ELECTRONIC SUPPORTING INFORMATION

Amyloidogenic model peptides as catalysts for stereoselective aldol reaction

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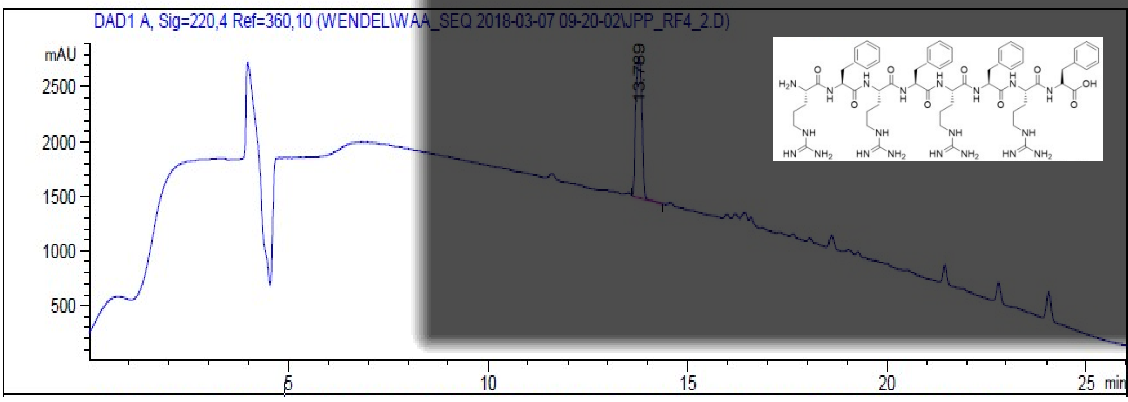
Mass spectrometry Analysis of the Peptides



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.789	VB	0.1829	1.40188e4	1288.73511	100.0000

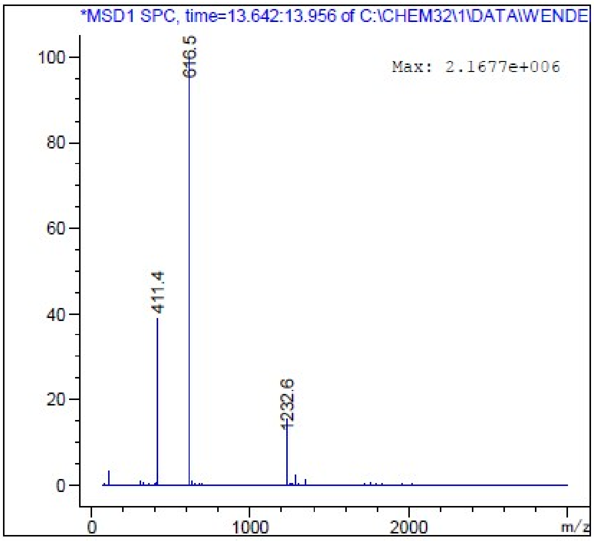
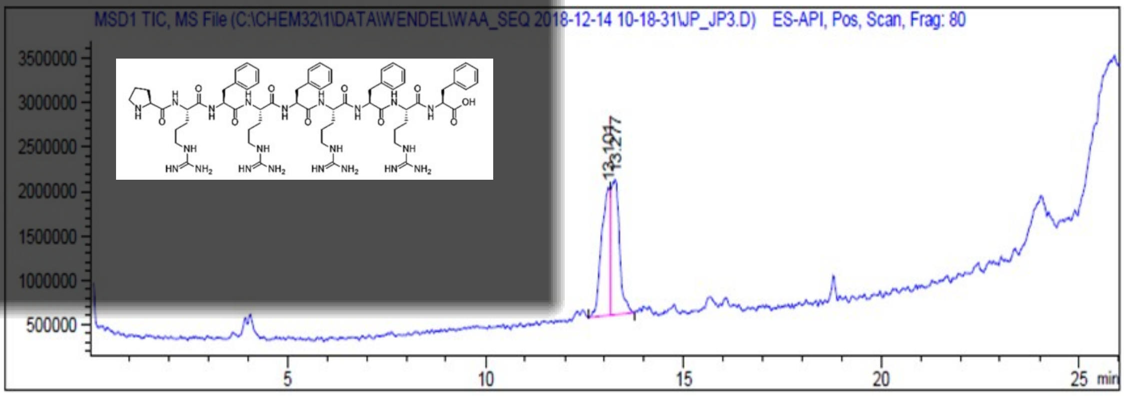


Figure S1. $[RF]_4$ chromatogram and mass spectrometry analysis.



Peak #	RetTime [min]	Type	Width [min]	Area	Height	Area %
1	13.101	BV	0.2089	2.18687e7	1.43885e6	49.6253
2	13.277	VB	0.2060	2.21990e7	1.51758e6	50.3747

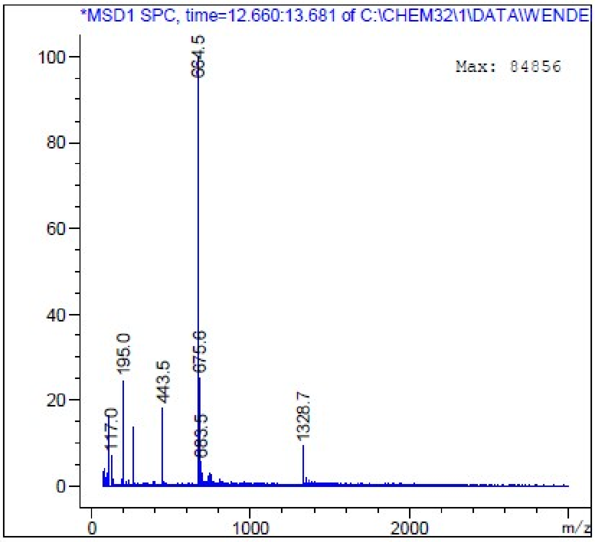


Figure S2. P[RF]$_4$ chromatogram and mass spectrometry analysis.

Estimation of Critical Concentrations by Fluorescence Spectroscopy

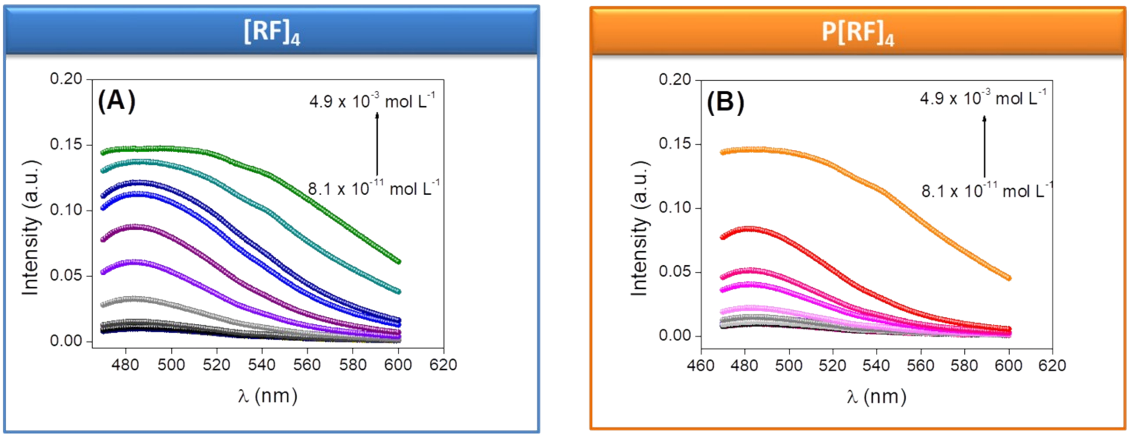


Figure S3. Emission spectrum for (A) $[RF]_4$ and (B) $P[RF]_4$ solutions with different concentration of peptides in an aqueous medium by using 0.01 mg·mL^{-1} ThT.

FTIR Spectroscopy

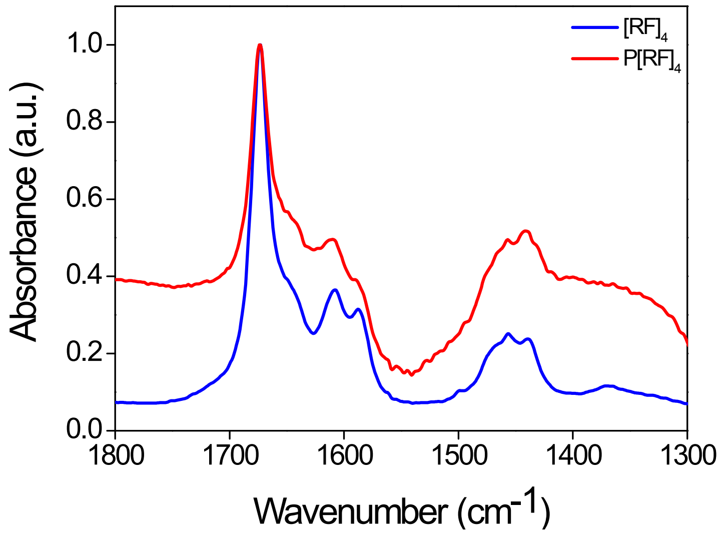


Figure S4. The absorbance FTIR spectra for $[RF]_4$ (blue line) and $P[RF]_4$ (red line) above *cac* in D_2O solutions.

DLS Assays

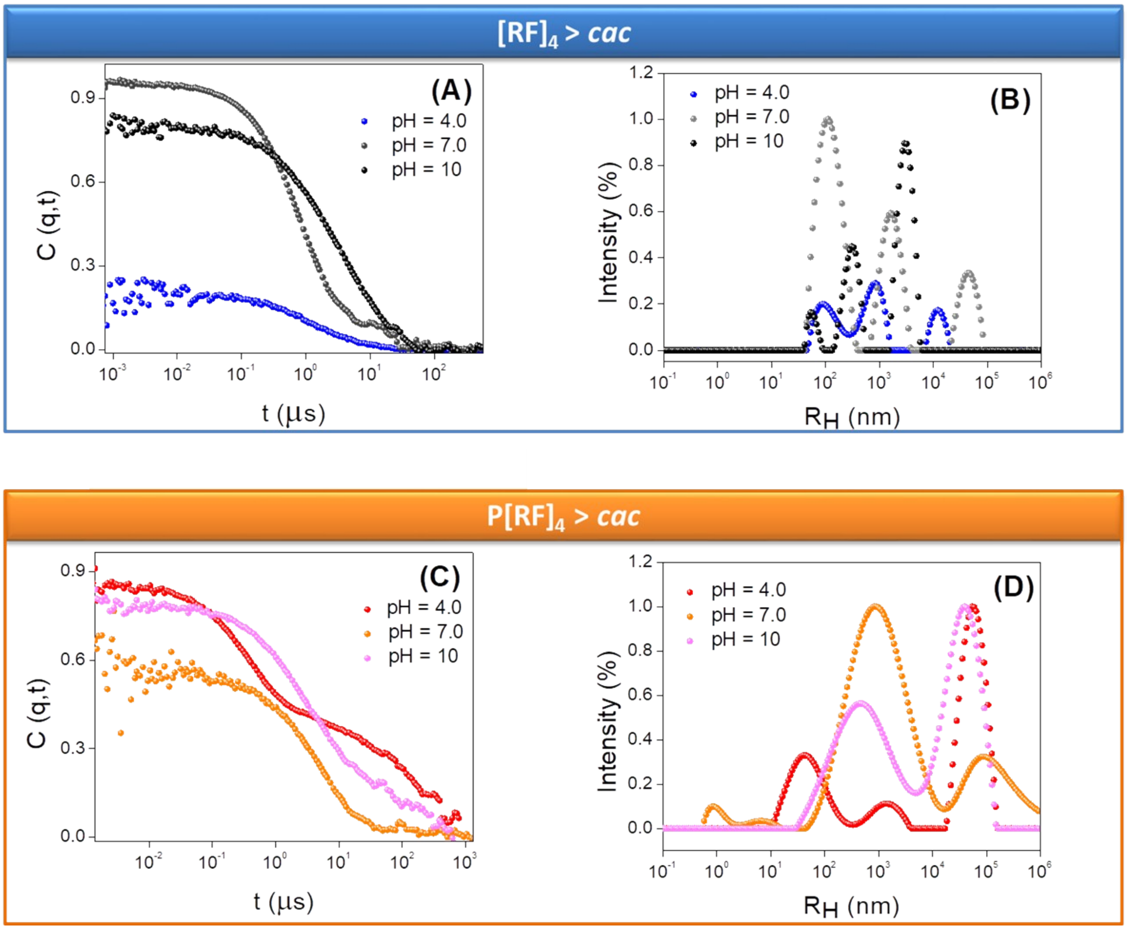


Figure S5. DLS correlation curves in function of decay time for (A) $[RF]_4$ and (C) $P[RF]_4$ in water solution at *cac*. Curves of intensity distribution as a function of ratio hydrodynamic for (B) $[RF]_4$ and (D) $P[RF]_4$, respectively, at *cac* in water.

Titration Curves

At low pH, the predominant ionic species is the fully protonated form, $^{+}H_3N$-peptides-COOH. When pH = pK_{a1}, equimolar concentrations of $^{+}H_3N$-peptides-COOH and $^{+}H_3N$-peptides-COO^{-} species are present at pH ≈ 2.0 for $[RF]_4$ and $P[RF]_4$ species. As the pH increases, the α-NH_3^{+} and guanidinium groups will be deprotonated at pK_{a2} ≈ 9.2 and pK_{a3} ≈ 12.3, respectively. The isoelectric point (pI) is the average of the pKas of the two most similar acids (value). Hence, pI = 1/2 (pK_{a2} + pK_{a3}) is ≈ 10.7 for both peptides.

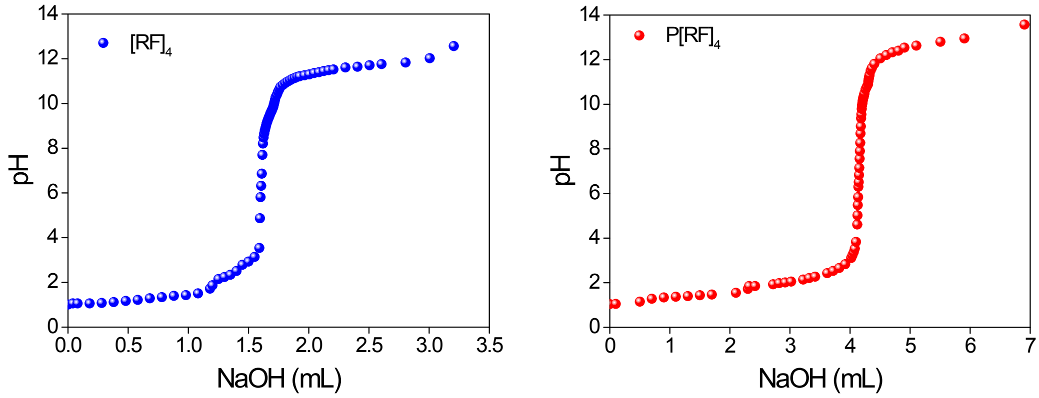
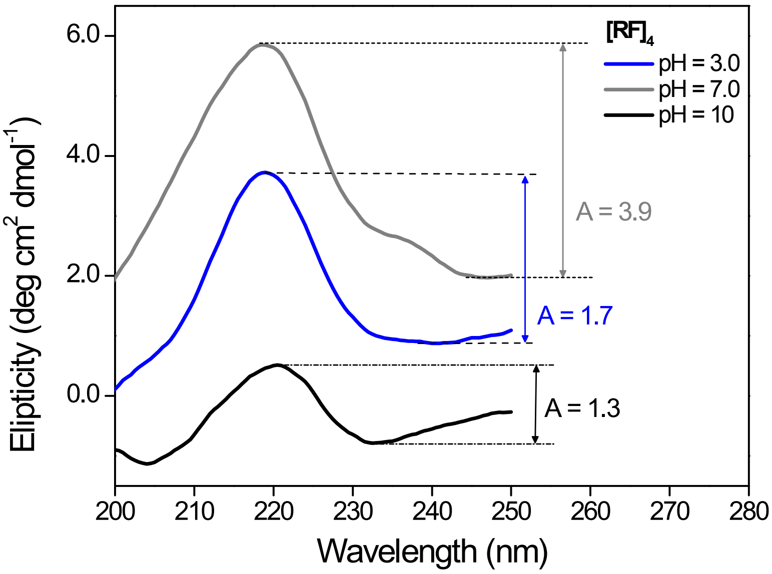


Figure S6. Titration curves for $[RF]_4$ and $P[RF]_4$ solutions at pH ranges of 1.0 to 14, by using 0.1 mol L^{-1} NaOH.

Circular Dichroism Spectroscopy



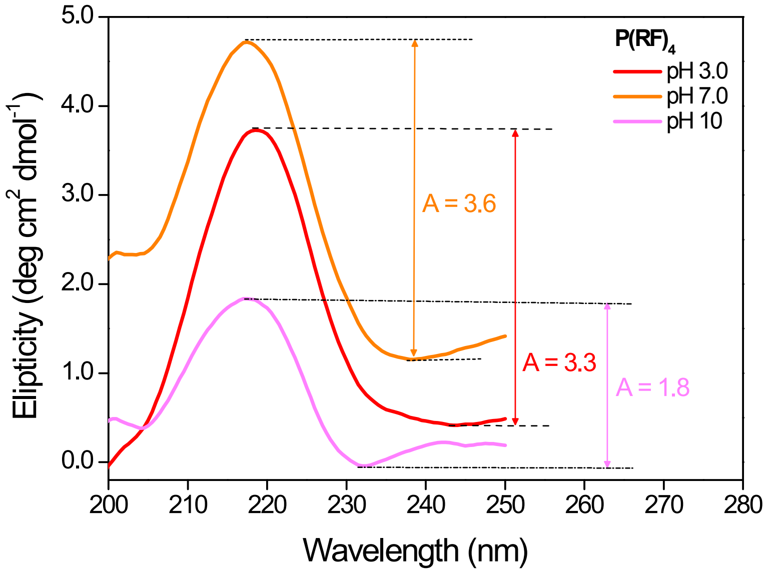
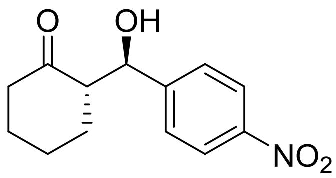


Figure S7. CD spectra of $[RF]_4$ and $P[RF]_4$ in aqueous solution above *cac* in different pHs.

ALDOL REACTIONS

Spectroscopic Data

(*S*)-2-((*R*)-Hydroxy(4-nitrophenyl)methyl)cyclohexan-1-one



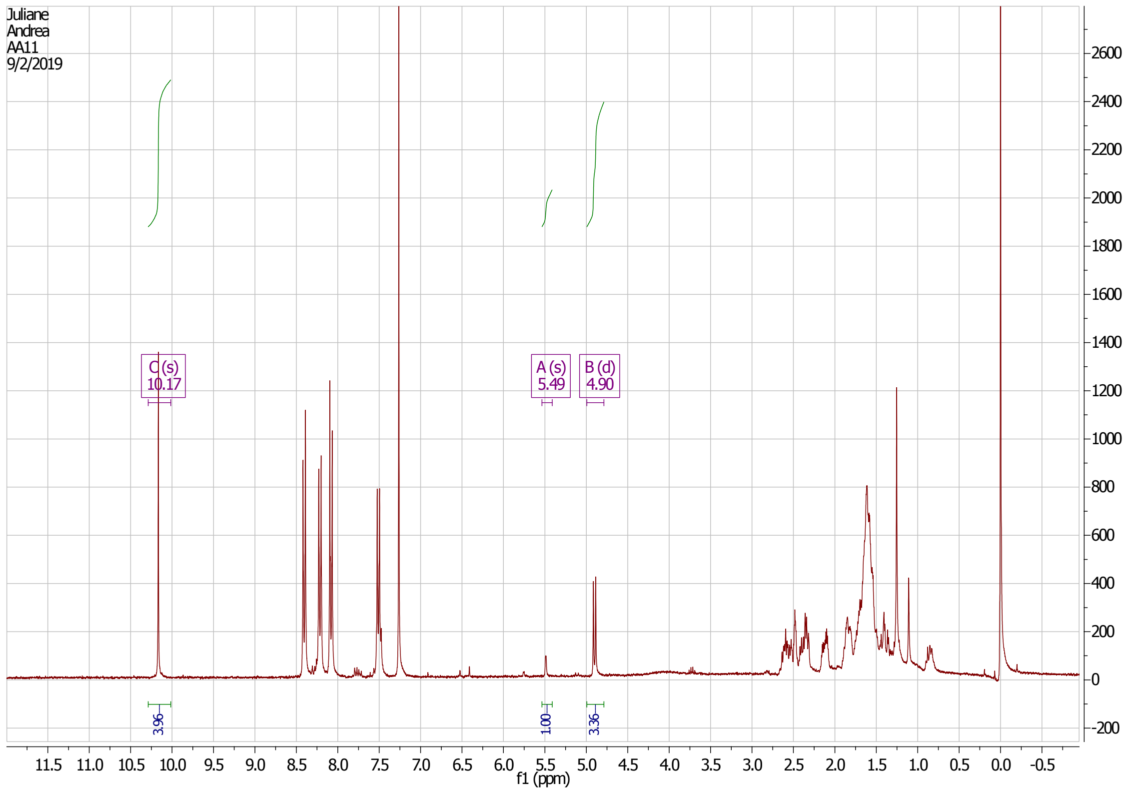
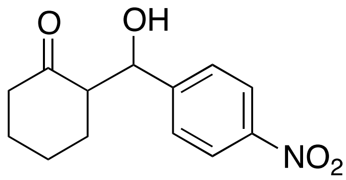


Figure S8. Representative H NMR spectra of crude aldol product.

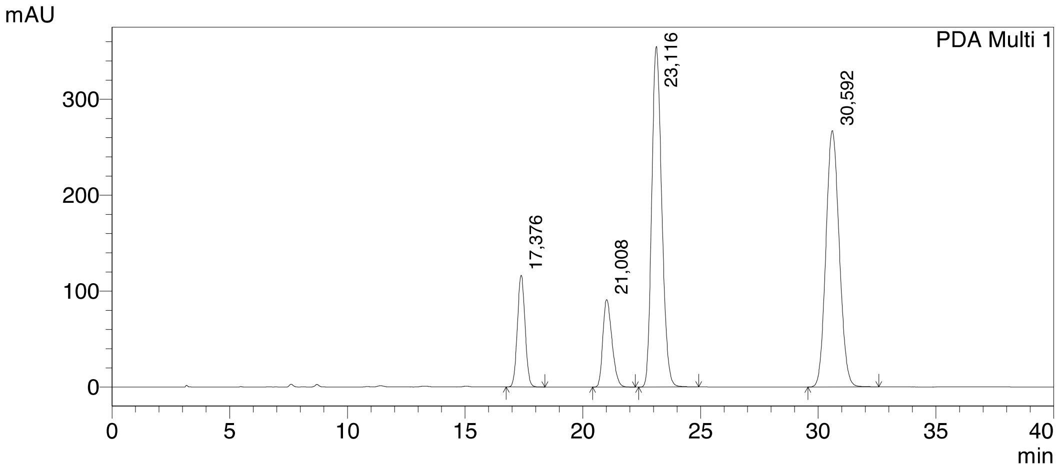
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22-8.18 (m, 2H, ArH), 7.51-7.47 (m, 2H, ArH), 5.49 (br s, 1H, C*H*OH of *syn* diastereoisomer), 4.90 (dd, J = 7.5 Hz, 3.0 Hz, 1H, CHOH of *anti* diastereoisomer), 2.66-2.30 (m, 1H, C*H*CHOH), 2.66-2.30 (m, 2H, $CH_2C(O)$), 2.16-1.24 (m, 6H, chex-H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 214.9, 148.5, 147.7, 128.0, 123.7, 74.1, 57.3, 42.8, 30.9, 27.8, 24.8.

Chiral-phase HPLC analysis



racemic



1 PDA Multi 1/254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17,376	2638133	116522	10,099	14,039
2	21,008	2453400	91192	9,391	10,987
3	23,116	10512709	355106	40,242	42,785
4	30,592	10519633	267163	40,268	32,189
Total		26123875	829983	100,000	100,000

3D Graph

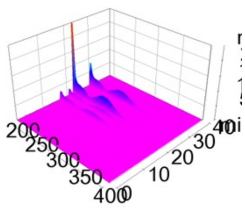
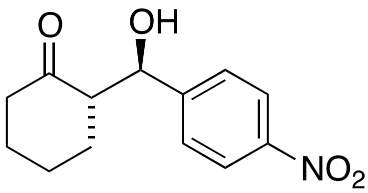
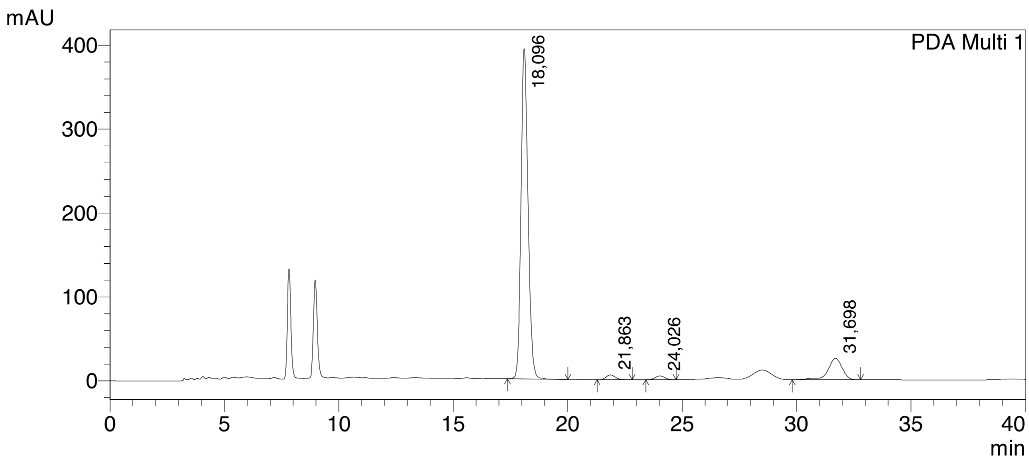


Figure S9. HPLC chromatogram for racemic aldol product. Conditions: Chiralpak AD-H, hexane/2-propanol (90/10); 1.0 mL·min^{-1}, λ= 254 nm.





1 PDA Multi 1/254nm,4nm

PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18,096	8384650	393801	85,638	91,644
2	21,863	164371	5862	1,679	1,364
3	24,026	133710	4558	1,366	1,061
4	31,698	1108055	25487	11,317	5,931
Total		9790787	429707	100,000	100,000

3D Graph

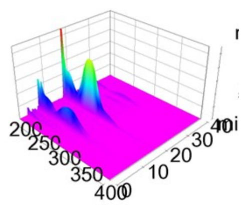


Figure S10. Representative HPLC chromatogram for chiral aldol product. Conditions: Chiralpak AD-H, hexane/2-propanol (90/10); 1.0 $mL\cdot min^{-1}$, λ= 254 nm.