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Chiral copper-salen complex grafted over functionalized mesoporous silica as an efficient catalyst for the asymmetric Henry reactions and synthesis of potent drug (R)-isoproterenol

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Section-I

1. GENERAL INFORMATION:

1.1 *Chemicals:*

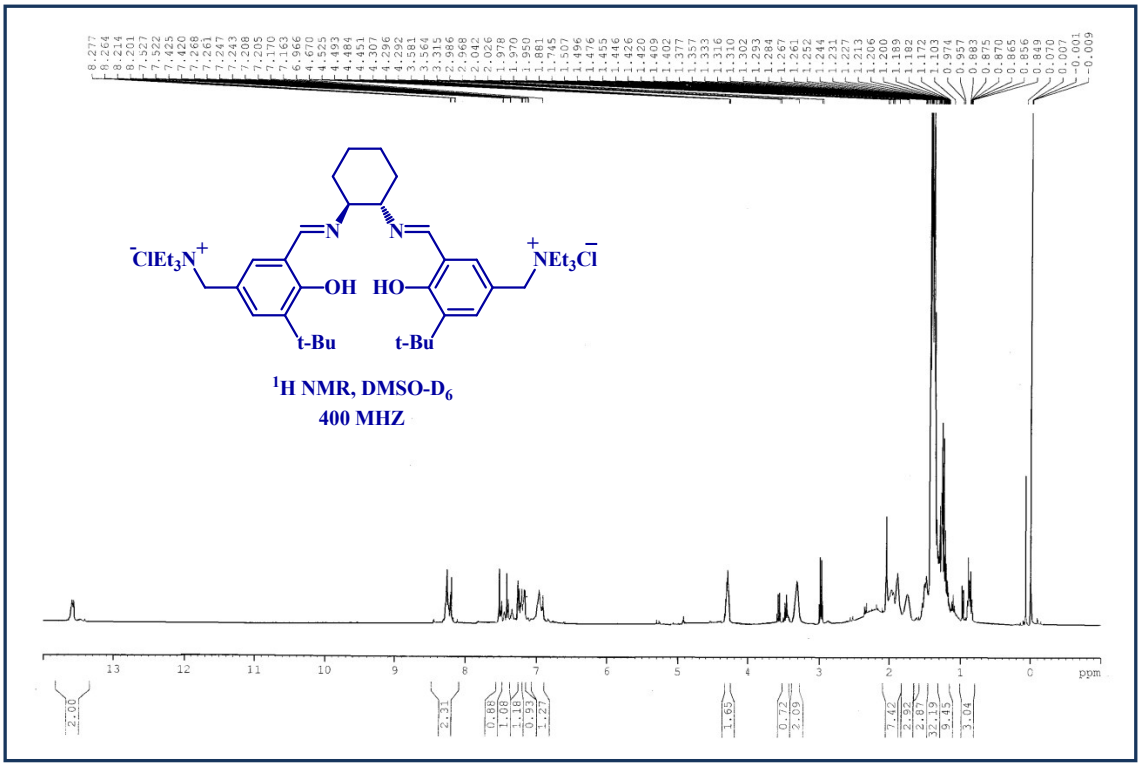
3-*tert*-butyl-2-hydroxybenzaldehyde (**1**), (1*S,* 2*S*)-(+)-1,2-diaminocyclohexane (**4**) Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, EO = ethylene oxide, PO = propyleneoxide, M_{av} = 5800), tetraethoxyorthosilicate (TEOS), 3-aminopropyl triethoxysilane (3-APTES, **8**), 4-formyl-benzoicacid, (**10**),$Cu(OAc)_2$.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

1.2 *Characterization techniques:*

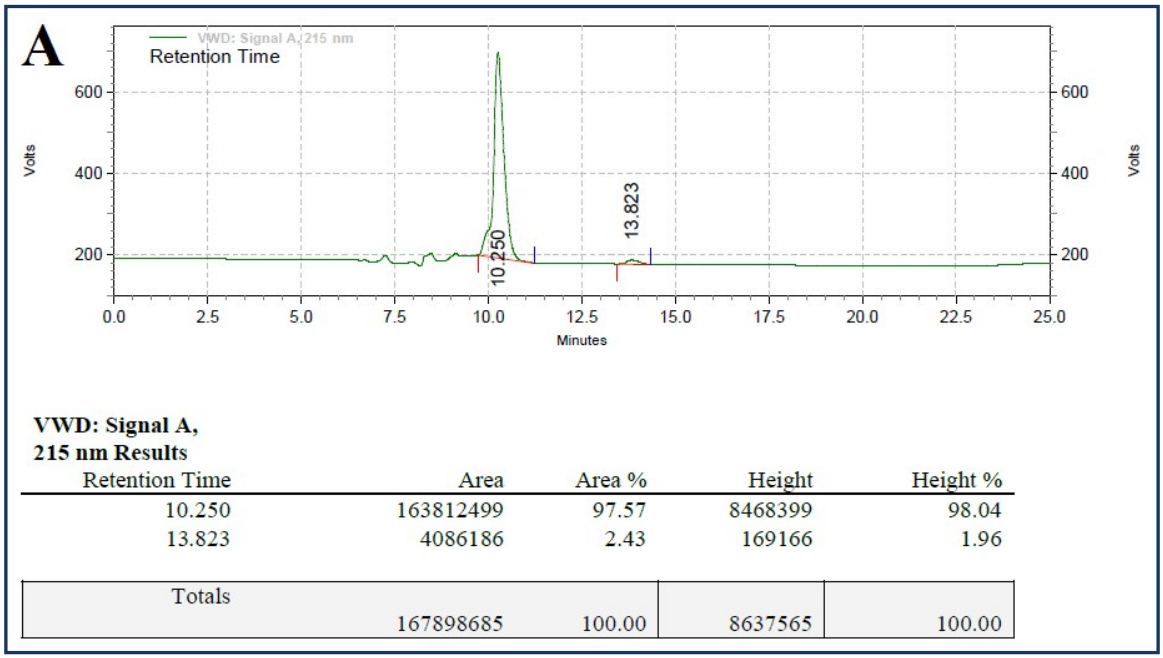
A Shimadzu UV 2401PC coupled with an integrating sphere attachment was used for the recording of UV-Visible spectra. $BaSO_4$ was applied as background standard. The Perkin-Elmer FT-IR 783 spectrophotometer was used to record FT-IR spectra of the samples in the range from 400 to 4000 cm^{-1} using KBr pellet as support. 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. TEM images of the mesoporous silica supported Cu-salen catalyst were obtained using a JEOL JEM 2010 transmission electron microscope. A Mettler Toledo TGA/DTA 851e device was used for TGA.A QuantachromeAutosorb 1C surface area analyzer was employed for N_2-sorption desorption analysis at 77 K. For the bulk elemental analysis, the Cu(II)@AFS-1 was digested with acid to dissolved them into clear liquid and then Cu content were analyzed by a Shimadzu AA-6300 atomic absorption spectrophotometer (AAS) fitted with a double beam monochromator. Carbon, hydrogen and nitrogen contents of Cu(II)@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 215 nm). 2-propanol/hexane system was used as eluent. Optical rotations were (described as: $[\alpha]_D^{25}$ (c = in g per 100 ml, solvent)) tested using Digipol 781 Automatic Polari meter Rudolph equipment.

2. CHARACTERISATION DATA OF THE Cu(II)@AFS-1CATALYST:

Fig. S1. ^{1}H NMR spectra of chiral Schiff base ligand **(1)**

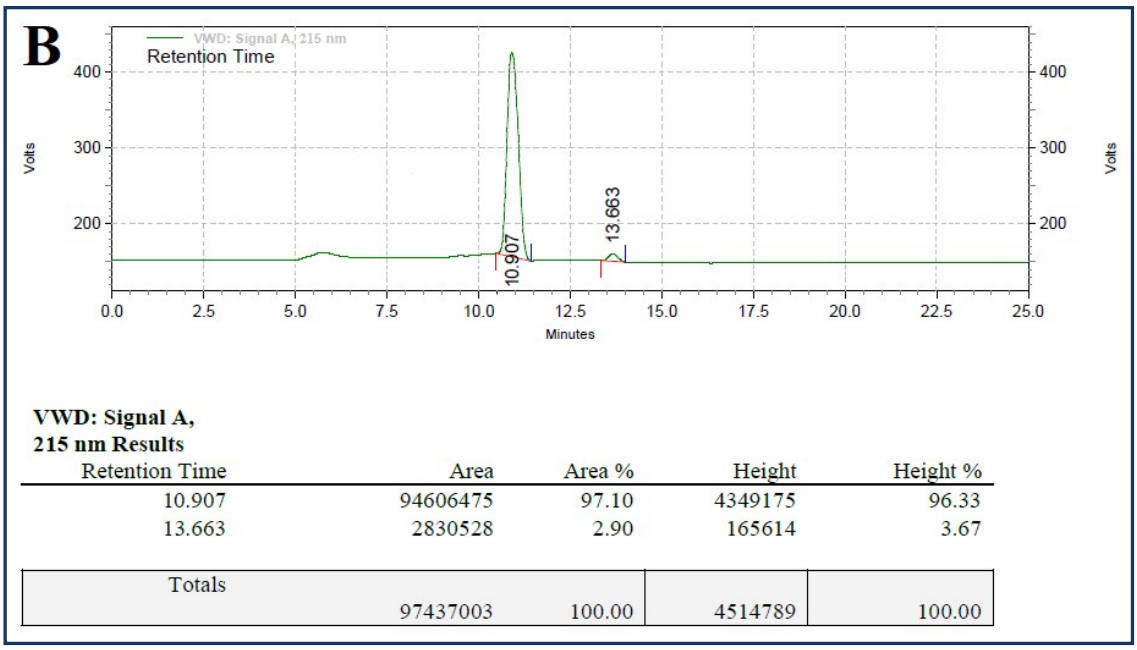


3.COMPARISON OF CATALYTIC ACTIVITY BETWEEN PhCHO AND CH_3NO_2 CATALYZED BY HOMOGENEOUS Cu(II)-SALEN COMPLEX (2) AND HETEROGENEOUS CHIRAL Cu(II)@AFS-1 CATALYST FOR THE HENRYREACTION[a]



VWD: Signal A, 215 nm Results

Retention Time	Area	Area %	Height	Height %
10.250	163812499	97.57	8468399	98.04
13.823	4086186	2.43	169166	1.96
Totals	167898685	100.00	8637565	100.00



VWD: Signal A, 215 nm Results

Retention Time	Area	Area %	Height	Height %
10.907	94606475	97.10	4349175	96.33
13.663	2830528	2.90	165614	3.67
Totals	97437003	100.00	4514789	100.00

Figure S2. HPLC chromatograms of (R)-2-nitro-1-phenylethanol (**2d**) over homogeneous chiral Cu(II) salen complex (**A**) and heterogeneous chiral Cu(II)@AFS-1 catalyst (**B**).

4. SYNTHESIS AND CHARACTERIZATION DATA OF CHIRAL DRUG (R)-ISOPROTERENOL

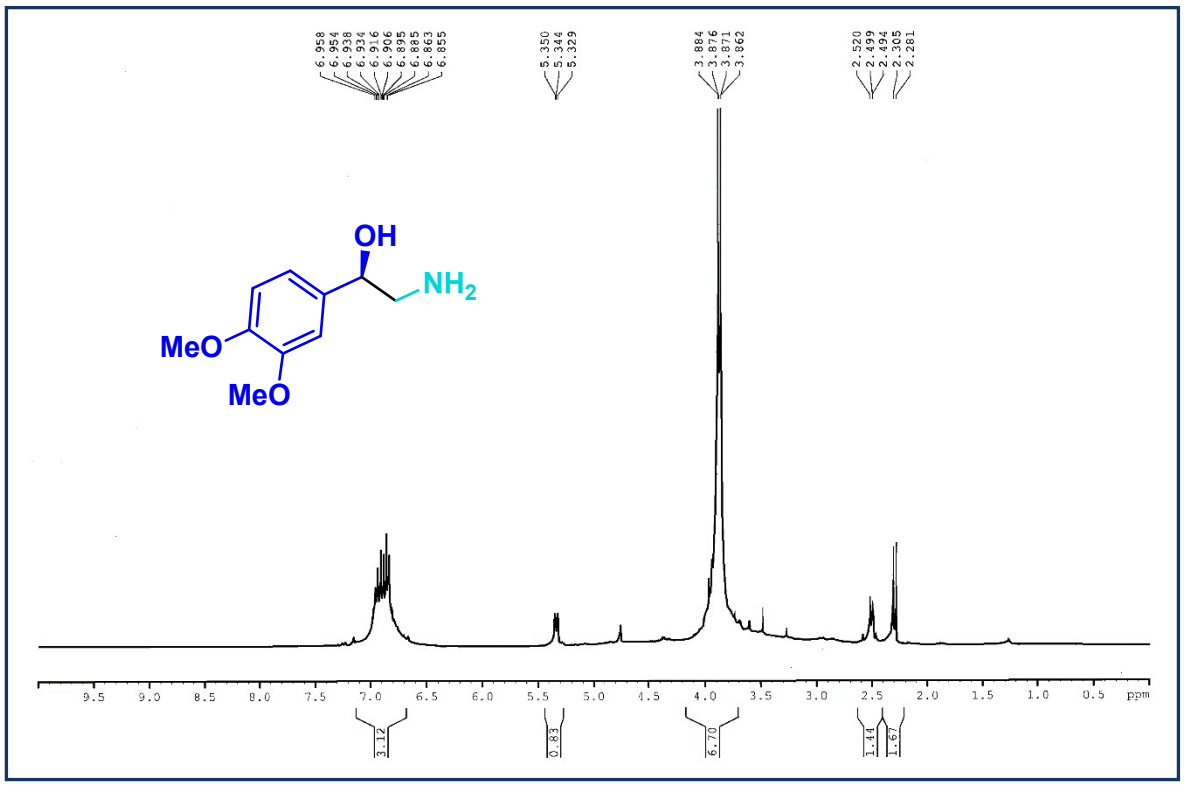
4.1 (R)-(-)-1-(3,4-dimethoxyphenyl)-2-nitroethanol (2f)[1]:

(R)-1-(3,4-dimethoxyphenyl)-2-nitroethanol (**2f**) was synthesized from 3,4-dimethoxy benzaldehyde and nitromethane according to our optimized reaction conditions as stated in Table 2. The characterization data of the compound 2f are stated in Section S2.

4.2(R)-(-)-2-Amino-1-(3,4-dimethoxyphenyl)ethanol (3)[1]:

10% Pd/C (230 mg) was slowly and cautiously added to the stirred ethanolic solution of 2f (2.95 mmol) under H_2 atmosphere for 24 h. After completion of the reaction catalyst was filtered out through the small pad of Celite. Then the solvent was removed under reduced pressure to furnish compound 3 (94% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ6.96-6.85 (m, 3H), 5.35-5.33 (m, 1H), 3.88 (bs, 3H), 3.86 (bs, 3H), 2.51 (d, J = 10.4 Hz, 1H), 2.29 (d, J = 9.6 Hz, 1H);$[\alpha]_D^{25}$ = -25.3 (*c* 1.0, EtOH)[1]{$[\alpha]_D^{25}$ = -24.0 (c 1.08, EtOH)}.

Fig. S3. ^{1}H NMR spectrum of (R)-(-)-2-Amino-1-(3,4-dimethoxyphenyl)ethanol (**3**):



4.3 (R)-(-)-1-(3,4-Dimethoxyphenyl)-2-(isopropylamino) ethanol (4)[1]

A mixture of compound 3 (2.2 mmol) and acetone (4.7 mmol) in ethanol (4 mL) was stirred at RT for 1 h. Then after cooling the mixture to 0 ºC (ice bath), $NaBH_4$ (3.3 mmol) was added to it. Thereafter the reaction mixture was further stirred for 1 h and finally the product compound (**4**) was separated through column chromatography (EtOAc/MeOH) as yellow coloured solid (95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ6.87-6.77 (m, 3H), 4.89 (bs, 1H), 3.79 (bs, 6H), 2.78-2.75 (m, 1H), 2.69-2.65 (m, 2H), 1.20-1.17 (m, 6H).$[\alpha]_D^{25}$ = -27.2 (c2.51, Acetone)[1]{$[\alpha]_D^{25}$ = -32.7 (c 3.00, Acetone)}, mp 126 ºC[2] mp:126-128 ºC], 91% ee; HPLC analysis was performed using Chiralcel OD-H column having 85/15 n-hexane/*i*-PrOH as mobile phase, flow rate 1.0 ml/min, retention time (*R*): 10.34 min (major), (*S*): 15.70 min (minor).

Fig. S4. ^{1}H NMR spectrum of (R)-(-)-1-(3,4-Dimethoxyphenyl)-2-(isopropylamino)ethanol (**4**):

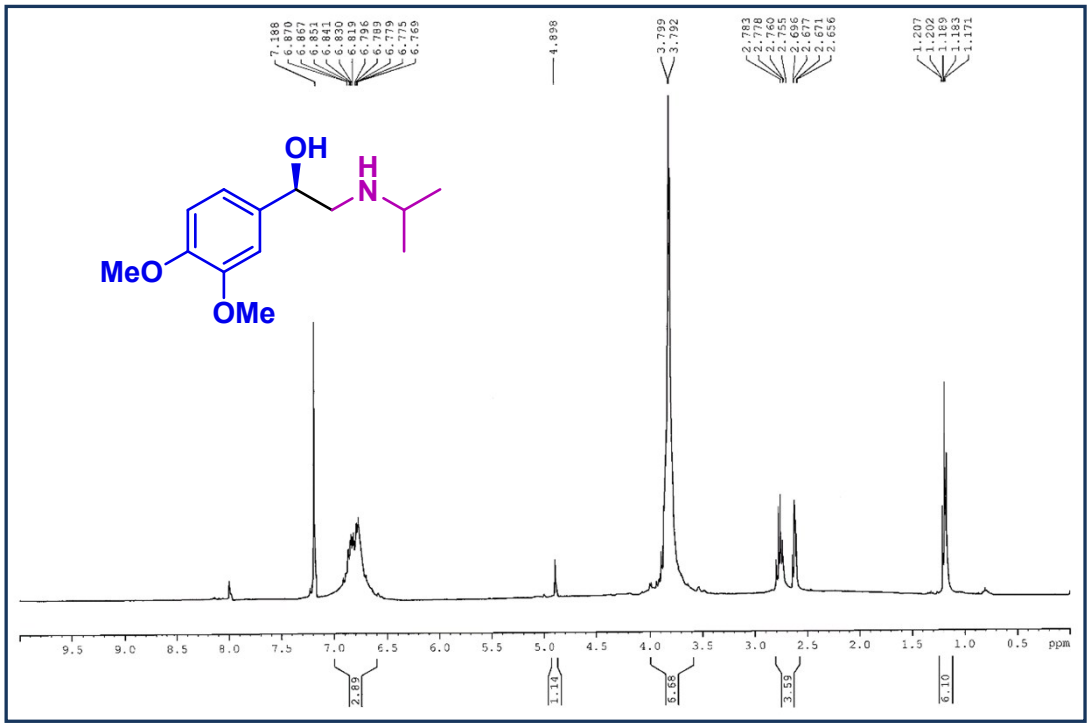
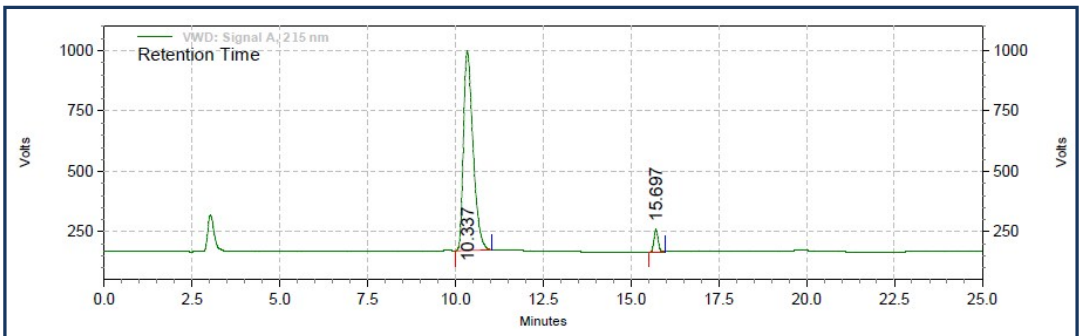


Fig. S5. HPLC chromatogram of **4**:



VWD: Signal A, 215 nm Results

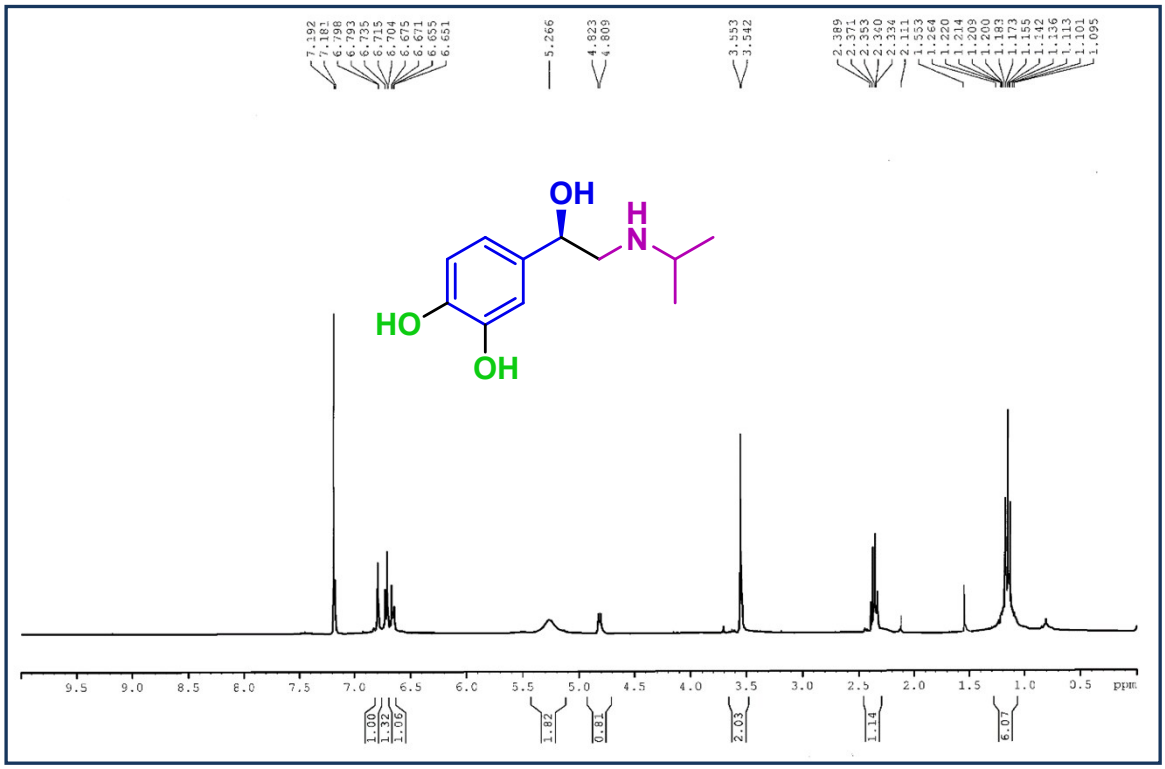
Retention Time	Area	Area %	Height	Height %
10.337	262901375	95.38	13833598	89.84
15.697	12747543	4.62	1564081	10.16
Totals	275648918	100.00	15397679	100.00

4.4 (R)-(-)-Isoproterenol[3-5]

The solution of EtSH (2 mL) in DCM was cooled to 0 °C (ice bath) and $AlCl_3$ (12 mmol) was added to it. Then the solution was warmed to RT and the compound **4** (0.578 mmol) was added. Thereafter stirring for 20 h the reaction mixture was poured into triple distilled water followed by acidified with dil. HCl and extracted with DCM. Then the solvent was evaporated and the product was collected by column chromatography ($CHCl_3$/MeOH) as a colourless solid (96% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ6.79-6.65 (m, 3H), 5.27 (br s, 2H), 4.81 (d, *J* = 5.6 Hz, 1H), 3.55-3.54 (m, 2H), 2.38-2.33 (m, 1H), 1.26-1.09 (m, 6H);

IR(neat): 3310, 2992, 1609, 1485, 1263, 1082, 889, 779 cm^{-1}; Anal. calcd. for $C_{11}H_{17}NO_3$: C 62.54, H 8.11, N 6.63; found: C 62.72, H 8.09, N 6.54%.$[\alpha]_D^{25}$ = -41.2 (*c* 1.06, 2M HCl)[3-5] $[\alpha]_D^{25}$ = -42.3 (c 1.00, 2M HCl), mp 162 ºC[3-5] mp:163-164 ºC. The overall yield of the drug molecule is 82%.

Fig. S6. ^{1}H NMR spectrum of (R)-(-)-Isoproterenol**:**



5. COMPARATIVE STUDY:

Table S1. Comparison of the catalytic activity of Cu(II)@AFS-1 with related catalysts:

Catalyst	Reaction Conditions	Yield[a] (%)	ee[b] (%)	TON	Ref
Chiral macrocyclic [H_4] salen ligand, $Cu(OAc)_2.H_2O$	Benzaldehyde, CH_3NO_2, THF, RT, 20 h	84	93	11.2	6
Fam-1 ligand, Et_2Zn	Benzaldehyde, CH_3NO_2, THF, -50 ºC, 16 h	83	87	1.53	7
Macrocyclic salen ligand, $CuCl_2 \cdot 2H_2O$	Benzaldehyde, CH_3NO_2, EtOH + DCM, 2,6-lutidine, RT, 30 h.	86	91	8.6	8
C_1-symmetric primary-secondary diamines ligand, CuBr	Benzaldehyde, CH_3NO_2, THF, NMM, RT, 24 h, N_2-atm.	81	82	8.1	9
Chiral tetrahydrosalen ligand, $(CuOTf)_2.C_6H_5CH_3$	Benzaldehyde, CH_3NO_2, MeOH, 4 Å MS, 40 ºC, 20 h	90	92	90	10
Heterogeneous chiral Cu(II)@AFS-1	**Benzaldehyde, CH_3NO_2, DCM, RT, 15 h**	**96**	**94**	**449**	**This work**

[a]Yields are referred to those of isolated pure products. [b]ee was determined from the HPLC analysis.

Section-II

1. CHARACTERIZATION DATA AND HPLC CHROMATOGRAMS OF THE PURE PRODUCTS:

(R)-2-nitro-1-(4-nitrophenyl)ethanol[11] (2a, Table 1)

The desired product was isolated by column chromatography over silica gel (ethyl acetate/hexane 15/85) as yellow oil. $[\alpha]_D^{25}$= -10.8(c 1.01, CH_2Cl_2), lit.[11] $[\alpha]_D^{25}$= -10.0 (c 1.06, CH_2Cl_2); 91% ee; HPLC analysis was performed using Chiralcel OD-H column having 85/15 n-hexane/^{i}PrOH as mobile phase, flow rate 1.0 ml/min, retention time (*R*): 17.79 min (major), (*S*): 24.53 min (minor).

Fig.S7. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz)**:**

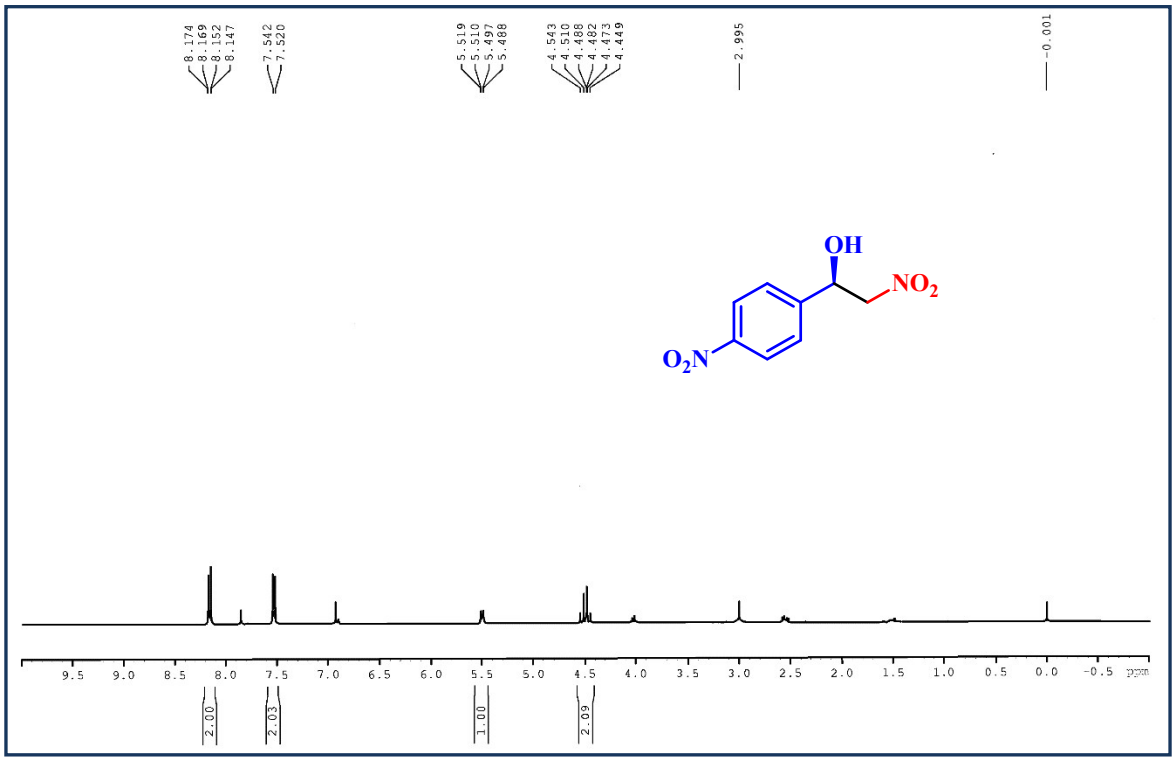
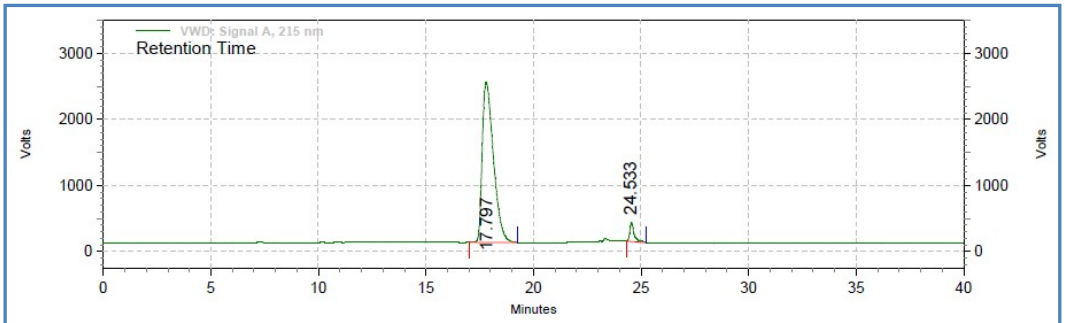


Fig. S8. HPLC chromatogram:



VWD: Signal A, 215 nm Results

Retention Time	Area	Area %	Height	Height %
17.797	1475919558	95.53	40792560	89.30
24.533	69067713	4.47	4888895	10.70
Totals	1544987271	100.00	45681455	100.00

(R)-1-(4-chlorophenyl)-2-nitroethanol[11] (2b, Table 1)

The desired product was isolated by column chromatography over silica gel (ethyl acetate/hexane 15/85) as yellowish oil. $[\alpha]_D^{25}$= -25.1(c 1.09, CH_2Cl_2), lit.[11]$[\alpha]_D^{25}$= +24.7 (c 1.13, CH_2Cl_2); 90% ee; HPLC analysis was performed using Chiralcel OD-H column having 85/15 n-hexane/*i*-PrOH as mobile phase, flow rate 1.0 ml/min, retention time (*R*): 10.39 min (major), (*S*): 12.46 min (minor).

Fig.S9. ^{1}H NMR spectrum($CDCl_3$, 400 MHz)**:**

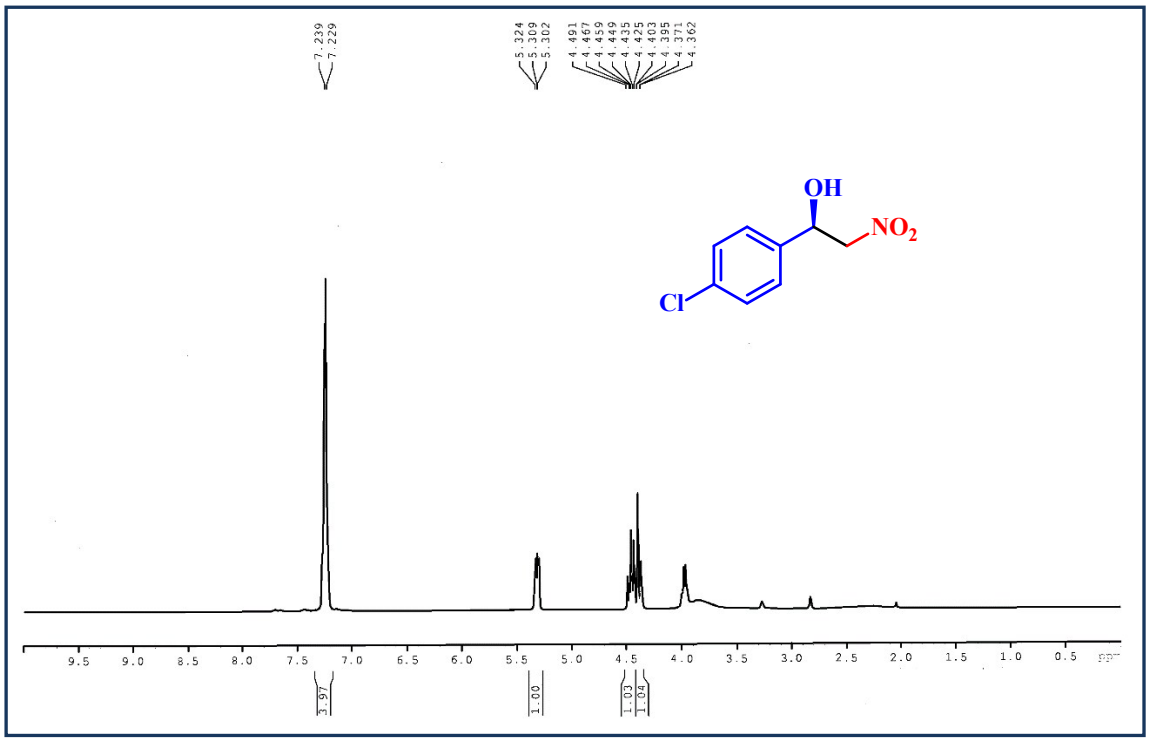
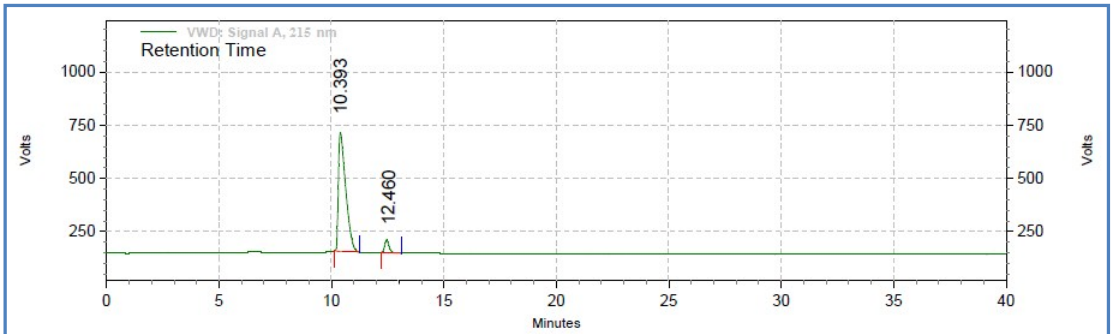


Fig. S10. HPLC chromatogram:



VWD: Signal A, 215 nm Results

Retention Time	Area	Area %	Height	Height %
10.393	206101000	94.89	9118017	90.01
12.460	11099701	5.11	1012012	9.99
Totals	217200701	100.00	10130029	100.00

(R)-2-nitro-1-(p-tolyl)ethanol[11] (2c, Table 1)

The desired product was isolated by column chromatography over silica gel (ethyl acetate/hexane 15/85) as yellowish oil. $[\alpha]_D^{25}$= -37.9(c 1.1, CH_2Cl_2), lit.[11]$[\alpha]_D^{25}$= -37.2(c 1.14, CH_2Cl_2); 87% ee; HPLC analysis was performed using Chiralcel OD-H column having 85/15 n-hexane/*i*-PrOH as mobile phase, flow rate 1.0 ml/min, retention time (*R*): 10.35 min (major), (*S*): 13.55 min (minor).

Fig.S11. ^{1}H NMR spectrum($CDCl_3$, 400 MHz)**:**

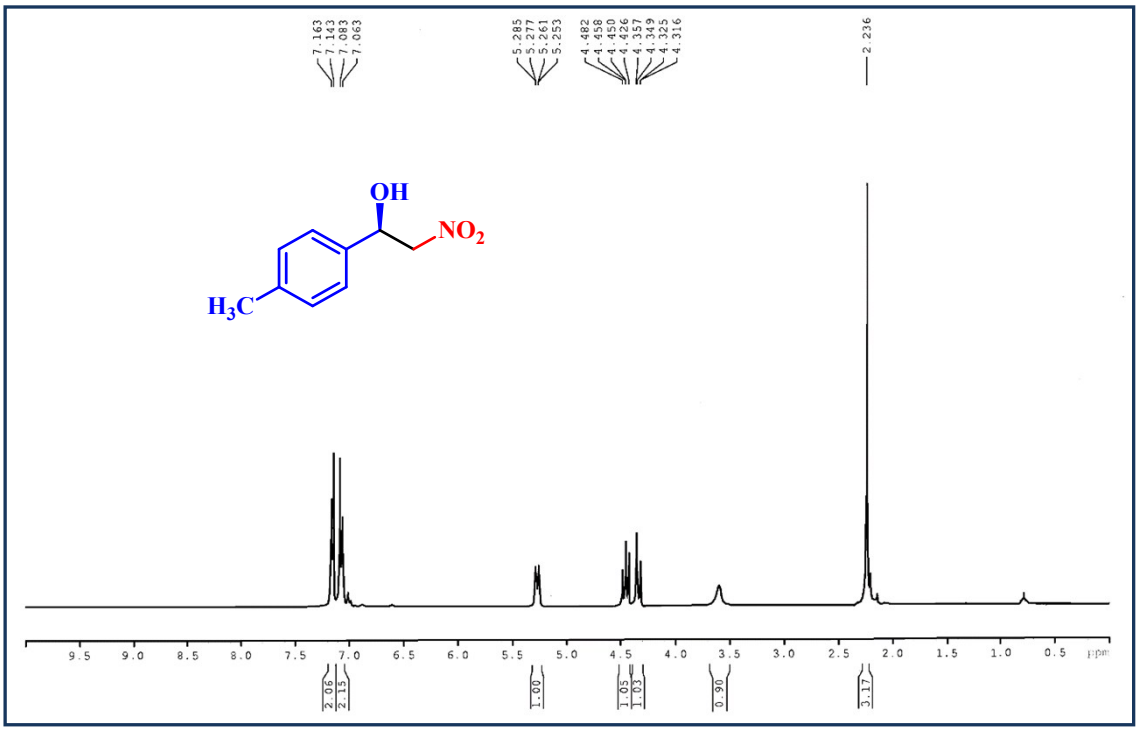
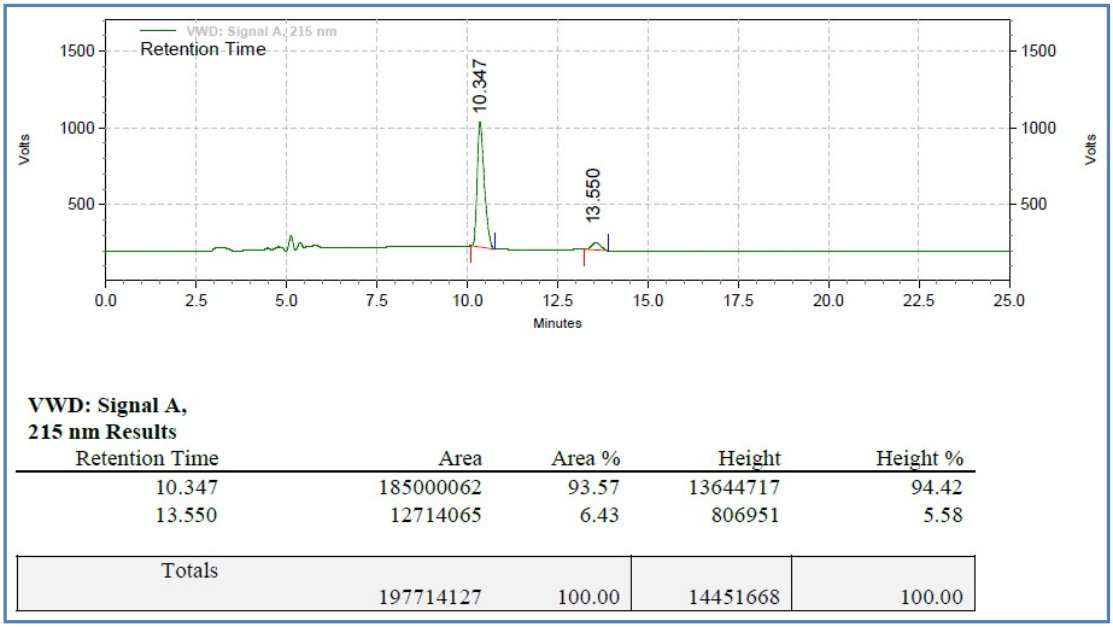


Fig. S12. HPLC chromatogram:



VWD: Signal A, 215 nm Results

Retention Time	Area	Area %	Height	Height %
10.347	185000062	93.57	13644717	94.42
13.550	12714065	6.43	806951	5.58
Totals	197714127	100.00	14451668	100.00

(R)-2-nitro-1-phenylethanol[10](2d, Table 1)

The desired product was isolated by column chromatography over silica gel (ethyl acetate/hexane 15/85) as pale-yellow oil. $[\alpha]_D^{25}$= -34.8(c 0.23, CH_2Cl_2), lit.[10] $[\alpha]_D^{25}$= - 39.5 (*c* 0.2, CH_2Cl_2); 94% ee; HPLC analysis was performed using Chiralcel OD-H column having 85/15 n-hexane/*i*-PrOH as mobile phase, flow rate 1.0 ml/min, retention time (*R*): 10.91 min (major), (*S*): 13.66 min (minor).

Fig.S13. ^{1}H NMR spectrum($CDCl_3$, 400 MHz)**:**

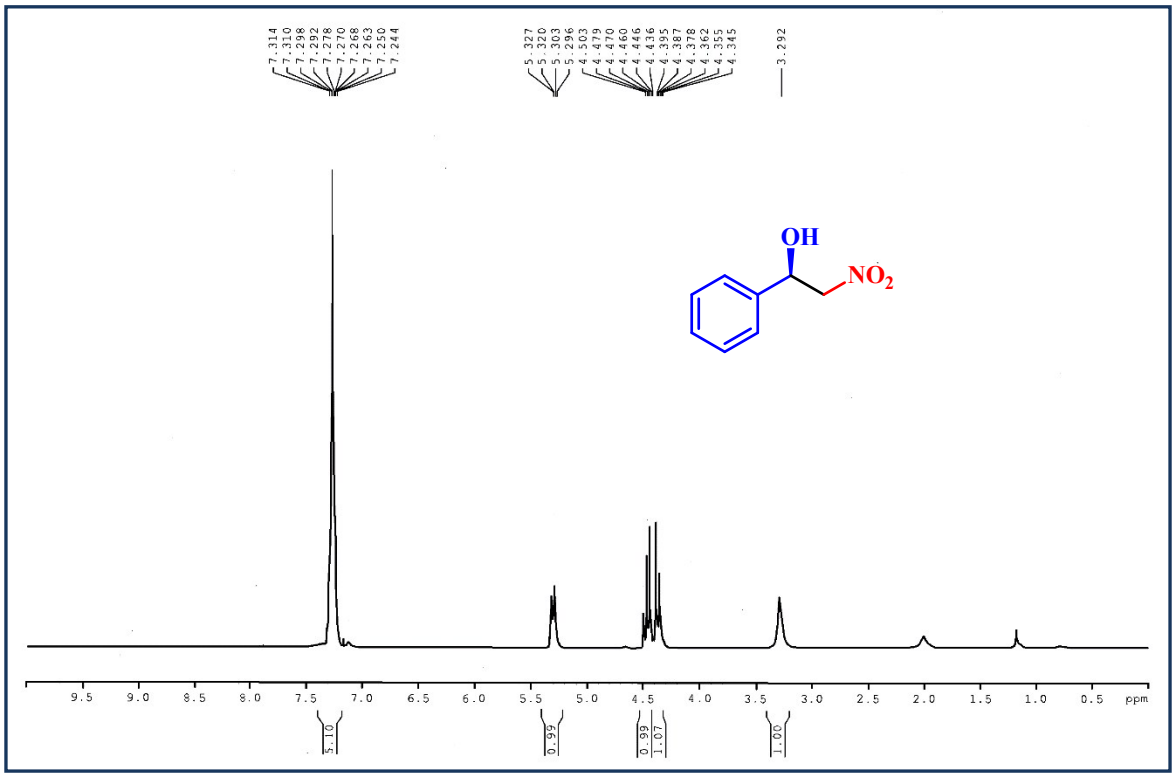
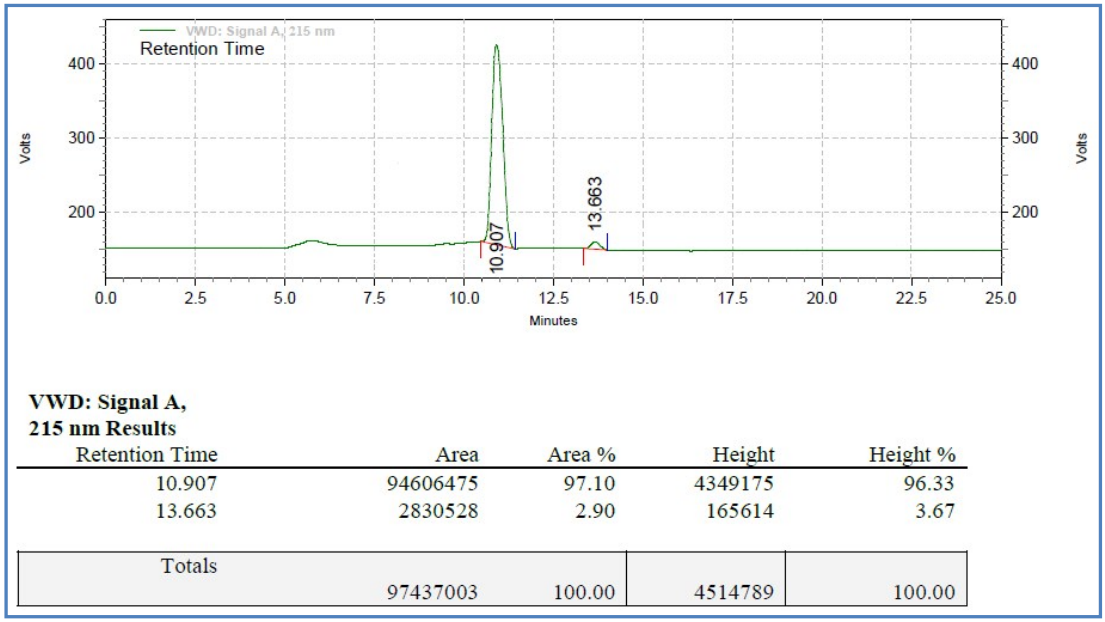


Fig. S14. HPLC chromatogram:



VWD: Signal A, 215 nm Results

Retention Time	Area	Area %	Height	Height %
10.907	94606475	97.10	4349175	96.33
13.663	2830528	2.90	165614	3.67
Totals	97437003	100.00	4514789	100.00

(R)-1-(4-methoxyphenyl)-2-nitroethanol[11](2e, Table 1)

The desired product was isolated by column chromatography over silica gel (ethyl acetate/hexane 15/85) as yellow oil. $[\alpha]_D^{25}$= -27.3(c 1.1, CH_2Cl_2), lit.[12] $[\alpha]_D^{25}$ = - 29.8 (*c* 1, CH_2Cl_2); 85% ee; HPLC analysis was performed using Chiralcel OD-H column having 85/15 n-hexane/*i*-PrOH as mobile phase, flow rate 1.0 ml/min, retention time (*R*): 10.39 min (major), (*S*): 14.10 min (minor).

Fig.S15. ^{1}H NMR spectrum($CDCl_3$, 400 MHz)**:**

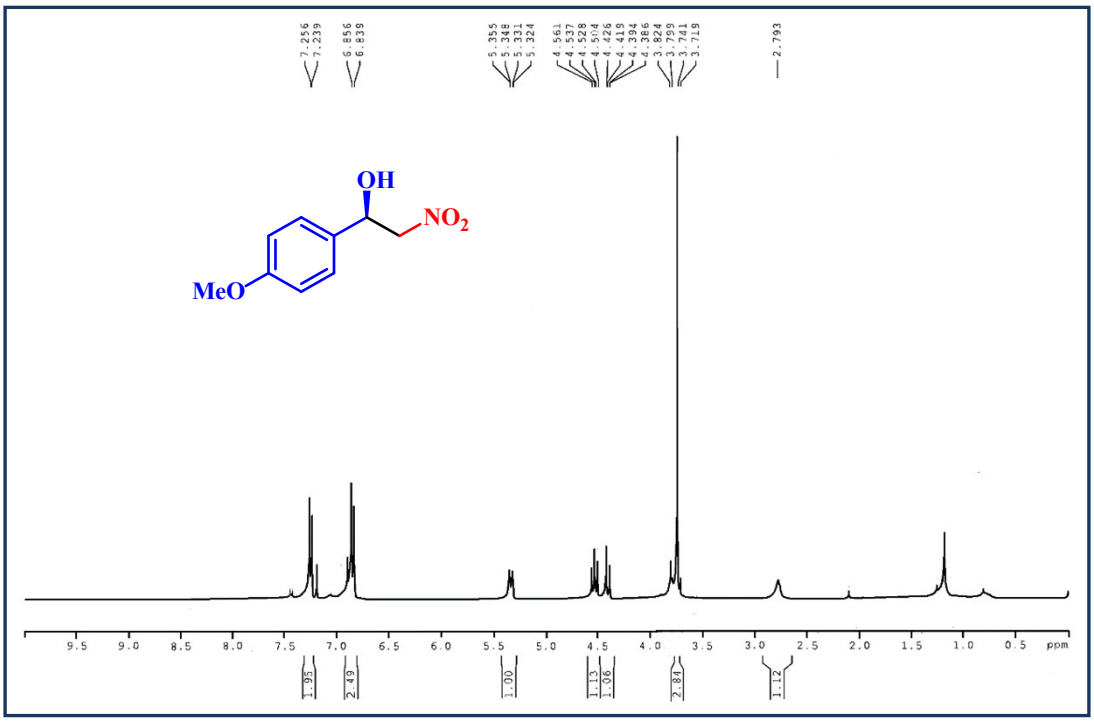
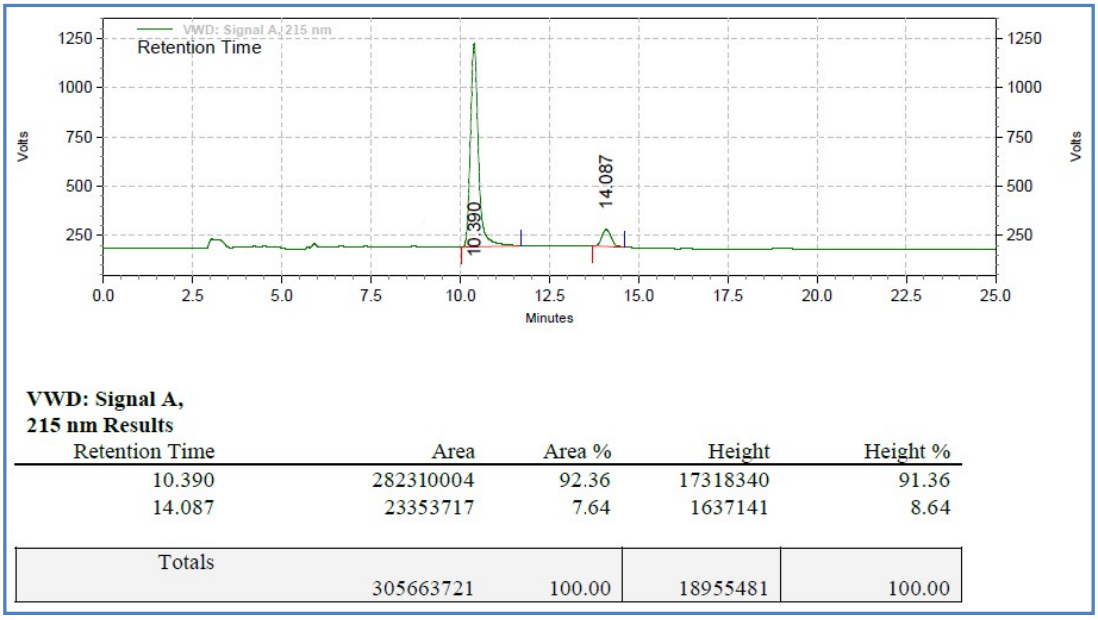


Fig. S16. HPLC chromatogram:



VWD: Signal A, 215 nm Results

Retention Time	Area	Area %	Height	Height %
10.390	282310004	92.36	17318340	91.36
14.087	23353717	7.64	1637141	8.64
Totals	305663721	100.00	18955481	100.00

(R)-1-(3,4-dimethoxyphenyl)-2-nitroethanol[1] (2f, Table 1)

The desired product was isolated by column chromatography over silica gel (ethyl acetate/hexane 15/85) as yellowish oil. $[\alpha]_D^{25}$= -28.0(c 1.98, CH_2Cl_2), lit.[1]$[\alpha]_D^{25}$= -27.1(c 2.01, CH_2Cl_2); 93% ee; HPLC analysis was performed using Chiralcel OD-H column having 85/15 n-hexane/*i*-PrOH as mobile phase, flow rate 1.0 ml/min, retention time (*R*): 16.52 min (major), (*S*): 22.16 min (minor).

Fig.S17. ^{1}H NMR spectrum($CDCl_3$, 400 MHz)**:**

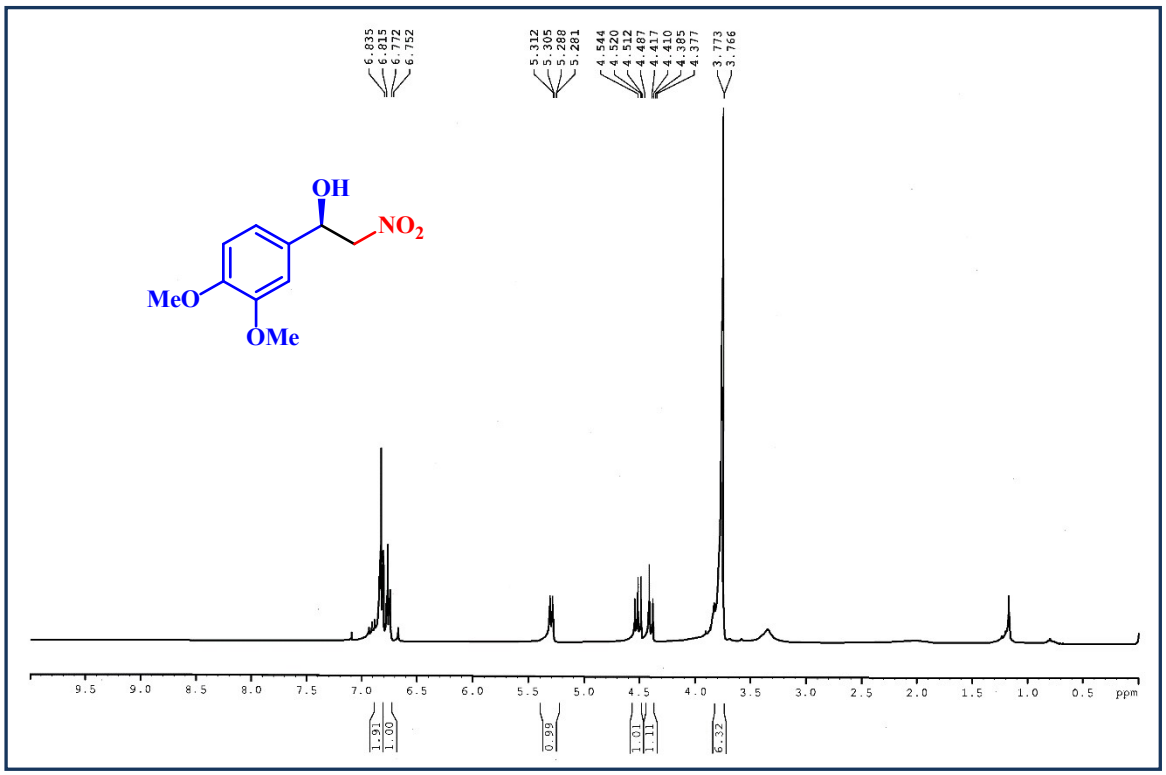
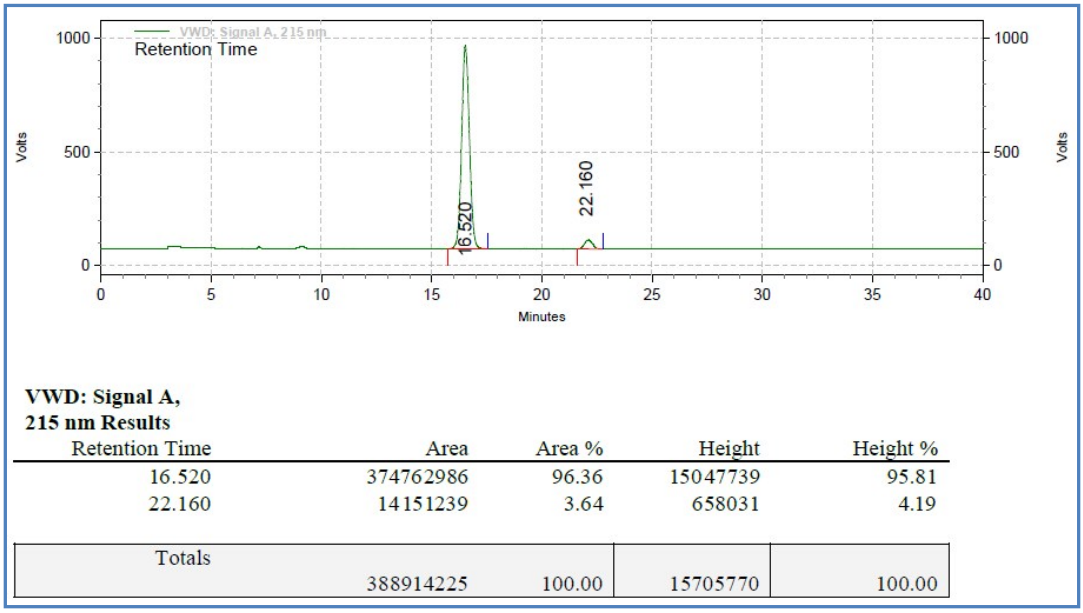


Fig. S18. HPLC chromatogram:



VWD: Signal A, 215 nm Results

Retention Time	Area	Area %	Height	Height %
16.520	374762986	96.36	15047739	95.81
22.160	14151239	3.64	658031	4.19
Totals	388914225	100.00	15705770	100.00

(R)-1-(3-chlorophenyl)-2-nitroethanol[11] (2g, Table 1)

The desired product was isolated by column chromatography over silica gel (ethyl acetate/hexane 15/85) as yellowish oil. $[\alpha]_D^{25}$= -28.6(c 1, CH_2Cl_2), lit.[11]$[\alpha]_D^{25}$= -27.2 (c 1.05, CH_2Cl_2); 93% ee; HPLC analysis was performed using Chiralcel OD-H column having 85/15 n-hexane/*i*PrOH as mobile phase, flow rate 1.0 ml/min, retention time (*R*):9.77 min (major), (*S*): 12.97 min (minor).

Fig.S19. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz)**:**

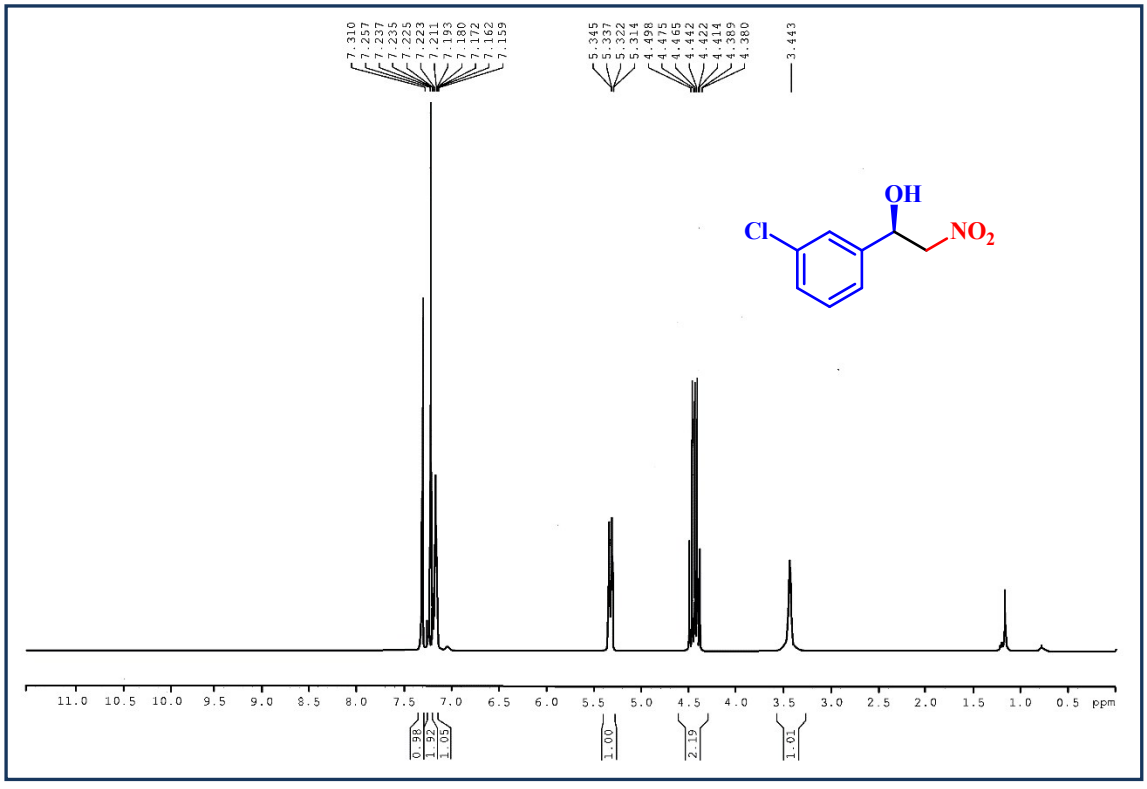
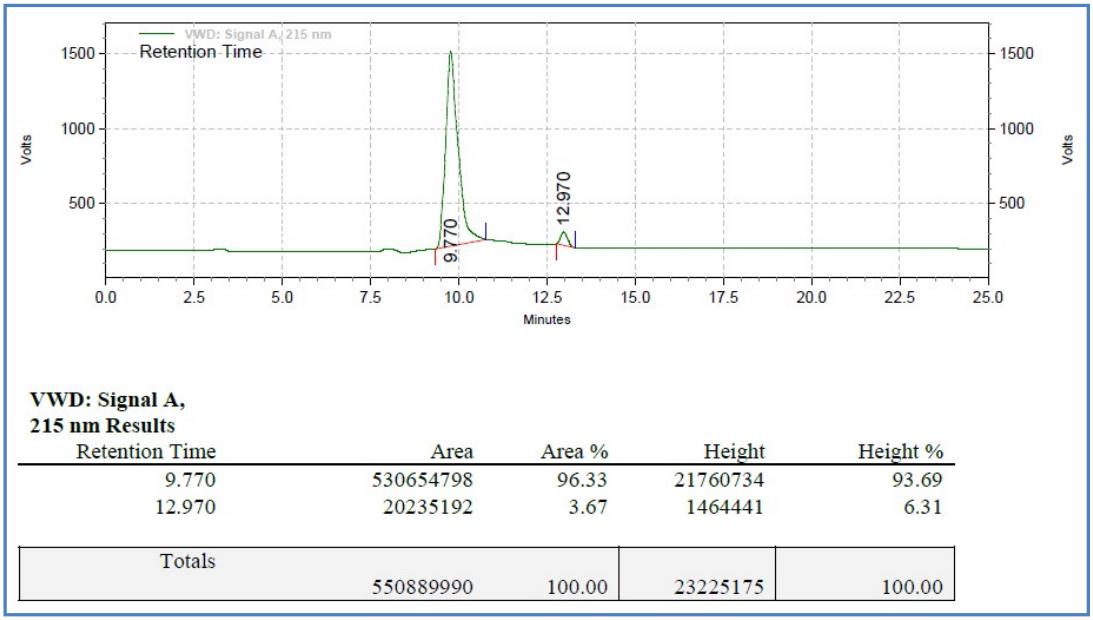


Fig. S20. HPLC chromatogram:



VWD: Signal A, 215 nm Results

Retention Time	Area	Area %	Height	Height %
9.770	530654798	96.33	21760734	93.69
12.970	20235192	3.67	1464441	6.31
Totals	550889990	100.00	23225175	100.00

(S)-1-(furan-2-yl)-2-nitroethanol[13] (2h, Table 1)

The desired product was isolated by column chromatography over silica gel (ethyl acetate/hexane 15/85) as pale-yellow oil. $[\alpha]_D^{25}$= -34.9(c 0.26, CH_2Cl_2),lit.[14] $[\alpha]_D^{25}$ = -37.1 (c 0.24, CH_2Cl_2); 88% ee; HPLC analysis was performed using Chiralcel OD-H column having 85/15 n-hexane/*i*PrOH as mobile phase, flow rate 1.0 ml/min, retention time (*S*): 18.59 min (major), (*R*): 22.46 min (minor).

Fig.S21. ^{1}H NMR spectrum($CDCl_3$, 400 MHz)**:**

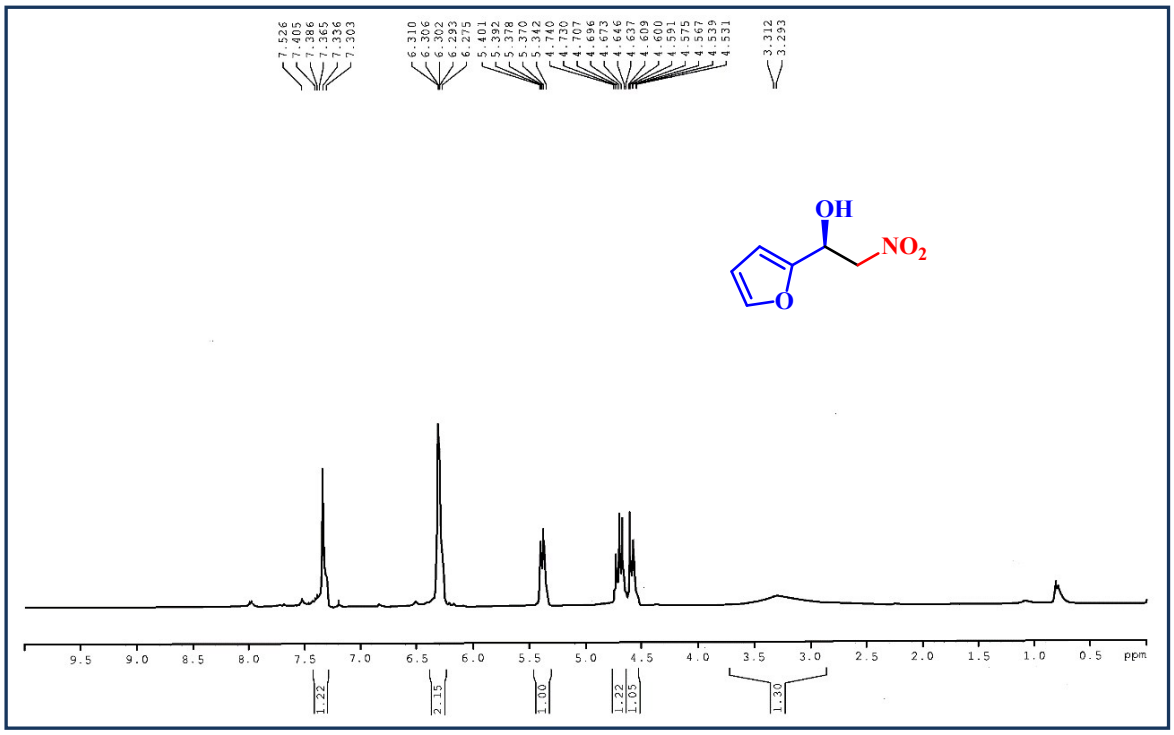
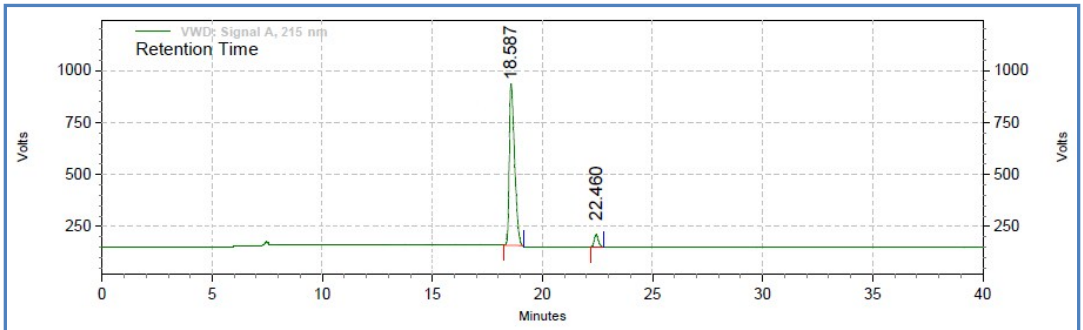


Fig. S22. HPLC chromatograms:



VWD: Signal A, 215 nm Results

Retention Time	Area	Area %	Height	Height %
18.587	205073611	93.98	12354469	92.50
22.460	13140749	6.02	1002268	7.50
Totals	218214360	100.00	13356737	100.00

(S)-2-nitro-1-(thiophen-2-yl)ethanol[13] (2i, Table 1)

The desired product was isolated by column chromatography over silica gel (ethyl acetate/hexane 15/85) as yellowish oil. $[\alpha]_D^{25}$= -35.9(c 0.33, CH_2Cl_2), lit.[14] $[\alpha]_D^{25}$ = -27.5 (c 0.28, CH_2Cl_2); 90% ee; HPLC analysis was performed using Chiralcel OD-H column having 85/15 n-hexane/*i*PrOH as mobile phase, flow rate 1.0 ml/min, retention time (*S*): 10.91 min (major), (*R*): 13.38 min (minor).

Fig.S23. ^{1}H NMR spectrum($CDCl_3$, 400 MHz)**:**

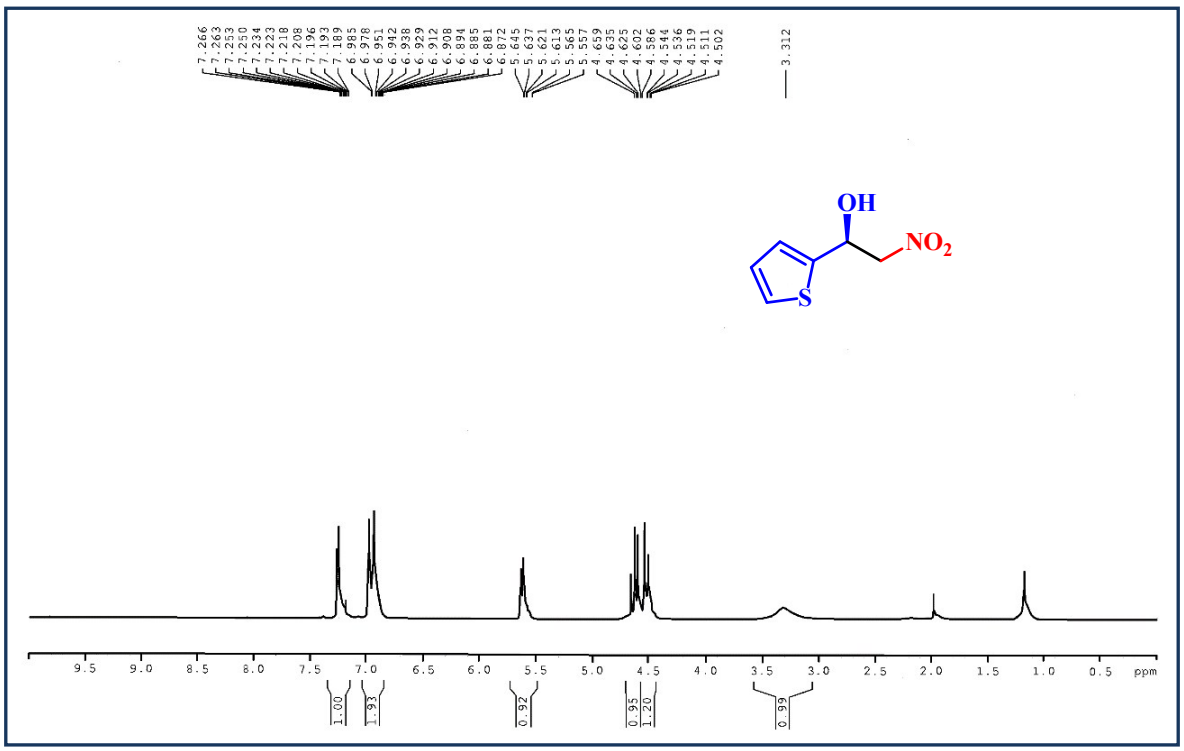
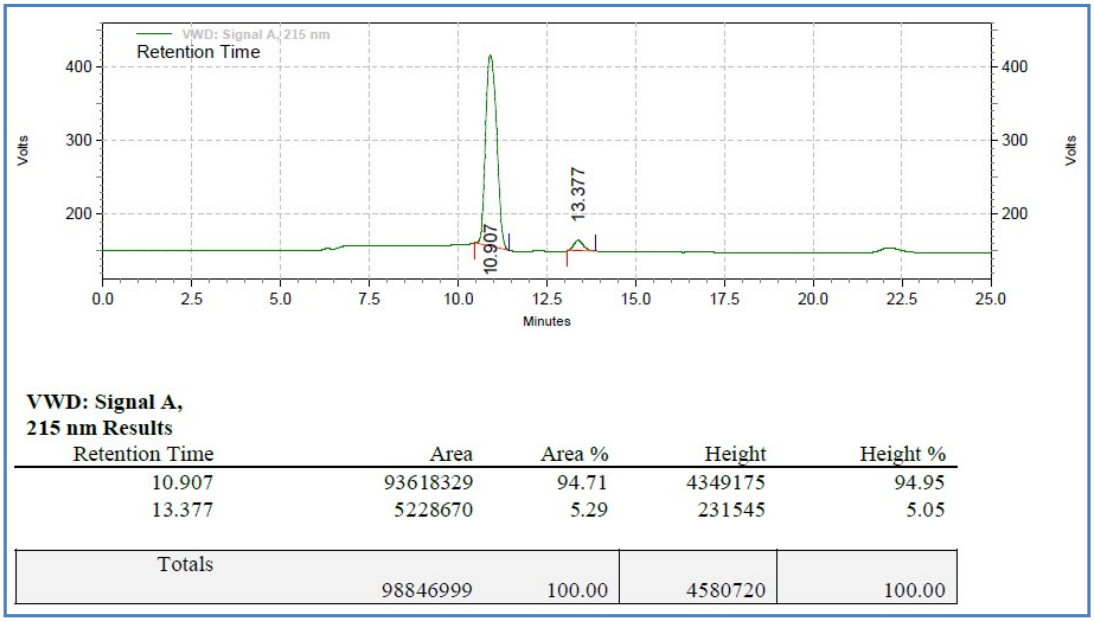


Fig. S24. HPLC chromatograms:



VWD: Signal A, 215 nm Results

Retention Time	Area	Area %	Height	Height %
10.907	93618329	94.71	4349175	94.95
13.377	5228670	5.29	231545	5.05
Totals	98846999	100.00	4580720	100.00

(R)-1-nitrooctan-2-ol[7] (2j, Table 2)

The desired product was isolated by column chromatography (ethyl acetate/hexane 10/90) as light yellowish oil. $[\alpha]_D^{25}$= -11.8 (c 1.09, CH_2Cl_2),lit.[15] $[\alpha]_D^{25}$ = -12.3 (c 1.2, CH_2Cl_2); 81% ee; HPLC analysis was performed using Chiralcel OD-H column having 90/10 n-hexane/*i*-PrOH as mobile phase, flow rate 0.8 ml/min, retention time (*R*): 9.31 min (major), (*S*): 14.53 min (minor).

Fig. S25. ^{1}H NMR spectrum($CDCl_3$, 400 MHz)**:**

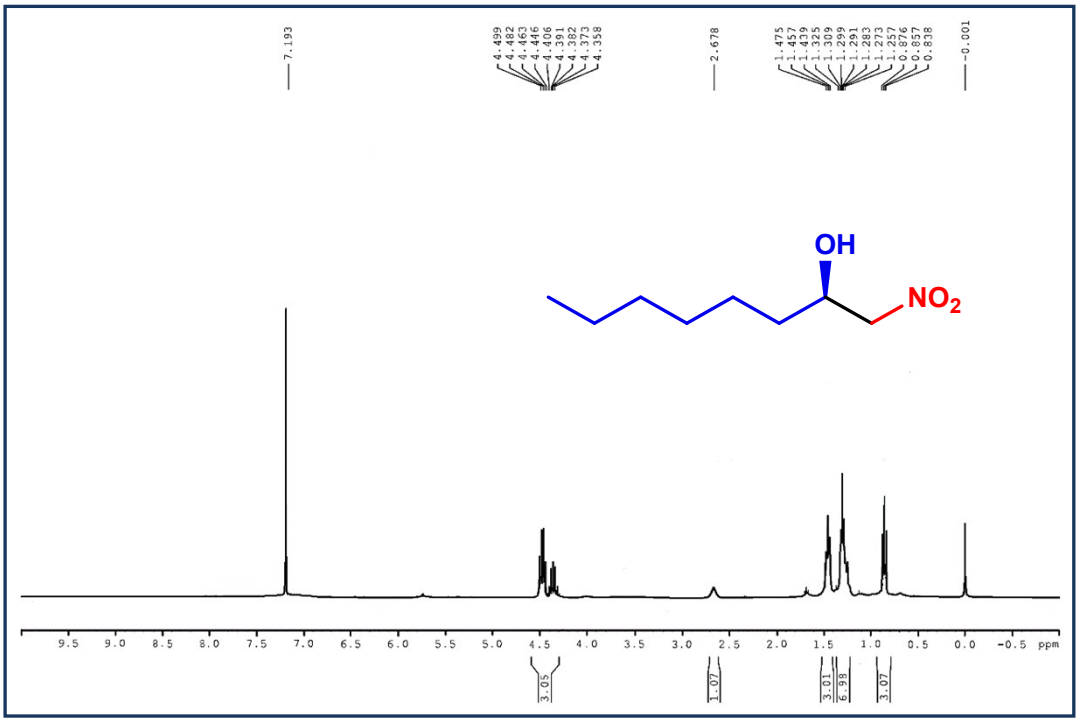
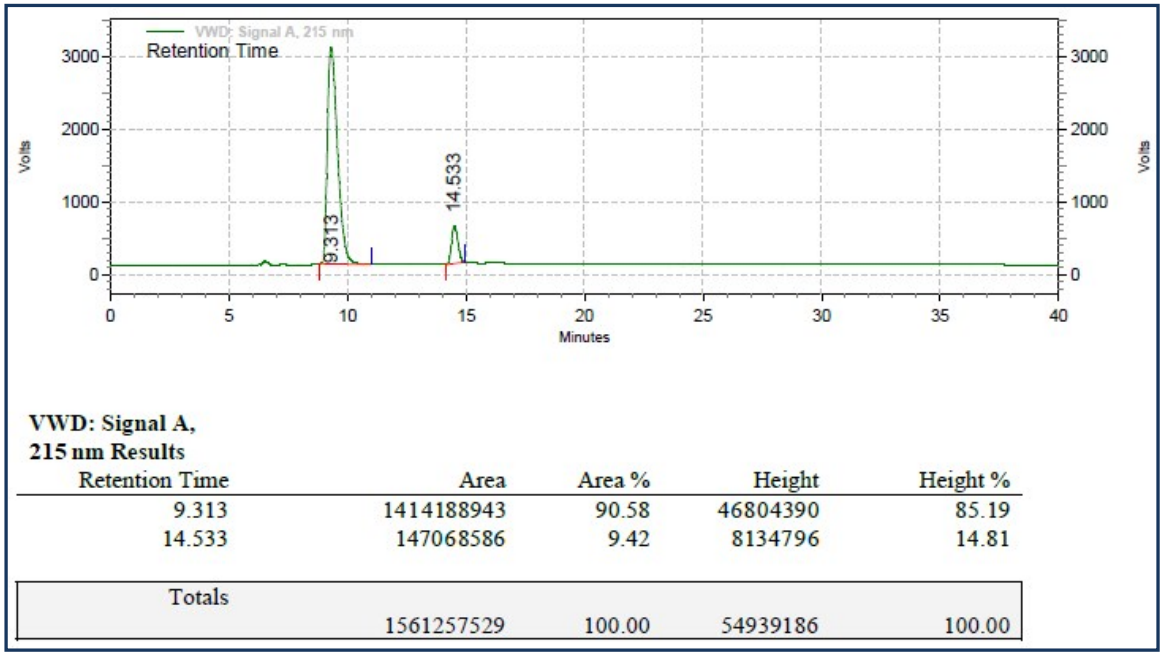


Fig. S26. HPLC chromatograms:



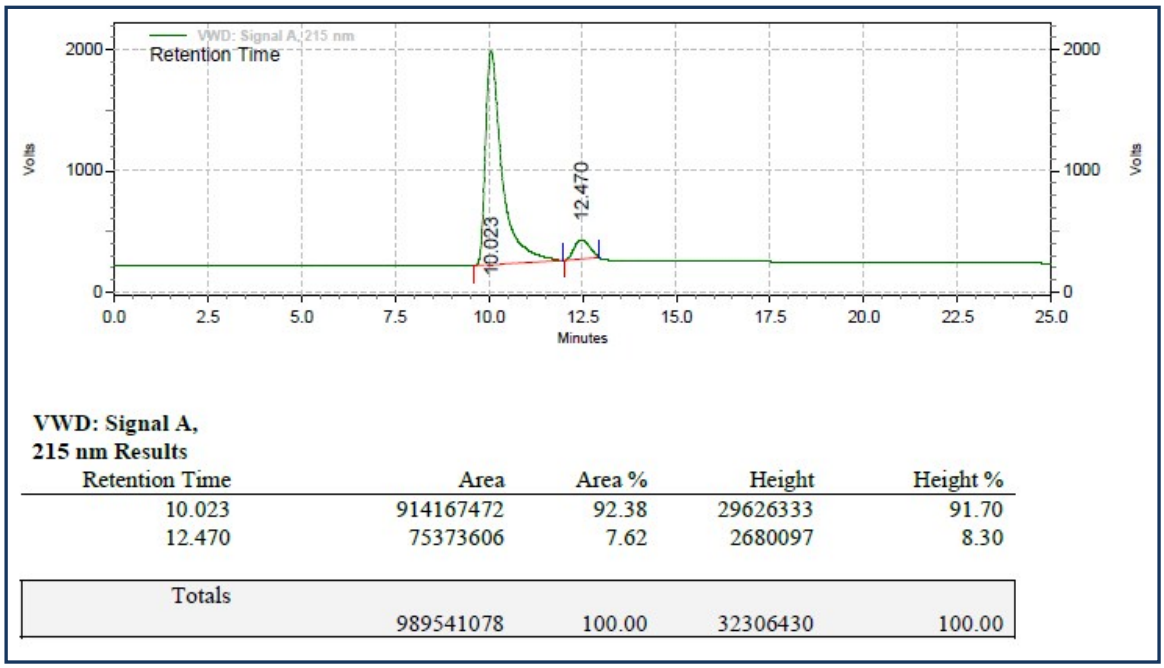
VWD: Signal A, 215 nm Results

Retention Time	Area	Area %	Height	Height %
9.313	1414188943	90.58	46804390	85.19
14.533	147068586	9.42	8134796	14.81
Totals	1561257529	100.00	54939186	100.00

(R)-1-cyclohexyl-2-nitroethanol[11] (2k, Table 2)

The desired product was isolated by column chromatography (ethyl acetate/hexane 10/90) as pale-yellow oil. $[\alpha]_D^{25}$= -15.2 (c 0.98, $CHCl_3$),lit.[11] $[\alpha]_D^{25}$ = -14.7 (c 1.03, $CHCl_3$); 85% ee; HPLC analysis was performed using Chiralcel OD-H column having 85/15 n-hexane/*i*-PrOH as mobile phase, flow rate 1.0 ml/min, retention time (*R*): 10.02 min (major), (*S*): 12.47 min (minor).

Fig. S27. HPLC chromatograms:



VWD: Signal A, 215 nm Results

Retention Time	Area	Area %	Height	Height %
10.023	914167472	92.38	29626333	91.70
12.470	75373606	7.62	2680097	8.30
Totals	989541078	100.00	32306430	100.00

2-Nitro-1-(4-nitrophenyl)propan-1-ol[5] (3a, Table 3)

The desired product was isolated by column chromatography over silica gel (ethyl acetate/hexane 15/85) as pale-yellow solid in 96% yield. Enantiomeric excess (ee_{syn}: 95%, ee_{anti}: 84%) of diastereomers were determined by HPLC analysis (Chiralcel OD-H, 85/15 n-hexane/*i*PrOH as mobile phase, flow rate 1.0 ml/min). Retention time, t_R (*anti* minor): 7.52 min, t_R (*anti* major): 9.56 min, t_R (*syn* major): 12.95 min, t_R (syn minor): 14.96min.Diastereomeric ratio (*syn*/*anti* = 3.2:1) was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$): δ =8.29-8.24 (m, 2H), 7.61-7.58 (m, 2H), 5.56 (d, *J* = 2.8 Hz, 0.29H, *anti*), 5.19 (d, *J* = 8.4 Hz, 0.91H, *syn*), 4.79-4.70 (m, 1H, *syn* + *anti*), 3.07-3.00 (br, 1H, *syn* + *anti*), 1.50-1.47 (m, 0.86H, *anti*), 1.43-1.37 (m, 2.76H, *syn*).

Fig. S28. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz)**:**

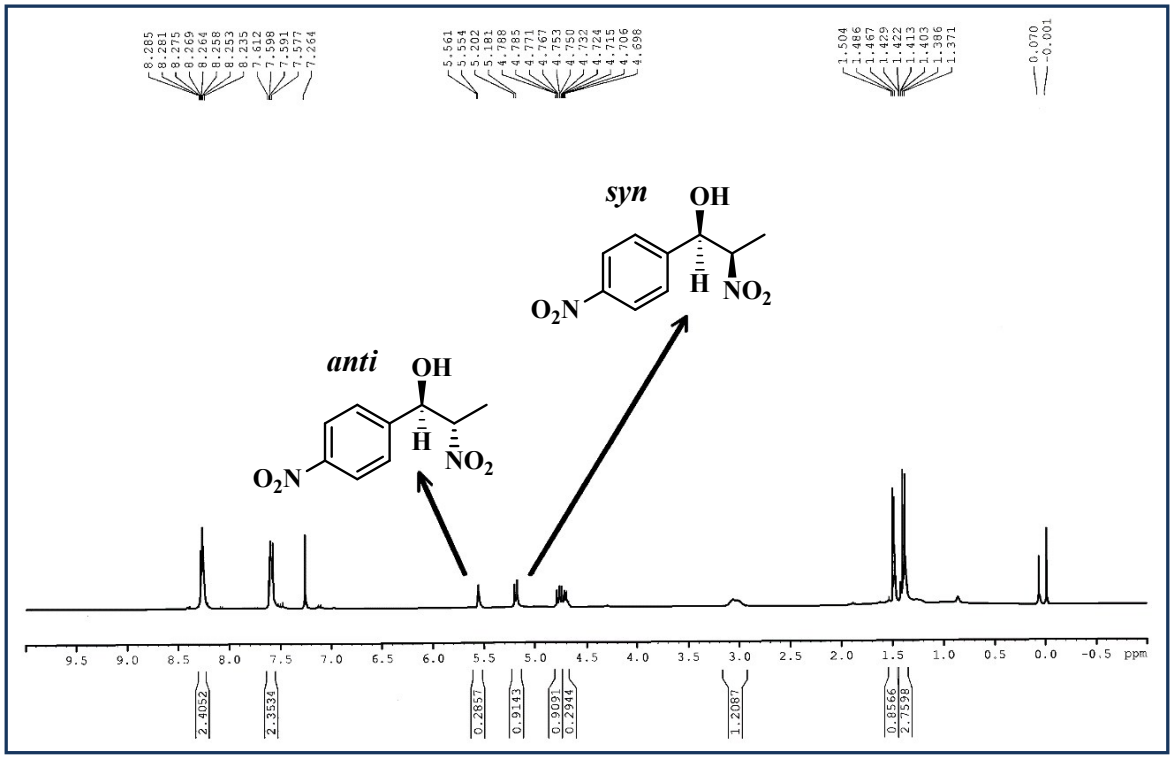
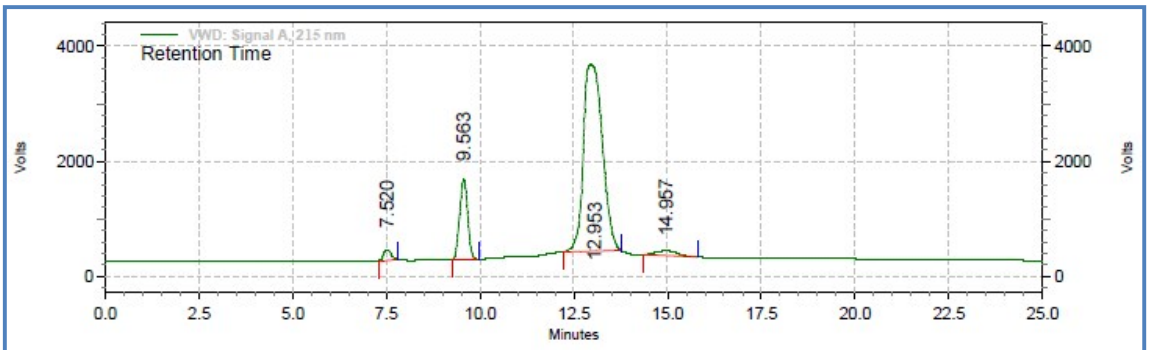


Fig. S29. HPLC chromatograms:



VWD: Signal A, 215 nm Results

Retention Time	Area	Area %	Height	Height %
7.520	29227681	1.43	2416947	3.17
9.563	356458382	16.43	23749615	31.17
12.953	1603088189	79.97	48627122	63.81
14.957	55980196	2.17	1409719	1.85
Totals	2044754448	100.00	76203403	100.00

1-(4-chlorophenyl)-2-nitropropan-1-ol[16] (3b, Table 3)

The desired product was isolated by column chromatography over silica gel (ethyl acetate/hexane 15/85) as pale-yellow solid in 95% yield. Enantiomeric excess (ee_{syn}: 95%, ee_{anti}: 66%) of diastereomers were determined by HPLC analysis (Chiralcel OD-H, 85/15 n-hexane/*i*PrOH as mobile phase, flow rate 1.0 ml/min). Retention time, t_R (*anti* minor): 4.54min, t_R (*anti* major): 5.54 min, t_R (*syn* major): 8.03 min, t_R (syn minor): 9.26 min. Diastereomeric ratio (*syn/anti*, 3:1 was determined by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30-7.20 (m, 4H), 5.28 (d, *J* = 3.2 Hz, 0.29H, *anti*), 4.92 (d, *J* = 8.8 Hz, 0.88H, *syn*), 4.66-4.62 (m, 0.88H, *syn*),4.59-4.55 (m, 0.29H,*anti*), 3.10 (br, 1H, *syn* + *anti*), 1.51-1.47 (m, 0.88H, *anti*), 1.40-1.39 (m, 2.63H, *syn*).

Fig. S30. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz)**:**

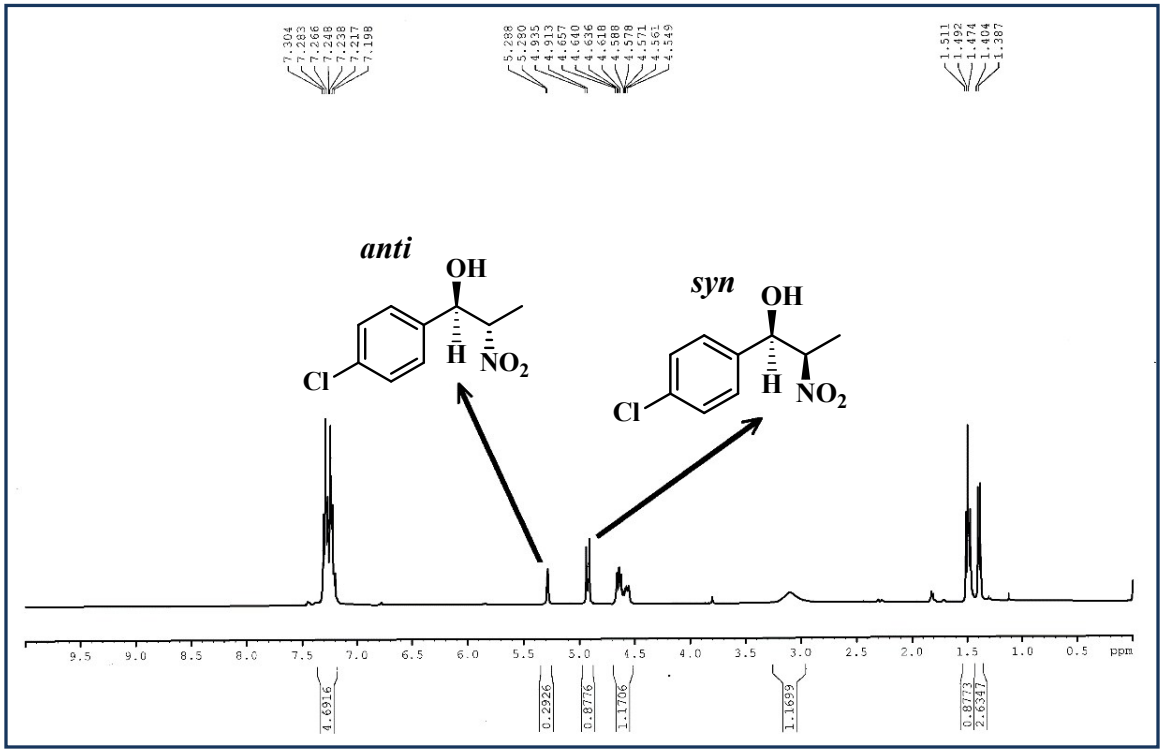
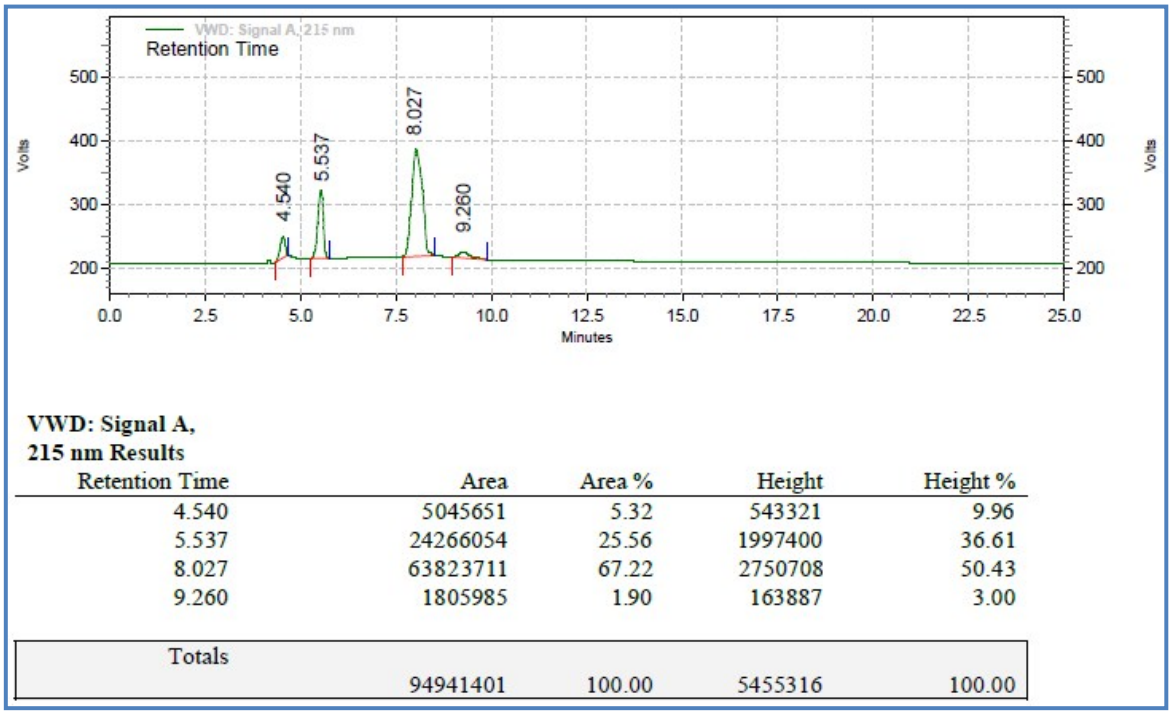


Fig. S31. HPLC chromatograms:



VWD: Signal A, 215 nm Results

Retention Time	Area	Area %	Height	Height %
4.540	5045651	5.32	543321	9.96
5.537	24266054	25.56	1997400	36.61
8.027	63823711	67.22	2750708	50.43
9.260	1805985	1.90	163887	3.00
Totals	94941401	100.00	5455316	100.00

2. FT-IR SPECTRUM OF THE REUSED Cu(II)@AFS-1 CATALYST:

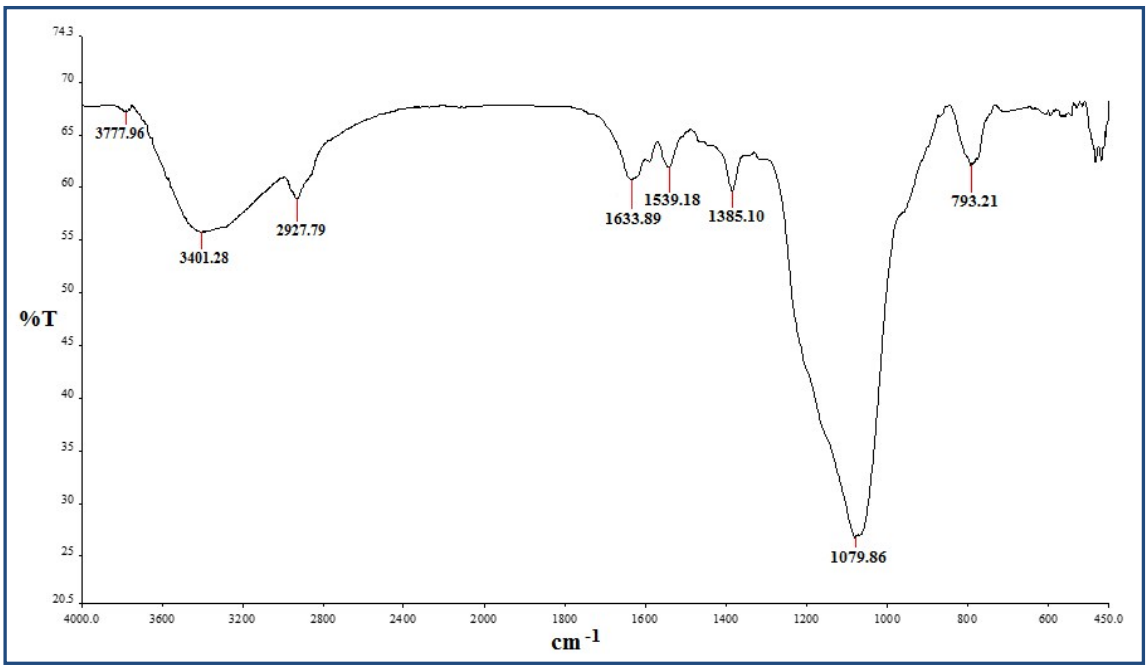


Fig. S32. FT-IR spectrum of the reused Cu(II)@AFS-1 catalyst.

REFERENCES:

1. G. Blay, V. Hernández-Olmos and J. R. Pedro, *Tetrahedron: Asymmetry,* 2010, **21**, 578.

2. C. P. Baird and P. C. Taylor, *J. Chem. Soc. Perkin.,*1998, **1**, 3399.

3. P. Kumar, R. K. Upadhyay and R. K. Pandey, *Tetrahedron: Asymmetry,* 2004, **15**, 3955.

4. E. J.Corey and J. O. Link, *Tetrahedron Lett.,*1990, **31**, 601.

5. A. Das, R. I. Kureshy, K. J. Prathap, M. K. Choudhary, G. V. S. Rao, N. H. Khan, S. H. R. Abdi and H. C. Bajaj, *Appl. Catal. A: Gen.,*2013, **459**, 97.

6. R. I. Kureshy, A. Das, N. H. Khan, S. H. R. Abdi, H. C. Bajaj, *ACS Catal*. **2011**, *1*, 1529.

7. A. Bulut, A. Aslan and O. Dogan, *J. Org. Chem.,* 2008, **73**, 7373.

8. R. I. Kureshy, B. Dangi, A. Das, N. H. Khan, S. H. R. Abdi and H. C. Bajaj, *Appl. Catal. A: Gen.,* 2012, **439-440**, 74.

9. L. Zhang, M. Liu, S. Ma, F. Y. Huang and Y. Wang, *Front. Chem. Sci. Eng*., 2013, **7**, 408.

10. J. D. White and S. Shaw, *Org. Lett*., 2012, **14**, 6270.

11. G. Blay, E. Climent, I. Fernández, V. Hernández-Olmos and J. Pedro, *Tetrahedron: Asymmetry,* 2007, **18**, 1603.

12. H. Maheswaran, K. L. Prasanth, G. G. Krishna, K. Ravikumar, B. Sridharb and M. L. Kantam, *Chem. Commun*., 2006, 4066.

13. H. -G. Cheng, L. -Q. Lu, T. Wang, J. -R. Chen and W. -J. Xiao, *Chem. Commun*., 2012, **48,** 5596.

14. B. Qin, X. Xiao, X. Liu, J. Huang, Y. Wen and X. Feng, *J. Org. Chem.,* 2007, **72**, 9323.

15. C. Palomo, M. Oiarbide and A. Laso, *Angew. Chem. Int. Ed.,* 2005, **44**, 3881.

16. W. Jin, X. Li, B. Wan, *J. Org. Chem*.,2011, **76**, 484.