Supporting Information:

CONVENIENT SYNTHESIS OF OPTICALLY PURE 8-METHOXY-2-METHYL-1,2,3,4-TETRAHYDROQUINOLINE AND 2-METHYL-1,2,3,4-TETRAHYDROQUINOLINE

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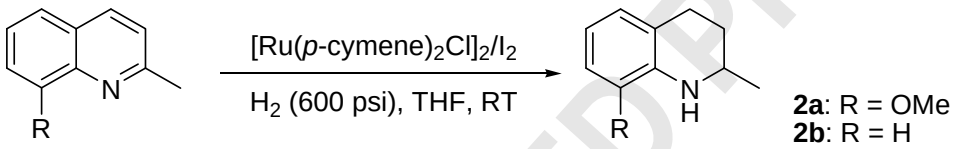
1. General and Materials

The chemical shifts for ^{1}H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard. Flash column chromatography was performed on silica gel (200-300 mesh). TLC analysis was performed using glass-backed plates coated with 0.2 mm silica. Optical rotations were measured with JASCO P-1010 polarimeter. 8-Methoxy-2-methyquinoline was synthesized by methylation of 8-hydroxy-2-methylquinoline with iodomethane. (C. Deraeve. *Chem. Eur. J*. 2008, **14**, 682).

2. The Synthesis of Racemates 2a and 2b



2a: R = OMe
2b: R = H

1) 8-Methoxy-2-methyl-1,2,3,4-tetrahydroquinoline (2a): In the air, to the reaction bottle A was added 8-methoxy-2-methylquinoline (12.470 g, 72 mmol) and I_2 (0.300 g), followed by 80 mL THF. The mixture was stirred until the iodine was dissolved. At the same time, to the reaction bottle B was added [Ru(*p*-cymene)Cl_2]$_2$ (0.050 g, 0.08 mmol) and 20 mL undistilled THF. The mixture was stirred until the solution is homogeneous. Then to the reaction bottle A was added the solution of [Ru(*p*-cymene)Cl_2]$_2$ of THF in bottle B. Then the resulting reaction mixture was placed in an autoclave, and the autoclave was pressurized to 600 psi hydrogen and stirred at room temperature for 16 h, after carefully releasing the hydrogen, the reaction mixture was concentrated to afford the crude product. Purification was performed by a silica gel column eluted with hexane/EtOAc to give pure product **2a** as light yellow oil (11.601 g, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.63-6.54 (m, 3H), 4.12 (s, 1H), 3.81 (s, 3H), 3.39-3.35 (m, 1H), 2.85-2.80 (m, 1H), 2.76-2.74 (m, 1H), 1.94-1.90 (m, 1H), 1.62-1.58 (m, 1H), 1.23 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1, 134.6, 121.5, 121.2, 115.9, 107.3, 55.3, 46.8, 30.2, 26.5, 22.7.

2) 2-Methyl-1,2,3,4-tetrahydroquinoline (2b): The synthesis of **2b** (99% yield) was similar to that of **2a**. (Known compound, see: W.-B. Wang, S.-M. Lu, P.-Y. Yang, X.-W. Han, Y.-G. Zhou, *J. Am. Chem. Soc.*, 2003, **125**, 10536). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95-6.93 (m, 2H), 6.61-6.57 (m, 1H), 6.46 (d, *J* = 8.2 Hz, 1H), 3.64 (br, 1H), 3.40-3.36 (m, 1H), 2.83-2.73 (m, 2H), 1.94-1.89 (m, 1H), 1.60-1.56 (m, 1H), 1.21-1.18 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ144.9, 129.4, 126.9, 121.3, 117.1, 114.1, 47.3, 30.3, 26.8, 22.8.

3. The Chemical Resolution of 2a and 2b

1) The chemical resolution of 8-methoxy-2-methyl-1,2,3,4-tetrahydro-quinoline (2a): Racemic 8-methoxy-2-methyl-1,2,3,4-tetrahydroquinoline **(2a)** (16.590 g, 93 mmol) was diluted by 70 mL acetone with heating to 50 ^{o}C. (*D*)-DTTA (35.656 g, 93 mmol) was dissolved in 100 mL acetone and the solution was dropped into the bottle of 8-methoxy-2-methyl-1,2,3,4-tetrahydroquinoline, keep stirring 30 minutes. Then the mixture was cooled to room temperature and crystals appeared. The crystals were filtered and the residue was washed with acetone (20 mL) and dried to afford the solid diastereoisomeric salt, workup of the diastereoisomeric salt was as follows: The crystals were suspended in NaOH aqueous solution (0.6 mol/L, 150 mL) and stirred for 30 min. The mixture was extracted with CH_2Cl_2 for three times. Then combined organic phase was dried over Na_2SO_4 and the solvent was removed *in vacuo* to afford the product. Repeating this operation twice gave the chiral (+)-8-methoxy-2-methyl- 1,2,3,4-tetrahydroquinoline **(2a)** (4.293 g, 52% yield, 99% *ee*), $[\alpha]^{21}_{D}$ = +68.4 (*c* 0.66, $CHCl_3$). HPLC (IC Column, Hexane/*i*-PrOH = 99.5/0.5, 0.5 mL/min, 30 ^{o}C, 254 nm): (+) t_1 = 9.4 min, (-) t_2 = 9.9 min.

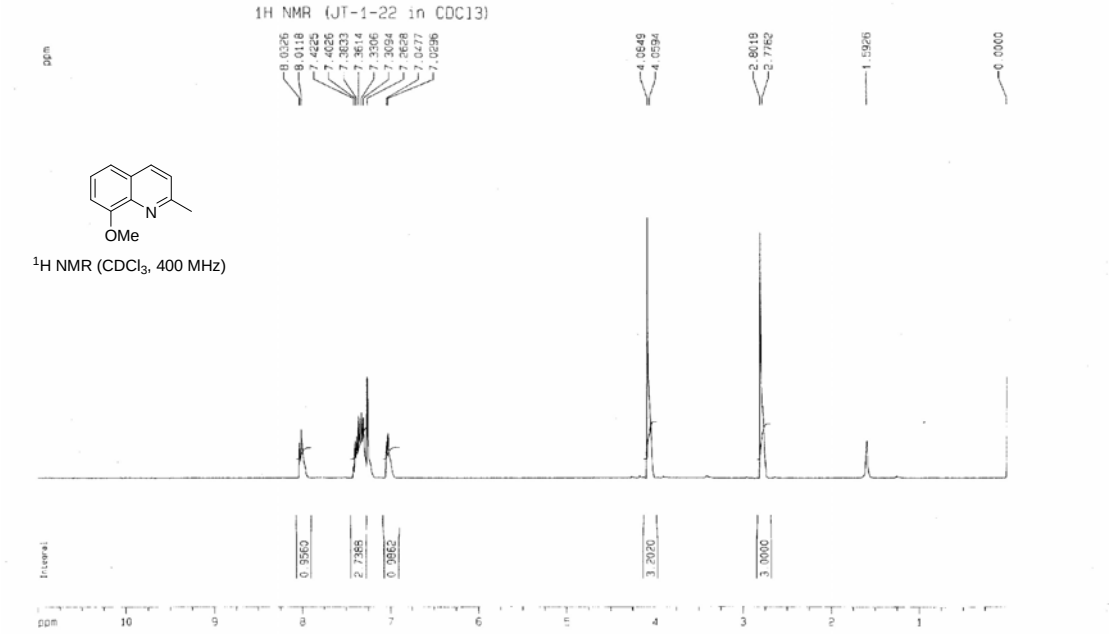
The filtrate after resolution was recovered and cracked by NaOH aqueous solution, the scalemic **2a** was obtained after extraction by CH_2Cl_2. Optically pure (-)-**2a** (88% yield, >99% *ee*) could be obtained by using the (*L*)-DTTA as resolution reagent with the same operation.

2) The chemical resolution of 2-methyl-1,2,3,4-tetrahydroquinoline (2b): Racemic 2-methyl-1,2,3,4-tetrahydroquinoline (24.673 g, 168 mmol) was diluted by

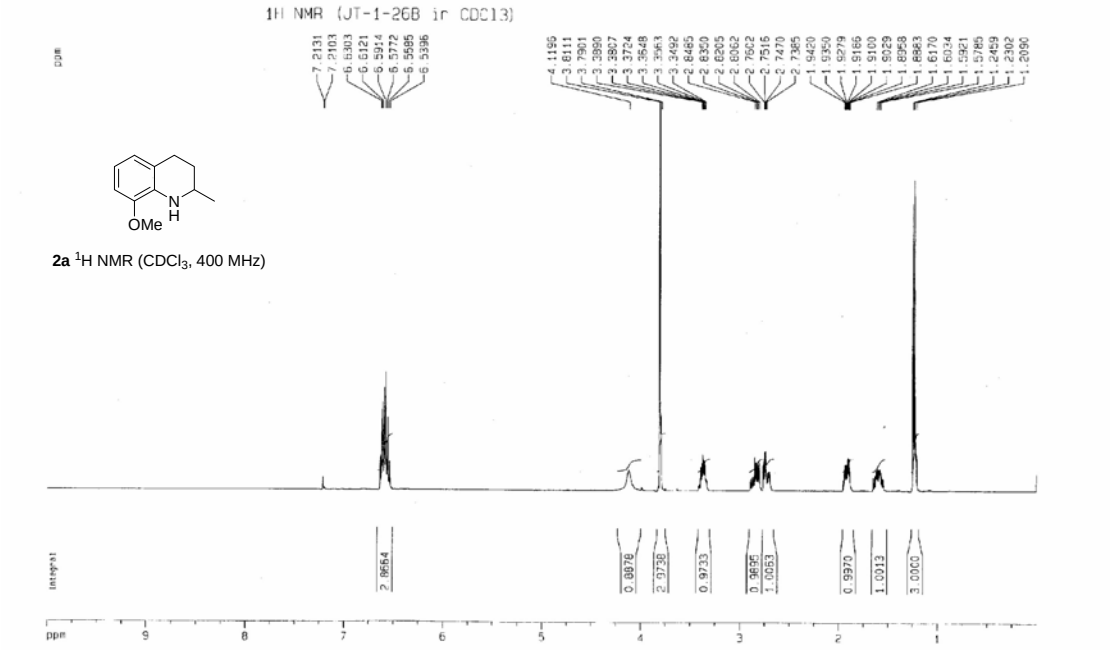
40 mL acetone with heating to 50 ^{o}C. (*D*)-DMTA (80.867 g, 168 mmol) was dissolved in 150 mL acetone and the solution was dropped into the bottle of 2-methyl-1,2,3,4-tetrahydroquinoline. keep stirring 30 minutes. Then the mixture was cooled to room temperature and crystals appeared. The crystals were filtered and the residue was washed with acetone (20 mL) and dried to afford the solid diastereoisomeric salt, workup of the diastereoisomeric salt was as follows: The crystals were suspended in NaOH aqueous solution (0.6 mol/L, 280 mL) and stirred for 30 min. The mixture was extracted with dichloromethane for three times. Then combined organic phase was dried over Na_2SO_4 and the solvent was removed *in vacuo* to afford the product. Repeating this operation three times gets (-)-(*S*)-2-methyl-1,2,3,4-tetrahydroquinoline **2b** (3.369 g, 28% yield, 99% *ee*). $[\alpha]^{20}_{D}$ = -91.7 (*c* 1.23, $CHCl_3$). HPLC (OJ-H Column, Hexane/*i*-PrOH = 95/5, 1.0 mL/min, 30 ^{o}C, 254 nm): (*S*)-(-) t_1 = 11.2 min, (*R*)-(+) t_2 = 12.3 min.

The filtrate after resolution was recovered and cracked by NaOH aqueous solution, the scalemic **2b** was obtained after extraction by CH_2Cl_2. Optically pure (*R*)-(+)-**2b** (31% yield, >99% *ee*) can be obtained by using the (*L*)-DMTA as resolution reagent with the same operation.

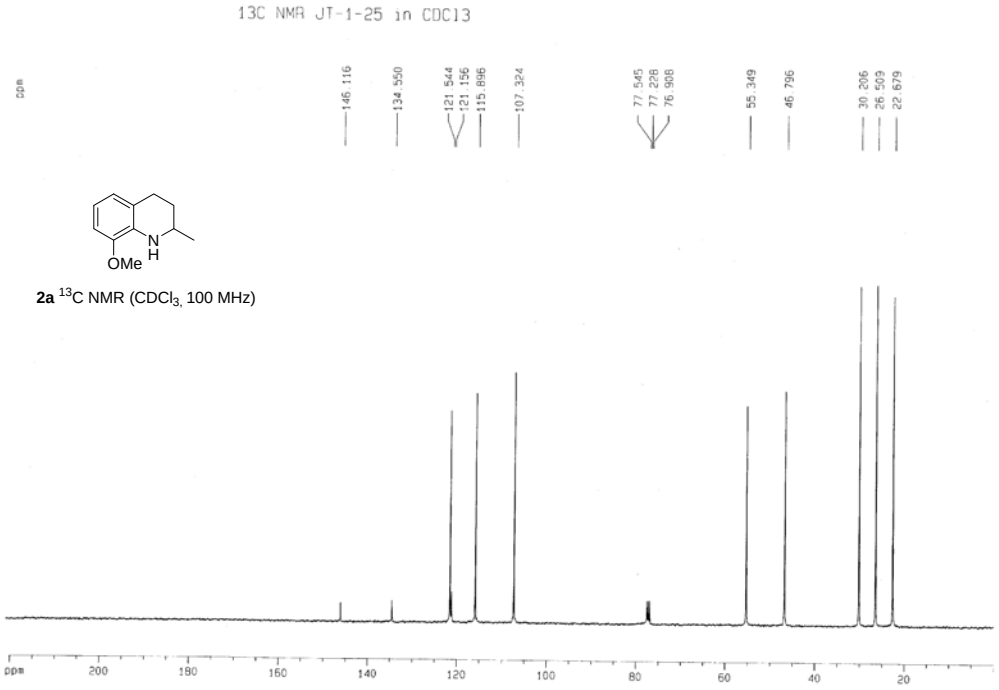
4. Copy of NMR and HPLC



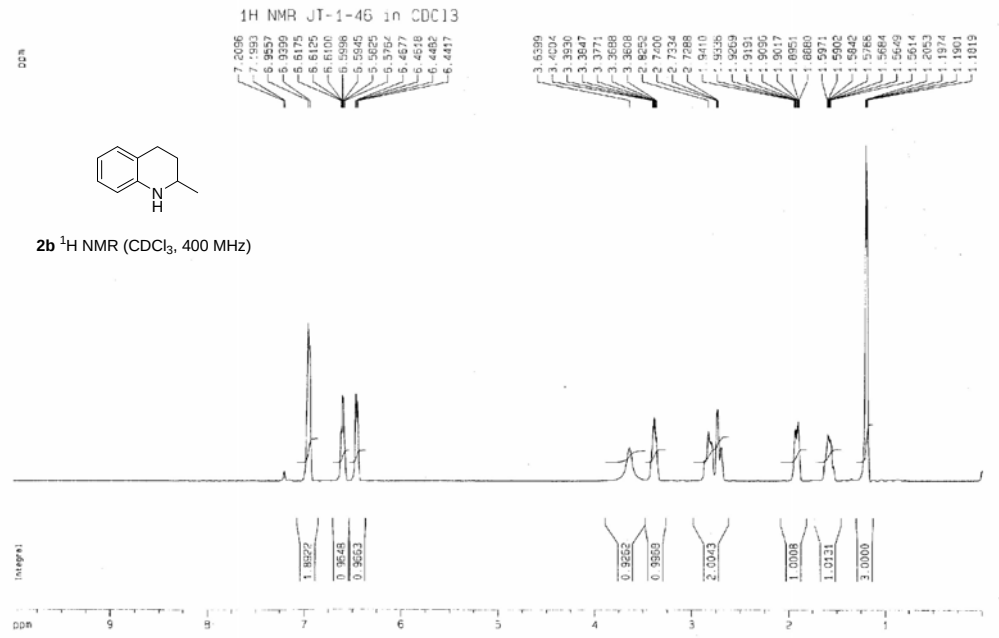
^{1}H NMR ($CDCl_3$, 400 MHz)



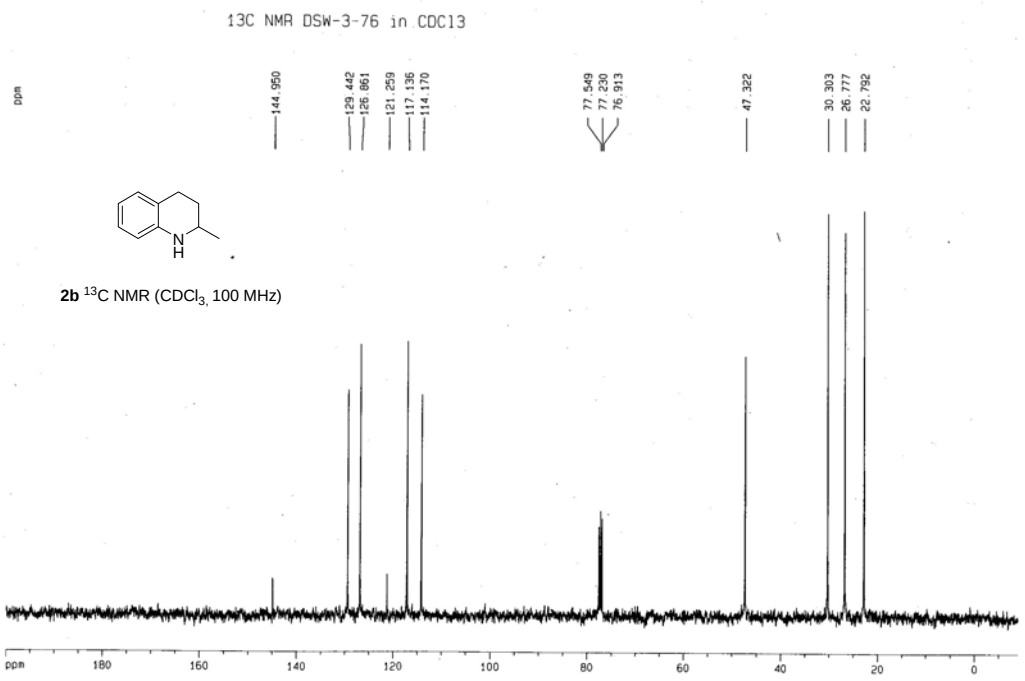
2a ^{1}H NMR ($CDCl_3$, 400 MHz)



2a ^{13}C NMR ($CDCl_3$, 100 MHz)



2b ^{1}H NMR ($CDCl_3$, 400 MHz)



2b ^{13}C NMR ($CDCl_3$, 100 MHz)

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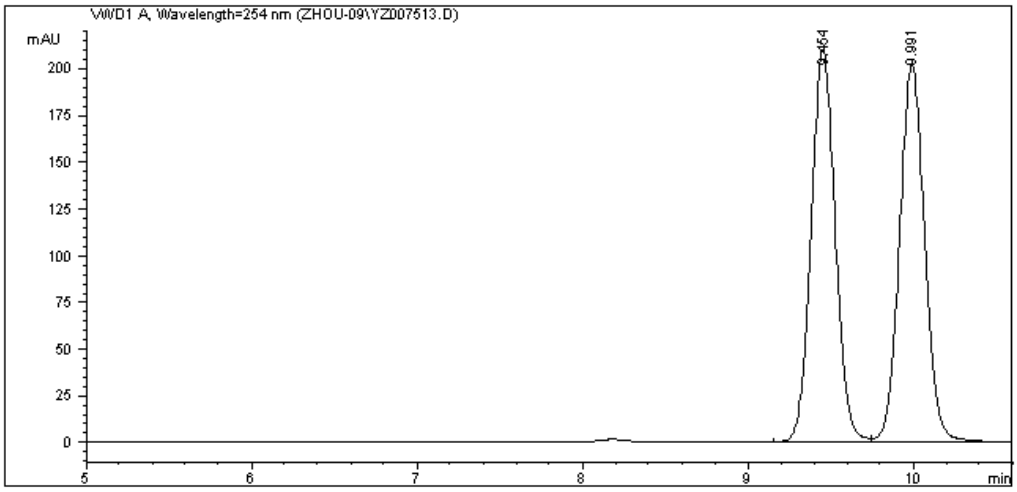


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Dilution              :      1.0000

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   2   9.991 VV    0.1646 2143.19775  201.95670  50.1966

Totals :                  4269.60815  411.82997

 Results obtained with enhanced integrator!
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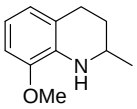

(+/-)-**2a**

Instrument 1 3/24/2010 9:18:46 PM Page 1 of 1

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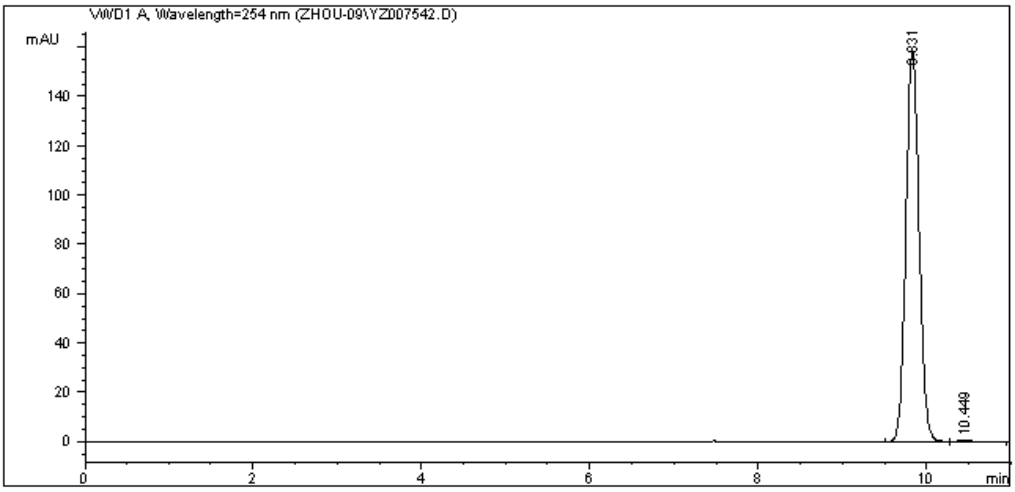


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   2  10.449 VB    0.2038    8.66741 6.37295e-1   0.4961

Totals :                  1746.98333  159.66645

 Results obtained with enhanced integrator!
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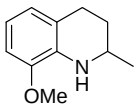

(+)-**2a**

Instrument 1 3/12/2010 5:04:46 PM Page 1 of 1

Data File C:\HPCHEM\1\DATA\ZHOU-09\YZ007569.D Sample Name: JT-1-31C

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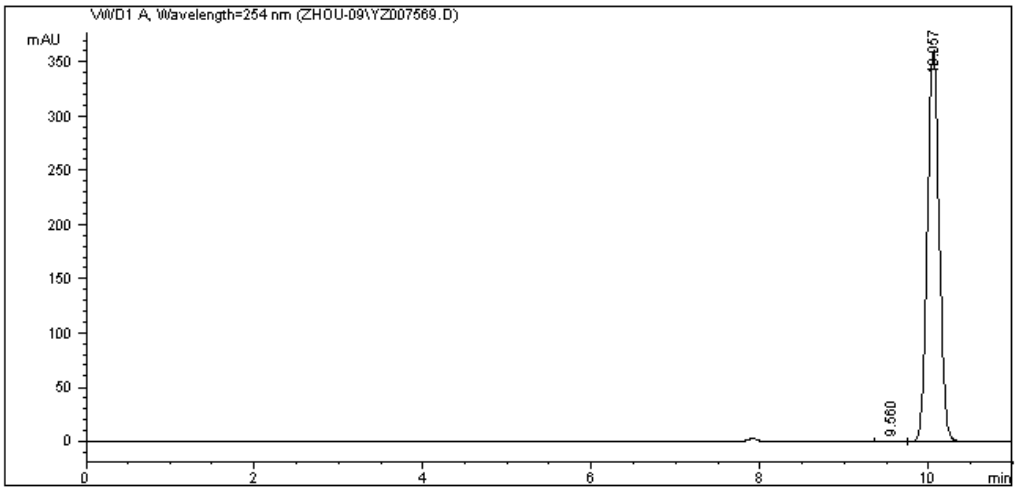


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   2  10.057 VP    0.1543 3560.07349  361.19980  99.8740

Totals :                  3564.56623  361.66933

 Results obtained with enhanced integrator!
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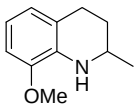

(-)-**2a**

Instrument 1 3/12/2010 5:06:20 PM Page 1 of 1

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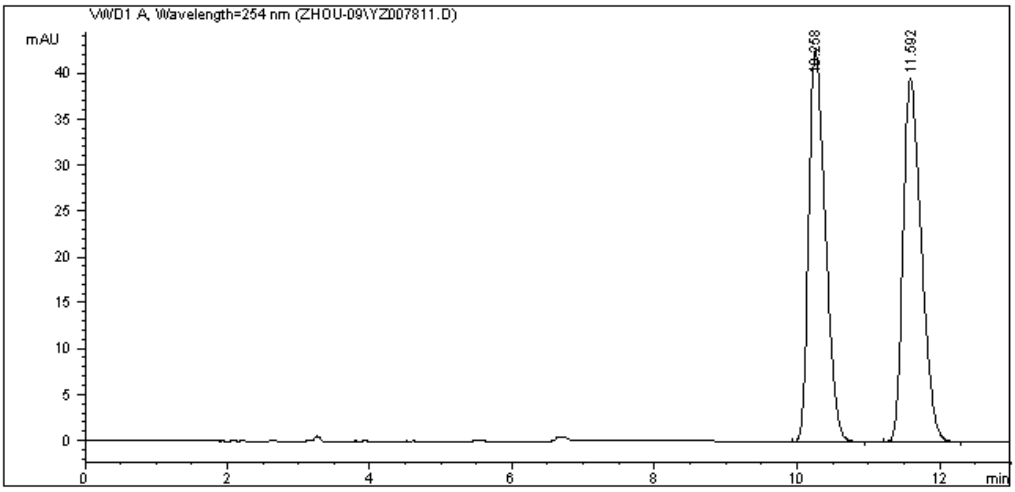


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   2  11.592 BB    0.2766  704.47668   39.48765  50.3953

Totals :                  1397.90240   82.12783

 Results obtained with enhanced integrator!
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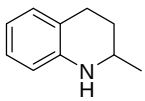

(+/-)-**2b**

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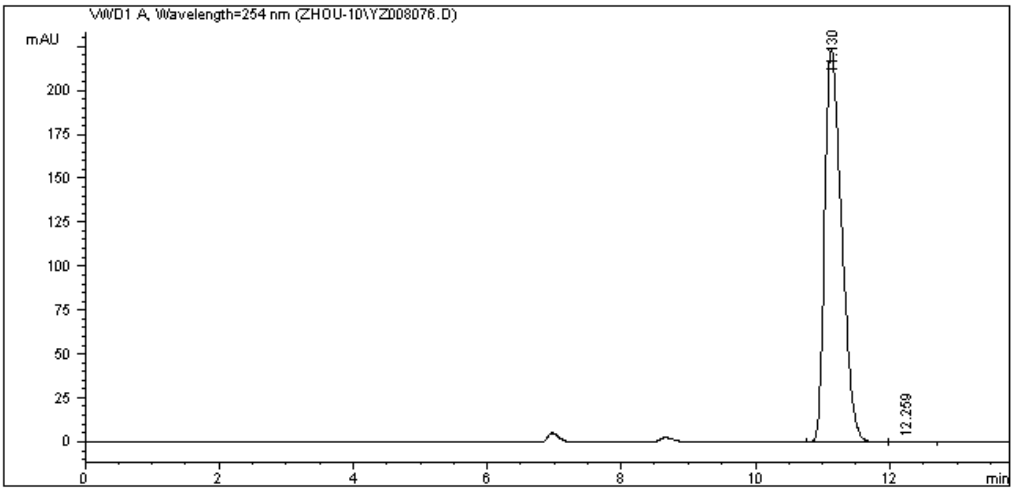


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 Results obtained with enhanced integrator!
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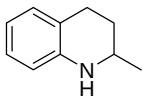

(-)-**2b**

Instrument 1 3/12/2010 4:56:57 PM Page 1 of 1

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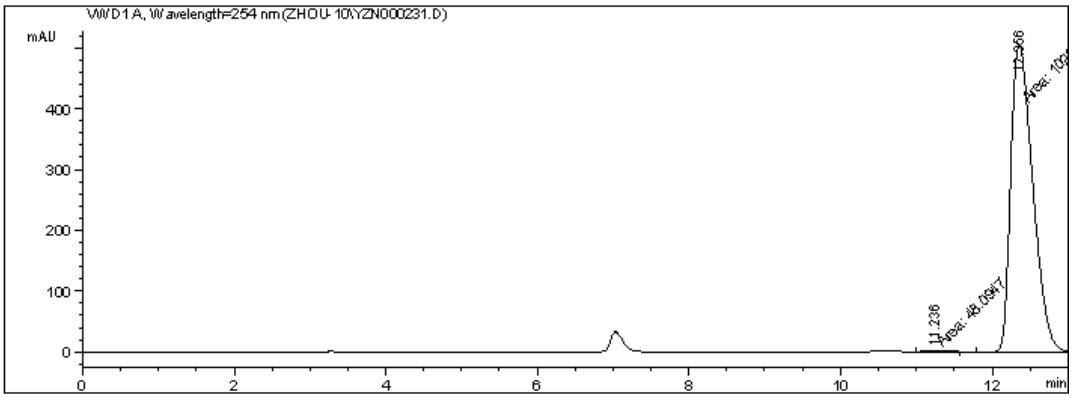


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    Use Multiplier & Dilution Factor with ISTDs


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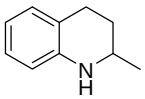

(+)-**2b**

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