

Direct Enantioselective Aldol-Tishchenko Reaction Catalyzed by Lithium Diphenylbinaphtholate

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Supporting Information

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1. General Methods

^1H and ^{13}C NMR spectra were measured in CDCl_3 with JEOL JNM-ECX400 spectrometer. Tetramethylsilane (TMS) ($\delta = 0$ ppm) and CDCl_3 ($\delta = 77.0$ ppm) were served as internal standards for ^1H and ^{13}C NMR, respectively. Infrared spectra were recorded on JEOL JIR 6500-W. Mass spectra were measured with JEOL JMS-DX303HF mass spectrometer. Optical rotations were recorded on JASCO P-1010 polarimeter. High-pressure liquid chromatography (HPLC) was performed on JASCO P-980 and UV-1575.

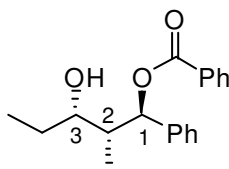
Thin-layer chromatography (TLC) analysis was carried out using Merck silica gel plates. Visualization was accomplished with UV light, phosphomolybdic acid and/or anisaldehyde. Column chromatography was performed using Kanto Chemical Silica Gel 60N (spherical, neutral, 63-210 μm).

Absolute configurations of **4aa**, **5aa**, **6aa** ~ **6ad**, **6ba**, **7da**, **12** were determined by the comparison of $[\alpha]_{\text{D}}$ data or HPLC data in the literatures. Absolute configurations of **6ae**, **6ca**, **7ea** were determined by analogy.

2. The aldol-Tishchenko reaction of 3-pentanone (**2a**) and benzaldehyde (**3a**).

Under an argon atmosphere, *n*-BuLi (0.094 mmol, 20 mol %) in hexane (0.17 M, 0.55 mL) was added to a solution of (*R*)-3,3'-diphenylbinaphthol (20.7 mg, 0.047 mmol, 10 mol %) in THF at 0 $^{\circ}\text{C}$, and the mixture was stirred for 5 min. Benzaldehyde (**3a**) (0.12 mL, 1.18 mmol, 2.5 equiv.) and 3-pentanone (**2a**) (0.05 mL, 0.47 mmol) were successively added to the above mixture at rt and the mixture was stirred for 3 h. The reaction was quenched with sat. NH_4Cl (2 mL) and the mixture was stirred for 5 min at rt. The aqueous layer was extracted with AcOEt and the combined organic layers were washed with brine (3 mL). After drying over Na_2SO_4 and concentration in vacuo, the residue was purified by column chromatography (SiO_2 , CH_2Cl_2) to afford monoacylated diol **4aa** (61 mg, 44% yield) and **5aa** (31 mg, 22% yield) both as a colorless oil.

(1*R*,2*R*,3*S*)-2-Methyl-1-phenyl-1,3-pentanediol 1-*O*-benzoate (**4aa**)¹.

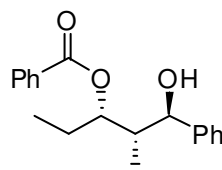


^1H NMR (CDCl_3 , 400 MHz) δ 0.75 (d, 3H, $J = 6.9$ Hz, $-\text{CHCH}_3$), 0.95 (t, 3H, $J = 7.3$ Hz, $-\text{CH}_2\text{CH}_3$), 1.38-1.49 (m, 1H, $-\text{CH}_2\text{CH}_3$), 1.57-1.68 (m, 1H, $-\text{CH}_2\text{CH}_3$), 2.08-2.16 (m, 1H, $-\text{CHCH}_3$), 2.47 (brs, 1H, $-\text{OH}$), 3.72-3.77 (m, 1H, $\text{HO}-\text{CH}$), 5.95 (d, 1H, $J = 10.1$ Hz, $\text{BzO}-\text{CHPh}$), 7.29-7.46 (m, 7H, $\text{Ar}-\text{H}$), 7.54-7.58 (m, 1H, $\text{Ar}-\text{H}$), 8.04-8.07 (m, 2H, $\text{Ar}-\text{H}$).

$[\alpha]_{\text{D}}^{30} +12.6$ (c 1.19, CHCl_3 , 85% ee), $[\alpha]_{\text{D}}^{30} +11.6$ (c 0.73, CH_2Cl_2 , 85% ee), [lit. 1: $[\alpha]_{\text{D}} -8.5$ (c 0.73, CH_2Cl_2 , 73% ee, 1*S*, 2*S*, 3*R*)]

HPLC (Daicel chiralcel OD-H, Hex/IPA = 97/3, 1.0 mL/min): t_{R} (min) 6.6 (major, 1*R*, 2*R*, 3*S*), 7.8 (minor, 1*S*, 2*S*, 3*R*), [lit. 1: 8.1 (1*R*, 2*R*, 3*S*), 8.7 (1*S*, 2*S*, 3*R*)].

(1*R*,2*R*,3*S*)-2-Methyl-1-phenyl-1,3-pentanediol 3-*O*-benzoate (**5aa**)¹.



^1H NMR (CDCl_3 , 400 MHz) δ 0.75 (d, 3H, $J = 6.9$ Hz, $-\text{CHCH}_3$), 1.00 (t, 3H, $J = 7.3$ Hz, $-\text{CH}_2\text{CH}_3$), 1.61-1.71 (m, 1H, $-\text{CH}_2\text{CH}_3$), 1.88-2.09 (m, 2H, $-\text{CH}_2\text{CH}_3$, $-\text{CHCH}_3$), 3.74 (d, 1H, $J = 3.6$ Hz, $-\text{OH}$), 4.19 (dd, 1H, $J = 9.6, 3.2$

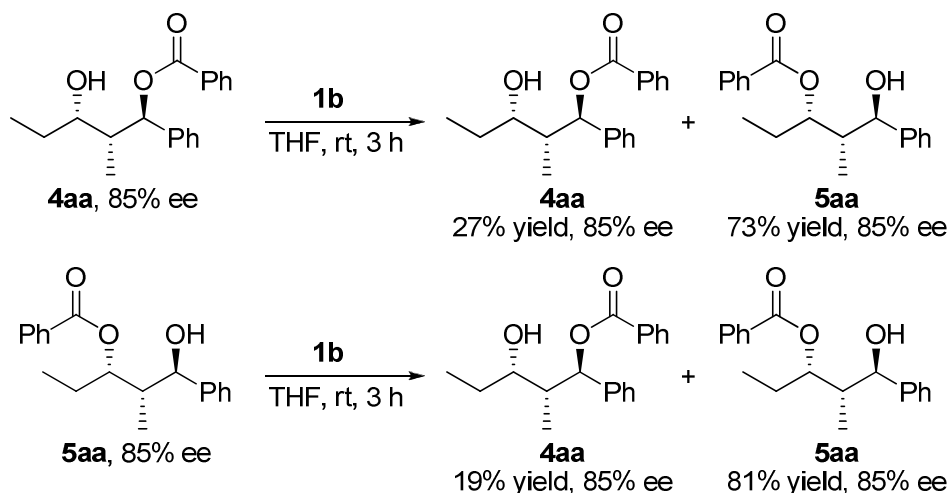
Hz, HO-CHPh), 5.62 (ddd, 1H, $J = 8.7, 5.0, 1.4$ Hz, BzO-CH), 7.24-7.37 (m, 5H, Ar-*H*), 7.47-7.51 (m, 2H, Ar-*H*), 7.59-7.63 (m, 1H, Ar-*H*), 8.10-8.13 (m, 2H, Ar-*H*).

$[\alpha]_D^{30} -0.3$ (c 1.07, CHCl₃, 85% ee), $[\alpha]_D^{31} +9.1$ (c 0.96, MeOH, 85% ee), $[\alpha]_D^{29} -3.7$ (c 1.09, CH₂Cl₂, 85% ee), [lit. 1: $[\alpha]_D +3.3$ (c 1.00, CH₂Cl₂, 72% ee, 1*S*, 2*S*, 3*R*)]

HPLC (Daicel chiralpak AD-H, Hex/IPA = 19/1, 1.0 mL/min): t_R (min) 12.1 (major, 1*R*, 2*R*, 3*S*), 20.5 (minor, 1*S*, 2*S*, 3*R*), [lit. 1: 12.3 (1*R*, 2*R*, 3*S*), 21.6 (1*S*, 2*S*, 3*R*)].

3. Isomerization of 4aa to 5aa and 5aa to 4aa.

Under an argon atmosphere, *n*-BuLi (0.094 mmol) in hexane (0.17 M, 0.55 mL) was added to a solution of (*R*)-3,3'-diphenylbinaphthol (20.7 mg, 0.047 mmol) and **4aa** (54.9 mg) or **5aa** (16.8 mg) in THF at 0 °C, and the mixture was stirred for 3 h. The reaction was quenched with sat. NH₄Cl (2 mL) and the mixture was stirred for 5 min at rt. The aqueous layer was extracted with AcOEt and the combined organic layers were washed with brine (3 mL). After drying over Na₂SO₄ and concentration in vacuo, the residue was purified by column chromatography (SiO₂, CH₂Cl₂) to afford monoacylated diol **4aa** and **5aa** both as a colorless oil.

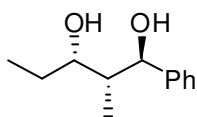


4. The aldol-Tishchenko reaction and subsequent deacylation.

Typical procedure:

Under an argon atmosphere, *n*-BuLi (0.094 mmol, 20 mol %) in hexane (0.17 M, 0.55 mL) was added to a solution of (*R*)-3,3'-diphenylbinaphthol (20.7 mg, 0.047 mmol, 10 mol %) in THF at 0 °C, and the mixture was stirred for 5 min. Benzaldehyde (**3a**) (0.12 mL, 1.18 mmol, 2.5 equiv.) and 3-pentanone (**2a**) (0.05 mL, 0.47 mmol) were successively added to the above mixture and the mixture was stirred for 48 h. The reaction was quenched with sat. NH₄Cl (2 mL) and the mixture was stirred for 5 min at rt. The aqueous layer was extracted with AcOEt and the combined organic layers were washed with brine (3 mL). After drying over Na₂SO₄ and concentration in vacuo, the residue was dissolved in MeOH (2 mL) and treated with NaOMe (0.05 mmol, 11 mol %) in MeOH (0.5 M, 0.1 mL). After 3 h, the mixture was diluted with AcOEt (20 mL), and washed with water (5 mL). The aqueous layer was extracted twice with AcOEt (10 mL x 2) and the combined organic layers were washed with brine (10 mL) and dried over Na₂SO₄. After concentration in vacuo, the residue was purified by column chromatography (SiO₂, hexane/AcOEt = 4/1) to give diol **6aa** (74 mg, 81%) as a colorless oil.

(1*R*,2*R*,3*S*)-2-Methyl-1-phenylpentane-1,3-diol (6aa**)¹.**

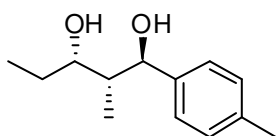


¹H NMR (CDCl₃, 400 MHz) δ 0.85 (d, 3H, J = 6.8 Hz, -CHCH₃), 0.89 (t, 3H, J = 7.3 Hz, CH₂CH₃), 1.36-1.56 (m, 2H, -CH₂CH₃), 1.88-1.95 (m, 1H, -CHCH₃), 2.91 (brs, 1H, -OH), 3.54 (brs, 1H, -OH), 3.70 (ddd, 1H, J = 8.7, 4.6, 2.3 Hz, HO-CH), 4.67 (d, 1H, J = 6.9 Hz, HO-CH), 7.22-7.36 (m, 5H, Ar-H).

$[\alpha]_D^{29} +45.4$ (c 1.22, CHCl₃, 91% ee), $[\alpha]_D^{29} +43.6$ (c 1.01, CH₂Cl₂, 91% ee), [lit. 1: $[\alpha]_D$ -36.2 (c 0.60, CH₂Cl₂, 75% ee, 1*S*, 2*S*, 3*R*)]

HPLC (Daicel chiralpak AD-H, Hex/IPA = 19/1, 1.0 mL/min): t_R (min) 14.7 (major, 1*R*, 2*R*, 3*S*), 20.3 (minor, 1*S*, 2*S*, 3*R*), [lit. 1: Hex/IPA = 9/1, 7.8 (1*R*, 2*R*, 3*S*), 10.1 (1*S*, 2*S*, 3*R*)].

(1*R*,2*R*,3*S*)-2-Methyl-1-(4-methylphenyl)pentane-1,3-diol (6ab**)¹.**



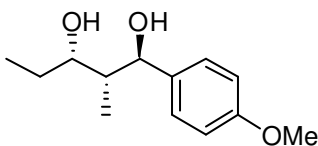
Following the typical procedure, the reaction of *p*-tolualdehyde (**3b**) (0.14 mL, 1.18 mmol, 2.5 equiv.) and 3-pentanone (**2a**) (0.05 mL, 0.47 mmol) gave diol **6ab** (85.3 mg, 87%) as a colorless oil.

¹H NMR (CDCl₃, 400 MHz) δ 0.81 (d, 3H, J = 7.3 Hz, -CHCH₃), 0.89 (t, 3H, J = 7.3 Hz, -CH₂CH₃), 1.35-1.58 (m, 2H, -CH₂CH₃), 1.85-1.92 (m, 1H, -CHCH₃), 2.33 (s, 3H, Ar-CH₃), 3.07 (brs, 1H, -OH), 3.53 (brs, 1H, -OH), 3.69 (ddd, 1H, J = 8.7, 4.6, 1.8 Hz, HO-CH), 4.62 (d, J = 6.8 Hz, HO-CHAr), 7.13 (d, 2H, J = 7.8 Hz, Ar-H), 7.20 (d, 2H, J = 7.8 Hz, Ar-H).

$[\alpha]_D^{29} +41.0$ (c 1.05, CHCl₃, 95% ee)

HPLC (Daicel chiralpak AD-H, Hex/IPA = 29/1, 1.0 mL/min): t_R (min) 24.6 (major, 1*R*, 2*R*, 3*S*), 29.4 (minor, 1*S*, 2*S*, 3*R*), [lit. 1: Hex/IPA = 9/1, 8.4 (1*R*, 2*R*, 3*S*), 9.1 (1*S*, 2*S*, 3*R*)].

(1*R*,2*R*,3*S*)-1-(4-methoxyphenyl)-2-Methylpentane-1,3-diol (6ac**)¹.**



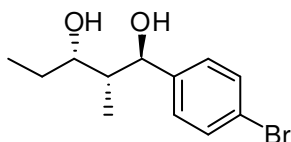
Following the typical procedure, the reaction of *p*-anisaldehyde (**3c**) (0.14 mL, 1.18 mmol, 2.5 equiv.) and 3-pentanone (**2a**) (0.05 mL, 0.47 mmol) gave diol **6ac** (84.9 mg, 81%) as a colorless oil.

¹H NMR (CDCl₃, 400 MHz) δ 0.79 (d, 3H, J = 7.4 Hz, -CHCH₃), 0.90 (t, 3H, J = 7.3 Hz, -CH₂CH₃), 1.38-1.58 (m, 2H, -CH₂CH₃), 1.83-1.91 (m, 1H, -CHCH₃), 3.12 (brs, 1H, -OH), 3.62 (brs, 1H, -OH), 3.69 (ddd, 1H, J = 8.2, 4.1, 1.8 Hz, HO-CH), 3.78 (s, 3H, -OCH₃), 4.60 (d, J = 7.3 Hz, HO-CHAr), 6.84-6.88 (m, 2H, Ar-H), 7.21-7.25 (m, 2H, Ar-H).

$[\alpha]_D^{29} +41.8$ (c 0.75, CHCl₃, 95% ee)

HPLC (Daicel chiralpak AD-H, Hex/IPA = 9/1, 1.0 mL/min): t_R (min) 11.0 (major, 1*R*, 2*R*, 3*S*), 12.4 (minor, 1*S*, 2*S*, 3*R*), [lit. 1: 11.3 (1*R*, 2*R*, 3*S*), 12.7 (1*S*, 2*S*, 3*R*)].

(1*R*,2*R*,3*S*)-1-(4-Bromophenyl)-2-methylpentane-1,3-diol (6ad)¹.



Following the typical procedure, the reaction of *p*-bromobenzaldehyde (**3d**) (212.4 mg, 1.18 mmol, 2.5 equiv.) and 3-pentanone (**2a**) (0.05 mL, 0.47 mmol) gave diol **6ad** (102.5 mg, 80%) as a colorless prism.

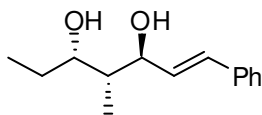
mp 96-97 °C

¹H NMR (CDCl₃, 400 MHz) δ 0.84-0.89 (m, 6H, -CHCH₃, -CH₂CH₃), 1.34-1.54 (m, 2H, -CH₂CH₃), 1.80-1.87 (m, 1H, -CHCH₃), 3.04 (brs, 1H, -OH), 3.63 (ddd, 1H, *J* = 8.7, 5.0, 2.3 Hz, HO-CH), 4.08 (brs, 1H, -OH), 4.60 (d, 1H, *J* = 6.4 Hz, HO-CHAr), 7.15-7.19 (m, 2H, Ar-*H*), 7.43-7.46 (m, 2H, Ar-*H*).

[α]_D²⁹ +34.5 (*c* 1.05, CHCl₃, 88% ee)

HPLC (Daicel chiralpak AS-H, Hex/IPA = 9/1, 1.0 mL/min): *t*_R (min) 7.2 (major, 1*R*, 2*R*, 3*S*), 10.2 (minor, 1*S*, 2*S*, 3*R*), [lit. 1: 6.3(1*R*, 2*R*, 3*S*), 10.1 (1*S*, 2*S*, 3*R*)].

(1*E*,3*R*,4*R*,5*S*)-4-Methyl-1-phenyl-1-heptane-3,5-diol (6ae).



Following the typical procedure, the reaction of *trans*-cinnamaldehyde (**3e**) (0.15 mL, 1.18 mmol, 2.5 equiv.) and 3-pentanone (**2a**) (0.05 mL, 0.47 mmol) gave diol **6ae** (62.8 mg, 61%) as a colorless oil.

¹H NMR (CDCl₃, 400 MHz) δ 0.92-0.98 (m, 6H, -CHCH₃, -CH₂CH₃), 1.49-1.61 (m, 2H, -CH₂CH₃), 1.73-1.80 (m, 1H, -CHCH₃), 2.85 (brs, 1H, -OH), 3.29 (brs, 1H, -OH), 3.84-3.88 (m, 1H, HO-CH), 4.30 (t, 1H, *J* = 6.4 Hz, HO-CH), 6.25 (dd, 1H, *J* = 16.0, 6.4 Hz, olefine-*H*), 6.62 (d, 1H, *J* = 15.6 Hz), 7.21-7.39 (m, 5H, Ar-*H*).

¹³C NMR (CDCl₃, 100 MHz) δ 10.63, 11.02, 26.71, 41.78, 74.10, 76.61, 126.41, 127.52, 128.50, 130.74, 131.60, 136.68.

IR (neat) ν 3552 cm⁻¹.

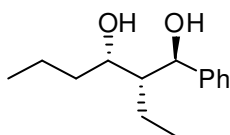
LR-FABMS (CHCl₃+NBA+NaI) 243 ((M+Na)⁺), 241, 176 (bp), 145, 136, 55.

HR-FABMS calcd for C₁₄H₂₀O₂Na ((M+Na)⁺) 243.1361, found 243.1340.

[α]_D²⁹ +6.9 (*c* 1.27, CHCl₃, 94% ee), [α]_D³¹ +15.4 (*c* 1.14, benzene, 94% ee)

HPLC (Daicel chiralpak AD-H, Hex/IPA = 19/1, 1.0 mL/min): *t*_R (min) 18.5 (major, 3*R*, 4*R*, 5*S*), 21.2 (minor, 3*S*, 4*S*, 5*R*).

(1*R*,2*R*,3*S*)-2-Ethyl-1-phenylhexane-1,3-diol (6ba)¹.



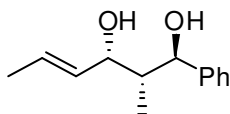
Following the typical procedure, the reaction of benzaldehyde (**3a**) (0.12 mL, 1.18 mmol, 2.5 equiv.) and 4-heptanone (**2b**) (0.07 mL, 0.47 mmol) gave diol **6ba** (69.4 mg, 71%) as a colorless oil.

¹H NMR (CDCl₃, 400 MHz) δ 0.82 (t, 3H, *J* = 6.9 Hz, -CHCH₂CH₃), 0.91 (t, 3H, *J* = 7.3 Hz, CH₂CH₂CH₃), 1.16-1.63 (m, 7H, -CHCH₂CH₃, -CH₂CH₂CH₃), 3.32 (brs, 1H, -OH), 3.74 (ddd, *J* = 9.2, 4.1, 1.8 Hz, HO-CH), 3.89 (brs, 1H, -OH), 4.85 (d, 1H, *J* = 5.5 Hz), 7.22-7.35 (m, 5H, Ar-*H*).

$[\alpha]_D^{28} +37.6$ (c 0.99, CHCl_3 , 91% ee)

HPLC (Daicel chiralpak AS-H, Hex/IPA = 19/1, 1.0 mL/min): t_R (min) 8.6 (major, 1*R*, 2*R*, 3*S*), 11.4 (minor, 1*S*, 2*S*, 3*R*), [lit. 1: Hex/IPA = 9/1, 5.1 (1*R*, 2*R*, 3*S*), 5.7 (1*S*, 2*S*, 3*R*)].

(1*R*,2*R*,3*S*,4*E*)-2-Methyl-1-phenyl-4-hexene-1,3-diol (6*ca*).



Following the typical procedure, the reaction of benzaldehyde (**3a**) (0.12 mL, 1.18 mmol, 2.5 equiv.) and 4-hexene-3-one (**2c**) (0.05 mL, 0.47 mmol) gave diol **6ca** (77.8 mg, 80%) as a colorless oil.

^1H NMR (CDCl_3 , 400 MHz) δ 0.69 (d, 3H, J = 7.3 Hz, $-\text{CHCH}_3$), 1.72 (d, 3H, J = 5.5 Hz, $-\text{CH}=\text{CHCH}_3$), 1.96-2.04 (m, 1H, $-\text{CHCH}_3$), 3.42 (brs, 1H, $-\text{OH}$), 3.87 (brs, 1H, $-\text{OH}$), 4.20-4.23 (m, 1H, $\text{HO}-\text{CH}$), 4.57 (d, 1H, J = 8.3 Hz), 5.56-5.89 (m, 2H, olefine- H), 7.23-7.34 (m, 5H, Ar- H).

^{13}C NMR (CDCl_3 , 100 MHz) δ 12.5, 17.8, 44.2, 75.0, 77.9, 126.6, 127.5, 127.7, 128.3, 130.7, 143.6.

IR (neat) ν 3354 cm^{-1} .

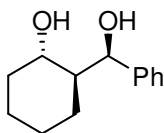
LR-FABMS (CHCl_3 +NBA+NaI) 229 ($(\text{M}+\text{Na})^+$, bp), 173, 149, 107, 55.

HR-FABMS calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2\text{Na}$ ($(\text{M}+\text{Na})^+$) 229.1204, found 229.1200.

$[\alpha]_D^{28} +5.7$ (c 1.34, CHCl_3 , 87% ee)

HPLC (Daicel chiralcel OD-H, Hex/IPA = 19/1, 1.0 mL/min): t_R 11.1 (minor, 1*S*, 2*S*, 3*R*), 12.2 (major, 1*R*, 2*R*, 3*S*).

(1*S*,2*S*, α *R*)- α -(2-Hydroxycyclohexyl)-benzenemethanol (7*da*)².



Following the typical procedure, the reaction of benzaldehyde (**3a**) (0.12 mL, 1.18 mmol, 2.5 equiv.) and cyclohexanone (**2d**) (0.05 mL, 0.47 mmol) in THF (3 mL) gave diol **7da** (87.5 mg, 87%) as colorless needles.

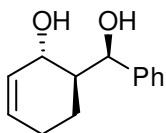
mp 122-124 °C

^1H NMR (CDCl_3 , 400 MHz) δ 0.78-0.92 (m, 1H), 1.02-1.15 (m, 2H), 1.25-1.35 (m, 1H), 1.50-1.65 (m, 3H), 1.74-1.81 (m, 1H), 1.89-1.93 (m, 1H), 3.23 (brs, 1H), 3.49 (dt, 1H, J = 10.5, 4.6 Hz), 3.70 (brs, 1H), 4.92 (s, 1H), 7.24-7.36 (m, 5H).

$[\alpha]_D^{27} +27.6$ (c 1.02, CHCl_3 , 90% ee), [lit. 2: $[\alpha]_D +32$ (c 0.95, CHCl_3 , 99% ee, 1*S*, 2*S*, α *R*)]

HPLC (Daicel chiralcel OD-H, Hex/IPA = 9/1, 1.0 mL/min): t_R (min) 7.3 (minor, 1*R*, 2*R*, α *S*), 8.7 (major, 1*S*, 2*S*, α *R*).

(1*S*,2*S*, α *R*)- α -(2-Hydroxycyclohex-3-enyl)-benzenemethanol (7ea).



Following the typical procedure, the reaction of benzaldehyde (**3a**) (0.12 mL, 1.18 mmol, 2.5 equiv.) and 2-cyclohexene-1-one (**2e**) (0.05 mL, 0.47 mmol) in THF (3mL) at -23 °C gave diol **6ea** (84.2 mg, 88%) as colorless needles.

mp 135-137 °C

¹H NMR (CDCl₃, 400 MHz) δ 1.15-1.24 (m, 1H), 1.62-1.67 (m, 1H), 1.93-2.09 (m, 3H), 2.71 (brs, 1H), 3.12 (brs, 1H), 4.24 (d, 1H, *J* = 8.7 Hz), 4.98 (s, 1H), 5.56-5.60 (m, 1H), 5.70-5.72 (m, 1H), 7.26-7.38 (m, 5H).

¹³C NMR (CDCl₃, 100 MHz) δ 22.2, 25.0, 47.4, 68.1, 76.2, 126.5, 127.4, 128.1, 128.8, 130.3, 142.0.

IR (KBr) ν 3313cm⁻¹.

LR-FABMS (CHCl₃+NBA+NaI) 227 ((M+Na)⁺, bp), 173, 149, 107, 77.

HR-FABMS calcd for C₁₃H₁₆O₂Na ((M+Na)⁺) 227.1048, found 227.1030.

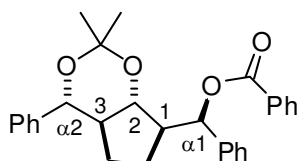
$[\alpha]_D^{27}$ -11.4 (*c* 0.99, CHCl₃, 85% ee)

HPLC (Daicel chiralcel OD-H, Hex/IPA = 9/1, 1.0 mL/min): *t*_R (min) 8.8 (minor, 1*R*, 6*R*, *S*), 11.3 (major, 1*S*, 6*S*, *R*).

5. The aldol-aldol-Tishchenko reaction of cyclopentanone (2f) and benzaldehyde (3a).

Under an argon atmosphere, *n*-BuLi (0.094 mmol, 20 mol %) in hexane (0.17 M, 0.55 mL) was added to a solution of (*R*)-3,3'-diphenylbinaphthol (20.7 mg, 0.047 mmol, 10 mol %) in THF at -23 °C, and the mixture was stirred for 5 min. Then benzaldehyde (**3a**) (0.17mL, 1.65 mmol, 3.5 equiv) and cyclopentanone (**2f**) (0.04 mL, 0.47 mmol) were added to the above mixture. After 24 h, the reaction was quenched with sat. NH₄Cl (2 mL) and the mixture was stirred for 5 min at rt. The aqueous layer was extracted with AcOEt and the combined organic layers were successively washed with brine (3 mL). Drying over Na₂SO₄ and concentration in vacuo, the residue was purified by column chromatography (SiO₂, CH₂Cl₂) to give an inseparable mixture of triol mono esters as a colorless oil. To the solution of the mono ethers, pyridinium *p*-toluenesulfonate (1.2 mg, 0.047 mmol, 10 mol %) and 2,2-dimethoxypropane (0.09 mL, 0.71 mmol, 1.5 equiv) was added and the mixture was stirred for 12 h. After diluted with AcOEt (20 mL), the mixture was washed with water (5 mL x 3) and brine (10 mL) and dried over Na₂SO₄. After concentration in vacuo, the residue was purified by column chromatography (SiO₂, hexane/toluene = 1/1) to give **8** (137 mg, 66%, 2 steps) as colorless needles and its diastereomer **8'** (46 mg, 22 %, 2 steps) as colorless needles.

(*rel*-1*S*,2*S*,3*R*,1 α *R*,2 α *R*)-2-Hydroxy- α 1, α 2-diphenyl-1,3-cyclopentanedimethanol 2, α 2-*O*,*O*-acetonide α 1-*O*-benzoate (8).



mp 114-115 °C

¹H NMR (CDCl₃, 400 MHz) δ 1.20-1.32 (m, 1H), 1.40-1.52 (m, 1H), 1.44 (s, 3H), 1.49 (s, 3H), 1.63-1.85 (m, 3H), 2.47-2.55 (m, 1H), 3.60 (t, 1H, *J* = 10.1 Hz), 4.60 (d, 1H, *J* = 10.1 Hz), 6.22 (d, 1H, *J* = 4.6 Hz), 7.21-7.33 (m,

8H), 7.39-7.42 (m, 2H), 7.45-7.49 (m, 2H), 7.55-7.60 (m, 1H), 8.13-8.16 (m, 2H).

^{13}C NMR (CDCl_3 , 100 MHz) δ 19.91, 21.10, 21.58, 29.90, 47.77, 48.63, 75.41, 75.70, 78.65, 100.50, 126.13, 126.40, 127.62, 127.70, 128.17, 128.32, 128.43, 129.60, 130.37, 133.00, 139.43, 140.71, 165.47.

IR (neat) ν 1718 cm^{-1} .

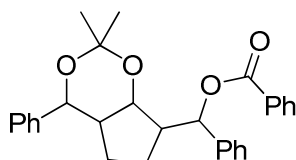
LR-FABMS (CHCl_3 +NBA+NaI) 465 ($(\text{M}+\text{Na})^+$), 413, 385, 329, 263, 245, 176, 154 (bp), 136, 105, 77.

HR-FABMS calcd for $\text{C}_{29}\text{H}_{30}\text{O}_4\text{Na}$ ($(\text{M}+\text{Na})^+$) 465.2042, found 465.2043.

$[\alpha]_{\text{D}}^{27}$ -8.2 (c 1.01, CHCl_3 , 99% ee)

HPLC (Daicel chiralpak AD-H, Hex/IPA = 99/1, 1.0 mL/min): t_{R} (min) 14.4 (major), 17.4 (minor).

diastereomer of **8** (**8'**).



mp 116-117 $^{\circ}\text{C}$

^1H NMR (CDCl_3 , 400 MHz) δ 1.19 (s, 3H), 1.33 (s, 3H), 1.45-1.57 (m, 2H), 1.71-1.78 (m, 1H), 1.92-1.99 (m, 1H), 2.24-2.33 (m, 1H), 2.61-2.69 (m, 1H), 4.08 (dd, 1H, J = 7.8, 5.0 Hz), 4.44 (d, 1H, J = 10.1 Hz), 6.08 (d, 1H, J = 7.3 Hz), 7.24-7.59 (m, 13H), 8.07-8.11 (m, 2H).

^{13}C NMR (CDCl_3 , 100 MHz) δ 23.61, 25.37, 27.11, 28.51, 49.41, 52.69, 73.61, 75.18, 77.60, 100.43, 126.58, 126.82, 127.59, 127.83, 128.23, 128.39, 129.62, 130.34, 133.01, 139.58, 141.20, 165.70.

IR (KBr) ν 1711 cm^{-1} .

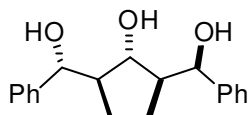
LR-FABMS (CHCl_3 +NBA+NaI) 466 ($(\text{M}+\text{Na})^+$), 414, 386, 329, 263, 245, 176, 105 (bp), 91. HR-FABMS calcd for $\text{C}_{29}\text{H}_{30}\text{O}_4\text{Na}$ ($(\text{M}+\text{Na})^+$) 465.2042, found 465.2046.

$[\alpha]_{\text{D}}^{27}$ -30.0 (c 1.52, CHCl_3 , 98% ee)

HPLC (Daicel chiralpak AD-H, Hex/IPA = 99/1, 1.0 mL/min): t_{R} (min) 19.0 (major), 25.8 (minor).

To the solution of **8** in MeOH (2 mL), NaOMe (0.05 mmol, 11 mol %) in MeOH (0.5 M, 0.1 mL) was added and the resulting homogeneous mixture was stirred for 12 h. The reaction was quenched with conc. HCl aq. (5 mL) and the mixture was stirred for 1 h at rt. The mixture was diluted with ethyl acetate (20 mL), and washed with water (5 mL). The aqueous layer was extracted twice with AcOEt (10 mL x 2) and the combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4 . After concentration in vacuo, the residue was purified by column chromatography (SiO_2 , hexane/AcOEt = 3/2) to give triol **9** (88 mg, 65%, from cyclopentanone (**2f**)) as colorless prisms.

(*rel*-1*S*,2*R*,3*R*,1*aR*,2*aR*)-2-Hydroxy- α 1, α 2-diphenyl-1,3-cyclopentanedimethanol (**9**).



mp 136-137 $^{\circ}\text{C}$

^1H NMR (CDCl_3 , 400 MHz) δ 1.04-1.14 (m, 1H), 1.23-1.32 (m, 1H), 1.45-1.61 (m, 2H), 2.09-2.18 (m, 1H), 2.30 (ddd, J = 18.8, 9.2, 5.0 Hz), 2.61 (d, 1H, J = 3.6 Hz), 3.05 (s, 1H), 3.10 (s, 1H), 4.01 (t, 1H, J = 9.2 Hz), 4.48 (d, 1H, J = 9.6 Hz), 4.86-4.88 (m, 1H), 7.24-7.37 (m, 10H).

^{13}C NMR (CDCl_3 , 100 MHz) δ 21.68, 23.85, 52.51, 52.71, 74.44, 79.14, 80.49, 126.30, 126.42, 127.52, 127.91,

128.37, 128.45, 142.95, 143.30.

IR (KBr) ν 3302 cm^{-1} .

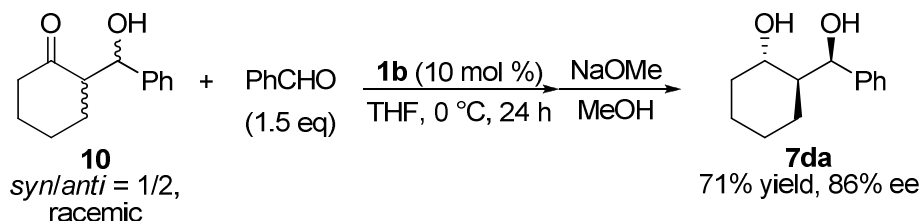
LR-FABMS ($\text{CHCl}_3 + \text{NBA} + \text{NaI}$) 321 ($(\text{M} + \text{Na})^+$), 263, 245, 176, 154 (bp), 136, 107, 69.

HR-FABMS calcd for $\text{C}_{19}\text{H}_{22}\text{O}_3\text{Na}$ ($(\text{M} + \text{Na})^+$) 321.1467, found 321.1475.

$[\alpha]_{\text{D}}^{30} +55.5$ (c 1.01, CHCl_3 , 99% ee)

Relative stereochemistry was determined by X-ray analysis (cf. S-26).

6. The Evans-Tishchenko reaction of racemic β -hydroxy ketone (**10**).

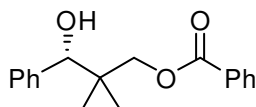


Under an argon atmosphere, *n*-BuLi (0.094 mmol, 20 mol %) in hexane (0.17 M, 0.55 mL) was added to a solution of (*R*)-3,3'-diphenylbinaphthol (20.7 mg, 0.047 mmol, 10 mol %) in THF (1 mL) at 0 °C, and the mixture was stirred for 5 min. Then benzaldehyde (**3a**) (0.07 mL, 0.07 mmol, 1.5 equiv.) and 2-(Hydroxyphenylmethyl)cyclohexanone (**10**) ($\text{syn/anti} = 1/2$, racemic) (96 mg, 0.47 mmol) in THF (2 mL) were successively added to the above mixture. After 24 h, the reaction was quenched with sat. NH_4Cl (2 mL) and the mixture was stirred for 5 min at rt. The aqueous layer was extracted with AcOEt and the combined organic layers were washed with brine (3 mL). After drying over Na_2SO_4 and concentration in vacuo, the residue was purified by column chromatography ($\text{SiO}_2, \text{CH}_2\text{Cl}_2$) to afford monoacylated diol as a colorless oil. The diol monoester was dissolved in MeOH (2 mL) and treated with NaOMe (0.05 mmol, 11 mol %) in MeOH (0.5 M, 0.1 mL) and the resulting homogeneous mixture was stirred for 3 h. The mixture was diluted with ethyl acetate (20 mL), and washed with water (5 mL). The aqueous layer was extracted twice with AcOEt (10 mL x 2) and the combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4 . After concentration in vacuo, the residue was purified by column chromatography (SiO_2 , hexane/AcOEt = 4/1) to give diol **7da** (68 mg, 71%, 86% ee) as colorless needles.

7. The Evans-Tishchenko reduction of β -hydroxy ketone (**11**).

Under an argon atmosphere, *n*-BuLi (0.094 mmol, 20 mol %) in hexane (0.17 M, 0.55 mL) was added to a solution of (*R*)-3,3'-diphenylbinaphthol (20.7 mg, 0.047 mmol, 10 mol %) in THF at -45 °C, and the mixture was stirred for 5 min. Then a solution of benzaldehyde (**3b**) (0.072 mL, 75 mg, 0.72 mmol, 1.5 equiv) and 2,2-dimethyl-3-hydroxy-1-phenylpropan-1-one (**11**) (0.073 mL, 0.47 mmol) were successively added to the above mixture. After 0.5 h, the reaction was quenched with sat. NH_4Cl aq and the mixture was stirred for 10 min at rt. The aqueous layer was extracted with AcOEt and the combined organic layer was washed with brine. After drying over Na_2SO_4 and evaporating the solvent, the residue was purified by silica gel column chromatography (SiO_2 , CH_2Cl_2) to afford the diol monoester product **12** (114 mg, 87% yield, 99% ee) as colorless prisms.

(S)-2,2-Dimethyl-1-phenylpropane-1,3-diol 3-O-benzoate (12)³.



mp 73-74 °C

¹H NMR (CDCl₃, 400 MHz) δ 0.97 (s, 3H, -CH₃), 1.04 (s, 3H, -CH₃), 2.45 (brs, 1H, -OH), 4.02 (d, 1H, *J* = 11.0 Hz, BzO-CH₂), 4.43 (d, 1H, *J* = 11.0 Hz, BzO-CH₂), 4.69 (s, 1H, HO-CHPh), 7.25-7.48 (m, 7H, Ar-*H*), 7.56-7.60 (m, 1H, Ar-*H*), 8.04-8.06 (m, 2H, Ar-*H*).

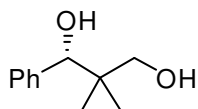
[α]_D³⁰ -23.1 (*c* 1.13, CHCl₃, 99% ee)

HPLC (Daicel chiralpak AD-H, Hex/IPA = 9/1, 1.0 mL/min): *t*_R 8.8 (major, *S*), 12.8 (minor, *R*).

Determination of the absolute configuration of 12.

To a solution of **12** (114 mg) in MeOH (2 mL), NaOMe (0.05 mmol, 11 mol %) in MeOH (0.5 M, 0.1 mL) was added and the resulting homogeneous mixture was stirred for 3 h. The mixture was diluted with ethyl acetate (20 mL), and washed with water (5 mL). The aqueous layer was extracted twice with ethyl acetate (10 mL x 2) and the combined organic layers were washed with brine (10 mL) and dried over Na₂SO₄. After concentration in vacuo, the residue was purified by column chromatography (SiO₂, hexane/ethyl acetate = 4/1) to give diol **13** (70 mg, 96%) as colorless needles. The optical rotation data shows (+)-**13** has *S*-configuration, which shows (-)-**12** has *S*-configuration.

(S)-2,2-Dimethyl-1-phenylpropane-1,3-diol (13)⁴.



mp 62-63 °C

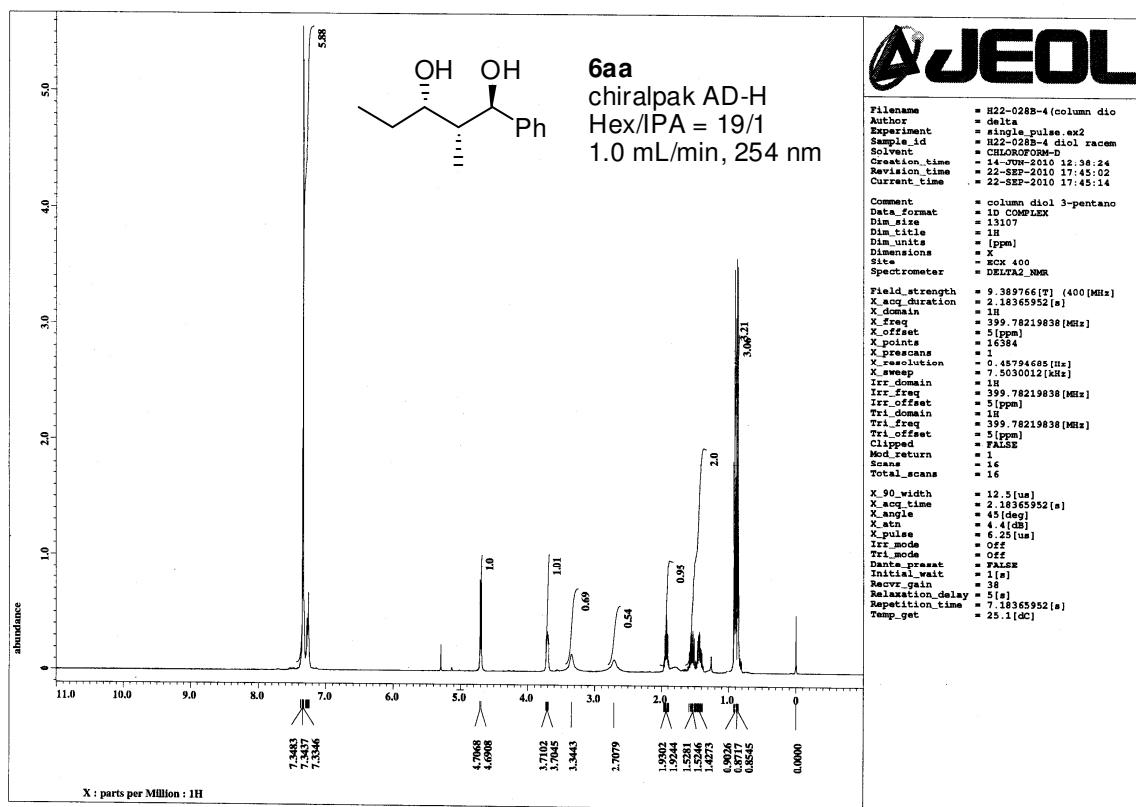
¹H NMR (CDCl₃, 400 MHz) δ 0.79 (s, 3H), 0.84 (s, 3H), 3.43 (d, 1H, *J* = 10.6 Hz), 3.50-3.58 (m, 2H), 3.77 (brs, 1H), 4.57 (s, 1H), 7.32-7.35 (m, 5H).

[α]_D³⁰ +44.7 (*c* 1.00, CHCl₃, 99% ee), [lit. 4: [α]_D³⁰ +21.7 (*c* 1.17, CHCl₃, 55% ee, *S*)]

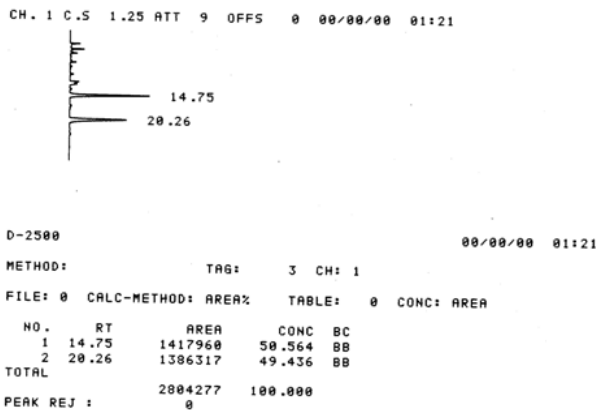
8. References

- (1) Mlynarski, J.; Rakiei, B.; Stodulski, M.; Suszczyńska, A.; Frelek, J. *Chem. Eur. J.* **2006**, *12*, 8158-8167.
- (2) Acetti, D.; Brenna, E.; Fuganti, C.; Gatti, F. G.; Serra, S. *Eur. J. Org. Chem.* **2010**, 142-151.
- (3) Markert, M.; Mahrwald, R. *Synthesis* **2004**, 1429-1433.
- (4) Kotani, S.; Shimoda, Y.; Sugiura, M.; Nakajima, M. *Tetrahedron Lett.* **2009**, *50*, 4602-4605.

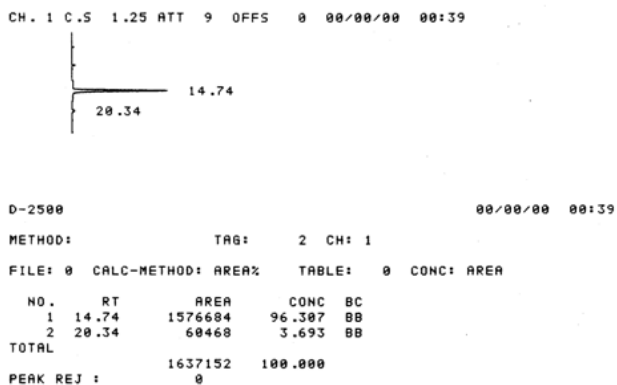
9. ^1H NMR and HPLC chart of the Tishchenko products

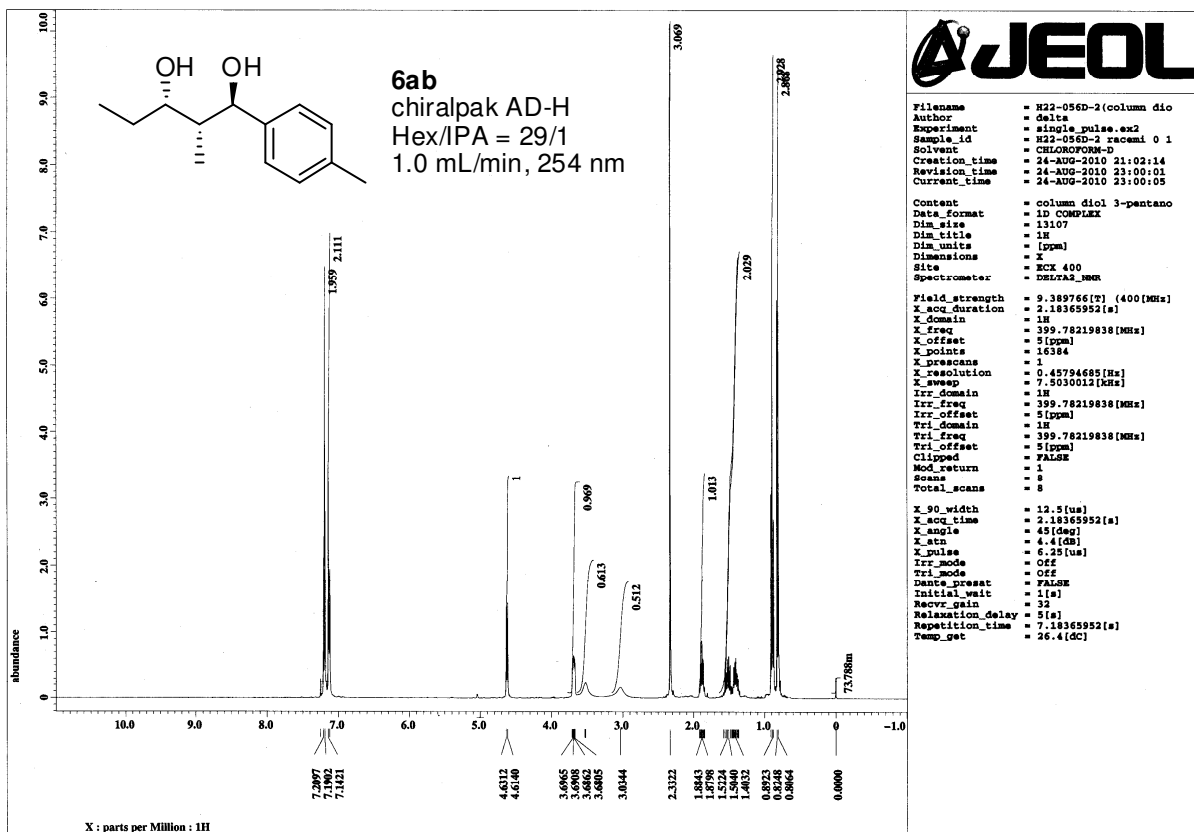


1. racemic



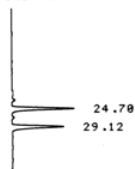
2. Optically active (93% ee)





1. racemic

CH. 1 C.5 1.25 ATT 8 OFFS 0 00/00/00 02:43



D-2500 00/00/00 02:43

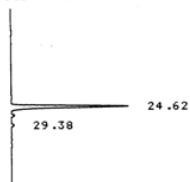
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2	29.12	1059139	49.775	BB
TOTAL		2127873	100.000	

PEAK REJ : 0

2. Optically active (95% ee)

CH. 1 C.5 1.25 ATT 8 OFFS 0 00/00/00 03:31

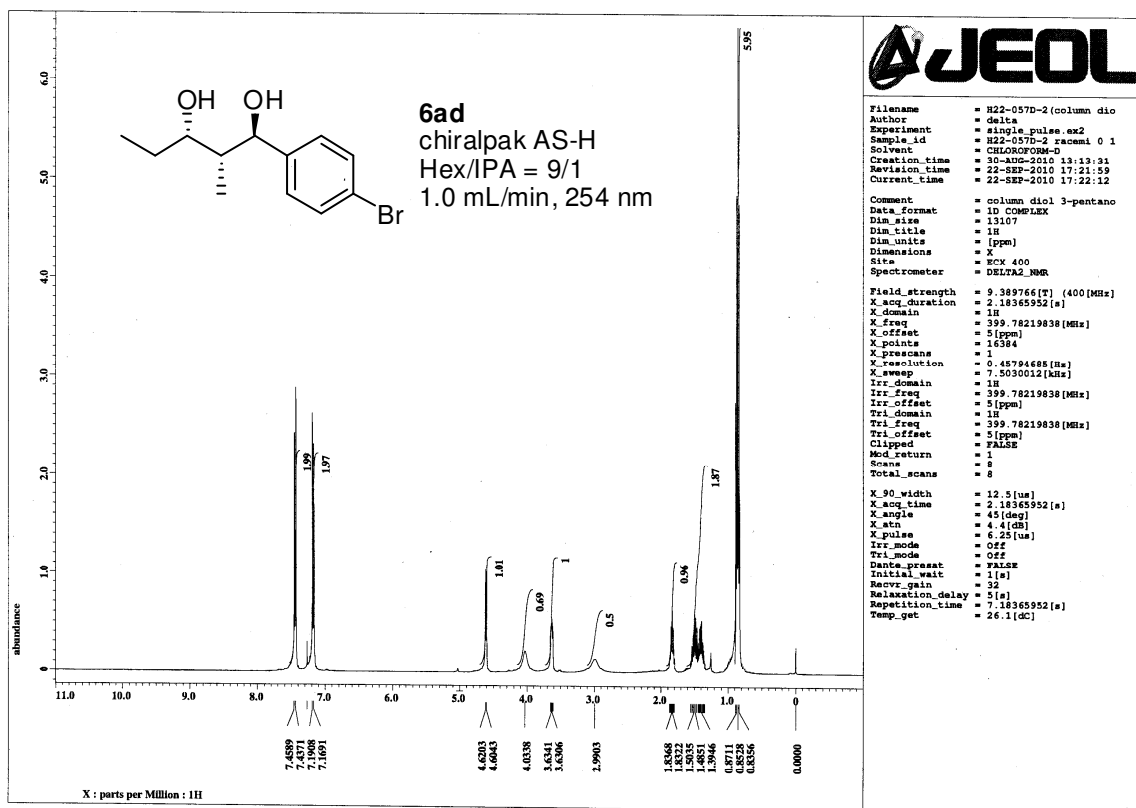


D-2500 00/00/00 03:31

METHOD: TAG: 10 CH: 1
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

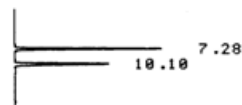
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2	29.38	58804	2.667	BB
TOTAL		2174639	100.000	

PEAK REJ : 0



1. racemic

CH. 1 C.S 1.25 ATT 9 OFFS 0 00/00/00 04:40



D-2500

00/00/00 04:40

METHOD: TAG: 3 CH: 1

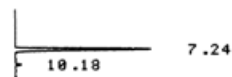
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	7.28	1222132	49.768	BB
2	10.10	1233505	50.232	BB

TOTAL 2455637 100.000
PEAK REJ : 1000

2. Optically active (88% ee)

CH. 1 C.S 1.25 ATT 10 OFFS 0 00/00/00 05:08



D-2500

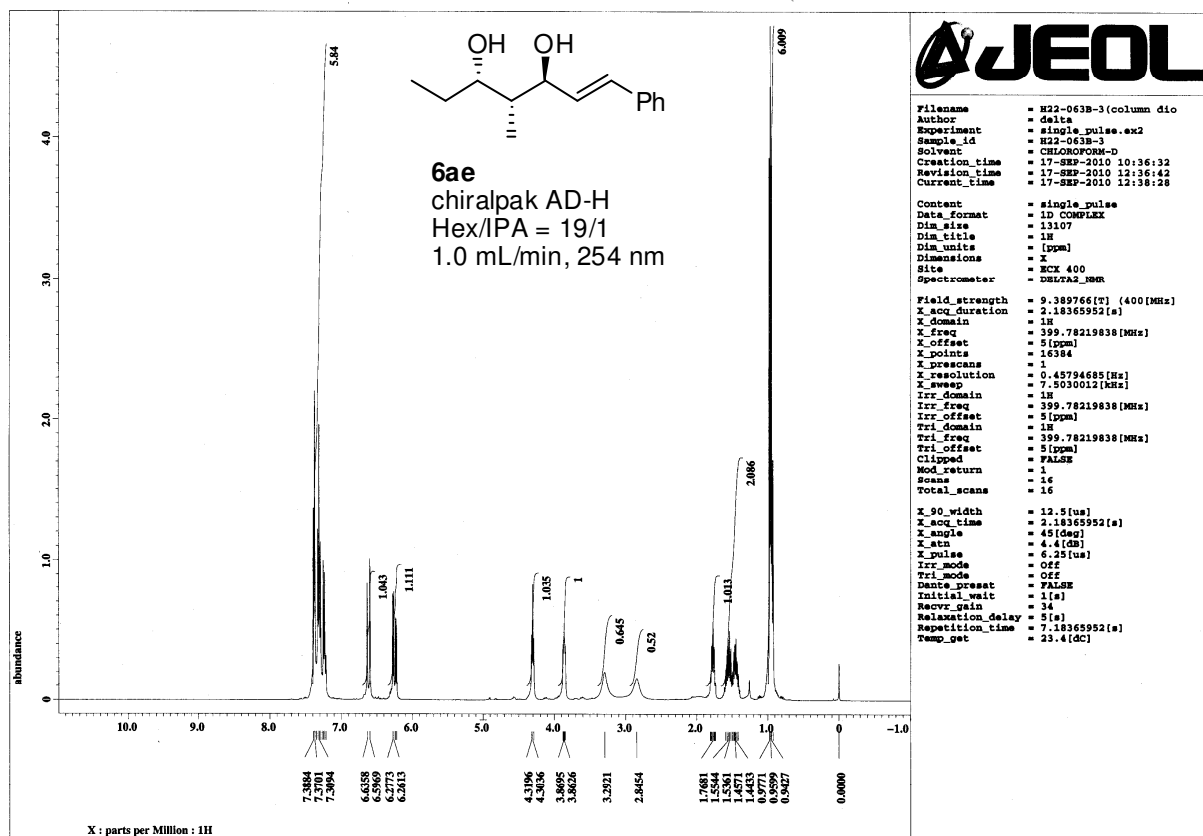
00/00/00 05:08

METHOD: TAG: 4 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

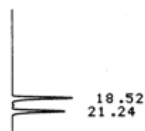
NO.	RT	AREA	CONC	BC
1	7.24	2374366	93.958	BB
2	10.18	152685	6.042	BB

TOTAL 2527051 100.000
PEAK REJ : 0



1. racemic

CH. 1 C.S 1.25 ATT 10 OFFS 0 00/00/00 04:30



D-2500

00/00/00 04:30

METHOD: TAG: 5 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

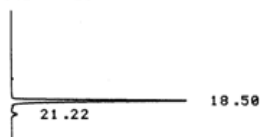
NO.	RT	AREA	CONC	BC
1	18.52	2631584	50.737	BB
2	21.24	2555151	49.263	BB

TOTAL 5186735 100.000

PEAK REJ : 0

2. Optically active (94% ee)

CH. 1 C.S 1.25 ATT 10 OFFS 0 00/00/00 05:05



D-2500

00/00/00 05:05

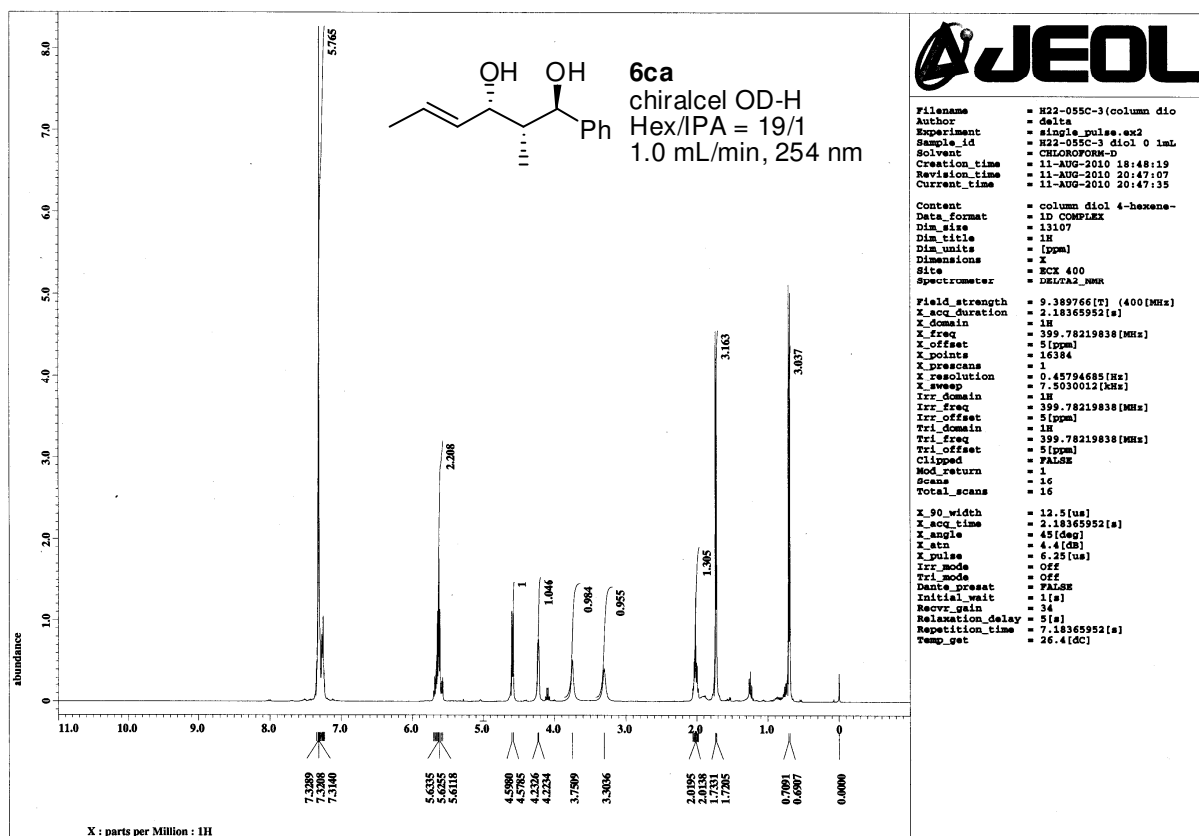
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FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
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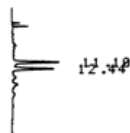
TOTAL 7569477 100.000

PEAK REJ : 0



1. racemic

CH. 1 C.S 1.25 ATT 6 OFFS 0 00/00/00 00:35



D-2500

00/00/00 00:35

METHOD: TAG: 3 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

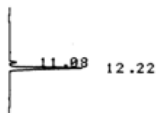
NO.	RT	AREA	CONC	BC
1	11.10	96360	50.426	BU
2	12.44	94731	49.574	UB

TOTAL 191091 100.000

PEAK REJ : 0

2. Optically active (87% ee)

CH. 1 C.S 1.25 ATT 9 OFFS 0 00/00/00 01:06



D-2500

00/00/00 01:06

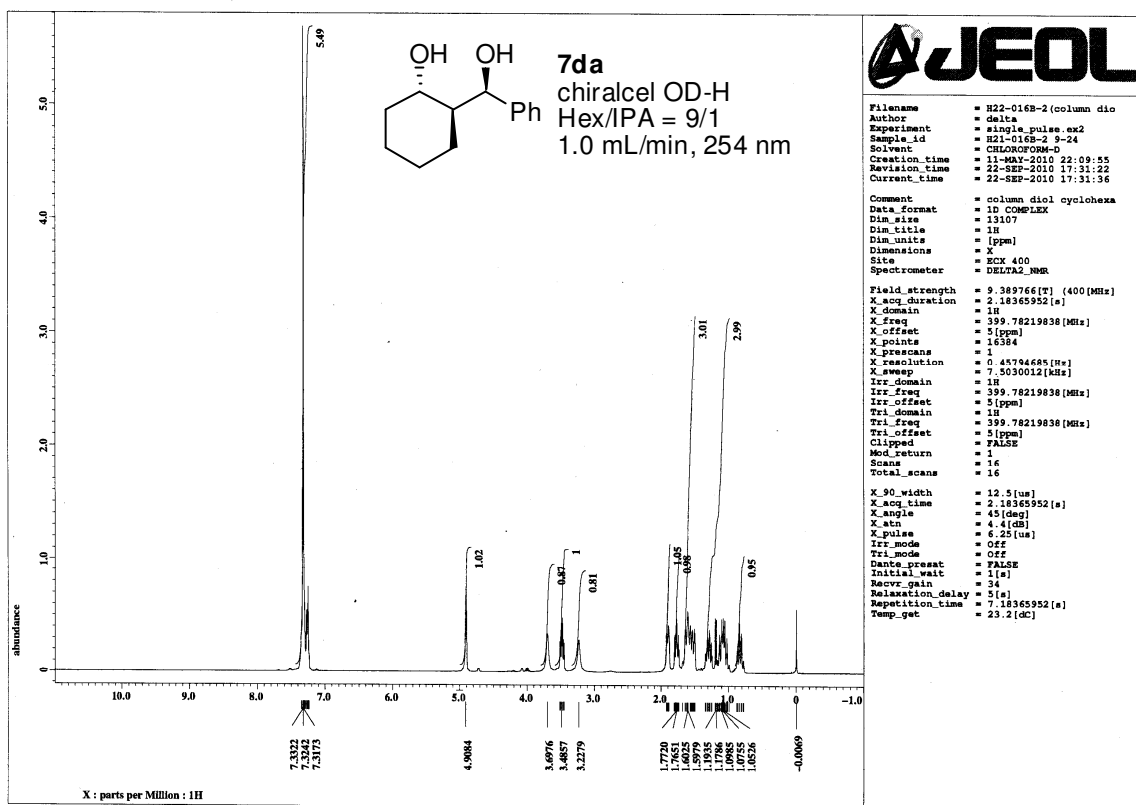
METHOD: TAG: 4 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	11.08	110640	6.659	BU
2	12.22	1550904	93.341	UB

TOTAL 1661544 100.000

PEAK REJ : 0



1. racemic

CH. 1 C.S 1.25 ATT 8 OFFS 0 00/00/00 05:18



D-2500

00/00/00 05:18

METHOD: TAG: 5 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

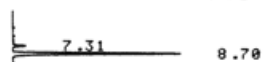
NO.	RT	AREA	CONC	BC
1	7.31	895968	48.488	BB
2	8.77	954886	51.592	BB

TOTAL 1850854 100.000

PEAK REJ : 0

2. Optically active (90% ee)

CH. 1 C.S 1.25 ATT 9 OFFS 0 00/00/00 06:39



D-2500

00/00/00 06:39

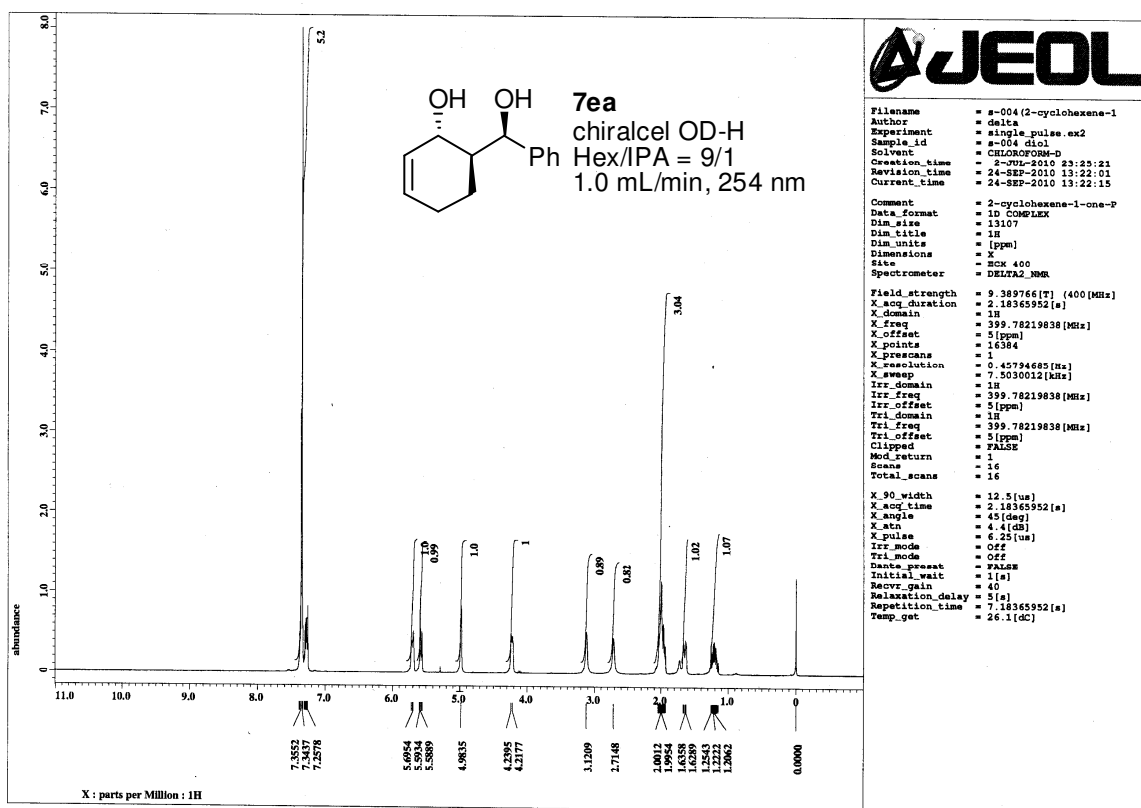
METHOD: TAG: 8 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	7.31	131929	5.196	BB
2	8.70	2407024	94.804	BB

TOTAL 2538953 100.000

PEAK REJ : 0



1. racemic

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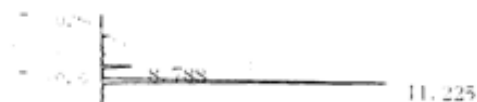
** CALCULATION REPORT **

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	7	11.321	501617	21850			49.3695	
TOTAL			1016046	50898			100	

C-RSA CHROMATOPAC CH=1 Report No.=2 DATA=1:9CHRM1.C00 10/07/03 16:05:08

2. Optically active (85% ee)

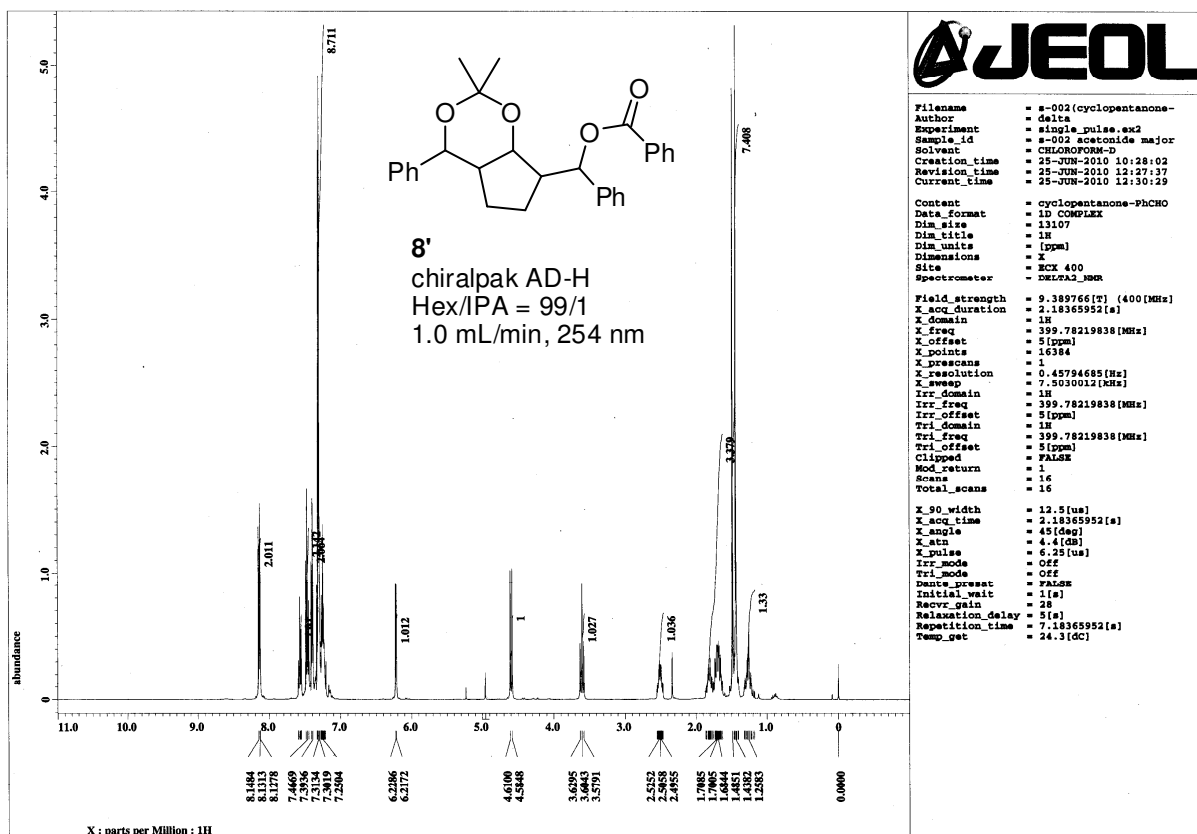
C-RSA CHROMATOPAC CH=1 Report No.=3 DATA=1:9CHRM1.C00 10/07/03 16:33:52



** CALCULATION REPORT **

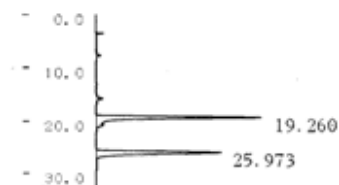
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	12	11.225	2111978	89015			92.3967	
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C-RSA CHROMATOPAC CH=1 Report No.=4 DATA=1:9CHRM1.C00 10/07/03 16:33:52



1. racemic

C-R8A CHROMATOPAC CH=1 Report No.=4 DATA=1:CHRM1.C00 10/07/06 16:58:00



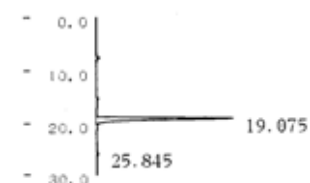
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	11	19.26	1824768	57678	S		52.5699	
	13	25.973	1646356	43834			47.43	
TOTAL			3471124	101512			100	

C-R8A CHROMATOPAC CH=1 Report No.=5 DATA=1:CHRM1.C00 10/07/06 16:58:00

2. Optically active (98% ee)

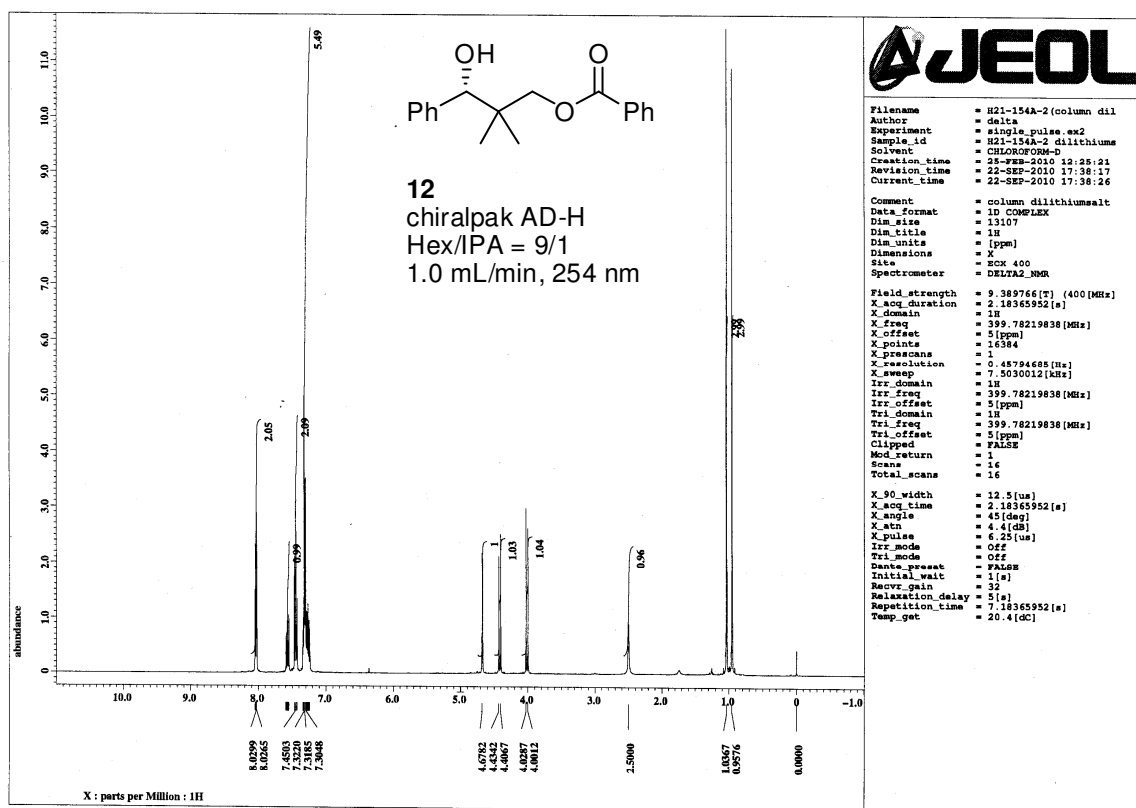
C-R8A CHROMATOPAC CH=1 Report No.=7 DATA=1:CHRM1.C00 10/07/06 17:33:20



** CALCULATION REPORT **

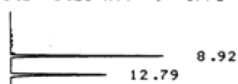
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	2	19.075	2880774	96253			99.1032	
	4	25.845	26068	829			0.8968	
TOTAL			2906842	97082			100	

C-R8A CHROMATOPAC CH=1 Report No.=8 DATA=1:CHRM1.C00 10/07/06 17:33:20



1. racemic

CH. 1 C.S 1.25 ATT 9 OFFS 0 00/00/00 00:24



D-2500

00/00/00 00:24

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

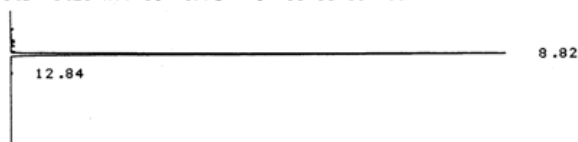
NO.	RT	AREA	CONC	BC
1	8.92	1504635	51.702	BB
2	12.79	1405558	48.298	BB

TOTAL 2910193 100.000

PEAK REJ : 0

2. Optically active (99% ee)

CH. 1 C.S 1.25 ATT 10 OFFS 0 00/00/00 00:55



D-2500

00/00/00 00:55

METHOD: TAG: 2 CH: 1

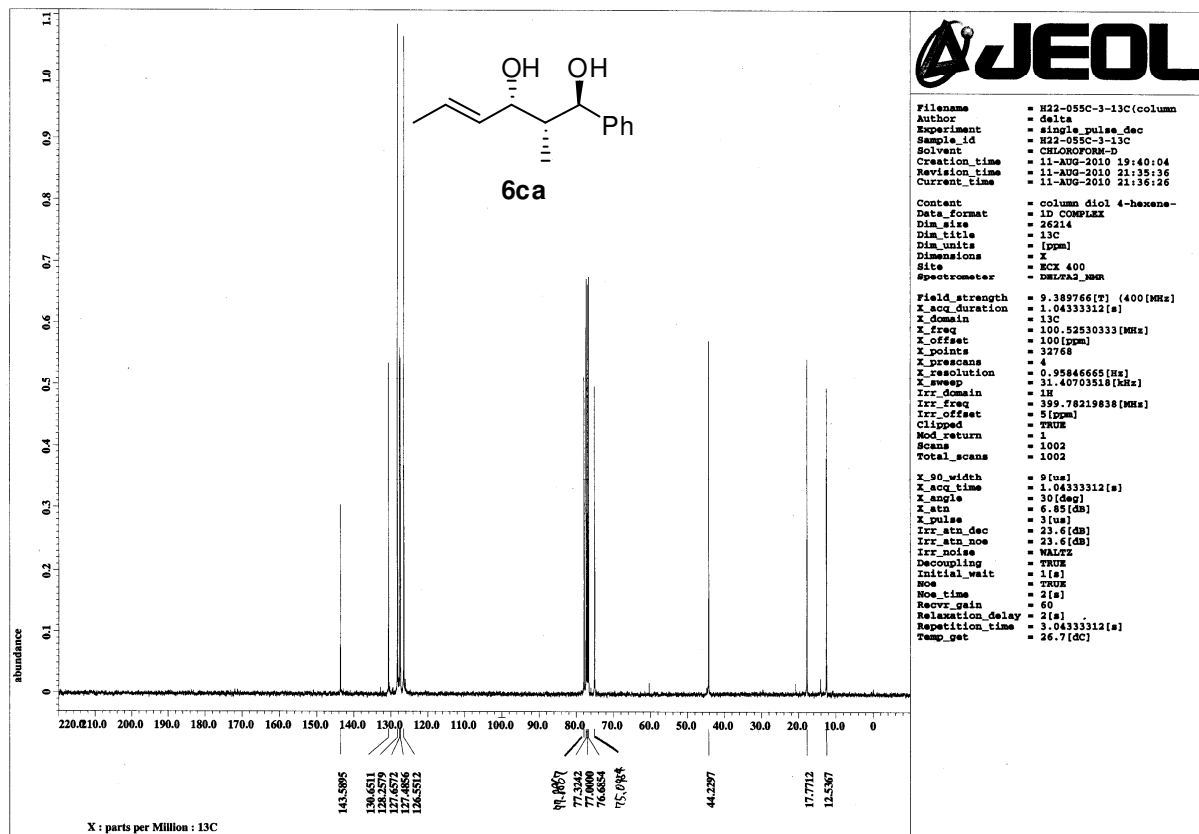
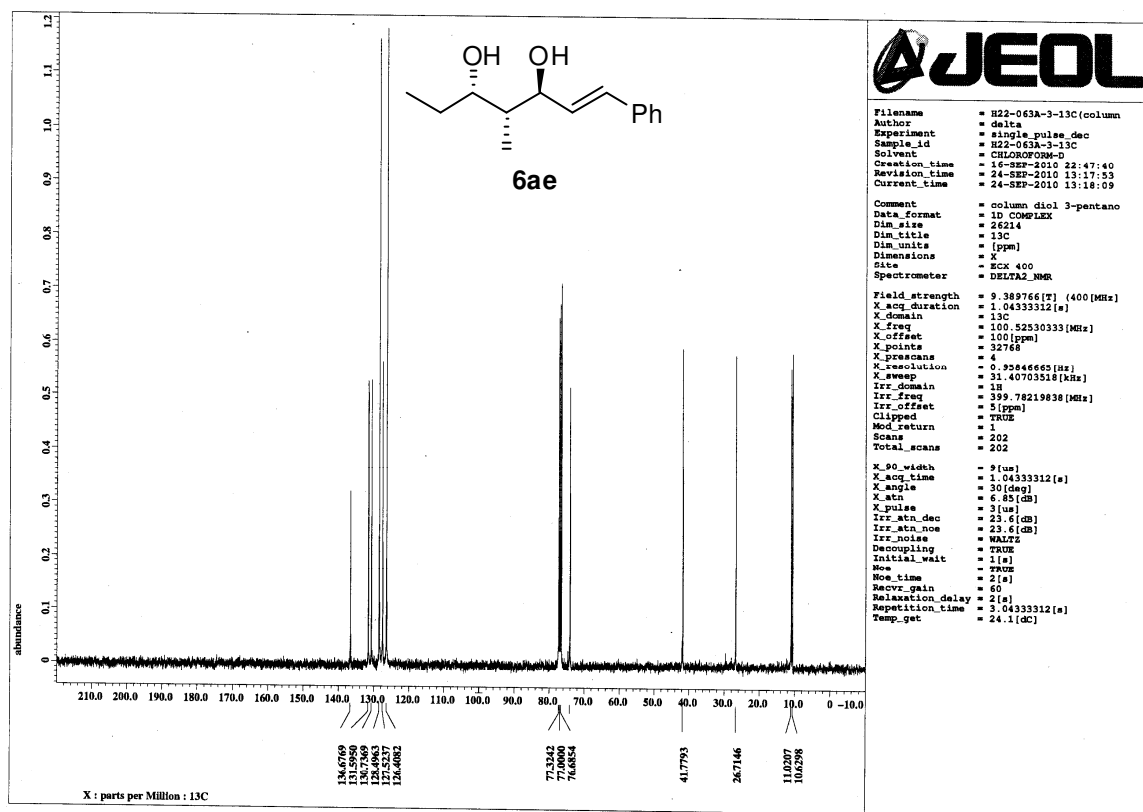
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

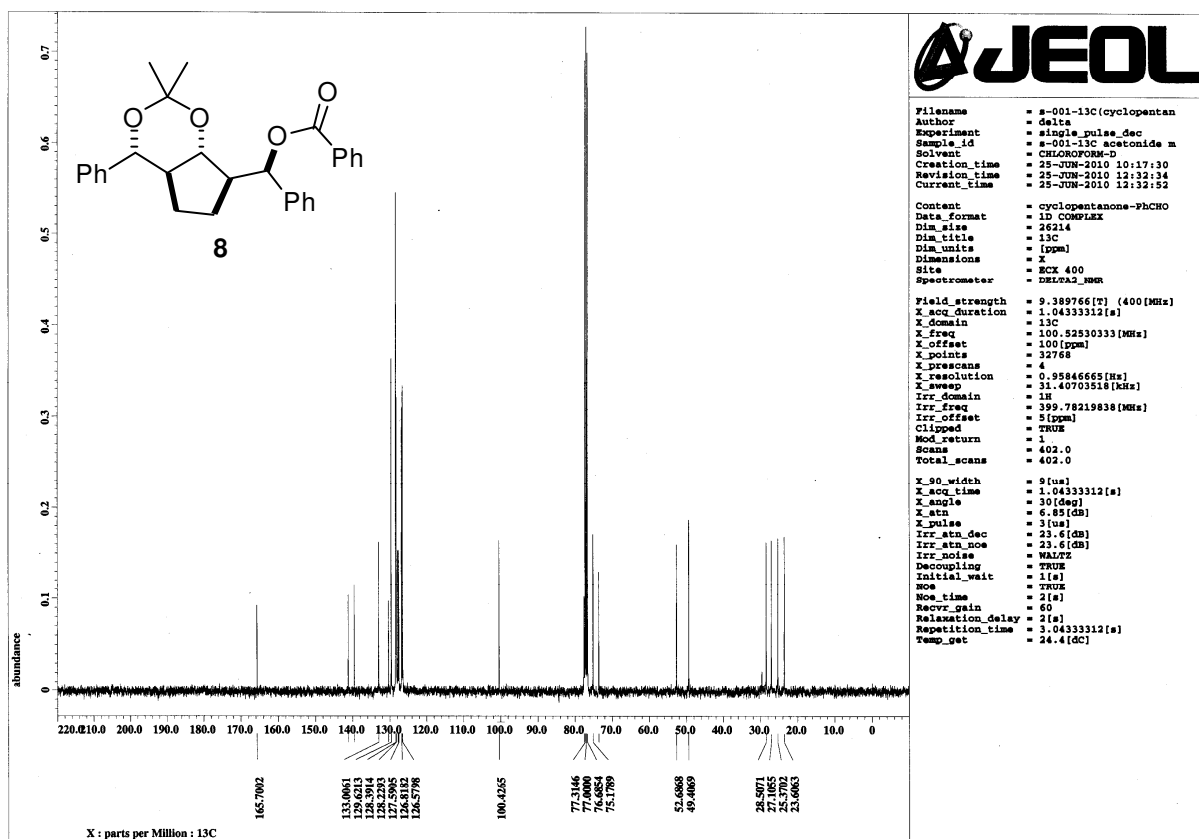
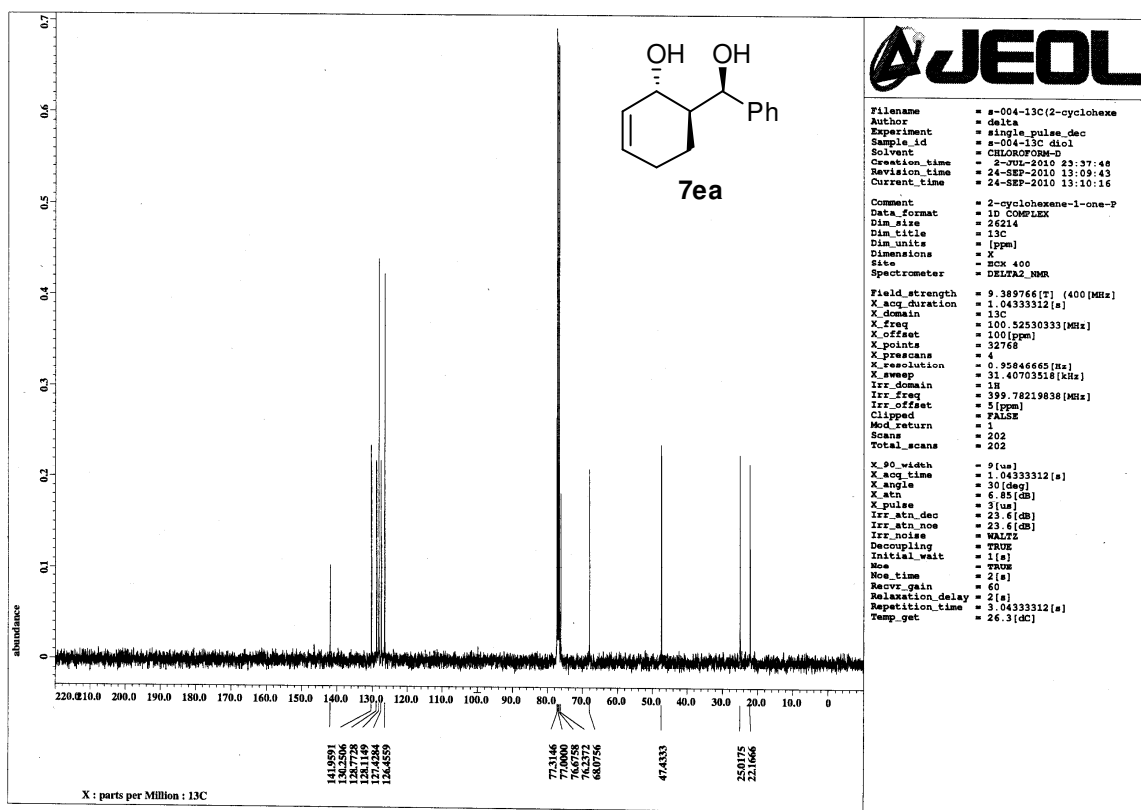
NO.	RT	AREA	CONC	BC
1	8.82	11095356	99.530	BB
2	12.84	52369	0.470	BB

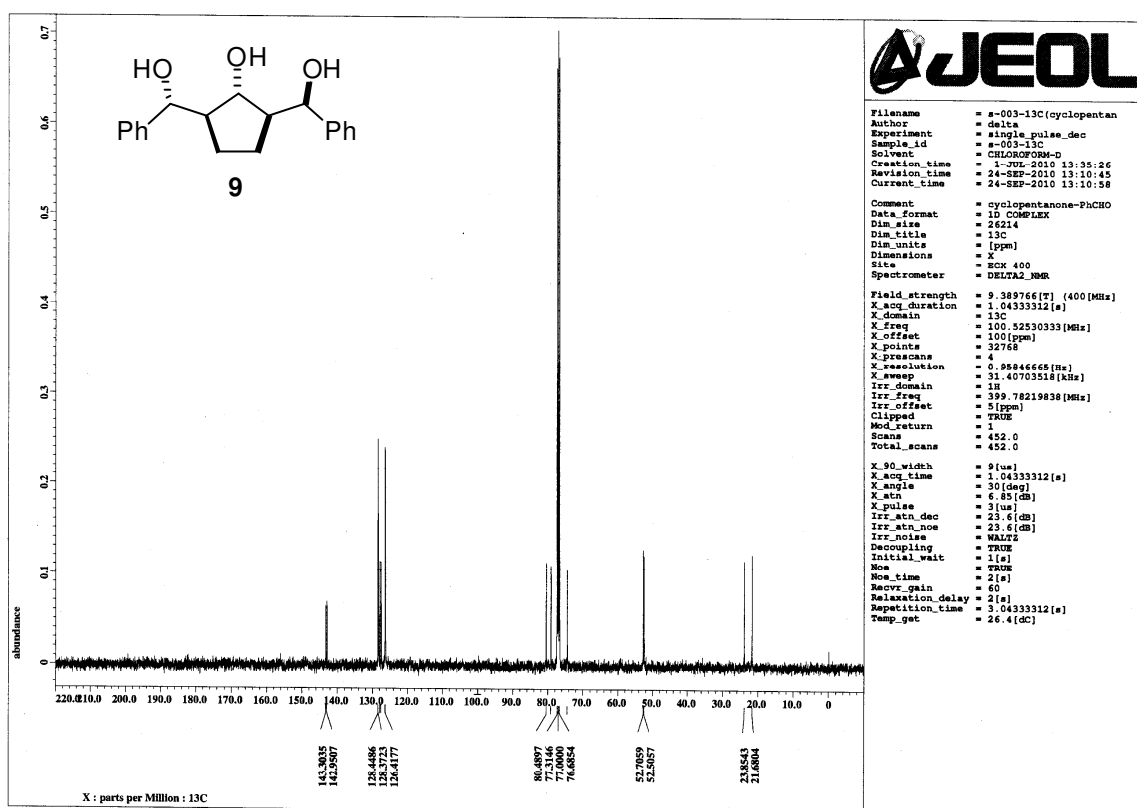
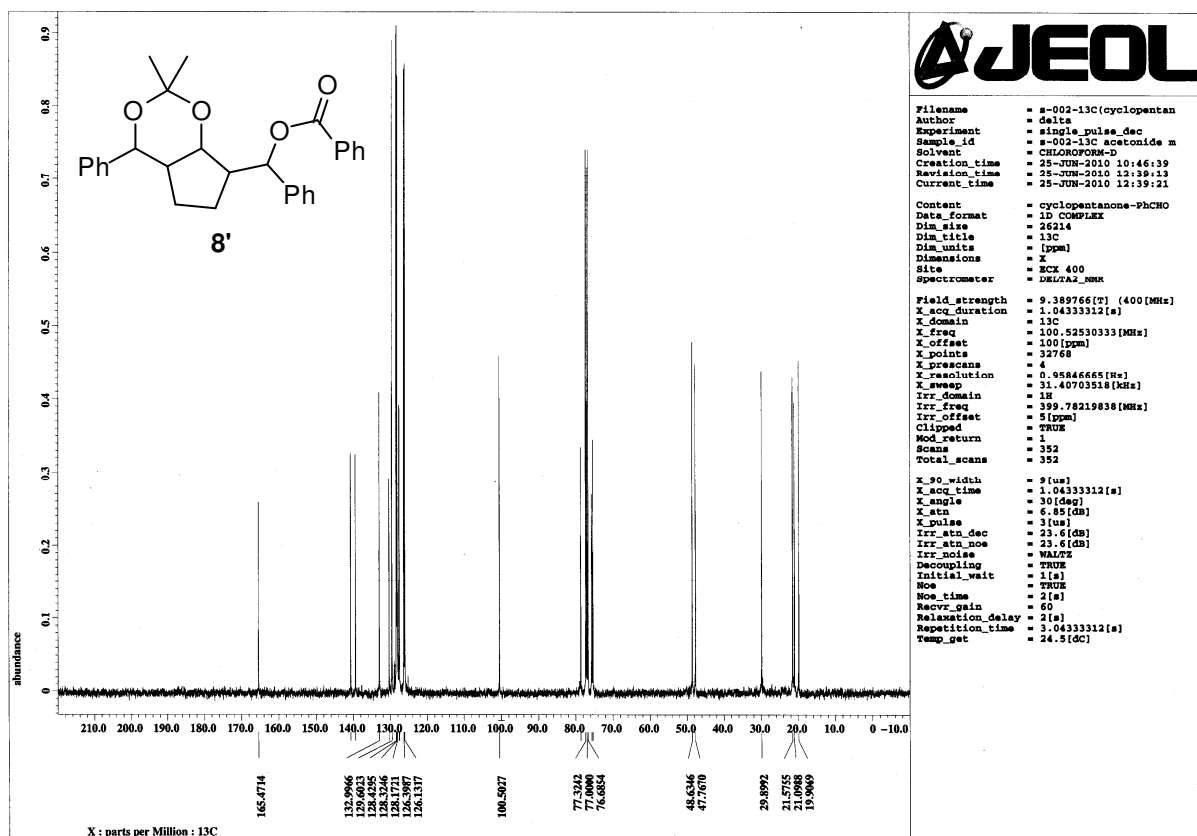
TOTAL 11147725 100.000

PEAK REJ : 0

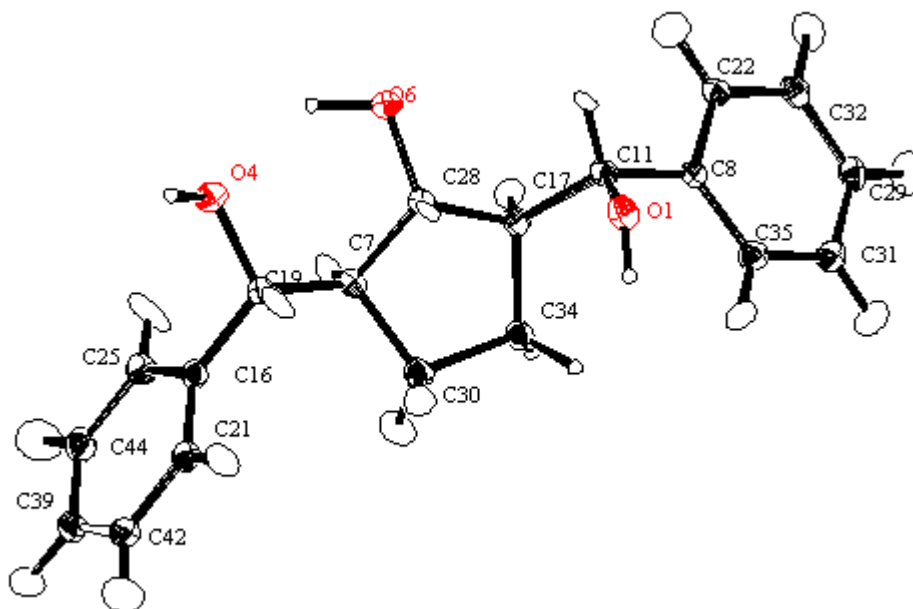
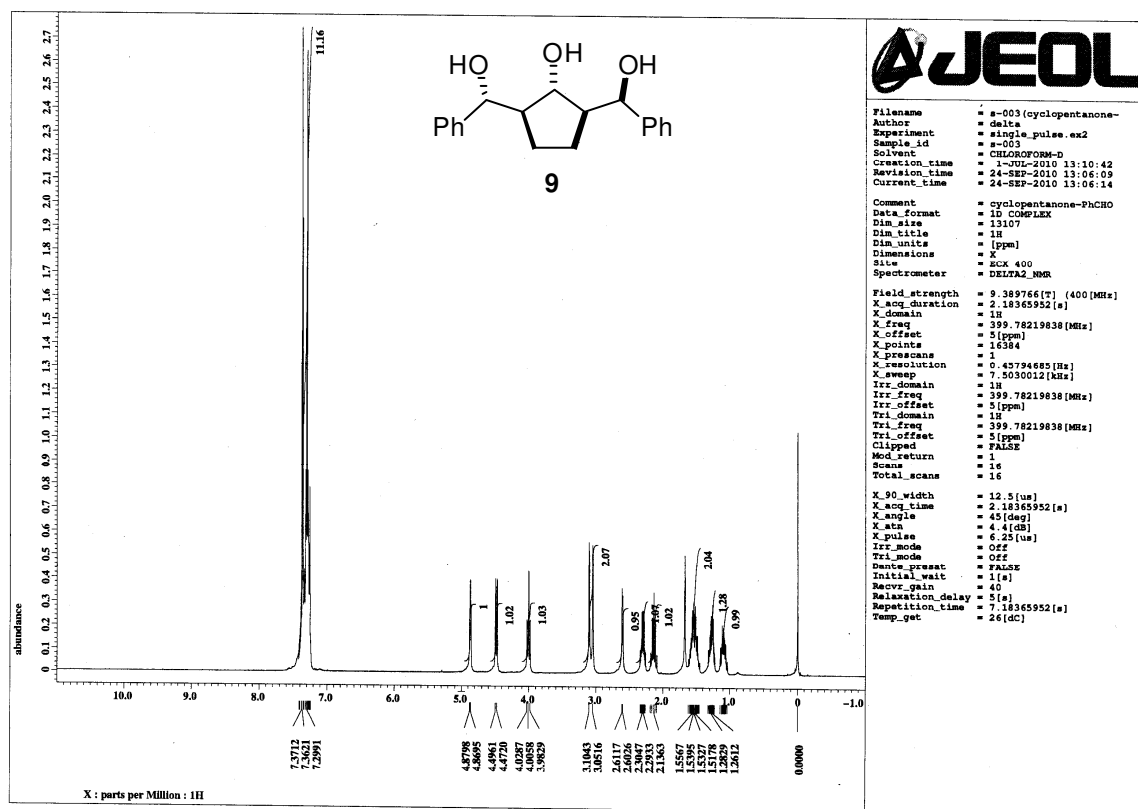
10. ^{13}C NMR chart of new compounds







11. ^1H NMR and X-ray structure report for 14



A. Crystal Data

Empirical Formula	C ₁₉ H ₂₂ O ₃
Formula Weight	298.38
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.30 X 0.30 X 0.30 mm
Crystal System	triclinic
Lattice Type	Primitive
Indexing Images	3 oscillations @ 60.0 seconds
Detector Position	127.40 mm
Pixel Size	0.100 mm
Lattice Parameters	a = 5.652(8) Å b = 13.457(8) Å c = 21.67(2) Å α = 82.23(4) ° β = 89.71(13) ° γ = 77.94(5) ° V = 1596.3(30) Å ³
Space Group	P-1 (#2)
Z value	4
D _{calc}	1.241 g/cm ³
F ₀₀₀	640.00
m(MoK α)	0.825 cm ⁻¹

B. Intensity Measurements

Diffractometer	Rigaku RAXIS-RAPID
Radiation	MoK α (λ = 0.71075 Å) graphite monochromated
Detector Aperture	280 mm x 256 mm
Data Images	44 exposures
ω oscillation Range (χ =45.0, ϕ =0.0)	130.0 - 190.0°
Exposure Rate	50.0 sec./°
ω oscillation Range (χ =45.0, ϕ =180.0)	0.0 - 160.0°
Exposure Rate	50.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
2 θ _{max}	54.9°
No. of Reflections Measured	Total: 15503 Unique: 7125 (R_{int} = 0.033)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.723 - 0.976)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F ²
Function Minimized	$\sum w (F_o^2 - F_c^2)^2$
Least Squares Weights	1/[0.0017F _o ² +1.0000 σ (F _o ²)]/(4F _o ²)
2 θ _{max} cutoff	54.9°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>2.00 σ (I))	6992
No. Variables	441
Reflection/Parameter Ratio	15.85
Residuals: R1 (I>2.00 σ (I))	0.0446
Residuals: wR2 (I>2.00 σ (I))	0.1180
Goodness of Fit Indicator	1.006
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.33 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.49 e ⁻ /Å ³