Supplementary Information (SI) for Organic & Biomolecular Chemistry.


# Sustainable biocatalytic synthesis of substituted muconic acids

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Electronic Supplementary Information

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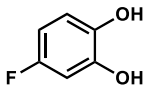
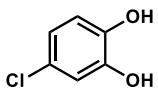
**Part I. Substrate synthesis information**

**General Information:** Chemicals and reagents were purchased from commercial suppliers (Sigma-Aldrich, Fisher Scientific, VWR, Twist Biosciences) and used without further purification unless otherwise noted. Some substrates were commercially available with the exception of **19**-**21** and **25-27**, which were synthesized using procedures outlined below. BL21 (DE3) E. coli cells were made chemically competent by $CaCl_2$ protocol and transformed with the relevant construct by heat-shock technique.[1] New Brunswick I26R, 120 V/60 Hz shaker incubators (Eppendorf) were used for cell growth. Optical density and UV-vis measurements were collected on a Cary 50 or Cary 60 UV-vis spectrophotometer using a quartz cuvette. Preparative flash chromatographic separations were performed on an Isolera One Flash Purification system (Biotage). High resolution mass spectrometry (HRMS) data were collected on an Agilent 6230 TOF LC/MS accurate-mass time-of-flight instrument (supported by NSF CHE-1429616 from Ripon College in Ripon, WI) with samples ionized by electrospray ionization (ESI). $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker AVANCE II-400 MHz spectrometer equipped with a 5 mm BBO/Z gradient broadband probe. $^{1}H$ chemical shifts are reported in ppm (δ) relative to the solvent resonance (i.e., δ $CDCl_3$ 7.26 ppm, δ acetone-$d_6$ 2.05 ppm, or δ MeOD 3.31 ppm). $^{13}C$ NMR data were acquired with $^{1}H$ decoupling and chemical shifts are reported in ppm (δ) relative to the solvent resonance (δ $CDCl_3$ 77.16 ppm, δ acetone-$d_6$ 29.84 ppm, δ MeOD 49.00 ppm). Data are reported as follows: chemical shift (multiplicity [singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), multiplet (m)], coupling constants [Hz], integration). All NMR spectra were recorded at ambient temperature (20–25 °C). IR spectra were recorded on a Thermo Scientific Nicolet iS5 FT-IR spectrometer with an iD7 attenuated total reflection (ATR) accessory.

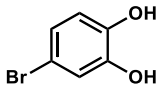



**4-fluorocatechol (19)**
The title compound was synthesized via Dakin oxidation from 5-fluorosalicylaldehyde. A 25 mL round bottom flask was equipped with a magnetic stir bar and charged with a solution of 5-fluorosalicylaldehyde (1.5 g, 10.7 mmoles) dissolved in a solvent blend containing 5.0 mL THF and 1.0 mL of deionized water. The mixture was set to stir and cooled to 0 °C in an icewater bath. A solution of NaOH (5 M, 2.33 mL, 11.7 mmoles) was produced and added slowly to the stirring flask, generating a bright yellow solution. The solution was stirred for 2 min at 0°C before dropwise addition of 30% $H_2O_2$ (1.05 mL, 13.4 mmoles). After 2 additional min, the icewater bath was removed and the reaction was allowed to warm to room temperature while stirring for 30 min. The resulting solution was then acidified to pH < 2 by HCl, extracted with diethyl ether and dried with anhydrous $Na_2SO_4$. After filtering off excess drying agent, the volume was concentrated under reduced pressure until only THF remained. The mixture was directly loaded onto a 50 g Biotage KP-Sil Snap Cartridge silica column for flash chromatographic separation using a hexanes/ethyl acetate gradient. Purification (gradient elution 10% to 50% ethyl acetate in hexanes) afforded 1.121 g (82% yield) of the title compound as an off-white solid. All spectroscopic data for the compound was consistent with literature values.[2] **$^{1}H$ NMR** (400 MHz, $CD_3OD$) δ 6.69 (dd, $J_{H-H}$ = 8.6, 5.7 Hz, 1H), 6.52 (dd, $J_{H-H}$ = 9.8, 2.6 Hz, 1H), 6.37 (td, $J_{H-H}$ = 8.6, 8.6 Hz, 1H).

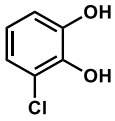



**4-chlorocatechol (20)**
The title compound was synthesized via Dakin oxidation from 5-chlorosalicylaldehyde. A 25 mL round bottom flask was equipped with a magnetic stir bar and charged with a solution of 5-chlorosalicylaldehyde (1.5 g, 9.6 mmoles) dissolved in a solvent blend containing 5.0 mL THF and 1.0 mL of deionized water. The mixture was set to stir and cooled to 0 °C in an icewater bath. A solution of NaOH (5 M, 2.12 mL, 10.6 mmoles) was produced and added slowly to the stirring flask, generating a bright yellow solution. The

solution was stirred for 2 min at 0°C before dropwise addition of 30% $H_2O_2$ (0.94 mL, 1.25 mmoles). After 2 additional min, the icewater bath was removed and the reaction was allowed to warm to room temperature while stirring for 30 min. The resulting solution was then acidified to pH < 2 by HCl, extracted with diethyl ether and dried with anhydrous $Na_2SO_4$. After filtering off excess drying agent, the volume was concentrated under reduced pressure until only THF remained. The mixture was directly loaded onto a 50 g Biotage KP-Sil Snap Cartridge silica column for flash chromatographic separation using a hexanes/ethyl acetate gradient. Purification (gradient elution 10% to 50% ethyl acetate in hexanes) afforded 995.2 mg (72% yield) of the title compound as an off-white solid. All spectroscopic data for the compound was consistent with literature values.[2] **$^1$H NMR** (400 MHz, $CD_3OD$) δ 6.75 (s, 1H), 6.70 (d, $J_{H-H}$ = 8.4 Hz, 1H), 6.63 (d, $J_{H-H}$ = 8.4 Hz, 1H).



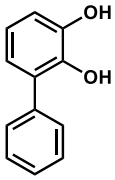

**4-bromocatechol (21)**
The title compound was synthesized via Dakin oxidation from 5-bromosalicylaldehyde. A 25 mL round bottom flask was equipped with a magnetic stir bar and charged with a solution of 5-bromosalicylaldehyde (1.5 g, 7.50 mmoles) dissolved in a solvent blend containing 5.0 mL THF and 1.0 mL of deionized water. The mixture was set to stir and cooled to 0 °C in an icewater bath. A solution of NaOH (5 M, 1.63 mL, 8.25 mmoles) was produced and added slowly to the stirring flask, generating a bright yellow solution. The solution was stirred for 2 min at 0°C before dropwise addition of 30% $H_2O_2$ (0.73 mL, 9.3 mmoles). After 2 additional min, the icewater bath was removed and the reaction was allowed to warm to room temperature while stirring for 30 min. The resulting solution was then acidified to pH < 2 by HCl, extracted with diethyl ether and dried with anhydrous $Na_2SO_4$. After filtering off excess drying agent, the volume was concentrated under reduced pressure until only THF remained. The mixture was directly loaded onto a 50 g Biotage KP-Sil Snap Cartridge silica column for flash chromatographic separation using a hexanes/ethyl acetate gradient. Purification (gradient elution 10% to 50% ethyl acetate in hexanes) afforded 810 mg (58% yield) of the title compound as an off-white solid. All spectroscopic data for the compound was consistent with literature values.[3] **$^1$H NMR** (400 MHz, $CD_3OD$) δ 6.89 (s, 1H), 6.77 (d, $J_{H-H}$ = 8.4 Hz, 1H), 6.66 (d, $J_{H-H}$ = 8.4 Hz, 1H).




**3-chlorocatechol (25)**
The title compound was synthesized via Dakin oxidation from 3-chlorosalicylaldehyde. A 25 mL round bottom flask was equipped with a magnetic stir bar and charged with a solution of 3-chlorosalicylaldehyde (1.5 g, 9.60 mmoles) dissolved in a solvent blend containing 5.0 mL THF and 1.0 mL of deionized water. The mixture was set to stir and cooled to 0 °C in an icewater bath. A solution of NaOH (5 M, 2.12 mL, 10.6 mmoles) was produced and added slowly to the stirring flask, generating a bright yellow solution. The solution was stirred for 2 min at 0°C before dropwise addition of 30% $H_2O_2$ (0.94 mL, 12.0 mmoles). After 2 additional min, the icewater bath was removed and the reaction was allowed to warm to room temperature while stirring for 30 min. The resulting solution was then acidified to pH < 2 by HCl, extracted with diethyl ether and dried with anhydrous $Na_2SO_4$. After filtering off excess drying agent, the volume was concentrated under reduced pressure until only THF remained. The mixture was directly loaded onto a 50 g Biotage KP-Sil Snap Cartridge silica column for flash chromatographic separation using a hexanes/ethyl acetate gradient. Purification (gradient elution 10% to 50% ethyl acetate in hexanes) afforded 739 mg (52% yield) of the title compound as an off-white solid. All spectroscopic data for the compound was consistent with literature values.[4] **$^1$H NMR** (400 MHz, $CD_3OD$) δ 6.76 (d, $J_{H-H}$ = 8.0 Hz ,1H), 6.70 (d, $J_{H-H}$ = 8.4 Hz, 1H), 6.62 (t, $J_{H-H}$ = 8.0 Hz, 1H).


**3-bromocatechol (26)**

The title compound was synthesized via Dakin oxidation from 3-bromosalicylaldehyde. A 25 mL round bottom flask was equipped with a magnetic stir bar and charged with a solution of 3-bromosalicylaldehyde (1.5 g, 7.46 mmoles) dissolved in a solvent blend containing 5.0 mL THF and 1.0 mL of deionized water. The mixture was set to stir and cooled to 0 °C in an icewater bath. A solution of NaOH (5 M, 1.64 mL, 8.21 mmoles) was produced and added slowly to the stirring flask, generating a bright yellow solution. The solution was stirred for 2 min at 0°C before dropwise addition of 30% $H_2O_2$ (0.73 mL, 9.33 mmoles). After 2 additional min, the icewater bath was removed and the reaction was allowed to warm to room temperature while stirring for 30 min. The resulting solution was then acidified to pH < 2 by HCl, extracted with diethyl ether and dried with anhydrous $Na_2SO_4$. After filtering off excess drying agent, the volume was concentrated under reduced pressure until only THF remained. The mixture was directly loaded onto a 50 g Biotage KP-Sil Snap Cartridge silica column for flash chromatographic separation using a hexanes/ethyl acetate gradient. Purification (gradient elution 10% to 50% ethyl acetate in hexanes) afforded 780 mg (55% yield) of the title compound as an off-white solid. All spectroscopic data for the compound was consistent with literature values.[3] **$^1$H NMR** (400 MHz, $CD_3OD$) δ 6.91 (d, $J_{H\text{-}H}$ = 8.0 Hz,1H), 6.73 (d, $J_{H\text{-}H}$ = 8.0 Hz, 1H), 6.57 (t, $J_{H\text{-}H}$ = 8.0 Hz, 1H).




**3-phenylcatechol (27)**

3-phenylcatechol was synthesized via a two-step process from 3-bromosalicylaldehyde. The first step was a Pd-catalyzed Suzuki-Miyaura coupling of 3-bromosalicylaldehyde with phenylboronic acid. A 250 mL round bottom flask was charged with 3-bromosalicylaldehyde (1.0 g, 4.97 mmol), phenylboronic acid (1.213 g, 9.95 mmol), 1 mol% $PdCl_2(PPh_3)_2$ (34.2 mg, 0.049 mmol), $K_2CO_3$ (1.375 g, 9.95 mmol), toluene (80 mL) and $dH_2O$ (20 mL). The reaction mixture was set to stir and a reflux condenser was attached. The mixture was refluxed for 18 h before cooling to room temperature. The mixture was acidified to pH 2 with 1M HCl and extracted with diethyl ether (3 x 25 mL). The majority of metal salts and impurities were removed by running the material over a silica gel plug and the remaining material (702 mg) was carried through to the second reaction. Dakin oxidation of 3-phenylsalicylaldehyde was performed to yield the title product. A 25 mL round bottom flask was equipped with a magnetic stir bar and charged with a solution of 3-phenylsalicylaldehyde (702 mg, 3.53 mmoles) dissolved in a solvent blend containing 5.0 mL THF and 1.0 mL of deionized water. The mixture was set to stir and cooled to 0 °C in an icewater bath. A solution of NaOH (5 M, 0.778 mL, 3.88 mmoles) was produced and added slowly to the stirring flask, generating a bright yellow solution. The solution was stirred for 2 min at 0°C before dropwise addition of 30% $H_2O_2$ (0.345 mL, 4.41 mmoles). After 2 additional min, the icewater bath was removed and the reaction was allowed to warm to room temperature while stirring for 30 min. The resulting solution was then acidified to pH < 2 by HCl, extracted with diethyl ether and dried with anhydrous $Na_2SO_4$. After filtering off excess drying agent, the volume was concentrated under reduced pressure until only THF remained. The mixture was directly loaded onto a 50 g Biotage KP-Sil Snap Cartridge silica column for flash chromatographic separation using a hexanes/ethyl acetate gradient. Purification (gradient elution 10% to 50% ethyl acetate in hexanes) afforded 252 mg (27% yield over 2 steps) of the title compound as an off-white solid. All spectroscopic data for the compound was consistent with literature values.[5] **$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.55 (d, $J_{H\text{-}H}$ = 7.7 Hz, 2H), 7.36 (t, $J_{H\text{-}H}$ = 7.6 Hz, 2H), 7.25 (t, $J_{H\text{-}H}$ = 7.7 Hz, 1H), 6.80 – 6.71 (m, 3H).

**Part II. Plasmid and protein information**

**Plasmid:** The gene encoding *catA* (catechol dioxygenase A from *P. putida* KT2440) was codon-optimized for overexpression in *E. coli* and synthesized by Twist Biosciences. The synthesized sequence was cloned by Twist Biosciences into individual pET-28a vectors containing the T7 expression system, kanamycin resistance, and N-terminal 6 x His-tag encoded upstream from the insert gene. No further modifications to this plasmid construct were necessary.

**Codon-Optimized *catA* Sequence (including 6 x His Tag)**

```
ATGGGCAGCAGCCATCATCATCATCATCACAGCAGCGGCCTGGTGCCGCGCGGCAGCCATATGGCTAGCATGACTGG
TGGACAGCAAATGGGTCGCGGATCCATGACGGTTAAAATCTCCCATACAGCTGATATCCAAGCTTTCTTTAATCGCG
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GCGCGGATGGACGATGGCACAGATCCTGGCGTTGTAATGTTTCTGCAAGGTCAGGTTTTTGACGCTGATGGTAAACC
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AATTTAATCTGCGACGTCGCATAATAACCGACGCCGAGGGTCGATATCGTGCACGCTCTATTGTGCCGAGTGGATAT
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ATTTTGCTTATGCAACCCGCGATGGTCTGATAGGAGAACTTCGATTTGTAGAAGATGCAGCCGCCGCACGCGACCGT
GGCGTTCAGGGAGAGCGTTTTGCTGAGCTCTCATTTGACTTCAGACTGCAGGGCGCTAAATCGCCGGATGCTGAAGC
ACGCTCTCATAGACCCCGGGCGTTGCAGGAGGGCTAA
```

**CatA Protein Sequence (including 6 x His Tag)**

```
MGSSHHHHHHSSGLVPRGSHMASMTGGQQMGRGSMTVKISHTADIQAFFNRVAGLDHAEGNPRFKQIILRVLQDTAR
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ARMDDGTDPGVVMFLQGQVFDADGKPLAGATVDLWHANTQGTYSYFDSTQSEFNLRRRIITDAEGRYRARSIVPSGY
GCDPQGPTQECLDLLGRHGQRPAHVHFFISAPGHRHLTTQINFAGDKYLWDDFAYATRDGLIGELRFVEDAAAARDR
GVQGERFAELSFDFRLQGAKSPDAEARSHRPRALQEG
```

**Expression of CatA (*P. putida* KT2440)**

The gene construct (pET-28a) containing codon-optimized gene for CatA (*P. putida* KT2440) was ordered from Twist Biosciences and used as received. Chemically competent BL21 (DE3) *E. coli* cells were transformed with 0.5 ng of plasmid DNA using the heat-shock technique. After 45 min of recovery in Luria-Burtani (LB) media at 37 °C, cells were plated onto LB plates with 50 µg/mL kanamycin (Kan) and incubated overnight. Single colonies were used to inoculate 5 mL LB + 50 µg/mL Kan, which were grown overnight at 37 °C, 200 rpm. Expression cultures, typically 1 L of Terrific Broth (TB) + 50 µg/mL Kan (TB-Kan), were inoculated from these starter cultures and shaken (200 rpm) at 37 °C. After 3 hours ($OD_{600}$ = ~0.6-0.8), the expression cultures were chilled on ice. After 30 min on ice, protein expression was induced with 0.5 mM IPTG and 0.2 mg/mL ferric ammonium citrate. The cultures were expressed for 16 hours at 20 °C with shaking at 200 rpm. Cells were then harvested by centrifugation at 4,000×*g* at 4 °C for 10 min. Cell pellets were resuspended and washed with a 50 mM Tris buffer (pH 8.0) to remove any remaining free iron from the expression medium. Cell pellets were frozen and stored at -80 °C if cells were used for protein purification.

**Purification of CatA**

To purify CatA, cell pellets were thawed on ice and then resuspended in lysis buffer (50 mM Tris buffer (pH = 8.0), 50 mM NaCl and 10 mM imidazole. A volume of 4 mL of lysis buffer per gram of wet cell pellet was used (250 mg pellet/mL buffer). The resulting solution was gently rocked at 0°C for 30 min, then transferred to a pre-chilled 250 mL metal beaker inside of an ice bath. Cell lysis was performed by sonic dismembration at 30% power for 5 min for a 5 sec on, 15 sec off cycle. The supernatant was then harvested by

centrifugation at 4,000×*g* at 4 °C for 30 min. Pre-rinsed Ni/NTA beads (GoldBio) were added to the supernatant and incubated on ice for 45 min prior to purification by Ni-affinity chromatography with a gravity column. The column was washed with 5 column volumes of 20 mM imidazole, 50 mM NaCl, 50 mM Tris buffer (pH = 8.0). Protein was eluted with 250 mM imidazole, 50 mM NaCl, 50 mM Tris buffer, pH 8.0. Elution of the desired protein product was monitored by the disappearance of its brownish purple color (resulting from the release of the dioxygenase) from the column. The protein product was desalted by PD-10 column by buffer exchange with storage buffer (50 mM Tris pH 8.0, 50 mM NaCl). Purified enzyme was flash frozen in pellet form by pipetting enzyme dropwise into a crystallization dish filled with liquid nitrogen. The enzyme was transferred to a plastic conical tube and stored at -80 °C until further use. The concentration of protein was determined by measuring the absorbance of the protein in 50 mM Tris pH 8.0 at 280 nm using the Beer-Lambert equation. The molar absorptivity of the protein was calculated using Expasy. Generally, this procedure yielded 75 – 100 mg protein per L culture. Protein purity was analyzed by sodium dodecyl sulfate-polyacrylamide (SDS-PAGE) gel electrophoresis using 8-12% polyacrylamide gels (Figure S1).

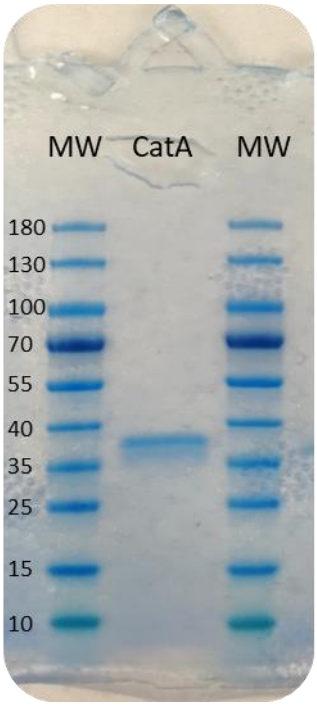



Figure S1: Denaturing gel electrophoresis (SDS-PAGE) of purified CatA. MW = molecular weight ladder (measured in KDa). Expected CatA size: 37.79 KDa

**Preparation of CatA clarified lysates**

To prepare clarified lysates of CatA, cell pellets were thawed on ice and then resuspended in lysis buffer (50 mM Tris buffer (pH = 8.4) and 50 mM NaCl. A volume of 4 mL of lysis buffer per gram of wet cell pellet was used (250 mg pellet/mL buffer). The resulting solution was transferred to a pre-chilled 250 mL metal beaker inside of an ice bath. Cell lysis was performed by sonic dismembration at 30% power for 5-7 min for a 5 sec on, 15 sec off cycle. Following cell lysis, the resulting solution was centrifuged at 4,000×*g* at 4 °C for 40 min to clarify the lysate of any cellular debris. The supernatant was flash frozen in pellet form by pipetting enzyme dropwise into a crystallization dish filled with liquid nitrogen. The enzyme was transferred to a plastic conical tube and stored at -80 °C until further use.

**Part III. Biocatalytic reaction procedures and products**

**Stock solutions:** Stock solutions of catechol substrates were prepared fresh in deionized water or MeOH. Solutions were not kept for more than 3-4 hours to avoid uncatalyzed substrate oxidation.

***In vitro* analytical-scale reactions:** For reaction condition optimization, each reaction (100 µL total volume) contained 20 mM buffer (Tris or carbonate) pH 6.8-10.0 (2.0 µL of a 1 M solution), 5 mM substrate (5.0 µL, 100 mM), 10 µM CatA (5.88 µL, 170 µM), and deionized water to a final volume of 100 µL. After optimization of reaction pH conditions, Tris pH 8.4 was used in all further reactions. Reactions were carried out at 30 °C for 4 h and quenched by the addition of 2 volumes of methanol. Precipitated biomolecules were pelleted by centrifugation (17,000 x g, 10 min). The supernatant was analyzed by UV-vis spectrophotometry and reaction yield obtained by the method described below in this section.

**Whole cell analytical-scale reactions:** For analytical scale reactions using wet whole cells, a 1.6 mL centrifuge tube was charged with 50 mM Tris buffer pH 8.4 (50 µL of 1M stock), 5 mM substrate (50 µL of 100 mM stock), 20 mg/mL whole cells harboring CatA (0.5-4 mg/mL final cell concentration), and deionized water to a final volume of 1.0 mL. Reactions were carried out at 30 °C for 4 h and quenched by the addition of 2 volumes of methanol. Precipitated biomolecules were pelleted by centrifugation (17,000 x g, 10 min). The supernatant was analyzed by UV-vis spectrophotometry and reaction yield obtained by the method described below in this section.

**Spectrophotometric quantification of percent yield:** To quantify the muconic acid product yield in CatA-catalyzed reactions, a 100 µL reaction aliquot was quenched by the addition of 200 µL of methanol and centrifugation at 17,000 x g for 10 min. The resulting supernatant was diluted so that the absorbance at 260 nm would not exceed the linear range for the spectrophotometer (typically a 50 x to 100 x dilution factor). The dilution mixture for this process was 20 mM Tris pH 8.4 to maintain the protonation state (and prevent isomerization) of the muconate product. Using a quartz cuvette, the spectrophotometer was baselined against the dilution mixture before the measurement of $A_{260}$ for the reaction mixture. Product concentration was calculated using the Beer-Lambert equation and multiplied by the dilution factor to determine the product yield. Literature or calculated values for muconate product molar absorptivity were used to determine product concentration. Calculated values for molar absorptivity were determined using the method established by Dorn and Knackmuss.[6]

**General procedure for whole cell preparative scale biocatalytic reactions:**

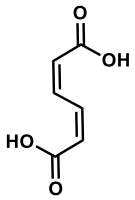
A 1 or 2 L (scale-dependent) Fernbach flask was charged with deionized water and Tris buffer at a final concentration of 50 mM (pH 8.4). The corresponding catechol, dissolved in deionized water (200 mM stock, 5 mM final concentration) was added to the solution. The reaction was initiated upon the addition of wet *E. coli* cells harboring expressed CatA (20 mg/mL final concentration, 2% w/v). The reaction vessel was placed in a shaking incubator (gentle shaking) at 30 °C for 16 h. Product formation was monitored by dilution and evaluation of absorbance at 260 nm, with quantification as described above for analytical scale reactions. After reaction completion, the reaction mixture was quenched with an equivalent volume of acetone and centrifuged (4,000 rpm, 15 min) to remove cellular debris. The supernatant was transferred to a clean beaker, acidified with 2N $H_2SO_4$ and extracted with ethyl acetate (3 x 30 mL). The remaining cell debris was resuspended in acidic water (pH < 2.0, $H_2SO_4$) and extracted three times with a 1:1 mixture of hexanes and ethyl acetate. The organic fraction was filtered to remove particulate matter and combined with organic layers from the supernatant extraction. The organic layer was dried over anhydrous $Na_2SO_4$ and the volume was reduced by rotary evaporation. Products were purified by repeat trituration with ice cold acetonitrile, as the products have limited solubility in these solvents. The remaining solid was dried under vacuum and analyzed directly without the need for further purification.

**General procedure for preparative scale biocatalytic reactions with clarified cell lysates:**

A 1 or 2 L (scale-dependent) Fernbach flask was charged with deionized water and Tris buffer at a final concentration of 50 mM (pH 8.4). The corresponding catechol, dissolved in deionized water (200 mM stock, 5 mM final concentration) was added to the solution. The reaction was initiated upon the addition of clarified

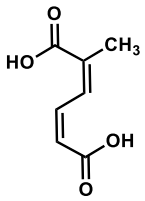
cell lysates harboring overexpressed CatA (8-12% v/v). The reaction vessel was placed in a shaking incubator (gentle shaking) at 30 °C for 16 h. Product formation was monitored by dilution and evaluation of absorbance at 260 nm, with quantification as described above for analytical scale reactions. After reaction completion, the reaction mixture was quenched with an equivalent volume of acetone and centrifuged (4,000 rpm, 15 min) to remove denatured protein materials. The supernatant was transferred to a clean beaker, acidified with 2N $H_2SO_4$ and extracted with ethyl acetate (3 x 30 mL). The organic layer was dried over anhydrous $Na_2SO_4$ and the volume was reduced by rotary evaporation. Products were purified by repeat trituration with ice cold acetonitrile, as the products have limited solubility in these solvents. The remaining solid was dried under vacuum and analyzed directly without the need for further purification.

**Biocatalytic reaction products**




**(2*Z*,4*Z*)-hexa-2,4-dienedioic acid (*cis*, *cis*, muconic acid, 10)**

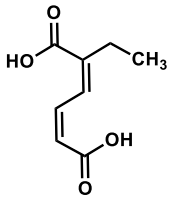
The compound was synthesized and purified using the general procedure for preparative scale biocatalytic reactions with clarified CatA lysate (10% v/v lysate). A 1000 mL Fernbach flask was charged with $dH_2O$ (149.9 mL) and Tris buffer pH 8.4 (9.1 mL of 1.0 M stock, final concentration 50 mM). Catechol (100 mg, 0.91 mmol) was dissolved in 4.54 mL of $dH_2O$ to produce a 200 mM solution that was then added to the Fernbach flask (final concentration: 5 mM). To initiate the reaction, clarified *E. coli* lysate harboring CatA was added to the reaction flask (18.2 mL, 10% v/v). The reaction was incubated at 30 °C for 16 h with gentle mixing (60 rpm shaking). After 16 h, the reaction mixture was quenched with an equivalent volume of acetone and centrifuged (4,000 rpm, 15 min) to remove denatured proteins. Supernatant was transferred to a clean beaker, acidified with 2N $H_2SO_4$ (pH < 2) and extracted with ethyl acetate (3 x 20 mL). The organic layer was dried over anhydrous $Na_2SO_4$ and the volume was reduced by rotary evaporation. The product was purified by repeat trituration with acetonitrile. The remaining white solid was dried under vacuum and analyzed directly without further purification. All spectroscopic data for the compound was consistent with literature values.[7] White powder, 125.4 mg, 97% yield. **$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.84 (d, $J_{H\text{-}H}$ = 8.4 Hz, 2H), 5.97 (d, $J_{H\text{-}H}$ = 8.5 Hz, 2H); **HR-ESI-MS**: m/z calcd for $C_6H_6O_4$ $[M+Na]^+$: 165.0158, found: 165.0163.




**(2*Z*,4*Z*)-2-methylhexa-2,4-dienedioic acid (28)**

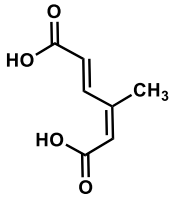
The compound was synthesized and purified using the general procedure for preparative scale biocatalytic reactions with clarified CatA lysate (10% v/v lysate). A 1000 mL Fernbach flask was charged with $dH_2O$ (132.9 mL) and Tris buffer pH 8.4 (8.05 mL of 1.0 M stock, final concentration 50 mM). 3-methylcatechol (100 mg, 0.81 mmol) was dissolved in 4.03 mL of $dH_2O$ to produce a 200 mM solution that was then added to the Fernbach flask (final concentration: 5 mM). To initiate the reaction, clarified *E. coli* lysate harboring CatA was added to the reaction flask (16.1 mL, 10% v/v). The reaction was incubated at 30 °C for 16 h with

gentle mixing (60 rpm shaking). After 16 h, the reaction mixture was quenched with an equivalent volume of acetone and centrifuged (4,000 rpm, 15 min) to remove denatured proteins. Supernatant was transferred to a clean beaker, acidified with 2N $H_2SO_4$ (pH < 2) and extracted with ethyl acetate (3 x 20 mL). The organic layer was dried over anhydrous $Na_2SO_4$ and the volume was reduced by rotary evaporation. The product was purified by repeat trituration with acetonitrile. The remaining white solid was dried under vacuum and analyzed directly without further purification. All spectroscopic data for the compound was consistent with literature values.[8] White powder, 114 mg, 91% yield. **$^1$H NMR** (400 MHz, acetone-d6) δ 7.74 (d, $J_{H\text{-}H}$ = 11.6 Hz, 1H), 7.60 (t, $J_{H\text{-}H}$ = 11.6 Hz, 1H), 5.86 (d, $J_{H\text{-}H}$ = 11.6 Hz, 1H), 2.06 (s, 3H); **$^{13}$C{$^1$H} NMR** (101 MHz, acetone-d6) δ 168.48, 167.24, 140.32, 136.19, 132.90, 121.84, 21.59; **HR-ESI-MS**: m/z calcd for $C_7H_8O_4$ $[M+Na]^+$: 179.0315, found: 179.0326.




**(2*Z*,4*Z*)-2-ethylhexa-2,4-dienedioic acid (29)**

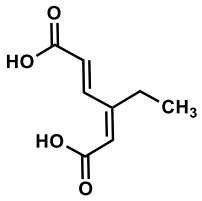
The compound was synthesized and purified using the general procedure for preparative scale biocatalytic reactions with clarified CatA lysate (12% v/v lysate). A 1000 mL Fernbach flask was charged with $dH_2O$ (116.4 mL) and Tris buffer pH 8.4 (7.24 mL of 1.0 M stock, final concentration 50 mM). 3-ethylcatechol (100 mg, 0.72 mmol) was dissolved in 3.62 mL of $dH_2O$ to produce a 200 mM solution that was then added to the Fernbach flask (final concentration: 5 mM). To initiate the reaction, clarified *E. coli* lysate harboring CatA was added to the reaction flask (17.4 mL, 12% v/v). The reaction was incubated at 30 °C for 16 h with gentle mixing (60 rpm shaking). After 16 h, the reaction mixture was quenched with an equivalent volume of acetone and centrifuged (4,000 rpm, 15 min) to remove denatured proteins. Supernatant was transferred to a clean beaker, acidified with 2N $H_2SO_4$ (pH < 2) and extracted with ethyl acetate (3 x 20 mL). The organic layer was dried over anhydrous $Na_2SO_4$ and the volume was reduced by rotary evaporation. The product was purified by repeat trituration with acetonitrile. White powder, 99.4 mg, 73% yield. **$^1$H NMR** (400 MHz, $CD_3OD$) δ 7.63 (d, $J_{HH}$ = 11.6 Hz, 1H), 7.42 (t, $J_{HH}$ = 11.6 Hz, 1H), 5.80 (d, $J_{HH}$ = 11.5 Hz, 1H), 2.41 (q, $J_{HH}$ = 7.5 Hz, 2H), 1.11 (t, $J_{HH}$ = 7.4 Hz, 3H); **$^{13}$C{$^1$H} NMR** (101 MHz, $CD_3OD$) δ 170.59, 169.28, 143.53, 140.78, 130.66, 121.97, 39.06, 13.42; **IR** (thin film)**:** 3093, 2979, 2921, 2589, 2238, 2083, 1672, 1625, 1579, 1275, 1251, 1226, 1043, 926, 836, 751, 707, 613, 539 $cm^{-1}$. **HR-ESI-MS**: m/z calcd for $C_8H_{10}O_4$ $[M+Na]^+$: 193.0471, found: 193.0473. **mp:** 150-151 °C.




**(2*Z*,4*E*)-3-methylhexa-2,4-dienedioic acid (15)**

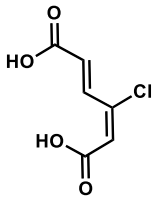
The compound was synthesized and purified using the general procedure for preparative scale biocatalytic reactions with clarified CatA lysate (10% v/v lysate). A 1000 mL Fernbach flask was charged with $dH_2O$ (132.9 mL) and Tris buffer pH 8.4 (8.05 mL of 1.0 M stock, final concentration 50 mM). 4-methylcatechol (100 mg, 0.81 mmol) was dissolved in 4.03 mL of $dH_2O$ to produce a 200 mM solution that was then added to the Fernbach flask (final concentration: 5 mM). To initiate the reaction, clarified *E. coli* lysate harboring CatA was added to the reaction flask (16.1 mL, 10% v/v). The reaction was incubated at 30 °C for 16 h with gentle mixing (60 rpm shaking). After 16 h, the reaction mixture was quenched with an equivalent volume of acetone and centrifuged (4,000 rpm, 15 min) to remove denatured proteins. Supernatant was transferred to a clean beaker, acidified with 2N $H_2SO_4$ (pH < 2) and extracted with ethyl acetate (3 x 20 mL). The organic layer was dried over anhydrous $Na_2SO_4$ and the volume was reduced by rotary evaporation. The product was purified by repeat trituration with acetonitrile. The remaining white solid was dried under

vacuum and analyzed directly without further purification. All spectroscopic data for the compound was consistent with literature values.[9] White powder, 113 mg, 90% yield. **$^{1}$H NMR** (400 MHz, $CD_3OD$) δ 8.62 (d, $J_{H\text{-}H}$ = 16.0 Hz, 1H), 6.19 (d, $J_{H\text{-}H}$ = 16.0 Hz, 1H), 5.99 (s, 1H), 2.06 (s, 3H); **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CD_3OD$ ) δ 169.98, 168.65, 148.59, 141.80, 125.40, 125.11, 20.52.; **HR-ESI-MS**: m/z calcd for $C_7H_8O_4$ $[M+Na]^+$: 179.0315, found: 179.0321.




**(2*Z*,4*E*)-3-ethylhexa-2,4-dienedioic acid (30)**

The compound was synthesized and purified using the general procedure for preparative scale biocatalytic reactions with clarified CatA lysate (10% v/v lysate). A 1000 mL Fernbach flask was charged with $dH_2O$ (119.4 mL) and Tris buffer pH 8.4 (7.24 mL of 1.0 M stock, final concentration 50 mM). 4-ethylcatechol (100 mg, 0.72 mmol) was dissolved in 3.62 mL of $dH_2O$ to produce a 200 mM solution that was then added to the Fernbach flask (final concentration: 5 mM). To initiate the reaction, clarified *E. coli* lysate harboring CatA was added to the reaction flask (14.5 mL, 10% v/v). The reaction was incubated at 30 °C for 16 h with gentle mixing (60 rpm shaking). After 16 h, the reaction mixture was quenched with an equivalent volume of acetone and centrifuged (4,000 rpm, 15 min) to remove denatured proteins. Supernatant was transferred to a clean beaker, acidified with 2N $H_2SO_4$ (pH < 2) and extracted with ethyl acetate (3 x 20 mL). The organic layer was dried over anhydrous $Na_2SO_4$ and the volume was reduced by rotary evaporation. The product was purified by repeat trituration with acetonitrile. All spectroscopic data for the compound was consistent with literature values.[8] White powder, 95.4 mg, 77% yield. **$^{1}$H NMR** (400 MHz, $CD_3OD$) δ 8.56 (d, $J_{H\text{-}H}$ = 16.4 Hz, 1H), 6.21 (d, $J_{H\text{-}H}$ = 16.2 Hz, 1H), 5.97 (s, 1H), 2.45 (q, $J_{H\text{-}H}$ = 7.5 Hz, 2H), 1.15 (t, $J_{H\text{-}H}$ = 7.6 Hz, 3H).; **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CD_3OD$) δ 170.04, 168.93, 154.20, 141.23, 124.59, 123.39, 27.53, 13.51; **HR-ESI-MS**: m/z calcd for $C_8H_{10}O_4$ $[M+Na]^+$: 193.0471, found: 193.0483.




**(2*E*,4*E*)-3-chlorohexa-2,4-dienedioic acid (31)**

The compound was synthesized and purified using the general procedure for preparative scale biocatalytic reactions with clarified CatA lysate (10% v/v lysate). A 1000 mL Fernbach flask was charged with $dH_2O$ (154.7 mL) and Tris buffer pH 8.4 (9.38 mL of 1.0 M stock, final concentration 50 mM). 4-chlorocatechol (135.5 mg, 0.94 mmol) was dissolved in 4.69 mL of $dH_2O$ to produce a 200 mM solution that was then added to the Fernbach flask (final concentration: 5 mM). To initiate the reaction, clarified *E. coli* lysate harboring CatA was added to the reaction flask (18.75 mL, 10% v/v). The reaction was incubated at 30 °C for 16 h with gentle mixing (60 rpm shaking). After 16 h, the reaction mixture was quenched with an equivalent volume of acetone and centrifuged (4,000 rpm, 15 min) to remove denatured proteins. Supernatant was transferred to a clean beaker, acidified with 2N $H_2SO_4$ (pH < 2) and extracted with ethyl acetate (3 x 20 mL). The organic layer was dried over anhydrous $Na_2SO_4$ and the volume was reduced by rotary evaporation. The product was purified by repeat trituration with acetonitrile. All spectroscopic data for the compound was consistent with literature values.[9] Off-white powder, 25.9 mg, 16% yield. **$^{1}$H NMR** (400 MHz, $CD_3OD$) δ 8.59 (d, $J_{H\text{-}H}$ = 15.2 Hz, 1H), 6.50 (d, $J_{H\text{-}H}$ = 15.2 Hz, 1H), 6.40 (s, 1H); **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CD_3OD$) δ 168.70, 166.17, 145.56, 137.43, 129.31, 126.29; **HR-ESI-MS**: m/z calcd for $C_6H_5ClO_4$ $[M+Na]^+$: 198.9769, found: 198.9773.

Figure S2: Gram-scale production of *cis, cis*-muconic acid (**10**) using CatA cell lysate.

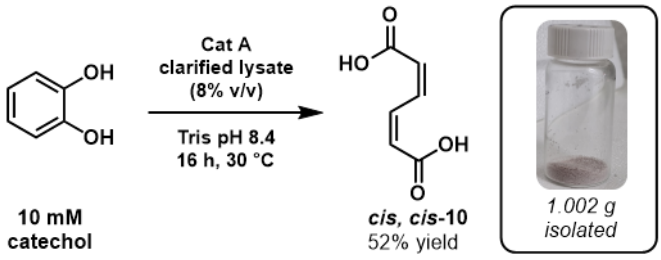
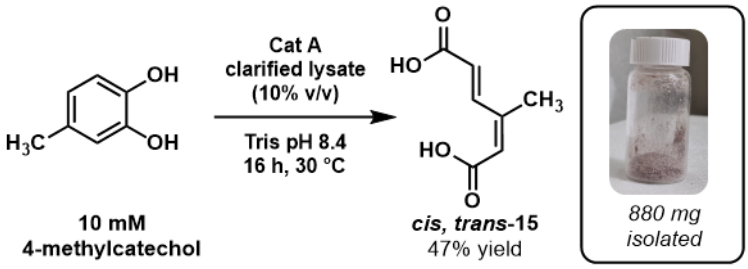


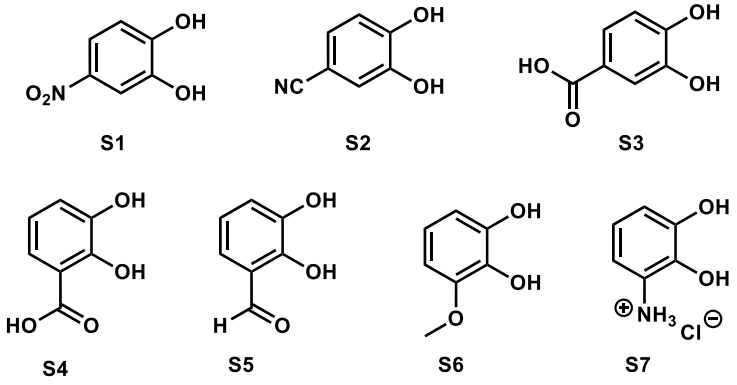

Figure S3: Milligram-scale production of *cis, trans*-3-methylmuconic acid (**15**) using CatA cell lysate.




**Procedure for larger scale reactions with CatA clarified lysates:**

The reactions shown in Figure S2 and Figure S3 were performed in a manner analogous to the "General procedure for preparative scale biocatalytic reactions with clarified cell lysates" featured above, except that the final concentration of catechol used in each reaction was increased to 10 mM. All other final concentrations and conditions were kept identical to smaller scale reactions (50 mM Tris pH 8.4, 8-10% v/v CatA lysate).

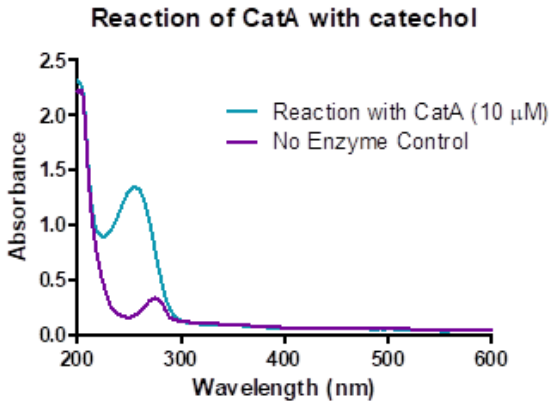
Figure S4: Compounds that were not substrates for CatA:



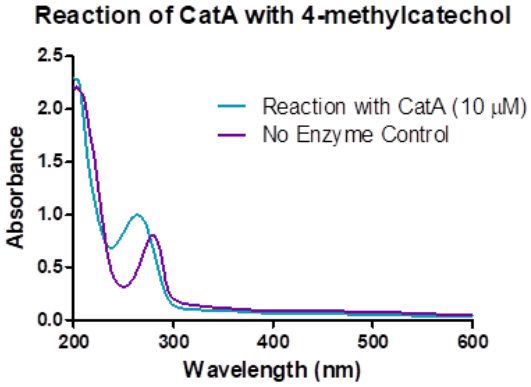
**Part IV. UV-vis spectroscopy of ring-cleaved products**

**General Procedure:** Data were collected between 600 and 200 nm on a Varian Cary 50 or Cary 60 spectrophotometer with a semi-micro (1 mL) quartz cuvette at 25 °C. Reactions were quenched by the addition of 2 volumes of methanol, followed by centrifugation at 17,000 x g. Reactions were then diluted 50-fold with a solution of 20 mM Tris pH 8.4 to maintain consistent pH. Controls with no enzyme added were performed, using $dH_2O$ used to replace the volume of CatA. The Beer-Lambert law was used to calculate the concentration of muconic acid based on the published or calculated extinction coefficients of ring-cleaved products.[6]

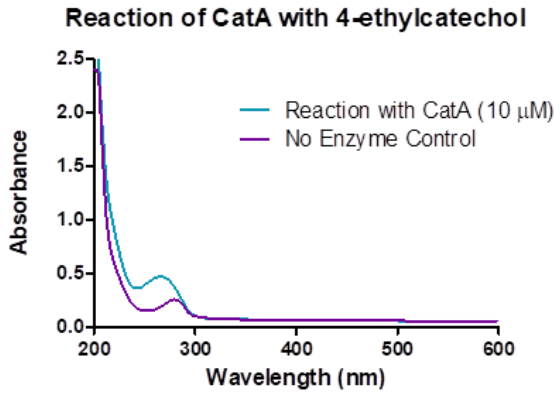
**Supplementary Figure S5.** UV-vis spectrum following reaction of CatA with catechol at 5 mM substrate loading. Overlay with control reaction without addition of CatA.



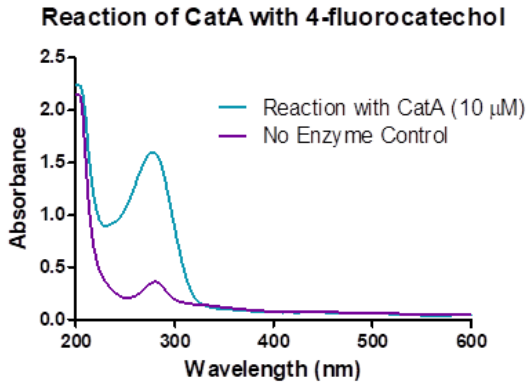

**Supplementary Figure S6.** UV-vis spectrum following reaction of CatA with 4-methylcatechol at 5 mM substrate loading. Overlay with control reaction without addition of CatA.



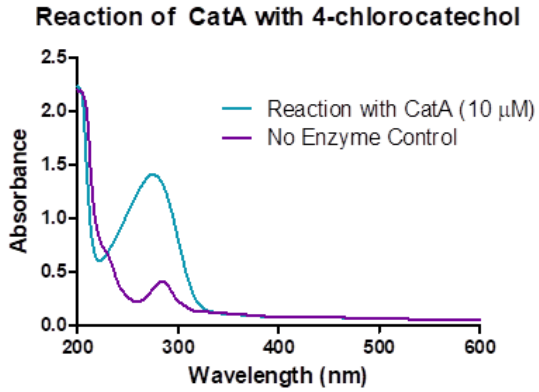
**Supplementary Figure S7.** UV-vis spectrum following reaction of CatA with 4-ethylcatechol at 5 mM substrate loading. Overlay with control reaction without addition of CatA.



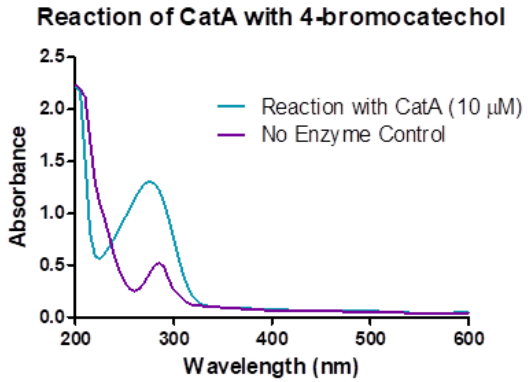

**Supplementary Figure S8.** UV-vis spectrum following reaction of CatA with 4-fluorocatechol at 5 mM substrate loading. Overlay with control reaction without addition of CatA.



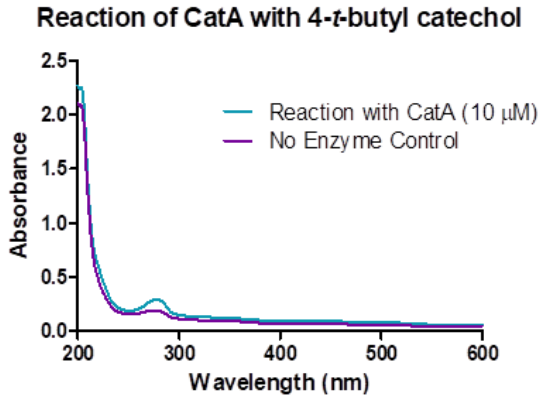

**Supplementary Figure S9.** UV-vis spectrum following reaction of CatA with 4-chlorocatechol at 5 mM substrate loading. Overlay with control reaction without addition of CatA.



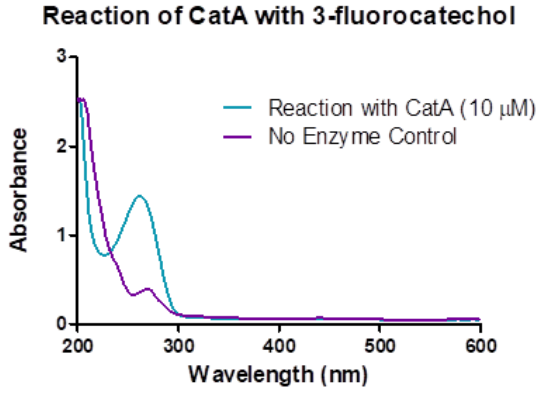
**Supplementary Figure S10.** UV-vis spectrum following reaction of CatA with 4-bromocatechol at 5 mM substrate loading. Overlay with control reaction without addition of CatA.



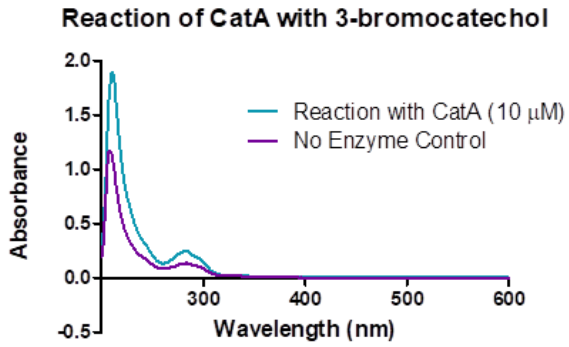

**Supplementary Figure S11.** UV-vis spectrum following reaction of CatA with 4-*t*-butylcatechol at 5 mM substrate loading. Overlay with control reaction without addition of CatA.



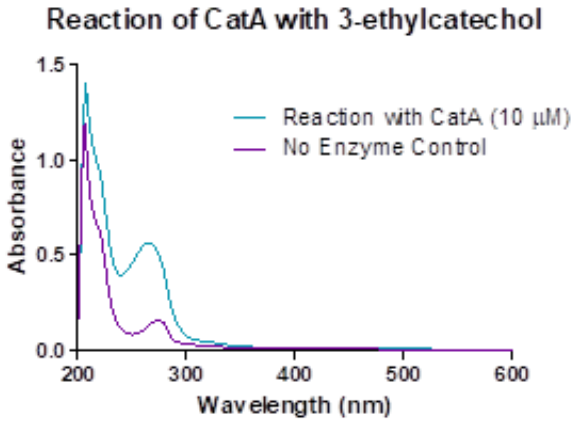

**Supplementary Figure S12.** UV-vis spectrum following reaction of CatA with 3-fluorocatechol at 5 mM substrate loading. Overlay with control reaction without addition of CatA.



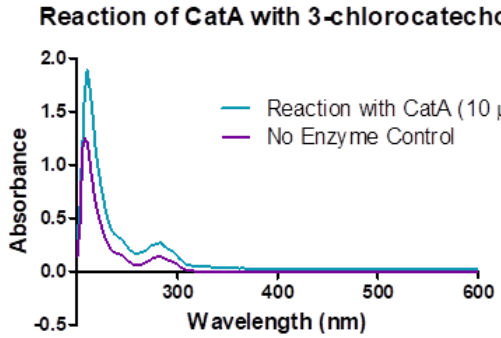
**Supplementary Figure S13.** UV-vis spectrum following reaction of CatA with 3-bromocatechol at 5 mM substrate loading. Overlay with control reaction without addition of CatA.




**Supplementary Figure S14.** UV-vis spectrum following reaction of CatA with 3-ethylcatechol at 5 mM substrate loading. Overlay with control reaction without addition of CatA.

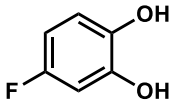



**Supplementary Figure S15.** UV-vis spectrum following reaction of CatA with 3-ethylcatechol at 5 mM substrate loading. Overlay with control reaction without addition of CatA.



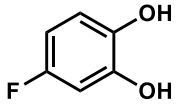
**Part V. NMR spectra of synthesized substrates**

400 MHz, $CD_3OD$

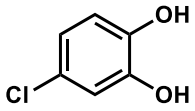


400 MHz, $CD_3OD$

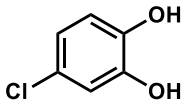
Zoom view



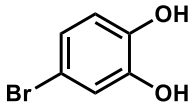
400 MHz, $CD_3OD$



400 MHz, $CD_3OD$
Zoom view

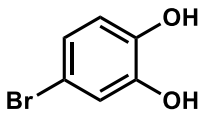


400 MHz, $CD_3OD$

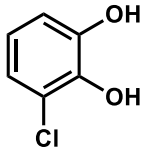


400 MHz, $CD_3OD$

Zoom view

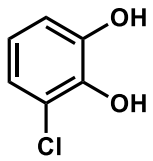


400 MHz, $CD_3OD$

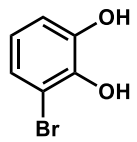


400 MHz, $CD_3OD$

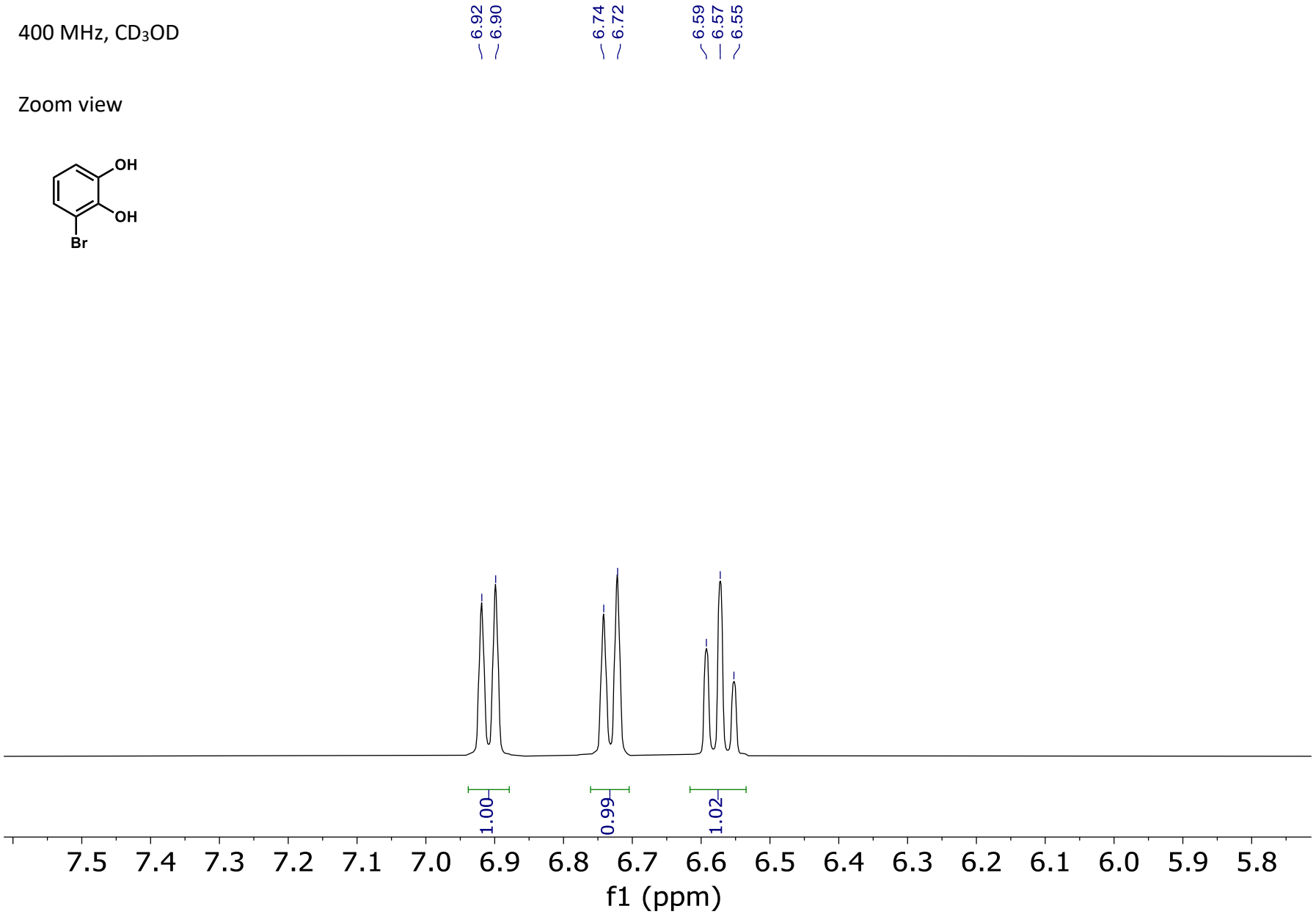
Zoom view



400 MHz, $CD_3OD$

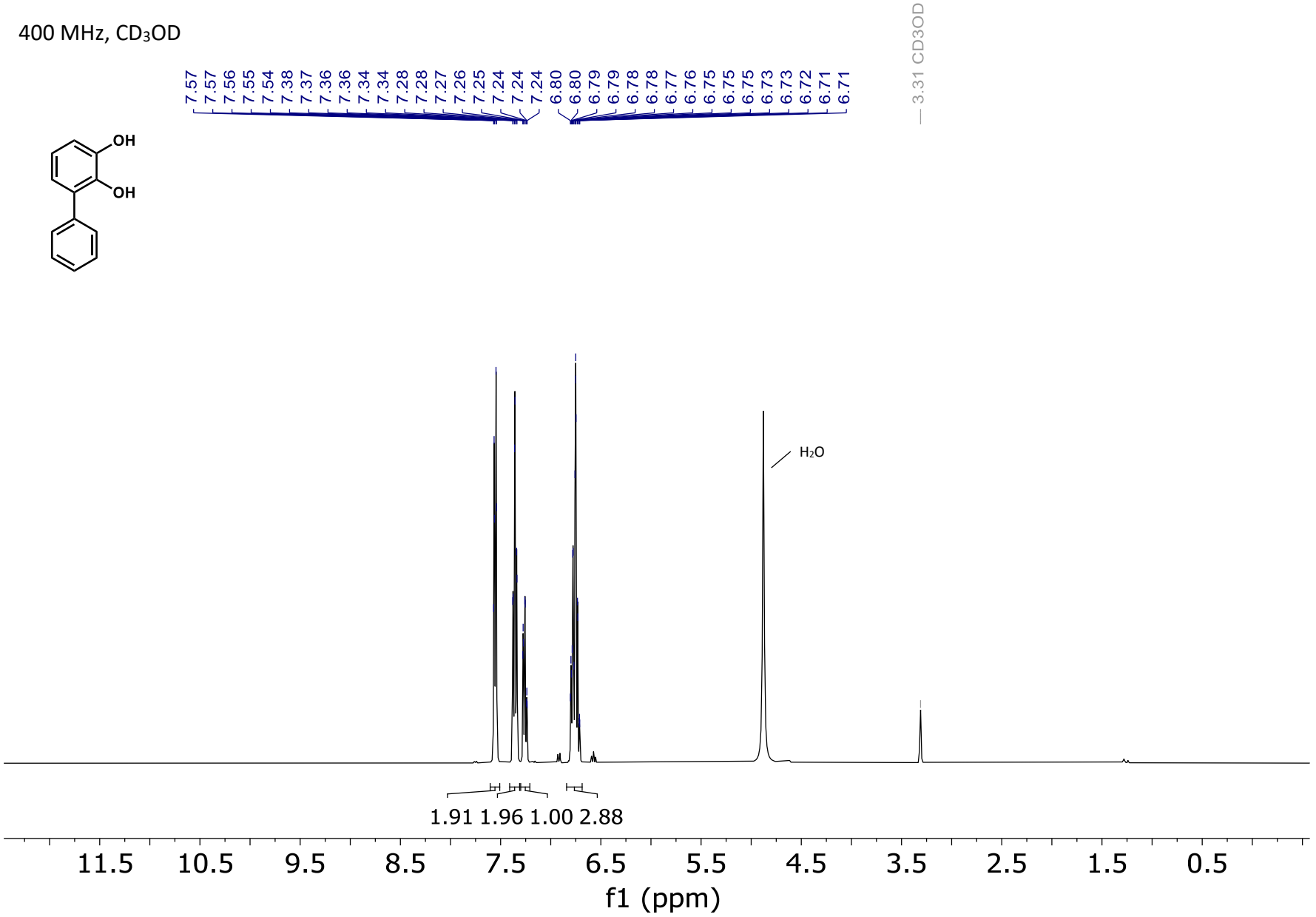


400 MHz, $CD_3OD$



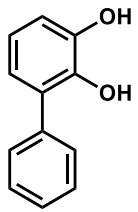

Zoom view

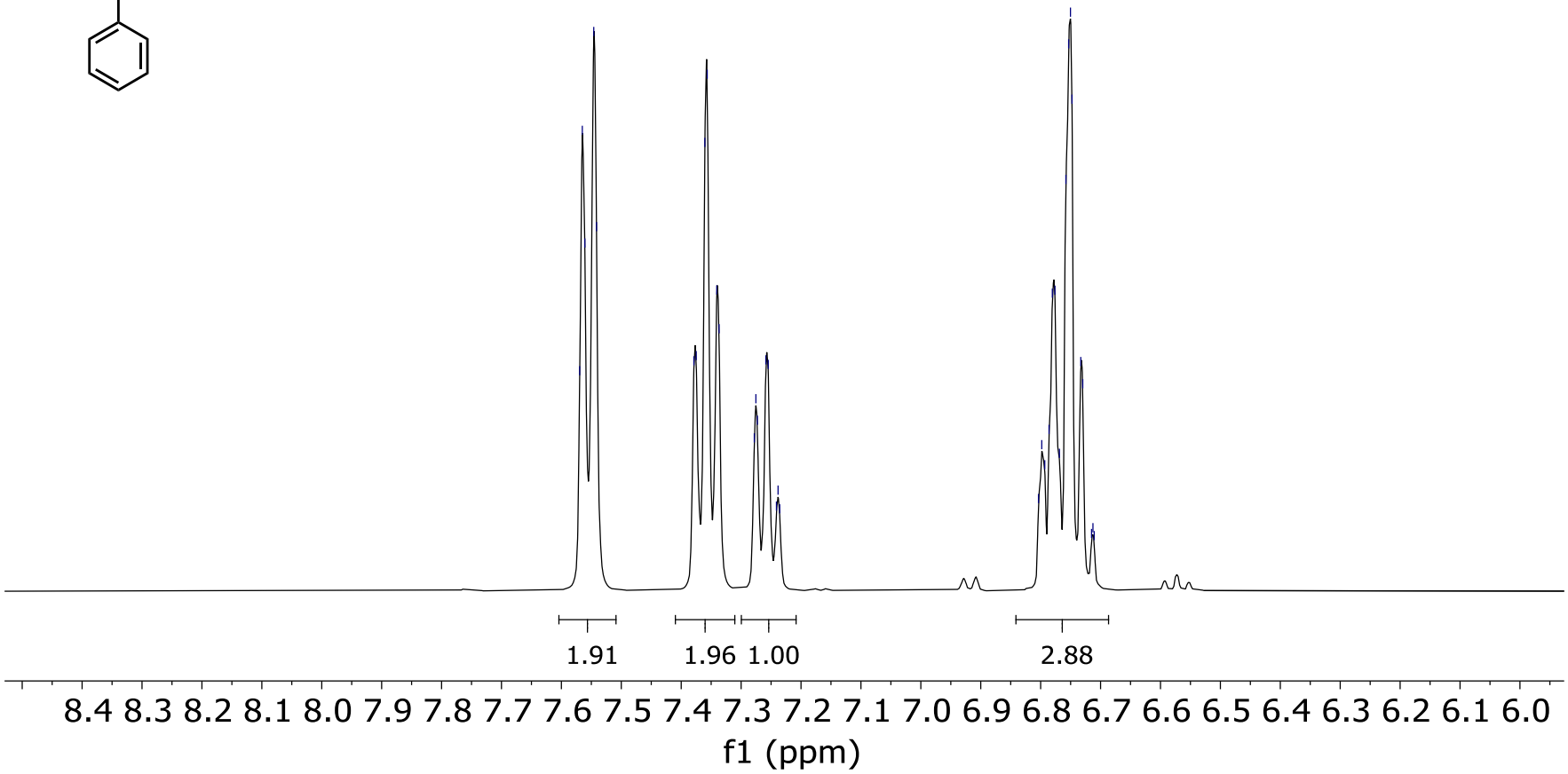
400 MHz, $CD_3OD$



400 MHz, $CD_3OD$

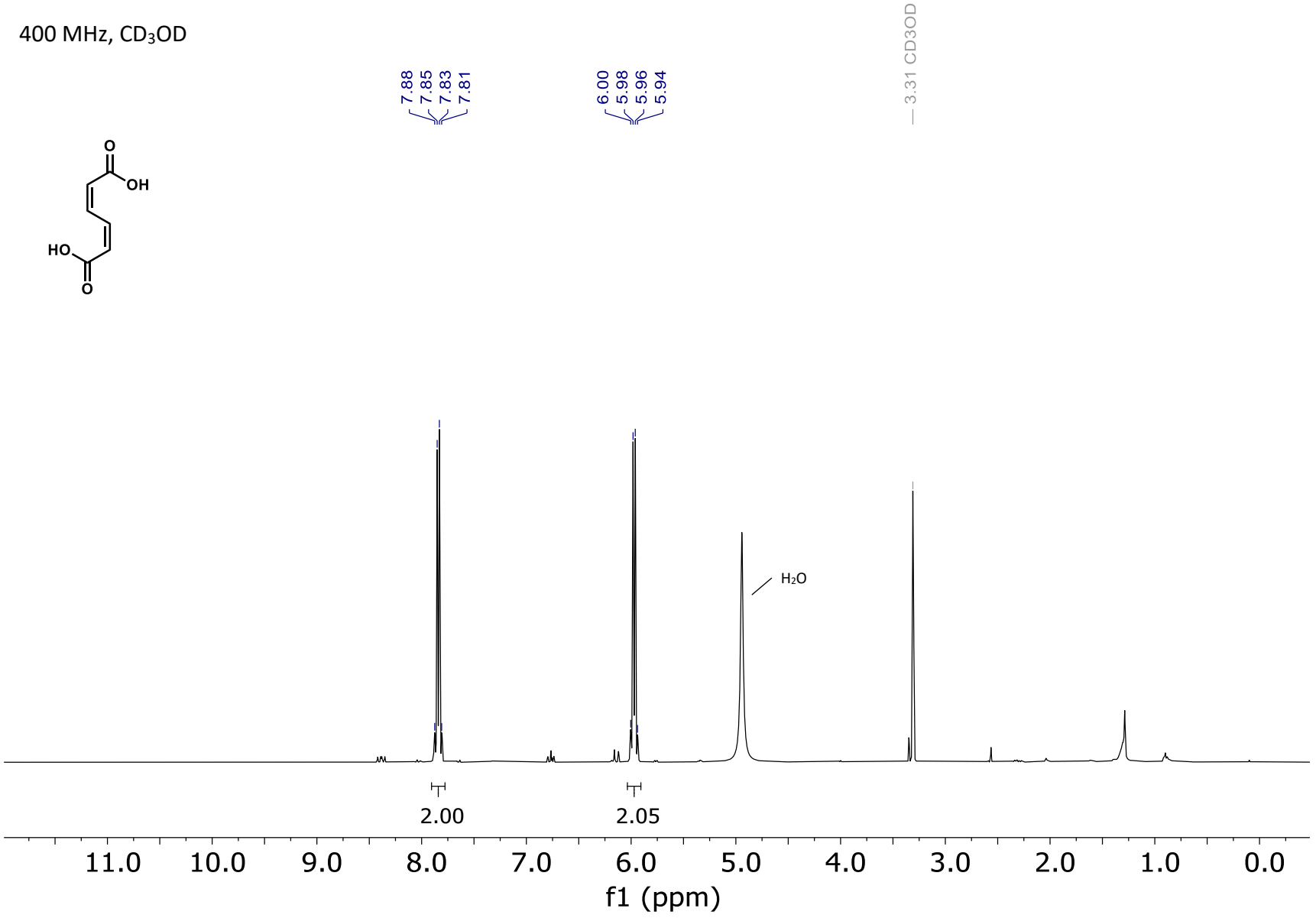
Zoom view

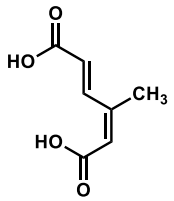



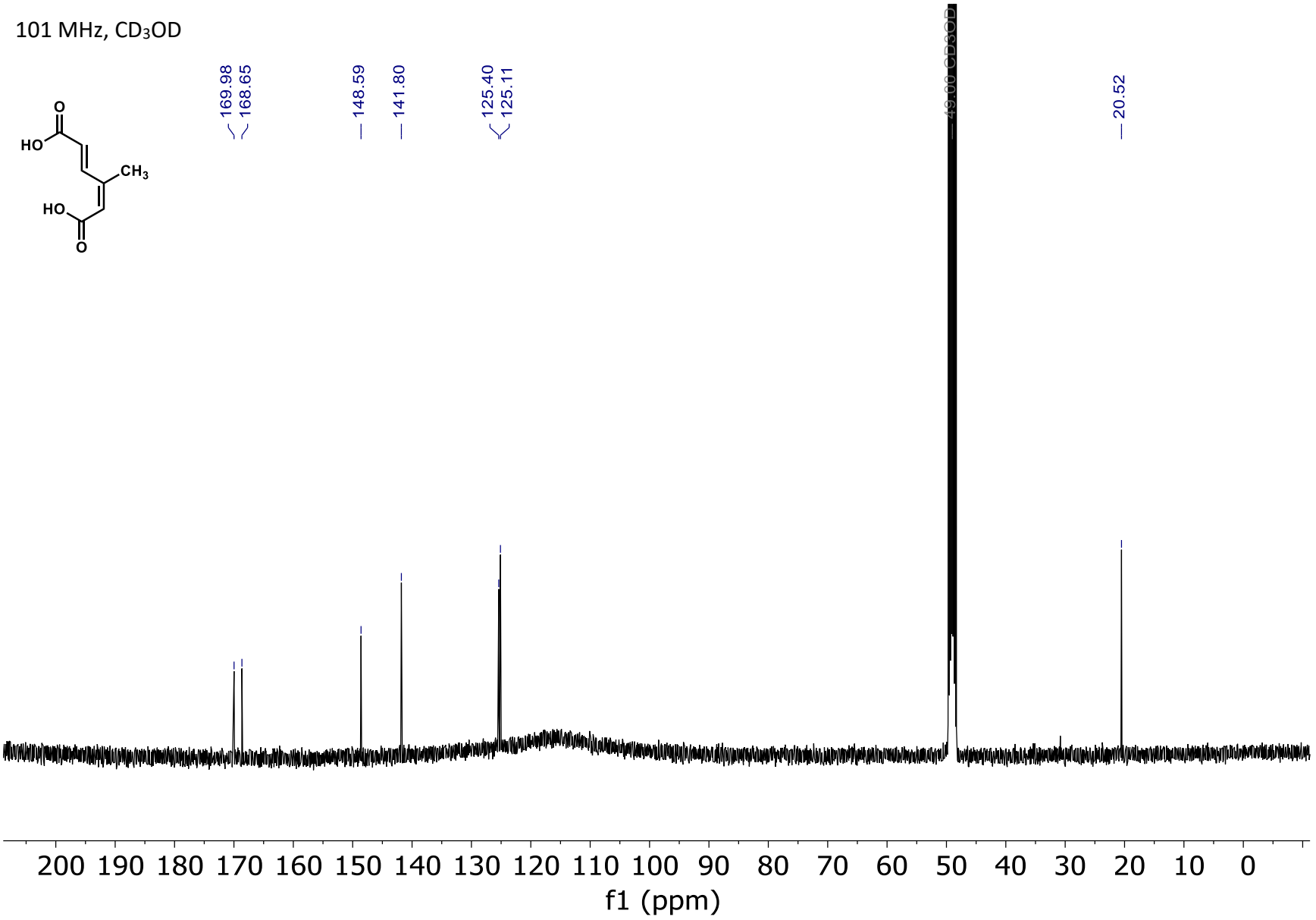
**Part VI. NMR spectra of biocatalytic reaction products**

400 MHz, $CD_3OD$

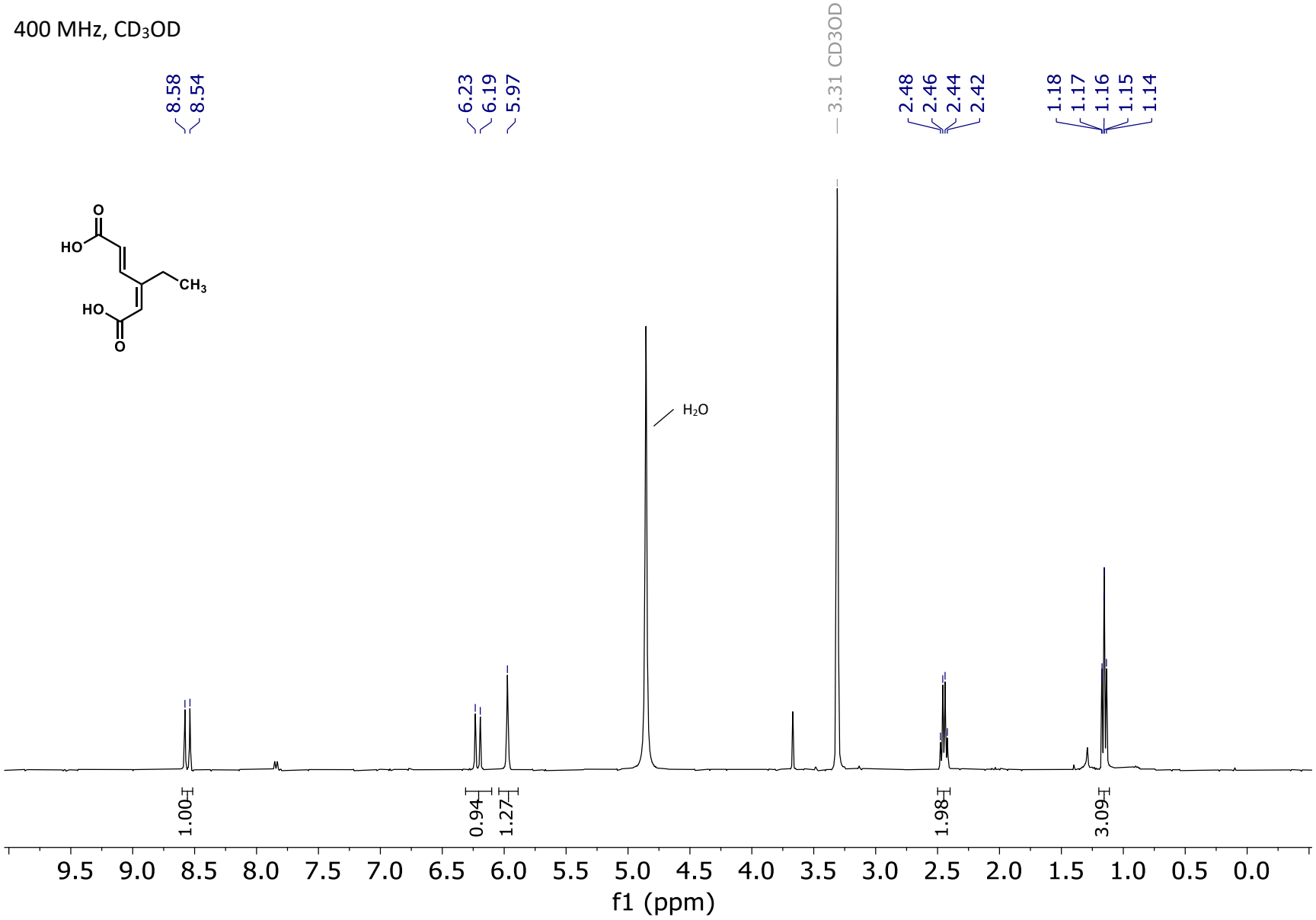


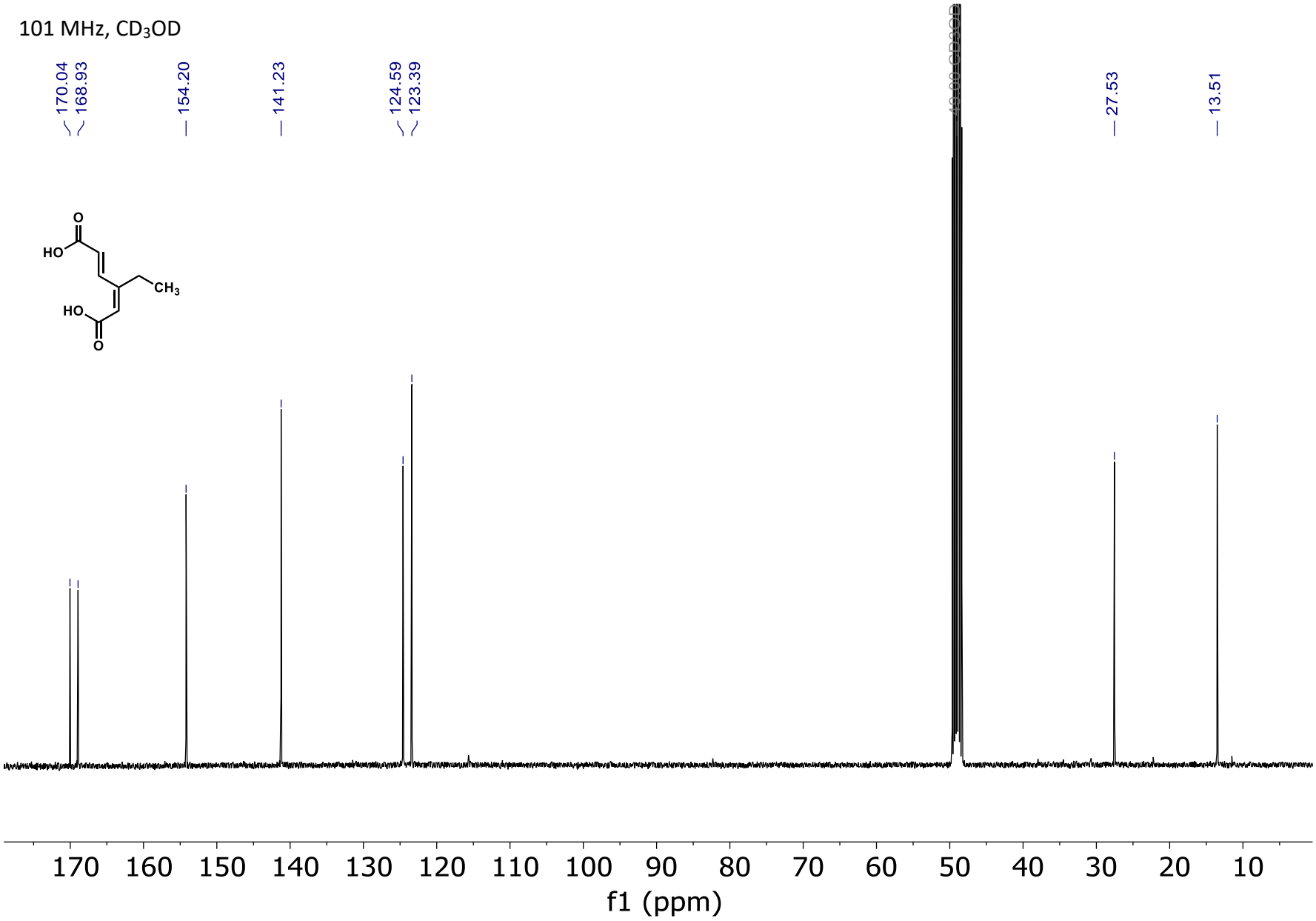
400 MHz, $CD_3OD$



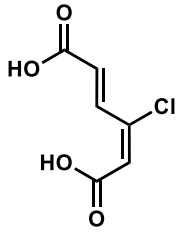

101 MHz, CD3OD
169.98
168.65
148.59
141.80
125.40
125.11
49.00 CD3OD
20.52
HO
O
CH3
HO
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

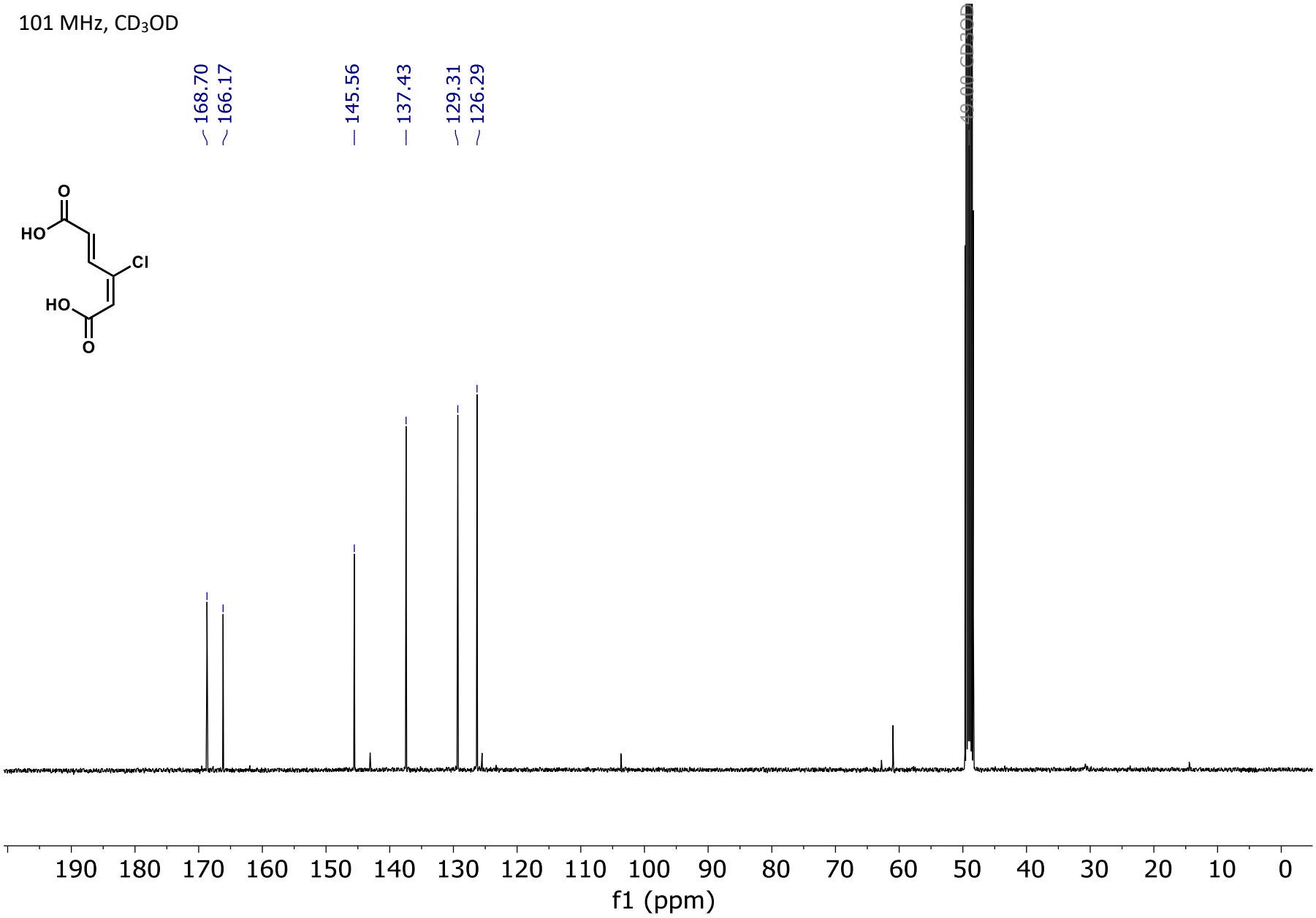
400 MHz, $CD_3OD$



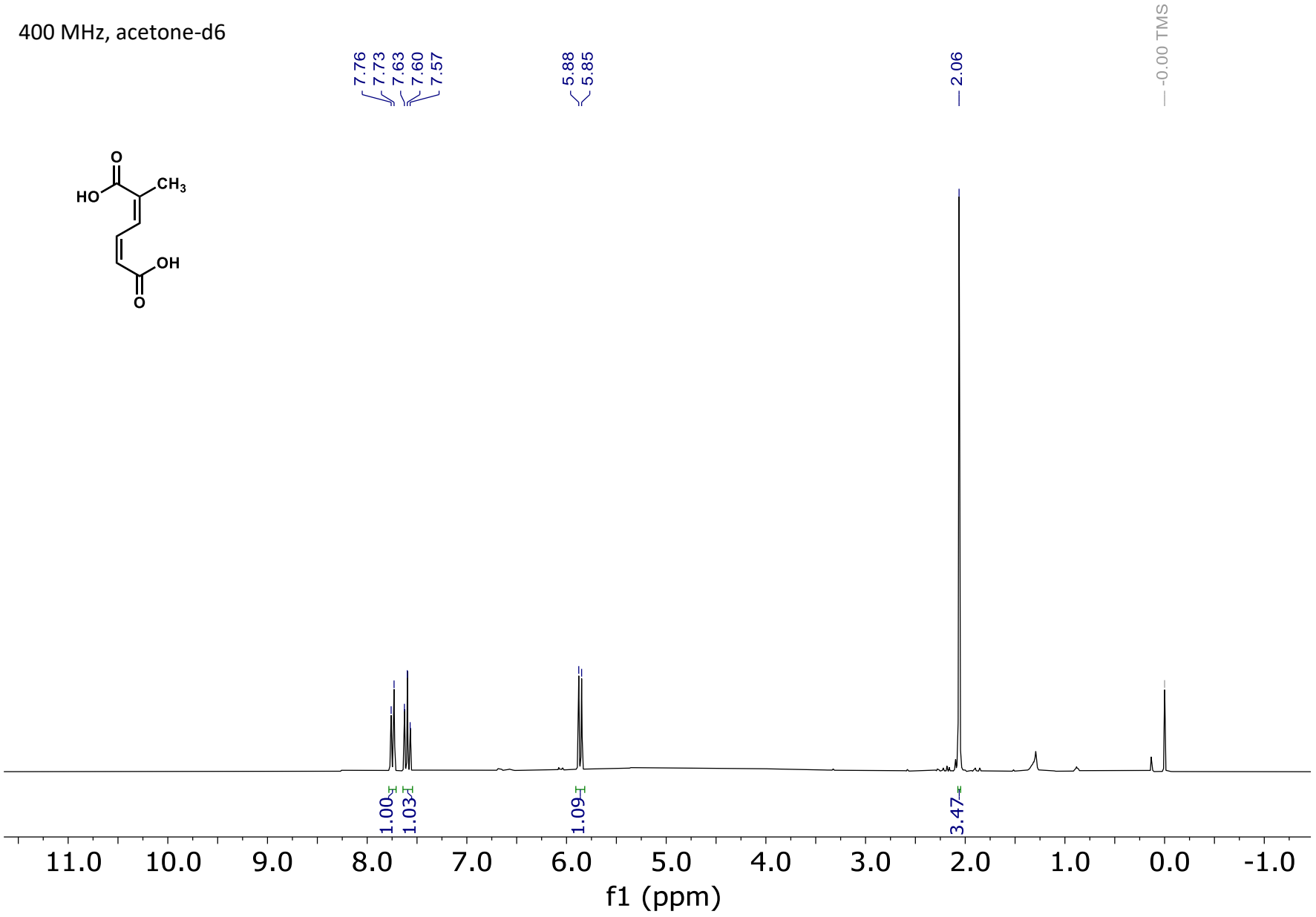

101 MHz, CD3OD
170.04
168.93
154.20
141.23
124.59
123.39
49.00 CD3OD
27.53
13.51
HO
O
CH3
HO
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

400 MHz, $CD_3OD$

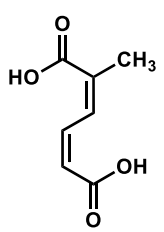



101 MHz, CD3OD
168.70
166.17
145.56
137.43
129.31
126.29
HO
O
Cl
HO
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

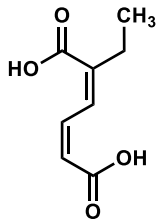
400 MHz, acetone-d6



101 MHz, acetone-d6

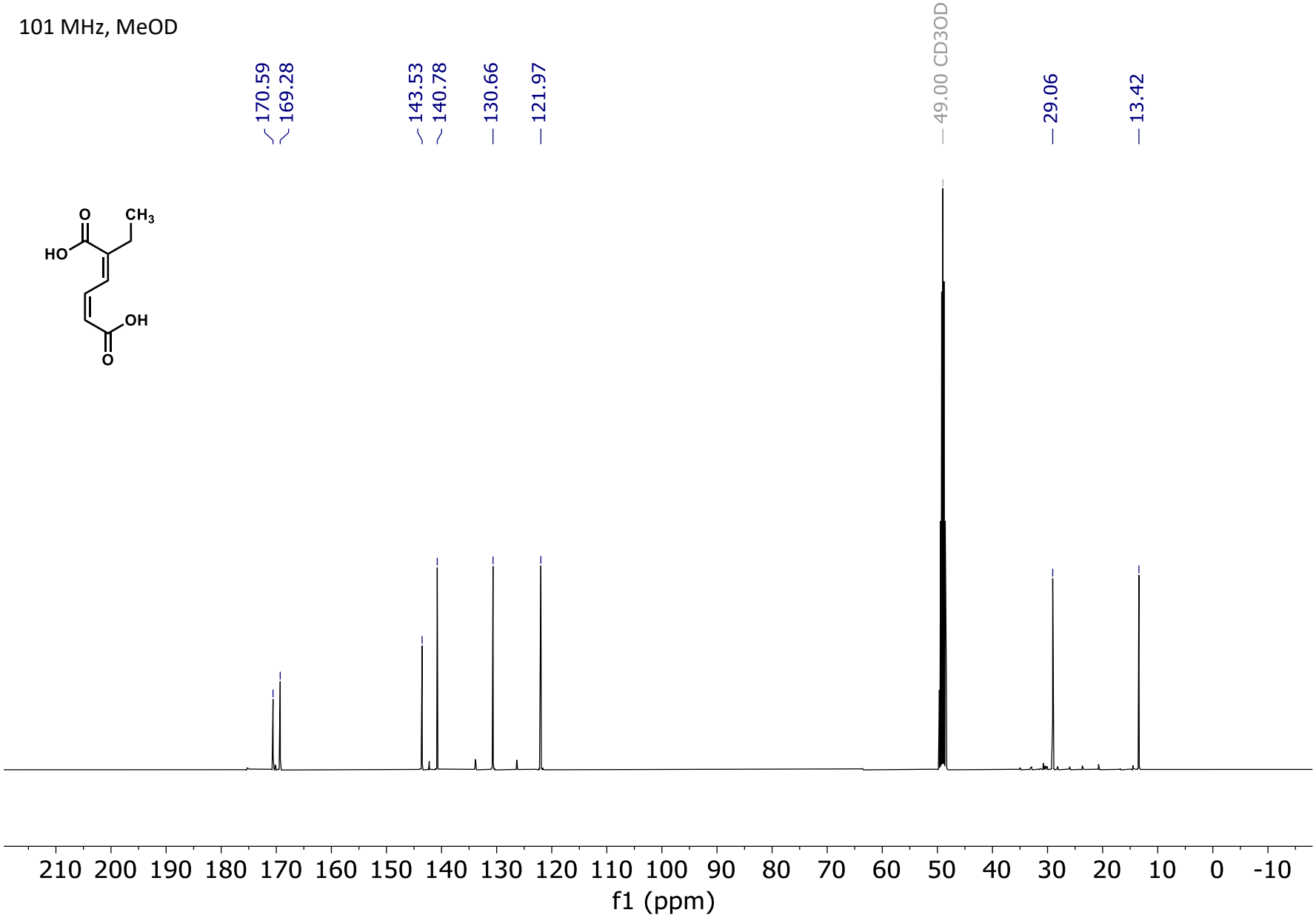


400 MHz, MeOD

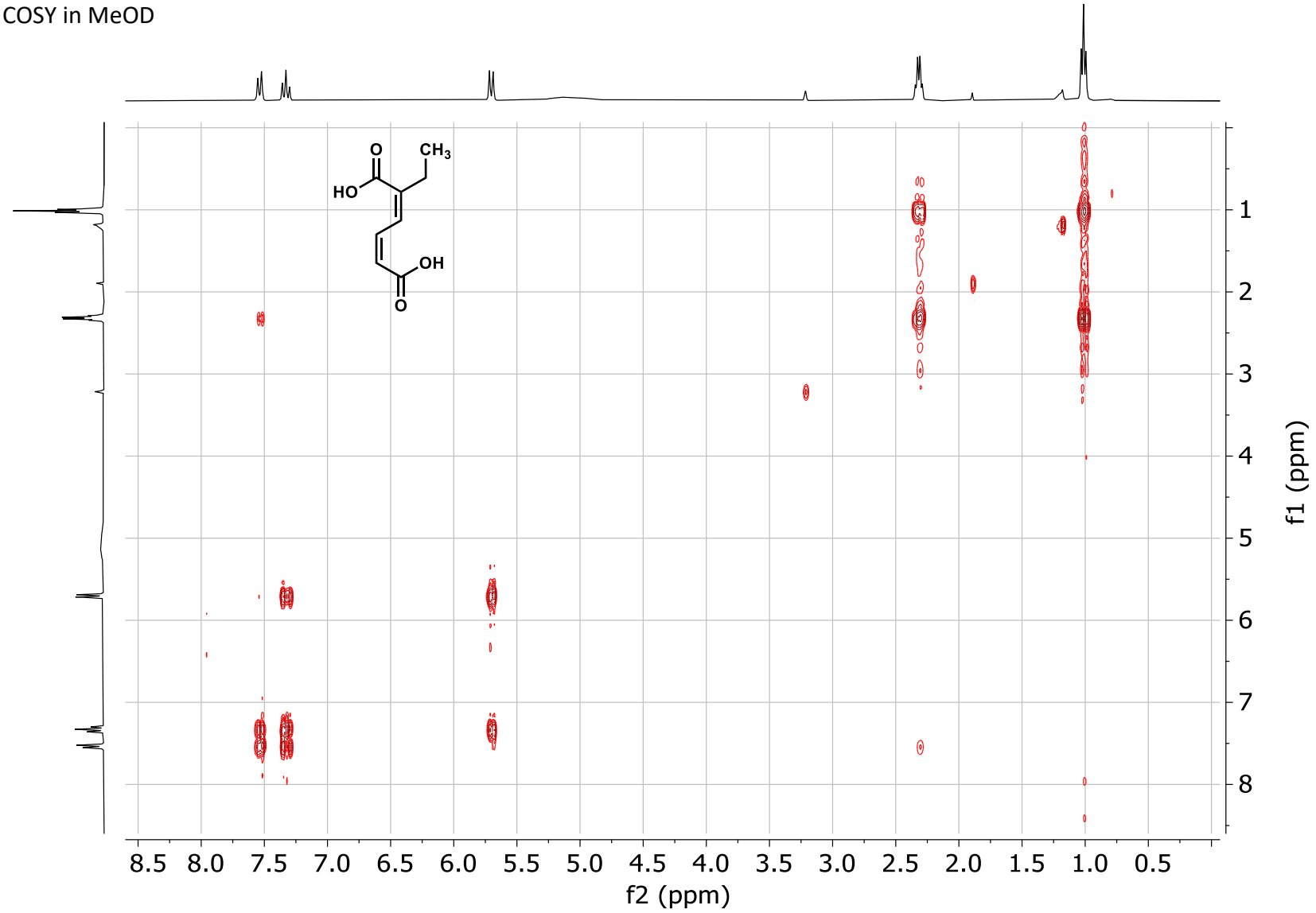

O
CH3
HO
OH
O


7.65
7.62
7.45
7.42
7.39
5.81
5.78
3.31 CD3OD
2.44
2.42
2.40
2.38
1.13
1.11
1.09
H2O
1.00
0.98
0.99
2.09
3.01
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

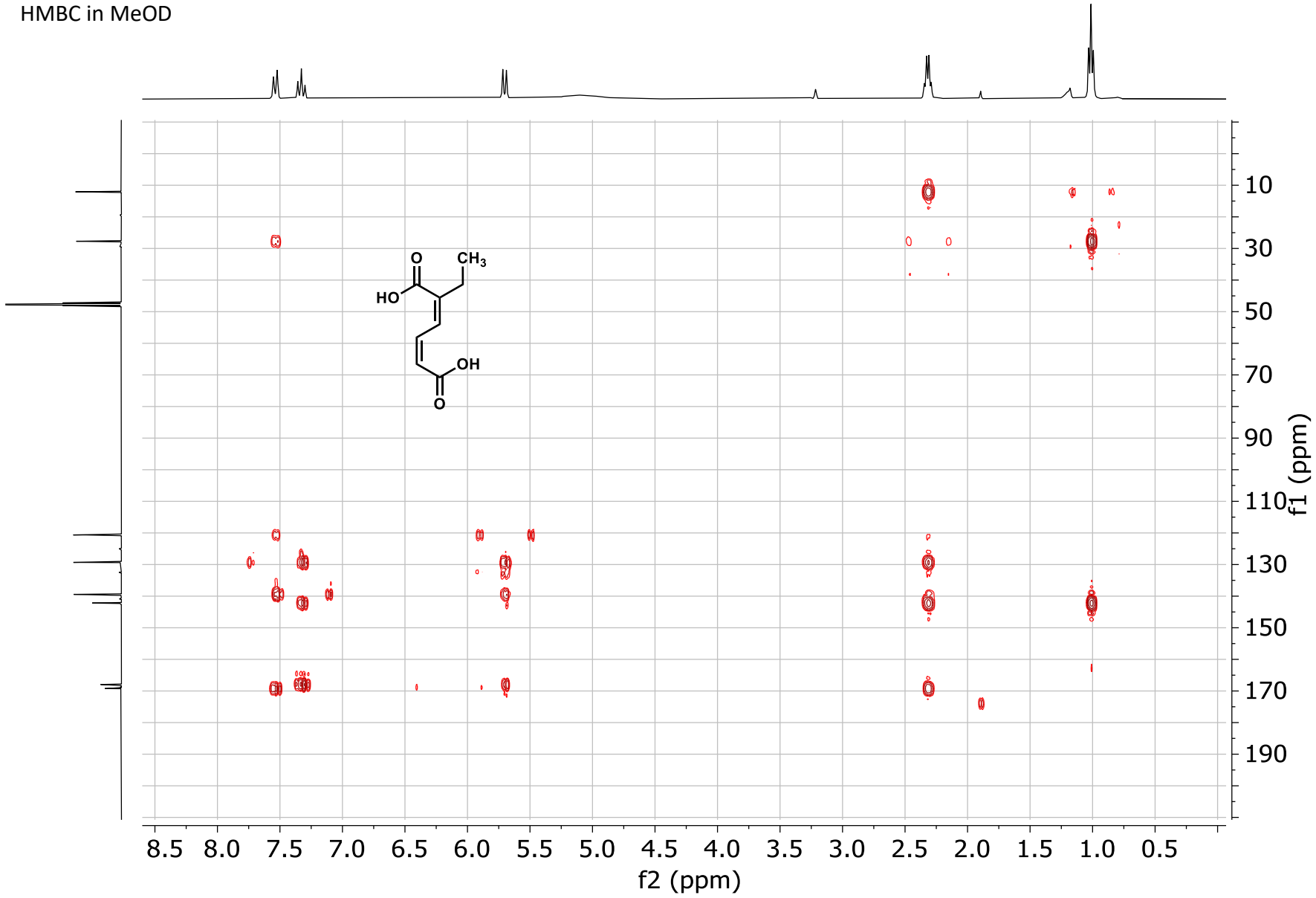
101 MHz, MeOD


170.59
169.28
143.53
140.78
130.66
121.97
49.00 CD3OD
29.06
13.42
O
CH3
HO
OH
O
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)

COSY in MeOD


HO
O
CH3
OH
O
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
f2 (ppm)
1 2 3 4 5 6 7 8
f1 (ppm)

HMBC in MeOD


HO
O
CH3
OH
O
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
f2 (ppm)
10 30 50 70 90 110 130 150 170 190
f1 (ppm)

**Part VII. References**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