

## Supporting Information

for

### **Enantioselective Conjugate Addition of Dialkylzinc and Diphenylzinc to Enones Catalyzed by a Copper(I)-Chiral Binaphthylthiophosphoramidate or Binaphthylselenophosphoramidate Ligand System**

Min Shi\* and Chun-Jiang Wang

*State Key Laboratory of Organometallic Chemistry,  
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences,  
354 Fenglin Lu, Shanghai 200032 China, mshi@pub.sioc.ac.cn  
Fax: 86-21-64166128*

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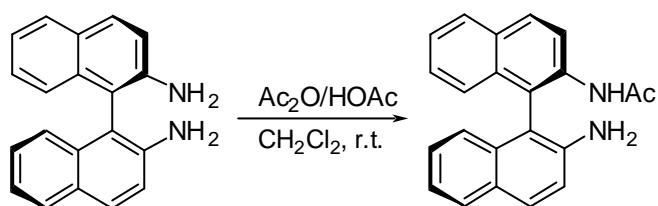
**General Remarks.** All reactions were conducted in oven (135 °C) and flame-dried glassware under an inert atmosphere of dry argon or nitrogen. Toluene was distilled from sodium metal; dichloromethane was distilled from calcium hydride; diethyl ether, tetrahydrofuran and benzene were distilled from sodium metal/benzophenone ketyl. <sup>1</sup>H NMR, <sup>13</sup>C NMR, and <sup>31</sup>P NMR spectra were recorded at 300, 75 and 121 MHz, respectively. Mass spectra were recorded by the EI method. All of the solid compounds reported in this paper gave satisfactory CHN microanalyses. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel coated plates. *P-Arus reagent* [prepared by dissolving *p*-anisaldehyde (10 mL), acetic acid (7.5 mL), and concentrated H<sub>2</sub>SO<sub>4</sub> (25 mL) in 95% ethanol (500 mL)] was used for those substrates that do not have absorption in UV region. Flash Column Chromatography was carried out using 200-300 mesh silica gel at increased pressure. Enantiomeric ratios were determined by chiral GLC or HPLC analysis. The absolute configuration was assigned by comparison the optical rotation with those reported date.<sup>[1]</sup> Racemic products were synthesized according to the literatures.<sup>[2,3]</sup> Melting points are uncorrected.

1) (a) S. J. Degrado, H. Mizutani, A. H. Hoveyda, *J. Am. Chem. Soc.* **2001**, *123*, 755-756; (b) X. Q. Hu, H. L. Chen, X. M. Zhang, *Acta. Chmica. Sinic.* **2000**, *58*, 1163-1167.

2) (a) A. Alexakis, J. Vastra, P. Mangeney, *Tetrahedron Lett.* **1997**, *38*, 7745-7748; (b) E. Della, W. Janowski, *Aust. J. Chem. Soc.* **1999**, *52*, 367-372.

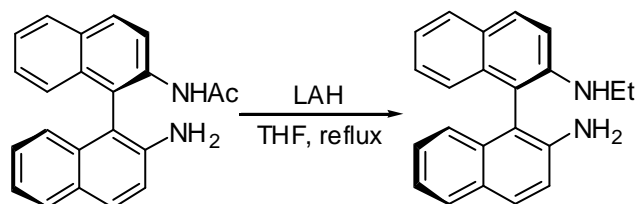
3) Y. Wang, J. A. Gladysz, *J. Org. Chem.* **1995**, *60*, 903-909.

**The synthesis of (*R*)-(+)-*N*-acetyl-1,1'-binaphthyl-2,2'-diamine.**



Acetic anhydride (208  $\mu$ L, 2.2 mmol) was added to a mixture of (*R*)-(+)-binaphthyldiamine (568 mg, 2 mmol), acetic acid (1.2 mL, 20 mmol) and dichloromethane (20.0 mL) with ice-cooling. The mixture was stirred at room temperature overnight, and 2.0 N NaOH was added until pH > 7. After extraction with dichloromethane, the combined organic layers were dried over MgSO<sub>4</sub>. The residue obtained upon evaporation was purified by column chromatography to afford the product as a colorless solid (509 mg, 78%). mp: 240-241 °C;  $[\alpha]_{\text{D}}^{25} = +40.0$  ( $c = 0.55$ , CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz)  $\delta$  = 1.85 (s, 3H, Me), 6.91-7.42 (m, 8H, ArH and NHCO), 7.81-8.03 (m, 4H, ArH), 8.58 (d,  $J = 9.0$  Hz, 2H, ArH); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, TMS, 75 MHz)  $\delta$  = 23.98, 110.31, 119.39, 121.93, 123.77, 124.48, 125.01, 125.03, 125.68, 126.18, 126.92, 127.91, 128.66, 128.71, 129.97, 130.03, 132.06, 133.14, 134.51, 136.16, 144.98, 169.53; IR (KBr)  $\nu$  = 3400, 1675, 1595, 1500, 1445, 1270, 1040, 965, 670 cm<sup>-1</sup>; MS (EI)  $m/z$  326 ([M]<sup>+</sup>, 43.47), 284 ([M-42]<sup>+</sup>, 25.13), 267 ([M-59]<sup>+</sup>, 100); Anal. Calcd. for C<sub>22</sub>H<sub>18</sub>ON<sub>2</sub> requires: C 80.98, H 5.52, N 8.59%; found: C 80.66, H 5.61, N 8.48%.

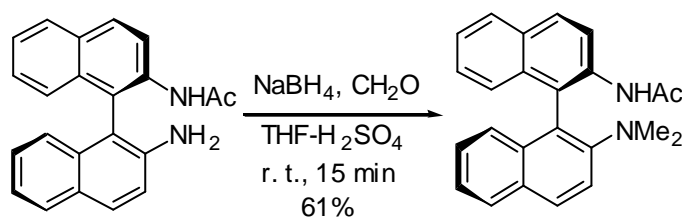
**The synthesis of (*R*)-(+)-*N*-ethyl-1,1'-binaphthyl-2,2'-diamine.**



To a stirred suspension of LiAlH<sub>4</sub> (280 mg, 7.37 mmol) in 30.0 mL of anhydrous THF was added dropwise a solution of (*R*)-(+)-*N*-acetyl-1,1'-binaphthyl-2,2'-diamine (509 mg, 1.56 mmol) in 10.0 mL of THF. The mixture was heated under reflux for 4 h. The reaction mixture was cooled in an ice-bath and the remaining hydride was carefully quenched by dropwise addition of water (5.0 mL) and then 10% NaOH (5.0 mL). A white precipitate was filtered off

and thoroughly washed with ethyl acetate. The combined filtrate and ethyl acetate washings were washed with brine and dried over  $\text{MgSO}_4$ . After the solvents were evaporated under reduced pressure, the product was purified by flash chromatography to afford the product (470 mg, 97%) as a colorless solid. m.p. 123-124 °C;  $[\alpha]_{\text{D}}^{25} = +175.2$  ( $c = 0.63$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\delta = 0.99$  (t,  $J = 7.5$  Hz, 3H, Me), 3.18 (q,  $J = 7.5$  Hz, 2H,  $\text{CH}_2$ ), 3.60 (br, 3H, amino-H), 6.96-7.25 (m, 8H, ArH), 7.75-7.87 (m, 4H, ArH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\delta = 15.57, 39.02, 112.62, 112.84, 114.69, 118.71, 122.28, 122.79, 124.15, 124.36, 127.09, 127.19, 128.03, 128.50, 128.54, 128.80, 129.86, 129.96, 134.01, 134.30, 143.35, 144.73$ ; IR(KBr)  $\nu = 3385, 3060, 2985, 2910, 1645, 1598, 1510, 1425, 1350, 1150, 915, 820$   $\text{cm}^{-1}$ ; MS (EI)  $m/z$  313 ( $[\text{M}+1]^+$ , 100.00), 297 ( $[\text{M}-15]^+$ , 34.21), 280 ( $[\text{M}-32]^+$ , 42.91), 267 ( $[\text{M}-45]^+$ , 25.99); Anal. Calcd. for  $\text{C}_{22}\text{H}_{20}\text{N}_2$  requires: C 84.62, H 6.41, N 8.97%; found: C 84.53, H 6.56, N 8.95%.

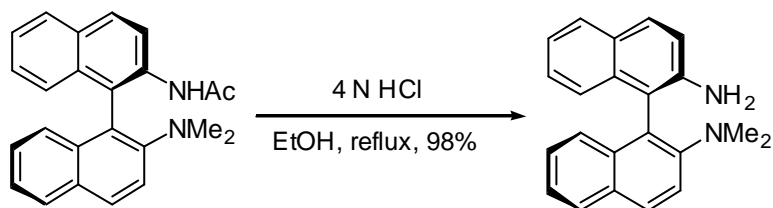
#### The synthesis of (*R*)-(+)-*N*-acetyl-*N*',*N*'-dimethyl-1,1'-binaphthyl-2,2'-diamine.



A solution of (*R*)-(+)-*N*-acetyl-1,1'-binaphthyl-2,2'-diamine (163 mg, 0.5 mmol) in THF (10 mL) and  $\text{NaBH}_4$  (133 mg, 3.5 mmol) were simultaneously added to a stirred solution of 20%  $\text{H}_2\text{SO}_4$  (0.5 mL) and 40% formaldehyde aqueous solution (0.5 mL, 6.0 mmol) in THF (20 mL) with ice-cooling over a period of 15 min. The mixture was stirred for an additional hour and then 1.0 N  $\text{NaOH}$  was added until  $\text{pH} > 7$ . After extraction with ethyl acetate, the combined organic layers were dried over  $\text{MgSO}_4$ . The residue obtained upon evaporation was purified by column chromatography to afford the product as a colorless solid (108 mg, 61%). m.p. 187-189 °C;  $[\alpha]_{\text{D}}^{25} = -244.5$  ( $c = 0.58$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\delta = 1.88$  (s, 3H, Me), 2.58 (s, 2Me), 6.95 (d,  $J = 8.7$  Hz, 1H, ArH), 7.12-7.55 (m, 6H, ArH), 7.84-7.80 (m, 4H, ArH), 8.49 (d,  $J = 9.0$  Hz, 1H, ArH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\delta = 24.85, 43.63, 119.02, 121.81, 124.30, 124.62, 125.02, 125.54, 126.64, 126.67, 126.74, 127.04, 128.17, 128.41, 128.84, 129.90, 130.36, 131.30, 133.62, 133.96, 134.12, 149.88, 168.52$ ; IR (KBr)  $\nu = 3402, 1684, 1596, 1501, 1427, 929, 669$   $\text{cm}^{-1}$ ; MS (EI)  $m/z$  354 ( $[\text{M}]^+$ , 58.79), 311 ( $[\text{M}-43]^+$ , 9.83), 296 ( $[\text{M}-58]^+$ , 17.65), 281 ( $[\text{M}-73]^+$ , 36.62); Anal. Calcd. for  $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}$  requires: C

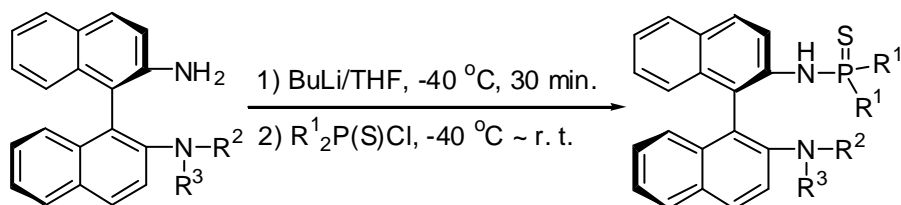
81.36, H 6.21, N 7.91%; found: C 81.40, H 6.39, N 7.80%.

**The synthesis of (*R*)-(+)-*N,N*-dimethyl-1,1'-binaphthyl-2,2'-diamine.**



(*R*)-(+)-*N*-Acetyl-*N'*,*N'*-dimethyl-1,1'-binaphthyl-2,2'-diamine (300 mg, 0.85 mmol) was added to a stirred solution of ethanol (25.0 mL) and 4.0 N HCl (9.0 mL), the mixture was heated under reflux for 12 h. After cooling to ambient temperature and removal of the ethanol *in vacuo*, 2.0 N NaOH was added until pH > 7. After extraction with dichloromethane, the combined organic layers were dried over MgSO<sub>4</sub>. The residue obtained upon evaporation was purified by column chromatography to afford the product as a colorless solid (262 mg, 99%). m.p. 116-118 °C; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +17.4 (*c* = 2.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz) **d** = 2.59 (s, 2Me), 7.0-7.29 (m, 7H, ArH), 7.47 (d, *J* = 9.0 Hz, 1H, ArH), 7.74-7.91 (m, 4H, ArH); <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz) **d** = 38.47, 111.70, 113.46, 114.65, 117.12, 117.17, 118.75, 119.91, 119.99, 121.36, 121.62, 122.98, 123.03, 123.32, 123.91, 124.28, 124.90, 128.71, 129.27, 136.94, 145.23; IR (KBr) **n** = 3395, 2794, 1621, 1507, 1426, 1380, 1143, 989, 930, 625 cm<sup>-1</sup>; MS (EI) *m/z* 312 ([M]<sup>+</sup>, 100.00), 297 ([M-15]<sup>+</sup>, 4.57), 280 ([M-32]<sup>+</sup>, 38.29), 267 ([M-45]<sup>+</sup>, 47.97); Anal. Calcd. for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub> requires: C 84.62, H 6.41, N 8.97%; found: C 84.70, H 6.55, N 8.92%.

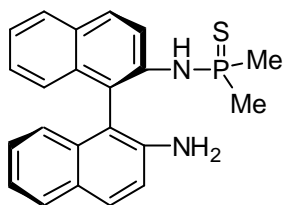
**The Representative Experimental Procedure for the Synthesis of Ligands 1-10.**



To a solution of (*R*)-(+)-*N*-ethyl-1,1'-binaphthyl-2,2'-diamine (200 mg, 0.64 mmol) in anhydrous THF (10.0 mL) was added dropwise *n*-butyllithium (1.12 mL, 1.8 mmol, 1.6 M solution in hexane) at -40 °C over 40 min, and the reaction mixture was stirred for 1 h at the same temperature. Then, diphenylthiophosphinic chloride (500 mg, 2.0 mmol) in 5.0 mL of

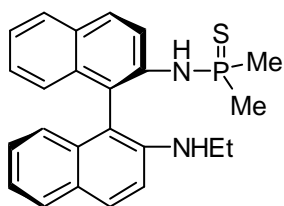
THF was added dropwise and the reaction solution was slowly allowed to warm to room temperature. After 2 h, the THF was removed *in vacuo*. The residue was purified by an alumina column chromatography to give the ligand (**L4**) as a colorless solid (314 mg, 93%).

### Ligand 1 (L1)



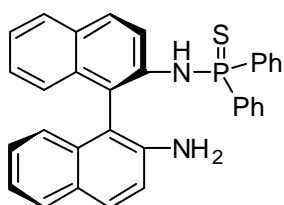
Yield 95%; m.p. 180-182 °C;  $[\alpha]_{\text{D}}^{25} = +65.8$  ( $c = 0.6$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\delta = 1.76$  (d,  $J = 13.5$  Hz, 3H, Me), 1.88 (d,  $J = 13.5$  Hz, 3H, Me), 4.61 (d,  $J = 6.6$  Hz, 1H, NH), 6.96 (d,  $J = 8.1$  Hz, 1H, ArH), 7.13-7.40 (m, 6H, ArH), 7.80-7.99 (m, 5H, ArH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\delta = 24.01$  (d,  $J = 68.6$  Hz), 24.60 (d,  $J = 68.6$  Hz), 110.16, 118.08, 118.97, 119.03, 122.54, 123.57, 124.25, 124.91, 126.95, 127.07, 128.09, 128.19, 128.21, 129.15, 129.97, 130.26, 133.04, 133.58, 137.62, 142.86;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 121 MHz, 85% $\text{H}_3\text{PO}_4$ )  $\delta = +56.96$ ; R (KBr)  $\tilde{\nu} = 3350, 1620, 1514, 1476, 1422, 927, 626$   $\text{cm}^{-1}$ ; MS (EI)  $m/z$  376 ( $[\text{M}]^+$ , 49.66), 284 ( $[\text{M}-92]^+$ , 16.13), 267 ( $[\text{M}-109]^+$ , 100); Anal. Calcd. for  $\text{C}_{22}\text{H}_{21}\text{N}_2\text{PS}$  requires: C 70.19, H 5.62, N 7.44%; found: C 69.84, H 5.82, N 7.65%.

### Ligand 2 (L2)



Yield 90%; m.p. 68-70 °C;  $[\alpha]_{\text{D}}^{25} = +30.4$  ( $c = 1.67$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\delta = 1.09$  (t,  $J = 7.2$  Hz, 3H, Me), 1.73 (d,  $J = 12.9$  Hz, 3H, Me), 1.89 (d,  $J = 12.9$  Hz, 3H, Me), 3.25 (q,  $J = 7.2$  Hz, 2H,  $\text{CH}_2$ ), 3.62 (br, 1H, NH), 4.61 (d,  $J = 7.2$  Hz, 1H, NH), 6.86 (d,  $J = 9.3$  Hz, 1H, ArH), 7.01-7.40 (m, 6H, ArH), 7.79-7.99 (m, 5H, ArH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\delta = 15.12, 23.96$  (d,  $J = 68.9$  Hz), 24.81 (d,  $J = 68.6$  Hz), 38.29, 109.60, 113.68, 118.89, 118.94, 119.61, 121.91, 123.35, 124.22, 124.94, 126.89, 126.94, 127.22, 128.19, 129.13, 129.99, 130.42, 133.26, 133.66, 137.83, 144.34;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 121 MHz, 85% $\text{H}_3\text{PO}_4$ )  $\delta = +56.68$ ; IR (KBr)  $\tilde{\nu} = 3345, 1620, 1598, 1514, 1427, 1345, 994, 926, 669$   $\text{cm}^{-1}$ ; MS (EI)  $m/z$  404 ( $[\text{M}]^+$ , 100.00), 389 ( $[\text{M}-15]^+$ , 5.87), 267 ( $[\text{M}-137]^+$ , 25.94); Anal. Calcd. for  $\text{C}_{24}\text{H}_{25}\text{N}_2\text{PS}$  requires: C 71.29, H 6.19, N 6.93%; found: C 71.65, H 6.57, N 6.49%.

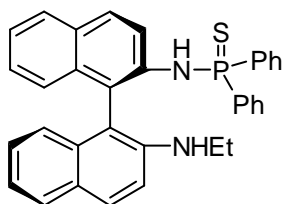
### Ligand 3 (L3)



Yield 92%; m.p. 175-177 °C;  $[\alpha]_{\text{D}}^{25} = -4.0$  ( $c = 1.20$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\delta = 4.10$  (s, br, 2H, NH), 5.12 (d,  $J =$

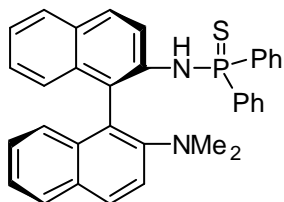
7.4 Hz, 1H, NH), 7.0-7.50 (m, 10H, ArH), 7.50-7.70 (m, 4H, ArH), 7.70-8.0 (m, 8H, ArH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\delta$  = 110.39, 118.25 (d,  $J$  = 4.4 Hz), 119.28 (d,  $J$  = 4.8 Hz), 119.84 (d,  $J$  = 8.9 Hz), 122.67, 124.00, 124.54 (d,  $J$  = 51.7 Hz), 127.12 (d,  $J$  = 27.8 Hz), 127.26, 128.28, 128.33, 128.52, 128.71, 128.95, 130.01 (d,  $J$  = 27.9 Hz), 130.80, 130.95, 131.62 (d,  $J$  = 11.5 Hz), 131.82, 131.86, 131.90, 133.15, 133.41 (d,  $J$  = 51.5 Hz), 133.57, 134.52, 134.93, 137.35, 143.16;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 121 MHz, 85%  $\text{H}_3\text{PO}_4$ )  $\delta$  = +53.37; IR (KBr)  $\nu$  = 3350, 1625, 1514, 1477, 1438, 1340, 929, 634  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  500 ( $[\text{M}]^+$ , 3.6); Anal. Calcd. for  $\text{C}_{32}\text{H}_{25}\text{N}_2\text{PS}$  requires: C 76.78, H 5.03, N 5.60%; found: C 76.65, H 5.07, N 5.74%.

#### Ligand 4 (L4)



Yield 93%; m.p. 78-80 °C;  $[\alpha]_{\text{D}}^{25}$  = -47.5 ( $c$  = 0.905,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\delta$  = 1.11 (t,  $J$  = 7.2 Hz, 3H, Me), 3.27 (q,  $J$  = 7.2 Hz, 2H,  $\text{CH}_2$ ), 3.78 (br, 1H, NH), 5.14 (d,  $J$  = 7.5 Hz, 1H, NH), 6.95-7.57 (m, 17 H, ArH), 7.75-7.91 (m, 5 H, ArH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\delta$  = 15.00, 38.31, 109.70, 113.64, 119.11 (d,  $J$  = 4.2 Hz), 119.46 (d,  $J$  = 7.9 Hz), 121.87, 123.63, 124.40 (d,  $J$  = 57.9 Hz), 126.73, 126.95, 127.26, 128.35, 128.36 (d,  $J$  = 28.8 Hz), 128.37, 128.52, 128.80, 130.14 (d,  $J$  = 51.6 Hz), 130.46 (d,  $J$  = 24.7 Hz), 131.48, 131.63, 131.67, 131.70, 131.74, 133.14, 133.31 (d,  $J$  = 38.3 Hz), 133.70, 134.68 (d,  $J$  = 37.1 Hz), 137.46, 144.37;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 121 MHz, 85%  $\text{H}_3\text{PO}_4$ )  $\delta$  = +53.28; IR (KBr)  $\nu$  = 1625, 1600, 1515, 1474, 1426, 1055, 898  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  528 ( $[\text{M}]^+$ , 2.13), 311 ( $[\text{M}-217]^+$ , 1.47), 267 ( $[\text{M}-261]^+$ , 11.27); Anal. Calcd. for  $\text{C}_{34}\text{H}_{29}\text{N}_2\text{PS}$  requires: C 77.27, H 5.49, N 5.30%; found: C 77.52, H 5.89, N 5.17%.

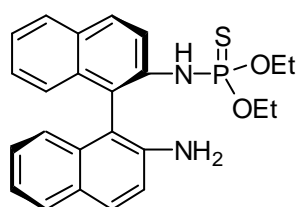
#### Ligand 5 (L5)



Yield 51%; m.p. 62-64 °C;  $[\alpha]_{\text{D}}^{25}$  = -180.1 ( $c$  = 1.83,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\delta$  = 2.53 (s, 6H, 2Me), 5.88 (d,  $J$  = 9.0 Hz, NH), 7.0 (d,  $J$  = 8.7 Hz, 1H, Ar), 7.14-7.43 (m, 12H, ArH), 7.56-7.75 (m, 5H, ArH), 7.79-7.98 (m, 4H, ArH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\delta$  = 43.27, 118.47, 120.41 (d,  $J$  = 4.8 Hz), 121.81, 123.92 (d,  $J$  = 2.6 Hz), 125.75, 126.56 (d,  $J$  = 8.3 Hz), 125.97, 128.34 (d,  $J$  = 18.6 Hz), 128.36, 128.37 (d,  $J$  = 24.0 Hz), 128.38 (d,  $J$  = 47.7 Hz), 128.41, 129.67, 129.84 (d,  $J$  = 2.8 Hz), 131.04, 131.20, 131.48, 131.52, 131.57, 131.68, 131.72, 132.99, 133.88, 134.03, 134.04 (d,  $J$  = 46.1 Hz), 135.25,

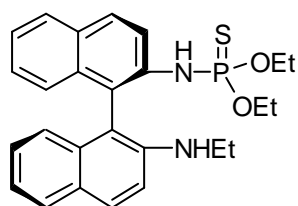
136.59, 149.87;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 121 MHz, 85% $\text{H}_3\text{PO}_4$ )  $\delta$  = +51.47; IR (KBr)  $\nu$  = 3350, 3054, 1619, 1595, 1507, 1438, 1422, 1338, 1219, 1153, 896, 817  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  528 ( $[\text{M}]^+$ , 46.79), 311 ( $[\text{M}-217]^+$ , 35.99), 267 ( $[\text{M}-261]^+$ , 100.00); Anal. Calcd. for  $\text{C}_{34}\text{H}_{29}\text{N}_2\text{PS}$  requires: C 77.27, H 5.49, N 5.30%; found: C 77.29, H 5.68, N 5.12%.

### Ligand 6 (L6)

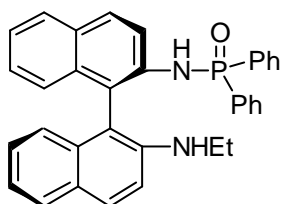


Yield 90%; m.p. 61-63 °C;  $[\alpha]_{\text{D}}^{25}$  = +41.3 ( $c$  = 2.07,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\delta$  = 1.28 (m, 6H, 2Me), 3.69 (br, 2H,  $\text{NH}_2$ ), 3.97-4.17 (m, 4H, 2 $\text{CH}_2$ ), 5.32 (d,  $J$  = 14.1 Hz, 1H, NH), 6.91 (d,  $J$  = 8.1 Hz, 1H, ArH), 7.12-7.37 (m, 6H, ArH), 7.80-7.96 (m, 5H, ArH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\delta$  = 15.61 (d,  $J$  = 8.4 Hz), 15.64 (d,  $J$  = 7.4 Hz), 63.19 (d,  $J$  = 4.1 Hz), 63.23 (d,  $J$  = 4.6 Hz), 110.08, 117.92, 117.96, 118.00, 118.04, 118.07, 122.44, 123.29, 124.12, 124.93, 126.84, 127.90, 128.15, 129.17, 129.75, 130.23, 132.83, 133.48, 136.31, 142.70;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 121 MHz, 85% $\text{H}_3\text{PO}_4$ )  $\delta$  = +66.63; IR (KBr)  $\nu$  = 3020, 1625, 1600, 1521, 1750, 1423, 1030, 929, 895  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  436 ( $[\text{M}]^+$ , 77.63), 284 ( $[\text{M}-152]^+$ , 52.04), 267 ( $[\text{M}-169]^+$ , 100); Anal. Calcd. for  $\text{C}_{24}\text{H}_{25}\text{N}_2\text{O}_2\text{PS}$  requires: C 66.10, H 5.73, N 6.42%; found: C 65.91, H 6.03, N 6.51%.

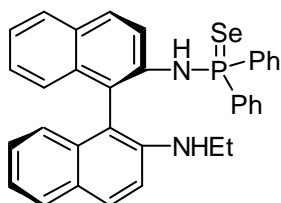
### Ligand 7 (L7)



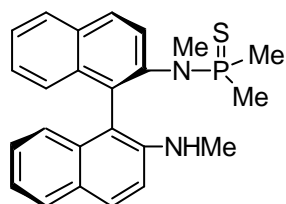
Yield 97%; Yellowish oil,  $[\alpha]_{\text{D}}^{25}$  = +13.7 ( $c$  = 2.57,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\delta$  = 1.06 (t,  $J$  = 6.9 Hz, Me), 1.28 (m, 6H, 2Me), 3.24 (q,  $J$  = 6.9 Hz,  $\text{CH}_2$ ), 3.51 (br, 1 H, NH), 3.95-4.13 (m, 4H, 2 $\text{CH}_2$ ), 5.31 (d,  $J$  = 13.2 Hz, 1H, NH), 6.81 (d,  $J$  = 8.4 Hz, 1H, ArH), 7.08-7.36 (m, 6H, ArH), 7.78-7.96 (m, 5H, ArH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\delta$  = 15.10, 15.73 (d,  $J$  = 7.9 Hz), 15.77 (d,  $J$  = 7.9 Hz), 38.32, 63.27 (d,  $J$  = 4.8 Hz), 63.30 (d,  $J$  = 4.2 Hz), 109.70, 113.88, 118.10, 118.13, 121.91, 123.20, 124.21, 125.13, 126.80, 126.92, 127.41, 127.99, 128.23, 129.28, 129.92, 130.46, 133.22, 133.65, 136.64, 144.38;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 121 MHz, 85% $\text{H}_3\text{PO}_4$ )  $\delta$  = +66.60; IR (KBr)  $\nu$  = 3360, 3020, 1630, 1598, 1514, 1476, 1427, 1346, 1022, 964, 801  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  464 ( $[\text{M}]^+$ , 100), 311 ( $[\text{M}-153]^+$ , 25.62), 267 ( $[\text{M}-197]^+$ , 70.09); Anal. Calcd. for  $\text{C}_{26}\text{H}_{29}\text{N}_2\text{O}_2\text{PS}$  requires: C 67.22, H 6.29, N 6.03%; found: C 67.36, H 6.45, N 5.75%; HRMS Calcd.  $\text{C}_{26}\text{H}_{30}\text{N}_2\text{O}_2\text{SP}$  ( $\text{M}^++1$ ): 465.1756, found: 465.1760.

**Ligand 8 (L8)**

Yield 99%; m.p. 57-58 °C;  $[\alpha]_{\text{D}}^{25} = -149.1$  ( $c = 0.9$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\delta = 1.07$  (t,  $J = 7.2$  Hz, 3H, Me), 3.25 (q,  $J = 7.2$  Hz, 2H,  $\text{CH}_2$ ), 3.75 (br, 1 H, NH), 5.46 (d,  $J = 10.8$  Hz, 1H, NH), 6.98-7.49 (m, 15 H, ArH), 7.64-7.94 (m, 7H, ArH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\delta = 14.77$ , 38.48, 113.90, 118.40 (d,  $J = 8.7$  Hz), 119.13 (d,  $J = 4.4$  Hz), 122.16 (d,  $J = 3.3$  Hz), 124.11, 124.32 (d,  $J = 84.3$  Hz), 126.97 (d,  $J = 5.9$  Hz), 127.54, 127.63, 128.25, 128.33, 128.98 (d,  $J = 71.4$  Hz), 128.66, 128.68, 129.41, 129.88, 130.35, 130.96, 131.19 (d,  $J = 10.3$  Hz), 131.50, 131.89, 131.98, 132.02, 132.68, 133.21, 133.52, 137.66, 144.32 (d,  $J = 2.3$  Hz);  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 121 MHz, 85%  $\text{H}_3\text{PO}_4$ )  $\delta = +17.89$ ; IR (KBr)  $\nu = 3350$ , 3020, 1619, 1598, 1517, 1475, 1424, 1378, 1216, 1045, 929, 811  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  512 ( $[\text{M}]^+$ , 53.62), 497 ( $[\text{M}-15]^+$ , 12.50), 295 ( $[\text{M}-217]^+$ , 92.79), 280 ( $[\text{M}-232]^+$ , 39.11); Anal. Calcd. for  $\text{C}_{34}\text{H}_{29}\text{N}_2\text{OP}$  requires: C 79.67, H 5.70, N 5.47%; found: C 79.33, H 6.03, N 5.07%; HRMS Calcd.  $\text{C}_{34}\text{H}_{29}\text{N}_2\text{OP}$  ( $\text{M}^+$ ): 512.2017, found: 512.2061.

**Ligand 9 (L9)**

Yield: 92%; m.p. 116-118 °C;  $[\alpha]_{\text{D}}^{25} = -28.1$  ( $c = 1.2$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\delta = 1.13$  (t,  $J = 7.2$  Hz, 3H, Me), 3.28 (q,  $J = 7.2$  Hz, 2H,  $\text{CH}_2$ ), 5.02 (d,  $J = 6.3$  Hz, 1H, NH), 7.22-7.51 (m, 17H, ArH), 7.76-7.90 (m, 5H, ArH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\delta = 15.15$ , 38.37, 109.44, 113.60, 119.41 (d,  $J = 5.1$  Hz), 120.05 (d,  $J = 8.0$  Hz), 121.85, 123.70, 124.15, 124.87, 127.01 (d,  $J = 34.5$  Hz), 127.03, 128.21 (d,  $J = 3.7$  Hz), 128.42, 128.60, 128.64 (d,  $J = 6.7$  Hz), 129.96, 130.61 (d,  $J = 33.9$  Hz), 130.68, 131.76, 131.81, 131.89, 131.92, 131.94, 133.10 (d,  $J = 47.0$  Hz), 133.18, 133.84, 134.37 (d,  $J = 46.5$  Hz), 137.60, 144.44;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 121 MHz, 85%  $\text{H}_3\text{PO}_4$ )  $\delta = +50.40$ ; IR (KBr)  $\nu = 3324$ , 3053, 2968, 1618, 1598, 1509, 1467, 1437, 1389, 1338, 1304, 1270, 1153, 1102, 991, 836, 809  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  575 ( $[\text{M}]^+$ , 14.42), 496 ( $[\text{M}-79]^+$ , 50.96), 311 ( $[\text{M}-264]^+$ , 87.08), 267 ( $[\text{M}-308]^+$ , 100.00); Anal. Calcd. for  $\text{C}_{34}\text{H}_{29}\text{N}_2\text{PS} \cdot \text{CH}_2\text{Cl}_2$  requires: C 63.64, H 4.70, N 4.24%; found: C 63.68, H 4.69, N 4.20%.

**Ligand 10 (L10)**

Yield: 81%; m.p. 120-122 °C;  $[\alpha]_D^{25} = -19.2$  ( $c = 0.55$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\delta$  1.44 (d,  $J = 12.6$  Hz, 3H, Me), 1.74 (d,  $J = 12.6$  Hz, 3H, Me), 2.58 (d,  $J = 10.8$  Hz, 3H,  $\text{CH}_3$ ), 2.82 (d,  $J = 4.8$  Hz, 3H,  $\text{CH}_3$ ), 3.82 (br, 1H, NH), 6.82 (d,  $J = 9.3$  Hz, 1H, ArH), 7.12-7.28 (m, 5H, ArH), 7.48 (m, 1H, ArH), 7.77-7.98 (m, 5H, ArH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\delta$  22.01 (d,  $J = 64.4$  Hz), 22.37 (d,  $J = 64.4$  Hz), 30.56, 36.87 (d,  $J = 14.1$  Hz), 112.82, 113.30, 121.26, 123.99, 125.91, 126.01, 126.08, 126.70, 126.80, 128.02, 128.04, 128.31, 128.74, 129.49, 132.47, 132.49, 133.47, 133.66, 143.41, 144.64;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ , 121 MHz, 85%  $\text{H}_3\text{PO}_4$ )  $\delta$  = +67.05; IR (KBr)  $\nu$  = 3350, 3025, 2817, 1617, 1598, 1499, 1422, 1344, 1297, 1170, 1153, 1054, 968, 943, 913  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  404 ( $[\text{M}]^+$ , 100.00), 311 ( $[\text{M}-93]^+$ , 28.15), 281 ( $[\text{M}-123]^+$ , 29.11), 265 ( $[\text{M}-139]^+$ , 4.82); HRMS Calcd.  $\text{C}_{34}\text{H}_{29}\text{N}_2\text{OP}$  ( $[\text{M}]^+$ ): 404.1476, found: 404.1440; Anal. Calcd. for  $\text{C}_{24}\text{H}_{25}\text{N}_2\text{PS}$  requires: C 71.29, H 6.19, N 6.93%; found: C 71.10, H 6.27, N 6.78%.

**General Procedure for the Cu-catalyzed Conjugate Addition and the Recovery of Chiral Ligand:**

A solution of  $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$  (4.7 mg, 0.015 mmol) and ligand **4** (16.0 mg, 0.03 mmol) in dry toluene (3 mL) was stirred for 1 h at room temperature under an argon atmosphere. Cyclohexenone **1** (48  $\mu\text{L}$ , 0.5 mmol) was added and the solution was stirred for a further 10 min, then  $\text{Et}_2\text{Zn}$  (0.75 mL, 0.75 mmol, 1.0 M solution in hexane) was added dropwise within 30 seconds. The resulting mixture was stirred for about 30 min, 1.0 N HCl (4.0 mL) was added. After extraction with ether (3 x 5.0 mL), the combined organic layers were dried over anhydrous  $\text{MgSO}_4$ . The residue obtained upon removal of volatiles in vacuo was purified by a flash column chromatography on silica gel (eluent: pentane/ether = 30/1) to afford (*R*)-(+)-ethylcyclohexanone **2** (59 mg, 94%) and to recover the ligand **L4** (13 mg, 82%).

**(*R*)-(+)-3-Ethylcyclohexanone 2 (Table 2, Entry 10).** 59 mg, 94%.  $[\alpha]_D^{25} = +10.5$  ( $c = 0.94$ ,  $\text{CHCl}_3$ ) for 97% ee;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\delta$  = 0.90 (t,  $J = 7.6$  Hz, Me), 1.44-1.25 (m, 3H), 1.58-1.70 (m, 2H), 1.85-2.10 (m, 3H), 2.20-2.46 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\delta$  = 10.76, 24.89, 28.88, 30.46, 40.37, 41.05, 47.39, 211.32; Chiraldex G-BP column, 20 m x 0.25 mm, 50 °C (2 min), 50-112 °C, 5 °C/min, 112 °C (2 min) 10.0 psi  $\text{N}_2$ ,  $t_R = 12.272$  min,  $t_S = 12.535$  min.

**(R)-(+)-3-Ethylcycloheptanone 4 (Table 3, Entry 2).** 67 mg, 96%.  $[\alpha]_{\text{D}}^{25} = +57.0$  ( $c = 1.55$ ,  $\text{CHCl}_3$ ) for 97% ee;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\mathbf{d} = 0.91$  (t,  $J = 7.5$  Hz, Me), 1.25-1.45 (m, 4H), 1.51-1.70 (m, 2H), 1.80-1.95 (m, 3H), 2.35-2.52 (m, 4H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\mathbf{d} = 11.35, 24.36, 28.51, 30.00, 36.42, 37.63, 43.86, 49.56, 214.86$ ; Chiraldex G-BP column, 20 m x 0.25 mm, 90 °C (30 min), 10.0 psi  $\text{N}_2$ ,  $t_{\text{R}} = 9.288$  min,  $t_{\text{S}} = 9.558$  min.

**(R)-(+)-3-Ethylcyclopentanone 6 (Table 4, Entry 3).** 42 mg, 75%.  $[\alpha]_{\text{D}}^{25} = +96.2$  ( $c = 1.60$ ,  $\text{CHCl}_3$ ) for 98% ee;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\mathbf{d} = 0.95$  (t,  $J = 7.5$  Hz, Me), 1.41-1.58 (m, 3H), 1.75-1.85 (m, 1H), 2.10-2.44 (m, 5H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\mathbf{d} = 12.09, 28.28, 28.30, 38.36, 38.76, 44.73, 219.68$ ; Rt- $\beta$ DDEXcst<sup>TM</sup>, 30 m x 0.25 mm, 70 °C (20 min), 70-115 °C, 1 °C/min, 115 °C (10 min), 8.4 psi  $\text{N}_2$ ,  $t_{\text{S}} = 61.900$  min,  $t_{\text{R}} = 62.052$  min.

**(S)-(+)-1,3-Diphenylpentan-1-one 8a (Table 5, Entry 3).** 117 mg, 98%.  $[\alpha]_{\text{D}}^{25} = +6.07$  ( $c = 5.85$ , EtOH) for 96% ee;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\mathbf{d} = 0.80$  (t,  $J = 7.5$  Hz, Me), 1.61-1.82 (m, 2H), 3.20-3.29 (m, 3H), 7.16-7.31 (m, 5H), 7.40-7.45 (m, 2H), 7.50-7.56 (m, 1H), 7.89-7.92 (m, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\mathbf{d} = 12.11, 29.21, 42.97, 45.59, 126.25, 127.63, 128.04, 128.39, 128.51, 132.91, 137.19, 144.64, 199.19$ ; Chiralpak AD, hexane/*i*-PrOH = 95/5, 0.7 mL/min,  $t_{\text{S}} = 9.42$  min,  $t_{\text{R}} = 11.29$  min.

**(-)-1-Naphthyl-3-phenylpentan-1-one 8b (Table 5, Entry 5).** 141 mg, 98%.  $[\alpha]_{\text{D}}^{25} = -57.2$  ( $c = 1.06$ , EtOH) for 96% ee;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\mathbf{d} = 0.84$  (t,  $J = 7.2$  Hz, Me), 1.62-1.92 (m, 2H), 3.26-3.43 (m, 3H), 7.16-7.35 (m, 5H), 7.54-7.61 (m, 2H), 7.85-8.01 (m, 4H), 8.41 (s, 1H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\mathbf{d} = 12.24, 29.31, 43.19, 45.70, 123.93, 126.34, 126.73, 127.73, 127.76, 128.39, 128.40, 128.48, 129.56, 129.72, 132.48, 134.56, 135.48, 144.76, 199.11$ ; Chiralpak AD, hexane/*i*-PrOH = 95/5, 0.7 mL/min,  $t_1 = 13.043$  min,  $t_2 = 16.977$  min.

**(+)-3-(4-Bromophenyl)-1-phenylpentan-1-one 8c (Table 5, Entry 6).** 157 mg, 99%.  $[\alpha]_{\text{D}}^{25} = +0.70$  ( $c = 2.78$ , EtOH) for 96% ee;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\mathbf{d} = 0.82$  (t,  $J = 7.2$  Hz, Me), 1.62-1.83 (m, 2H), 3.20-3.29 (m, 3H), 7.13 (d,  $J = 8.4$  Hz, 2H), 7.40-7.48 (m, 4H), 7.54-7.59 (m, 1H), 7.90 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\mathbf{d} = 12.05, 29.19, 42.33, 45.26, 119.88, 127.98, 128.56, 129.44, 131.42, 133.04, 137.01, 143.68, 198.68$ ; Chiralpak AD, hexane/*i*-PrOH = 95/5, 0.7 mL/min,  $t_1 = 10.583$  min,  $t_2 = 14.963$  min.

**(S)-(+)-(4-Methoxyphenyl)-1-phenylpentan-1-one 8d (Table 5, Entry 7).** 132 mg, 98%.  $[\alpha]_{\text{D}}^{25} = +15.5$  ( $c = 0.98$ , EtOH) for 96% ee;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\mathbf{d} = 0.81$  (t,  $J = 7.2$  Hz, Me), 1.60-1.83 (m, 2H), 3.19-3.29 (m, 3H), 3.79 (s, 3H), 6.84 (d,  $J = 8.7$  Hz, 2H), 7.15 (d,  $J = 8.7$  Hz, 2H), 7.42-7.48 (m, 2H), 7.5-7.58 (m, 1H), 7.91 (d,  $J = 7.2$  Hz, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\mathbf{d} = 12.06, 29.30, 42.16, 45.72, 55.04, 113.67, 127.96, 128.41, 128.43, 132.80, 136.55, 137.15, 157.86, 199.25$ ; Chiralpak AD, hexane/*i*-PrOH = 95/5, 0.7 mL/min,  $t_{\text{S}} = 12.743$  min,  $t_{\text{R}} = 18.343$  min.

**(-)-1-(4-Bromophenyl)-3-phenylpentan-1-one 8e (Table 5, Entry 8).** 153 mg, 97%.  $[\alpha]_{\text{D}}^{25} = -6.33$  ( $c = 4.25$ , EtOH) for 95% ee;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\mathbf{d} = 0.80$  (t,  $J = 7.2$  Hz, Me), 1.62-1.82 (m, 2H), 3.16-3.29 (m, 3H), 7.16-7.32 (m, 5H), 7.57 (d,  $J = 12.9$  Hz, 2H), 7.77 (d,  $J = 12.9$  Hz, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\mathbf{d} = 12.03, 29.13, 42.92, 45.45, 126.27, 127.50, 127.96, 128.35, 129.50, 131.70, 135.79, 144.28, 198.08$ ; Chiralpak AD, hexane/*i*-PrOH = 95/5, 0.7 mL/min,  $t_1 = 11.563$  min,  $t_2 = 13.943$  min.

**(S)-(-)-1-(4-Methoxyphenyl)-3-phenylpentan-1-one 8f (Table 5, Entry 9).** 119 mg, 87%.  $[\alpha]_{\text{D}}^{25} = -4.0$  ( $c = 2.2$ , EtOH) for 97% ee;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\mathbf{d} = 0.81$  (t,  $J = 7.5$  Hz, Me), 1.64-1.88 (m, 2H), 3.18-3.28 (m, 3H), 3.87 (s, 3H), 6.91 (d,  $J = 8.7$  Hz, 2H), 7.17-7.38 (m, 5H), 7.91 (d,  $J = 8.7$  Hz, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\mathbf{d} = 12.11, 29.18, 43.17, 45.22, 55.39, 113.61, 126.18, 127.62, 128.35, 130.28, 130.31, 144.78, 163.30, 197.75$ ; Chiralpak AD, hexane/*i*-PrOH = 95/5, 0.7 mL/min,  $t_{\text{S}} = 19.077$  min,  $t_{\text{R}} = 28.437$  min.

**(-)-4-Ethyl-octan-2-one 10a (Table 6, Entry 3).** 69 mg, 89%.  $[\alpha]_{\text{D}}^{25} = -2.5$  ( $c = 1.05$ ,  $\text{CHCl}_3$ ) for 93% ee;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\mathbf{d} = 0.86$  (m, 6H, 2Me), 1.26 (m, 8H, 4CH<sub>2</sub>), 1.83 (m, 1H, CH), 2.12 (s, 3H, Me), 2.31 (d,  $J = 6.6$  Hz, 2H, CH<sub>2</sub>);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\mathbf{d} = 10.76, 14.03, 22.89, 26.30, 28.79, 30.35, 33.12, 35.24, 48.36, 209.46$ ; IR (neat)  $\mathbf{n} = 2958, 1716, 1463, 1410, 1376, 1143, 1060, 1022, 966, 723$  cm<sup>-1</sup>; MS (EI)  $m/z$  157 ([M+1]<sup>+</sup>, 42.0), 141 ([M-15]<sup>+</sup>, 8.0), 127 ([M-29]<sup>+</sup>, 10.0), 113 ([M-43]<sup>+</sup>, 7.0); HRMS Calcd. C<sub>10</sub>H<sub>20</sub>O (M<sup>+</sup>): 156.1514, found: 156.1488; Chirasil-DEX CB, 25 m x 0.25 mm, 100 °C (30 min), 8.0 psi N<sub>2</sub>,  $t_1 = 16.478$  min,  $t_2 = 17.443$  min.

**(-)-4-Ethyl-5-methylhexan-2-one 10b (Table 6, Entry 4).** 58 mg, 82%.  $[\alpha]_{\text{D}}^{25} = -1.0$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ) for 89% ee;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\mathbf{d} = 0.86$  (m, 9H, 3Me), 1.20 (m, 1H,

CH), 1.32 (m, 1H, CH), 1.75 (m, 2H, 2CH), 2.16 (s, 3H, Me), 2.35 (dd,  $J = 6.6$  and  $16.2$  Hz, 1H, CH), 2.39 (dd,  $J = 6.6$  and  $16.2$  Hz, 1H, CH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\mathbf{d} = 11.68, 18.38, 19.50, 23.83, 29.17, 30.24, 41.07, 45.06, 209.65$ ; MS (EI)  $m/z$  143 ( $[\text{M}+1]^+$ , 23.0), 127 ( $[\text{M}-15]^+$ , 2.0), 99 ( $[\text{M}-43]^+$ , 4.0), 84 ( $[\text{M}-58]^+$ , 41.0); HRMS Calcd.  $\text{C}_9\text{H}_{18}\text{O}$  ( $\text{M}^+$ ): 142.1358, found: 142.1364; CHIRASIL-DEX CB, 25 m x 0.25 mm, 80 °C (20 min), 80-150 °C, 1 °C/min, 150 °C (10 min), 8.0 psi  $\text{N}_2$ ,  $t_1 = 24.635$  min,  $t_2 = 24.852$  min.

**(-)-6-Ethyl-2-methyldecan-4-one 10c (Table 6, Entry 5).** 91 mg, 92%.  $[\alpha]_{\text{D}}^{25} = -6.0$  ( $c = 0.3$ ,  $\text{CHCl}_3$ ) for 85% ee;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\mathbf{d} = 0.87$  (m, 12H, 4Me), 1.27 (m, 8H, 4 $\text{CH}_2$ ), 1.85 (m, 1H, CH), 2.13 (m, 1H, CH), 2.25 (d,  $J = 6.3$  Hz, 2H,  $\text{CH}_2$ ), 2.27 (d,  $J = 6.9$  Hz, 2H,  $\text{CH}_2$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\mathbf{d} = 10.81, 14.07, 22.58, 22.94, 24.48, 26.33, 28.83, 33.12, 35.03, 47.91, 52.34, 211.28$ ; IR (neat)  $\mathbf{n} = 2958, 2873, 1713, 1465, 1408, 1367, 1289, 1203, 1170, 1144, 1051$   $\text{cm}^{-1}$ ; MS (EI)  $m/z$  199 ( $[\text{M}+1]^+$ , 79.0), 141 ( $[\text{M}-57]^+$ , 58.0), 113 ( $[\text{M}-85]^+$ , 6.0), 85 ( $[\text{M}-113]^+$ , 64.0); HRMS Calcd.  $\text{C}_{13}\text{H}_{26}\text{O}$  ( $\text{M}^+$ ): 198.1984, found: 198.2007; Chirasil-DEX CB, 25 m x 0.25 mm, 80 °C (20 min), 80-180 °C, 1 °C/min, 180 °C (2 min), 8.0 psi  $\text{N}_2$ ,  $t_1 = 60.477$  min,  $t_2 = 61.215$  min.

**(-)-5-Ethyl-2-methylnonan-3-one 10d (Table 6, Entry 6).** 85 mg, 92%.  $[\alpha]_{\text{D}}^{25} = -3.0$  ( $c = 0.23$ ,  $\text{CHCl}_3$ ) for 80% ee;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\mathbf{d} = 0.87$  (m, 6H, 2Me), 1.10 (d,  $J = 6.3$  Hz, 6H, 2Me), 1.28 (m, 8H, 4 $\text{CH}_2$ ), 1.89 (m, 1H, CH), 2.36 (d,  $J = 6.6$  Hz, 2H,  $\text{CH}_2$ ), 2.60 (m, 1H, CH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\mathbf{d} = 10.77, 13.98, 18.12, 22.87, 26.29, 28.80, 33.09, 34.73, 40.99, 44.98, 214.93$ ; IR (neat)  $\mathbf{n} = 2963, 2930, 2874, 1713, 1466, 1408, 1381, 1366, 1105, 1048, 733$   $\text{cm}^{-1}$ ; MS (EI)  $m/e$  185 ( $[\text{M}+1]^+$ , 43.0), 141 ( $[\text{M}-43]^+$ , 64.0), 113 ( $[\text{M}-71]^+$ , 5.0), 71 ( $[\text{M}-113]^+$ , 100.0); HRMS Calcd.  $\text{C}_{12}\text{H}_{24}\text{O}$  ( $\text{M}^+$ ): 184.1827, found: 184.1819; CHIRASIL-DEX CB, 25 m x 0.25 mm, 60 °C (20 min), 80-160 °C, 1 °C/min, 160 °C (10 min), 8.0 psi  $\text{N}_2$ ,  $t_1 = 68.878$  min,  $t_2 = 69.587$  min.

**(R)-(+)-3-Methylcyclohexanone 11a (Table 7, Entry 2).** 40 mg, 71%.  $[\alpha]_{\text{D}}^{25} = +13.6$  ( $c = 1.55$ ,  $\text{CHCl}_3$ ) for 87% ee.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\mathbf{d} = 0.98$  (d,  $J = 6.0$  Hz, Me), 1.26-1.36 (m, 1H), 1.57-1.70 (m, 1H), 1.79-2.08 (m, 4H), 2.14-2.38 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz)  $\mathbf{d} = 22.01, 25.23, 33.19, 34.12, 41.04, 49.90, 212.00$ ; The product was then treated with (+)-(2*R*, 3*R*)-diethyl tartrate to form the corresponding ketal.<sup>[3]</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz)  $\mathbf{d} = 0.92$  (d,  $J = 6.3$  Hz, Me), 1.24-1.85 (m, 15H), 4.24-4.32 (m, 4H), 4.76-4.83 (m, 2H); The diastereoisomeric purity of the ketal was assayed by GC and was

assumed to be identical to the ee of the product. Alltech EC-5, 30 m x 0.32 mm, 150 °C (30 min), 10.0 psi N<sub>2</sub>,  $t_1 = 24.2148$  min,  $t_2 = 25.290$  min. or Rt- $\beta$ DEXcst<sup>TM</sup>, 30 m x 0.25 mm, 130 °C (60 min), 130-160 °C, 5 °C/min, 160 °C (120 min), 10.0 psi N<sub>2</sub>,  $t_1 = 130.543$  min,  $t_2 = 133.170$  min.

**(R)-(+)-3-Phenylcyclohexanone 11b (Table 7, Entry 5).** 85 mg, 98%.  $[\alpha]_D^{25} = +19.9$  ( $c = 1.50$ , CHCl<sub>3</sub>) for 90% ee; <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz)  $\delta = 1.76$ -1.92 (m, 2H), 2.07-2.22 (m, 2H), 2.35-2.64 (m, 4H), 3.01 (m, 1H), 7.21-7.35 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz)  $\delta = 25.45, 32.65, 41.09, 44.64, 48.84, 126.47, 126.58, 128.57, 144.23, 210.98$ ; Chiralpak AD, hexane/i-PrOH = 50/1, 0.7 mL/min,  $t_S = 16.043$  min,  $t_R = 19.083$  min.

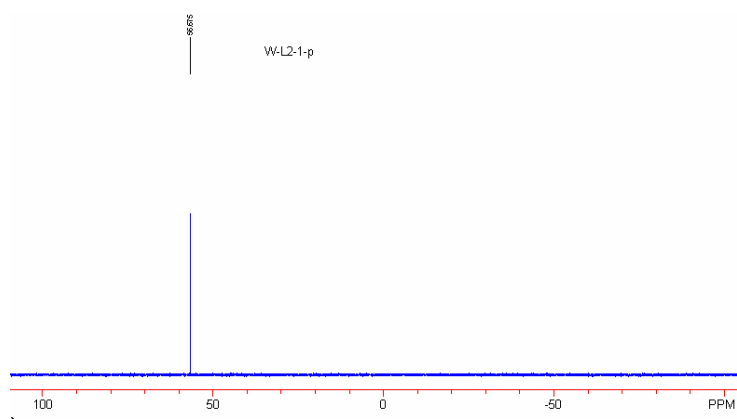
### The General Experiments Procedure on Linear Effect for the Cu-catalyzed Conjugate Addition to Chalcone with Et<sub>2</sub>Zn:

A solution of Cu(CH<sub>3</sub>CN)<sub>4</sub>BF<sub>4</sub> (4.7 mg, 0.015 mmol) and various ligand **L4** with different ee (8.0 mg, 0.015 mmol) in dry toluene (3 mL) was stirred for 1 h at room temperature under an argon atmosphere. Chalcone **7a** (104 mg, 0.5 mmol) was added and the solution was stirred for a further 10 min, then Et<sub>2</sub>Zn (0.75 mL, 0.75 mmol, 1.0 M solution in hexane) was added dropwise within 30 seconds. The resulting mixture was stirred for 10 min, then 1.0 N HCl (4.0 mL) was added into the reaction solution. After extraction with ether (3 x 5.0 mL), the combined organic layers were dried over anhydrous MgSO<sub>4</sub>. The residue obtained upon removal of volatiles in *vacuo* was purified by a flash column chromatography on silica gel (eluent: pentane/ether = 30/1) to afford the 1,3-diphenyl-pentan-1-one **8a** in quantitative yield (96-98%) with different ee. The results were summarized in Table 1.

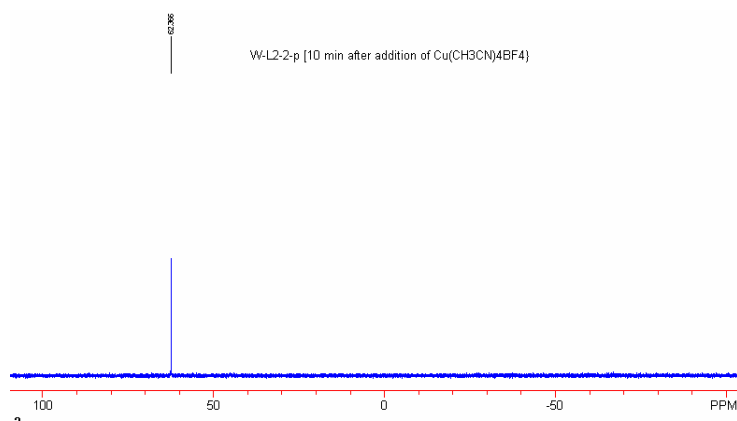
**Table 1.** The correlation between the ee of the ligand **L4** and the ee of **8a**.

entry	1	2	3	4	5	6	7	8
1 <sup>a)</sup>	0	12.6	28	47	61.5	73.5	88	98
2 <sup>b)</sup>	0	10	30	45	62	72	89	96

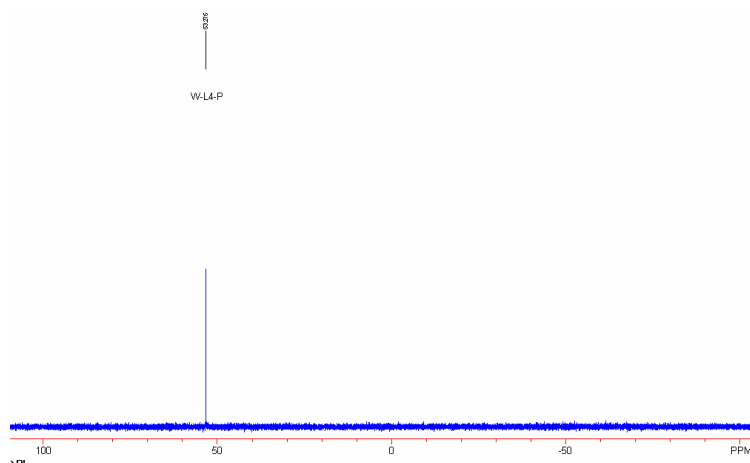
<sup>a)</sup>The ee of the ligand **L4**. <sup>b)</sup>The ee of the **8a**.



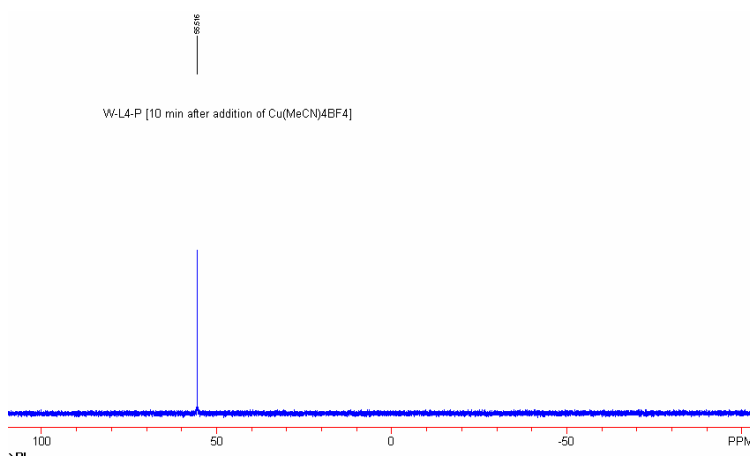
**Figure 1.** The  $^{31}\text{P}$  NMR of **L2**.



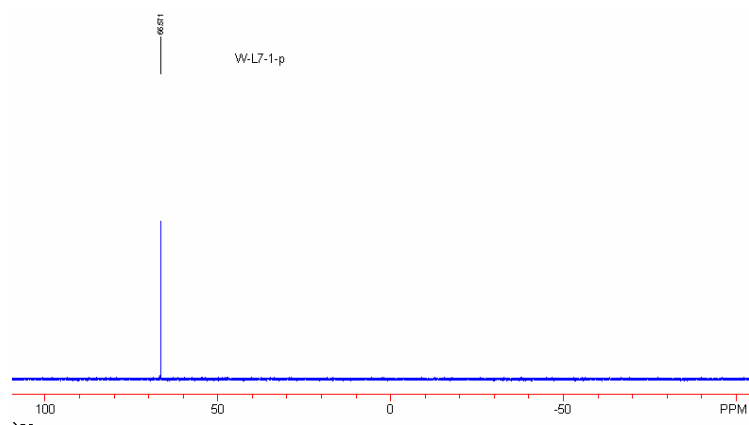
**Figure 2.** The  $^{31}\text{P}$  NMR of the mixture of **L2** and  $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ .



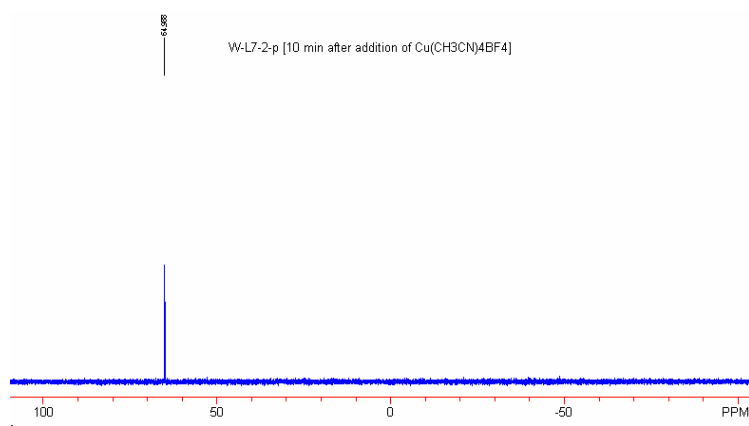
**Figure 3.** The  $^{31}\text{P}$  NMR of **L4**.



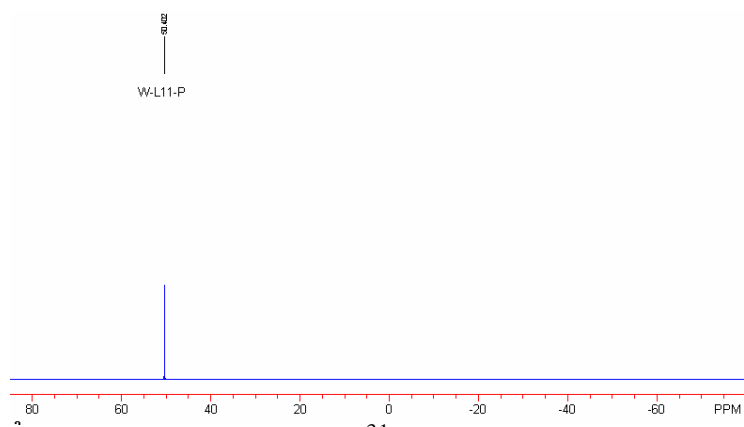
**Figure 4.** The  $^{31}\text{P}$  NMR of the mixture of **L4** and  $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ .



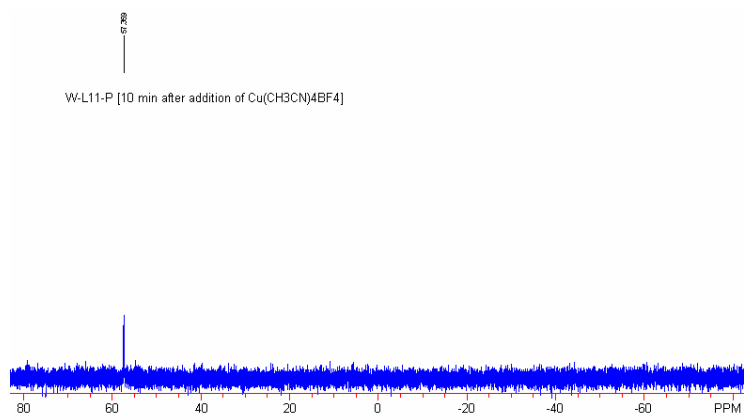
**Figure 5.** The  $^{31}\text{P}$  NMR of **L7**.



**Figure 6.** The  $^{31}\text{P}$  NMR of the mixture of **L7** and  $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ .



**Figure 7.** The  $^{31}\text{P}$  NMR of **L9**.



**Figure 8.** The  $^{31}\text{P}$  NMR of the mixture of **L9** and  $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ .

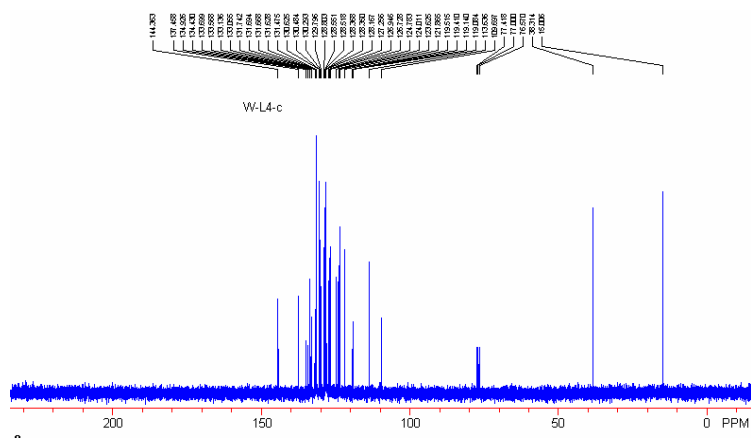
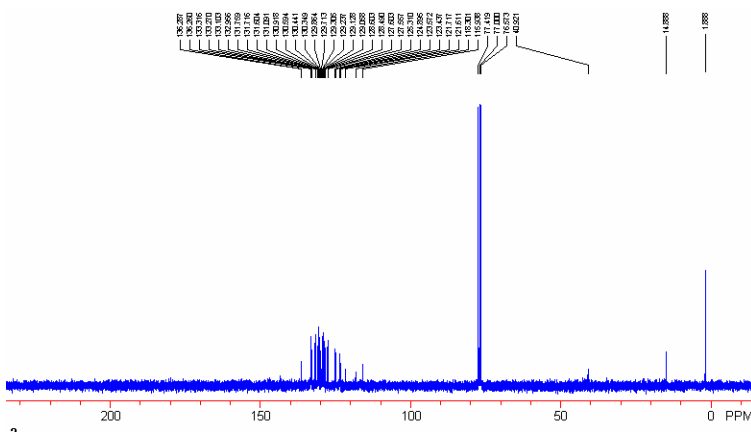


Figure 9. The  $^{13}\text{C}$  NMR of L4.



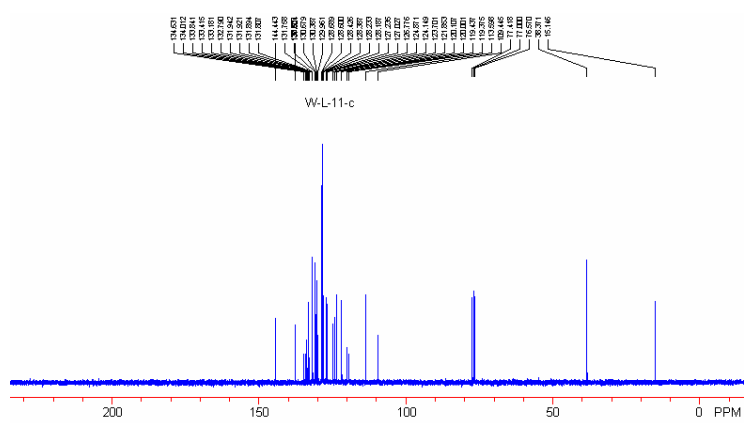


Figure 11. The  $^{13}\text{C}$  NMR of **L9**.

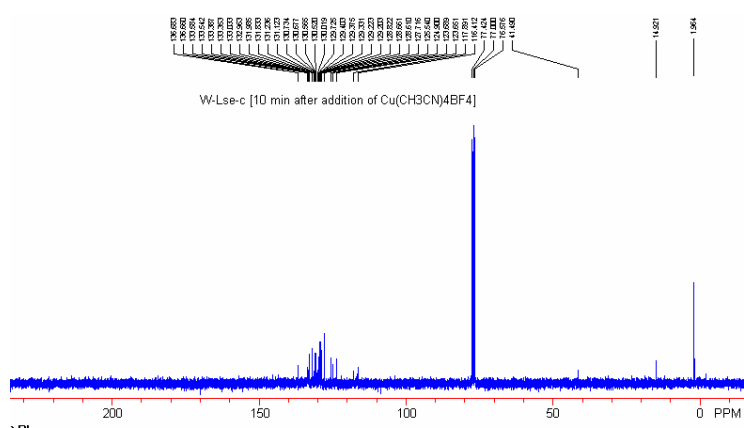


Figure 12. The  $^{13}\text{C}$  NMR of the mixture of **L9** and  $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ .

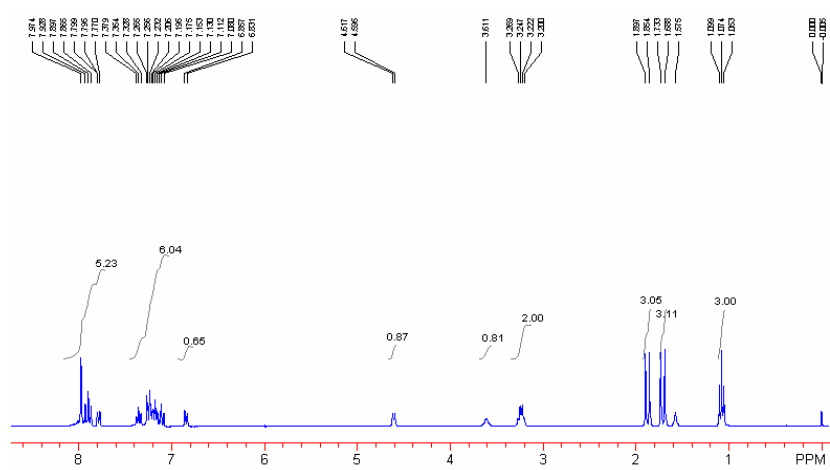


Figure 13. The  $^1\text{H}$  NMR of Ligand **L2** in  $\text{CDCl}_3$ .

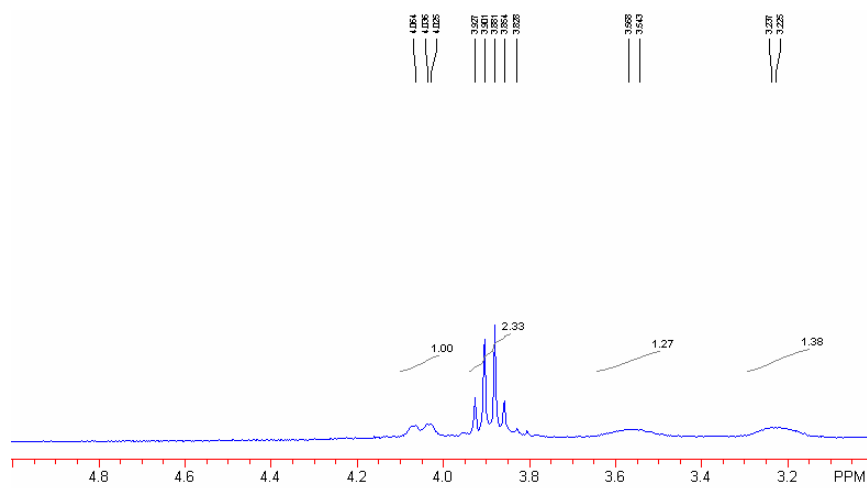


Figure 14. The part of  $^1\text{H}$  NMR of Ligand **L2** and  $\text{Et}_2\text{Zn}$  in  $\text{CDCl}_3$ .

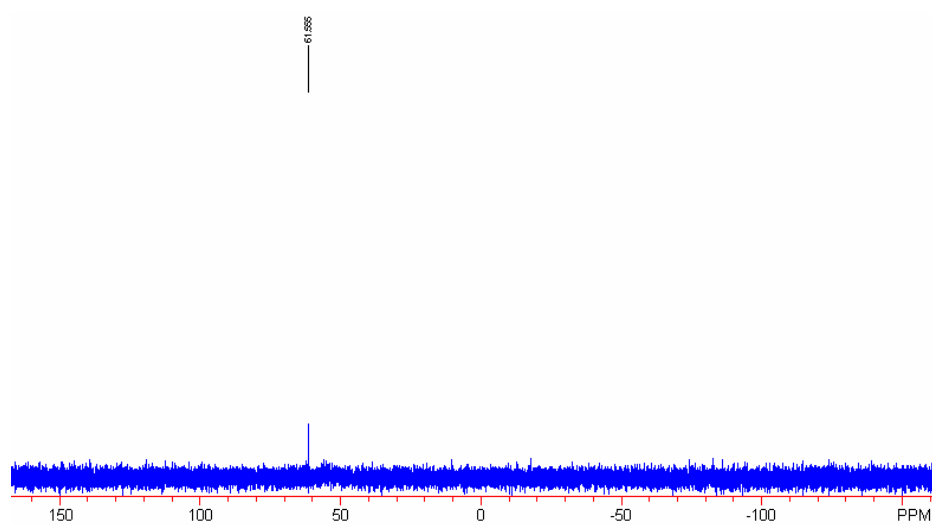


Figure 15. The  $^{31}\text{P}$  NMR of Ligand **L2** with  $\text{Cu}(\text{CH}_3\text{CN})\text{BF}_4$  and  $\text{Et}_2\text{Zn}$  in  $\text{CDCl}_3$ .

File : S10\_91.D01  
Run : 01

Collection : 13:09:36 Oct 22 2002 Method : XWD

w-外消

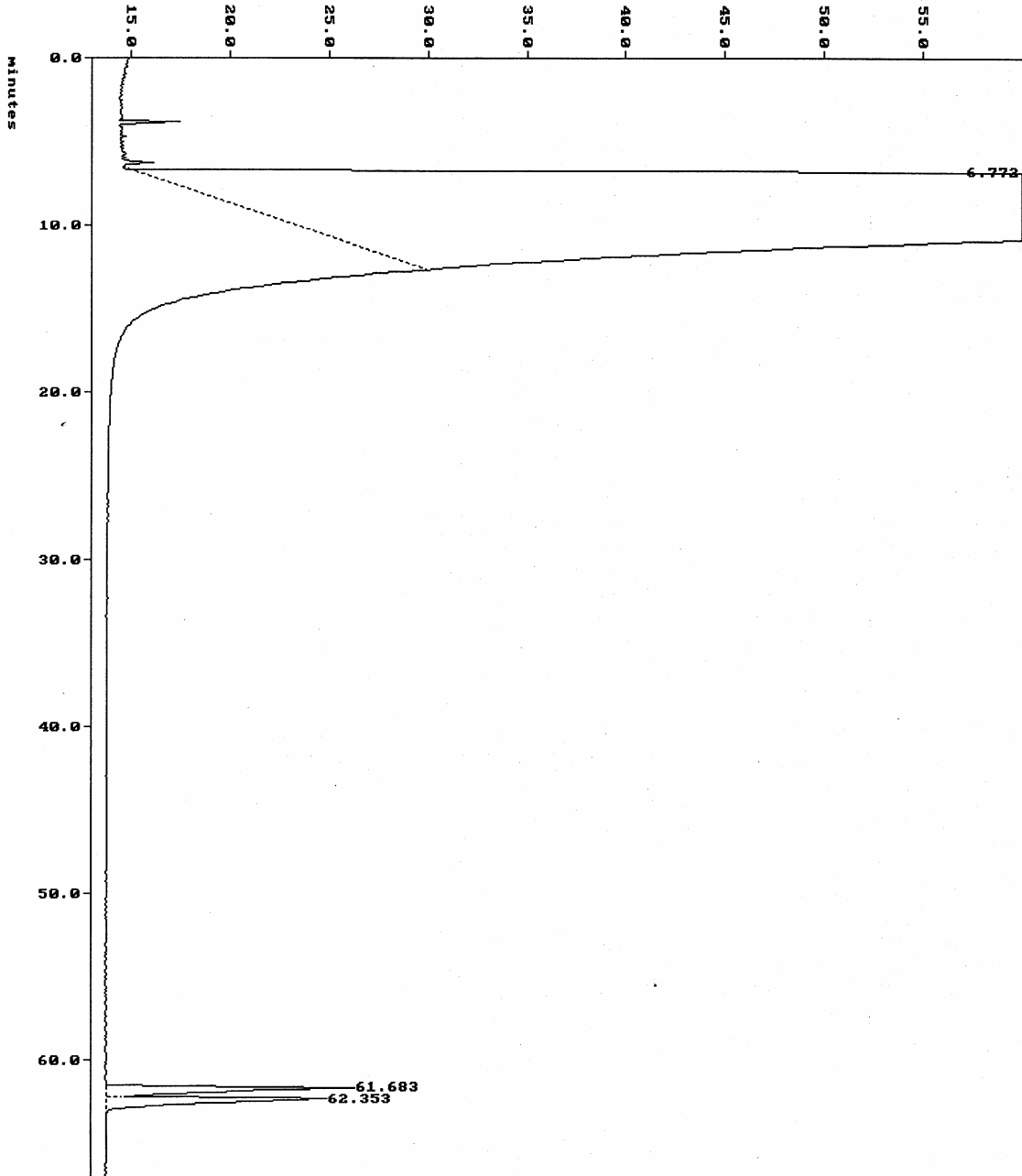


Type : Sample  
[ 08:03:19 Oct 22 2002 ]

Rt- $\beta$ DEX cst<sup>TM</sup>, 30m x 0.25 mm

(S10\_91.D01) MV

70°C (20 min), 70~115°C, 1°C/min  
115°C (10 min), 8.4 psi N<sub>2</sub>



\*\*\*\*\* MODEL 1022 RUNLOG for run: S10\_\_85 \*\*\*\*\*

Run terminated manually on Channel A.

\*\*\*\*\* MODEL 1022 RUNLOG for run: S10\_\_86 \*\*\*\*\*

Run terminated manually on Channel A.

\*\*\*\*\* MODEL 1022 RUNLOG for run: S10\_\_87 \*\*\*\*\*

Run terminated manually on Channel A.

\*\*\*\*\* MODEL 1022 RUNLOG for run: S10\_\_88 \*\*\*\*\*

Run terminated manually on Channel A.

\*\*\*\*\* MODEL 1022 RUNLOG for run: S10\_\_89 \*\*\*\*\*

Run terminated manually on Channel A.

\*\*\*\*\* MODEL 1022 RUNLOG for run: S10\_\_90 \*\*\*\*\*

Run terminated manually on Channel A.

\*\*\*\*\* MODEL 1022 RUNLOG for run: S10\_\_91 \*\*\*\*\*

Run terminated manually on Channel A.

File : S10\_\_91.D01

Run : 01

Path : C:\\$T\$

Collection : 13:09:36 Oct 22 2002 Method : XWD

Integration: 13:09:36 Oct 22 2002 Method : XWD

Report : 14:21:34 Oct 22 2002 Method : XWD

Type : Sampl  
Inst : 1022 LC Plu

[ 08:03:19 Oct 22 2002 ]

[ 08:03:19 Oct 22 2002 ]

[ 08:03:19 Oct 22 2002 ]

PERCENT ( AREA ) \ MANUALLY ALTERED

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	6.772	302510208	242.8732		98.5246	91.0980
2	61.683	2233637	12.5590	T	0.7275	4.7107
3	62.353	2296515	11.1743		0.7480	4.1913

3 Peaks > Area Reject 307040352 Total Area  
3 Peaks > Height Reject 266.607 Total Height

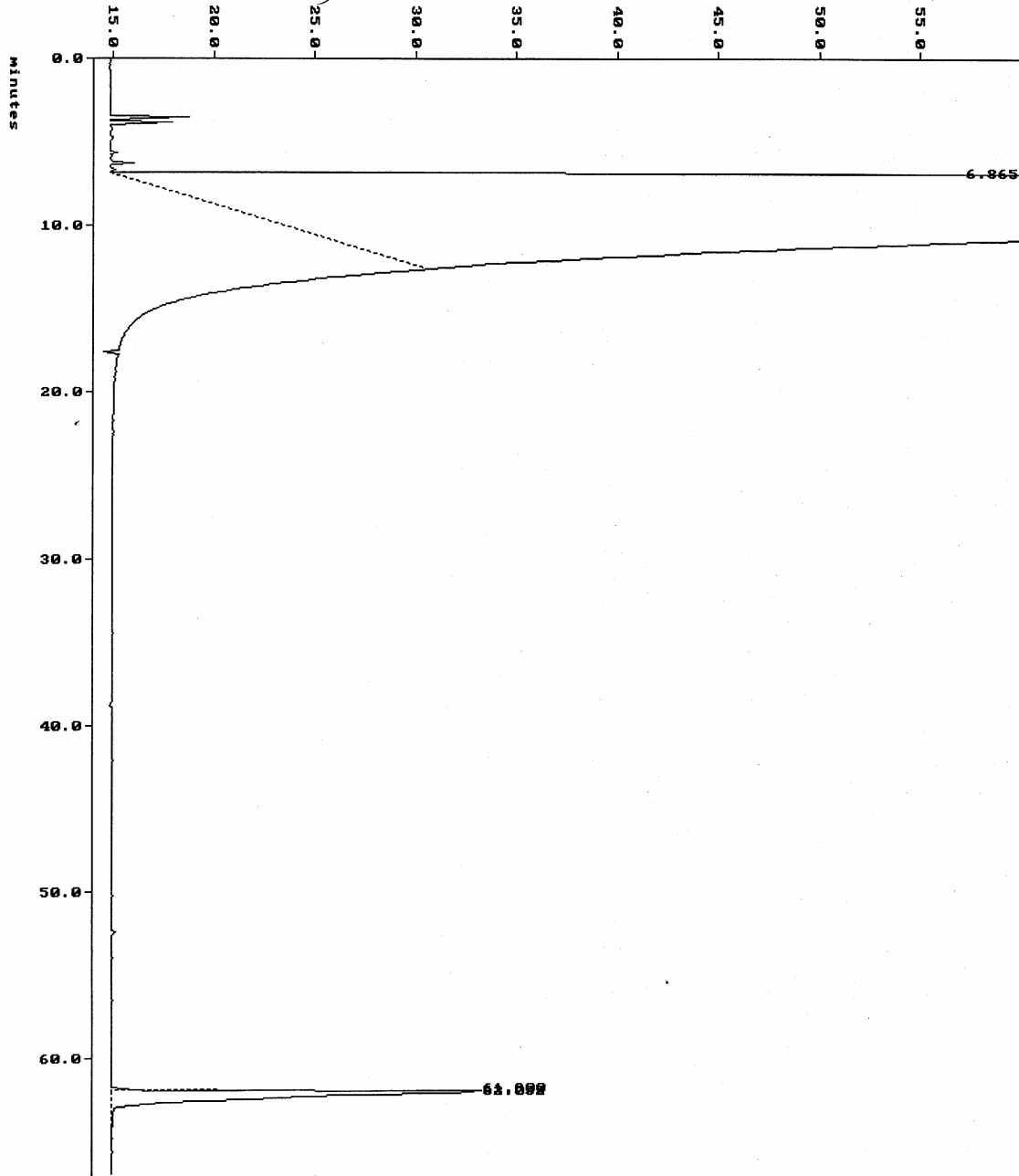


File : S10\_92.D01 w-9-10-46  
Run : 01  
Collection : 14:28:06 Oct 22 2002 Method : XWD

Type : Sample  
[ 08:03:19 Oct 22 2002 ]  
Rt-βDEX cst™, 30m x 0.25mm,  
70°C (20 min), 70-115°C, 1°C/min  
115°C (10 min), 8.4psi N<sub>2</sub>

(S10\_92.D01) MV

from addition







File : S13\_22.D01

Cui-8-61

Run : 01

Collection : 13:26:41 Dec 02 2002

Method : XWD

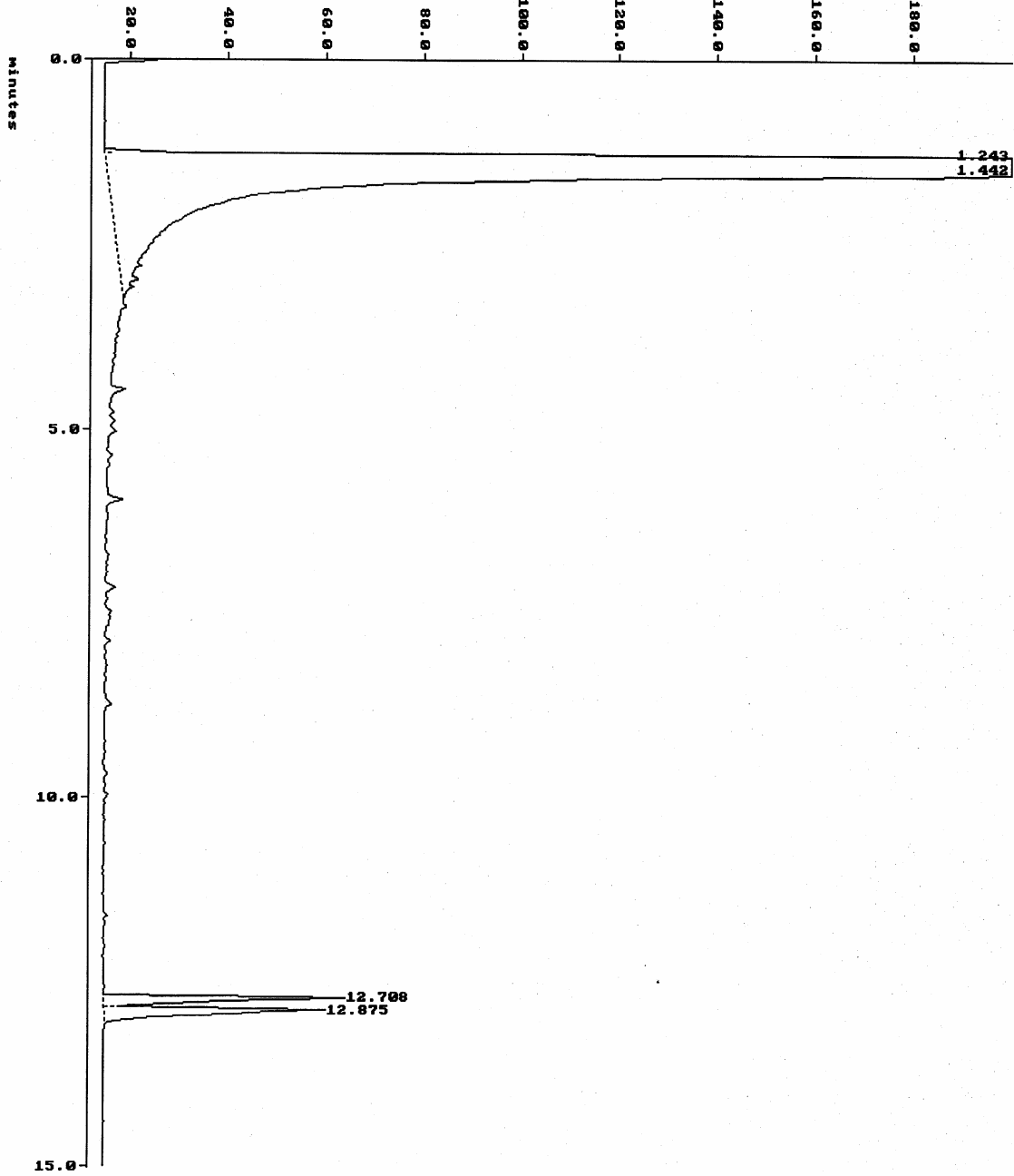
Type : Sample

[ 07:15:02 Dec 02 2002 ]  
Chiraldex G-BP 20 m x 0.25 mm

(S13\_22.D01) MU

50°C (2 min) , 50-112°C , 5°C/min  
112°C (2 min) , 10.0 psi N<sub>2</sub>

authentic racemic



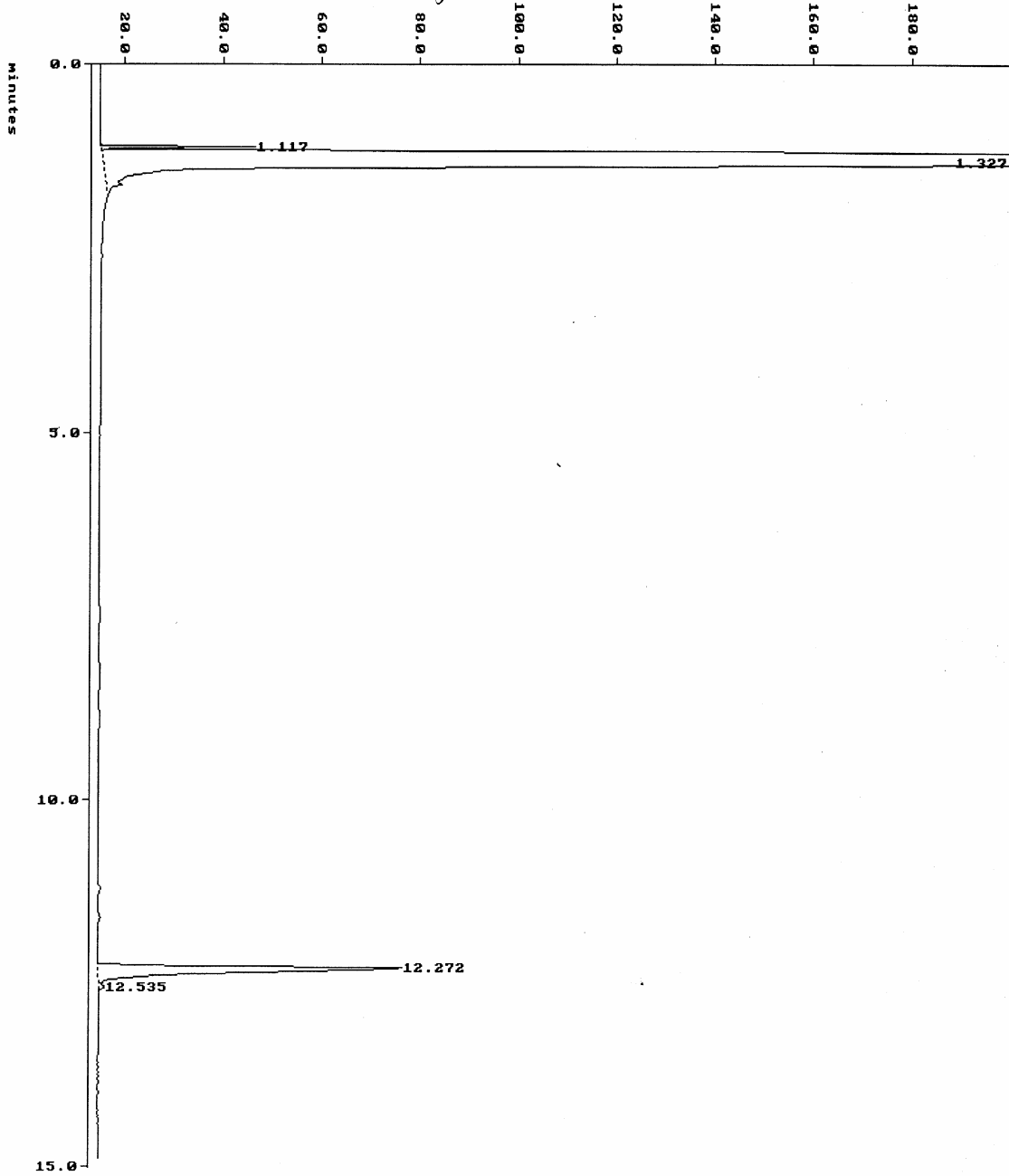




File : S19\_32.D01 w-10-753-1  
Run : 01  
Collection : 14:18:18 Mar 10 2003 Method : XWD

Type : Sample  
[ 07:51:38 Mar 10 2003 ]  
Chiraldex G-BP, 20m x 0.25 mm,  
50°C (2min), 50-112°C, 5°C/min,  
112°C (2min)

(S19\_32.D01) MU  
*from addition*



\*\*\*\*\* MODEL 1022 RUNLOG for run: S19\_\_25 \*\*\*\*\*

Run terminated manually on Channel A.

\*\*\*\*\* MODEL 1022 RUNLOG for run: S19\_\_26 \*\*\*\*\*

Run terminated manually on Channel A.

\*\*\*\*\* MODEL 1022 RUNLOG for run: S19\_\_27 \*\*\*\*\*

Run terminated manually on Channel A.

\*\*\*\*\* MODEL 1022 RUNLOG for run: S19\_\_28 \*\*\*\*\*

Run terminated manually on Channel A.

\*\*\*\*\* MODEL 1022 RUNLOG for run: S19\_\_29 \*\*\*\*\*

Run terminated manually on Channel A.

\*\*\*\*\* MODEL 1022 RUNLOG for run: S19\_\_30 \*\*\*\*\*

Run terminated manually on Channel A.

\*\*\*\*\* MODEL 1022 RUNLOG for run: S19\_\_31 \*\*\*\*\*

Run terminated manually on Channel A.

\*\*\*\*\* MODEL 1022 RUNLOG for run: S19\_\_32 \*\*\*\*\*

Run terminated manually on Channel A.

File : S19\_\_32.D01

w-10-753-1

Run : 01

Path : C:\\$T\$

Type : Sampl

Inst : 1022 LC Plu

Collection : 14:18:18 Mar 10 2003 Method : XWD [ 07:51:38 Mar 10 2003 ]

Integration: 14:18:18 Mar 10 2003 Method : XWD [ 07:51:38 Mar 10 2003 ]

Report : 14:34:33 Mar 10 2003 Method : XWD [ 07:51:38 Mar 10 2003 ]

PERCENT ( AREA ) \ MANUALLY ALTERED

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	1.117	315810	31.5253	T	0.2880	2.8967
2	1.327	105839936	994.3459		96.5143	91.3655
3	12.272	3459667	61.4176	T	3.1548	5.6434
4	12.535	47001	1.0281		0.0429	0.0945

4 Peaks > Area Reject 109662416 Total Area

4 Peaks > Height Reject 1088.317 Total Height



File : S19\_34.D01

w-7

Run : 01

Type : Sample

Collection : 14:59:23 Mar 10 2003 Method : XWD

[ 07:51:38 Mar 10 2003 ]

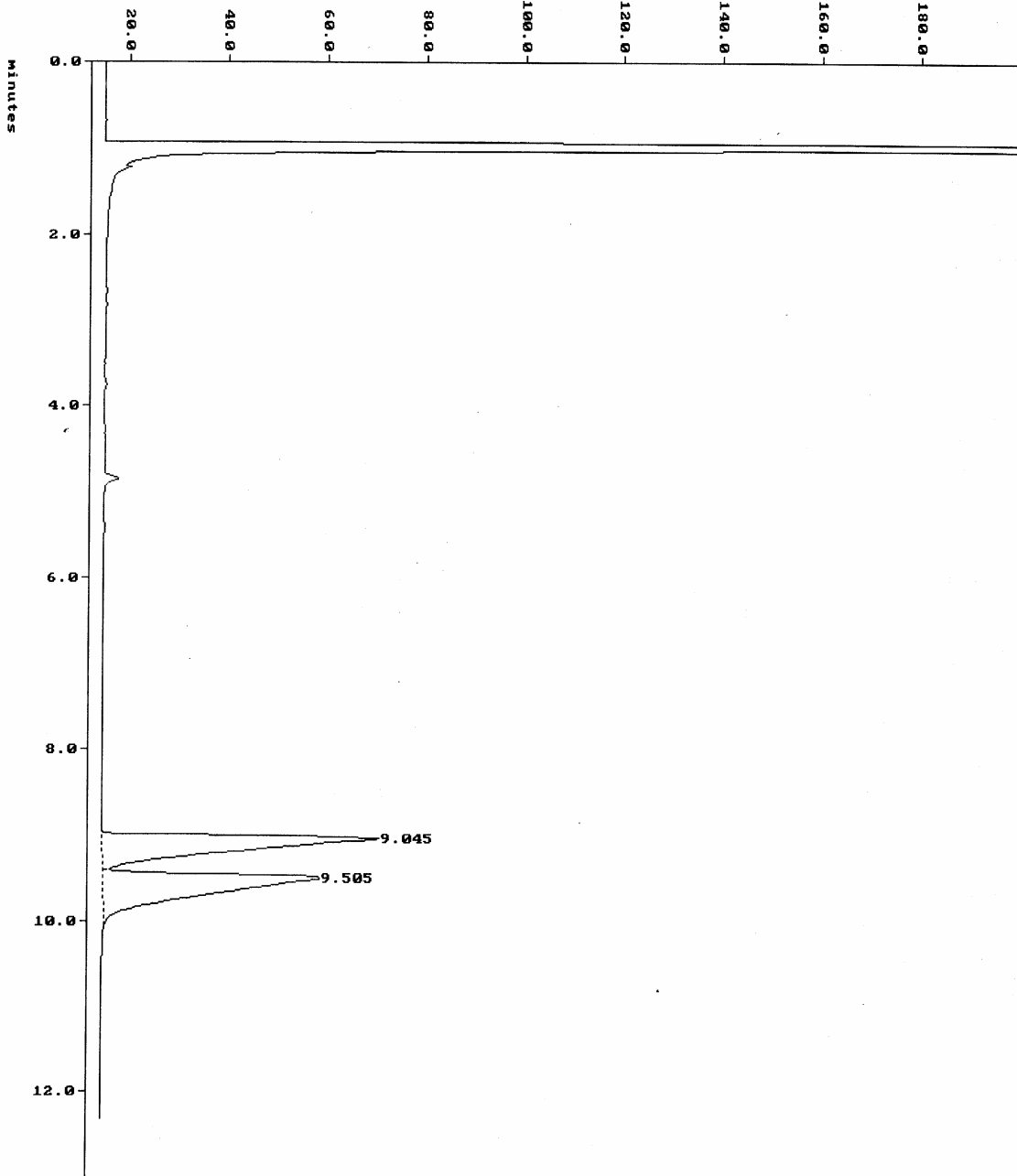
Chiraldex G-BP 20m x 0.25mm,

(S19\_34.D01)

MU

90°C (30min) 10.0 psi N<sub>2</sub>

authentic racemic





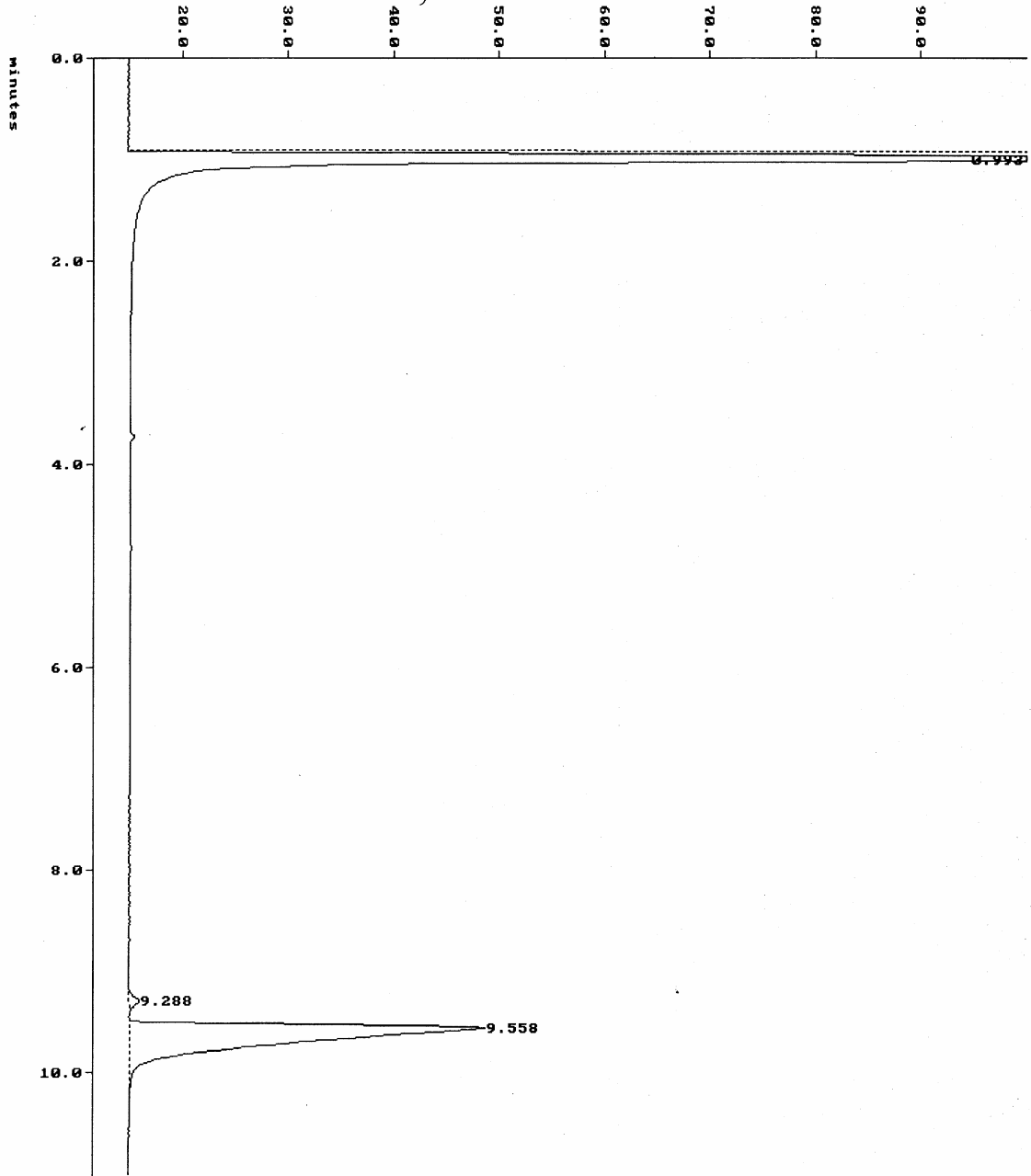


File : S19\_35.D01 w-10-751  
Run : 01  
Collection : 15:18:45 Mar 10 2003 Method : XWD

Type : Sample  
I 07:51:38 Mar 10 2003 I  
Chiraldex G-BP 20m x 0.25mm  
90°C (30min) 10.0 psi N<sub>2</sub>

(S19\_35.D01) mU

from addition



File : S19\_\_\_35.D01 w-10-751  
Run : 01  
Path : C:\\$T\$ Type : Sampl  
Collection : 15:18:45 Mar 10 2003 Method : XWD [ 07:51:38 Mar 10 2003 ]  
Integration: 15:18:45 Mar 10 2003 Method : XWD [ 07:51:38 Mar 10 2003 ]  
Report : 09:00:55 Mar 11 2003 Method : XWD [ 07:15:16 Mar 11 2003 ]

## PERCENT ( AREA ) \ MANUALLY ALTERED

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	0.993	19624732	502.4642		83.7309	93.5654
2	9.288	60843	0.9376	V	0.2596	0.1746
3	9.558	3752277	33.6174		16.0095	6.2600
3 Peaks > Area Reject			23437852	Total Area		
3 Peaks > Height Reject			537.019	Total Height		

\*\*\*\*\* MODEL 1022 RUNLOG for run: CH-6\_02 \*\*\*\*\*  
 Run terminated manually on Channel A.



Chiralpak AD  
 hexane/i-PrOH = 50/1  
 0.5 mL/min, 254 nm 1

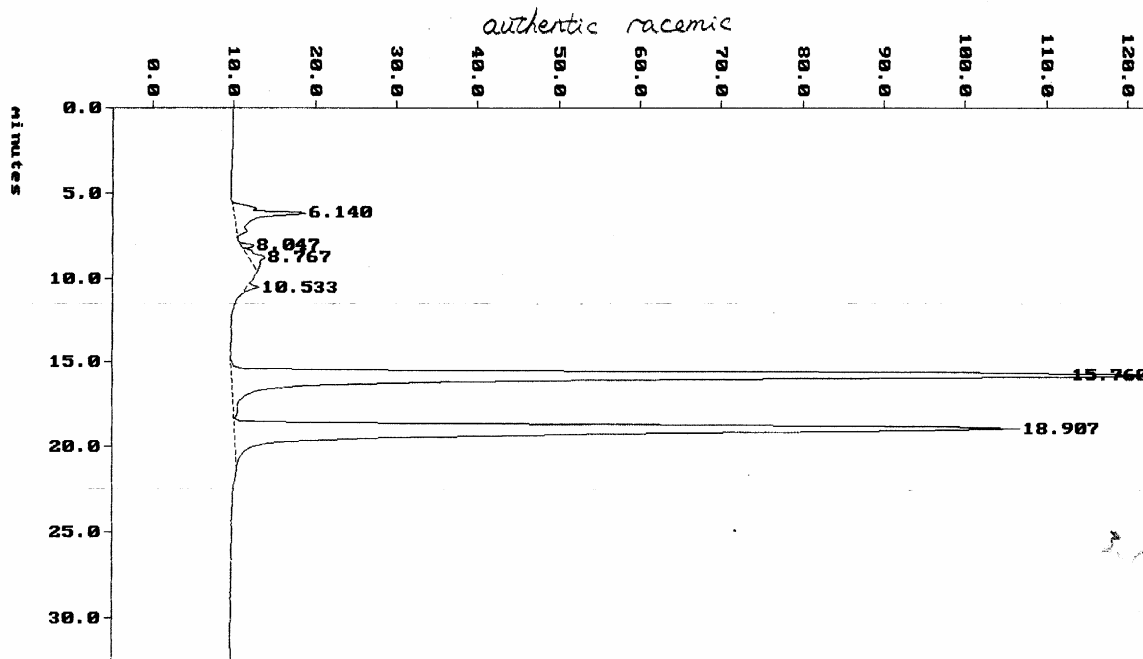
File : CH-6\_02.D01 w10-64rac  
 Run : 02 Type : Sample  
 Path : C:\CH-5 Inst : 1022 LC Plus  
 Collection : 12:25:01 Jan 21 2003 Method : LCTEST [ 11:36:44 Jan 21 2003 ]  
 Integration: 12:25:01 Jan 21 2003 Method : LCTEST [ 11:36:44 Jan 21 2003 ]  
 Report : 13:07:28 Jan 21 2003 Method : LCTEST [ 11:36:44 Jan 21 2003 ]

## PERCENT ( AREA )

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	6.140	2640531	8.7952	V	3.2693	3.7688
2	8.047	204164	1.6005	T	0.2528	0.6858
3	8.767	762833	1.9729		0.9445	0.8454
4	10.533	255317	1.5096		0.3161	0.6469
5	15.760	34864496	113.1095	T	43.1665	48.4687
6	18.907	34440664	96.6574		42.6418	41.4188
7	35.880	4095354	4.7773	T	5.0706	2.0471
8	39.853	3504050	4.9435		4.3384	2.1184

8 Peaks > Area Reject 80767408 Total Area  
 8 Peaks > Height Reject 233.366 Total Height

(CH-6\_02.D01) MV



\*\*\*\*\* MODEL 1022 RUNLOG for run: CH-6\_04 \*\*\*\*\*

Run terminated manually on Channel A.



Chiralpak AD

hexane/i-PrOH = 50/1

0.5 ml/min, 254nm

File : CH-6\_04.D01

W10-64A

1

Run : 02

Type : Sample

Path : C:\CH-5

Inst : 1022 LC Plus

Collection : 13:49:02 Jan 21 2003 Method : LCTEST [ 11:36:44 Jan 21 2003 ]

Integration: 13:49:02 Jan 21 2003 Method : LCTEST [ 11:36:44 Jan 21 2003 ]

Report : 14:12:08 Jan 21 2003 Method : LCTEST [ 11:36:44 Jan 21 2003 ]

PERCENT ( AREA )

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	6.130	1069728	6.0523		2.0712	4.0299
2	8.030	184635	0.7704	T	0.3575	0.5130
3	8.697	198580	0.8602		0.3845	0.5728
4	10.610	601540	3.2235		1.1647	2.1464
5	16.043	2823714	9.7369		5.4673	6.4834
6	19.083	46769192	129.5393		90.5548	86.2546

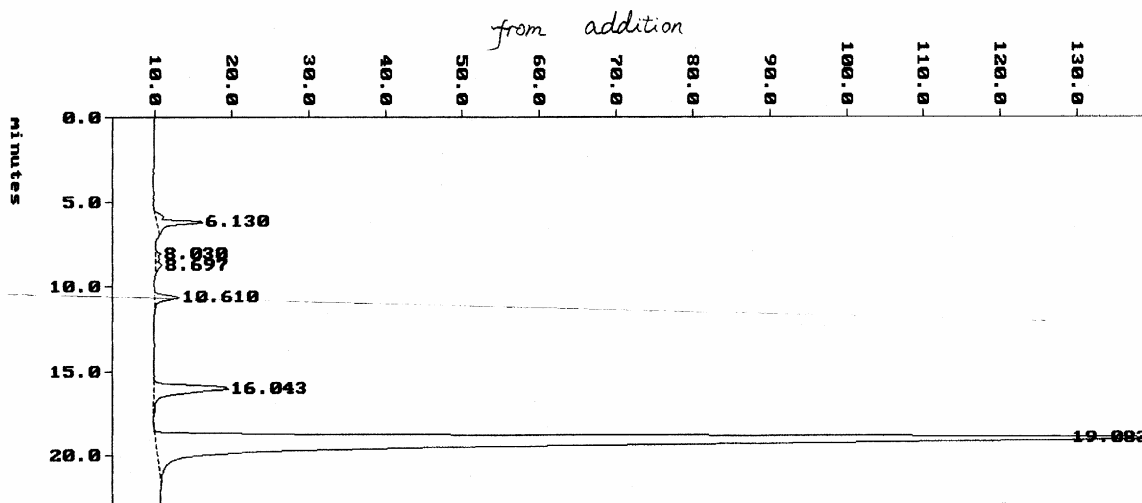
6 Peaks > Area Reject

51647388 Total Area

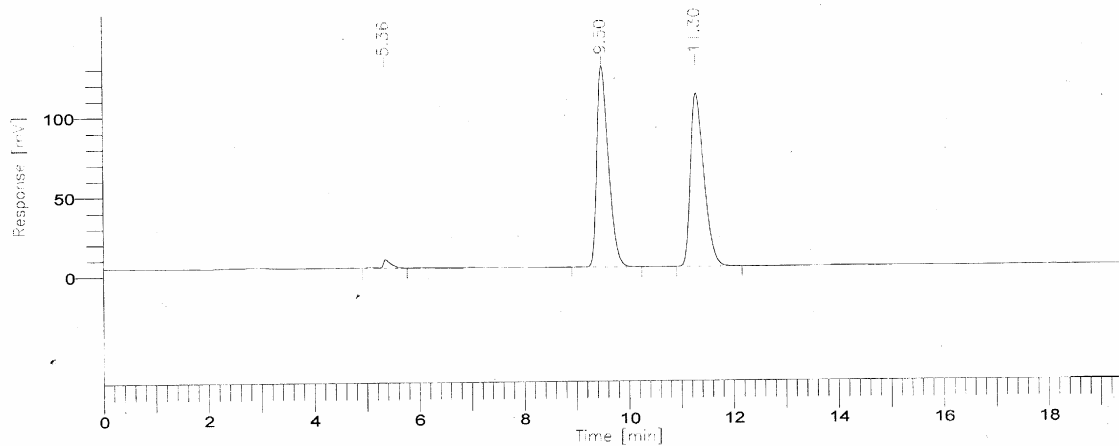
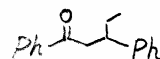
6 Peaks > Height Reject

150.182 Total Height

(CH-6\_04.D01) mU



Software Version: 4.1<2F12> *Chiralpak, hexane/i-PrOH = 95/5*  
 Date: 02-9-26 15:08 *0.7 ml/min, 254 nm*  
 Sample Name : ~~LM7162AC~~ *W-9-9-245 外消*  
 Data File : D:\TC4\DATA\CAO\CAO\_314V.RAW Date: 02-7-3 13:43  
 Sequence File: D:\TC4\DATA\CAO\CAO.SEQ Cycle: 1 Channel : A  
 Instrument : 970A - 0 Rack/Vial: 0/0 Operator: CAO  
 Sample Amount : 1.0000 Dilution Factor : 1.00

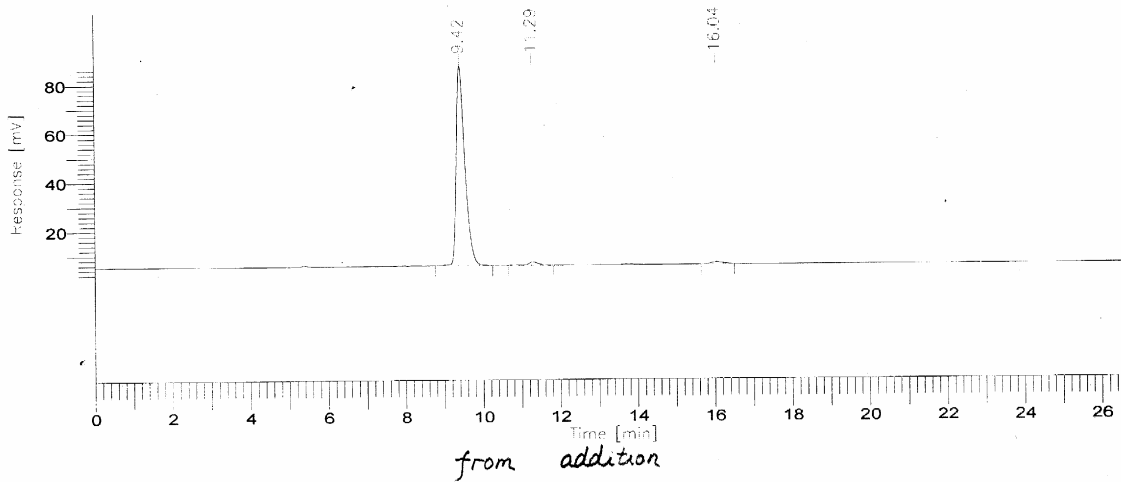


*authentic racemic*

### REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Area BL	Area/Height [sec]
1	5.362	62759.00	5512.13	1.59	0.00	BB	11.3856
2	9.498	1936399.00	125963.77	49.07	0.00	BB	15.3727
3	11.299	1946804.50	108510.77	49.34	0.00	BB	17.9411
		3945962.50	239986.67	100.00	0.00		

Software Version: 4.1<2F12> *Chiralpak, hexane/i-PrOH = 95/5*  
 Date: 02-9-26 13:24 *0.7 ml/min, 254 nm* Ph-C(=O)-C(C)C-Ph  
 Sample Name : w9-9-245  
 Data File : D:\TC4\DATA\CAO\CA0\_328.RAW Date: 02-9-25 16:04  
 Sequence File: D:\TC4\DATA\CAO\CA0.SEQ Cycle: 1 Channel : A  
 Instrument : 970A\_0 Rack/Vial: 0/0 Operator: CAO  
 Sample Amount : 1.0000 Dilution Factor : 1.00



## REPORT

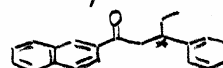
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Area BL	Area/Height [sec]
1	9.415	1274505.00	82093.15	96.60	0.00	BB	15.5251
2	11.289	26948.00	1391.79	2.04	0.00	BB	19.3621
3	16.042	17968.75	812.80	1.36	0.00	BB	22.1073
		1319421.75	84297.73	100.00	0.00		

95.9%

\*\*\*\*\* MODEL 1022 RUNLOG for run: CH-9\_92 \*\*\*\*\*

Run terminated manually on Channel A.

Chiralpak AD, hexane/i-PrOH  
= 95/5  
0.7 mL/min  
254 nm



File : CH-9\_92.D01 w9-10-10b (外消) 1  
Run : 01 Type : Sample  
Path : C:\CH-4 Inst : 1022 LC Plus  
Collection : 13:17:10 Oct 14 2002 Method : LCTEST [ 10:04:38 Oct 14 2002 ]  
Integration : 13:17:10 Oct 14 2002 Method : LCTEST [ 10:04:38 Oct 14 2002 ]  
Report : 13:48:49 Oct 14 2002 Method : LCTEST [ 10:04:38 Oct 14 2002 ]

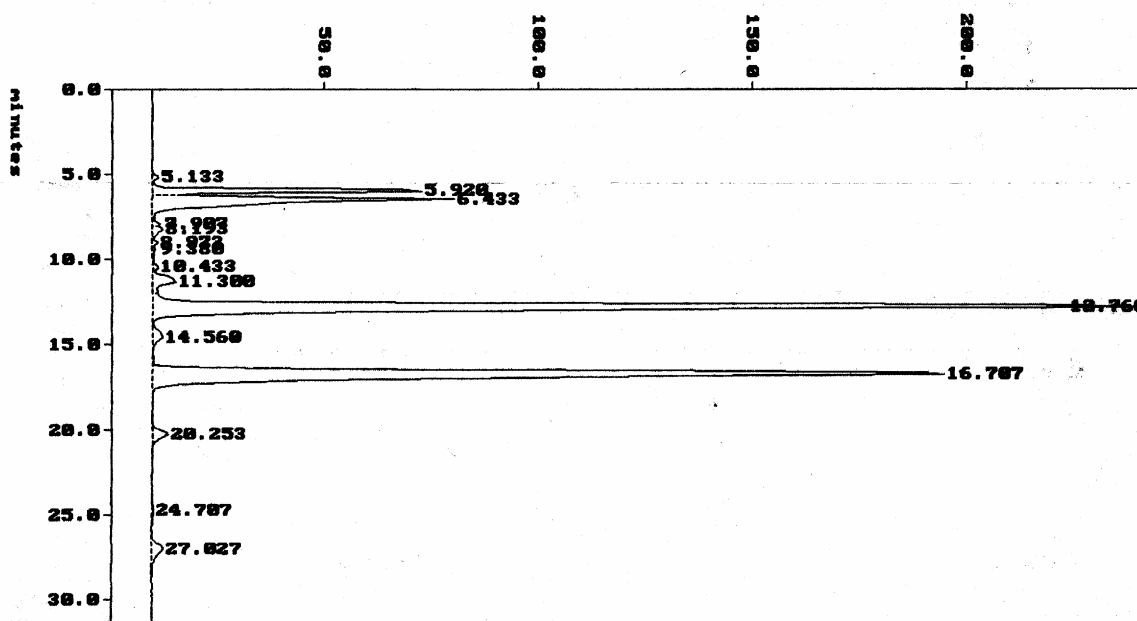
PERCENT ( AREA )

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	5.133	246723	1.5235	T	0.1856	0.2658
2	5.920	7560013	62.8971	T	5.6873	10.9737
3	6.433	14857027	70.4506	T	11.1768	12.2916
4	7.907	240343	1.7196	T	0.1808	0.3000
5	8.193	581392	2.3240	T	0.4374	0.4055
6	8.973	220165	1.1568	T	0.1656	0.2018
7	9.380	182398	0.7174	T	0.1372	0.1252
8	10.433	307755	1.2187	T	0.2315	0.2126
9	11.300	1980516	5.4886	T	1.4899	0.9576
10	12.760	52173020	232.5014	T	39.2492	40.5647
11	14.560	941927	2.1567		0.7086	0.3763
12	16.707	51171208	184.7512		38.4956	32.2337
13	20.253	1153540	3.5035		0.8678	0.6113
14	24.707	129712	0.2893		0.0976	0.0505
15	27.027	1181778	2.4639		0.8890	0.4299

15 Peaks > Area Reject 132927520 Total Area  
15 Peaks > Height Reject 573.162 Total Height

(CH-9\_92.D01) .HU

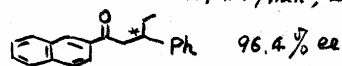
authentic racemic



\*\*\*\* MODEL 1022 RUNLOG for run: CH-9\_93 \*\*\*\*

Run terminated manually on Channel A.

Chiralpak AD, hexane/i-PrOH = 95/5  
0.7 mL/min, 254nm



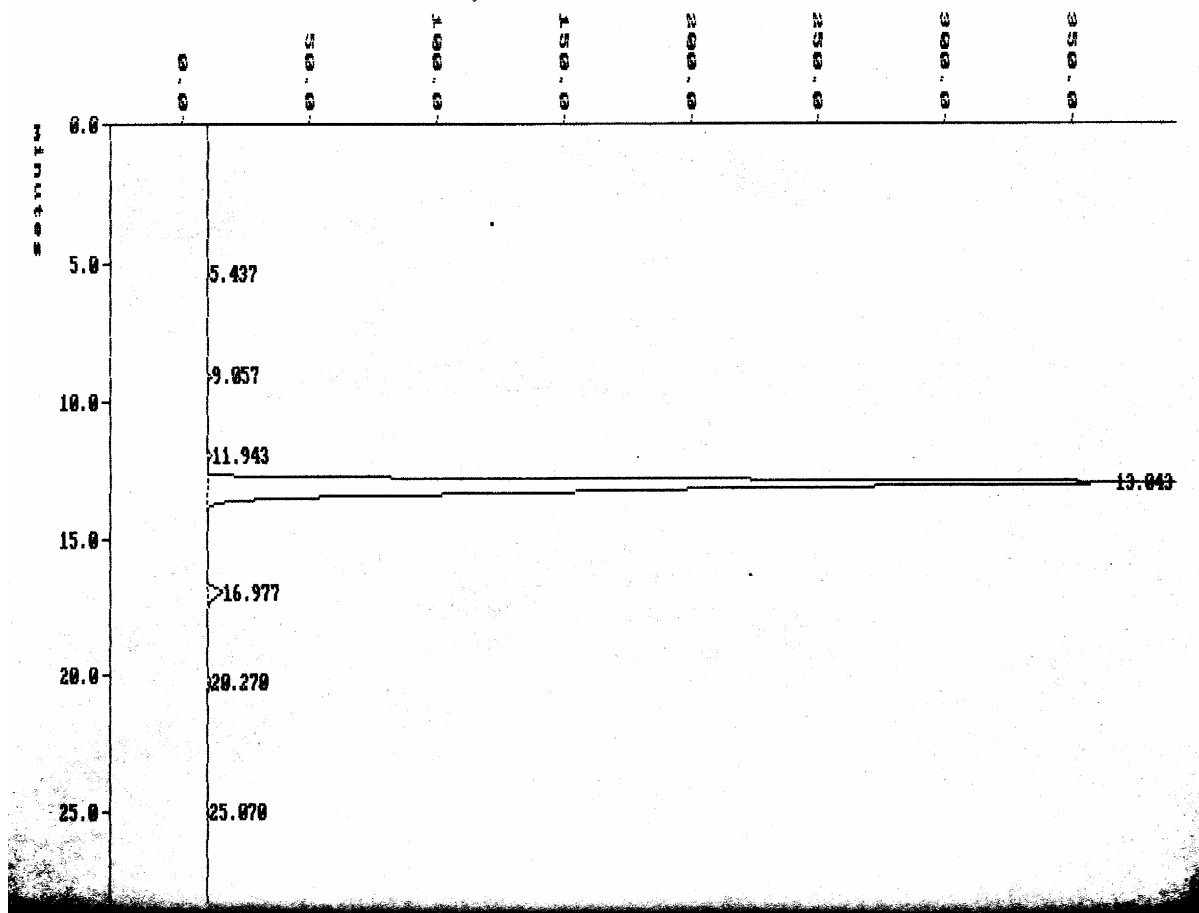
File : CH-9\_93.D01 w9-10-10b 1  
Run : 02 Type : Sample  
Path : C:\CH-4 Inst : 1022 LC Plus  
Collection : 13:57:10 Oct 14 2002 Method : LCTEST [ 10:04:38 Oct 14 2002 ]  
Integration: 13:57:10 Oct 14 2002 Method : LCTEST [ 10:04:38 Oct 14 2002 ]  
Report : 14:25:44 Oct 14 2002 Method : LCTEST [ 10:04:38 Oct 14 2002 ]

PERCENT ( AREA )

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	5.437	69501	0.5629		0.0802	0.1437
2	9.057	174690	1.2664		0.2017	0.3233
3	11.943	257138	1.2683	V	0.2969	0.3238
4	13.043	84081648	381.2719		97.0773	97.3323
5	16.977	1535687	5.8332		1.7730	1.4891
6	20.270	332471	1.1000		0.3839	0.2808
7	25.070	161935	0.4191		0.1870	0.1070

7 Peaks > Area Reject 86613072 Total Area  
7 Peaks > Height Reject 391.722 Total Height

from addition



File : CH-2\_81.D01 W2153E-RAC 1  
 Run : 01 Type : Sample  
 Path : C:\CH-4 Inst : 1022 LC Plus  
 Collection : 14:42:13 Feb 28 2002 Method : LCTEST [ 08:55:51 Feb 28 2002 ]  
 Integration : 16:41:45 Nov 01 2002 Method : LCTEST [ 13:28:18 Nov 01 2002 ]  
 Report : 16:41:47 Nov 01 2002 Method : LCTEST [ 13:28:18 Nov 01 2002 ]

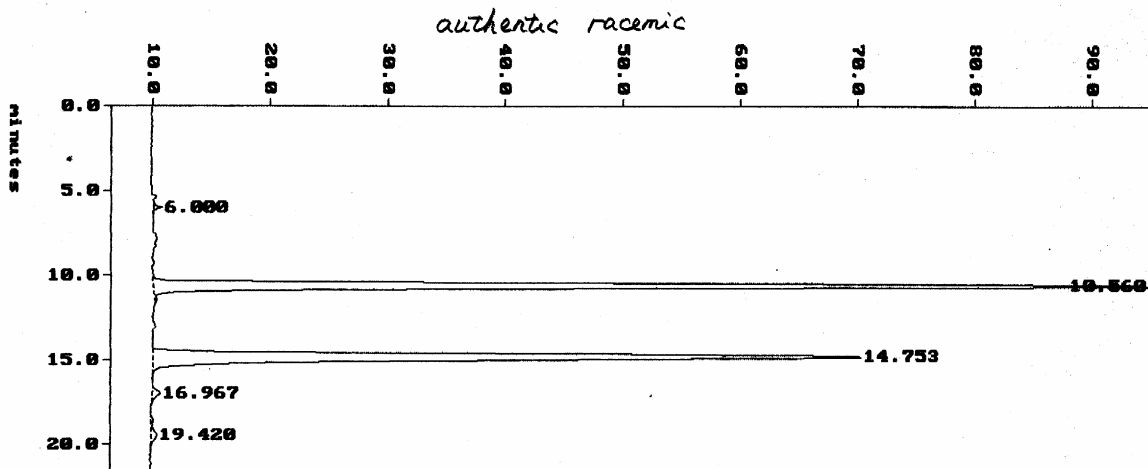
## PERCENT ( AREA )

Pk #	RT	Area	Height	BC	Area Percent	Height Percent (外消)
1	6.000	62430	0.6563		0.2156	0.4471
2	10.560	14227934	84.7207		49.1321	57.7097
3	14.753	14262233	60.2732		49.2506	41.0567
4	16.967	171722	0.6497		0.5930	0.4426
5	19.420	234186	0.5051		0.8087	0.3441

5 Peaks > Area Reject 28958504 Total Area  
 5 Peaks > Height Reject 146.805 Total Height

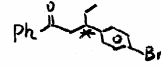
Chiralpak AD,  
 hexane / i-PrOH = 95/5  
 0.7 mL/min, 254 nm.

(CH-2\_81.D01) MV



\*\*\*\*\* MODEL 1022 RUNLOG for run: CH-9\_57 \*\*\*\*\*

Run terminated manually on Channel A.



File : CH-9\_57.D01 w9-10-7a 1  
 Run : 01 Type : Sample  
 Path : C:\CH-4 Inst : 1022 LC Plus  
 Collection : 13:22:26 Oct 09 2002 Method : LCTEST [ 11:40:03 Oct 09 2002 ]  
 Integration : 13:22:26 Oct 09 2002 Method : LCTEST [ 11:40:03 Oct 09 2002 ]  
 Report : 13:45:57 Oct 09 2002 Method : LCTEST [ 11:40:03 Oct 09 2002 ]

PERCENT ( AREA )

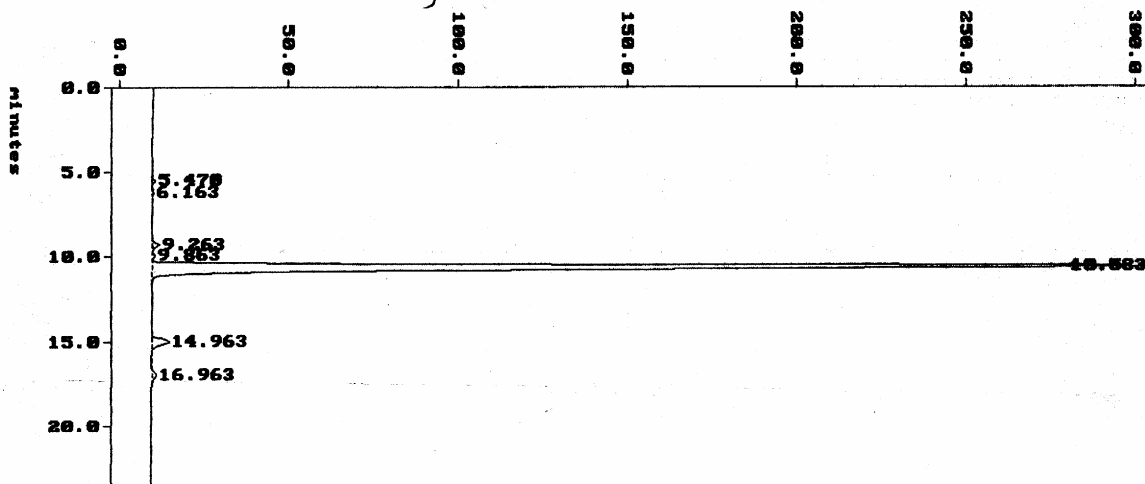
PK #	RT	Area	Height	BC	Area Percent	Height Percent
1	5.470	109704	0.9251	T	0.2031	0.3034
2	6.163	61810	0.3673		0.1144	0.1204
3	9.263	320233	2.0274	T	0.5929	0.6648
4	9.863	96516	0.6318	T	0.1787	0.2072
5	10.583	51893412	294.5019		96.0773	96.5675
6	14.963	1190958	5.1670		2.2050	1.6943
7	16.963	339500	1.3495		0.6286	0.4425

7 Peaks > Area Reject 54012136 Total Area  
 7 Peaks > Height Reject 304.970 Total Height

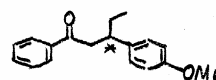
*Chiralpak AD,  
 hexane/i-PrOH = 95/5  
 0.7 mL/min, 254 nm*

(CH-9\_57.D01) WU

*from addition*



Chiralpak AD, hexane/i-PrOH = 95/5  
0.7 mL/min, 254 nm

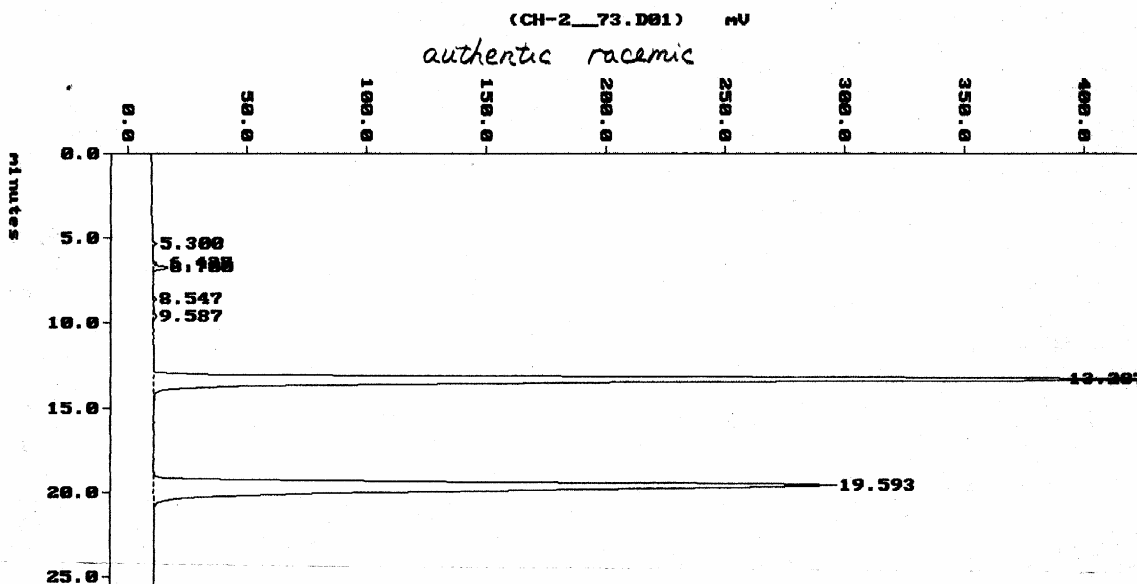


File : CH-2\_73.D01 W2153A-RAC 1  
Run : 01 Type : Sample  
Path : C:\CH-4 Inst : 1022 LC Plus  
Collection : 09:01:46 Feb 28 2002 Method : LCTEST [ 08:55:51 Feb 28 2002 ]  
Integration: 16:36:01 Nov 01 2002 Method : LCTEST [ 13:28:18 Nov 01 2002 ]  
Report : 16:36:08 Nov 01 2002 Method : LCTEST [ 13:28:18 Nov 01 2002 ]

## PERCENT ( AREA )

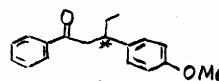
Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	5.300	211168	2.0265		0.1125	0.2841
2	6.427	130973	1.4098	T	0.0698	0.1977
3	6.700	661565	5.8154		0.3524	0.8154
4	8.547	198028	1.3154	T	0.1055	0.1844
5	9.587	286134	1.2462		0.1524	0.1747
6	13.287	92189568	415.9774		49.1087	58.3275
7	19.593	94047904	285.3846		50.0987	40.0161

7 Peaks > Area Reject 187725344 Total Area  
7 Peaks > Height Reject 713.175 Total Height



Chiralpak AD, hexane/i-Pr-OH = 95/5  
0.7 mL/min, 254 nm

\*\*\*\*\* MODEL 1022 RUNLOG for run: CH-9\_58 \*\*\*\*\*  
Run terminated manually on Channel A.



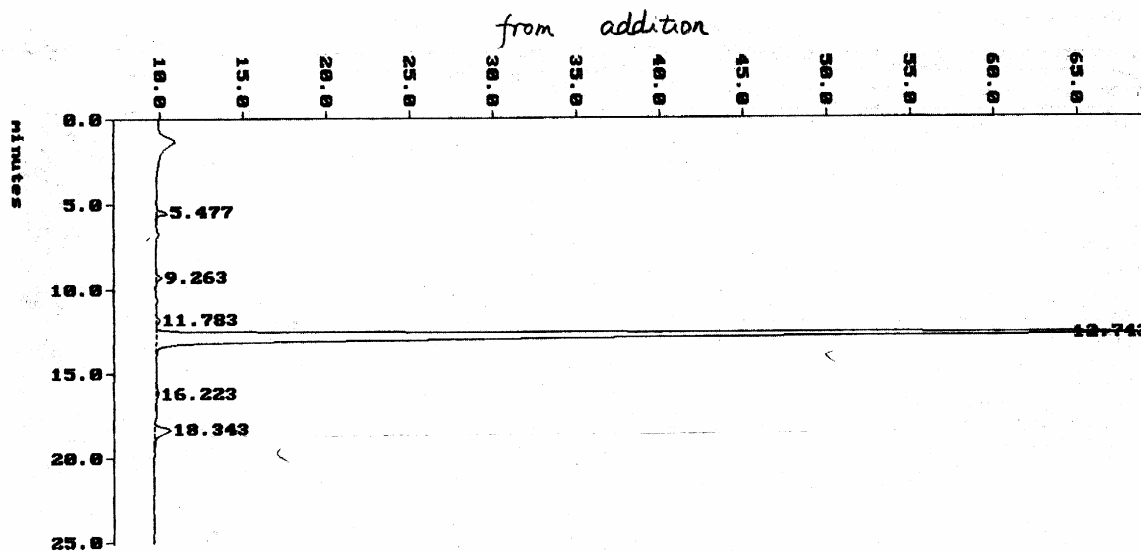
File : CH-9\_58.D01 w9-10-7b 1  
Run : 01 Type : Sample  
Path : C:\CH-4 Inst : 1022 LC Plus  
Collection : 13:47:18 Oct 09 2002 Method : LCTEST [ 11:40:03 Oct 09 2002 ]  
Integration: 13:47:18 Oct 09 2002 Method : LCTEST [ 11:40:03 Oct 09 2002 ]  
Report : 14:12:23 Oct 09 2002 Method : LCTEST [ 11:40:03 Oct 09 2002 ]

PERCENT ( AREA )

PK #	RT	Area	Height	BC	Area Percent	Height Percent
1	5.477	78151	0.6639		0.6281	1.0715
2	9.263	51747	0.3353		0.4159	0.5412
3	11.783	42503	0.2093	T	0.3416	0.3379
4	12.743	11995181	59.6948		96.4062	96.3463
5	16.223	16764	0.1120		0.1347	0.1808
6	18.343	257981	0.9432		2.0734	1.5223

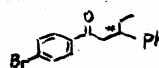
6 Peaks > Area Reject 12442328 Total Area  
6 Peaks > Height Reject 61.959 Total Height

(CH-9\_58.D01) nU



\*\*\*\*\* MODEL 1022 RUNLOG for run: CH-9\_88 \*\*\*\*\*

Run terminated manually on Channel A.



95.1% ee

File : CH-9\_88.D01

w9-10-10a

1

Run : 01

Type : Sample

Path : C:\CH-4

Inst : 1022 LC Plus

Collection : 10:05:40 Oct 14 2002 Method : LCTEST [ 10:04:38 Oct 14 2002 ]

Integration: 10:05:40 Oct 14 2002 Method : LCTEST [ 10:04:38 Oct 14 2002 ]

Report : 10:25:13 Oct 14 2002 Method : LCTEST [ 10:04:38 Oct 14 2002 ]

PERCENT ( AREA )

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	5.490	30328	0.4034		0.0250	0.0614
2	6.550	64178	0.5542		0.0528	0.0843
3	8.170	125943	0.9320	T	0.1036	0.1418
4	9.090	112811	0.4217		0.0928	0.0641
5	10.750	798677	4.0507	T	0.6572	0.6162
6	11.563	117354792	636.7339		96.5633	96.8658
7	13.943	2945391	13.7032	V	2.4236	2.0847
8	15.037	99329	0.5374		0.0817	0.0817

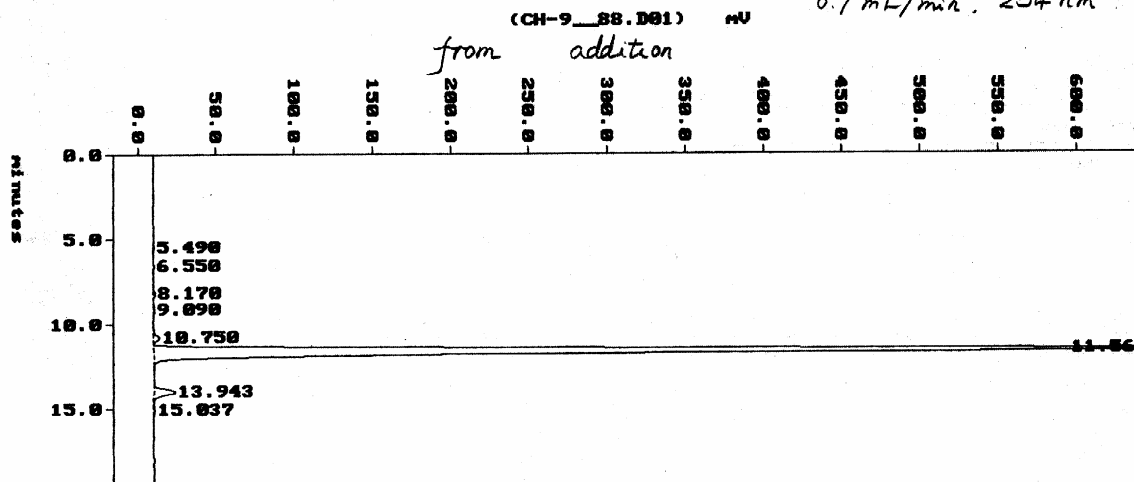
8 Peaks > Area Reject

121531448 Total Area

8 Peaks > Height Reject

657.336 Total Height

Chiralpak AD,  
hexane/i-PrOH = 95/5  
0.7 mL/min, 254 nm



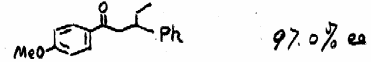
\*\*\*\*\* MODEL 1022 RUNLOG for run: CH-9\_89 \*\*\*\*\*

Run terminated manually on Channel A.

*Chiralpak AD,  
Hexane/i-PrOH = 95/5,  
0.7 ml/min, 254 nm*

File : CH-9\_89.D01 w9-10-10c 1  
Run : 01 Type : Sample  
Path : C:\CH-4 Inst : 1022 LC Plus  
Collection : 10:26:00 Oct 14 2002 Method : LCTEST [ 10:04:38 Oct 14 2002 ]  
Integration: 10:26:00 Oct 14 2002 Method : LCTEST [ 10:04:38 Oct 14 2002 ]  
Report : 11:04:20 Oct 14 2002 Method : LCTEST [ 10:04:38 Oct 14 2002 ]

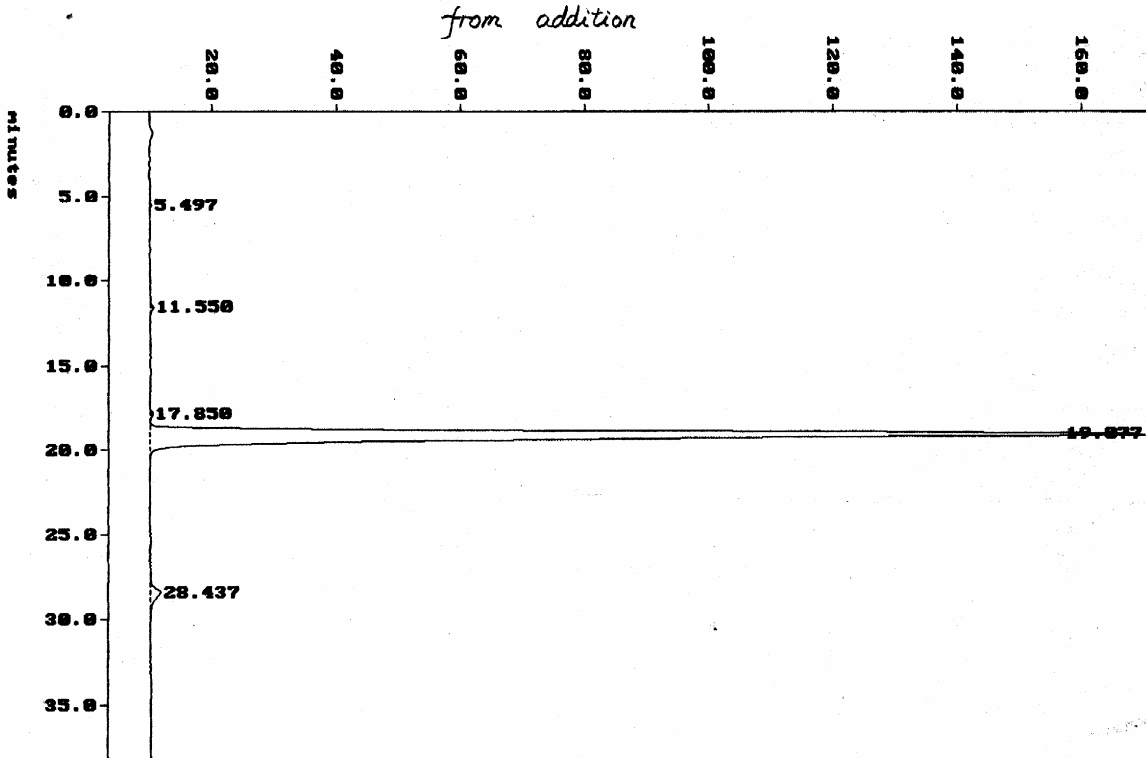
PERCENT ( AREA )

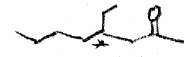


Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	5.497	27180	0.2745		0.0561	0.1682
2	11.550	98381	0.5660		0.2030	0.3469
3	17.850	102047	0.3764	T	0.2106	0.2307
4	19.077	47493480	160.2653		98.0188	98.2298
5	28.437	732326	1.6712		1.5114	1.0243

5 Peaks > Area Reject 48453416 Total Area  
5 Peaks > Height Reject 163.153 Total Height

(CH-9\_89.D01) .NU





File : S11\_54.D01

w9-69-b

Run : 03

Type : Sample

Collection : 10:35:41 Nov 11 2002

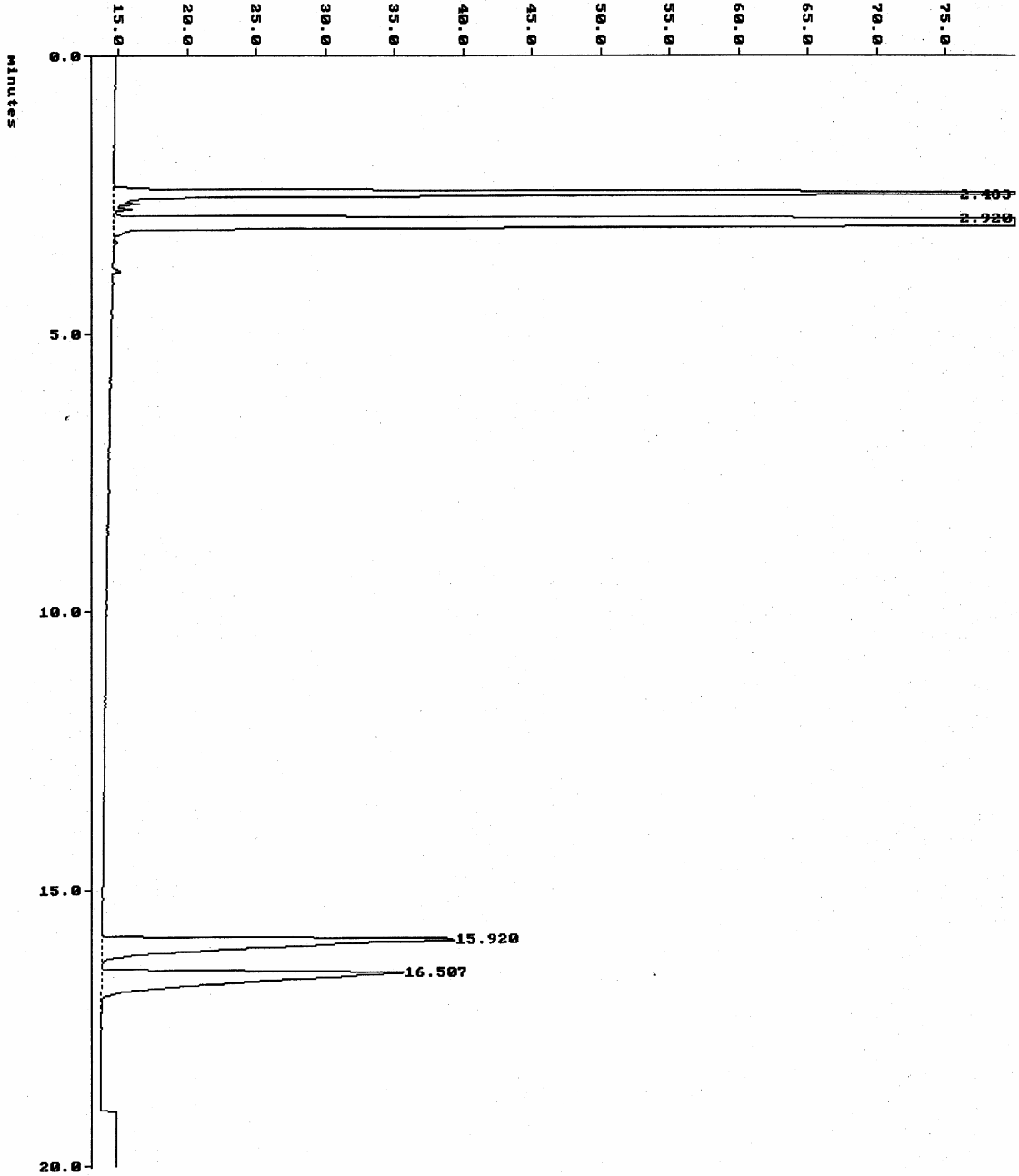
Method : XWD

[ 08:18:02 Nov 11 2002 ]

Chirasil-DEX CB, 25m x 0.25mm,

(S11\_54.D01) mU 100°C (30min), 8.0psi N<sub>2</sub>

authentic racemic



\*\*\*\*\* MODEL 1022 RUNLOG for run: S11\_\_58 \*\*\*\*\*

Run terminated manually on Channel A.

\*\*\*\*\* MODEL 1022 RUNLOG for run: S11\_\_59 \*\*\*\*\*

Run terminated manually on Channel A.

\*\*\*\*\* MODEL 1022 RUNLOG for run: S11\_\_60 \*\*\*\*\*

Run terminated manually on Channel A.

\*\*\*\*\* MODEL 1022 RUNLOG for run: S11\_\_61 \*\*\*\*\*

Run terminated manually on Channel A.

\*\*\*\*\* MODEL 1022 RUNLOG for run: S11\_\_62 \*\*\*\*\*

Run terminated manually on Channel A.

File : S11\_\_54.D01

w9-69-b

Run : 03

Type : Sampl

Path : C:\\$T\$

Inst : 1022 LC Plu

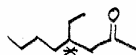
Collection : 10:35:41 Nov 11 2002 Method : XWD [ 08:18:02 Nov 11 2002 ]

Integration: 10:35:41 Nov 11 2002 Method : XWD [ 08:18:02 Nov 11 2002 ]

Report : 14:32:00 Nov 11 2002 Method : XWD [ 08:18:02 Nov 11 2002 ]

PERCENT ( AREA )

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	2.483	49905224	995.2268	T	60.6822	64.8972
2	2.920	26863990	491.3793		32.6652	32.0421
3	15.920	2738977	25.2992	T	3.3305	1.6497
4	16.507	2732152	21.6371		3.3222	1.4109
4 Peaks > Area Reject			82240344 Total Area			
4 Peaks > Height Reject			1533.542 Total Height			



File : S11\_84.D01  
Run : 01  
Collection : 13:42:22 Nov 14 2002

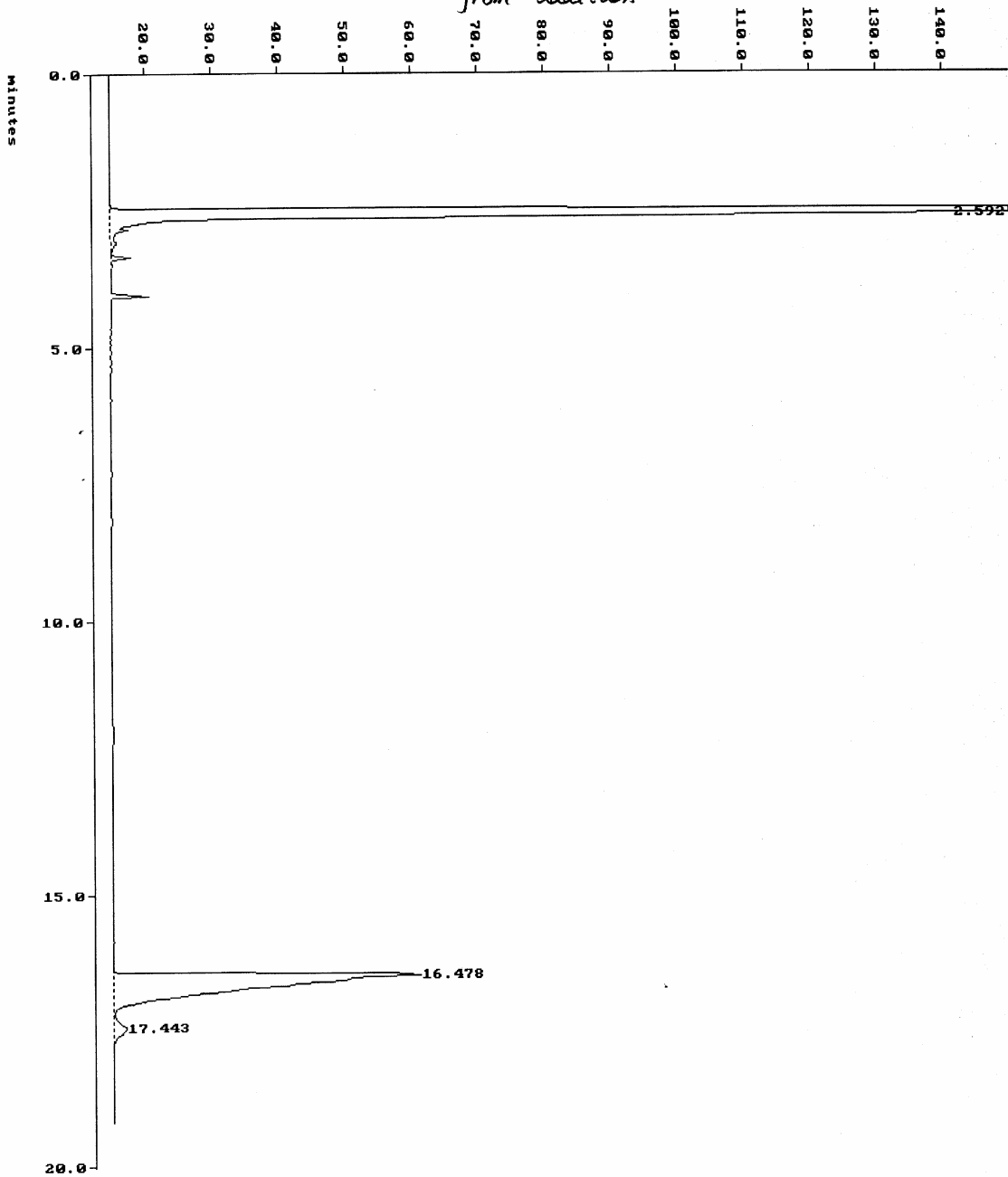
w9-73-B  
Method : XWD

Type : Sample  
[ 08:06:39 Nov 14 2002 ]

Chiralcel-DEX CB, 25m x 0.25mm  
100°C (30min), 8.0psi N<sub>2</sub>

(S11\_84.D01) MV

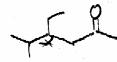
from addition



File : S11\_\_84.D01 w9-73-B  
Run : 01  
Path : C:\\$T\$ Type : Sampl  
Collection : 13:42:22 Nov 14 2002 Method : XWD Inst : 1022 LC Plu  
Integration: 13:42:22 Nov 14 2002 Method : XWD [ 08:06:39 Nov 14 2002 ]  
Report : 10:45:09 Apr 15 2003 Method : XWD [ 08:06:39 Nov 14 2002 ]  
[ 07:39:59 Apr 15 2003 ]

## PERCENT ( AREA ) \ MANUALLY ALTERED

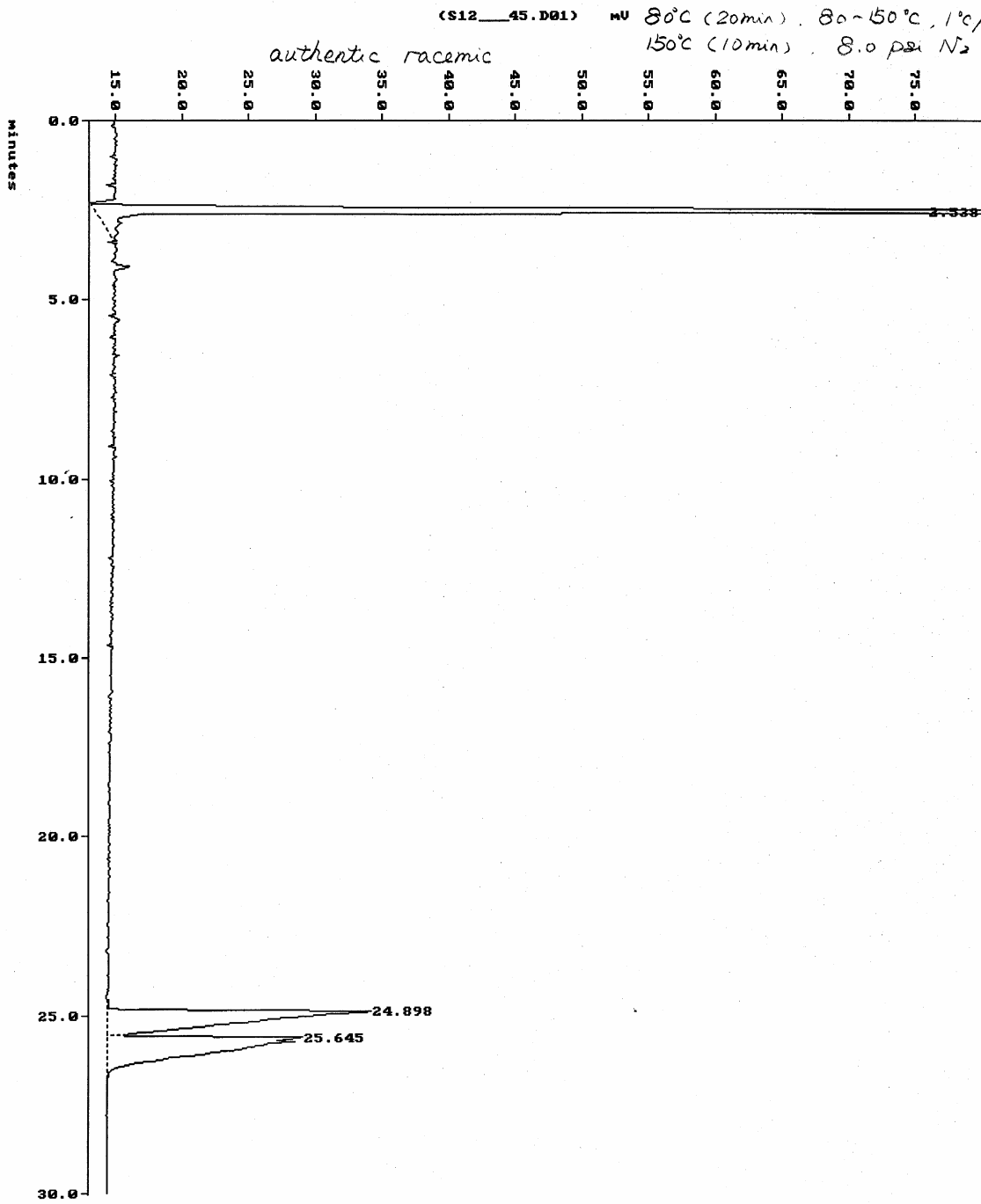
Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	2.592	65937704	995.0563		89.5845	95.5282
2	16.478	7388903	44.6094	T	10.0387	4.2826
3	17.443	277341	1.9700		0.3768	0.1891
3 Peaks > Area Reject			73603952	Total Area		
3 Peaks > Height Reject			1041.636	Total Height		



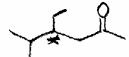
File : S12\_45.D01  
Run : 01

W9-82-b  
Method : XWD

Type : Sample  
[ 07:30:32 Nov 22 2002 ]  
Chiralcel-DEX CB, 25 m x 0.25 mm  
80°C (20min), 80-150°C, 1°C/min  
150°C (10min), 8.0 psi N<sub>2</sub>







File : S12\_46.D01

w9-82

Run : 01

Type : Sample

Collection : 08:59:24 Nov 22 2002 Method : XWD

[ 07:30:32 Nov 22 2002 ]

Chirasil - DEX CB, 25 m x 0.25 mm

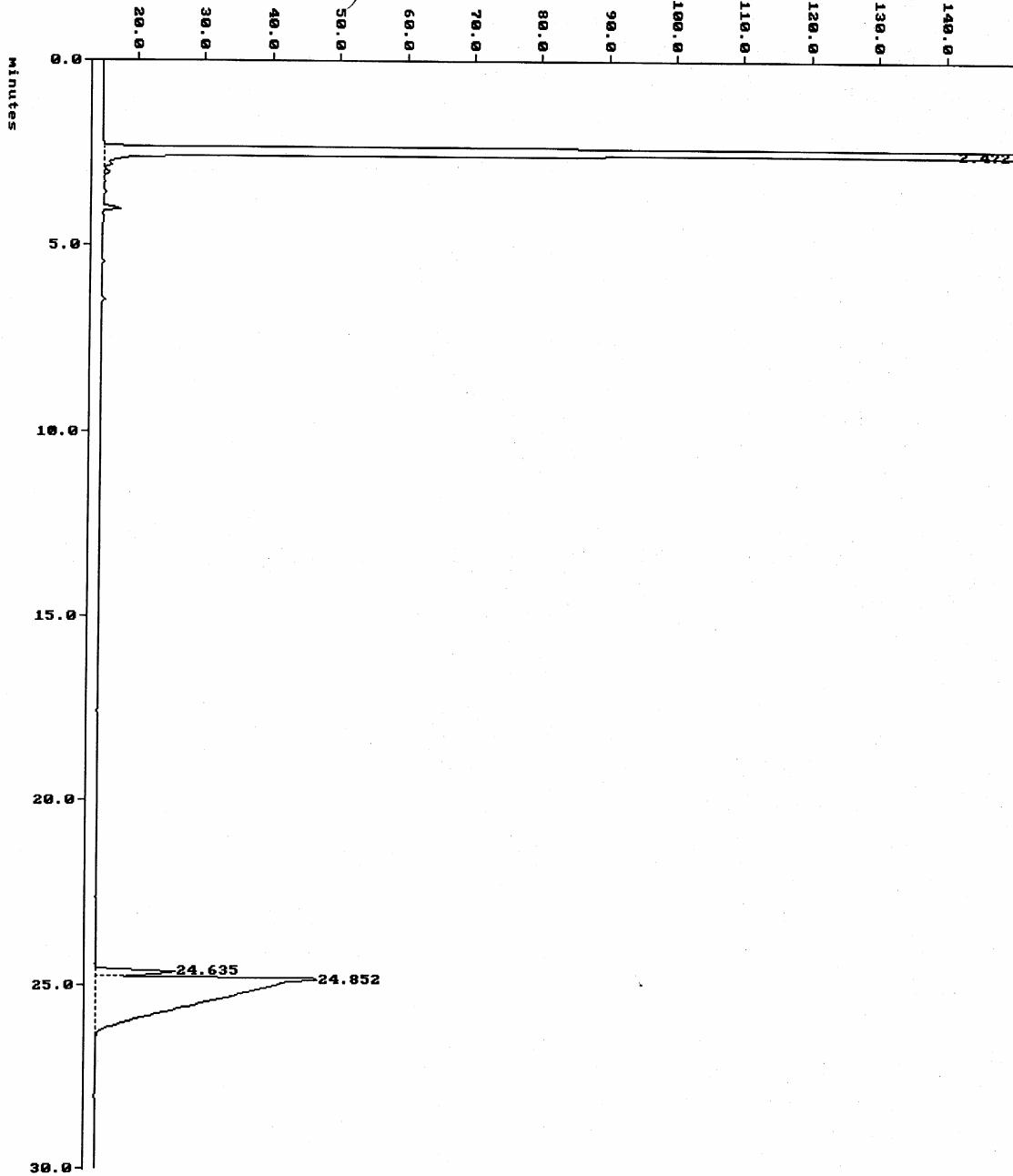
(S12\_46.D01)

MU

80°C (20min), 80-150°C, 1°C/min,

150°C (10min), 8.0 psi N<sub>2</sub>

from addition









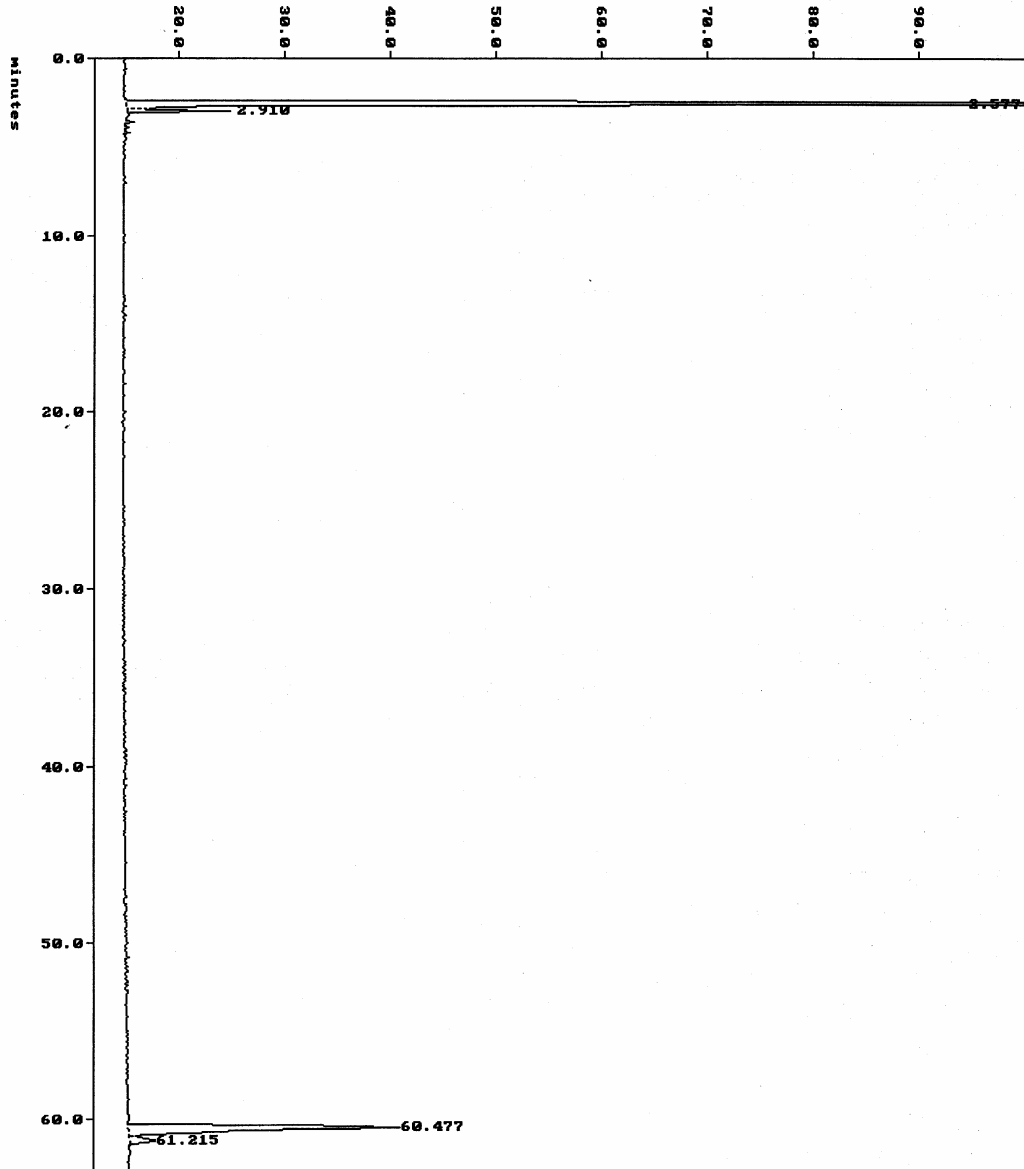
File : S12\_99.D01  
Run : 01  
Collection : 15:29:32 Nov 28 2002

w-9-96  
Method : XMD

Type : Sample  
[ 07:21:59 Nov 28 2002 ]

*Chiralcel-DEX CB, 25m x 0.25mm*  
*80°C (20min), 80-180°C, 1°C/min,*  
*180°C (2min), 8.0 psi N<sub>2</sub>*

(S12\_99.D01) MU  
*from addition*



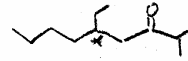
File : S12\_\_99.D01 w-9-96  
Run : 01 Type : Sampl  
Path : C:\\$T\$ Inst : 1022 LC Plu  
Collection : 15:29:32 Nov 28 2002 Method : XWD [ 07:21:59 Nov 28 2002 ]  
Integration: 15:29:32 Nov 28 2002 Method : XWD [ 07:21:59 Nov 28 2002 ]  
Report : 07:51:13 Nov 29 2002 Method : XWD [ 07:11:27 Nov 29 2002 ]

## PERCENT ( AREA ) \ MANUALLY ALTERED

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	2.577	88931496	994.7877	T	94.4199	96.3755
2	2.910	378026	9.6893		0.4014	0.9387
3	60.477	4502482	25.2342	T	4.7804	2.4447
4	61.215	375256	2.4890		0.3984	0.2411

4 Peaks > Area Reject 94187264 Total Area  
4 Peaks > Height Reject 1032.200 Total Height

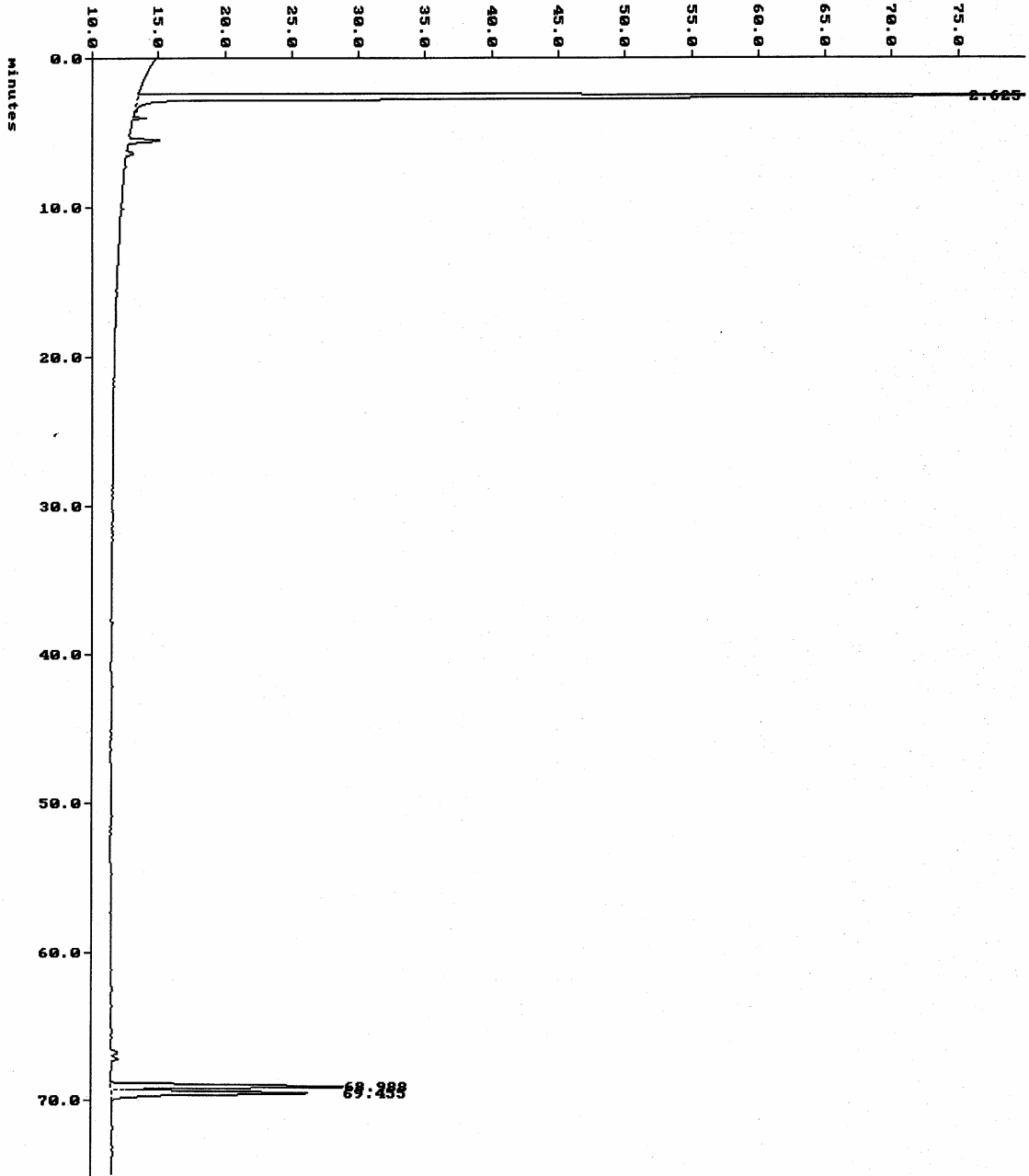
812 ec



File : S13\_20.D01 w-10-4-rac  
Run : 01  
Collection : 10:19:27 Dec 02 2002 Method : XWD

Type : Sample  
[ 07:15:02 Dec 02 2002 ]  
Chiralcel-DEX CB, 25m x 0.25mm

(S13\_20.D01) WU 60°C (20min), 80-160°C, 1°C/min,  
authentic racemic 160°C (10min), 8.0 psi N<sub>2</sub>





File : S13\_21.D01  
Run : 02  
Collection : 11:43:56 Dec 02 2002

w-10-4  
Method : XWD

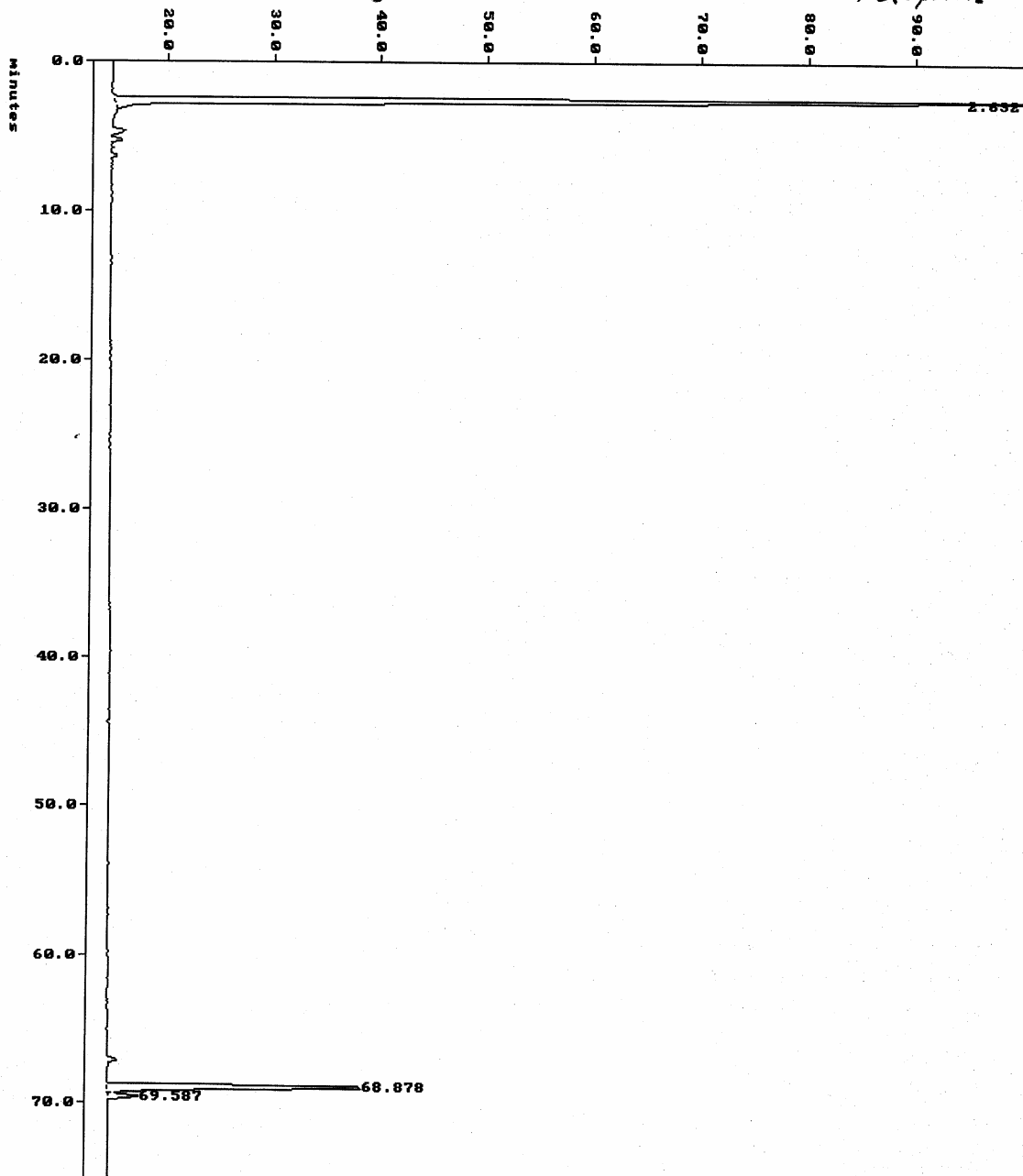
Type : Sample  
[ 07:15:02 Dec 02 2002 ]



(S13\_21.D01) MU

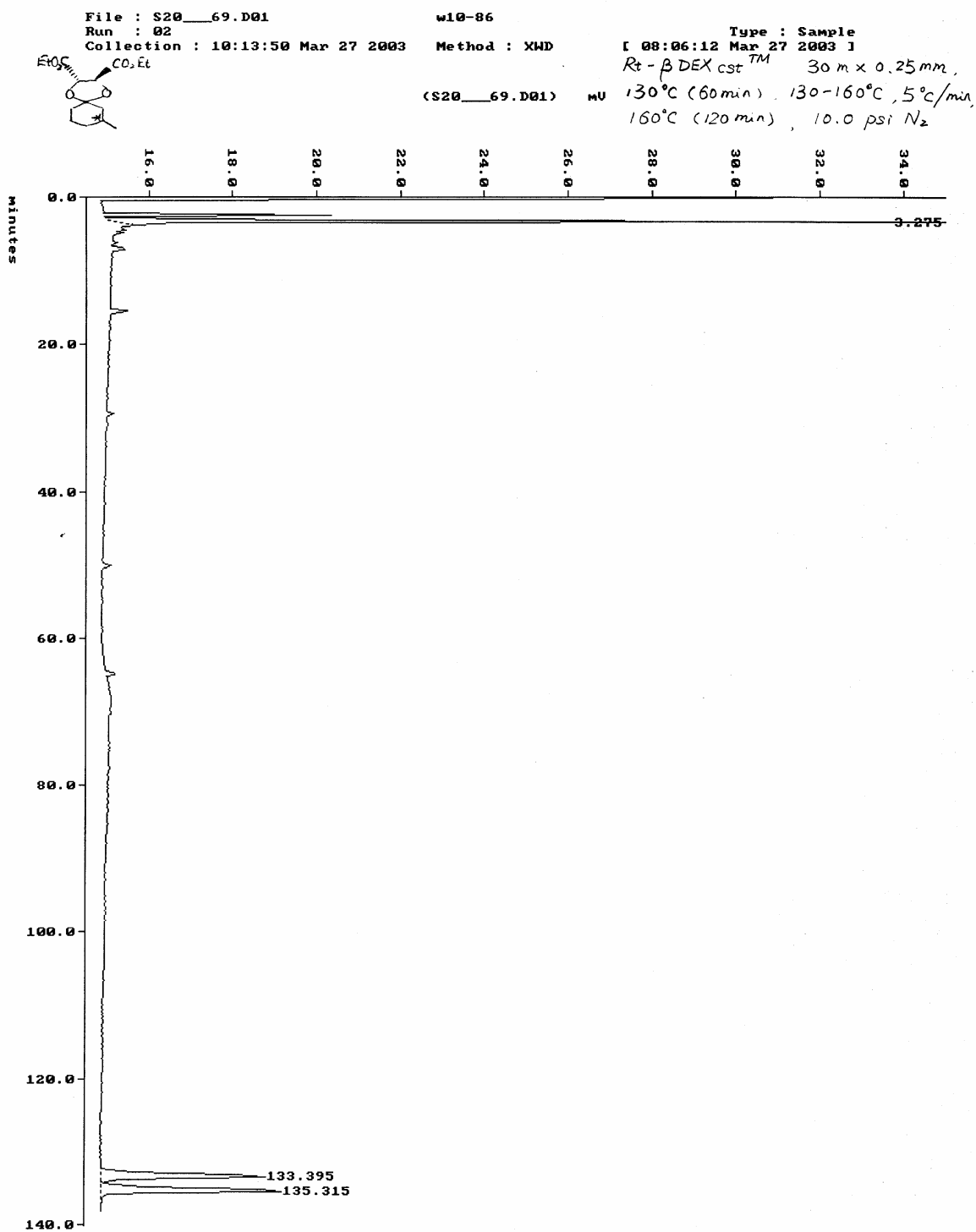
Chiralcel-DEX CB, 25 m x 0.25 mm  
60°C (20 min), 80-160°C 1°C/min  
160°C (10 min), 8.0 psi N<sub>2</sub>

from addition



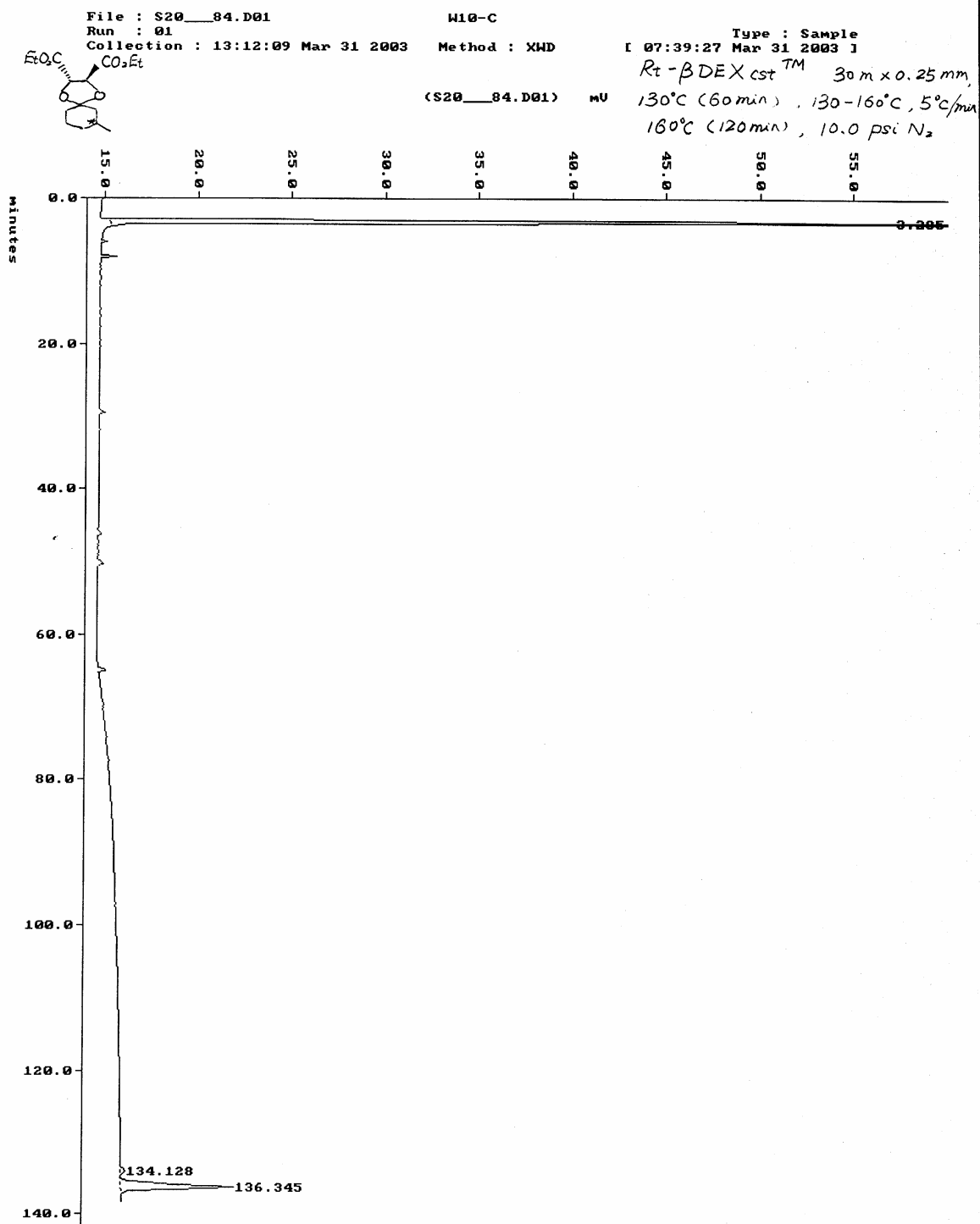


*the corresponding ketal of authentic racemic*



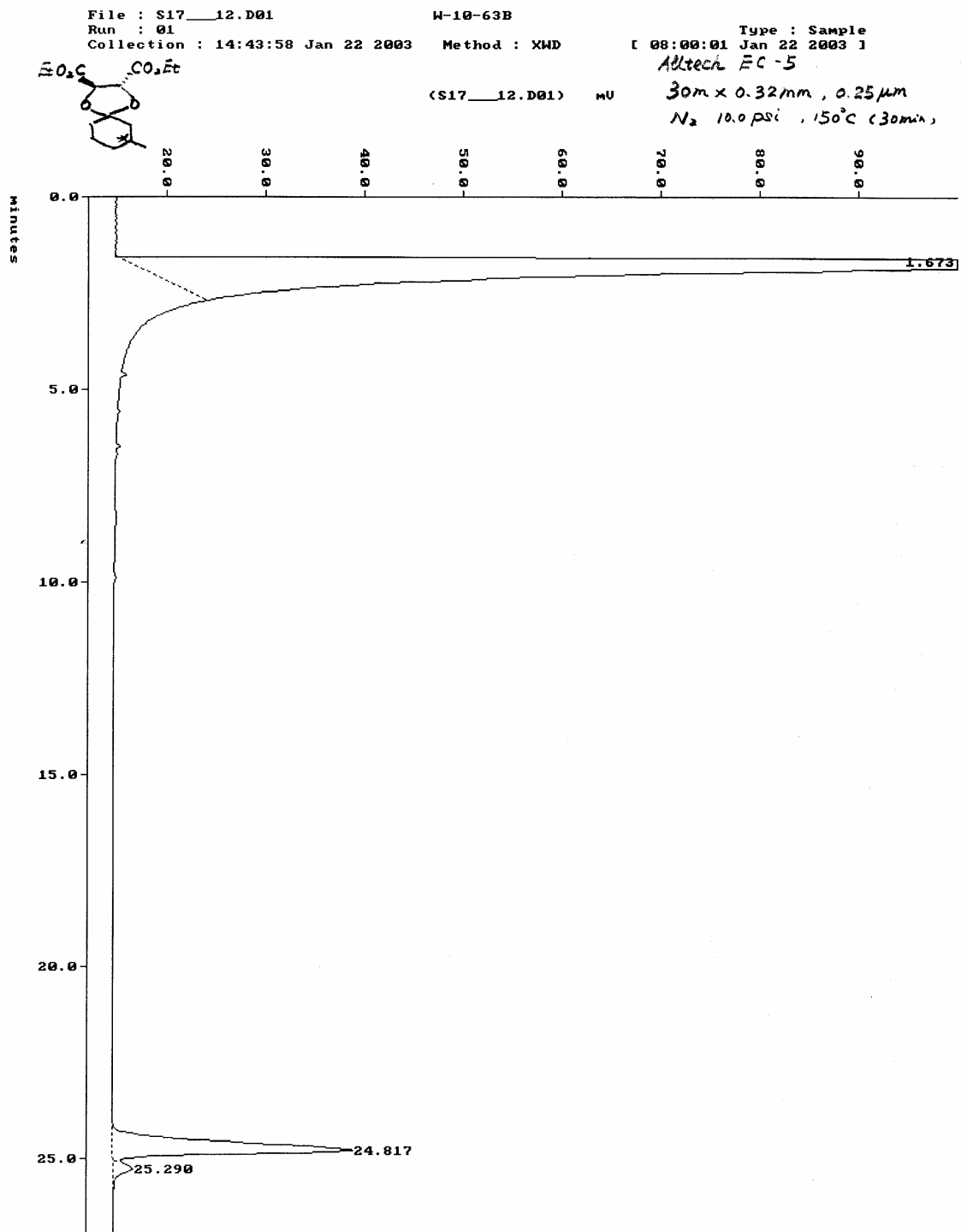


*the corresponding ketal of asymmetri addition product*





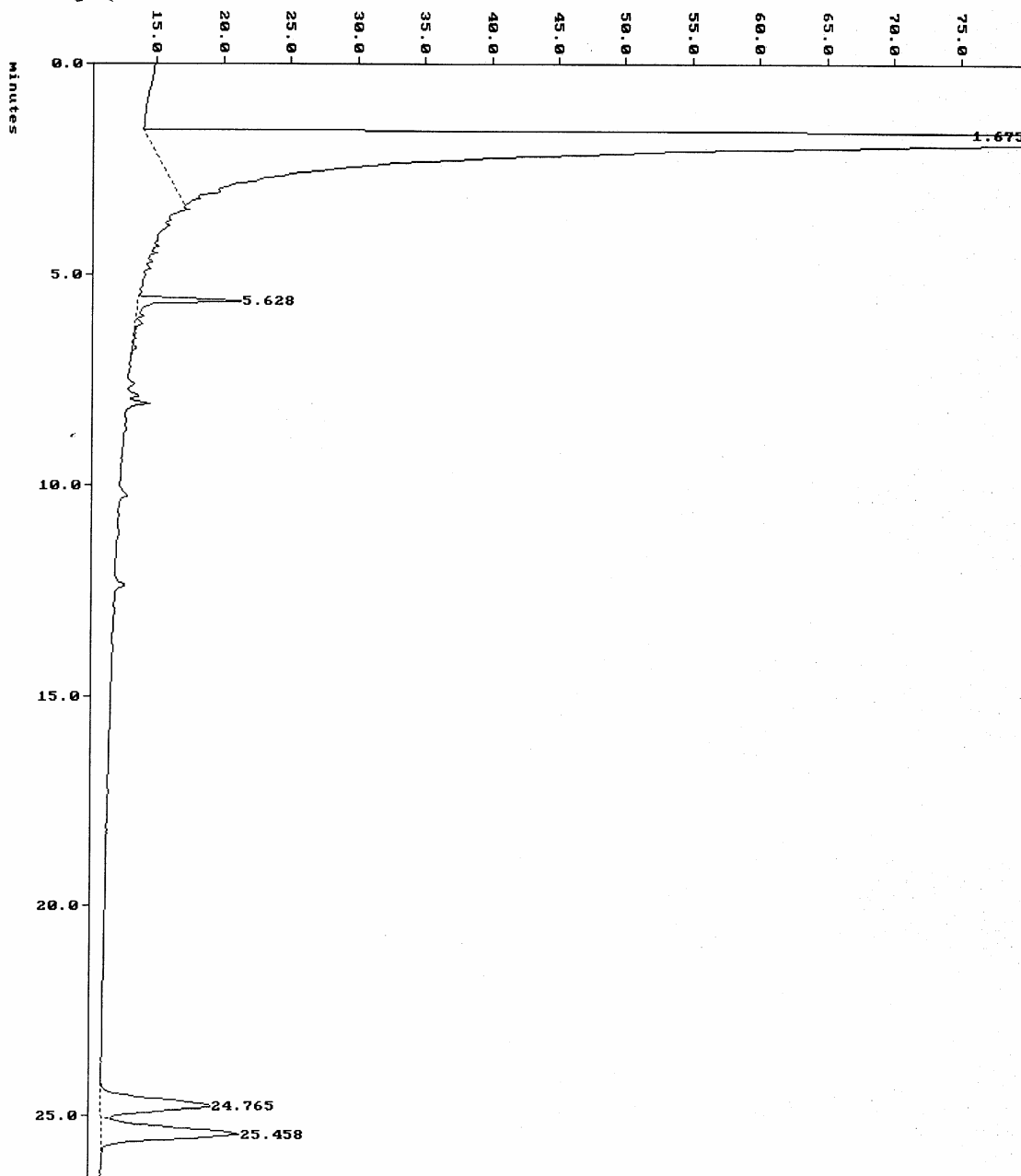
*the corresponding ketal of asymmetric addition product*





the corresponding ketal of authentic racemic

File : S17\_09.D01      Wang cj      Type : Sample  
Run : 01      Collection : 13:15:05 Jan 22 2003      Method : XWD      [ 08:00:01 Jan 22 2003 ]  
EtOC      CO<sub>2</sub>Et  
COC(=O)[C@H]1[C@@H](OC(=O)C)[C@@H]2[C@H](OC(=O)C)CC[C@H]12  
(S17\_09.D01)      mU      Alltech EC-5  
30 m x 0.32 mm, 0.25 μm  
N<sub>2</sub> 10.0 psi, 150°C (30 min)



File : S17\_\_\_09.D01                      Wang cj  
Run : 01  
Path : C:\\$T\$                              Type : Sampl  
Collection : 13:15:05 Jan 22 2003      Method : XWD      [ 08:00:01 Jan 22 2003 ]  
Integration: 13:15:05 Jan 22 2003      Method : XWD      [ 08:00:01 Jan 22 2003 ]  
Report : 15:27:56 Apr 11 2003      Method : XWD      [ 12:47:52 Apr 11 2003 ]

## PERCENT ( AREA ) \ MANUALLY ALTERED

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	1.675	84016888	995.7156		95.3732	97.4557
2	5.628	561454	7.6605		0.6373	0.7498
3	24.765	1603196	8.1017	T	1.8199	0.7930
4	25.458	1911205	10.2329		2.1695	1.0015

4 Peaks > Area Reject      88092744 Total Area  
4 Peaks > Height Reject    1021.711 Total Height



File : S20\_\_44.D01 w10-63rac  
Run : 01 Type : Sampl  
Path : C:\\$T\$ Inst : 1022 LC Plu  
Collection : 10:04:00 Mar 21 2003 Method : XWD [ 08:40:39 Mar 21 2003 ]  
Integration: 10:04:00 Mar 21 2003 Method : XWD [ 08:40:39 Mar 21 2003 ]  
Report : 12:56:21 Mar 21 2003 Method : XWD [ 08:40:39 Mar 21 2003 ]

## PERCENT ( AREA ) \ MANUALLY ALTERED

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	3.252	129841904	994.8225		97.8544	99.2380
2	14.738	393571	1.3894		0.2966	0.1386
3	130.418	1127290	2.9443	T	0.8496	0.2937
4	133.538	1326168	3.3053		0.9995	0.3297
4 Peaks > Area Reject			132688936	Total Area		
4 Peaks > Height Reject			1002.462	Total Height		

the corresponding ketal of asymmetric addition product

