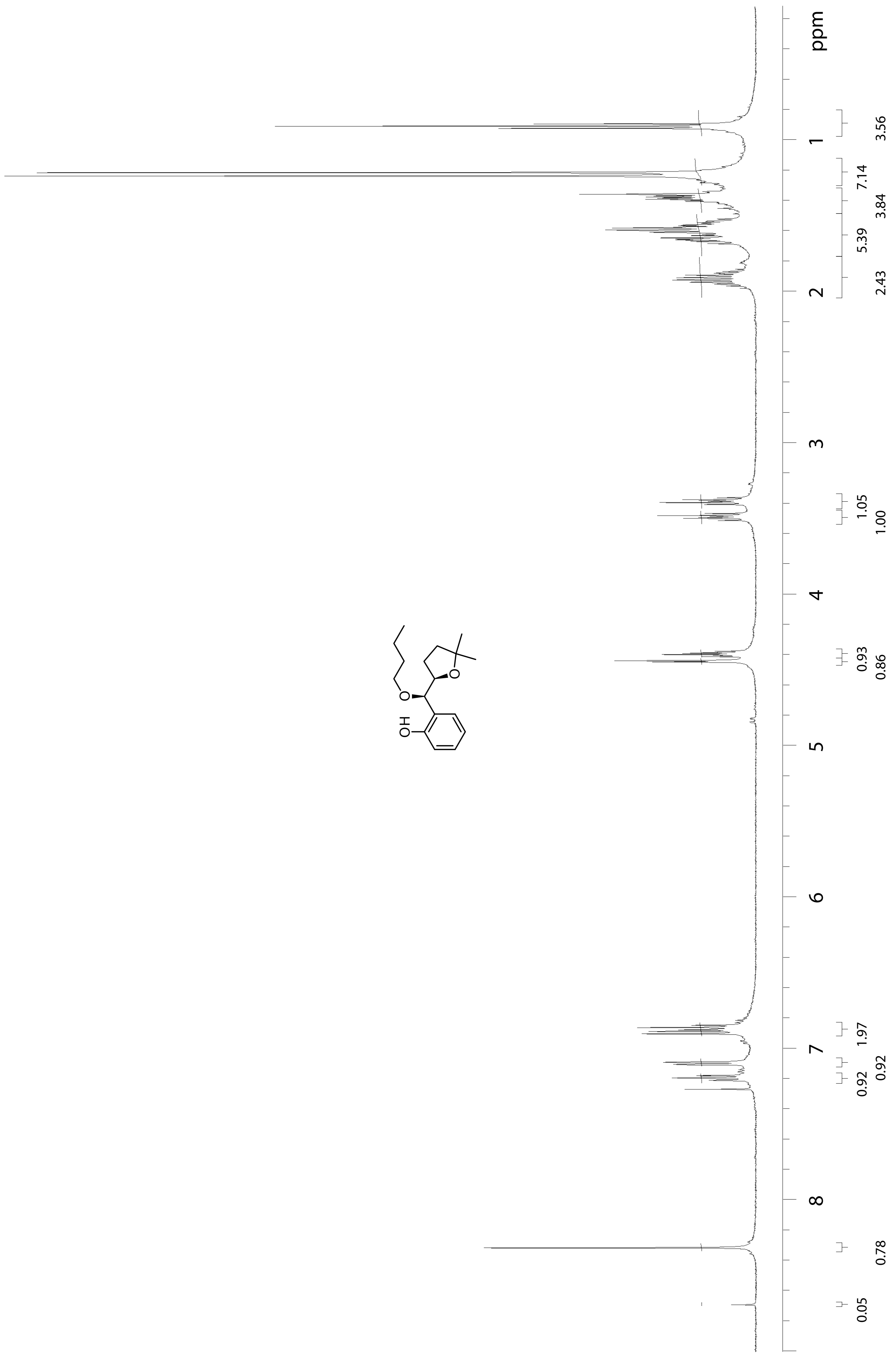
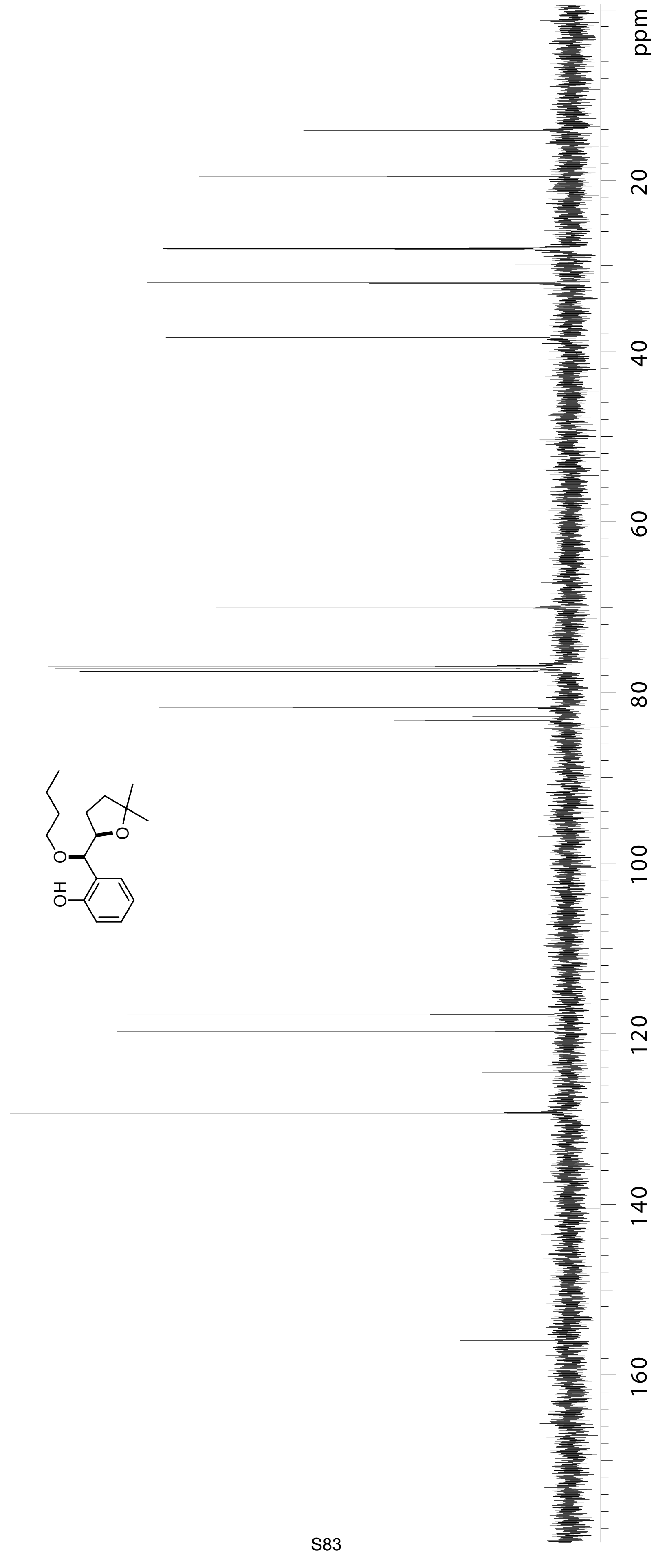
40
60
80
100
120
140
160
ppm


ppm
1
2
3
4
5
6
7
8
3.56
7.14
3.84
5.39
2.43
1.05
1.00
0.93
0.86
1.97
0.92
0.92
0.78
0.05
OH
O
O


ppm
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40
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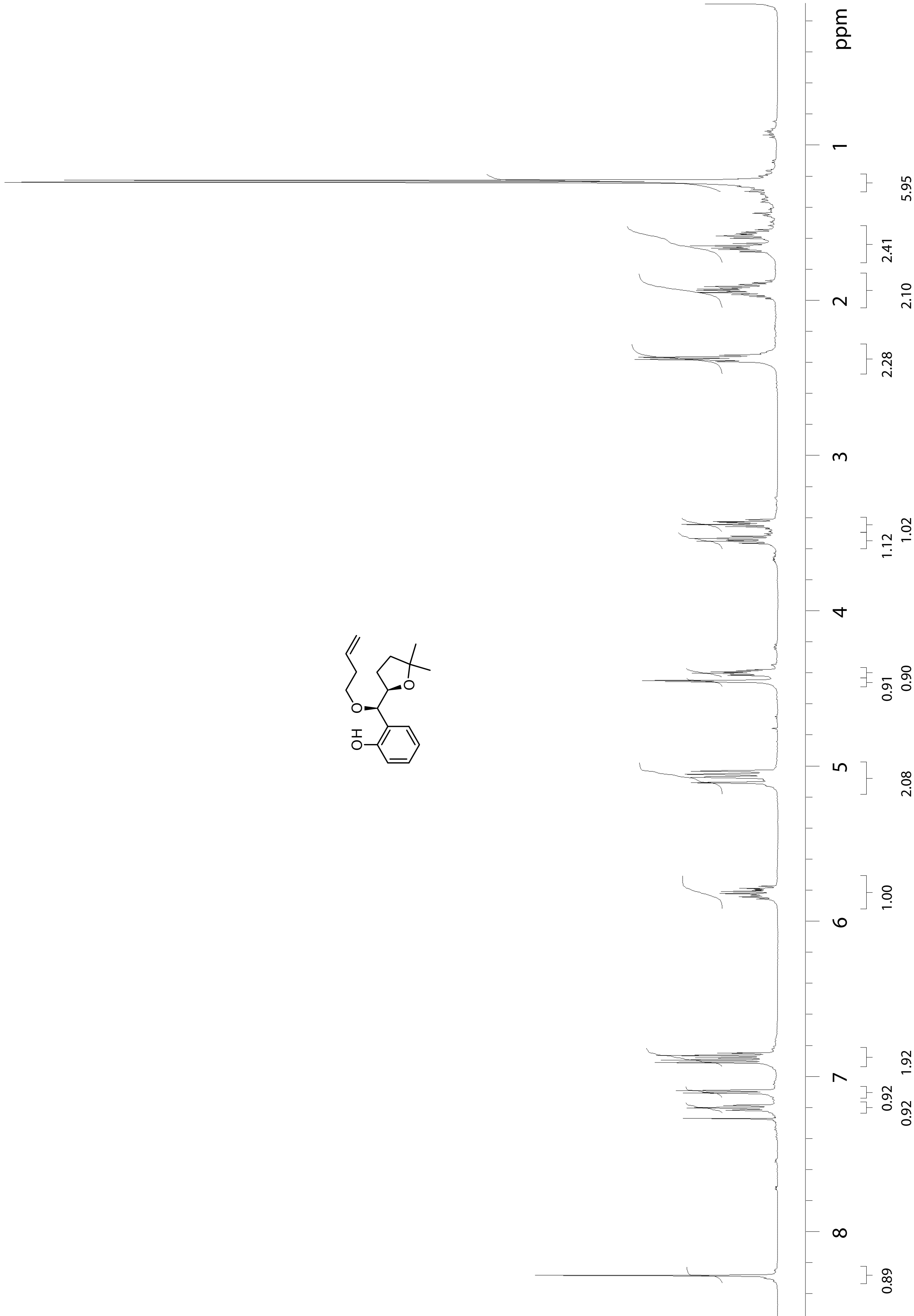
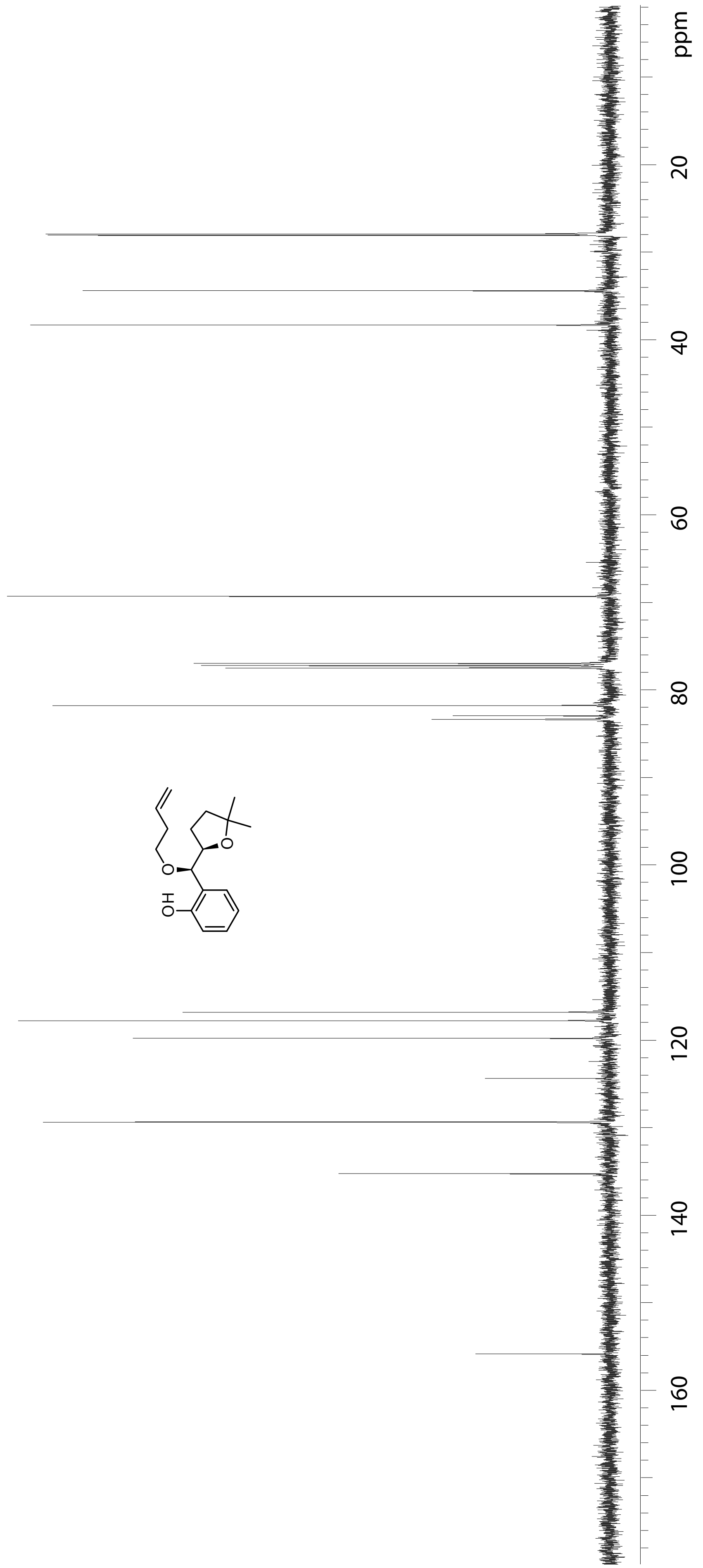
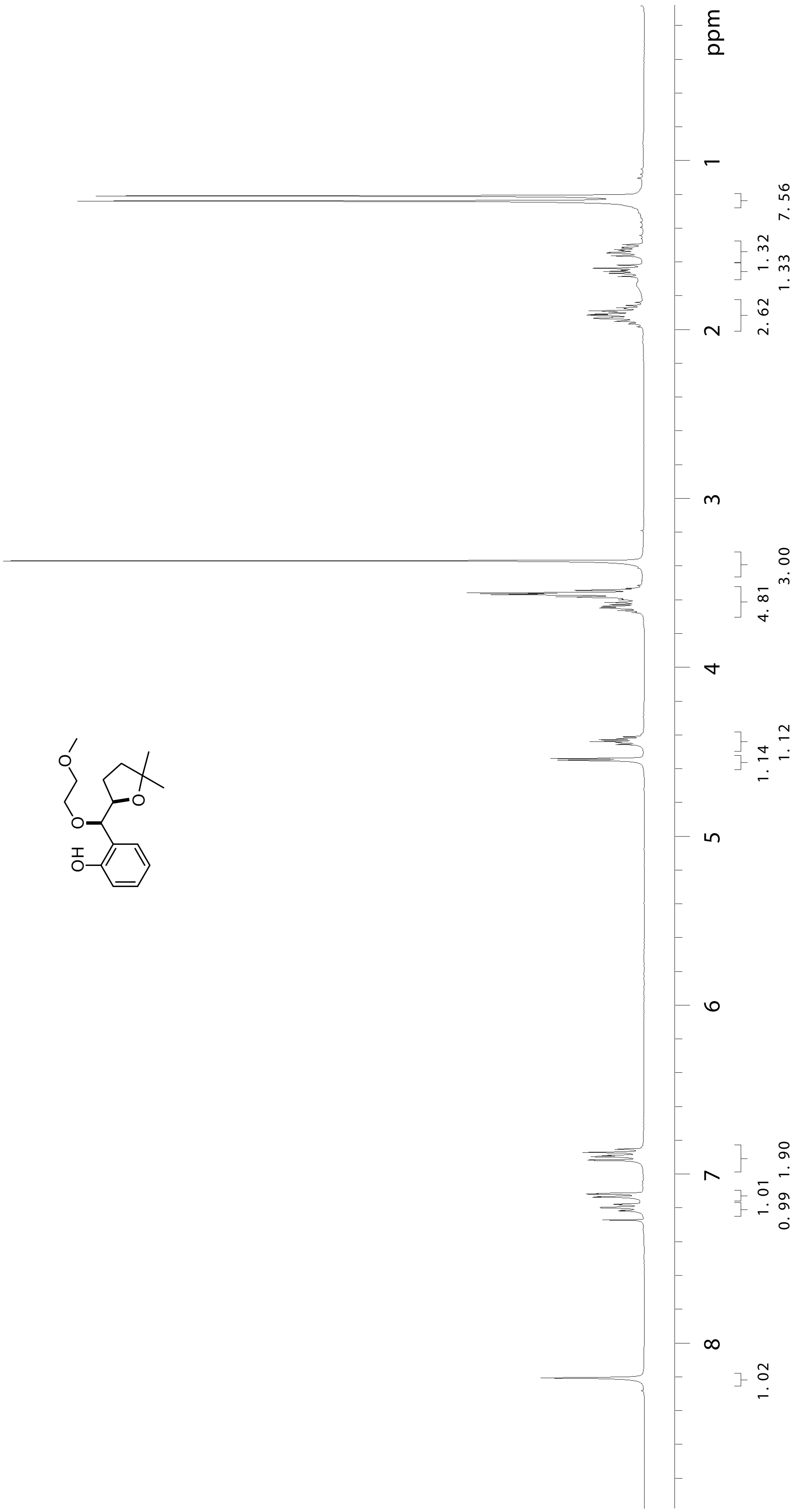
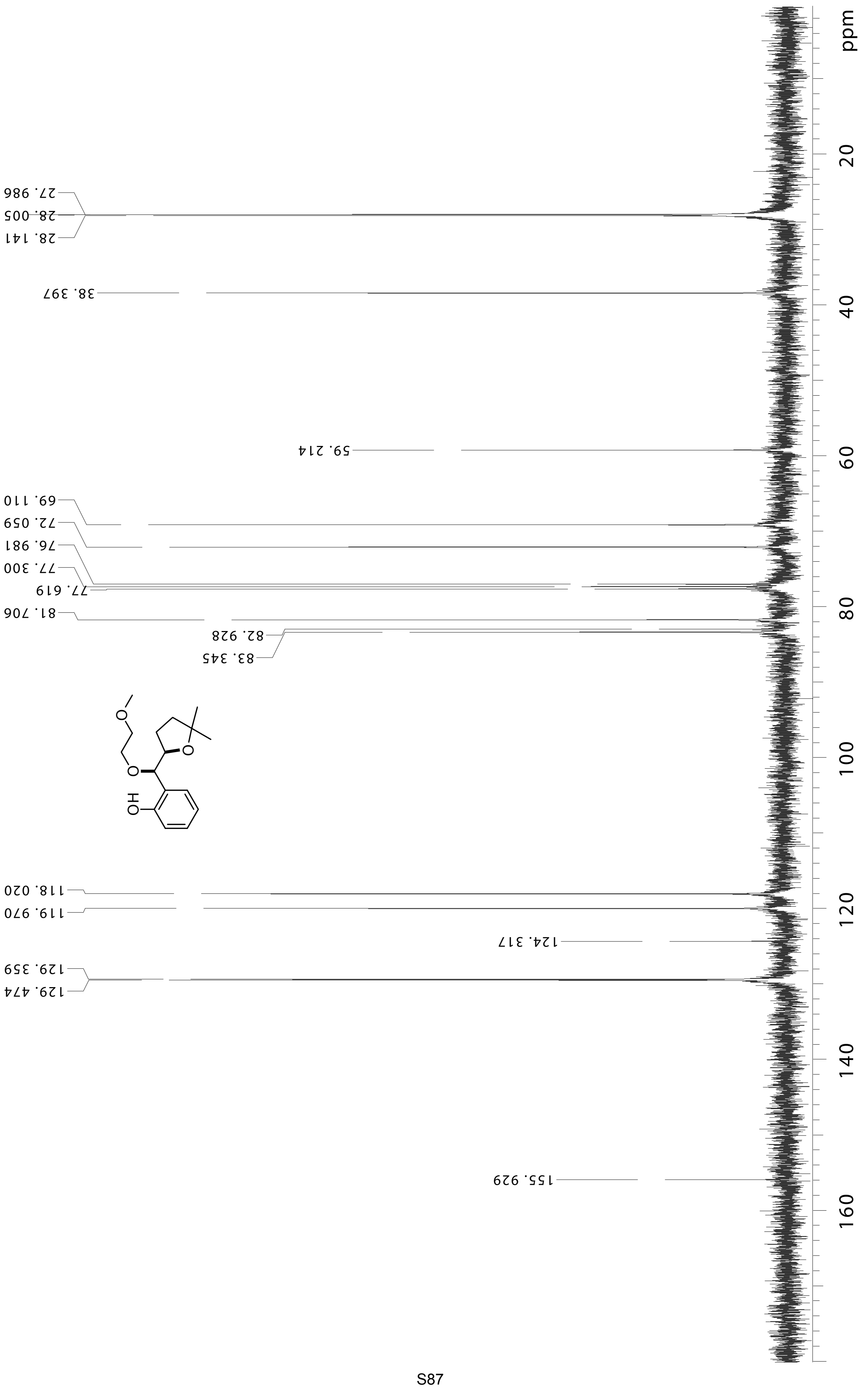
80
100
120
140
160
OH
O
O

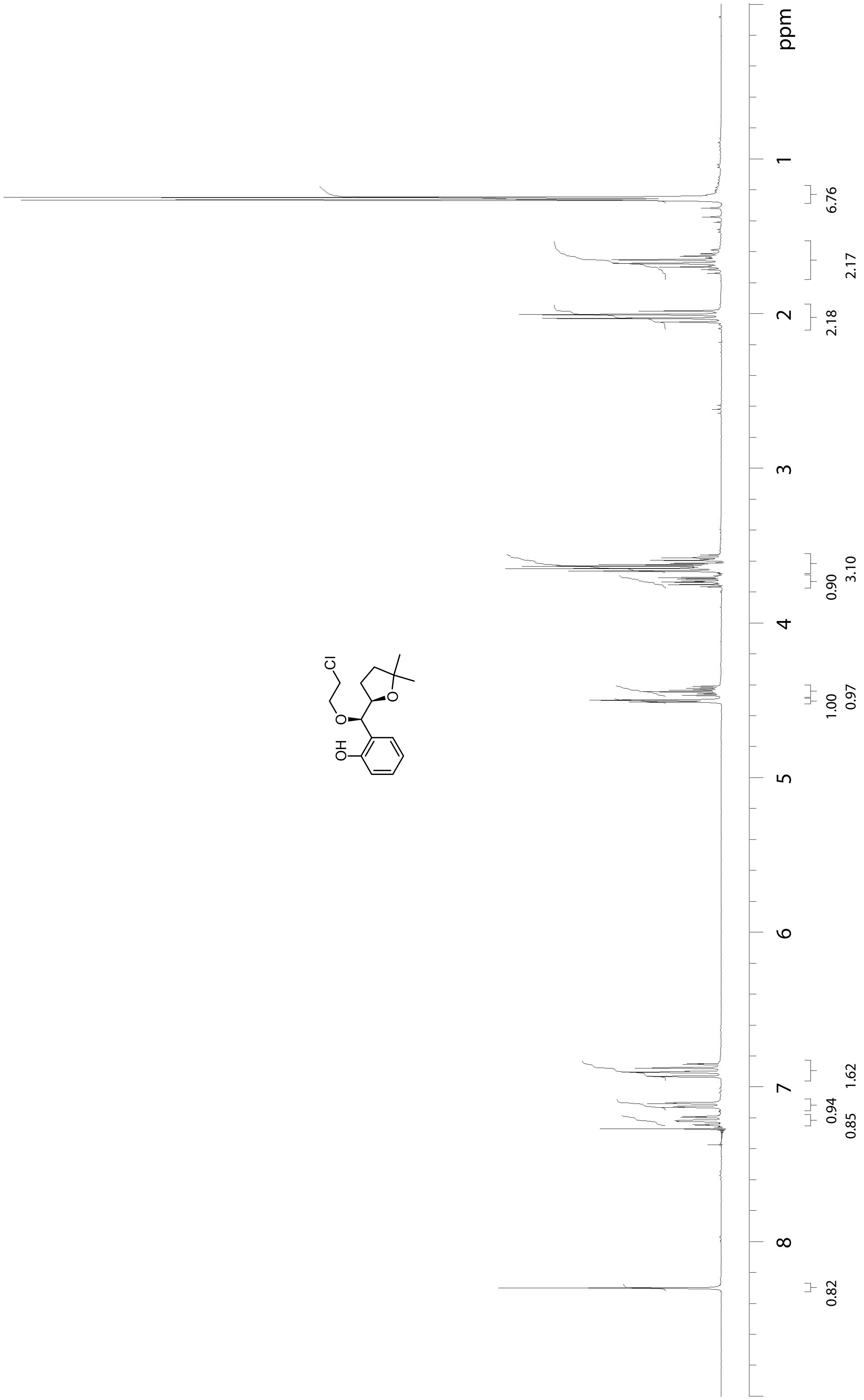

ppm
1
2
3
4
5
6
7
8
5.95
2.41
2.10
2.28
1.12
1.02
0.91
0.90
2.08
1.00
1.92
0.92
0.92
0.89
OH
O
O

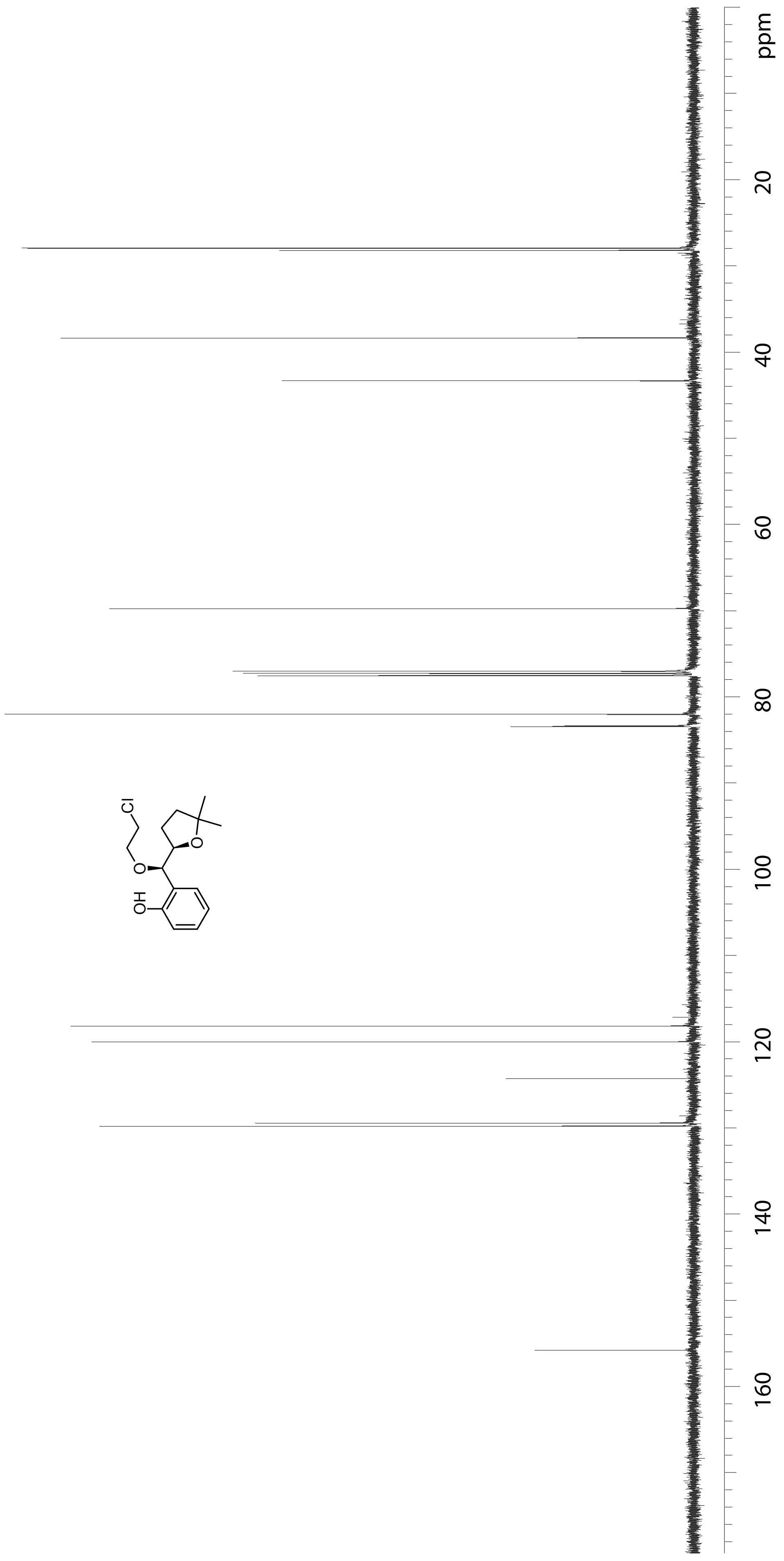

ppm
20
40
60
80
100
120
140
160
OH
O
O

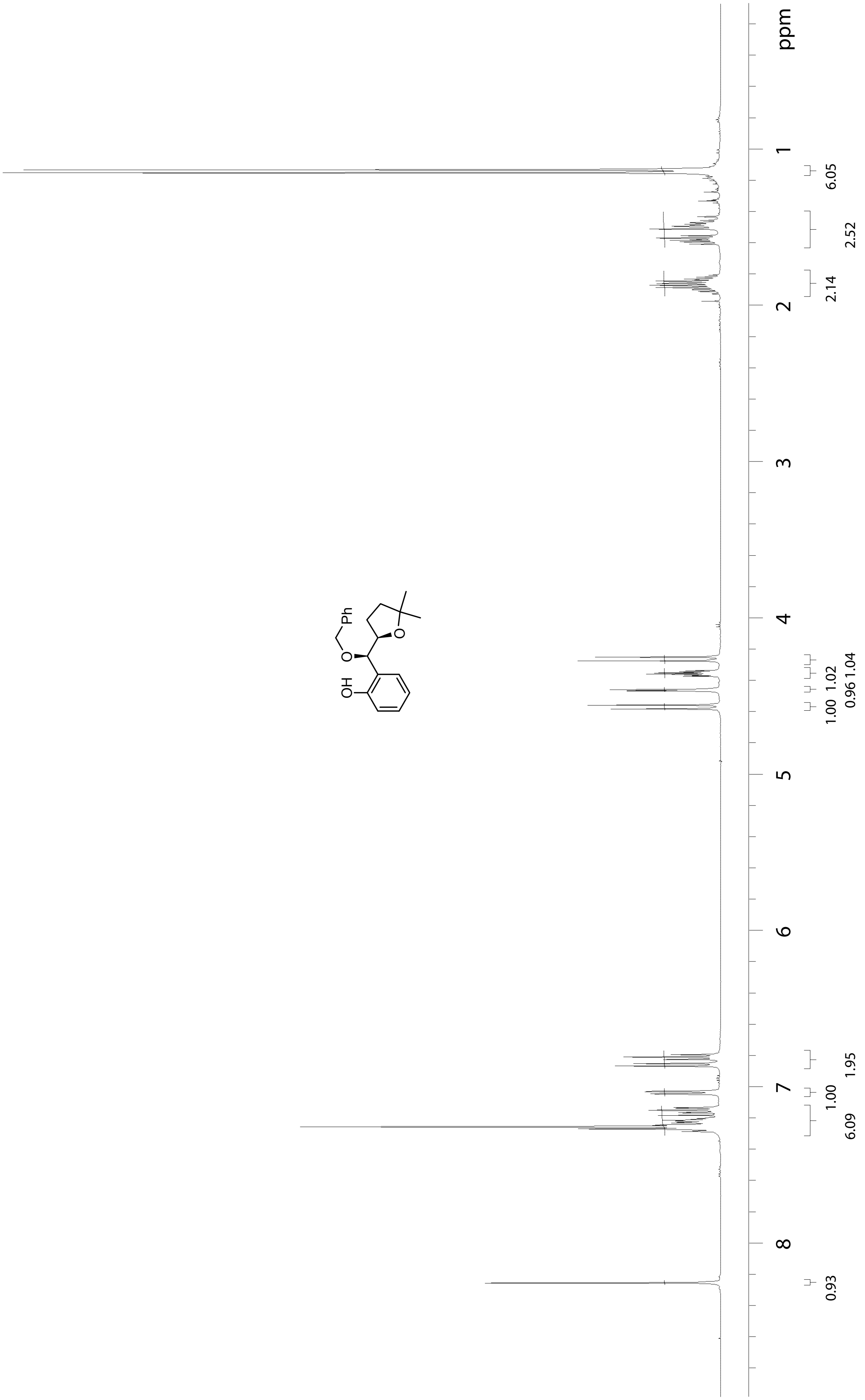


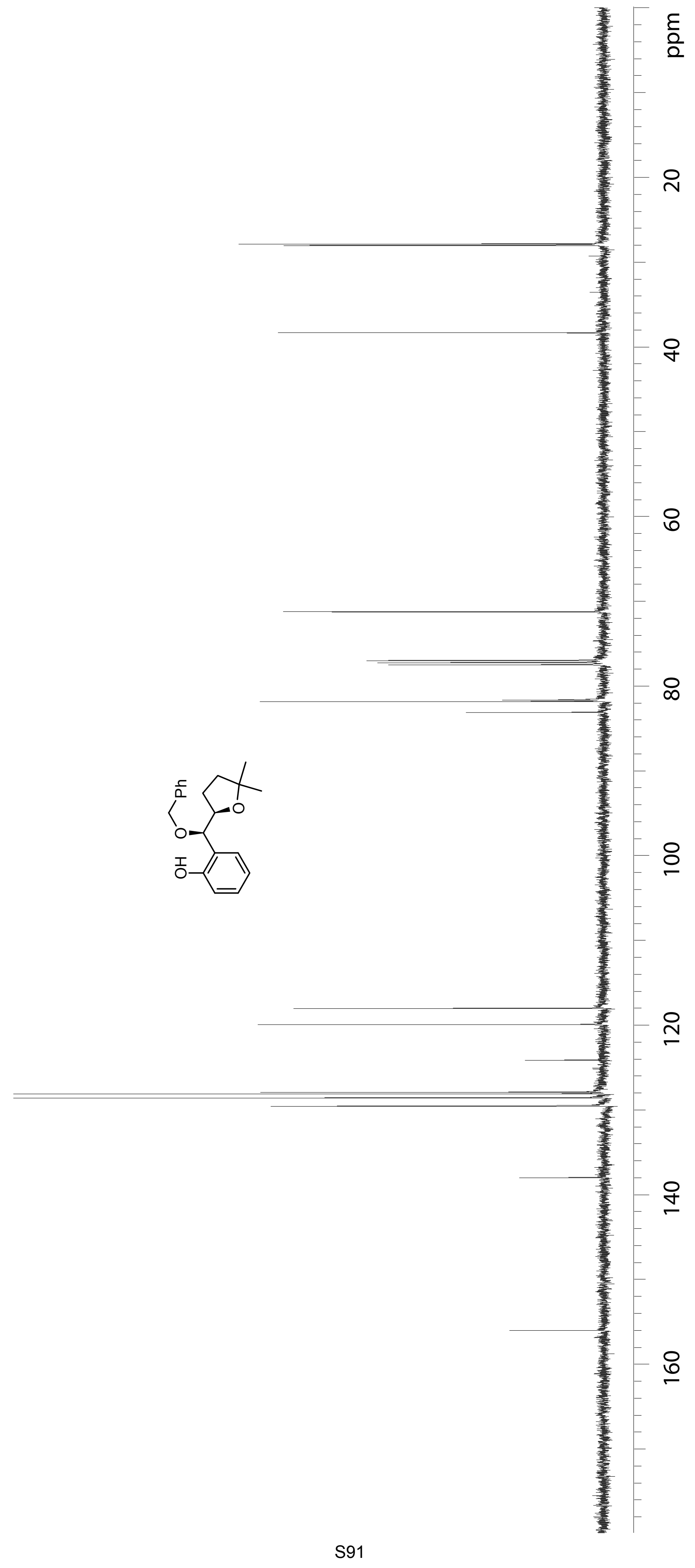
ppm
1
2
3
4
5
6
7
8
7.56
1.32
1.33
2.62
3.00
4.81
1.14
1.12
1.90
1.01
0.99
1.02
OH
O
O
O

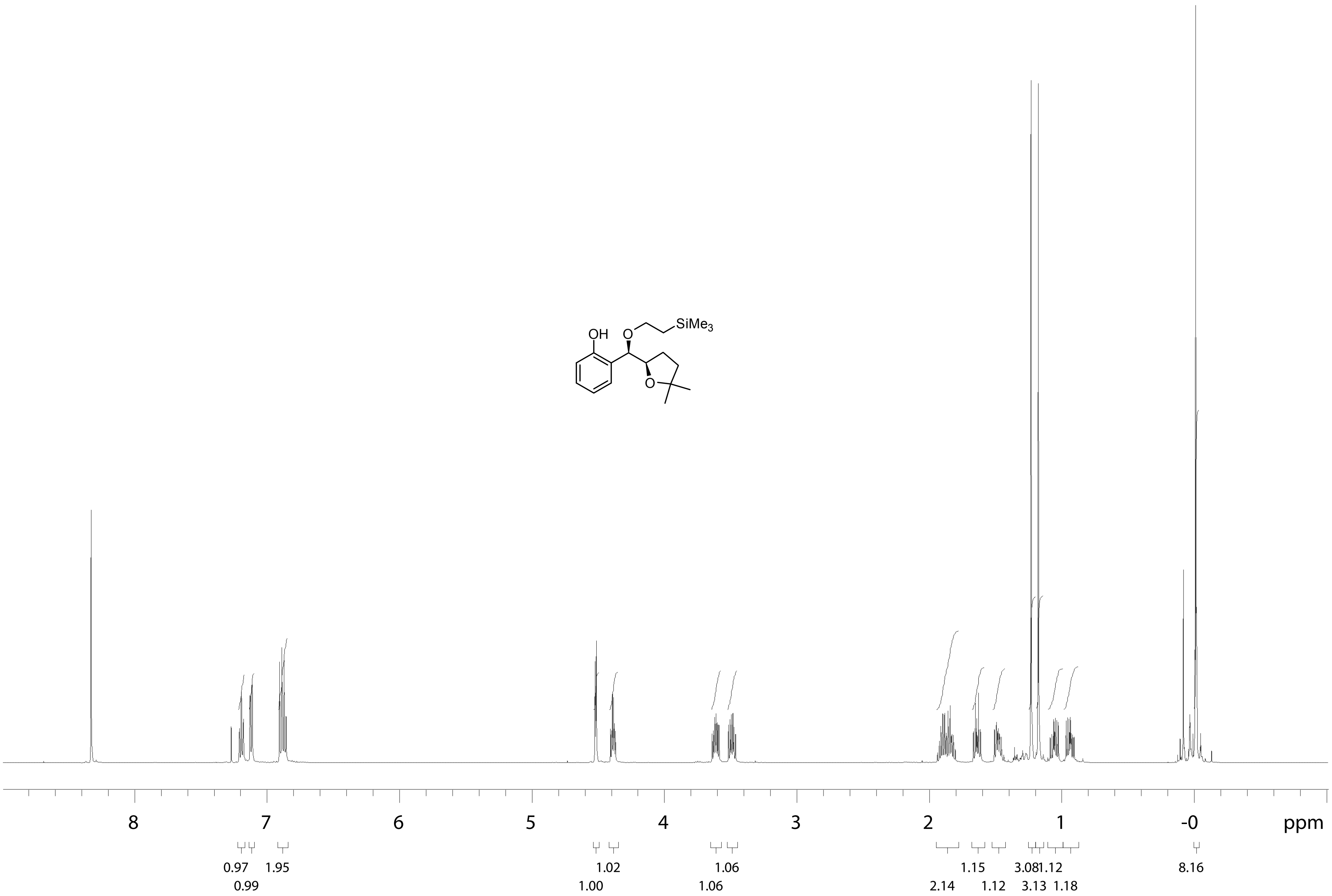

ppm
20
40
60
80
100
120
140
160
27.986
28.005
28.141
38.397
59.214
69.110
72.059
76.981
77.300
77.619
81.706
82.928
83.345
118.020
119.970
124.317
129.359
129.474
155.929
OH
O
O
O

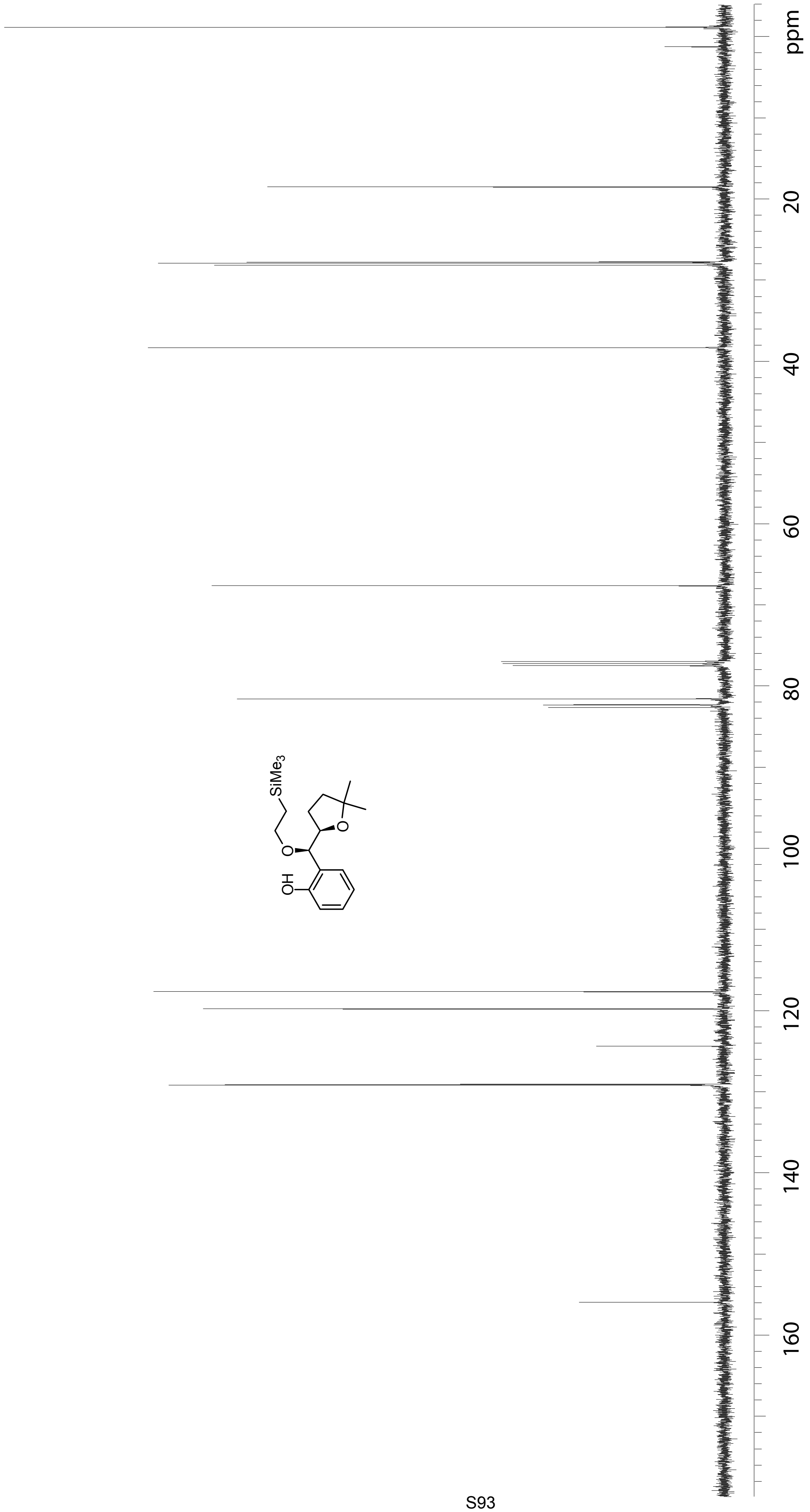

ppm
1
2
3
4
5
6
7
8
6.76
2.17
2.18
0.90
3.10
1.00
0.97
1.62
0.94
0.85
0.82
OH
O
O
Cl


ppm
20
40
60
80
100
120
140
160
OH
O
Cl
O


ppm
1
2
3
4
5
6
7
8
6.05
2.52
2.14
1.00 1.02
0.96 1.04
1.95
1.00
6.09
0.93
OH
O
Ph
O


ppm
20
40
60
80
100
120
140
160
OH
O
Ph
O


OH
O
SiMe3
O
8
7
6
5
4
3
2
1
-0
ppm
0.97
0.99
1.95
1.00
1.02
1.06
1.06
2.14
1.15
1.12
3.08
3.13
1.12
1.18
8.16


ppm
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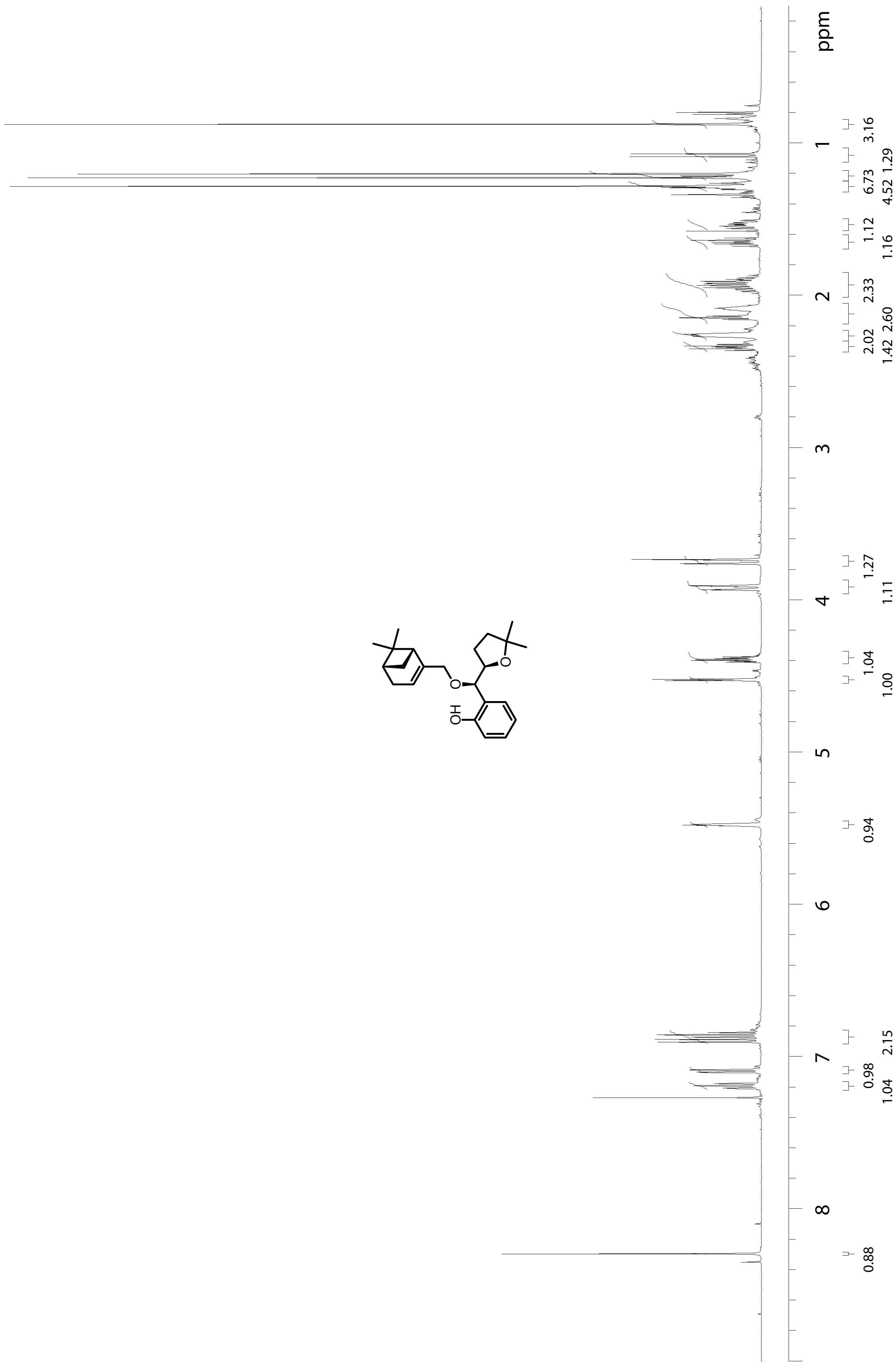
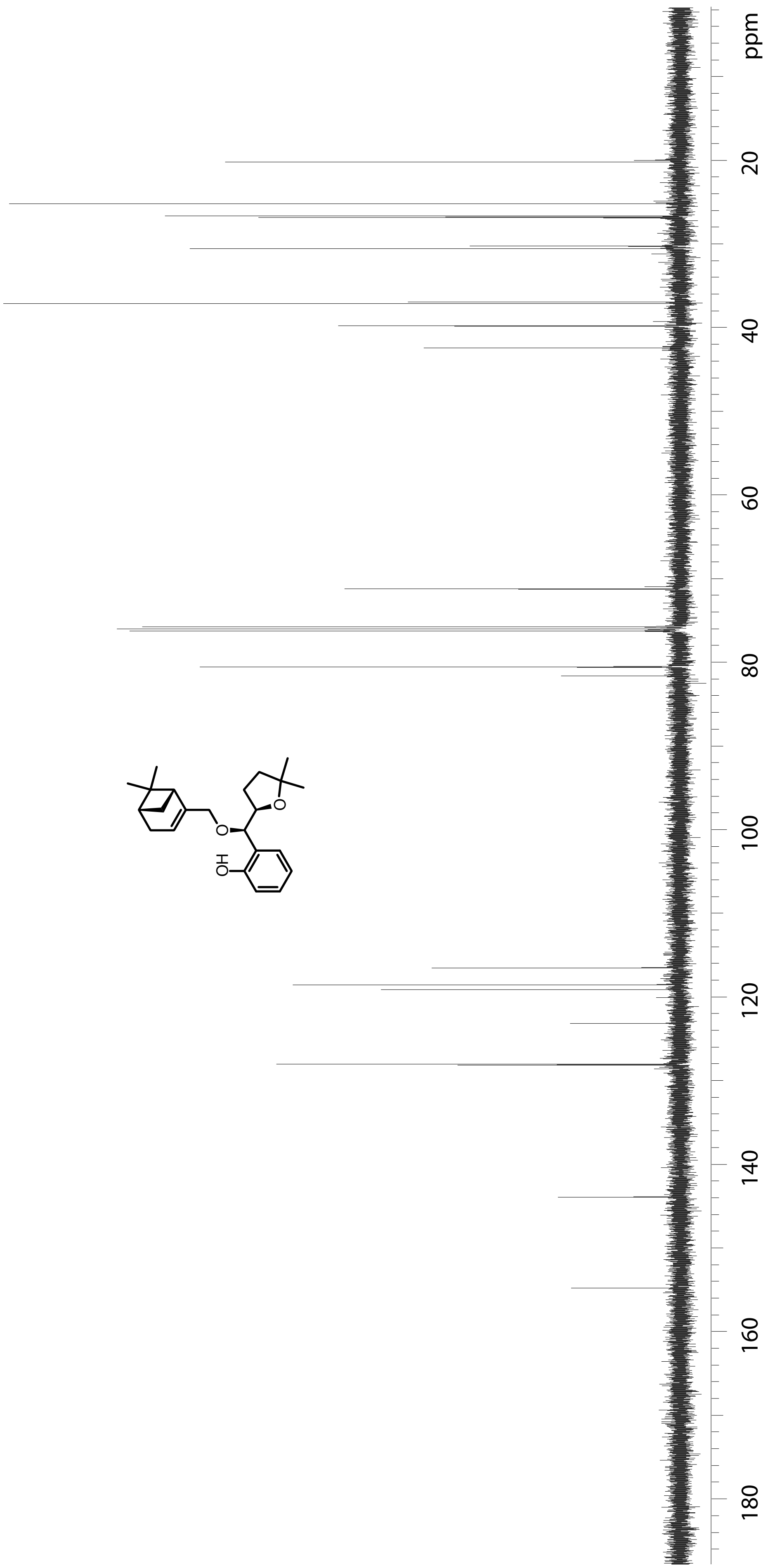
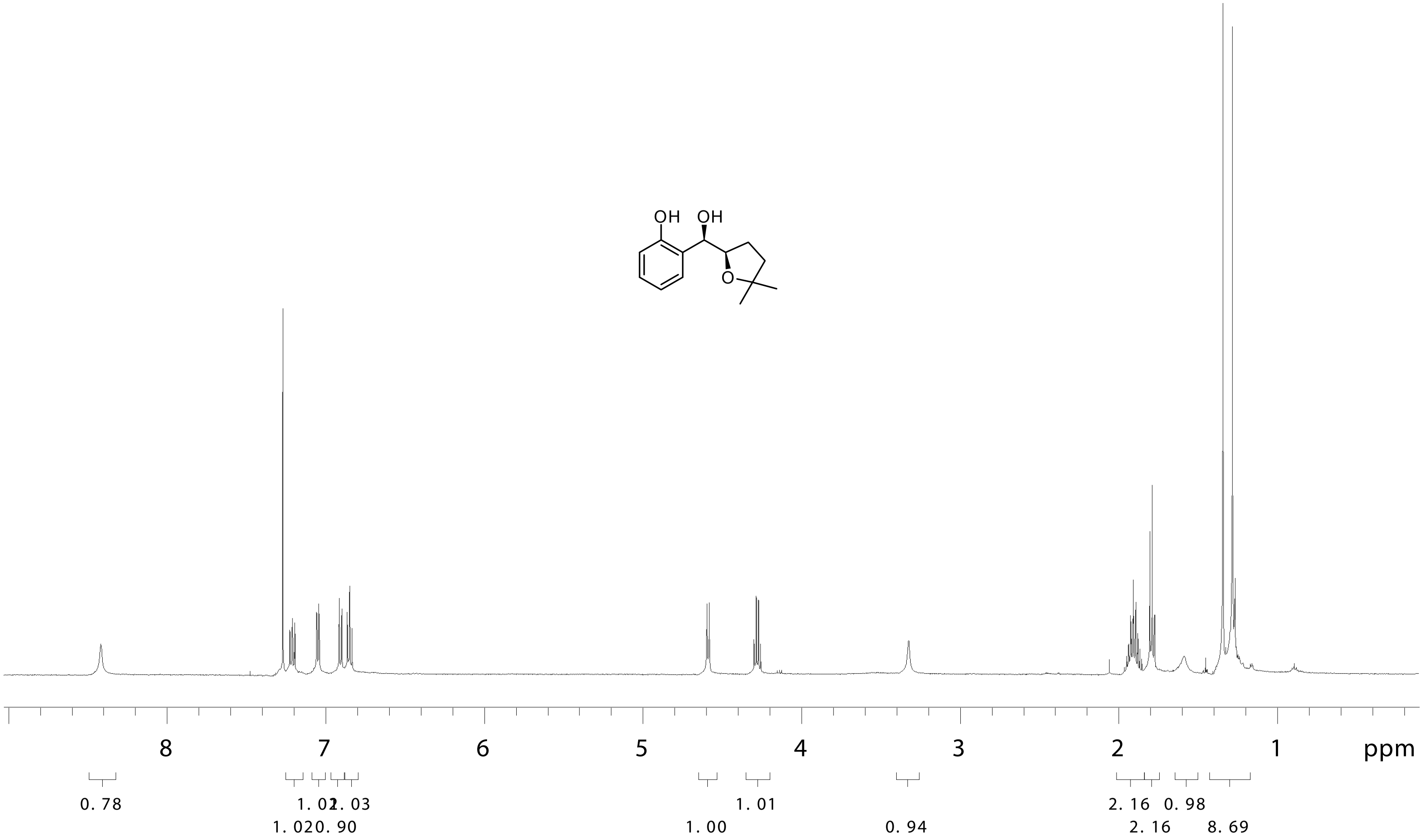
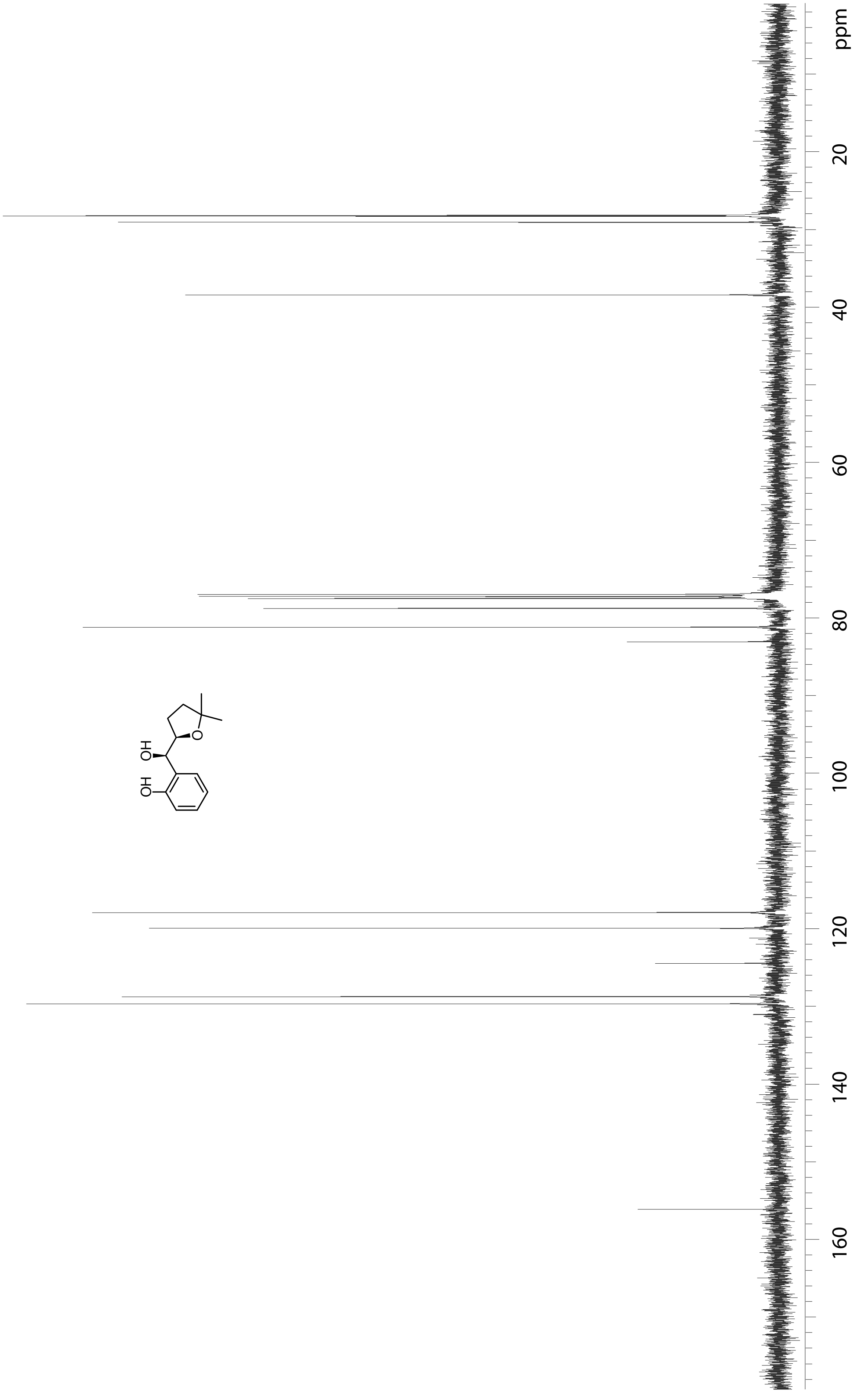
40
60
80
100
120
140
160
OH
O
SiMe3
O


ppm
1
2
3
4
5
6
7
8
3.16
1.29
6.73
4.52
1.12
1.16
2.33
2.60
2.02
1.42
1.27
1.11
1.04
1.00
0.94
2.15
0.98
1.04
0.88
O
O
OH



OH
O
O
ppm
20
40
60
80
100
120
140
160
180


OH
OH
O
8
7
6
5
4
3
2
1
ppm
0. 78
1. 02
1. 03
1. 02
0. 90
1. 00
1. 01
0. 94
2. 16
2. 16
0. 98
8. 69


ppm
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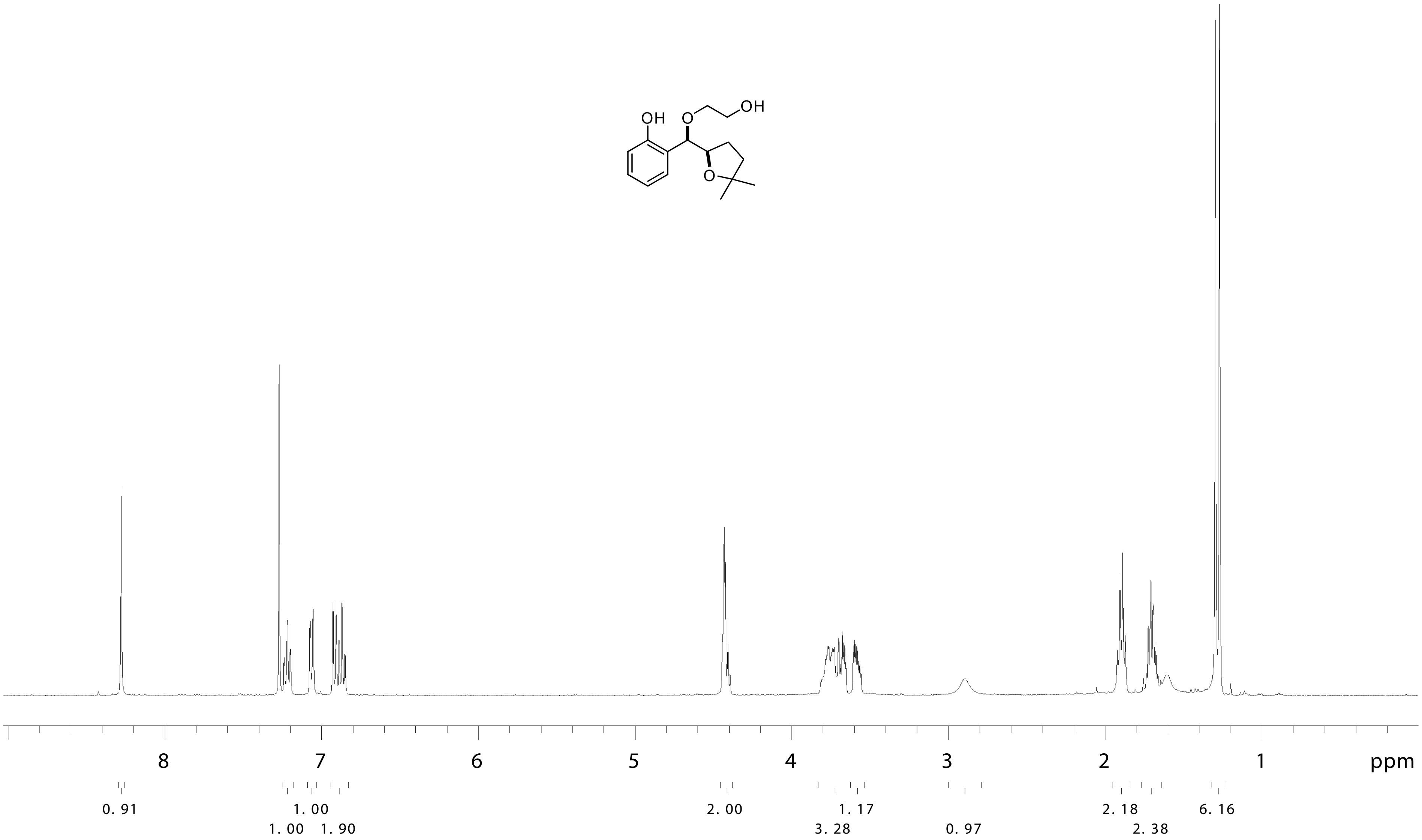
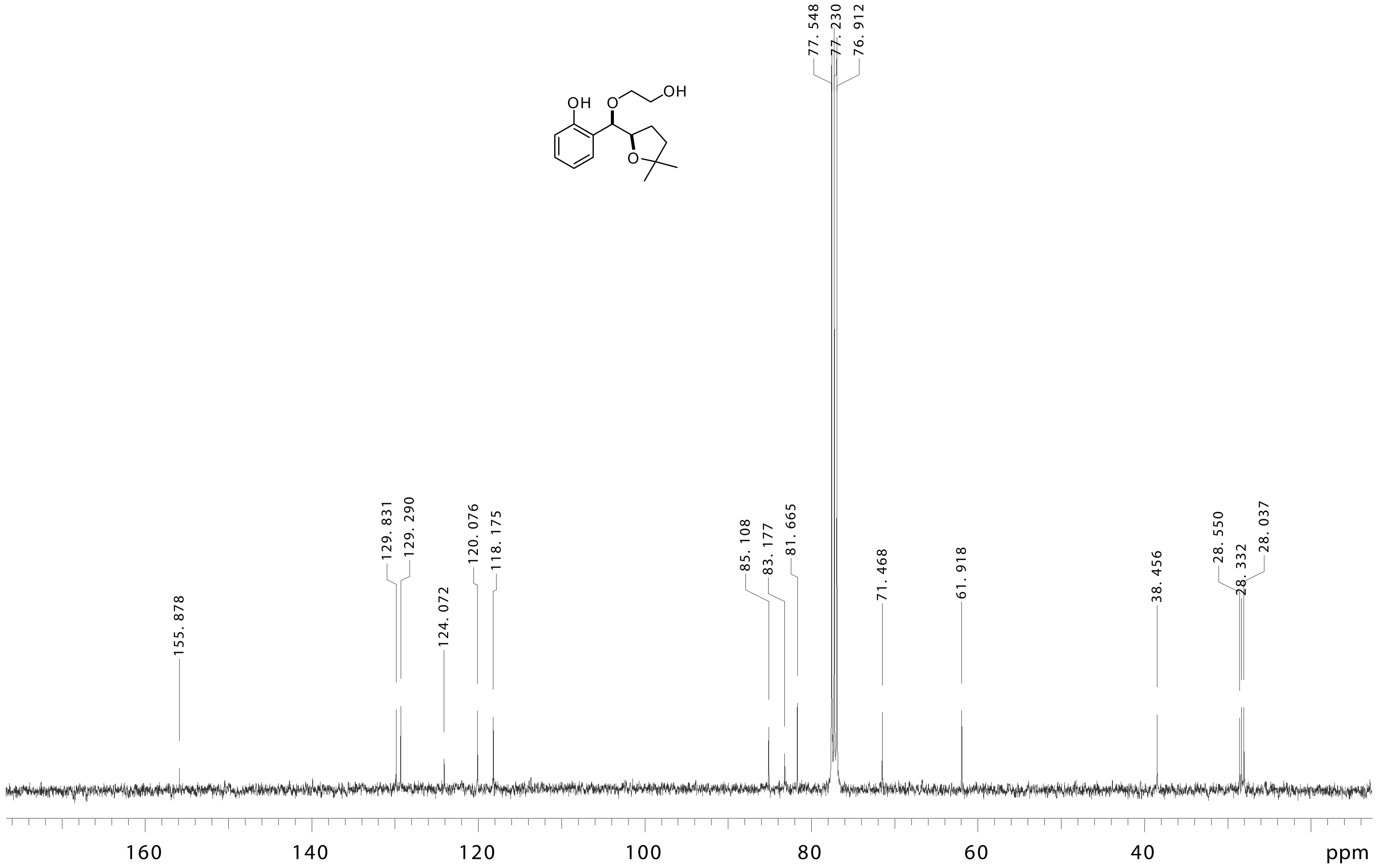
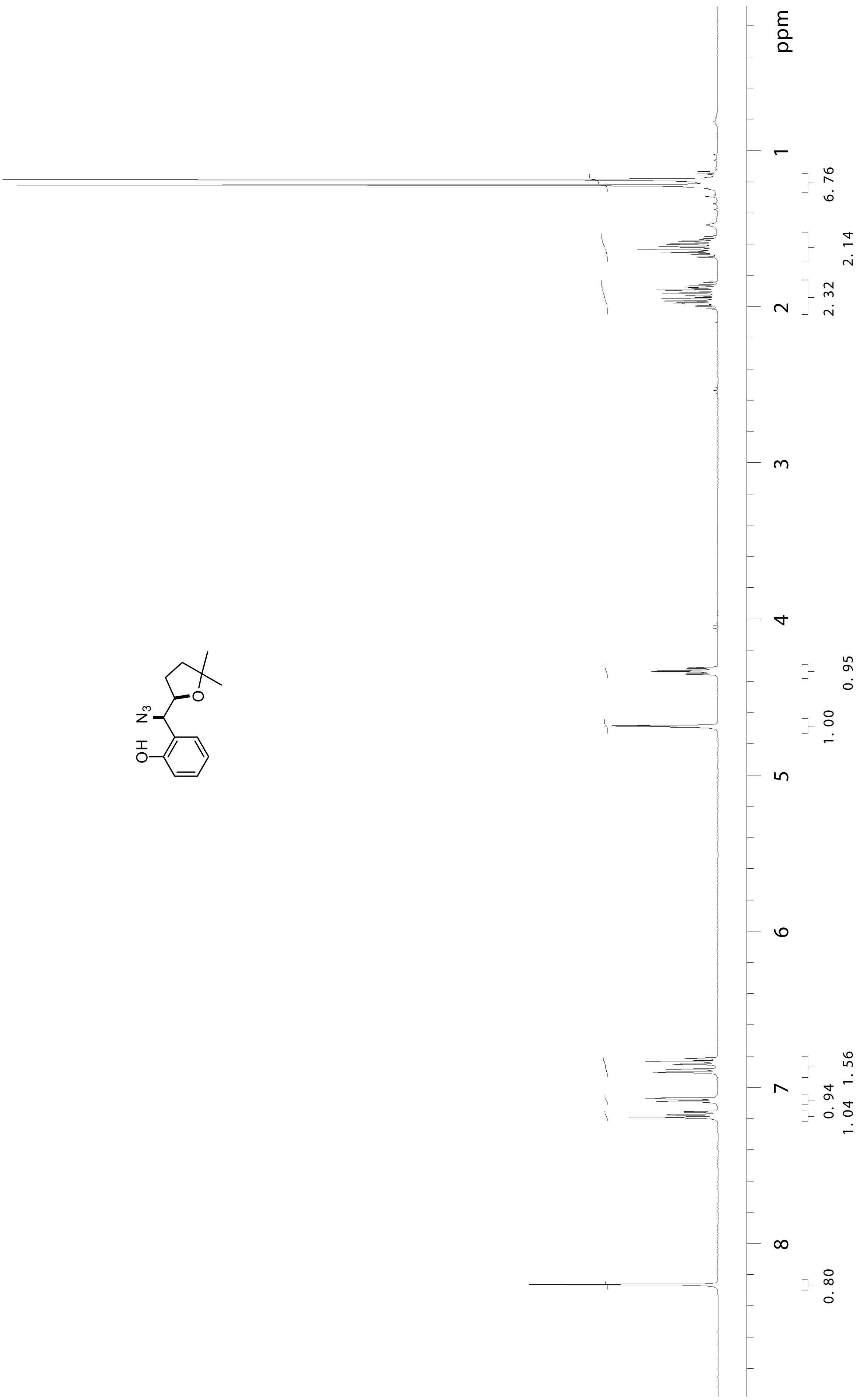
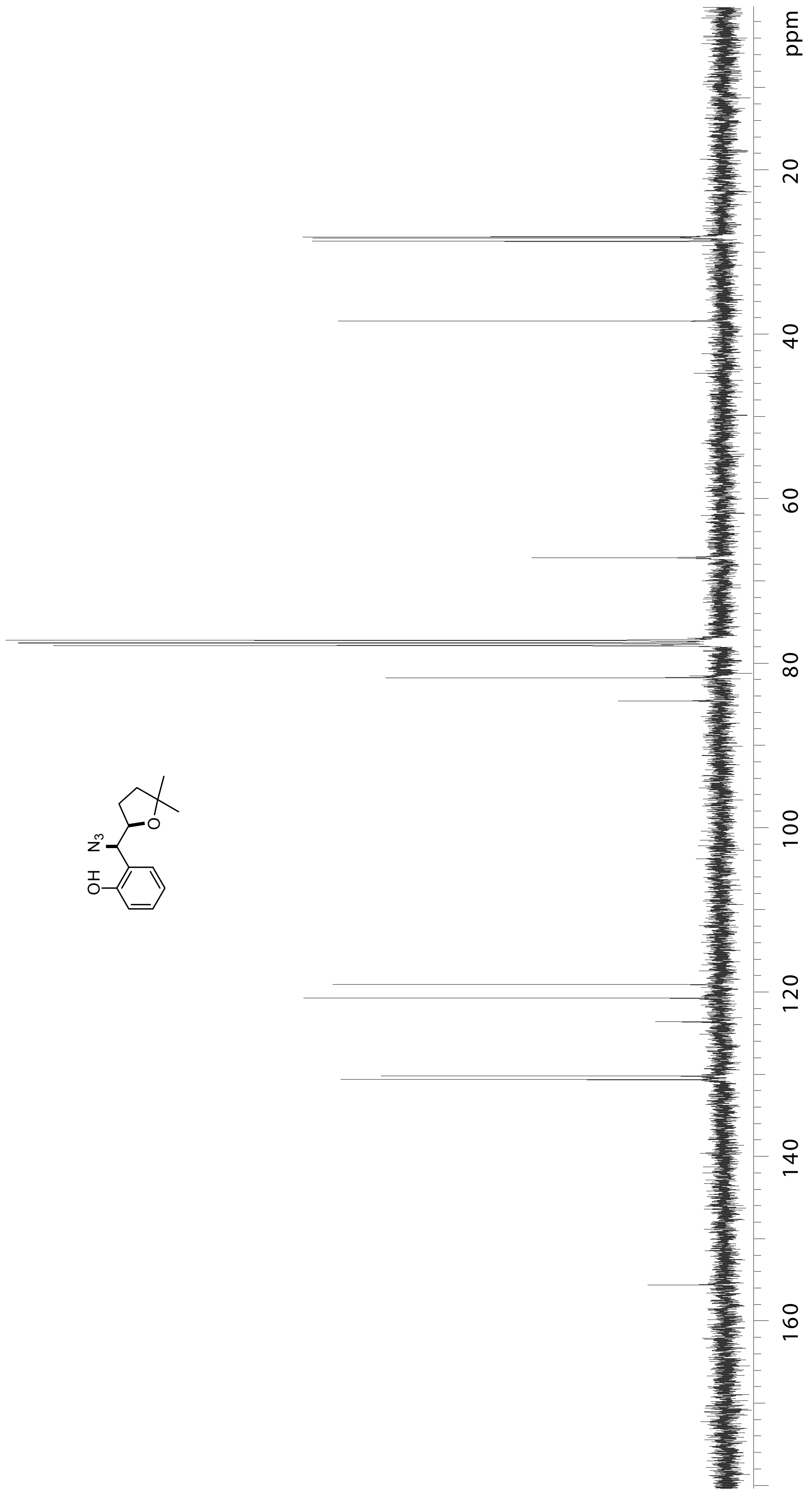
40
60
80
100
120
140
160
OH
OH
O

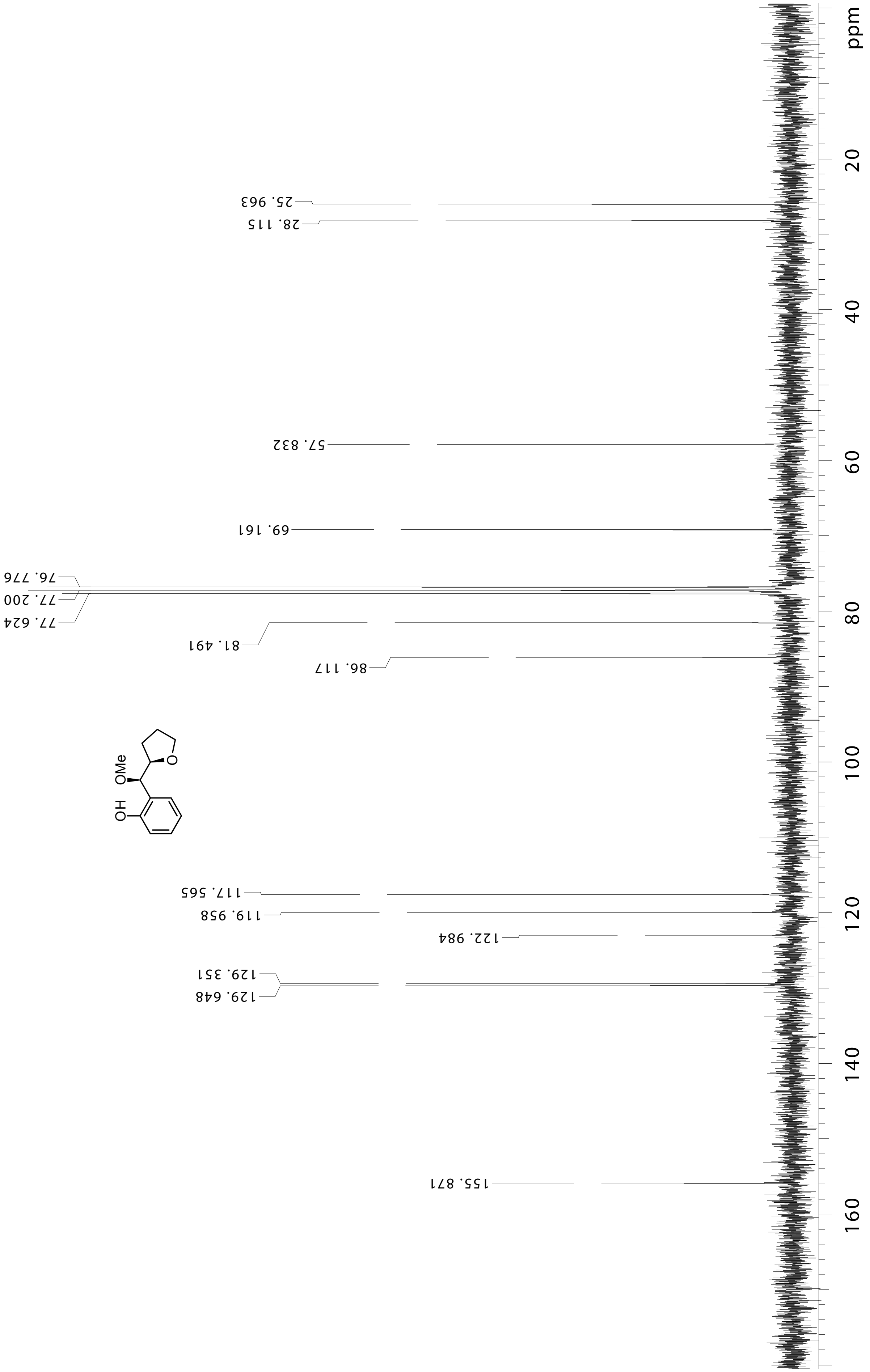

8
7
6
5
4
3
2
1
ppm
0. 91
1. 00
1. 00
1. 90
2. 00
1. 17
3. 28
0. 97
2. 18
2. 38
6. 16
OH
O
OH
O

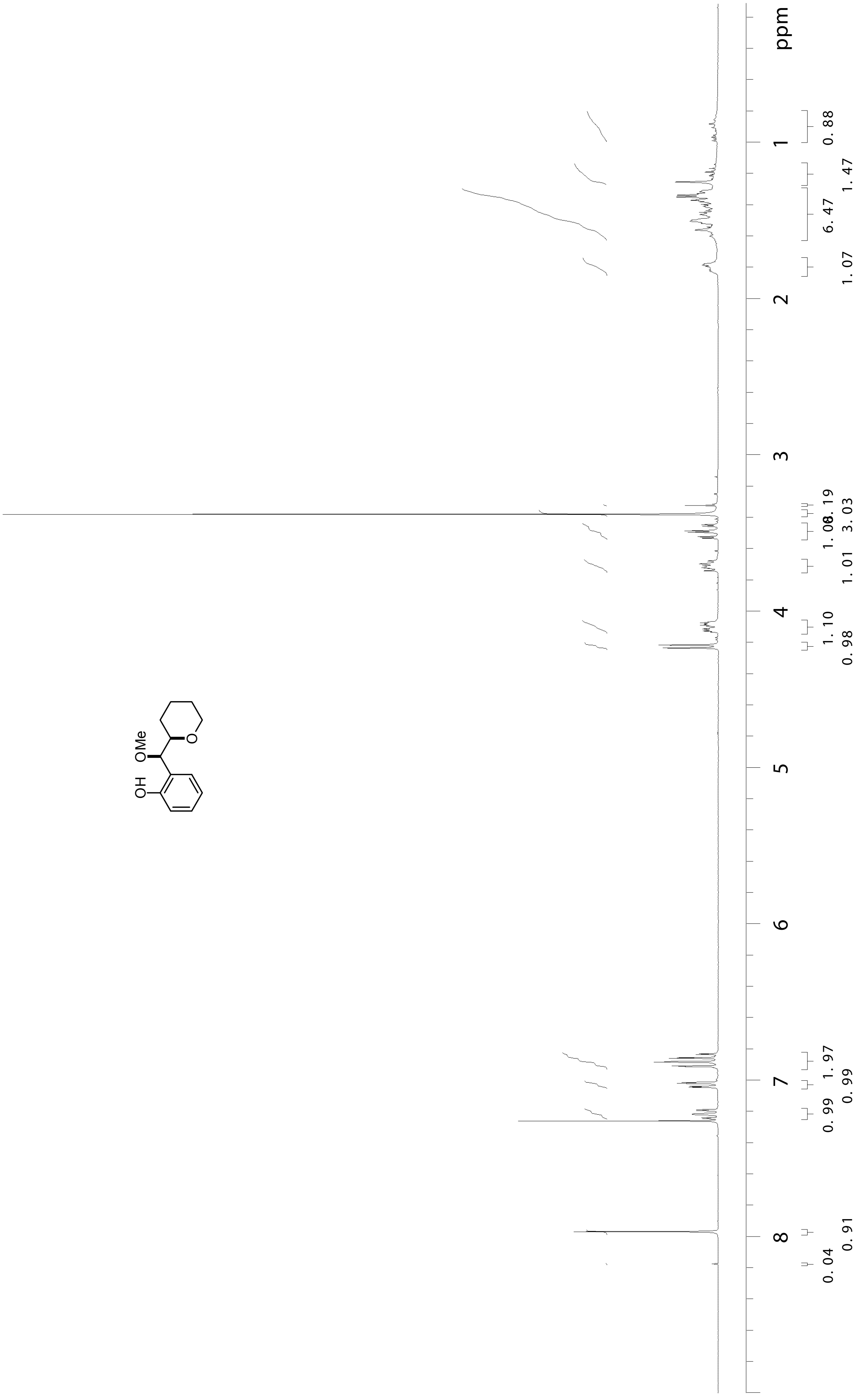

155. 878
129. 831
129. 290
124. 072
120. 076
118. 175
85. 108
83. 177
81. 665
77. 548
77. 230
76. 912
71. 468
61. 918
38. 456
28. 550
28. 332
28. 037
OH
O
OH
O
160
140
120
100
80
60
40
ppm

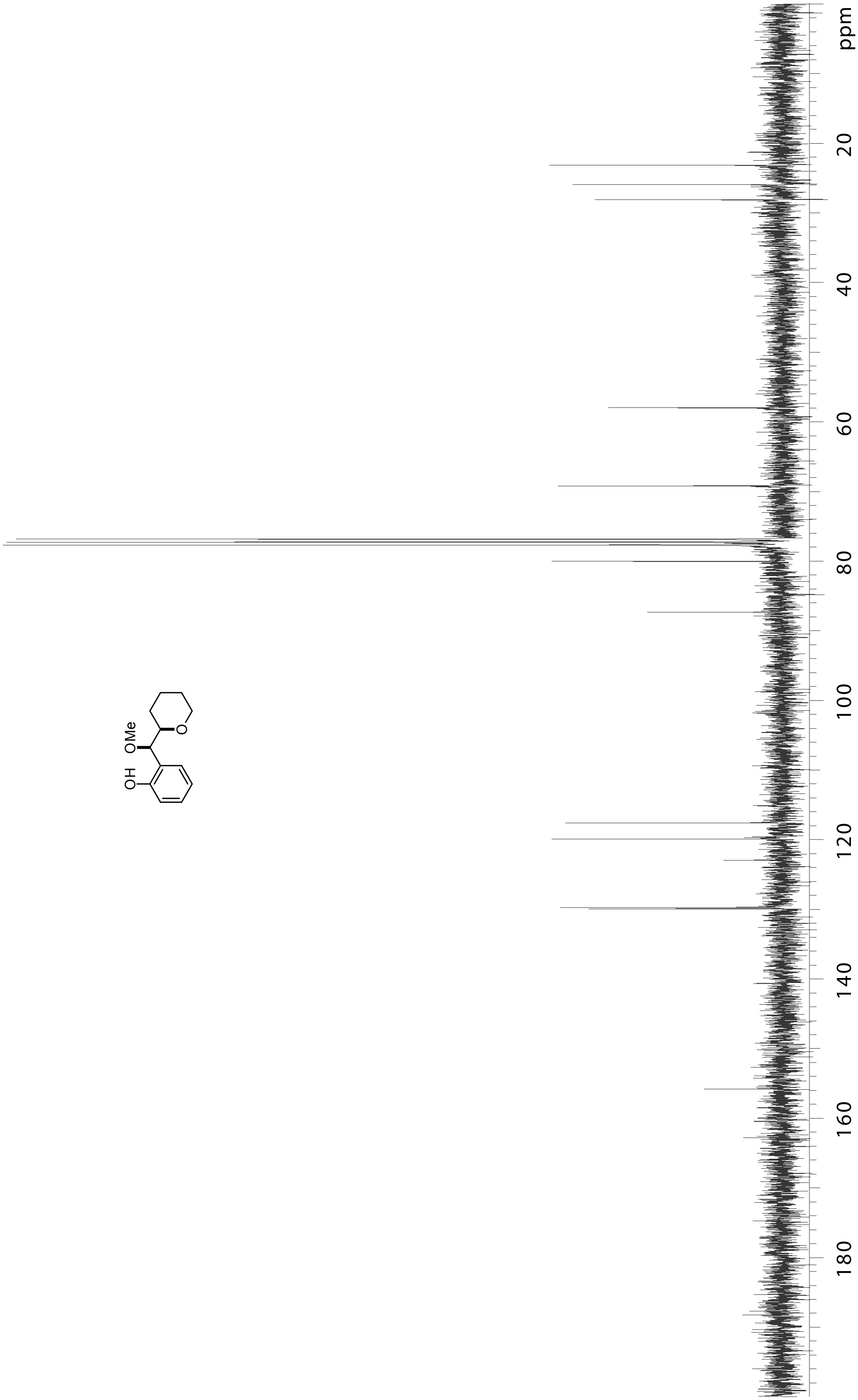

ppm
1
2
3
4
5
6
7
8
6.76
2.14
2.32
0.95
1.00
1.56
0.94
1.04
0.80
OH
N3
O

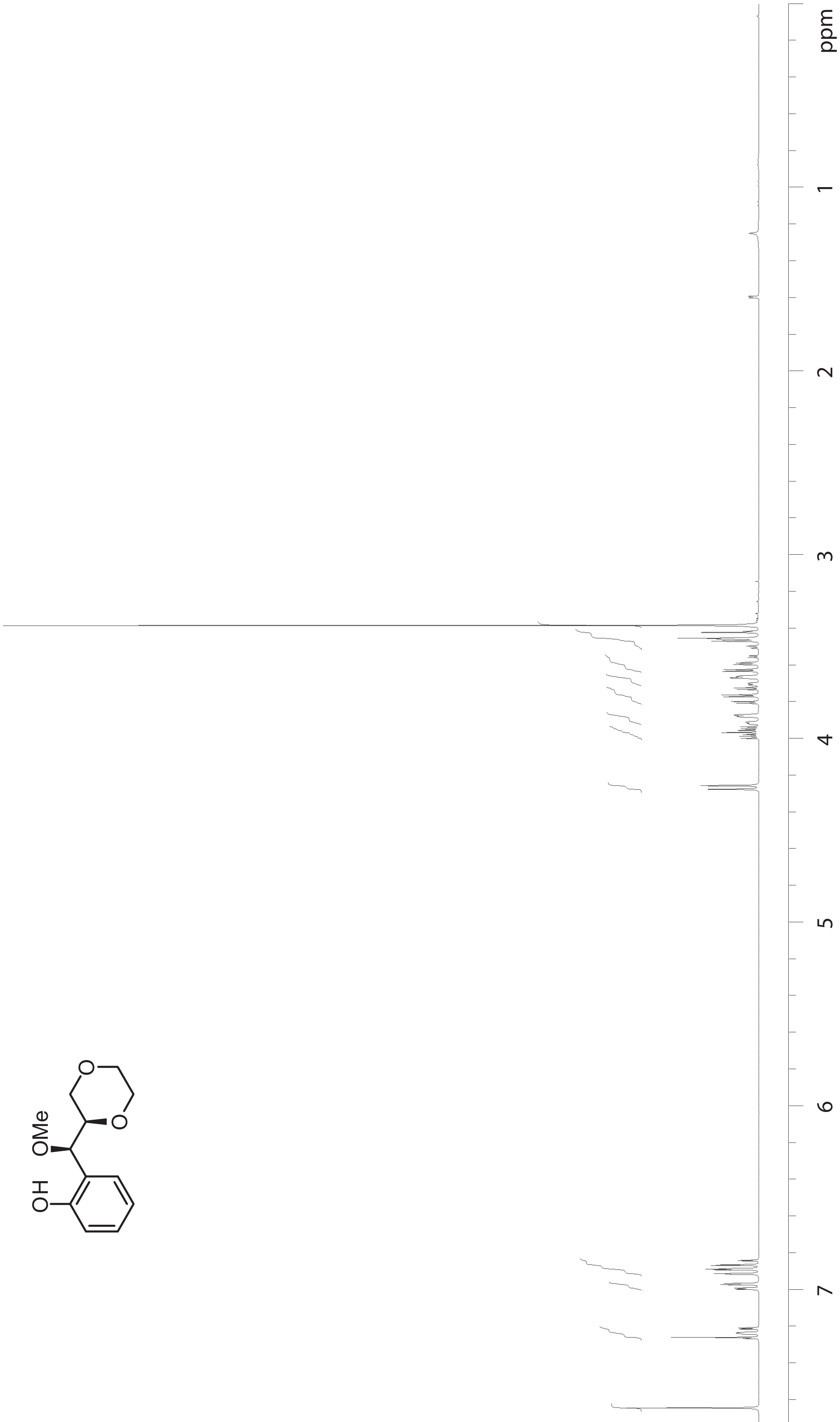

OH
N3
O
ppm
20
40
60
80
100
120
140
160

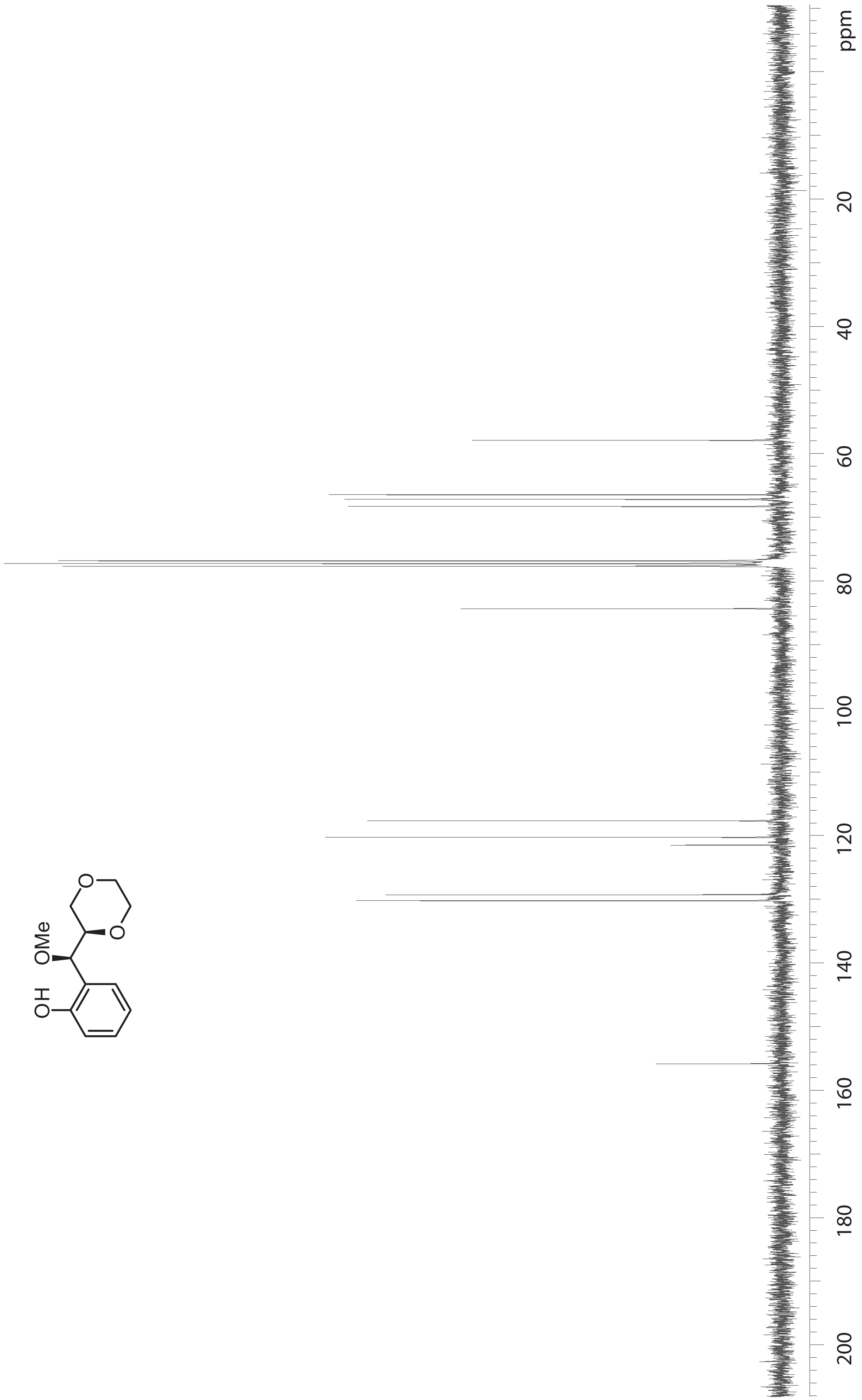
ppm
1
2
3
4
5
6
7
8
4.32
3.00
2.10
2.06
1.75
0.97
0.92
0.87
OH
OMe
O

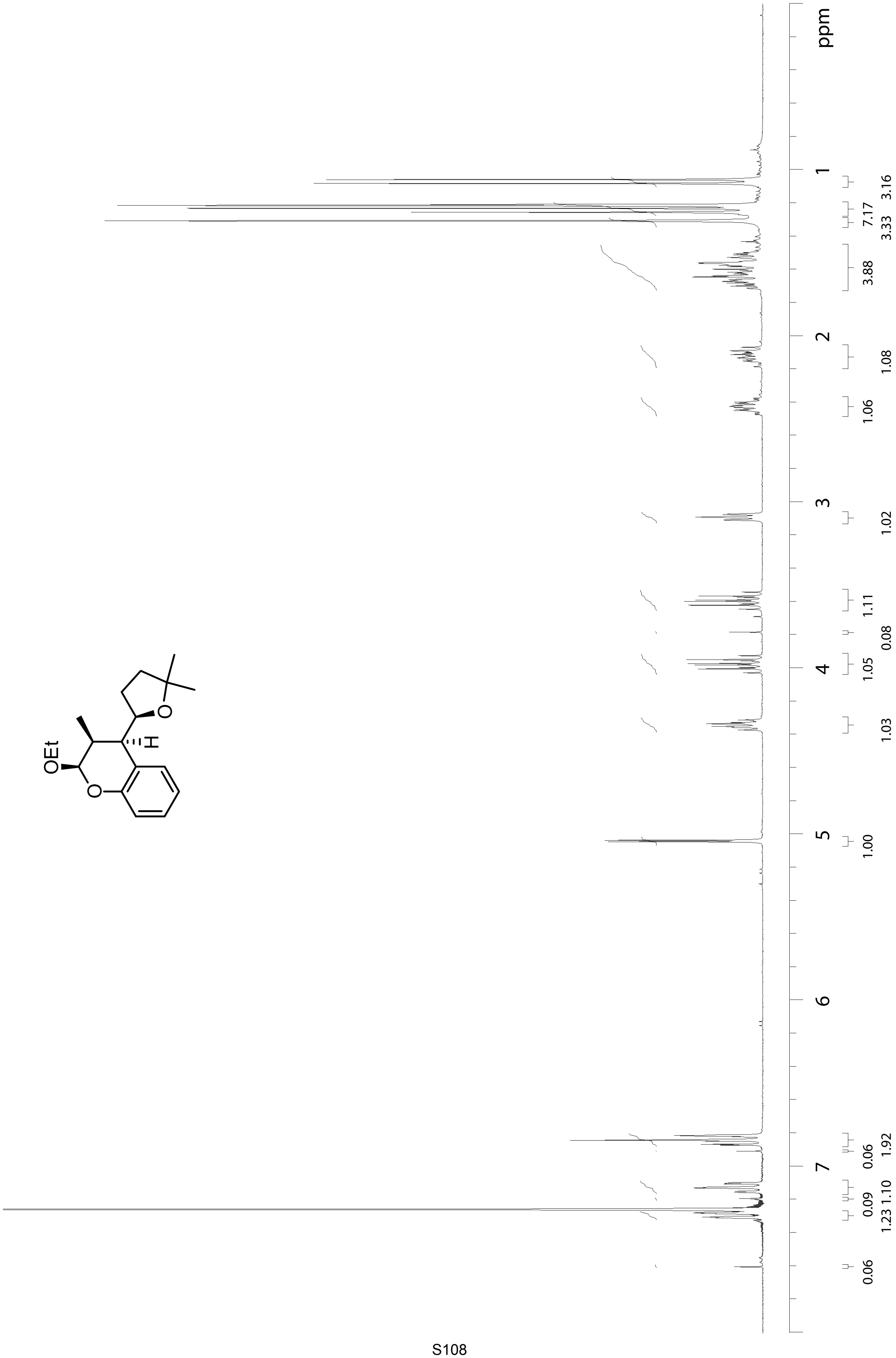

25.963
28.115
57.832
69.161
76.776
77.200
77.624
81.491
86.117
117.565
119.958
122.984
129.351
129.648
155.871
OH
OMe
O
ppm
20
40
60
80
100
120
140
160

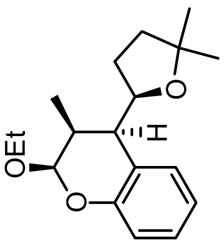

OH
OMe
O
ppm
1
2
3
4
5
6
7
8
0.88
1.47
6.47
1.07
1.08.19
3.03
1.01
1.10
0.98
1.97
0.99
0.99
0.04
0.91


OH
OMe
O
ppm
20
40
60
80
100
120
140
160
180

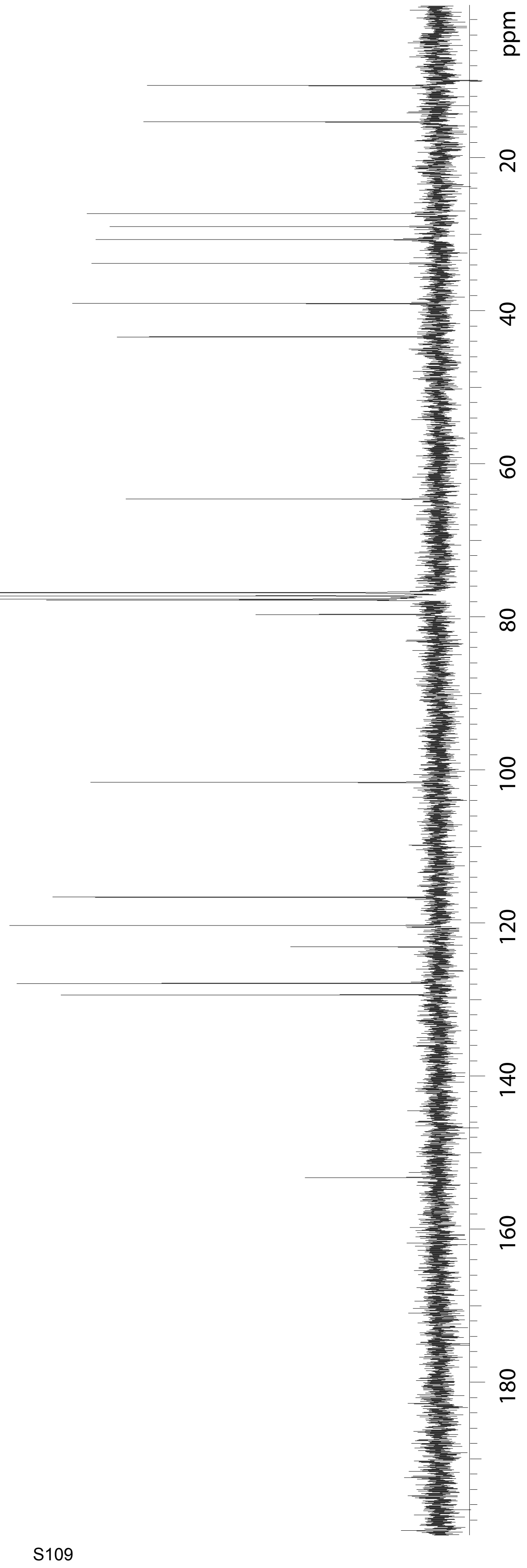

OH
OMe
O
O
ppm
1
2
3
4
5
6
7


OH
OMe
O
O
ppm
20
40
60
80
100
120
140
160
180
200


OEt
O
O
H
ppm
1
2
3
4
5
6
7
3.16
7.17
3.33
3.88
1.08
1.06
1.02
1.11
0.08
1.05
1.03
1.00
1.92
0.06
1.10
0.09
1.23
0.06



OEt
O
H
O



ppm
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120
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160
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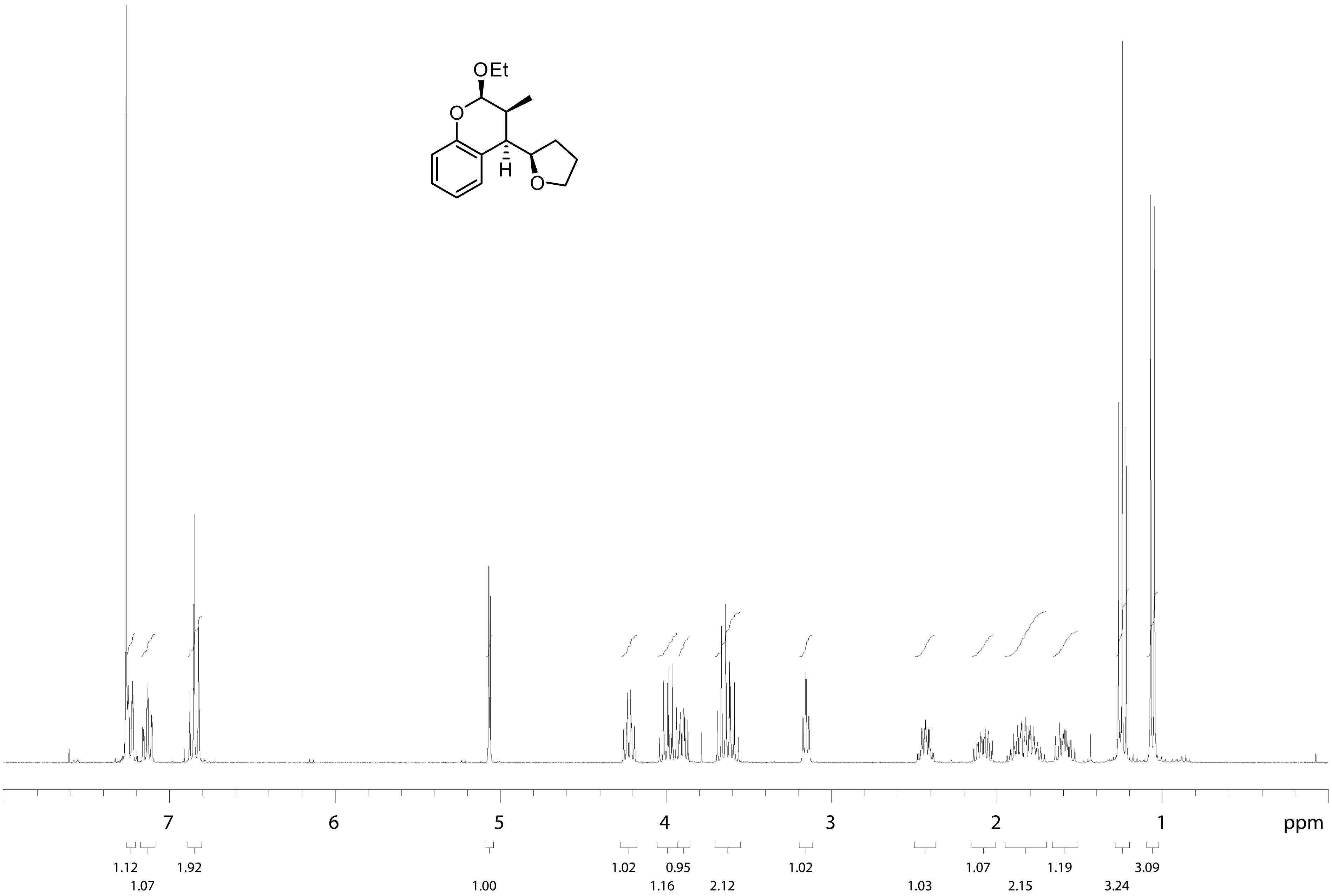
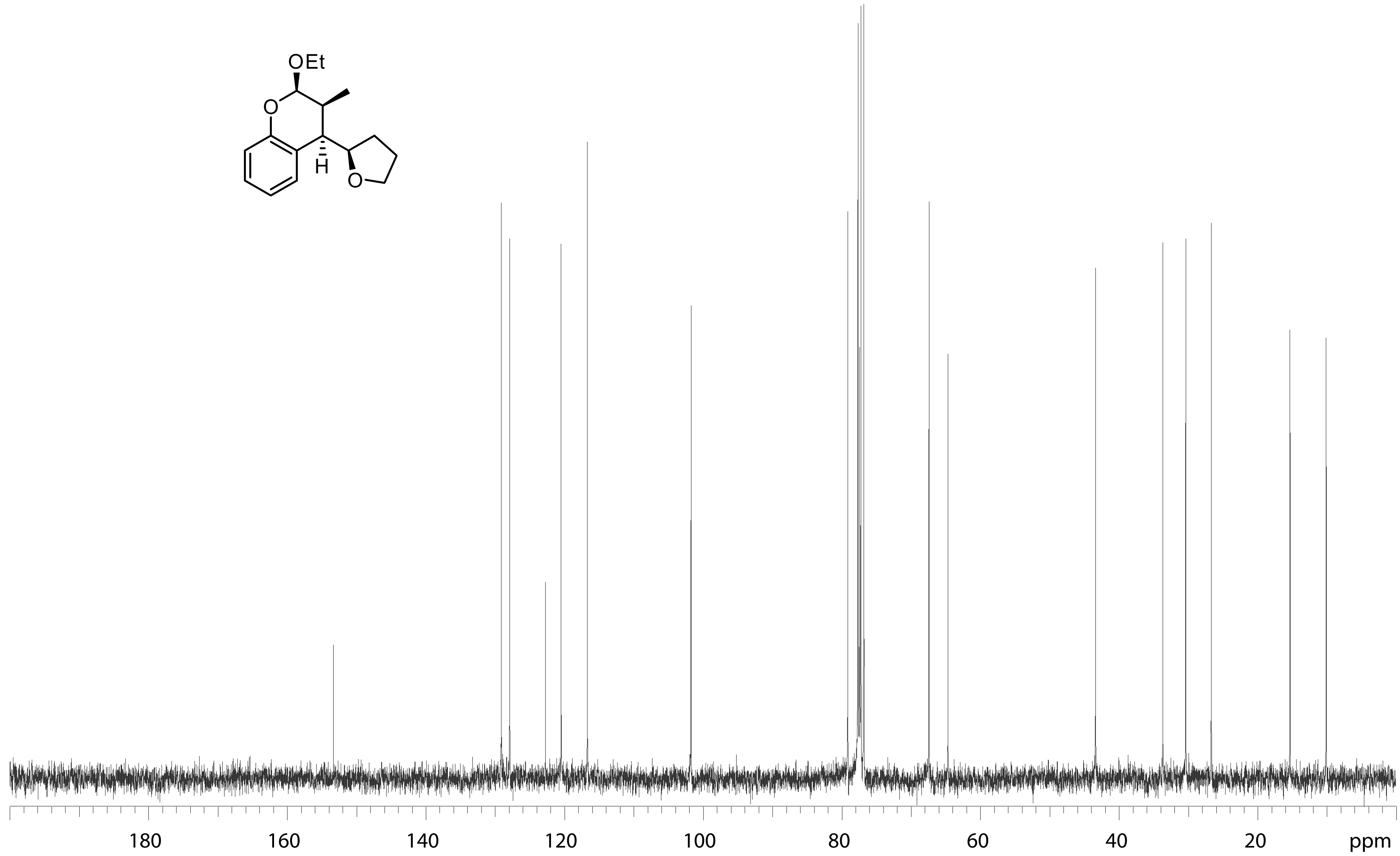
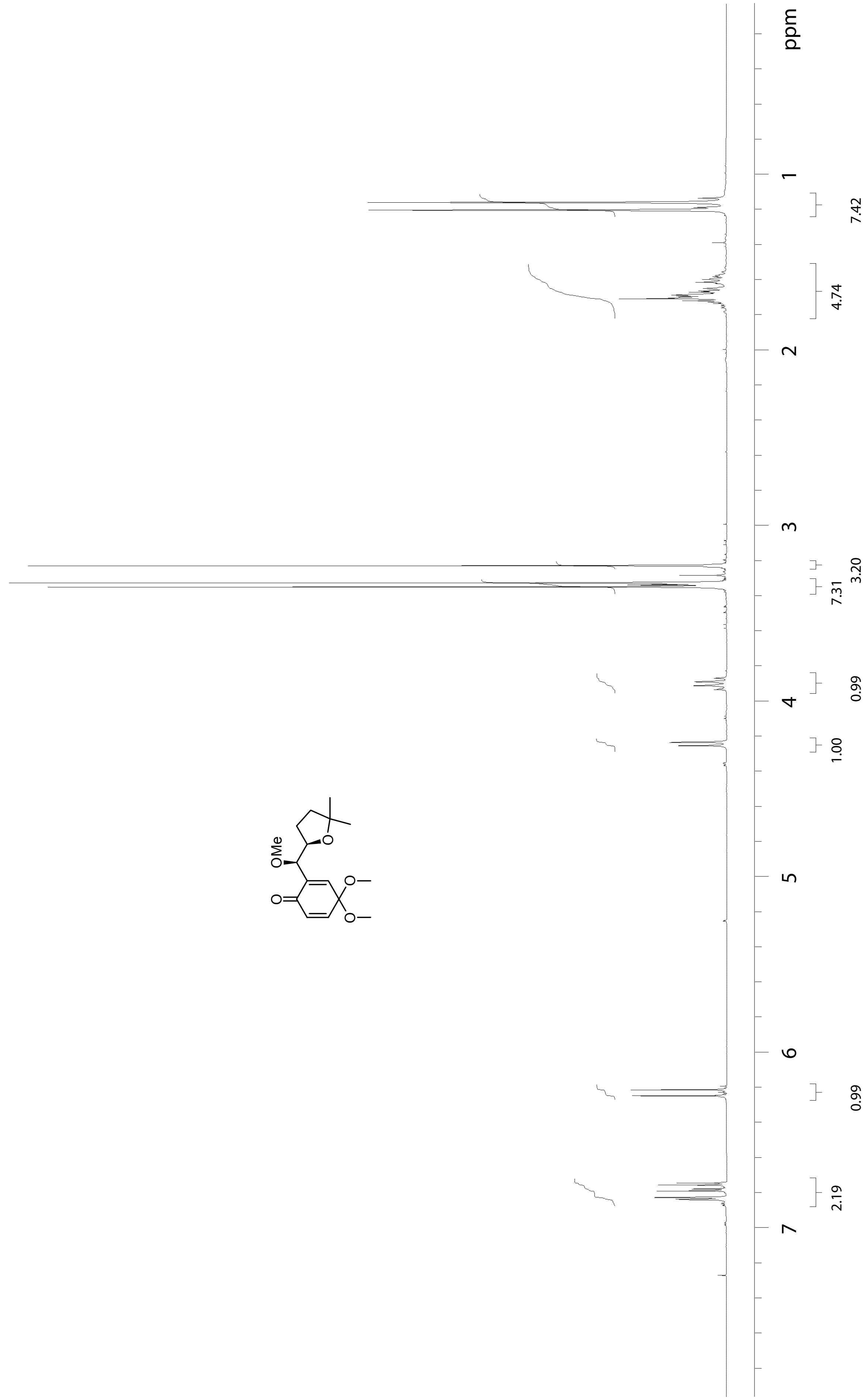
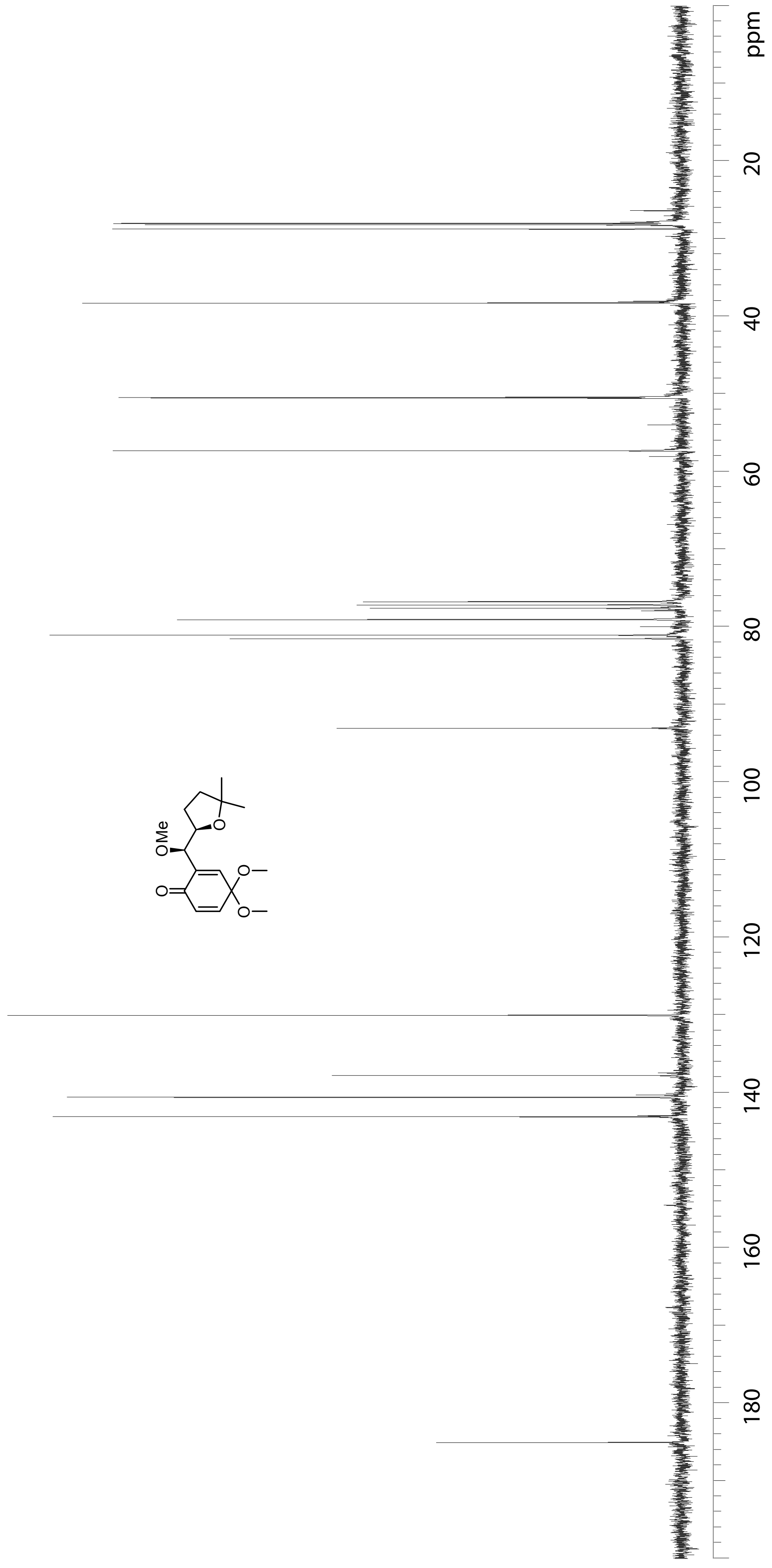
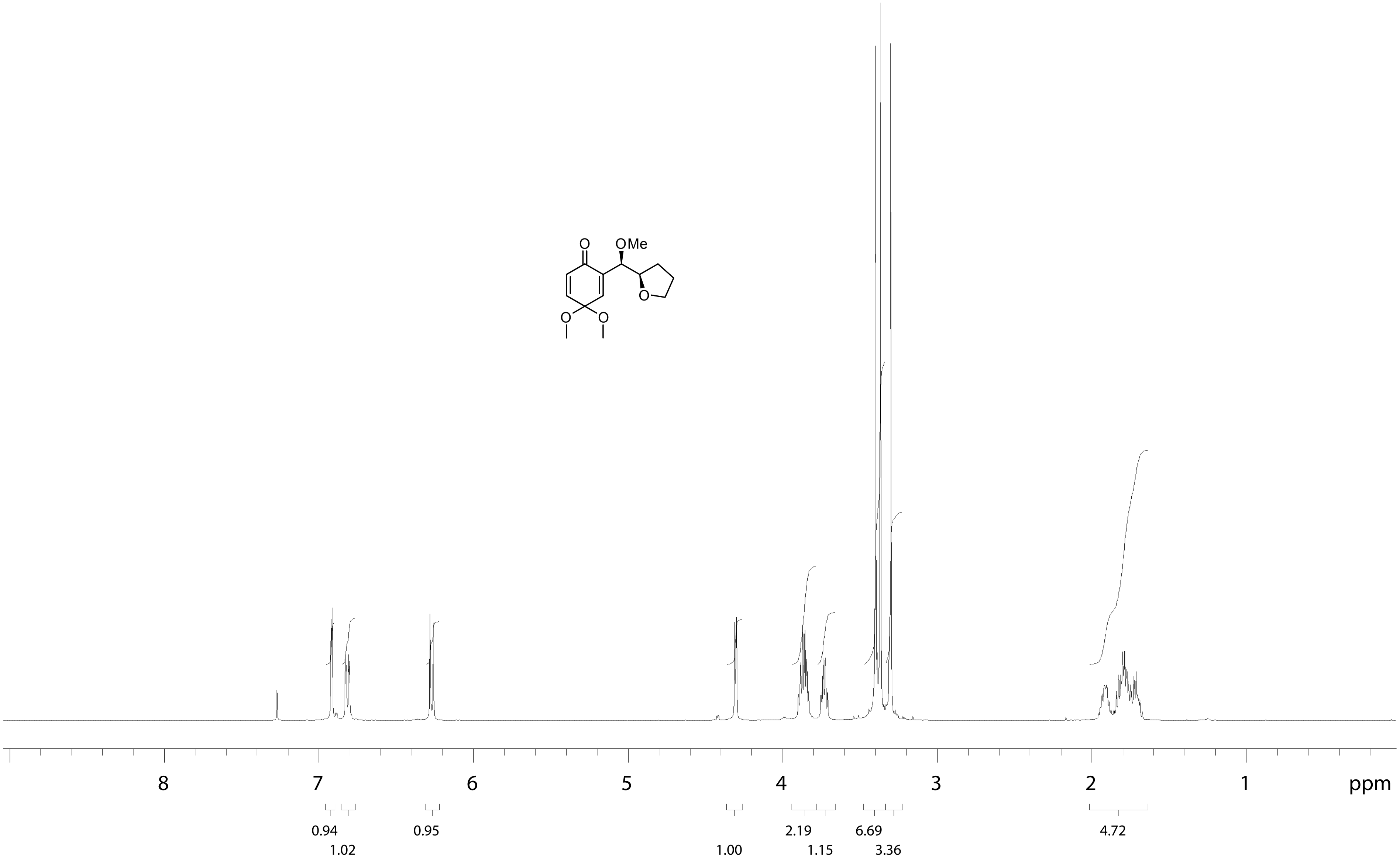
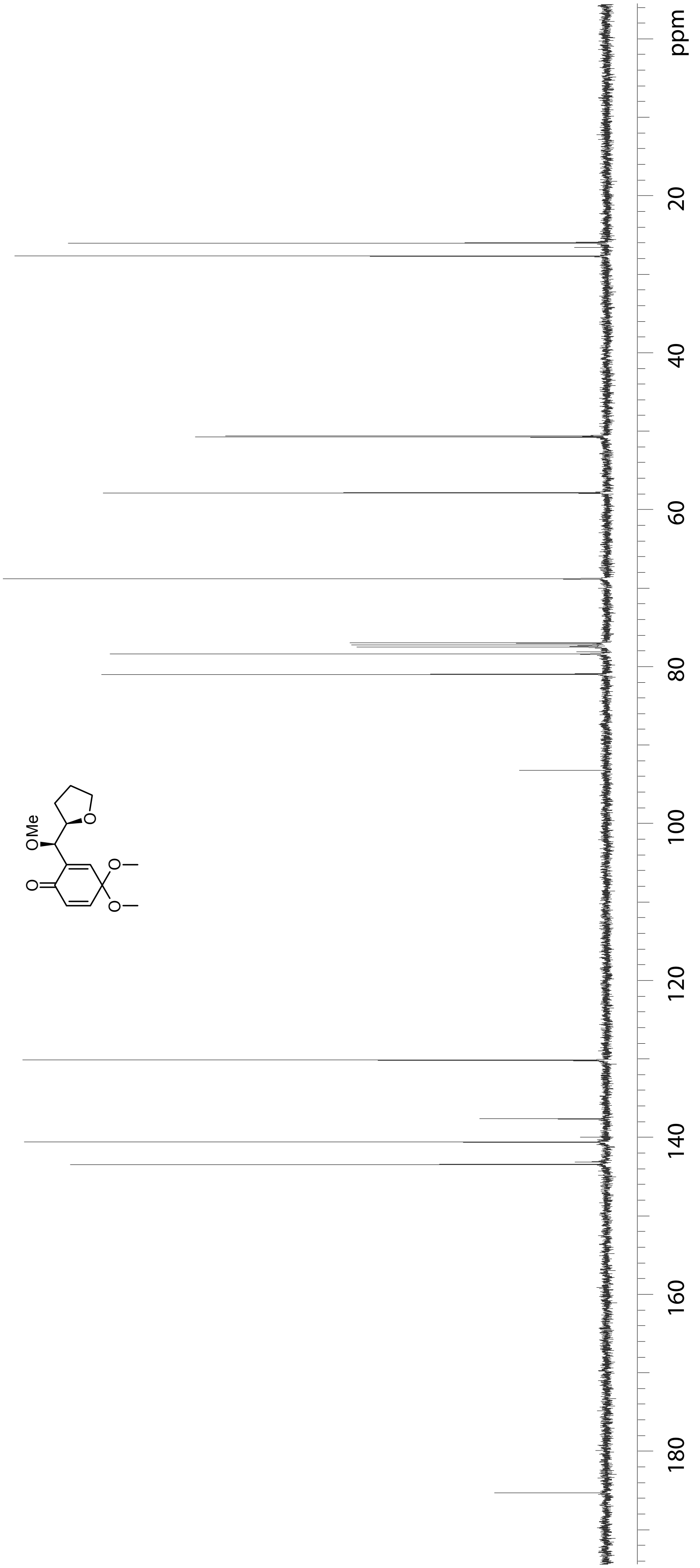

OEt
O
H
O
7
6
5
4
3
2
1
ppm
1.12
1.07
1.92
1.00
1.02
1.16
0.95
2.12
1.02
1.03
1.07
2.15
1.19
3.24
3.09


OEt
O
H
O
180
160
140
120
100
80
60
40
20
ppm


ppm
1
2
3
4
5
6
7
7.42
4.74
3.20
7.31
0.99
1.00
0.99
2.19
OMe
O
O
O
O

ppm
20
40
60
80
100
120
140
160
180
OMe
O
O
O
O


O
OMe
O
O
O
8
7
6
5
4
3
2
1
ppm
0.94
1.02
0.95
1.00
2.19
1.15
6.69
3.36
4.72


ppm
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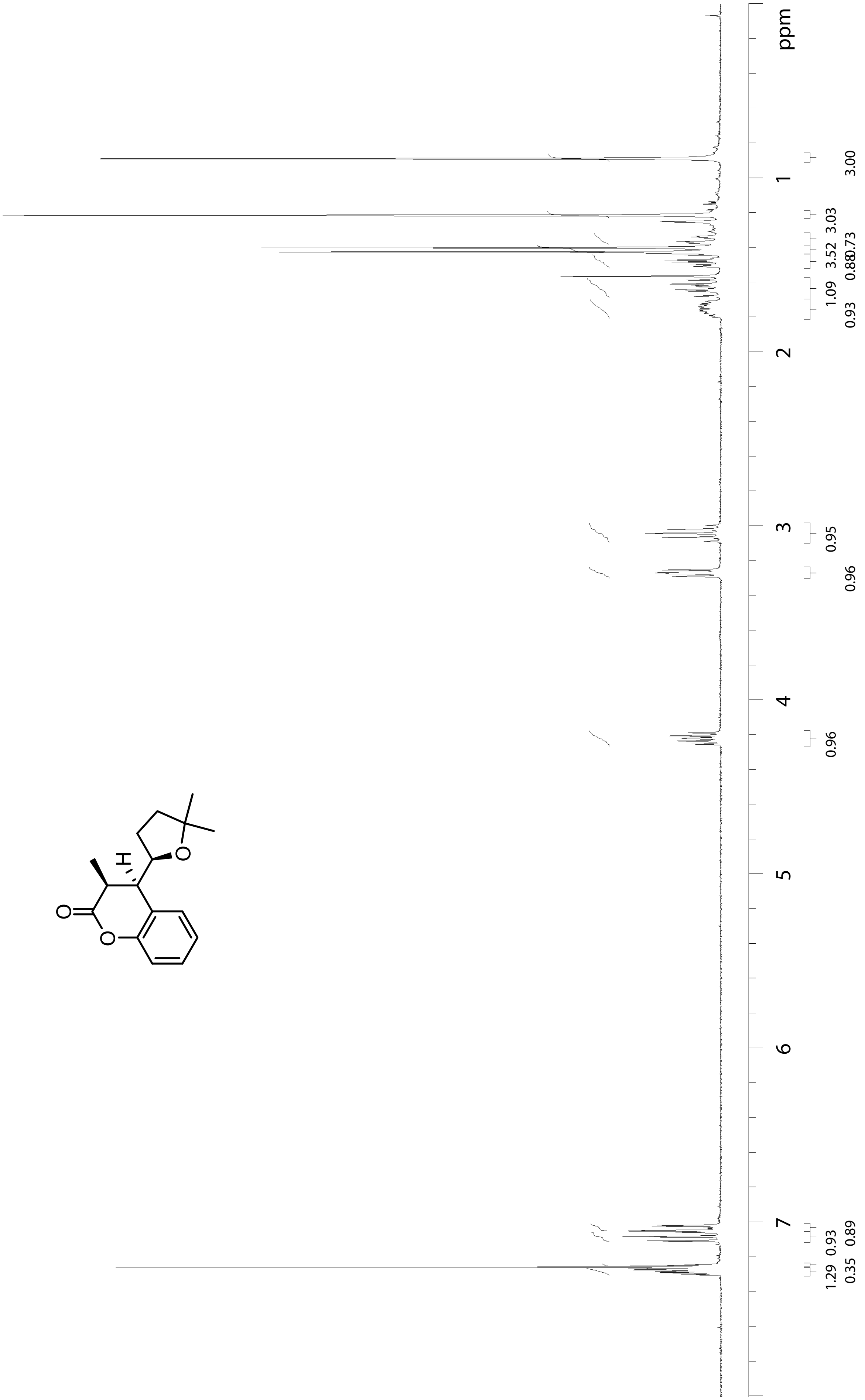
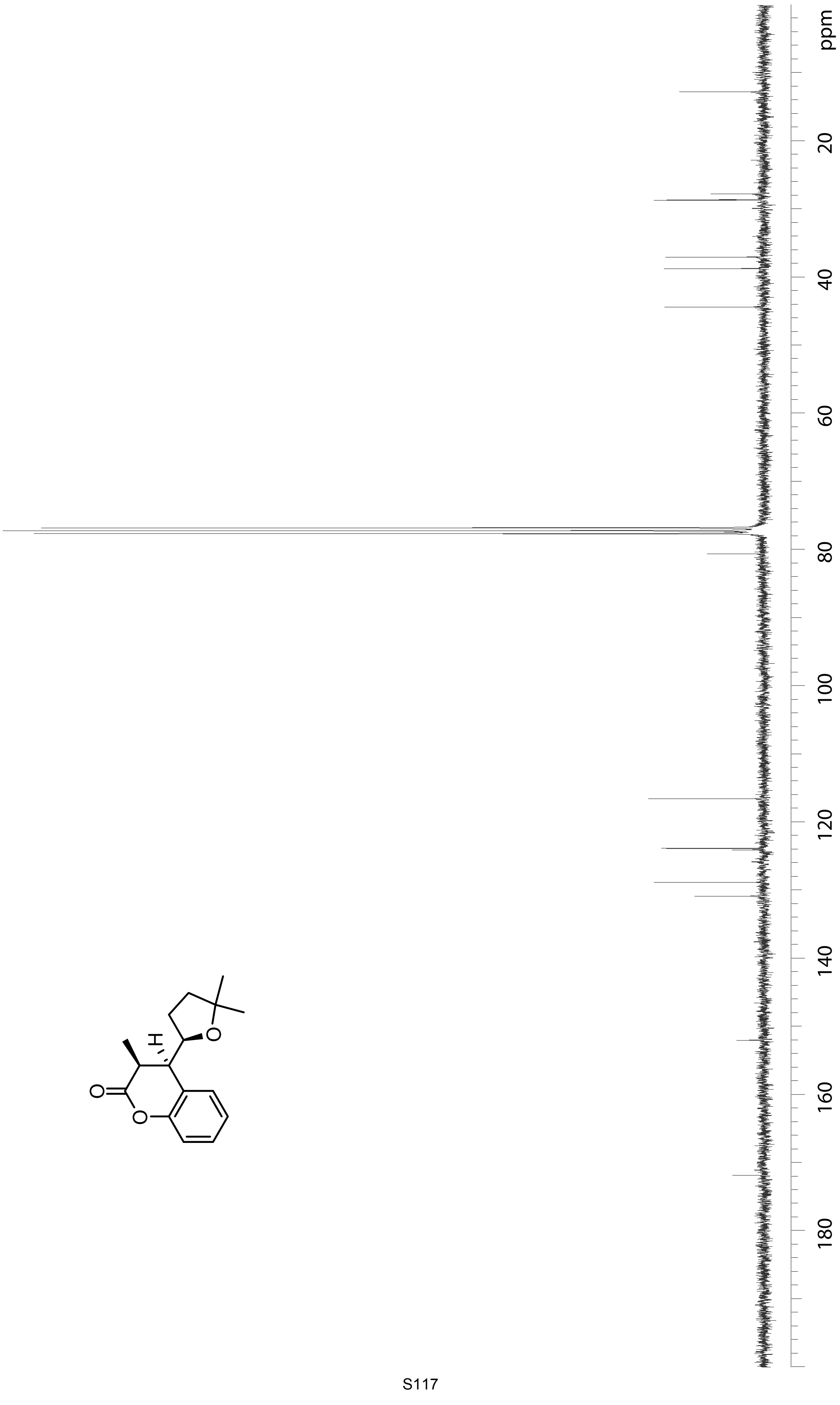
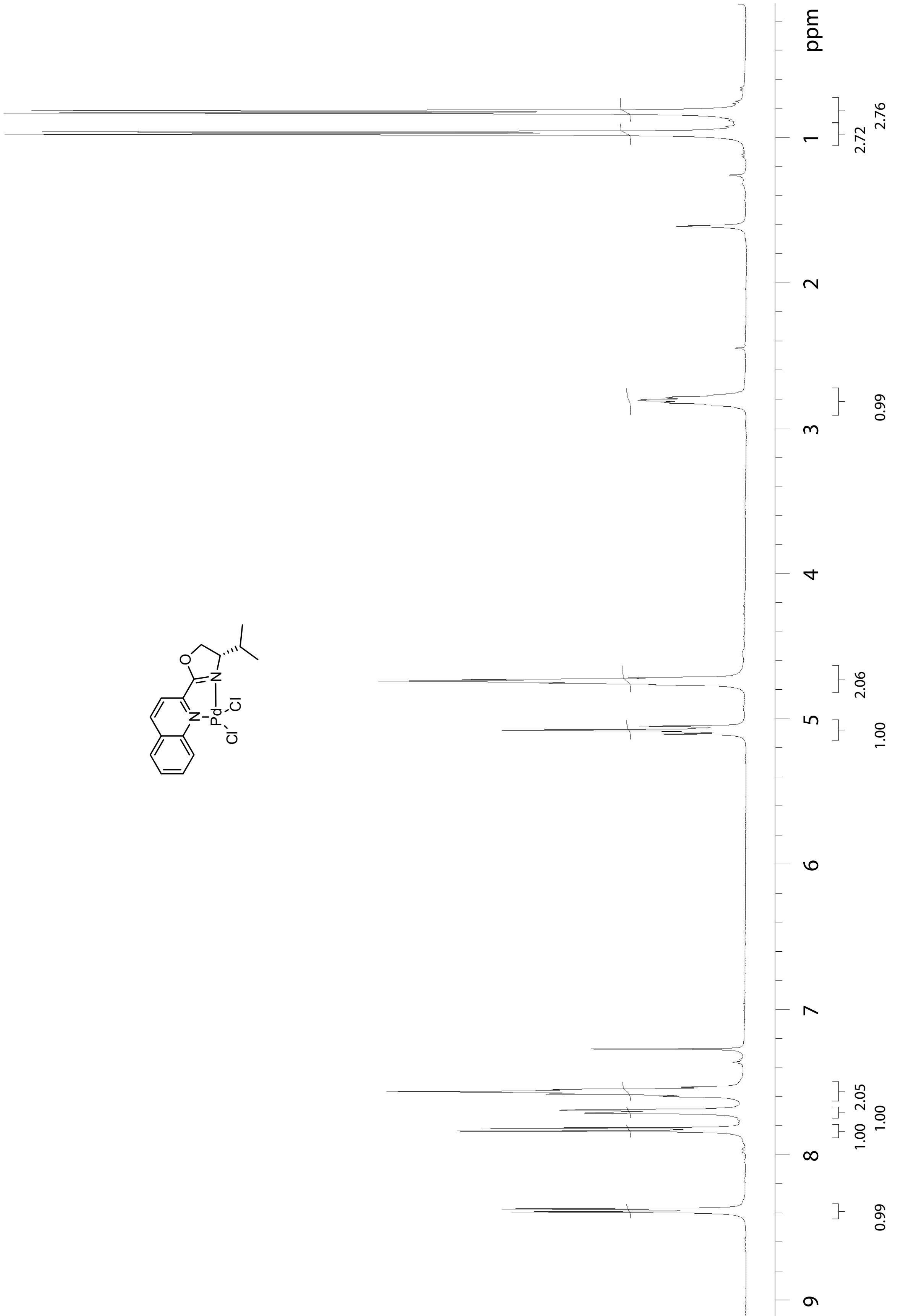
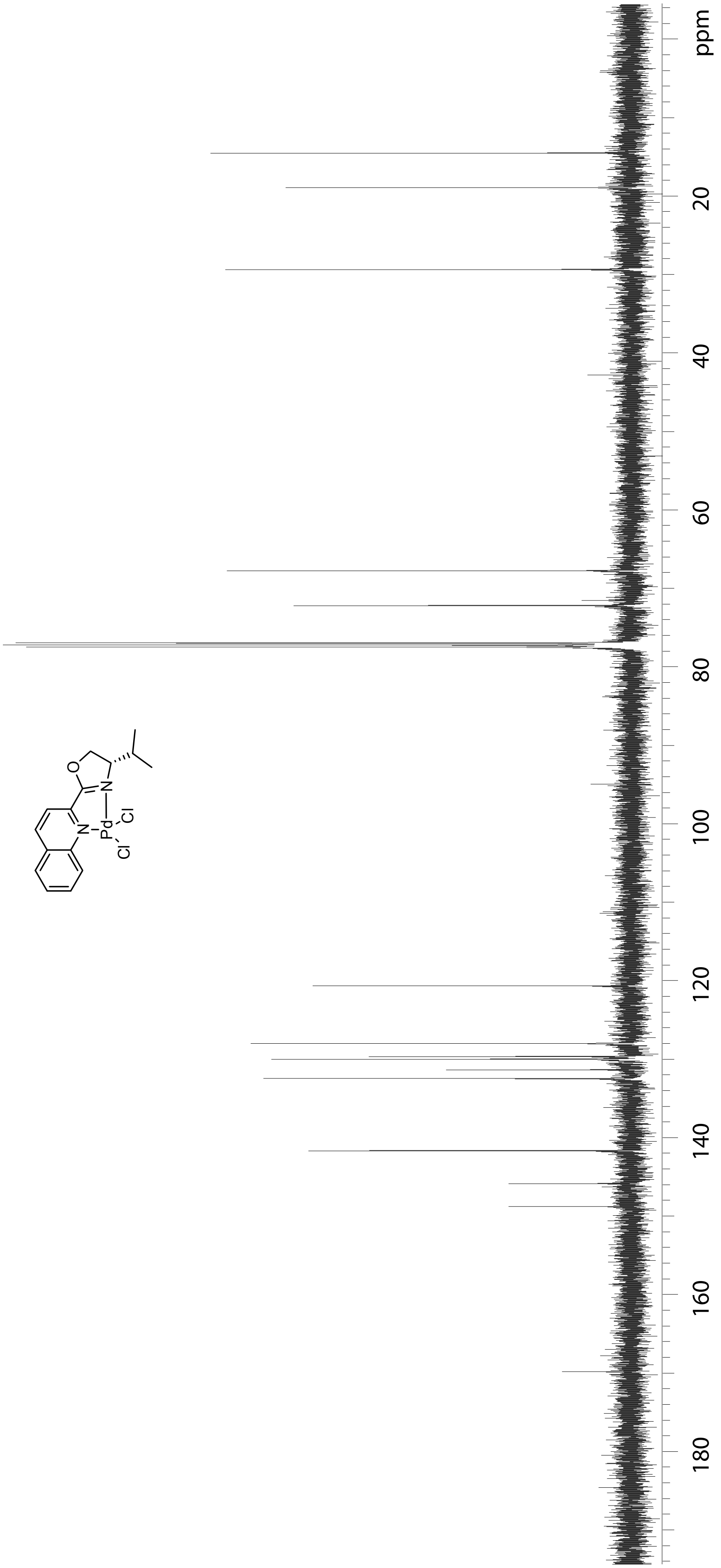
40
60
80
100
120
140
160
180
OMe
O
O
O
O


ppm
1
2
3
4
5
6
7
3.00
3.03
3.52
0.80
0.73
1.09
0.93
0.95
0.96
0.96
0.93
0.89
1.29
0.35
O
O
O
H


ppm
20
40
60
80
100
120
140
160
180
O
O
O
H


ppm
1
2
3
4
5
6
7
8
9
2.76
2.72
0.99
2.06
1.00
2.05
1.00
1.00
0.99
1.01
O
N
N
Pd
Cl
Cl


O
N
N
Pd
Cl
Cl
ppm
20
40
60
80
100
120
140
160
180