Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

H_2O_2-Driven Enzymatic Oxyfunctionalization of Tertiary C-H Bonds

Yawen Huang[a][b], Huanhuan Li[c], Pengpeng Zhang[a][b], Yalan Zhang[b], Peigao Duan[c], Wuyuan Zhang*[a][b][d]

[a] University of Chinese Academy of Sciences, Beijing 100049, China

[b] Key Laboratory of Engineering Biology for Low-carbon Manufacturing, Tianjin Institute of Industrial Biotechnology, Chinese Academy of Sciences, 32 West 7th Avenue, Tianjin 300308, China

[c] School of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an 710049, China

[d] National Innovation Center for Synthetic Biotechnology, 32 West 7th Avenue, Tianjin 300308, China

*E-mail: zhangwy@tib.cas.cn

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Experimental Procedures

1.1 Materials

All chemicals including tris(hydroxymethyl) aminomethane (Tris), hydrogen chloride (HCl), acetonitrile, substrates with tertiary C-H groups and their corresponding tertiary alcohols, hydrogen peroxide (H_2O_2), isobutyrophenone, propiophenone, sodium borohydride ($NaBH_4$), sulbactam, 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC•HCl), 3-chloroperbenzoic acid (*m*-CPBA), sodium bicarbonate ($NaHCO_3$), sodium sulfate (Na_2SO_4), sulfuric acid (H_2SO_4), 4-dimethylaminopyridine (DMAP), N,O-bis (trimethylsilyl) trifluoroacetamide (BSTFA), pyridine, dichloromethane (CH_2Cl_2), methanol, ethyl acetate (EA), petroleum ether (PE), etc., were purchased from commercial sources (Sigma–Aldrich, Alfa Aesar, TCI chemicals, etc.) and used directly in all experiments unless otherwise noted. For the compounds synthesized in-house (**1a, 2, 5, 6, 11, 21, 24, etc.,**), detailed procedures and characterizations were included in this Supporting Information file.

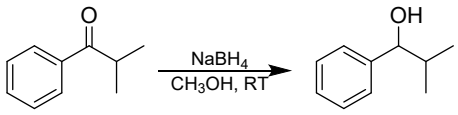
1.2 Enzyme preparation

The expression and preparation of the unspecific peroxygenase from *A. aegerita* (PaDa-I variant) in *P. pastoris* were adopted according to the previous methods.[1] The procedures were: single colony from the *P. pastoris* clones were picked and inoculated in YPD medium (5 mL), and incubated for 36 h at 30 °C, 220 rpm. Then BMGY medium (100 mL) was inoculated with the preculture (1 mL) for 24 h till OD600 was around 15. The cells were collected by centrifugation at 3000 rpm for 5 min and the supernatant was removed. The cells were reinoculated in BMMY medium (50 mL) and methanol was added. After the fermentation process, the culture broth of *P. pastoris* cells containing r*Aae*UPO was separated by centrifugation at 10000 rpm at 4 °C for 1 h. The supernatant was filtered through a 0.22 μm filter and kept at -80 °C for later use.

1.3 Substrate synthesis

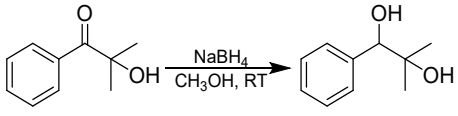
All substrates and intermediate compounds used for enzymatic reactions were obtained by either commercial purchase or synthesis in-house. For the latter, the procedures of the synthesis of noncommercially available substrates, using either chemical or enzymatic methods, are shown as follows. The characterization of the as-synthesized compounds using ^1H and ^{13}C NMR was included in Supporting Information.

Synthesis of 2-methyl-1-phenylpropan-1-ol



The procedures were adapted from reported protocols[2]:
Isobutyrophenone (1776 mg, 12 mmol, 1.0 equiv.) was dissolved in methanol (40 mL) in an ice bath and NaBH4 (590 mg, 15.6 mmol, 1.3 equiv.) was added under stirring. Over 10 min, the cooling bath was removed and the reaction mixture was stirred at room temperature. The reaction process was monitored by TLC. Next, the reaction mixture was concentrated by evaporation of methanol and the remaining oil was extracted with CH_2Cl_2 and brine, and the aqueous phase was extracted with further CH_2Cl_2. Subsequently, the collected CH_2Cl_2 phase was dried over Na_2SO_4 and concentrated in vacuo. Finally, crude mixture was purified by silica gel column chromatography (EA:PE=1:5).

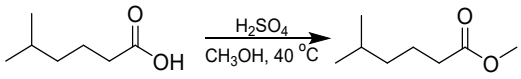
Synthesis of 2-methyl-1-phenylpropane-1,2-diol



The procedures were adapted from reported protocols[2]:

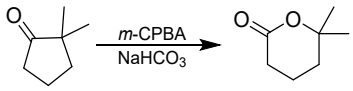
Propiophenone (1968 mg, 12 mmol, 1.0 equiv) was dissolved in methanol (40 mL) in an ice bath and $NaBH_4$ (590 mg, 15.6 mmol, 1.3 equiv) was added under stirring. Over 10 min, the cooling bath was removed and the reaction mixture was stirred at room temperature. The reaction process was monitored by TLC. Next, the reaction mixture was concentrated by evaporation of methanol and the remaining was extract with CH_2Cl_2 and brine, and the aqueous phase was extracted with further CH_2Cl_2. Subsequently, the collected CH_2Cl_2 phase was dried over Na_2SO_4 and concentrated in vacuo. Finally, crude mixture was purified by silica gel column chromatography (EA:PE=1:5).

Synthesis of methyl 5-methylhexanoate



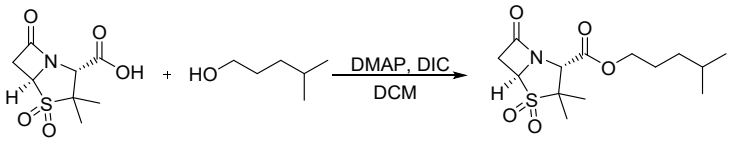
Concentrated sulfuric acid (0.1 mL) was added to methanol (20 mL) under stirring, then 5-methylhexanoic acid (1000 mg, 7.69 mmol) was added. The mixture was stirred at 40°C. The reaction process was monitored by TLC (Iodine bath). Next, the reaction mixture was concentrated by evaporation of methanol and the remaining was washed with saturated $NaHCO_3$ and brine, and the aqueous phase was extracted with EA. Subsequently, the collected EA phase was dried over Na_2SO_4 and concentrated in vacuo. Finally, crude mixture was purified by silica gel column chromatography (EA:PE=1:5).

Synthesis of 6,6-dimethyltetrahydro-2H-pyran-2-one



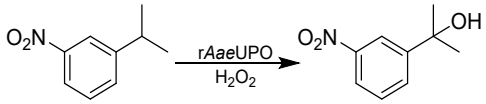
The procedures were adapted from the literature[3]:
Ketone (560 mg, 5.0 mmol, 1.0 equiv) and $NaHCO_3$ (836 mg, 9.95 mmol, 1.99 equiv) were added to CH_2Cl_2 (15 mL), then *m*-CPBA (949 mg, 5.5 mmol, 1.1 equiv) was added in an ice bath under stirring. Over 10 min, the cooling bath was removed and the reaction mixture was stirred at room temperature. The reaction process was monitored by TLC (Iodine bath). Next, the reaction mixture was washed with saturated $NaHCO_3$ and brine, and the aqueous phase was extracted with CH_2Cl_2. Subsequently, the collected CH_2Cl_2 phase was dried over Na_2SO_4 and concentrated in vacuo. Finally, crude mixture was purified by silica gel column chromatography (EA: CH_2Cl_2= 2:98).

Synthesis of sulbactam analogues



The procedures were adapted from the literature[4]:
sulbactam (400 mg, 1.7 mmol, 1.0 equiv) and 4-dimethylamino pyridine (20.7 mg, 0.17 mmol, 0.10 equiv) were added to a flask. Then CH_2Cl_2 (30 mL) and 4-methylpentan-1-ol (173.7 mg, 1.7 mmol, 1.0 equiv) were added under stirring, followed by N,N'-diisopropylcarbodiimide (DIC) (214.5 mg, 1.7 mmol, 1.0 equiv). The reaction stirred at room temperature overnight, before filtering and concentrating under reduced pressure. The crude residue was directly purified by flash-column chromatography (SiO_2) to (99:1 to 98:2 CH_2Cl_2: EA).

Synthesis of 2-(3-nitrophenyl)propan-2-ol



The reactions were carried out on a 0.5 mmol scale. 1-isopropyl-3-nitrobenzene (82.5 mg, 10 mM) and r*Aae*UPO (500 nM at first, replenished every 12 hours) were added to 50 mL of Tris HCl buffer (50 mM, pH 8.0) with 30% MeCN. Then, the H_2O_2

from a stock solution (1000 mM) was dosed by a syringe pump at a rate of 6.67 μL min^{-1}. Then, the reaction was sealed and stirred in a water bath at 320 rpm and 30°C for 30 h. When the substrate was no longer reduced in 6 hours, the reaction mixture was extracted with ethyl acetate (three times). The organic phase was combined and dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (EA:PE=1:5).

1.4 Enzymatic reactions

Oxyfunctionalization of tertiary C-H bonds using r*Aae*UPO.

Unless otherwise specified, 10 mM substrate and 500 nM r*Aae*UPO were added to Tris HCl buffer (50 mM, pH = 8) with 10% MeCN in a total volume of 1 mL. Then, 6 mM h^{-1} H_2O_2 was continuously added with syringe pump for 12 h. The reaction vial was sealed and reacted in a thermal shaker at 800 rpm and 30°C. After the reaction, 100 μL of the reaction mixture was withdrawn and extracted with 200 μL ethyl acetate, which contained 5 mM acetophenone as an internal standard. The organic phase was dried over anhydrous Na_2SO_4 and subjected to GC. Experiments were performed as twice.

Oxyfunctionalization of pharmaceutical molecules using r*Aae*UPO.

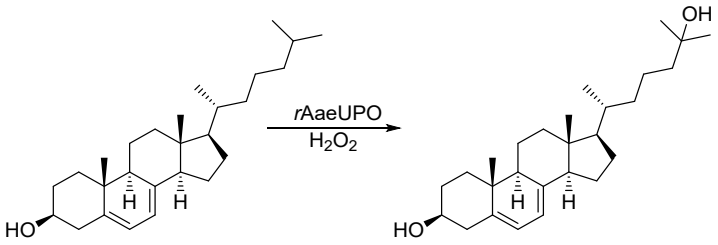
Unless otherwise specified, 2.5 mM substrate and 500 nM rAaeUPO were added to Tris HCl buffer (50 mM, pH = 8) with 30% MeCN in a total volume of 1 mL. Then, 2 mM h^{-1} H_2O_2 was continuously added with syringe pump for 6 h. The reaction vial was sealed and reacted in a thermal shaker at 800 rpm and 30 °C. After the reaction, 100 μL of the reaction mixture was withdrawn and extracted with 200 μL ethyl acetate, which contained 5 mM acetophenone as an internal standard. The organic phase was dried over anhydrous Na_2SO_4 and subjected to GC-MS. Experiments were performed as twice.

follow-up chemistry.

To perform Pinacol rearrangement reaction, H_2O_2-driven enzymztic oxyfunctionlization of **11** was carried out as the first step using the method mentioned above. After 12 h, the glass bottles were exposed to blue light for 20 min to eliminate the remaining H_2O_2 due to a background reaction observed with H_2O_2. Then 3 M HCl (final concentration) was added to start the pinacol rearrangement in 80 °C, 800 rpm for another 3 h. The same procedures shown in substrate scope study were used for lactonization reaction.

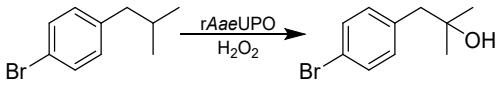
1.5 Semipreparative scale synthesis

25-OH-7-DHC



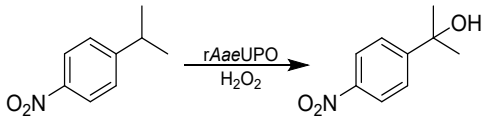
The reactions were carried out on a 1.30 mmol scale. 7-DHC (0.4996 g, 2.60 mM) and r*Aae*UPO (500 nM) were added to 500 mL of Tris HCl buffer (50 mM, pH 8.0) with 30% MeCN. Then, the H_2O_2 from a stock solution (400 mM) was dosed by a syringe pump at a rate of 6.67 μL min^{-1}. The reaction was sealed and stirred in a water bath at 670 rpm and 30°C for 30 h. When the substrate was no longer reduced in 10 hours, the reaction mixture was extracted with ethyl acetate (three times). The organic phase was combined and dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (EA:PE=1:4). 81.5mg of the desired product was obtained, corresponding to 16.3 % isolated yield.

1-(4-bromophenyl)-2-methylpropan-2-ol



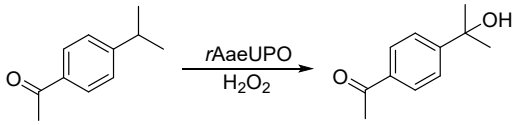
The reactions were carried out on a 10 mmol scale. 1-bromo-4-isobutylbenzene (0.4163, 10 mM) and r*Aae*UPO (500 nM) were added to 200 mL of Tris HCl buffer (50 mM, pH 8.0) with 30% MeCN. Then, the H_2O_2 from a stock solution (1000 mM) was dosed by a syringe pump at a rate of 20 µL min^{-1}. The reaction was sealed and stirred in a water bath at 510 rpm and 30°C for 12 h. When the substrate ran out, the reaction mixture was extracted with ethyl acetate (three times). The organic phase was combined and dried over anhydrous Na2SO4 and evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (PE:EA=5:1). 0.1767 mg of the desired product was obtained, corresponding to 42.45 % isolated yield.

2-(4-nitrophenyl)propan-2-ol



The reactions were carried out on a 2 mmol scale. 1-isopropyl-4-nitrobenzene (0.3304 mg, 10 mM) and r*Aae*UPO (500 nM at first, replenished every 12 hour2) were added to 200 mL of Tris HCl buffer (50 mM, pH 8.0) with 30% MeCN. Then, the H_2O_2 from a stock solution (1000 mM) was dosed by a syringe pump at a rate of 20 µL min^{-1}. Then, the reaction was sealed and stirred in a water bath at 410 rpm and 30°C for 12 h. When the substrate was no longer reduced in 5 hours, the reaction mixture was extracted with ethyl acetate (three times). The organic phase was combined and dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (EA:PE=2:15). 0.1781 mg of the desired product was obtained, corresponding to 53.90 % isolated yield.

1-(4-(2-hydroxypropan-2-yl)phenyl)ethan-1-one



The reactions were carried out on a 2 mmol scale. 1-(4-isopropylphenyl)ethan-1-one (0.3242 g, 10 mM) and rAaeUPO (500 nM) were added to 200 mL of Tris HCl buffer (50 mM, pH 8.0) with 30% MeCN. Then, the H_2O_2 from a stock solution (1000 mM) was dosed by a syringe pump at a rate of 20 µL min^{-1}. The reaction was sealed and stirred in a water bath at 410 rpm and 30°C for 10 h. When the substrate was no longer reduced in 5 hours, the reaction mixture was extracted with ethyl acetate (three times). The organic phase was combined and dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (PE:EA=10:1). 0.2045 mg of the desired product was obtained, corresponding to 63.08 % isolated yield.

1.6 Analytics methods

Gas chromatography methods

Gas chromatography equipped with a flame ionization detector (FID) was used to quantify the concentration of each compound and determine the yield of the reaction. Nitrogen was used as the carrier gas, and a column flow at 3 mL min^{-1} and split ratio of 30:1 was used in all analyses. Suitable columns (A and B) were used depending on the compounds.
Column A: SH-Rtx-1 column (30 m length, 0.25 mm inner diameter, 1 µm film thickness).
Column B: Chiral CP7503 column (25 m length, 0.32 mm inner diameter, 0.25 µm film thickness).

Entry	Column	Temperature profile	Compound
1	A	120°C hold 0.5 min, 20°C min^{-1} to 205°C hold 2.5 min, 30°C min^{-1} to 320°C hold 0.5min.	**1-14, 15-17**

2	A	160°C hold 0.5 min, 20°C min^{-1} to 205°C hold 1.5 min, 30°C min^{-1} to 310°C hold 8.2min.	**16**
3	B	80°C hold 0.5 min, 5°C min^{-1} to 110°C hold 2 min, 20°C min^{-1} to 170°C hold 1 min.	**9**

Derivatization of the tertiary alcohol products

After the reaction, 100 µL of the reaction mixture was withdrawn and extracted with 200 µL of ethyl acetate. Then the organic phase was dried over anhydrous Na_2SO_4 and vacuum rotary. Next, 100 µL of BSTFA was added and reacted at 90°C for 1 h. After derivatization, 100 µL of ethyl acetate was added before the samples were subjected to GC or GC-MS.

GC–MS analysis

The electron ionization (EI) GC–MS data were collected on GCMS-QP2010 SE with a Agilent J&W DB-5ms column (30 m length, 0.25 mm inner diameter, 0.25 µm film thickness) The GC program was listed in the following table.

Temperature profile	**Compound**
100°C hold 2.5 min, 15°C min^{-1} to 280°C hold 5 min, 30°C min^{-1} to 310°C hold 10 min	7-DHC, Tacalcitol, Propofol, and Sulbactam and their products

NMR spectroscopy analysis

NMR spectra were recorded at 298.2 K on a Bruker AVANCE III 400 MHz NMR spectrometer (Bruker Bio spin, Germany) operating at 400 MHz for proton frequency and 101 MHz for carbon frequency. TMS was used as an internal standard, and $CDCl_3$ was used as the solvent unless otherwise specified.

Molecular docking.

The structure of r*Aae*UPO (PDB ID: 5OXU) was used for molecular docking[3]. Isobutylbenzene and 2-methyl-1-phenylpropan-1-ol were docked into r*Aae*UPO with AutoDock Vina (version 1.1.2) The ligand was embedded in a three-dimensional grid with 40*40*40 and the grid center was 11.314, 2.954, 9.653 for xyz-coordinates. All the results were treated with PyMOL Molecular Graphics System.

Results and Discussion

Figure S1. Experimental facility for enzymatic reactions with H_2O_2 dosing.

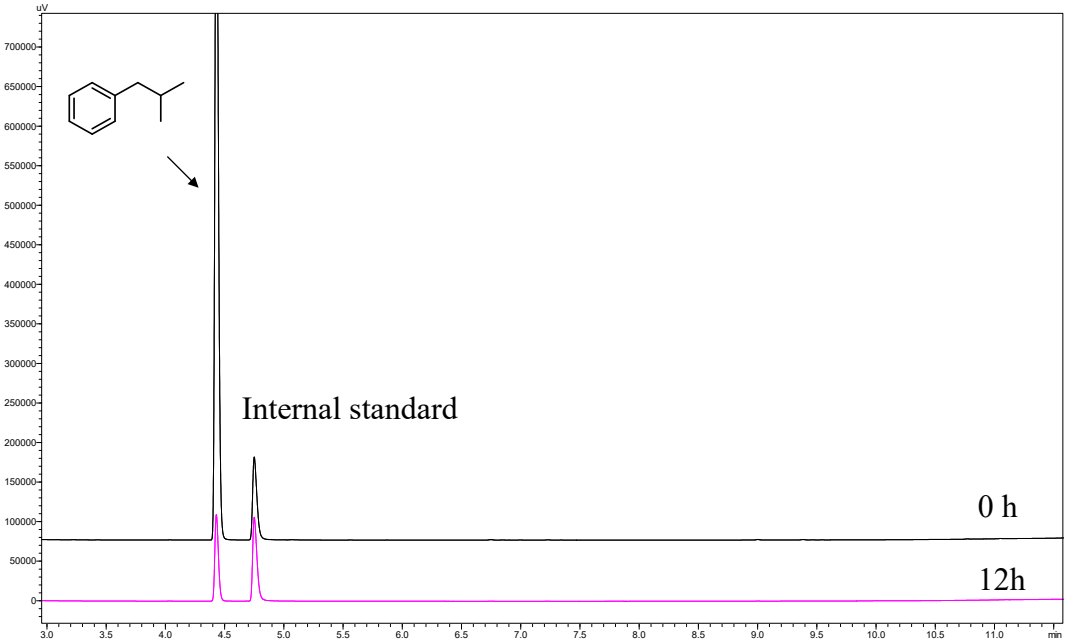


Figure S2. Example of GC chromatogram showing the evaporation of the substrate isobutylbenzene after 12 h shaking in a thermal shaker.

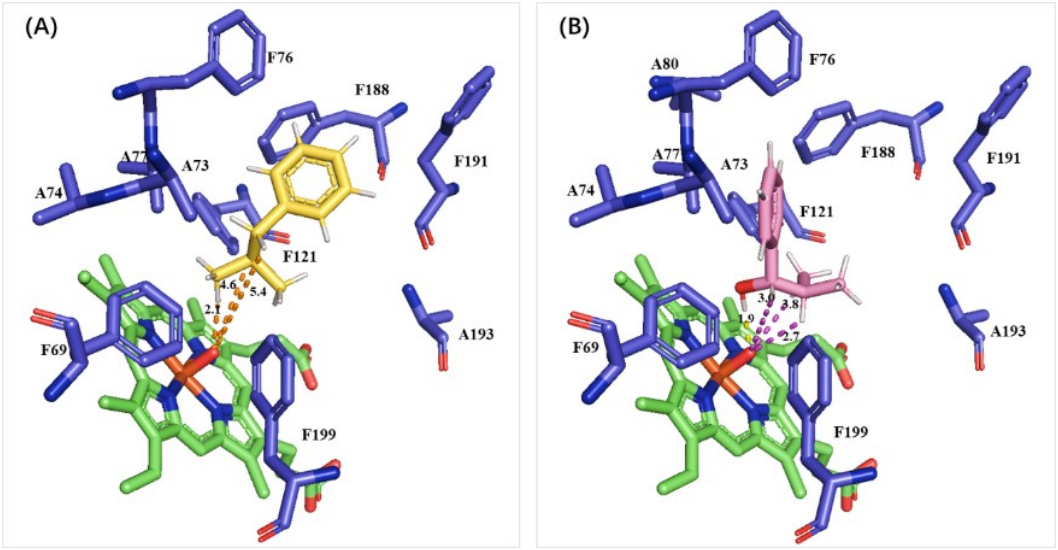


Figure S3. Active sites of r*Aae*UPO in complex with isobutylbenzene (A, yellow) and 2-methyl-1-phenylpropan-1-ol (B, pink) predicted by Autodock. Ligands and important catalytic residues are shown in sticks. The dashed lines indicate distances (in Å) from oxoferryl-heme.

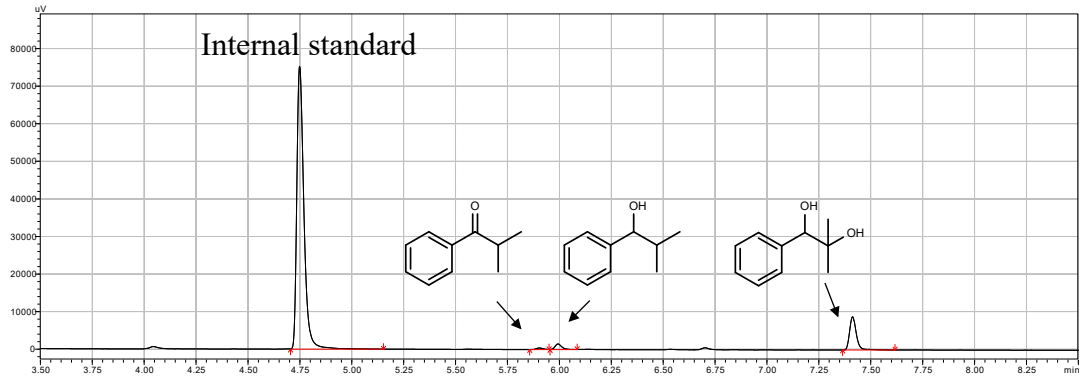


Figure S4. GC chromatogram of the r*Aae*UPO-catalyzed hydroxylation of 2-methyl-1-phenylpropan-1-ol to desired diol and the possible ketone product.

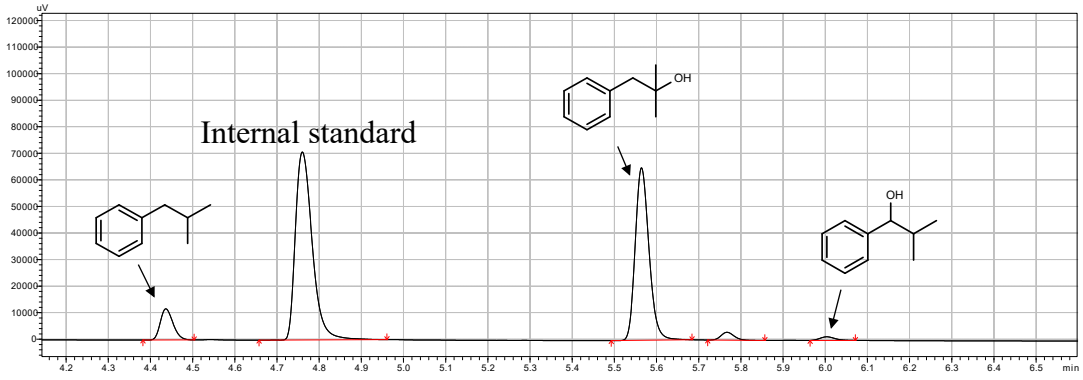


Figure S5. GC chromatogram of r*Aae*UPO-catalyzed oxyfunctionalization reaction to alcohol **1**.

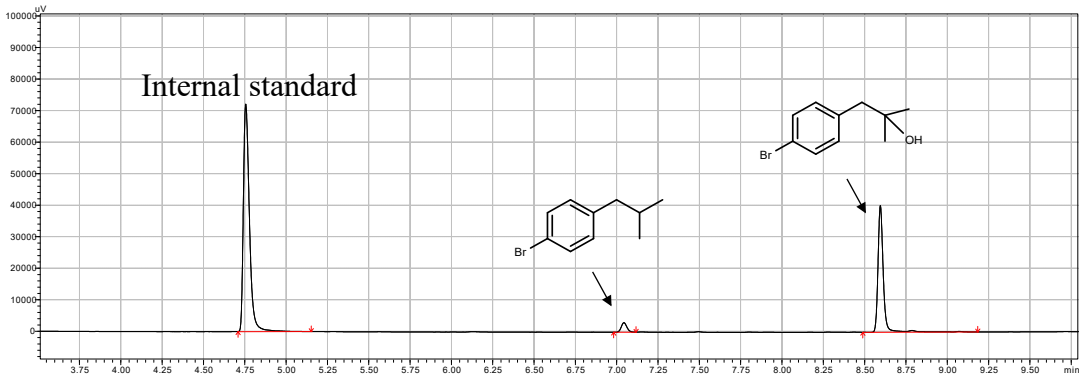


Figure S6. GC chromatogram of r*Aae*UPO-catalyzed oxyfunctionalization reaction to alcohol **2.**

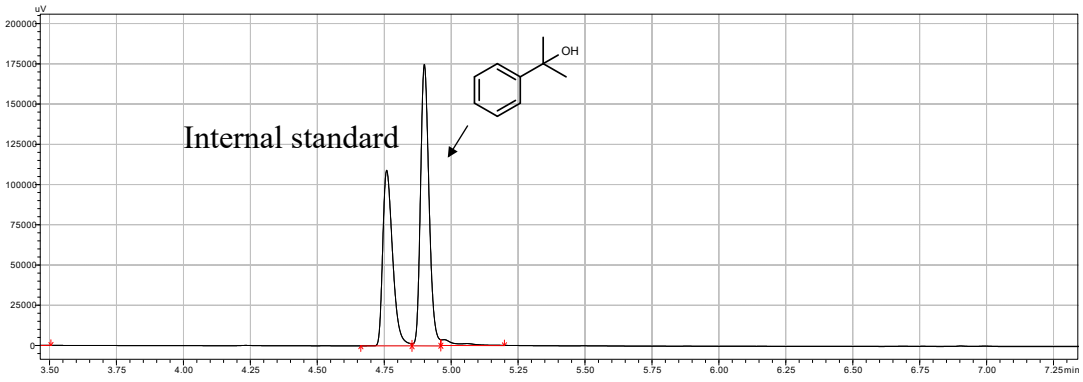


Figure S7. GC chromatogram of r*Aae*UPO-catalyzed oxyfunctionalization reaction to alcohol **3**.

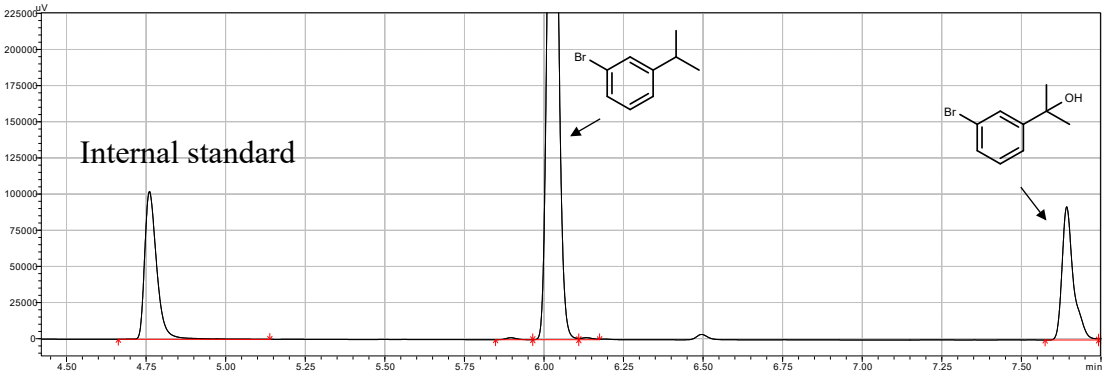


Figure S8. GC chromatogram of r*Aae*UPO-catalyzed oxyfunctionalization reaction to alcohol **4.**

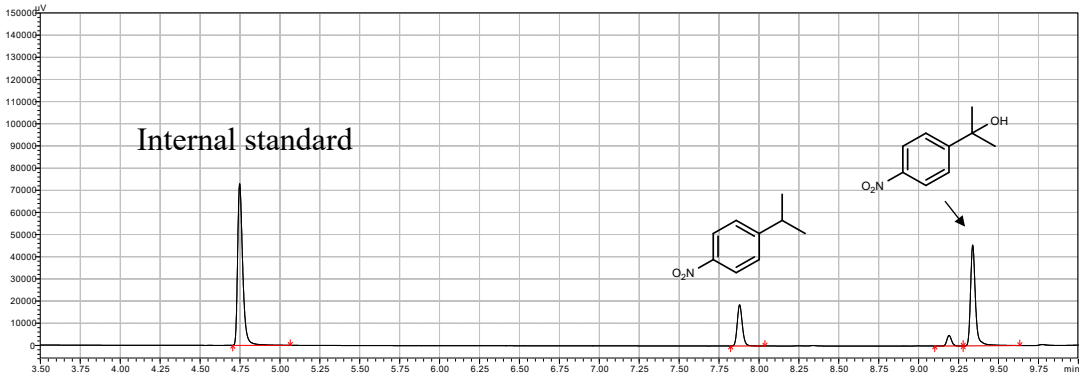


Figure S9. GC chromatogram of r*Aae*UPO-catalyzed oxyfunctionalization reaction to alcohol **5**.

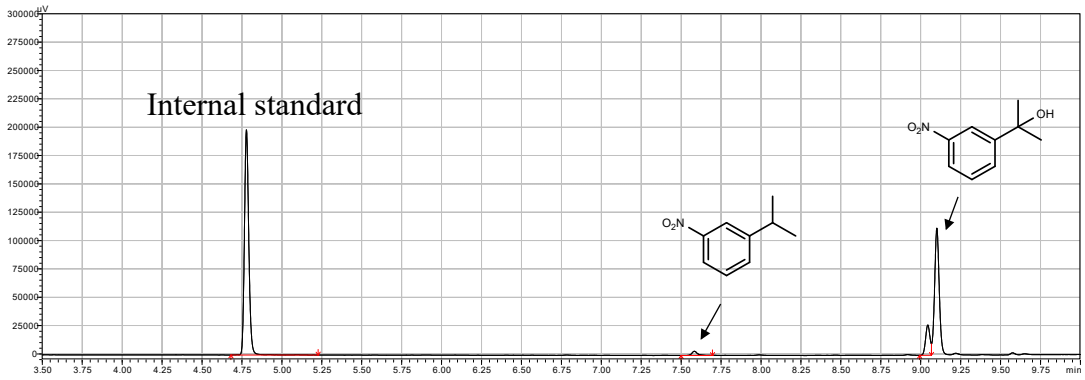


Figure S10. GC chromatogram of r*Aae*UPO-catalyzed oxyfunctionalization reaction to alcohol **6.**

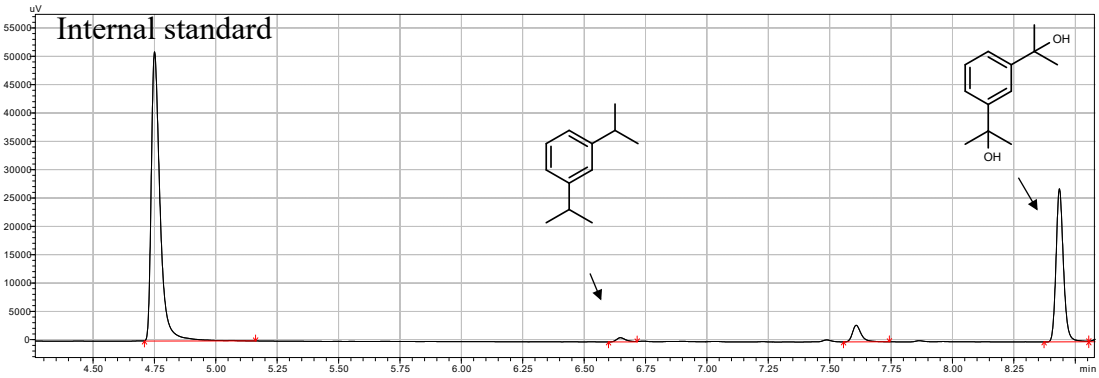


Figure S11. GC chromatogram of r*Aae*UPO-catalyzed oxyfunctionalization reaction to alcohol **7.**

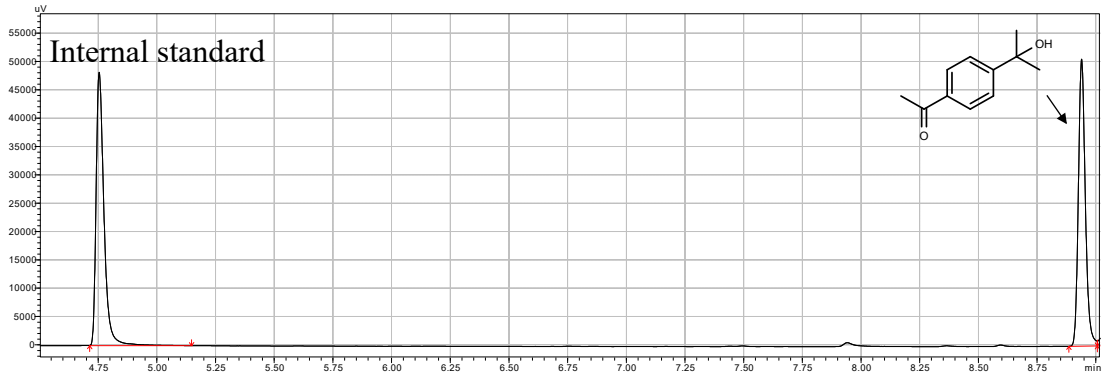


Figure S12. GC chromatogram of r*Aae*UPO-catalyzed oxyfunctionalization reaction to alcohol **8**.

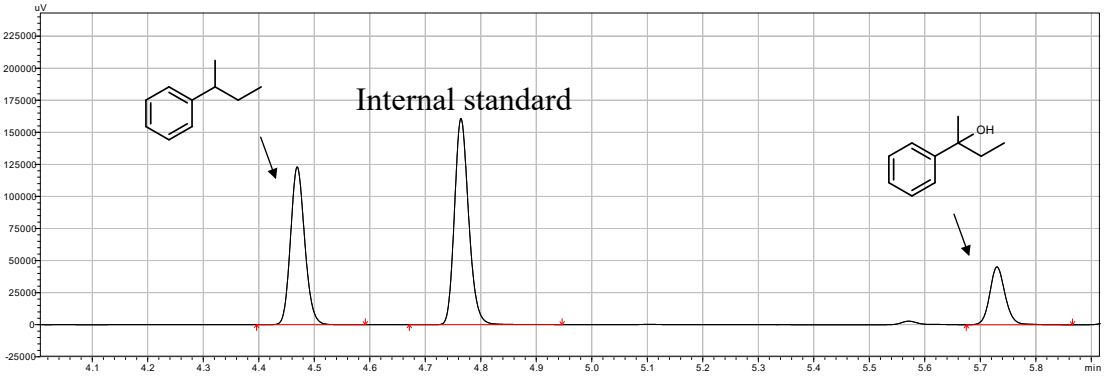


Figure S13. GC chromatogram of r*Aae*UPO-catalyzed oxyfunctionalization reaction to alcohol **9.**

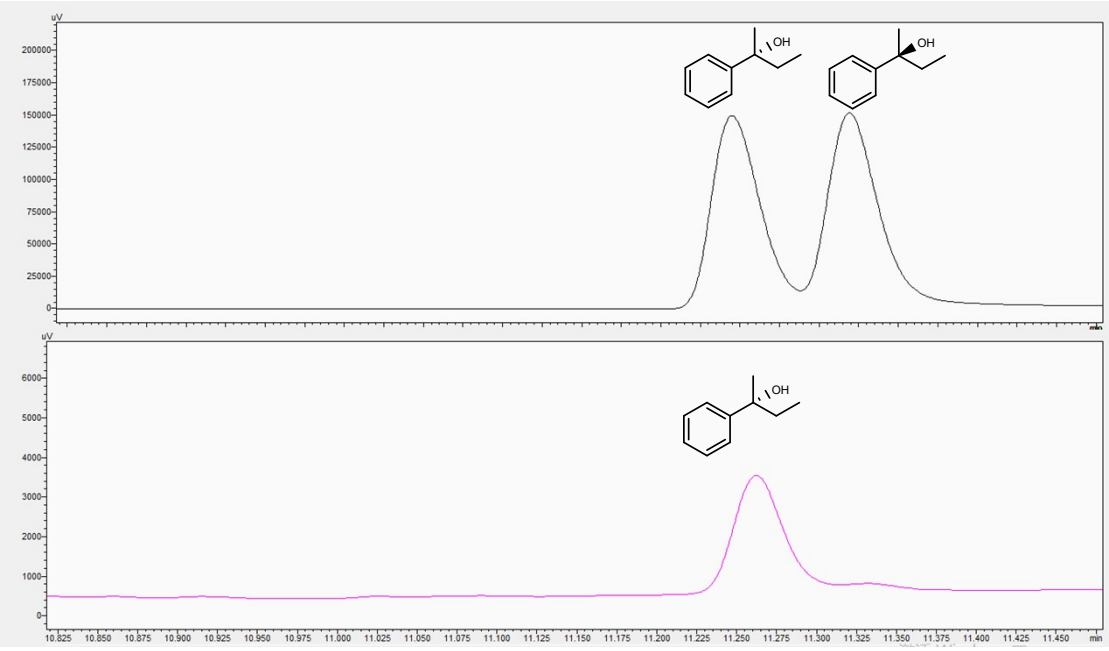


Figure S14. GC chromatogram of chiral **9**.

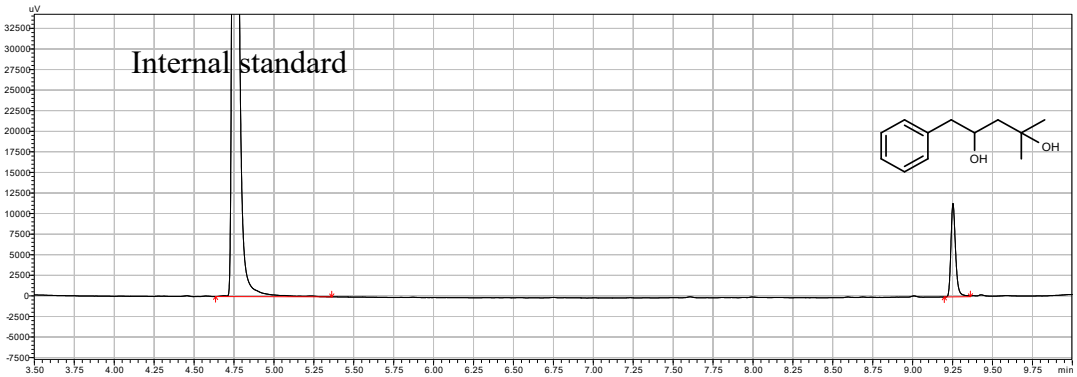


Figure S15. GC chromatogram of r*Aae*UPO-catalyzed oxyfunctionalization reaction to alcohol **10.**

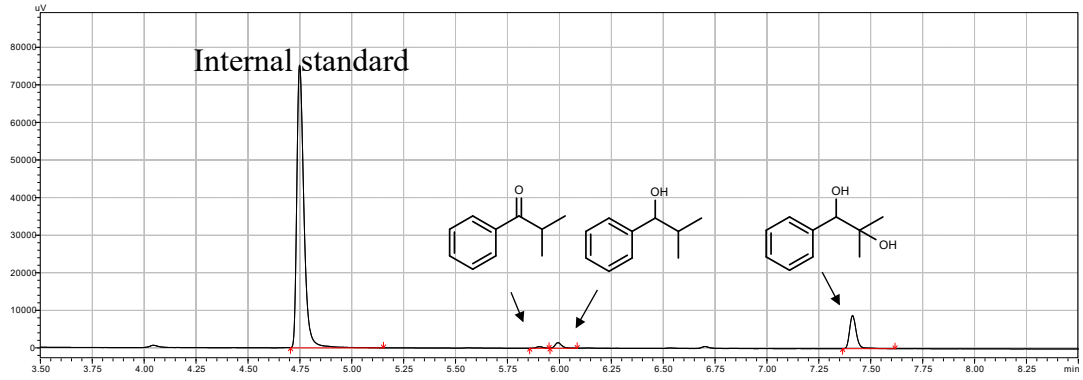


Figure S16. GC chromatogram of r*Aae*UPO-catalyzed oxyfunctionalization reaction to alcohol **11**.

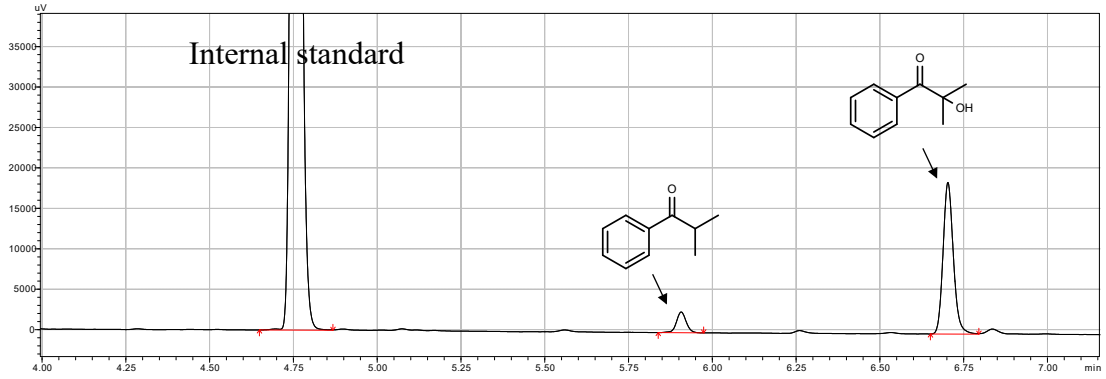


Figure S17. GC chromatogram of r*Aae*UPO-catalyzed oxyfunctionalization reaction to alcohol **12**.

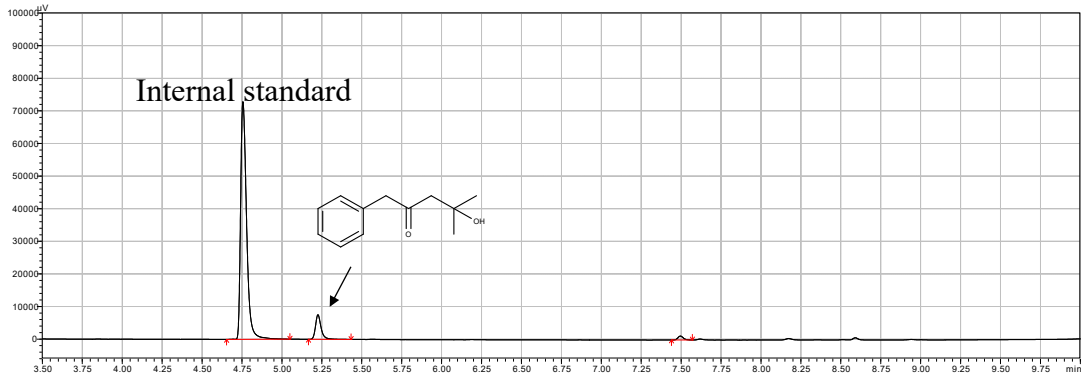


Figure S18. GC chromatogram of r*Aae*UPO-catalyzed oxyfunctionalization reaction to alcohol **13.**

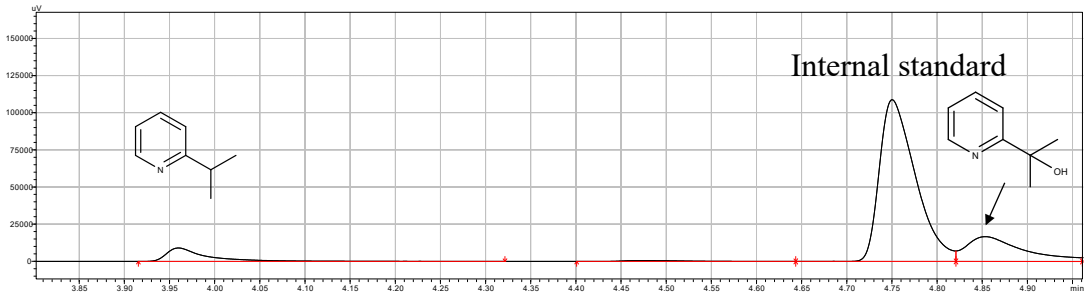


Figure S19. GC chromatogram of r*Aae*UPO-catalyzed oxyfunctionalization reaction to alcohol **14.**

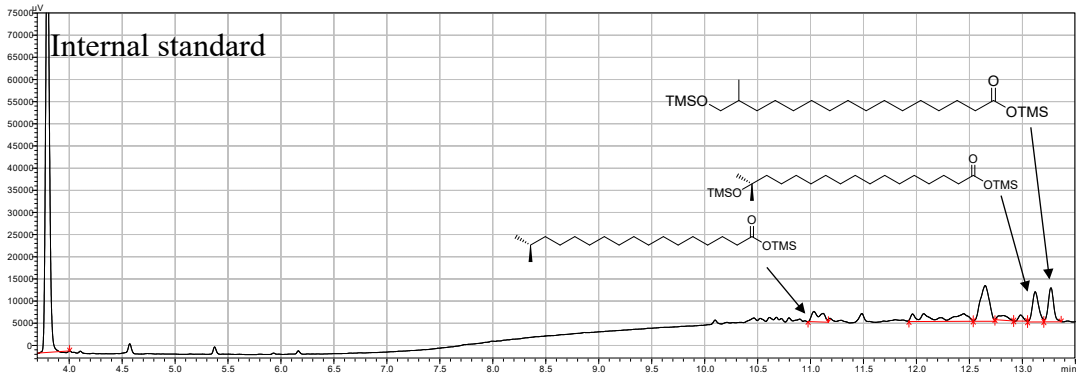


Figure S20. GC chromatogram of r*Aae*UPO-catalyzed oxyfunctionalization reaction to alcohol **15**. The unidentified peaks were mostly caused by the impurities introduced during the silylation procedures[4].

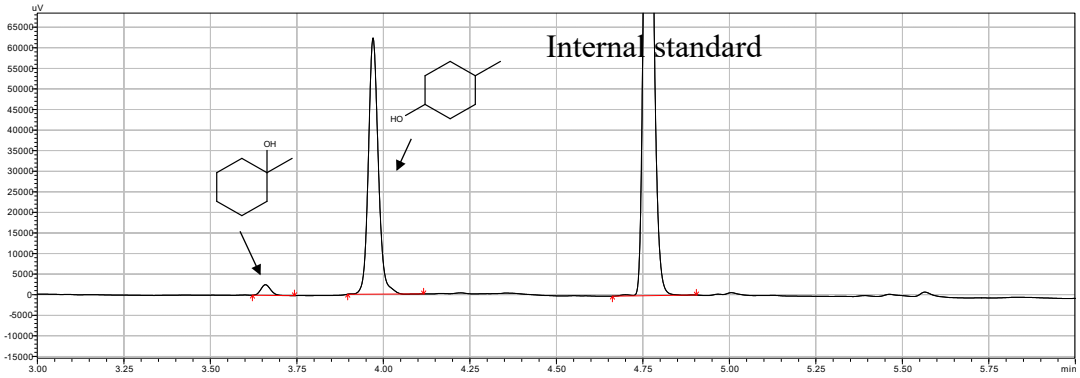


Figure S21. GC chromatogram of r*Aae*UPO-catalyzed oxyfunctionalization reaction to alcohol **16.**

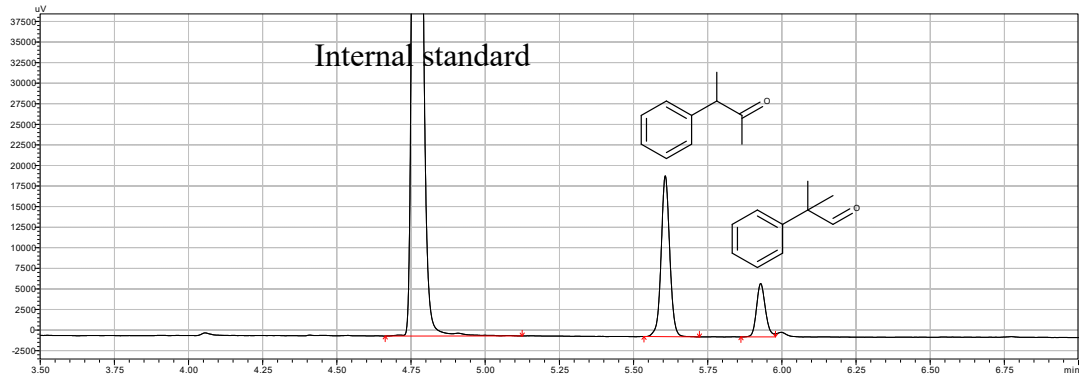


Figure S22. GC chromatogram of pinacol rearrangement to carbonyl products **(18 and 19).**

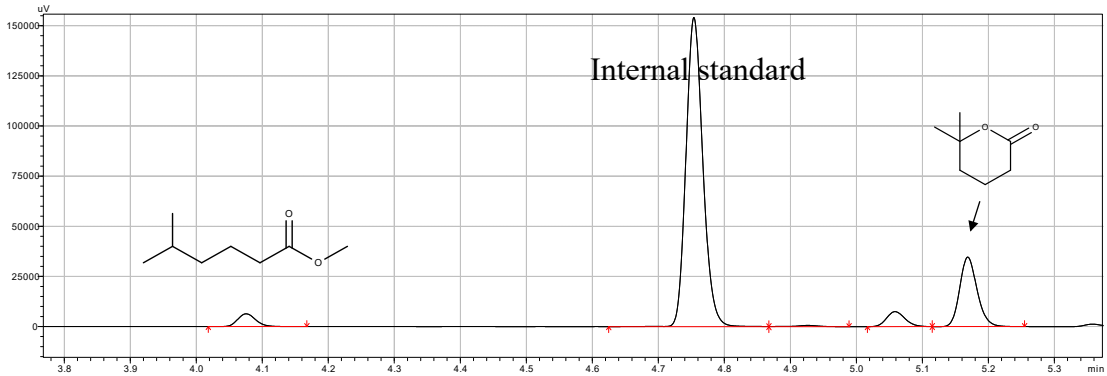


Figure S23. GC chromatogram of the lactonization yielding the lactone **21.**

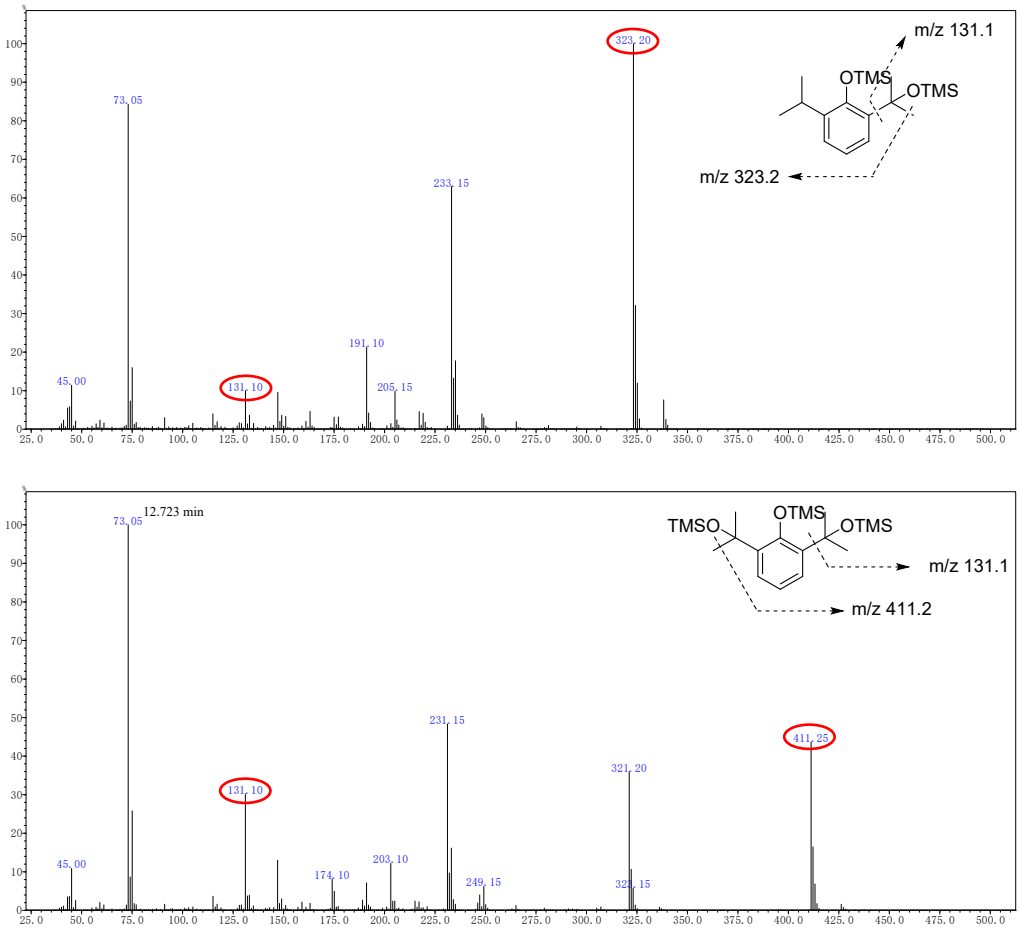


Figure S24. GC-MS of oxyfunctionalization of Propofol (**22**). The analysis of the fragments was based on the literature.[4]

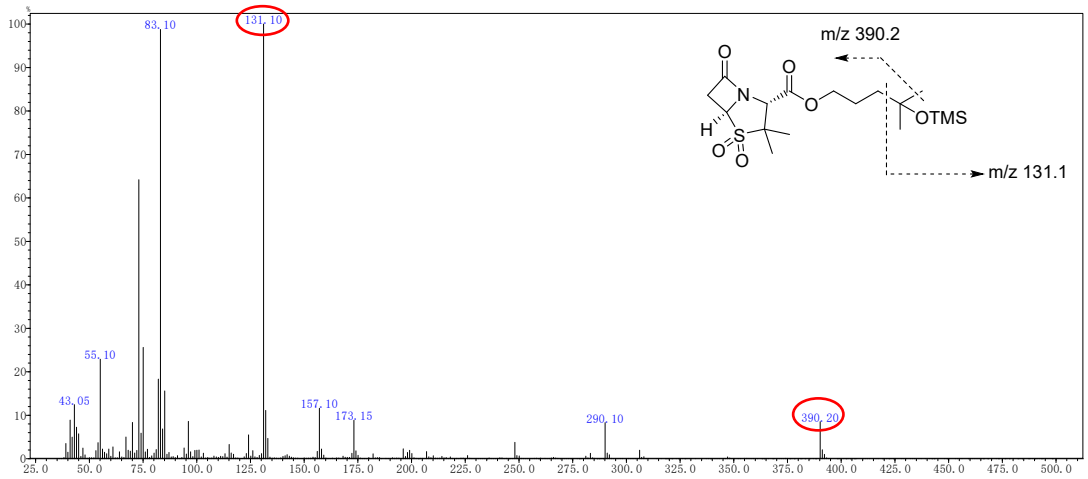


Figure S25. GC-MS of oxyfunctionalization of Sulbactam (**23**)**.**

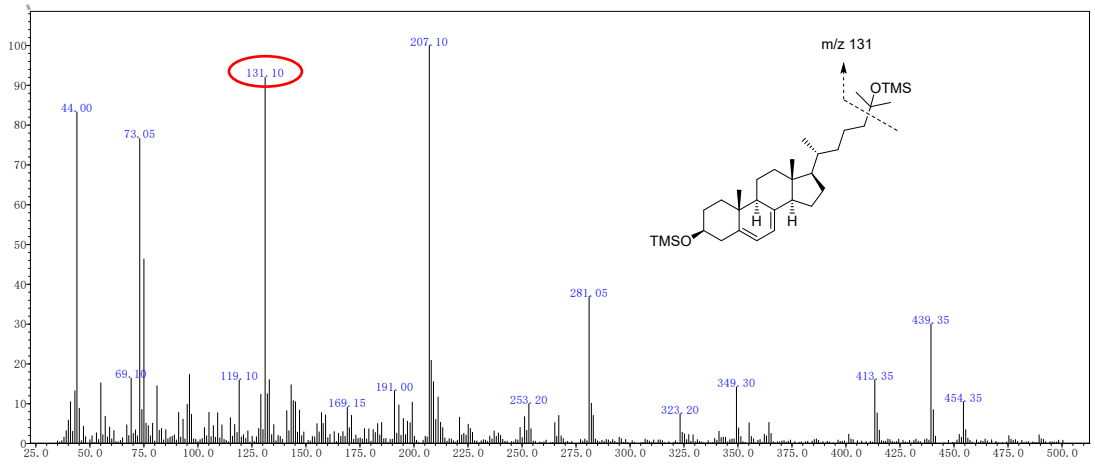


Figure S26. GC-MS of oxyfunctionalization of 7-Dehydrocholesterol (**24**).

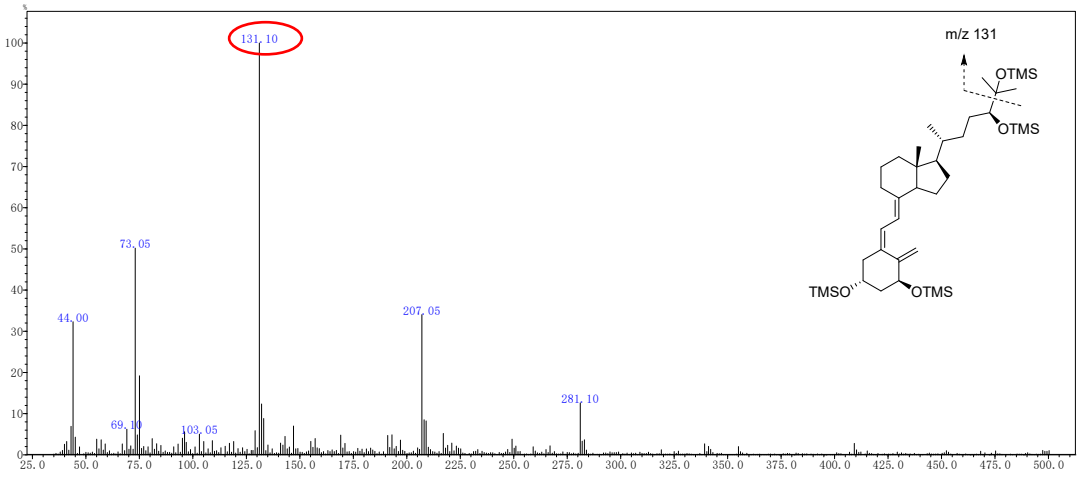


Figure S27. GC-MS of oxyfunctionalization of Tacalcitol (**25**).

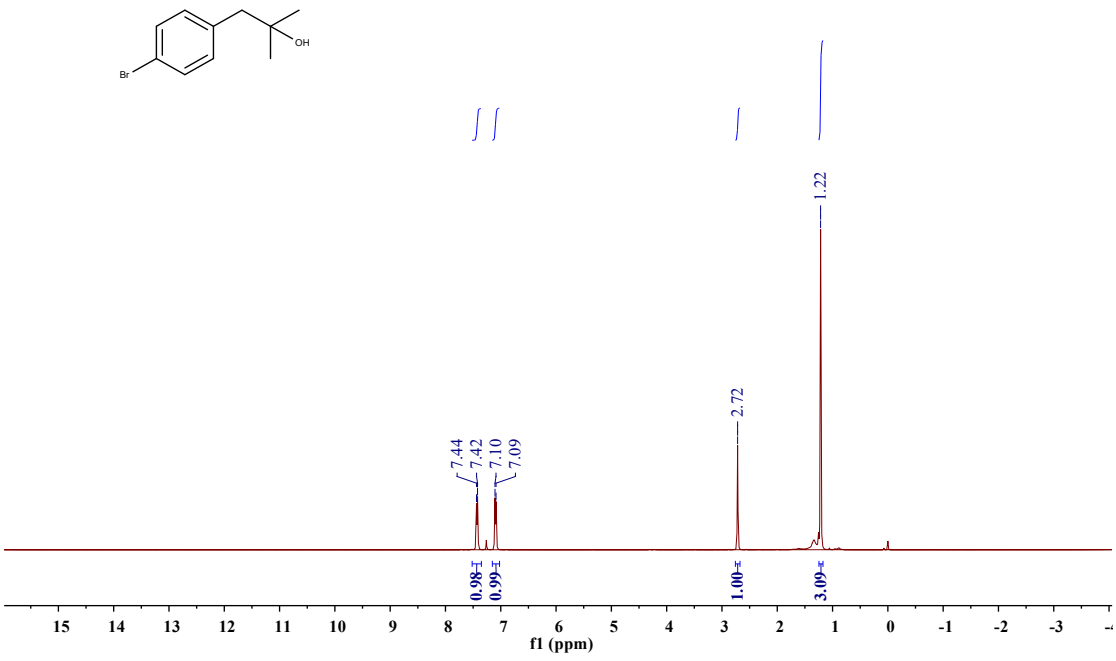


Figure S28. ^{1}H NMR of 1-(4-bromophenyl)-2-methylpropan-2-ol**.**

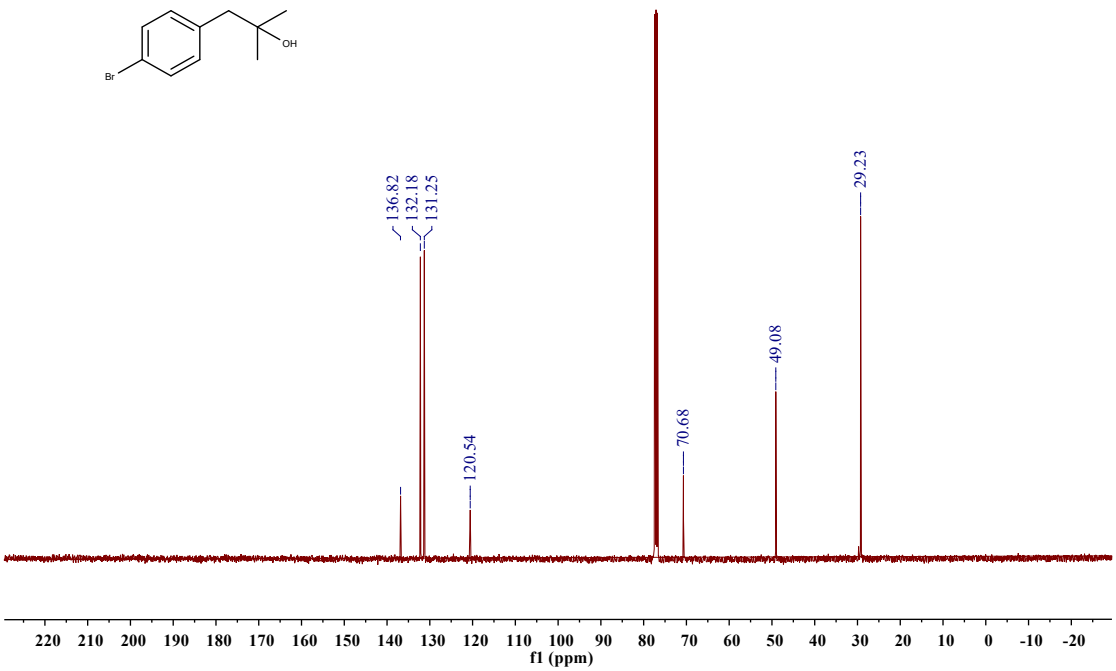


Figure S29. ^{13}C NMR of 1-(4-bromophenyl)-2-methylpropan-2-ol.

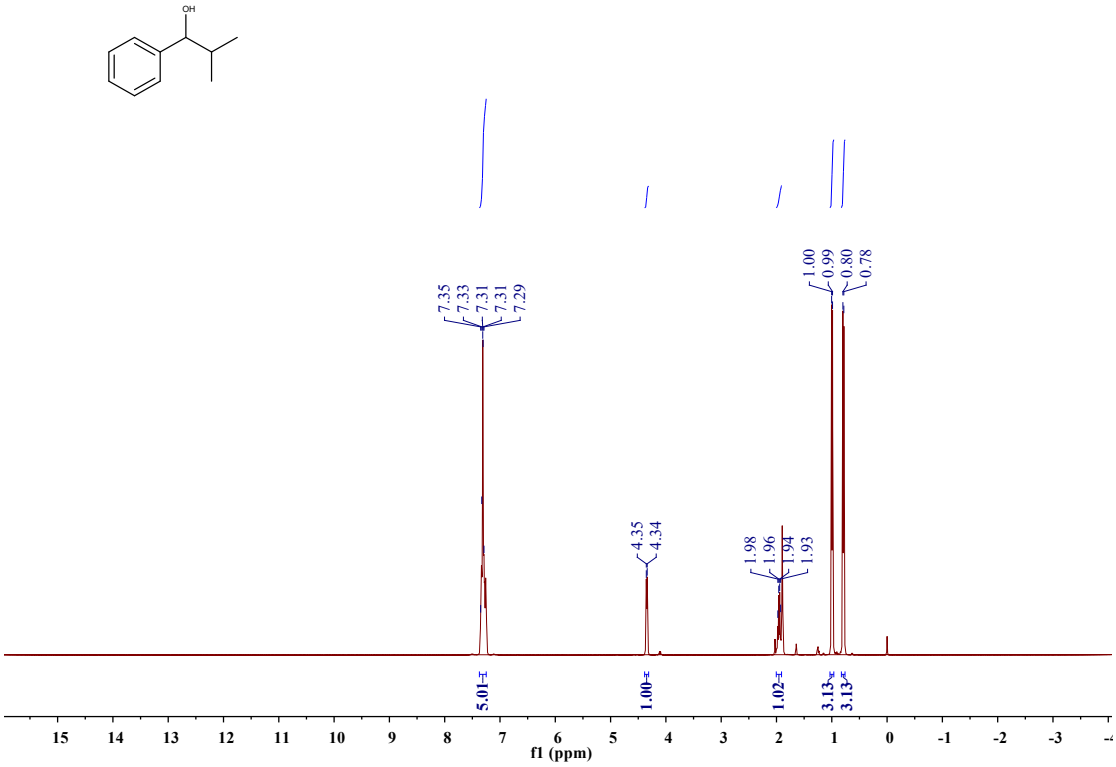


Figure S30. ^{1}H NMR of 2-methyl-1-phenylpropan-1-ol.

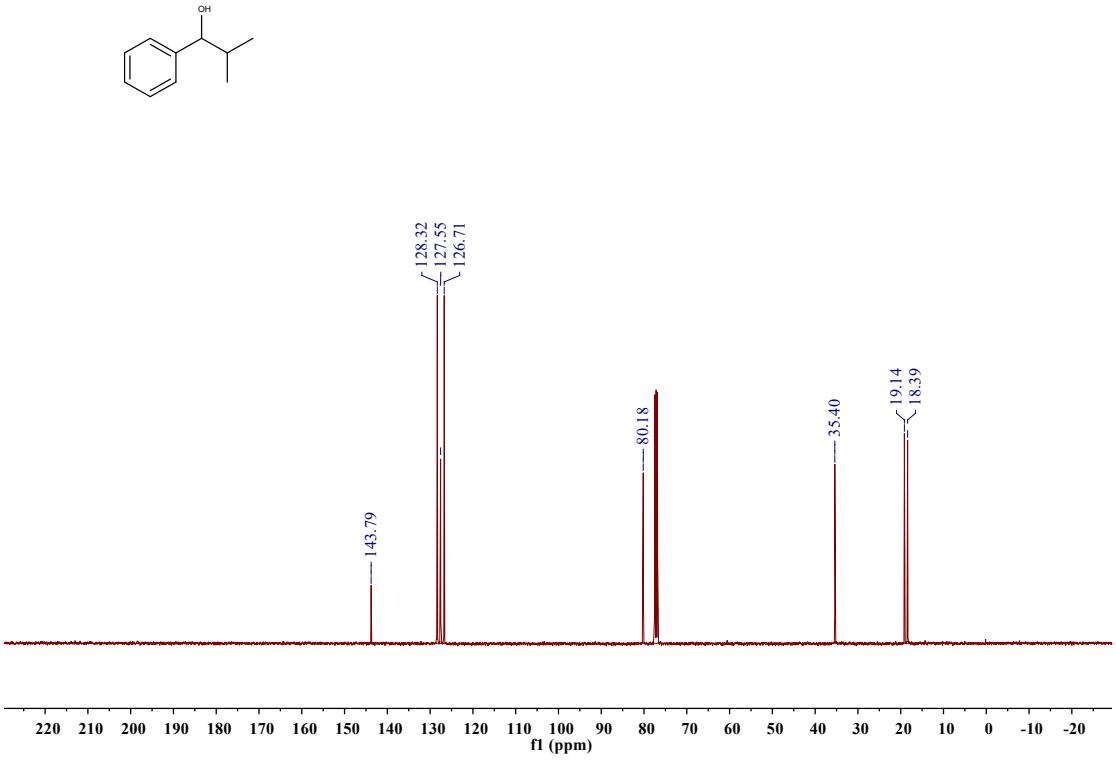


Figure S31. ^{13}C NMR of 2-methyl-1-phenylpropan-1-ol.

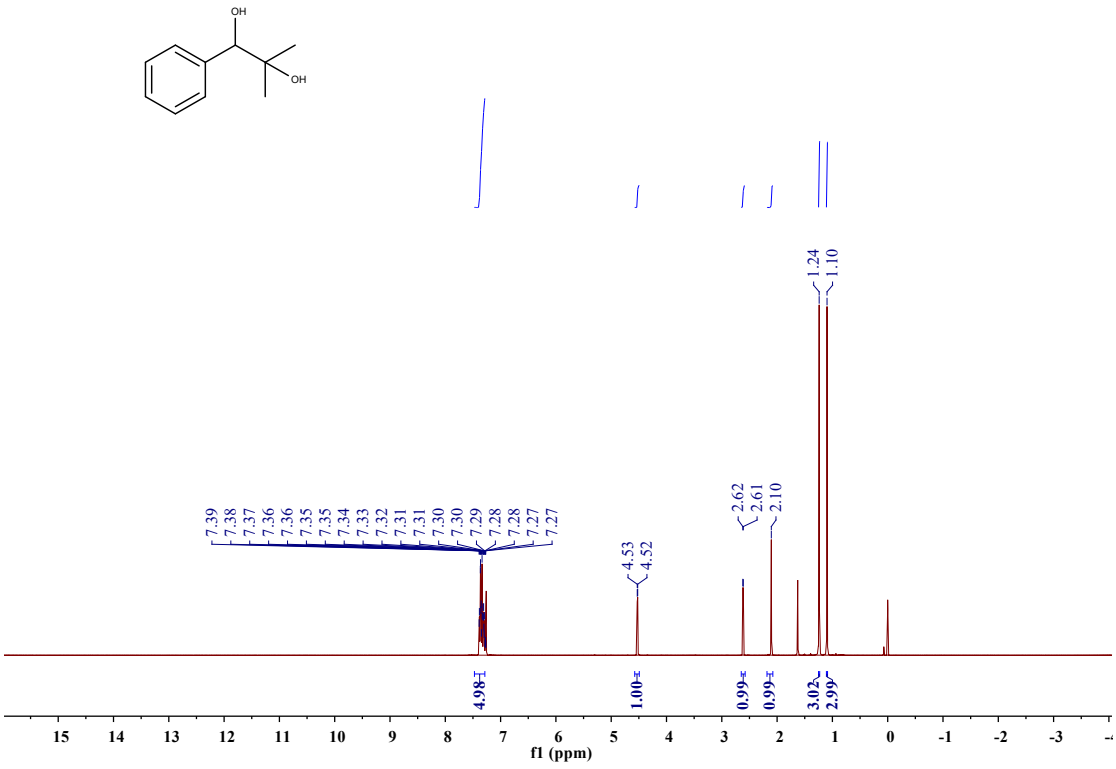


Figure S32. ^{1}H NMR of 2-methyl-1-phenylpropane-1,2-diol.

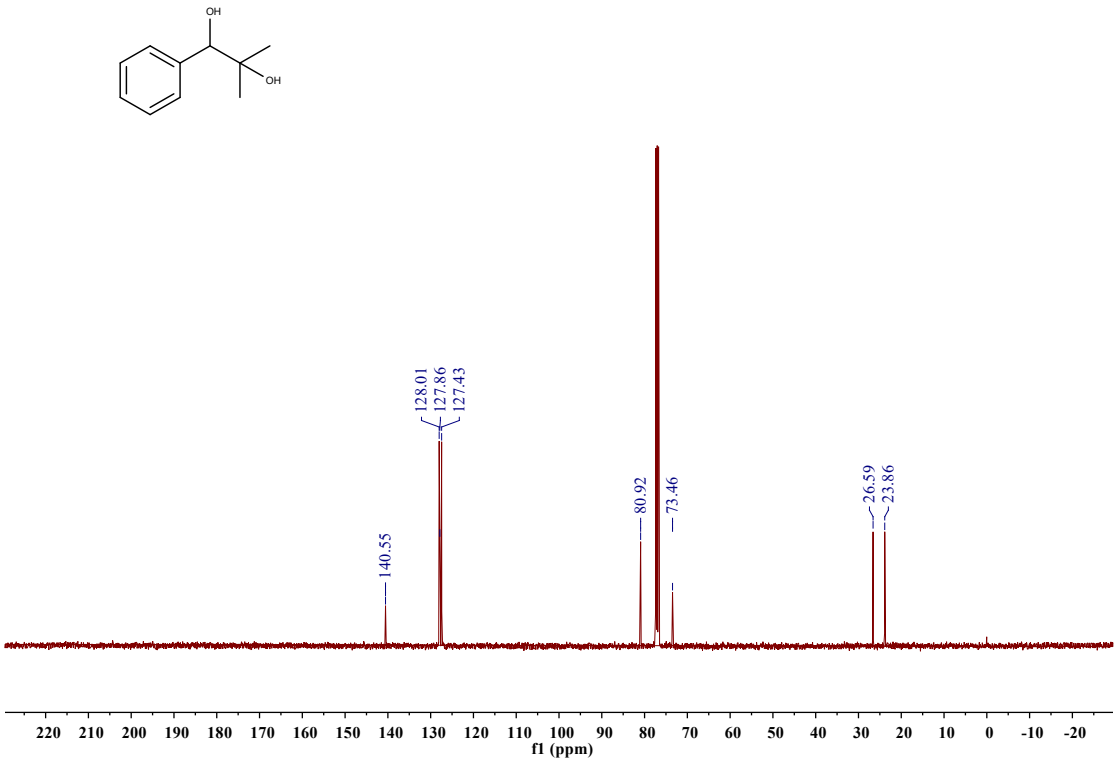


Figure S33. ^{13}C NMR of 2-methyl-1-phenylpropane-1,2-diol.

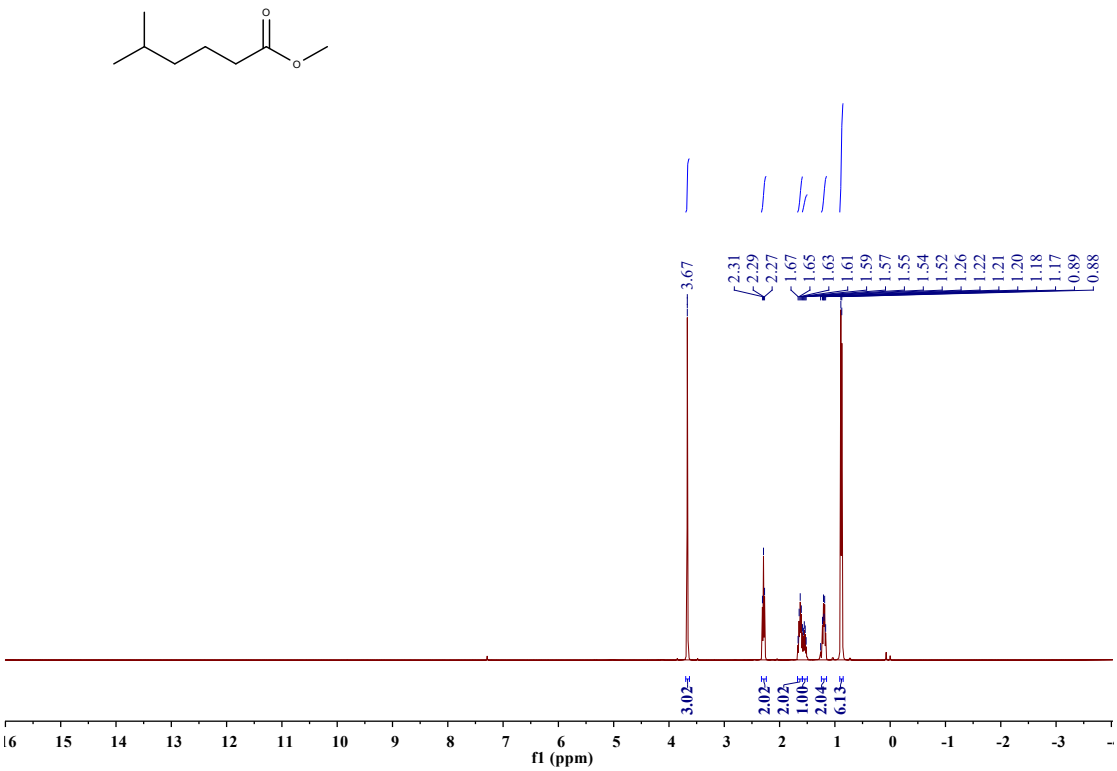


Figure S34. ^{1}H NMR of methyl 5-methylhexanoate.

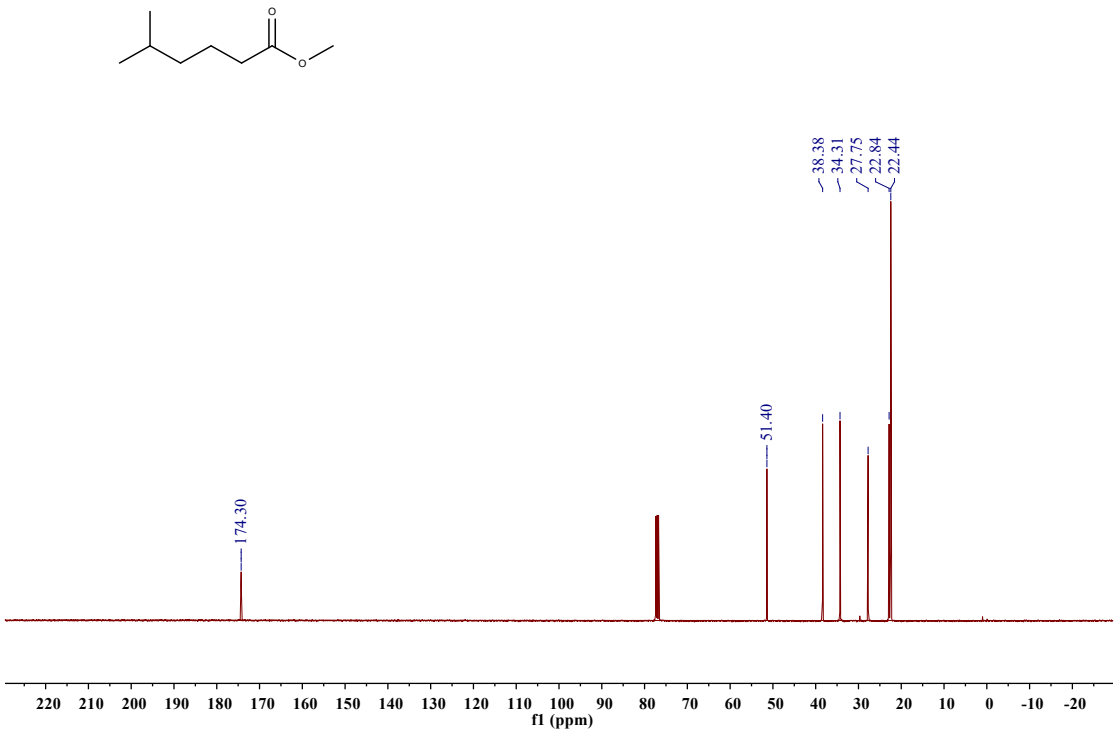


Figure S35. ^{13}C NMR of methyl 5-methylhexanoate.

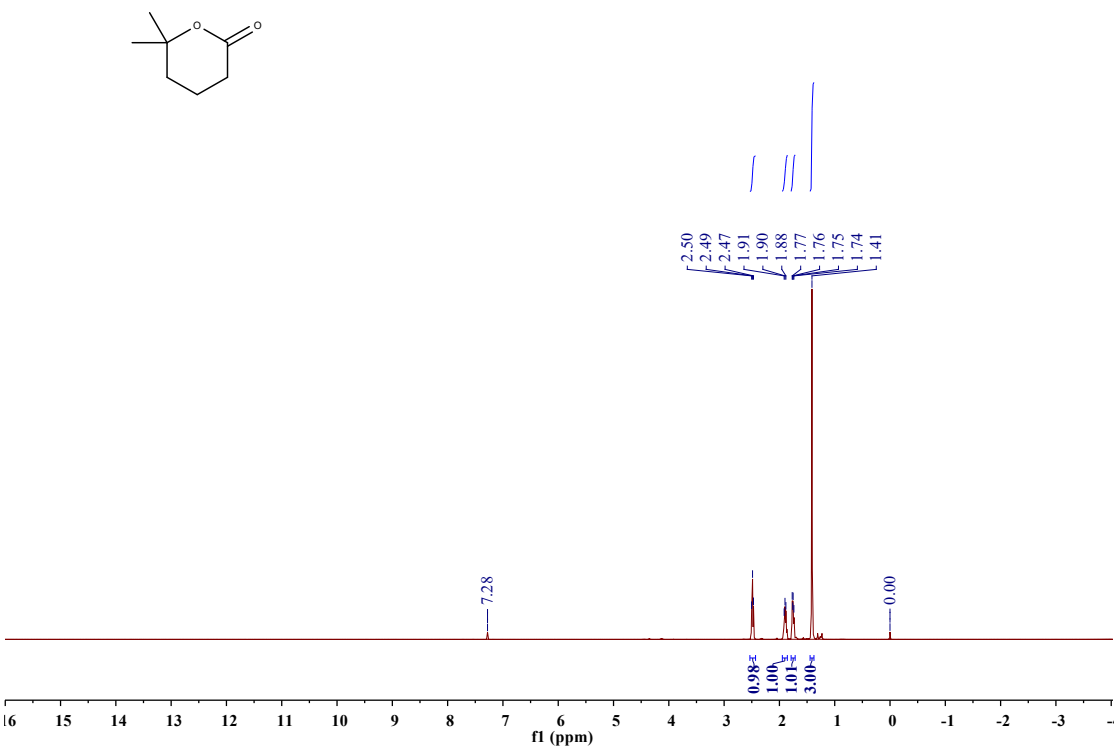


Figure S36. ^{1}H NMR of 6,6-dimethyltetrahydro-2H-pyran-2-one.

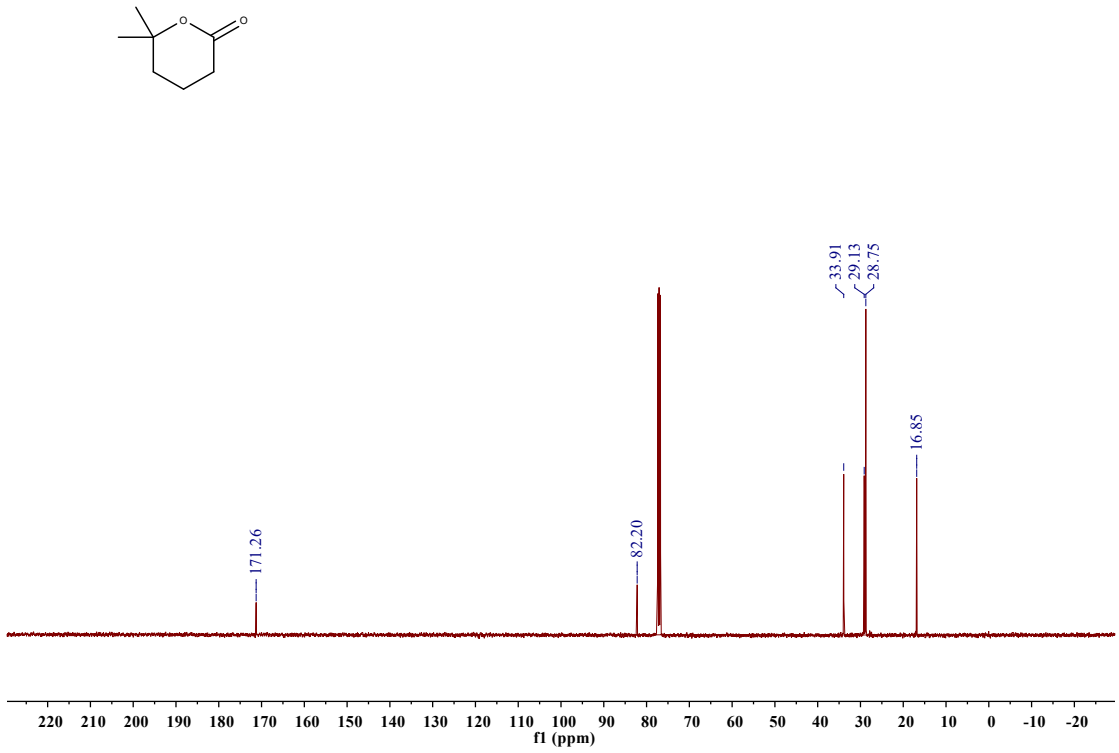


Figure S37. ^{13}C NMR of 6,6-dimethyltetrahydro-2H-pyran-2-one.

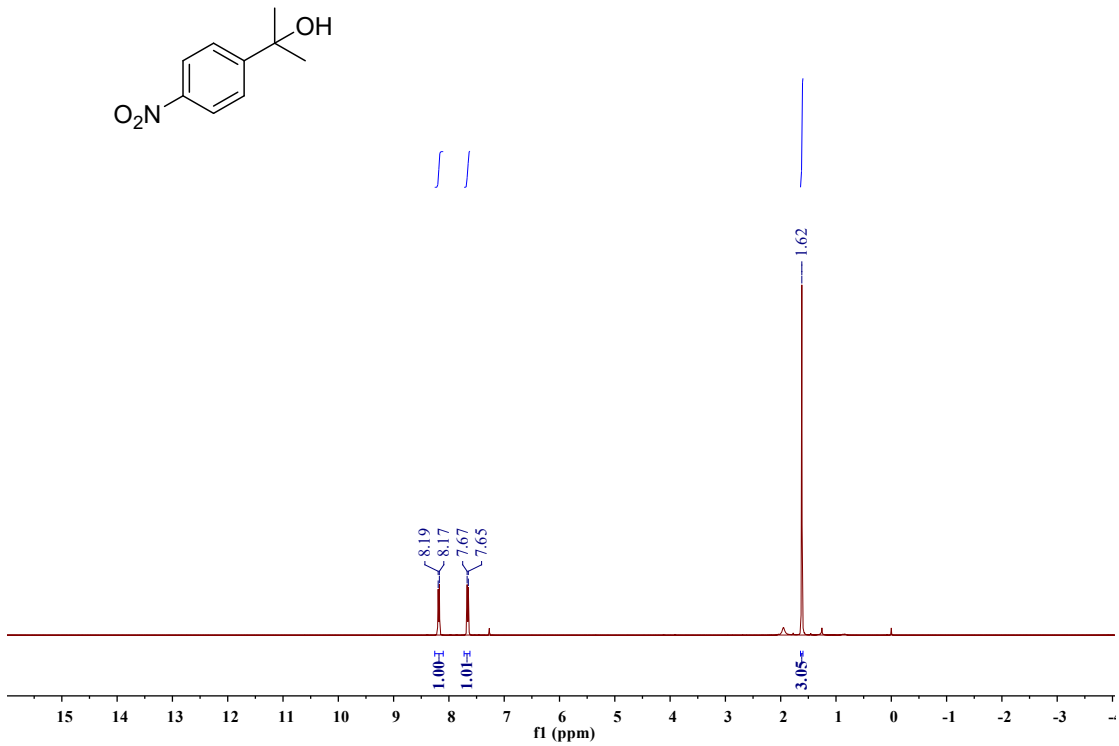


Figure S38. ^{1}H NMR of 2-(4-nitrophenyl)propan-2-ol.

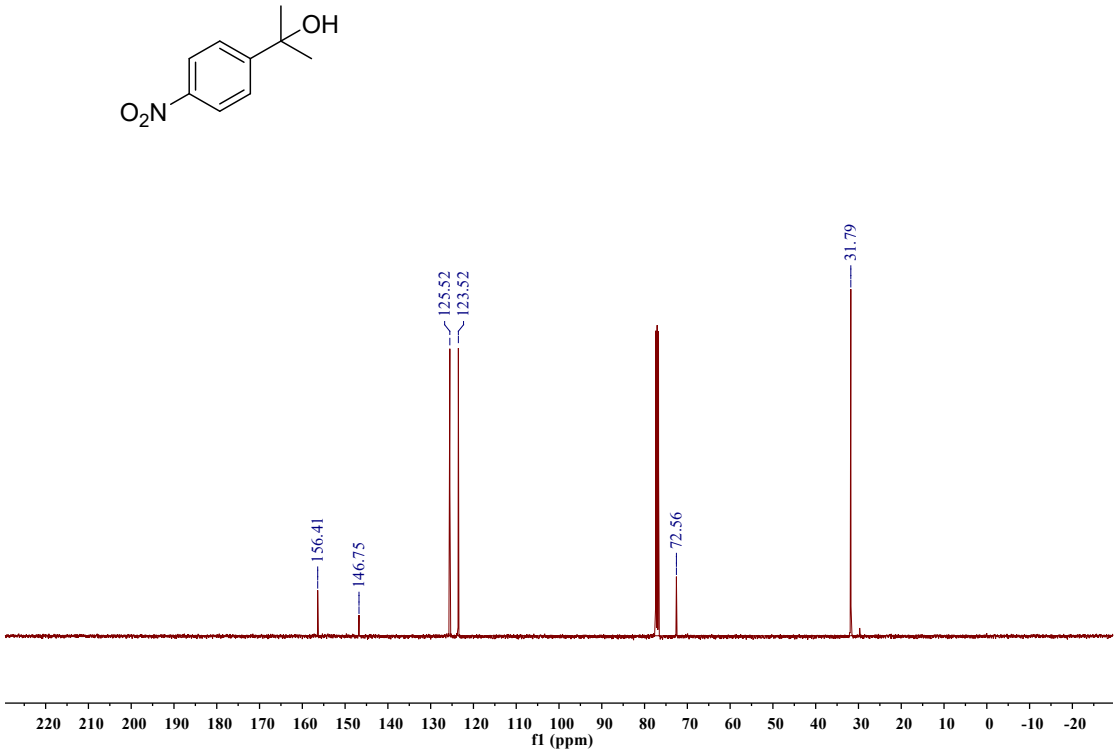


Figure S39. ^{13}C NMR of 2-(4-nitrophenyl)propan-2-ol.

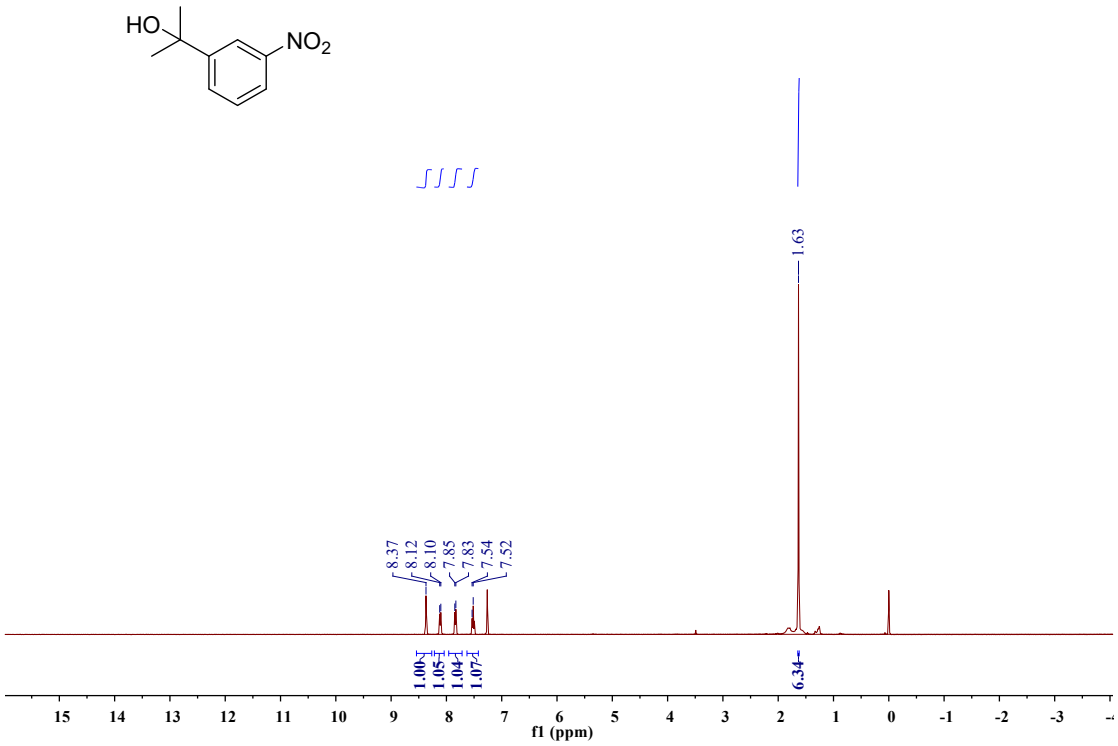


Figure S40. ^{1}H NMR of 2-(3-nitrophenyl)propan-2-ol.

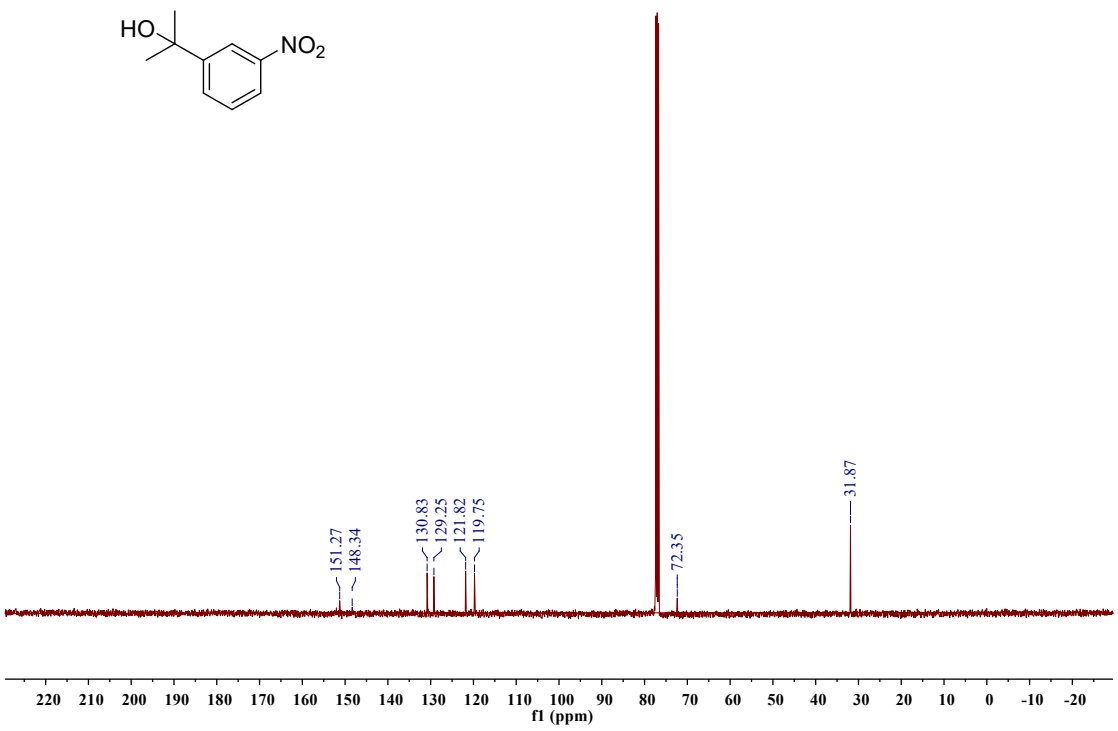


Figure S41. ^{13}C NMR of 2-(3-nitrophenyl)propan-2-ol.

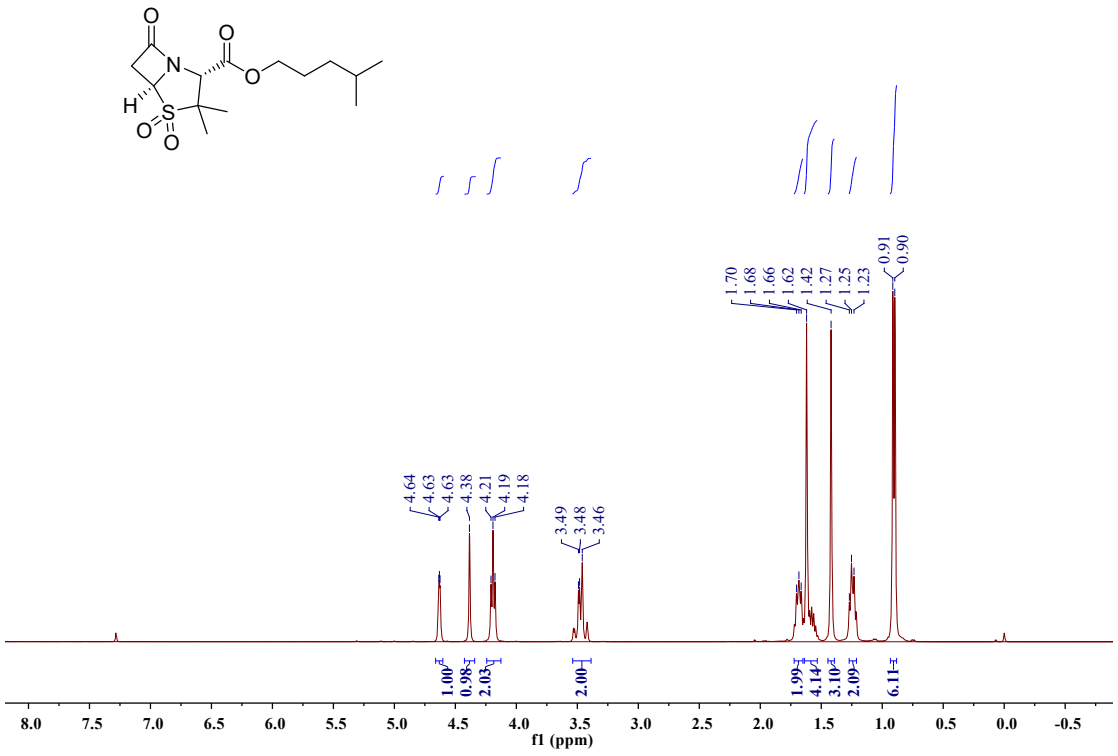


Figure S42. ^{1}H NMR of 4-Methylpentyl (2S,5R)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide.

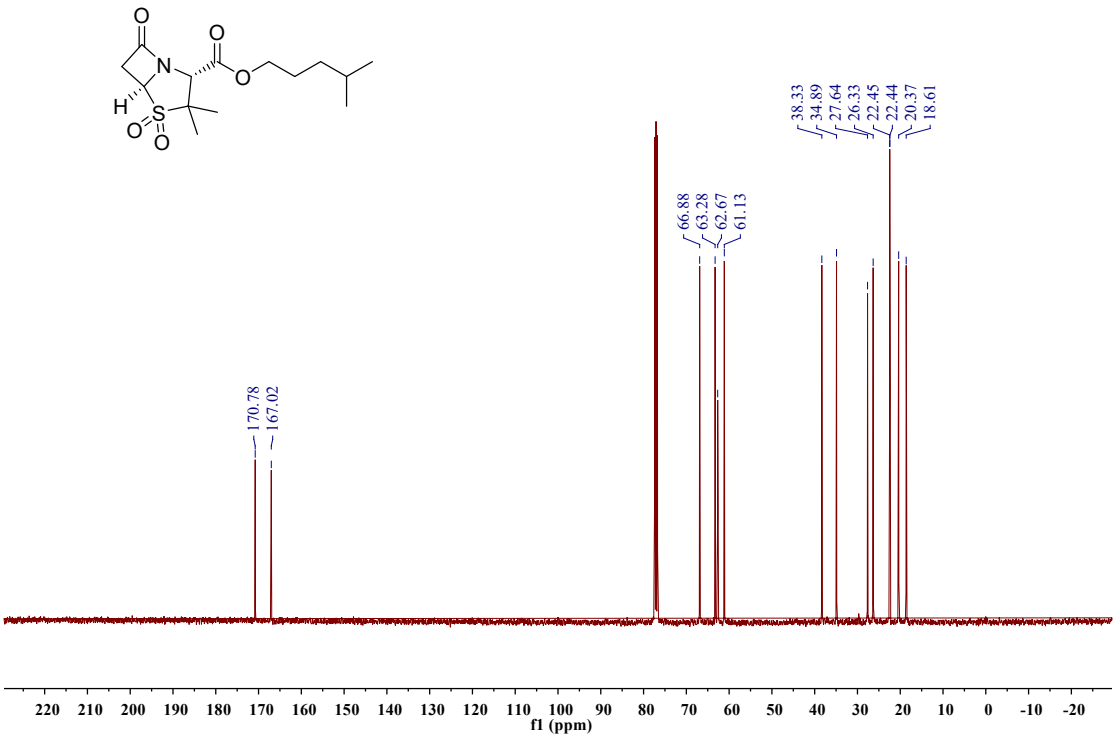


Figure S43. ^{13}C NMR of 4-Methylpentyl (2S,5R)-3,3-dimethyl-7-oxo-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylate 4,4-dioxide.

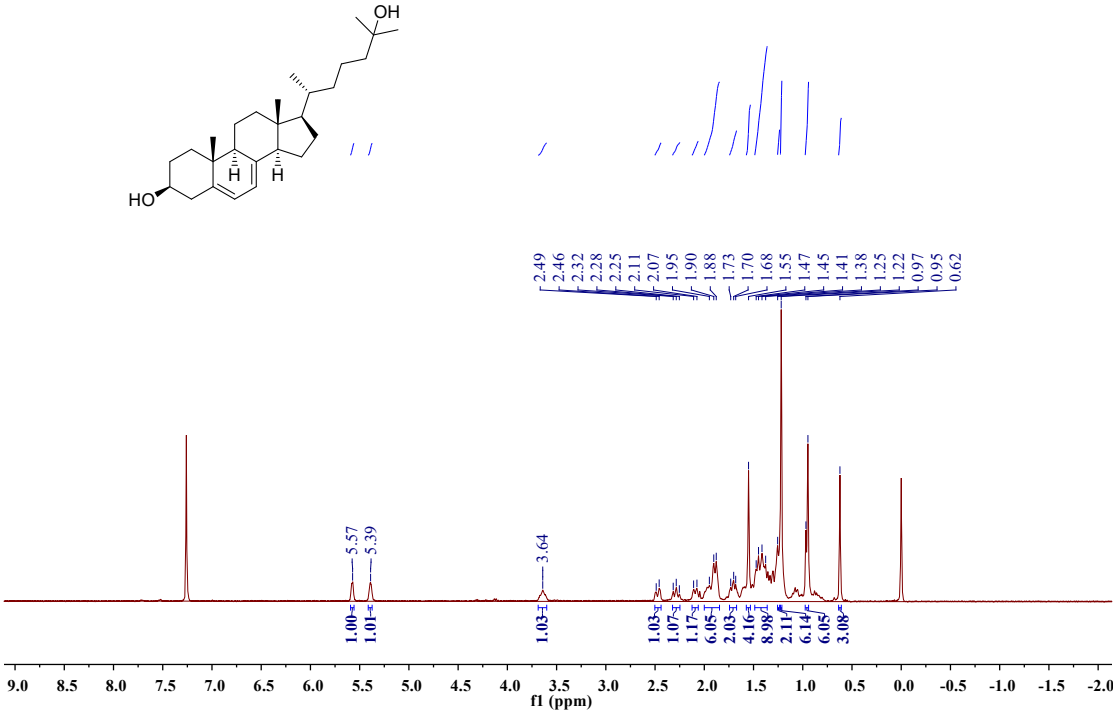


Figure S44. ^{1}H NMR of 25-hydroxy-7-DHC.

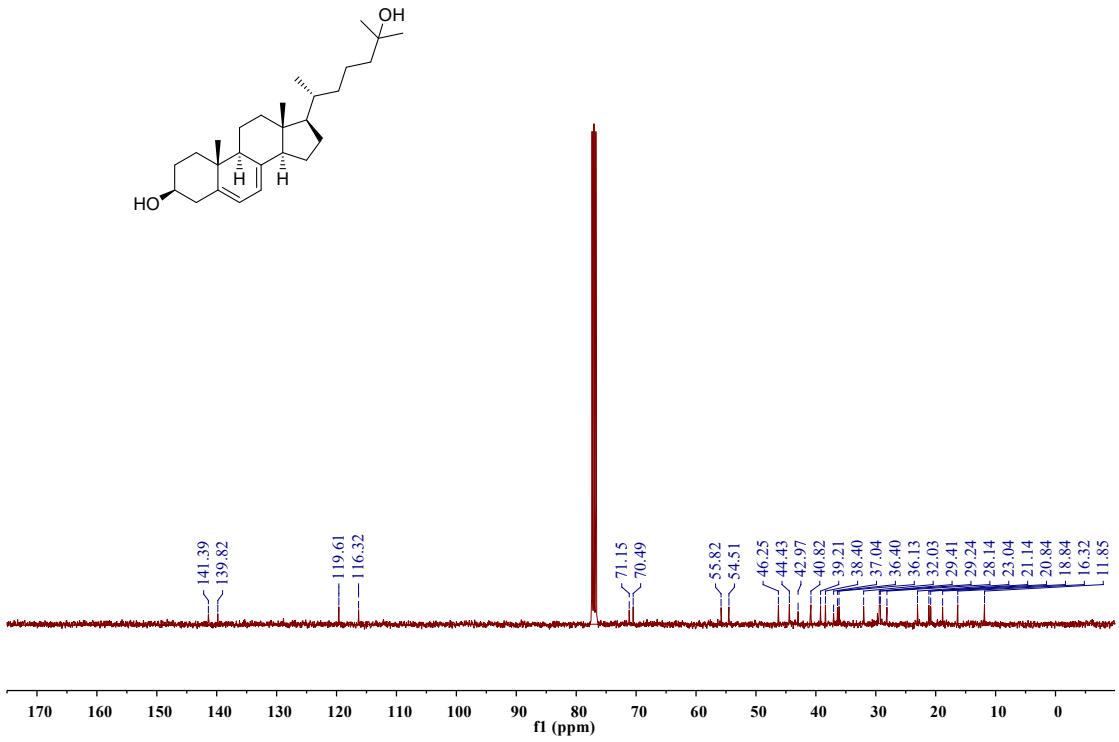
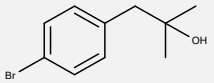
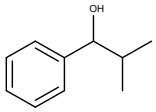
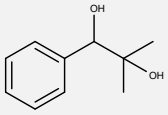
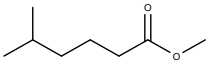
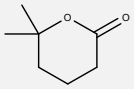
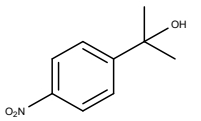
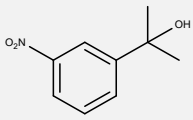
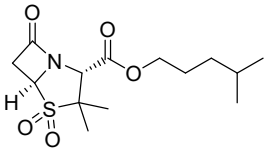
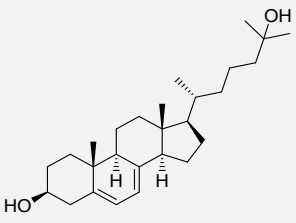


Figure S45. ^{13}C NMR of 25-hydroxy-7-DHC.

Table S1. List of NRM chemical shift

Compound	^{1}H NMR chemical shift	^{13}C NRM chemical shift
	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 1H), 2.72 (s, 1H), 1.22 (s, 3H).	^{13}C NMR (101 MHz, $CDCl_3$) δ 136.82 (s), 132.18 (s), 131.25 (s), 120.54 (s), 70.68 (s), 49.08 (s), 29.23 (s).
	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 5H), 4.35 (d, *J* = 6.6 Hz, 1H), 1.95 (dd, *J* = 13.5, 6.7 Hz, 1H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 3H).	^{13}C NMR (101 MHz, $CDCl_3$) δ 143.79 (s), 128.32 (s), 127.55 (s), 126.71 (s), 80.18 (s), 35.40 (s), 19.14 (s), 18.39 (s).
	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.28 (m, 5H), 4.52 (d, *J* = 3.2 Hz, 1H), 2.62 (d, *J* = 3.3 Hz, 1H), 2.10 (s, 1H), 1.24 (s, 3H), 1.10 (s, 3H).	^{13}C NMR (101 MHz, $CDCl_3$) δ 140.55 (s), 127.93 (d, *J* = 15.8 Hz), 127.43 (s), 80.92 (s), 73.46 (s), 26.59 (s), 23.86 (s).
	^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 3H), 2.29 (t, *J* = 7.6 Hz, 2H), 1.64 (dd, *J* = 15.6, 7.8 Hz, 2H), 1.59 – 1.50 (m, 1H), 1.24 – 1.15 (m, 2H), 0.88 (d, *J* = 6.6 Hz, 6H).	^{13}C NMR (101 MHz, $CDCl_3$) δ 174.30 (s), 51.40 (s), 38.38 (s), 34.31 (s), 27.75 (s), 22.84 (s), 22.44 (s).
	^{1}H NMR (400 MHz, $CDCl_3$) δ 2.49 (t, *J* = 6.9 Hz, 1H), 1.95 – 1.86 (m, 1H), 1.75 (dd, *J* = 7.6, 4.7 Hz, 1H), 1.41 (s, 3H).	^{13}C NMR (101 MHz, $CDCl_3$) δ 171.26 (s), 82.20 (s), 33.91 (s), 29.13 (s), 28.75 (s), 16.85 (s).
	^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.7 Hz, 1H), 7.66 (d, *J* = 8.7 Hz, 1H), 1.62 (s, 3H).	^{13}C NMR (101 MHz, $CDCl_3$) δ 156.41 (s), 146.75 (s), 125.52 (s), 123.52 (s), 72.56 (s), 31.79 (s).
	^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 1.63 (s, 6H).	^{13}C NMR (101 MHz, $CDCl_3$) δ 151.27 (s), 148.34 (s), 130.83 (s), 129.25 (s), 121.82 (s), 119.75 (s), 72.35 (s), 31.87 (s).
	^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (dd, *J* = 11.0, 7.7 Hz, 1H NMR (400 MHz, CDCl3) δ 4.66 – 4.60 (m, 1H), 4.38 (s, 1H), 4.19 (t, J = 6.6 Hz, 2H), 3.54 – 3.39 (m, 2H), 1.72 – 1.65 (m, 2H), 1.62 (s, 4H), 1.42 (s, 3H), 1.27 – 1.21 (m, 2H), 0.91 (d, J = 6.5 Hz, 6H).	^{13}C NMR (101 MHz, $CDCl_3$) δ 170.78 (s), 167.02 (s), 66.88 (s), 63.28 (s), 62.67 (s), 61.13 (s), 38.33 (s), 34.89 (s), 27.64 (s), 26.33 (s), 22.44 (d, *J* = 1.6 Hz), 20.37 (s), 18.61 (s).
	^{1}H NMR (400 MHz, $CDCl_3$) δ 5.57 (s, 1H), 5.39 (s, 1H), 3.64 (s, 1H), 2.47 (d, *J* = 12.0 Hz, 1H), 2.28 (t, *J* = 12.5 Hz, 1H), 2.09 (d, *J* = 13.5 Hz, 1H), 2.00 – 1.85 (m, 6H), 1.74 – 1.67 (m, 2H), 1.55 (s, 4H), 1.43 (dd, *J* = 26.3, 12.2 Hz, 9H), 1.24 (s, 2H), 1.22 (s, 6H), 0.96 (d, *J* = 8.1 Hz, 6H), 0.62 (s, 3H).	^{13}C NMR (101 MHz, $CDCl_3$) δ 141.39 (s), 119.61 (s), 116.32 (s), 71.15 (s), 70.49 (s), 55.82 (s), 54.51 (s), 46.25 (s), 44.43 (s), 42.97 (s), 40.82 (s), 39.21 (s), 38.40 (s), 37.04 (s), 36.40 (s), 36.13 (s), 32.03 (s), 29.32 (d, *J* = 17.3 Hz), 28.14 (s), 23.04 (s), 21.14 (s), 20.84 (s), 18.84 (s), 16.32 (s), 11.85 (s).

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