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Highly Enantioselective Asymmetric Darzens Reaction Catalysed by Proline Based Efficient Organocatalysts for Synthesis of di- and tri-substituted Epoxides

Veeramanoharan Ashokkumar, Ayyanar Siva* and Rishinaradamangalam Ramaswamy Chidambaram

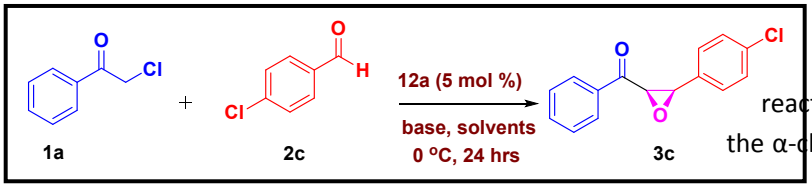
Supramolecular and Organometallic Chemistry Lab, Department of Inorganic Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai-625 021, Tamil Nadu, India.

E-mail: drasiva@gmail.com

Supporting Information

Table of Contents

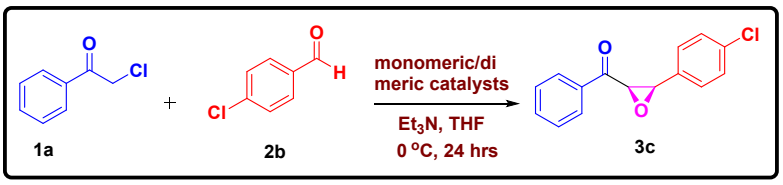
Table S1: Optimization of solvent and base for asymmetric Darzens reaction.[a]



[a] The Darzens reaction was carried out between the α-chloro ketone (0.2 mmol), 4-chlorobenzaldehyde (0.24 mmol), various bases (0.8 mmol) and different solvents (2 mL) with **12a** (5 mol %) at 0 °C temperature. [b] Isolated yield of purified material. [c] Enantiopurity was determined by HPLC analysis of epoxide product using a chiral column (Chiralcel OD-H) with hexane-IPA as an eluent. [d] Absolute configuration was determined by comparison of the HPLC retention time using known literature data.[1-7] [e] no reaction

Entry	Solvents	Base	Yield (%) [b]	ee's (%)[c]	Abs. Conf.[d]
1	THF	KOH	nr[e]	-	(2*S*, 3*R*)
2	THF	K^{t}OBu	trace	-	(2*S*, 3*R*)
3	THF	NaOH	nr[e]	-	(2*S*, 3*R*)
4	THF	K_2CO_3	40	30	(2*S*, 3*R*)
5	THF	morpholine	70	86	(2*S*, 3*R*)
6	THF	Et_3N	96	99	(2*S*, 3*R*)
7	THF	pyridine	75	78	(2*S*, 3*R*)
8	CH_3CN	Et_3N	90	91	(2*S*, 3*R*)
9	CH_3OH	Et_3N	72	81	(2*S*, 3*R*)
10	$CHCl_3$	Et_3N	70	84	(2*S*, 3*R*)
11	cyclohexane	Et_3N	65	71	(2*S*, 3*R*)
12	Toluene	Et_3N	60	63	(2*S*, 3*R*)

Table S2: comparisons of monomeric/dimeric catalysts for asymmetric Darzens reaction.

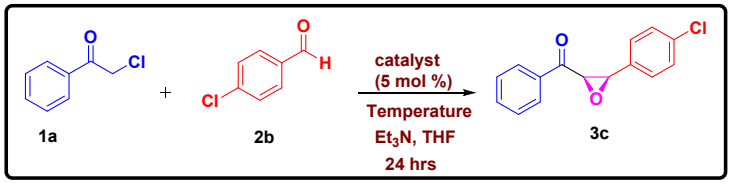


Entry	Catalysts (momeric/dimeric)	Mol % of catalyst	Yield (%)[b]	ee's (%)[c]	Abs. Conf.[d]
1	***N*-benzyl-L-proline**	5 mol%	60	53	(2*S*, 3*R*)
2	***N*-benzyl-L-proline**	10 mol%	62	58	(2*S*, 3*R*)
3	***N*-benzyl-L-proline ethyl ester**	5 mol%	55	40	(2*S*, 3*R*)
4	***N*-benzyl-L-proline ethyl ester**	10 mol%	58	47	(2*S*, 3*R*)
5	**11a**	5 mol%	87	91	(2*S*, 3*R*)
6	**11b**	5 mol%	85	83	(2*S*, 3*R*)
7	**12a**	5 mol%	96	99	(2*S*, 3*R*)
8	**12b**	5 mol%	90	92	(2*S*, 3*R*)

[a] The Darzens reaction was carried out between the α-chloro ketone (0.2 mmol), 4-chlorobenzaldehyde (0.24 mmol), Et_3N (0.8 mmol) and THF (2 mL) with various catalysts in different concentration (5 and 10

mol %) at 0 °C condition. [b] Isolated yield of purified material.[c] Enantiopurity was determined by HPLC analysis of epoxide product using a chiral column (Chiralcel OD-H) with hexane-IPA as an eluent. [d] Absolute configuration was determined by comparison of the HPLC retention time using known literature data.[1-7]

Table S3: Catalyst screening and temperature optimization for asymmetric Darzens reaction.



Entry	Catalysts	Temperature (°C)	Yield (%)[b]	ee's (%)[c]	Abs. Conf.[d]
1	**11a**	60 °C	65	61	(2*S*, 3*R*)
2	**11b**	60 °C	60	47	(2*S*, 3*R*)
3	**12a**	60 °C	70	67	(2*S*, 3*R*)
4	**12b**	60 °C	65	58	(2*S*, 3*R*)
5	**11a**	30 °C	72	84	(2*S*, 3*R*)
6	**11b**	30 °C	75	78	(2*S*, 3*R*)
7	**12a**	30 °C	85	86	(2*S*, 3*R*)
8	**12b**	30 °C	80	81	(2*S*, 3*R*)
9	**11a**	0 °C	87	91	(2*S*, 3*R*)
10	**11b**	0 °C	85	83	(2*S*, 3*R*)
11	**12a**	0 °C	96	99	(2*S*, 3*R*)
12	**12b**	0 °C	90	92	(2*S*, 3*R*)

[a] The Darzens reaction was carried out between the α-chloro ketone (0.2 mmol), 4-chlorobenzaldehyde (0.24 mmol), Et_3N (0.8 mmol) and THF (2 mL) with different catalysts (5 mol %) at various temperature condition. [b] Isolated yield of purified material. [c] Enantiopurity was determined by HPLC analysis of epoxide product using a chiral column (Chiralcel OD-H) with hexane-IPA as an eluent. [d] Absolute configuration was determined by comparison of the HPLC retention time using known literature data.[1-7]

1. Experimental Section

1.1. Materials and Methods

All the chemicals and reagents used in this work were of analytical grade. Benzaldehyde, 4-Chlorobenzaldehyde, 3-Chlorobenzaldehyde 2-Chlorobenzaldehyde, 4-Bromobenzaldehyde, 4-Methoxybenzaldehyde, 4-Methylbenzaldehyde, 2-Methylbenzaldehyde, 1-Naphthaldehyde, Formaldehyde, Propionaldehyde, 2-Chloroacetophenone, 4'-bromo-2-chloroacetophenone, 2-Chlorotetralin-1-one were purchased from Sigma Aldrich. L-proline and L-proline ethyl ester were purchased from TCI chemicals. N-bromosuccinimide and AIBN were obtained from Alfa Aesar, acetic acid and $ZnCl_2$ were purchased from Merck and all the solvents were obtained from Laboratory Grade.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker (Avance) 300 and 400 MHz NMR instrument using TMS as an internal standard and $CDCl_3$ as a solvent. Standard Bruker software was used throughout. Chemical shifts are given in parts per million (δ-scale) and the coupling constants are given in Hertz. Silica gel-G plates (Merck) were used for TLC analysis with a mixture of n-hexane and ethyl acetate as an eluent. Column chromatography was carried out on silica gel (60-120 mesh size) using n-hexane and ethyl acetate as an eluent. High Resolution mass spectroscopic (HRMS) data were obtained using Bruker Apex IV RTMS. The HPLC was recorded in SHIMADZU LC-6AD with chiral column (Chiralcel OD-H), using HPLC grade n-hexane and isopropanol as solvents. Optical rotations were measured on Rudolph Research Analytical AUTOPOL-II (readability ± 0.01°) and AUTOPOL-IV (readability ± 0.001°) automatic polarimeters.

2. Experimental procedure for the synthesis of core and organocatalysts.

2.1. Preparation of compound 8a.

About 1 g (7.3 mmol) of pentaerythritol was dissolved in 1:1 ratio of ethanol and acetic acid at 80 °C under constant stirring. Then 1.64 mL (14.7 mmol) of *o*-tolualdehyde was added and followed by the addition of anhydrous $ZnCl_2$ in a catalytic amount. Then, the mixture was allowed to reflux for about 12 hours. After completion of the reaction, the reaction mixture was extracted with ethyl acetate and the solvent was removed under vacuum. The crude reaction mass was purified by column chromatography using pet.ether and ethyl acetate as an eluent, isolated yield of **8a** is 1.9 g, 78 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 2.29 (s, 6H), 3.69 (s, 8H), 5.97 (s, 2H), 7.15-7.23 (m, 4H), 7.32 (d, *J* = 6.0 Hz, 2H), 7.38 (d, *J* = 6.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 139.85, 135.23, 130.34, 129.12, 127.76, 125.67, 108.89, 65.27, 31.84, 19.44.

2.2. Preparation of compound 8b.

About 1 g (7.3 mmol) of pentaerythritol was dissolved in 1:1 ratio of ethanol and acetic acid at 80 °C under constant stirring. Then 1.64 mL (14.7 mmol) of *p*-tolualdehyde was added and followed by the addition of anhydrous $ZnCl_2$ in a catalytic amount. Then, the mixture was allowed to reflux for about 12 hours. After completion of the reaction, the reaction mixture was extracted with ethyl acetate and the solvent was removed under vacuum. The crude reaction mass was purified by column chromatography using pet. ether and ethyl acetate as an eluent, isolated yield of **8b** is 2 g, 80 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 2.19 (s, 6H), 3.74 (s, 8H), 5.99 (s, 2H), 7.11 (d, *J* = 6.0 Hz, 4H), 7.38 (d, *J* = 6.1 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 137.58, 134.31, 128.86, 127.33, 109.34, 68.67, 31.90, 21.33.

2.3. Preparation of compound 9a.

Compound **8a** (1g, 2.9 mmol), NBS (1.1g 6.1 mmol) and the catalytic amount of AIBN and benzene (15 ml) were taken in a 100 ml RB flask. The reaction mixture was refluxed for about 6 h at 70 °C. The reaction was monitored by TLC, after completion of the reaction, and the reaction mixture was poured into 10% sodium bicarbonate solution and extracted with ethyl acetate, washed with brine solution and dried over sodium sulphate. The product was concentrated and purified by column chromatography using pet. ether and ethyl acetate as an eluent. The isolated yield of **9a** is 0.9 g, 70 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 3.70 (s, 8H), 4.56 (s, 4H), 5.97 (s, 2H), 7.30-7.33 (m, 6H), 7.46 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 139.85, 136.42, 132.02, 129.51, 128.83, 128.20, 125.72, 108.21, 65.24, 31.98, 31.40.

2.4. Preparation of compound 9b.

Compound **8b** (1g, 2.9 mmol), NBS (1.1g 6.1 mmol) and the catalytic amount of AIBN and benzene (15 ml) were taken in a 100 ml RB flask. The reaction mixture was refluxed for about 6 h at 70 °C. The reaction was monitored by TLC, after completion of reaction, and the reaction mixture was poured into 10% sodium bicarbonate solution and extracted with ethyl acetate, washed with brine and dried over sodium sulphate. The product was concentrated and purified by column chromatography using pet. ether and ethyl acetate as an eluent. The isolated yield of **9b** is 1.05 g, 72 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 3.74 (s, 8H), 4.56 (s, 4H), 5.98 (s, 2H), 7.32 (d, *J* = 6.2 Hz, 4H), 7.46 (d, *J* = 6.0 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 137.13, 128.89, 127.71, 109.32, 68.53, 33.33, 31.87.

2.5. Synthesis of proline based *o*-substituted chiral organocatalyst (11a).

A mixture of compound **9a** (1.0 g, 2 mmol), L-proline **10a** (0.48 g, 4.17 mmol) was dissolved in 1: 1 ratio of DMF: ACN solvent mixture and then added K_2CO_3 (0.82 g, 5.93 mmol) heated to reflux for overnight. The reaction was monitored by TLC, after completion of reaction, and the reaction mixture was poured into cold water and extracted with ethyl acetate, washed with brine and dried over sodium sulphate. The product was concentrated and purified by column chromatography using pet. ether and ethyl acetate as an eluent. The isolated yield of **11a** is 0.97 g, 85 % yield. $[\alpha]\ ^{25}_{D}$ = +163.4 (c= 0.12, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 12.39 (br, 2H), 7.40-7.46 (m, 6H), 7.30 (d, *J* = 7.8 Hz, 2H), 5.98 (s, 2H), 3.73 (s, 8H), 3.62 (s, 4H), 3.22 (t, *J* = 7.7 Hz, 2H), 2.30-2.40 (m, 4H), 1.75-1.95 (m, 4H), 1.54-1.64 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 174.75, 139.65, 132.90, 128.92, 127.57, 127.36, 127.11, 108.99, 73.71, 65.26, 57.54, 31.91, 29.14, 22.04. HRMS (ESI/$[M+Na]^+$) Calculated for: $C_{31}H_{38}N_2O_8Na$: 589.2525. Found: 589.2521.

2.6. Synthesis of proline based *o*-substituted chiral organocatalyst (11b).

A mixture of compound **9a** (1.0 g, 2 mmol), L-proline ethyl ester **10b** (0.75 g, 4.17 mmol) was dissolved in 1: 1 ratio of DMF: ACN solvent mixture and then added K_2CO_3 (0.82 g, 5.93 mmol) heated to reflux for overnight. The reaction was monitored by TLC, after completion of reaction, and the reaction mixture was poured into cold water and extracted with ethyl acetate, washed with brine and dried over sodium sulphate. The product was concentrated and purified by column chromatography using pet. ether and ethyl acetate as an eluent. The isolated yield of **11b** is 1.04 g, 83 % yield. [α] $^{25}_{D}$ = +127.1 (c= 0.14, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.41-7.46 (m, 6H), 7.30 (d, *J* = 7.3 Hz, 2H), 5.98 (s, 2H), 4.11 (q, *J* = 8.4 Hz, 4H), 3.73 (s, 8H), 3.62 (s, 4H), 3.17 (t, *J* = 7.4 Hz, 2H), 2.30-2.39 (m, 4H), 1.81-2.06 (m, 4H), 1.54-1.64 (m, 4H), 1.21(t, *J* = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 173.53, 139.68, 132.96, 128.92, 127.84, 127.52, 127.21, 108.91, 71.52, 65.20, 61.31, 57.73, 31.91, 26.65, 22.02, 14.12. HRMS (ESI/[M+Na]$^+$) Calculated for: $C_{35}H_{46}N_2O_8Na$: 645.3151. Found: 645.3156.

2.7. Synthesis of proline based *p*-substituted chiral organocatalyst (12a).

A mixture of compound **9b** (1.0 g, 2 mmol), L-proline **10a** (0.48 g, 4.17 mmol) was dissolved in 1: 1 ratio of DMF: ACN solvent mixture and then added K_2CO_3 (0.82 g, 5.93 mmol) heated to reflux for overnight. The reaction was monitored by TLC, after completion of reaction, and the reaction mixture was poured into cold water and extracted with ethyl acetate, washed with brine and dried over sodium sulphate. The product was concentrated and purified by column chromatography using pet. ether and ethyl acetate as an eluent. The isolated yield of **12a** is 0.98 g, 86 % yield. [α] $^{25}_{D}$ = +204.2 (c= 0.15, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 12.39 (br, 2H), 7.46 (d, *J* = 9.6 Hz, 4H), 7.27 (d, *J* = 9.4 Hz, 4H), 5.98 (s, 2H), 3.73 (s, 8H), 3.63 (s, 4H), 3.21 (t, *J* = 5.2 Hz, 2H), 2.30-2.40 (m, 4H), 1.70-1.95 (m, 4H), 1.54-1.64 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 22.02, 29.14, 31.92, 57.54, 62.21, 65.24, 73.71, 109.37, 127.14, 130.00, 135.81, 137.76, 174.75. HRMS (ESI/[M+Na]$^+$) Calculated for: $C_{31}H_{38}N_2O_8Na$: 589.2525. Found: 589.2529.

2.8. Synthesis of proline based *p*-substituted chiral organocatalyst (12b).

A mixture of compound **9b** (1.0 g, 2 mmol), L-proline ethyl ester **10b** (0.75 g, 4.17 mmol) was dissolved in 1:1 ratio of DMF: ACN solvent mixture and then added K_2CO_3 (0.82 g, 5.93 mmol) heated to reflux for overnight. The reaction was monitored by TLC, after completion of reaction, and the reaction mixture was poured into cold water and extracted with ethyl acetate, washed with brine and dried over sodium sulphate. The product was concentrated and purified by column chromatography using pet. ether and ethyl acetate as an eluent. The isolated yield of 12b is 1.08 g, 87 % yield. [α] $^{25}_{D}$ = +138.1 (c= 0.17, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.45 (d, *J* = 7.6 Hz, 4H), 7.27 (d, *J* = 7.4 Hz, 4H), 5.98 (s, 2H), 4.11 (q, *J* = 7.3 Hz, 4H), 3.73 (s, 8H), 3.62 (s, 4H), 3.18 (t, *J* = 6.7 Hz, 2H), 2.29-2.40 (m, 4H), 1.81-2.05 (m, 4H), 1.54-1.64 (m, 4H), 1.20 (t, *J* = 6.4 Hz, 6H); ^{13}C NMR

(100 MHz, DMSO-d_6) δ_C 14.12, 22.04, 26.67, 31.91, 57.55, 61.33, 62.21, 71.52, 109.34, 127.11, 130.07, 135.65, 137.69, 173.54. HRMS (ESI/[M+Na]$^+$) Calculated for: $C_{35}H_{46}N_2O_8Na$: 645.3151. Found: 645.3159.

3. General reaction procedure for asymmetric Darzens reaction in the preparation of di-substituted epoxides.

To a solution of α-chloro ketones **1** (0.2 mmol), Et_3N (0.8mmol) an organocatalyst **12a** (5 mol %) in THF (2 mL) was added, after stirring at 0°C for 30 min, then various aldehydes **2a-j** (0.24mmol), were added and the reaction mixture was stirred vigorously at 0 °C for 24 h. The reaction was quenched with 1 N HCl (2mL), and the mixture was extracted with ethyl acetate (3mL X 3), washed with brine, and dried over $MgSO_4$. Removal of the solvent followed by column chromatography using pet.ether and ethyl acetate as an eluent, gave the desired di-substituted epoxide products (**3a**-**3j**).

3.1. Characterization of di-substituted epoxides.

3.1.1. phenyl((2*S*,3*R*)-3-(*p*-tolyl)oxiran-2-yl)methanone (3a).

White solid, Yield 82 % ; ee 91 % ; $[\alpha]^{25}_D$ = +212.4 (c= 0.17, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.82 (d, *J* = 7.8 Hz, 2H), 7.42 (t, *J* = 6.3 Hz, 1H), 7.34 (t, *J* = 6.7 Hz, 2H), 7.06 (d, *J* = 7.7 Hz, 2H), 6.96 (d, *J*= 7.7 Hz, 2H), 4.42 (d, *J* = 8.2 Hz, 1H), 4.32 (d, *J* = 8.1 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 197.59, 137.35, 136.87, 136.65, 133.01, 129.05, 128.12, 128.02, 65.14, 58.21, 21.07. HRMS (ESI/[M+Na]$^+$) Calculated for: $C_{16}H_{14}O_2Na$: 261.0892. Found: 239.0898. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 16.01 min (major) and 30.21 min (minor). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3*R*) by comparison of the known literature reported value. [1-7]

3.1.2. ((2*S*,3*R*)-3-(4-methoxyphenyl)oxiran-2yl)(phenyl)methanone (3b).

Light yellow solid, Yield 84 % ; ee 94 % ; $[\alpha]^{25}_D$ = +207.1 (c= 0.14, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.11 (d, *J* = 4.0 Hz, 2H), 7.71 (m, 3H), 7.61 (d, *J* = 7.0 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 4.42 (d, *J* = 8.2 Hz, 1H), 4.32 (d, *J* = 8.1 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 197.64, 161.54, 144.58, 132.36, 130.15, 128.39, 128.23, 119.57, 114.27, 65.10, 58.30, 55.25. HRMS (ESI/[M+Na]$^+$) Calculated for: $C_{16}H_{14}O_3Na$: 277.0841. Found: 277.0856. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 20.74 min (major) and 36.46 min (minor). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3*R*) by comparison of the known literature reported value.[1-7]

3.1.3. ((2*S*,3*R*)-3-(4-chlorophenyl)oxiran-2yl)(phenyl)methanone (3c).

Yellow solid, Yield 96 % ; ee 99 % ; [α] $^{25}_{D}$ = +234.0 (c= 0.21, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.03 (d, *J* = 7.8 Hz, 2H), 7.60 (m, 3H), 7.54 (m, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 4.42 (d, *J* = 8.2 Hz, 1H), 4.33 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 197.62, 138.21, 137.92, 133.29, 132.87, 129.53, 129.19, 128.55, 128.44, 65.17, 58.21. HRMS (ESI/[M+Na]$^+$) Calculated for: $C_{15}H_{11}ClO_2Na$: 281.0346. Found: 281.0357. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 24.93 min (major) and 40.38 min (minor). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3*R*) by comparison of the known literature reported value. [1-7]

3.1.4. ((2*S*,3*R*)-3-(4-nitrophenyl)oxiran-2yl)(phenyl)methanone (3d).

Yellow solid, Yield 97 % ; ee 98 % ; [α] $^{25}_{D}$ = +274.2 (c= 0.23, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.29 (d, *J* = 8.5 Hz, 2H), 7.80 (dd, *J* = 15.0, 10.5 Hz, 3H), 7.61 (dd, *J* = 14.0, 5.0 Hz, 2H), 7.53 (m, 2H), 4.42 (d, *J* = 8.6 Hz, 1H), 4.33 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 197.69, 148.58, 141.07, 137.56, 133.36, 128.91, 128.82, 128.60, 124.24, 65.16, 58.21. HRMS (ESI/[M+Na]$^+$) Calculated for: $C_{15}H_{11}NO_4Na$: 292.0586. Found: 292.0597. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 26.02 min (major) and 45.07 min (minor). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3*R*) by comparison of the known literature reported value. [1-7]

3.1.5. (2*S*,3*R*)-1-(3-phenyloxiran-2-yl)ethanone (3e).

Light yellow liquid, Yield 80 % ; ee 90 % ; [α] $^{25}_{D}$ = +14.1 (c= 0.19, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.77 (m, 3H), 7.63 (m, 2H), 3.94 (d, *J* = 3.9 Hz, 1H), 3.17 (q, *J* = 7.4 Hz, 1H), 1.17 (d, *J* = 9.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$); δ_C 192.76, 135.12, 128.89, 127.41, 126.74, 126.65, 125.55, 60.08, 58.92, 18.08. HRMS (ESI/[M+Na]$^+$) Calculated for: $C_{10}H_{10}O_2Na$: 185.0579. Found: 185.0572. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 18.02 min (major) and 30.78 min (minor). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,* 3*R*) by comparison of the known literature reported value. [1-7]

3.1.6. (2*S*,3*R*)- (3-ethyloxiran-2-yl)(phenyl)methanone (3f).

Yellow liquid, Yield 82 % ; ee 93 % ; [α] $^{25}_{D}$ = +11.4 (c= 0.17, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.97 (d, *J* = 7.0 Hz, 2H), 7.47 (m, 3H), 4.04 (d, *J* = 3.2 Hz, 1H), 3.01 (m, 1H), 1.31 (m, 2H), 1.06 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 192.08, 134.84, 133.04, 128.86, 127.33, 126.75, 125.56, 60.52, 59.32, 22.95, 12.11. HRMS (ESI/[M+Na]$^+$) Calculated for: $C_{11}H_{12}O_2Na$: 199.0735. Found: 199.0730. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 19.46 min (major) and 37.57 min (minor). The absolute

stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3*R*) by comparison of the known literature reported value. [1-7]

3.1.7. (4-bromophenyl)((2*S*,3*R*)-3-(*p*-tolyl)oxiran-2-yl)methanone (3g).

White solid, Yield 85 % ; ee 92 % ; $[\alpha]^{25}_{D}$ = +141.2 (c= 0.19, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.87 (d, *J* = 8.7 Hz, 2H), 7.62 (m, 4H), 6.94 (d, *J* = 9.0 Hz, 2H), 4.42 (d, *J* = 8.2 Hz, 1H), 4.32 (d, *J* = 8.1 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 197.78, 161.81, 137.22, 131.87, 130.37, 129.95, 127.43, 118.99, 114.36, 65.50, 58.21, 21.04. HRMS (ESI/$[M+Na]^+$) Calculated for: $C_{16}H_{13}BrO_2Na$: 338.9997. Found: 338.9991.The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 20.94 min (major) and 43.03 min (minor). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3*R*) by comparison of the known literature reported value. [1-7]

3.1.8. (4-bromophenyl)((2*S*,3*R*)-3-(4-methoxyphenyl)oxiran-2-yl)methanone (3h).

Light yellow solid, Yield 87 % ; ee 95 % ; $[\alpha]^{25}_{D}$ = +147.1 (c= 0.21, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.87 (d, *J* = 6.8 Hz, 2H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 6.5 Hz, 2H), 7.23 (d, *J* = 6.6 Hz, 2H), 4.42 (d, *J* = 8.6 Hz, 1H), 4.33 (d, *J* = 8.7 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 197.79, 145.34, 137.13, 131.94, 129.99, 129.72, 128.55, 127.66, 65.15, 58.25, 21.25. HRMS (ESI/$[M+Na]^+$) Calculated for: $C_{16}H_{13}BrO_3Na$: 354.9946 Found: 354.9954. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 22.47 min (major) and 46.02 min (minor). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3*R*) by comparison of the known literature reported value. [1-7]

3.1.9. (4-bromophenyl)((2*S*,3*R*)-3-(4-chlorophenyl)oxiran-2-yl)methanone (3i).

White solid, Yield 96 % ; ee 98 % ; $[\alpha]^{25}_{D}$ = +139.4 (c= 0.12, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.87 (d, *J* = 6.8 Hz, 2H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 6.0 Hz, 2H), 7.39 (d, *J* = 9.0 Hz, 2H), 4.42 (d, *J* = 8.2 Hz, 1H), 4.33 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 197.64, 136.59, 133.07, 131.88, 129.92, 129.56, 129.22, 128.07, 65.15, 58.20. HRMS (ESI/$[M+Na]^+$) Calculated for: $C_{15}H_{10}BrClO_2Na$: 358.9451. Found: 358.9460. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 31.17 min (major) and 48.54 min (minor). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3*R*) by comparison of the known literature reported value. [1-7]

3.1.10. (4-bromophenyl)((2*S*,3*R*)-3-(4-nitrophenyl)oxiran-2-yl)methanone (3j).

Yellow solid, Yield 97 % ; ee 99 % ; $[\alpha]^{25}_{D}$ = +134.1 (c= 0.17, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.29 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 11.4 Hz, 2H), 4.42 (d, *J* = 8.2 Hz, 1H), 4.33 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 197.69, 148.55, 141.07, 137.56, 133.38, 128.91, 128.82, 128.62, 124.23, 65.15, 58.25. HRMS (ESI/$[M+Na]^+$) Calculated for:

$C_{15}H_{10}BrNO_4Na$: 369.9691. Found: 369.9698. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 26.42 min (major) and 42.38 min (minor). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3*R*) by comparison of the known literature reported value. [1-7]

3.1.11. 4-((2*S*,3*R*)-3-(4-chlorobenzoyl)oxiran-2-yl)benzonitrile (3k).

Yellow liquid, Yield 95 % ; ee 98 % ; [α] $^{25}_D$ = +174.1 (c= 0.18, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.06 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 6.8 Hz, 2H), 7.60 (d, *J* = 6.4 Hz, 2H), 7.46 (d, *J* = 6.0 Hz, 2H), 4.42 (d, *J* = 8.1 Hz, 1H), 4.33 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 197.07, 139.85, 138.71, 132.31, 132.16, 130.23, 128.76, 124.47, 118.65, 112.14, 66.10, 59.40. HRMS (ESI/$[M+Na]^+$) Calculated for: $C_{16}H_{10}ClNO_2Na$: 306.0297. Found: 306.0293. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 17.98 min (major) and 34.20 min (minor). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3*R*) by comparison of the known literature reported value.[1-7]

3.1.12. (4-chlorophenyl)((2*S*,3*R*)-3-(4-hydroxyphenyl)oxiran-2-yl)methanone (3l).

Yellow oil, Yield 87 % ; ee 93 % ; [α] $^{25}_D$ = +181.4 (c= 0.24, $CHCl_3$); ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 9.06 (br, 1H), 8.06 (d, *J* = 6.0 Hz, 2H), 7.62 (d, *J* = 6.2 Hz, 2H), 7.11 (d, *J* = 5.3 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 4.42 (d, *J* = 7.8 Hz, 1H), 4.33 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C 197.00, 158.02, 138.76, 132.43, 130.23, 128.72, 128.11, 125.50, 115.86, 66.10, 59.40. HRMS (ESI/$[M+Na]^+$) Calculated for: $C_{15}H_{11}ClO_3Na$: 297.0294. Found: 297.0298. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 15.09 min (major) and 28.26 min (minor). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3*R*) by comparison of the known literature reported value.[1-7]

3.1.13. ((2*S*,3*R*)-3-(4-aminophenyl)oxiran-2-yl)(4-chlorophenyl)methanone (3m).

Yellow liquid, Yield 84 % ; ee 92 % ; [α] $^{25}_D$ = +169.1 (c= 0.21, $CHCl_3$); ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 8.06 (d, *J* = 6.0 Hz, 2H), 7.61 (d, *J* = 6.2 Hz, 2H), 7.13 (d, *J* = 6.5 Hz, 2H), 6.48 (d, *J* = 7.0 Hz, 2H), 4.71 (s, 2H), 4.42 (d, *J* = 7.9 Hz, 1H), 4.32 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C 197.04, 147.92, 138.72, 132.39, 130.26, 128.76, 125.52, 124.24, 120.72, 66.10, 59.46. HRMS (ESI/$[M+Na]^+$) Calculated for: $C_{15}H_{12}ClNO_2Na$: 296.0454. Found: 296.0459. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 21.61 min (major) and 39.06 min (minor). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3*R*) by comparison of the known literature reported value.[1-7]

3.1.14. methyl 4-((2*S*,3*R*)-3-(4-chlorobenzoyl)oxiran-2-yl)benzoate (3n).

White solid, Yield 92 % ; ee 97 % ; [α] $^{25}_D$ = +187.1 (c= 0.19, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.06 (d, *J* = 8.5 Hz, 2H), 7.96 (d, *J* = 6.4 Hz, 2H), 7.60 (d, *J* = 6.1 Hz, 2H), 7.21 (d, *J* = 6.0 Hz, 2H), 4.42 (d,

J = 7.5 Hz, 1H), 4.32 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 197.05, 165.98, 139.80, 138.74, 132.31, 130.21, 128.73, 125.12, 66.11, 59.45, 51.55. HRMS (ESI/[M+Na]$^+$) Calculated for: $C_{17}H_{13}ClO_4Na$: 339.0399. Found: 339.0391. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 25.98 min (major) and 37.20 min (minor). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3*R*) by comparison of the known literature reported value.[1-7]

3.1.15. (4-fluorophenyl)((2*S*,3*R*)-3-(furan-2-yl)oxiran-2-yl)methanone (3o).

Light yellow solid, Yield 85 % ; ee 96 % ; [α] $^{25}_D$ = +191.4 (c= 0.32, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 8.15 (d, *J* = 7.3 Hz, 2H), 7.58 (d, *J* = 5.7 Hz, 1H), 7.37 (d, *J* = 6.7 Hz, 2H), 6.40-6.42 (m, 2H), 4.56 (d, *J* = 8.0 Hz, 1H), 4.42 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 197.05, 167.39, 153.53, 141.55, 130.48, 129.85, 115.45, 110.27, 69.61, 55.30. HRMS (ESI/[M+Na]$^+$) Calculated for: $C_{13}H_9FO_3Na$: 255.0433. Found: 255.0437. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 22.10 min (major) and 34.64 min (minor). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3*R*) by comparison of the known literature reported value.[1-7]

3.1.16. (4-fluorophenyl)((2*S*,3*R*)-3-(naphthalen-2-yl)oxiran-2-yl)methanone (3p).

Yellow solid, Yield 87 % ; ee 94 % ; [α] $^{25}_D$ = +187.1 (c= 0.27, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.97-7.99 (m, 2H), 7.86-7.90 (m, 4H), 7.40-7.54 (m, 5H), 4.42 (d, *J* = 7.6 Hz, 1H), 4.42 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 197.08, 167.42, 133.48, 131.82, 130.48, 129.83, 18.05, 127.57, 126.72, 126.01, 125.31, 125.12, 123.07, 115.40, 66.12, 59.41. HRMS (ESI/[M+Na]$^+$) Calculated for: $C_{19}H_{13}FO_2Na$: 315.0797. Found: 315.0791. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 27.60 min (major) and 50.74 min (minor). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3*R*) by comparison of the known literature reported value.[1-7]

4. General reaction procedure for asymmetric Darzens reaction in the preparation of tri-substituted epoxides

To a solution of α-substituted α-chloro ketones **4** (0.2 mmol), Et_3N (0.8mmol) and organocatalyst **12a** (5 mol %) in THF (2 mL) was added, after stirring at 0°C for 1 h, then various aldehydes **2** (0.24mmol), were added and the reaction mixture was stirred vigorously at 0 °C for 36 h. The reaction was quenched with 1 N HCl (2mL), and the mixture was extracted with ethyl acetate (3mL X 3), washed with brine, and dried over $MgSO_4$. Removal of the solvent followed by column chromatography using pet.ether and ethyl acetate as an eluent, gave the desired tri-substituted epoxide products (**5a**-**5j**).

4.1. Characterization of tri-substituted epoxides.

4.1.1. (2*S*,3'*R*)-3'-phenyl-3,4-dihydro-1*H*-spiro[naphthalene-2,2'-oxiran]-1-one (5a).

White solid, Yield 96 %; ee 97 %; [α] $^{25}_{D}$ = +114.1 (c= 0.31, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 1.83-1.88 (m, 1 H), 2.20-2.31 (m, 1H), 2.39-2.48 (m, 2H), 4.37 (s, 1H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.34-7.41 (m, 6H), 7.50-7.54 (m, 1H), 8.11-8.13 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 192.06, 142.96, 136.50, 134.13, 132.91, 132.16, 129.03, 128.44, 128.17, 127.20, 127.08, 125.89, 125.28, 65.02, 64.21, 27.32, 25.54. HRMS (ESI/[M+Na]$^+$) Calculated for: $C_{17}H_{14}O_2Na$: 273.0892. Found: 273.0897. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 10.25 min (minor) and 15.19 min (major). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3'*R*) by comparison of the known literature reported value. [1-7]

4.1.2. (2*S*,3'*R*)-3'-(4-chlorophenyl)-3,4-dihydro-1*H*-spiro[naphthalene-2,2'-oxiran]-1-one (5b).

White solid, Yield 94 %; ee 98 %; [α] $^{25}_{D}$ = +167.4 (c= 0.37, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 1.78-1.84 (m, 1 H), 2.40-2.48 (m, 1H), 2.81-2.89 (m, 2H), 4.34 (s, 1H) 7.24 (d, *J* = 6.1 Hz, 1H), 7.31-7.39 (m, 5H), 7.50-7.53 (m, 1H), 8.11-8.13 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 193.45, 143.43, 134.63, 132.98, 132.82, 129.08, 128.88, 128.25, 127.95, 127.36, 64.66, 63.82, 27.51, 25.32. HRMS (ESI/[M+Na]$^+$) Calculated for: $C_{17}H_{13}ClNaO_2$: 307.0502. Found: 307.0527. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 14.13 min (minor) and 18.81 min (major). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3'*R*) by comparison of the known literature reported value. [1-7]

4.1.3. (2*S*,3'*R*)-3'-(3-chlorophenyl)-3,4-dihydro-1*H*-spiro[naphthalene-2,2'-oxiran]-1-one (5c).

White solid, Yield 92 %; ee 95 %; [α] $^{25}_{D}$ = +117.2 (c= 0.41, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 1.81-1.87 (m, 1 H), 2.43-2.48 (m, 1H), 2.83-2.91 (m, 2H), 4.33 (s, 1H), 7.23-7.40 (m, 6H), 7.52-7.54 (m, 1H), 8.11-8.13 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 193.37, 143.57, 136.64, 134.80, 134.62, 132.83, 129.94, 129.06, 128.88, 127.96, 127.34, 126.94, 125.12, 64.56, 63.43, 27.56, 25.69. HRMS (ESI/[M+Na]$^+$) Calculated for: $C_{17}H_{13}ClNaO_2$: 307.0502. Found: 307.0543. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 12.07 min (minor) and 17.18 min (major). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3'*R*) by comparison of the known literature reported value. [1-7]

4.1.4. (2*S*,3'*R*)-3'-(2-chlorophenyl)-3,4-dihydro-1*H*-spiro[naphthalene-2,2'-oxiran]-1-one (5d).

White solid, Yield 87 %; ee 90 %; [α] $^{25}_{D}$ = +79.4 (c= 0.32, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 1.62-1.67 (m, 1 H), 2.37-2.44 (m, 1H), 2.82-2.87 (m, 1H), 2.98-3.03 (m, 1H), 4.44 (s, 1H), 7.25 (d, *J* = 6.9 Hz, 1H), 7.31-7.43 (m, 5H), 7.52-7.55 (m, 1H), 8.12-8.16 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 193.34, 143.68, 134.55, 133.49, 132.90, 129.48, 129.07, 128.75, 128.08, 127.27, 126.98, 64.33, 63.06, 27.90, 26.25. HRMS (ESI/[M+Na]$^+$) Calculated for: $C_{17}H_{13}ClNaO_2$: 307.0502. Found: 307.0519. The enantiomeric

excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 9.03 min (minor) and 14.26 min (major). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3'*R*) by comparison of the known literature reported value. [1-7]

4.1.5. (2*S*,3'*R*)-3'-(*o*-tolyl)-3,4-dihydro-1*H*-spiro[naphthalene-2,2'-oxiran]-1-one (5e).

White solid, Yield 82 %; ee 85 %; [α] $^{25}_{D}$ = +74.1 (c= 0.27, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 1.84-1.89 (m, 1 H), 2.38 (s, 3H) 2.39-2.48 (m, 1H), 2.81-2.84 (m, 2H), 4.32 (s, 1H), 7.19-7.28 (m, 5H), 7.35-7.39 (m, 1H), 7.50-7.54 (m, 1H), 8.11-8.13 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 183.16, 143.65, 138.44, 134.46, 131.31, 129.24, 128.94, 127.97, 127.24, 126.82, 64.61, 64.45, 27.93, 25.68, 21.41. HRMS (ESI/$[M+Na]^+$) Calculated for: $C_{18}H_{16}NaO_2$: 287.1048. Found: 287.1051. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 11.56 min (major) and 16.24 min (minor). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3'*R*) by comparison of the known literature reported value. [1-7]

4.1.6. (2*S*,3'*R*)-3'-(naphthalen-1-yl)-3,4-dihydro-1*H*-spiro[naphthalene-2,2'-oxiran]-1-one (5f).

White solid, Yield 90 %; ee 94 %; [α] $^{25}_{D}$ = +83.1 (c= 0.33, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 1.67-1.73 (m, 1 H), 2.36-2.42 (m, 1H), 2.68-2.76 (m, 2H), 4.86 (s, 1H), 7.17-7.19 (m, 1H), 7.41-7.61 (m, 6H), 7.78-7.92 (m, 3H), 8.16-8.20 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 193.98, 143.76, 134.62, 133.40, 130.36, 129.26, 129.08, 128.92, 128.87, 127.26, 126.95, 126.39, 125.52, 124.94, 122.72, 64.77, 63.50, 28.15, 26.08. HRMS (ESI/$[M+Na]^+$) Calculated for: $C_{21}H_{16}NaO_2$: 323.1048. Found: 323.1059. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 7.21 min (minor) and 13.35 min (major). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3'*R*) by comparison of the known literature reported value. [1-7]

4.1.7. **(2*S*,3'*R*)-3'-propyl-3,4-dihydro-1*H*-spiro[naphthalene-2,2'-oxiran]-1-one (5g).**

White solid, Yield 80 %; ee 92 %; [α] $^{25}_{D}$ = +21.4 (c= 0.14, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 0.91 (t, *J* = 4.2 Hz, 3H), 1.43-1.52 (m, 2 H), 1.68-1.73 (m, 1H), 2.04-2.31 (m, 1H), 2.51-2.54 (m, 1H), 2.91-2.95 (m, 1H), 3.15-3.18 (m, 1H), 3.34-3.40 (m, 1H), 4.34 (d, *J* = 8.0 Hz, 1H), 7.26-7.37 (m, 2H), 7.51-7.55 (m, 1H), 8.07-8.08 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 192.51, 143.44, 134.59, 130.32, 129.06, 127.81, 127.27, 74.71, 33.96, 30.69, 25.57, 21.28, 20.07, 14.41, 14.16. HRMS (ESI/$[M+Na]^+$) Calculated for: $C_{14}H_{16}O_2Na$: 239.1048. Found: 239.1057. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 10.42 min (minor) and 20.26 min (major). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3'*R*) by comparison of the known literature reported value. [1-7]

4.1.8. (2*S*,3'*R*)-3'-hexyl-3,4-dihydro-1*H*-spiro[naphthalene-2,2'-oxiran]-1-one (5h).

White solid, Yield 84 %; ee 93 %; [α] $^{25}_{D}$ = +27.1 (c= 0.15, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 0.89 (t, *J* = 3.9 Hz, 3H), 1.30-1.64 (m, 8 H), 2.31-2.34 (m, 1H), 2.51-2.64 (m, 1H), 2.91-2.96 (m, 1H), 3.26-3.36 (m, 1H), 4.32 (d, *J* = 6.8 Hz, 1H),7.26-7.36 (m, 2H), 7.52-7.54 (m, 1H), 8.08-8.13 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 192.88, 143.47, 134.54, 129.78, 128.97, 127.42, 127.23, 74.93, 32.07, 31.88, 29.54, 29.16, 26.82, 25.41, 22.90, 14.33. HRMS (ESI/$[M+Na]^+$) Calculated for: $C_{17}H_{22}O_2Na$: 281.1518. Found: 281.1547. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 8.60 min (minor) and 14.77 min (major). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3'*R*) by comparison of the known literature reported value. [1-7]

4.1.9. (2*S*,3'*R*)-6-methoxy-3'-phenyl-3,4-dihydro-1*H*-spiro[naphthalene-2,2'-oxiran]-1-one (5i).

White solid, Yield 85 %; ee 92 %; [α] $^{25}_{D}$ = +67.0 (c= 0.21, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 1.75-1.86 (m, 1 H), 2.20-2.34 (m, 1H), 2.74-2.85 (m, 2H), 3.69 (s, 3H), 4.24 (s, 1H), 6.91-6.97 (m, 2H), 7.24-7.32 (m, 5H), 8.11 (d, *J* = 5.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 192.15, 164.84, 134.12, 129.68, 128.52, 128.15, 126.24, 125.47, 113.27, 111.52, 68.13, 65.69, 55.64, 27.88, 25.36. HRMS (ESI/$[M+Na]^+$) Calculated for: $C_{18}H_{16}O_3Na$: 303.0996. Found: 303.0991. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 17.63 min (minor) and 35.77 min (major). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3'*R*) by comparison of the known literature reported value. [1-7]

4.1.10. (2*S*,3'*R*)-3'-(4-bromophenyl)-6-methoxy-3,4-dihydro-1*H*-spiro[naphthalene-2,2'-oxiran]-1-one (5j).

White solid, Yield 90 %; ee 96 %; [α] $^{25}_{D}$ = +74.1 (c= 0.27, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 1.74-1.84 (m, 1 H), 2.21-2.32 (m, 1H), 2.72-2.83 (m, 2H), 3.70 (s, 3H), 4.25 (s, 1H), 6.91-6.96 (m, 2H), 7.17 (d, *J* = 5.4 Hz, 2H), 7.85 (d, *J* = 6.3 Hz, 2H), 8.13 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 192.34, 164.84, 133.11, 131.53, 129.75, 128.20, 126.22, 120.33, 113.21, 111.41, 68.53, 65.79, 55.86, 27.27, 25.55. HRMS (ESI/$[M+Na]^+$) Calculated for: $C_{18}H_{15}BrO_3Na$: 381.0102. Found: 381.0112. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 21.39 min (minor) and 37.24 min (major). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S,*3'*R*) by comparison of the known literature reported value.[1-7]

4.1.11. (2*S*,3'*R*)-6-methoxy-3'-(pyridin-4-yl)-3,4-dihydro-1*H*-spiro[naphthalene-2,2'-oxiran]-1-one (5k).

White solid, Yield 78 %; ee 83 %; [α] $^{25}_{D}$ = +54.1 (c= 0.21, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 1.75-1.85 (m, 1 H), 1.95-2.10 (m, 1H), 2.75-2.85 (m, 2H), 3.70 (s, 3H), 4.25 (s, 1H), 6.91-6.97 (m, 2H), 7.46 (d,

J = 6.0 Hz, 2H), 8.11 (d, *J* = 7.4 Hz, 1H), 8.61 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 192.05, 164.81, 149.14, 147.01, 129.69, 128.43, 126.29, 122.08, 113.10, 111.40, 67.21, 65.81, 55.88, 27.62, 25.56. HRMS (ESI/[M+Na]$^+$) Calculated for: $C_{17}H_{15}NO_3Na$: 304.0949. Found: 304.0942. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 16.07 min (minor) and 30.34 min (major). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S*,3'*R*) by comparison of the known literature reported value.[1-7]

4.1.12. (2*S*,3'*R*)-3'-(4-acetylphenyl)-6-methoxy-3,4-dihydro-1H-spiro[naphthalene-2,2'-oxiran]-1-one (5l).

White solid, Yield 80 %; ee 87 %; [α] $^{25}_D$ = +61.4 (c= 0.27, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) 1.75-1.84 (m, 1 H), 1.98-2.06 (m, 1H), 2.51 (s, 3H), 2.75-2.85 (m, 2H), 3.70 (s, 3H), 4.25 (s, 1H),6.77 (d, *J* = 5.8 Hz, 2H), 6.91-6.97 (m, 2H), 7.23 (d, *J* = 6.6 Hz, 2H), 8.11 (d, *J* = 6.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 192.05, 164.81, 149.14, 147.01, 129.69, 128.43, 126.29, 122.08, 113.10, 111.40, 67.21, 65.81, 55.88, 27.62, 25.56. HRMS (ESI/[M+Na]$^+$) Calculated for: $C_{20}H_{18}O_4Na$: 345.1102. Found: 345.1109. The enantiomeric excess was determined by HPLC, Chiralcel (OD-H), 254 nm, Hexane: IPA 95: 5, flow rate: 1 mL min^{-1}, retention time: 18.16 min (minor) and 39.26 min (major). The absolute stereochemistry of the α,β-epoxy ketone was assigned as (2*S*,3'*R*) by comparison of the known literature reported value.[1-7]

5. References

1. Y. Liu, B. A. Provencher, K. J. Bartelson, L. Deng, *Chem. Sci*., 2011, **2**, 1301.
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4. S. Arai, Y. Shirai, T. Ishida, T. Shioiri, *Tetrahedron,* 1999, **55**, 6375.
5. X. Wang, L. Shi, M. Li, K. Ding, *Angew. Chem. Int. Ed.,* 2005, **44**, 6362.
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7. R. Chen, C. Qian, J. G. Vries, *Tetrahedron,* 2001, **57**, 9837.

NMR spectra for core and organocatalysts

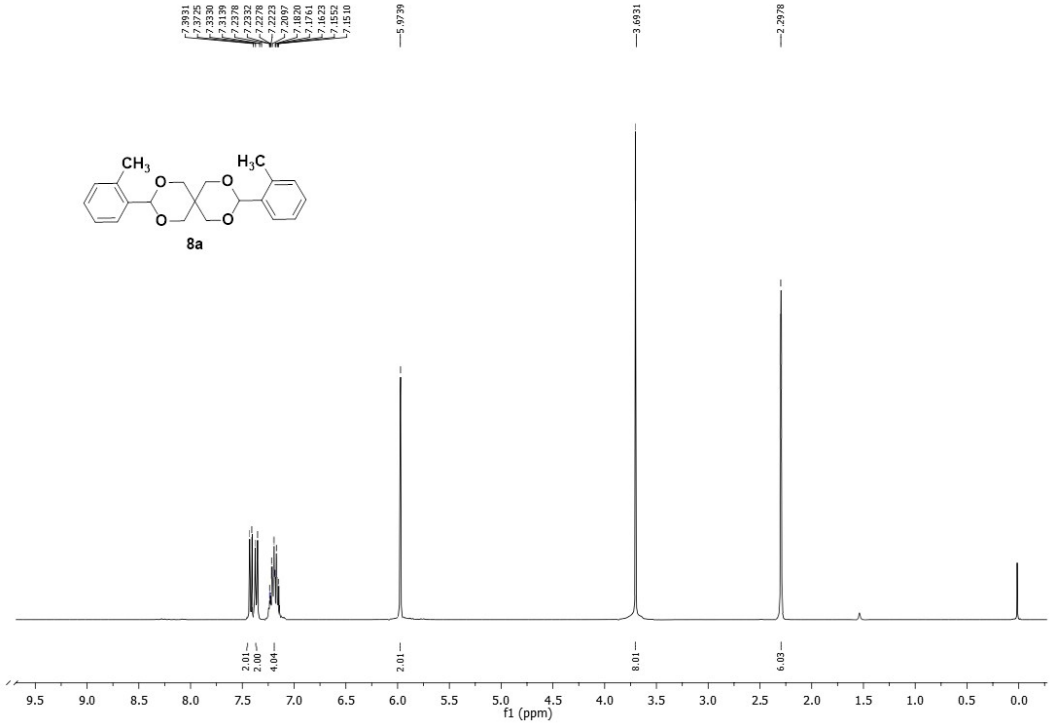


Figure S1: 1H NMR spectrum of compound **8a**.

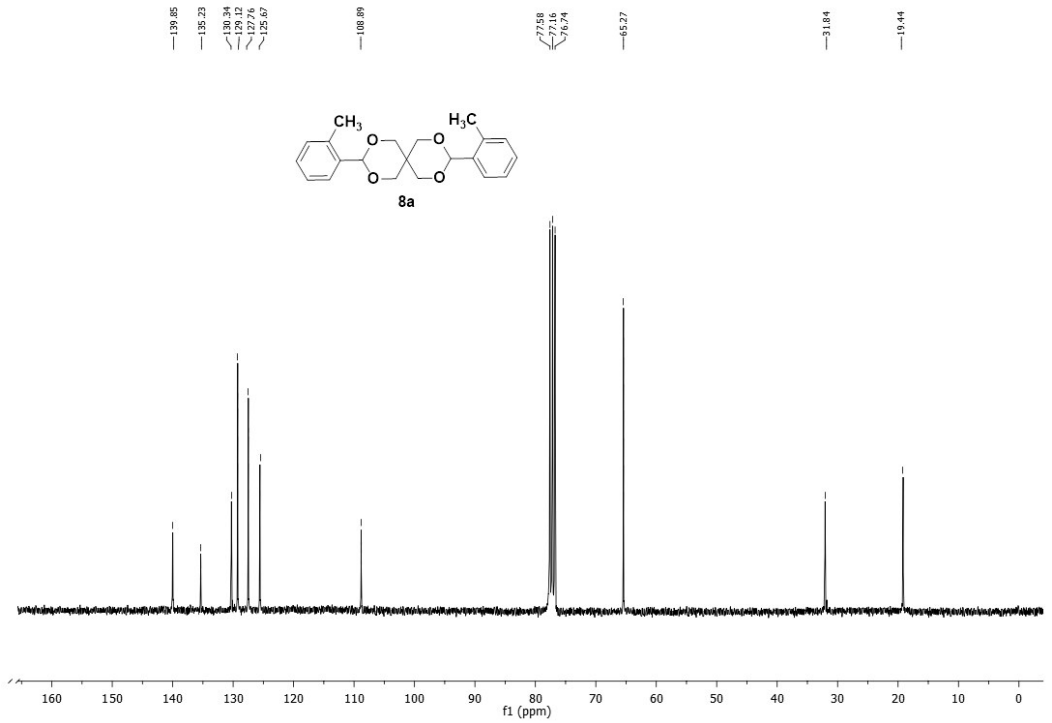


Figure S2: 13C NMR spectrum of compound **8a**.

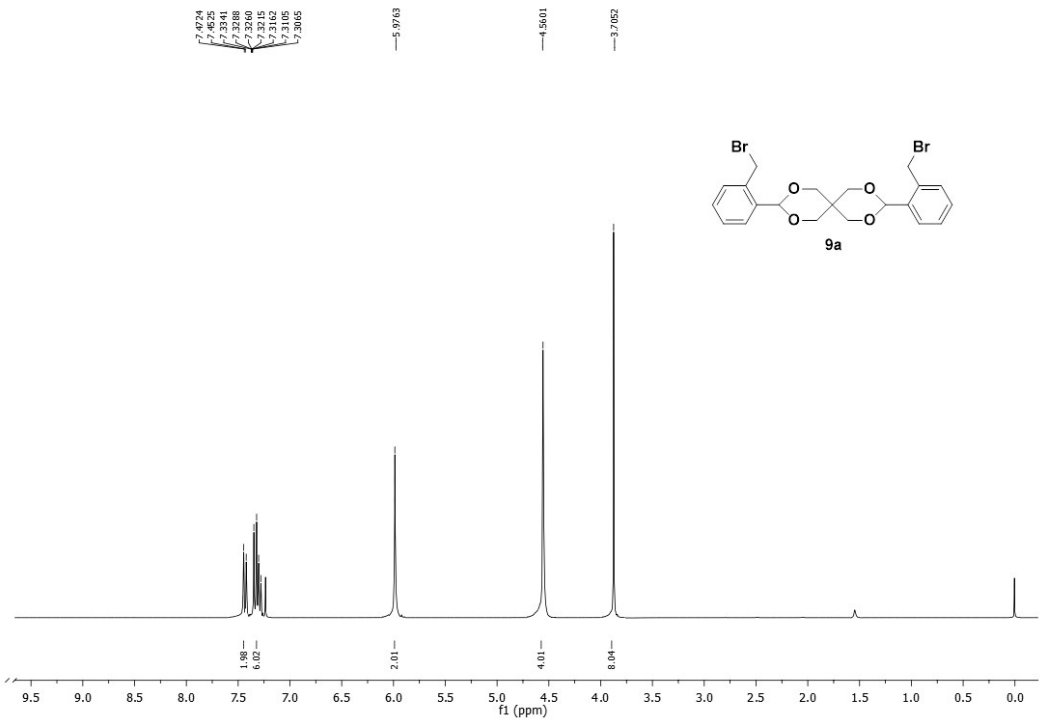


Figure S3: 1H NMR spectrum of compound **9a**.

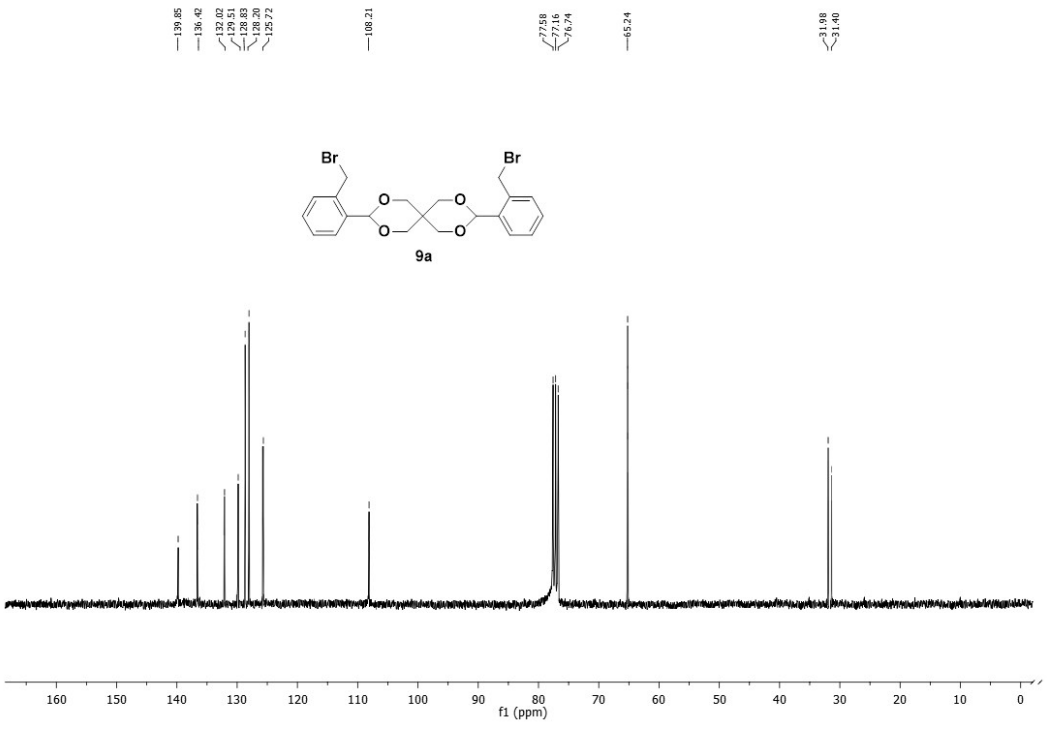


Figure S4: 13C NMR spectrum of compound **9a**.

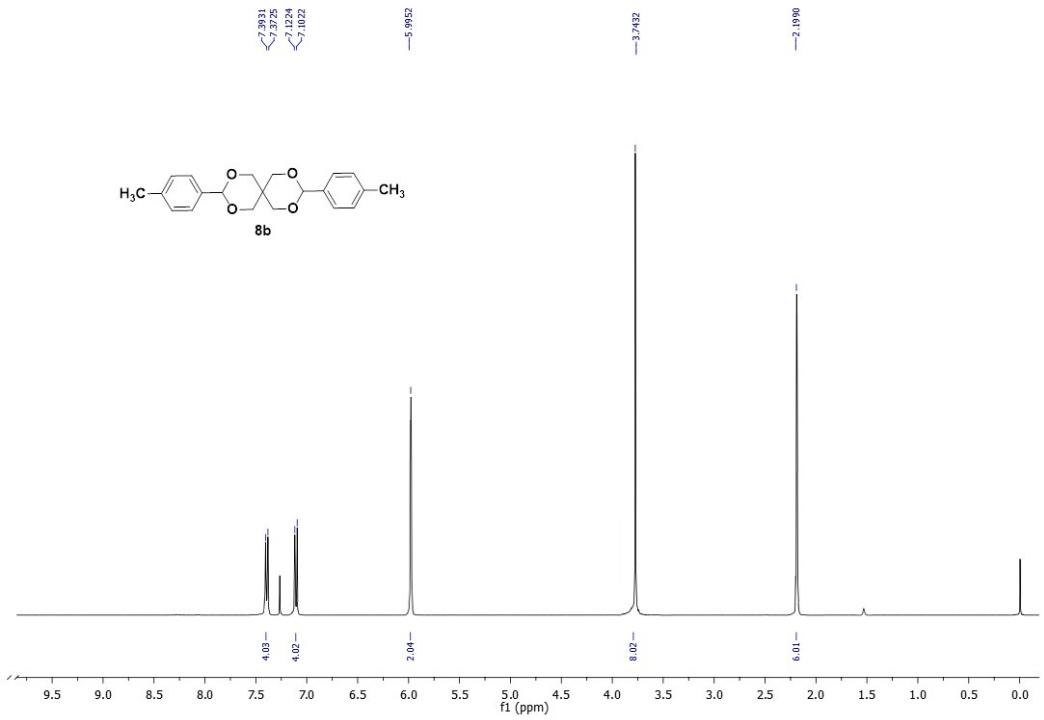


Figure S5: 1H NMR spectrum of compound **8b**.

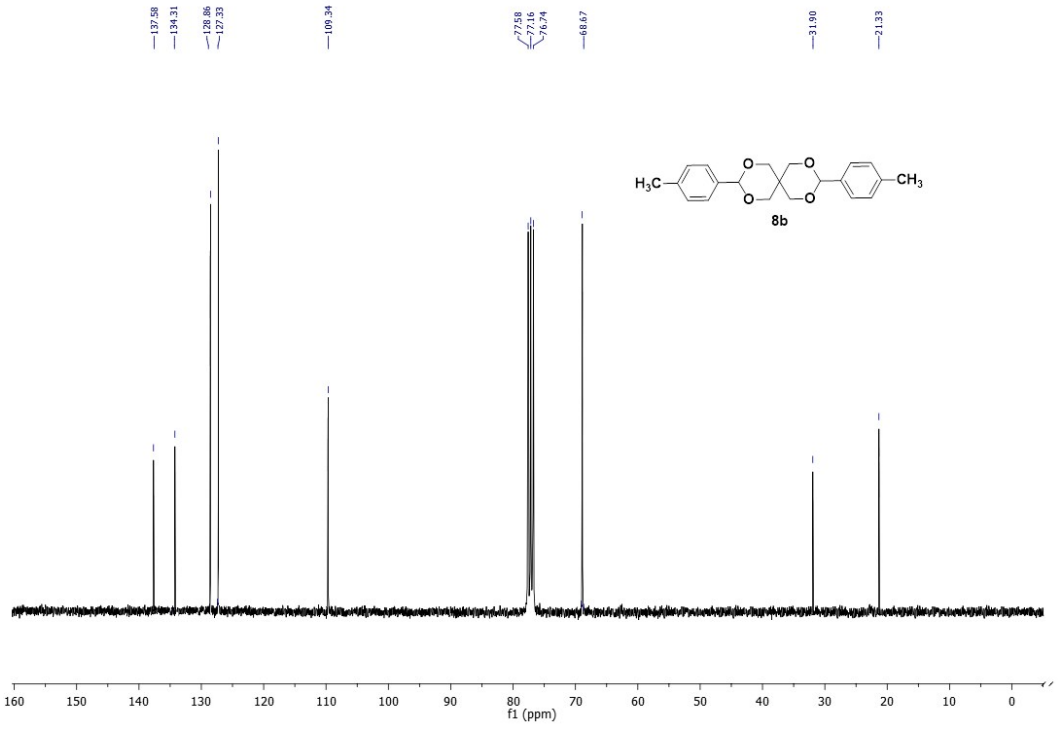


Figure S6: 13C NMR spectrum of compound **8b**.

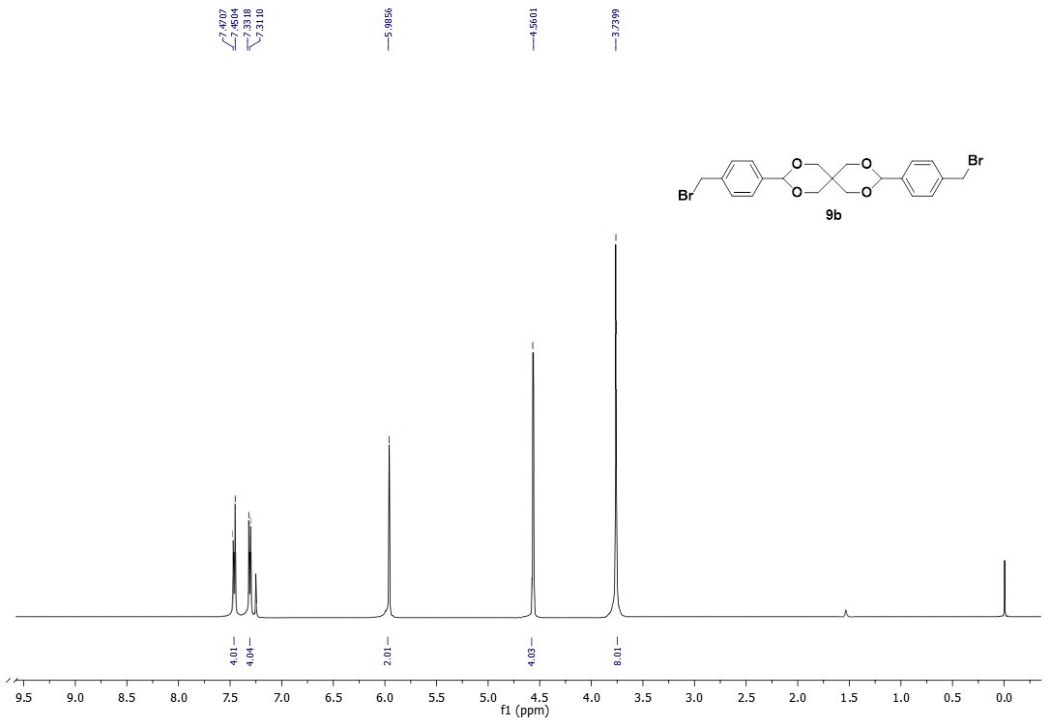


Figure S7: 1H NMR spectrum of compound **9b**.

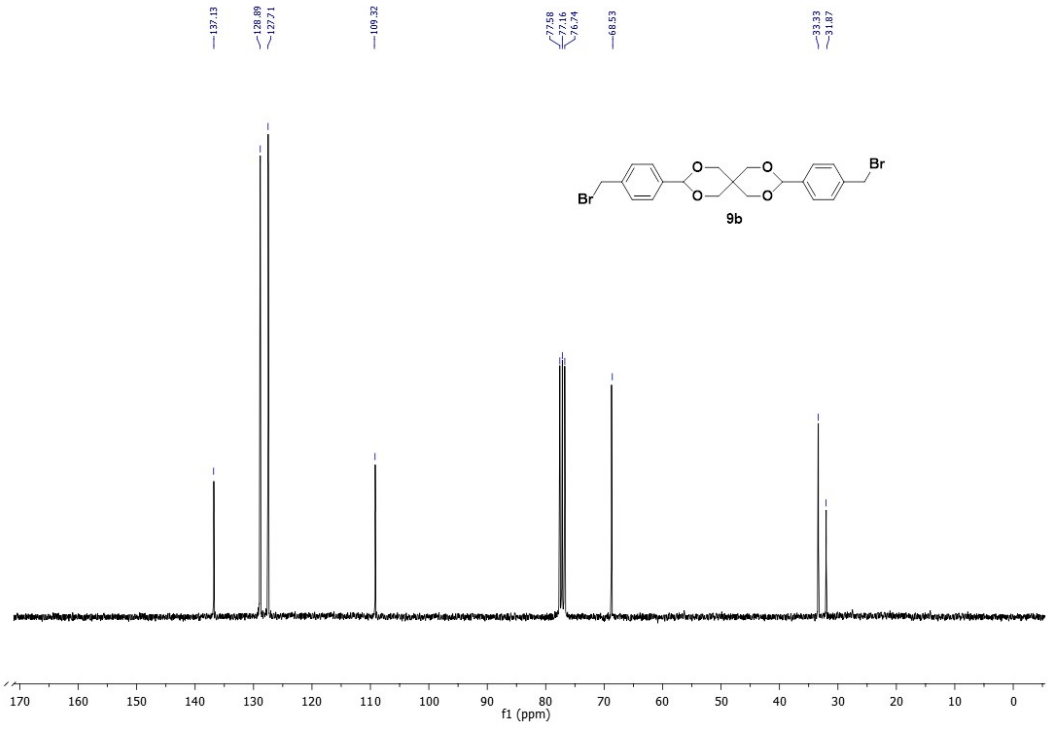


Figure S8: 13C NMR spectrum of compound **9b**.

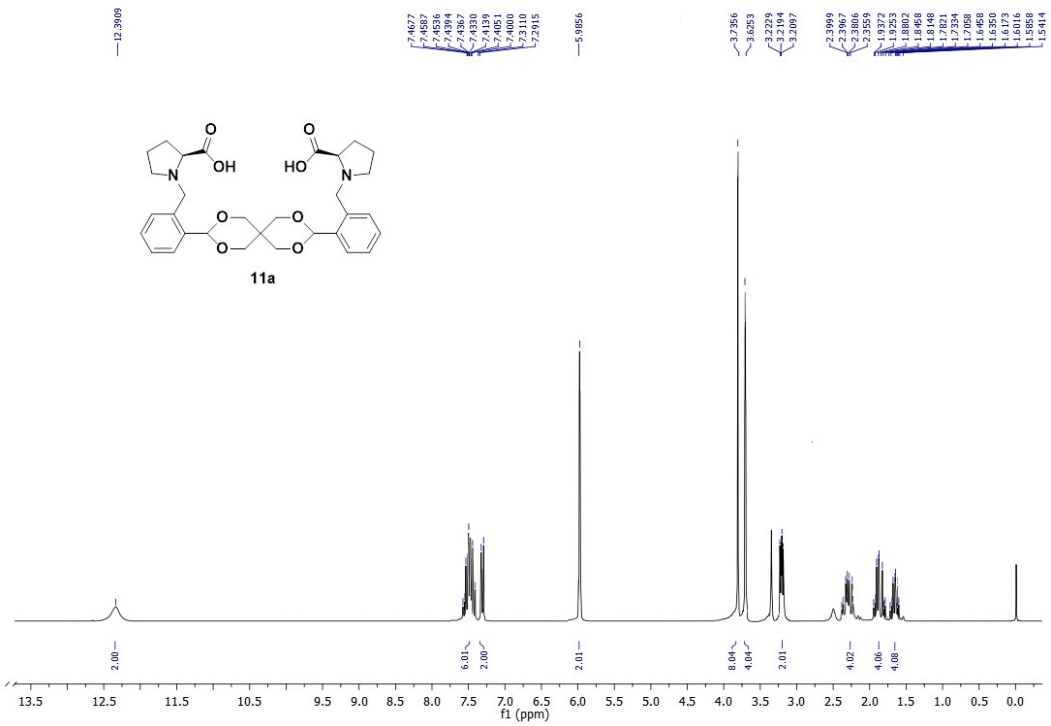


Figure S9: 1H NMR spectrum of organocatalyst **11a**.

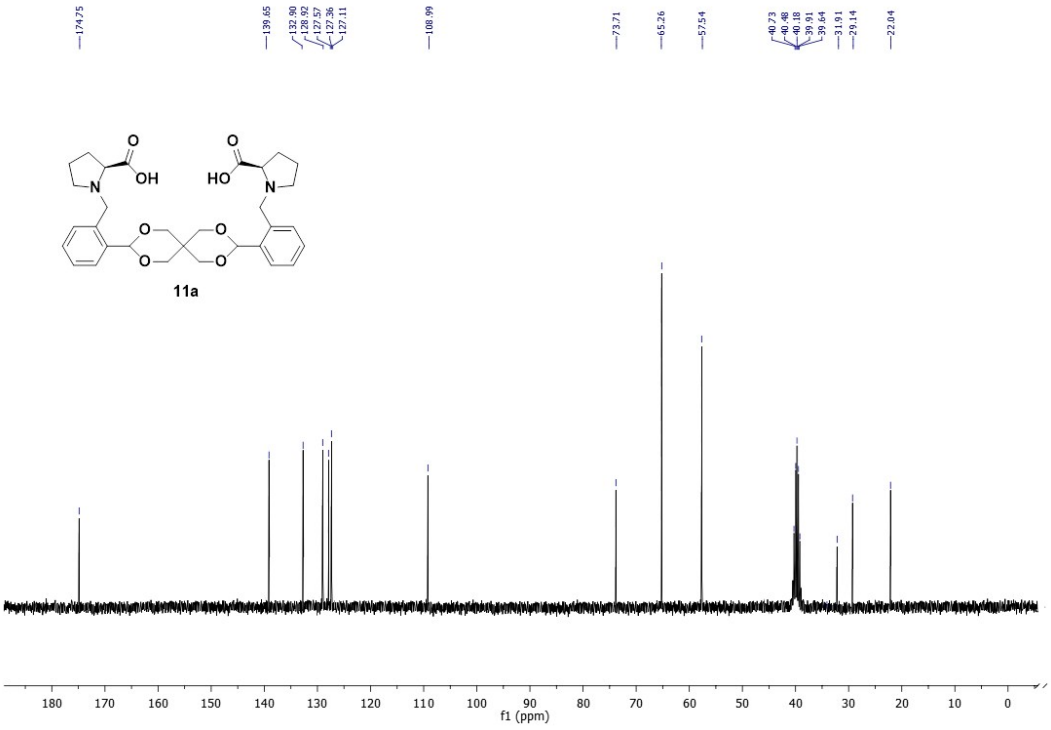


Figure S10: 13C NMR spectrum of organocatalyst **11a**.

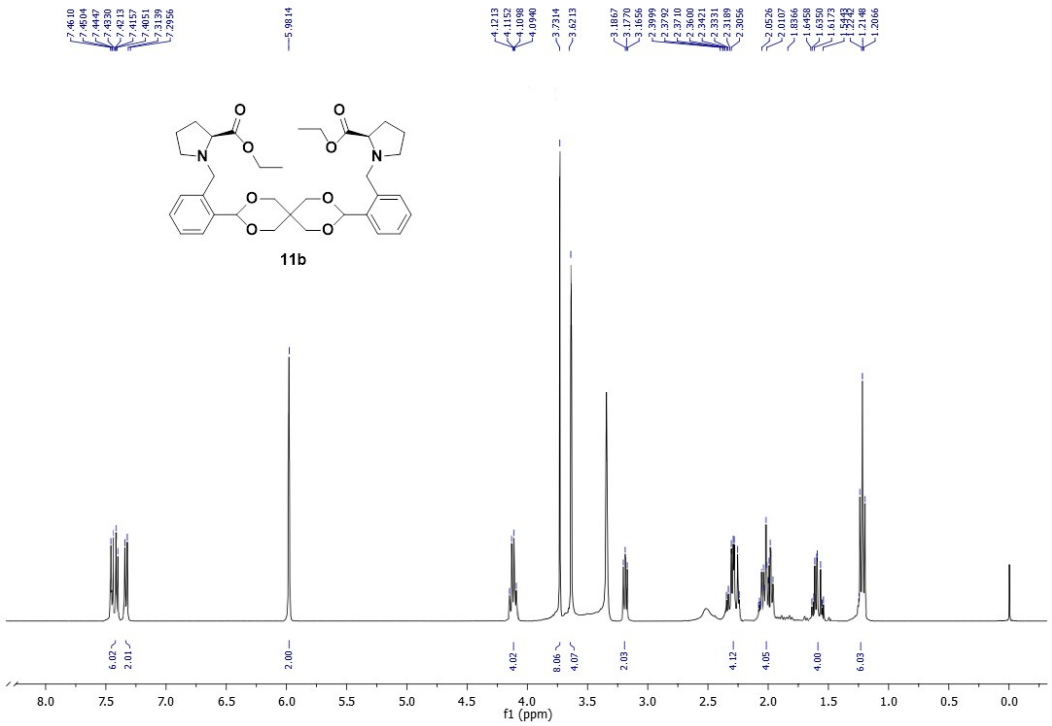


Figure S11: 1H NMR spectrum of organocatalyst **11b**.

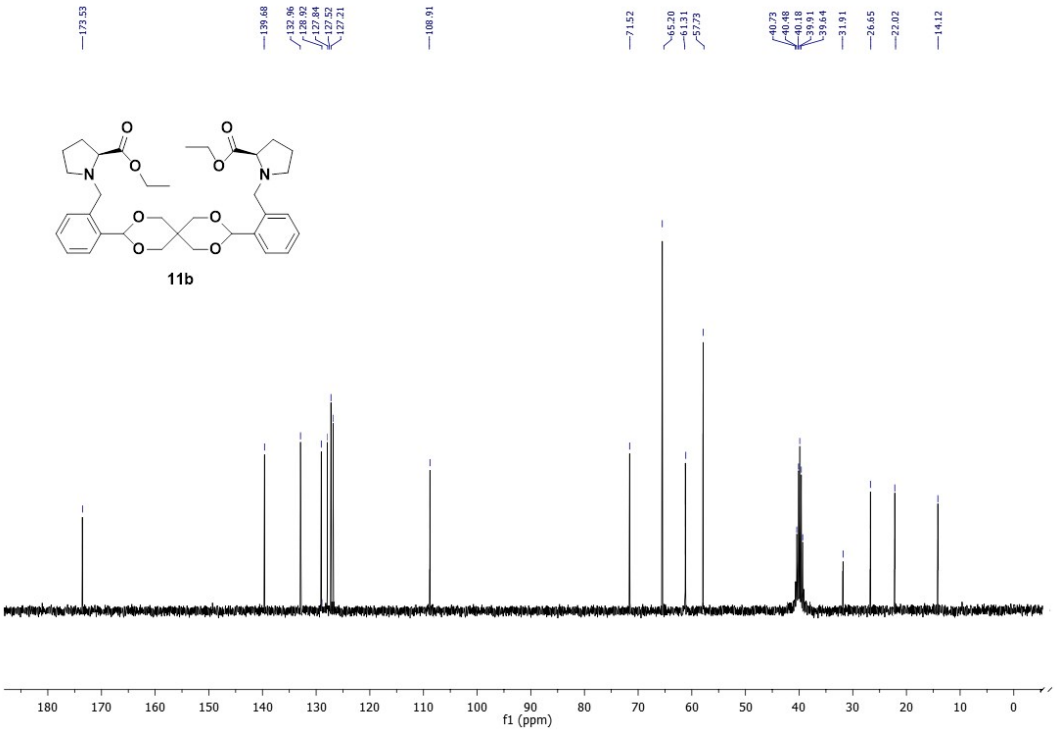


Figure S12: 13C NMR spectrum of organocatalyst **11b**.

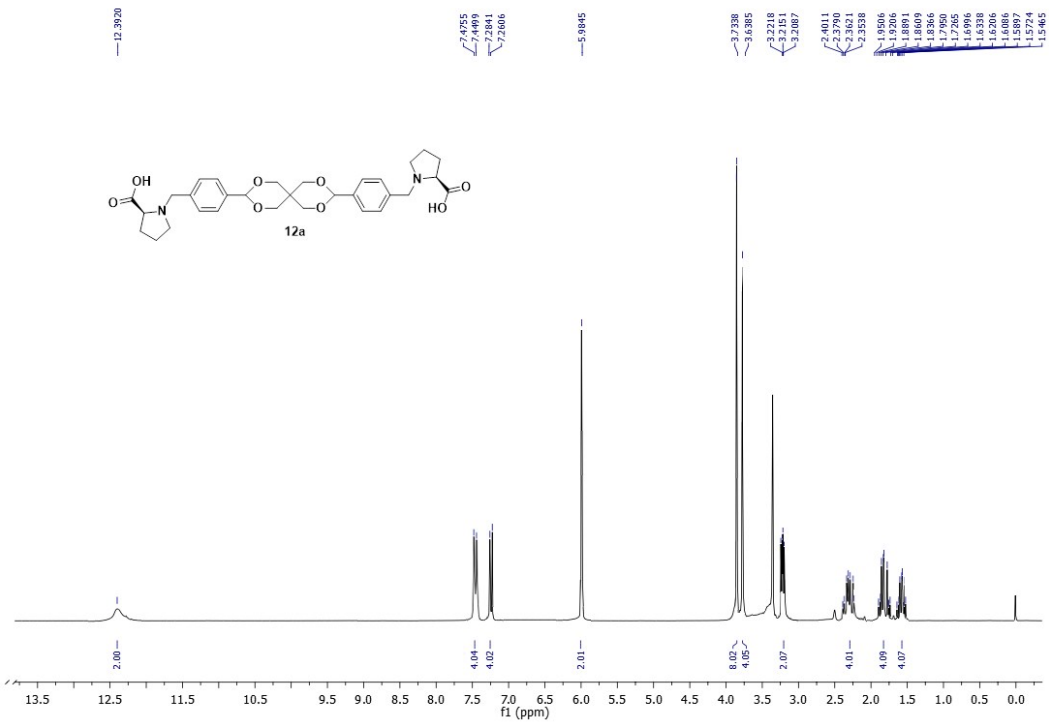


Figure S13: 1H NMR spectrum of organocatalyst **12a**.

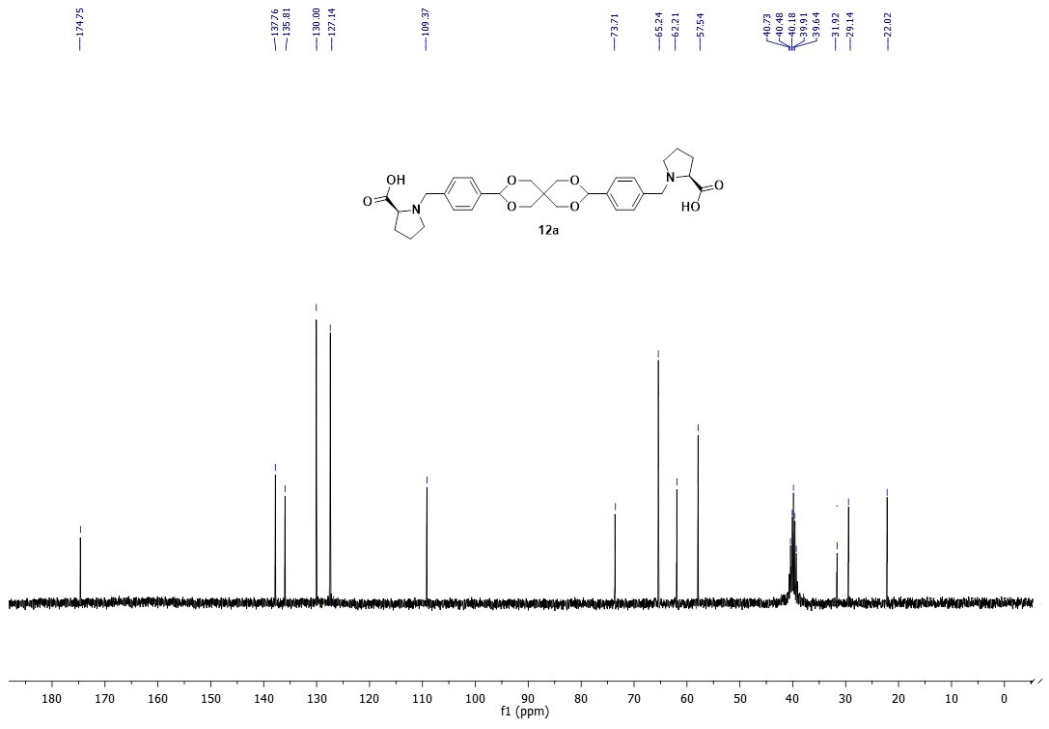


Figure S14: 13C NMR spectrum of organocatalyst **12a**.

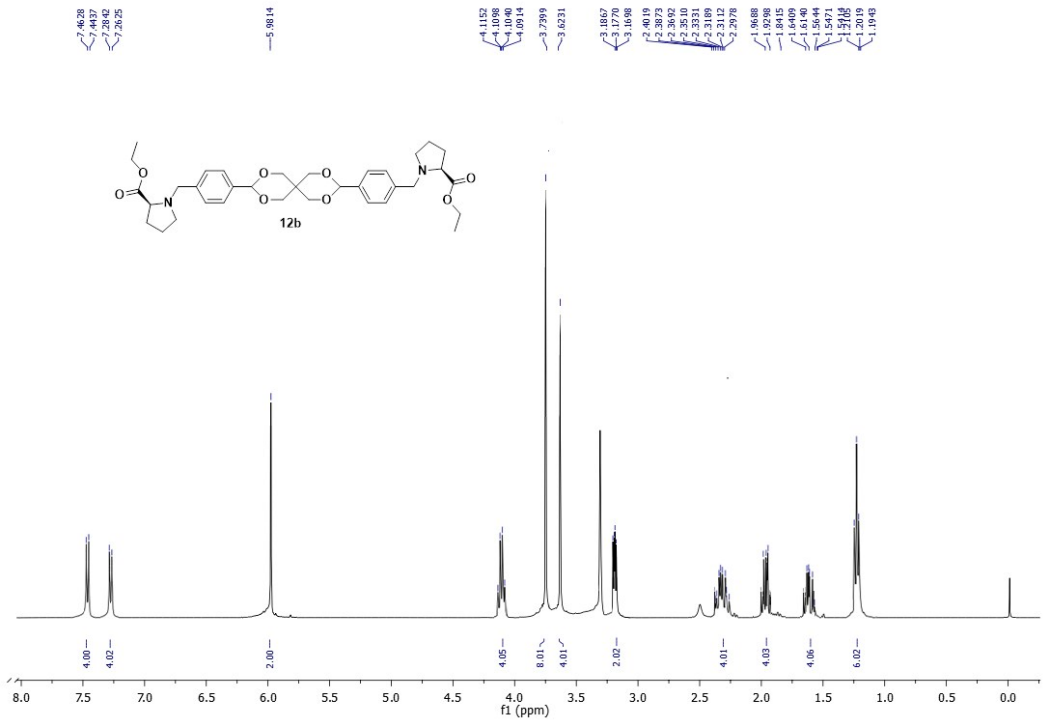


Figure S15: 1H NMR spectrum of organocatalyst **12b**.

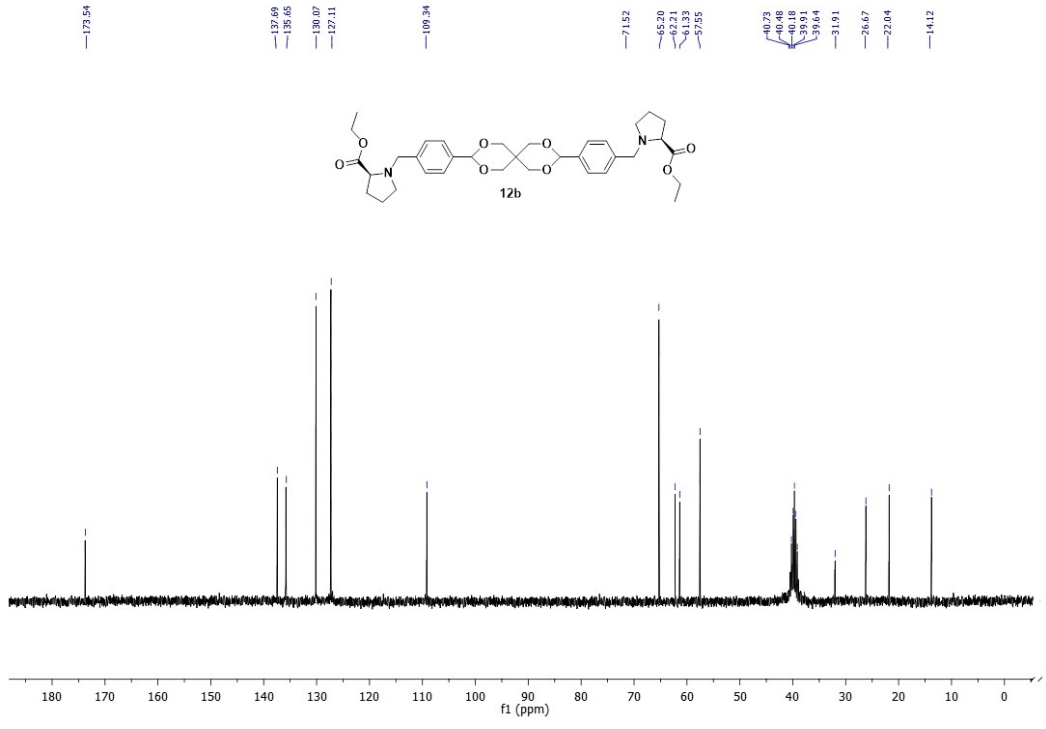


Figure S16: 13C NMR spectrum of organocatalyst **12b**.

NMR spectra and HPLC chromatograms for di and tri substituted epoxides

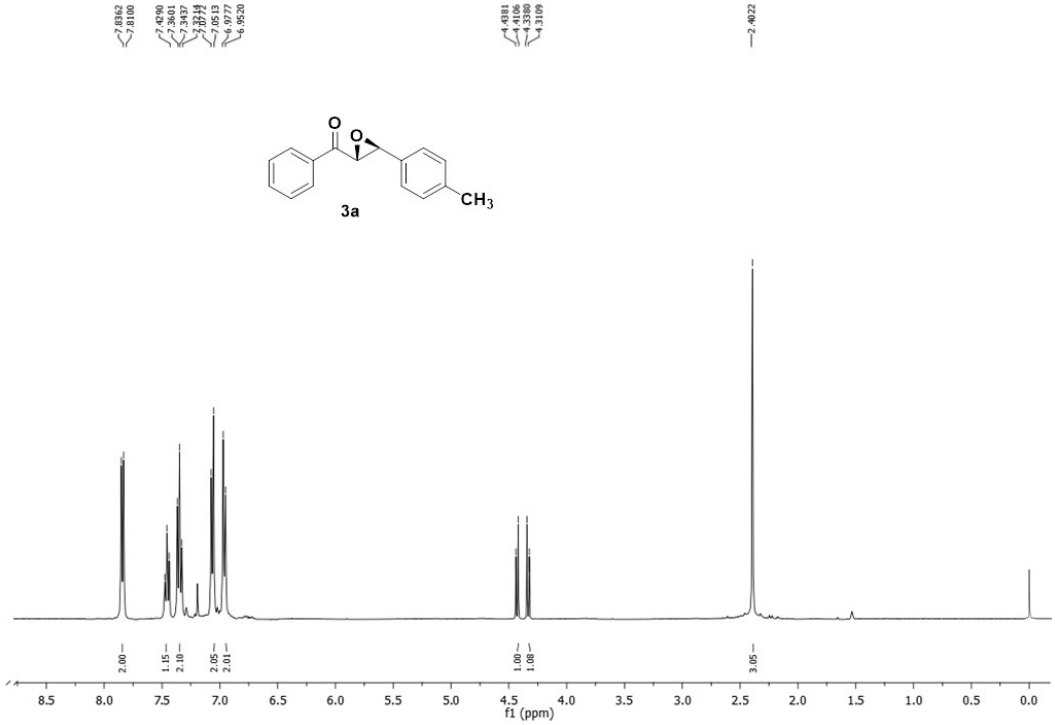


Figure S17: 1H NMR spectrum of epoxide **3a**.

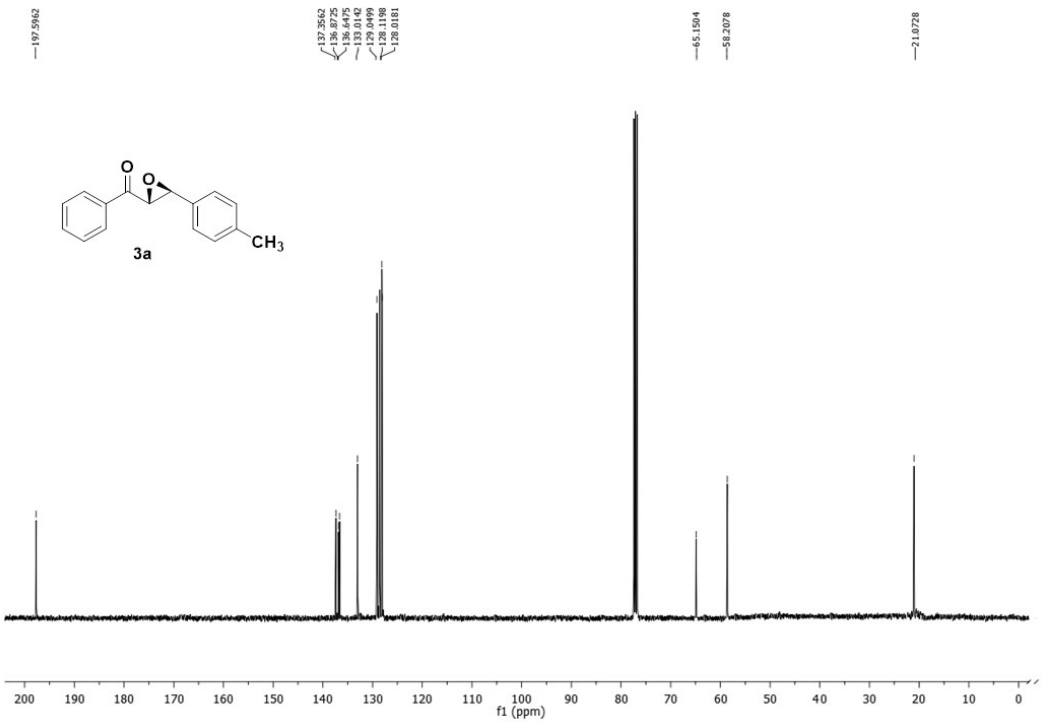
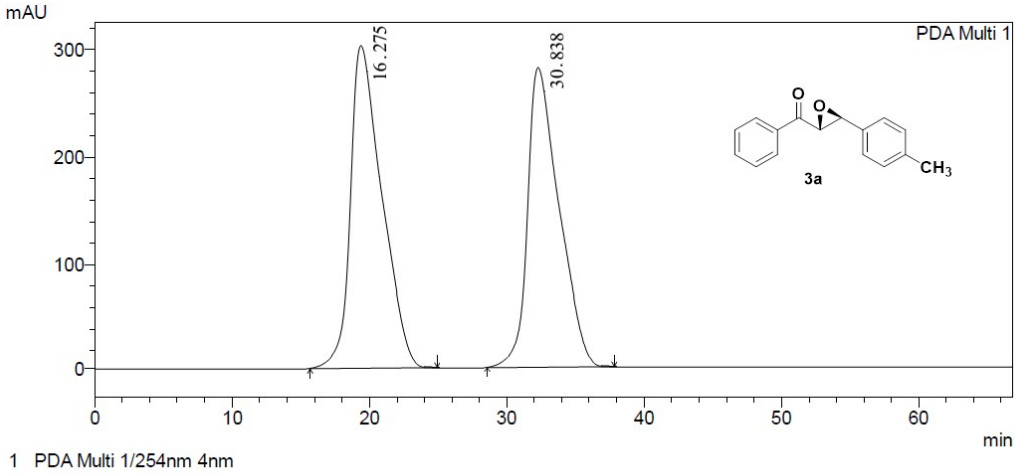


Figure S18: 13C NMR spectrum of epoxide **3a**.

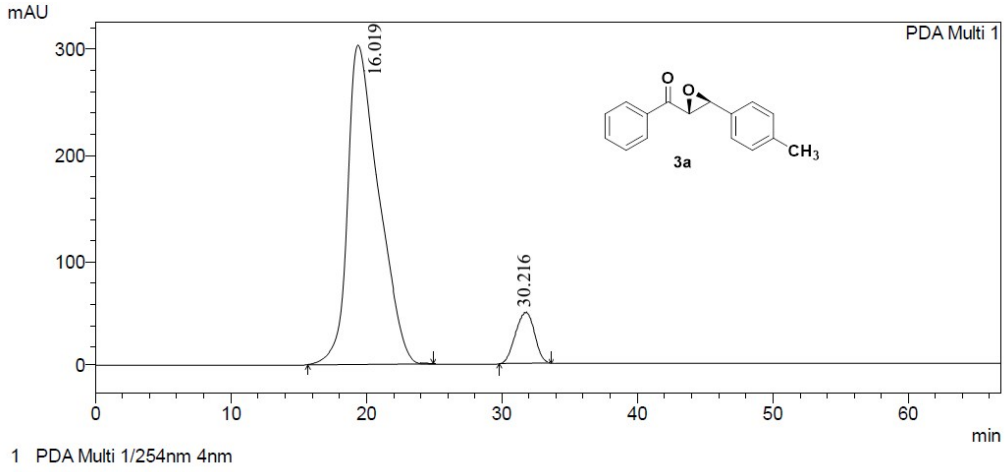


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.275	6412071	85516	50.674	51.910
2	30.838	6338383	83187	49.326	48.090
Total		12750455	168703	100.000	100.000

Figure S19: HPLC chromatogram of epoxide **3a** (Racemic mixture).



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.019	59390085	2019427	95.537	92.263
2	30.216	2774362	169346	4.463	7.737
Total		62164448	2188773	100.000	100.000

Figure S20: HPLC chromatogram of epoxide **3a** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 ^oC condition.

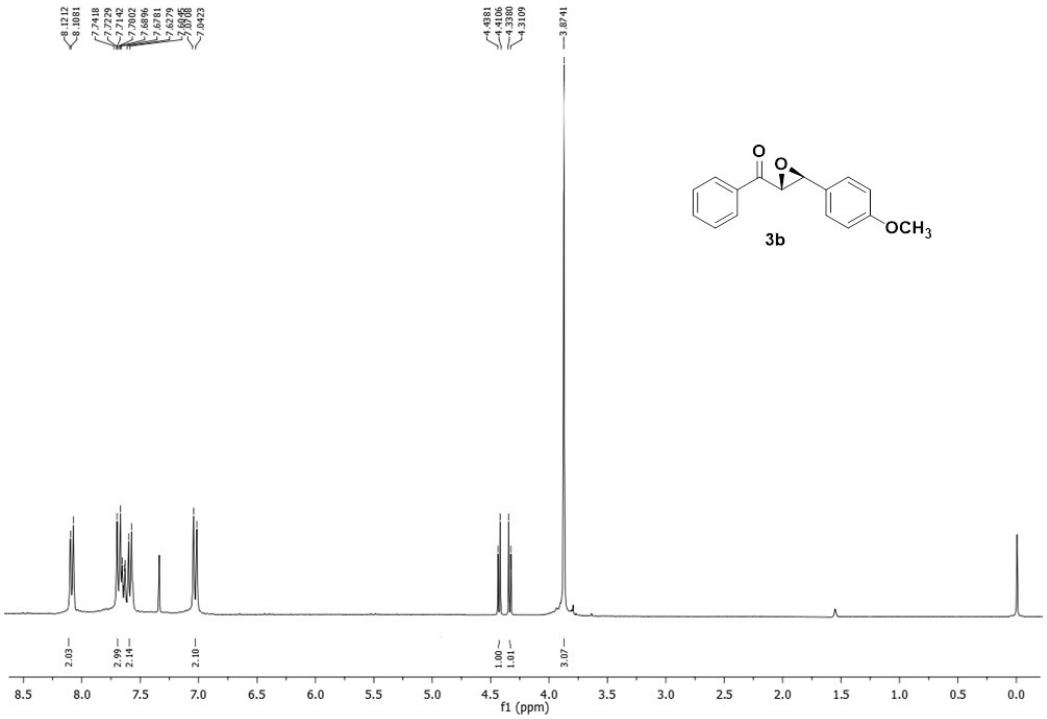


Figure S21: 1H NMR spectrum of epoxide **3b**.

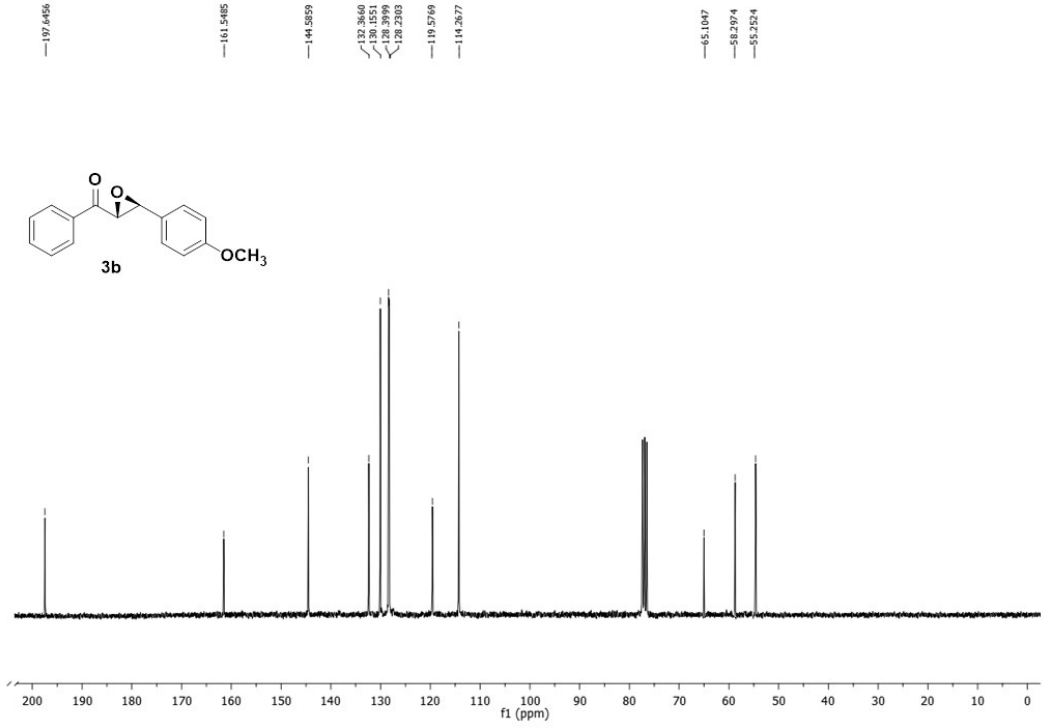
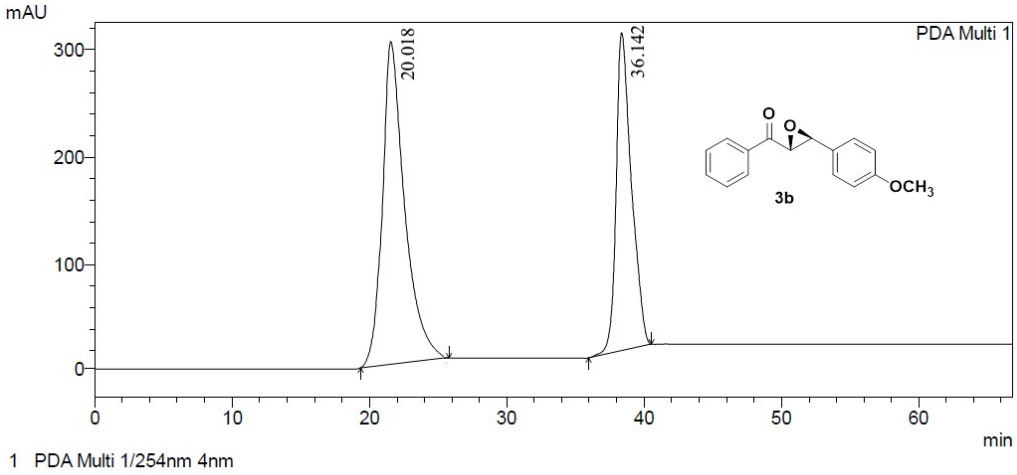


Figure S22: 13C NMR spectrum of epoxide **3b**.

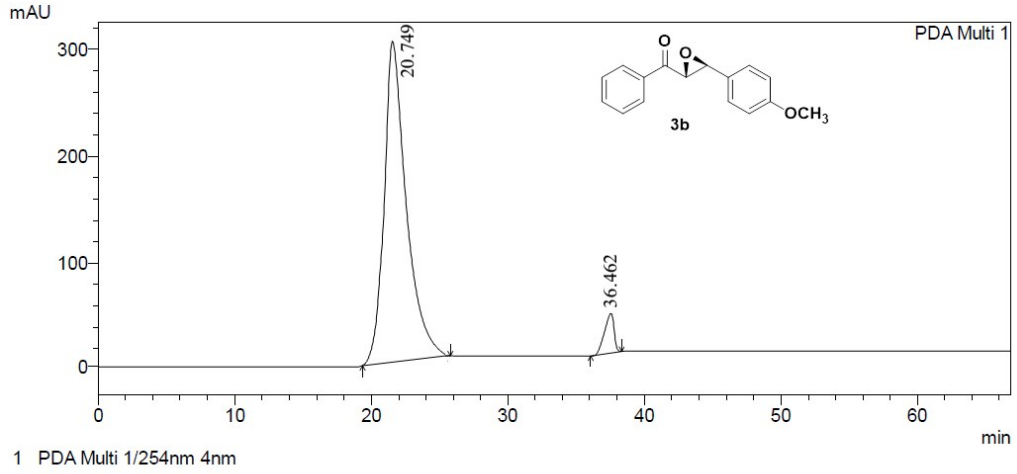


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.018	9236738	103209	50.607	51.001
2	36.142	9187611	102591	49.393	48.999
Total		18424349	205800	100.000	100.000

Figure S23: HPLC chromatogram of epoxide **3b** (Racemic mixture).



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.749	61357098	746211	97.057	93.606
2	36.462	61860393	50970	2.943	6.394
Total		63217491	797180	100.000	100.000

Figure S24: HPLC chromatogram of epoxide **3b** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 ^oC condition.

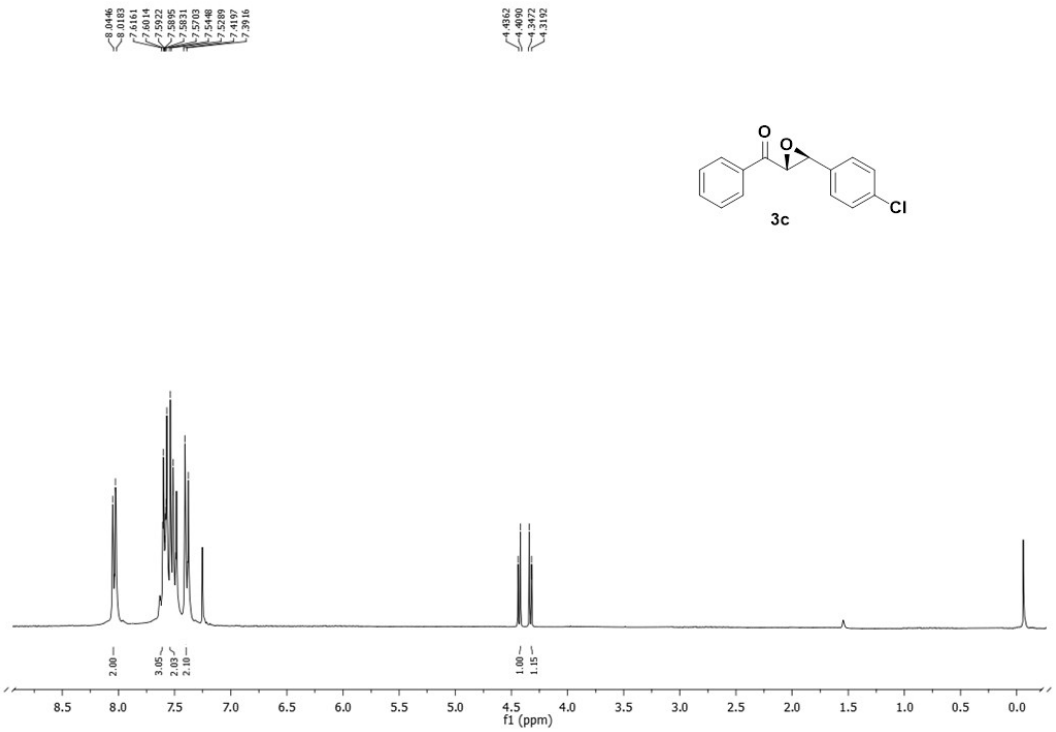


Figure S25: 1H NMR spectrum of epoxide **3c**.

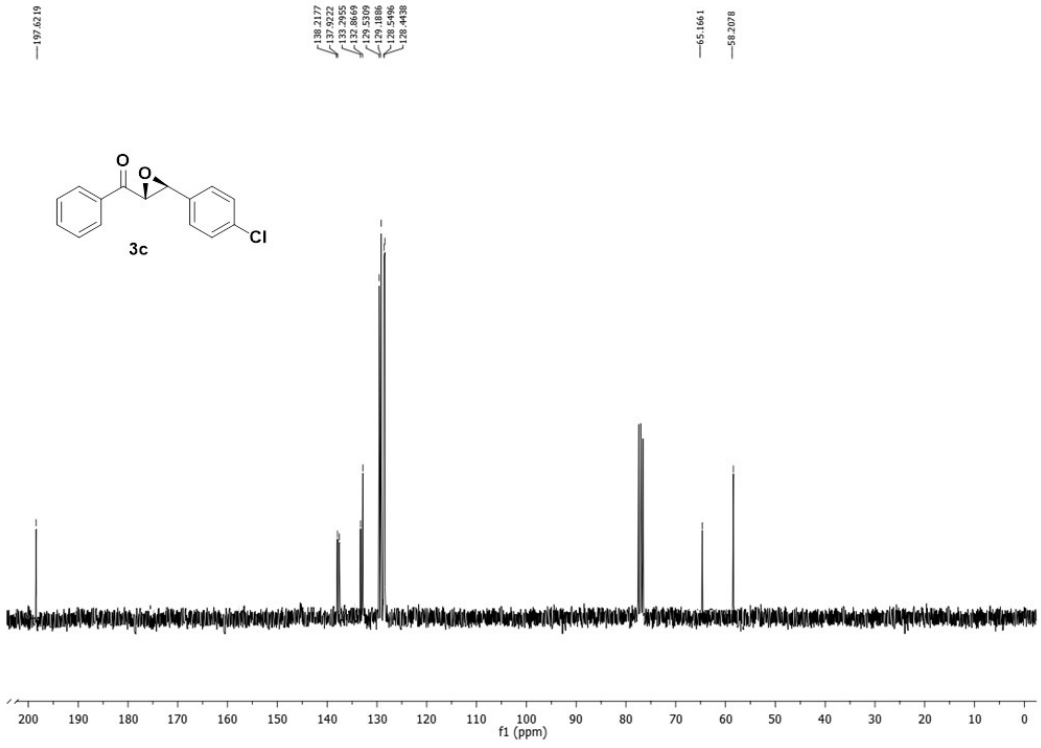
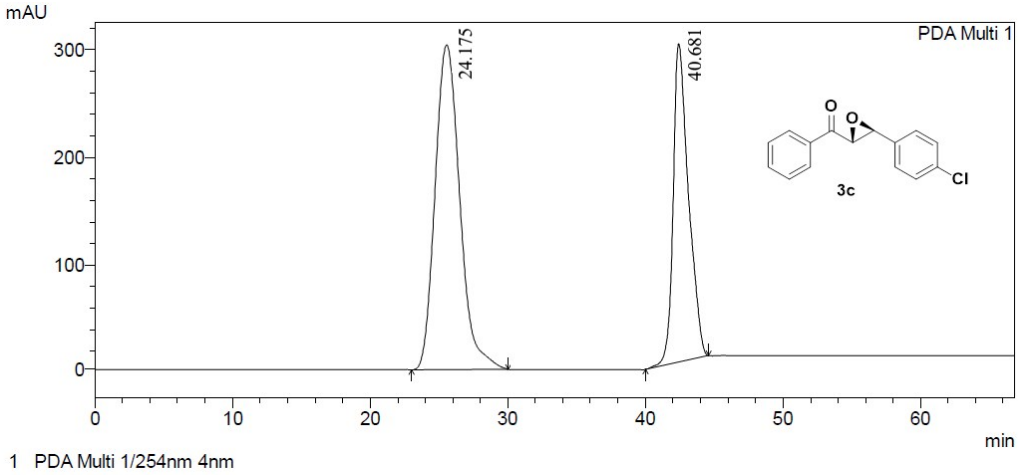


Figure S26: 13C NMR spectrum of epoxide **3c**.

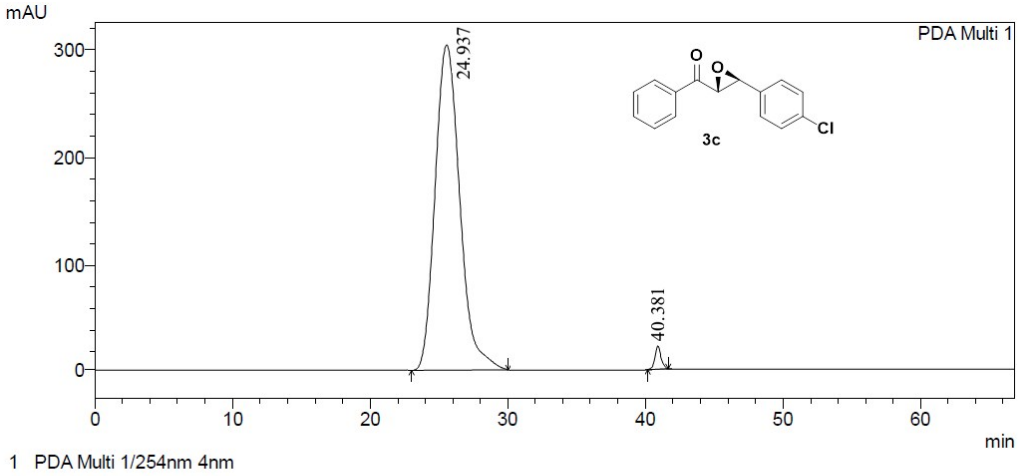


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.175	5653681	104342	50.162	51.369
2	40.681	5517457	97410	49.838	48.631
Total		11171138	201752	100.000	100.000

Figure S27: HPLC chromatogram of epoxide **3c** (Racemic mixture).



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.937	331381981	389212	99.687	98.851
2	40.381	44433	4523	0.313	1.149
Total		331426414	393735	100.000	100.000

Figure S28: HPLC chromatogram of epoxide **3c** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 ^oC condition.

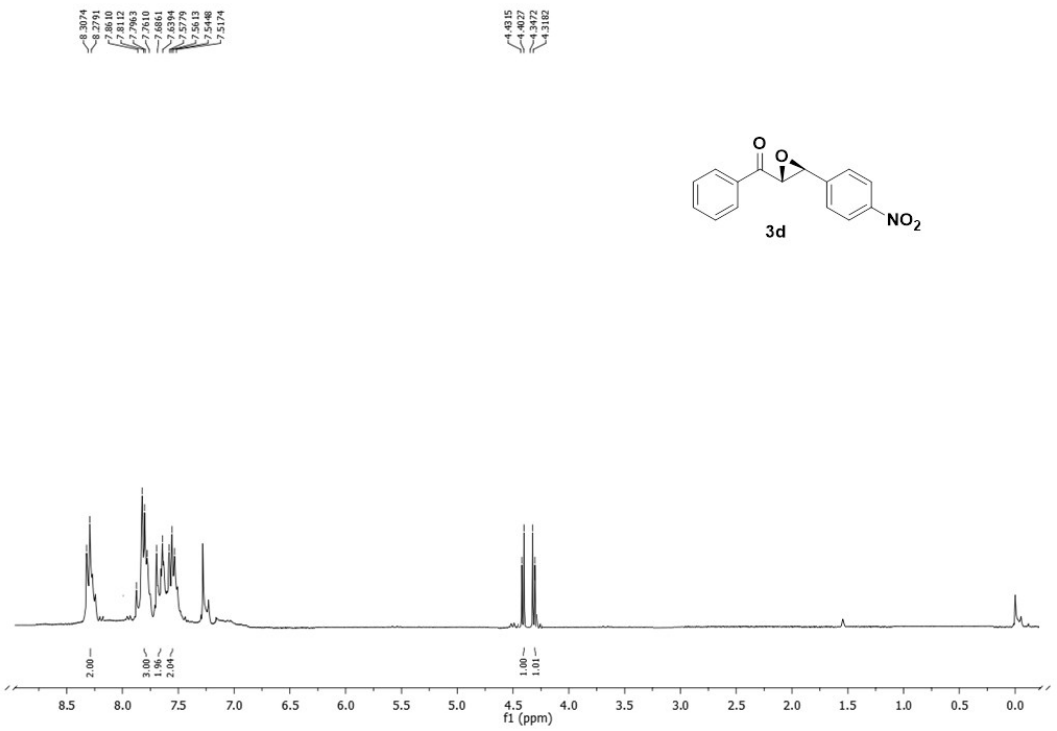


Figure S29: 1H NMR spectrum of epoxide **3d**.

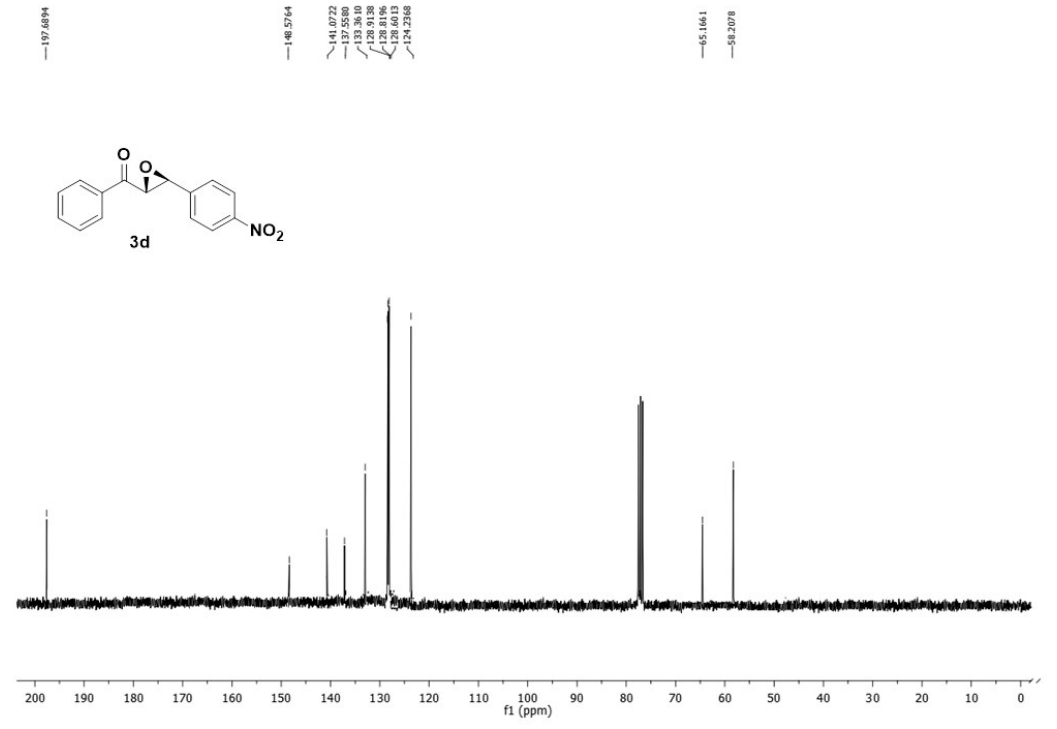
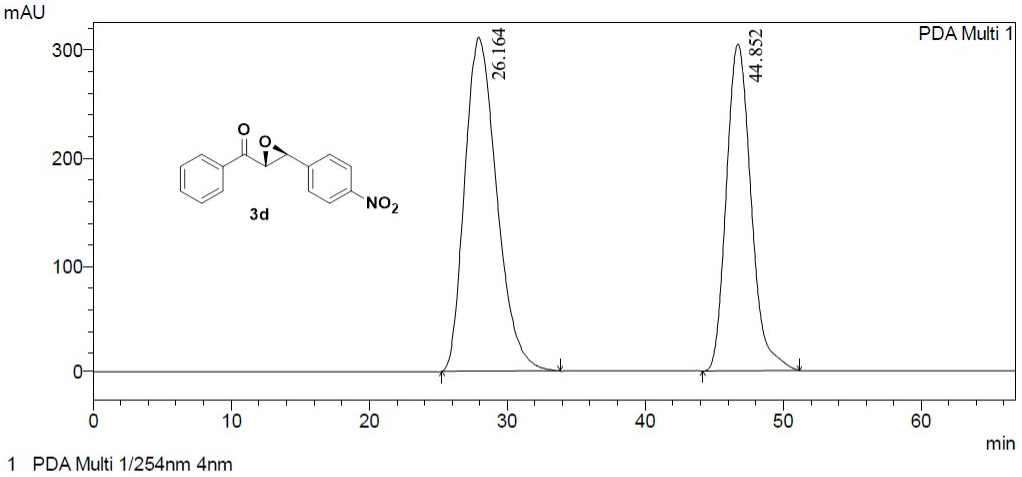


Figure S30: 13C NMR spectrum of epoxide **3d**.

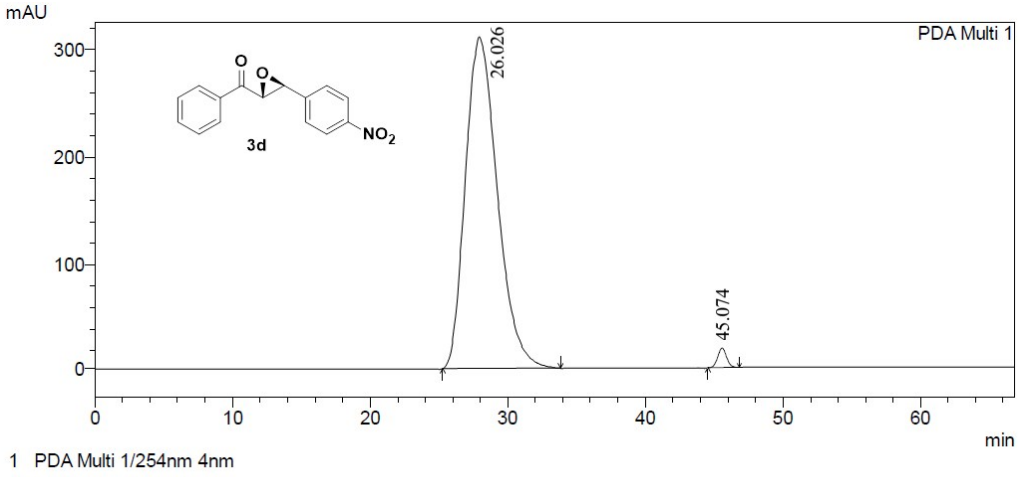


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.164	36525852	399404	50.753	51.826
2	44.852	35721829	371448	49.247	48.174
Total		72247681	770851	100.000	100.000

Figure S31: HPLC chromatogram of epoxide **3d** (Racemic mixture).



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.026	72949890	507459	99.113	98.604
2	45.074	652804	7184	0.887	1.396
Total		73602695	514642	100.000	100.000

Figure S32: HPLC chromatogram of epoxide **3d** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 ^oC condition.

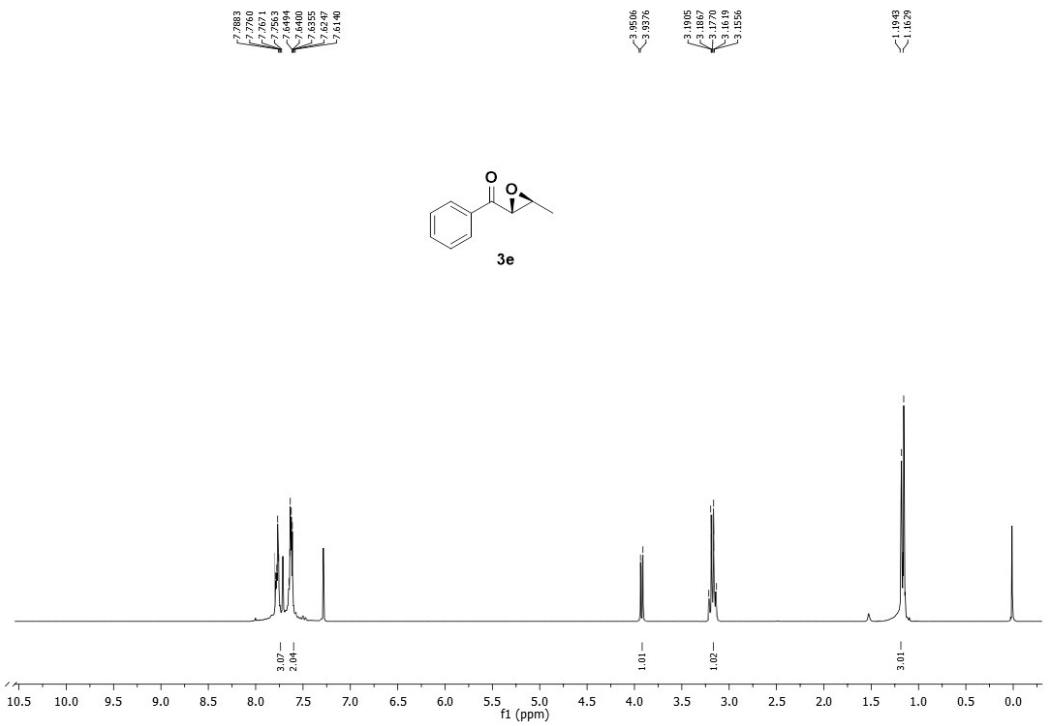


Figure S33: 1H NMR spectrum of epoxide **3e**.

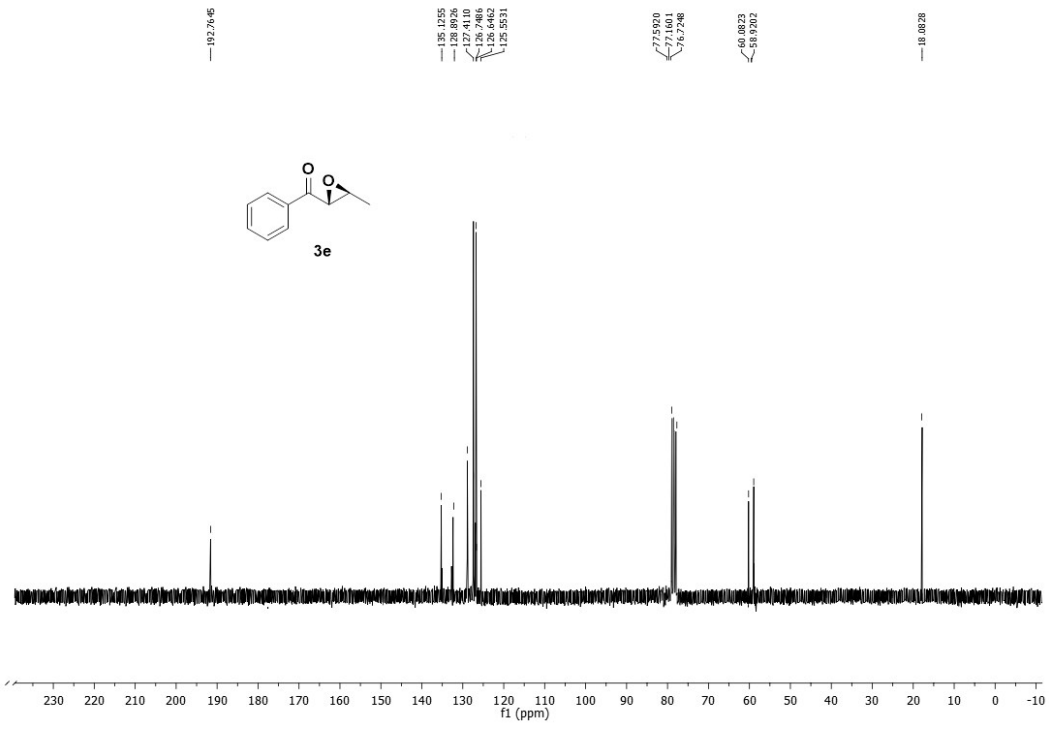
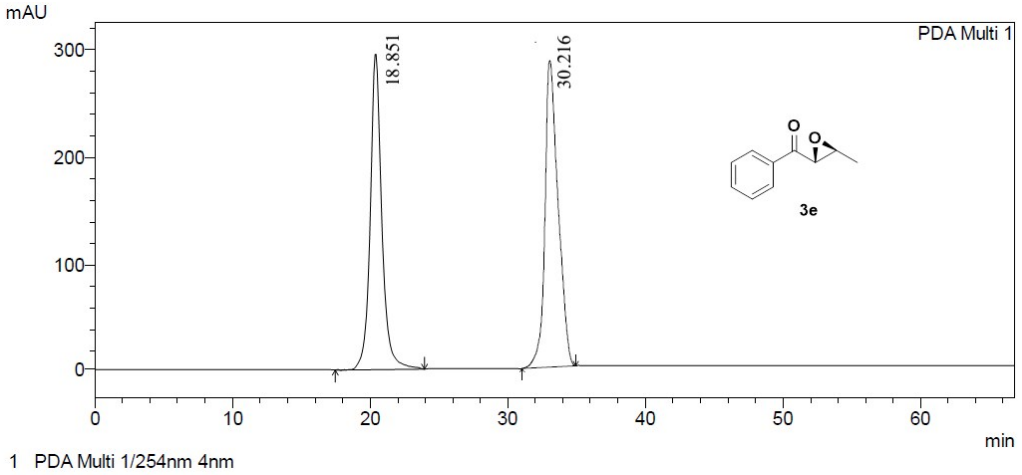


Figure S34: 13C NMR spectrum of epoxide **3e**.

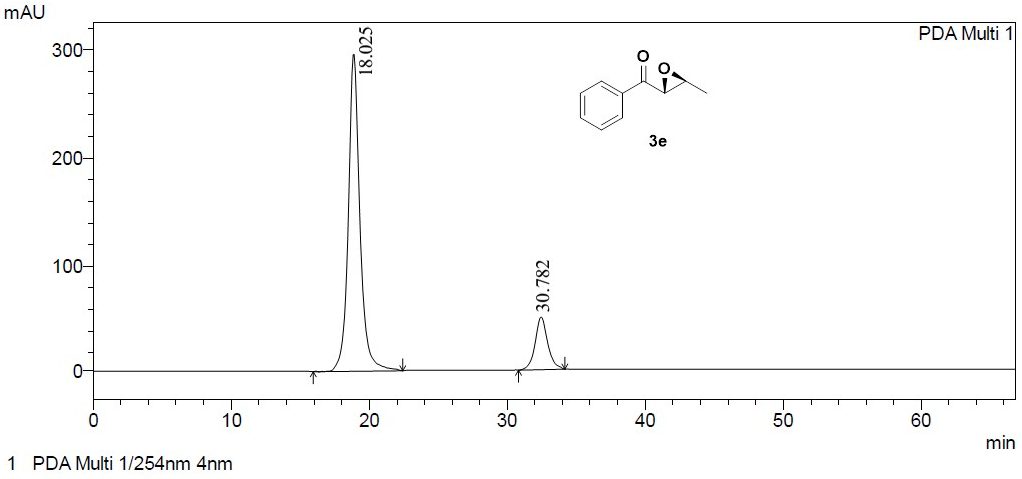


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.851	1973568	8839	50.216	51.640
2	30.216	1877623	8633	49.784	48.360
Total		3851191	17472	100.000	100.000

Figure S35: HPLC chromatogram of epoxide **3e** (Racemic mixture).



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.025	138778209	1462970	94.807	94.445
2	30.782	7602045	86041	5.193	5.555
Total		146380254	1549011	100.000	100.000

Figure S36: HPLC chromatogram of epoxide **3e** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 ^oC condition.

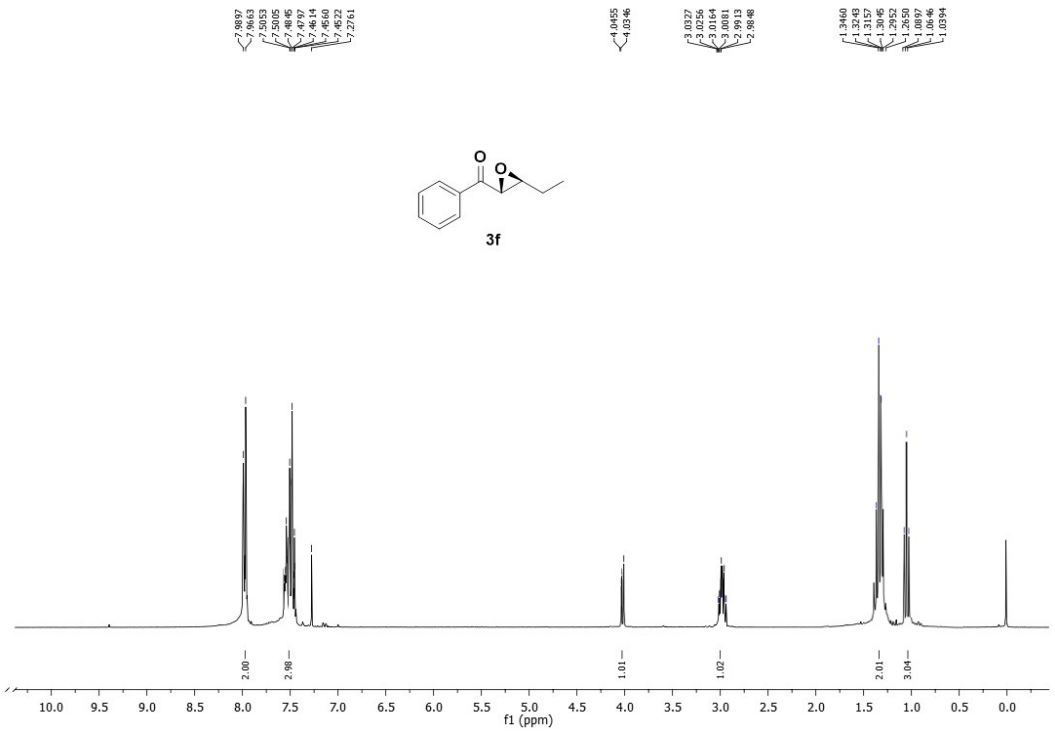


Figure S37: 1H NMR spectrum of epoxide **3f**.

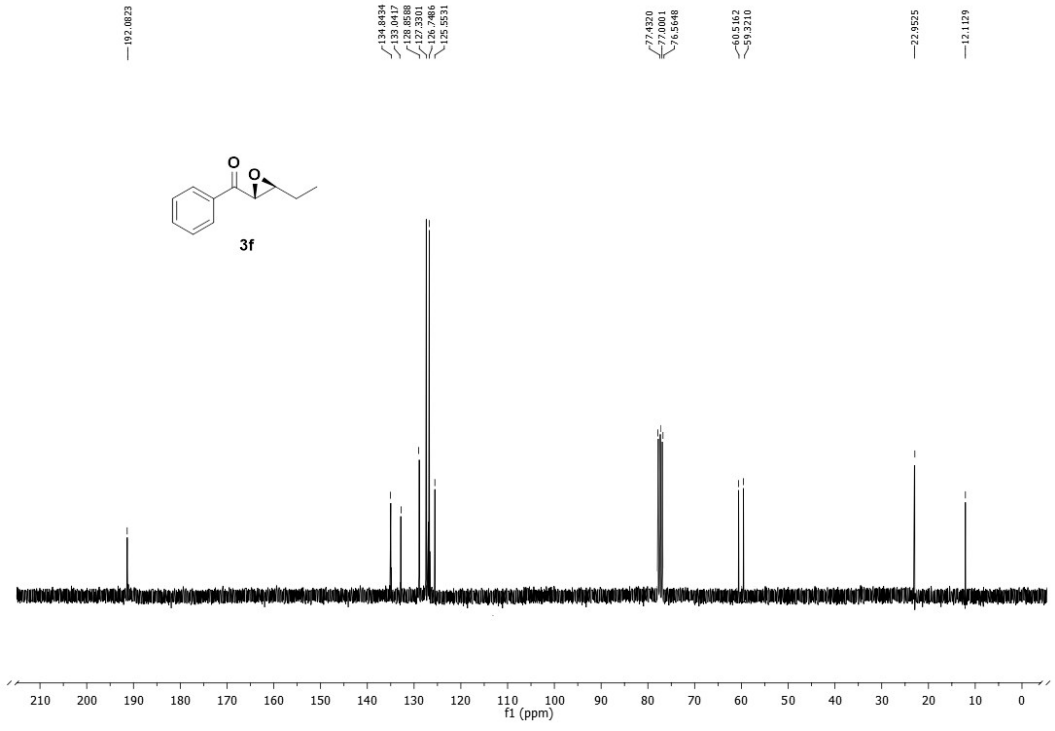
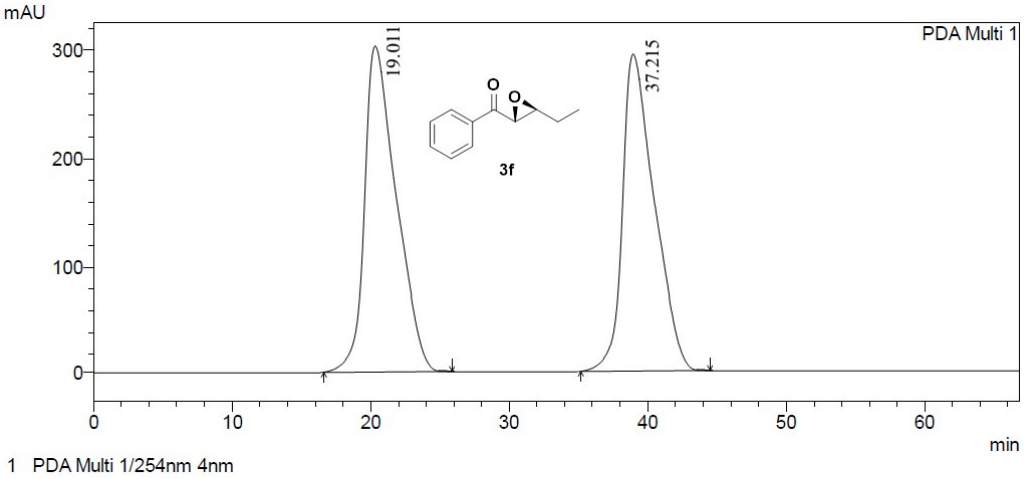


Figure S38: 13C NMR spectrum of epoxide **3f**.

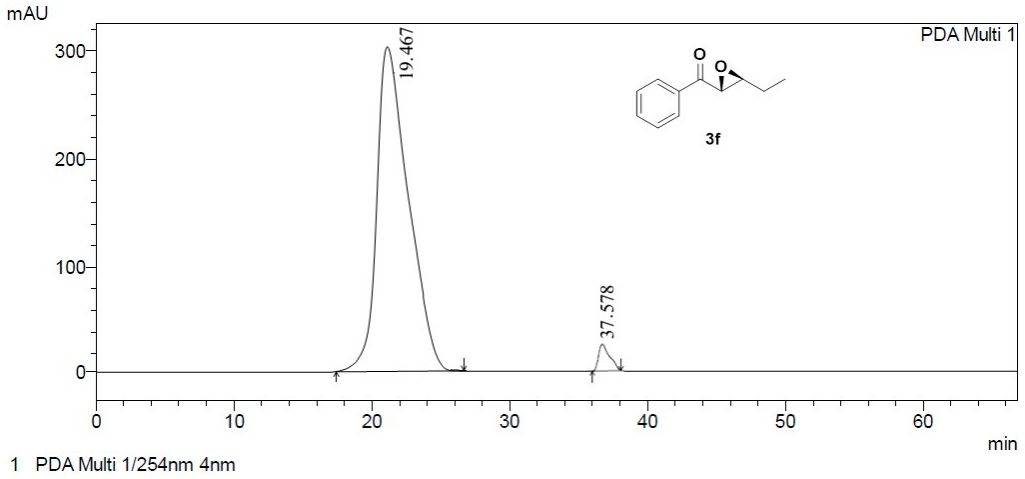


PeakTable

PDA Ch1 244nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.011	4120354	196930	50.914	52.714
2	37.215	4011796	185535	49.086	47.286
Total		8132150	382465	100.000	100.000

Figure S39: HPLC chromatogram of epoxide **3f** (Racemic mixture).



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.467	3904352	75789	96.378	95.441
2	37.578	146742	3620	3.622	4.559
Total		4051094	79409	100.000	100.000

Figure S40: HPLC chromatogram of epoxide **3f** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 ºC condition.

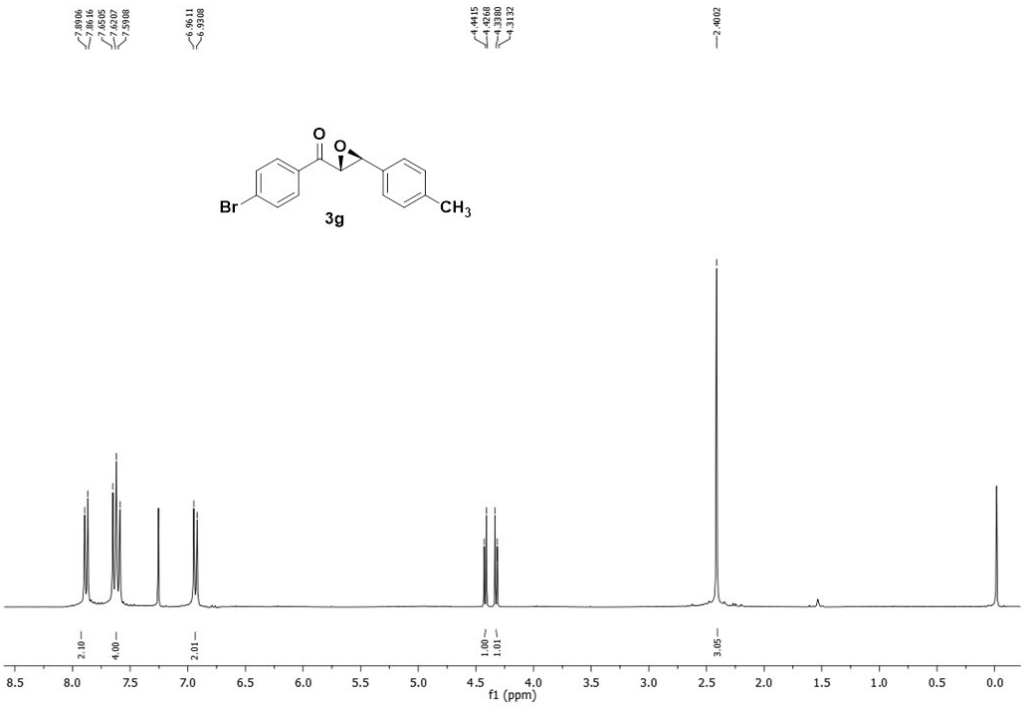


Figure S41: 1H NMR spectrum of epoxide **3g**.

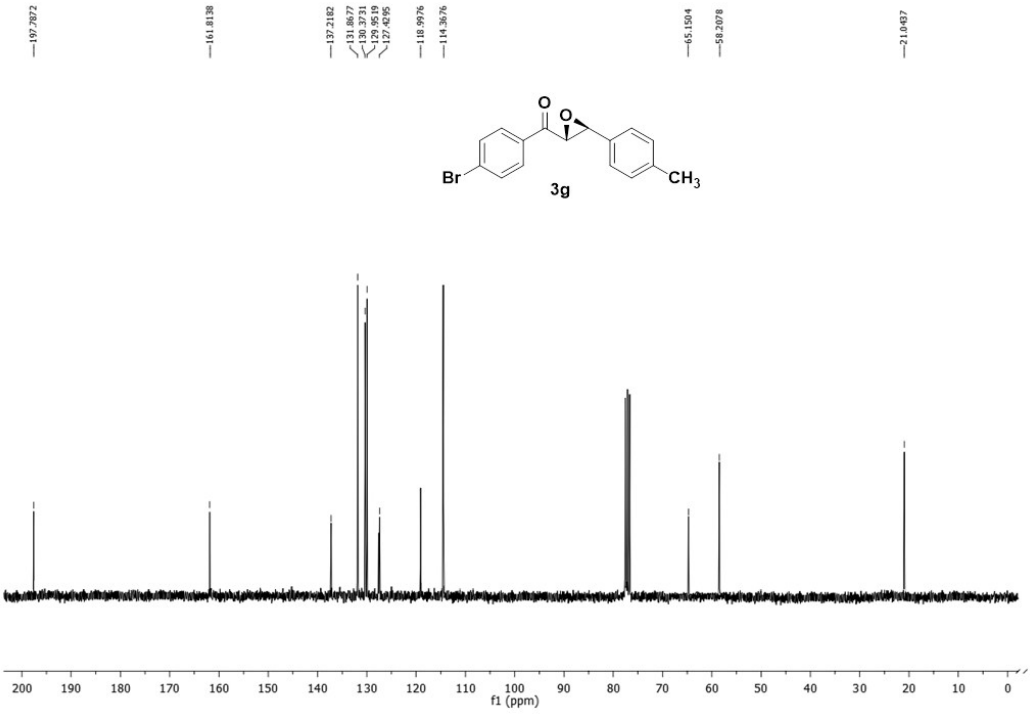
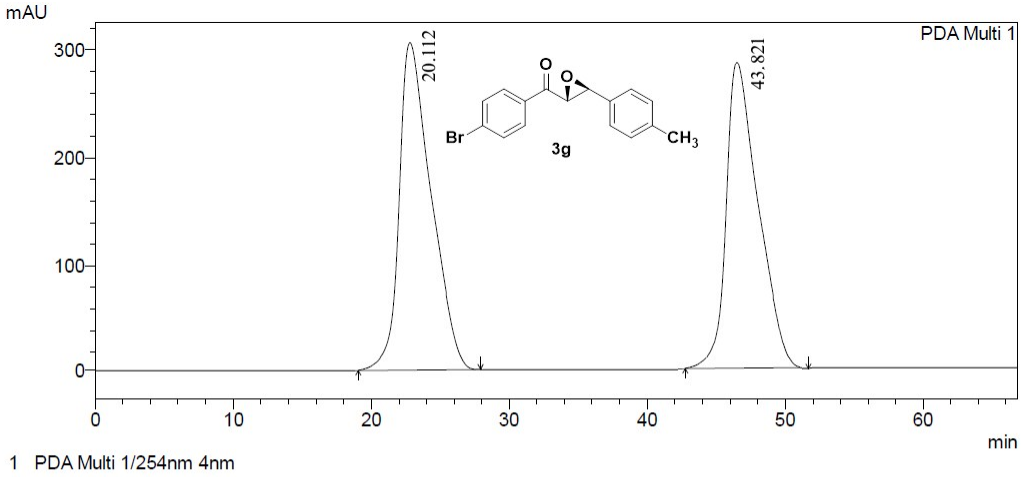


Figure S42: 13C NMR spectrum of epoxide **3g**.

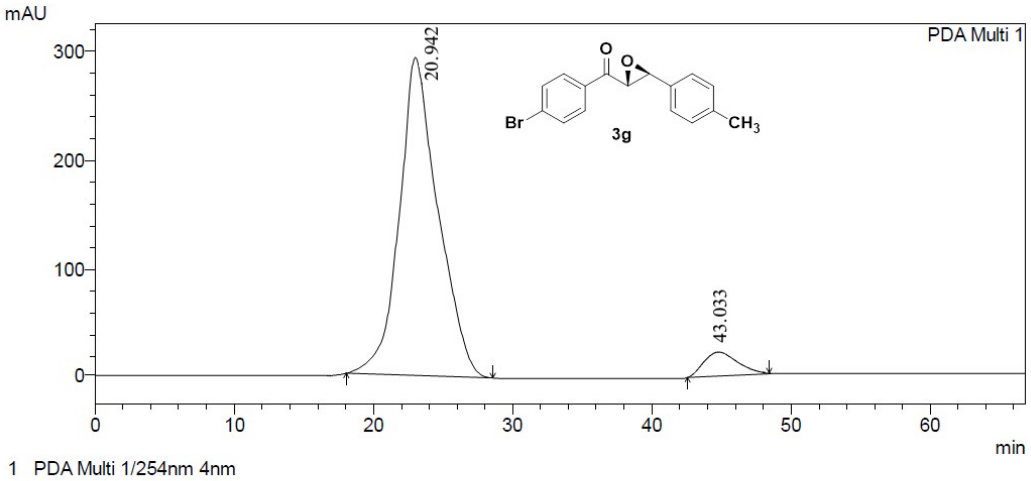


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.112	9151863	102571	50.394	51.420
2	43.821	9065393	95256	49.606	48.580
Total		18217256	197826	100.000	100.000

Figure S43: HPLC chromatogram of epoxide **3g** (Racemic mixture).



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.942	82677818	834234	96.067	92.270
2	43.033	3384812	69886	3.933	7.730
Total		86062630	904119	100.000	100.000

Figure S44: HPLC chromatogram of epoxide **3g** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 ^oC condition.

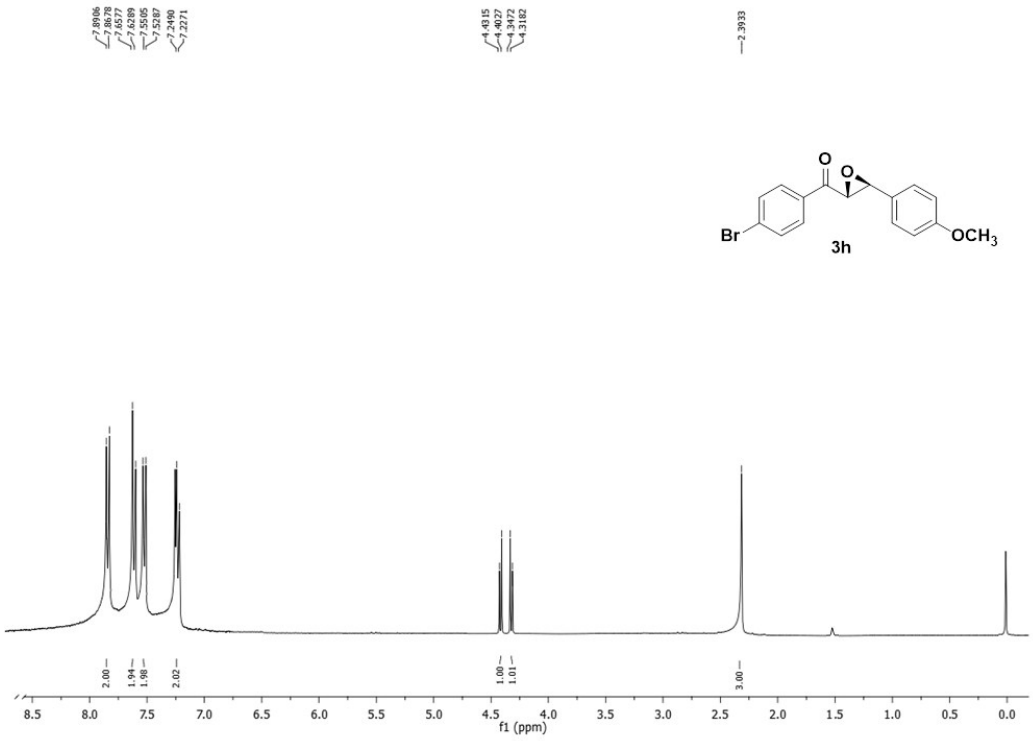


Figure S45: 1H NMR spectrum of epoxide **3h**.

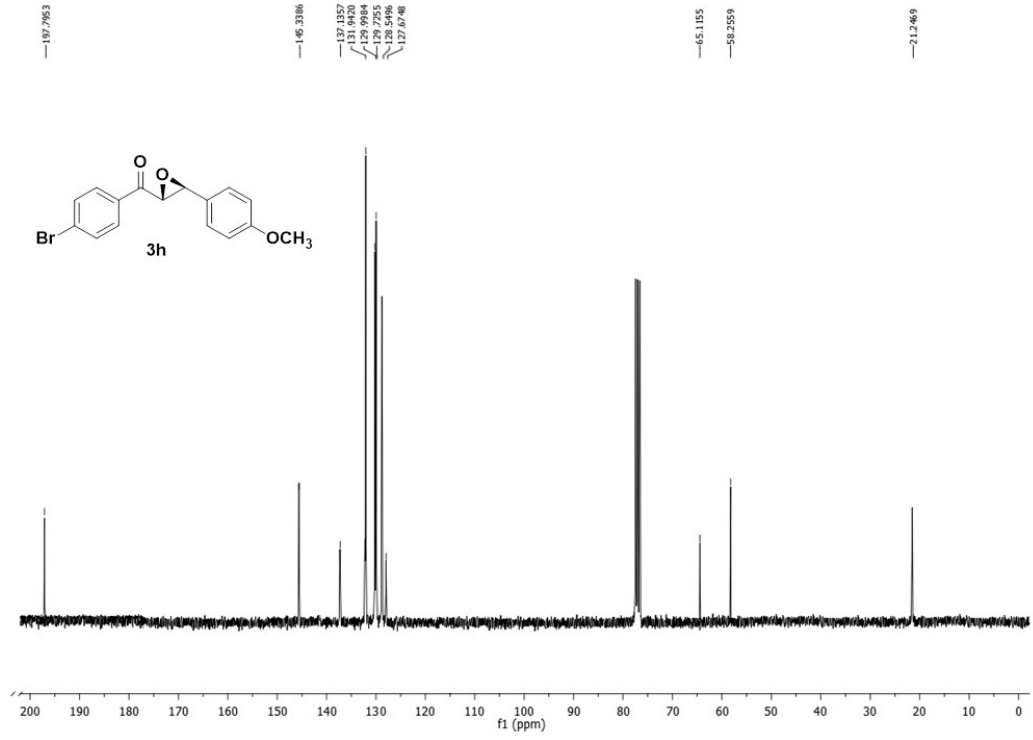
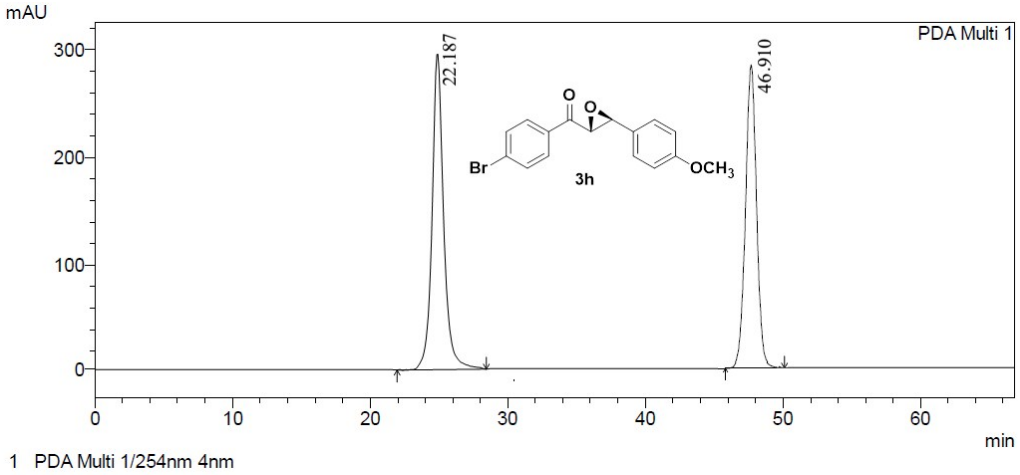


Figure S46: 13C NMR spectrum of epoxide **3h**.

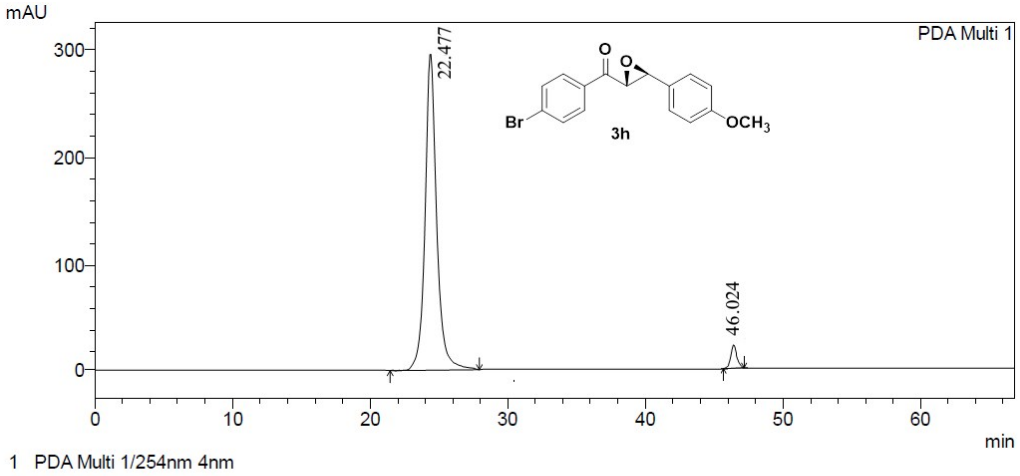


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.187	6412071	85516	50.674	51.910
2	46.910	6338383	83187	49.326	48.090
Total		12750455	168703	100.000	100.000

Figure S47: HPLC chromatogram of epoxide **3h** (Racemic mixture).



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.477	59989641	2024905	97.580	95.203
2	46.024	1487822	102027	2.420	4.797
Total		61477464	2126932	100.000	100.000

Figure S48: HPLC chromatogram of epoxide **3h** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 ^oC condition.

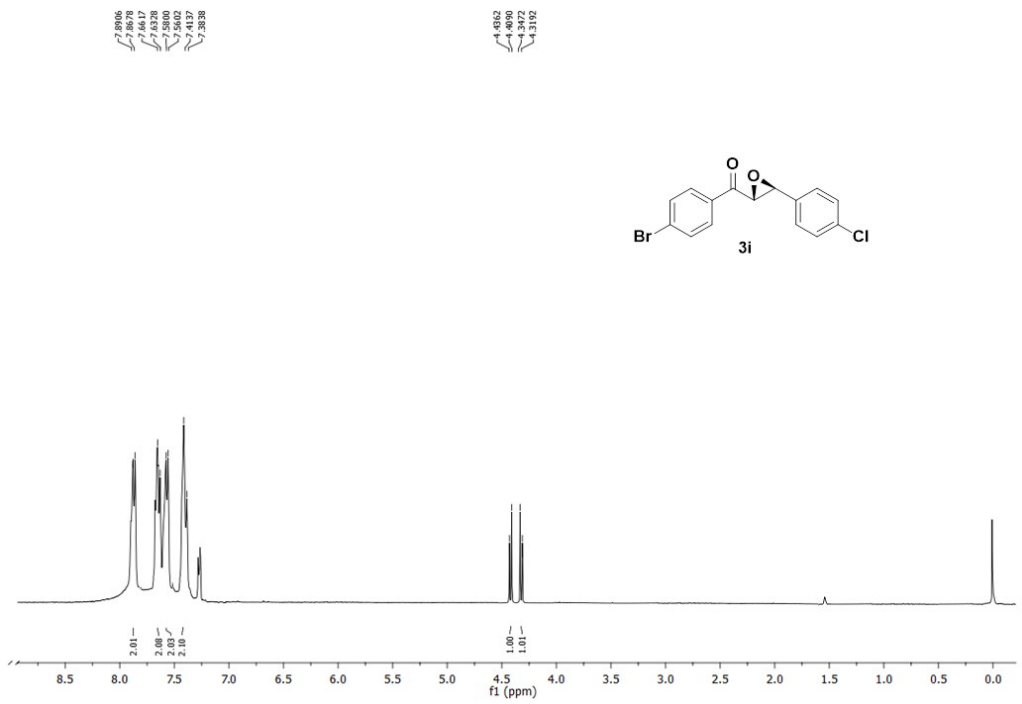


Figure S49: 1H NMR spectrum of epoxide **3i**.

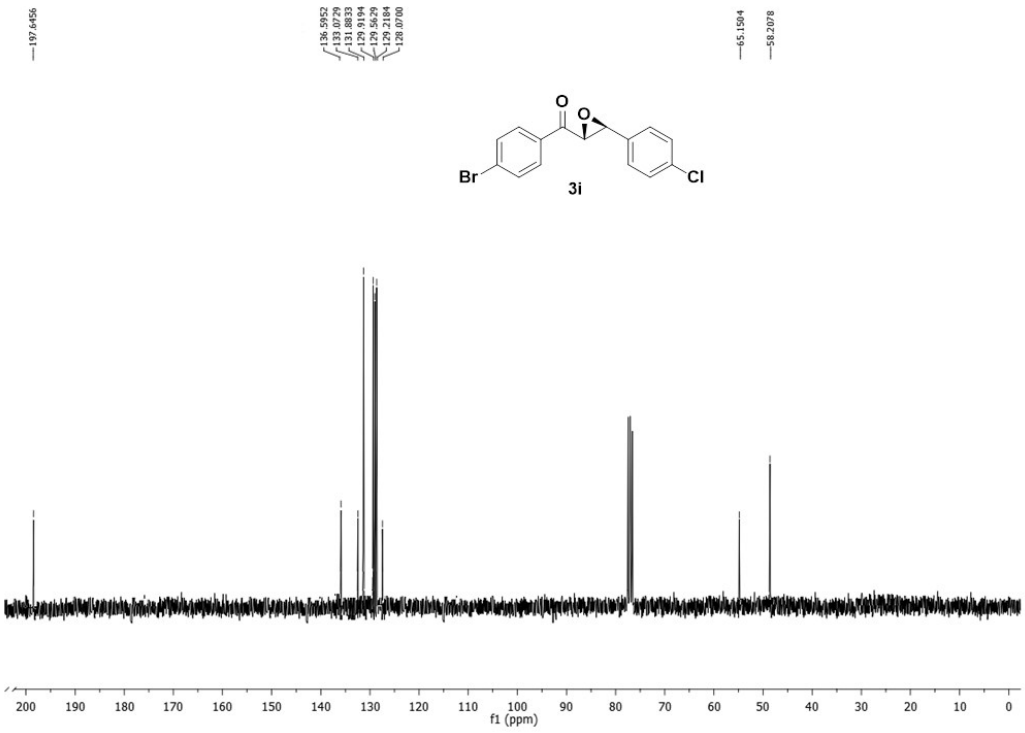
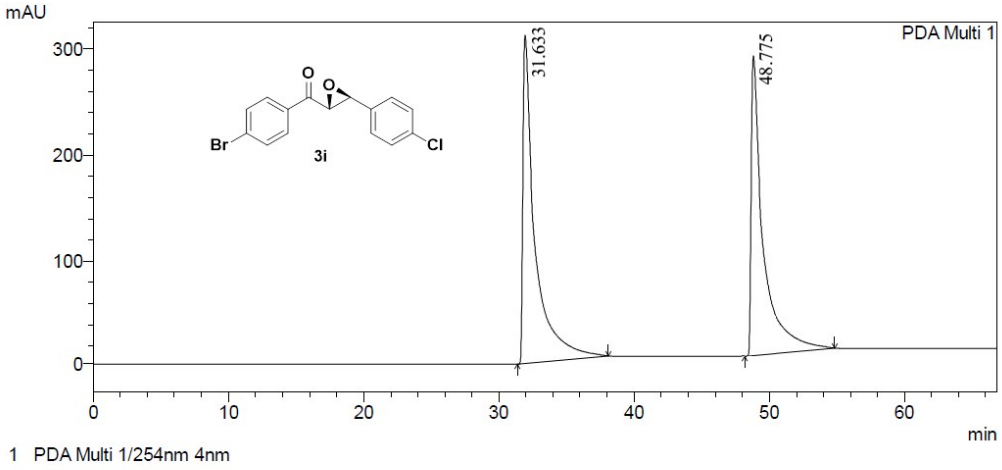


Figure S50: 13C NMR spectrum of epoxide **3i**.

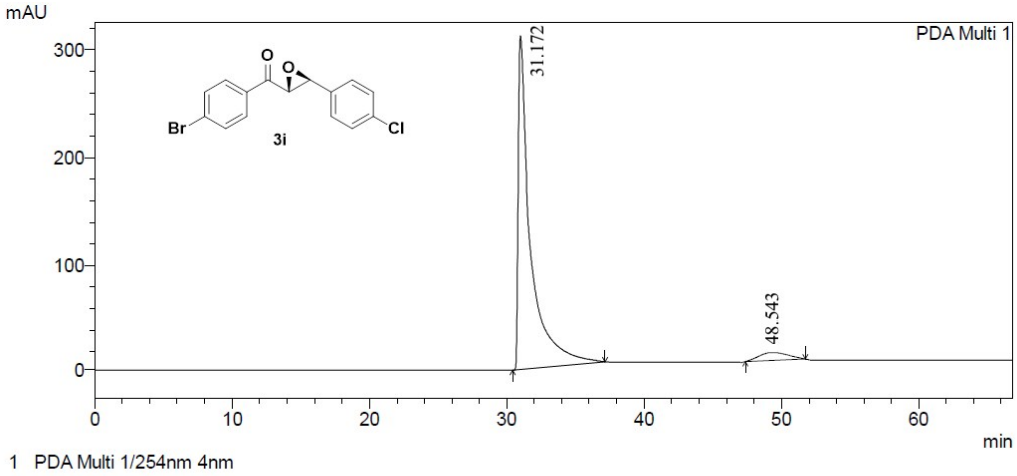


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.633	1973568	8839	50.216	51.640
2	48.775	1877623	8633	49.784	48.360
Total		3851191	17472	100.000	100.000

Figure S51: HPLC chromatogram of epoxide **3i** (Racemic mixture).



PeakTable

PDA Ch1 254nm 4nm

Name	Peak#	Ret. Time	Area	Height	Area %	Height %
	1	31.172	104833728	545438	99.270	97.639
	2	48.543	770444	13187	0.730	2.361
	Total		105604172	558624	100.000	100.000

Figure S52: HPLC chromatogram of epoxide **3i** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 ^oC condition.

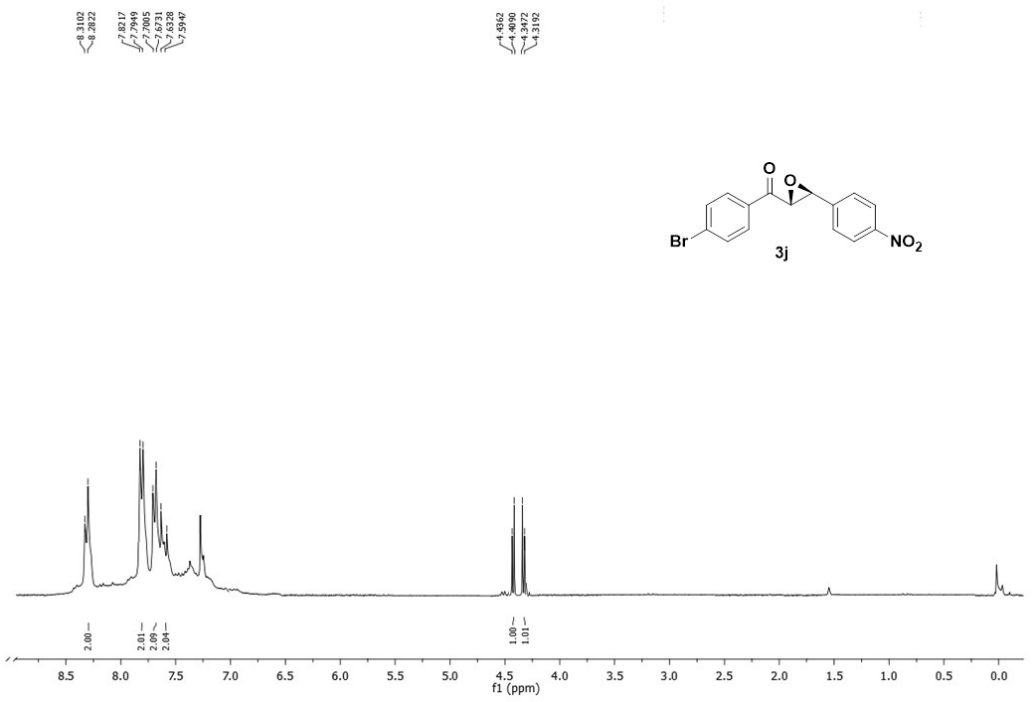


Figure S53: 1H NMR spectrum of epoxide **3j**.

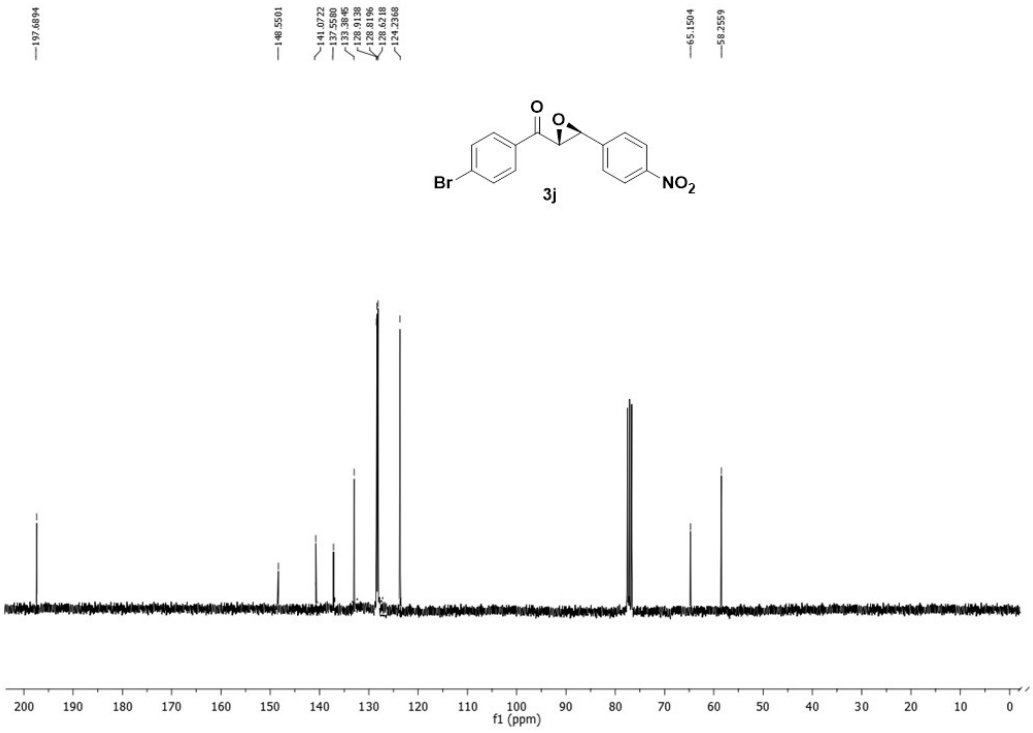
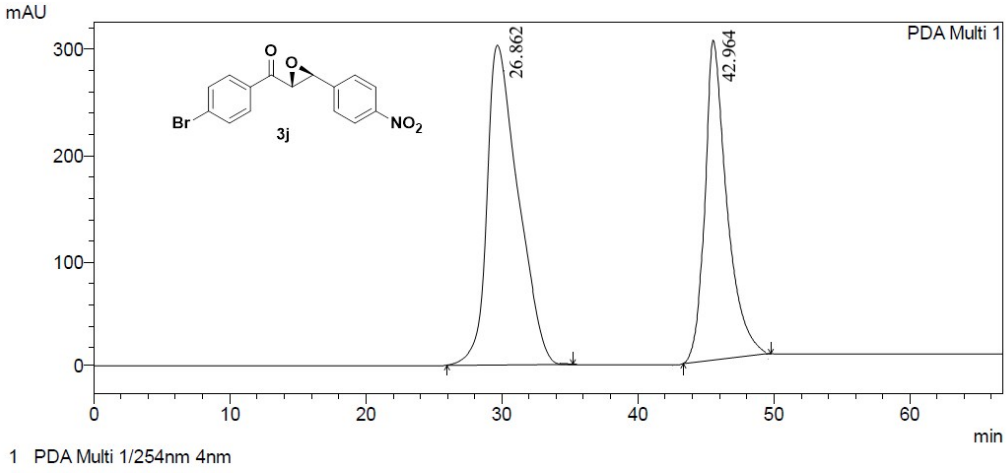


Figure S54: 13C NMR spectrum of epoxide **3j**.

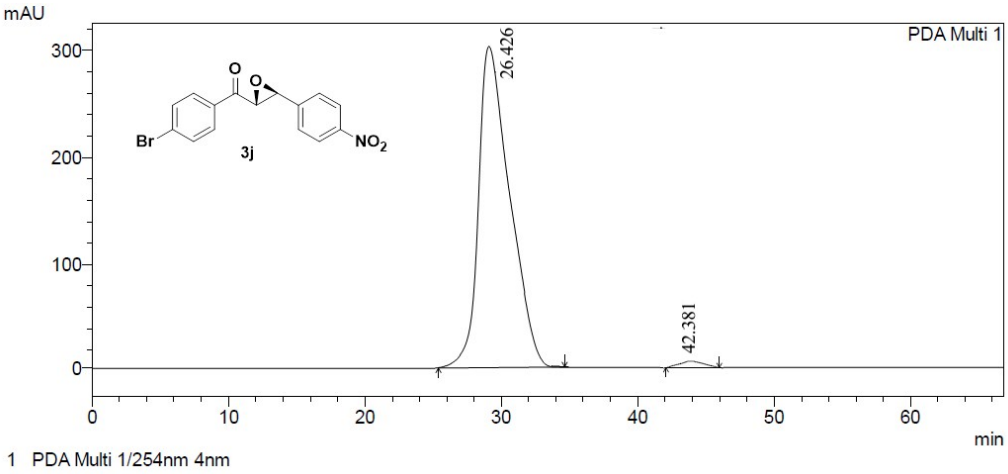


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.862	143622513	1483220	50.741	51.794
2	42.964	142638897	1365126	49.259	48.206
Total		286261409	2848346	100.000	100.000

Figure S55: HPLC chromatogram of epoxide **3j** (Racemic mixture).



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.426	331381981	389212	99.687	98.851
2	42.381	44433	4523	0.313	1.149
Total		331426414	393735	100.000	100.000

Figure S56: HPLC chromatogram of epoxide **3j** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 °C condition.

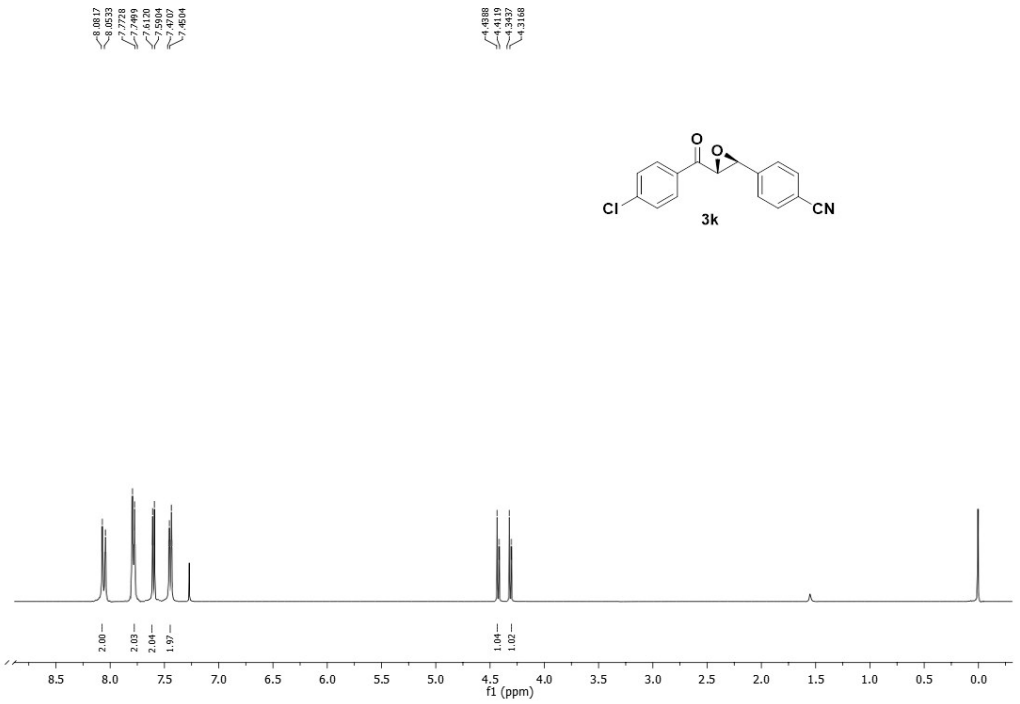


Figure S57: 1H NMR spectrum of epoxide **3k**.

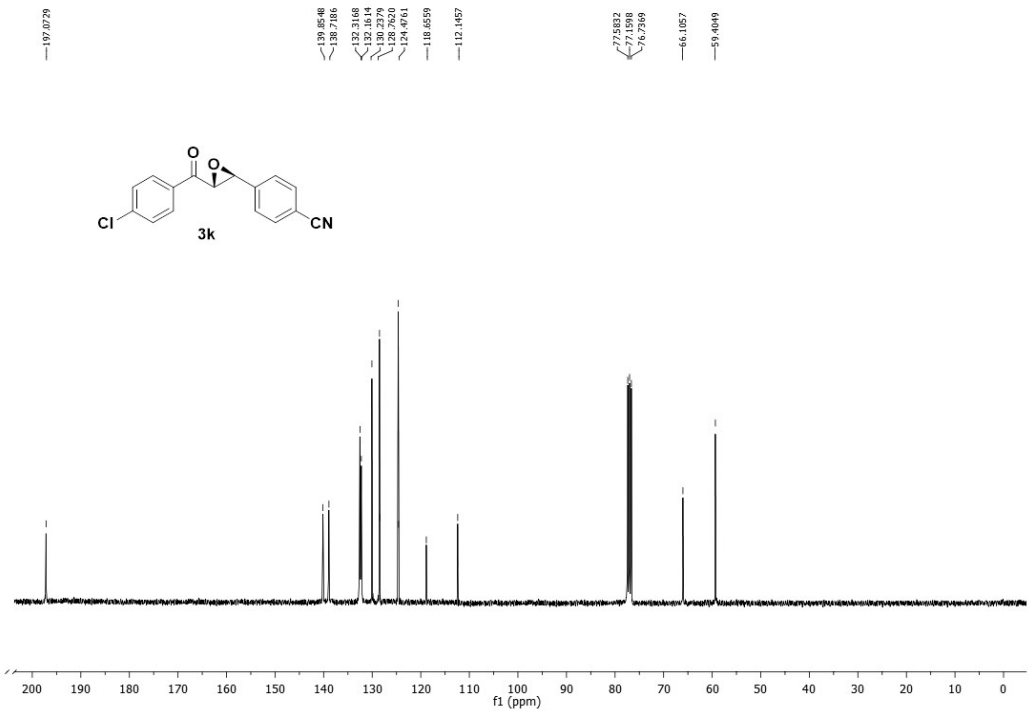
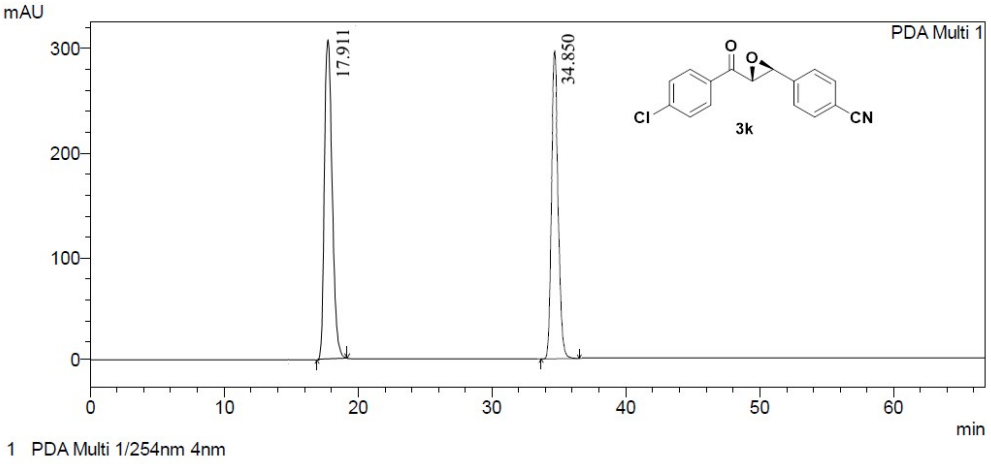


Figure S58: 13C NMR spectrum of epoxide **3k**.

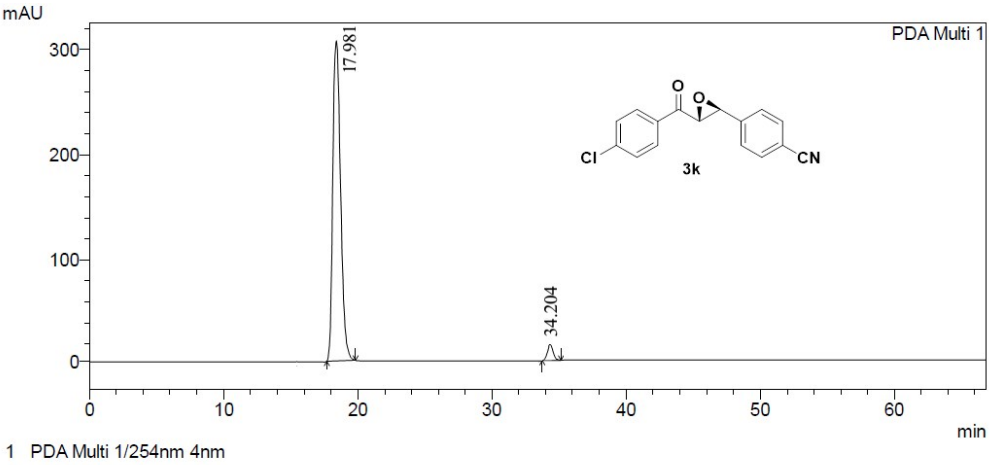


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.911	5653681	104342	50.162	51.369
2	34.850	5517457	97410	49.838	48.631
Total		11171138	201752	100.000	100.000

Figure S59: HPLC chromatogram of epoxide **3k** (Racemic mixture).



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.981	27835219	399135	98.789	94.977
2	34.204	427069	21110	1.211	5.023
Total		28262287	420246	100.000	100.000

Figure S60: HPLC chromatogram of epoxide **3k** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 ^oC condition.

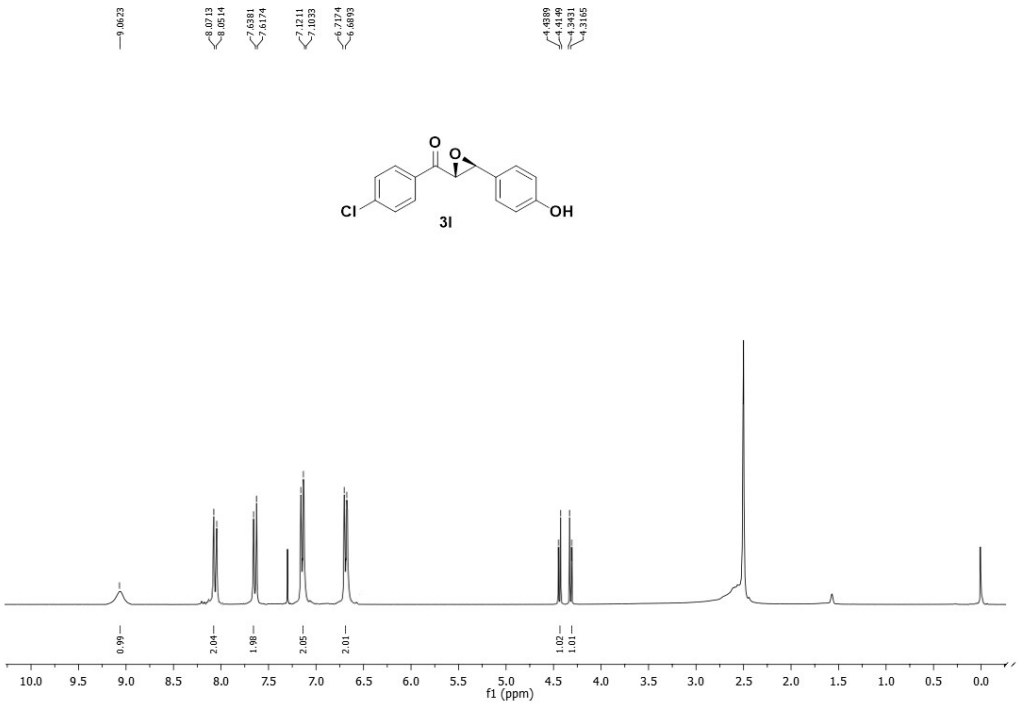


Figure S61: 1H NMR spectrum of epoxide **3l**.

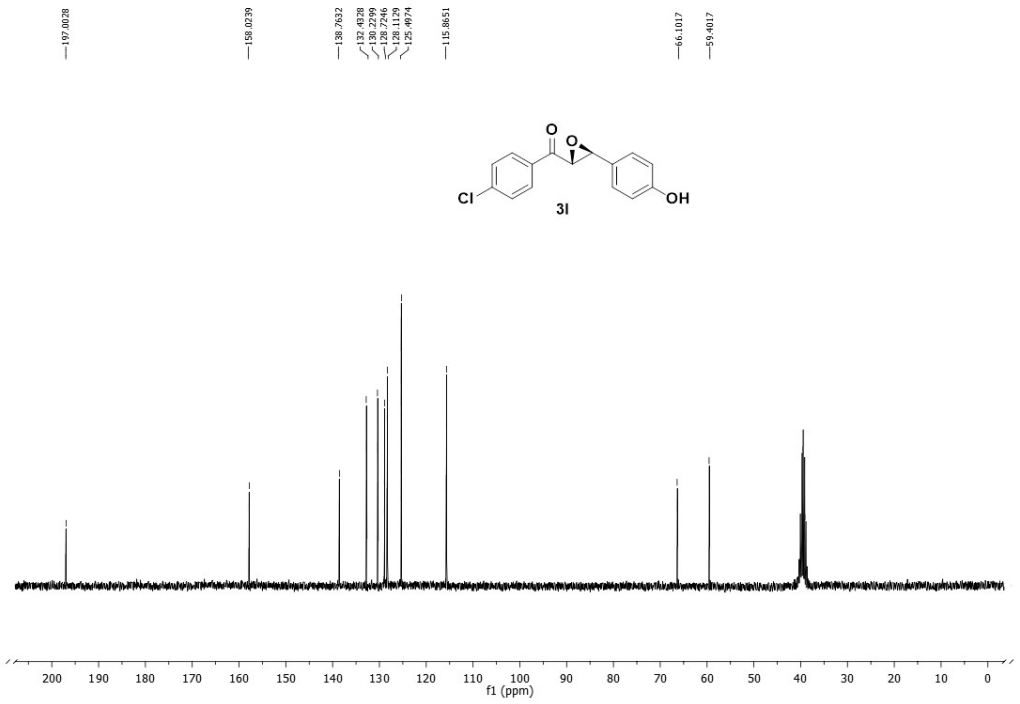
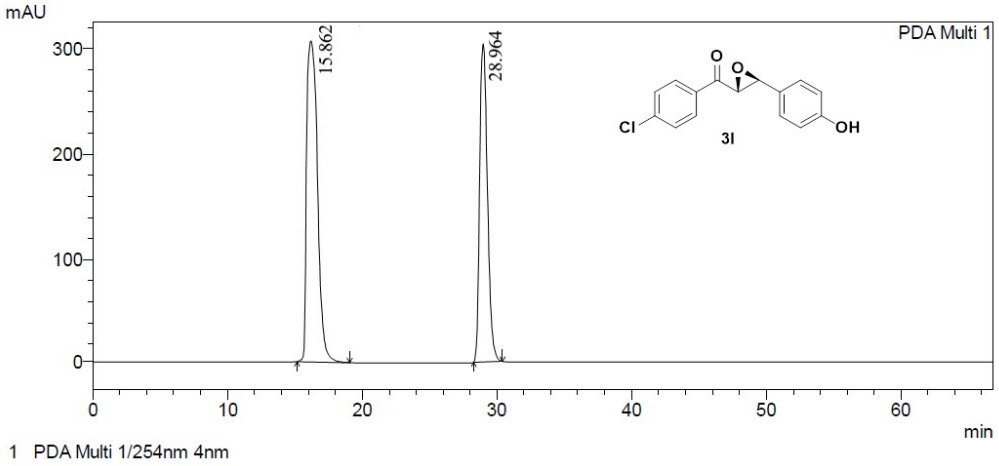


Figure S62: 13C NMR spectrum of epoxide **3l**.

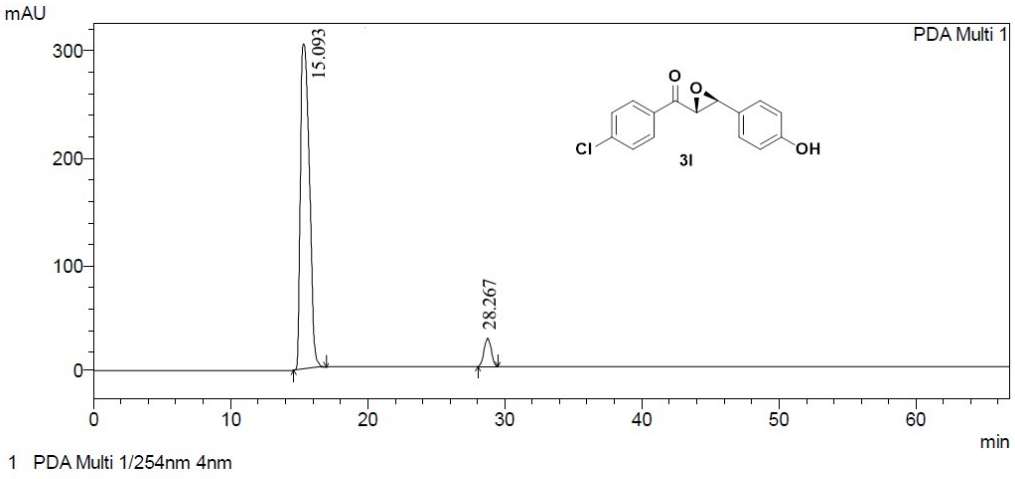


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.862	143622513	1483220	50.741	51.794
2	28.964	142638897	1365126	49.259	48.206
Total		286261409	2848346	100.000	100.000

Figure S63: HPLC chromatogram of epoxide **3l** (Racemic mixture).



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.093	143622513	1483220	96.741	95.794
2	28.267	4838897	65126	3.259	4.206
Total		148461409	1548346	100.000	100.000

Figure S64: HPLC chromatogram of epoxide **3l** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 ^oC condition.

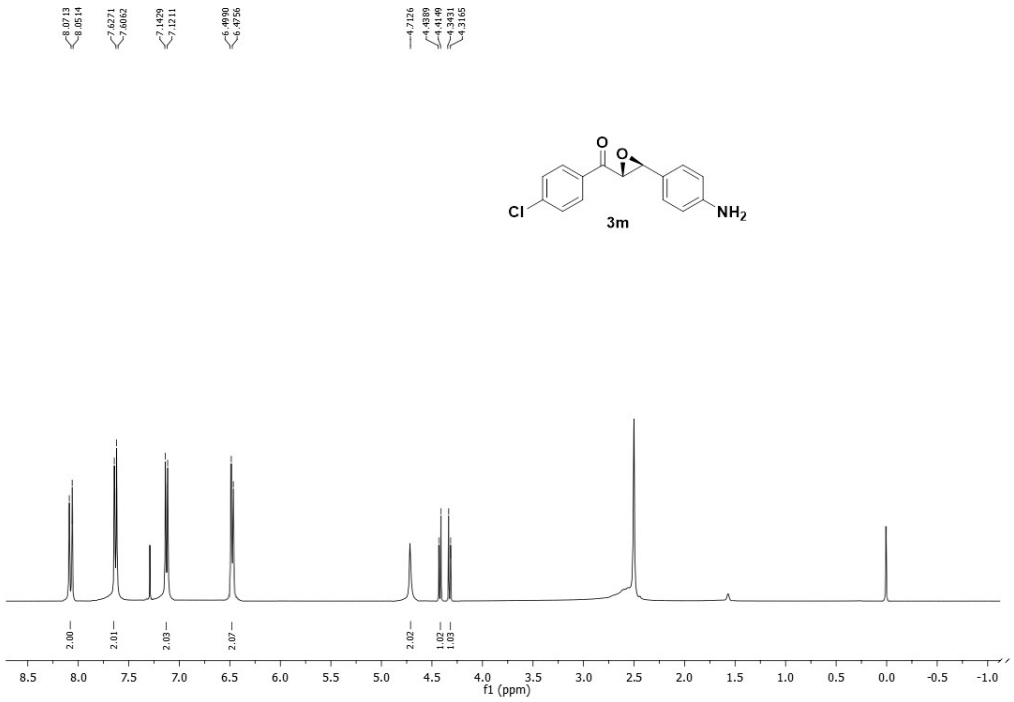


Figure S65: 1H NMR spectrum of epoxide **3m**.

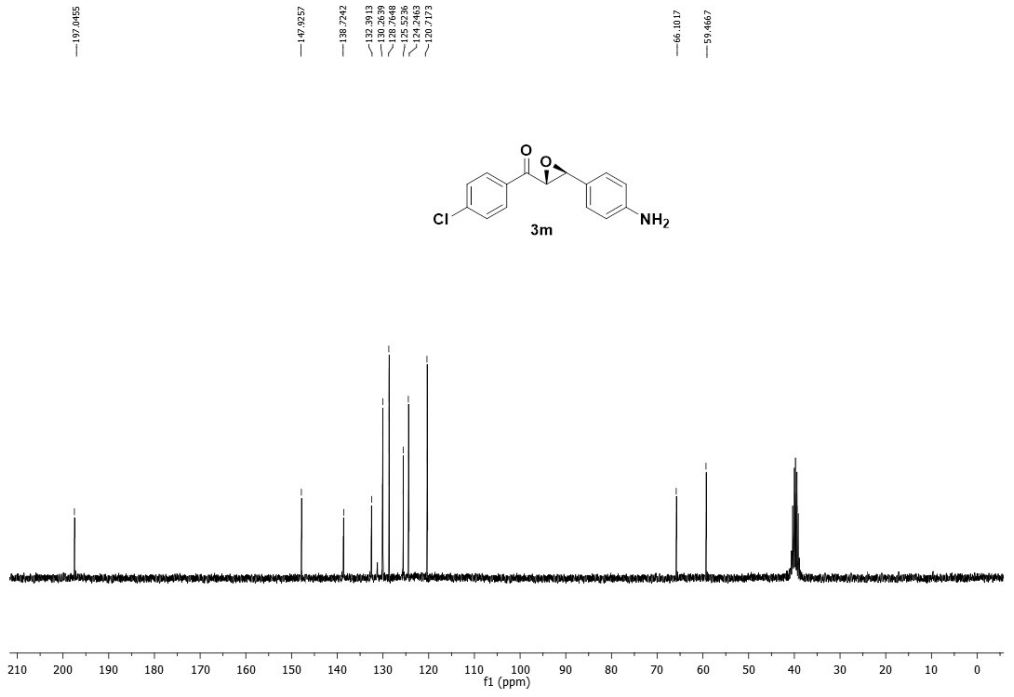
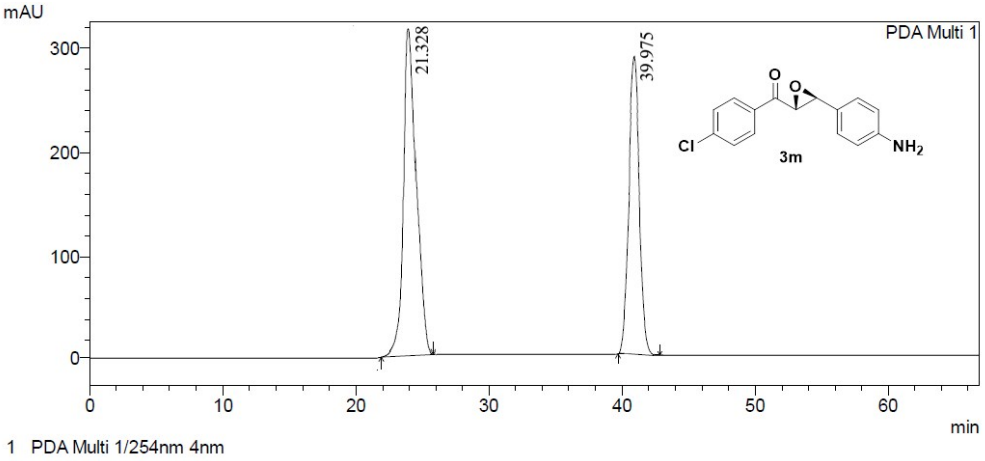


Figure S66: 13C NMR spectrum of epoxide **3m**.



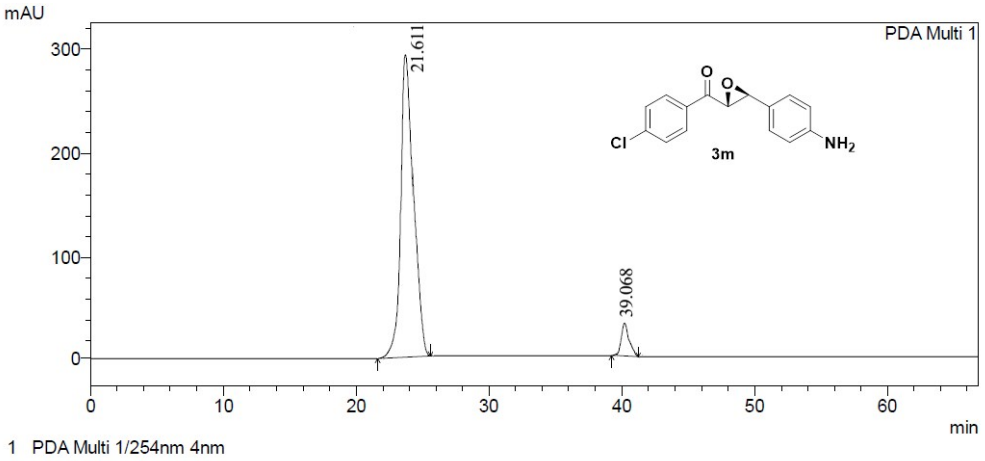
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.328	4120354	196930	50.914	52.714
2	39.975	4011796	185535	49.086	47.286
Total		8132150	382465	100.000	100.000

Figure S67: HPLC chromatogram of epoxide **3m** (Racemic mixture).



1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.611	2753234	112968	95.961	98.933
2	39.068	115892	1219	4.039	1.067
Total		2869127	114187	100.000	100.000

Figure S68: HPLC chromatogram of epoxide **3m** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 °C condition.

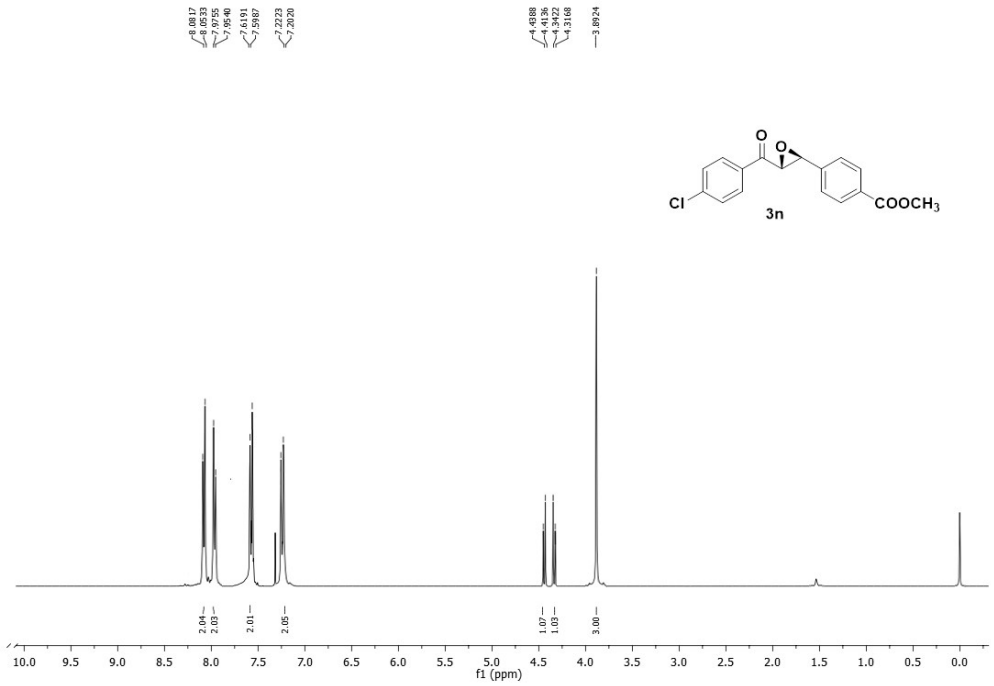


Figure S69: 1H NMR spectrum of epoxide **3n**.

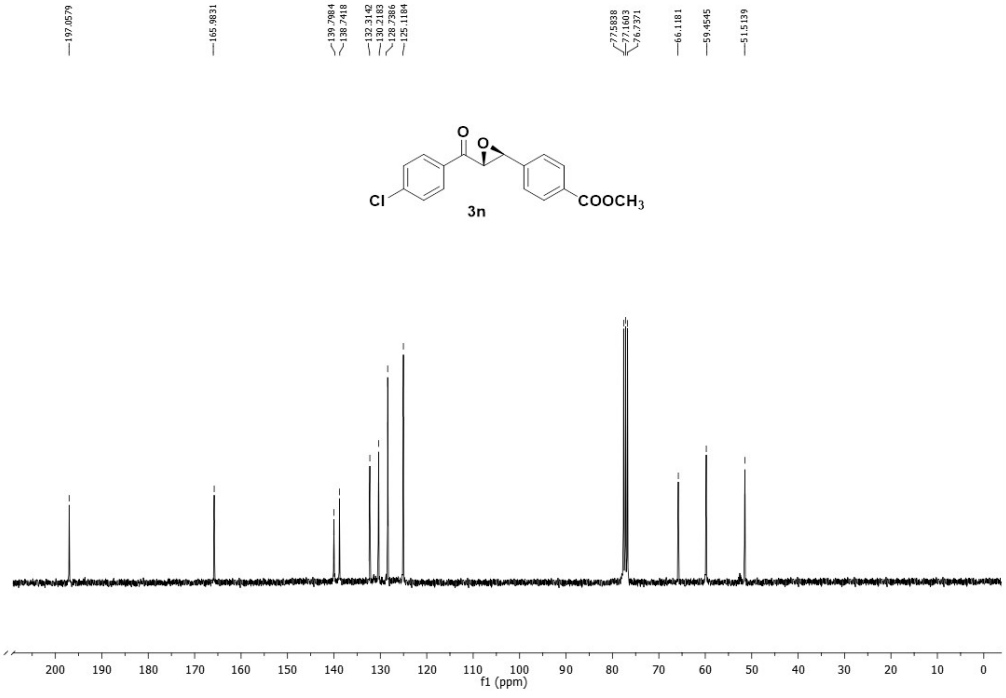
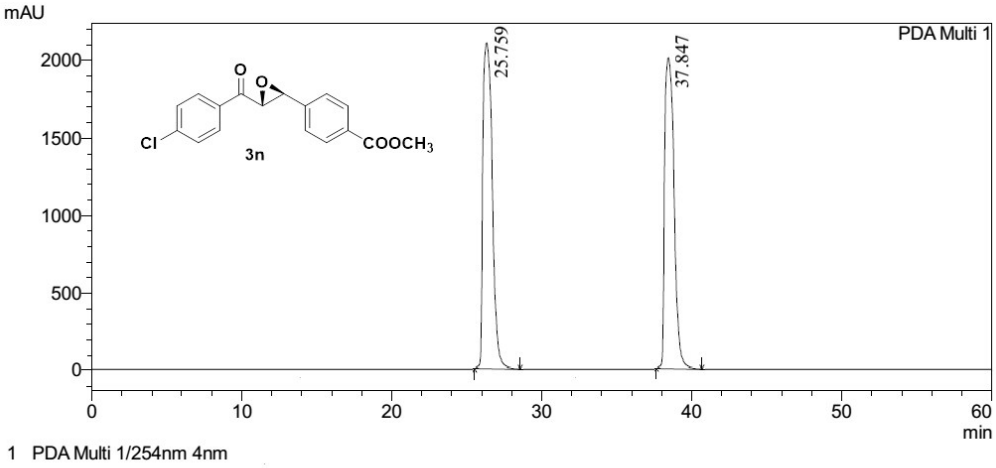


Figure S70: 13C NMR spectrum of epoxide **3n**.

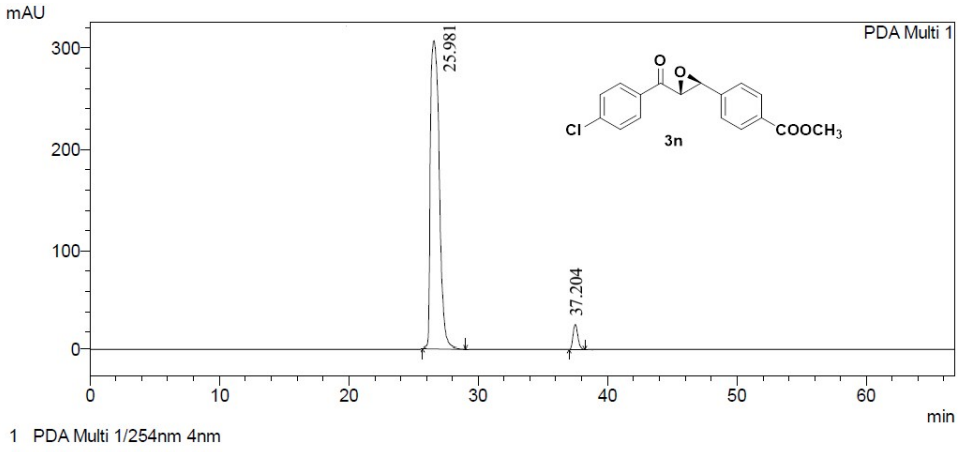


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.759	1362622	9131	50.357	51.296
2	37.847	1222762	8981	49.643	48.704
Total		2585384	18112	100.000	100.000

Figure S71: HPLC chromatogram of epoxide **3n** (Racemic mixture).



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.981	27835219	399135	98.489	94.977
2	37.204	427069	21110	1.511	5.023
Total		28262287	420246	100.000	100.000

Figure S72: HPLC chromatogram of epoxide **3n** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 ^oC condition.

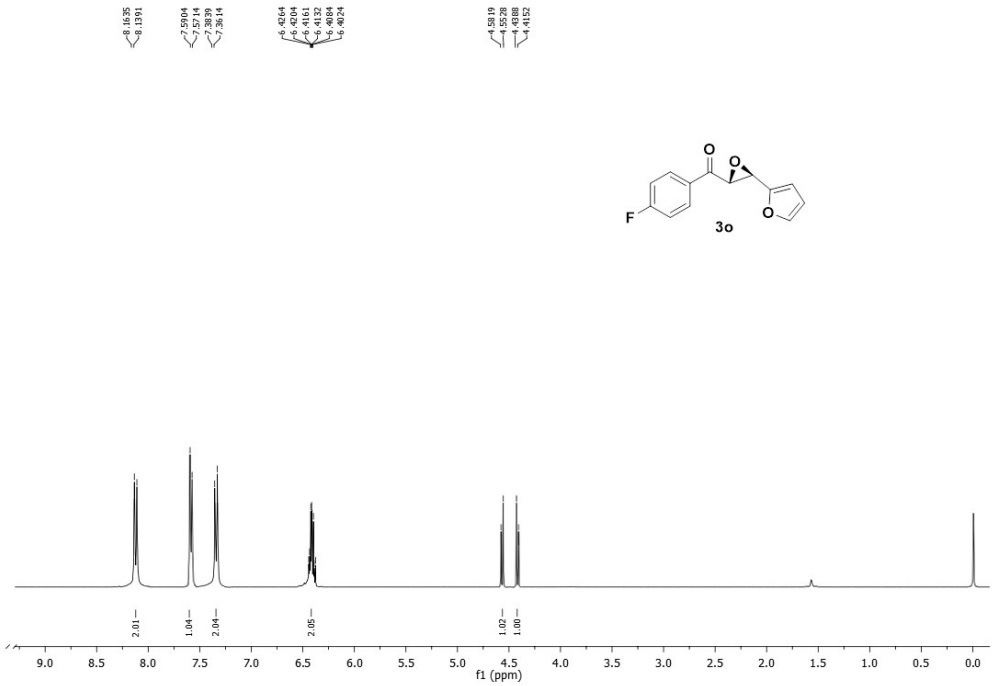


Figure S73: 1H NMR spectrum of epoxide **3o**.

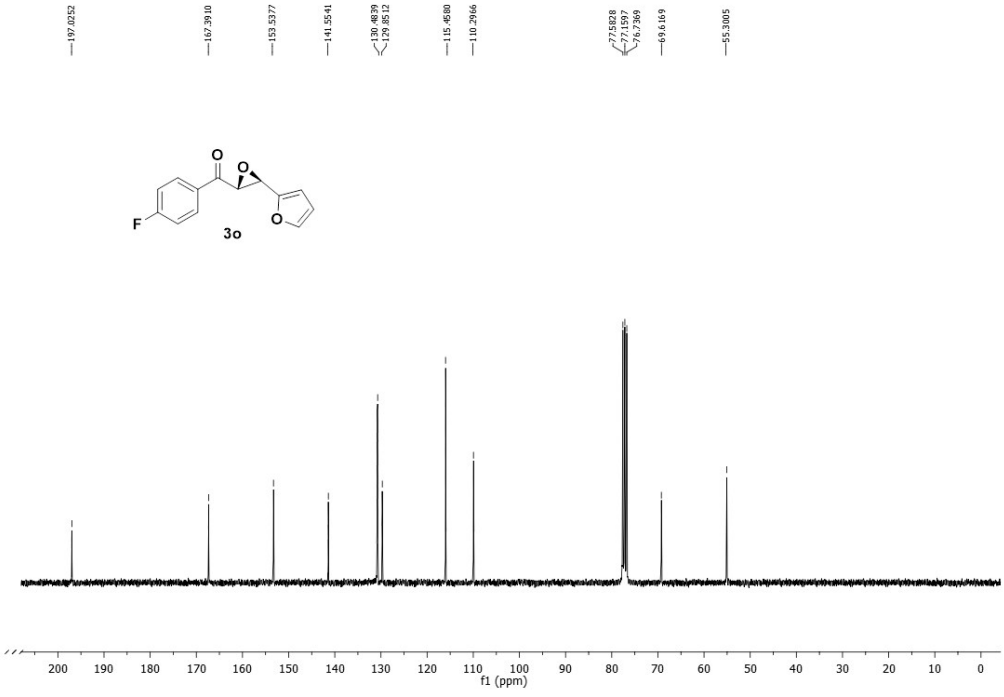
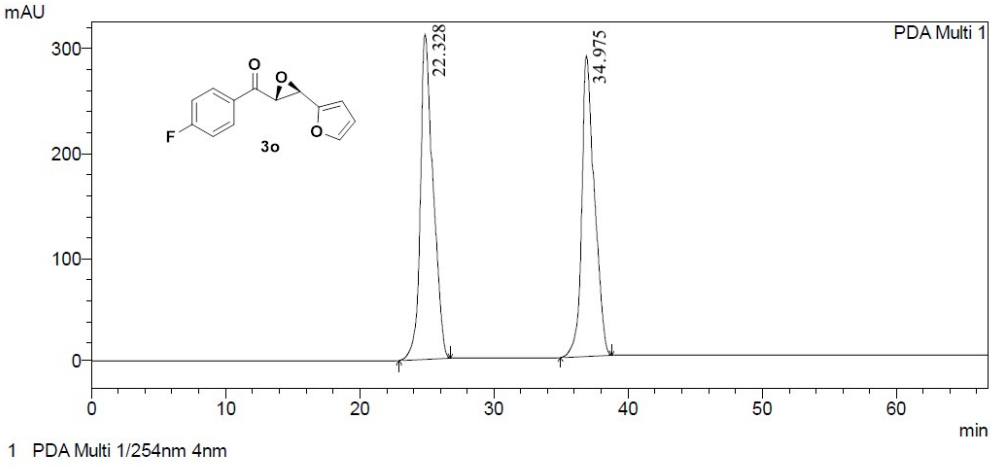


Figure S74: 13C NMR spectrum of epoxide **3o**.

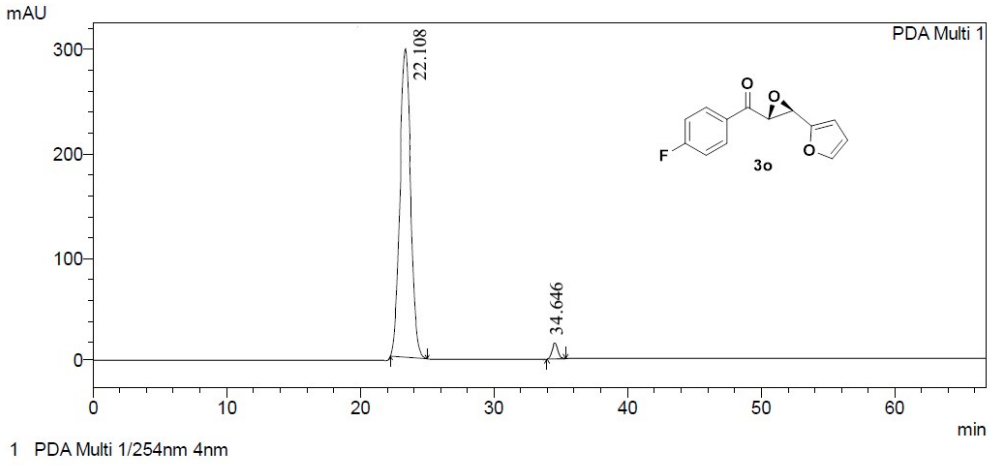


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.328	4120354	196930	50.914	52.714
2	34.975	4011796	185535	49.086	47.286
Total		8132150	382465	100.000	100.000

Figure S75: HPLC chromatogram of epoxide **3o** (Racemic mixture).



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.108	68931819	2182365	98.416	98.087
2	34.646	989860	42564	1.584	1.913
Total		69921680	2224929	100.000	100.000

Figure S76: HPLC chromatogram of epoxide **3o** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 °C condition.

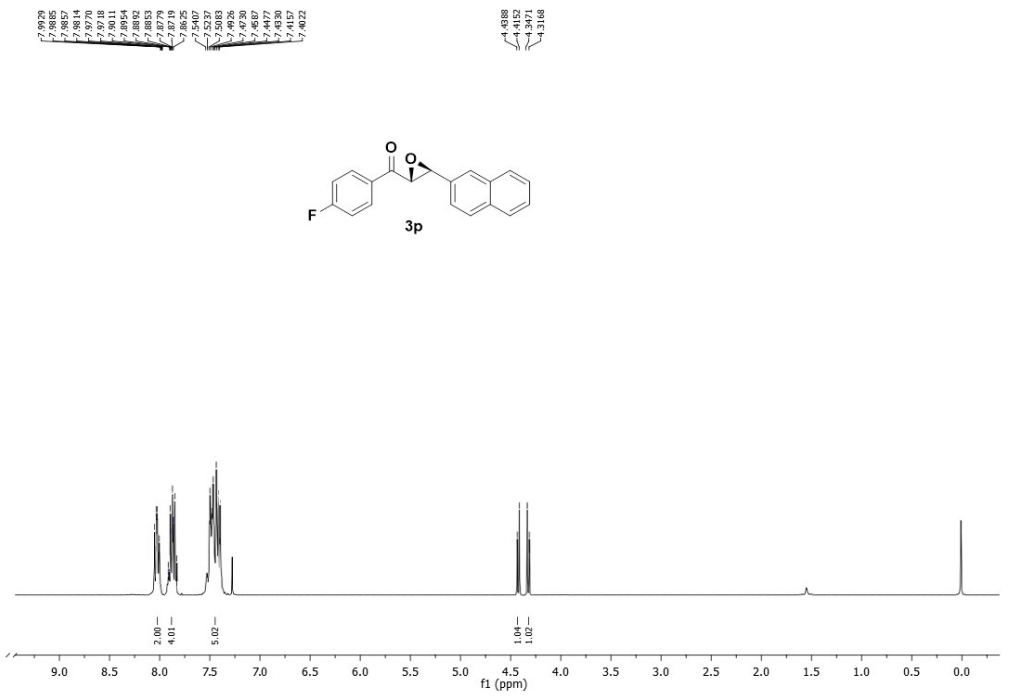


Figure S77: 1H NMR spectrum of epoxide **3p**.

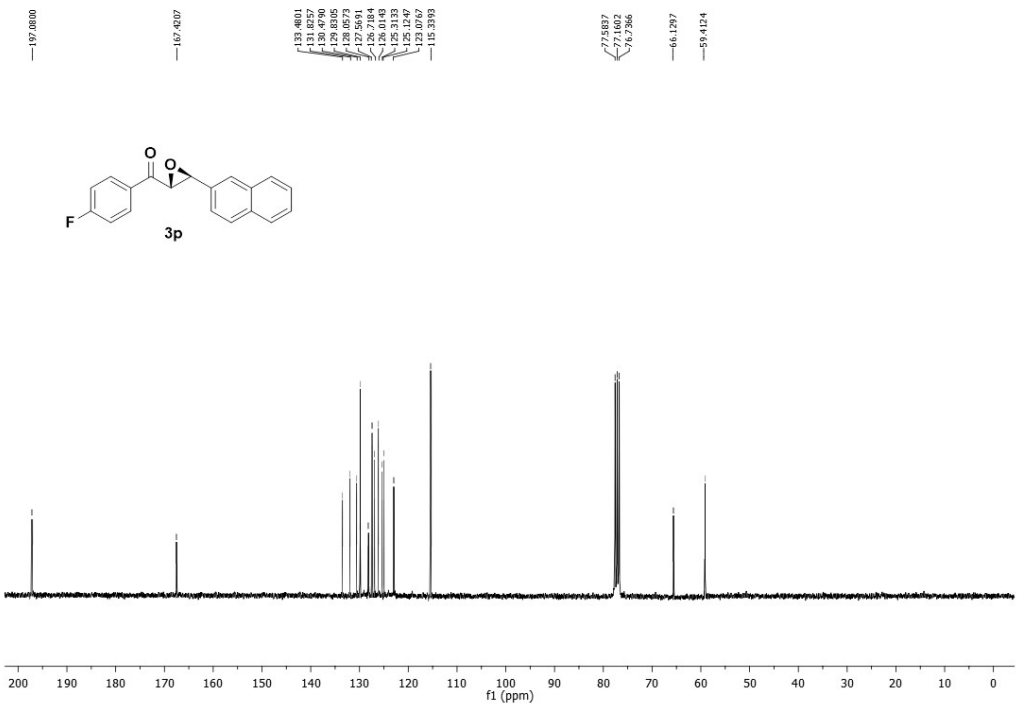
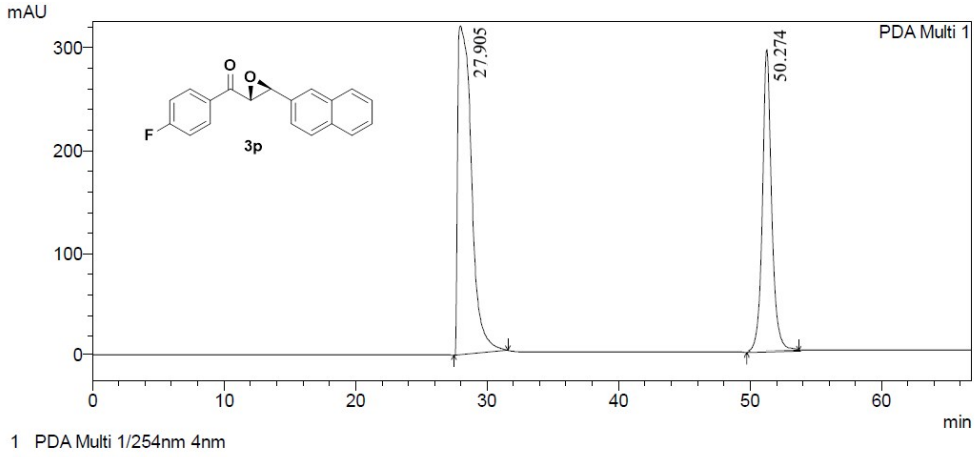


Figure S78: 13C NMR spectrum of epoxide **3p**.

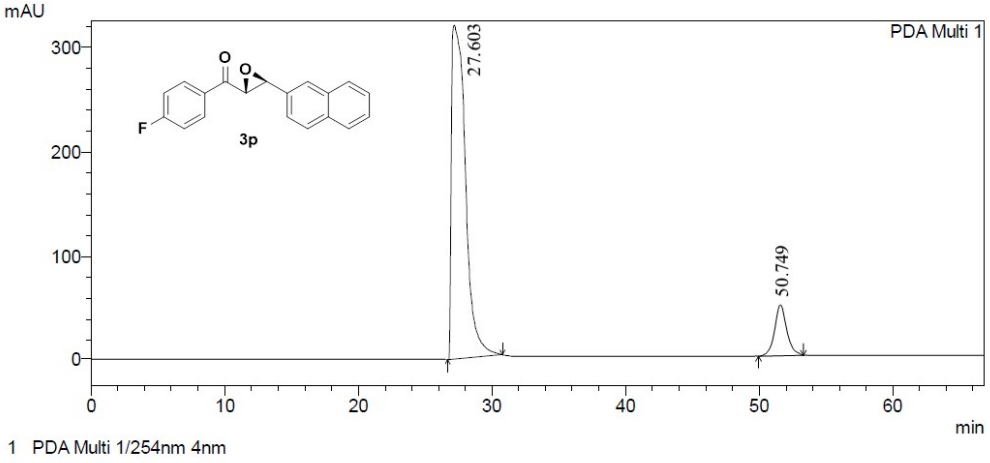


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.905	3986453	97339	50.611	51.579
2	50.274	3859166	95403	49.389	48.421
Total		7845619	192742	100.000	100.000

Figure S79: HPLC chromatogram of epoxide **3p** (Racemic mixture).



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.603	61357098	746211	97.057	93.606
2	50.749	4860393	50970	2.943	6.394
Total		66217491	797180	100.000	100.000

Figure S80: HPLC chromatogram of epoxide **3p** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 °C condition.

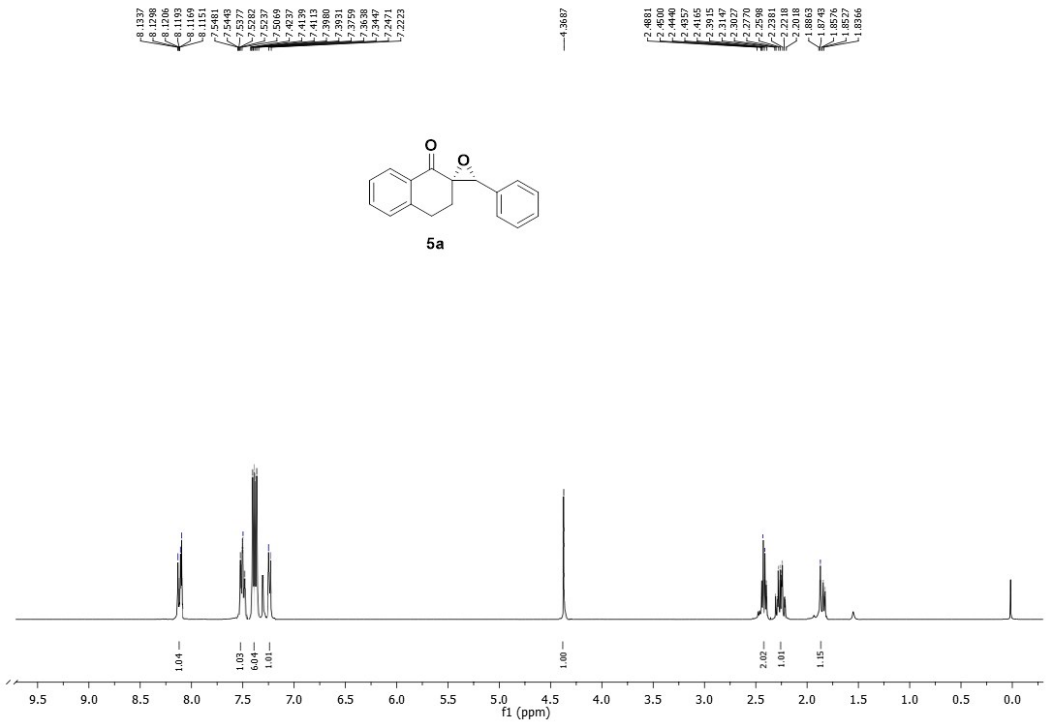


Figure S81: 1H NMR spectrum of epoxide **5a**.

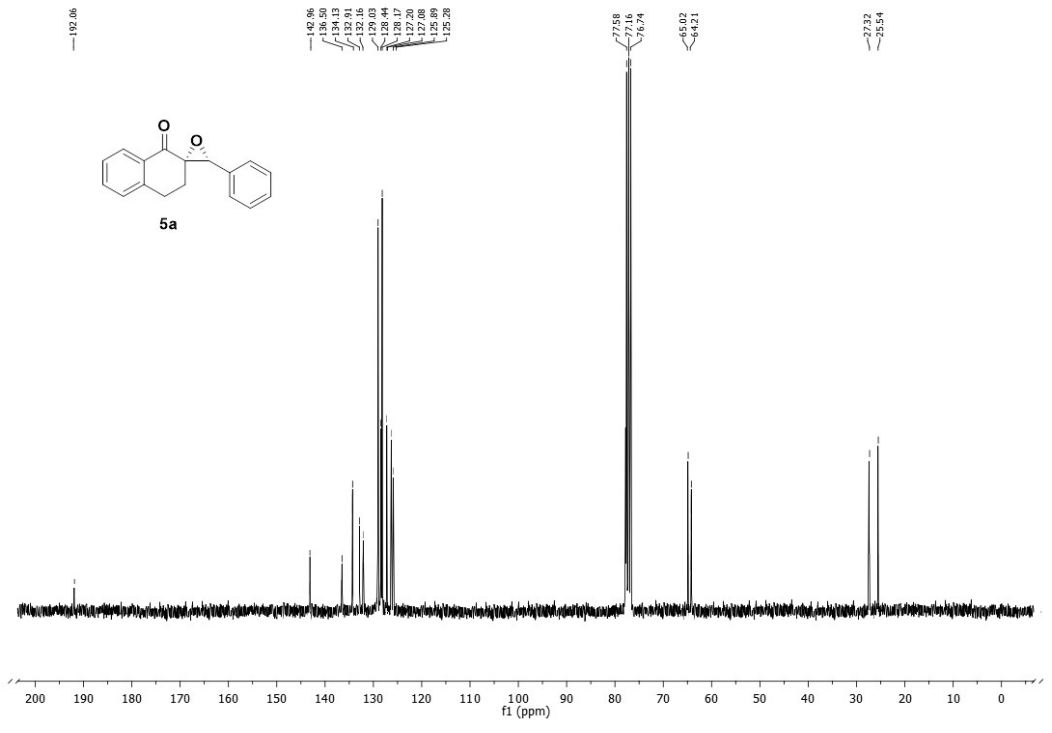
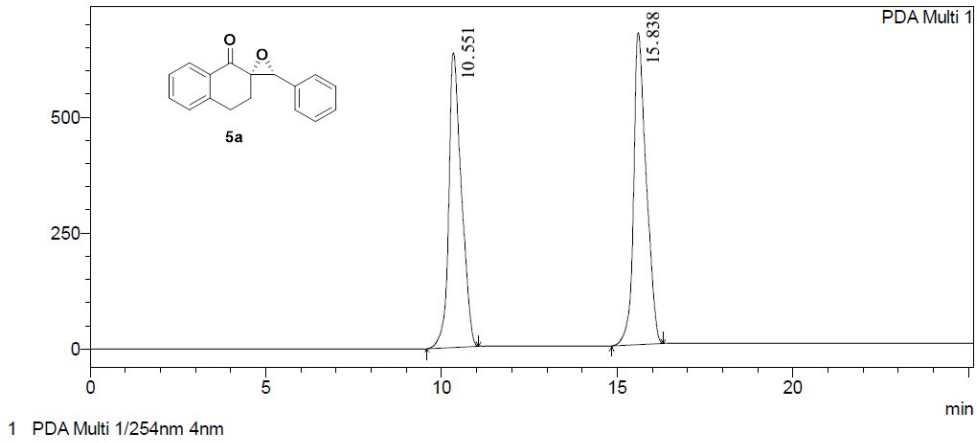


Figure S82: 13C NMR spectrum of epoxide **5a**.



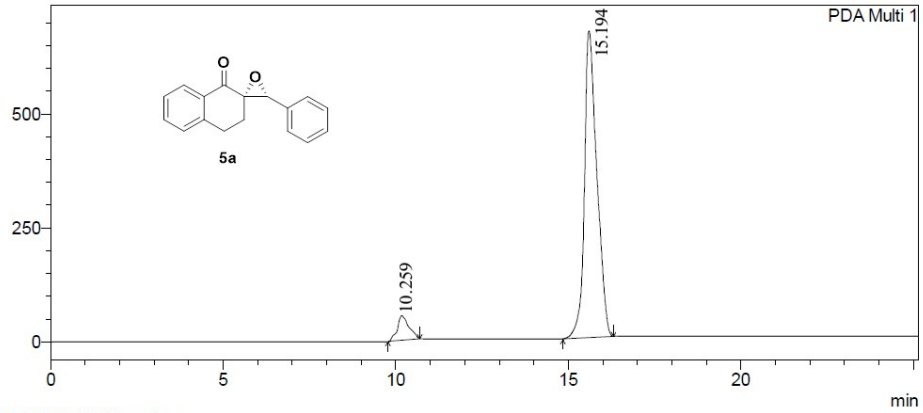
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.551	6338383	83187	49.326	48.090
2	15.838	6412071	85516	50.674	51.910
Total		12750455	168703	100.000	100.000

Figure S83: HPLC chromatogram of epoxide **5a** (Racemic mixture).



1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.259	84159	819	1.470	0.779
2	15.194	5641798	104287	98.530	99.221
Total		5725958	105106	100.000	100.000

Figure S84: HPLC chromatogram of epoxide **5a** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 ^oC condition.

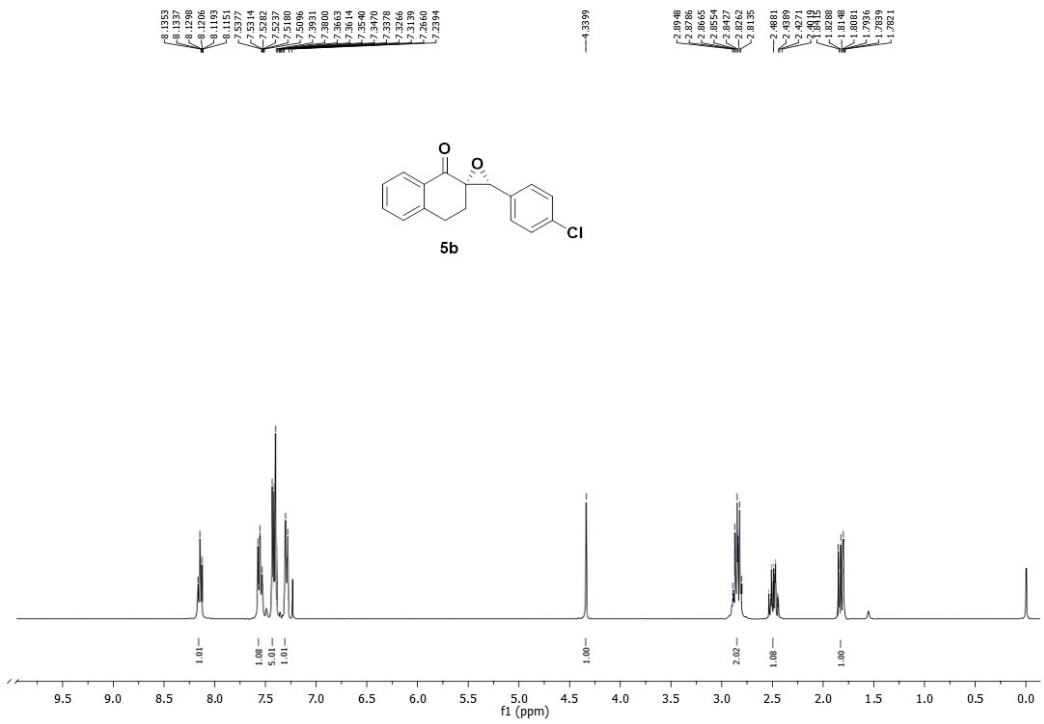


Figure S85: 1H NMR spectrum of epoxide **5b**.

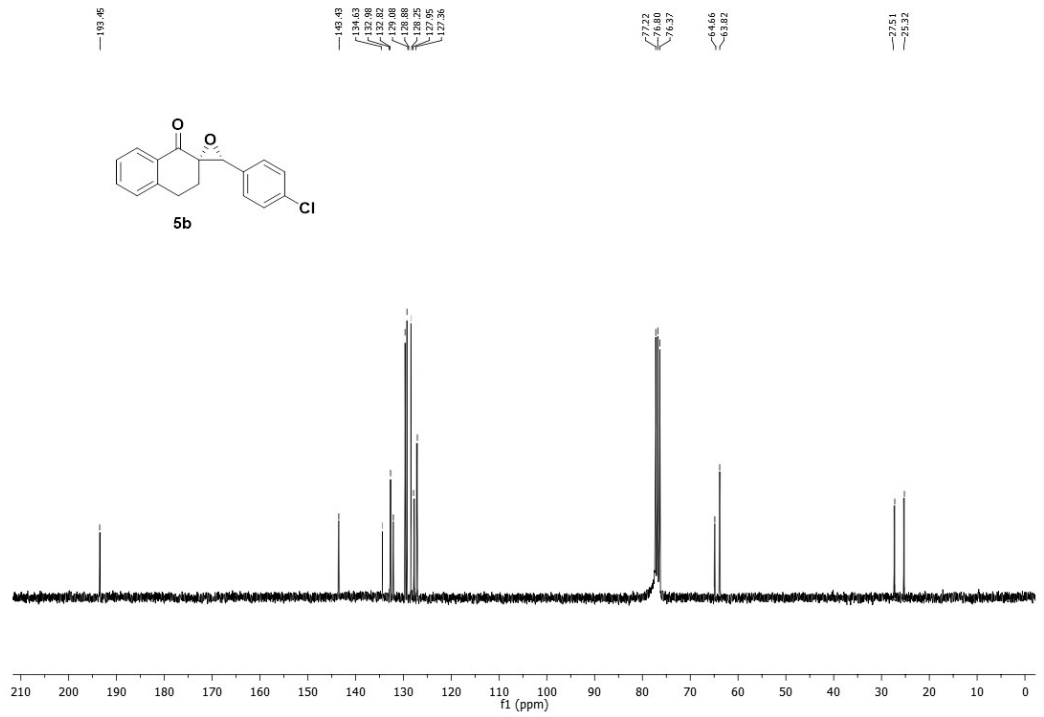
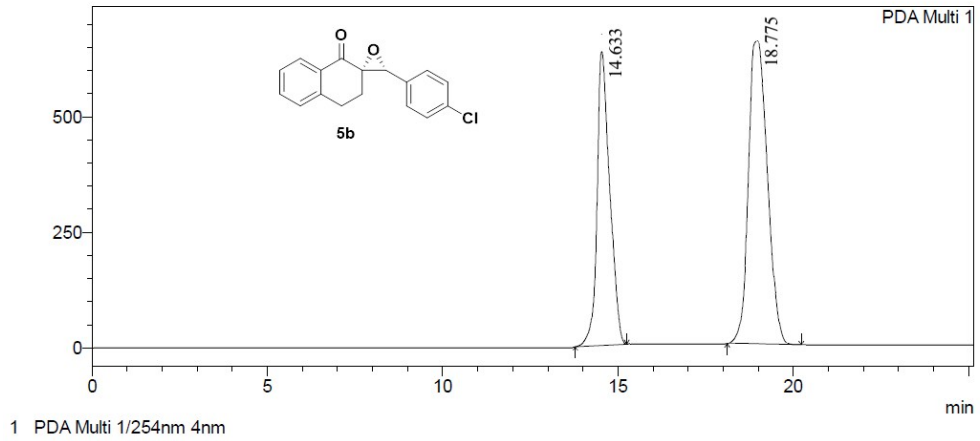


Figure S86: 13C NMR spectrum of epoxide **5b**.



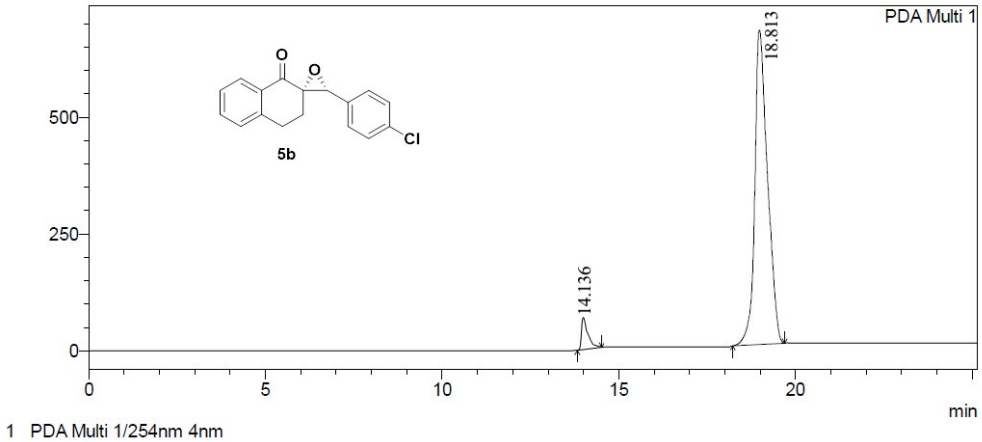
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.633	1877623	8633	49.784	48.360
2	18.775	1973568	8839	50.216	51.640
Total		3851191	17472	100.000	100.000

Figure S87: HPLC chromatogram of epoxide **5b** (Racemic mixture).



1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.136	751420	46813	1.182	5.836
2	18.813	62830428	755323	98.818	94.164
Total		63581847	802136	100.000	100.000

Figure S88: HPLC chromatogram of epoxide **5b** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 ^oC condition.

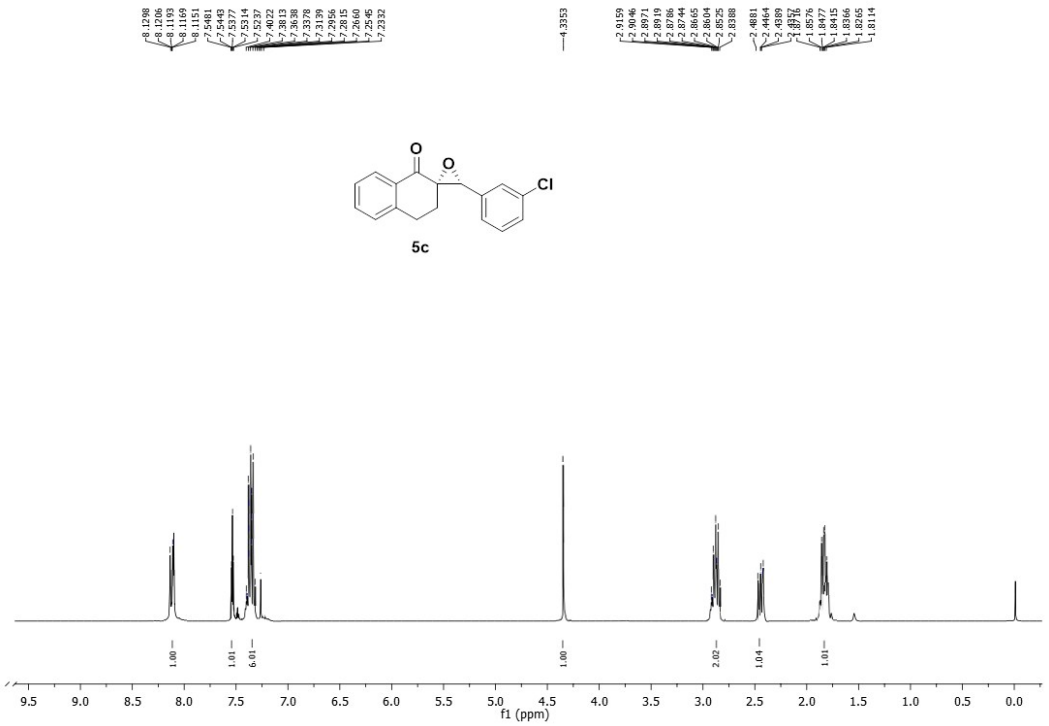


Figure S89: 1H NMR spectrum of epoxide **5c**.

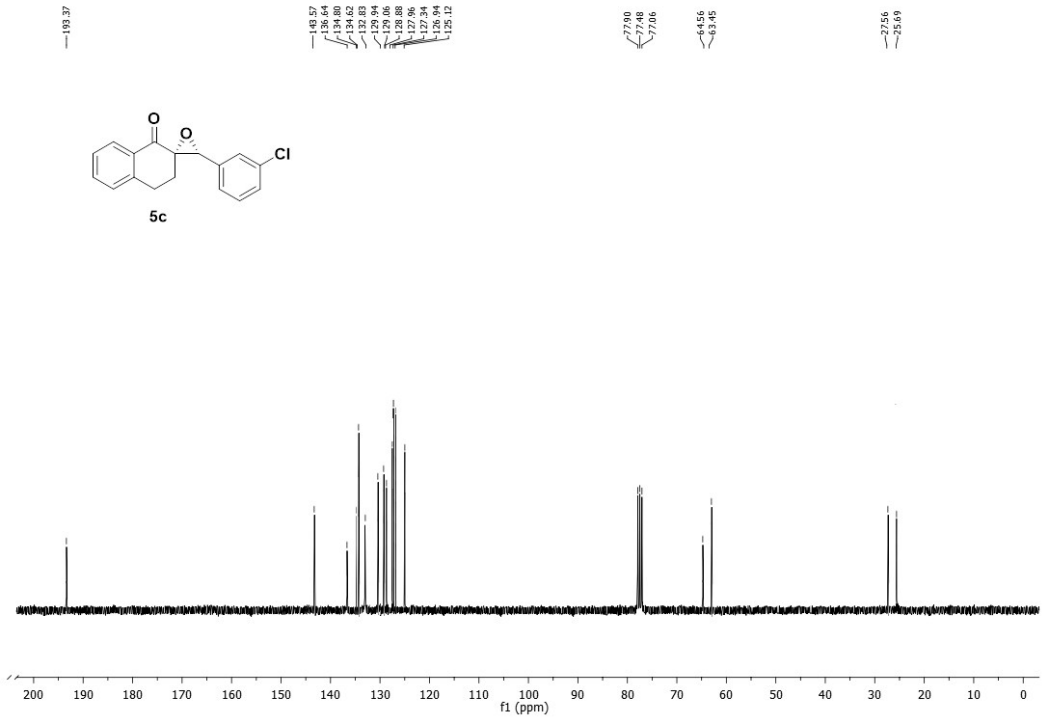
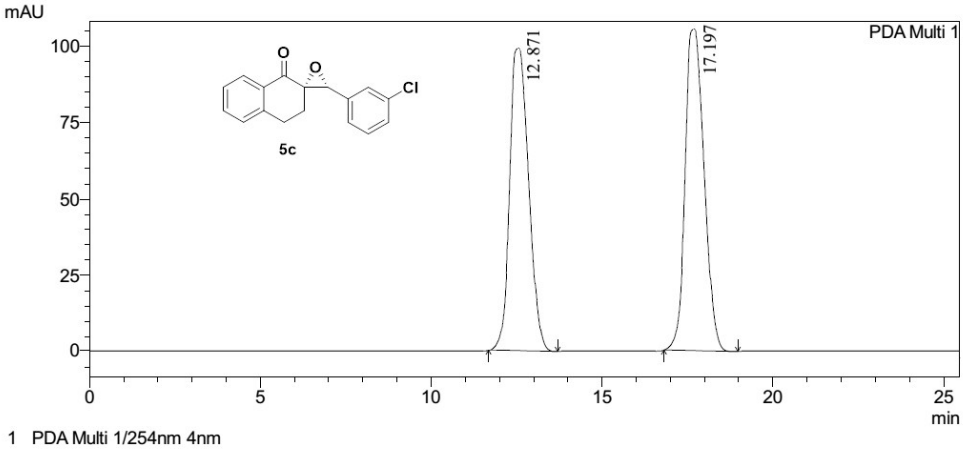


Figure S90: 13C NMR spectrum of epoxide **5c**.



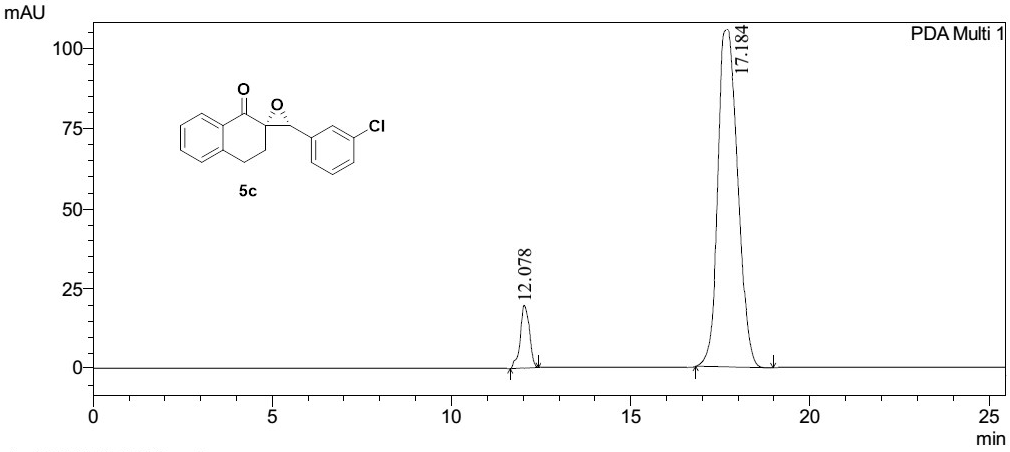
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.871	2066695	115427	2.129	27.502
2	17.197	95011537	304278	97.871	72.498
Total		97078231	419705	100.000	100.000

Figure S91: HPLC chromatogram of epoxide **5c** (Racemic mixture).



1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.078	2066695	115427	2.129	27.502
2	17.184	95011537	304278	97.871	72.498
Total		97078231	419705	100.000	100.000

Figure S92: HPLC chromatogram of epoxide **5c** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 °C condition.

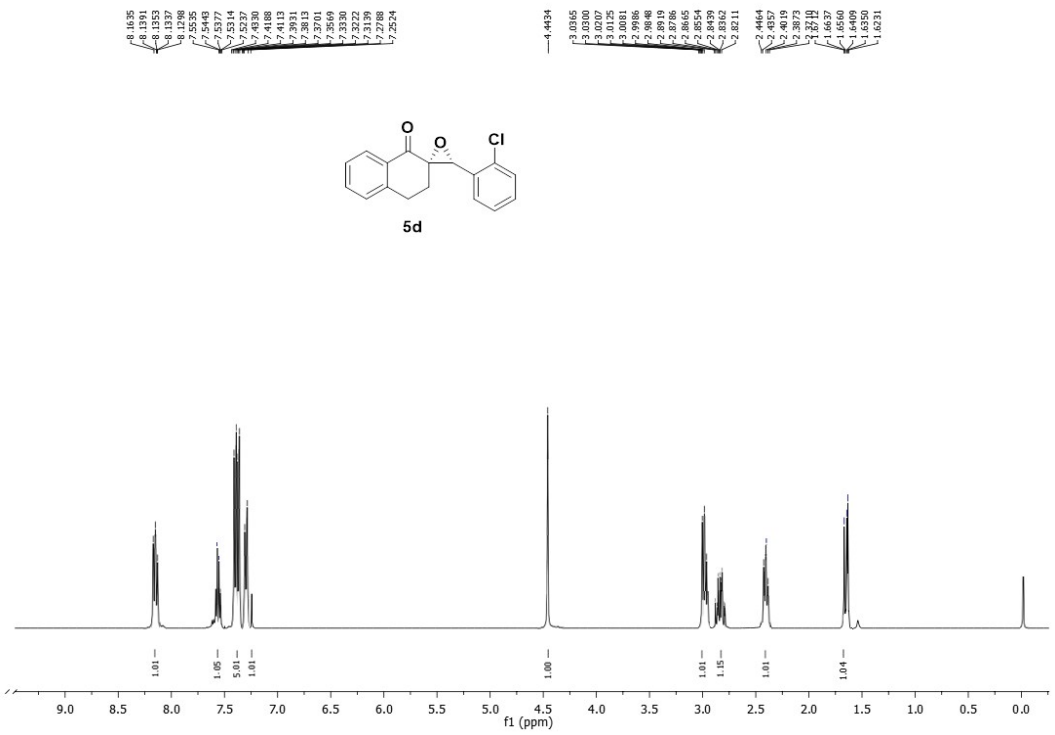


Figure S93: 1H NMR spectrum of epoxide **5d**.

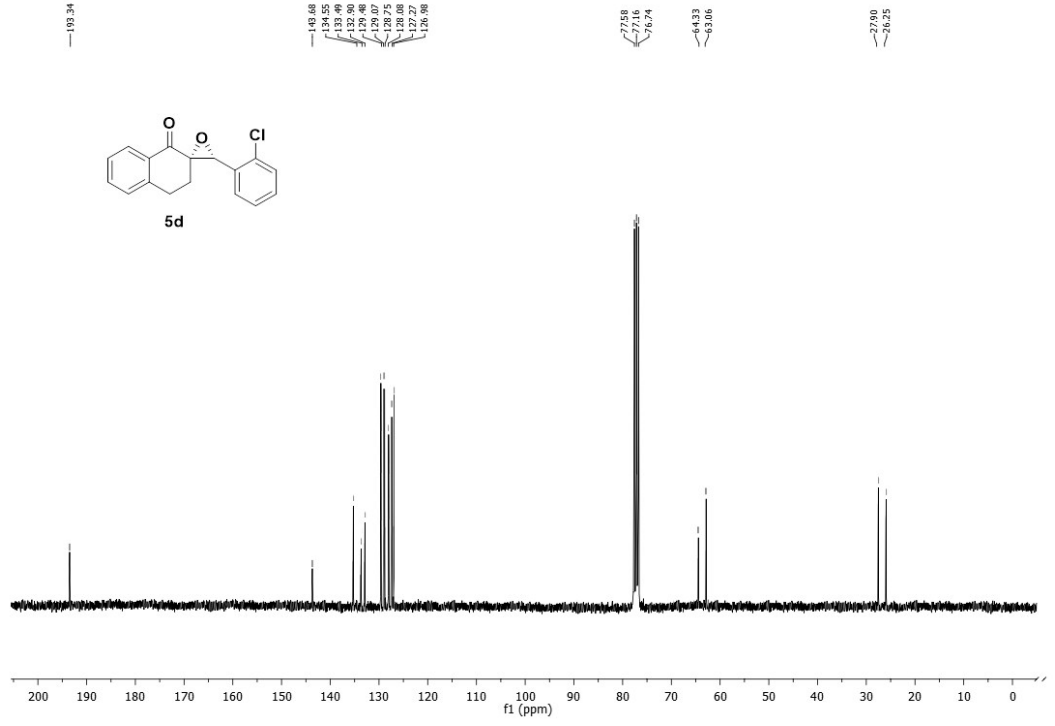
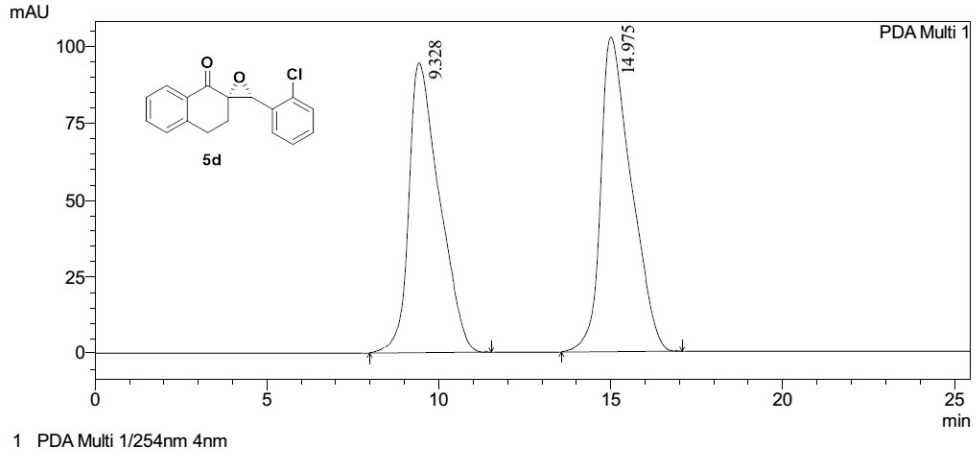


Figure S94: 13C NMR spectrum of epoxide **5d**.



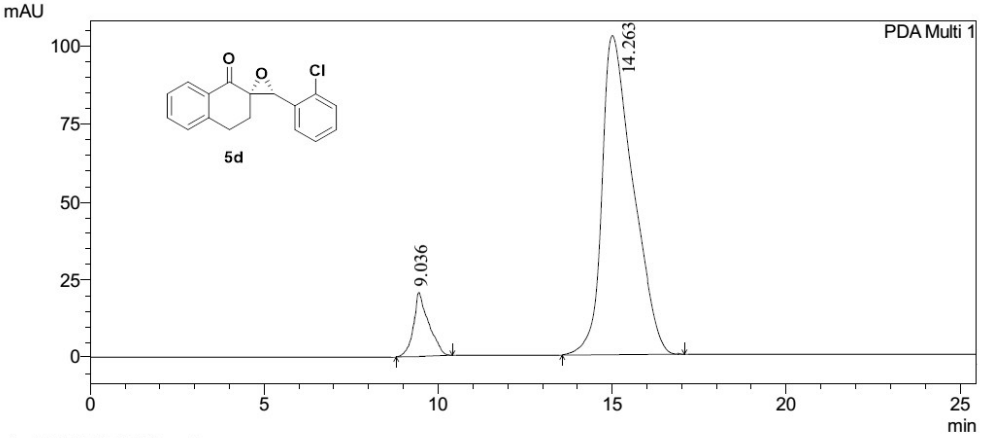
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 244nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.328	4011796	185535	49.086	47.286
2	14.975	4120354	196930	50.914	52.714
Total		8132150	382465	100.000	100.000

Figure S95: HPLC chromatogram of epoxide **5d** (Racemic mixture).



1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.036	54454	605	4.791	15.650
2	14.263	1082036	3263	95.209	84.350
Total		1136491	3868	100.000	100.000

Figure S96: HPLC chromatogram of epoxide **5d** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 ^oC condition.

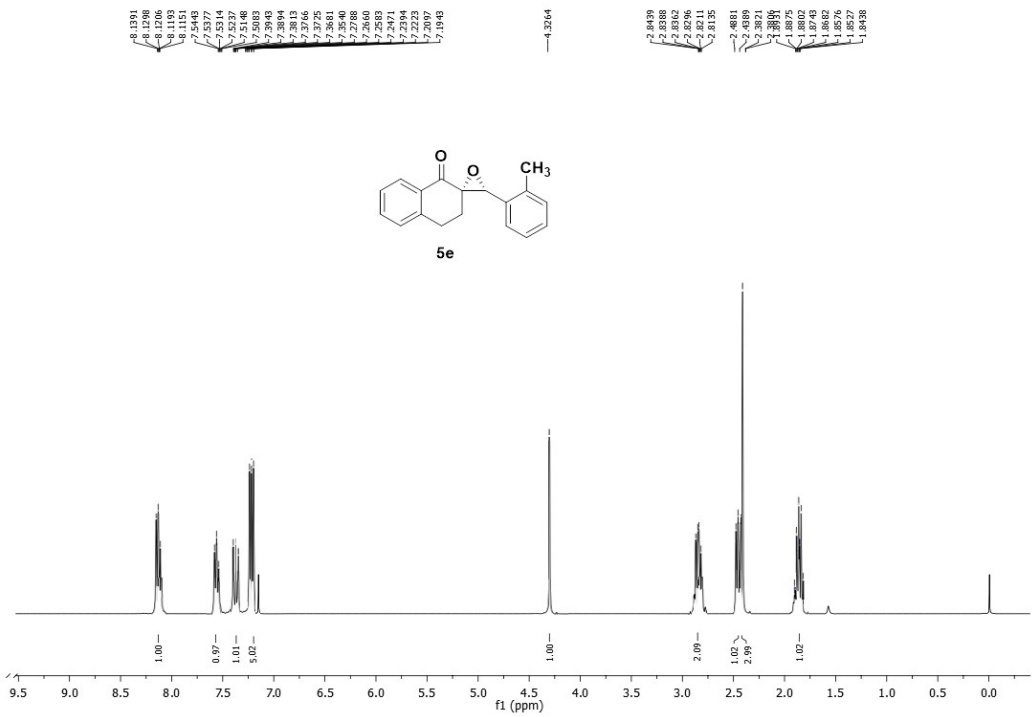


Figure S97: 1H NMR spectrum of epoxide **5e**.

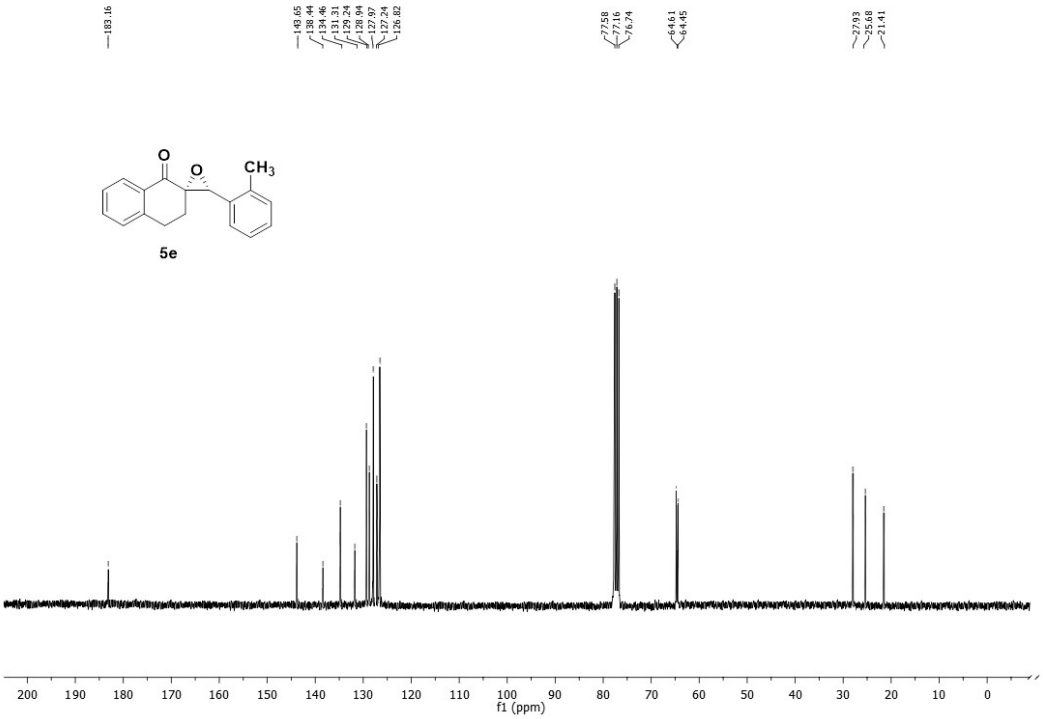
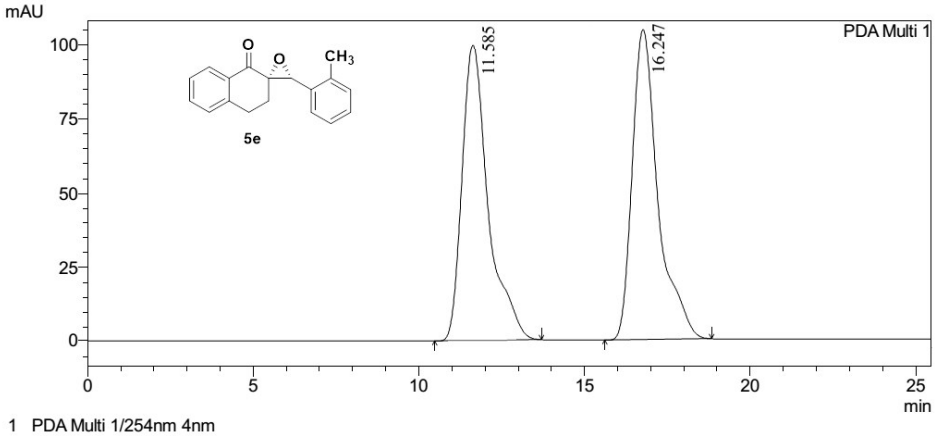


Figure S98: 13C NMR spectrum of epoxide **5e**.



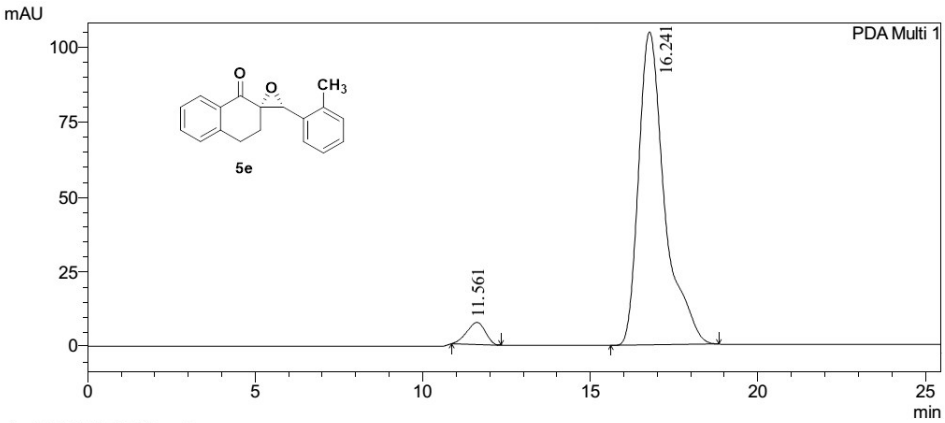
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.585	35721829	371448	49.247	48.174
2	16.247	36525852	399404	50.753	51.826
Total		72247681	770851	100.000	100.000

Figure S99: HPLC chromatogram of epoxide **5e** (Racemic mixture).



1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.561	11972419	110813	7.683	6.949
2	16.241	143863194	1483918	92.317	93.051
Total		155835613	1594731	100.000	100.000

Figure S100: HPLC chromatogram of epoxide **5e** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 ^oC condition.

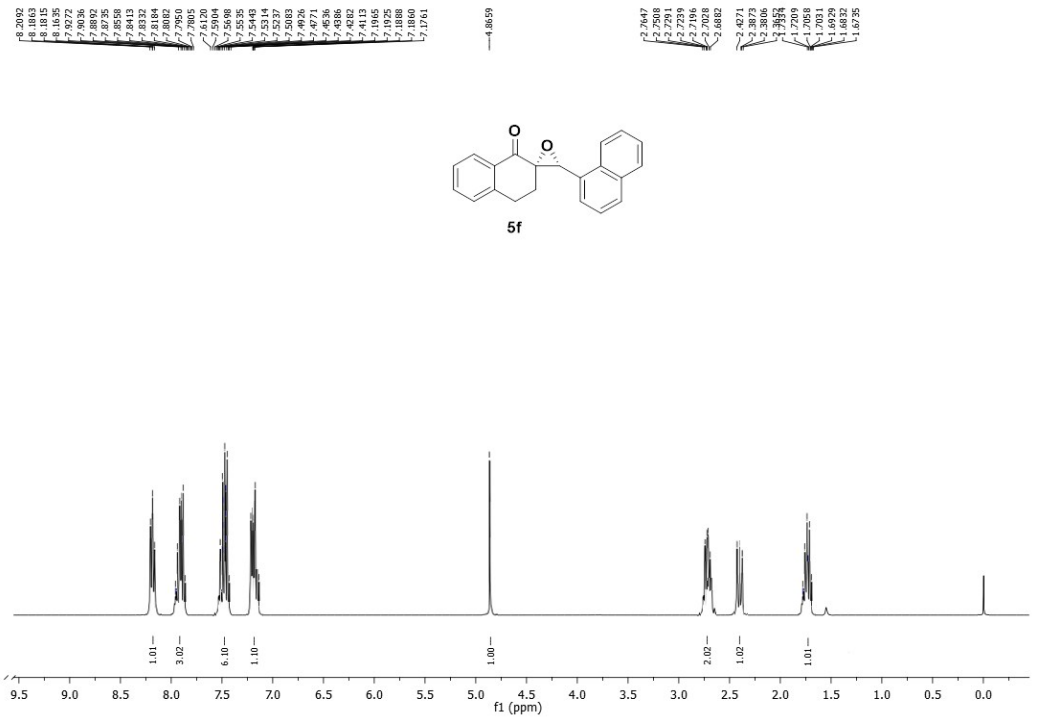


Figure S101: 1H NMR spectrum of epoxide **5f**.

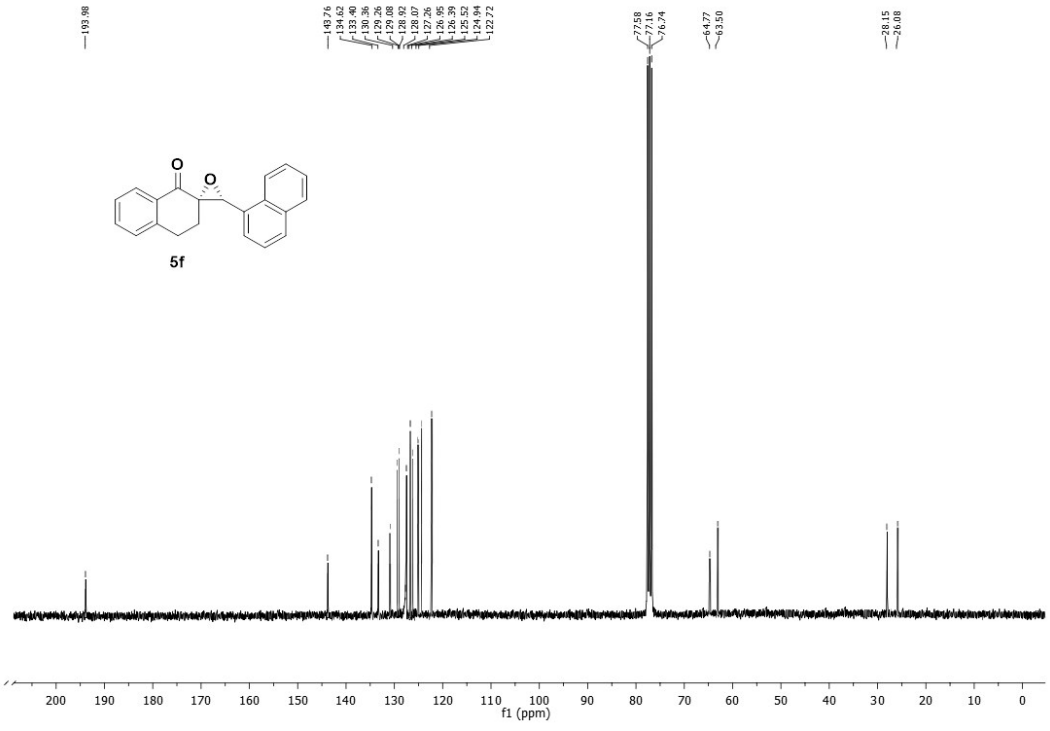
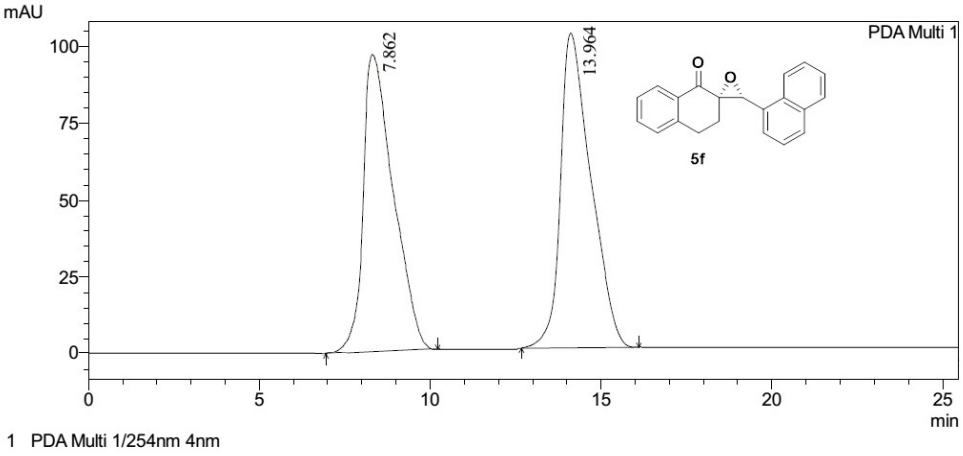


Figure S102: 13C NMR spectrum of epoxide **5f**.



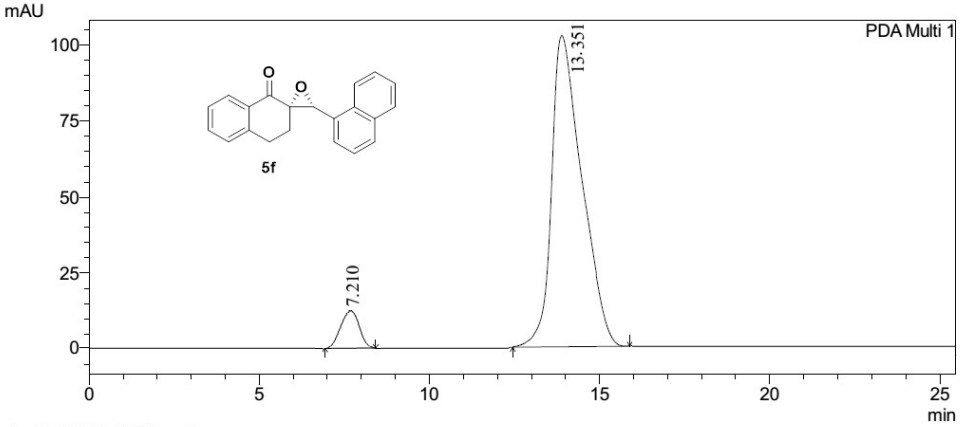
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.862	142638897	1365126	49.259	48.206
2	13.964	143622513	1483220	50.741	51.794
Total		286261409	2848346	100.000	100.000

Figure S103: HPLC chromatogram of epoxide **5f** (Racemic mixture).



1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.210	838351	21549	2.999	5.171
2	13.351	27112859	395206	97.001	94.829
Total		27951210	416755	100.000	100.000

Figure S104: HPLC chromatogram of epoxide **5f** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 ^oC condition.

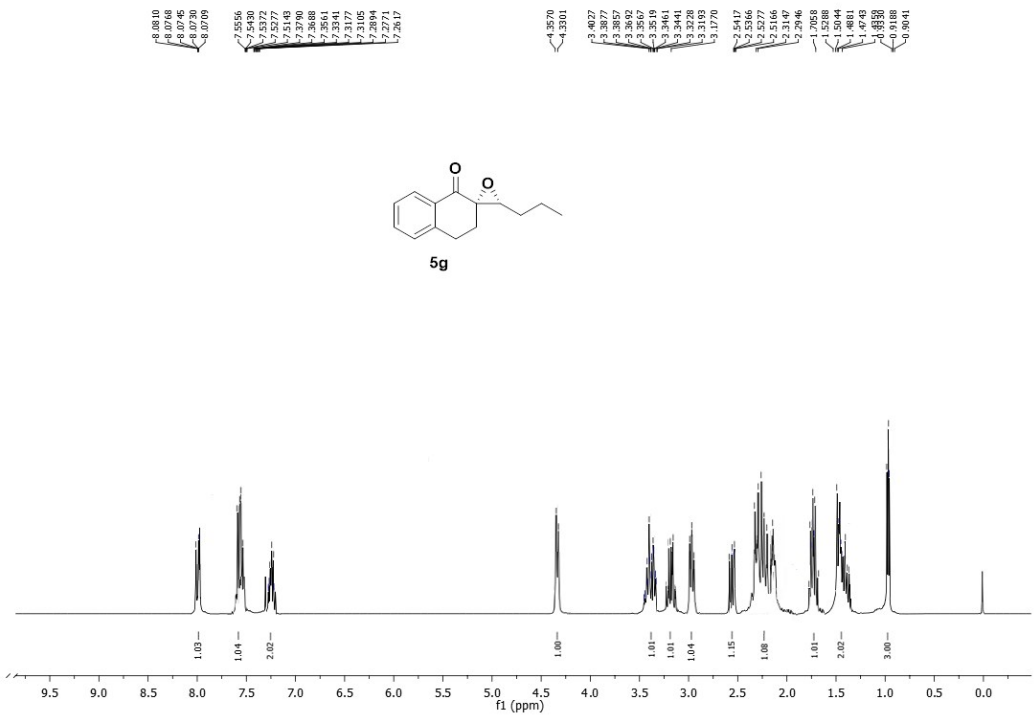


Figure S105: 1H NMR spectrum of epoxide **5g**.

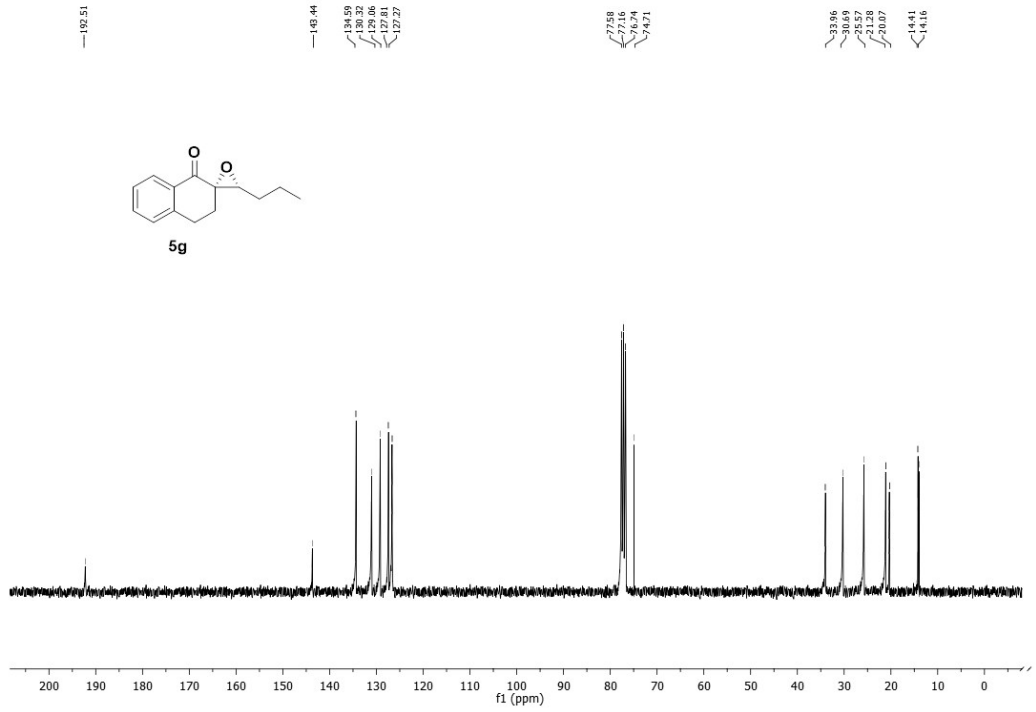
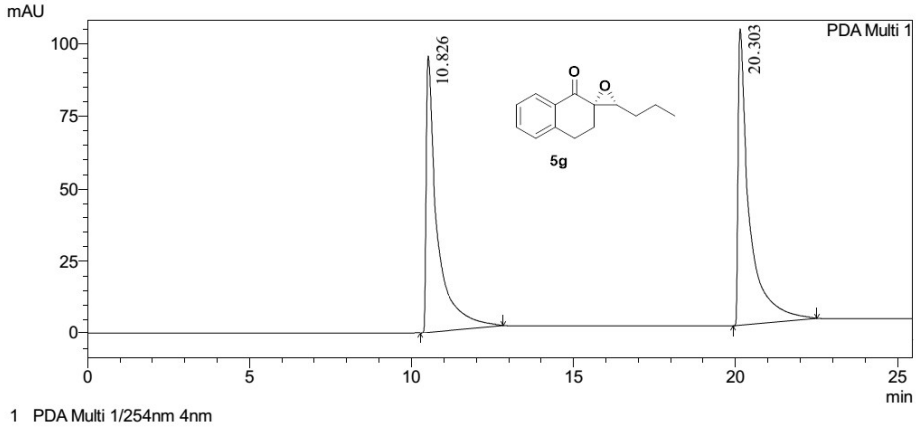


Figure S106: 13C NMR spectrum of epoxide **5g**.

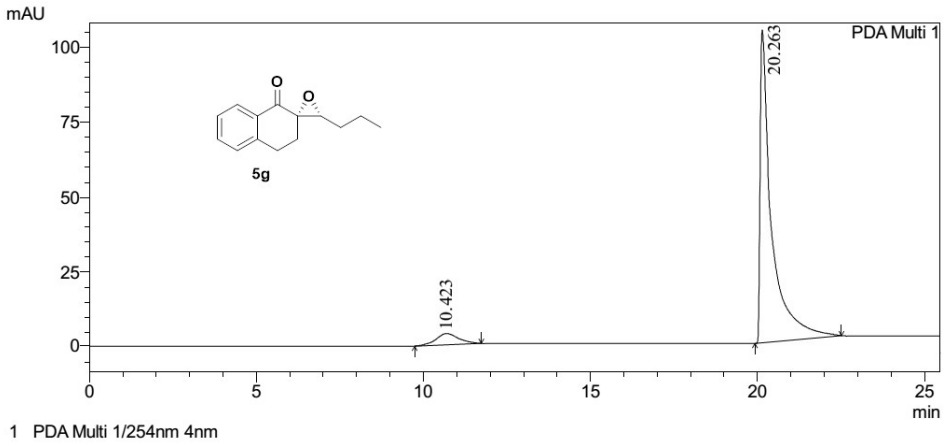


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.826	6338383	83187	49.326	48.090
2	20.303	6412071	85516	50.674	51.910
Total		12750455	168703	100.000	100.000

Figure S107: HPLC chromatogram of epoxide **5g** (Racemic mixture).



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.423	3384812	69886	3.933	7.730
2	20.263	82677818	834234	96.067	92.270
Total		86062630	904119	100.000	100.000

Figure S108: HPLC chromatogram of epoxide **5g** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in –10 °C condition.

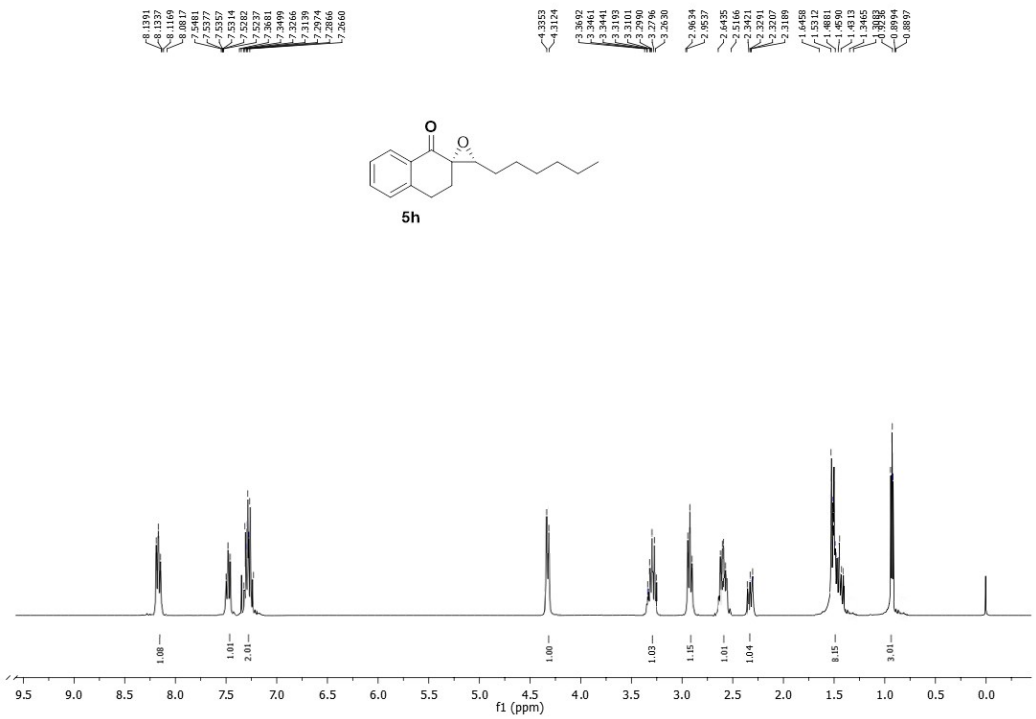


Figure S109: 1H NMR spectrum of epoxide **5h**.

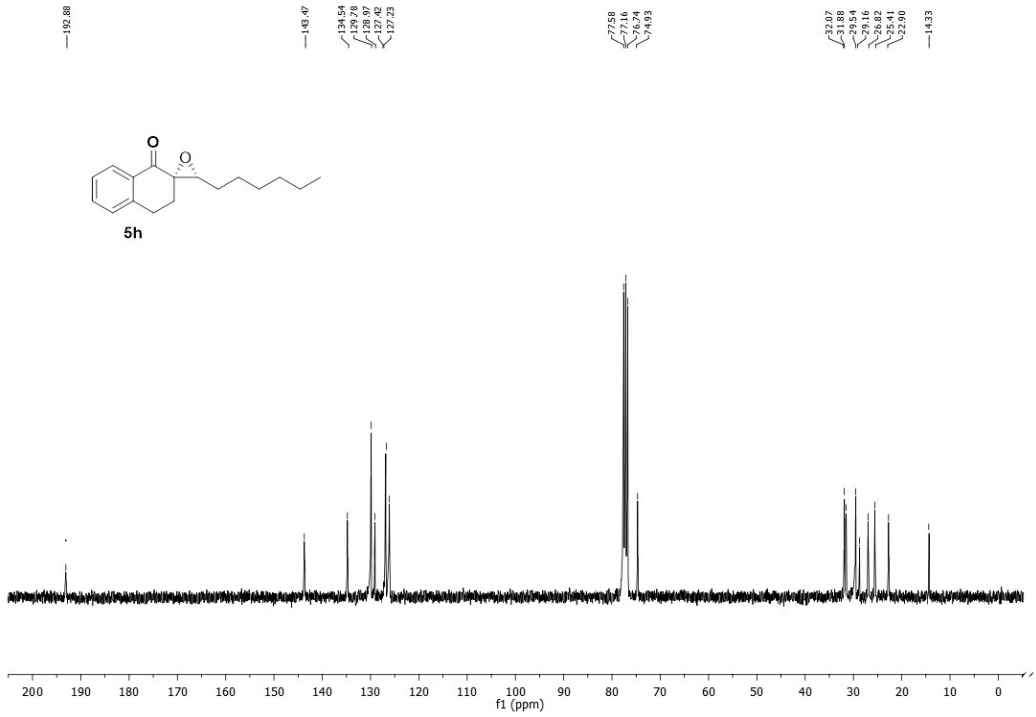
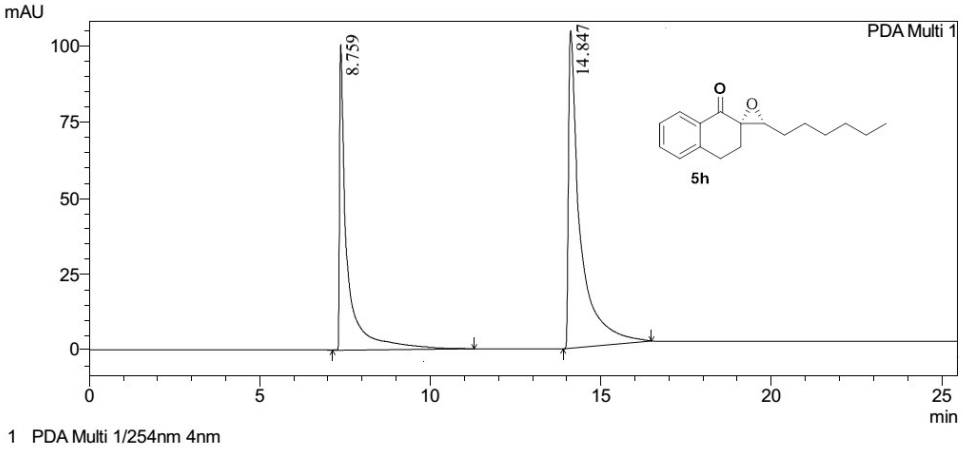


Figure S110: 13C NMR spectrum of epoxide **5h**.

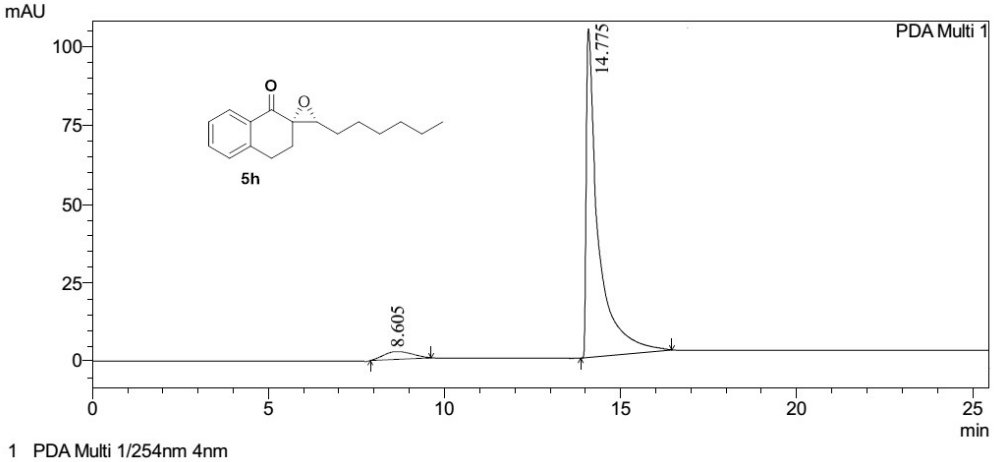


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.759	1222762	8981	49.643	48.704
2	14.847	1362622	9131	50.357	51.296
Total		2585384	18112	100.000	100.000

Figure S111: HPLC chromatogram of epoxide **5h** (Racemic mixture).



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.605	148617	5305	3.481	2.623
2	14.775	4120354	196930	96.519	97.377
Total		4268971	202235	100.000	100.000

Figure S112: HPLC chromatogram of epoxide **5h** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in –10 ^oC condition.

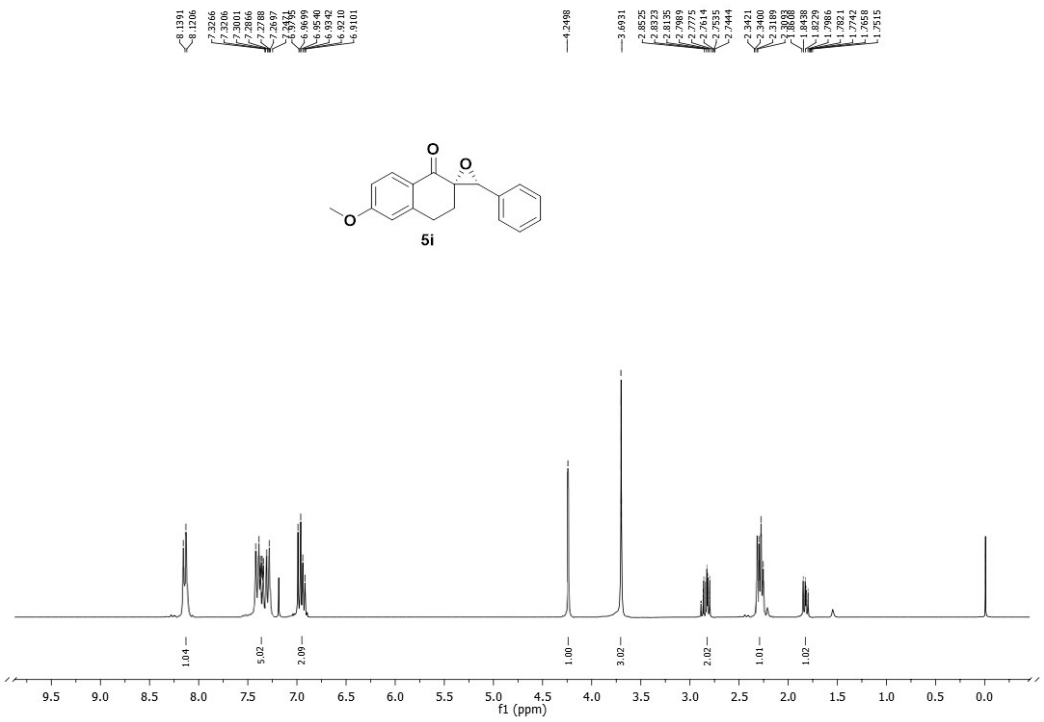


Figure S113: 1H NMR spectrum of epoxide **5i**.

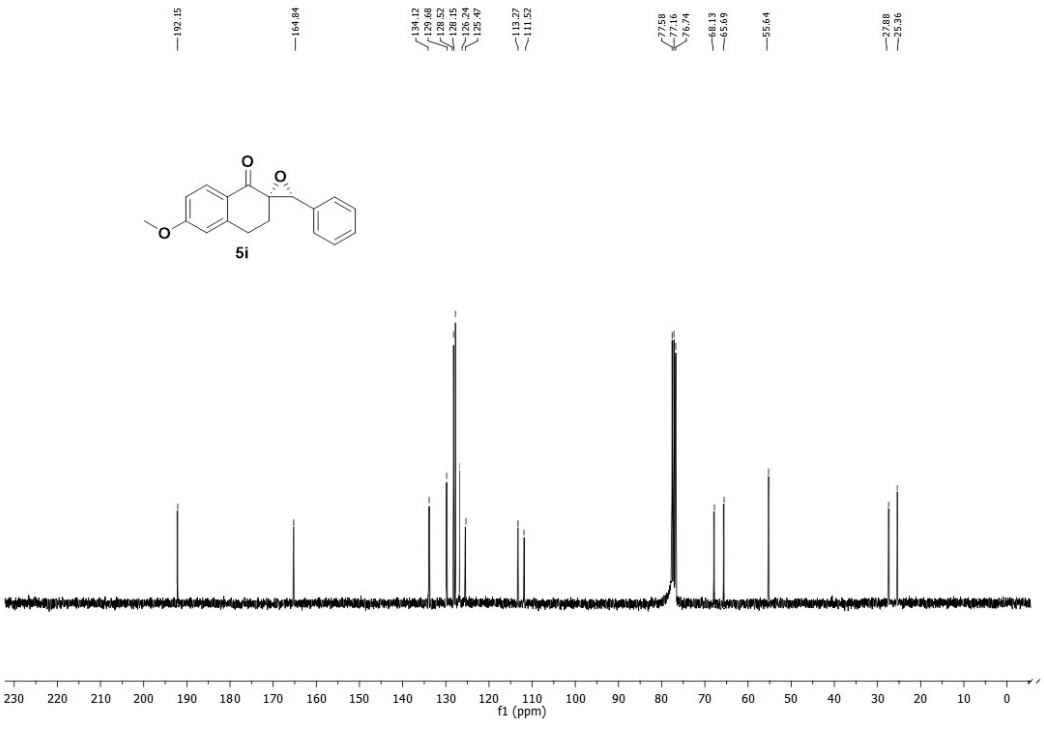
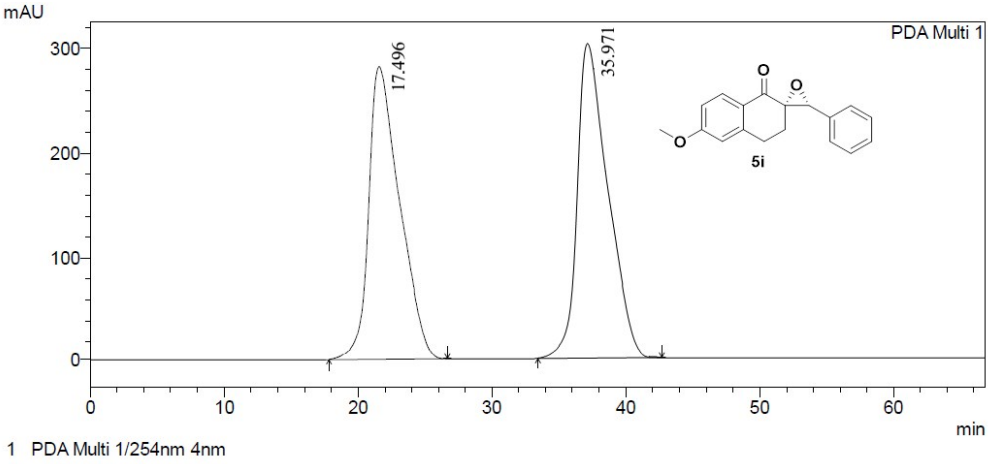


Figure S114: 13C NMR spectrum of epoxide **5i**.

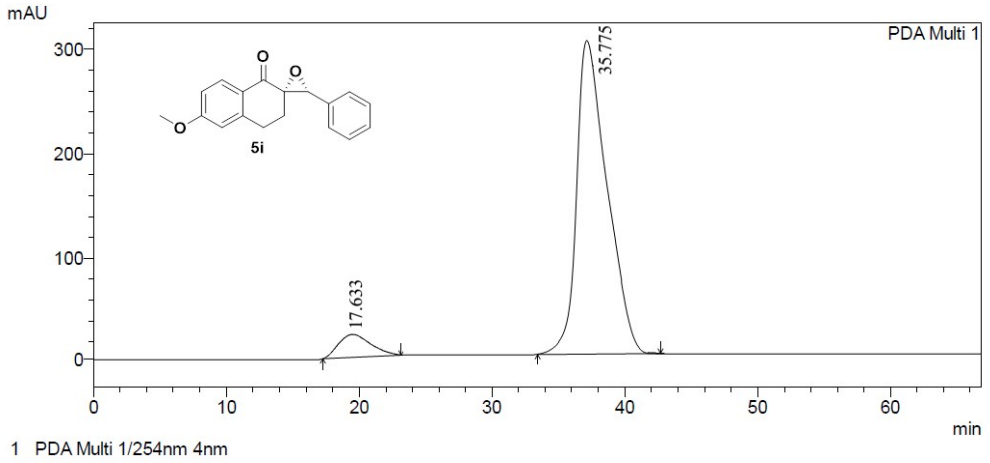


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.496	19741162	230817	49.786	48.630
2	35.971	20622334	254758	50.214	51.370
Total		40363496	485575	100.000	100.000

Figure S115: HPLC chromatogram of epoxide **5i** (Racemic mixture).



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.633	77623	1133	3.784	11.360
2	35.775	1973568	8839	96.216	88.640
Total		2051191	9971	100.000	100.000

Figure S116: HPLC chromatogram of epoxide **5i** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 ^oC condition.

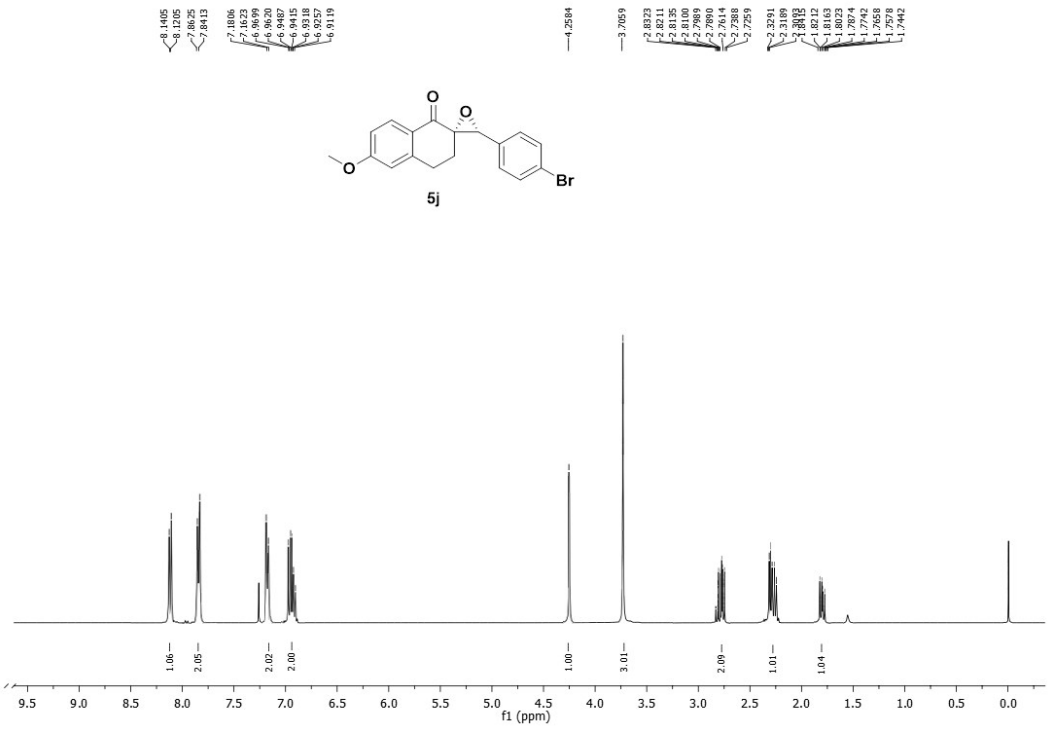


Figure S117: 1H NMR spectrum of epoxide **5j**.

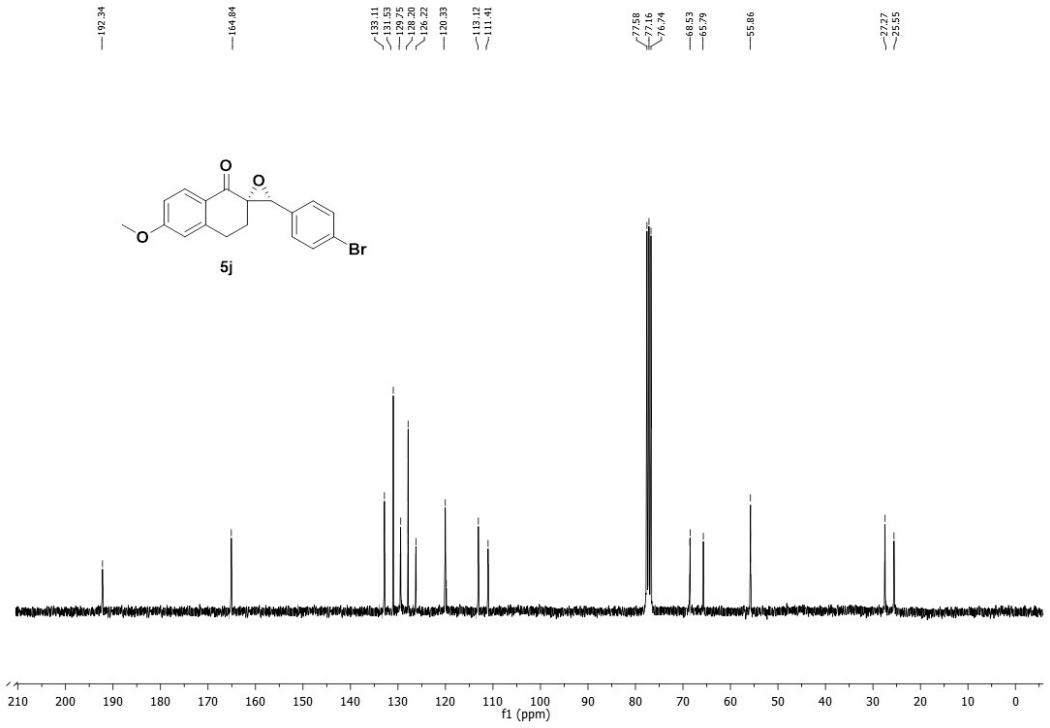
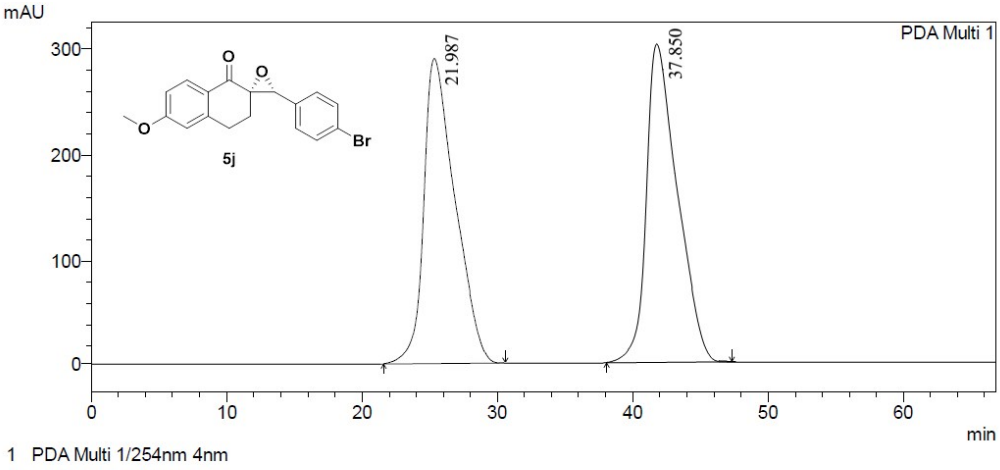


Figure S118 13C NMR spectrum of epoxide **5j**.

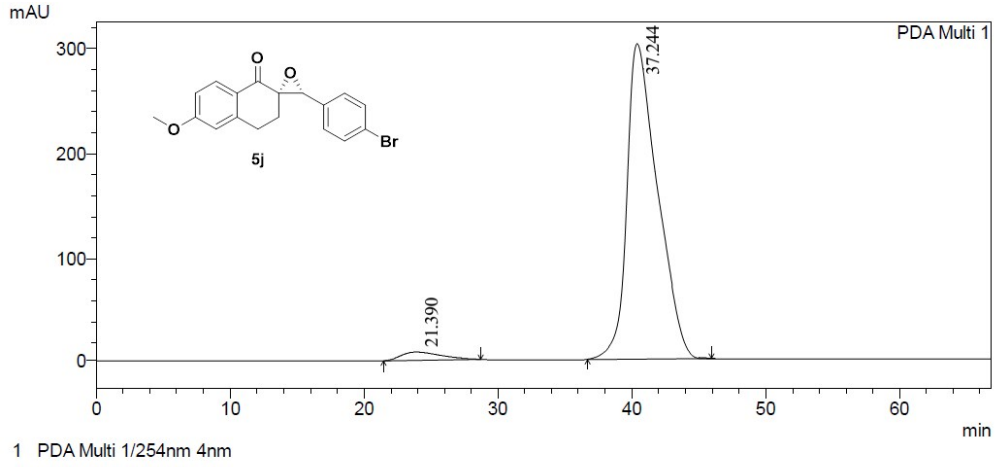


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.987	5517457	97410	49.838	48.631
2	37.850	5653681	104342	50.162	51.369
Total		11171138	201752	100.000	100.000

Figure S119: HPLC chromatogram of epoxide **5j** (Racemic mixture).



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.390	983580	48963	2.555	6.111
2	37.244	62251896	752263	98.445	93.889
Total		63235475	801226	100.000	100.000

Figure S120: HPLC chromatogram of epoxide **5j** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 ^oC condition.

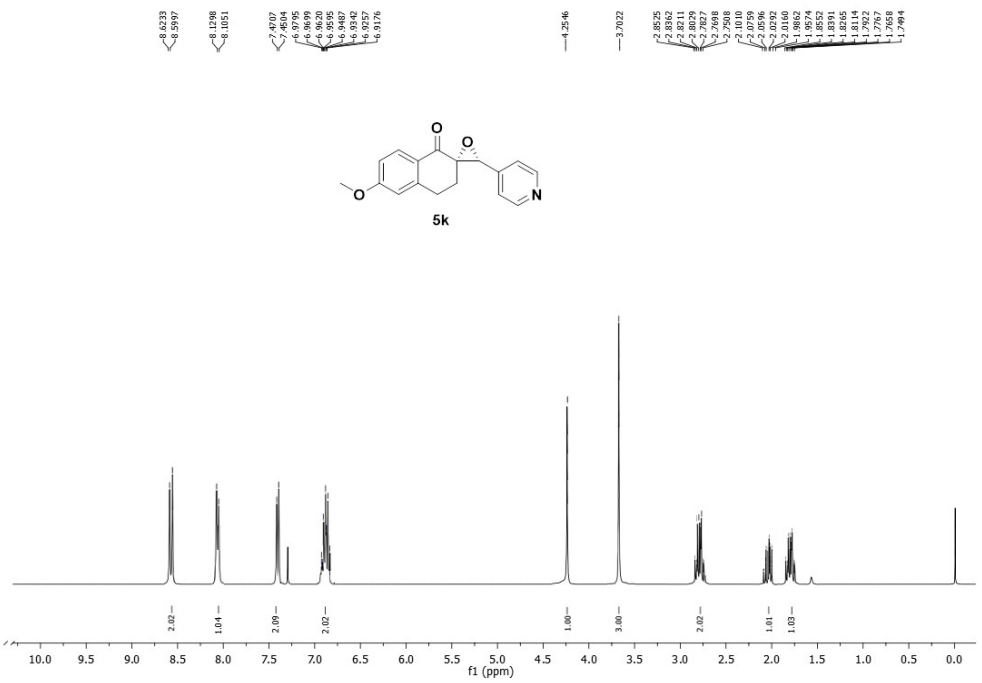


Figure S121: 1H NMR spectrum of epoxide **5k**.

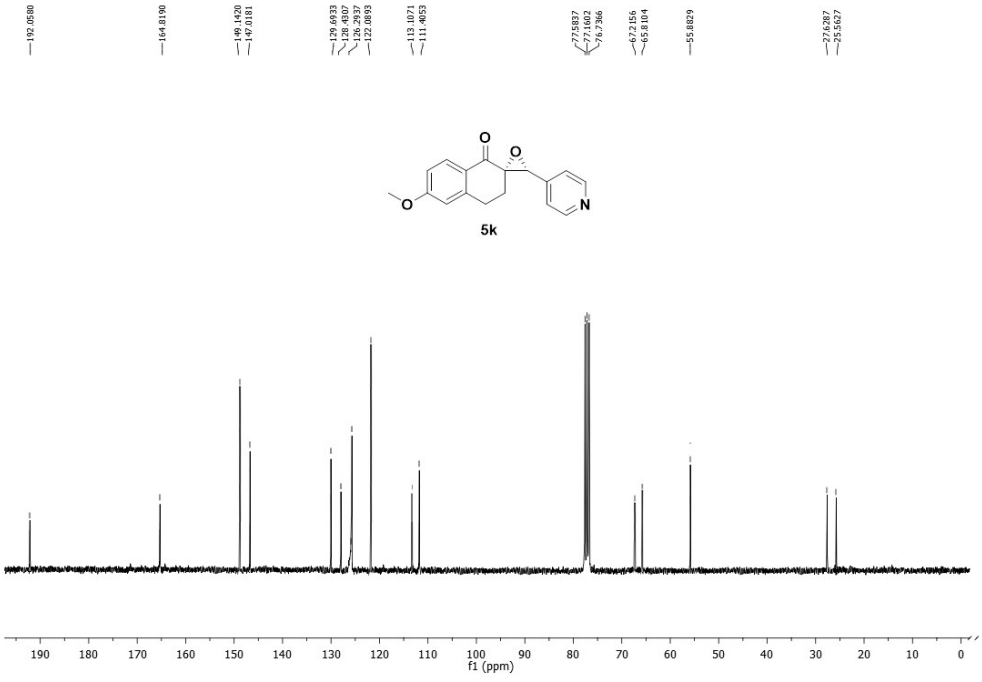
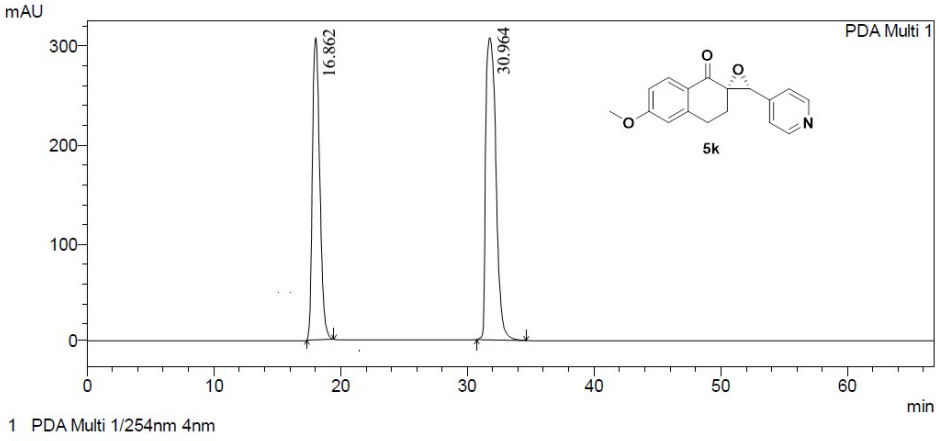


Figure S122: 13C NMR spectrum of epoxide **5k**.

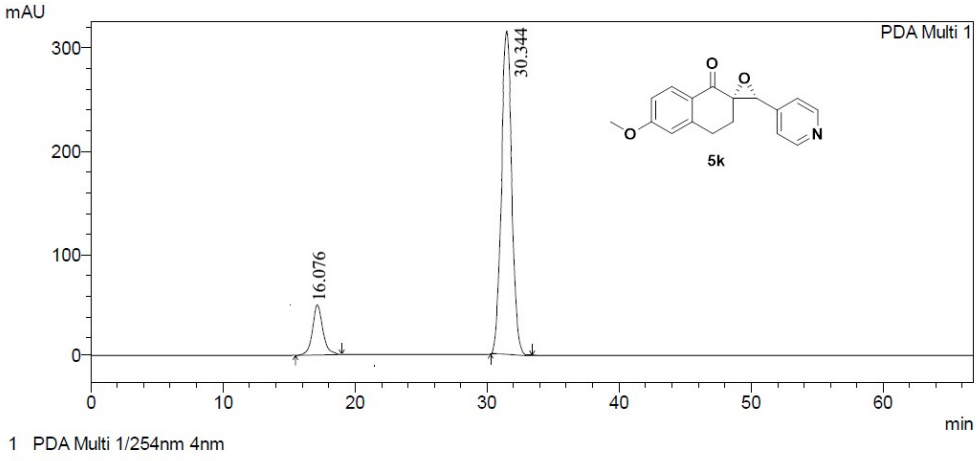


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.862	142638897	1365126	49.259	48.206
2	30.964	143622513	1483220	50.741	51.794
Total		286261409	2848346	100.000	100.000

Figure S123: HPLC chromatogram of epoxide **5k** (Racemic mixture).



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.076	1297389	19932	8.115	3.541
2	30.344	14690360	1273254	91.885	96.459
Total		63235475	801226	100.000	100.000

Figure S124: HPLC chromatogram of epoxide **5k** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 ^oC condition.

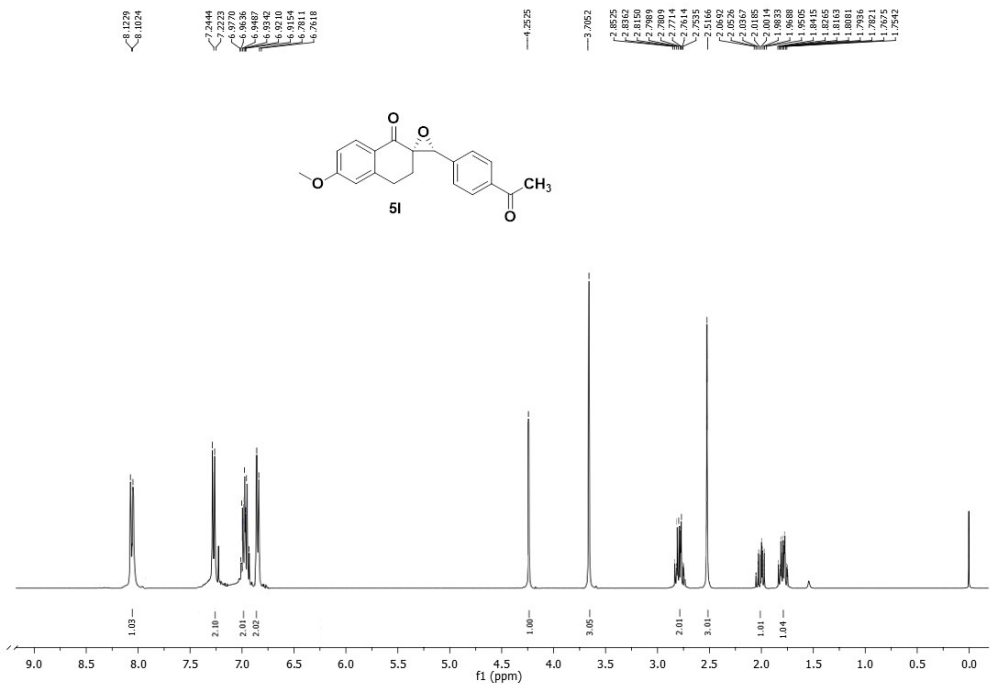


Figure S125: 1H NMR spectrum of epoxide **5l**.

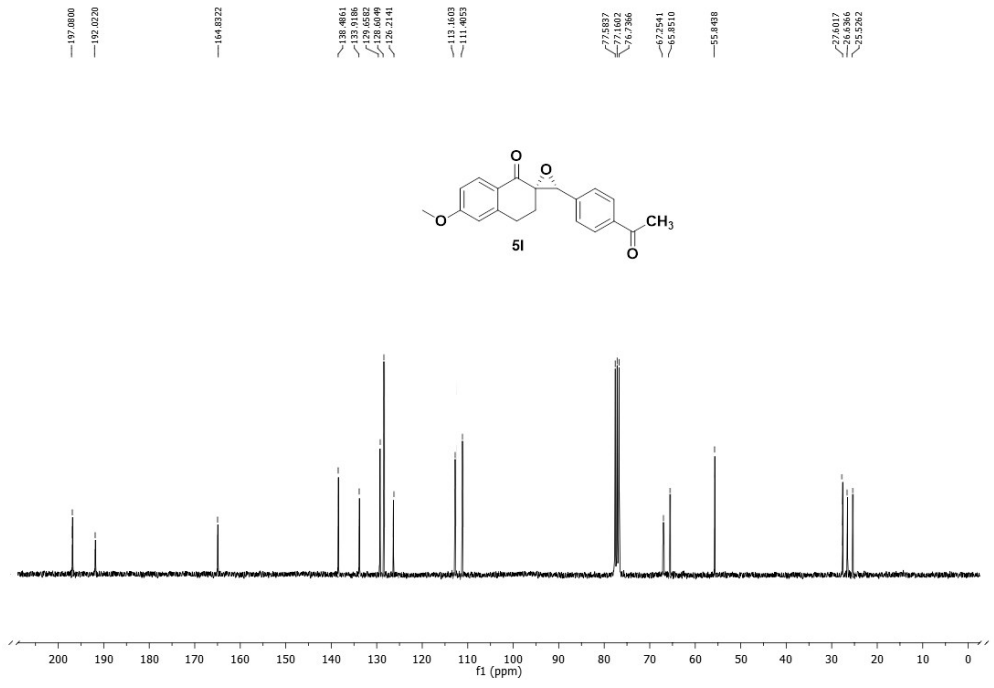
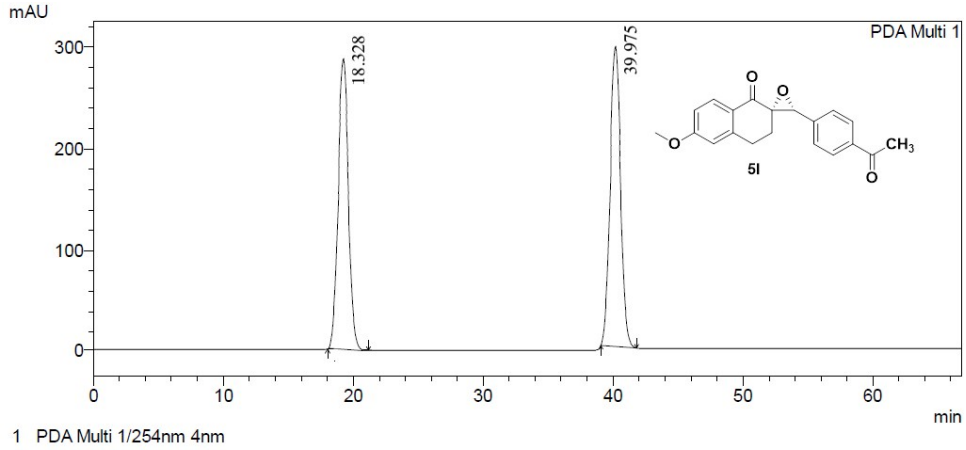


Figure S126: 13C NMR spectrum of epoxide **5l**.

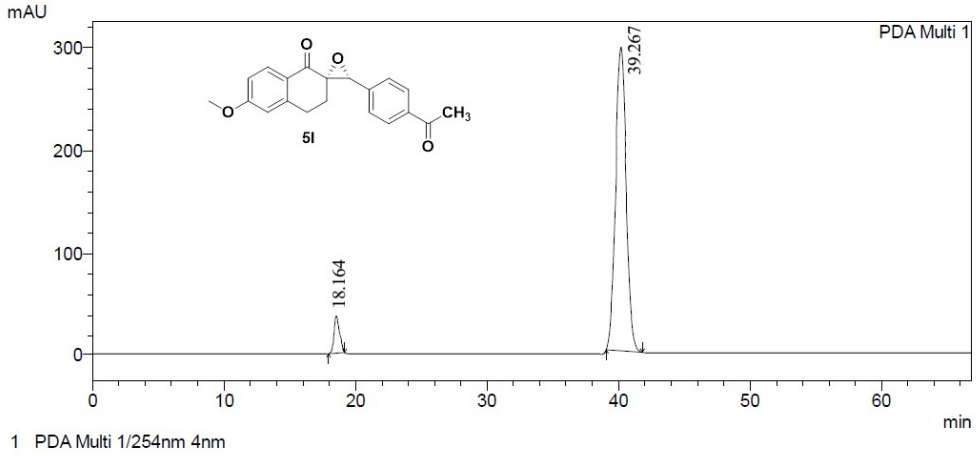


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.328	4011796	185535	49.086	47.286
2	39.975	4120354	196930	50.914	52.714
Total		8132150	382465	100.000	100.000

Figure S127: HPLC chromatogram of epoxide **5l** (Racemic mixture).



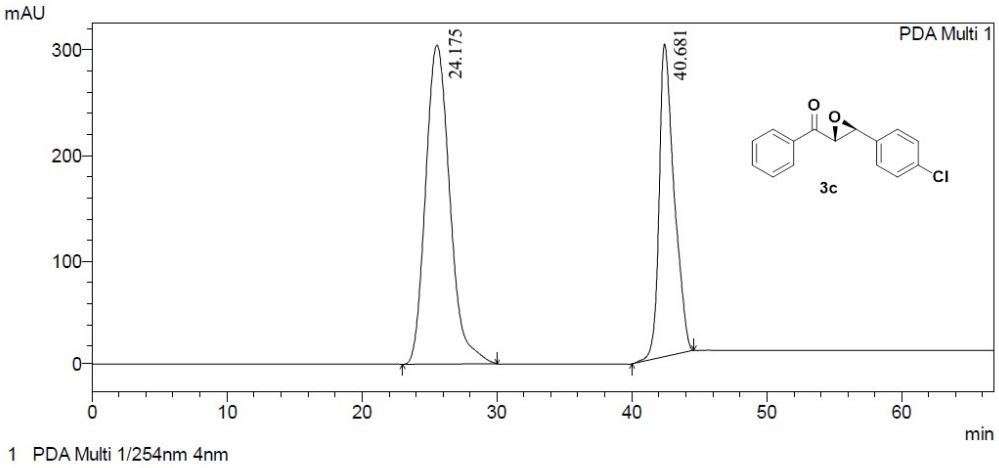
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.164	2416824	64531	6.184	14.619
2	39.267	36665482	376897	93.816	85.381
Total		39082306	441428	100.000	100.000

Figure S128: HPLC chromatogram of epoxide **5l** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N/THF in 0 ^oC condition.

HPLC chromatograms for optimization of reaction condition for highly Enantioselective asymmetric Darzens reaction

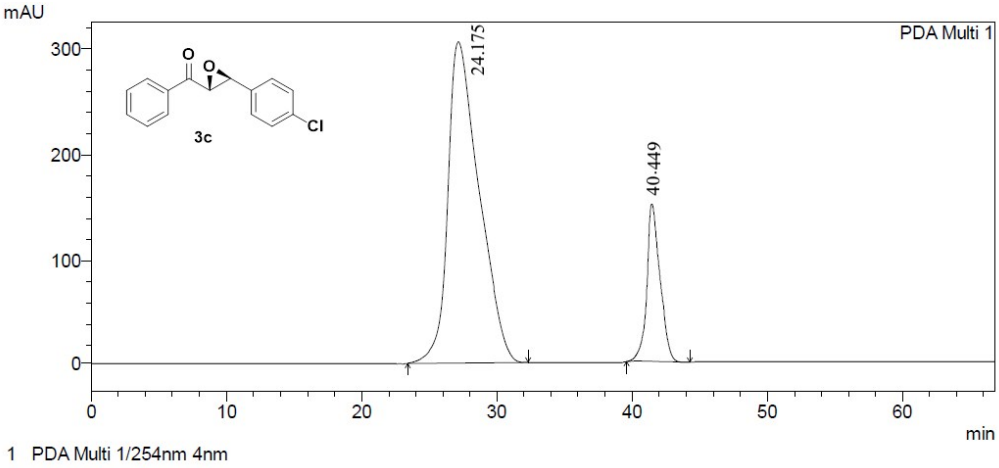


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.175	5653681	104342	50.162	51.369
2	40.681	5517457	97410	49.838	48.631
Total		11171138	201752	100.000	100.000

Figure S129: HPLC chromatogram of epoxide **3c** (Racemic mixture).

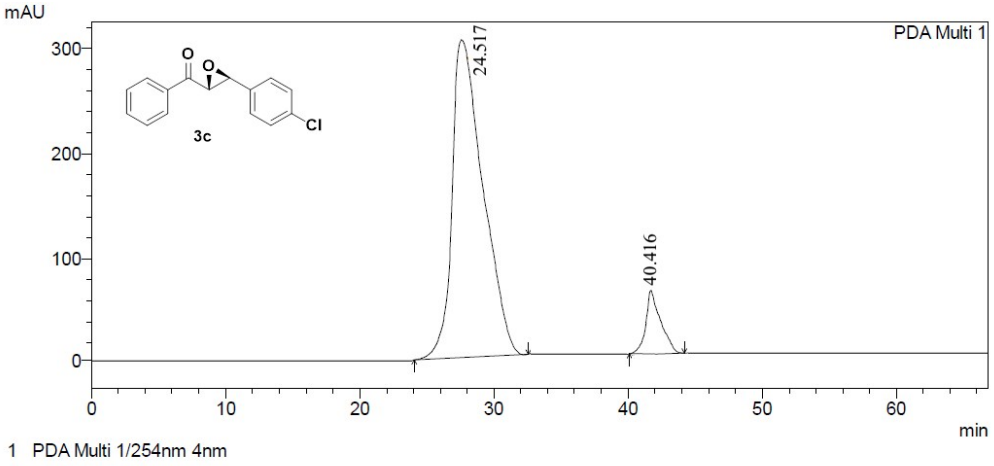


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.175	179449516	2323261	65.208	63.542
2	40.449	83641572	1791754	34.792	36.458
Total		263091088	4115015	100.000	100.000

Figure S130: HPLC chromatogram of epoxide **3c** in the presence 5 mol % of organocatalyst (12a) and **K_2CO_3**/THF in 0 ^oC condition.

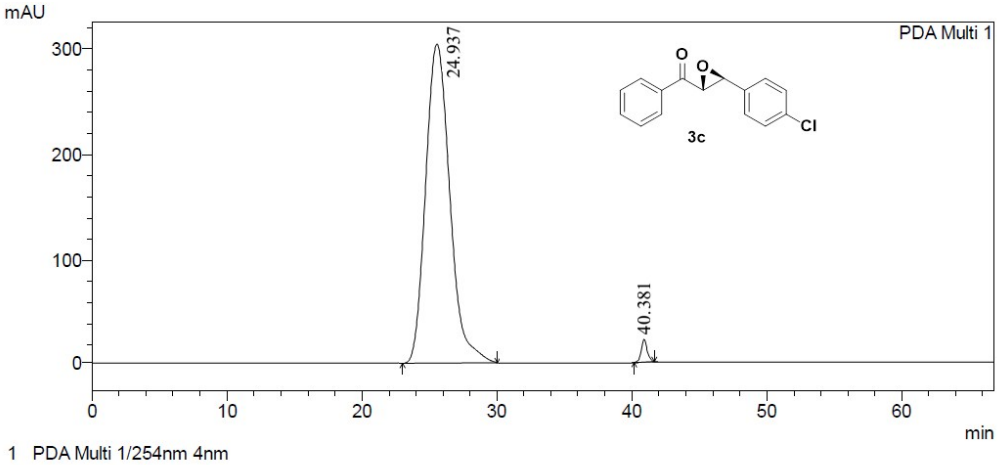


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.517	16288090	453694	93.044	88.009
2	40.416	1217689	61815	6.956	11.991
Total		17505779	515509	100.000	100.000

Figure S131: HPLC chromatogram of epoxide **3c** in the presence 5 mol % of organocatalyst (12a) and **morpholine**/THF in 0 ºC condition.

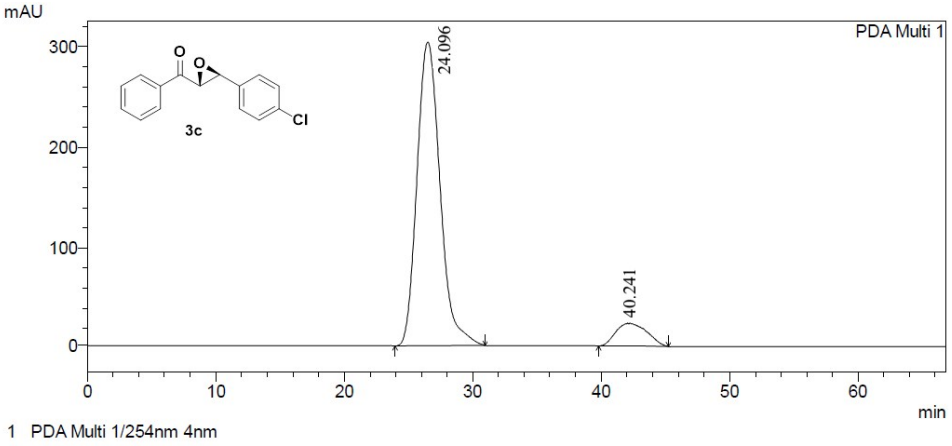


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.937	331381981	389212	99.687	98.851
2	40.381	44433	4523	0.313	1.149
Total		331426414	393735	100.000	100.000

Figure S132: HPLC chromatogram of epoxide **3c** in the presence 5 mol % of organocatalyst (12a) and **Et_3N** /THF in 0 ºC condition.

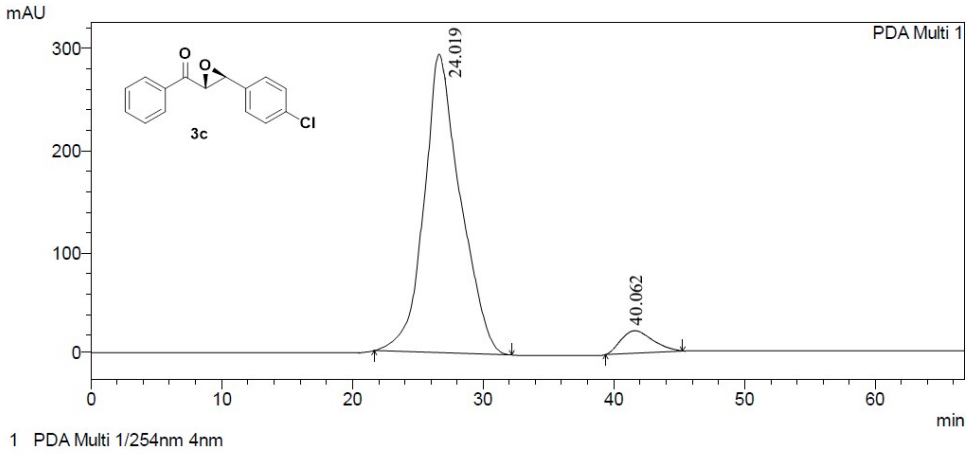


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.096	5687279	212415	89.025	97.258
2	40.241	633682	5989	10.975	2.742
Total		6320961	218404	100.000	100.000

Figure S133: HPLC chromatogram of epoxide **3c** in the presence 5 mol % of organocatalyst (12a) and **Pyridine** /THF in 0 °C condition.

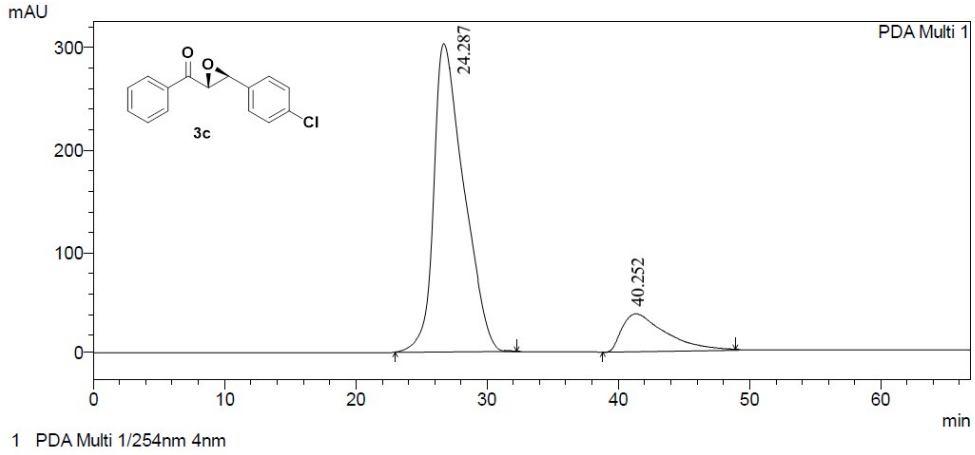


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.019	59390085	2019427	95.537	92.263
2	40.062	2774362	169346	4.463	7.737
Total		62164448	2188773	100.000	100.000

Figure S134: HPLC chromatogram of epoxide **3c** in the presence 5 mol % of organocatalyst (12a) and Et_3N /**CH_3CN** in 0 °C condition.

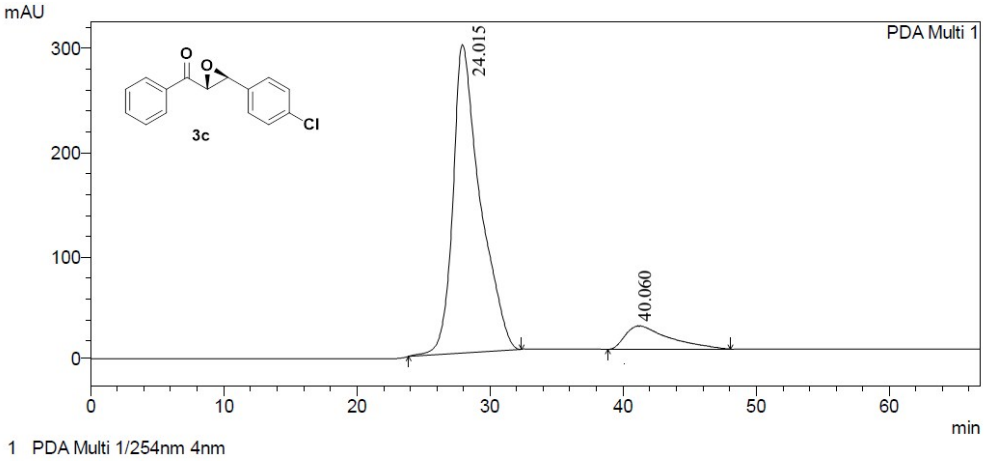


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.287	9057877	113602	90.339	77.358
2	40.252	968610	33250	9.661	22.642
Total		10026487	146852	100.000	100.000

Figure S135: HPLC chromatogram of epoxide **3c** in the presence 5 mol % of organocatalyst (12a) and Et_3N /**CH_3OH** in 0 °C condition.

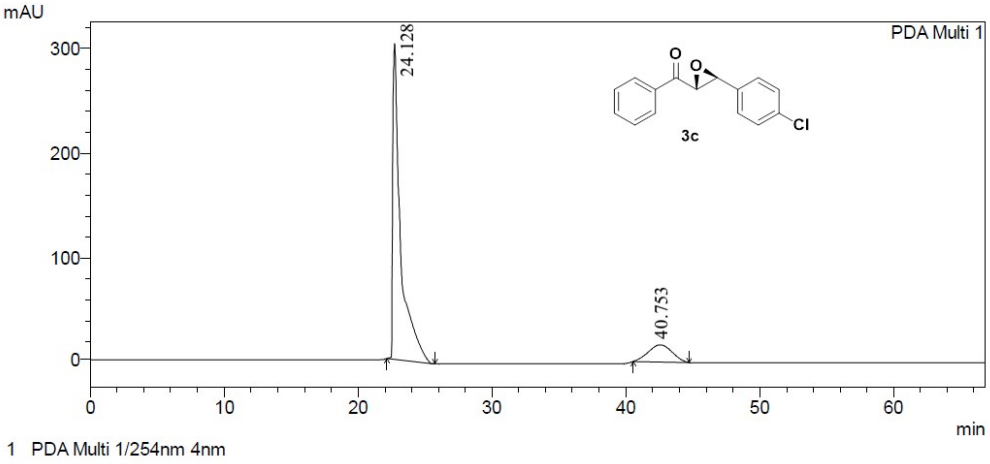


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.015	20622334	254758	92.214	83.370
2	40.060	1741162	50817	7.786	16.630
Total		22363496	305575	100.000	100.000

Figure S136: HPLC chromatogram of epoxide **3c** in the presence 5 mol % of organocatalyst (12a) and Et_3N /**$CHCl_3$** in 0 °C condition.

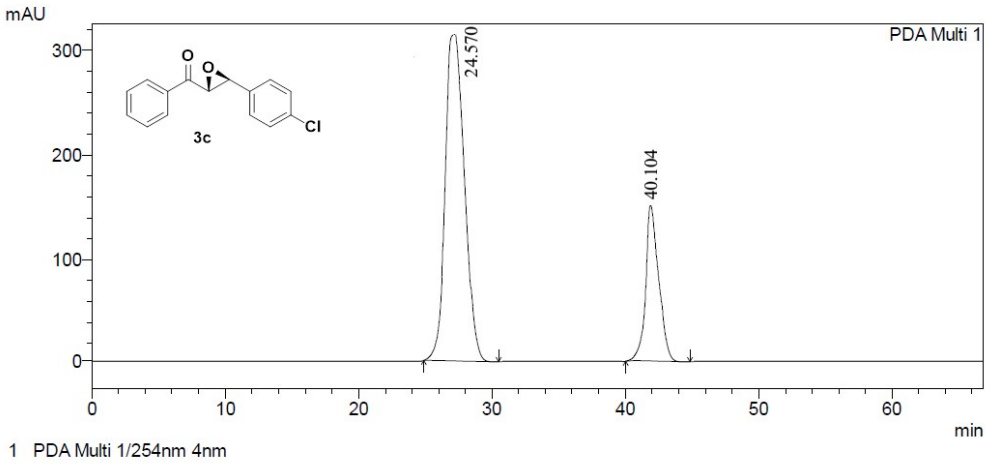


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.128	6770649	261063	85.713	94.819
2	40.753	1128573	14265	14.287	5.181
Total		7899222	275328	100.000	100.000

Figure S137: HPLC chromatogram of epoxide **3c** in the presence 5 mol % of organocatalyst (12a) and Et_3N /**Cyclohexane** in 0 ºC condition.

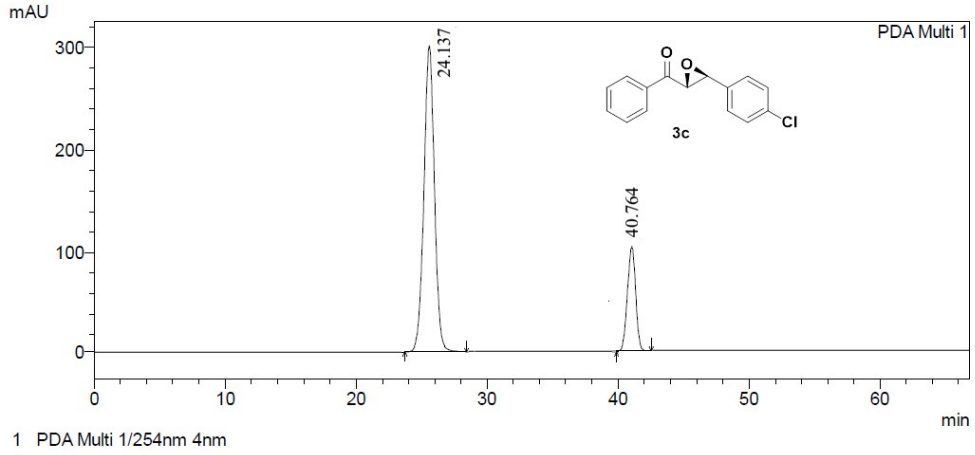


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.570	9427796	104252	81.483	73.552
2	40.104	1647576	36770	16.279	25.283
Total		11570271	141740	100.000	100.000

Figure S138: HPLC chromatogram of epoxide **3c** in the presence 5 mol % of organocatalyst (12a) and Et_3N / **Toluene** in 0 ºC condition.

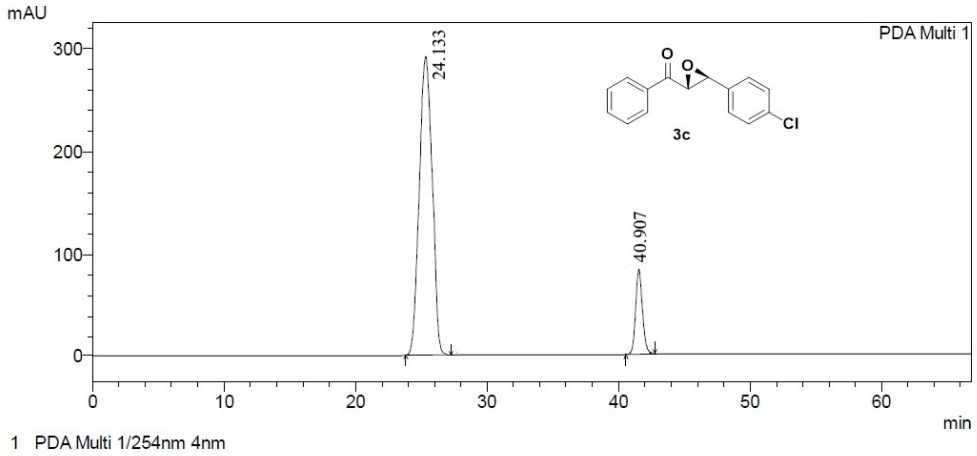


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.137	3986453	97339	76.611	85.579
2	40.764	1659166	16403	23.389	14.421
Total		5645619	113742	100.000	100.000

Figure S139: HPLC chromatogram of epoxide **3c** in the presence **5 mol %** of ***N*-benzyl-L-proline** catalyst and Et_3N /THF in 0 °C condition.

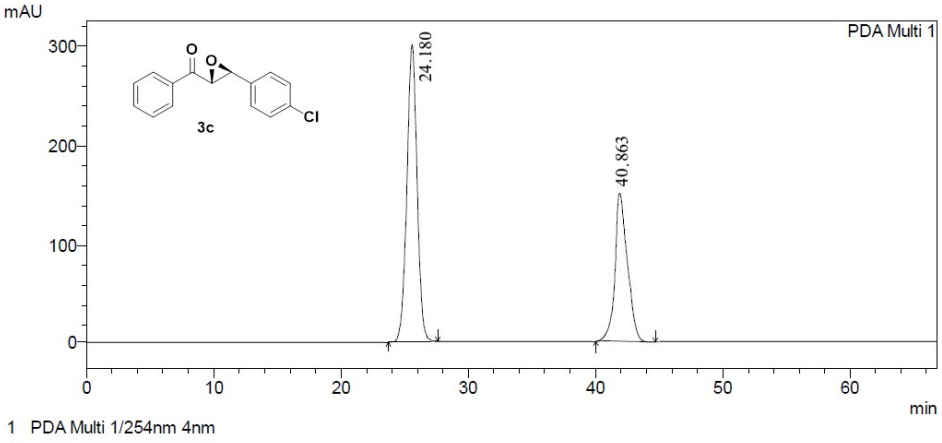


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.133	96059467	1381057	79.036	85.671
2	40.907	25478902	230994	20.964	14.329
Total		121538368	1612051	100.000	100.000

Figure S140: HPLC chromatogram of epoxide **3c** in the presence **10 mol %** of ***N*-benzyl-L-proline** catalyst and Et_3N /THF in 0 °C condition.



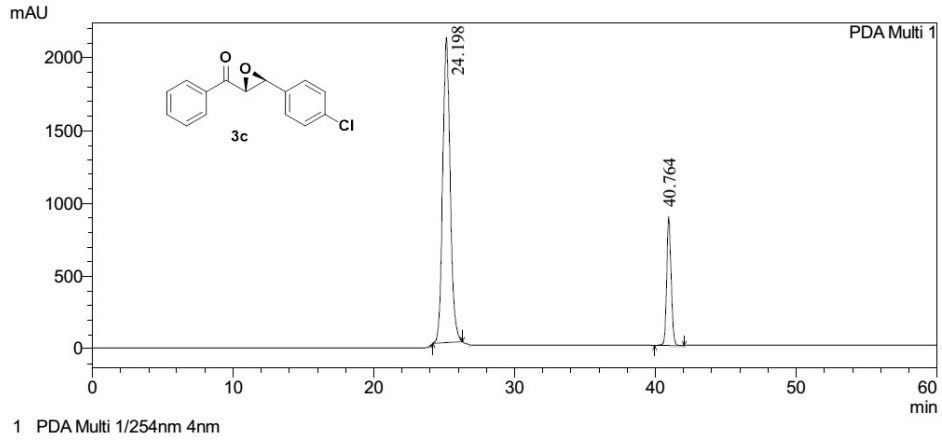
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.180	16023952	101826	70.379	59.796
2	40.863	13643082	70856	29.621	40.204
Total		19667034	172683	100.000	100.000

Figure S141: HPLC chromatogram of epoxide **3c** in the presence **5 mol %** of ***N*-benzyl-L-proline ethyl ester** catalyst and Et_3N /THF in 0 °C condition.



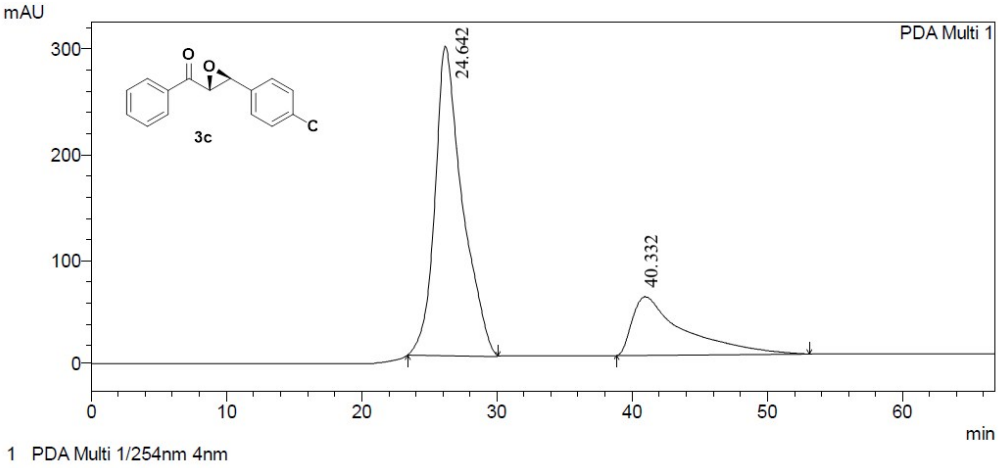
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.198	3986453	97339	73.611	85.579
2	40.764	1659166	16403	26.389	14.421
Total		5645619	113742	100.000	100.000

Figure S142: HPLC chromatogram of epoxide **3c** in the presence **10 mol %** of ***N*-benzyl-L-proline ethyl ester** catalyst and Et_3N /THF in 0 °C condition.

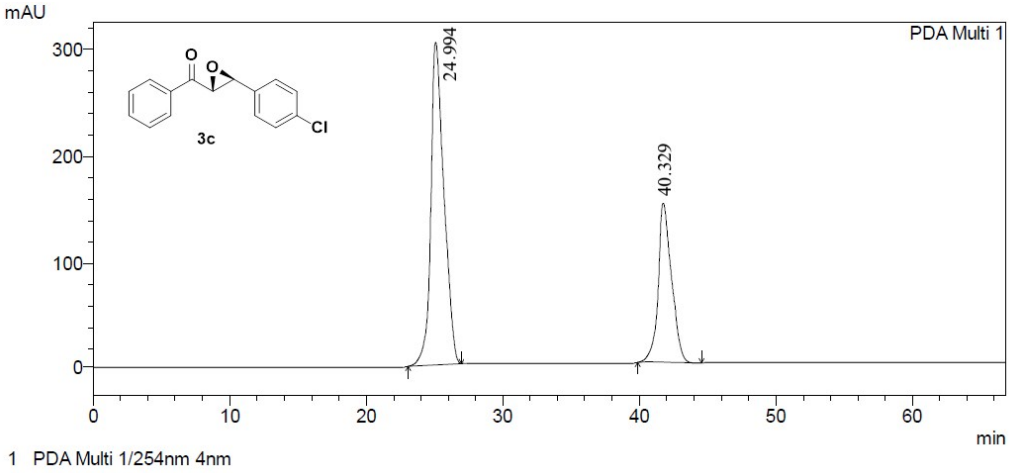


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.642	94686876	1249027	80.942	89.034
2	40.332	23585725	153840	19.058	10.966
Total		118272601	1402868	100.000	100.000

Figure S143: HPLC chromatogram of epoxide **3c** in the presence 5 mol % of organocatalyst (**11a**) and Et_3N /THF in **60 °C** condition.

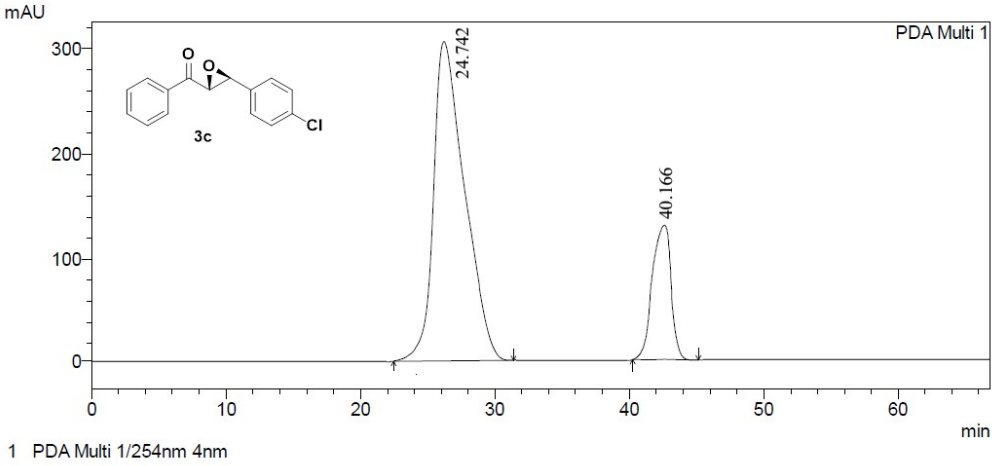


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.994	3986453	97339	73.611	85.579
2	40.329	1659166	16403	26.389	14.421
Total		5645619	113742	100.000	100.000

Figure S144: HPLC chromatogram of epoxide **3c** in the presence 5 mol % of organocatalyst (**11b**) and Et_3N /THF in **60 °C** condition.

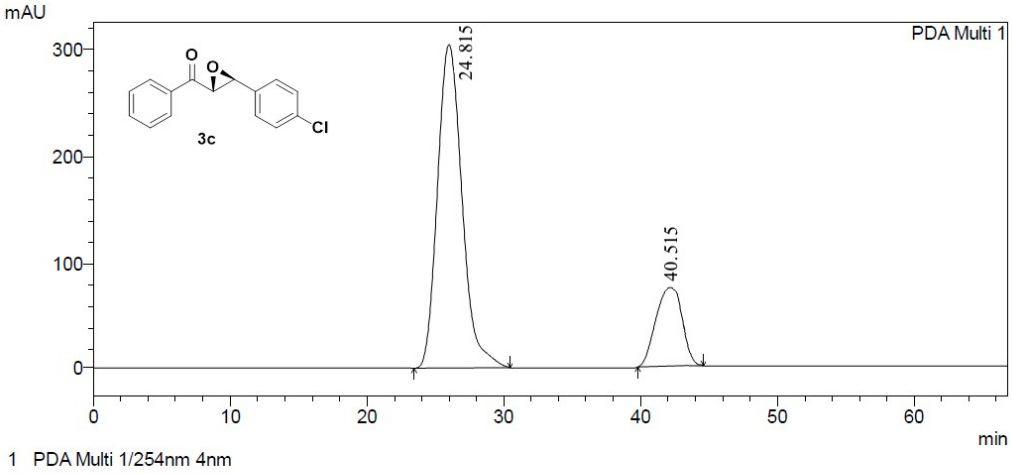


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.742	8473498	108659	83.721	74.717
2	40.166	1647576	36770	16.279	25.283
Total		10121074	145429	100.000	100.000

Figure S145: HPLC chromatogram of epoxide **3c** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N /THF in **60 °C** condition.



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.815	96059467	1381057	79.036	85.671
2	40.515	25478902	230994	20.964	14.329
Total		121538368	1612051	100.000	100.000

Figure S146: HPLC chromatogram of epoxide **3c** in the presence 5 mol % of organocatalyst (**12b**) and Et_3N /THF in **60 °C** condition.

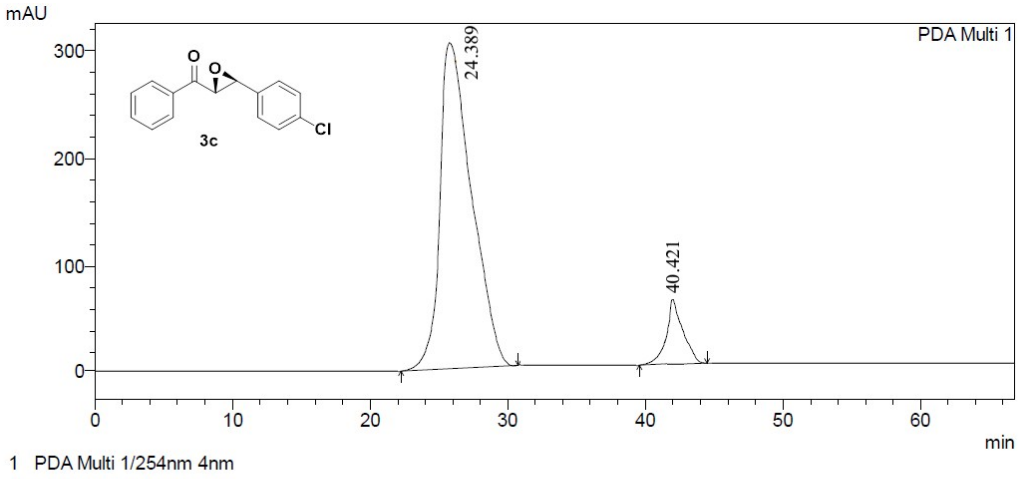
Figure S147: HPLC chromatogram of epoxide **3c** in the presence 5 mol % of organocatalyst (**11a**) and Et_3N /THF in **30 °C** condition.

Figure S148: HPLC chromatogram of epoxide **3c** in the presence 5 mol % of organocatalyst (**11b**) and Et_3N /THF in **30 °C** condition.

Figure S149: HPLC chromatogram of epoxide **3c** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N /THF in **30 °C** condition.

Figure S150: HPLC chromatogram of epoxide **3c** in the presence 5 mol % of organocatalyst (**12b**) and Et_3N /THF in **30 °C** condition.

Figure S151: HPLC chromatogram of epoxide **3c** in the presence 5 mol % of organocatalyst (**11a**) and Et_3N /THF in **0 °C** condition.



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.389	20622334	254758	94.214	83.370
2	40.421	1741162	50817	10.786	16.630
Total		22363496	305575	100.000	100.000

Figure S152: HPLC chromatogram of epoxide **3c** in the presence 5 mol % of organocatalyst (**11b**) and Et_3N /THF in **0 °C** condition.

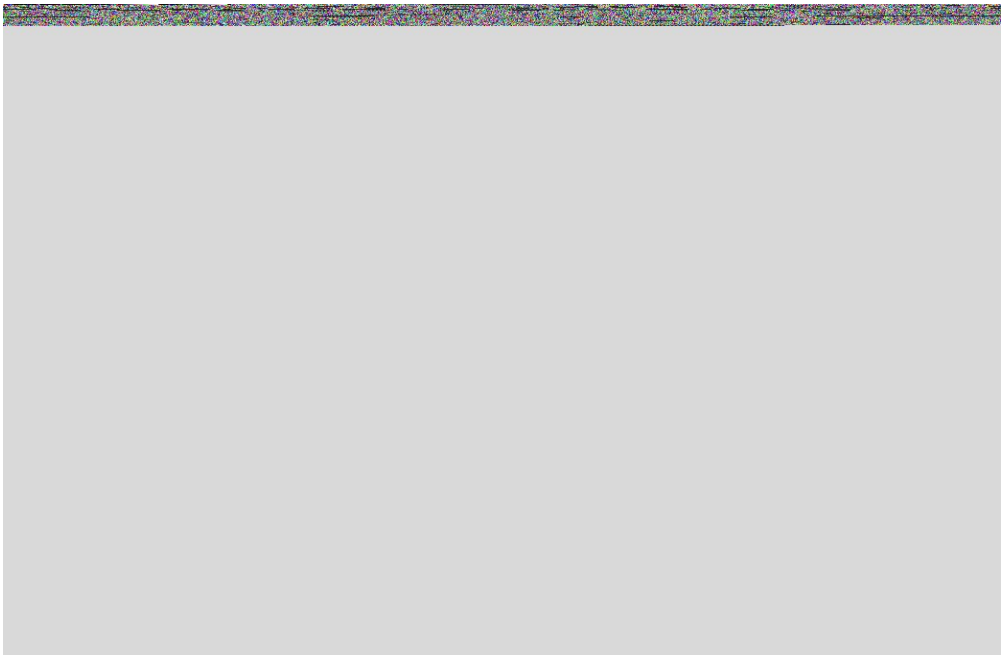
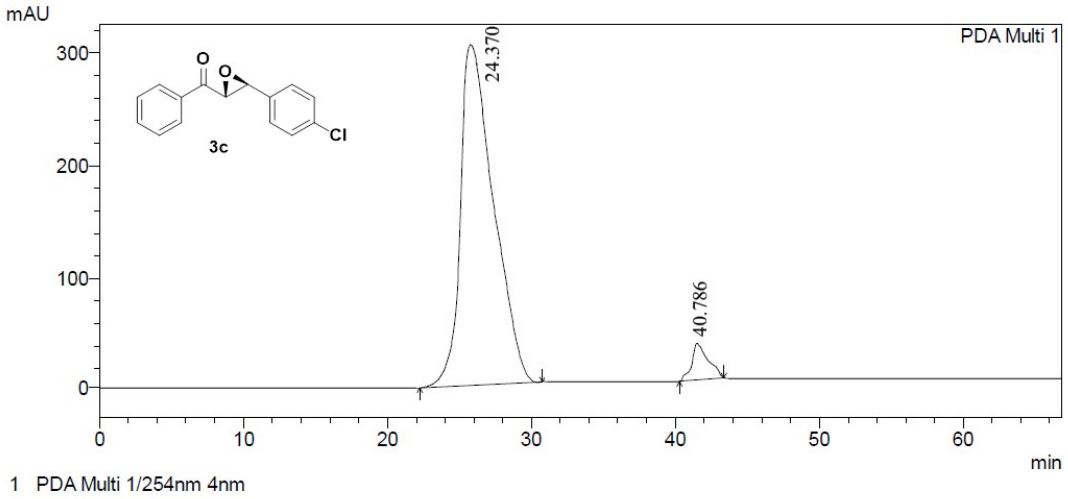


Figure S153: HPLC chromatogram of epoxide **3c** in the presence 5 mol % of organocatalyst (**12a**) and Et_3N /THF in **0 °C** condition.



PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.370	1973568	8839	96.216	88.640
2	40.786	77623	1133	3.784	11.360
Total		2051191	9971	100.000	100.000

Figure S154: HPLC chromatogram of epoxide **3c** in the presence 5 mol % of organocatalyst (**12b**) and Et_3N /THF in **0 °C** condition.