

Supporting Information

Synthesis of Novel Axially Chiral Rh-NHC Complexes Derived from BINAM and Application in the Enantioselective Hydrosilylation of Methyl Ketones**

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General Remarks. ¹H NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in CDCl₃ with tetramethylsilane (TMS) as an internal standard; *J*-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-241 MC digital polarimeter; [α]_D-values are given in unit of 10⁻¹ deg cm² g⁻¹. THF and toluene were distilled from Na under Ar atmosphere. All of the solid compounds reported in this paper gave satisfactory CHN microanalyses with a Carlo-Erba 1106 analyzer. [RhCl(COD)]₂ was prepared according to the literature.¹ Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF₂₅₄ silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. Enantiomeric ratios were determined by chiral GC or HPLC analysis. The absolute configuration was assigned by comparison the optical rotation with those reported date. Racemic products were synthesized from the reduction of corresponding ketones in THF with LiAlH₄ or NaBH₄.

1) G. Giordano, R. H. Crabtree, *Inorg. Synth.* **1988**, 28, 88.

Synthesis of (S)-(+)-*N*², *N*^{2'}-bis(2-nitrophenyl)-1,1'-binaphthalenyl-2,2'-diamine 2.

Under argon atmosphere, a mixture of (S)-1,1'-binaphthalenyl-2,2'-diamine **1** (142 mg, 0.50 mmol), 2-bromo-nitrobenzene (303 mg, 1.5 mmol), Pd₂(dba)₃ (12 mg, 0.0125 mmol), DPE-phos (20 mg, 0.0375 mmol), and Cs₂CO₃ (520 mg, 1.6 mmol) were stirred in anhydrous toluene (4.0 mL) at 80 °C for 48 h. After the reaction mixture was cooled to room temperature, the reaction was quenched by addition of 10 mL H₂O. The organic compound was extracted with EtOAc (2 x 20 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: hexane/ethyl acetate= 20/1) to remove excess raw material, and then with eluent: hexane/ethyl acetate= 4/1 to give **2** as a red solid; Yield: 263 mg (100%). [α]_D²⁰ = 522.4 (c 0.33, CHCl₃); IR (KBr) ν 3317, 1613, 1498, 1244, 736 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS) δ 6.58-6.64 (m, 2H, ArH), 7.10-7.30 (m, 6H, ArH), 7.31-7.37 (m, 2H, ArH), 7.46-7.51 (m, 2H, ArH), 7.68 (d, *J* = 8.7 Hz, 2H, ArH), 7.92-7.98 (m, 4H, ArH), 8.02 (d, *J* = 9.0 Hz, 2H, ArH), 9.04 (s, 2H, NH); ¹³C NMR (75 MHz, CDCl₃, TMS) δ 115.65, 117.74, 122.09, 124.82, 125.64, 125.74, 126.16, 127.48, 128.44, 129.71, 131.31, 133.30, 133.43, 135.16, 135.37, 141.49; MS (CI) *m/e* 527 (M⁺+1, 100), 480 (M⁺-46, 9.14), 389 (M⁺-137, 8.64), 341 (M⁺-185, 20.95); Anal. Calcd. for C₃₂H₂₂N₄O₄ requires: C 72.99, H 4.21, N 10.64. Found: C 72.89, H 4.07, N 10.49%.

Synthesis of (S)-(-)-*N*², *N*^{2'}-bis(2-aminophenyl)-1,1'-binaphthalenyl-2,2'-diamine 3.

A mixture of **2** (144 mg, 0.25 mmol), 10% Pd-C (15 mg) in mixed solution of EtOAc (15 mL) and EtOH (45 mL) were stirred under H₂ atmosphere (1.0 atm) at 60 °C for 24 h. After cooling to room temperature, Pd-C was removed by filtration. The solvent was evaporated under reduced pressure. The residue was purified by a silica gel flash column chromatography (eluent: hexane/ethyl acetate, 2/1–1/1) to give **3** as a white solid; Yield: 107 mg (92%). [α]_D²⁰ = -199.0 (c 0.52, CHCl₃); IR (KBr) ν 3368, 1618, 1593, 1500, 1299, 817, 745 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS) δ 3.69 (br, 4H, NH₂), 5.15 (br, 2H, NH), 6.67-6.74 (m, 4H, ArH), 6.98-7.05 (m, 4H, ArH), 7.15 (d, *J* = 8.7 Hz, 2H, ArH), 7.24-7.29 (m, 6H, ArH), 7.80-7.83 (m, 4H, ArH), ¹³C NMR (75 MHz, CDCl₃, TMS) δ 113.33, 115.78, 116.17, 118.77, 122.81, 123.68, 126.62, 126.85, 127.04, 127.45, 128.37, 128.70, 129.69, 133.76, 142.66, 143.06; MS (EI) *m/e* 466 (M⁺, 100), 359 (M⁺-107, 34.75), 266 (M⁺-200, 36.18); Anal. Calcd. for C₃₂H₂₆N₄ requires: C 82.38, H 5.62, N 12.01. Found: C 81.98, H 5.65, N 11.97%.

Synthesis of (S)-(-)-1,1'-(1,1'-binaphthanelyl)dibenzimidazole 4.

The compound **3** (233 mg, 0.50 mmol) and triethyl orthoformate [HC(OC₂H₅)₃] (5.0 mL)

containing a little TsOH were heated at 100 °C for 24 h. After the excess amount of triethyl orthoformate was removed under reduced pressure, the residue was purified by a silica gel flash column chromatography (eluent: hexane/ethyl acetate, 2/3) to give **4** as a white solid; Yield: 221 mg (91%). $[\alpha]_D^{20} = -490.10$ (c 0.52, CHCl₃); IR (KBr) ν 3057, 1612, 1490, 1232, 820, 734 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS) δ 6.10 (d, 2H, $J = 8.4$ Hz, ArH), 6.40-6.52 (m, 2H, ArH), 6.93-6.99 (m, 2H, ArH), 6.99 (s, 2H, NCHN), 7.44 (d, $J = 8.7$ Hz, 2H, ArH), 7.48-7.57 (m, 6H, ArH), 7.64-7.69 (m, 2H, ArH), 8.07 (d, $J = 8.4$ Hz, 4H, ArH); ¹³C NMR (75 MHz, CDCl₃, TMS) δ 108.67, 119.06, 122.06, 123.40, 123.63, 126.16, 126.96, 128.01, 128.18, 128.77, 130.69, 132.19, 132.38, 133.78, 134.38, 141.42, 142.13; MS (EI) m/e 486 (M⁺, 100), 368 (M⁺-118, 78.13), 243 (M⁺-143, 20.75); Anal. Calcd. for C₃₄H₂₂N₄ requires: C 83.93, H 4.56, N 11.51. Found: C 83.97, H 4.55, N 11.45%.

Synthesis of (S)-1,1'-(1,1'-binaphthyl)-3,3'-dimethyldibenzimidazolium diiodide **5**.

The compound **4** (97 mg, 0.20 mmol) and CH₃I (0.24 mL, 4 mmol) in CH₃CN (4.0 mL) were stirred under reflux for 5 h. After cooling to room temperature, volatiles were removed under reduced pressure and the obtained solid compound **5** was used for the next reaction without further purification. MS (ESI) m/e 643.2 (M⁺-I), 258.1 (M-2I)/2.

Synthesis of Rh(I) complex **6** and Rh(III) complex **7**.

A mixture of **5** (154 mg, 0.20 mmol), [RhCl(COD)]₂ (48 mg, 0.10 mmol), NaOAc (132 mg, 0.80 mmol), and KI (66 mg, 0.40 mmol) was stirred in CH₃CN (12 ml) under reflux for 24 h. After cooling, volatiles were removed under reduce pressure and the residue was purified by a silica gel flash column chromatography (eluent: hexane/ethyl acetate= 8/1) to give a [RhX(COD)]₂ fraction (X = Cl, I). The subsequent elution with hexane/ethyl acetate (6/1) gave a yellow solid Rh(I) complex **6**. The further elution with hexane/ ethyl acetate (1/1) gave a orange solid Rh(III) complex **7**.

(S)-(-)-Diiodo-[1,1'-(1,1'-binaphthyl)-3,3'-dimethyldibenzimidazoline-2,2'-diylidene]bis-(η^4 -1,5-cyclooctadiene)dirhodium(I) **6.** A crystal suitable for X-ray analysis was obtained by recrystallization from CH₂Cl₂. $[\alpha]_D^{20} = -14.1$ (c 1.22, CHCl₃); IR (KBr) ν 2847, 1601, 1483, 1333, 1218, 799, 738 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS) δ 1.43-1.55 (m, 4H, cod-CH₂), 1.69-1.73 (m, 4H, cod-CH₂), 1.83-1.87 (m, 2H, cod-CH₂), 2.02-2.18 (m, 6H, cod-CH₂), 3.09-3.11(m, 2H, cod-CH), 3.39-4.44 (m, 2H, cod-CH), 4.02-4.09 (m, 2H, cod-CH), 4.17 (s, 6H, CH₃), 5.16-5.20 (m, 2H, cod-CH), 6.59-6.65 (m, 4H, ArH), 6.76-6.81 (m, 2H, ArH), 6.88 (d, $J = 9.0$ Hz, 2H, ArH), 7.41-7.52 (m, 4H, ArH), 7.60-7.67 (m, 4H, ArH), 7.97 (d, $J = 8.7$ Hz, 2H, ArH), 8.03 (d, $J = 7.8$

Hz, 2H, ArH); ^{13}C NMR (75 MHz, CDCl_3 , TMS) δ 28.86, 29.63, 31.62, 32.70, 36.50, 70.37 (d, $^1J(^{103}\text{Rh},\text{C}) = 13.4$ Hz, cod-CH), 71.88 (d, $^1J(^{103}\text{Rh},\text{C}) = 14.8$ Hz, cod-CH), 96.14 (d, $^1J(^{103}\text{Rh},\text{C}) = 6.1$ Hz, cod-CH), 98.33 (d, $^1J(^{103}\text{Rh},\text{C}) = 7.1$ Hz, cod-CH), 107.90, 111.89, 121.16, 122.67, 126.39, 126.82, 127.29, 128.66, 129.11, 130.73, 131.64, 133.85, 134.12, 136.11, 137.01, 138.02, 196.35 (d, $^1J(^{103}\text{Rh},\text{C}) = 49.1$ Hz, CN_2); MS (ESI) m/e 1063.1 (M^+ -I); Anal. Calcd. for $\text{C}_{52}\text{H}_{50}\text{I}_2\text{N}_4\text{Rh}_2 \cdot \text{H}_2\text{O}$ requires: C 51.68, H 4.34, N 4.64. Found: C 51.84, H 4.62, N 4.54%.

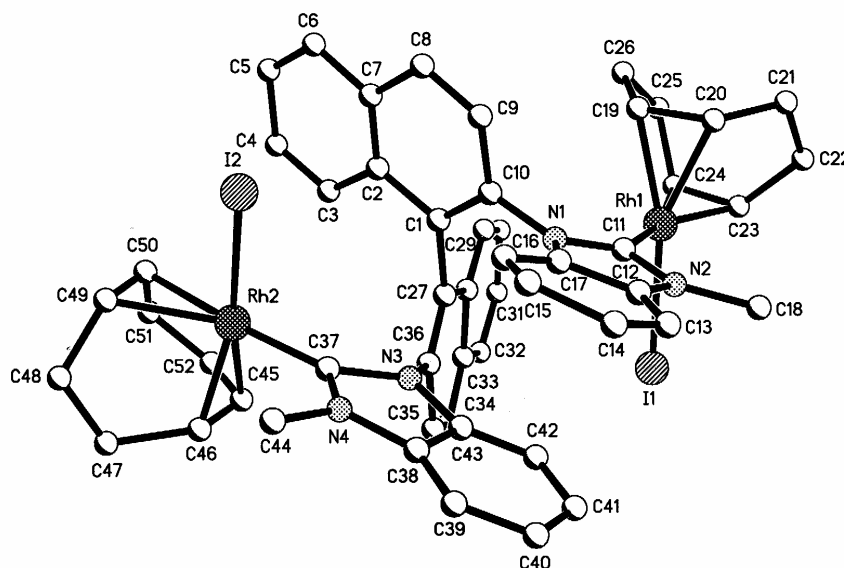


Figure 1: The ORTEP draw of Rh(I)-NHC complex **6**.

Selected bond lengths and angles: Rh-C(carbene) 2.059(12) and 1.924(19) Å,
I1-Rh1-C11(carbene) 90.1(4)°.

The crystal data for Rh(I)-NHC complex **6**: empirical formula: $\text{C}_{52}\text{H}_{50}\text{N}_4\text{I}_2\text{Rh}_2$, formula weight: 1190.58, temperature: 293(2) K, crystal system, space group: Orthorhombic, $\text{P}2(1)2(1)2(1)$, unit cell dimensions: $a = 12.1794(19)\text{Å}$, $b = 19.027(3)\text{Å}$, $c = 20.291(3)\text{Å}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 4702.0(13)\text{Å}^3$, $Z_{\text{value}} = 4$, $D_{\text{calc}} = 1.682 \text{ g/cm}^3$, $F_{000} = 2344$, Crystal size: 0.432 x 0.201 x 0.126 mm, Data/restraints/parameters = 8726/0/544, Final R indices [$I > 2\sigma(I)$]: $R1 = 0.0651$, $wR2 = 0.1366$, R indices (all data): $R1 = 0.1070$; $wR2 = 0.1508$. Its crystal structure has been deposited at the Cambridge Crystallographic Data Center and has been allocated the deposition numbers: CCDC 209244.

(S)-(+)-Diiodo-[1,1'-(1,1'-binaphthyl)-3,3'-dimethyldibenzimidazoline-2,2'-diylidene] acetato Rh(III) 7. Yield: 47 mg (25%). A crystal suitable for X-ray analysis was obtained by recrystallization from hexane/THF (1/1). $[\alpha]_{\text{D}}^{20} = 8$ (c 1.03, CHCl_3); IR (KBr) ν 3057, 1591, 1464,

1333, 1088, 739, 689 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3 , TMS) δ 4.28 (s, 6H, CH_3), 6.70 (d, $J = 8.1$ Hz, 2H, ArH), 6.90-7.12 (m, 10H, ArH), 7.28-7.33 (m, 2H, ArH), 7.74 (d, $J = 8.1$ Hz, 2H, ArH), 7.94 (d, $J = 8.7$ Hz, 2H, ArH), 8.36 (d, $J = 9.0$ Hz, 2H, ArH); ^{13}C NMR (75MHz, CDCl_3 , TMS) δ 24.94, 38.04, 109.70, 111.32, 122.82, 123.32, 126.16, 126.62, 127.08, 127.71, 127.98, 129.36, 130.93, 132.81, 132.99, 134.37, 134.63, 136.25, 166.89 (d, $^1J(^{103}\text{Rh},\text{C}) = 47.6$ Hz, CN_2), 188.84; MS (ESI) m/e 870.9 ($\text{M}^+ - \text{OAc}$), 803.0 ($\text{M}^+ - \text{I}$); Anal. Calcd. for $\text{C}_{38}\text{H}_{29}\text{I}_2\text{N}_4\text{O}_2\text{Rh}$ requires: C 49.06, H 3.14, N 6.02. Found: C 49.42, H 3.23, N 5.70%.

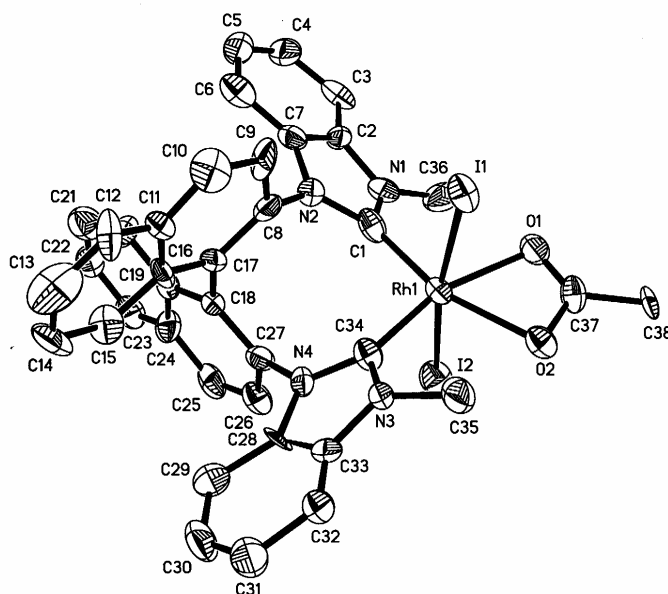


Figure 2: The ORTEP draw of Rh(III)-NHC complex 7.

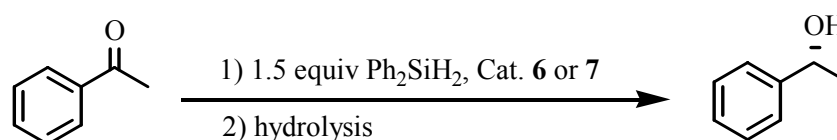
Selected bond lengths and angles: Rh-C(carbene) 1.956(14) and 1.972(13) Å,
Rh-O 2.175(9) and 2.174(9) Å, C1-Rh1-C34 98.1°.

The crystal data for Rh(III)-NHC complex 7: empirical formula: $\text{C}_{40}\text{H}_{33}\text{N}_4\text{O}_{2.5}\text{I}_2\text{Rh}$, formula weight: 966.41, temperature: 293(2) K, crystal system, space group: Orthorhombic, $\text{P}2(1)2(1)2(1)$, unit cell dimensions: $a = 17.4433(9)\text{Å}$, $b = 17.9331(9)\text{Å}$, $c = 27.9530(14)\text{Å}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 8744.0(8)\text{Å}^3$, $Z_{\text{value}} = 8$, $D_{\text{calc}} = 1.468 \text{ g/cm}^3$, $F_{000} = 3776$, Crystal size: 0.215 x 0.098 x 0.062 mm, Data/restraints/parameters = 20291/5/874, Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0663$, $wR_2 = 0.1599$, R indices (all data): $R_1 = 0.1872$; $wR_2 = 0.1940$. Its crystal structure has been deposited at the Cambridge Crystallographic Data Center and has been allocated the deposition numbers: CCDC 209243.

The Rh-catalyzed Enantioselective Hydrosilylation Reaction:

For an initial investigation of catalysts **6** and **7** (1.0 mol%) in the reduction of acetophenone with diphenylsilane disclosed that chiral Rh(III) complex **7** resulted in higher enantioselectivity (Table 1, entry 2), while chiral Rh(I) complex **6** gave poor result under the same conditions (Table 1, entry 1). The solvent effect has been examined as well. We found that THF is the best solvent among toluene, ether and dichloromethane (Table 1, entries 2-5). The reaction temperature did not significantly affect the enantiomeric excess (Table 1, entries 6-8). Using 2.0 mol% of catalyst **7**, the reaction can be completed within 24 h and the corresponding (*R*)-1-phenyl ethanol can be obtained in 98% ee and 87% yield (Table 1, entry 6).

Table 1. Axially chiral Rh complexes catalyzed enantioselective hydrosilylation of acetophenone.

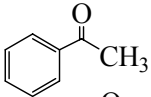
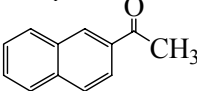
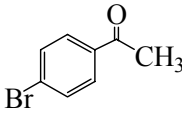
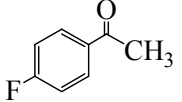
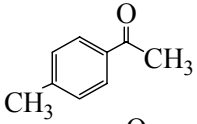
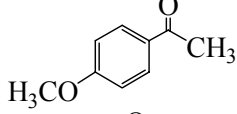
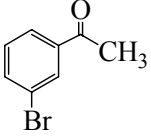
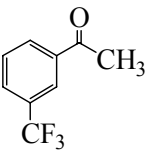
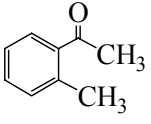
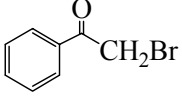


Entry	Catalysts (mol%)	Solvent	Temp./(^o C)	Time/(h)	Yield/(%) ^a	ee/(%) ^b	Config. ^c
1	6 (1 mol%)	THF	15	48	77	23	<i>R</i>
2	7 (1 mol%)	THF	15	48	77	98	<i>R</i>
3	7 (1 mol%)	Toluene	15	48	74	96	<i>R</i>
4	7 (1 mol%)	Et ₂ O	15	48	64	96	<i>R</i>
5	7 (1 mol%)	CH ₂ Cl ₂	15	48	33	49	<i>R</i>
6	7 (2 mol%)	THF	15	24	87	98	<i>R</i>
7	7 (2 mol%)	THF	0	24	66	98	<i>R</i>
8	7 (2 mol%)	THF	45	24	82	94	<i>R</i>

[a] Isolated yields. [b] Determined by chiral HPLC analysis. [c] Absolute stereochemistry determined by comparison of the sign of optical rotation to literature values.

Under the optimized reaction conditions, we subsequently examined the reduction of other aryl alkyl ketones. The results were summarized in Table 2. Various aryl alkyl ketones can be smoothly reduced to give the corresponding *sec*-alcohol in >92% ee and good yields under mild conditions (Table 2, entries 1-9). 2-Bromoacetophenone was also reduced in 97% ee and 92% yield under the same conditions (Table 2, entry 10).

Table 2. The chiral Rh complexes catalyzed enantioselective hydrosilylation of ketones

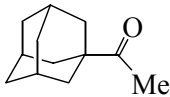
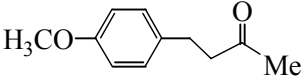
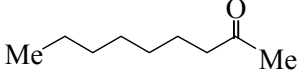
$\text{R}^1\text{-C(=O)-R}^2 \xrightarrow[\text{2) hydrolysis}]{\text{1) 1.5 equiv Ph}_2\text{SiH}_2, \text{7 (2 mol\%), THF, 15 }^\circ\text{C, 24 h}}$ $\text{R}^1\text{-CH(OH)-R}^2$				
$\mathbf{8a-j}$		$(\mathbf{R})\text{-}\mathbf{9a-j}$		
Entry	Substrates	No.	Yield (%) ^a	ee (%) ^b
		$\mathbf{9}$		
1		a	87	98
2		b	91	96
3		c	88	95
4		d	86	95
5		e	93	98
6		f	96	92
7		g	93	98
8		h	82	98
9		i	85	92
10		j	92	97

[a] Isolated yields; [b] Determined by chiral HPLC.

For more challenging substrates such as dialkyl ketones, adamantyl methyl ketone **8k** was reduced in 96% ee and 96% yield under the same mild conditions (Table 3, entry 1). Other dialkyl

ketones **8l** and **8m** also can be reduced in good enantiomeric excesses and yields under the same conditions (Table 3, entries 2 and 3).

Table 3. The chiral Rh complexes catalyzed enantioselective hydrosilylation of aliphatic ketones

Entry	Substrates	No.	Yield (%) ^a		ee (%) ^b	
			9	9		
1		k	96	96 ^c		
2		l	87	71		
3		m	86	67 ^d		

[a] Isolated yields. [b] Determined by chiral HPLC or GC. [c] Determined by chiral HPLC analysis of its *N*-phenyl carbamate derivative. [d] Determined by chiral GC analysis of its acetate derivative.

General Procedure for the Rh-catalyzed Enantioselective Hydrosilylation Reaction:

Under an Ar atmosphere, the ketones (0.5 mmol) and PhSiH₂ (138 mg, 0.75 mmol) were added to a solution of the Rh complex (0.01 mmol) in 2 mL of anhydrous THF. The reaction mixture was stirred at reaction temperature. The reaction was quenched by addition of H₂O (1 mL) and 0.5 N HCl (0.5 mL). The resulting aqueous solution was stirred for 0.5 h at room temperature and extracted with Et₂O (2 x 10 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: pentane/Et₂O= 10:1 – 4:1) to give the corresponding *sec*-alcohols. The enantiomeric excess of the obtained alcohols was determined by chiral HPLC or GC.

(R)-1-Phenylethanol (9a): Yield: 87% (53 mg). ¹H NMR (300 MHz, CDCl₃, TMS) δ 1.50 (d, *J* = 6.6 Hz, 3H, CH₃), 1.95 (br, 1H, OH), 4.89 (q, *J* = 6.6 Hz, 1H, CH), 7.22-7.40 (m, 5H, ArH); [α]_D²⁰ = 47.4 (c 2.60, CHCl₃) for 98% ee; Chiralcel OJ, hexane/*i*-PrOH = 95/5, 0.7 mL/min, 254 nm, *t*_S = 19.457 min, *t*_R = 21.737 min.

(R)-1-(Naphthalen-2-yl)ethanol (9b): Yield: 91% (78 mg). ¹H NMR (300 MHz, CDCl₃, TMS) δ

1.55 (d, $J = 6.6$ Hz, 3H, CH₃), 2.10 (br, 1H, OH), 5.02 (q, $J = 6.6$ Hz, 1H, CH), 7.40-7.55 (m, 3H, ArH), 7.77-7.86 (m, 4H, ArH); $[\alpha]_{\text{D}}^{20} = 34.95$ (c 3.85, EtOH) for 96% ee; Chiralcel OJ, hexane/*i*-PrOH = 95/5, 0.7 mL/min, 254 nm, $t_{\text{S}} = 23.031$ min, $t_{\text{R}} = 29.146$ min.

(R)-1-(4-Bromophenyl)ethanol (9c): Yield: 88% (89 mg). ¹H NMR (300 MHz, CDCl₃, TMS) δ 1.45 (d, $J = 6.3$ Hz, 3H, CH₃), 2.17 (br, 1H, OH), 4.82 (q, $J = 6.3$ Hz, 1H, CH), 7.20-7.27 (m, 2H, ArH); 7.42-7.50 (m, 2H, ArH); $[\alpha]_{\text{D}}^{20} = 45.3$ (c 1.0, CHCl₃) for 95% ee; Chiralcel OJ, hexane/*i*-PrOH = 95/5, 0.7 mL/min, 254 nm, $t_{\text{S}} = 18.579$ min, $t_{\text{R}} = 20.060$ min.

(R)-1-(4-Fluorophenyl)ethanol (9d): Yield: 86% (61 mg). ¹H NMR (300 MHz, CDCl₃, TMS) δ 1.48 (d, $J = 6.3$ Hz, 3H, CH₃), 1.90 (br, 1H, OH), 4.88 (q, $J = 6.3$ Hz, 1H, CH), 6.99-7.06 (m, 2H, ArH), 7.30-7.37 (m, 2H, ArH); $[\alpha]_{\text{D}}^{20} = 34.0$ (c 1.65, CHCl₃) for 95% ee; Chiralpak AS, hexane/*i*-PrOH = 95/5, 0.7 mL/min, 254 nm, $t_{\text{R}} = 9.580$ min, $t_{\text{S}} = 10.607$ min.

(R)-1-(4-Methylphenyl)ethanol (9e): Yield: 93% (63 mg). ¹H NMR (300 MHz, CDCl₃, TMS) δ 1.45 (d, $J = 6.6$ Hz, 3H, CH₃), 2.17 (br, 1H, OH), 2.33 (s, 3H, CH₃), 4.81 (q, $J = 6.6$ Hz, 1H, CH), 7.12-7.19 (m, 2H, ArH), 7.20-7.28 (m, 2H, ArH); $[\alpha]_{\text{D}}^{20} = 46.8$ (c 2.9, CHCl₃) for 98% ee; Chiralcel OJ, hexane/*i*-PrOH = 95/5, 0.7 mL/min, 254 nm, $t_{\text{S}} = 23.500$ min, $t_{\text{R}} = 26.473$ min.

(R)-1-(4-Methoxyphenyl)ethanol (9f): Yield: 96% (73 mg). ¹H NMR (300 MHz, CDCl₃, TMS) δ 1.44 (d, $J = 6.3$ Hz, 3H, CH₃), 2.76 (br, 1H, OH), 3.77 (s, 3H, CH₃), 4.78 (q, $J = 6.3$ Hz, 1H, CH), 6.83-6.91 (d, $J = 8.3$ Hz, 2H, ArH), 7.22-7.31 (d, $J = 8.3$ Hz, 2H, ArH); $[\alpha]_{\text{D}}^{20} = 44.87$ (c 3.2, CHCl₃) for 92% ee; Chiralpak AS, hexane/*i*-PrOH = 90/10, 0.7 mL/min, $t_{\text{R}} = 14.885$ min, $t_{\text{S}} = 18.491$ min □

(R)-1-(3-Bromophenyl)ethanol (9g): Yield: 93% (94 mg). ¹H NMR (300 MHz, CDCl₃, TMS) δ 1.50 (d, $J = 6.6$ Hz, 3H, CH₃), 2.12 (br, 1H, OH), 4.96 (q, $J = 6.6$ Hz, 1H, CH), 7.44-7.57 (m, 3H, ArH); 7.65 (s, 1H, ArH); $[\alpha]_{\text{D}}^{20} = 27.5$ (c 2.2, CH₃OH) for 98% ee; Chiralcel OJ, hexane/*i*-PrOH = 95/5, 0.7 mL/min, 254 nm, $t_{\text{S}} = 22.192$ min, $t_{\text{R}} = 25.838$ min.

(R)-1-(3-Trifluoromethylphenyl)ethanol (9h): Yield: 82% (78 mg). ¹H NMR (300 MHz, CDCl₃, TMS) δ 1.50 (d, $J = 6.6$ Hz, 3H, CH₃), 1.89 (br, 1H, OH), 4.87 (q, $J = 6.6$ Hz, 1H, CH), 7.19-7.38 (m, 2H, ArH), 7.38-7.52 (m, 1H, ArH), 7.53-7.55 (m, 1H, ArH); $[\alpha]_{\text{D}}^{20} = 25.4$ (c 1.35, CH₃OH)

for 98% ee; Chiralcel OJ, hexane/*i*-PrOH = 100/1, 0.7 mL/min, 254 nm, $t_S = 27.539$ min, $t_R = 33.094$ min.

(R)-1-(2-Methylphenyl)ethanol (9i): Yield: 85% (58 mg). $^1\text{H NMR}$ (300 MHz, CDCl_3 , TMS) δ 1.47 (d, $J = 6.3$ Hz, 3H, CH_3), 1.76 (br, 1H, OH), 2.35 (s, 3H, CH_3), 5.14 (q, $J = 6.6$ Hz, 1H, CH), 7.12-7.26 (m, 3H, ArH), 7.52 (d, $J = 7.2$ Hz, 1H, ArH); $[\alpha]_D^{20} = 54.1$ (c 1.6, EtOH) for 92% ee; Chiralpak AD, hexane/*i*-PrOH = 95/5, 0.7 mL/min, 254 nm, $t_R = 10.837$ min, $t_S = 12.083$ min.

(R)-2-Bromo-1-phenylethanol (9j): Yield: 92% (93 mg). $^1\text{H NMR}$ (300 MHz, CDCl_3 , TMS) δ 2.69 (d, $J = 3.6$ Hz, 1H, OH), 3.54 (dd, $J_1 = 8.7$ Hz, $J_2 = 10.5$ Hz, 1H, CH_2Br), 3.64 (dd, $J_1 = 3.3$ Hz, $J_2 = 10.5$ Hz, 1H, CH_2Br), 4.92 (dt, $J_1 = 3.3$ Hz, $J_2 = 8.7$ Hz, 1H, CH), 7.33-7.40 (m, 5H, ArH); $[\alpha]_D^{20} = 48.4$ (c 2.6, CHCl_3) for 97% ee; Chiralcel OJ, hexane/*i*-PrOH = 95/5, 0.7 mL/min, 254 nm, $t_S = 28.360$ min, $t_R = 30.360$ min.

(R)-1-(Adamantly)ethanol (9k): Yield: 96% (85 mg). $^1\text{H NMR}$ (300 MHz, CDCl_3 , TMS) δ 1.10 (d, $J = 6.3$ Hz, 3H, CH_3), 1.25 (br, 1H, OH), 1.44-1.74 (m, 12H), 1.95-2.02 (m, 3H), 3.29 (q, $J = 6.3$ Hz, 1H, CH); $[\alpha]_D^{20} = 1.0$ (c 2.0, CHCl_3) for 96% ee;

Derivation with phenyl isocyanate: the alcohol (0.4 mmol), phenyl isocyanate (0.4 mmol) and Et_3N (0.5 mmol) were stirred in anhydrous CH_2Cl_2 (5 mL) at room temperature for 12 h. Volatiles were removed under reduced pressure and residue was purified by a silica gel flash column chromatography (eluent: hexane/EtOAc = 25/1) to afford the corresponding carbamate derivative for the HPLC determination of enantiomeric excess. Chiralcel OJ, hexane/*i*-PrOH = 95/5, 0.7 mL/min, 254 nm, $t_S = 7.043$ min, $t_R = 9.042$ min.

(R)-4-(4-Methoxyphenyl)-2-butanol (9l): Yield: 87% (78 mg). $^1\text{H NMR}$ (300 MHz, CDCl_3 , TMS) δ 1.22 (d, $J = 6.0$ Hz, 3H, CH_3), 1.69-1.77 (m, 2H, CH_2), 2.59-2.70 (m, 2H, CH_2), 3.78 (s, 3H, CH_3), 3.81 (q, $J = 6.0$ Hz, 1H, CH), 6.81-6.86 (m, 2H, ArH), 7.10-7.14 (m, 2H, ArH); $[\alpha]_D^{20} = -11.20$ (c 3.5, CHCl_3) for 71% ee; Chiralpak AD, hexane/*i*-PrOH = 95/5, 0.7 mL/min, 254 nm, $t_S = 15.900$ min, $t_R = 16.673$ min.

(R)-Noan-2-ol (9m): Yield: 86% (62 mg). $^1\text{H NMR}$ (300 MHz, CDCl_3 , TMS) δ 0.88 (t, $J = 7.2$ Hz, 3H, CH_3), 1.17 (d, $J = 6.3$ Hz, 3H, CHCH_3), 1.23-1.50 (m, 12H, $(\text{CH}_2)_6$), 1.96 (br, 1H, OH), 3.73-3.80 (m, 1H, CH); $[\alpha]_D^{20} = -5.32$ (c 3.1, CHCl_3) for 67% ee;

Derivation with acetyl chloride: The alcohol (0.4 mmol) was dissolved in anhydrous THF (4 mL),

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acetyl chloride (2.0 mmol) and Et₃N (2.0 mmol) were added and the mixture kept at ambient temperature for 12 h. The reaction was quenched by addition of H₂O. The organic compound was extracted with Et₂O (2 x 10 mL) and dried over anhydrous Na₂SO₄. The filtrate was used for the GC determination of the enantiomeric excess. Rt-βDexcstTM 30 m x 0.25 mm x 0.25 μm, 110 °C, Carrier: N₂ 10psi. *t*_S = 15.960 min, *t*_R = 17.250 min.

Software Version: 4.1<2F12>

Date: 03-4-14 9:45

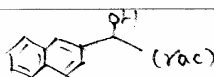
Sample Name : D198-RAC

Data File : D:\TC4\DATA\CAO\CAP_008K.RAW Date: 03-4-14 9:01

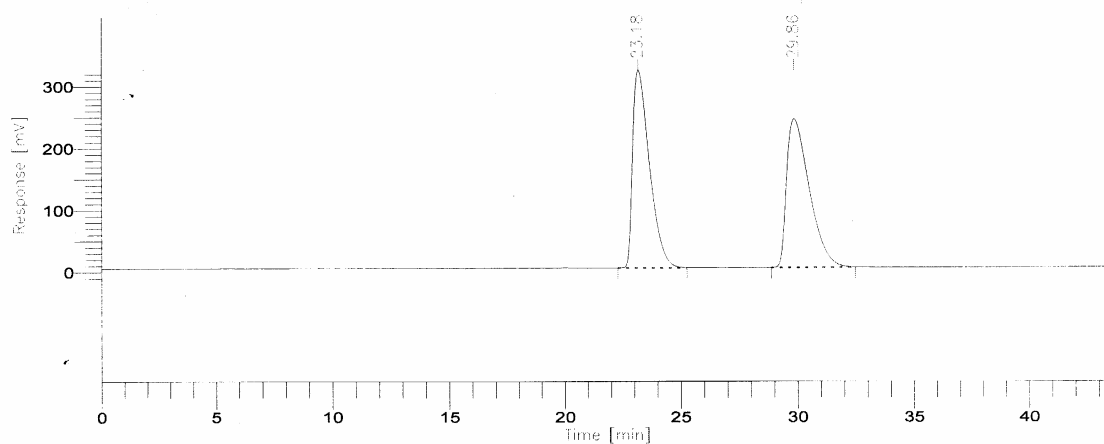
Sequence File: D:\TC4\DATA\CAO\CAP.SEQ Cycle: 1 Channel : A

Instrument : 970A_0 Rack/Vial: 0/0 Operator: cao

Sample Amount : 1.0000 Dilution Factor : 1.00



Chiralcel OJ 254mm 2.7ml/min
Hexane:2-proH = 75:25



REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Area BL	Area/Height [sec]
1	23.184	16045640.75	319195.59	49.88	0.00	BB	50.2690
2	29.861	16123704.50	239871.14	50.12	0.00	BB	67.2182
		32169345.25	559066.73	100.00	0.00		

Software Version: 4.1<2F12>

Date: 03-4-14 13:21

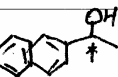
Sample Name : D198-101

Data File : D:\TC4\DATA\CAO\CAP_008M.RAW Date: 03-4-14 10:31

Sequence File: D:\TC4\DATA\CAO\CAP.SEQ Cycle: 1 Channel : A

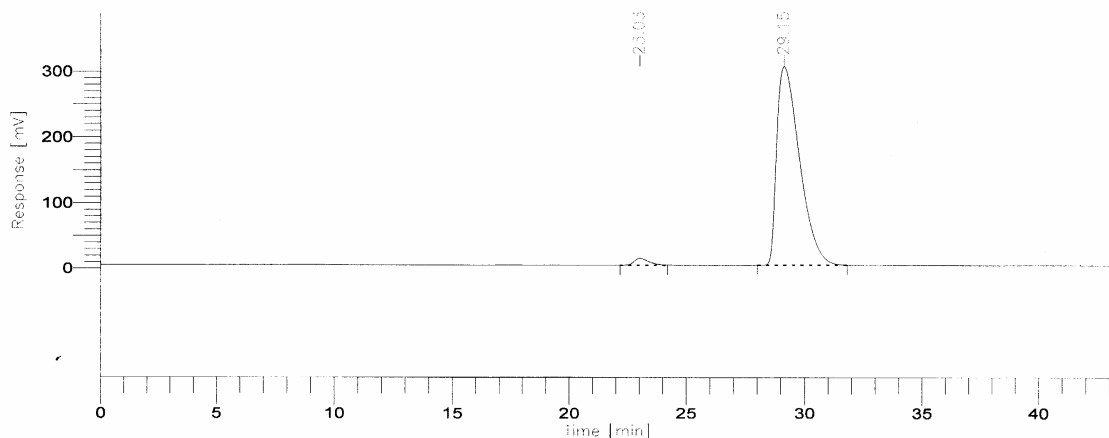
Instrument : 970A_0 Rack/Vial: 0/0 Operator: cao

Sample Amount : 1.0000



96% ee
chiralcel OJ 254nm
0.7 mL/min Hexane: i-PrOH
= 95:5

Dilution Factor : 1.00



REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Area BL	Area/Height [sec]
1	23.031	448689.50	10770.67	2.16	0.00	BB	41.6585
2	29.146	20309990.00	302515.29	97.84	0.00	BB	67.1371
		20758679.50	313285.96	100.00	0.00		

Software Version: 4.1<2F12>

Date: 03-4-17 14:20

Sample Name : d199-rac

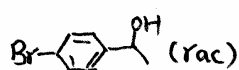
Data File : D:\TC4\DATA\CAO\CAP_009G.RAW Date: 03-4-17 13:48

Sequence File: D:\TC4\DATA\CAO\CAP.SEQ Cycle: 1 Channel : A

Instrument : 970A - 0 Rack/Vial: 0/0 Operator: cao

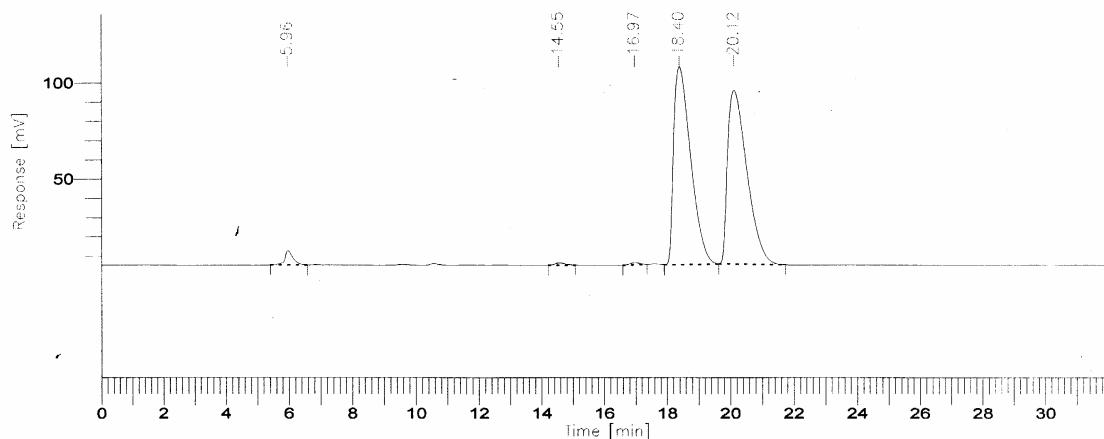
Sample Amount : 1.0000

Dilution Factor : 1.00



Chiracel OJ 254nm 0.7ml/min

Hexane : i-PrOH = 95 : 5



REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Area BL	Area/Height [sec]
1	5.964	133871.50	7366.33	1.71	0.00	BB	18.1734
2	14.551	26437.50	1201.58	0.34	0.00	BB	22.0023
3	16.973	22781.75	1064.82	0.29	0.00	BB	21.3949
4	18.397	3833404.50	102367.01	48.89	0.00	BB	37.4477
5	20.121	3824602.25	90183.44	48.78	0.00	BB	42.4091
		7841097.50	202183.17	100.00	0.00		

Software Version: 4.1<2F12>

Date: 03-4-17 15:43

Sample Name : d-199-104-1

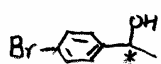
Data File : D:\TC4\DATA\CAO\CAP_009H.RAW Date: 03-4-17 14:27

Sequence File: D:\TC4\DATA\CAO\CAP.SEQ Cycle: 1 Channel : A

Instrument : 970A_0 Rack/Vial: 0/0 Operator: cao

Sample Amount : 1.0000

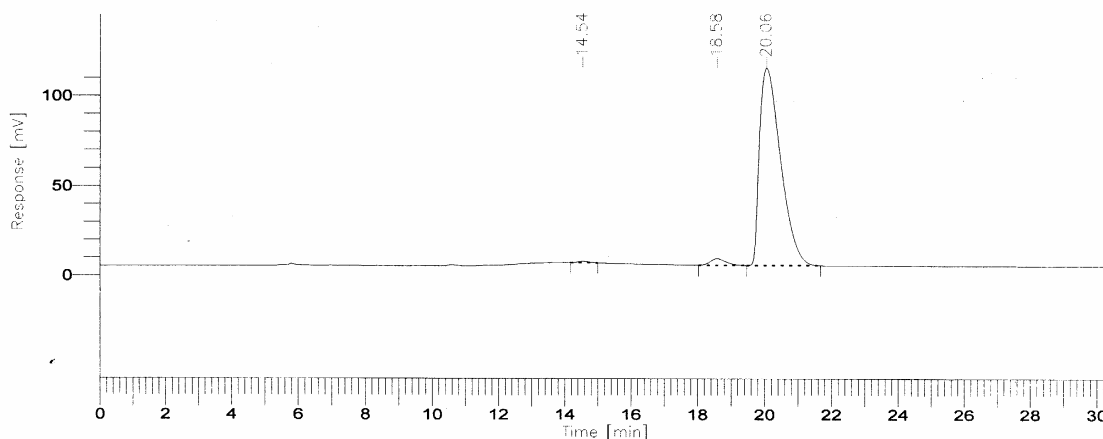
Dilution Factor : 1.00



95% ee

Chiracel OJ 254nm 0.7ml/min

Hexane: i-PrOH = 95:5



REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Area BL	Area/Height [sec]
1	14.543	18136.25	815.98	0.37	0.00	BB	22.2265
2	18.579	122717.50	3816.40	2.48	0.00	BB	32.1553
3	20.060	4808804.00	109724.61	97.15	0.00	BB	43.8261
		4949657.75	114356.98	100.00	0.00		

***** MODEL 1022 RUNLOG for run: CH-9_66 *****

Run terminated via Button or External Stop.



Chiracel OJ 254nm
0.7 ml/min
Hexane : i-PrOH = 95 : 5

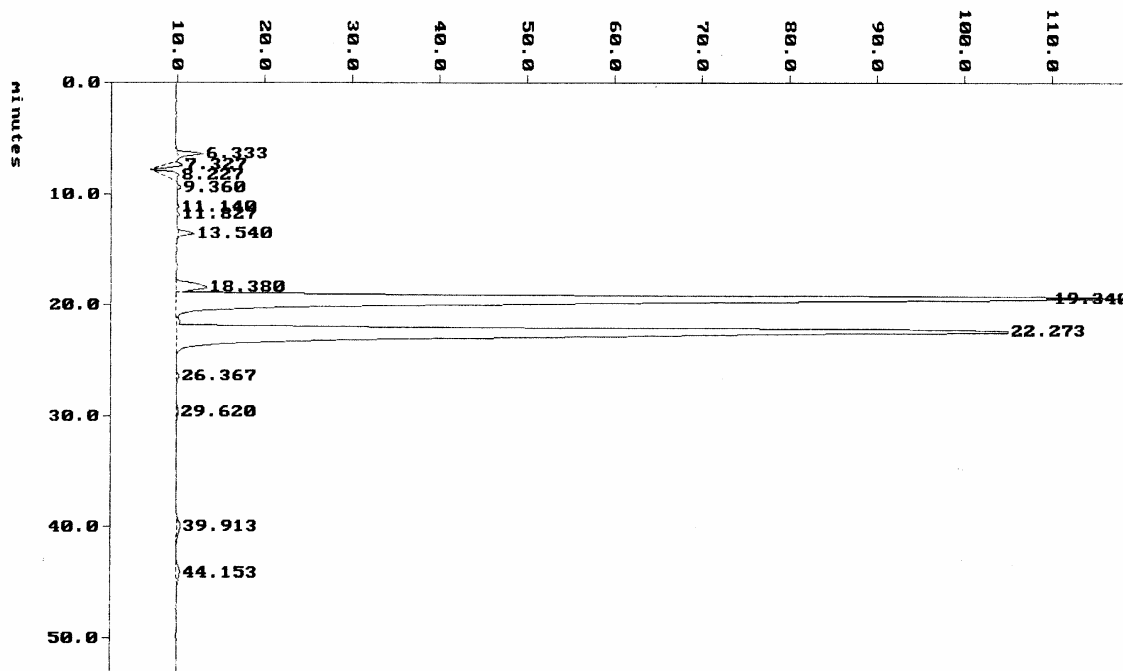
File : CH-9_66.D01 D-194RAC
Run : 01 Type : Sample
Path : C:\CH-5 Inst : 1022 LC Plus
Collection : 14:09:55 Apr 28 2003 Method : LCTEST [14:09:45 Apr 28 2003]
Integration : 14:09:55 Apr 28 2003 Method : LCTEST [14:09:45 Apr 28 2003]
Report : 15:03:16 Apr 28 2003 Method : LCTEST [14:09:45 Apr 28 2003]

PERCENT (AREA)

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	6.333	462836	2.9051		0.4624	1.3303
2	7.327	497537	1.6148	V	0.4971	0.7395
3	8.227	777507	2.0150		0.7768	0.9227
4	9.360	80636	0.4153		0.0806	0.1902
5	11.140	31900	0.1742	T	0.0319	0.0798
6	11.827	70433	0.3357		0.0704	0.1537
7	13.540	371263	1.8486		0.3709	0.8465
8	18.380	1349842	3.5246	T	1.3485	1.6140
9	19.340	47686880	109.1875	T	47.6408	50.0002
10	22.273	47848076	95.0631		47.8018	43.5322
11	26.367	118562	0.2623		0.1184	0.1201
12	29.620	123472	0.1938		0.1234	0.0887
13	39.913	314710	0.4166		0.3144	0.1908
14	44.153	363054	0.4177		0.3627	0.1913

14 Peaks > Area Reject 100096712 Total Area
14 Peaks > Height Reject 218.374 Total Height

(CH-9_66.D01) MU



Chiracel OJ 254nm 0.7ml/min
Hexane : i-PrOH = 95:5



***** MODEL 1022 RUNLOG for run: CH-9_67 *****

Run terminated manually on Channel A.

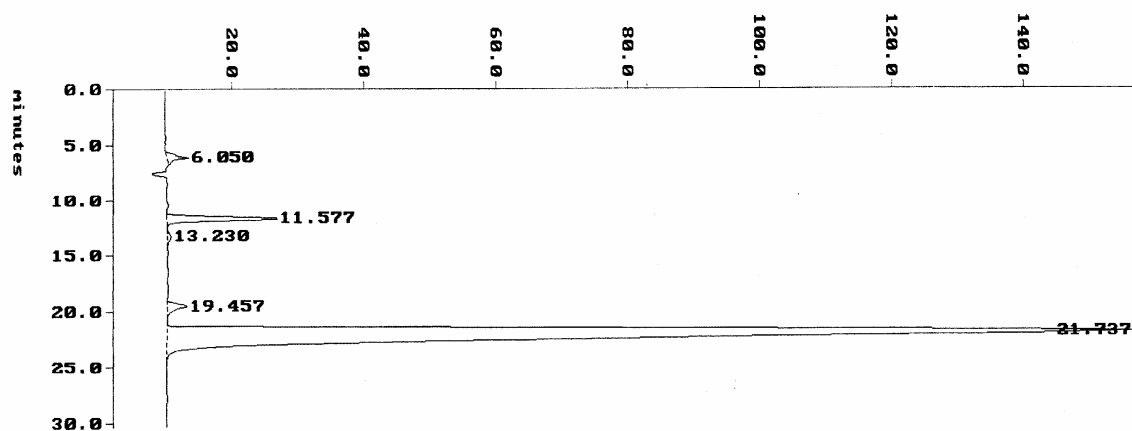
File : CH-9_67.D01 D-194-106 1
Run : 01 Type : Sample
Path : C:\CH-5 Inst : 1022 LC Plus
Collection : 15:03:32 Apr 28 2003 Method : LCTEST [14:09:45 Apr 28 2003]
Integration: 15:03:32 Apr 28 2003 Method : LCTEST [14:09:45 Apr 28 2003]
Report : 15:33:50 Apr 28 2003 Method : LCTEST [14:09:45 Apr 28 2003]

PERCENT (AREA)

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	6.050	782533	3.2772		0.9059	1.9259
2	11.577	3336053	16.6617		3.8619	9.7918
3	13.230	209283	0.6028		0.2423	0.3542
4	19.457	950921	2.9691		1.1008	1.7449
5	21.737	81105552	146.6485		93.8892	86.1831

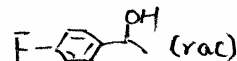
5 Peaks > Area Reject 86384344 Total Area
5 Peaks > Height Reject 170.159 Total Height

(CH-9_67.D01) mV



Chirapak As 254nm 0.7ml/min
Hexane : i-PrOH = 95 : 5

***** MODEL 1022 RUNLOG for run: CH-2__11 *****
Run terminated manually on Channel A.



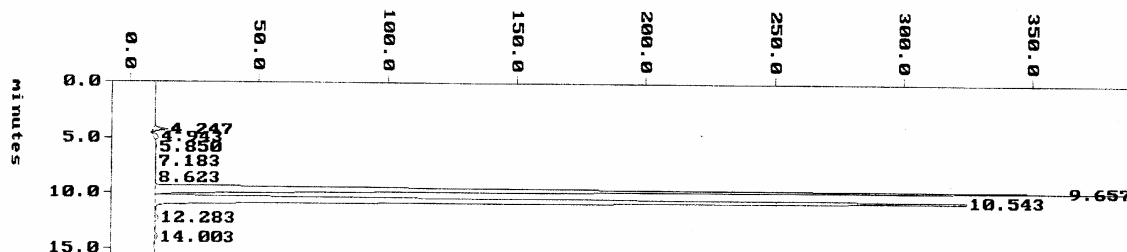
File : CH-2__11.D01 d-206rpack 1
Run : 01 Type : Sample
Path : C:\CH-6 Inst : 1022 LC Plus
Collection : 15:50:58 May 29 2003 Method : LCTEST [08:22:43 May 29 2003]
Integration : 15:50:58 May 29 2003 Method : LCTEST [08:22:43 May 29 2003]
Report : 16:06:35 May 29 2003 Method : LCTEST [08:22:43 May 29 2003]

PERCENT (AREA)

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	4.247	779871	5.4404		0.6344	0.7722
2	4.943	512951	1.9999		0.4172	0.2839
3	5.850	62020	0.4459		0.0504	0.0633
4	7.183	24865	0.1522		0.0202	0.0216
5	8.623	53437	0.2002	V	0.0435	0.0284
6	9.657	60944580	379.4578	T	49.5730	53.8604
7	10.543	60107416	314.7272		48.8921	44.6725
8	12.283	231004	1.0991		0.1879	0.1560
9	14.003	222854	0.9983		0.1813	0.1417

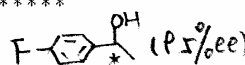
9 Peaks > Area Reject 122939000 Total Area
9 Peaks > Height Reject 704.521 Total Height

(CH-2__11.D01) mU



***** MODEL 1022 RUNLOG for run: CH-2__12 *****

Run terminated manually on Channel A.



Chira pak As 254nm

0.7ml/min

Hexane: 2-proH = 95:5

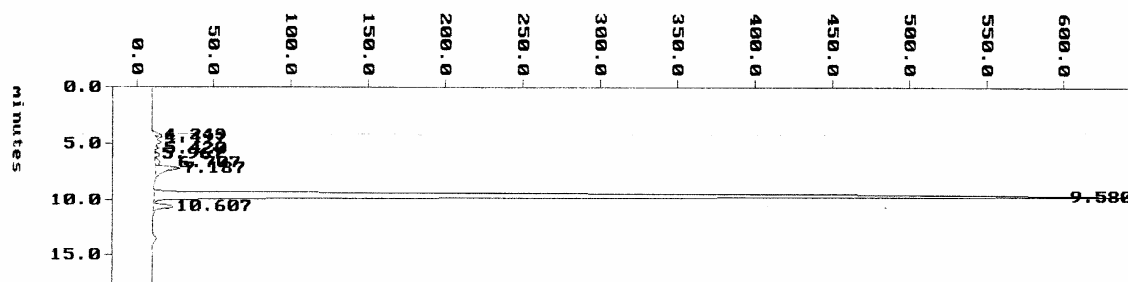
File : CH-2__12.D01 d-206-110
Run : 01 Type : Sample
Path : C:\CH-6 Inst : 1022 LC Plus
Collection : 16:07:30 May 29 2003 Method : LCTEST [08:22:43 May 29 2003]
Integration: 16:07:30 May 29 2003 Method : LCTEST [08:22:43 May 29 2003]
Report : 16:25:37 May 29 2003 Method : LCTEST [08:22:43 May 29 2003]

PERCENT (AREA)

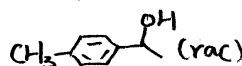
Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	4.243	535797	4.2482	T	0.4531	0.6259
2	4.497	163133	1.6304	V	0.1380	0.2402
3	5.420	301039	2.4046	V	0.2546	0.3543
4	5.967	430346	2.6842	T	0.3639	0.3955
5	6.707	836939	3.1751	T	0.7078	0.4678
6	7.187	3739345	16.2362		3.1624	2.3922
7	9.580	109336464	635.0581	T	92.4663	93.5691
8	10.607	2901545	13.2684		2.4538	1.9550

8 Peaks > Area Reject 118244608 Total Area
8 Peaks > Height Reject 678.705 Total Height

(CH-2__12.D01) AU



***** MODEL 1022 RUNLOG for run: CH-2__68 *****



Run terminated manually on Channel A.

Chiracel OJ 254nm 0.7ml/min

File : CH-2__68.D01

d-201-rac

Hexane : i-proh = 95 : 5

Run : 01

Type : Sample

Path : C:\CH-6

Inst : 1022 LC Plus

Collection : 10:08:58 Jun 11 2003 Method : LCTEST [09:28:19 Jun 11 2003]

Integration : 10:08:58 Jun 11 2003 Method : LCTEST [09:28:19 Jun 11 2003]

Report : 10:55:35 Jun 11 2003 Method : LCTEST [09:28:19 Jun 11 2003]

PERCENT (AREA)

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	4.813	80954	0.6140	T	0.0962	0.4175
2	5.193	110713	1.1061	T	0.1316	0.7520
3	5.420	272782	1.8205		0.3241	1.2377
4	9.713	156060	0.9315		0.1854	0.6333
5	11.267	293514	1.6073		0.3488	1.0928
6	17.887	921037	3.4495	T	1.0944	2.3452
7	18.473	1009556	3.2764	T	1.1996	2.2276
8	19.687	1922607	5.6637	T	2.2845	3.8506
9	21.420	1912632	5.3350		2.2726	3.6271
10	24.127	38620792	66.0974		45.8902	44.9378
11	27.940	38780868	56.9497		46.0804	38.7185
12	33.553	77644	0.2353		0.0923	0.1600

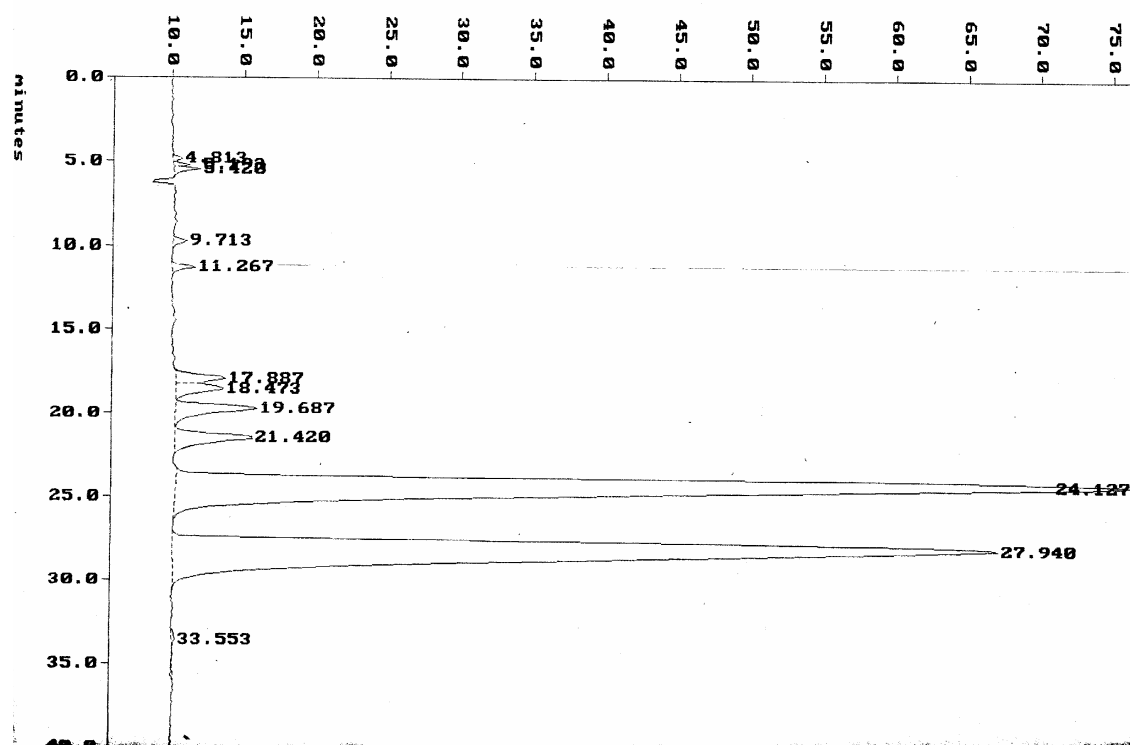
12 Peaks > Area Reject

84159160 Total Area

12 Peaks > Height Reject

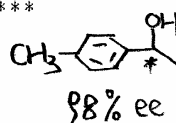
147.086 Total Height

(CH-2__68.D01) AU



***** MODEL 1022 RUNLOG for run: CH-2_70 *****

Run terminated manually on Channel A.



Chiralcel OJ 254nm

0.7 mL/min

Hexane : i-PrOH = 95:5

File : CH-2_70.D01

d-201-120

Run : 02

Path : C:\CH-6

Type : Sample

Inst : 1022 LC Plus

Collection : 14:08:16 Jun 11 2003 Method : LCTEST [09:28:19 Jun 11 2003]

Integration : 14:08:16 Jun 11 2003 Method : LCTEST [09:28:19 Jun 11 2003]

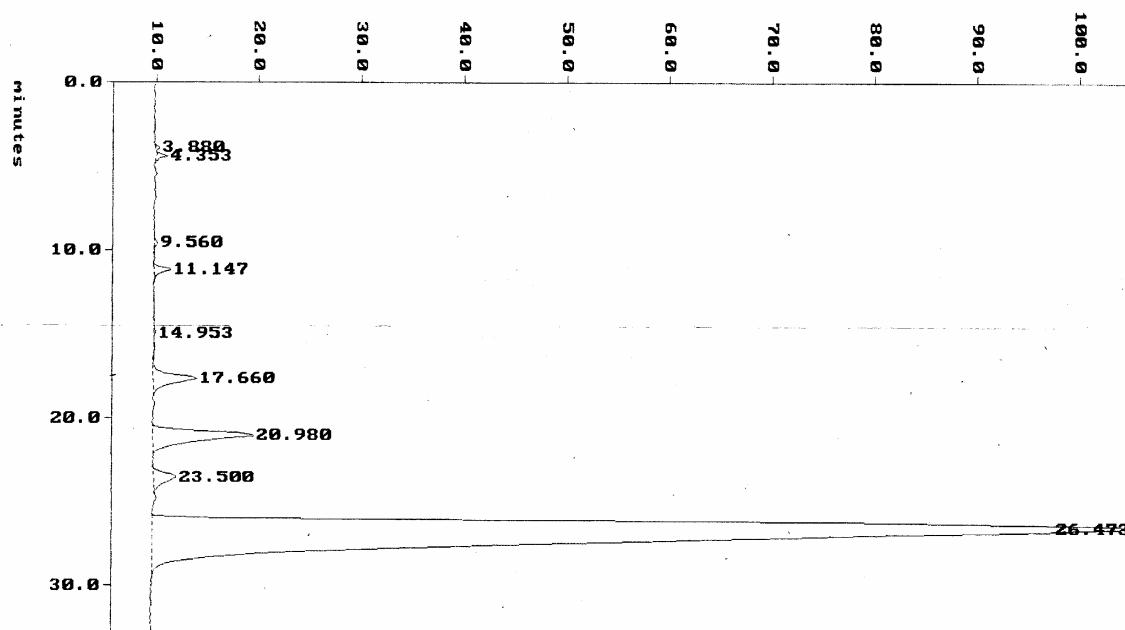
Report : 14:41:22 Jun 11 2003 Method : LCTEST [09:28:19 Jun 11 2003]

PERCENT (AREA)

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	3.880	45856	0.3969		0.0588	0.3439
2	4.353	151791	1.0581		0.1948	0.9170
3	9.560	57944	0.3038		0.0744	0.2633
4	11.147	327310	1.6395		0.4200	1.4208
5	14.953	72667	0.1425		0.0932	0.1235
6	17.660	1504079	4.2457		1.9300	3.6793
7	20.980	3754988	9.7777		4.8184	8.4731
8	23.500	868616	2.2424		1.1146	1.9432
9	26.473	71147248	95.5894		91.2958	82.8359

9 Peaks > Area Reject 77930496 Total Area
9 Peaks > Height Reject 115.396 Total Height

(CH-2_70.D01) MV



Software Version: 4.1<2F12>

Date: 03-6-6 13:56

Sample Name : d-202rac

Data File : D:\TC4\DATA\CAO\CAP_018T.RAW Date: 03-6-6 13:30

Sequence File: D:\TC4\DATA\CAO\CAP.SEQ Cycle: 1 Channel : A

Instrument : 970A - 0 Rack/Vial: 0/0 Operator: cao

Sample Amount : 1.0000

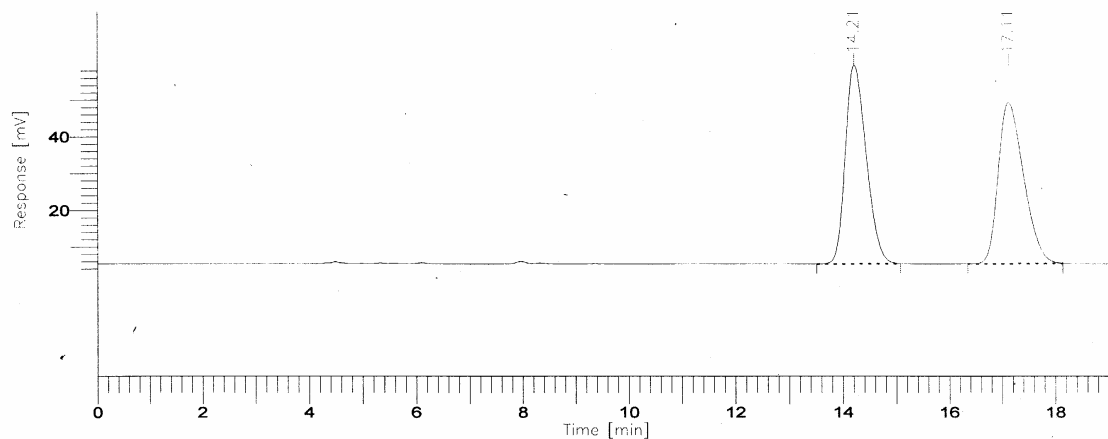
Dilution Factor : 1.00



Chirapak As 254mm

0.7mL/min

Hexane : i-proh = 90:10



REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Area BL	Area/Height [sec]
1	14.208	1466007.25	54186.44	49.99	0.00	BB	27.0549
2	17.113	1466662.00	43933.82	50.01	0.00	BB	33.3834
		2932669.25	98120.26	100.00	0.00		

Software Version: 4.1<2F12>

Date: 03-6-6 14:17

Sample Name : d-202-106

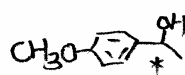
Data File : D:\TC4\DATA\CAO\CAP_018U.RAW Date: 03-6-6 13:52

Sequence File: D:\TC4\DATA\CAO\CAP.SEQ Cycle: 1 Channel : A

Instrument : 970A_0 Rack/Vial: 0/0 Operator: cao

Sample Amount : 1.0000

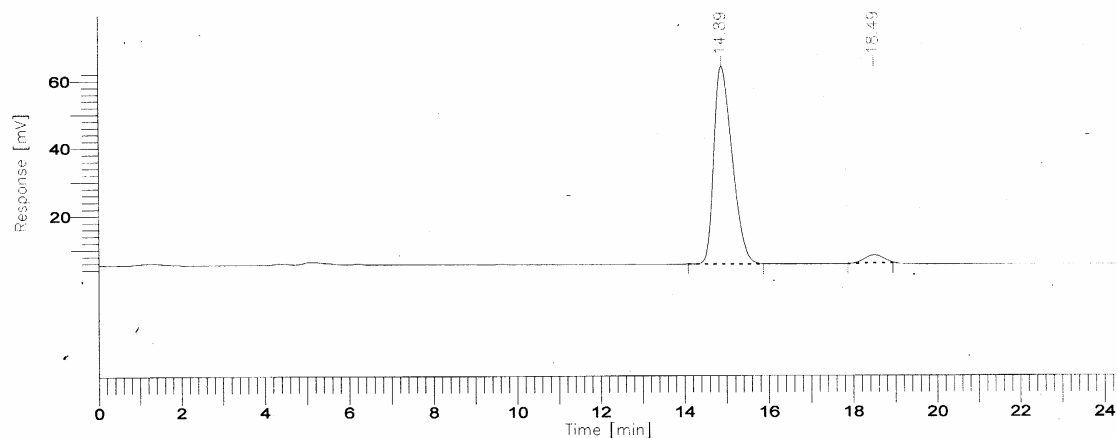
Dilution Factor : 1.00



Chiralpak AS 254nm

0.7 ml/min

Hexane: i-PrOH = 90:10



REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Area BL	Area/Height [sec]
1	14.885	1766035.00	58489.43	96.11	0.00	BB	30.1941
2	18.491	71538.00	2362.00	3.89	0.00	BB	30.2871
		1837573.00	60851.43	100.00	0.00		

Software Version: 4.1<2F12>

Date: 03-6-12 16:22

Sample Name : d-207rac

Data File : D:\TC4\DATA\CAO\CAP_019Q.RAW Date: 03-6-12 15:17

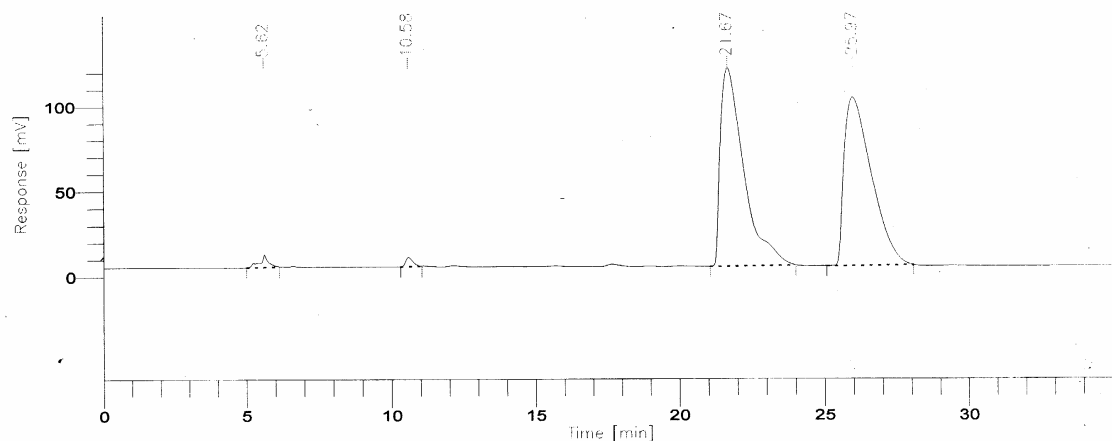
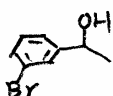
Sequence File: D:\TC4\DATA\CAO\CAP.SEQ Cycle: 1 Channel : A

Instrument : 970A_0 Rack/Vial: 0/0 Operator: cao

Sample Amount : 1.0000

Chiralcel OJ 254 nm 0.7ml/min

Hexane : i-PrOH = 95:5



REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Area BL	Area/Height [sec]
1	5.621	145266.00	7308.11	1.10	0.00	BB	19.8774
2	10.584	92014.00	5379.62	0.70	0.00	BB	17.1042
3	21.672	6488531.00	116414.13	49.19	0.00	BB	55.7366
4	25.974	6464067.00	98854.16	49.01	0.00	BB	65.3899
		13189878.00	227956.02	100.00	0.00		

Software Version: 4.1<2F12>

Date: 03-6-12 16:28

Sample Name : d-207-120

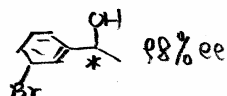
Data File : D:\TC4\DATA\CAO\CAP_019R.RAW Date: 03-6-12 15:55

Sequence File: D:\TC4\DATA\CAO\CAP.SEQ Cycle: 1 Channel : A

Instrument : 970A_0 Rack/Vial: 0/0 Operator: cao

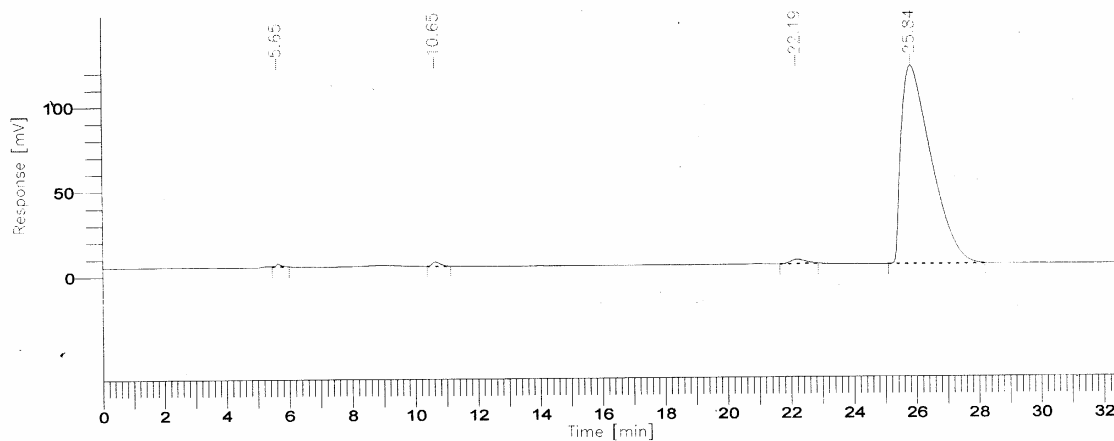
Sample Amount : 1.0000

Dilution Factor : 1.00



Chiracel OJ 254nm 0.7ml/min

Hexane : 2-propr = 95:5



REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Area BL	Area/Height [sec]
1	5.645	17623.00	1704.48	0.22	0.00	BB	10.3392
2	10.645	44362.00	2516.44	0.56	0.00	BB	17.6289
3	22.192	82201.50	2512.46	1.04	0.00	BB	32.7176
4	25.838	7742756.50	116513.31	98.17	0.00	BB	66.4538
		7886943.00	123246.68	100.00	0.00		

Software Version: 4.1<2F12>

Date: 03-6-2 13:13

Sample Name : d-208rac

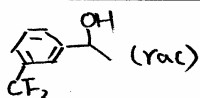
Data File : D:\TC4\DATA\CAO\CAP_017N.RAW Date: 03-6-2 12:23

Sequence File: D:\TC4\DATA\CAO\CAP_SEQ Cycle: 1 Channel : A

Instrument : 970A_0 Rack/Vial: 0/0 Operator: cao

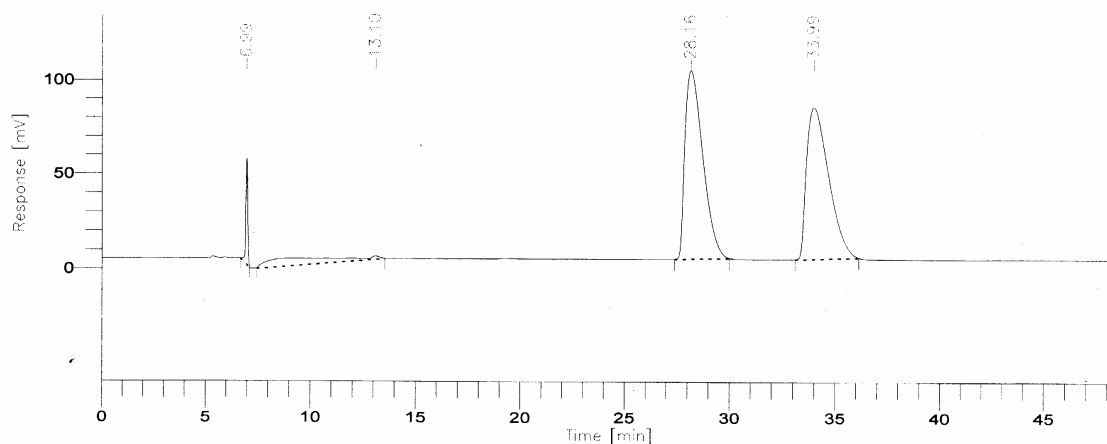
Sample Amount : 1.0000

Dilution Factor : 1.00



Chiralcel OJ 254nm 0.7ml/min

Hexane : 2-proH = 100 : 1



REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Area BL	Area/Height [sec]
1	6.987	361468.00	56527.78	2.78	0.00	BB	6.3945
2	13.103	875117.75	1639.58	6.73	0.00	BB	533.7456
3	28.163	5900763.25	99827.61	45.40	0.00	BB	59.1095
4	33.992	5860093.00	80222.09	45.09	0.00	BB	73.0484
		12997442.00	238217.05	100.00	0.00		

Software Version: 4.1<2F12>

Date: 03-6-2 14:08

Sample Name : d-208-110

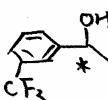
Data File : D:\TC4\DATA\CAO\CAP_0170.RAW Date: 03-6-2 13:23

Sequence File: D:\TC4\DATA\CAO\CAP.SEQ Cycle: 1 Channel : A

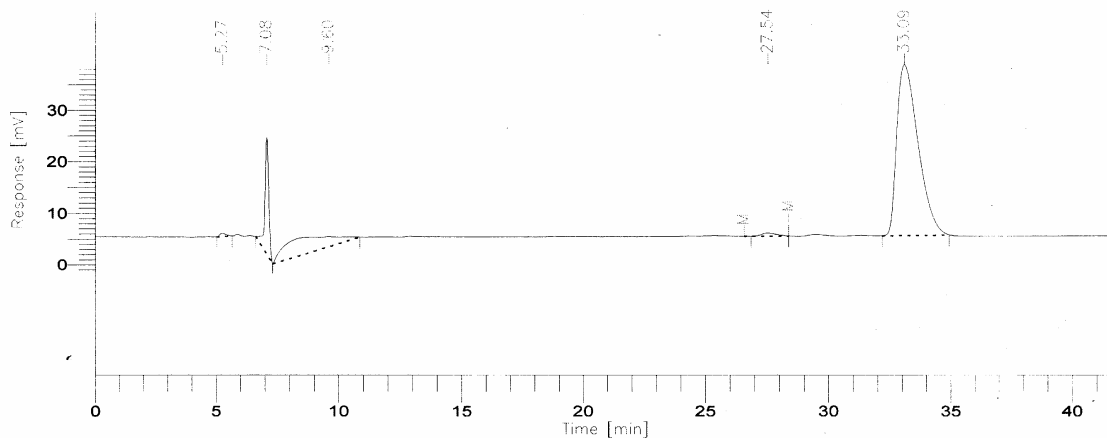
Instrument : 970A_0 Rack/Vial: 0/0 Operator: cao

Sample Amount : 1.0000

Dilution Factor : 1.00

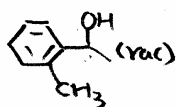


98% ee Chiralcel OJ 254nm 0.7ml/min
Hexane: i-PrOH = 100:1



REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Area BL	Area/Height [sec]
1	5.267	11360.50	672.11	0.42	0.00	BB	16.9029
2	7.079	251399.50	22639.38	9.21	0.00	BB	11.1045
3	9.599	429915.00	1912.06	15.75	0.00	BB	224.8437
4	27.539	25211.27	619.90	0.92	0.00	*BB	40.6700
5	33.094	2012158.50	33100.79	73.70	0.00	BB	60.7888
		2730044.77	58944.23	100.00	0.00		



Chiropak AD 254 nm 0.7 mL/min

Hexane : i-proh = 95 : 5

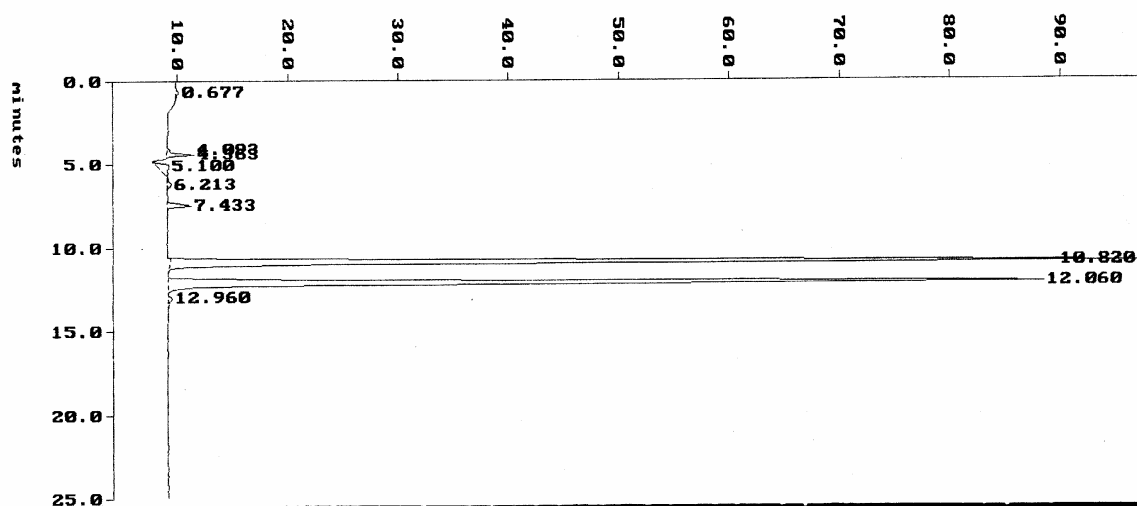
File : CH-2_18.D01 d-211 1
Run : 01 Type : Sample
Path : C:\CH-6 Inst : 1022 LC Plus
Collection : 10:36:23 May 30 2003 Method : LCTEST [08:22:11 May 30 2003]
Integration : 09:51:46 Jun 02 2003 Method : LCTEST [08:47:45 Jun 02 2003]
Report : 09:51:49 Jun 02 2003 Method : LCTEST [08:47:45 Jun 02 2003]

PERCENT (AREA)

PK #	RT	Area	Height	BC	Area Percent	Height Percent
1	0.677	36313	0.2828		0.1635	0.1627
2	4.093	19811	0.2304	T	0.0892	0.1325
3	4.363	181260	2.4578		0.8162	1.4136
4	5.100	370154	1.0971		1.6668	0.6310
5	6.213	63928	0.3455		0.2879	0.1987
6	7.433	170447	2.1110		0.7675	1.2141
7	10.820	10575318	87.6955		47.6216	50.4361
8	12.060	10713716	79.3120	T	48.2449	45.6145
9	12.960	76009	0.3424		0.3423	0.1969

9 Peaks > Area Reject 22206958 Total Area
9 Peaks > Height Reject 173.874 Total Height

(CH-2_18.D01) mV



***** MODEL 1022 RUNLOG *****

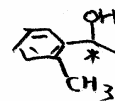
Run CH-2__20 abandoned at 13:33:48 Fri May 30 2003

***** MODEL 1022 RUNLOG for run: CH-2__20 *****

Run terminated manually on Channel A.

File : CH-2__20.D01 d-211-114
Run : 02 Type : Sample
Path : C:\CH-6 Inst : 1022 LC Plus
Collection : 13:34:58 May 30 2003 Method : LCTEST [11:13:06 May 30 2003]
Integration: 13:34:58 May 30 2003 Method : LCTEST [11:13:06 May 30 2003]
Report : 13:51:11 May 30 2003 Method : LCTEST [11:13:06 May 30 2003]

Chirapak AD 254nm 0.7ml/min
Hexane : i-proh = 95 : 5
92% ee

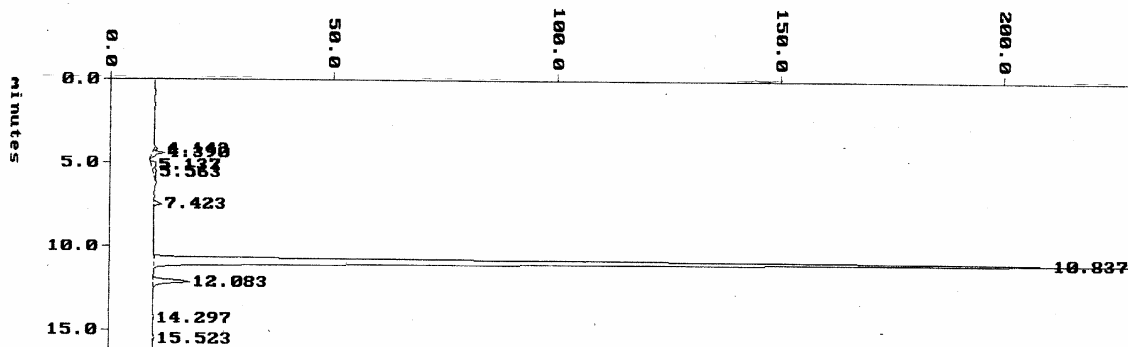


PERCENT (AREA)

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	4.143	79221	0.6916	T	0.2734	0.2951
2	4.390	358888	2.7803	V	1.2384	1.1864
3	5.137	305240	1.0726	T	1.0533	0.4577
4	5.563	166737	0.6856		0.5754	0.2926
5	7.423	140412	1.7071		0.4845	0.7284
6	10.837	26694280	218.6694		92.1144	93.3088
7	12.083	1154797	8.2658		3.9849	3.5271
8	14.297	44039	0.2325	V	0.1520	0.0992
9	15.523	35865	0.2454		0.1238	0.1047

9 Peaks > Area Reject 28979480 Total Area
9 Peaks > Height Reject 234.350 Total Height

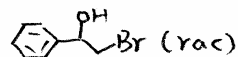
(CH-2__20.D01) mU



Chiralcel OJ 254nm 0.7ml/min
Hexane : i-PrOH = 15 : 5

***** MODEL 1022 RUNLOG for run: CH-2__09 *****

Run terminated manually on Channel A.



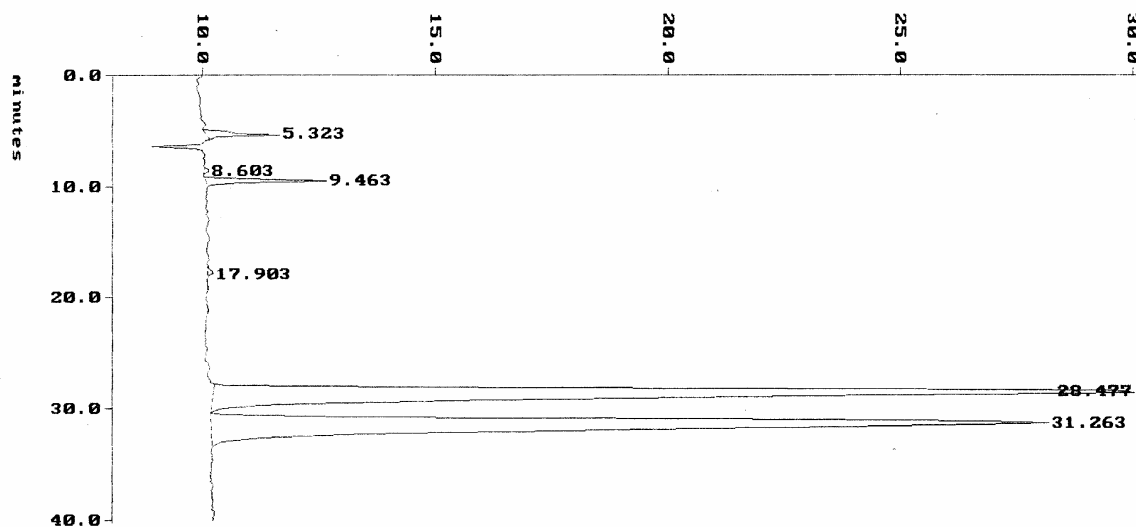
File : CH-2__09.D01 d-210 1
Run : 01 Type : Sample
Path : C:\CH-6 Inst : 1022 LC Plus
Collection : 13:55:52 May 29 2003 Method : LCTEST [08:22:43 May 29 2003]
Integration: 13:55:52 May 29 2003 Method : LCTEST [08:22:43 May 29 2003]
Report : 14:36:09 May 29 2003 Method : LCTEST [08:22:43 May 29 2003]

PERCENT (AREA)

PK #	RT	Area	Height	BC	Area Percent	Height Percent
1	5.323	260983	1.5802		1.1595	3.7478
2	8.603	18749	0.0822	V	0.0833	0.1948
3	9.463	409443	2.6021		1.8190	6.1715
4	17.903	24608	0.0786		0.1093	0.1865
5	28.477	10857188	19.8024	V	48.2350	46.9666
6	31.263	10937976	18.0173		48.5939	42.7327

6 Peaks > Area Reject 22508948 Total Area
6 Peaks > Height Reject 42.163 Total Height

(CH-2__09.D01) mU



Chiracel OJ 254nm 0.7mL/min

***** MODEL 1022 RUNLOG for run: CH-2__10 *****
Run terminated manually on Channel A.

Hexane : i-PrOH = 95 : 5



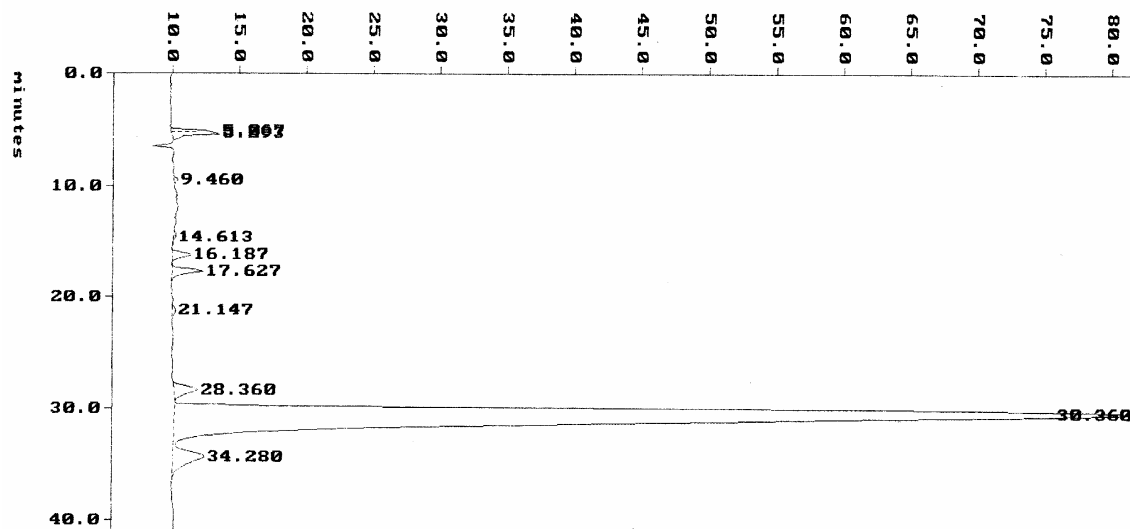
File : CH-2__10.D01 d-210-112 1
Run : 01 Type : Sample
Path : C:\CH-6 Inst : 1022 LC Plus
Collection : 14:41:00 May 29 2003 Method : LCTEST [08:22:43 May 29 2003]
Integration: 14:41:00 May 29 2003 Method : LCTEST [08:22:43 May 29 2003]
Report : 15:22:19 May 29 2003 Method : LCTEST [08:22:43 May 29 2003]

PERCENT (AREA)

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	5.067	328918	2.5551	T	0.5329	2.9726
2	5.293	610607	3.5451		0.9893	4.1243
3	9.460	60330	0.2867		0.0977	0.3336
4	14.613	37003	0.1554		0.0600	0.1808
5	16.187	336490	1.3539		0.5452	1.5751
6	17.627	652619	2.2785		1.0574	2.6508
7	21.147	109065	0.2430		0.1767	0.2827
8	28.360	750894	1.7828		1.2166	2.0740
9	30.360	57169968	71.4255	T	92.6256	83.0958
10	34.280	1665682	2.3295		2.6987	2.7102

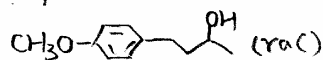
10 Peaks > Area Reject 61721576 Total Area
10 Peaks > Height Reject 85.956 Total Height

(CH-2__10.D01) UV



Chiralpak AD Hexane : i-proH = 95 : 5

0.7 mL/min 254 nm



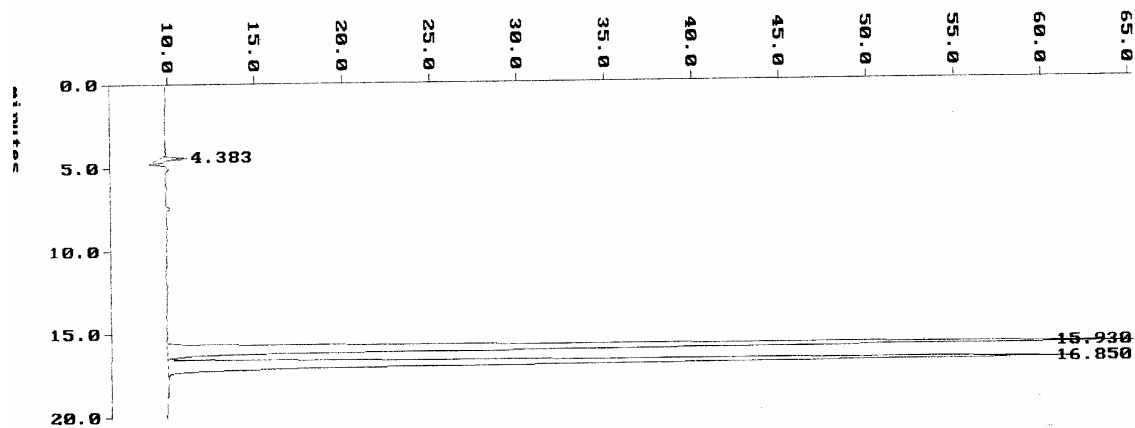
File : CH-2_21.D01 d-212rac Type : Sample
Run : 01 Inst : 1022 LC Plus
Path : C:\CH-6
Collection : 13:57:36 May 30 2003 Method : LCTEST [11:13:06 May 30 2003]
Integration : 14:43:10 May 30 2003 Method : LCTEST [14:42:39 May 30 2003]
Report : 14:43:12 May 30 2003 Method : LCTEST [14:42:39 May 30 2003]

PERCENT (AREA)

PK #	RT	Area	Height	BC	Area Percent	Height Percent
1	4.383	190048	1.5612	V	0.9721	1.4396
2	15.930	9673524	55.2446	T	49.4813	50.9401
3	16.850	9686280	51.6442		49.5466	47.6203

3 Peaks > Area Reject 19549852 Total Area
3 Peaks > Height Reject 108.450 Total Height

(CH-2_21.D01) AU



Software Version: 4.1<2F12>

Date: 03-6-12 14:18

Sample Name : d-215-rac

Data File : D:\TC4\DATA\CAO\CAP_0190.RAW Date: 03-6-12 13:59

Sequence File: D:\TC4\DATA\CAO\CAP.SEQ Cycle: 1 Channel : A

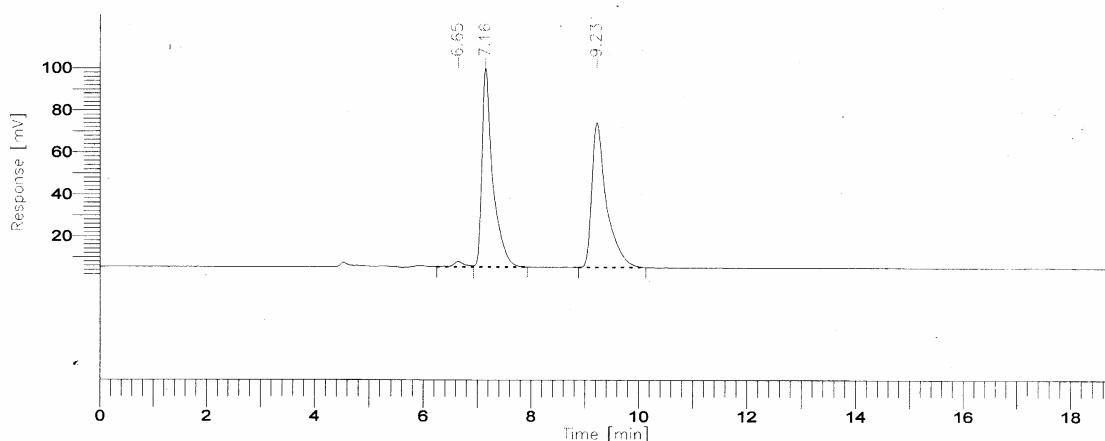
Instrument : 970A_-0 Rack/Vial: 0/0 Operator: cao

Sample Amount : 1.0000

(rac)

chiracel OJ 254nm 0.7ml/min

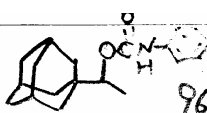
Hexane : i-proH = 95 : 5



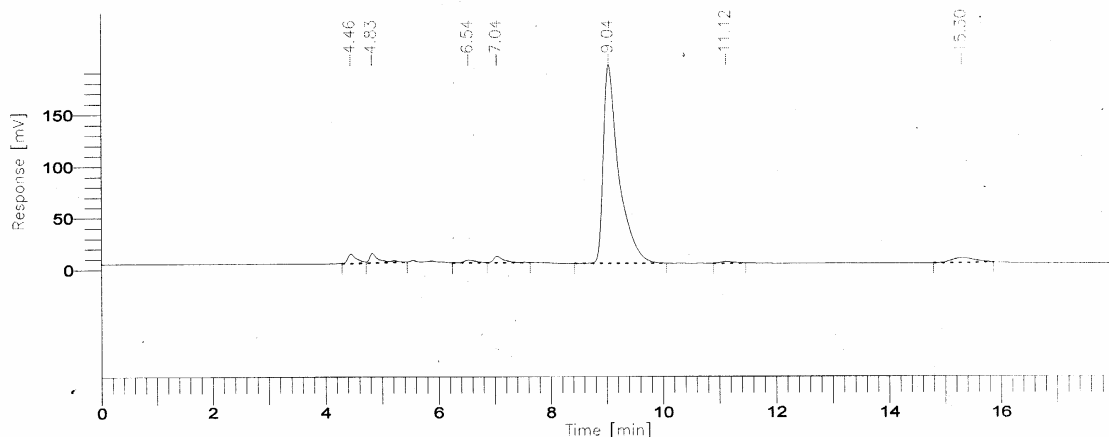
REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL	Area/Height [sec]
1	6.647	33597.56	2462.34	1.26	0.00	BV	13.6446
2	7.155	1323046.94	94662.19	49.59	0.00	VB	13.9765
3	9.228	1311405.00	68995.95	49.15	0.00	BB	19.0070
		2668049.50	166120.48	100.00	0.00		

Software Version: 4.1<2F12>
 Date: 03-6-12 14:42
 Sample Name : d-215-117
 Data File : D:\TC4\DATA\CAO\CAP_019P.RAW Date: 03-6-12 14:23
 Sequence File: D:\TC4\DATA\CAO\CAP.SEQ Cycle: 1 Channel : A
 Instrument : 970A_0 Rack/Vial: 0/0 Operator: cao
 Sample Amount : 1.0000 Dilution Factor : 1.00



Chiralcel OJ 254nm 0.7ml/min
 96% ee Hexane : i-ProH = 95 : 5



REPORT

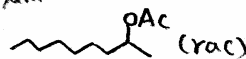
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Area BL	Area/Height [sec]
1	4.457	97593.67	9047.65	2.34	0.00	BV	10.7866
2	4.833	103638.33	9190.16	2.49	0.00	VB	11.2771
3	6.540	38667.60	2639.77	0.93	0.00	BV	14.6481
4	7.043	78349.90	6401.38	1.88	0.00	VB	12.2395
5	9.042	3687155.00	191309.21	88.46	0.00	BB	19.2733
6	11.123	29655.00	1943.56	0.71	0.00	BB	15.2581
7	15.299	133259.25	4620.73	3.20	0.00	BB	28.8395
		4168318.75	225152.44	100.00	0.00		

Rt- β Dexcsst 30m x 0.25mm x 0.25 μ m

File : S22_24.D01

110°C N₂ : 10 ps

D-203-107a



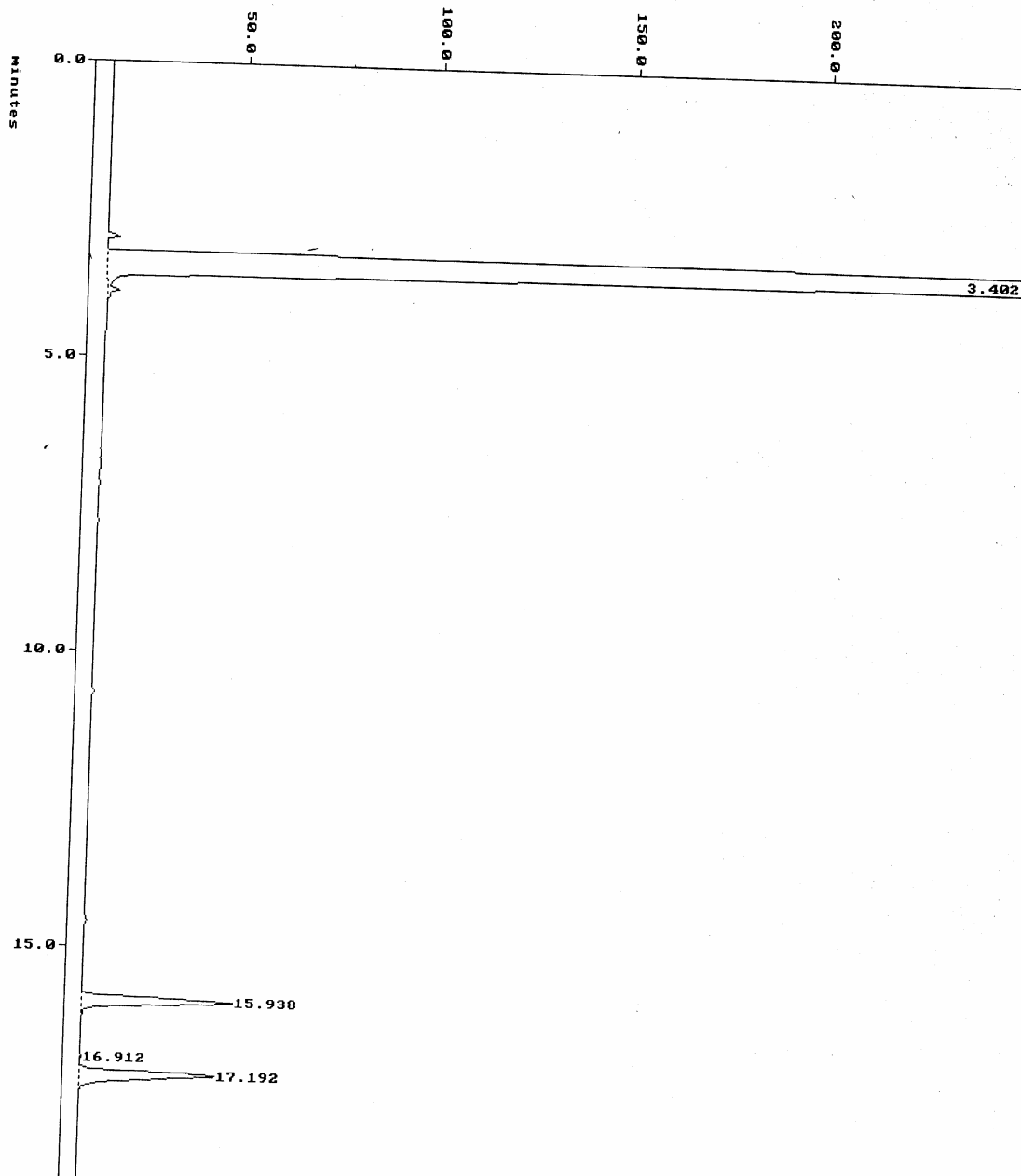
Run : 02

Collection : 10:40:00 Apr 28 2003

Method : XWD

Type : Sample
[07:20:18 Apr 28 2003]

(S22_24.D01) MU



***** MODEL 1022 RUNLOG for run: S22__29 *****

Run terminated manually on Channel A.

***** MODEL 1022 RUNLOG for run: S22__30 *****

Run terminated manually on Channel A.

***** MODEL 1022 RUNLOG for run: S22__31 *****

Run terminated manually on Channel A.

***** MODEL 1022 RUNLOG *****

Run S22__32 abandoned at 09:05:41 Tue Apr 29 2003

***** MODEL 1022 RUNLOG for run: S22__32 *****

Run terminated manually on Channel A.

***** MODEL 1022 RUNLOG for run: S22__33 *****

Run terminated manually on Channel A.

***** MODEL 1022 RUNLOG for run: S22__34 *****

Run terminated manually on Channel A.

***** MODEL 1022 RUNLOG for run: S22__35 *****

Run terminated manually on Channel A.

***** MODEL 1022 RUNLOG for run: S22__36 *****

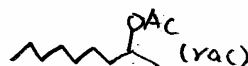
Run terminated manually on Channel A.

***** MODEL 1022 RUNLOG for run: S22__37 *****

Run terminated manually on Channel A.

File : S22__24.D01

D-203-107a



Run : 02

Type : Sampl

Path : C:\\$T\$

Inst : 1022 LC Plu

Collection : 10:40:00 Apr 28 2003 Method : XWD [07:20:18 Apr 28 2003]

Integration: 10:40:00 Apr 28 2003 Method : XWD [07:20:18 Apr 28 2003]

Report : 13:11:51 Apr 29 2003 Method : XWD [07:36:59 Apr 29 2003]

PERCENT (AREA) \ MANUALLY ALTERED

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	3.402	150159344	995.1762		96.2104	93.1150
2	15.938	2945611	38.8359	T	1.8873	3.6337
3	16.912	24902	0.2981	T	0.0160	0.0279
4	17.192	2944042	34.4503		1.8863	3.2234

4 Peaks > Area Reject 156073904 Total Area

4 Peaks > Height Reject 1068.760 Total Height

Rt- β Dex_{cs}t 30m x 0.25mm x 0.25 μ m

110°C N₂: 10psi



67% ee

File : S22_35.D01

D-203-105

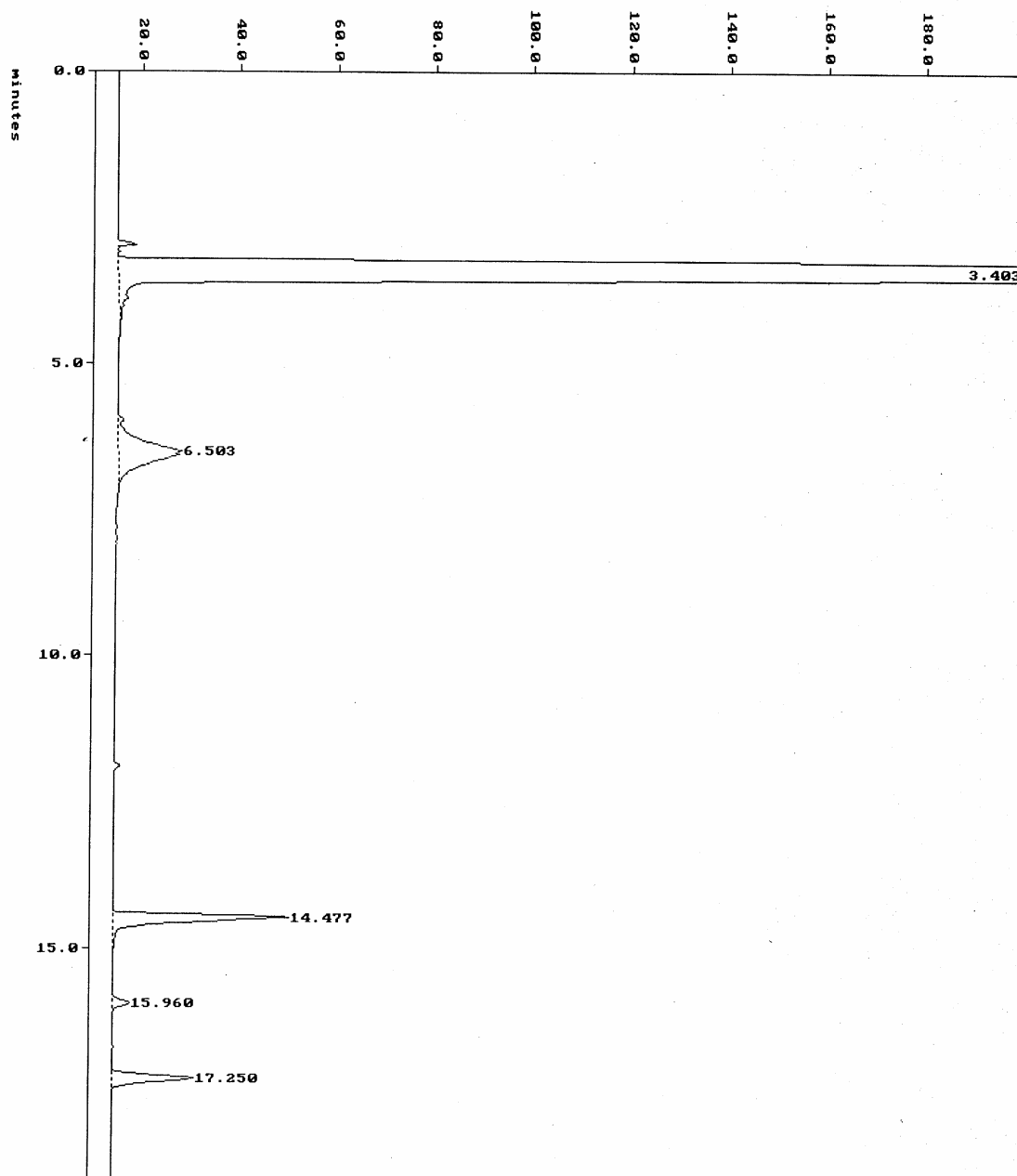
Run : 01

Type : Sample

Collection : 11:10:46 Apr 29 2003 Method : XWD

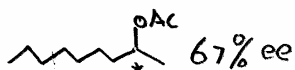
[07:36:59 Apr 29 2003]

(S22_35.D01) MU



File : S22__35.D01

D-203-105



Run : 01

Type : Sampl

Path : C:\\$T\$

Inst : 1022 LC Plu

Collection : 11:10:46 Apr 29 2003 Method : XWD

[07:36:59 Apr 29 2003]

Integration: 11:10:46 Apr 29 2003 Method : XWD

[07:36:59 Apr 29 2003]

Report : 13:14:09 Apr 29 2003 Method : XWD

[07:36:59 Apr 29 2003]

PERCENT (AREA) \ MANUALLY ALTERED

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	3.403	165268704	995.0167		95.5927	93.5084
2	6.503	3113643	13.0103		1.8010	1.2227
3	14.477	2874628	35.9979		1.6627	3.3830
4	15.960	265290	3.5533		0.1534	0.3339
5	17.250	1366159	16.5157		0.7902	1.5521

5 Peaks > Area Reject 172888416 Total Area
5 Peaks > Height Reject 1064.094 Total Height