Supporting Information for

Enantiocomplementary Synthesis of Chiral 2,3-Dihydroxy Aryl Ketones via ThDP-Dependent Enzymatic Catalysis

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1. General information

Reagents for molecular biology were obtained from TOYOBO, Thermo Scientific and Omega Biotek. Kanamycin, Ampicillin and isopropyl-*β*-D-thiogalactopyranoside (IPTG) were purchased from Shanghai Yuanye Biotechnology *Co. Ltd.* The medium used in the laboratory is lysogeny broth medium (LB) containing 10 g/L tryptone, 5 g/L yeast extract and 10 g/L NaCl. All chemical reagents and all substrates were obtained from commercial sources unless otherwise noted, including aromatic aldehyde.

Thin-layer chromatography (TLC) analysis was carried out on silica gel GF254 plates, with visualization under UV light at 254 nm. The column chromatography separation was carried out using 200-300 mesh silica gel. The samples were analyzed by an Agilent HPLC system equipped with a variable wavelength detector (VWD), using Avantor ACE 5 C18-PFP column (250 mm × 4.6 mm, 5 μm, Agilent) and chiral Daicel Chiralpak IA column (250 mm × 4.6 mm, 5 μm). ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded on a Bruker AMX400 spectrometer. The following reference values were used: $CDCl_3$ (^{1}H NMR: δ 7.26; ^{13}C NMR: δ 77.16), DMSO-d_6 (^{1}H NMR: δ 2.50; ^{13}C NMR: δ 39.52) D_2O (^{1}H NMR: δ 4.79), Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets. High resolution mass spectra (HRMS) (EI－) were recorded on Thermo Scientific Q Exactive Orbitrap mass spectrometer. The enantiomeric excess (ee.) was determined by normal phase-high performance liquid chromatography using *n*-hexane and isopropanol as mobile phase. The yields measured by reversed phase-high performance liquid chromatography (RP-HPLC) were calculated with calibration curves. The mobile phase used in RP-HPLC was formic acid water (0.1%） and acetonitrile (60% : 40% respectively).

2. Expression of recombinant ThDP-dependent enzymes

The genes of the ThDP-dependent enzymes were all synthesized by Nanjing Genscript Biotechnology *Co., Ltd.* Recombinant ThDP-dependent enzymes cloned into pET28a (+) or pET21a (+) were expressed in *E. coli* BL21 (DE3) cell and were cultivated overnight at 37 °C in 4 mL LB supplemented with 50 μg/mL ampicillin or kanamycin. Then the culture was transferred into 100 mL LB containing 50 μg/mL ampicillin or kanamycin at a 1% inoculation volume in a 250 mL baffled flask and incubated at 37 ℃ and 220 rpm. When the OD_{600} reached 0.6~0.8, it was then cooled in an ice bath for 25 minutes and 1.0 mM IPTG (final concentration) was to induce protein expression at 16 ℃ for 18-20 h. The cells were collected by centrifugation at 9,000 rpm and pour out the upper liquid, then the stored at -40 ℃ for the purity of enzymes or the subsequent whole-cell reaction immediately.

3. Screening procedure of wild-type ThDP-dependent enzymes

The analytical reaction mixture contained benzaldehyde (**1a**, 0.04 mmol, 100 mM), 1,4-dioxane-2,5-diol (**2**, 0.04 mmol, 100 mM), 5% DMSO (v/v), 0.15 mM ThDP, 2.5 mM $MgSO_4$ and whole cell of wild-type enzymes in potassium phosphate buffer (100 mg/mL, PBS, 50 mM, pH 8.0, 0.4 mL). For the *Pa*BAL reaction condition: (**1a**, 0.02 mmol, 50 mM), 1,4-dioxane-2,5-diol (**2**, 0.02 mmol, 50 mM), 5% DMSO (v/v), 0.15 mM ThDP, 2.5 mM $MgSO_4$ and whole cell (200 mg/mL, PBS, 50 mM, pH 8.0, 0.4 mL). The reaction mixture was shaken at 30 ℃ for 12 h or 24 h and then added 1 mL MeOH to quench the reaction and the yields were measured using HPLC based on the calibration curves.

4. Construction of *Pf*BAL and *Pa*BAL libraries

4.1 Molecular docking

The crystal structure of *Pf*BAL (PDB code: 3D7K) was gained in the PDB database (as receptor) and the homology model of *Pa*BAL was constructed by AlphaFold 2[1](as receptor) and the volume of the binding pocket were shown online (https://proteins.plus/), assisting in handling docking ligand (the product of the Breslow intermediate attacking the **1a**) into the receptor. Molecular docking study was performed with the AutoDock vina (1.1.2) software[2]. Then *Pf*BAL and *Pa*BAL molecular was removed water and added hydrogen atoms and the energy of ligand was minimized by Chemdraw 3D for the docking. To include all possible binding conformations, a large grid box centered at the sulfur atom of ThDP comprising 70 × 70 × 70 girds with the grid spacing of 0.375 Å was used for the docking calculations. The lowest-energy conformation was selected and visualized in PyMOL. The selected hot sites within 4 Å of the *Pf*BAL active pocket were A28, L112, Q113 and the optional sites within 4 Å of the *Pa*BAL active pocket were L116, Q117, G396, H417, G421, M480, M556, Y571 for site-directed saturation mutagenesis (SSM) (**Figure S2A** and **S2B**).

4.2 PCR procedure of *Pf*BAL and *Pa*BAL

To construct the *Pf*BAL and *Pa*BAL mutants, specific primers were designed based on the intended amino acid substitutions (**Tables S2-S4**, **S6-S14**). The wild-type *Pf*BAL and *Pa*BAL plasmid or constructed mutant plasmids served as the templates for PCR amplification. PCR was performed in a total volume of 25 μL, containing 0.5 μL plasmid template, 1 μL of each forward and reverse primer, 12.5 μL of KOD One™ PCR Master Mix, and 11 μL of ddH_2O. The thermal cycling conditions were as follows: initial denaturation at 98 °C for 45 s; 30 cycles of 98 °C for 15 s, annealing at (minimum Tm-5) °C for 30 s, and extension at 68 °C for 150 s; followed by a final extension at 68 °C for 150 s. The PCR products were purified using a PCR Clean-Up Kit and directly transformed into *E. coli* BL21 (DE3) competent cells. The transformation mixture was spread on LB-agar plates supplemented with 50 μg/mL ampicillin or kanamycin and

incubated overnight at 37 °C. Single colony from each plate was picked into 4 mL of LB broth containing 50 μg/mL ampicillin or kanamycin in 10 mL culture tubes and grown overnight at 37 °C. Then DNA was sequenced by Tsingke Biotech (Beijing, China) and subsequently used for large-scale culture.

5. Screening of *Pf*BAL and *Pa*BAL mutant libraries and purification of *Pa*BAL M3 mutants

For *Pf*BAL mutant libraries: The analytical reaction mixture was composed of **1a** (0.04 mmol, 100 mM), compound **2** (0.04 mmol, 100 mM), 5% (v/v) DMSO, ThDP (0.15 mM), $MgSO_4$ (2.5 mM), and 0.4 mL of 50 mM PBS (pH 8.0) containing 60 mg/mL whole cells of *Pf*BAL mutants.The reaction mixture was shaken at 30 °C for 6 h and then added 1 mL MeOH to quench the reaction and the yields were determined using RP-HPLC analysis based on the calibration curves.

For *Pa*BAL mutant libraries: The analytical reaction mixture was composed of **1a** (0.02 mmol, 50 mM), compound **2** (0.02 mmol, 50 mM), 5% (v/v) DMSO, ThDP (0.15 mM), $MgSO_4$ (2.5 mM), and 0.4 mL of 50 mM PBS (pH 8.0) containing 200 mg/mL whole cells of *Pa*BAL mutants. The reaction mixture was shaken at 30 °C for 24 h and then added 1 mL MeOH to quench the reaction and the yields were determined using RP-HPLC analysis based on the calibration curves.

Purification of *Pa*BAL M3 mutants

The fresh wet cells containing *Pa*BAL M3 mutants were resuspended in 50 mM phosphate buffer (PBS). After sonication, the crude lysate containing 6×His-tagged proteins were loaded into Ni-NTA affinity chromatography. The target proteins were subsequently eluted with elution buffer containing 200 mM imidazole, 50 mM potassium phosphate (pH 8.0). The eluted fraction was dialyzed using 30 kDa molecular weight cut-off (MWCO) ultrafiltration tubes centrifuged at 3,200 rpm for 4 times. The final protein concentration was determined in triplicate by measuring the absorbance at 280 nm using a NanoDrop spectrophotometer, with extinction coefficients corrected via the ExPASy ProtParam tool (https://web.expasy.org/protparam/). The purified enzymes were stored at –80 °C for subsequent assays (SDS-PAGE in **Figure S7**).

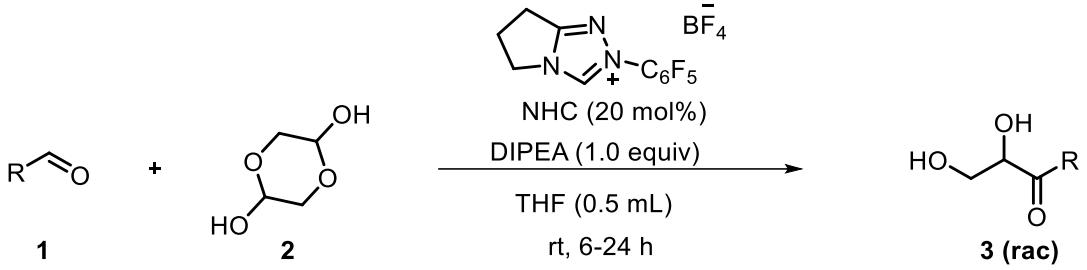
6. The activity assay of *Pa*BAL and *Pa*BAL M3

One unit (U) is defined as the amount of enzyme that catalyzes the formation of 1 μmol of 2,3-dihydroxy aryl ketone from aldehydes per minute at 30 °C.

The reaction mixture (400 μL) was composed of **1a** (5 mM or 10 mM), compound **2** (5 mM or 10mM), 5% (v/v) DMSO, ThDP (0.15 mM), $MgSO_4$ (2.5 mM), 50 mM PBS (pH 8.0). The reaction was initiated by adding pure enzyme (1 mg). After all additions, shake the reaction at 30 °C for 10-30 minutes. It was then quenched with 1 mL of MeOH

and centrifuged at 12,000 rpm for 1 minutes. The product was analyzed by RP-HPLC using an ACE 5 C18-PFP column (mobile phase: H_2O with 0.1% formic acid and CH_3CN in a 60 : 40 ratio) based on the calibration curves.

7. General procedure for the synthesis of racemic 2, 3-dihydroxyketone



To a solution of aldehyde **1** (0.05 mmol) and **2** (2.0 equiv.) in THF (0.5 mL) was added NHC (20 mol%), followed by *N,N*-diisopropylethylamine (DIPEA, 1.0 equiv.). The mixture was stirred at room temperature for 24 h. The reaction mixture was then directly subjected to preparative thin-layer chromatography (prep-TLC) to obtain the racemic products **3**. The silica gel band containing the target product **3** was collected, and the product was eluted with ethanol. The resulting solution was filtered through a membrane filter to prepare a sample for HPLC analysis for chiral resolution.

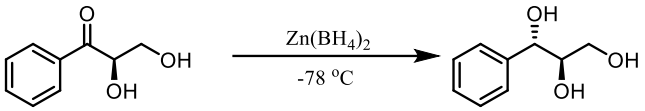
8. General procedure for exploring the substrate scope

***Pf*BAL_A28S**: The reaction mixture contains substrate **1** (0.04 mmol, 100 mM), **2** (0.04 mmol, 100 mM), DMSO (5%, v/v), ThDP (0.15 mM), $MgSO_4$ (2.5 mM) and PBS (50 mM, pH 8.0, 0.4 mL) supplemented with 60 mg/mL whole cell of *Pf*BAL_A28S. And the reactions were shaken at 1000 rpm, 30 °C for 12 h on the dry thermostat metal bath JX-10. (The reaction of **1k**, **1o** and **1s** used at the 120 mg/mL whole cell of *Pf*BAL_A28S and the reaction time for 24 h). Then 1mL EtOAc was added to the reaction (three times) and extracted the products by centrifugation at 12,000 rpm for 1 min. The product was concentrated by the rotary evaporator and added 0.5 mL EtOAc containing 1,3,5-trimethoxybenzene (0.5 equiv.) as internal standard. The yields were determined by ^{1}H NMR.

***Pa*BAL M3**: The reaction mixture contains substrate **1** (0.02 mmol, 33 mM), **2** (0.02 mmol, 33 mM), DMSO (5%, v/v), ThDP (0.15 mM), $MgSO_4$ (2.5 mM), 0.3% loading of the *Pa*BAL M3 purified enzyme and PBS (50 mM, pH 8.0, 384.75 μL) in total 0.5 mL. And the reactions were shaken at 1000 rpm and 30 °C for 24 h on the dry thermostat metal bath JX-10. 1 mL MeOH was added into the mixture and centrifuge mixture at 12,000 rpm for 1 min. The yields were determined based on the calibration curves using RP-HPLC.

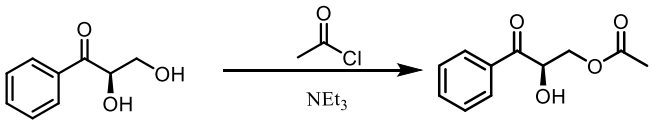
9. Transformation

9.1 The chemical transformation of chiral 2, 3-dihydroxy aryl ketone 3a[3]



3a **4a**

3a (0.6 mmol) was dissolved in dry DCM (4 mL) and placed in -78 °C stirring for 5 min under N_2 atmosphere, $Zn(BH_4)_2$ (2 equiv.) was added drowisely with stirring. The reaction was stirred for 2 h at this temperature before being quenched by the addition of saturated aqueous solution of ammonium chloride (approximately 5 mL). The mixture was extracted with DCM (note: most of product **4a** exist in aqueous phase) and the pure compound **4a** was purified by silica gel flash chromatography.



3a **4b**

To the solution of **3a** (0.6 mmol) dissolved in a 10 mL round bottomed flask was added NEt_3(1.5 equiv.), acetyl chloride (1.02 equiv.) was added dropwise at 0 °C. Then the reaction warmed to room temperature with stirring for 2 h and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography to afford product **4b**.

9.2 Scaled-up biotransformation of 3a, 3c, 3d and 3o

A 40 mL-scale preparative reaction consisted of substrate **1a** (4 mmol), **2** (4 mmol), 5% (v/v) DMSO, 0.15 mM ThDP, 2.5 mM $MgSO_4$, and 40 mL of 60 mg/mL *Pf*BAL_A28S whole-cell suspension in 50 mM PBS buffer (pH 8.0). The mixture was shaken at 220 rpm and 30 °C for 24 h. The reaction mixture was extracted with EtOAc (80 mL × 4), dried over anhydrous Na_2SO_4, and concentrated by rotary evaporation. The residue was purified via column chromatography to yield product **3a** (0.59 g, 89% ee). The procedure of products **3c, 3d** and **3o** was similar to that of **3a.**

10. Supplementary Figures

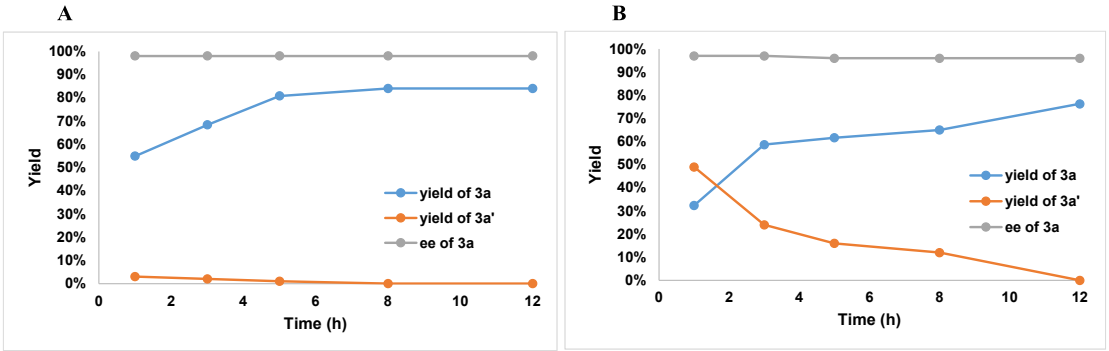


Figure S1. Reaction progress curve. A) process of *Pf*BAL_A28S catalysis; B) process

of wild-type *Pf*BAL catalysis.

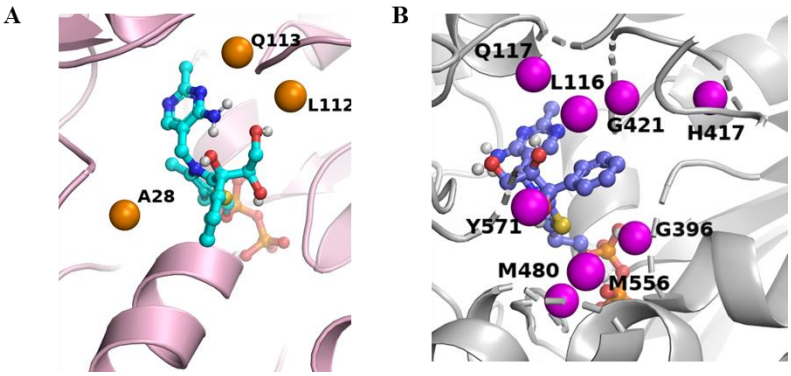


Figure S2. (**A**) Three hotpots of *Pf*BAL active pocket, shown in orange spheres; (**B**) Eight hotpots of *Pa*BAL active pocket, shown in magenta spheres.

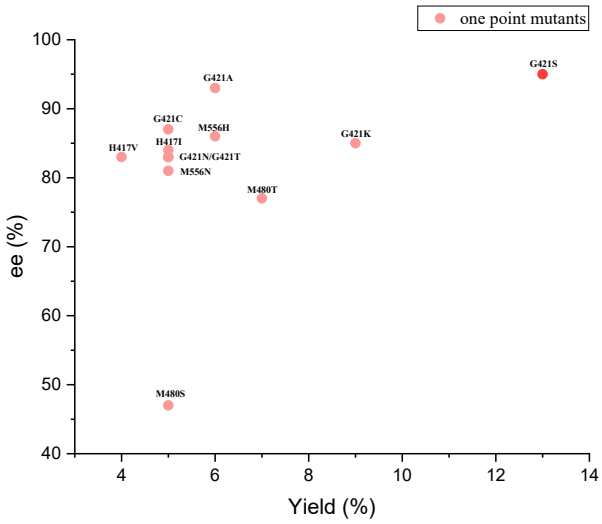


Figure S3. The result of the first round of mutation of *Pa*ABL. Only the part of mutants that showed a response were displayed and *Pa*BAL_G421S was the best mutant that showed by red colour. And the other mutants not shown had no or trace response. The reaction condition: **1a** (0.02 mmol, 50 mM), **2** (0.02 mmol, 50 mM), DMSO (5%, v/v), ThDP (0.15 mM), $MgSO_4$ (2.5 mM) and PBS (50 mM, pH 8.0, 0.4 mL) containing 200 mg/mL whole cell of *Pa*BAL mutants, 30 °C, 24 h.

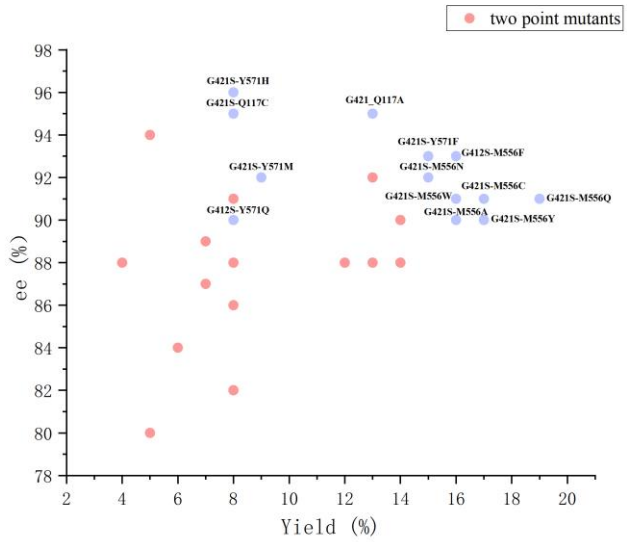


Figure S4. The result of the second round of mutation of *Pa*ABL. Only the part of mutants that showed a response were displayed. The magenta spheres respectively indicated the best second round of mutants of G421_Q117, G421_M556 and G421_Y571. The reaction reaction: **1a** (0.02 mmol, 50 mM), **2** (0.02 mmol, 50 mM), DMSO (5%, v/v), ThDP (0.15 mM), $MgSO_4$ (2.5 mM) and PBS (50 mM, pH 8.0, 0.4 mL) containing 200 mg/mL whole cell of *Pa*BAL mutants, 30 ℃, 24 h.

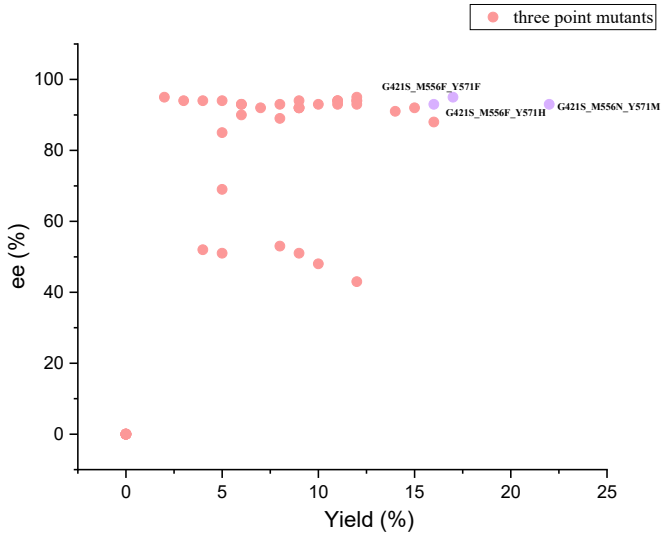


Figure S5. The result of the third of mutation of *Pa*ABL. Some points overlap multiple mutants. The pink spheres respectively indicated the relatively good third round of mutants of G421_M556F_571F, G421_M556N_571M and G421_M556F_Y571H. The reaction reaction: **1a** (0.02 mmol, 50 mM), **2** (0.02 mmol, 50 mM), DMSO (5 %, v/v), ThDP (0.15 mM), $MgSO_4$ (2.5 mM) and PBS (50 mM, pH 8.0, 0.4 mL) containing 200 mg/mL whole cell of *Pa*BAL mutants, 30 ℃, 24 h.

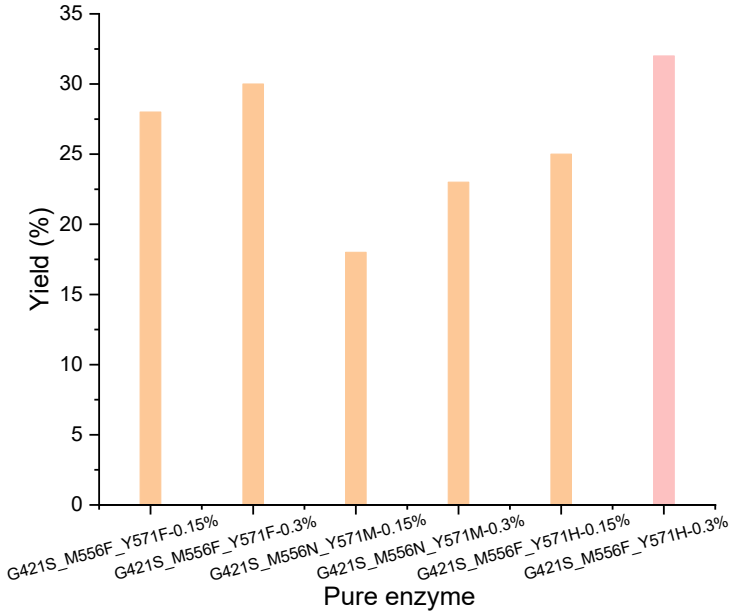


Figure S6. The result of different loading of pure *Pa*ABL mutants in the third round campaign. The reaction reaction: **1a** (0.02 mmol, 50 mM), **2** (0.02 mmol, 50 mM), DMSO (5%, v/v), ThDP (0.15 mM), $MgSO_4$ (2.5 mM) and 0.15% or 0.3% loading pure *Pa*BAL mutants, 30 ℃, 24 h.

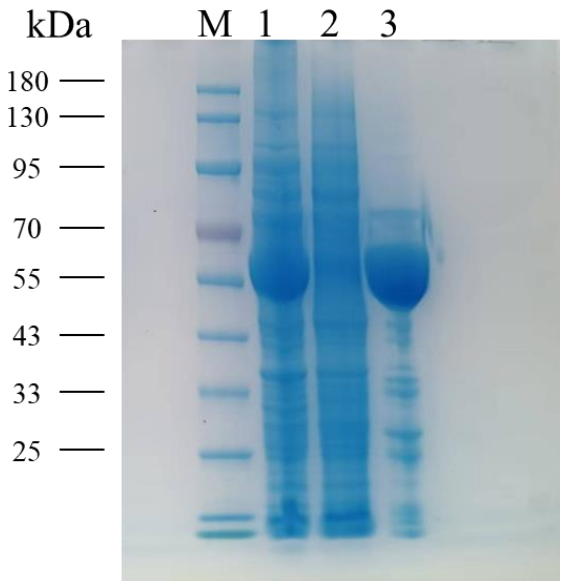


Figure S7. SDS-PAGE. M: protein maker; 1: crude *Pf*BAL_A28S; 2: crude *Pa*BAL; 3: *Pa*BAL M3 (pure). (Molecular weight of *Pf*BAL: 58.9 kDa; *Pa*BAL: 59.5 kDa)

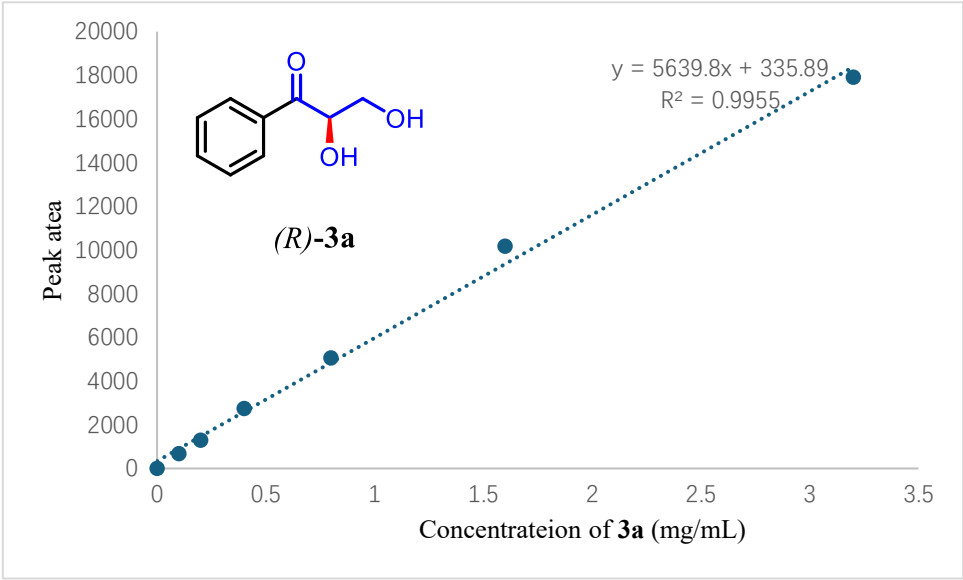


Figure S8. Calibration curve of **3a** used for yield determination by RP-HPLC

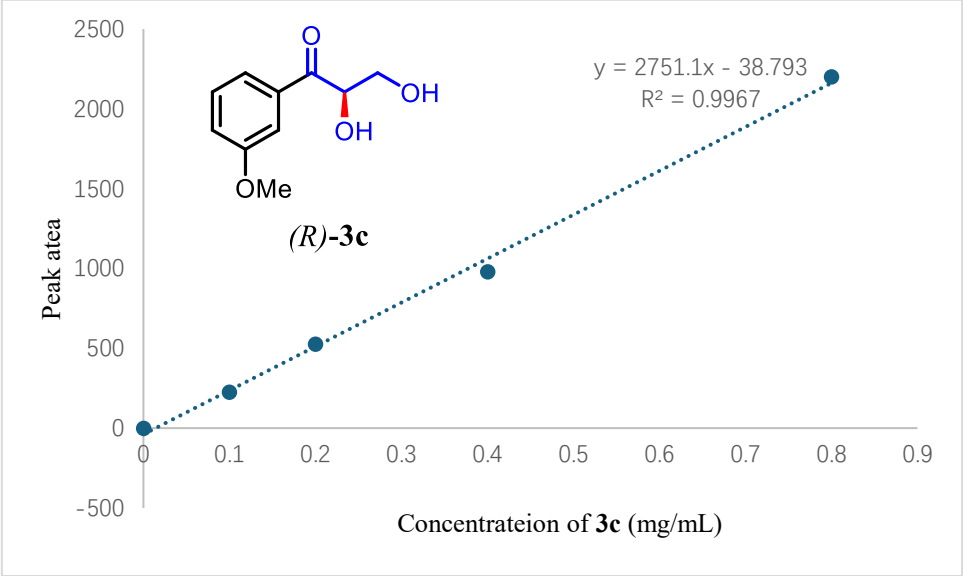


Figure S9. Calibration curve of **3c** used for yield determination by RP-HPLC.

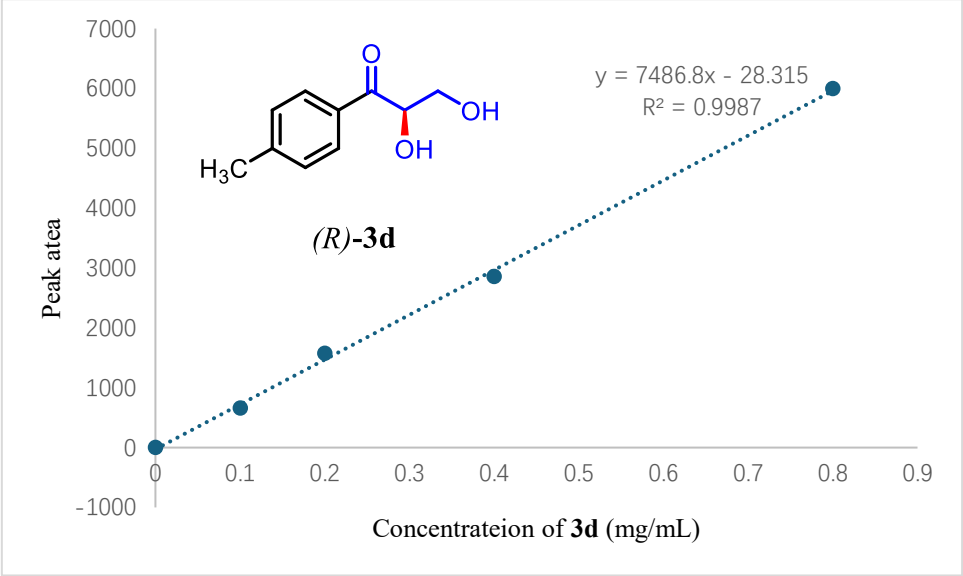


Figure S10. Calibration curve of **3d** used for yield determination by RP-HPLC.

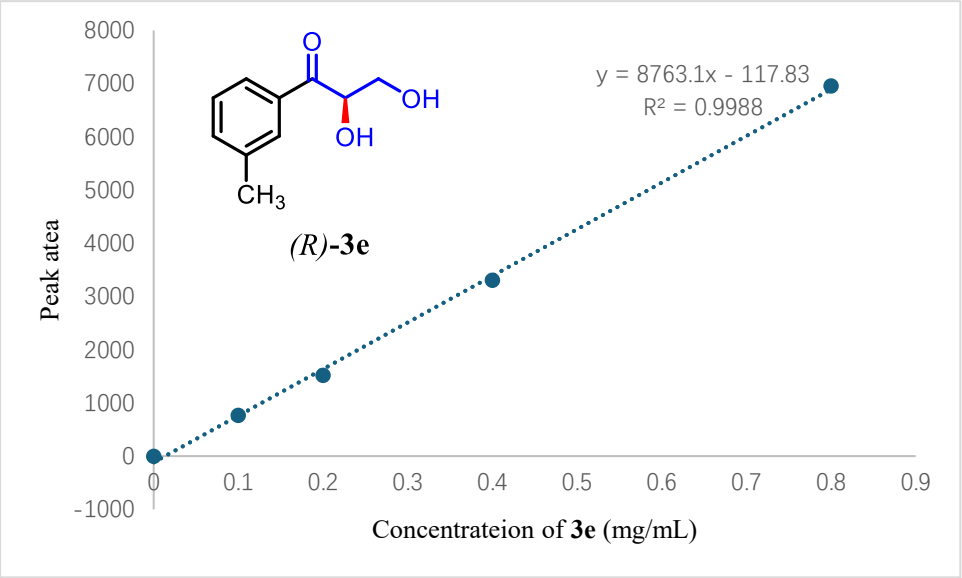


Figure S11. Calibration curve of **3e** used for yield determination by RP-HPLC.

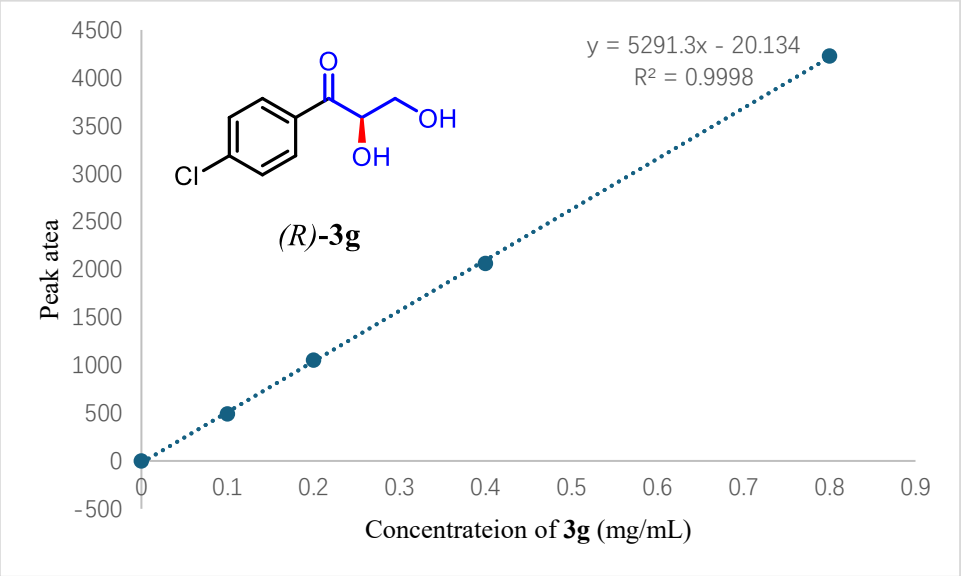


Figure S12. Calibration curve of **3g** used for yield determination by RP-HPLC.

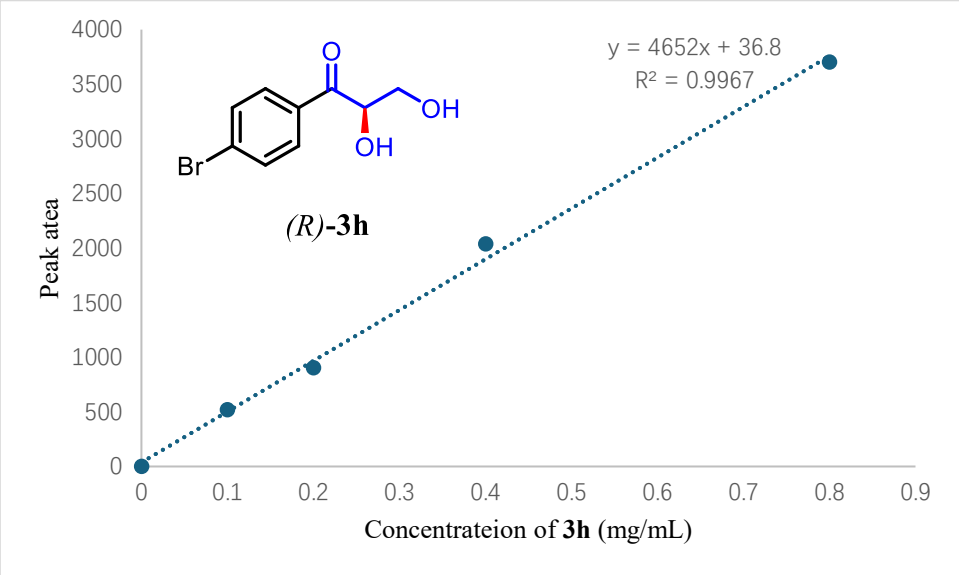


Figure S13. Calibration curve of **3h** used for yield determination by RP-HPLC.

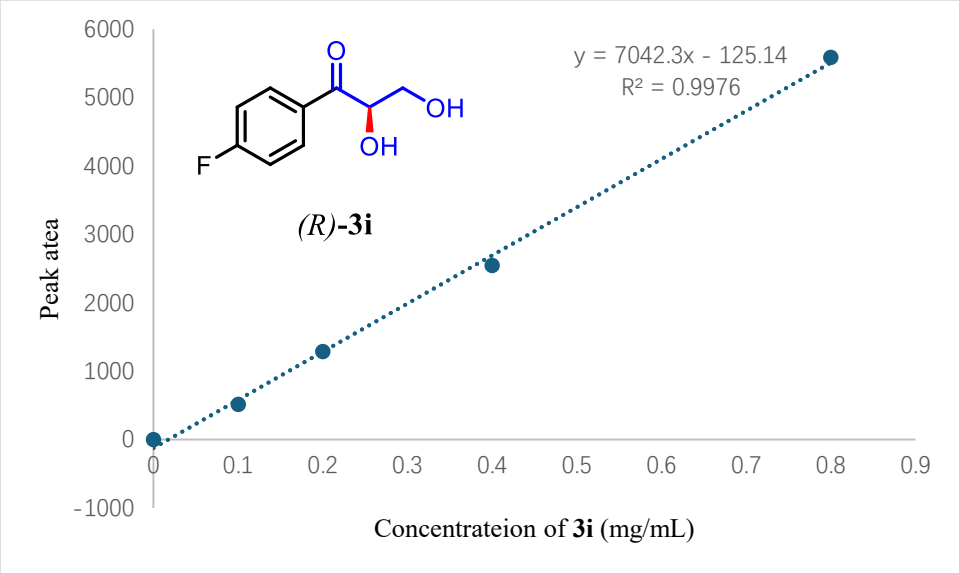


Figure S14. Calibration curve of **3i** used for yield determination by RP-HPLC.

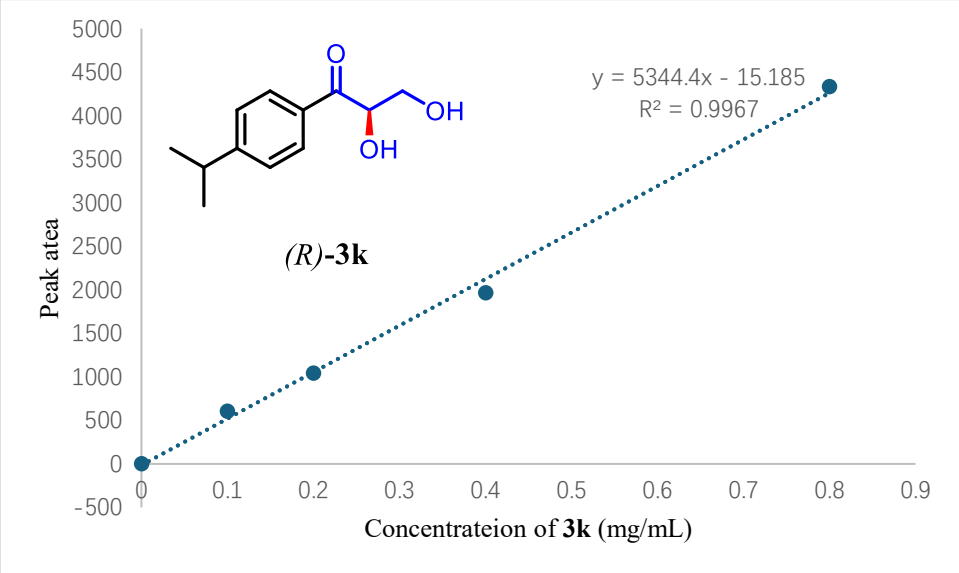


Figure S15. Calibration curve of **3k** used for yield determination by RP-HPLC.

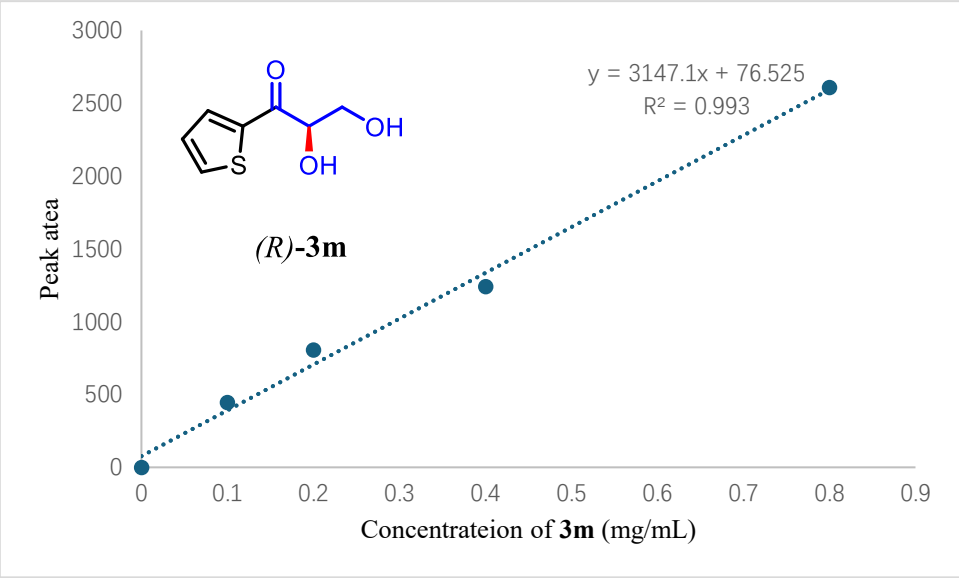


Figure S16. Calibration curve of **3m** used for yield determination by RP-HPLC.

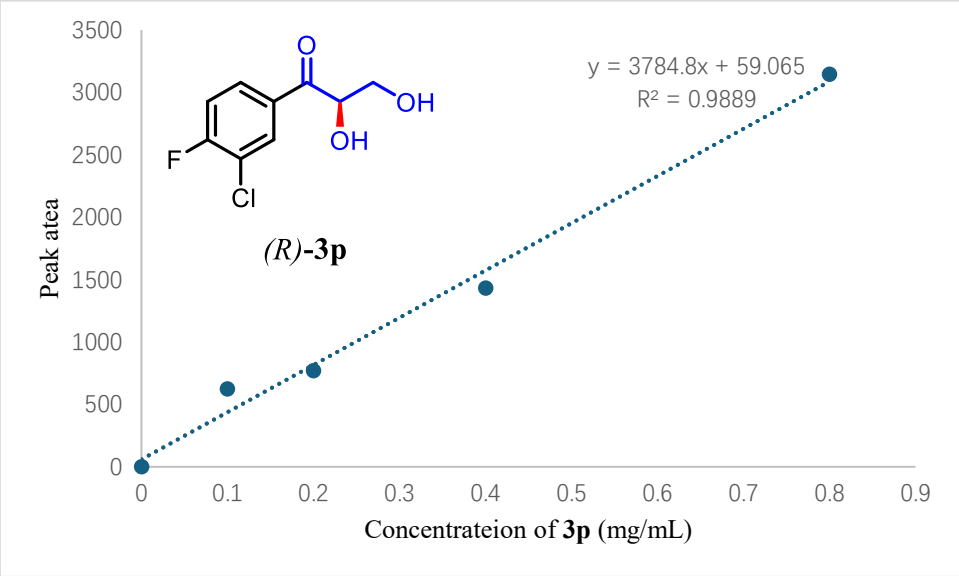


Figure S17. Calibration curve of **3p** used for yield determination by RP-HPLC.

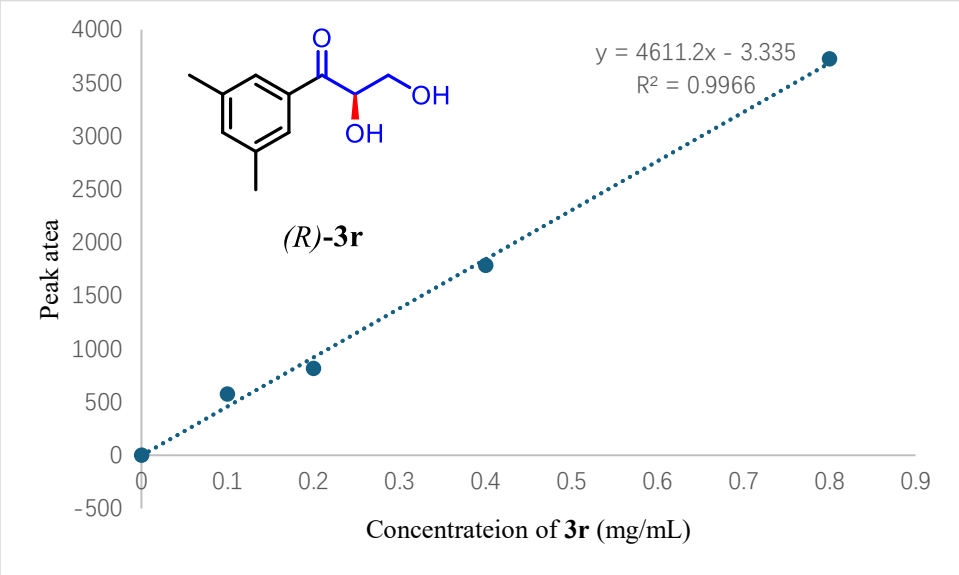


Figure S18. Calibration curve of **3r** used for yield determination by RP-HPLC.

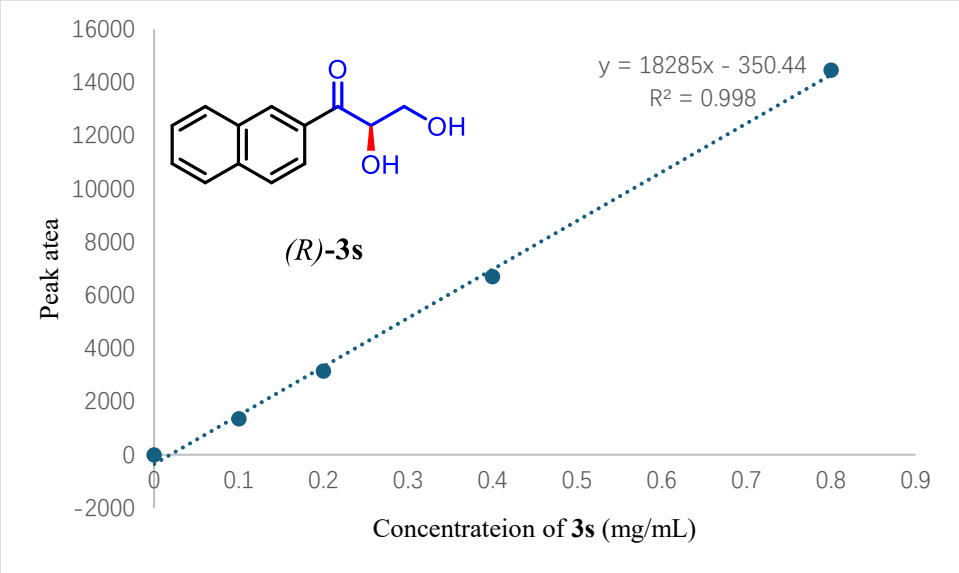


Figure S19. Calibration curve of **3s** used for yield determination by RP-HPLC.

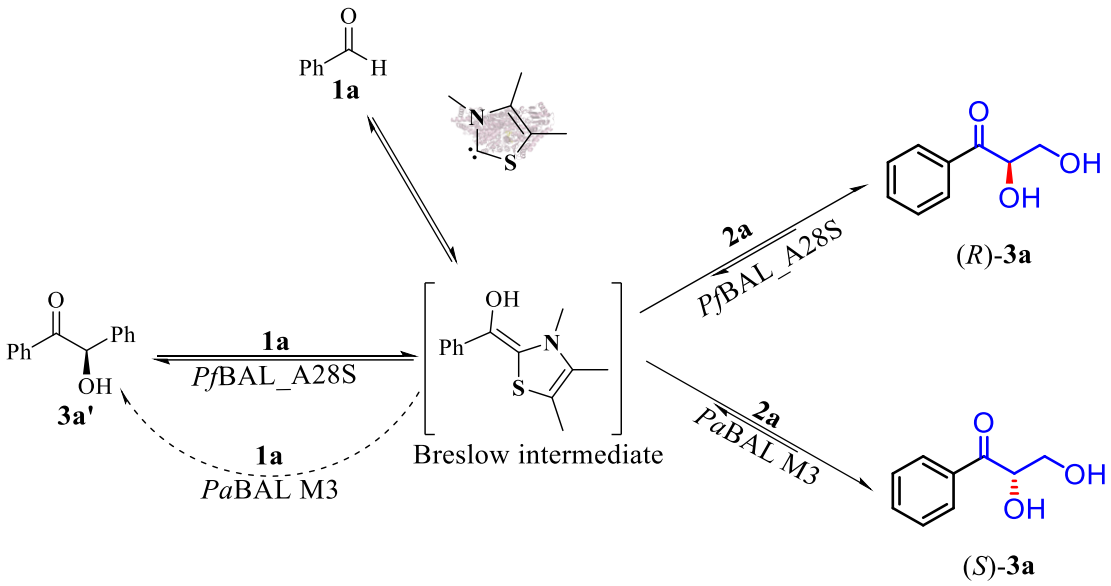


Figure S20. The reaction pathway.

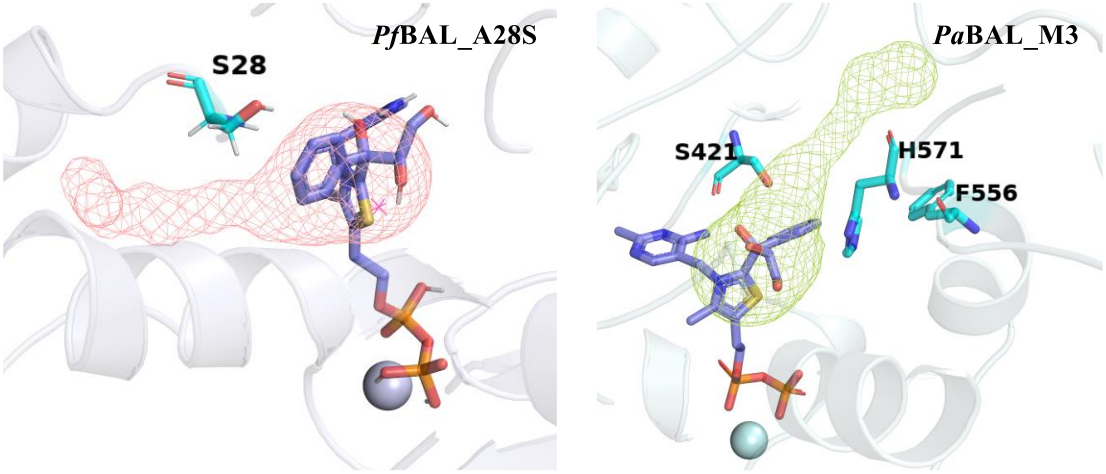
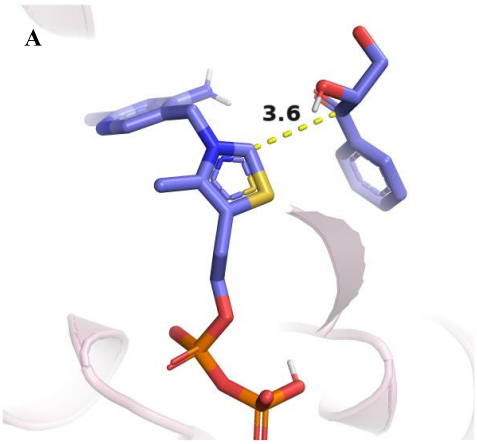
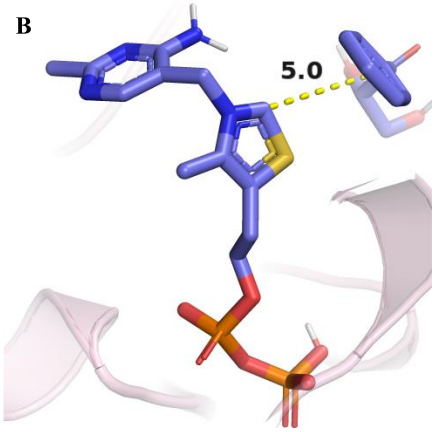


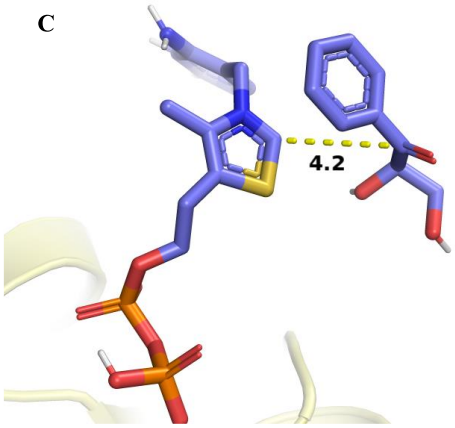
Figure S21. The substrate tunnel of *Pf*BAL_A28S and *Pa*BAL M3 respectively.



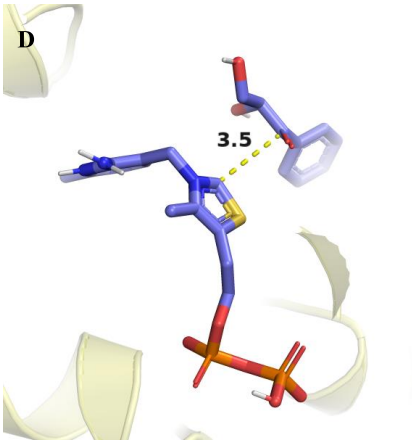
*Pf*BAL_A28S-ThDP-(*R*)-**3a**
Catalytic distance: 3.6 Å
$\Delta G_{binding}$ = -4.7 kal/mol



*Pf*BAL_A28S-ThDP-(*S*)-**3a**
Catalytic distance: 5.0 Å
$\Delta G_{binding}$ = -4.2 kal/mol



*Pa*BAL_M3-ThDP-(*R*)-**3a**
Catalytic distance: 4.2 Å
$\Delta G_{binding}$ = -1.5 kal/mol



*Pa*BAL_M3-ThDP-(*S*)-**3a**
Catalytic distance: 3.5 Å
$\Delta G_{binding}$ = -3.0 kal/mol

Figure S22. Molecular dockings of *Pf*BAL_A28S/*Pa*BAL M3 with (*R*)-**3a** or (*S*)-**3a** (ThDP and **3a** were presented in sticks; distances were showed in dashed lines). The reversible processes is demonstrated. To understand the different stereoselectivities of two enzyme pairs from the perspective of reverse reaction, molecular docking studies were performed for *Pa*BAL M3 and *Pf*BAL_A28S with both (*S*)- and (*R*)-enantiomers of **3a**, respectively. The docking results showed that the distance between the C2 of ThDP and carbonyl C of (*R*)-**3a** were 3.6 Å, clearly shorter than that of (*S*)-**3a** (5.0 Å). An opposite result was observed for *Pa*BAL M3 ($d_{ThDP-(R)\text{-}3a}$ = 4.2 Å > $d_{ThDP-(S)\text{-}3a}$ = 3.5 Å). The large distance might prevent (*S*)-**3a** from being attacked by ThDP cofactor in *Pf*BAL_A28S and prevent (*R*)-**3a** from being attacked by ThDP cofactor in *Pa*BAL M3. Therefore, *Pf*BAL_A28S just accepted (*R*)-**3a** as raw material, and *Pa*BAL M3 just accepted (*S*)-**3a** as raw material for the reverse reaction.

11. Supplementary Tables

Table S1. The information of different ThDP-dependent enzymes (existing this research group) used in this study

Entry	enzyme	source	Protein identifier
1	*Ss*BAL	*Streptomyces sp*. BK335	WP_133047913.1
2	*Su*BAL	*Streptomyces umbrinus*	WP_189844730.1
3	*As*BAL	*Actinomadura sp. KC345*	WP_131875833.1
4	*Pa*BAL	*Polymorphobacter arshaanensis*	WP_135246357.1
5	*Ec*Mend	*Escherichia coli K-12*	2JLC
6	*Ss*BFD	*Streptomyces sp. Tu 4128*	WP_122617744.1
7	*KdcA*	*Lactococcus lactis*	2VBF
8	*An*PDC	*Acinetobacter nectaris*	WP_023273611.1
9	*EcTK*	*Escherichia coli*	2R8P
10	*ScTK*	*S. cerivisiae (yeast)*	1TKA
11	*Pf*BAL	*Pseudomonas fluorescens*	3D7K

Table S2. Primers used for 28 site of *Pf*BAL

Entry	Mutants	Forward Primer (5'-3')	Reverse Primer (5'-3')
1	A28C	tgtttggtcttcacggtTGTcacattgataccatc	
2	A28D	tgtttggtcttcacggtGATcacattgataccatc	
3	A28E	tgtttggtcttcacggtGAAcacattgataccatc	
4	A28F	tgtttggtcttcacggtTTTcacattgataccatc	
5	A28G	tgtttggtcttcacggtGGTcacattgataccatc	
6	A28H	tgtttggtcttcacggtCATcacattgataccatc	
7	A28I	tgtttggtcttcacggtATTcacattgataccatc	
8	A28K	tgtttggtcttcacggtAAAcacattgataccatc	
9	A28L	tgtttggtcttcacggtCTGcacattgataccatc	
10	A28M	tgtttggtcttcacggtATGcacattgataccatc	accgtgaagaccaaacaggtgctcgacgcct
11	A28N	tgtttggtcttcacggtAATcacattgataccatc	
12	A28P	tgtttggtcttcacggtCCGcacattgataccatc	
13	A28Q	tgtttggtcttcacggtCAGcacattgataccatc	
14	A28R	tgtttggtcttcacggtCGTcacattgataccatc	
15	A28S	tgtttggtcttcacggtAGCcacattgataccatc	
16	A28T	tgtttggtcttcacggtACCcacattgataccatc	
17	A28V	tgtttggtcttcacggtGTTcacattgataccatc	
18	A28W	tgtttggtcttcacggtTGGcacattgataccatc	
19	A28Y	tgtttggtcttcacggtTATcacattgataccatc	

Table S3. Primers used for 112 site of *Pf*BAL

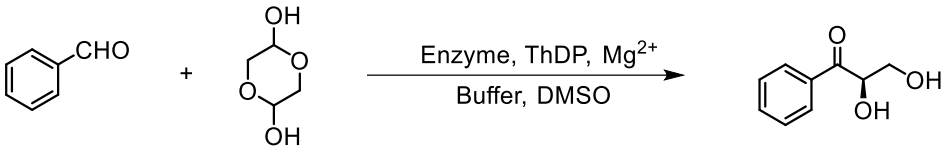
Entry	Mutants	Forward Primer (5'-3')	Reverse Primer (5'-3')
1	L112A	tgatgagacaaataccGCAcaagcgggcattga	
2	L112C	tgatgagacaaataccTGTcaagcgggcattga	
3	L112D	tgatgagacaaataccGATcaagcgggcattga	
4	L112E	tgatgagacaaataccGAAcaagcgggcattga	
5	L112F	tgatgagacaaataccTTTcaagcgggcattga	
6	L112G	tgatgagacaaataccGGTcaagcgggcattga	
7	L112H	tgatgagacaaataccCATcaagcgggcattga	
8	L112I	tgatgagacaaataccATTcaagcgggcattga	
9	L112K	tgatgagacaaataccAAAcaagcgggcattga	
10	L112M	tgatgagacaaataccATGcaagcgggcattga	ggtatttgtctcatcatcacgcagagcgccg
11	L112N	tgatgagacaaataccAATcaagcgggcattga	
12	L112P	tgatgagacaaataccCCGcaagcgggcattga	
13	L112Q	tgatgagacaaataccCAGcaagcgggcattga	
14	L112R	tgatgagacaaataccCGTcaagcgggcattga	
15	L112S	tgatgagacaaataccAGCcaagcgggcattga	
16	L112T	tgatgagacaaataccACCcaagcgggcattga	
17	L112V	tgatgagacaaataccGTTcaagcgggcattga	
18	L112W	tgatgagacaaataccTGGcaagcgggcattga	
19	L112Y	tgatgagacaaataccTATcaagcgggcattga	

Table S4. Primers used for 113 site of *Pf*BAL

Entry	Mutants	Forward Primer (5'-3')	Reverse Primer (5'-3')
1	Q113A	gagacaaataccctcGCAgcgggcattgaccaa	
2	Q113C	gagacaaataccctcTGTgcgggcattgaccaa	
3	Q113D	gagacaaataccctcGATgcgggcattgaccaa	
4	Q113E	gagacaaataccctcGAAgcgggcattgaccaa	
5	Q113F	gagacaaataccctcTTTgcgggcattgaccaa	
6	Q113G	gagacaaataccctcGGTgcgggcattgaccaa	
7	Q113H	gagacaaataccctcCATgcgggcattgaccaa	ggtatttgtctcatcatcacgcagagcgcc
8	Q113I	gagacaaataccctcATTgcgggcattgaccaa	
9	Q113K	gagacaaataccctcAAAgcgggcattgaccaa	
10	Q113L	gagacaaataccctcCTGgcgggcattgaccaa	
11	Q113M	gagacaaataccctcATGgcgggcattgaccaa	
12	Q113N	gagacaaataccctcAATgcgggcattgaccaa	
13	Q113P	gagacaaataccctcCCGgcgggcattgaccaa	
14	Q113R	gagacaaataccctcCGTgcgggcattgaccaa	

15	Q113S	gagacaaataccctcAGCgcgggcattgaccaa
16	Q113T	gagacaaataccctcACCgcgggcattgaccaa
17	Q113V	gagacaaataccctcGTTgcgggcattgaccaa
18	Q113W	gagacaaataccctcTGGgcgggcattgaccaa
19	Q113Y	gagacaaataccctcTATgcgggcattgaccaa

Table S5. The results of mutants at the amino acid residue L112 and Q113



1a **2** **3a**

		1a⟶3a				1a⟶3a	
Entry	enzyme	yield	ee.	Entry	enzyme	yield	ee.
1	L112A	0	-	1	Q113A	0	-
2	L112C	11%	91%	2	Q113C	0	-
3	L112D	0	-	3	Q113D	0	-
4	L112E	0	-	4	Q113E	0	-
5	L112F	12%	85%	5	Q113F	0	-
6	L112G	0	-	6	Q113G	0	-
7	L112H	0	-	7	Q113H	0	-
8	L112I	31%	88%	8	Q113I	0	-
9	L112K	0	-	9	Q113K	0	-
10	L112M	6%	93%	10	Q113L	0	-
11	L112N	24%	89%	11	Q113M	0	-
12	L112P	0	-	12	Q113N	0	-
13	L112Q	0	-	13	Q113P	0	-
14	L112R	0	-	14	Q113R	trace	-
15	L112S	9%	78%	15	Q113S	0	-
16	L112T	trace	-	16	Q113T	0	-
17	L112V	9%	90%	17	Q113V	0	-
18	L112W	0	-	18	Q113W	0	-
19	L112Y	0	-	19	Q113Y	0	-

Reaction conditions: **1a** (0.04 mmol, 100 mM), **2** (0.04 mmol, 100 mM), whole cell (400 uL, 60 mg/mL), ThDP (0.15 mM), $MgSO_4$ (2.5 mM), PBS buffer (50 mM, pH 8.0), DMSO (5%, v/v), 1000 rpm, 30 °C, 24 h; Yields and ee were determined by HPLC.

Table S6. Primers used for 116 site of *Pa*BAL

Entry	Mutants	Forward Primer (5'-3')	Reverse Primer (5'-3')
1	L116A	agttgaaacaaatccgGCAcagggcggtattgatca	
2	L116C	agttgaaacaaatccgTGTcagggcggtattgatca	
3	L116D	agttgaaacaaatccgGATcagggcggtattgatca	
4	L116E	agttgaaacaaatccgGAAcagggcggtattgatca	
5	L116F	agttgaaacaaatccgTTTcagggcggtattgatca	
6	L116G	agttgaaacaaatccgGGTcagggcggtattgatca	
7	L116H	agttgaaacaaatccgCATcagggcggtattgatca	
8	L116I	agttgaaacaaatccgATTcagggcggtattgatca	
9	L116K	AgttgaaacaaatccgAAAcagggcggtattgatca	
10	L116M	AgttgaaacaaatccgATGcagggcggtattgatca	cggatttgtttcaacttctctcagaggcggggcgc
11	L116N	agttgaaacaaatccgAATcagggcggtattgatca	
12	L116P	agttgaaacaaatccgCCGcagggcggtattgatca	
13	L116Q	agttgaaacaaatccgCAGcagggcggtattgatca	
14	L116R	agttgaaacaaatccgCGTcagggcggtattgatca	
15	L116S	agttgaaacaaatccgAGCcagggcggtattgatca	
16	L116T	agttgaaacaaatccgACCcagggcggtattgatca	
17	L116V	agttgaaacaaatccgGTTcagggcggtattgatca	
18	L116W	agttgaaacaaatccgTGGcagggcggtattgatca	
19	L116Y	agttgaaacaaatccgTATcagggcggtattgatca	

Table S7. Primers used for 117 site of *Pa*BAL

Entry	Mutants	Forward Primer (5'-3')	Reverse Primer (5'-3')
1	Q117A	gttgaaacaaatccgctgGCAggcggtattgatcag	
2	Q117C	gttgaaacaaatccgctgTGTggcggtattgatcag	
3	Q117D	gttgaaacaaatccgctgGATggcggtattgatcag	
4	Q117E	gttgaaacaaatccgctgGAAggcggtattgatcag	
5	Q117F	gttgaaacaaatccgctgTTTggcggtattgatcag	
6	Q117G	gttgaaacaaatccgctgGGTggcggtattgatcag	
7	Q117H	gttgaaacaaatccgctgCATggcggtattgatcag	cagcggatttgtttcaacttctctcagaggcggggc
8	Q117I	gttgaaacaaatccgctgATTggcggtattgatcag	
9	Q117K	gttgaaacaaatccgctgAAAggcggtattgatcag	
10	Q117L	gttgaaacaaatccgctgCTGggcggtattgatcag	
11	Q117M	gttgaaacaaatccgctgATGggcggtattgatcag	
12	Q117N	gttgaaacaaatccgctgAATggcggtattgatcag	
13	Q117P	gttgaaacaaatccgctgCCGggcggtattgatcag	
14	Q117R	gttgaaacaaatccgctgCGTggcggtattgatcag	

15	Q117S	gttgaaacaaatccgctgAGCggcggtattgatcag	
16	Q117T	gttgaaacaaatccgctgACCggcggtattgatcag	
17	Q117V	gttgaaacaaatccgctgGTTggcggtattgatcag	
18	Q117W	gttgaaacaaatccgctgTGGggcggtattgatcag	
19	Q117Y	gttgaaacaaatccgctgTATggcggtattgatcag	

Table S8. Primers used for 396 site of *Pa*BAL

Entry	Mutants	Forward Primer (5'-3')	Reverse Primer (5'-3')
1	G396A	ttatgtgtttgatggcGCAgaaagcagtagctgggg	
2	G396C	ttatgtgtttgatggcTGTgaaagcagtagctgggg	
3	G396D	ttatgtgtttgatggcGATgaaagcagtagctgggg	
4	G396E	ttatgtgtttgatggcGAAgaaagcagtagctgggg	
5	G396F	ttatgtgtttgatggcTTTgaaagcagtagctgggg	
6	G396H	ttatgtgtttgatggcCATgaaagcagtagctgggg	
7	G396I	ttatgtgtttgatggcATTgaaagcagtagctgggg	
8	G396K	ttatgtgtttgatggcAAAgaaagcagtagctgggg	
9	G396L	ttatgtgtttgatggcCTGgaaagcagtagctgggg	
10	G396M	ttatgtgtttgatggcATGgaaagcagtagctgggg	gccatcaaacacataagcagcatcctgaccggc
11	G396N	ttatgtgtttgatggcAATgaaagcagtagctgggg	
12	G396P	ttatgtgtttgatggcCCGgaaagcagtagctgggg	
13	G396Q	ttatgtgtttgatggcCAGgaaagcagtagctgggg	
14	G396R	ttatgtgtttgatggcCGTgaaagcagtagctgggg	
15	G396S	ttatgtgtttgatggcAGCgaaagcagtagctgggg	
16	G396T	ttatgtgtttgatggcACCgaaagcagtagctgggg	
17	G396V	ttatgtgtttgatggcGTTgaaagcagtagctgggg	
18	G396W	ttatgtgtttgatggcTGGgaaagcagtagctgggg	
19	G396Y	ttatgtgtttgatggcTATgaaagcagtagctgggg	

Table S9. Primers used for 417 site of *Pa*BAL

Entry	Mutants	Forward Primer (5'-3')	Reverse Primer (5'-3')
1	H417A	cctgcaagagttctgagtGCAggttatctgggctgc	
2	H417C	cctgcaagagttctgagtTGTggttatctgggctgc	
3	H417D	cctgcaagagttctgagtGATggttatctgggctgc	
4	H417E	cctgcaagagttctgagtGAAggttatctgggctgc	
5	H417F	cctgcaagagttctgagtTTTggttatctgggctgc	actcagaactcttgcaggtgcatccactgccac
6	H417G	cctgcaagagttctgagtGGTggttatctgggctgc	
7	H417I	cctgcaagagttctgagtATTggttatctgggctgc	
8	H417K	cctgcaagagttctgagtAAAggttatctgggctgc	
9	H417L	cctgcaagagttctgagtCTGggttatctgggctgc	

10	H417M	cctgcaagagttctgagtATGggttatctgggctgc	
11	H417N	cctgcaagagttctgagtAATggttatctgggctgc	
12	H417P	cctgcaagagttctgagtCCGggttatctgggctgc	
13	H417Q	cctgcaagagttctgagtCATggttatctgggctgc	
14	H417R	cctgcaagagttctgagtCGTggttatctgggctgc	
15	H417S	cctgcaagagttctgagtAGCggttatctgggctgc	
16	H417T	cctgcaagagttctgagtACCggttatctgggctgc	
17	H417V	cctgcaagagttctgagtGTTggttatctgggctgc	
18	H417W	cctgcaagagttctgagtTGGggttatctgggctgc	
19	H417Y	cctgcaagagttctgagtTATggttatctgggctgc	

Table S10. Primers used for 421 site of *Pa*BAL

Entry	Mutants	Forward Primer (5'-3')	Reverse Primer (5'-3')
1	G421A	gagtcatggttatctgGCAtgcctgggcattggtcc	
2	G421C	gagtcatggttatctgTGTtgcctgggcattggtcc	
3	G421D	gagtcatggttatctgGATtgcctgggcattggtcc	
4	G421E	gagtcatggttatctgGAAtgcctgggcattggtcc	
5	G421F	gagtcatggttatctgTTTtgcctgggcattggtcc	
6	G421H	gagtcatggttatctgCATtgcctgggcattggtcc	
7	G421I	gagtcatggttatctgATTtgcctgggcattggtcc	
8	G421K	gagtcatggttatctgAAAtgcctgggcattggtcc	
9	G421L	gagtcatggttatctgCTGtgcctgggcattggtcc	
10	G421M	gagtcatggttatctgATGtgcctgggcattggtcc	cagataaccatgactcagaactcttgcaggtgc
11	G421N	gagtcatggttatctgAATtgcctgggcattggtcc	
12	G421P	gagtcatggttatctgCCGtgcctgggcattggtcc	
13	G421Q	gagtcatggttatctgCATtgcctgggcattggtcc	
14	G421R	gagtcatggttatctgCGTtgcctgggcattggtcc	
15	G421S	gagtcatggttatctgAGCtgcctgggcattggtcc	
16	G421T	gagtcatggttatctgACCtgcctgggcattggtcc	
17	G421V	gagtcatggttatctgGTTtgcctgggcattggtcc	
18	G421W	gagtcatggttatctgTGGtgcctgggcattggtcc	
19	G421Y	gagtcatggttatctgTATtgcctgggcattggtcc	

Table S11. Primers used for 480 site of *Pa*BAL

Entry	Mutants	Forward Primer (5'-3')	Reverse Primer (5'-3')
1	M480A	ataatcaggtgtggggcGCAagtattcatggccag	gccccacacctgattattcagaatcacggt
2	M480C	ataatcaggtgtggggcTGTagtattcatggccag	
3	M480D	ataatcaggtgtggggcGATagtattcatggccag	
4	M480E	ataatcaggtgtggggcGAAagtattcatggccag	

5	M480F	ataatcaggtgtggggcTTTagtattcatggccag
6	M480G	ataatcaggtgtggggcGGTagtattcatggccag
7	M480H	ataatcaggtgtggggcCATagtattcatggccag
8	M480I	ataatcaggtgtggggcATTagtattcatggccag
9	M480K	ataatcaggtgtggggcAAAagtattcatggccag
10	M480L	ataatcaggtgtggggcCTGagtattcatggccag
11	M480N	ataatcaggtgtggggcAATagtattcatggccag
12	M480P	ataatcaggtgtggggcCCGagtattcatggccag
13	M480Q	ataatcaggtgtggggcCAGagtattcatggccag
14	M480R	ataatcaggtgtggggcCGTagtattcatggccag
15	M480S	ataatcaggtgtggggcAGCagtattcatggccag
16	M480T	ataatcaggtgtggggcACCagtattcatggccag
17	M480V	ataatcaggtgtggggcGTTagtattcatggccag
18	M480W	ataatcaggtgtggggcTGGagtattcatggccag
19	M480Y	ataatcaggtgtggggcTATagtattcatggccag

Table S12. Primers used for 556 site of *Pa*BAL

Entry	Mutants	Forward Primer (5'-3')	Reverse Primer (5'-3')
1	M556A	atccggccaccgttgcaGCActgggtcaattag	
2	M556C	atccggccaccgttgcaTGTctgggtcaattag	
3	M556D	atccggccaccgttgcaGATctgggtcaattag	
4	M556E	atccggccaccgttgcaGAActgggtcaattag	
5	M556F	atccggccaccgttgcaTTTctgggtcaattag	
6	M556G	atccggccaccgttgcaGGTctgggtcaattag	
7	M556H	atccggccaccgttgcaCATctgggtcaattag	
8	M556I	atccggccaccgttgcaATTctgggtcaattag	
9	M556K	atccggccaccgttgcaAAActgggtcaattag	
10	M556L	atccggccaccgttgcaCTGctgggtcaattag	tgcaacggtggccggatgaacaacatcgg
11	M556N	atccggccaccgttgcaAATctgggtcaattag	
12	M556P	atccggccaccgttgcaCCGctgggtcaattag	
13	M556Q	atccggccaccgttgcaCAGctgggtcaattag	
14	M556R	atccggccaccgttgcaCGTctgggtcaattag	
15	M556S	atccggccaccgttgcaAGCctgggtcaattag	
16	M556T	atccggccaccgttgcaACCctgggtcaattag	
17	M556V	atccggccaccgttgcaGTTctgggtcaattag	
18	M556W	atccggccaccgttgcaTGGctgggtcaattag	
19	M556Y	atccggccaccgttgcaTATctgggtcaattag	

Table S13. Primers used for 571 site of *Pa*BAL

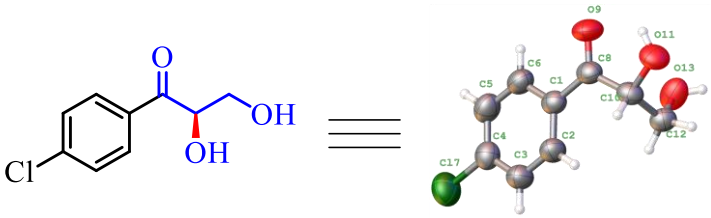
Entry	Mutants	Forward Primer (5'-3')	Reverse Primer (5'-3')
1	Y571A	gccgtgatattatgattccgGCAtacgagaacatc	cggaatcataatatcacggctaccttcggctaat
2	Y571C	gccgtgatattatgattccgTGTtacgagaacatc	
3	Y571D	gccgtgatattatgattccgGATtacgagaacatc	
4	Y571E	gccgtgatattatgattccgGAAtacgagaacatc	
5	Y571F	gccgtgatattatgattccgTTTtacgagaacatc	
6	Y571G	gccgtgatattatgattccgGGTtacgagaacatc	
7	Y571H	gccgtgatattatgattccgCATtacgagaacatc	
8	Y571I	gccgtgatattatgattccgATTtacgagaacatc	
9	Y571K	gccgtgatattatgattccgAAAtacgagaacatc	
10	Y571L	gccgtgatattatgattccgCTGtacgagaacatc	
11	Y571M	gccgtgatattatgattccgATGtacgagaacatc	
12	Y571N	gccgtgatattatgattccgAATtacgagaacatc	
13	Y571P	gccgtgatattatgattccgCCGtacgagaacatc	
14	Y571Q	gccgtgatattatgattccgCAGtacgagaacatc	
15	Y571R	gccgtgatattatgattccgCGTtacgagaacatc	
16	Y571S	gccgtgatattatgattccgAGCtacgagaacatc	
17	Y571T	gccgtgatattatgattccgACCtacgagaacatc	
18	Y571V	gccgtgatattatgattccgGTTtacgagaacatc	
19	Y571W	gccgtgatattatgattccgTGGtacgagaacatc	

Table S14. Primers used for mutants G421S_H417 of *Pa*BAL

Entry	Mutants	Forward Primer (5'-3')	Reverse Primer (5'-3')
1	H417A_G421S	aagagttctgagtGCAggttatctgAGCtgcc	actcagaactcttgcaggtgcatccactgccac
2	H417C_G421S	aagagttctgagtTGTggttatctgAGCtgcc	
3	H417D_G421S	aagagttctgagtGATggttatctgAGCtgcc	
4	H417E_G421S	aagagttctgagtGAAggttatctgAGCtgcc	
5	H417F_G421S	aagagttctgagtTTTggttatctgAGCtgcc	
6	H417G_G421S	aagagttctgagtGGTggttatctgAGCtgcc	
7	H417I_G421S	aagagttctgagtATTggttatctgAGCtgcc	
8	H417K_G421S	aagagttctgagtAAAggttatctgAGCtgcc	
9	H417L_G421S	aagagttctgagtCTGggttatctgAGCtgcc	
10	H417M_G421S	aagagttctgagtATGggttatctgAGCtgcc	
11	H417N_G421S	aagagttctgagtAATggttatctgAGCtgcc	
12	H417P_G421S	aagagttctgagtCCGggttatctgAGCtgcc	
13	H417Q_G421S	aagagttctgagtCAGggttatctgAGCtgcc	
14	H417R_G421S	aagagttctgagtCGTggttatctgAGCtgcc	

15	H417S_G421S	aagagttctgagtAGCggttatctgAGCtgcc
16	H417T_G421S	aagagttctgagtACCggttatctgAGCtgcc
17	H417V_G421S	aagagttctgagtGTTggttatctgAGCtgcc
18	H417W_G421S	aagagttctgagtTGGggttatctgAGCtgcc
19	H417Y_G421S	aagagttctgagtTATggttatctgAGCtgcc

Table S15. Crystal data and structure refinement for *(R)*-**3g**



X-ray of (*R*)-**3g**

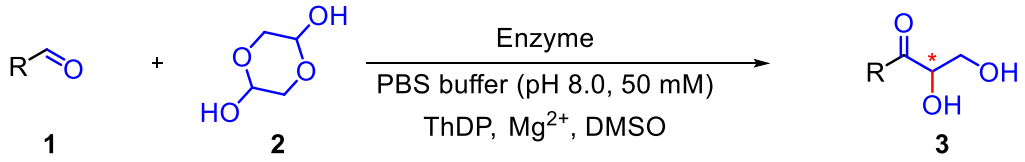
CCDC number	2494126
Empirical formula	$C_9H_9ClO_3$
Formula weight	200.61
Temperature/K	273.15
Crystal system	monoclinic
Space group	$P2_1$
a/Å	4.8781(3)
b/Å	5.6405(3)
c/Å	16.7996(9)
α/°	90
β/°	94.538(2)
γ/°	90
Volume/Å^3	460.79(4)
Z	2
ρ_{calc}g/cm^3	1.446
μ/mm^{-1}	3.458
F(000)	208.0
Crystal size/mm^3	0.58 × 0.36 × 0.01
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.276 to 136.922
Index ranges	$-5 \le h \le 5$, $-6 \le k \le 6$, $-19 \le l \le 19$
Reflections collected	7841
Independent reflections	1555 [R_{int} = 0.0414, R_{sigma} = 0.0410]
Data/restraints/parameters	1555/1/121
Goodness-of-fit on F^2	1.109
Final R indexes [I>=2σ (I)]	R_1 = 0.0415, wR_2 = 0.1086

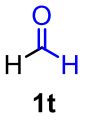
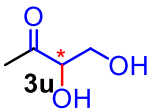
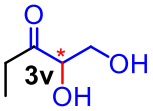
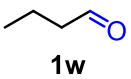
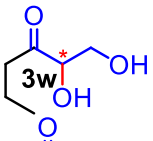
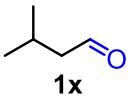
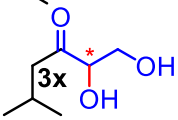
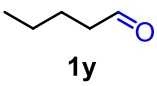
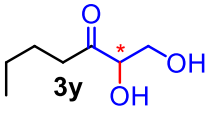
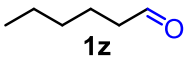
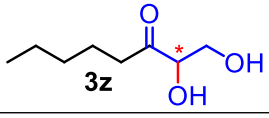
Final R indexes [all data]	R_1 = 0.0425, wR_2 = 0.1096
Largest diff. peak/hole / e Å^{-3}	0.22/-0.18
Flack parameter	0.120(11)

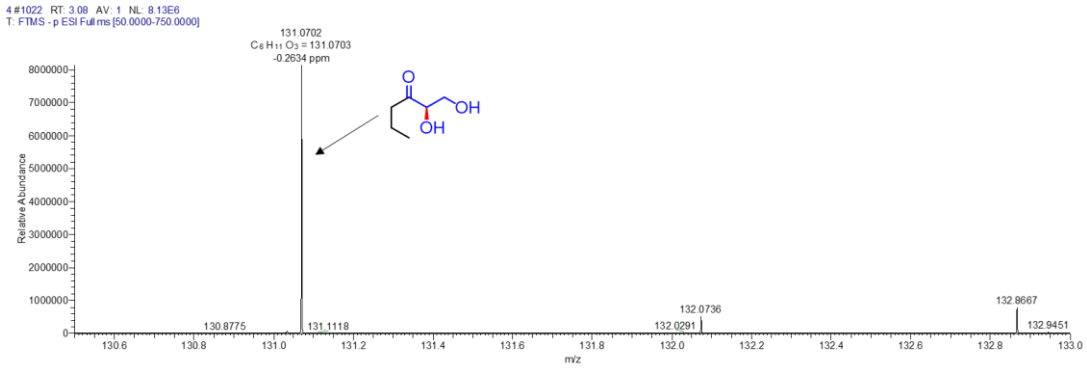
12. Substrate Scope of Aliphatic Aldehydes

The reaction mixture contains substrate **1** (0.01 mmol), **2** (0.01 mmol), DMSO (5%, v/v), ThDP (0.15 mM), $MgSO_4$ (2.5 mM) and PBS (50 mM, pH 8.0, 0.4 mL) supplemented with 200 mg/mL whole cell of *Pf*BAL_A28S. And the reactions were shaken at 1000 rpm, 30 °C for 24 h on the dry thermostat metal bath JX-10. Then 1mL EtOAc was added to the reaction extracted the products by centrifugation at 12,000 rpm for 1 min. The product was concentrated by the rotary evaporator and added 0.5 mL MeOH. Product identification by TLC and HRMS.

Table S16. The results of evaluation on substrate scope of aliphatic aldehydes

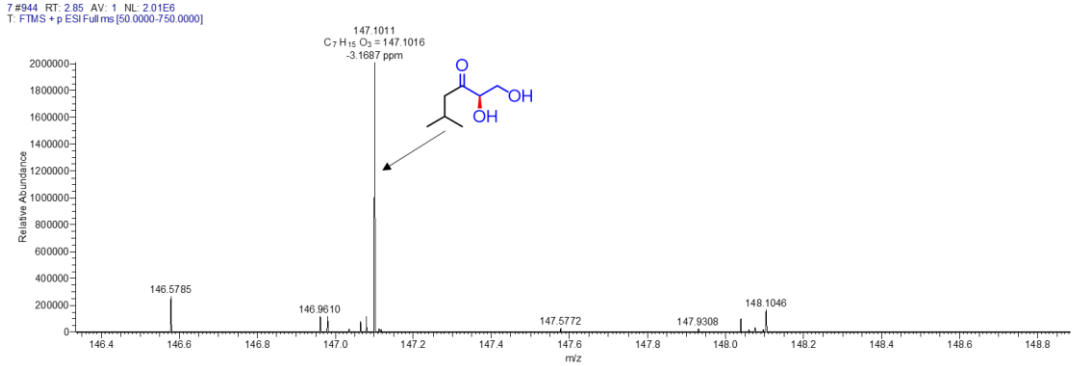


Aliphatic aldehyde	Product	*Pf*BAL_A28S (yield)	*Pa*BAL M3 (yield)
 1t	 3t	-	-
 1u	 3u	-	-
 1v	 3v	-	-
 1w	 3w	trace	-
 1x	 3x	trace	-
 1y	 3y	trace	-
 1z	 3z	trace	-



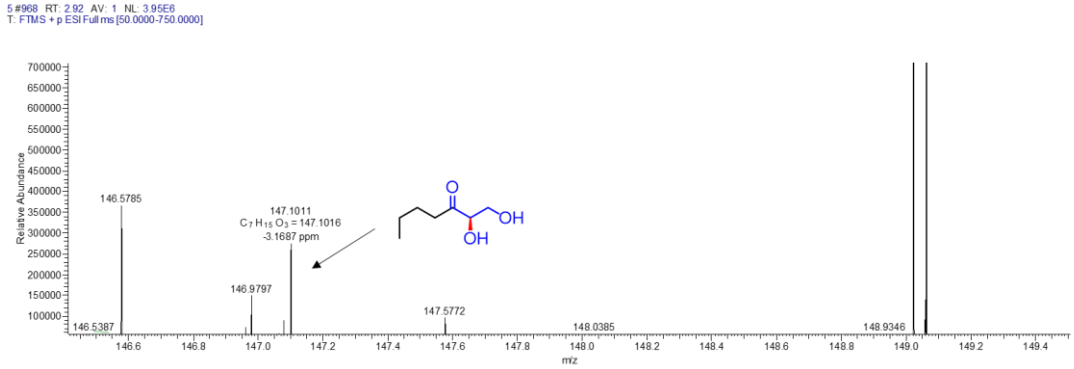
HRMS (ESI, m/z): calcd for $C_6H_{11}O_3$ $[M-H]^-$: 131.0703, found: 131.0702.

HRMS of **3w**



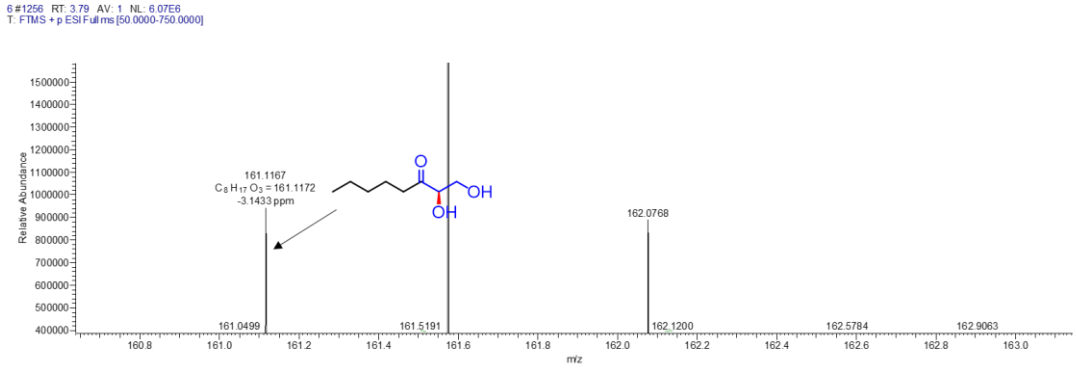
HRMS (ESI, m/z): calcd for $C_7H_{15}O_3$ $[M+H]^+$: 147.1016, found: 147.1011.

HRMS of **3x**



HRMS (ESI, m/z): calcd for $C_7H_{15}O_3$ $[M+H]^+$: 147.1016, found: 147.1011.

HRMS of **3y**



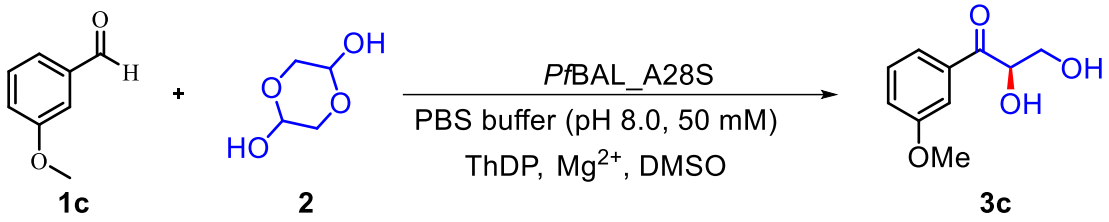
HRMS (ESI, m/z): calcd for $C_8H_{17}O_3$ $[M+H]^+$: 161.1172, found: 161.1167.

HRMS of **3z**

13. The higher substrate concentrations of 1c and 2 for *Pf*BAL_A28S

Different concentrations of **1c** or **2** (final concentrations: 200 Mm, 300 mM, 400 mM, 500 mM, 600 mM and 800 mM) were added to the reaction. The reaction mixture also contains DMSO (5%, v/v), ThDP (0.15 mM), $MgSO_4$ (2.5 mM) and PBS (50 mM, pH 8.0, 0.4 mL) supplemented with 60 mg/mL whole cell of *Pf*BAL_A28S. And the reactions were shaken at 1000 rpm, 30 °C for 24 h on the dry thermostat metal bath JX-10. Then 1mL EtOAc was added to the reaction (three times) and extracted the products by centrifugation at 12,000 rpm for 1 min. The product was concentrated by the rotary evaporator and added 0.5 mL EtOAc containing 1,3,5-trimethoxybenzene (0.5 equiv.) as internal standard. The yields were determined by ^{1}H NMR and ee were determined by HPLC.

A 40 mL-scale preparative reaction consisted of substrate **1c** (500 mM) and **2** (500 mM) also was conducted, the procedure of products was similar to that as described above.



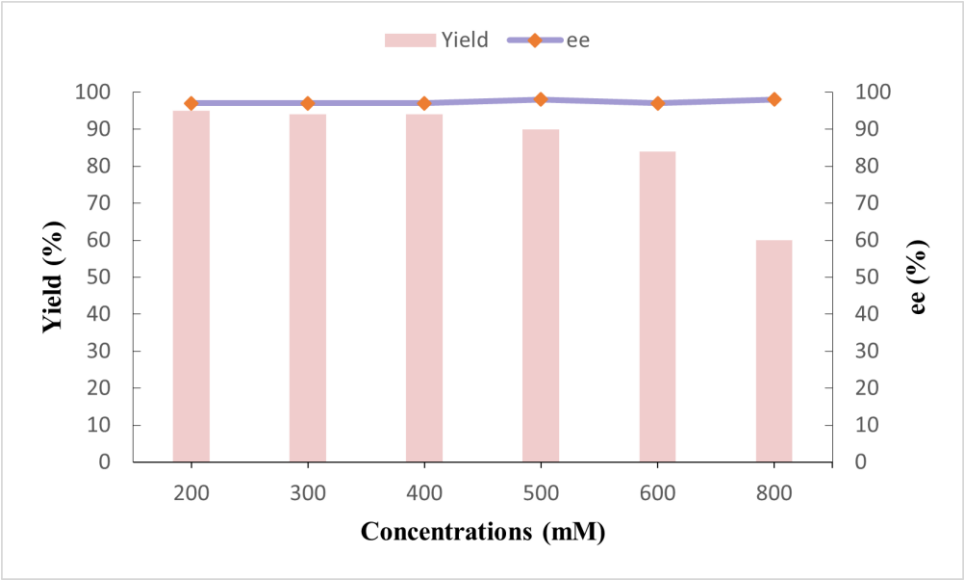


Figure S23. The results of *Pf*BAL_A28S catalysis at different substrate concentrations.

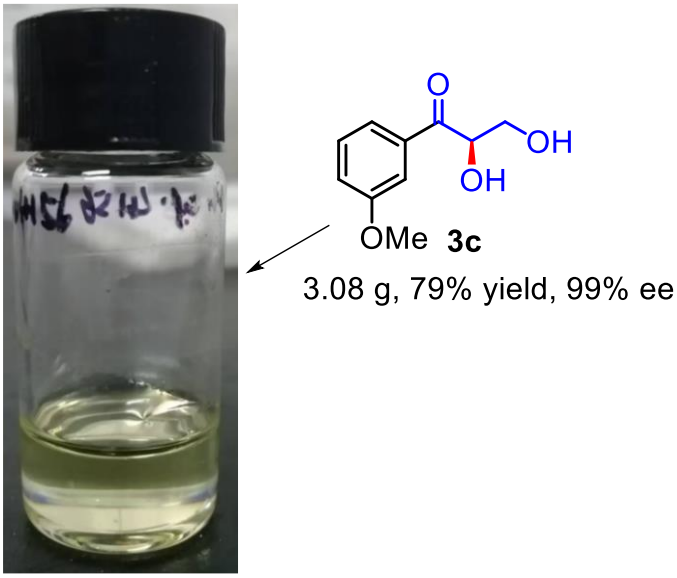
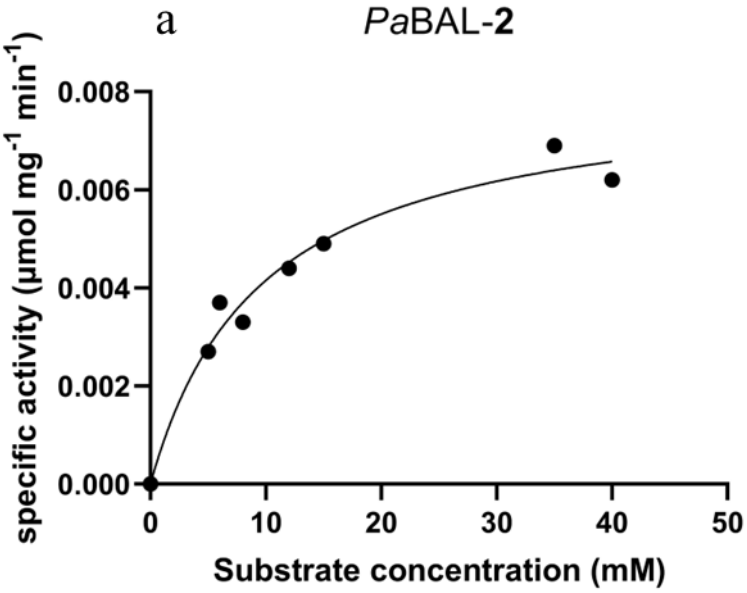


Figure S24. Compound **3c** produced at a 40 mL-scale preparative reaction containing 500 mM substrates.

14. Kinetic characterisation of positive wild-type *Pa*BAL and *Pa*BAL M3 towards 1a or 2

The reaction mixture contained 1~3 mg purified enzyme, 50 mM **1a** or **2**, 0.15 mM ThDP, 2.5 mM $MgSO_4$, 5% DMSO (v/v) and PBS (50 mM, pH 8.0). Different concentrations of **1a** or **2** were added to start the reaction and maintain conversion below 20% during each reaction. The yields were determined by RP-HPLC.



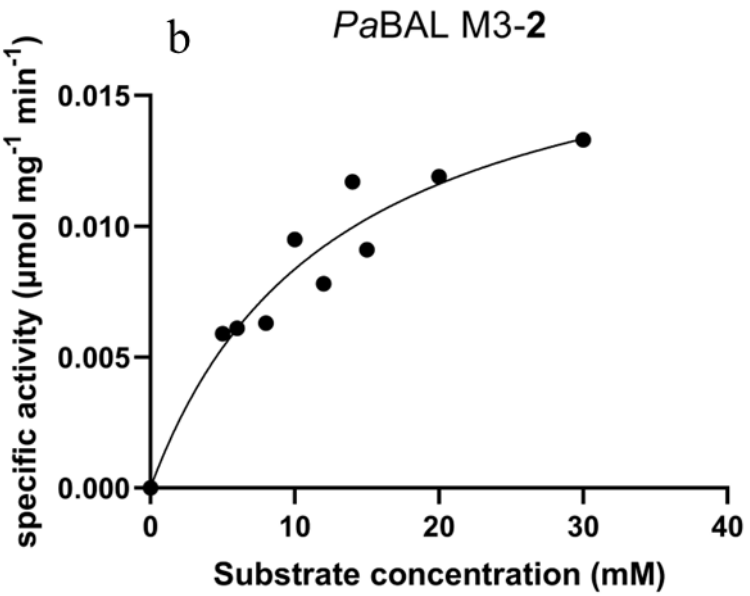
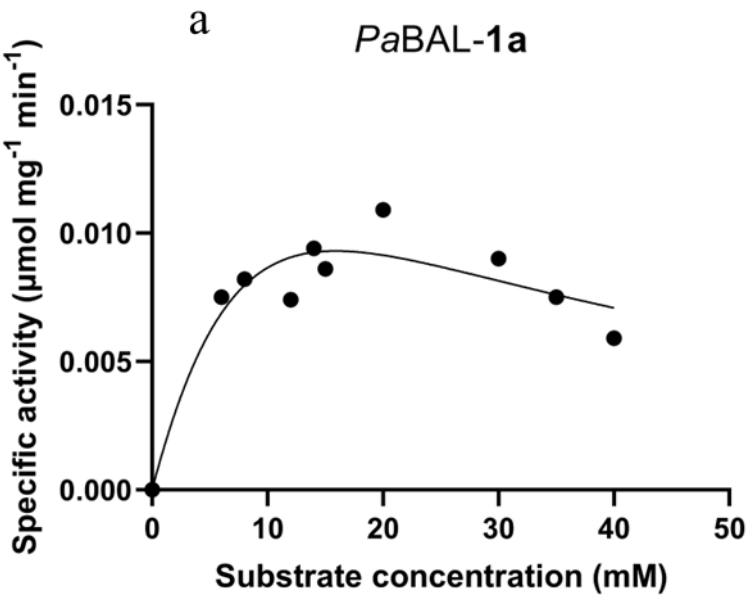


Figure S25. Dynamic fitting curve of different concentrations **2** and 50 mM **1a**. a, wild-type *Pa*BAL. b, *Pa*BAL M3.



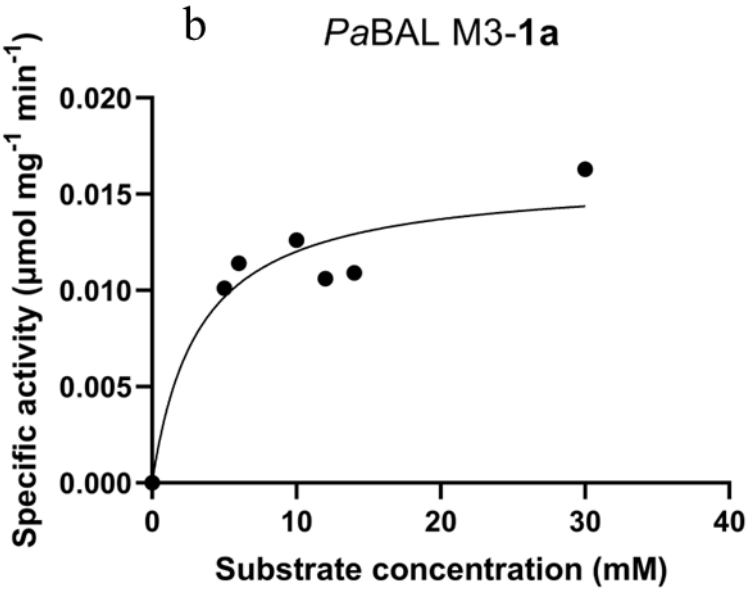
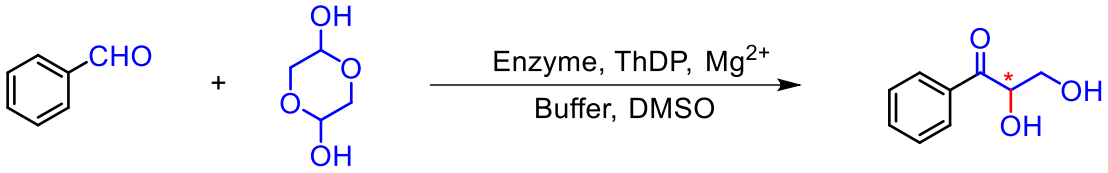


Figure S26. Dynamic fitting curve of different concentrations **2** and 50 mM **1a**. a, wild-type *Pa*BAL. b, *Pa*BAL M3.

Table S17. Kinetic data for wild-type *Pa*BAL and *Pa*BAL M3 towards **1a** or **2** as substrates



1a **2** **3a**

Enzyme-Substrate	K_i (mM)	K_m (mM)	k_{cat} (s^{-1})	k_{cat}/K_m (s^{-1} mM^{-1})
*Pa*BAL-**2**	-	9.05	8.12×10^{-3}	8.97×10^{-4}
*Pa*BAL M3-**2**	-	12.75	1.89×10^{-2}	1.48×10^{-3}
*Pa*BAL-**1a**	14.57	17.38	2.94×10^{-2}	1.69×10^{-3}
*Pa*BAL M3-**1a**	-	3.26	1.58×10^{-2}	4.85×10^{-3}

15. Molecular dynamic simulations

Molecular dynamics (MD) simulations were performed using the GROMACS 2025.1 software package[5]. The initial structures of the protein and ligand were obtained from molecular docking. The system was solvated in a box filled with TIP3P water molecules and chloride counterions to neutralize the charge[6]. A minimum distance of 1.0 nm between the protein and periodic box boundary was maintained to avoid artificial interactions with periodic images. The final box size was approximately 10.8

× 12.5 × 10.0 nm, containing about 130,000 atoms in total.

The Amber14SB force field was used to simulate the protein[7], while the Generalized Amber Force Field (GAFF) was applied to the ligand[5], with the topology files generated using Sobtop. The equilibrium geometry of each ligand was optimized at the B3LYP--D3(BJ)/def2-SVP level using Gaussian16 (A.0.3)[8], and the atomic charges were derived via the RESP2$_{0.5}$ method based on the electrostatic potential calculated from B3LYP/def2-TZVP level using Multiwfn[9] In MD simulations, the system was first energy-minimized, followed by linear heating from 0 K to 298.15 K over 1 ns to equilibrate the solvent environment. In this stage, the temperature and pressure were maintained via the velocity-rescale thermostat and Berendsen's barostat[10] Subsequently, a pre-equilibration simulation of 50 ns was conducted under NPT conditions using the velocity-rescale thermostat and Parrinello-Rahman isotropic barostat to relax the protein structure and reach conformational equilibrium[11]. And finally a simulation of 150 ns was conducted and treated as the equilibrated ensemble for statistical analysis. The binding free energy was calculated using GMX_MMPBSA code[12].

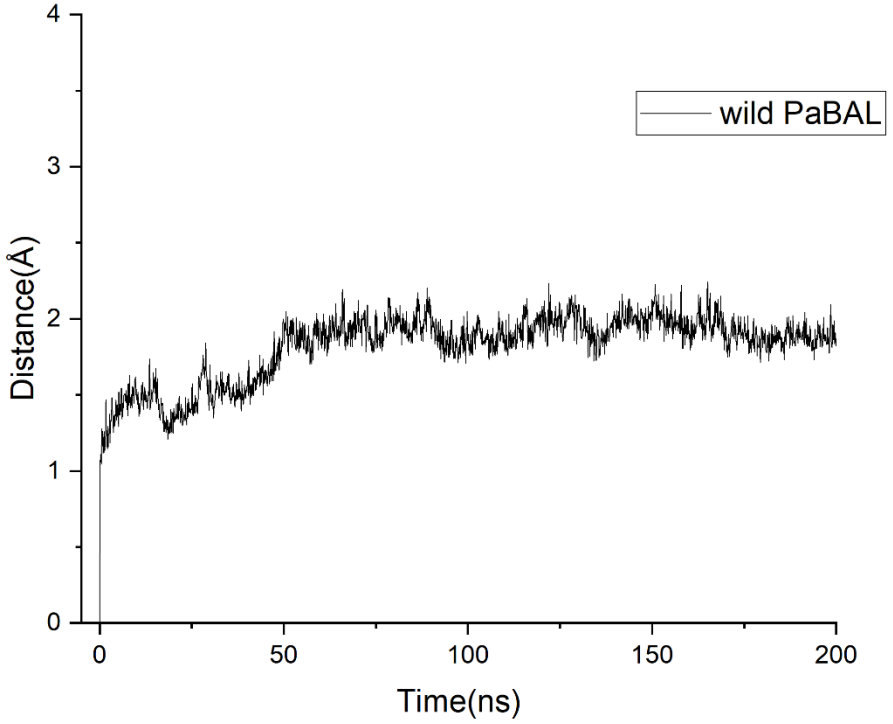


Figure S27. The root mean square deviation (RMSD) of wild *Pa*BAL backbone heavy atoms relative to the first snapshot during the 200 ns MD simulation.

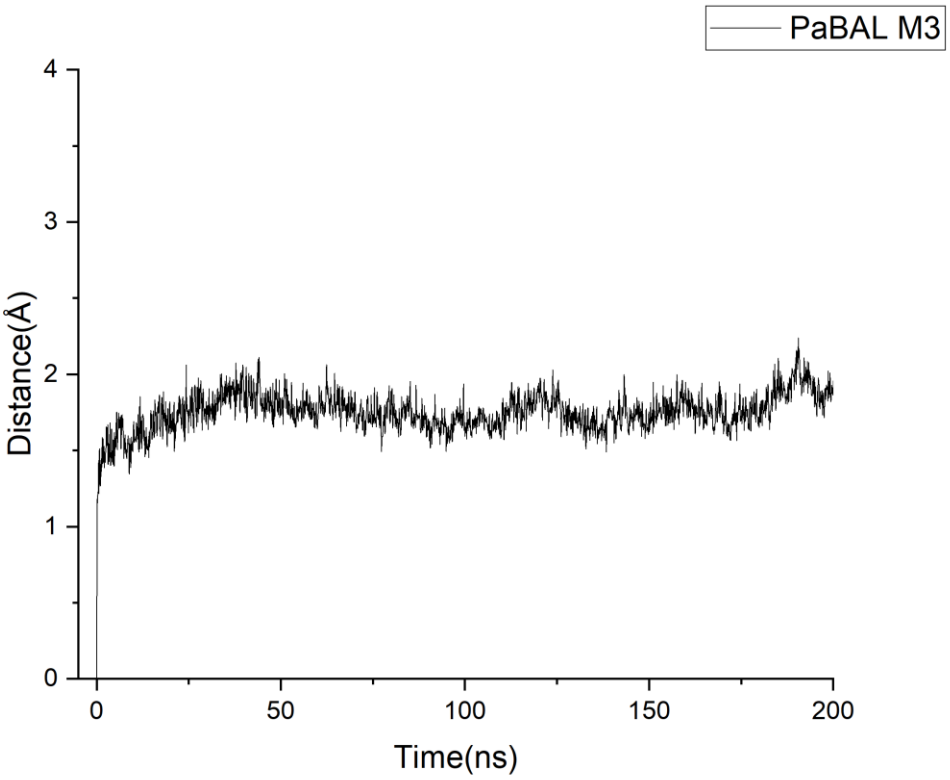
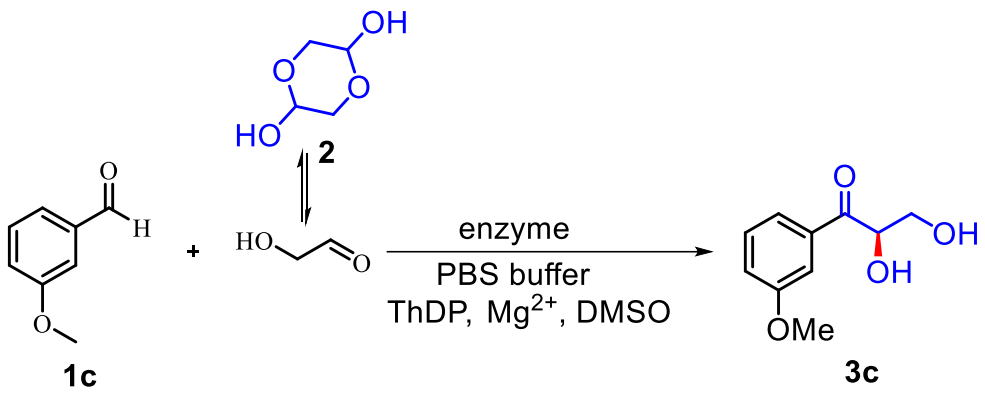


Figure S28. The root mean square deviation (RMSD) of wild *Pa*BAL M3 backbone heavy atoms relative to the first snapshot during the 200 ns MD simulation.

Table S18. Binding energies of wild-type *Pa*BAL and *Pa*BAL M3 with Breslow intermediate, computed using the MM-PBSA method.

Energy (kcal/mol)	wild-type *Pa*BAL	*Pa*BAL M3
ΔE_{vdw}	-53.19 ± 2.43	-54.56 ± 2.11
ΔE_{elec}	-36.29 ± 0.65	-48.98 ± 1.33
$\Delta E_{pb,\ elec}$	37.62 ± 0.17	46.37 ± 0.68
ΔE_{npolar}	-7.66 ± 0.05	-8.21 ± 0.02
ΔG_{bind}	-59.53 ± 2.52	-65.37 ± 2.59

16. The cost and economic analysis



$$AE = \frac{molecular\ weight\ of\ the\ product}{sun\ of\ molecular\ weights\ of\ all\ the\ stoichiomettic\ reagents}$$

$$\text{E-factor} = \frac{mass\ of\ waste}{mass\ of\ the\ product}$$

Table S19. Cost Statistics for Producing 9.72 g of **3c**

Entry	unit price	cost (CNY)
Substrate-**1c**	1.024 CNY/g	8.36
Substrate-**2**	19.032 CNY/g	137.03
ThDP	81.75 CNY/g	3.58
$MgSO_4$	0.116 CNY/g	0.02
Na_2HPO_4	0.043 CNY/g	0.15
KH_2PO_4	0.0765 CNY/g	0.1
NaCl	0.0425 CNY/g	1.34
KCl	0.585 CNY/g	0.01
DMSO	0.0442 CNY/mL	1.11
Tryptone	0.64 CNY/g	19.2
Yeast Extract	0.336 CNY/g	5.04
Wahaha Purified Water	1.38 CNY/L	4.14
Ethyl Acetate	13 CNY/L	1.3
Na_2SO_4	0.05 CNY/g	0.05
Silica gel	0.0475 CNY/g	0.1
Power charge	0.53 CNY/kWh	14.76
	Total Cost: 196.28 CNY	
	Cost for producing 1 g of **3c**: ¥20.19	

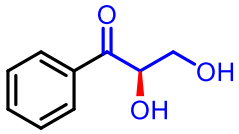
Table S20. Some metrics for enzymatic synthesis of compound **3c**

AE (atom economy)	E-factor	Cost

	*Pf*BAL_A28S	Organic NHC	
100%	6.1	271	20.19 CNY/g

We mainly summarized the metrics from the preparative reaction at a 500 mL scale. The substrate **2** can be hydrolyzed in water to glycolaldehyde and then participate in the reaction. No loss of atoms was observed. The E-factor of the synthetic route employing organic NHC is significantly higher than that of the enzymatic synthesis. The reason lies in the poor recoverability of organic solvents like THF in the chemical synthetic route, and low yield. The calculated cost for producing 1 g of compound **3c** is 20.19 RMB.

17. Characterization data of the products



(R)-**3a**

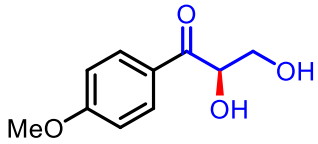
(*R*)-2,3-dihydroxy-1-phenylpropan-1-one: slightly yellow oil, 88% yield (*Pf*BAL_A28S), 32% yield (*Pa*BAL M3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.88 (m, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.4 Hz, 2H), 5.18 (dd, J = 5.0, 3.1 Hz, 1H), 3.99 (dd, J = 11.9, 3.1 Hz, 1H), 3.76 – 3.71 (m, J = 5.0, 11.9 Hz 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.7, 134.2, 133.7, 128.9, 128.6, 74.9, 65.2.

HPLC analysis: 97% ee (*Pf*BAL_A28S, *R*), 95% ee (*Pa*BAL M3, *S*); DAICEL IA (*n*-hexane: *i*-PrOH = 95:5, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 32.950 min (*Pf*BAL_A28S) and $t_{R\text{-major}}$ = 29.670 min (*Pa*BAL M3).

HRMS (ESI, m/z): calcd for $C_9H_9O_3$ $[M\text{-}H]^-$: 165.0548, found: 165.0546.



(R)-**3b**

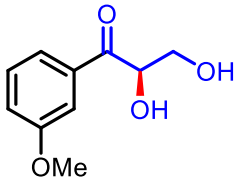
(*R*)-2,3-dihydroxy-1-(4-methoxyphenyl)propan-1-one: slightly yellow oil, 66% yield (*Pf*BAL_A28S).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 9.0 Hz, 2H), 6.96 (d, J = 9.0 Hz, 2H), 5.14 – 5.09 (m, 1H), 4.02 – 3.97 (m, 1H), 3.87 (s, 3H), 3.71 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 164.6, 131.1, 126.4, 114.3, 74.3, 65.8, 55.7.

HPLC analysis: 99% ee (*Pf*BAL_A28S, *R*); DAICEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 32.892 min (*Pf*BAL_A28S).

HRMS (ESI, m/z): calcd for $C_{10}H_{11}O_4$ $[M\text{-}H]^-$: 195.0656, found: 195.0652.



(R)-**3c**

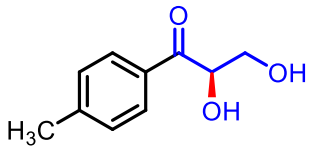
(*R*)-2,3-dihydroxy-1-(3-methoxyphenyl)propan-1-one: slightly yellow oil, 93% yield (*Pf*BAL_A28S), 55% yield (*Pa*BAL M3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.37 (t, J = 7.9 Hz, 1H), 7.13 (dd, J = 7.9 Hz, 1H), 5.14 (dd, J = 4.9, 3.2 Hz, 1H), 3.99 (dd, J = 11.8, 3.2 Hz, 1H), 3.82 (s, 3H), 3.75 (dd, J = 11.8, 4.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.5, 160.0, 135.0, 130.0, 121.1, 120.7, 113.0, 75.0, 65.4, 55.5.

HPLC analysis: 94% ee (*Pf*BAL_A28S, *R*), 92% ee (*Pa*BAL M3, *S*); DAICEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 24.040 min (*Pf*BAL_A28S) and $t_{R\text{-major}}$ = 26.410 min (*Pa*BAL M3).

HRMS (ESI, m/z): calcd for $C_{10}H_{11}O_4$ $[M\text{-}H]^-$: 195.0656, found: 195.0652.



(R)-**3d**

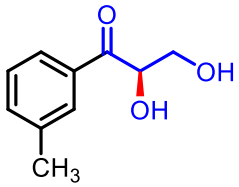
(*R*)-2,3-dihydroxy-1-(p-tolyl)propan-1-one: slightly yellow oil, 92% yield (*Pf*BAL_A28S), 36% yield (*Pa*BAL M3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 5.14 (dd, J = 5.2, 3.2 Hz, 1H), 4.00 (dd, J = 11.7, 3.2 Hz, 1H), 3.73 (dd, J = 11.7, 5.2 Hz, 1H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 145.6, 131.0, 129.8, 128.8, 74.6, 65.6, 21.9.

HPLC analysis: 99% ee (*Pf*BAL_A28S, *R*), 94% ee (*Pa*BAL M3, *S*); DAICEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 21.617 min (*Pf*BAL_A28S) and $t_{R\text{-major}}$ = 19.718 min (*Pa*BAL M3).

HRMS (ESI, m/z): calcd for $C_{10}H_{11}O_3$ $[M\text{-}H]^-$: 179.0704, found: 179.0703.



(R)-**3e**

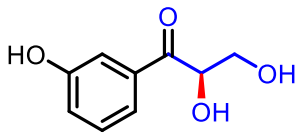
(*R*)-2,3-dihydroxy-1-(m-tolyl)propan-1-one: slightly yellow oil, 89% yield (*Pf*BAL_A28S), 30% yield (*Pa*BAL M3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.38 (dd, J = 7.6, 8.0 Hz, 1H), 5.16 (dd, J = 5.0, 3.2 Hz, 1H), 4.01 (dd, J = 11.8, 3.2 Hz, 1H), 3.74 (dd, J = 11.8, 5.0 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.7, 139.1, 135.2, 133.6, 129.2, 128.9, 125.9, 74.8, 65.5, 21.4.

HPLC analysis: 98% ee (*Pf*BAL_A28S, *R*), 90% ee (*Pa*BAL M3, *S*); DAICEL OD-H (*n*-hexane: *i*-PrOH = 95:5, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 28.420 min (*Pf*BAL_A28S) and $t_{R\text{-major}}$ = 24.627 min (*Pa*BAL M3).

HRMS (ESI, m/z): calcd for $C_{10}H_{11}O_3$ $[M\text{-}H]^-$: 179.0704, found: 179.0703.



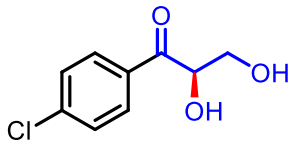
(R)-**3f**

(*R*)-2,3-dihydroxy-1-(3-hydroxyphenyl)propan-1-one: slightly yellow oil, 87% yield (*Pf*BAL_A28S).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.77 (s, 1H), 7.42 (m, 1H), 7.34 – 7.27 (m, 2H), 7.02 (m, 1H), 5.18 (d, J = 6.6 Hz, 1H), 4.96 – 4.88 (m, 1H), 4.77 (m, 1H), 3.74 – 3.65 (m, 1H), 3.59 (m, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 200.4, 157.5, 136.7, 129.7, 120.3, 119.4, 114.7, 74.6, 64.1.

HRMS (ESI, m/z): calcd for $C_9H_9O_4$ $[M\text{-}H]^-$: 181.0494, found: 181.0495.



(R)-**3g**

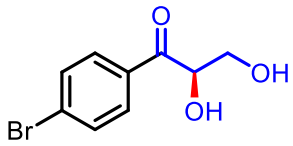
(*R*)-1-(4-chlorophenyl)-2,3-dihydroxypropan-1-one: slightly yellow oil, 80% yield (*Pf*BAL_A28S), 15% yield (*Pa*BAL M3).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.01 (d, J = 8.7 Hz, 2H), 7.59 (d, J = 8.7 Hz, 2H), 5.38 (s, 1H), 4.93 (m, 1H), 4.82 (s, 1H), 3.73 – 3.58 (m, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 199.8, 138.0, 134.2, 130.5, 128.7, 74.8, 63.9.

HPLC analysis: 97% ee (*Pf*BAL_A28S, *R*), 80% ee (*Pa*BAL M3, *S*); DAICEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 22.861 min (*Pf*BAL_A28S) and $t_{R\text{-major}}$ = 19.363 min (*Pa*BAL M3).

HRMS (ESI, m/z): calcd for $C_9H_8O_3Cl$ $[M\text{-}H]^-$: 199.0157, found: 199.0157.



(R)-**3h**

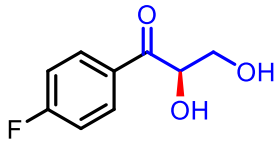
(*R*)-1-(4-bromophenyl)-2,3-dihydroxypropan-1-one: slightly yellow oil, 64% yield (*Pf*BAL_A28S), 15% yield (*Pa*BAL M3).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.92 (d, J = 8.5 Hz, 2H), 7.73 (d, J = 8.5 Hz, 2H), 5.38 (d, J = 6.5 Hz, 1H), 4.92 (m, 1H), 4.82 (t, J = 5.8 Hz, 1H), 3.66 (m, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 200.0, 134.5, 131.6, 130.6, 127.2, 74.8, 63.9.

HPLC analysis: 97% ee (*Pf*BAL_A28S, *R*), 79% ee (*Pa*BAL M3, *S*); DAICEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 24.624 min (*Pf*BAL_A28S) and $t_{R\text{-major}}$ = 20.936 min (*Pa*BAL M3).

HRMS (ESI, m/z): calcd for $C_9H_8O_3Br$ $[M\text{-}H]^-$: 242.9656 found: 242.9651.



(R)-**3i**

(*R*)-1-(4-fluorophenyl)-2,3-dihydroxypropan-1-one: slightly yellow oil, 84% yield (*Pf*BAL_A28S), 13% yield (*Pa*BAL M3).

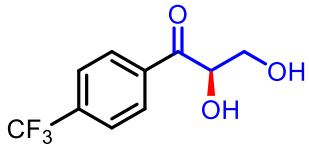
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.07 (d, J = 8.8 Hz, 2H), 7.34 (t, J = 8.8 Hz, 2H), 5.33 (d, J = 6.5 Hz, 1H), 4.96 – 4.90 (m, 1H), 4.80 (t, J = 5.8 Hz, 1H), 3.66 (m, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 199.3, 165.0 (d, J = 251.8 Hz), 132.2 (d, J = 2.9 Hz), 131.6 (d, J = 9.4 Hz), 115.6 (d, J = 21.7 Hz), 74.7, 64.0.

^{19}F NMR (376 MHz, DMSO-d_6) δ -106.00.

HPLC analysis: 98% ee (*Pf*BAL_A28S, *R*), 86% ee (*Pa*BAL M3, *S*); DAICEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 21.962 min (*Pf*BAL_A28S) and $t_{R\text{-major}}$ = 18.701 min (*Pa*BAL M3).

HRMS (ESI, m/z): calcd for $C_9H_8O_3F$ $[M\text{-}H]^-$: 183.0450, found: 183.0452.



(R)-**3j**

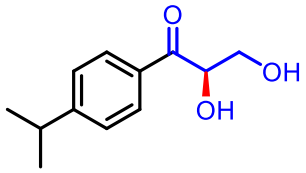
(*R*)-2,3-dihydroxy-1-(4-(trifluoromethyl)phenyl)propan-1-one: slightly yellow oil, 92% yield (*Pf*BAL_A28S).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.16 (d, J = 8.2 Hz, 2H), 7.89 (d, J = 8.2 Hz, 2H), 5.49 (d, J = 6.4 Hz, 1H), 4.99 – 4.94 (m, 1H), 4.86 (t, J = 5.7 Hz, 1H), 3.70 (m, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 200.6, 139.0, 132.3 (q, J = 31.9 Hz), 129.4, 125.5 (d, J = 3.7 Hz), 123.8 (q, J = 251.3 Hz), 75.1, 63.8.

^{19}F NMR (376 MHz, DMSO-d_6) δ -61.60.

HRMS (ESI, m/z): calcd for $C_{10}H_8O_3F_3$ $[M-H]^-$: 233.0421, found: 233.0420.



(R)-**3k**

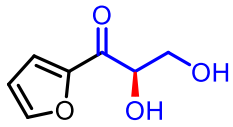
(*R*)-2,3-dihydroxy-1-(4-isopropylphenyl)propan-1-one: slightly yellow oil, 54% yield (*Pf*BAL_A28S), 44% yield (*Pa*BAL M3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 5.15 (dd, J = 5.1, 3.2 Hz, 1H), 4.01 (dd, J = 11.8, 3.2 Hz, 1H), 3.73 (dd, J = 11.8, 5.1 Hz, 1H), 2.96 (m, J = 6.9 Hz, 1H), 1.25 (d, J = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 158.5, 130.9, 128.7, 126.1, 74.7, 65.6, 35.4, 31.1.

HPLC analysis: 98% ee (*Pf*BAL_A28S, *R*), 95% ee (*Pa*BAL M3, *S*); DAICEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 18.308 min (*Pf*BAL_A28S) and $t_{R\text{-major}}$ = 14.746 min (*Pa*BAL M3).

HRMS (ESI, m/z): calcd for $C_{12}H_{15}O_3$[M-H]$^-$: 207.1019, found: 207.1016.



(R)-**3l**

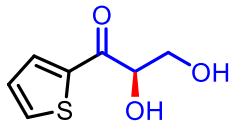
(*R*)-1-(furan-2-yl)-2,3-dihydroxypropan-1-one: slightly yellow oil, 42% yield (*Pf*BAL_A28S).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.00 (s, 1H), 7.54 (d, J = 3.6 Hz, 1H), 6.73 – 6.70 (m, 1H), 5.40 (d, J = 6.2 Hz, 1H), 4.81 (t, J = 5.9 Hz, 1H), 4.63 (m, 1H), 3.65 (m, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 188.9, 150.8, 147.8, 119.9, 112.4, 74.8, 64.0.

HPLC analysis: 84% ee (*Pf*BAL_A28S, *R*); DAICEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 27.557 min (*Pf*BAL_A28S).

HRMS (ESI, m/z): calcd for $C_7H_7O_4$ $[M-H]^-$: 155.0340, found: 155.0339.



(R)-**3m**

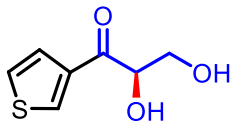
(*R*)-2,3-dihydroxy-1-(thiophen-2-yl)propan-1-one: slightly yellow oil, 72% yield (*Pf*BAL_A28S), 9% yield (*Pa*BAL M3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 3.9 Hz, 1H), 7.77 (d, J = 5.0 Hz, 1H), 7.23 – 7.18 (m, J = 3.9, 5.0 Hz 1H), 4.99 – 4.95 (m, 1H), 4.06 (dd, J = 11.7, 3.4 Hz, 1H), 3.87 (dd, J = 11.7, 5.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8 139.8 135.5 133.5, 128.7, 75.3, 66.2.

HPLC analysis: 93% ee (*Pf*BAL_A28S, *R*), 92% ee (*Pa*BAL M3, *S*); DAICEL IC (*n*-hexane: *i*-PrOH = 85:15, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 23.483 min (*Pf*BAL_A28S) and $t_{R\text{-major}}$ = 27.507 min (*Pa*BAL M3).

HRMS (ESI, m/z): calcd for $C_7H_7O_3S$ $[M\text{-}H]^-$: 171.0109, found: 171.0110.



(R)-**3n**

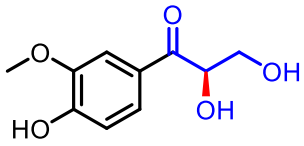
(*R*)-2,3-dihydroxy-1-(thiophen-3-yl)propan-1-one: slightly yellow oil, 76% yield (*Pf*BAL_A28S).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, J = 2.9, 1.3 Hz, 1H), 7.56 (dd, J = 5.1, 1.3 Hz, 1H), 7.38 (dd, J = 5.1, 2.9 Hz, 1H), 4.96 (m, 1H), 4.02 (dd, J = 11.8, 3.3 Hz, 1H), 3.80 (dd, J = 11.8, 5.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 138.1, 133.9, 127.2, 127.0, 75.7, 65.7.

HPLC analysis: 95% ee (*Pf*BAL_A28S, *R*); DAICEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 27.178 min (*Pf*BAL_A28S).

HRMS (ESI, m/z): calcd for $C_7H_7O_3S$ $[M\text{-}H]^-$: 171.0109, found: 171.0110.



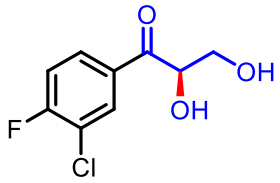
(R)-**3o**

(*R*)-2,3-dihydroxy-1-(4-hydroxy-3-methoxyphenyl)propan-1-one: slightly yellow oil, 88% yield (*Pf*BAL_A28S).

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.02 (s, 1H), 7.58 (d, J = 8.3 Hz, 1H), 7.51 (s, 1H), 6.89 (d, J = 8.3 Hz, 1H), 5.06 (s, 1H), 4.99 (m, J = 4.2, 11.3 Hz,1H), 4.76 (s, 1H), 3.83 (s, 3H), 3.72 (d, J = 11.3 Hz, 1H), 3.64 (d, J = 4.2 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 198.5, 152.0, 147.7, 127.1, 123.8, 115.1, 111.9, 74.1, 64.7, 55.8.

HRMS (ESI, m/z): calcd for $C_{10}H_{11}O_5$ $[M\text{-}H]^-$: 211.0600, found: 211.0601.



(R)-**3p**

(*R*)-1-(3-chloro-4-fluorophenyl)-2,3-dihydroxypropan-1-one: slightly yellow oil, 81% yield (*Pf*BAL_A28S), 24% yield (*Pa*BAL M3).

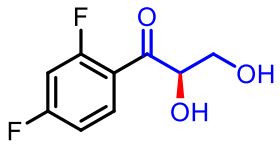
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 7.0, 2.2 Hz, 1H), 7.81 (dd, J = 8.7, 2.2 Hz, 1H), 7.21 (t, J = 8.5 Hz, 1H), 5.15 – 5.11 (m, 1H), 3.98 (dd, J = 12.0, 3.2 Hz, 1H), 3.76 (dd, J = 12.0, 4.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 161.6 (d, J = 259.0 Hz), 131.6, 131.1 (d, J = 3.7 Hz), 129.2 (d, J = 8.6 Hz), 122.4 (d, J = 18.3 Hz), 117.3 (d, J = 21.8 Hz), 75.0, 64.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -104.90.

HPLC analysis: 97% ee (*Pf*BAL_A28S, *R*), 84% ee (*Pa*BAL M3, *S*); DAICEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 18.463 min (*Pf*BAL_A28S) and $t_{R\text{-major}}$ = 16.105 min (*Pa*BAL M3).

HRMS (ESI, m/z): calcd for $C_9H_7O_3ClF$ $[M\text{-}H]^-$: 217.0025, found: 217.0062.



(R)-**3q**

(*R*)-1-(2,4-difluorophenyl)-2,3-dihydroxypropan-1-one: slightly yellow oil, 66% yield (*Pf*BAL_A28S).

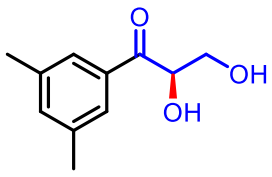
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.93 (m, 1H), 7.04 – 6.97 (m, 1H), 6.90 (m, 1H), 5.01 (m, J = 1.8, 3.3 Hz, 1H), 3.99 (dd, J = 12.1, 1.8 Hz, 1H), 3.80 (m, J = 12.1, 3.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8 (d, J = 4.6 Hz), 166.7 (dd, J = 12.5, 259.2 Hz), 162.6 (dd, J = 12.6, 257.1 Hz), 133.4 (dd, J = 4.4, 10.8 Hz), 119.0 (dd, J = 3.6, 13.5 Hz), 113.1 (dd, J = 3.2, 21.7 Hz), 105.1, 77.8 (d, J = 8.6 Hz), 64.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -99.14, -103.98.

HPLC analysis: 96% ee (*Pf*BAL_A28S, *R*); DAICEL IA (*n*-hexane: *i*-PrOH = 93:7, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 25.577 min (*Pf*BAL_A28S).

HRMS (ESI, m/z): calcd for $C_9H_7F_2O_3$ $[M\text{-}H]^-$: 201.0358, found: 201.0358.



(R)-**3r**

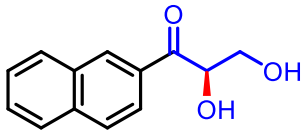
(*R*)-1-(3,5-dimethylphenyl)-2,3-dihydroxypropan-1-one: slightly yellow oil, 77% yield (*Pf*BAL_A28S), 37% yield (*Pa*BAL M3).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.58 (s, 2H), 7.26 (s, 1H), 5.15 (d, J = 6.7 Hz, 1H), 4.99 (q, J = 5.7, 4.7 Hz, 1H), 4.76 (t, J = 5.8 Hz, 1H), 3.71 (m, J = 11.1, 4. Hz, 1H), 3.61 (m, J = 11.1, 5.7 Hz, 1H), 2.33 (s, 6H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 200.7, 137.9, 135.5, 134.5, 126.1, 74.5, 64.2, 20.8.

HPLC analysis: 98% ee (*Pf*BAL_A28S, *R*), 93% ee (*Pa*BAL M3, *S*); DAICEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 13.426 min (*Pf*BAL_A28S) and $t_{R\text{-major}}$ = 12.747 min (*Pa*BAL M3).

HRMS (ESI, m/z): calcd for $C_{11}H_{13}O_3[M\text{-}H]^-$: 193.0859, found: 183.0859.



(R)-**3s**

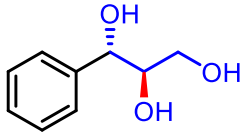
(*R*)-2,3-dihydroxy-1-(naphthalen-2-yl)propan-1-one: slightly yellow oil, 33% yield (*Pf*BAL_A28S), 24% yield (*Pa*BAL M3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.93 (m, 4H), 7.61 m, 2H), 5.34 (d, J = 5.2 Hz, 1H), 4.10 (dd, J = 11.8, 3.2 Hz, 1H), 3.82 (dd, J = 11.8, 5.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.4, 136.2, 132.5, 130.9, 130.8, 129.8, 129.3, 129.1, 128.0, 127.4, 123.9, 74.8, 65.7.

HPLC analysis: 97% ee (*Pf*BAL_A28S, *R*), 95% ee (*Pa*BAL M3, *S*); DAUCEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 28.121 min (*Pf*BAL_A28S) and $t_{R\text{-major}}$ = 25.978 min (*Pa*BAL M3).

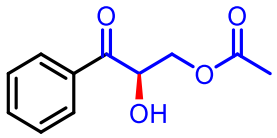
HRMS (ESI, m/z): calcd for $C_{13}H_{11}O_3[M\text{-}H]^-$: 215.0704, found: 215.0703.



4a

(1*S*,2*R*)-1-phenylpropane-1,2,3-triol[4]: slightly yellow oil, 60% yield, dr=7:1.

^{1}H NMR (400 MHz, D_2O) δ 7.48 – 7.36 (m, 5H), 4.65 (d, J = 7.0 Hz, 1H), 3.92 (td, J = 7.0, 3.2 Hz, 1H), 3.80 (dd, J = 11.8, 3.3 Hz, 1H), 3.62 (dd, J = 11.8, 6.8 Hz, 1H).



4b

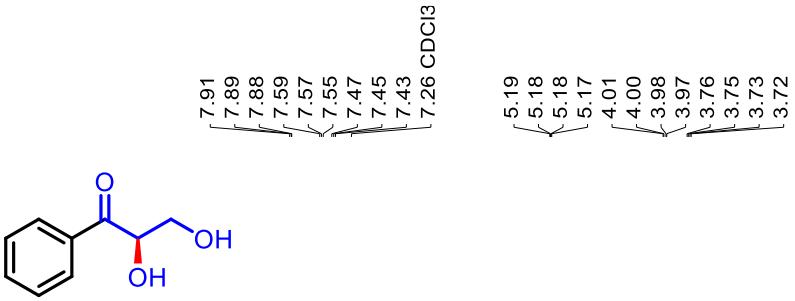
(*R*)-2-hydroxy-3-oxo-3-phenylpropyl acetate: slightly yellow oil, 40% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.0 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.52

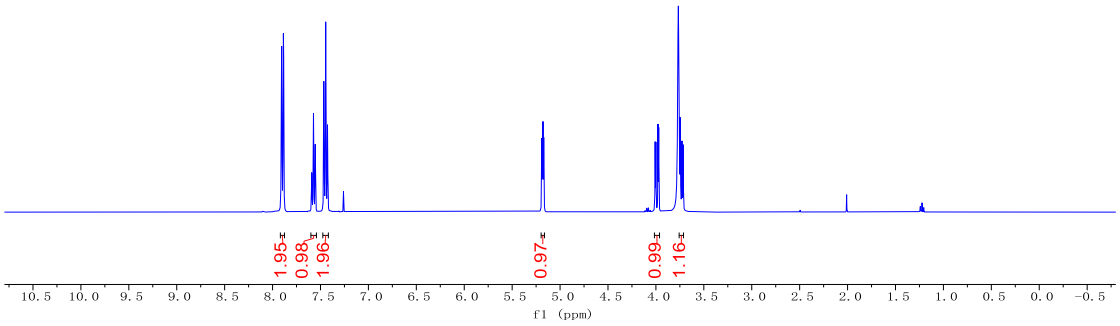
(t, J = 7.8 Hz, 2H), 5.30 (dd, J = 5.8, 3.2 Hz, 1H), 4.56 (dd, J = 11.7, 3.1 Hz, 1H), 4.12 (dd, J = 11.8, 5.8 Hz, 1H), 2.02 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.6, 171.0, 134.6, 133.5, 129.2, 128.8, 72.1, 66.9, 20.8.

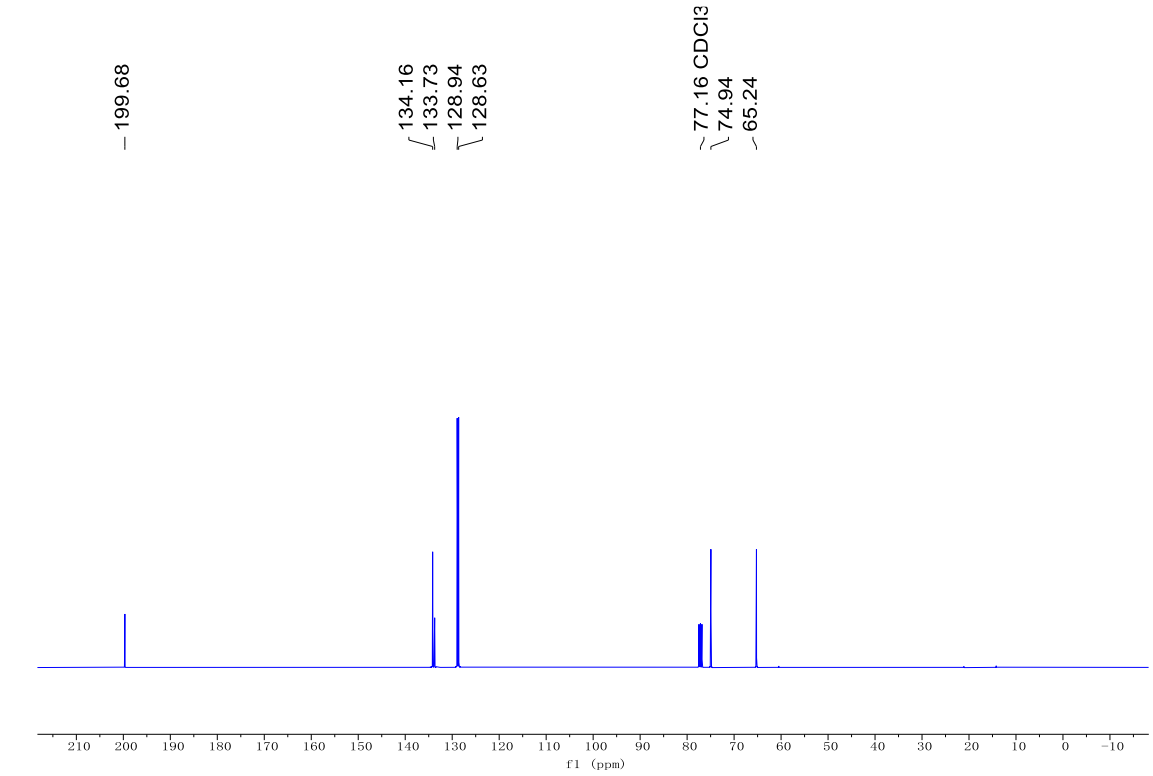
18. NMR Spectra of products



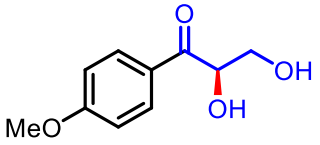
(R)-**3a**



^{1}H NMR of (*R*)-**3a**

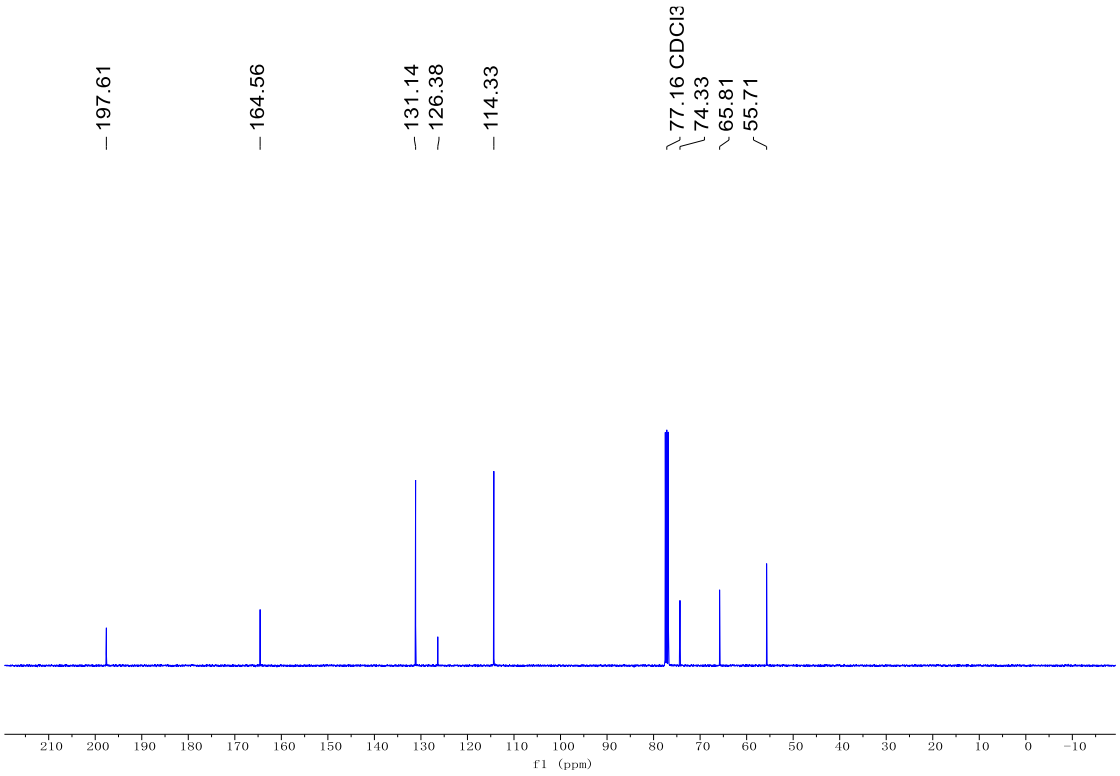


^{13}C NMR of (*R*)-**3a**

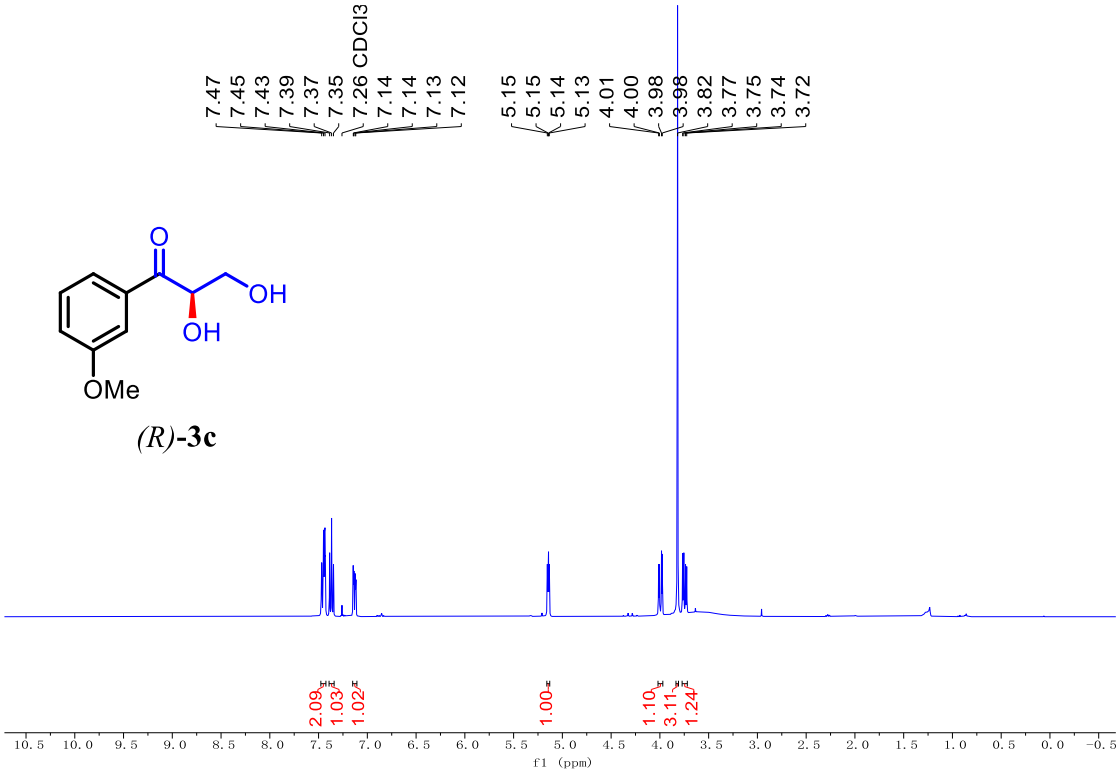


(R)-**3b**

^{1}H NMR of (*R*)-**3b**

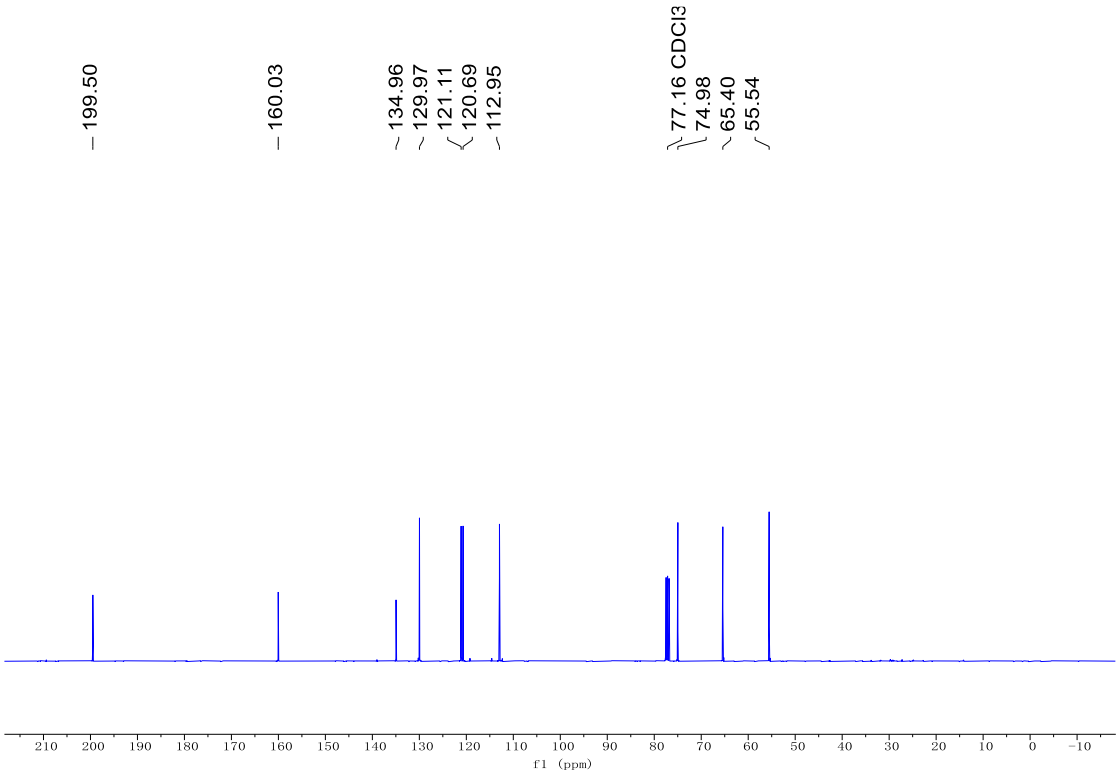


^{13}C NMR of (*R*)-**3b**

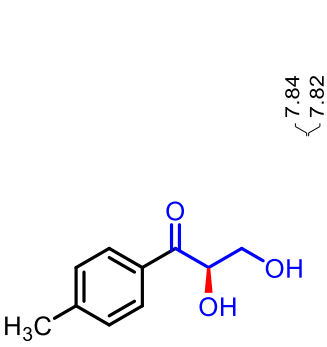


(R)-**3c**

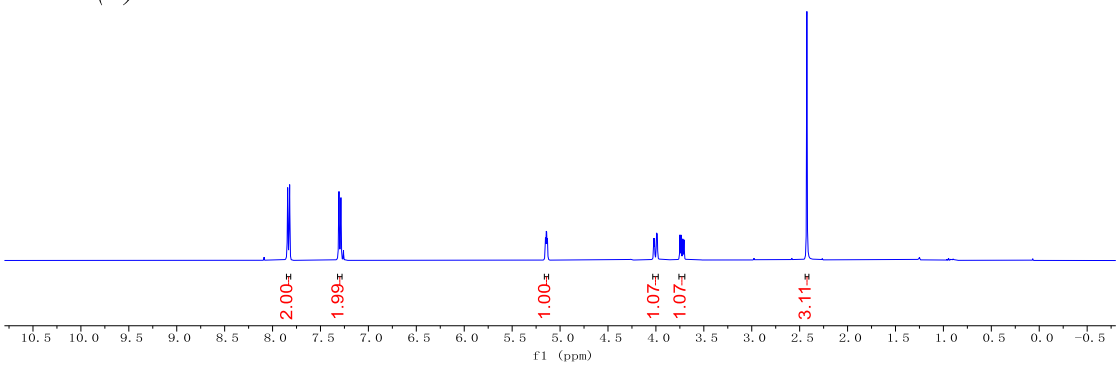
^{1}H NMR of (*R*)-**3c**



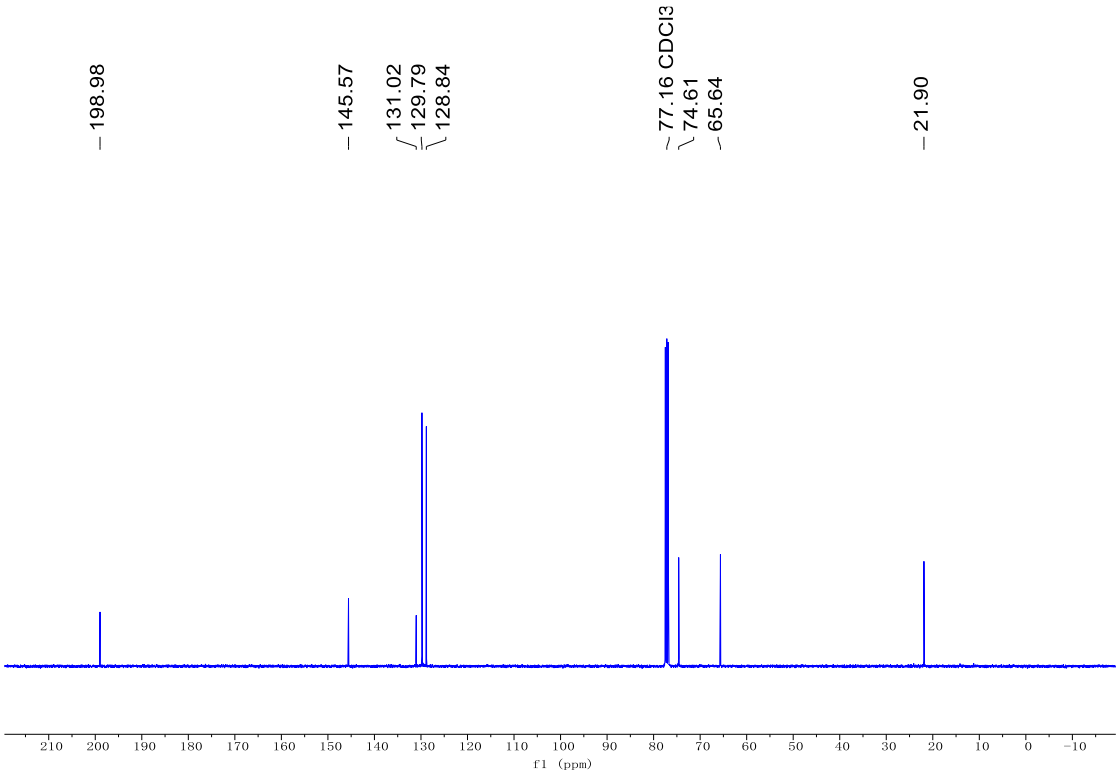
^{13}C NMR of (*R*)-**3c**



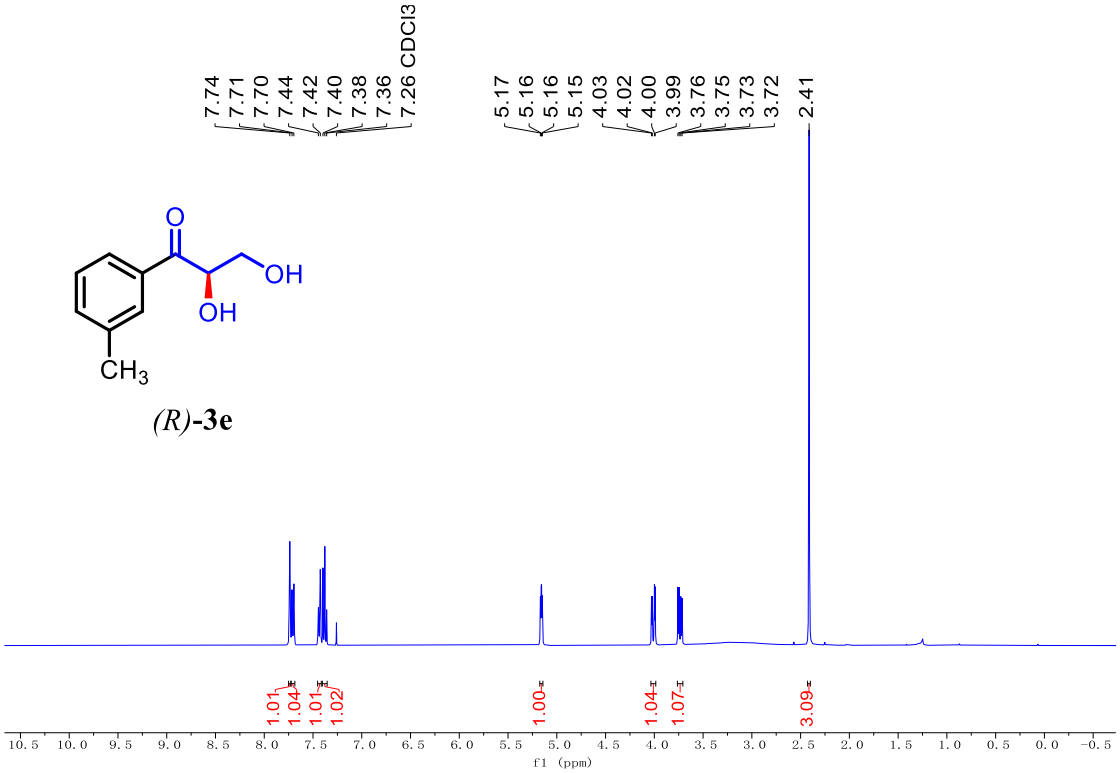
(R)-**3d**



^{1}H NMR of (*R*)-**3d**

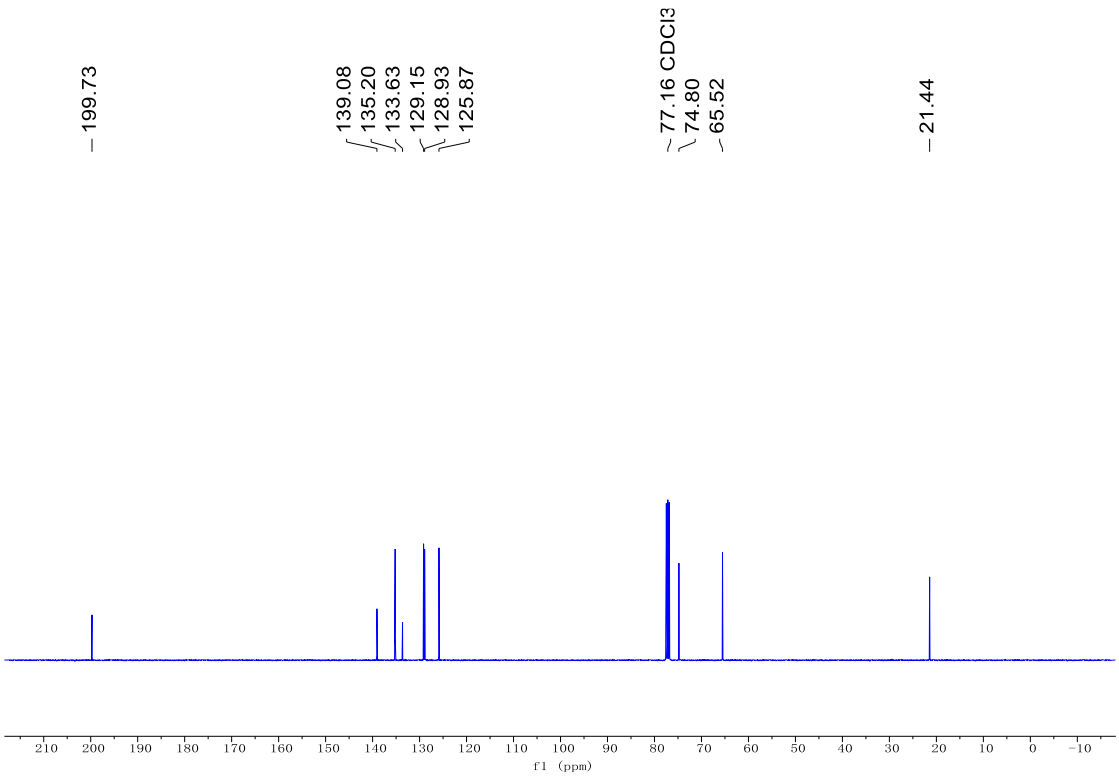


^{13}C NMR of (*R*)-**3d**

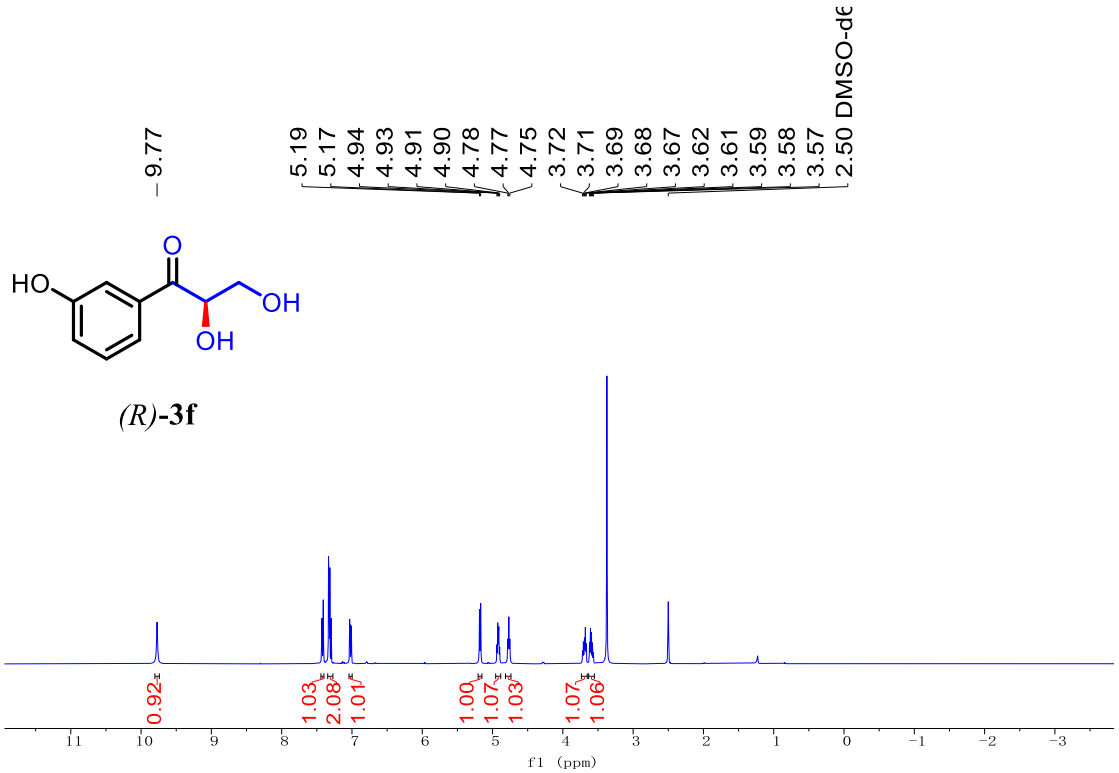


(R)-**3e**

^{1}H NMR of (*R*)-**3e**

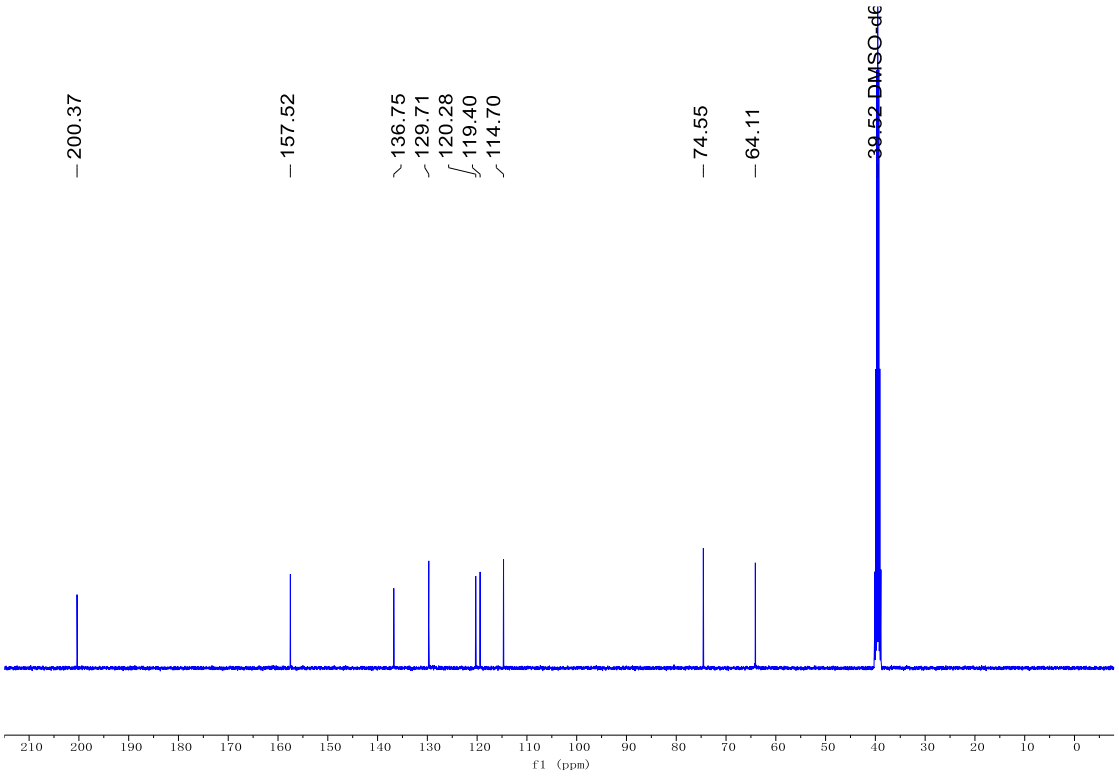


^{13}C NMR of (*R*)-**3e**

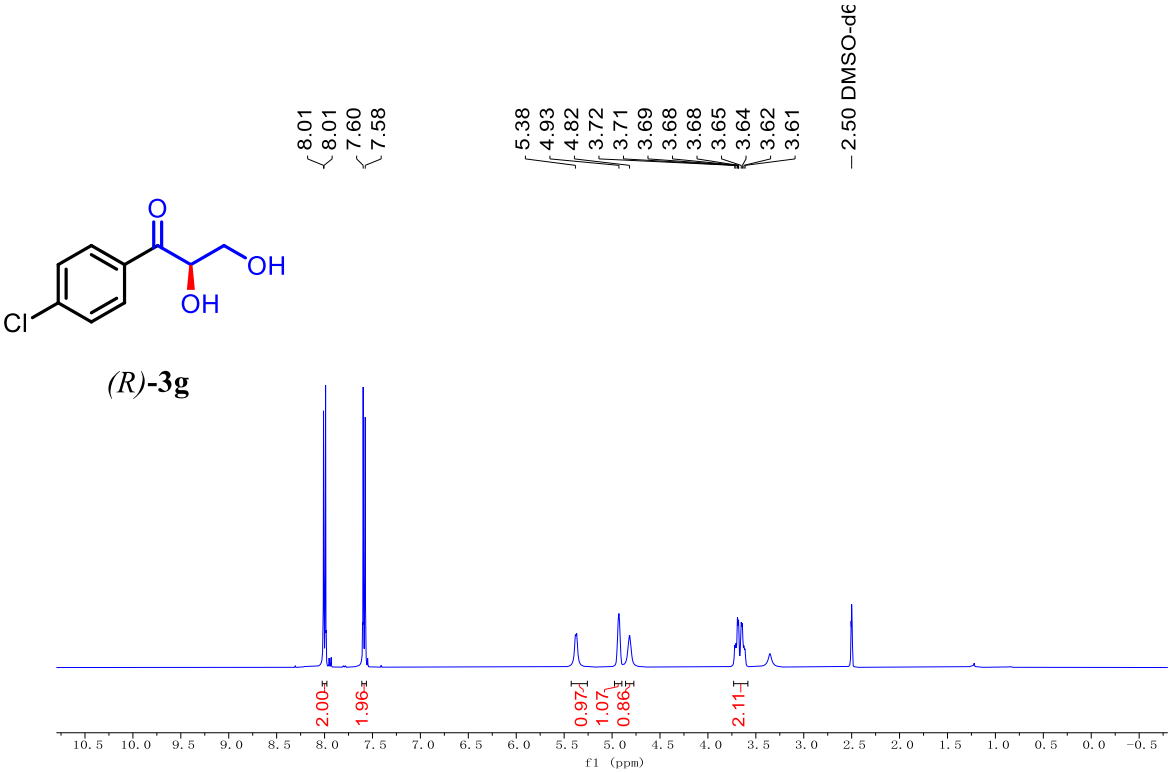


(R)-**3f**

^{1}H NMR of (*R*)-**3f**

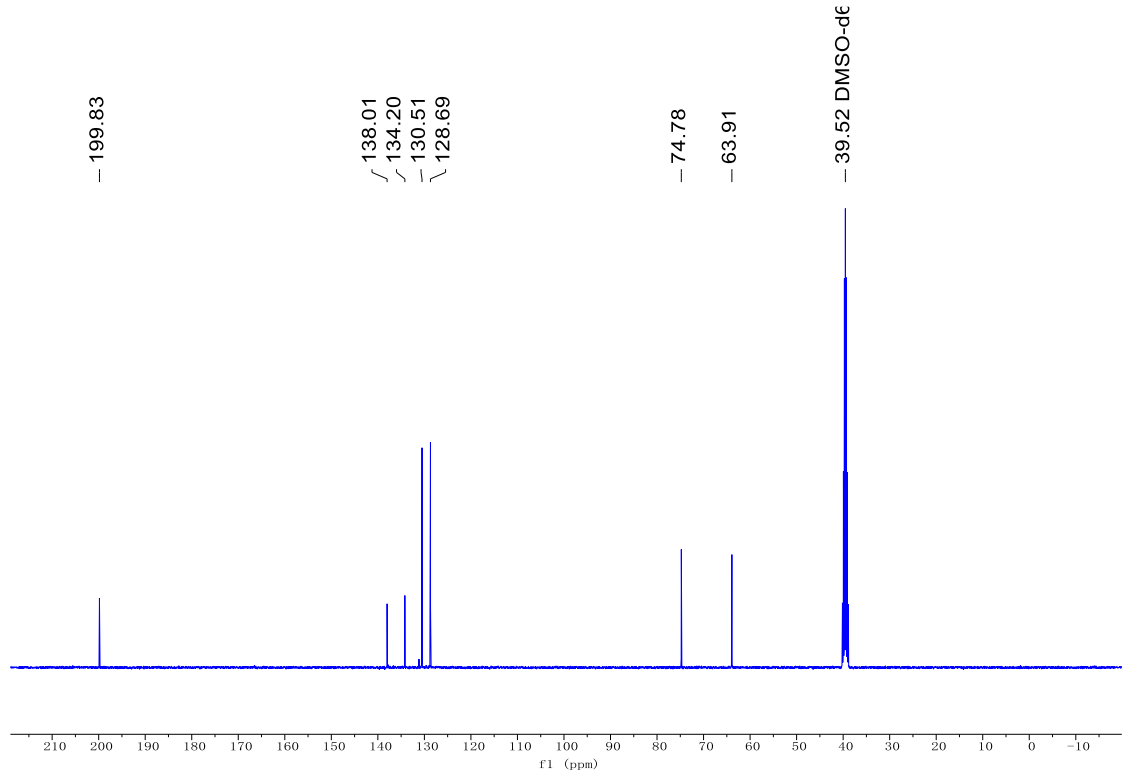


^{13}C NMR of (*R*)-**3f**

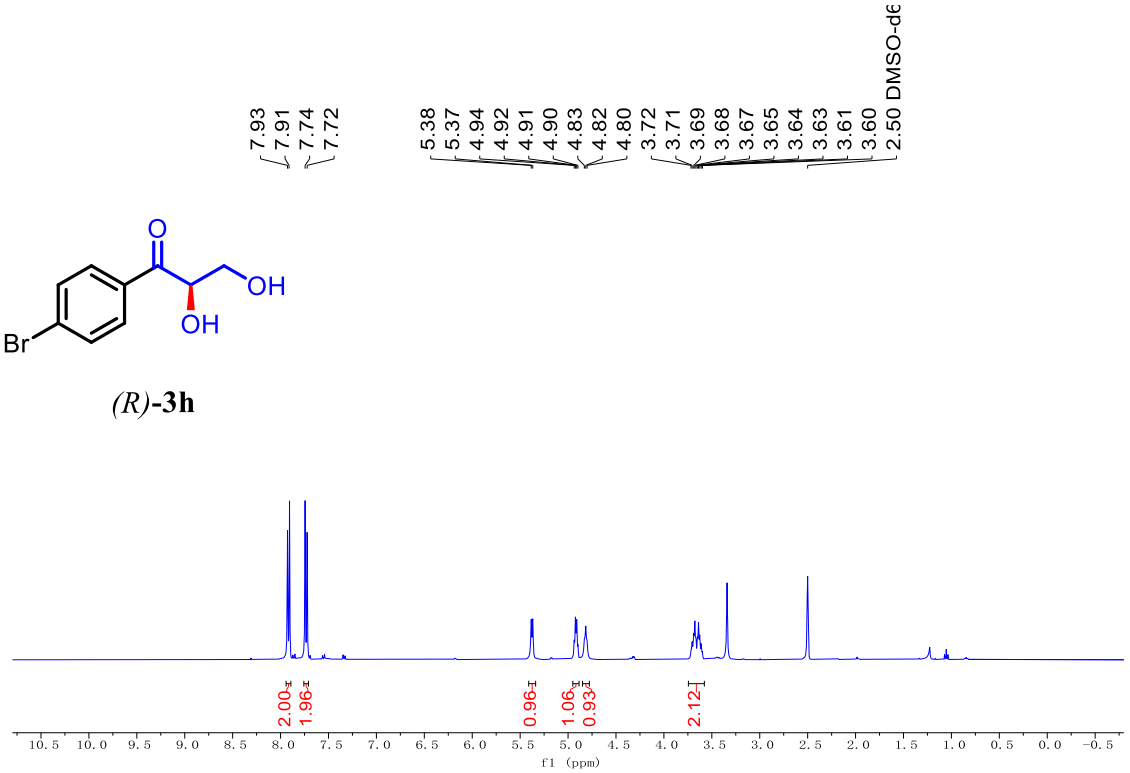


(R)-**3g**

^{1}H NMR of (*R*)-**3g**

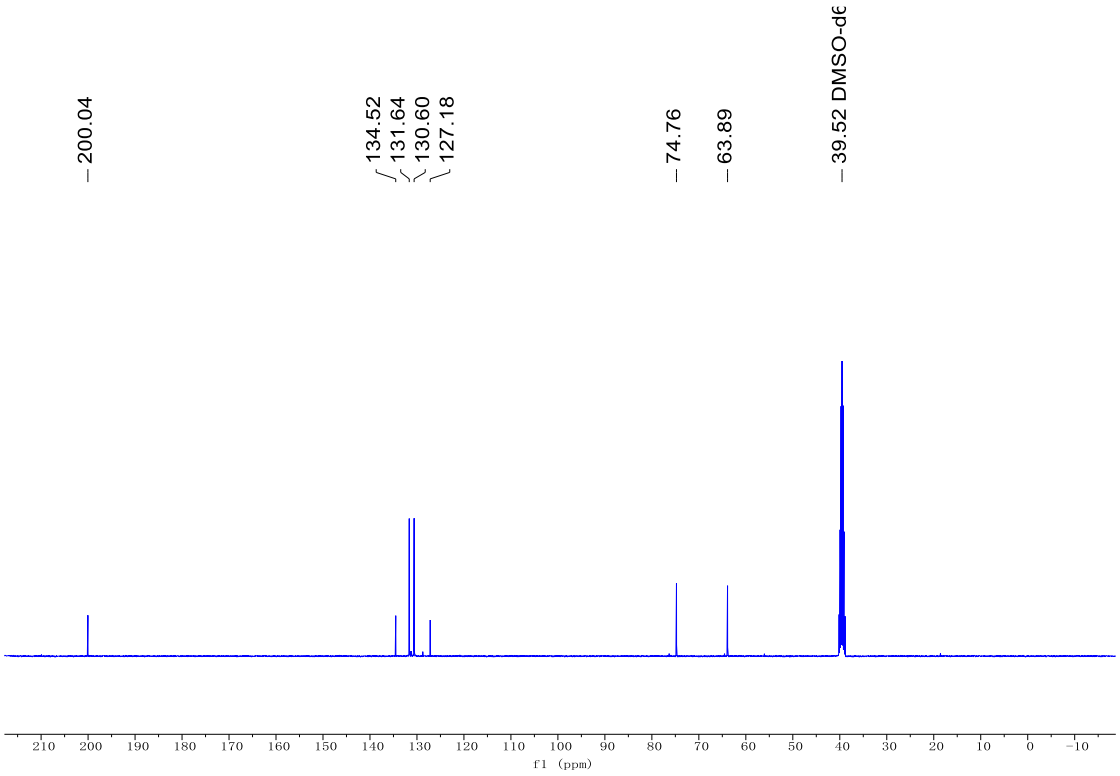


^{13}C NMR of (*R*)-**3g**

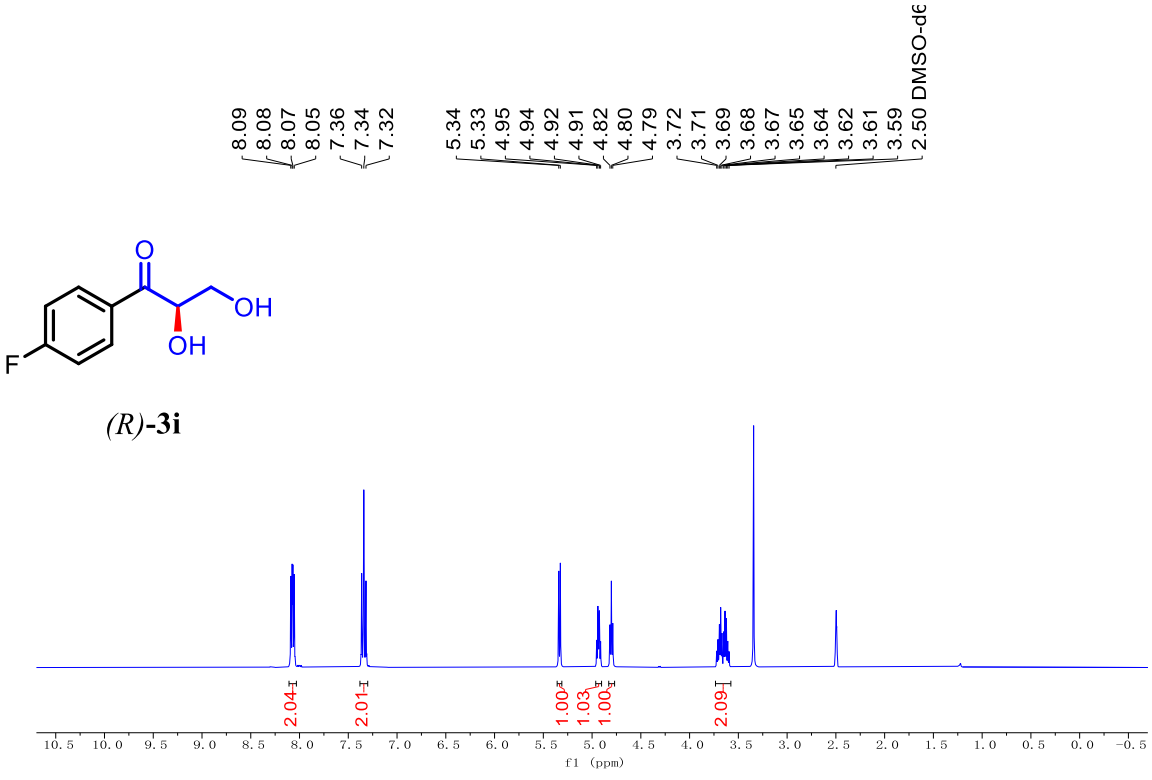


(R)-**3h**

^{1}H NMR of (*R*)-**3h**

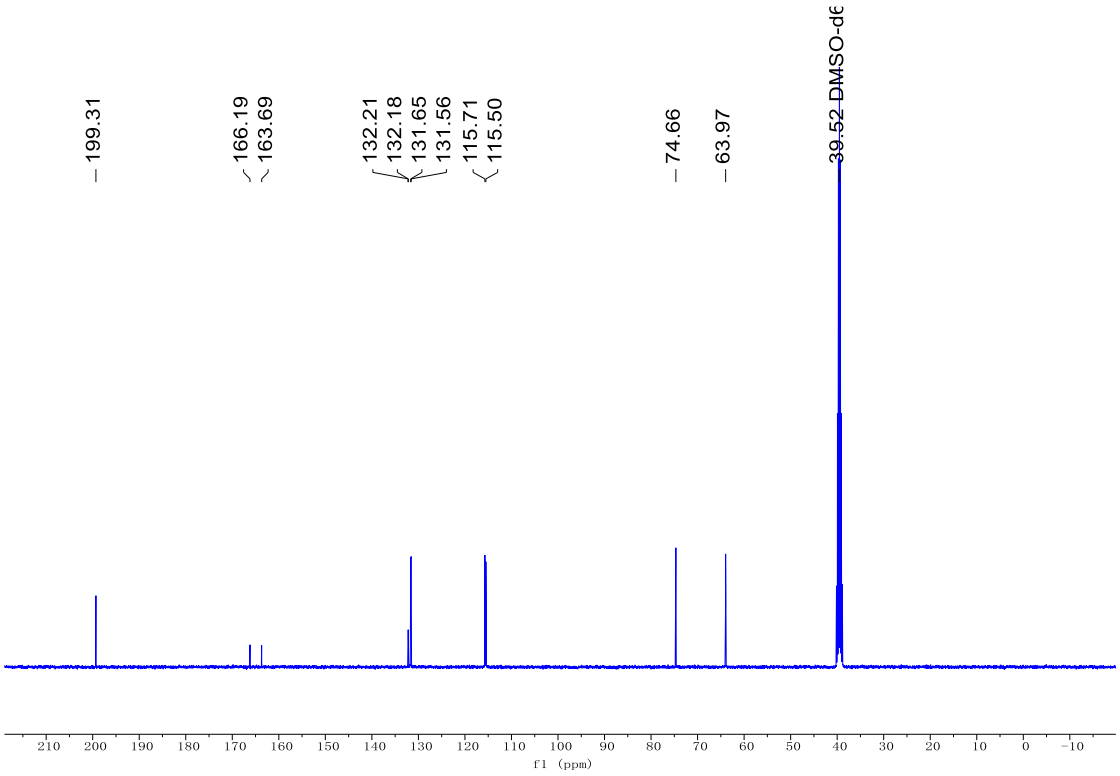


^{13}C NMR of (*R*)-**3h**

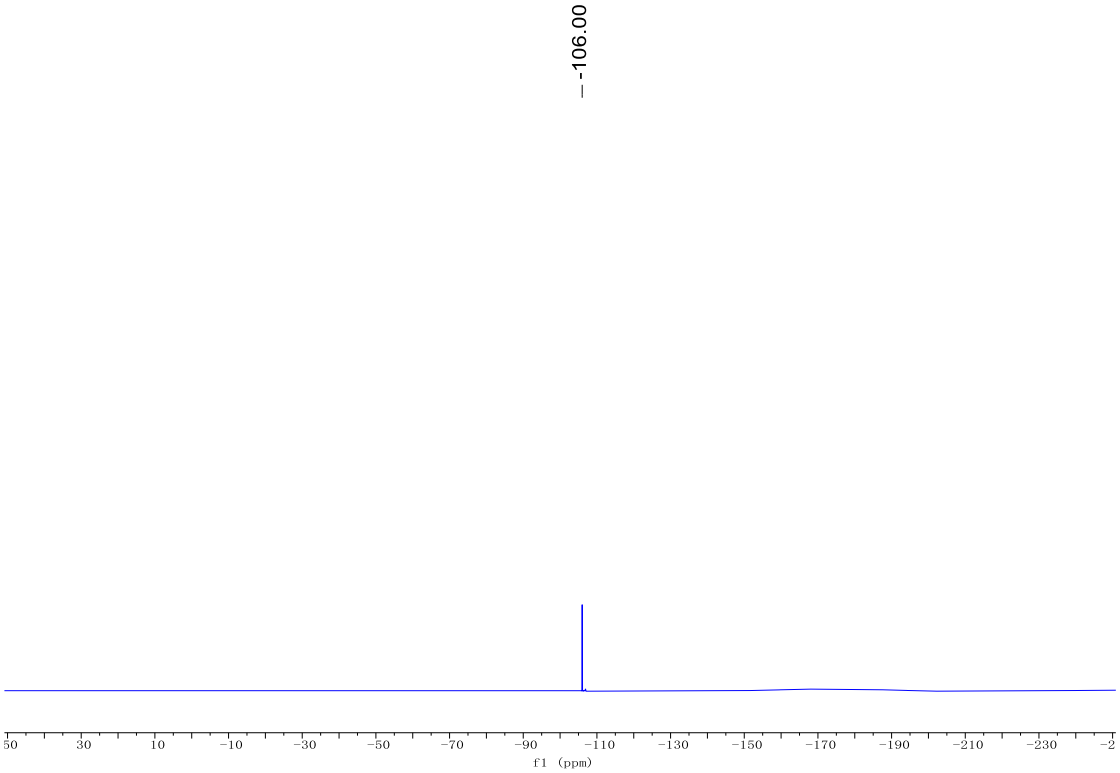


(R)-**3i**

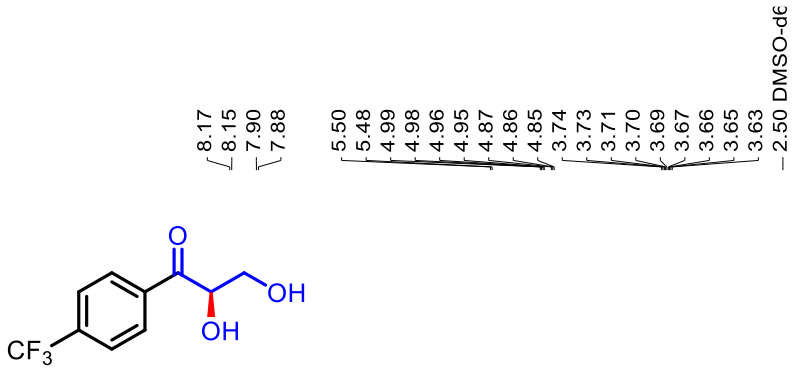
^{1}H NMR of (*R*)-**3i**



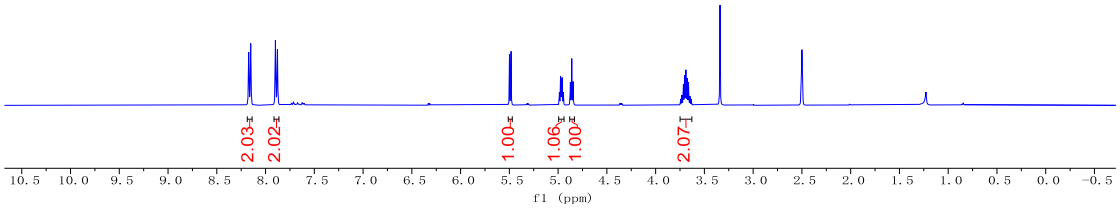
^{13}C NMR of (*R*)-**3i**



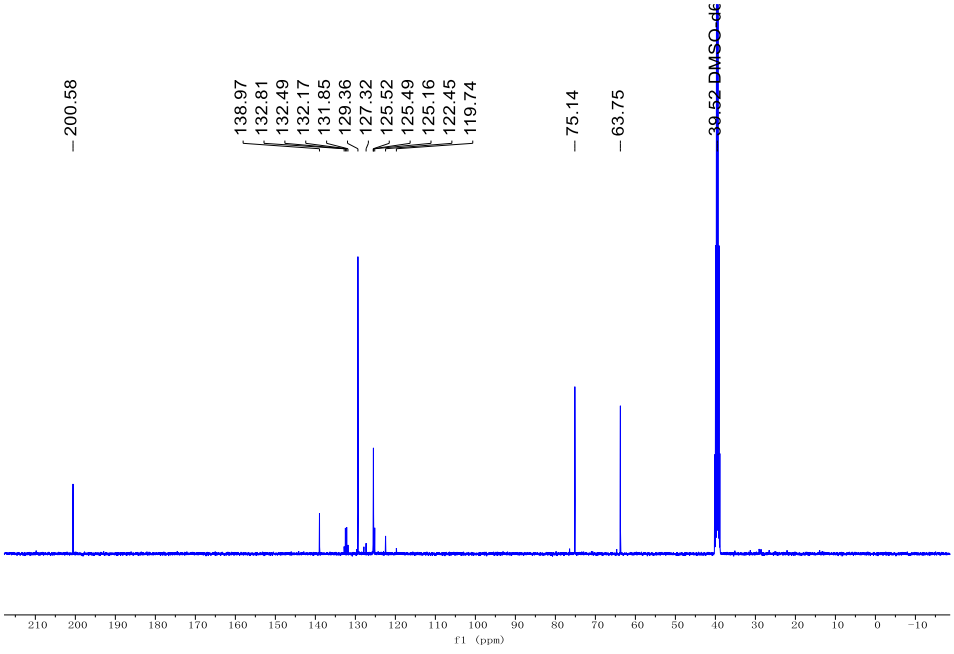
^{19}F NMR of (*R*)-**3i**



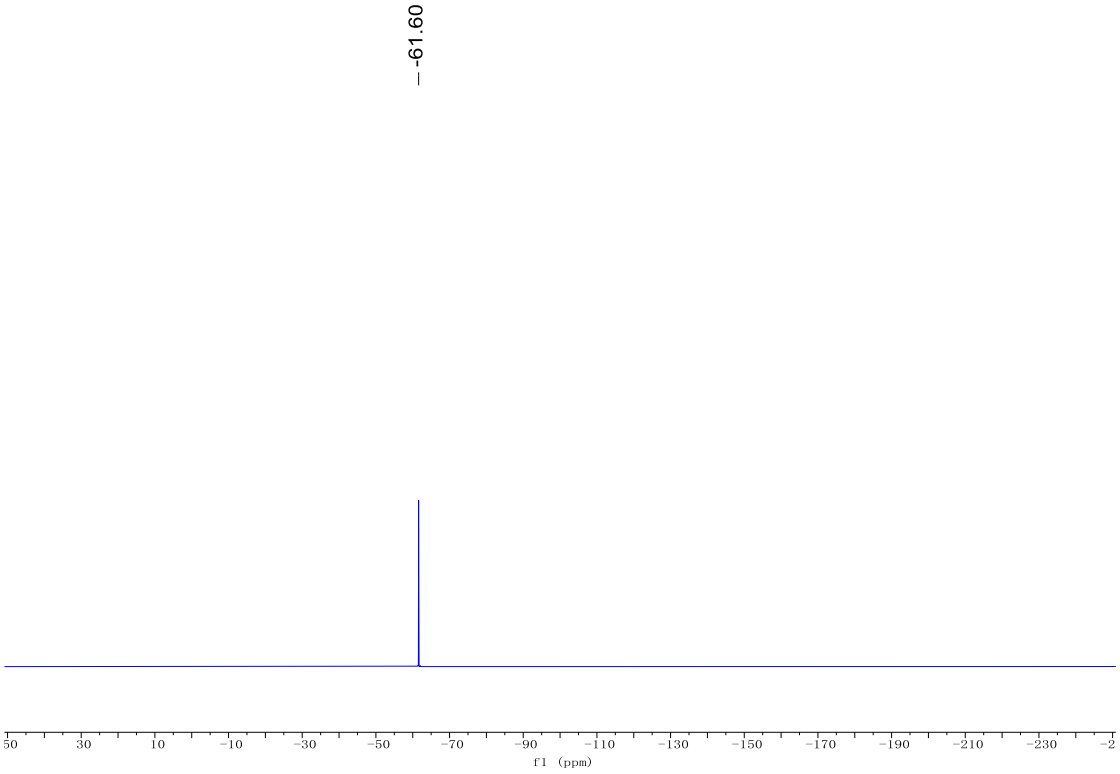
(R)-**3j**



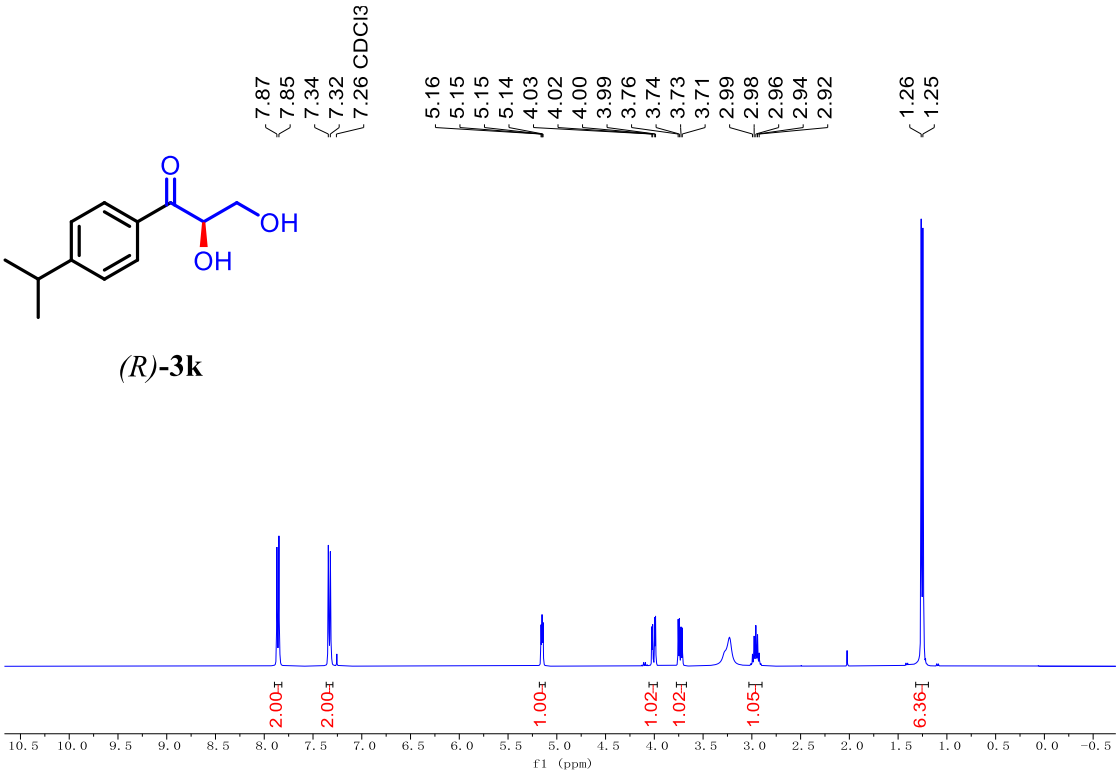
^{1}H NMR of (*R*)-**3j**



^{13}C NMR of (*R*)-**3j**

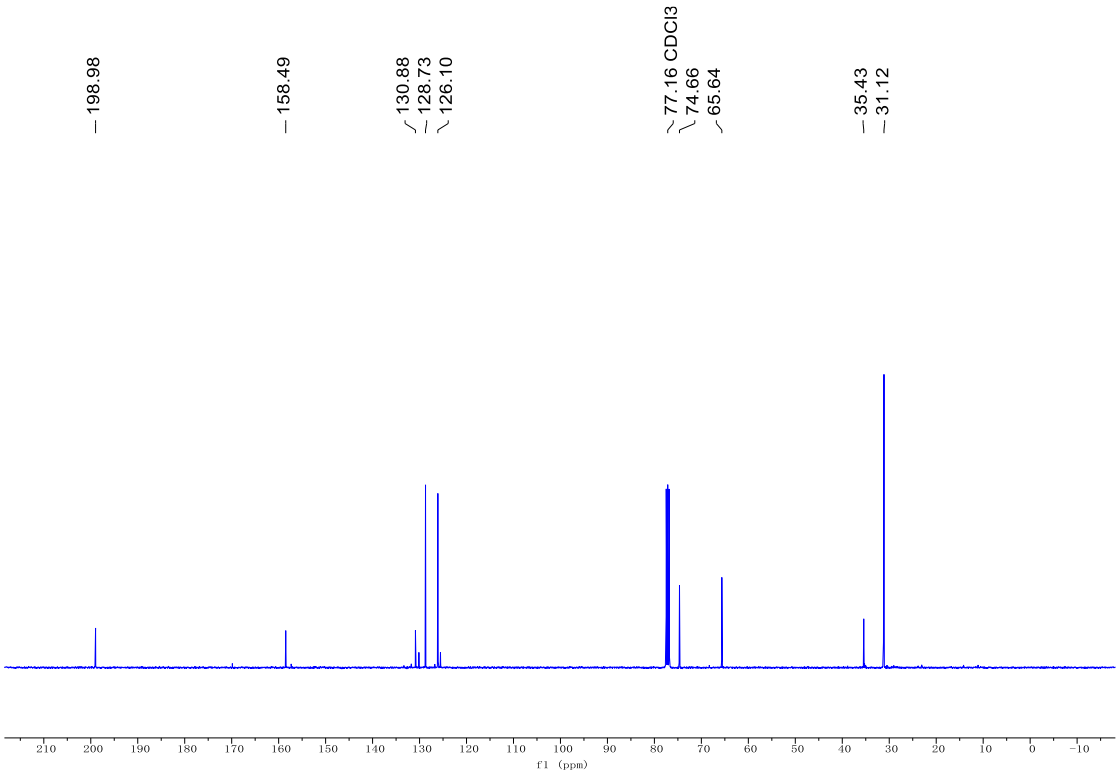


^{19}F NMR of (*R*)-**3j**

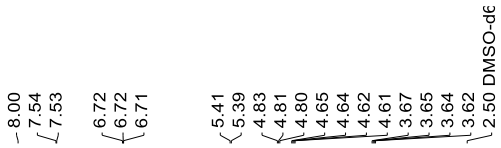


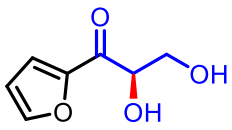
(R)-**3k**

^{1}H NMR of (*R*)-**3k**

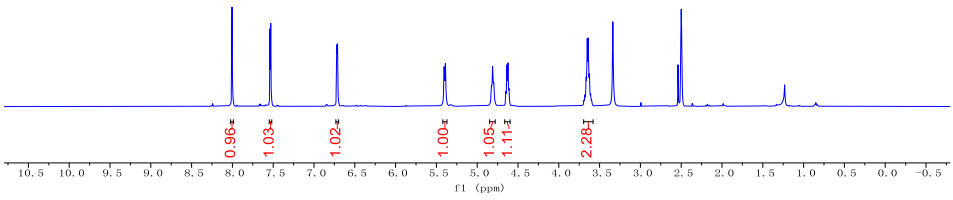


^{13}C NMR of (*R*)-**3k**

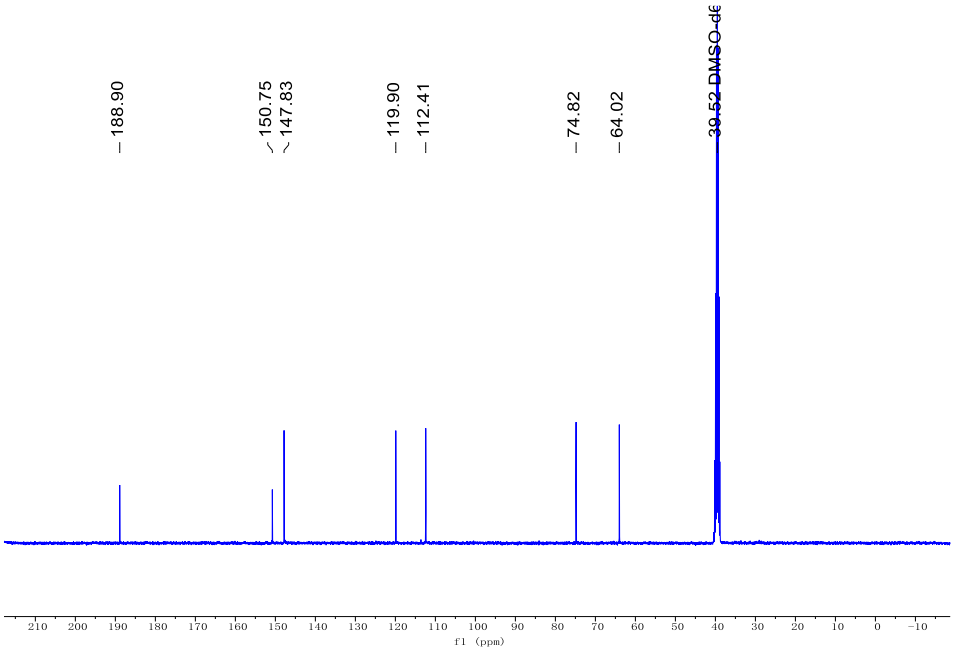




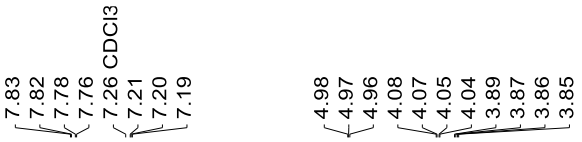
(R)-**3l**

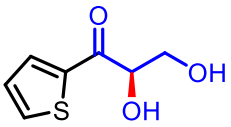


^{1}H NMR of (*R*)-**3l**

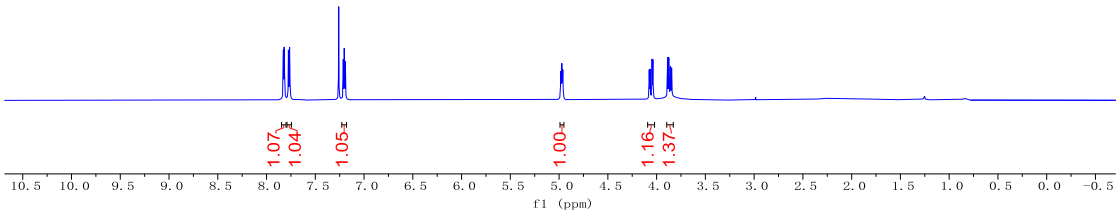


^{13}C NMR of (*R*)-**3l**

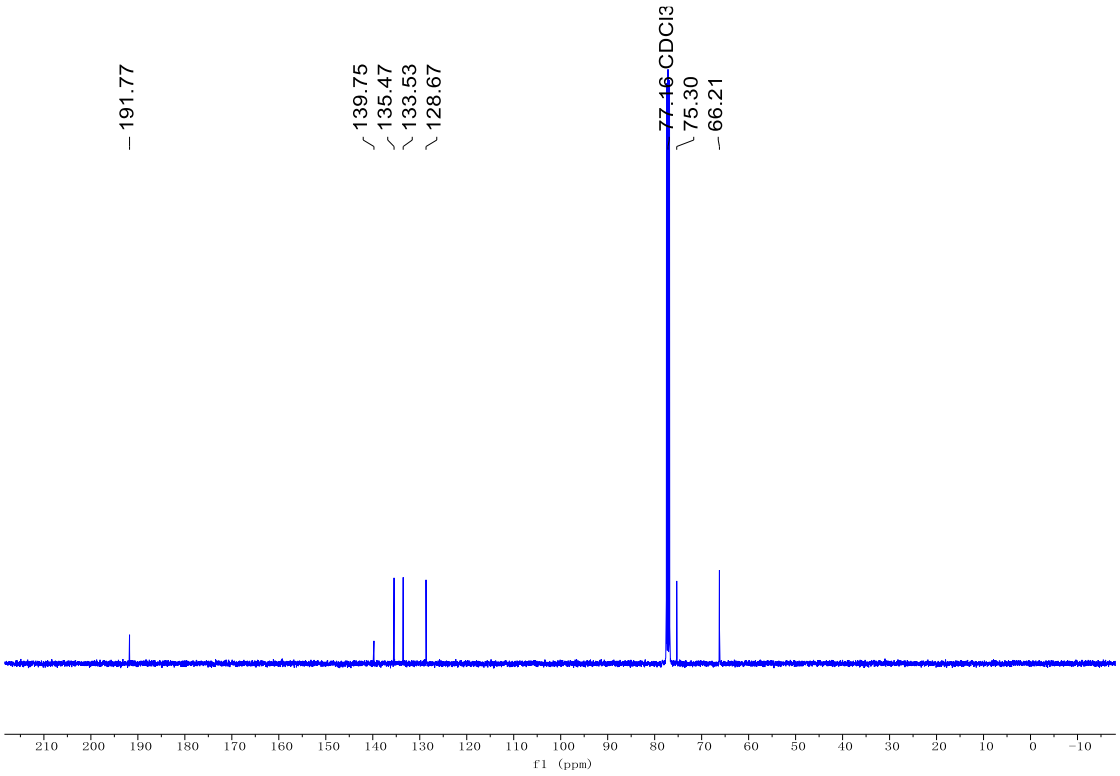




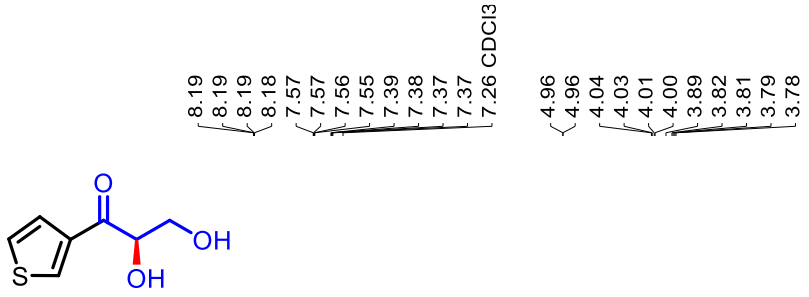
(R)-**3m**



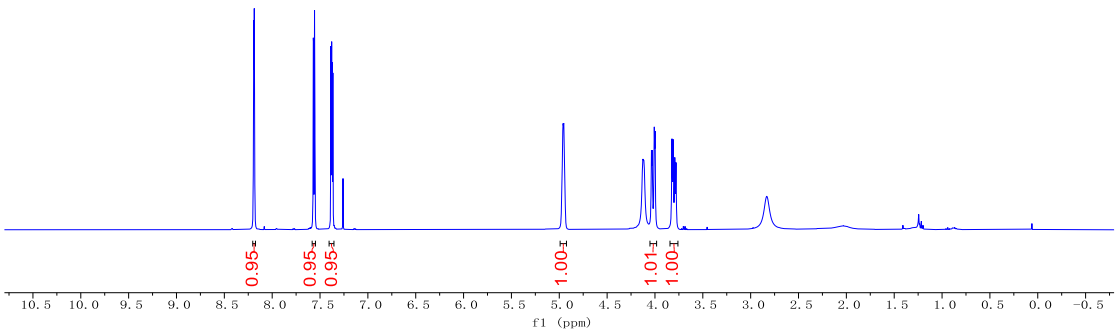
^{1}H NMR of (*R*)-**3m**



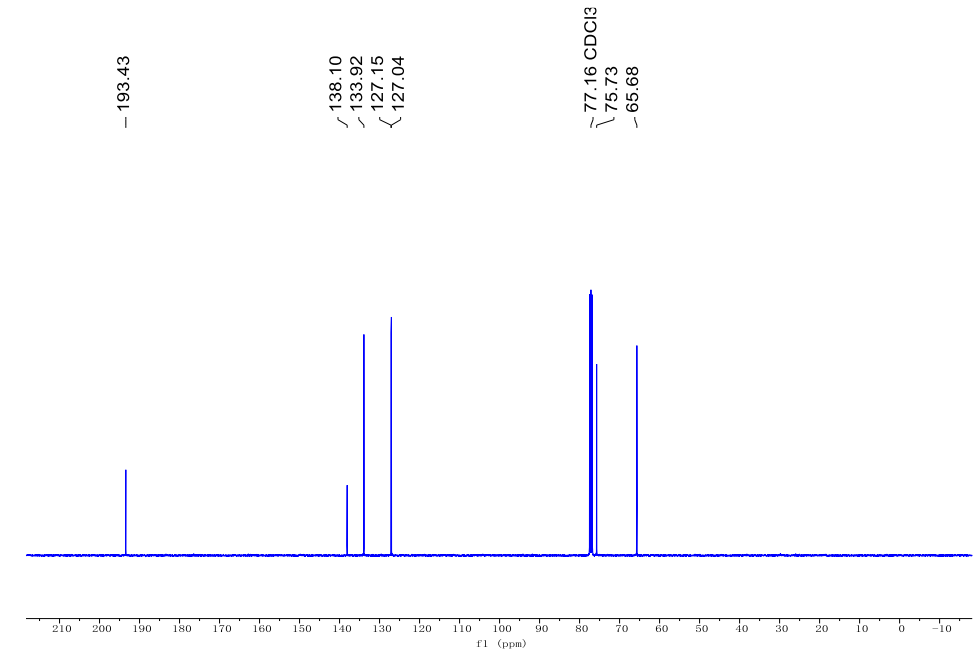
^{13}C NMR of (*R*)-**3m**



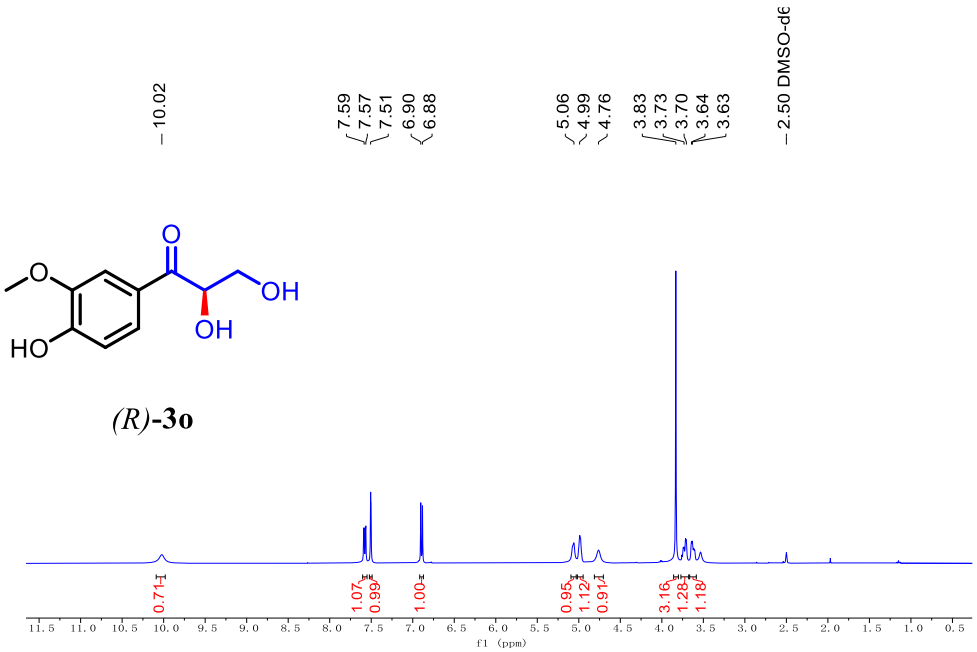
(R)-**3n**



^{1}H NMR of (*R*)-**3n**

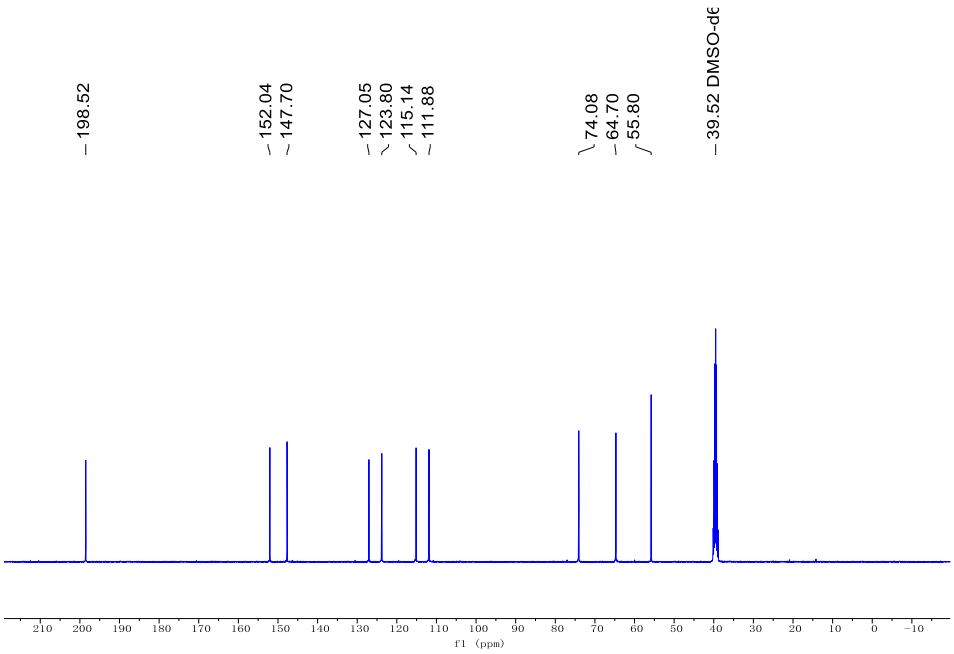


^{13}C NMR of (*R*)-**3n**

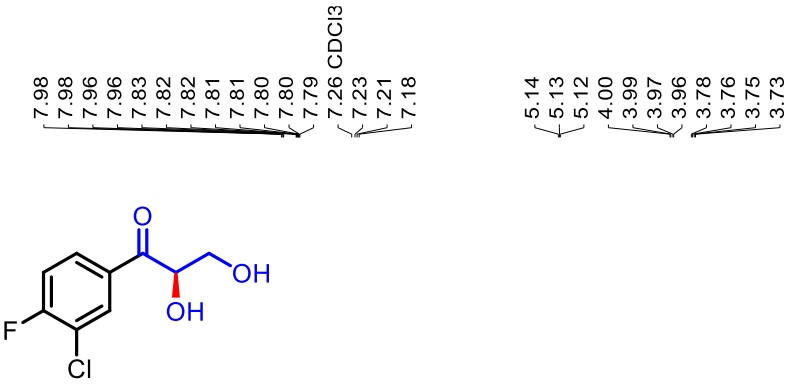


(R)-**3o**

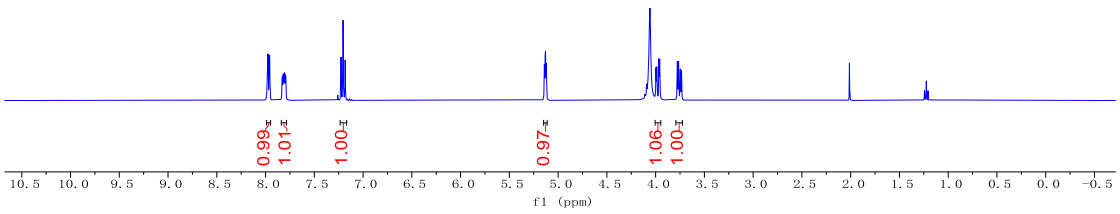
^{1}H NMR of (*R*)-**3o**



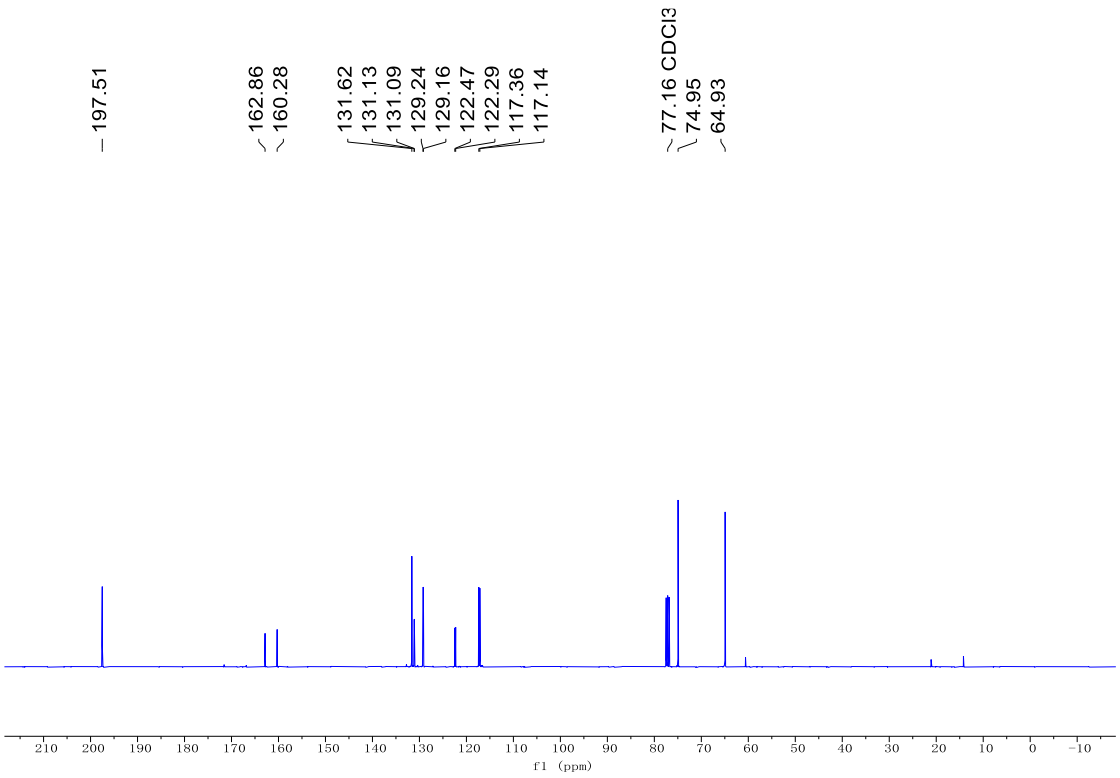
^{13}C NMR of (*R*)-**3o**



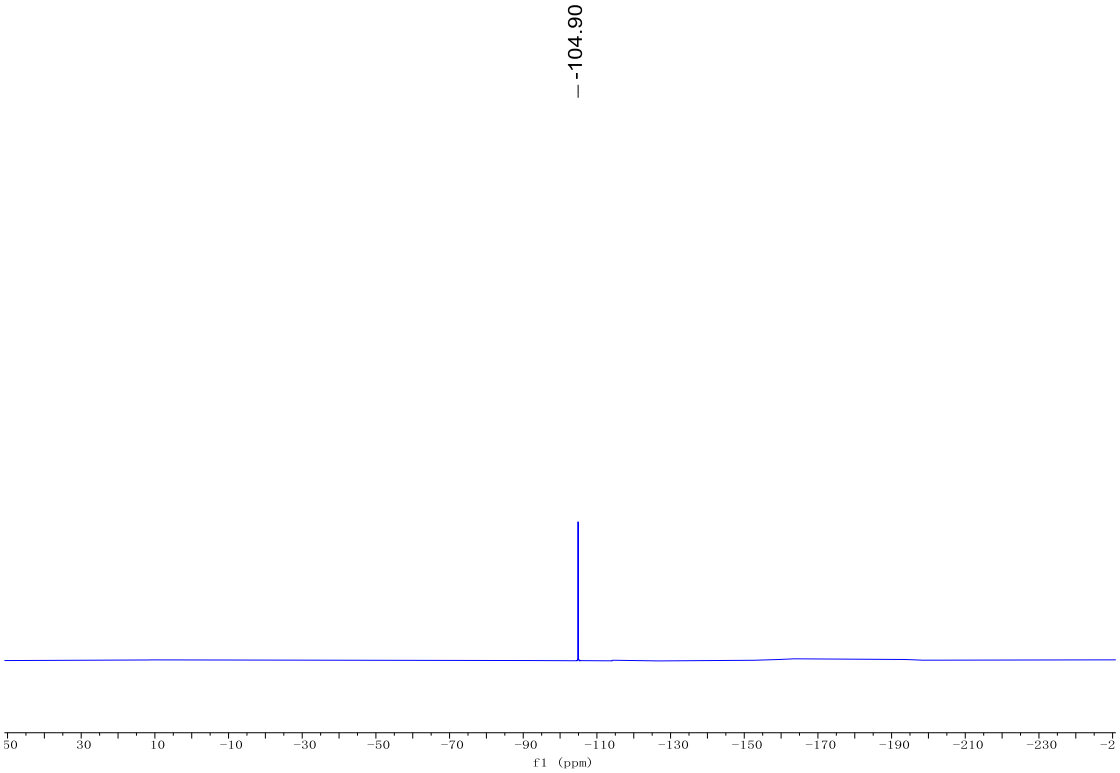
(R)-**3p**



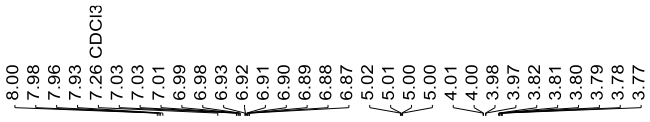
^{1}H NMR of (*R*)-**3p**

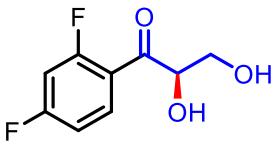


^{13}C NMR of (*R*)-**3p**

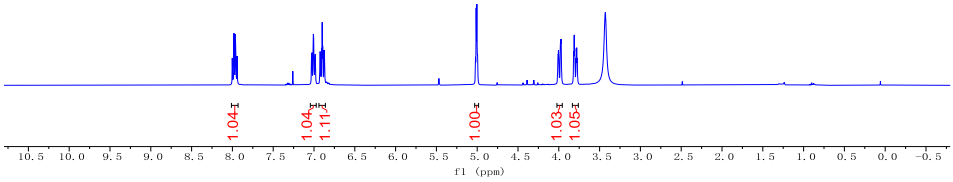


^{19}F NMR of (*R*)-**3p**

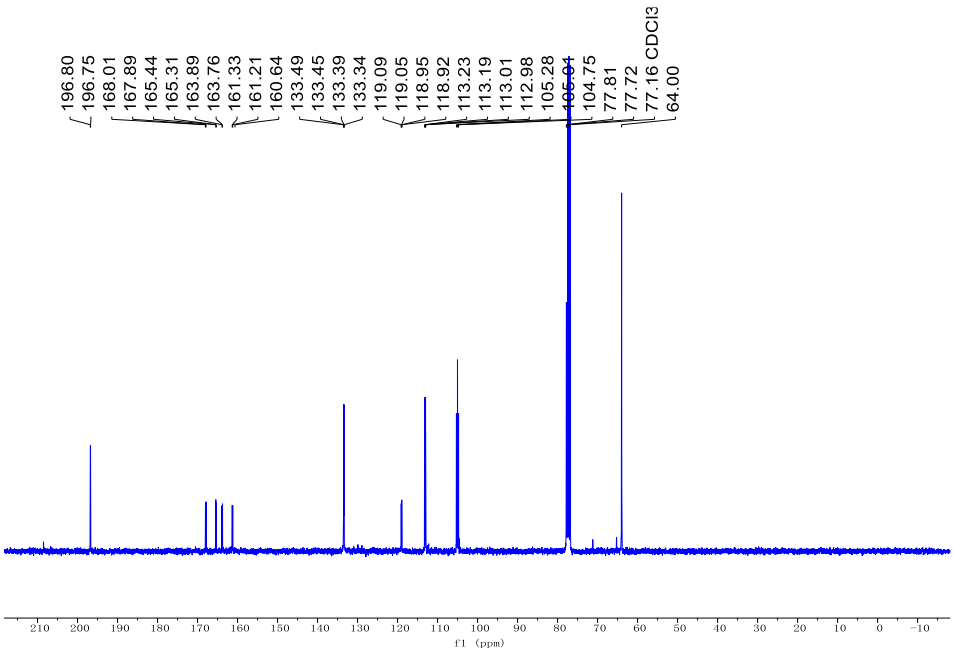




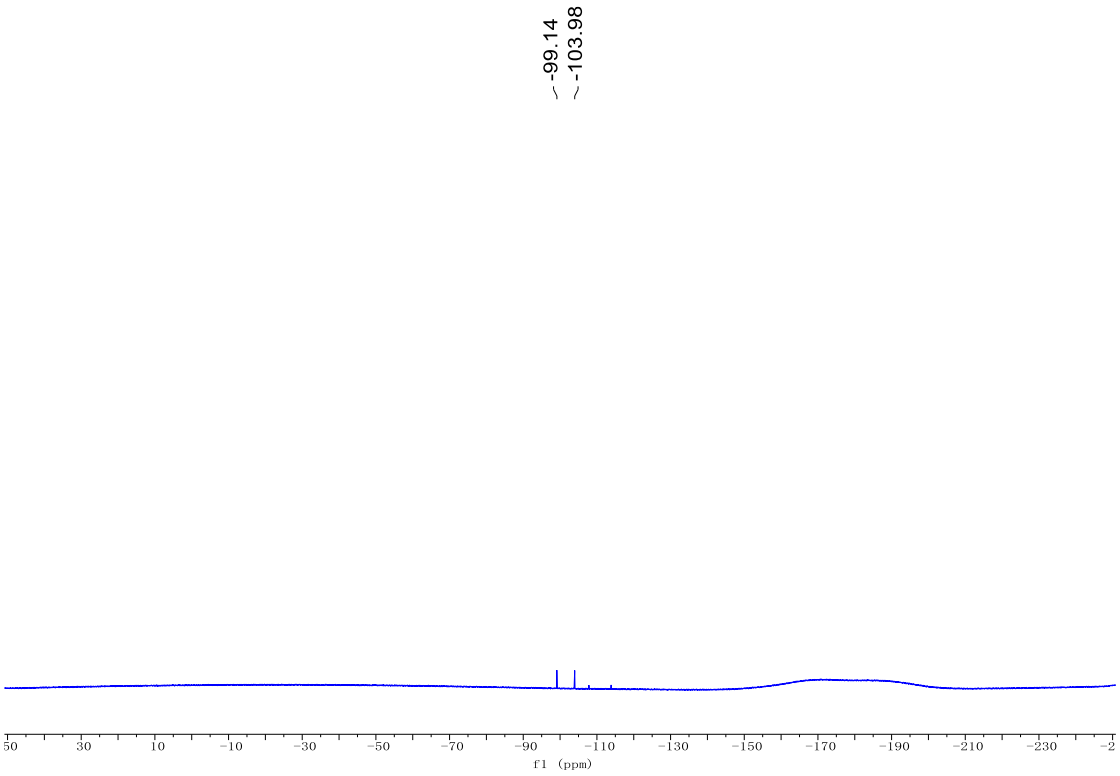
(R)-**3q**



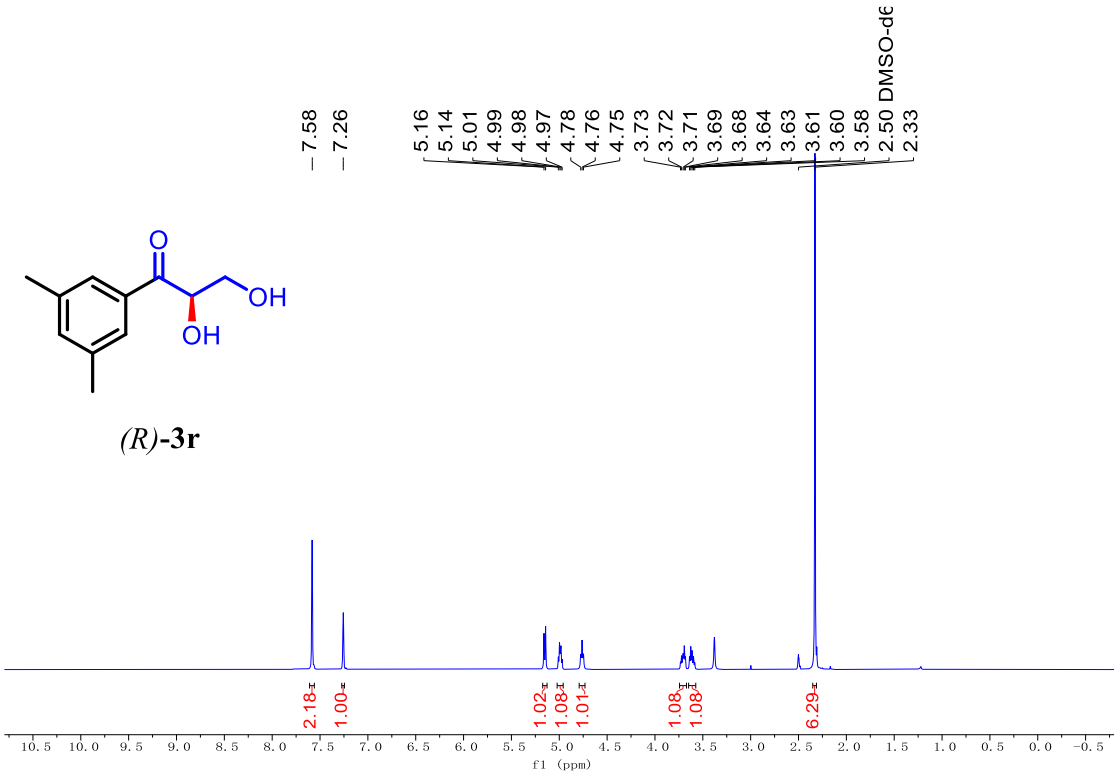
^{1}H NMR of (*R*)-**3q**



^{13}C NMR of (*R*)-**3q**

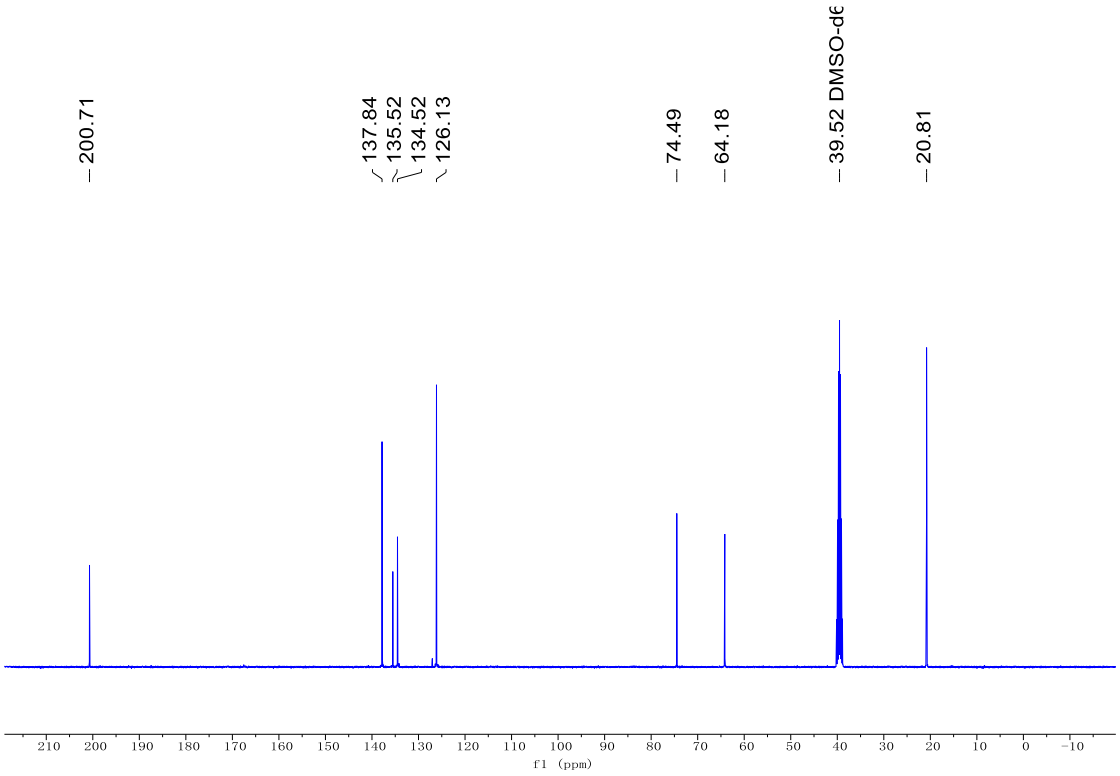


^{19}F NMR of (*R*)-**3q**

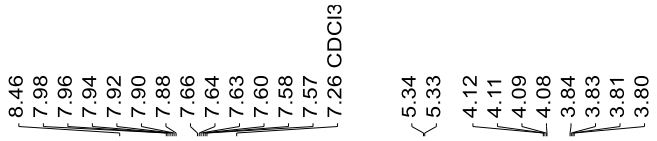


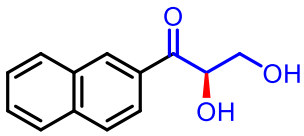
(R)-**3r**

^{1}H NMR of (*R*)-**3r**

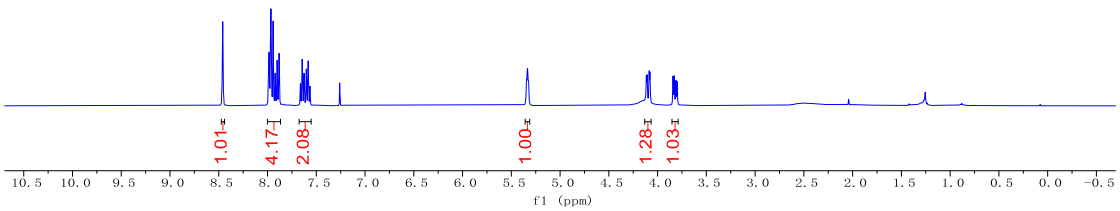


^{13}C NMR of (*R*)-**3r**

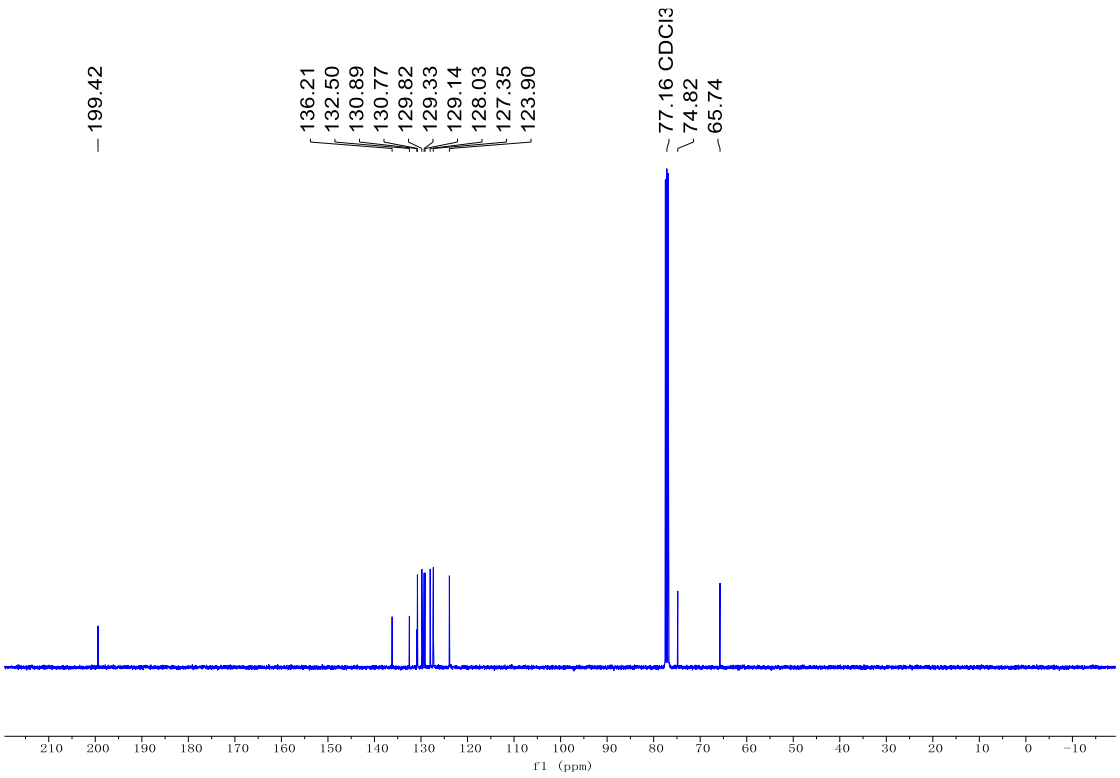




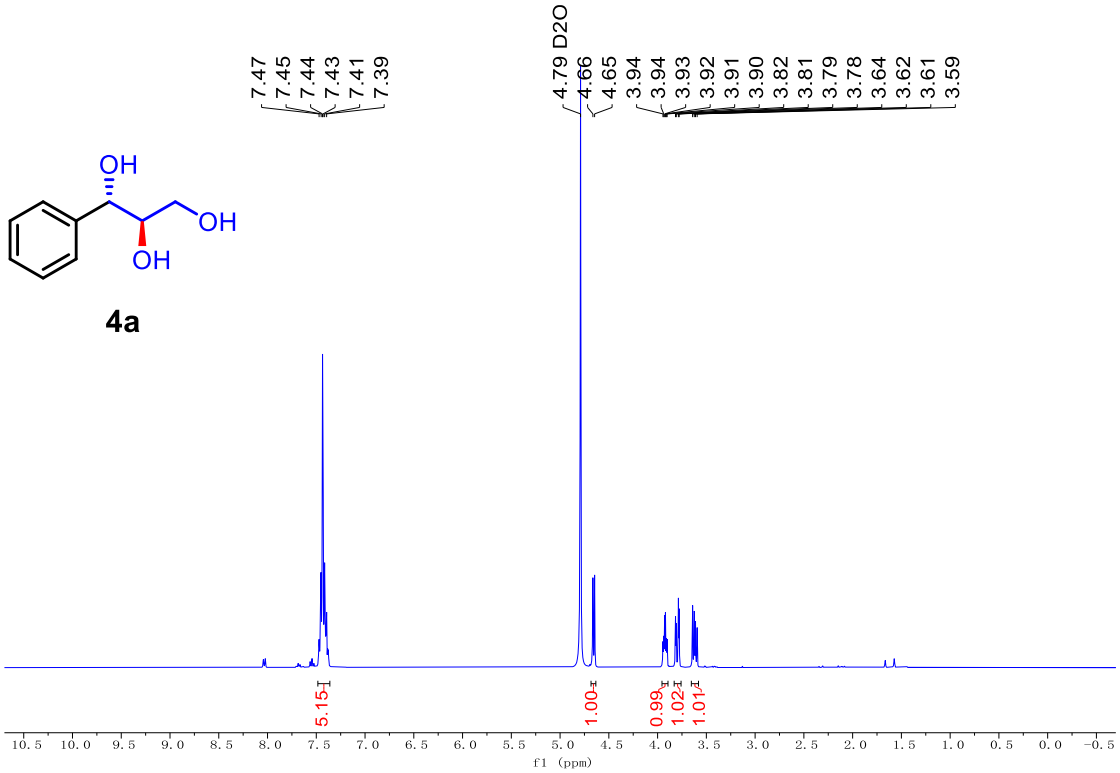
(R)-**3s**



^{1}H NMR of (*R*)-**3s**

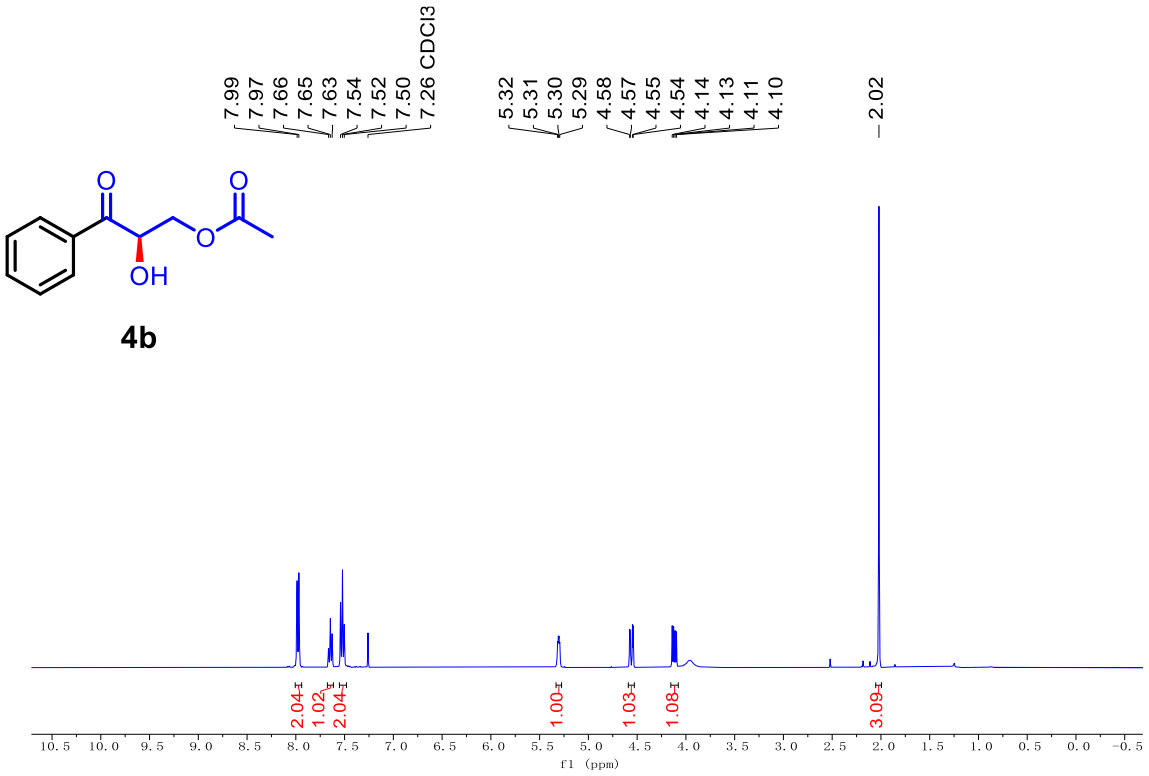


^{13}C NMR of (*R*)-**3s**



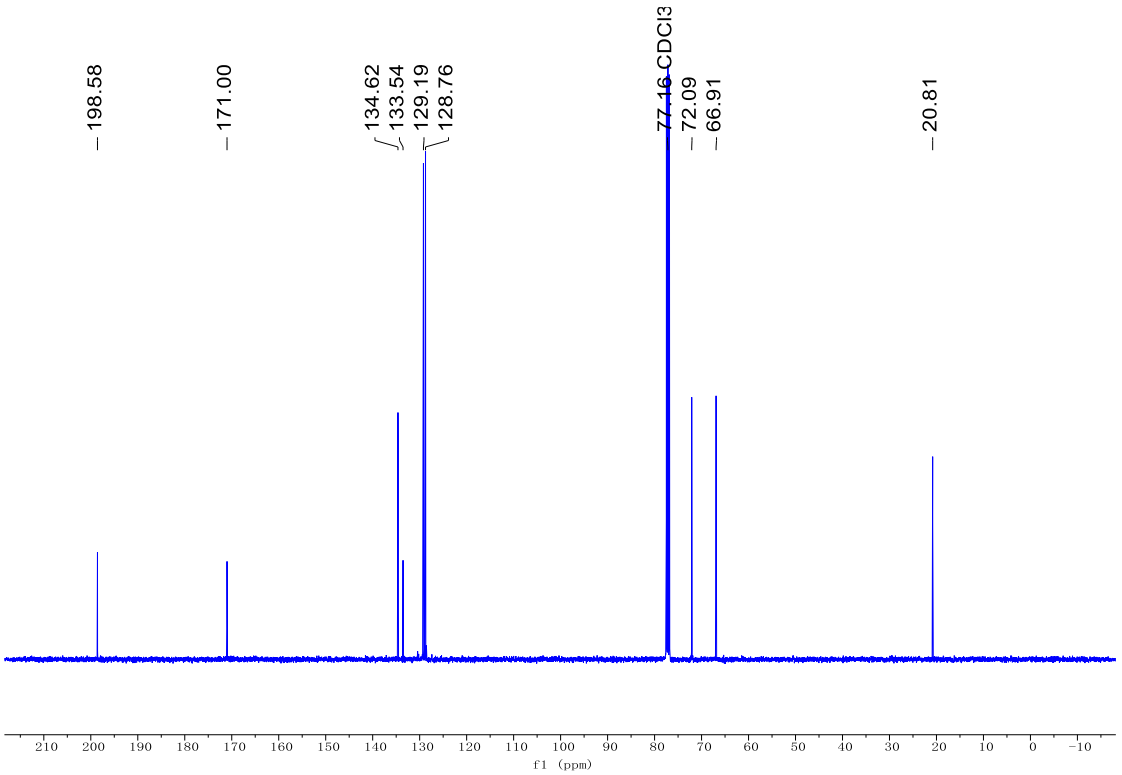
4a

^{1}H NMR of **4a**



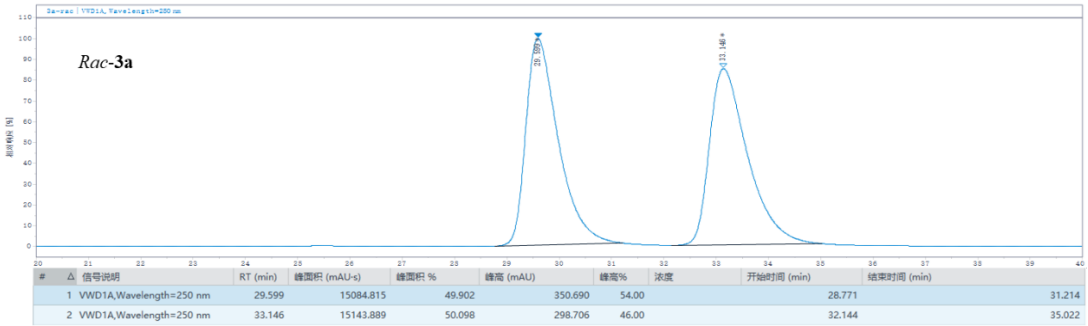
4b

^{1}H NMR of **4b**

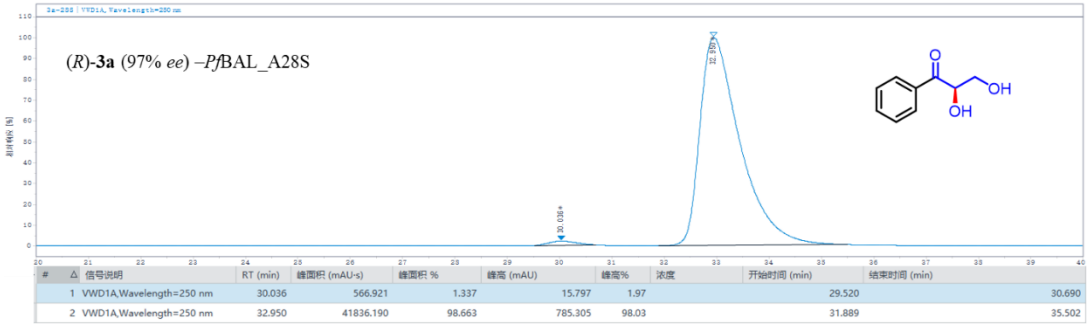


^{13}C NMR of **4b**

19. HPLC Spectra of chiral compounds



#	Δ	信号说明	RT (min)	峰面积 (mAU-s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1		VWD1A,Wavelength=250 nm	29.599	15084.815	49.902	350.690	54.00		28.771	31.214
2		VWD1A,Wavelength=250 nm	33.146	15143.889	50.098	298.706	46.00		32.144	35.022



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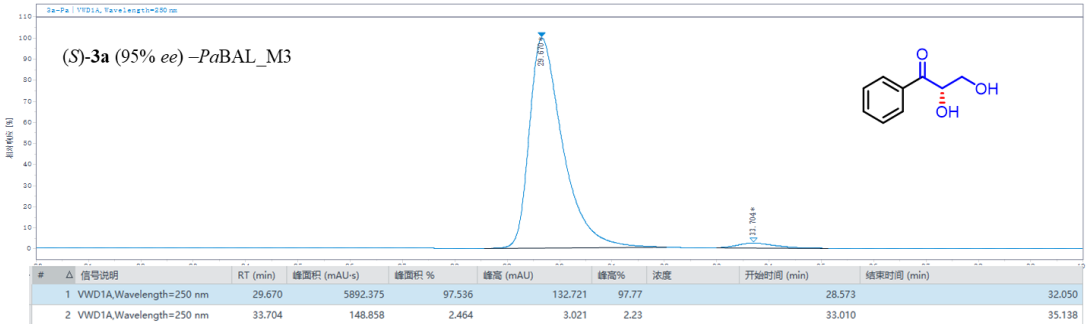
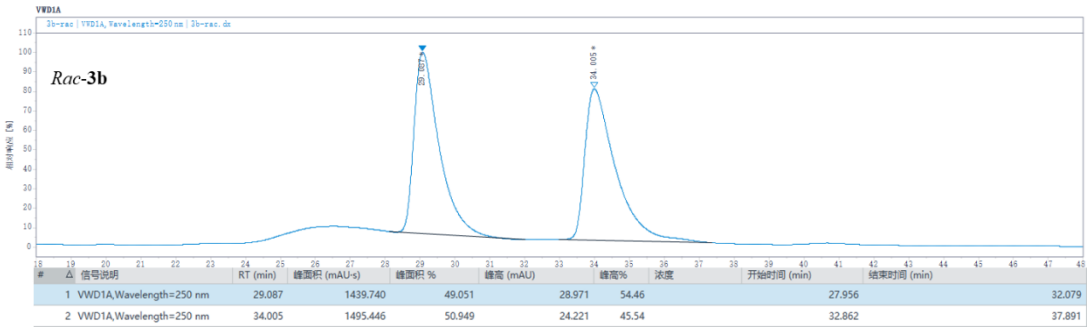
1		VWD1A,Wavelength=250 nm	30.036	566.921	1.337	15.797	1.97		29.520	30.690
2		VWD1A,Wavelength=250 nm	32.950	41836.190	98.663	785.305	98.03		31.889	35.502

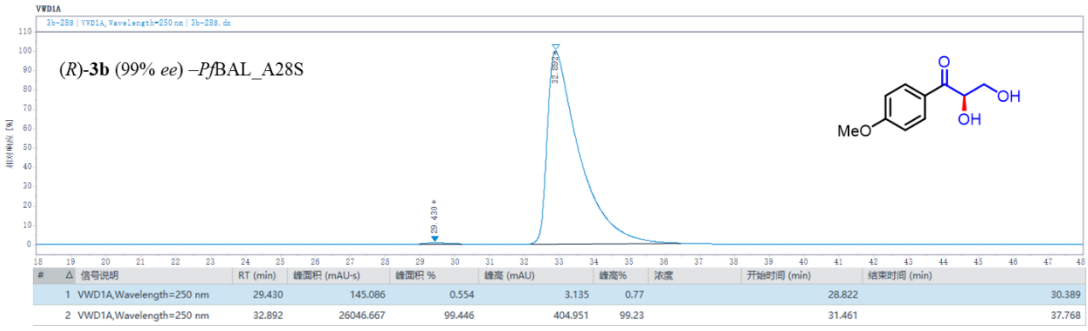


#	Δ	信号说明	RT (min)	峰面积 (mAU-s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1		VWD1A,Wavelength=250 nm	29.670	5892.375	97.536	132.721	97.77		28.573	32.050
2		VWD1A,Wavelength=250 nm	33.704	148.858	2.464	3.021	2.23		33.010	35.138

HPLC chromatogram of racemate of 2,3-dihydroxy-1-phenylpropan-1-one (**3a**), products of *Pf*BAL_A28S ((*R*)-**3a**) and *Pa*BAL M3 ((*S*)-**3a**). HPLC conditions: DAICEL IA (*n*-hexane: *i*-PrOH = 95:5, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 32.950 min (*Pf*BAL_A28S) and $t_{R\text{-major}}$ = 29.670 min (*Pa*BAL M3).

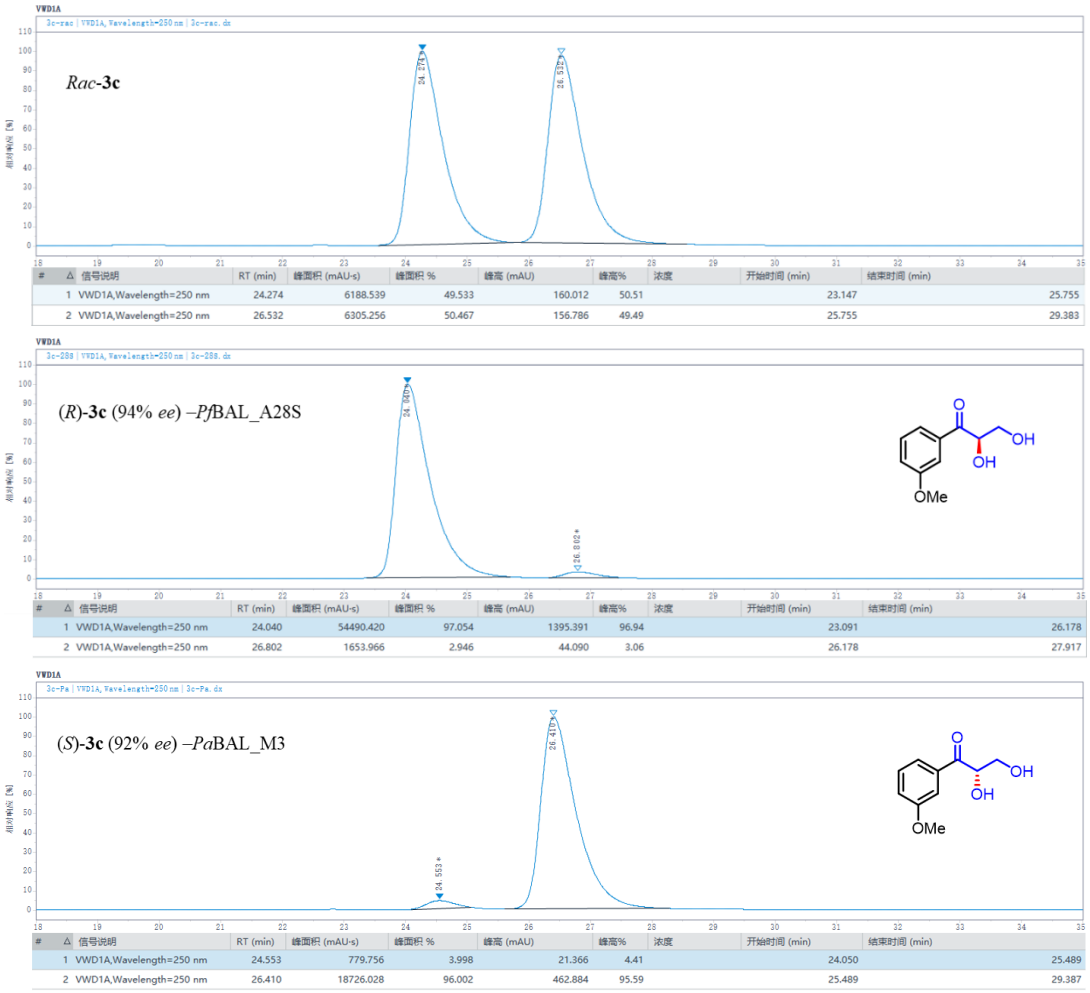


#	Δ	信号说明	RT (min)	峰面积 (mAU-s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1		VWD1A,Wavelength=250 nm	29.087	1439.740	49.051	28.971	54.46		27.956	32.079
2		VWD1A,Wavelength=250 nm	34.005	1495.446	50.949	24.221	45.54		32.862	37.891



#	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1	VWD1A,Wavelength=250 nm	29.430	145.086	0.554	3.135	0.77		28.822	30.389
2	VWD1A,Wavelength=250 nm	32.892	26046.667	99.446	404.951	99.23		31.461	37.768

HPLC chromatogram of racemate of 2,3-dihydroxy-1-(4-methoxyphenyl)propan-1-one(**3b**), products of *Pf*BAL_A28S: ((*R*)-**3b**). HPLC conditions: DAICEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 32.892 min (*Pf*BAL_A28S).



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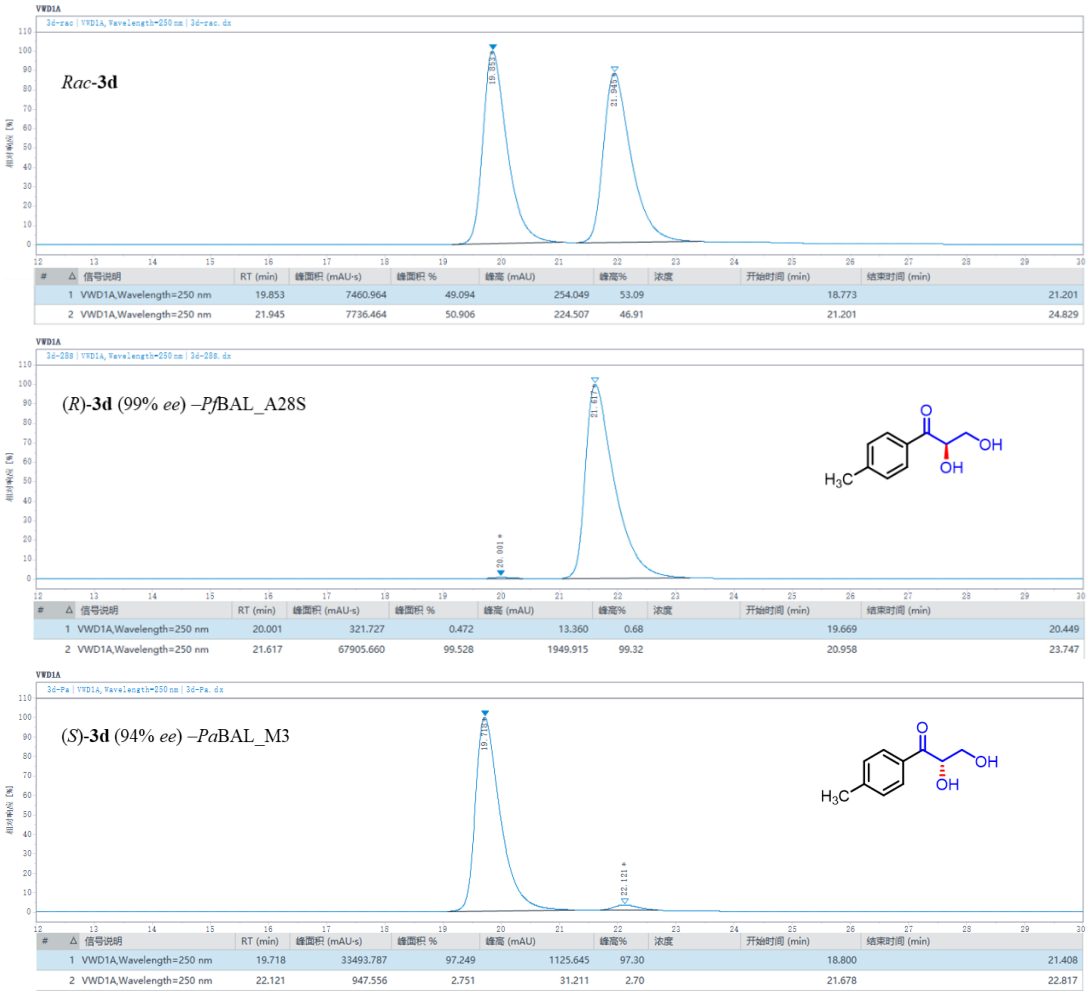
1	VWD1A,Wavelength=250 nm	24.274	6188.539	49.533	160.012	50.51		23.147	25.755
2	VWD1A,Wavelength=250 nm	26.532	6305.256	50.467	156.786	49.49		25.755	29.383

#	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1	VWD1A,Wavelength=250 nm	24.040	54490.420	97.054	1395.391	96.94		23.091	26.178
2	VWD1A,Wavelength=250 nm	26.802	1653.966	2.946	44.090	3.06		26.178	27.917

#	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1	VWD1A,Wavelength=250 nm	24.553	779.756	3.998	21.366	4.41		24.050	25.489
2	VWD1A,Wavelength=250 nm	26.410	18726.028	96.002	462.884	95.59		25.489	29.387

HPLC chromatogram of racemate of 2,3-dihydroxy-1-(3-methoxyphenyl)propan-1-one(**3c**), products of *Pf*BAL_A28S ((*R*)-**3c**) and *Pa*BAL M3 ((*S*)-**3c**). HPLC conditions: DAICEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 24.040 min (*Pf*BAL_A28S) and $t_{R\text{-major}}$ = 26.410 min (*Pa*BAL M3).



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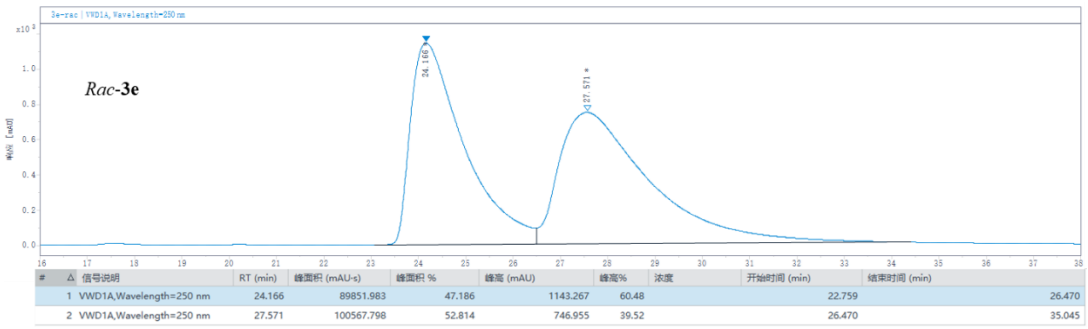
1	VWD1A,Wavelength=250 nm	19.853	7460.964	49.094	254.049	53.09		18.773	21.201
2	VWD1A,Wavelength=250 nm	21.945	7736.464	50.906	224.507	46.91		21.201	24.829

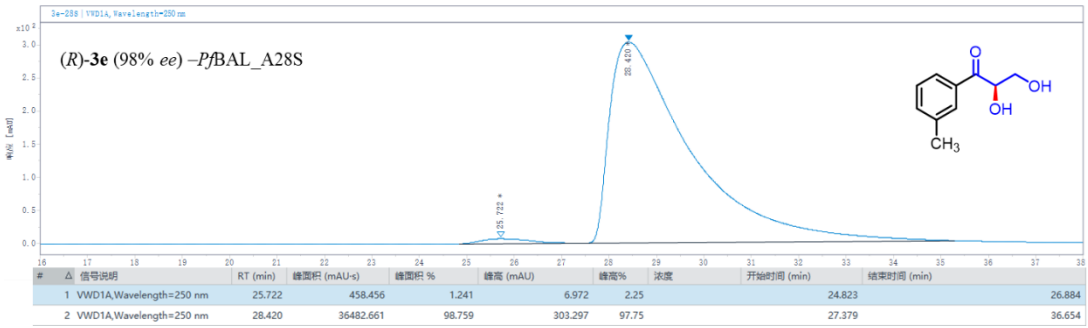
#	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1	VWD1A,Wavelength=250 nm	20.001	321.727	0.472	13.360	0.68		19.669	20.449
2	VWD1A,Wavelength=250 nm	21.617	67905.660	99.528	1949.915	99.32		20.958	23.747

#	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1	VWD1A,Wavelength=250 nm	19.718	33493.787	97.249	1125.645	97.30		18.800	21.408
2	VWD1A,Wavelength=250 nm	22.121	947.556	2.751	31.211	2.70		21.678	22.817

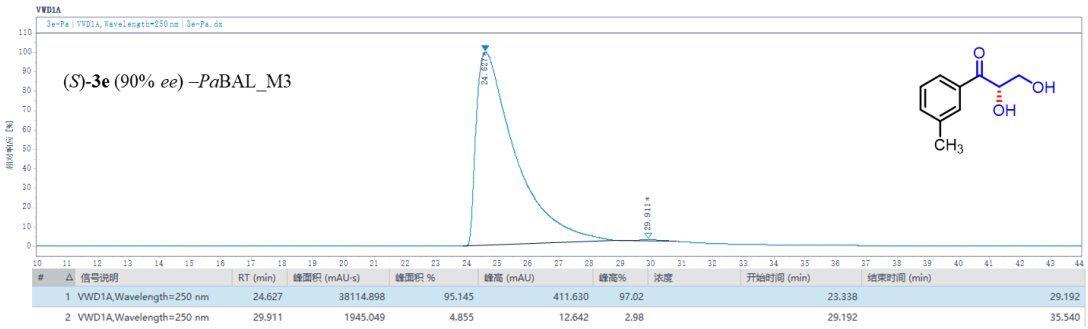
HPLC chromatogram of racemate of Products of *Pf*BAL_A28S ((*R*)-**3d**) and *Pa*BAL M3 ((*S*)-**3d**). HPLC conditions: DAICEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 21.617 min (*Pf*BAL_A28S) and $t_{R\text{-major}}$ = 19.718 min (*Pa*BAL M3).



#	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1	VWD1A,Wavelength=250 nm	24.166	89851.983	47.186	1143.267	60.48		22.759	26.470
2	VWD1A,Wavelength=250 nm	27.571	100567.798	52.814	746.955	39.52		26.470	35.045

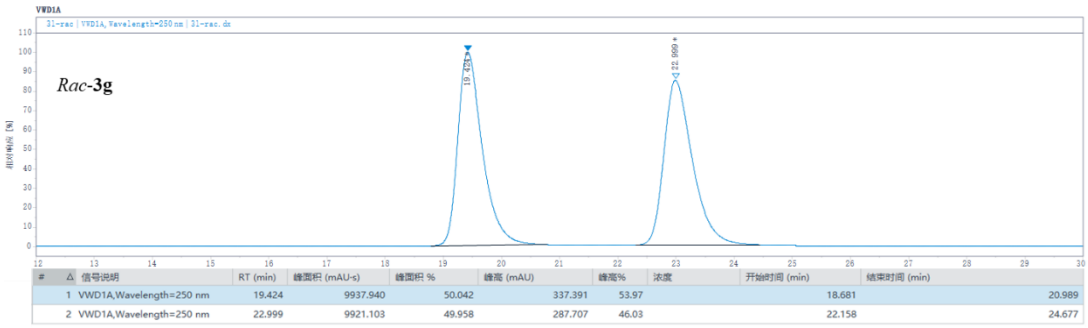


#	Δ	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1		VWD1A,Wavelength=250 nm	25.722	458.456	1.241	6.972	2.25		24.823	26.884
2		VWD1A,Wavelength=250 nm	28.420	36482.661	98.759	303.297	97.75		27.379	36.654

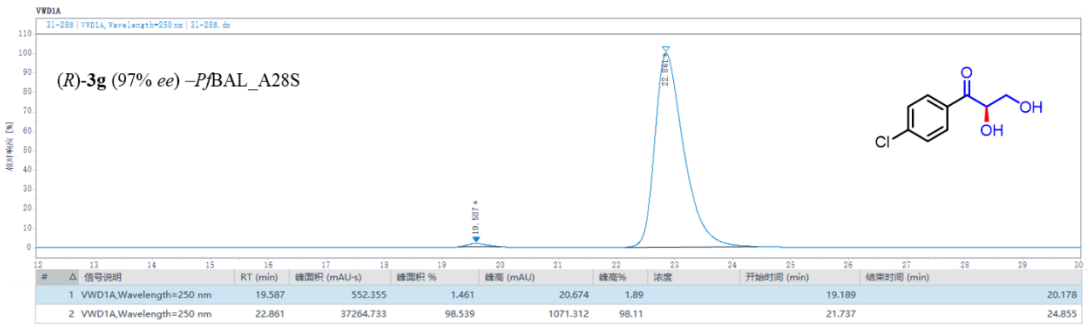


#	Δ	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1		VWD1A,Wavelength=250 nm	24.627	38114.898	95.145	411.630	97.02		23.338	29.192
2		VWD1A,Wavelength=250 nm	29.911	1945.049	4.855	12.642	2.98		29.192	35.540

HPLC chromatogram of racemate of 2,3-dihydroxy-1-(m-tolyl)propan-1-one (**3e**), products of *Pf*BAL_A28S ((*R*)-**3e**) and *Pa*BAL M3 ((*S*)-**3e**). HPLC conditions: DAICEL OD-H (*n*-hexane: *i*-PrOH = 95:5, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-}major}$ = 28.420 min (*Pf*BAL_A28S) and $t_{R\text{-}major}$ = 24.627 min (*Pa*BAL M3).



#	Δ	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1		VWD1A,Wavelength=250 nm	19.424	9937.940	50.042	337.391	53.97		18.681	20.989
2		VWD1A,Wavelength=250 nm	22.999	9921.103	49.958	287.707	46.03		22.158	24.677



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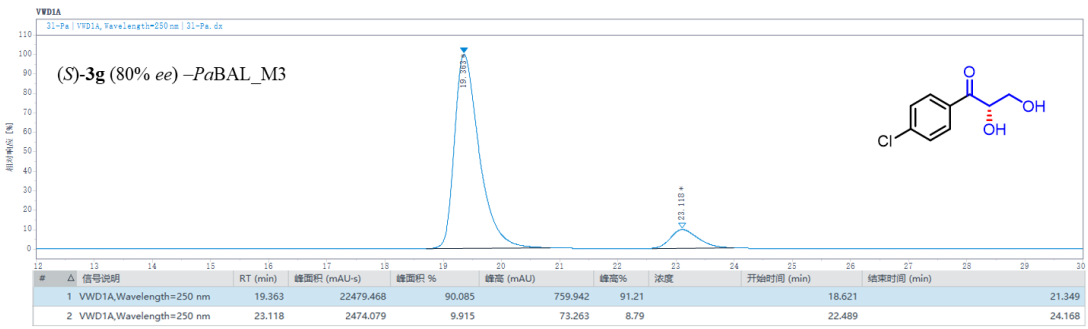
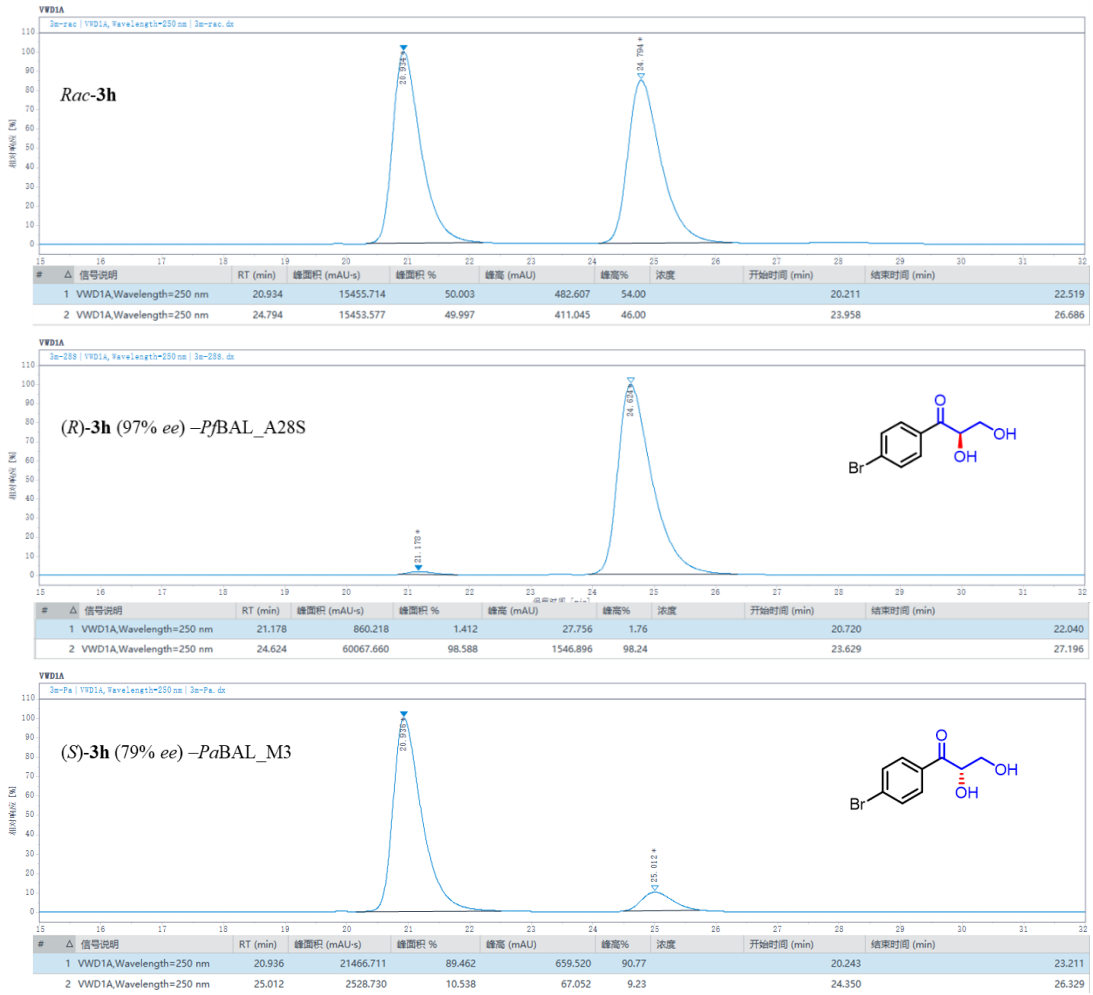
1		VWD1A,Wavelength=250 nm	19.587	552.355	1.461	20.674	1.89		19.189	20.178
2		VWD1A,Wavelength=250 nm	22.861	37264.733	98.539	1071.312	98.11		21.737	24.855



#	Δ	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1		VWD1A,Wavelength=250 nm	19.363	22479.468	90.085	759.942	91.21		18.621	21.349
2		VWD1A,Wavelength=250 nm	23.118	2474.079	9.915	73.263	8.79		22.489	24.168

HPLC chromatogram of racemate of 1-(4-chlorophenyl)-2,3-dihydroxypropan-1-one (**3g**), products of *Pf*BAL_A28S ((*R*)-**3g**) and *Pa*BAL M3 ((*S*)-**3g**). HPLC conditions: DAICEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-}major}$ = 22.861 min (*Pf*BAL_A28S) and $t_{R\text{-}major}$ = 19.363 min (*Pa*BAL M3).

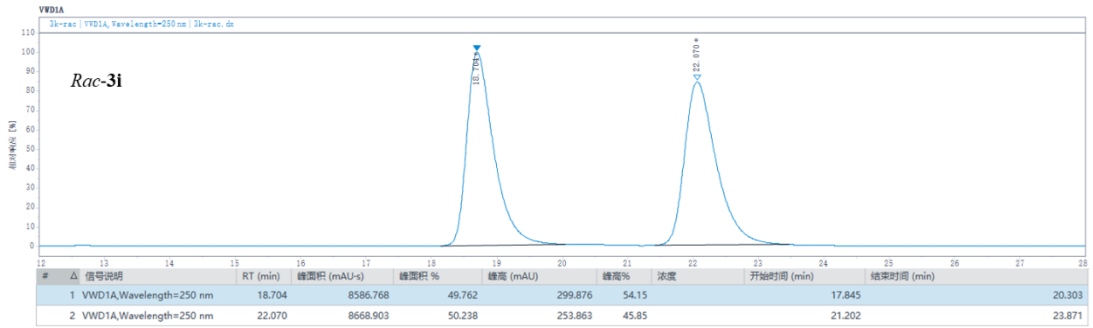


#	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1	VWD1A,Wavelength=250 nm	20.934	15455.714	50.003	482.607	54.00		20.211	22.519
2	VWD1A,Wavelength=250 nm	24.794	15453.577	49.997	411.045	46.00		23.958	26.686

#	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1	VWD1A,Wavelength=250 nm	21.178	860.218	1.412	27.756	1.76		20.720	22.040
2	VWD1A,Wavelength=250 nm	24.624	60067.660	98.588	1546.896	98.24		23.629	27.196

#	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1	VWD1A,Wavelength=250 nm	20.936	21466.711	89.462	659.520	90.77		20.243	23.211
2	VWD1A,Wavelength=250 nm	25.012	2528.730	10.538	67.052	9.23		24.350	26.329

HPLC chromatogram of racemate of 1-(4-bromophenyl)-2,3-dihydroxypropan-1-one (**3h**), products of *Pf*BAL_A28S ((*R*)-**3h**) and *Pa*BAL M3 ((*S*)-**3h**). HPLC conditions: DAICEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-}major}$ = 24.624 min (*Pf*BAL_A28S) and $t_{R\text{-}major}$ = 20.936 min (*Pa*BAL M3).



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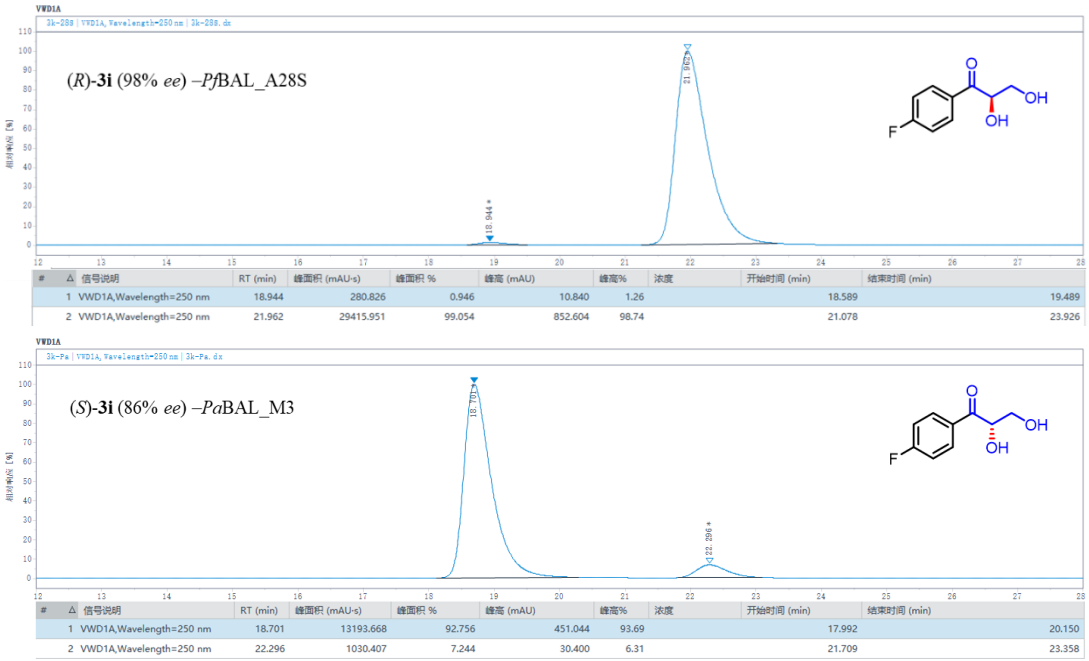
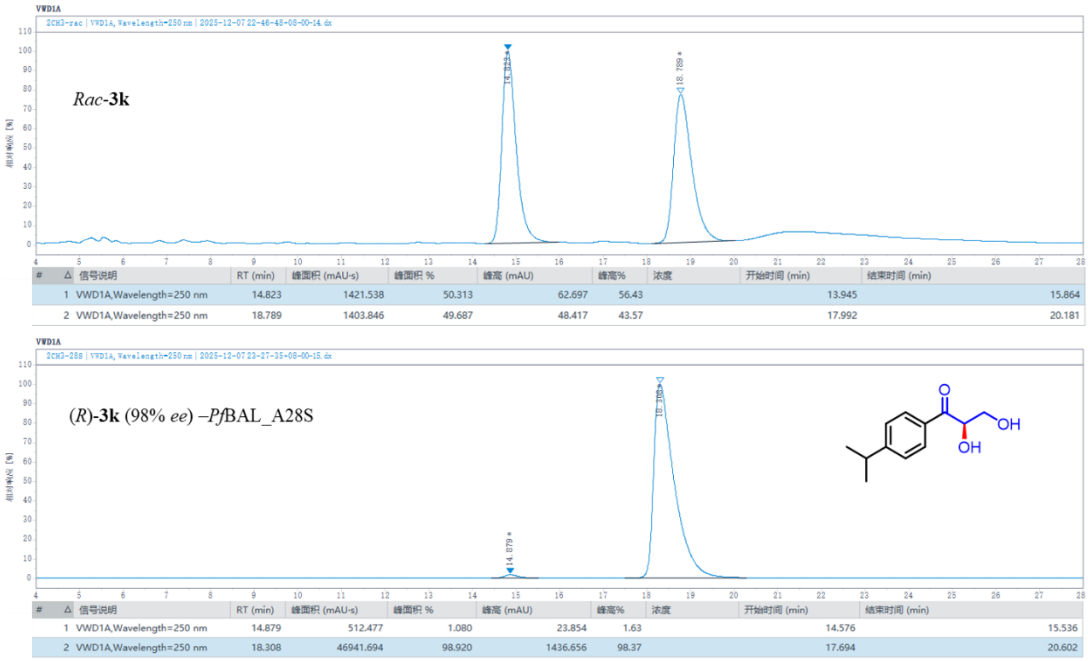
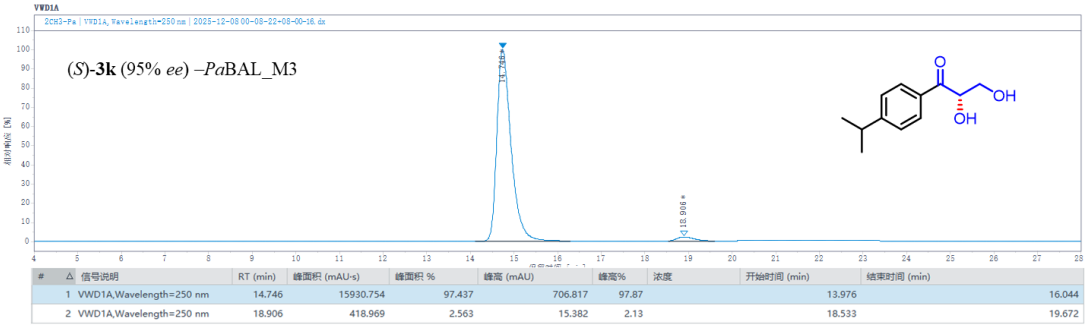
1	VWD1A,Wavelength=250 nm	18.704	8586.768	49.762	299.876	54.15		17.845	20.303
2	VWD1A,Wavelength=250 nm	22.070	8668.903	50.238	253.863	45.85		21.202	23.871



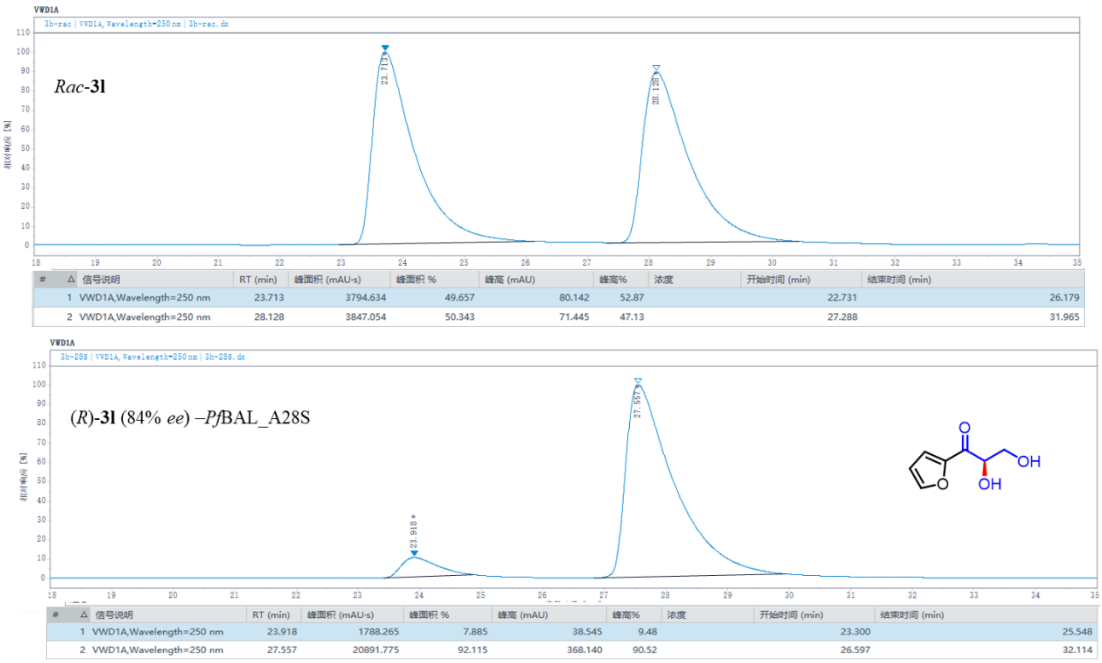
HPLC chromatogram of racemate of 1-(4-fluorophenyl)-2,3-dihydroxypropan-1-one (**3i**), products of *Pf*BAL_A28S ((*R*)-**3i**) and *Pa*BAL M3 ((*S*)-**3i**). HPLC conditions: DAICEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-}major}$ = 21.962 min (*Pf*BAL_A28S) and $t_{R\text{-}major}$ = 18.701 min (*Pa*BAL M3).





#	信号说明	RT (min)	峰面积 (mAU-s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1	VWD1A,Wavelength=250 nm	14.746	15930.754	97.437	706.817	97.87		13.976	16.044
2	VWD1A,Wavelength=250 nm	18.906	418.969	2.563	15.382	2.13		18.533	19.672

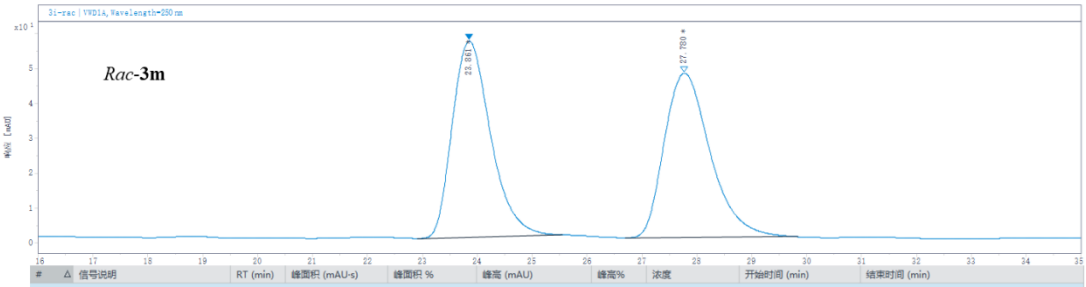
HPLC chromatogram of racemate of 2,3-dihydroxy-1-(4-isopropylphenyl)propan-1-one (**3k**), products of *Pf*BAL_A28S ((*R*)-**3k**) and *Pa*BAL M3 ((*S*)-**3k**). HPLC conditions: DAICEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 18.308 min (*Pf*BAL_A28S) and $t_{R\text{-major}}$ = 14.746 min (*Pa*BAL M3).



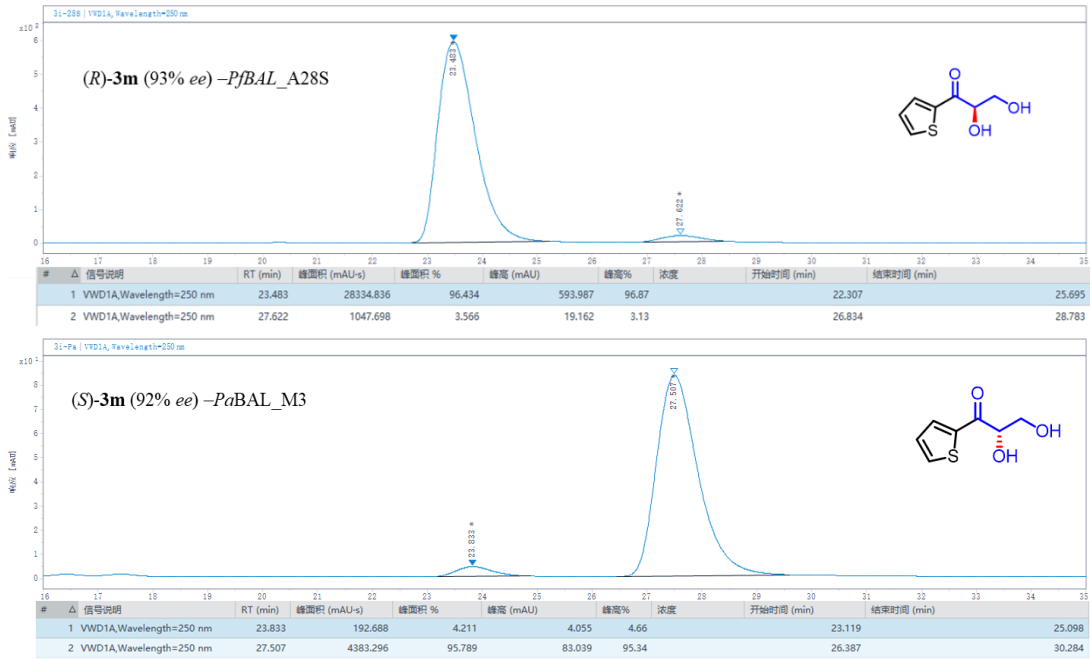
#	信号说明	RT (min)	峰面积 (mAU-s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1	VWD1A,Wavelength=250 nm	23.713	3794.634	49.657	80.142	52.87		22.731	26.179
2	VWD1A,Wavelength=250 nm	28.128	3847.054	50.343	71.445	47.13		27.288	31.965

#	信号说明	RT (min)	峰面积 (mAU-s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1	VWD1A,Wavelength=250 nm	23.918	1788.265	7.885	38.545	9.48		23.300	25.548
2	VWD1A,Wavelength=250 nm	27.557	20891.775	92.115	368.140	90.52		26.597	32.114

HPLC chromatogram of racemate of 1-(furan-2-yl)-2,3-dihydroxypropan-1-one (**3l**), products of *Pf*BAL_A28S ((*R*)-**3l**). HPLC conditions: DAICEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 27.557 min (*Pf*BAL_A28S).



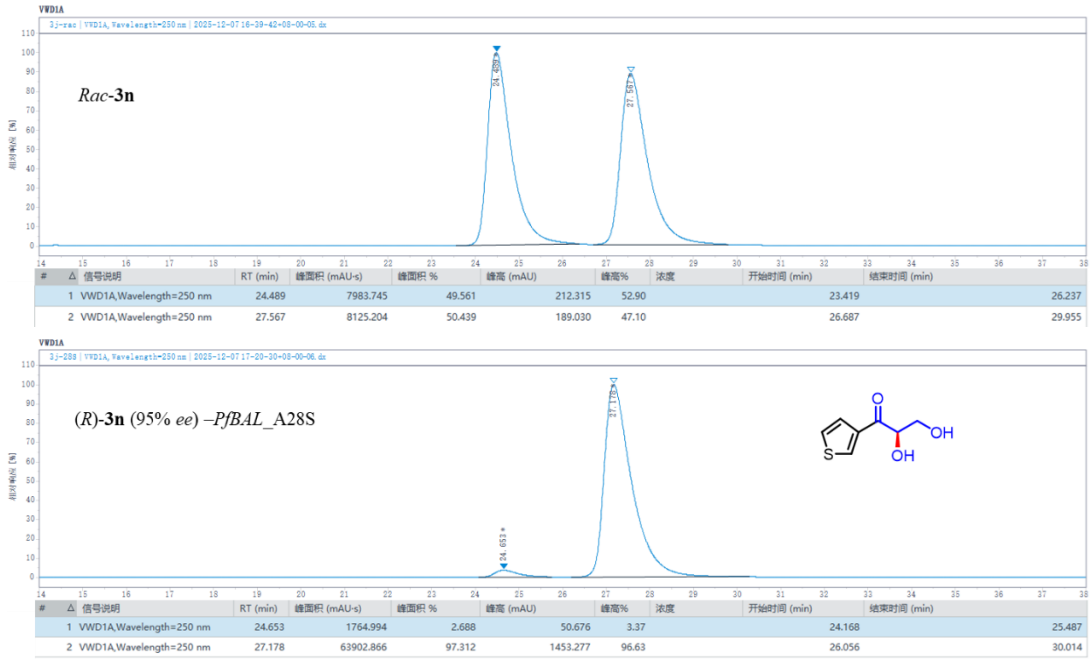
#	信号说明	RT (min)	峰面积 (mAU-s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1	VWD1A,Wavelength=250 nm	23.861	2729.302	49.643	56.150	54.32		22.459	25.967
2	VWD1A,Wavelength=250 nm	27.780	2768.602	50.357	47.222	45.68		26.717	30.435



#	Δ	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1		VWD1A,Wavelength=250 nm	23.483	28334.836	96.434	593.987	96.87		22.307	25.695
2		VWD1A,Wavelength=250 nm	27.622	1047.698	3.566	19.162	3.13		26.834	28.783

#	Δ	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1		VWD1A,Wavelength=250 nm	23.833	192.688	4.211	4.055	4.66		23.119	25.098
2		VWD1A,Wavelength=250 nm	27.507	4383.296	95.789	83.039	95.34		26.387	30.284

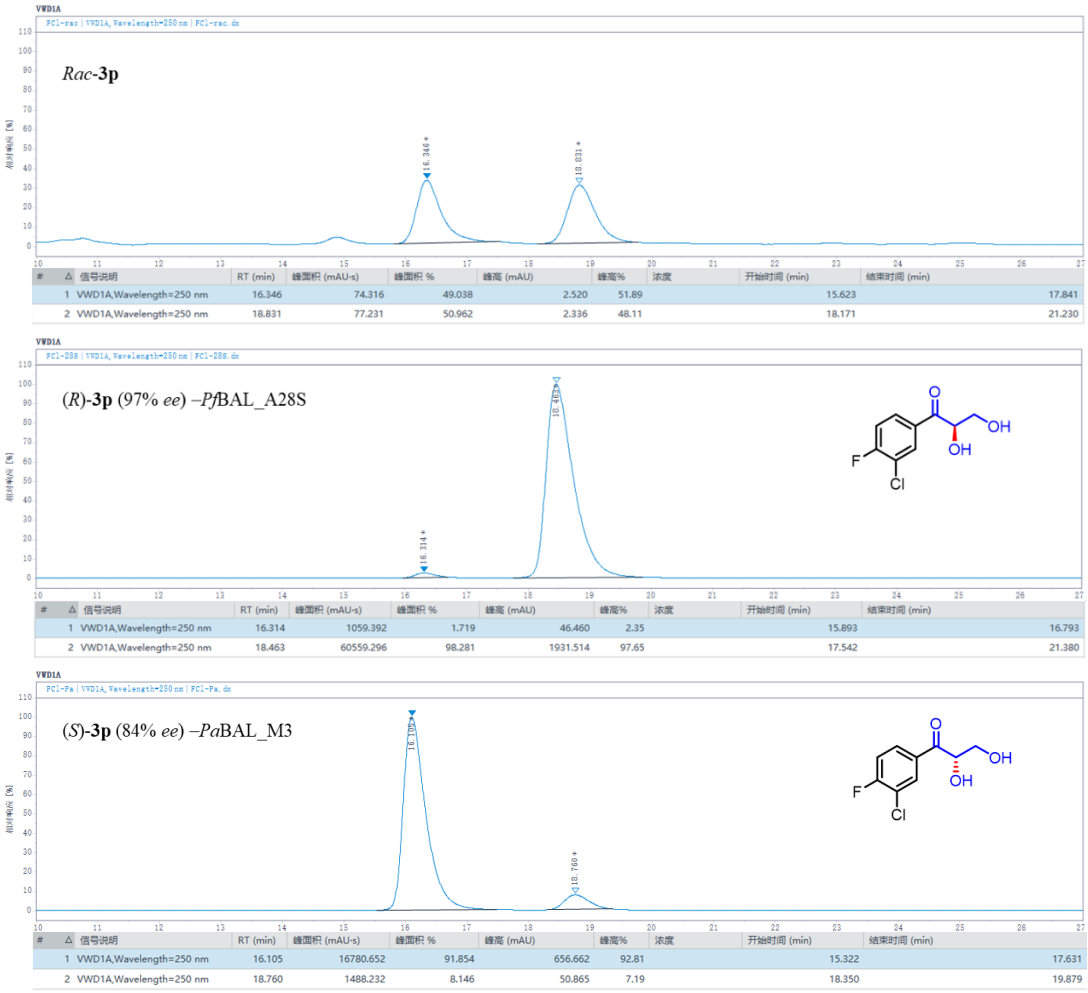
HPLC chromatogram of racemate of 1-(3-chloro-4-fluorophenyl)-2,3-dihydroxypropan-1-one (**3m**), products of *Pf*BAL_A28S ((*R*)-**3m**) and *Pa*BAL M3 ((*S*)-**3m**). HPLC conditions: DAICEL IC (*n*-hexane: *i*-PrOH = 85:15, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 23.483 min (*Pf*BAL_A28S) and $t_{R\text{-major}}$ = 27.507 min (*Pa*BAL M3).



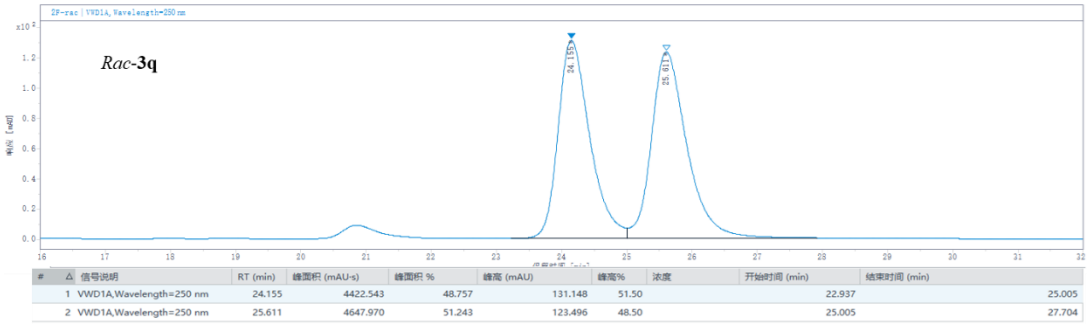
#	Δ	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1		VWD1A,Wavelength=250 nm	24.489	7983.745	49.561	212.315	52.90		23.419	26.237
2		VWD1A,Wavelength=250 nm	27.567	8125.204	50.439	189.030	47.10		26.687	29.955

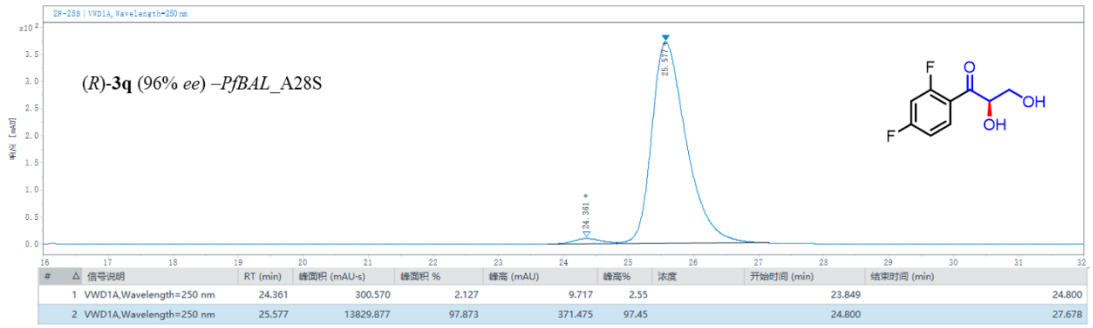
#	Δ	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1		VWD1A,Wavelength=250 nm	24.653	1764.994	2.688	50.676	3.37		24.168	25.487
2		VWD1A,Wavelength=250 nm	27.178	63902.866	97.312	1453.277	96.63		26.056	30.014

HPLC chromatogram of racemate of 2,3-dihydroxy-1-(thiophen-3-yl)propan-1-one (**3n**), products of *Pf*BAL_A28S ((*R*)-**3n**). HPLC conditions: DAICEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 27.178 min (*Pf*BAL_A28S).



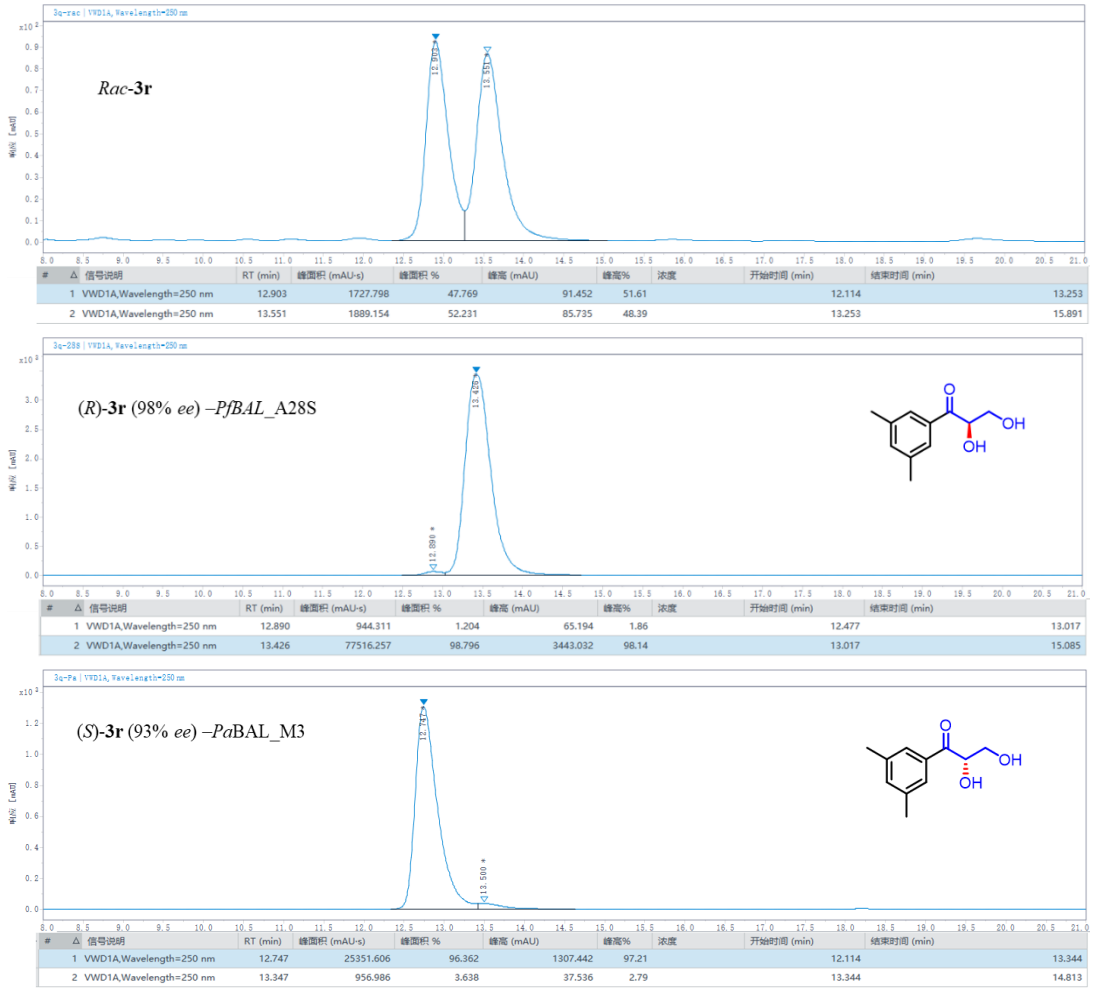
HPLC chromatogram of racemate of 1-(3-chloro-4-fluorophenyl)-2,3-dihydroxypropan-1-one (**3p**), products of *Pf*BAL_A28S ((*R*)-**3p**) and *Pa*BAL M3 ((*S*)-**3p**). HPLC conditions: DAICEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 18.463 min (*Pf*BAL_A28S) and $t_{R\text{-major}}$ = 16.105 min (*Pa*BAL M3).





#	Δ	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1		VWD1A,Wavelength=250 nm	24.361	300.570	2.127	9.717	2.55		23.849	24.800
2		VWD1A,Wavelength=250 nm	25.577	13829.877	97.873	371.475	97.45		24.800	27.678

HPLC chromatogram of racemate of 1-(3-chloro-4-fluorophenyl)-2,3-dihydroxypropan-1-one (**3q**), products of *Pf*BAL_A28S ((*R*)-**3q**). HPLC conditions: DAICEL IA (*n*-hexane: *i*-PrOH = 93:7, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 25.577 min (*Pf*BAL_A28S).

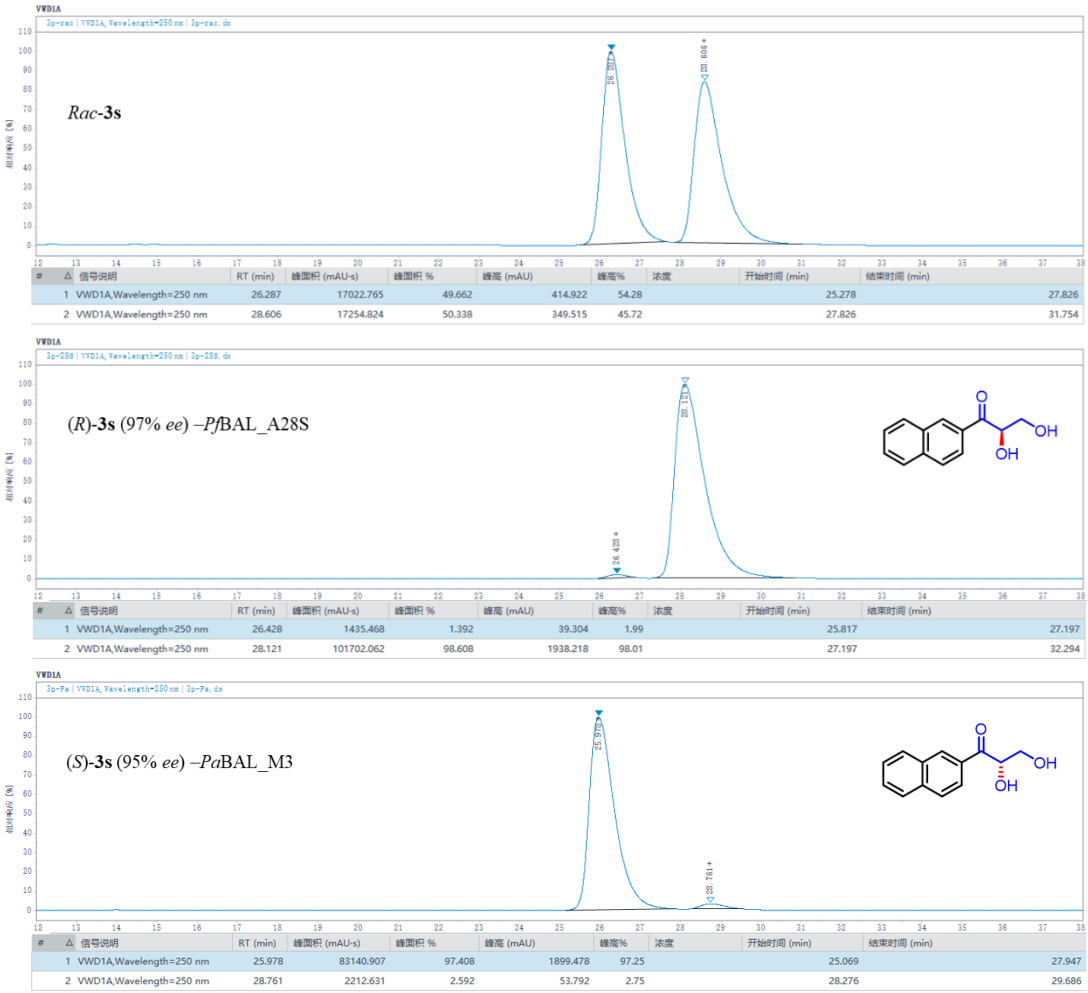


#	Δ	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1		VWD1A,Wavelength=250 nm	12.903	1727.798	47.769	91.452	51.61		12.114	13.253
2		VWD1A,Wavelength=250 nm	13.551	1889.154	52.231	85.735	48.39		13.253	15.891

#	Δ	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1		VWD1A,Wavelength=250 nm	12.890	944.311	1.204	65.194	1.86		12.477	13.017
2		VWD1A,Wavelength=250 nm	13.426	77516.257	98.796	3443.032	98.14		13.017	15.085

#	Δ	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1		VWD1A,Wavelength=250 nm	12.747	25351.606	96.362	1307.442	97.21		12.114	13.344
2		VWD1A,Wavelength=250 nm	13.347	956.986	3.638	37.536	2.79		13.344	14.813

HPLC chromatogram of racemate of 1-(3,5-dimethylphenyl)-2,3-dihydroxypropan-1-one (**3r**), products of *Pf*BAL_A28S ((*R*)-**3r**) and *Pa*BAL M3 ((*S*)-**3r**). HPLC conditions: DAICEL IA (*n*-hexane: *i*PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-major}}$ = 13.426 min (*Pf*BAL_A28S) and $t_{R\text{-major}}$ = 12.747 min (*Pa*BAL M3).

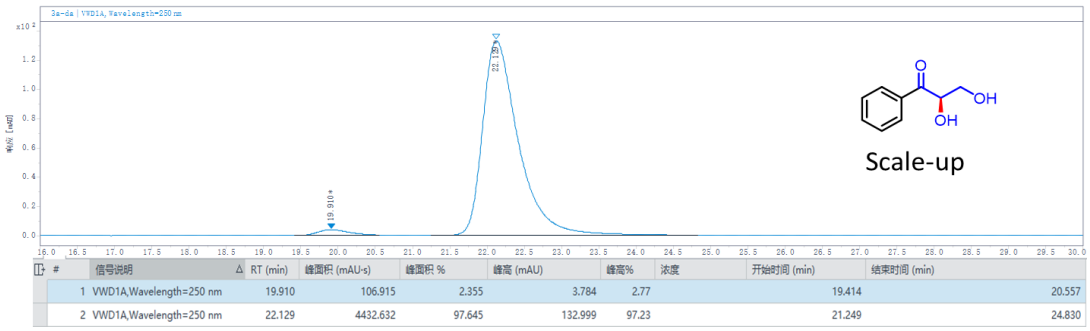


#	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1	VWD1A,Wavelength=250 nm	26.287	17022.765	49.662	414.922	54.28		25.278	27.826
2	VWD1A,Wavelength=250 nm	28.606	17254.824	50.338	349.515	45.72		27.826	31.754

#	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1	VWD1A,Wavelength=250 nm	26.428	1435.468	1.392	39.304	1.99		25.817	27.197
2	VWD1A,Wavelength=250 nm	28.121	101702.062	98.608	1938.218	98.01		27.197	32.294

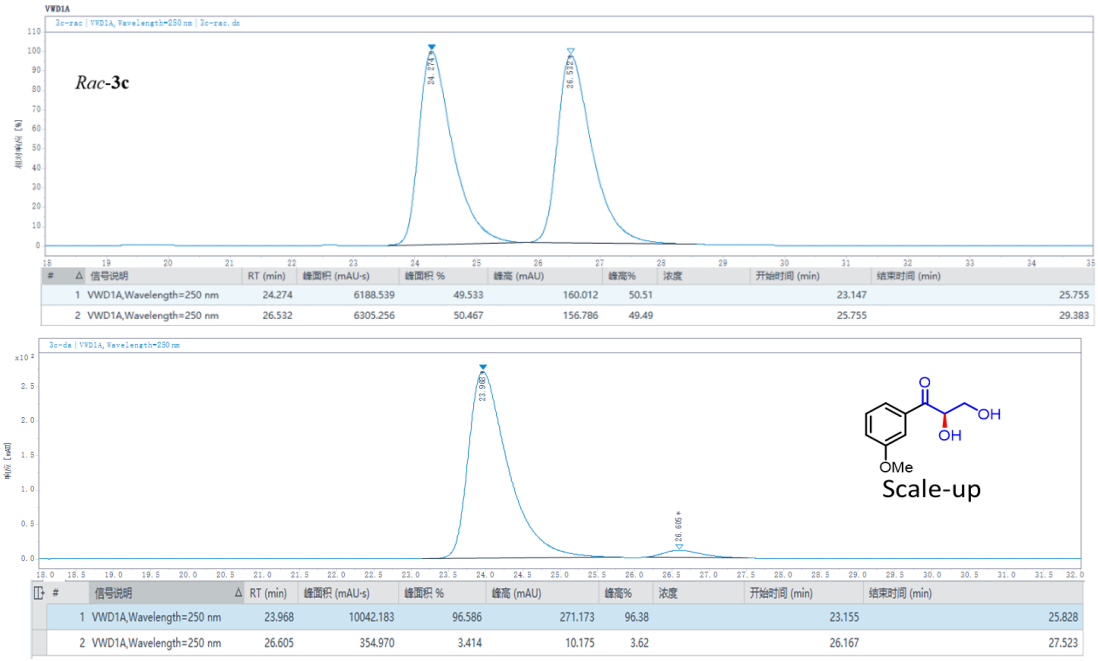
#	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1	VWD1A,Wavelength=250 nm	25.978	83140.907	97.408	1899.478	97.25		25.069	27.947
2	VWD1A,Wavelength=250 nm	28.761	2212.631	2.592	53.792	2.75		28.276	29.686

HPLC chromatogram of racemate of 2,3-dihydroxy-1-(naphthalen-2-yl)propan-1-one (**3s**), products of *Pf*BAL_A28S ((*R*)-**3s**) and *Pa*BAL M3 ((*S*)-**3s**). HPLC conditions: DAICEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-}major}$ = 28.121 min (*Pf*BAL_A28S) and $t_{R\text{-major}}$ = 25.978 min (*Pa*BAL M3).



#	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1	VWD1A,Wavelength=250 nm	19.910	106.915	2.355	3.784	2.77		19.414	20.557
2	VWD1A,Wavelength=250 nm	22.129	4432.632	97.645	132.999	97.23		21.249	24.830

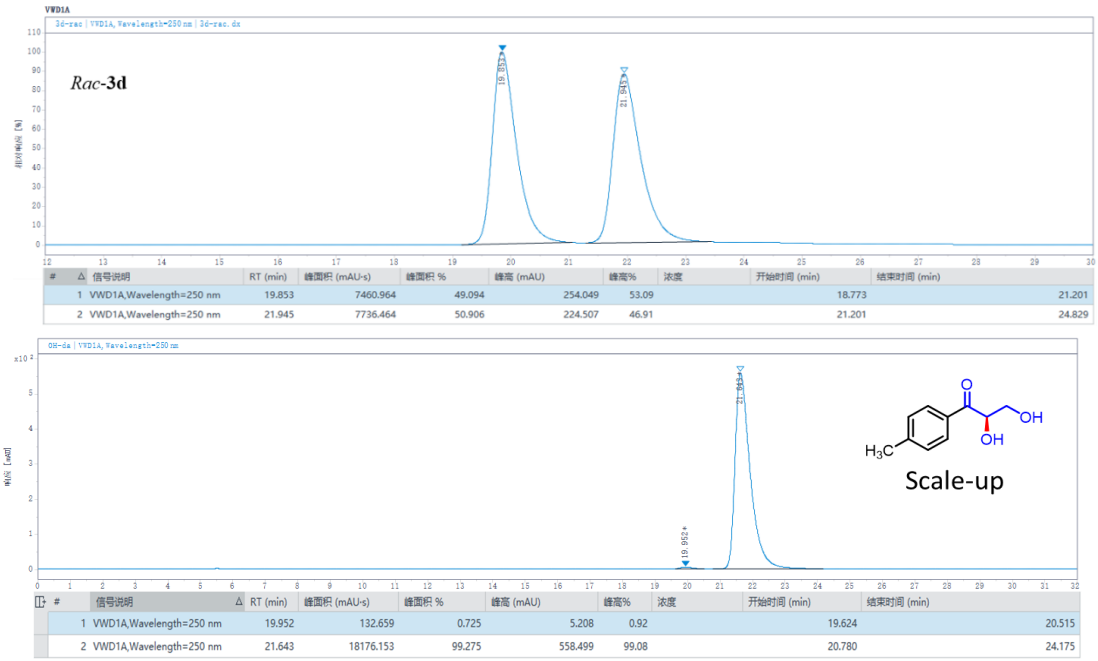
HPLC chromatogram of scale-up biotransformation product of **3a**. HPLC conditions: DAICEL IA (*n*-hexane: *i*-PrOH = 90:10, Flow rate = 0.8 mL/min, UV = 250 nm): $t_{R\text{-}major}$ = 22.129 min and $t_{R\text{-major}}$ = 19.910 min



#	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1	VWD1A,Wavelength=250 nm	24.274	6188.539	49.533	160.012	50.51		23.147	25.755
2	VWD1A,Wavelength=250 nm	26.532	6305.256	50.467	156.786	49.49		25.755	29.383

#	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1	VWD1A,Wavelength=250 nm	23.968	10042.183	96.586	271.173	96.38		23.155	25.828
2	VWD1A,Wavelength=250 nm	26.605	354.970	3.414	10.175	3.62		26.167	27.523

HPLC chromatogram of scale-up biotransformation product of **3c**.



#	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1	VWD1A,Wavelength=250 nm	19.853	7460.964	49.094	254.049	53.09		18.773	21.201
2	VWD1A,Wavelength=250 nm	21.945	7736.464	50.906	224.507	46.91		21.201	24.829

#	信号说明	RT (min)	峰面积 (mAU·s)	峰面积 %	峰高 (mAU)	峰高%	浓度	开始时间 (min)	结束时间 (min)
1	VWD1A,Wavelength=250 nm	19.952	132.659	0.725	5.208	0.92		19.624	20.515
2	VWD1A,Wavelength=250 nm	21.643	18176.153	99.275	558.499	99.08		20.780	24.175

HPLC chromatogram of scale-up biotransformation product of **3d**.

20. Supplementary References

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21. Sequences of proteins

Protein sequence of *Ss*BAL

MPLVSGGELVVRLLQQAGVDRMFGINGAHIDAVYQAALDHRLPIVDTRHEM
NAGHAAEGYARVRNALGVALLTAGGGFTNAVTSMANAHLDRTPVLYLAASG
PLADDQTNTLQAGLDQVAIATPVTKWAHRVTRASLIPRILARAIRTALSAPRGP
VLVDIPWDVLTEQVDLPDLATELLHGADHGPGLSQAGADRILALLSEARRPVV
AVGSEVPRSGAGGEVRAFAERLGVPLLSDYEGLGAISPSPMNFGLVQSLHGLP
AGAEPDLVIMAGLRFGLTTAHGSGALIPRTARVLQIDPSGAELGHLQPVALSVA
ADPLPVFQDLNRVLAVRQSAARPDLADWRDTLHAHLRRRREAVAAQVVQDE
RVHPYDAVCVIAEALPDASVVVADGALTYLWLSETISSAPVSAFLCHGYLGSM
GVGMGIALGAQAAVEPGTNVVLVTGDGSVGYSLGEFDSMVRAGLGAVVVVL
NNRAWGATLHAQEIMHGKDRVVNNRLENGSYAAAAIALGADGYQVRTLDEL
APALAKALRSGRPSCVEVHVSLDPIPPEERVIMGGSPF

Protein sequence of *Su*BAL

MATVTGSGLVVRTLQRAGVHVAFGLPGAHIDPILQEALDAKLRVVDVRHEMN
AGHAAEGYARVTGDLGVAVVTAGGGFTNVLTSITNAYLDRTPVLYIAGSGPLD
RDQINDQQAGFDQVAMAAPVTRFAHRVTRADLIPRLVAQAIRTAQSEPKGPVL
LDIPWDVLRQTVDVDEVEDYRVQIDGTGIAPAGAVDRILEALSAARRPIALVG
KSFVTAEARAQLHEFSARTGVPLFSDWEGLGAIVGSEQHAGLVQSLATVPEDE
RPDLVLLLGLRFGMMTQFGTGGLMPKSARIFQIDPDGRELGRLQEVELGIQAD
PIGTIGLLNERLGDSPVPPGRDDWLKTLRDVSAARRSALAAETQHHEGAIHPY
LAVRTIAESVPDGATVLVDGALTELWLSETIALAPLAHYLNHGYLSSMGSNFG
VALGAQYATPDKATILVTGDGAVGYSLAEFDTLVRARLPVIVIVLNNRAWGAT
LHTQQFLFGQDRVTNNRLENGSYSGVARALGADGVDVTELDQLRPAIEAALA
ARRPTCIDLRVSLEPIPPEERVMSGKAPFDVVQTDA

Protein sequence of *As*BAL

MDPNGGILLARTLAEIAPIVFTLHGGHLDSFYRGCADEGIELLDFRHEAAAVN
AADGYARVTGGLGVAAVTSGPGFANGFAGITNAYADGVPLLVVVAAPPLREAE
TRELQGGIDQIAALKPVTKWAHRITDPARIPDLVGLAVRRALSDRPGPVALELP
IDVAFAPVDPARVRPAGRPDLGARTGPGRRALAGALRALDGAERPVVLAGEG
LRWSRDRRILIDFAEASGIPVLSGGPASRGLPPGHPLNGRGVATLAALAMSGGA
TPDVVMLLGFTPGMHSGGRPGAVIPADAEIVQVDPDAAEIGRLGPVHVAVQA
DPAETLAAMLAAHDGPWPARKEWAETLMGASRLPDLLFADAPDVVNGRIHP
HHATREALAALDPGSIVVADGGESLAWTMSAAFSADIDLVVGLGHQGHLGVG
HGFAIGAQRAEPGRRVVQITGDGAVGFHIQELDTMVRHELPIVTVVLSNDTW
GMSIHSQDVLFGAGNDIVTRLAPTRYEKVAEAFGAYGEHVEKPGEIGPAIRRA
LDSGRPALINVAISNEVVHPVTTSMLGDVTTTDEIVIPYYENIPLR

Protein sequence of *Pa*BAL

MSSPEARYTGGDLLAQTLHDAGVTKIFALHGGHHEALFKGCIDQGIDLIDFRH
EAAAGHAADAYARTTGKLGVCIITAGPGFTNAISAIANAQLDASPVLFLIGAPP
LREVETNPLQGGIDQIAMARPAAKWALSIPSTERVRDLTAMAIRKAMTGRKGP
VVLEIPIDILHMSVTGAQATPSAGLAVRPQPAPAPEEVAALAELLLRAERPVIVA
GLESASAATAVALRALVAKLPLPVFAKPQAYGLLPAGHACDAGAAGNLAVLPII
GAGAPDLVILLGARLGLMLGGRSGALVPHDAHVVQIYSDASEIGRLRDIDLPI
AADCAQTLTALTKALAAVDLPDTSAWTARAAGAKALAASAWPDAEVAGGIH
PYHAAKAVANAAGQDAAYVFDGGESSSWGTATVAVDAPARVLSHGYLGCLGI
GPGFAIGMQIAHPDRRVVQVTGDGAMGFHIQEFDTMVRHRLPIVTVILNNQV
WGMSIHGQQMMYGANYNVITKLGSTQYASIAAAFGCHAERVTAFAEIAPAM
ARAFASGKPALVEIMTDADVVHPATVAMLGQLAEGSRDIMIPYYENIAAS

Protein sequence of *Ec*Mend

MSVSAFNRRWAAVILEALTRHGVRHICIAPGSRSTPLTLAAAENSAFIHHTHF
DERGLGHLALGLAKVSKQPVAVIVTSGTAVANLYPALIEAGLTGEKLILLTAD
RPPELIDCGANQAIRQPGMFASHPTHSISLPRPTQDIPARWLVSTIDHALGTLH
AGGVHINCPFAEPLYGEMDDTGLSWQQRLGDWWQDDKPWLREAPRLESEK
QRDWFFWRQKRGVVVAGRMSAEEGKKVALWAQTLGWPLIGDVLSQTGQPL
PCADLWLGNAKATSELQQAQIVVQLGSSLTGKRLLQWQASCEPEEYWIVDDI
EGRLDPAHHRGRRLIANIADWLELHPAEKRQPWCVEIPRLAEQAMQAVIARR
DAFGEAQLAHRICDYLPEQGQLFVGNSLVVRLIDALSQLPAGYPVYSNRGAS
GIDGLLSTAAGVQRASGKPTLAIVGDLSALYDLNALALLRQVSAPLVLIVVNN
NGGQIFSLLPTPQSERERFYLMPQNVHFEHAAAMFELKYHRPQNWQELETAF
ADAWRTPTTTVIEMVVNDTDGAQTLQQLLAQVSHL

Protein sequence of *Ss*BFD

MSSVRRVSHDFLERQGLTTVFGNPGSNELPFLAGLPEGFRYVLGLHEGAVVG
MADGYAQATGRPVLVNLHAASGSGNAMGALTNAVAARTPLVVLAGQQVRPA
IGPEANLASVDAPALMKPLVGWAAEPACAEDVPRALAQAVFEARLQRRPTYL
SVPYDDWSAEAGDNAAAVLDRRVELAAVPGAGQGQRLVERVAAARRPALVL
GGDIDSDGLFDDAVHLAERLGAPVWAAPSLFRLPFPNRHPQFQGVLPAGIAPV
SAAFEGHDLVLVLGAPVFRYHEHLPGAYLPEGTRLVQVTGDASAAARAPMGE
ALVADPSAVVDLLLKSLDAPARPAPPYRPVPAPLTAEGPGLHPEQVFAALRDEL
PEDTAYVVESTSTNAAWWRQMDLRRPGSYYFPAAGGLGFGLPGAVGVAMAR
PDRPVVAVVGDGSANYGITALWTAAQHRIPLTVVLLRNGTYGALRWFGGLLG
VPDAPGLDIPGLDFTRIAEGYGVAARHVEGAEELRAVLAEPAAGPRLIQVDTA
LTTPS

Protein sequence of *KdcA*

MYTVGDYLLDRLHELGIEEIFGVPGDYNLQFLDQIISREDMKWIGNANELNASYMADGYA
RTKKAAAFLTTFGVGELSAINGLAGSYAENLPVVEIVGSPTSKVQNDGKFVHHTLADGDF
KHFMKMHEPVTAARTLLTAENATYEIDRVLSQLLKERKPVYINLPVDVAAAKAEKPALSLE
KESSTTNTTEQVILSKIEESLKNAQKPVVIAGHEVISFGLEKTVTQFVSETKLPITTLNFGK
SAVDESLPSFLGIYNGKLSEISLKNFVESADFILMLGVKLTDSSTGAFTHHLDENKMISLNI
DEGIIFNKVVEDFDFRAVVSSLSELKGIEYEGQYIDKQYEEFIPSSAPLSQDRLWQAVESL
TQSNETIVAEQGTSFFGASTIFLKSNSRFIGQPLWGSIGYTFPAALGSQIADKESRHLLFIG
DGSLQLTVQELGLSIREKLNPICFIINNDGYTVEREIHGPTQSYNDIPMWNYSKLPETFGA
TEDRVVSKIVRTENEFVSVMKEAQADVNRMYWIELVLEKEDAPKLLKKMGKLFAEQNK

Protein sequence of *An*PDC

MYIEIGNFLNQRLKQAGISHIFGVPGDFNLAYLEQIEADTELQFIGTCNELNGA
YAADGYARIQNLSVMVTTYGVGDLSAINGIAGAYSEHIPVVHISGIPPLHAVKN
GAQLHHTLLDGNYDHIMNCMKPFTVAQTRLTPENAAYEIDRVLQACLTYKRPI
HIQLPSDITHIKIQTPTHPFQYKPYVTEPSYLNTVVHKLKDKLASAQKPTLLID
HLAQKFGFANIIQNISEQYKIPLVSLGTAKNIINEAAPNYLGVYSGASSPTDIKN
AVEQSDCLLCIGTQFADVNTAIFSQNIPYQNTILIQPYDVKLNHEYYEGIEATTL
LKHIFNIHEQPLENINSEKQAPTHKNSKEPLSNATLWPQISSFLRDGDIVLGEAG
CSSSGLNGISLPFKAKYISQPIWGSIGYTLPALVGTLFAQPQARHILFIGDGSLQL
TAQEISTIVRYKLKPIIFILNNGGYTIERKILGAEAKYNDIHNWRYTELAHVFYG
EAQTFHVETLKELHQTLSTLDTPNQLTLIELKLPKLDAPESLNKFGPIVAQYDY
GKHTMSQIKKD

Protein sequence of *Ec*TK

MSSRKELANAIRALSMDAVQKAKSGHPGAPMGMADIAEVLWRDFLKHNPQN
PSWADRDRFVLSNGHGSMLIYSLLHLTGYDLPMEELKNFRQLHSKTPGHPEV
GYTAGVETTTGPLGQGIANAVGMAIAEKTLAAQFNRPGHDIVDHYTYAFMGD
GCMMEGISHEVCSLAGTLKLGKLIAFYDDNGISIDGHVEGWFTDDTAMRFEA
YGWHVIRDIDGHDAASIKRAVEEARAVTDKPSLLMCKTIIGFGSPNKAGTHDS
HGAPLGDAEIALTREQLGWKYAPFEIPSEIYAQWDAKEAGQAKESAWNEKFA
AYAKAYPQEAAEFTRRMKGEMPSDFDAKAKEFIAKLQANPAKIASRKASQNA
IEAFGPLLPEFLGGSADLAPSNLTLWSGSKAINEDAAGNYIHYGVREFGMTAIA
NGISLHGGFLPYTSTFLMFVEYARNAVRMAALMKQRQVMVYTHDSIGLGED
GPTHQPVEQVASLRVTPNMSTWRPCDQVESAVAWKYGVERQDGPTALILSRQ
NLAQQERTEEQLANIARGGYVLKDCAGQPELIFIATGSEVELAVAAYEKLTAEG
VKARVVSMPSTDAFDKQDAAYRESVLPKAVTARVAVEAGIADYWYKYVGLN
GAIVGMTTFGESAPAELLFEEFGFTVDNVVAKAKELL

Protein sequence of *Sc*TK

MTQFTDIDKLAVSTIRILAVDTVSKANSGHPGAPLGMAPAAHVLWSQMRMNP
TNPDWINRDRFVLSNGHAVALLYSMLHLTGYDLSIEDLKQFRQLGSRTPGHPE
FELPGVEVTTGPLGQGISNAVGMAMAQANLAATYNKPGFTLSDNYTYVFLGD
GCLQEGISSEASSLAGHLKLGNLIAIYDDNKITIDGATSISFDEDVAKRYEAYG
WEVLYVENGNEDLAGIAKAIAQAKLSKDKPTLIKMTTTIGYGSLHAGSHSVH
GAPLKADDVKQLKSKFGFNPDKSFVVPQEVYDHYQKTILKPGVEANNKWNK
LFSEYQKKFPELGAELARRLSGQLPANWESKLPTYTAKDSAVATRKLSETVLE
DVYNQLPELIGGSADLTPSNLTRWKEALDFQPPSSGSGNYSGRYIRYGIREHA
MGAIMNGISAFGANYKPYGGTFLNFVSYAAGAVRLSALSGHPVIWVATHDSIG
VGEDGPTHQPIETLAHFRSLPNIQVWRPADGNEVSAAYKNSLESKHTPSIIALS
RQNLPQLEGSSIESASKGGYVLQDVANPDIILVATGSEVSLSVEAAKTLAAKNI
KARVVSLPDFFTFDKQPLEYRLSVLPDNVPIMSVEVLATTCWGKYAHQSFGID
RFGASGKAPEVFKFFGFTPEGVAERAQKTIAFYKGDKLISPLKKAF

Protein sequence of *Pf*BAL

MAMITGGELVVRTLIKAGVEHLFGLHGAHIDTIFQACLDHDVPIIDTRHEAAA
GHAAEGYARAGAKLGVALVTAGGGFTNAVTPIANAWLDRTPVLFLTGSGALR
DDETNTLQAGIDQVAMAAPITKWAHRVMATEHIPRLVMQAIRAALSAPRGPV
LLDLPWDILMNQIDEDSVIIPDLVLSAHGARPDPADLDQALALLRKAERPVIVL
GSEASRTARKTALSAFVAATGVPVFADYEGLSMLSGLPDAMRGGLVQNLYSFA
KADAAPDLVLMLGARFGLNTGHGSGQLIPHSAQVIQVDPDACELGRLQGIAL
GIVADVGGTIEALAQATAQDAAWPDRGDWCAKVTDLAQERYASIAAKSSSEH
ALHPFHASQVIAKHVDAGVTVVADGALTYLWLSEVMSRVKPGGFLCHGYLG
SMGVGFGTALGAQVADLEAGRRTILVTGDGSVGYSIGEFDTLVRKQLPLIVIIM

NNQSWGATLHFQQLAVGPNRVTGTRLENGSYHGVAAAFGADGYHVDSVESF
SAALAQALAHNRPACINVAVALDPIPPEELILIGMDPFA