Supporting Information

'Highly Stereoselective C-C Bond Formation by Rhodium Catalyzed Tandem Ylide Formation/[2,3]-Sigmatropic Rearrangement Between Donor/Acceptor Carbenoids and Chiral Allylic Alcohols'

*Zhanjie Li, Brendan T. Parr and Huw M. L. Davies**

Department of Chemistry, Emory University, 440 Atwood Hall, 1515 Dickey Drive, Atlanta, GA 30322.

* To whom correspondence should be addressed: hmdavie@emory.edu

Table of Contents

1. Experimental Section

1.1 General Considerations

All reactions were conducted in oven-dried glassware under an inert atmosphere of dry argon. All chemicals were purchased from either Sigma-Aldrich, TCI America or Acros and were used as received. Pentane, tetrahydrofuran and diethyl ether were obtained from a Grubbs-type solvent purification system. ^{1}H NMR spectra were recorded at either 400 MHz on an INOVA-400 spectrometer or at 600 MHz on an INOVA-600 spectrometer. ^{13}C NMR spectra were recorded at 100 MHz on an INOVA-400 spectrometer. NMR spectra were recorded in deuterated chloroform ($CDCl_3$) solutions, with residual chloroform (δ 7.27 ppm for ^{1}H NMR and δ 77.23 ppm for ^{13}C NMR) or tetramethylsilane (δ 0.00 ppm for ^{1}H NMR) taken as the internal standard, and were reported in parts per million (ppm). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants were taken from the spectra directly and are uncorrected. IR spectra were collected on a Nicolet iS10 FT-IR spectrometer as neat films. Mass spectra determinations were carried out on a Thermo Finnigan LTQ-FTMS spectrometer with electrospray (ESI) or atmospheric pressure chemical (APCI) ionization. Optical rotations were measured on JASCO P-2000 polarimeter. Gas chromatography (GC) analysis was performed on an Agilent 7890A; column conditions: 30 ^{o}C for 1 min, then increasing to 180 ^{o}C at a rate of 5 ^{o}C/min, then 180 ^{o}C for 5 min. Analytical thin layer chromatography (TLC) was performed on silica gel plates using UV light or stained with 10% vanillin/1% sulfuric acid/ethanol solution. Flash column chromatography was performed with silica gel 60 A (230-400 mesh) according to the literature procedure.[1] Substrates **2** and **4c**[2], Rh_2(*S*-DOSP)$_4$ and Rh_2(*R*-DOSP)$_4$[3], **4a-b**[4], **4d-e**[5] and **4f**[6] were all synthesized according to published procedures.

1.2 General Procedures

1.2.1 Enzymatic Kinetic Resolution of Secondary Allylic Alcohols[7]

To a vigorously stirred solution of racemic allylic alcohol (1.0 equiv) and vinyl acetate (2.7 equiv) in hexanes (100 mL) was added Amano AK (30 wt %) and molecular sieves (50 wt %). The mixture was stirred at room temperature with periodic analysis of aliquots by chiral GC or HPLC. After the enantiomeric excess of the alcohol exceeded 98%, the mixture was filtered and concentrated *in vacuo*. Flash chromatography of the crude material on silica gel afforded the enantiomerically pure (*S*)-alcohol.

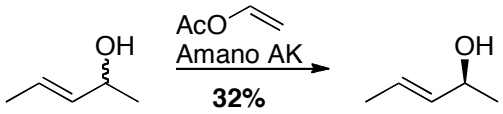
1.2.2 Sharpless Enantioselective Epoxidation/Kinetic Resolution of Secondary Alcohols[8]

To a solution of racemic allylic alcohol (10.0 mmol, 1.0 equiv) and *D*-(-)-DIPT (2.55 mL, 12.0 mmol, 1.2 equiv) in dichloromethane (100 mL) at -20 ^{o}C was slowly added Ti(O*i*-Pr)$_4$ (3.00 mL, 10.0 mmol, 1.0 equiv). The solution was stirred for 30 min prior to the slow addition of TBHP (5.5 M in decane, 1.1 mL, 6.0 mmol, 0.60 equiv). The reaction mixture was then stirred at -20 ^{o}C for 15 h before quenching with cold aqueous citric acid (11 g)/$FeSO_4$ (33 g) solution (100 mL). The mixture was stirred vigorously at room temperature until two layers became apparent. The organic layer was set aside and the aqueous layer was extracted with dichloromethane. The combined organic fractions were concentrated *in vacuo*, and the crude residue was dissolved in diethyl ether (100 mL). To the ether solution was added aqueous NaOH (30 g)/NaCl (5 g) solution (90 mL) at 0 ^{o}C. The mixture was then stirred at 0 ^{o}C for 1h before addition of H_2O (100 mL). The layers were separated and the organic was dried over $MgSO_4$ and concentrated *in vacuo*. Flash chromatography of the crude material on silica gel afforded the enantiomerically pure (*S*)-alcohol.

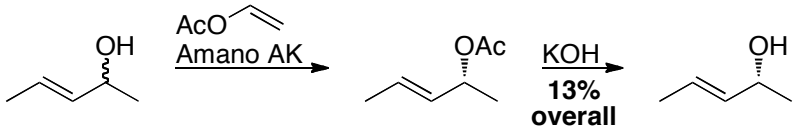
1.2.3 Rhodium(II)-Catalyzed [2,3]-Sigmatropic Rearrangement of Allylic Alcohols

An oven-dried, 25 mL round-bottomed flask, equipped with a stir bar, was capped with a rubber septum and placed under a dry argon atmosphere. The reaction vessel was charged with Rh_2(*S*-DOSP)$_4$ (10 mg, 0.0050 mmol, 0.010 equiv) and the allyl alcohol (0.5 mmol, 1.0 equiv) in pentane (1.0 mL). The solution was cooled to 0 ^oC in an ice bath before adding a pentane solution (9 mL) of the diazo compound (1.0 mmol, 2.0 equiv) drop-wise over 1.5 h. Following addition, the reaction was stirred at 0 ^oC for 1 h before warming to room temperature and concentrating *in vacuo*. The product was purified by flash chromatography.

2. Procedures and Characterization Data

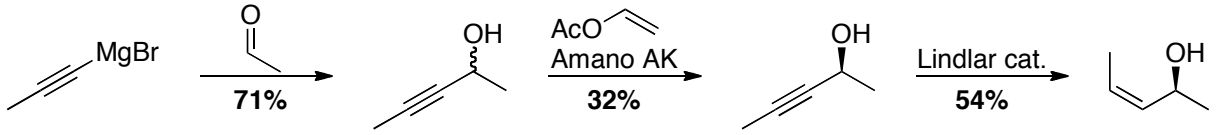


(*S*,*E*)-pent-3-en-2-ol ((*S*,*E*)-1). Prepared by procedure *1.2.1* with *racemic* **(*E*)-1** (3.0 g, 35 mmol, 1.0 equiv), vinyl acetate (8.7 mL, 94 mmol, 2.7 equiv) and Amano AK enzyme (1.0 g, 30 wt %). The reaction mixture was stirred for 8 h at ambient temperature and filtered. After concentration of the filtrate, the residue was purified by flash chromatography (pentane/diethyl ether, 5:1 → 2:1) to afford the title compound as a colorless oil (0.95 g, 32% yield). $[\alpha]^{20}_{D}$ -14.5° (*c* 3.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.66 (dq, J = 15.2, 6.4 Hz, 1H), 5.53 (dd, J = 15.2, 6.4 Hz, 1H), 4.26 (m, 1H), 1.69 (d, J = 6.4 Hz, 3H), 1.29 (d, J = 6.4 Hz, 3H). Chiral Capillary GC analysis: 99% ee, (CHIRALDEX BP-M). t_R = 5.10 min (minor), 5.27 min (major).



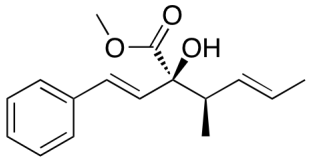
(*R*,*E*)-pent-3-en-2-ol ((*R*,*E*)-1). Prepared by procedure *1.2.1* with *racemic* **(*E*)-1** (3.0 g, 35 mmol, 1.0 equiv), vinyl acetate (8.7 mL, 94 mmol, 2.7 equiv) and Amano AK enzyme (1.0 g, 30 wt %). The reaction mixture was stirred for 2 h at ambient temperature and filtered. After concentration of the filtrate, the residue was purified by flash chromatography (pentane/diethyl ether, 5:1 → 2:1) to afford (*R*,*E*)-pent-3-en-2-yl acetate. The acetate was dissolved with potassium hydroxide solution (3.9 g KOH in 10 mL EtOH/H_2O, 7:3) and heated to reflux for 3.5 h. Upon cooling to room temperature, the solution was carefully neutralized with aqueous HCl and extracted with diethyl ether. The combined organic fractions were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the title compound as a colorless oil (0.19 g, 13%

yield). Spectral data was consistent with that for **(*S*,*E*)-1**. Chiral Capillary GC analysis: 97% ee, (CHIRALDEX BP-M). t_R = 5.10 min (major), 5.27 min (minor).

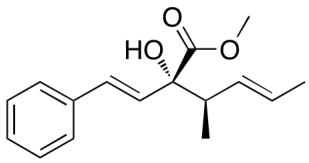


(*S*,*Z*)-pent-3-en-2-ol ((*S*,*Z*)-1). To a solution of 1-propynylmagnesium bromide (0.5 M in THF, 200 mL, 100 mmol, 1.0 equiv) was slowly added acetaldehyde (5.6 mL, 150 mmol, 1.5 equiv) as a diethyl ether solution (20 mL) at 0 ^oC. After addition, the reaction was allowed to warm to room temperature over 5 h and was subsequently quenched with careful addition of saturated aqueous NH_4Cl. The resultant layers were separated and the organic was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The product was purified by short path vacuum distillation (20 mm Hg, 55 ^oC) to afford *racemic* 3-pentyn-2-ol (6.00 g, 71% yield). The enzymatic kinetic resolution of 3-pentyn-2-ol was performed according to procedure *1.2.1* with *racemic* 3-pentyn-2-ol (1.35 g, 11.9 mmol, 1.0 equiv), vinyl acetate (3.0 mL, 32 mmol, 2.7 equiv) and Amano AK enzyme (0.46 g, 30 wt %). The reaction mixture was stirred for 20 h at 30 ^oC and filtered. After concentration of the filtrate, the residue was purified by flash chromatography (pentane/diethyl ether, 10:1 → 3:1) to afford (*S*)-3-pentyn-2-ol as a colorless oil (0.43 g, 32% yield). $[\alpha]^{20}_D$ -36.9^o (*c* 6.9, $CHCl_3$). Chiral Capillary GC analysis: 98% ee, (CHIRALDEX BP-M). t_R = 7.21 min (minor), 7.38 min (major). To a solution of (*S*)-3-pentyn-2-ol (215 mg, 2.56 mmol, 1.0 equiv) in pentane (2 mL) was added Pd/$CaCO_3$ poisoned with Pb (12 mg) and quinoline (one drop). The reaction vessel was purged with H_2 and stirred at ambient temperature for 20 h. The suspension was filtered and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography (pentane/diethyl ether, 5:1 → 3:1) to afford the

title compound as a colorless oil (120 mg, 54% yield). Spectral data were consistent with the literature.

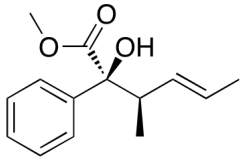


(2*R*,3*R*,*E*)-methyl 2-hydroxy-3-methyl-2-((*E*)-styryl)hex-4-enoate (2*R*,3*R*)-3). Prepared by procedure *1.2.3* with **(*S*,*E*)-1** (44 mg, 0.50 mmol, 1.0 equiv) and **2** (205 mg, 1.0 mmol, 2.0 equiv). The crude residue was purified by flash chromatography (pentane/diethyl ether, 10:1) to afford the title compound as a colorless oil (93 mg, 70%). $[\alpha]^{20}_{D}$ +19.7° (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.41 (m, 2H), 7.35-7.31 (m, 2H), 7.25-7.23 (m, 1H), 6.85 (d, *J* = 15.6 Hz, 1H), 6.26 (d, *J* = 15.6 Hz, 1H), 5.52 (dq, *J* = 15.2, 6.0 Hz, 1H), 5.40 (ddq, *J* = 15.2, 8.4, 1.6 Hz, 1H), 3.78 (s, 3H), 3.33 (s, 1H), 2.70-2.63 (m, 1H), 1.67 (dd, *J* = 6.0, 1.6 Hz, 3H), 1.02 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.6, 137.7, 131.4, 130.8, 129.2, 128.7, 127.9, 127.3, 126.8, 80.5, 53.1, 44.9, 18.3, 14.2. FTIR (neat): ν_{max}/cm^{-1} 3514, 1731, 1448, 1436, 1144. HRMS (p-APCI): *m/z* 243.1379 [$(M\text{-}OH)^+$ requires 243.1380]. HPLC analysis: >99% ee (CHIRALCEL OD-H, 0.5% isopropanol/hexanes, 0.7 mL/min, UV: 254 nm). t_R = 17.6 min (major), 21.9 min (minor).

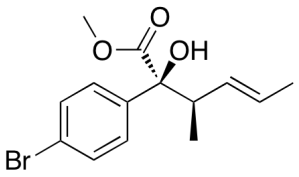


(2*S*,3*R*,*E*)-methyl 2-hydroxy-3-methyl-2-((*E*)-styryl)hex-4-enoate ((2*S*,3*R*)-3). Prepared by procedure *1.2.3* with **(*S*,*E*)-1** (45 mg, 0.50 mmol, 1.0 equiv), **2** (202 mg, 1.0 mmol, 2.0 equiv) and Rh_2(*R*-DOSP)$_4$ (9.5 mg, 0.0050 mmol, 001 equiv). The crude residue was purified by flash chromatography (pentane/diethyl ether, 15:1) to afford the title compound as a colorless oil (73

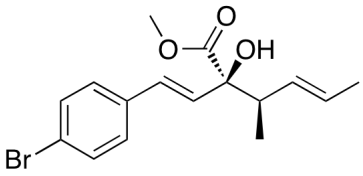
mg, 54%). $[\alpha]^{20}_D$ +53.1° (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.41-7.39(m, 2H), 7.34-7.31 (m, 2H), 7.27-7.23 (m, 1H), 6.78 (d, *J* = 15.6 Hz, 1H), 6.28 (d, *J* = 15.6 Hz, 1H), 5.52 (dq, *J* = 15.6, 6.4 Hz, 1H), 5.40 (ddq, *J* = 15.2, 7.6, 1.6 Hz, 1H), 3.82 (s, 3H), 3.38 (s, 1H), 2.74-2.67 (m, 1H), 1.65 (dd, *J* = 6.0, 1.6 Hz, 3H), 1.01 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.6, 136.8, 130.5, 130.4, 129.9, 128.7, 127.8, 127.4, 126.8, 79.9, 53.3, 44.9, 18.3, 15.3. FTIR (neat): ν_{max}/cm^{-1} 3515, 1727, 1448, 1436, 1152. HRMS (p-APCI): *m/z* 243.1380 $[(M\text{-}OH)^+$ requires 243.1380]. HPLC analysis: >99% ee (CHIRALCEL OD-H, 0.5% isopropanol/hexanes, 0.7 mL/min, UV: 254 nm). t_R = 18.5 min (minor), 19.9 min (major).



(2*S*,3*R*,*E*)-methyl 2-hydroxy-3-methyl-2-phenylhex-4-enoate (5a). Prepared by procedure *1.2.3* with **(*S*,*E*)-1** (43 mg, 0.50 mmol, 1.0 equiv) and **4a** (175 mg, 1.0 mmol, 2.0 equiv). The crude residue was purified by flash chromatography (pentane/diethyl ether, 10:1) to afford the title compound as a colorless oil (66 mg, 56%). $[\alpha]^{20}_D$ +70.9° (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.69-7.66 (m, 2H), 7.38-7.34 (m, 2H), 7.31-7.27 (m, 1H), 5.59 (dq, *J* = 15.6, 6.4 Hz, 1H), 5.50 (m, 1H), 3.74 (s, 3H), 3.67 (s, 1H), 3.10 (m, 1H), 1.69 (dd, *J* = 6.4, 1.6 Hz, 3H), 0.81 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.9, 140.4, 131.6, 128.3, 127.7, 127.4, 126.3, 81.2, 53.3, 45.2, 18.4, 14.2. FTIR (neat): ν_{max}/cm^{-1} 3507, 1724, 1447, 1435, 1140, 1005. HRMS (p-APCI): *m/z* 252.1596 $[(M+NH_4)^+$ requires 252.1594]. HPLC analysis: >99% ee (S,S-WHELK, 0.5% isopropanol/hexanes, 0.7 mL/min, UV: 230 nm). t_R = 9.2 min (major), 10.6 min (minor).

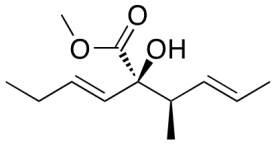


(2*S*,3*R*,*E*)-methyl 2-(4-bromophenyl)-2-hydroxy-3-methylhex-4-enoate (5b). Prepared by procedure *1.2.3* with **(*S*,*E*)-1** (45 mg, 0.50 mmol, 1.0 equiv) and **4b** (259 mg, 1.0 mmol, 2.0 equiv). The crude residue was purified by flash chromatography (pentane/diethyl ether, 20:1) to afford the title compound as a colorless oil (109 mg, 66%). $[\alpha]^{20}_{D}$ +80.3° (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 5.59 (dq, *J* = 15.2, 6.4 Hz, 1H), 5.46 (ddq, *J* = 15.2, 8.4, 1.6 Hz, 1H), 3.74 (s, 3H), 3.66 (s, 1H), 3.02 (m, 1H), 1.68 (dd, *J* = 6.4, 1.2 Hz, 3H), 0.78 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.4, 139.5, 131.4, 131.3, 128.3, 127.7, 121.9, 81.0, 53.5, 45.3, 18.4, 14.1. FTIR (neat): ν_{max}/cm^{-1} 3503, 1728, 1486, 1436, 1090, 1075, 1010. HRMS (p-APCI): *m/z* 295.0331 [$(M\text{-}OH)^+$ requires 295.0328]. HPLC analysis: >99% ee (CHIRALPAK AD-H, 1.0% isopropanol/hexanes, 0.7 mL/min, UV: 230 nm). t_R = 13.8 min (minor), 17.5 min (major).

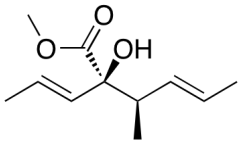


(2*R*,3*R*,*E*)-methyl 2-((*E*)-4-bromostyryl)-2-hydroxy-3-methylhex-4-enoate (5c). Prepared by procedure *1.2.3* with **(*S*,*E*)-1** (44 mg, 0.50 mmol, 1.0 equiv) and **4c** (281 mg, 1.0 mmol, 2.0 equiv). The crude residue was purified by flash chromatography (pentane/diethyl ether, 10:1) to afford the title compound as a white solid (119 mg, 69%). MP = 76-78 °C. $[\alpha]^{20}_{D}$ +35.2° (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 15.6 Hz, 1H), 6.24 (d, *J* = 15.6 Hz, 1H), 5.51 (dq, *J* = 15.2, 6.0 Hz, 1H), 5.38 (ddq, *J* = 15.2, 8.8, 1.6 Hz, 1H), 3.77 (s, 3H), 3.32 (s, 1H), 2.68-2.60 (m, 1H), 1.65 (dd, *J* = 6.4, 1.6 Hz,

3H), 0.99 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.4, 135.6, 131.8, 131.2, 130.0, 129.7, 128.4, 127.5, 121.7, 80.5, 53.2, 44.9, 18.3, 14.2. FTIR (neat): ν_{max}/cm^{-1} 3512, 1731, 1487, 1435, 1072, 1009. HRMS (p-APCI): *m/z* 321.0492 [(M-OH)$^+$ requires 321.0485]. HPLC analysis: >99% ee (CHIRALCEL OD-H, 0.5% isopropanol/hexanes, 0.7 mL/min, UV: 230 nm). t_R = 13.8 min (minor), 14.9 min (major).

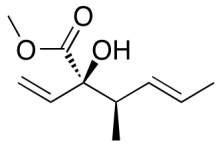


(*R*,*E*)-methyl 2-hydroxy-2-((*R*,*E*)-pent-3-en-2-yl)hex-3-enoate (5d). Prepared by procedure *1.2.3* with **(*S*,*E*)-1** (43 mg, 0.50 mmol, 1.0 equiv) and **4d** (155 mg, 1.0 mmol, 2.0 equiv). The crude residue was purified by flash chromatography (pentane/diethyl ether, 12:1) to afford the title compound as a colorless oil (64 mg, 60%). $[\alpha]^{20}_D$ -31.0^o (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.94 (dt, J = 15.6, 6.4 Hz, 1H), 5.51-5.54 (m, 2H), 5.35 (ddd, J = 15.6, 8.4, 1.2 Hz, 1H), 3.74 (s, 3H), 3.12 (s, 1H), 2.52 (dq, J = 6.8, 6.8 Hz, 1H), 2.11-2.04 (m, 2H), 1.62 (dd, J = 6.2, 1.2 Hz, 3H), 0.99 (t, J = 7.6 Hz, 3H), 0.95 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.2, 133.8, 131.6, 128.4, 127.0, 80.1, 52.9, 44.5, 25.3, 18.3, 13.9, 13.7. FTIR (neat): ν_{max}/cm^{-1} 3521, 2965, 2935, 2875, 1732, 1437, 1157. HRMS (p-APCI): *m/z* 195.1380 [(M-OH)$^+$ requires 195.1380]. HPLC analysis: >99% ee (CHIRALPAK AD-H, 0.5% isopropanol/hexanes, 0.5 mL/min, UV: 210 nm). t_R = 21.6 min (minor), 23.4 min (major).

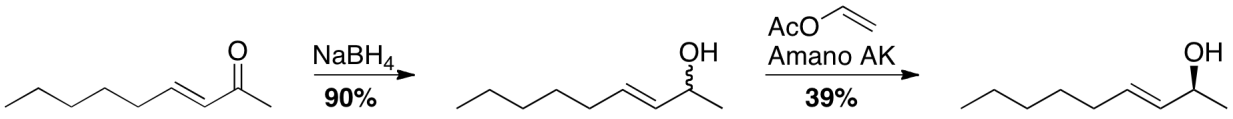


(2*R*,3*R*,*E*)-methyl 2-hydroxy-3-methyl-2-((*E*)-prop-1-en-1-yl)hex-4-enoate (5e). Prepared by procedure *1.2.3* with **(*S*,*E*)-1** (43 mg, 0.50 mmol, 1.0 equiv) and **4e** (141 mg, 1.0 mmol, 2.0

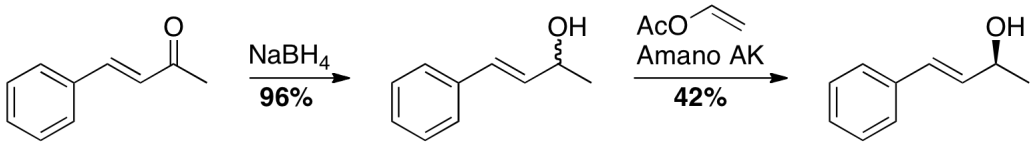
equiv). The crude residue was purified by flash chromatography (pentane/diethyl ether, 12:1) to afford the title compound as a colorless oil (55 mg, 55%). $[\alpha]^{20}_{D}$ -20.6° (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.94 (dq, *J* = 15.6, 6.6 Hz, 1H), 5.53-5.49 (m, 1H), 5.48-5.45 (m, 1H), 5.38-5.33 (m, 1H), 3.74 (s, 3H), 3.12 (s, 1H), 2.52 (dq, *J* = 7.2, 7.2 Hz, 1H), 1.73 (dd, *J* = 7.2, 1.8 Hz, 3H), 1.63 (dd, *J* = 6.0, 1.8 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.1, 131.6, 130.6, 127.1, 127.0, 80.1, 52.9, 44.5, 18.3, 17.8, 14.0. FTIR (neat): ν_{max}/cm^{-1} 3522, 2969, 2919, 2857, 1732, 1438, 1156. HRMS (p-APCI): *m/z* 181.1225 [$(M\text{-}OH)^+$ requires 181.1223]. HPLC analysis: >99% ee (CHIRALPAK AD-H, 0.5% isopropanol/hexanes, 0.5 mL/min, UV: 210 nm). t_R = 19.2 min (minor), 20.3 min (major).



(2*R*,3*R*,*E*)-methyl 2-hydroxy-3-methyl-2-vinylhex-4-enoate (5f). Prepared by procedure *1.2.3* with **(*S*,*E*)-1** (45 mg, 0.50 mmol, 1.0 equiv) and **4f** (160 mg, 1.25 mmol, 2.5 equiv). The crude residue was purified by flash chromatography (pentane/diethyl ether, 20:1) to afford the title compound as a colorless oil (41 mg, 43%). $[\alpha]^{20}_{D}$ -52.8° (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.91 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.54-5.44 (m, 2H), 5.39-5.33 (m, 1H), 5.24 (dd, *J* = 10.4, 1.6 Hz, 1H), 3.75 (s, 3H), 3.15 (s, 1H), 2.56 (m, 1H), 1.64 (dd, *J* = 6.4, 1.2 Hz, 3H), 0.96 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.6, 137.7, 131.4, 127.2, 116.2, 80.6, 53.0, 44.3, 18.3, 14.0. FTIR (neat): ν_{max}/cm^{-1} 3519, 2975, 2935, 1732, 1437, 1159. HRMS (p-APCI): *m/z* 185.1173 [$(M+H)^+$ requires 185.1172]. Chiral Capillary GC analysis: >99% ee (CHIRALDEX BP-M). t_R = 14.7 min (major), 15.2 min (minor).

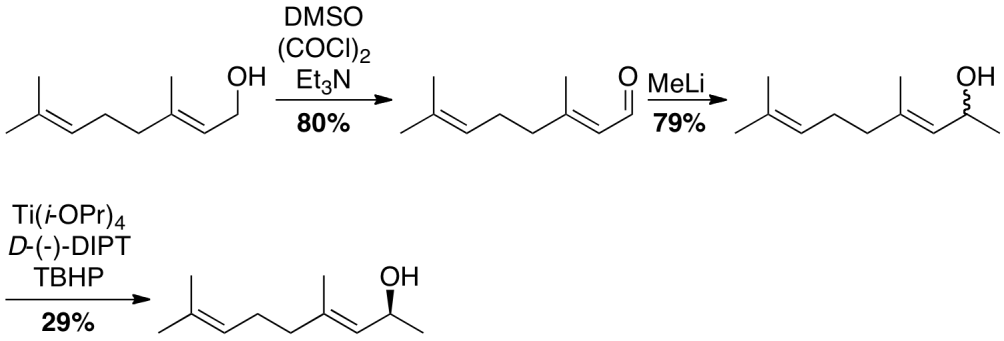


(*S*,*E*)-non-3-en-2-ol (6a). To a solution of (*E*)-3-nonen-2-one (3.0 g, 21 mmol, 1.0 equiv) in methanol (30 mL) at 0 ^{o}C was added sodium borohydride (0.9 g, 23 mmol, 1.1 equiv) in methanol (30 mL). The reaction was gradually warmed to room temperature over 3 h and subsequently quenched with saturated aqueous NH_4Cl. The resultant mixture was concentrated *in vacuo* and the residue was extracted with diethyl ether. The combined organic fractions were washed with brine, drived over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography (pentane/diethyl ether, 5:1 → 3:1) to afford *racemic* **6a** as a colorless oil (2.7 g, 90% yield). The enzymatic kinetic resolution was performed according to procedure *1.2.1* with *racemic* **6a** (2.0 g, 15 mmol, 1.0 equiv), vinyl acetate (3.7 mL, 40 mmol, 2.7 equiv) and Amano AK enzyme (0.60 g, 30 wt %). The reaction mixture was stirred for 3 h at ambient temperature and filtered. After concentration of the filtrate, the residue was purified by flash chromatography (pentane/diethyl ether, 5:1 → 3:1) to afford the title compound as a colorless oil (0.77 g, 39% yield). Spectral data were consistent with the literature. Chiral Capillary GC analysis: 99% ee (CHIRALDEX BP-M). t_R = 14.17 min (major), 15.10 min (minor).



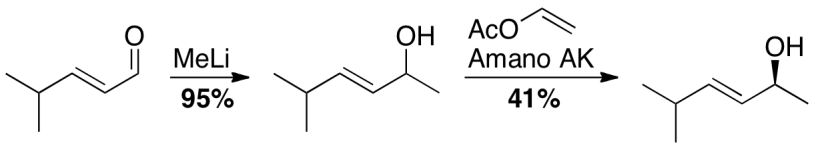
(*S*,*E*)-4-phenylbut-3-en-2-ol (6b). To a solution of (*E*)-4-phenylbut-3-en-2-one (5.0 g, 34 mmol, 1.0 equiv) in methanol (50 mL) was slowly added sodium borohydride (1.4 g, 37 mmol, 1.1 equiv) in methanol (50 mL) at 0 ^{o}C. The reaction mixture was gradually warmed to room temperature over 2 h and was subsequently quenched with saturated aqueous NH_4Cl. The resultant mixture was concentrated *in vacuo* and the residue was extracted with diethyl ether. The combined organic fractions were washed with brine, drived over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography (hexanes/ethyl acetate, 3:1) to afford

racemic **6b** as a white solid (4.9 g, 96% yield). The enzymatic kinetic resolution was performed according to procedure *1.2.1* with *racemic* **6b** (1.0 g, 6.7 mmol, 1.0 equiv), vinyl acetate (1.7 mL, 18 mmol, 2.7 equiv) and Amano AK enzyme (0.50 g, 50 wt %). The reaction mixture was stirred for 24 h at ambient temperature and filtered. After concentration of the filtrate, the residue was purified by flash chromatography (pentane/diethyl ether, 3:1) to afford the title compound as a white solid (0.43 g, 42% yield). Spectral data were consistent with the literature. HPLC analysis: 99% ee (CHIRALCEL OD-H, 5% isopropanol/hexanes, 0.6 mL/min, UV: 254 nm). t_R = 21.9 min (minor), 35.6 min (major).



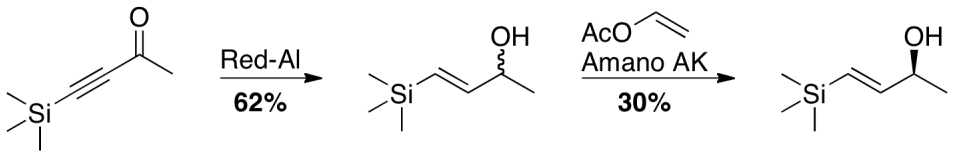
(*S*,*E*)-4,8-dimethylnona-3,7-dien-2-ol (6c). To a dichloromethane solution (40 mL) of oxalyl chloride (4.1 mL, 49 mmol, 1.5 equiv) at -78 ^oC was slowly added dimethyl sulfoxide (6.5 mL, 91 mmol, 2.8 equiv). The solution was stirred for 1.5 h before adding geraniol (5.0 g, 32 mmol, 1.0 equiv) in dichloromethane (60 mL) dropwise. The solution was stirred an additional 2 h at -78 ^oC, and then triethylamine (24.0 mL, 172 mmol, 5.3 equiv) was slowly added. The solution was allowed to warm to room temperature overnight. The reaction mixture was poured over H_2O (100 mL) and the layers were separated. The organic layer was washed with saturated aqueous NH_4Cl, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography (pentane/diethyl ether, 7:1) to afford (*E*)-geranial as a colorless oil (3.9 g, 80% yield). To a diethyl ether solution (150 mL) of (*E*)-geranial (3.9 g, 26 mmol, 1.0 equiv) at -78 ^oC

was slowly added methyl lithium solution (1.6 M in diethyl ether, 21 mL, 33 mmol, 1.3 equiv). After 1.5 h, the reaction was quenched with HCl (*conc.*, 1 mL). The organic layer was then washed sequentially with H_2O and brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash chromatography (pentane/diethyl ether, 6:1 → 3:1) to afford *racemic* **6c** as a colorless oil (3.4 g, 79% yield). The Sharpless kinetic resolution was performed according to procedure *1.2.2* with *racemic* **6c** (1.68 g, 10.0 mmol, 1.0 equiv). The crude residue was purified by flash chromatography (pentane/diethyl ether, 5:1 → 3:1) to afford the title compound as a colorless oil (0.49 g, 29% yield). Spectral data were consistent with the literature. Chiral Capillary GC analysis: 99% ee, (CHIRALDEX BP-M). t_R = 18.92 min (minor), 19.32 min (major).

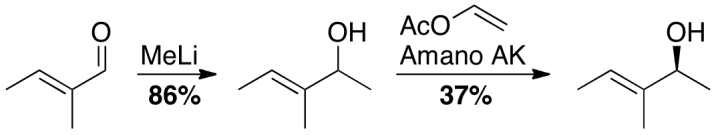


(*S*,*E*)-5-methylhex-3-en-2-ol (6d). To a tetrahydrofuran solution (100 mL) of (*E*)-4-methylpent-2-enal (4.91 g, 50.0 mmol, 1.0 equiv) at 0 ^oC was slowly added methyllithium (1.6 M in diethyl ether, 48 mL, 76 mmol, 1.5 equiv). After 1 h, the reaction was quenched by careful addition of saturated aqueous NH_4Cl. The resultant layers were separated and the aqueous was extracted with diethyl ether. The combined organic fractions were washed sequentially with H_2O and brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude residue was purified by flash chromatography (pentane/diethyl ether, 3:1) to afford *racemic* **6d** as a colorless oil (5.40g, 95% yield). The enzymatic kinetic resolution was performed according to procedure *1.2.1* with *racemic* **6d** (3.20 g, 28.0 mmol, 1.0 equiv), vinyl acetate (7.80 mL, 84.3 mmol, 3.0 equiv) and Amano AK enzyme (1.60 g, 50 wt %). The reaction mixture was stirred for 2 h at ambient temperature and filtered. After concentration of the filtrate, the residue was purified by flash

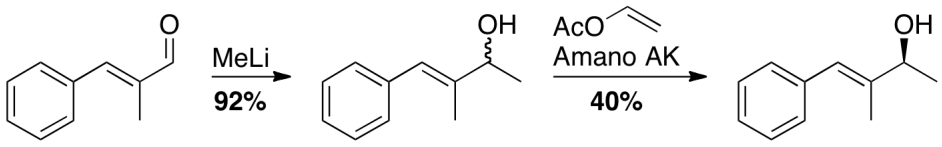
chromatography (pentane/diethyl ether, 2:1) to afford the title compound as a colorless oil (1.31 g, 41% yield). Spectral data were consistent with the literature. Chiral Capillary GC analysis: 99% ee, (CHIRALDEX BP-M). t_R = 9.23 min (major), 9.38 min (minor).



(*S*,*E*)-4-(trimethylsilyl)but-3-en-2-ol (6e). To a solution of 4-(trimethylsilyl)but-3-yn-2-ol (2.6 g, 18 mmol, 1.0 equiv) in diethyl ether (40 mL) was added Red-Al (11.0 mL, 36.4 mmol, 2.0 equiv) at 0 ^{o}C. The reaction mixture was allowed to warm to room temperature over 2 h and was subsequently quenched with H_2O (1 mL) and aqueous H_2SO_4 (2 mL, 3.6 M) at 0 ^{o}C. The resultant layers were separated and the aqueous was extracted with diethyl ether. The combined organic fractions were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography (pentane/diethyl ether, 10:1 → 5:1) to afford *racemic* **6e** as a colorless oil (1.62 g, 62% yield). The enzymatic kinetic resolution was performed according to procedure *1.2.1* with *racemic* **6e** (1.0 g, 6.9 mmol, 1.0 equiv), vinyl acetate (3.2 mL, 35 mmol, 5.0 equiv) and Amano AK enzyme (0.50 g, 50 wt %). The reaction mixture was stirred for 15 h at 35 ^{o}C and filtered. After concentration of the filtrate, the residue was purified by flash chromatography (pentane/diethyl ether, 10:1 → 5:1) to afford the title compound as a colorless oil (0.30 g, 30% yield). Spectral data were consistent with the literature. Chiral Capillary GC analysis: 99% ee, (CHIRALDEX BP-M). t_R = 11.58 min (major), 11.89 min (minor).

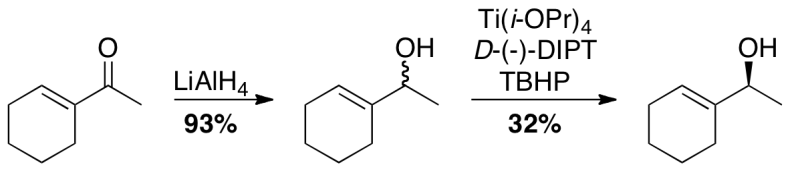


(*S*,*E*)-3-methylpent-3-en-2-ol (6f). To a solution of (*E*)-2-methylbut-2-enal (4.4 g, 52 mmol, 1.0 equiv) in tetrahydrofuran (100 mL) was slowly added methyllithium solution (1.6 M in diethyl ether, 39 mL, 63 mmol, 1.2 equiv) at 0 ^{o}C. The reaction was stirred at 0 ^{o}C for 4 h and then quenched with saturated aqueous NH_4Cl. The resultant layers were separated and the aqueous was extracted with diethyl ether. The combined organic fractions were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography (pentane/diethyl ether, 3:1) to afford *racemic* **6f** as a colorless oil (4.5 g, 86% yield). The enzymatic kinetic resolution was performed according to procedure *1.2.1* with *racemic* **6f** (3.5 g, 35 mmol, 1.0 equiv), vinyl acetate (8.7 mL, 94 mmol, 2.7 equiv) and Amano AK enzyme (1.0 g, 29 wt %). The reaction mixture was stirred for 12 h at ambient temperature and filtered. After concentration of the filtrate, the residue was purified by flash chromatography (pentane/diethyl ether, 3:1) to afford the title compound as a colorless oil (1.29 g, 37% yield). Spectral data were consistent with the literature. Chiral Capillary GC analysis: 99% ee, (CHIRALDEX BP-M). t_R = 8.76 min (minor), 8.98 min (major).

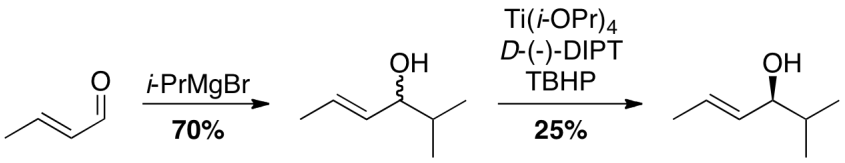


(*S*,*E*)-3-methyl-4-phenylbut-3-en-2-ol (6g). To a tetrahydrofuran solution (250 mL) of (*E*)-α-methylcinnamaldehyde (7.30 mL, 52.0 mmol, 1.0 equiv) at 0 ^{o}C was slowly added methyllithium solution (1.6 M in diethyl ether, 60 mL, 96 mmol, 1.8 equiv). After 2 h, the reaction was carefully quenched with saturated aqueous NH_4Cl. The resultant layers were separated and the aqueous was extracted with diethyl ether. The combined organic fractions were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography (hexanes/ethyl acetate, 4:1) to afford *racemic* **6g** as a colorless oil (7.76 g, 92%

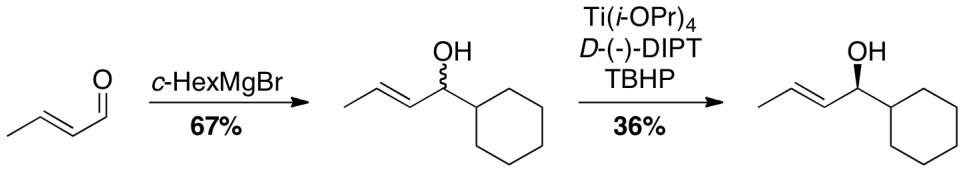
yield). The enzymatic kinetic resolution was performed according to procedure *1.2.1* with *racemic* **6g** (2.33 g, 14.3 mmol, 1.0 equiv), vinyl acetate (3.60 mL, 38.9 mmol, 2.7 equiv) and Amano AK enzyme (0.70 g, 30 wt %). The reaction mixture was stirred for 12 h at ambient temperature and filtered. After concentration of the filtrate, the residue was purified by flash chromatography (hexanes/ethyl acetate, 3:1) to afford the title compound as a colorless oil (0.93 g, 40% yield). Spectral data were consistent with the literature. HPLC analysis: 99% ee (S,S-WHELK, 1.5% isopropanol/hexanes, 1.0 mL/min, UV: 254 nm). t_R = 9.7 min (minor), 10.8 min (major).



(*S*)-1-(cyclohex-1-en-1-yl)ethanol (6h). To a lithium aluminum hydride (0.6 g, 17 mmol, 0.5 equiv) in diethyl ether (15 mL) at 0 ^oC was slowly added 1-acetylcyclohexene (4.0 g, 32 mmol, 1.0 equiv) as a diethyl ether solution (15 mL). Following addition, the reaction mixture was warmed to room temperature and stirred for an additional 1 h. The reaction vessel was again cooled to 0 ^oC and carefully quenched with cold H_2O followed by aqueous H_2SO_4 (10%, 5 mL). The resultant layers were separated and the organic was washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by short path vacuum distillation (20 mm Hg, 100 ^oC) to afford *racemic* **6h** as a colorless oil (3.8 g, 93% yield). The Sharpless kinetic resolution was performed according to procedure *1.2.2* with *racemic* **6h** (1.20 g, 10.0 mmol, 1.0 equiv). The crude residue was purified by flash chromatography (pentane/diethyl ether, 5:1) to afford the title compound as a colorless oil (0.39 g, 32% yield). Spectral data were consistent with the literature. Chiral Capillary GC analysis: 99% ee, (CHIRALDEX BP-M). t_R = 16.50 min (minor), 16.60 min (major).

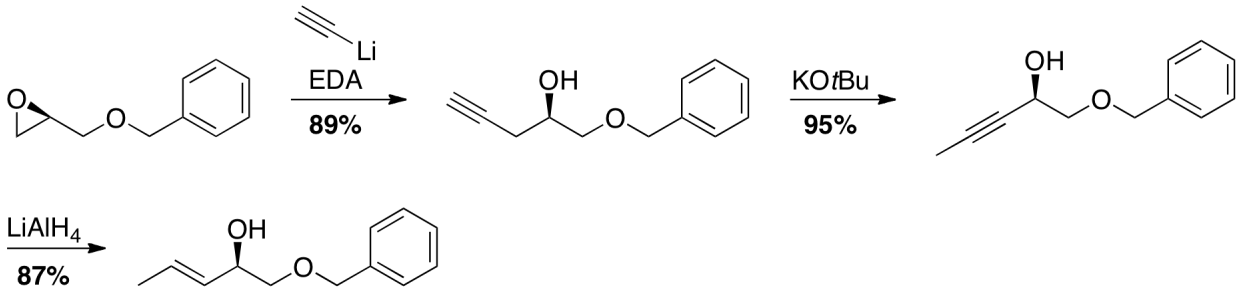


(*S*,*E*)-2-methylhex-4-en-3-ol (6i). To an isopropylmagnesium bromide solution (2.0 M in diethyl ether, 43 mL, 86 mmol, 1.2 equiv) at 0 °C was slowly added crotonaldehyde (5.0 g, 71 mmol, 1.0 equiv) in diethyl ether (10 mL). The solution was then allowed to warm to room temperature and stirred for an additional 1 h. The reaction was carefully quenched with saturated aqueous NH_4Cl and the resultant layers were separated. The aqueous was extracted with diethyl ether and the combined organic fractions were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by short path vacuum distillation (20 mm Hg, 65 °C) to afford *racemic* **6i** as a colorless oil (5.7 g, 70% yield). The Sharpless kinetic resolution was performed according to procedure *1.2.2* with *racemic* **6i** (1.14 g, 10.0 mmol, 1.0 equiv). The crude residue was purified by flash chromatography (pentane/diethyl ether, 10:1 → 5:1) to afford the title compound as a colorless oil (0.28 g, 25% yield). Spectral data were consistent with the literature. Chiral Capillary GC analysis: 99% ee, (CHIRALDEX BP-M). t_R = 9.83 min (minor), 9.85 min (major).



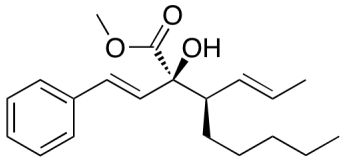
(*S*,*E*)-1-cyclohexylbut-2-en-1-ol (6j). To a cyclohexylmagnesium bromide solution (1.0 M in tetrahydrofuran, 32 mL, 32 mmol, 1.5 equiv) at 0 °C was slowly added crotonaldehyde (1.5 g, 21 mmol, 1.0 equiv) in tetrahydrofuran (10 mL). The solution was then allowed to warm to room temperature and stirred for an additional 1 h. The reaction was carefully quenched with saturated aqueous NH_4Cl and the resultant layers were separated. The aqueous was extracted with diethyl

ether and the combined organic fractions were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography (pentane/diethyl ether, 5:1) to afford *racemic* **6j** as a colorless oil (2.2 g, 67% yield). The Sharpless kinetic resolution was performed according to procedure *1.2.2* with *racemic* **6i** (1.54 g, 10.0 mmol, 1.0 equiv). The crude residue was purified by flash chromatography (pentane/diethyl ether, 5:1) to afford the title compound as a colorless oil (0.55 g, 36% yield). Spectral data were consistent with the literature. Mosher ester ^{1}H NMR analysis: 99% ee.



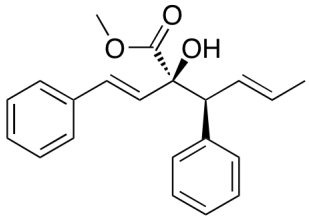
(*R*,*E*)-1-(benzyloxy)pent-3-en-2-ol (6k). To a solution of benzyl (*R*)-(-)-glycidyl ether (3.5 g, 21 mmol, 1.0 equiv) in dimethyl sulfoxide (40 mL) at 0 ^{o}C was added lithium acetylide ethylenediamine complex (3.3 g, 33 mmol, 1.6 equiv) in several portions. After 1 h, the reaction was quenched by sequential addition of brine and aqueous HCl (5.0 M). The aqueous was extracted with diethyl ether and the combined organic fractions were washed with aqueous $NaHCO_3$ (5%) and brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography (pentane/diethyl ether, 2:1) to afford (*R*)-1-(benzyloxy)pent-4-yn-2-ol as a pale yellow oil (3.54 g, 89% yield). To a dimethyl sulfoxide (5 mL) solution of (*R*)-1-(benzyloxy)pent-4-yn-2-ol (3.0 g, 16 mmol, 1.0 equiv) was added potassium *tert*-butoxide (3.7 g, 32, 2.0 equiv) as a dimethyl sulfoxide (20 mL) solution. The reaction was stirred at ambient temperature for 1 h before quenching sequentially with brine and HCl (5.0 M). The aqueous was extracted with diethyl ether and the combined organic fractions were washed with aqueous

$NaHCO_3$ (5%) and brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography (pentane/diethyl ether, 2:1) to afford (*R*)-1-(benzyloxy)pent-3-yn-2-ol (2.86 g, 95% yield). To a tetrahydrofuran (5 mL) of lithium aluminum hydride (333 mg, 8.77 mmol, 2.0 equiv) was slowly added (*R*)-1-(benzyloxy)pent-3-yn-2-ol (833 mg, 4.38 mmol, 1.0 equiv) as a tetrahydrofuran (5 mL) solution. Following addition, the reaction was heated to reflux for 4 h. Upon cooling to ambient temperature, the reaction was quenched with aqueous ammonium hydroxide (30%) and the aqueous was extracted with diethyl ether. The organic fractions were combined, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography (pentane/diethyl ether, 3:1 → 2:1) to afford the title compound as a colorless oil (730 mg, 87% yield). Spectral data were consistent with the literature. Mosher ester ^{1}H NMR analysis: 99% ee.

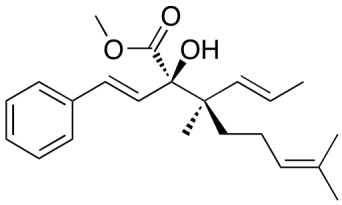


(2*R*,3*R*)-methyl 2-hydroxy-3-((*E*)-prop-1-en-1-yl)-2-((*E*)-styryl)octanoate (7a). Prepared by procedure *1.2.3* with **6a** (71 mg, 0.50 mmol, 1.0 equiv) and **2** (206 mg, 1.0 mmol, 2.0 equiv). The crude residue was purified by flash chromatography (pentane/diethyl ether, 30:1 → 20:1) to afford the title compound as a colorless oil (131 mg, 83%). $[\alpha]^{20}_D$ -4.5° (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.39 (m, 2H), 7.34-7.30 (m, 2H), 7.26-7.22 (m, 1H), 6.84 (d, J = 16.0 Hz, 1H), 6.24 (d, J = 16.0 Hz, 1H), 5.48 (dq, J = 15.2, 6.4 Hz, 1H), 5.31 (ddq, J = 15.2, 9.2, 1.6 Hz, 1H), 3.75 (s, 3H), 3.40 (s, 1H), 2.39 (t, J = 11.2 Hz, 1H), 1.67 (dd, J = 6.4, 1.6 Hz, 3H), 1.53-1.50 (m, 1H), 1.31-1.08 (m, 7H), 0.84 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.6, 136.7, 130.8, 130.2, 129.4, 128.7, 127.8, 126.8, 80.9, 53.1, 50.9, 31.9, 27.7, 27.4, 22.8, 18.3, 14.2. FTIR (neat): ν_{max}/cm^{-1} 3515, 1731, 1447, 1436, 1136. HRMS (p-APCI): *m/z* 299.2003

[$(M+H)^+$ requires 299.2006]. HPLC analysis: >99% ee (CHIRALCEL OD-H, 0.5% isopropanol/hexanes, 0.7 mL/min, UV: 254 nm). t_R = 13.7 min (major), 16.8 min (minor).

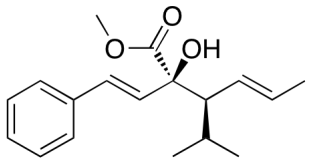


(2*R*,3*S*,*E*)-methyl 2-hydroxy-3-phenyl-2-((*E*)-styryl)hex-4-enoate (7b). Prepared by procedure *1.2.3* with **6b** (77 mg, 0.50 mmol, 1.0 equiv) and **2** (203 mg, 1.0 mmol, 2.0 equiv). The crude residue was purified by flash chromatography (pentane/diethyl ether, 30:1 → 10:1) to afford the title compound as a white solid (119 mg, 71%). MP = 112-114 °C. $[\alpha]^{20}_D$ -148.5° (*c* 1.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.34-7.32 (m, 2H), 7.27-7.14 (m, 8H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.26 (d, *J* = 16.0 Hz, 1H), 5.94 (ddq, *J* = 15.2, 9.2, 1.6 Hz), 5.31 (dq, *J* = 15.2, 6.8 Hz, 1H), 3.82 (s, 3H), 3.81 (d, *J* = 9.2 Hz, 1H), 3.59 (s, 1H), 1.69 (dd, *J* = 6.4, 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.1, 139.4, 136.7, 130.8, 129.5, 129.1, 129.0, 128.8, 128.6, 128.2, 127.7, 127.0, 126.7, 80.9, 57.2, 53.3, 18.4. FTIR (neat): ν_{max}/cm^{-1} 3506, 1728, 1448, 1436, 1140, 1118. HRMS (p-APCI): *m/z* 305.1535 [$(M-OH)^+$ requires 305.1536]. HPLC analysis: >99% ee (CHIRALCEL OD-H, 0.5% isopropanol/hexanes, 0.7 mL/min, UV: 254 nm). t_R = 25.3 min (major), 32.0 min (minor).



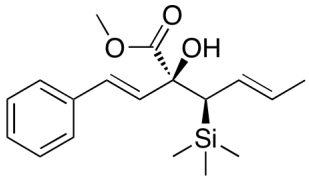
(2*R*,3*R*)-methyl 2-hydroxy-3,7-dimethyl-3-((*E*)-prop-1-en-1-yl)-2-((*E*)-styryl)oct-6-enoate (7c). Prepared by procedure *1.2.3* with **6c** (85 mg, 0.50 mmol, 1.0 equiv) and **2** (200 mg, 1.0 mmol, 2.0 equiv). The crude residue was purified by flash chromatography (pentane/diethyl

ether, 30:1 → 10:1) to afford the title compound as a colorless oil (140 mg, 82%). $[\alpha]^{20}_{D}$ -29.4° (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.2 Hz, 2H), 7.31 (d, *J* = 7.2 Hz, 2H), 7.24-7.21 (m, 1H), 6.81 (d, *J* = 15.6 Hz, 1H), 6.46 (d, *J* = 15.6 Hz, 1H), 5.55 (d, *J* = 15.6 Hz, 1H), 5.43 (dq, *J* = 15.6, 6.0 Hz, 1H), 5.07 (t, *J* = 7.6 Hz, 1H), 3.79 (s, 3H), 3.50 (s, 1H), 1.84-1.77 (m, 2H), 1.74 (d, *J* = 6.0 Hz, 3H), 1.65 (s, 3H), 1.61-1.56 (m, 1H), 1.42-1.34 (m, 1H), 1.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.2, 137.0, 134.8, 131.3, 130.9, 128.7, 127.8, 127.7, 126.9, 125.9, 125.1, 82.4, 53.0, 47.6, 35.2, 25.9, 23.0, 18.6, 17.8, 17.7. FTIR (neat): ν_{max}/cm^{-1} 3507, 1721, 1445, 1436, 1144. HRMS (p-APCI): *m/z* 343.2264 [$(M+H)^+$ requires 343.2268]. HPLC analysis: >99% ee (CHIRALPAK OD-H, 0.3% isopropanol/hexanes, 0.7 mL/min, UV: 254 nm). t_R = 18.1 min (major), 29.7 min (minor).

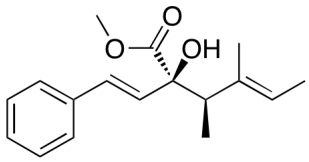


(2*R*,3*R*,*E*)-methyl 2-hydroxy-3-isopropyl-2-((*E*)-styryl)hex-4-enoate (7d). Prepared by procedure *1.2.3* with **6d** (57 mg, 0.50 mmol, 1.0 equiv) and **2** (202 mg, 1.0 mmol, 2.0 equiv). The crude residue was purified by flash chromatography (pentane/diethyl ether, 15:1) to afford the title compound as a white solid (100 mg, 70%). MP = 47-48 °C. $[\alpha]^{20}_{D}$ -26.9° (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.40 (m, 2H), 7.34-7.30 (m, 2H), 7.26-7.22 (m, 1H), 6.88 (d, *J* = 16.0 Hz, 1H), 6.29 (d, *J* = 16.0 Hz, 1H), 5.53-5.40 (m, 2H), 3.74 (s, 3H), 3.47 (s, 1H), 2.37 (dd, *J* = 9.0, 3.0 Hz, 1H), 2.05 (dqq, *J* = 6.8, 6.8, 2.8 Hz, 1H), 1.69 (d, *J* = 4.8 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.6, 136.6, 130.2, 129.7, 129.5, 128.6, 127.6, 126.7, 126.2, 81.5, 55.4, 53.0, 27.1, 23.3, 18.4, 18.2. FTIR (neat): ν_{max}/cm^{-1} 3508, 3026, 2954, 2873, 1728, 1448, 1436, 1145. HRMS (p-APCI): *m/z*

271.1697 [(M-OH)$^+$ requires 271.1693]. HPLC analysis: >99% ee (CHIRALPAK AD-H, 0.3% isopropanol/hexanes, 0.8 mL/min, UV: 230 nm). t_R = 14.6 min (major), 19.2 min (minor).

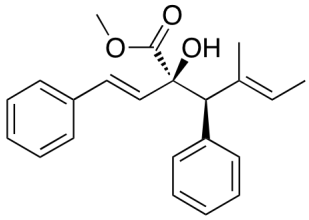


(2*S*,3*R*,*E*)-methyl 2-hydroxy-2-((*E*)-styryl)-3-(trimethylsilyl)hex-4-enoate (7e). Prepared by procedure *1.2.3* with **6e** (73 mg, 0.50 mmol, 1.0 equiv) and **2** (208 mg, 1.0 mmol, 2.0 equiv). The crude residue was purified by flash chromatography (pentane/diethyl ether, 30:1 → 20:1) to afford the title compound as a white solid (68 mg, 42%). MP = 58-60 ^{o}C. $[\alpha]^{20}_D$ -67.3^o (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.38 (m, 2H), 7.35-7.31 (m, 2H), 7.26-7.23 (m, 1H), 6.82 (d, *J* = 15.6 Hz, 1H), 6.26 (d, *J* = 15.6 Hz, 1H), 5.50-5.34 (m, 2H), 3.72 (s, 3H), 3.61 (s, 1H), 2.12 (d, *J* = 7.0 Hz, 1H), 1.67 (d, *J* = 4.8 Hz, 3H), 0.02 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.1, 136.8, 131.1, 129.8, 128.8, 127.8, 127.5, 126.8, 80.5, 53.1, 43.9, 18.4, -0.3. FTIR (neat): ν_{max}/cm^{-1} 3512, 2953, 1728, 1448,1436, 1099. HRMS (p-APCI): *m/z* 301.1620 [(M-OH)$^+$ requires 301.1618]. HPLC analysis: >99% ee (CHIRALCEL OD-H, 0.5% isopropanol/hexanes, 0.7 mL/min, UV: 254 nm). t_R = 13.1 min (major), 16.5 min (minor).

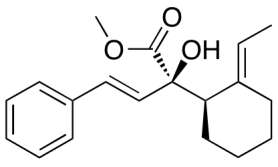


(2*R*,3*R*,*E*)-methyl 2-hydroxy-3,4-dimethyl-2-((*E*)-styryl)hex-4-enoate (7f). Prepared by procedure *1.2.3* with **6f** (45 mg, 0.50 mmol, 1.0 equiv) and **2** (214 mg, 1.0 mmol, 2.0 equiv). The crude residue was purified by flash chromatography (pentane/diethyl ether, 20:1) to afford the title compound as a colorless oil (86 mg, 61%). $[\alpha]^{20}_D$ +29.4^o (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.41 (m, 2H), 7.35-7.31 (m, 2H), 7.27-7.23 (m, 1H), 6.84 (d, *J* = 16.0 Hz,

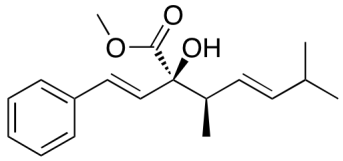
1H), 6.28 (d, J = 16.0 Hz, 1H), 5.38 (dq, J = 6.8, 1.2 Hz, 1H), 3.76 (s, 3H), 3.32 (s, 1H), 2.70 (q, J = 7.2 Hz, 1H), 1.65 (t, J = 1.2, 3H), 1.58 (dd, J = 6.8, 0.8 Hz, 3H), 1.08 (d, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.8, 136.8, 136.7, 130.5, 129.8, 128.7, 126.8, 122.3, 81.3, 52.9, 49.7, 14.0, 13.6, 12.8. FTIR (neat): ν_{max}/cm^{-1} 3513, 1729, 1448, 1436, 1145. HRMS (p-APCI): m/z 257.1536 [(M-OH)$^+$ requires 257.1536]. HPLC analysis: >99% ee (CHIRALCEL OD-H, 0.5% isopropanol/hexanes, 0.7 mL/min, UV: 254 nm). t_R = 17.3 min (major), 33.4 min (minor).



(2*R*,3*S*,*E*)-methyl 2-hydroxy-4-methyl-3-phenyl-2-((*E*)-styryl)hex-4-enoate (7g). Prepared by procedure *1.2.3* with **6g** (81 mg, 0.50 mmol, 1.0 equiv) and **2** (202 mg, 1.0 mmol, 2.0 equiv). The crude residue was purified by flash chromatography (hexanes/ethyl acetate, 10:1) to afford the title compound as a white solid (114 mg, 68%). MP = 106-108 ^{o}C. $[\alpha]^{20}_D$ -101.2 ^{o} (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.40 (m, 2H), 7.26-7.12 (m, 8H), 6.63 (d, J = 16.0 Hz, 1H), 6.18 (d, J = 16.0 Hz, 1H), 5.75 (q, J = 7.2 Hz, 1H), 3.89 (s, 1H), 3.81 (s, 3H), 3.62 (s, 1H), 1.60 (d, J = 7.2 Hz, 3H), 1.58 (d, J = 1.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.5, 138.3, 136.5, 135.6, 130.7, 130.3, 130.2, 128.4, 127.7, 127.5, 126.6, 126.5, 122.2, 81.1, 60.1, 53.1, 15.8, 13.7. FTIR (neat): ν_{max}/cm^{-1} . HRMS (p-APCI): m/z 337.1806 [(M+H)$^+$ requires 337.1798]. HPLC analysis: >99% ee (CHIRALPAK AD-H, 1.0% isopropanol/hexanes, 1.0 mL/min, UV: 254 nm). t_R = 19.2 min (minor), 21.2 min (major).

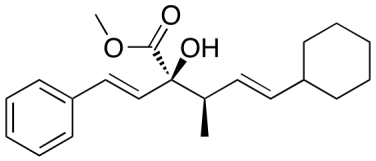


(*R*,*E*)-methyl 2-((*R*,*E*)-2-ethylidenecyclohexyl)-2-hydroxy-4-phenylbut-3-enoate (7h). Prepared by procedure *1.2.3* with **6h** (64 mg, 0.50 mmol, 1.0 equiv) and **2** (202 mg, 1.0 mmol, 2.0 equiv). The crude residue was purified by flash chromatography (pentane/diethyl ether, 30:1) to afford the title compound as a white solid (117 mg, 77%). MP = 136-137 ^{o}C. $[\alpha]^{20}_{D}$ -58.6^{o} (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.39 (m, 2H), 7.33-7.29 (m, 2H), 7.25-7.21 (m, 1H), 6.86 (d, *J* = 16.0 Hz, 1H), 6.24 (d, *J* = 16.0 Hz, 1H), 5.24 (q, *J* = 6.8 Hz, 1H), 3.74 (s, 3H), 3.40 (s, 1H), 2.61 (t, *J* = 5.2 Hz, 1H), 2.30-2.25 (m, 2H), 1.89-1.82 (m, 2H), 1.68-1.53 (m, 2H), 1.57 (d, *J* = 6.8 Hz, 3H), 1.44-1.32 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.1, 139.3, 136.7, 130.8, 130.6, 128.7, 127.9, 126.9, 118.5, 82.6, 53.1, 48.9, 27.5, 27.4, 27.3, 24.0, 13.1. FTIR (neat): ν_{max}/cm^{-1} 3503, 1729, 1447, 1133. HRMS (p-APCI): *m/z* 283.1690 [$(M\text{-}OH)^+$ requires 283.1693]. HPLC analysis: >99% ee (CHIRALPAK AD-H, 0.3% isopropanol/hexanes, 0.7 mL/min, UV: 254 nm). t_R = 29.7 min (minor), 33.1 min (major).

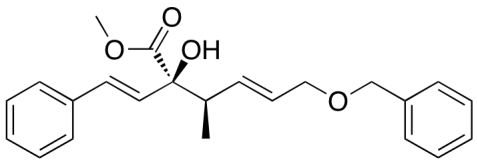


(2*R*,3*R*,*E*)-methyl 2-hydroxy-3,6-dimethyl-2-((*E*)-styryl)hept-4-enoate (7i). Prepared by procedure *1.2.3* with **6i** (59 mg, 0.50 mmol, 1.0 equiv) and **2** (201 mg, 1.0 mmol, 2.0 equiv). The crude residue was purified by flash chromatography (pentane/diethyl ether, 30:1 → 20:1) to afford the title compound as a colorless oil (112 mg, 75%). $[\alpha]^{20}_{D}$ +28.8^{o} (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.41 (m, 2H), 7.35-7.31 (m, 2H), 7.27-7.23 (m, 1H), 6.86 (d, *J* = 16.0 Hz, 1H), 6.26 (d, *J* = 16.0 Hz, 1H), 5.46 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.34 (dd, *J* = 16.0, 8.8 Hz, 1H), 3.77 (s, 3H), 3.36 (s, 1H), 2.66-2.59 (m, 1H), 2.29-2.21 (m, 1H), 1.02 (d, *J* = 7.2 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.6, 140.2, 136.7, 130.8, 129.3, 128.7, 127.9, 127.3, 126.9, 80.7, 53.0, 45.0, 31.3, 22.9, 22.8, 14.2.

FTIR (neat): ν_{max}/cm^{-1} 3515, 1731, 1448, 1436, 1142. HRMS (p-APCI): *m/z* 271.1694 [(M-OH)$^+$ requires 271.1693]. HPLC analysis: >99% ee (CHIRALCEL OD-H, 0.5% isopropanol/hexanes, 0.7 mL/min, UV: 254 nm). t_R = 15.9 min (minor), 19.6 min (major).

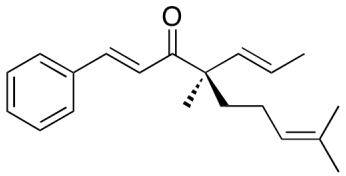


(2*R*,3*R*,*E*)-methyl 5-cyclohexyl-2-hydroxy-3-methyl-2-((*E*)-styryl)pent-4-enoate (7j). Prepared by procedure *1.2.3* with **6j** (78 mg, 0.50 mmol, 1.0 equiv) and **2** (204 mg, 1.0 mmol, 2.0 equiv). The crude residue was purified by flash chromatography (pentane/diethyl ether, 20:1 → 10:1) to afford the title compound as a white solid (143 mg, 86%). MP = 130-131 ^{o}C. $[\alpha]^{20}_D$ +34.1^o (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.41 (m, 2H), 7.34-7.31 (m, 2H), 7.26-7.23 (m, 1H), 6.86 (d, *J* = 16.0 Hz, 1H), 6.26 (d, *J* = 16.0 Hz, 1H), 5.43 (dd, *J* = 15.6, 6.4 Hz, 1H), 5.34 (dd, *J* = 15.6, 8.4 Hz, 1H), 3.77 (s, 3H), 3.35 (s, 1H), 2.66-2.58 (m, 1H), 1.92-1.88 (m, 1H), 1.74-1.64 (m, 1H), 1.31-1.13 (m, 4H), 1.08-1.04 (m, 1H), 1.02 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.6, 139.0 136.7, 130.8, 129.2, 128.8, 127.9, 127.8, 126.8, 80.8, 53.1, 45.1, 40.9, 33.4, 33.3, 26.3, 26.2, 26.1, 14.2. FTIR (neat): ν_{max}/cm^{-1} 3516, 2922, 2849, 1730, 1447,114. HRMS (p-APCI): *m/z* 311.2005 [(M-OH)$^+$ requires 311.2006]. HPLC analysis: >99% ee (CHIRALCEL OD-H, 0.5% isopropanol/hexanes, 0.7 mL/min, UV: 254 nm). t_R = 16.4 min (major), 19.9 min (minor).



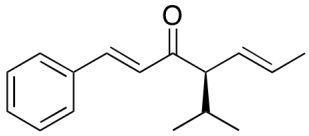
(2*R*,3*R*,*E*)-methyl 6-(benzyloxy)-2-hydroxy-3-methyl-2-((*E*)-styryl)hex-4-enoate (7k). Prepared by procedure *1.2.3* with **6k** (96 mg, 0.50 mmol, 1.0 equiv) and **2** (202 mg, 1.0 mmol,

2.0 equiv). The crude residue was purified by flash chromatography (pentane/diethyl ether, 10:1) to afford the title compound as a colorless oil (129 mg, 70%). MP = 130-131 ^{o}C. $[\alpha]^{20}_{D}$ +34.1^{o} (*c* 1.0, $CHCl_3$). $[\alpha]^{20}_{D}$ +13.1^{o} (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.39 (m, 2H), 7.36-7.22 (m, 8H), 6.86 (d, *J* = 15.6 Hz, 1H), 6.25 (d, *J* = 15.6 Hz, 1H), 5.73-5.62 (m, 2H), 4.51-4.44 (m, 2H), 4.02 -3.92 (m, 2H), 3.77 (s, 3H), 3.39 (s, 1H), 2.79-2.71 (m, 1H), 1.06 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.5, 138.6, 136.6, 134.4, 131.2, 129.0, 128.8, 128.6, 128.0, 127.9, 127.8, 126.9, 80.3, 71.9, 70.7, 83.3, 44.8, 14.0. FTIR (neat): ν_{max}/cm^{-1} 3512, 3027, 2951, 2852, 1730,1496, 1449, 1144. HRMS (p-APCI): *m/z* 367.1910 [$(M+H)^+$ requires 367.1917]. HPLC analysis: >99% ee (CHIRALCEL AD-H, 1.0% isopropanol/hexanes, 1.0 mL/min, UV: 254 nm). t_R = 22.7 min (minor), 23.9 min (major).



(*R*,*E*)-4,8-dimethyl-1-phenyl-4-((*E*)-prop-1-en-1-yl)nona-1,7-dien-3-one (8a). To a tetrahydrofuran (4 mL) solution of **7c** (270 mg, 0.79 mmol, 1.0 equiv) at 0 ^{o}C was added lithium aluminum hydride solution (1.0 M in tetrahydrofuran, 2.4 mL, 2.4 mmol, 3.0 equiv) dropwise over 30 min. Following addition, the reaction was allowed to warm to room temperature and stirred for an additional 4 h. The reaction vessel was again cooled to 0 ^{o}C and the reaction was carefully quenched by sequential addition of ethyl acetate (2 mL) and saturated aqueous sodium potassium tartrate (10 mL). The mixture was partitioned between H_2O (15 mL) and ethyl acetate (15 mL) and stirred until two distinct layers formed. The layers were separated and the aqueous was extracted with ethyl acetate. The organic fractions were combined and washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude residue was dissolved in

tetrahydrofuran/H_2O (1:1, 10 mL) and sodium periodate (338 mg, 1.58 mmol, 2.0 equiv) was added in one portion with vigorous stirring. The reaction was stirred at room temperature for 6 h and the quenched with addition of aqueous sodium thiosulfate solution (20 mL). The aqueous was extracted with ethyl acetate and the combined organic fractions were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude residue was purified by flash chromatography (pentane/diethyl ether, 20:1 → 10:1) to afford the title compound as a colorless oil (200 mg, 90% yield). $[\alpha]^{20}_D$ +2.4^o (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 15.8 Hz, 1H), 7.56-7.53 (m, 2H), 7.39-7.36 (m, 3H), 7.04 (d, J = 15.8 Hz, 1H), 5.64-5.53 (m, 2H), 5.11-5.07 (m, 1H), 2.00-1.89 (m, 1H) 1.88-1.76 (m, 2H), 1.74 (d, J = 4.8 Hz, 3H), 1.68-1.61 (m, 1H), 1.65 (s, 3H), 1.55 (s, 3H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.6, 142.3, 135.3, 134.7, 132.0, 130.3, 129.0, 128.5, 126.4, 124.5, 122.5, 52.7, 38.0, 25.9, 23.3, 20.9, 18.7, 17.8. FTIR (neat): ν_{max}/cm^{-1} 3026, 2966, 2915, 2855, 1683, 1608, 1576, 1495, 1448, 1049. HRMS (p-APCI): *m/z* 283.2055 [$(M+H)^+$ requires 283.2056].

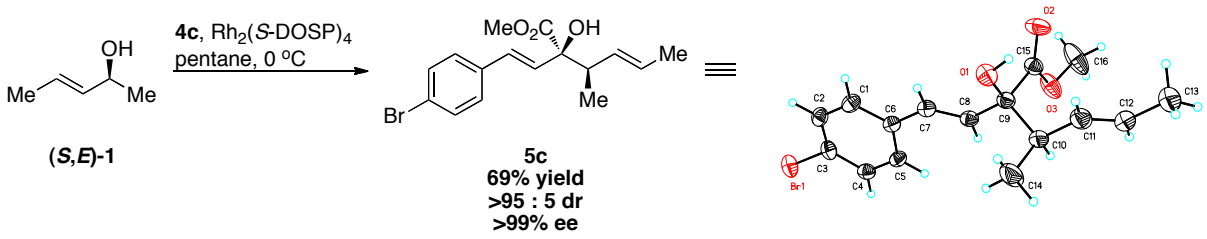


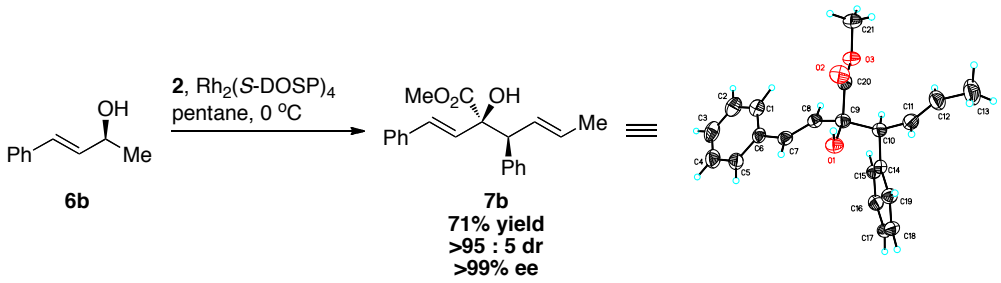
(*R*,1*E*,5*E*)-4-isopropyl-1-phenylhepta-1,5-dien-3-one (8b). To a tetrahydrofuran (4 mL) solution of **7d** (240 mg, 0.83 mmol, 1.0 equiv) at 0 ^{o}C was added lithium aluminum hydride solution (1.0 M in tetrahydrofuran, 2.5 mL, 2.5 mmol, 3.0 equiv) dropwise over 30 min. Following addition, the reaction was allowed to warm to room temperature and stirred for an additional 4 h. The reaction vessel was again cooled to 0 ^{o}C and the reaction was carefully quenched by sequential addition of ethyl acetate (5 mL) and saturated aqueous sodium potassium tartrate (25 mL). The mixture was further dilute with ethyl acetate (20 mL) and stirred until two distinct layers formed. The layers were separated and the aqueous was extracted with ethyl

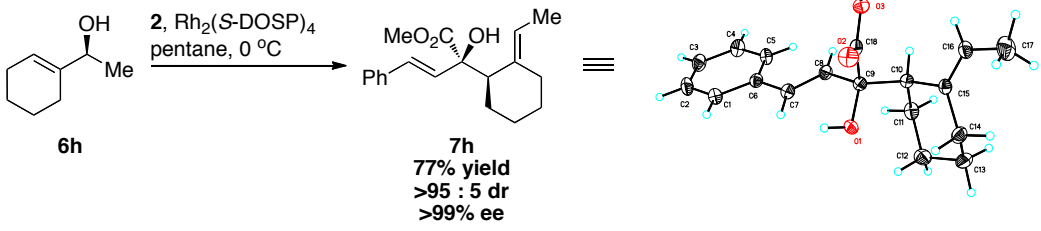
acetate. The organic fractions were combined and washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude residue was dissolved in tetrahydrofuran/H_2O (1:1, 10 mL) and sodium periodate (355 mg, 1.66 mmol, 2.0 equiv) was added in one portion with vigorous stirring. The reaction was stirred at room temperature for 4 h and the quenched with addition of aqueous sodium thiosulfate solution (25 mL). The aqueous was extracted with ethyl acetate and the combined organic fractions were washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by flash chromatography (pentane/diethyl ether, 15:1) to afford the title compound as a colorless oil (169 mg, 89% yield). $[\alpha]^{20}_D$ -74.2^o (*c* 2.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 16.0 Hz, 1h), 7.57-7.55 (m, 2H), 7.39-7.37 (m, 3H), 6.80 (d, J = 16.0 Hz, 1H), 5.60 (dq, J = 15.2, 6.4 Hz, 1H), 5.43 (m, 1H), 3.02 (t, J = 9.0 Hz, 1H), 2.17-2.05 (m, 1H), 1.71 (dd, J = 6.4, 1.6 Hz, 3H), 0.92 (d, J = 1.6 Hz, 3H), 0.90 (d, J = 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.0, 142.5, 134.9, 130.5, 129.8, 129.1, 128.5, 128.4, 125.6, 63.1, 30.1, 21.4, 20.1, 18.3. FTIR (neat): ν_{max}/cm^{-1} 3026, 2959, 2870, 1685, 1652, 1607, 1576, 1465. HRMS (p-APCI): *m/z* 229.1591 [$(M+H)^+$ requires 229.1587]. HPLC analysis: >99% ee (CHIRALCEL AD-H, 0.4% isopropanol/hexanes, 0.4 mL/min, UV: 254 nm). t_R = 22.6 min (major), 24.9 min (minor).

3. Stereochemical Rationale

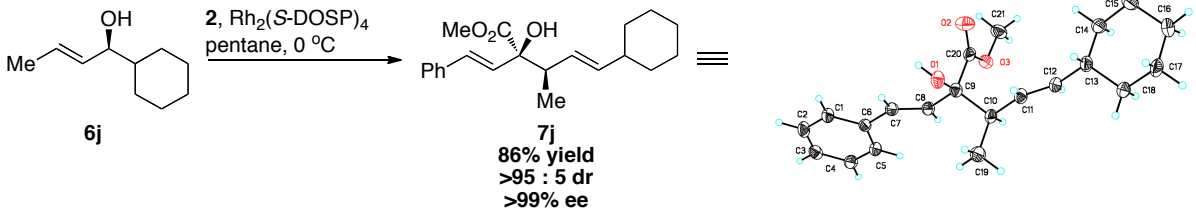
The absolute configuration of compounds **5c**, **7b** and **7h** were each determined by X-ray diffraction and applied to all other products of the same enantiomeric series by analogy.





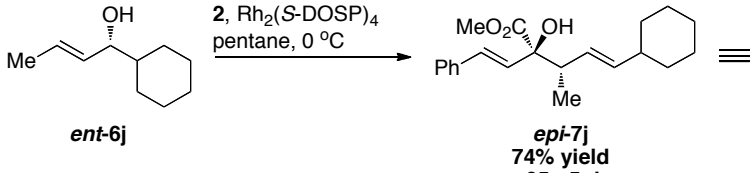


The [2,3]-sigmatropic rearrangement was conducted with both **6j** and *ent*-**6j** and **2** catalyzed by Rh_2(*S*-DOSP)$_4$, to prepare the two C_3-diastereoisomers of **7j**. Analysis of each product by X-Ray crystallography verified that, indeed, the configuration of the C_2-stereocenter was governed by the rhodium catalyst and the C_3-stereocenter by the alcohol geometry. The stereochemistry of products in Table 1 was assigned by inference from these results. Complete crystallographic data is available in Section 5.



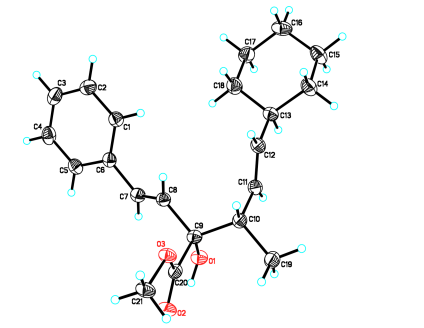
6j

7j
86% yield
>95 : 5 dr
>99% ee



***ent*-6j**

***epi*-7j**
74% yield
>95 : 5 dr
>99% ee



4. References

1. Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

2. Davies, J. M. L.; Yang, J.; Manning, J. R. *Tetrahedron: Asymmetry* **2006**, *17*, 665.

3. Davies, H. M. L.; Bruzinski, P.; Hutcheson, D. K.; Fall, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 6897.

4. Davies, H. M. L.; Hansen, T.; Churchill, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 3063.

5. Bulugahapitiya, P; Landais, Y.; Para-Rapado, L.; Planchenault, D.; Weber, V. *J. Org. Chem.* **1997**, *62*, 1630.

6. Davies, H. M. L.; Hougland, P. W.; Cantrell Jr., W. R. *Synth. Commun.* **1992**, *22*, 971.

7. Wood, J. L.; Moniz, G. A.; Pflum, D. A.; Stoltz, B. M.; Holubec, A. A.; Dietrich, H.-J. *J. Am. Chem. Soc.* **1999**, *121*, 1748.

8. Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237.

5. Crude NMR Data

Table 1, Entry 1

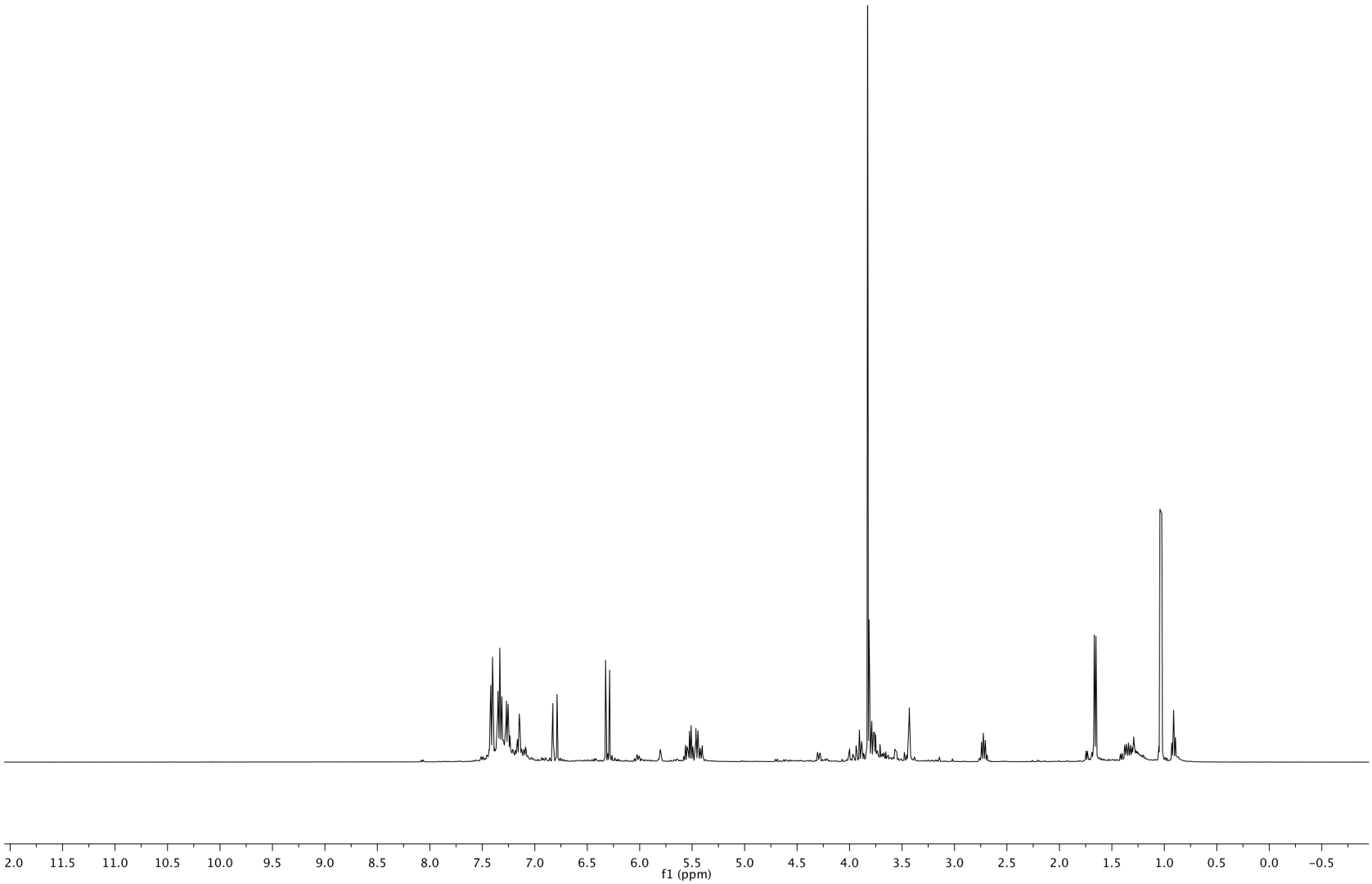


Table 1, Entry 3

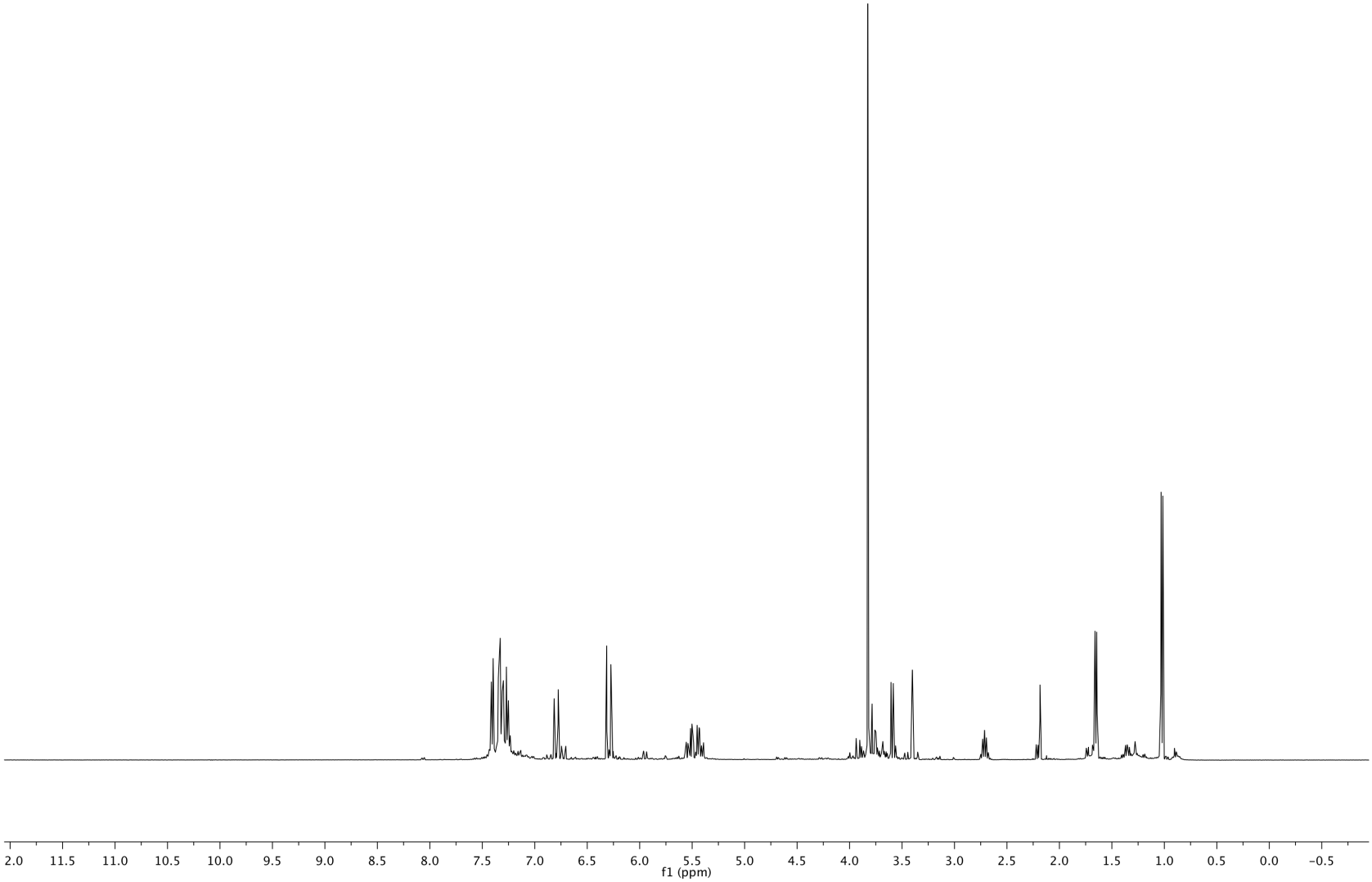
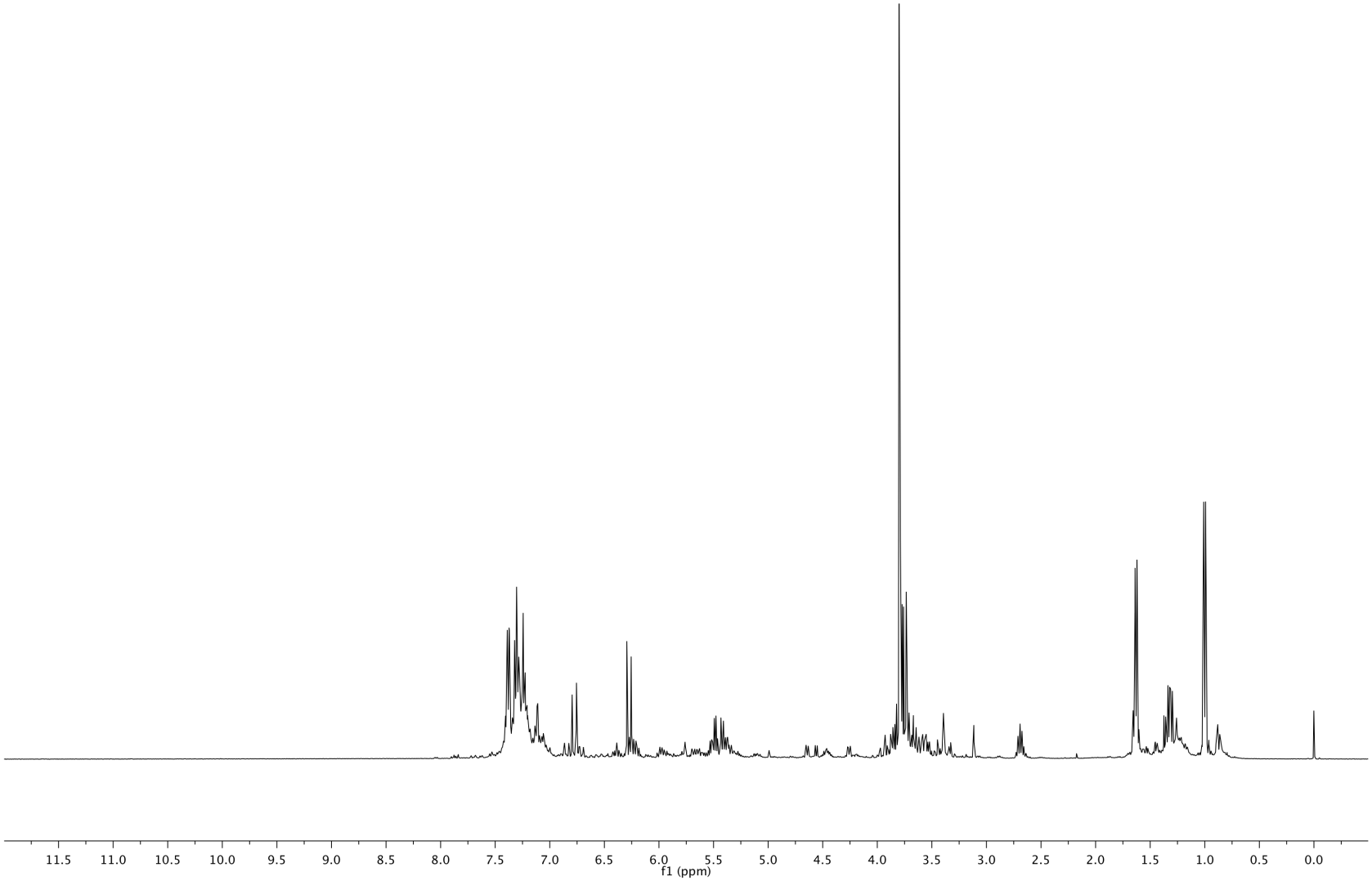
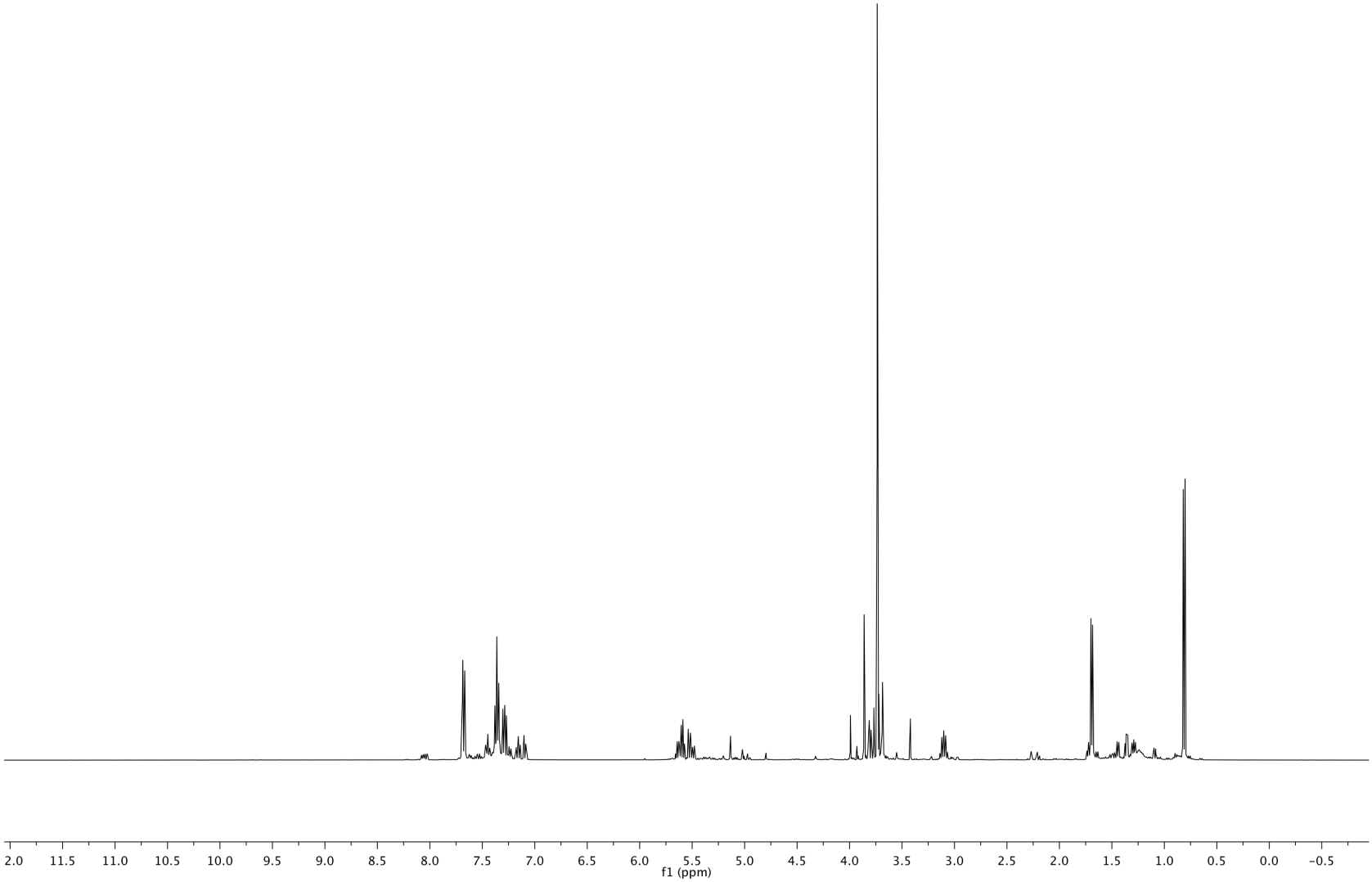


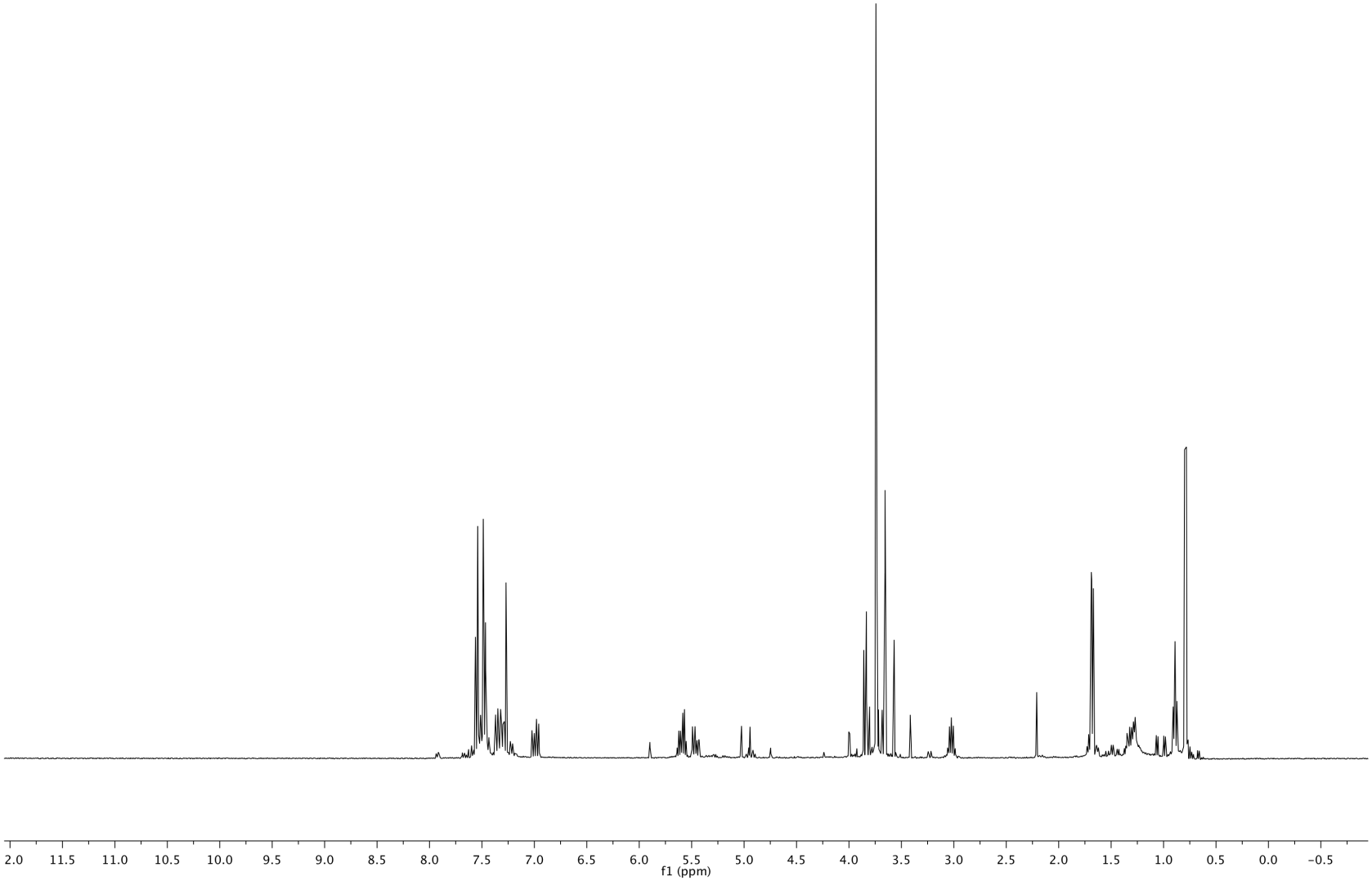
Table 1, Entry 6



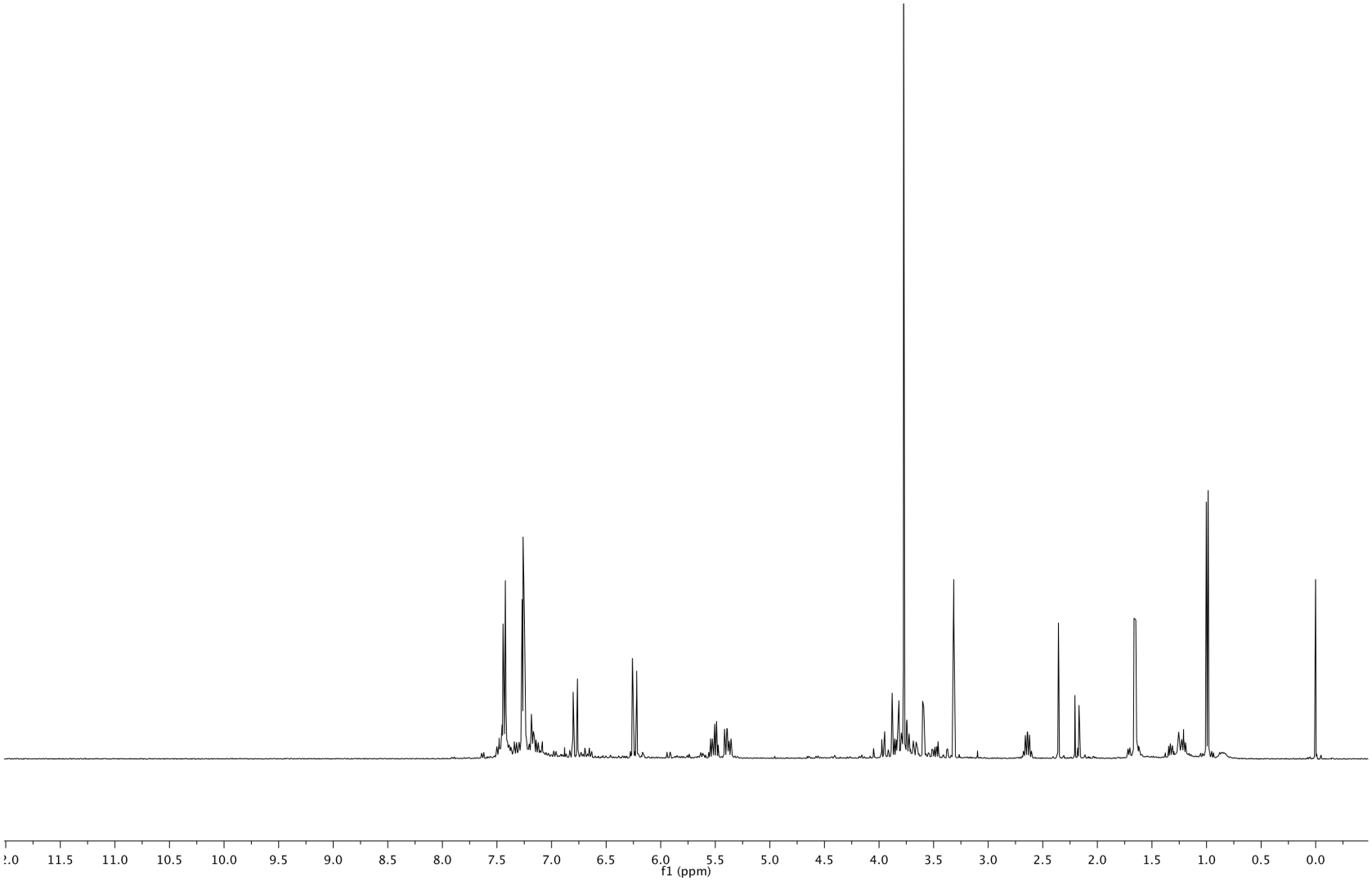
5a crude


2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

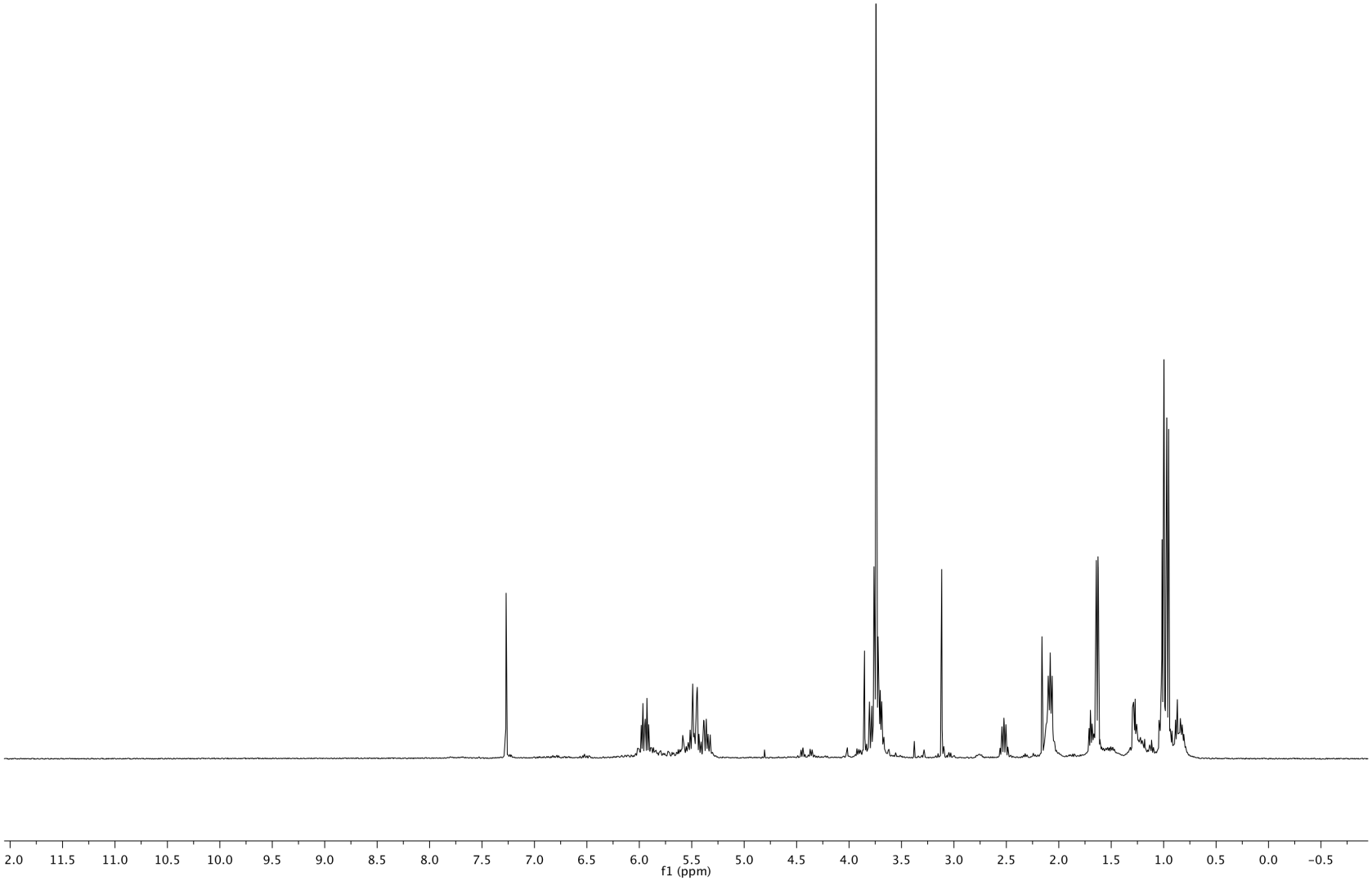
5b crude


2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

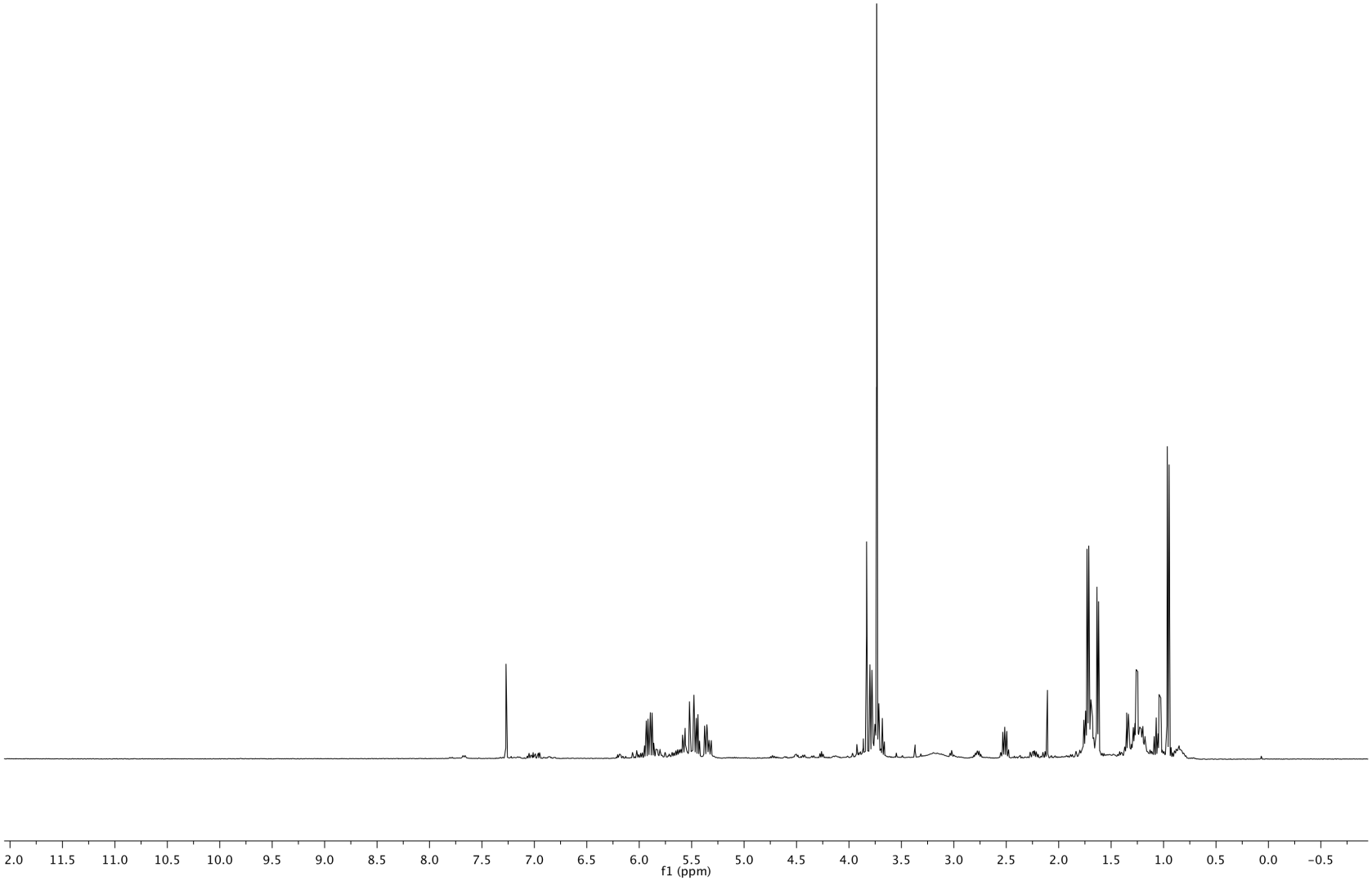
5c crude


12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

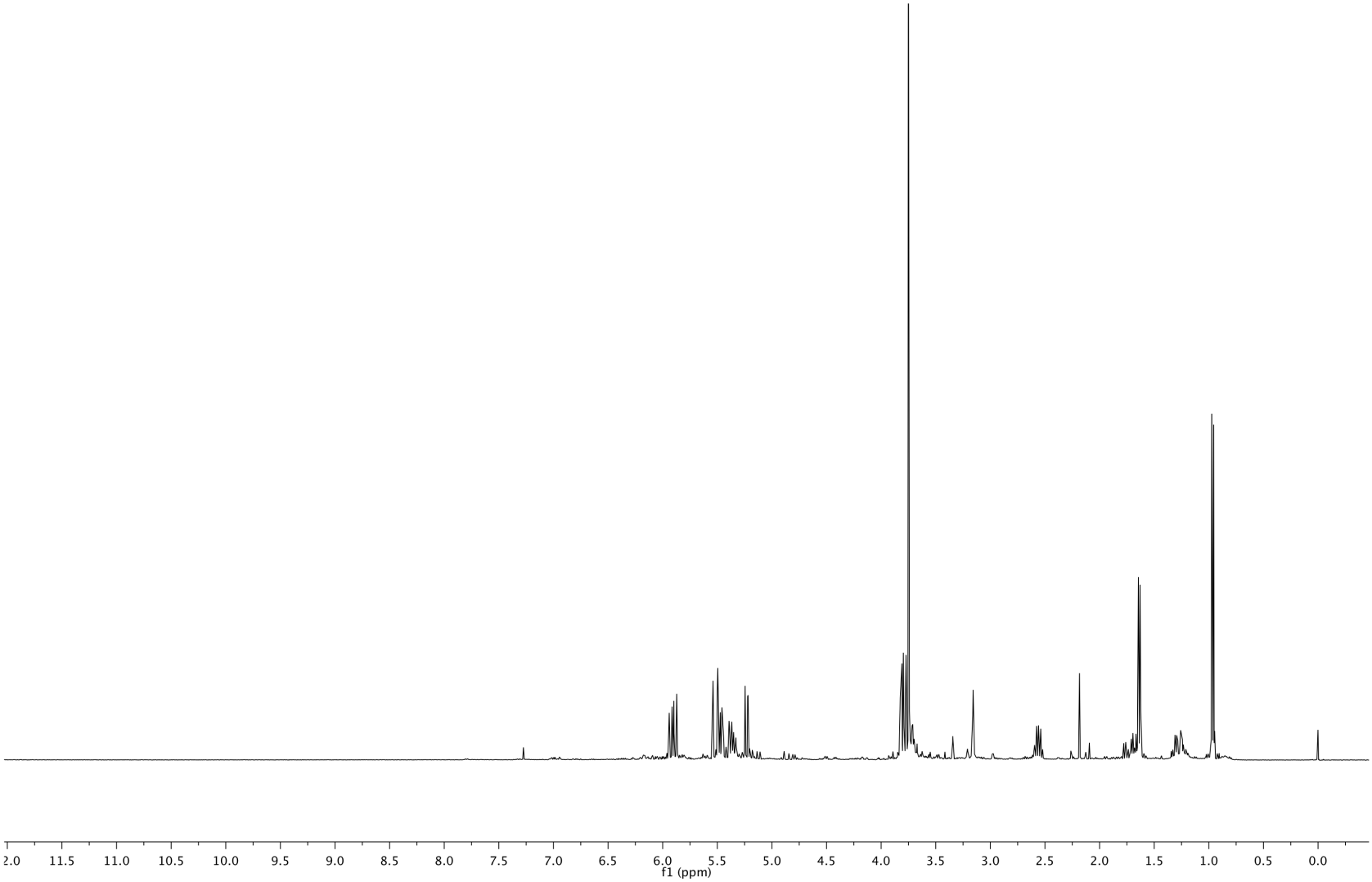
5d crude


2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

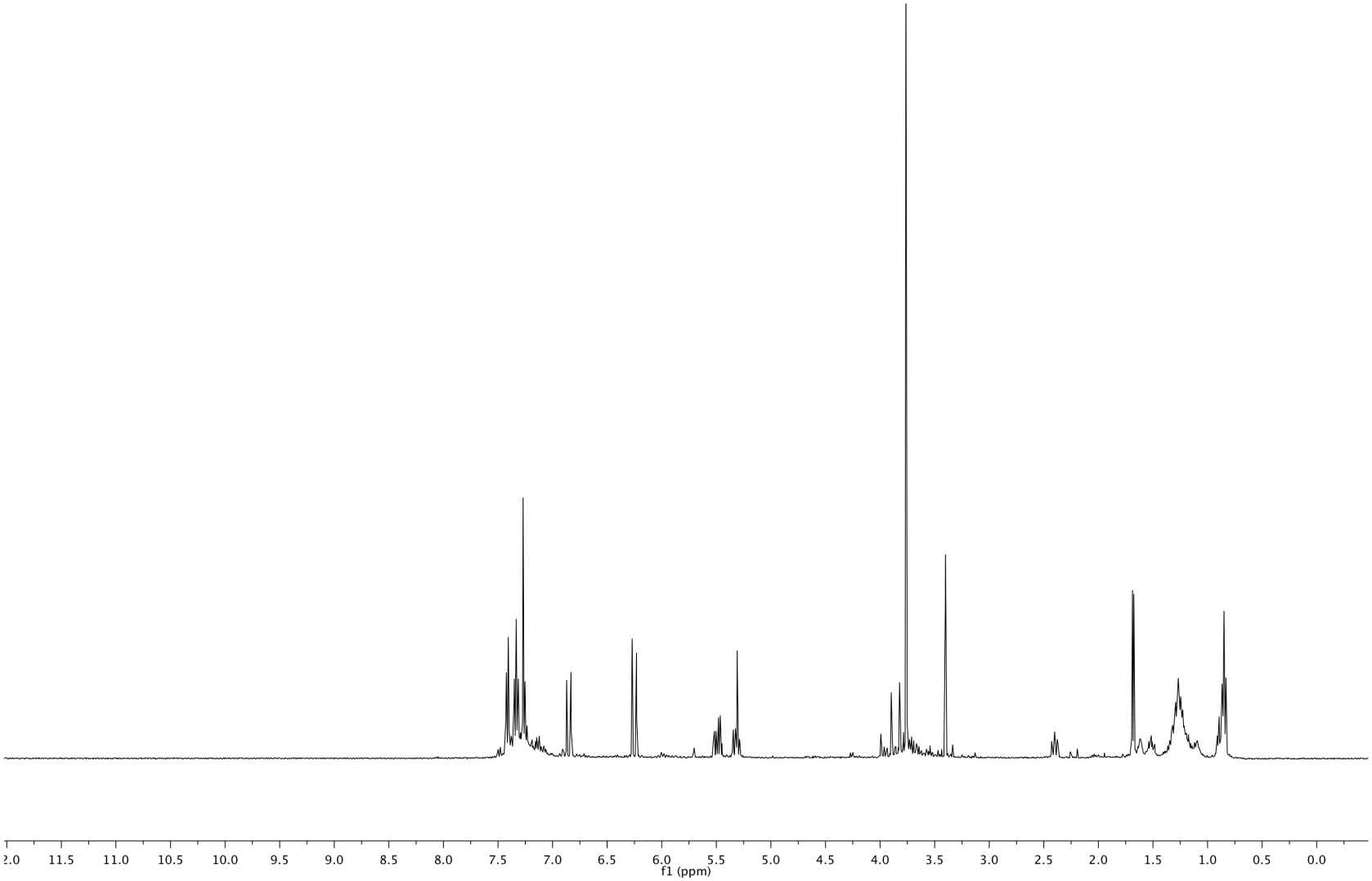
5e crude


2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

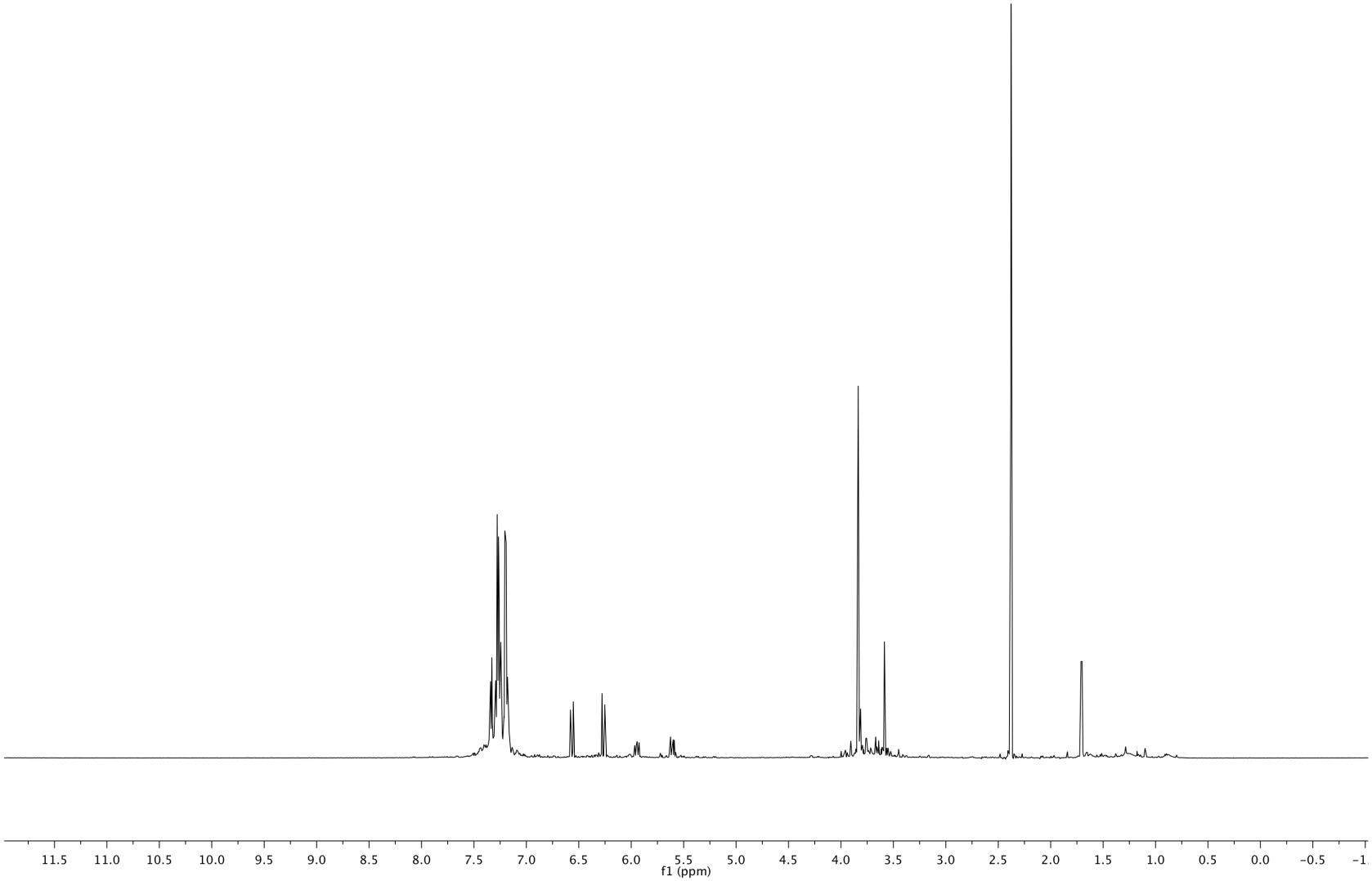
5f crude


2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

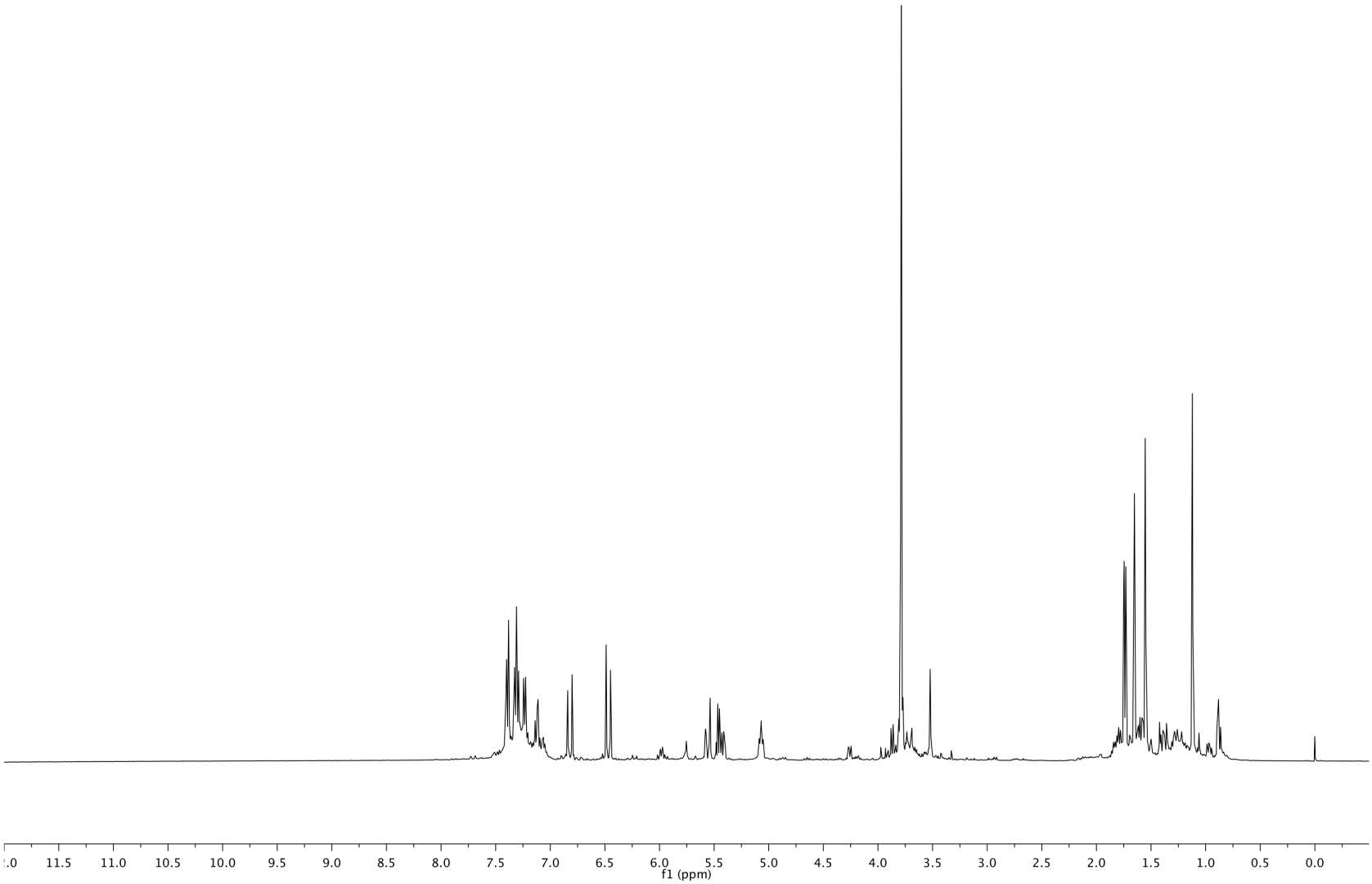
7a crude


12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

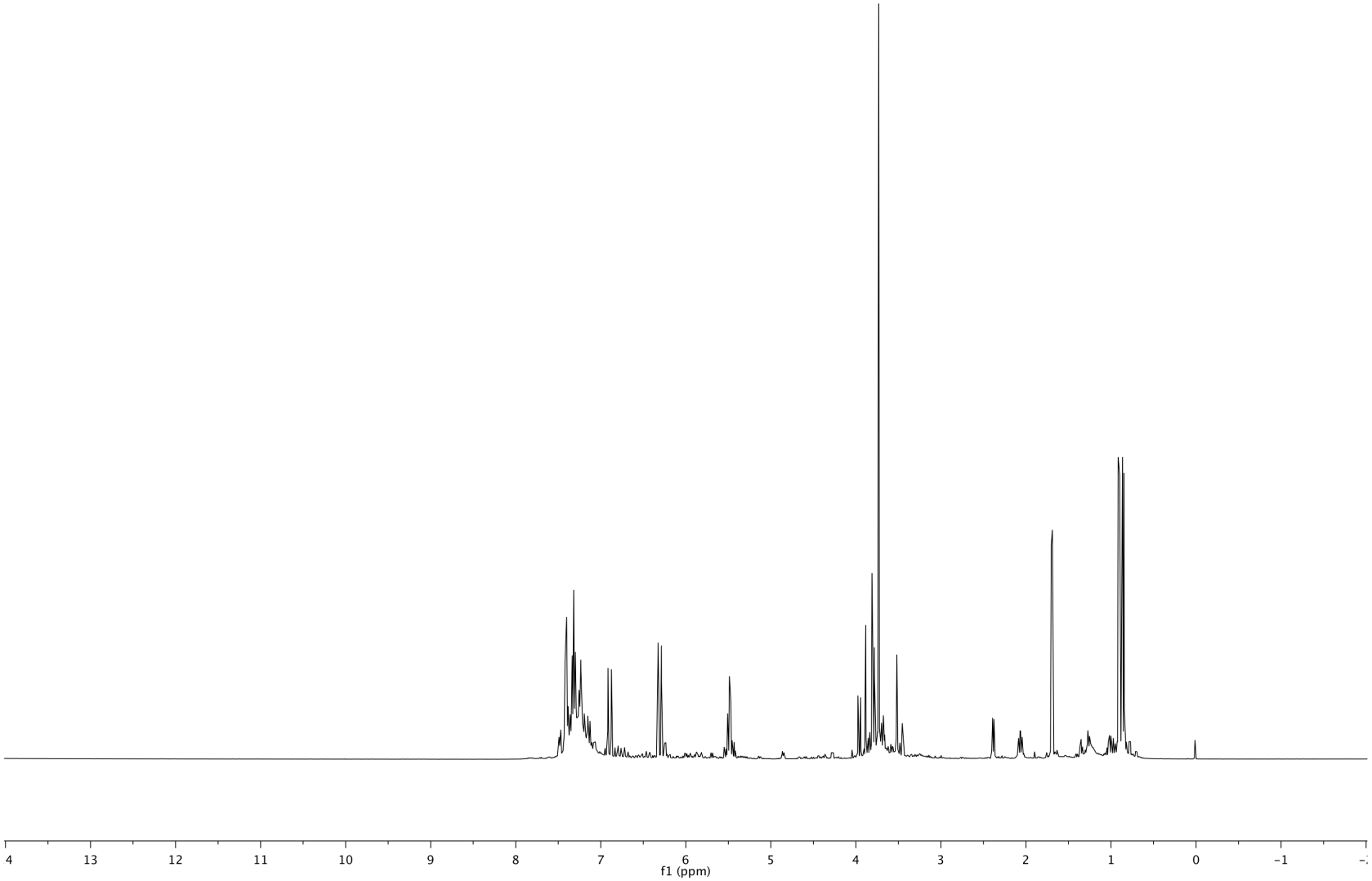
7b crude


11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)

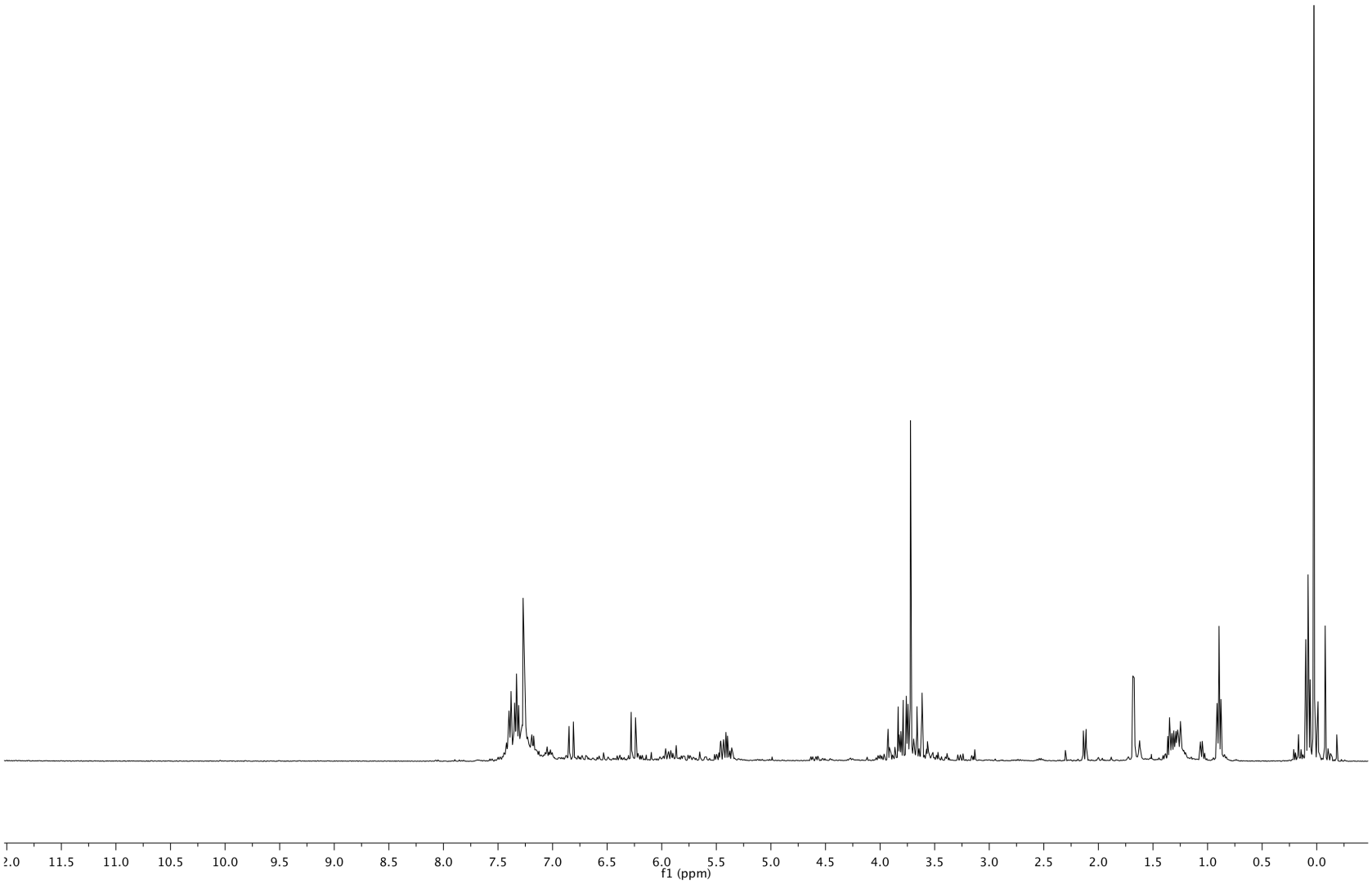
7c crude


11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

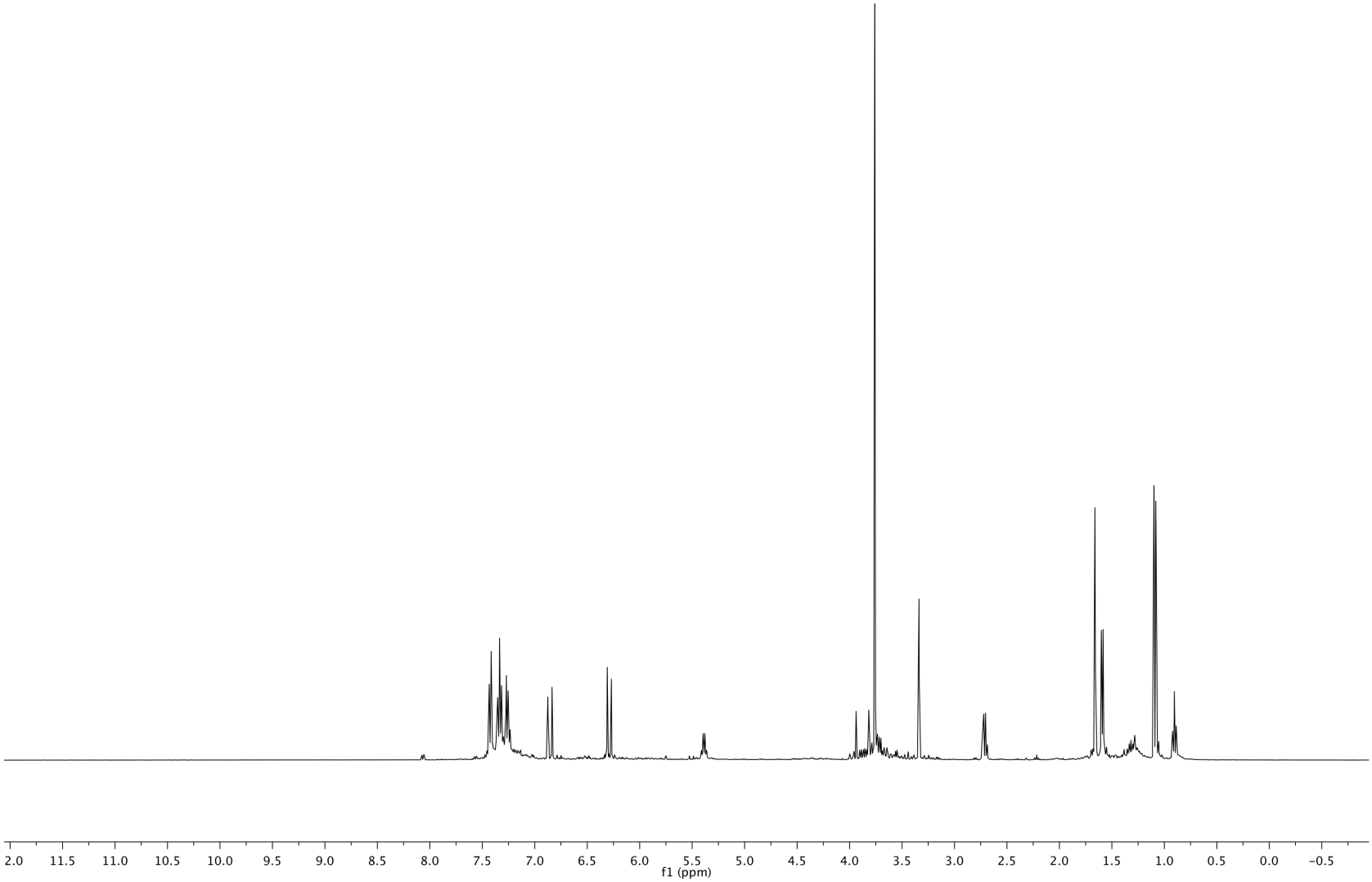
7d crude



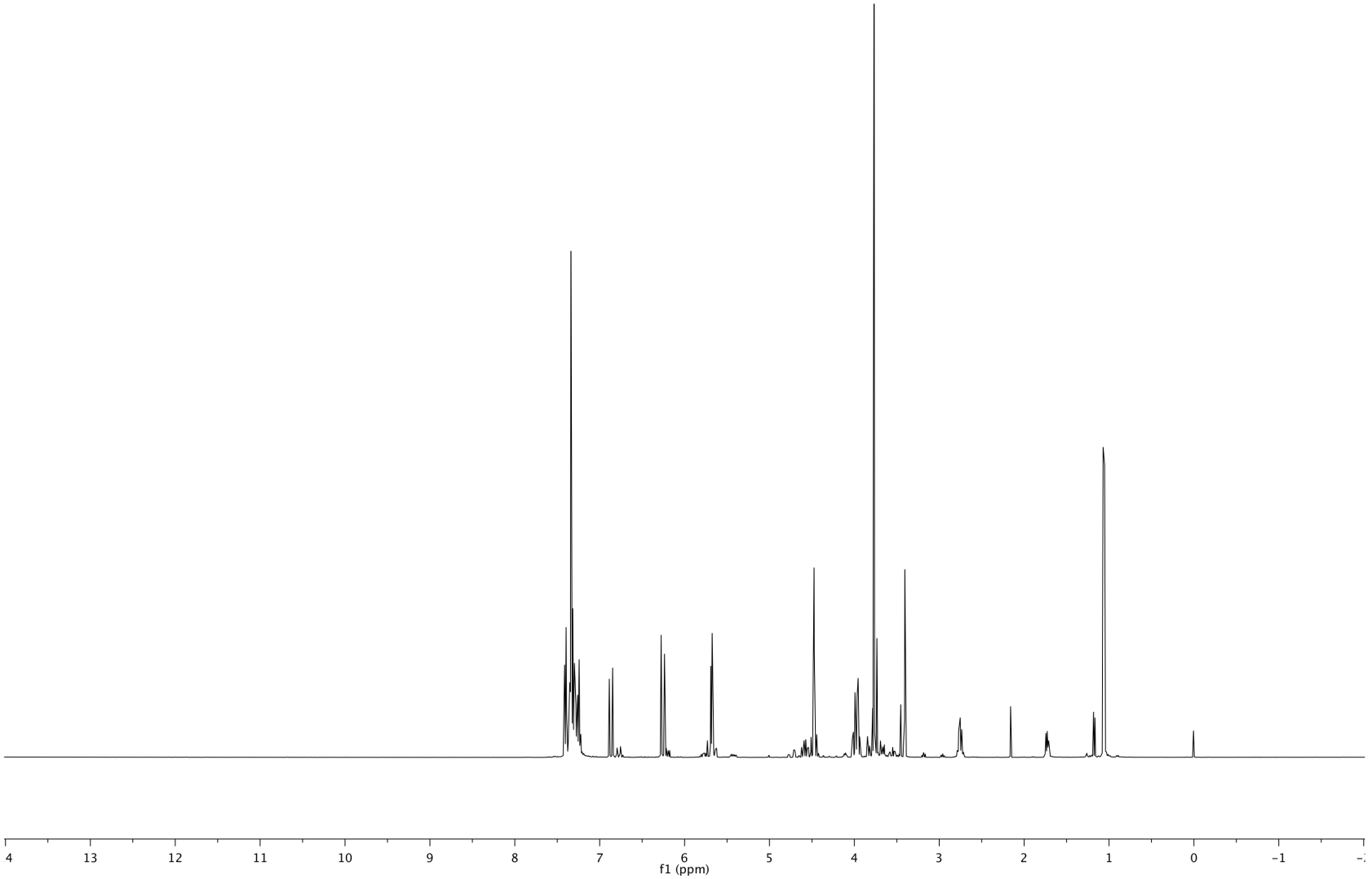
7e crude


12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

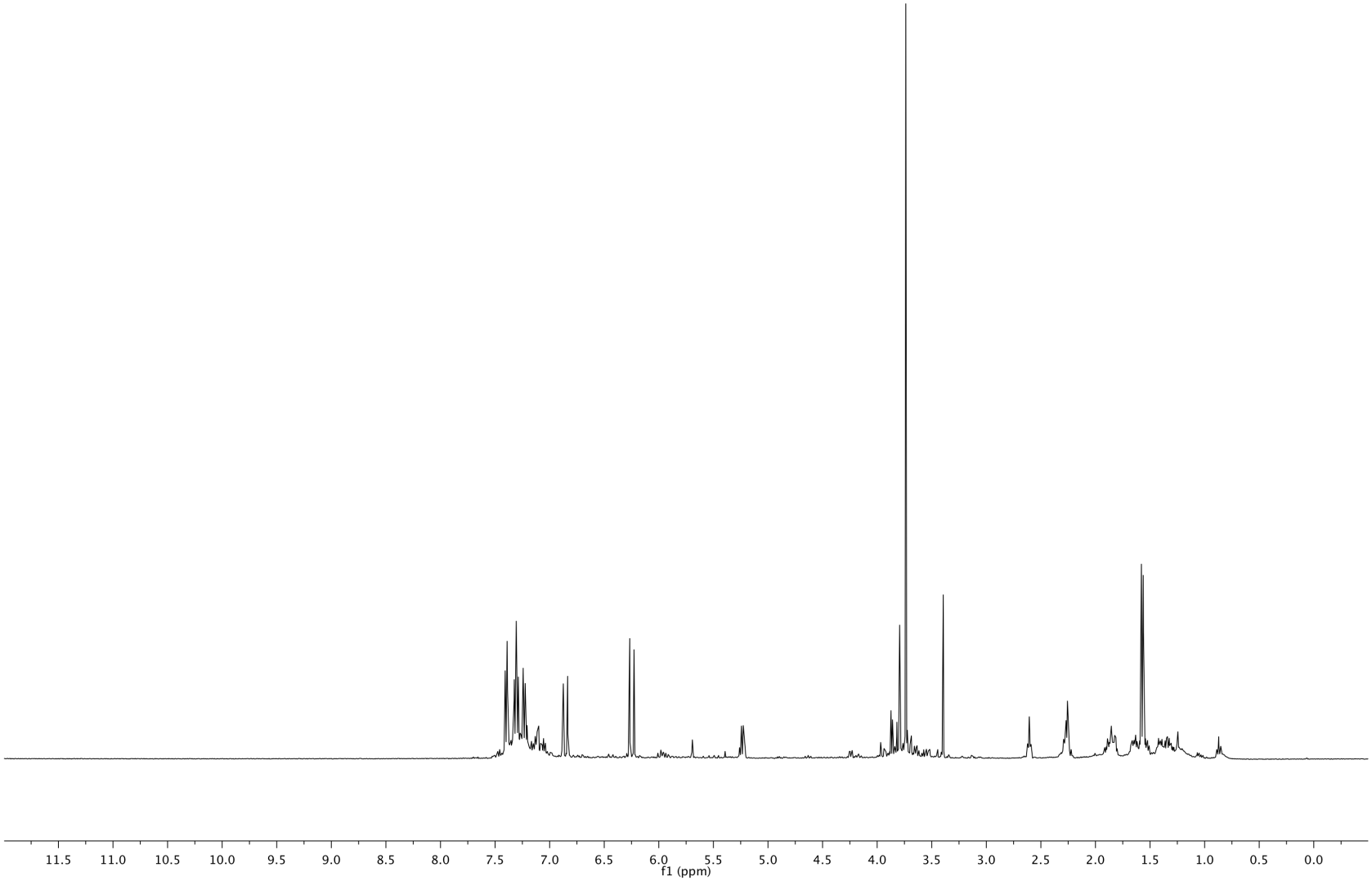
7f crude


2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

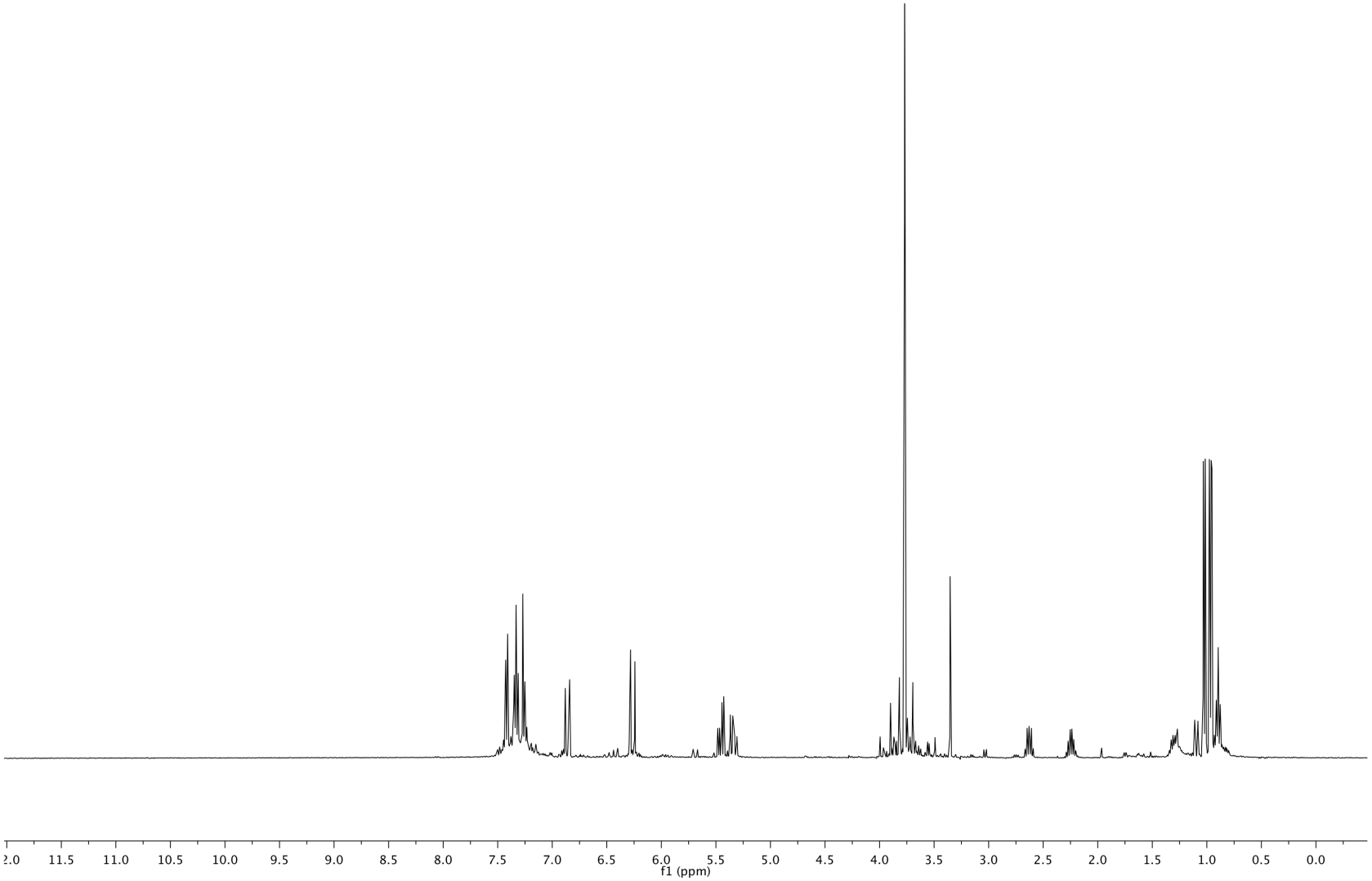
7g crude



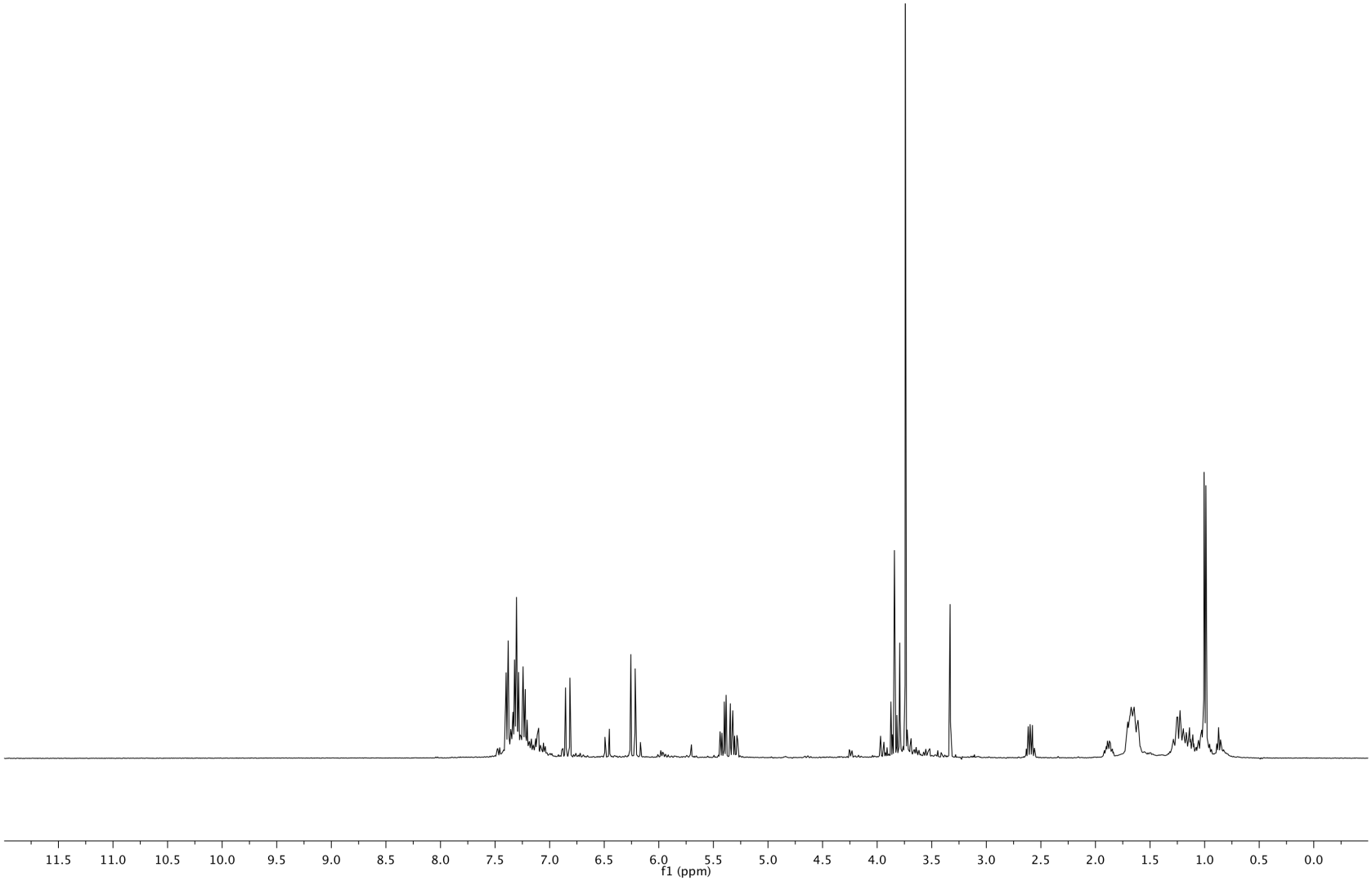
7h crude


11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

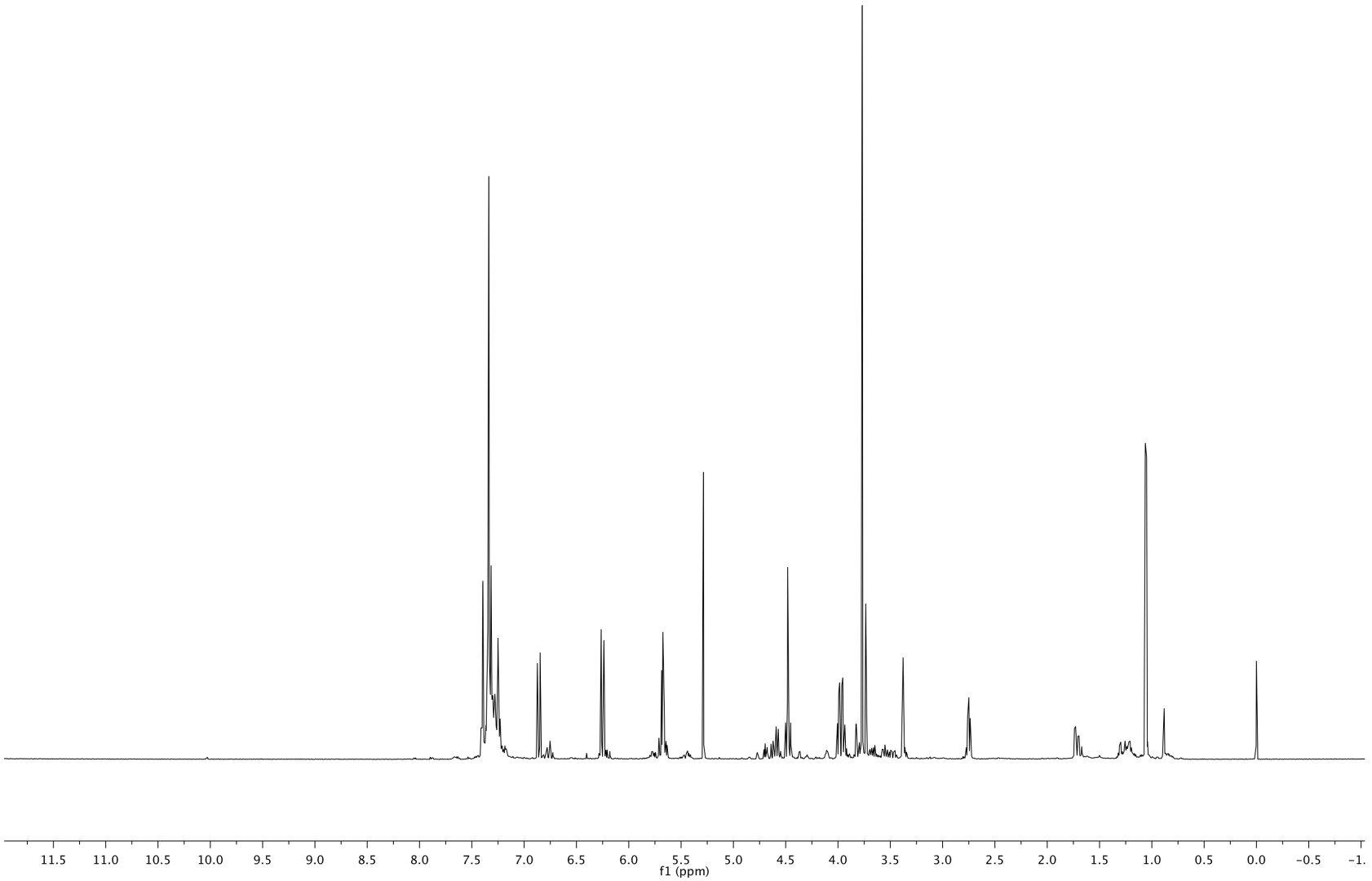
7i crude


2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

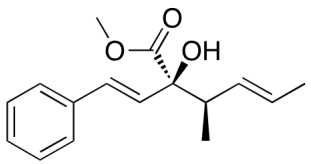
7j crude


11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

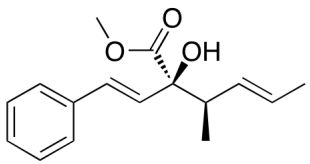
7k crude


11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.
f1 (ppm)

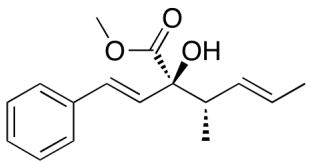
6. NMR Data for New Compounds



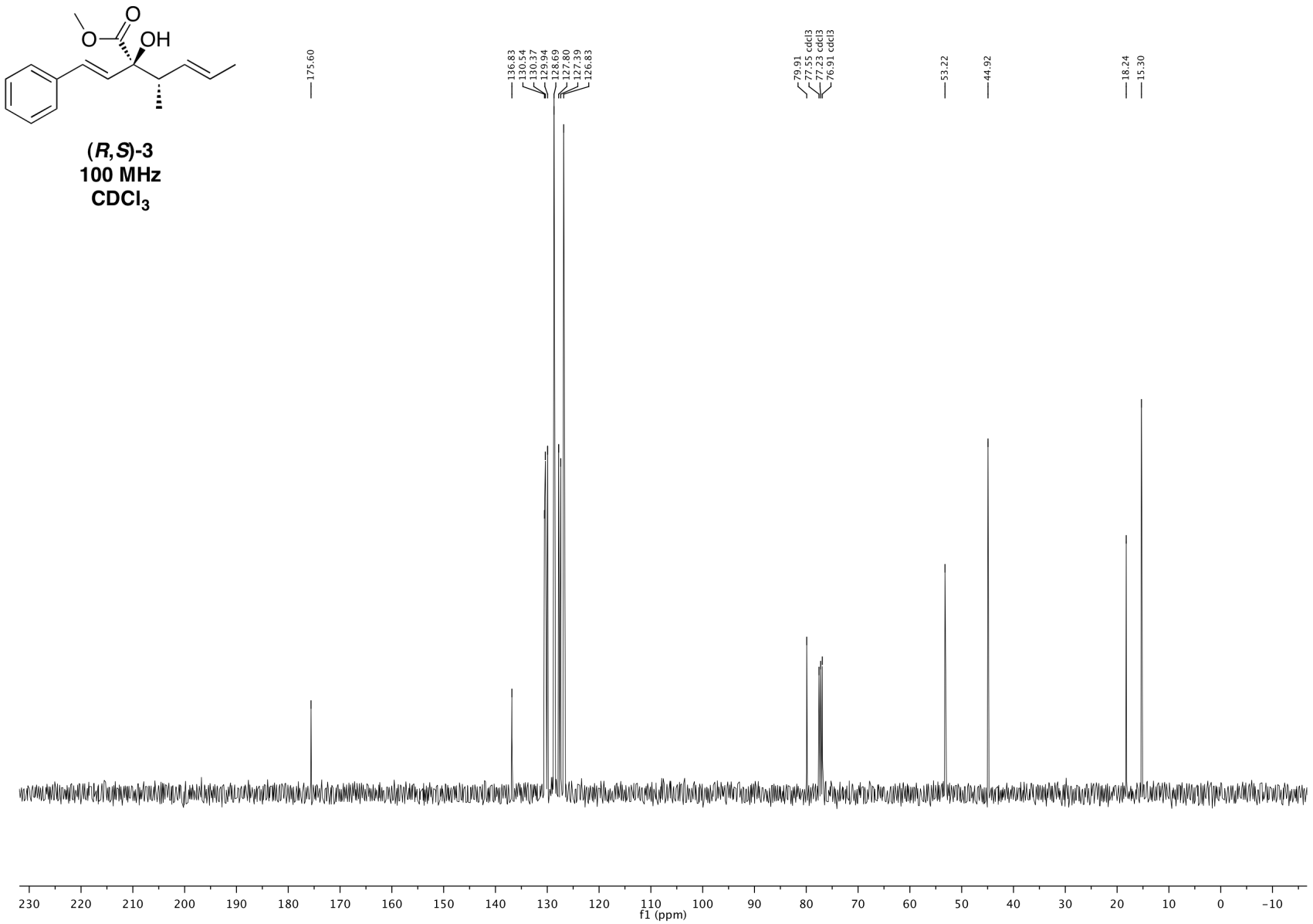
(*R*,*R*)-3
400 MHz
$CDCl_3$

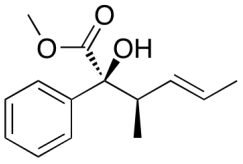


(*R*,*R*)-3
100 MHz
$CDCl_3$

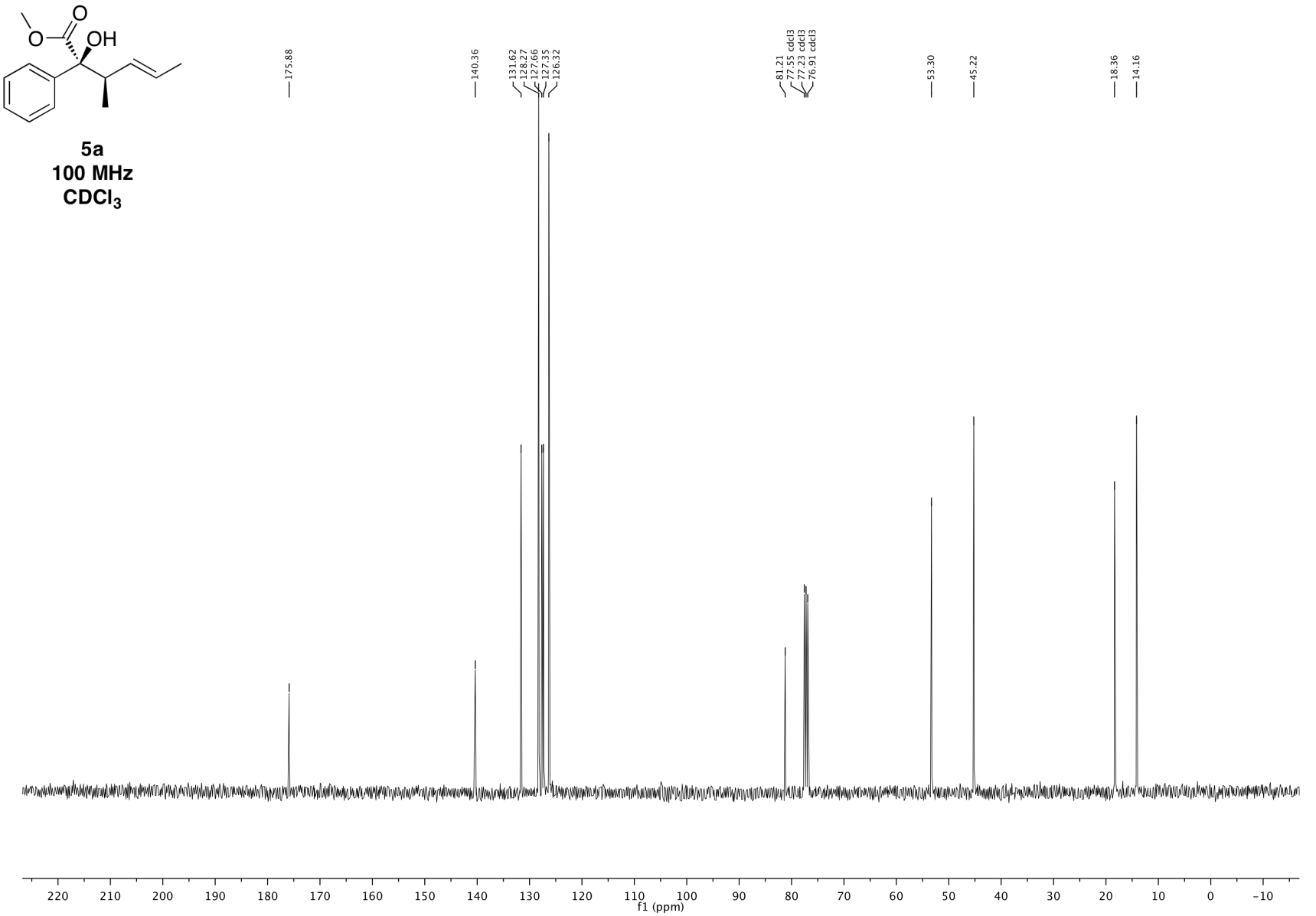


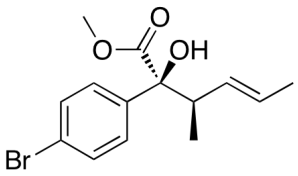
(*R*,*S*)-3
400 MHz
$CDCl_3$


O
O
OH
(R,S)-3
100 MHz
CDCl3
175.60
136.83
130.54
130.37
129.94
128.69
127.80
127.39
126.83
79.91
77.55 cdcl3
77.23 cdcl3
76.91 cdcl3
53.22
44.92
18.24
15.30
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

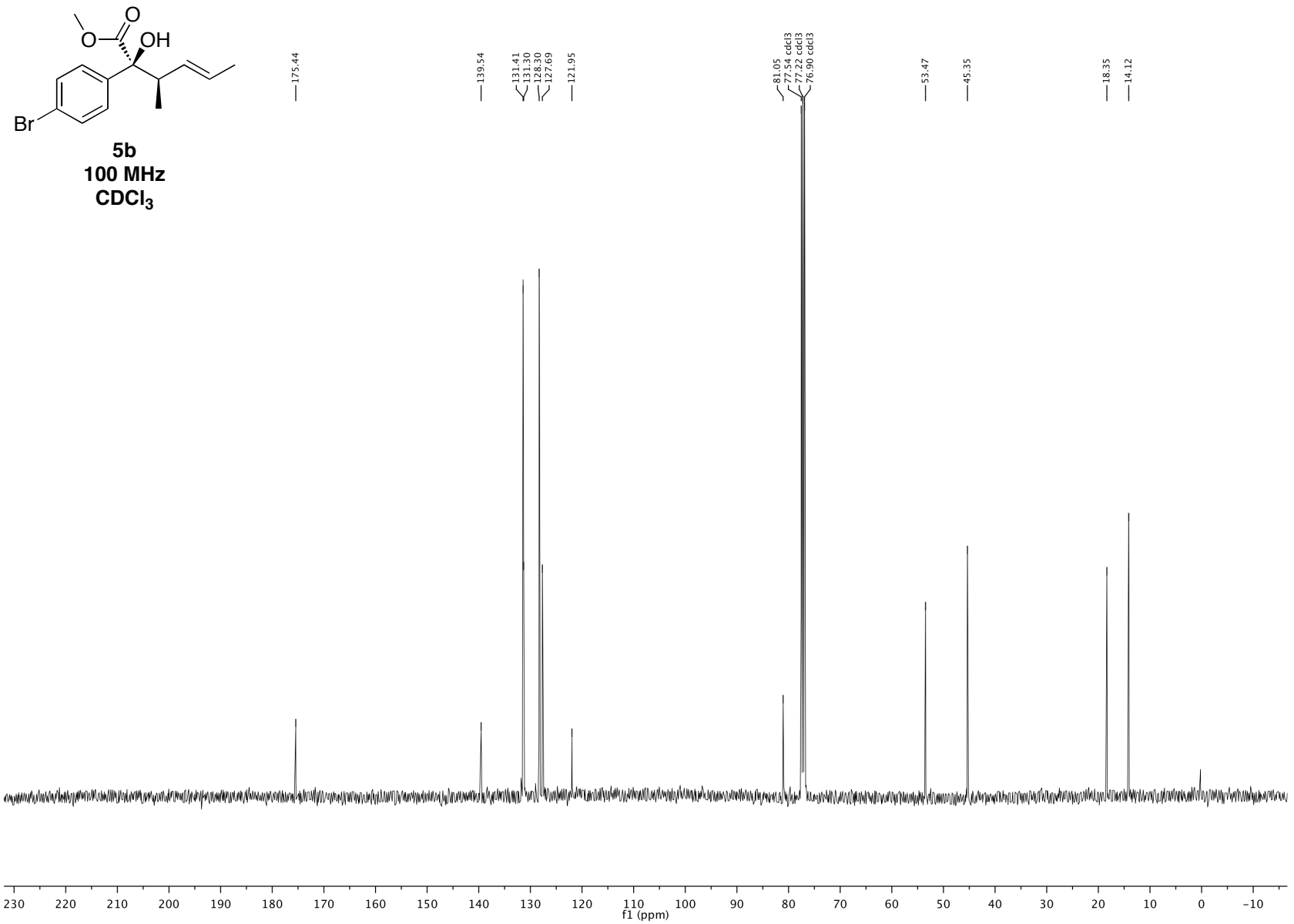


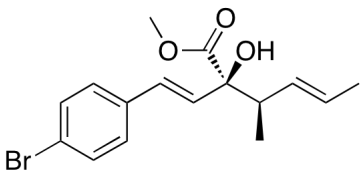
5a
400 MHz
$CDCl_3$


5a
100 MHz
CDCl3
175.88
140.36
131.62
128.27
127.66
127.35
126.32
81.21
77.55 cdcl3
77.23 cdcl3
76.91 cdcl3
53.30
45.22
18.36
14.16
f1 (ppm)

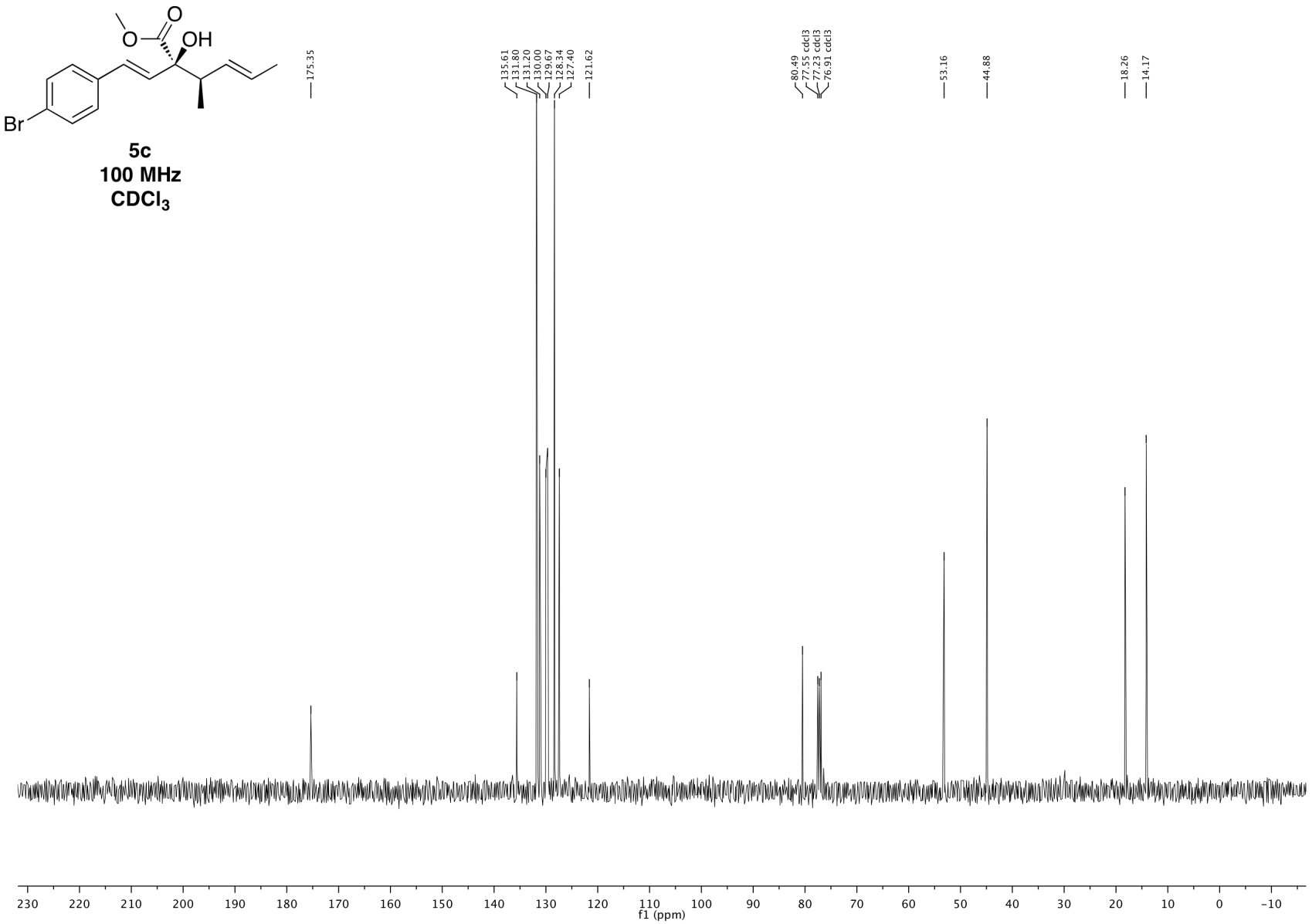


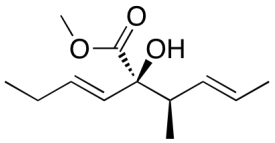
5b
400 MHz
$CDCl_3$


O
O
OH
Br
5b
100 MHz
CDCl3
175.44
139.54
131.41
131.30
128.30
127.69
121.95
81.05
77.54 cdcl3
77.22 cdcl3
76.90 cdcl3
53.47
45.35
18.35
14.12
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

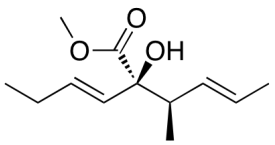


5c
400 MHz
$CDCl_3$

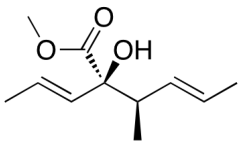

O
O
OH
Br
5c
100 MHz
CDCl3
175.35
135.61
131.80
131.20
130.00
129.67
128.34
127.40
121.62
80.49
77.55 cdcl3
77.23 cdcl3
76.91 cdcl3
53.16
44.88
18.26
14.17
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



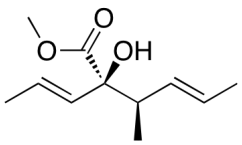
5d
400 MHz
$CDCl_3$



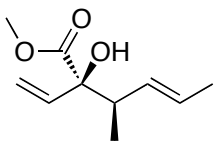
5d
100 MHz
$CDCl_3$



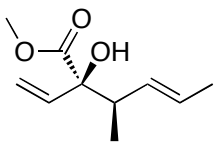
5e
400 MHz
$CDCl_3$



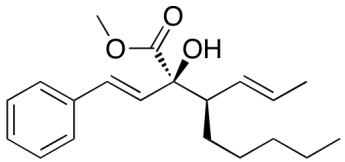
5e
100 MHz
$CDCl_3$



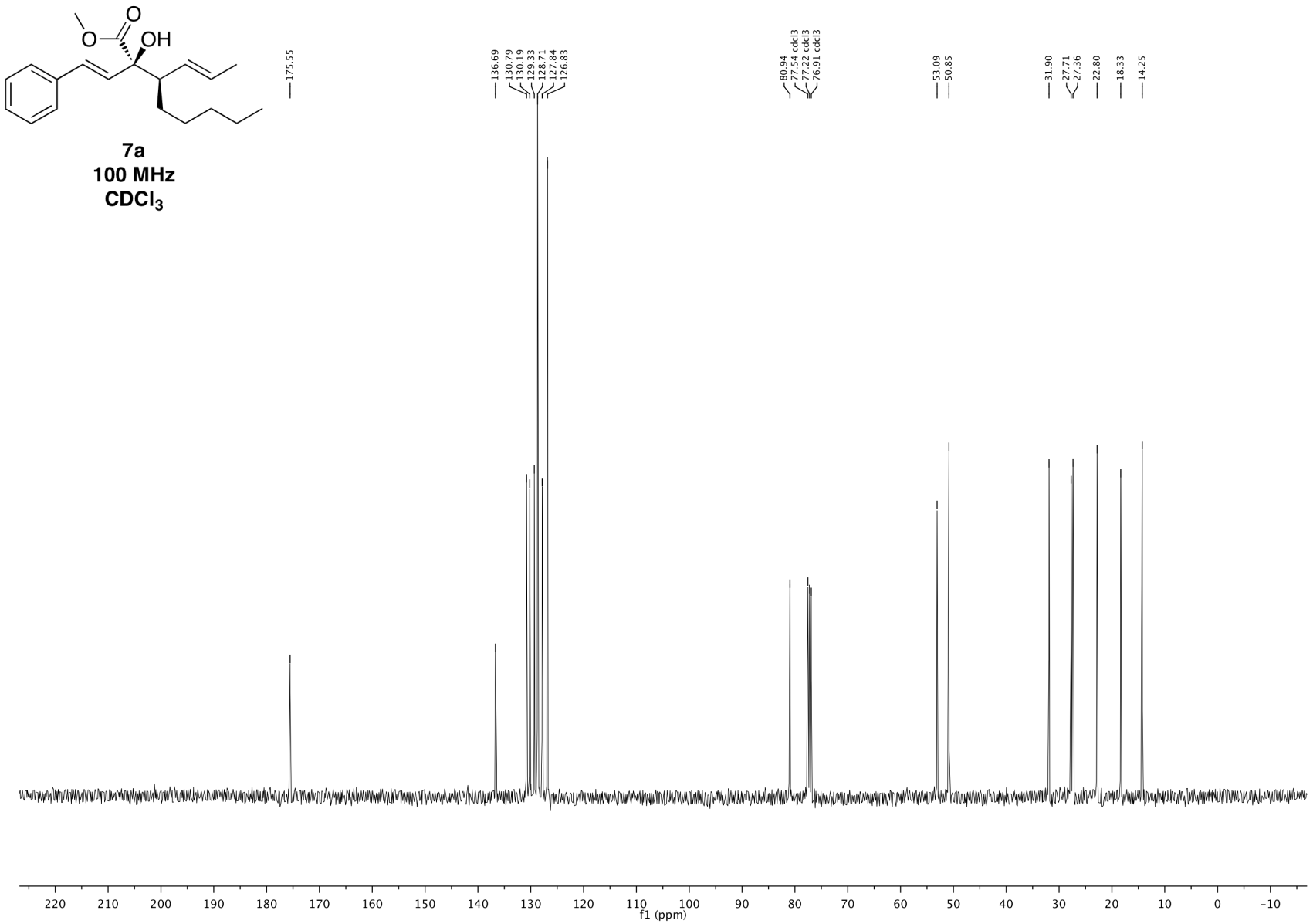
5f
400 MHz
$CDCl_3$

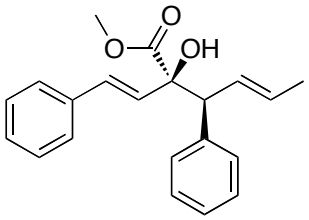


5f
100 MHz
$CDCl_3$

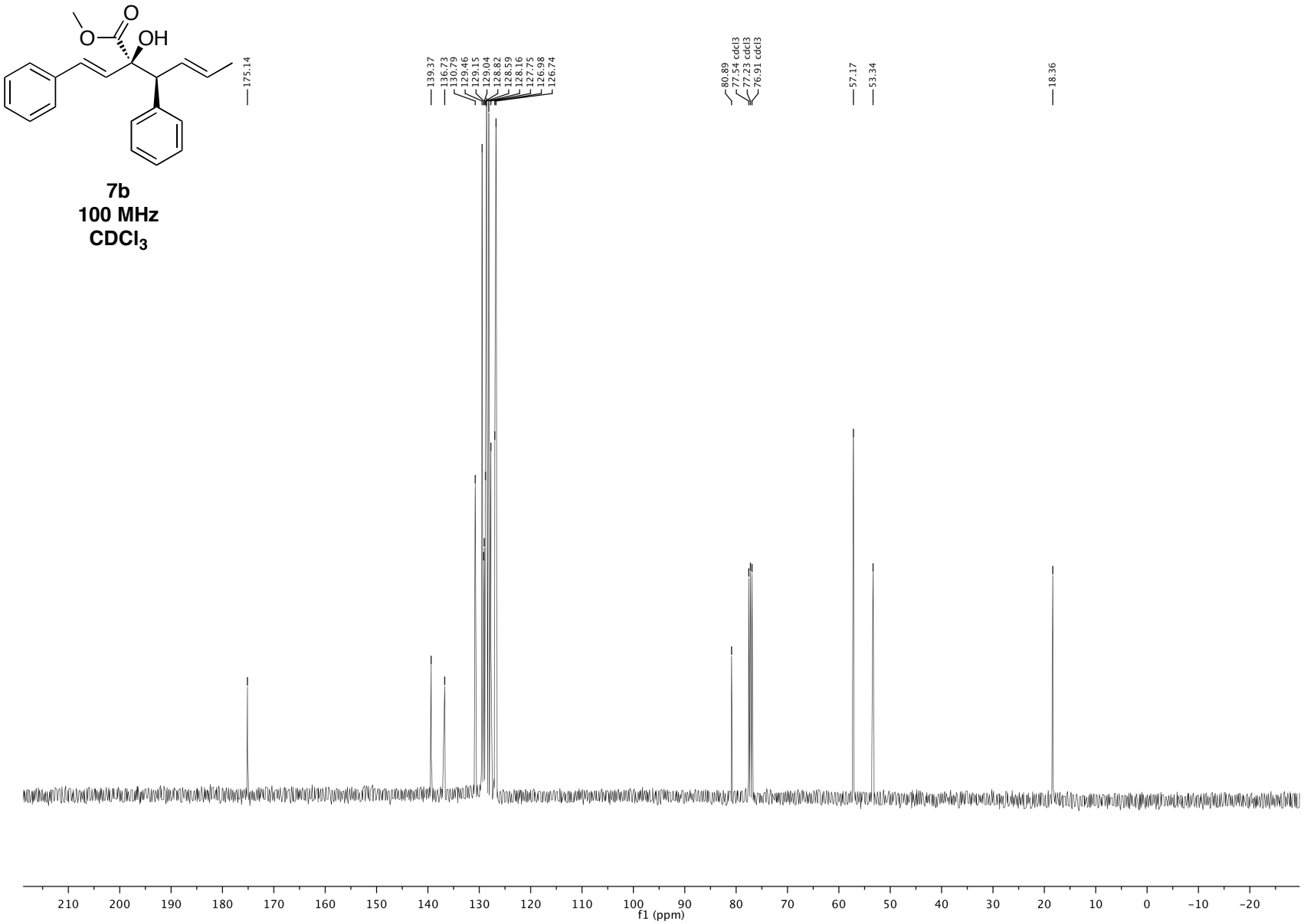


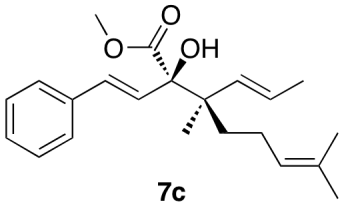
7a
400 MHz
$CDCl_3$


7a
100 MHz
CDCl3
175.55
136.69
130.79
130.19
129.33
128.71
127.84
126.83
80.94
77.54 cdcl3
77.22 cdcl3
76.91 cdcl3
53.09
50.85
31.90
27.71
27.36
22.80
18.33
14.25
f1 (ppm)

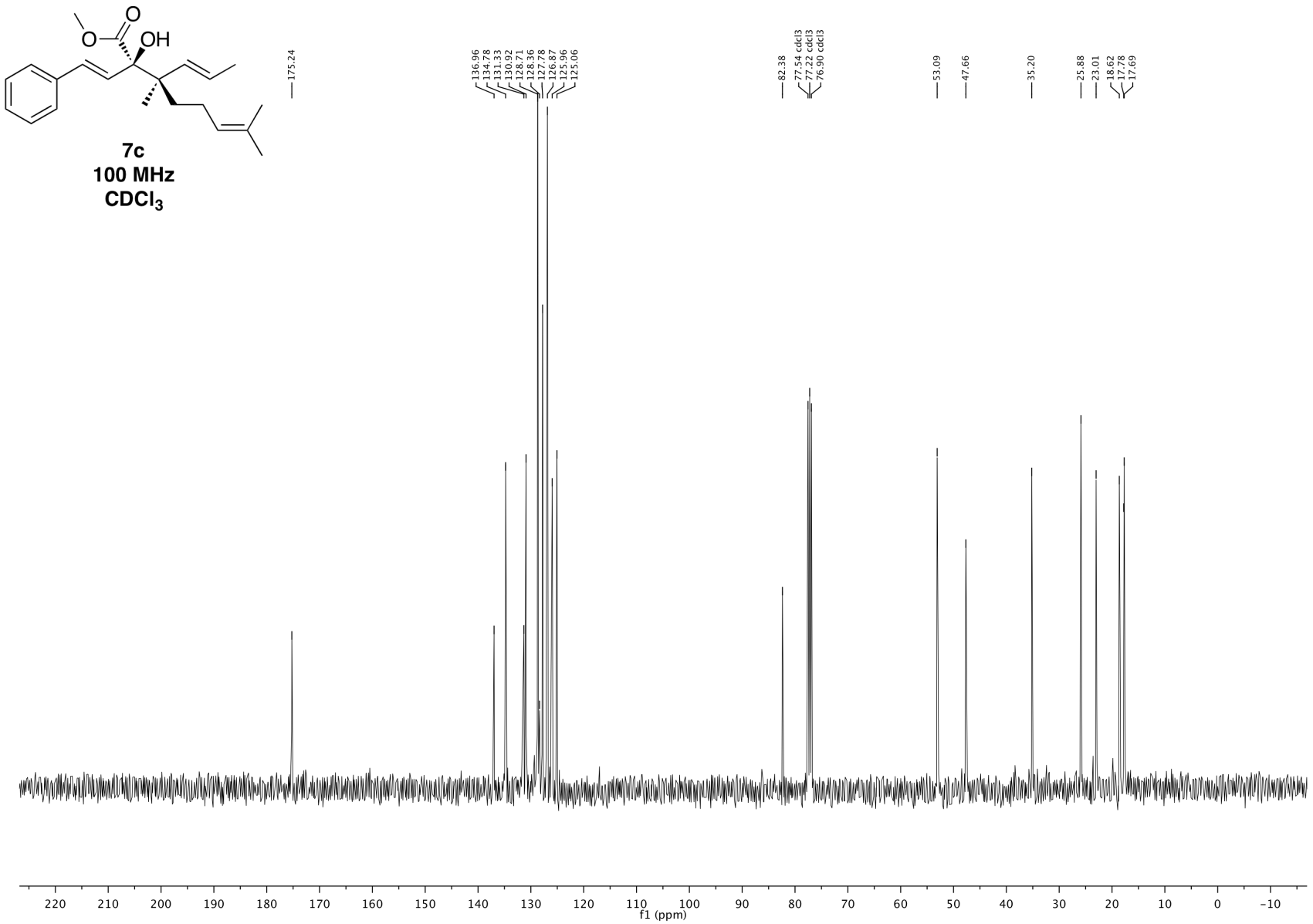


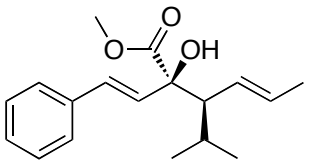
7b
400 MHz
$CDCl_3$


O
O
OH
175.14
139.37
136.73
130.79
129.46
129.15
129.04
128.82
128.59
128.16
127.75
126.98
126.74
80.89
77.54 cdcl3
77.23 cdcl3
76.91 cdcl3
57.17
53.34
18.36
7b
100 MHz
CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

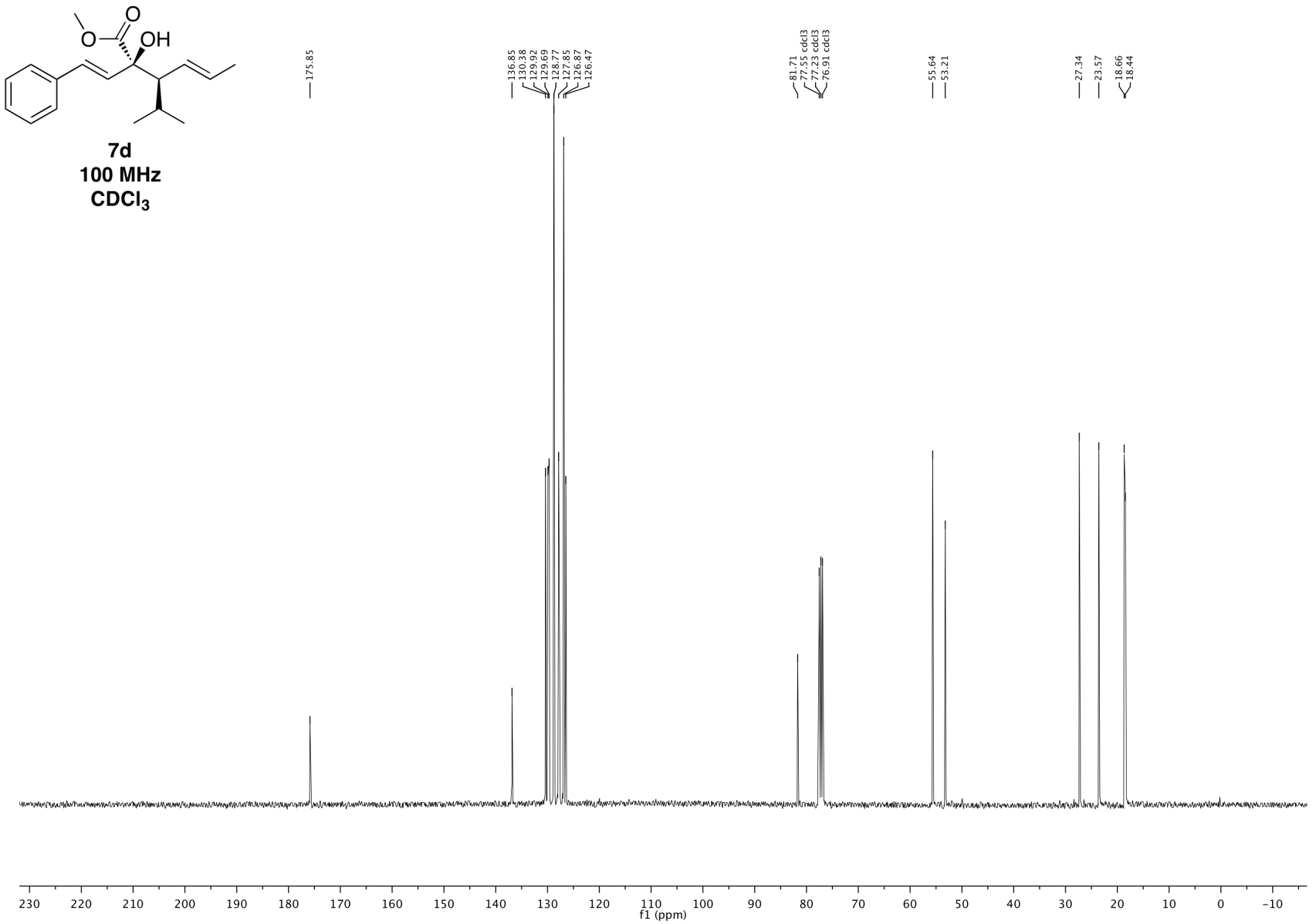


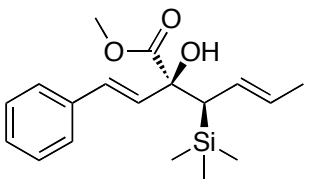
7c
400 MHz
$CDCl_3$


7c
100 MHz
CDCl3
175.24
136.96
134.78
131.33
130.92
128.71
128.36
127.78
126.87
125.96
125.06
82.38
77.54 cdcl3
77.22 cdcl3
76.90 cdcl3
53.09
47.66
35.20
25.88
23.01
18.62
17.78
17.69
f1 (ppm)

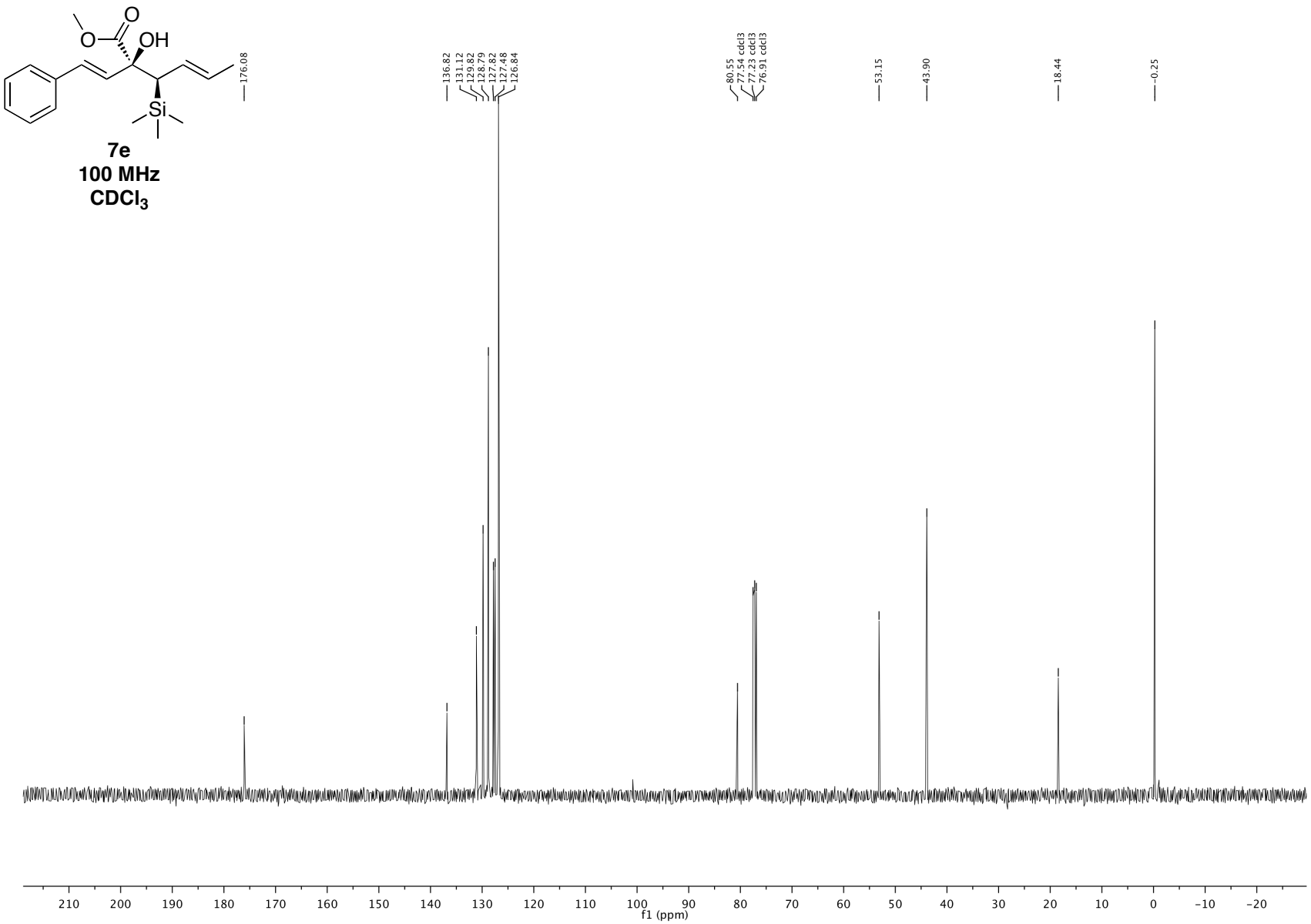


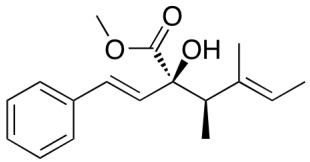
7d
400 MHz
$CDCl_3$


7d
100 MHz
CDCl3
175.85
136.85
130.38
129.92
129.69
128.77
127.85
126.87
126.47
81.71
77.55 cdcl3
77.23 cdcl3
76.91 cdcl3
55.64
53.21
27.34
23.57
18.66
18.44
f1 (ppm)

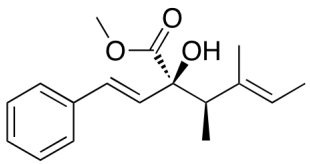


7e
400 MHz
$CDCl_3$

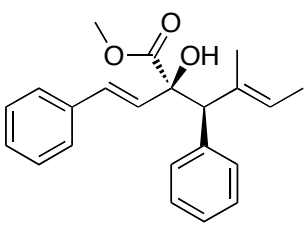

O
O
OH
Si
7e
100 MHz
CDCl3
176.08
136.82
131.12
129.82
128.79
127.82
127.48
126.84
80.55
77.54 cdcl3
77.23 cdcl3
76.91 cdcl3
53.15
43.90
18.44
-0.25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



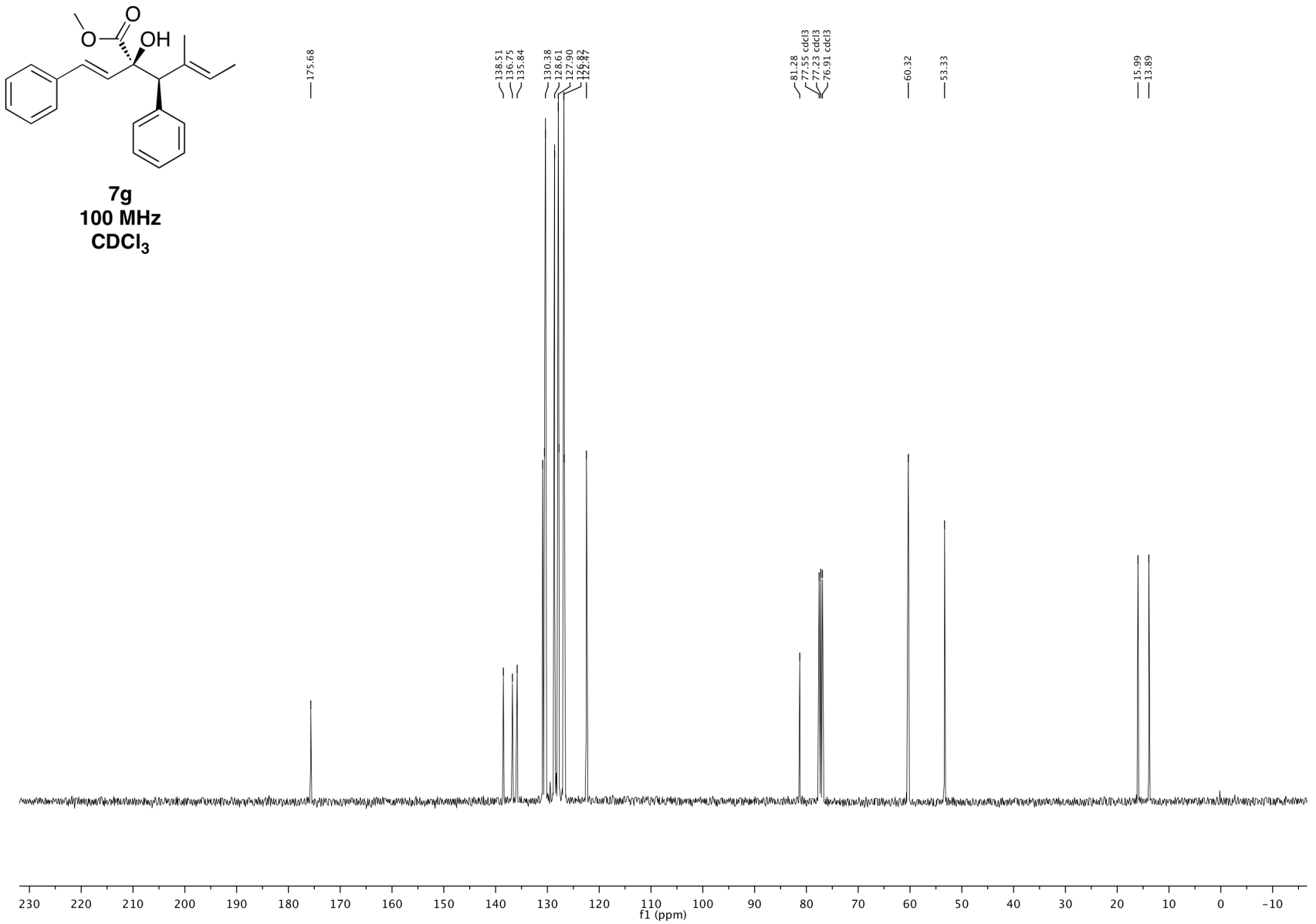
7f
400 MHz
$CDCl_3$

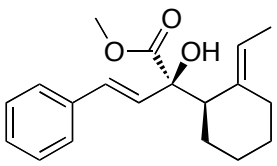


7f
100 MHz
$CDCl_3$

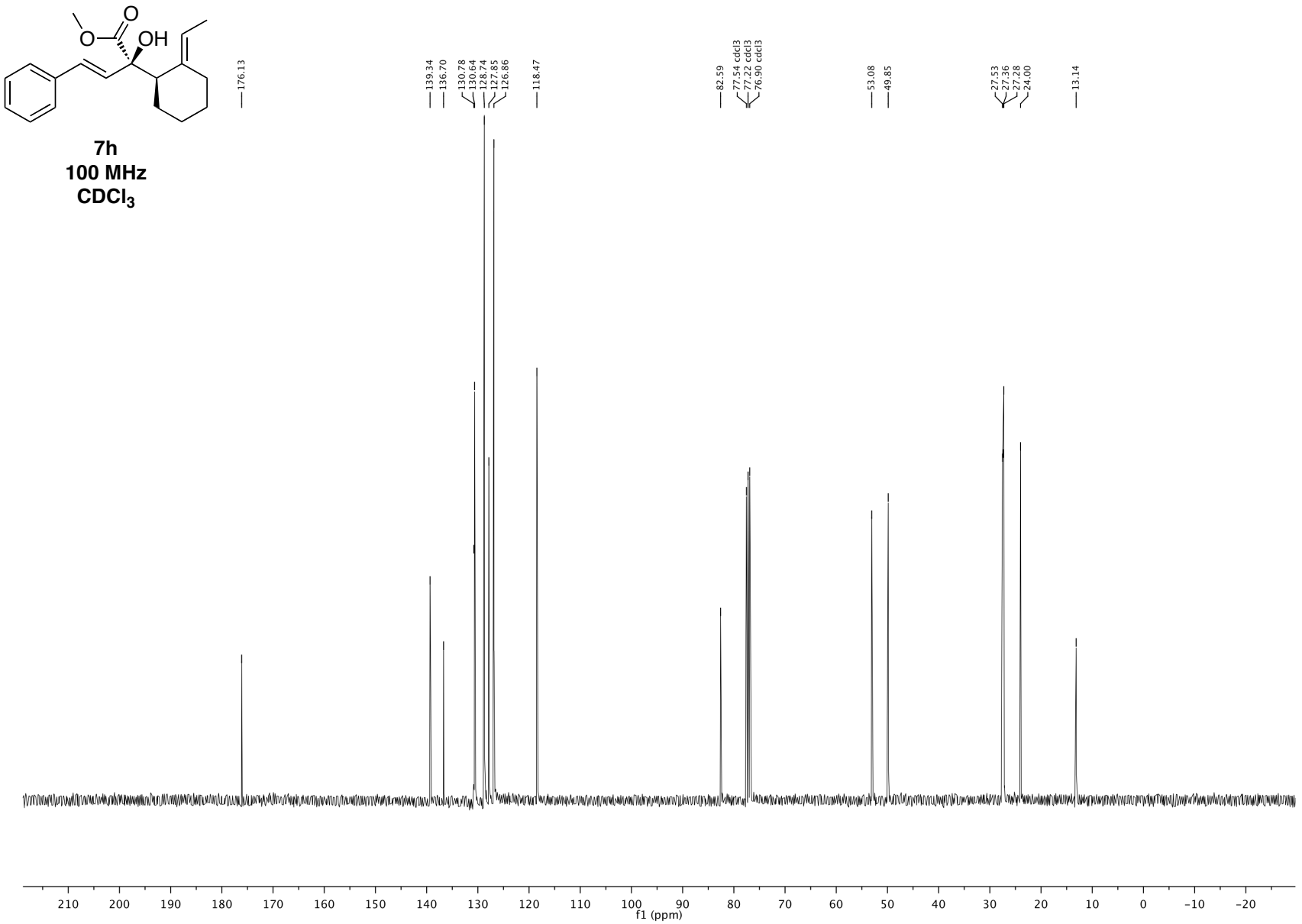


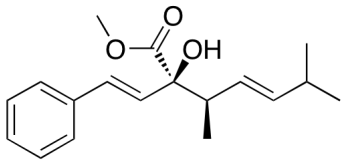
7g
400 MHz
$CDCl_3$


O
O
OH
7g
100 MHz
CDCl3
175.68
138.51
136.75
135.84
130.38
128.61
127.90
126.82
122.47
81.28
77.55 cdcl3
77.23 cdcl3
76.91 cdcl3
60.32
53.33
15.99
13.89
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

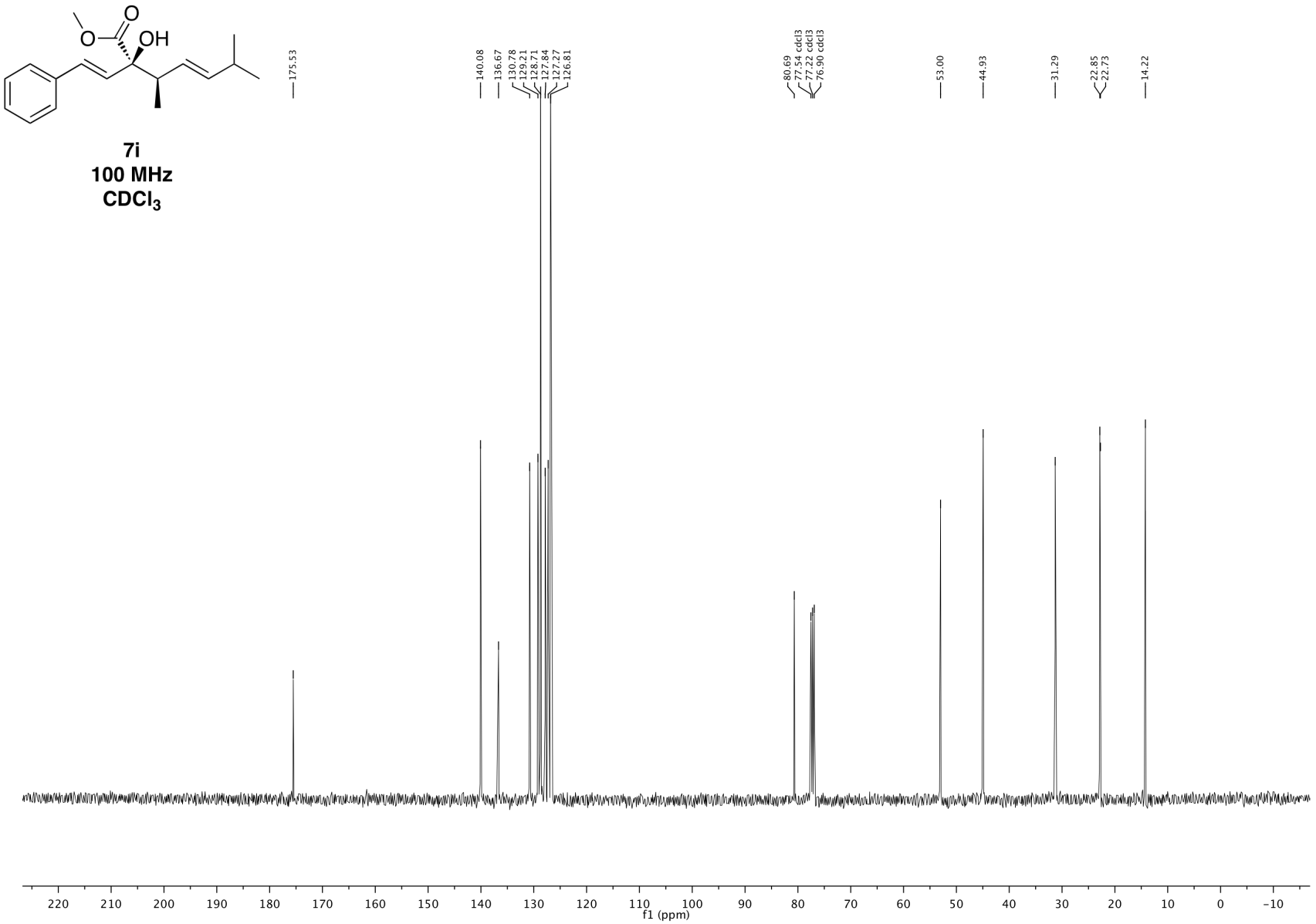


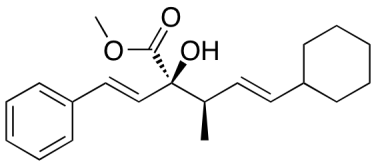
7h
400 MHz
$CDCl_3$


7h
100 MHz
CDCl3
176.13
139.34
136.70
130.78
130.64
128.74
127.85
126.86
118.47
82.59
77.54 cdcl3
77.22 cdcl3
76.90 cdcl3
53.08
49.85
27.53
27.36
27.28
24.00
13.14
f1 (ppm)

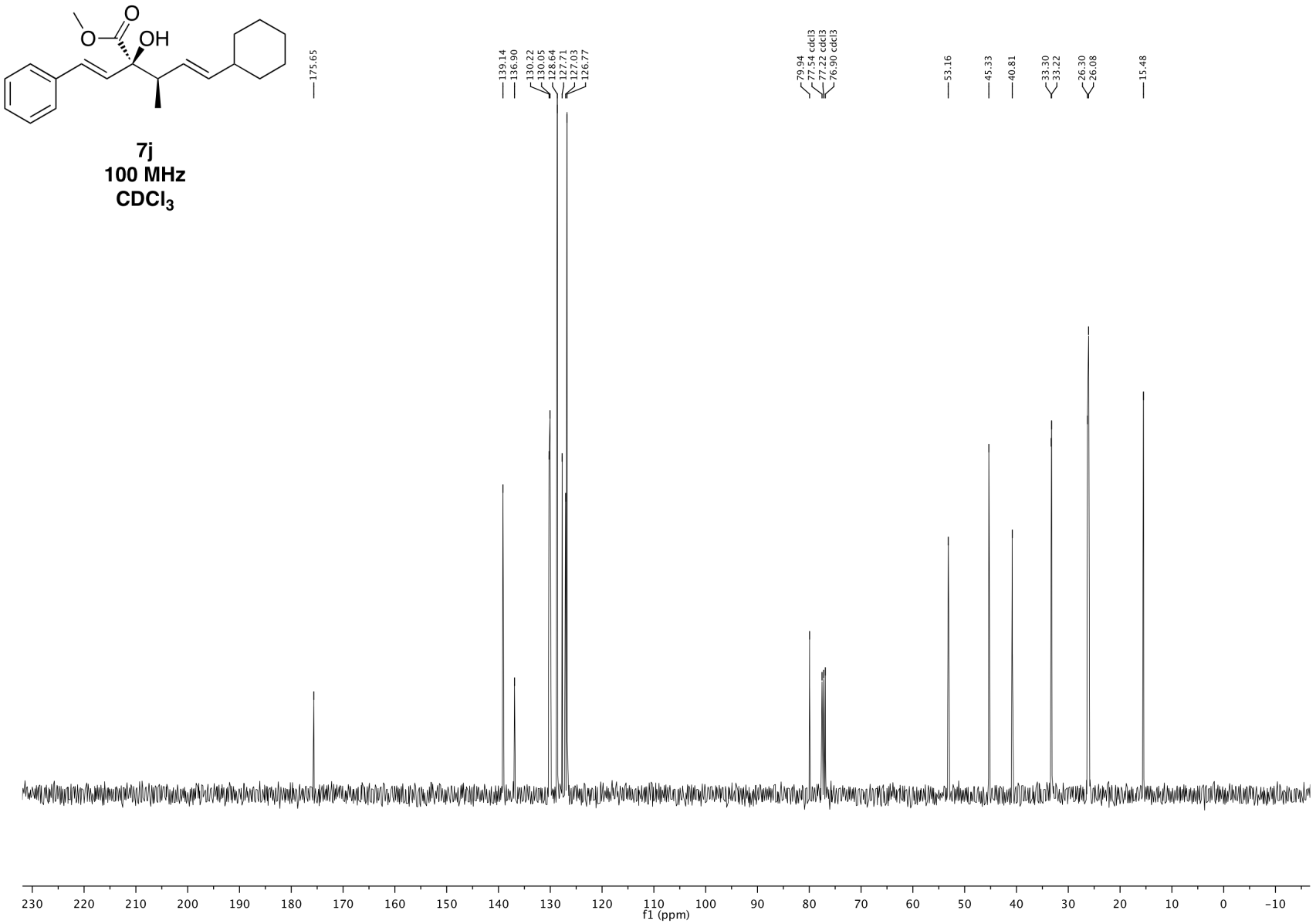


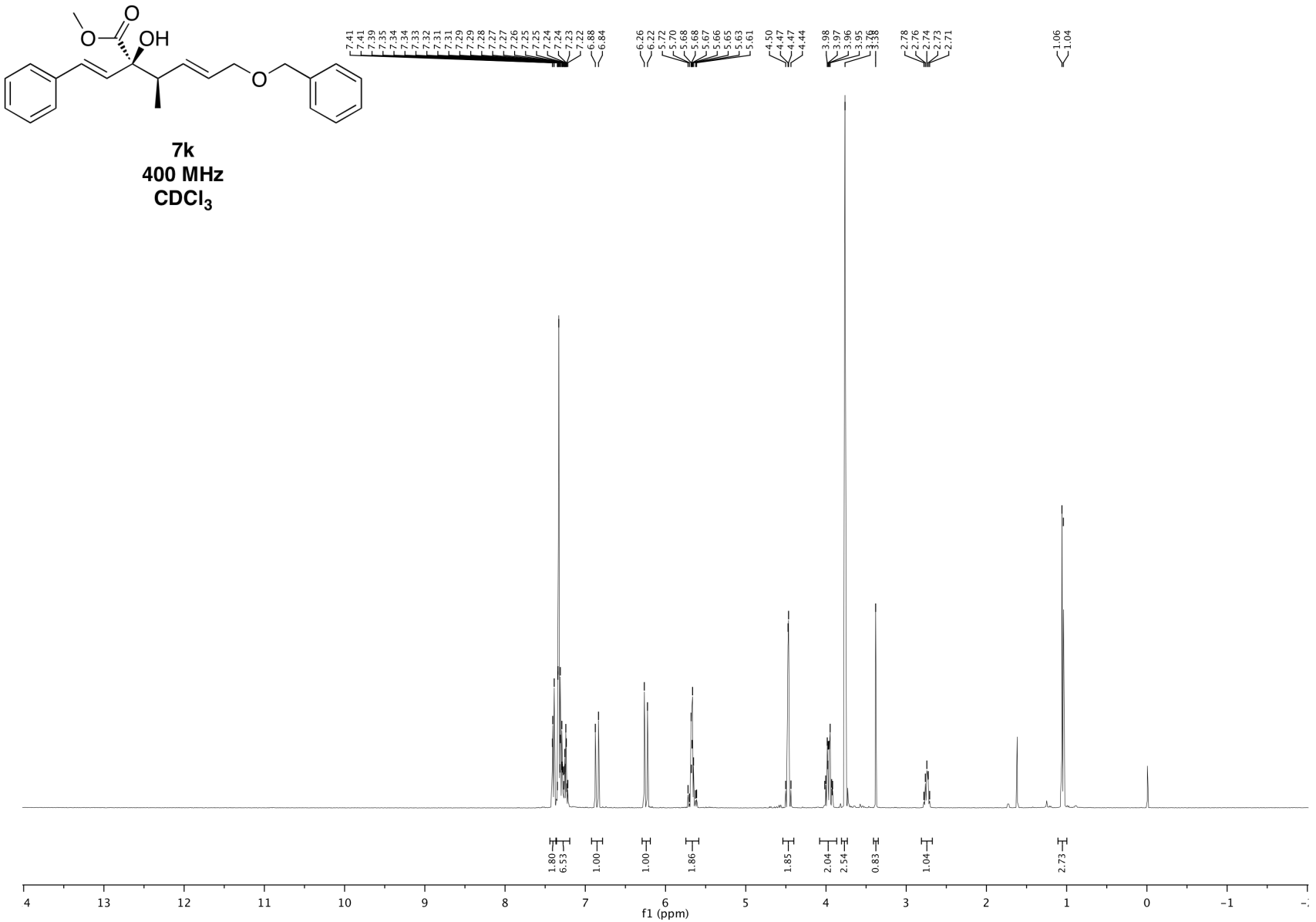
7i
400 MHz
$CDCl_3$

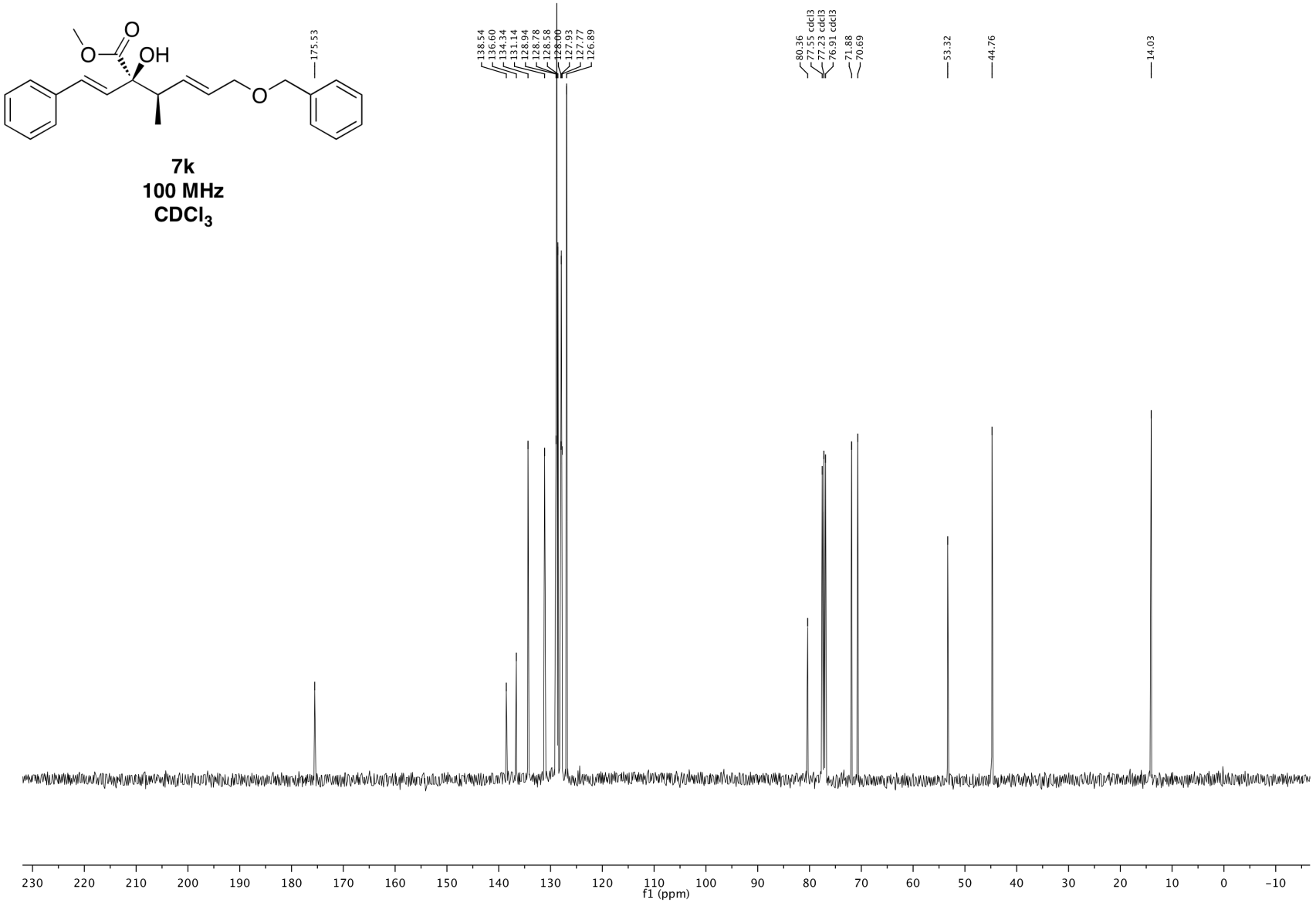

O
O
OH
7i
100 MHz
CDCl3
175.53
140.08
136.67
130.78
129.21
128.71
127.84
127.27
126.81
80.69
77.54 cdcl3
77.22 cdcl3
76.90 cdcl3
53.00
44.93
31.29
22.85
22.73
14.22
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

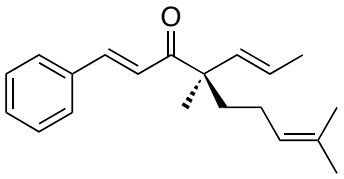


7j
400 MHz
$CDCl_3$

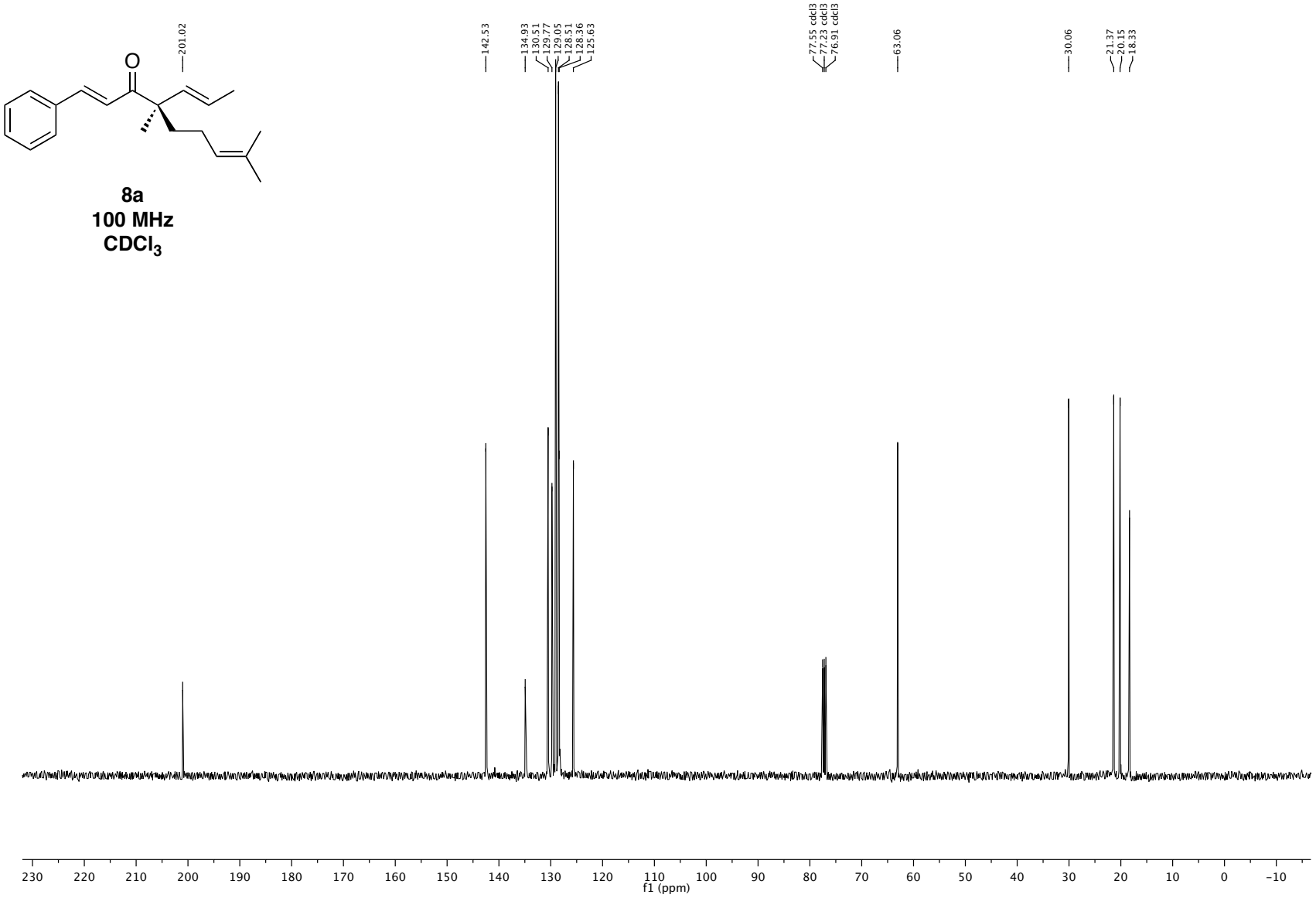

7j
100 MHz
CDCl3
175.65
139.14
136.90
130.22
130.05
128.64
127.71
127.03
126.77
79.94
77.54 cdcl3
77.22 cdcl3
76.90 cdcl3
53.16
45.33
40.81
33.30
33.22
26.30
26.08
15.48
f1 (ppm)

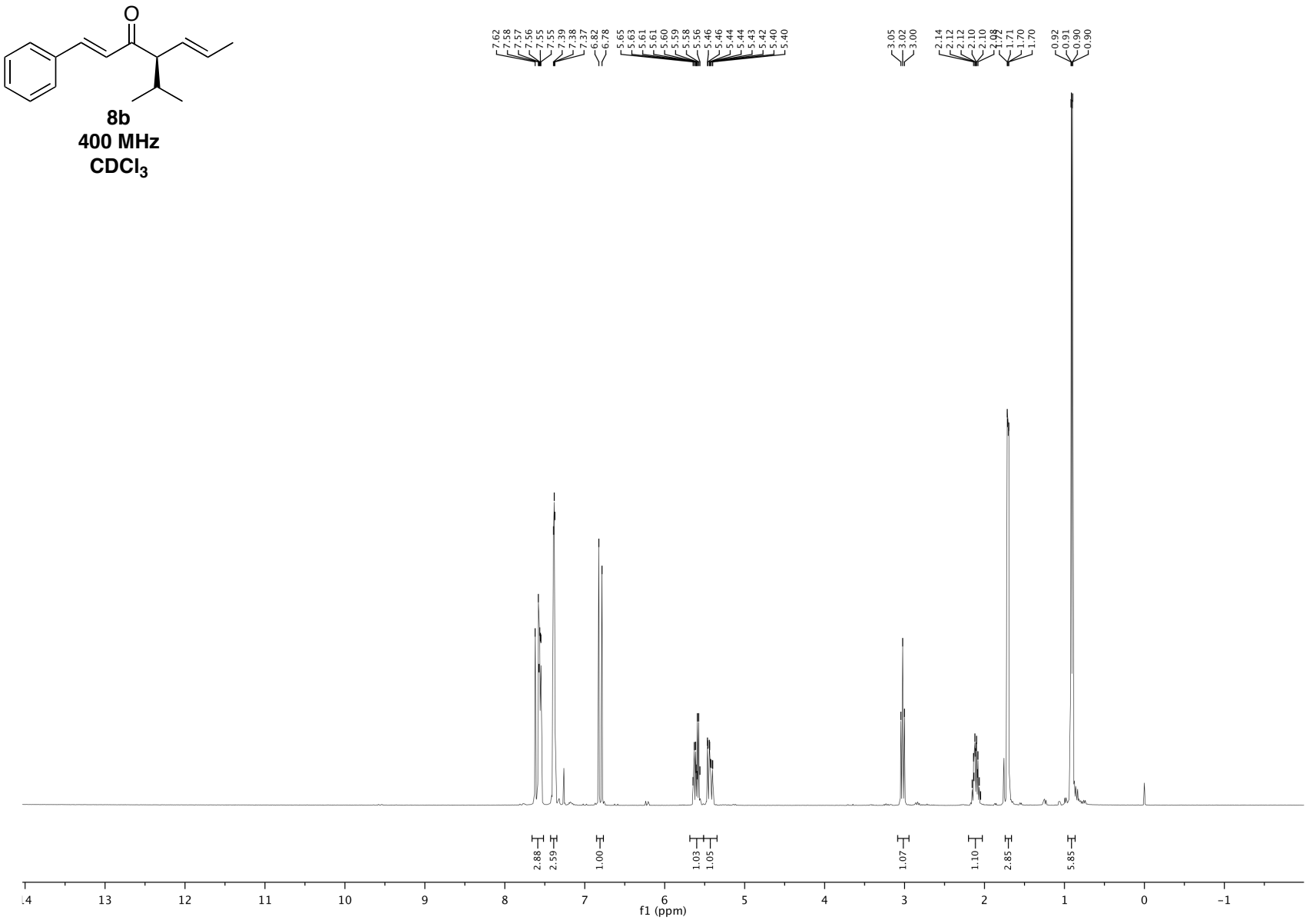

7k
400 MHz
CDCl3
f1 (ppm)

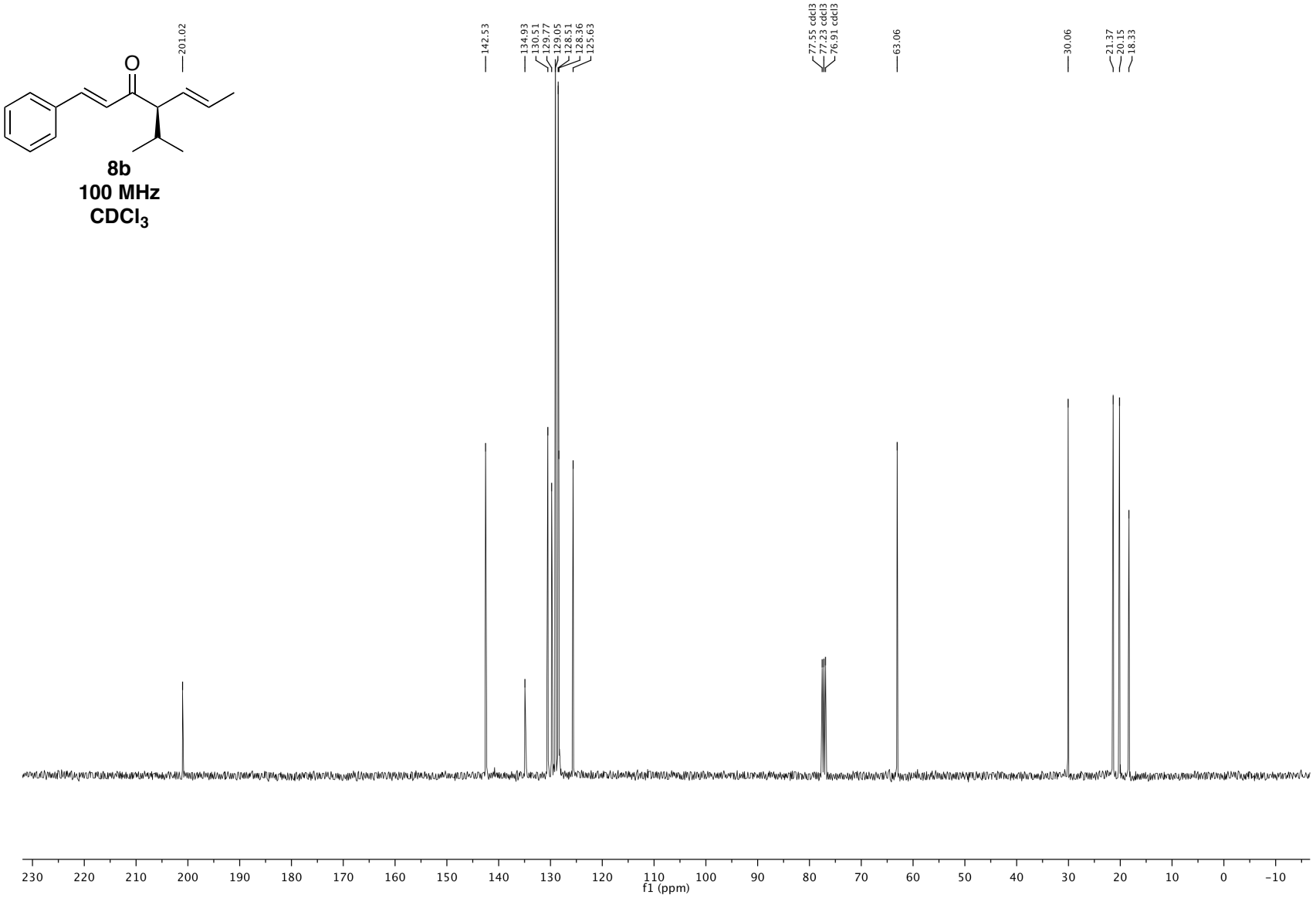

7k
100 MHz
CDCl3
175.53
138.54
136.60
134.34
131.14
128.94
128.78
128.58
128.00
127.93
127.77
126.89
80.36
77.55 cdcl3
77.23 cdcl3
76.91 cdcl3
71.88
70.69
53.32
44.76
14.03
f1 (ppm)



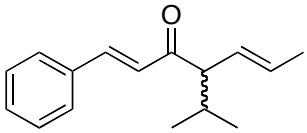
8a
400 MHz
$CDCl_3$


O
201.02
142.53
134.93
130.51
129.77
129.05
128.51
128.36
125.63
77.55 cdcl3
77.23 cdcl3
76.91 cdcl3
63.06
30.06
21.37
20.15
18.33
8a
100 MHz
CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

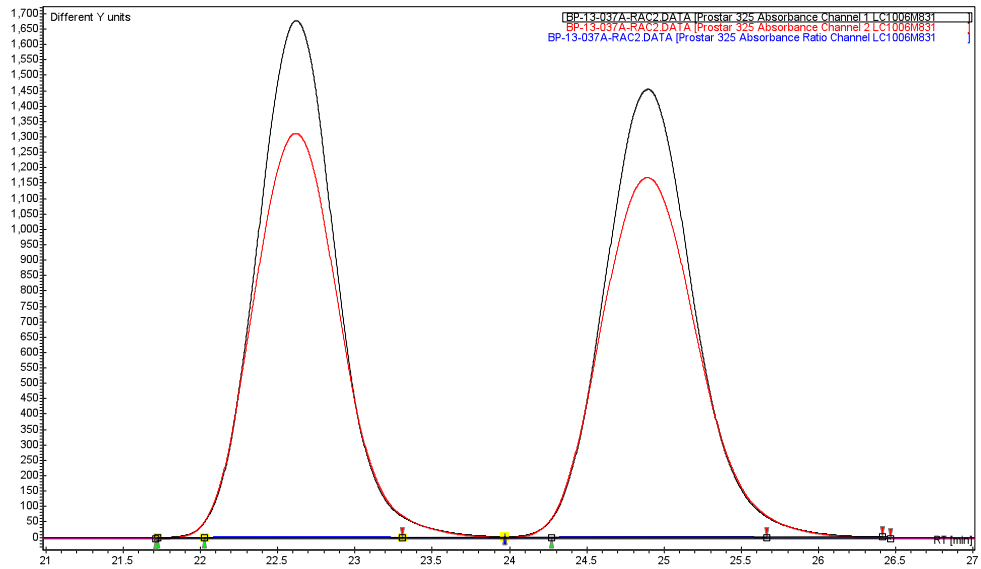

8b
400 MHz
CDCl3
7.62
7.58
7.57
7.56
7.55
7.55
7.39
7.38
7.37
6.82
6.78
5.65
5.63
5.61
5.61
5.60
5.59
5.58
5.56
5.46
5.46
5.44
5.43
5.42
5.40
5.40
3.05
3.02
3.00
2.14
2.12
2.12
2.10
2.10
1.71
1.70
1.70
0.92
0.91
0.90
0.90
2.88
2.59
1.00
1.03
1.05
1.07
1.10
2.85
5.85
f1 (ppm)


O
201.02
142.53
134.93
130.51
129.77
129.05
128.51
128.36
125.63
77.55 cdcl3
77.23 cdcl3
76.91 cdcl3
63.06
30.06
21.37
20.15
18.33
8b
100 MHz
CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

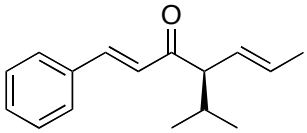
7. HPLC Traces for Compound 8b



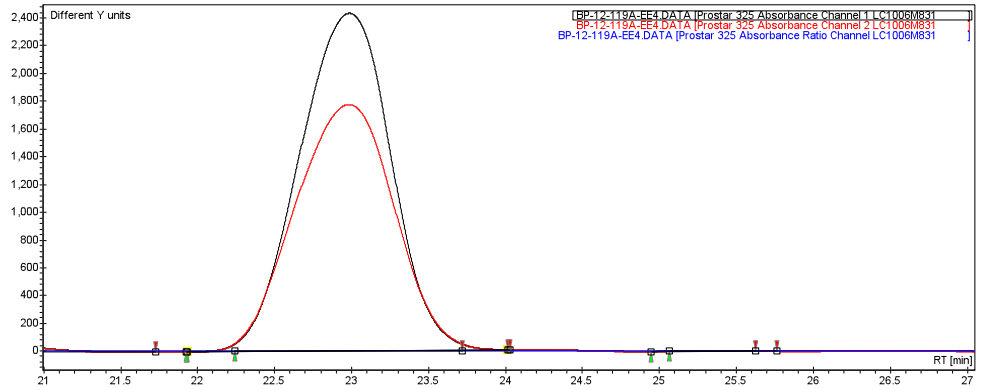
***rac*-8b**



ENTRY	TIME (MIN)	QUANTITY (%)
1	22.62	50.69
2	24.90	49.31



8b



ENTRY	TIME (MIN)	QUANTITY (%)
1	22.99	99.93
2	25.35	0.07

8. X-Ray Crystallography Data

5c

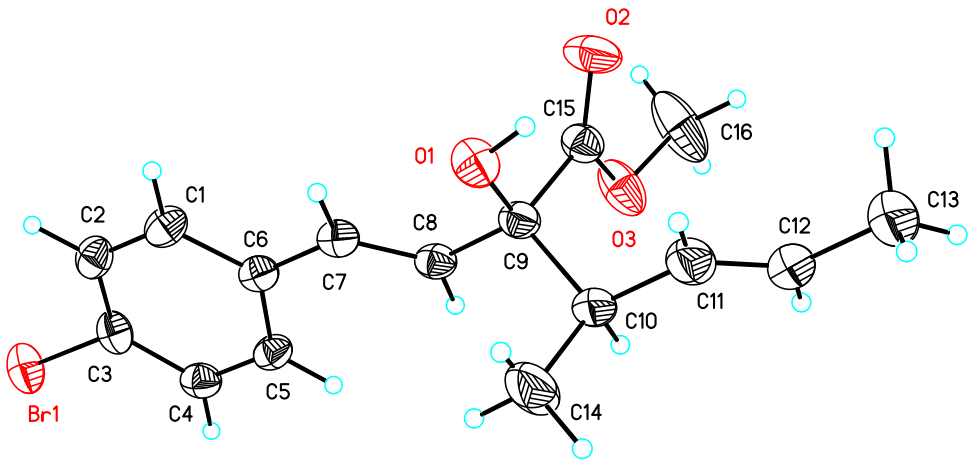


Table 1. Crystal data and structure refinement for **5c**.

Identification code	**5c**	
Empirical formula	C16 H19 Br O3	
Formula weight	339.22	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2	
Unit cell dimensions	a = 7.9626(3) Å	α= 90°.
	b = 36.6534(11) Å	β= 90°.
	c = 5.6635(2) Å	γ = 90°.
Volume	1652.93(10) $Å^3$	
Z	4	
Density (calculated)	1.363 Mg/m^3	
Absorption coefficient	3.427 mm^{-1}	
F(000)	696	
Crystal size	0.48 x 0.12 x 0.03 mm^3	
Theta range for data collection	2.41 to 67.55°.	
Index ranges	-8<=h<=8, -43<=k<=43, -6<=l<=6	
Reflections collected	10887	
Independent reflections	2788 [R(int) = 0.0324]	

Completeness to theta = 67.55°	94.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9042 and 0.2900
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2788 / 0 / 181
Goodness-of-fit on F^2	1.089
Final R indices [I>2sigma(I)]	R1 = 0.0368, wR2 = 0.0913
R indices (all data)	R1 = 0.0401, wR2 = 0.0926
Absolute structure parameter	0.02(3)
Largest diff. peak and hole	0.452 and -0.340 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **5c**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	3150(1)	1730(1)	4087(1)	52(1)
C(1)	1866(6)	2456(1)	9409(6)	40(1)
C(2)	2084(6)	2139(1)	8096(6)	40(1)
C(3)	2888(5)	2159(1)	5959(7)	37(1)
C(4)	3519(5)	2485(1)	5108(7)	38(1)
C(5)	3278(5)	2800(1)	6423(6)	35(1)
C(6)	2434(5)	2791(1)	8582(6)	32(1)
C(7)	2186(5)	3119(1)	10048(6)	34(1)
C(8)	2353(5)	3461(1)	9390(6)	33(1)
C(9)	2057(5)	3783(1)	10984(7)	35(1)
C(10)	3501(5)	4062(1)	10910(10)	48(1)
C(11)	3081(6)	4395(1)	12314(9)	52(1)
C(12)	2888(6)	4727(1)	11509(10)	63(1)
C(13)	2480(8)	5057(1)	12972(12)	80(2)
C(14)	5113(6)	3886(1)	11784(14)	90(2)
C(15)	420(5)	3973(1)	10211(6)	37(1)
C(16)	-950(8)	4287(2)	7148(9)	84(2)
O(1)	1834(4)	3667(1)	13352(4)	43(1)
O(2)	-765(4)	4008(1)	11467(6)	58(1)
O(3)	513(5)	4094(1)	8025(5)	59(1)

Table 3. Bond lengths [Å] and angles [°] for **5c**.

Br(1)-C(3)	1.906(3)
C(1)-C(2)	1.389(5)
C(1)-C(6)	1.392(5)
C(1)-H(1A)	0.9500
C(2)-C(3)	1.371(6)
C(2)-H(2A)	0.9500
C(3)-C(4)	1.383(5)
C(4)-C(5)	1.388(5)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.395(5)
C(5)-H(5A)	0.9500
C(6)-C(7)	1.475(5)
C(7)-C(8)	1.315(5)
C(7)-H(7A)	0.9500
C(8)-C(9)	1.504(5)
C(8)-H(8A)	0.9500
C(9)-O(1)	1.419(4)
C(9)-C(10)	1.540(5)
C(9)-C(15)	1.541(5)
C(10)-C(11)	1.494(6)
C(10)-C(14)	1.521(6)
C(10)-H(10A)	1.0000
C(11)-C(12)	1.308(6)
C(11)-H(11A)	0.9500
C(12)-C(13)	1.501(7)
C(12)-H(12A)	0.9500
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-O(2)	1.189(5)
C(15)-O(3)	1.318(4)

C(16)-O(3)	1.450(6)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
O(1)-H(1B)	0.8400

C(2)-C(1)-C(6)	121.2(3)
C(2)-C(1)-H(1A)	119.4
C(6)-C(1)-H(1A)	119.4
C(3)-C(2)-C(1)	119.1(3)
C(3)-C(2)-H(2A)	120.4
C(1)-C(2)-H(2A)	120.4
C(2)-C(3)-C(4)	121.5(3)
C(2)-C(3)-Br(1)	119.9(3)
C(4)-C(3)-Br(1)	118.6(3)
C(3)-C(4)-C(5)	118.8(3)
C(3)-C(4)-H(4A)	120.6
C(5)-C(4)-H(4A)	120.6
C(4)-C(5)-C(6)	121.1(3)
C(4)-C(5)-H(5A)	119.4
C(6)-C(5)-H(5A)	119.4
C(1)-C(6)-C(5)	118.2(3)
C(1)-C(6)-C(7)	119.2(3)
C(5)-C(6)-C(7)	122.6(3)
C(8)-C(7)-C(6)	127.2(3)
C(8)-C(7)-H(7A)	116.4
C(6)-C(7)-H(7A)	116.4
C(7)-C(8)-C(9)	124.2(3)
C(7)-C(8)-H(8A)	117.9
C(9)-C(8)-H(8A)	117.9
O(1)-C(9)-C(8)	110.6(3)
O(1)-C(9)-C(10)	108.6(3)
C(8)-C(9)-C(10)	112.8(3)
O(1)-C(9)-C(15)	107.4(3)
C(8)-C(9)-C(15)	108.5(3)
C(10)-C(9)-C(15)	108.9(3)

C(11)-C(10)-C(14)	111.3(4)
C(11)-C(10)-C(9)	111.2(3)
C(14)-C(10)-C(9)	109.8(3)
C(11)-C(10)-H(10A)	108.1
C(14)-C(10)-H(10A)	108.1
C(9)-C(10)-H(10A)	108.1
C(12)-C(11)-C(10)	126.9(5)
C(12)-C(11)-H(11A)	116.5
C(10)-C(11)-H(11A)	116.5
C(11)-C(12)-C(13)	125.6(5)
C(11)-C(12)-H(12A)	117.2
C(13)-C(12)-H(12A)	117.2
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(10)-C(14)-H(14A)	109.5
C(10)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(10)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
O(2)-C(15)-O(3)	124.8(4)
O(2)-C(15)-C(9)	123.4(3)
O(3)-C(15)-C(9)	111.8(4)
O(3)-C(16)-H(16A)	109.5
O(3)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
O(3)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(9)-O(1)-H(1B)	109.5
C(15)-O(3)-C(16)	116.2(4)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	69(1)	41(1)	46(1)	-2(1)	-4(1)	13(1)
C(1)	45(2)	46(2)	28(2)	6(2)	2(2)	-5(2)
C(2)	45(3)	39(2)	34(2)	9(2)	-3(2)	0(2)
C(3)	42(2)	35(2)	33(2)	-2(2)	-11(2)	6(2)
C(4)	32(2)	48(2)	33(2)	4(2)	0(2)	2(2)
C(5)	33(2)	40(2)	31(2)	6(1)	1(2)	-4(2)
C(6)	27(2)	42(2)	28(2)	6(1)	-6(1)	0(1)
C(7)	31(2)	43(2)	28(2)	3(1)	-2(2)	0(2)
C(8)	30(2)	43(2)	27(2)	4(2)	2(1)	3(1)
C(9)	30(2)	40(2)	35(2)	4(2)	2(2)	4(1)
C(10)	30(3)	41(2)	72(3)	-4(2)	7(2)	-2(2)
C(11)	40(3)	49(2)	68(3)	-12(2)	0(3)	-1(2)
C(12)	53(3)	46(2)	90(4)	-4(2)	24(3)	-6(2)
C(13)	65(4)	52(3)	123(5)	-21(3)	20(3)	-2(2)
C(14)	34(3)	55(3)	183(8)	-25(4)	-6(4)	5(2)
C(15)	37(3)	42(2)	33(2)	0(2)	3(2)	5(2)
C(16)	114(5)	85(4)	53(3)	-10(3)	-28(3)	61(4)
O(1)	54(2)	48(1)	28(1)	-1(1)	1(1)	8(1)
O(2)	33(2)	79(2)	60(2)	7(2)	10(2)	12(2)
O(3)	82(3)	60(2)	36(2)	3(1)	0(2)	34(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **5c**.

	x	y	z	U(eq)
H(1A)	1320	2443	10898	48
H(2A)	1681	1912	8671	48
H(4A)	4106	2493	3649	45
H(5A)	3695	3026	5843	42
H(7A)	1871	3079	11645	41
H(8A)	2682	3508	7806	40
H(10A)	3674	4138	9230	57
H(11A)	2939	4362	13965	63
H(12A)	3017	4762	9857	76
H(13A)	2410	5272	11949	120
H(13B)	3364	5094	14153	120
H(13C)	1402	5020	13770	120
H(14A)	6031	4064	11718	136
H(14B)	5387	3676	10781	136
H(14C)	4960	3803	13416	136
H(16A)	-749	4364	5516	126
H(16B)	-1162	4501	8135	126
H(16C)	-1928	4125	7199	126
H(1B)	1469	3841	14166	65

Table 6. Torsion angles [°] for **5c**.

C(6)-C(1)-C(2)-C(3)	0.6(6)
C(1)-C(2)-C(3)-C(4)	1.5(6)
C(1)-C(2)-C(3)-Br(1)	-178.4(3)
C(2)-C(3)-C(4)-C(5)	-2.2(6)
Br(1)-C(3)-C(4)-C(5)	177.7(3)
C(3)-C(4)-C(5)-C(6)	0.8(6)
C(2)-C(1)-C(6)-C(5)	-1.9(6)
C(2)-C(1)-C(6)-C(7)	-179.5(4)
C(4)-C(5)-C(6)-C(1)	1.2(6)
C(4)-C(5)-C(6)-C(7)	178.7(3)
C(1)-C(6)-C(7)-C(8)	-166.5(4)
C(5)-C(6)-C(7)-C(8)	16.0(6)
C(6)-C(7)-C(8)-C(9)	179.2(3)
C(7)-C(8)-C(9)-O(1)	9.0(5)
C(7)-C(8)-C(9)-C(10)	130.9(4)
C(7)-C(8)-C(9)-C(15)	-108.4(4)
O(1)-C(9)-C(10)-C(11)	-63.0(4)
C(8)-C(9)-C(10)-C(11)	174.0(4)
C(15)-C(9)-C(10)-C(11)	53.5(5)
O(1)-C(9)-C(10)-C(14)	60.6(5)
C(8)-C(9)-C(10)-C(14)	-62.4(5)
C(15)-C(9)-C(10)-C(14)	177.2(4)
C(14)-C(10)-C(11)-C(12)	121.6(6)
C(9)-C(10)-C(11)-C(12)	-115.7(5)
C(10)-C(11)-C(12)-C(13)	-179.4(5)
O(1)-C(9)-C(15)-O(2)	0.2(5)
C(8)-C(9)-C(15)-O(2)	119.7(4)
C(10)-C(9)-C(15)-O(2)	-117.2(4)
O(1)-C(9)-C(15)-O(3)	179.5(3)
C(8)-C(9)-C(15)-O(3)	-61.1(4)
C(10)-C(9)-C(15)-O(3)	62.1(4)
O(2)-C(15)-O(3)-C(16)	0.8(7)
C(9)-C(15)-O(3)-C(16)	-178.4(4)

Table 7. Hydrogen bonds for **5c** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1B)...O(3)#1	0.84	2.49	3.250(4)	150.5

Symmetry transformations used to generate equivalent atoms:
#1 x,y,z+1

7b

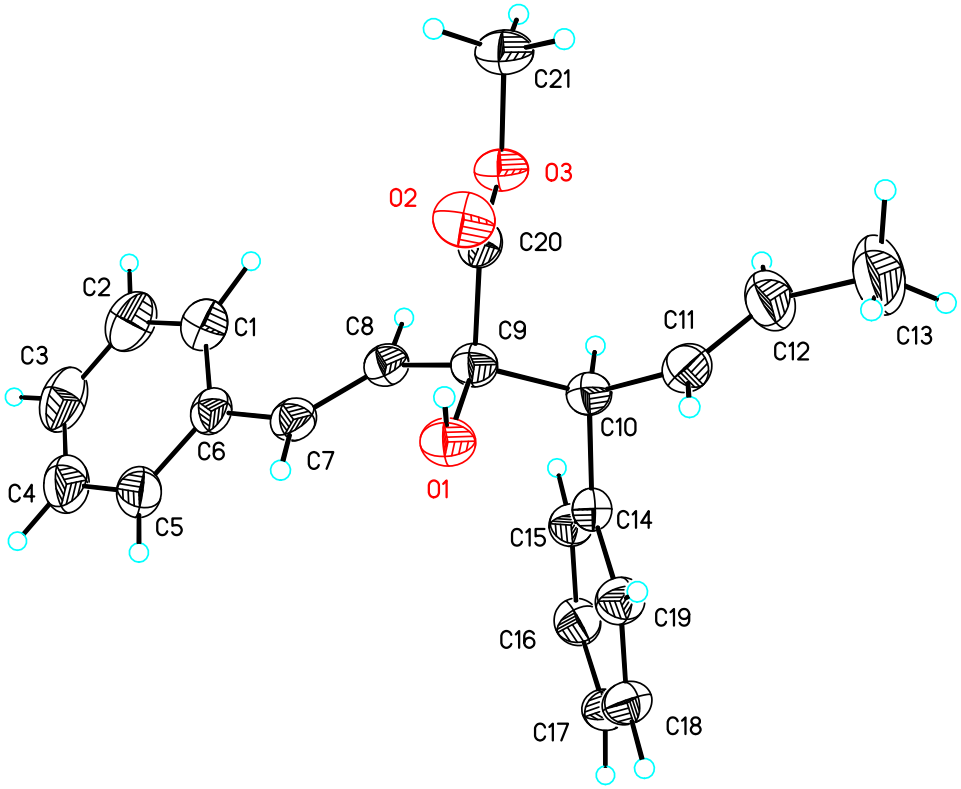


Table 1. Crystal data and structure refinement for **7b**.

Identification code	**7b**	
Empirical formula	C21 H22 O3	
Formula weight	322.39	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 11.1117(5) Å	α= 90°.
	b = 5.5288(3) Å	β= 104.084(2)°.
	c = 14.6321(7) Å	γ = 90°.
Volume	871.89(7) $Å^3$	
Z	2	
Density (calculated)	1.228 Mg/m^3	

Absorption coefficient	0.646 mm^{-1}
F(000)	344
Crystal size	0.42 x 0.17 x 0.16 mm^3
Theta range for data collection	3.11 to 68.04°.
Index ranges	-12<=h<=13, -6<=k<=5, -16<=l<=17
Reflections collected	6114
Independent reflections	2555 [R(int) = 0.0138]
Completeness to theta = 68.04°	95.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9038 and 0.7732
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2555 / 1 / 305
Goodness-of-fit on F^2	1.013
Final R indices [I>2sigma(I)]	R1 = 0.0254, wR2 = 0.0692
R indices (all data)	R1 = 0.0258, wR2 = 0.0697
Absolute structure parameter	-0.20(16)
Largest diff. peak and hole	0.143 and -0.133 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **7b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7838(1)	8078(3)	2616(1)	44(1)
C(2)	9030(2)	9020(4)	2923(1)	54(1)
C(3)	9910(2)	7803(4)	3599(1)	56(1)
C(4)	9602(1)	5691(4)	3974(1)	54(1)
C(5)	8419(1)	4749(4)	3671(1)	43(1)
C(6)	7514(1)	5921(3)	2990(1)	33(1)
C(7)	6265(1)	4860(3)	2673(1)	33(1)
C(8)	5242(1)	6061(3)	2264(1)	31(1)
C(9)	3985(1)	4929(3)	1864(1)	31(1)
C(10)	2952(1)	6164(3)	2259(1)	31(1)
C(11)	1674(1)	5447(3)	1697(1)	39(1)
C(12)	817(2)	6987(4)	1279(1)	53(1)
C(13)	-479(2)	6317(7)	57(2)	79(1)
C(14)	3127(1)	5696(3)	3307(1)	30(1)
C(15)	3716(1)	7413(3)	3955(1)	34(1)
C(16)	3844(1)	7080(3)	4914(1)	39(1)
C(17)	3377(1)	5013(3)	5233(1)	39(1)
C(18)	2799(1)	3283(3)	4598(1)	40(1)
C(19)	2679(1)	3610(3)	3639(1)	36(1)
C(20)	3670(1)	5295(3)	790(1)	30(1)
C(21)	3394(2)	8006(3)	-470(1)	40(1)
O(1)	4001(1)	2406(2)	2035(1)	36(1)
O(2)	3484(1)	3623(2)	245(1)	41(1)
O(3)	3649(1)	7599(2)	539(1)	35(1)

Table 3. Bond lengths [Å] and angles [°] for **7b**.

C(1)-C(2)	1.392(2)
C(1)-C(6)	1.395(2)
C(1)-H(1)	1.031(19)
C(2)-C(3)	1.384(3)
C(2)-H(2)	0.97(3)
C(3)-C(4)	1.368(3)
C(3)-H(3)	0.93(2)
C(4)-C(5)	1.383(2)
C(4)-H(4)	0.99(2)
C(5)-C(6)	1.392(2)
C(5)-H(5)	0.94(2)
C(6)-C(7)	1.4737(19)
C(7)-C(8)	1.327(2)
C(7)-H(7)	0.96(2)
C(8)-C(9)	1.5122(18)
C(8)-H(8)	0.989(19)
C(9)-O(1)	1.4166(18)
C(9)-C(20)	1.5388(17)
C(9)-C(10)	1.5624(19)
C(10)-C(11)	1.5100(18)
C(10)-C(14)	1.5198(17)
C(10)-H(10)	0.979(18)
C(11)-C(12)	1.313(2)
C(11)-H(11)	0.95(2)
C(12)-C(13)	1.503(3)
C(12)-H(12)	1.04(3)
C(13)-H(13A)	0.98(3)
C(13)-H(13B)	1.00(3)
C(13)-H(13C)	1.00(4)
C(14)-C(15)	1.388(2)
C(14)-C(19)	1.390(2)
C(15)-C(16)	1.387(2)
C(15)-H(15)	0.942(17)
C(16)-C(17)	1.383(2)

C(16)-H(16)	0.948(19)
C(17)-C(18)	1.379(2)
C(17)-H(17)	0.949(18)
C(18)-C(19)	1.388(2)
C(18)-H(18)	0.95(2)
C(19)-H(19)	0.964(18)
C(20)-O(2)	1.2049(17)
C(20)-O(3)	1.3240(18)
C(21)-O(3)	1.4510(16)
C(21)-H(21A)	0.96(2)
C(21)-H(21B)	0.966(17)
C(21)-H(21C)	0.94(2)
O(1)-H(1O)	0.882(19)

C(2)-C(1)-C(6)	57(16)
C(2)-C(1)-H(1)	118.5(11)
C(6)-C(1)-H(1)	120.8(11)
C(3)-C(2)-C(1)	120.01(19)
C(3)-C(2)-H(2)	122.3(12)
C(1)-C(2)-H(2)	117.6(12)
C(4)-C(3)-C(2)	119.94(16)
C(4)-C(3)-H(3)	117.6(13)
C(2)-C(3)-H(3)	122.3(13)
C(3)-C(4)-C(5)	120.25(17)
C(3)-C(4)-H(4)	120.3(13)
C(5)-C(4)-H(4)	119.5(13)
C(4)-C(5)-C(6)	121.27(18)
C(4)-C(5)-H(5)	119.9(11)
C(6)-C(5)-H(5)	118.7(11)
C(5)-C(6)-C(1)	117.94(14)
C(5)-C(6)-C(7)	120.07(14)
C(1)-C(6)-C(7)	121.97(13)
C(8)-C(7)-C(6)	125.48(14)
C(8)-C(7)-H(7)	116.8(10)
C(6)-C(7)-H(7)	117.7(10)
C(7)-C(8)-C(9)	125.22(14)

C(7)-C(8)-H(8)	121.4(9)
C(9)-C(8)-H(8)	113.3(9)
O(1)-C(9)-C(8)	111.60(11)
O(1)-C(9)-C(20)	107.45(11)
C(8)-C(9)-C(20)	107.41(10)
O(1)-C(9)-C(10)	110.14(11)
C(8)-C(9)-C(10)	111.64(11)
C(20)-C(9)-C(10)	108.42(10)
C(11)-C(10)-C(14)	112.18(11)
C(11)-C(10)-C(9)	111.19(12)
C(14)-C(10)-C(9)	111.91(10)
C(11)-C(10)-H(10)	107.3(8)
C(14)-C(10)-H(10)	107.9(8)
C(9)-C(10)-H(10)	106.0(9)
C(12)-C(11)-C(10)	124.24(18)
C(12)-C(11)-H(11)	119.5(11)
C(10)-C(11)-H(11)	116.2(11)
C(11)-C(12)-C(13)	125.0(2)
C(11)-C(12)-H(12)	117.8(13)
C(13)-C(12)-H(12)	117.2(13)
C(12)-C(13)-H(13A)	107.7(17)
C(12)-C(13)-H(13B)	109.3(14)
H(13A)-C(13)-H(13B)	109(2)
C(12)-C(13)-H(13C)	107.6(18)
H(13A)-C(13)-H(13C)	108(3)
H(13B)-C(13)-H(13C)	115(3)
C(15)-C(14)-C(19)	118.54(12)
C(15)-C(14)-C(10)	119.76(12)
C(19)-C(14)-C(10)	121.67(12)
C(16)-C(15)-C(14)	121.04(14)
C(16)-C(15)-H(15)	119.7(9)
C(14)-C(15)-H(15)	119.2(9)
C(17)-C(16)-C(15)	119.82(14)
C(17)-C(16)-H(16)	119.5(10)
C(15)-C(16)-H(16)	120.7(10)
C(18)-C(17)-C(16)	119.78(13)

C(18)-C(17)-H(17)	120.9(12)
C(16)-C(17)-H(17)	119.2(12)
C(17)-C(18)-C(19)	120.37(15)
C(17)-C(18)-H(18)	120.2(11)
C(19)-C(18)-H(18)	119.4(11)
C(18)-C(19)-C(14)	120.44(14)
C(18)-C(19)-H(19)	121.0(10)
C(14)-C(19)-H(19)	118.6(10)
O(2)-C(20)-O(3)	124.49(12)
O(2)-C(20)-C(9)	122.31(13)
O(3)-C(20)-C(9)	113.19(11)
O(3)-C(21)-H(21A)	104.5(11)
O(3)-C(21)-H(21B)	109.5(10)
H(21A)-C(21)-H(21B)	112.5(16)
O(3)-C(21)-H(21C)	110.5(11)
H(21A)-C(21)-H(21C)	109.6(18)
H(21B)-C(21)-H(21C)	110.1(15)
C(9)-O(1)-H(1O)	103.7(12)
C(20)-O(3)-C(21)	114.63(12)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **7b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	41(1)	47(1)	47(1)	-1(1)	15(1)	0(1)
C(2)	48(1)	54(1)	65(1)	-10(1)	24(1)	-12(1)
C(3)	36(1)	79(1)	56(1)	-23(1)	14(1)	-11(1)
C(4)	35(1)	78(1)	46(1)	-4(1)	7(1)	7(1)
C(5)	38(1)	53(1)	40(1)	0(1)	11(1)	7(1)
C(6)	33(1)	40(1)	30(1)	-6(1)	11(1)	3(1)
C(7)	37(1)	34(1)	30(1)	0(1)	12(1)	1(1)
C(8)	34(1)	31(1)	29(1)	-1(1)	10(1)	0(1)
C(9)	33(1)	28(1)	31(1)	2(1)	8(1)	0(1)
C(10)	32(1)	31(1)	31(1)	3(1)	8(1)	0(1)
C(11)	35(1)	49(1)	35(1)	2(1)	10(1)	-4(1)
C(12)	38(1)	75(1)	41(1)	-3(1)	2(1)	11(1)
C(13)	37(1)	134(3)	58(1)	-13(2)	-1(1)	13(1)
C(14)	27(1)	33(1)	32(1)	3(1)	9(1)	3(1)
C(15)	35(1)	32(1)	35(1)	3(1)	10(1)	0(1)
C(16)	40(1)	42(1)	34(1)	-3(1)	8(1)	4(1)
C(17)	42(1)	46(1)	31(1)	8(1)	14(1)	10(1)
C(18)	43(1)	39(1)	43(1)	11(1)	19(1)	4(1)
C(19)	38(1)	34(1)	38(1)	2(1)	11(1)	-2(1)
C(20)	28(1)	31(1)	31(1)	-2(1)	8(1)	-1(1)
C(21)	52(1)	41(1)	28(1)	0(1)	10(1)	0(1)
O(1)	44(1)	28(1)	36(1)	1(1)	10(1)	-1(1)
O(2)	50(1)	36(1)	37(1)	-6(1)	7(1)	-3(1)
O(3)	45(1)	32(1)	27(1)	1(1)	9(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **7b**.

	x	y	z	U(eq)
H(1)	7223(17)	8940(40)	2071(13)	54(5)
H(2)	9218(19)	10500(50)	2631(14)	64(6)
H(3)	10726(19)	8320(40)	3791(13)	62(5)
H(4)	10229(19)	4810(40)	4457(14)	65(6)
H(5)	8227(17)	3240(40)	3901(13)	53(5)
H(7)	6178(15)	3150(40)	2770(11)	40(4)
H(8)	5251(13)	7830(30)	2167(10)	35(4)
H(10)	3039(13)	7910(30)	2171(10)	28(4)
H(11)	1492(16)	3760(40)	1672(12)	46(5)
H(12)	1050(20)	8810(50)	1302(16)	77(7)
H(13A)	-620(30)	6980(60)	120(20)	111(10)
H(13B)	-1080(20)	7070(50)	1078(18)	99(9)
H(13C)	-520(30)	4510(70)	700(20)	103(10)
H(15)	3987(14)	8870(30)	3736(11)	31(4)
H(16)	4249(15)	8260(40)	5353(12)	43(4)
H(17)	3508(16)	4760(30)	5892(13)	48(5)
H(18)	2514(16)	1830(40)	4815(12)	45(5)
H(19)	2267(15)	2420(40)	3189(11)	39(4)
H(21A)	3422(17)	9740(40)	-534(13)	54(5)
H(21B)	2591(16)	7340(40)	-770(11)	43(4)
H(21C)	4009(16)	7290(40)	-719(12)	48(5)
H(1O)	3795(16)	1770(30)	1466(13)	48(5)

Table 6. Torsion angles [°] for **7b**.

C(6)-C(1)-C(2)-C(3)	0.7(2)
C(1)-C(2)-C(3)-C(4)	-0.9(3)
C(2)-C(3)-C(4)-C(5)	0.9(3)
C(3)-C(4)-C(5)-C(6)	-0.6(3)
C(4)-C(5)-C(6)-C(1)	0.4(2)
C(4)-C(5)-C(6)-C(7)	179.27(14)
C(2)-C(1)-C(6)-C(5)	-0.5(2)
C(2)-C(1)-C(6)-C(7)	-179.30(14)
C(5)-C(6)-C(7)-C(8)	158.53(14)
C(1)-C(6)-C(7)-C(8)	-22.7(2)
C(6)-C(7)-C(8)-C(9)	174.43(12)
C(7)-C(8)-C(9)-O(1)	4.06(19)
C(7)-C(8)-C(9)-C(20)	-113.46(14)
C(7)-C(8)-C(9)-C(10)	127.81(14)
O(1)-C(9)-C(10)-C(11)	-68.77(14)
C(8)-C(9)-C(10)-C(11)	166.66(12)
C(20)-C(9)-C(10)-C(11)	48.54(15)
O(1)-C(9)-C(10)-C(14)	57.56(14)
C(8)-C(9)-C(10)-C(14)	-67.01(14)
C(20)-C(9)-C(10)-C(14)	174.87(11)
C(14)-C(10)-C(11)-C(12)	110.54(17)
C(9)-C(10)-C(11)-C(12)	-123.28(16)
C(10)-C(11)-C(12)-C(13)	-176.81(16)
C(11)-C(10)-C(14)-C(15)	-137.08(14)
C(9)-C(10)-C(14)-C(15)	97.13(14)
C(11)-C(10)-C(14)-C(19)	40.96(18)
C(9)-C(10)-C(14)-C(19)	-84.83(15)
C(19)-C(14)-C(15)-C(16)	-0.78(19)
C(10)-C(14)-C(15)-C(16)	177.33(12)
C(14)-C(15)-C(16)-C(17)	-0.2(2)
C(15)-C(16)-C(17)-C(18)	0.7(2)
C(16)-C(17)-C(18)-C(19)	-0.3(2)
C(17)-C(18)-C(19)-C(14)	-0.7(2)
C(15)-C(14)-C(19)-C(18)	1.22(19)

C(10)-C(14)-C(19)-C(18)	-176.84(12)
O(1)-C(9)-C(20)-O(2)	0.15(16)
C(8)-C(9)-C(20)-O(2)	120.35(14)
C(10)-C(9)-C(20)-O(2)	-118.87(14)
O(1)-C(9)-C(20)-O(3)	-178.85(11)
C(8)-C(9)-C(20)-O(3)	-58.65(14)
C(10)-C(9)-C(20)-O(3)	62.13(13)
O(2)-C(20)-O(3)-C(21)	-0.83(18)
C(9)-C(20)-O(3)-C(21)	178.15(11)

Table 7. Hydrogen bonds for **7b** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1O)...O(2)	0.882(19)	2.014(19)	2.6288(14)	125.7(16)

7h

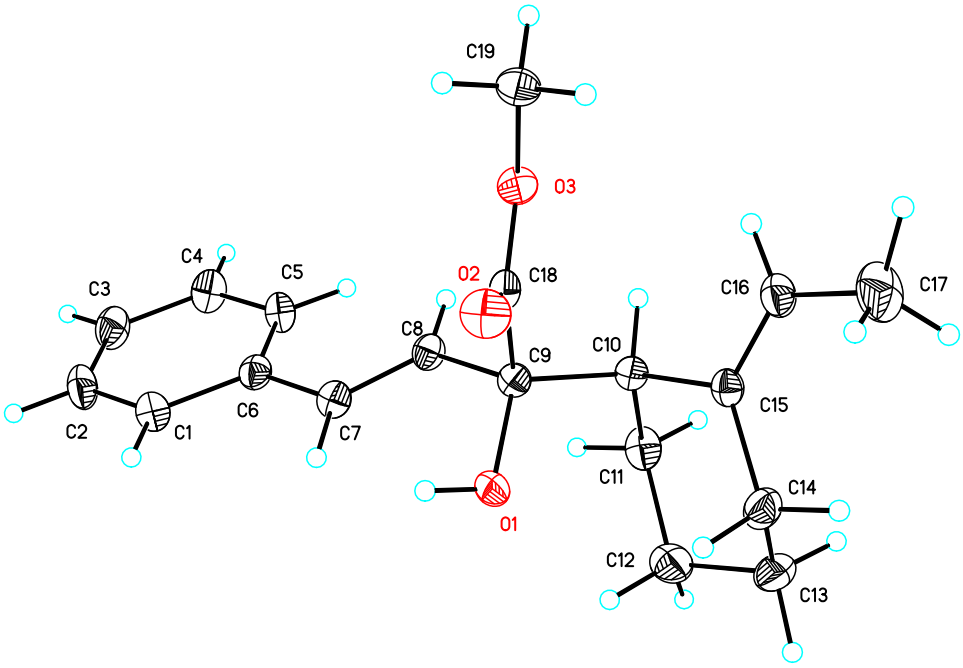


Table 1. Crystal data and structure refinement for **7h**.

Identification code	**7h**	
Empirical formula	C19 H24 O3	
Formula weight	300.38	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 5.7546(12) Å	α= 104.48(2)°.
	b = 12.147(2) Å	β= 90.08(3)°.
	c = 12.151(2) Å	γ = 90.16(3)°.
Volume	822.4(3) $Å^3$	
Z	2	
Density (calculated)	1.213 Mg/m^3	
Absorption coefficient	0.641 mm^{-1}	
F(000)	324	
Crystal size	0.34 x 0.10 x 0.09 mm^3	

Theta range for data collection	3.76 to 65.09°.
Index ranges	-6<=h<=5, -14<=k<=14, -14<=l<=13
Reflections collected	8095
Independent reflections	3637 [R(int) = 0.0146]
Completeness to theta = 65.09°	87.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9446 and 0.8115
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3637 / 3 / 398
Goodness-of-fit on F^2	1.020
Final R indices [I>2sigma(I)]	R1 = 0.0299, wR2 = 0.0860
R indices (all data)	R1 = 0.0300, wR2 = 0.0861
Absolute structure parameter	-0.02(16)
Extinction coefficient	0.0100(9)
Largest diff. peak and hole	0.194 and -0.138 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **7h**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-4649(4)	-10986(2)	-2261(2)	34(1)
C(2)	-6004(4)	-11964(2)	-2567(2)	38(1)
C(3)	-8104(4)	-11946(2)	-3097(2)	38(1)
C(4)	-8882(4)	-10946(2)	-3323(2)	37(1)
C(5)	-7531(4)	-9966(2)	-3029(2)	33(1)
C(6)	-5408(4)	-9967(2)	-2482(2)	27(1)
C(7)	-3926(4)	-8946(2)	-2136(2)	28(1)
C(8)	-4577(4)	-7892(2)	-2085(2)	26(1)
C(9)	-3022(3)	-6859(2)	-1670(2)	24(1)
C(10)	-3470(4)	-5963(2)	-2371(2)	25(1)
C(11)	-3018(4)	-6423(2)	-3647(2)	32(1)
C(12)	-493(4)	-6412(2)	-4000(2)	39(1)
C(13)	534(4)	-5221(2)	-3549(2)	41(1)
C(14)	317(4)	-4825(2)	-2261(2)	34(1)
C(15)	-2139(4)	-4862(2)	-1875(2)	25(1)
C(16)	-3171(4)	-4012(2)	-1138(2)	32(1)
C(17)	-2059(5)	-2903(2)	-520(3)	50(1)
C(18)	-3627(4)	-6326(2)	-421(2)	26(1)
C(19)	-6572(4)	-5466(2)	853(2)	35(1)
O(1)	-660(2)	-7197(1)	-1711(1)	29(1)
O(2)	-2234(3)	-6195(1)	336(2)	37(1)
O(3)	-5870(3)	-6047(1)	-287(1)	29(1)
C(1B)	-4419(4)	-4075(2)	-5532(2)	34(1)
C(2B)	-3119(5)	-3082(2)	-5360(2)	40(1)
C(3B)	-1047(5)	-3076(2)	-5918(2)	42(1)
C(4B)	-262(5)	-4052(2)	-6648(2)	40(1)
C(5B)	-1546(4)	-5054(2)	-6829(2)	35(1)
C(6B)	-3637(4)	-5079(2)	-6271(2)	28(1)
C(7B)	-5067(4)	-6121(2)	-6431(2)	27(1)
C(8B)	-4320(4)	-7171(2)	-6886(2)	26(1)
C(9B)	-5828(4)	-8222(2)	-7011(2)	26(1)

C(10B)	-5282(4)	-9103(2)	-8161(2)	25(1)
C(11B)	-5836(4)	-8652(2)	-9207(2)	33(1)
C(12B)	-8385(5)	-8737(2)	-9569(2)	41(1)
C(13B)	-9288(4)	-9943(2)	-9707(2)	42(1)
C(14B)	-8965(4)	-10334(2)	-8609(2)	36(1)
C(15B)	-6450(4)	-10245(2)	-8239(2)	27(1)
C(16B)	-5264(4)	-11087(2)	-7996(2)	32(1)
C(17B)	-6157(5)	-12257(2)	-8002(3)	52(1)
C(18B)	-5225(4)	-8773(2)	-6040(2)	27(1)
C(19B)	-2321(4)	-9659(2)	-5204(2)	37(1)
O(1B)	-8199(2)	-7920(1)	-6907(1)	29(1)
O(2B)	-6649(3)	-8945(1)	-5377(2)	38(1)
O(3B)	-2979(3)	-9029(1)	-6022(1)	30(1)

Table 3. Bond lengths [Å] and angles [°] for **7h**.

C(1)-C(2)	1.390(3)
C(1)-C(6)	1.401(3)
C(1)-H(1A)	0.9500
C(2)-C(3)	1.372(4)
C(2)-H(2A)	0.9500
C(3)-C(4)	1.386(3)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.390(3)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.390(3)
C(5)-H(5A)	0.9500
C(6)-C(7)	1.474(3)
C(7)-C(8)	1.321(3)
C(7)-H(7A)	0.9500
C(8)-C(9)	1.518(3)
C(8)-H(8A)	0.9500
C(9)-O(1)	1.419(2)
C(9)-C(18)	1.535(3)
C(9)-C(10)	1.562(3)
C(10)-C(15)	1.526(3)
C(10)-C(11)	1.534(3)
C(10)-H(10A)	1.0000
C(11)-C(12)	1.516(3)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(13)	1.530(3)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(14)	1.524(4)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.494(3)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900

C(15)-C(16)	1.327(3)
C(16)-C(17)	1.509(3)
C(16)-H(16A)	0.9500
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-O(2)	1.199(3)
C(18)-O(3)	1.335(3)
C(19)-O(3)	1.447(3)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
O(1)-H(1B)	0.8400
C(1B)-C(2B)	1.388(3)
C(1B)-C(6B)	1.398(3)
C(1B)-H(1BA)	0.9500
C(2B)-C(3B)	1.373(4)
C(2B)-H(2BA)	0.9500
C(3B)-C(4B)	1.370(4)
C(3B)-H(3BA)	0.9500
C(4B)-C(5B)	1.391(3)
C(4B)-H(4BA)	0.9500
C(5B)-C(6B)	1.386(3)
C(5B)-H(5BA)	0.9500
C(6B)-C(7B)	1.479(3)
C(7B)-C(8B)	1.329(3)
C(7B)-H(7BA)	0.9500
C(8B)-C(9B)	1.518(3)
C(8B)-H(8BA)	0.9500
C(9B)-O(1B)	1.411(3)
C(9B)-C(18B)	1.535(3)
C(9B)-C(10B)	1.566(3)
C(10B)-C(15B)	1.521(3)
C(10B)-C(11B)	1.539(3)
C(10B)-H(10B)	1.0000
C(11B)-C(12B)	1.527(3)

C(11B)-H(11C)	0.9900
C(11B)-H(11D)	0.9900
C(12B)-C(13B)	1.522(4)
C(12B)-H(12C)	0.9900
C(12B)-H(12D)	0.9900
C(13B)-C(14B)	1.535(4)
C(13B)-H(13C)	0.9900
C(13B)-H(13D)	0.9900
C(14B)-C(15B)	1.511(3)
C(14B)-H(14C)	0.9900
C(14B)-H(14D)	0.9900
C(15B)-C(16B)	1.324(3)
C(16B)-C(17B)	1.509(3)
C(16B)-H(16B)	0.9500
C(17B)-H(17D)	0.9800
C(17B)-H(17E)	0.9800
C(17B)-H(17F)	0.9800
C(18B)-O(2B)	1.204(3)
C(18B)-O(3B)	1.332(3)
C(19B)-O(3B)	1.449(3)
C(19B)-H(19D)	0.9800
C(19B)-H(19E)	0.9800
C(19B)-H(19F)	0.9800
O(1B)-H(1BB)	0.8400

C(2)-C(1)-C(6)	120.7(2)
C(2)-C(1)-H(1A)	119.6
C(6)-C(1)-H(1A)	119.6
C(3)-C(2)-C(1)	120.2(2)
C(3)-C(2)-H(2A)	119.9
C(1)-C(2)-H(2A)	119.9
C(2)-C(3)-C(4)	119.8(2)
C(2)-C(3)-H(3A)	120.1
C(4)-C(3)-H(3A)	120.1
C(3)-C(4)-C(5)	120.4(2)
C(3)-C(4)-H(4A)	119.8

C(5)-C(4)-H(4A)	119.8
C(6)-C(5)-C(4)	120.53(19)
C(6)-C(5)-H(5A)	119.7
C(4)-C(5)-H(5A)	119.7
C(5)-C(6)-C(1)	118.31(18)
C(5)-C(6)-C(7)	122.69(18)
C(1)-C(6)-C(7)	119.0(2)
C(8)-C(7)-C(6)	125.8(2)
C(8)-C(7)-H(7A)	117.1
C(6)-C(7)-H(7A)	117.1
C(7)-C(8)-C(9)	124.0(2)
C(7)-C(8)-H(8A)	118.0
C(9)-C(8)-H(8A)	118.0
O(1)-C(9)-C(8)	110.04(16)
O(1)-C(9)-C(18)	107.53(16)
C(8)-C(9)-C(18)	107.64(16)
O(1)-C(9)-C(10)	112.04(16)
C(8)-C(9)-C(10)	110.64(16)
C(18)-C(9)-C(10)	108.79(16)
C(15)-C(10)-C(11)	112.04(17)
C(15)-C(10)-C(9)	111.29(16)
C(11)-C(10)-C(9)	113.30(17)
C(15)-C(10)-H(10A)	106.6
C(11)-C(10)-H(10A)	106.6
C(9)-C(10)-H(10A)	106.6
C(12)-C(11)-C(10)	115.09(19)
C(12)-C(11)-H(11A)	108.5
C(10)-C(11)-H(11A)	108.5
C(12)-C(11)-H(11B)	108.5
C(10)-C(11)-H(11B)	108.5
H(11A)-C(11)-H(11B)	107.5
C(11)-C(12)-C(13)	109.88(19)
C(11)-C(12)-H(12A)	109.7
C(13)-C(12)-H(12A)	109.7
C(11)-C(12)-H(12B)	109.7
C(13)-C(12)-H(12B)	109.7

H(12A)-C(12)-H(12B)	108.2
C(14)-C(13)-C(12)	111.32(18)
C(14)-C(13)-H(13A)	109.4
C(12)-C(13)-H(13A)	109.4
C(14)-C(13)-H(13B)	109.4
C(12)-C(13)-H(13B)	109.4
H(13A)-C(13)-H(13B)	108.0
C(15)-C(14)-C(13)	112.08(19)
C(15)-C(14)-H(14A)	109.2
C(13)-C(14)-H(14A)	109.2
C(15)-C(14)-H(14B)	109.2
C(13)-C(14)-H(14B)	109.2
H(14A)-C(14)-H(14B)	107.9
C(16)-C(15)-C(14)	123.95(19)
C(16)-C(15)-C(10)	119.94(19)
C(14)-C(15)-C(10)	116.10(18)
C(15)-C(16)-C(17)	126.4(2)
C(15)-C(16)-H(16A)	116.8
C(17)-C(16)-H(16A)	116.8
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
O(2)-C(18)-O(3)	124.8(2)
O(2)-C(18)-C(9)	123.2(2)
O(3)-C(18)-C(9)	111.93(17)
O(3)-C(19)-H(19A)	109.5
O(3)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
O(3)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(9)-O(1)-H(1B)	109.5
C(18)-O(3)-C(19)	115.93(18)

C(2B)-C(1B)-C(6B)	120.5(2)
C(2B)-C(1B)-H(1BA)	119.7
C(6B)-C(1B)-H(1BA)	119.7
C(3B)-C(2B)-C(1B)	120.3(2)
C(3B)-C(2B)-H(2BA)	119.9
C(1B)-C(2B)-H(2BA)	119.9
C(4B)-C(3B)-C(2B)	119.9(2)
C(4B)-C(3B)-H(3BA)	120.1
C(2B)-C(3B)-H(3BA)	120.1
C(3B)-C(4B)-C(5B)	120.5(2)
C(3B)-C(4B)-H(4BA)	119.7
C(5B)-C(4B)-H(4BA)	119.7
C(6B)-C(5B)-C(4B)	120.5(2)
C(6B)-C(5B)-H(5BA)	119.8
C(4B)-C(5B)-H(5BA)	119.8
C(5B)-C(6B)-C(1B)	118.33(19)
C(5B)-C(6B)-C(7B)	122.67(19)
C(1B)-C(6B)-C(7B)	119.0(2)
C(8B)-C(7B)-C(6B)	125.0(2)
C(8B)-C(7B)-H(7BA)	117.5
C(6B)-C(7B)-H(7BA)	117.5
C(7B)-C(8B)-C(9B)	123.4(2)
C(7B)-C(8B)-H(8BA)	118.3
C(9B)-C(8B)-H(8BA)	118.3
O(1B)-C(9B)-C(8B)	110.44(16)
O(1B)-C(9B)-C(18B)	107.68(16)
C(8B)-C(9B)-C(18B)	108.20(16)
O(1B)-C(9B)-C(10B)	112.41(17)
C(8B)-C(9B)-C(10B)	110.07(17)
C(18B)-C(9B)-C(10B)	107.89(15)
C(15B)-C(10B)-C(11B)	111.44(17)
C(15B)-C(10B)-C(9B)	112.03(16)
C(11B)-C(10B)-C(9B)	112.95(16)
C(15B)-C(10B)-H(10B)	106.6
C(11B)-C(10B)-H(10B)	106.6
C(9B)-C(10B)-H(10B)	106.6

C(12B)-C(11B)-C(10B)	115.12(19)
C(12B)-C(11B)-H(11C)	108.5
C(10B)-C(11B)-H(11C)	108.5
C(12B)-C(11B)-H(11D)	108.5
C(10B)-C(11B)-H(11D)	108.5
H(11C)-C(11B)-H(11D)	107.5
C(13B)-C(12B)-C(11B)	110.50(18)
C(13B)-C(12B)-H(12C)	109.6
C(11B)-C(12B)-H(12C)	109.6
C(13B)-C(12B)-H(12D)	109.6
C(11B)-C(12B)-H(12D)	109.6
H(12C)-C(12B)-H(12D)	108.1
C(12B)-C(13B)-C(14B)	111.24(19)
C(12B)-C(13B)-H(13C)	109.4
C(14B)-C(13B)-H(13C)	109.4
C(12B)-C(13B)-H(13D)	109.4
C(14B)-C(13B)-H(13D)	109.4
H(13C)-C(13B)-H(13D)	108.0
C(15B)-C(14B)-C(13B)	111.1(2)
C(15B)-C(14B)-H(14C)	109.4
C(13B)-C(14B)-H(14C)	109.4
C(15B)-C(14B)-H(14D)	109.4
C(13B)-C(14B)-H(14D)	109.4
H(14C)-C(14B)-H(14D)	108.0
C(16B)-C(15B)-C(14B)	124.08(19)
C(16B)-C(15B)-C(10B)	120.13(19)
C(14B)-C(15B)-C(10B)	115.79(18)
C(15B)-C(16B)-C(17B)	127.1(2)
C(15B)-C(16B)-H(16B)	116.4
C(17B)-C(16B)-H(16B)	116.4
C(16B)-C(17B)-H(17D)	109.5
C(16B)-C(17B)-H(17E)	109.5
H(17D)-C(17B)-H(17E)	109.5
C(16B)-C(17B)-H(17F)	109.5
H(17D)-C(17B)-H(17F)	109.5
H(17E)-C(17B)-H(17F)	109.5

O(2B)-C(18B)-O(3B)	124.8(2)
O(2B)-C(18B)-C(9B)	122.9(2)
O(3B)-C(18B)-C(9B)	112.39(17)
O(3B)-C(19B)-H(19D)	109.5
O(3B)-C(19B)-H(19E)	109.5
H(19D)-C(19B)-H(19E)	109.5
O(3B)-C(19B)-H(19F)	109.5
H(19D)-C(19B)-H(19F)	109.5
H(19E)-C(19B)-H(19F)	109.5
C(9B)-O(1B)-H(1BB)	109.5
C(18B)-O(3B)-C(19B)	115.55(18)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **7h**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	36(1)	29(1)	35(1)	8(1)	0(1)	2(1)
C(2)	48(2)	25(1)	44(2)	13(1)	1(1)	0(1)
C(3)	47(1)	28(1)	38(1)	7(1)	-1(1)	-10(1)
C(4)	39(1)	36(1)	36(1)	11(1)	-7(1)	-10(1)
C(5)	38(1)	26(1)	35(1)	10(1)	-3(1)	-2(1)
C(6)	34(1)	25(1)	23(1)	5(1)	6(1)	-1(1)
C(7)	31(1)	29(1)	25(1)	8(1)	-2(1)	-1(1)
C(8)	28(1)	27(1)	24(1)	6(1)	0(1)	-2(1)
C(9)	22(1)	26(1)	24(1)	6(1)	0(1)	1(1)
C(10)	24(1)	25(1)	26(1)	5(1)	-2(1)	-1(1)
C(11)	42(1)	31(1)	23(1)	7(1)	-3(1)	-1(1)
C(12)	46(2)	43(1)	28(1)	10(1)	9(1)	11(1)
C(13)	34(1)	46(1)	46(2)	21(1)	13(1)	3(1)
C(14)	28(1)	33(1)	45(2)	16(1)	-2(1)	-4(1)
C(15)	26(1)	24(1)	27(1)	10(1)	-3(1)	-1(1)
C(16)	39(1)	24(1)	32(1)	7(1)	-1(1)	-1(1)
C(17)	67(2)	29(1)	48(2)	-2(1)	-2(2)	-6(1)
C(18)	29(1)	21(1)	29(1)	10(1)	-3(1)	-3(1)
C(19)	41(1)	32(1)	29(1)	3(1)	8(1)	3(1)
O(1)	23(1)	28(1)	36(1)	9(1)	-2(1)	2(1)
O(2)	37(1)	45(1)	29(1)	8(1)	-9(1)	0(1)
O(3)	31(1)	29(1)	25(1)	4(1)	2(1)	1(1)
C(1B)	39(1)	30(1)	34(1)	7(1)	4(1)	2(1)
C(2B)	52(2)	26(1)	37(1)	-1(1)	3(1)	-1(1)
C(3B)	53(2)	30(1)	41(2)	7(1)	-4(1)	-15(1)
C(4B)	41(1)	38(1)	39(1)	8(1)	2(1)	-11(1)
C(5B)	39(1)	29(1)	33(1)	3(1)	3(1)	-3(1)
C(6B)	33(1)	28(1)	24(1)	10(1)	-5(1)	-2(1)
C(7B)	32(1)	27(1)	23(1)	7(1)	-1(1)	-1(1)
C(8B)	26(1)	28(1)	24(1)	8(1)	-1(1)	0(1)
C(9B)	25(1)	25(1)	26(1)	5(1)	2(1)	1(1)

C(10B)	23(1)	24(1)	26(1)	6(1)	4(1)	0(1)
C(11B)	41(1)	32(1)	27(1)	9(1)	4(1)	3(1)
C(12B)	46(2)	47(1)	30(1)	11(1)	-3(1)	14(1)
C(13B)	33(1)	50(1)	36(1)	-2(1)	-9(1)	5(1)
C(14B)	28(1)	33(1)	41(1)	1(1)	-1(1)	-3(1)
C(15B)	26(1)	27(1)	25(1)	2(1)	4(1)	-3(1)
C(16B)	33(1)	26(1)	35(1)	6(1)	3(1)	1(1)
C(17B)	61(2)	33(1)	63(2)	17(1)	5(2)	-6(1)
C(18B)	30(1)	24(1)	25(1)	3(1)	1(1)	-4(1)
C(19B)	42(1)	38(1)	36(1)	18(1)	-4(1)	2(1)
O(1B)	25(1)	28(1)	31(1)	5(1)	3(1)	0(1)
O(2B)	37(1)	49(1)	32(1)	17(1)	7(1)	-2(1)
O(3B)	30(1)	31(1)	30(1)	12(1)	-1(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **7h**.

	x	y	z	U(eq)
H(1A)	-3192	-11007	-1899	40
H(2A)	-5473	-12648	-2408	46
H(3A)	-9023	-12617	-3310	45
H(4A)	-10348	-10931	-3679	44
H(5A)	-8062	-9289	-3204	39
H(7A)	-2366	-9056	-1931	33
H(8A)	-6109	-7774	-2322	32
H(10A)	-5159	-5770	-2289	30
H(11A)	-3603	-7214	-3884	38
H(11B)	-3927	-5966	-4064	38
H(12A)	-380	-6638	-4840	46
H(12B)	397	-6966	-3694	46
H(13A)	2194	-5227	-3763	49
H(13B)	-286	-4681	-3902	49
H(14A)	1285	-5315	-1907	41
H(14B)	914	-4037	-2002	41
H(16A)	-4765	-4112	-986	38
H(17A)	-3211	-2429	-27	75
H(17B)	-1484	-2504	-1075	75
H(17C)	-759	-3055	-58	75
H(19A)	-8236	-5297	858	52
H(19B)	-5691	-4756	1103	52
H(19C)	-6263	-5954	1369	52
H(1B)	112	-6712	-1235	43
H(1BA)	-5853	-4072	-5144	41
H(2BA)	-3665	-2405	-4855	48
H(3BA)	-159	-2395	-5797	50
H(4BA)	1170	-4045	-7034	48
H(5BA)	-985	-5726	-7338	42
H(7BA)	-6640	-6034	-6189	33

H(8BA)	-2761	-7268	-7147	31
H(10B)	-3568	-9240	-8171	29
H(11C)	-5351	-7845	-9045	39
H(11D)	-4891	-9079	-9854	39
H(12C)	-9320	-8203	-8990	49
H(12D)	-8549	-8519	-10298	49
H(13C)	-8445	-10465	-10334	50
H(13D)	-10958	-9974	-9910	50
H(14C)	-9931	-9858	-7999	43
H(14D)	-9495	-11132	-8735	43
H(16B)	-3676	-10937	-7796	38
H(17D)	-4889	-12711	-7805	77
H(17E)	-6752	-12629	-8760	77
H(17F)	-7409	-12193	-7444	77
H(19D)	-647	-9810	-5258	55
H(19E)	-3174	-10382	-5364	55
H(19F)	-2696	-9213	-4435	55
H(1BB)	-8936	-8396	-6646	43

Table 6. Torsion angles [°] for **7h**.

C(6)-C(1)-C(2)-C(3)	0.4(4)
C(1)-C(2)-C(3)-C(4)	-0.4(4)
C(2)-C(3)-C(4)-C(5)	1.0(4)
C(3)-C(4)-C(5)-C(6)	-1.5(4)
C(4)-C(5)-C(6)-C(1)	1.5(3)
C(4)-C(5)-C(6)-C(7)	-179.0(2)
C(2)-C(1)-C(6)-C(5)	-1.0(3)
C(2)-C(1)-C(6)-C(7)	179.5(2)
C(5)-C(6)-C(7)-C(8)	14.3(4)
C(1)-C(6)-C(7)-C(8)	-166.2(2)
C(6)-C(7)-C(8)-C(9)	177.0(2)
C(7)-C(8)-C(9)-O(1)	19.1(3)
C(7)-C(8)-C(9)-C(18)	-97.8(2)
C(7)-C(8)-C(9)-C(10)	143.5(2)
O(1)-C(9)-C(10)-C(15)	-63.7(2)
C(8)-C(9)-C(10)-C(15)	173.14(18)
C(18)-C(9)-C(10)-C(15)	55.1(2)
O(1)-C(9)-C(10)-C(11)	63.7(2)
C(8)-C(9)-C(10)-C(11)	-59.5(2)
C(18)-C(9)-C(10)-C(11)	-177.58(17)
C(15)-C(10)-C(11)-C(12)	45.0(2)
C(9)-C(10)-C(11)-C(12)	-82.0(2)
C(10)-C(11)-C(12)-C(13)	-52.9(3)
C(11)-C(12)-C(13)-C(14)	57.4(3)
C(12)-C(13)-C(14)-C(15)	-55.7(3)
C(13)-C(14)-C(15)-C(16)	-131.9(2)
C(13)-C(14)-C(15)-C(10)	48.6(2)
C(11)-C(10)-C(15)-C(16)	138.0(2)
C(9)-C(10)-C(15)-C(16)	-94.0(2)
C(11)-C(10)-C(15)-C(14)	-42.5(3)
C(9)-C(10)-C(15)-C(14)	85.5(2)
C(14)-C(15)-C(16)-C(17)	-3.4(4)
C(10)-C(15)-C(16)-C(17)	176.0(2)
O(1)-C(9)-C(18)-O(2)	3.3(2)

C(8)-C(9)-C(18)-O(2)	121.8(2)
C(10)-C(9)-C(18)-O(2)	-118.3(2)
O(1)-C(9)-C(18)-O(3)	-175.92(13)
C(8)-C(9)-C(18)-O(3)	-57.4(2)
C(10)-C(9)-C(18)-O(3)	62.53(19)
O(2)-C(18)-O(3)-C(19)	4.9(3)
C(9)-C(18)-O(3)-C(19)	-175.89(15)
C(6B)-C(1B)-C(2B)-C(3B)	0.1(4)
C(1B)-C(2B)-C(3B)-C(4B)	0.2(4)
C(2B)-C(3B)-C(4B)-C(5B)	-0.2(4)
C(3B)-C(4B)-C(5B)-C(6B)	-0.1(4)
C(4B)-C(5B)-C(6B)-C(1B)	0.4(3)
C(4B)-C(5B)-C(6B)-C(7B)	-179.9(2)
C(2B)-C(1B)-C(6B)-C(5B)	-0.4(3)
C(2B)-C(1B)-C(6B)-C(7B)	179.9(2)
C(5B)-C(6B)-C(7B)-C(8B)	16.5(3)
C(1B)-C(6B)-C(7B)-C(8B)	-163.8(2)
C(6B)-C(7B)-C(8B)-C(9B)	178.52(19)
C(7B)-C(8B)-C(9B)-O(1B)	17.5(3)
C(7B)-C(8B)-C(9B)-C(18B)	-100.1(2)
C(7B)-C(8B)-C(9B)-C(10B)	142.2(2)
O(1B)-C(9B)-C(10B)-C(15B)	-65.9(2)
C(8B)-C(9B)-C(10B)-C(15B)	170.57(17)
C(18B)-C(9B)-C(10B)-C(15B)	52.7(2)
O(1B)-C(9B)-C(10B)-C(11B)	61.0(2)
C(8B)-C(9B)-C(10B)-C(11B)	-62.6(2)
C(18B)-C(9B)-C(10B)-C(11B)	179.53(17)
C(15B)-C(10B)-C(11B)-C(12B)	45.6(3)
C(9B)-C(10B)-C(11B)-C(12B)	-81.5(2)
C(10B)-C(11B)-C(12B)-C(13B)	-52.2(3)
C(11B)-C(12B)-C(13B)-C(14B)	56.7(3)
C(12B)-C(13B)-C(14B)-C(15B)	-56.4(3)
C(13B)-C(14B)-C(15B)-C(16B)	-128.3(2)
C(13B)-C(14B)-C(15B)-C(10B)	51.3(2)
C(11B)-C(10B)-C(15B)-C(16B)	134.3(2)
C(9B)-C(10B)-C(15B)-C(16B)	-98.1(2)

C(11B)-C(10B)-C(15B)-C(14B)	-45.3(3)
C(9B)-C(10B)-C(15B)-C(14B)	82.4(2)
C(14B)-C(15B)-C(16B)-C(17B)	-2.0(4)
C(10B)-C(15B)-C(16B)-C(17B)	178.5(2)
O(1B)-C(9B)-C(18B)-O(2B)	3.6(2)
C(8B)-C(9B)-C(18B)-O(2B)	123.0(2)
C(10B)-C(9B)-C(18B)-O(2B)	-118.0(2)
O(1B)-C(9B)-C(18B)-O(3B)	-176.29(16)
C(8B)-C(9B)-C(18B)-O(3B)	-56.9(2)
C(10B)-C(9B)-C(18B)-O(3B)	62.15(19)
O(2B)-C(18B)-O(3B)-C(19B)	6.3(3)
C(9B)-C(18B)-O(3B)-C(19B)	-173.82(17)

Table 7. Hydrogen bonds for **7h** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1B)...O(3)#1	0.84	2.62	3.361(2)	148.5
O(1B)-H(1BB)...O(3B)#2	0.84	2.62	3.354(2)	146.7

Symmetry transformations used to generate equivalent atoms:
#1 x+1,y,z #2 x-1,y,z

7j

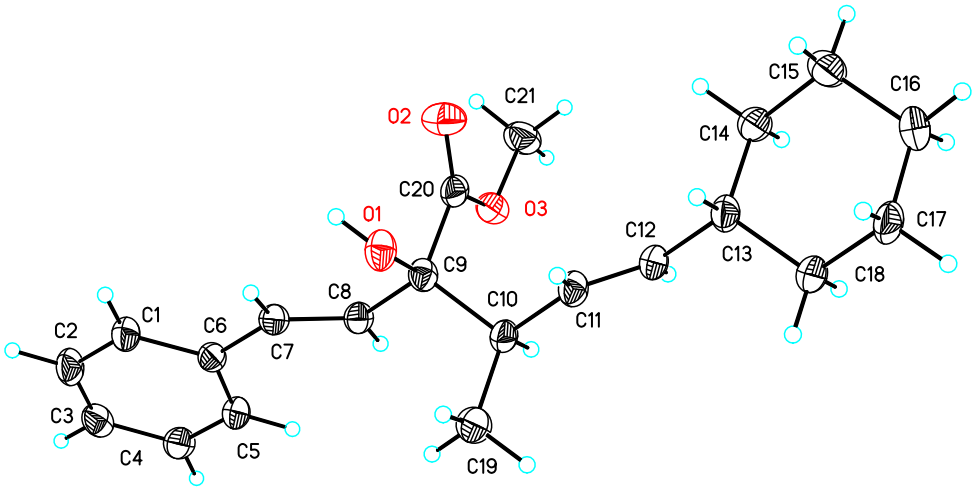


Table 1. Crystal data and structure refinement for **7j**.

Identification code	**7j**	
Empirical formula	C21 H28 O3	
Formula weight	328.43	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 5.5849(4) Å	α= 116.623(5)°.
	b = 9.4558(6) Å	β= 94.611(6)°.
	c = 9.9361(7) Å	γ = 90.704(4)°.
Volume	466.88(6) $Å^3$	
Z	1	
Density (calculated)	1.168 Mg/m^3	
Absorption coefficient	0.604 mm^{-1}	
F(000)	178	
Crystal size	0.25 x 0.18 x 0.09 mm^3	
Theta range for data collection	5.00 to 67.44°.	
Index ranges	-6<=h<=6, -11<=k<=11, -11<=l<=11	
Reflections collected	3568	
Independent reflections	1969 [R(int) = 0.0221]	

Completeness to theta = 67.44°	82.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9477 and 0.8637
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1969 / 3 / 217
Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0448, wR2 = 0.1175
R indices (all data)	R1 = 0.0484, wR2 = 0.1214
Absolute structure parameter	0.0(3)
Largest diff. peak and hole	0.200 and -0.203 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **7j**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-2307(5)	-9699(3)	-4730(4)	36(1)
C(2)	-640(6)	-10279(4)	-3999(4)	41(1)
C(3)	1493(5)	-9456(4)	-3307(4)	39(1)
C(4)	2021(5)	-8038(4)	-3343(4)	37(1)
C(5)	392(5)	-7454(3)	-4079(4)	33(1)
C(6)	-1791(5)	-8280(3)	-4788(3)	30(1)
C(7)	-3563(5)	-7712(3)	-5591(3)	30(1)
C(8)	-3141(4)	-6641(3)	-6066(3)	29(1)
C(9)	-5058(4)	-6134(3)	-6907(3)	29(1)
C(10)	-5068(4)	-4302(3)	-6244(3)	30(1)
C(11)	-6930(5)	-3852(3)	-7143(3)	32(1)
C(12)	-6537(5)	-3162(3)	-8004(3)	32(1)
C(13)	-8505(5)	-2727(3)	-8861(3)	33(1)
C(14)	-8172(6)	-3432(3)	-10550(3)	40(1)
C(15)	-10283(6)	-3052(4)	-11404(4)	47(1)
C(16)	-10576(6)	-1272(4)	-10739(4)	46(1)
C(17)	-10812(5)	-540(4)	-9054(4)	41(1)
C(18)	-8694(5)	-939(3)	-8215(4)	37(1)
C(19)	-5555(6)	-3570(4)	-4580(4)	41(1)
C(20)	-4571(5)	-6847(3)	-8577(4)	31(1)
C(21)	-1845(6)	-6927(4)	-10283(4)	44(1)
O(1)	-7369(3)	-6737(2)	-6853(3)	36(1)
O(2)	-5972(4)	-7755(3)	-9582(3)	49(1)
O(3)	-2447(3)	-6335(2)	-8750(2)	35(1)

Table 3. Bond lengths [Å] and angles [°] for **7j**.

C(1)-C(6)	1.396(4)
C(1)-C(2)	1.399(4)
C(1)-H(1A)	0.9500
C(2)-C(3)	1.365(5)
C(2)-H(2A)	0.9500
C(3)-C(4)	1.387(4)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.390(4)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.393(4)
C(5)-H(5A)	0.9500
C(6)-C(7)	1.475(4)
C(7)-C(8)	1.321(4)
C(7)-H(7A)	0.9500
C(8)-C(9)	1.517(3)
C(8)-H(8A)	0.9500
C(9)-O(1)	1.419(3)
C(9)-C(20)	1.535(4)
C(9)-C(10)	1.553(3)
C(10)-C(11)	1.504(3)
C(10)-C(19)	1.529(4)
C(10)-H(10A)	1.0000
C(11)-C(12)	1.317(4)
C(11)-H(11A)	0.9500
C(12)-C(13)	1.508(4)
C(12)-H(12A)	0.9500
C(13)-C(18)	1.524(4)
C(13)-C(14)	1.531(4)
C(13)-H(13A)	1.0000
C(14)-C(15)	1.537(4)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.524(4)
C(15)-H(15A)	0.9900

C(15)-H(15B)	0.9900
C(16)-C(17)	1.516(5)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-C(18)	1.540(4)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-O(2)	1.198(4)
C(20)-O(3)	1.329(3)
C(21)-O(3)	1.439(4)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
O(1)-H(1B)	0.8400

C(6)-C(1)-C(2)	120.4(3)
C(6)-C(1)-H(1A)	119.8
C(2)-C(1)-H(1A)	119.8
C(3)-C(2)-C(1)	120.7(3)
C(3)-C(2)-H(2A)	119.6
C(1)-C(2)-H(2A)	119.6
C(2)-C(3)-C(4)	119.6(3)
C(2)-C(3)-H(3A)	120.2
C(4)-C(3)-H(3A)	120.2
C(3)-C(4)-C(5)	120.3(3)
C(3)-C(4)-H(4A)	119.8
C(5)-C(4)-H(4A)	119.8
C(4)-C(5)-C(6)	120.7(2)
C(4)-C(5)-H(5A)	119.7
C(6)-C(5)-H(5A)	119.7
C(5)-C(6)-C(1)	118.3(2)

C(5)-C(6)-C(7)	122.5(2)
C(1)-C(6)-C(7)	119.2(2)
C(8)-C(7)-C(6)	126.2(2)
C(8)-C(7)-H(7A)	116.9
C(6)-C(7)-H(7A)	116.9
C(7)-C(8)-C(9)	123.1(2)
C(7)-C(8)-H(8A)	118.4
C(9)-C(8)-H(8A)	118.4
O(1)-C(9)-C(8)	110.6(2)
O(1)-C(9)-C(20)	107.2(2)
C(8)-C(9)-C(20)	108.6(2)
O(1)-C(9)-C(10)	109.1(2)
C(8)-C(9)-C(10)	111.7(2)
C(20)-C(9)-C(10)	109.49(18)
C(11)-C(10)-C(19)	110.6(2)
C(11)-C(10)-C(9)	110.0(2)
C(19)-C(10)-C(9)	110.3(2)
C(11)-C(10)-H(10A)	108.6
C(19)-C(10)-H(10A)	108.6
C(9)-C(10)-H(10A)	108.6
C(12)-C(11)-C(10)	126.9(2)
C(12)-C(11)-H(11A)	116.5
C(10)-C(11)-H(11A)	116.5
C(11)-C(12)-C(13)	124.0(2)
C(11)-C(12)-H(12A)	118.0
C(13)-C(12)-H(12A)	118.0
C(12)-C(13)-C(18)	112.1(2)
C(12)-C(13)-C(14)	111.8(2)
C(18)-C(13)-C(14)	109.8(2)
C(12)-C(13)-H(13A)	107.7
C(18)-C(13)-H(13A)	107.7
C(14)-C(13)-H(13A)	107.7
C(13)-C(14)-C(15)	110.5(2)
C(13)-C(14)-H(14A)	109.5
C(15)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5

C(15)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	108.1
C(16)-C(15)-C(14)	111.2(3)
C(16)-C(15)-H(15A)	109.4
C(14)-C(15)-H(15A)	109.4
C(16)-C(15)-H(15B)	109.4
C(14)-C(15)-H(15B)	109.4
H(15A)-C(15)-H(15B)	108.0
C(17)-C(16)-C(15)	111.9(2)
C(17)-C(16)-H(16A)	109.2
C(15)-C(16)-H(16A)	109.2
C(17)-C(16)-H(16B)	109.2
C(15)-C(16)-H(16B)	109.2
H(16A)-C(16)-H(16B)	107.9
C(16)-C(17)-C(18)	111.1(3)
C(16)-C(17)-H(17A)	109.4
C(18)-C(17)-H(17A)	109.4
C(16)-C(17)-H(17B)	109.4
C(18)-C(17)-H(17B)	109.4
H(17A)-C(17)-H(17B)	108.0
C(13)-C(18)-C(17)	110.7(2)
C(13)-C(18)-H(18A)	109.5
C(17)-C(18)-H(18A)	109.5
C(13)-C(18)-H(18B)	109.5
C(17)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	108.1
C(10)-C(19)-H(19A)	109.5
C(10)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(10)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
O(2)-C(20)-O(3)	125.3(3)
O(2)-C(20)-C(9)	122.8(2)
O(3)-C(20)-C(9)	111.9(2)
O(3)-C(21)-H(21A)	109.5

O(3)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
O(3)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(9)-O(1)-H(1B)	109.5
C(20)-O(3)-C(21)	115.9(2)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **7j**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	44(1)	30(1)	38(2)	19(1)	5(1)	4(1)
C(2)	58(2)	32(2)	44(2)	24(1)	11(2)	14(1)
C(3)	48(2)	38(2)	35(2)	20(1)	7(1)	19(1)
C(4)	41(1)	33(1)	37(2)	15(1)	3(1)	8(1)
C(5)	38(1)	29(1)	37(2)	17(1)	3(1)	5(1)
C(6)	40(1)	25(1)	27(2)	12(1)	7(1)	9(1)
C(7)	31(1)	28(1)	30(2)	13(1)	2(1)	5(1)
C(8)	29(1)	27(1)	32(2)	14(1)	3(1)	6(1)
C(9)	25(1)	30(1)	34(2)	18(1)	-1(1)	3(1)
C(10)	34(1)	24(1)	34(2)	15(1)	1(1)	4(1)
C(11)	33(1)	28(1)	37(2)	17(1)	3(1)	8(1)
C(12)	37(1)	26(1)	36(2)	15(1)	3(1)	7(1)
C(13)	37(1)	28(1)	38(2)	19(1)	3(1)	6(1)
C(14)	52(2)	30(2)	33(2)	11(1)	2(1)	14(1)
C(15)	59(2)	45(2)	34(2)	16(2)	-4(2)	12(2)
C(16)	58(2)	41(2)	49(2)	30(2)	-2(2)	9(1)
C(17)	45(1)	27(1)	52(2)	21(1)	-1(1)	10(1)
C(18)	45(1)	27(1)	38(2)	15(1)	2(1)	9(1)
C(19)	51(2)	36(2)	37(2)	16(1)	5(1)	13(1)
C(20)	33(1)	25(1)	36(2)	15(1)	-3(1)	5(1)
C(21)	52(2)	49(2)	30(2)	16(1)	8(1)	7(1)
O(1)	29(1)	37(1)	49(1)	27(1)	2(1)	3(1)
O(2)	48(1)	51(1)	38(1)	12(1)	-5(1)	-6(1)
O(3)	36(1)	38(1)	31(1)	16(1)	2(1)	4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **7j**.

	x	y	z	U(eq)
H(1A)	-3799	-10273	-5188	43
H(2A)	-996	-11257	-3984	50
H(3A)	2609	-9853	-2804	46
H(4A)	3504	-7461	-2863	44
H(5A)	773	-6481	-4097	40
H(7A)	-5161	-8159	-5785	35
H(8A)	-1561	-6166	-5872	35
H(10A)	-3450	-3890	-6316	36
H(11A)	-8563	-4093	-7084	38
H(12A)	-4917	-2922	-8091	39
H(13A)	-10065	-3183	-8758	39
H(14A)	-8075	-4595	-10968	48
H(14B)	-6647	-2992	-10688	48
H(15A)	-9997	-3470	-12483	56
H(15B)	-11784	-3582	-11348	56
H(16A)	-9165	-762	-10922	56
H(16B)	-12025	-1071	-11256	56
H(17A)	-12341	-940	-8876	49
H(17B)	-10859	625	-8649	49
H(18A)	-7178	-455	-8314	44
H(18B)	-8928	-490	-7127	44
H(19A)	-5565	-2416	-4177	62
H(19B)	-4293	-3841	-4005	62
H(19C)	-7121	-3984	-4492	62
H(21A)	-257	-6478	-10288	66
H(21B)	-3050	-6621	-10863	66
H(21C)	-1818	-8084	-10743	66
H(1B)	-7372	-7727	-7209	54

Table 6. Torsion angles [°] for **7j**.

C(6)-C(1)-C(2)-C(3)	1.3(4)
C(1)-C(2)-C(3)-C(4)	-0.7(5)
C(2)-C(3)-C(4)-C(5)	0.0(5)
C(3)-C(4)-C(5)-C(6)	0.0(4)
C(4)-C(5)-C(6)-C(1)	0.6(4)
C(4)-C(5)-C(6)-C(7)	-179.5(3)
C(2)-C(1)-C(6)-C(5)	-1.2(4)
C(2)-C(1)-C(6)-C(7)	178.9(3)
C(5)-C(6)-C(7)-C(8)	17.8(4)
C(1)-C(6)-C(7)-C(8)	-162.3(3)
C(6)-C(7)-C(8)-C(9)	179.1(2)
C(7)-C(8)-C(9)-O(1)	10.7(4)
C(7)-C(8)-C(9)-C(20)	-106.7(3)
C(7)-C(8)-C(9)-C(10)	132.4(3)
O(1)-C(9)-C(10)-C(11)	-59.4(3)
C(8)-C(9)-C(10)-C(11)	178.0(2)
C(20)-C(9)-C(10)-C(11)	57.7(2)
O(1)-C(9)-C(10)-C(19)	62.8(3)
C(8)-C(9)-C(10)-C(19)	-59.8(3)
C(20)-C(9)-C(10)-C(19)	179.9(2)
C(19)-C(10)-C(11)-C(12)	124.9(3)
C(9)-C(10)-C(11)-C(12)	-113.0(3)
C(10)-C(11)-C(12)-C(13)	-179.2(3)
C(11)-C(12)-C(13)-C(18)	110.9(3)
C(11)-C(12)-C(13)-C(14)	-125.4(3)
C(12)-C(13)-C(14)-C(15)	176.6(2)
C(18)-C(13)-C(14)-C(15)	-58.3(3)
C(13)-C(14)-C(15)-C(16)	56.2(3)
C(14)-C(15)-C(16)-C(17)	-54.3(4)
C(15)-C(16)-C(17)-C(18)	54.3(4)
C(12)-C(13)-C(18)-C(17)	-176.6(2)
C(14)-C(13)-C(18)-C(17)	58.5(3)
C(16)-C(17)-C(18)-C(13)	-56.6(3)
O(1)-C(9)-C(20)-O(2)	-0.9(3)

C(8)-C(9)-C(20)-O(2)	118.7(3)
C(10)-C(9)-C(20)-O(2)	-119.1(3)
O(1)-C(9)-C(20)-O(3)	179.2(2)
C(8)-C(9)-C(20)-O(3)	-61.3(2)
C(10)-C(9)-C(20)-O(3)	60.9(2)
O(2)-C(20)-O(3)-C(21)	0.7(4)
C(9)-C(20)-O(3)-C(21)	-179.3(2)

***epi*-7j**

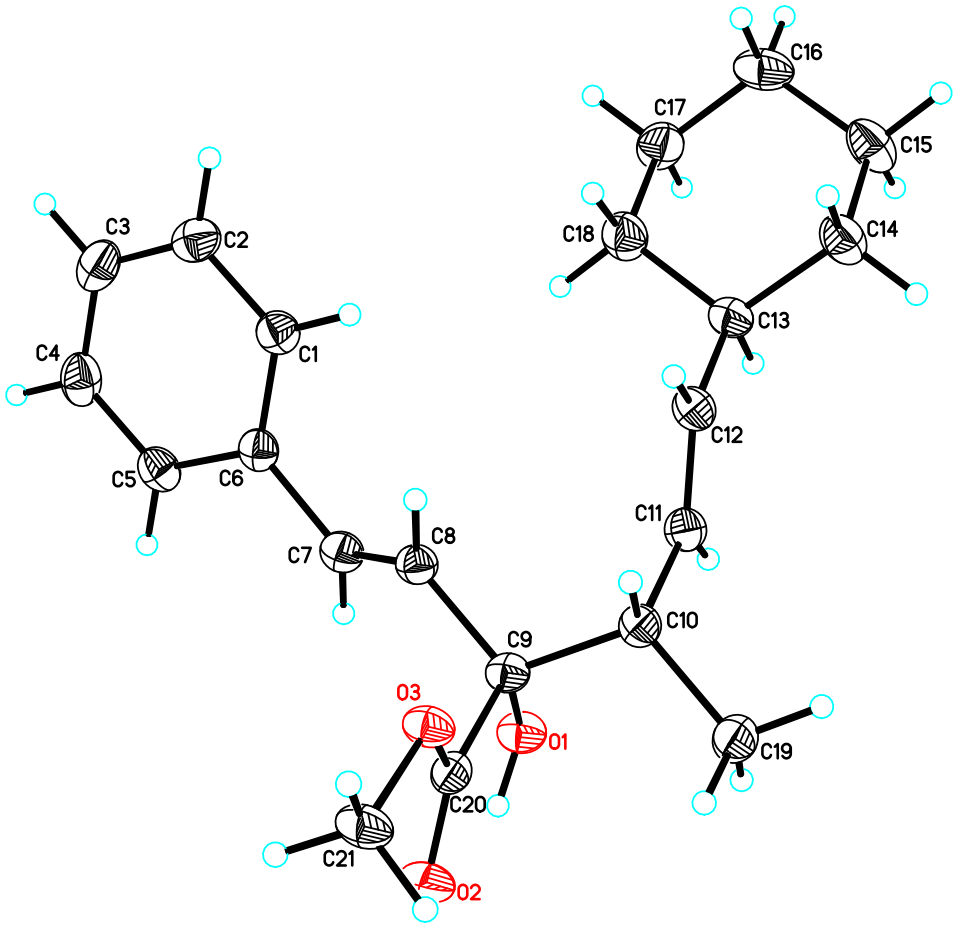


Table 1. Crystal data and structure refinement for ***epi*-7j**.

Identification code	***epi*-7j**	
Empirical formula	C21 H28 O3	
Formula weight	328.43	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 5.4496(4) Å	α= 90°.
	b = 13.7116(8) Å	β= 90°.
	c = 25.4795(15) Å	γ = 90°.

Volume	1903.9(2) $Å^3$
Z	4
Density (calculated)	1.146 Mg/m^3
Absorption coefficient	0.592 mm^{-1}
F(000)	712
Crystal size	0.41 x 0.09 x 0.07 mm^3
Theta range for data collection	3.47 to 65.51°.
Index ranges	-6<=h<=4, -16<=k<=16, -29<=l<=30
Reflections collected	16001
Independent reflections	3218 [R(int) = 0.0341]
Completeness to theta = 65.51°	99.6 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3218 / 0 / 218
Goodness-of-fit on F^2	1.176
Final R indices [I>2sigma(I)]	R1 = 0.0356, wR2 = 0.0832
R indices (all data)	R1 = 0.0527, wR2 = 0.0970
Absolute structure parameter	0.1(3)
Extinction coefficient	0.0037(4)
Largest diff. peak and hole	0.176 and -0.195 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ***epi*-7j**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	8707(4)	4366(2)	9942(1)	39(1)
C(2)	9687(5)	4390(2)	10444(1)	45(1)
C(3)	8532(5)	3911(2)	10849(1)	50(1)
C(4)	6391(5)	3402(2)	10756(1)	48(1)
C(5)	5397(4)	3381(2)	10258(1)	40(1)
C(6)	6552(4)	3852(1)	9840(1)	34(1)
C(7)	5471(4)	3795(1)	9311(1)	37(1)
C(8)	6693(4)	3878(1)	8867(1)	34(1)
C(9)	5552(4)	3836(1)	8328(1)	32(1)
C(10)	6691(4)	4619(1)	7963(1)	35(1)
C(11)	6344(4)	5612(1)	8204(1)	37(1)
C(12)	8112(4)	6139(1)	8411(1)	37(1)
C(13)	7841(4)	7110(1)	8676(1)	38(1)
C(14)	9447(5)	7891(2)	8415(1)	50(1)
C(15)	9342(5)	8861(2)	8704(1)	56(1)
C(16)	10009(5)	8744(2)	9277(1)	55(1)
C(17)	8346(5)	8008(2)	9538(1)	52(1)
C(18)	8466(5)	7028(2)	9258(1)	49(1)
C(19)	5614(4)	4556(2)	7408(1)	45(1)
C(20)	5968(4)	2821(1)	8100(1)	33(1)
C(21)	8802(4)	1616(1)	7852(1)	42(1)
O(1)	2969(3)	3980(1)	8360(1)	40(1)
O(2)	4317(3)	2279(1)	7980(1)	45(1)
O(3)	8343(3)	2590(1)	8052(1)	36(1)

Table 3. Bond lengths [Å] and angles [°] for ***epi*-7j**.

C(1)-C(2)	1.387(3)
C(1)-C(6)	1.393(3)
C(1)-H(1A)	0.9500
C(2)-C(3)	1.376(3)
C(2)-H(2A)	0.9500
C(3)-C(4)	1.380(3)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.379(3)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.395(3)
C(5)-H(5A)	0.9500
C(6)-C(7)	1.473(2)
C(7)-C(8)	1.318(3)
C(7)-H(7A)	0.9500
C(8)-C(9)	1.510(2)
C(8)-H(8A)	0.9500
C(9)-O(1)	1.424(2)
C(9)-C(20)	1.525(3)
C(9)-C(10)	1.549(3)
C(10)-C(11)	1.506(3)
C(10)-C(19)	1.533(3)
C(10)-H(10A)	1.0000
C(11)-C(12)	1.315(3)
C(11)-H(11A)	0.9500
C(12)-C(13)	1.500(3)
C(12)-H(12A)	0.9500
C(13)-C(18)	1.527(3)
C(13)-C(14)	1.534(3)
C(13)-H(13A)	1.0000
C(14)-C(15)	1.522(3)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.512(3)
C(15)-H(15A)	0.9900

C(15)-H(15B)	0.9900
C(16)-C(17)	1.511(3)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-C(18)	1.523(3)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-O(2)	1.207(2)
C(20)-O(3)	1.338(2)
C(21)-O(3)	1.451(2)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
O(1)-H(1B)	0.8400

C(2)-C(1)-C(6)	120.52(19)
C(2)-C(1)-H(1A)	119.7
C(6)-C(1)-H(1A)	119.7
C(3)-C(2)-C(1)	120.3(2)
C(3)-C(2)-H(2A)	119.9
C(1)-C(2)-H(2A)	119.9
C(2)-C(3)-C(4)	119.93(19)
C(2)-C(3)-H(3A)	120.0
C(4)-C(3)-H(3A)	120.0
C(5)-C(4)-C(3)	120.1(2)
C(5)-C(4)-H(4A)	120.0
C(3)-C(4)-H(4A)	120.0
C(4)-C(5)-C(6)	121.0(2)
C(4)-C(5)-H(5A)	119.5
C(6)-C(5)-H(5A)	119.5
C(1)-C(6)-C(5)	118.22(17)

C(1)-C(6)-C(7)	122.28(17)
C(5)-C(6)-C(7)	119.50(19)
C(8)-C(7)-C(6)	125.4(2)
C(8)-C(7)-H(7A)	117.3
C(6)-C(7)-H(7A)	117.3
C(7)-C(8)-C(9)	124.8(2)
C(7)-C(8)-H(8A)	117.6
C(9)-C(8)-H(8A)	117.6
O(1)-C(9)-C(8)	110.42(16)
O(1)-C(9)-C(20)	107.19(16)
C(8)-C(9)-C(20)	108.66(15)
O(1)-C(9)-C(10)	109.60(16)
C(8)-C(9)-C(10)	110.78(16)
C(20)-C(9)-C(10)	110.11(15)
C(11)-C(10)-C(19)	112.23(16)
C(11)-C(10)-C(9)	109.36(15)
C(19)-C(10)-C(9)	111.16(17)
C(11)-C(10)-H(10A)	108.0
C(19)-C(10)-H(10A)	108.0
C(9)-C(10)-H(10A)	108.0
C(12)-C(11)-C(10)	124.7(2)
C(12)-C(11)-H(11A)	117.7
C(10)-C(11)-H(11A)	117.7
C(11)-C(12)-C(13)	126.6(2)
C(11)-C(12)-H(12A)	116.7
C(13)-C(12)-H(12A)	116.7
C(12)-C(13)-C(18)	110.45(16)
C(12)-C(13)-C(14)	111.61(17)
C(18)-C(13)-C(14)	110.21(19)
C(12)-C(13)-H(13A)	108.2
C(18)-C(13)-H(13A)	108.2
C(14)-C(13)-H(13A)	108.2
C(15)-C(14)-C(13)	112.27(18)
C(15)-C(14)-H(14A)	109.2
C(13)-C(14)-H(14A)	109.2
C(15)-C(14)-H(14B)	109.2

C(13)-C(14)-H(14B)	109.2
H(14A)-C(14)-H(14B)	107.9
C(16)-C(15)-C(14)	111.4(2)
C(16)-C(15)-H(15A)	109.3
C(14)-C(15)-H(15A)	109.3
C(16)-C(15)-H(15B)	109.3
C(14)-C(15)-H(15B)	109.3
H(15A)-C(15)-H(15B)	108.0
C(17)-C(16)-C(15)	110.6(2)
C(17)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16A)	109.5
C(17)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	108.1
C(16)-C(17)-C(18)	110.97(19)
C(16)-C(17)-H(17A)	109.4
C(18)-C(17)-H(17A)	109.4
C(16)-C(17)-H(17B)	109.4
C(18)-C(17)-H(17B)	109.4
H(17A)-C(17)-H(17B)	108.0
C(17)-C(18)-C(13)	112.35(17)
C(17)-C(18)-H(18A)	109.1
C(13)-C(18)-H(18A)	109.1
C(17)-C(18)-H(18B)	109.1
C(13)-C(18)-H(18B)	109.1
H(18A)-C(18)-H(18B)	107.9
C(10)-C(19)-H(19A)	109.5
C(10)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(10)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
O(2)-C(20)-O(3)	123.51(18)
O(2)-C(20)-C(9)	123.23(19)
O(3)-C(20)-C(9)	113.26(17)
O(3)-C(21)-H(21A)	109.5

O(3)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
O(3)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(9)-O(1)-H(1B)	109.5
C(20)-O(3)-C(21)	114.62(16)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for ***epi*-7j**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	42(2)	37(1)	38(1)	-2(1)	2(1)	0(1)
C(2)	42(2)	44(1)	49(1)	-8(1)	-7(1)	6(1)
C(3)	64(2)	48(1)	37(1)	-3(1)	-8(1)	16(1)
C(4)	68(2)	42(1)	35(1)	3(1)	10(1)	8(1)
C(5)	45(2)	34(1)	41(1)	-2(1)	8(1)	-1(1)
C(6)	39(1)	29(1)	34(1)	-3(1)	3(1)	6(1)
C(7)	35(1)	34(1)	40(1)	-3(1)	1(1)	1(1)
C(8)	33(1)	31(1)	37(1)	-2(1)	-3(1)	1(1)
C(9)	24(1)	34(1)	38(1)	-3(1)	-2(1)	2(1)
C(10)	37(1)	32(1)	35(1)	-1(1)	-1(1)	3(1)
C(11)	38(1)	33(1)	39(1)	0(1)	-1(1)	3(1)
C(12)	38(1)	32(1)	41(1)	-1(1)	3(1)	2(1)
C(13)	38(1)	33(1)	44(1)	-3(1)	-1(1)	-2(1)
C(14)	61(2)	36(1)	52(1)	-1(1)	8(1)	-6(1)
C(15)	69(2)	35(1)	63(1)	-4(1)	16(1)	-7(1)
C(16)	48(2)	44(1)	73(2)	-21(1)	-5(1)	-1(1)
C(17)	67(2)	44(1)	44(1)	-7(1)	-5(1)	4(1)
C(18)	63(2)	39(1)	46(1)	-3(1)	2(1)	0(1)
C(19)	57(2)	40(1)	38(1)	0(1)	-4(1)	2(1)
C(20)	35(1)	36(1)	29(1)	2(1)	-2(1)	0(1)
C(21)	43(2)	31(1)	52(1)	-13(1)	-1(1)	1(1)
O(1)	30(1)	41(1)	49(1)	-6(1)	-2(1)	3(1)
O(2)	38(1)	40(1)	58(1)	-10(1)	-4(1)	-8(1)
O(3)	30(1)	31(1)	46(1)	-9(1)	-1(1)	1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for ***epi*-7j**.

	x	y	z	U(eq)
H(1A)	9510	4702	9665	47
H(2A)	11162	4739	10508	54
H(3A)	9208	3931	11192	60
H(4A)	5601	3066	11034	58
H(5A)	3903	3041	10199	48
H(7A)	3752	3688	9288	44
H(8A)	8417	3972	8888	40
H(10A)	8494	4490	7938	41
H(11A)	4734	5877	8206	44
H(12A)	9725	5878	8391	44
H(13A)	6088	7318	8645	46
H(14A)	11168	7660	8405	59
H(14B)	8894	7987	8049	59
H(15A)	10492	9326	8537	67
H(15B)	7666	9135	8676	67
H(16A)	11735	8526	9307	66
H(16B)	9856	9381	9457	66
H(17A)	6637	8252	9534	62
H(17B)	8846	7924	9909	62
H(18A)	7304	6570	9428	59
H(18B)	10138	6754	9296	59
H(19A)	6367	5056	7186	68
H(19B)	3837	4662	7423	68
H(19C)	5949	3910	7260	68
H(21A)	10575	1507	7827	63
H(21B)	8058	1548	7504	63
H(21C)	8081	1135	8092	63
H(1B)	2243	3481	8249	60

Table 6. Torsion angles [°] for ***epi*-7j**.

C(6)-C(1)-C(2)-C(3)	-0.4(3)
C(1)-C(2)-C(3)-C(4)	0.1(3)
C(2)-C(3)-C(4)-C(5)	-0.6(3)
C(3)-C(4)-C(5)-C(6)	1.4(3)
C(2)-C(1)-C(6)-C(5)	1.1(3)
C(2)-C(1)-C(6)-C(7)	-179.01(18)
C(4)-C(5)-C(6)-C(1)	-1.6(3)
C(4)-C(5)-C(6)-C(7)	178.51(19)
C(1)-C(6)-C(7)-C(8)	26.0(3)
C(5)-C(6)-C(7)-C(8)	-154.1(2)
C(6)-C(7)-C(8)-C(9)	-178.80(18)
C(7)-C(8)-C(9)-O(1)	16.9(3)
C(7)-C(8)-C(9)-C(20)	-100.4(2)
C(7)-C(8)-C(9)-C(10)	138.6(2)
O(1)-C(9)-C(10)-C(11)	64.4(2)
C(8)-C(9)-C(10)-C(11)	-57.7(2)
C(20)-C(9)-C(10)-C(11)	-177.93(17)
O(1)-C(9)-C(10)-C(19)	-60.1(2)
C(8)-C(9)-C(10)-C(19)	177.83(16)
C(20)-C(9)-C(10)-C(19)	57.6(2)
C(19)-C(10)-C(11)-C(12)	-127.8(2)
C(9)-C(10)-C(11)-C(12)	108.4(2)
C(10)-C(11)-C(12)-C(13)	-177.13(17)
C(11)-C(12)-C(13)-C(18)	113.9(2)
C(11)-C(12)-C(13)-C(14)	-123.1(2)
C(12)-C(13)-C(14)-C(15)	-175.66(19)
C(18)-C(13)-C(14)-C(15)	-52.5(3)
C(13)-C(14)-C(15)-C(16)	55.1(3)
C(14)-C(15)-C(16)-C(17)	-56.8(3)
C(15)-C(16)-C(17)-C(18)	57.2(3)
C(16)-C(17)-C(18)-C(13)	-56.2(3)
C(12)-C(13)-C(18)-C(17)	177.0(2)
C(14)-C(13)-C(18)-C(17)	53.2(3)
O(1)-C(9)-C(20)-O(2)	-0.2(2)

C(8)-C(9)-C(20)-O(2)	119.2(2)
C(10)-C(9)-C(20)-O(2)	-119.3(2)
O(1)-C(9)-C(20)-O(3)	-179.55(15)
C(8)-C(9)-C(20)-O(3)	-60.2(2)
C(10)-C(9)-C(20)-O(3)	61.3(2)
O(2)-C(20)-O(3)-C(21)	-1.4(2)
C(9)-C(20)-O(3)-C(21)	178.03(14)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for ***epi*-7j** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1B)...O(2)	0.84	2.11	2.6306(19)	119.5
O(1)-H(1B)...O(3)#1	0.84	2.50	3.2562(19)	150.0

Symmetry transformations used to generate equivalent atoms:
#1 x-1,y,z