Enantioselective syntheses of β-amino alcohols catalyzed by recyclable chiral Fe(III) metal complex

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1. General Information

$Fe(acac)_3$, $FeCl_3$, (*S*)-1,1'-binaphthyl-2,2'-diol / (*R*)-1,1'-binaphthyl-2,2'-diol, aniline, 2-methoxyaniline, 4-methoxyaniline, 4-methylaniline, 2-chloroaniline, 4-nitroaniline, 4-ethylaniline, *meso*-stilbene oxide, *cis*-butene oxide and cyclohexene oxide were purchased from

Aldrich Chemicals and were used as received. All the solvents used in the present study were dried by known purification technique. NMR spectra were obtained with 500 MHz / 200 MHz and are referenced internally with TMS. Enantiomeric excess (ee) were determined by HPLC using Daicel Chiralpak OD, OJ and AD chiral columns with 2-propanol/hexane as eluent. FT-IR spectra were carried out using KBr. Optical rotations were determined by automatic polarimeter (Digipol 781). For the product purification flash chromatography was performed using silica gel 100-200 mesh. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, m =multiplet, br = broad, q = Quintet, coupling constants are given in Hertz (Hz).

2. Synthesis and characterization of the ligands:

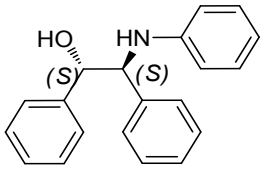
Chiral ligands $\mathbf{L_1}$-$\mathbf{L_7}$ were prepared according to the methods reported in the literature. For the characterization of the ligands.[1-4]

3. Typical experimental procedure for ring opening of epoxides

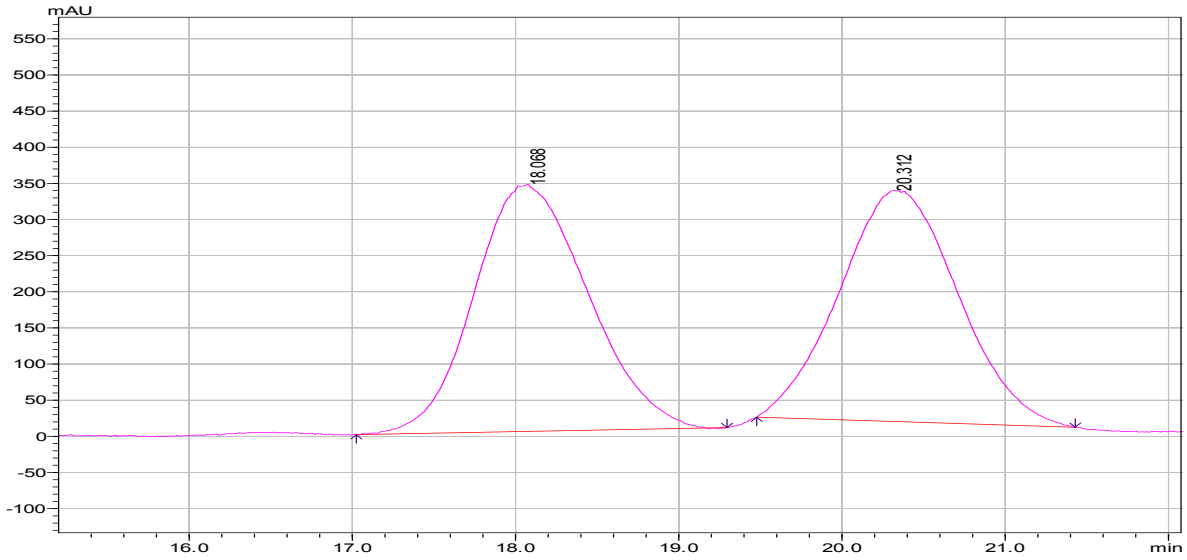
To a 5 ml round bottom flask fitted with rubber septum and equipped with a magnetic stirring bar, a solution of chiral ligands $\mathbf{L_1}$-$\mathbf{L_7}$ (0.005 mmol) in DCM, 0.8 ml and iron salts (0.01 mmol) were charged and the resulting solution was allowed to stir at room temperature (27±2 °C) for 1 h. Subsequently, an appropriate epoxide viz., *meso*-stilbene oxide **5**/ *cis*-butene oxide **7**/cyclohexene oxide **8** (0.2 mmol) was added to the above stirring solution and after a gap of 10 min, appropriate anilines **6a-l** (0.22 mmol) was added and the reaction mixture was allowed to stir for the specified time. The progress of the reaction was checked on TLC using hexane/ethyl acetate (8/2) as mobile phase. After the completion of reaction, solvent was removed under vacuum and the product was purified by column chromatography using silica gel 100-200 mesh as stationary phase and hexane: ethyl acetate (8:2) as mobile phase.

4. Characterization data and HPLC profile of products:

(1S,2S)-1,2-Diphenyl-2-(phenylamino)-ethanol [6'a] [1,3] :



The title compound was isolated by column chromatography (hexane/AcOEt: 90/10) as a white solid; Melting point: 100–102 °C; The *ee* >99% on HPLC (Chiralpak AD column) mobile phase 92/8 n-hexane/*i*-PrOH; flow rate 0.6 mL/min., retention time, (*1S,2S*): 17.31 min., (*1R,2R*): 20.8 min.; ^{1}H NMR (200MHz, $CDCl_3$, δ ppm): δ = 7.17–7.27 (m, 10 H), 7.03–7.11 (t, *J* = 8.0 Hz, 2 H), 6.60 (t, *J* = 8.0 Hz, 1 H), 6.52 (d, *J* = 8.0 Hz, 2 H), 4.86 (d, *J* = 5.8 Hz, 1 H), 4.52 (d, *J* = 5.8 Hz, 1 H), 2.64 (bs, OH); ^{13}C NMR (200 MHz, $CDCl_3$, δ ppm): δ = 148.91, 141.87, 137.42, 130.72, 130.22, 129.91, 129.56, 129.18, 128.94, 128.22, 119.56, 115.79, 79.72, 66.38; FTIR (KBr): ν = 3545, 3405, 3026, 2883, 2847, 1600, 1502, 1450, 1427, 1322, 1030, 753, 696 cm^{-1}; TOF-MS (ESI+): m/z 290 $[M+H]^+$, 272 (base peak) $[M–OH]^+$.



Peak	Ret. Time	Area	Peak Start	Peak End	Area%
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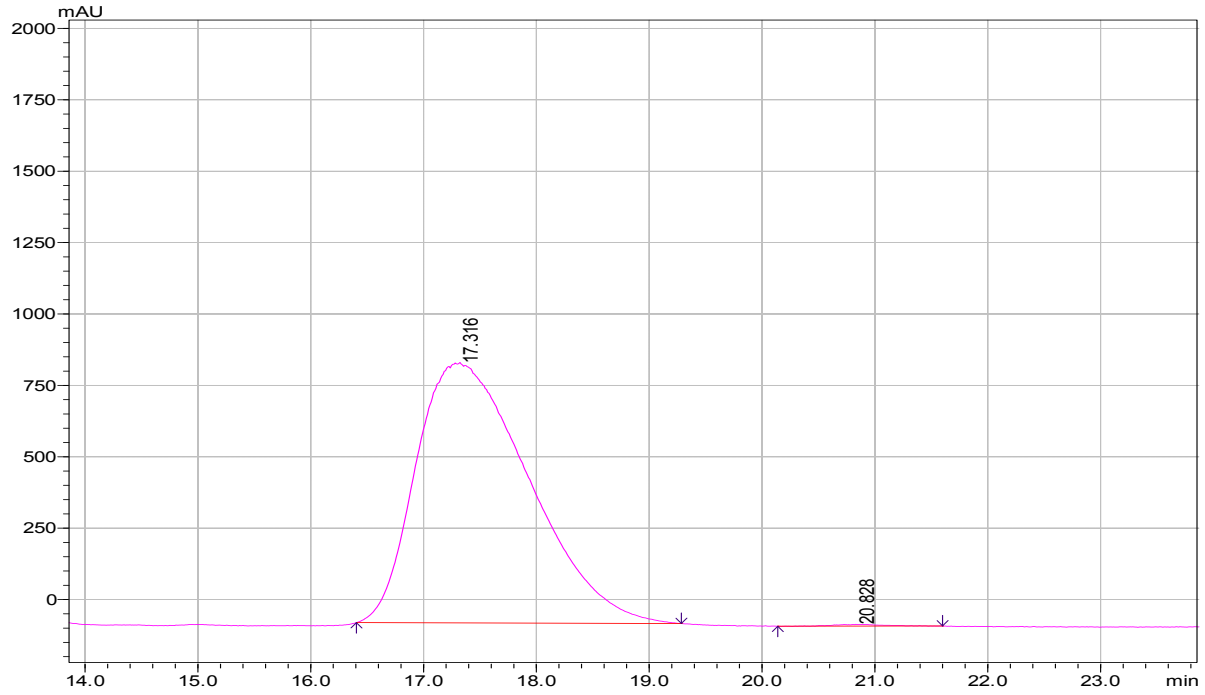
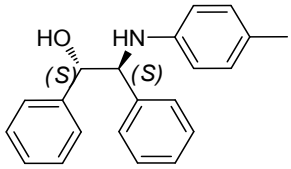
2	20.312	16187629	19.477	21.429	49.4402



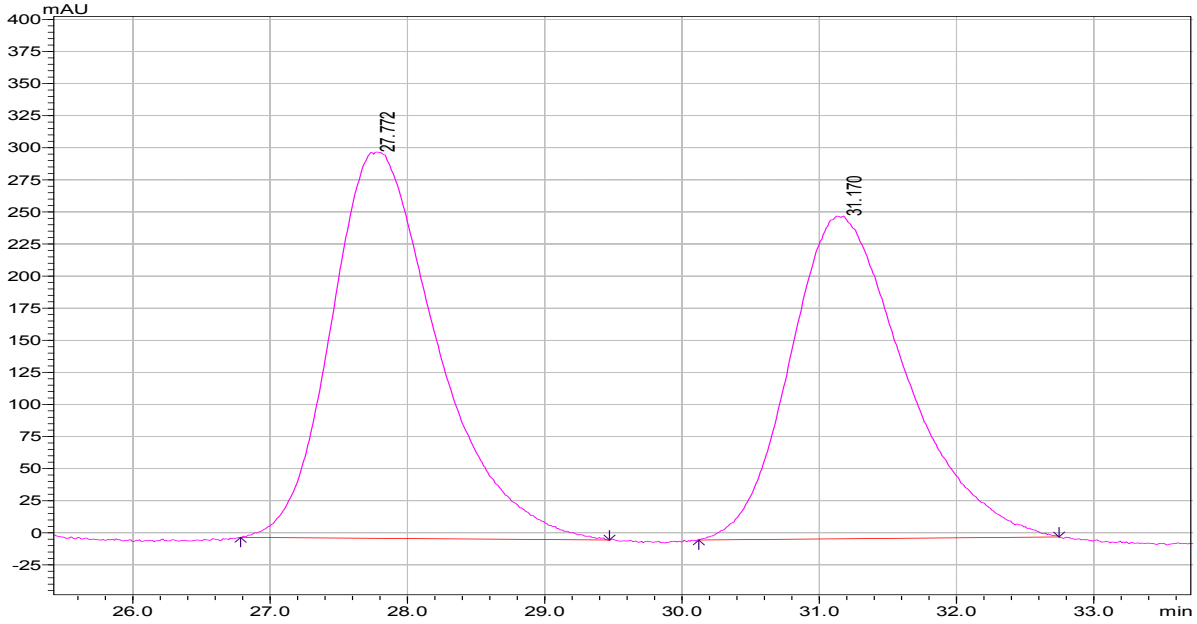
Peak	Ret. Time	Area	Peak Start	Peak End	Area%
1	17.316	63445475	16.405	19.285	99.7351
2	20.828	168484	20.139	21.600	0.2649

(1*S*,2*S*)-1,2-Diphenyl-2-(4-methyl-phenylamino)-ethanol [6'b] [1,3]:

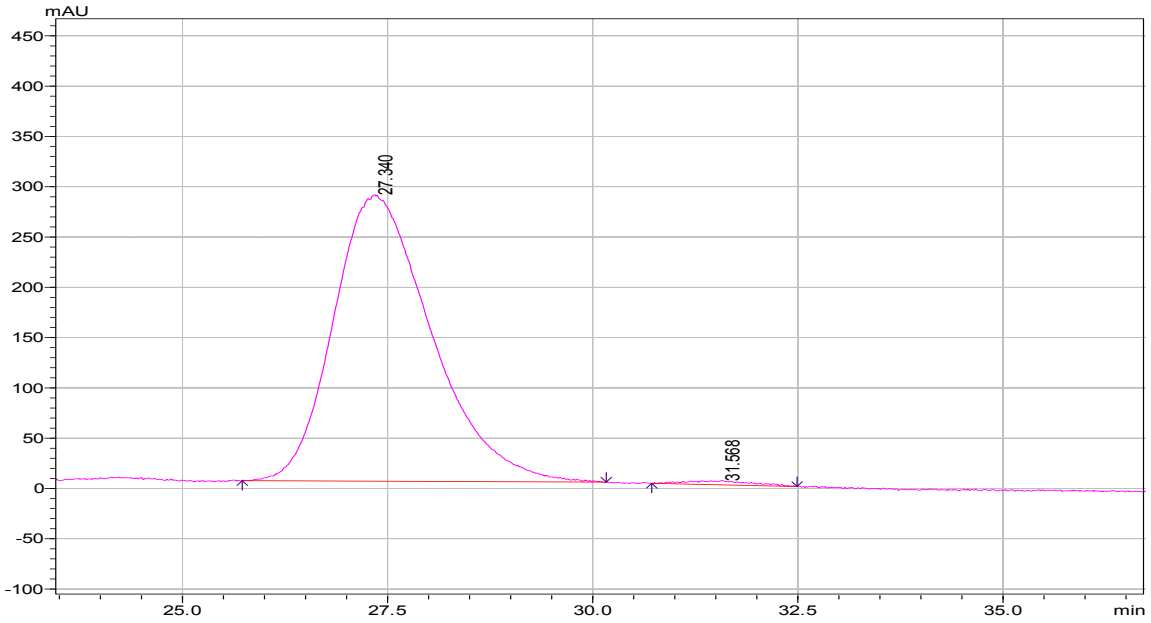


The title compound was isolated by column chromatography (hexane/AcOEt 90/10) as a white solid; Melting point: 85°C; The *ee* >99% on HPLC (Chiralpak OD column,) mobile phase, 92/8 hexane/*i*-PrOH; flow rate 0.6 mL/min., retention time (*1S,2S*): 27.3 min., (*1R,2R*): 31.5 min.; ^{1}H

NMR (200 MHz, $CDCl_3$, δ ppm): δ = 7.21–7.25 (m, 10 H), 6.85 (d, *J* = 8.0 Hz, 2 H), 6.44 (d, *J* = 8.0 Hz, 2 H), 4.82 (d, *J* = 6.2 Hz, 1 H), 4.46 (d, *J* = 6.2 Hz, 1 H), 2.67 (bs, 1 H), 2.16 (s, 3 H); ^{13}C NMR (200 MHz, $CDCl_3$, δ ppm): δ = 144.9, 140.5, 140.2, 129.6, 128.5, 128.2, 127.8, 127.3, 126.6, 114.3, 78.0, 65.2, 20.3; FTIR (KBr): ν = 3398, 3062, 3028, 2858, 2832, 1816, 1615, 1517, 1491, 1258, 1043, 814, 763, 700 cm^{-1}; TOF-MS (ESI+): m/z 304 $[M+H]^+$, 286 $[M–OH]^+$.

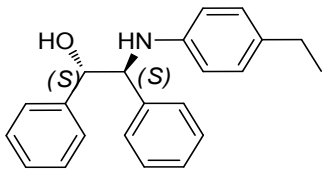


Peak	Ret. Time	Area	Peak Start	Peak End	Area%
1	27.772	16170220	26.784	29.472	52.4441
2	31.170	14663037	30.123	32.747	47.5559



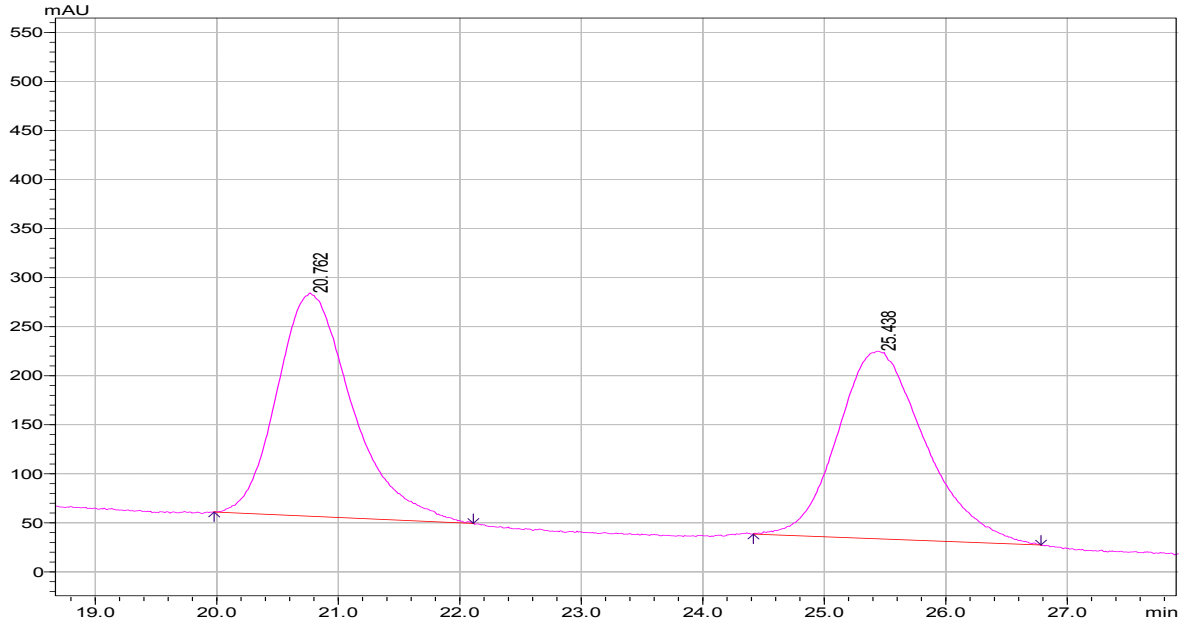
Peak	Ret. Time	Area	Peak Start	Peak End	Area%
1	27.340	23565831	25.728	30.165	99.5854
2	31.568	217516	30.720	32.491	0.4146

(1*S*,2*S*)-1,2-diphenyl-2-(4-ethyl-phenylamino)-ethanol [6'c] [1,3]**:**

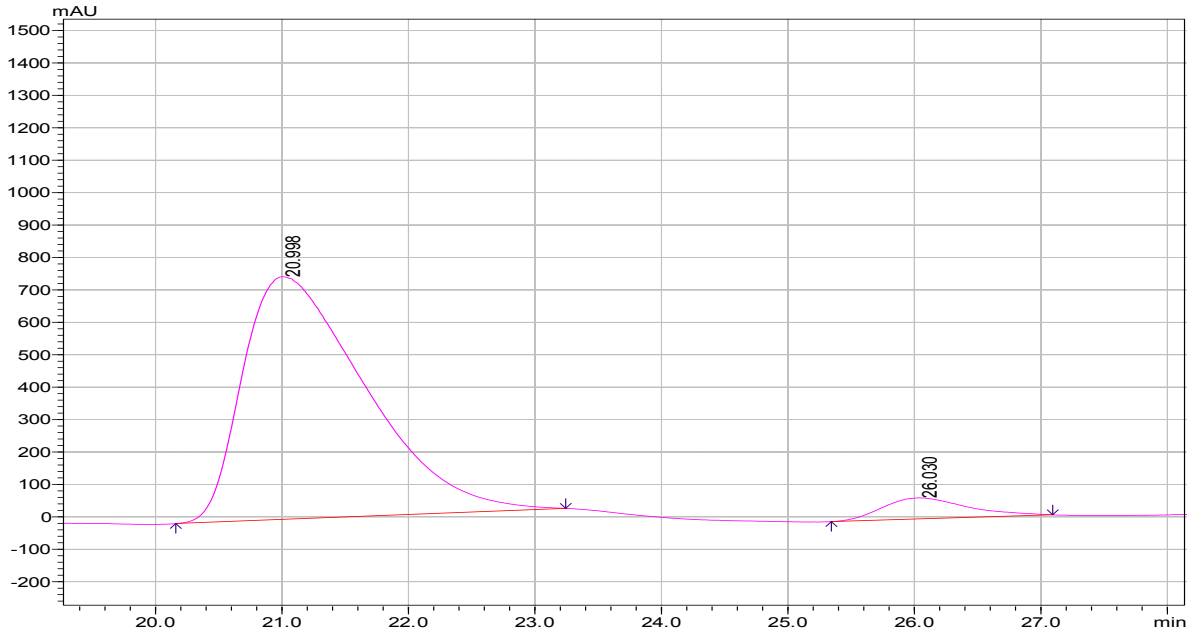


The title compound was isolated by column chromatography (hexane/AcOEt 90/10) as a white solid; Melting point: 85°C; The *ee* 90% on HPLC (Chiralpak OD column,) mobile phase, 92/8 hexane/*i*-PrOH; flow rate 0.6 mL/min., retention time (*1S,2S*): 20.9 min., (*1R,2R*): 26.03 min.; ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): δ = 7.25–7.06 (m, 10 H), 6.88 (d, *J* = 8.5 Hz, 2 H), 6.44 (d, *J* = 8.5 Hz, 2 H), 5.00 (d, *J* = 5.0 Hz, 1 H), 4.61 (d, *J* = 5.0 Hz, 1 H), 2.19 (q, 2 H), 1.102 (t, *J* =

15.0 Hz, 3 H), ^{13}C NMR (200 MHz, $CDCl_3$, δ ppm): δ = 144.69, 140.07, 138.81, 133.82, 128.26, 128.22, 127.96, 127.91, 127.57, 114.14, 78.0, 64.04, 27.87,15.81; FTIR (KBr): ν = 3398, 3062, 3028, 2857, 2832, 1814, 1616, 1519, 1492, 1257, 1045, 816, 769, 701 cm^{-1}; TOF-MS (ESI+): m/z 318 $[M+H]^+$, 334 $[M–OH]^+$.

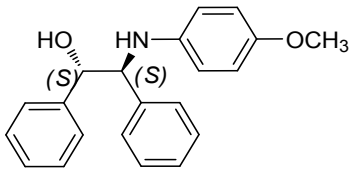


Peak	Ret. Time	Area	Peak Start	Peak End	Area%
1	20.762	9774345	19.979	22.112	50.3976
2	25.438	9620109	24.416	26.784	49.6024



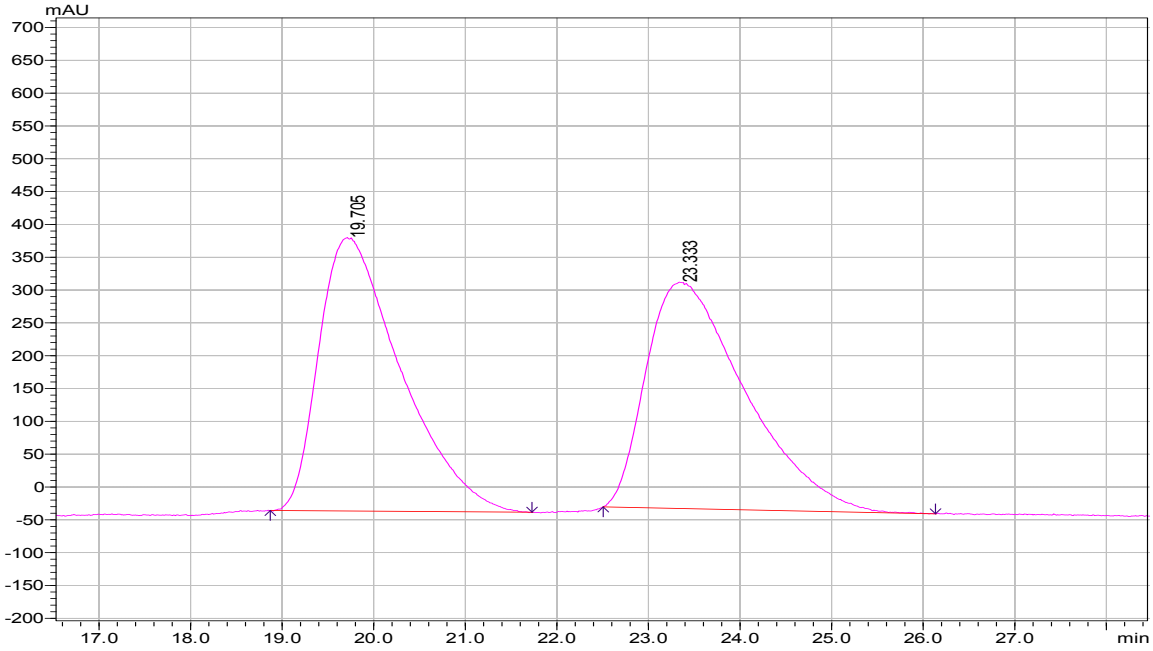
Peak	Ret. Time	Area	Peak Start	Peak End	Area%
1	20.998	50374644	20.160	23.243	95.3926
2	26.030	2992523	25.344	27.093	4.6074

(1*S*,2*S*)-1,2-Diphenyl-2-(4-methoxy-phenylamino)-ethanol [6'd] [1,3]**:**

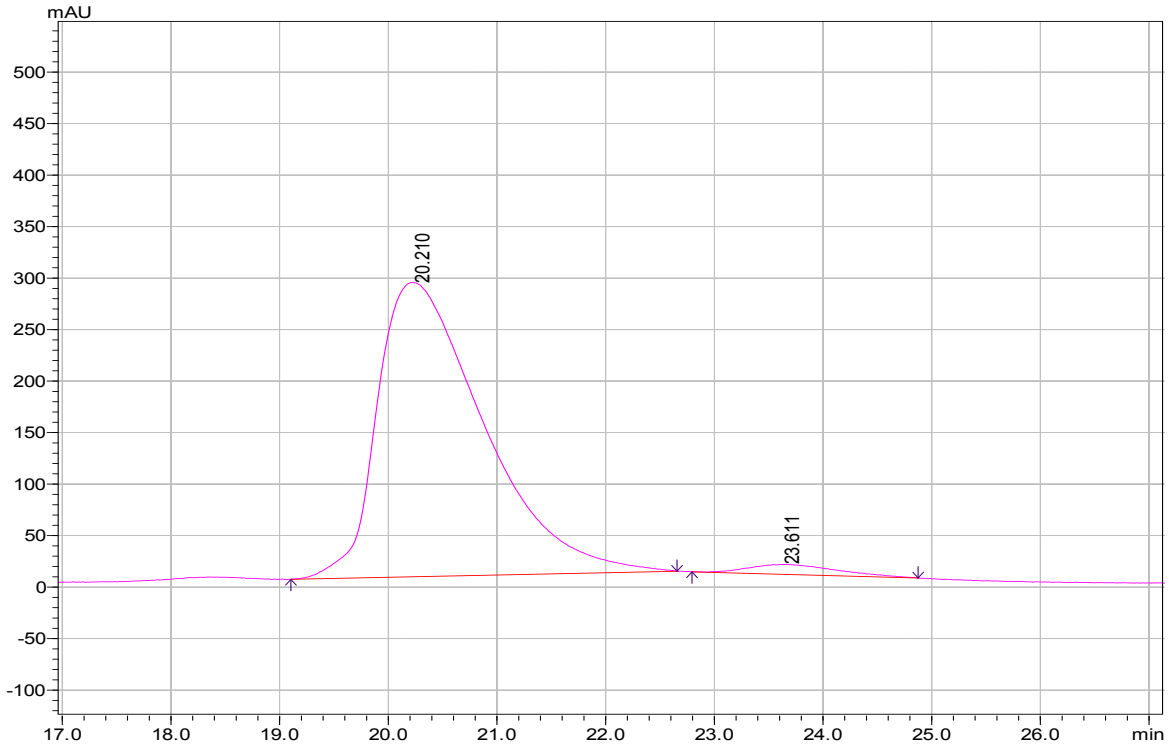


The title compound was isolated by column chromatography (hexane/AcOEt 90/10) as a yellow solid; Melting point: 98–102°C; The *ee* 95% on HPLC (Chiralpak OD column) mobile phase, 90/10 n-hexane/*i*-PrOH; flow rate 1 mL/min., retention time, (*1S,2S*): 20.21 min., (*1R,2R*): 23.61 min., ^{1}H NMR (200 MHz, $CDCl_3$, δ ppm): δ = 7.20–7.26 (m, 10 H), 6.66 (d, *J* = 8.8 Hz, 2 H), 6.50 (d, *J* = 8.8 Hz, 2 H), 4.82 (d, *J* = 6.4 Hz, 1 H), 4.41 (d, *J* = 6.4 Hz, 1 H), 3.69 (s, 3 H), ^{13}C NMR (200 MHz, $CDCl_3$, δ ppm): δ = 152.52, 141.28, 140.55, 140.19, 128.46, 128.15, 127.44,

127.32, 126.66, 115.75, 114.64, 78.09, 66.17, 55.65, 29.67; FTIR (KBr): v = 3483, 3393, 3026, 2964, 2833, 1807, 1510, 1453, 1254, 1024, 819, 753, 700 cm^{-1}; TOF-MS (ESI+): m/z 320 $[M+H]^+$.

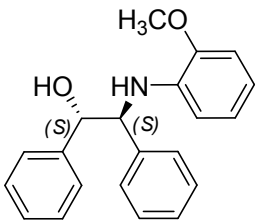


Peak	Ret. Time	Area	Peak Start	Peak End	Area%
1	19.705	25848481	18.869	21.728	49.8879
2	23.333	25964631	22.507	26.133	50.1121



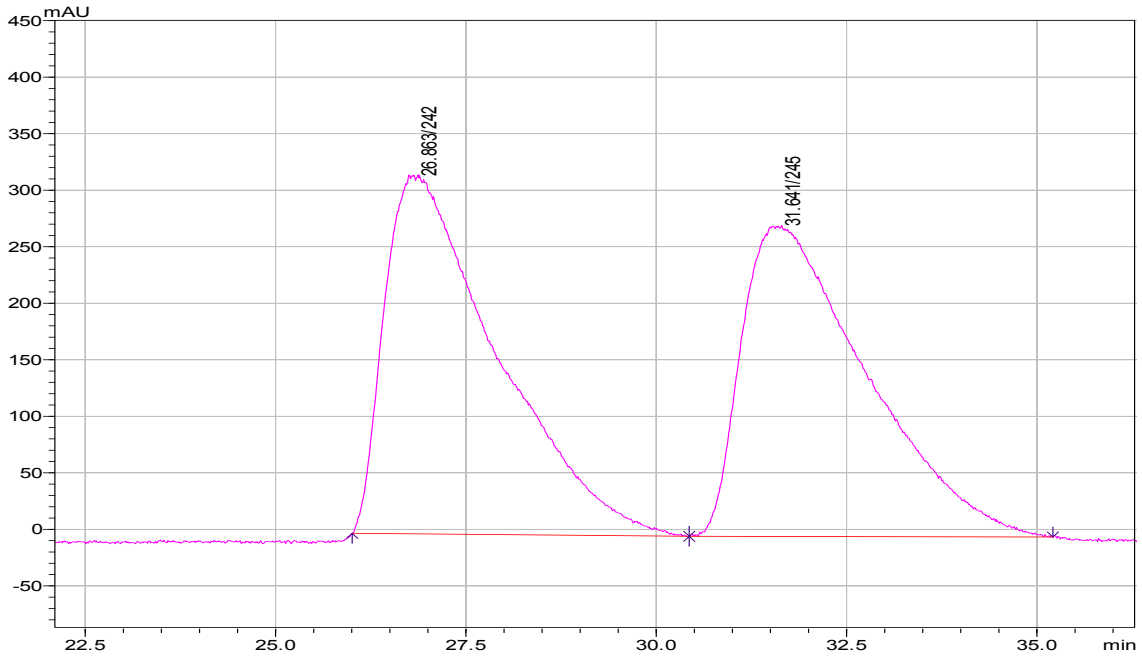
Peak	Ret. Time	Area	Peak Start	Peak End	Area%
1	20.210	19443320	19.104	22.656	97.2354
2	23.611	552823	22.795	24.875	2.7646

(1*S*,2*S*)-1,2-Diphenyl-2-(2-methoxy-phenylamino)-ethanol [6'e] [1,3]**:**

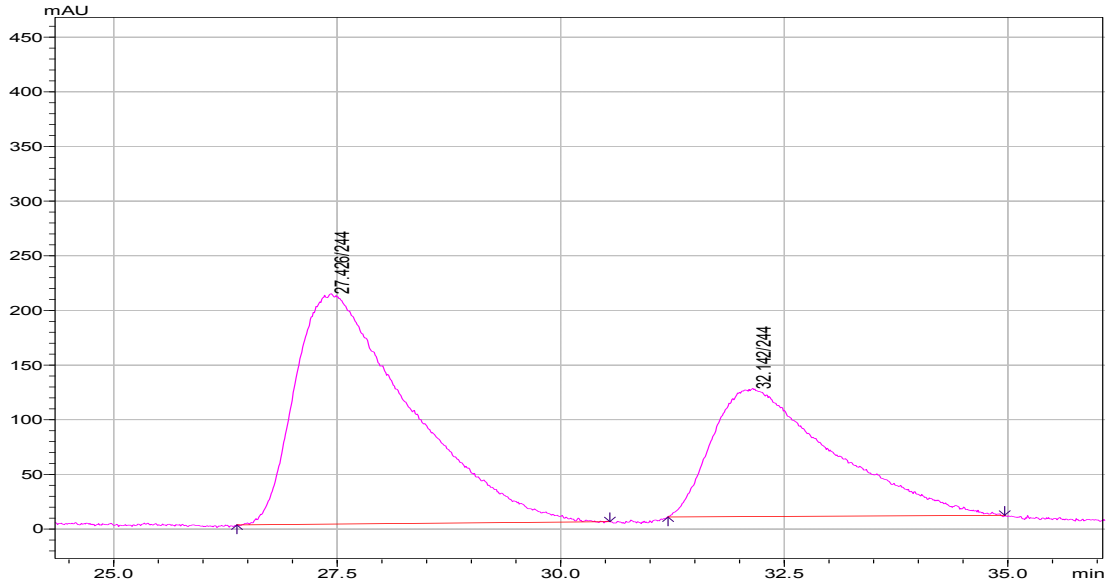


The title compound was isolated by column chromatography (hexane/AcOEt 90/10) as a white solid, Melting point: 93-95°C, ee 28% on HPLC (Chiralpak OD column) mobile phase 80/20 hexane/*i*-PrOH, flow rate 0.8 mL/min, retention time, (*1S, 2S*): 27.42 min, (*1R,2R*): 32.14 min.; ^{1}H NMR (200 MHz, $CDCl_3$, δ ppm): δ = 7.21–7.26 (m, 10 H), 6.74 (d, *J* = 8.0 Hz, 1 H), 6.62 (t,

J = 6.4 Hz, 2 H), 6.38 (d, *J* = 7.2 Hz, 1 H**),** 5.19 (bs, NH), 4.87 (d, *J* = 6.4 Hz, 1 H), 4.50 (d, *J* = 6.4 Hz, 1 H), 3.88 (s, 3 H), ^{13}C NMR (200 MHz, $CDCl_3$, δ ppm): δ = 147.42, 140.63, 140.14, 137.11, 129.76, 129.00, 128.40, 128.10, 127.79, 127.39, 127.31, 126.75, 121.05, 117.20, 109.60, 78.33, 64.94, 55.62 ; FT-IR (KBr): v = 3407, 3062, 3030, 2936, 2835, 1810, 1698, 1601, 1515, 1248, 1027, 846, 740, 700 cm^{-1}; TOF-MS (ESI+): m/z 320 $[M+H]^+$, 302 $[M-OH]^+$.

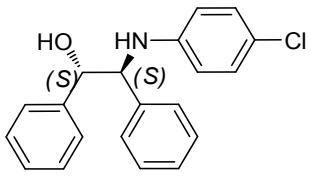


Peak	Ret. Time	Area	Peak Start	Peak End	Area%
1	26.863	32531113	26.005	30.432	50.9541
2	31.641	31312832	30.432	35.211	49.0459



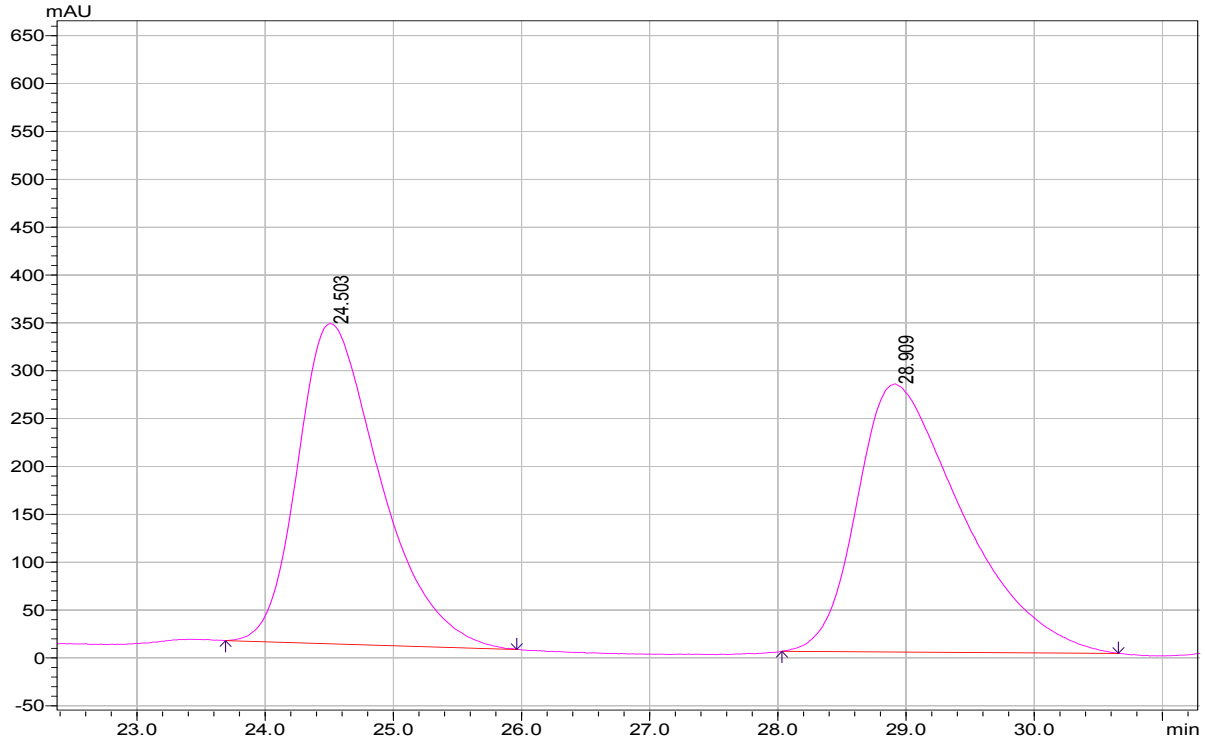
Peak	Ret. Time	Area	Peak Start	Peak End	Area%
1	27.426	18736196	26.379	30.549	64.0062
2	32.142	11000869	31.200	34.965	35.9938

(1*S*,2*S*)-1,2-diphenyl-2-(4-chloro-phenylamino)-ethanol [6'f] [1,3]**:**

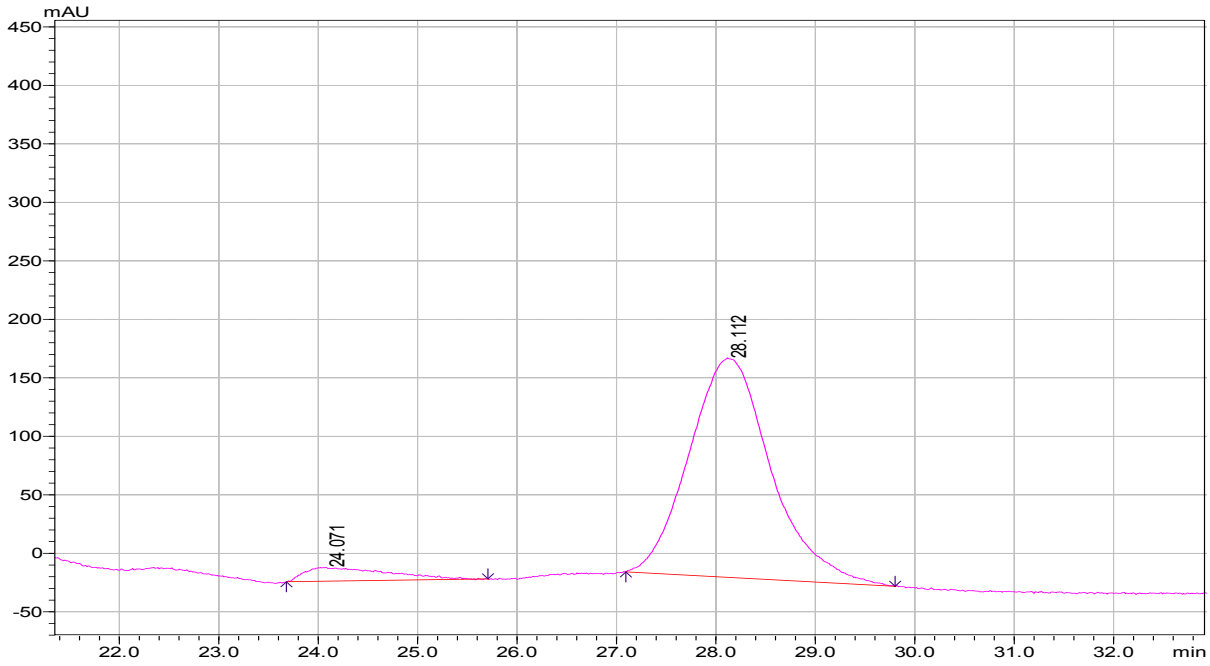


The title compound was isolated by column chromatography (hexane/ AcOEt, 90:10) as a white solid; m.p. 95°C; The *ee* 90% on HPLC (Chiralpak AD Column) mobile phase 90:10 hexane/*i*PrOH; flow rate 0.8 mL/min., retention time (1*S*,2*S*) 24.07 min., (1*R*,2*R*): 28.11 min.; ^{1}H NMR (500 MHz, CDCl3, δ ppm): δ = 7.16–7.26 (m, 10 H), 6.95 (d, *J* = 8.0 Hz, 2 H), 6.39 (d, *J* = 8.8 Hz, 2 H), 4.82 (d, *J* = 5.6 Hz, 1 H), 4.72 (br. s, 1 H), 4.44 (d, *J* = 5.6 Hz, 1 H), 2.50 (br. s, 1 H); ^{13}C NMR (200 MHz, CDCl3, δ ppm): δ = 144.9, 142.3, 141.6, 130.5, 130.2, 129.92, 129.59 129.43, 129.11,121.8,114.7, 79.9, 66.2; FTIR (KBr): ν = 3396, 3063, 3031, 2960, 2929, 2860,

1812, 1722, 1599, 1496, 1268, 1073, 820, 739, 700 cm^{-1}; TOF-MS (ESI+): m/z = 324 $[M+H]^+$, 347 $[M+Na]^+$.

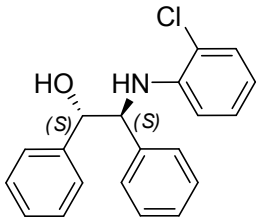


Peak	Ret. Time	Area	Peak Start	Peak End	Area%
1	24.503	15004590	23.691	25.963	48.4154
2	28.909	15986780	28.032	30.656	51.5846



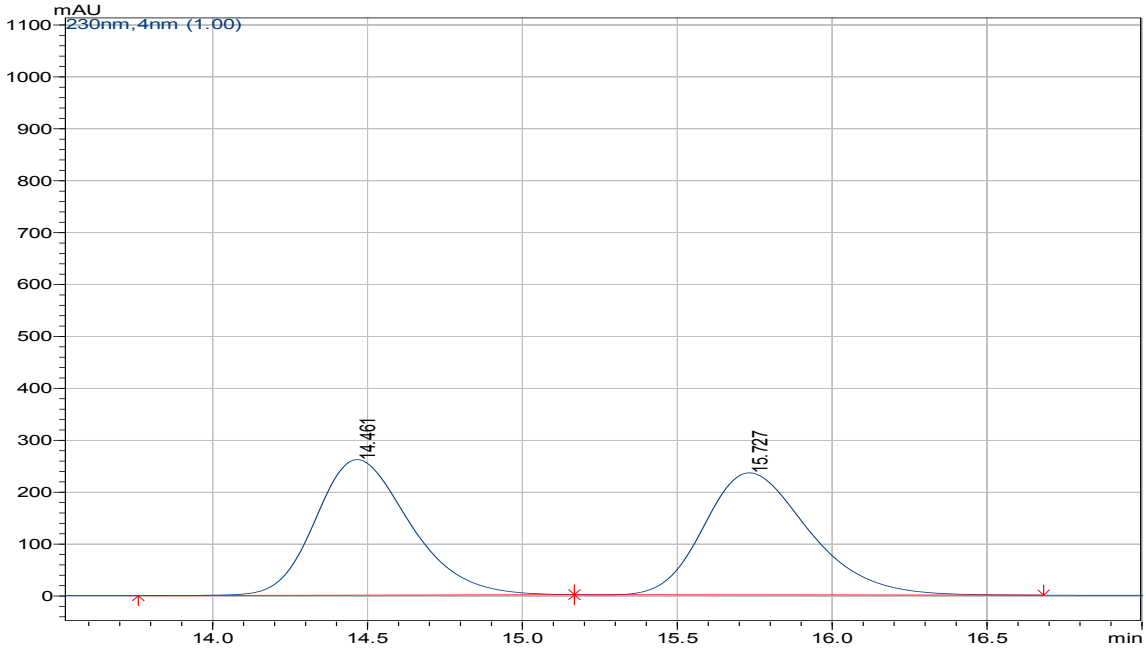
Peak	Ret. Time	Area	Peak Start	Peak End	Area%
1	24.071	673759	23.680	25.707	4.9194
2	28.112	10708500	27.093	29.803	95.0806

(1*S*,2*S*)-2-(2-Chlorophenylamino)-1,2-diphenylethanol [6'g] [1,3]**:**

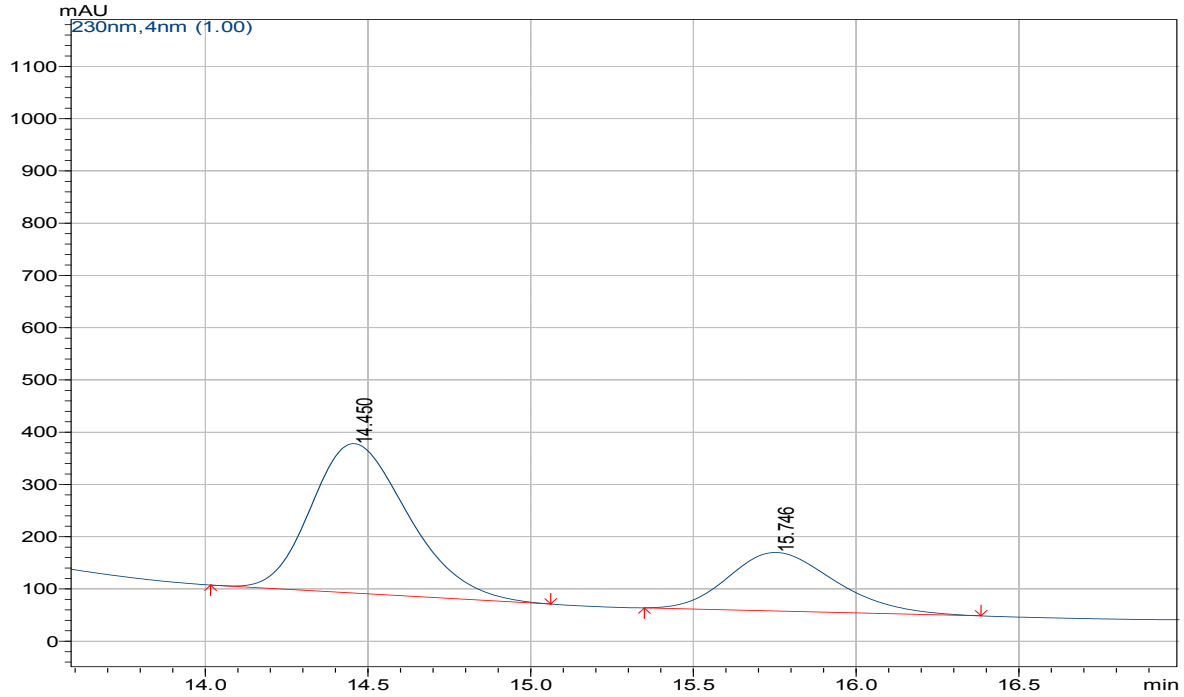


The title compound was isolated by column chromatography (hexane/AcOEt, 90:10) as a white solid; m.p. 95 °C; *ee* 38 % on HPLC(Chiralpak OD Column) mobile phase 80:20 hexane/*i*PrOH; flow rate 1 mL/min, retention time (1*S*,2*S*) 10.15 min,(1*R*,2*R*): 10.94 min. ^{1}H NMR (200 MHz, $CDCl_3$): δ= 7.16–7.25 (m, 11 H),), 6.81 (t, J = 8.0 Hz, 1 H), 6.47 (t, J = 8.0 Hz, 1 H), 5.41 (bs, 1 H), 4.88 (d, J = 5.0 Hz, 1 H), 4.51 (d, J = 5.0 Hz, 1 H), 2.44 (bs, 1H): ^{13}C NMR (200 MHz,

$CDCl_3$): δ = 144.98, 142.39, 141.62, 130.54, 130.21, 129.92, 129.59, 129.43, 129.11,128.43, 121.84, 119.51, 114.7, 79.93, 66.20: FTIR (KBr): v = 3396, 3063, 3031, 2960, 2929, 2860,1812, 1722, 1599, 1496, 1268, 1073, 820, 739, 700 cm^{-1}; TOF-MS (ESI+): *m/z* 324 [M + H]+.

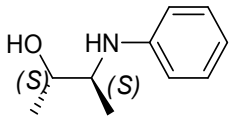


Peak#	Ret. Time	Area	Peak Start	Peak End	Area%
1	14.461	19206379	13.760	15.168	50.0494
2	15.727	19168499	15.168	16.683	49.9506



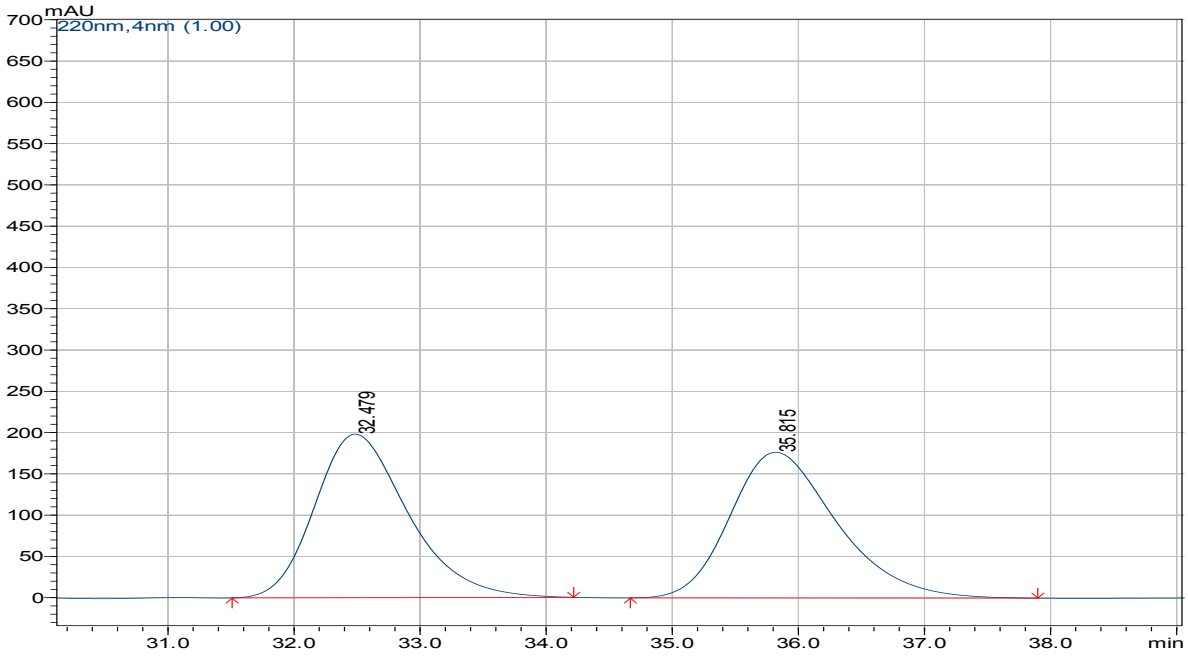
Peak#	Ret. Time	Area	Peak Start	Peak End	Area%
1	14.450	5940613	14.016	15.061	68.9479
2	15.746	2552294	15.349	16.384	31.0521

(2*S*,3*S*)-3-(Phenylamino)butan-2-ol [7'a] [1,3]**:**

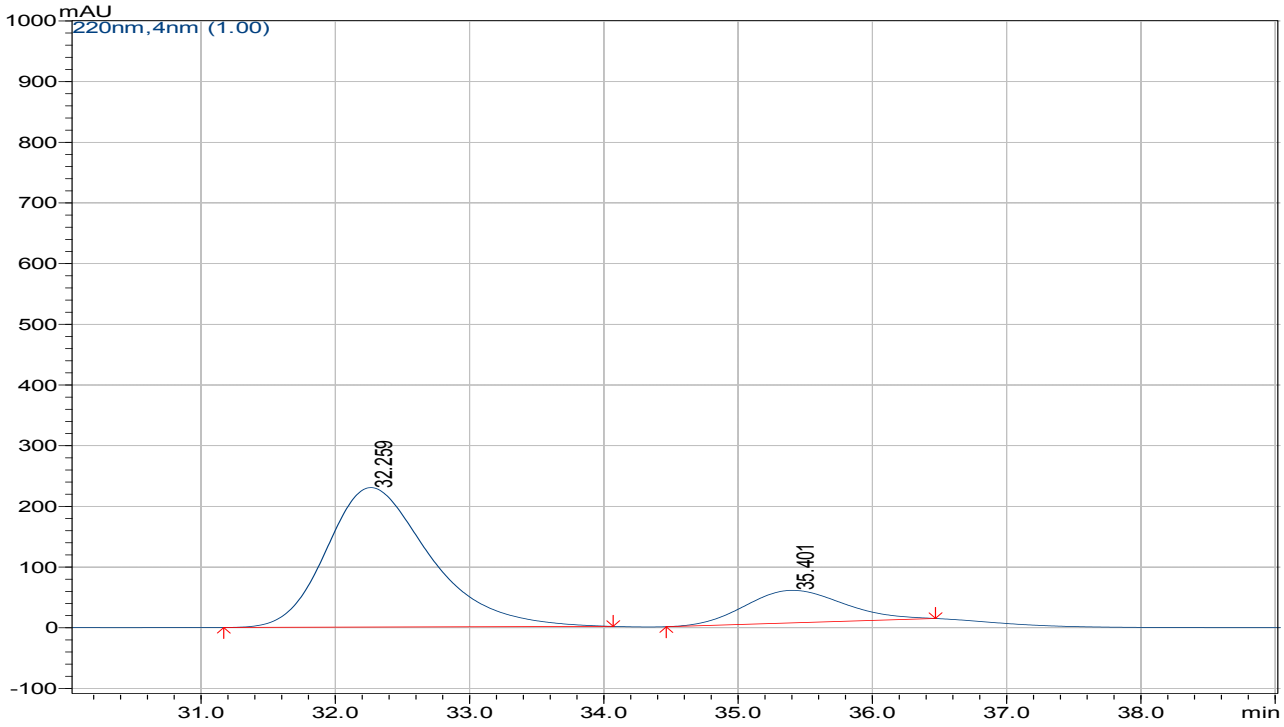


The title compound was isolated by column chromatography (hexane/AcOEt 90/10) as oil; The *ee* 62% on HPLC (Chiralpak OD column,) mobile phase, 97/2 hexane/*i*-PrOH; flow rate 0.8 mL/min., retention time (*2S,3S*): 32.25 min., (2*R,3R*): 35.40 min.; ^{1}H NMR (200 MHz, $CDCl_3$, δ ppm): δ = 7.25 (t, *J* = 7.5 Hz, 2 H), 6.81 (t, *J* = 7.5 Hz, 1 H), 6.74 (d, *J* = 3.2 Hz, 2 H), 3.68 (m, 1 H), 3.37 (m, 1 H), 2.84 (bs, 2 H), 1.32 (d, *J* = 2.6 Hz, 1 H) 1.22 (d, *J* = 2.6 Hz, 1 H); ^{13}C NMR

(200 MHz, $CDCl_3$, δ ppm): δ = 147.77, 129.38, 118.29, 114.35, 71.42, 56.15, 19.56, 17.33; FTIR (KBr): v = 3397, 3055, 2975, 2925, 1924, 1603, 1502, 1438, 1376, 1318, 1256, 1007, 903, 752, 699 cm^{-1}; TOF-MS (ESI+): m/z 166 $[M+H]^+$.

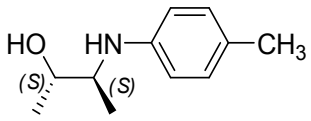


Peak#	Ret. Time	Area	Peak Start	Peak End	Area%
1	32.479	10202178	31.509	34.219	49.4997
2	35.815	10408411	34.667	37.899	50.5003



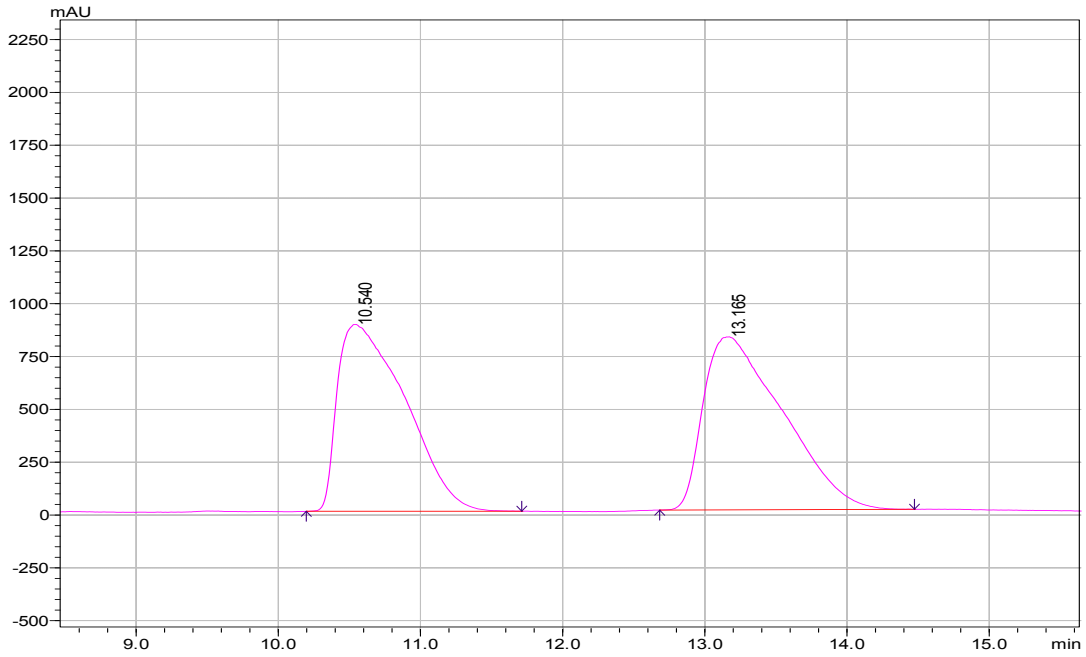
Peak#	Ret. Time	Area	Peak Start	Peak End	Area%
1	32.259	12324422	31.168	34.069	80.9234
2	35.401	2719420	34.464	36.469	19.0766

(2*S*,3*S*)-3-(4-Methylphenylamino)butan-2-ol [7'b] [1,3]**:**

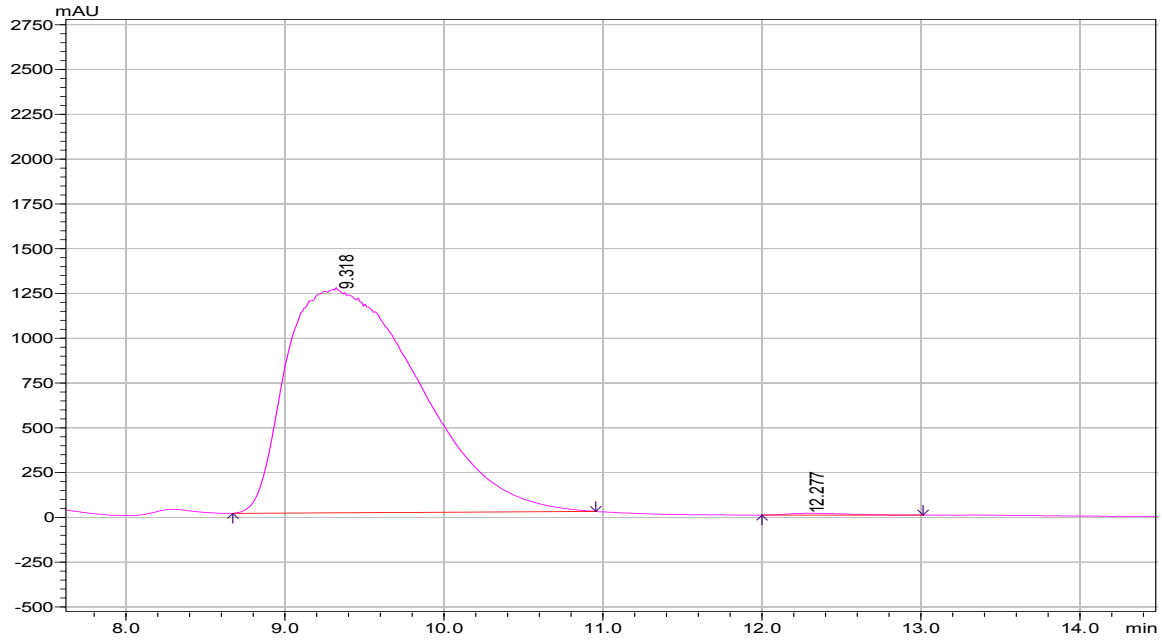


The title compound was isolated by column chromatography (hexane/AcOEt, 90:10) as an oil; The *ee* 99% on HPLC (Chiralpak OD column) mobile phase, 90:10 hexane/^{i}PrOH; flow rate 1 mL/min, retention time (2*S*,3*S*): 9.31 min., (2*R*,3*R*): 12.27 min.; ^{1}H NMR (200 MHz, $CDCl_3$, δ ppm): δ = 6.99 (d, *J* = 8.2 Hz, 2 H), 6.60 (d, *J* = 8.2 Hz, 2 H), 3.54-3.67 (m, 1 H), 3.21-3.34 (m, 1 H), 2.88 (bs, 2 H), 2.26 (s, 3 H), 1.25 (d, *J* = 6.0 Hz, 3 H), 1.12 (d, *J* = 6.0 Hz, 3 H); ^{13}C NMR

(200 MHz, $CDCl_3$, δ ppm): δ= 145.37, 129.85, 127.71, 114.73, 71.36, 56.78, 20.40, 19.46, 17.20; FTIR (KBr): ν = 3288, 2955, 1620, 1523, 1445, 1354, 1236, 1157, 1037, 823, 791 cm^{-1}; TOF-MS (ESI+): *m/z* 180 $[M+H]^+$.

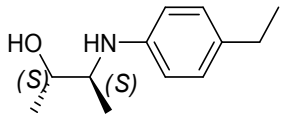


Peak	Ret. Time	Area	Peak Start	Peak End	Area%
1	10.540	29287430	10.197	11.712	47.9435
2	13.165	31799900	12.683	14.475	52.0565



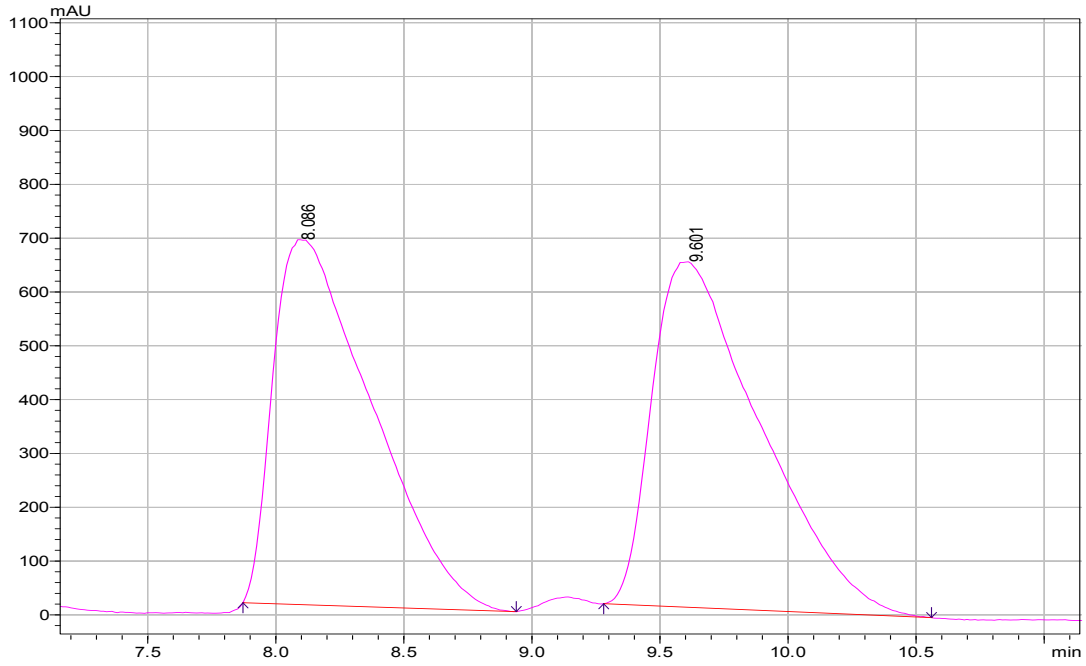
Peak	Ret. Time	Area	Peak Start	Peak End	Area%
1	9.318	72819545	8.672	10.955	99.6441
2	12.277	260120	12.000	13.013	0.3559

(2*S*,3*S*)-3-(4-ethylphenylamino)butan-2-ol [7'c] [1,3]**:**

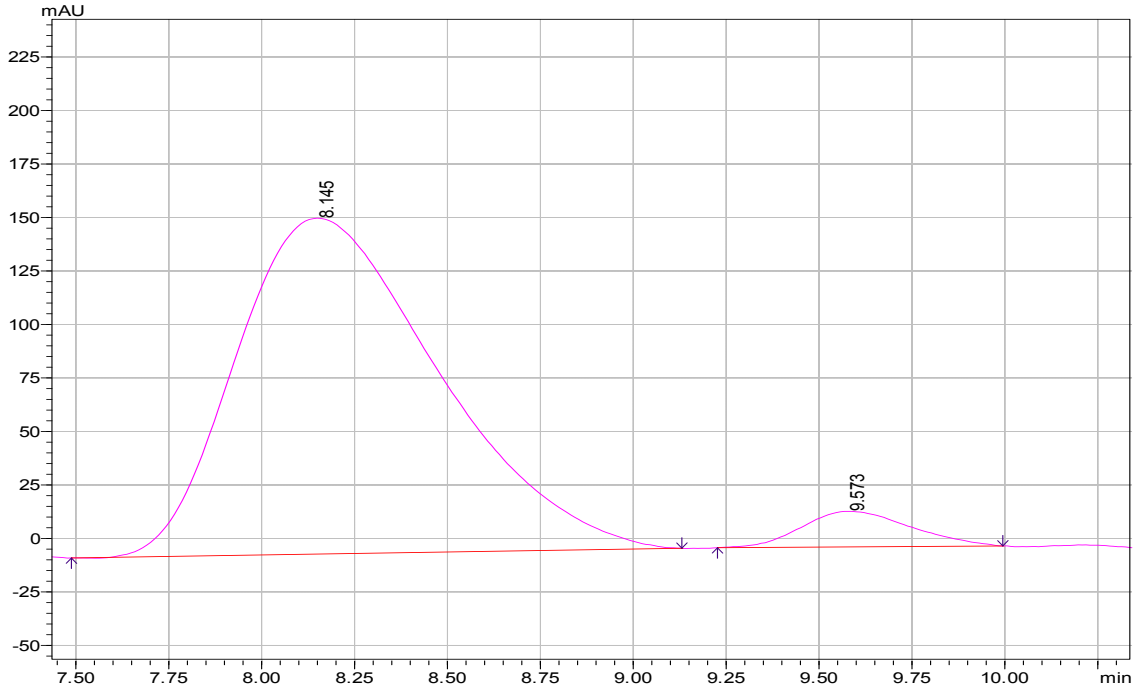


The title compound was isolated by column chromatography (hexane/AcOEt, 90:10) as an oil; The *ee* 90% on HPLC (Chiralpak OD column) mobile phase, 90:10 hexane/^{i}PrOH; flow rate 1 mL/min., retention time (2*S*,3*S*): 8.14 min., (2*R*,3*R*): 9.57 min.; ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): δ = 6.93–6.87 (d, *J* = 8.0 Hz, 2 H), 6.52–6.48 (d, *J* = 8.0 Hz, 2 H), 3.48-3.45 (m, 1 H), 3.19-3.12 (m, 3 H), 2.49-2.37 (q, 2 H), 1.43-1.09 (m, 6 H), 1.05-0.99 (d, *J* = 6.0 Hz, 3 H).; ^{13}C NMR (200 MHz, $CDCl_3$, δ ppm): δ = 145.68, 134.35, 128.65, 114.72, 74.48, 60.58, 33.13,

31.64, 27.99, 25.08, 24.3, 15.9; FTIR (KBr): ν = 3288, 2956, 1620, 1523, 1445, 1354, 1236, 1158, 1037, 822, 791 cm^{-1}; TOF-MS (ESI+): *m/z* 194 $[M+H]^+$.

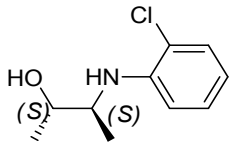


Peak	Ret. Time	Area	Peak Start	Peak End	Area%
1	8.086	18159147	7.872	8.939	48.9799
2	9.601	18915538	9.280	10.560	51.0201



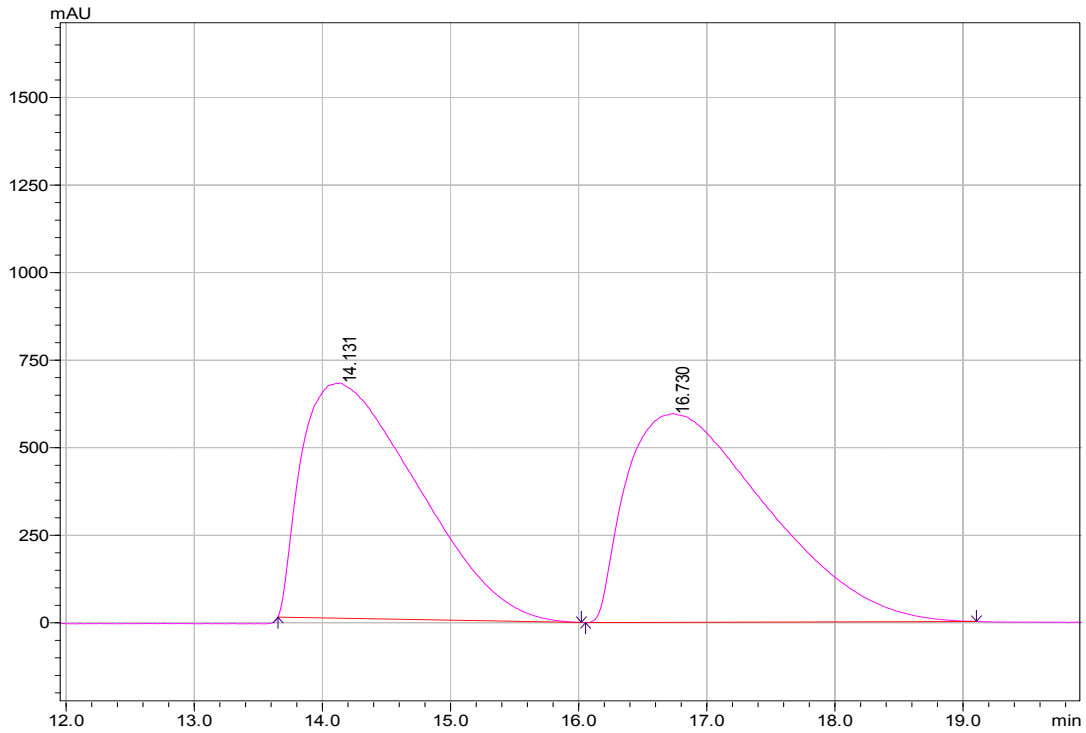
Peak	Ret. Time	Area	Peak Start	Peak End	Area%
1	8.145	5927431	7.488	9.131	94.6034
2	9.573	338129	9.227	9.995	5.3966

(2*S*,3*S*)-3-(2-chlorophenylamino)butan-2-ol [7'd] [1,3]**:**

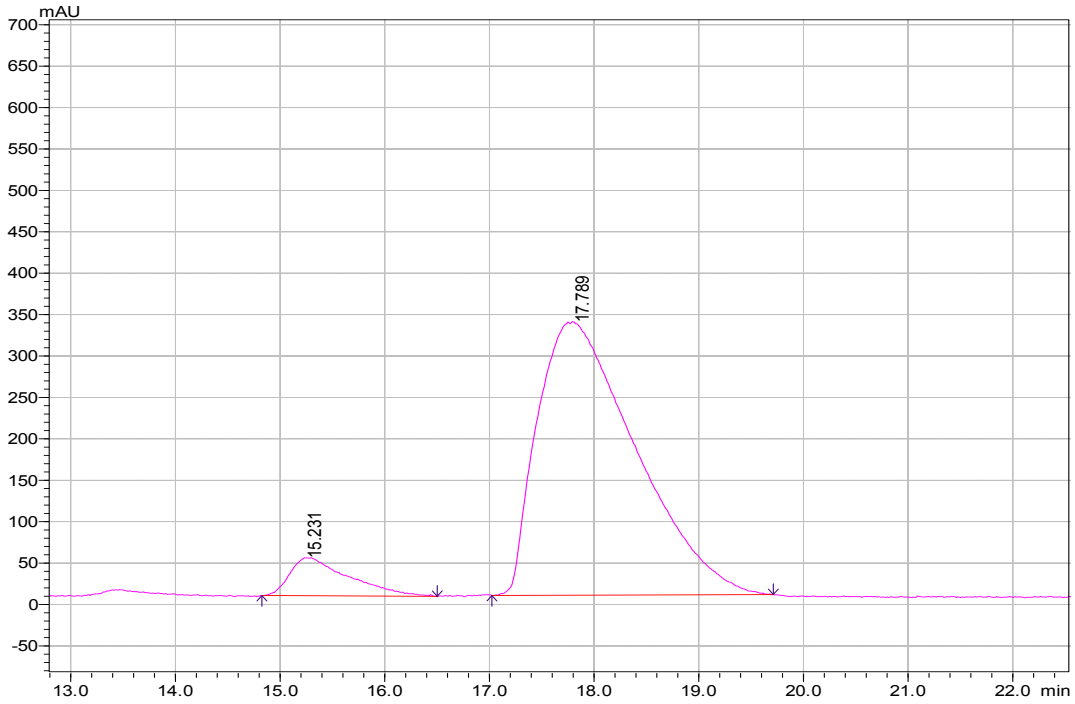


The title compound was isolated by column chromatography (hexane/AcOEt, 90:10) as an oil; The *ee* 86% on HPLC (Chiralpak OD column)mobile phase, 97:3 hexane/*i*PrOH; flow rate 0.8 mL/min., retention time (2*S*,3*S*): 15.21 min., (2*R*,3*R*): 17.78 min.; ^{1}HNMR (200 MHz, $CDCl_3$, δ ppm): δ= 7.25–7.29 (m, 1 H), 7.11–7.14 (m, 1 H), 6.76 (d, *J* = 8.0 Hz, 1 H), 6.66-6.70 (m, 1 H), 4.23 (bs, 1 H), 3.41 (m, 1 H), 2.48 (bs, 1 H), 1.22 (d, *J* = 6.2 Hz, 3 H), 1.18 (d, *J* = 6.2 Hz, 3 H);

^{13}C NMR (200 MHz, $CDCl_3$, δ ppm): δ =143.88, 129.53, 127.81, 120.33, 118.01, 112.80, 71.34, 55.66, 19.70, 17.55; FTIR (KBr): ν = 3287, 2955, 1620, 1522, 1445, 1354, 1236, 1159, 1037, 823, 791; TOF-MS (ESI+): *m*/*z* 180 $[M\text{-}OH]^+$.

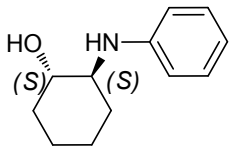


Peak	Ret. Time	Area	Peak Start	Peak End	Area%
1	14.131	42181163	13.653	16.021	48.0827
2	16.730	45545177	16.053	19.104	51.9173



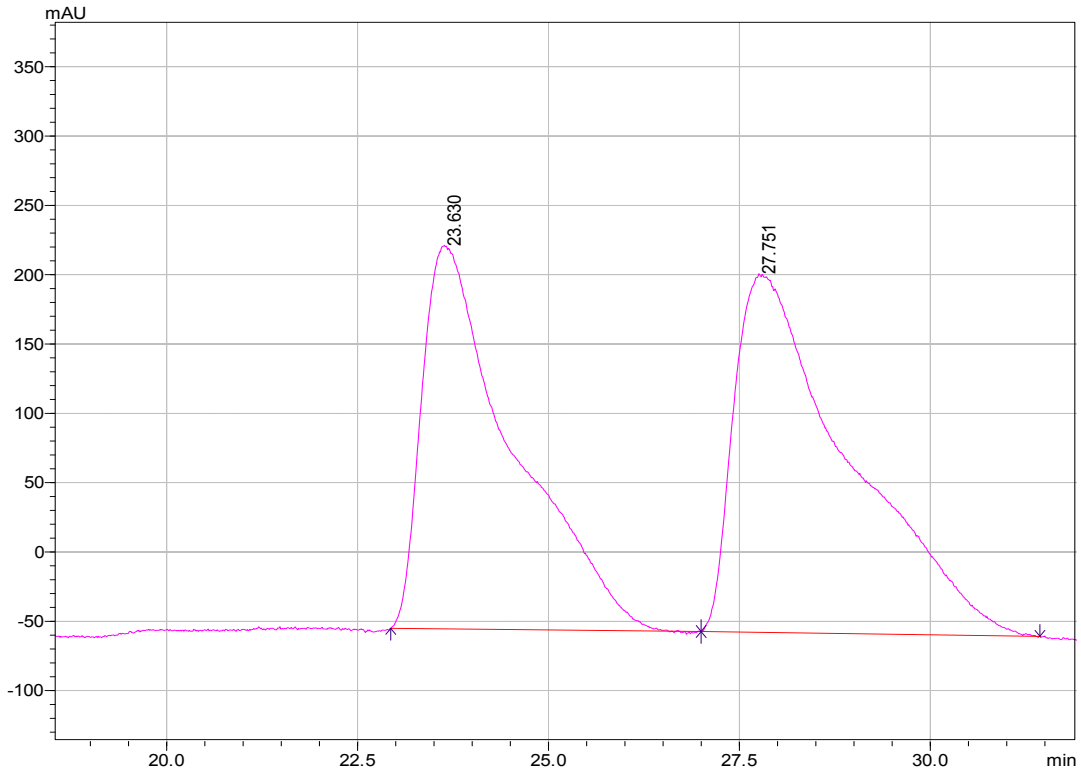
Peak	Ret. Time	Area	Peak Start	Peak End	Area%
1	15.231	1790065	14.827	16.501	7.6794
2	17.789	21519903	17.024	19.712	92.3206

(1*S*,2*S*)-2-(phenylamino)-cyclohexene-1-ol [8'a] [1,3]**:**

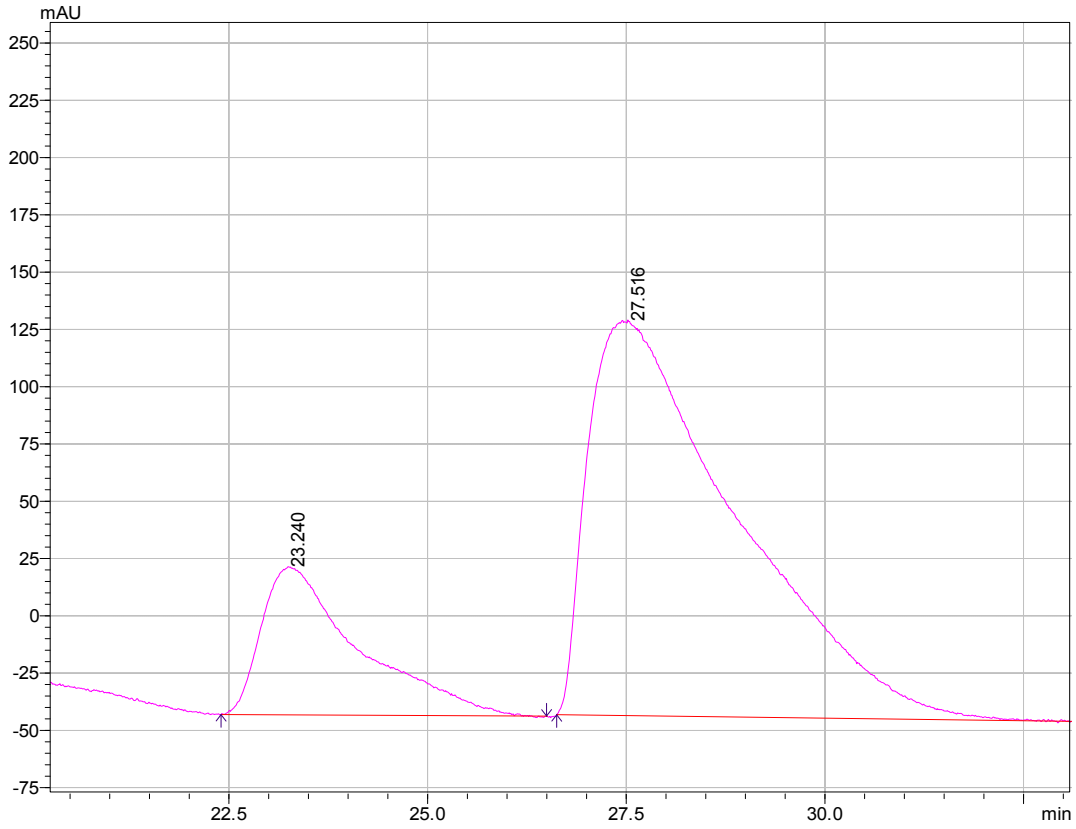


The title compound was isolated by column chromatography (hexane/AcOEt 90/10) as a white solid; Melting point: 58–60°C; The *ee* 63% on HPLC (Chiralpak OD column) mobile phase, 96/4 hexane/*i*-PrOH; flow rate 0.7 mL/min., retention time. (*1S,2S*): 23.24 min., (*1R,2R*): 27.51 min.; ^{1}H NMR (200 MHz, $CDCl_3$, δ ppm): δ= 7.09 (t, *J*= 3 Hz, 2H), 6.64–6.69 (m, 3 H), 3.26 (m , 1 H), 3.08 (m, 1 H), 2.66 (bs, 1 H), 2.03–2.06 (m, 2 H), 1.70–1.71 (m, 1 H),1.64–1.66 (m, 1 H),

1.51(bs, 1H), 1.29–1.37 (m, 1 H), 1.18–1.26 (m, 1 H); ^{13}C NMR (200 MHz, $CDCl_3$, δ ppm): δ= 147.82, 129.35, 118.41, 114.40, 74.58, 60.18, 33.12, 31.53, 25.04, 24.27; FTIR (KBr): v = 3356, 2933, 2858, 1602, 1501, 1448, 1320, 1067, 748 cm^{-1}; TOF-MS (ESI+): m/z 192 $[M+H]^+$,

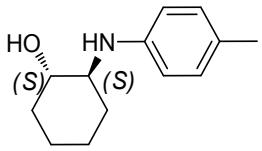


Peak	Ret. Time	Area	Peak Start	Peak End	Area%
1	23.630	22847919	22.933	26.997	45.8611
2	27.751	26971872	26.997	31.435	54.1389



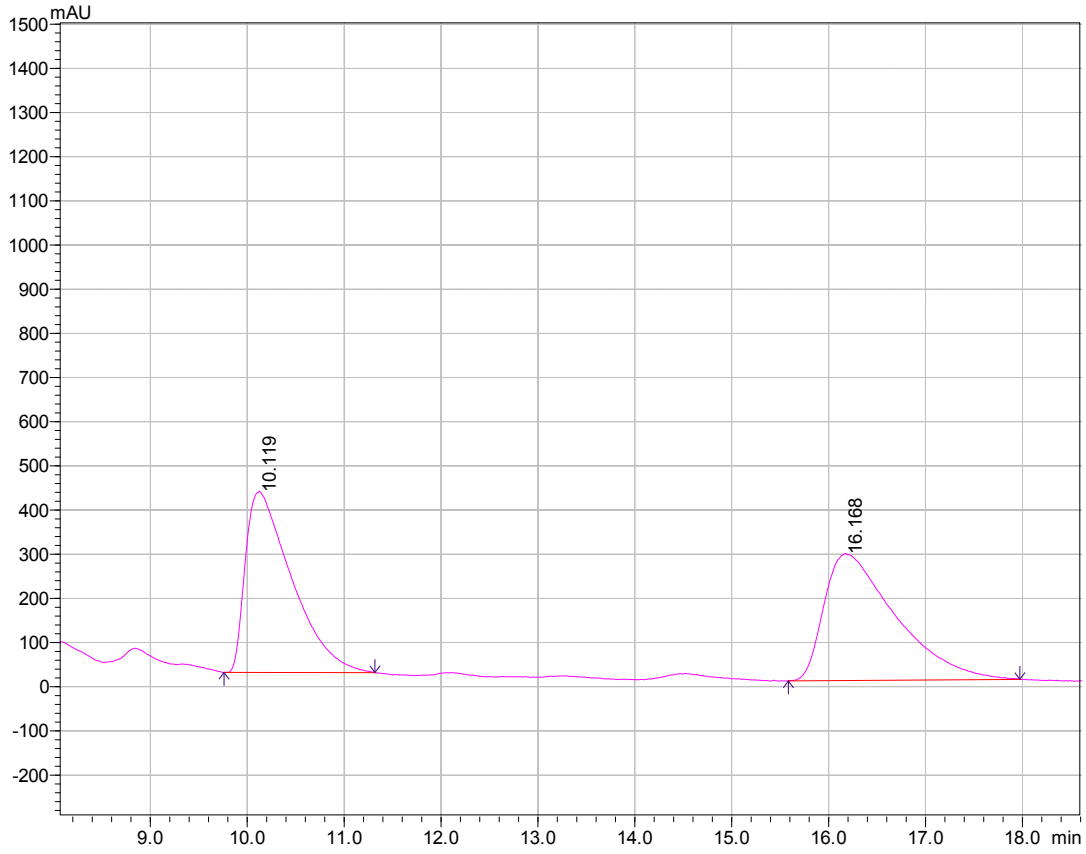
Peak	Ret. Time	Area	Peak Start	Peak End	Area%
1	23.240	5488248	22.400	26.496	18.7122
2	27.516	22353666	26.624	34.091	81.2878

(1*S*,2*S*)-2-(4-Methylphenylamino)-cyclohexane-1-ol [8'b] [1,3]:

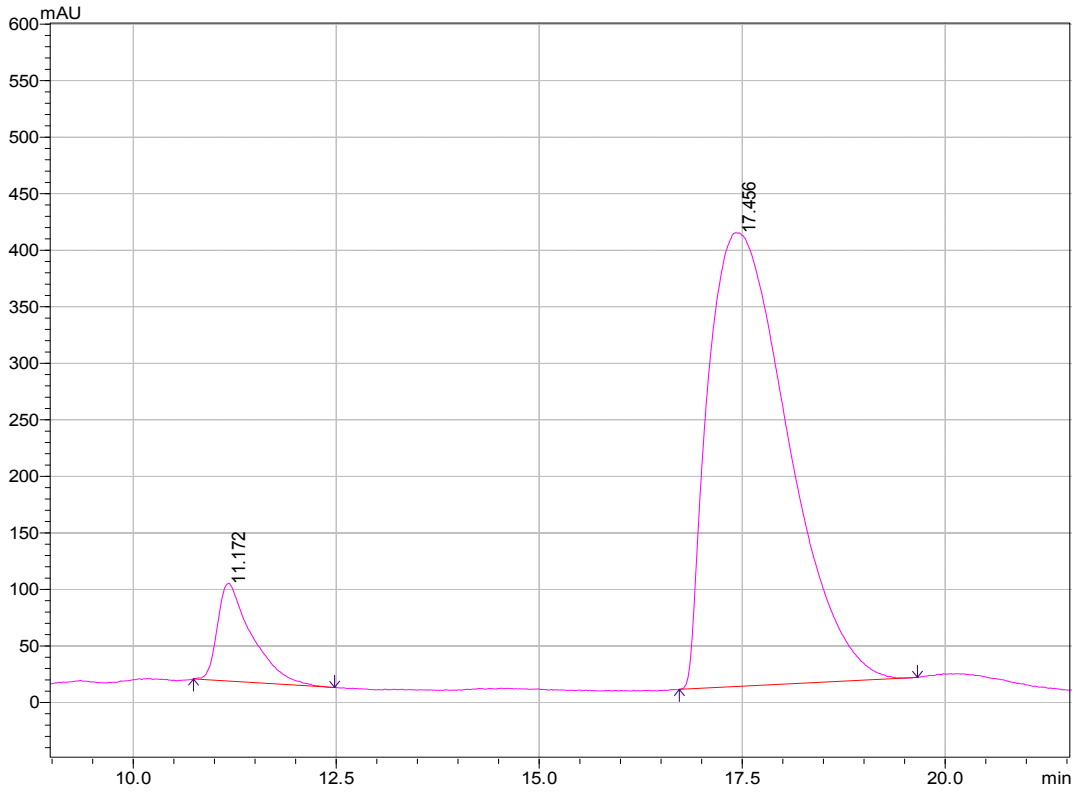


The title compound was isolated by column chromatography (hexane/AcOEt 90/10) as a brownish liquid; The ee 85 % on HPLC (Chiralpak OD column) mobile phase, 90/10 hexane/ *i*-PrOH: flow rate 0.8 mL/min., retention time (1*S*,2*S*): 11.17 min. (1*R*,2*R*):17.4 min.; ^{1}H NMR

(200 MHz, $CDCl_3$, δ ppm): δ = 7.0 (d, *J* = 3.2 Hz, 2 H), 6.65 (d, *J* = 3.2 Hz, 2 H), 3.33-3.37 (m, 1 H), 3.08-3.12 (m, 1 H), 2.48 (bs, 2 H), 2.26 (s, 3 H), 2.12–2.13 (m, 2 H), 1.78–1.79 (m, 1 H), 1.72–1.73 (m, 1 H), 1.27-1.42 (m, 3 H), 1.01-1.06 (m, 1 H).; ^{13}C NMR (200 MHz, $CDCl_3$, δ ppm): δ = 145.41, 129.92, 127.97, 114.94, 74.56, 60.83, 33.20, 31.63, 25.17, 24.38, 20.48; FTIR (KBr): ν = 3665, 3390, 3105, 3019, 2928, 2860, 2734, 1866, 1617, 1519, 1451, 1451, 1405, 1300, 1252, 1183, 1129, 1068, 938 cm^{-1}; TOF-MS (ESI+): m/z 206 $[M+H]^+$.

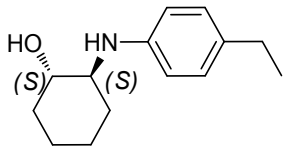


Peak	Ret. Time	Area	Peak Start	Peak End	Area%
1	10.119	13613603	9.760	11.317	48.0981
2	16.168	14690215	15.584	17.973	51.9019



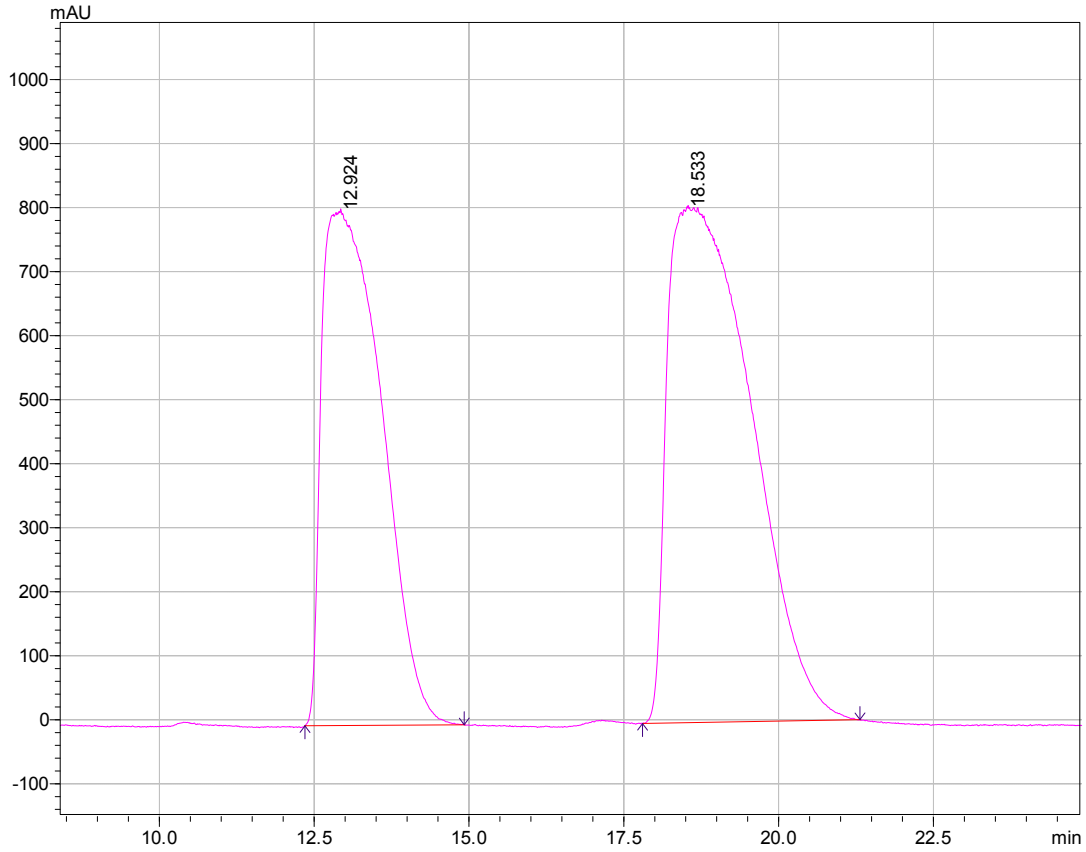
Peak	Ret. Time	Area	Peak Start	Peak End	Area%
1	11.172	2529479	10.741	12.480	7.4515
2	17.456	27400027	16.725	19.659	92.5485

(1S,2S)-2-(4-ethylphenylamino)-cyclohexan-1-ol [8'c] [1,3]:

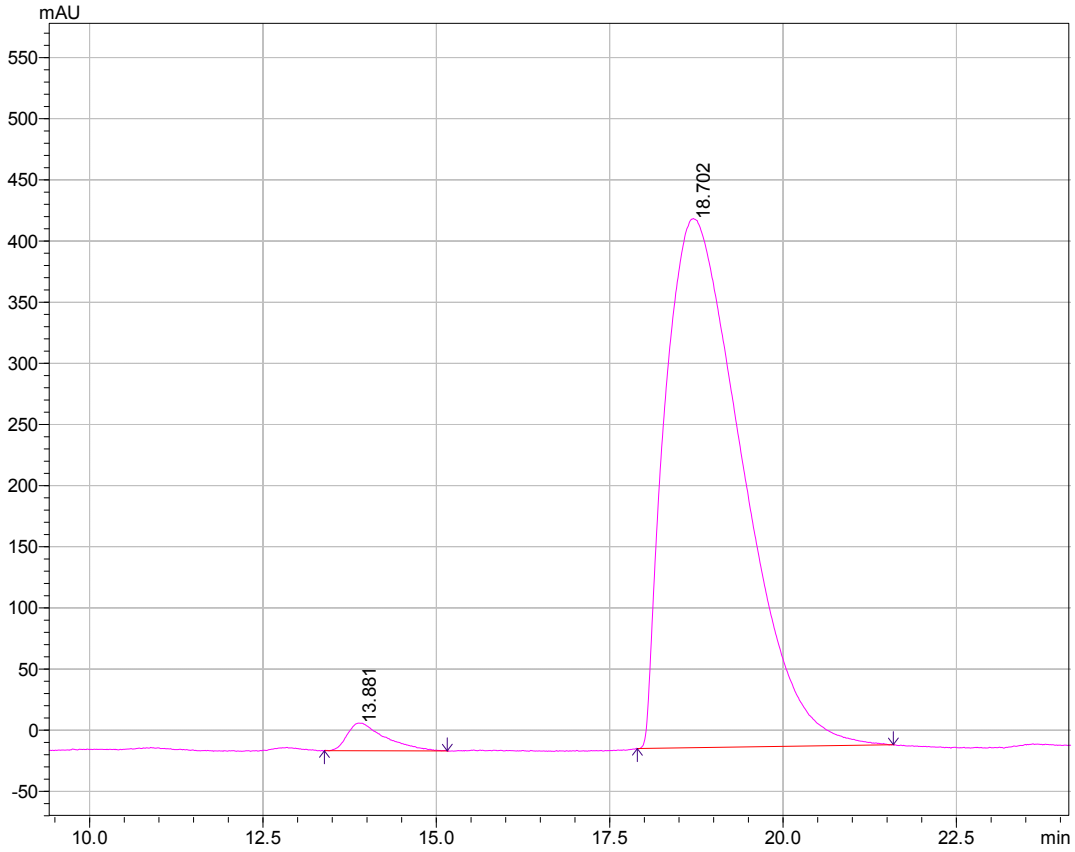


The title compound was isolated by column chromatography (hexane/AcoEt 90/10) as a brownish liquid; The ee 95% on HPLC (Chiralpak OD column) mobile phase, 94/6 hexane/i-PrOH: flow rate 0.8 mL/min., retention time (1*S*,2*S*): 13.88 min., (1*R*,2*R*): 18.70 min.; ^{1}H NMR (200 MHz, $CDCl_3$, δ ppm): δ = 7.05 (d, *J* = 8.4 Hz, 2 H), 6.68 (d, *J* = 8.1 Hz, 2 H), 3.37-3.33

(m, 1 H), 3.15-3.05 (m, 3 H), 2.62 (q, J = 7.5 Hz, 2 H), 2.15-2.09 (m, 2 H), 1.78-1.72 (m, 2 H), 1.43-1.28 (m, 3 H), 1.24 (t, J = 7.5 Hz, 3 H), 1.06-0.1.0 (m, 1 H); ^{13}C NMR (CDCl3, 200 MHz, δ ppm): δ = 145.67, 134.34, 128.65, 114.70, 74.47, 60.58, 33.14, 31.62, 29.68, 27.94, 25.07, 24.32, 15.97; FT-IR (KBr) ν = 3393, 2958, 2927, 2855, 1616, 1539, 1517, 1488, 1455, 1418, 1321, 1257, 1068 cm^{-1}; TOF-MS (ESI+): m/z 220 $[M+H]^+$

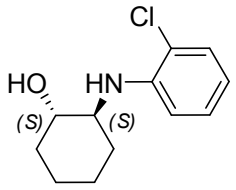


Peak	Ret. Time	Area	Peak Start	Peak End	Area%
1	12.924	64150650	12.352	14.923	45.5743
2	18.533	76099519	17.803	21.312	54.4257



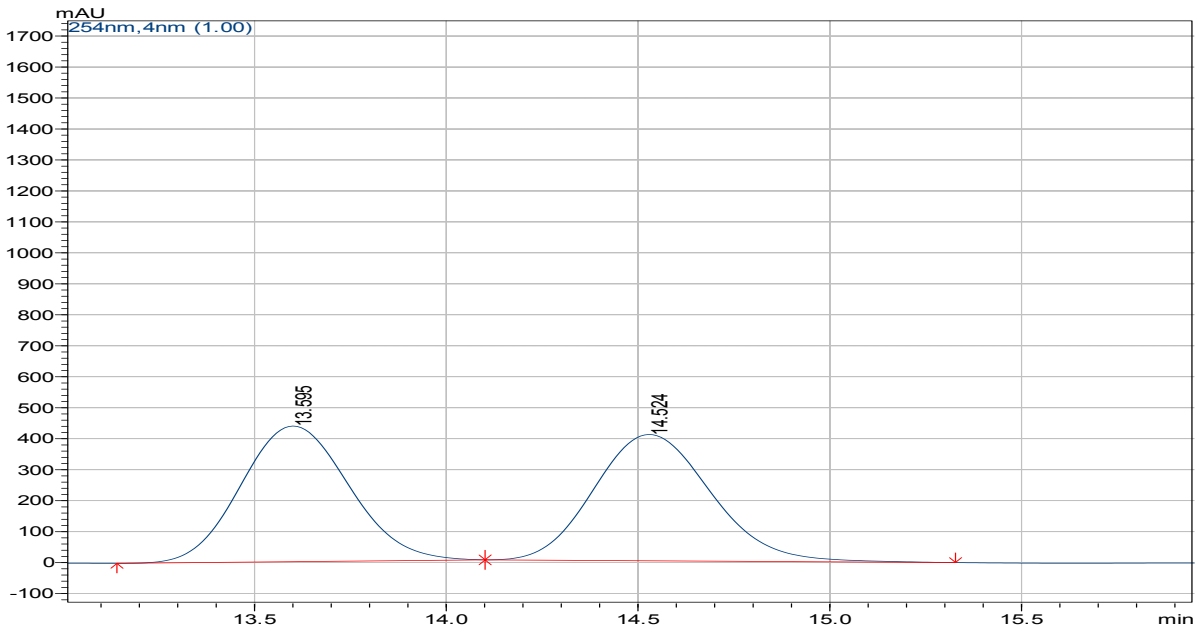
Peak	Ret. Time	Area	Peak Start	Peak End	Area%
1	13.881	860286	13.387	15.157	2.5129
2	18.702	33374796	17.899	21.589	97.4871

(*1S,2S*)-2-(2-chlorophenylamino)-cyclohexane-1-ol [8'd] [1,3]:

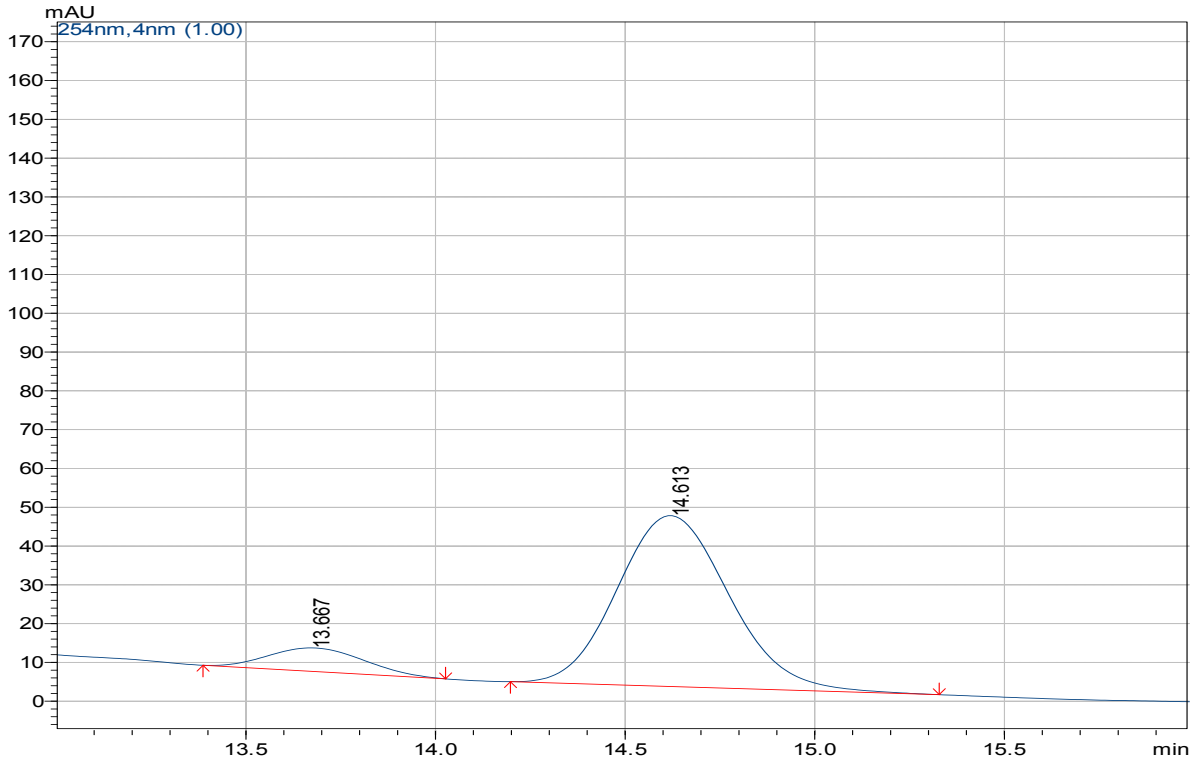


The title compound was isolated by column chromatography (hexane/AcOEt 90/10) as a brownish liquid. The ee 80 % on HPLC (Chiralpak OD column) mobile phase, 90/10 hexane/i-PrOH: flow rate 1 ml/min, retention time (1*S*,2*S*):13.66 min, (1*R*,2*R*):14.61 min.; ^{1}H NMR(200

MHz, $CDCl_3$,): δ = 7.16 (d, J = 8.0 Hz, 1 H), 7.05 (t, J = 8.0 Hz, 1 H), 6.74 (d, J = 8.0 Hz, 1 H), 6.53 (t, J = 8.0 Hz, 1 H), 3.99 (bs, 1H), 3.31-3.42 (m, 1 H), 3.05-3.17 (m, 1 H), 2.73 (bs, 1H), 1.97-2.03 (m, 2H), 1.63–1.71 (m, 2 H), 0.82–1.43 (m, 6 H): ^{13}C NMR (200 MHz, $CDCl_3$): δ= 153.83, 143.84, 129.32, 127.84, 120.20, 117.98, 112.83, 111.60, 74.46, 59.75, 33.21, 31.67, 24.92, 24.21, 20.38: FTIR(KBr): v = 3370, 3005, 2956, 2845, 2774, 1866, 1619, 1524, 1467, 1451, 1402, 1252, 1182, 1126, 1054, 930 cm^{-1}; TOF-MS (ESI+): m/z 226 $[M+H]^+$.



Peak#	Ret. Time	Area	Peak Start	Peak End	Area%
1	13.595	8587514	13.141	14.101	49.8409
2	14.524	8642334	14.101	15.328	50.1591

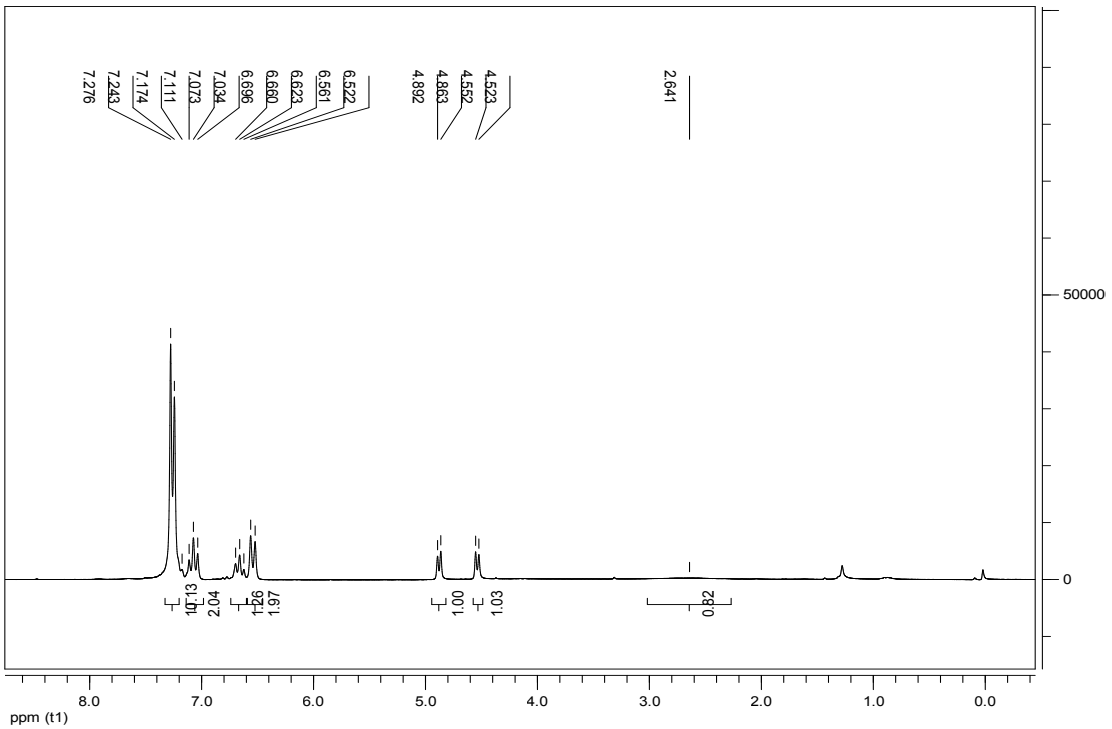


Peak#	Ret. Time	Area	Peak Start	Peak End	Area%
1	13.667	104866	13.387	14.027	10.0996
2	14.613	903496	14.197	15.328	89.9004

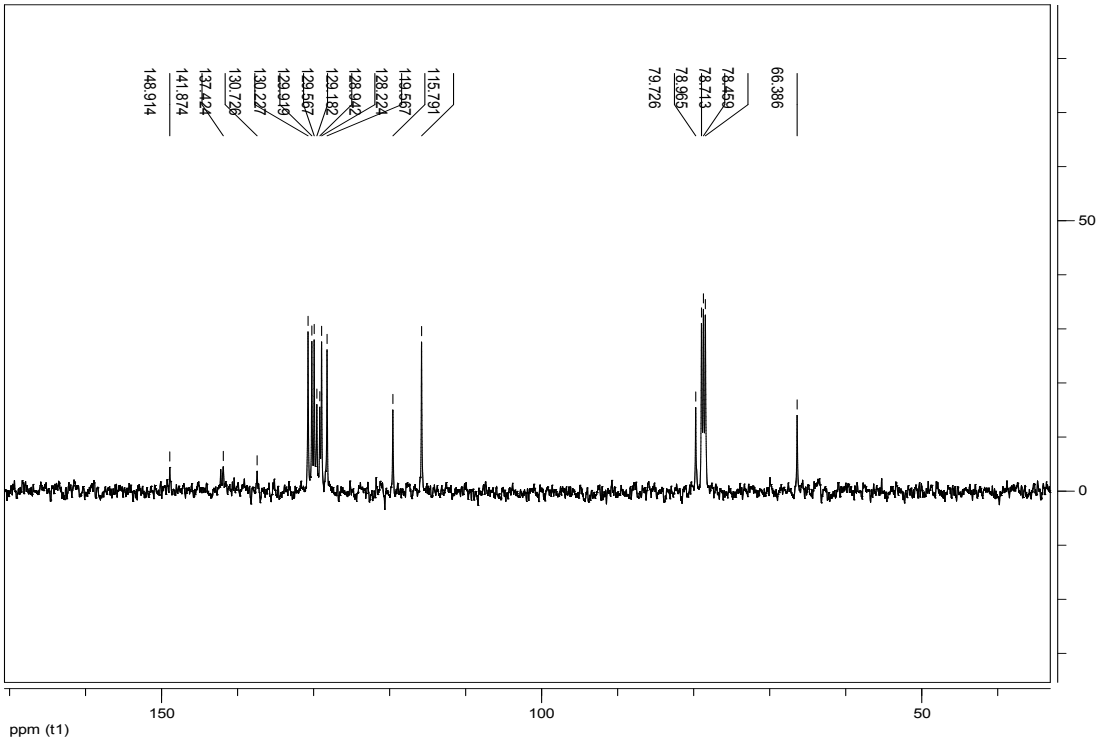
5. ^{1}H and ^{13}C NMR spectra of Products :

(1S,2S)-1,2-Diphenyl-2-(phenylamino)-ethanol [6'a]

^{1}H NMR

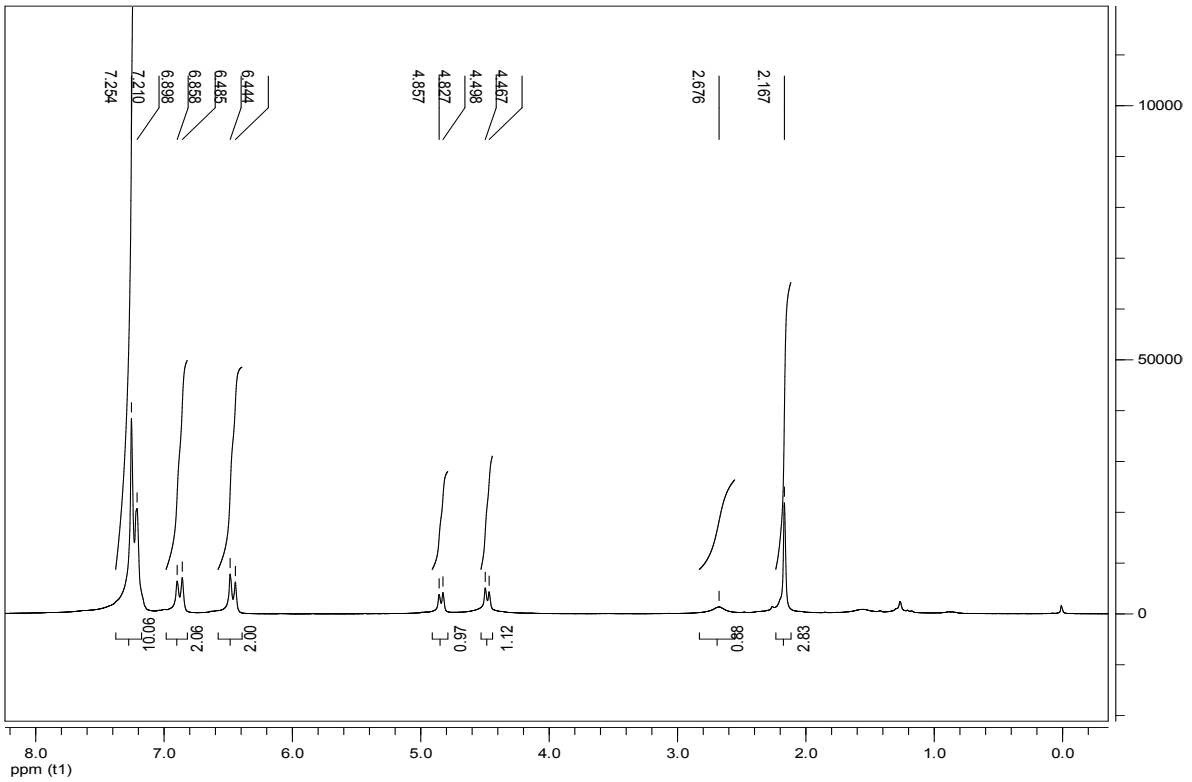


^{13}C NMR

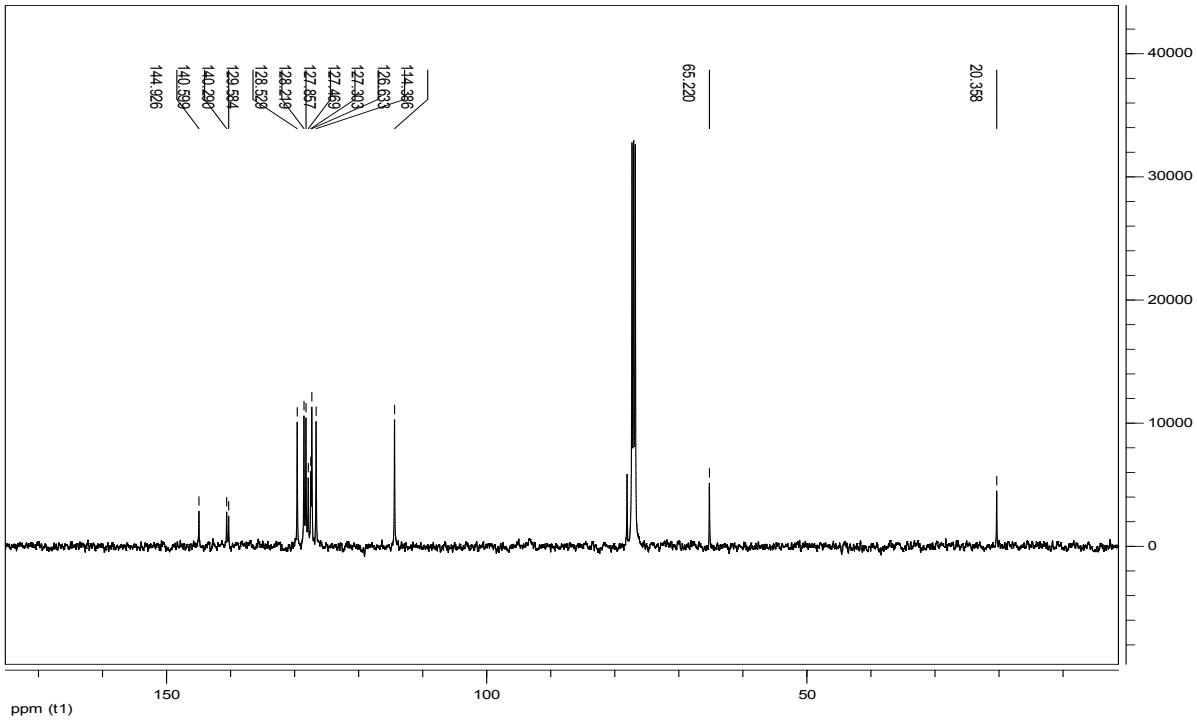


(1*S*,2*S*)-1,2-Diphenyl-2-(4-methyl-phenylamino)-ethanol [6'b]

^{1}H NMR

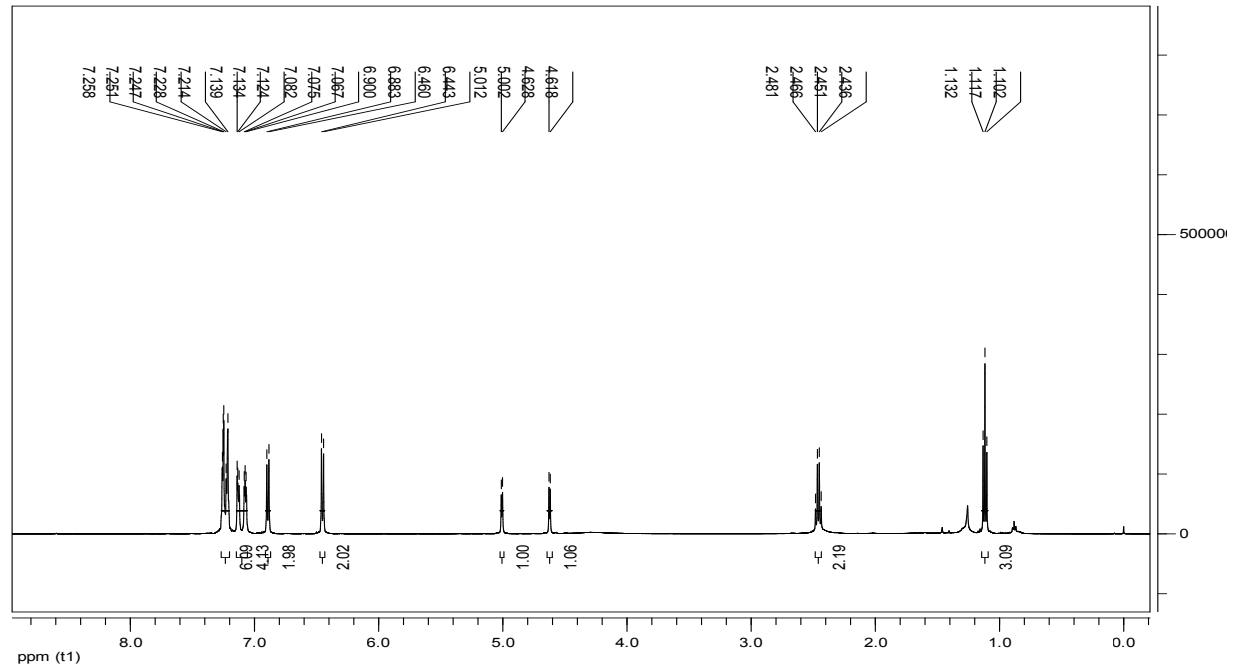


^{13}C NMR

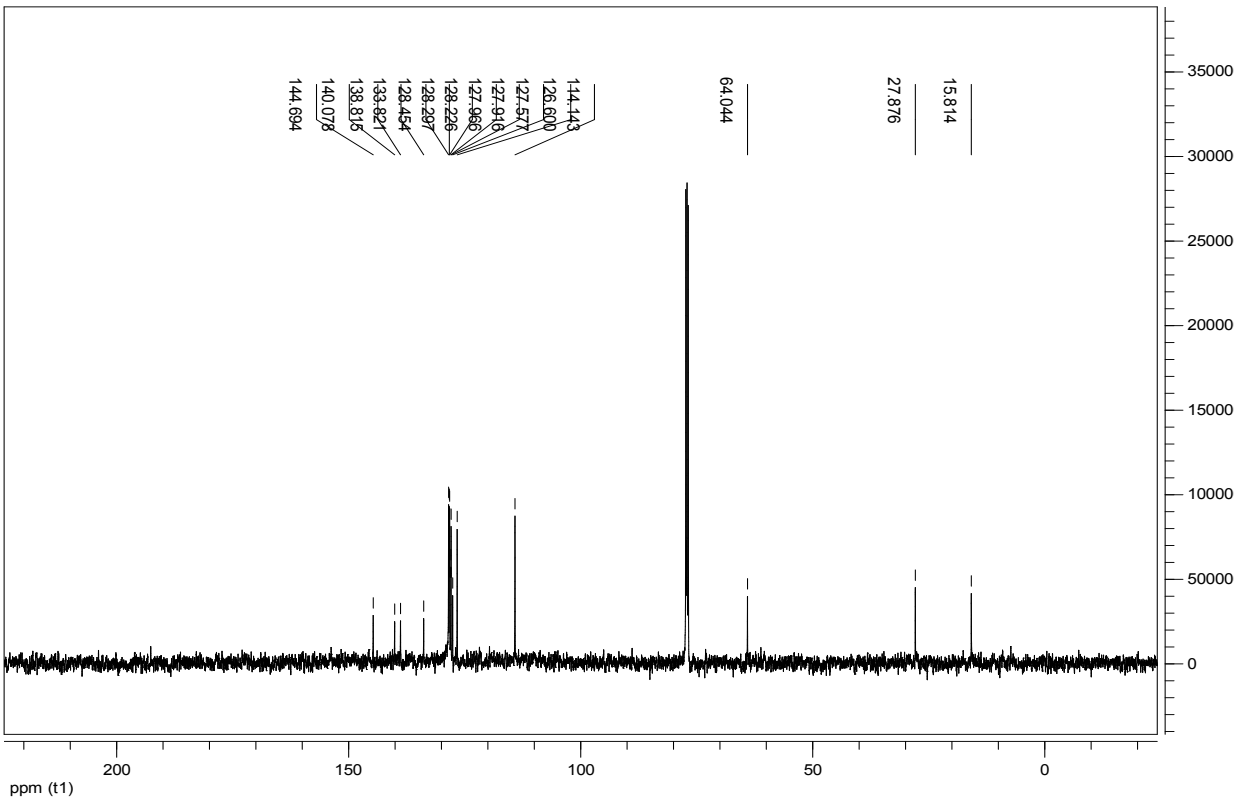


(1*S*,2*S*)-1,2-diphenyl-2-(4-ethyl-phenylamino)-ethanol [6'c]

^{1}H NMR

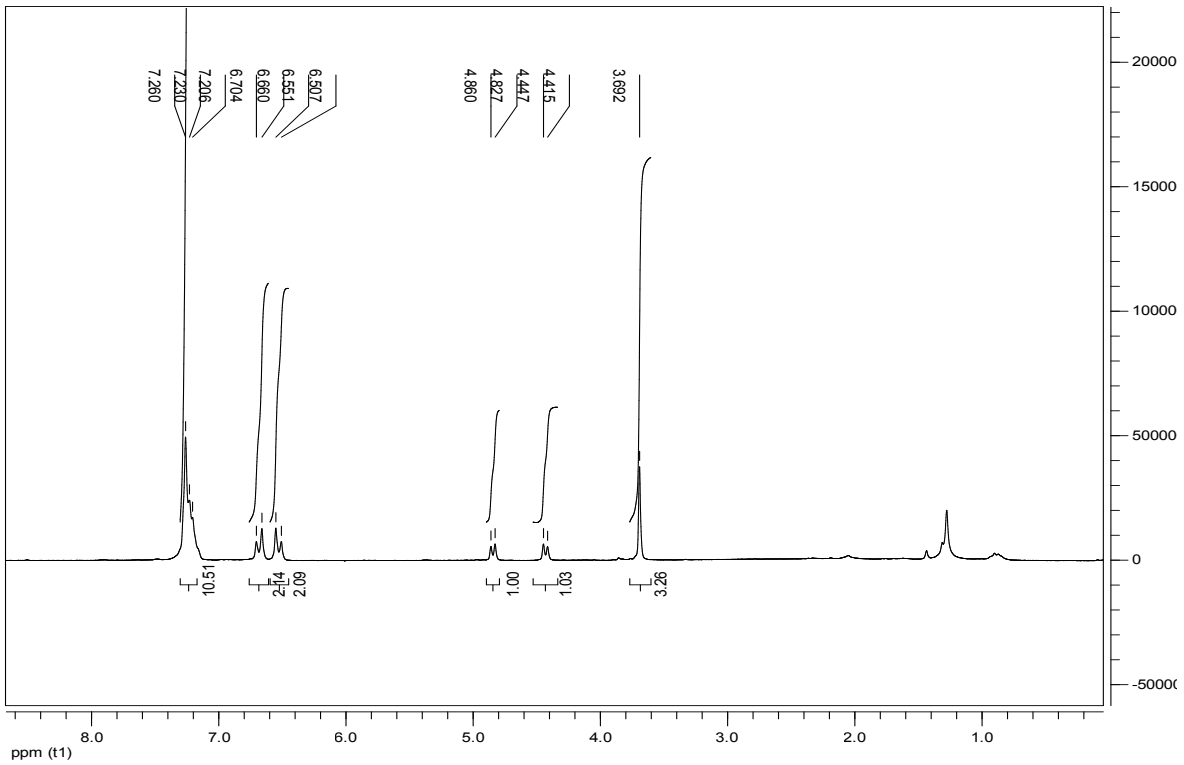


^{13}C NMR

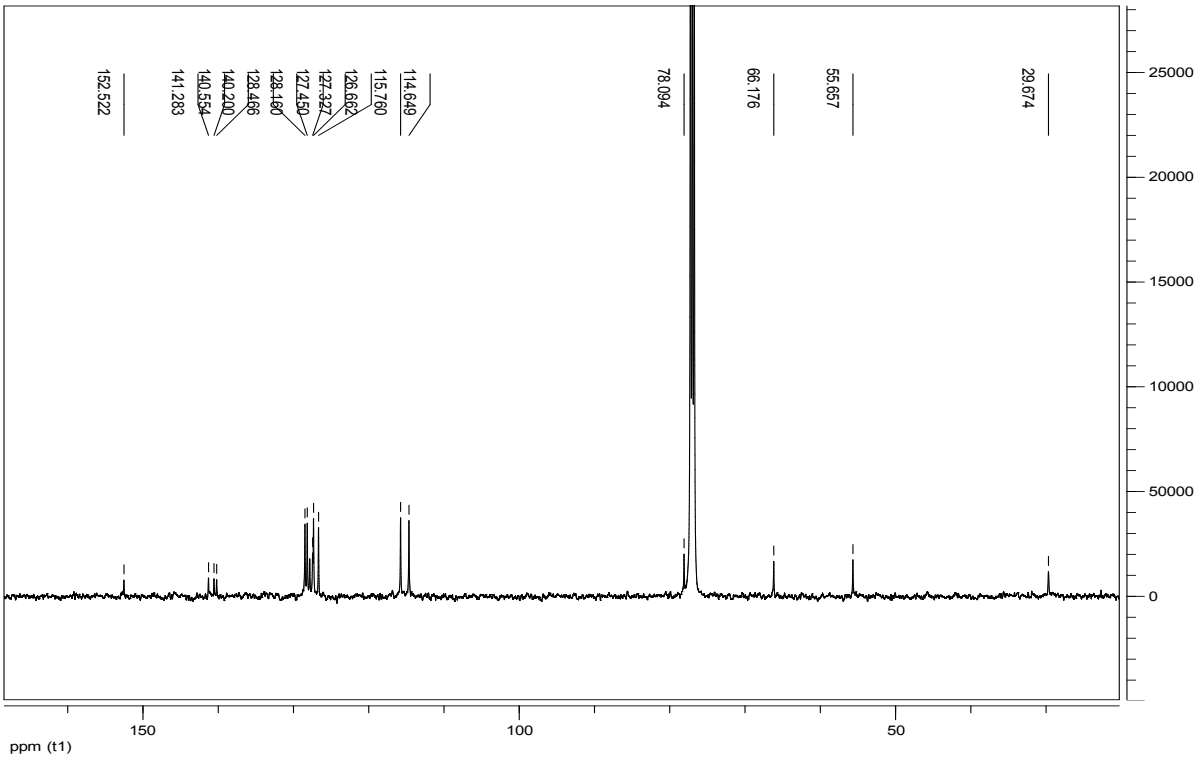


(1*S*,2*S*)-1,2-Diphenyl-2-(4-methoxy-phenylamino)-ethanol [6'd]

^{1}H NMR

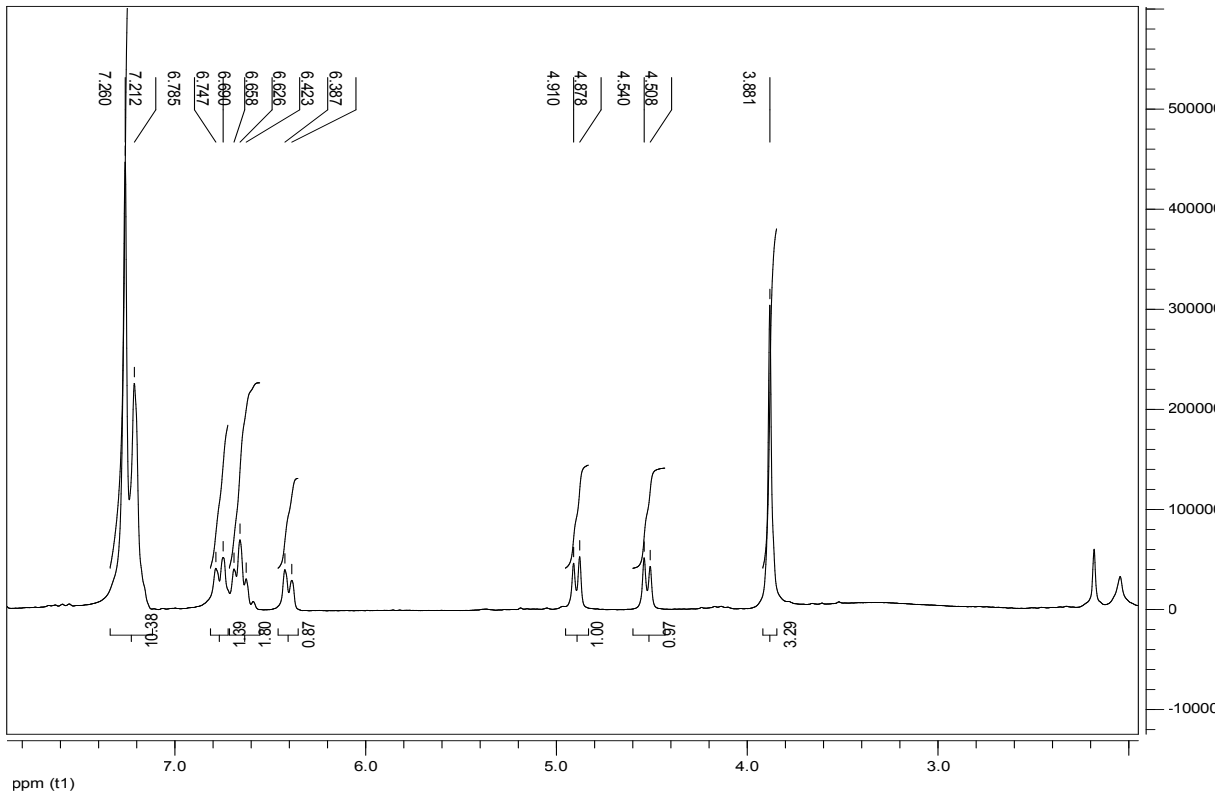


^{13}C NMR

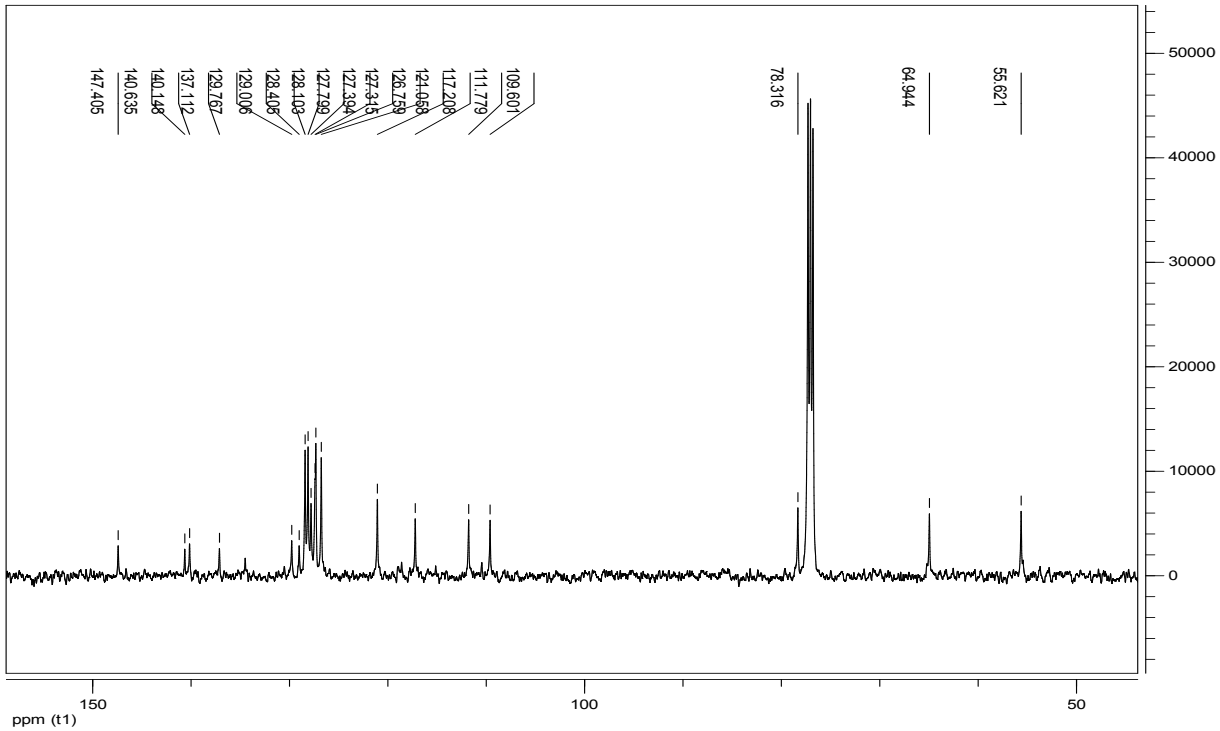


(1*S*,2*S*)-1,2-Diphenyl-2-(2-methoxy-phenylamino)-ethanol [6'e]

^{1}H NMR

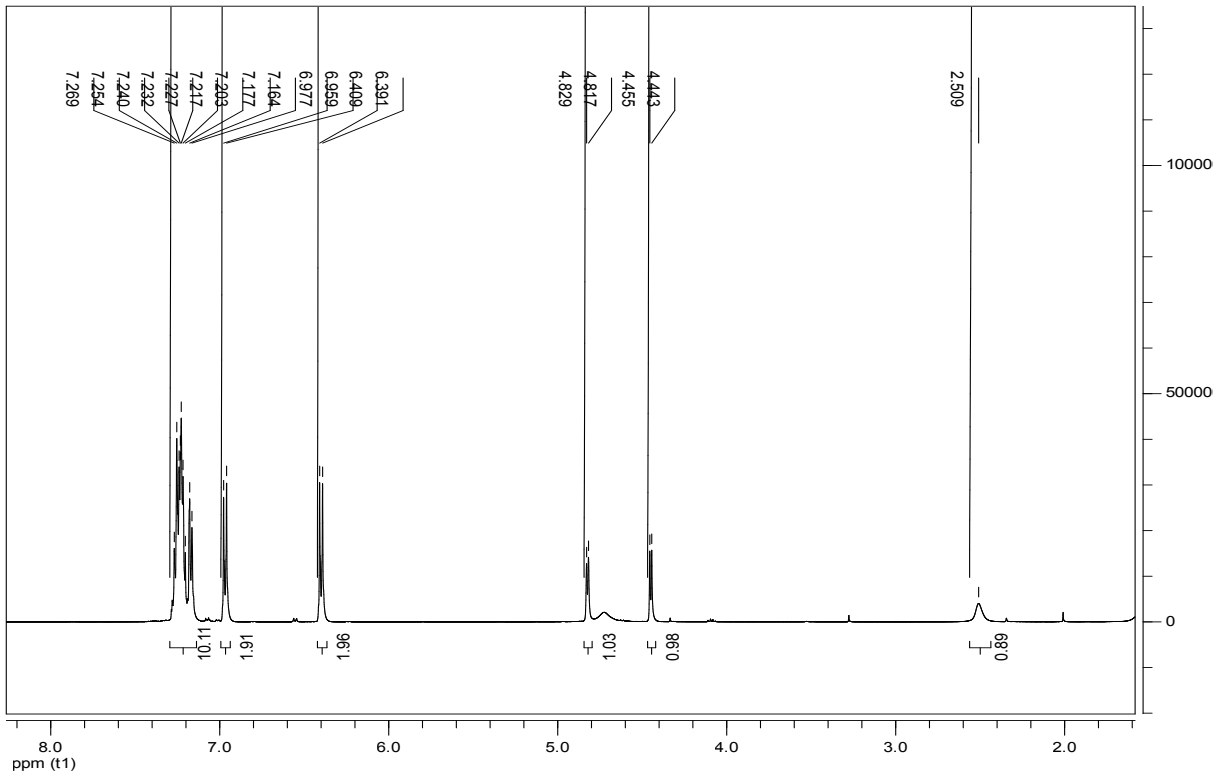


^{13}C NMR

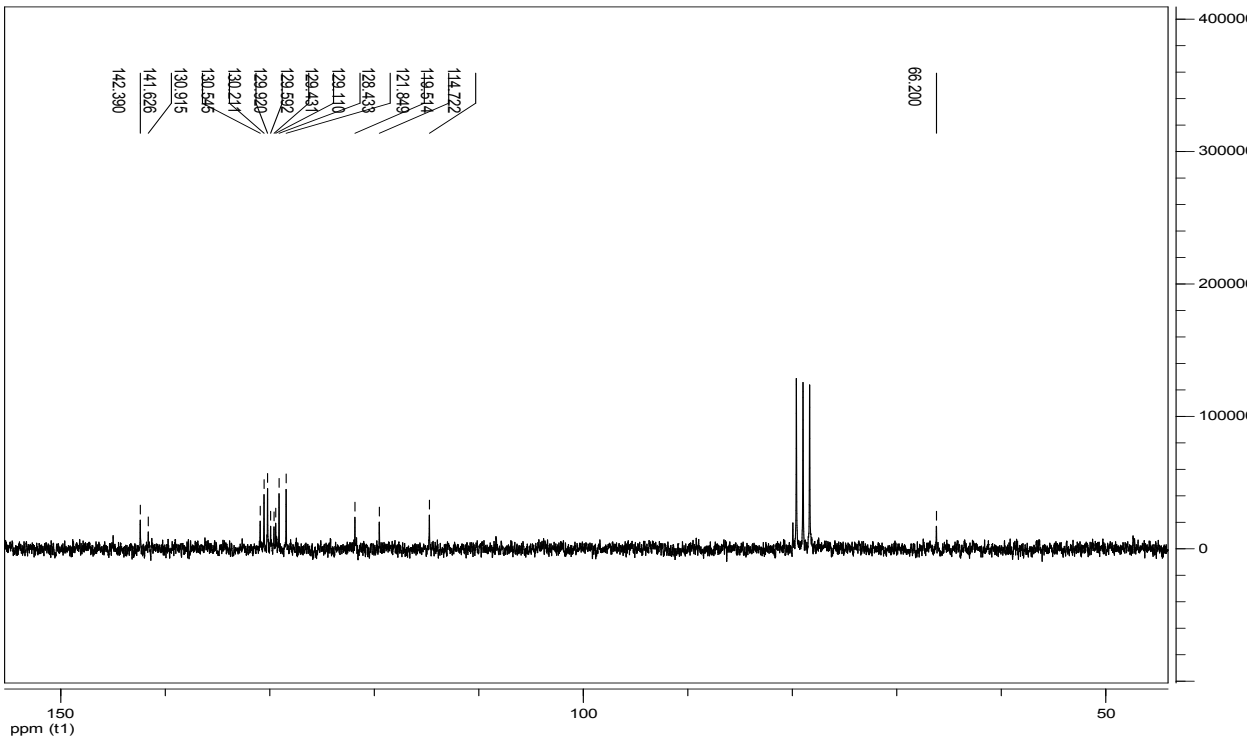


(1*S*,2*S*)-2-(4-Chlorophenylamino)-1,2-diphenylethanol [6'f]

^{1}H NMR

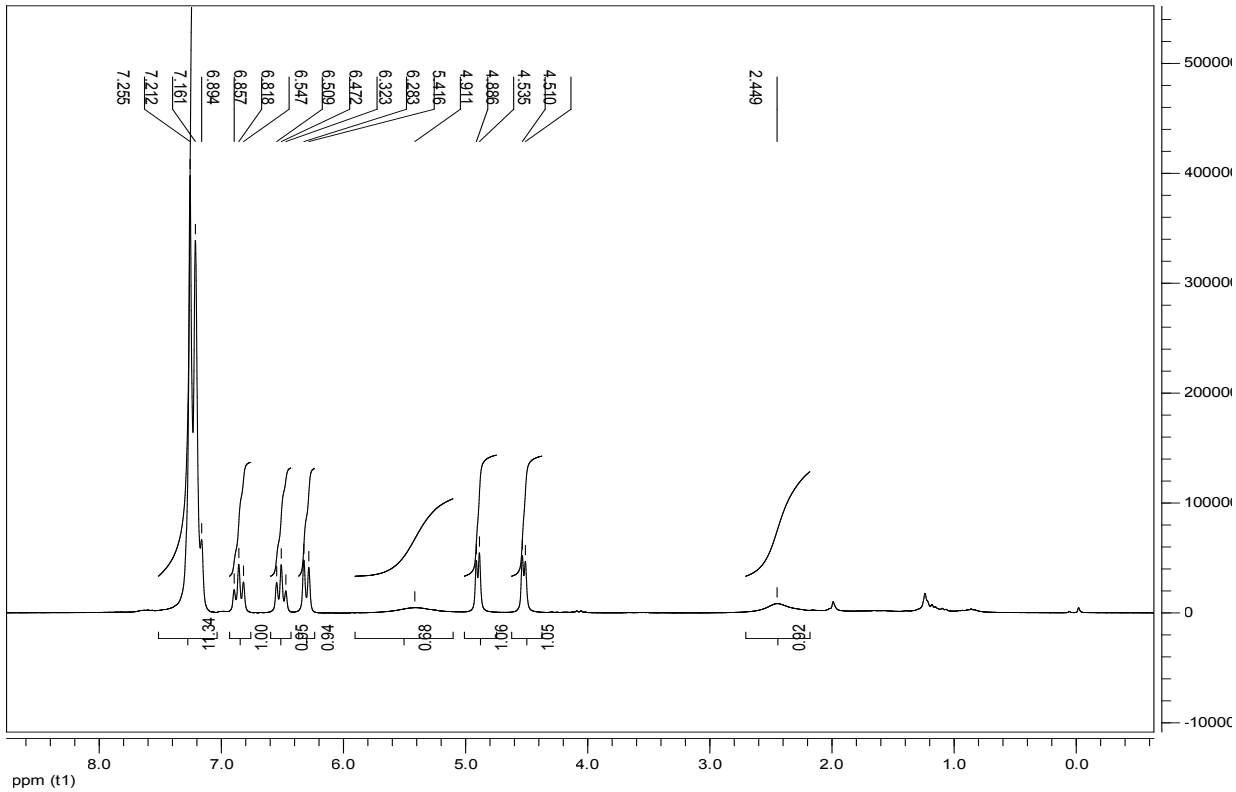


^{13}C NMR

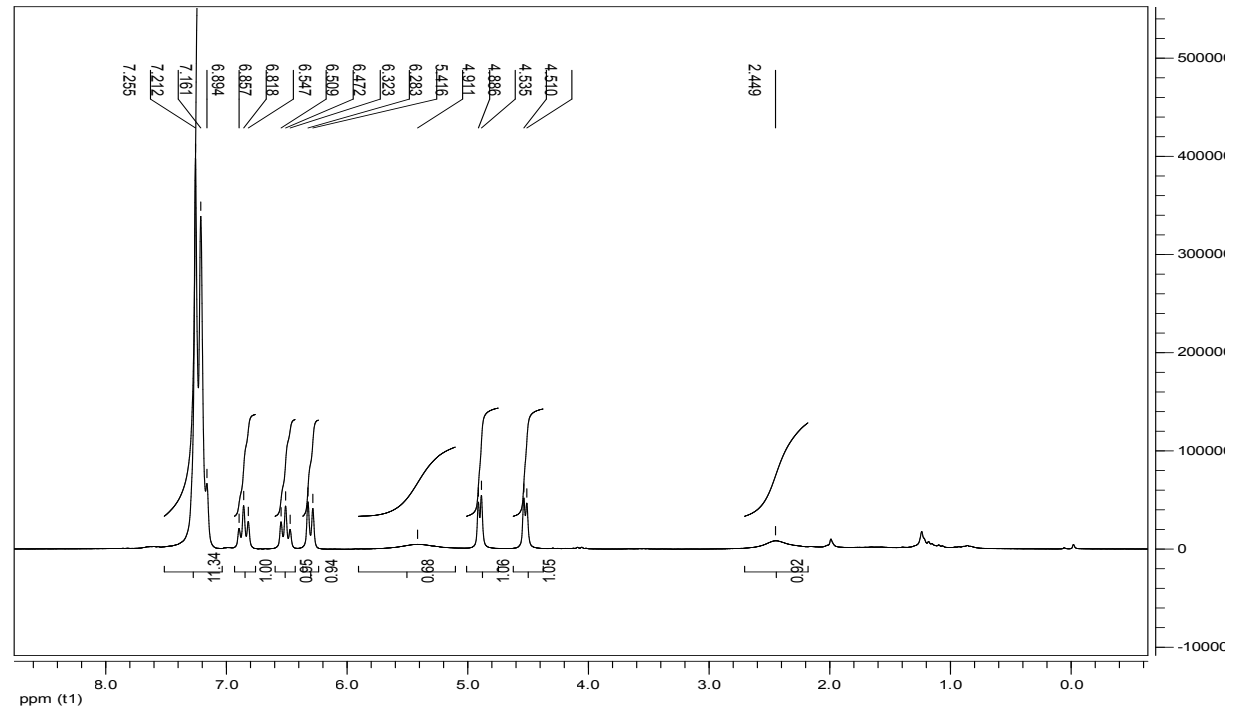


(1*S*,2*S*)-2-(2-Chlorophenylamino)-1,2-diphenylethanol [6'g]

^{1}H NMR

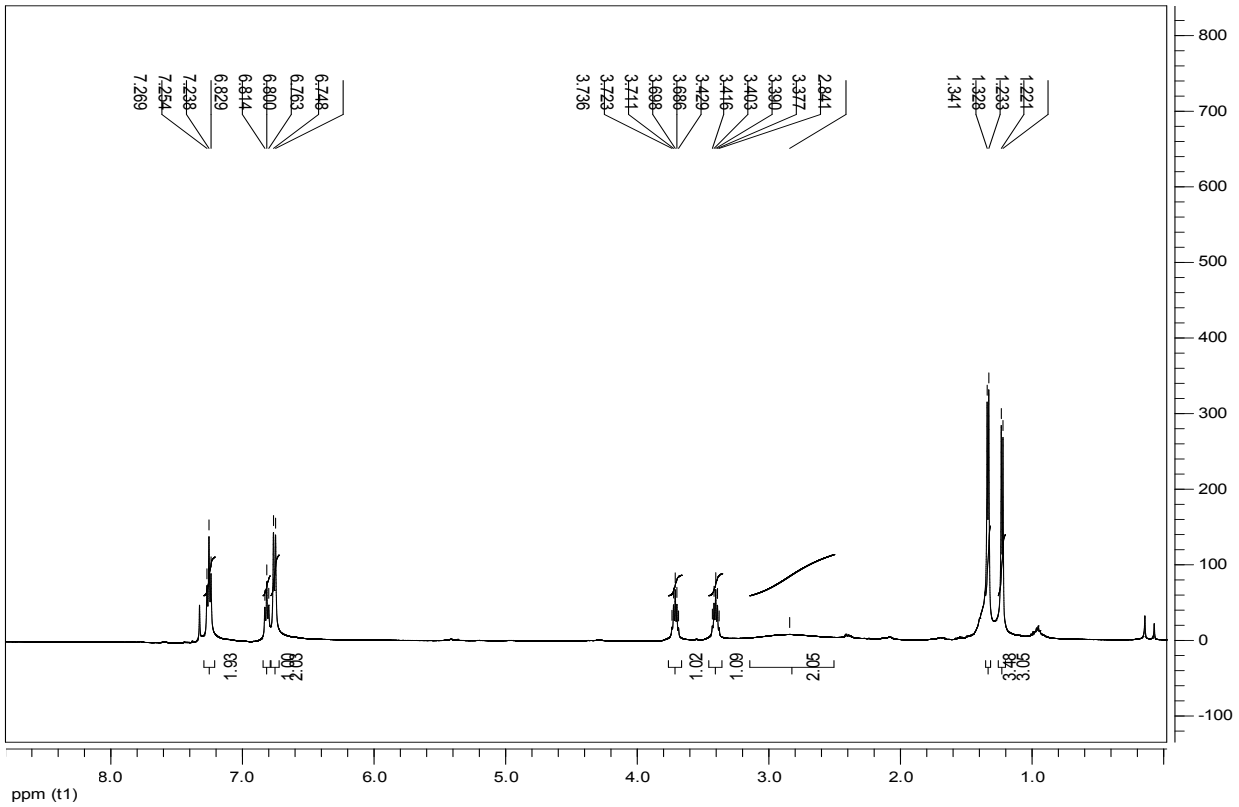


^{13}C NMR

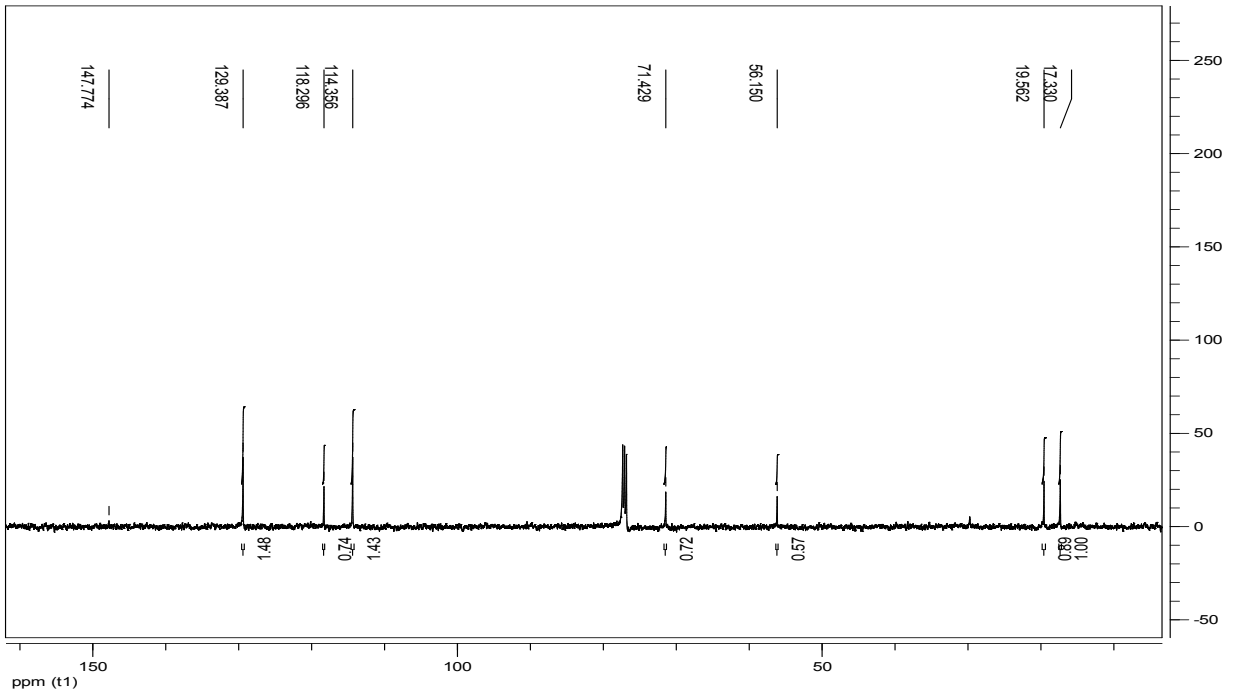


(2*S*,3*S*)-3-(Phenylamino) butan-2-ol [7'a]

^{1}H NMR

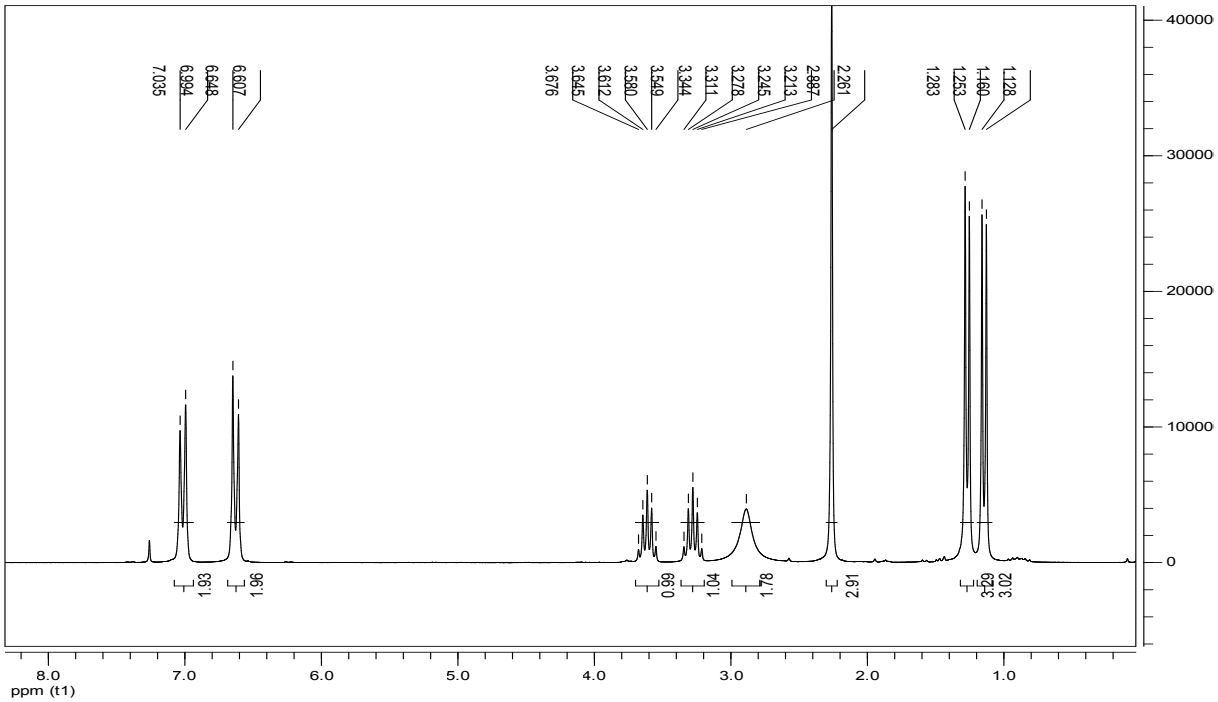


^{13}C NMR

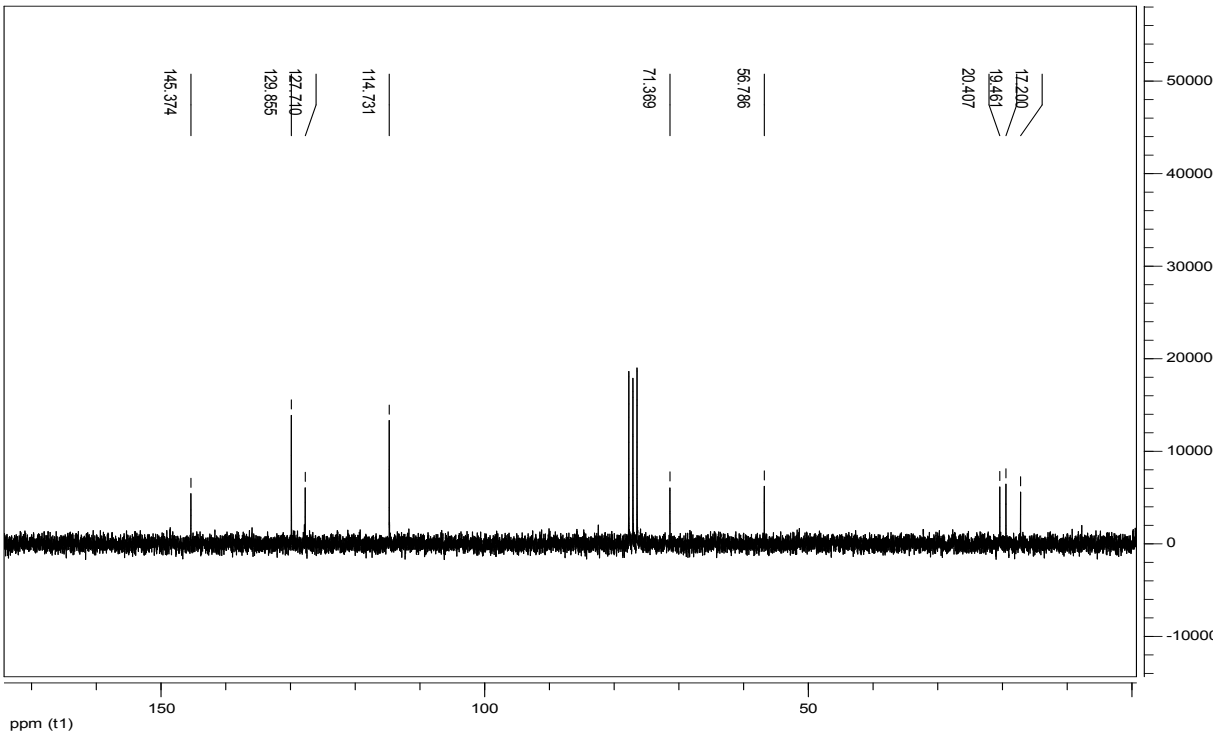


(2*S*,3*S*)-3-(4-Methylphenylamino)butan-2-ol [7'b]

^{1}H NMR

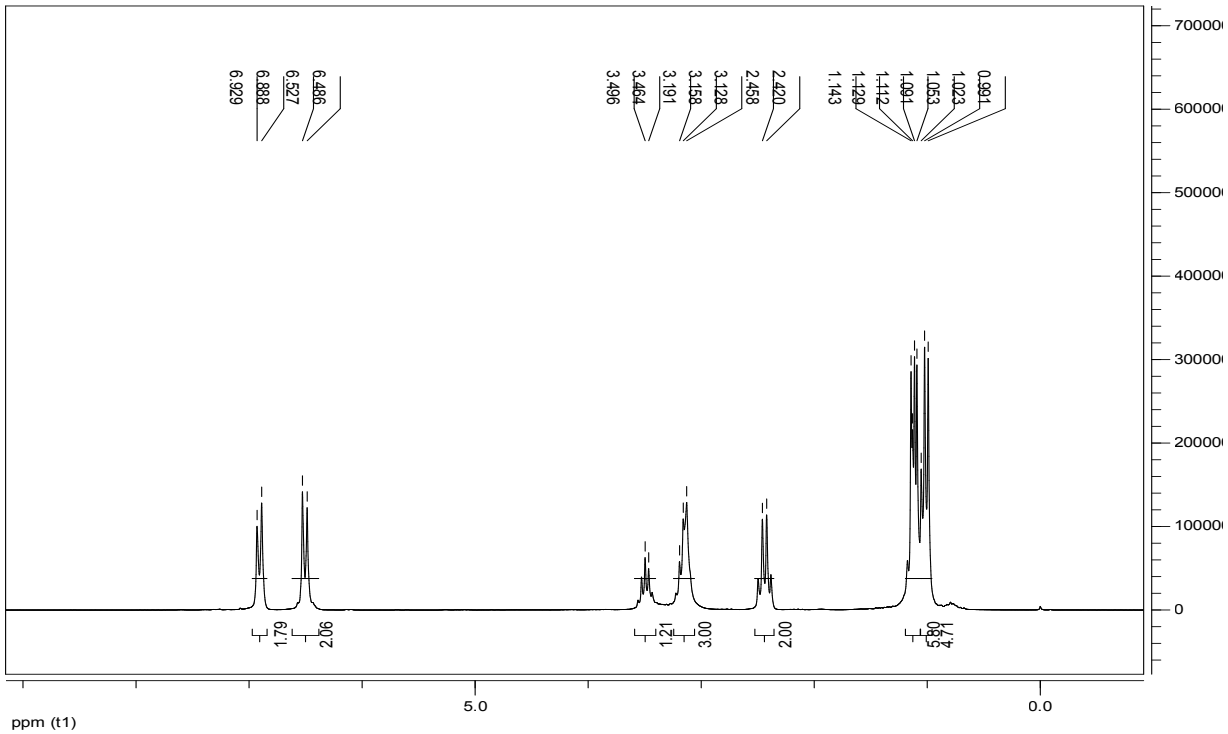


^{13}C NMR

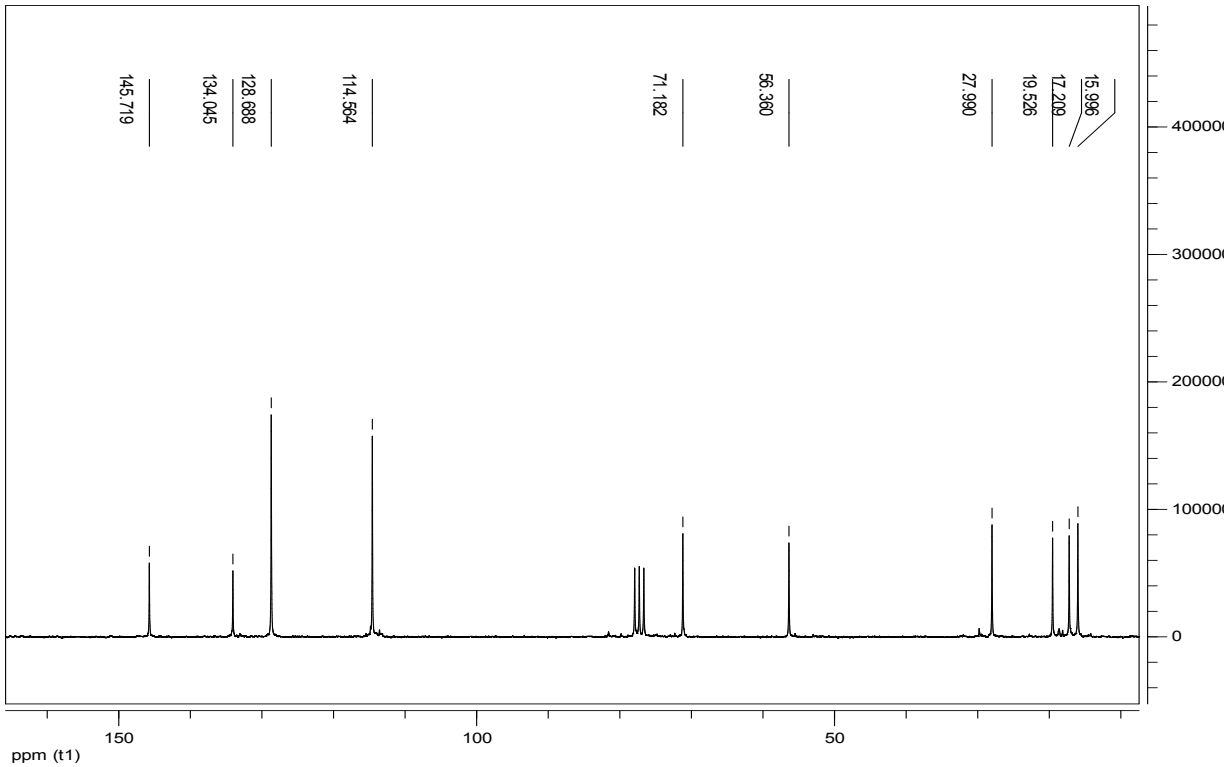


(2*S*,3*S*)-3-(4-ethylphenylamino)butan-2-ol [7'c]

^{1}H NMR

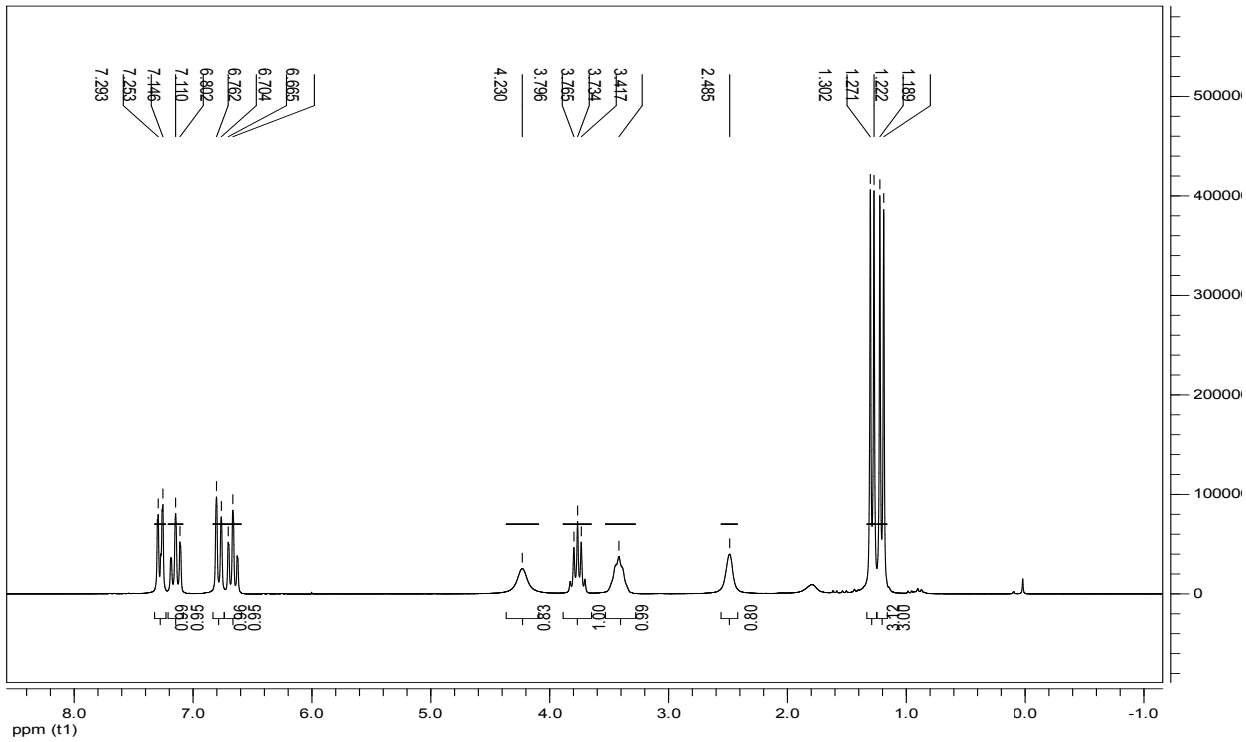


^{13}C NMR

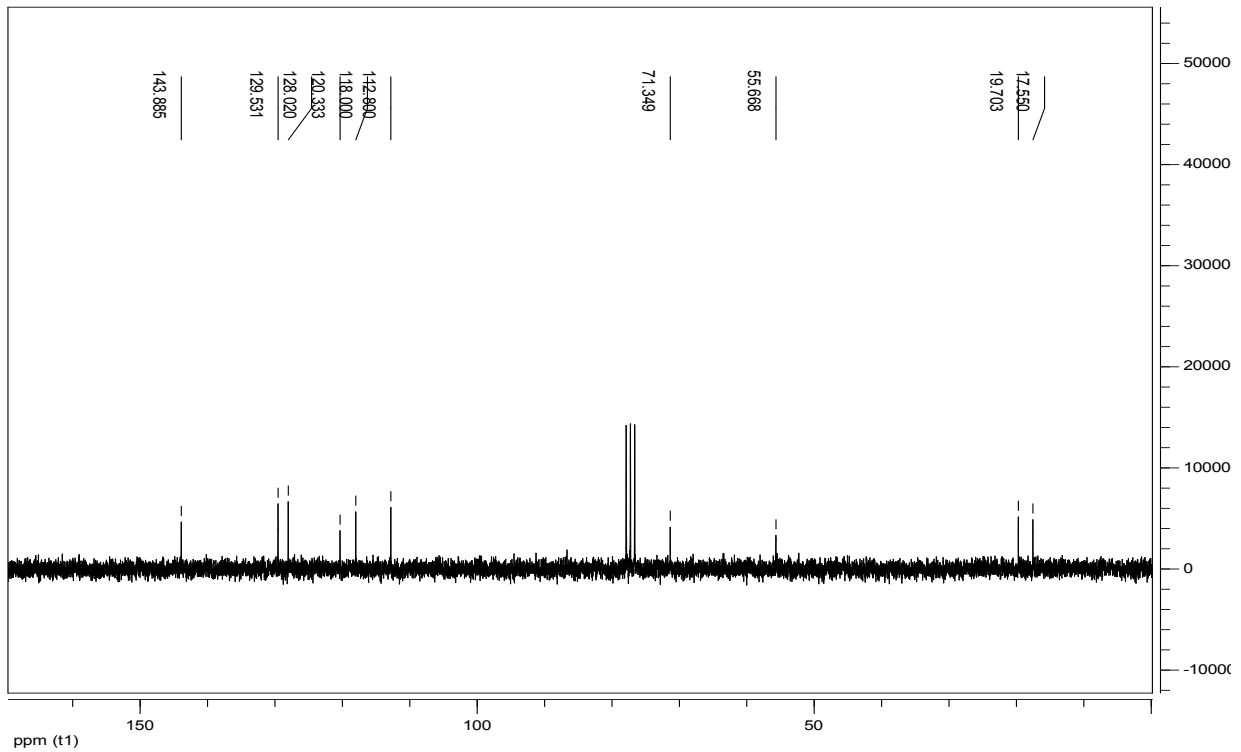


(2*S*,3*S*)-3-(2-chlorothoxyphenylamino)butan-2-ol [7'g]

^{1}H NMR

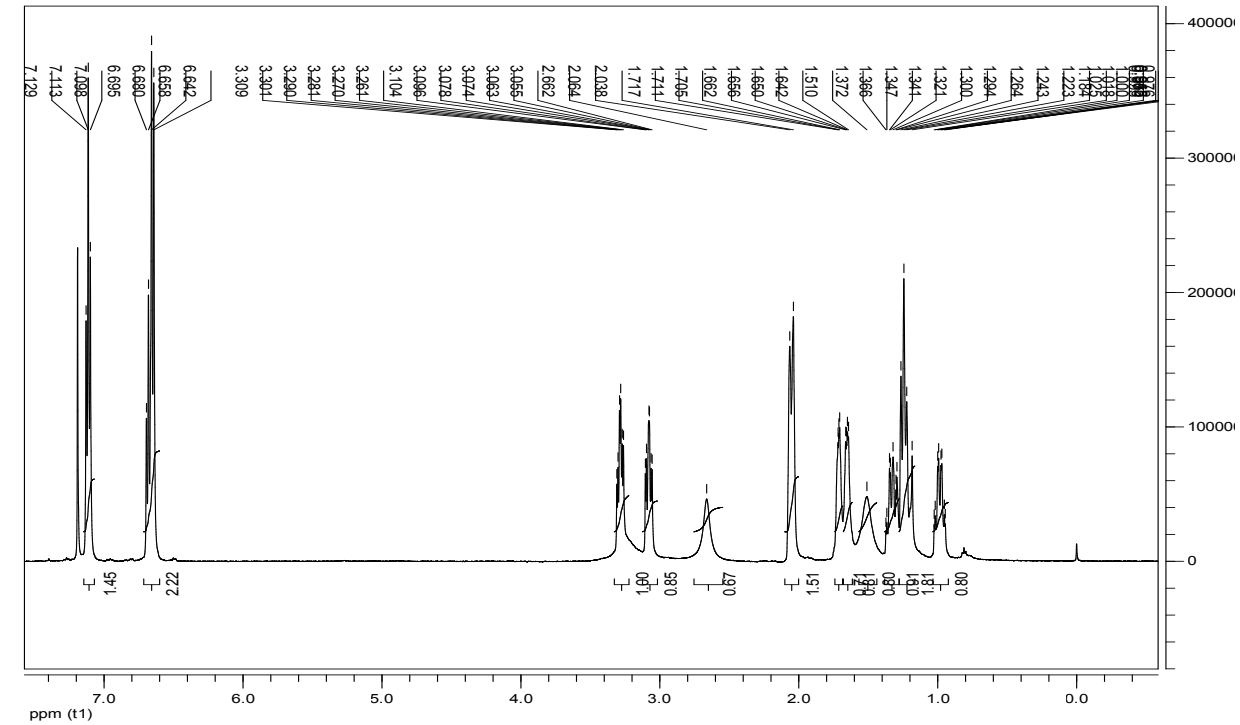


^{13}C NMR

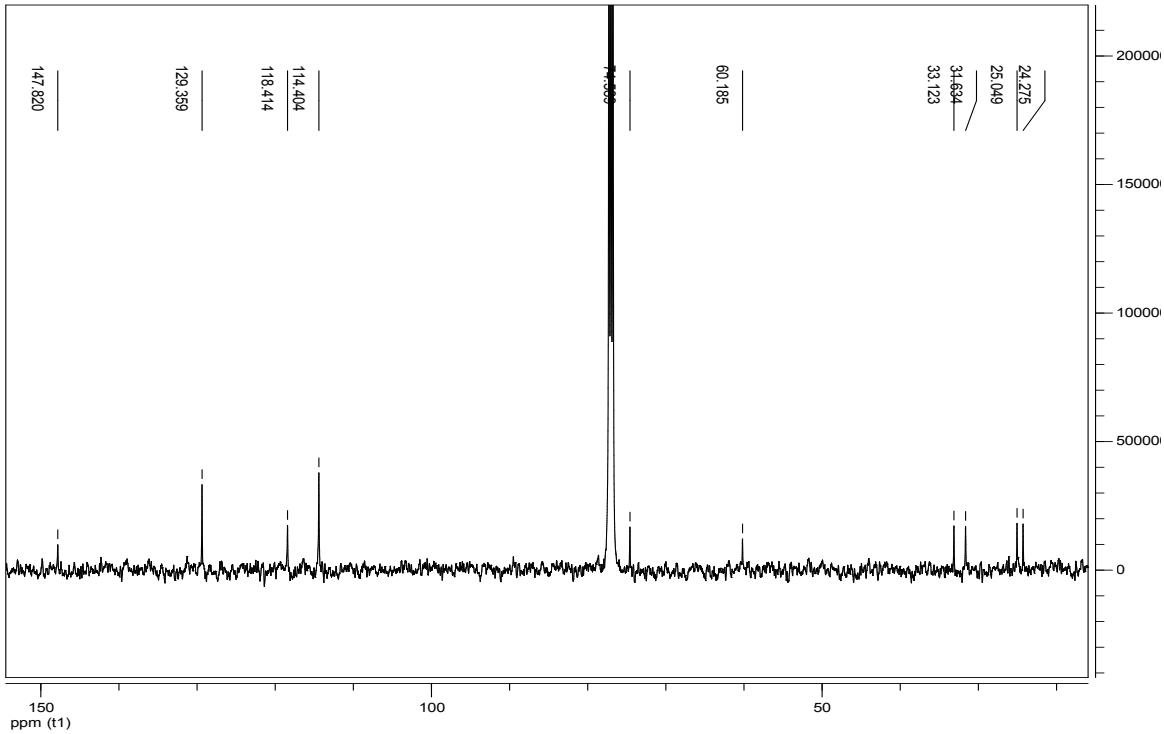


(1*S*,2*S*)-2-(phenylamino)-cyclohexene-1-ol [8'a]

^{1}H NMR

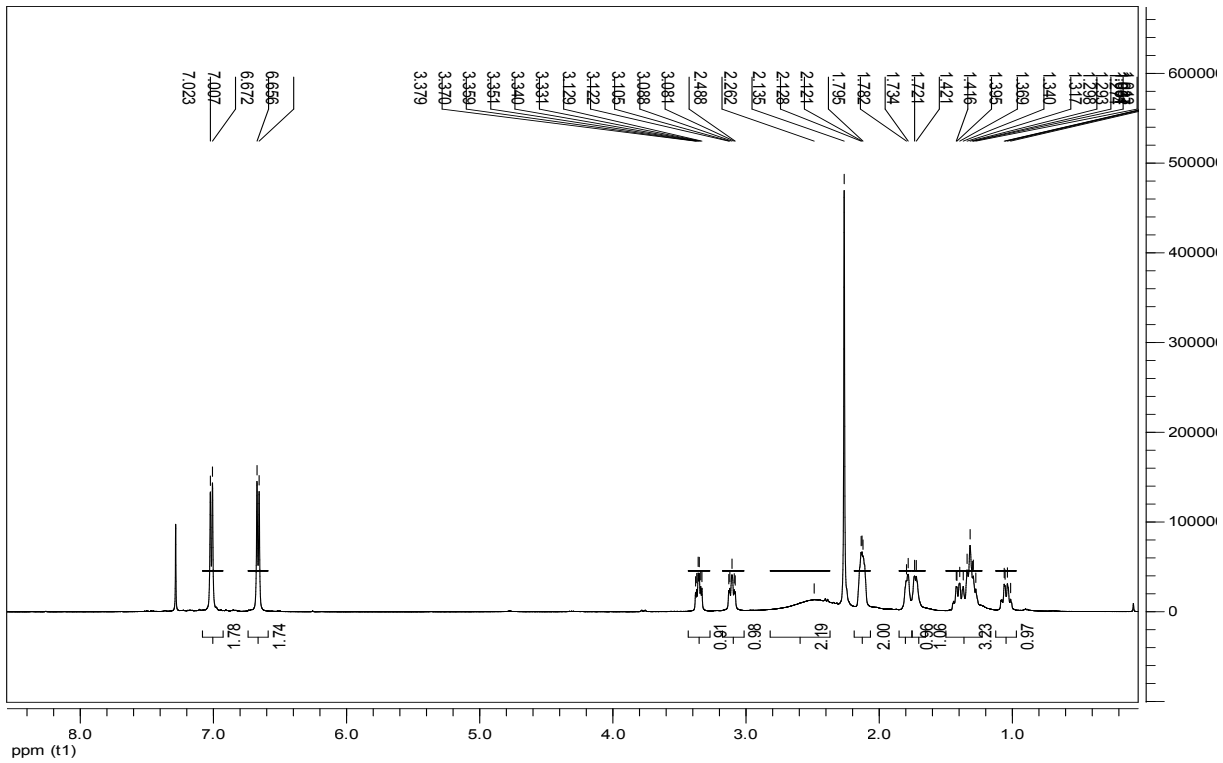


^{13}C NMR

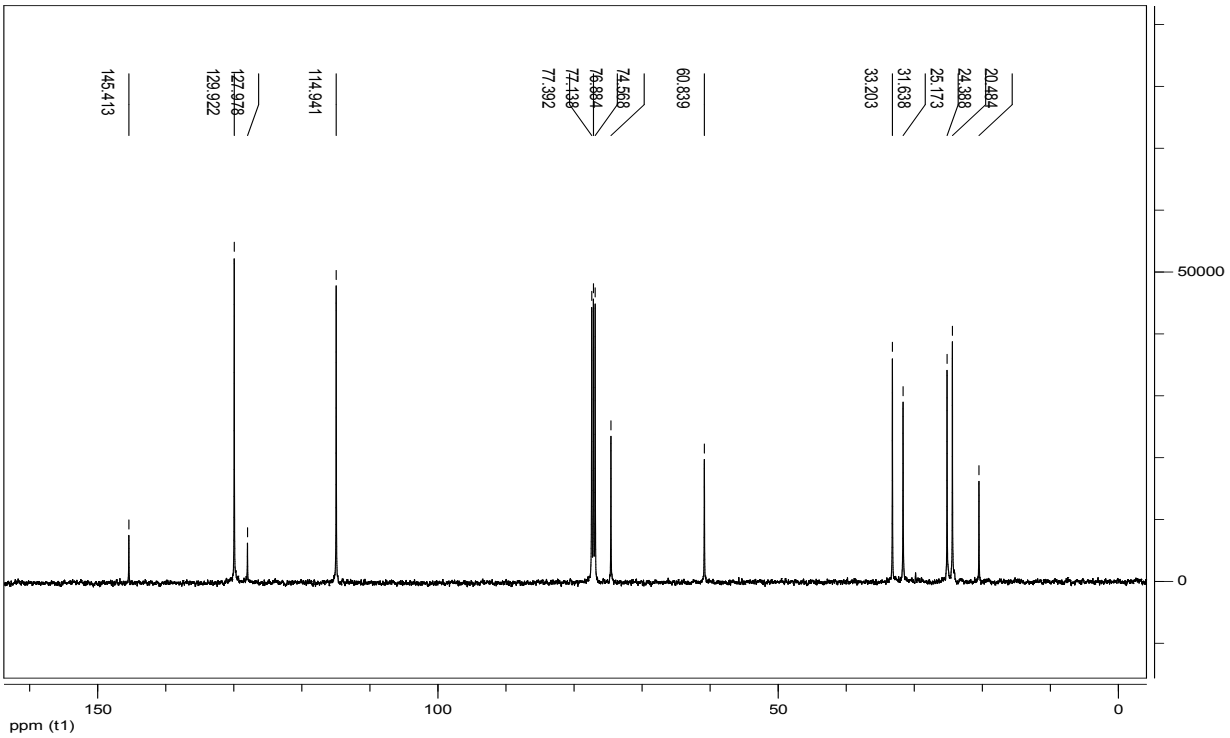


(1*S*,2*S*)-2-(4-methylphenylamino)-cyclohexan-1-ol [8'b]

^{1}H NMR

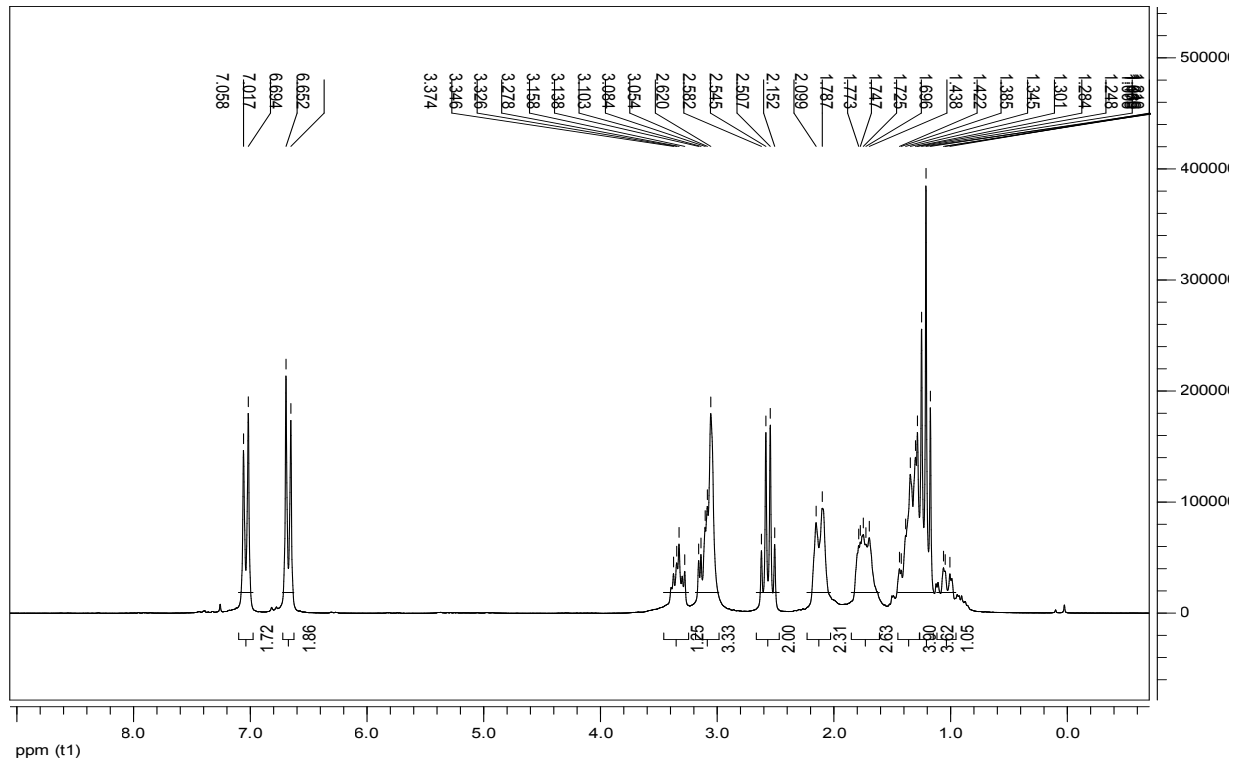


^{13}C NMR

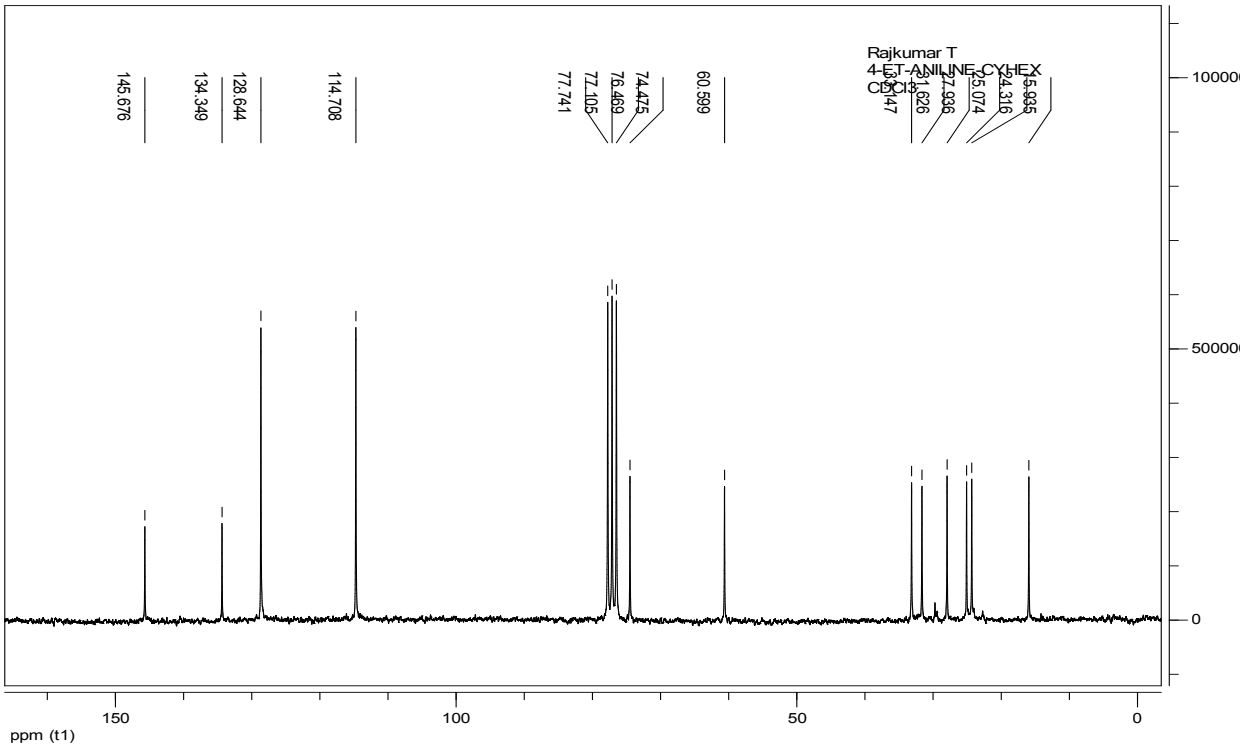


(1*S*,2*S*)-2-(4-ethylphenylamino)-cyclohexan-1-ol [8'c]

^{1}H NMR

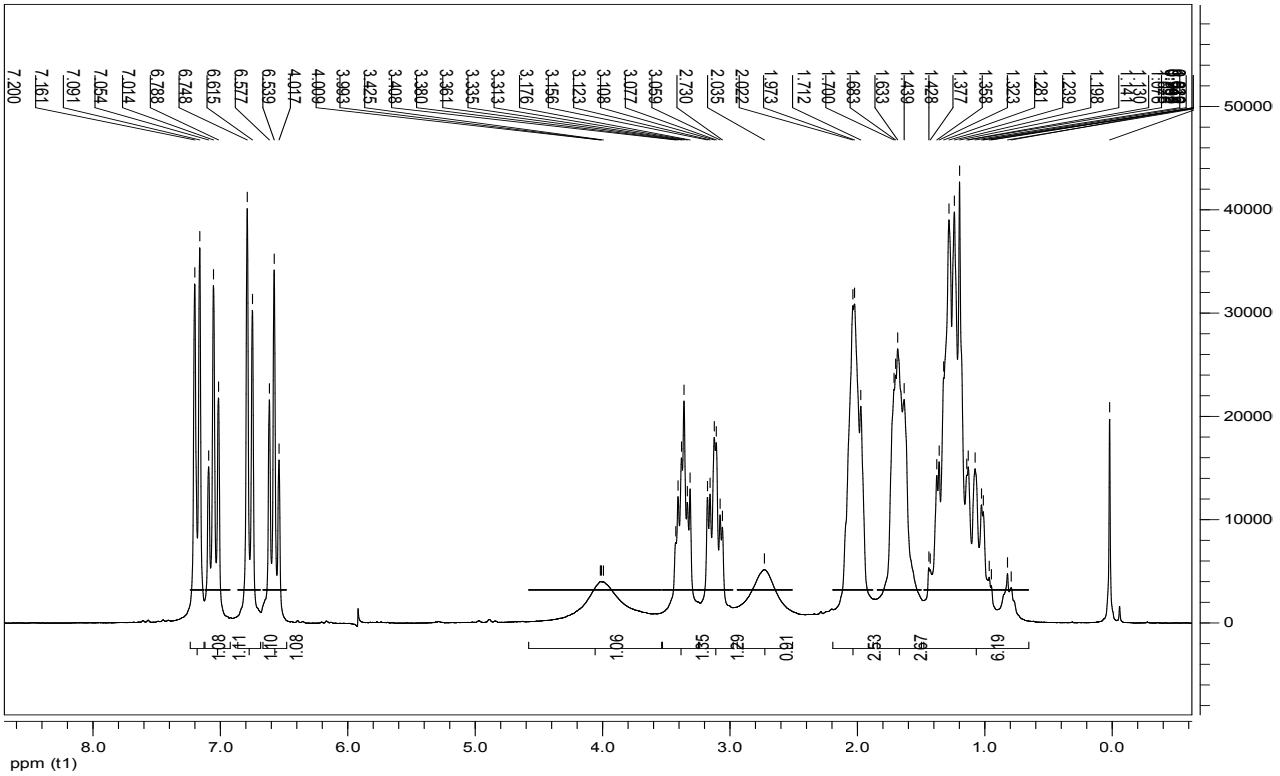


^{13}C NMR

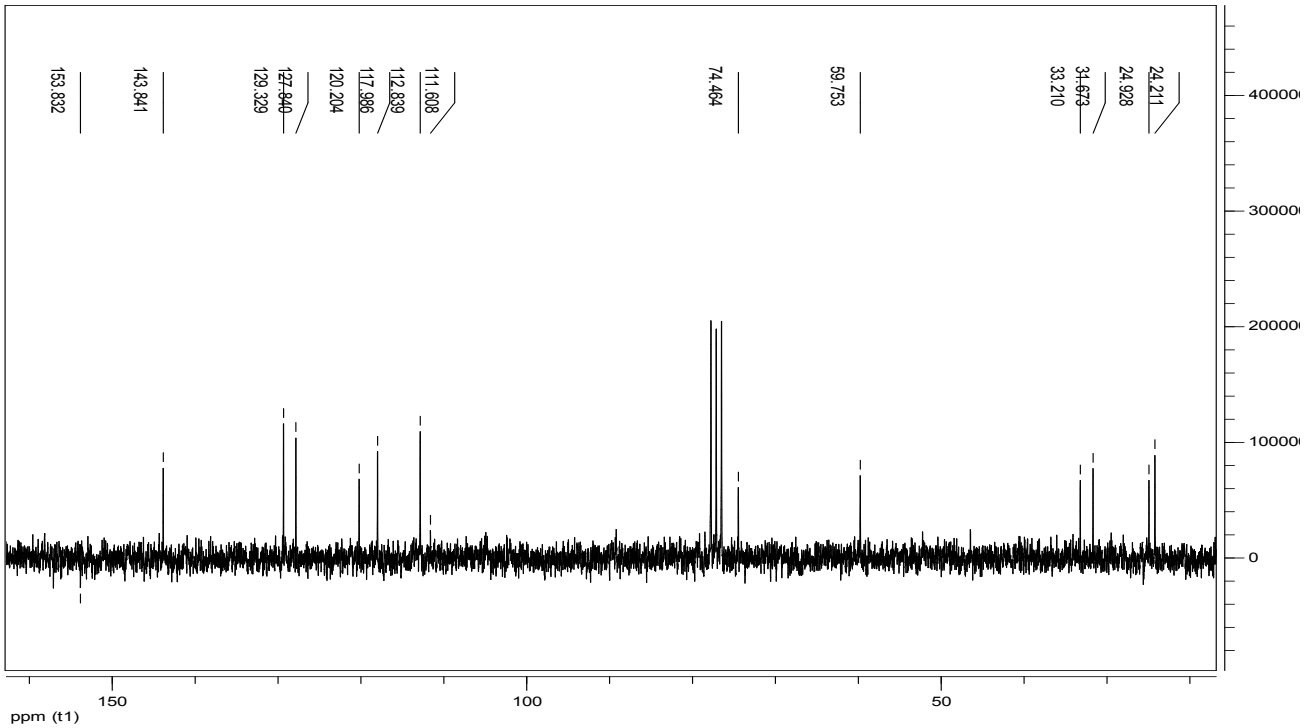


(1*S*,2*S*)-2-(2-chlorophenylamino)-cyclohexane-1-ol [8'g]

^{1}H NMR



^{13}C NMR



6. UV-Vis titration using Job's method :

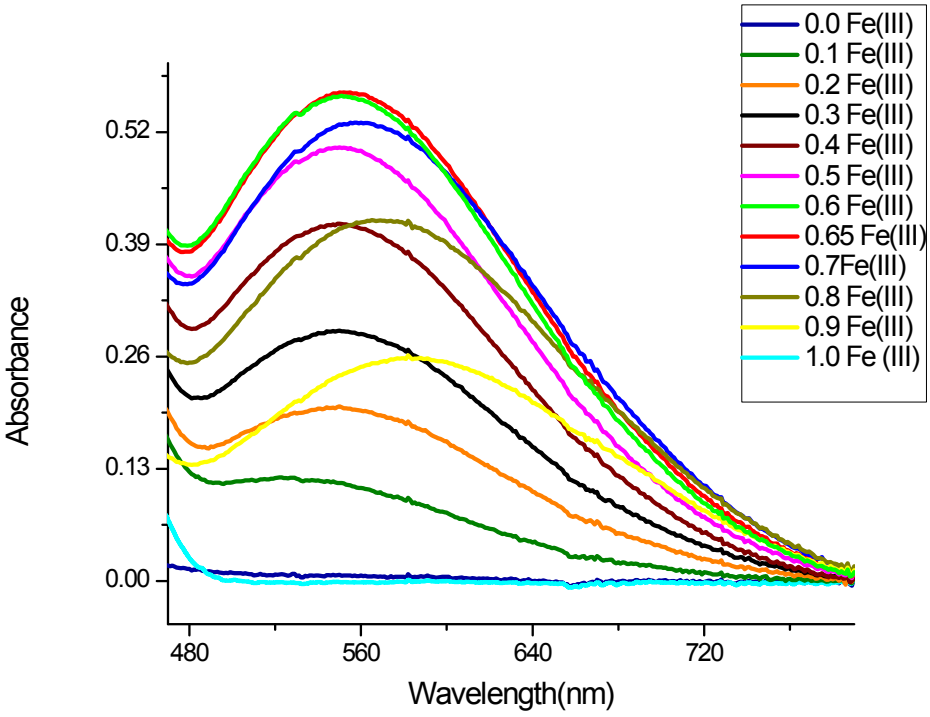


Figure S-1. UV-Vis titration using Job's method

7. Plausible structure, MS and MALDI spectra of the complex $[Fe_2L_5a(acac)_2]$

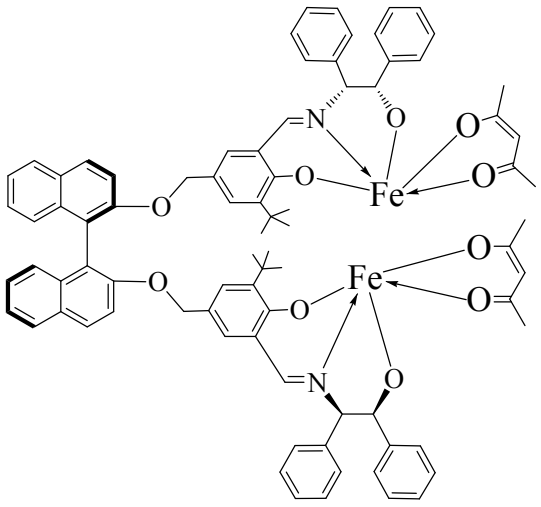


Figure S-2. Plausible structure of complex **$[Fe_2L_5a(acac)_2]$**

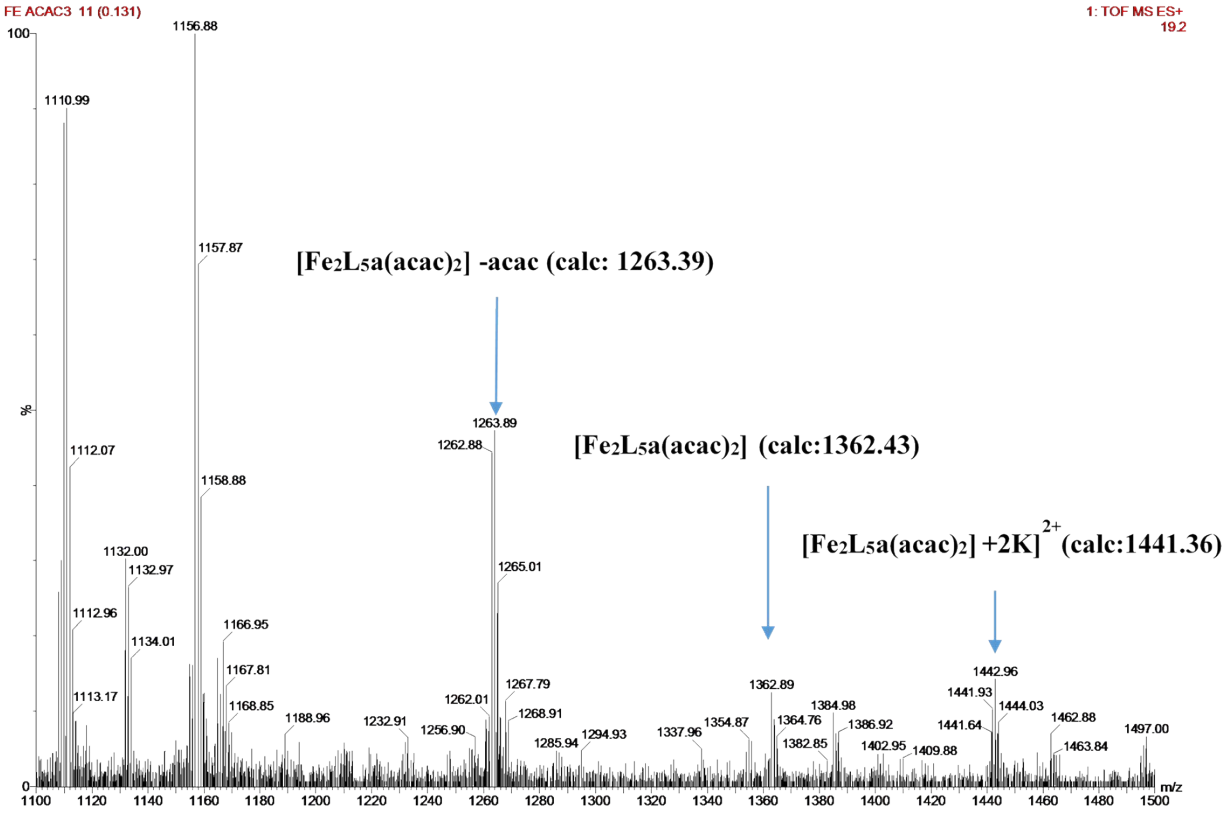


Figure S-3. MS spectra of complex **[$Fe_2L_5a(acac)_2$]**

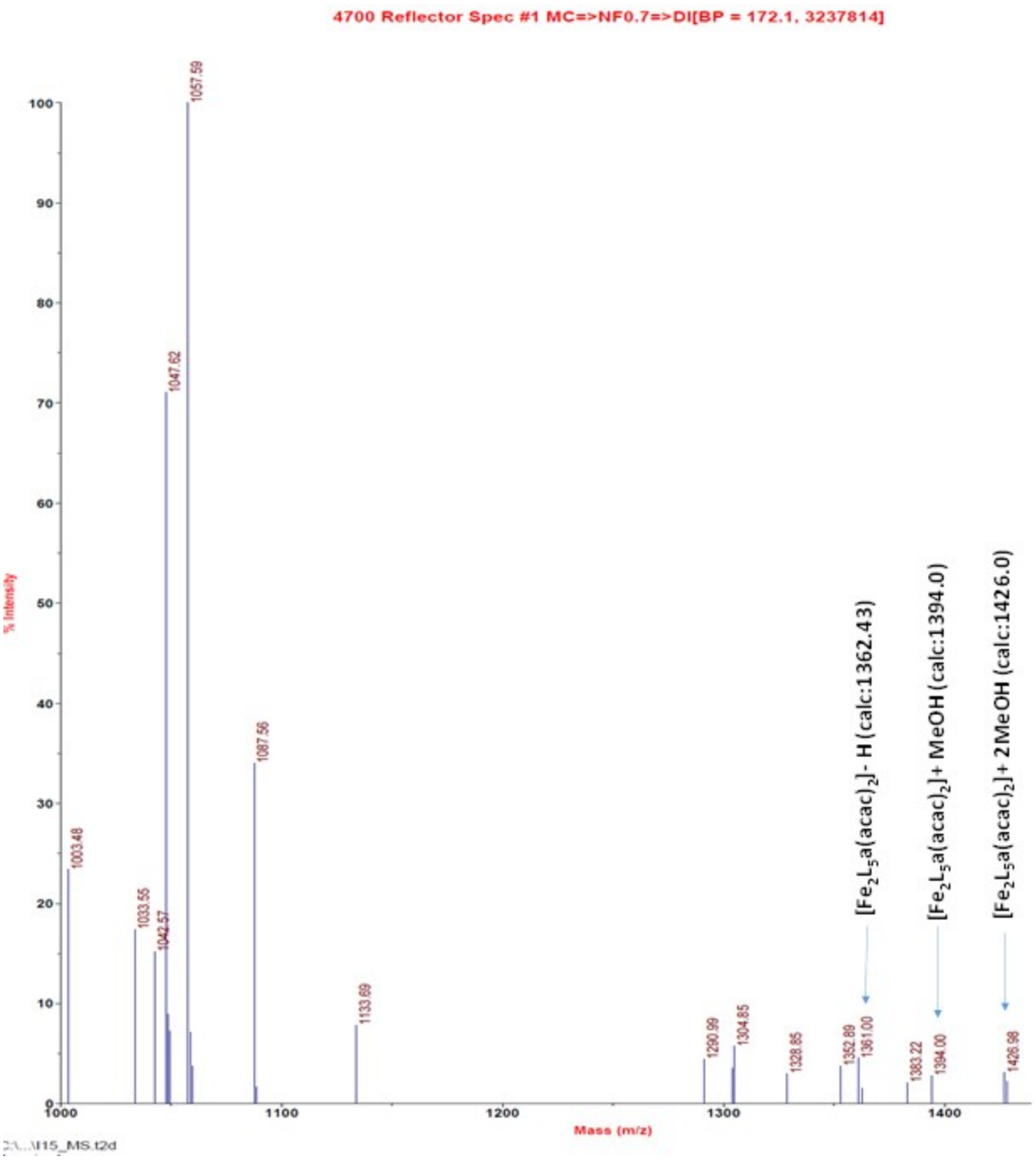


Figure S-4. MALDI spectra of complex **$[Fe_2L_5a(acac)_2]$**

8. Recyclability of the complex

The catalyst recyclability experiment was carried out by precipitating the catalyst (*in situ* generated Fe_2(**L_4h**)) from the reaction mixture by the addition of hexane after the first catalytic run for the ring opening of *cis*-butene oxide **7** with 4-methyl aniline **6b** at 1 mmol level under the optimized reaction conditions (Table 5, entry 2). The precipitated complex was washed thoroughly with hexane and dried under vacuum before its reuse in the next cycle. From the recycling experiments it is evident that the *in situ* formed catalyst is fairly stable and do not deteriorate during the course of ARO reaction (**Figure 5**).

9. ICP analysis

To check the leaching of the metal from the complex derived from **L_4h** with $FeCl_3$ was done by using inductively coupled plasma (ICP) spectrometer. The supernatant obtained after removing the catalyst and the product was concentrated to remove organic solvent and then treated with conc. HNO_3 to digest the metal present in the solution. This solution was make up to 100 ml with deionised water and used for ICP. The ICP results have shown no trace of metal in the supernatant obtained after removing the catalyst confirming that no metal is leached out during ARO reaction which further confirms the stability of the complex in the catalytic reaction.

10. Reference:

1. M. Kumar, R. I. Kureshy, D. Ghosh, N. H. Khan, S. H. R. Abdi and H. C. Bajaj, *ChemCatChem.,* 2013, **5**, 2336.
2. M. K. Choudhary, A. Das, R. I. Kureshy, M. Kumar, N. H. Khan, S. H. R. Abdi and H.C. Bajaj, *Catal. Sci. Techno*l , 2014, **4**, 548.

3. R. I. Kureshy, K. J. Prathap, S. Agrawal, N. H. Khan, S. H. R. Abdi and R. V. Jasra, *Eur. J. Org. Chem*., 2008, 3118.
4. P. K. Bera, P. Kumari, S. H. R. Abdi, N. H. Khan, R. I. Kureshy, P. S. Subramanian and H. C. Bajaj, *RSC Adv*., 2014, **4**, 61550.