

Supplementary Information

First enantioselective organocatalytic allylation of simple aldimines with allyltrichlorosilane

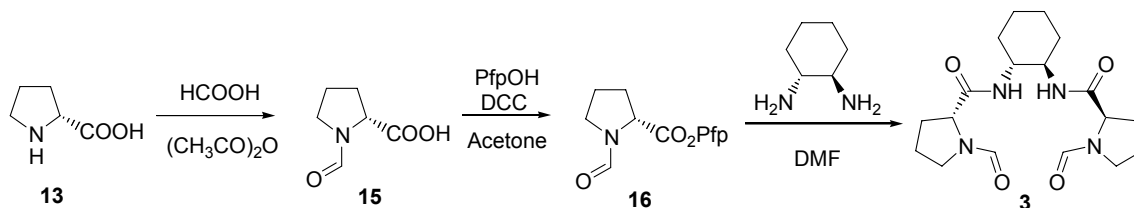
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General: All solvents were purified by standard procedures and distilled prior to use. Reagents obtained from commercial sources were used without further purification. TLC chromatography was performed on precoated aluminium silica gel SIL G/UV₂₅₄ plates (Marcherey, Nagel & Co.) or silica gel 60-F₂₅₄ precoated glass plates (Merck). ¹H NMR spectra were recorded with a Varian Unity 300. ESI mass spectra were recorded with a LCQ Finnigan spectrometer. High-resolution mass spectra were measured with a Bruker APEX IV 7T FT-ICR instrument. A Perkin-Elmer 241 polarimeter was used for optical rotation measurements.



Compound 15: D-Proline (3 g, 26.05 mmol) was dissolved in 85% formic acid (55 mL) and cooled to 0 °C. Acetic anhydride (18 mL) was added and the mixture was stirred at room temperature for 2 h. Ice cold water (21 mL) was then added and the solvent was removed under reduced pressure. The residual pale yellow oil was dissolved in methanol and the solvent was removed under reduced pressure to give the product **15** as a white powder. Yield 3.4 g (91%). $[\alpha]_D^{20} = +121.5^\circ$ (c = 1.2, EtOH). ¹H NMR (300 MHz, CDCl₃): $\delta = 1.82$ -2.28 (m, 4H), 3.49-3.69 (m, 2H), 4.39-4.48 (m, 1H), 8.23 and 8.28 (two

singlets, 1H, CHO), 10.73 (s, 1H, COOH) ppm. ESI-MS (positive ion): $m/z = 144.0 [M + H]^+$, 166.0 $[M + Na]^+$, 308.8 $[2M + Na]^+$.

Compound 16: The cooled solution of *N,N*-dicyclohexylcarbodiimide (DCC) (4.76 g, 23.06 mmol) in acetone (15 mL) was added dropwise to the stirred solution of **15** (3 g, 20.96 mmol) and pentafluorophenol (PfpOH) (4.25 g, 23.09 mmol) in acetone (25 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 5 h. The precipitate formed (urea) was filtered off and washed with acetone (15 mL).

The urea which precipitated was removed by filtration and the solvent was subsequently removed under vacuum. The oily residue was dissolved in acetone (15 mL), cooled to 0°C and more of the urea was able to be removed by filtration. The filtrate was concentrated to dryness under reduced pressure to give the product **16** as a white solid, which was used without further purification. Yield 5.96 g (92%). ¹H NMR (300 MHz, CDCl₃): $\delta = 1.98-2.48$ (m, 4 H), 3.58-3.74 (m, 2 H), 4.73-4.79 (m, 1 H), 8.32 and 8.34 (two singlets, 1H, CHO) ppm.

Bisformamide 3: To a stirred solution of (*R,R*)-1,2-diaminocyclohexane (481 mg, 4.21 mmol) in DMF (10 mL) was added the solution of **16** (3 g, 9.70 mmol) in DMF (15 mL). The reaction mixture was stirred at room temperature for 12 h. The white precipitated product was filtered off, washed with cold ethyl acetate and dried under vacuum to give a white powder. Yield 1.23 g (80%). $[\alpha]_D^{20} = +245.6^\circ$ ($c = 0.73$, CHCl₃).

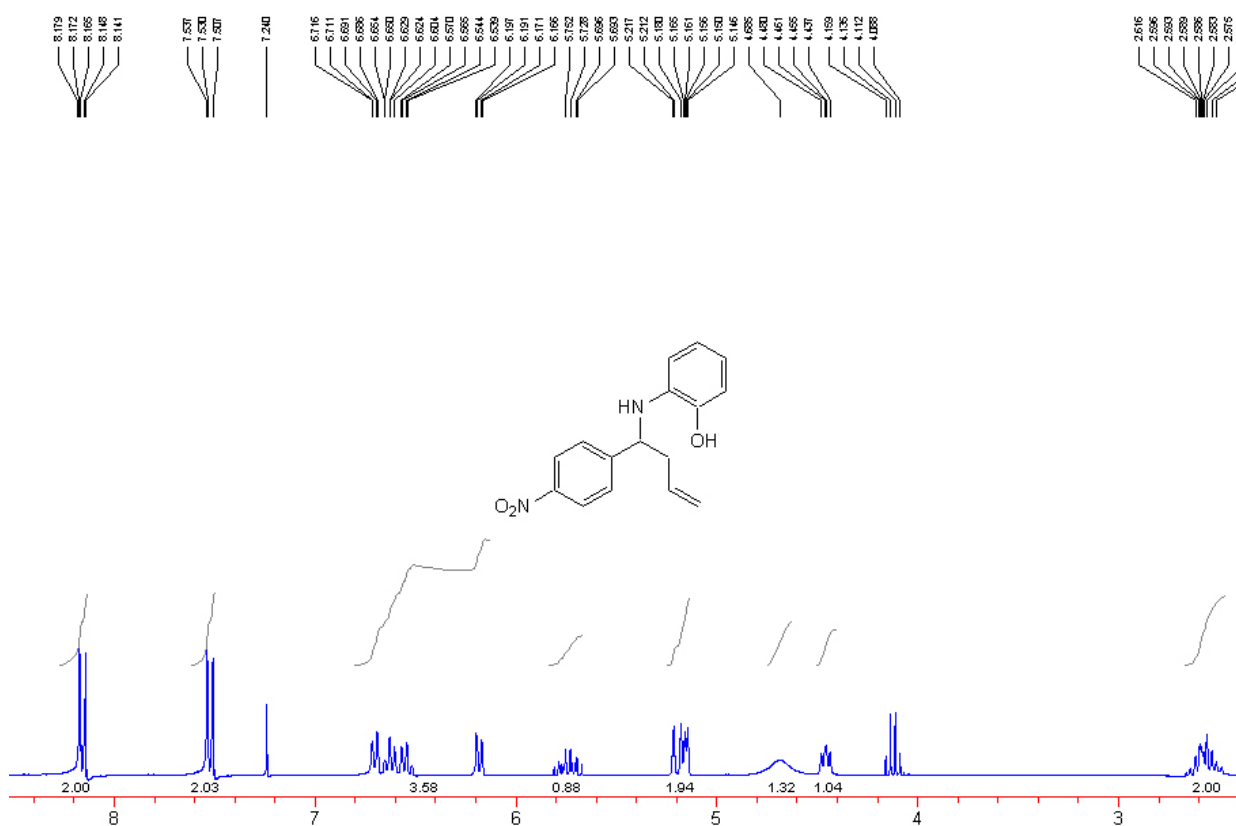
¹H NMR (300 MHz, CDCl₃): $\delta = 1.15-1.35$ (m, 4H), 1.60-2.29 (m, 12H), 3.40-3.62 (m, 6H), 4.30-4.41 (m, 2H), 6.86-7.22 (m, 2H, 2 x NH), 8.16-8.28 (three singlets, 2H, 2 x CHO) ppm. ESI-MS (positive ion): $m/z = 365.2 [M + H]^+$, 387.3 $[M + Na]^+$, 751.0 $[2M + Na]^+$. ESI-MS (negative ion): $m/z = 363.3 [M - H]^-$. HRMS (ESI): calcd. for C₁₈H₂₈N₄O₄ $[M + H]^+$ 365.21833, found 365.21860. Anal. Calcd. for C₁₈H₂₈N₄O₄: C, 59.32; H, 7.74; N, 15.37, found C, 59.01; H, 7.95; N, 15.21.

General procedure for the allylation of simple aldimines with allyltrichlorosilane:

To a solution of aldimine (0.0825 mmol), bisformamide **3** (0.165 mmol, 2 equiv) and L-proline (0.165 mmol, 2 equiv) in CH₂Cl₂ (0.165 mL) was added allyltrichlorosilane

(0.124 mmol, 1.5 equiv). After stirring vigorously at room temperature for 4 hours, triethylamine (0.06 mL) in methanol (0.3 mL) was added to quench the reaction. The mixture was diluted with diethyl ether (11 mL) and water (5 mL). The organic layer was separated, washed twice with water (5 mL), dried over anhydrous Na₂SO₄, filtered, and purified by column chromatography (hexane/ethyl acetate) to give the product.

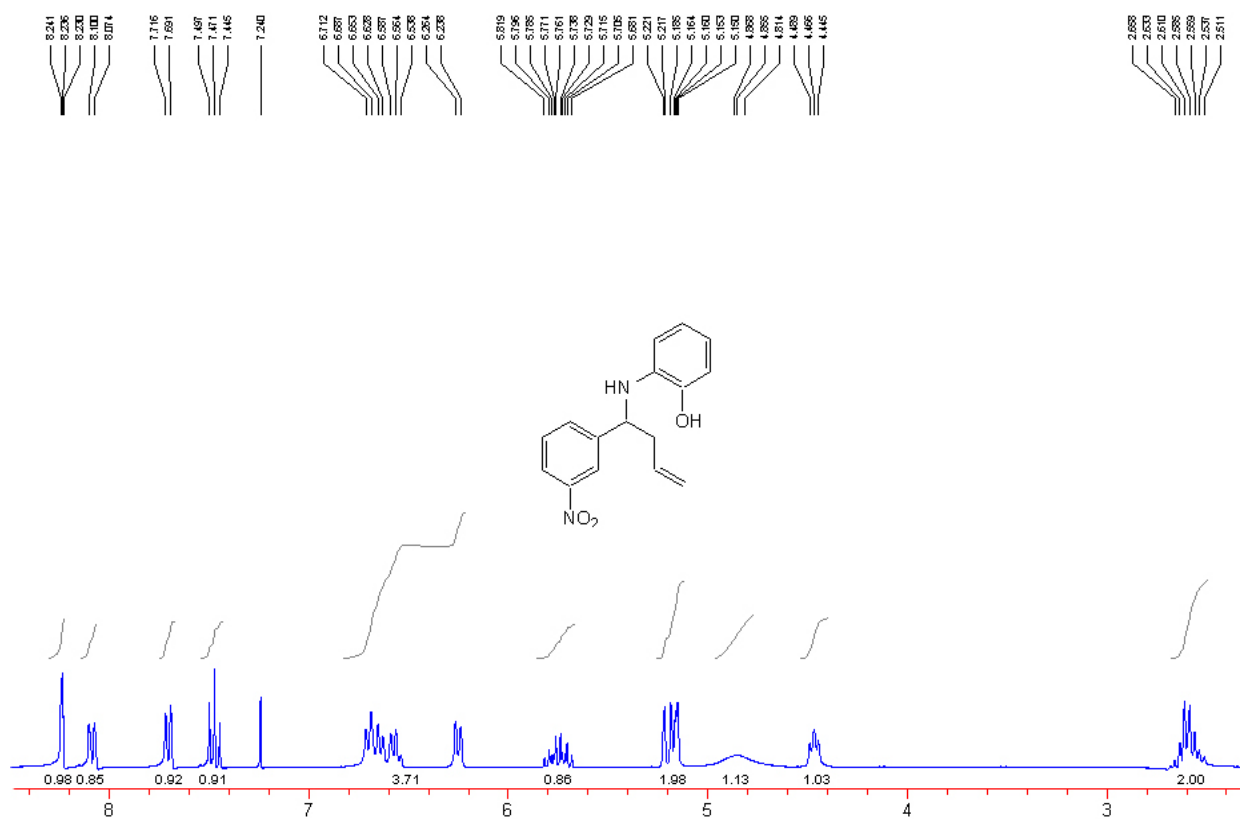
¹H NMR (300 MHz, CDCl₃):



ESI-MS (positive ion): $m/z = 307.3$ [M + Na]⁺.

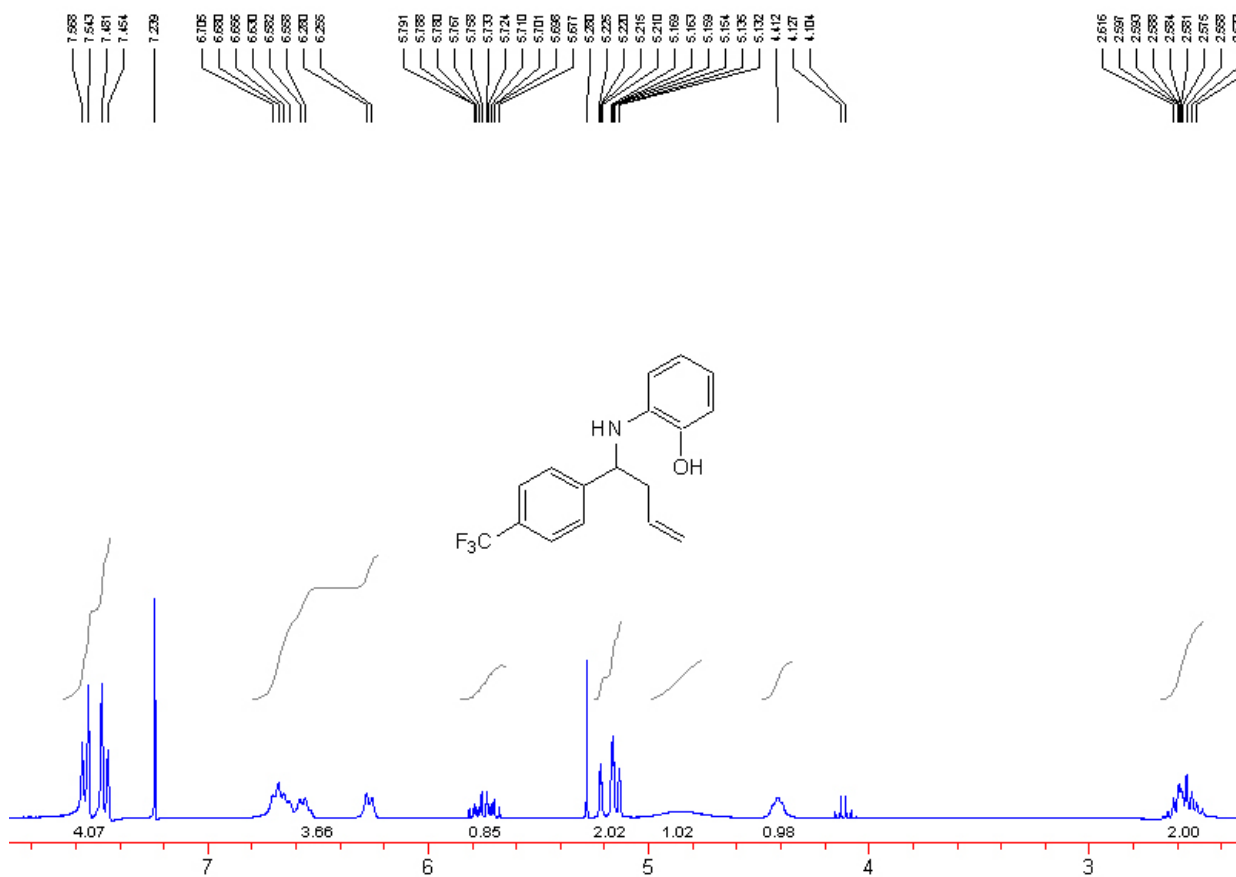
ESI-MS (negative ion): $m/z = 283.0$ [M - H]⁻.

$^1\text{H NMR}$ (300 MHz, CDCl_3):



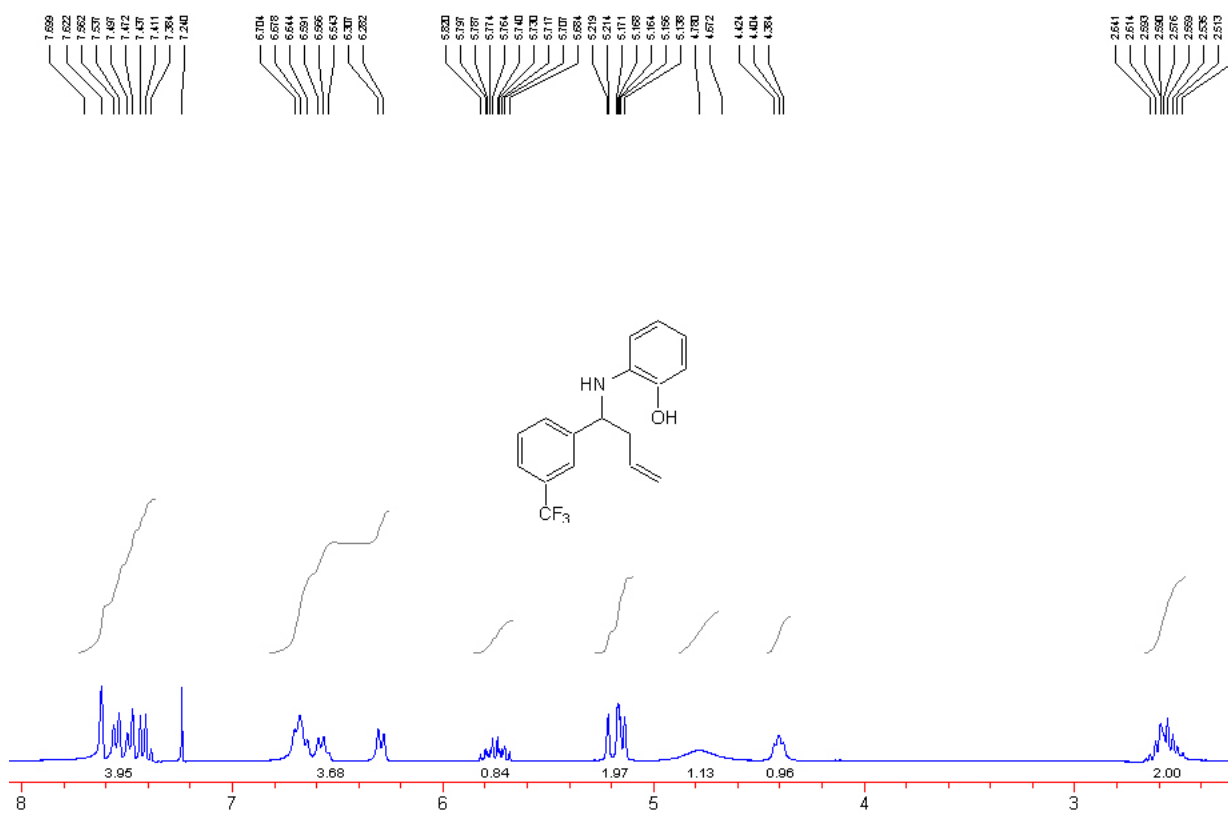
ESI-MS (negative ion): $m/z = 283.0$ $[\text{M} - \text{H}]^-$, 566.9 $[2\text{M} - \text{H}]^-$.

^1H NMR (300 MHz, CDCl_3):



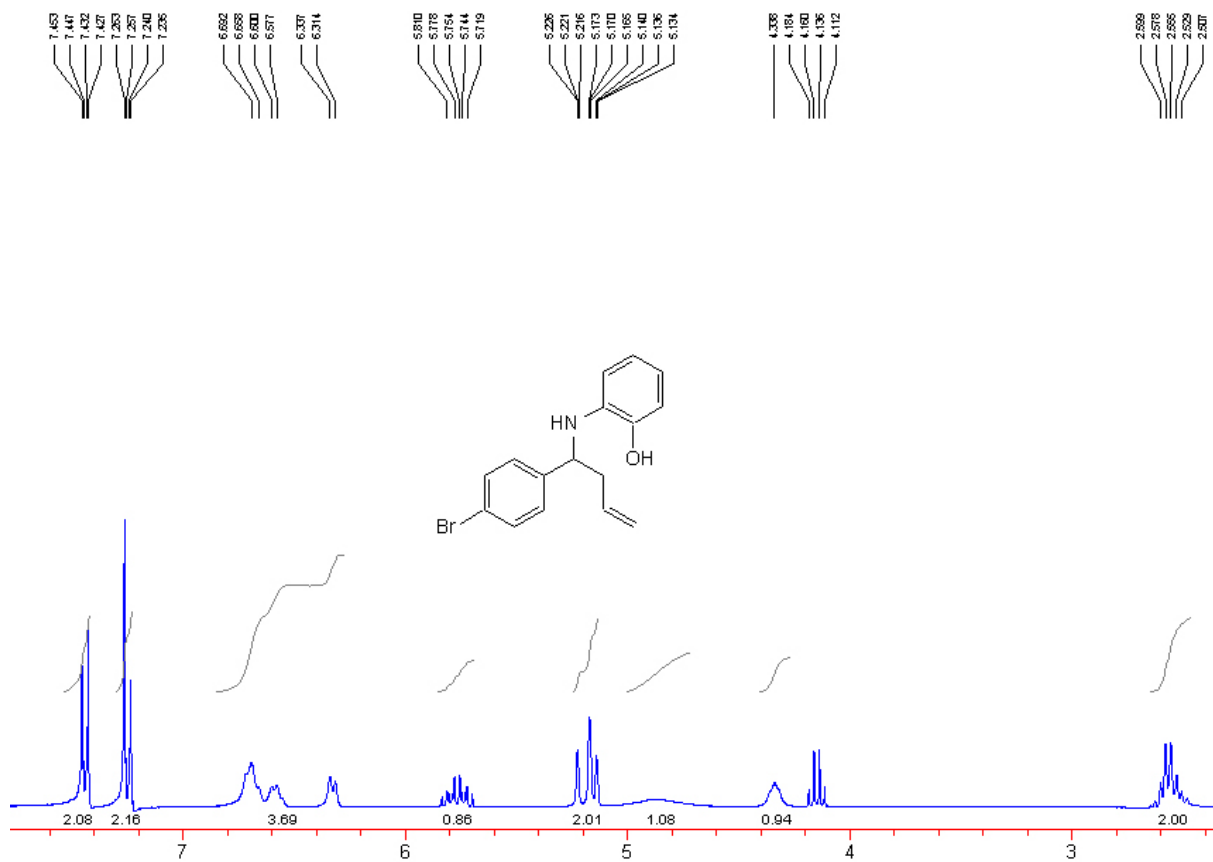
ESI-MS (negative ion): $m/z = 306.1$ $[\text{M} - \text{H}]^-$, 612.9 $[2\text{M} - \text{H}]^-$.

^1H NMR (300 MHz, CDCl_3):



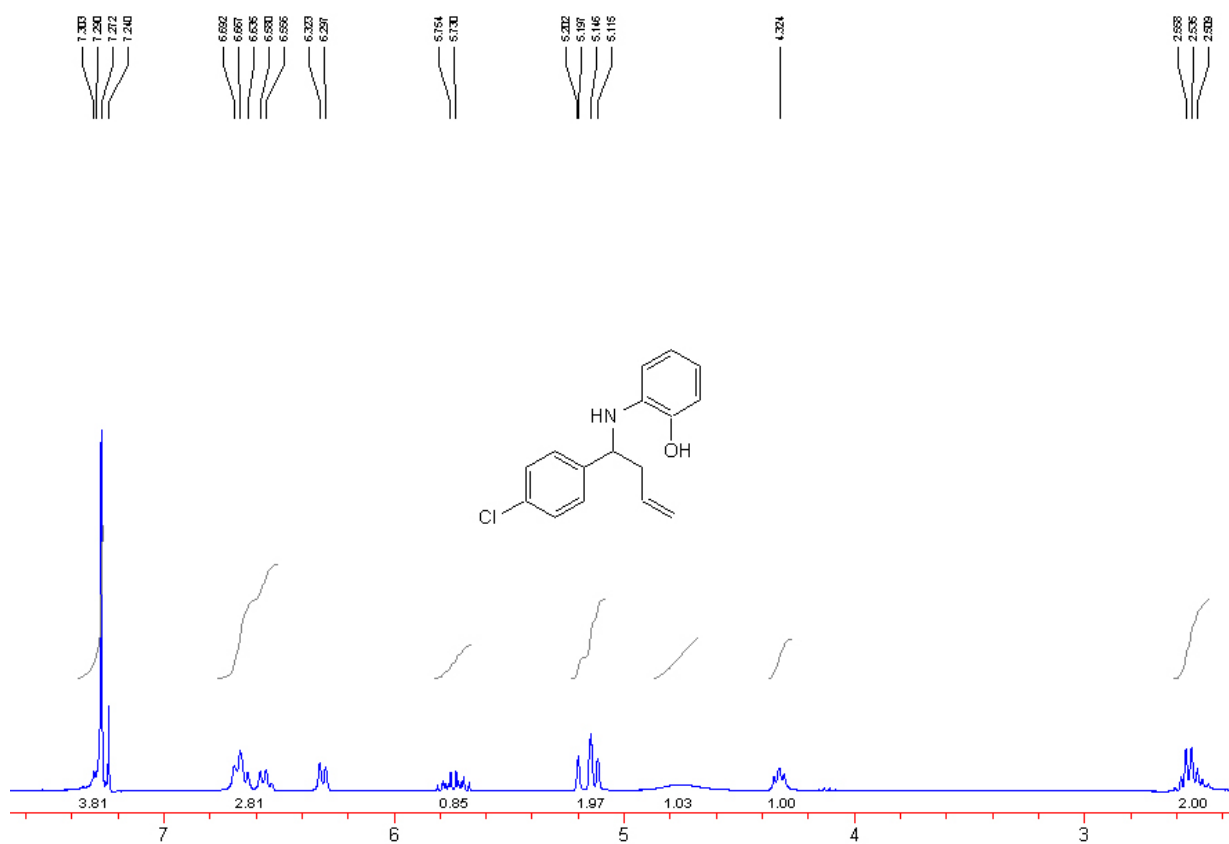
ESI-MS (negative ion): $m/z = 306.1$ $[\text{M} - \text{H}]^-$, 612.9 $[2\text{M} - \text{H}]^-$.

^1H NMR (300 MHz, CDCl_3):



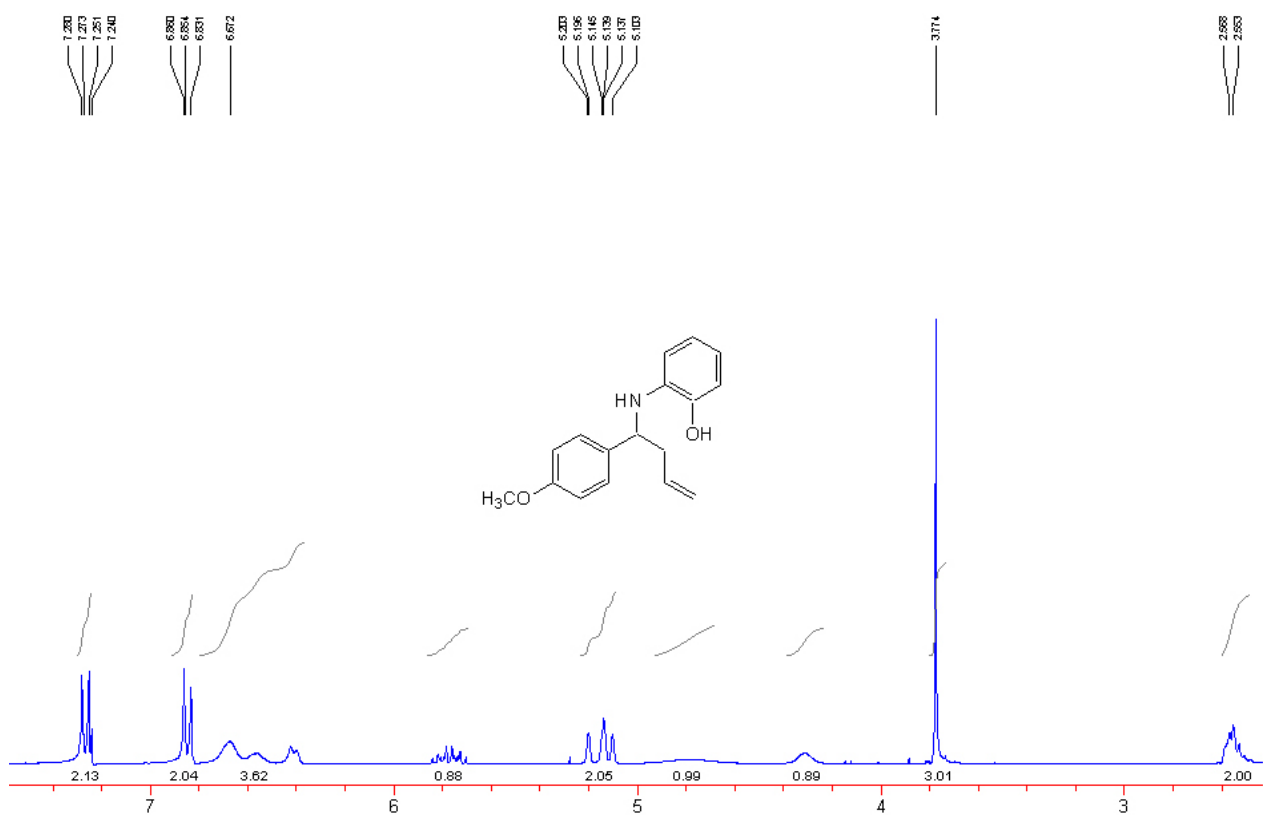
ESI-MS (negative ion): $m/z = 316.0$ [$\text{M} - \text{H}$], 634.7 [$2\text{M} - \text{H}$].

^1H NMR (300 MHz, CDCl_3):



ESI-MS (negative ion): $m/z = 272.0$ $[\text{M} - \text{H}]^-$, 544.9 $[2\text{M} - \text{H}]^-$.

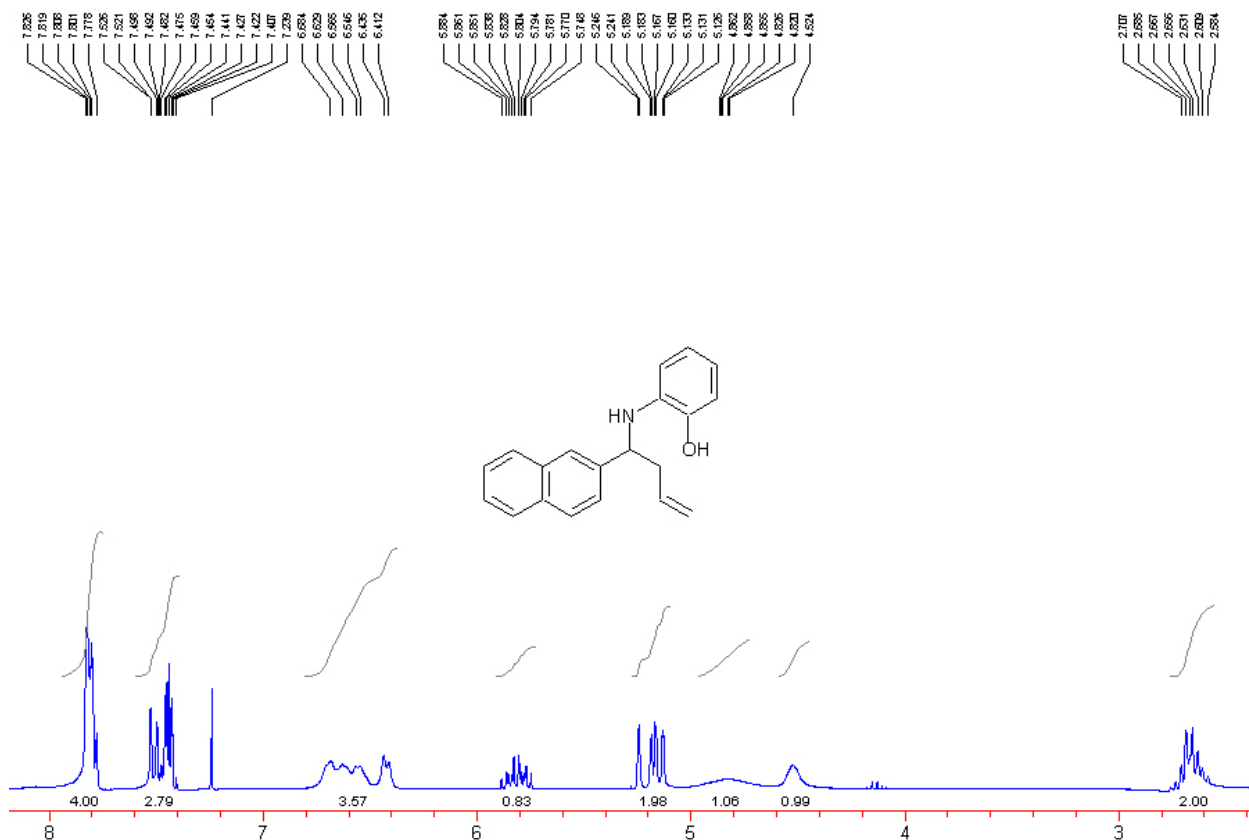
^1H NMR (300 MHz, CDCl_3):



ESI-MS (positive ion): $m/z = 269.8$ $[\text{M} + \text{H}]^+$, 291.9 $[\text{M} + \text{Na}]^+$.

ESI-MS (negative ion): $m/z = 268.1$ $[\text{M} - \text{H}]^-$.

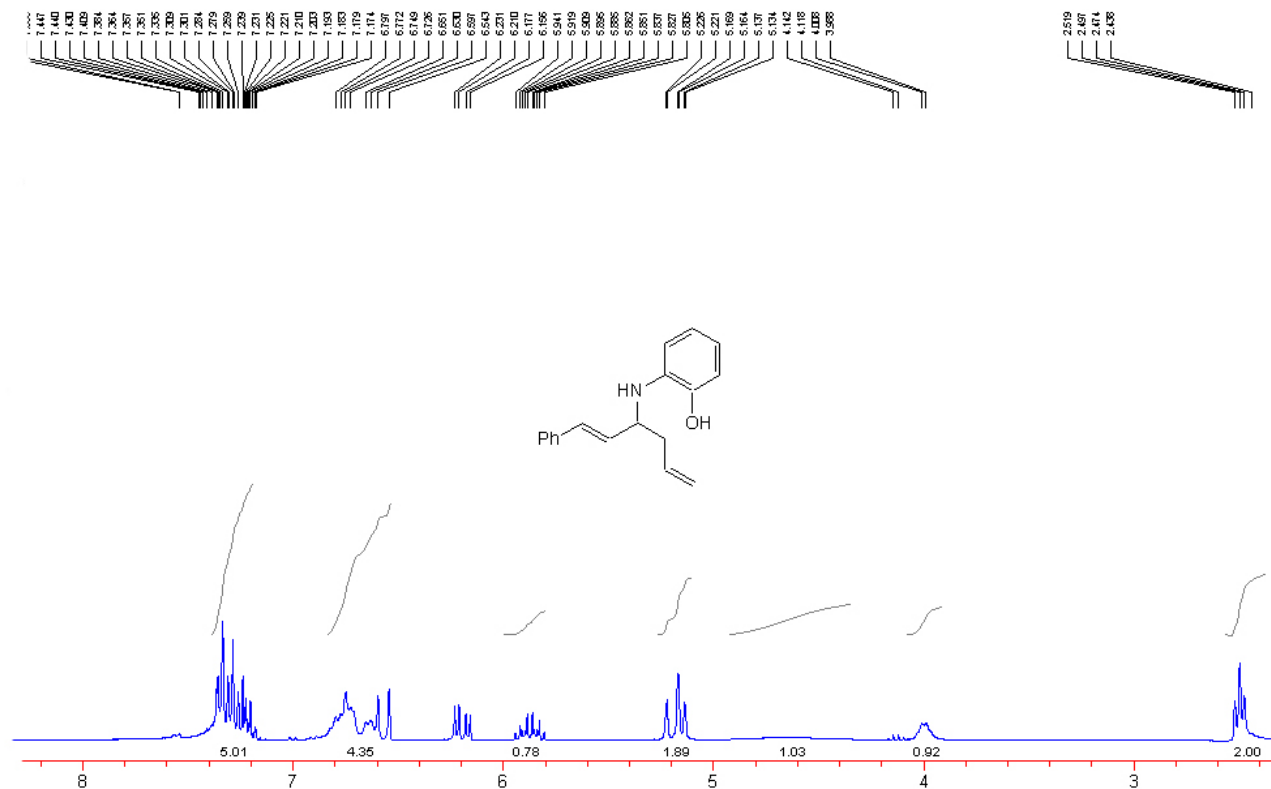
^1H NMR (300 MHz, CDCl_3):



ESI-MS (positive ion): $m/z = 289.8$ $[\text{M} + \text{H}]^+$.

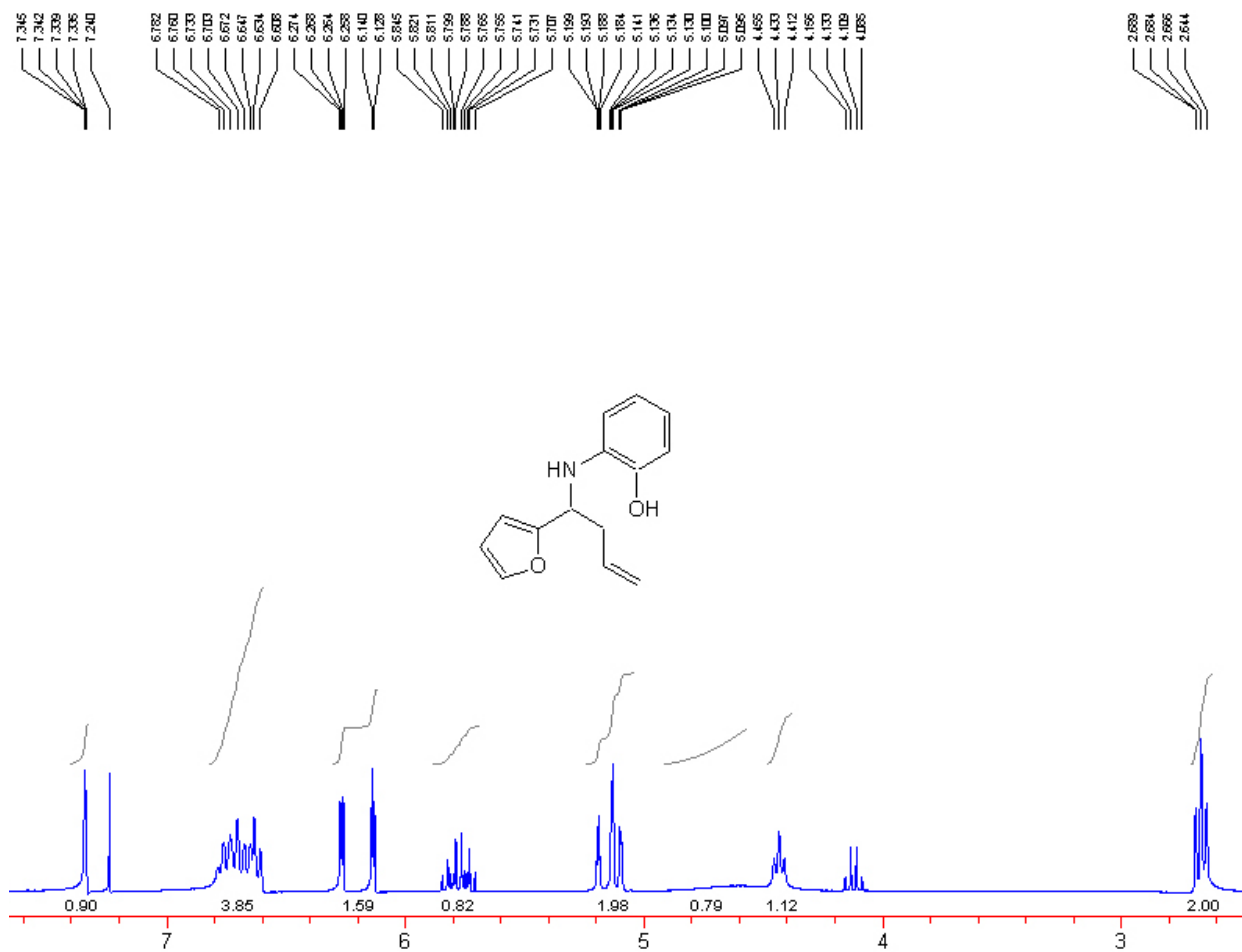
ESI-MS (negative ion): $m/z = 288.1$ $[\text{M} - \text{H}]^-$.

^1H NMR (300 MHz, CDCl_3):



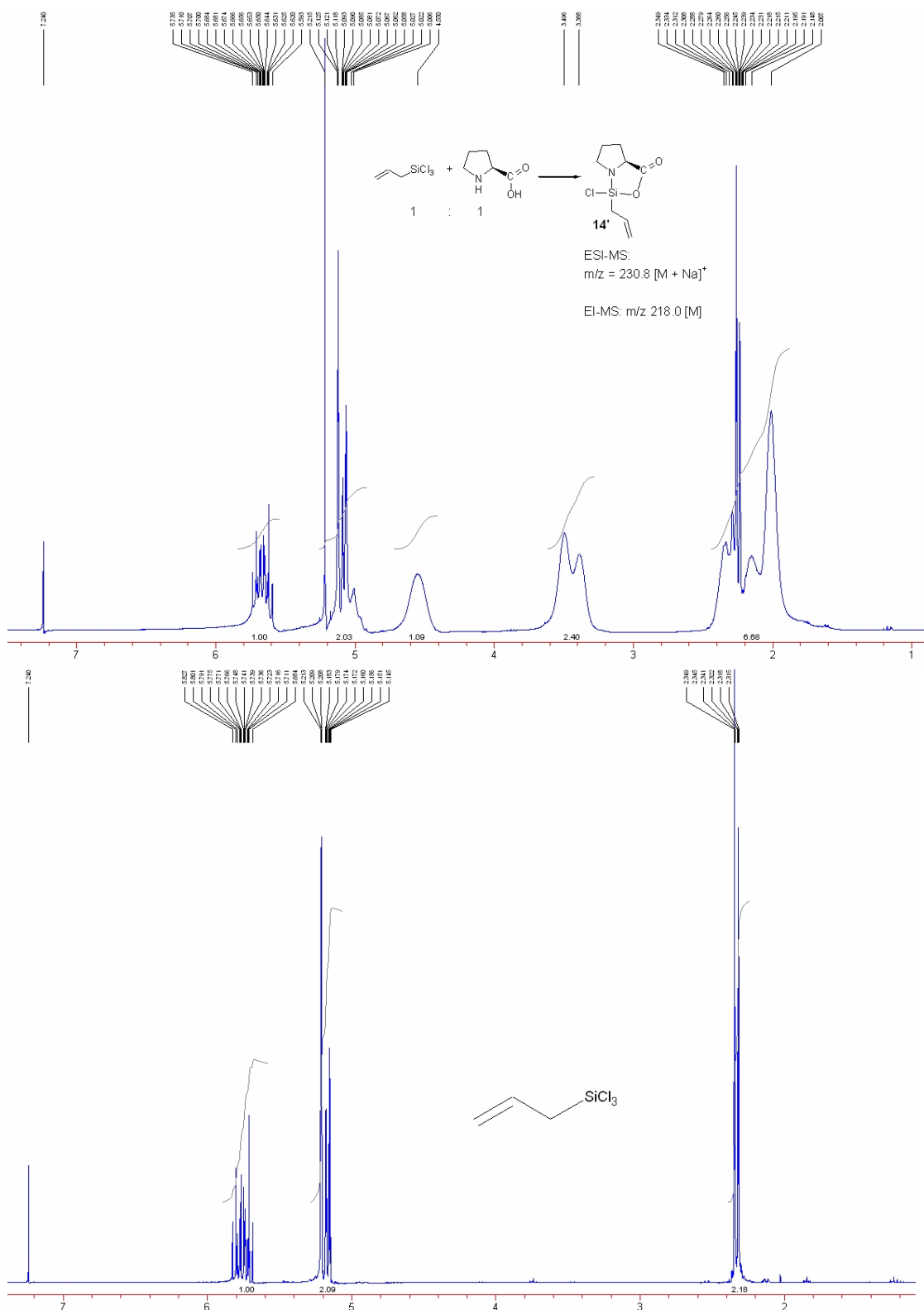
ESI-MS (negative ion): $m/z = 264.0$ [$\text{M} - \text{H}$], 529.0 [$2\text{M} - \text{H}$].

^1H NMR (300 MHz, CDCl_3):

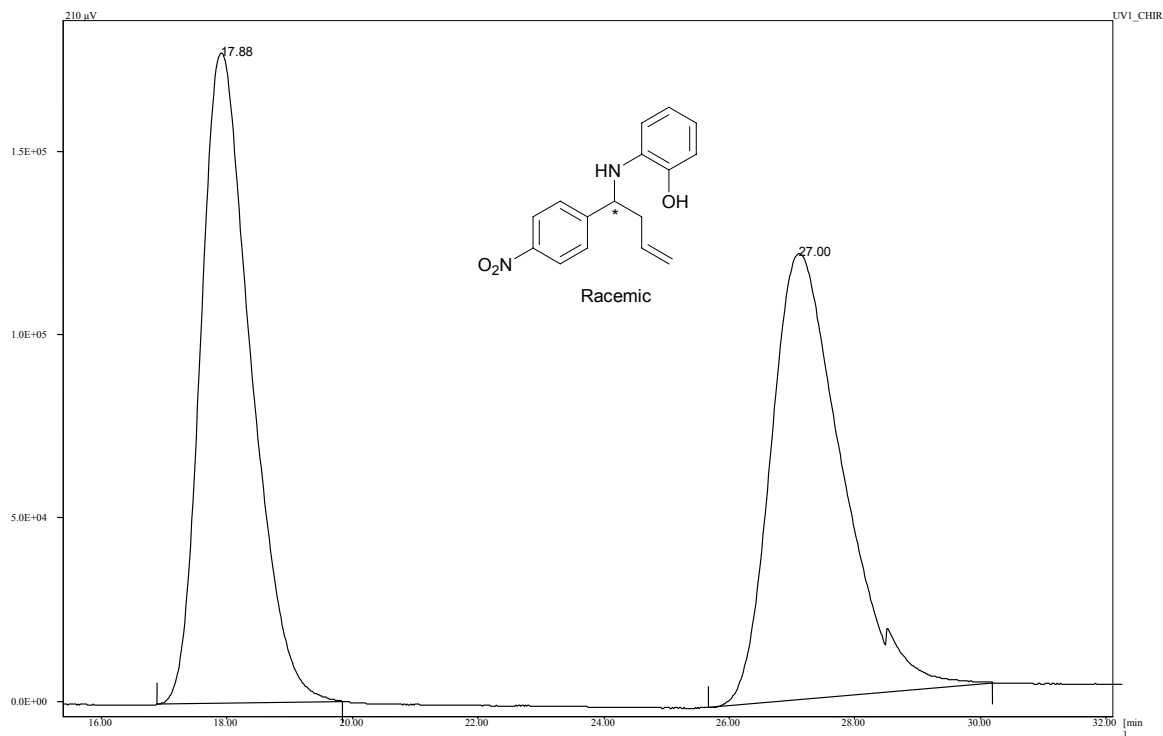


ESI-MS (negative ion): $m/z = 228.0$ $[\text{M} - \text{H}]^-$, 456.7 $[2\text{M} - \text{H}]^-$.

^1H NMR (300 MHz, CDCl_3):



n-Hexane/ 2-Propanol = 90:10, flow rate 1 ml/ min, $\lambda = 210$ nm (Daicel Chiralpak AD column)

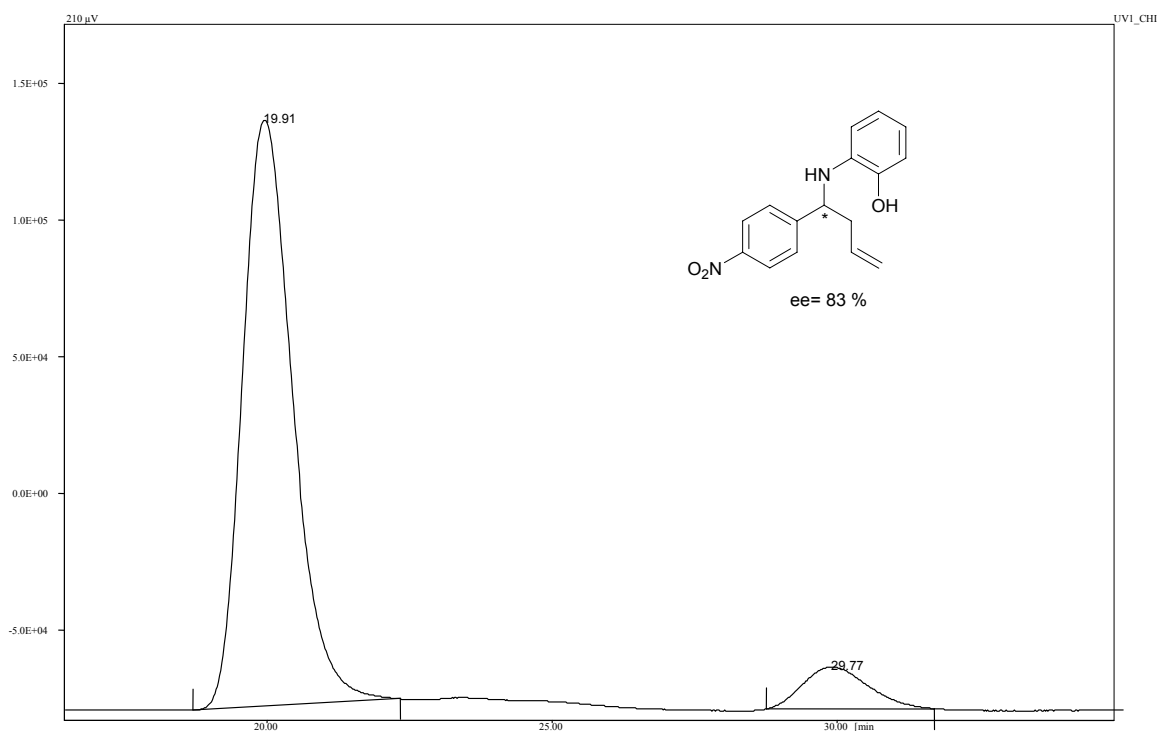


File name : RANO2001
Control Method : 90-10-1M

#	Name	Rt	Area	%Area
1	Peak 1	17,88	9590732,000	50,456
2	Peak 2	27,00	9417262,250	49,544

Total Area of Peak = 19007994.25

n-Hexane/ 2-Propanol = 90:10, flow rate 1 ml/ min, $\lambda = 210$ nm (Daicel Chiralpak AD column)

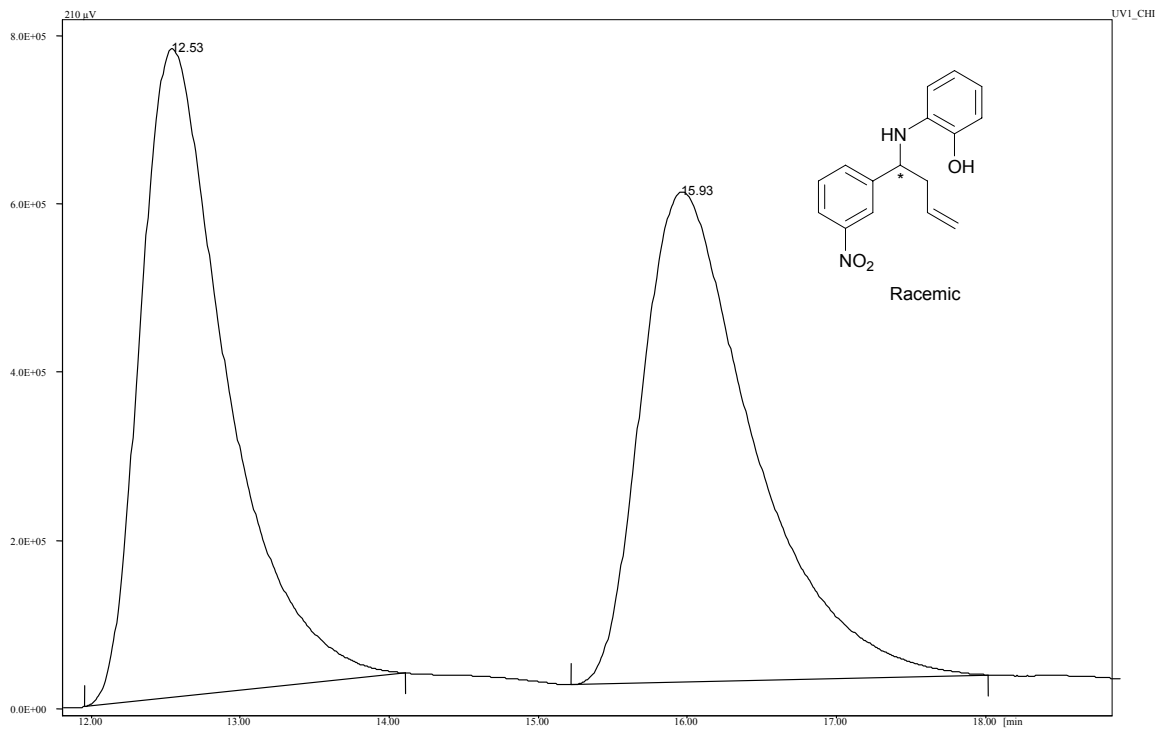


File name : S390C001
Control Method : 90-10-1M

#	Name	Rt	Area	%Area
1	Peak 1	19,91	12855646,001	91,449
2	Peak 2	29,77	1202149,749	8,551

Total Area of Peak = 14057795.75

n-Hexane/ 2-Propanol = 90:10, flow rate 1 ml/ min, $\lambda = 210$ nm (Daicel Chiralpak OD column)

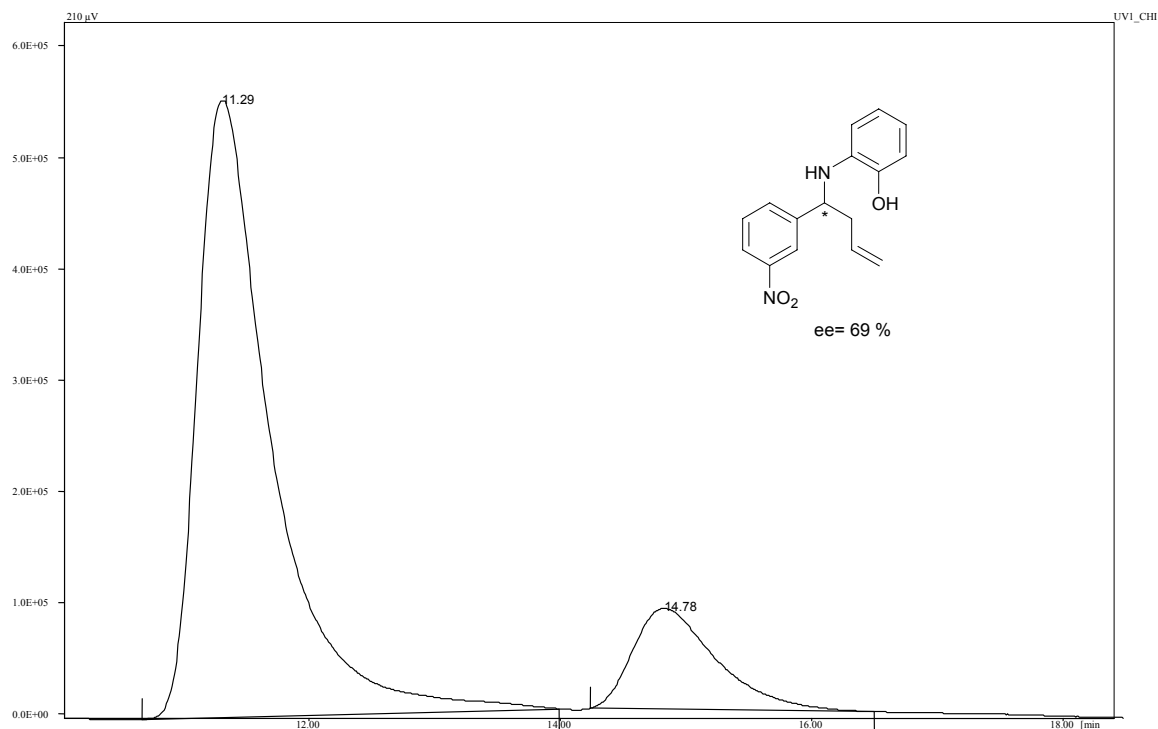


File name : SJ417001
Control Method : 90-10-1M

#	Name	Rt	Area	%Area
1	Peak 1	12,53	30937820,000	50,550
2	Peak 2	15,93	30264833,500	49,450

Total Area of Peak = 61202653.50

n-Hexane/ 2-Propanol = 90:10, flow rate 1 ml/ min, $\lambda = 210$ nm (Daicel Chiralpak OD column)

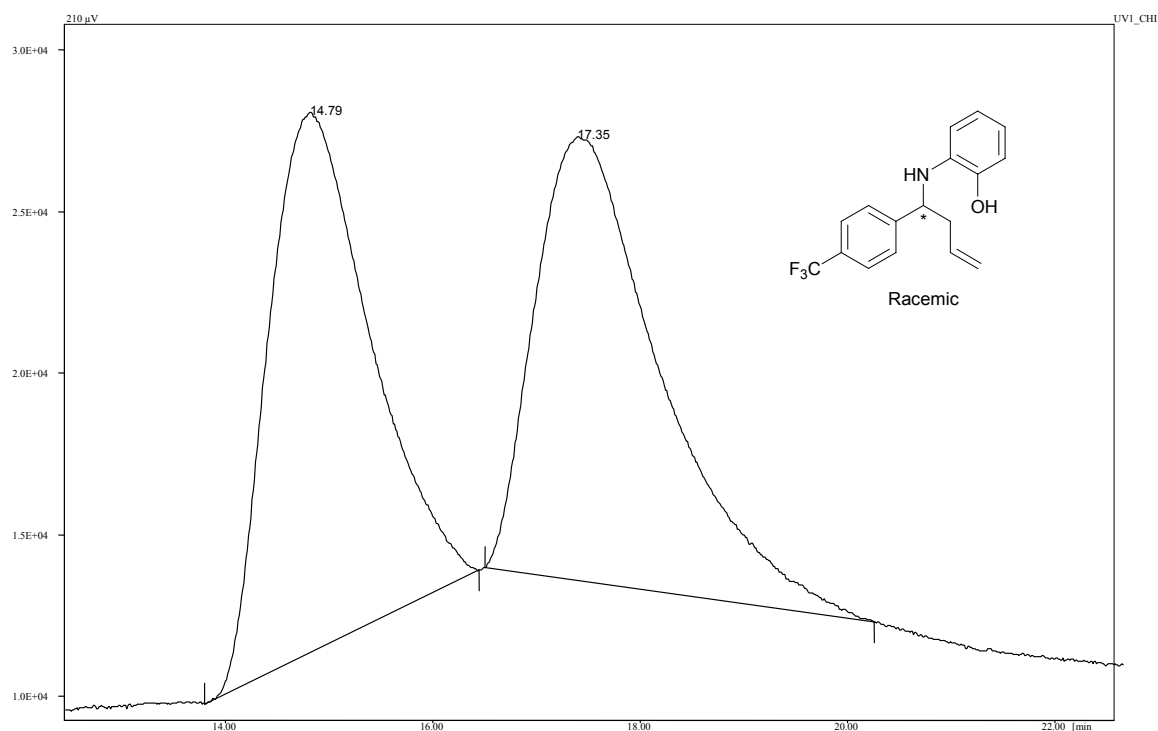


File name : SJ418001
Control Method : 90-10-1M

#	Name	Rt	Area	%Area
1	Peak 1	11,29	22241340,250	84,414
2	Peak 2	14,78	4106676,500	15,586

Total Area of Peak = 26348016.75

n-Hexane/ 2-Propanol = 90:10, flow rate 0.5 ml/ min, $\lambda = 210$ nm (Daicel Chiralpak OD column)

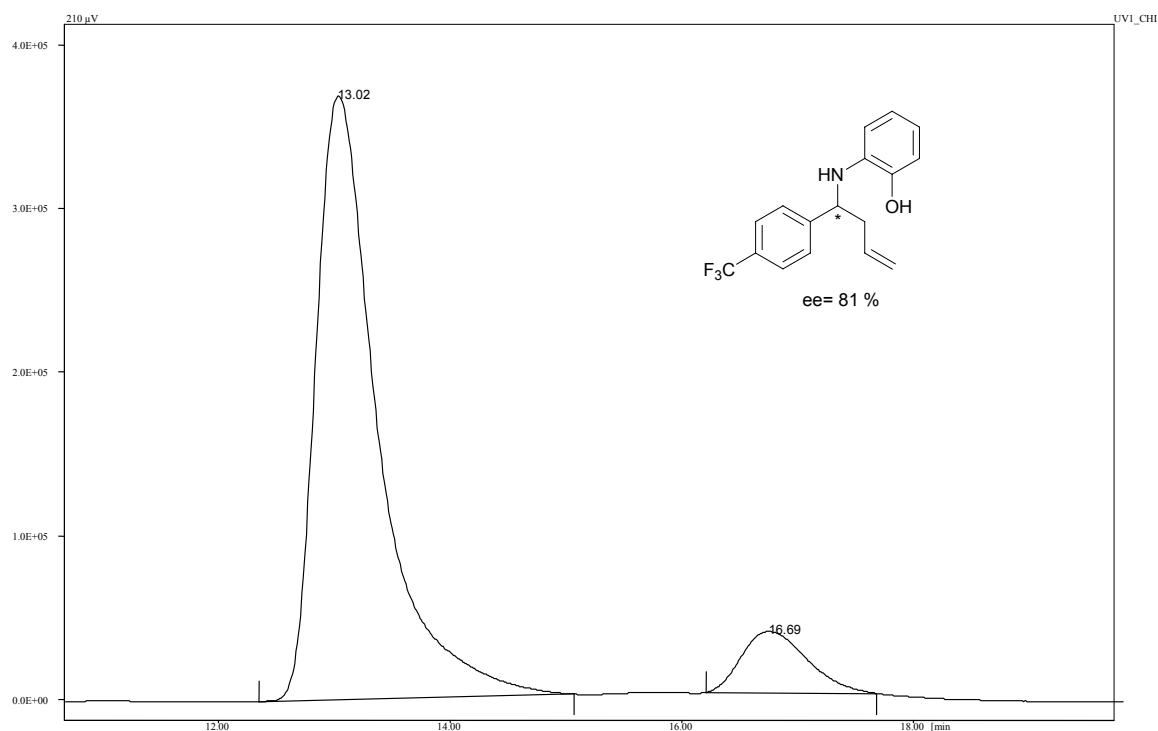


File name : SJ404002
Control Method :90-10-05

#	Name	Rt	Area	%Area
1	Peak 1	14,79	1125885,500	49,622
2	peak 2	17,35	1143030,000	50,378

Total Area of Peak = 2268915.50

n-Hexane/ 2-Propanol = 90:10, flow rate 0.5 ml/ min, $\lambda = 210$ nm (Daicel Chiralpak OD column)

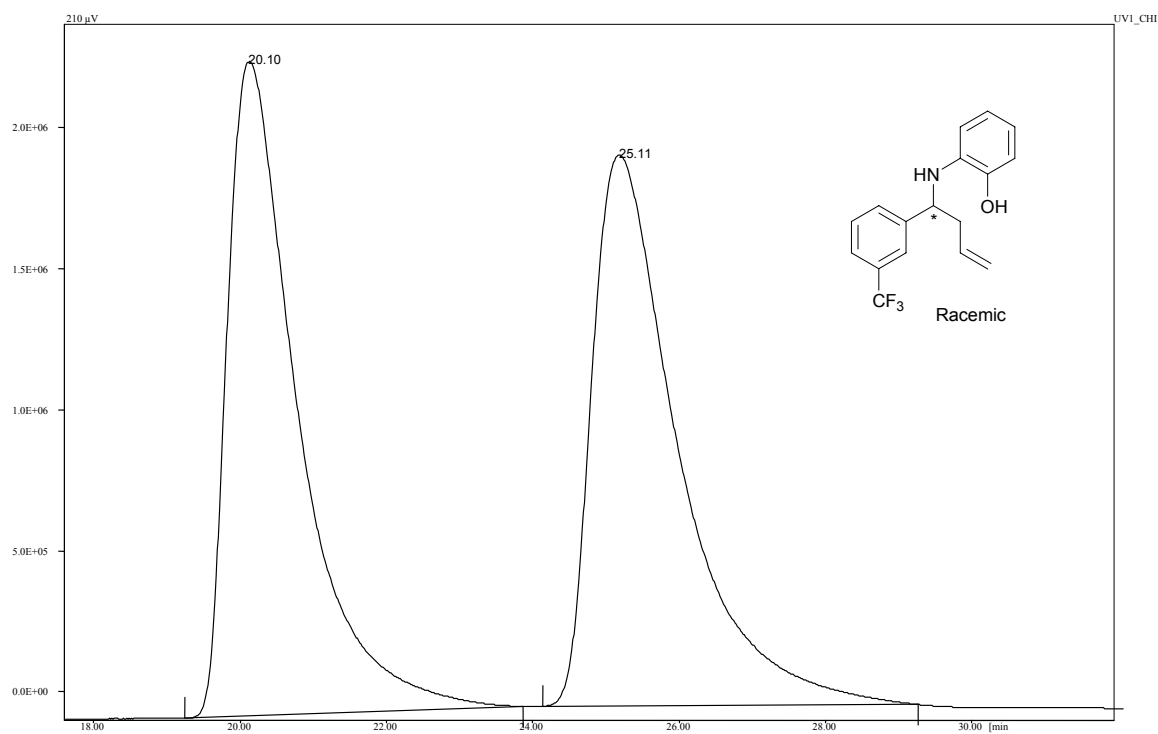


File name : SJ406002
Control Method :90-10-05

#	Name	Rt	Area	%Area
1	Peak 1	13,02	13424531,000	90,328
2	Peak 2	16,69	1437390,000	9,672

Total Area of Peak = 14861921.00

n-Hexane/ 2-Propanol = 95:05, flow rate 0.5 ml/ min, $\lambda = 210$ nm (Daicel Chiralpak OD column)

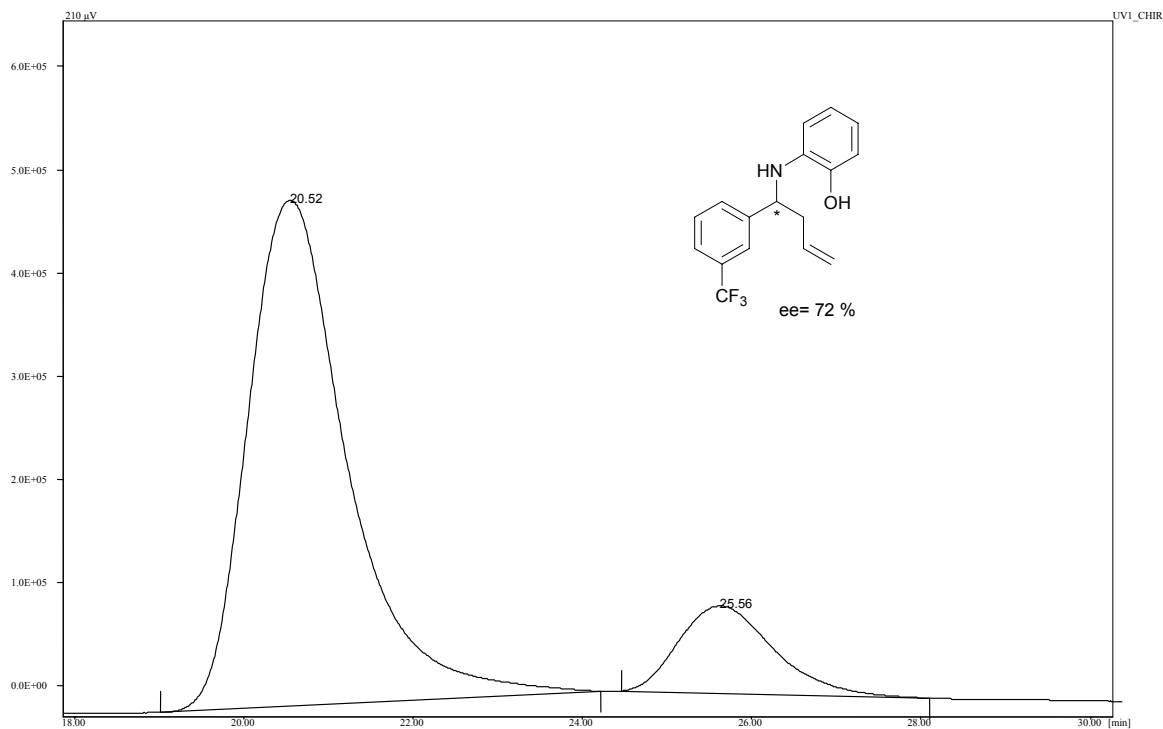


File name : SJ419001
Control Method :95_05_05

#	Name	Rt	Area	%Area
1	Peak 1	20,10	151598371,000	49,188
2	Peak 2	25,11	156603189,000	50,812

Total Area of Peak = 308201560.00

n-Hexane/ 2-Propanol = 95:05, flow rate 0.5 ml/ min, $\lambda = 210$ nm (Daicel Chiralpak OD column)

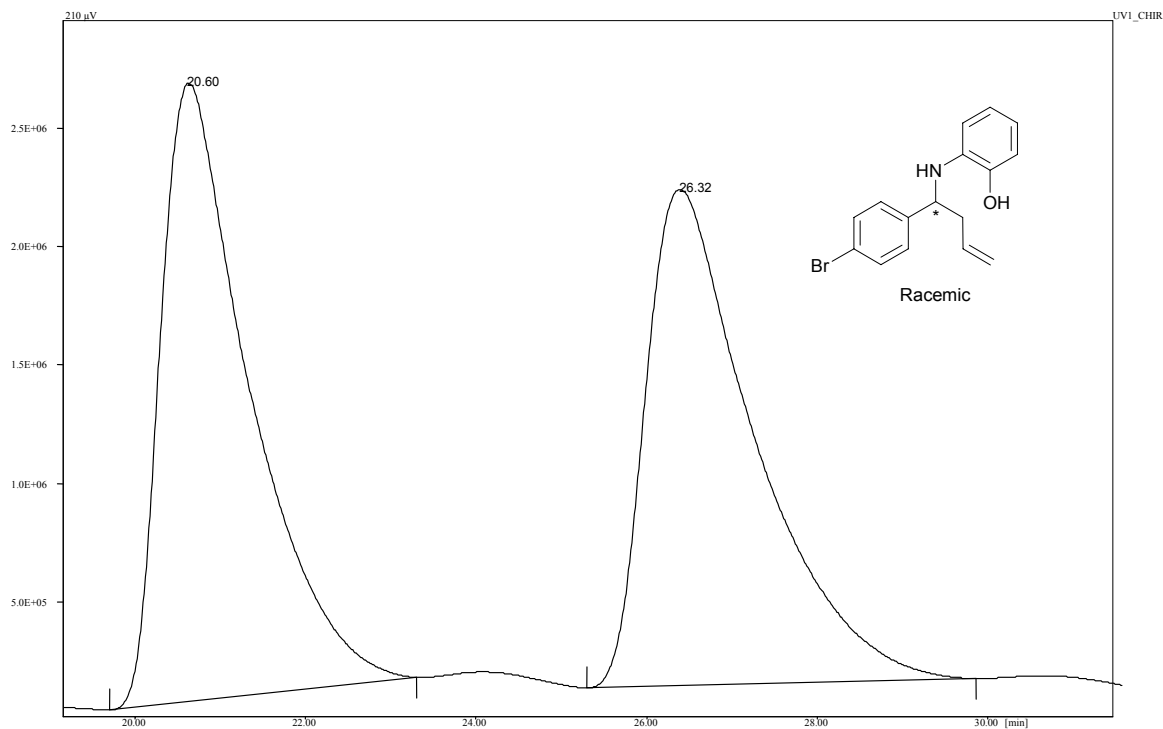


File name : SJ420001
Control Method :95_05_05

#	Name	Rt	Area	%Area
1	Peak 1	20,52	39496601,250	85,871
2	Peak 2	25,56	6498418,000	14,129

Total Area of Peak = 45995019.25

n-Hexane/ 2-Propanol = 95:05, flow rate 0.5 ml/ min, $\lambda = 210$ nm (Daicel Chiralpak OD column)

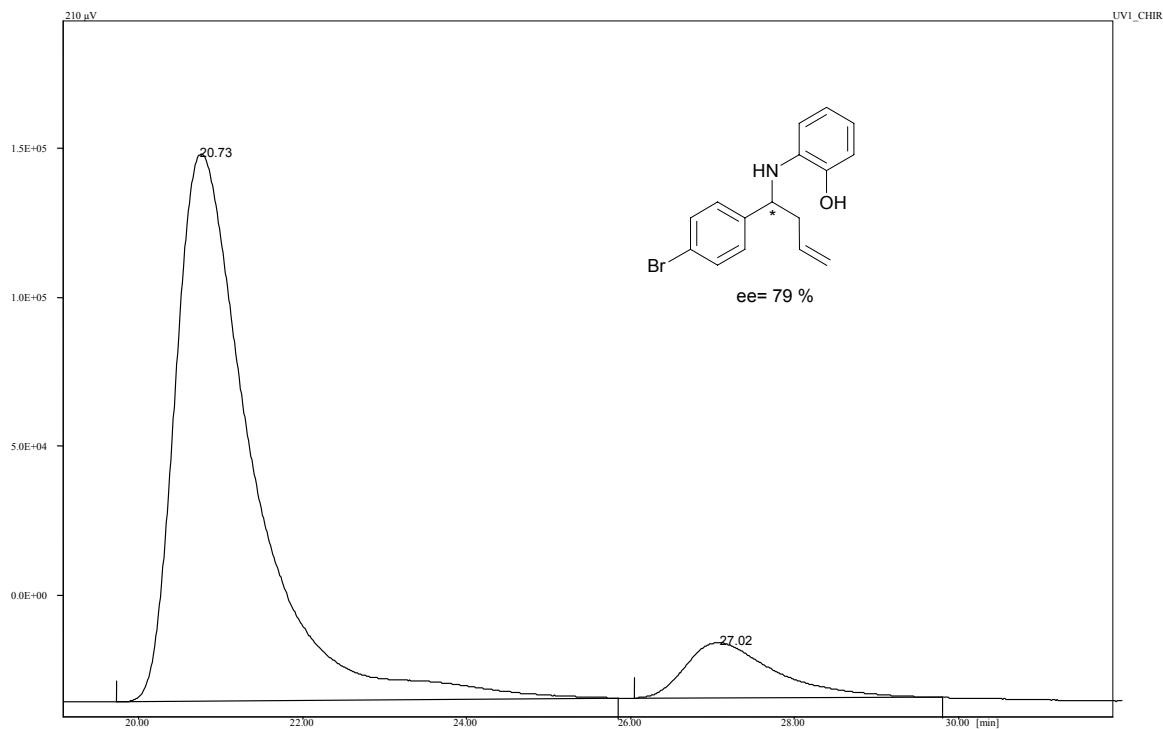


File name : SJ398002
Control Method :95_05_05

#	Name	Rt	Area	%Area
1	Peak 1	20,60	185906406,000	50,384
2	Peak 2	26,32	183074728,500	49,616

Total Area of Peak = 368981134.50

n-Hexane/ 2-Propanol = 95:05, flow rate 0.5 ml/ min, $\lambda = 210$ nm (Daicel Chiralpak OD column)

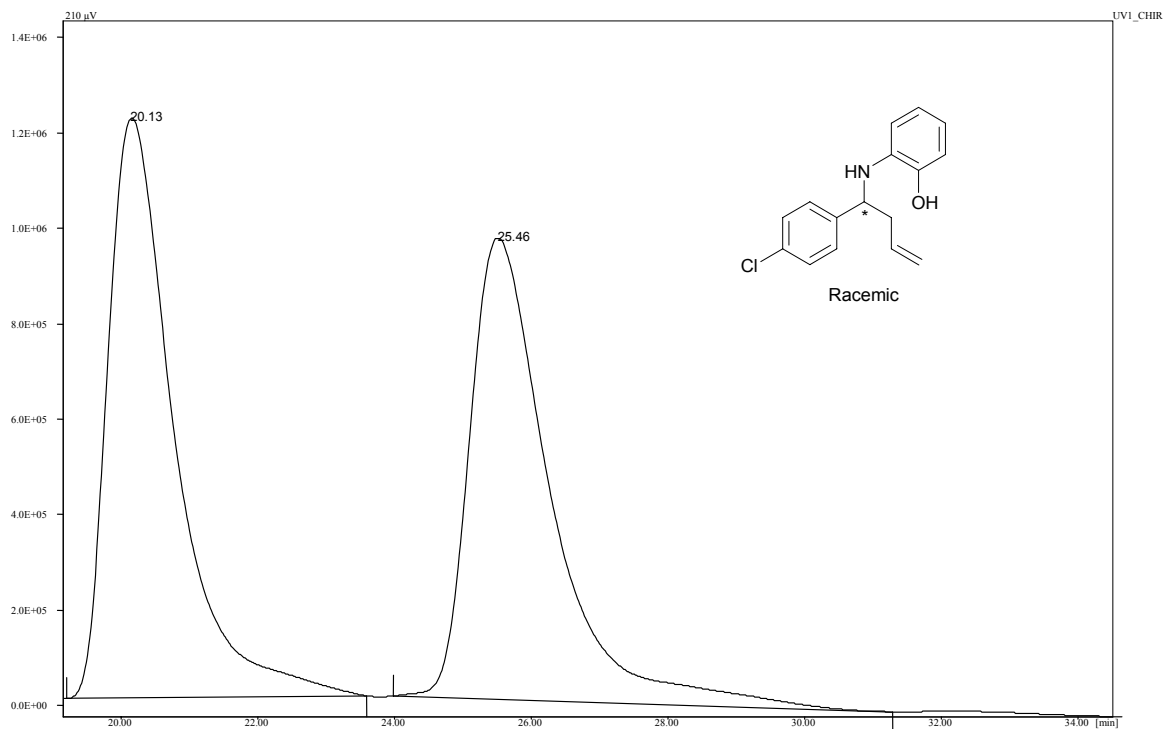


File name : SJ410001
Control Method :95_05_05

#	Name	Rt	Area	%Area
1	Peak 1	20,73	11912952,001	89,450
2	Peak 2	27,02	1405115,501	10,550

Total Area of Peak = 13318067.50

n-Hexane/ 2-Propanol = 95:05, flow rate 0.5 ml/ min, $\lambda = 210$ nm (Daicel Chiralpak OD column)

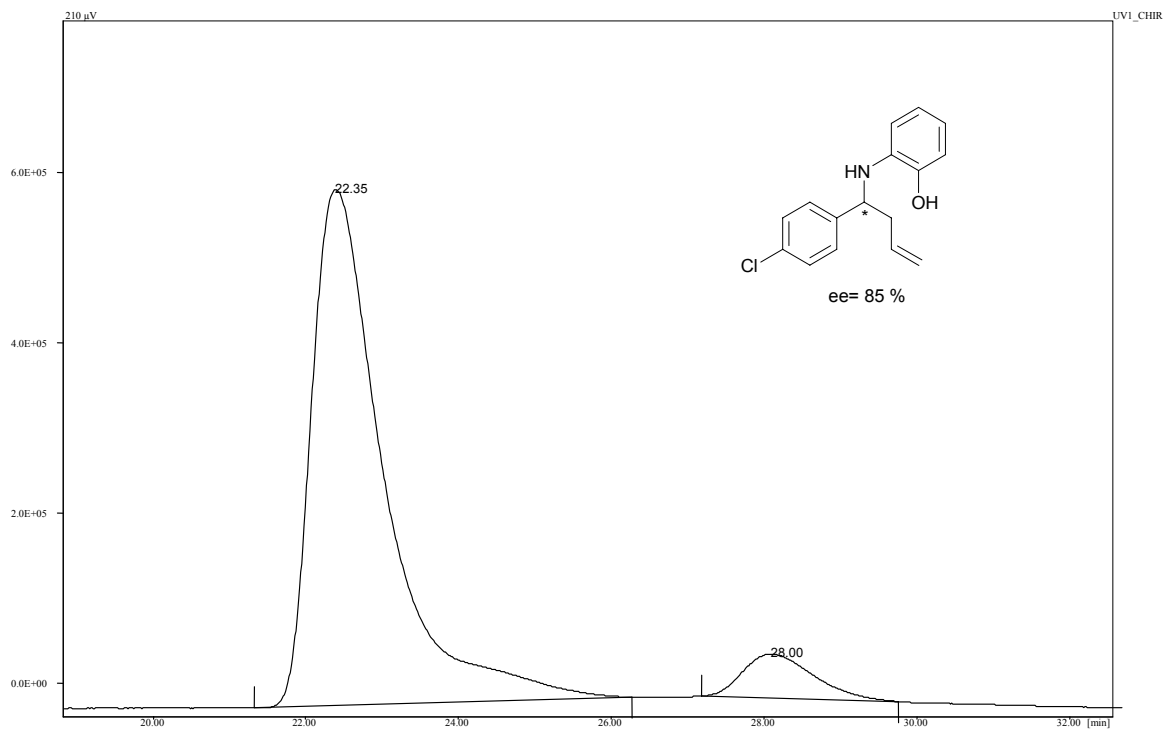


File name : SJ414001
Control Method :95_05_05

#	Name	Rt	Area	%Area
1	Peak 1	20,13	80021344,000	50,627
2	Peak 2	25,46	78037798,500	49,373

Total Area of Peak = 158059142.50

n-Hexane/ 2-Propanol = 95:05, flow rate 0.5 ml/ min, $\lambda = 210$ nm(Daicel Chiralpak OD column)

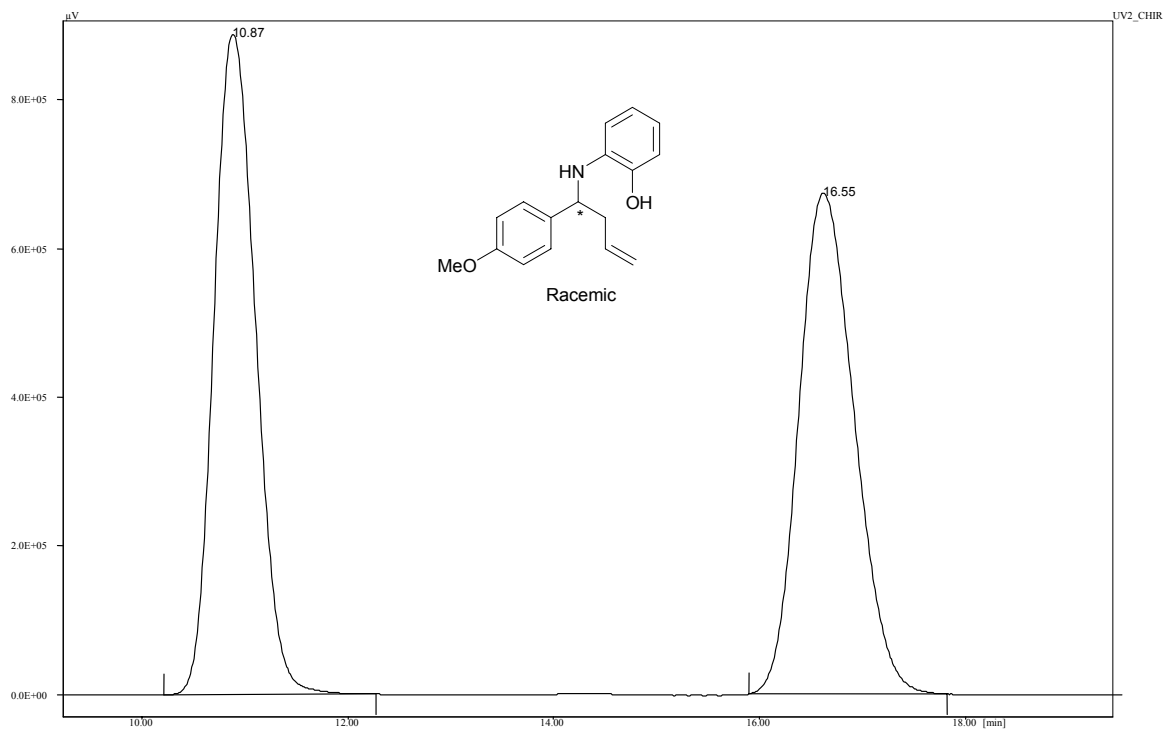


File name : SJ413001
Control Method :95_05_05

#	Name	Rt	Area	%Area
1	Peak 1	22,35	39293195,750	92,330
2	Peak 2	28,00	3264158,250	7,670

Total Area of Peak = 42557354.00

n-Hexane/ 2-Propanol = 90:10, flow rate 1 ml/ min, $\lambda = 210$ nm (Daicel Chiralpak AD column)

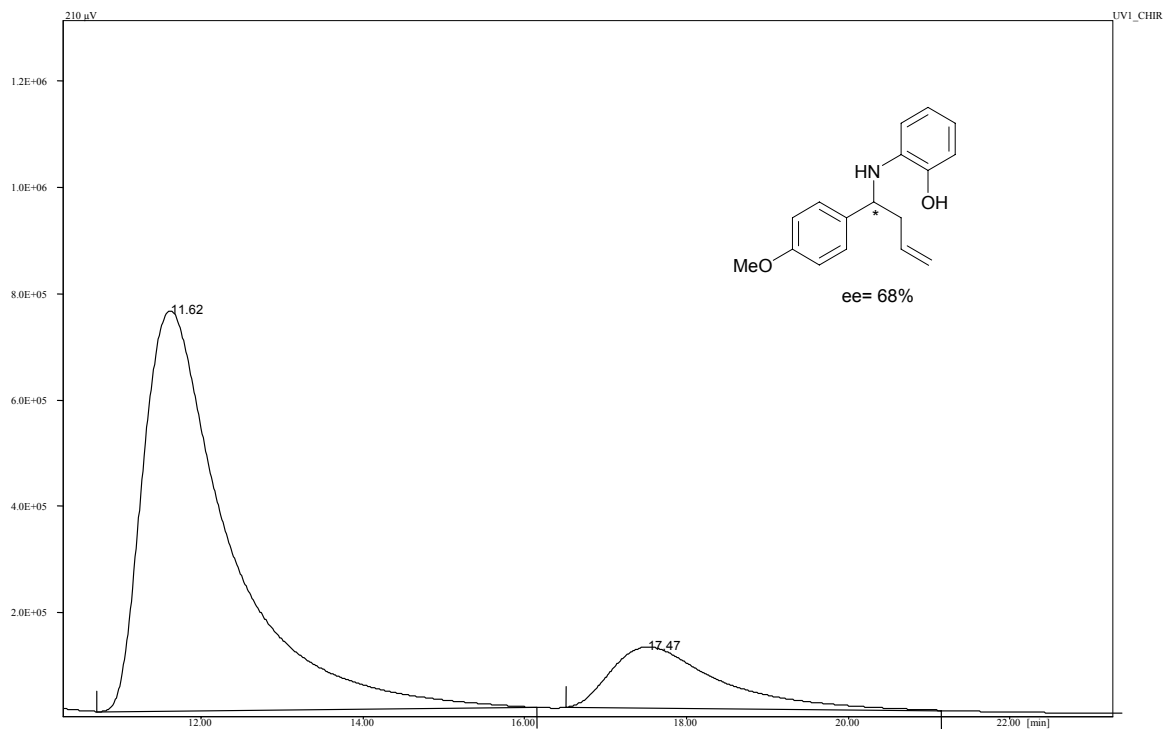


File name : CB050001
Control Method :90-10-1M

#	Name	Rt	Area	%Area
1	Peak 1	10,87	24272635,75	49,66
2	Peak 2	16,55	24607561,50	50,34

Total Area of Peak = 48880197.25

n-Hexane/ 2-Propanol = 90:10, flow rate 1 ml/ min, $\lambda = 210$ nm (Daicel Chiralpak AD column)

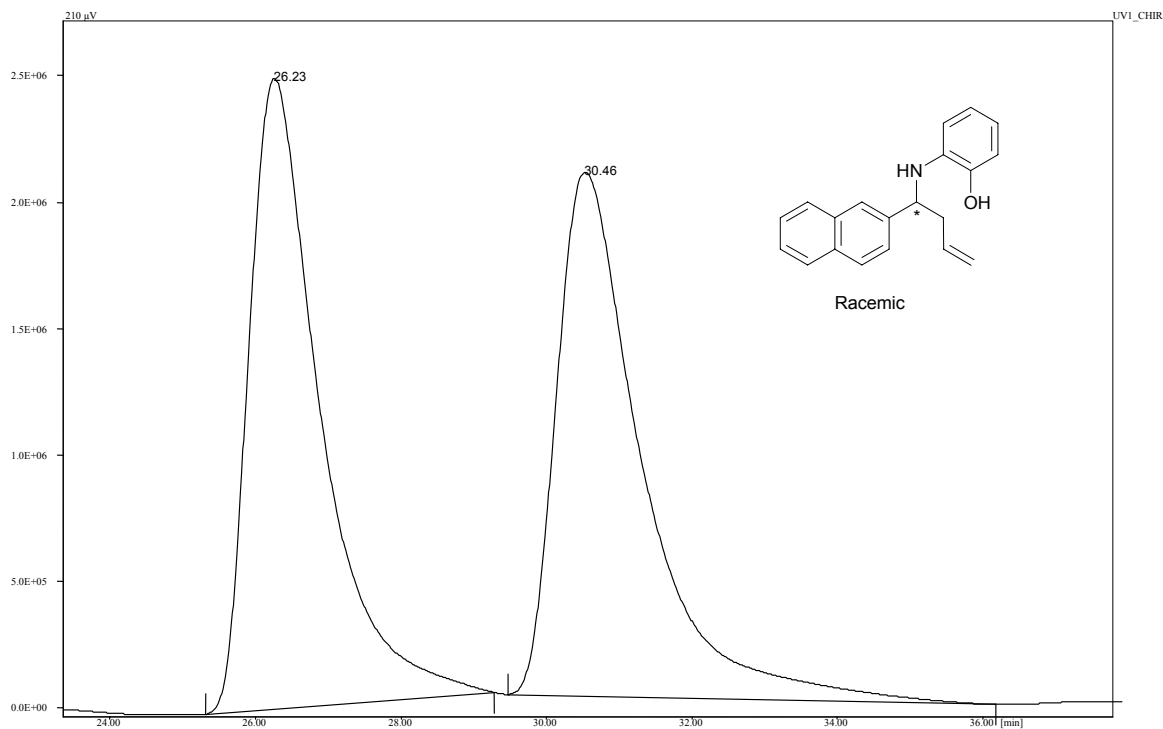


File name : SJ405002
Control Method :90-10-1M

#	Name	Rt	Area	%Area
1	Peak 1	11,62	55039797,250	84,014
2	Peak 2	17,47	10472482,001	15,986

Total Area of Peak = 65512279.25

n-Hexane/ 2-Propanol = 95:05, flow rate 0.5 ml/ min, $\lambda = 210$ nm (Daicel Chiralpak OD column)

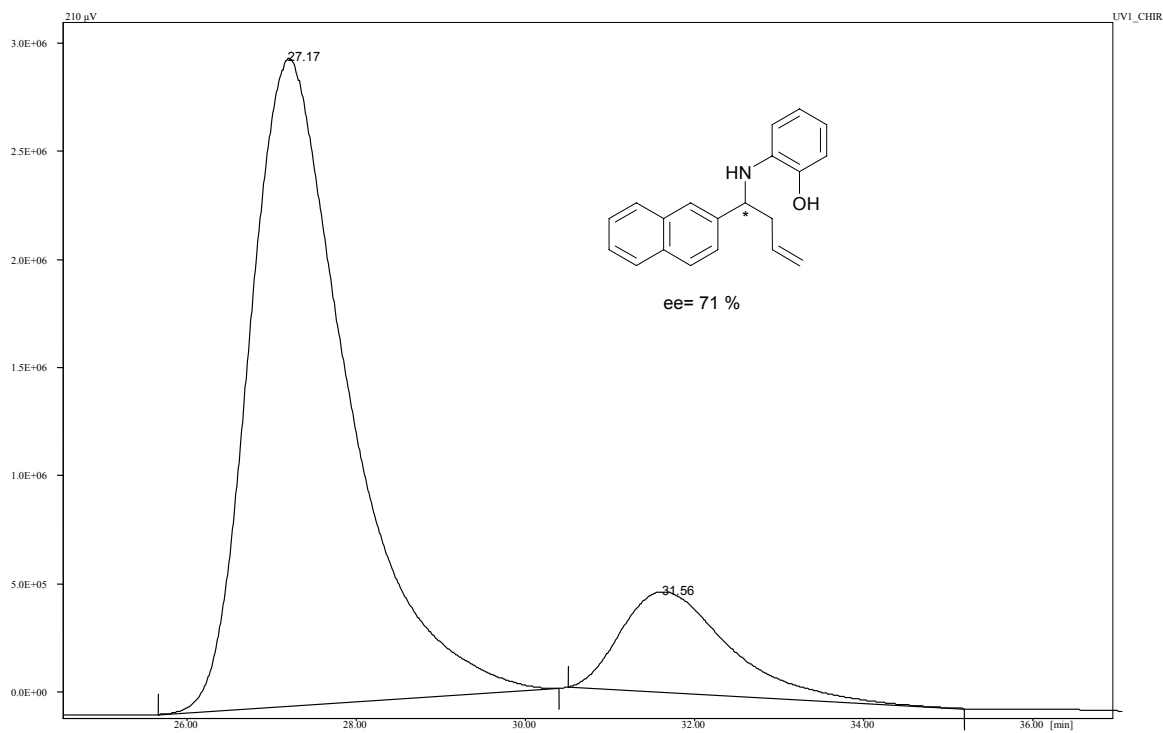


File name : S407C008
Control Method :95_05_05

#	Name	Rt	Area	%Area
1	Peak 1	26,23	166152150,750	50,014
2	Peak 2	30,46	166057582,750	49,986

Total Area of Peak = 332209733.50

n-Hexane/ 2-Propanol = 95:05, flow rate 0.5 ml/ min, $\lambda = 210$ nm (Daicel Chiralpak OD column)

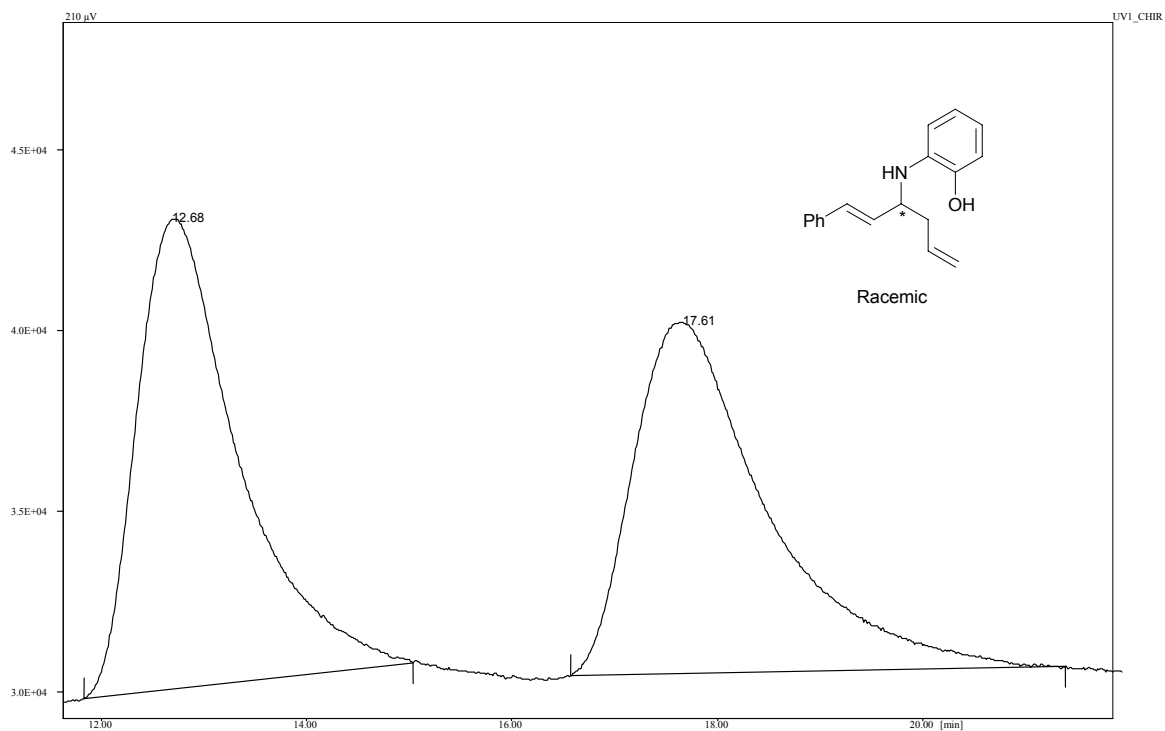


File name : SJ402004
Control Method :95_05_05

#	Name	Rt	Area	%Area
1	Peak 1	27,17	238321094,500	85,546
2	Peak 2	31,56	40266230,000	14,454

Total Area of Peak = 278587324.50

n-Hexane/ 2-Propanol = 90:10, flow rate 1 ml/ min, λ = 210 nm (Daicel Chiralpak AD column)

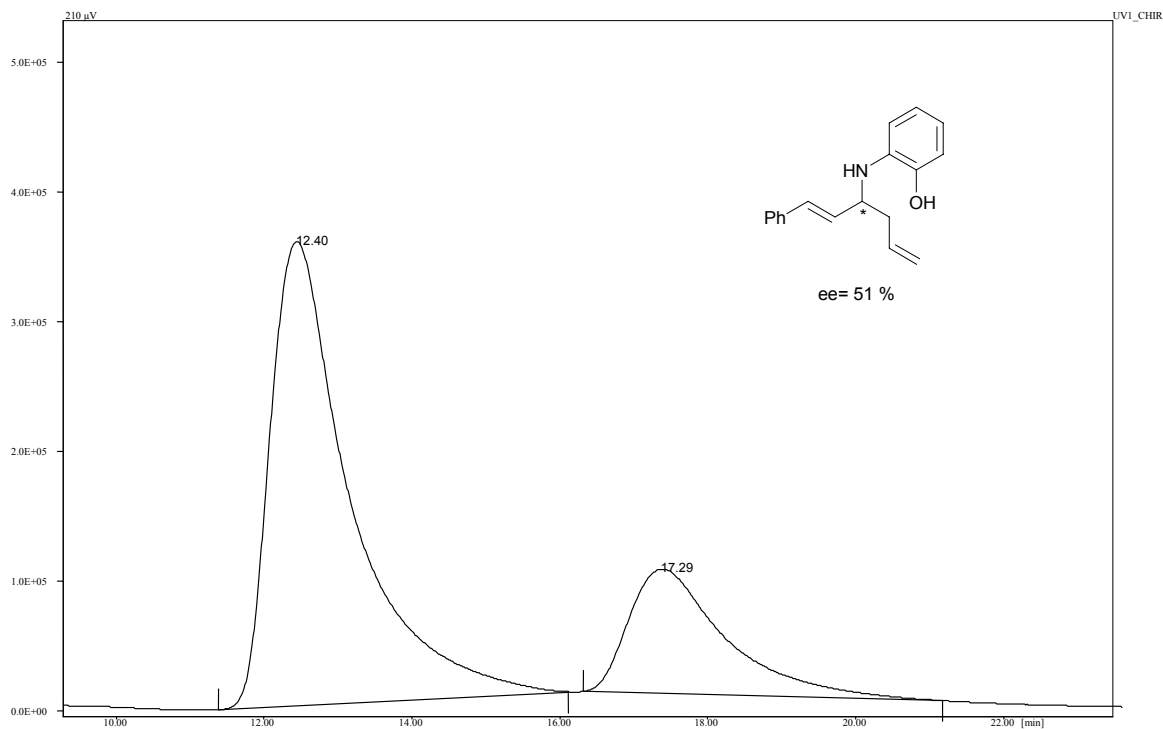


File name : S407A001
Control Method : 90-10-1M

#	Name	Rt	Area	%Area
1	Peak 1	12,68	881668,000	50,416
2	Peak 2	17,61	867119,500	49,584

Total Area of Peak = 1748787.50

n-Hexane/ 2-Propanol = 90:10, flow rate 1 ml/ min, $\lambda = 210$ nm (Daicel Chiralpak AD column)

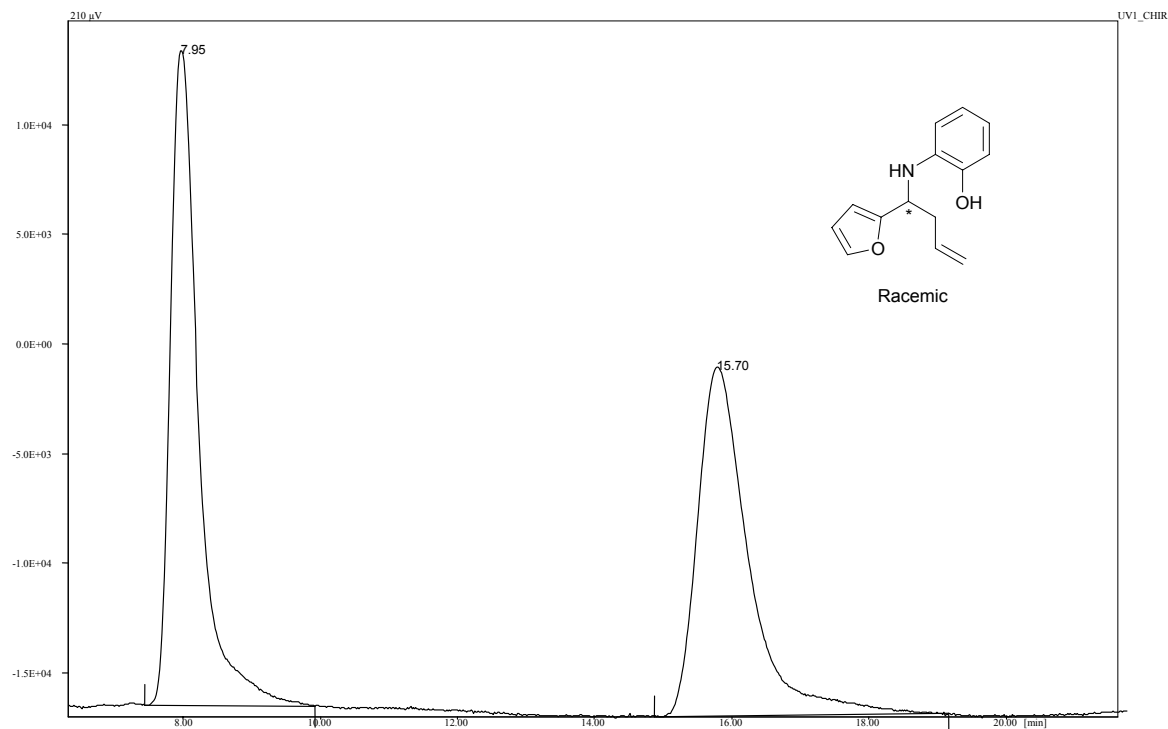


File name : SJ403001
Control Method :90-10-1M

#	Name	Rt	Area	%Area
1	Peak 1	12,40	26626444,000	75,712
2	Peak 2	17,29	8541809,250	24,288

Total Area of Peak = 35168253.25

n-Hexane/ 2-Propanol = 90:10, flow rate 1 ml/ min, $\lambda = 210$ nm (Daicel Chiralpak OD column)

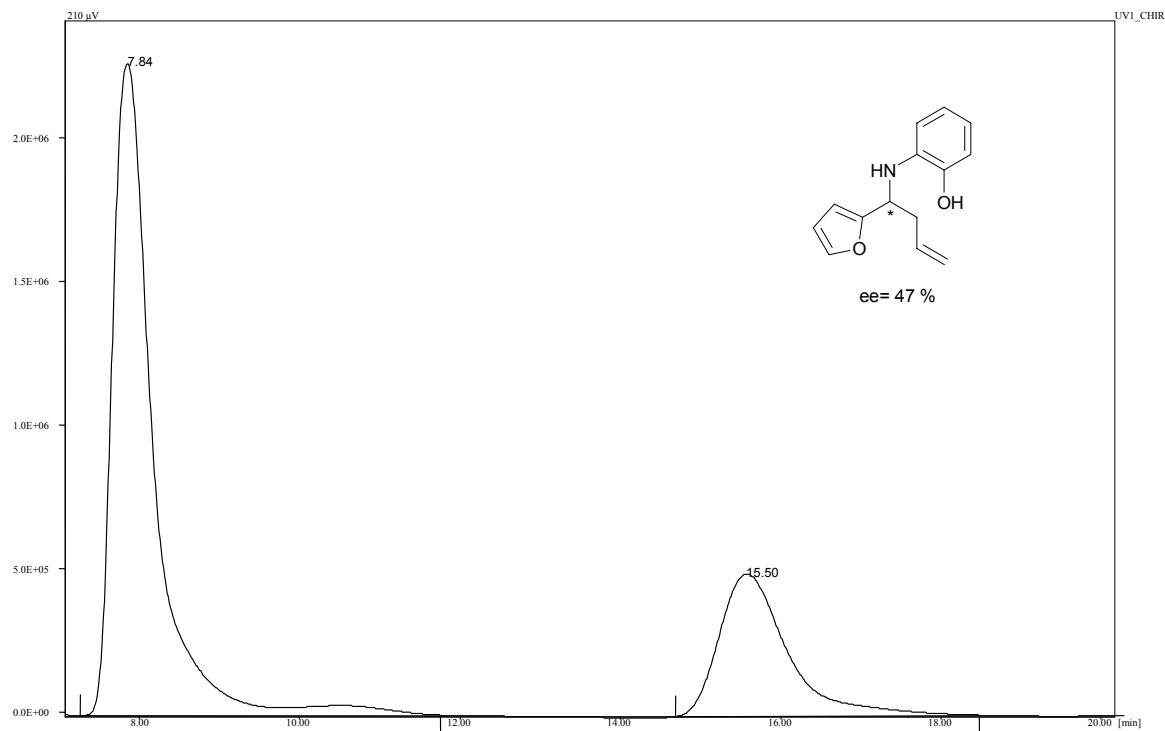


File name : S407D001
Control Method :90-10-1M

#	Name	Rt	Area	%Area
1	Peak 1	7,95	828735,500	50,580
2	Peak 2	15,70	809725,500	49,420

Total Area of Peak = 1638461.00

n-Hexane/ 2-Propanol = 90:10, flow rate 1 ml/ min, $\lambda = 210$ nm (Daicel Chiralpak OD column)



File name : SJ412003
Control Method :90-10-1M

#	Name	Rt	Area	%Area
1	Peak 1	7,84	78129487,000	73,271
2	Peak 2	15,50	28502058,000	26,729

Total Area of Peak = 106631545.00