Supporting information

Chiral Co(III)-salen complex supported over highly ordered functionalized mesoporous silica for enantioselectiveaminolysis of racemic epoxides

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List of Contents **Page No**

SECTION-S1

1. GENERAL INFORMATION:

1.1 Chemicals:

3-*tert*-butyl-2-hydroxybenzaldehyde (1), (1*S, 2S*)-(+)-1,2-diaminocyclohexane (4) Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, EO = ethylene oxide, PO = propyleneoxide, M_{av} = 5800), tetraethoxyorthosilicate (TEOS), 3-aminopropyl triethoxysilane (3-APTES, 8), 4-formyl-benzoic acid, (10),$Co(OAc)_2.4H_2O$, all epoxides and anilines were acquired as reagent grade and were used devoid of additional purification. All the solvents were dried according to standard procedures. TLC-analysis' were performed using TLC Silica gel 60 F_{254}.

1.2Characterization techniques:

The Perkin-Elmer FT-IR 783 spectrophotometer was used to record FT-IR spectra of the samples in the range from 400 to 4000 cm^{-1} using KBr pellet as support. A Shimadzu UV 2401PC coupled with an integrating sphere attachment was used for the recording of UV–Visible spectra. $BaSO_4$ was applied as background standard. Powder X-ray diffraction (PXRD) patterns of the sample was tested with a Bruker D8 Advance X-ray diffractometer operated at a voltage of 40 kV and a current of 40 mA using Ni–filtered Cu Kα (λ=0.15406 nm) radiation. A Mettler Toledo TGA/DTA 851e device was used for TGA. TEM images of the mesoporous silica supported Co-salen catalyst were obtained using a JEOL JEM 2010 transmission electron microscope. A Quantachrome Autosorb 1C surface area analyzer was employed for N_2-sorption desorption analysis at 77 K. For the bulk elemental analysis the Co(III)@AFS-1 was digested with acid to dissolved them into clear liquid and then Co content were analyzed by a Shimadzu AA-6300 atomic absorption spectrophotometer (AAS) fitted with a double beam monochromator. Carbon, hydrogen and nitrogen contents of Co(III)@AFS-1 were examined utilizing a Perkin Elmer 2400 Series II CHN analyzer. ^1H spectrums of the products were recorded on 400 MHz NMR instruments using $CDCl_3$ as solvent. Enantiomeric excesses were examined by HPLC (Agilent, Model 1220) using Ultron using a Chiralcel ® OD-H column (wavelengths 254 nm). 2-propanol/hexane system was used as eluent. Optical rotations were (described as: $[\alpha]_D^{27}$ (c = in g per 100 ml, solvent)) tested using Digipol 781 Automatic Polarimeter Rudolph equipment.

1.3 General procedure for asymmetric ring opening (ARO) of epoxide with aniline:

A mixture of cyclohexene oxide (1.0 mmol), aniline (1.0 mmol) and Co(III)@AFS-1 catalyst (25 mg) were stirred at room temperature (27 2 °C) for 1.5 h under neat condition. The progress of the reaction was monitored by TLC. After completion of reaction, the catalyst was removed by simple filtration and ethyl acetate was added. The organic phase was washed with water and brine, and finally dried over Na_2SO_4. Then the product was separated by column chromatography over silica gel with pet ether/ethyl acetate (90:10) as eluent. All the products were characterized on the basis of their ^1H NMR data and their spectroscopic data are in agreement with those previously reported. Enantiomeric excess (ee) was determined by HPLC analysis using Chiralpak OD-H column.

1.4 Comparative Study:

Table S1. Comparison of the catalytic activity of Co(III)@AFS-1 with related catalysts

Catalyst	Reaction Condition	Yield[a] (%)	ee[b] (%)	TOF (h^{-1})	Ref
Hetergeneous chiral Fe(III) salen complex (Fe@SBSAL)	Cyclohexene oxide (1 mmol), Aniline (1 mmol), Fe@SBSAL (0.4 mo% of Fe), without solvent, RT, 2 h.	96	99	121	1(a)
Chiral organocatalyst	Catalyst(20mol%),Cyclohexene oxide (0.2 mmol), anilines (0.22 mmol) in DCM, 24 h, rt.	95	89	0.04	2
Macrocyclic Chiral Cr(III) salen complex	Catalyst (0.5 mol%), cyclohexene oxide (1 mmol), anilines (1 mmol) in DCM+MeOH, 24 h, rt.	98	75	8.16	3
Homogeneous chiral Vanadium–Salan Complex	Catalyst (10 mol%), cyclohexene oxide (1.0 mmol), anilines (1.0 mmol) in DCM, 24 h, 0 °C.	84	62	0.35	4
Recyclable Chiral Ti complex	Chiral ligand (0.015 mmol), $Ti(OiPr)_4$ (0.03 mmol), cyclohexene oxide (0.2 mmol), anilines (0.22 mmol) in DCM, 15 h, RT	95	82	211	5

Recyclable chiral Fe(III) metal complex	Chiral ligand (0.005 mmol), $FeCl_3$ (0.01 mmol), cyclohexene oxide (0.2 mmol), anilines (0.22 mmol) in DCM, 15 h, RT	97	63	646	6
Hetergeneous chiral Co(III) SalanComplexCo(III)@AFS-1	Cyclohexene oxide (1 mmol), Aniline (1 mmol), Co(III)@AFS-1 (25 mg, 2.46 x 10^{-6} mol Co or 0.246 mol % Co), without solvent, RT, 1.5 h.	97	>99	262.6	**Present study**

[a]Yields are referred to those of isolated pure products.

[b]Enantiomeric excess was determined from the HPLC analysis using Chiralpak OD-H column.

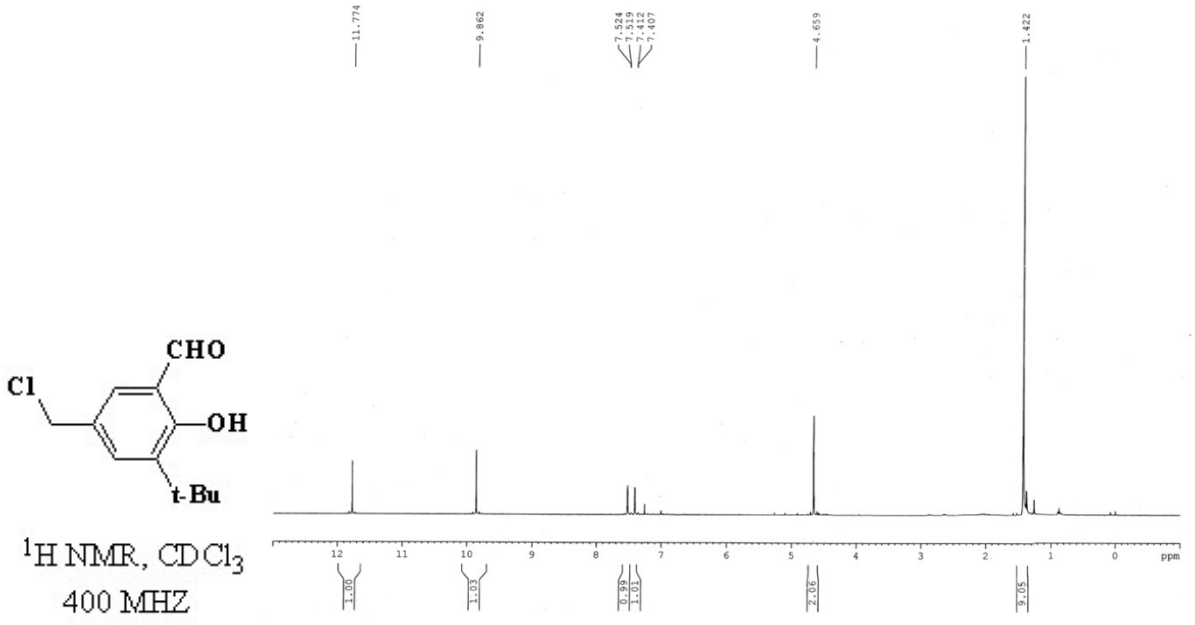
2. CHARACTERISATION DATA OF THE CATALYST

2.1 ^{1}H NMR Spectrum

^{1}H NMR data of 3-tert-butyl-5-chloromethyl-2-hydroxybenzaldehyde **(2)**

^{1}H NMR ($CDCl_3$, 400 MHz):δ (ppm)11.77 (s, 1H), 9.86 (s, 1H), 7.52 (d, *J*= 2 Hz, 1H), 7.41 (d, *J*= 2 Hz, 1H), 4.66 (s, 2H), 1.42 (s, 9H),

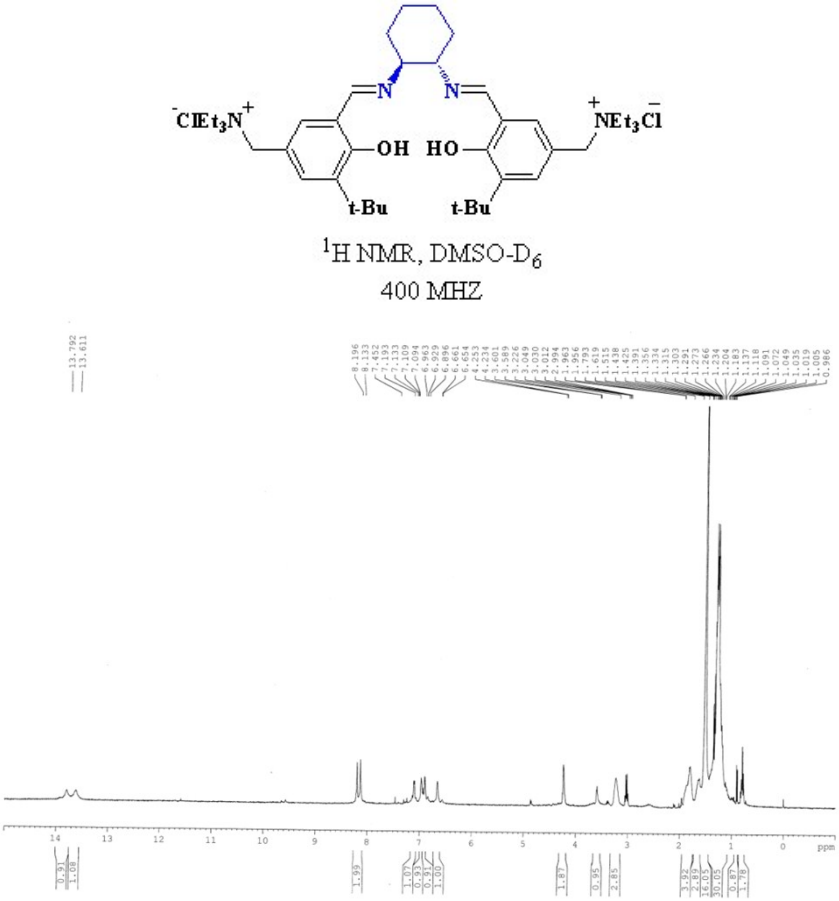
Fig. S1. ^{1}H NMR spectra of 3-tert-butyl-5-chloromethyl-2-hydroxybenzaldehyde **(2)**



[1]H NMR data of chiral Schiff base ligand ***(5)***

[1]H NMR (DMSO-D_6, 400 MHz): δ (ppm) 13.79 (bs, 1H), 13.61 (bs, 1H), 8.16 (d, 2H), 7.13-7.09 (bs, 1H), 6.96-6.89 (m, 2H), 6.66 (bs, 1H), 4.24 (bs, 2H), 3.60-3.59 (bs, 1H), 3.23(m, 3H), 1.96-1.79 (m, 4H), 1.62-1.51(m, 3H), 1.44-1.42 (m, 16H), 1.39-0.98 (m, 30H), 0.95-0.86 (m, 1H), 0.85-0.72 (m, 2H).

Fig. S2. [1]H NMR spectra of chiral Schiff base ligand **(5)**



2.2 Mass and FT-IR data of the homogeneous chiral Co(III) salen complex (6)

TOF-MS *m/z*: calcd ($C_{42}H_{68}Cl_3CoN_4O_2$) 789.41 (M^+, -Cl), found 789.79 (M^+, -Cl). FT-IR (KBr): 3406, 2933, 2860, 1629, 1531, 1439, 1386, 1318, 1203, 1162, 1061, 772 cm-[1].

2.3 Elemental data of the Co(III)@AFS-1

CHN analysis: C =15.97 %, H = 2.94 %, N = 3.07 %.Atomic absorption spectroscopy analysis suggested Co-loading of 0.0984mmol g^{-1} (0.58 wt%) in Co(III)@AFS-1. FT-IR (KBr): 3417, 2939, 1637, 1544, 1387, 1074, 801 cm^{-1}.

2.4 UV-Vis DRS analysis

The DRS UV-Vis absorption spectra of AFS-1 and Co(III)@AFS-1 (**Fig. S3**) have been recorded as $MgCO_3/BaSO_4$ disc. A new broad band near 360 to 450 nm indicates the surface bound Co(III) in the catalyst.

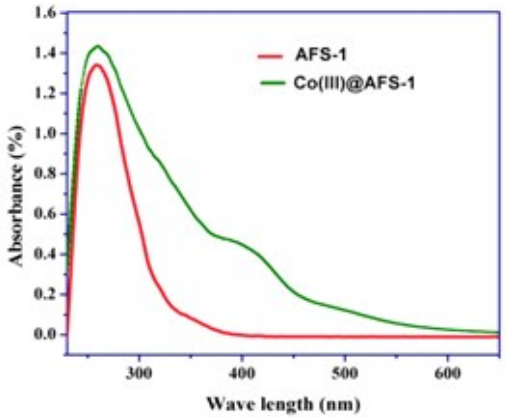


Fig. S3. The DRS-UV-vis absorption spectrum of Co(III)@AFS-1.

2.5 FT-IR Spectrum

The representative FT-IR spectra of SBA-15, 3-APTES functionalized SBA-15, acid functionalized mesoporous material AFS-1, homogeneous Co(III)-salen complex(Co-SAL) and heterogeneous chiral catalyst Co(III)@AFS-1 itself are shown in **Fig. S4**. The broad peak near 2900 to 3000 cm^{-1} (**a**, **Fig. S4)** indicates the presence of aliphatic C–H stretching vibrations and with further modification of SBA-15 to Co(III)@AFS-1, the intensity of this peak gradually increases. The broad band near 1081 cm^{-1} for Si–O–Si bond and 3440 cm^{-1} for the Si–OH bond (**a**, **Fig. S4)** clearly indicates the presence of SBA-15 material. In the spectra the band near 1557 cm^{-1} can be assigned for the deformed N-H vibrations of amido-groups of 3-APTES functionalized SBA-15 (**b, Fig. S4**). The peaks near 1400 cm^{-1} to 1600 cm^{-1} in the

IR spectra (**c, d, e, Fig. S4**) indicate the –C=N– stretching of the modified catalyst. Therefore FT-IR spectra indicates the successful stepwise modification of SBA-15 to Co(III)@AFS-1 catalyst.

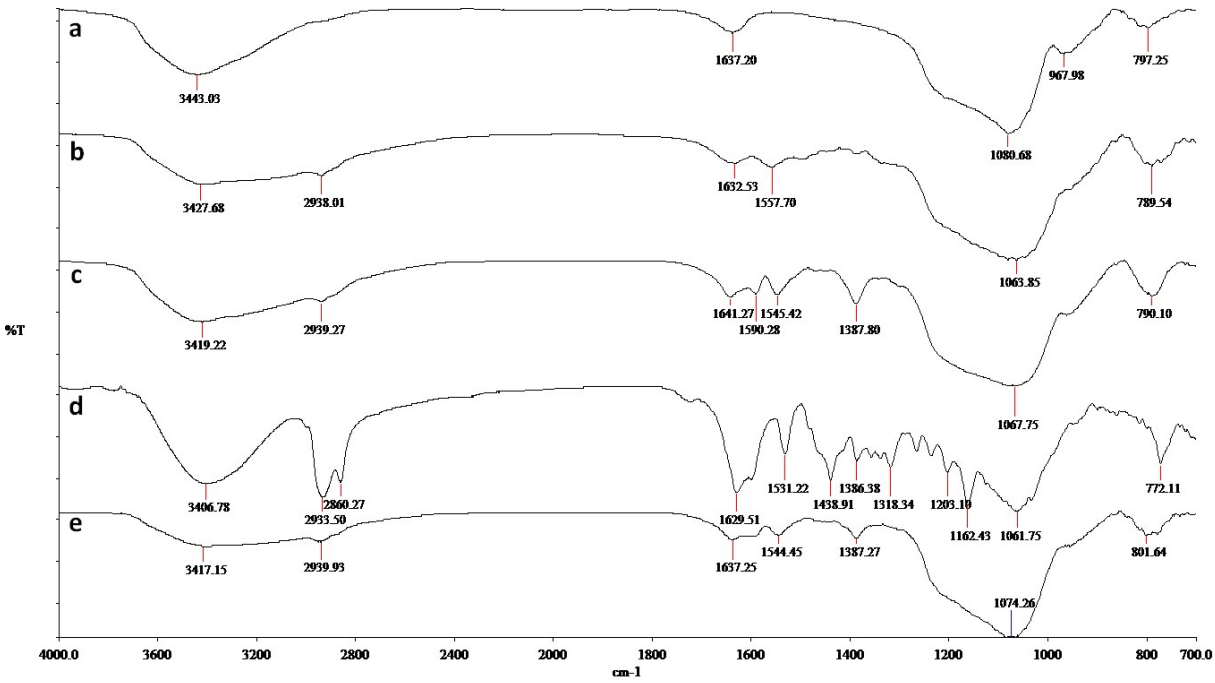


Fig. S4. FT IR spectra of (a) SBA-15 (b) 3-APTES functionalized SBA-15 (c) acid functionalized mesoporous material AFS-1, (d) homogeneous Co(III)-salen complex(Co-SAL) (e) heterogeneous chiral catalyst Co(III)@AFS-1.

2.6 Electron Paramagnetic Resonance (EPR)

Here we have shown the EPR spectrum ofCo(III)@AFS-1 catalyst in the **Fig. S5**. There is no characteristics peak in the spectrum as here Co(III) (d^6 system) forms low-spin complex, having all paired electrons.

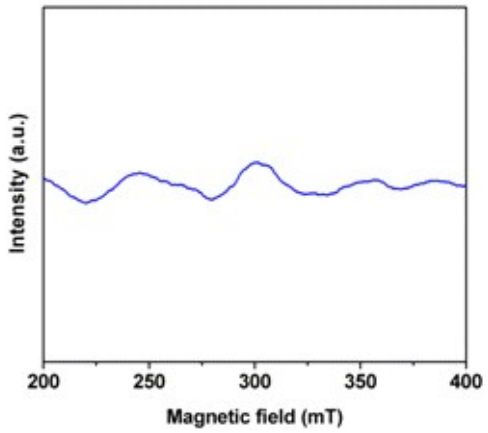


Fig. S5. EPR spectrum ofchiral catalyst Co(III)@AFS-1 at 298 K.

2.7 Wide angle powder XRD of chiral catalyst Co(III)@AFS-1

The wide angle powder X-ray diffraction pattern of Co(III)@AFS-1 material is shown in Fig. S6. The broad peak is appeared at 2θ value of 22°, suggesting the Co(III)@AFS-1 material is amorphous in nature.

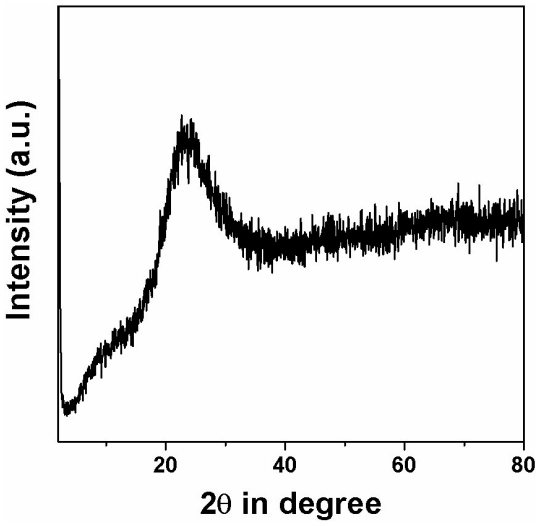


Fig. S6. Wide angle powder XRDofchiral catalyst Co(III)@AFS-1.

2.8 Nitrogen adsorption-desorption isotherm and pore size distribution of mesoporous SBA-15.

The nitrogen adsorption/desorption isotherm of pure SBA-15 material is shown in Figure S7, where the isotherms are classified as type IV with a large H1 hysteresis loop. As noticed from the figure the N_2 uptake at 0.75-0.90 bar pressure region indicates the presence of mesoporosity in SBA-15 material. The total Brunauer–Emmett–Teller (BET) surface area and pore volume of pure SBA-15 were obtained to be 710 $m^2 g^{-1}$ and 0.8185 cc g^{-1}. The pore size distribution plot is obtained using NLDFT (non-local distribution functional theory) method, shown in the inset of Fig. S7. The pore diameter of pure SBA-15 was estimated to be 11.2 nm.

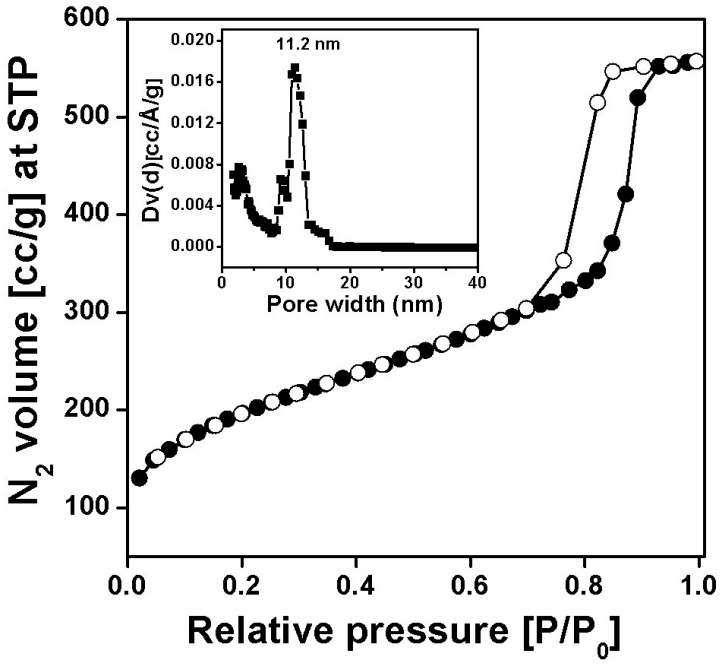


Fig. S7. The N_2 adsorption-desorption isotherm of mesoporous SBA-15. The PSD estimated by NLDFT method is given inset.

2.9. Solid UV-Vis and FT-IR spectroscopic data of reused Co(III)@AFS-1 catalyst after fifth cycle.

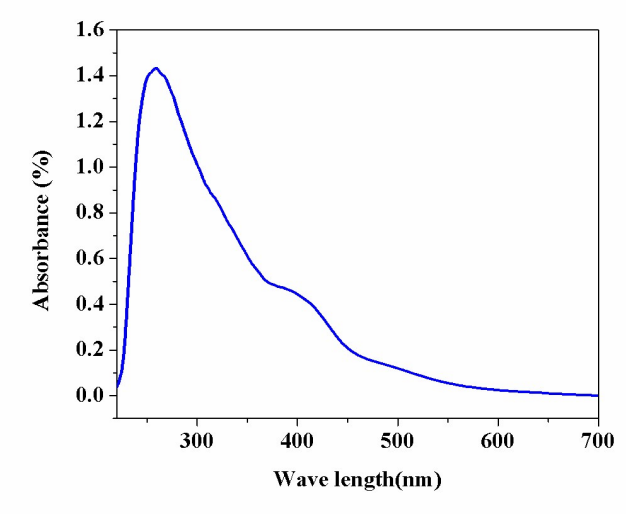


Fig. S8: UV-Vis Spectrum of reused Co(III)@AFS-1 catalyst.

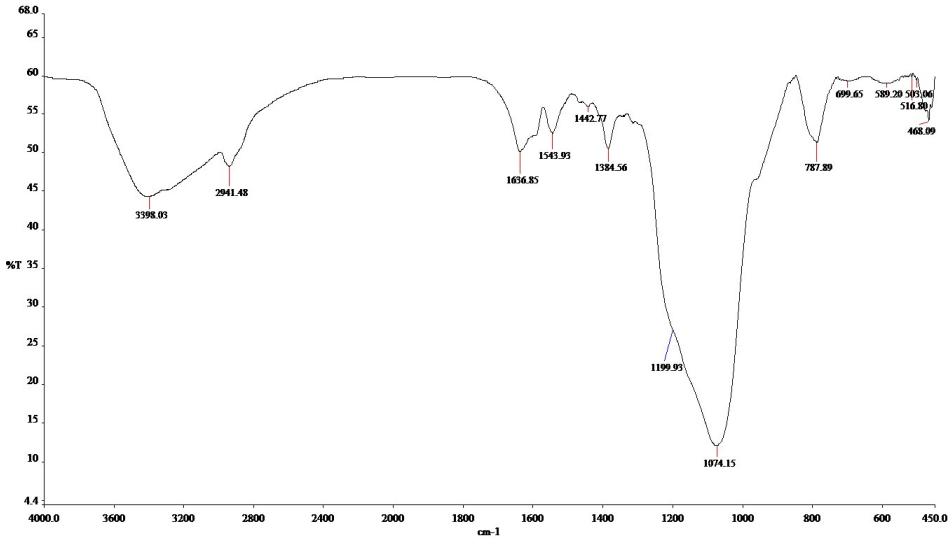


Fig. S9: FT IR Spectrum of reused Co(III)@AFS-1 catalyst.

3. The possible reaction pathway for ARO of epoxide with amine.

Figure S10 represents the probable reaction pathway for the ARO of meso and terminal epoxide with amines. The probable path way follows the well recognized mechanisms reported in literature[7].

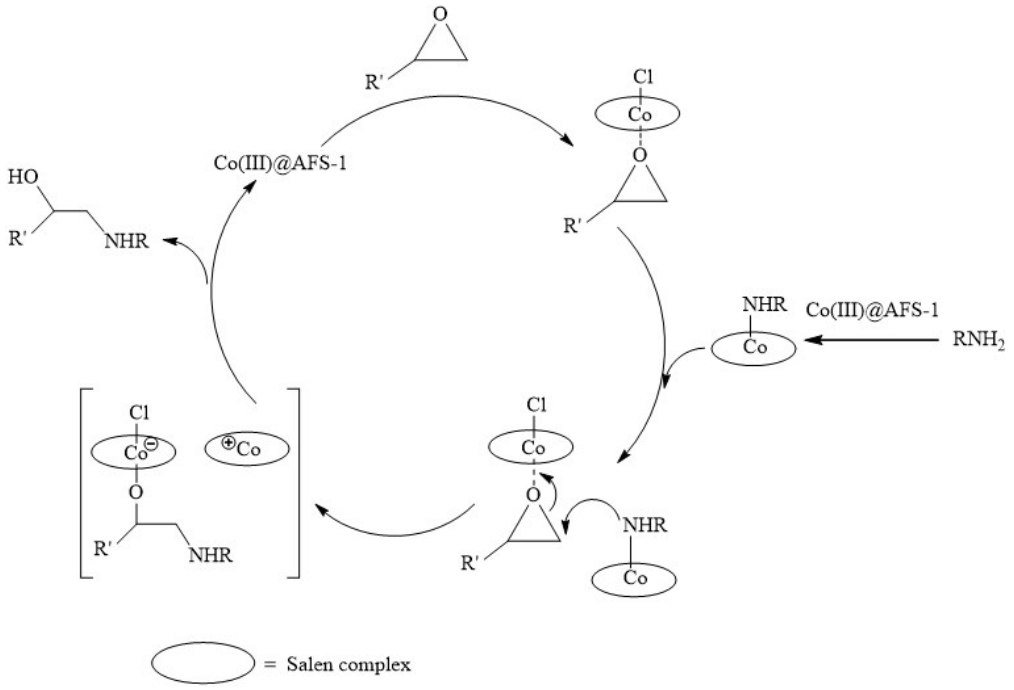


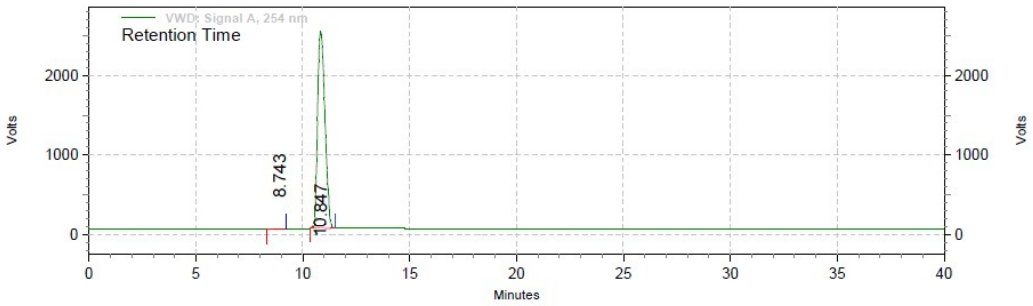
Fig. S10: The probable reaction pathway.

4. Comparison of catalytic activity between cyclohexene oxide and aniline catalyzed by homogeneous Co(III) salen complex (6) and heterogeneous chiral Co(III)@AFS-1 catalyst for the ARO reaction[a]

Catalyst	Time (h)	Yield[b] (%)	ee[c] (%)
Homogeneous Co(III) salen complex	1	97	>99
Heterogeneous chiral Co(III)@AFS-1 catalyst	1.5	97	>99

[a]Reaction conditions: Cyclohexene oxide (1.0 equvt.), Aniline (1.0 equvt.), Co(III) catalyst (0.246 mol % Co), without solvent, RT; [b]Isolated Yield, [c]Determined by chiral HPLC analysis using Chiralpak OD-H column.

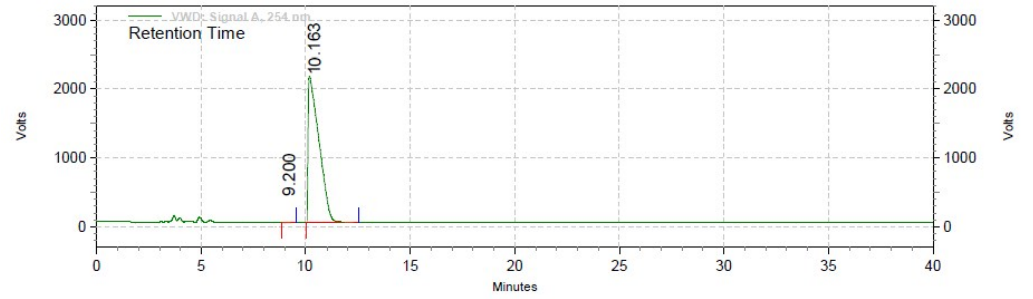
Fig. S11. HPLC chromatograms of (*1R,2R*)-2-(phenylamino)cyclohexanol (3a) synthesized by homogeneous chiral Co(III) salen complex:



VWD: Signal A,
254 nm Results

Retention Time	Area	Area %	Height	Height %
8.743	1266781	0.15	64164	0.16
10.847	867956992	99.85	39467712	99.84
Totals	869223773	100.00	39531876	100.00

Fig. 12. HPLC chromatograms of (*1R,2R*)-2-(phenylamino)cyclohexanol (3a) synthesized by heterogeneous chiral Co(III)@AFS-1 catalyst



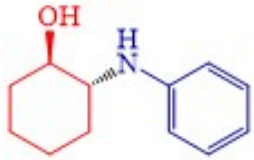
VWD: Signal A,
254 nm Results

Retention Time	Area	Area %	Height	Height %
9.200	2464564	0.19	150500	0.42
10.163	1285194005	99.81	35724007	99.58
Totals	1287658569	100.00	35874507	100.00

SECTION-S2

Characterization data and HPLC chromatograms of the pure products

(*1R,2R*)-2-(phenylamino)cyclohexanol[1a] (3a, Table 2)



The desired product was isolated by column chromatography over silica gel (ethyl acetate/hexane 10/90) as white solid. $[\alpha]_D^{27}$ -35.6 (c = 0.5, $CHCl_3$); >99% ee; HPLC analysis was performed using Chiralpak OD-H column having 90/10 n-hexane/^{i}-PrOH as mobile phase, flow rate 1.0 ml/min, retention time (*1S,2S*): 9.20 min (minor), (*1R,2R*): 10.16 min (major).

Fig.S13.^{1}H NMR spectra:

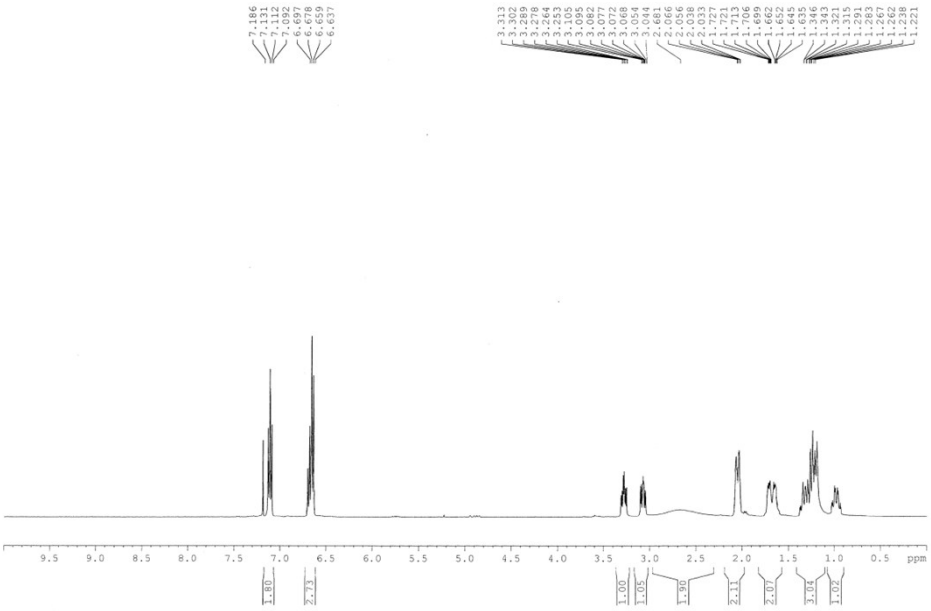
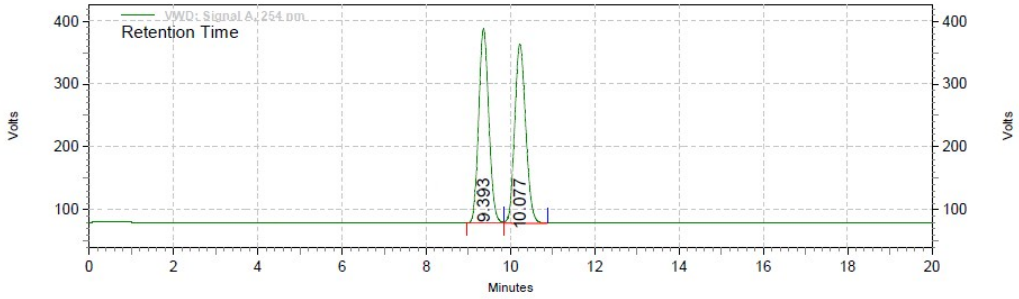
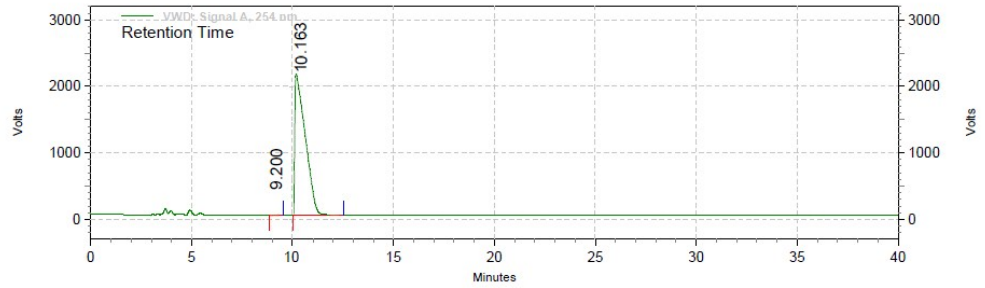


Fig. S14. HPLC chromatograms:



VWD: Signal A, 254 nm Results

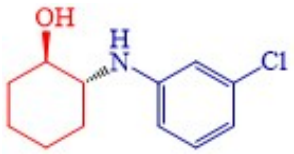
Retention Time	Area	Area %	Height	Height %
9.393	87167788	49.87	5195414	52.04
10.077	87636672	50.13	4788044	47.96
Totals	174804460	100.00	9983458	100.00



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %	Height	Height %
9.200	2464564	0.19	150500	0.42
10.163	1285194005	99.81	35724007	99.58
Totals	1287658569	100.00	35874507	100.00

(*1R,2R*)-2-((3-chlorophenyl)amino)cyclohexanol[1a] (3b, Table 2)



The desired product was isolated by column chromatography over silica gel (ethyl acetate/hexane 10/90). $[\alpha]_D^{27}$ -28.9 (c = 0.5, $CHCl_3$); 98% ee; HPLC analysis was performed

using Chiralpak OD-H column having 90/10 n-hexane/^{i}-PrOH as mobile phase, flow rate 1.0 ml/min, retention time (*1S,2S*): 7.83 min (minor), (*1R,2R*): 9.23 min (major).

Fig. S15.^{1}H NMR spectra:

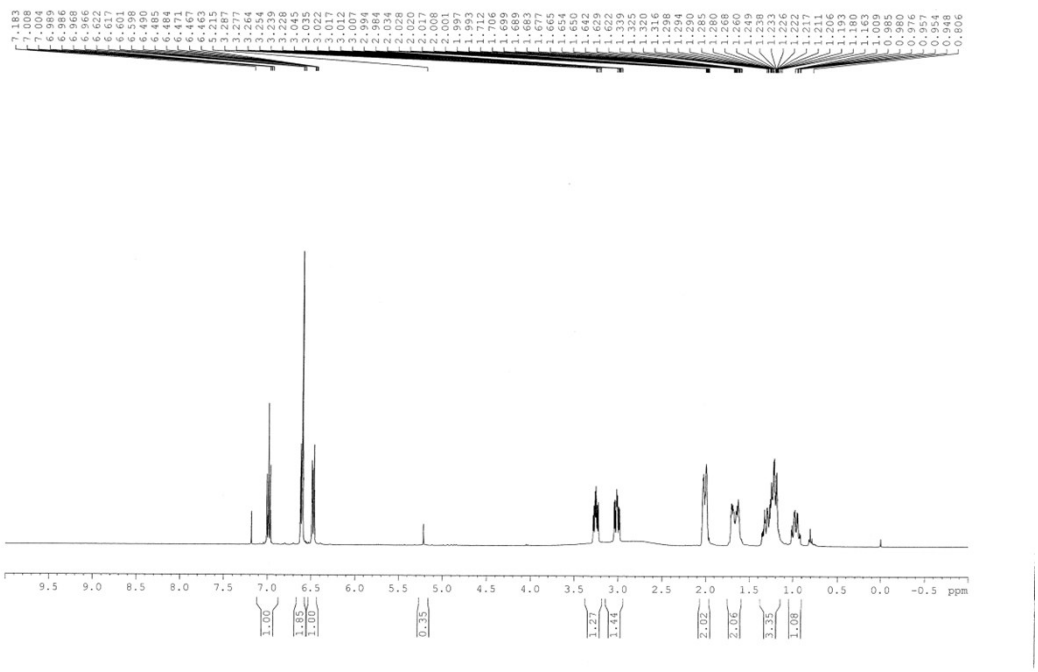
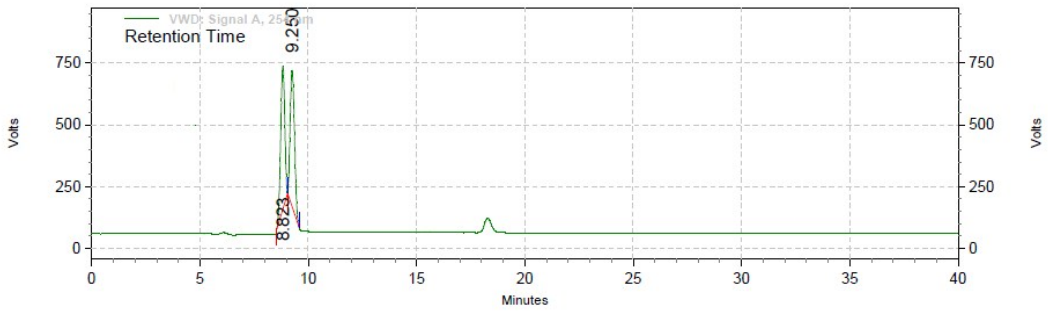
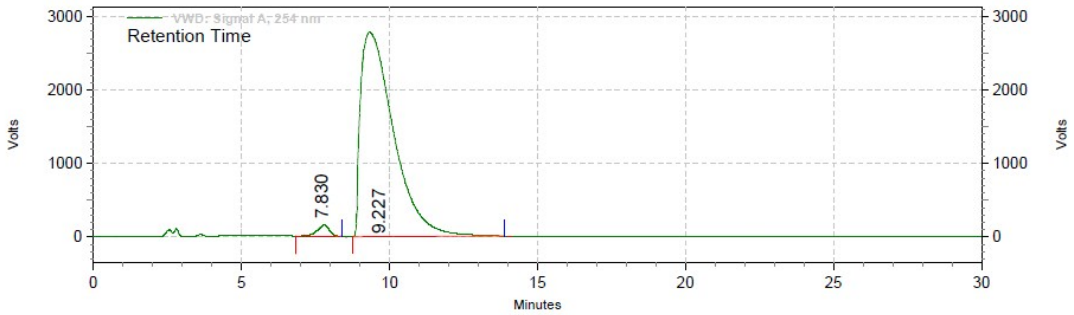


Fig. S16. HPLC chromatograms:



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %	Height	Height %
8.823	125658039	49.10	9670339	51.03
9.250	130261058	50.90	9278945	48.97
Totals	255919097	100.00	18949284	100.00



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %	Height	Height %
7.830	84245789	2.13	2436163	4.95
9.227	3870769908	97.87	46781246	95.05
Totals	3955015697	100.00	49217409	100.00

(*1R,2R*)-2-morpholinocyclohexanol[1b] (3c, Table 2)

The compound was isolated by column chromatography over silica gel (ethyl acetate/hexane 25/75) as colourless oil. $[\alpha]_D^{27}$ -48.6 (c = 3.00, $CHCl_3$); 77% ee; HPLC analysis was performed using Chiralpak OD-H column having 90/20 n-hexane/^{i}-PrOH as mobile phase, flow rate 1.0 ml/min, retention time: 17.13 min (major), 19.21 min (minor).

Fig. S17.^{1}H NMR spectra:

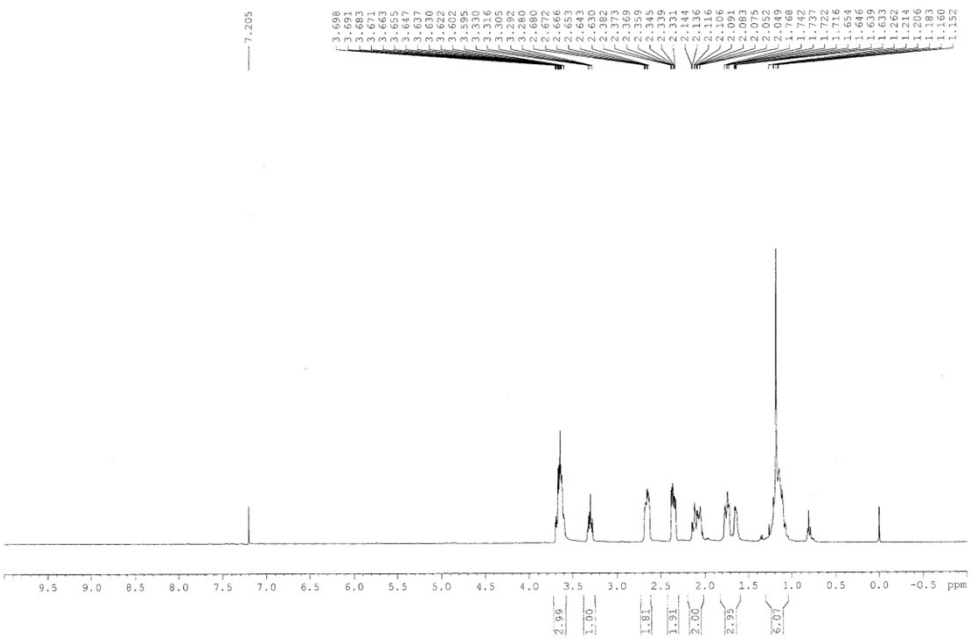
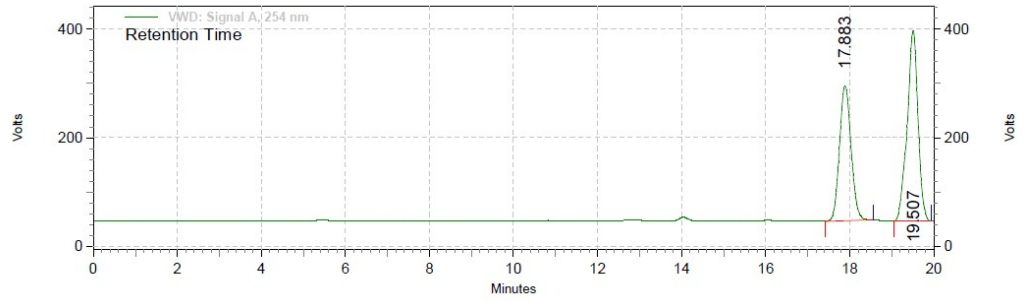
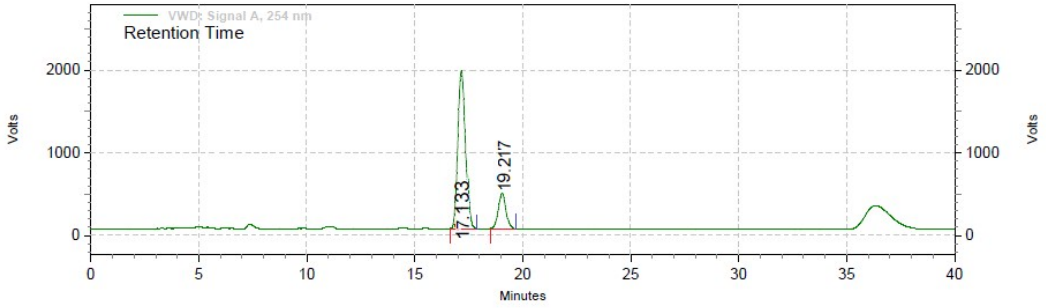


Fig. S18. HPLC chromatograms:



VWD: Signal A, 254 nm Results

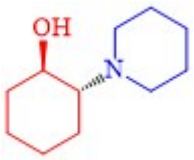
Retention Time	Area	Area %	Height	Height %
17.883	79743410	44.54	4168856	42.14
19.507	99289903	55.46	5722966	57.86
Totals	179033313	100.00	9891822	100.00



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %	Height	Height %
17.133	674876123	77.02	27398615	76.04
19.217	201318433	22.98	8633815	23.96
Totals	876194556	100.00	36032430	100.00

(*1R,2R*)-2-(piperidin-1-yl)cyclohexanol[1b] (3d, Table 2)



The compound was isolated by column chromatography over silica gel (ethyl acetate/hexane 25/75) as colourless oil. $[\alpha]_D^{27}$ -52.3 (c = 3.03, $CHCl_3$); 80% ee; HPLC analysis was

performed using Chiralpak OD-H column having 90/20 n-hexane/^{i}-PrOH as mobile phase, flow rate 1.0 ml/min, retention time: 16.10 min (major), 18.69 min (minor).

Fig. S19. ^{1}H NMR spectra:

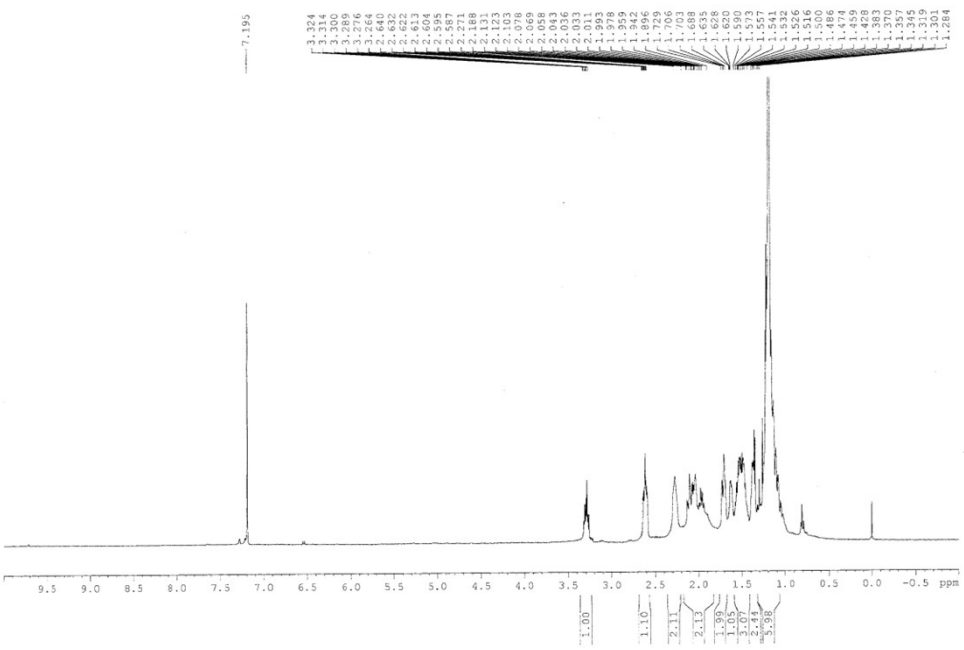
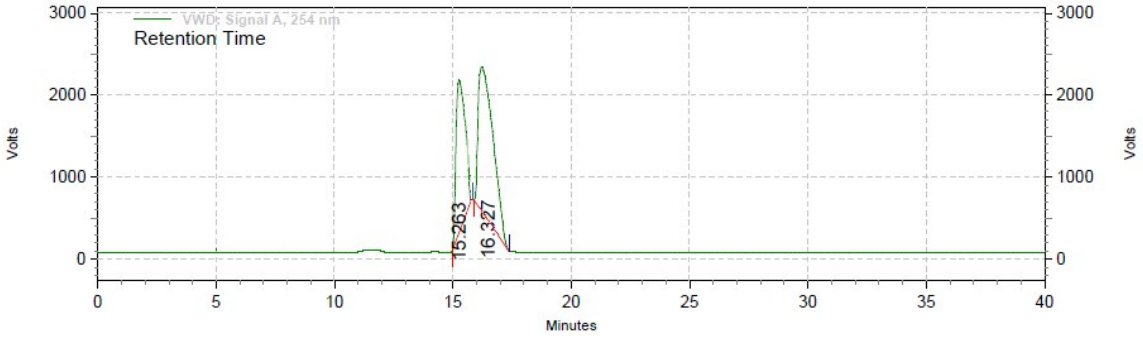
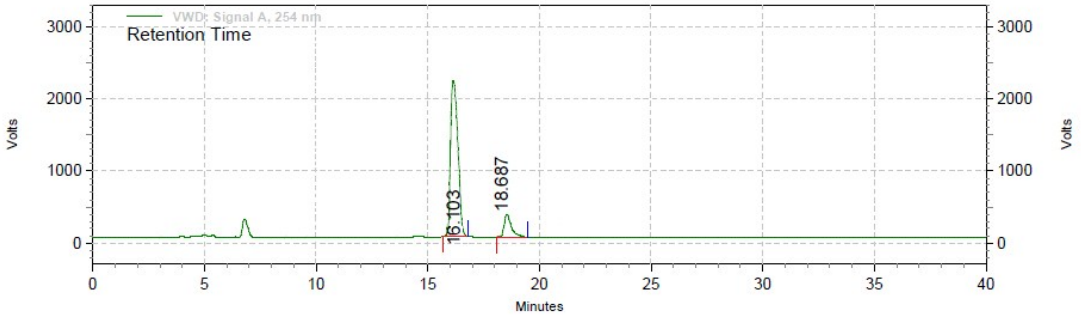


Fig. S20. HPLC chromatograms:



VWD: Signal A, 254 nm Results

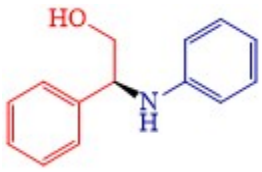
Retention Time	Area	Area %	Height	Height %
15.263	1055197943	48.85	31917663	48.72
16.327	1104894322	51.15	33592858	51.28
Totals	2160092265	100.00	65510521	100.00



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %	Height	Height %
16.103	862592212	80.53	41187656	84.57
18.687	208605716	19.47	7516507	15.43
Totals	1071197928	100.00	48704163	100.00

(*S*)-2-phenyl-2-(phenylamino)ethanol[1a] (3e, Table 2)



The compound was isolated by column chromatography over silica gel (ethyl acetate/hexane 10/90) as paleyellow viscous oil. $[\alpha]_D^{27}$ +29.8 (c = 0.5, $CHCl_3$); 98% ee; HPLC analysis was performed using Chiralpak OD-H column having 90/10 n-hexane/^{i}-PrOH as mobile phase, flow rate 1.0 ml/min, retention time : 11.74 min (minor), 14.87 min (major).

Fig. S21. ^{1}H NMR spectra:

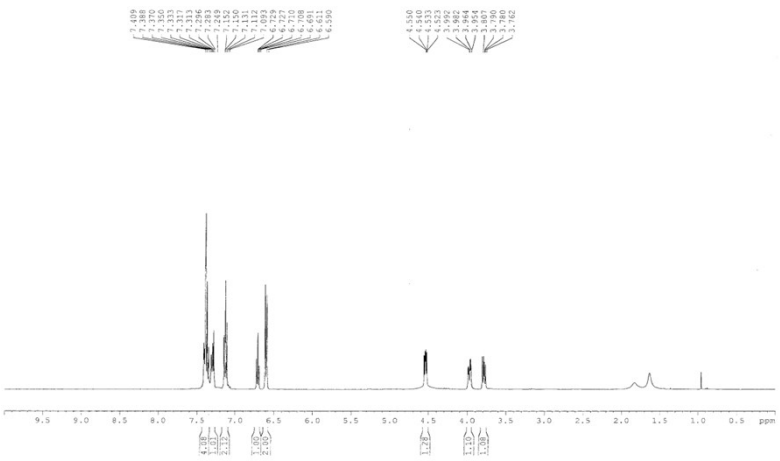
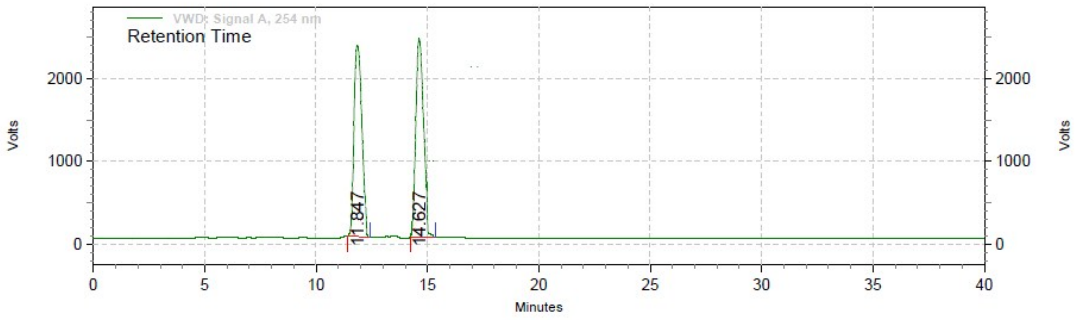
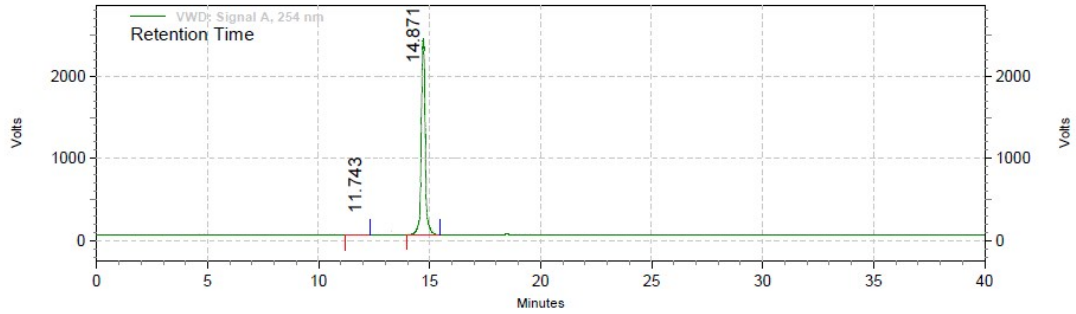


Fig. S22. HPLC chromatograms:



VWD: Signal A, 254 nm Results

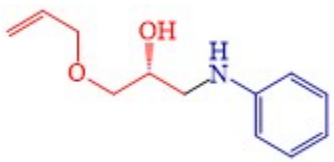
Retention Time	Area	Area %	Height	Height %
11.847	751928293	46.99	33076087	46.07
14.627	848361772	53.01	38714939	53.93
Totals	1600290065	100.00	71791026	100.00



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %	Height	Height %
11.743	43129611	1.60	2004713	5.07
14.871	2652471055	98.40	37527163	94.93
Totals	2695600666	100.00	39531876	100.00

(*R*)-1-(allyloxy)-3-(phenylamino)propan-2-ol[1a] (3f, Table 2)



The compound was isolated by column chromatography over silica gel (ethyl acetate/hexane 10/90) as pale yellow viscous liquid. $[\alpha]_D^{27}$ -38.0 (c 1.5, $CHCl_3$); 94% ee; HPLC analysis was

performed using Chiralpak OD-H column having 90/10 n-hexane/^{i}-PrOH as mobile phase, flow rate 1.0 ml/min, retention time : 9.90 min (major), 12.61 min (minor).

Fig. S23. ^{1}H NMR spectra:

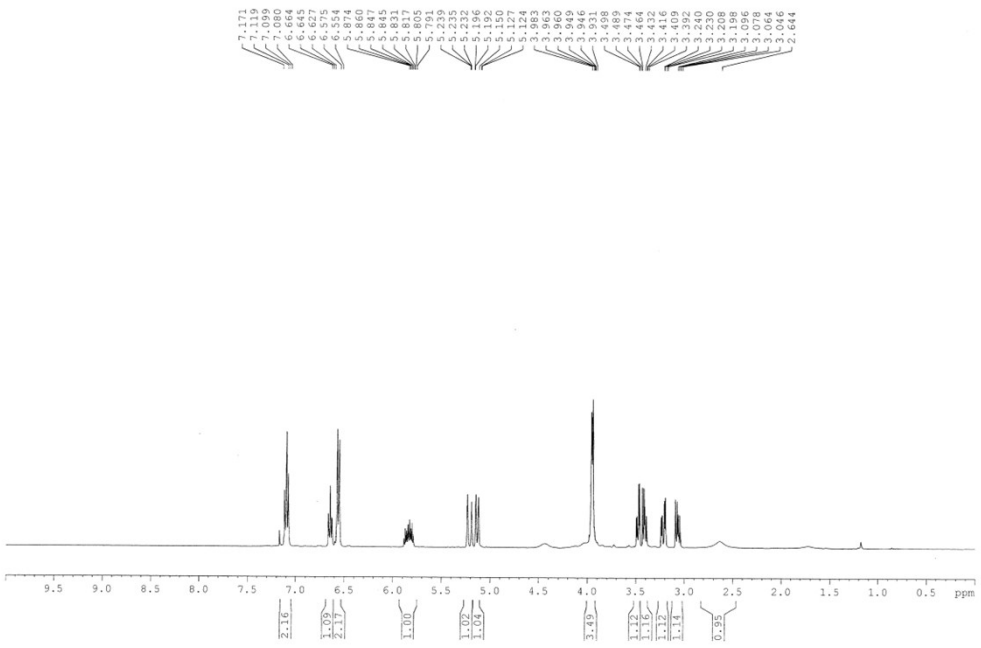
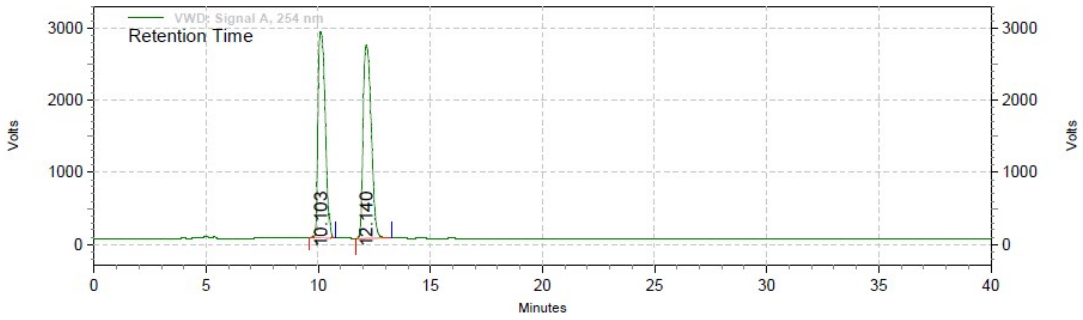
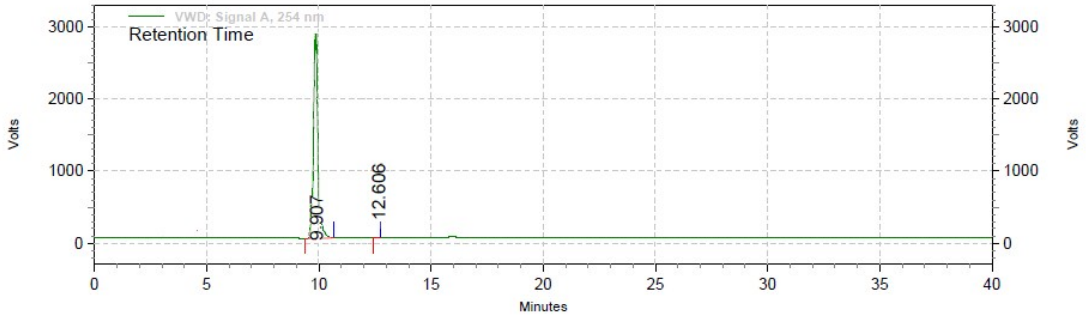


Fig. S24. HPLC chromatograms



VWD: Signal A, 254 nm Results

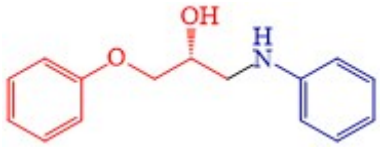
Retention Time	Area	Area %	Height	Height %
10.103	1023271901	47.34	47032156	51.02
12.140	1138283230	52.66	45144951	48.98
Totals	2161555131	100.00	92177107	100.00



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %	Height	Height %
9.907	1139609152	93.80	49026009	98.80
12.606	75356627	6.20	594778	1.20
Totals	1214965779	100.00	49620787	100.00

(*R*)-1-phenoxy-3-(phenylamino)propan-2-ol[1a] (3g, Table 2)



The compound was isolated by column chromatography over silica gel (ethyl acetate/hexane 10/90) as pale yellow liquid. $[\alpha]_D^{27}$ -33.7 (c = 0.5, $CHCl_3$); >99% ee; HPLC analysis was performed using Chiralpak OD-H column having 90/10 n-hexane/^{i}-PrOH as mobile phase, flow rate 1.0 ml/min, retention time: 19.29 min (minor), 25.41 min (major).

Fig. S25. ^{1}H NMR spectra:

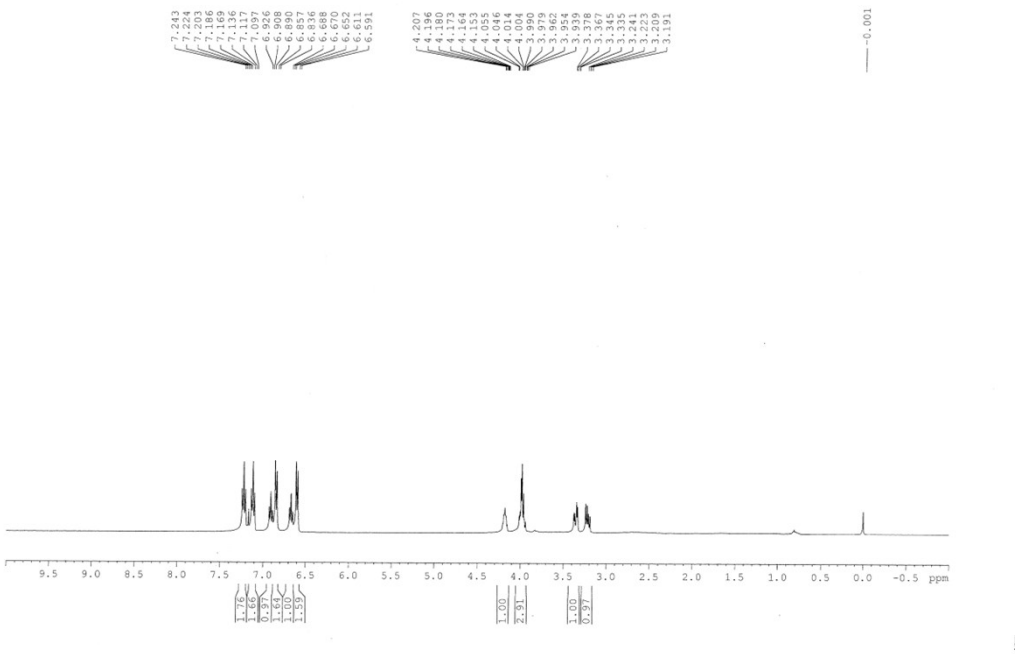
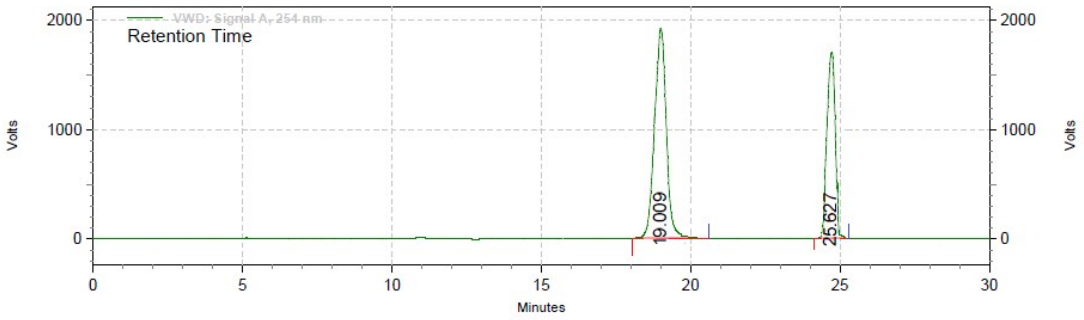
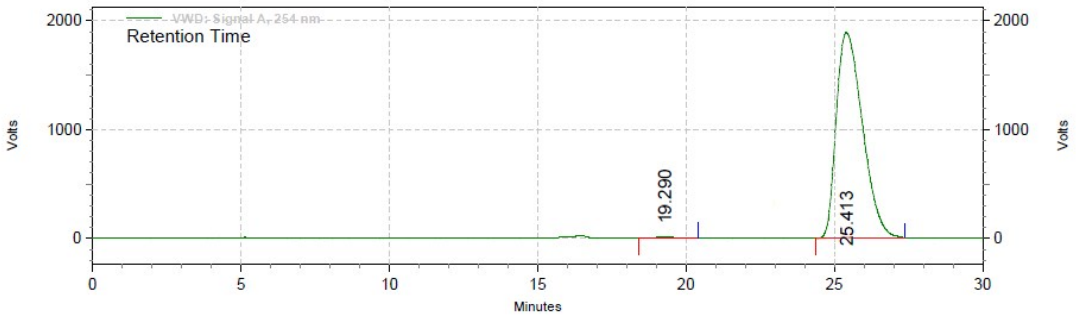


Fig. S26. HPLC chromatograms:



VWD: Signal A, 254 nm Results

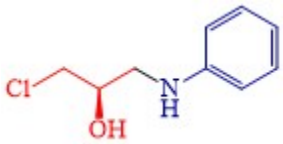
Retention Time	Area	Area %	Height	Height %
19.009	919090601	56.99	38398609	53.03
25.627	693691412	43.01	34009108	46.97
Totals	1612782013	100.00	72407717	100.00



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %	Height	Height %
19.290	12288796	0.64	291656	0.92
25.413	1910523233	99.36	31503764	99.08
Totals	1922812029	100.00	31795420	100.00

(*R*)-1-chloro-3-(phenylamino)propan-2-ol[1a] (3h, Table 2)



The compound was isolated by column chromatography over silica gel (ethyl acetate/hexane 10/90) as pale yellow liquid. $[\alpha]_D^{27}$ -29.0 (c = 1.04, $CHCl_3$); 98% ee; HPLC analysis was performed using Chiralpak OD-H column having 90/10 n-hexane/^{i}-PrOH as mobile phase, flow rate 1.0 ml/min, retention time: 14.80 min (minor), 17.18 min (major).

Fig. S27. ^{1}H NMR spectra:

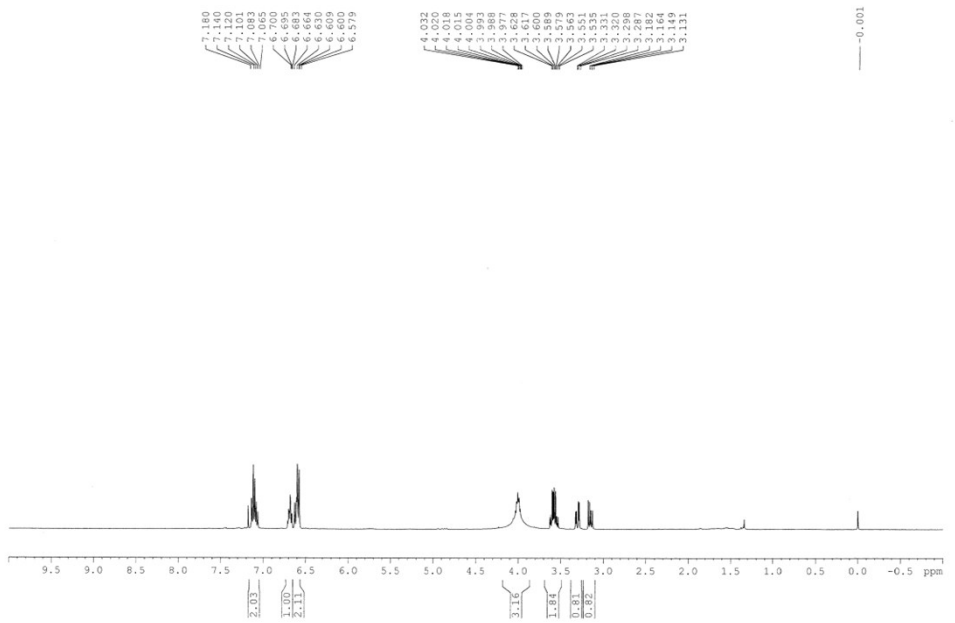
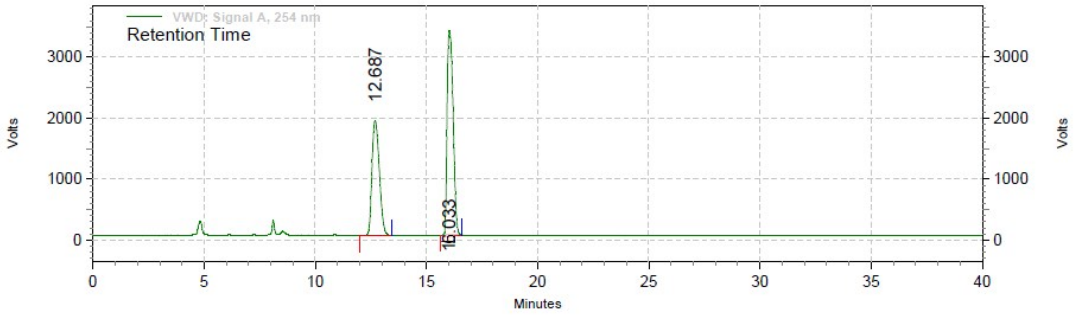
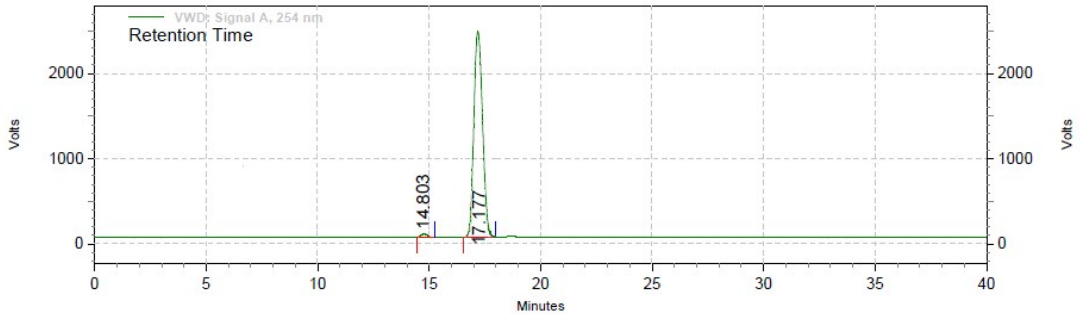


Fig. S28.HPLC chromatograms:



VWD: Signal A, 254 nm Results

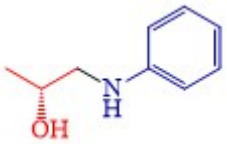
Retention Time	Area	Area %	Height	Height %
12.687	733994534	41.18	31734630	36.14
16.033	1048265466	58.82	56082980	63.86
Totals	1782260000	100.00	87817610	100.00



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %	Height	Height %
14.803	13743162	1.57	706194	1.96
17.177	862451394	98.43	35326236	98.04
Totals	876194556	100.00	36032430	100.00

(*R*)-1-(phenylamino)propan-2-ol[1a] (3i, Table 2)



The compound was isolated by column chromatography over silica gel (ethyl acetate/hexane 10/90) as pale yellow liquid. $[\alpha]_D^{27}$ -28.9 (c = 1.0, $CHCl_3$); 98% ee; HPLC analysis was performed using Chiralpak OD-H column having 90/10 n-hexane/^{i}PrOH as mobile phase, flow rate 1.0 ml/min, retention time: 12.52 min (major), 14.16 min (minor).

Fig. S29. ^{1}H NMR spectra:

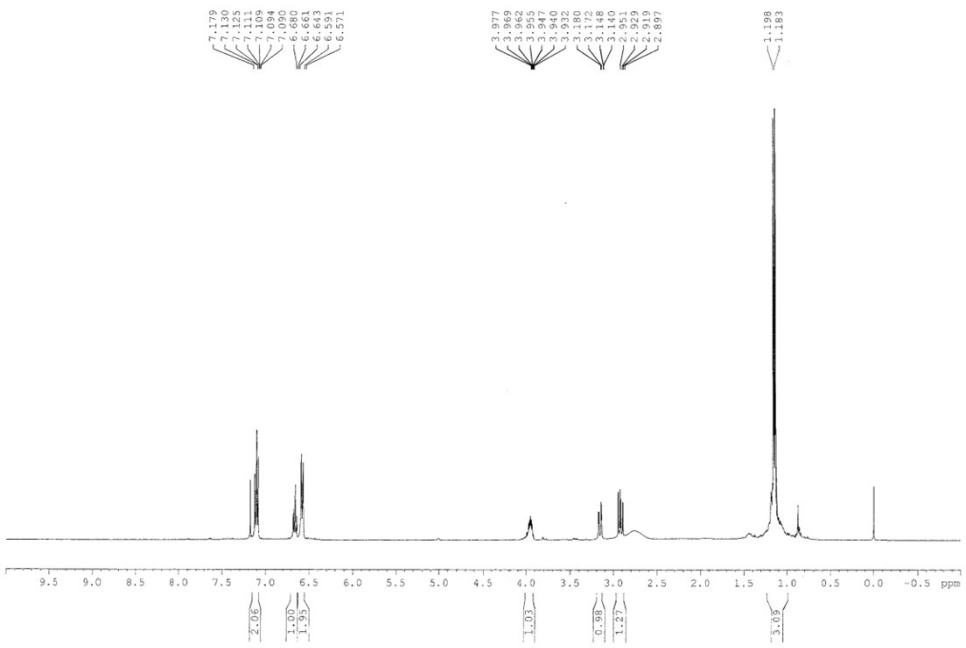
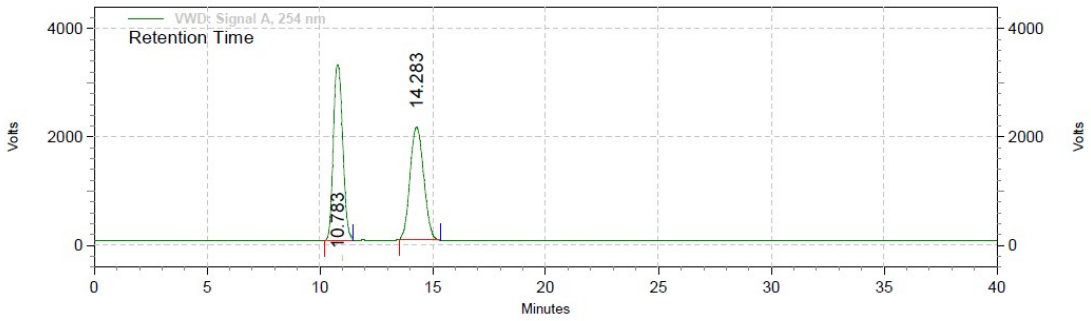
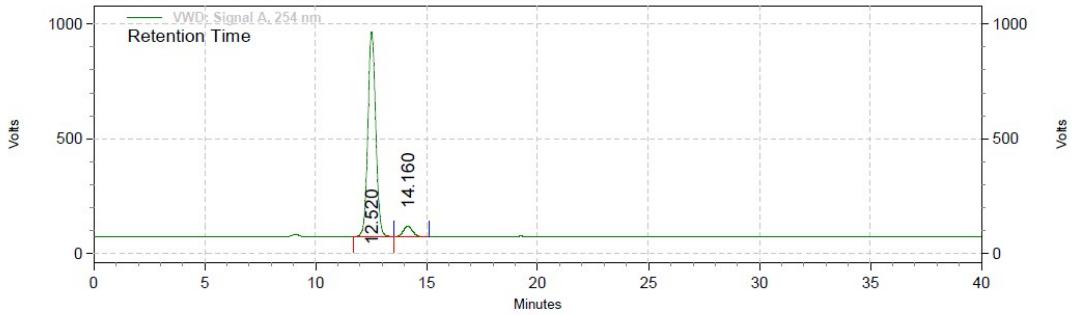


Fig. S30. HPLC chromatograms:



VWD: Signal A, 254 nm Results

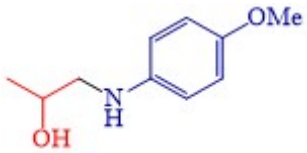
Retention Time	Area	Area %	Height	Height %
10.783	1517660074	51.45	53759244	60.93
14.283	1431881027	48.55	34465416	39.07
Totals				
	2949541101	100.00	88224660	100.00



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %	Height	Height %
12.520	383058228	98.34	14960109	95.19
14.160	6455987	1.66	755641	4.81
Totals	389514215	100.00	15715750	100.00

(-) 1-((4-methoxyphenyl)amino)propan-2-ol (3j, Table 2)



The compound was isolated by column chromatography over silica gel (ethyl acetate/hexane 10/90) as yellow liquid. $[]^{27}_{D}$= -25.8 (c = 1.0, $CHCl_3$); 98% ee; HPLC analysis was performed using Chiralpak OD-H column having 90/10 n-hexane/^{i}-PrOH as mobile phase, flow rate 1.0 ml/min, retention time: 12.92 min (major), 14.08 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$): 6.73-6.70 (m, 2H), 6.58-6.55 (m, 2H), 3.99-3.91 (m, 3H), 3.68 (s, 3H), 3.14-3.10 (m, 1H), 2.91-2.85 (m, 1H), 1.14 (d, J = 2.8 Hz, 3H).

Fig. S31. ^{1}H NMR spectra:

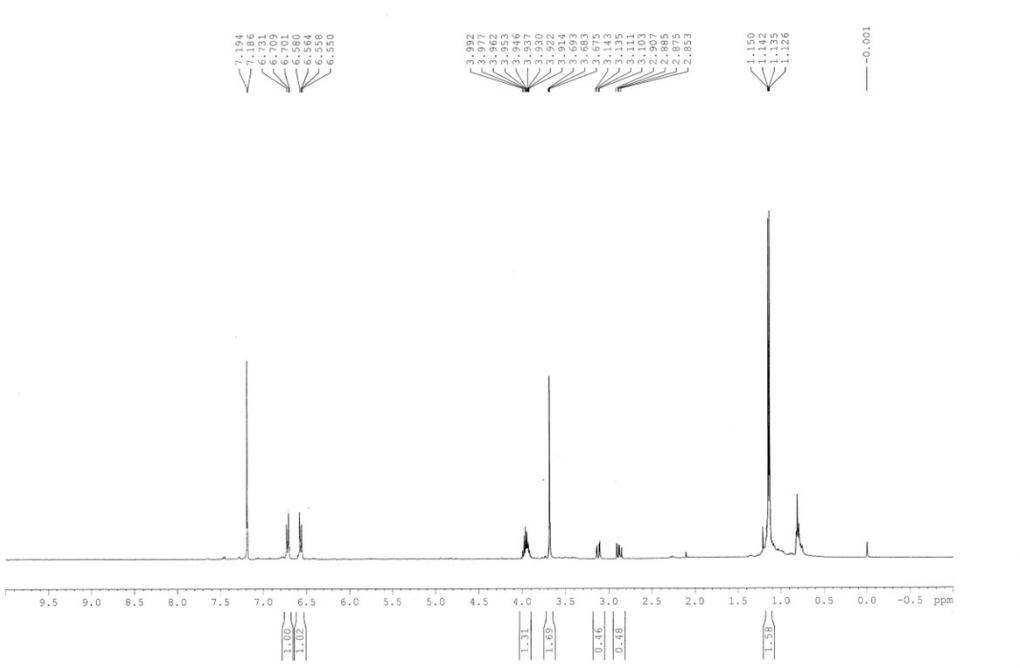
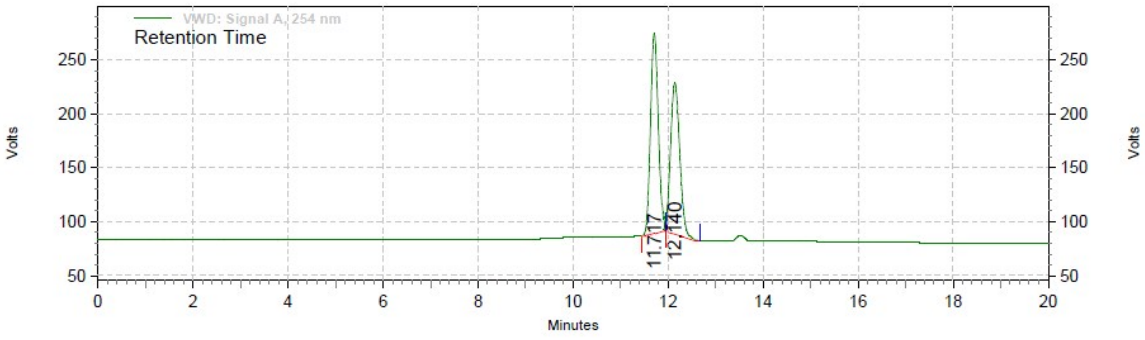
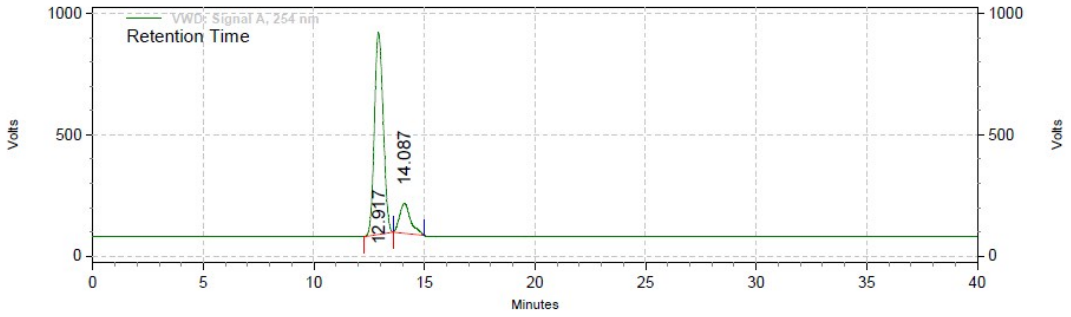


Fig. S32. HPLC chromatograms:



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %	Height	Height %
11.717	39933596	56.36	3143941	56.32
12.140	30921830	43.64	2438632	43.68
Totals	70855426	100.00	5582573	100.00



VWD: Signal A, 254 nm Results

Retention Time	Area	Area %	Height	Height %
12.917	398779694	87.30	13966503	87.09
14.087	58017506	12.70	2069925	12.91
Totals	456797200	100.00	16036428	100.00

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1. (a) S. Roy, P. Bhanja, S. S. Islam, A. Bhaumik and S. M. Islam, *Chem. Commun*., 2016, **52**, 1871. (b) L.W. Nicholsona, C.D. Pfeiffer, C.T. Goralskib, and B. Singaram, *J. Chromatography A*, 1996, **719**, 315.

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