

Supporting Information

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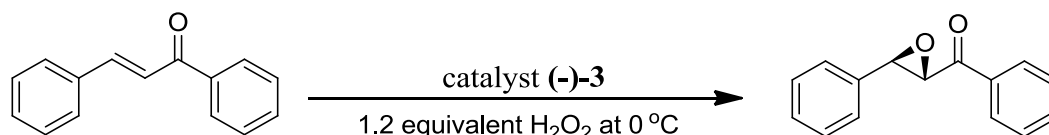
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General Information

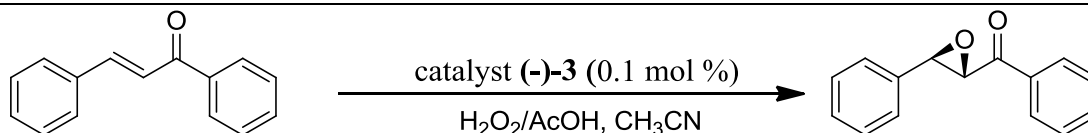
Manganese bistrifluoromethanesulfonate ($\text{Mn}(\text{OTf})_2$), styrene, *cis*- β -methyl styrene and Indene were bought from Sigma Aldrich and were used as such. (*1R,2R*)-(-)-1,2-diaminocyclohexane and (*1S,2S*)-(+)-1,2-diaminocyclohexane, 2-acetyl pyridine and pyridine-2-carboxaldehyde were procured from Sigma Aldrich. All chromenes and chalcones [1,2 and 3] were synthesized according to the reported procedures. All the solvents were purified before use [4]. Microanalysis of the products was carried out on a Perkin Elmer 2400 CHNS analyzer. The ^1H NMR and ^{13}C NMR spectra were recorded on Bruker 200 MHz or 500 MHz instruments at ambient temperature. The chemical shifts are reported in ppm relative to TMS ($\delta = 0.00$) for ^1H NMR and relative to the central CDCl_3 resonance ($\delta = 77.0$) for ^{13}C NMR. FT-IR spectra were recorded on Perkin Elmer Spectrum GX spectrophotometer in KBr window. Electronic spectra of complex were recorded in HPLC grade acetonitrile (CH_3CN) on a Shimadzu UV-Vis-NIR spectrophotometer (Serial No. A108446). TOFF mass of the catalysts and intermediates were determined on a Micromass Q-TOF-micro instrument. Optical rotations of chiral complexes and their ligand precursors were recorded on an Automatic Polarimeter (Digipol 781, Rudolph) Instrument. All the melting points reported here were determined on Thermo Scientific MET-TEMP (Model No. 1002D) and were uncorrected. The purity of the solvents and alkenes and the analysis of the epoxide product were determined by gas chromatography (GC) by a Bruker 450-GC instrument using Factor four capillary column VF-1ms, 15m 0.25mm, 0.25 μm (part no. CP8907) and equipped with an FID detector. Ultrapure nitrogen was the carrier gas (rate 30 mL/min). Injection port and detector temperature were kept at 200 $^\circ\text{C}$. For the product analysis of styrene, *cis*- β -Methyl styrene and indene the column temperature was programmed at 70 to 140 $^\circ\text{C}$, while for chromene it was kept at 140 $^\circ\text{C}$ (isothermal). Synthetic standards of the

products were used to determine the conversions by comparing the peak height and area. Flash chromatography (FC) was carried out using Neutral alumina (Grade-1). Enantiomeric excesses (ee) of chromenes and chalcones were determined by HPLC (Shimadzu SCL-10AVP) using Daicel Chiralpak OD, IC column with 2-propanol/hexane as eluent. Enantiomeric excess of styrene and *cis*- β -styrene was determined by gas chromatography using a Shimadzu GC 2010 instrument with a Supelco Astec Chiral DEXTM G-TA column. Optical rotations are reported as follow: $[\alpha]_D^t$ (c in g per 100 mL, solvent). The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, ddd= triple doublets, t = triplet, m = multiplet, br = broad, coupling constants are given in Hertz (Hz). NMR data of known compounds is in agreement with literature values.[5,6] HPLC and GC traces were compared to racemic samples prepared by racemic complex. Ligand C1' is synthesized according to the reported procedure. [7]

Table S1. Optimization of catalyst and AcOH amount

Entry	Catalyst loading, mol %	Time, min	Conversion[%] ^b	ee [%] ^c	Configuration
1 ^a	0.025	60	69	50	2 <i>R</i> ,3 <i>S</i>
2 ^a	0.05	60	77	75	2 <i>R</i> ,3 <i>S</i>
3 ^a	0.1	60	96	86	2 <i>R</i> ,3 <i>S</i>
4 ^a	0.2	60	99	78	2 <i>R</i> ,3 <i>S</i>
5 ^a	0.5	60	>99	76	2 <i>R</i> ,3 <i>S</i>
6 ^d	0.1	60	65	78	2 <i>R</i> ,3 <i>S</i>
7 ^e	0.1	45	>99	68	2 <i>R</i> ,3 <i>S</i>
8 ^f	0.1	60	10	20	-
9 ^g	0.1	60	4	8	-
10 ^h	0.1	60	33	71	2 <i>R</i> ,3 <i>S</i>
11 ⁱ	0.1	60	<1	NA	NA

^aReaction condition: catalyst (0.1 mol%, 1mL CH₃CN), chalcone (1.4 mmol), 1.2 equiv. of 50% H₂O₂, AcOH (3 equiv.); ^b Determined on ¹H NMR; ^cDetermined on HPLC using Diacel IC column; ^dReaction condition: catalyst (0.1 mol%, 1 mL CH₃CN), chalcone (1.4 mmol), 1.2 equiv. of 50% H₂O₂, AcOH (1equiv.); ^eReaction condition: catalyst (0.1 mol%, 1 mL CH₃CN), chalcone (1.4 mmol), 1.2 equiv. of 50% H₂O₂, AcOH (5 equiv.); ^fReaction condition: catalyst (0.1 mol%, 1 mL CH₃CN), chalcone (1.4 mmol), 1.2 equiv. of 50% H₂O₂, no AcOH; ^gReaction condition: catalyst (0.1 mol%), 1 mL 2.0 x 10⁻⁷ M trifluoroacetic acid CH₃CN solution of pH ~ 3.3); ^hReaction condition: catalyst (0.1 mol%) 1 mL 0.087 M benzoic acid CH₃CN solution of pH ~ 3.4); ⁱReaction condition: catalyst (0.1 mol%, 1mL CH₃CN, 3 equivalent of trifluoroacetic acid)

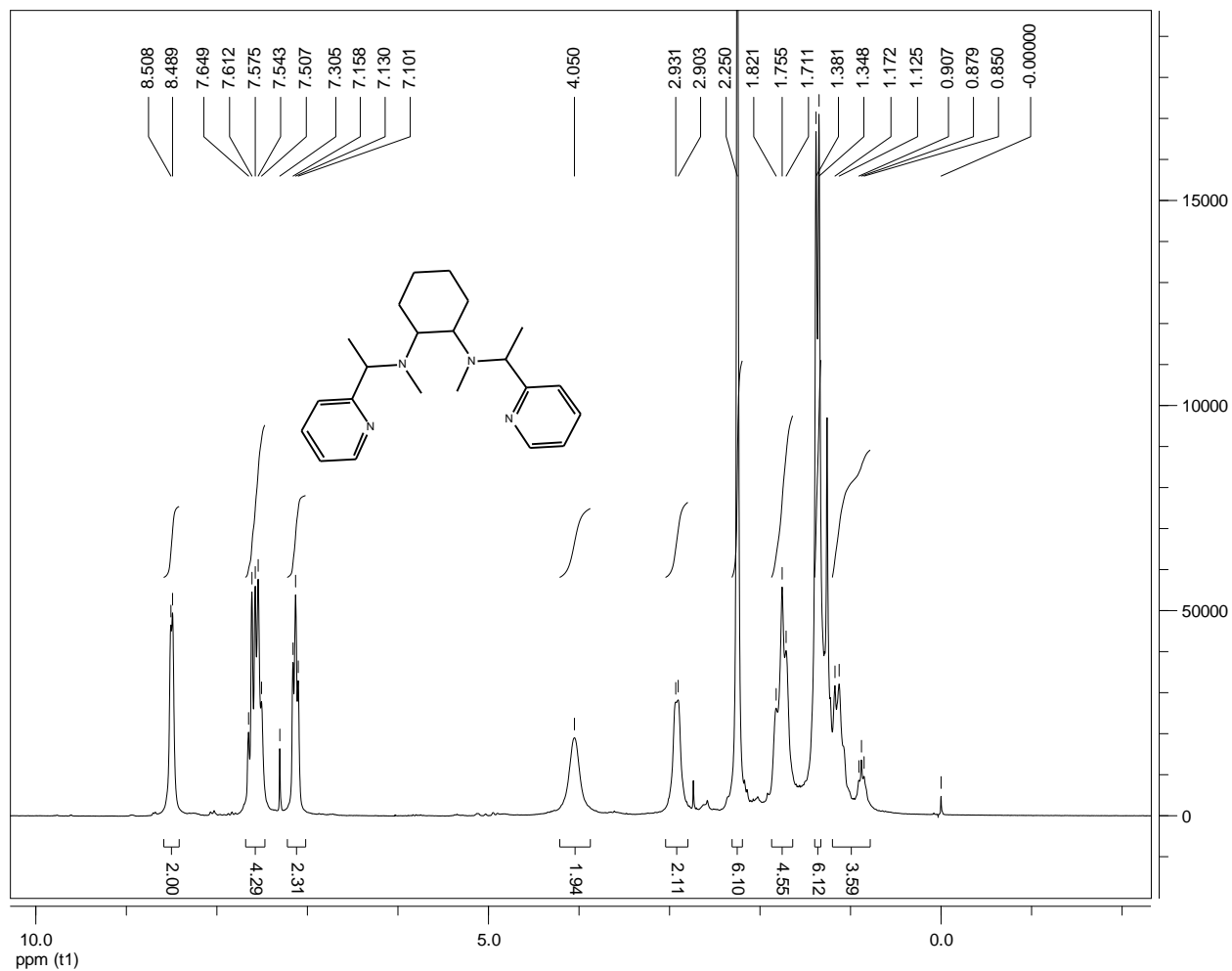
Table S2. Temperature variation using catalyst (-)-3^a

Entry	Temp, °C	Time, min	Yield[%] ^b	ee[%] ^c	Config.
1	10	60	>99	76	2 <i>R</i> ,3 <i>S</i>
2	0	60	95	86	-
3	-5	60	80	82	-
4	-10	60	60	70	-

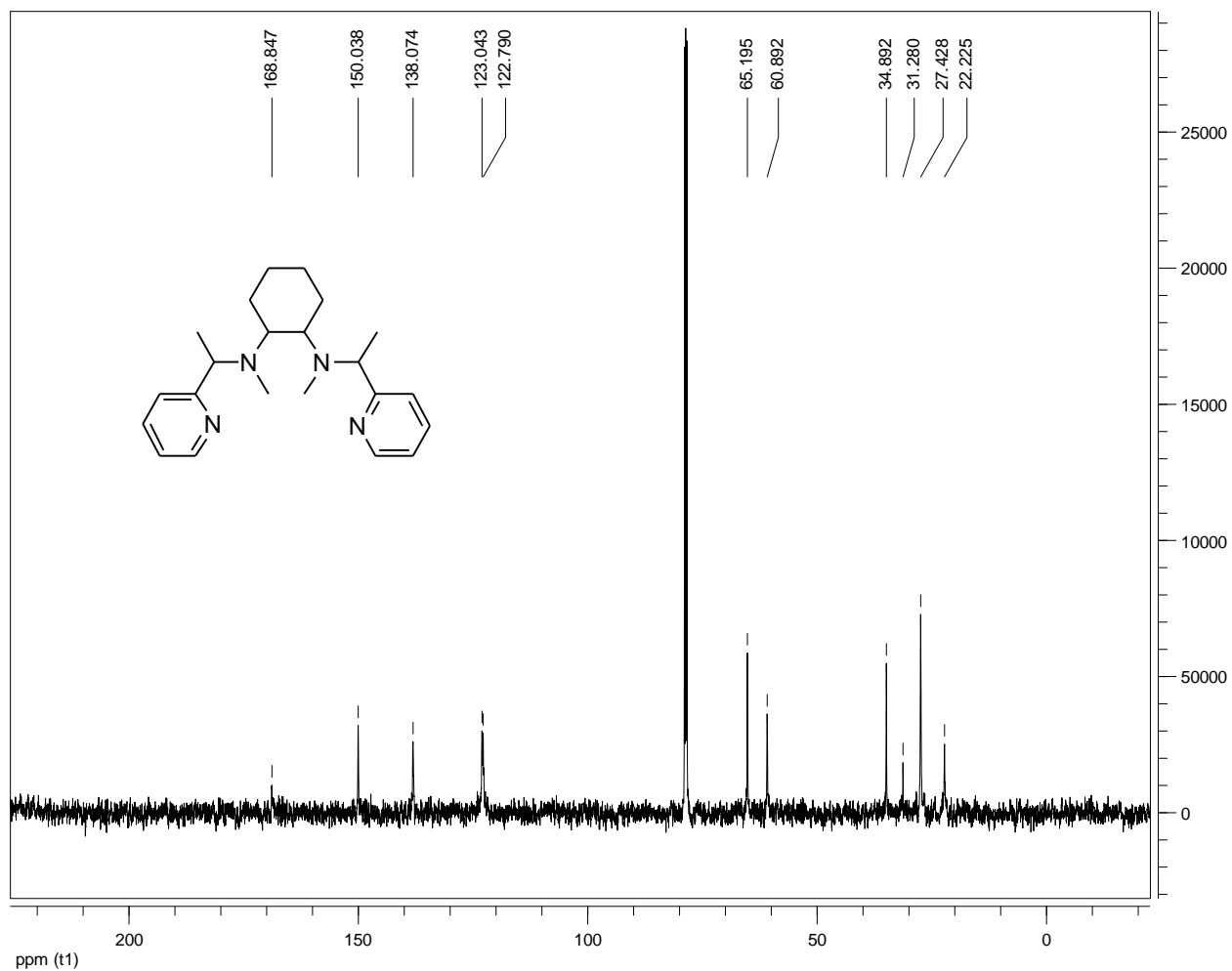
^aReaction condition: catalyst (0.1 mol%, 1mL CH₃CN), chalcone (1.4 mmol), 50% H₂O₂ (1.2 equiv.), AcOH (3 equiv.); ^bDetermined on ¹H NMR; ^cDetermined on HPLC using Diacel IC column.

NMR Profiles:

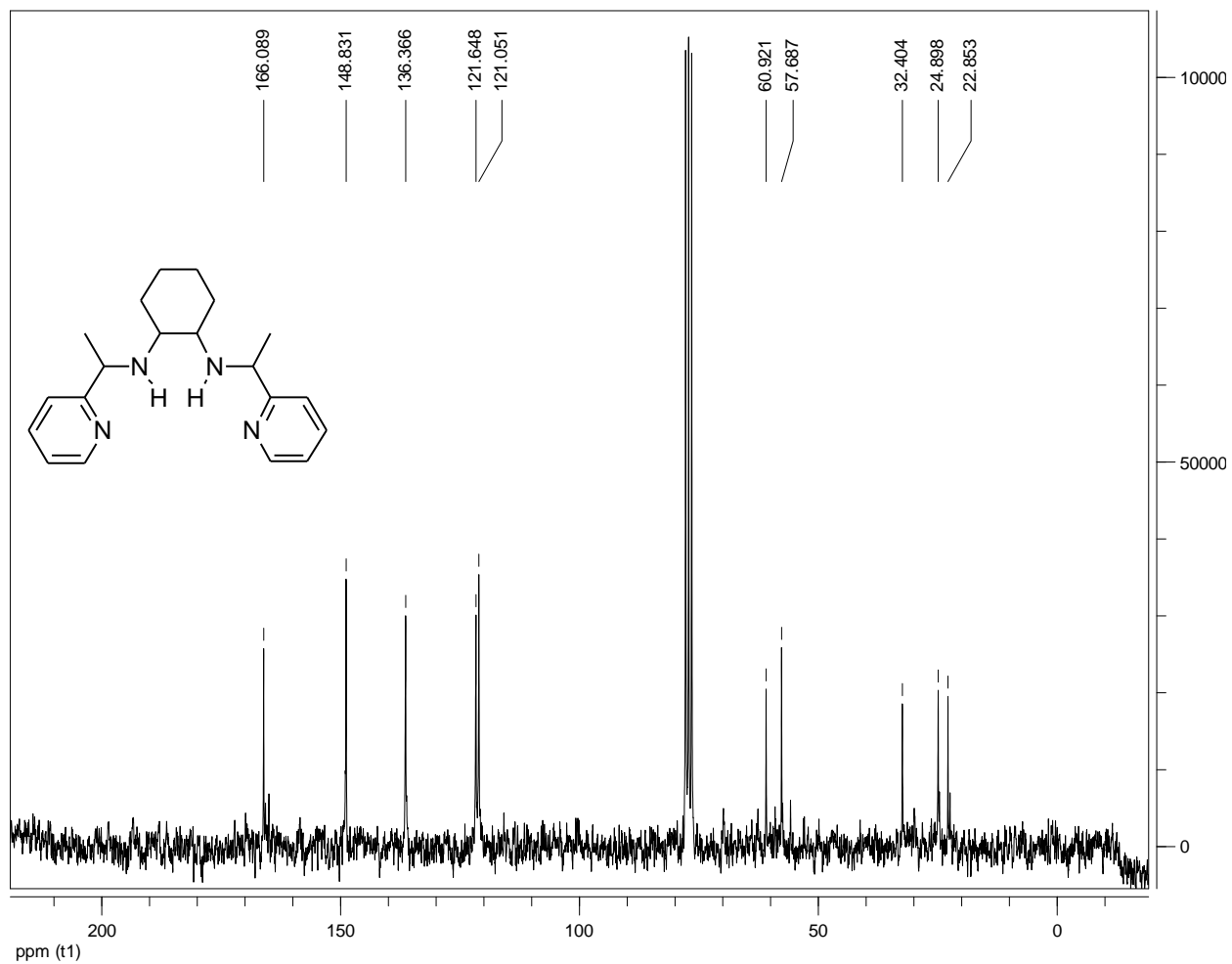
^1H NMR of **7S,1S,2S,7'R-C3'**:



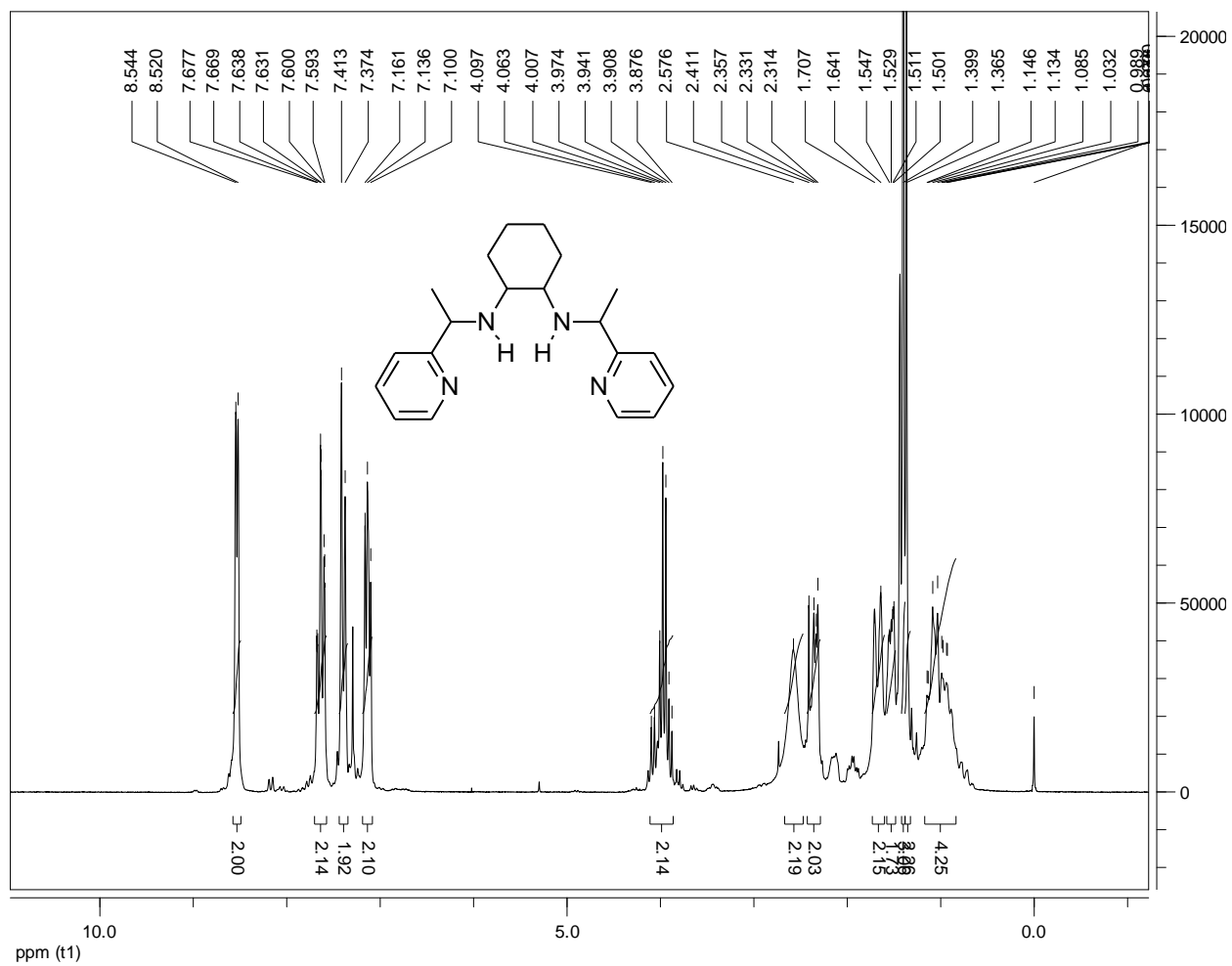
^{13}C NMR of **7S,1S,2S,7'R-C3'**:



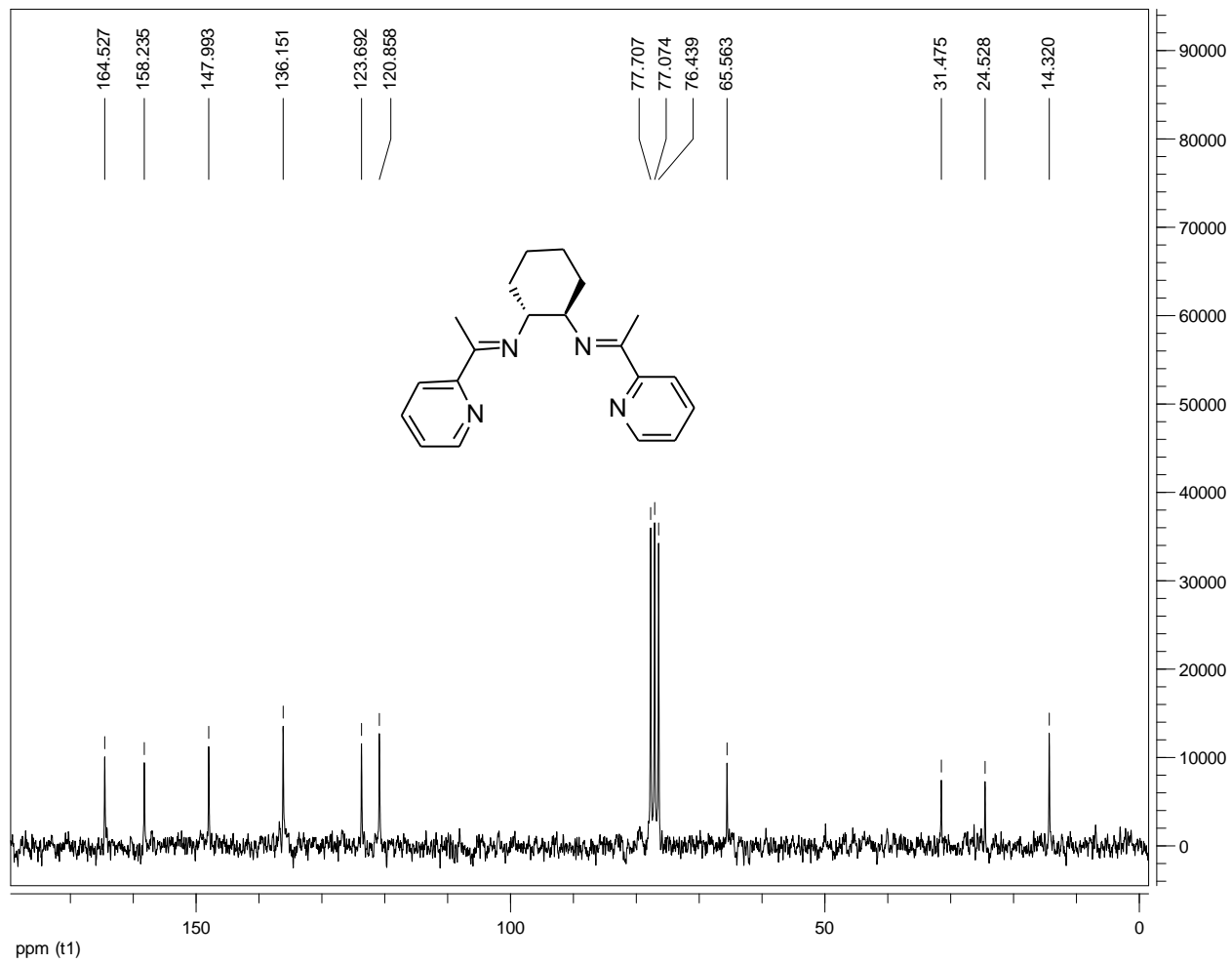
^{13}C NMR of **7S,1S,2S,7'R-C3'**:



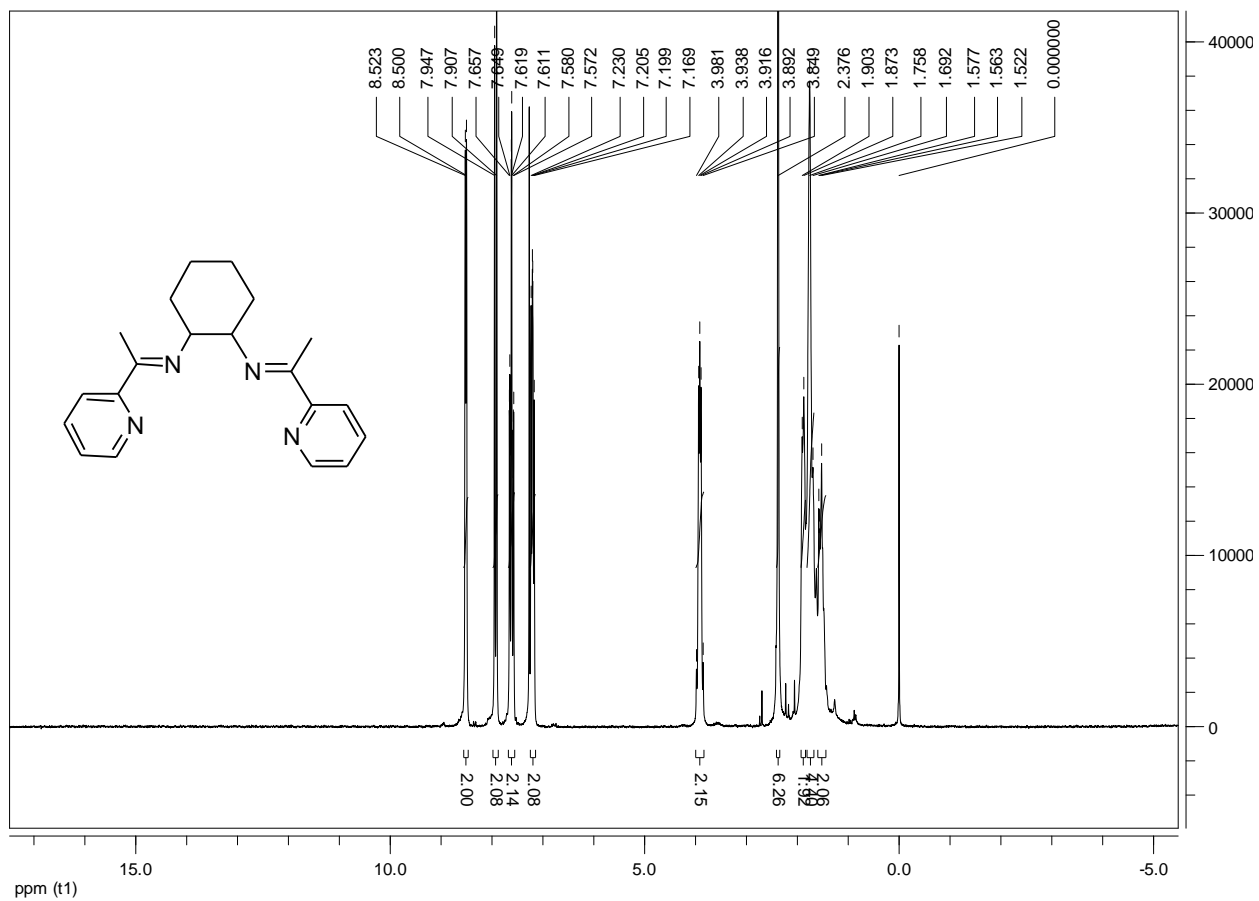
^1H NMR of **7S,1S,2S,7'R-C3''**:



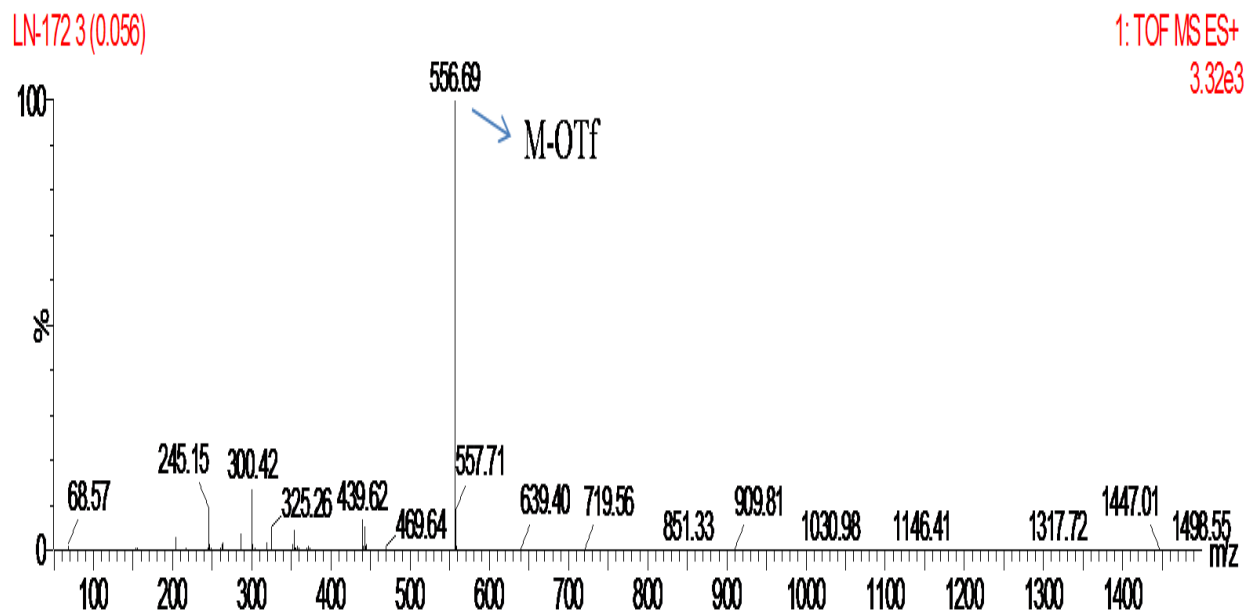
^{13}C NMR of **1S,2S-C3'''**:



^1H NMR of **1S,2S-C3'''**:



LCMS Profiles:

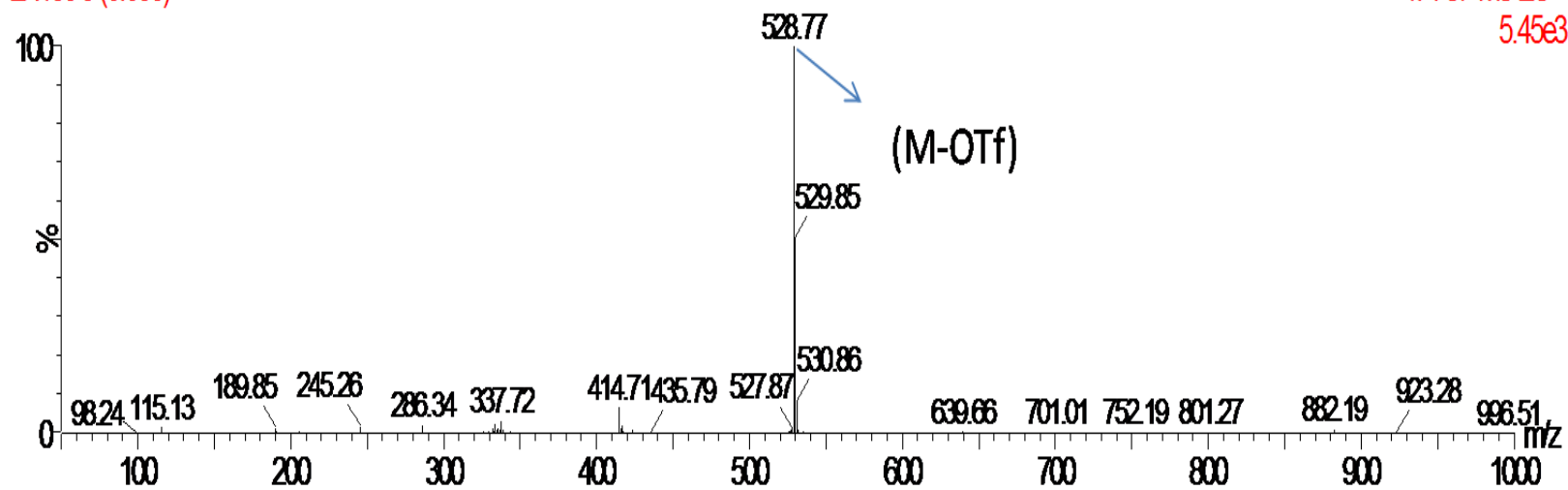


LCMS of catalyst (-)-3:

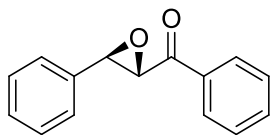
LCMS of catalyst (+)-2:

LN1863 (0.056)

1: TOFMS⁺
5.45e3

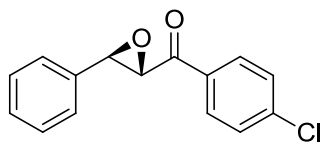


NMR data of the products:



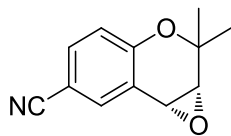
^1H NMR (500 MHz, CDCl_3) δ ppm: 7.93 (q, $J=8.25$, 1.0, 2H), 7.53 (t, $J=7.5$, 1H), 7.40 (t, $J=8$, 2H), 7.32-7.28 (m, 5H), 4.22 (d, $J=2$, 1H), 3.99 (d, $J=1.5$, 1H).

^{13}C (125 MHz, CDCl_3) δ ppm: 193.1, 135.5, 134.0, 129.1, 128.9, 128.8, 128.4, 125.8, 61.0, 59.4.



^1H NMR (500 MHz, CDCl_3) δ ppm: 7.97 (d, $J=8.5$, 2H), 7.47 (d, $J=8.5$, 2H), 7.42-7.35 (m, 5H), 4.24 (d, $J=2$, 1H), 4.08 (d, $J=2$, 1H).

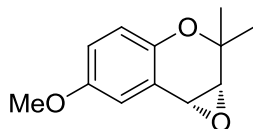
^{13}C NMR (125 MHz, CDCl_3) δ ppm: 192.1, 140.6, 135.2, 133.7, 129.8, 129.3, 129.2, 128.8, 125.8, 61.0, 59.4.



^1H NMR (200 MHz, CDCl_3) δ ppm: 7.66 (s, 1H), 7.54 (d, $J=8.2$, 1H), 6.87 (d, $J=8.4$, 1H), 3.92

(d, $J=4.2$, 1H), 3.55 (d, $J=4.2$, 1H), 1.61 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ

172.4, 156.7, 133.6, 133.2, 130.0, 120.8, 118.5, 104.0, 79.9, 73.176, 25.8, 21.2.



^1H NMR (200 MHz, CDCl_3) δ ppm: 6.89 (d, $J=2.4$, 1H), 6.81 (d, $J=9$, 1H), 6.74 (d, $J=8.8$, 1H),

3.86 (d, $J=4.4$, 1H), 3.47 (d, $J=4.4$, 1H), 1.58 (s, 3H), 1.57 (s, 3H), 1.22 (s, 3H).

^{13}C NMR (50 MHz, CDCl_3) δ ppm: 153.9, 146.2, 120.7, 118.7, 115.6, 114.7, 72.7, 62.8, 55.8, 51.1, 25.7, 22.3.

1,2-epoxy hexane:

^1H NMR (500 MHz, CDCl_3) δ ppm: 2.89 (s, 1H), 2.73 (d, $J=3.5$ Hz, 1H), 2.42 (s, 1H), 1.53 (t, $J=6$ Hz, 2H), 1.45-1.37 (m, 4H), 0.92 (t, $J=7$ Hz, 3H)

^{13}C NMR (125 MHz, CDCl_3) δ ppm: 52.2, 46.9, 32.1, 28.0, 22.4, 13.8.

1,2-Epoxy hexane

Column: SUPELCO ASTEC CHIRAL DEXTM G-TA (45944-01B), Length: 30 M.

Injector Temperature: 200 °C

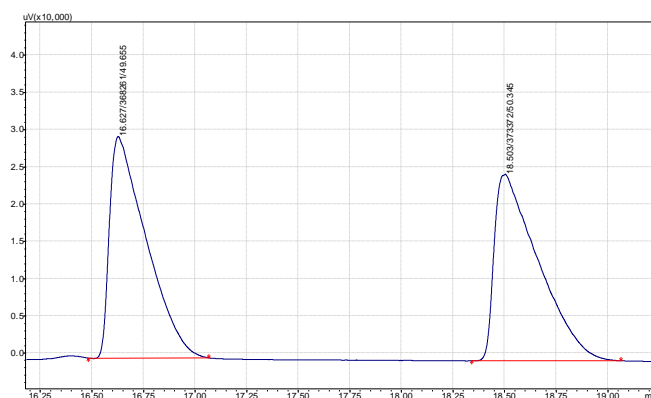
Detector Temperature: 200 °C

Pressure: 101.1 kPa.

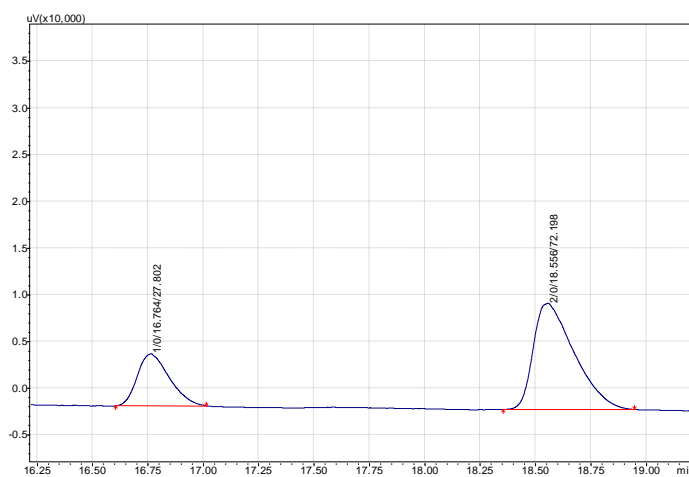
Linear Velocity: 46.4cm/sec.

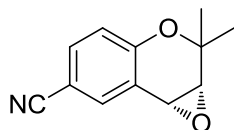
Column temperature: 40 °C

Racemic 1,2-epoxy hexane



Chiral 1,2-epoxy hexane, 44% ee (Table 4, entry 7)





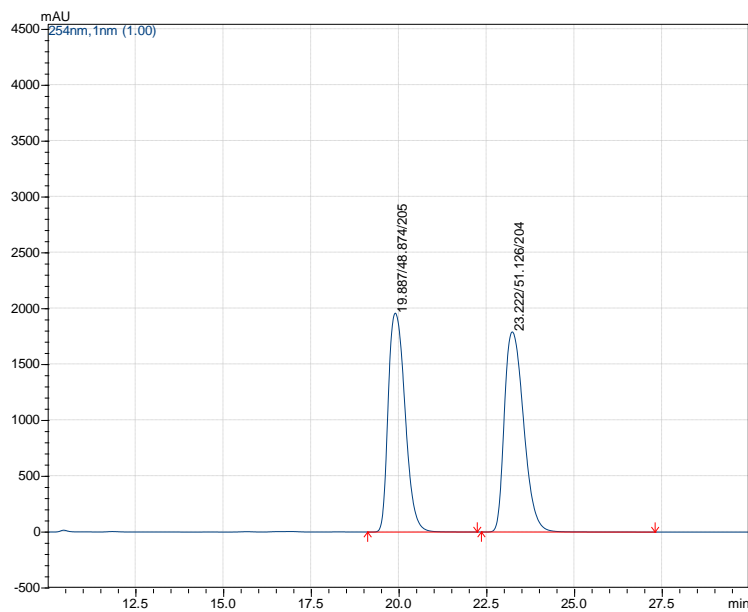
Column: Daicel OD (No. OD00CE-IL045)

IPA: Hexane: 5:95

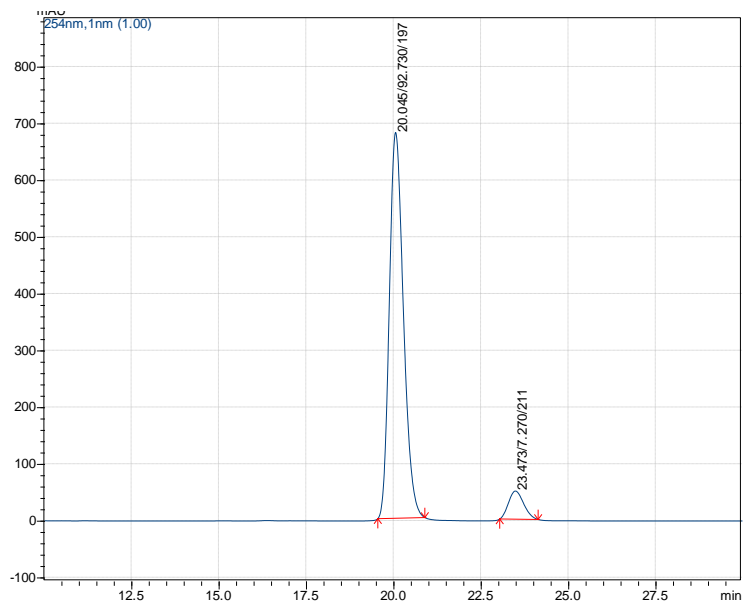
Flow rate: 0.6ml/min

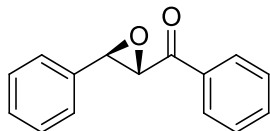
Wave Length: 254nm

Racemic epoxide:



Chiral CN-CHR epoxide ee 86% (Table 4, entry 3)





Column: Daicel IC (No. IC00CE-PI031)

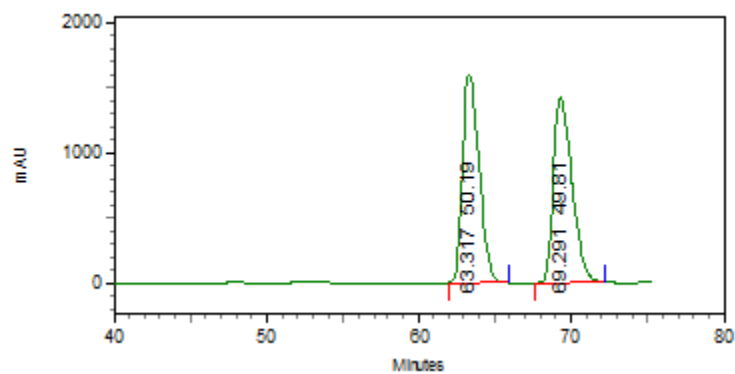
IPA: Hexane: 10:90

Flow rate: 0.3 ml/min

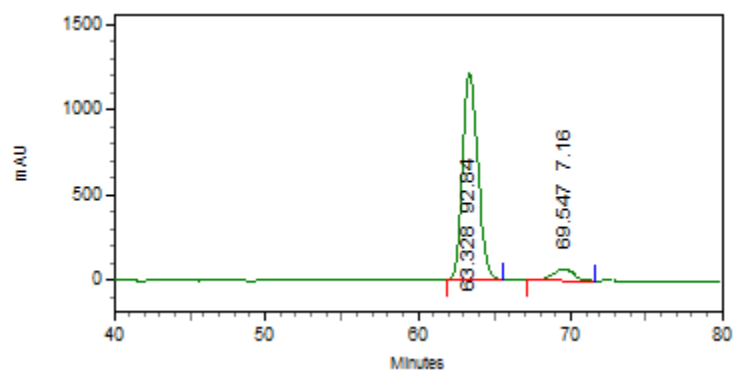
Wave Length: 254 nm

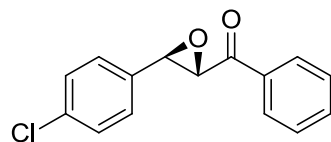
Racemic epoxide:

Racemic epoxide



chiral chalcone epoxide ee 86% (Table 4, entry 1)





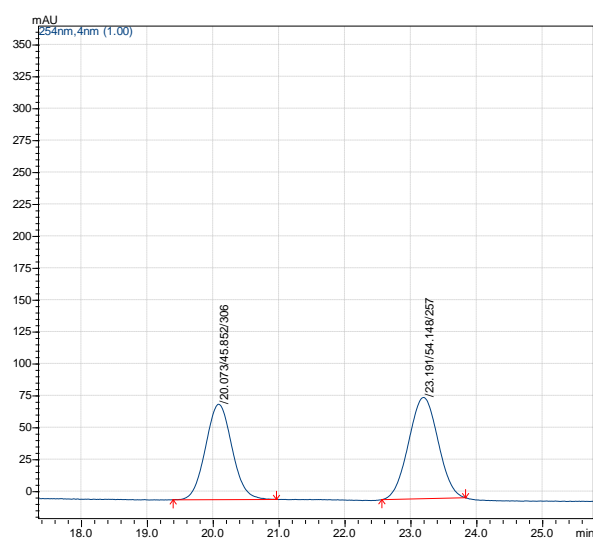
Column: Daicel IC (No. IC00CE-PI031)

IPA: Hexane: 4:96

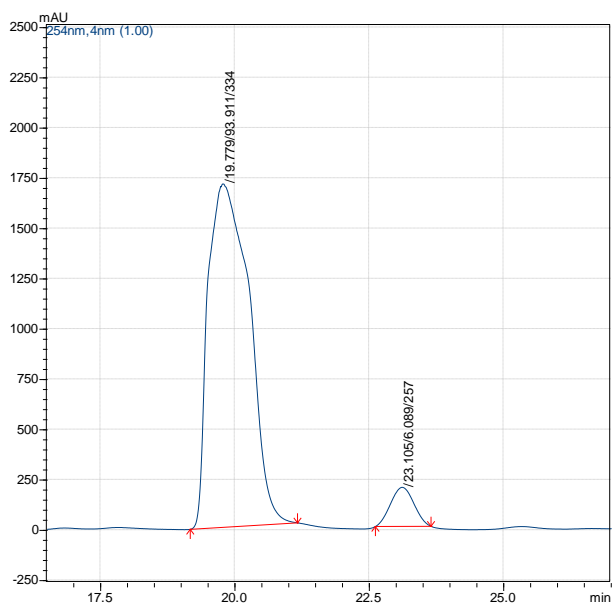
Flow rate: 1 ml/min

Wave Length: 254 nm

Racemic epoxide:



Chiral epoxide ee 88% (Table 4, entry 2)



Cis - β -methyl styrene:

Column: SUPELCO ASTEC CHIRAL DEXTM G-TA (NO. 45944-01B), Length: 30 M.

Injector Temperature: 200 °C

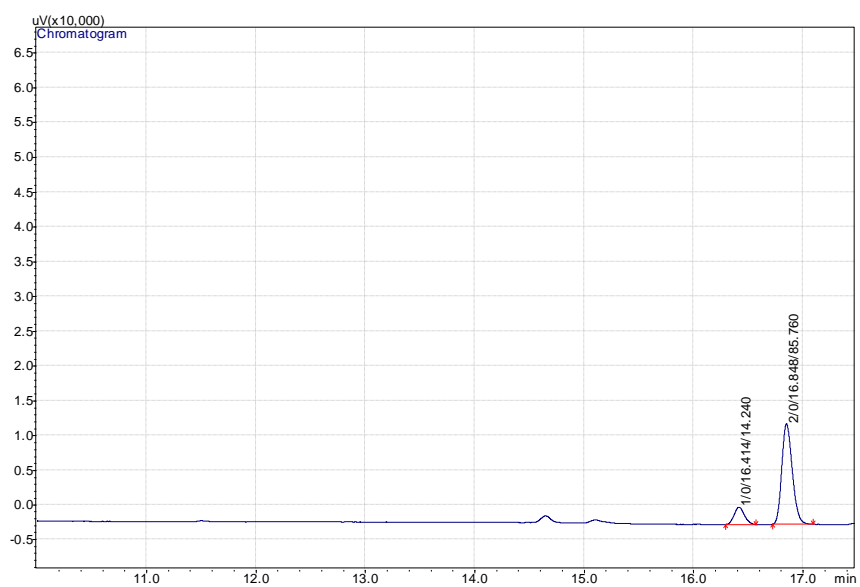
Detector Temperature: 200 °C

Pressure: 122.2 kPa.

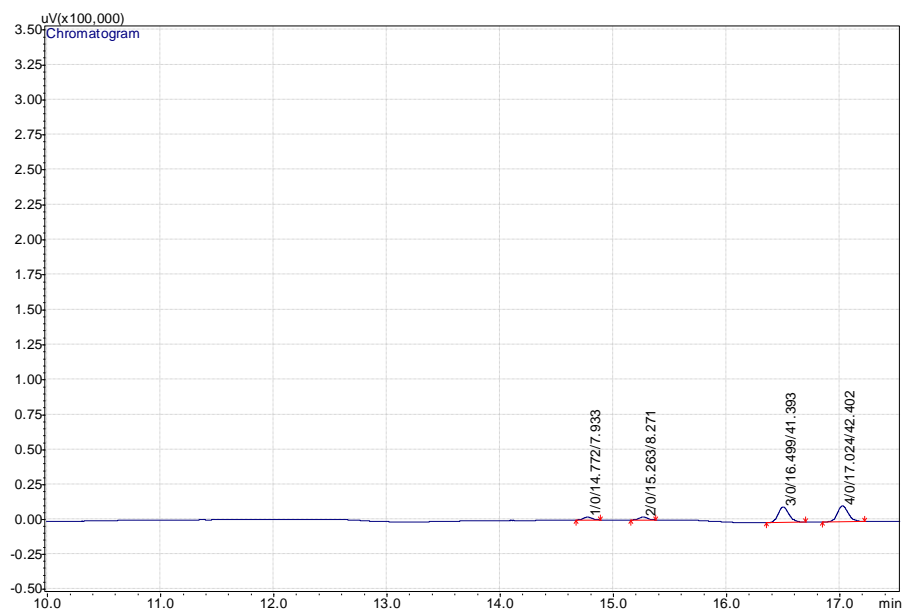
Linear Velocity: 52.4 cm/sec.

Heating rate: 70 °C to 140 °C at 2 °C/min.

Chiral epoxide ee 71% (Table 4, entry 6)



Racemic epoxide



Styrene oxide:

Column: SUPELCO ASTEC CHIRAL DEXTM G-TA (45944-01B), Length: 30 M.

Injector Temperature: 200 °C

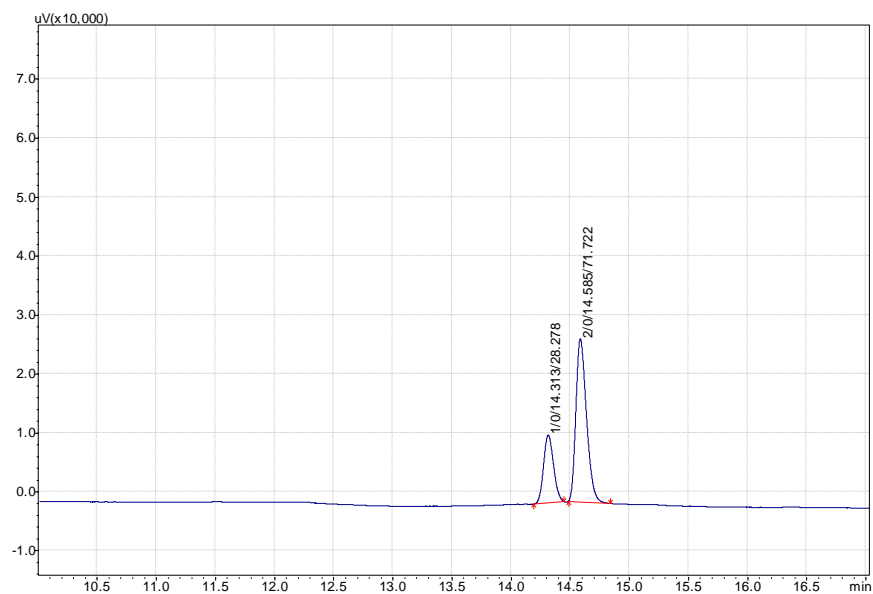
Detector Temperature: 200 °C

Pressure: 101.1 kPa.

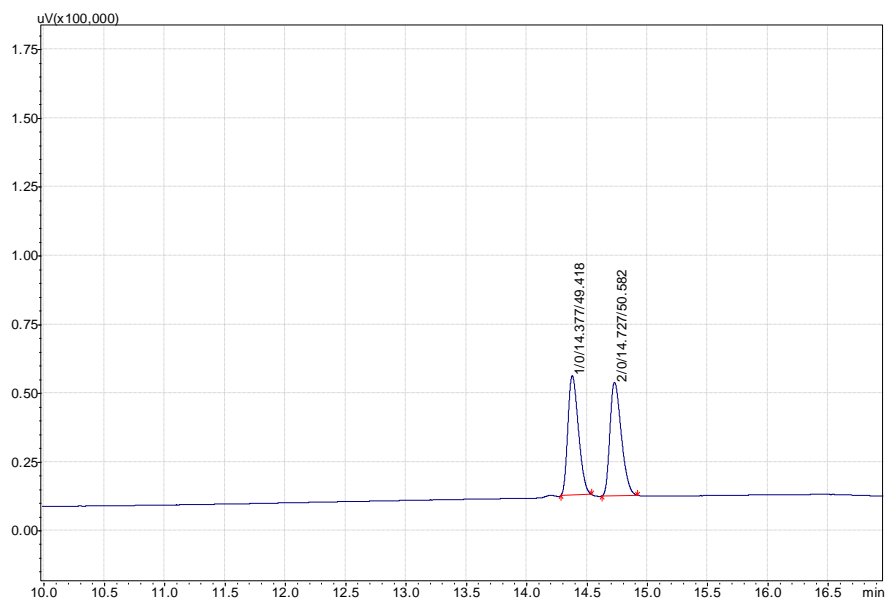
Linear Velocity: 46.4 cm/sec.

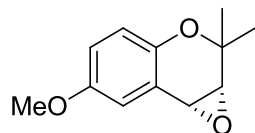
Column temperature: 70 -140 °C, 3 °C/min

Chiral styrene epoxide ee 44% (Table 4, entry 8)



Racemic styrene epoxide





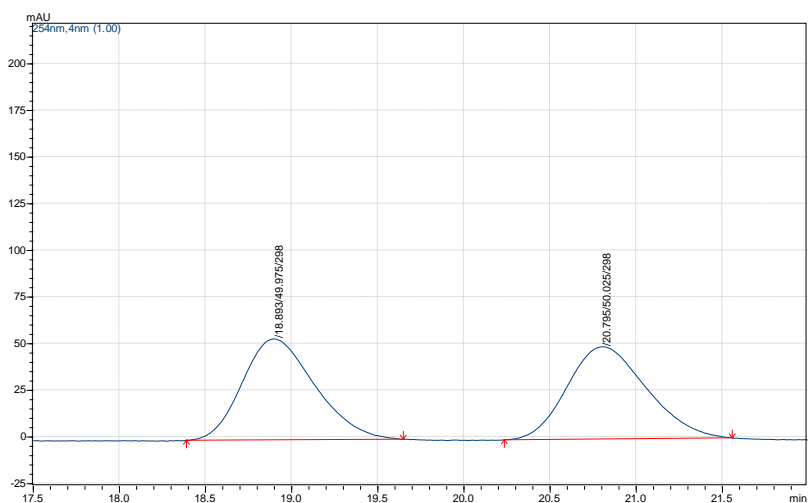
Column: Daicel OD (No. OD00CE-IL045)

IPA: Hexane: 5:95

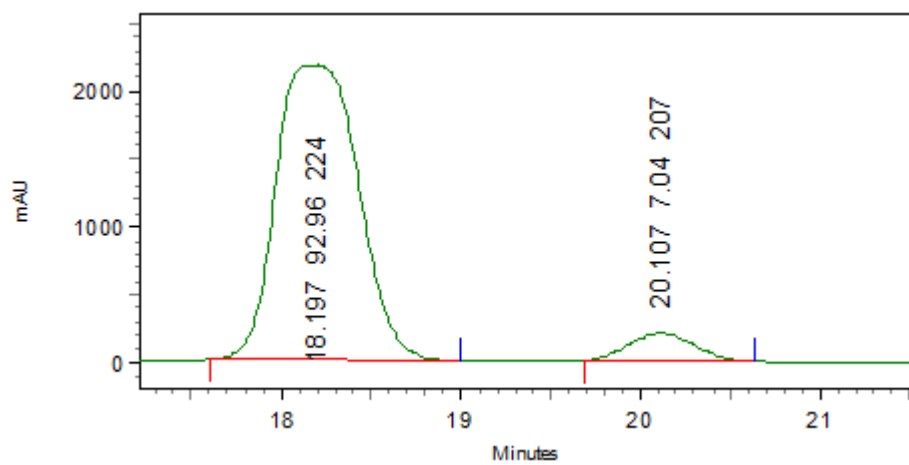
Flow rate: 0.4 ml/min

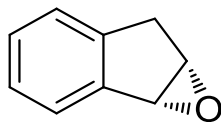
Wave Length: 220 nm

Racemic epoxide:



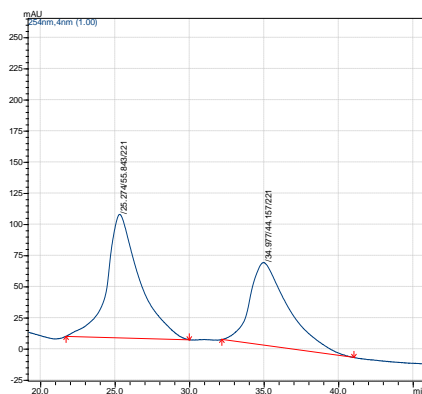
Chiral MeO-CHR epoxide ee 86% (table 4, entry 4)



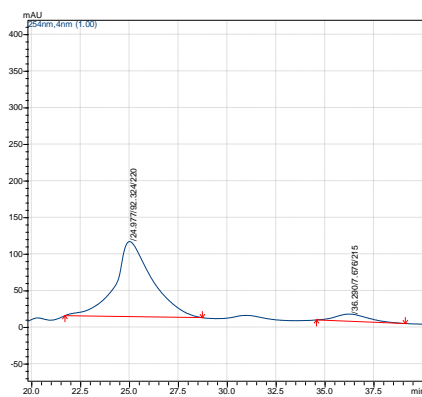


Column: Daicel OB
IPA: Hexane: 3:97
Flow rate: 0.5 ml/min
Wave Length: 254 nm

racemic indene epoxide



chiral indene oxide 84% ee (table 4, entry 5)



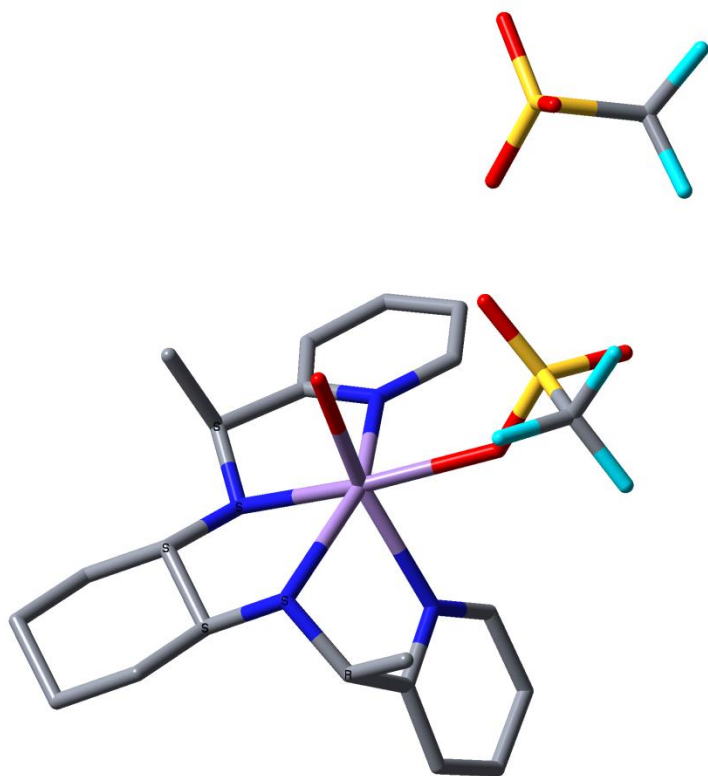
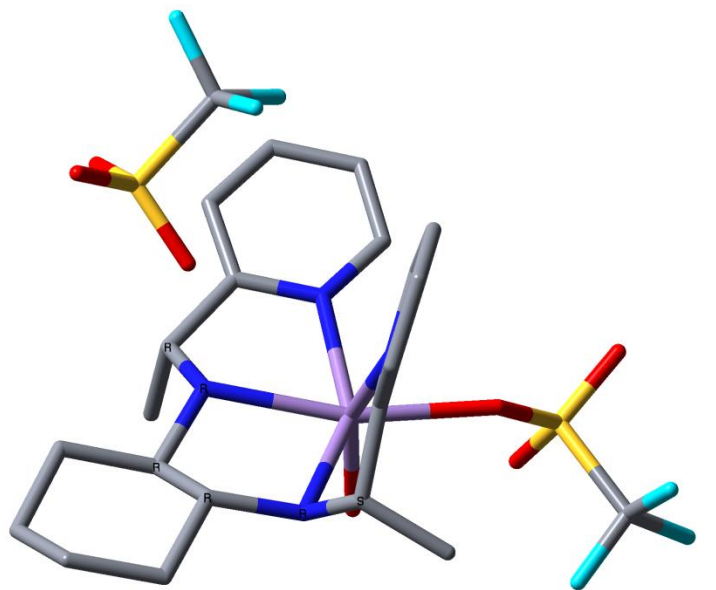


Figure S1. Crystal structure of Δ -(+)-**2** and Λ -(-)-**2** which are non super imposable mirror image (straight line depicts the plane of mirror, and Hydrogen atoms are omitted to improve clarity)

References:

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