

Supporting information

A New Recyclable Functionalized Mesoporous SBA-15 Catalyst grafted with Chiral Fe(III) Sites for the Enantioselective Aminolysis of Racemic Epoxides under Solvent free Conditions

Mita Halder,^{a,c} Piyali Bhanja,^b Susmita Roy,^c Swarbhanu Ghosh,^c Sudipta Kundu,^b Md. Mominul Islam,^c and Sk. Manirul Islam^{*c}

^a*Department of Chemistry, University of Calcutta, 92 APC Road, Kolkata 700 009, India.*

^b*Department of Materials Science, Indian Association for the Cultivation of Science, 2A & B, Raja S.C. Mullick Road, Jadavpur, Kolkata– 700032, India*

^c*Department of Chemistry, University of Kalyani, Kalyani, Nadia, 741235, W.B., India.*

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Section-S1

1. General Information

1.1 Chemicals:

Pluronic P123 (EO₂₀PO₇₀EO₂₀, EO = ethylene oxide, PO = propylene oxide, M_{av} = 5800), tetraethylorthosilicate (TEOS), 3-aminopropyl triethoxysilane (3-APTES), (S)-(+)-epichlorohydrine and all racemic epoxides were purchased from Aldrich Chemical Co. FeCl₃·6H₂O and all anilines were purchased from E-Merck. All the reagents were analytical grade and used as such without further purification. Solvents were purified and dried according to standard procedures. Thin layer chromatography was done using commercial (MERCK) plates with silica gel 60 F₂₅₄.

1.2 Characterizations:

Powder X-ray diffraction (PXRD) patterns of different samples were recorded 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 K α ($\lambda=0.15406$ nm) radiation. UV-visible diffuse reflectance spectra were recorded on a Shimadzu UV 2401PC coupled with an integrating sphere attachment. BaSO₄ was used as background standard. Transmission electron microscopy (TEM) images of the mesoporous mixed oxide were obtained using a JEOL JEM 2010 transmission electron microscope with operating voltage 200 kV. The samples were prepared by dropping a colloidal solution onto the carbon-coated copper grids followed by drying under high vacuum. For the bulk elemental analysis the Fe@SBEP was digested with acid to dissolve them into clear liquid and then Fe content were analyzed by using a Shimadzu AA-6300 atomic absorption spectrophotometer (AAS) fitted with a double beam monochromator. Carbon, hydrogen and nitrogen contents of Fe@SBEP were analyzed using a Perkin Elmer 2400 Series II CHN analyzer. Nitrogen sorption isotherms were obtained using a Quantachrome Autosorb 1C surface area analyzer at 77 K. Prior to the measurement, the

samples were degassed at 423 K for approximately 4 h under high vacuum. ¹H NMR spectra were recorded on a Bruker DPX-400 instrument. The FT-IR spectra of the samples were recorded on a Perkin-Elmer FT-IR 783 spectrophotometer. Enantiomeric excesses (ee) were determined by HPLC (Agilent, Model 1220) using Ultron using a Chiralcel ® OD-H column (wavelengths 254 nm) with 2-propanol/hexane as eluent. Optical rotations are reported as follows: $[\alpha]_D^{27}$ (c = in g per 100 ml, solvent) were measured with a Digipol 781 Automatic Polarimeter Rudolph Instruments.

1.3 General procedure for asymmetric ring opening (ARO) of epoxides with amines:

In a typical procedure, a mixture comprising of a chiral catalyst Fe@SBEP (15 mg), an epoxide (1 mmol) and an amine (1 mmol) were taken in a 5 mL round bottom flask and stirred vigorously for a given time period (monitored by TLC) under solvent free condition. 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 Na₂SO₄. 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 **Fe(III) catalyst (Fe@SBEP)** with other reported catalysts

Catalyst	Reaction condition	Yield (%)	ee (%)	TOF (h ⁻¹)	Ref
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	1
Chiral organocatalyst	Catalyst 20mol%, Cyclohexene oxide (0.2 mmol), anilines (0.22 mmol)	95	89	0.04	2

	in DCM, 24 h, rt.				
Homogeneous chiral Vanadium–Salan complex	Catalyst(10mol%), Cyclohexene oxide (1.0 mmol), anilines(1.0 mmol) in DCM, 24 h, 0 oC.	84	62	0.35	3
Heterogeneous chiral Fe(III) catalyst (Fe@SBEP)	Cyclohexene oxide (1 mmol), Aniline (1 mmol), Fe@SBEP (0.5 mo% of Fe), without solvent, RT, 2 h.	96	98	96.0	Present study

^aYields are referred to those of isolated pure products.

^bEnantiomeric excess was determined from the HPLC analysis using Chiralpak OD-H column.

2. Characterization of the Fe@SBSAL Catalyst:

2.1 ¹H NMR Spectrum data of chiral (2'S)-N-(2', 3'-epoxypropyl)-3-(aminopropyl)-triethoxysilane (3):

¹H NMR (400 MHz, CDCl₃): δ (ppm) 0.61 (t, J = 8.00, 2H), 1.25 (t, J = 7.01, 3H), 1.49–1.65 (m, 2H), 2.67 (t, J = 7.28, 2H), 2.77 (d, J = 3.98, 1H), 2.84–2.91 (m, 1H), 3.57 (d, J = 5.55, 1H), 3.70 (q, J = 6.95, 14.00, 2H), 3.85 (q, J = 7.01, 14.01, 2H); FT IR (KBr): 3412, 2930, 1650, 1445, 1080, 775, 697 cm⁻¹.

2.2 FT-IR and elemental analysis data of Fe@SBEP (6).

FT-IR (KBr): 3391, 2975, 1632, 1457, 1078, 795, 771, 682, 570 cm⁻¹; CHN analysis: C = 12.92 %, H = 2.61 %, N = 1.88 %.

2.3 FT-IR spectrum:

The FT-IR spectra of SBA-15-supported (S)-amino alcohol and the heterogeneous catalyst Fe@SBSAL are shown in ESI Figure S1 (a-b), respectively. The FT-IR spectrum of chiral ligand showed band at 1459 and 1637 cm⁻¹, due to ν (C–N) and ν (C=C) of aromatic ring respectively (**Figure S1a**). The chiral ligand showed the characteristic band of SBA-15 at 1087 cm⁻¹ for Si–O–Si and 3403 cm⁻¹ for the Si–OH bond. On complexation with Fe(III) metal ion the IR band centred around 3391 cm⁻¹ due to ν (O–H) merged with Si–O–Si bands.

Further a decrease in intensity could be attributed to the coordination with phenolic oxygen to the metal ion (**Figure S1b**).

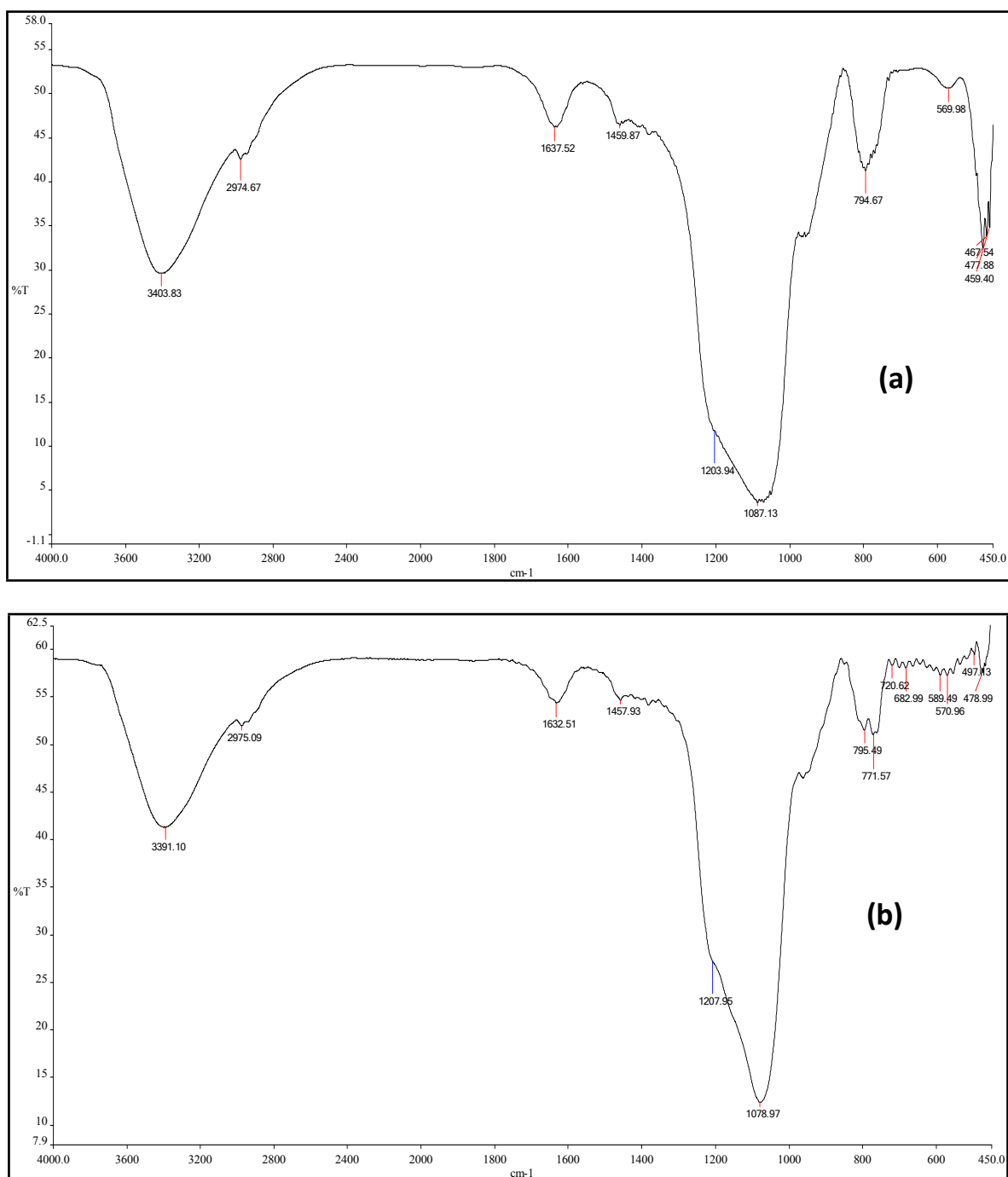


Figure S1. FT IR spectra of (a) SBA-15 supported (S)-amino alcohol and (b) heterogeneous chiral catalyst Fe@SBEP.

2.4 UV-Vis DRS analysis:

The UV–Vis absorption spectrum of the Fe@SBEP is recorded in diffuse reflectance mode as a BaSO₄ disk due to its solubility limitations in common organic solvents. The UV spectrum of Fe@SBEP is given in Figure S2. In this case the vibrational bands at 200-300 nm and 330 nm could be attributed due to the n- π^* transitions and the ligand π - π^* transition of phenolic group. An absorption band near 600 nm was observed from metal-to-ligand charge transfer due to complexation with Fe(III) metal ion.

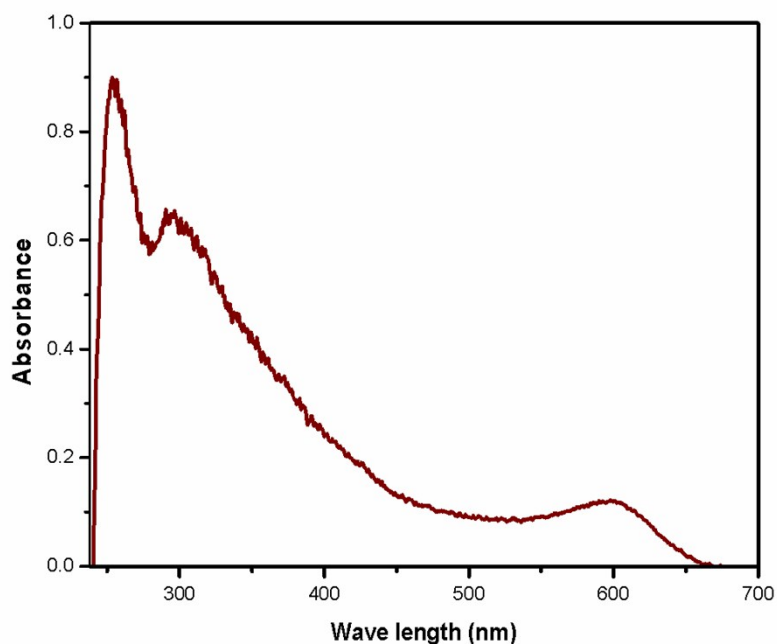
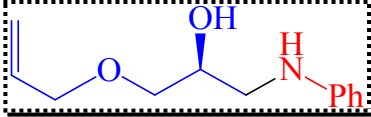
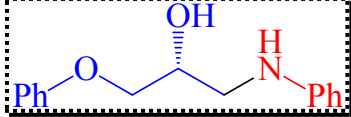
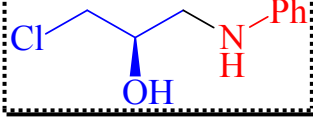
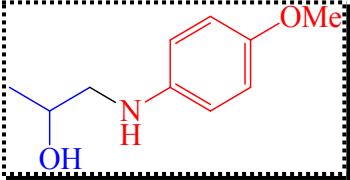
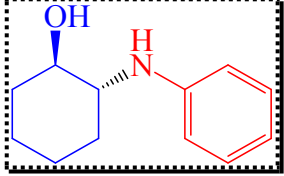
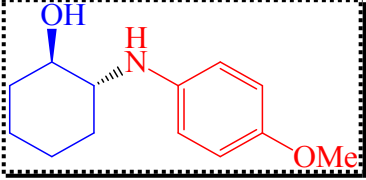


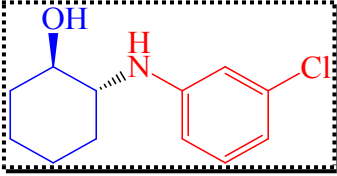
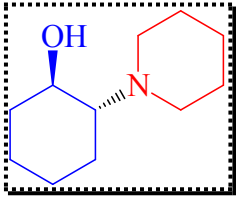
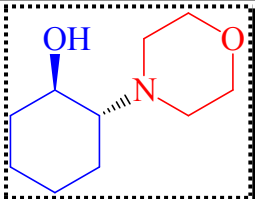
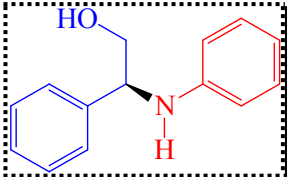
Figure S2. The DRS-UV-visible absorption spectrum of Fe@SBEP material

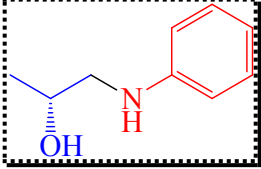
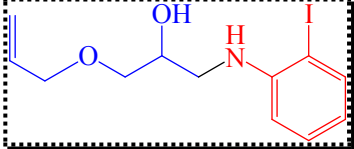
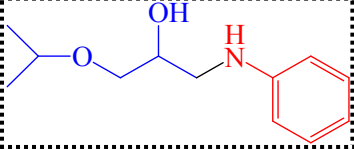
Section-S2

¹H NMR and HPLC data of isolated pure products

	<p>The compound was isolated by column chromatography (hexane/AcOEt 90/10) as a yellow liquid; $[\alpha]_D^{27} = +30.8$ ($c = 1.0$, CHCl_3); ee 72% on HPLC (Chiralpak OD-H column) mobile phase 90/10 hexane/<i>i</i>-PrOH; flow rate 1 ml/min, retention time. : 13.34 min (minor), 15.68 min. (major); ¹H NMR (400 MHz, CDCl_3): 3.03-3.08 (m, 1H), 3.23 (dd, $J = 4.5, 8.8$ Hz, 1H), 3.38-3.42 (m, 1H), 3.45-3.48 (m, 1H), 3.92-4.04 (m, 3H), 5.12-5.23 (m, 2H), 5.78-5.88 (m, 1H), 6.55-6.57 (m, 2H), 6.62-6.66 (m, 1H), 7.07-7.16 (m, 2H).</p>
	<p>The compound was isolated by column chromatography (hexane/AcOEt 90/10) as pale yellow liquid; $[\alpha]_D^{27} = -25.0$ ($c = 1.0$, CHCl_3); The ee 93% on HPLC (Chiralpak OD-H column) mobile phase 92/8 hexane/<i>i</i>-PrOH; flow rate 0.8 ml/min, retention time: 9.84 min (minor), 14.40 min. (major); ¹H NMR (400 MHz, CDCl_3): δ 3.28-3.38 (m, 2H), 3.46 (dd, $J = 4.4, 8.4$ Hz 1H), 4.04-4.17 (m, 2H), 4.26-4.31 (m, 1H), 6.70-6.73 (m, 2H), 6.77-6.82 (m, 1H), 6.95-7.04 (m, 2H), 7.17-7.35 (m, 3H).</p>
	<p>The compound was isolated by column chromatography (hexane/AcOEt 90/10) as pale yellow liquid; $[\alpha]_D^{27} = -27.3$ ($c = 0.5$, CHCl_3); ee >99% on HPLC (Chiralpak OD-H column) mobile phase 90/10 hexane/<i>i</i>-PrOH; flow rate 0.8 ml/min, retention time: 16.69 min (minor), 18.14 min. (major); ¹H NMR (400 MHz, CDCl_3): δ 3.06 (s, br, 1H), 3.11-3.16 (m, 1H), 3.29 (dd, $J = 4.5, 9.1$ Hz, 1H), 3.53-3.61 (m, 2H), 3.96-4.01 (m, 1H), 6.58-6.62 (m, 2H), 6.66-6.70 (m, 1H), 7.10-7.17 (m, 2H).</p>

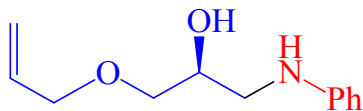
	<p>The compound was isolated by column chromatography (hexane/AcOEt 92/8) as pale yellow liquid; $[\alpha]_D^{27} = -25.6$ ($c = 1.0$, CHCl_3); ee 88% on HPLC (Chiralpak OD column) mobile phase 90/10 hexane/<i>i</i>-PrOH; flow rate 1 ml/min, retention time: 14.89 min (major), 18.40 min. (minor); ^1H NMR (400 MHz, CDCl_3): δ 1.12-1.37 (d, $J = 6.6$ Hz, 3H), 2.51 (bs, 1H), 2.83-2.89 (dd, $J = 4.3$-8.7, 1H), 3.07-3.13 (dd, $J = 3.1$-9.5, 1H), 3.67 (s, 3H), 3.93-3.95 (m, 1H), 6.56-6.57 (m, 2H), 6.67-6.74 (m, 2H).</p>
	<p>The compound was isolated by column chromatography (hexane/AcOEt 90/10) as white solid. $[\alpha]_D^{27} = -31.3$ ($c = 1.0$, CHCl_3); ee 97% on HPLC (Chiralpak OD column) mobile phase 95/5 hexane/<i>i</i>-PrOH; flow rate 0.6 ml/min, retention time. (<i>1S,2S</i>): 13.48 min (minor), (<i>1R,2R</i>): 15.87 min. (major); ^1H NMR (400 MHz, CDCl_3): δ 1.12-1.17 (m, 1H), 1.27-1.46 (m, 3H), 1.73-1.75 (m, 2H), 1.81-2.16 (m, 2H), 2.02-2.04 (m, 2H), 2.91 (br s, 1H), 3.13-3.19 (m, 1H), 3.34-3.40 (m, 1H), 6.70-6.79 (m, 2H), 7.19-7.28 (m, 2H).</p>
	<p>The compound was isolated by column chromatography (hexane/AcOEt 92/8) as white solid. $[\alpha]_D^{27} = -30.1$ ($c = 1.0$, CHCl_3); ee >99% on HPLC (Chiralpak OD-H column) mobile phase 90/10 hexane/<i>i</i>-PrOH; flow rate 1 ml/min, retention time (<i>1S,2S</i>): 8.86 min (minor), (<i>1R,2R</i>): 12.72 min. (major); ^1H NMR (400 MHz, CDCl_3): δ 1.31-1.42 (m, 4H), 1.68-1.78 (m, 2H), 2.04-2.14 (m, 2H), 2.84 (br s, 1H), 2.95-3.02 (m, 1H), 3.29-3.36 (m, 1H), 3.74 (s, 3H), 6.65-6.70 (m, 2H), 6.75-6.80 (m, 2H).</p>

	<p>The compound was isolated by column chromatography (hexane/AcOEt 90/10) as yellow liquid; $[\alpha]_D^{27} = -31.5$ ($c = 1.0$, CHCl_3); ee >99% on HPLC (Chiralpak OD-H column) mobile phase 90/10 hexane/<i>i</i>-PrOH; flow rate 0.8 ml/min, retention time (<i>1S,2S</i>): 8.64 min (minor), (<i>1R,2R</i>): 10.17 min. (major); ^1H NMR (400 MHz, CDCl_3): δ 1.10-1.15 (m, 1H), 1.23-1.46 (m, 3H), 1.50-1.58 (m, 1H), 1.73-1.80 (m, 1H), 2.08-2.13 (m, 2H), 3.08-3.14 (m, 1H), 3.35-3.41 (m, 1H), 3.74 (s, 3H), 6.69-6.61 (dd, $J = 1.2, 2.8$ Hz, 1H), 6.71-6.73 (m, 2H), 7.09 (t, 1H).</p>
	<p>The compound was isolated by column chromatography (hexane/AcOEt 90/10) as colourless oil; $[\alpha]_D^{27} = -52.4$ ($c = 3.03$, CHCl_3); ee 82 % on HPLC (Chiralpak OD-H column) mobile phase 90/20 hexane/<i>i</i>-PrOH; flow rate 1 ml/min, retention time: 16.59 min (major), 20.74 min (minor). ^1H NMR (400 MHz, CDCl_3): δ 1.06-1.3 (m, 6H), 1.32-1.39 (m, 2H), 1.47-1.51 (m, 3H), 1.52-1.52 (m, 1H), 1.52-1.53 (m, 2 H), 1.54-2.15 (m, 2H), 2.28-2.30 (m, 2H), 2.59-2.65 (m, 1H), 3.29-3.32 (m, 1H).</p>
	<p>The compound was isolated by column chromatography (hexane/AcOEt 90/10) as colourless oil; $[\alpha]_D^{27} = -48.7$ ($c = 3.00$, CHCl_3); ee 76% on HPLC (Chiralpak OD-H column) mobile phase 90/20 hexane/<i>i</i>-PrOH; flow rate 1 ml/min, retention time: 15.57 min (major), 19.77 min (minor). ^1H NMR (400 MHz, CDCl_3): δ 1.08-1.26 (m, 6H), 1.64-1.77 (m, 3H), 2.02-2.14 (m, 2H), 2.33-2.38 (m, 2H), 2.63-2.66 (m, 2H), 3.28-3.34 (m, 1H), 3.62-3.70 (m, 2H).</p>
	<p>The compound was isolated by column chromatography (hexane/AcOEt 90/10) as pale yellow viscous oil. $[\alpha]_D^{27} +29.9$ ($c = 0.5$, CHCl_3); 98% ee; HPLC analysis was performed using Chiralpak OD-H column having 90/10 <i>n</i>-hexane/<i>i</i>-PrOH as mobile phase, flow rate 1.0 ml/min, retention time : 11.25 min (minor), 14.31 min (major). ^1H</p>

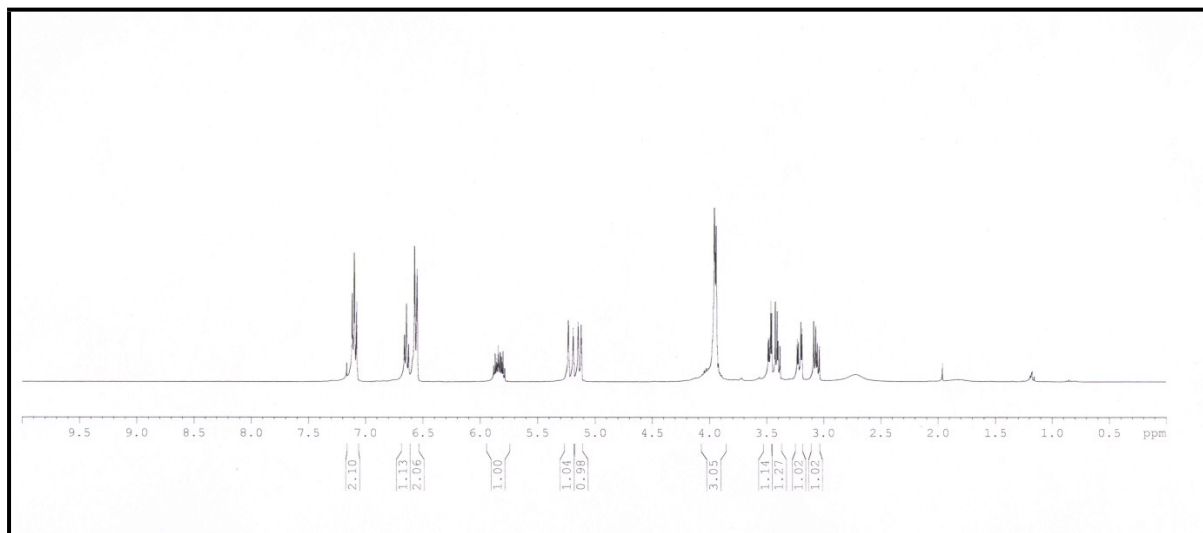
	<p>NMR (400 MHz, CDCl₃): δ 2.75 (bs, 1H), 3.63-3.67 (m, 1H), 3.82-3.86 (m, 1H), 3.91-3.95 (m, 1H), 4.39-4.42 (m, 1H), 6.59-6.61 (m, 3H), 6.68-6.70 (m, 1H), 7.07-7.09 (m, 1H), 7.17-7.20 (m, 1H), 7.23-7.29 (m, 4H).</p>
	<p>The compound was isolated by column chromatography (hexane/AcOEt 90/10) as pale yellow liquid. $[\alpha]_D^{27}$ -28.9 (c = 1.0, CHCl₃); 89% ee; HPLC analysis was performed using Chiralpak OD-H column having 90/10 n-hexane/<i>i</i>-PrOH as mobile phase, flow rate 1.0 ml/min, retention time : 12.92 min (major), 15.42 min (minor). ¹H NMR (400 MHz, CDCl₃): δ 1.20-1.21 (m, 3H), 2.64 (bs, 1H), 2.90-2.95 (m, 1H), 3.14-3.18 (m, 1H), 3.93-3.98 (m, 1H), 6.57-6.59 (m, 2H), 6.64-6.68 (m, 1H), 7.09-7.13 (m, 2H).</p>
	<p>The compound was isolated by column chromatography (hexane/AcOEt 90/10) as dark brown liquid. $[\alpha]_D^{27}$ +36.1 (c = 1.3, CHCl₃); 78% ee; HPLC analysis was performed using Chiralpak OD-H column having 90/10 n-hexane/<i>i</i>-PrOH as mobile phase, flow rate 1.0 ml/min, retention time : 13.51 min (minor), 16.24 min (major). ¹H NMR (400 MHz, CDCl₃): δ 2.61 (bs, 1H), 3.12-3.24 (m, 1H), 3.25-3.28 (m, 1H), 3.43-3.52 (m, 2H), 3.96-3.98 (m, 3H), 4.50 (bs, 1H), 5.13-5.24 (m, 2H), 5.8-5.89 (m, 1H), 6.36-6.39 (m, 1H), 6.51-6.53 (m, 1H), 7.10-7.18 (m, 1H), 7.57-7.59 (m, 1H).</p>
	<p>The compound was isolated by column chromatography (hexane/AcOEt 90/10) as brown viscous oil. $[\alpha]_D^{27}$ -29.8 (c = 0.1, CHCl₃); 95% ee; HPLC analysis was performed using Chiralpak OD-H column having 90/10 n-hexane/<i>i</i>-PrOH as mobile phase, flow rate 1.0 ml/min, retention time : 9.58 min (minor), 13.52 min (major). ¹H NMR (400 MHz, CDCl₃): δ 1.10 (d, <i>J</i> = 6, 6H), 3.03-3.08 (m, 1H), 3.18-3.23 (m, 1H), 3.35-3.39 (m, 1H), 3.45-3.48 (m, 1H), 3.51-3.55 (m, 1H), 3.89-3.92 (m, 1H), 6.55-6.57 (m, 2H), 6.62-6.65 (m, 1H), 7.07-7.11 (m, 2H).</p>

Section-S3

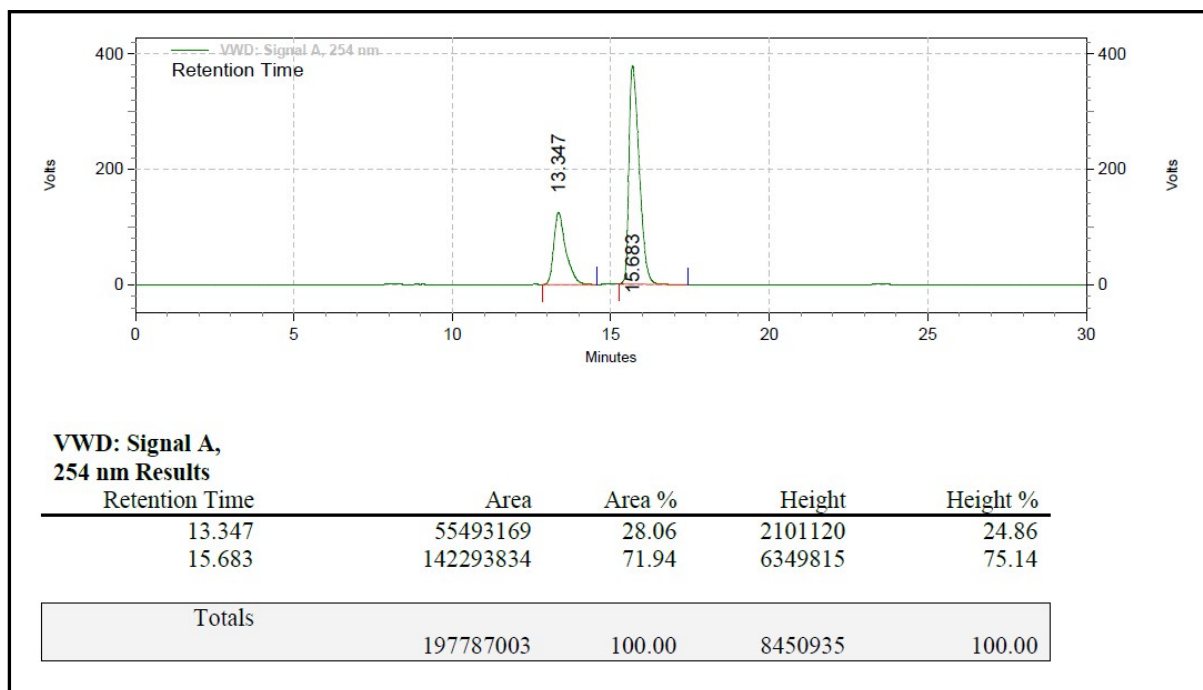
(S)-1-(allyloxy)-3-(phenylamino)propan-2-ol ⁴ (Table 2, entry 1)



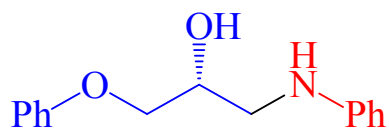
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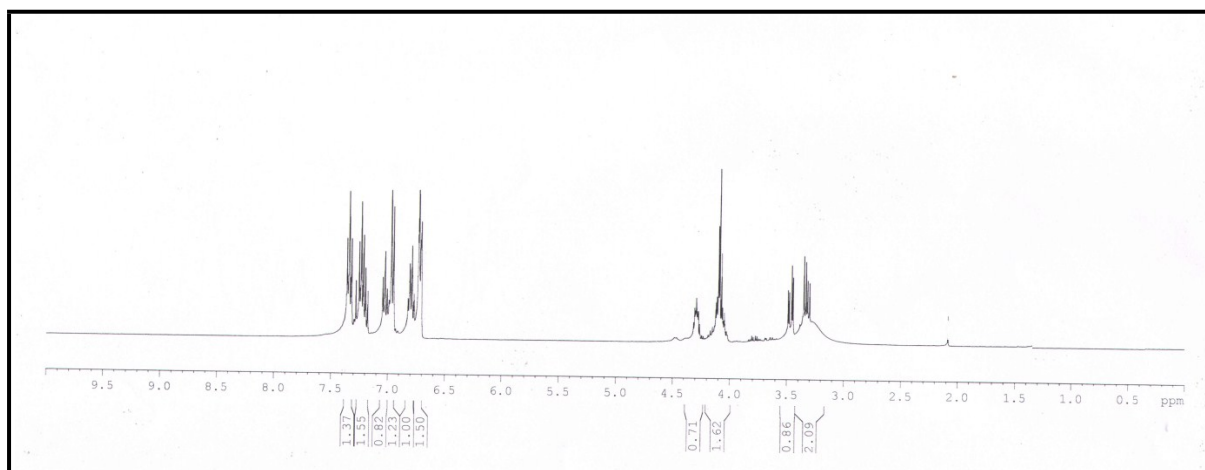
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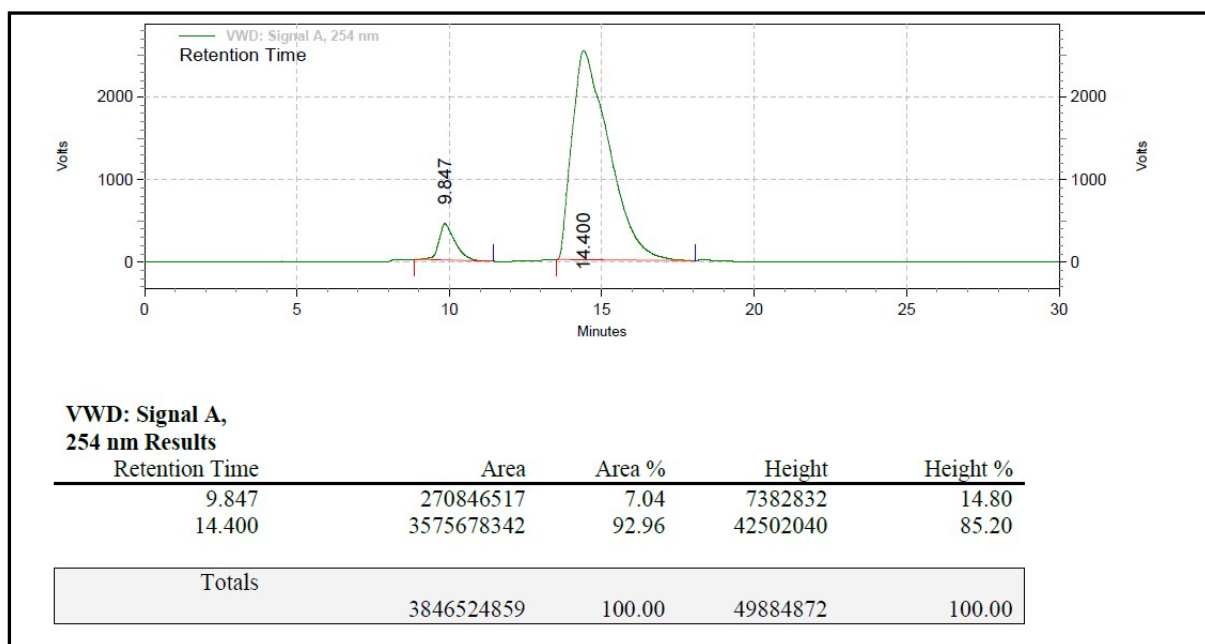
(R)-1-phenoxy-3-(phenylamino)propan-2-ol ⁴ (Table 2, entry 2)



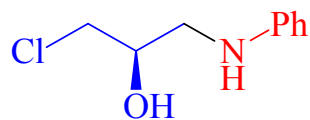
¹H NMR spectra:



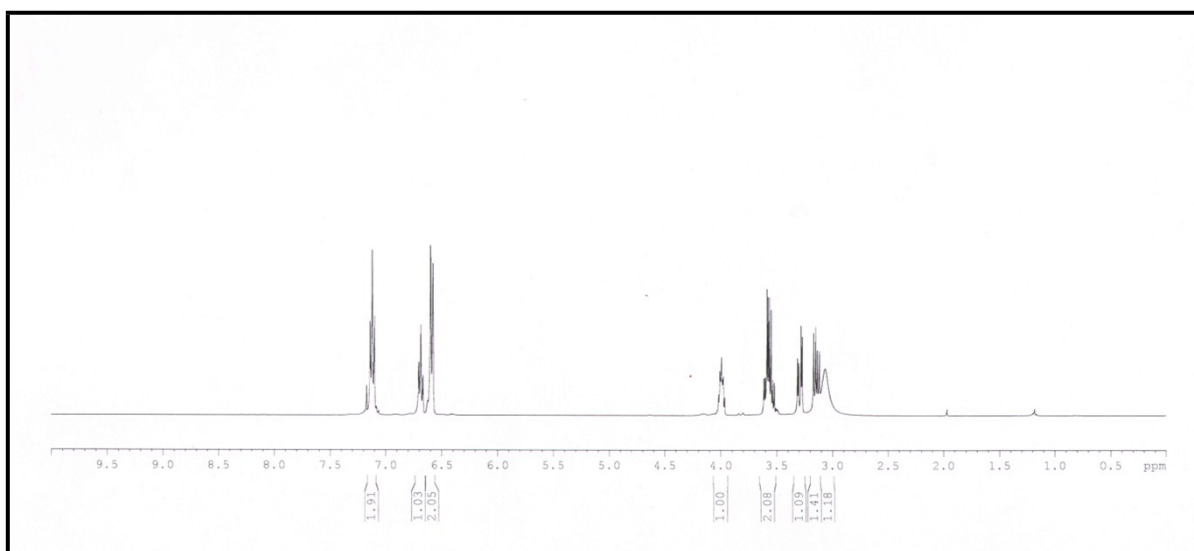
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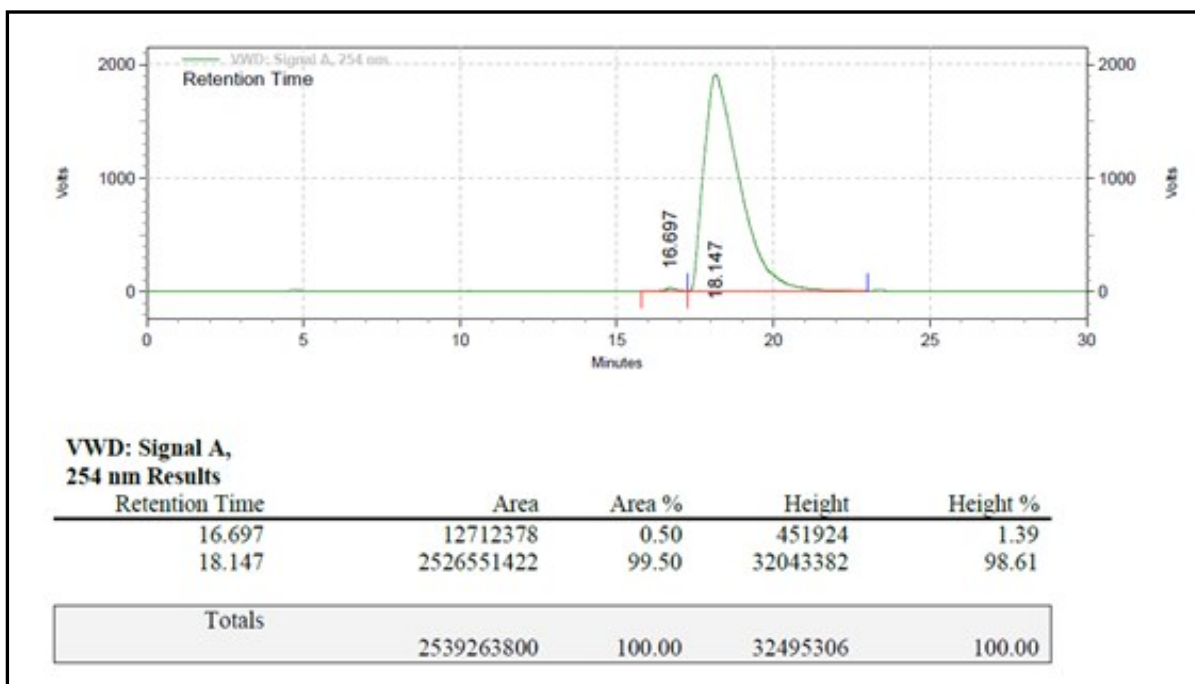
(R)-1-chloro-3-(phenylamino)propan-2-ol ⁴ (Table 2, entry 3)



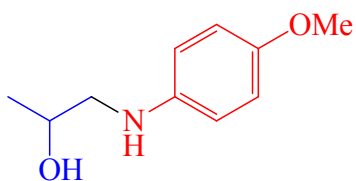
¹H NMR spectra:



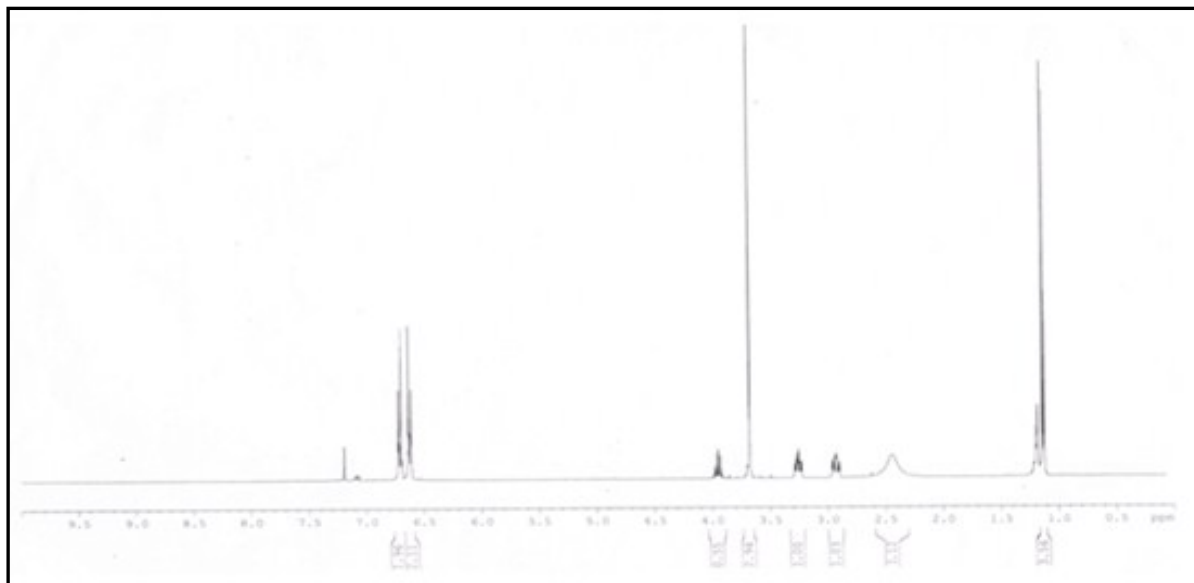
HPLC chromatogram:



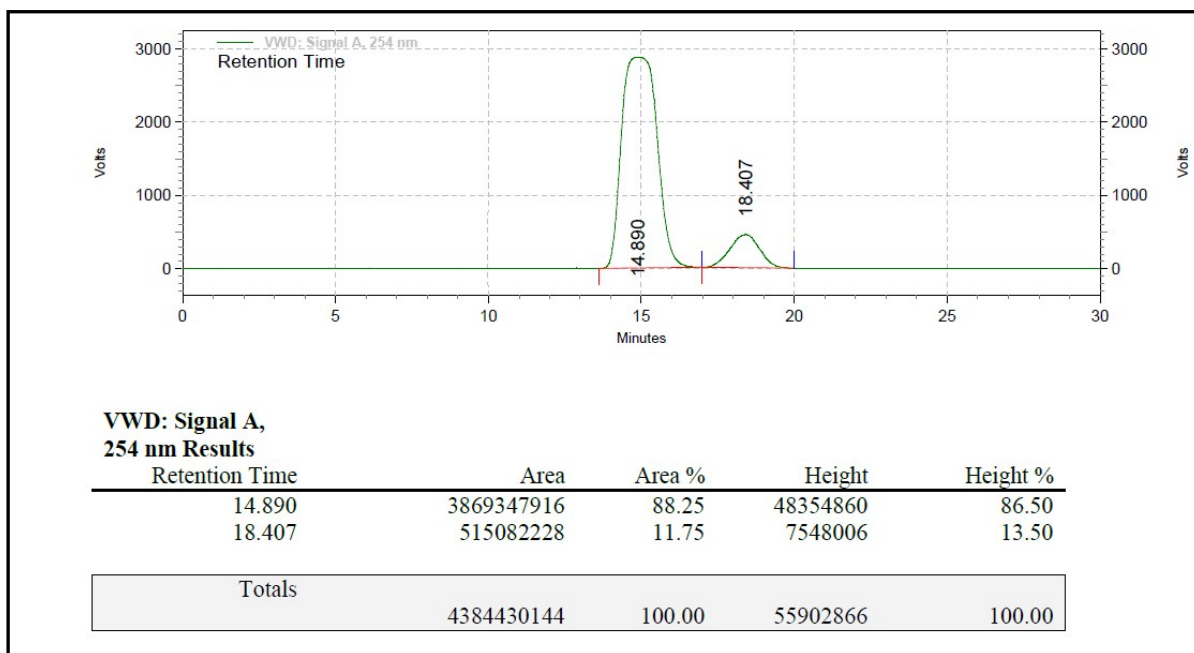
(-) 1-(4-methoxyphenylamino)propan-2-ol (Table 2, entry 4)



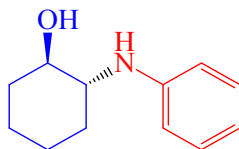
¹H NMR spectra:



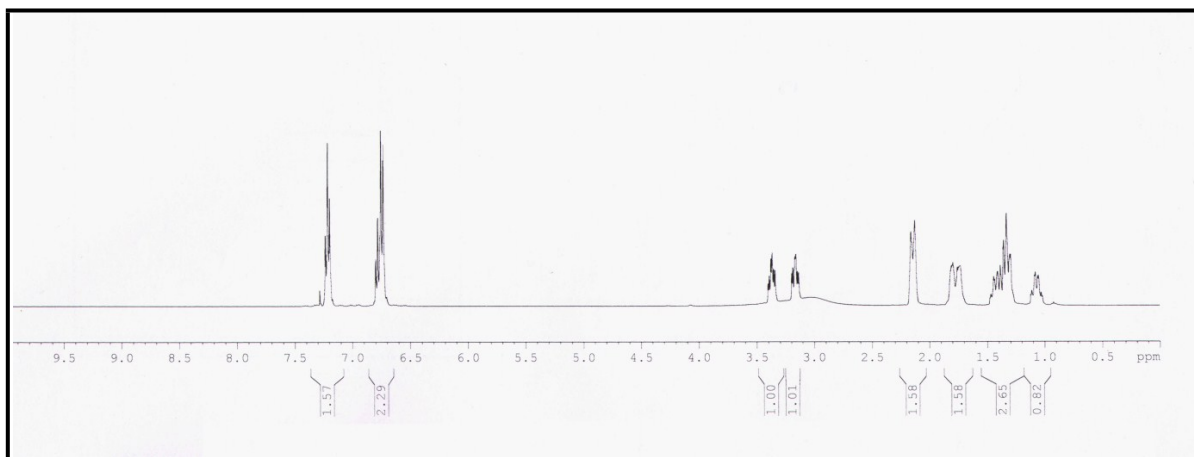
HPLC chromatogram:



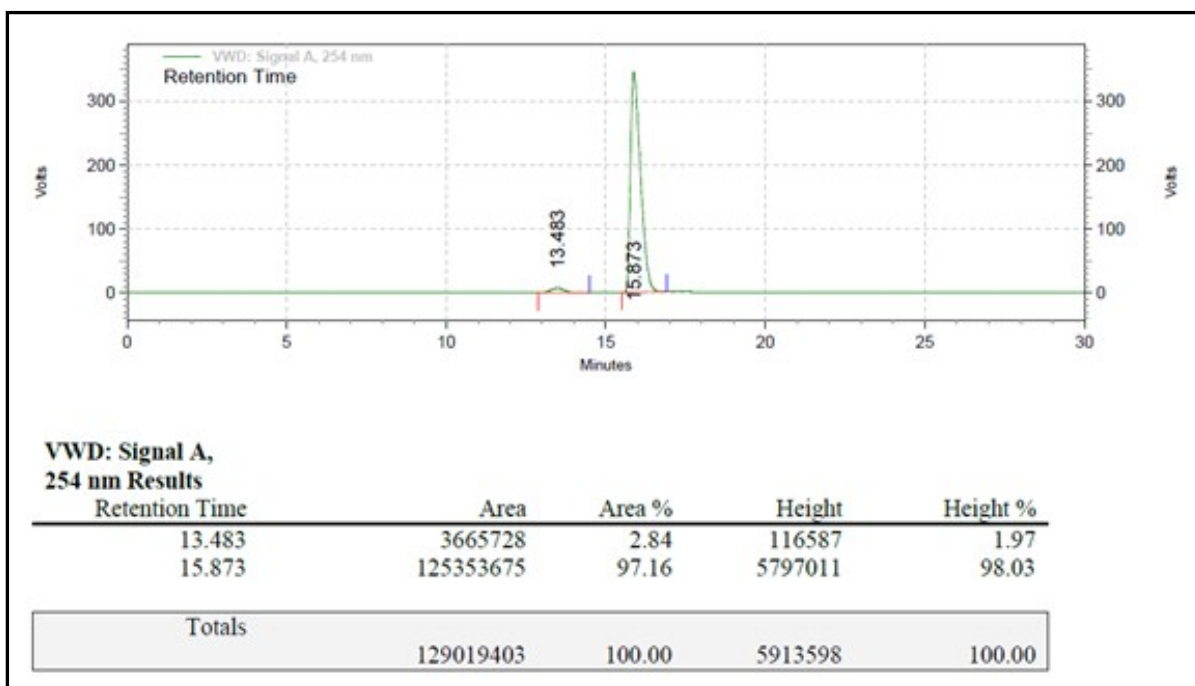
(1R,2R)-2-(phenylamino)cyclohexanol⁴ (Table 2, entry 5)



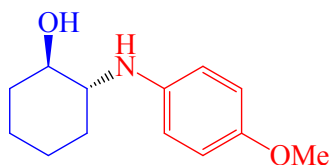
¹H NMR spectra:



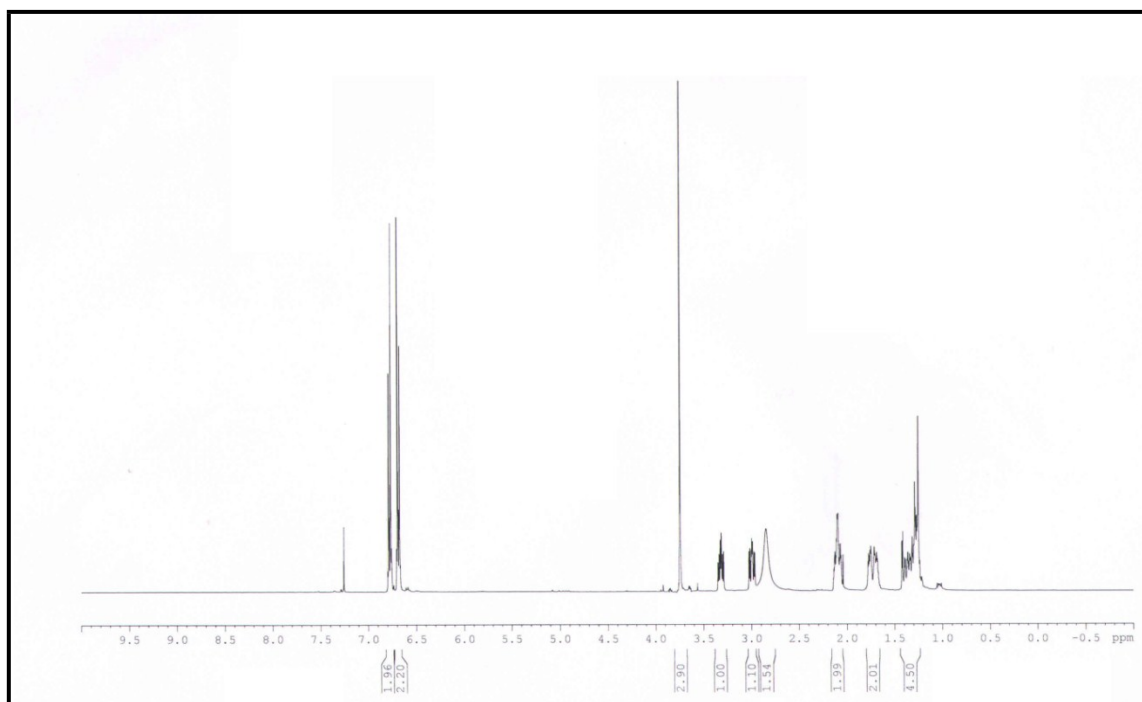
HPLC chromatogram:



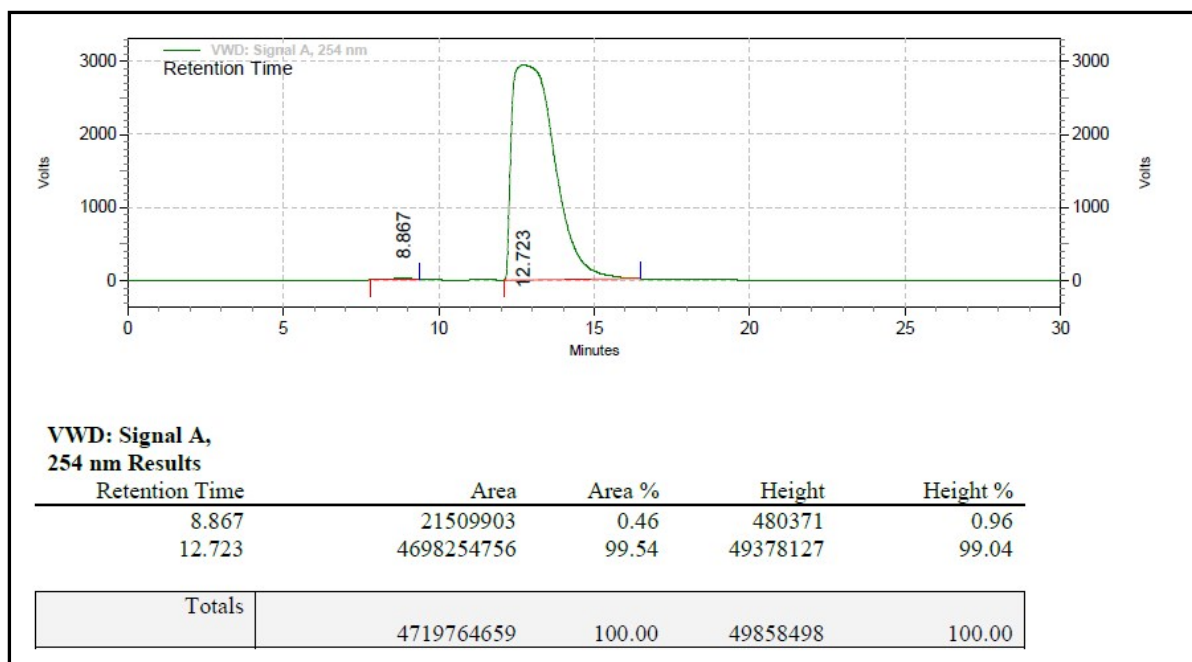
(1*R*,2*R*)-2-(4-methoxyphenylamino)cyclohexanol ⁴ (Table 2, entry 6)



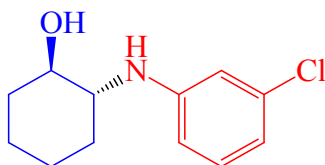
¹H NMR spectra:



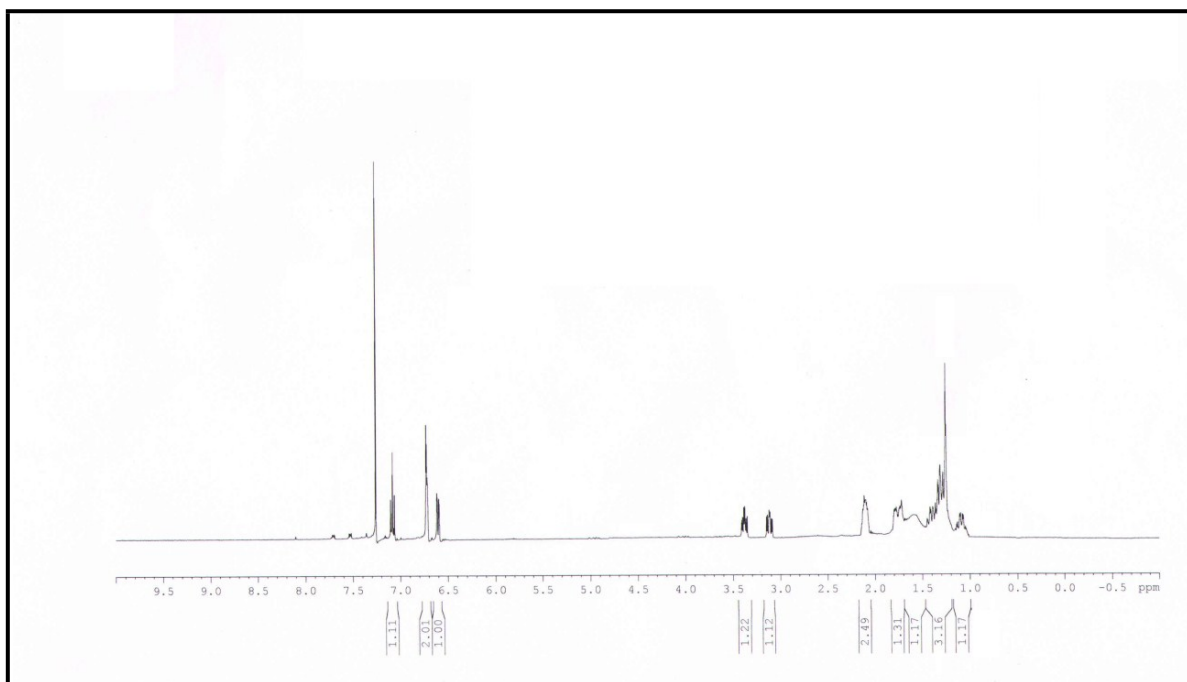
HPLC chromatogram:



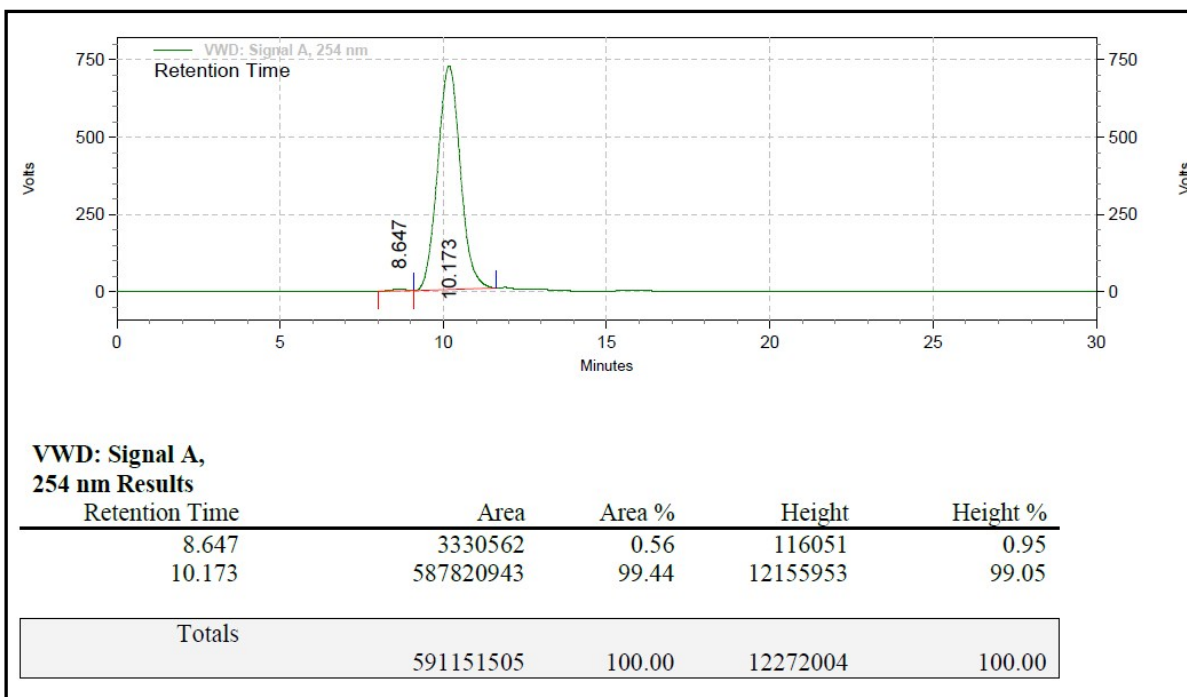
(1*R*,2*R*)-2-(3-chlorophenylamino)cyclohexanol ⁴ (Table 2, entry 7)



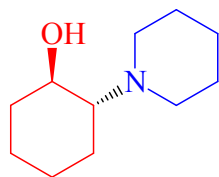
¹H NMR spectra:



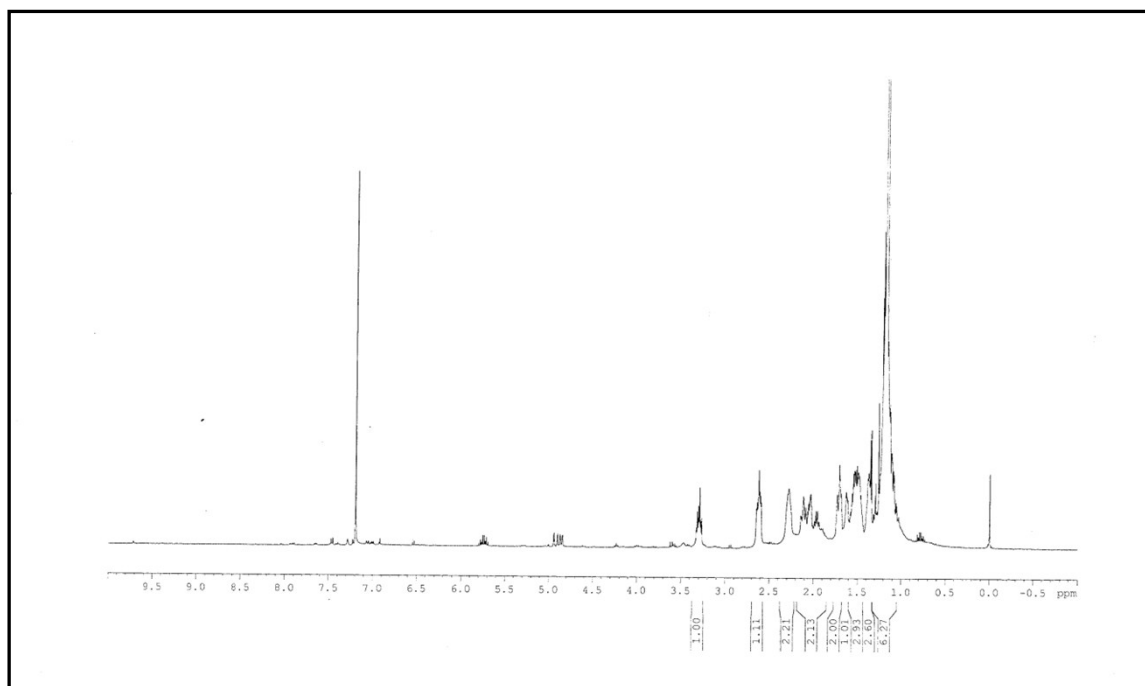
HPLC chromatogram:



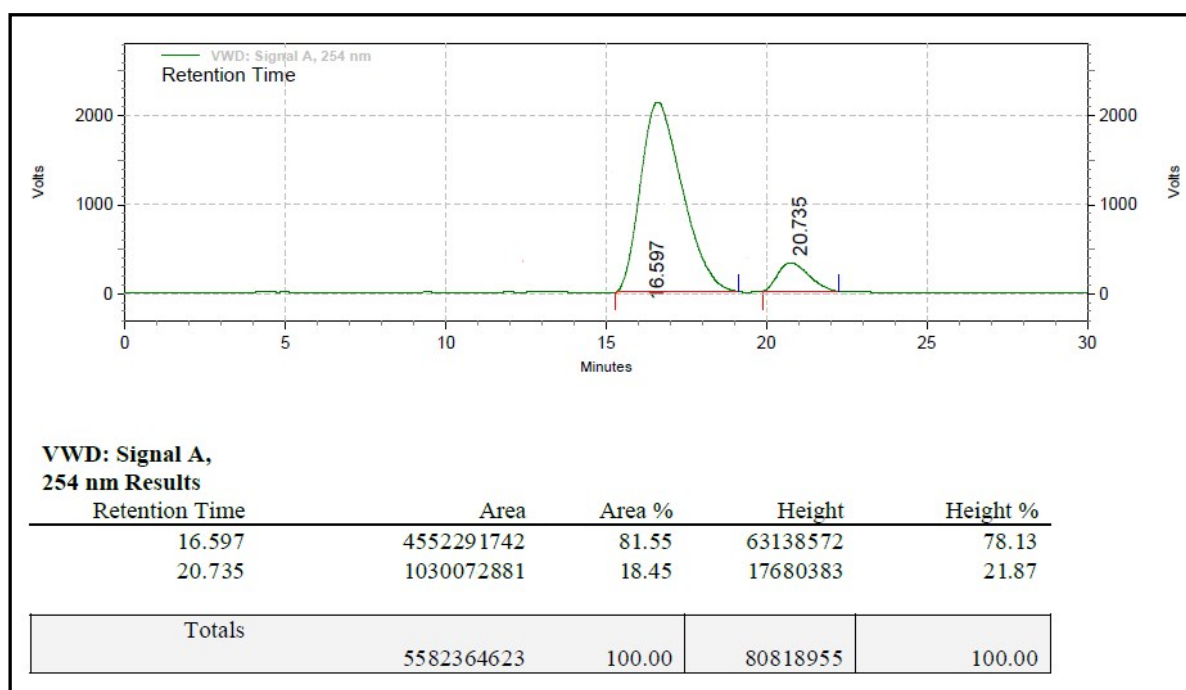
(1*R*,2*R*)-2-(piperidin-1-yl)cyclohexanol ⁵ (Table 2, entry 8)



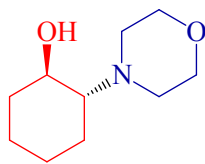
¹H NMR spectra:



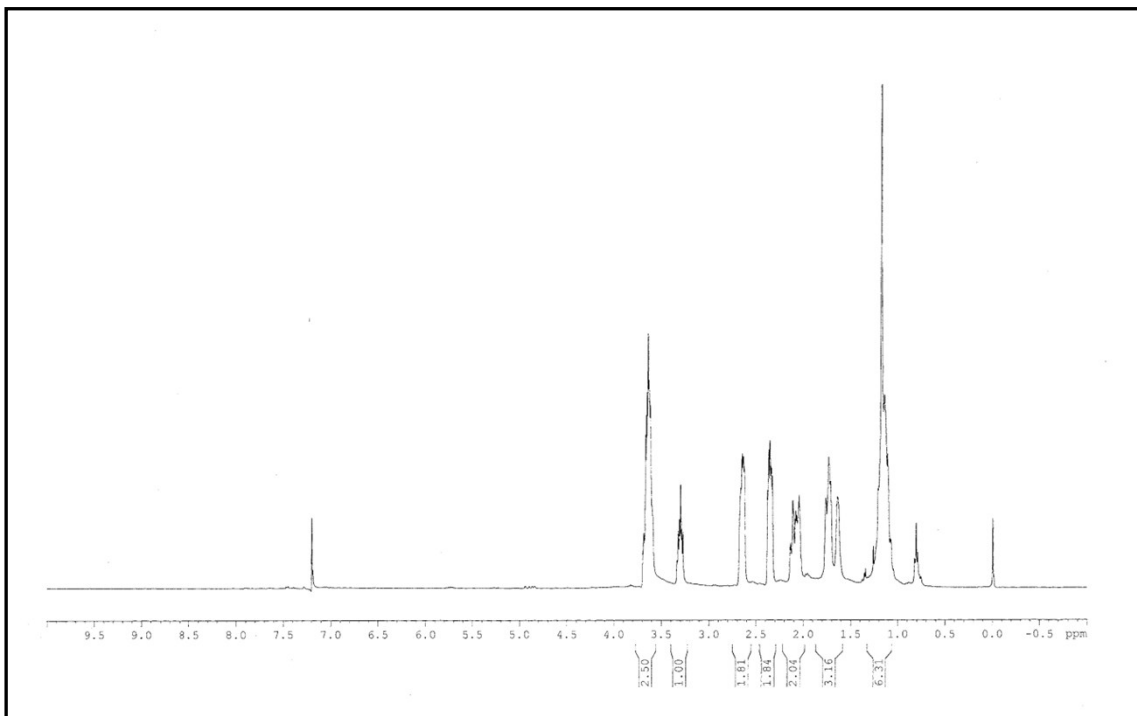
HPLC chromatograms:



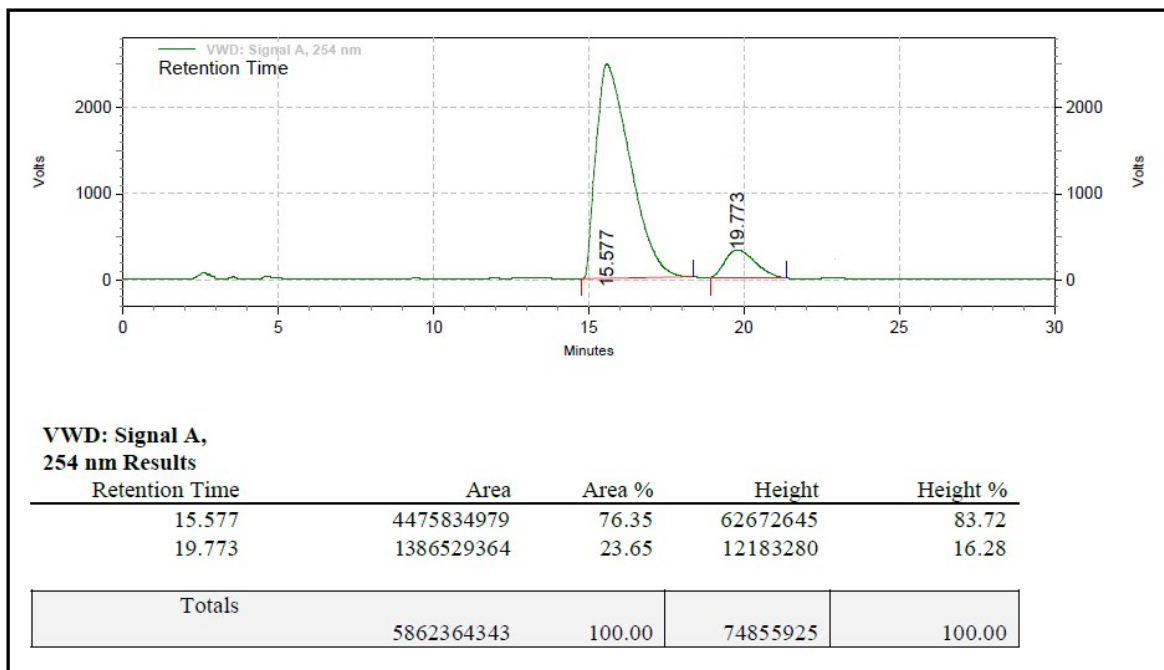
(1*R*,2*R*)-2-morpholinocyclohexanol ⁵ (Table 2, entry 9)



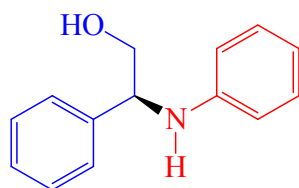
¹H NMR spectra:



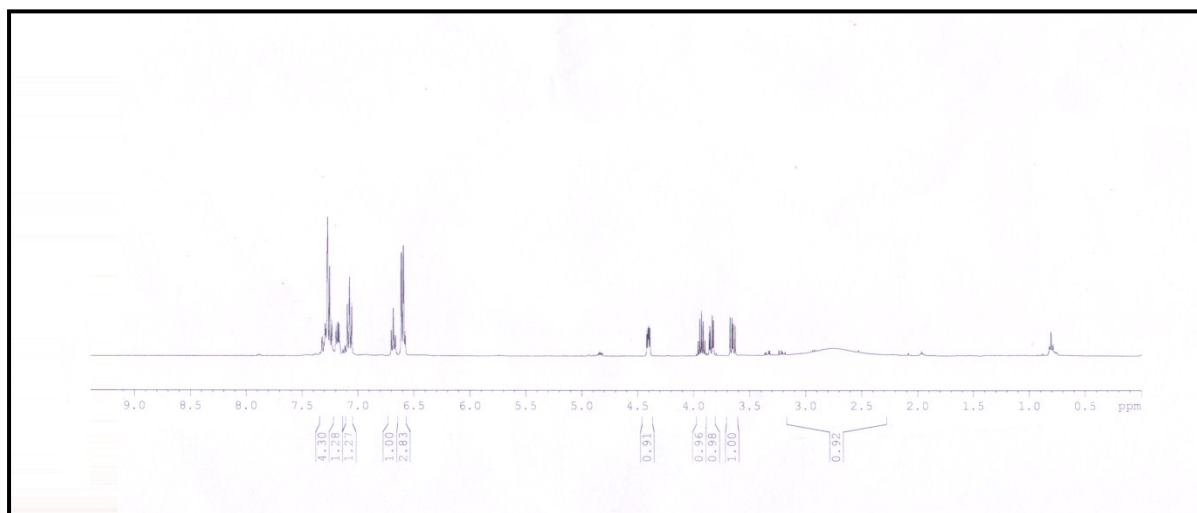
HPLC chromatograms:



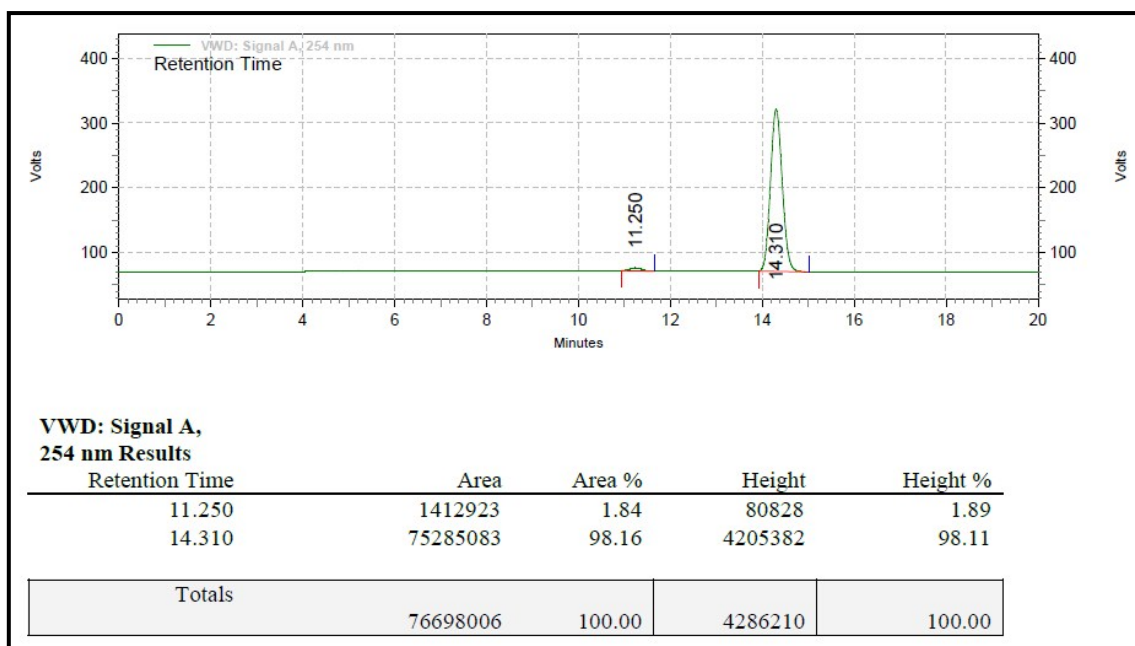
(S)-2-phenyl-2-(phenylamino)ethanol⁴ (Table 2, entry 10)



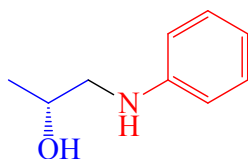
¹H NMR spectra:



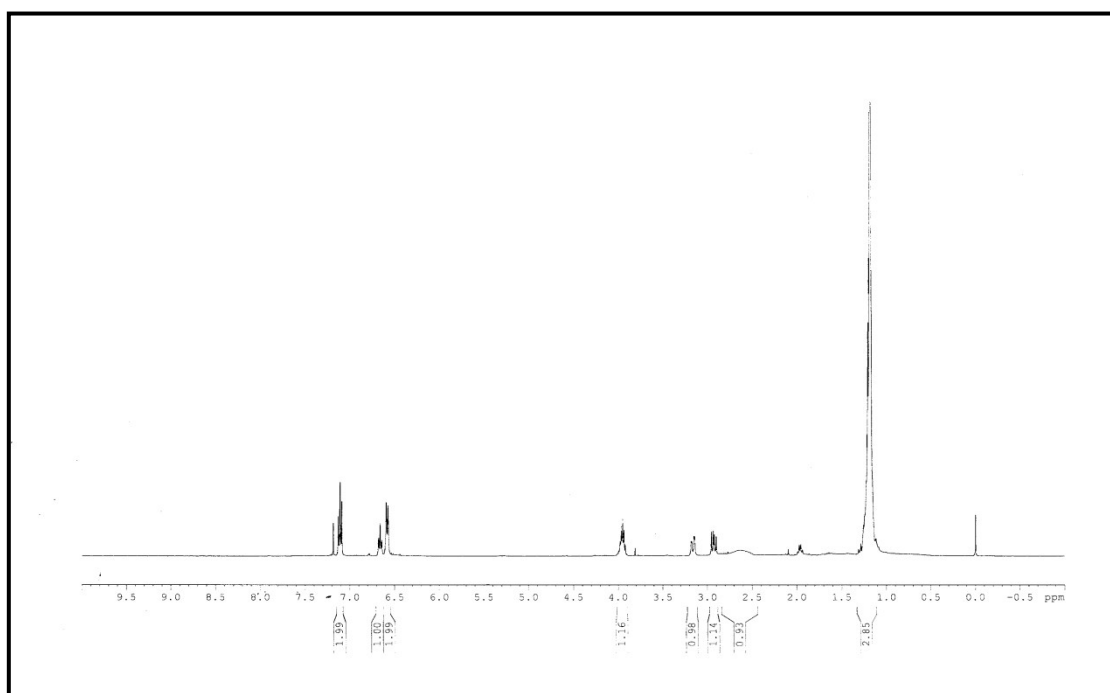
HPLC chromatograms:



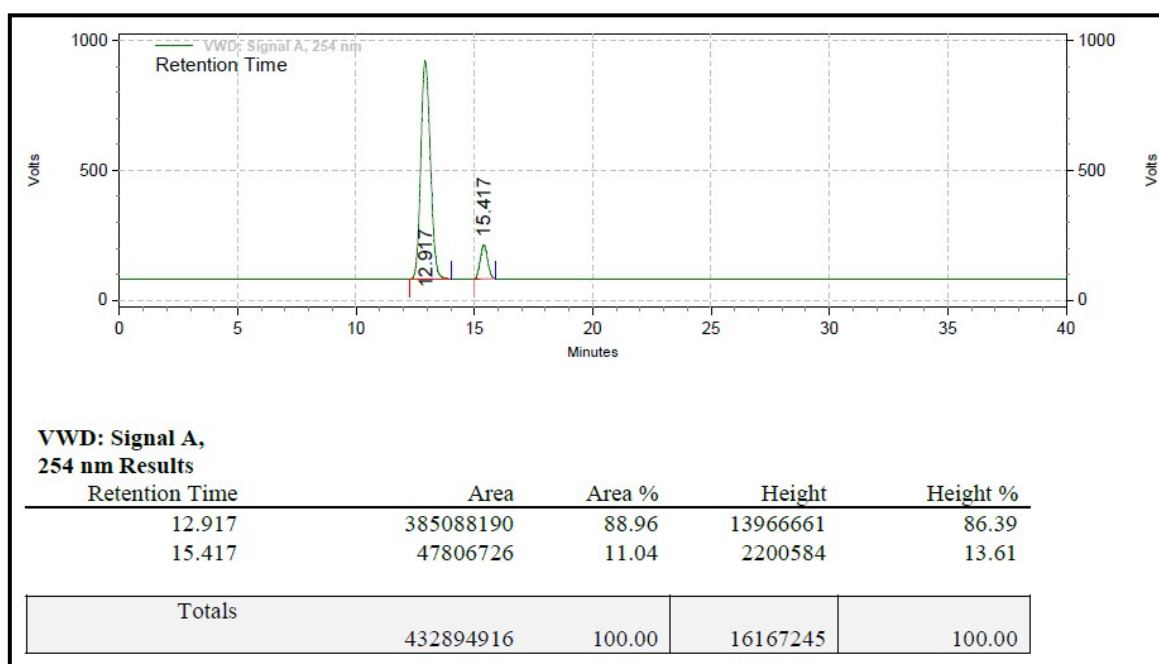
(R)-1-(phenylamino)propan-2-ol⁴ (Table 2, entry 13)



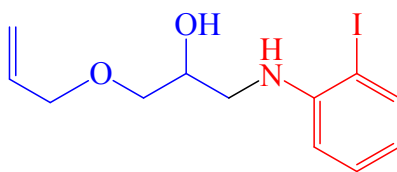
¹H NMR spectra:



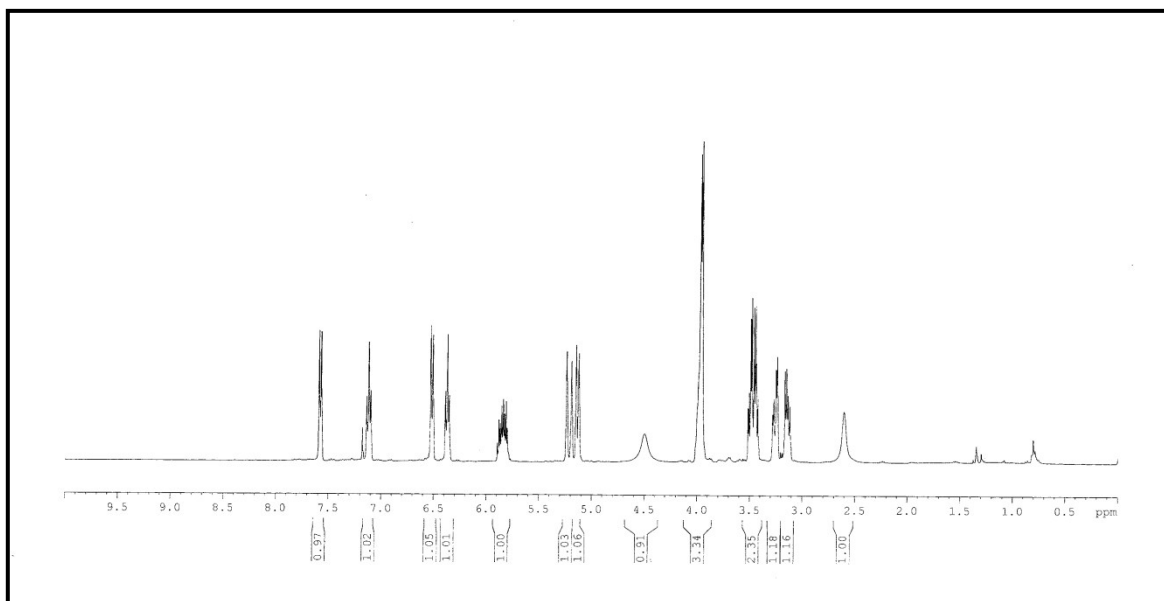
HPLC chromatograms:



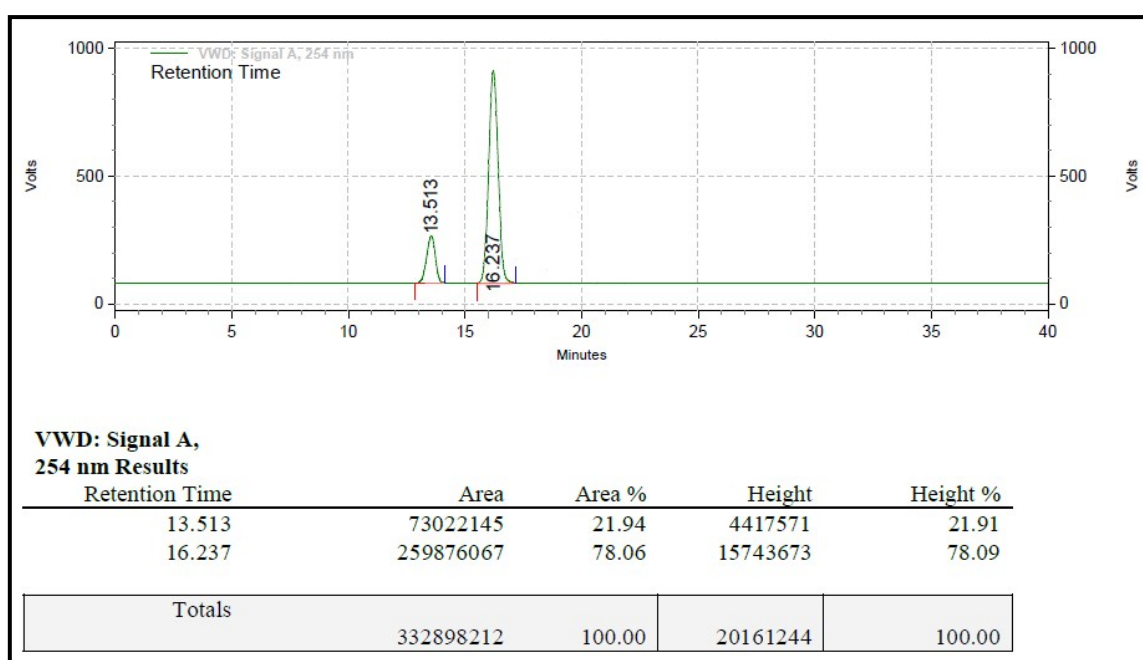
(+)-1-(allyloxy)-3-((2-iodophenyl)amino)propan-2-ol (Table 2, entry 14)



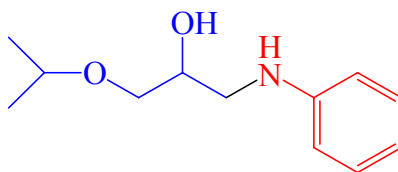
¹H NMR spectra:



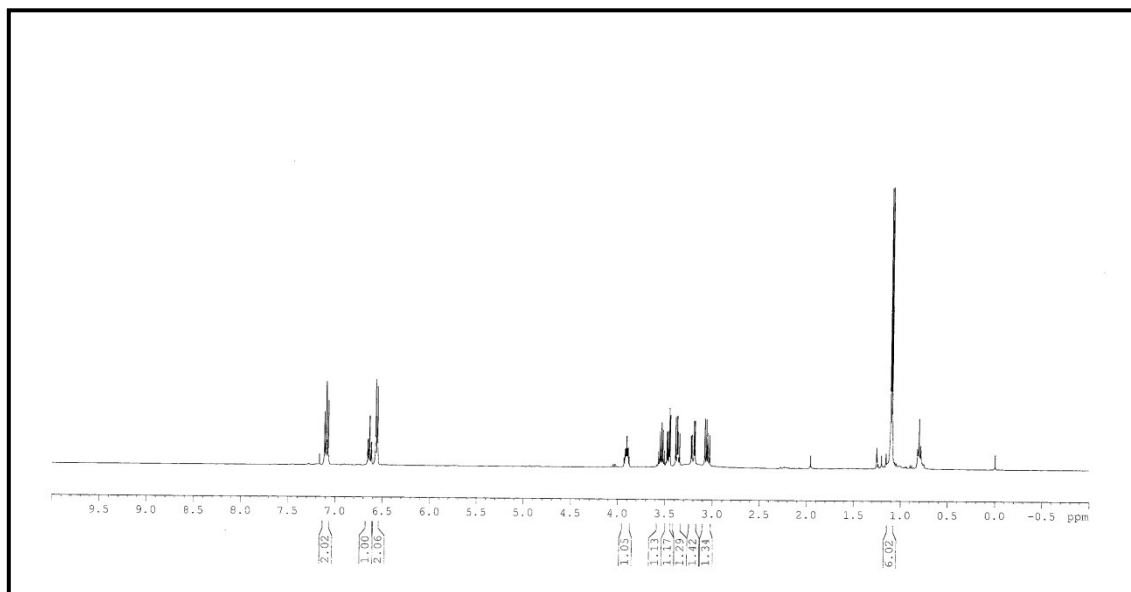
HPLC chromatograms:



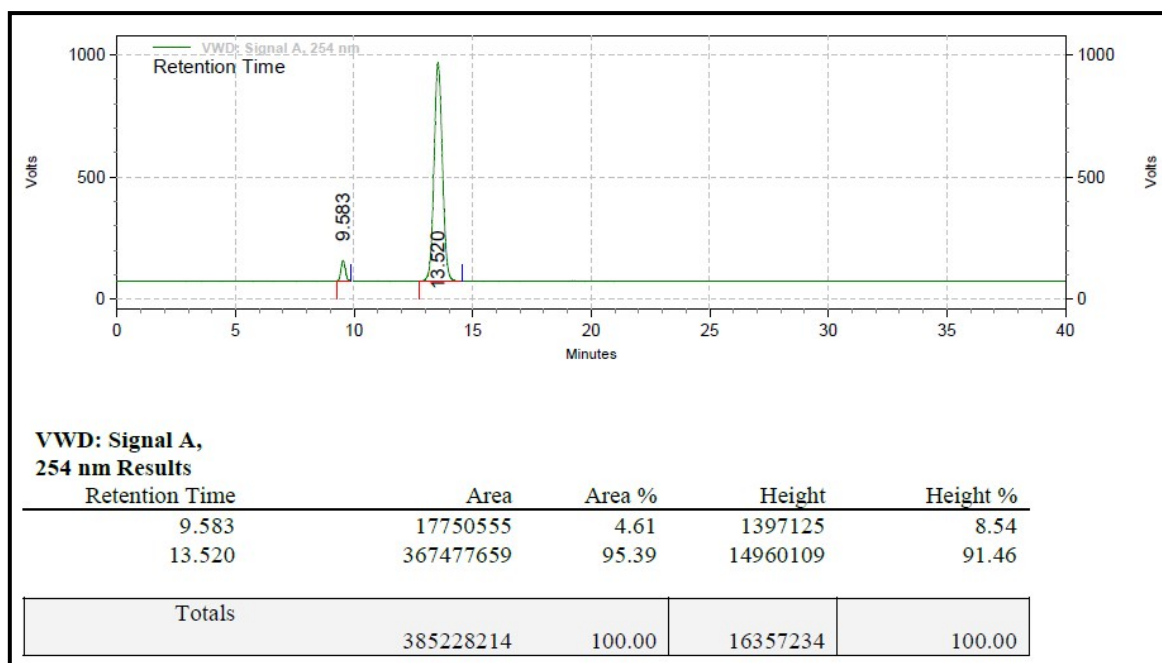
(-)-1-isopropoxy-3-(phenylamino)propan-2-ol (Table 2, entry 15)



¹H NMR spectra:



HPLC chromatograms:



Reference:

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2. M. Kumar, R. I. Kureshy, S. Saravanan, S. Verma, A. Jakhar, N. H. Khan, S. H. R. Abdi and H. C. Bajaj, *Org. Lett.*, 2014, **16**, 2798.
3. J. Sun, Z. Dai, M. Yang, X. Pan and C. Zhu, *Synthesis*, 2008, **13**, 2100.
4. S. Roy, P. Bhanja, S. S. Islam, A. Bhaumik and S. M. Islam, *Chem. Commun.*, 2016, **52**, 1871.
5. L. W. Nicholsona, C. D. Pfeiffer, C. T. Goralskib and B. Singaram, *Journal of Chromatography A*, 1996, **719**, 315.