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Supporting Information

L-Proline as an efficient enantioinduction organo-catalyst in the solvent-free synthesis of pyrazolo[3,4-*b*]quinoline derivatives *via* one-pot multi-component reaction

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EXPERIMENTAL

All commercially available chemicals and reagents were purchased from Sigma Aldrich, Merck and were used without further purification. Purity of the products were confirmed by infrared (IR), ^{1}H-NMR, ^{13}C-NMR and mass spectra. IR spectra were recorded in KBr pellets on a Perkin Elmer Spectrum 400 FTIR instrument, and the frequencies are expressed in cm^{-1}. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker Avance II-400 spectrometer in DMSO-d_6 (Chemical shifts in δ with TMS as internal standard).Mass spectral data were obtained with a JEOL D-300 (ESI) mass spectrometer. All reactions were monitored by thin layer chromatography (TLC) using precoated aluminium sheets (silica gel 60 F_{254} 0.2-mm thickness).HPLC analyses were performed on Waters M515 series equipped with a Agela chiral ADV analytical column (5 μm, 1000 Å, 4.6x250 mm,). UV-detection at 254 nm was used to analyse the data. The analytical separation was carried out at 25°C using a mobile phase (A) of isopropanol and (B) of n-Hexane as eluent, the all solvents were HPLC-grade.TFA was of analytical grade. The flow rate applied was 0.5 mL/min.

X-ray crystallography

The X-ray data of **4j** was collected at 293 K with a Agilent Xcalibur (Eos, Gemini) diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The data was collected and reduced in CrysAlis PRO (Agilent, 2011) software and cell refinement was done in CrysAlis PRO software. The absorption was corrected by SCALE3 ABSPACK multi-scan method in CrysAlisPro. The structures were solved by direct methods using the program SHELXS-2013 and refined by full matrix least-squares calculations (F2) by using the SHELXL-2013 software. All non-H atoms were refined anisotropically against F2 for all reflections. All hydrogen atoms were placed at their calculated positions and refined isotropically. ORTEP image of **4j** is shown in Figure 1

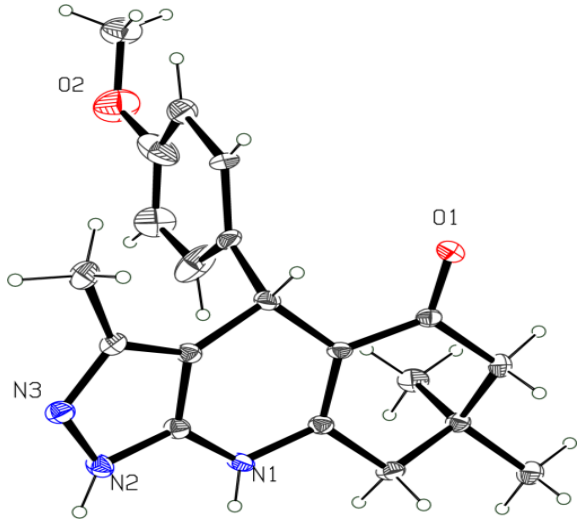


Fig. 1. ORTEP Image of **4j** (CCDC 1410800)

Table1. X-ray crystallography data for compound **4j**

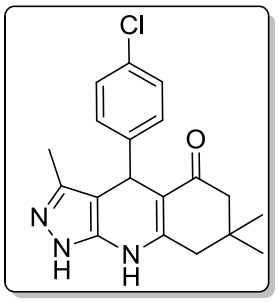
Empirical formula	$C_{20}\ H_{23}\ N_3\ O_2$
Formula weight	337.41
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 8.7142(7) Å α= 90°.
	b = 14.7858(8) Å β = 106.346(7)°.
	c = 14.5751(9) Å α = 90°.
Volume	1.802(2) nm^3
Z	4
Density (calculated)	1.244 Mg/m^3
Absorption coefficient	0.082 mm^{-1}
F(000)	720
Theta range for data collection	3.117 to 26.370°.
Index ranges	-10<=h<=10, -14<=k<=18, -13<=l<=18
Reflections collected	7891
Independent reflections	3566 [R(int) = 0.0339]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3566 / 0 / 234
Goodness-of-fit on F^2	1.407
Final R indices [I>2sigma(I)]	R1 = 0.1321, wR2 = 0.3486
R indices (all data)	R1 = 0.1686, wR2 = 0.3845

General procedure for the synthesis of 4 (a–u)

A pre-stirred mixture of aldehyde 1 (2.1 mmol), dimedone 2 (2.0 mmol) and 3-methyl-1*H*-pyrazol-5-amine 3 (2.0 mmol) was irradiated in a Chem Discover microwave reactor at 110°C, for 15 min, in the presence of L-proline (10 mol %). The completion of the reaction was monitored by TLC. After the completion of the reaction, it was worked up using ethyl acetate, washed with brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo to give the crude mass. The crude compound was then purified by silica gel column chromatography to afford the pyrazoloquinolinones **4** in pure form.

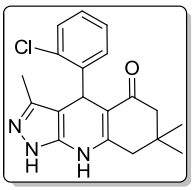
Analytical data for the substituted pyrazolo derivative derivatives

4-(4-chlorophenyl)-3,7,7-trimethyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin 5(4H)-one , (4a) .



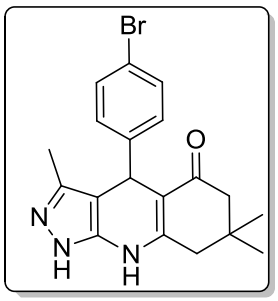
White solid. mp : 305-306 ^{o}C. IR ν_{max} (KBr): 3258, 3073, 2952, 1573, 1547, 1255, 770 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ_H (ppm) 0.67 (s, 3H, CH_3), 0.76 (s, 3H, CH_3), 1.85(s, 3H, CH_3), 2.17-2.30 (m, 2H, CH_2), 5.32 (s, 1H, 4*H*), 5.81(s,1 H, NH), 6.86 (d, 2H, *J* = 8 Hz, Ar-H), 7.07 (d, 2H, *J* = 8 Hz, Ar-H), 10.19 (s, 1H, NH); ^{13}C NMR (100 MHz, ACETONE-d_6): δ_C (ppm) 14.21, 27.46, 29.34, 32.86, 33.12 40.98, 50.93, 106.00, 113.08, 128.63, 128.87, 129.58, 132.99, 143.46, 149.28, 150.31, 193.40 ; MS (ES$^+$) : calcd for $C_{19}H_{20}ClN_3O$ 341.13 found *m/z* 342.40 $(M + H)^+$.

4-(2-chlorophenyl)-3,7,7-trimethyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one , (4b)



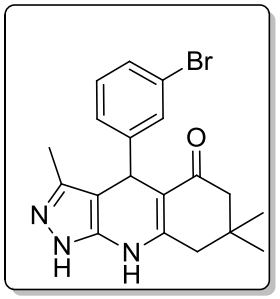
White solid. mp : 302-304 ^{o}C. IR ν_{max} (KBr):3258, 3067, 2957, 1579, 1548, 1257, 748cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 0.99(s, 3H, CH_3), 1.04 (s, 3H, CH_3) 1.91(s, 3H, CH_3), 2.11 (d, 1H, *J* = 16 Hz, CH_2), 2.18 (d, 1H, *J* = 16 Hz, CH_2), 2.38-2.60(m, 2H, CH_2), 4.06 (s, 1H, NH), 5.46 (s, 1H, 4*H*), 7.00-7.57 (m, 4H, Ar-H) 11.55 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$+DMSO-D_6): δ_C (ppm) 13.53, 26.28, 26.85, 28.59, 31.91, 41.24, 49.87, 106.84, 113.07, 126.13, 128.08, 129.28, 130.10, 137.29, 139.96, 144.17, 149.24, 154.66, 193.84; MS (ES$^+$) calcd for $C_{19}H_{20}ClN_3O$ 341.13 found *m/z* 342.40 $(M + H)^+$.

4-(4-bromophenyl)-3,7,7-trimethyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one, (4c)



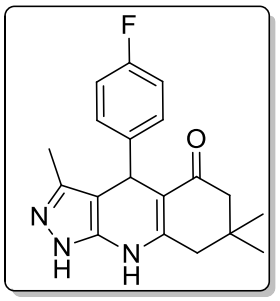
White solid. mp : 314-315 ^{o}C. IR ν_{max} (KBr): 3235, 3125, 2954, 1578, 1548, 1252, 796 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 0.98 (s, 3H, CH_3), 1.09 (s, 3H, CH_3) 2.05-2.07 (m, 2H, CH_2), 2.17 (s, 3H, CH_3), 2.22 (d, 1H, *J* = 16 Hz, CH_2), 2.34 (d, 1H, *J* = 16 Hz, CH_2), 5.47 (s, 1H, 4*H*), 6.30 (s, 1H, NH), 7.09 (d, 2H, *J* = 8 Hz, Ar-H), 7.38 (d, 2H, *J* = 8 Hz, Ar-H), 7.75 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C (ppm) 14.52, 26.08, 27.52, 32.11, 34.03, 39.40, 55.74, 109.36, 112.77, 117.98, 128.28, 131.35, 133.19, 145.65, 146.27, 151.31, 198.62; MS (ES$^+$) calcd $C_{19}H_{20}BrN_3O$ 385.08 found *m/z* 386.20 $(M + H)^+$.

4-(3-bromophenyl)-3,7,7-trimethyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one , (4d)



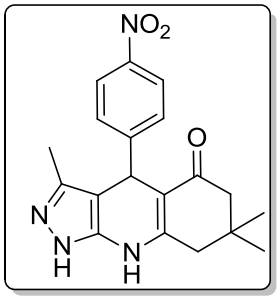
White solid. mp : 315-317 ^{o}C. IR ν_{max} (KBr): 3271, 3067, 2956, 1578, 1540, 1247, 753 cm^{-1}; ^{1}H NMR (400 MHz, ACETONE-D_6): δ_H (ppm) 0.74 (s, 3H, CH_3), 0.86 (s, 3H, CH_3), 1.82 (s, 3H, CH_3), 1.96 (d, 1H, *J* = 16 Hz, CH_2), 2.04 (d, 1H, *J* = 16 Hz, CH_2), 2.31 (d, 1H, *J* = 16 Hz, CH_2), 2.37 (d, 1H, *J* = 16 Hz, CH_2), 4.05 (s, 1H, NH), 5.30 (s, 1H, 4*H*), 5.94 (s, 1H, NH), 7.07 (d, 1H, *J* = 8 Hz, Ar-H), 7.16 (t, 1H, Ar-H.), 7.22 (d, 1H, *J* = 8 Hz, Ar-H), 7.82 (s, 1H, Ar-H); ^{13}C NMR (100 MHz, CDCl3): δ_C (ppm) 13.94, 27.42, 28.96, 29.70, 32.72, 41.09, 50.26, 101.09, 113.73, 119.17, 125.87, 129.71, 130.65, 134.01, 144.49, 148.05, 149.67, 154.88, 197.73; MS (ES$^+$) calcd $C_{19}H_{20}BrN_3O$ 385.08 found *m/z* 386.08 $(M + H)^+$.

4-(4-fluorophenyl)-3,7,7-trimethyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one , (4e)



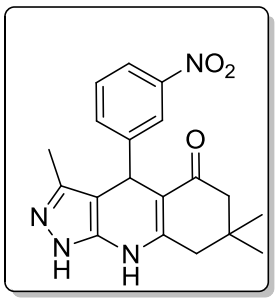
Yellowish solid. mp : 339-341 ^{o}C. IR ν_{max} (KBr): 3259, 3069, 2960, 1580, 1508, 1252, 757, cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 0.93 (s, 3H, CH_3), 1.01 (s, 3H, CH_3) 1.89 (s, 3H, CH_3), 2.05 (d, 1H, *J* = 16 Hz, CH_2), 2.15 (d, 1H, *J* = 16 Hz, CH_2), 2.27-2.30 (m, 2H, CH_2), 5.38 (s, 1H, 4*H*), 6.25 (s, H, NH), 6.81-7.12 (m, 4H, Ar-H), 11.83 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ_C (ppm) 14.47, 25.95, 27.32, 32.02, 34.30, 39.69 51.57, 110.28, 114.92, 119.47, 128.62, 133.34, 140.36, 142.59, 153.33, 157.88, 197.72 ; MS (ES$^+$) calcd $C_{19}H_{20}FN_3O$ 325.16 found *m/z* 326.01 $(M + H)^+$.

3,7,7-trimethyl-4-(4-nitrophenyl)-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one , (4f)



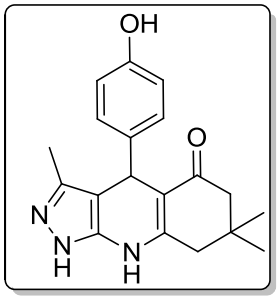
Yellowish solid. mp : 300-301 ^{o}C. IR ν_{max} (KBr): 3262, 3078, 2959, 1591, 1513, 1252, 733 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 1.04 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 2.16 (s, 3H, CH_3) , 2.26(d, 1H, *J* = 16 Hz, CH_2), 2.34(d, 1H, *J* = 16 Hz, CH_2), 2.40-2.45 (m, 4H, CH_2), 5.41 (s, 1H, 4*H*), 7.18 (d, 2H, *J* = 8 Hz, Ar-H), 8.07 (d, 2H, *J* = 8 Hz, Ar-H.), 11.74 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C (ppm) 11.56, 27.45, 29.44, 31.47, 33.25, 40.83 50.58, 106.58, 114.91, 123.53, 127.63, 129.34, 140.30, 146.10, 146.55, 158.17, 190.97 ; MS (ES^+) calcd $C_{19}H_{20}N_4O_3$ 352.15 found *m/z* 353.57 $(M + H)^+$ and 375.72 $(M+23)^+$.

3,7,7-trimethyl-4-(3-nitrophenyl)-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one , (4g)



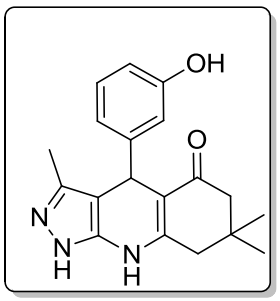
Yellow solid. mp : 299-300 ^{o}C. IR ν_{max} (KBr):3215, 3065, 2957, 1578, 1529, 1252, 730 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6): δ_H (ppm) 0.91 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 2.04 (d, 1H, *J* = 16 Hz, CH_2), 2.10 (s, 3H, CH_3), 2.17 (d, 1H, *J* = 16 Hz, CH_2), 2.41-2.51 (m, 2H, CH_2), 5.50 (s, 1H, 4*H*), 6.27 (s, H, NH), 7.38 (t, 1H, Ar-H), 7.51(d, 1H , *J* = 8 Hz, Ar-H.), 7.66 (s, 1H, Ar-H), 7.93 (d, 1H, *J* = 8 Hz Ar-H), 10.12 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ_C (ppm) 10.11, 23.64, 32.04, 33.81, 34.25, 37.31, 49.79, 105.66, 109.27, 120.45, 126.39, 127.00, 134.24, 138.14, 142.60, 145.97, 150.09, 153.78, 197.53; MS (ES^+) calcd $C_{19}H_{20}N_4O_3$ 352.15 found *m/z* 353.92 $(M + H)^+$.

4-(4-hydroxyphenyl)-3,7,7-trimethyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one , (4h)



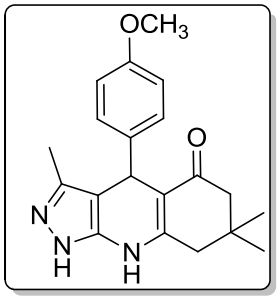
White solid. mp : 273-275 ^{o}C. IR ν_{max} (KBr): 3252, 3134, 2961, 1596, 1514, 1245, 838 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 0.94 (s, 3H, CH_3), 1.03 (s, 3H, CH_3) ,1.98 (s, 3H, CH_3), 2.12-2.15 (m, 2H, CH_2), 2.30-2.39 (m, 2H, CH_2), 3.42 (s, H, OH), 4.60 (s, 1H, *4H*), 6.60 (d, 2H, *J* = 8 Hz, Ar-H), 7.07 (d, 2H, *J* = 8 Hz, Ar-H.), 9.06 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C (ppm) 9.03, 31.94, 32.95, 33.99, 36.88, 45.44, 52.45, 98.56, 115.48, 119.72, 124.94, 133.94, 139.86, 146.08, 151.08, 154.14, 201.20; MS (ES$^+$) calcd $C_{19}H_{21}N_3O_2$ 323.16 found *m/z* 323.00 $(M)^+$.

4-(3-hydroxyphenyl)-3,7,7-trimethyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one , (4i).



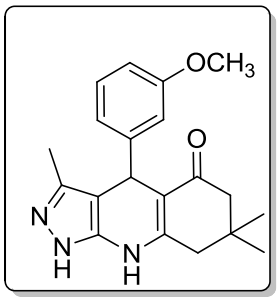
Yellow solid. mp : 271-272 ^{o}C. IR ν_{max} (KBr): 3260, 3068, 2959, 1575, 1544, 1254, 775 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 0.95 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 1.80 (s, 3H, CH_3), 2.03(d, 1H, *J* = 16 Hz, CH_2), 2.12(d, 1H, *J* = 16 Hz, CH_2), 2.35-2.40 (m, 2H, CH_2), 4.91 (s, 1H, 4*H*), 5.42 (s, 1H, OH), 6.46 (d, 1H, *J* = 8 Hz, Ar-H), 6.61 (d, 1H, *J* = 8 Hz, Ar-H), 6.89-6.95 (m, 1H, Ar-H.), 7.46 (s, 1H, Ar-H), 9.00(s, H, NH), 9.77 (s, 1H, NH); ^{13}C NMR (100 MHz, CDCl3): δ_C (ppm) 14.60, 25.94, 27.34, 33.93, 37.03, 40.21, 52.92, 109.30, 110.58, 112.72, 117.42, 123.42, 133.38, 140.53, 141.40, 142.55, 153.02, 158.03, 198.88; MS (ES$^+$) $C_{19}H_{21}N_3O_2$ 323.16 found *m/z* 324.05 $(M + H)^+$.

4-(4-methoxyphenyl)-3,7,7-trimethyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one, (4j).



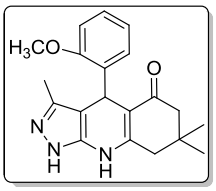
Yellow Crystal. mp : 298 ^{o}C. IR ν_{max} (KBr): 3238, 3065, 2962, 1590, 1546, 1253, 761 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6): δ_H (ppm) 0.93 (s, 3H, CH_3), 0.99 (s, 3H, CH_3) 1.88 (s, 3H, CH_3), 1.97 (d, 1H, *J* = 16 Hz, CH_2), 2.08 (d, 1H, *J* = 16 Hz, CH_2), 2.37-2.51 (m, 2H, CH_2), 3.64 (s,3H,CH_3), 4.89 (s, 1H, 4*H*), 6.62 (d, 2H, *J* = 8 Hz, Ar-H), 7.03 (d, 2H, *J* = 8 Hz, Ar-H), 7.74 (s, 1H, NH), 9.27 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ_C (ppm) 14.51, 32.10, 32.98, 34.01,36.99, 39.38, 55.73, 59.84, 109.34, 112.76, 117.96 , 133.18, 133.56, 140.22, 145.64, 151.30, 157.85, 198.62; MS (ES$^+$) calcd $C_{20}H_{23}N_3O_2$ 337.18 found *m/z* 338.0 $(M + H)^+$, 360.0$(M+Na)^+$.

4-(3-methoxyphenyl)-3,7,7-trimethyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one , (4k)



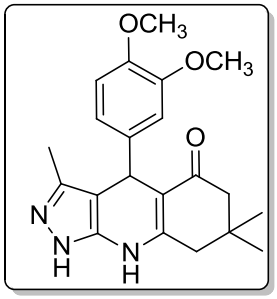
White solid. mp : 292-294 ^{o}C. IR ν_{max} (KBr): 3214, 3064, 2957, 1576, 1529, 1252, 730 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6): δ_H (ppm) 0.93 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 2.10 (d, 1H, *J* = 16 Hz, CH_2), 2.17(d, 1H, *J* = 16 Hz, CH_2), 2.24-2.30 (m, 2H, CH_2), 3.67 (s, 3H, CH_3), 5.79 (s, H, NH), 5.83 (s, 1H, 4*H*), 6.20 (d, 1H , *J* = 8 Hz, Ar-H.), 6.48 (d, 1H, *J* = 8 Hz Ar-H), 6.82 (t, 1H, Ar-H), 7.35 (s, 1H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C (ppm) 14.20, 27.34, 29.72, 32.50, 38.38, 41.00, 50.78, 55.09, 105.54, 110.86, 112.75, 113.74, 120.26, 129.01, 137.30, 138.22, 139.13, 151.11, 159.41, 198.28; MS (ES$^+$) calcd $C_{20}H_{23}N_3O_2$ 337.18 found *m/z* 338.75 $(M + H)^+$.

4-(2-methoxyphenyl)-3,7,7-trimethyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one , (4l)



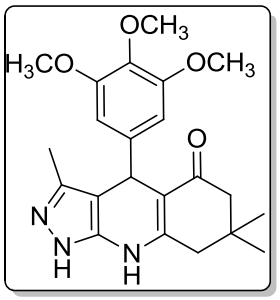
White solid. mp : 297-300 ^{o}C. IR ν_{max} (KBr):3387, 3060, 2957, 2929, 1557, 1249, 744 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 0.93 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 2.05-2.27 (m, 2H, CH_2), 2.32-241 (m, 2H, CH_2), 3.64 (s, 3H, CH_3), 5.50 (s, 1H, 4*H*), 6.73 (d, 1H, *J* = 8 Hz, Ar-H), 6.82 (t, 1H, Ar-H), 7.13 (t, 1H, Ar-H), 7.19 (d, 1H, *J* = 8Hz, Ar-H), 10.41 (s, 1H, NH), 11.84 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C (ppm) 18.88, 27.15, 31.88, 34.29, 37.35, 40.88, 51.45, 58.26, 106.04, 113.02, 114.82, 120.99, 124.61, 131.12, 135.49, 142.24, 144.15, 158.28, 193.57; MS (ES$^+$) calcd $C_{20}H_{23}N_3O_2$ 337.18 found *m/z* 360.89 $(M + 23)^+$.

4-(3,4-dimethoxyphenyl)-3,7,7-trimethyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one , (4m)



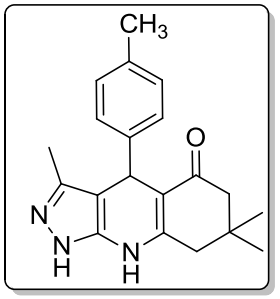
White solid. mp : 307-309 ^{o}C. IR ν_{max} (KBr): 3257, 3066, 2957, 1577, 1546, 1256, 744 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6): δ_H (ppm) 0.81 (s, 3H, CH_3), 0.86 (s, 3H, CH_3) , 1.79 (s, 3H, CH_3) , 1.97 (d, 1H, *J* = 16 Hz, CH_2), 2.02 (d, 1H, *J* = 16 Hz, CH_2), 2.21-2.28 (m, 2H, CH_2), 3.57-3.59 (m, 6H, CH_3), 4.84 (s, 1H, 4*H*), 6.05 (s, H, NH), 6.47 - 6.67 (m, 2H, Ar-H), 7.14 (s, 1H, Ar-H.), 8.14 (s, 1H, NH); ^{13}C NMR (100 MHz,CDCl3): δ_C (ppm) 13.37, 26.18, 27.17, 28.17, 31.52, 41.21, 49.41, 53.11, 54.81, 109.67, 110.04, 117.85, 118.62, 121.83, 134.27, 137.31, 141.40, 147.50, 147.76, 157.71, 195.99; MS (ES$^+$) calcd $C_{21}H_{25}N_3O_3$ 367.19 found *m/z* 368.0 $(M + H)^+$; 390.0 $(M+23)^+$.

3,7,7-trimethyl-4-(3,4,5-trimethoxyphenyl)-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one, (4n)



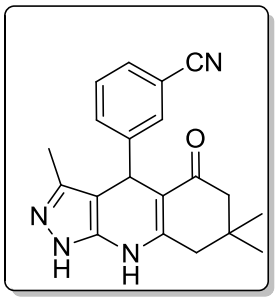
White solid. mp : 319-321 ^{o}C. IR ν_{max} (KBr):3242, 3066, 2962 , 1591, 1539, 1252, 755cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 0.93 (s, 3H, CH_3), 0.95 (s, 3H, CH_3) , 2.11 (s, 3H, CH_3), 2.17 (d, 1H, *J* = 16 Hz, CH_2), 2.27 (d, 1H, *J* = 16 Hz, CH_2), 2.31 (d, 1H, *J* = 16 Hz, CH_2), 2.36 (d, 1H, *J* = 16 Hz, CH_2), 3.69 (s, 9H, CH_3), 4.28 (s, H, NH), 5.43 (s, 1H, 4*H*), 6.22 (s, 1H, Ar-H), 6.37 (s, 1H, Ar-H), 7.88 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ_C (ppm) 8.74, 26.87, 27.15, 34.30, 36.48, 43.28, 50.56, 52.37, 55.21, 100.87, 109.19, 113.61, 132.60, 133.25, 136.59, 141.82, 143.65, 147.52, 149.53, 190.88; MS (ES$^+$) calcd $C_{22}H_{27}N_3O_4$ 397.20 found *m/z* 398.0 $(M + H)^+$.

3,7,7-trimethyl-4-(p-tolyl)-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one, (4o)



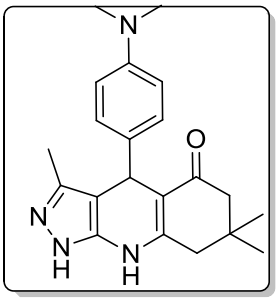
White solid. mp : 309-311 ^{o}C. IR ν_{max} (KBr): 3236, 3025, 2957, 1578, 1545, 1249, 770cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 0.92 (s, 3H, CH_3), 1.03 (s, 3H, CH_3) 2.01 (s, 3H, CH_3), 2.08 (d, 1H, *J* = 16 Hz, CH_2), 2.14(d, 1H, *J* = 16 Hz, CH_2), 2.39-2.46 (m, 2H, CH_2), 2.59 (s, 3H,CH_3), 6.02 (s, 1H, 4*H*), 6.37 (s, H, NH), 6.97 (d, 2H, *J* = 8 Hz, Ar-H), 7.18 (d, 2H, *J* = 8 Hz, Ar-H), 11.28 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C (ppm) 13.16, 21.13, 27.28, 29.02, 29.70, 32.61, 40.70, 50.35, 105.68, 106.95, 126.77, 129.12, 137.52, 138.79, 148.21, 148.66, 151.41, 193.62; MS (ES$^+$) calcd $C_{20}H_{23}N_3O$ 321.18 found *m/z* 322.40 $(M + H)^+$.

3-(3,7,7-trimethyl-5-oxo-4,5,6,7,8,9-hexahydro-1H-pyrazolo[3,4-b]quinolin-4-yl)benzonitrile, (4p)



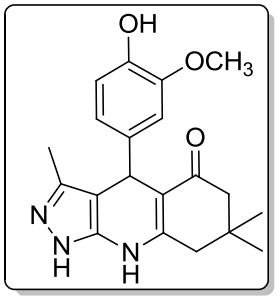
Yellow solid. mp : 287-289 ^{o}C. IR ν_{max} (KBr): 3216, 3073, 2957, 2232, 1579, 1539, 791 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 0.94 (s, 3H, CH_3), 1.06 (s, 3H, CH_3) 1.98(s, 3H, CH_3), 2.11-2.28 (m, 2H, CH_2), 2.40-247 (m, 2H, CH_2), 6.08 (s, 1H, 4*H*), 6.52 (s, H, NH), 7.31-7.38 (m, 1H, Ar-H), 7.48 (d, 1H, *J* = 8 Hz, Ar-H), 7.55 (d, 1H, *J* = 8 Hz, Ar-H), 7.65 (s, 1H, Ar-H), 10.93 (s, 1H, NH); ^{13}C NMR (100 MHz, CDCl3): δ_C (ppm) 13.80, 27.42, 28.87 , 32.68, 33.22, 40.70, 50.10, 103.76, 105.78, 112.19, 118.82, 129.20, 129.89, 131.66, 133.08, 137.66, 141.66, 143.79, 151.58, 196.54; ; MS (ES^{+}) $C_{20}H_{20}N_4O$ 332.16 found *m/z* 333.00 (M + H)$^{+}$.

4-(4-(dimethylamino)phenyl)-3,7,7-trimethyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one, (4q)



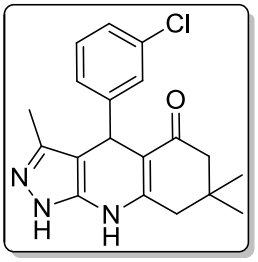
White solid. mp : 257-259 ^{o}C. IR ν_{max} (KBr): 3254, 3077, 2958, 1586, 1545, 1252, 794 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 0.95 (s, 3H, CH_3), 0.99 (s, 3H, CH_3) 1.92 (s, 3H, CH_3), 2.06 (d, 1H, *J* = 16 Hz, CH_2), 2.14(d, 1H, *J* = 16 Hz, CH_2), 2.30-2.42 (m, 2H, CH_2), 2.80 (s, 6H,CH_3), 3.60 (s, 1H, NH), 4.95 (s, 1H, 4*H*), 6.68 (d, 2H, *J* = 8 Hz, Ar-H), 7.04 (d, 2H, *J* = 8 Hz, Ar-H), 8.20 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C (ppm) 14.78, 27.39, 28.19, 32.21, 34.40, 40.52, 42.01, 42.47, 50.84, 105.60, 111.62, 114.81, 128.45, 131.05, 137.56, 147.57,149.86, 155.92, 194.97; MS (ES^{+}) calcd $C_{21}H_{26}N_4O$ 350.21 found *m/z* 373.22 (M + Na)$^{+}$.

4-(4-hydroxy-3-methoxyphenyl)-3,7,7-trimethyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one, (4t)



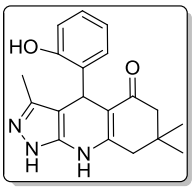
White solid. mp : 281-283 ^{o}C. IR ν_{max} (KBr): 3245, 3125, 2970, 1587, 1562, 1265, 767cm^{-1}; δ_H (ppm) ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6): δ_H (ppm) 0.87 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 1.93 (d, 1H, *J* = 16 Hz, CH_2), 2.13 (d, 1H, *J* = 16 Hz, CH_2), 2.32-2.38 (m, 2H, CH_2), 3.04 (s, 1H, OH), 4.02 (s, 1H, NH), 4.99 (s, 1H, 4*H*), 5.16 (s, 3H, CH_3), 6.56 (d, 1H, *J* = 8 Hz, Ar-H), 6.70 (d, 1H, *J* = 8Hz, Ar-H), 7.77 (s, 1H, Ar-H), 9.94 (s, 1H, NH); ^{13}C NMR (100 MHz,CDCl3): δ_C (ppm) 19.11, 27.34, 32.93, 34.30, 36.98, 38.86, 52.96, 58.91, 103.31, 116.11, 117.83, 119.66, 124.90, 130.02, 133.68, 139.97, 145.89, 149.38, 157.31, 195.37; MS (ES$^+$) calcd $C_{20}H_{23}N_3O_3$ 353.17 found *m/z* 354.97 $(M + H)^+$.

4-(3-chlorophenyl)-3,7,7-trimethyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one , (4s)



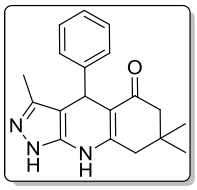
White solid. mp: 301-303 ^{o}C. IR ν_{max} (KBr): 3271, 3068, 2961, 1575, 1543, 1258, 752 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 0.92 (s, 3H, CH_3), 1.02 (s, 3H, CH_3) 1.88 (s, 3H, CH_3), 2.12 (d, 1H, *J* = 16 Hz, CH_2), 2.20 (d, 1H, *J* = 16 Hz, CH_2), 2.32-2.40 (m, 2H, CH_2), 4.02 (s, 1H, NH), 5.41 (s, 1H, 4*H*), 6.24 (s, 1H, NH), 7.09 (d, 1H, *J* = 8 Hz, Ar-H), 7.35 (t, 1H, Ar-H), 7.91 (d, 1H, *J* = 8 Hz, Ar-H), 8.0 (s, 1H, Ar-H); ^{13}C NMR (100 MHz, CDCl3): δ_C (ppm) 10.19, 27.41, 28.95, 29.70, 33.83, 41.15, 50.21, 99.85, 105.83, 125.44, 127.77, 128.22, 130.18,1 33.54, 144.12, 147.66, 155.49, 159.17, 194.47; MS (ES$^+$) calcd. for $C_{19}H_{20}ClN_3O$ 341.13 found *m/z* 342.16 $(M + H)^+$.

4-(2-hydroxyphenyl)-3,7,7-trimethyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one , (4t)



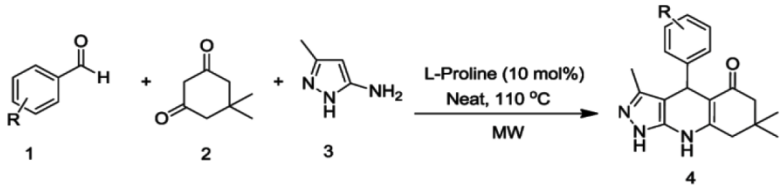
White solid. mp: 268-270 ^{o}C. IR ν_{max} (KBr): 3266, 3076, 2961, 1584, 1549, 1253, 752cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$+ DMSO-d_6): δ_H (ppm) 0.87 (s, 3H, CH_3), 0.99 (s, 3H, CH_3) ,1.75 (s, 3H, CH_3), 2.08 (d, 1H, *J* = 16 Hz, CH_2), 2.17 (d, 1H, *J* = 16 Hz, CH_2), 2.35(d, 1H, *J* = 16 Hz, CH_2), 2.40 (d, 1H, *J* = 16 Hz, CH_2), 4.01 (s,1 H, NH), 5.16 (s, 1H, *4H*), 6.55 (d, 1H, *J* = 8Hz, Ar-H), 6.69 (d, 1H, *J* = 8 Hz, Ar-H), 6.81-6.88 (m, 2H, Ar-H), 7.76 (s, 1H, OH), 9.93 (s, 1H, NH); ^{13}C NMR (100 MHz, CDCl3+ DMSO-d_6): δ_C (ppm) 14.22, 32.22, 33.45, 34.27, 37.10, 40.48, 52.92, 105.81, 109.23, 112.50, 120.10, 122.05, 124.85, 131.46, 134.11, 139.86, 153.74, 158.33, 200.27 ;MS (ES^+) $C_{19}H_{21}N_3O_2$ 323.16 found *m/z* 324.16 $(M + H)^+$.

3,7,7-trimethyl-4-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one ,(4u)

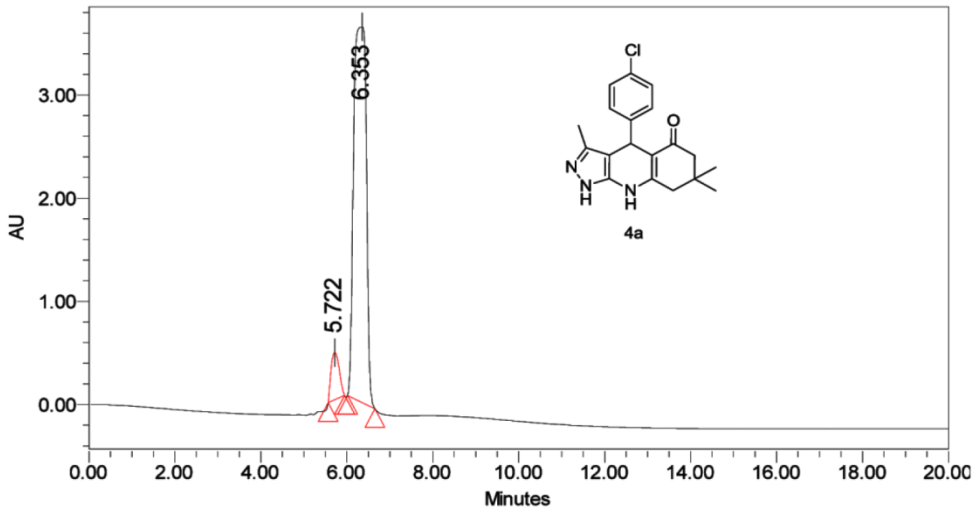


White solid. mp: 231-233 ^{o}C. IR ν_{max} (KBr): 3239, 3061, 2958, 1587, 1549, 1251,752cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 0.91 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 1.99-2.02 (m, 2H, CH_2), 2.09 (d, *J* = 16Hz, 1H), 2.16 (d, *J* =16Hz, 1H), 5.39 (s, 1H, *4H*), 6.26 (s,1 H, NH), 7.01-7.39 (m, 5H, Ar-H), 9.81 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6): δ_C (ppm) 14.20, 27.30, 29.13, 32.46, 34.94, 40.50, 50.50, 106.27, 115.40, 128.03, 129.84, 137.50, 142.61, 149.08, 158.23, 195.97; MS (ES^+) $C_{19}H_{21}N_3O$ 307.17 found *m/z* 308.15 $(M + H)^+$.

HPLC ANALYSIS:



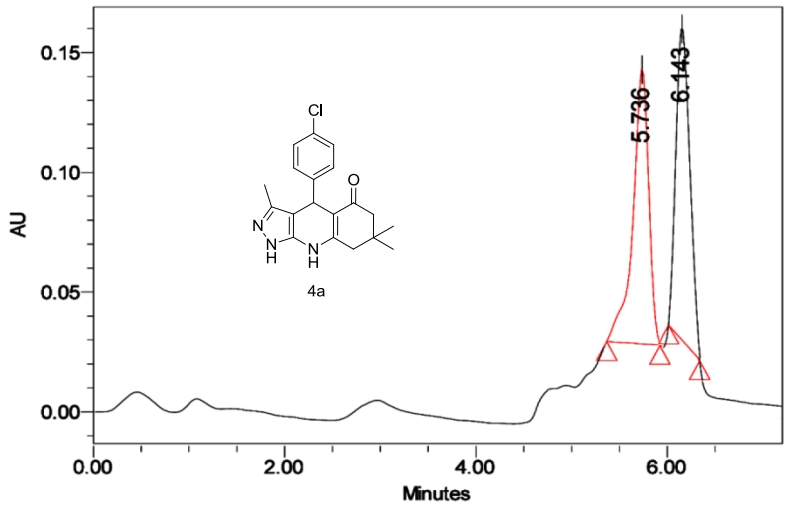
Enantiomeric ratio (08:92) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (20: 80), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		5.722	6060697	7.58	458915
2		6.353	73941090	92.42	3646059

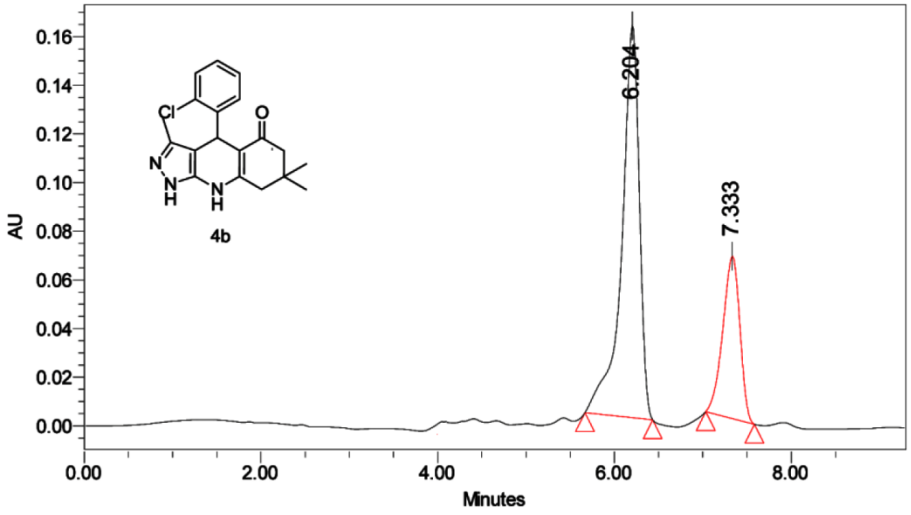
Racemic Mixture:

Enantiomeric ratio (49.81:50.19) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (20: 80), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		5.736	1320809	49.81	114818
2		6.143	1330940	50.19	130308

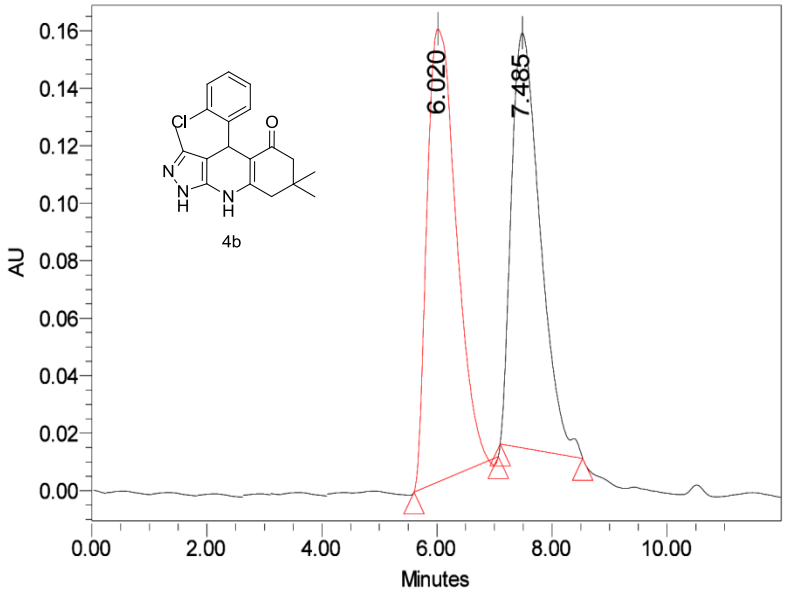
Enantiomeric ratio (71:29) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		6.204	2245976	71.45	161558
2		7.333	897256	28.55	66827

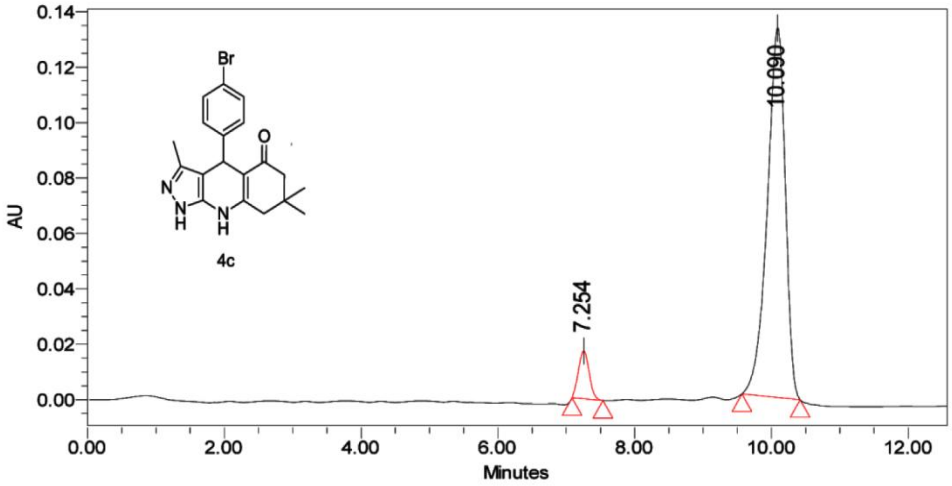
Racemic Mixture:

Enantiomeric ratio (52.65:47.35) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		6.020	5597017	52.65	157677
2		7.485	5033941	47.35	144386

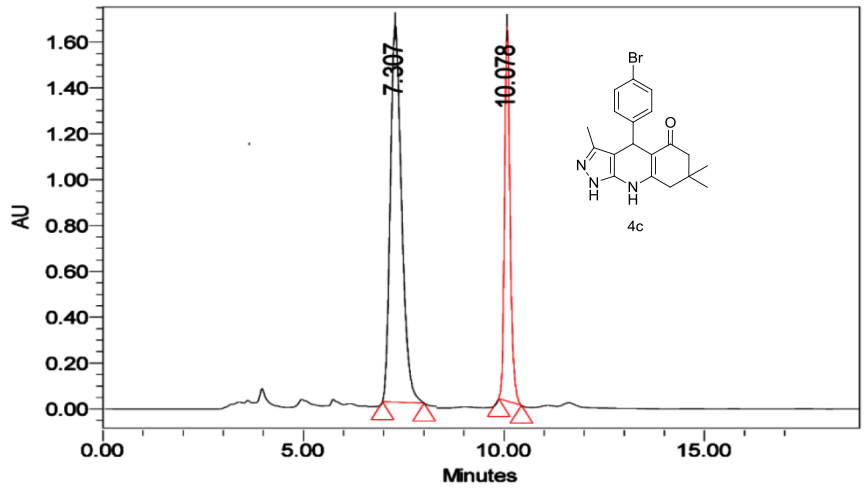
Enantiomeric ratio (07:93) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (14: 86), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		7.254	188874	7.17	17346
2		10.090	2446728	92.83	133567

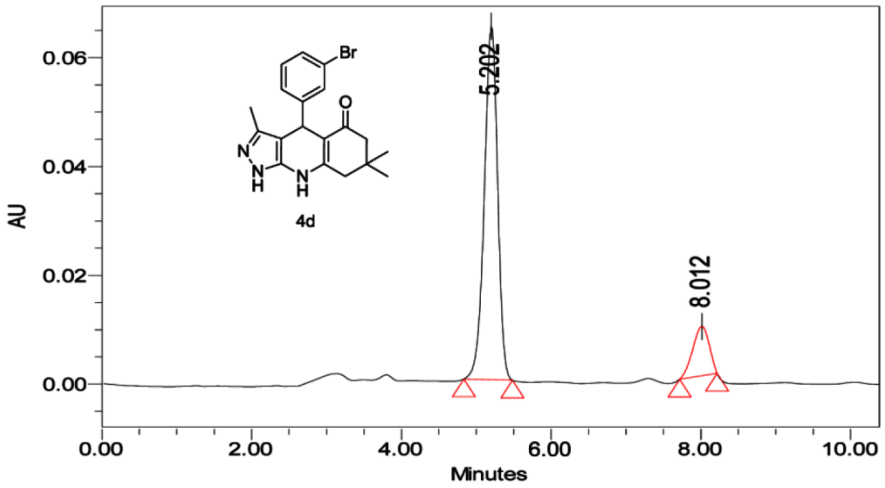
Racemic Mixture:

Enantiomeric ratio (51.22:48.78) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (14: 86), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		7.307	16507143	51.22	1657928
2		10.078	15720890	48.78	1637936

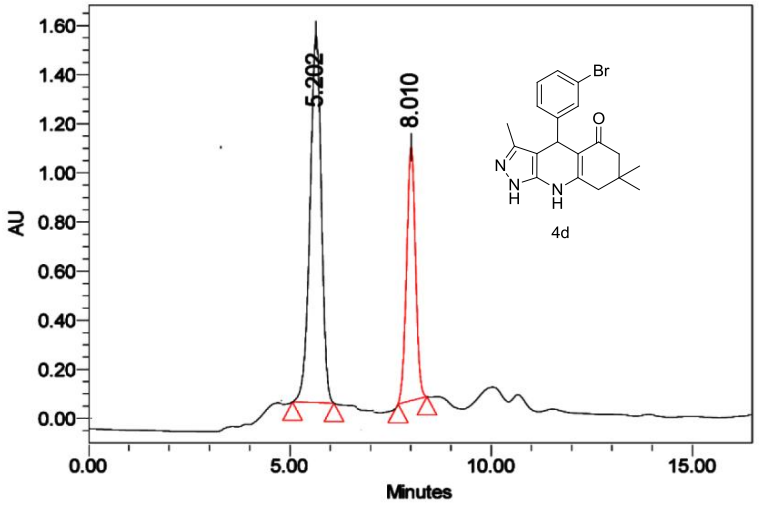
Enantiomeric ratio (85:15) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (14: 86), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		5.202	801033	85.30	65085
2		8.012	137993	14.70	9102

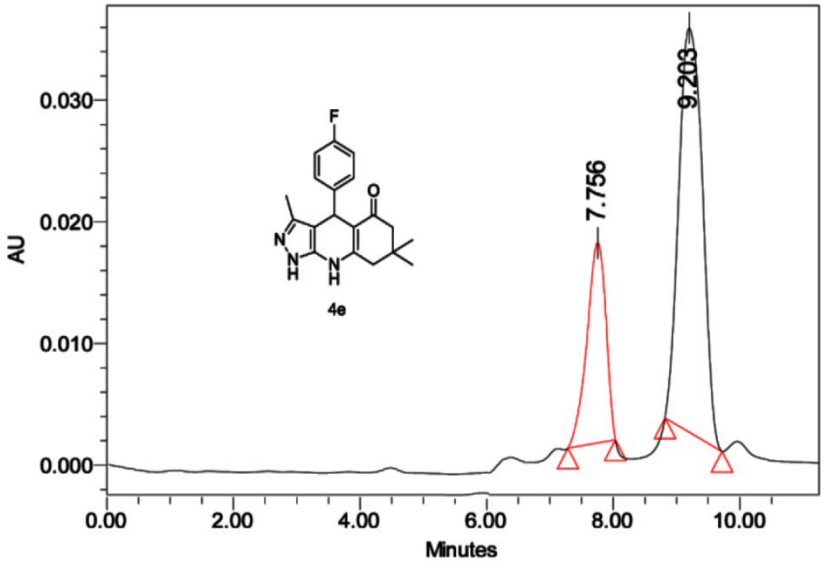
Racemic Mixture:

Enantiomeric ratio (53.63:46.37) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (14: 86), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		5.202	18412002	53.63	1566132
2		8.010	15916534	46.37	1035726

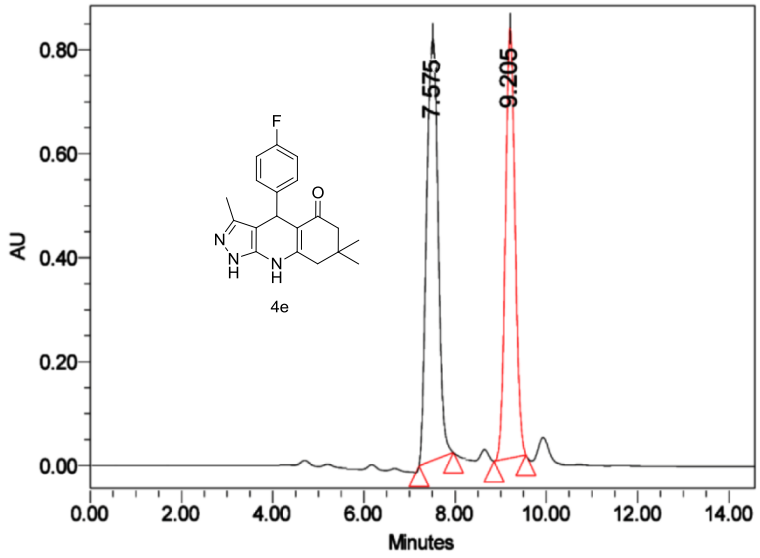
Enantiomeric ratio (28:72) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		7.756	341840	28.32	16469
2		9.203	865157	71.68	33245

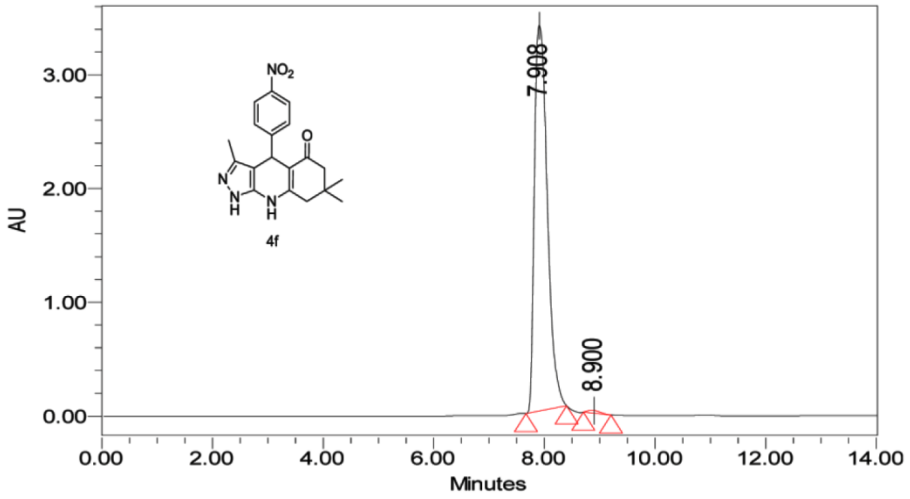
Racemic Mixture:

Enantiomeric ratio (49.61:50.39) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		7.575	12017504	49.61	817594
2		9.205	12206207	50.39	828958

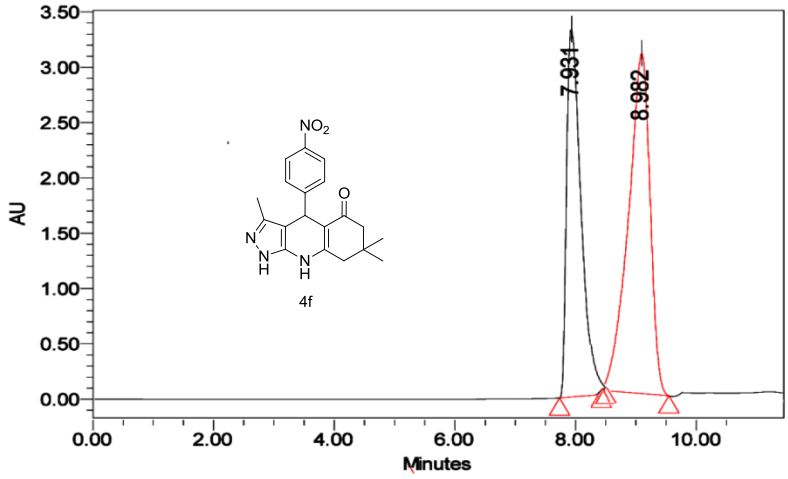
Enantiomeric ratio (99.3:0.7) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		7.908	55317444	99.30	3396999
2		8.900	389499	0.70	24089

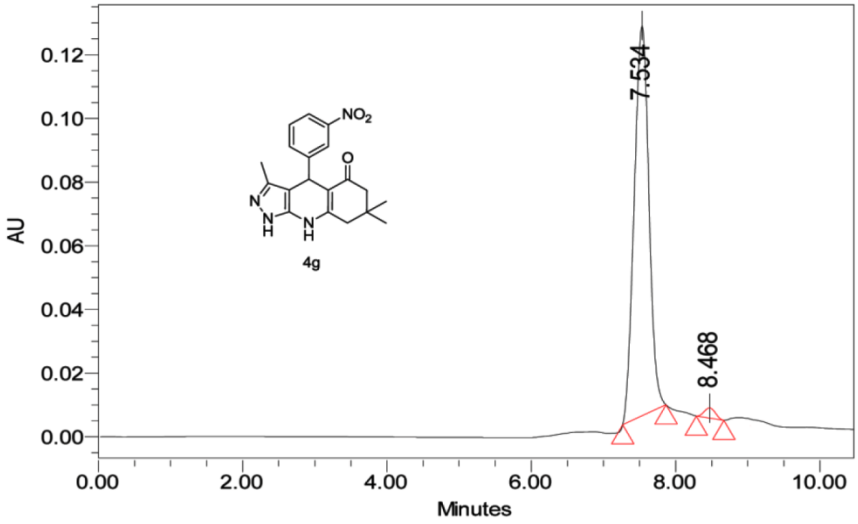
Racemic Mixture:

Enantiomeric ratio (47.72:52.28) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		7.931	550908	47.72	3328096
2		8.982	603719	52.28	3126126

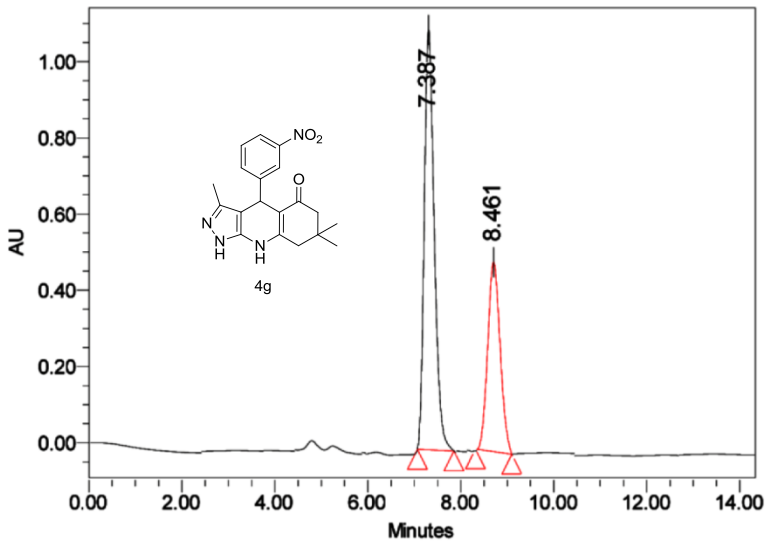
Enantiomeric ratio (98:02) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		7.534	1737088	98.09	122623
2		8.468	33822	1.91	3176

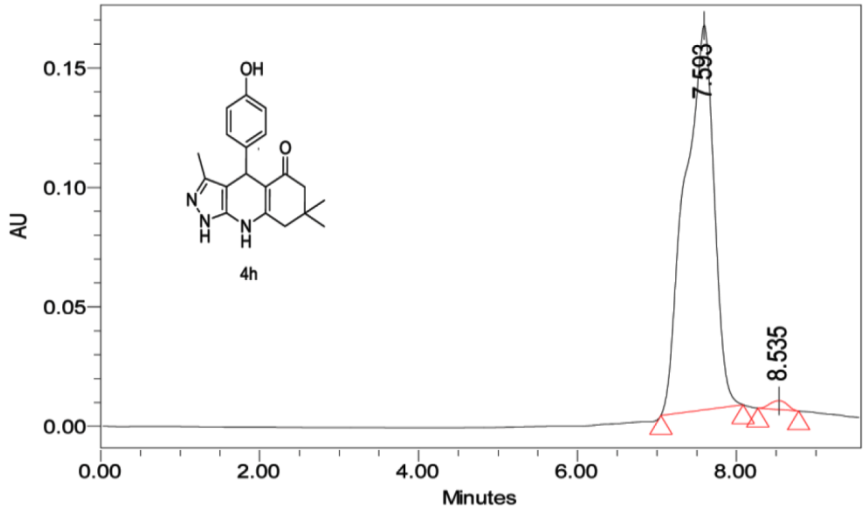
Racemic Mixture:

Enantiomeric ratio (55.38:44.62) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		7.387	16507143	55.38	1105704
2		8.461	13298724	44.62	482062

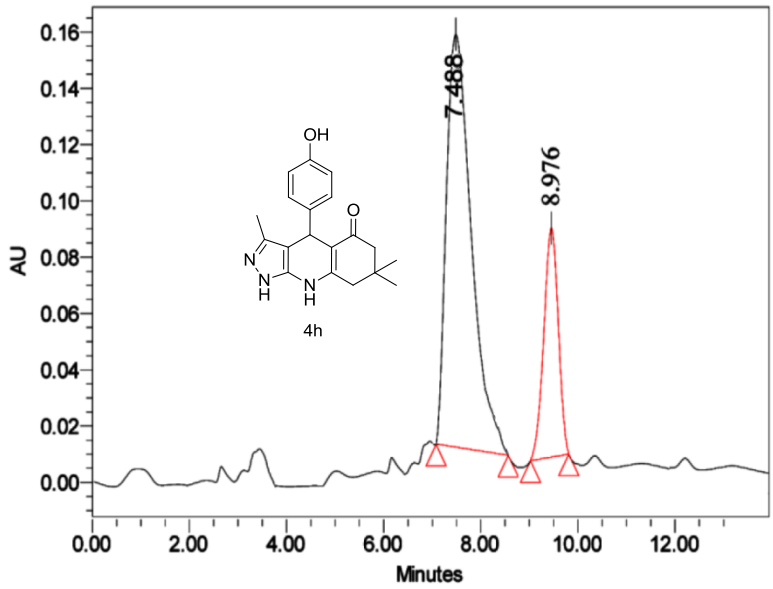
Enantiomeric ratio (98.64:1.36) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		7.593	4073832	98.64	161206
2		8.535	56300	1.36	3725

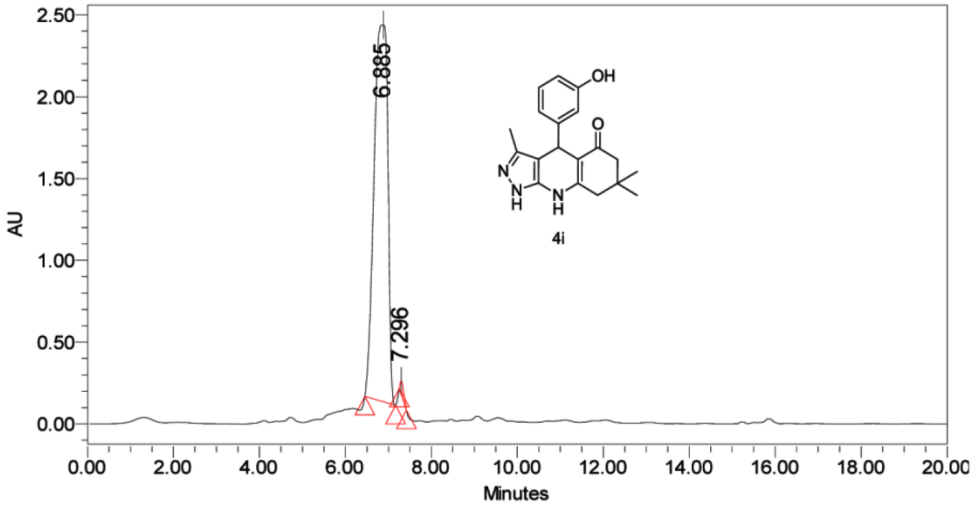
Racemic Mixture:

Enantiomeric ratio (54.68:45.32) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		7.488	5015003	54.68	147048
2		8.976	4156915	45.32	817875

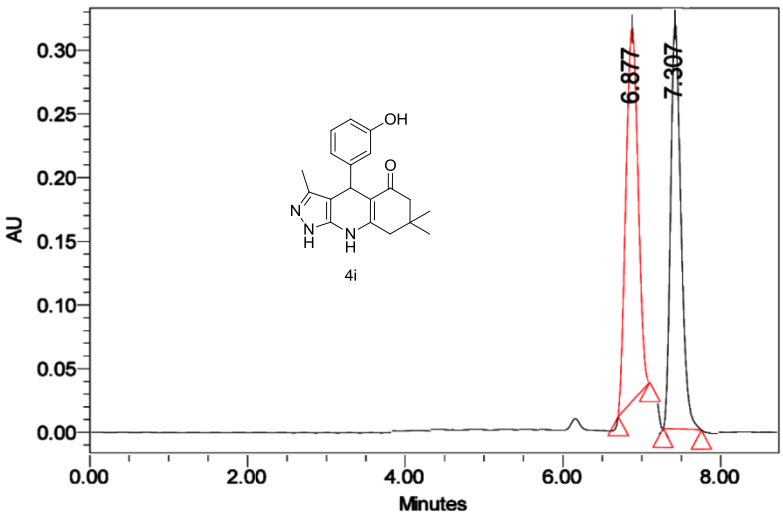
Enantiomeric ratio (99.01:0.99) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (18: 82), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		6.885	51284829	99.01	2307717
2		7.296	512465	0.99	81797

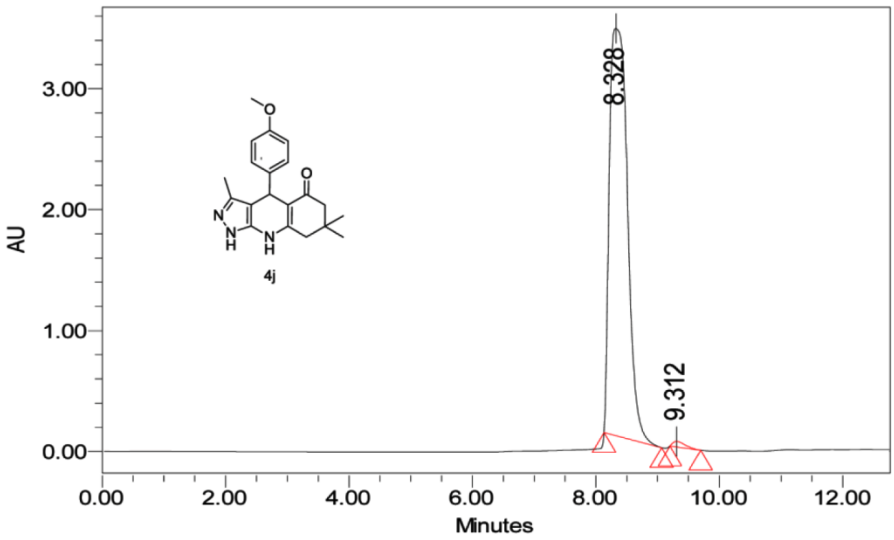
Racemic Mixture:

Enantiomeric ratio (48.61:51.39) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (18: 82), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		6.877	3128282	48.61	293627
2		7.307	3307143	51.39	295125

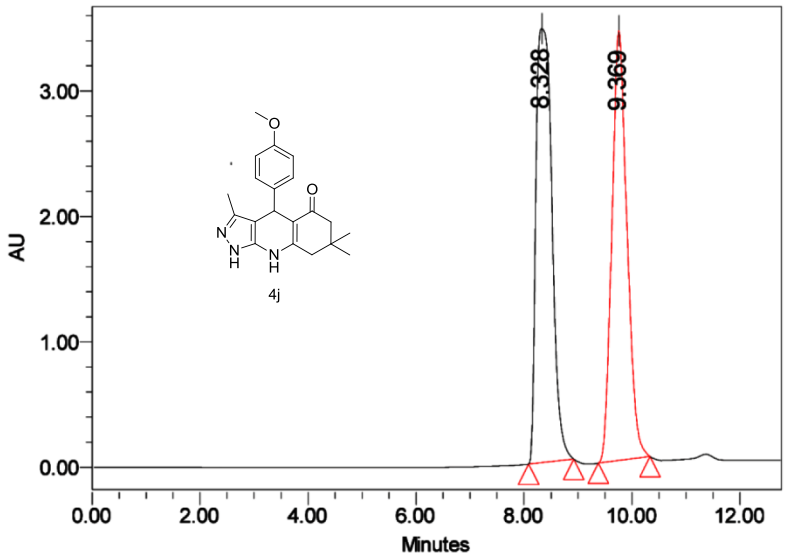
Enantiomeric ratio (99.06:0.94) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Retention Time	Area	% Area	Height
1	8.328	68635889	99.06	3366449
2	9.312	654647	0.94	47336

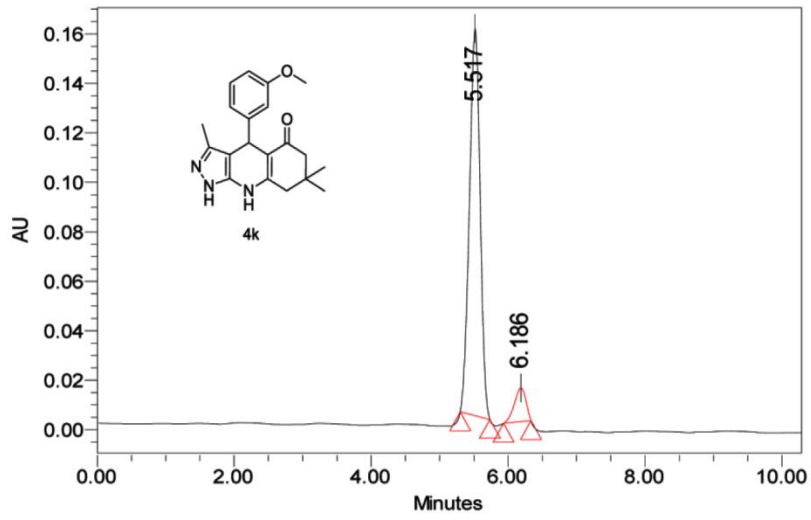
Racemic Mixture:

Enantiomeric ratio (49.78:50.22) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		8.328	71437728	49.78	3465094
2		9.369	72078520	50.22	3425094

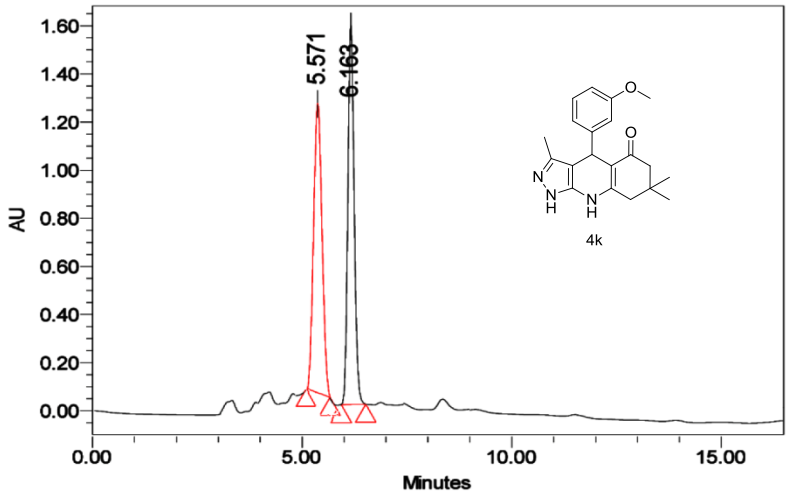
Enantiomeric ratio (91.44:8.56) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (14: 86), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		5.517	1700048	91.44	156612
2		6.186	159116	8.56	13661

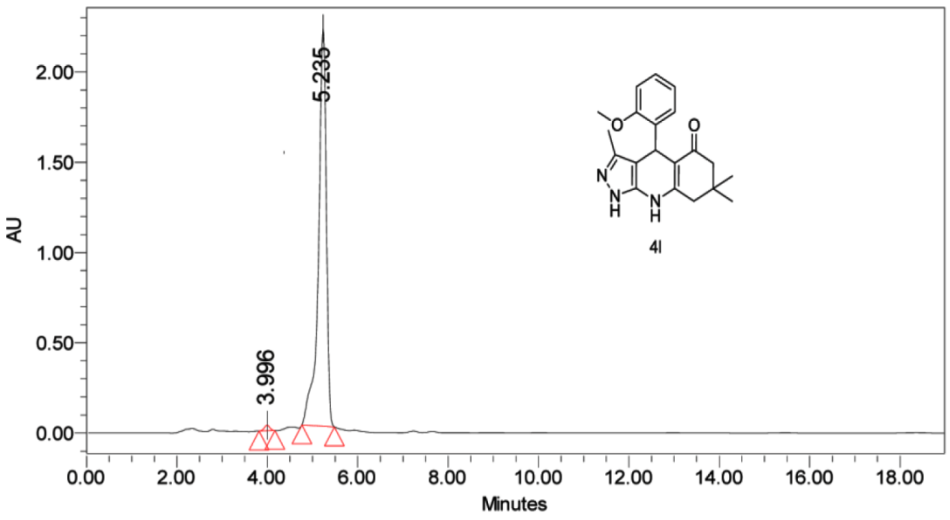
Racemic Mixture:

Enantiomeric ratio (48.19:51.81) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (14: 86), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		5.571	15264888	48.19	1307716
2		6.163	16412002	51.81	1576132

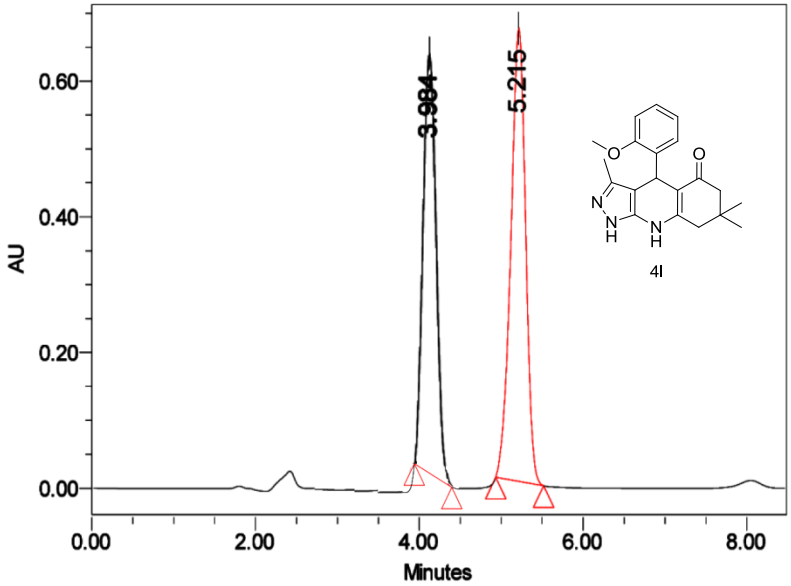
Enantiomeric ratio (0.93:99.07) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (20: 80), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		3.996	252704	0.93	30674
2		5.235	26804403	99.07	2204147

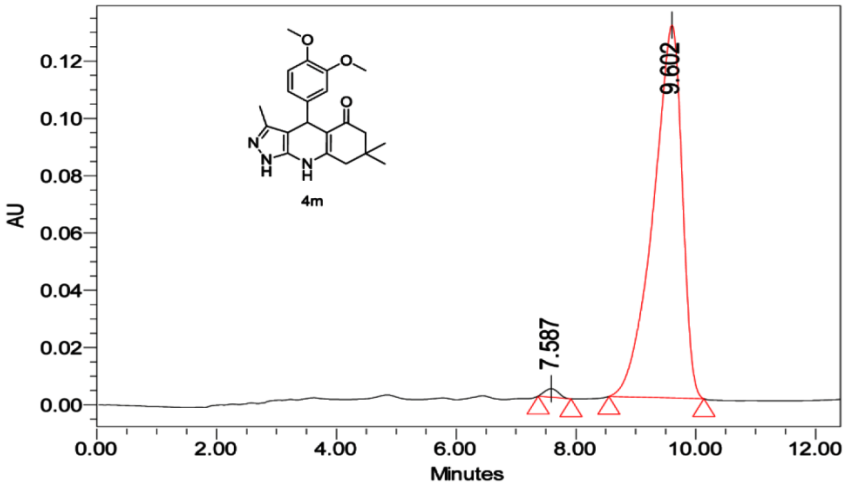
Racemic Mixture:

Enantiomeric ratio (49.62:50.38) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (20: 80), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		3.984	8235762	49.62	646417
2		5.215	8363262	50.38	668131

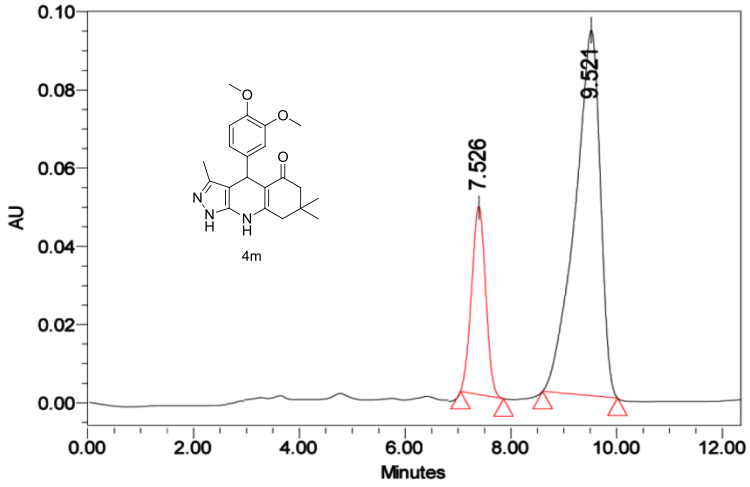
Enantiomeric ratio (1.08:98.92) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		7.587	47456	1.08	2966
2		9.602	4357965	98.92	130197

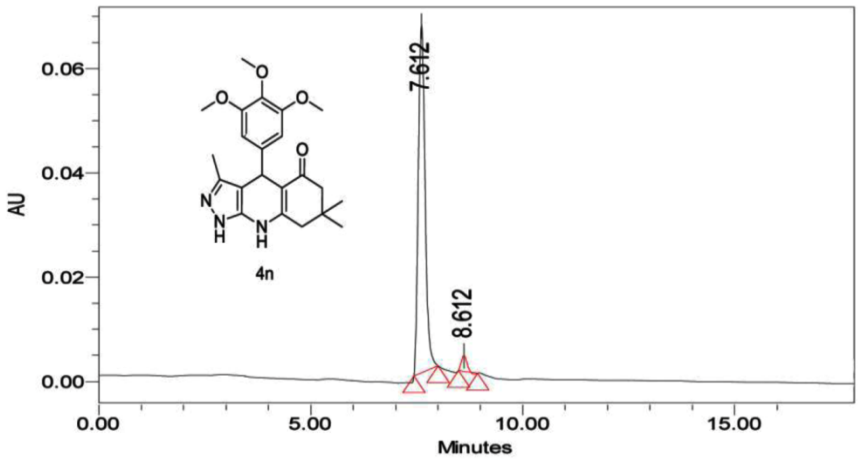
Racemic Mixture:

Enantiomeric ratio (29.50:70.50) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		7.526	1299028	29.50	50072
2		9.521	3104394	70.50	93470

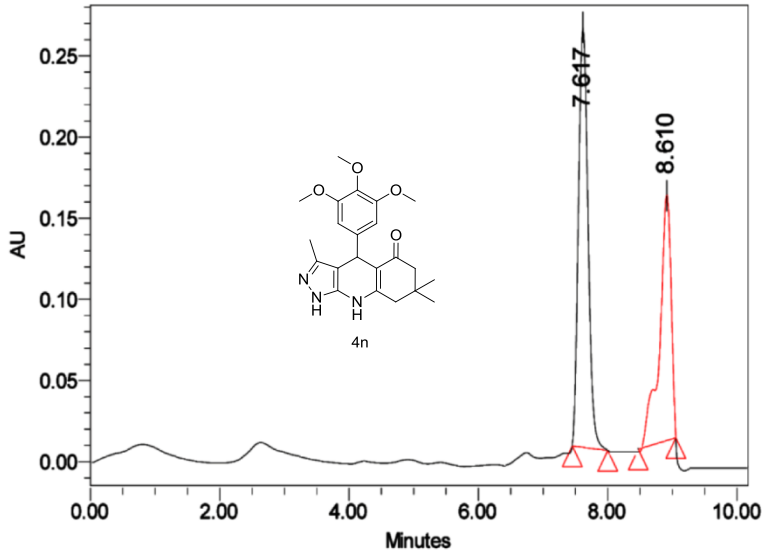
Enantiomeric ratio (96.22:3.78) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (18: 82), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		7.612	741349	96.22	66747
2		8.612	29102	3.78	2968

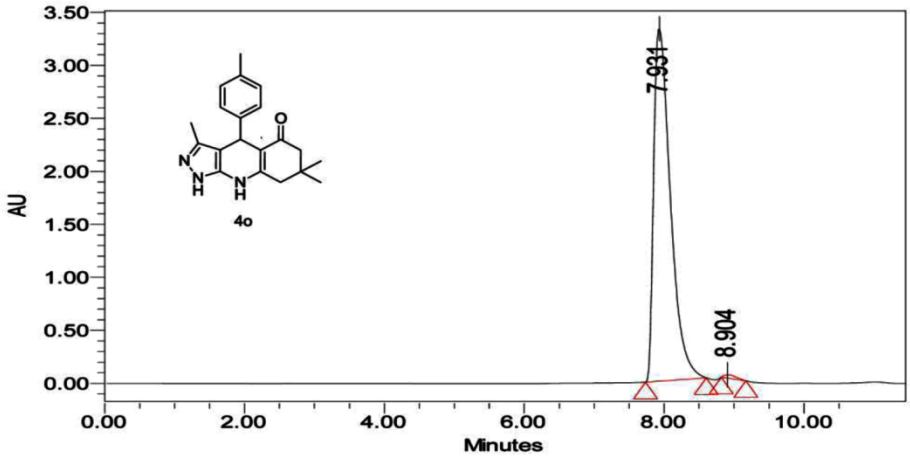
Racemic Mixture:

Enantiomeric ratio (55.07:44.93) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (18: 82), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		7.617	427603	55.07	258839
2		8.610	348884	44.93	159799

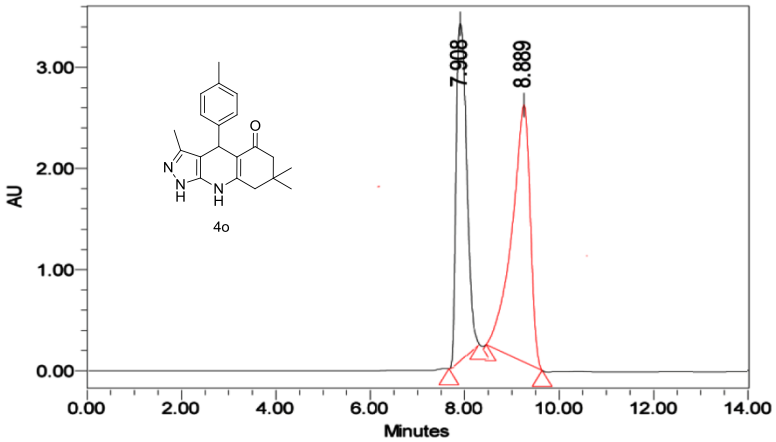
Enantiomeric ratio (99.29:0.71) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		7.931	55520908	99.29	3328096
2		8.904	396877	0.71	31274

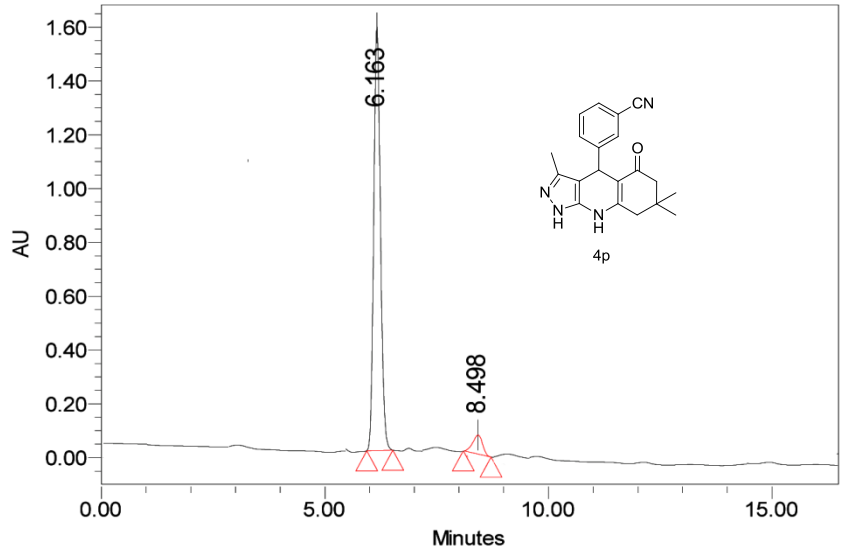
Racemic Mixture:

Enantiomeric ratio (47.45:52.55) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		7.908	47317444	47.45	3396999
2		8.889	52399499	52.55	2620000

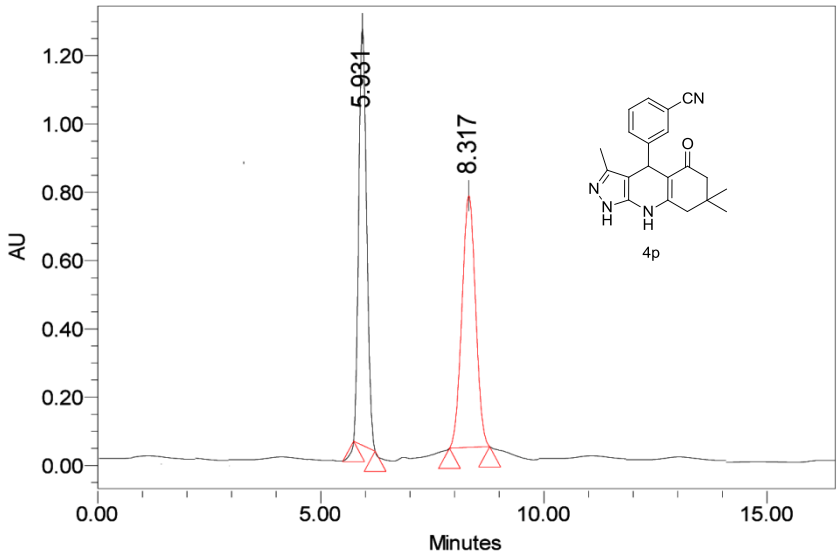
Enantiomeric ratio (98.15:1.85) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		6.163	5271706	98.15	1576132
2		8.498	99153	1.85	8101

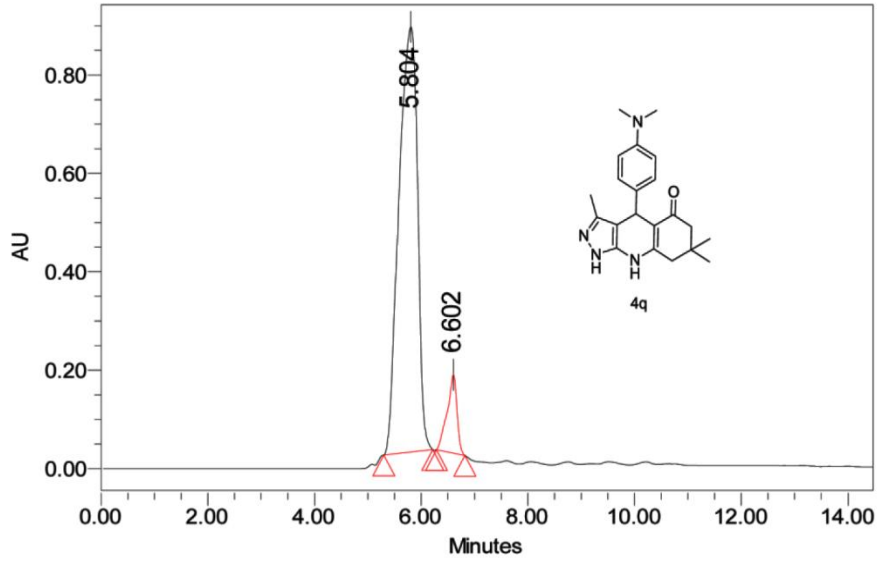
Racemic Mixture:

Enantiomeric ratio (48.82:51.18) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		5.931	14957808	48.82	1221773
2		8.317	15681364	51.18	737149

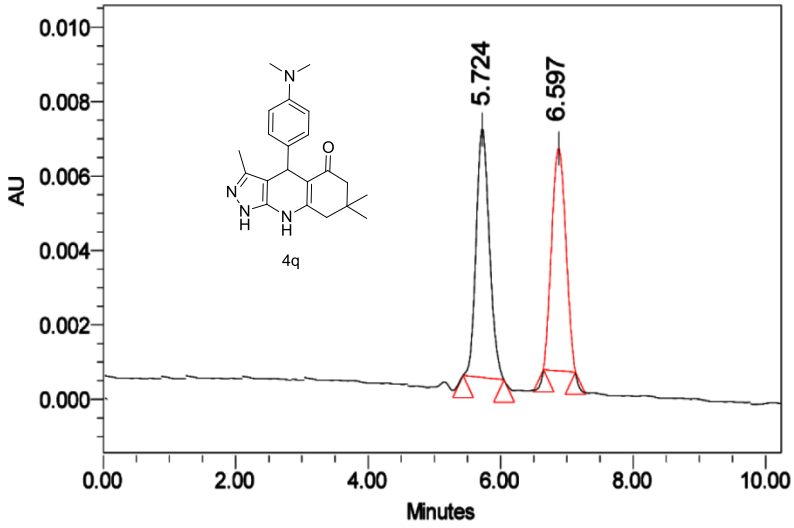
Enantiomeric ratio (91.08:8.92) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		5.804	20924403	91.08	864509
2		6.602	2049066	8.92	159696

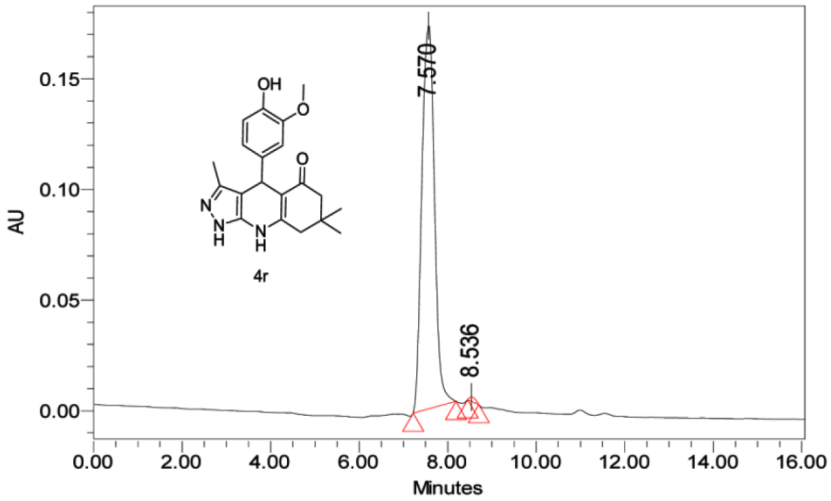
Racemic Mixture:

Enantiomeric ratio (51.12:48.88) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		5.724	92843	51.12	6694
2		6.597	88787	48.88	5989

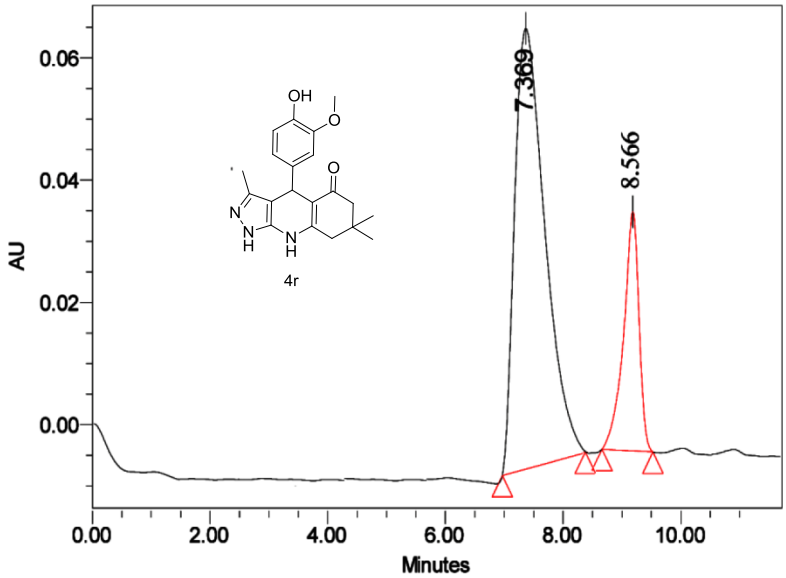
Enantiomeric ratio (99.43:0.57) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		7.570	3427626	99.43	173178
2		8.536	19807	0.57	1950

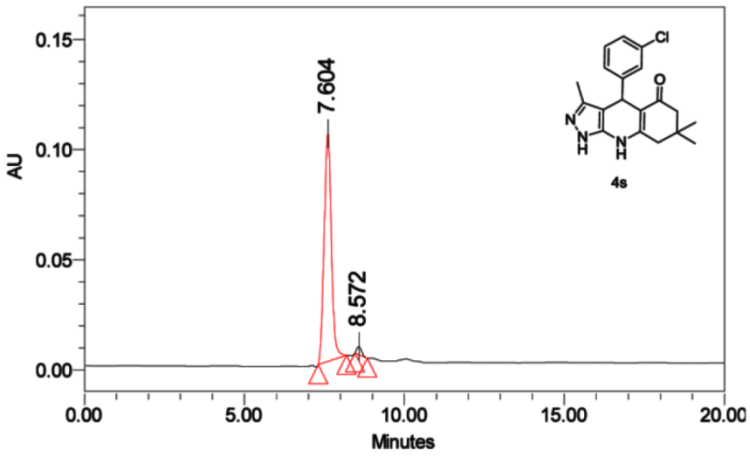
Racemic Mixture:

Enantiomeric ratio (55.37:44.63) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		7.369	2567094	55.37	72018
2		8.566	2069493	44.63	32584

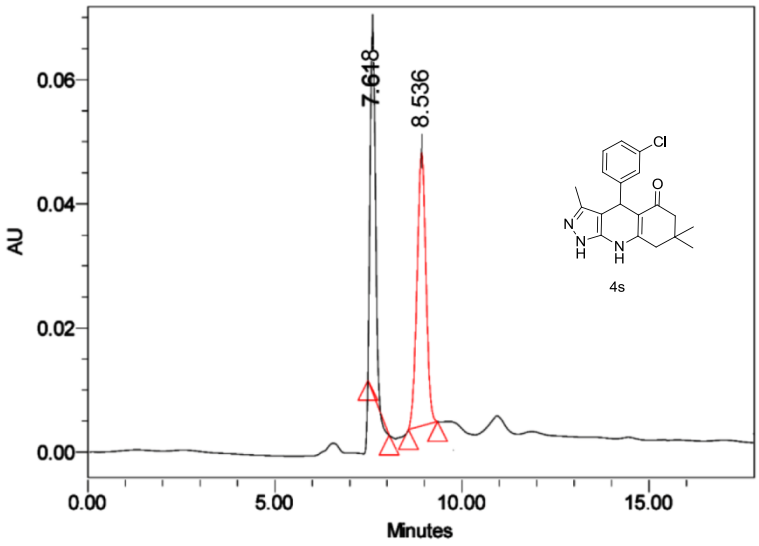
Enantiomeric ratio (97.75:2.25) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		7.604	1625621	97.75	103593
2		8.572	37345	2.25	3621

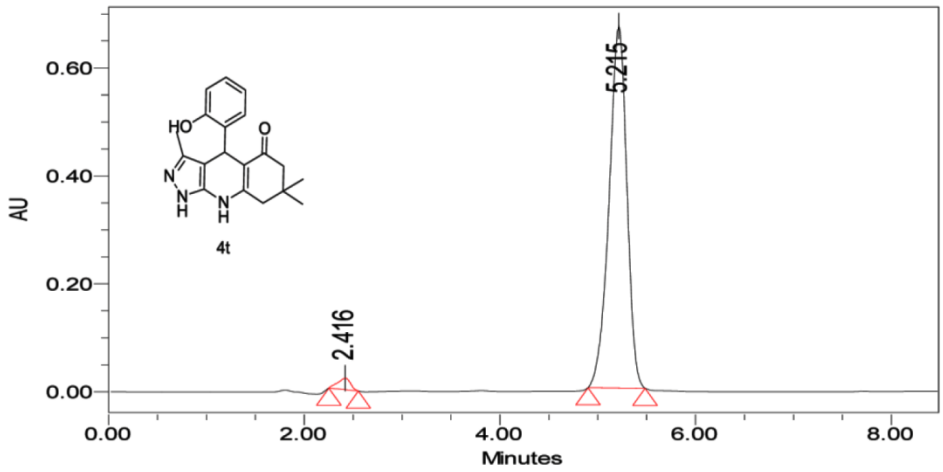
Racemic Mixture:

Enantiomeric ratio (49.28:50.72) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		7.618	579541	49.28	54877
2		8.536	596534	50.72	44734

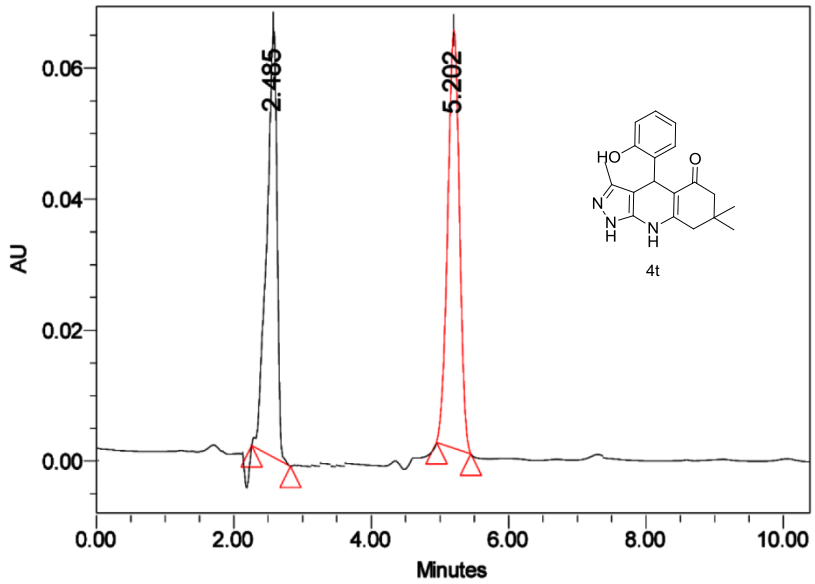
Enantiomeric ratio (2.20:97.80) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		2.416	191237	2.20	21313
2		5.215	8487866	97.80	671573

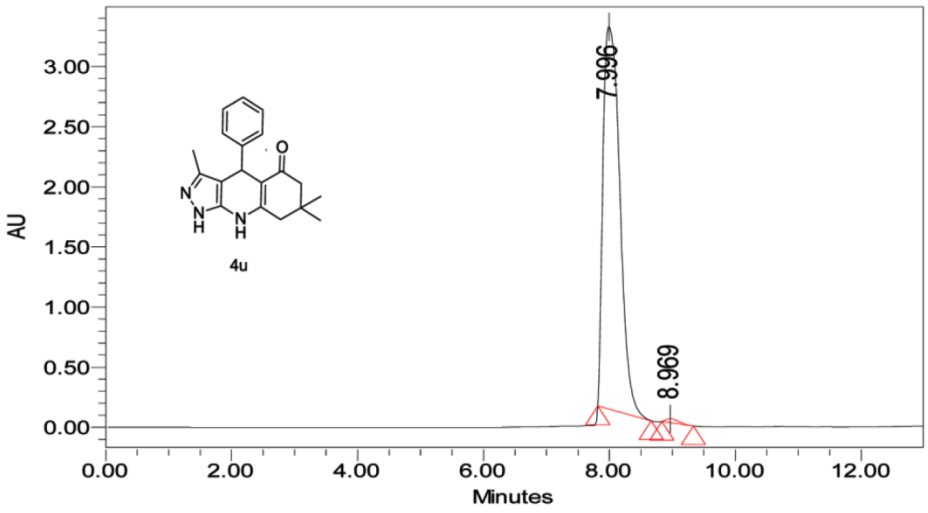
Racemic Mixture:

Enantiomeric ratio (49.18:50.82) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (12: 88), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		2.485	125725	49.18	64650
2		5.202	129928	50.82	64105

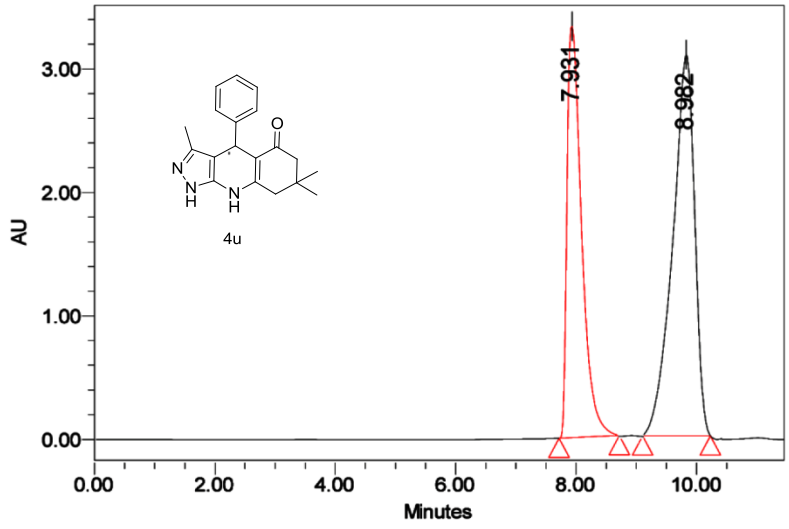
Enantiomeric ratio (99.22:0.78) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (20: 80), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		7.996	59097135	99.22	3179580
2		8.969	461814	0.78	32194

Racemic Mixture:

Enantiomeric ratio (48.05:51.95) was determined by chiral HPLC analysis on AGELA CHIRAL ADV column, isopropanol: n- hexane (20: 80), flow 0.5 ml/min, UV 254 nm.



	Name	Retention Time	Area	% Area	Height
1		7.931	792122	48.05	322276
2		8.982	856386	51.95	306114

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