

Supplementary Materials

# Selectivity in Catalytic Asymmetric Formal [3 + 3] Annulation of 2-Enoyl-Pyridine *N*-Oxide with Benzyl Methyl Ketone

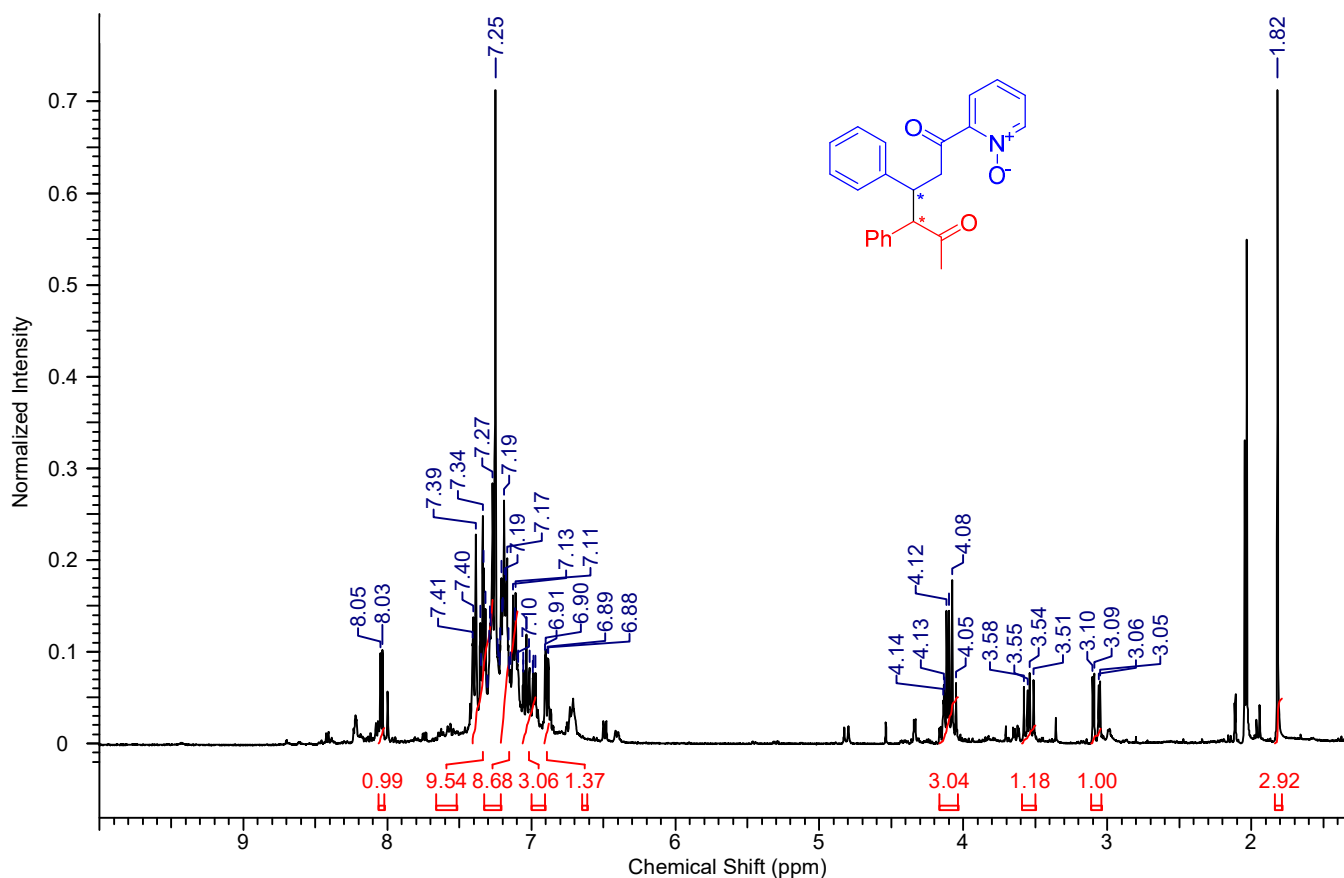
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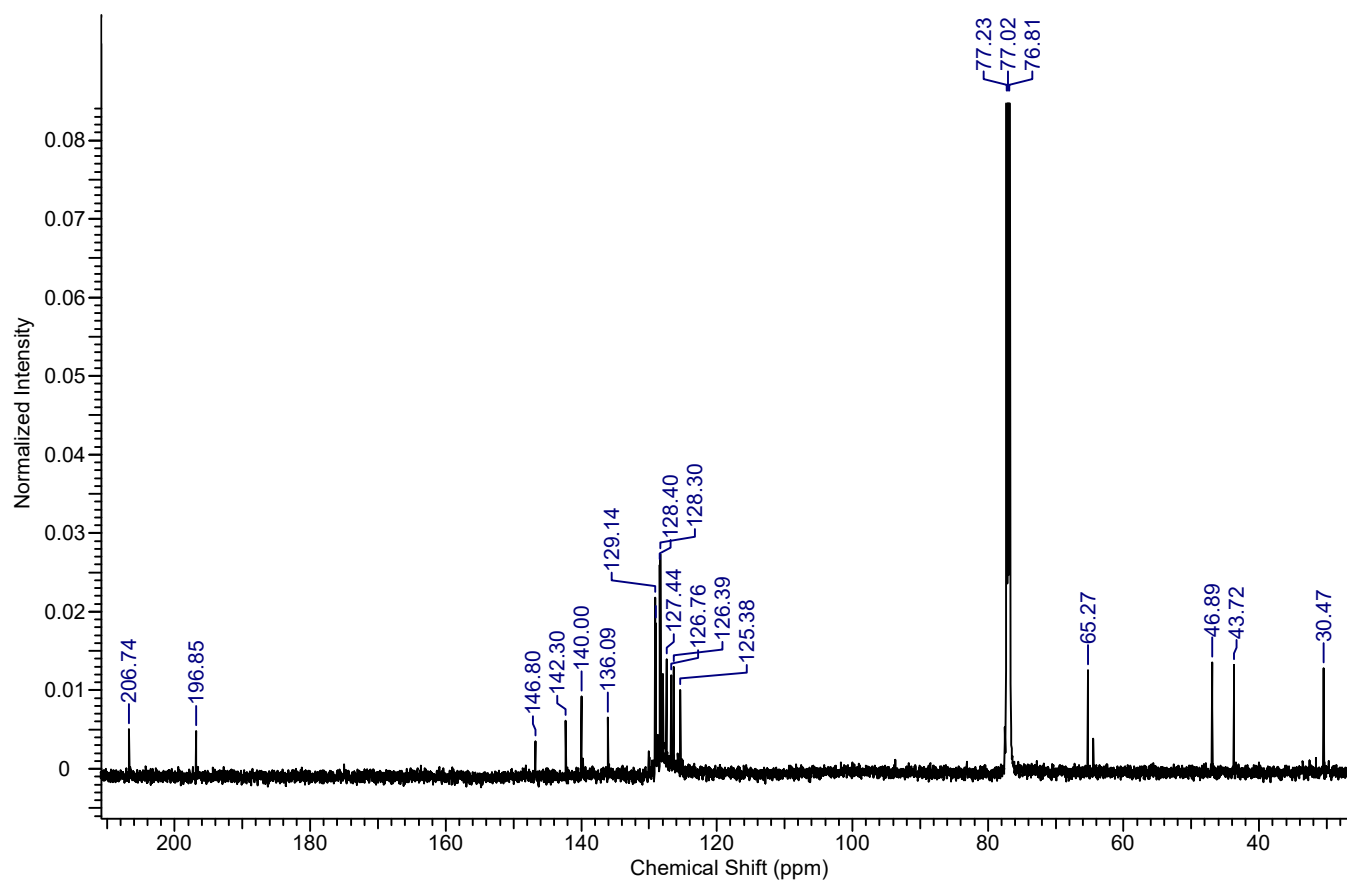
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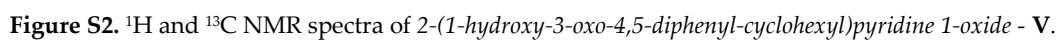
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## 1. Spectral Data





**Figure S1.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 2-(5-oxo-3,4-diphenyl-hexanoyl)pyridine 1-oxide - I.



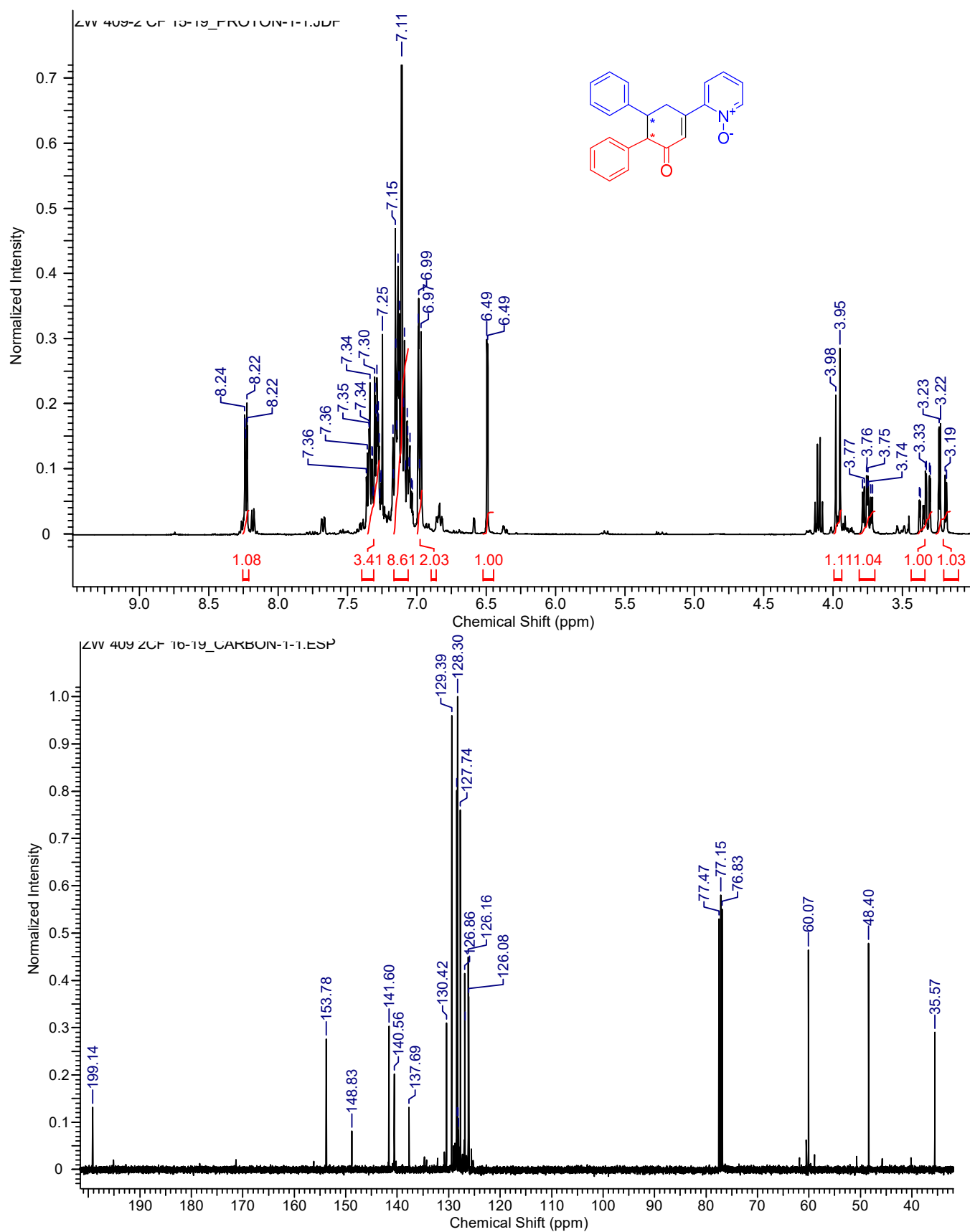
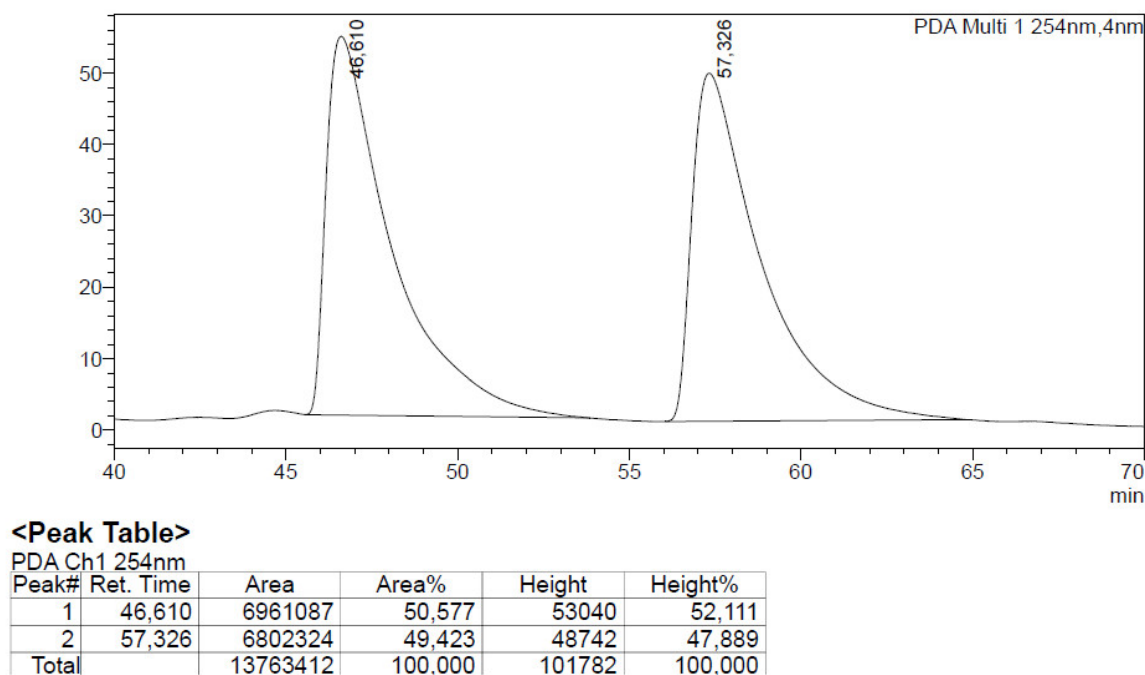


Figure S3. <sup>1</sup>H and <sup>13</sup>C NMR spectra of 2-(3-oxo-4,5-diphenyl-cyclohex-1-en-yl)pyridine 1-oxide - III.

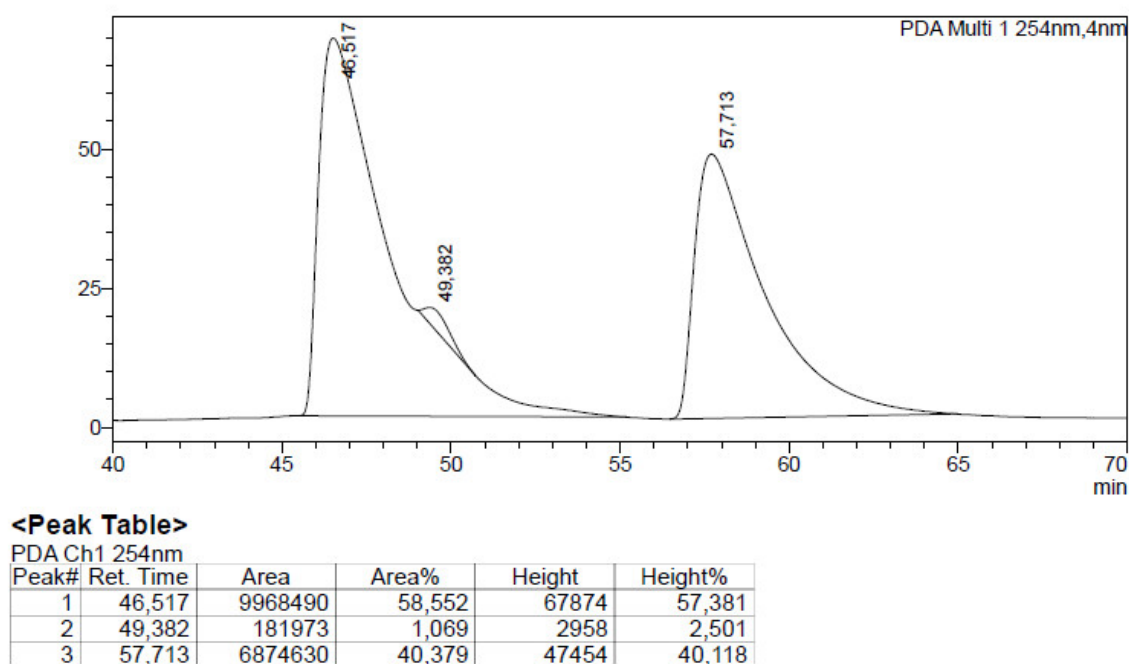
## 2. HPLC Data

### 2.1. Formal [3+3] annulation of 2-cinammoylpyridine N-oxide and BMK

(Chiralpak IA-3 column, hexane/*i*-PrOH 8:2, flow rate 1.0 mL/min)



**Figure S4.** HPLC chromatogram obtained with catalyst D/L-Phe-K (racemate).



**Figure S5.** HPLC chromatogram obtained with catalyst L-Phe-K (18% ee).

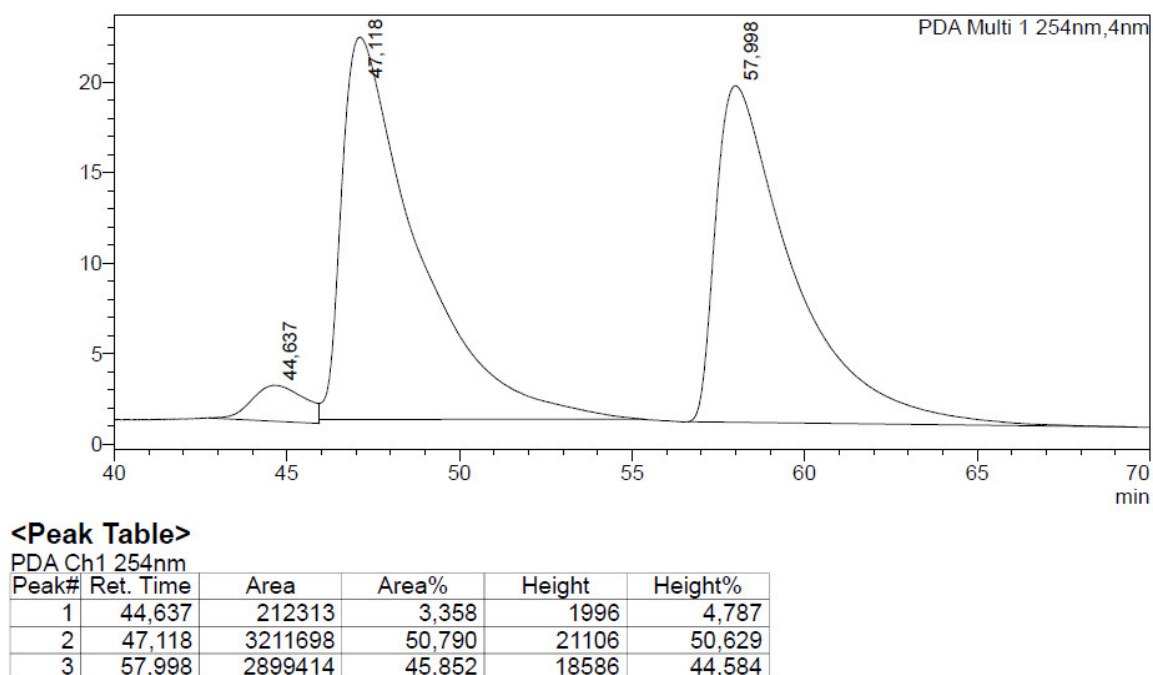


Figure S6. HPLC chromatogram obtained with catalyst L-Pro-K (5% ee).

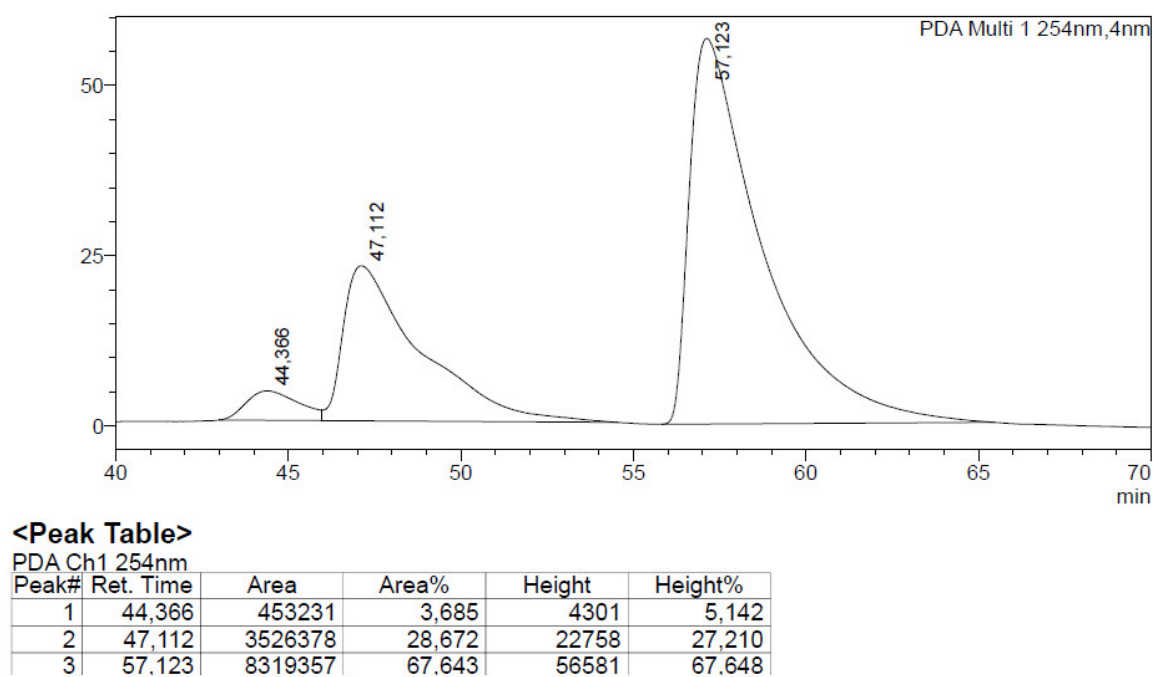
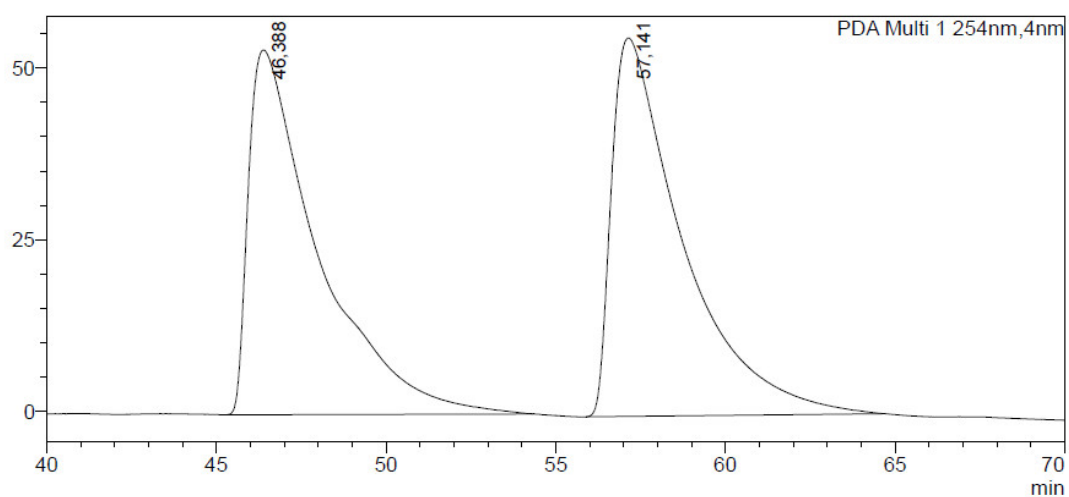


Figure S7. HPLC chromatogram obtained with catalyst L-*tert*-Leu-K (40% ee).

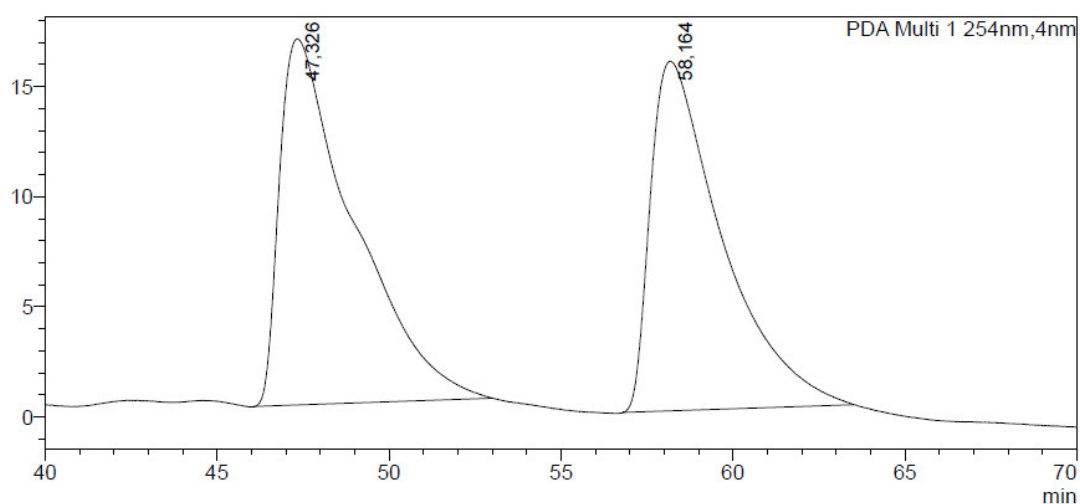


#### <Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	46,388	7572949	48,645	53087	49,077
2	57,141	7994885	51,355	55084	50,923
Total		15567834	100.000	108170	100.000

Figure S8. HPLC chromatogram obtained with catalyst L-Phe-K (in 1,2-dichloroethane, 3% ee).



#### <Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height	Height%
1	47,326	2482178	51,903	16634	51,153
2	58,164	2300186	48,097	15885	48,847
Total		4782364	100.000	32519	100.000

Figure S9. HPLC chromatogram obtained with catalyst L-Phe-Na (3% ee).

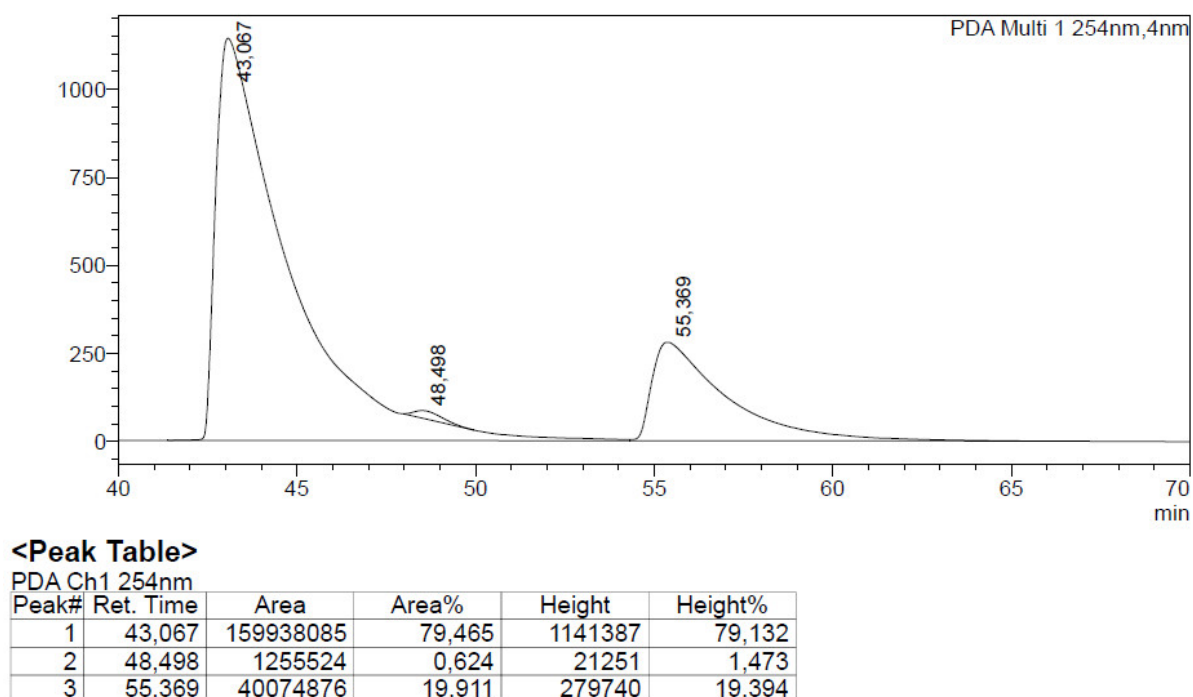


Figure S10. HPLC chromatogram obtained with catalyst TM-2 (60% ee).

### 3. Computational Data

Table S1. Values of relative free energies between main compounds.

	Compound III				Compound IV
Number of Structure	1	2	3	4	
Free energy ( $E_h$ )	-1092.7530	-1092.7530	-1092.7520	-1092.7520	-1092.7497
Relative free energy (kcal/mol)	-	-	0,69	0,68	2,12
Structures of compound III					-



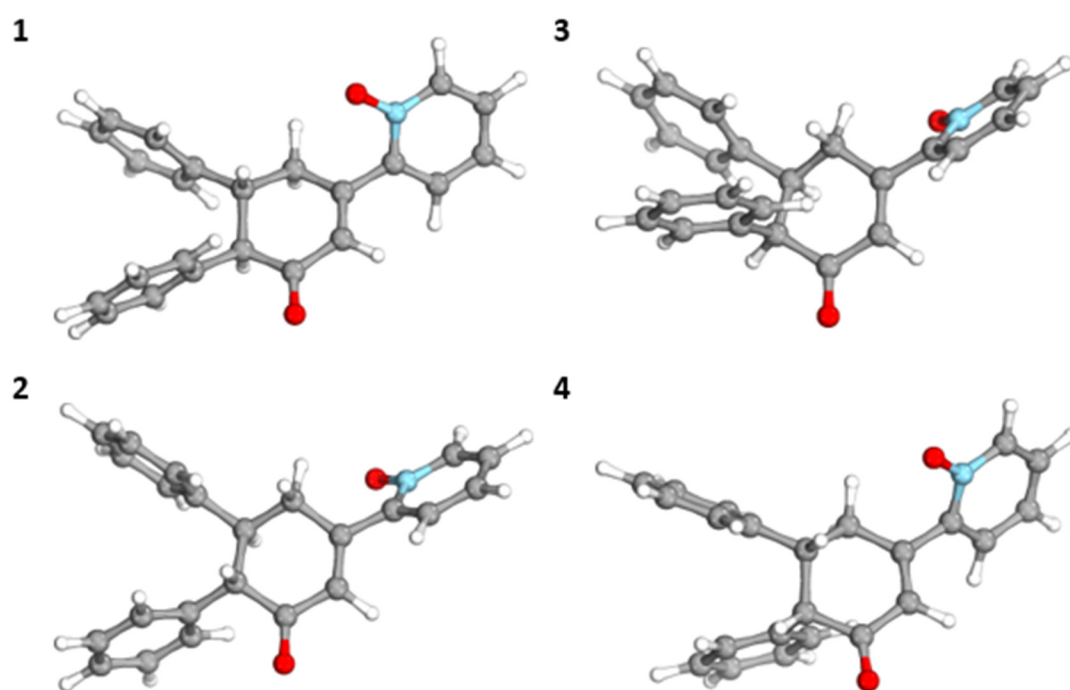


Figure S11. 3D structures of optimized geometries of diastereomers of compound III.