Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary information

Diastereoselective Synthesis of 2,5-Disubstituted-3-Hydroxy-Tetrahydrofurans Through Counterion-Directed Tsuji-Trost Reaction

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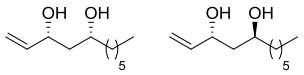
1. Materials and Methods

All reactions were conducted in flame-dried glassware under an argon atmosphere with dry solvents, unless otherwise noted. All reagents and starting materials were purchased from commercial sources and used as supplied, unless otherwise indicated. Anhydrous tetrahydrofuran (THF) is obtained through distillation over sodium/benzophenone under argon, dichloromethane (CH_2Cl_2) is obtained through distillation over CaH_2 under argon, and toluene (PhMe) were dried over 4 Å molecular sieves and degazed under argon.

Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. Flash column chromatography was performed on Silica Gel 60Å. Thin layer chromatography (TLC) analyses were performed on EMD TLC Silica gel 60 F254 Glass Plates and the spots were visualized by UV-light (254 nm) or appropriate stains, including vanillin, phosphomolybdic acid or potassium permanganate. ^{1}H NMR data were recorded on Bruker Avance 400 MHz and 300 MHz spectrometers (BBFO probe) with calibration of spectra to tetramethylsilane (0.00 ppm). ^{13}C NMR data were recorded at 100 MHz with calibration to the central line of CDCl3 (77.16 ppm). Two-dimensional NMR spectra, including COSY and NOESY were recorded on a Bruker Avance 400 MHz spectrometer (BBFO probe). Infrared spectra (IR) were recorded on a Perkin-Elmer FT-IR system equipped with a Dura SamplIR II diamond window, and the data are reported in reciprocal centimeters (ν, cm^{-1}). HRMS (ESI-TOF) analyses were performed at the mass spectrometry laboratory of UMR 8638 at the Faculty of Pharmacy. All compounds purified by chromatography were sufficiently pure for use in further experiments, unless indicated otherwise.

2. Experimental procedures

Undec-1-ene-3,5-diol (6-*syn* and 6-*anti*)

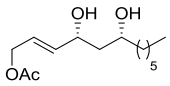


A solution of *n*Buli (1.7 mL, 2.5 M/hexane) was added to a suspension of trimethylsulfonium iodide (876.7 mg, 4.296 mmol) in THF (9 mL) cooled at –10 °C under an argon atmosphere. The resulting solution was stirred for 15 min before addition at room temperature of the epoxide **5** (205 mg, 1.161 mmol) dissolved in THF (2.5 mL) under an argon atmosphere. The reaction medium was stirred overnight before quenching with H_2O. After extraction by Et_2O, the combined organic phases were dried over Na_2SO_4. The crude product was purified by preparative HPLC (Heptane/EtOAc 2/1) to afford **6-*syn*** (78 mg, 36%) and of **6-*anti*** (95.6 mg, 44%) as colorless oils.
All spectral data are in agreement with those of the literature.[1]

6-*syn*: IR (neat) *v*: 3336, 2925, 2855, 1457, 1070, 989, 921 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ= 5.89 (ddd, *J* = 6.1, 10.3, 17.1 Hz, 1H), 5.26 (td, *J* = 1.6, 17.1 Hz, 1H), 5.11 (td, *J* = 1.6, 10.5 Hz, 1H), 4.38 (ddd, *J* = 3.0, 6.0, 9.6 Hz, 1H), 3.89 (ddd, *J* = 4.3, 7.1, 9.1 Hz, 1H), 2.76 (br, 2H), 1.54-1.69 (m, 3H), 1.33-1.50 (m, 3H), 1.28 (bs, 8H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 14.2, 22.7, 25.5, 29.4, 29.7, 31.9, 38.2, 42.9, 72.5, 73.7, 114.4, 140.8. HRMS (ESI) calcd for $C_{12}H_{24}O_2Na$: 223.1674, found 223.1674.

6-*anti*: IR (neat) *v*: 3338, 2925, 2855, 1457, 1427, 1068, 990, 921cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ= 5.94 (ddd, *J* = 5.1, 10.2, 17.2 Hz, 1H), 5.3 (qd, *J* = 1.7, 17.2 Hz, 1H), 5.15 (td, *J* = 1.8, 10.3 Hz, 1H), 4.48 (td, *J* = 5.0, 6.8 Hz, 1H), 3.93 (tdd, *J* = 3.8, 7.5, 8.8 Hz, 1H), 2.35 (bs, 2H), 1.71 (m, 2H), 1.37-1.58 (m, 4H), 1.28 (bs, 8H), 0.88 (t, *J*= 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 14.2, 22.8, 25.8, 29.4, 29.7, 31.2, 37.7, 42.3, 69.3, 70.6, 114.3, 140.9. HRMS (ESI) calcd for $C_{12}H_{24}O_2Na$: 223.1674, found 223.1679.

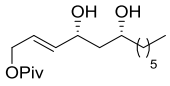
(*E*)-5,7-(*syn*)-dihydroxydodec-2-enyl acetate (7b)



(Procedure A) 1,4-diacetoxy-cis-2-butene (340 µL, 1.915 mmol) was added to dec-1-ene-3,5-(*syn*)-diol (71.4 mg, 0.383 mmol) and the Grubbs' catalyst 2nd generation (8.1 mg, 2.5% mol) under argon and the resulting mixture was stirred at 40 °C for 1h. The crude product was purified by column chromatography (Cyclohexane/EtOAc) to afford 87 mg (88%) of **7b** as yellowish oil.

IR (neat) *v*: 3362, 2928, 2857, 1740, 1440, 1379, 1364, 1227, 1136, 1025, 968 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ= 5.8 (q, *J*= 2.6 Hz, 2H), 4.56 (d, *J* = 4.4 Hz, 2H), 3.87 (s, 1H), 3.48 (s, 1H), 3.00 (s, 1H), 2.07 (s, 3H), 1.46 (m, 12H), 0.88 (t, *J*= 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 171.0, 136.9, 124.2, 72.7, 64.4, 43.0, 38.3, 31.9, 29.4, 25.4, 22.7, 21.1, 14.2. LRMS (ESI) m/z = 281 [$(M+Na)^+$] HRMS (ESI) calcd for $C_{14}H_{26}O_4Na$: 281.1729, found 281.1736.

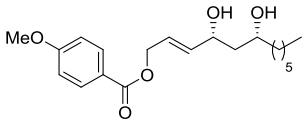
(E)-5,7-(*syn*)-dihydroxydodec-2-enyl pivalate (7a)



Procedure A using (Z)-but-2-ene-1,4-diyl-bis-(2,2-pivalate).[2] The crude product was purified by preparative HPLC (Heptane/EtOAc 2/1) to afford 73.9 mg (73%) of **7a** as yellowish oil.

IR (neat) *v*: 3360, 2957, 2929, 2858, 1729, 1480, 1460, 1398, 1366, 1282, 1150, 1098, 1061, 1032, 967 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ= 5.79 (dd, *J* = 5.7, 3.8 Hz, 2H), 4.56 (d, *J* = 4.2 Hz, 2H), 4.41 (ddd, *J* = 3.3, 4.2, 9.4 Hz, 1H), 3.88 (s, 1H), 3.08 (s, 1H), 2.63 (s, 1H), 1.46 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 178.5, 136.2, 124.5, 72.7, 72.6, 64.2, 42.9, 38.9, 38.2, 31.9, 29.4, 27.3, 25.4, 22.7, 14.2. LRMS (ESI) m/z = 323 [(M+Na)+]. HRMS (ESI) calcd for $C_{17}H_{32}O_4Na$: 323.2198, found 323.2197.

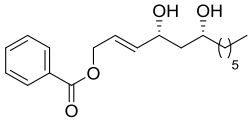
(*E*)-4,6-(*syn*)-dihydroxydodec-2-en-1-yl 4-methoxybenzoate (7c)



Procedure A using (Z)-but-2-ene-1,4-diyl bis(4-methoxybenzoate). The crude product was purified by preparative HPLC (Heptane/EtOAc 1/1) to afford 55.5 mg (67%) of **7c** as yellowish oil.

IR (neat) *v*: 3377, 2929, 2856, 1710, 1606, 1511, 1252, 1166, 1099 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ= 8.0 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 5.92, dt, *J*= 15.5, 4.8 Hz, 1H), 5.86, dt, *J*= 15.5, 4.8 Hz, 1H), 4.79 (d, *J*= 4.8 Hz, 2H), 4.43 (td, *J*= 5.1, 9.7 Hz, 1H), 3.87 (m, 1H), 3.86 (s, 3H), 3.30 (bs, 2H), 1.63 (m, 2H), 1.44 (m, 2H), 1.28 (m, 8H), 0.88 (t, *J*= 6.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 14.2, 22.7, 25.4, 29.4, 31.9, 38.3, 43.0, 55.5, 64.5, 72.7, 72.8, 113.7, 122.6, 124.6, 131.8, 136.6, 163.5, 166.2. HRMS (ESI) calcd for $C_{20}H_{30}O_5Na$: 373.1991, found 373.1992.

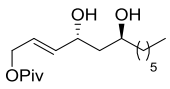
(*E*)-4,6-(*syn*)-dihydroxydodec-2-en-1-yl benzoate (7d)



Procedure A using (Z)-but-2-ene-1,4-diyl dibenzoate. The crude product was purified by preparative HPLC (Heptane/EtOAc 1/1) to afford 50.8 mg (70%) of **7d** as yellowish oil.

IR (neat) *v*: 3349, 2928, 2856, 1718, 1451, 1268, 1110, 1098, 709 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ= 8.05 (d, *J* = 7.9 Hz, 2H), 7.56 (dd, *J* = 6.7, 7.7 Hz, 1H), 7.43 (dd, *J* = 7.3, 8.1 Hz, 2H), 5.89 (m, 2H), 4.82 (d, *J* = 4.8 Hz, 2H), 4.43 (ddd, *J* = 2.9, 4.8, 9.6 Hz, 1H), 3.87 (td, *J* = 6.1, 9.4 Hz, 1H), 3.65 (bs, 1H), 3.25 (bs, 1H), 1.63 (m, 2H), 1.44 (m, 2H), 1.27 (m, 8H), 0.87 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 14.2, 22.7, 25.4, 29.4, 31.9, 38.3, 42.9, 64.8, 72.7, 72.8, 124.2, 128.5, 129.7, 130.2, 133.1, 136.9, 166.5. HRMS (ESI) calcd for $C_{19}H_{28}O_4Na$: 343.1877, found 343.1885.

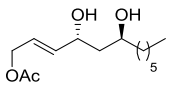
(*E*)-5,7-(*anti*)-dihydroxydodec-2-enyl pivalate (8a)



Procedure A using (Z)-but-2-ene-1,4-diyl-bis-(2,2-pivalate). The crude product was purified by preparative HPLC (Heptane/EtOAc 2/1) to afford 91 mg (69%) of **8a** as yellowish oil.

IR (neat) *v*: 3359, 2957, 2930, 2873, 2858, 1729, 1712, 1282, 1150 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ= 5.83 (m, 2H), 4.58 (d, *J*= 3.2 Hz, 2H), 4.51 (m, 1H), 3.92 (tt, *J*= 4.3, 7.61 Hz, 1H), 1.70 (m, 2H), 1.46 (m, 2H), 1.29 (m, 8H), 1.21 (s, 9H), 0.88 (t, *J*= 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 14.2, 22.7, 25.7, 27.3, 29.4, 31.9, 37.6, 38.9, 42.4, 64.3, 69.2, 69.4, 124.4, 136.4, 178.5. HRMS (ESI) calcd for $C_{17}H_{32}O_4Na$: 323.2198, found 323.2204.

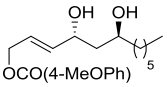
(*E*)-5,7-(*anti*)-dihydroxydodec-2-enyl acetate (8b)



Procedure A. The crude product was purified by column chromatography eluting with Cyclohexane/EtOAc 1/1 to afford (51.8 mg, 69%) of **8b** as yellowish oil.

IR (neat) *v*: 3380, 2928, 2857, 1740, 1457, 1379, 1364, 1229, 1125, 1026, 968 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ= 5.85 (quint d, *J* = 1.7, 2.8 Hz, 2H), 4.59 (d, *J* = 3.3 Hz, 2H), 4.50 (s, 1H), 3.92 (s, 1H), 2.68 (s, 1H), 2.16, (s, 1H), 2.08(s, 3H), 1.7 (td, *J* = 3.8, 7.1 Hz, 2H), 1.30 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 171.0, 137.1, 124.0, 69.4, 69.2, 64.5, 42.2, 37.6, 31.8, 29.3, 25.6, 22.6, 21.1, 14.1. LRMS (ESI) m/z = 281 [$(M+Na)^+$]. HRMS (ESI) calcd for $C_{14}H_{26}O_4Na$: 281.1729, found 281.1717.

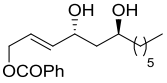
(*E*)-4,6-(*anti*)-dihydroxydodec-2-en-1-yl 4-methoxybenzoate (8c)



Procedure A using (Z)-but-2-ene-1,4-diyl bis(4-methoxybenzoate). The crude product was purified by preparative HPLC (Heptane/EtOAc 1/1) to afford 93 mg (62%) of **8c** as yellowish oil.

IR (neat) *v*: 3375, 2929, 2856, 1709, 1606, 1511, 1253, 1167 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ= 8.01 (d, *J*= 8.8 Hz, 2H), 6.92 (d, *J*= 8.8 Hz, 2H), 5.94 (m, 2H), 4.81 (d, *J*= 4.8 Hz, 2H), 4.53 (ddd, *J* = 3.7, 4.7, 6.5 Hz, 1H), 3.94 (tt, *J*= 4.9, 7.1 Hz, 1H), 3.87 (s, 3H), 2.08 (bs, 2H), 1.72 (m, 2H), 1.43 (m, 3H), 1.28 (m, 7H), 0.88 (t, *J*= 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 14.2, 22.7, 25.7, 29.4, 31.9, 37.6, 42.3, 55.5, 64.6, 69.2, 69.5, 113.7, 122.5, 124.3, 131.7, 136.9, 163.5, 166.3. HRMS (ESI) calcd for $C_{20}H_{30}O_5Na$: 373.1991, found 373.2002.

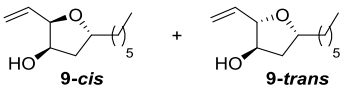
(*E*)-4,6-(*anti*)-dihydroxydodec-2-en-1-yl benzoate (8d)



Procedure A using (Z)-but-2-ene-1,4-diyl dibenzoate. The crude product was purified by preparative HPLC (Heptane/EtOAc 2/1) to afford 108 mg (76%) of **8d** as yellowish oil.

IR (neat) *v*: 3377, 2928, 2856, 1718, 1451, 1268, 1111, 1097, 709 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ= 8.06 (d, *J*= 7.6 Hz, 2H), 7.57 (dd, *J*= 7.2, 7.9 Hz, 1H), 7.45 (t, *J*= 7.6 H, 1H), 5.96 (m, 2H), 4.85 (d, *J*= 4.4 Hz, 2H), 4.54 (q, *J*= 4.3 Hz, 1H), 3.94 (tt, *J*= 4.7, 7.7 Hz, 1H), 1.98 (bs, 2H), 1.72 (m, 2H), 1.47 (m, 3H), 1.28 (m, 7H), 0.88 (t, *J*= 6.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 14.16, 22.7, 25.7, 29.4, 31.9, 37.6, 42.3, 64.9, 69.2, 69.5, 124.1, 128.5, 129.7, 130.2, 133.1, 137.2, 166.5. HRMS (ESI) calcd for $C_{19}H_{28}O_4Na$: 343.1885, found 343.1895.

5-hexyl-2-vinyltetrahydrofuran-3-ol (9-*cis* and 9-*trans*)

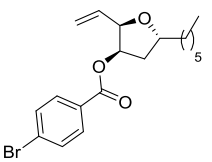


$P(4\text{-MeOPh})_3$ (8% mol) and $Pd_2(dba)_3$ (2% mol) were dissolved in THF (*c* 0.1M) and added to allyl acetate **7b** (87 mg, 0.374 mmol) under argon. The solution was stirred at 40 °C until total consumption of the starting material (1h) and then directly filtered over a silica pad, eluting with EtOAc and then purified by HPLC (19 mL/min, eluting with Hexane/EtOAc 3/2) to afford of **9-*cis* (**48.2 mg, 72%) and **9-*trans*** (10.2 mg, 15%) as colorless oils. (*dr*: 83 /17 determined by ^1H NMR experiment on the crude).

9-*cis*: IR (neat) *v*: 3403, 2927, 2857, 1459, 1405, 1378, 1271, 1193, 1039, 991, 925 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ= 5.91 (ddd, *J* = 5.63, 10.58, 17.35 Hz, 1H), 5.46 (td, *J* = 1.72, 17.37 Hz, 1H), 5.36 (td, *J* = 1.7, 10.64 Hz, 1H), 4.44 (m, 1H), 4.28 (m, 2H), 2.15 (dd, *J* = 5.8, 13.1 Hz, 1H), 1.72 (ddd, *J* = 4.9, 9.4, 12.8 Hz, 1H), 1.64 (d, *J* = 4.4 Hz, 2H), 1.37 (m, 9H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 134.1, 118.5, 83.0, 78.2, 741, 44.4, 36.3, 32.0, 29.5, 26.1, 22.8, 14.2. LRMS (ESI) m/z = 221.15 [$(M+Na)^+$]. HRMS (ESI) calcd for $C_{12}H_{22}O_2Na$: 221.1517, found: 221.1511.

9-*trans*: IR (neat) *v*: 3388, 2956, 2927, 2858, 1458, 1098, 1036, 922 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ= 5.84 (ddd, *J* = 6.2, 10.4, 17.2 Hz, 1H), 5.35 (td, *J* = 1.6, 17.1 Hz, 1H), 5.16 (td, *J* = 1.6, 10.5 Hz, 1H), 4.15 (m, 3H), 1.93 (m, *J*= 5.7, 2.3 Hz, 2H), 1.72 (m, *J*= 9.6, 6.2 Hz, 2H), 1.47 (m, 2H), 1.29 (m, 6H), 0.88 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 14.2, 22.7, 26.2, 29.5, 31.9, 36.0, 40.4, 77.0, 78.7, 87.5, 116.6, 137.3. HRMS (ESI) calcd for $C_{12}H_{22}O_2Na$: 221.1517, found 221.1521.

5-hexyl-2-vinyltetrahydrofuran-3-yl 4-bromobenzoate (9-*cis*-ester):

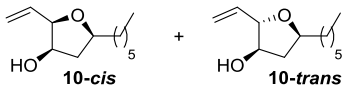


To a solution of **9-*cis*** (24.0 mg, 0.121 mmol) in CH_2Cl_2 (1.2 mL) was added NEt_3 (34 mL, 0.242 mmol), 4-DMAP (2.0 mg, 0.012 mmol), and 4-bromobenzoylchloride (40 mg, 0.1815 mmol). After 20h of stirring at RT, the reaction medium was

evaporated to dryness over silica gel and the resulting powder was put on the top of a silica gel column (Hexane/EtOAc 8/1). Purification gave ester **9-*cis*-ester** (45.5 mg, 99%) as colorless oils.

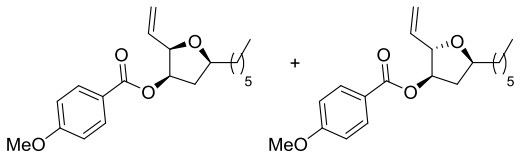
9-*cis*: IR (neat) *v*: 2955, 2927, 2857, 1719, 1591, 1266, 1101, 1012, 754 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ= 7.88 (d, *J*= 8.4 Hz, 1H), 7.58 (d, *J*= 8.4 Hz, 1H), 5.88 (ddd, *J*= 6.6, 10.4, 17.2 Hz, 1H), 5.60 (td, *J*= 4.4, 1.5 Hz, 1H), 5.38 (td, *J*=1.6, 17.2 Hz, 1H), 5.19 (dd, *J*=1.7, 10.4 Hz, 1H), 4.6 (ddd, *J*= 4.2, 5.5, 0.9 Hz, 1H), 4.31 (dtd, *J*= 9.6, 6.5, 5.4 Hz, 1H), 2.27 (ddd, *J*= 1.5, 5.8, 13.7 Hz, 1H), 1.96 (ddd, *J*= 5.2, 9.6, 13.9 Hz, 1H), 1.68 (m, 1H), 1.39-1.56 (m, 2H), 1.23-1.37 (m, 8H), 0.88 (t, *J*= 6.5 Hz, 1H).^{13}C NMR ($CDCl_3$, 100 MHz) δ= 14.2, 22.7, 26.1, 29.5, 31.9, 36.1, 39.3, 78.4, 81.9, 118.3, 128.4, 129.1, 131.3, 131.9, 133.3, 165.2. HRMS (ESI) calcd for $C_{19}H_{25}O_3NaBr$: 403.0885, found: 403.0897.

5-hexyl-2-vinyltetrahydrofuran-3-ol (10-*cis* and 10-*trans*):



From *anti*-diol **8b** using the same procedure as for the synthesis of **9**. Purification by preparative HPLC afford the mixture of diastereoisomers **10-*cis*** and **10-*trans*** as a colourless oil (31.9 mg, 84%), 86/14 *dr* determined by ^1H NMR experiment. These products being inseparable even by HPLC they were transformed into 4-methoxy-benzoyl esters **11** that were separated.

5-hexyl-2-vinyltetrahydrofuran-3-yl 4-methoxybenzoate (10-*trans* ester and 10-*cis* ester):

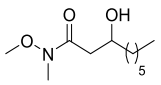


Et_3N (30.4 µL, 0.217 mmol) followed by DMAP (1 mg, 6% mol) and *para*-methoxybenzyl chloride (27.3 mg, 0.159 mmol) dissolved in dry DCM was added to the THF **10** (28.8 mg, 0.145 mmol) dissolved in dry DCM. The resulting solution was heated to reflux for 1 day before quenching with water acidified by HCl 1M. The aqueous phase was extracted with Et_2O, the combined organic phases were dried over Na_2SO_4. The crude product was purified by HPLC (heptane/EtOAc 8/1) to afford 4 mg (8%) of the minor diastereoisomer **10-*trans* ester** and 36.3 mg (76%) of the major diastereoisomer **11-*cis* ester** as colorless oils.

10-*cis* ester: IR (neat) *v*: 2929, 2857, 1709, 1606, 1582, 1511, 1459, 1421, 1357, 1316, 1252, 1166, 1112, 1100, 1030, 990, 926 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ= 7.98 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 5.95 (ddd, *J* = 6.4, 10.5, 17.3 Hz, 1H), 5.51 (ddd, *J* = 3.2, 4.6, 6.8 Hz, 1H), 5.4 (dd, *J* = 1.8, 17.3 Hz, 1H), 5.22 (dd, *J* = 1.8, 10.5 Hz, 1H), 4.36 (dd, *J* = 4.5, 6.6 Hz, 1H), 3.96 (tt, *J* = 6.2, 7.2 Hz, 1H), 3.85 (s, 3H), 2.56 (td, *J* = 7.1, 13.8 Hz, 1H), 1.78 (ddd, *J* = 2.7, 6.7 Hz, 13.8, 2H), 1.60 (m, 1H), 1.45 (m, 1H), 1.30 (m, 7H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 165.7, 163.6, 133.2, 131.8, 122.7, 118.7, 113.7, 82.7, 78.1, 76.0, 55.6, 39.0, 36.2, 31.9, 29.5, 26.1, 22.7, 14.2. LRMS (ESI) m/z = 355 [$(M+Na)^+$]. HRMS (ESI) calcd for $C_{20}H_{29}O_4$: 333.2066, found 333.2079.

10-*trans* ester: IR (neat) *v*: 2954, 2927, 2856, 1710,1606, 1511, 1252, 1166, 1099, 1030 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ= 8.0 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 5.92 (ddd, *J* = 5.1, 10.5, 17.2 Hz, 1H), 5.38 (td, *J* = 1.7, 17.2 Hz, 1H), 5.26 (td, *J* = 3.4, 6.9 Hz, 1H), 5.21 (td, *J* = 1.8, 10.7 Hz, 1H), 4.61 (dd, *J* = 2.8, 5.3 Hz, 1H), 4.19 (m, *J* = 6.6 Hz, 1H), 3.87 (s, 3H), 2.51 (m, *J* = 6.8 Hz, 1H), 1.79 (br. m, 2H), 1.25-1.61 (br. m, 9H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 14.1, 22.6, 26.1, 29.3, 31.9, 36.4, 37.0, 55.5, 78.5, 78.8, 83.6, 113.7, 116.1, 122.4, 131.7, 135.9, 163.5, 166.0. HRMS (ESI) calcd for $C_{20}H_{28}O_4$: 355.1885, found 355.1881.

3-hydroxy-N-methoxy-N-methylnonanamide (12):

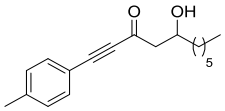


Triisobutylaluminum (1M / PhMe, 9.27 mL, 9.27 mmol) was added drop wise to a suspension of MeNHOMe•HCl (904 mg, 9.27 mmol) in THF (6 mL) at –10 °C under argon. After 1h of stirring at RT, the solution of β-hydroxyester **11** (852 mg, 4.213 mmol), in THF (6 mL) was introduced. One hour and a half later, the reaction medium was poured into a saturated

solution on sodium/potassium tartrate (25 mL) and vigorously stirred during 1 h. After extraction by CH_2Cl_2, drying over Na_2SO_4 and filtration, the crude was purified by MPLC (Cyclohexane/EtOAc : 1/1) and **12** was obtained as a colourless oil (789.4 mg, 86%).

IR (neat) *v*: 3453, 2926, 2856, 1642, 1463, 1420 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ= 4.02 (dddd, *J* = 2.3, 4.0, 7.52, 9.7 Hz, 1H), 3.69 (s, 3H), 3.20 (s, 3H), 2.67 (dd, *J* = 2.2, 17.0 Hz, 1H), 2.44 (dd, *J* = 8.9, 16.7 Hz, 1H), 12.6-1.58 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 14.2, 22.7, 25.6, 29.4, 29.8, 31.9, 36.7, 38.3, 61.3, 68.0, 174.0. HRMS (ESI) calcd for $C_{11}H_{23}NO_3Na$: 240.1576, found 240.1575.

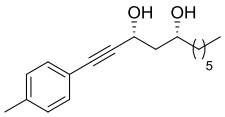
5-hydroxy-1-(*p*-tolyl)undec-1-yn-3-one (13):



To a THF solution (30 mL) of 1-ethynyl-4-methylbenzene (430 μL, 3.39 mmol) at 0 °C under argon was added nBuLi (2.12 mL, 3.39 mmol). After 30 min of stirring at 0 °C, the temperature was dropped down to –78 °C and then a THF solution (10 mL) of Weinreb amide **12** (245.6 mg, 1.13 mmol) was introduced. The temperature was allowed to slowing reach RT and then the reaction medium was poured into a saturated solution of NH_4Cl. After extraction by CH_2Cl_2, drying over Na_2SO_4, and filtration, the crude was purified by MPLC (Cyclohexane/EtOAC : 5/1) to give ketone **13** as a colorless oil (305.5 mg, 99%).

IR (neat) *v*: 3438, 2956, 2926, 2857, 2198, 1660, 1288, 1082, 815 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ= 7.47 (d, *J* = 8.04 Hz, 2H), 7.2 (d, *J* = 8.09 Hz, 2H), 4.18 (m, 1H), 2.89 (dd, *J*= 17.4, 3.5 Hz, 1H), 2.80 (dd, *J*= 17.4, 8.3 Hz, 1H), 2.71 (d, *J*= 2.3 Hz, 1H), 2.39 (s, 3H), 1.29-1.55 (m, 10 H), 0.89 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ= 14.0, 21.6, 22.5, 25.4, 29.1, 31.7, 36.5, 52.4, 67.6, 87.8, 92.2, 116.5, 129.3, 133.1, 141.6, 187.3. HRMS (ESI) calcd for $C_{18}H_{23}O_2$: 271.1698, found 271.1705.

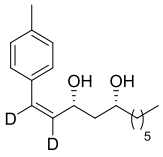
1-(*p*-tolyl)undec-1-yne-3,5-(*syn*)-diol (14):



A solution of DIBAL (1 m / PhMe, 1.747 mL, 1.747 mmol), was added to a THF solution (8 mL) of ketone 13 (190.7 mg, 0.699 mmol) at –78 °C under argon. after 45 min of strirring, the reaction medium was poured into a saturated solution on sodium/potassium tartrate (20 mL) and vigorously stirred during 1 h. after extraction by CH_2Cl_2, drying over Na_2SO_4 and filtration, the crude was purified by HPLC (heptane/EtOAc : 2/1) and **14** was obtained as a colorless oil (172.6 mg, *anti*/*syn* : 8/92, 90%).

IR (neat) *v*: 3267, 2934, 2854, 1509, 1338, 1023, 1013 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ= 7.32 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 4.85 (dd, *J* = 6.1, 7.0 Hz, 1H), 3.94 (tt, *J* = 5.3, 6.8 Hz, 1H), 2.34 (s, 3H), 1.95 (m, 2H), 1.25-1.95 (m, 8 H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 14.2, 21.6, 22.7, 25.4, 29.4, 31.9, 38.0, 44.3, 62.9, 71.8, 85.2, 89.0, 119.5, 129.1, 131.7, 138.7. HRMS (ESI) calcd for $C_{18}H_{26}NaO_2$: 297.1825, found 297.1825.

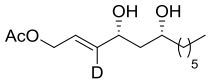
(*Z*)-1-(*p*-tolyl)undec-1-ene-1,2-D2-3,5-(*syn*)-diol (15):



To a solution of propargylic alcohol **14** (172.0 mg, 0.627 mmol), and freshly distilled quinoline (60 µl) in EtOAc was added Lindlar catalyst (45 mg) under argon. The reaction mixture was cooled down to 0 °C and was purged with D_2. After 5h of vigorous stirring at 0 °C, D_2 was removed using argon and the reaction mixture was filtered through 1 cm of silica gel using AcOEt. HPLC purification (heptane/EtOAc: 2/1) allow separating desired **15** (117.8 mg, 67%) as a pure *syn*-isomer.

IR (neat) *v*: 3341, 2926, 2856, 1510, 1456, 1059, 819 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ= 7.20 (d, *J*= 8.0 Hz, 2H), 7.16 (d, *J*= 8.0 Hz, 2H), 4.85 (dd, *J* = 4.2, 8.8 Hz, 1H), 3.89 (dddd, *J* = 3.4, 5.2, 7.0, 8.7 Hz, 1H), 2.80 (bs, 2H), 2.25 (s, 3H), 1.69-1.74 (m, 2H), 1.40-1.49 (m, 2H), 1.28 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 14.2, 21.3, 22.7, 25.4, 29.4, 31.9, 38.2, 43.2, 69.0, 72.5, 128.8, 129.1, 130.0 (t, *J*= 23.3 Hz), 133.0 (t, *J*= 23.3 Hz), 133.7, 137.2. HRMS (ESI) calcd for $C_{18}H_{26}D_2NaO_2$: 301.2107, found 301.2105.

(*E*)-4,6-(*syn*)-dihydroxydodec-2-en-1-yl-3-*d* acetate (7b*)



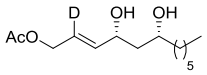
To a solution of alkene **14** (117.8 mg, 0.423 mmol) in (*Z*)-but-2-ene-1,4-diyl diacetate (340 μL, 2.12 mmol) under argon, was added a catalytic amount of Grubbs 'catalyst of second generation (9.0 mg, 0.011 mmol, 2.5 mol%). after 4 h of stirring at 40 °C, the reaction medium was introduced at the top of a silica-gel column and eluted (cyclohexane/EtOAc : 1/1) which gave **7b*** as a colorless oil (99.6 mg, 91%).

IR (neat) *v*: 3378, 2928, 2857, 1739, 1228, 1025 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ= 5.8 (t, *J*= 6.0 Hz, 1H), 4.57 (d, *J* = 6.0 Hz, 2H), 4.41 (dd, *J*= 3.0, 9.7 Hz, 2H), 3.88 (dddd, *J*= 2.4, 5.0, 6.8, 9.8 Hz, 1H), 2.08 (s, 3H), 1.67 (dt, *J*= 14.6, 2.7 Hz, 1H), 1.58 (m, 1H), 1.39-1.45 (m, 2H), 1.29 (m, 8H), 0.89 (t, *J*= 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 14.1, 21.0, 22.7, 25.3, 29.4, 31.9, 38.2, 42.8, 64.4, 72.5, 123.9, 136.6 (t, *J*= 23.6 Hz), 171.0. HRMS (ESI) calcd for $C_{14}H_{25}DNaO_4$: 282.1786, found 282.1786.

5-hexyl-2-vinyltetrahydrofuran-2-*d*-3-ol (9*-*trans* and 9*-*cis*)

From diol **7b*** (46.5 mg, 0.179 mmol) using the same procedure as for the synthesis of **9**. Purification by preparative HPLC afford the mixture of diastereoisomers **9*-*cis*** and **9*-*trans*** as a colorless oil (33.4 mg, 93.5 %), 83/17 *dr* determined by ^1H NMR experiment.

9*-*cis*: IR (neat) *v*: 3420, 2926, 2857, 1466, 1059, 920 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ= 5.91 (dd, *J*= 10.2, 17.4 Hz, 2H), 5.45 (dd, *J*= 1.9, 17.2 Hz, 1H), 5.35 (dd, *J*= 2.1, 10.7 Hz, 1H), 4.27 (m, 2H), 2.15 (dd, *J*= 5.8, 13.2 Hz, 1H), 1.72 (ddd + br, *J*= 12.8, 9.7, 4.5 Hz, 2H), 1.65 (m, 1H), 1.37-1.51 (m, 2H), 1.24-1.36 (m, 8H), 0.88 (t, *J*= 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 14.2, 22.7, 26.1, 29.5, 31.9, 36.3, 41.4, 74.0, 78.2, 82.6 (t, *J*= 22.1 Hz), 118.5, 134.0. HRMS (ESI) calcd for $C_{12}H_{21}DNaO_2$: 222.1575, found 222.1575.

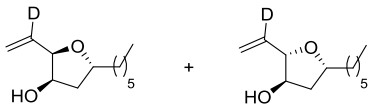


(4R,6R,E)-4,6-dihydroxydodec-2-en-1-yl-2-*d* acetate (7b$^\bullet$)

Procedure A using (*Z*)-but-2-ene-1,4-diyl-2,3-D_2 diacetate and **6-*syn***. The crude product was purified by column chromatography eluting with Heptane/EtOAc 1/1 to afford (91.4 mg, 84 %) of **7b$^\bullet$** as yellowish oil.

IR (neat) *v*: 3371, 2928, 2856, 1739, 1227 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ= 5.79 (m, *J*= 2.2 Hz, 1H), 4.56 (s, 2H), 4.41 (ddd, *J*= 2.9, 5.9, 9.8 Hz, 1H), 3.88 (dddd, *J*= 2.4, 5.1, 6.8, 9.8 Hz, 1H), 2.68 (bs, 2H), 2.07 (s, 3H), 1.67 (td, *J*= 2.8, 14.4 Hz, 1H), 1.58 (td, *J*= 9.8, 14.6 Hz, 1H), 1.25-1.52 (m, 10H), 0.89 (t, *J*= 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 14.2, 21.1, 22.7, 25.4, 29.4, 31.9, 38.4, 43.0, 64.3, 72.8, 124.0 (t, *J*= 23.9 Hz), 136.8, 170.9. HRMS (ESI) calcd for $C_{14}H_{25}DNaO_4$: 282.1792, found 282.1809.

5-hexyl-2-(vinyl-1-*d*)tetrahydrofuran-3-ol (9$^\bullet$-*trans* and 9$^\bullet$-*cis*)



From diol **7b$^\bullet$** (91.4 mg, 0.352 mmol) using the same procedure as for the synthesis of **9**. Purification by preparative HPLC (Heptane/EtOAc : 2/1) afford the mixture of diastereoisomers **9$^\bullet$-*cis*** and **9$^\bullet$-*trans*** as a colorless oil (33.4 mg, 93.5 %), 80.5/19.5 *dr* determined by ^1H NMR experiment.

9•-*cis*: ir (neat) *v*: 3413, 2955, 2926, 2857, 1042 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 5.44 (td, *J*= 2.1, 3.0 Hz, 1H), 5.34 (t, *J*= 1.8 Hz, 1H), 4.42 (td, *J*= 1.5, 3.5 Hz,1H), 4.23-4.30 (m, 2H), 2.14 (dd, *J*= 1.1, 5.9, 13.2 Hz, 1H), 1.84 (s, 1H), 1.72 (ddd, *J* = 4.7, 9.7, 13.2 Hz, 1H), 1.64 (m ,1H), 1.26-1.50 (m, 9H), 0.88 (t, *J*= 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 Mhz) δ= 14.2, 22.7, 26.0, 29.5, 31.9, 36.3, 41.4, 74.0, 78.2, 82.9, 118.3, 133.78 (t, *J*= 24.0 Hz). HRMS (ESI) calcd for $C_{12}H_{21}DNaO_2$: 222.1575, found 222.1585.

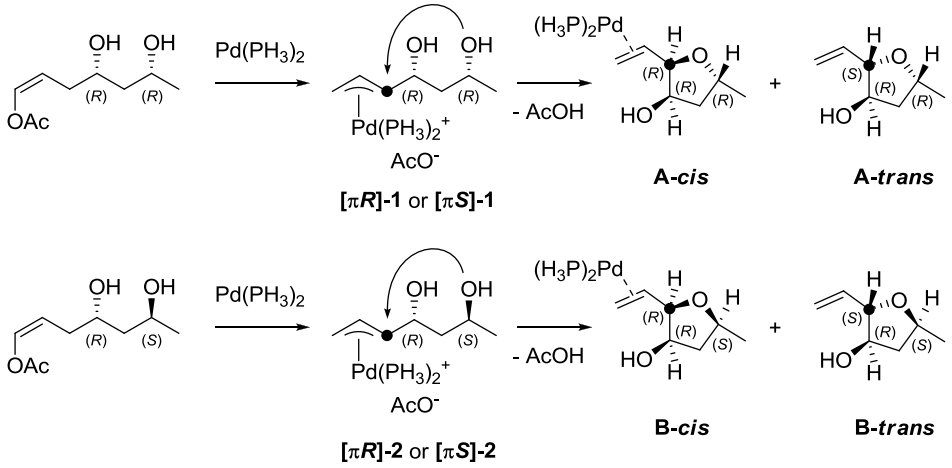
9•-*trans*: IR (neat) *v*: 3399, 2956, 2928, 2858, 1063 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz) δ= 5.34 (tt, *J*= 1.9, 2.7 Hz, 1H), 5.16 (t, *j*= 1.6 Hz, 1H), 4.10-4.19 (m, 3H), 1.93 (ddd, *J*= 2.6, 5.7, 13.1 Hz, 1H), 1.75 (brs, 1H), 1.73 (ddd, *J*= 9.6, 6.3, 13.1 Hz, 1H), 1.65 (m, 1H), 1.24-1.54 (m, 10 H), 0.88 (t, *J*= 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ= 14.2, 22.8, 26.2, 29.5, 31.9, 36.0, 40.4, 78.7, 87.5, 116.4, 137.0 (t, *J*= 24.0 Hz). HRMS (ESI) calcd for $C_{12}H_{21}DNaO_2$: 222.1575, found 222.1548.

3. Calculations

DFT computations were carried out to rationalize the stereochemistry observed in the cyclizations. All computations were performed with the Gaussian '09 software package, revision D01.[3] Optimizations were carried out using the B3LYP functional.[4] The atoms H, C, O, and P were described with the 6-31+G(d,p)[5] basis set. The Pd atom was described by the quasi relativistic ECP28MWB basis set (*(8s7p6d2f1g)/[6s5p3d2f1g]*).[6] This combination of basis sets is denoted BS1 in the manuscript. Single point energies were calculated with the M06L functional,[7] the ECP28MWB basis set for Pd and the 6-311+G(2d,2p)[8] basis set for the other elements. This combination of basis sets is denoted BS2 in the manuscript. Zero-point correction (ZPC) and thermal correction (298 K) to the Gibbs free energy were obtained from the optimization level. Solvation correction (THF) were obtained by the PCM method at the M06L/BS2 level. $Pd(PH_3)_2$ was used as model species for $Pd(p\text{-}MeOPh)_3P)_2$. The results presented are Gibbs free energies (ΔG_{298}, kcal/mol).

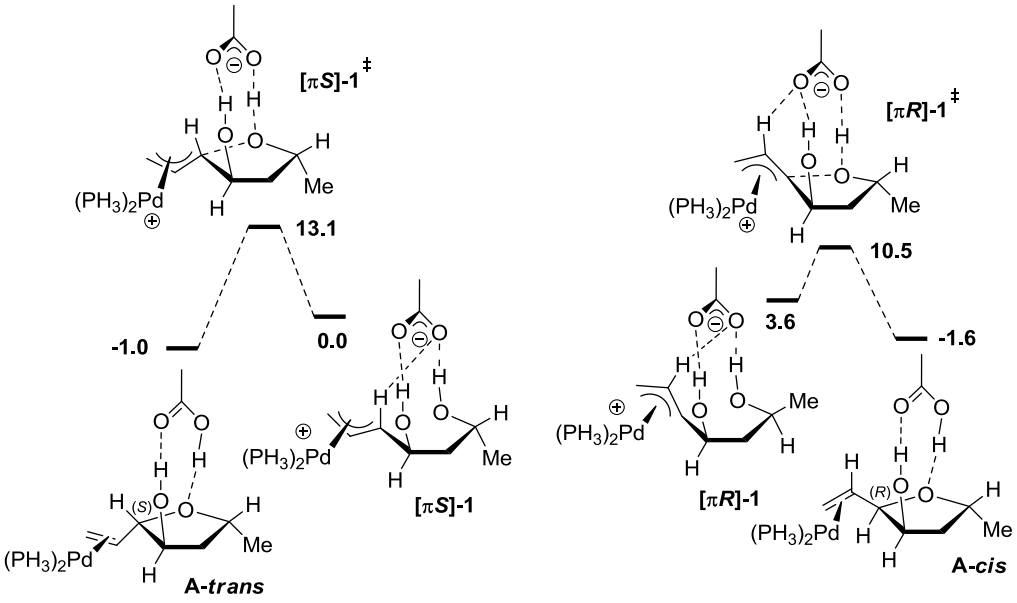
We focused on the two diastereomeric diols displayed in Scheme 1. From each diol, a pair of diastereomers is expected after cyclization. It depends on the enantioface of the intermediate π-allyl palladium that is attacked by the terminal alcohol function. Attack of the *Si* face of the π-allyl palladium leads to *R* stereocenters as in **A-*cis*** and **B-*cis***, which corresponds to the major products obtained experimentally. The corresponding conformation of the π-allyl palladium complexes have thus been denoted **[π*R*]-1** and **[π*R*]-2**. Accordingly, the **[π*S*]-1** and **[π*S*]-2** conformations would give rise to the minor isomers **A-*trans*** and **B-*trans*** respectively.

Scheme 1. Reactions studied by computations



We started our investigations with the **[π*R*]-1** and **[π*S*]-1** conformers (see Scheme 2 and Figure 1 for the geometries). As in our previous study,[9] we were unable to obtain a cyclization transition state in the absence of the acetate counterion. On the other hand, having the acetate H-bonded to the two alcohol functionalities allowed us to locate **[π*R*]-1**‡ and **[π*S*]-1**‡ on the potential energy surface. The two strong H-bonds between the acetate oxygens and the hydrogens of the alcohol functions are also present in the starting π-allyl complexes **[π*R*]-1** and **[π*S*]-1**. In **[π*R*]-1**, a third H-bond is established between the rear oxygen atom of the acetate and the central C-H fragment of the π-allyl moiety. According to the geometrical parameters and the maximum electron density,[10] this H-bond is moderately strong but not negligible compared to the two O···H-O hydrogen bond (O···H-C 2.16 Å; OHC 176.0°; ρ_{max} = 0.016 e/Å^{-3} vs 0.044 e/Å^{-3} for the two O···H-O hydrogen bonds). In **[π*S*]-1**, the rear acetate oxygen also interacts with the π-allyl moiety, yet this time with the internal CH fragment. Nevertheless, this bond is also quite strong (O···H-C 2.13 Å; OHC 162.3°; ρ_{max} = 0.019 e/Å^{-3} vs 0.044 e/Å^{-3} for the two O···H-O hydrogen bonds). In both **[π*R*]-1** and **[π*S*]-1**, these networks of hydrogen bonds preorganize the complexes for cyclization. In the transition state **[π*R*]-1**‡, the O···H-C hydrogen bond remains but passes for the rear oxygen to the front one. It is also weaker than in **[π*R*]-1** (O···H-C 2.38 Å; OHC 136.6°; ρ_{max} = 0.012 e/Å^{-3}). On the other hand, a O···H-C interaction is unworkable in **[π*S*]-1**‡. Also in the products **A-*cis*** and **A-*trans***, this extra H-bond does not exist anymore. Although **[π*S*]-1** is more stable than **[π*R*]-1** by 3.6 kcal/mol, it is **[π*R*]-1**‡ that is the lowest lying transition state ($\Delta\Delta G_{298}^{‡}$ = 2.6 kcal/mol). This could be due, among other factors, to the fact that the extra O···H-C bond still exists in the transition state, conferring additional stability. Both transformations are moderately exergonic. Under kinetic control, the calculations predict **A-*cis*** type products to be the major ones, which is corroborated experimentally.

Scheme 2. Computed reaction profiles at the PCM^{THF}/M06-L/BS2//B3LYP/BS1 level corresponding to the transformation of conformers [π*R*]-1 and [π*S*]-1 into A-*cis* and A-*trans* (Gibbs free energies, kcal/mol).



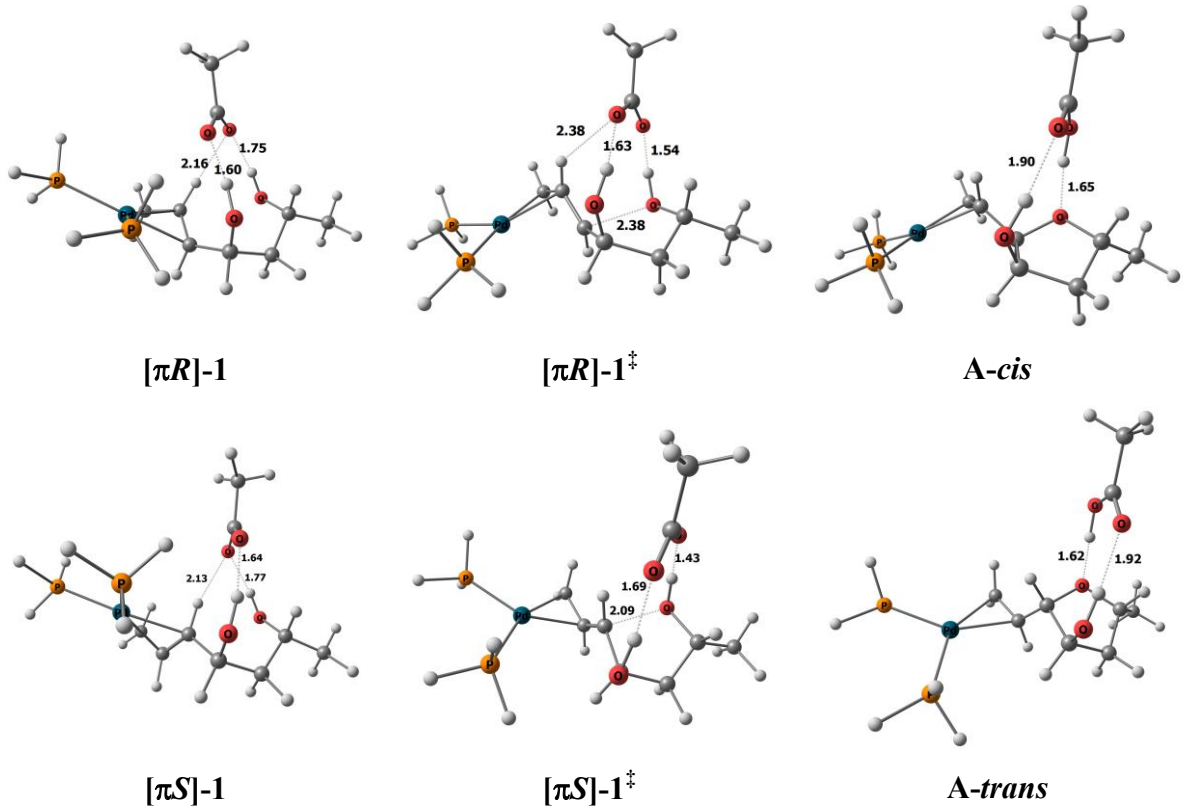
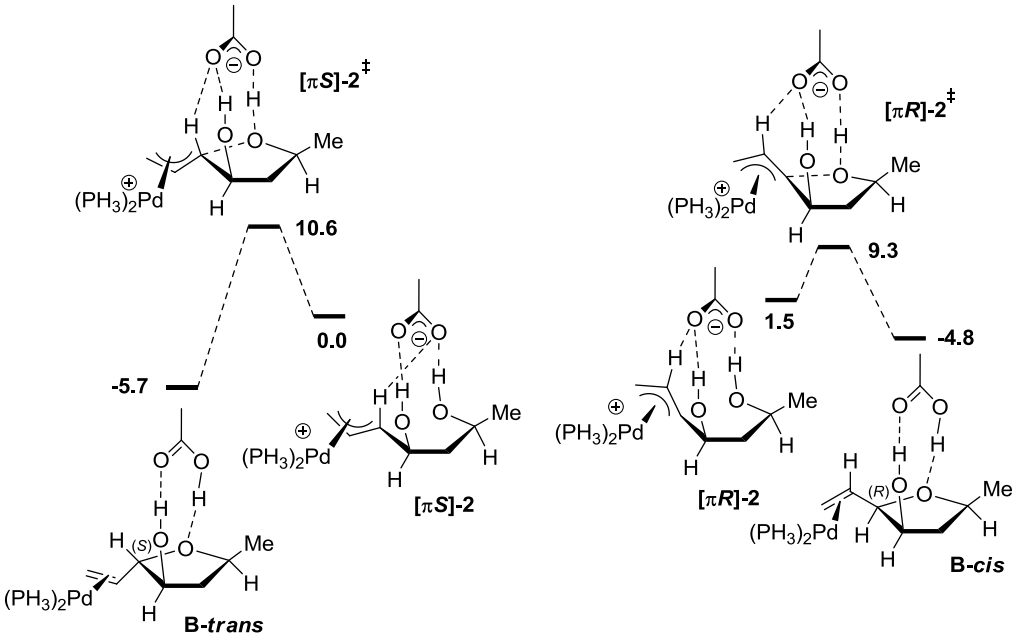


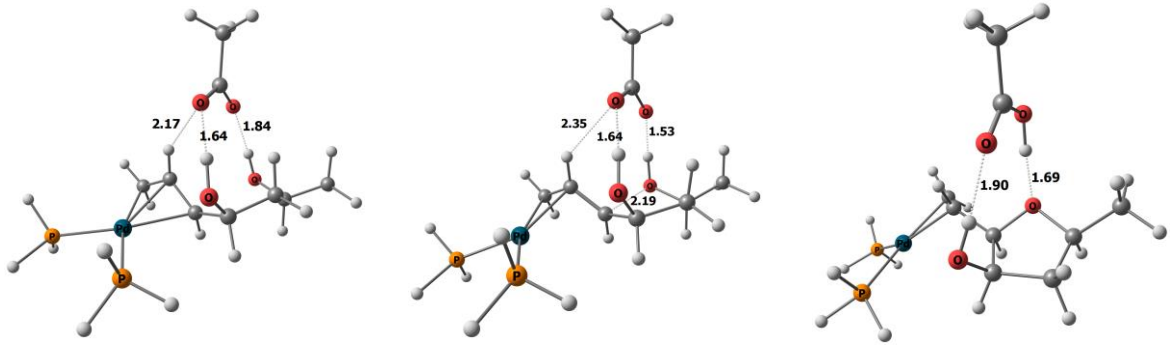
Figure 1. Geometries of the computed species related to Scheme 2 (distances in Å) at the B3LYP/BS1 level

The calculations regarding the **[π*R*]-2** and **[π*S*]-2** conformers are summarized in Scheme 3 and Figure 2. Again, the starting complexes are preorganized for cyclization and exhibit two

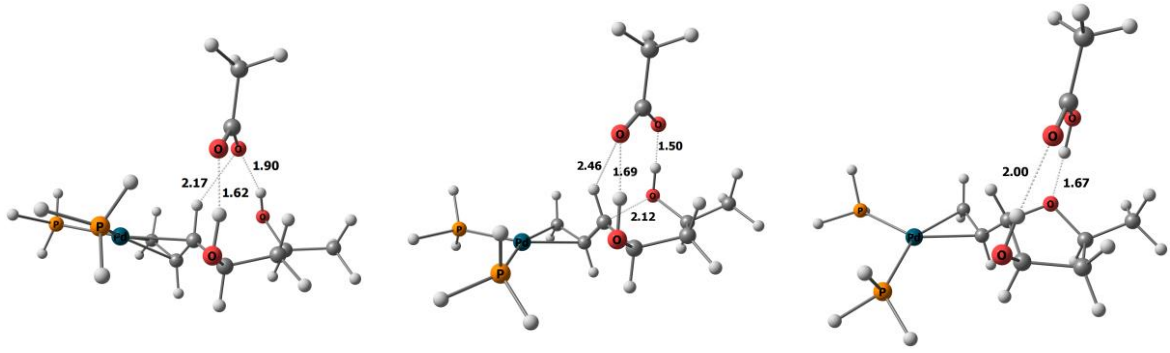
O···H-O and one O···H-C hydrogen bonds. In **[π*R*]-2**, the extra H-bond is established between the front acetate oxygen and the central C-H fragment of the π-allyl moiety (O···H-C 2.17 Å; OHC 147.8°; ρ_{max} = 0.019 e/Å^{-3}). In **[π*S*]-2**, it is the rear oxygen and the internal C-H bond that are concerned (O···H-C 2.17 Å; OHC 144.5°; ρ_{max} = 0.019 e/Å^{-3}). Interestingly, in this series, the extra hydrogen bonds are not lost in the transition states, which might partly explain why the activation free energies are both significantly lower than those corresponding to **[π*S*]-1**‡. In **[π*R*]-2**‡, the extra H-bond remains at the front oxygen (O···H-C 2.35 Å; OHC 137.9°; ρ_{max} = 0.016 e/Å^{-3}). In **[π*S*]-2**‡, it passes from the rear to the front (O···H-C 2.46 Å; OHC 125.0°; ρ_{max} = 0.012 e/Å^{-3}). On the basis of geometrical parameters and maximum electron density, the O···H-C hydrogen bond in **[π*S*]-2**‡ is weaker than in **[π*R*]-2**‡. This is consistent with the fact that **[π*R*]-2**‡ is the lowest lying transition state. The energy difference between the two transition states is twice less than in the previous series but remains sufficient to ensure a good diastereoselectivity in favor of the *cis* isomer as observed experimentally ($\Delta\Delta G_{298}^{‡}$ = 1.3 kcal/mol). The 1.3 kcal/mol difference in Gibbs free energy of activation between the transition states leads to an estimated ratio of 9 : 1 which is in line with the experimental one. In the previous case however, the difference was 2.6 kcal/mol, which gives a computed ratio of 81 : 1 way higher that the observed one. Nevertheless, model substrates have been used so these estimates can only reflect a general trend.[11]

Scheme 3. Computed reaction profiles at the PCM^{THF}/M06-L/BS2//B3LYP/BS1 level corresponding to the transformation of conformers [π*R*]-2 and [π*S*]-2 into B-*cis* and B-*trans* (Gibbs free energies, kcal/mol).





[πR]-2 [πR]-2‡ B-*cis*



[πS]-2 [πS]-2‡ B-*trans*

Figure 2. Geometry of the computed species related to Scheme 3 (distances in Å) at the B3LYP/BS1 level

Supporting Information

Table S1. Coordinates (x,y,z) of the computed species

[πR]-1 E(RM06L) = -1467.94490538				**[πR]-1‡** E(RM06L) = -1467.93700241; Frequency -91.3810			
O	-3.183673000	0.093123000	-1.289491000	O	-2.589272000	-0.531216000	-1.482738000
C	-0.359417000	-1.450394000	-0.647844000	C	-0.383143000	-0.766649000	-0.619914000
C	-3.605915000	-0.553251000	-0.093174000	C	-3.271991000	-1.416446000	-0.599426000
C	-2.793846000	-1.834616000	0.152461000	C	-2.220096000	-2.388323000	-0.059762000
C	-1.296699000	-1.663939000	0.540211000	C	-0.975488000	-1.631859000	0.465047000
Pd	1.627148000	-0.490446000	-0.295685000	Pd	2.059861000	0.069822000	-0.167261000
P	3.677783000	0.598474000	-0.606165000	P	4.113277000	0.935116000	-0.860594000
C	-0.229995000	-0.294296000	-1.446114000	C	-0.041992000	0.590721000	-0.511210000
C	0.861492000	-0.238413000	-2.339668000	C	0.793787000	1.202510000	-1.482439000
O	-1.102970000	-0.749648000	1.597561000	O	-1.162014000	-0.973939000	1.684419000
C	-5.101133000	-0.872948000	-0.198731000	C	-4.412966000	-2.131663000	-1.325723000
P	1.671698000	-0.966960000	2.021599000	P	2.480111000	-1.309601000	1.723226000
O	-0.579671000	1.740968000	1.170753000	O	-2.476571000	1.301324000	1.533304000
C	-1.131910000	2.615803000	0.426159000	C	-3.040065000	2.044187000	0.673872000
O	-1.861690000	2.370061000	-0.574745000	O	-3.159259000	1.792885000	-0.564808000
C	-0.897815000	4.082956000	0.785868000	C	-3.651286000	3.351042000	1.176906000
H	-3.257600000	-2.377316000	0.985766000	H	-2.612425000	-3.004409000	0.756381000
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H	1.062502000	0.686679000	-2.872136000	H	0.938794000	2.278708000	-1.447857000
H	0.002308000	-2.381484000	-1.093067000	H	-0.127971000	-1.280719000	-1.544465000
H	-0.900585000	4.705886000	-0.112269000	H	-3.678346000	4.099755000	0.381501000
H	0.033917000	4.209762000	1.343112000	H	-3.104403000	3.726358000	2.045501000
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H	-3.450476000	0.119034000	0.761884000	H	-3.682234000	-0.836520000	0.238191000
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H	-5.665073000	0.049363000	-0.367466000	H	-5.144762000	-1.403561000	-1.687773000
H	2.943034000	-1.150083000	2.626671000	H	3.679491000	-2.043382000	1.891577000
H	1.023419000	-2.091715000	2.560578000	H	1.576711000	-2.335427000	2.079273000
H	1.175050000	0.065458000	2.833236000	H	2.503562000	-0.630513000	2.961699000
H	4.525020000	0.178445000	-1.656207000	H	4.459700000	0.829233000	-2.227781000
H	4.652685000	0.654637000	0.416515000	H	5.356255000	0.513458000	-0.329252000
H	3.638393000	1.975349000	-0.916332000	H	4.325597000	2.326357000	-0.725044000
H	-0.771118000	0.616759000	-1.200239000	H	-0.423034000	1.154236000	0.335513000
H	-2.870721000	-2.478749000	-0.734525000	H	-1.906968000	-3.062831000	-0.869974000
H	-1.037359000	0.217126000	1.305771000	H	-1.728522000	-0.150678000	1.579329000
H	-0.995393000	-2.638749000	0.951621000	H	-0.226285000	-2.419787000	0.648667000
H	-2.792992000	0.966741000	-1.052798000	H	-2.788774000	0.422670000	-1.169849000
A-*cis* E(RM06L) = -1467.96927962				**[πS]-1** E(RM06L) = -1467.94944438			
O	-2.097262000	-0.787677000	-1.037195000	O	-3.076071000	-0.767166000	-1.366123000

C	-0.726256000	-0.975649000	-0.524020000	C	-0.416918000	-1.042260000	-0.104523000
C	-3.014402000	-1.733294000	-0.404863000	C	-3.577009000	-0.841973000	-0.032414000
C	-2.154976000	-2.515845000	0.602564000	C	-2.682333000	-1.749551000	0.827263000
C	-0.953002000	-1.594373000	0.867382000	C	-1.259439000	-1.218798000	1.143907000
Pd	2.148696000	0.193483000	-0.151019000	Pd	1.754482000	-0.421205000	-0.022972000
P	4.290697000	0.397601000	-1.063450000	P	3.947320000	0.065266000	-0.653932000
C	0.019843000	0.325485000	-0.615548000	C	0.393154000	-2.064234000	-0.625674000
C	0.768520000	0.655119000	-1.759378000	C	1.290346000	-1.771477000	-1.677534000
O	-1.182757000	-0.647343000	1.894229000	O	-1.281739000	-0.033932000	1.913621000
C	-3.699909000	-2.578620000	-1.469852000	C	-5.010159000	-1.377091000	-0.081923000
P	2.282486000	-0.215064000	2.168717000	P	1.436784000	1.041233000	1.824436000
O	-3.142139000	1.351985000	1.236662000	O	-1.539483000	2.247045000	0.644020000
C	-3.494743000	1.984753000	0.245444000	C	-1.584675000	2.455885000	-0.610869000
O	-3.255356000	1.595383000	-1.003385000	O	-1.627608000	1.558311000	-1.502095000
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H	3.513032000	-0.313817000	2.872998000	H	-5.449250000	-1.440542000	0.920357000
H	1.682565000	-1.350378000	2.767046000	H	-5.631855000	-0.718079000	-0.695171000
H	1.690943000	0.740845000	3.028534000	H	1.119368000	0.515782000	3.088226000
H	4.738983000	-0.594593000	-1.973908000	H	0.449026000	2.031996000	1.650365000
H	5.491547000	0.434152000	-0.303204000	H	2.557291000	1.832116000	2.183796000
H	4.622994000	1.504370000	-1.887833000	H	4.889981000	-0.984731000	-0.728117000
H	-0.374618000	1.125602000	0.007212000	H	4.732915000	0.977996000	0.086455000
H	-1.810486000	-3.457572000	0.156368000	H	4.162683000	0.615567000	-1.937310000
H	-1.885824000	-0.018040000	1.638426000	H	-2.599408000	-2.724241000	0.326260000
H	-0.072125000	-2.163291000	1.176753000	H	-1.516376000	0.770408000	1.354808000
H	-2.749585000	0.724926000	-1.016484000	H	-0.780091000	-1.979409000	1.777038000
[πS]-1‡ E(RM06L) = -1467.93720378; Frequency -191.0234				**A-*trans*** E(RM06L) = -1467.96531997			
O	-2.453594000	-0.708677000	-1.159412000	O	-2.032713000	-0.417811000	-1.020212000
C	-0.572627000	-0.715555000	-0.245808000	C	-0.806644000	-0.421238000	-0.194634000
C	-3.311724000	-1.271858000	-0.159235000	C	-2.851347000	-1.600526000	-0.766828000
C	-2.401492000	-2.164169000	0.680977000	C	-1.962085000	-2.507352000	0.086746000
C	-1.108300000	-1.390022000	1.011093000	C	-1.070323000	-1.518002000	0.856861000
Pd	2.000414000	-0.224676000	-0.184617000	Pd	2.274922000	0.100725000	-0.187661000
P	3.965346000	0.800664000	-0.906930000	P	3.995764000	1.651222000	-0.553298000

C	0.341332000	-1.356770000	-1.120812000	C	0.404958000	-0.637640000	-1.070221000
C	1.090642000	-0.646992000	-2.089390000	C	0.935949000	0.394558000	-1.862270000
O	-1.256883000	-0.450340000	2.055473000	O	-1.681158000	-1.020848000	2.035523000
C	-4.476113000	-2.016121000	-0.810082000	C	-3.320422000	-2.182795000	-2.091533000
P	1.979816000	-0.025401000	2.191639000	P	2.690703000	-1.029903000	1.826624000
O	-2.185837000	1.851722000	1.029945000	O	-3.676321000	0.981262000	1.426983000
C	-2.628314000	2.369144000	-0.031441000	C	-3.900737000	1.835201000	0.574777000
O	-2.816966000	1.754855000	-1.136705000	O	-3.435100000	1.776142000	-0.670578000
C	-2.988441000	3.851185000	-0.022668000	C	-4.736950000	3.064805000	0.830239000
H	-2.618782000	0.337782000	-1.188689000	H	-2.888467000	0.937934000	-0.810600000
H	-2.872757000	-2.488441000	1.614640000	H	-2.531778000	-3.142315000	0.769984000
H	0.459751000	-2.435791000	-1.037813000	H	0.563867000	-1.666707000	-1.394927000
H	1.689229000	-1.205185000	-2.804228000	H	1.462852000	0.161486000	-2.784643000
H	0.735190000	0.321217000	-2.438196000	H	0.500712000	1.391839000	-1.820468000
H	-0.651432000	0.365283000	-0.279256000	H	-0.757237000	0.562611000	0.281998000
H	-2.635858000	4.334639000	0.890303000	H	-5.112711000	3.052311000	1.853049000
H	-4.077902000	3.952600000	-0.084390000	H	-5.570638000	3.101675000	0.122217000
H	-2.569191000	4.346136000	-0.903851000	H	-4.131710000	3.961958000	0.665257000
H	-3.701269000	-0.457826000	0.467311000	H	-3.719093000	-1.271078000	-0.178702000
H	-4.103607000	-2.808871000	-1.468322000	H	-2.466416000	-2.500814000	-2.698540000
H	-5.120406000	-2.467944000	-0.046512000	H	-3.966265000	-3.050205000	-1.912455000
H	-5.081780000	-1.329082000	-1.408449000	H	-3.892894000	-1.444510000	-2.661773000
H	1.426330000	-1.030322000	3.013493000	H	2.488969000	-2.429077000	1.953834000
H	1.289635000	1.079645000	2.729819000	H	1.924940000	-0.668308000	2.963080000
H	3.200888000	0.140557000	2.891135000	H	3.949719000	-1.014719000	2.483853000
H	4.836833000	0.077176000	-1.755160000	H	4.621480000	1.728089000	-1.824522000
H	4.957410000	1.280266000	-0.016410000	H	5.202663000	1.713652000	0.195026000
H	3.871437000	1.966121000	-1.704004000	H	3.701997000	3.035751000	-0.454654000
H	-2.142878000	-3.060770000	0.099854000	H	-1.347849000	-3.150300000	-0.556728000
H	-1.683543000	0.376023000	1.701848000	H	-2.389835000	-0.387291000	1.812084000
H	-0.367341000	-2.120586000	1.358400000	H	-0.137812000	-1.987168000	1.177581000
[πR]-2 E(RM06L) = -1467.94047445				**[πR]-2‡** E(RM06L) = -1467.93524185; Frequency -146.7323			
O	2.684843000	-1.012816000	-1.768905000	O	2.363460000	-0.891176000	-1.562731000
C	0.234397000	-0.825581000	-0.484322000	C	0.437712000	-0.801744000	-0.526235000
C	2.992894000	-1.957914000	-0.748083000	C	2.891492000	-1.990250000	-0.819048000
C	2.495089000	-1.462627000	0.615408000	C	2.501704000	-1.772282000	0.644232000
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Pd	-1.927673000	-0.084322000	-0.246963000	Pd	-2.068603000	0.064858000	-0.184142000
P	-4.030850000	0.802000000	-0.786035000	P	-4.206606000	0.555877000	-0.964602000
C	0.077175000	0.505271000	-0.907688000	C	-0.004747000	0.519394000	-0.743067000
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O	0.674901000	-0.427876000	1.873701000	O	0.824371000	-0.458296000	1.865012000
C	4.495266000	-2.262625000	-0.711925000	C	4.399486000	-2.136858000	-1.026326000
P	-2.232571000	-1.065602000	1.885739000	P	-2.268852000	-0.759972000	2.042389000
O	1.837391000	1.884262000	1.309569000	O	2.253439000	1.681629000	1.263164000

C	2.754967000	2.174308000	0.469478000	C	3.139328000	1.947904000	0.397345000
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C	3.569572000	3.434558000	0.767681000	C	3.971539000	3.211129000	0.609495000
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H	4.167524000	3.730439000	-0.096956000	H	4.225909000	3.670442000	-0.349245000
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O	2.019346000	-0.800943000	-1.199994000	O	2.831517000	-1.497866000	-1.216041000
C	0.677391000	-0.970031000	-0.631679000	C	0.434396000	-0.837962000	0.105996000
C	2.712673000	-2.042611000	-0.936518000	C	3.271654000	-1.807418000	0.106021000
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C	0.953125000	-1.642605000	0.737992000	C	1.251692000	-0.671409000	1.376693000
Pd	-2.170795000	0.198496000	-0.143116000	Pd	-1.787429000	-0.378972000	-0.007587000
P	-4.335669000	0.459909000	-0.979647000	P	-3.975406000	-0.227191000	-0.794947000
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O	1.060180000	-0.738106000	1.821986000	O	0.955585000	0.563062000	2.005385000
C	4.208462000	-1.859362000	-1.131227000	C	4.798220000	-1.946310000	0.145852000
P	-2.241960000	-0.333830000	2.155582000	P	-1.673889000	1.494120000	1.449522000
O	3.085794000	1.238662000	1.321518000	O	1.455756000	2.511609000	0.327716000
C	3.507539000	1.883315000	0.366794000	C	1.944355000	2.370060000	-0.843215000
O	3.327170000	1.529673000	-0.903651000	O	2.159066000	1.267730000	-1.420408000
C	4.289461000	3.165698000	0.508194000	C	2.317221000	3.654021000	-1.585931000
H	2.812151000	0.673518000	-0.970426000	H	2.793423000	-0.526095000	-1.335648000
H	2.110866000	-3.524126000	0.568483000	H	3.252774000	-0.944531000	2.095654000
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H	3.003819000	-2.150952000	1.231628000	H	3.116804000	0.218247000	0.780590000
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C	1.136319000	-0.757929000	1.362674000	C	1.088435000	-1.363416000	0.942388000
Pd	-2.040191000	-0.241214000	-0.106854000	Pd	-2.233417000	-0.011041000	-0.233434000
P	-3.998930000	0.404816000	-1.180699000	P	-4.026848000	1.401038000	-0.750822000
C	-0.409146000	-1.680539000	-0.483812000	C	-0.426682000	-0.893972000	-1.095564000
C	-1.202554000	-1.472747000	-1.642963000	C	-1.030536000	-0.040232000	-2.034946000
O	0.870620000	0.488212000	1.985645000	O	1.073524000	-0.609186000	2.142769000
C	4.505310000	-2.124461000	-0.061987000	C	4.021324000	-2.019150000	-1.393796000
P	-2.069144000	0.921164000	1.978544000	P	-2.436584000	-0.645046000	2.025299000
O	1.980169000	2.126215000	0.188218000	O	3.055492000	1.416559000	1.343139000
C	2.880115000	2.066236000	-0.698532000	C	3.614147000	1.957863000	0.395787000
O	3.284137000	1.008757000	-1.283489000	O	3.544886000	1.515013000	-0.859049000
C	3.572201000	3.367644000	-1.096947000	C	4.459486000	3.201442000	0.524589000
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H	4.690483000	-2.735358000	-0.950636000	H	4.037047000	-1.842141000	-2.473688000
H	-3.325893000	1.364546000	2.467574000	H	-3.706872000	-0.806430000	2.640423000
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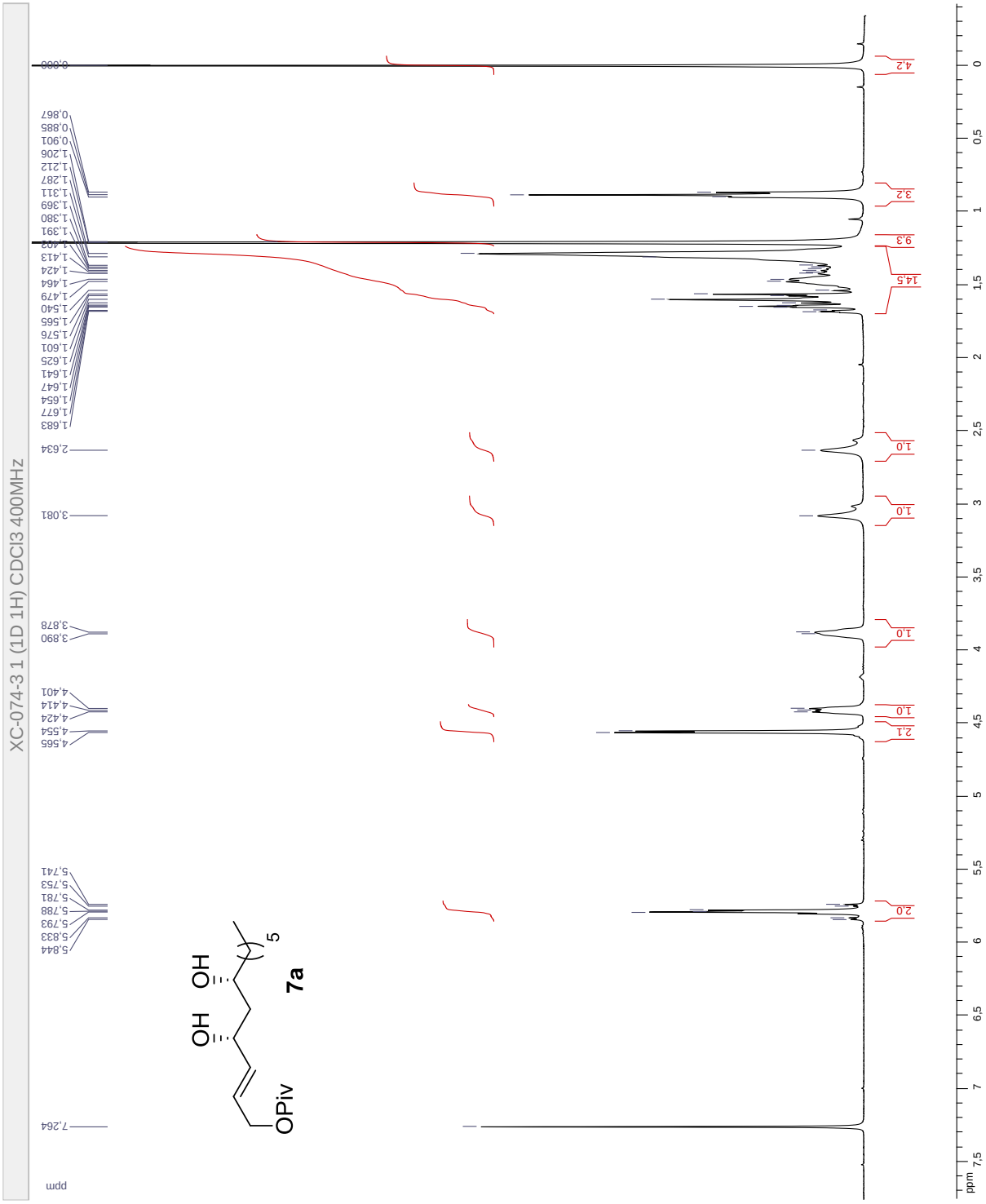
4. NMR spectra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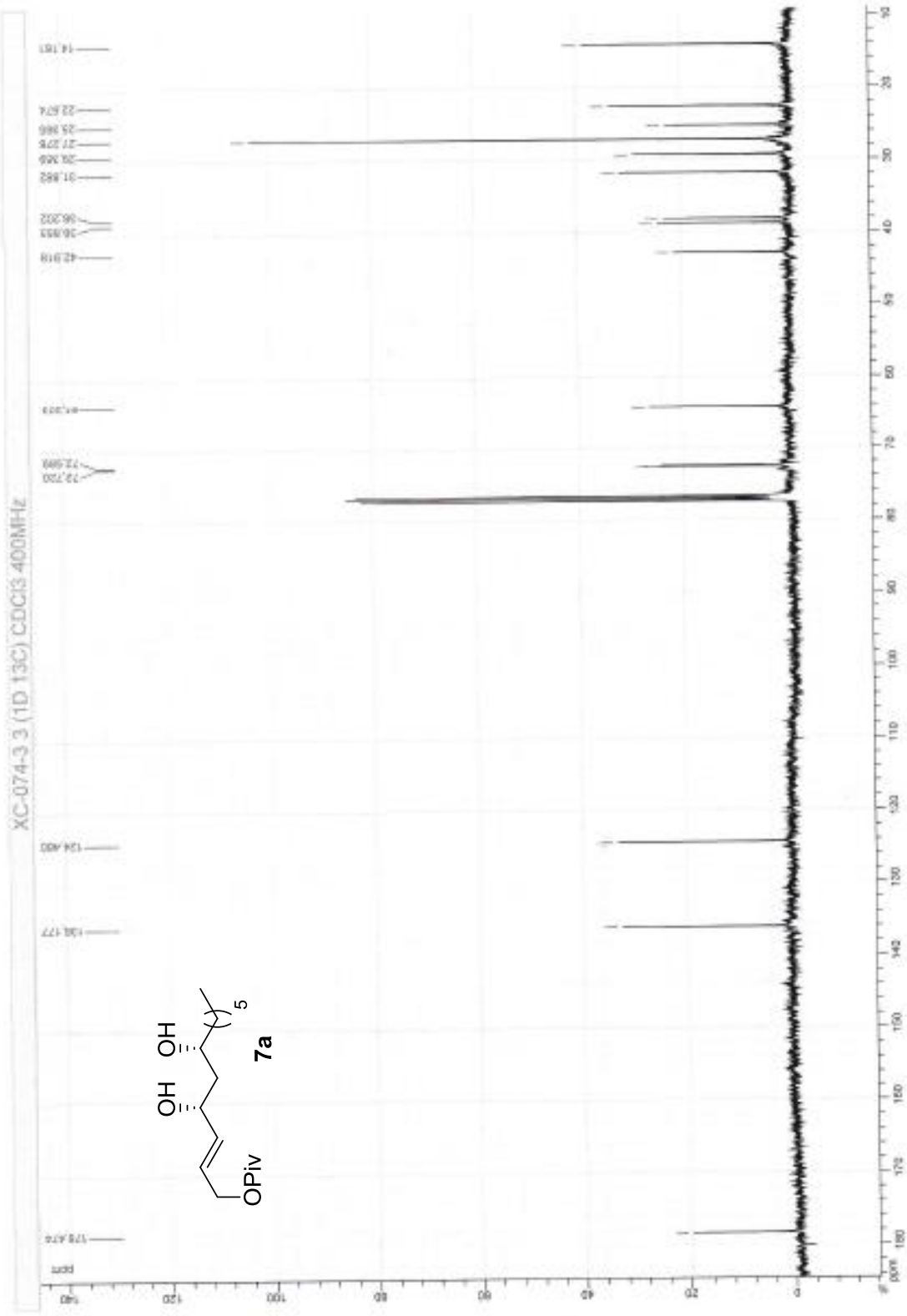
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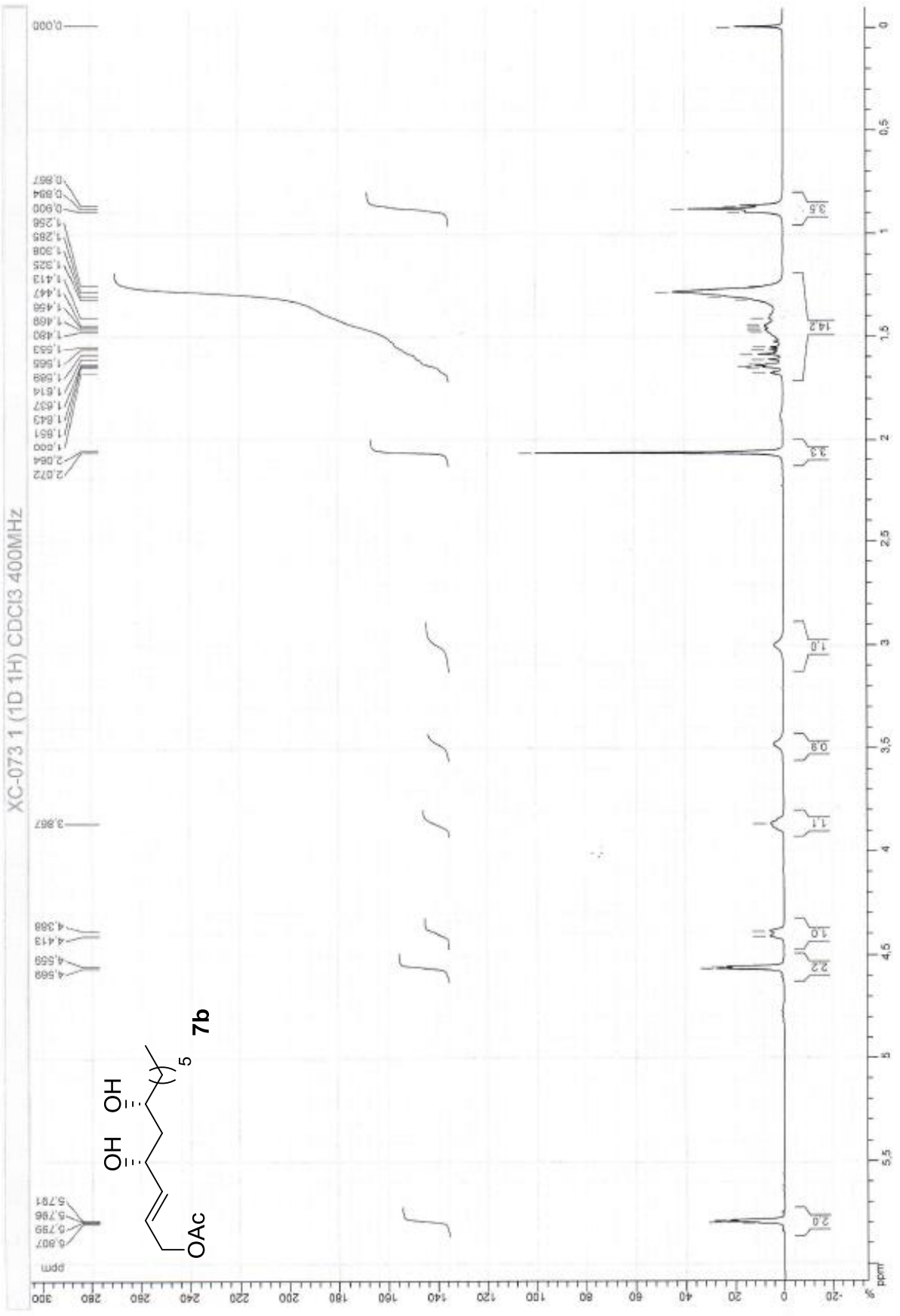
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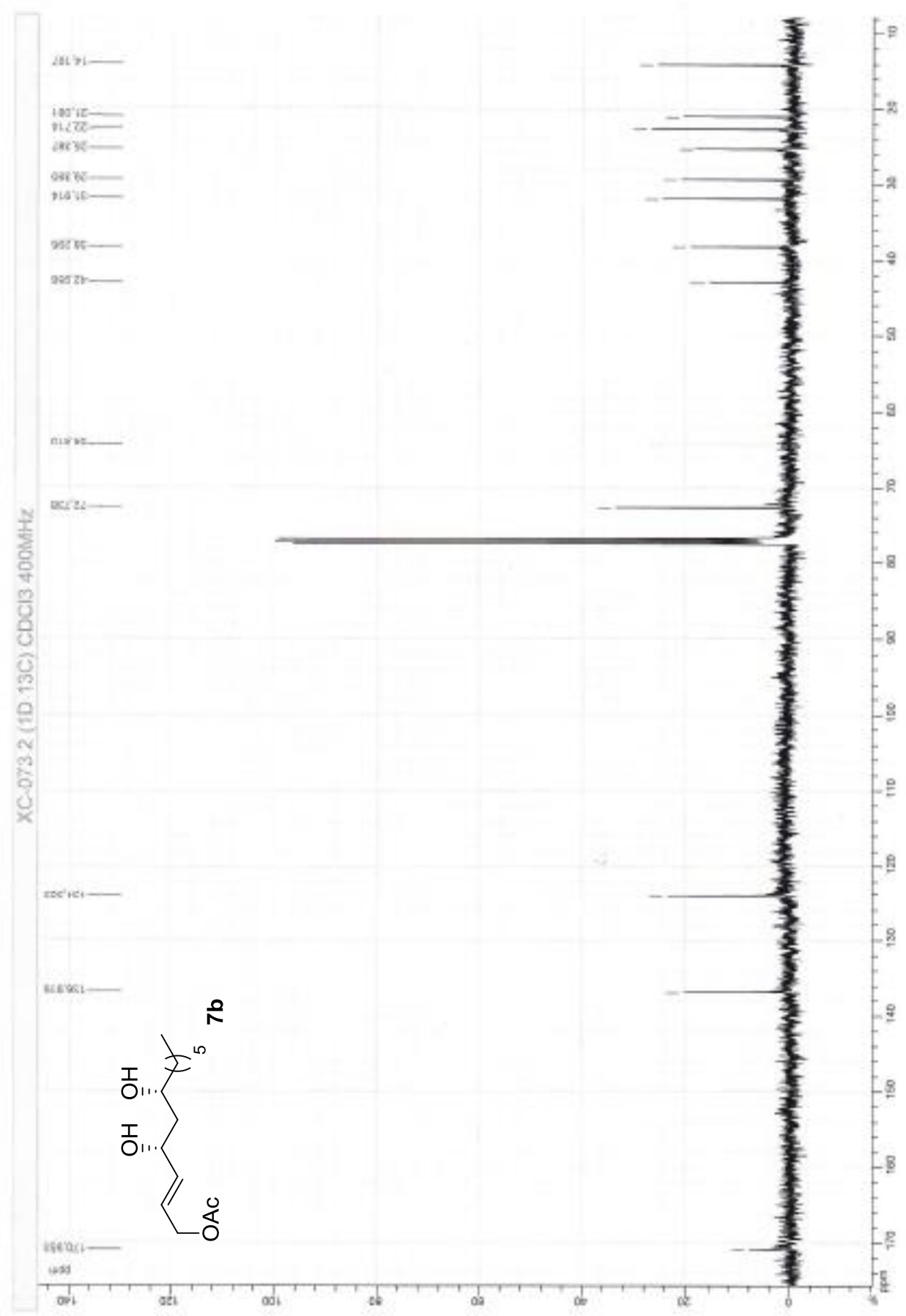
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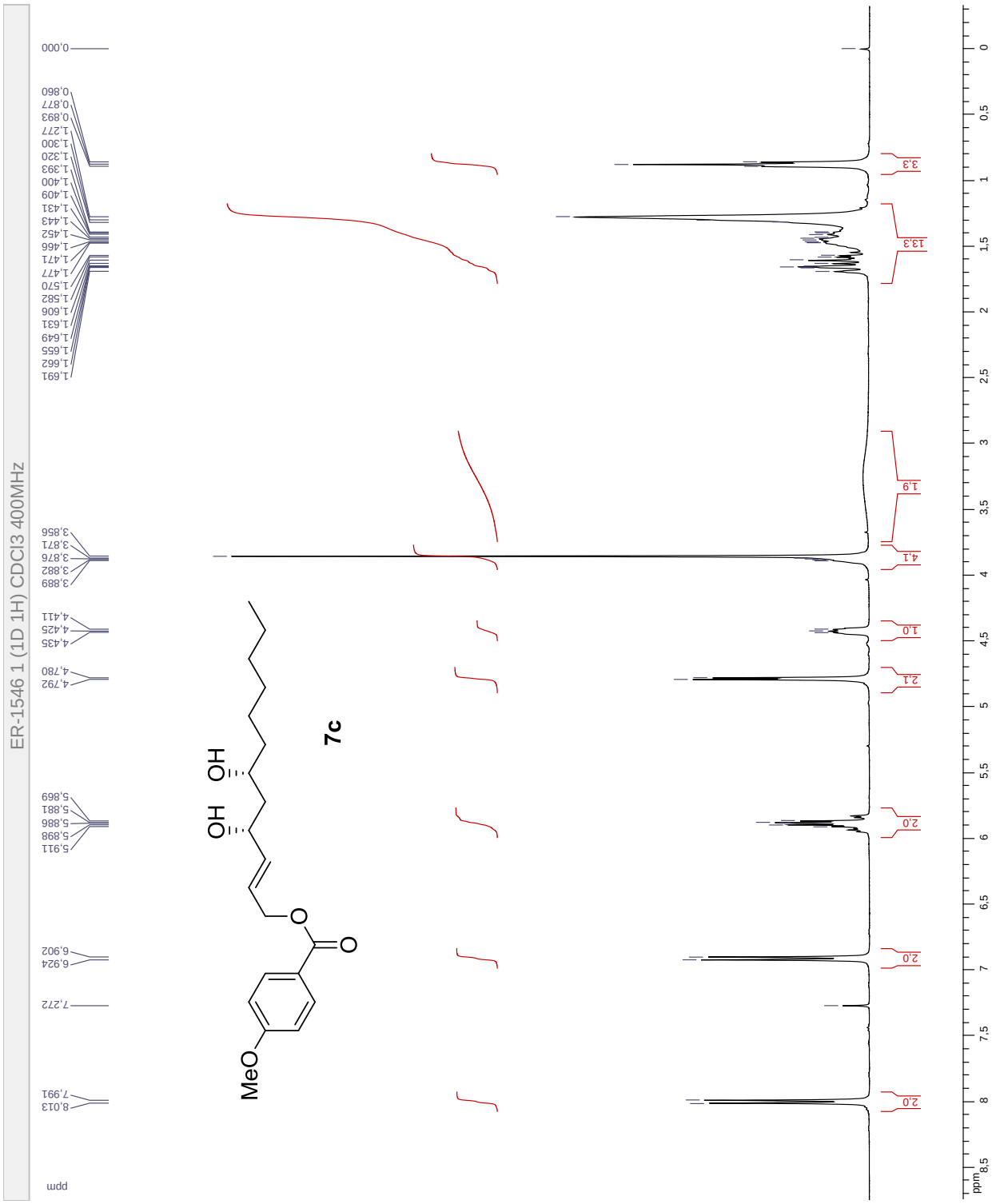
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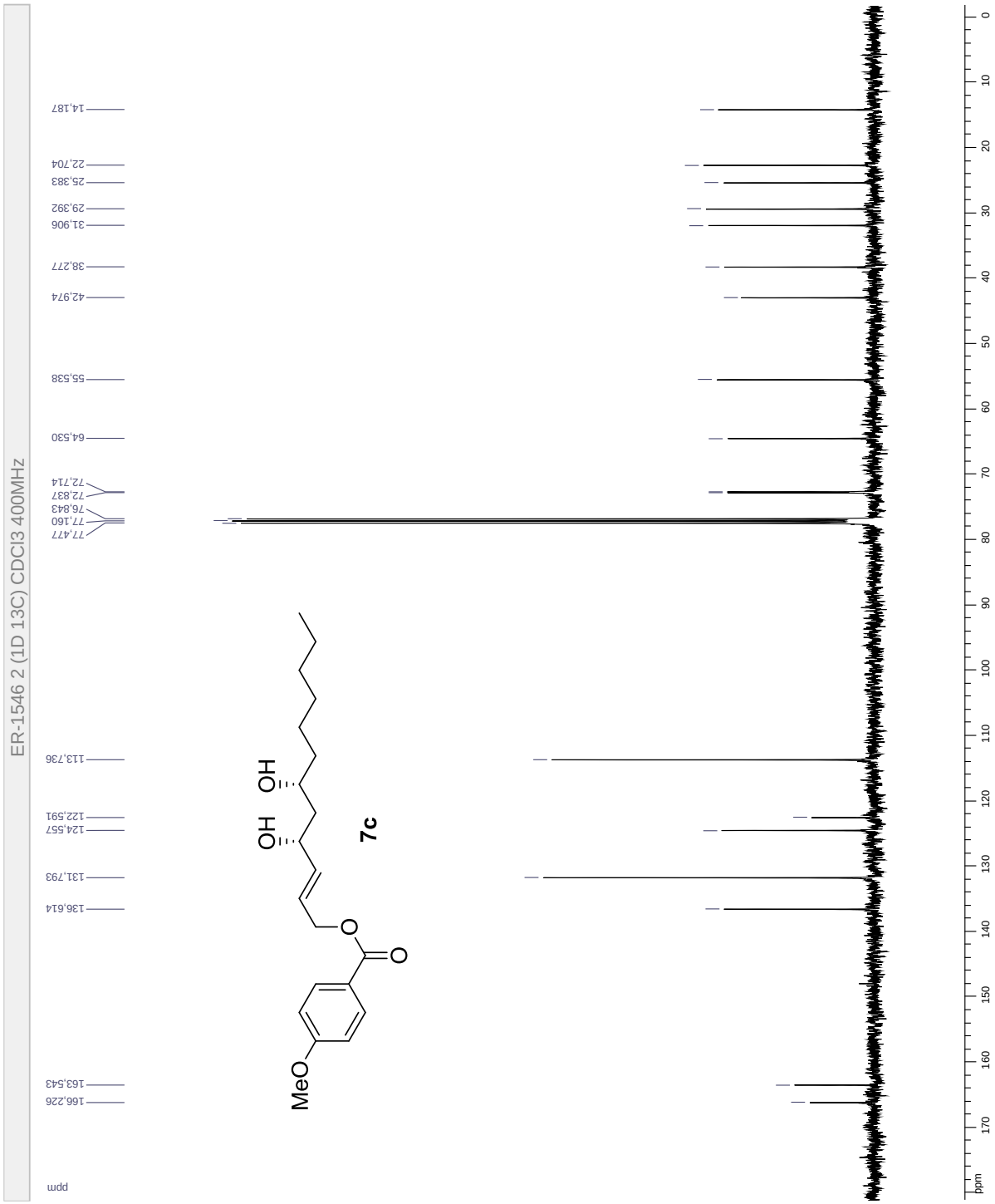
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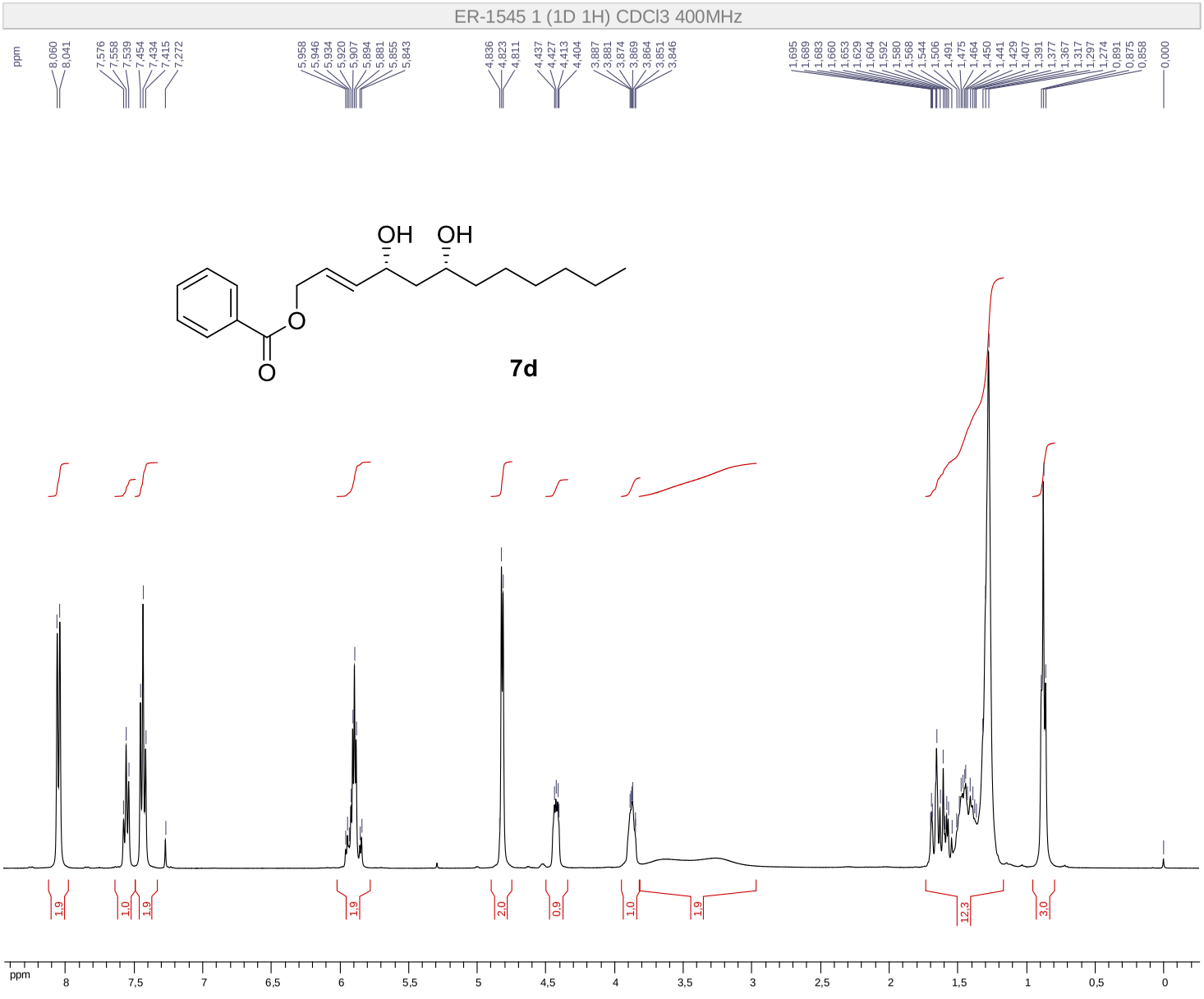
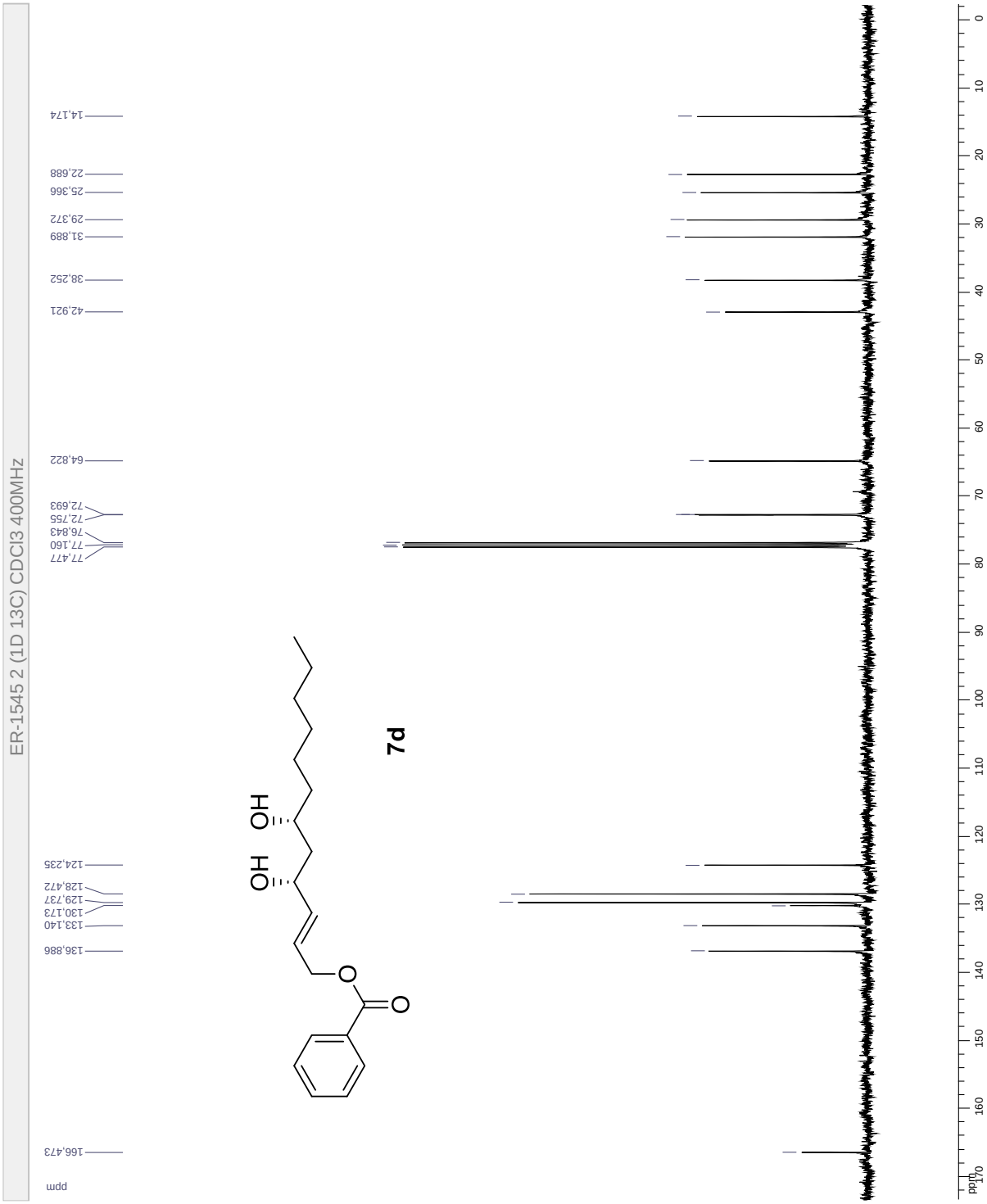
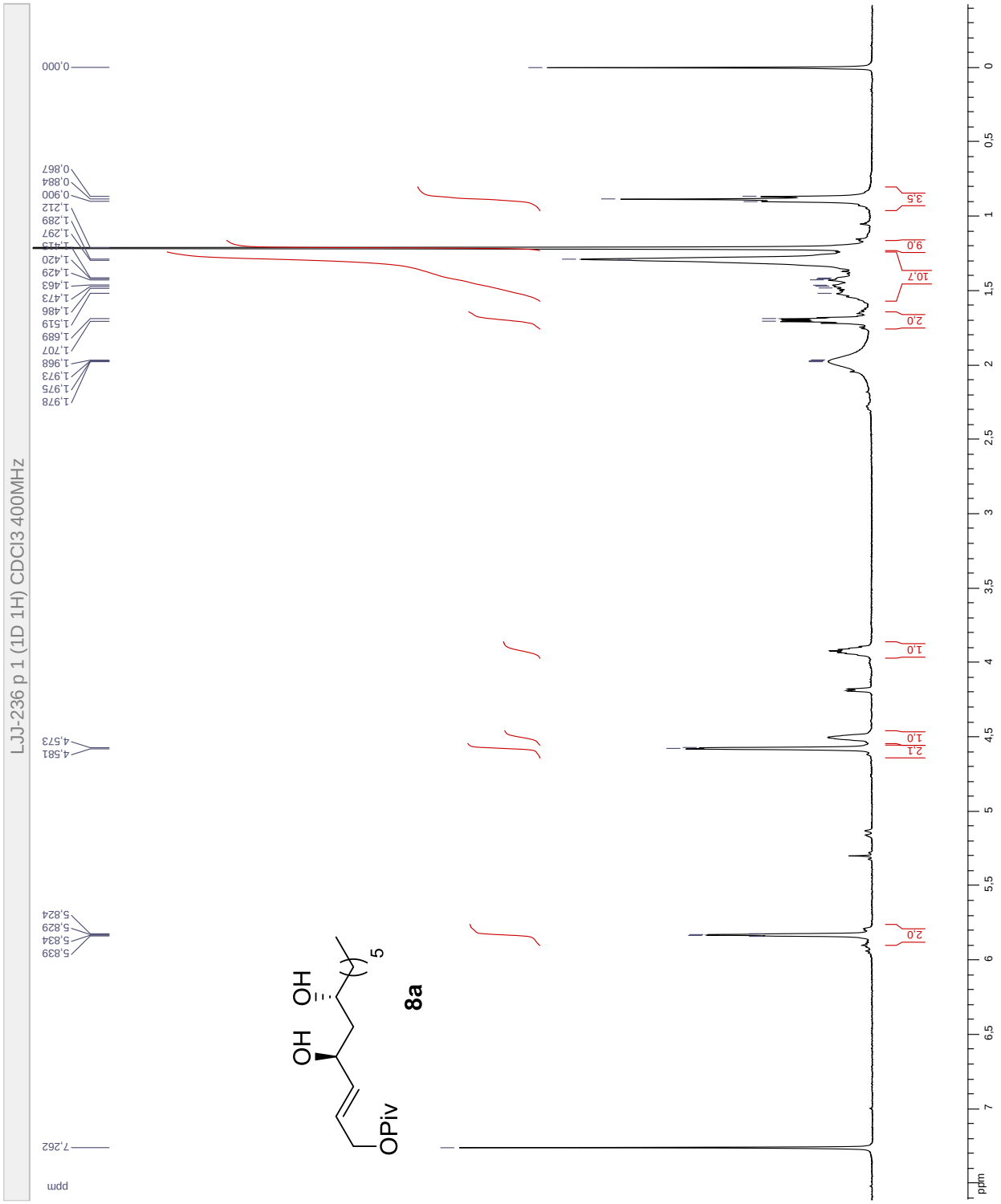
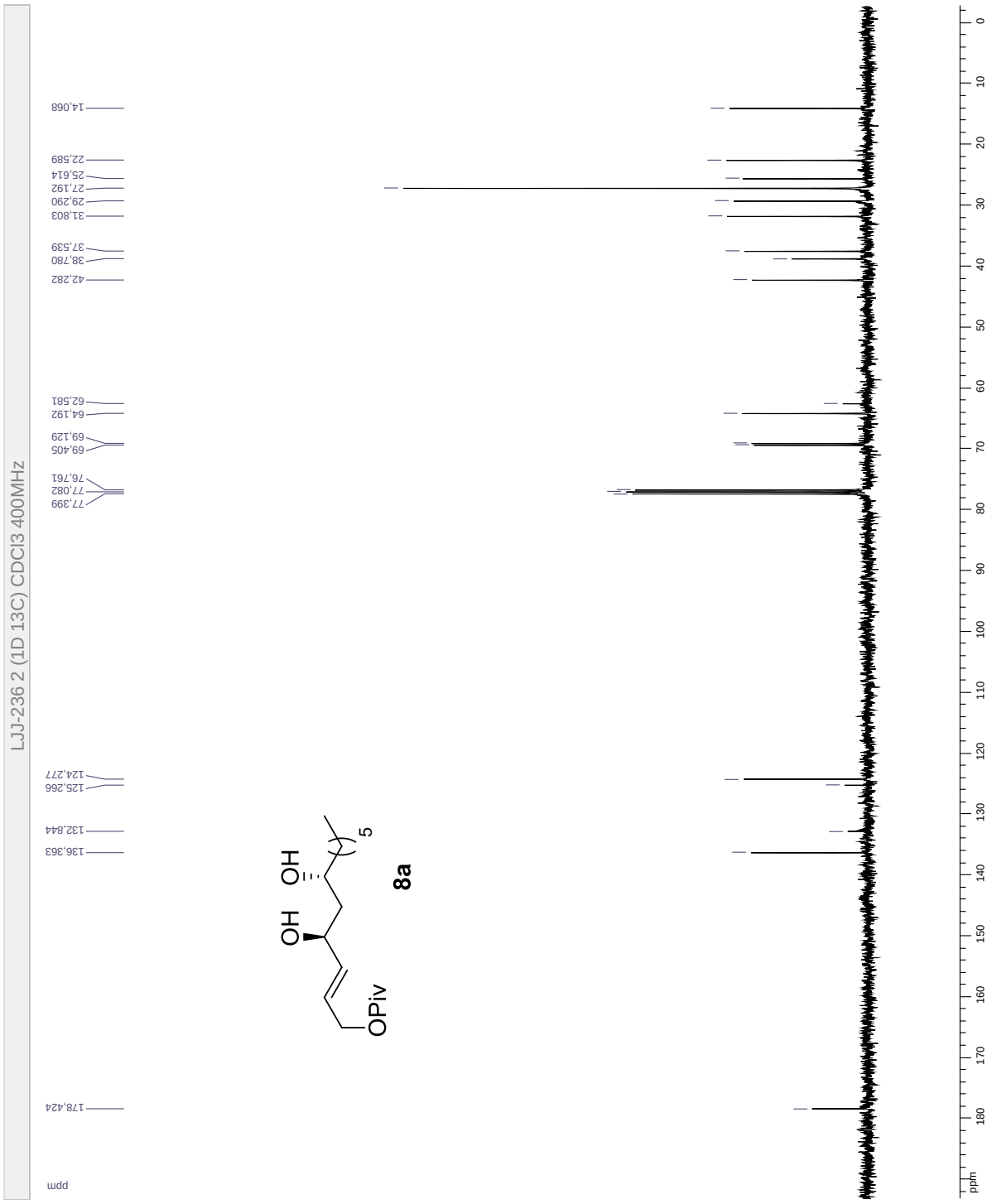
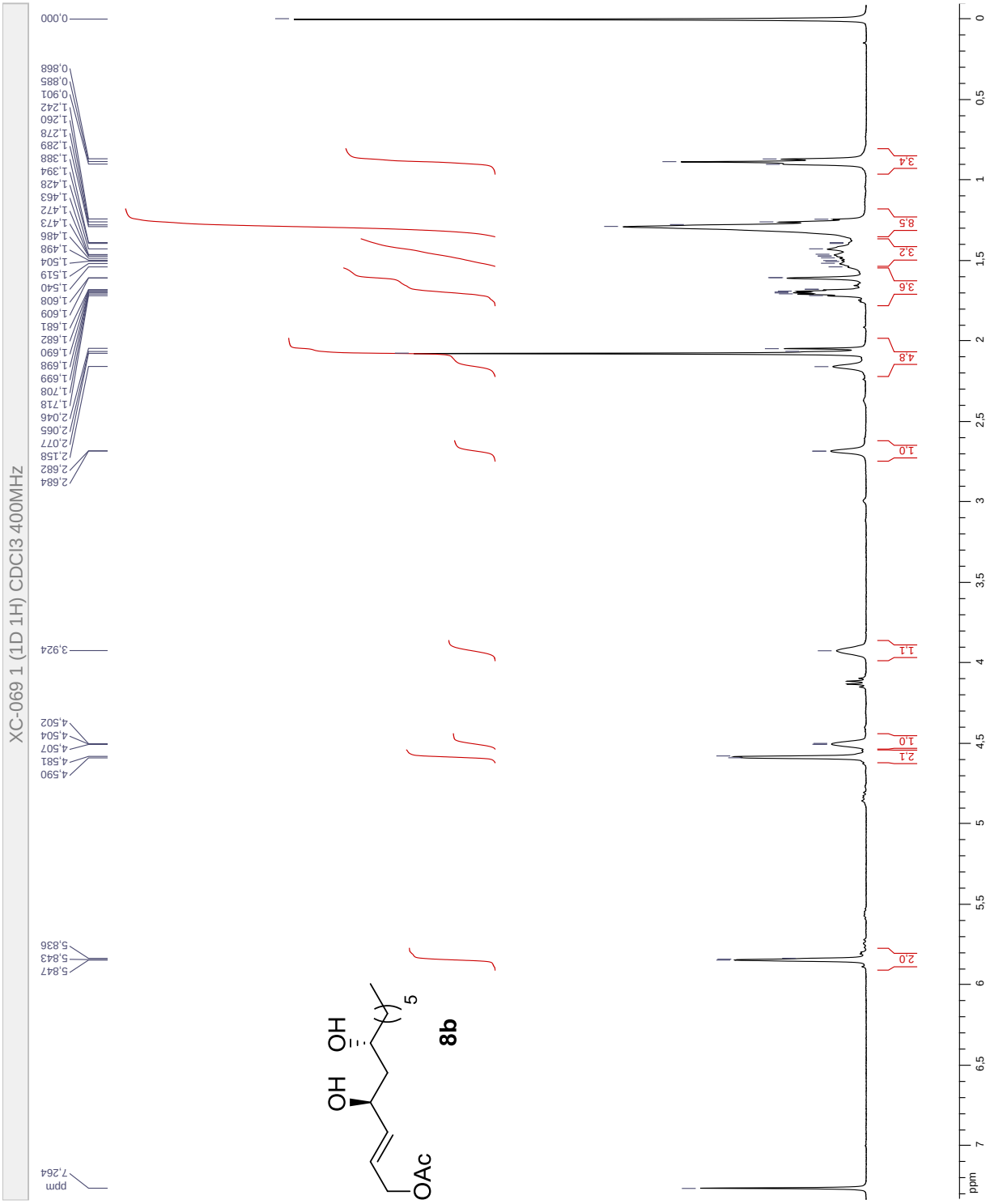
7c
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
ppm

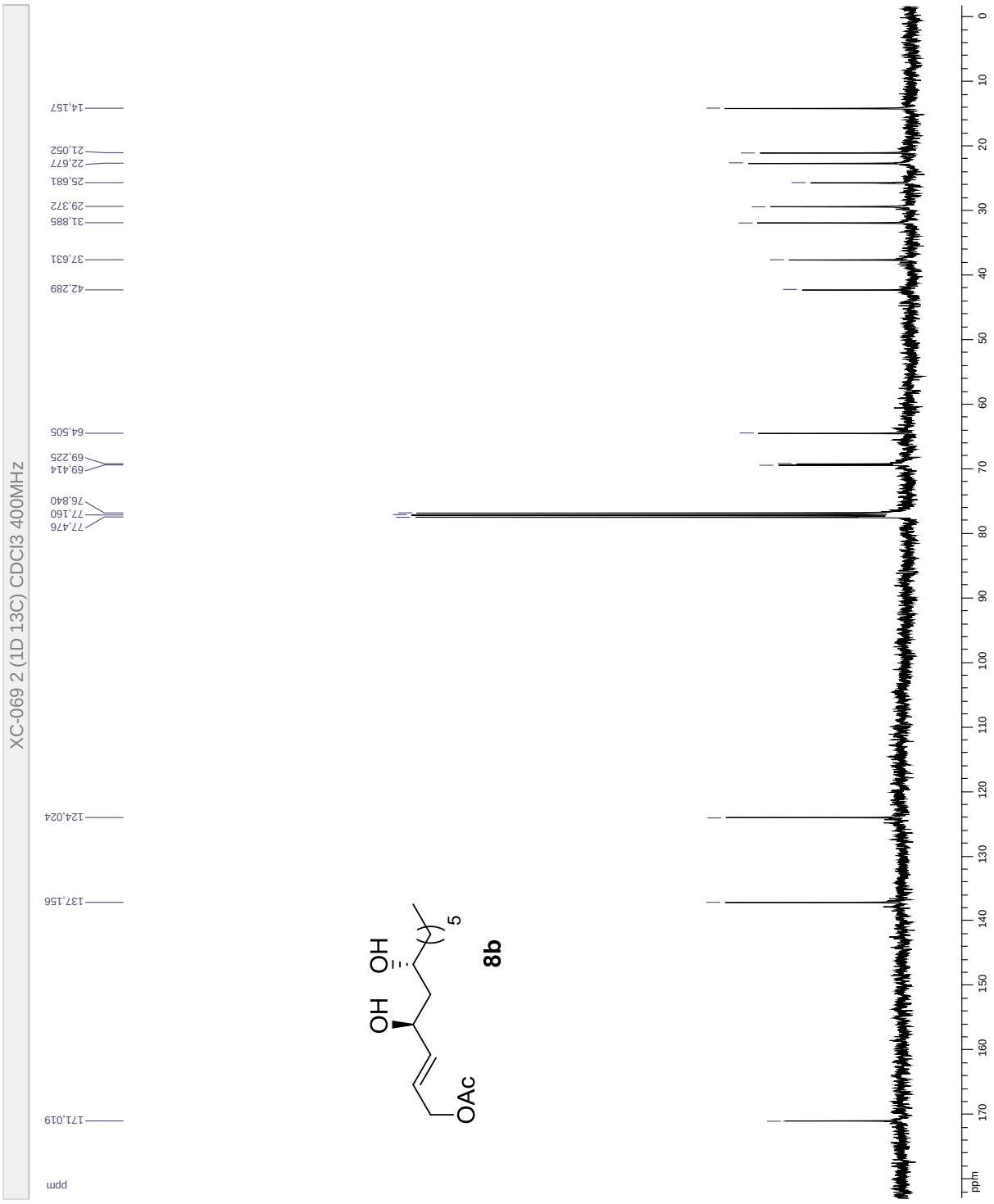

ER-1545 1 (1D 1H) CDCl3 400MHz
ppm
8,060
8,041
7,576
7,558
7,539
7,454
7,434
7,415
7,272
5,958
5,946
5,934
5,920
5,907
5,894
5,881
5,855
5,843
4,836
4,823
4,811
4,437
4,427
4,413
4,404
3,887
3,881
3,874
3,869
3,864
3,851
3,846
1,695
1,689
1,683
1,660
1,653
1,629
1,604
1,592
1,580
1,568
1,544
1,506
1,491
1,475
1,464
1,450
1,441
1,429
1,407
1,391
1,377
1,367
1,317
1,297
1,274
0,891
0,875
0,858
0,000
OH
OH
O
O
7d
1,9
1,0
1,9
1,9
2,0
0,9
1,0
1,9
12,3
3,0
ppm
8
7,5
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0

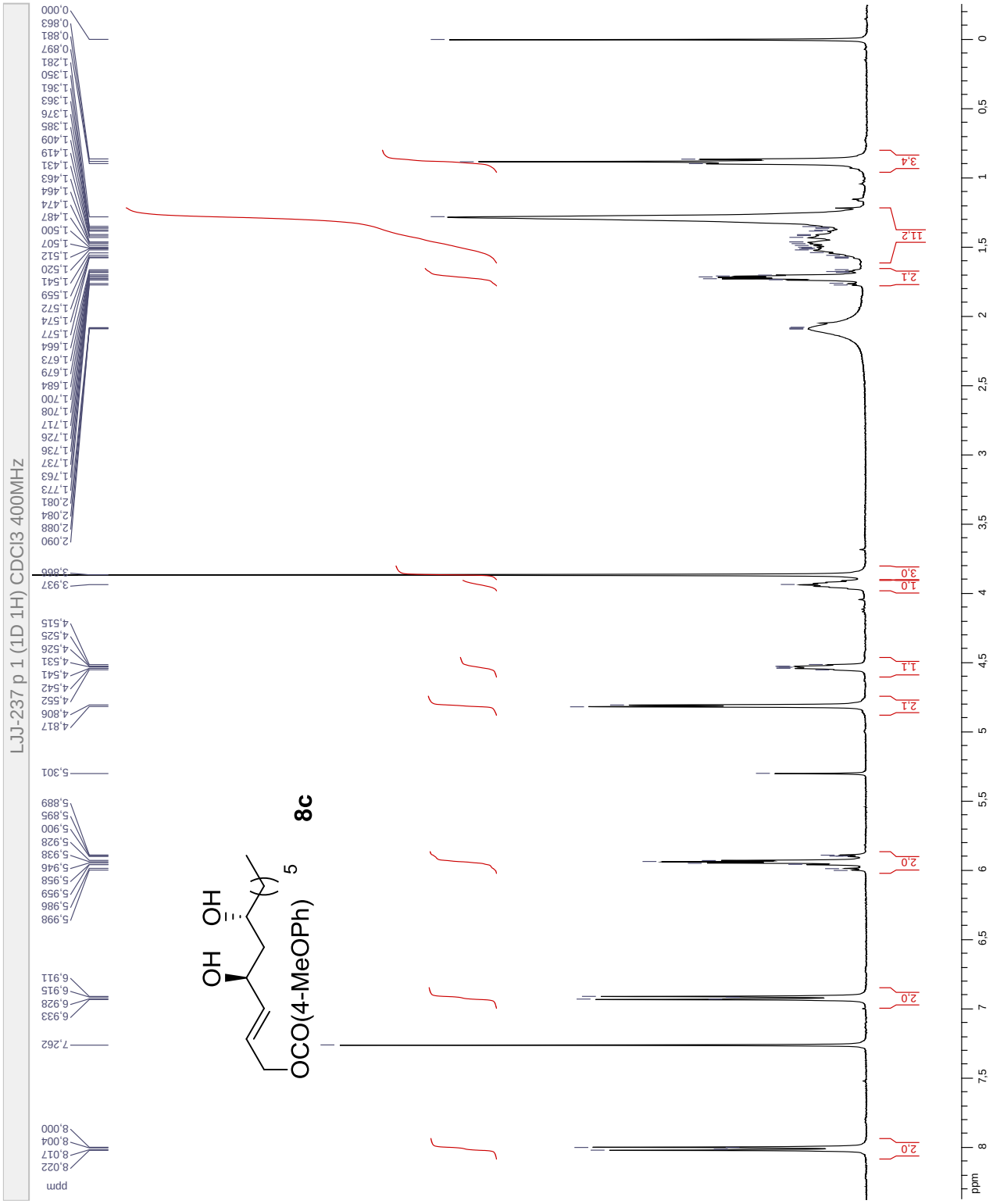

ER-1545 2 (1D 13C) CDCl3 400MHz
14,174
22,688
25,366
29,372
31,889
38,252
42,921
64,822
72,693
72,755
76,843
77,160
77,477
124,235
128,472
129,737
130,173
133,140
136,886
166,473
ppm
7d
OH
OH
O
O
ppm

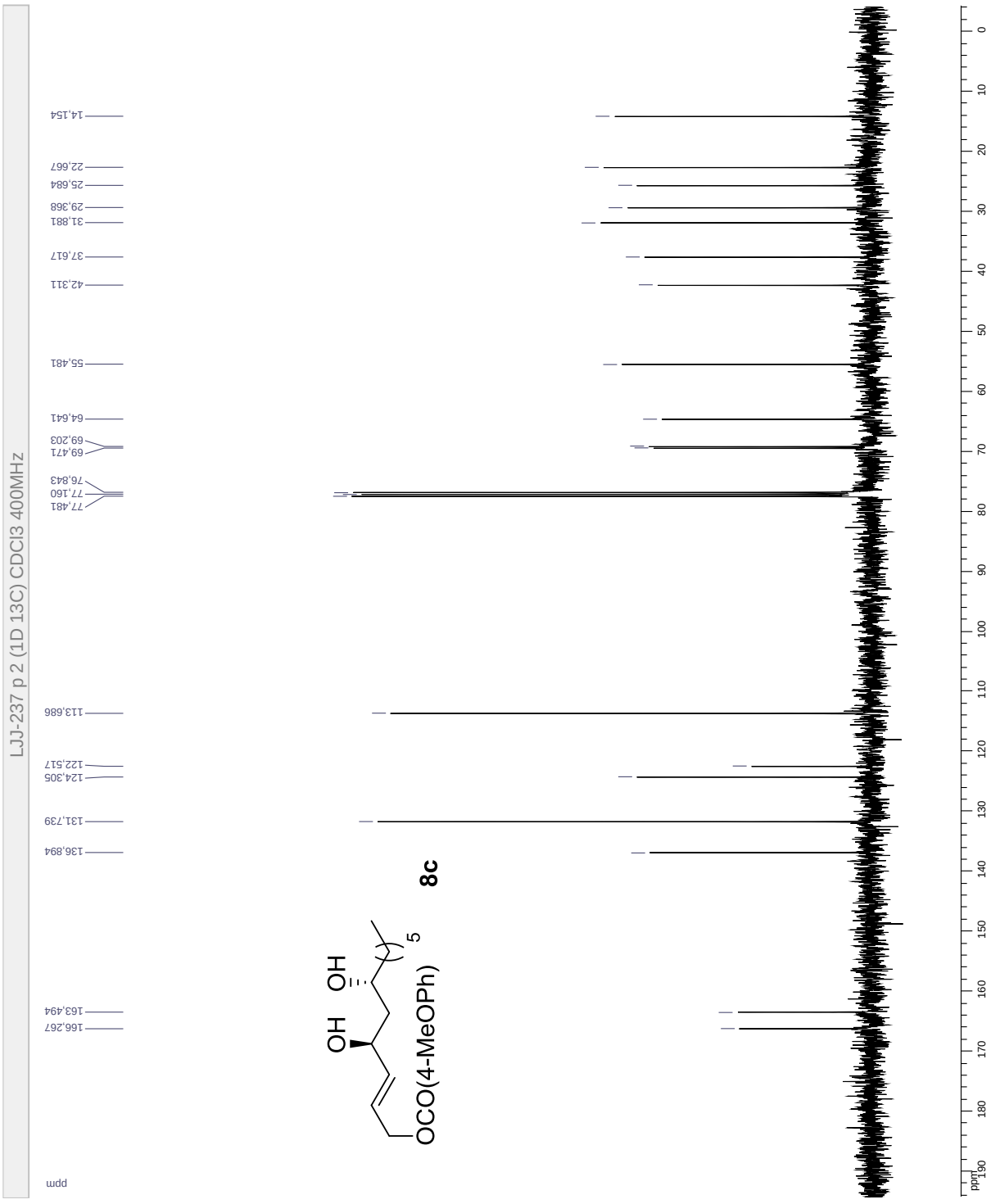

LJ-236 p 1 (1D 1H) CDCl3 400MHz
ppm
7,262
5,839
5,834
5,829
5,824
4,581
4,573
1,978
1,975
1,973
1,968
1,707
1,689
1,519
1,486
1,473
1,463
1,429
1,420
1,413
1,297
1,289
1,212
0,900
0,884
0,867
0,000
OH
OH
OPiv
5
8a
3,5
9,0
10,7
2,0
1,0
2,1
1,0
2,0

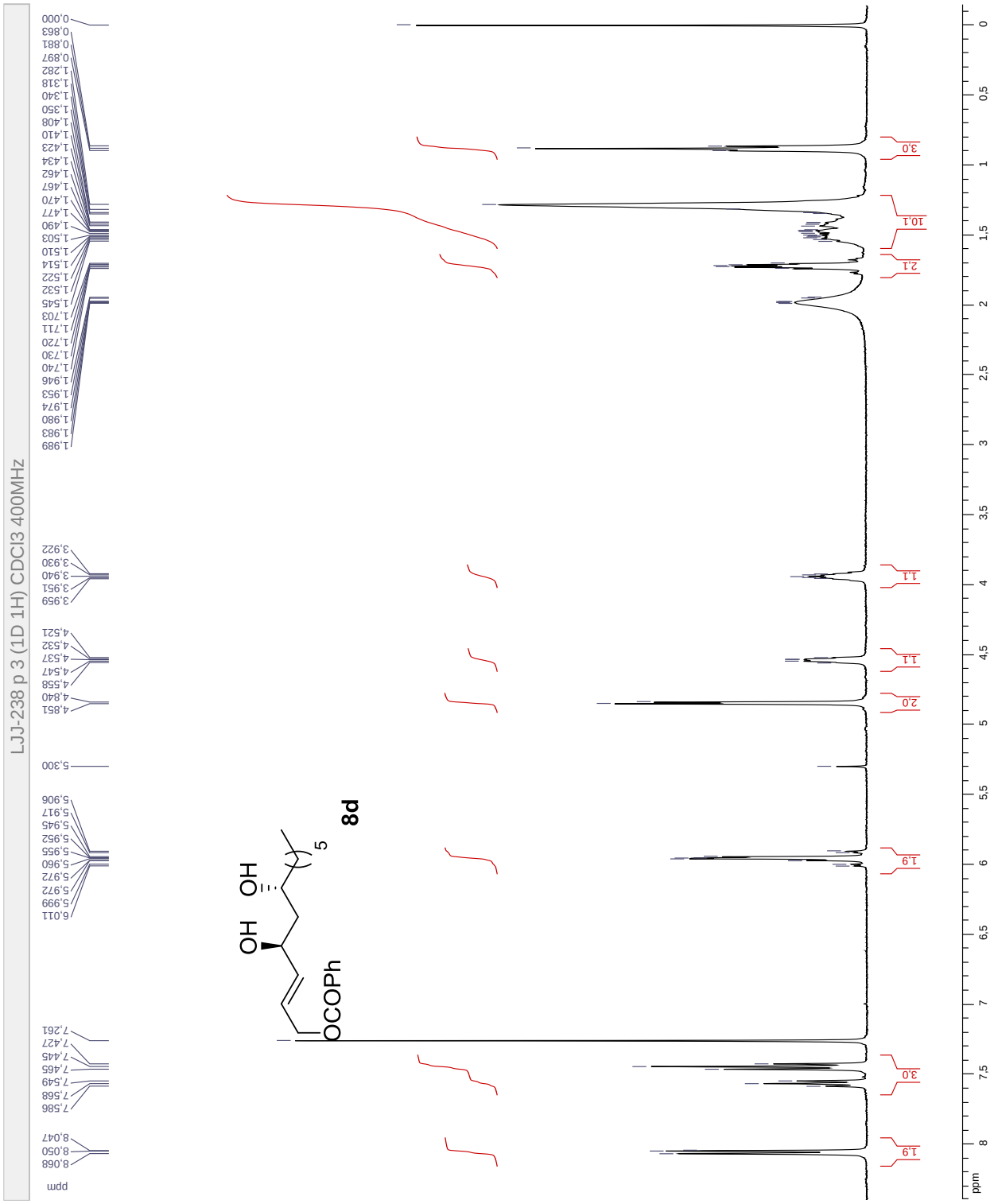

LJJ-236 2 (1D 13C) CDCl3 400MHz
ppm
178,424
136,363
132,844
125,266
124,277
77,399
77,082
76,761
69,405
69,129
64,192
62,581
42,282
38,780
37,539
31,803
29,290
27,192
25,614
22,589
14,068
OH
OH
OPiv
5
8a

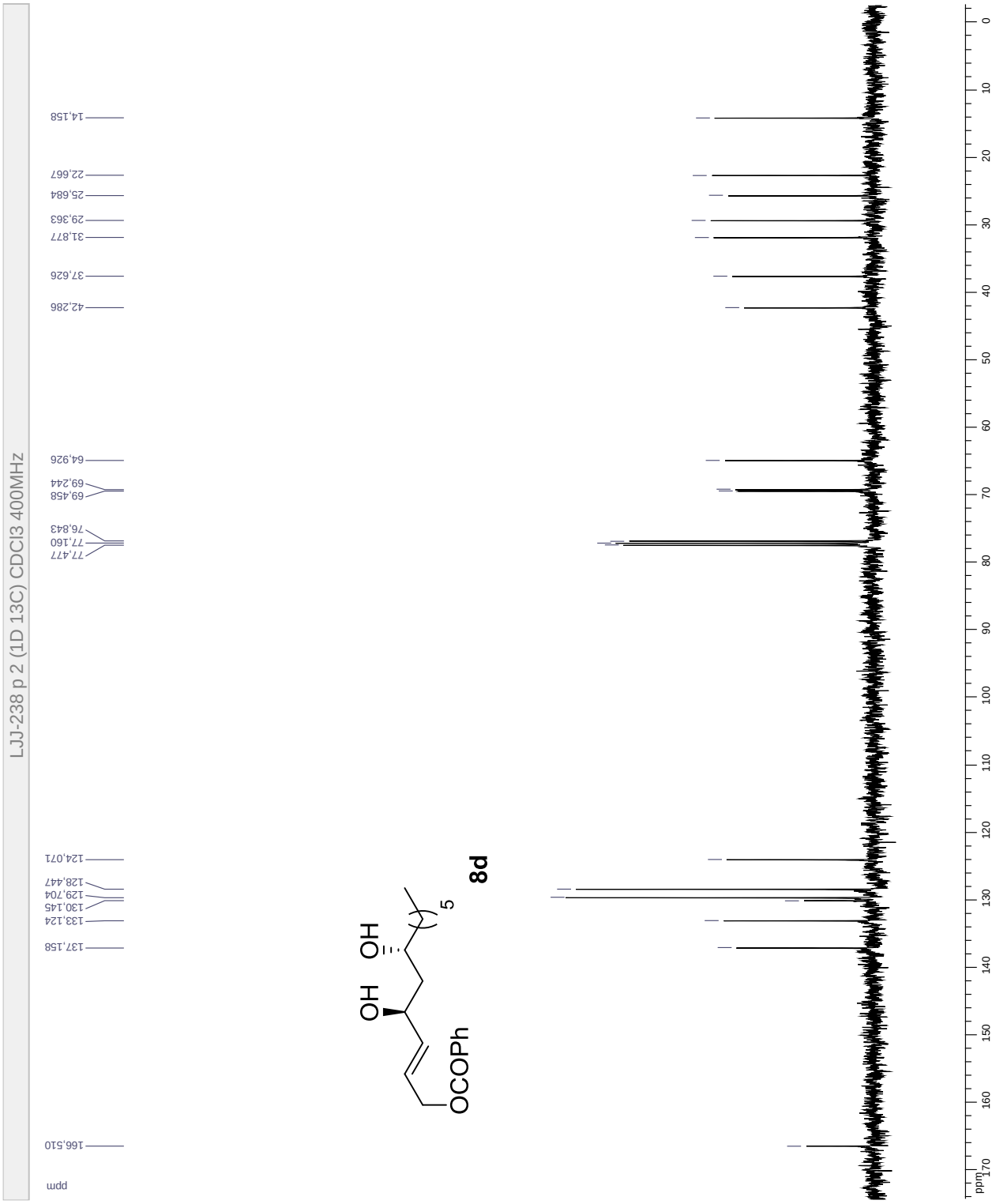

XC-069 1 (1D 1H) CDCl3 400MHz
8b
OAc
OH
OH
5

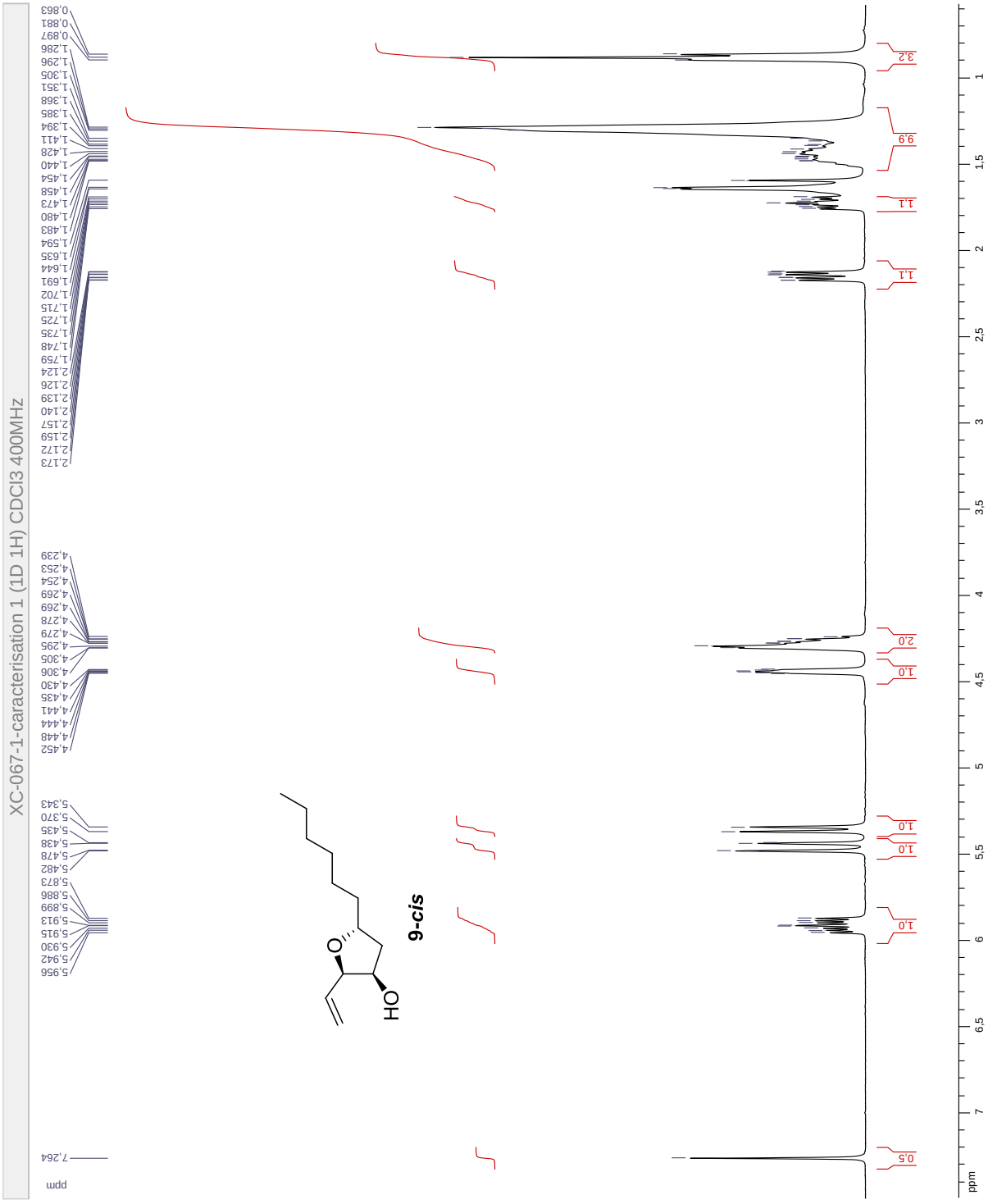

XC-069 2 (1D 13C) CDCl3 400MHz
14,157
21,052
22,677
25,681
29,372
31,885
37,631
42,289
64,505
69,225
69,414
76,840
77,160
77,476
124,024
137,156
171,019
ppm
OH
OH
OAc
5
8b

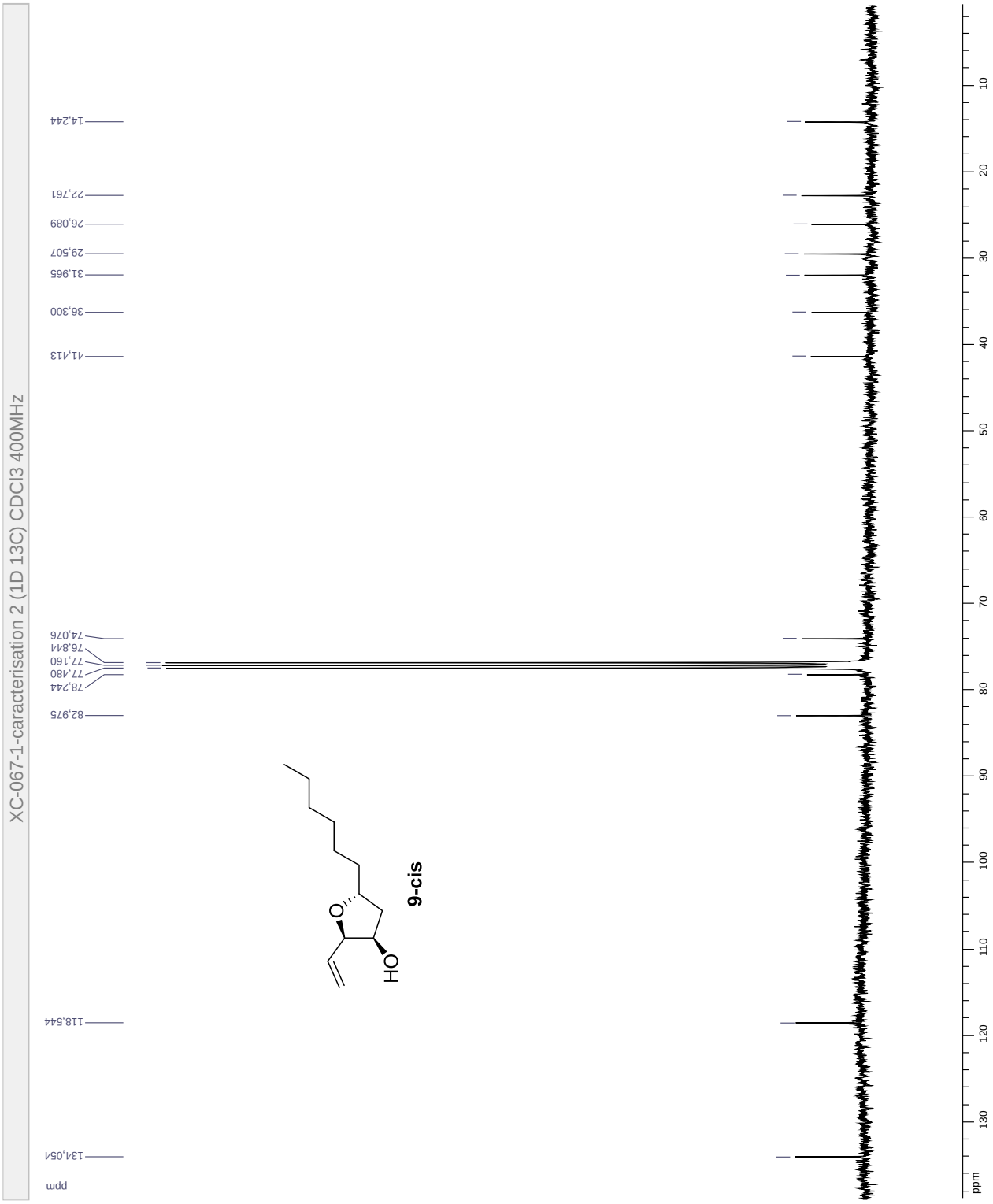

LJJ-237 p 1 (1D 1H) CDCl3 400MHz
OH
OH
OCO(4-MeOPh)
5
8c

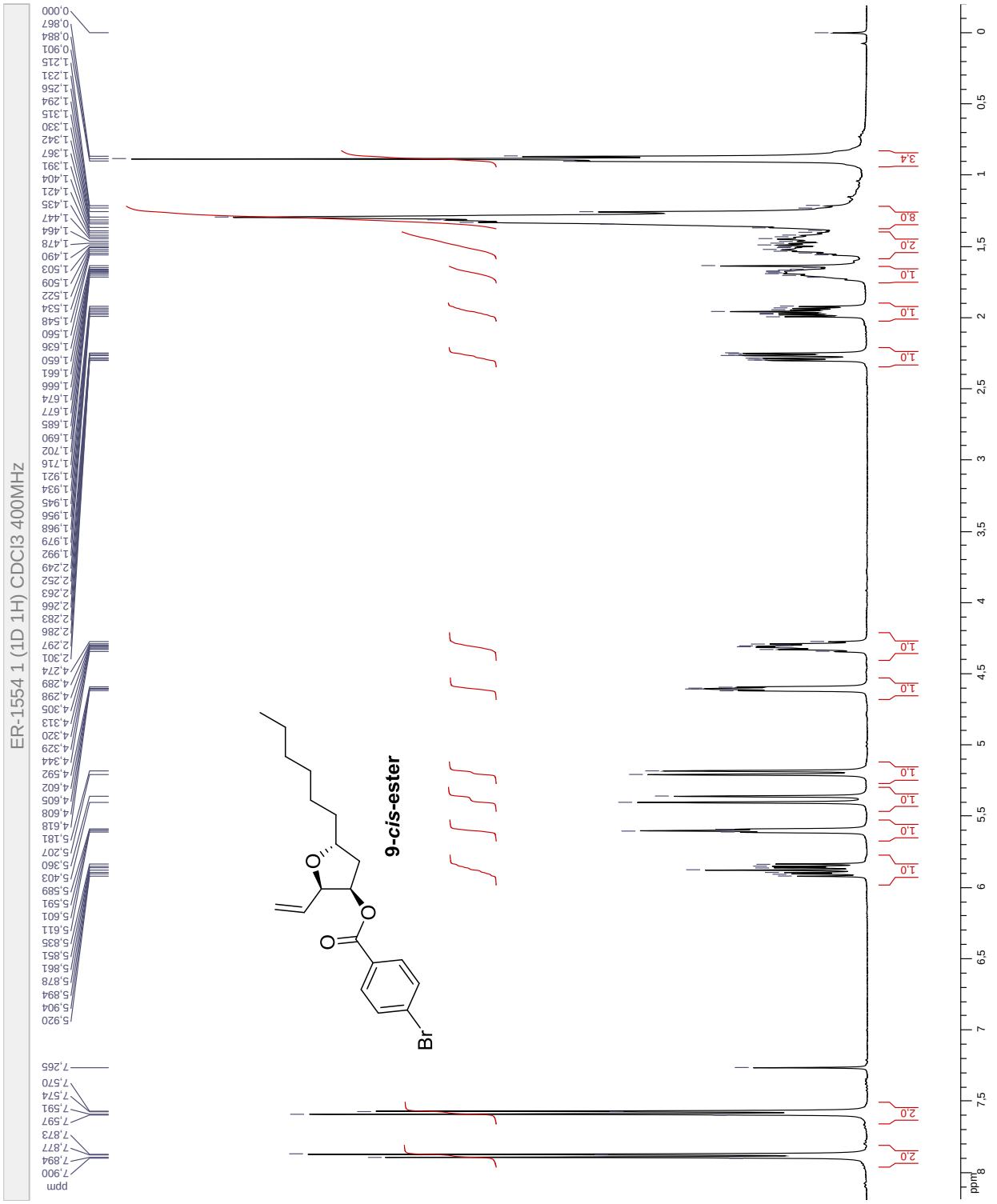

LJJ-237 p 2 (1D 13C) CDCl3 400MHz
14,154
22,667
25,684
29,368
31,881
37,617
42,311
55,481
64,641
69,203
69,471
76,843
77,160
77,481
113,686
122,517
124,305
131,739
136,894
163,494
166,267
ppm
OH
OH
5
OCO(4-MeOPh)
8c

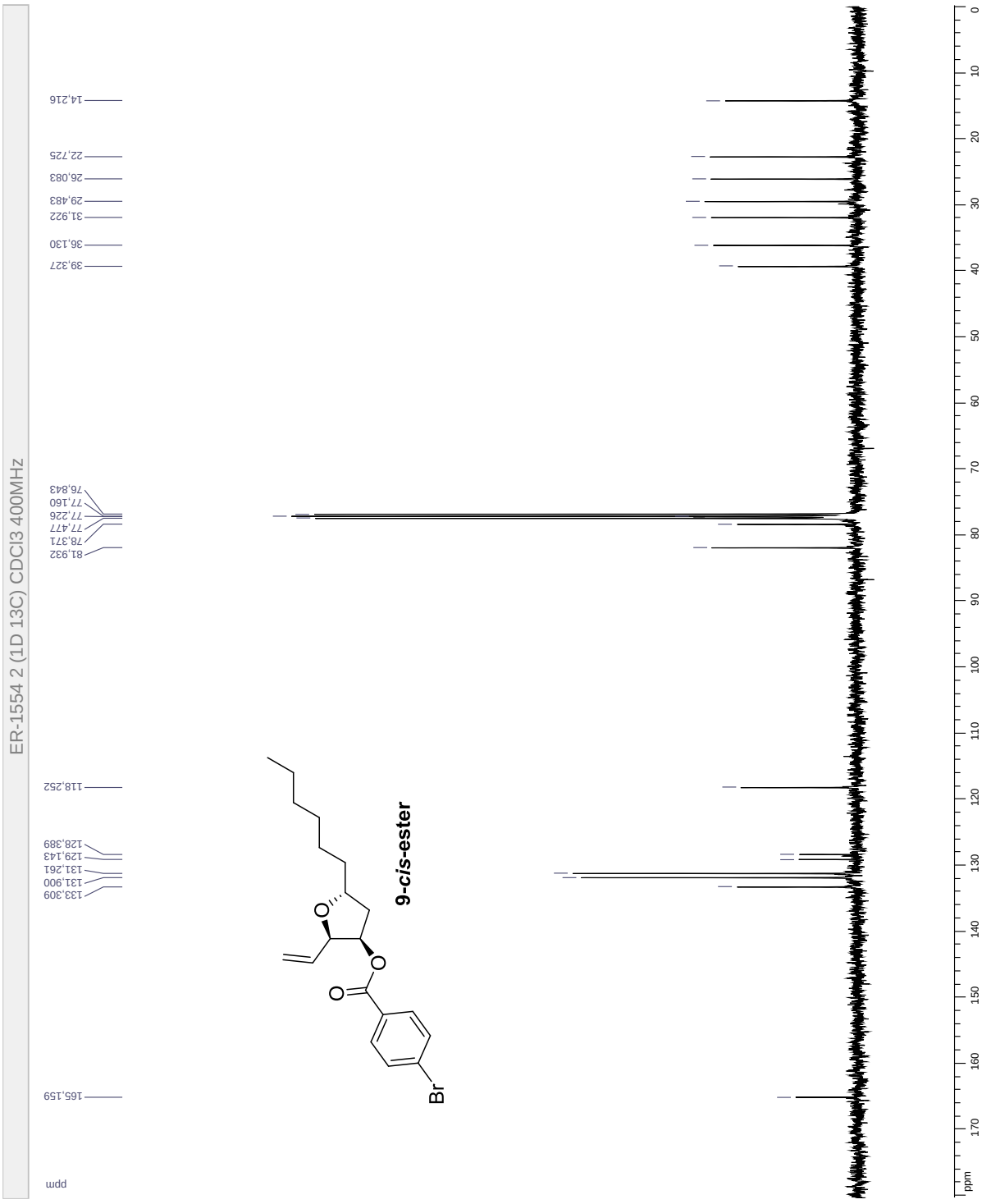

LJJ-238 p 3 (1D 1H) CDCl3 400MHz
8d
OH
OH
OCOPh
5
ppm

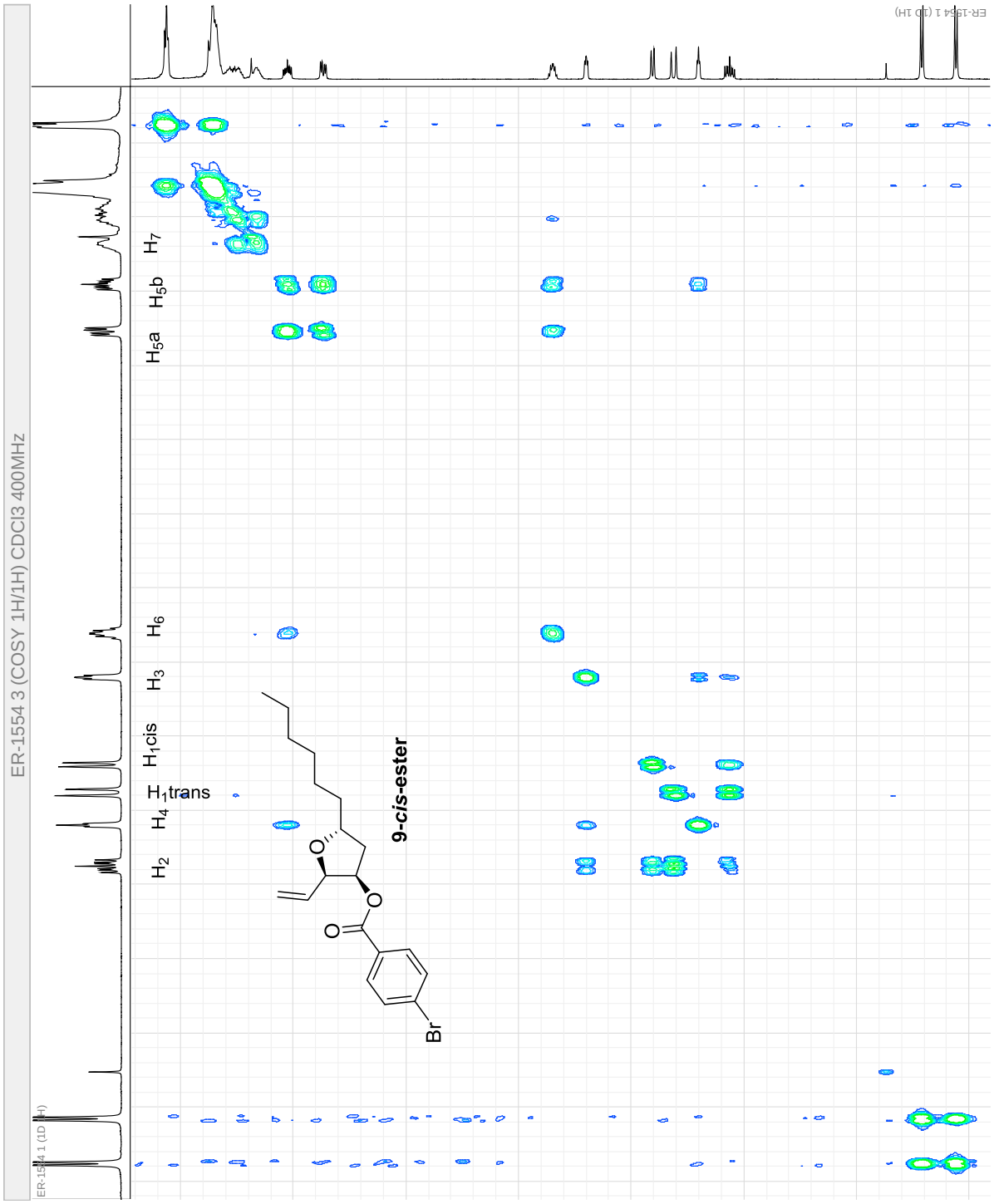

LJJ-238 p 2 (1D 13C) CDCl3 400MHz
14,158
22,667
25,684
29,363
31,877
37,626
42,286
64,926
69,458
69,244
76,843
77,160
77,477
124,071
128,447
129,704
130,145
133,124
137,158
166,510
ppm
OH
OH
5
OCOPh
8d

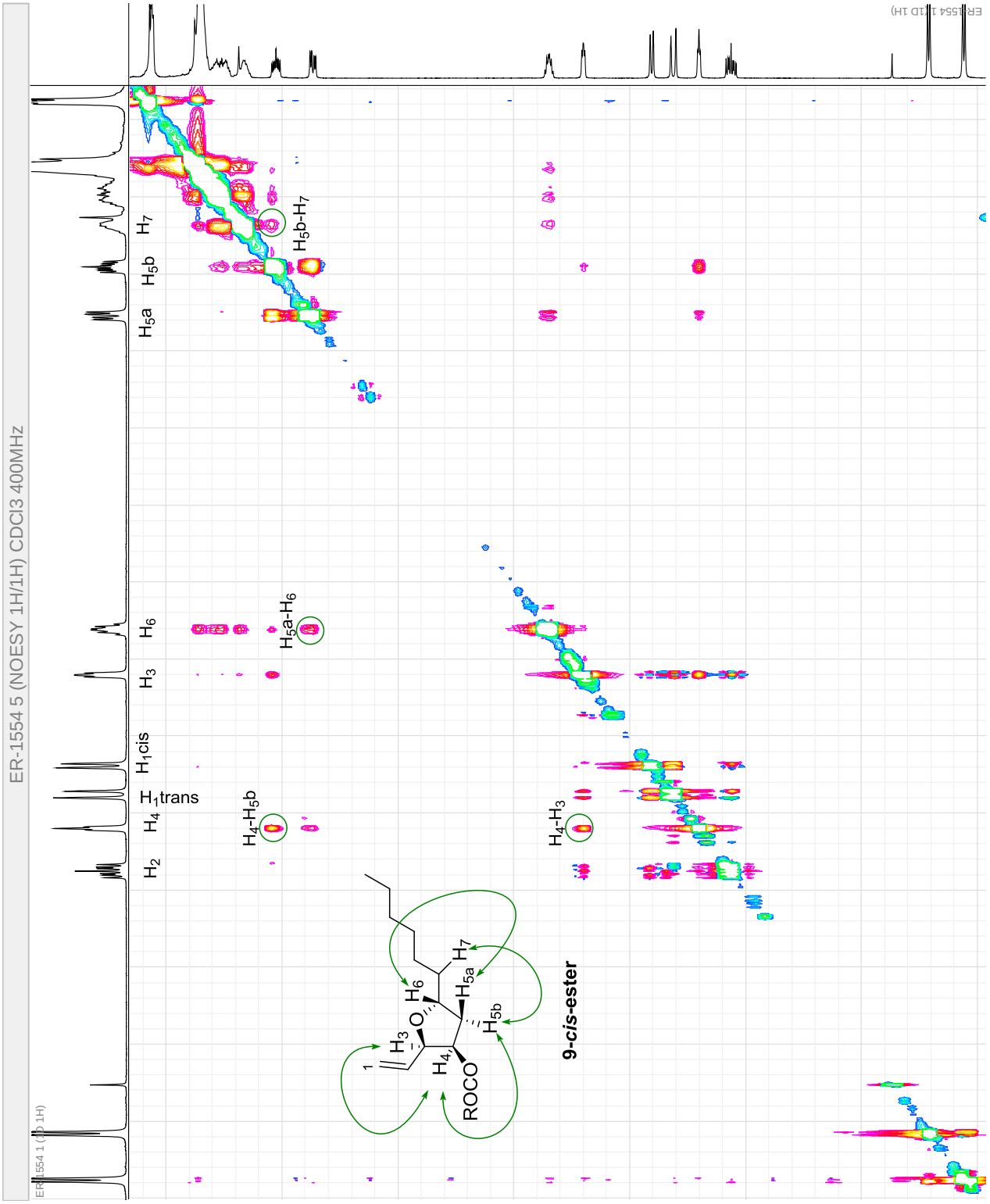

XC-067-1-caracterisation 1 (1D 1H) CDCl3 400MHz
9-cis
OH
O
ppm

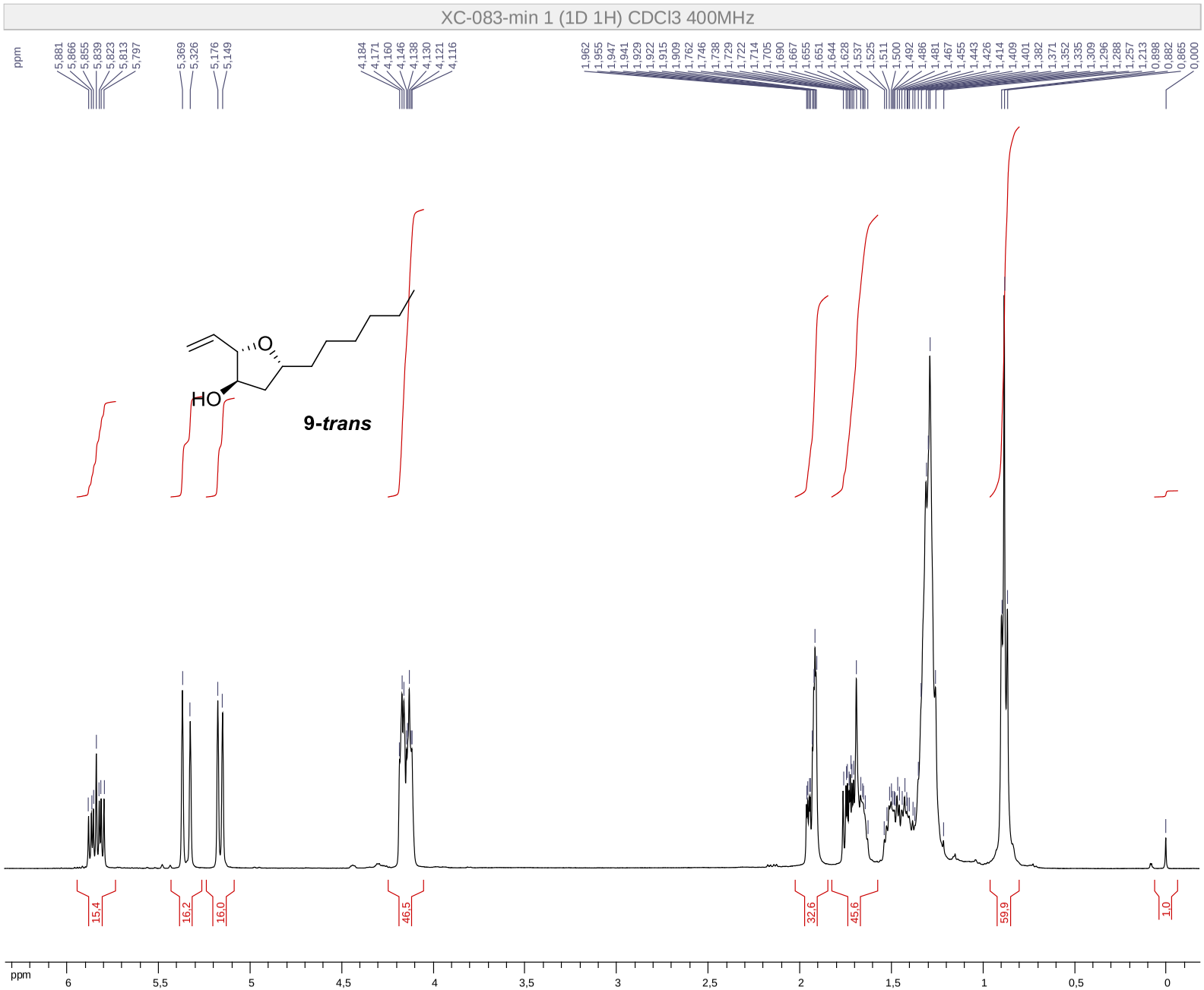

XC-067-1-caracterisation 2 (1D 13C) CDCl3 400MHz
ppm
134,054
118,544
82,975
78,244
77,480
77,160
76,844
74,076
41,413
36,300
31,965
29,507
26,089
22,761
14,244
9-cis
OH
O
ppm

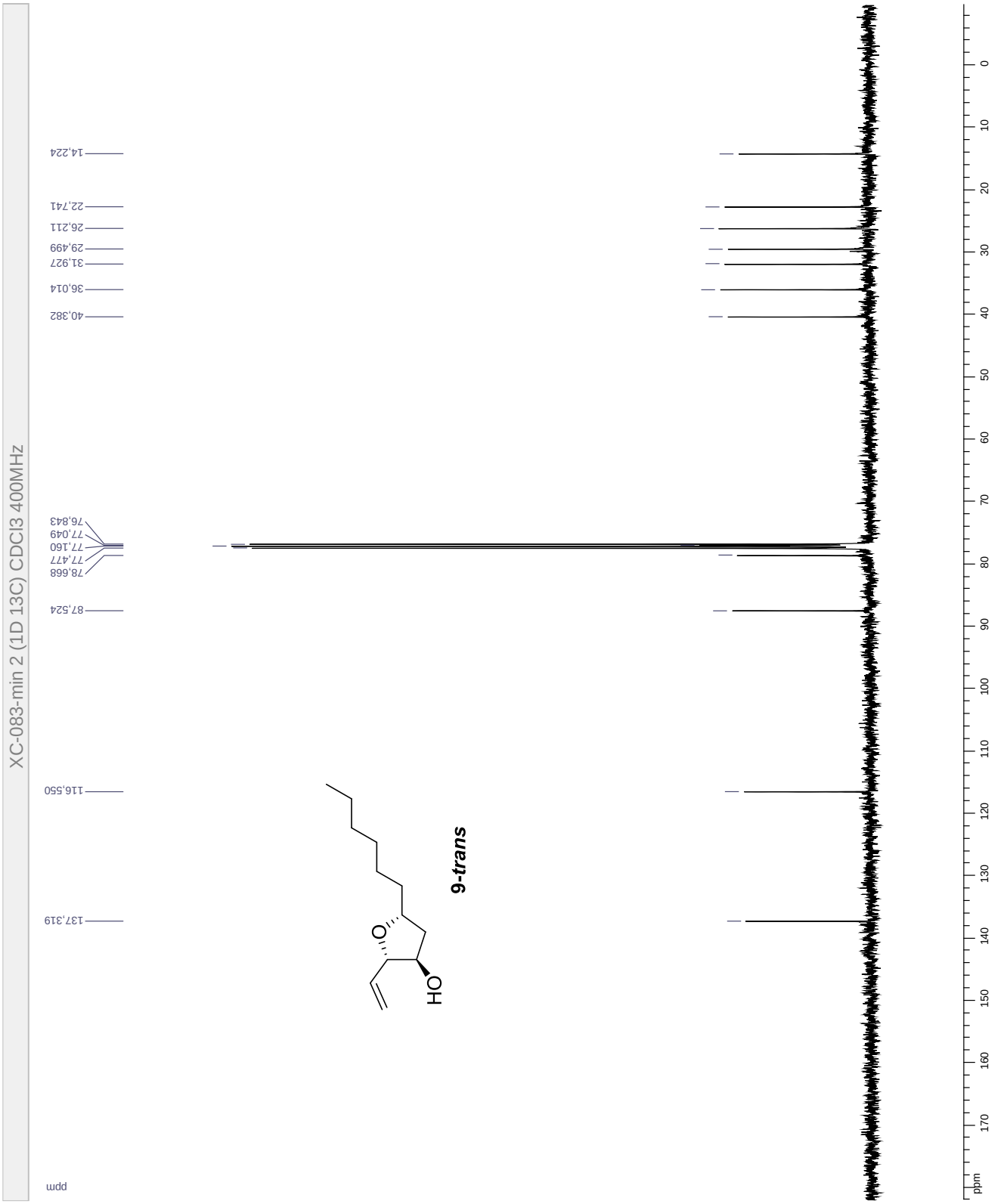

ER-1554 1 (1D 1H) CDCl3 400MHz
9-cis-ester
Br
O
O
O
ppm

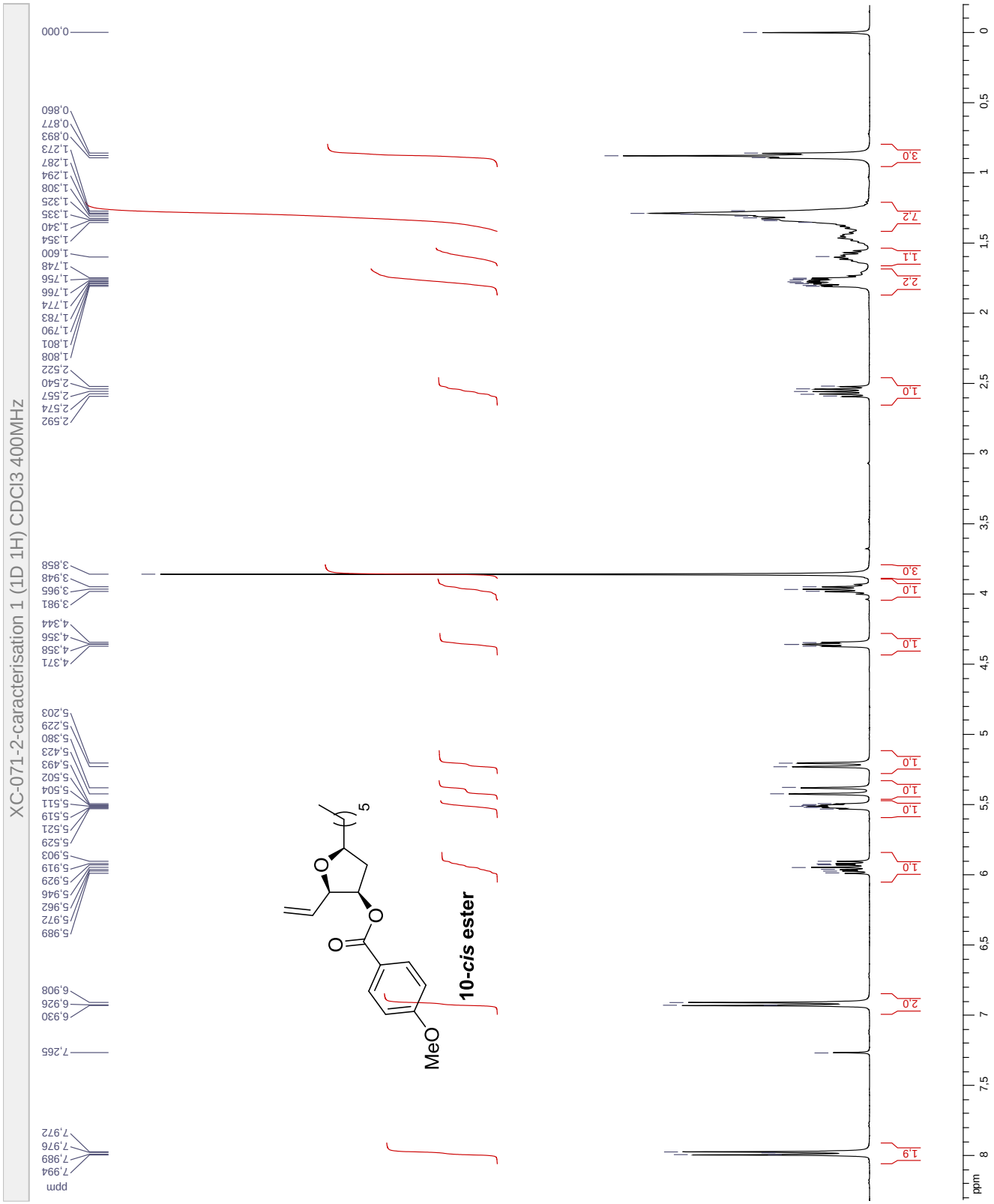

ER-1554 2 (1D 13C) CDCl3 400MHz
14,216
22,725
26,083
29,483
31,922
36,130
39,327
76,843
77,160
77,226
77,477
78,371
81,932
118,252
128,389
129,143
131,261
131,900
133,309
165,159
ppm
9-cis-ester
Br
O
O
O
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
ppm

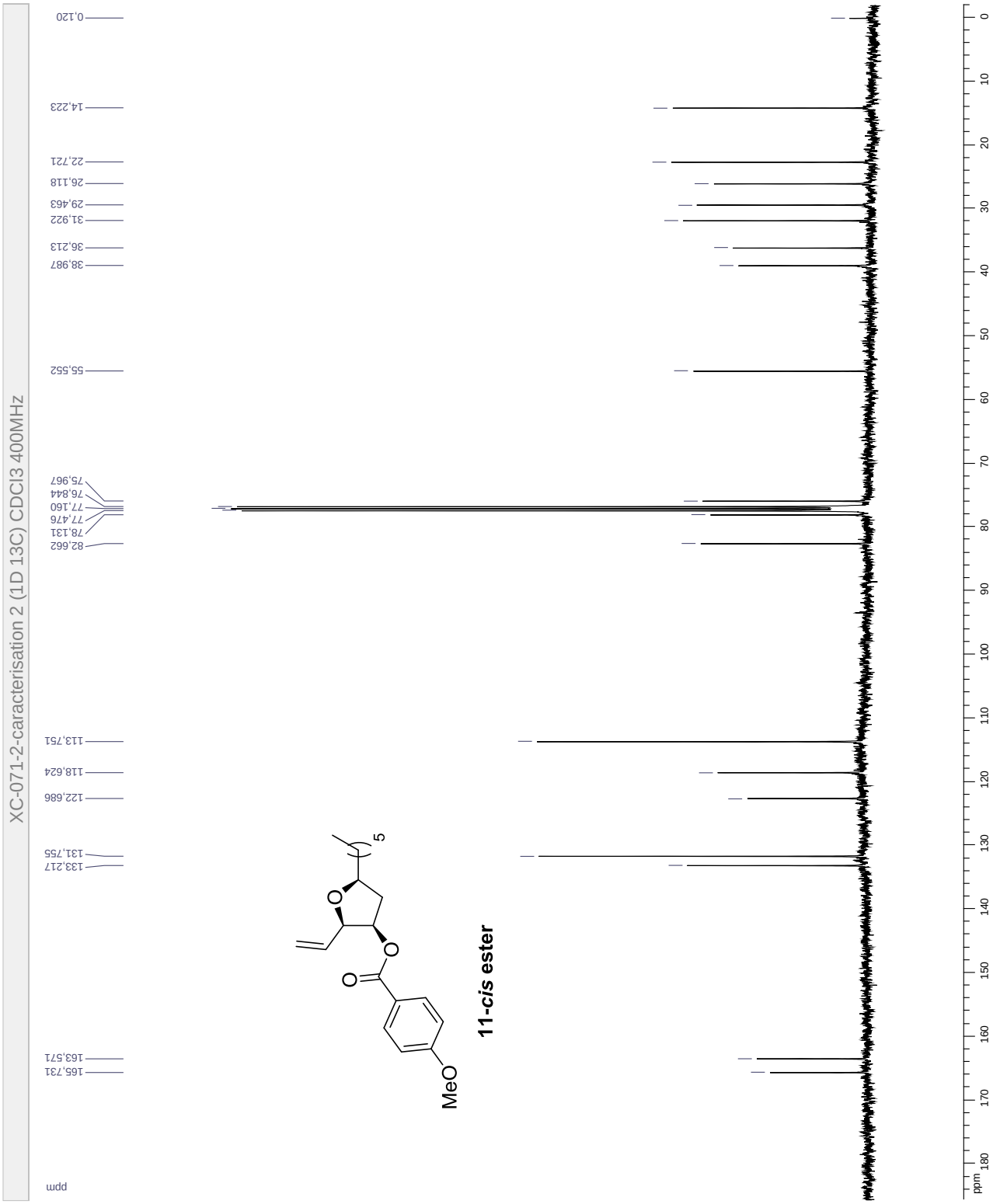

ER-1554 3 (COSY 1H/1H) CDCl3 400MHz
H7
H5b
H5a
H6
H3
H1cis
H1trans
H4
H2
9-cis-ester
O
O
O
Br

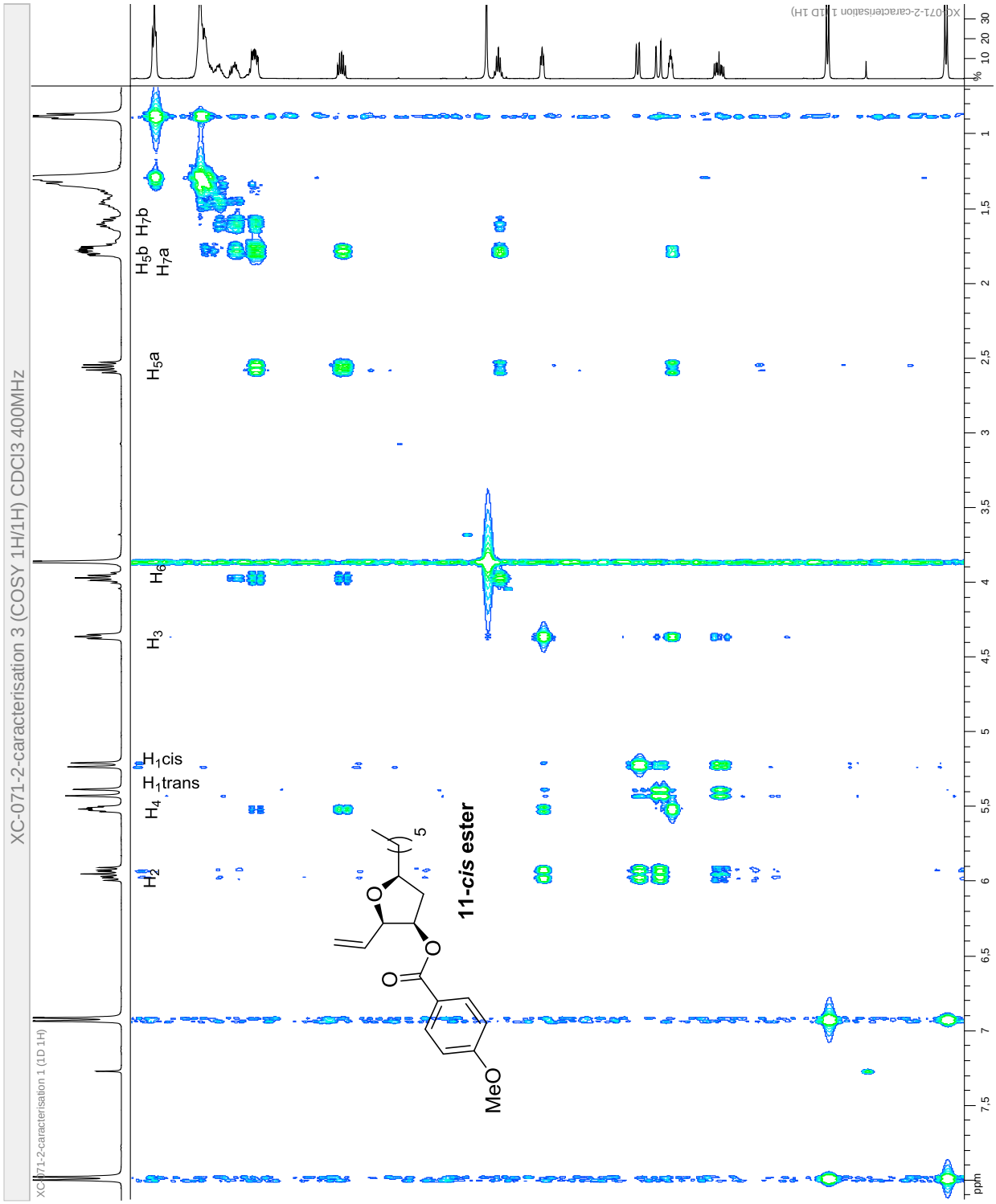

ER-1554 5 (NOESY 1H/1H) CDCl3 400MHz
H7
H5b
H5a
H6
H3
H1cis
H1trans
H4
H2
H5b-H7
H5a-H6
H4-H5b
H4-H3
H7
H6
H5a
H5b
H3
O
H4
ROCO
1
9-cis-ester

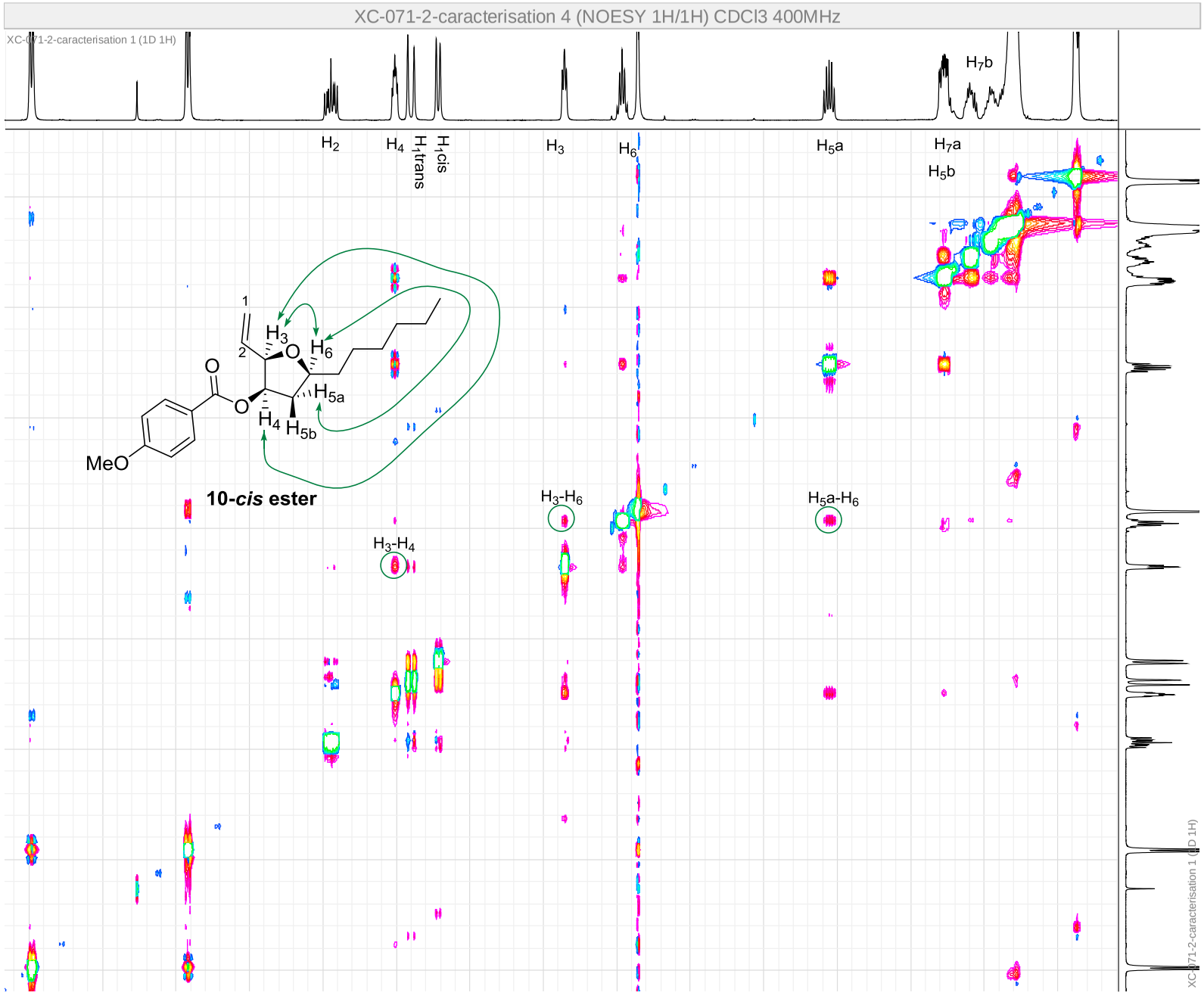

XC-083-min 1 (1D 1H) CDCl3 400MHz
ppm
5.881
5.866
5.855
5.839
5.823
5.813
5.797
5.369
5.326
5.176
5.149
4.184
4.171
4.160
4.146
4.138
4.130
4.121
4.116
1.962
1.955
1.947
1.941
1.929
1.922
1.915
1.909
1.762
1.746
1.738
1.729
1.722
1.714
1.705
1.690
1.667
1.655
1.651
1.644
1.628
1.537
1.525
1.511
1.500
1.492
1.486
1.481
1.467
1.455
1.443
1.426
1.414
1.409
1.401
1.382
1.371
1.352
1.335
1.309
1.296
1.288
1.257
1.213
0.898
0.882
0.865
0.000
O
HO
9-trans
15.4
16.2
16.0
46.5
32.6
45.6
59.9
1.0
ppm
6
5,5
5
4,5
4
3,5
3
2,5
2
1,5
1
0,5
0


XC-083-min 2 (1D 13C) CDCl3 400MHz
14,224
22,741
26,211
29,499
31,927
36,014
40,382
76,843
77,049
77,160
77,477
78,668
87,524
116,550
137,319
ppm
9-trans
OH
O
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
ppm

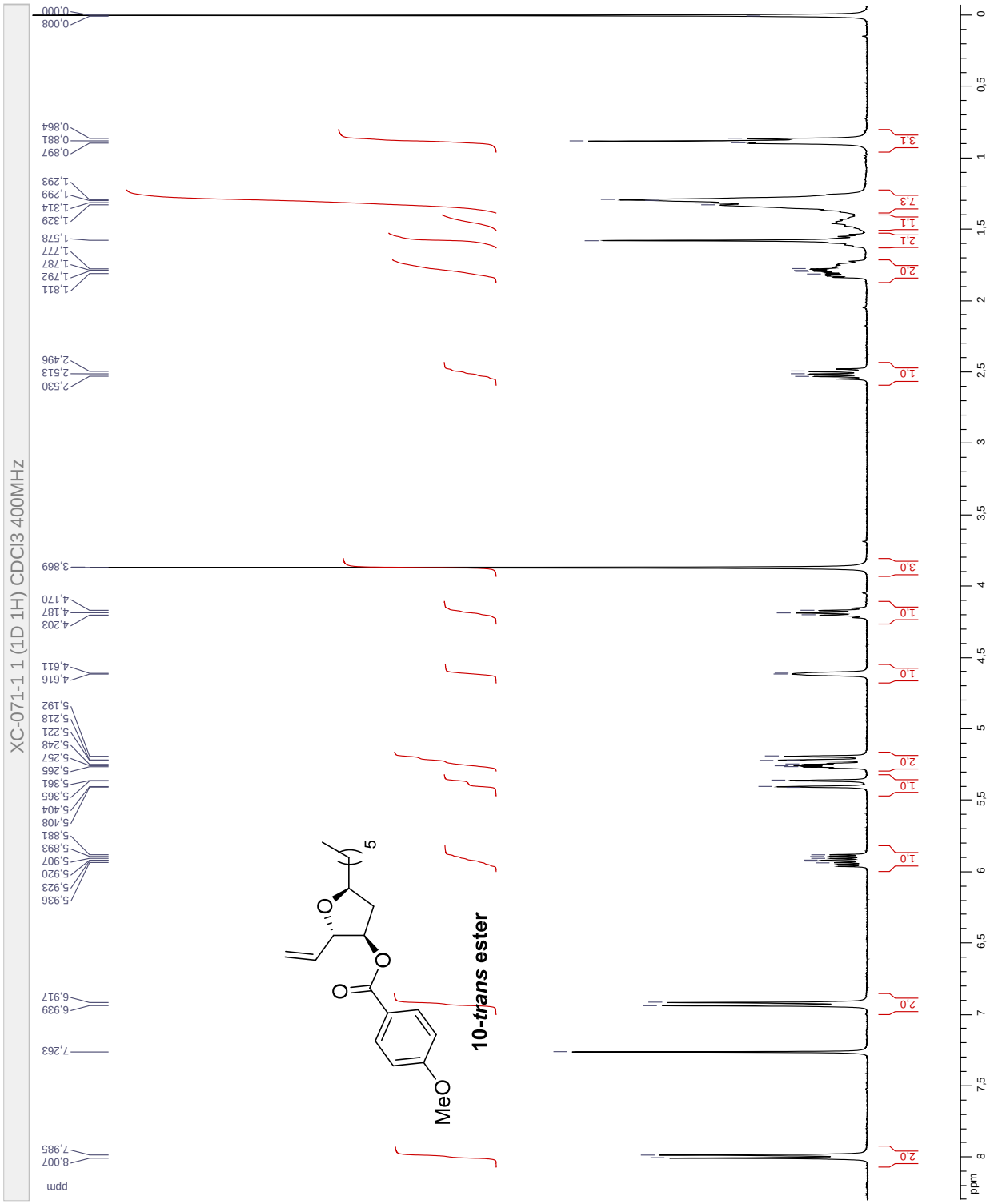

XC-071-2-caracterisation 1 (1D 1H) CDCl3 400MHz
10-cis ester
MeO
O
O
O
5
ppm

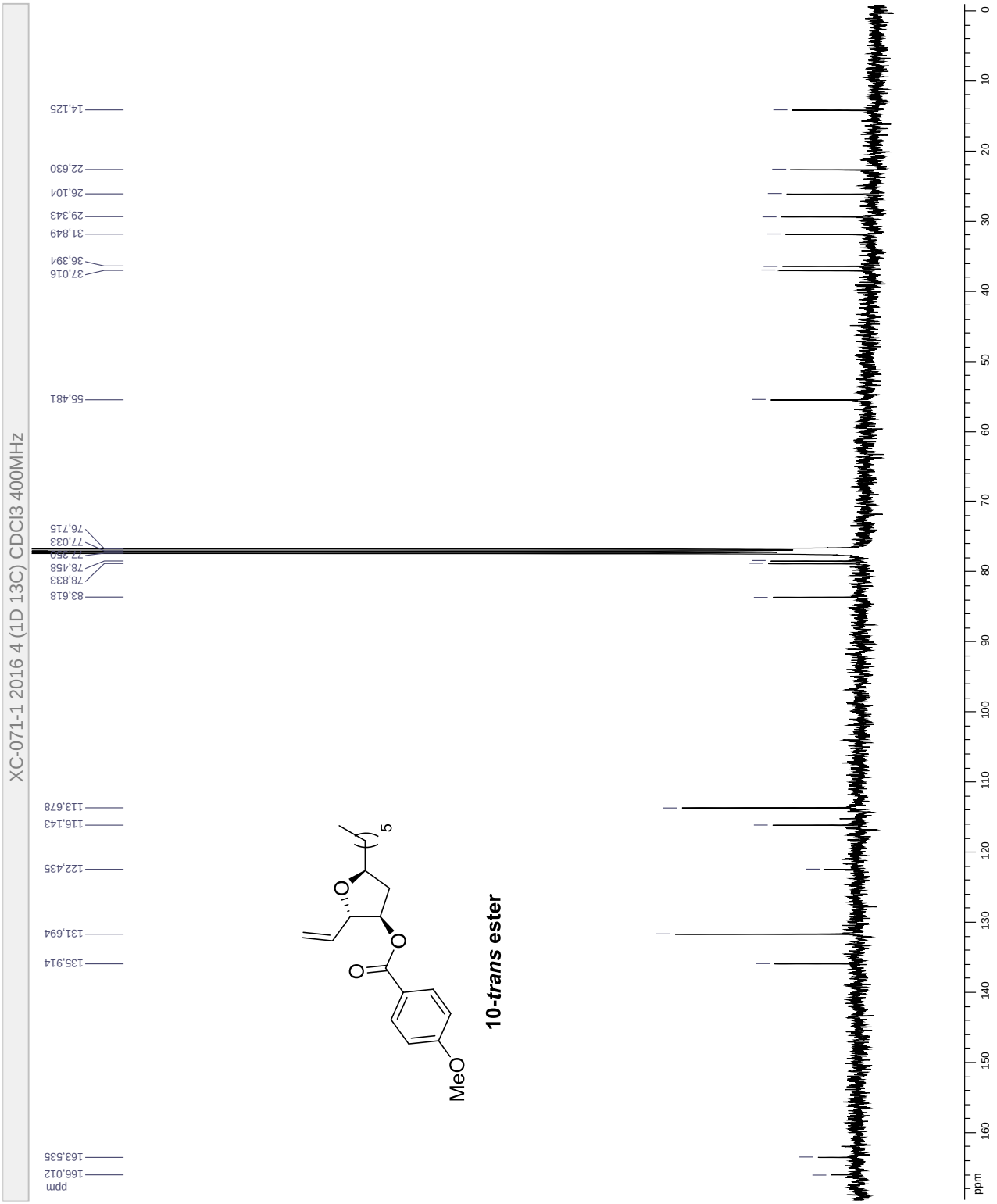

XC-071-2-caracterisation 2 (1D 13C) CDCl3 400MHz
ppm
0.120
14.223
22.721
26.118
29.463
31.922
36.213
38.987
55.552
75.967
76.844
77.160
77.476
78.131
82.662
113.751
118.624
122.686
131.755
133.217
163.571
165.731
MeO
11-cis ester

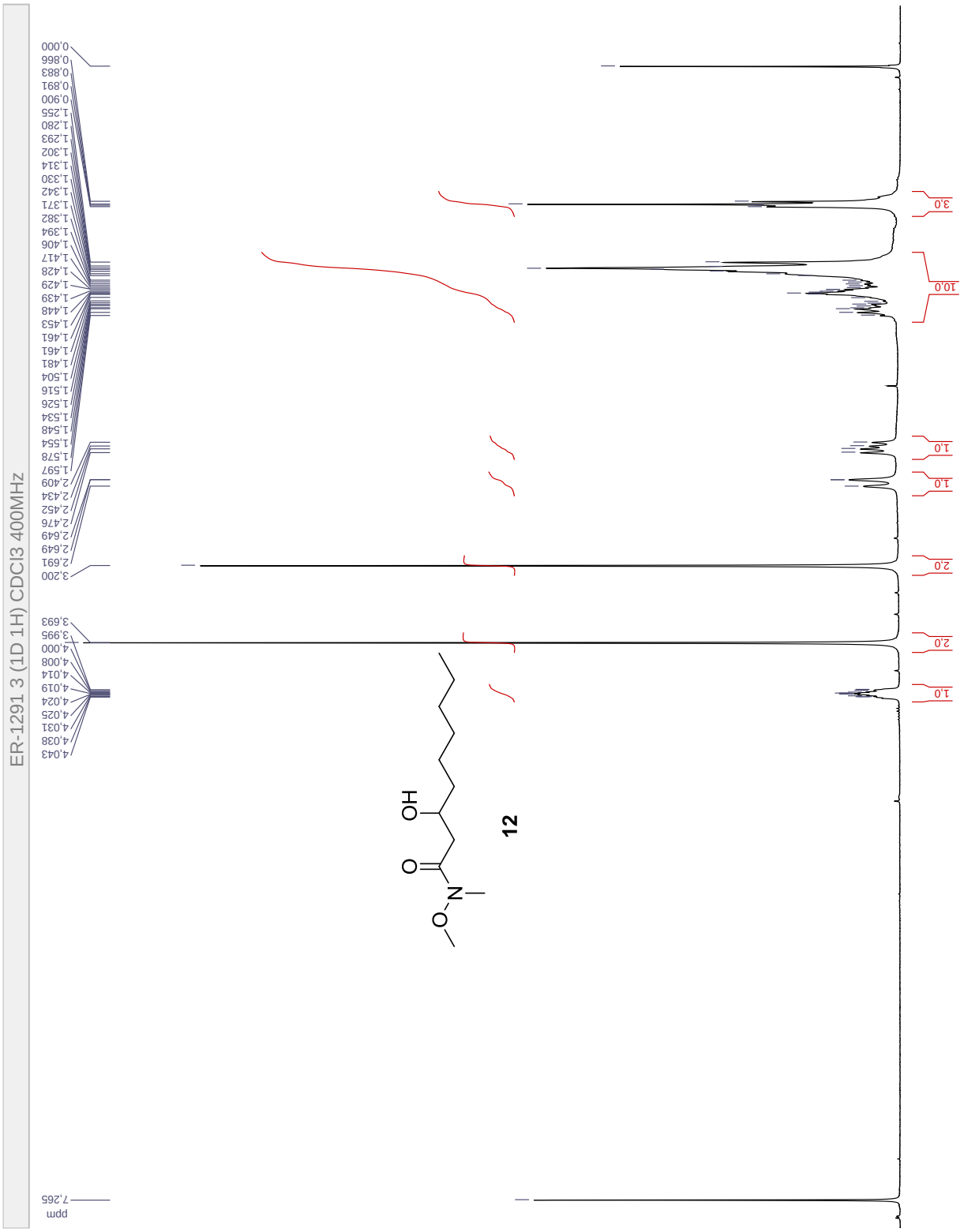

XC-071-2-caracterisation 3 (COSY 1H/1H) CDCl3 400MHz
XC-071-2-caracterisation 1 (1D 1H)
H5b H7b
H7a
H5a
H6
H3
H1cis
H1trans
H4
H2
11-cis ester
MeO
ppm

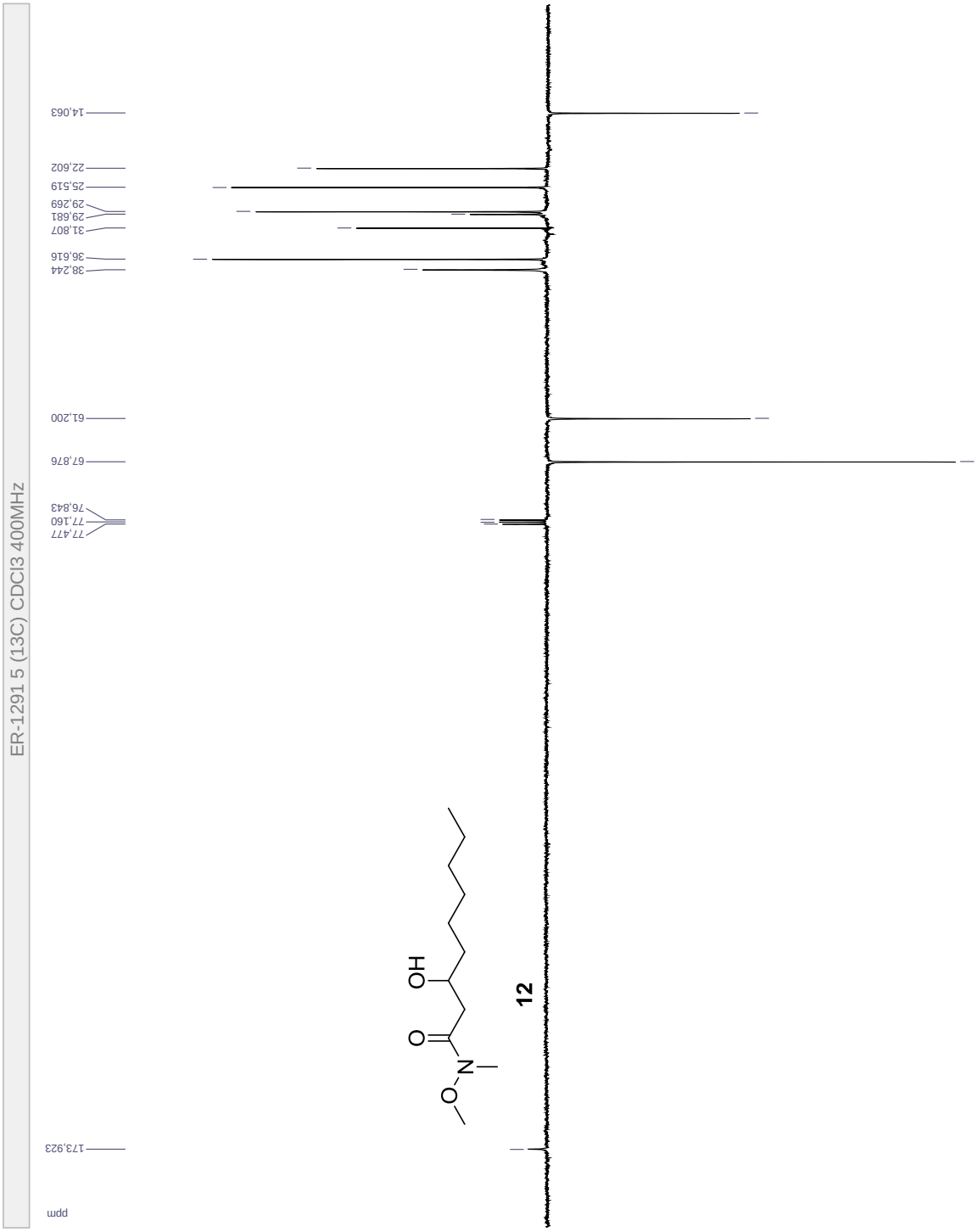

XC-071-2-caracterisation 4 (NOESY 1H/1H) CDCl3 400MHz
XC-071-2-caracterisation 1 (1D 1H)
H7b
H2
H4
H1trans
H1cis
H3
H6
H5a
H7a
H5b
H3-H6
H5a-H6
H3-H4
10-cis ester
MeO
XC-071-2-caracterisation 1 (1D 1H)

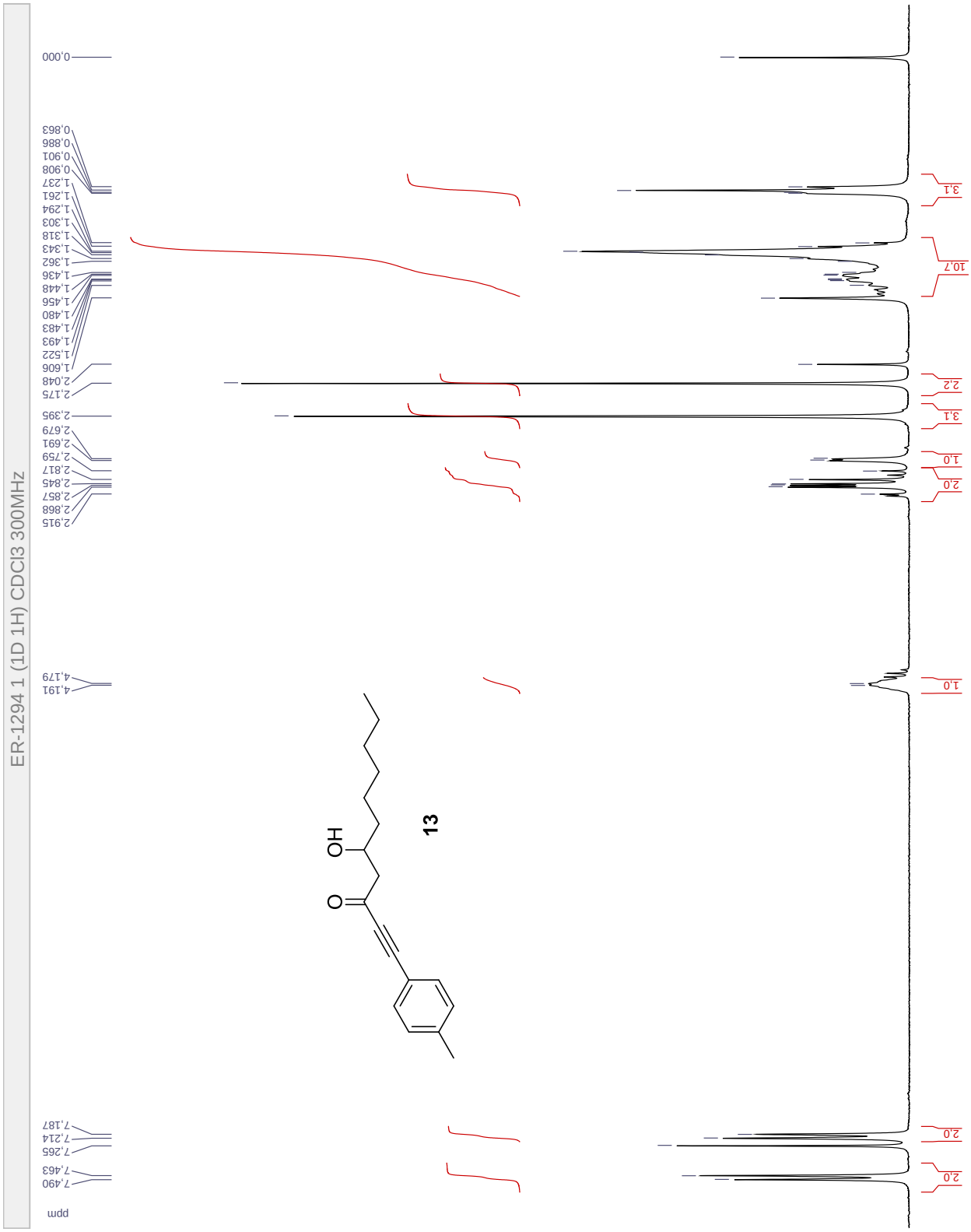
H1cis

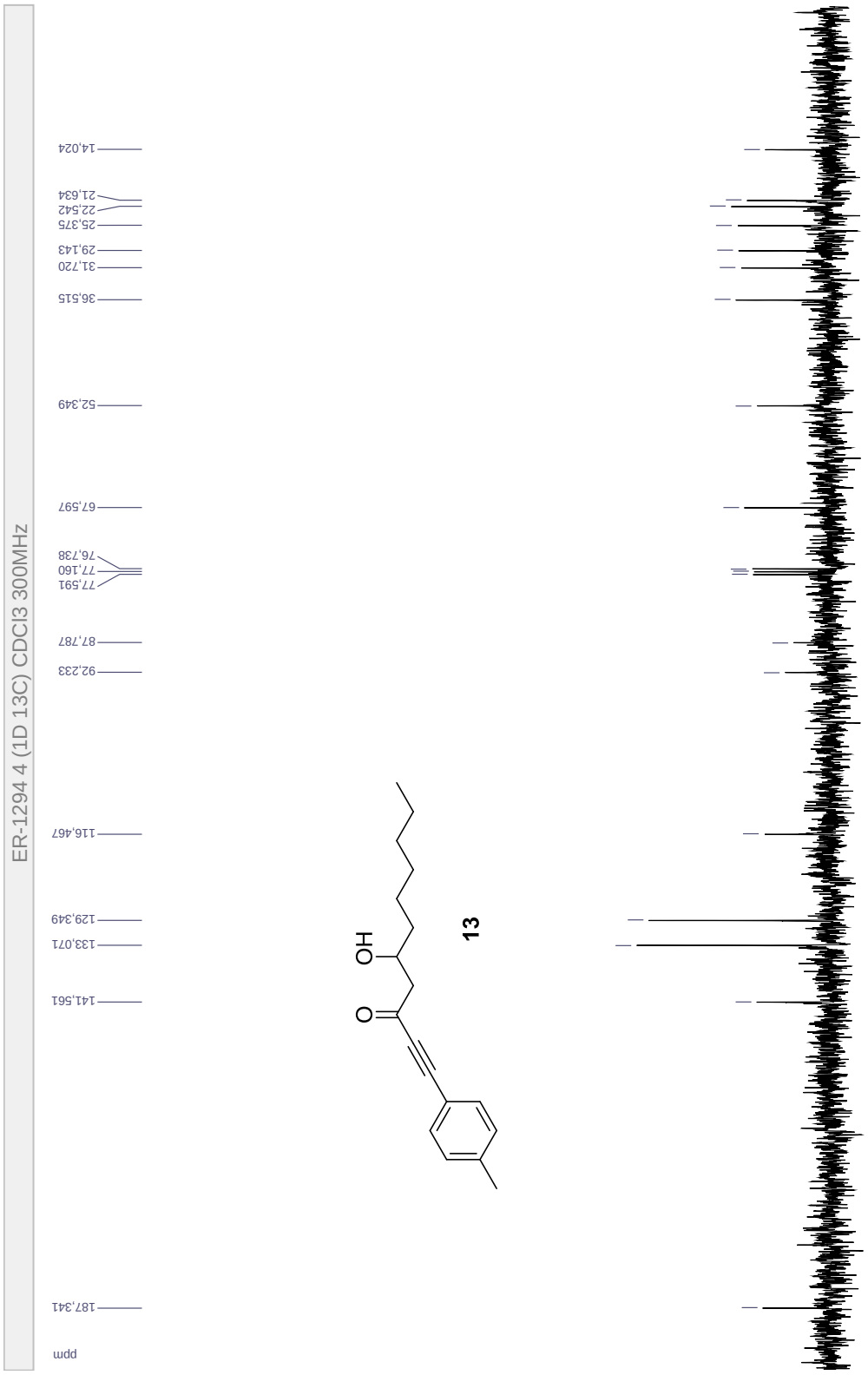

XC-071-1 1 (1D 1H) CDCl3 400MHz
10-trans ester
MeO
O
O
5
ppm

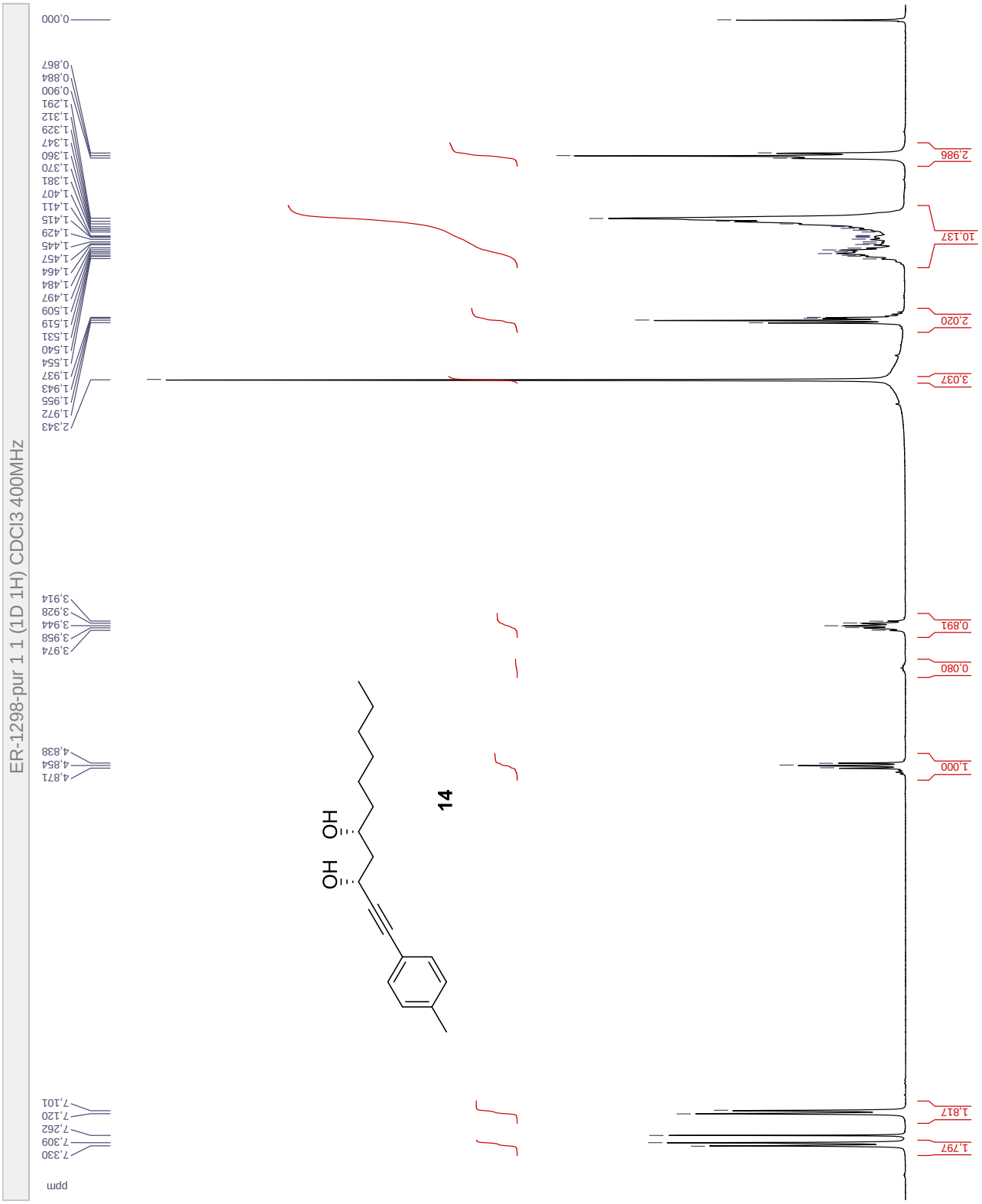

XC-071-1 2016 4 (1D 13C) CDCl3 400MHz
14.125
22.630
26.104
29.343
31.849
36.394
37.016
55.481
76.715
77.033
77.350
78.458
78.833
83.618
113.678
116.143
122.435
131.694
135.914
163.535
166.012
ppm
MeO
10-trans ester

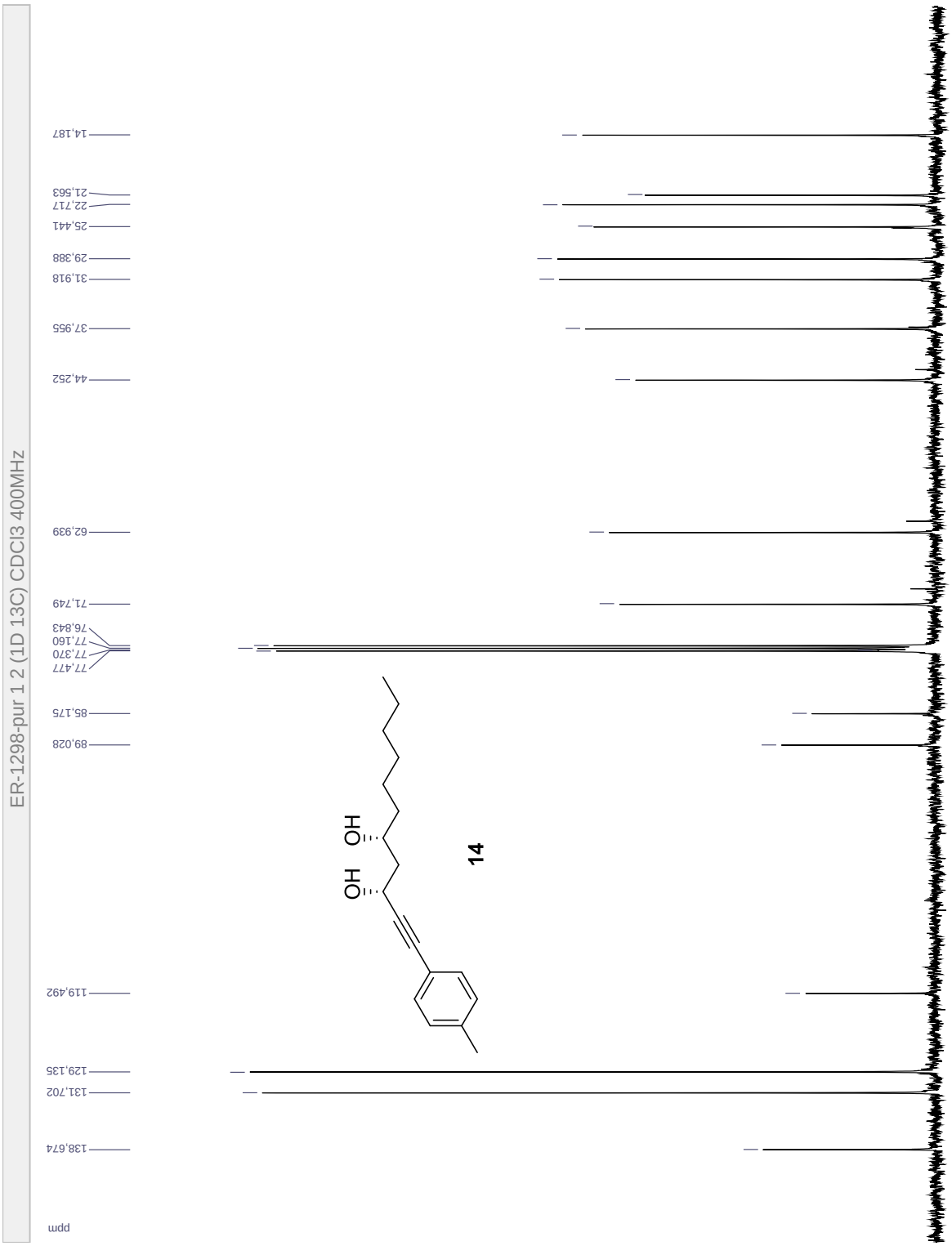

ER-1291 3 (1D 1H) CDCl3 400MHz
ppm
7,265
3,200
2,691
2,649
2,649
2,476
2,452
2,434
2,409
1,597
1,578
1,554
1,548
1,534
1,526
1,516
1,504
1,481
1,461
1,461
1,453
1,448
1,439
1,429
1,428
1,417
1,406
1,394
1,382
1,371
1,342
1,330
1,314
1,302
1,293
1,280
1,255
0,900
0,891
0,883
0,866
0,000
4,043
4,038
4,031
4,025
4,024
4,019
4,014
4,008
4,000
3,995
3,693
3,0
10,0
1,0
1,0
2,0
2,0
1,0
OH
O
N
O
12

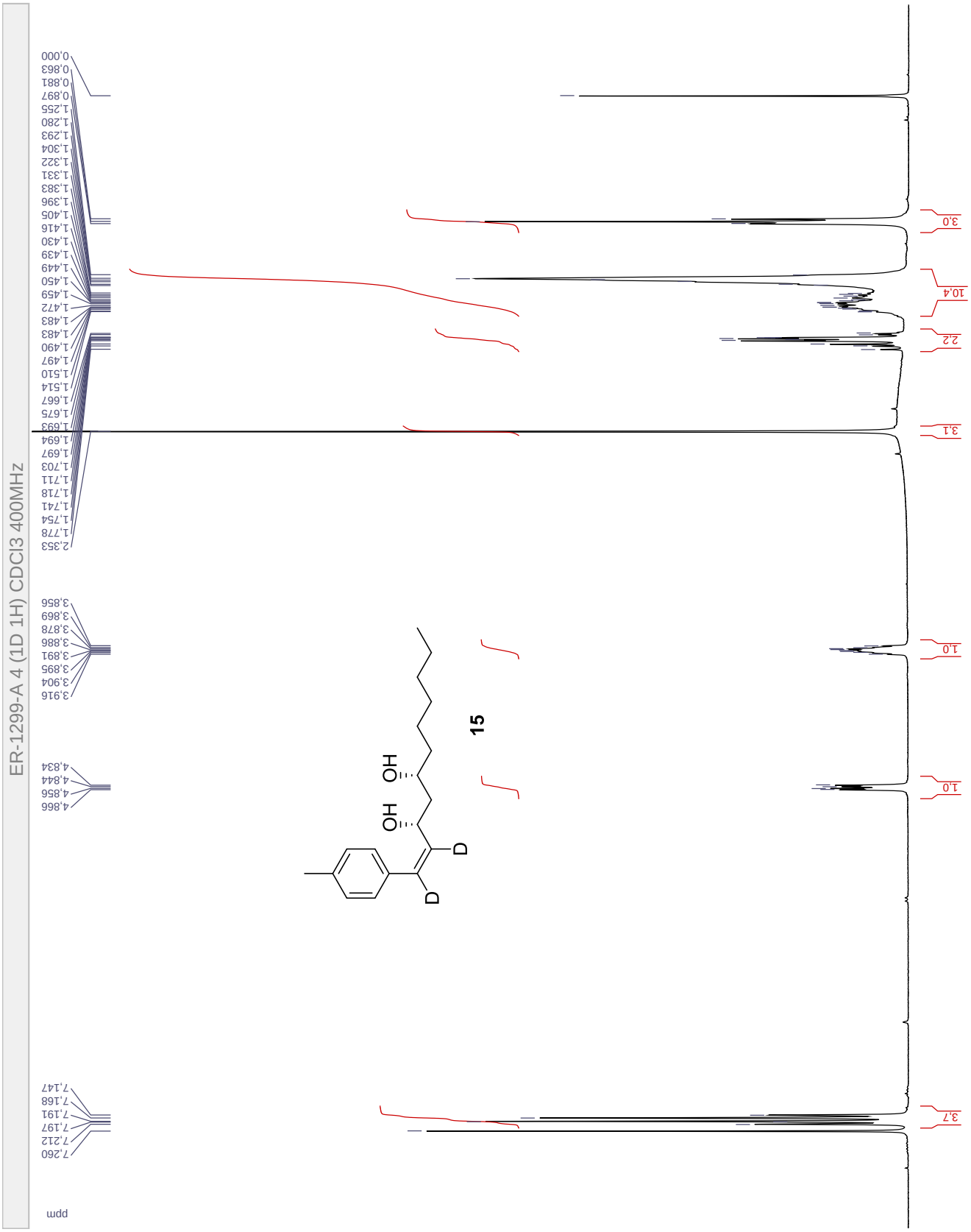

ER-1291 5 (13C) CDCl3 400MHz
14.063
22.602
25.519
29.269
29.681
31.807
36.516
38.244
61.200
67.876
76.843
77.160
77.477
173.923
ppm
12
OH
O
N
O

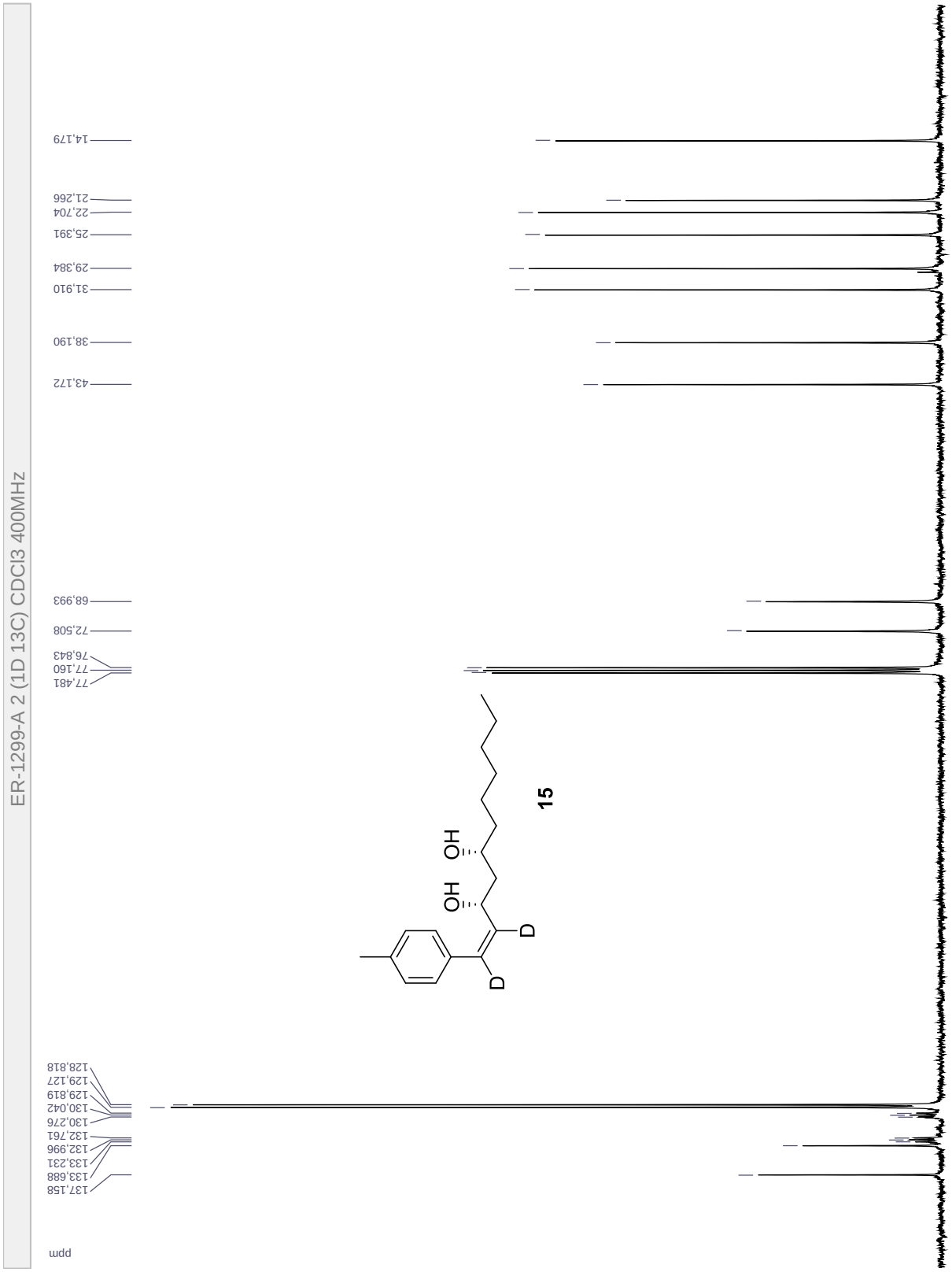

ER-1294 1 (1D 1H) CDCl3 300MHz
ppm
0.000
0.863
0.886
0.901
0.908
1.237
1.261
1.294
1.303
1.318
1.343
1.362
1.436
1.448
1.456
1.480
1.483
1.493
1.522
1.606
2.048
2.175
2.395
2.679
2.691
2.759
2.817
2.845
2.857
2.868
2.915
4.179
4.191
7.187
7.214
7.265
7.463
7.490
3.1
10.7
2.2
3.1
1.0
2.0
1.0
2.0
2.0
OH
O
13

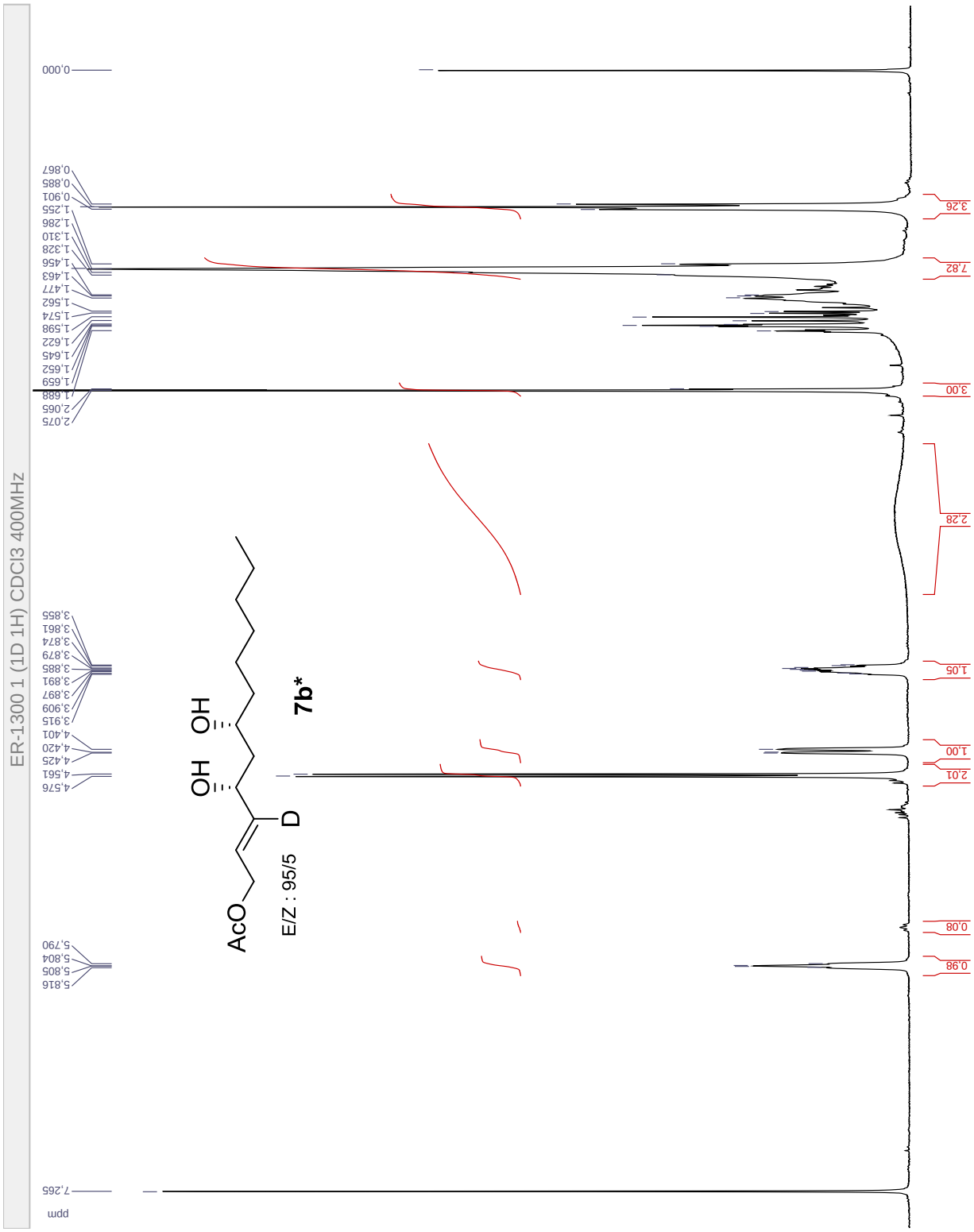

ER-1294 4 (1D 13C) CDCl3 300MHz
ppm
187,341
141,561
133,071
129,349
116,467
92,233
87,787
77,591
77,160
76,738
67,597
52,349
36,515
31,720
29,143
25,375
22,542
21,634
14,024
OH
O
13

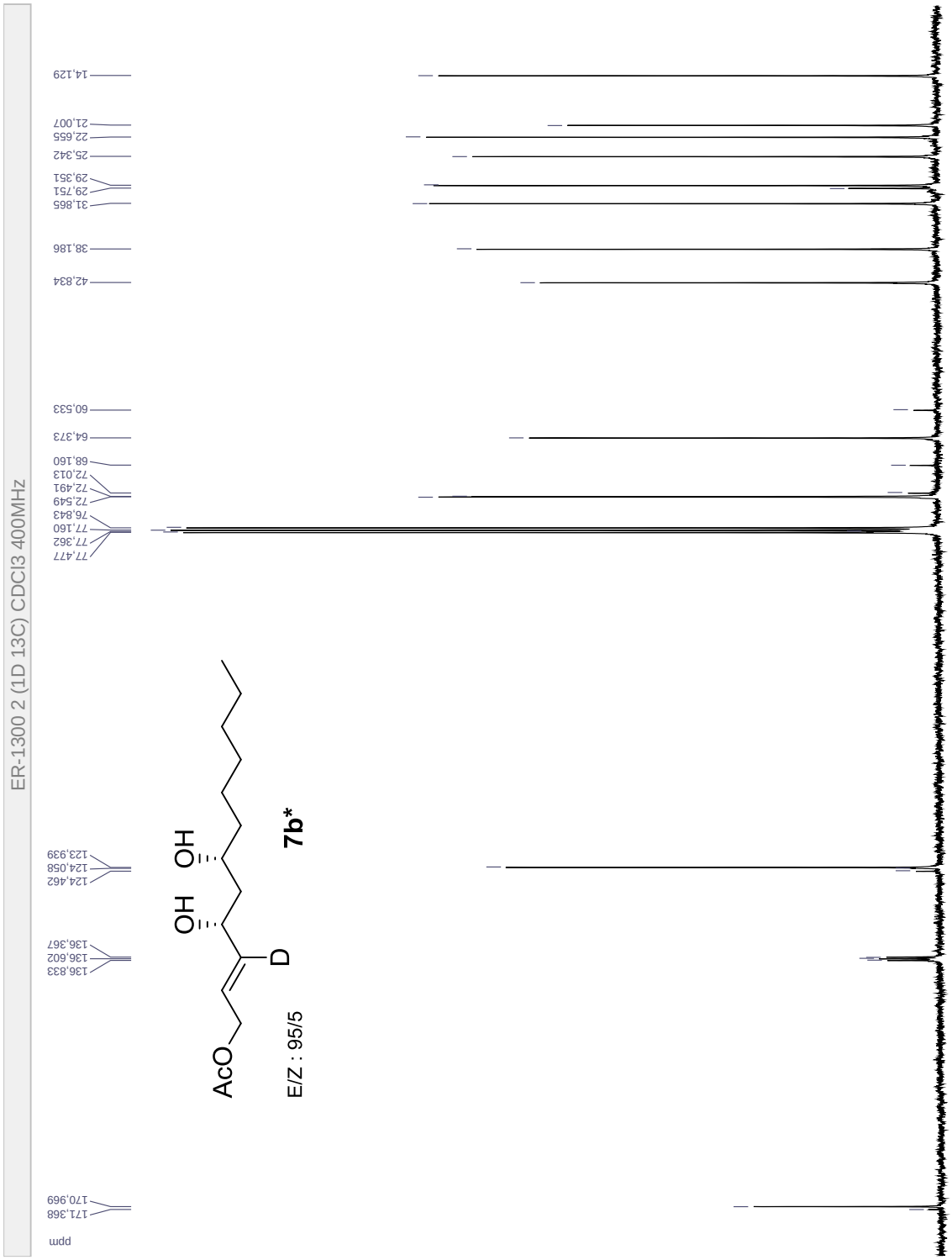

ER-1298-pur 1 1 (1D 1H) CDCl3 400MHz
ppm
0.000
0.867
0.884
0.900
1.291
1.312
1.329
1.347
1.360
1.370
1.381
1.407
1.411
1.415
1.429
1.445
1.457
1.464
1.484
1.497
1.509
1.519
1.531
1.540
1.554
1.937
1.943
1.955
1.972
2.343
3.914
3.928
3.944
3.958
3.974
4.838
4.854
4.871
7.101
7.120
7.262
7.309
7.330
OH
OH
14
2.986
10.137
2.020
3.037
0.891
0.080
1.000
1.817
1.797

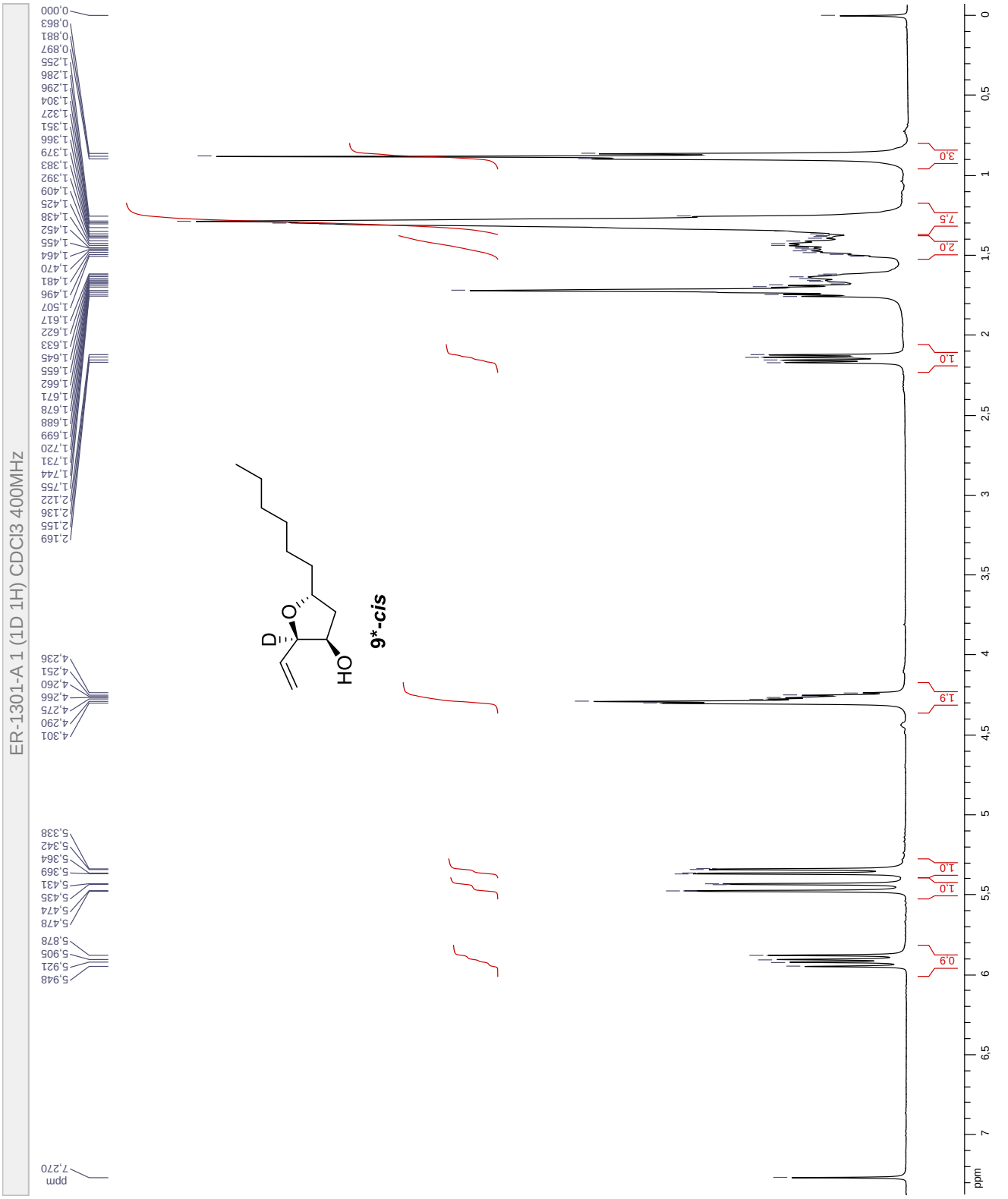

ER-1298-pur 1 2 (1D 13C) CDCl3 400MHz
14.187
21.563
22.717
25.441
29.388
31.918
37.955
44.252
62.939
71.749
76.843
77.160
77.370
77.477
85.175
89.028
119.492
129.135
131.702
138.674
ppm
OH
OH
14

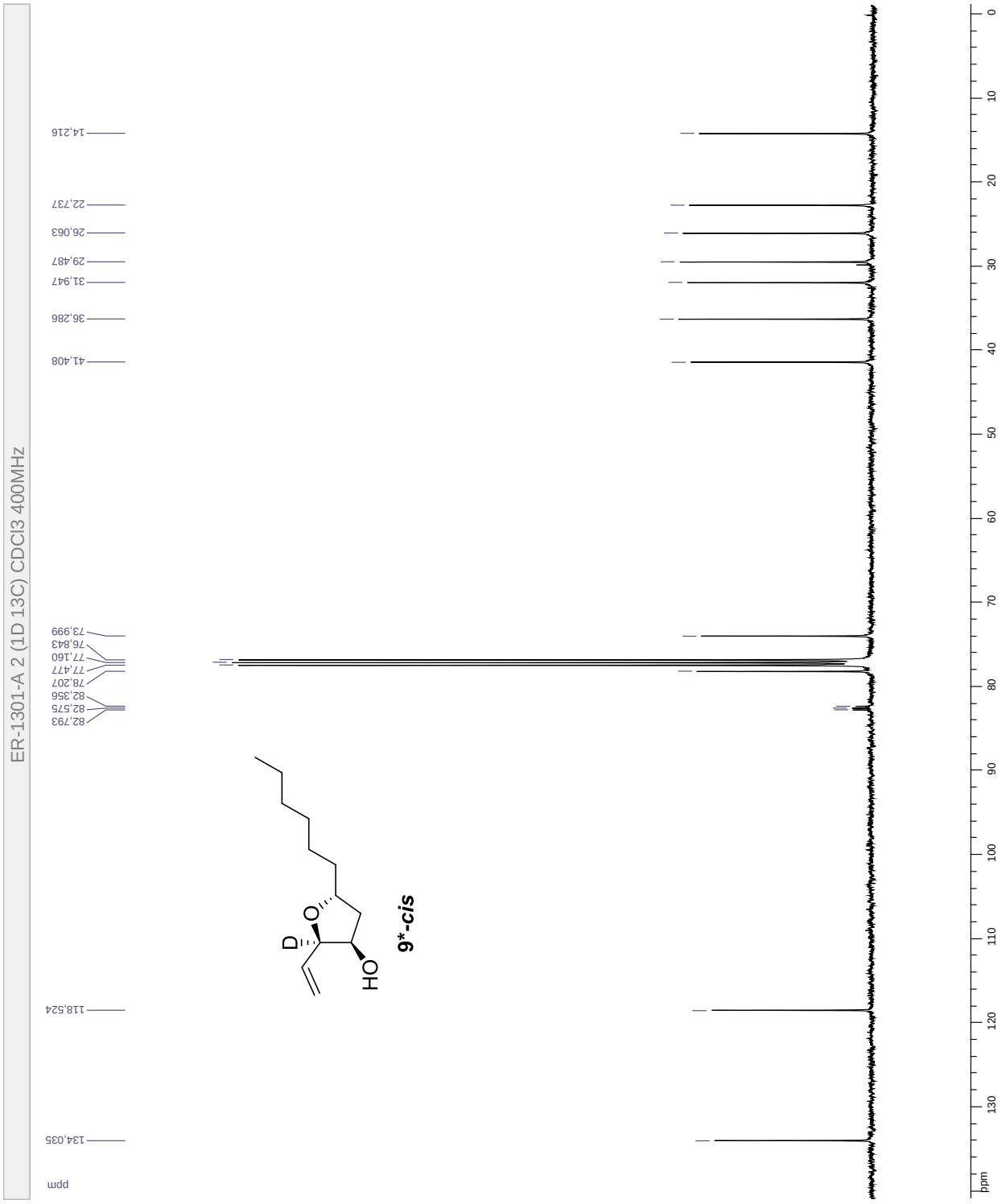

ER-1299-A 4 (1D 1H) CDCl3 400MHz
ppm
7,260
7,212
7,197
7,191
7,168
7,147
4,866
4,856
4,844
4,834
3,916
3,904
3,895
3,891
3,886
3,878
3,869
3,856
2,353
1,778
1,754
1,741
1,718
1,711
1,703
1,697
1,694
1,693
1,675
1,667
1,514
1,510
1,497
1,490
1,483
1,483
1,472
1,459
1,450
1,449
1,439
1,430
1,416
1,405
1,396
1,383
1,331
1,322
1,304
1,293
1,280
1,255
0,897
0,881
0,863
0,000
3,0
10,4
2,2
3,1
1,0
1,0
3,7
OH
OH
D
D
15

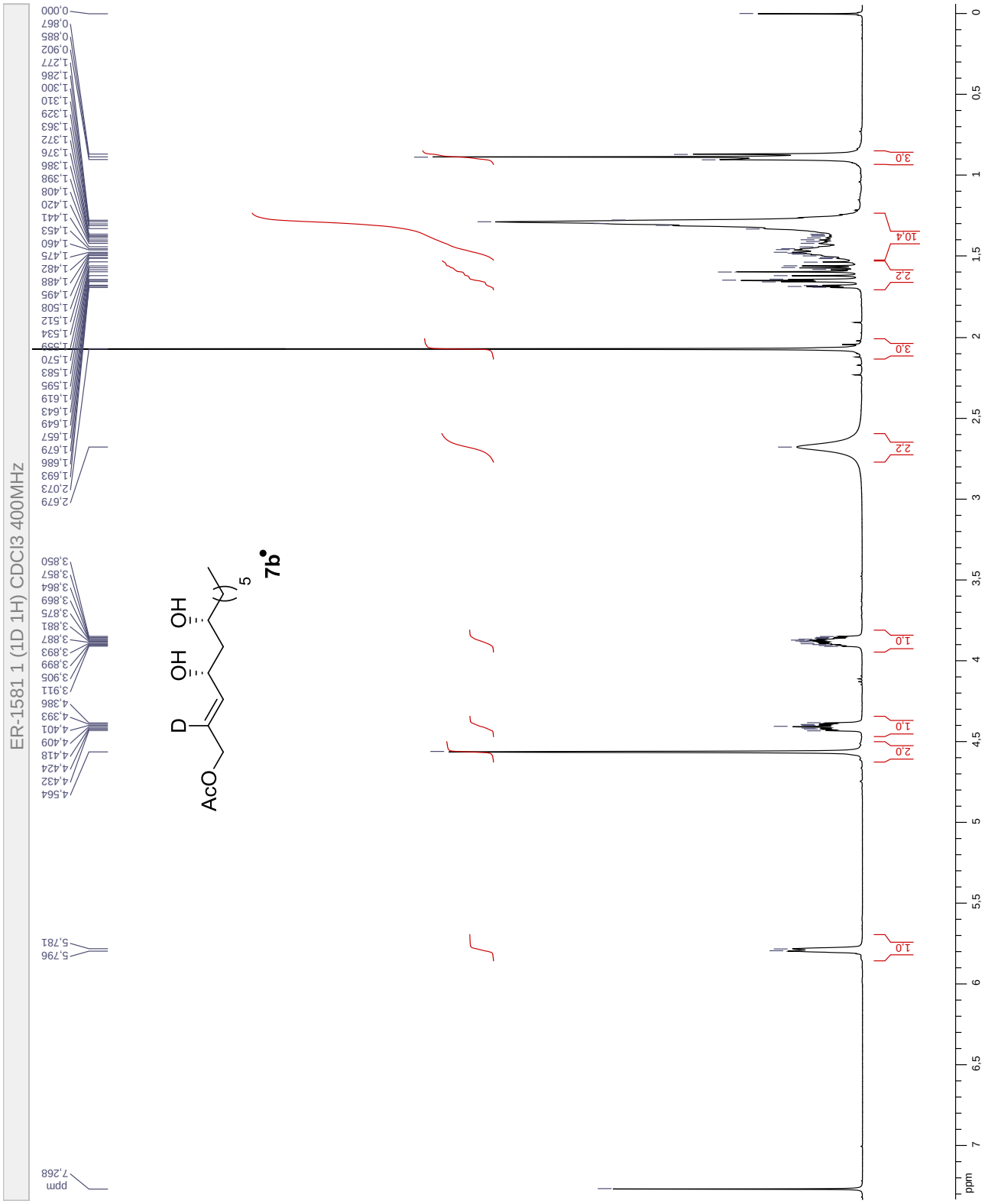

ER-1299-A 2 (1D 13C) CDCl3 400MHz
ppm
14,179
21,266
22,704
25,391
29,384
31,910
38,190
43,172
68,993
72,508
76,843
77,160
77,481
128,818
129,127
129,819
130,042
130,276
132,761
132,996
133,231
133,688
137,158
OH
OH
D
D
15

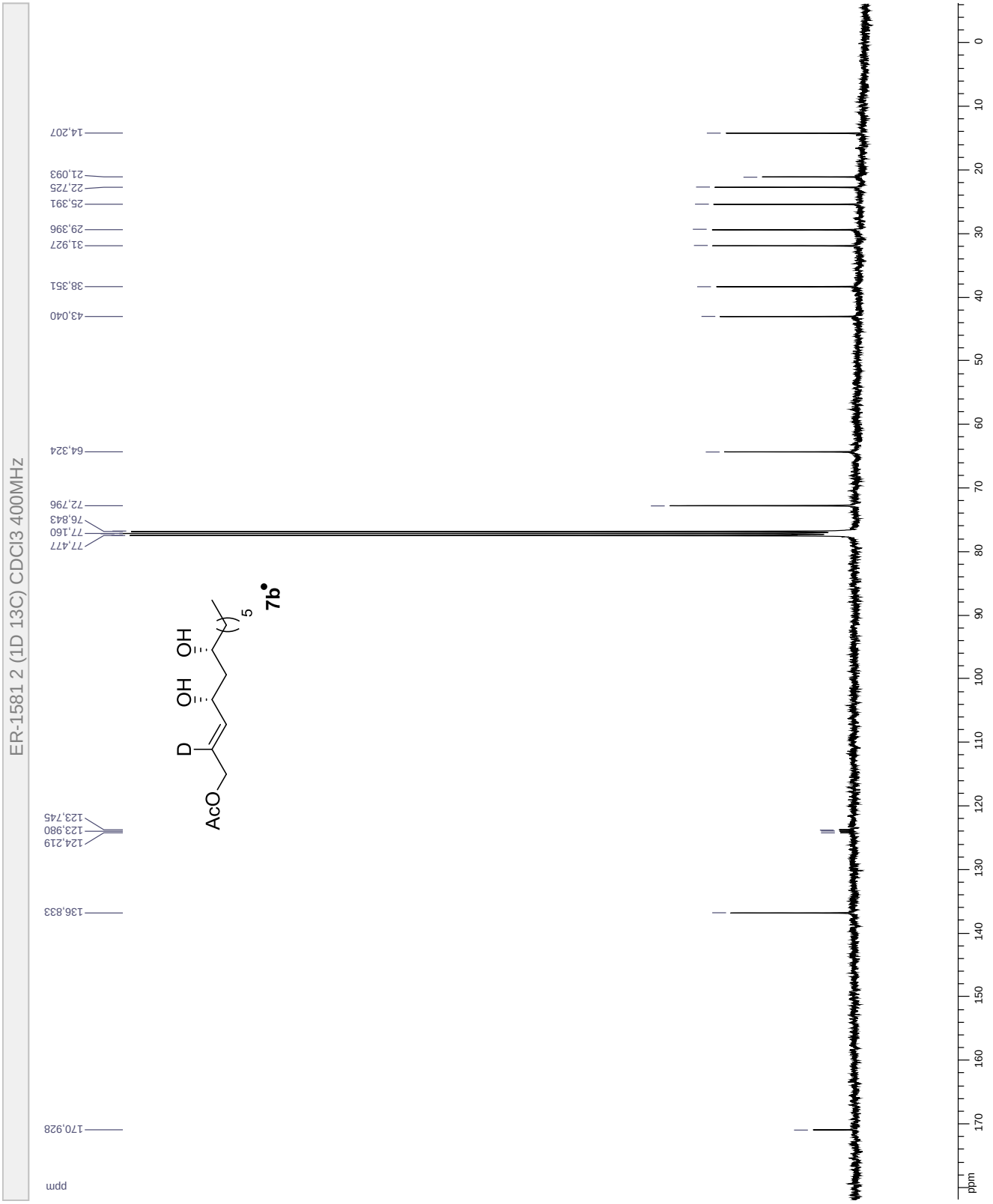

ER-1300 1 (1D 1H) CDCl3 400MHz
ppm
7,265
5,816
5,805
5,804
5,790
4,576
4,561
4,425
4,420
4,401
3,915
3,909
3,897
3,891
3,885
3,879
3,874
3,861
3,855
2,075
2,065
1,688
1,659
1,652
1,645
1,622
1,598
1,574
1,562
1,477
1,463
1,456
1,328
1,310
1,286
1,255
0,901
0,885
0,867
0,000
3,26
7,82
3,00
2,28
1,05
1,00
2,01
0,08
0,98
AcO
OH
OH
D
E/Z : 95/5
7b*

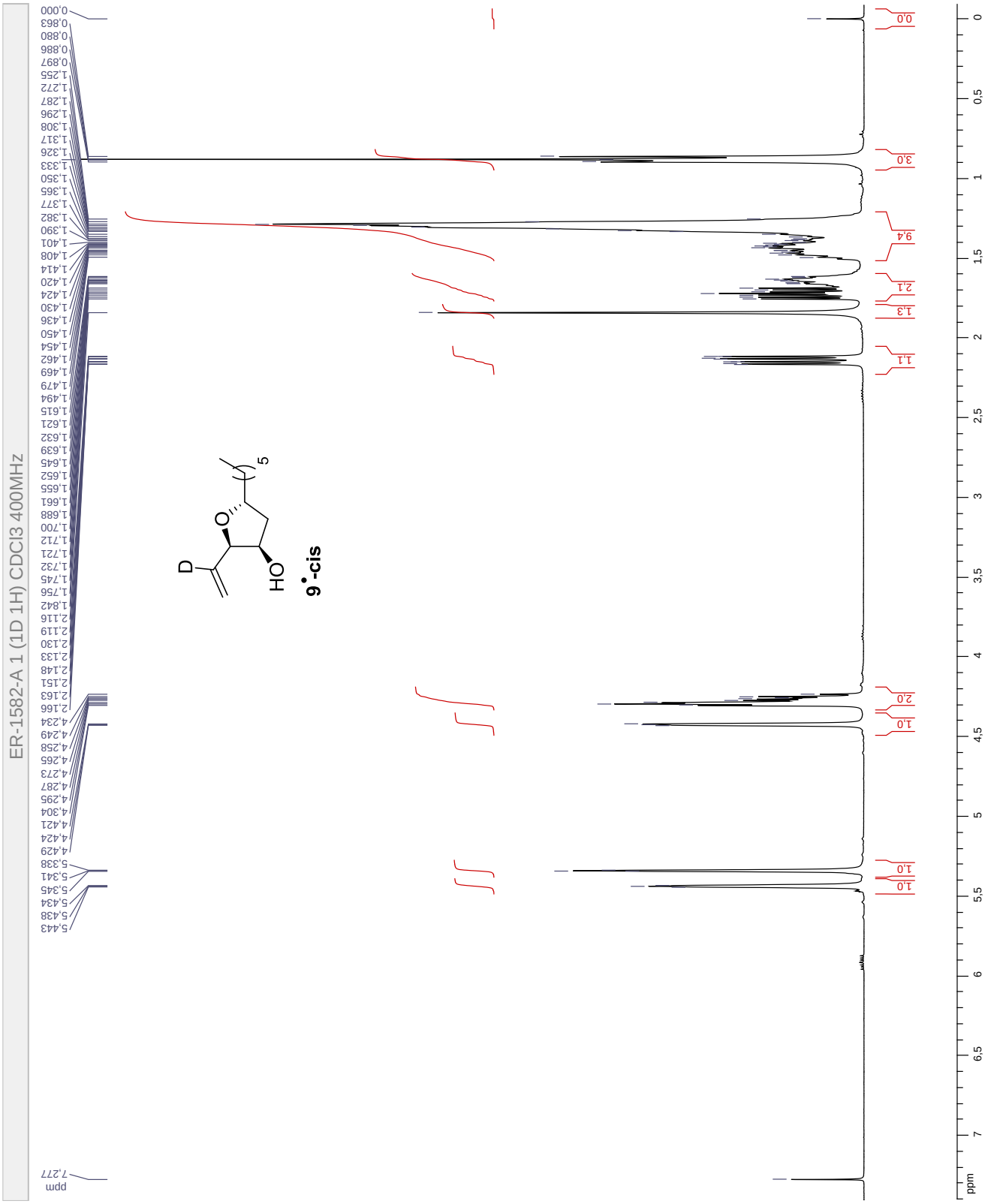

ER-1300 2 (1D 13C) CDCl3 400MHz
14,129
21,007
22,655
25,342
29,351
29,751
31,865
38,186
42,834
60,533
64,373
68,160
72,013
72,491
72,549
76,843
77,160
77,362
77,477
123,939
124,058
124,462
136,367
136,602
136,833
170,969
171,368
ppm
AcO
OH
OH
D
7b*
E/Z : 95/5

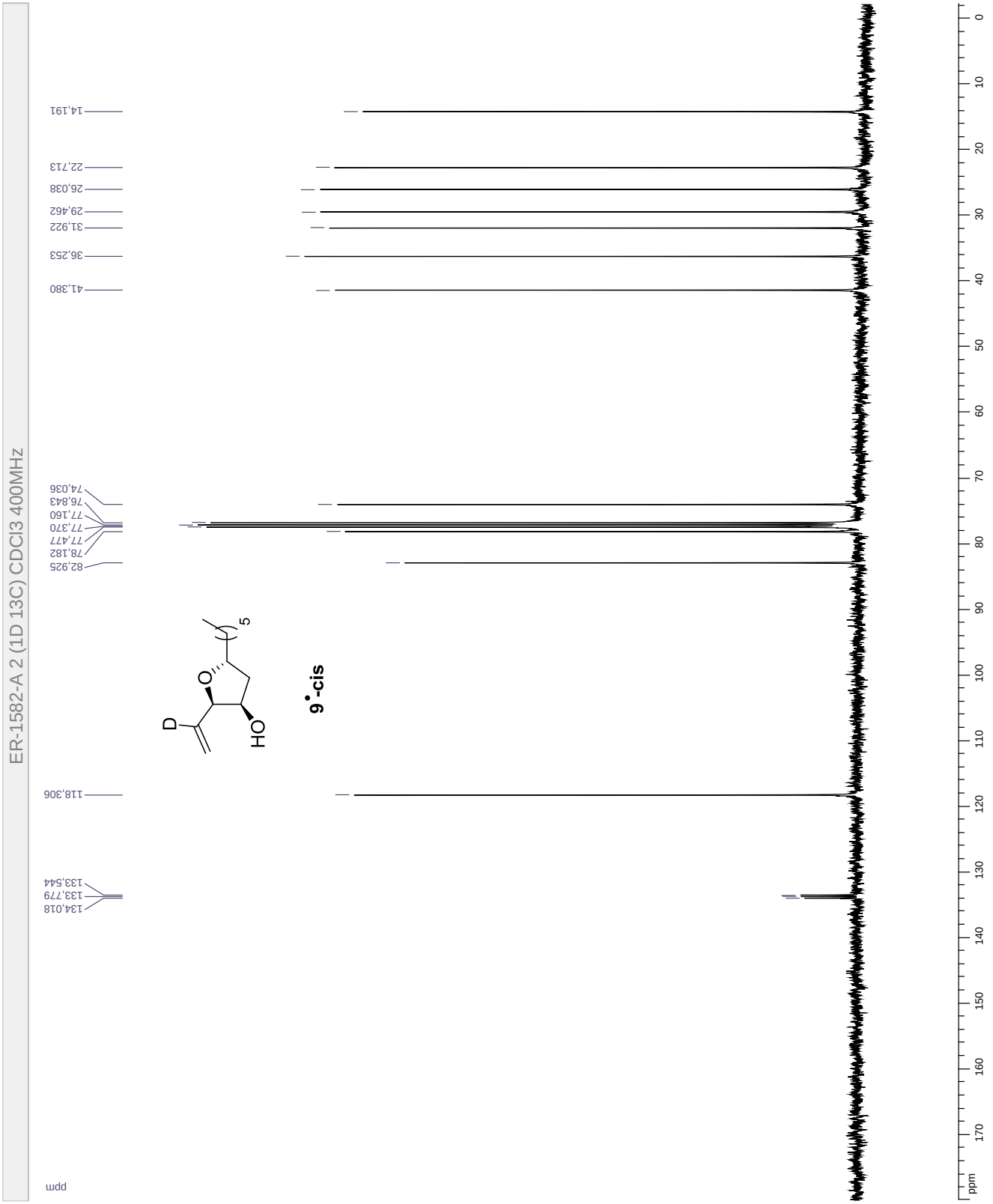

ER-1301-A 1 (1D 1H) CDCl3 400MHz
9*-cis
D
OH
ppm

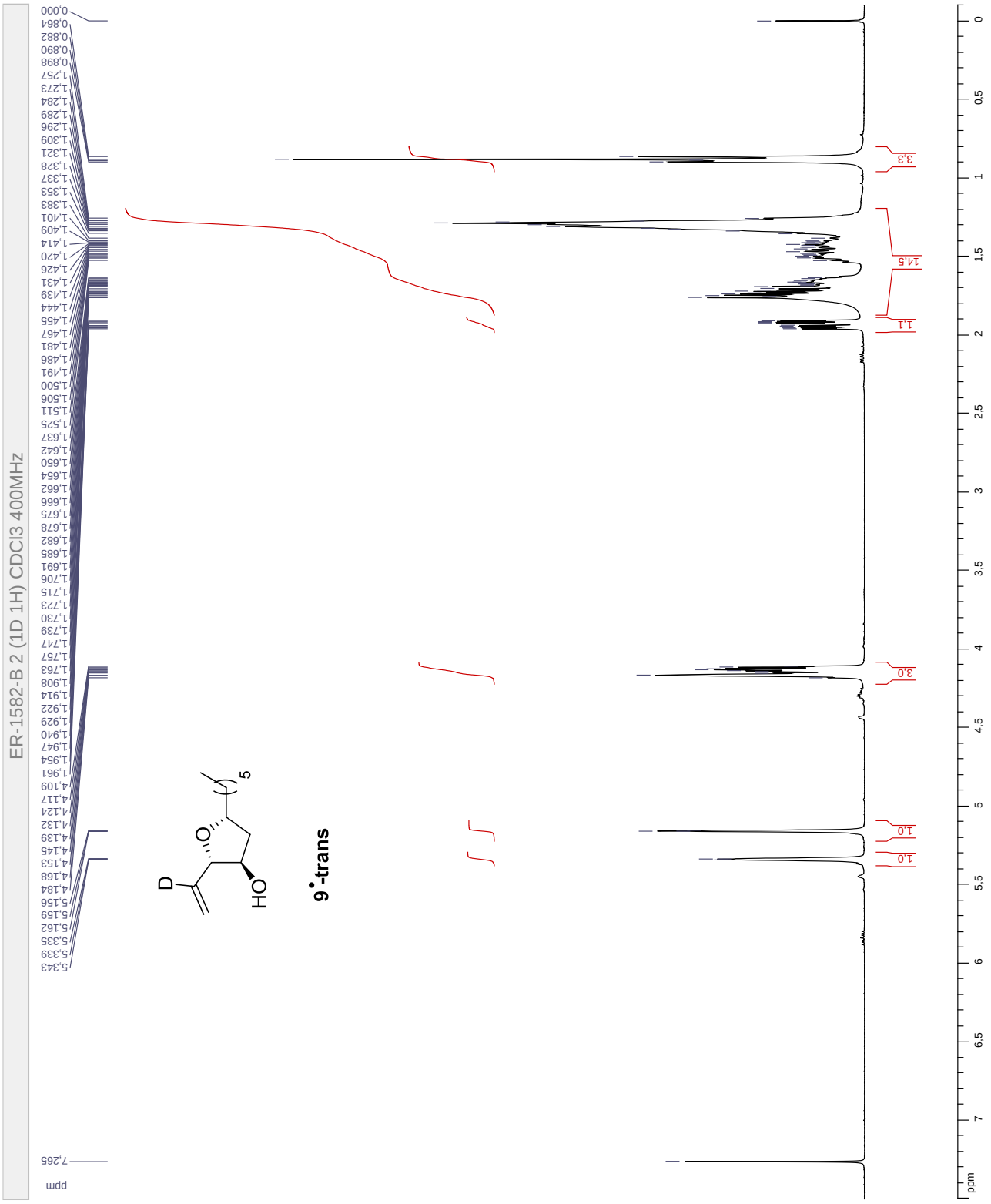

ER-1301-A 2 (1D 13C) CDCl3 400MHz
14,216
22,737
26,063
29,487
31,947
36,286
41,408
73,999
76,843
77,160
77,477
78,207
82,356
82,575
82,793
118,524
134,035
ppm
D
O
HO
9*-cis
0
10
20
30
40
50
60
70
80
90
100
110
120
130
ppm

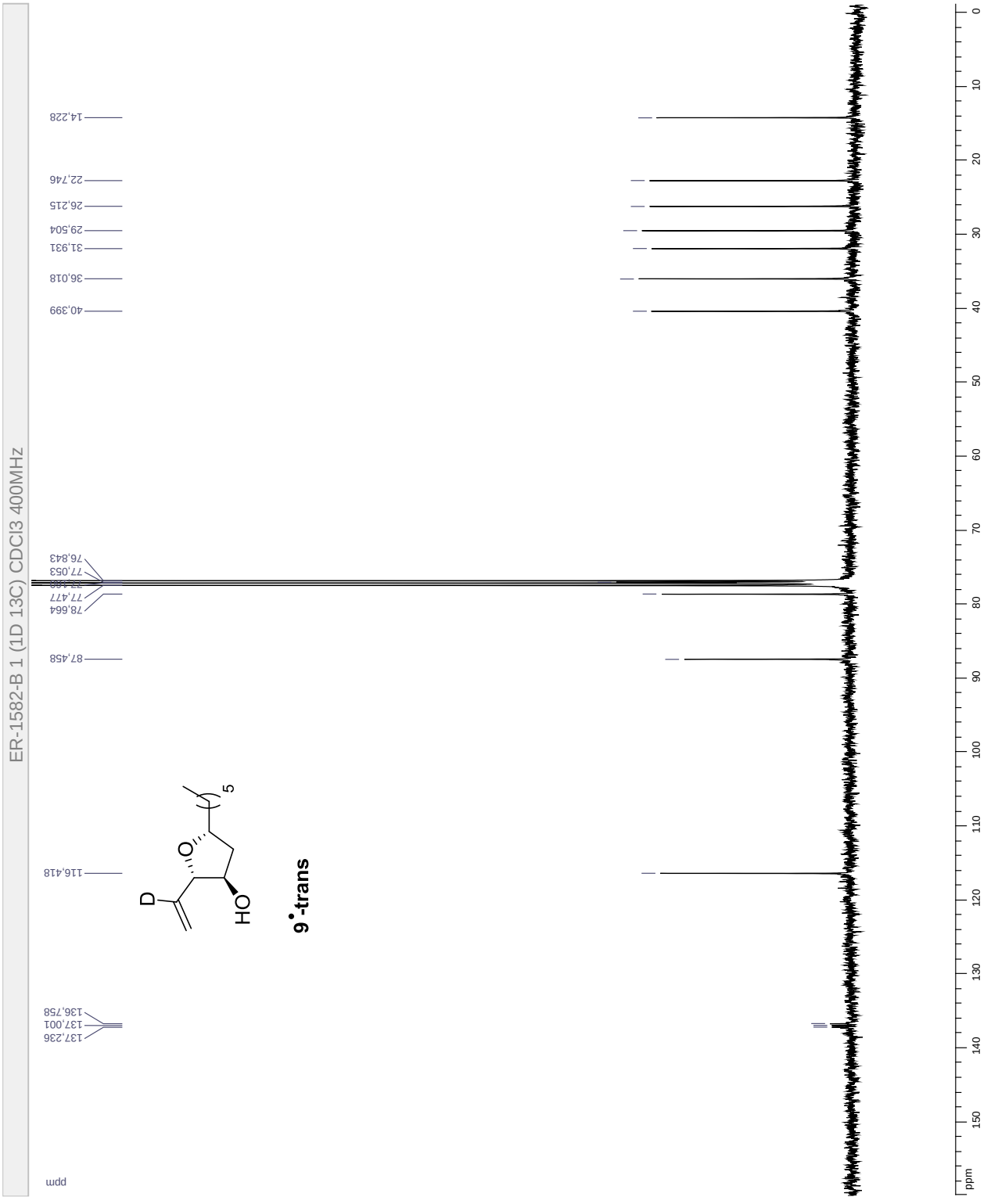

ER-1581 1 (1D 1H) CDCl3 400MHz
ppm
7,268
5,796
5,781
4,564
4,432
4,424
4,418
4,409
4,401
4,393
4,386
3,911
3,905
3,899
3,893
3,887
3,881
3,875
3,869
3,864
3,857
3,850
2,679
2,073
1,693
1,686
1,679
1,657
1,649
1,643
1,619
1,595
1,583
1,570
1,559
1,534
1,512
1,508
1,495
1,488
1,482
1,475
1,460
1,453
1,441
1,420
1,408
1,398
1,386
1,376
1,372
1,363
1,329
1,310
1,300
1,286
1,277
0,902
0,885
0,867
0,000
3,0
10,4
2,2
3,0
2,2
1,0
1,0
2,0
1,0
AcO
D
OH
OH
5
7b
ppm


ER-1581 2 (1D 13C) CDCl3 400MHz
14,207
21,093
22,725
25,391
29,396
31,927
38,351
43,040
64,324
72,796
76,843
77,160
77,477
123,745
123,980
124,219
136,833
170,928
ppm
AcO
D
OH
OH
5
7b•


ER-1582-A 1 (1D 1H) CDCl3 400MHz
ppm
7,277
5,443
5,438
5,434
5,345
5,341
5,338
4,429
4,424
4,421
4,304
4,295
4,287
4,273
4,265
4,258
4,249
4,234
2,166
2,163
2,151
2,148
2,133
2,130
2,119
2,116
1,842
1,756
1,745
1,732
1,721
1,712
1,700
1,688
1,661
1,655
1,652
1,645
1,639
1,632
1,621
1,615
1,494
1,479
1,469
1,462
1,454
1,450
1,436
1,430
1,424
1,420
1,414
1,408
1,401
1,390
1,382
1,377
1,365
1,350
1,333
1,326
1,317
1,308
1,296
1,287
1,272
1,255
0,897
0,886
0,880
0,863
0,000
D
O
HO
5
9 •-cis
0,0
3,0
9,4
2,1
1,3
1,1
2,0
1,0
1,0
1,0
ppm
0
0,5
1
1,5
2
2,5
3
3,5
4
4,5
5
5,5
6
6,5
7


ER-1582-A 2 (1D 13C) CDCl3 400MHz
14,191
22,713
26,038
29,462
31,922
36,253
41,380
74,036
76,843
77,160
77,370
77,477
78,182
82,925
118,306
133,544
133,779
134,018
D
HO
5
9-cis
ppm


ER-1582-B 2 (1D 1H) CDCl3 400MHz
9•-trans
D
HO
O
5
3.3
14.5
1.1
3.0
1.0
1.0
ppm


ER-1582-B 1 (1D 13C) CDCl3 400MHz
14,228
22,746
26,215
29,504
31,931
36,018
40,399
76,843
77,053
77,477
78,664
87,458
116,418
136,758
137,001
137,236
D
HO
O
5
9-trans
ppm