Supporting Information

Chiral Cu(II)-Amino Alcohol Based Complexes for Asymmetric Aza-Henry Reaction of *N*-Ts Imines

Manoj K. Choudhary,[a,b] Anjan Das,[a,b] Rukhsana I. Kureshy,*[a,b] Manish Kumar,[a,b] Noor-ul H. Khan,[a,b] Sayed H. R.Abdi,[a,b] and Hari C. Bajaj[a,b]

[a] Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute (CSMCRI), Council of Scientific & Industrial Research (CSIR), Bhavnagar- 364 002, Gujarat, India. E-mail: *rukhsana93@yahoo.co.in*, Fax: 0278-2566970.

[b] Academy of Scientific and innovative research (AcSIR), CSIR-CSMCRI, Bhavnagar- 364 002, Gujarat

1.General information:

All starting materials and reagents were used as received without any further purification. All the solvents used in the present study were dried by known purification technique.[1-5] Chemical reactions (which have been mentioned) were conducted under anhydrous conditions using nitrogen atmosphere and oven-dried glassware's unless otherwise stated. Enantiomeric excess (ee) of the products and intermediates were determined by using programmable high performance liquid chromatography (HPLC). 200 MHz or 500 MHz spectrometers were used to record the ^{1}H and ^{13}C NMR spectra. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$ = 7.26). Spectra are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration, and assignment.

2. General procedures for the preparation of *N*-Ts imines:

N-Ts imines **(2a-k)** were prepared according to the reported literature.[6-]

3. Synthesis and characterization of the ligands :

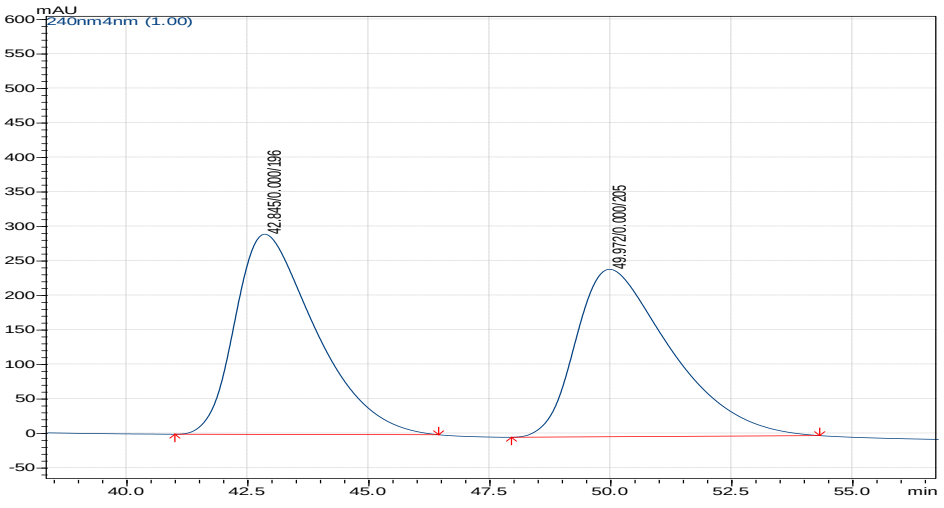
Chiral ligands **1A-C, 2A-B, 3A-B, 4A** were prepared according to the methods reported in the literature. For the characterization of the ligands.[10]

4. Typical experimental procedure for the Aza-Henry reaction : Typical Experimental Procedure for Asymmetric Aza-Henry reaction: Chiral BINOL **1A-C, 2A-B, 3A-B, 4A** (10 mol%) and $Cu(OAc)_2.H_2O$ (15 mol%) were added to a screw-capped vial containing a stirring magnetic bar. Anhydrous Toluene (0.8 mL) was then added, and a clear green solution formed was stirred for 2 h at RT. To the resulting solution nitromethane or nitroethane (5.0 mmol, 10 equiv) and desired *N*-Ts imines (0.2 mmol, 1equiv) were added. After running the reaction for the specified time as given in Table 4 and Table 5, the volatile components were removed under reduced pressure, and the crude product was purified by flash column chromatography.(AcOEt : Hexane =1:9).

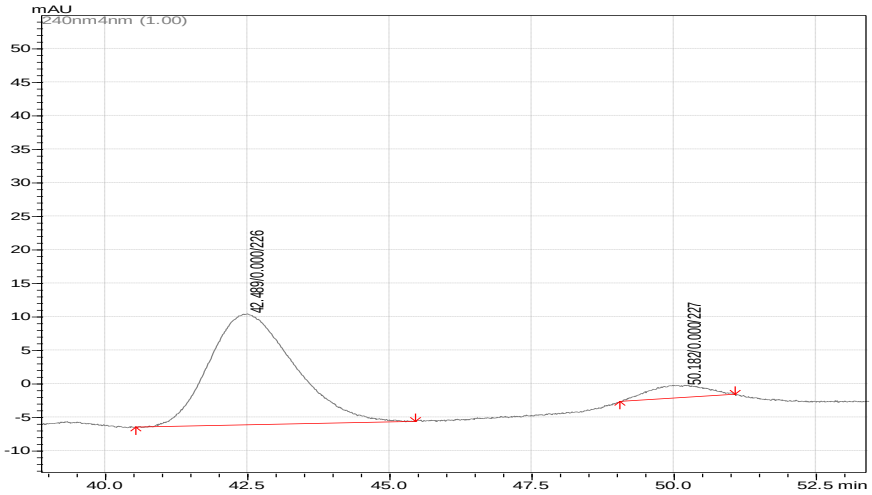
5. Characterization and HPLC profiles of the products:

(i). 2-Nitro-1-phenyl-*N*-tosylethanamine **(2a)**

White solid, 86% ee; ^{1}H NMR (200 MHz, $CDCl_3$, δ ppm) δ 7.66 (d, 2H, *J* = 8.0 Hz), 7.27-7.20 (m, 5H), 7.10-7.08 (d, 2H), 5.37-5.34 (d, 1H, *J*= 7.2 Hz), 4.98 (q, 1H, *J*= 6.6 Hz), 4.86 (dd, 1H, = 13, 6.4 Hz), 4.69 (dd, 1H, *J*= 13, 6.4 Hz), 2.4 (S, 3H); ^{13}C NMR (200 MHz, $CDCl_3$, δ ppm) δ 144.02, 136.42, 135.26, 129.73, 129.18, 127.13, 126.45, 78.95, 55.42, 21.5. HPLC (Chiralcel OD-H, hexane/2-propanol = 90/10, flow 0.80 mL/min, λ =240 nm) $t_{(major)}$ = 42.2 min. and $t_{(minor)}$ = 50.3 min.



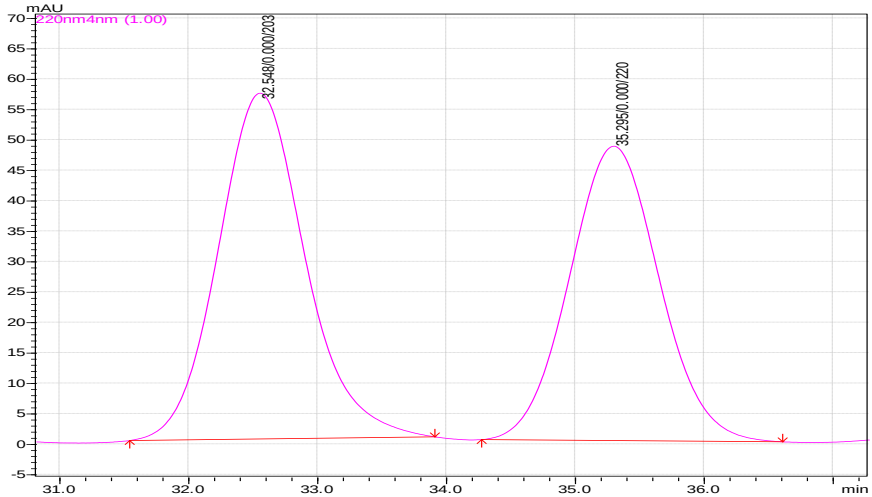
Racemic



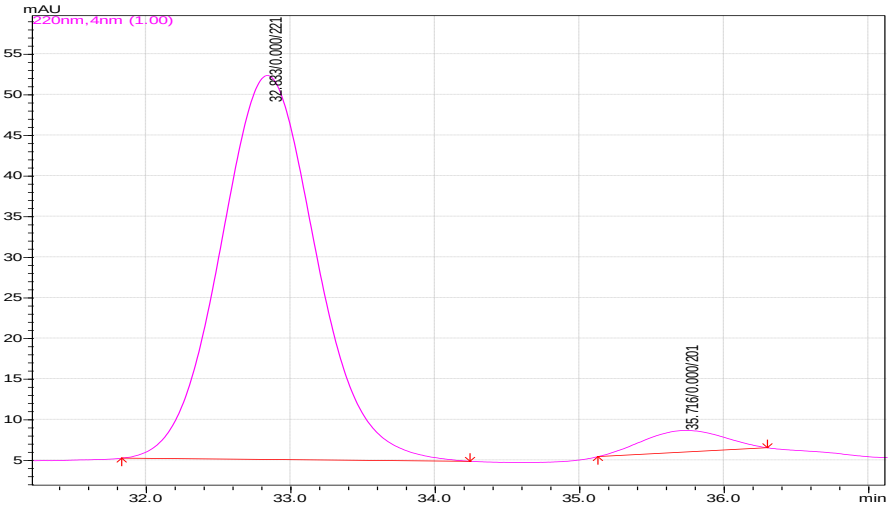
Chiral

(ii). 2-Nitro-1-(2'-methoxyphenyl)-*N*-tosylethanamine **(2b)**

White solid, 91% ee; ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) δ 7.82-7.81 (d, 1H, *J*= 8.0 Hz), 7.56-7.55 (d, 2H, *J*= 8.0 Hz), 7.21-7.18 (m, 1H), 7.12-7.10 (d, 2H, *J*= 8.0 Hz), 6.94-6.93 (d, 1H, *J*=7.5 Hz), 6.78-6.73 (m, 2H), 5.88-5.86 (d, 1H, *J*= 10 Hz), 5.13 (q, 1H, *J*= 7 Hz), 4.83-4.82 (dd, 1H, *J*= 12.5, 7.5 Hz), 4.66-4.65 (dd, 1H, *J*= 12.5,6.5 Hz), 3.81 (S, 3H), 2.34 (S, 3H); ^{13}C NMR (500 MHz, $CDCl_3$, δ ppm) δ 156.08, 143.18, 136.58, 129.89, 129.40, 129.06, 126.63, 122.20, 120.71, 110.56, 77.49, 55.11, 54.41, 21.16; HPLC (Chiralcel OD-H, hexane/2-propanol = 70/30, flow 0.60 mL/min, λ= 220 nm) $t_{(major)}$ = 32.8 min and $t_{(minor)}$ =36.7 min.



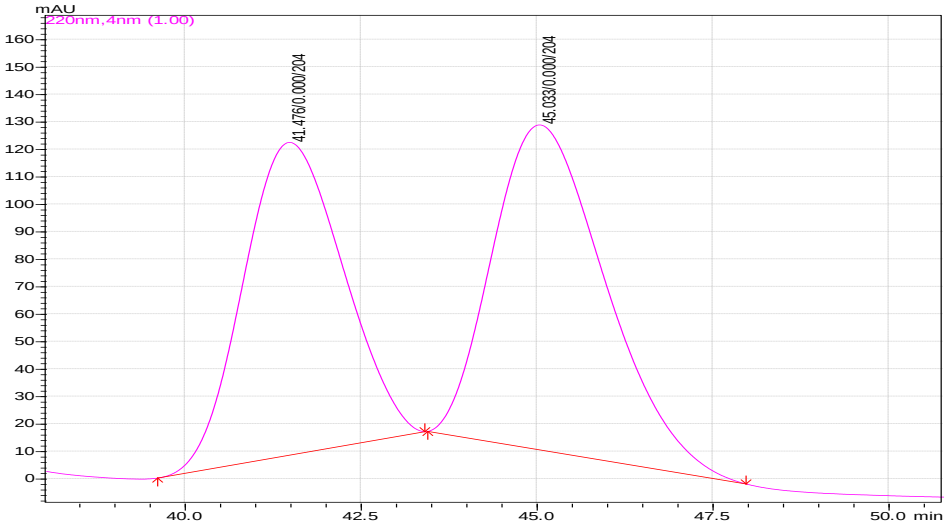
Racemic



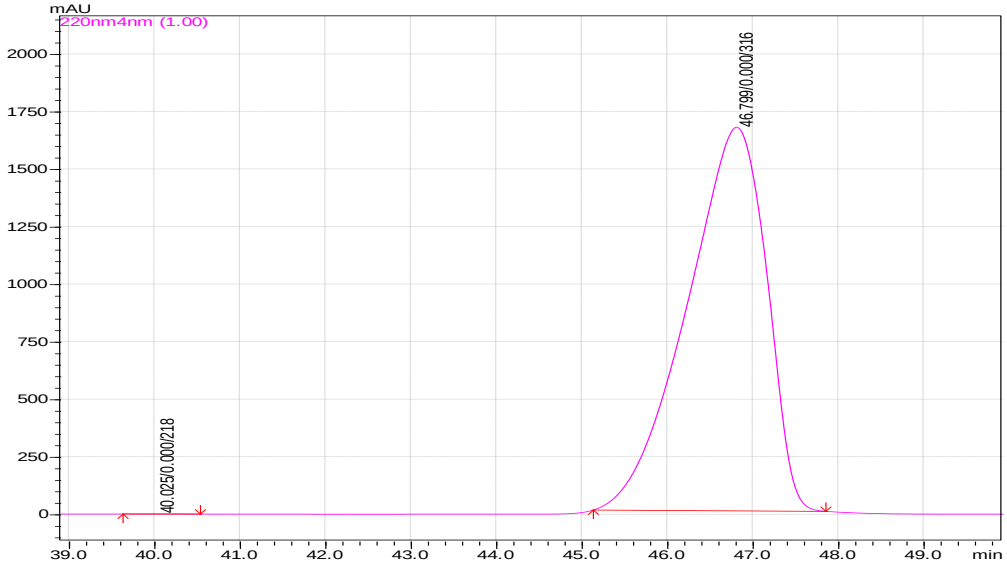
Chiral

(iii). 2-Nitro-1-(4'-methoxyphenyl)-*N*-tosylethanamine **(2c)**

White solid, >99% ee; ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) δ 7.66 (d, 2H, *J*= 8.0 Hz), 7.26-7.24 (m, 2H,), 7.00-6.98 (d, 2H,*J*= 8.5 Hz), 6.77-6.75 (m, 2H), 5.29-5.27 (d, 1H, *J*= 7.0 Hz), 4.92 (q, 1H, *J*= 6.5 Hz), 4.85 (dd, 1H, *J*= 13, 6.5 Hz), 4.66 (dd, 1H, *J*= 13, 6.5 Hz), 3.75 (S, 3H), 2.41 (S, 3H); ^{13}C NMR (500 MHz, $CDCl_3$, δ ppm) δ 160.26, 144.24, 136.65, 129.99, 127.97, 127.41, 114.79, 79.19, 55.54, 55.15, 21.71; HPLC (Chiralcel OD-H, hexane/2-propanol = 85/15, flow 0.80 mL/min, λ= 220 nm) $t_{(major)}$= 46.7 min and $t_{(minor)}$=41.5 min.



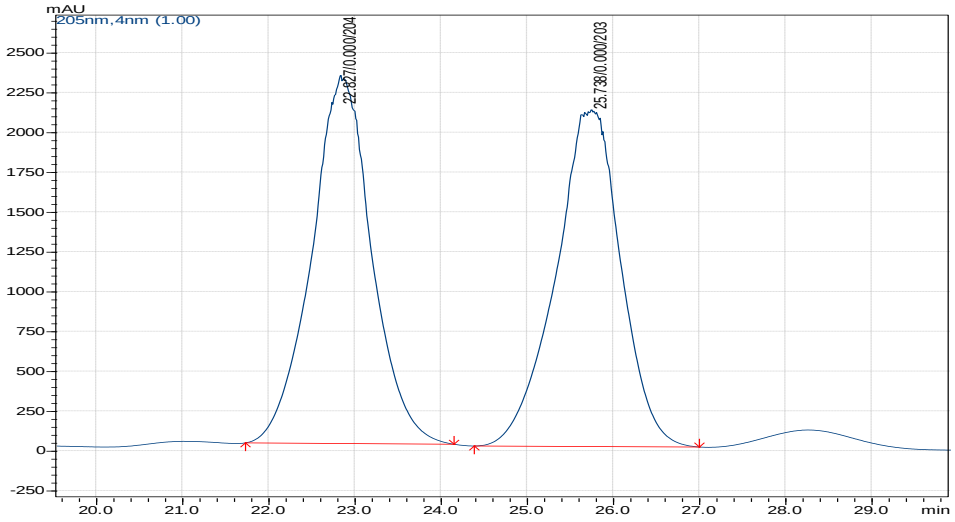
Racemic



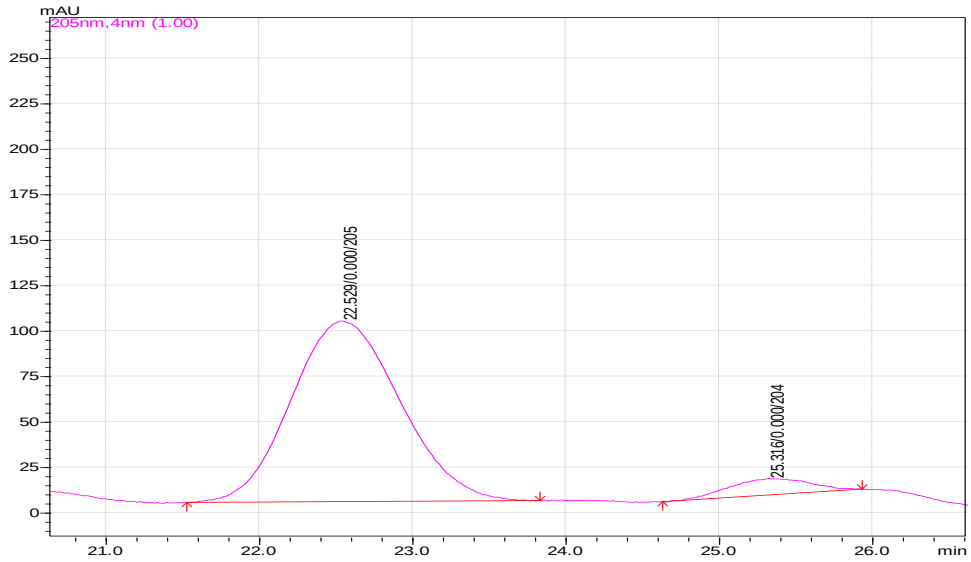
Chiral

(iv). 2-Nitro-1-o-tolyl-*N*-tosylethanamine **(2d)**

White solid, 89% ee; ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) δ 7.65 (d, 2H, *J*= 8.5 Hz), 7.25 (d, 2H, *J*= 8.0 Hz), 7.17-7.12 (m, 3H), 7.08 (d, 1H, *J*=7.0 Hz), 5.24 (q, 1H, *J*=6.5 Hz), 5.07-5.06 (d, 1H, *J*=6.0 Hz), 4.90-4.89 (dd, 1H, *J*= 13, 6.5 Hz), 4.70-4.69 (dd, 1H, *J*= 13, 7.0 Hz), 2.41 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$, δ ppm) δ 145.89, 136.77,135.49, 131.56, 130.80, 129.01, 128.86, 127.43, 80.35, 53.22, 23.36, 20.62; HPLC (Chiralcel AD-H, hexane/2-propanol = 90/10, flow 0.80 mL/min, λ=230 nm) $t_{(major)}$ = 22.5 min and $t_{(minor)}$= 25.3 min.



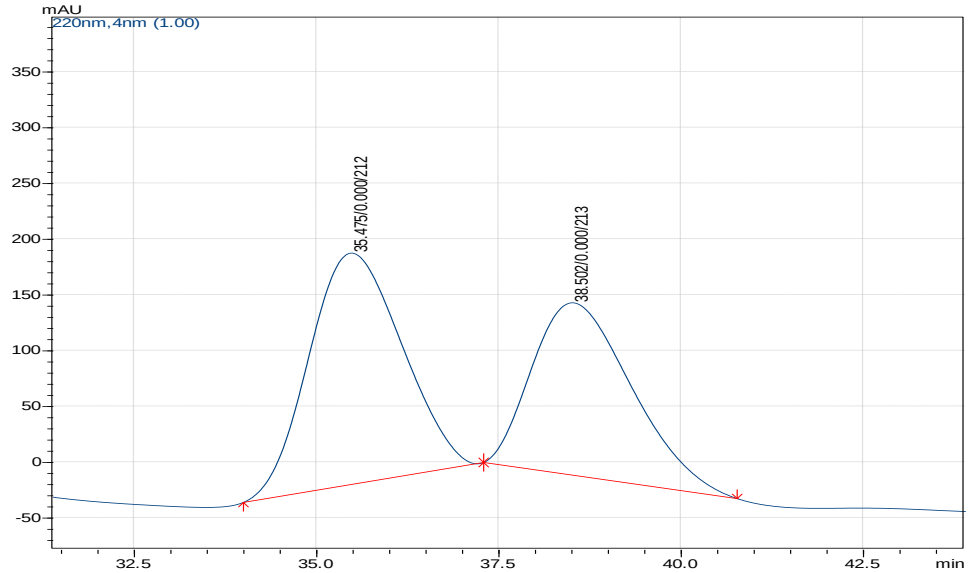
Racemic



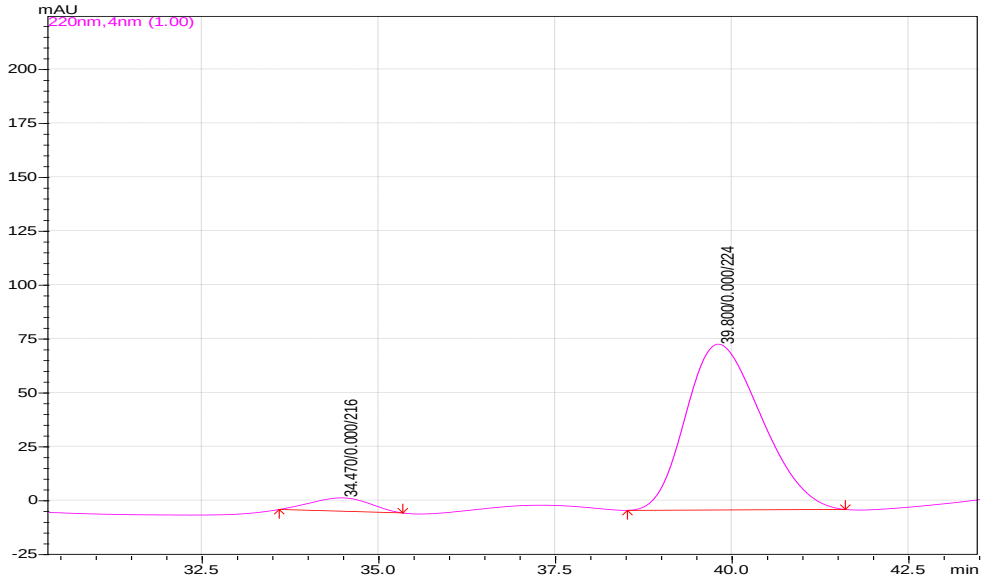
Chiral

(v). 2-Nitro-1-p-tolyl-*N*-tosylethanamine **(2e)**

White solid, 90% ee; ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) δ 7.66 (d, 2H, *J*= 8.0 Hz), 7.26-7.24 (m, 2H), 7.07 (d, 2H, *J*= 8.0 Hz), 6.97 (d, 2H, *J*= 8.0 Hz), 5.26 (d, 1H, *J*= 7.0 Hz), 4.94 (q, 1H, *J*= 7.0 Hz), 4.86-4.84 (dd, 1H, *J*= 13, 6.5 Hz), 4.68-4.67 (dd, 1H, *J*= 13, 6.5 Hz), 2.42 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$, δ ppm) δ 144.26, 139.35,136.63, 132.52, 130.10, 129.99, 127.41, 126.54, 79.17, 55.37, 21.78, 21.29; HPLC (Chiralcel OD-H, hexane/2-propanol = 90/10, flow 1.0 mL/min, λ=220 nm) $t_{(major)}$ = 34.4 min and $t_{(minor)}$ = 39.8 min.



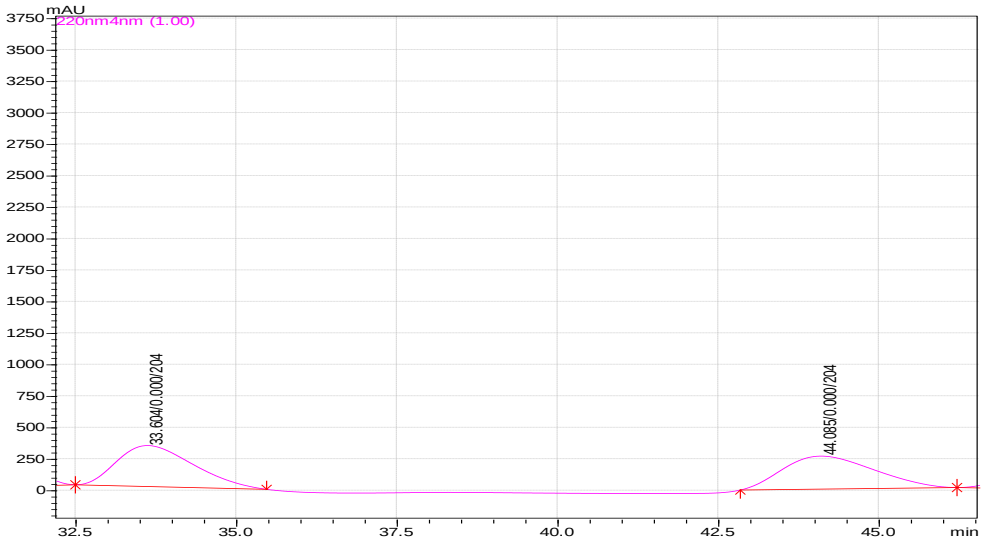
Racemic



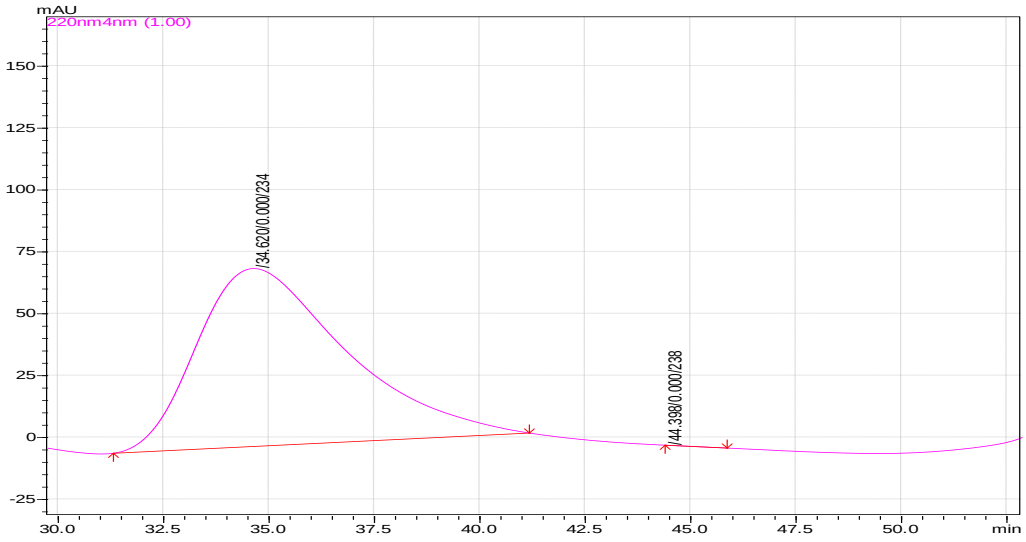
Chiral

(vi). 2-Nitro-1-(2'-fluorophenyl)-*N*-tosylethanamine **(2f)**

White solid, 99% ee; ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) δ 7.62 (d, 2H, *J*= 8.5 Hz), 7.26 (m, 1H), 7.17 (d, 2H, *J*= 8.0 Hz), 7.13 (m, 1H), 7.01-6.92 (m, 1H), 5.78 (d, 1H, *J*= 9.5 Hz), 5.27 (q, 1H, *J*= 6.5 Hz), 4.81-4.78 (dd, 1H, *J*= 13.5, 7.5 Hz), 4.67-4.64 (dd, 1H, *J*= 13, 6.0 Hz), 2.36 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$, δ ppm) δ 159.56, 141.41,136.52, 130.79, 129.66, 128.068, 128.28, 127.61, 127.01, 126.53, 124.76, 11608, 115.91, 83.79, 51.52, 20.10;HPLC (Chiralcel OD-H, hexane/2-propanol = 90/10, flow 0.80 mL/min, λ=220 nm) $t_{(major)}$ = 34.6 min and $t_{(minor)}$ = 44.1 min.



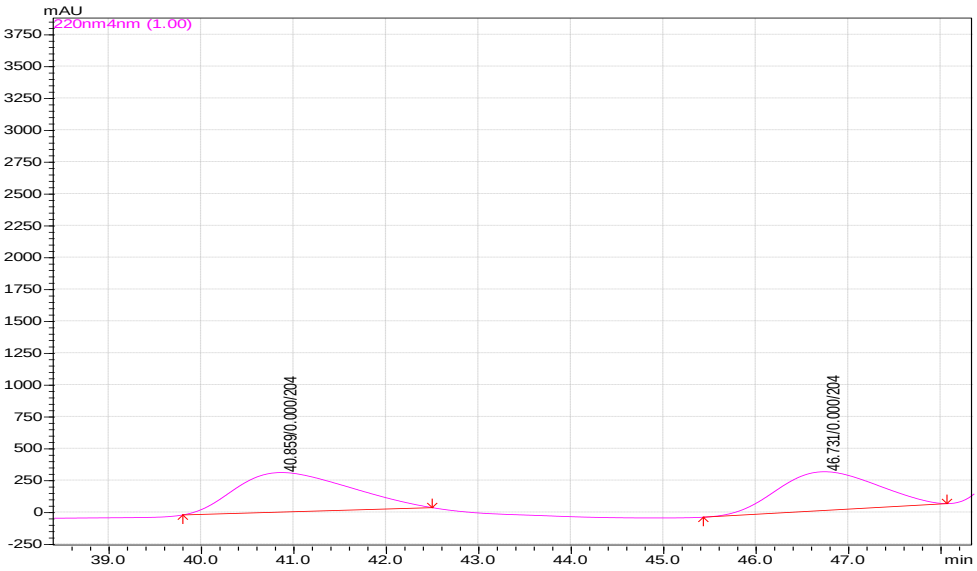
Racemic



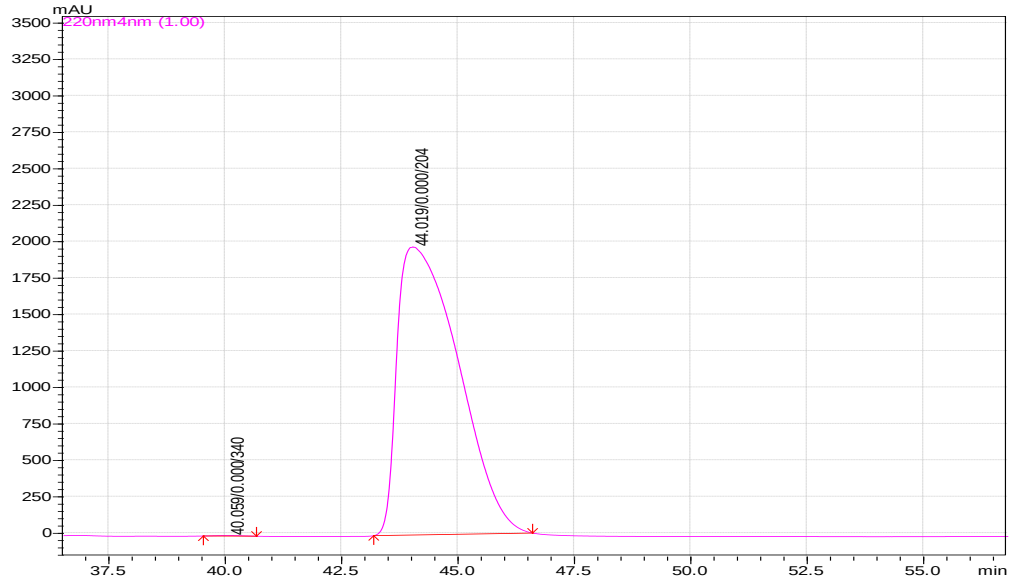
Chiral

(vii). 2-Nitro-1-(4'-fluorophenyl)-*N*-tosylethanamine **(2g)**

White solid, 99% ee; ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) δ 7.82 (d, 1H, *J*= 8.5 Hz), 7.64 (d, 2H, *J*= 8.5 Hz), 7.25 (d, 2H, *J*= 8.5 Hz), 7.09-7.07 (m, 2H), 6.96-6.92 (m, 2H), 5.50 (d, 1H, *J*= 7.0 Hz), 5.0 (q, 1H, *J*= 7.0 Hz), 4.81-4.80 (dd, 1H, *J*= 13, 6.5 Hz), 4.65-4.64 (dd, 1H, *J*= 13, 6.0 Hz), 2.41 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$, δ ppm) δ 163.12, 146.08, 138.28, 131.68, 130.29(d, *J*= 33Hz),129.00, 128.35, 118.18 (d, *J*= 87 Hz), 80.76, 56.60, 23.43; HPLC (Chiralcel IC, hexane/2-propanol = 80/20, flow 0.70 mL/min, λ=220 nm) $t_{(major)}$ = 44 min and $t_{(minor)}$ = 40 min.



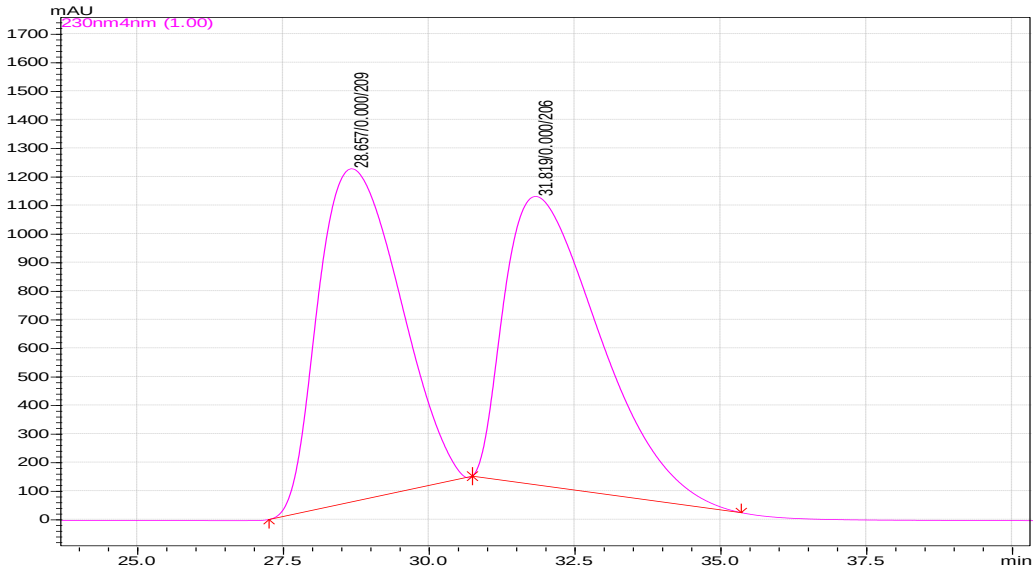
Racemic



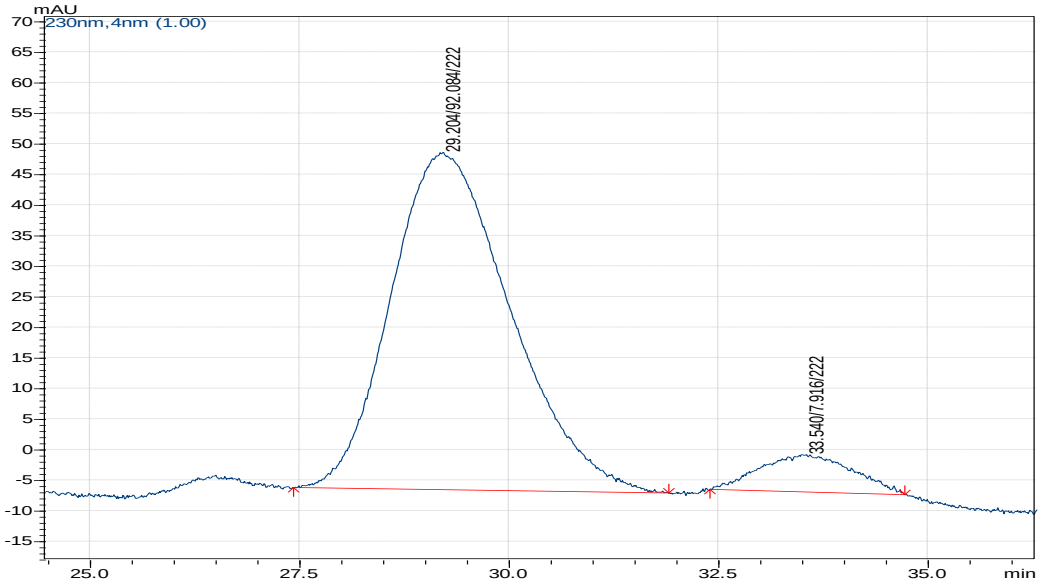
Chiral

(viii). 2-Nitro-(1-naphtyl)-*N*-tosylethanamine **(2h)**

White solid, 99% ee; ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) δ 7.82 (d, 1H, *J*= 8.0 Hz), 7.76 (d, 2H, *J*= 8.0 Hz), 7.55 (d, 2H, *J*= 8.0 Hz), 7.50-7.44 (m, 2H), 7.36-7.30 (m, 2H), 7.07 (d, 2H, *J*= 8.0 Hz), 5.88-5.83 (q, 1H, *J*= 6.5 Hz), 5.76 (d, 1H, *J*= 7.5 Hz), 4.98-4.97 (dd, 1H, *J*= 13.0, 7.5 Hz), 4.87-4.86 (dd, 1H, *J*= 13.0, 6.0 Hz), 2.32 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$, δ ppm) δ 143.84, 136.12, 133.86, 130.71, 129.82, 129.72, 129.51, 129.20, 127.21, 127.13, 126.22, 125.18, 124.55, 121.55, 78.60, 51.72, 21.46; HPLC (Chiralcel OD-H, hexane/2-propanol = 80/20, flow 1.0 mL/min, λ =240 nm) $t_{(major)}$ = 30.07 min and $t_{(minor)}$ = 24.8 min.



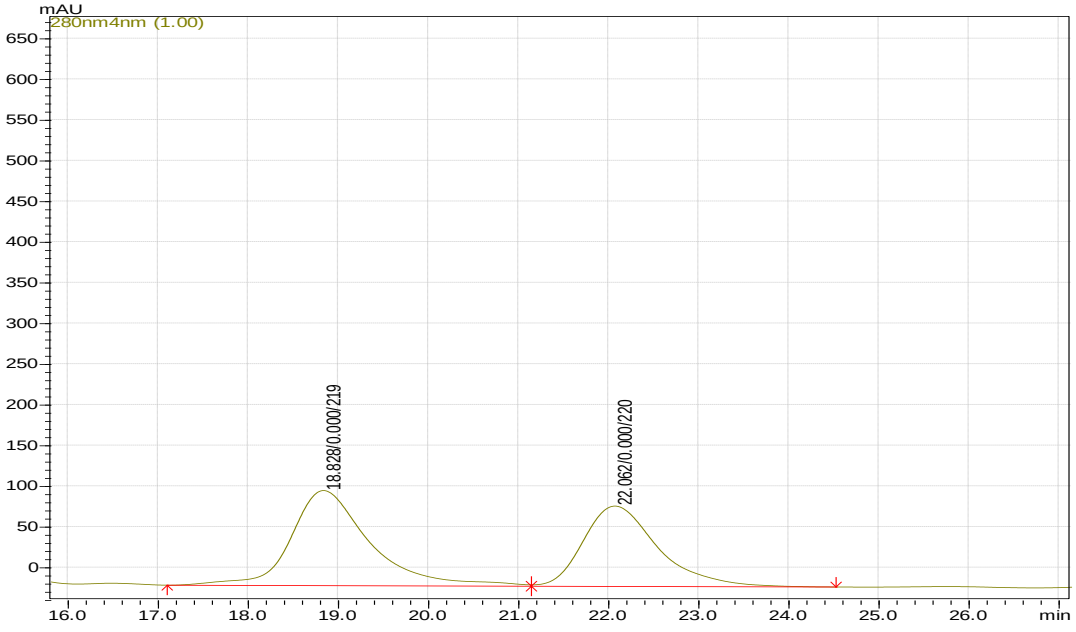
Racemic



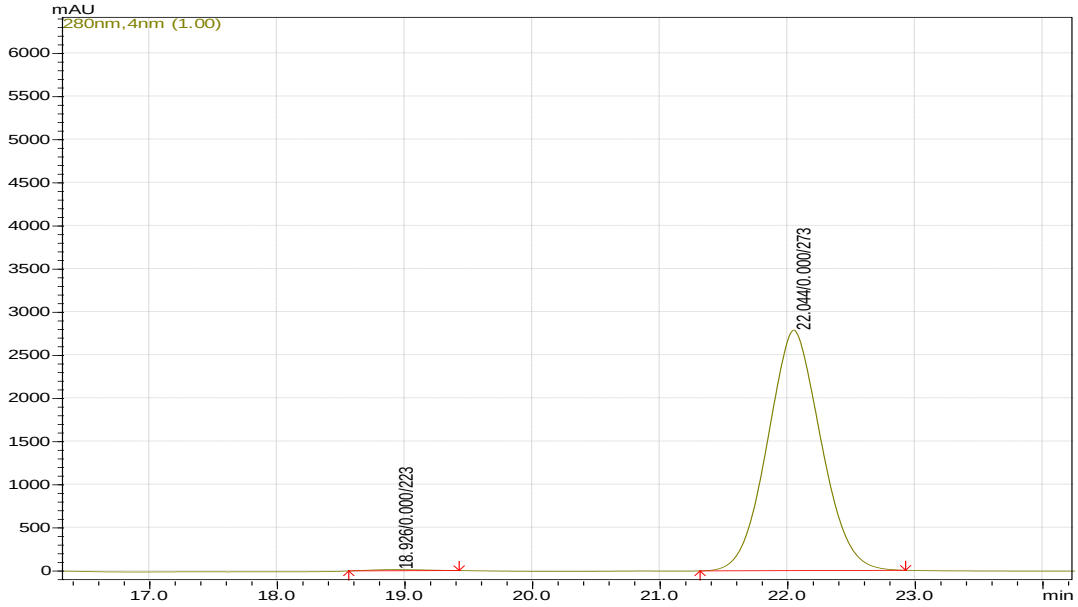
Chiral

(ix). 2-Nitro-(2-naphtyl)-*N*-tosylethanamine **(2i)**

White solid, 99% ee; ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) δ 7.79 (m, 2H), 7.75-7.73 (d, 1H, *J*= 8.5 Hz), 7.69 (m, 1H), 7.63-7.61 (d, 1H, *J*= 8.5 Hz), 7.50 (m, 3H), 7.17 (m, 3H), 5.45-5.43 (d, 1H, *J*= 7.0 Hz), 5.15-5.14 (q, 1H, *J*= 7.0 Hz), 4.94-4.91 (dd, 1H, *J*= 13.0, 6.5 Hz), 4.79-4.77 (dd, 1H, *J*= 13.0, 6.0 Hz), 2.30 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$, δ ppm) δ 143.49, 135.84, 132.60, 132.37,131.66, 129.10, 128.80, 127.40, 127.07, 126.57, 126.35, 126.25, 126.06, 122.72, 78.31, 54.98, 20.85; HPLC (Chiralcel AD-H, hexane/2-propanol = 85/15, flow 1.0 mL/min, λ =280 nm) $t_{(major)}$ = 22.0 min and $t_{(minor)}$ = 18.9 min.



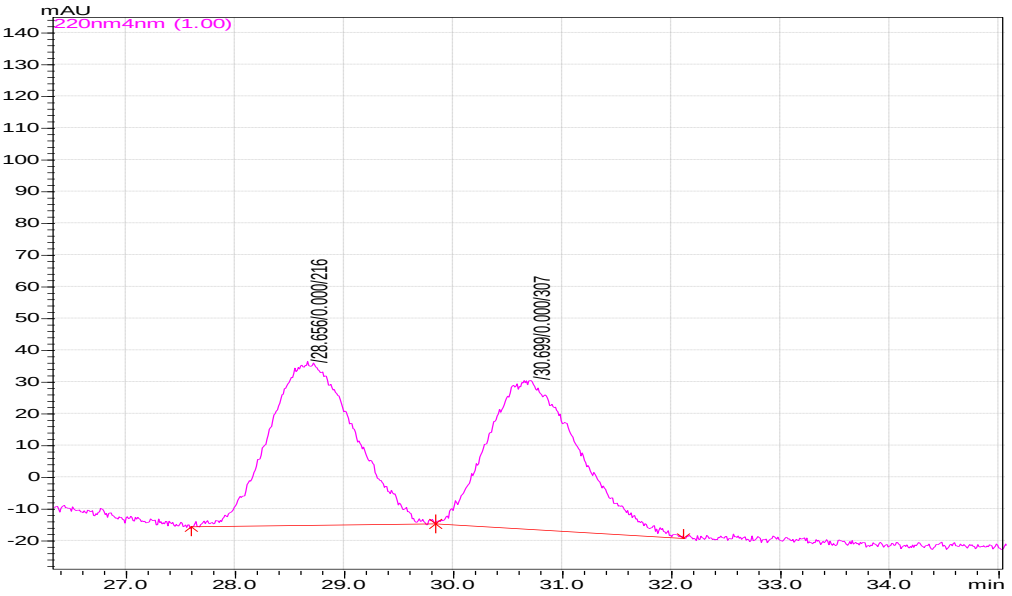
Racemic



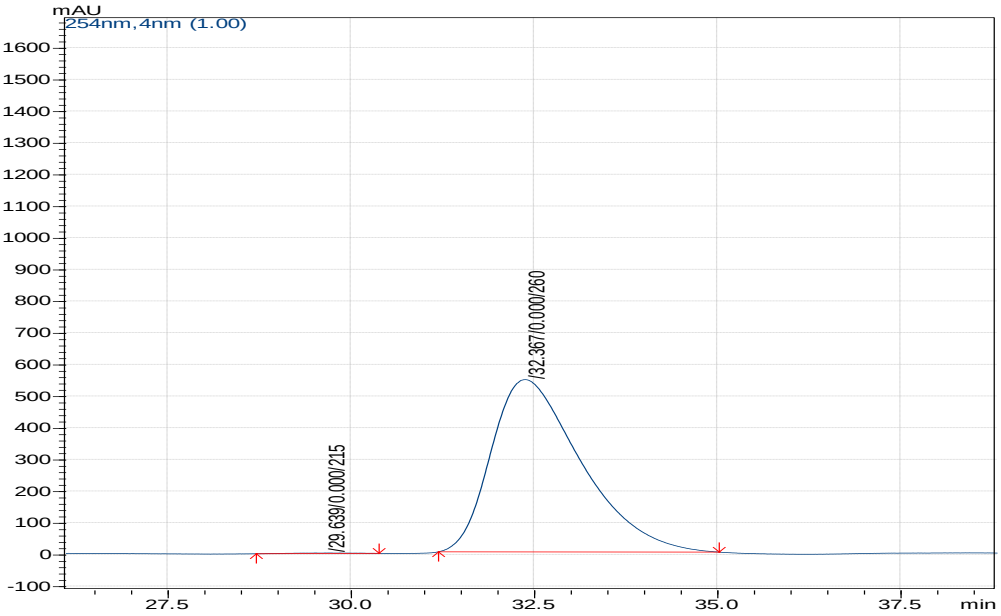
Chiral

(x). 2-Nitro-1-ethylbenzen-*N*-tosylethanamine **(2j)**

White solid, 99% ee; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.75-7.73 (m, 3H), 7.29-7.25 (m, 3H), 7.19-7.18 (m, 4H), 4.43-4.33 (m, 1H), 3.77-3.57 (m, 1H), 2.41-2.39 (m, 3H), 2.35 (s, 3H), 2.16-2.10 (m, 2H), ^{13}C NMR (200 MHz, $CDCl_3$, δ ppm) δ 144.26, 143.26, 139.20, 137.12, 129.93, 129.60, 128.55, 127.12, 126.36, 78.40, 51.27, 33.97; 31.50, 30.95, 21.57. HPLC (Chiralcel OD-H, hexane/2-propanol = 90/10, flow 0.8 mL/min, λ =220 nm) $t_{(major)}$ = 28.6.0 min and $t_{(minor)}$ = 30.6 min



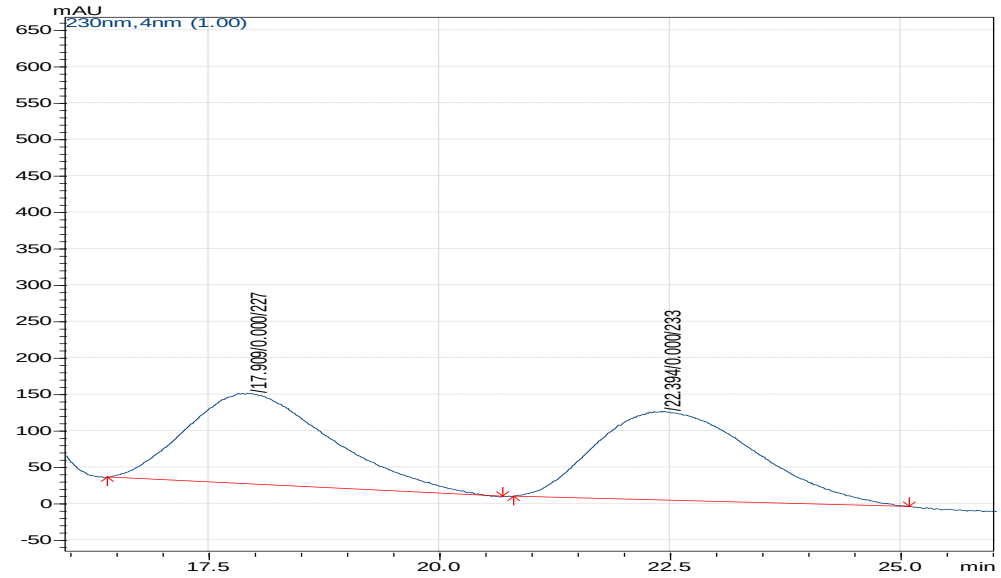
Racemic



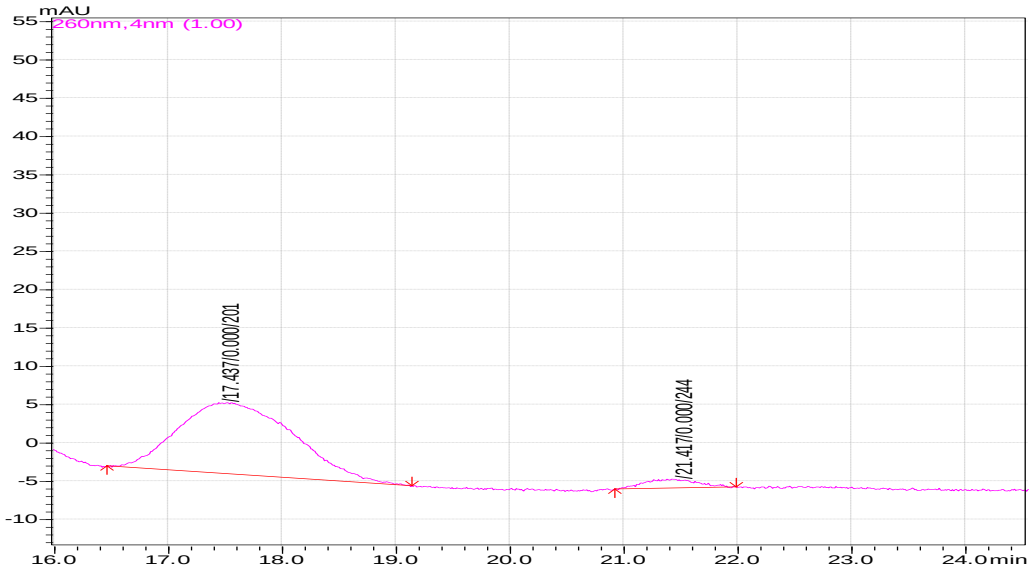
Chiral

(xi). 2-Nitro-1-octane-*N*-tosylethanamine **(2k)**

White solid, 91% ee; ^{1}H NMR (200 MHz, $CDCl_3$**)** δ 7.81-7.74 (m, 2H), 7.30-7.27 (m, 2H), 4.47-4.32 (m, 2H), 3.74 (m, 2H), 2.42 (s, 3H), 1.85 (m, 1H), 1.49-1.09 (m, 12H), 0.88 (m, 3H), ^{13}C NMR (500 MHz, $CDCl_3$, δ ppm) δ 143.50, 139.15, 129.68, 126.39, 80.74, 44.59, 31.79, 29.36, 25.26, 22.62, 21.51, 14.08.; HPLC (Chiralcel OD-H, hexane/2-propanol = 90/10, flow 0.8 mL/min, λ =230 nm) $t_{(major)}$ = 17.9 min and $t_{(minor)}$ = 22.3 min.



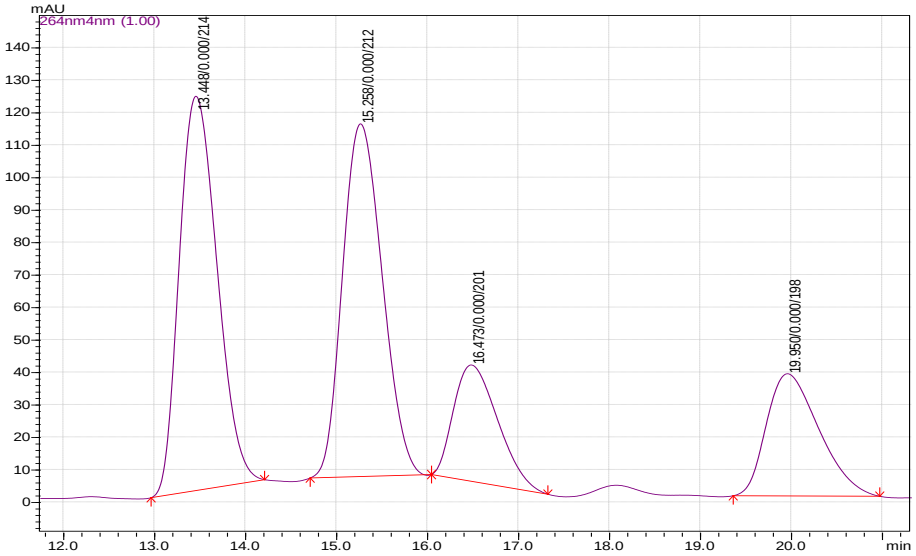
Racemic



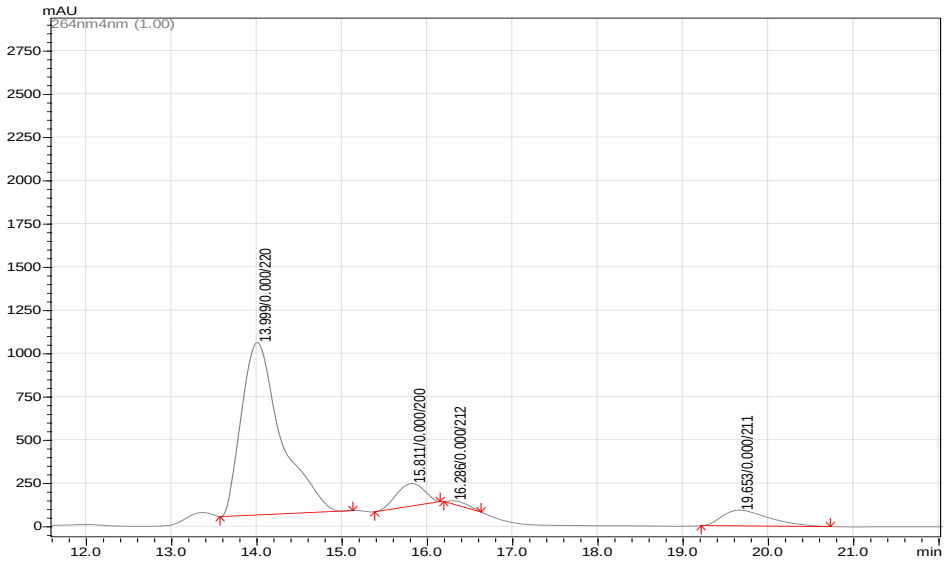
Chiral

(xii). 2-Methyl-2-Nitro-1-phenyl-*N*-tosylethanamine **(2a)**

Yield: 82%; Diastereomeric ratio (*anti*/*syn*, 10:90 was determined by HPLC; Enantiomeric excess of diastereomers were determined by two different chiral HPLC (Chiralpak IA, hexan/2-propanol = 85:15, 0.8 mL/min); Ee_{syn}: 81%, Ee_{anti}: 85%, t_r(*anti*) = 15.81(minor), t_r(*anti*) = 13.92 (major); t_r(*syn*) = 19.63(major), t_r(*syn*) = 16.20 (minor); ^{1}H NMR (500 MHz, $CDCl_3$,δ ppm): δ 7.53-7.51 (m, 2H), 7.17-7.07 (m, 5H), 7.01-6.99 (m, 2H), 6.14-6.13 (m, 1H), 5.97-5.96 (brS, 1H), 4.86-4.74 (m, 2H), 2.33 (d, 3H, *J*= 7.0 Hz), 1.52 (d, 1H, *J*= 6.5 Hz), 1.43 (d, 1H, *J*= 6.5 Hz), ^{13}C NMR (500 MHz, $CDCl_3$) δ 143.48, 136.85, 136.67, 135.29, 135.05, 129.48, 129.38, 128.92, 128.75, 128.53, 127.00, 126.72, 86.83, 86.19, 60.56, 21.44, 16.89;



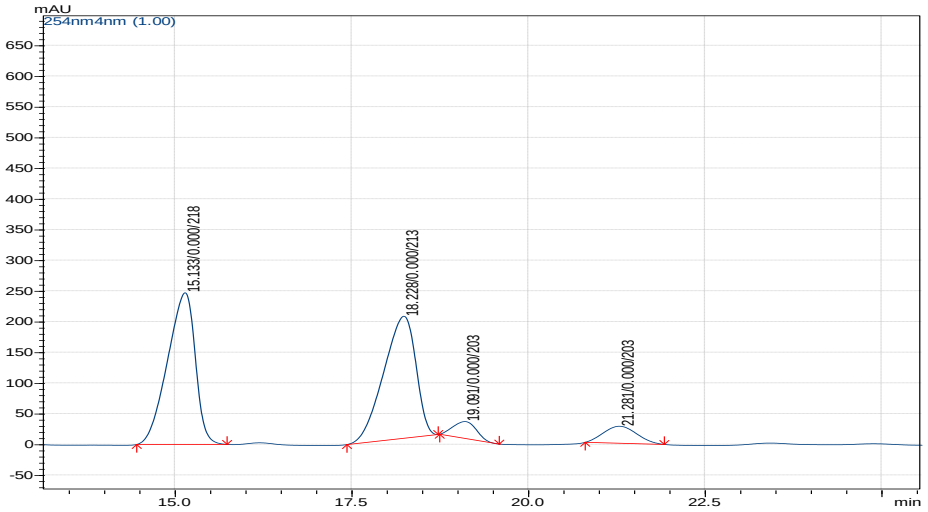
Racemic



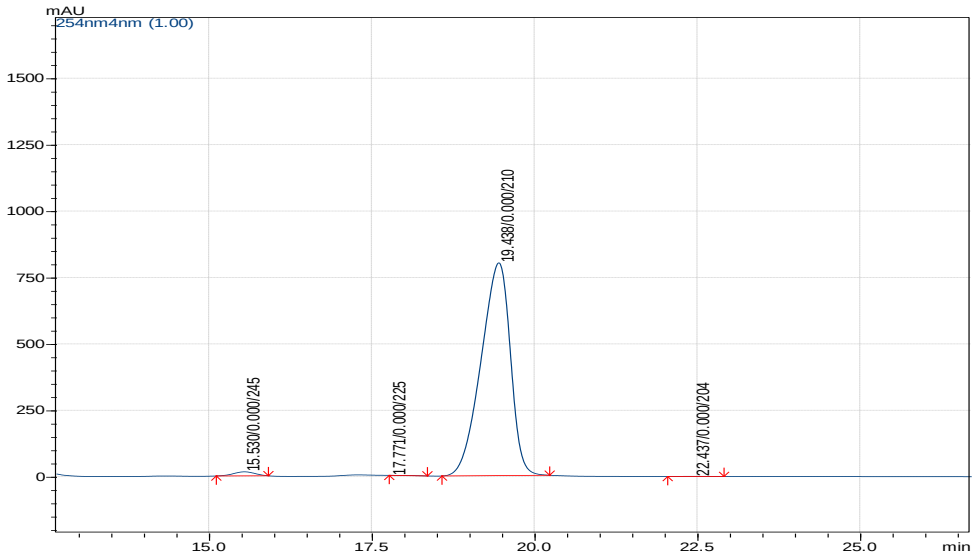
Chiral

(xiii). 2-Methyl-2-Nitro-1-(2'-methoxyphenyl)-*N*-tosylethanamine **(2b)**

Yield: 78%; Diastereomeric ratio (anti/syn, 03:97 was determined by HPLC; Enantiomeric excess of diastereomers were determined by two different chiral HPLC (Chiralpak AD-H, hexan/2-propanol = 85:15, 0.8 mL/min); Ee(syn): 99%, Ee(anti): 69%, t_r(anti) = 17.77(minor), t_r(anti) = 15.53(major); t_r(syn) = 19.43(major), t_r(syn) = 22.43(minor); ^{1}H NMR (200 MHz, $CDCl_3$, δ ppm): δ 7.42-7.38 (m, 2H), 7.19-6.81 (m, 4H), 6.69-6.53 (m, 2H), 6.13 (dd, 1H, *J*= 10.6 Hz, 10.4 Hz), 5.02-4.95 (m,1H), 4.79-4.48 (m, 1H), 3.73 (d, 3H, *J*= 6.8 Hz), 2.21 (s, 3H), 2.30 (s, 3H), 1.65 (d, 1H, *J*= 6.6 Hz), 1.33 (d, 3H, *J*= 6.6 Hz), ^{13}C NMR (500 MHz, $CDCl_3$, δ ppm) δ 156.1, 143.35, 143.05, 137.03, 136.73, 129.93, 129.06, 126.84, 122.49, 120.84, 110.81, 110.69, 85.07, 59.98, 55.37, 21.40, 17.49.



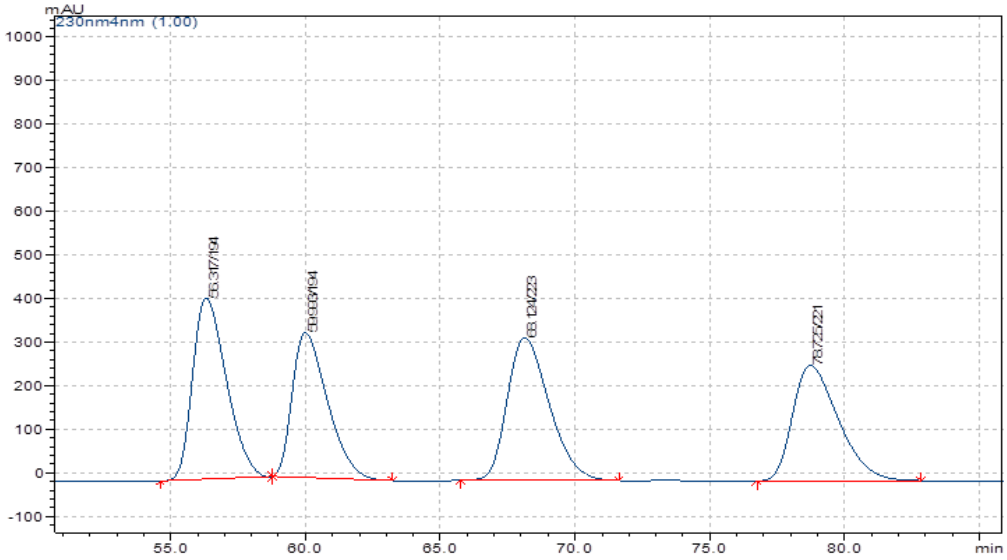
Racemic



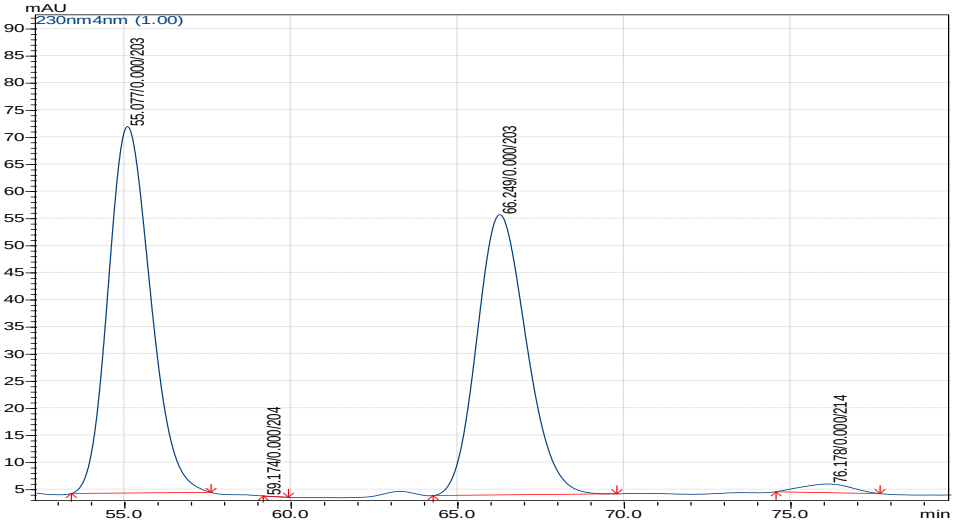
Chiral

(xiv). 2-Methyl-2-Nitro-1-(4'-methoxyphenyl)-*N*-tosylethanamine **(2c)**

Yield: 72%; Diastereomeric ratio (anti/syn, 48:52 was determined by HPLC; Enantiomeric excess of diastereomers were determined by two different chiral HPLC (Chiralpak AD-H, hexan/2-propanol =90:10, 0.8 mL/min); Ee(syn): 93%, Ee(anti): 99%, t_r(anti) = 59.23(minor), t_r(anti) = 55.07(major); t_r(syn) = 66.20(major), t_r(syn) = 76.17(minor); ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): δ 7.52-7.45 (m, 2H), 7.09-6.84 (m, 4H), 6.75-6.58 (m, 2H), 6.31-6.10 (m, 1H), 5.15-4.58 (m, 2H), 3.80-3.70 (m, 3H), 2.32 (d, 3H, J= 7.4 Hz), 1.72 (d, 1H, J= 6.6 Hz), 1.59 (d, 1H, J= 6.0 Hz), ^{13}C NMR (200 MHz, $CDCl_3$) δ 159.60, 143.48, 136.97, 130.26, 129.94, 129.31, 129.06, 128.11, 127.04, 126.83, 120.79, 114.22, 85.11, 60.30, 55.24, 21.39, 17.44.



Racemic

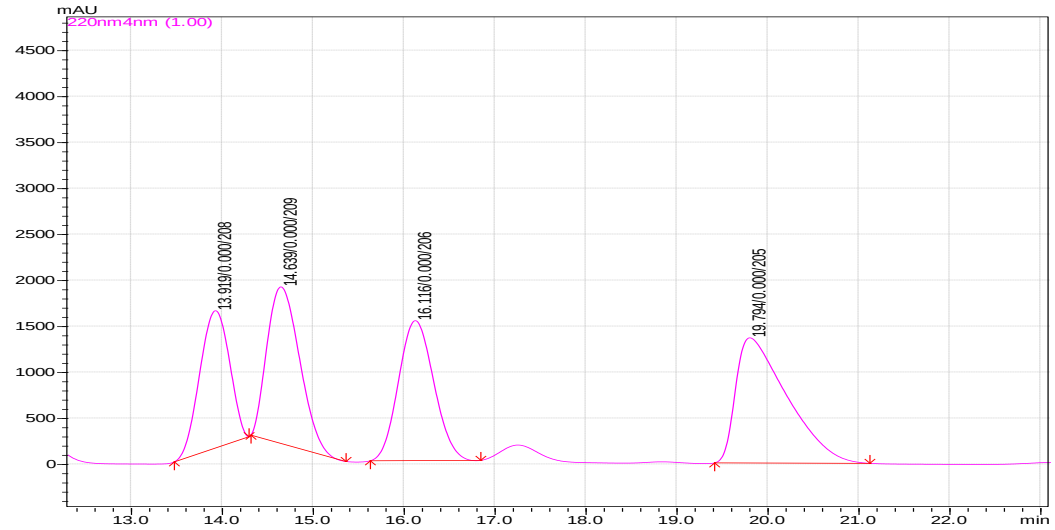


Chiral

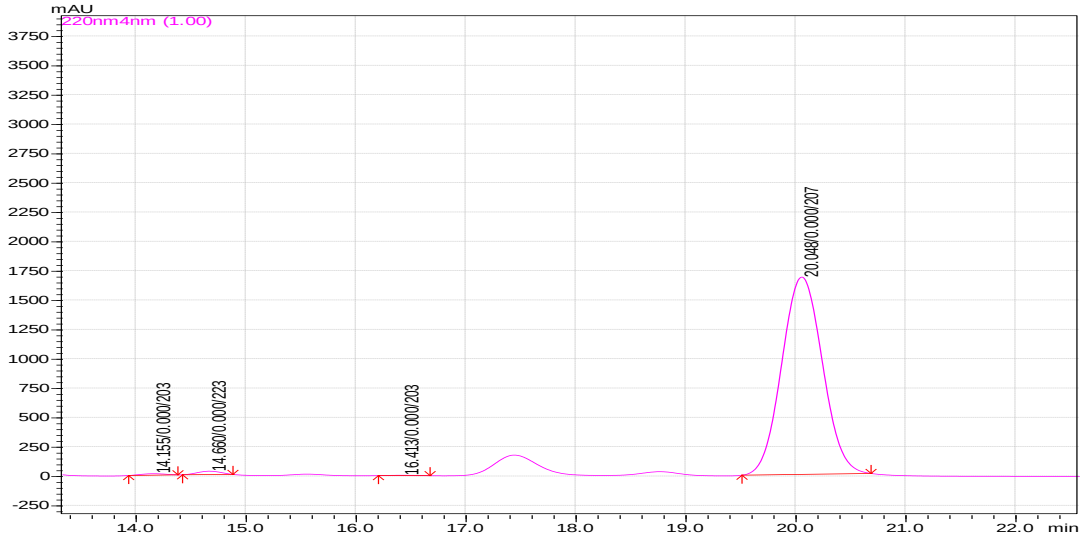
(xv). 2-Methyl-2-Nitro-1-p-tolyl-*N*-tosylethanamine **(2e)**

Yield: 68%; Diastereomeric ratio (anti/syn, 02:98 was determined by HPLC; Enantiomeric excess of diastereomers were determined by two different chiral HPLC (Chiralpak AD-H, hexan/2-propanol =85:15, 0.8 mL/min); Ee(syn): 99%, Ee(anti): 45%, t_r(anti) = 14.15(minor), t_r(anti) = 14.66(major); t_r(syn) = 20.04(major), t_r(syn) = 16.41(minor); ^{1}H NMR (200 MHz, $CDCl_3$, δ ppm): δ 7.54 (d, 2H, *J*= 8.0 Hz), 7.13-7.09 (m, 2H), 7.01-

6.78 (m, 4H), 5.78 (d, 1H, *J*= 9.2 Hz), 5.58 (d, 1H, *J*= 8.8 Hz), 4.85-4.66 (m, 2H), 2.35 (s, 3H), 2.26 (s, 3H), 1.59 (d, 1H, *J*= 6.6 Hz), 1.47 (d, 1H, *J*= 6.4 Hz), ^{13}C NMR (500 MHz, $CDCl_3$) δ 143.61, 143.41, 138.47, 136.88, 136.71, 132.21, 132.02, 129.55, 129.38, 129.34, 127.11, 127.04, 126.71, 126.64, 86.83, 86.26, 60.40, 21.03, 16.81.



Racemic

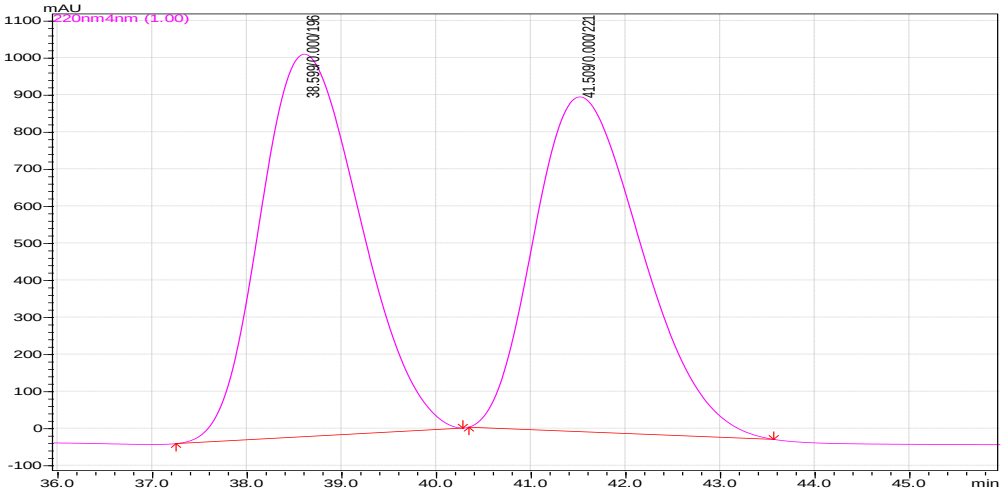


Chiral

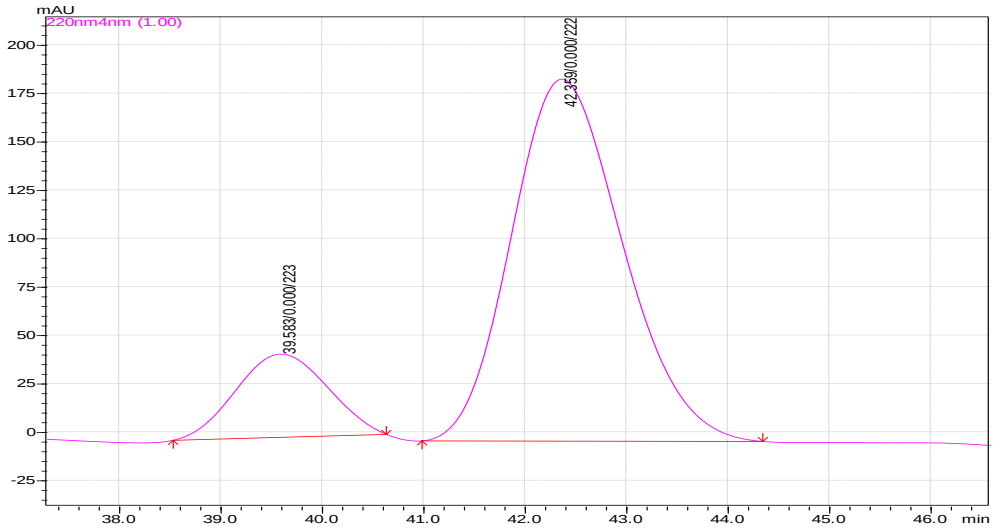
(xvi). 2-Methyl- 2-Nitro-(2-naphtyl)-*N*-tosylethanamine **(2i)**

Yield: 70%; Diastereomeric ratio (anti/syn, 07:93 was determined by HPLC; Enantiomeric excess of diastereomers were determined by two different chiral HPLC (Chiralpak IC, hexan/2-propanol =90:10, 1.0 mL/min); Ee(syn): 89%, Ee(anti): 65%, t_r(anti) = 39.58 (minor), t_r(anti) = 42.32 (major); t_r(syn) = 85.48 (major), t_r(syn) = 124.72 (minor); ^{1}H NMR (200 MHz, $CDCl_3$, δ ppm): δ 7.76-7.71 (m, 1H), 7.66-7.57 (m, 2H),

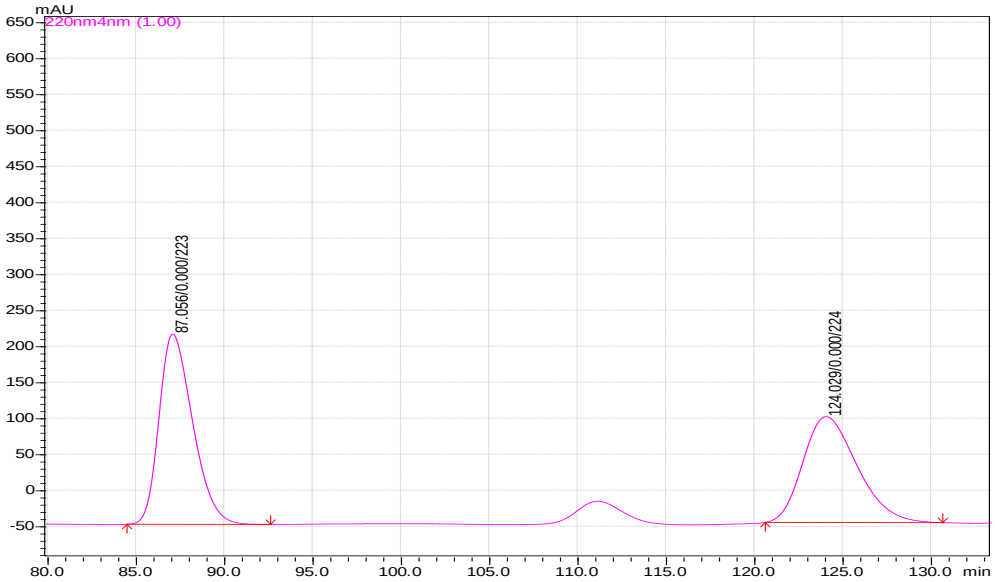
7.48-7.45 (m, 4H), 7.28 (brS, 1H), 7.09-7.04 (m, 1H), 6.94-6.90 (m, 2H), 5.95-5.91 (m, 1H), 5.71-5.67 (m, 1H), 4.93-4.90 (m, 2H), 2.17 (s, 3H), 2.14 (d, 3H, *J*= 6.4 Hz), 1.66 (d, 2H, *J*= 6.5 Hz), 1.52 (d, 1H, *J*= 6.0 Hz), ^{13}C NMR (500 MHz, $CDCl_3$) δ 143.72, 141.24, 136.52, 132.74, 131.90, 129.33, 129.21, 128.95, 127.92, 127.53, 127.03, 126.68, 126.56, 123.44, 117.36, 108.96, 108.68, 108.48, 85.8, 60.53, 21.23, 15.72.



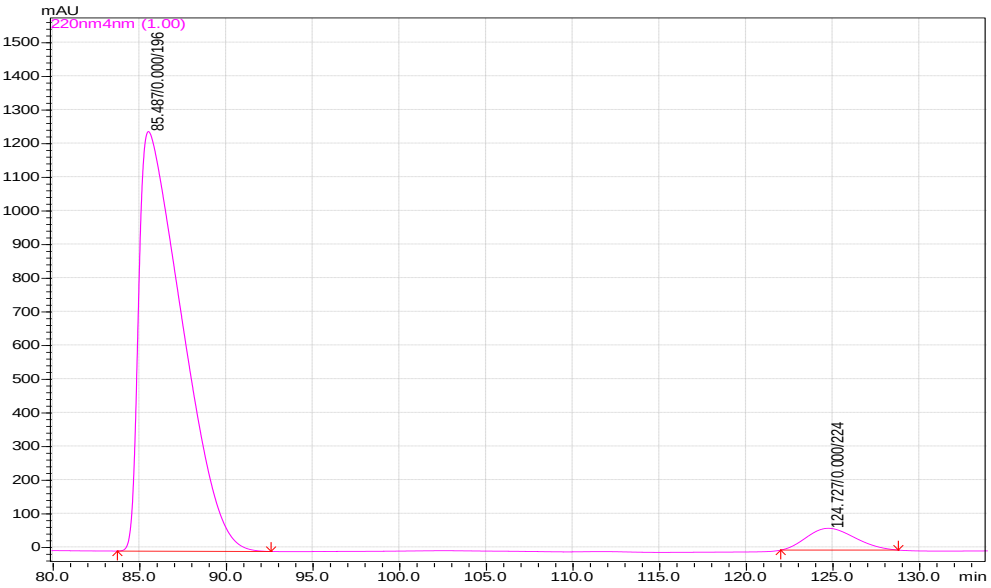
Racemic



Chiral



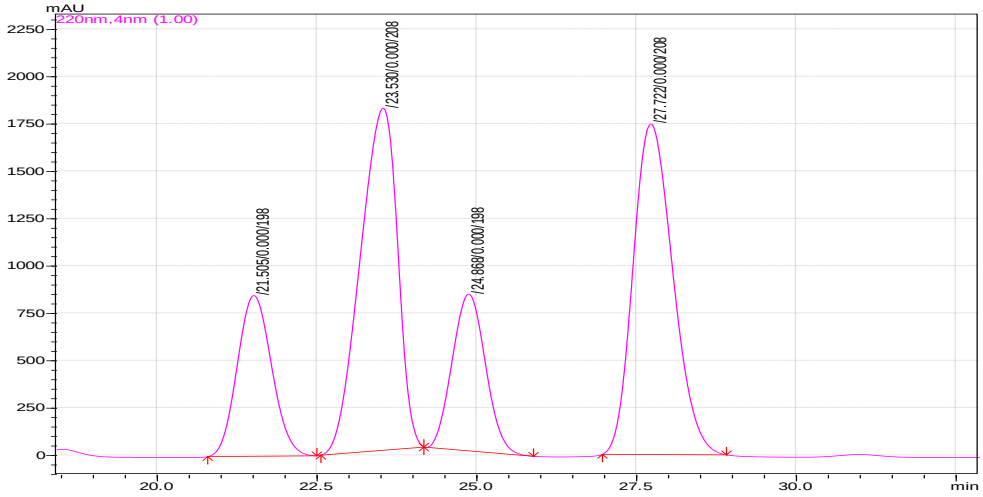
Racemic



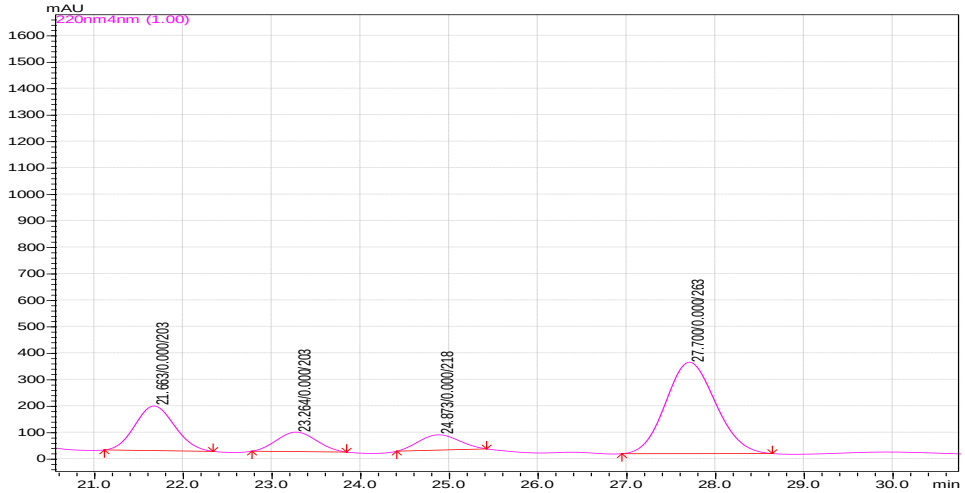
Chiral

(xvii). 2-Methyl-2-Nitro-1-(2'-cholrophenyl)-*N*-tosylethanamine **(2j)**

Yield: 65%; Diastereomeric ratio (anti/syn, 30:70 was determined by HPLC; Enantiomeric excess of diastereomers were determined by two different chiral HPLC (Chiralpak AD-H, hexan/2-propanol =90:10, 0.8 mL/min); Ee(syn): 69%, Ee(anti): 46%, t_r(anti) = 24.80 (minor), t_r(anti) = 21.62 (major); t_r(syn) = 27.72 (major), t_r(syn) = 23.25 (minor); ^{1}H NMR (200 MHz, $CDCl_3$, δ ppm): δ 7.55-7.51 (d, 2H, *J*= 8.0 Hz), 7.25-7.04 (m, 6H), 6.21-6.07 (m, 2H), 5.23-5.14 (m, 1H), 4.99-4.93 (m, 1H), 2.29 (s, 3H), 1.55 (d, 3H, *J*= 6.6 Hz), 0.87-0.84 (m, 1H), ^{13}C NMR (500 MHz, $CDCl_3$) δ 143.26, 136.29, 132.70, 132.10, 129.57, 129.34, 129.16, 129.07, 127.17, 126.70, 126.61, 85.25, 83.74, 56.89, 21.12, 16.73.



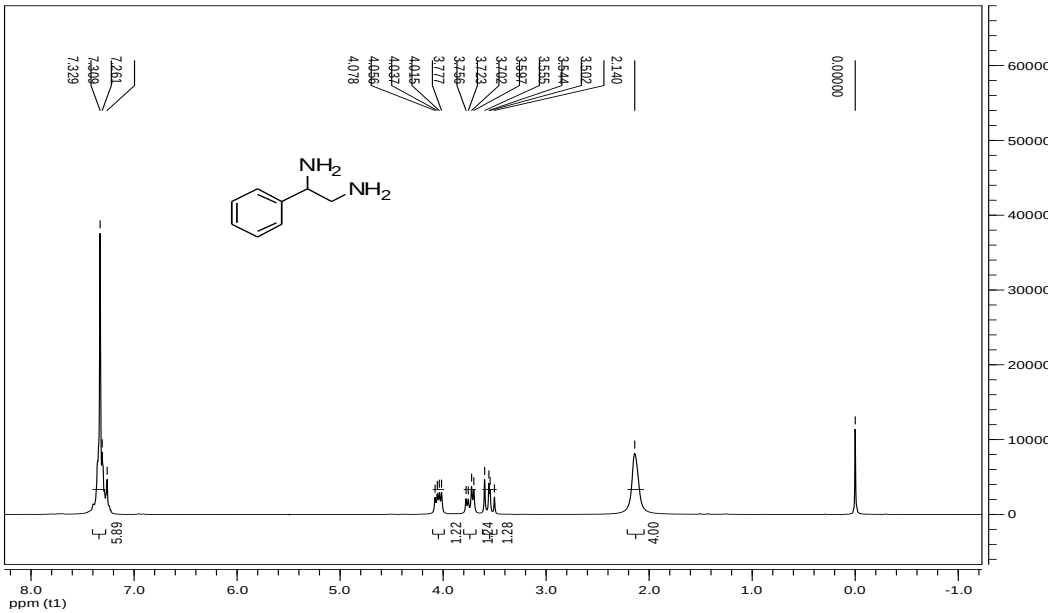
Racemic

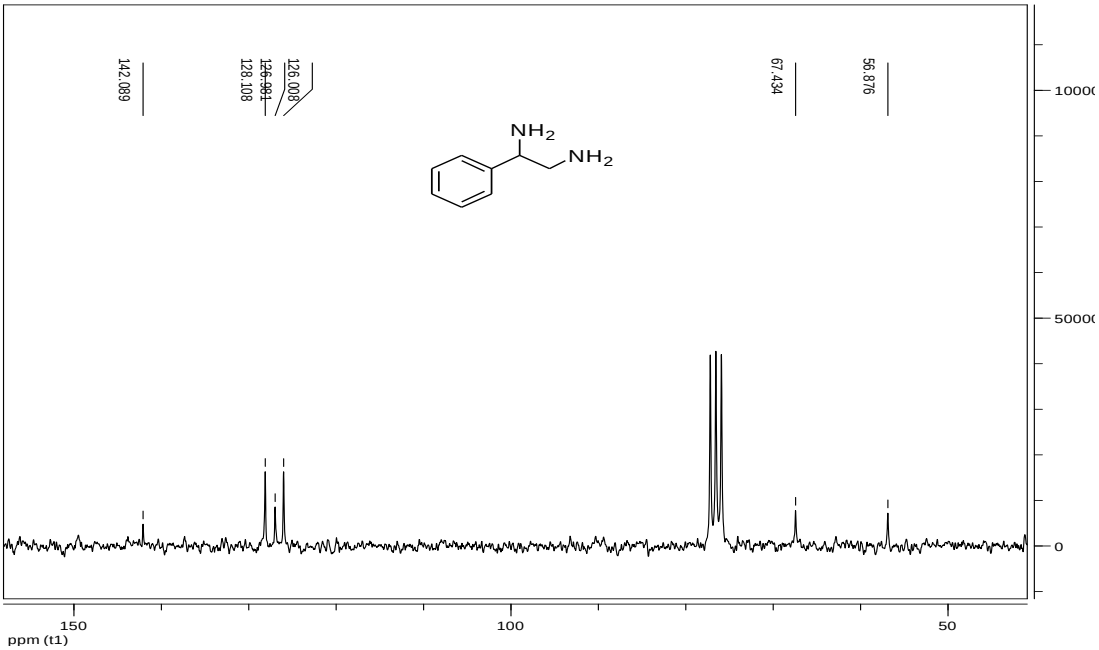


Chiral

6.^{1}H-NMR and ^{13}C-NMR spectra of 1, 2- Diamine

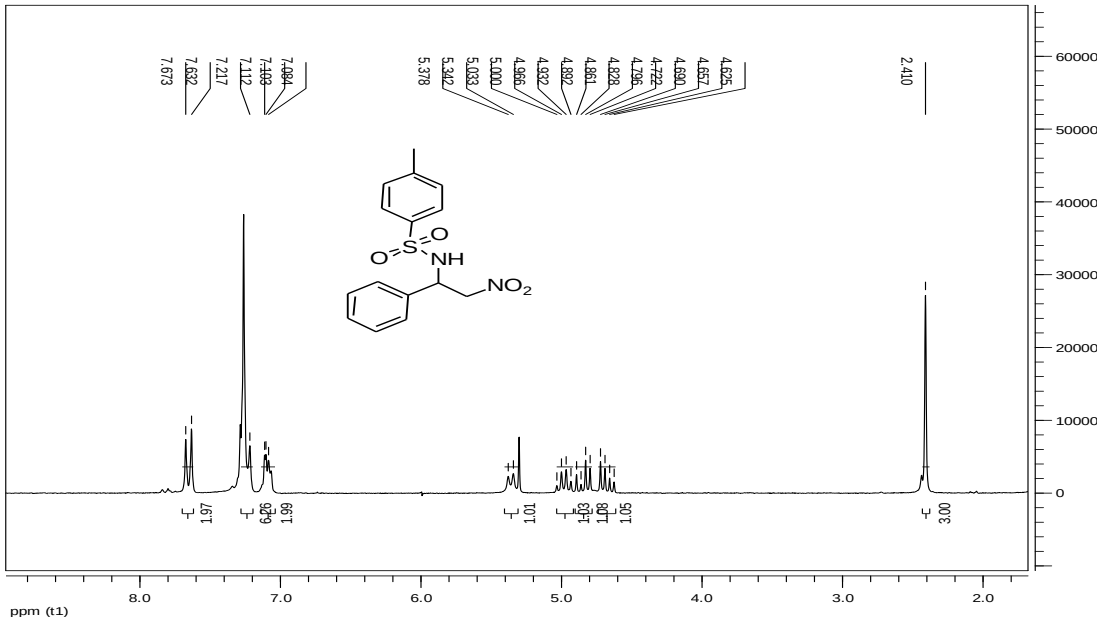
White solid, ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.28-7.35 (m, 5H), 4.01-4.07 (m, 1H), 3.70-3.77 (m, 1H), 3.50-3.59 (m, 1H), 2.14 (br, 4H); ^{13}C NMR (200 MHz, $CDCl_3$, δ ppm) δ 142.09, 128.14, 126.0, 67.43, 57.87;



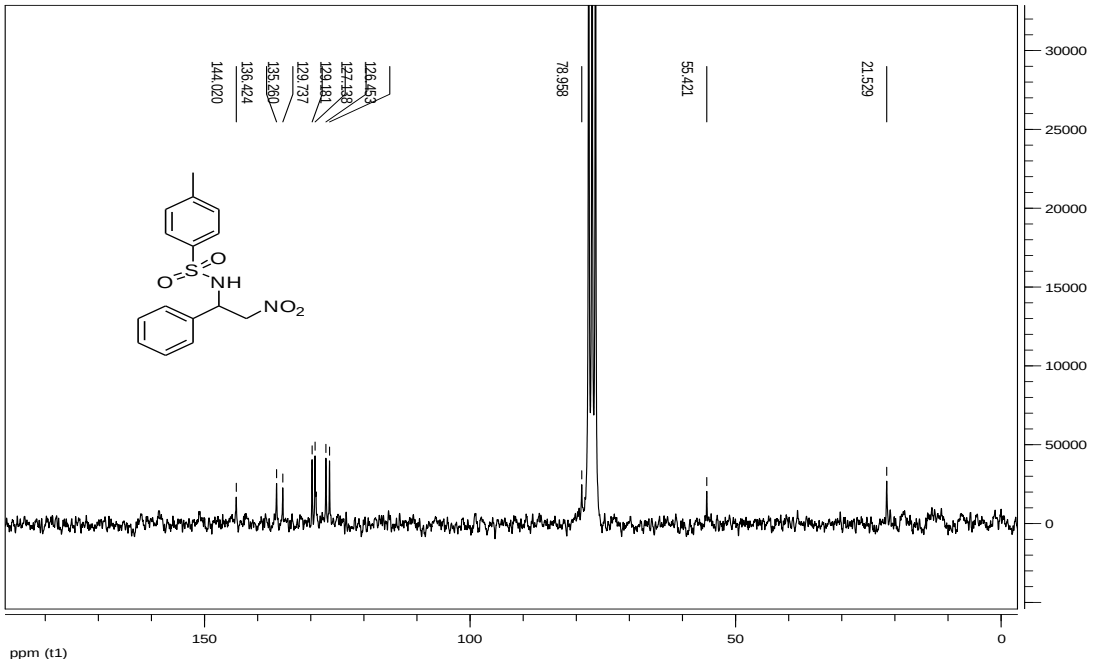


7. ^{1}H-NMR and ^{13}C-NMR spectra of Aza-Henry Products

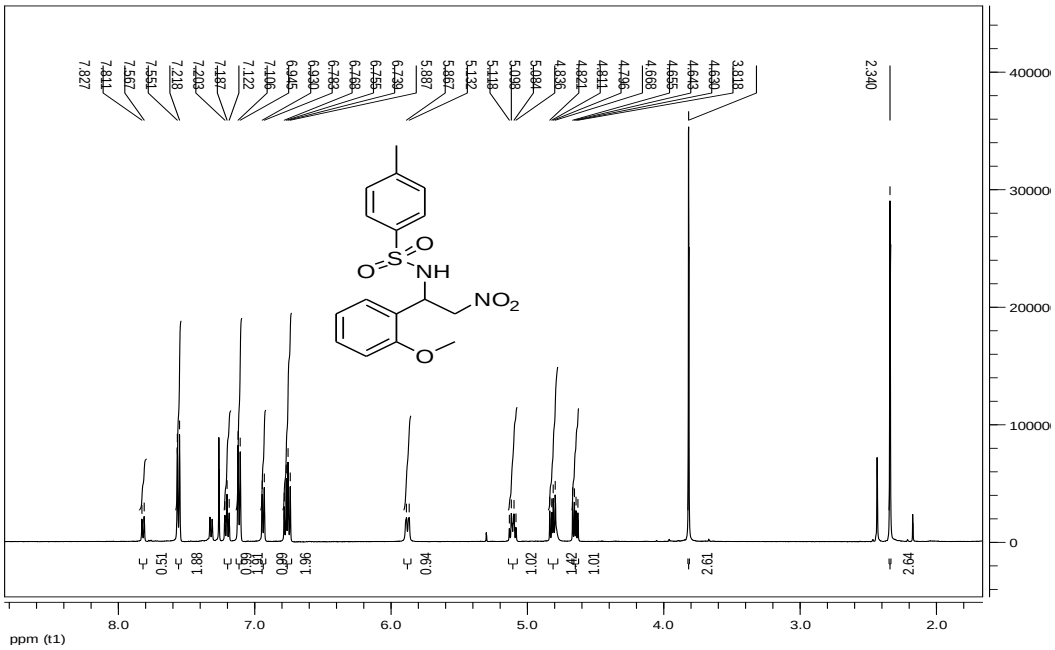
(7.1) ^{1}H-NMR spectra of 2-Nitro-1-phenyl-*N*-tosylethanamine



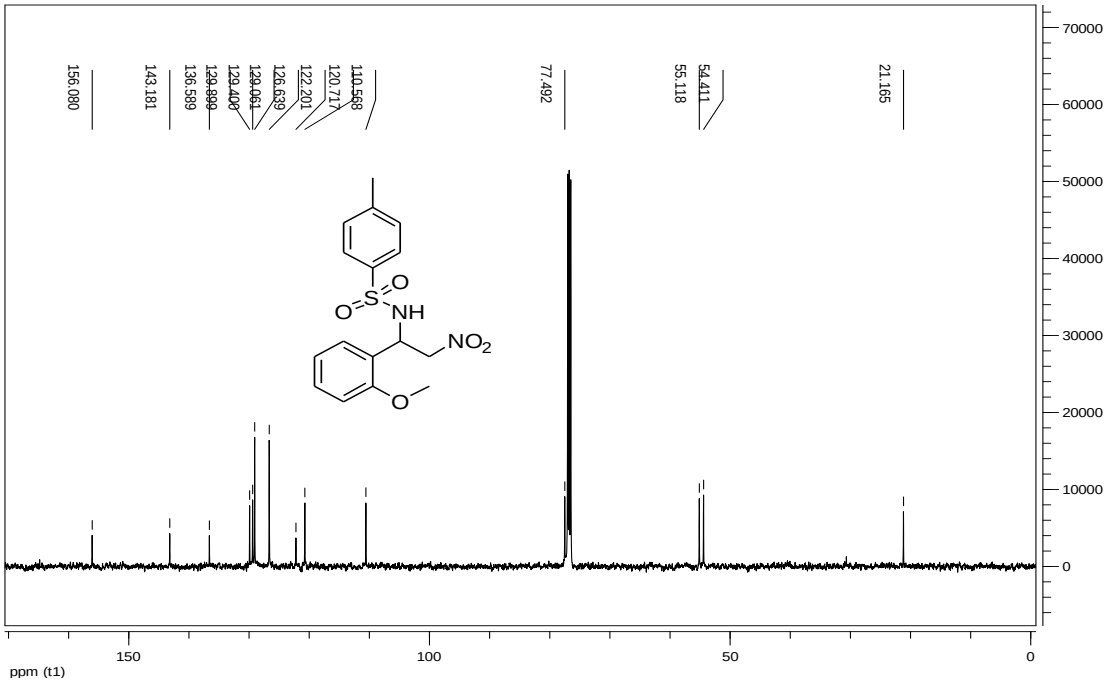
(7.2) ^{13}C-NMR spectra of 2-Nitro-1-phenyl-*N*-tosylethanamine



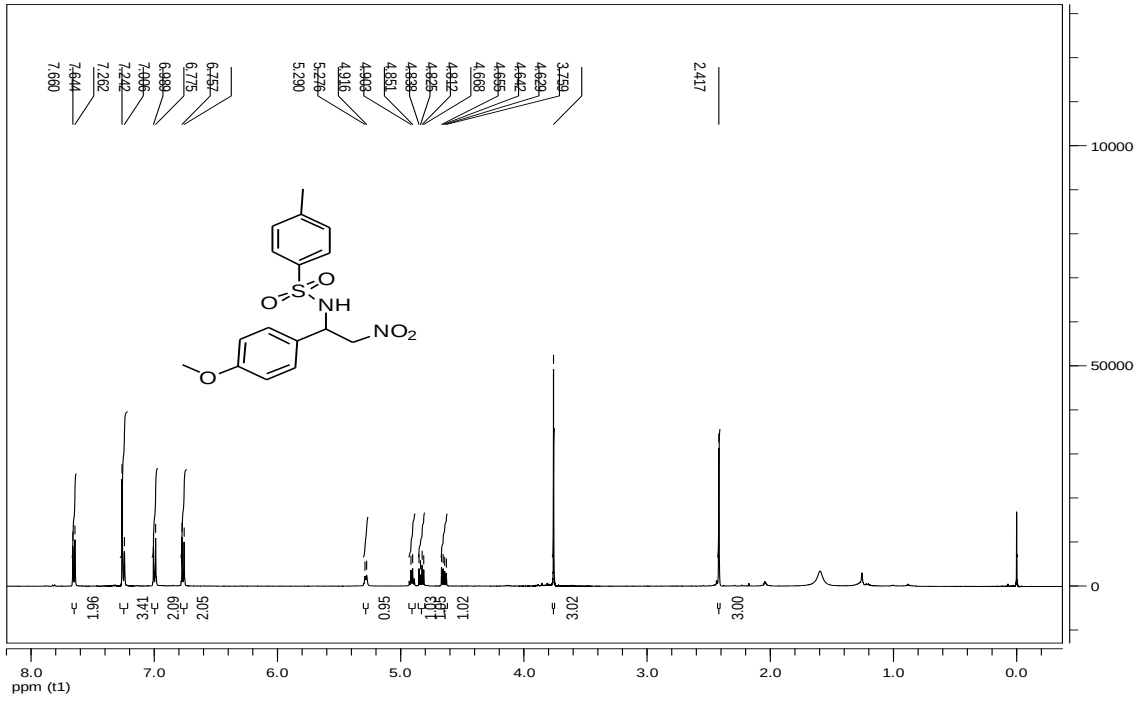
(7.3) ^{1}H-NMR spectra of 2-Nitro-1-(2'-methoxyphenyl)-*N*-tosylethanamine



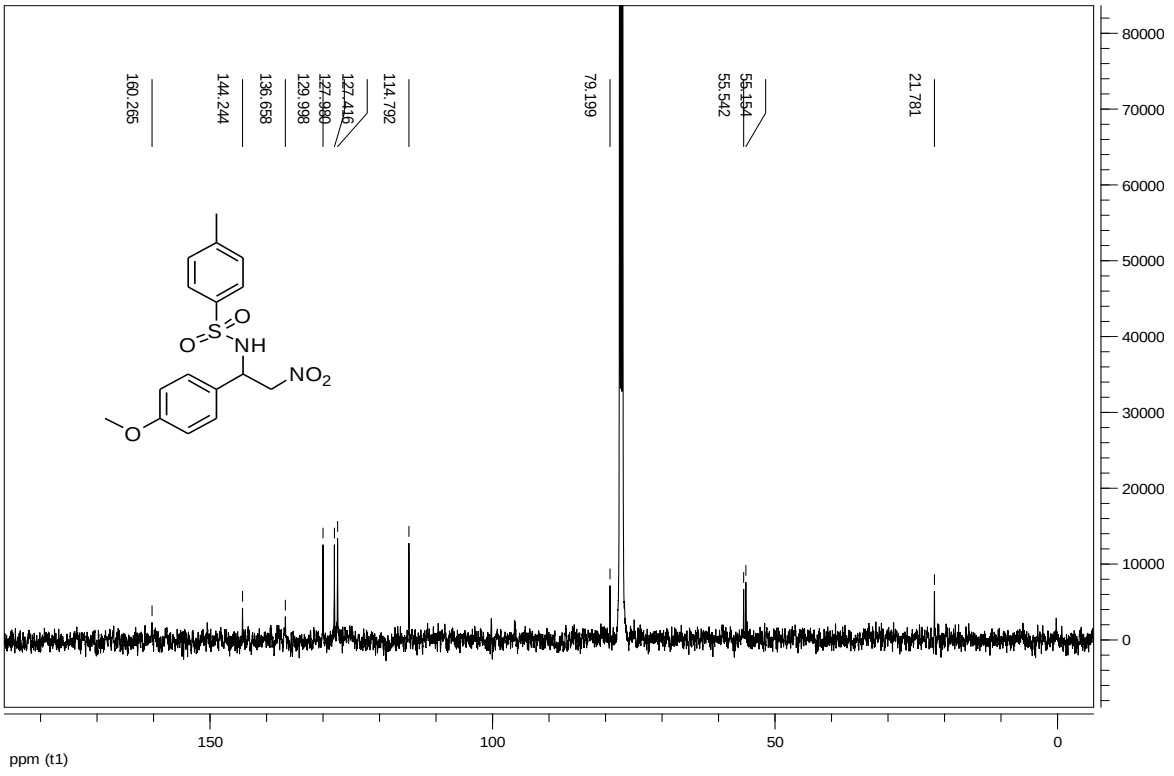
(7.4) ^{13}C-NMR spectra of 2-Nitro-1-(2'-methoxyphenyl)-*N*-tosylethanamine



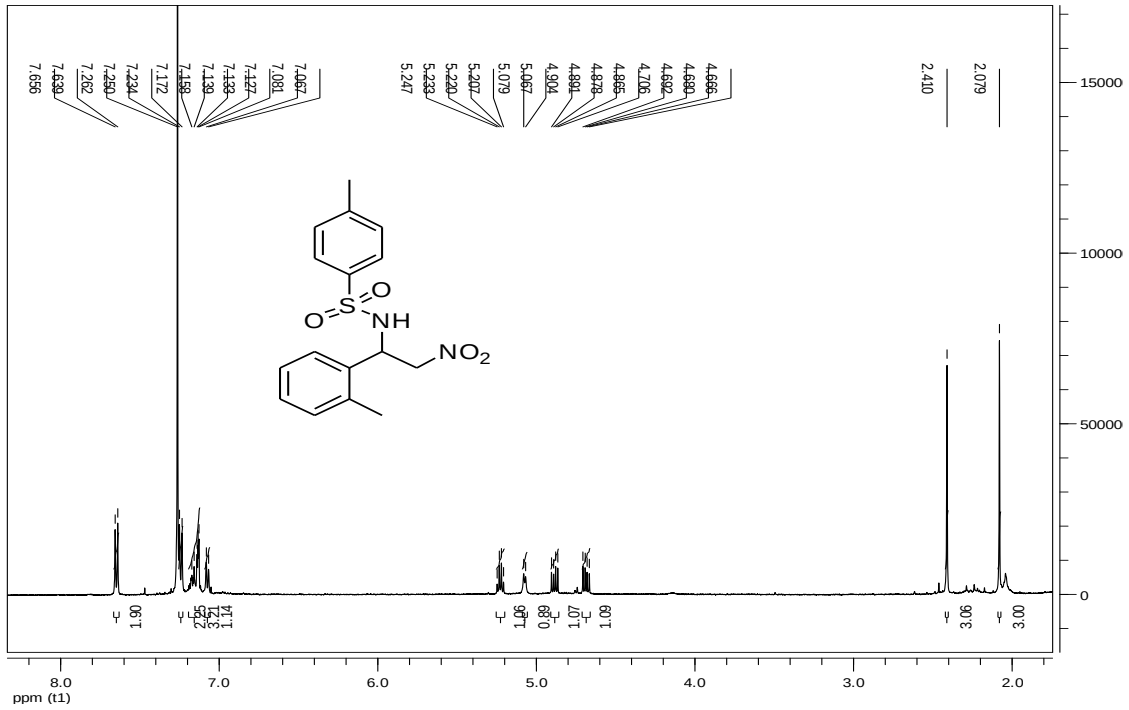
(7.5) ^{1}H-NMR spectra of 2-Nitro-1-(4'-methoxyphenyl)-*N*-tosylethanamine



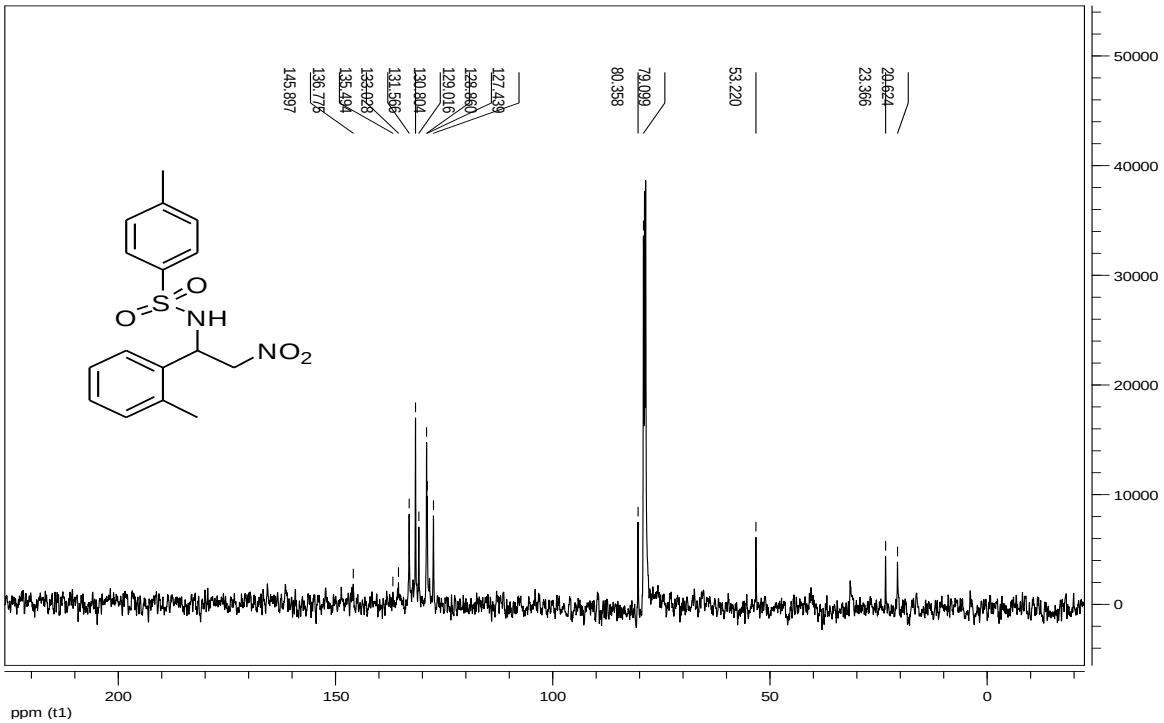
(7.6) ^{13}C-NMR spectra of 2-Nitro-1-(4'-methoxyphenyl)-*N*-tosylethanamine



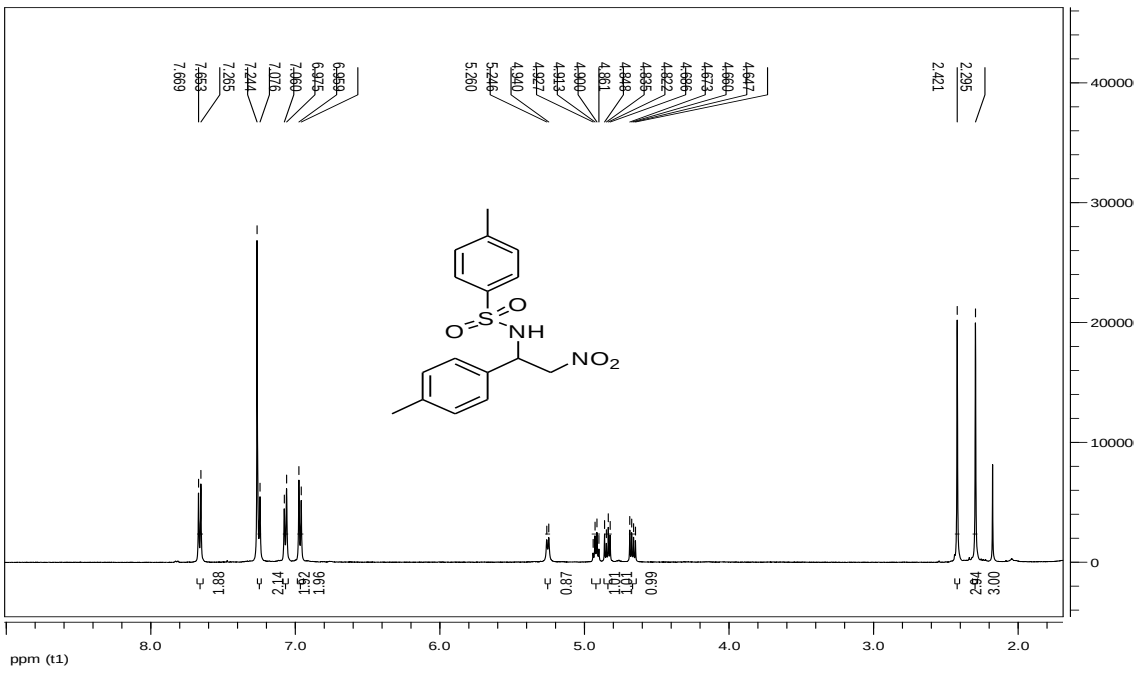
(7.7) ^{1}H-NMR spectra of Nitro-1-o-tolyl-*N*-tosylethanamine



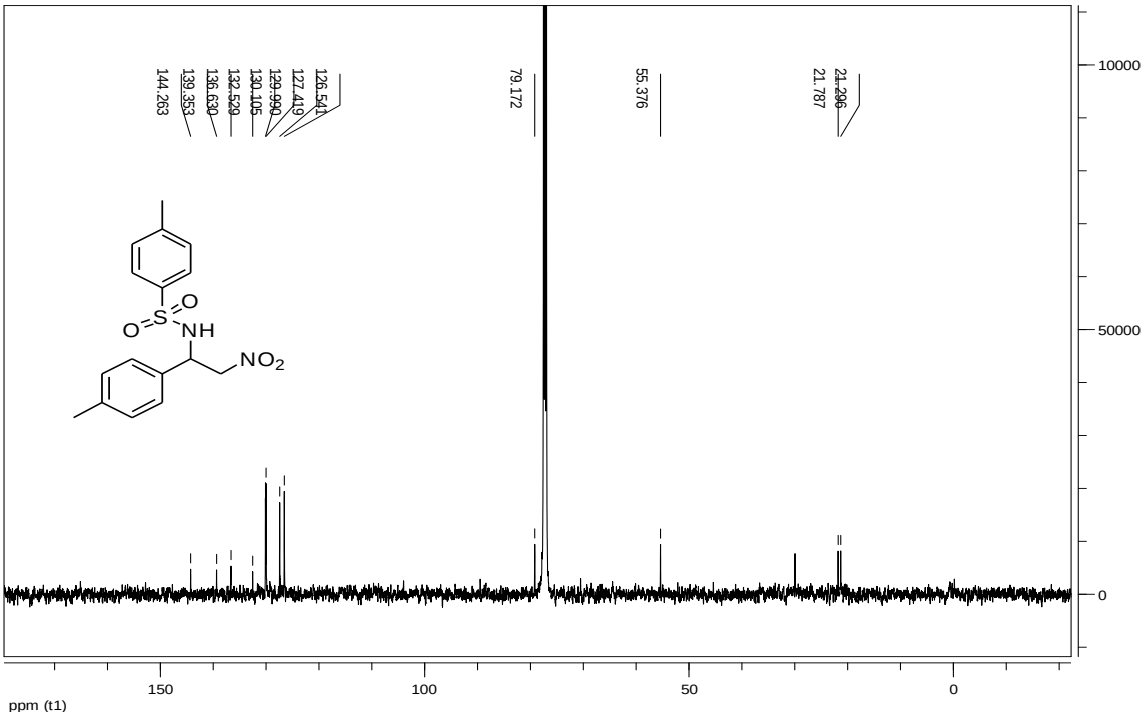
(7.8) ^{13}C-NMR spectra of Nitro-1-o-tolyl-*N*-tosylethanamine



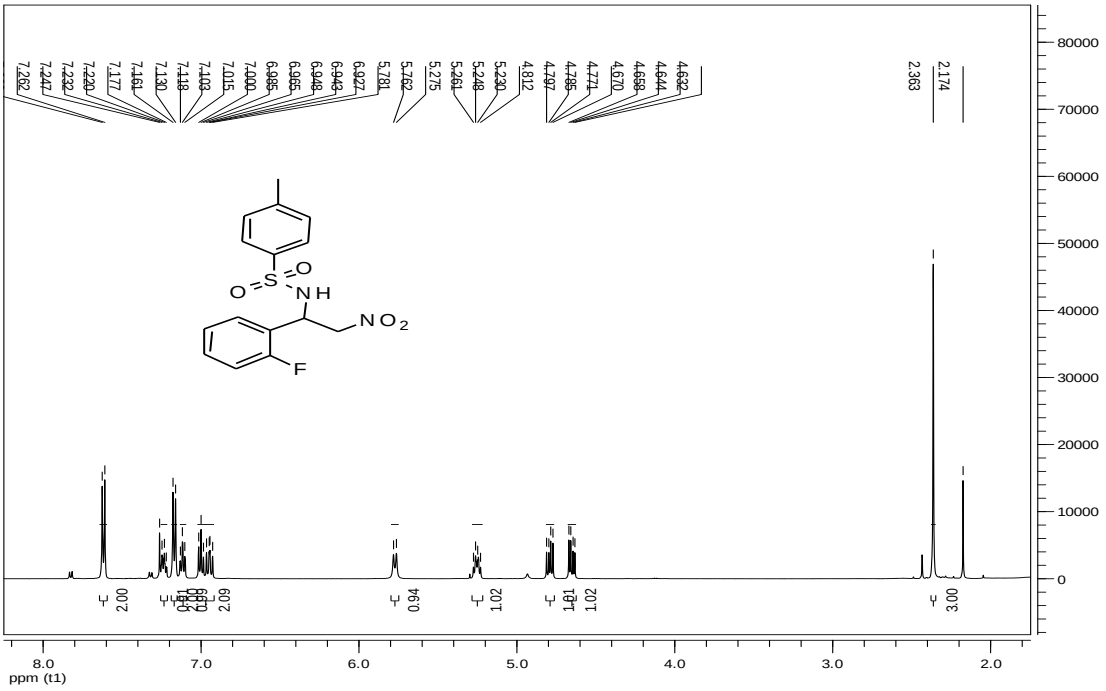
(7.9) ^{1}H-NMR spectra of Nitro-1-p-tolyl-*N*-tosylethanamine



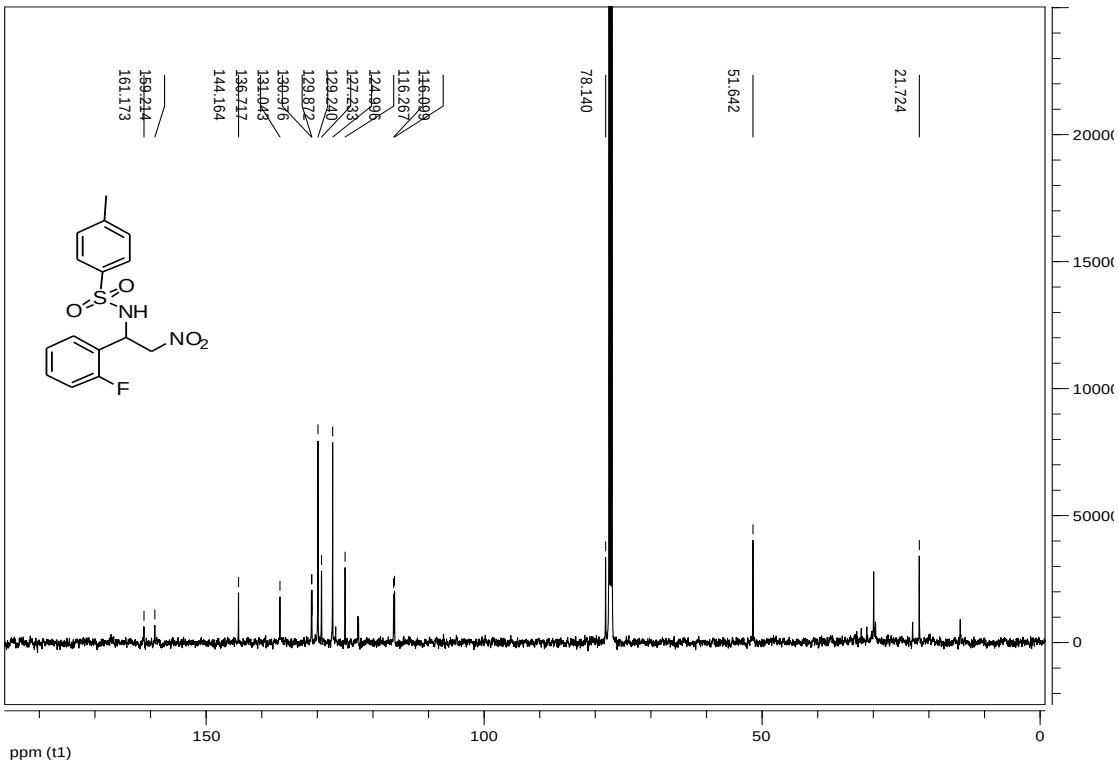
(7.10) ^{13}C-NMR spectra of Nitro-1-p-tolyl-*N*-tosylethanamine



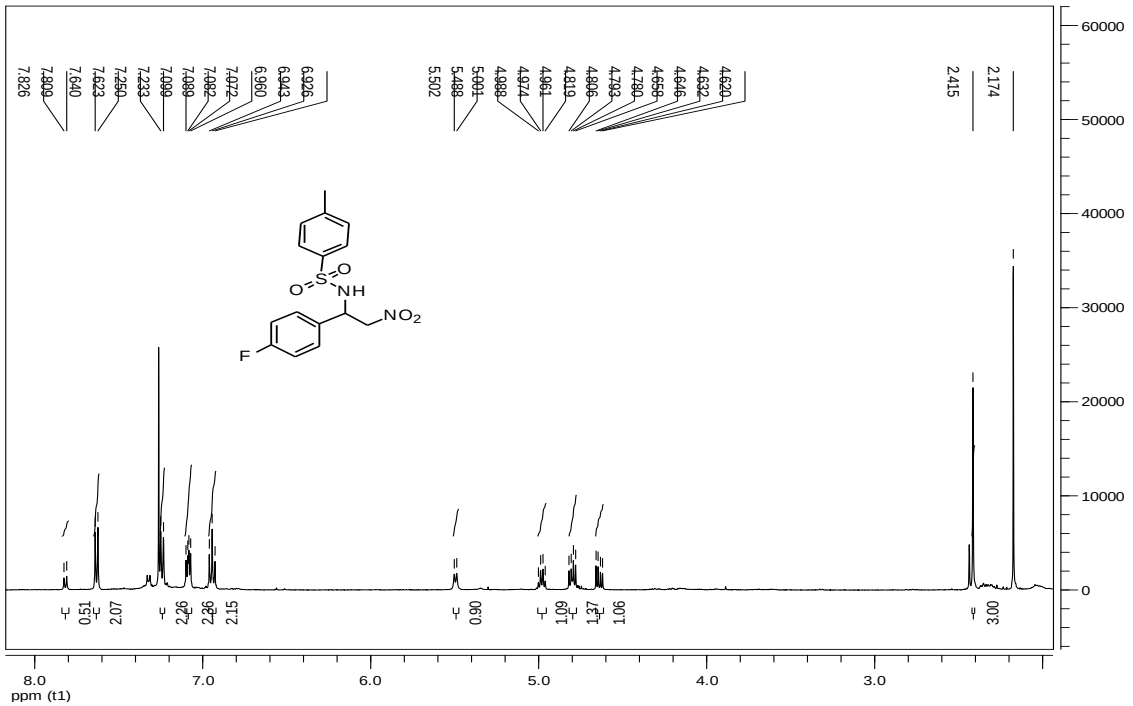
(7.11) ^{1}H-NMR spectra of 2-Nitro-1-(2'-fluorophenyl)-*N*-tosylethanamine



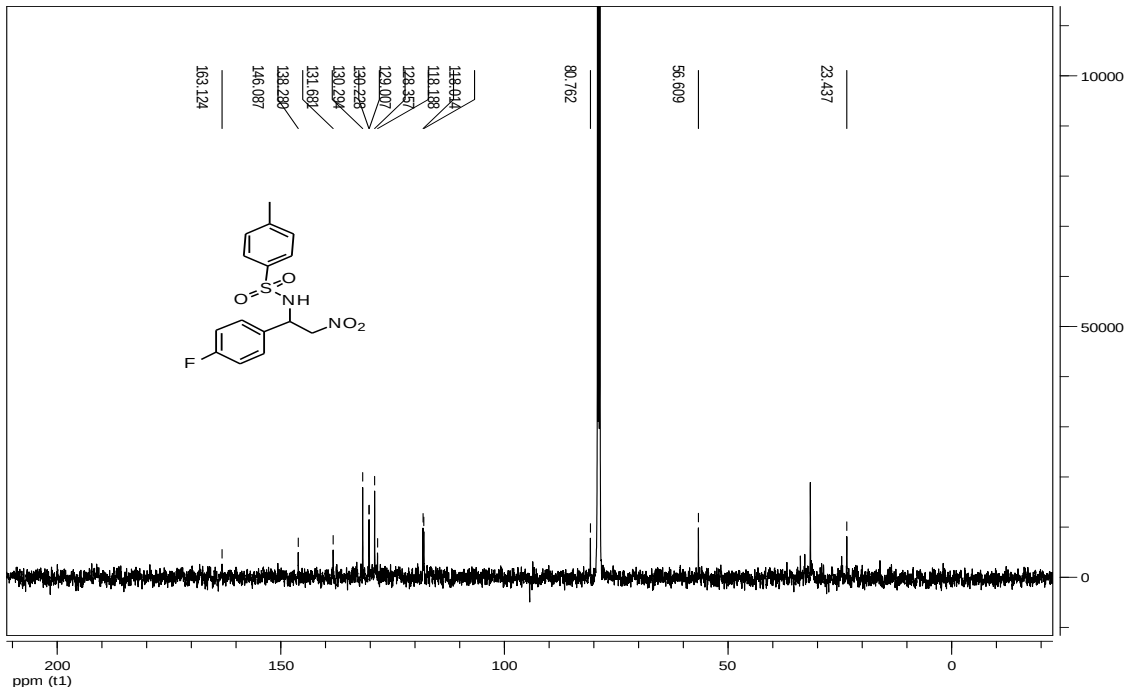
(7.12) ^{13}C-NMR spectraof 2-Nitro-1-(2'-fluorophenyl)-*N*-tosylethanamine



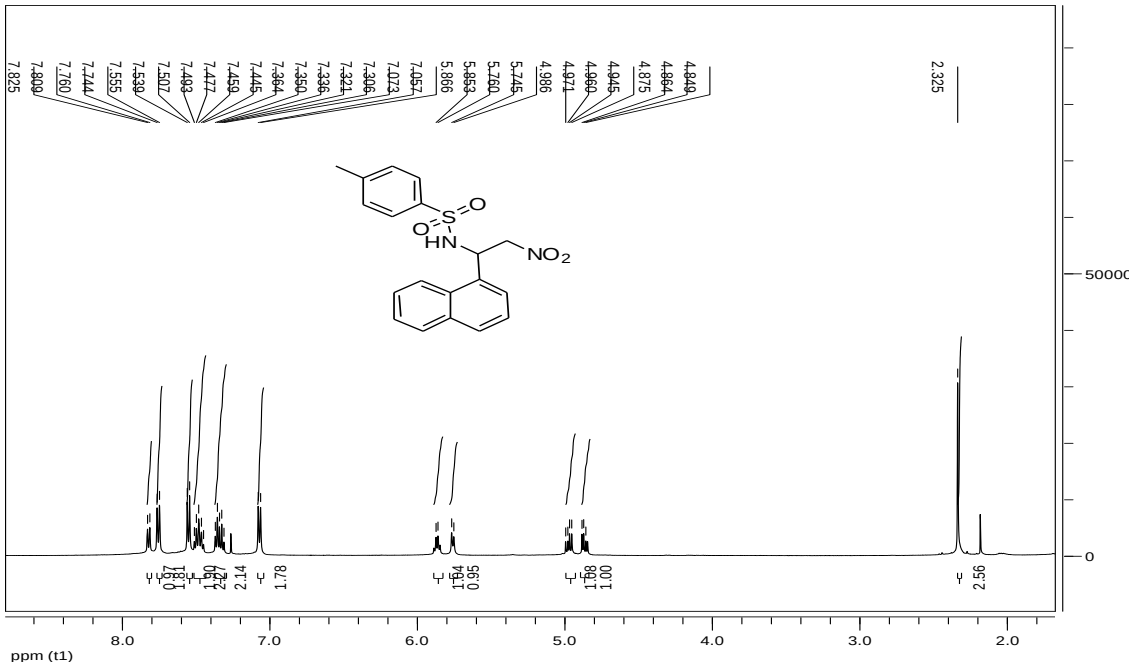
(7.13) ^{1}H-NMR spectraof 2-Nitro-1-(4'-fluorophenyl)-*N*-tosylethanamine



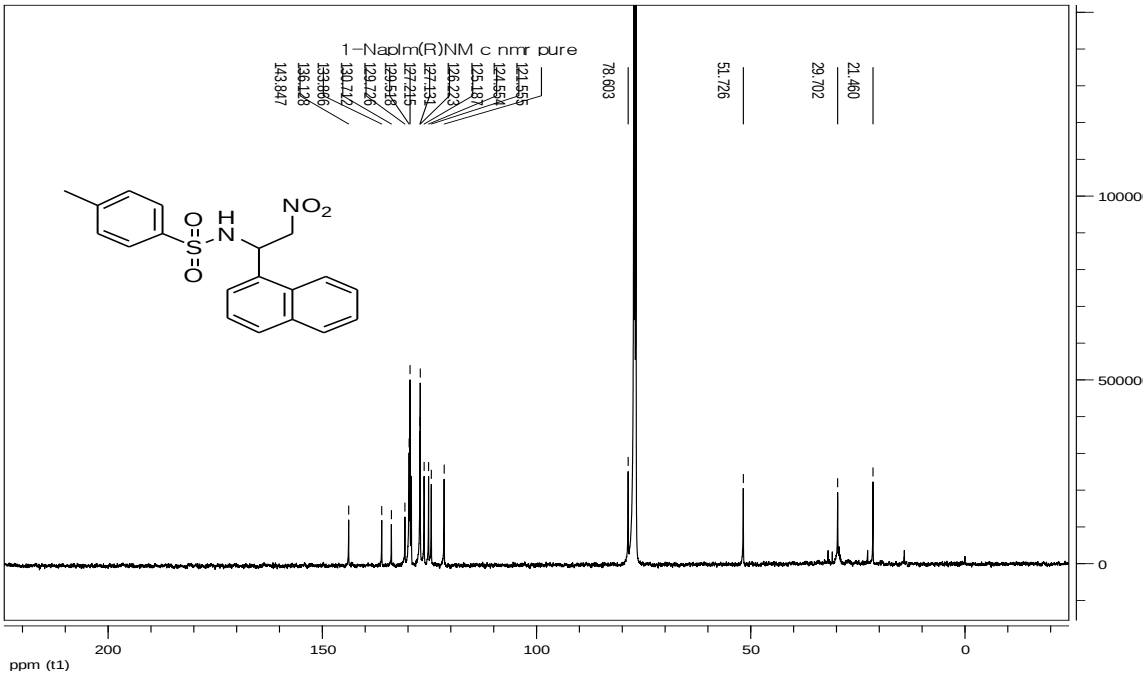
(7.14) ^{13}C-NMR spectraof 2-Nitro-1-(4'-fluorophenyl)-*N*-tosylethanamine



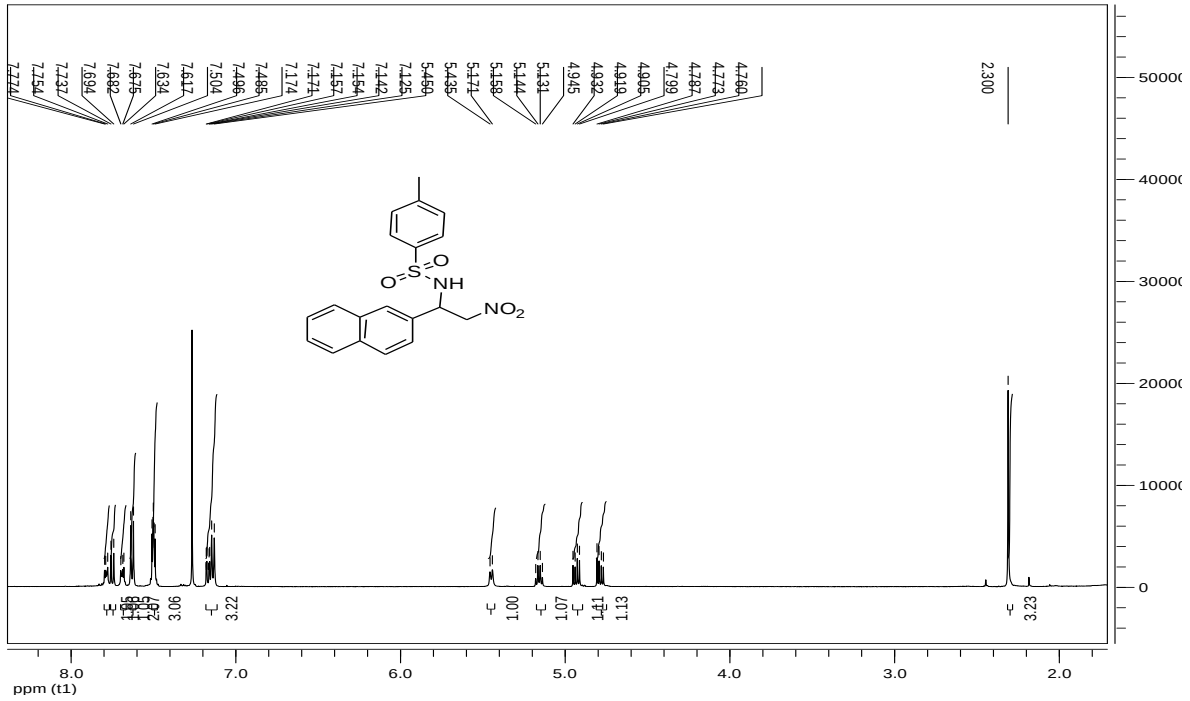
(7.15) ^{1}H-NMR spectraof 2-Nitro-(1-naphtyl)-*N*-tosylethanamine



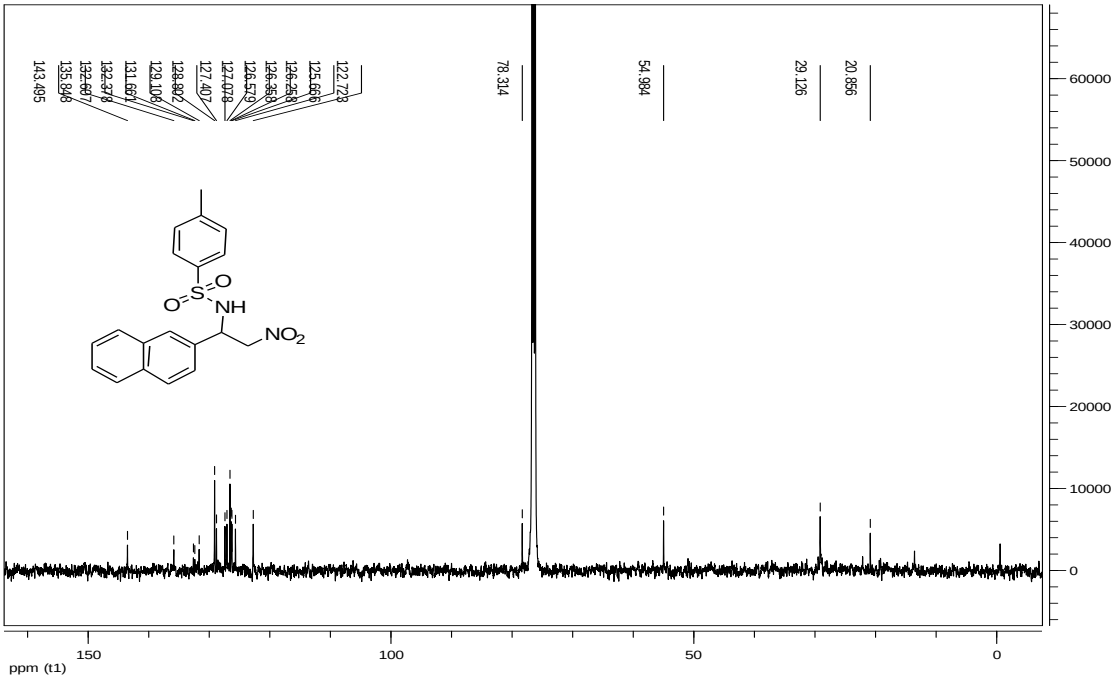
(7.16) ^{13}C-NMR spectraof 2-Nitro-(1-naphtyl)-*N*-tosylethanamine



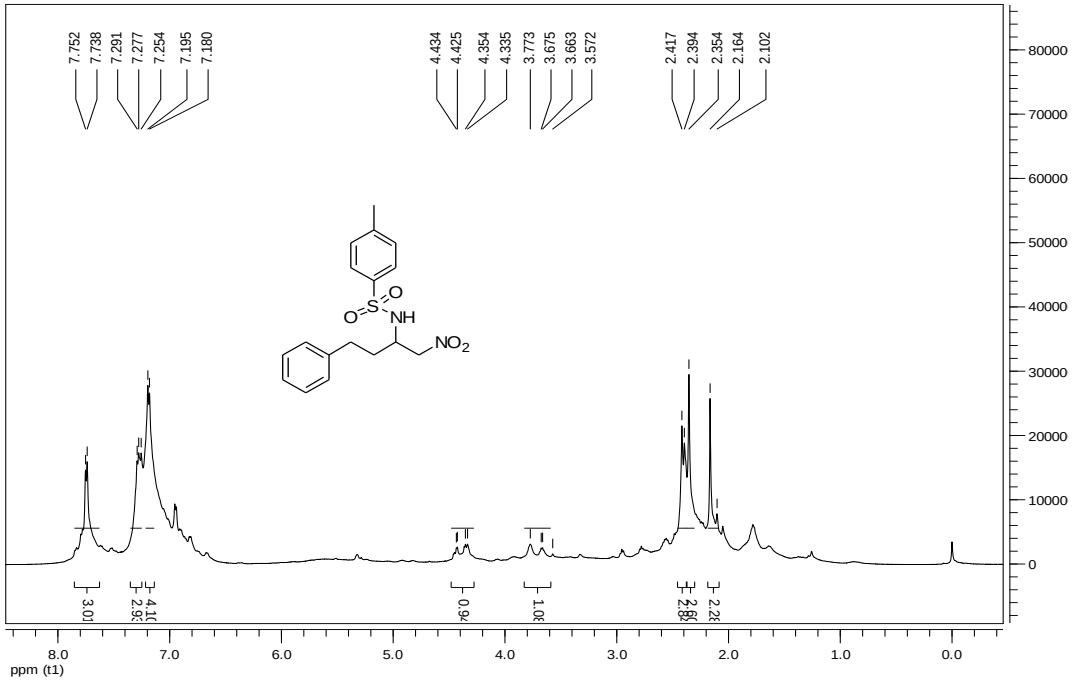
(7.17) ^{1}H-NMR spectra of 2-Nitro-(2-naphtyl)-*N*-tosylethanamine



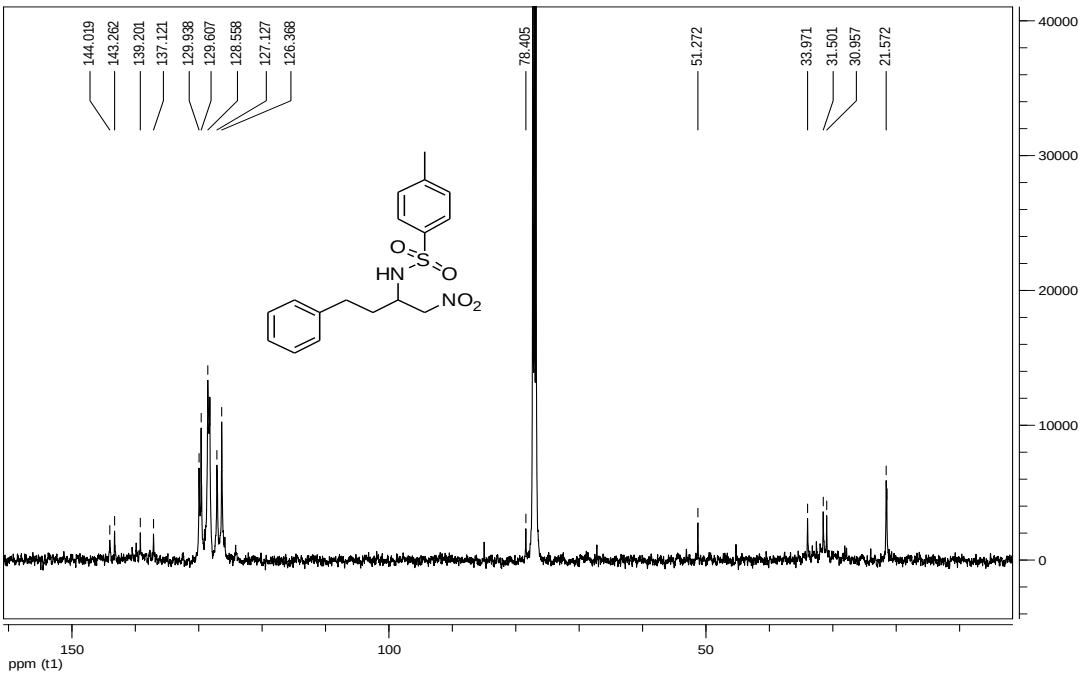
(7.18) ^{1}H-NMR spectraof 2-Nitro-(2-naphtyl)-*N*-tosylethanamine



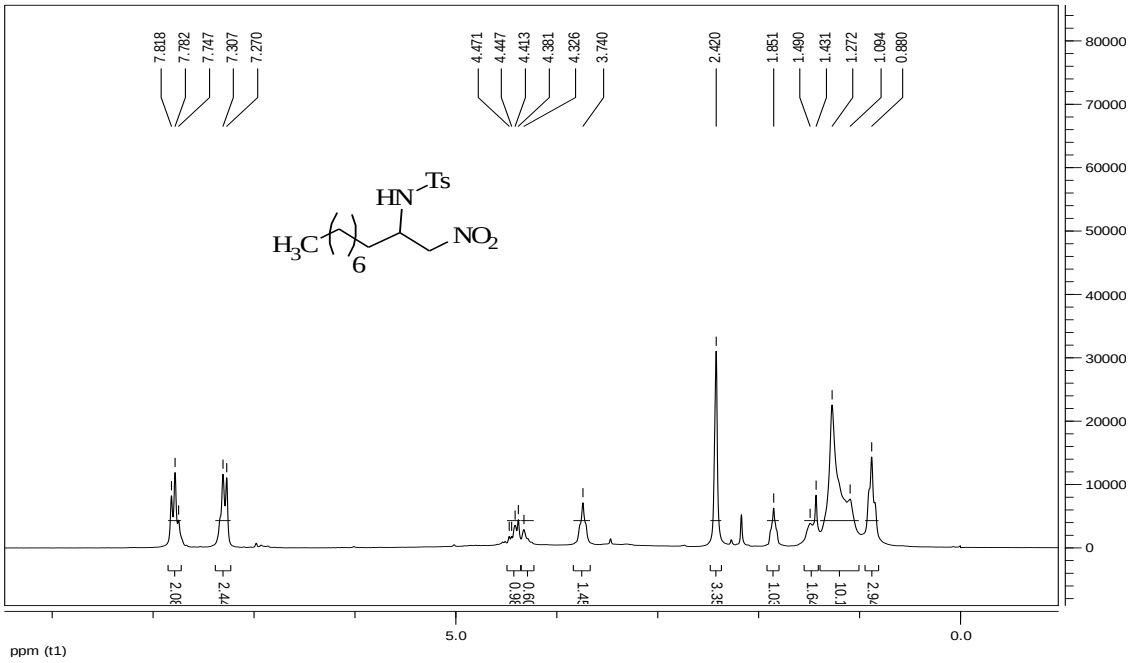
(7.19) ^{1}H-NMR spectra of 2-Nitro-1-ethylbenzen-*N*-tosylethanamine



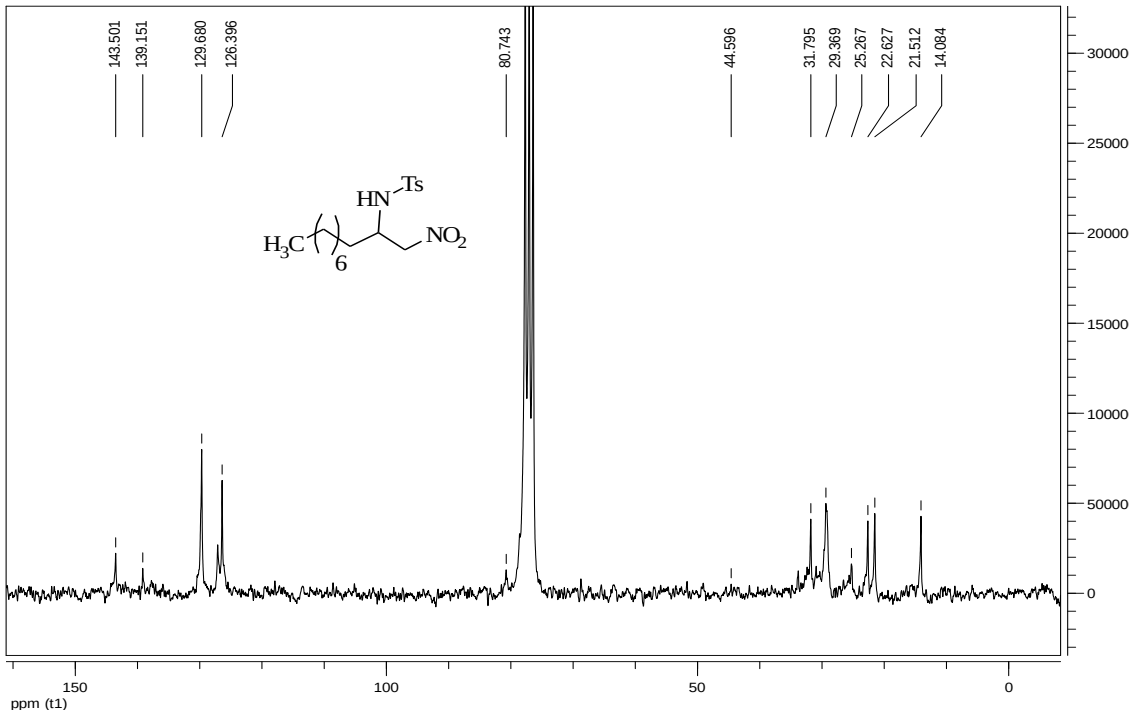
(7.20) ^{13}C-NMR spectra of 2-Nitro-1-ethylbenzen-*N*-tosylethanamine



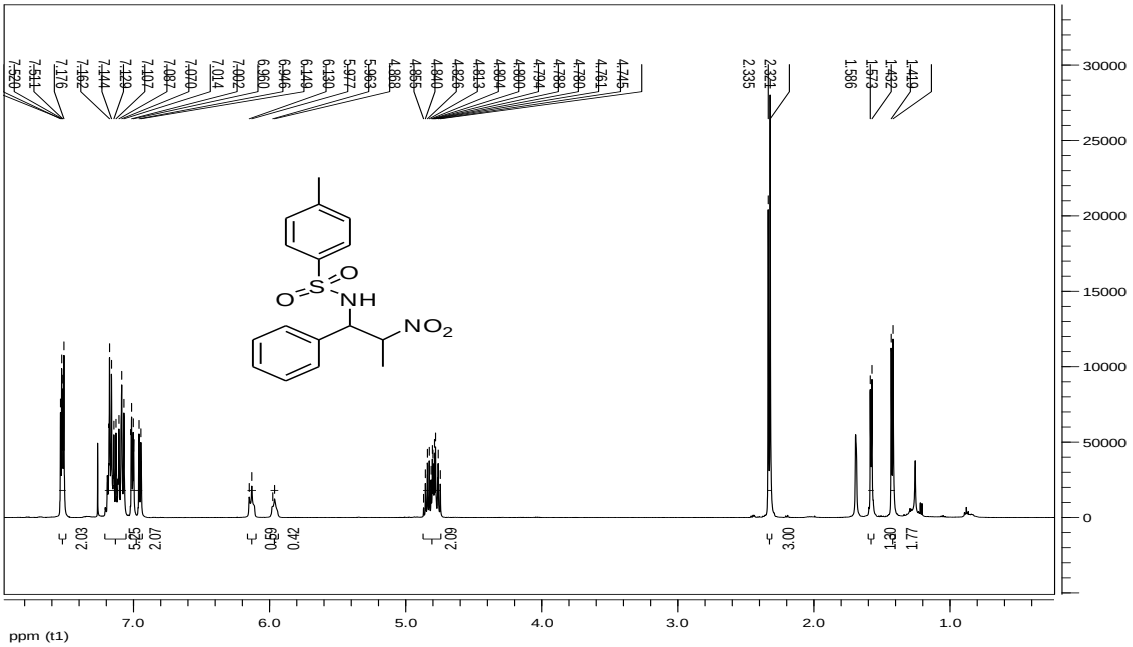
(7.21) ^{1}H-NMR spectra of 2-Nitro-1-octane-*N*-tosylethanamine



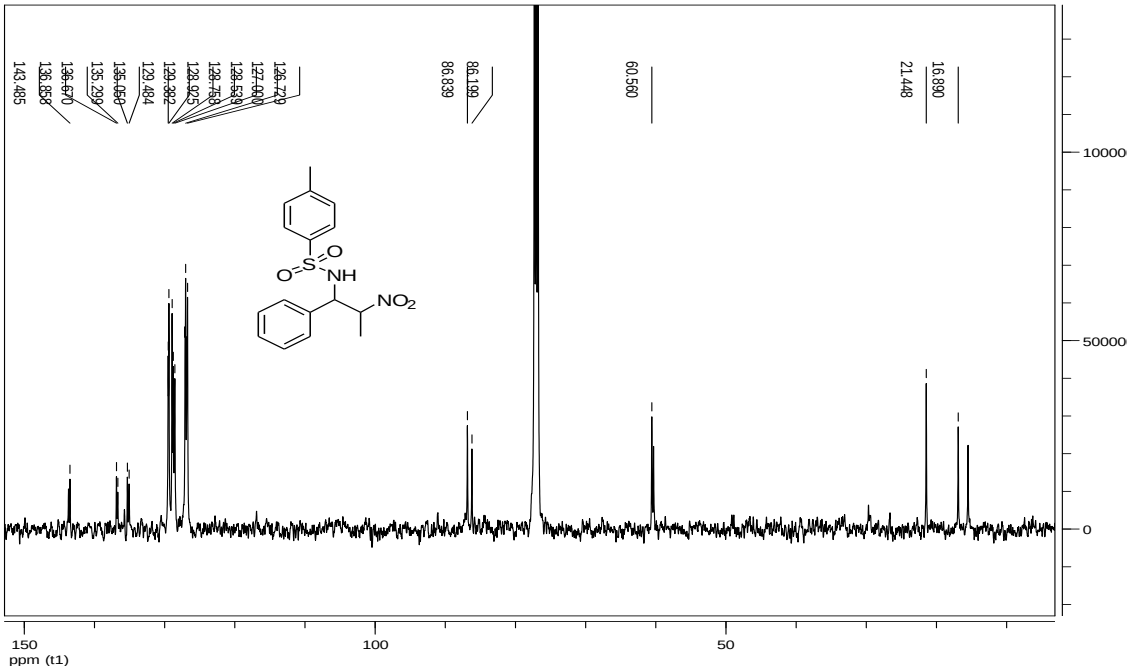
(7.22) ^{13}C-NMR spectra of 2-Nitro-1-octane-*N*-tosylethanamine



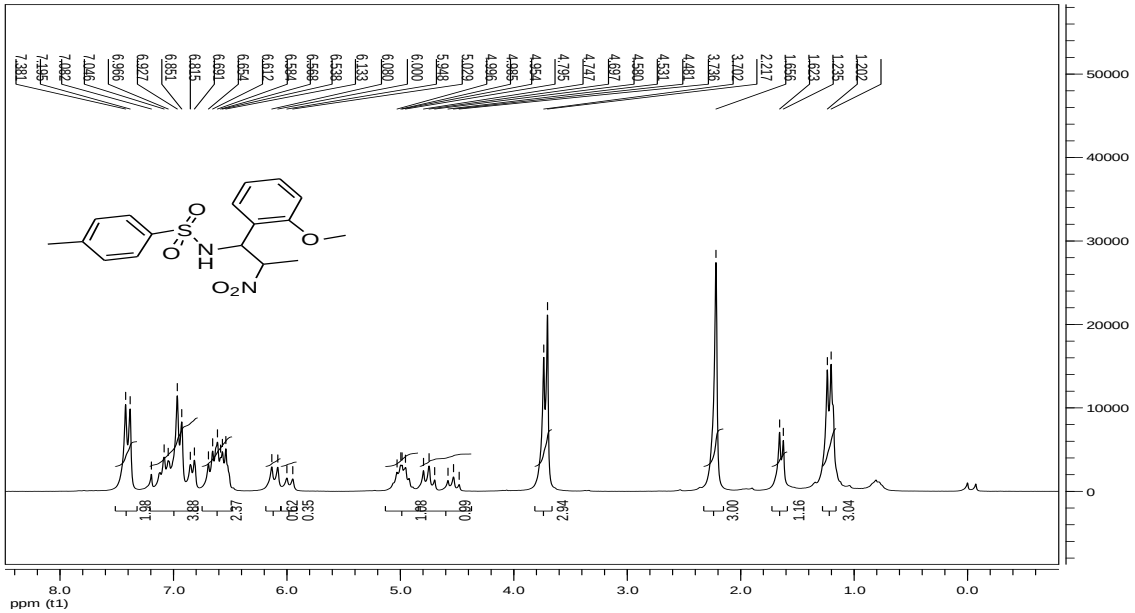
(7.23) ^{1}H-NMR spectraof 2-Methyl-2-Nitro-1-phenyl-*N*-tosylethanamine



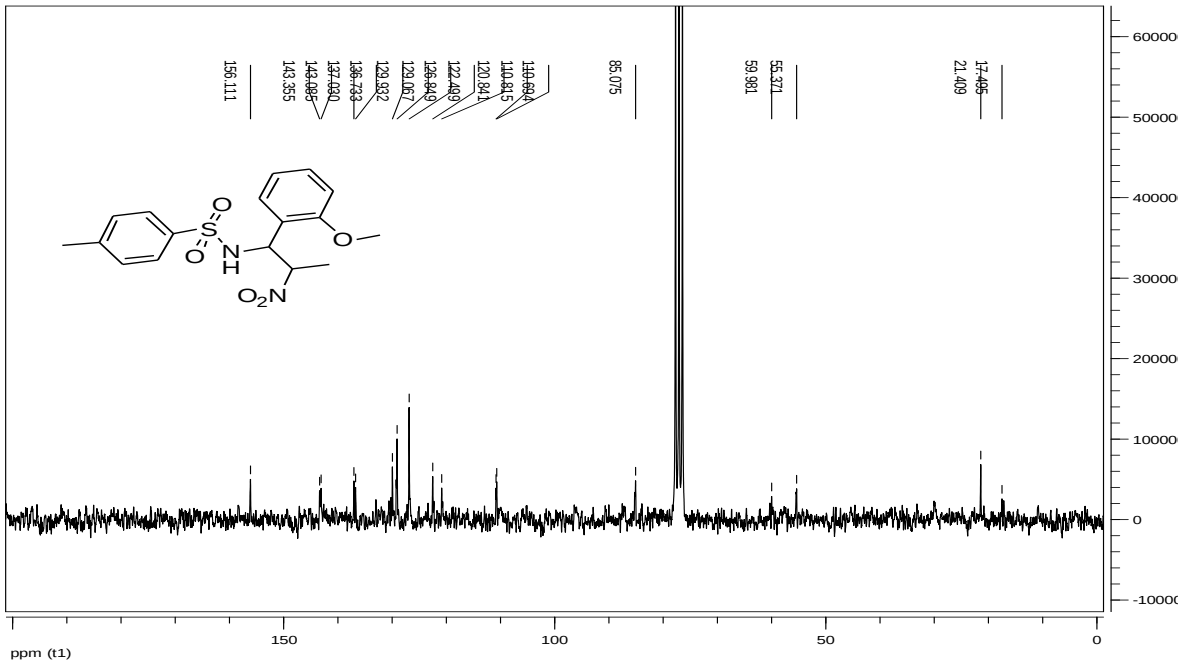
(7.24) ^{13}C-NMR spectraof 2-Methyl-2-Nitro-1-phenyl-*N*-tosylethanamine



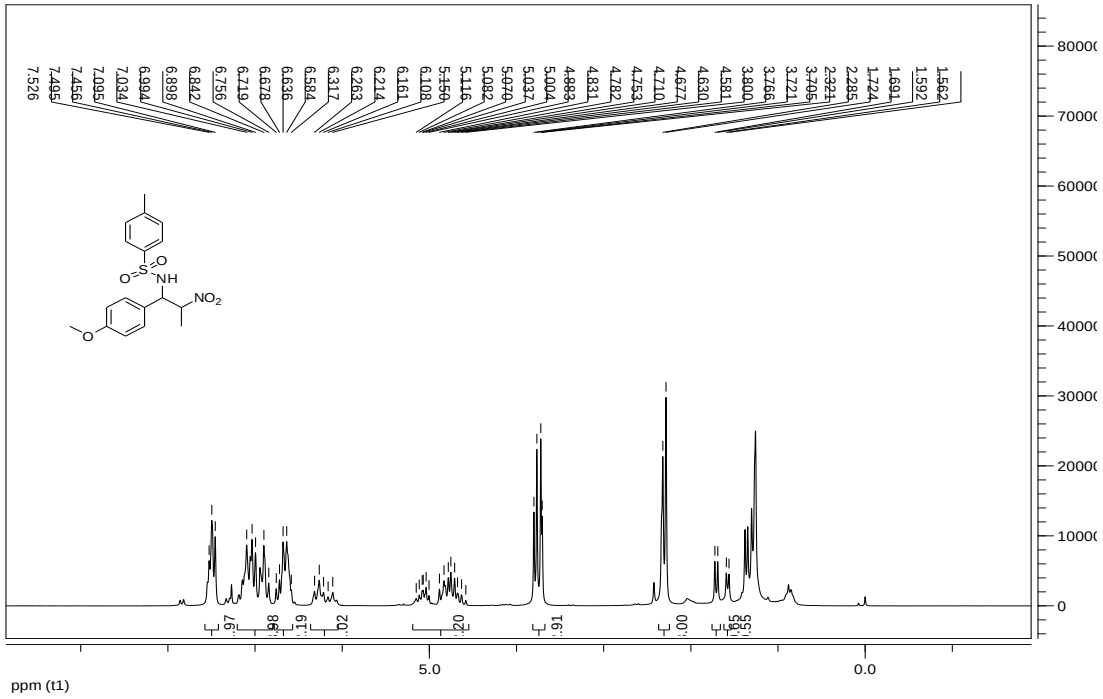
(7.25) ^{1}H-NMR spectraof 2-Methyl-2-Nitro-1-(2'-methoxyphenyl)-*N*-tosylethanamine



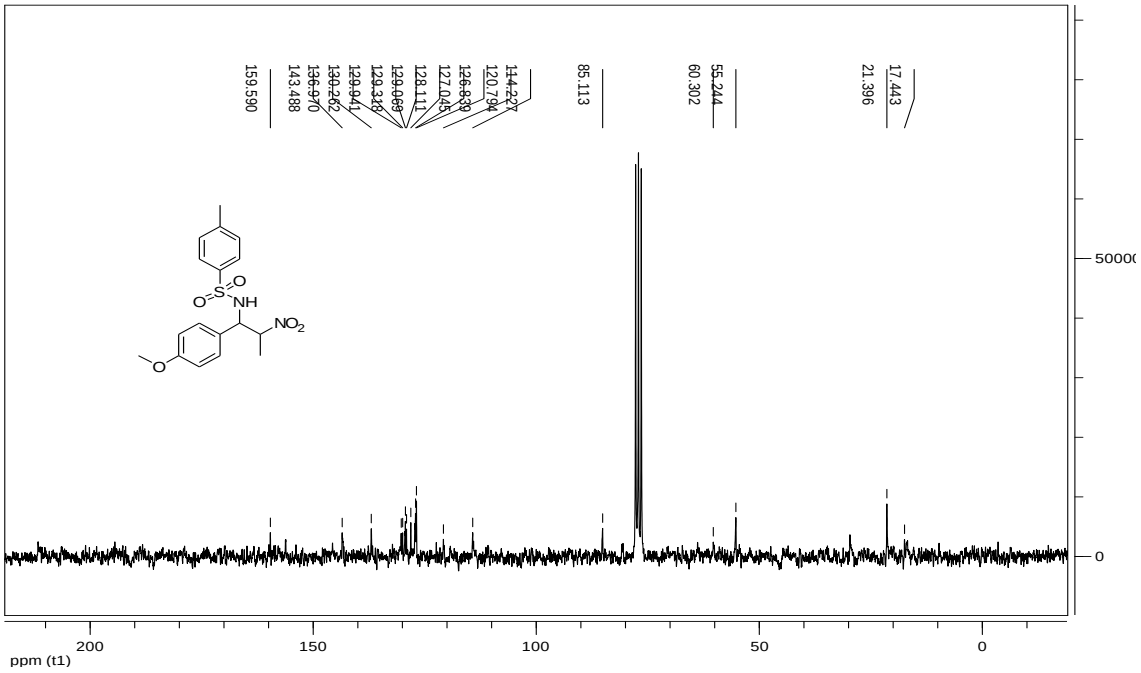
(7.26) ^{13}C-NMR spectraof 2-Methyl-2-Nitro-1-(2'-methoxyphenyl)-*N*-tosylethanamine



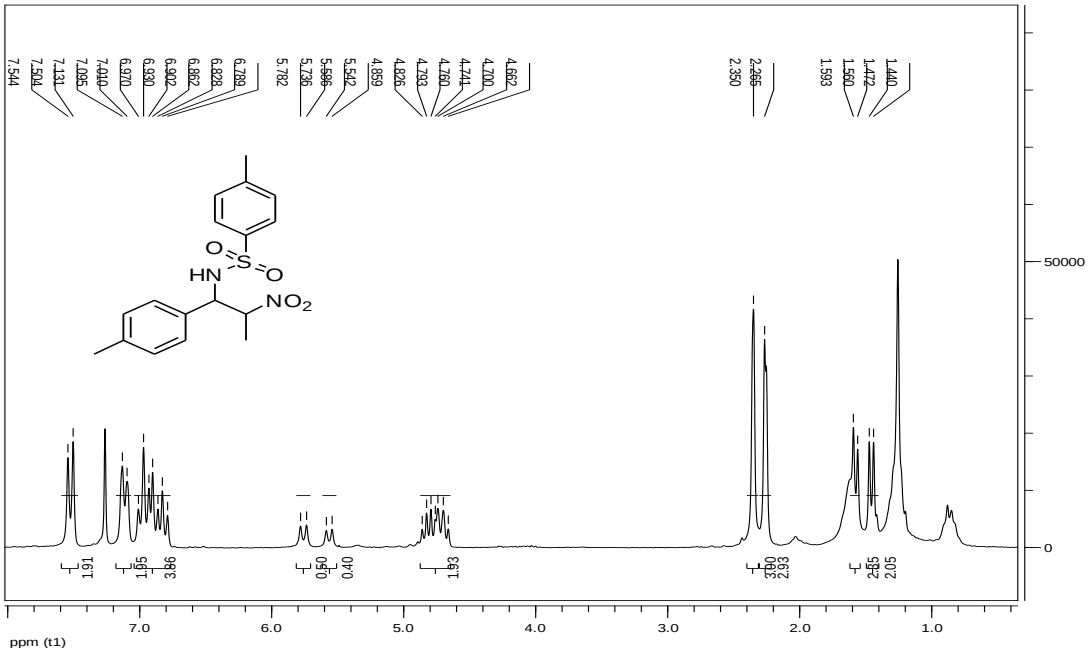
(7.27) ^{1}H-NMR spectraof 2-Methyl-2-Nitro-1-(4'-methoxyphenyl)-*N*-tosylethanamine



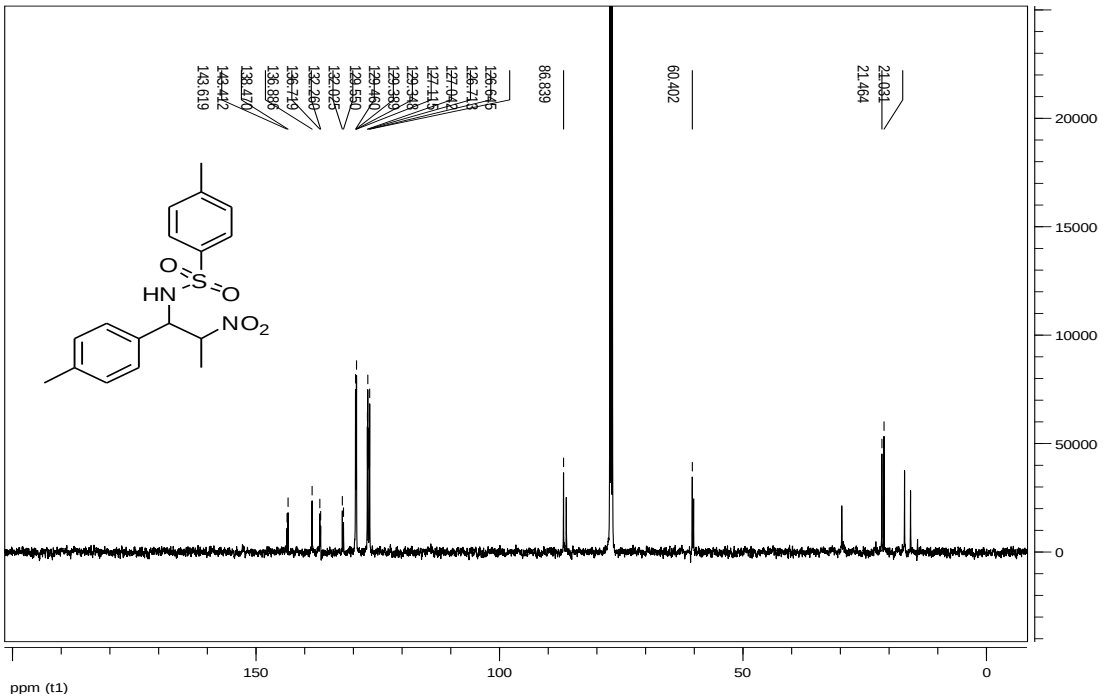
(7.28) ^{13}C-NMR spectraof 2-Methyl-2-Nitro-1-(4'-methoxyphenyl)-*N*-tosylethanamine



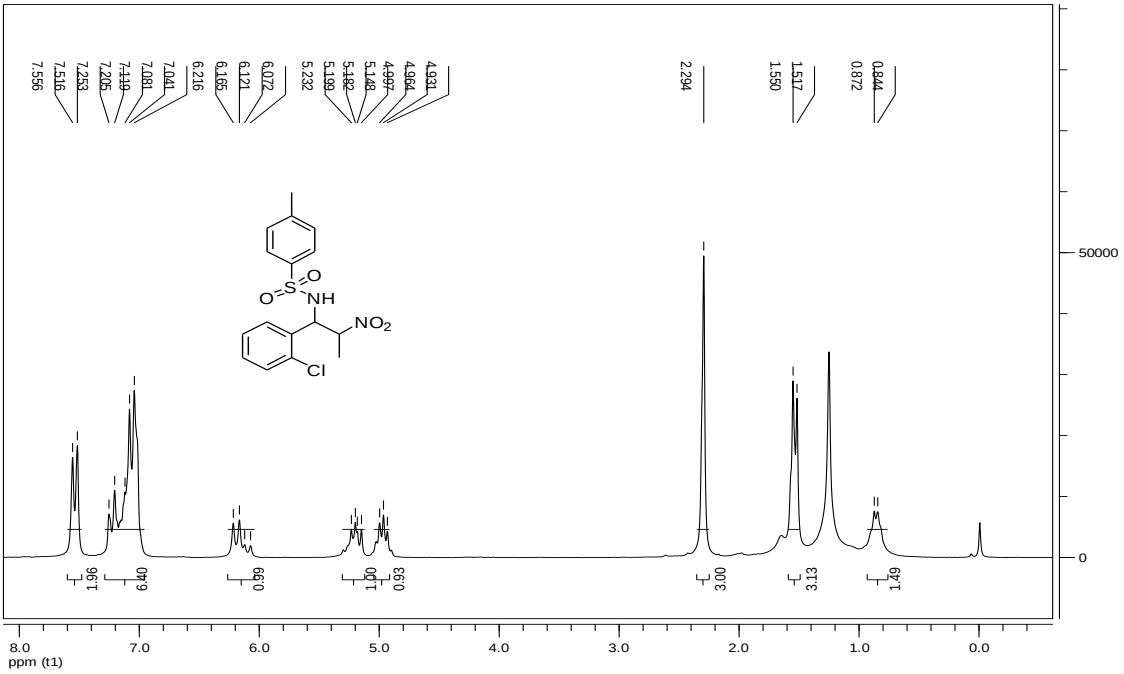
(7.29) ^{1}H-NMR spectra of 2-Methyl-2-Nitro-1-p-tolyl-*N*-tosylethanamine



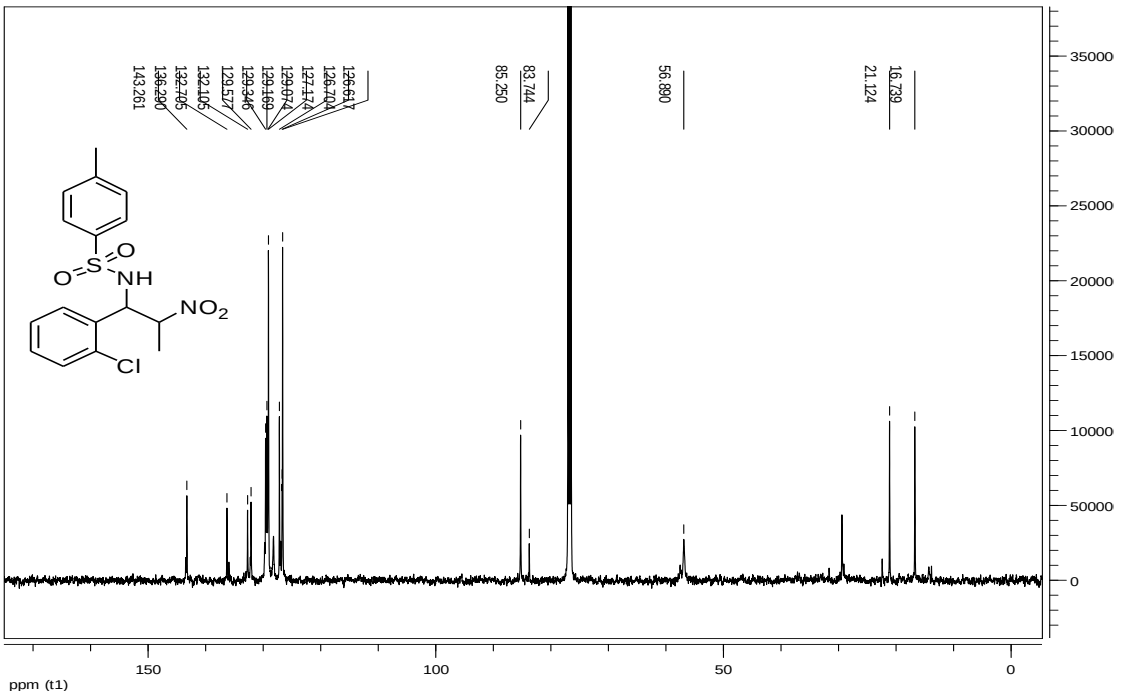
(7.30) ^{1}H-NMR spectra of 2-Methyl-2-Nitro-1-p-tolyl-*N*-tosylethanamine



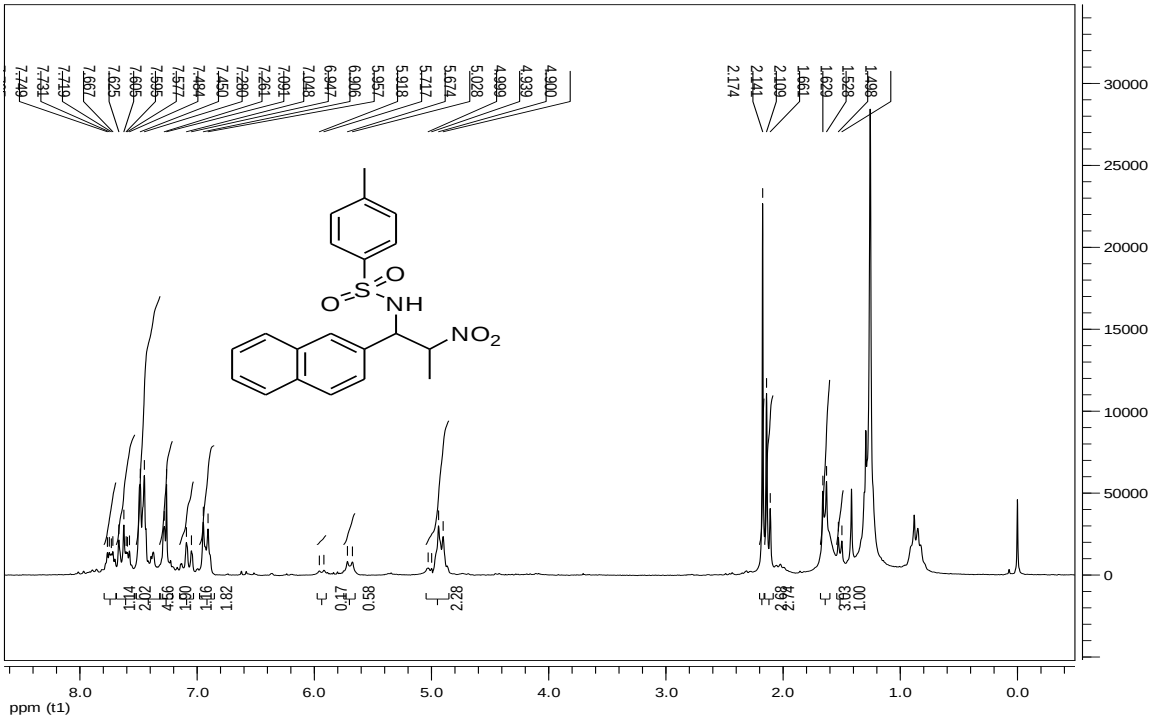
(7.31) ^{1}H-NMR spectra of 2-Methyl-2-Nitro-1-(2'-cholrophenyl)-*N*-tosylethanamine



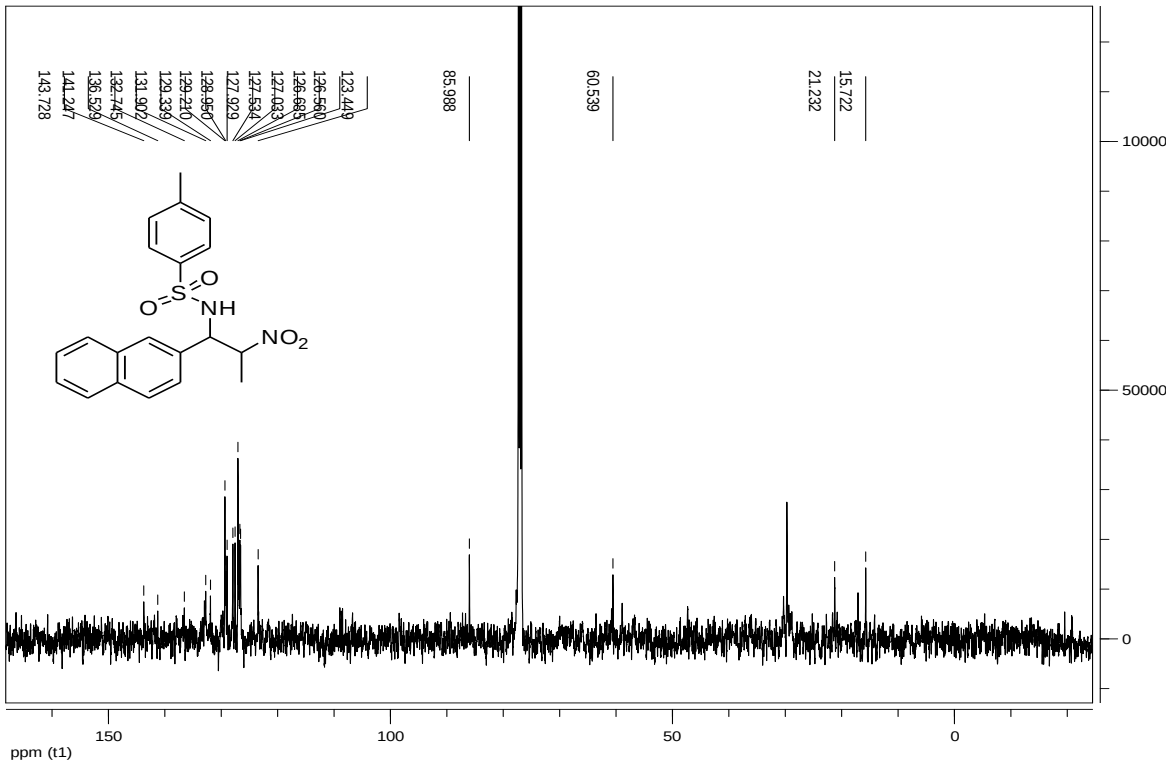
(7.32) ^{13}C-NMR spectra of 2-Methyl-2-Nitro-1-(2'-cholrophenyl)-*N*-tosylethanamine



(7.33) ^{1}H-NMR spectra of 2-Methyl- 2-Nitro-(2-naphtyl)-*N*-tosylethanamine



(7.34) ^{1}H-NMR spectra of 2-Methyl- 2-Nitro-(2-naphtyl)-*N*-tosylethanamine



8. References

1. T. P. Yoon and E. N. Jacobsen, *Angew. Chem., Int. Ed.*, 2005, **44**, 466-468.
2. X. Xu, T. Furukawa, T. Okino, H. Miyabe and Y. Takemoto, *Chem. Eur. J.*, 2006, **12**, 466-476.
3. T. Okino, S. Nakamura, T. Furukawa and Y. Takemoto, *Org. Lett.*, 2004, **6**, 625-627.
4. Y. Chang, J. Yang, J. Dang and Y. Xue, *Synlett*, 2007, 2283-2285.
5. J. Luis, G. Ruano, M. Topp, J. López-Cantarero, J. Alemán, M. J. Remuiñán and M. B. Cid, *Org.Lett.*, 2005, **7**, 4407.
6. W. B. Jennings and C. J. Lovely, *Tetrahedron*, 1991, **47**, 5561-5568.
7. F. Chemla, V. Hebbe and J. F. Normant, *Synthesis*, 2000, **1**, *75*-77.
8. T. Ooi, Y. Uematsu and K. Maruoka, *J. Am. Chem. Soc.*, 2006, **128**, 2548-2549.
9. J. L. G. Ruano, J. AlemOn, M. B.Cid and A. Parra, *Org. Lett*., 2005, **7**, 179 – 182
10. M. Kumar, R. I. Kureshy, D. Ghosh, N. H. Khan, S. H. R. Abdi and H. C. Bajaj, *ChemCatChem.*, 2013, ***5***, 2336-2342.