

## Supporting Information

### Chiral phosphine Lewis base catalyzed asymmetric aza-Baylis-Hillman reaction of *N*-sulfonated imines with activated olefins

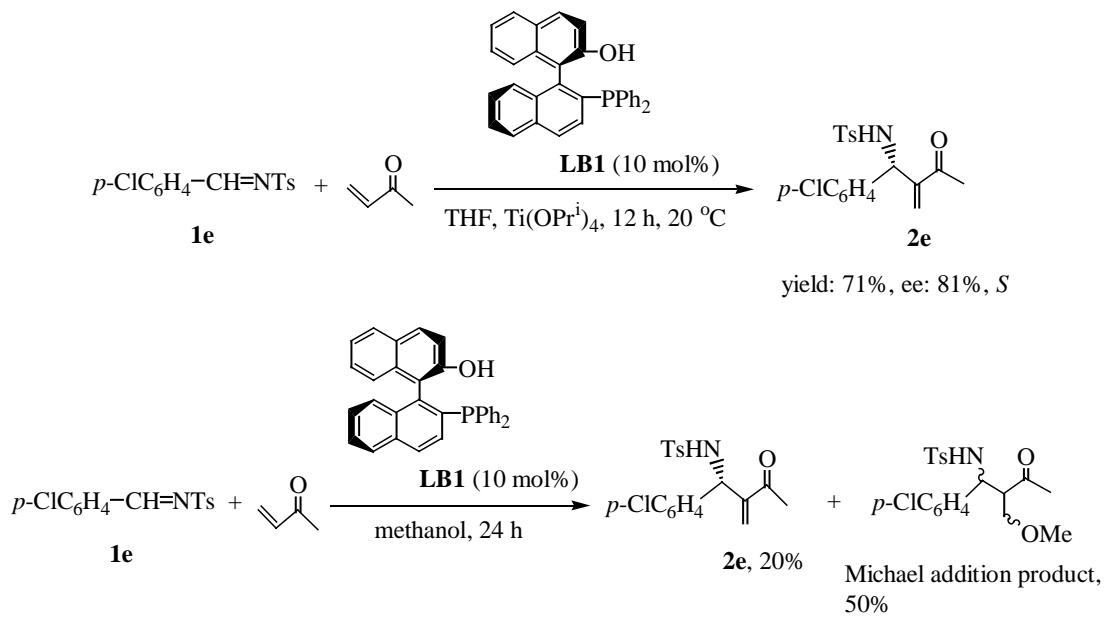
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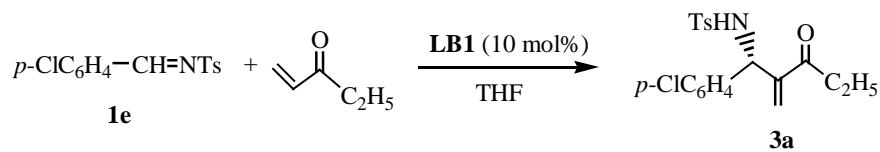
1) *Aza-Baylis-Hillman reaction of **1e** with MVK in THF in the presence of Lewis acid  $Ti(OPr^i)_4$  and in methanol.*



2) Optimization of the reaction conditions for the aza-Baylis-Hillman reaction of *N*-(4-chlorobenzylidene)-4-methylbenzenesulfonamide **1e** with ethyl vinyl ketone.

As can be seen from this Table, we found that similar results were obtained as those of MVK. At -20 °C and -30 °C, the corresponding aza-Baylis-Hillman adduct **3a** was obtained in 87% ee and 58% yield for 24 h and 92% ee and 49% yield for 72 h, respectively with S configuration (entries 3 and 4). In the presence of MS 4A at -20 °C, the yield of **3a** reached 77% in 86% ee (entry 5). However, at -30 °C, the yield of **3a** was 56% in 88% ee even for 7 days (entry 6).

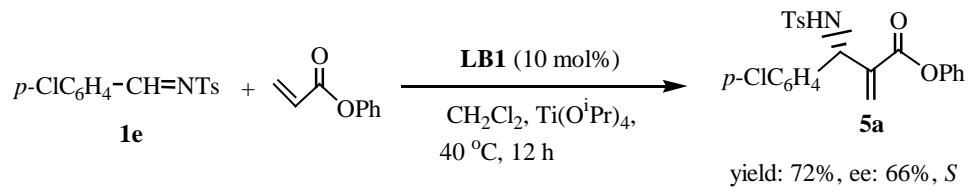
Table. aza-Baylis-Hillman reactions of *N*-(4-chlorobenzylidene)-4-methyl benzenesulfonamide **1e** (1.0 equiv.) with ethyl vinyl ketone (2.0 equiv.) in the presence of chiral Lewis base **LB1** (10 mol%).



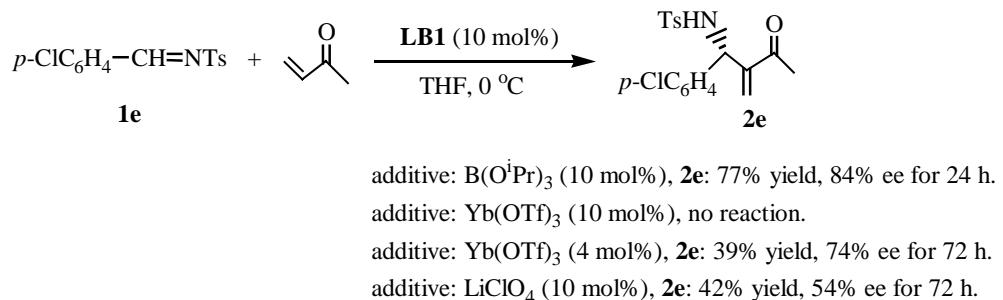
entry	temp. (°C)	time/h	yield[%] <sup>a)</sup> <b>3a</b>	ee/% <sup>b)</sup>	absolute configuration
1	r.t.	12	76	77	S
2	0	38	74	83	S
3	-20	24	58	87	S
4	-30	72	48	92	S
5	-20, MS 4A	48	77	86	S
6	-30, MS 4A	7d	56	88	S

<sup>a)</sup>Isolated yield. <sup>b)</sup>Determined by chiral HPLC.

3) Aza-Baylis-Hillman reaction of **1e** with phenyl acrylate in  $\text{CH}_2\text{Cl}_2$  in the presence of Lewis acid  $\text{Ti}(\text{O}^{\text{i}}\text{Pr})_4$  at  $40\text{ }^{\circ}\text{C}$  for 12 h.

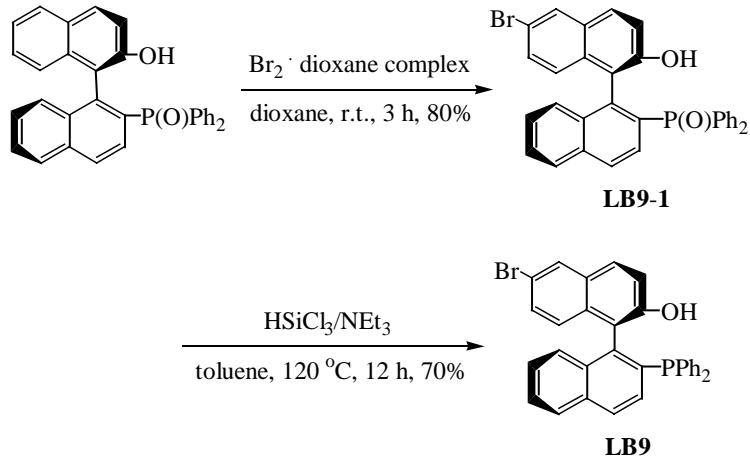


4) The additives effects on this catalytic, asymmetric aza-Baylis-Hillman reaction.

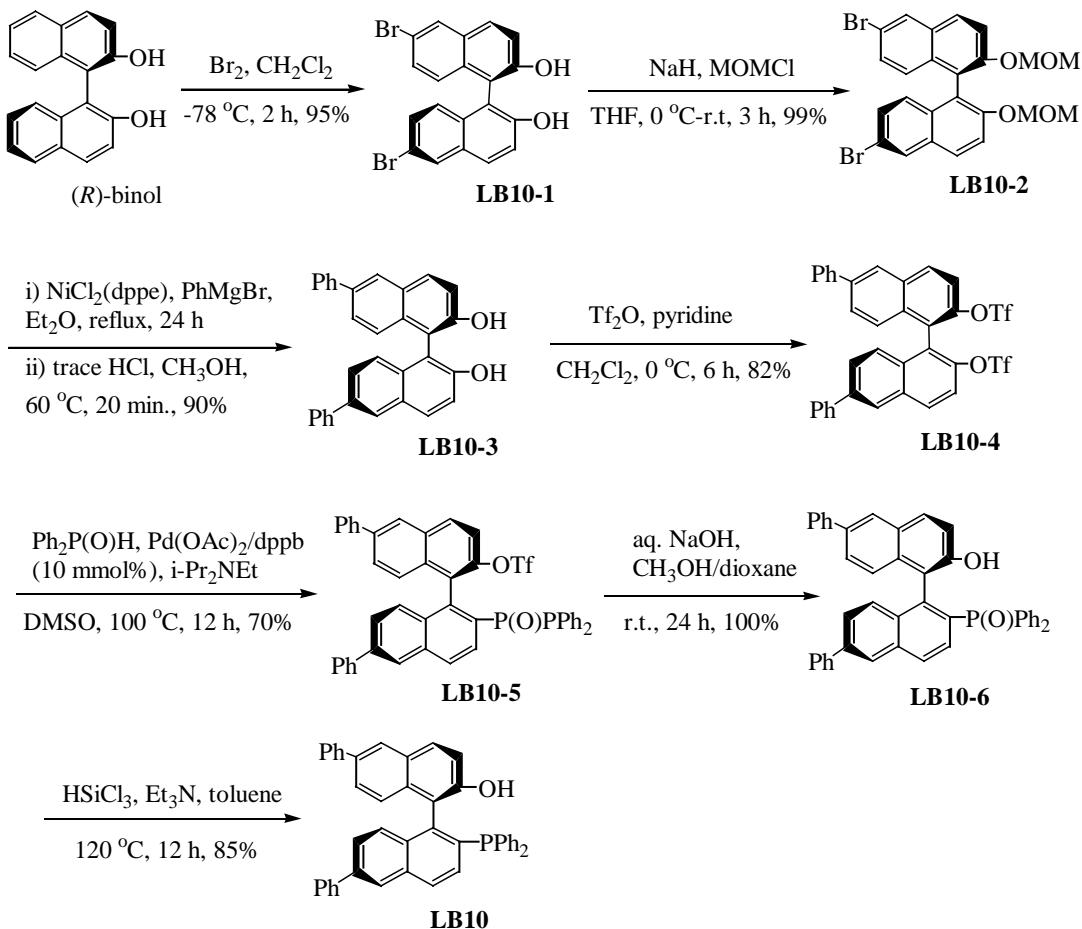


5) The modification of the structure of chiral Lewis base **LBI** and their results in catalytic, asymmetric aza-Baylis-Hillman reaction.

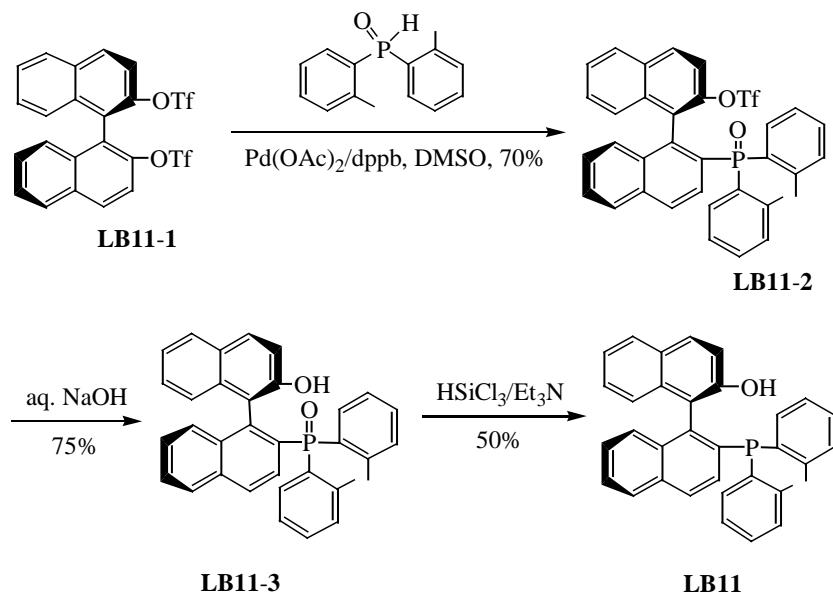
Scheme SI-1



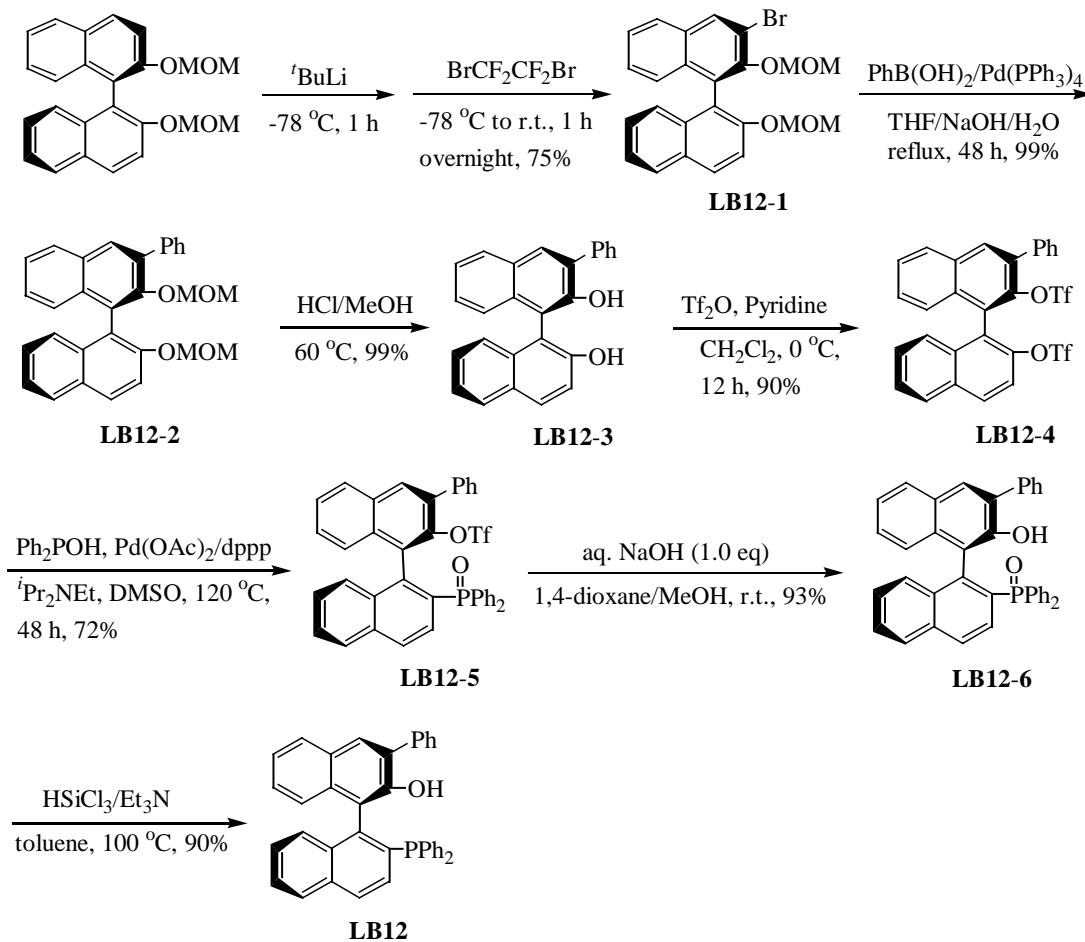
Scheme SI-2



Scheme SI-3



Scheme SI-4



These chiral phosphine Lewis bases **LB9-LB12** were employed in the same catalytic, asymmetric aza-Baylis-Hillman reaction of *N*-sulfonated imines **1** with MVK or phenyl acrylate. The results using **LB9** and **LB10** as chiral Lewis base promoters are summarized in Tables SI-1 and SI-2, respectively. As can be seen from Tables SI-1 and SI-2, the chiral phosphine Lewis bases **LB9** and **LB10** gave similar results in the aza-Baylis-Hillman reaction of *N*-sulfonated imines **1** with MVK. But for the aza-Baylis-Hillman reaction of *N*-sulfonated imines **1** with phenyl acrylate in dichloromethane, **LB9** is slightly more effective than **LB10** under the same conditions (Tables SI-1 and SI-2). The outcomes for comparison of **LB1**, **LB9** and **LB10** in the aza-Baylis-Hillman reaction of *N*-(4-chlorobenzylidene)-4-methylbenzenesulfonamide **1e** with MVK and phenyl acrylate at

various temperatures are elucidated in Table SI-3. **LB9** and **LB10** are similarly effective as **LB1** in the aza-Baylis-Hillman reaction using MVK as a Michael acceptor. In addition, they have similar enantioselective induction ability in this reaction. On the other hand, in the aza-Baylis-Hillman reaction using phenyl acrylate as a Michael acceptor, **LB1** has the similar catalytic activity as **LB9**. However, **LB1** and **LB9** are slightly more effective than **LB10** (Table SI-3). Moreover, we found that **LB11** has no catalytic ability for this reaction. These results suggest that Br and phenyl substituents on the 6,6'-position of binaphthalene framework do not significantly affect the reaction rate and enantioselectivity in this catalytic, asymmetric reaction, but the steric bulkiness around phosphine atom plays a key role to initiate the reaction. It should be pointed out that using **LB1**, **LB9** and **LB10** as Lewis base promoters in this reaction, we found that they are gradually oxidized into the corresponding phosphine oxide during reaction.

The results using chiral phosphine Lewis base **LB12** having a phenyl substituent on the 3-position adjacent to the phenolic hydroxy group in the aza-Baylis-Hillman reaction of *N*-sulfonated imines **1** with MVK and phenyl acrylate are summarized in Tables SI-4 and SI-5, respectively. **LB12** is slightly less effective than **LB1** because at -20 °C, **2e** was obtained in 60% yield after 3 days in THF (Table SI-4, entry 3). However, at 0 °C or 25 °C, **2e** was obtained in 91% yield with 86% and 85% ee, respectively after 12 h (Table SI-4, entries 1 and 2). The best reaction temperature is 0 °C. For other reactions of *N*-sulfonated imines **1** with MVK at 0 °C, the corresponding aza-Baylis-Hillman adducts **2** were obtained in good yields with 83~93% ee as *S* configuration (Table SI-4, entries 4-8). At relatively higher temperature, this reaction proceeded smoothly to give the adduct in good enantioselectivity. Therefore, no MS 4A is required in this catalytic system. In the aza-Baylis-Hillman reaction of *N*-sulfonated imines **1** with phenyl acrylate in dichloromethane, the corresponding adduct **5a** was obtained in high yield at 40 °C (Table SI-5, entries 1-4). At any rate, we found that at various reaction temperatures (-20 °C-40 °C), the similar good results were obtained as **LB1** in this reaction

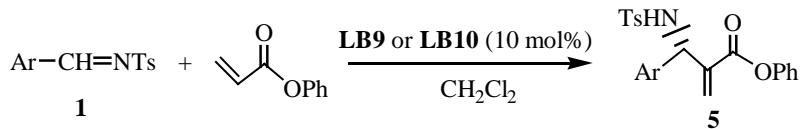
(Table SI-5, entries 1-4). For other reactions of *N*-sulfonated imines **1** with phenyl acrylate at 25 °C, the corresponding aza-Baylis-Hillman adducts **5** were obtained in good yields with 56~78% ee as *S* configuration (Table SI-5, entries 5-8). Overall, we found that chiral Lewis base **LB12** having a phenyl substituent adjacent to the phenolic hydroxy group produced the adducts in relatively higher ee under slightly milder conditions (0 °C and 25 °C) in the aza-Baylis-Hillman reaction using MVK as a Michael acceptor. We also confirmed that this Lewis base promoter is difficult to be oxidized to the phosphine oxide during reaction under identical conditions as **LB1**, **LB9** and **LB10**. It is still active and can be reused again for this reaction after recovery by a column chromatography (Table SI-4, entry 4).

Table SI-1. aza-Baylis-Hillman reactions of *N*-sulfonated imines **1** (1.0 equiv.) with MVK (3.0 equiv.) in the presence of chiral Lewis bases **LB9** and **LB10** (10 mol%) in THF.

entry	Ar	No.	reaction conditions	yield[%] <sup>a)</sup>		ee/% <sup>b)</sup>		absolute configuration
				LB9	LB10	LB9	LB10	
1	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<b>1e</b>	r.t., 12 h	<b>2e</b> , 96	<b>2e</b> , 83	86	84	<i>S</i>
2	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<b>1e</b>	0 °C, 12 h	<b>2e</b> , 88	<b>2e</b> , 87	91	87	<i>S</i>
3	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<b>1e</b>	-20 °C, 24 h	<b>2e</b> , 82	<b>2e</b> , 77	88	90	<i>S</i>
4	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	<b>1f</b>	-20 °C, 24 h	<b>2f</b> , 60	<b>2f</b> , 72	86	88	<i>S</i>
5	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<b>1i</b>	-20 °C, 24 h	<b>2i</b> , 78	<b>2i</b> , 86	92	92	<i>S</i>
6	<i>m</i> -FC <sub>6</sub> H <sub>4</sub>	<b>1g</b>	-20 °C, 24 h	<b>2g</b> , 76	<b>2g</b> , 72	84	87	<i>S</i>
7	<i>m</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<b>1j</b>	-20 °C, 24 h	<b>2j</b> , 94	<b>2j</b> , 86	87	94	<i>S</i>
8	C <sub>6</sub> H <sub>5</sub>	<b>1a</b>	-20 °C, 48 h	<b>2a</b> , 79	<b>2a</b> , 80	50	65	<i>S</i>

<sup>a)</sup>Isolated yield. <sup>b)</sup>Determined by chiral HPLC.

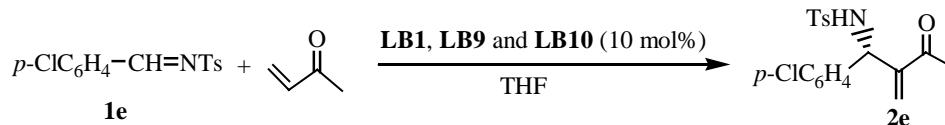
Table SI-2. aza-Baylis-Hillman reactions of *N*-sulfonated imines **1** (1.0 equiv.) with phenyl acrylate (1.5 equiv.) in the presence of chiral Lewis bases **LB9** and **LB10** (10 mol%) in CH<sub>2</sub>Cl<sub>2</sub>.



entry	Ar	No.	reaction conditions	yield[%] <sup>a)</sup>		ee/% <sup>b)</sup>		absolute configuration
				LB9	LB10	LB9	LB10	
1	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<b>1e</b>	40 °C, 12 h	<b>5a</b> , 92	<b>5a</b> , 82	70	51	<i>S</i>
2	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<b>1e</b>	r.t., 12 h	<b>5a</b> , 72	<b>5a</b> , 61	74	65	<i>S</i>
3	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<b>1e</b>	0 °C, 24 h	<b>5a</b> , 34	<b>5a</b> , 27	69	62	<i>S</i>
4	<i>p</i> -FC <sub>6</sub> H <sub>4</sub>	<b>1d</b>	r.t., 12 h	<b>5d</b> , 57	<b>5d</b> , 56	69	67	<i>S</i>
5	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	<b>1f</b>	r.t., 12 h	<b>5e</b> , 72	<b>5e</b> , 66	72	64	<i>S</i>
6	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<b>1i</b>	r.t., 12 h	<b>5h</b> , 72	<b>5h</b> , 71	75	71	<i>S</i>
7	C <sub>6</sub> H <sub>5</sub>	<b>1a</b>	r.t., 12 h	<b>5b</b> , 62	<b>5b</b> , 60	64	54	<i>S</i>

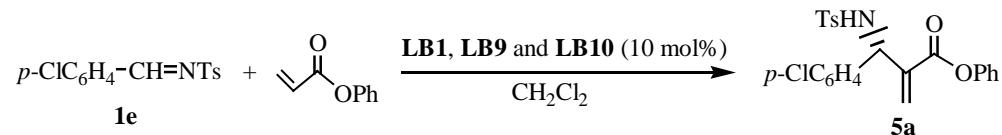
<sup>a)</sup>Isolated yield. <sup>b)</sup>Determined by chiral HPLC.

Table SI-3. the comparions of aza-Baylis-Hillman reactions of *N*-sulfonated imine **1e** (1.0 equiv.) with MVK (3.0 equiv.) and phenyl acrylate (1.5 equiv.) in the presence of chiral Lewis bases **LB1**, **LB9** and **LB10** (10 mol%) in THF or CH<sub>2</sub>Cl<sub>2</sub>.



entry	temp./°C	time/h	yield[%] <sup>a)</sup>			ee/% <sup>b)</sup>		
			LB1	LB9	LB10	LB1	LB9	LB10
1	r.t.	12	86	96	83	84	86	84
2	0	12	84	88	87	90	91	87
3	-20	24	70	82	77	94	88	90

<sup>a)</sup>Isolated yield. <sup>b)</sup>Determined by chiral HPLC.



entry	temp./°C	time/h	yield[%] <sup>a)</sup>			ee/(%) <sup>b)</sup>		
			LB1	LB9	LB10	LB1	LB9	LB10
1	40	12	94	92	82	67	70	51
2	r.t.	12	70	72	61	71	74	65
3	0	24	59	34	27	67	69	62

<sup>a)</sup>Isolated yield. <sup>b)</sup>Determined by chiral HPLC.

Table SI-4. aza-Baylis-Hillman reactions of *N*-sulfonated imines **1** (1.0 equiv.) with methyl vinyl ketone (3.0 equiv.) in the presence of chiral Lewis base **LB12** (10 mol%).

entry	Ar	No.	temp. (°C)	time/h	$\frac{\text{yield}[\%]^{\text{a)}}{2}$	ee/% <sup>b</sup>	absolute configuration
					<b>2</b>		
1	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<b>1e</b>	25	12	<b>2e</b> , 91	85	<i>S</i>
2	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<b>1e</b>	0	12	<b>2e</b> , 91	86	<i>S</i>
3	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<b>1e</b>	-20	72	<b>2e</b> , 60	87	<i>S</i>
4	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	<b>1f</b>	0	36	<b>2f</b> , 84 (80) <sup>c</sup>	93 (92) <sup>c</sup>	<i>S</i>
5	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<b>1i</b>	0	36	<b>2i</b> , 85	90	<i>S</i>
6	<i>m</i> -FC <sub>6</sub> H <sub>4</sub>	<b>1g</b>	0	36	<b>2g</b> , 86	92	<i>S</i>
7	<i>m</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<b>1j</b>	0	36	<b>2j</b> , 85	92	<i>S</i>
8	C <sub>6</sub> H <sub>5</sub>	<b>1a</b>	0	36	<b>2a</b> , 73	83	<i>S</i>

<sup>a</sup>Isolated yield. <sup>b</sup>Determined by chiral HPLC. <sup>c</sup>Recovered **LB12** was employed..

Table SI-5. aza-Baylis-Hillman reactions of *N*-sulfonated imines **1** (1.0 equiv.) with phenyl acrylate (1.5 equiv.) in the presence of chiral Lewis base **LB12** (10 mol%).

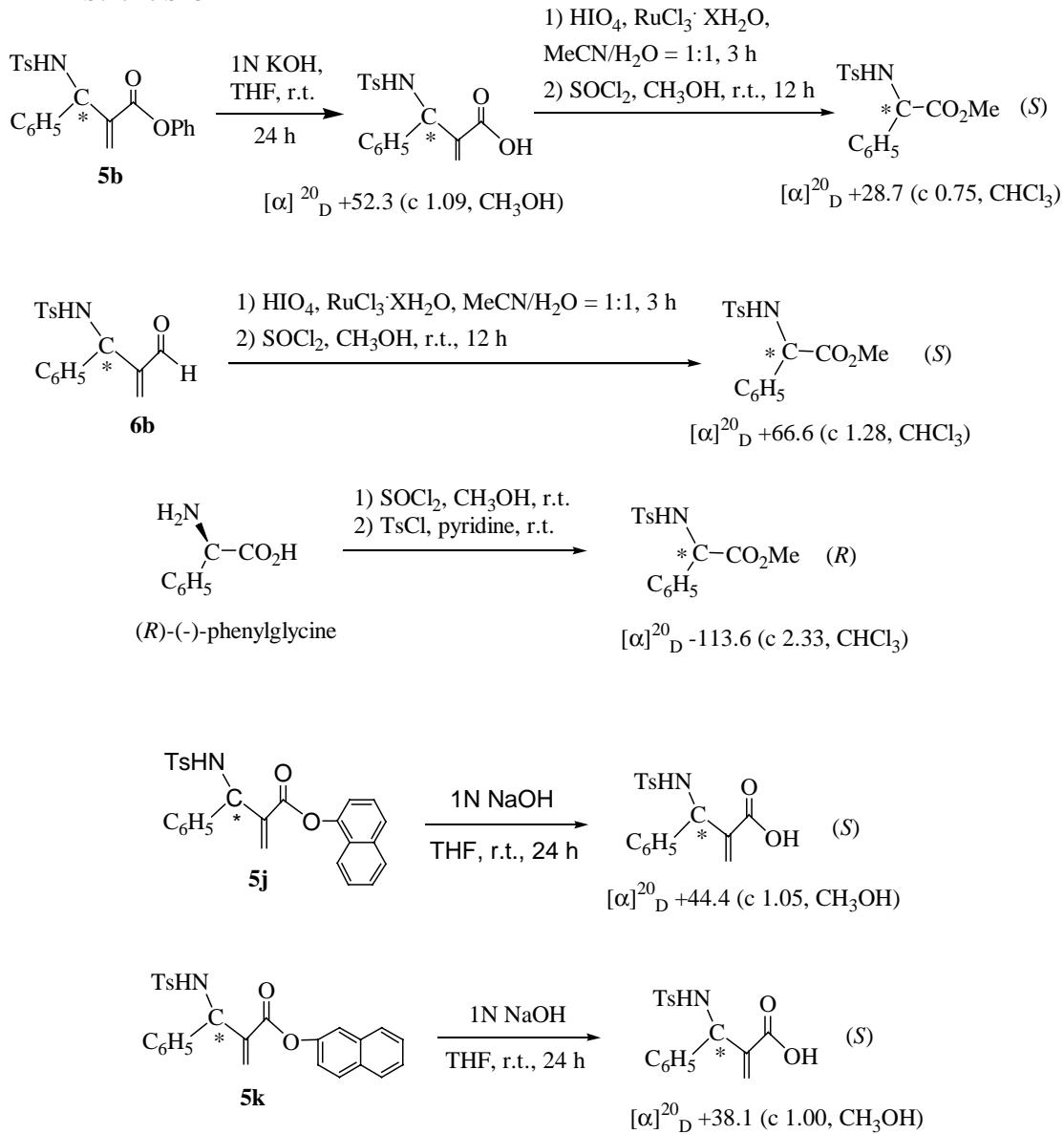
entry	Ar	No.	temp. (°C)	time/h	$\frac{\text{yield}[\%]^{\text{a)}}{5}$	ee/% <sup>b</sup>	absolute configuration
					<b>5</b>		
1	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<b>1e</b>	25	48	<b>5a</b> , 70	59	<i>S</i>
2	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<b>1e</b>	40	12	<b>5a</b> , 97	59	<i>S</i>
3	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<b>1e</b>	0	72	<b>5a</b> , 77	64	<i>S</i>
4	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<b>1e</b>	-20	60	<b>5a</b> , 59	67	<i>S</i>
5	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<b>1i</b>	25	12	<b>5h</b> , 71	71	<i>S</i>
6	<i>p</i> -FC <sub>6</sub> H <sub>4</sub>	<b>1d</b>	25	12	<b>5d</b> , 75	78	<i>S</i>
7	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub>	<b>1f</b>	25	12	<b>5e</b> , 79	56	<i>S</i>
8	C <sub>6</sub> H <sub>5</sub>	<b>1a</b>	25	12	<b>5b</b> , 88	76	<i>S</i>

<sup>a</sup>Isolated yield. <sup>b</sup>Determined by chiral HPLC.

6) *Determination of absolute configuration.*

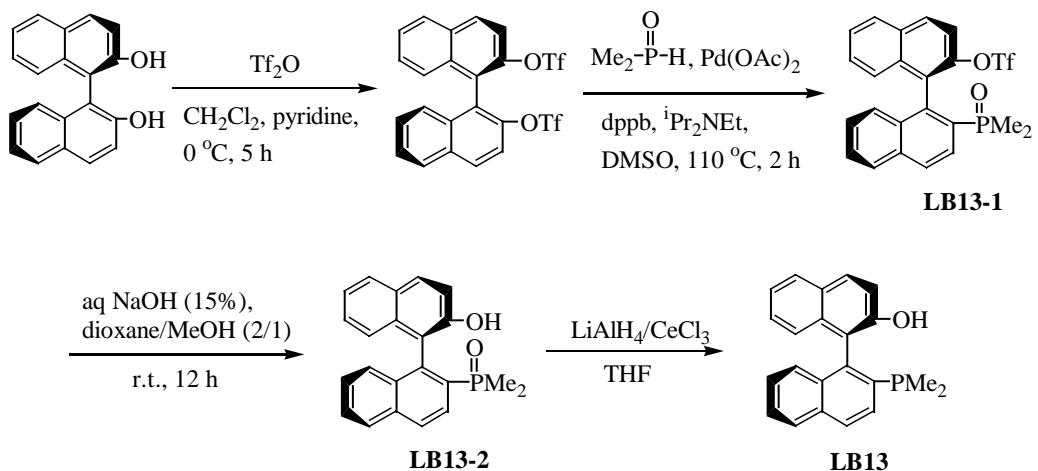
The absolute configuration of adduct **2** was determined to be (*S*)-enriched by comparison of the sign of specific rotation with its antipode. For adducts **5** and **6**, the absolute configuration was unambiguously confirmed to be (*S*)-enriched by the method reported by Li and Hatakeyama, namely, transforming the products to the corresponding phenylglycine derivatives and comparing them to authentic samples prepared from (*R*)-phenylglycine as shown in Scheme SI-5. Adducts **5j** and **5k** can be assigned as (*S*)-enriched configuration in the same way (Scheme SI-5).

Scheme SI-5



7) Preparation of chiral phosphine Lewis base **LB13**.

Scheme SI-6



## Experimental Section

**General Remarks.** MPs were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. Unless otherwise stated, all reactions were carried out under argon atmosphere. All solvents were purified by distillation. Infrared spectra were measured on a PERKIN-ELMER 983 spectrometer.  $^1\text{H}$  NMR spectra were recorded on a Bruker AM-300 spectrometer as a solution in  $\text{CDCl}_3$  with tetramethylsilane (TMS) as an internal standard; J-values are in Hz. Mass spectra were recorded with a HP-5989 instrument and HRMS was measured by a Finnigan MA+ mass spectrometer. *N*-Sulfonated imines **1** were prepared according to the literature.<sup>1</sup> 2-Cyclopenten-1-one was obtained from Tokyo Chemical Industry (Tokyo Kasei Co. Ltd.) and used without purification. The chiral phosphine catalyst **LB1** is a known compound which can be easily prepared according to the literature.<sup>2</sup> All of the solid compounds reported in this paper gave satisfactory CHN microanalyses with a Carlo-Erba 1106 analyzer. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF<sub>254</sub> silica gel coated plates. Flash column chromatography was carried out using 200-300 mesh silica gel at increased pressure. The optical purities of the Baylis-Hillman adducts were determined by HPLC analysis using a chiral stationary phase column (column, Daicel Co. Chiralcel AD, AS, TBB and OJ; eluent: hexane/2-propanol mixture; flow rate, 0.7 mL min<sup>-1</sup>; detection, 254 nm or 220 nm light) and the absolute configuration of the major enantiomer was assigned according to the sign of the specific rotation. For adducts **7a**, the reversed phase chiral HPLC column (TBB KR 100 5CHI-TBB (250 mm x 4.6 mm and Chiralcel OJ-R) was employed because it is insoluble in petroleum ether/isopropyl alcohol.

These chiral Lewis bases **LB1-LB13** are prepared by the known synthetic methods as elucidated in Schemes. Chiral Lewis bases **LB1-LB9** are the known compounds. For new ligands **LB10-LB13**, their spectroscopic data are shown as belows.

*General procedure for the preparation of aryl triflates.*

To a solution of substituted (*R*)-1,1'-bi-2-naphthol (5.0 mmol) and pyridine (1.24 mL, 15.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was added trifluoromethanesulfonic anhydride (3.38 g, 2.0 mL, 12.0 mmol) at 0 °C, and the mixture was stirred for 6 h at room temperature. After removal of the solvent, the residue was diluted with 150 mL of EtOAc and then washed with 5% HCl, saturated NaHCO<sub>3</sub>, and brine (once for each). The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure, and chromatographed on silica gel (EtOAc/Petroleum ether, 1/20) to give the product as a white solid.

(*R*)-(-)-6,6' -Diphenyl-2,2'-trifluoromethansulfonyloxy-[1,1']binaphthalenyl **LB10-4**: This compound was prepared in the same manner as that described above. yield: 82%. [α]<sup>20</sup><sub>D</sub> -213 (c 1.05, CHCl<sub>3</sub>). mp. 76-78 °C. IR (KBr): ν 3055, 1595, 1493, 1442, 1248, 1216, 1175, 1139, 967, 943 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS): δ 7.35-7.43 (4H, m), 7.47-7.52 (4H, dd, J<sub>1</sub> = 7.8 Hz, J<sub>2</sub> = 6.9 Hz), 7.64-7.73 (8H, m), 8.2-8.23 (4H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75.45 MHz): δ 118.14 (d, J<sub>C-F</sub> = 320.9 Hz), 119.76, 123.36, 125.99, 127.31, 127.38, 127.71, 127.93, 128.96, 132.22, 132.69, 139.86, 140.00, 145.30; MS (EI): *m/e* 702 (M<sup>+</sup>, 12.60), 569 (M<sup>+</sup>-133, 6.19), 436 (M<sup>+</sup>-266, 12.13), 420 (M<sup>+</sup>-282, 100), 218 (M<sup>+</sup>-266-218, 12.13), 77 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 12.26). Anal. Calcd. for C<sub>34</sub>H<sub>20</sub>F<sub>6</sub>O<sub>6</sub>S<sub>2</sub>: requires C, 58.12; H, 2.87%; Found: C, 58.46; H, 2.93%.

*General procedure for the palladium-catalyzed coupling of diphenylphosphine oxide with aryl triflates.*

A three-necked round-bottom flask charged with a mixture of triflate (4.0 mmol), 8.0 mmol of diphenylphosphine oxide, 1,3-bis(diphenylphosphino)propane (dppp) (0.4 mmol), Pd(OAc)<sub>2</sub> (0.4 mmol) and diisopropylethylamine (20 mmol) in 20 mL of DMSO was heated to 120 °C for 24 h under argon atmosphere. The solvent was removed under reduced pressure. To the residue were added water (50 mL) and EtOAc (200 mL), and the organic phase was washed with 10%

HCl (3 x 50 mL), brine, and water and finally dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation to dryness yielded a crude material which was purified by flash column chromatography (SiO<sub>2</sub>, eluent: EtOAc/Petroleum ether from 1/4 to 1/2) to yield the pure product as a colorless solid.

*(R)-(-)-6,6'-Diphenyl-2'-(diphenylphosphinoyl)-2-trifluoromethansulfonyloxy-[1,1']binaphthalenyl* **LB10-5**: This compound was prepared in the same manner as that described above. yield: 70%. [α]<sup>20</sup><sub>D</sub> -62 (c 1.10, CHCl<sub>3</sub>). mp. 140-142 °C. IR (KBr): ν 3055, 1642, 1598, 1489, 1417, 1248, 1210, 1173, 1139, 960, 946 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS): δ 7.07 (1H, d, J = 8.7 Hz), 7.25-7.72 (25H, m), 7.99 (1H, J = 9.3 Hz), 8.03-8.09 (2H, m), 8.15 (1H, d, J = 1.2 Hz). <sup>31</sup>P NMR (121.45 MHz, CDCl<sub>3</sub>, 85% H<sub>3</sub>PO<sub>4</sub>): δ +29.38. <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75.45 MHz): δ 118.01 (d, J<sub>C-F</sub> = 320.2 Hz), 119.31, 125.60, 125.77, 126.90, 127.27, 127.29, 127.33, 127.37, 127.65, 127.68, 127.70, 127.76, 127.86, 127.95, 128.03, 128.12, 128.19, 128.76, 128.82, 128.85, 128.98, 129.06, 130.40, 131.21, 131.37, 131.41, 131.48, 131.51, 131.71, 131.73, 131.84, 131.85, 132.01, 132.04, 132.14, 132.29, 132.86, 132.93, 133.39, 134.80, 134.83, 136.96, 137.06, 139.22, 139.95, 140.36, 140.86, 145.54. MS (EI): *m/e* 605 (M<sup>+</sup>-149, 100), 420 (M<sup>+</sup>-133-201, 15.42), 201 (Ph<sub>2</sub>PO<sup>+</sup>, 39.85), 77 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 7.60). Anal. Calcd. for C<sub>45</sub>H<sub>30</sub>F<sub>3</sub>O<sub>4</sub>PS: requires C, 71.61; H, 4.01%; Found: C, 71.38; H, 4.02%.

*General procedure for the deprotection of phosphine oxides triflates.*

To a solution of the phosphine oxides triflate (2.0 mmol) in 2/1 mixture of 1,4-dioxane and MeOH (30 mL) was added 3 N aqueous NaOH solution (3.0 mL) at room temperature. The reaction mixture was stirred for 24 h, acidified to pH = 1 by addition of conc. HCl, and then extracted twice with EtOAc. The organic phase was dried over MgSO<sub>4</sub>, concentrated under reduced pressure, and chromatographed on silica gel (EtOAc/Petroleum ether, from 1/2 to 1/1) to give the product as a white solid.

*(R)-(-)-6,6'-Diphenyl-2'-(diphenylphosphinoyl)-[1,1']binaphthalenyl-2-ol* **LB10-6**: This

compound was prepared in the same manner as that described above. yield: 100%.  $[\alpha]^{20}_D$  -187.0 (c 1.06, CHCl<sub>3</sub>). mp. 156-158 °C. IR (KBr):  $\nu$  3392, 3055, 1621, 1592, 1491, 1437, 1353, 1231, 1158, 1143, 1116, 756, 728, 696 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  6.57 (1H, d, *J* = 8.6 Hz), 6.72-6.79 (3H, m), 7.20-7.70 (22H, *m*), 7.91-8.0 (3H, m), 8.11 (1H, s), 9.03 (1H, s, OH). <sup>31</sup>P NMR (121.45 MHz, CDCl<sub>3</sub>, 85% H<sub>3</sub>PO<sub>4</sub>):  $\delta$  +31.80. <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75.45 MHz):  $\delta$  122.85, 122.91, 123.55, 125.05, 125.42, 125.56, 126.32, 126.88, 127.00, 127.04, 127.24, 127.33, 127.40, 127.76, 127.98, 128.16, 128.22, 128.33, 128.57, 128.73, 128.76, 128.79, 128.84, 129.12, 129.62, 129.65, 129.78, 129.86, 129.99, 130.05, 130.61, 131.24, 131.39, 132.04, 132.08, 132.16, 132.55, 132.60, 132.70, 135.44, 135.47, 135.92, 140.13, 140.80, 141.07, 141.10, 141.20, 153.87. MS (EI): *m/e* 622 (M<sup>+</sup>, 16.21), 421 (M<sup>+</sup>-201, 35.67), 420 (M<sup>+</sup>-201-1, 100), 201 (Ph<sub>2</sub>PO<sup>+</sup>, 18.47), 77 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 18.86). HRMS (EI) (M<sup>+</sup>) Calcd. for C<sub>44</sub>H<sub>31</sub>O<sub>2</sub>P requires 622.2039, Found: 622.2056.

*General procedure for the reduction of the phosphine oxides.*

At 0 °C, HSiCl<sub>3</sub> (10 mmol, 1.0 mL) was carefully added to a mixture of phosphine oxide (2.0 mmol) and triethylamine (48 mmol, 2.1 mL) in toluene (50 mL) in a three-necked round-bottom flask under argon atmosphere. The mixture was heated to reflux for 16-24 h. To the cooled mixture was added ether and sodium bicarbonate. Solids were removed by filtration and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (SiO<sub>2</sub>, EtOAc/Petroleum ether, 1/20) to give the product as a colorless solid.

(*R*)-(-)-6,6'-Diphenyl-2'-(diphenylphosphanyl)-[1,1']binaphthalenyl-2-ol **LB10**: This compound was prepared in the same manner as that described above. yield: 85%.  $[\alpha]^{20}_D$  -111.0 (c 1.10, CHCl<sub>3</sub>). mp. 120-122 °C. IR (KBr):  $\nu$  3395, 3053, 1681, 1622, 1596, 1491, 1435, 1358, 1157, 1117, 756, 695 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  4.66 (1H, s, OH), 6.84 (1H, d,

$J = 8.6$  Hz), 7.06-7.69 (25H, m), 7.98-8.01 (3H, m), 8.13 (1H, d,  $J = 1.7$  Hz).  $^{31}\text{P}$  NMR (121.45 MHz,  $\text{CDCl}_3$ , 85%  $\text{H}_3\text{PO}_4$ ):  $\delta$  -12.42.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75.45 MHz):  $\delta$  117.89, 125.35, 125.89, 125.99, 126.73, 126.89, 126.95, 127.16, 127.36, 127.65, 128.16, 128.24, 128.36, 128.51, 128.59, 128.63, 128.73, 128.89, 129.00, 129.42, 130.57, 130.63, 133.45, 133.54, 133.72, 133.80, 134.26, 135.88, 139.98, 140.49, 141.17, 151.19, 151.22. MS (ESI):  $m/e$  607.1 ( $\text{M}^+ + 1$ , 100). HRMS (ESI) ( $\text{M}^+ + \text{H}$ ) Calcd. for  $\text{C}_{44}\text{H}_{32}\text{O}_2\text{P}$  requires 607.2187, Found: 607.2185.

(*R*)-(+)-2'-(Di-*o*-tolylphosphinoyl)-2-trifluoromethansulfonyloxy-[1,1']binaphthalenyl

**LB11-2:** This compound was prepared in the same manner as that described above. yield: 70%.  $[\alpha]^{20}_D +9.1$  (c 0.99,  $\text{CHCl}_3$ ). mp. 123-125 °C. IR (KBr):  $\nu$  3056, 2958, 1593, 1509, 1452, 1417, 1248, 1211, 1174, 1140, 956, 941  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  2.13 (3H, s, Me), 2.50 (3H, s, Me), 6.88-7.43 (15H, m), 7.59 (1H, dd,  $J_1 = 7.4$  Hz,  $J_2 = 7.3$  Hz), 7.86 (1H, d,  $J = 8.6$  Hz), 7.95-7.99 (3H, m).  $^{31}\text{P}$  NMR (121.45 MHz,  $\text{CDCl}_3$ , 85%  $\text{H}_3\text{PO}_4$ ):  $\delta$  +34.52.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75.45 MHz):  $\delta$  21.54 (d,  $J_{\text{C}-\text{P}} = 3.8$  Hz), 21.68 (d,  $J_{\text{C}-\text{P}} = 4.5$  Hz), 117.82 (d,  $J_{\text{C}-\text{F}} = 319.9$  Hz), 118.89, 124.59, 124.75, 124.85, 125.01, 126.04, 126.39, 126.67, 126.94, 126.97, 127.70, 127.75, 128.07, 128.19, 128.24, 128.42, 129.48, 129.58, 130.54, 130.63, 130.78, 130.95, 131.22, 131.26, 131.47, 131.62, 132.60, 132.74, 132.76, 132.90, 133.13, 133.23, 133.27, 134.14, 134.16, 137.64, 137.72, 142.96, 143.05, 143.12, 143.22, 145.64, 170.92. MS (EI):  $m/e$  497 ( $\text{M}^+ - 133$ , 4.19), 481 ( $\text{M}^+ - 149$ , 100), 268 ( $\text{M}^+ - 133 - 229$ , 9.20), 229 [ $(\text{C}_6\text{H}_4\text{CH}_3)_2\text{PO}^+$ , 9.22], 91 ( $\text{C}_6\text{H}_4\text{CH}_3^+$ , 6.31). Anal. Calcd. for  $\text{C}_{35}\text{H}_{26}\text{F}_3\text{O}_4\text{PS}$ : requires C, 66.66; H, 4.16%; Found: C, 66.98; H, 4.33%.

(*R*)-(-)-2'-(Di-*o*-tolylphosphinoyl)-[1,1']binaphthalenyl-2-ol **LB11-3:** This compound was prepared in the same manner as that described above. yield: 75%.  $[\alpha]^{20}_D -59.8$  (c 1.11,  $\text{CHCl}_3$ ). mp. 150-152 °C. IR (KBr):  $\nu$  3055, 2957, 1621, 1593, 1513, 1451, 1435, 1348, 1277, 1175, 1138, 871, 746  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  2.01 (3H, s, Me), 2.75 (3H, s, Me),

6.21 (1H, d,  $J = 8.6$  Hz), 6.54-6.62 (2H, m), 6.75-6.82 (2H, m), 7.03-7.25 (6H, m), 7.39-7.58 (6H, m), 7.69 (1H, d,  $J = 8.6$  Hz), 7.90-7.96 (2H, m), 9.40 (1H, s, OH).  $^{31}\text{P}$  NMR (121.45 MHz,  $\text{CDCl}_3$ , 85%  $\text{H}_3\text{PO}_4$ ):  $\delta$  +37.82.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75.45 MHz):  $\delta$  22.24 (d,  $J_{\text{C-P}} = 4.5$  Hz), 22.62 (d,  $J_{\text{C-P}} = 3.6$  Hz), 122.51, 122.60, 122.80, 124.59, 124.75, 124.79, 124.83, 125.04, 125.10, 125.36, 125.54, 125.79, 126.87, 127.16, 127.23, 127.32, 127.35, 127.49, 127.63, 127.80, 127.95, 128.03, 128.83, 128.91, 129.77, 129.83, 130.64, 130.68, 130.74, 130.89, 131.18, 132.03, 132.12, 132.15, 132.41, 132.54, 132.78, 132.98, 133.52, 133.78, 133.93, 134.64, 134.67, 137.59, 141.37, 141.47, 143.99, 144.08, 153.51. MS (EI):  $m/e$  498 ( $\text{M}^+$ , 73.69), 483 ( $\text{M}^+-15$ , 57.22), 268 ( $\text{M}^+-230$ , 100), 215 ( $\text{M}^+-230-53$ , 56.65), 229 [ $(\text{C}_6\text{H}_4\text{CH}_3)_2\text{PO}^+$ , 13.53], 91 ( $\text{C}_6\text{H}_4\text{CH}_3^+$ , 24.68). Anal. Calcd. for  $\text{C}_{34}\text{H}_{27}\text{O}_2\text{P}$ : requires C, 81.91; H, 5.46%; Found: C, 81.71; H, 5.55%.

*(R)*-(+)-2'-(Di-*o*-tolylphosphanyl)-[1,1']binaphthalenyl-2-ol **LB11**: This compound was prepared in the same manner as that described above. yield: 50%.  $[\alpha]^{20}_{\text{D}} +28.3$  (c 1.08,  $\text{CHCl}_3$ ). mp. 83-85 °C. IR (KBr):  $\nu$  3053, 2957, 1621, 1595, 1466, 1450, 1379, 1347, 1269, 1205, 1175, 1148, 817, 747  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  1.96 (3H, s, Me), 2.17 (3H, s, Me), 4.38 (1H, s, OH), 6.70 (1H, d,  $J = 7.9$  Hz), 6.86-7.39 (14H, m), 7.52-7.57 (1H, m), 7.83 (1H, d,  $J = 8.1$  Hz), 7.90 (1H, d,  $J = 8.8$  Hz), 7.96 (2H, d,  $J = 8.3$  Hz).  $^{31}\text{P}$  NMR (121.45 MHz,  $\text{CDCl}_3$ , 85%  $\text{H}_3\text{PO}_4$ ):  $\delta$  -30.73.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75.45 MHz):  $\delta$  21.12 (d,  $J = 12.8$  Hz), 21.43 (d,  $J = 12.6$  Hz), 117.46, 118.05, 118.16, 123.06, 124.95, 125.75, 125.79, 125.91, 125.96, 126.16, 126.96, 127.07, 127.63, 128.10, 128.37, 128.41, 128.76, 128.84, 129.00, 129.47, 129.76, 129.83, 130.04, 130.19, 130.25, 133.43, 133.49, 133.51, 133.80, 134.02, 135.26, 135.44, 137.19, 137.61, 138.33, 138.49, 142.74, 142.83, 142.99, 143.21, 143.35, 151.25. MS (EI):  $m/e$  482 ( $\text{M}^+$ , 100), 481 ( $\text{M}^+-1$ , 86.75), 467 ( $\text{M}^+-15$ , 86.75), 268 ( $\text{M}^+-213-1$ , 65.90), 252 ( $\text{M}^+-213-17$ , 24.98), 215 ( $\text{M}^+-214-53$ , 13.07), 91 ( $\text{C}_6\text{H}_4\text{CH}_3^+$ , 24.68). Anal. Calcd. for  $\text{C}_{34}\text{H}_{27}\text{OP}$ : requires C, 84.63; H, 5.64%; Found: C, 84.36; H, 5.69%.

(*R*)-(-)-3-Phenyl-2,2'-trifluoromethansulfonyloxy-[1,1']binaphthalenyl **LB12-4**: This compound was prepared in the same manner as that described above. yield: 90%.  $[\alpha]^{20}_D$  -194.4 (c 1.95, CHCl<sub>3</sub>). mp. 65-67 °C. IR (KBr):  $\nu$  3053, 1510, 1498, 1420, 1362, 1214, 1138, 1069, 973, 940 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  7.24 (2H, dd,  $J_1$  = 8.7 Hz,  $J_2$  = 9.9 Hz), 6.36-7.65 (10H, m), 8.01 (2H, d,  $J$  = 8.1 Hz), 8.11-8.18 (2H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75.45 MHz):  $\delta$  117.45 (d,  $J_{C-F}$  = 320.0 Hz), 118.22 (d,  $J_{C-F}$  = 320.0 Hz), 119.37, 120.77 (d,  $J_{C-F}$  = 292.0 Hz), 124.00, 124.80, 126.88, 127.21, 127.28, 127.35, 127.56, 127.61, 127.78, 128.25, 128.29, 128.38, 128.52, 129.79, 132.14, 132.30, 132.34, 132.38, 133.00, 133.49, 134.44, 136.11, 143.51, 145.58. MS (EI): *m/e* 626 (M<sup>+</sup>, 15.16), 493 (M<sup>+</sup>-133, 8.95), 360 (M<sup>+</sup>-266, 16.33), 344 (M<sup>+</sup>-282, 100). Anal. Calcd. for C<sub>28</sub>H<sub>16</sub>F<sub>6</sub>O<sub>6</sub>S<sub>2</sub>: requires C, 53.68; H, 2.57%; Found: C, 53.72; H, 2.91%.

(*R*)-(-)-3-Phenyl-2'-(diphenylphosphinoyl)-2-trifluoromethansulfonyloxy-[1,1']binaphthalenyl **LB12-5**: This compound was prepared in the same manner as that described above. yield: 72%.  $[\alpha]^{20}_D$  -80.4 (c 1.02, CHCl<sub>3</sub>). mp. 125-127 °C. IR (KBr):  $\nu$  1437, 1411, 1204, 1133, 970, 939 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  6.88 (1H, d,  $J$  = 8.4 Hz), 7.08-7.14 (3H, m), 7.20-7.27 (1H, m), 7.30-7.52 (11H, m), 7.55-7.65 (4H, m), 7.69-7.80 (3H, m), 7.88 (1H, s), 7.95 (1H, d,  $J$  = 8.1 Hz), 8.02 (1H, dd,  $J_1$  = 8.7 Hz,  $J_2$  = 2.4 Hz). <sup>31</sup>P NMR (121.45 MHz, CDCl<sub>3</sub>, 85% H<sub>3</sub>PO<sub>4</sub>):  $\delta$  +29.09. <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75.45 MHz):  $\delta$  117.42 (d,  $J$  = 321.0 Hz), 126.63, 126.81, 126.90, 126.93, 126.97, 127.77, 127.80, 127.84, 127.92, 127.96, 127.98, 128.05, 128.19, 128.26, 128.30, 128.34, 128.64, 128.81, 128.98, 129.13, 129.19, 129.71, 129.90, 131.05, 131.08, 131.12, 131.32, 131.45, 131.53, 131.56, 131.70, 131.93, 132.05, 132.77, 132.97, 133.33, 133.54, 133.68, 134.13, 134.50, 134.53, 136.53, 137.64, 137.73, 143.95. MS (EI): *m/e* 545 (M<sup>+</sup>-133, 1.98), 529 (M<sup>+</sup>-149, 100), 344 (M<sup>+</sup>-133-201, 15.42), 201 (Ph<sub>2</sub>PO<sup>+</sup>, 41.34), 77 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 10.54). Anal. Calcd. for C<sub>39</sub>H<sub>26</sub>F<sub>3</sub>O<sub>4</sub>PS:

requires C, 69.02; H, 3.86%; Found: C, 69.30; H, 4.12%.

**(R)-(-)-3-Phenyl-2'-(diphenylphosphinoyl)-[1,1']binaphthalenyl-2-ol **LB12-6**:** This compound was prepared in the same manner as that described above. yield: 93%.  $[\alpha]^{20}_D$  -130.8 (c 0.98, CHCl<sub>3</sub>). mp. 220-222 °C. IR (KBr):  $\nu$  3053, 1497, 1438, 1250, 1151, 1116, 748, 702 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  6.46 (1H, d, *J* = 8.1 Hz), 6.70-6.76 (2H, m), 6.82-6.88 (1H, m), 6.92-6.98 (1H, m), 7.11-7.16 (1H, m), 7.24-7.31 (4H, m), 7.36-7.65 (9H, m), 7.67 (1H, s), 7.81-7.96 (6H, m), 8.73 (1H, s). <sup>31</sup>P NMR (121.45 MHz, CDCl<sub>3</sub>, 85% H<sub>3</sub>PO<sub>4</sub>):  $\delta$  +32.14. <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75.45 MHz):  $\delta$  123.48, 124.59, 124.66, 125.18, 125.48, 126.74, 126.77, 126.90, 127.00, 127.17, 127.38, 127.46, 127.55, 127.73, 127.77, 127.94, 128.09, 128.41, 128.57, 128.84, 129.15, 129.30, 129.43, 129.61, 129.80, 129.89, 129.92, 130.51, 130.99, 131.17, 131.78, 131.90, 131.96, 132.71, 133.10, 133.24, 134.92, 134.95, 135.25, 138.76, 141.43, 141.54, 151.10. MS (EI): *m/e* 546 (M<sup>+</sup>, 14.40), 345 (M<sup>+</sup>-201, 29.30), 344 (M<sup>+</sup>-201-1, 100), 201 (Ph<sub>2</sub>PO<sup>+</sup>, 8.09), 77 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 4.21). Anal. Calcd. for C<sub>38</sub>H<sub>27</sub>O<sub>2</sub>P: requires C, 83.50; H, 4.98%; Found: C, 83.48; H, 5.14%.

**(R)-(+)-3-Phenyl-2'-(diphenylphosphanyl)-[1,1']binaphthalenyl-2-ol **LB12**:** This compound was prepared in the same manner as that described above. yield: 90%.  $[\alpha]^{20}_D$  +24.0 (c 1.08, CHCl<sub>3</sub>). mp. 110-112 °C. IR (KBr):  $\nu$  3532, 3051, 1622, 1601, 1583, 1497, 1479, 1432, 1352, 1258, 1240, 1196, 1128, 743, 697 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  6.87 (1H, d, *J* = 8.1 Hz), 7.08-7.15 (3H, m), 7.16-7.24 (3H, m), 7.26-7.56 (16H, m), 7.87 (1H, d, *J* = 8.1 Hz), 7.91-7.96 (3H, m). <sup>31</sup>P NMR (121.45 MHz, CDCl<sub>3</sub>, 85% H<sub>3</sub>PO<sub>4</sub>):  $\delta$  -12.25. <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75.45 MHz):  $\delta$  118.98, 119.08, 123.55, 124.72, 126.10, 126.14, 126.30, 126.96, 127.08, 127.46, 127.92, 128.08, 128.16, 128.19, 128.33, 128.37, 128.42, 128.51, 128.63, 128.66, 128.72, 128.79, 128.81, 128.95, 129.41, 130.05, 130.14, 130.16, 130.31, 132.94, 133.02, 133.29, 133.31, 133.34, 133.52, 133.56, 133.79, 133.80, 137.00, 137.17, 137.35, 137.55,

137.83, 138.00, 138.90, 139.35, 148.66, 148.69. MS (EI): *m/e* 530 ( $M^+$ , 52.50), 344 ( $M^+$ -185-1, 82.48), 328 ( $M^+$ -16-185-1, 100), 108 ( $C_6H_5^+$ +31, 11.85), 77 ( $C_6H_5^+$ , 18.81). Anal. Calcd. for  $C_{38}H_{27}OP$ : requires C, 86.02; H, 5.13%; Found: C, 85.65; H, 5.13%.

(*R*)-2'-Dimethylphosphanyl-[1,1']binaphthalenyl-2-ol **LB13**: a viscous oily compound;  $[\alpha]_D^{20}$  -147.2 (c 0.79,  $CHCl_3$ ). IR ( $CHCl_3$ ):  $\nu$  3197, 3044, 1619, 1510, 1429, 1337, 1268, 810  $cm^{-1}$  ( $C=C$ );  $^1H$  NMR ( $CDCl_3$ , TMS, 300 MHz):  $\delta$  0.97 (3H, d,  $J$  = 3.3 Hz, Me), 1.25 (3H, d,  $J$  = 3.3 Hz, Me), 4.80 (1H, s, OH), 6.89 (1H, d,  $J$  = 8.4 Hz, Ar), 7.20-7.38 (4H, m, Ar), 7.50 (1H, t,  $J$  = 6.9 Hz, Ar), 7.75-7.96 (4H, m, Ar), 8.04 (2H, d,  $J$  = 8.4 Hz, Ar).  $^{13}C$  NMR ( $CD_3C(O)CD_3$ , TMS, 75 MHz):  $\delta$  13.90 (d,  $J$  = 13.6 Hz), 14.27 (d,  $J$  = 13.6 Hz), 117.45, 123.21, 123.26, 124.76, 125.82, 125.84, 126.40, 126.44, 126.73, 127.0, 128.0, 128.08, 128.76, 129.10, 130.12, 132.86, 132.94, 133.64, 133.96, 133.98, 150.86.  $^{31}P$  NMR ( $CDCl_3$ , 85%  $H_3PO_4$ , 300 MHz):  $\delta$  -51.8. MS (EI): *m/e* 330 ( $M^+$ , 26.87), 313 ( $M^+$ -17, 100), 268 ( $M^+$ -62, 17.60). HRMS (EI) Calcd. for  $C_{22}H_{19}OP$  requires M, 330.1174, Found: 330.1187 ( $M^+$ ).

*Typical reaction procedure for (*R*)-2'-diphenylphosphanyl-[1,1']binaphthalenyl-2-ol **LB1** catalyzed aza-Baylis-Hillman reaction of *N*-(benzylidene)-4-methylbenzenesulfonamide **1a** with MVK.*

A 10 mL Schlenk tube containing *N*-(benzylidene)-4-methylbenzenesulfonamide **1a** (0.5 mmol) and (*R*)-2'-diphenylphosphanyl-[1,1']binaphthalenyl-2-ol **LB1** (23 mg, 0.05 mmol) was degassed and the reaction vessel was protected under argon atmosphere. Then, THF (1.0 mL) was added. After the reaction mixture was cooled to -30 °C, methyl vinyl ketone (MVK) (125  $\mu$ L, 1.5 mmol) was added into the Schlenk tube. The reaction mixture was stirred at -30 °C for 12-36 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography ( $SiO_2$ , eluent: EtOAc/Petroleum ether = 1/5) to yield the corresponding aza-Baylis-Hillman adduct as a colorless solid which was immediately

subjected to the chiral HPLC for the analysis of the achieved enantiomeric excess. For microanalysis, all these products were recrystallized from acetone and n-hexane.

**4-Methyl-N-(2-methylene-3-oxo-1-phenylbutyl)benzenesulfonamide 2a:** a colorless solid, 81 mg, yield: 49%. mp. 124-126 °C.  $[\alpha]_D^{20} +28.3$  (c 0.95, CHCl<sub>3</sub>). IR (CHCl<sub>3</sub>):  $\nu$  3266, 3025, 1667 (C=O), 1597, 1491, 1449, 1366, 1323, 1304, 1161, 750, 667 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz):  $\delta$  2.16 (3H, s, Me), 2.42 (3H, s, Me), 5.26 (1H, d, *J* = 8.6 Hz), 5.61 (1H, d, *J* = 8.6 Hz), 6.10 (1H, s), 6.11 (1H, s), 7.11 (2H, m, Ar), 7.20-7.27 (5H, m, Ar), 7.66 (2H, d, *J* = 8.1 Hz, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz):  $\delta$  21.74, 26.51, 58.64, 126.78, 127.48, 127.75, 128.44, 128.67, 129.72, 137.72, 139.18, 143.56, 146.81, 199.05. MS (EI): *m/e* 260 (M<sup>+</sup>-69, 14.09), 174 (M<sup>+</sup>-155, 100), 155 (SO<sub>2</sub>PhMe<sup>+</sup>, 29.60). Anal. Calcd. for C<sub>18</sub>H<sub>19</sub>NO<sub>3</sub>S: C, 65.63; H, 5.81; N, 4.25%. Found: C, 65.64; H, 5.74; N, 4.14%. HPLC: AD column;  $\lambda$  = 254 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min; t<sub>major</sub> = 17.14 min, t<sub>minor</sub> = 18.80 min; ee% = 83%.

**4-Methyl-N-(2-methylene-3-oxo-1-p-tolylbutyl)benzenesulfonamide 2b:** a colorless solid, 90 mg, yield: 53%. mp: 114-116 °C.  $[\alpha]_D^{20} +38.4$  (c 1.06, CHCl<sub>3</sub>). IR (KBr):  $\nu$  3219, 3023, 2924, 2884, 1918, 1664 (C=O), 1598, 1512, 1456, 1369, 1323, 1271, 1158, 1095, 1069, 963, 932, 824, 812, 663 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz):  $\delta$  2.16 (3H, s, Me), 2.27 (3H, s, Me), 2.42 (3H, s, Me), 5.23 (1H, d, *J* = 8.4 Hz), 5.56 (1H, d, *J* = 8.4 Hz), 6.10 (2H, s), 6.95 (2H, d, *J* = 8.2 Hz, Ar), 7.00 (2H, d, *J* = 8.2 Hz, Ar), 7.24 (2H, d, *J* = 8.2 Hz, Ar), 7.65 (2H, d, *J* = 8.2 Hz, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz):  $\delta$  21.55, 22.07, 26.88, 58.81, 127.01, 127.84, 128.48, 129.73, 130.04, 136.58, 137.83, 138.09, 143.84, 147.31, 199.39. MS (EI): *m/e* 274 (M<sup>+</sup>-69, 4.44), 188 (M<sup>+</sup>-155, 100), 91 (PhMe<sup>+</sup>, 50.98). Anal. Calcd. for C<sub>19</sub>H<sub>21</sub>NO<sub>3</sub>S: C, 66.47; H, 6.12; N, 4.08%; Found: C, 66.74; H, 6.47; N, 3.89%. HPLC: AD column;  $\lambda$  = 254 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min; t<sub>major</sub> = 17.42 min, t<sub>minor</sub> = 18.81

min; ee% = 80%.

**N-[1-(4-Ethylphenyl)-2-methylene-3-oxobutyl]-4-methylbenzenesulfonamide 2c:** a colorless solid, 110 mg, yield: 62%. mp: 110-114 °C;  $[\alpha]_D^{20} +38.4$  (c 1.05, CHCl<sub>3</sub>). IR (CHCl<sub>3</sub>):  $\nu$  3375, 3020, 2966, 1674 (C=O), 1423, 1334, 1215, 1160, 1092, 953, 814, 756, 667 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz):  $\delta$  1.23 (3H, t, *J* = 7.6 Hz, Me), 2.15 (3H, s, Me), 2.39 (3H, s, Me), 2.54 (2H, q, *J* = 7.6 Hz, CH<sub>2</sub>), 5.20 (1H, d, *J* = 6.1 Hz, CH), 5.51 (1H, d, *J* = 8.4 Hz, NH), 6.09 (2H, s), 6.97 (2H, d, *J* = 6.1 Hz, Ar), 6.98 (2H, *J* = 6.1 Hz, Ar), 7.21 (2H, d, *J* = 8.4 Hz, Ar), 7.63 (2H, d, *J* = 8.4 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz):  $\delta$  15.51, 21.42, 26.25, 28.29, 58.29, 126.44, 127.22, 127.89, 129.08, 129.38, 136.09, 137.44, 143.16, 143.54, 146.66, 198.26. MS (EI): *m/e* 358 (M<sup>+</sup>-1, 0.5), 288 (M<sup>+</sup>-69, 5.6), 202 (M<sup>+</sup>-155, 100). Anal. Calcd. for C<sub>20</sub>H<sub>23</sub>NO<sub>3</sub>S: C, 67.20; H, 6.49; N, 3.92%. Found: C, 67.04; H, 6.42; N, 3.74%. HPLC: TBB column;  $\lambda$  = 254 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min; t<sub>minor</sub> = 10.84 min; t<sub>major</sub> = 11.52 min, ee% = 76%.

**N-[1-(4-Fluorophenyl)-2-methylene-3-oxobutyl]-4-methylbenzenesulfonamide 2d:** a colorless solid, 146 mg, yield: 84%. mp: 104-106 °C.  $[\alpha]_D^{20} +22.1$  (c 1.2, CHCl<sub>3</sub>). IR (KCl):  $\nu$  3255 (N-H), 1663 (C=O), 1600, 1510, 1437, 1367, 1325, 1228, 1159, 1094, 1065, 960, 812, 666, 550 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz):  $\delta$  2.15 (3H, s, Me), 2.41 (3H, s, Me), 5.24 (1H, d, *J* = 8.7 Hz), 5.75 (1H, d, *J* = 8.7 Hz), 6.07 (1H, s), 6.09 (1H, s), 6.84-6.9 (2H, dd, *J*<sub>1</sub> = 9.0 Hz, *J*<sub>2</sub> = 8.6 Hz), 7.04-7.09 (2H, dd, *J*<sub>1</sub> = 8.6 Hz, *J*<sub>2</sub> = 5.2 Hz), 7.23 (2H, d, *J* = 8.1 Hz), 7.63 (2H, *J* = 8.1 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz):  $\delta$  21.09, 25.88, 57.74, 114.88 (d, *J* = 21.8 Hz), 126.83, 127.78, 127.87 (d, *J* = 2.7 Hz), 129.11, 134.35, 137.01, 143.07, 146.03, 161.64 (d, *J* = 244 Hz), 198.38. MS (EI): *m/e* 192 (M<sup>+</sup>-155, 8.79), 155 (M<sup>+</sup>-192, 7.08), 95 (M<sup>+</sup>-155-97, 11.72), 91 (M<sup>+</sup>-192-64, 70.98), 65 (M<sup>+</sup>-155-64-26, 45.32), 43 (M<sup>+</sup>-304, 100). Anal. Calcd. for C<sub>18</sub>H<sub>18</sub>FNO<sub>3</sub>S: C, 62.24; H, 5.22; N, 4.03%. Found: C, 61.98; H, 5.29; N, 4.04%. HPLC: AD

column;  $\lambda = 254$  nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min;  $t_{\text{major}} = 13.15$  min,  $t_{\text{minor}} = 14.26$  min; ee% = 81%.

**N-[1-(4-Chlorophenyl)-2-methylene-3-oxobutyl]-4-methylbenzenesulfonamide 2e:** a colorless solid, 131 mg, yield: 72%. mp: 89-92 °C.  $[\alpha]_D^{20} +25.3$  (c 1.07, CHCl<sub>3</sub>). IR (CHCl<sub>3</sub>):  $\nu$  3282, 3022, 1674 (C=O), 1596, 1489, 1419, 1366, 1332, 1216, 1161, 1092, 1068, 1015, 955, 814, 756, 667 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz):  $\delta$  2.11 (3H, s, Me), 2.38 (3H, s, Me), 5.24 (1H, d,  $J = 9.1$  Hz, NH), 5.99 (1H, d,  $J = 9.1$  Hz, CH), 6.03 (1H, s), 6.06 (1H, s,), 7.01 (2H, d,  $J = 8.6$  Hz, Ar), 7.12 (2H, d,  $J = 8.6$  Hz, Ar), 7.19 (2H, d,  $J = 8.1$  Hz, Ar), 7.59 (2H, d,  $J = 8.1$  Hz, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz):  $\delta$  21.42, 26.18, 58.14, 127.14, 127.85, 128.38, 128.48, 129.46, 133.34, 137.33, 137.44, 143.44, 146.17, 198.66. MS (EI): *m/e* 294 (M<sup>+</sup>-69, 2.36), 208 (M<sup>+</sup>-155, 100), 91 (PhMe<sup>+</sup>, 39.81). Anal. Calcd. for C<sub>18</sub>H<sub>18</sub>ClNO<sub>3</sub>S C, 59.42; H, 4.99; N, 3.85%. Found: C, 59.43; H, 4.94; N, 3.78%. HPLC: AS column;  $\lambda = 254$  nm; eluent: Hexane/Isopropanol = 65/35; Flow rate: 0.7 mL/min;  $t_{\text{major}} = 24.437$  min,  $t_{\text{minor}} = 32.41$  min; ee% = 94%.

**N-[1-(4-Bromophenyl)-2-methylene-3-oxobutyl]-4-methylbenzenesulfonamide 2f:** a colorless solid, 173 mg, yield: 85%. mp: 98-100 °C.  $[\alpha]_D^{20} +27.8$  (c 1.08, CHCl<sub>3</sub>). IR (KCl):  $\nu$  3295 (N-H), 1669 (C=O), 1696, 1485, 1441, 1324, 1162, 1069, 1010, 960, 814, 664 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz):  $\delta$  2.15 (3H, s, Me), 2.41 (3H, s, Me), 5.19 (1H, d,  $J = 9.1$  Hz), 5.71 (1H, d,  $J = 9.1$  Hz), 6.06 (1H, s), 6.09 (1H, s), 6.98 (2H, d,  $J = 7.8$  Hz), 7.26 (2H, d,  $J = 8.0$  Hz), 7.31 (2H, dd,  $J_1 = 7.8$  Hz,  $J_2 = 2.0$  Hz), 7.62 (2H,  $J = 8.0$  Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz):  $\delta$  20.99, 25.73, 57.84, 121.05, 126.68, 127.70, 127.99, 129.01, 130.99, 136.87, 137.48, 143.01, 145.63, 198.21. MS (EI): *m/e* 254 (M<sup>+</sup>+2-155, 10.96), 252 (M<sup>+</sup>-155, 10.67), 208 (M<sup>+</sup>-155-44, 3.87), 184 (M<sup>+</sup>-155-68, 9.58), 155 (M<sup>+</sup>-253, 15.5), 130 (M<sup>+</sup>-155-43-79, 47.22), 91 (M<sup>+</sup>-252-64, 100), 65 (M<sup>+</sup>-252-64-26, 47.08), 43 (M<sup>+</sup>-365, 74.05). Anal. Calcd. for

$C_{18}H_{18}BrNO_3S$ : C, 52.95; H, 4.44; N, 3.43%. Found: C, 53.12; H, 4.60; N, 3.33%. HPLC: AD column;  $\lambda = 254$  nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min;  $t_{\text{major}} = 23.16$  min,  $t_{\text{minor}} = 25.65$  min; ee% = 83%.

**N-[1-(3-Fluorophenyl)-2-methylene-3-oxobutyl]-4-methylbenzenesulfonamide 2g:** a colorless solid, 45 mg, yield: 26%. mp: 109-111 °C.  $[\alpha]_D^{20} +10.6$  (c 1.03,  $CHCl_3$ ). IR ( $CHCl_3$ ):  $\nu$  3357, 3302, 1925, 1673 (C=O), 1609, 1592, 1482, 1439, 1372, 1329, 1242, 1160, 1096, 1067, 988, 919, 821, 781, 672  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ , TMS, 300 MHz):  $\delta$  2.16 (3H, s, Me), 2.41 (3H, s, Me), 5.24 (1H, d,  $J = 9.2$  Hz, NH), 5.78 (1H, d,  $J = 9.2$  Hz), 6.06 (1H, s), 6.11 (1H, s), 6.79-6.92 (3H, m, Ar), 7.14-7.23 (3H, m, Ar), 7.65 (2H, d,  $J = 8.6$  Hz, Ar).  $^{13}C$  NMR ( $CDCl_3$ , TMS, 75 MHz):  $\delta$  21.38, 26.13, 58.22, 113.51 (d,  $J = 22.8$  Hz), 114.34 (d,  $J = 21.2$  Hz), 121.94 (d,  $J = 2.8$  Hz), 127.13, 128.65, 129.44, 129.90 (d,  $J = 8.4$  Hz), 137.35, 141.48 (d,  $J = 6.8$  Hz), 143.45, 145.97, 162.59 (d,  $J = 245$  Hz), 198.67. MS (EI):  $m/e$  278 ( $M^+ - 69$ , 7.84), 192 ( $M^+ - 155$ , 100), 155 ( $SO_2PhMe^+$ , 44.33). Anal. Calcd. for  $C_{18}H_{18}FNO_3S$ : C, 62.23; H, 5.22; N, 4.03%. Found: C, 62.38; H, 5.34; N, 3.82%. HPLC: AD column;  $\lambda = 254$  nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min;  $t_{\text{major}} = 17.65$  min,  $t_{\text{minor}} = 18.11$  min; ee% = 91%.

**N-[1-(3-Chlorophenyl)-2-methylene-3-oxobutyl]-4-methylbenzenesulfonamide 2h:** a colorless solid, 112 mg, yield: 62%. mp: 89-92 °C.  $[\alpha]_D^{20} +17.5$  (c 1.12,  $CHCl_3$ ). IR (KCl):  $\nu$  3305 (N-H), 1667 (C=O), 1596, 1480, 1443, 1324, 1217, 1161, 1070, 984, 959, 924, 801, 696  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ , TMS, 300 MHz):  $\delta$  2.16 (3H, s, Me), 2.41 (3H, s, Me), 5.20 (1H, d,  $J = 9.0$  Hz), 5.69 (1H, d,  $J = 9.0$  Hz), 6.08 (1H, s), 6.12 (1H, s), 7.0-7.03 (2H, m), 7.13-7.15 (2H, m), 7.24 (2H, d,  $J = 8.2$  Hz), 7.63 (2H,  $J = 8.2$  Hz).  $^{13}C$  NMR ( $CDCl_3$ , TMS, 75 MHz):  $\delta$  21.73, 26.43, 58.21, 124.90, 127.03, 127.40, 127.83, 128.99, 129.73, 129.94, 134.43, 137.54, 141.26, 143.79, 146.26, 198.88. MS (EI):  $m/e$  208 ( $M^+ - 155$ , 7.61), 155 ( $M^+ - 208$ , 9.04), 91

(M<sup>+</sup>-208-64, 76.55), 65 (M<sup>+</sup>-208-64-26, 44.72), 43 (M<sup>+</sup>-360, 100). Anal. Calcd. for C<sub>18</sub>H<sub>18</sub>ClNO<sub>3</sub>S: C, 59.42; H, 4.98; N, 3.85%. Found: C, 59.49; H, 5.17; N, 3.81%. HPLC: AD column; λ = 254 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min; t<sub>major</sub> = 17.65 min, t<sub>minor</sub> = 20.81 min; ee% = 88%.

**4-Methyl-N-[2-methylene-1-(4-nitrophenyl)-3-oxobutyl]benzenesulfonamide 2i:** a colorless solid, 110 mg, yield: 60%. mp: 120-122 °C. [α]<sub>D</sub><sup>20</sup> +2.5 (c 0.98, CHCl<sub>3</sub>). IR (CHCl<sub>3</sub>): ν 3328, 3021, 1674 (C=O), 1597, 1520, 1418, 1348, 1215, 1186, 1162, 1077, 926, 854, 759, 668 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz): δ 2.15 (3H, s, Me), 2.44 (3H, s, Me), 5.32 (1H, d, J = 9.4 Hz), 5.94 (1H, d, J = 9.4 Hz), 6.08 (1H, s), 6.14 (1H, s), 7.25 (2H, d, J = 8.3 Hz, Ar), 7.34 (2H, d, J = 8.7 Hz, Ar), 7.65 (2H, d, J = 8.3 Hz, Ar), 8.07 (2H, d, J = 8.7 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz): δ 21.37, 25.99, 58.32, 123.43, 127.04, 127.27, 129.35, 129.50, 137.19, 143.72, 145.47, 146.21, 146.98, 198.50. MS (EI): m/e 305 (M<sup>+</sup>-69, 3.77), 219 (M<sup>+</sup>-155, 100), 155 (SO<sub>2</sub>PhMe<sup>+</sup>, 29.96). Anal. Calcd. for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>5</sub>S: C, 57.74; H, 4.85; N, 7.48%. Found: C, 57.62; H, 4.84; N, 7.39%. HPLC: OJ column; λ = 254 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.7 mL/min; t<sub>major</sub> = 13.15 min, t<sub>minor</sub> = 14.26 min; ee% = 94%.

**4-Methyl-N-[2-methylene-1-(3-nitrophenyl)-3-oxobutyl]benzenesulfonamide 2j:** a colorless solid, 101 mg, yield: 54%. mp: 122-124 °C. [α]<sub>D</sub><sup>20</sup> +10.1 (c 1.04, CHCl<sub>3</sub>). IR (KCl): ν 3317 (N-H), 1671 (C=O), 1595, 1538, 1432, 1349, 1323, 1160, 1087, 1066, 981, 956, 919, 812, 689 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz): δ 2.18 (3H, s, Me), 2.41 (3H, s, Me), 5.32 (1H, d, J = 9.4 Hz), 5.89 (1H, d, J = 9.4 Hz), 6.12 (1H, s), 6.18 (1H, s), 7.25 (2H, d, J = 8.6 Hz), 7.44 (1H, dd, J<sub>1</sub> = 8.2 Hz, J<sub>2</sub> = 7.8 Hz), 7.61 (1H, d, J = 7.8 Hz), 7.65 (2H, d, J = 8.6 Hz), 7.89 (1H, s), 8.05 (1H, d, J = 8.2 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz): δ 21.65, 26.33, 58.10, 121.76, 122.61, 127.34, 129.63, 129.79, 129.85, 133.01, 137.41, 141.49, 144.00, 145.81,

148.24, 198.88. MS (EI):  $m/e$  91 ( $M^+$ -283, 52.79), 65 ( $M^+$ -283-26, 37.97), 43 ( $M^+$ -331, 100). Anal. Calcd. for  $C_{18}H_{18}N_2O_5S$ : C, 57.74; H, 4.84; N, 7.48%. Found: C, 57.74; H, 5.07; N, 7.34%. HPLC: AD column;  $\lambda$  = 254 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min;  $t_{\text{major}}$  = 23.60 min,  $t_{\text{minor}}$  = 29.04 min; ee% = 90%.

***N*-[2-Acetyl-1-(2-chlorophenyl)allyl]-4-methylbenzenesulfonamide 2k:** a colorless solid, 154 mg, yield: 85%. mp: 155-158 °C.  $[\alpha]_D^{23}$  +24.1 (c 1.06,  $CHCl_3$ ). IR ( $CHCl_3$ ):  $\nu$  3247, 3060, 1678 (C=O), 1597, 1473, 1444, 1366, 1336, 1159, 1093, 1074, 959, 815, 757, 671  $\text{cm}^{-1}$ .  $^1H$  NMR ( $CDCl_3$ , TMS, 300 MHz):  $\delta$  2.21 (3H, s, Me), 2.37 (3H, s, Me), 5.68 (1H, d,  $J$  = 8.6 Hz), 5.78 (1H, d,  $J$  = 8.6 Hz), 6.16 (1H, s), 6.17 (1H, s), 7.06-7.15 (2H, m, Ar), 7.20 (2H, d,  $J$  = 8.4 Hz, Ar), 7.21-7.24 (1H, m, Ar), 7.30-7.33 (1H, m, Ar), 7.63 (2H, d,  $J$  = 8.4 Hz, Ar).  $^{13}C$  NMR ( $CDCl_3$ , TMS, 75 MHz):  $\delta$  21.43, 26.37, 55.55, 126.74, 127.15, 128.76, 129.05, 129.23, 129.31, 129.61, 132.65, 135.87, 137.06, 143.25, 145.35, 198.79. MS (EI):  $m/e$  364 ( $M^+$ +1, 0.70), 294 ( $M^+$ -69, 5.04), 208 ( $M^+$ -155, 100), 210 ( $M^+$ +2-155, 34.99), 193 ( $M^+$ -170, 3.60), 155 ( $M^+$ -208, 18.25), 91 (PhMe $^+$ , 51.57). Anal. Calcd. for  $C_{18}H_{18}ClNO_3S$ : C, 59.42; H, 4.99; N, 3.85%. Found: C, 59.37; H, 5.16; N, 3.68%. HPLC: AD column;  $\lambda$  = 254 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min;  $t_{\text{major}}$  = 22.13 min,  $t_{\text{minor}}$  = 24.46 min; ee% = 61%.

***N*-[2-Acetyl-1-(2-nitrophenyl)allyl]-4-methylbenzenesulfonamide 2l:** a yellow solid, 165 mg, yield: 88%. mp: 141-143 °C.  $[\alpha]_D^{23}$  +58.2 (c 0.99,  $CHCl_3$ ). IR ( $CHCl_3$ ):  $\nu$  3264, 2924, 1683 (C=O), 1598, 1578, 1528, 1445, 1350, 1160, 1091, 1063, 958, 916, 858, 816, 671  $\text{cm}^{-1}$ .  $^1H$  NMR ( $CDCl_3$ , TMS, 300 MHz):  $\delta$  2.17 (3H, s, Me), 2.40 (3H, s, Me), 5.91 (1H, d,  $J$  = 9.0 Hz), 5.96 (1H, s), 5.97 (1H, d,  $J$  = 9.0 Hz), 6.08 (1H, s), 7.23 (2H, d,  $J$  = 8.1 Hz, Ar), 7.36 (1H, ddd,  $J_1$  = 7.8 Hz,  $J_2$  = 7.5 Hz,  $J_3$  = 1.5 Hz, Ar), 7.50 (1H, ddd,  $J_1$  = 7.8 Hz,  $J_2$  = 7.5 Hz,  $J_3$  = 1.2 Hz, Ar), 7.64 (1H, dd,  $J_1$  = 7.8 Hz,  $J_2$  = 1.2 Hz, Ar), 7.68 (2H, d,  $J$  = 8.1 Hz, Ar), 7.75 (1H, dd,

$J_1 = 7.8$  Hz,  $J_2 = 1.2$  Hz, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz):  $\delta$  21.51, 26.21, 54.51, 124.71, 127.18, 128.57, 129.42, 129.54, 130.41, 132.95, 133.22, 137.01, 143.60, 144.82, 148.04, 198.58. MS (EI):  $m/e$  305 ( $M^+$ -69, 0.79), 219 ( $M^+$ -155, 20.77), 201 ( $M^+$ -173, 38.50), 159 ( $M^+$ -170-46+1, 49.75), 155 ( $M^+$ -219, 21.37), 91 ( $\text{PhMe}^+$ , 51.57), 77 ( $\text{Ph}^+$ , 14.80). Anal. Calcd. for  $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_5\text{S}$ : C, 57.74; H, 4.85; N, 7.48%. Found: C, 57.60; H, 4.77; N, 7.44%. HPLC: AS column;  $\lambda = 254$  nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.7 mL/min;  $t_{\text{major}} = 30.88$  min,  $t_{\text{minor}} = 78.03$  min; ee% = 84%.

**N-[2-Acetyl-1-styryl-allyl]-4-methylbenzenesulfonamide 2m:** a colorless solid, 166 mg, yield: 94%. mp: 141-143 °C.  $[\alpha]_D^{23} +6.0$  (c 1.08,  $\text{CHCl}_3$ ). IR ( $\text{CHCl}_3$ ):  $\nu$  3276, 3026, 2924, 1674 (C=O), 1598, 1495, 1424, 1366, 1329, 1161, 1093, 1050, 967, 815, 750, 694, 669  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz):  $\delta$  2.19 (3H, s, Me), 2.33 (3H, s, Me), 4.76 (1H, dd,  $J_1 = 6.9$  Hz,  $J_2 = 9.6$  Hz, CH), 5.61 (1H, d,  $J = 9.6$  Hz, NH), 5.98 (1H, s), 5.99 (1H, dd,  $J_1 = 6.9$  Hz,  $J_2 = 15.9$  Hz), 6.00 (1H, s), 6.28 (1H, d,  $J = 15.9$  Hz), 7.14-7.28 (7H, m, Ar), 7.69 (2H, d,  $J = 8.1$  Hz, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz):  $\delta$  21.30, 26.09, 58.12, 126.34, 126.90, 127.23, 127.74, 128.17, 128.30, 129.39, 131.74, 135.86, 137.69, 143.21, 146.06, 198.98. MS (EI):  $m/e$  355 ( $M^+$ , 0.61), 270 ( $M^+$ -70-15, 16.78), 200 ( $M^+$ -155, 61.16), 184 ( $M^+$ -171, 6.38), 171 ( $M^+$ -184, 2.90), 156 ( $M^+$ -199, 18.41), 155 ( $M^+$ -200, 16.98), 91 ( $\text{PhMe}^+$ , 100), 77 ( $\text{Ph}^+$ , 14.51). Anal. Calcd. for  $\text{C}_{20}\text{H}_{21}\text{NO}_3\text{S}$ : C, 67.58; H, 5.95; N, 3.94%. Found: C, 67.34; H, 6.10; N, 7.35%. HPLC: AD column;  $\lambda = 254$  nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min;  $t_{\text{major}} = 23.30$  min,  $t_{\text{minor}} = 26.88$  min; ee% = 95%.

**N-[2-Acetyl-1-(4-chlorophenyl)allyl]methanesulfonamide 2n:** a colorless solid, 135 mg, yield: 94%. mp: 130-132 °C.  $[\alpha]_D^{23} -3.7$  (c 1.09,  $\text{CHCl}_3$ ). IR ( $\text{CHCl}_3$ ):  $\nu$  3285, 2927, 1676 (C=O), 1491, 1441, 1367, 1323, 1154, 1092, 1069, 1014, 978, 859, 759, 517  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz):  $\delta$  2.34 (3H, s, Me), 2.88 (3H, s, Me), 5.41 (1H, d,  $J = 9.0$  Hz), 5.64

(1H, d,  $J = 9.0$  Hz), 6.18 (1H, s), 6.29 (1H, s), 7.25-7.34 (4H, m, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz):  $\delta$  26.39, 41.50, 57.62, 127.99, 128.48, 128.73, 133.51, 137.86, 147.12, 198.70. MS (EI):  $m/e$  220 ( $M^+-69+2$ , 3.32), 218 ( $M^+-69$ , 8.53), 210 ( $M^+-79+2$ , 33.04), 208 ( $M^+-79$ , 100), 192 ( $M^+-95$ , 1.08), 172 ( $M^+-79-35-1$ , 4.44), 164 (95+69, 5.45), 149 (79+69+1, 16.06), 140 ( $M^+-147$ , 23.51), 96 (95+1, 3.30), 79 (14.80), 43 ( $M^+-244$ , 26.49). Anal. Calcd. for  $\text{C}_{12}\text{H}_{14}\text{ClNO}_3\text{S}$ : C, 50.09; H, 4.90; N, 4.87%. Found: C, 50.04; H, 5.16; N, 4.72%. HPLC: OD column;  $\lambda = 254$  nm; eluent: Hexane/Isopropanol = 85/15; Flow rate: 0.7 mL/min;  $t_{\text{minor}} = 24.03$  min,  $t_{\text{major}} = 25.54$  min; ee% = 82%.

**N-[2-Acetyl-1-(4-chlorophenyl)allyl]-4-chlorobenzenesulfonamide 2o:** a colorless syrup, 180 mg, yield: 94%. 90-93 °C.  $[\alpha]_D^{23} +24.4$  (c 1.10,  $\text{CHCl}_3$ ). IR ( $\text{CHCl}_3$ ):  $\nu$  3278, 3092, 2924, 1676 (C=O), 1586, 1491, 1477, 1422, 1397, 1366, 1338, 1278, 1164, 1093, 1067, 1014, 954, 827, 754, 627  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz):  $\delta$  2.17 (3H, s, Me), 5.29 (1H, d,  $J = 9.0$  Hz), 6.05 (1H, s), 6.11 (1H, s), 6.20 (1H, d,  $J = 9.0$  Hz), 7.05 (2H, d,  $J = 8.1$  Hz, Ar), 7.16 (2H, d,  $J = 8.1$  Hz, Ar), 7.39 (2H, d,  $J = 8.1$  Hz, Ar), 7.67 (2H, d,  $J = 8.1$  Hz, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz):  $\delta$  26.21, 58.14, 127.80, 128.50, 128.55, 129.10, 133.49, 137.06, 138.81, 139.04, 145.97, 198.71. MS (EI):  $m/e$  316 ( $M^+-69+2$ , 100), 314 ( $M^+-69$ , 2.39), 278 ( $M^+-36-69$ , 2.11), 210 ( $M^+-175+2$ , 33.48), 208 ( $M^+-175$ , 1.08), 193 ( $M^+-190$ , 5.56), 175 ( $M^+-208$ , 12.23), 149 ( $M^+-234$ , 10.44), 130 ( $M^+-253$ , 21.39), 111 (35+76, 28.38). HRMS (MALDI) ( $M^++\text{Na}$ ) calcd for  $\text{C}_{17}\text{H}_{15}\text{Cl}_2\text{NO}_3\text{SNa}^+$  requires 406.00419, Found 406.0056. HPLC: AD column;  $\lambda = 254$  nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min;  $t_{\text{major}} = 29.91$  min,  $t_{\text{minor}} = 32.94$  min; ee% = 89%.

**2-Trimethylsilanyleethanesulfonic acid [2-acetyl-1-(4-chlorophenyl)allyl]amide 2q:** a colorless solid, 50 mg, yield: 53%. mp: 99-102 °C.  $[\alpha]_D^{23} +9.8$  (c 1.06,  $\text{CHCl}_3$ ). IR ( $\text{CHCl}_3$ ):  $\nu$  3280, 2954, 2898, 1679 (C=O), 1632, 1595, 1491, 1421, 1366, 1323, 1264, 1251, 1169, 1145,

1092, 1069, 1015, 955, 893, 860, 740, 699 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz): δ -0.01 (9H, s, Me), 0.86-0.93 (2H, m, CH<sub>2</sub>), 2.34 (3H, s, Me), 2.81-2.87 (2H, m, CH<sub>2</sub>), 5.35 (1H, d, *J* = 9.0 Hz), 5.49 (1H, d, *J* = 9.0 Hz), 6.20 (1H, s), 6.28 (1H, s), 7.28-7.33 (4H, m, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75 MHz): δ -2.01, 10.43, 26.52, 49.95, 58.41, 127.93, 128.25, 128.80, 133.66, 138.14, 147.33, 198.87. MS (EI): *m/e* 280 (M<sup>+</sup>-93, 2.77), 266 (M<sup>+</sup>-107, 3.07), 210 (M<sup>+</sup>-165+2, 34.76), 208 (M<sup>+</sup>-165, 100), 193 (M<sup>+</sup>-180, 3.01), 166 (M<sup>+</sup>-207, 2.94), 149 (M<sup>+</sup>-224, 4.28), 138 (M<sup>+</sup>-165-70, 3.86), 130 (M<sup>+</sup>-243, 8.13), 73 [(CH<sub>3</sub>)<sub>3</sub>Si<sup>+</sup>, 79.83], 43 (M<sup>+</sup>-330, 26.30). HRMS (MALDI) (M<sup>+</sup>+Na) calcd for C<sub>16</sub>H<sub>24</sub>CINO<sub>3</sub>SSiNa<sup>+</sup> requires 396.08269, Found 396.0844. HPLC: AS column; λ = 254 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min; t<sub>major</sub> = 19.38 min, t<sub>minor</sub> = 26.04 min; ee% = 89%.

In the coexistence of molecular sieve 4A (100 mg), these reactions were carried out in the same manner as that described above.

*Typical reaction procedure for (R)-2'-diphenylphosphanyl-[1,1']binaphthalenyl-2-ol **LB1** catalyzed aza-Baylis-Hillman reaction of N-(benzylidene)-4-methylbenzenesulfonamide **1a** with EVK.*

A 10 mL Schlenk tube containing *N*-(benzylidene)-4-methylbenzenesulfonamide **1a** (0.5 mmol) and (R)-2'-diphenylphosphanyl-[1,1']binaphthalenyl-2-ol **LB1** (23 mg, 0.05 mmol) was degassed and the reaction vessel was protected under argon atmosphere. Then, THF (1.0 mL) was added. After the reaction mixture was cooled to -20 °C, ethyl vinyl ketone (EVK) (100 μL, 1.0 mmol) was added into the Schlenk tube. The reaction mixture was stirred at -20 °C for 1-7 days. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (SiO<sub>2</sub>, eluent: EtOAc/Petroleum ether = 1/6) to yield the corresponding aza-Baylis-Hillman adduct as a colorless solid which was immediately subjected to the chiral HPLC for the analysis of the achieved enantiomeric excess. For

microanalysis, all these products were recrystallized from acetone and n-hexane.

**4-Methyl-N-[1-(4-chlorophenyl)-2-methylene-3-oxo-pentyl]benzenesulfonamide 3a:** a colorless solid (90 mg, 48%).  $[\alpha]^{20}_D +17.1$  (c 1.03, CHCl<sub>3</sub>). mp. 112-113 °C. IR (CHCl<sub>3</sub>): ν 3282, 3023, 2980, 2940, 1678 (C=O), 1598, 1492, 1410, 1335, 1216, 1161, 1092, 1015, 952, 814, 756, 667 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz): δ 0.95 (3H, t, *J* = 7.2 Hz, Me), 2.41 (3H, s, Me), 2.43-2.61 (2H, m, CH<sub>2</sub>), 5.23 (1H, d, *J* = 9.0 Hz), 5.75 (1H, d, *J* = 9.0 Hz), 6.03 (1H, s), 6.10 (1H, s), 7.07 (2H, d, *J* = 8.4 Hz, Ar), 7.18 (2H, d, *J* = 8.4 Hz, Ar), 7.26 (2H, d, *J* = 8.1 Hz, Ar), 7.65 (2H, d, *J* = 8.1 Hz, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75.44 MHz): δ 7.72, 21.49, 31.25, 58.51, 127.16, 127.19, 127.79, 128.50, 129.45, 133.29, 137.31, 137.49, 143.47, 145.50, 201.40. MS (EI): *m/e* 294 (M<sup>+</sup>-83, 4.57), 222 (M<sup>+</sup>-155, 100), 155 (MePhSO<sub>2</sub><sup>+</sup>, 27.67). Anal. Calcd. for C<sub>19</sub>H<sub>20</sub>ClNO<sub>3</sub>S: requires C, 60.39; H, 5.33; N, 3.71%. Found: C, 60.39; H, 5.50; N, 3.61%. HPLC: OD column; λ = 254 nm; eluent: Hexane/Isopropanol = 90/10; Flow rate: 0.7 mL/min; t<sub>minor</sub> = 24.71 min; t<sub>major</sub> = 27.58 min, ee% = 92%.

**4-Methyl-N-(1-phenyl-2-methylene-3-oxo-pentyl)benzenesulfonamide 3b:** a colorless solid (90 mg, 52%).  $[\alpha]^{20}_D +15.5$  (c 1.0, CHCl<sub>3</sub>). mp. 84-86 °C. IR (CHCl<sub>3</sub>): ν 3285, 3025, 2981, 2940, 1677 (C=O), 1599, 1495, 1452, 1411, 1332, 1216, 1161, 1092, 1066, 950, 814, 755, 699, 669 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz): δ 0.93 (3H, t, *J* = 7.4 Hz, Me), 2.41 (3H, s, Me), 2.46-2.55 (2H, m, CH<sub>2</sub>), 5.32 (1H, d, *J* = 8.0 Hz), 5.89 (1H, d, *J* = 8.0 Hz), 6.05 (1H, s), 6.09 (1H, s), 7.10-7.14 (2H, m, Ar), 7.18-7.20 (3H, m, Ar), 7.23 (2H, d, *J* = 8.4 Hz, Ar), 7.66 (2H, d, *J* = 8.4 Hz, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75.44 MHz): δ 8.04, 21.73, 31.56, 59.23, 126.65, 127.09, 127.49, 127.75, 128.70, 129.68, 137.75, 139.20, 143.54, 146.18, 201.74. MS (EI): *m/e* 344 (M<sup>+</sup>+1, 1.91), 188 (M<sup>+</sup>-155, 100), 155 (MePhSO<sub>2</sub><sup>+</sup>, 12.97). Anal. Calcd. for C<sub>19</sub>H<sub>21</sub>NO<sub>3</sub>S: requires C, 66.45; H, 6.16; N, 4.08%. Found: C, 65.97; H, 6.09; N, 3.99%. HPLC: OJ column; λ = 254 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min; t<sub>minor</sub> = 19.74 min,

$t_{\text{major}} = 30.04 \text{ min}$ , ee% = 80%.

**4-Methyl-N-[1-(4-fluorophenyl)-2-methylene-3-oxo-pentyl]benzenesulfonamide 3c:** a colorless solid (93 mg, 56%).  $[\alpha]^{20}_{\text{D}} +12.2$  (c 1.1,  $\text{CHCl}_3$ ), mp. 111-112 °C. IR ( $\text{CHCl}_3$ ):  $\nu$  3298, 2986, 2945, 1672 (C=O), 1598, 1510, 1446, 1409, 1346, 1308, 1294, 1222, 1214, 1189, 1164, 1096, 1074, 983, 955, 921, 867, 815, 675  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz):  $\delta$  0.95 (3H, t,  $J = 7.2 \text{ Hz}$ , Me), 2.43 (3H, s, Me), 2.44-2.62 (2H, m,  $\text{CH}_2$ ), 5.26 (1H, d,  $J = 9.0 \text{ Hz}$ ), 5.77 (1H, d,  $J = 9.0 \text{ Hz}$ ), 6.04 (1H, s), 6.10 (1H, s), 6.87-6.93 (2H, m, Ar), 7.08-7.12 (2H, m, Ar), 7.26 (2H, d,  $J = 8.1 \text{ Hz}$ , Ar), 7.66 (2H, d,  $J = 8.1 \text{ Hz}$ , Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75.44 MHz):  $\delta$  7.70, 21.45, 31.27, 58.48, 115.23 (1C, d,  $J_{\text{C}-\text{F}} = 21.7 \text{ Hz}$ ), 126.96, 127.15, 128.07 (1C, d,  $J_{\text{C}-\text{F}} = 7.5 \text{ Hz}$ ), 129.42, 134.69 (1C, d,  $J_{\text{C}-\text{F}} = 3.4 \text{ Hz}$ ), 137.33, 143.38, 145.66, 161.94 (1C, d,  $J_{\text{C}-\text{F}} = 246.8 \text{ Hz}$ ), 201.46. MS (EI):  $m/e$  278 ( $\text{M}^+ - 83$ , 4.09), 206 ( $\text{M}^+ - 155$ , 100), 155 ( $\text{MePhSO}_2^+$ , 13.72). Anal. Calcd. for  $\text{C}_{19}\text{H}_{20}\text{FNO}_3\text{S}$ : requires C, 63.14; H, 5.58; N, 3.88%. Found: C, 63.20; H, 5.59; N, 3.62%. HPLC: AS column;  $\lambda = 254 \text{ nm}$ ; eluent: Hexane/Isopropanol = 75/25; Flow rate: 0.7 mL/min;  $t_{\text{major}} = 22.56 \text{ min}$ ,  $t_{\text{minor}} = 25.86 \text{ min}$ ; ee% = 86%.

**4-Methyl-N-[1-(4-bromophenyl)-2-methylene-3-oxo-pentyl]benzenesulfonamide 3d:** a colorless solid (139 mg, 66%).  $[\alpha]^{20}_{\text{D}} +17.7$  (c 1.10,  $\text{CHCl}_3$ ). mp. 122-124 °C. IR (KBr):  $\nu$  3230 (NH), 2980, 2937, 1684 (C=O), 1598, 1490, 1448, 1321, 1160, 1073, 860, 820, 670  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz):  $\delta$  0.93 (3H, t,  $J = 7.3 \text{ Hz}$ , Me), 2.41 (3H, s, Me), 2.46-2.61 (2H, m,  $\text{CH}_2$ ), 5.20 (1H, d,  $J = 8.9 \text{ Hz}$ ), 5.73 (1H, d,  $J = 8.9 \text{ Hz}$ ), 6.00 (1H, s), 6.08 (1H, s), 6.99 (2H, d,  $J = 8.3 \text{ Hz}$ , Ar), 7.22 (2H, d,  $J = 8.0 \text{ Hz}$ , Ar), 7.32 (2H, d,  $J = 8.3 \text{ Hz}$ , Ar), 7.63 (2H, d,  $J = 8.0 \text{ Hz}$ , Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75.44 MHz):  $\delta$  7.69, 21.45, 31.24, 58.62, 121.46, 127.13, 127.19, 128.11, 129.43, 131.44, 137.32, 138.00, 143.43, 145.44, 201.36. MS (EI):  $m/e$  266 ( $\text{M}^+ - 155$ , 100), 268 ( $\text{M}^+ + 2 - 155$ , 94.77), 155 ( $\text{MePhSO}_2^+$ , 30.32), 130 ( $\text{M}^+ - 155 - 79 - 29 - 28$ , 71.41), 91 ( $\text{M}^+ - 266 - 64$ , 87.08). Anal. Calcd. for  $\text{C}_{19}\text{H}_{20}\text{BrNO}_3\text{S}$ : requires C, 54.03; H, 4.77; N,

3.32%. Found: C, 54.41; H, 4.90; N, 3.25%. HPLC: OD column;  $\lambda = 254$  nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min;  $t_{\text{minor}} = 11.89$  min;  $t_{\text{major}} = 13.12$  min, ee% = 86%.

**4-Methyl-N-[1-(3-fluorophenyl)-2-methylene-3-oxo-pentyl]benzenesulfonamide 3e:** a colorless solid (110 mg, 61%).  $[\alpha]^{20}_{\text{D}} +1.7$  (c 1.02,  $\text{CHCl}_3$ ). mp. 94-96 °C. IR (KBr):  $\nu$  3246 (NH), 2990, 2940, 1681 (C=O), 1594, 1485, 1450, 1439, 1327, 1165, 1085, 917, 819, 782, 708, 673  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz):  $\delta$  0.94 (3H, t,  $J = 7.2$  Hz, Me), 2.41 (3H, s, Me), 2.43-2.60 (2H, m,  $\text{CH}_2$ ), 5.23 (1H, d,  $J = 9.1$  Hz), 5.77 (1H, d,  $J = 9.1$  Hz), 6.01 (1H, s), 6.10 (1H, s), 6.79-6.93 (3H, m, Ar), 7.17-7.26 (3H, m, Ar), 7.65 (2H, d,  $J = 8.0$  Hz, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75.44 MHz):  $\delta$  7.70, 21.43, 31.23, 58.74, 113.45 (1C, d,  $J_{\text{C}-\text{F}} = 22.7$  Hz), 114.34 (1C, d,  $J_{\text{C}-\text{F}} = 21.3$  Hz), 121.89, 127.16, 127.46, 129.44, 129.94 (1C, d,  $J_{\text{C}-\text{F}} = 8.3$  Hz), 137.38, 141.53 (1C, d,  $J_{\text{C}-\text{F}} = 7.1$  Hz), 143.45, 145.31, 162.63 (1C, d,  $J_{\text{C}-\text{F}} = 244.8$  Hz), 201.41. MS (EI):  $m/e$  206 ( $\text{M}^+ - 155$ , 100), 155 ( $\text{MePhSO}_2^+$ , 15.32), 91 ( $\text{M}^+ - 266 - 64$ , 42.83). Anal. Calcd. for  $\text{C}_{19}\text{H}_{20}\text{FNO}_3\text{S}$ : requires C, 63.14; H, 5.58; N, 3.88%. Found: C, 62.93; H, 5.75; N, 3.79%. HPLC: AD column;  $\lambda = 254$  nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min;  $t_{\text{major}} = 18.57$  min,  $t_{\text{minor}} = 20.24$  min; ee% = 89%.

**4-Methyl-N-[1-(3-chlorophenyl)-2-methylene-3-oxo-pentyl]benzenesulfonamide 3f:** a colorless solid (115 mg, 61%).  $[\alpha]^{20}_{\text{D}} +9.1$  (c 1.02,  $\text{CHCl}_3$ ). mp. 101-103 °C. IR (KBr):  $\nu$  3300 (NH), 3300, 2984, 2944, 1670 (C=O), 1595, 1573, 1490, 1477, 1447, 1407, 1343, 1210, 1187, 1162, 1097, 1079, 956, 925, 893, 813, 674  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz):  $\delta$  0.94 (3H, t,  $J = 7.2$  Hz, Me), 2.41 (3H, s, Me), 2.44-2.61 (2H, m,  $\text{CH}_2$ ), 5.22 (1H, d,  $J = 9.2$  Hz), 5.72 (1H, d,  $J = 9.2$  Hz), 6.03 (1H, s), 6.11 (1H, s), 7.01-7.04 (2H, m, Ar), 7.14-7.16 (2H, m, Ar), 7.24 (2H, d,  $J = 8.2$  Hz, Ar), 7.64 (2H, d,  $J = 8.2$  Hz, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75.44 MHz):  $\delta$  7.34, 21.07, 30.79, 57.89, 124.16, 126.32, 126.73, 127.04, 127.14, 129.08, 129.27,

133.78, 136.87, 140.65, 143.12, 144.96, 200.88. MS (EI): *m/e* 224 ( $M^+ + 2 - 155$ , 36.20), 222 ( $M^+ - 155$ , 100), 155 ( $MePhSO_2^+$ , 20.22), 91 ( $M^+ - 223 - 64$ , 52.70). Anal. Calcd. for  $C_{19}H_{20}ClNO_3S$ : requires C, 60.39; H, 5.33; N, 3.71%. Found: C, 60.18; H, 5.45; N, 3.58%. HPLC: AD column;  $\lambda = 254$  nm; eluent: Hexane/Isopropanol = 75/25; Flow rate: 0.7 mL/min;  $t_{\text{major}} = 13.05$  min,  $t_{\text{minor}} = 14.85$  min; ee% = 92%.

**4-Methyl-N-[1-(4-nitrophenyl)-2-methylene-3-oxo-pentyl]benzenesulfonamide 3g:** a colorless solid (164 mg, 85%).  $[\alpha]^{20}_D +5.7$  (c 1.08,  $CHCl_3$ ). mp. 147-149 °C. IR (KBr):  $\nu$  3284 (NH), 2990, 2950, 1670 (C=O), 1597, 1516, 1447, 1355, 1344, 1206, 1163, 1099, 1076, 962, 924, 876, 855, 813, 675  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $CDCl_3$ , TMS, 300 MHz):  $\delta$  0.92 (3H, t,  $J = 7.0$  Hz, Me), 2.41 (3H, s, Me), 2.44-2.61 (2H, m,  $CH_2$ ), 5.31 (1H, d,  $J = 9.4$  Hz), 5.94 (1H, d,  $J = 9.4$  Hz), 6.04 (1H, s), 6.13 (1H, s), 7.24 (2H, d,  $J = 8.0$  Hz, Ar), 7.34 (2H, d,  $J = 8.9$  Hz, Ar), 7.64 (2H, d,  $J = 8.0$  Hz, Ar), 8.07 (2H, d,  $J = 8.9$  Hz, Ar).  $^{13}\text{C}$  NMR ( $CDCl_3$ , TMS, 75.44 MHz):  $\delta$  7.64, 21.47, 31.17, 58.95, 123.56, 126.33, 127.12, 127.21, 128.29, 129.55, 137.27, 143.76, 144.83, 146.30, 201.34. MS (EI): *m/e* 233 ( $M^+ - 155$ , 100), 155 ( $MePhSO_2^+$ , 15.94), 91 ( $M^+ - 233 - 64$ , 49.17). Anal. Calcd. for  $C_{19}H_{20}N_2O_5S$ : requires C, 58.75; H, 5.19; N, 7.21%. Found: C, 58.83; H, 4.96; N, 7.34%. HPLC: AS column;  $\lambda = 254$  nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.7 mL/min;  $t_{\text{major}} = 34.33$  min,  $t_{\text{minor}} = 48.25$  min; ee% = 88%.

*Typical reaction procedure for (R)-2'-diphenylphosphanyl-[1,1']binaphthalenyl-2-ol **LB1** catalyzed aza-Baylis-Hillman reaction of N-(benzylidene)-4-methylbenzenesulfonamide **1a** with phenyl acrylate.*

A 10 mL Schlenk tube containing *N*-(benzylidene)-4-methylbenzenesulfonamide **1a** (0.5 mmol) and (R)-2'-diphenylphosphanyl-[1,1']binaphthalenyl-2-ol **LB1** (23 mg, 0.05 mmol) was degassed and the reaction vessel was protected under argon atmosphere. Then,  $CH_2Cl_2$  (2.0 mL)

was added. After the mixtures were heated to 40 °C, phenyl acrylate (100 µL, 0.75 mmol) was added into the Schlenk tube. The reaction mixture was stirred at 40 °C for 12 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (SiO<sub>2</sub>, eluent: EtOAc/Petroleum ether = 1/8) to yield the corresponding Baylis-Hillman adduct **5b** as a colorless solid which was immediately subjected to the chiral HPLC for the analysis of the achieved enantiomeric excess. For microanalysis, all these products were recrystallized from EtOAc and n-hexane.

**2-[(4-Chlorophenyl)-(toluene-4-sulfonylamino)methyl]acrylic acid phenyl ester 5a:** a colorless solid, 208 mg, yield: 94%. mp: 120-122 °C.  $[\alpha]_D^{20} +3.4$  (c 0.97, CHCl<sub>3</sub>). IR (KCl):  $\nu$  3296 (N-H), 1721 (C=O), 1640, 1599, 1491, 1460, 1327, 1191, 1164, 1081, 815, 755, 567 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz):  $\delta$  2.44 (3H, s, Me), 5.38 (1H, d, *J* = 9.0 Hz), 5.64 (1H, d, *J* = 9.0 Hz), 6.05 (1H, s), 6.50 (1H, s), 6.87-6.90 (2H, m), 7.12-7.16 (2H, m), 7.20-7.28 (5H, m), 7.33-7.38 (2H, m), 7.69-7.71 (2H, m). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75.4 MHz):  $\delta$  21.5, 58.3, 121.2, 126.1, 127.1, 128.0, 128.7, 129.4, 129.5, 129.6, 133.7, 137.0, 137.3, 138.2, 143.6, 150.0, 163.7. MS (EI): *m/e* 348 (M<sup>+</sup>-93, 30.24), 294 (M<sup>+</sup>-93-54, 19.66), 177 (M<sup>+</sup>-93-171, 65.22), 155 (M<sup>+</sup>-286, 81.92), 115 (M<sup>+</sup>-93-170-28-35, 33.60), 91 (M<sup>+</sup>-350, 100), 65 (M<sup>+</sup>-350-26, 50.99). Anal. Calcd. for C<sub>23</sub>H<sub>20</sub>ClNO<sub>4</sub>S: C, 62.51; H, 4.56; N, 3.17%. Found: C, 62.48; H, 4.56; N, 3.12%. HPLC: AS column;  $\lambda$  = 254 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.7 mL/min; t<sub>major</sub> = 21.4 min, t<sub>minor</sub> = 28.9 min; ee% = 67%.

**2-[Phenyl-(toluene-4-sulfonylamino)methyl]acrylic acid phenyl ester 5b:** a colorless solid, 170 mg, yield: 84%. mp: 110-112 °C.  $[\alpha]_D^{20} +0.4$  (c 1.01, CHCl<sub>3</sub>). IR (KCl):  $\nu$  3300 (N-H), 1724 (C=O), 1600, 1492, 1456, 1327, 1271, 1192, 1162, 1087, 1071, 960, 814, 754, 693, 564 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz):  $\delta$  2.42 (3H, s, Me), 5.41 (1H, d, *J* = 8.6 Hz), 5.55 (1H, d, *J* = 8.6 Hz), 6.08 (1H, s), 6.50 (1H, s), 6.83-6.86 (2H, m), 7.15-7.35 (10H, m),

7.71 (2H, d,  $J = 8.1$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75.4 MHz):  $\delta$  21.5, 58.8, 121.3, 126.0, 126.6, 127.2, 127.9, 128.6, 129.1, 129.3, 129.5, 137.5, 138.4, 138.6, 143.4, 150.1, 163.8. MS (EI):  $m/e$  314 ( $M^+$ -93, 36.26), 260 ( $M^+$ -93-54, 30.46), 155 ( $M^+$ -252, 65.23), 143 ( $M^+$ -93-171, 84.77), 115 ( $M^+$ -93-171-28, 39.57), 91 ( $M^+$ -316, 100), 77 ( $M^+$ -330, 22.85), 65 ( $M^+$ -316-26, 52.65). Anal. Calcd. for  $\text{C}_{23}\text{H}_{21}\text{NO}_4\text{S}$ : C, 67.80; H, 5.19; N, 3.44%. Found: C, 67.83; H, 5.40; N, 3.32%. HPLC: AS column;  $\lambda = 254$  nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.7 mL/min;  $t_{\text{major}} = 23.04$  min,  $t_{\text{minor}} = 31.4$  min; ee% = 61%.

**2-[(4-Ethylphenyl)-(toluene-4-sulfonylamino)methyl]acrylic acid phenyl ester 5c:** a colorless solid, 130 mg, yield: 60%. mp: 96-98 °C.  $[\alpha]_D^{20} +8.6$  (c 1.16,  $\text{CHCl}_3$ ). IR (KCl):  $\nu$  3318 (N-H), 2966, 1732 (C=O), 1591, 1492, 1434, 1323, 1276, 1196, 1162, 1131, 1053, 961, 812, 756, 667, 577, 550  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz):  $\delta$  1.19 (3H, t,  $J = 7.5$  Hz), 2.41 (3H, s), 2.57 (2H, q,  $J = 7.5$  Hz), 5.38 (1H, d,  $J = 8.5$  Hz), 5.58 (1H, d,  $J = 8.5$  Hz), 6.08 (1H, s), 6.49 (1H, s), 6.86 (2H, d,  $J = 7.8$  Hz), 7.06 (4H, s), 7.19-7.26 (3H, m), 7.32 (2H, t,  $J = 7.8$  Hz), 7.7 (2H, d,  $J = 8.3$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75.4 MHz):  $\delta$  15.8, 21.8, 28.7, 58.9, 121.6, 126.3, 126.9, 127.5, 128.4, 129.2, 129.6, 129.8, 135.9, 137.7, 139.0, 143.7, 144.3, 150.4, 164.2. MS (EI):  $m/e$  342 ( $M^+$ -93, 31.65), 288 ( $M^+$ -93-54, 23.94), 171 ( $M^+$ -264, 100), 155 ( $M^+$ -280, 31.89), 91 ( $M^+$ -280-64, 68.19), 65 ( $M^+$ -280-64-26, 26.26). Anal. Calcd. for  $\text{C}_{25}\text{H}_{25}\text{NO}_4\text{S}$ : C, 68.94; H, 5.78; N, 3.22%. Found: C, 68.91; H, 5.80; N, 3.09%. HPLC: AS column;  $\lambda = 254$  nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.7 mL/min;  $t_{\text{major}} = 18.98$  min,  $t_{\text{minor}} = 27.39$  min; ee% = 53%.

**2-[(4-Fluorophenyl)-(toluene-4-sulfonylamino)methyl]acrylic acid phenyl ester 5d:** a colorless solid, 170 mg, yield: 80%. mp: 119-122 °C.  $[\alpha]_D^{20} -1.6$  (c 1.03,  $\text{CHCl}_3$ ). IR (KCl):  $\nu$  3298 (N-H), 1721 (C=O), 1640, 1599, 1510, 1453, 1326, 1270, 1231, 1188, 1159, 1094, 1081, 961, 815, 754, 725, 678, 573, 553  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz):  $\delta$  2.43 (3H, s,

Me), 5.38 (1H, d,  $J$  = 8.8 Hz), 5.53 (1H, d,  $J$  = 8.8 Hz), 6.05 (1H, s), 6.49 (1H, s), 6.86-6.89 (2H, m), 6.91-6.97 (2H, t,  $J$  = 8.6 Hz), 7.14-7.18 (2H, m), 7.22-7.28 (3H, m), 7.31-7.36 (2H, dd,  $J_1$  = 7.3 Hz,  $J_2$  = 8.2 Hz), 7.70 (2H, d,  $J$  = 8.1 Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75.44 MHz):  $\delta$  21.45, 58.29, 115.46 (d,  $J$  = 21.3 Hz), 121.19, 126.06, 127.15, 128.32 (d,  $J$  = 8.2 Hz), 129.20, 129.36, 129.53, 134.22 (d,  $J$  = 3.5 Hz), 137.38, 138.36, 143.56, 150.00, 162.20 (d,  $J$  = 246.6 Hz), 163.73. MS (EI):  $m/e$  332 ( $M^+$ -93, 66.78), 278 ( $M^+$ -93-54, 37.48), 161 ( $M^+$ -93-171, 90.79), 155 ( $M^+$ -270, 95.58), 133 ( $M^+$ -93-171-28, 42.46), 91 ( $M^+$ -270-64, 100), 65 ( $M^+$ -270-64-26, 30.55). Anal. Calcd. for  $\text{C}_{23}\text{H}_{20}\text{FNO}_4\text{S}$ : C, 64.93; H, 4.74; N, 3.29%. Found: C, 65.00; H, 4.96; N, 3.21%. HPLC: AS column;  $\lambda$  = 254 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.7 mL/min;  $t_{\text{major}}$  = 27.03 min,  $t_{\text{minor}}$  = 38.93 min; ee% = 69%.

**2-[(4-Bromophenyl)-(toluene-4-sulfonylamino)methyl]acrylic acid phenyl ester 5e:** a colorless solid, 206 mg, yield: 85%. mp: 120-122 °C.  $[\alpha]_D^{20}$  +5.7 (c 1.12,  $\text{CHCl}_3$ ). IR (KCl):  $\nu$  3296 (N-H), 1721 (C=O), 1599, 1590, 1486, 1453, 1334, 1291, 1267, 1192, 1163, 1082, 1012, 815, 755, 565  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz):  $\delta$  2.42 (3H, s, Me), 5.35 (1H, d,  $J$  = 8.8 Hz), 5.59 (1H, d,  $J$  = 8.8 Hz), 6.04 (1H, s), 6.49 (1H, s), 6.87 (2H, dd,  $J_1$  = 7.0 Hz,  $J_2$  = 1.1 Hz), 7.06 (2H, dd,  $J_1$  = 8.6 Hz,  $J_2$  = 1.7 Hz), 7.22-7.26 (3H, m), 7.31-7.39 (4H, m), 7.68 (2H, dd,  $J_1$  = 8.5 Hz,  $J_2$  = 1.9 Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75.44 MHz):  $\delta$  21.48, 58.33, 121.20, 121.36, 126.07, 127.12, 128.35, 128.37, 129.37, 129.56, 131.54, 137.33, 137.50, 138.16, 143.52, 150.02, 163.65. MS (EI):  $m/e$  394 ( $M^+$ +2-93, 24.68), 392 ( $M^+$ -93, 24.30), 340 ( $M^+$ +2-93-54, 13.62), 338 ( $M^+$ -93-54, 13.17), 313 ( $M^+$ -93-79, 79), 223 ( $M^+$ +2-93-171, 24.60), 221 ( $M^+$ -93-171, 32.55), 196 ( $M^+$ +2-93-171-28, 10.52), 194 ( $M^+$ -93-171-28, 11.36), 155 ( $M^+$ -330, 83.88), 115 ( $M^+$ -93-170-28-79, 35.96), 91 ( $M^+$ -330-64, 100), 65 ( $M^+$ -330-64-26, 44.97). Anal. Calcd. for  $\text{C}_{23}\text{H}_{20}\text{BrNO}_4\text{S}$ : C, 56.80; H, 4.14; N, 2.88%. Found: C, 57.06; H, 4.38; N, 2.81%. HPLC: AS column;  $\lambda$  = 254 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.7 mL/min;  $t_{\text{major}}$  = 18.48 min,  $t_{\text{minor}}$  = 24.13 min; ee% = 77%.

**2-[(3-Fluorophenyl)-(toluene-4-sulfonylamino)methyl]acrylic acid phenyl ester 5f:** a colorless solid, 190 mg, yield: 89%. mp: 104-106 °C.  $[\alpha]_D^{20} -8.5$  (c 1.01, CHCl<sub>3</sub>). IR (KCl): ν 3297 (N-H), 1720 (C=O), 1592, 1486, 1444, 1336, 1269, 1255, 1188, 1162, 1090, 1070, 952, 814, 755, 692, 563, 544 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz): δ 2.42 (3H, s, Me), 5.39 (1H, d, *J* = 9.3 Hz), 5.67 (1H, d, *J* = 9.3 Hz), 6.05 (1H, s), 6.51 (1H, s), 6.88-7.01 (4H, m), 7.20-7.37 (7H, m), 7.71 (2H, d, *J* = 8.7 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75.4 MHz): δ 21.5, 58.4, 113.7 (d, *J*<sub>C-F</sub> = 0.3 Hz), 114.8 (d, *J*<sub>C-F</sub> = 0.3 Hz), 121.2, 122.1 (d, *J*<sub>C-F</sub> = 0.04 Hz), 126.1, 127.1, 129.5 (d, *J*<sub>C-F</sub> = 0.2 Hz), 129.7, 130.2 (d, *J*<sub>C-F</sub> = 0.1 Hz), 137.3, 138.0, 140.9, 141.0, 143.7, 150.0, 162.7 (d, *J*<sub>C-F</sub> = 3.3 Hz), 163.6. MS (EI): *m/e* 332 (M<sup>+</sup>-93, 70.61), 278 (M<sup>+</sup>-93-54, 31.24), 161 (M<sup>+</sup>-93-171, 79.78), 155 (M<sup>+</sup>-270, 88.28), 91 (M<sup>+</sup>-270-64, 100), 65 (M<sup>+</sup>-270-64-26, 40.82). Anal. Calcd. for C<sub>23</sub>H<sub>20</sub>FNO<sub>4</sub>S: C, 64.93; H, 4.74; N, 3.29%. Found: C, 64.85; H, 4.89; N, 3.21%. HPLC: AS column; λ = 254 nm; eluent: Hexane/Isopropanol = 60/40; Flow rate: 0.7 mL/min; t<sub>major</sub> = 23.96 min, t<sub>minor</sub> = 37.82 min; ee% = 63%.

**2-[(3-Chlorophenyl)-(toluene-4-sulfonylamino)methyl]acrylic acid phenyl ester 5g:** a colorless solid, 210 mg, yield: 95%. mp: 96-98 °C.  $[\alpha]_D^{20} \approx 0$  (c 0.97, CHCl<sub>3</sub>). IR (KCl): ν 3298 (N-H), 1717 (C=O), 1593, 1492, 1450, 1334, 1267, 1234, 1188, 1164, 1093, 1073, 961, 814, 756, 702, 687, 660, 562, 543 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz): δ 2.42 (3H, s, Me), 5.37 (1H, d, *J* = 9.4 Hz), 5.70 (1H, d, *J* = 9.4 Hz), 6.06 (1H, s), 6.51 (1H, s), 6.89 (2H, d, *J* = 8.2 Hz), 7.08-7.27 (7H, m), 7.32-7.37 (2H, dd, *J*<sub>1</sub> = 8.1 Hz, *J*<sub>2</sub> = 7.5 Hz), 7.69 (2H, d, *J* = 8.7 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75.44 MHz): δ 21.47, 58.34, 121.23, 124.71, 126.08, 126.91, 127.12, 127.96, 129.37, 129.57, 129.64, 129.86, 134.43, 137.26, 138.04, 140.43, 143.68, 150.02, 163.63. MS (EI): *m/e* 348 (M<sup>+</sup>-93, 15.26), 294 (M<sup>+</sup>-93-54, 13.09), 177 (M<sup>+</sup>-93-171, 48.89), 155 (M<sup>+</sup>-286, 70.56), 115 (M<sup>+</sup>-93-170-28-35, 22.90), 91 (M<sup>+</sup>-286-64, 100), 65 (M<sup>+</sup>-286-64-26, 67.24). Anal. Calcd. for C<sub>23</sub>H<sub>20</sub>ClNO<sub>4</sub>S: C, 62.51; H, 4.56; N, 3.17%. Found: C, 62.76; H, 4.61;

N, 3.04%. HPLC: AD column;  $\lambda = 254$  nm; eluent: Hexane/ Isopropanol = 80/20; Flow rate: 0.7 mL/min;  $t_{\text{major}} = 14.27$  min,  $t_{\text{minor}} = 17.01$  min; ee% = 58%.

**2-[(4-Nitrophenyl)-(toluene-4-sulfonylamino)methyl]acrylic acid phenyl ester 5h:** a colorless solid, 220 mg, yield: 97%. mp: 122-124 °C.  $[\alpha]_D^{20} -2.4$  (c 1.05, CHCl<sub>3</sub>). IR (KCl):  $\nu$  3273 (N-H), 1730 (C=O), 1597, 1522, 1492, 1435, 1348, 1243, 1193, 1162, 1135, 1061, 817, 749, 693, 667, 568 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz):  $\delta$  2.42 (3H, s, Me), 5.48 (1H, d, *J* = 9.1 Hz), 5.87 (1H, d, *J* = 9.1 Hz), 6.06 (1H, s), 6.53 (1H, s), 6.87-6.90 (2H, m), 7.23-7.37 (5H, m), 7.43 (2H, d, *J* = 8.7 Hz), 7.70 (2H, d, *J* = 8.7 Hz), 8.12 (2H, dd, *J*<sub>1</sub> = 8.7 Hz, *J*<sub>2</sub> = 2.0 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75.4 MHz):  $\delta$  21.3, 58.2, 121.0, 123.5, 126.1, 127.0, 129.3, 129.6, 130.3, 137.0, 137.4, 143.8, 145.6, 147.1, 149.8, 163.3. MS (EI): *m/e* 359 (M<sup>+</sup>-93, 9.48), 188 (M<sup>+</sup>-93-171, 9.97), 155 (M<sup>+</sup>-297, 38.73), 115 (M<sup>+</sup>-93-170-28-46, 15.69), 91(M<sup>+</sup>-361, 100), 77 (M<sup>+</sup>-375, 19.28), 65 (M<sup>+</sup>-361-26, 77.45). Anal. Calcd. for C<sub>23</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub>S: C, 61.05; H, 4.45; N, 6.19%. Found: C, 61.06; H, 4.51; N, 6.05%. HPLC: AS column;  $\lambda = 254$  nm; eluent: Hexane/ Isopropanol = 60/40; Flow rate: 0.7 mL/min;  $t_{\text{major}} = 28.32$  min,  $t_{\text{minor}} = 49.30$  min; ee% = 75%.

**2-[(3-Nitrophenyl)-(toluene-4-sulfonylamino)-methyl]acrylic acid phenyl ester 5i:** a colorless solid, 200 mg, yield: 89%. mp: 118-120 °C.  $[\alpha]_D^{20} -1.6$  (c 1.25, CHCl<sub>3</sub>). IR (KCl):  $\nu$  3235 (N-H), 1733 (C=O), 1596, 1530, 1492, 1446, 1349, 1244, 1194, 1163, 1135, 1091, 1063, 915, 811, 740, 689, 665, 549 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz):  $\delta$  2.41 (3H, s, Me), 5.48 (1H, d, *J* = 9.0 Hz), 5.94 (1H, d, *J* = 9.0 Hz), 6.10 (1H, s), 6.56 (1H, s), 6.90 (2H, d, *J* = 8.3 Hz), 7.23-7.27 (3H, m), 7.35 (2H, t, *J* = 7.6 Hz), 7.46 (1H, t, *J*<sub>1</sub> = 8.1 Hz, *J*<sub>2</sub> = 7.7 Hz), 7.64-7.71 (3H, m), 7.97 (1H, m), 8.09 (2H, d, *J* = 7.7 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75.44 MHz):  $\delta$  21.40, 58.25, 121.13, 121.63, 122.71, 126.17, 127.07, 129.40, 129.56, 129.65, 130.41, 132.79, 137.12, 137.50, 140.66, 143.90, 148.12, 149.90, 163.47. MS (EI): *m/e* 359 (M<sup>+</sup>-93, 22.43), 305 (M<sup>+</sup>-93-54, 9.51), 188 (M<sup>+</sup>-93-171, 13.33), 155 (M<sup>+</sup>-297, 62.05), 115

(M<sup>+</sup>-93-170-28-46, 13.38), 91 (M<sup>+</sup>-361, 100), 77 (M<sup>+</sup>-375, 13.48), 65 (M<sup>+</sup>-361-26, 57.68).

Anal. Calcd. for C<sub>23</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub>S: C, 61.05; H, 4.45; N, 6.19%. Found: C, 61.04; H, 4.52; N, 6.10%. HPLC: AD column; λ = 254 nm; eluent: Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min; t<sub>major</sub> = 22.7 min, t<sub>minor</sub> = 27.3 min; ee% = 52%.

**α-Naphthyl 2-[phenyl(toluene-4-sulfonylamino)methyl]acrylate 5j.** a colorless solid, yield: 49%; mp. 130-132 °C. [α]<sub>D</sub><sup>20</sup> -5.3 (c 1.04, CHCl<sub>3</sub>). IR (CHCl<sub>3</sub>) ν 1735 cm<sup>-1</sup> (C=O); <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz): δ 2.42 (3H, s, Me), 5.50 (1H, d, J = 8.8 Hz), 5.57 (1H, d, J = 8.8 Hz), 6.18 (1H, s), 6.66 (1H, s), 7.02 (1H, d, J = 7.6 Hz, Ar), 7.19-7.46 (9H, m, Ar), 7.71 (2H, d, J = 9.1 Hz, Ar), 7.75 (2H, d, J = 8.5 Hz, Ar), 7.82 (1H, J = 8.5 Hz, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75.45 MHz): δ 21.44, 58.73, 117.83, 120.75, 125.13, 126.15, 126.34, 126.37, 126.65, 127.13, 127.84, 127.92, 128.71, 129.18, 129.51, 134.41, 137.37, 138.33, 138.43, 143.43, 145.93, 163.95. MS (EI): m/e 457 (M<sup>+</sup>, 4.91), 314 (M<sup>+</sup>-143, 7.80). Anal. Calcd. for C<sub>27</sub>H<sub>23</sub>NO<sub>4</sub>S requires C, 70.88; H, 5.07; N, 3.06%. Found: C, 71.14; H, 5.41; N, 3.04%. HPLC: AS column; λ = 254 nm; eluent: Hexane : Isopropanol = 60:40; Flow rate: 0.7mL/min; t<sub>major</sub> = 28.88 min, t<sub>minor</sub> = 41.74 min; ee% = 58%.

**β-Naphthyl 2-[phenyl-(toluene-4-sulfonylamino)-methyl]acrylate 5k.** a colorless solid , yield: 57%. mp. 120-122 °C; [α]<sub>D</sub><sup>20</sup> -10.5 (c 0.97, CHCl<sub>3</sub>). IR (CHCl<sub>3</sub>): ν 3293, 3059, 1728 (C=O), 1629, 1599, 1510, 1494, 1448, 1274, 1240, 1208, 1162, 1063, 959, 907, 814, 705, 669, 558 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz): δ 2.42 (3H, s, Me), 5.46 (1H, d, J = 8.7 Hz), 5.59 (1H, d, J = 8.7 Hz), 6.12 (1H, s), 6.57 (1H, s), 6.97 (1H, dd, J<sub>1</sub> = 9.0 Hz, J<sub>2</sub> = 2.1 Hz, Ar), 7.19-7.35 (8H, m, Ar), 7.43-7.50 (2H, m, Ar), 7.72-7.83 (5H, m, Ar). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75.45 MHz): δ 21.46, 58.81, 118.33, 120.60, 125.77, 126.55, 127.18, 127.51, 127.65, 127.87, 128.64, 129.29, 129.31, 129.51, 131.35, 133.45, 137.37, 138.35, 138.54, 143.43, 147.65, 163.93. MS (EI): m/e 457 (M<sup>+</sup>, 0.52), 314 (M<sup>+</sup>-143, 1.21), 260 (M<sup>+</sup>-197, 7.62), 155 (M<sup>+</sup>-302,

23.00), 144 ( $M^+$ -313, 100), 143 ( $M^+$ -314, 1.21), 115 ( $M^+$ -342, 37.30), 91 ( $M^+$ -366, 56.30). Anal. Calcd. for  $C_{27}H_{23}NO_4S$  requires C, 70.88; H, 5.07; N, 3.06%. Found: C, 70.88; H, 5.12; N, 2.96%. HPLC: AS column;  $\lambda = 254$  nm; eluent: Hexane : Isopropanol = 60:40; Flow rate: 0.7mL/min;  $t_{\text{major}} = 32.85$  min,  $t_{\text{minor}} = 45.31$  min; ee% = 53%.

*Typical reaction procedure for (R)-2'-diphenylphosphanyl-[1,1']binaphthalenyl-2-ol **LB1** catalyzed aza-Baylis-Hillman reaction of N-benzylidene-4-methylbenzenesulfonamide **1a** with acrolein.*

A 10 mL Schlenk tube contained with *N*-(benzylidene)-4-methylbenzenesulfonamide **1a** (0.5 mmol) and (R)-2'-diphenylphosphanyl-[1,1']binaphthalenyl-2-ol **LB1** (23 mg, 0.05 mmol) was degassed and the reaction vessel was protected under argon atmosphere. Then, THF (1.0 mL) and acrolein (67  $\mu$ L, 1.0 mmol) was added into the Schlenk tube at room temperature. The reaction was monitored by TLC, when the imine disappeared, the solvent was removed under reduced pressure and the residue was purified by flash chromatography ( $\text{SiO}_2$ , EtOAc-Petroleum ether = 1/5) to yield the product as a colorless solid which was immediately subjected to the chiral HPLC for the analysis of the achieved enantiomeric excess. For microanalysis, all these products were recrystallized from acetone and n-hexane.

***N*-[1-(4-Chlorophenyl)-2-formyl-allyl]-4-methylbenzenesulfonamide **6a**: a colorless solid (165 mg, 94%).  $[\alpha]_D^{20} +52.3$  (c 0.94,  $\text{CHCl}_3$ ). mp. 101-102 °C; IR ( $\text{CHCl}_3$ ):  $\nu$  3276, 3022, 1691 (C=O), 1598, 1493, 1432, 1331, 1216, 1162, 1093, 1015, 964, 928, 886, 814, 757, 668, 569  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz):  $\delta$  2.46 (3H, s, Me), 5.26 (1H, d,  $J = 8.6$  Hz), 5.62 (1H, d,  $J = 8.6$  Hz), 6.12 (1H, s), 6.52 (1H, s), 7.04 (2H, d,  $J = 8.4$  Hz, Ar), 7.19 (2H, d,  $J = 8.4$  Hz, Ar), 7.25 (2H, d,  $J = 8.6$  Hz, Ar), 7.64 (2H, d,  $J = 8.6$  Hz, Ar), 9.38 (1H, s).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75.44 MHz):  $\delta$  21.41, 56.19, 127.10, 128.06, 128.65, 129.51, 133.76, 136.02, 136.53, 136.97, 143.66, 147.56, 192.69. MS (EI):  $m/e$  294 ( $M^+ - 55$ , 15.60), 194 ( $M^+ - 155$ , 100).**

Anal. Calcd. for C<sub>17</sub>H<sub>16</sub>ClNO<sub>3</sub>S: requires C, 58.37; H, 4.61; N, 4.01%. Found: C, 58.57; H, 4.84; N, 3.90%. HPLC: AS column;  $\lambda$  = 254 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min; t<sub>major</sub> = 31.18 min, t<sub>minor</sub> = 44.35 min; ee% = 81%.

**N-(1-Phenyl-2-formyl-allyl)-4-methylbenzenesulfonamide 6b:** a colorless solid (140 mg, 88%).  $[\alpha]_D^{20}$  +47.2 (c 1.06, CHCl<sub>3</sub>). mp. 107-108 °C. IR (CHCl<sub>3</sub>):  $\nu$  3280, 3028, 2924, 2833, 1690 (C=O), 1599, 1494, 1454, 1326, 1217, 1161, 1090, 1066, 964, 882, 843, 814, 755, 699, 670, 567 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz):  $\delta$  2.46 (3H, s, Me), 5.26 (1H, d,  $J$  = 8.1 Hz), 5.49 (1H, d,  $J$  = 8.1 Hz), 6.12 (1H, s), 6.54 (1H, s), 7.06-7.09 (2H, m, Ar), 7.19-7.22 (3H, m, Ar), 7.25 (2H, d,  $J$  = 8.7 Hz, Ar), 7.66 (2H, d,  $J$  = 8.7 Hz, Ar), 9.39 (1H, s). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75.44 MHz):  $\delta$  21.46, 56.70, 126.68, 127.20, 127.87, 128.60, 129.51, 135.89, 137.09, 138.02, 143.50, 147.99, 192.83. MS (EI): *m/e* 314 (M<sup>+</sup>-1, 4.05), 91 (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub><sup>+</sup>, 100). Anal. Calcd. for C<sub>17</sub>H<sub>17</sub>NO<sub>3</sub>S: requires C, 64.76; H, 5.39; N, 4.44%. Found: C, 64.77; H, 5.53; N, 4.33%. HPLC: AS column;  $\lambda$  = 254 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min; t<sub>major</sub> = 45.80 min, t<sub>minor</sub> = 61.32 min; ee% = 86%.

**N-[1-(4-Methylphenyl)-2-formyl-allyl]-4-methylbenzenesulfonamide 6c:** a colorless solid (160 mg, 97%).  $[\alpha]_D^{20}$  +62.0 (c 1.02, CHCl<sub>3</sub>). mp. 108-109 °C; IR (CHCl<sub>3</sub>):  $\nu$  3278, 3021, 2925, 2832, 2401, 1691 (C=O), 1599, 1495, 1420, 1333, 1216, 1161, 1094, 1073, 962, 928, 814, 760, 668 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz):  $\delta$  2.26 (3H, s, Me), 2.41 (3H, s, Me), 5.22 (1H, d,  $J$  = 8.0 Hz), 5.45 (1H, d,  $J$  = 8.0 Hz), 6.10 (1H, s), 6.53 (1H, s), 6.93 (2H, d,  $J$  = 8.2 Hz, Ar), 7.01 (2H, d,  $J$  = 8.2 Hz, Ar), 7.23 (2H, d,  $J$  = 8.4 Hz, Ar), 7.64 (2H, d,  $J$  = 8.4 Hz, Ar), 9.41 (1H, s). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75.44 MHz):  $\delta$  20.95, 21.47, 56.57, 126.60, 127.25, 129.33, 129.52, 135.09, 135.75, 137.12, 137.79, 143.50, 148.15, 192.91. MS (EI): *m/e* 274 (M<sup>+</sup>-55, 7.41), 174 (M<sup>+</sup>-155, 100). Anal. Calcd. for C<sub>18</sub>H<sub>19</sub>NO<sub>3</sub>S: requires C, 65.65; H, 5.78; N, 4.26%. Found: C, 65.80; H, 5.50; N, 4.09%. HPLC: AS column;  $\lambda$  = 254 nm; eluent:

Hexane/Isopropanol = 65/35; Flow rate: 0.7 mL/min;  $t_{\text{major}} = 42.59$  min;  $t_{\text{minor}} = 65.60$  min; ee% = 76%.

**N-[1-(4-Methoxyphenyl)-2-formyl-allyl]-4-methylbenzenesulfonamide 6d:** a colorless solid (170 mg, 99%).  $[\alpha]_D^{20} +63.6$  (c 0.99, CHCl<sub>3</sub>). mp. 120-122 °C. IR (CHCl<sub>3</sub>):  $\nu$  3277, 3021, 2838, 1691 (C=O), 1611, 1512, 1440, 1332, 1252, 1216, 1161, 1094, 1070, 1035, 924, 814, 756, 668, 566 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz):  $\delta$  2.44 (3H, s, Me), 3.76 (3H, s, Me), 5.22 (1H, d,  $J = 7.8$  Hz), 5.37 (1H, d,  $J = 7.8$  Hz), 6.12 (1H, s), 6.57 (1H, s), 6.75 (2H, d,  $J = 8.8$  Hz, Ar), 6.98 (2H, d,  $J = 8.8$  Hz, Ar), 7.27 (2H, d,  $J = 8.5$  Hz, Ar), 7.66 (2H, d,  $J = 8.5$  Hz, Ar), 9.41 (1H, s). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75.44 MHz):  $\delta$  21.50, 55.21, 56.29, 114.00, 127.25, 127.98, 129.54, 130.07, 135.68, 137.05, 143.52, 148.16, 159.23, 192.96. MS (EI): *m/e* 290 (M<sup>+</sup> -55, 7.64), 190 (M<sup>+</sup>-155, 100). Anal. Calcd. for C<sub>18</sub>H<sub>19</sub>BNO<sub>3</sub>S: requires C, 62.59; H, 5.54; N, 4.06%. Found: C, 62.80; H, 5.71; N, 3.97%, HPLC: OD column;  $\lambda = 254$  nm; eluent: Hexane/Isopropanol = 65/35; Flow rate: 0.7 mL/min;  $t_{\text{minor}} = 15.67$  min;  $t_{\text{major}} = 21.95$  min; ee% = 78%.

**N-[1-(4-Fluorophenyl)-2-formyl-allyl]-4-methylbenzenesulfonamide 6e:** a colorless solid (143 mg, 86%).  $[\alpha]_D^{20} +48.0$  (c 1.05, CHCl<sub>3</sub>). mp. 135-136 °C. IR (CHCl<sub>3</sub>):  $\nu$  3272, 3021, 1690 (C=O), 1602, 1510, 1425, 1330, 1216, 1161, 1094, 925, 760, 668, 549 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz):  $\delta$  2.42 (3H, s, Me), 5.26 (1H, d,  $J = 7.8$  Hz), 5.61 (1H, d,  $J = 7.8$  Hz), 6.12 (1H, s), 6.52 (1H, s), 6.90 (2H, dd,  $J = 8.4, 8.3$  Hz, Ar), 7.07 (2H, dd,  $J = 8.3, 5.8$  Hz, Ar), 7.25 (2H, d,  $J = 8.4$  Hz, Ar), 7.64 (2H, d,  $J = 8.4$  Hz, Ar), 9.38 (1H, s). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75.44 MHz):  $\delta$  21.36, 55.61, 115.27 (d,  $J_{\text{C-F}} = 21.2$  Hz), 127.01, 128.44, 128.54, 129.43, 133.82 (d,  $J_{\text{C-F}} = 2.5$  Hz), 136.32 (d,  $J_{\text{C-F}} = 79.5$  Hz), 143.55, 147.80, 161.97 (d,  $J_{\text{C-F}} = 242.5$  Hz), 192.66. MS (EI): *m/e* 278 (M<sup>+</sup> -55, 4.51), 178 (M<sup>+</sup>-155, 82.25). Anal. Calcd. for C<sub>17</sub>H<sub>16</sub>FNO<sub>3</sub>S: requires C, 61.25; H, 4.84; N, 4.20%. Found: C, 61.36; H, 5.05; N, 4.12%,

HPLC: OJ column;  $\lambda = 254$  nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min;  $t_{\text{minor}} = 28.84$  min;  $t_{\text{major}} = 32.41$  min, ee% = 84%.

**N-[1-(4-Bromophenyl)-2-formyl-allyl]-4-methylbenzenesulfonamide 6f:** a colorless solid (190 mg, 96%).  $[\alpha]_D^{20} +43.4$  (c 1.06, CHCl<sub>3</sub>). mp. 106-107 °C; IR (CHCl<sub>3</sub>): ν 3277, 3025, 2924, 2852, 1690 (C=O), 1628, 1597, 1488, 1436, 1330, 1216, 1161, 1093, 1074, 1011, 965, 927, 886, 814, 757, 669, 568 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz): δ 2.45 (3H, s, Me), 5.25 (1H, d, *J* = 8.3 Hz), 5.56 (1H, d, *J* = 8.3 Hz), 6.14 (1H, s), 6.53 (1H, s), 7.00 (2H, d, *J* = 8.4 Hz, Ar), 7.27 (2H, d, *J* = 8.5 Hz, Ar), 7.36 (2H, d, *J* = 8.4 Hz, Ar), 7.65 (2H, d, *J* = 8.5 Hz, Ar), 9.40 (1H, s). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75.44 MHz): δ 21.50, 55.98, 121.86, 127.11, 128.53, 129.57, 131.60, 136.08, 136.93, 137.14, 143.73, 147.57, 192.70. MS (EI): *m/e* 339 (M<sup>+</sup> -55, 3.39), 337 (M<sup>+</sup>-57, 3.15). Anal. Calcd. for C<sub>17</sub>H<sub>16</sub>BrNO<sub>3</sub>S: requires C, 51.79; H, 4.09; N, 3.55%. Found: C, 51.90; H, 4.27; N, 3.48%. HPLC: AS column;  $\lambda = 254$  nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min;  $t_{\text{major}} = 30.78$  min,  $t_{\text{minor}} = 42.31$  min; ee% = 79%.

**N-[1-(3-Chlorophenyl)-2-formyl-allyl]-4-methylbenzenesulfonamide 6g:** a colorless solid (130 mg, 74%).  $[\alpha]_D^{20} +38.6$  (c 0.96, CHCl<sub>3</sub>). mp. 112-114 °C. IR (CHCl<sub>3</sub>): ν 3273, 3021, 2926, 2834, 2400, 1691 (C=O), 1597, 1576, 1477, 1434, 1332, 1216, 1162, 1093, 963, 933, 888, 814, 760, 669, 571, 549 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz): δ 2.49 (3H, s, Me), 5.32 (1H, d, *J* = 8.1 Hz), 5.65 (1H, d, *J* = 8.1 Hz), 6.20 (1H, s), 6.57 (1H, s), 7.06-7.09 (2H, m, Ar), 7.22-7.25 (2H, m, Ar), 7.32 (2H, d, *J* = 8.7 Hz, Ar), 7.70 (2H, d, *J* = 8.7 Hz, Ar), 9.45 (1H, s). <sup>13</sup>C NMR (CDCl<sub>3</sub>, TMS, 75.44 MHz): δ 21.49, 56.46, 124.81, 126.94, 127.17, 128.06, 129.60, 129.88, 134.50, 136.34, 137.01, 140.02, 143.79, 147.37, 192.73. MS (EI): *m/e* 294 (M<sup>+</sup>-56, 4.34), 194 (M<sup>+</sup>-156, 100). Anal. Calcd. for C<sub>17</sub>H<sub>16</sub>ClNO<sub>3</sub>S: requires C, 58.37; H, 4.61; N, 4.00%. Found: C, 58.45; H, 4.51; N, 4.13%. HPLC: OD column;  $\lambda = 254$  nm; eluent: Hexane/Isopropanol = 65/35; Flow rate: 0.7 mL/min;  $t_{\text{major}} = 11.84$  min;  $t_{\text{minor}} = 15.67$  min; ee% = 82%.

*The general procedure for the determination of the absolute configuration of the reaction products.*

2-[Phenyl-(toluene-4-sulfonylamino)methyl]acrylic acid phenyl ester **5b** (264 mg, 0.65 mmol) was dissolved in THF (2.3 mL), and then 1.0 N NaOH aqueous solution (1.5 mL) was added. After the reaction mixture was stirred at room temperature for 24 hours, HCl (10%) was added into the reaction solution and the organic products were extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL x 3). The organic layer was dried with MgSO<sub>4</sub> and concentrated with rotary evaporator. The crude product was purified by flash column chromatography (SiO<sub>2</sub>, eluent: EtOAc/Petroleum ether = 1/1) to yield the corresponding product **5b-1** as a colorless solid (200 mg, 93% yield):  $[\alpha]^{20}_D$  +52.3 (c 1.09, CH<sub>3</sub>OH). <sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS, 300 MHz):  $\delta$  2.40 (3H, s), 5.28 (1H, d, *J* = 8.6 Hz), 5.75 (1H, d, *J* = 8.6 Hz), 5.94 (1H, s), 6.35 (1H, s), 7.12-7.15 (2H, m), 7.21-7.24 (5H, m), 7.66 (2H, d, *J* = 7.8 Hz), 13.5 (1H, br).

2-[Phenyl-(toluene-4-sulfonylamino)methyl]acrylic acid (compound **5b-1**) (200 mg, 0.6 mmol) was dissolved in MeCN/H<sub>2</sub>O (1:1) (5.3 mL), and then HIO<sub>4</sub> (624 mg, 3.25 mmol), RuCl<sub>3</sub> · nH<sub>2</sub>O (17 mg, 0.08 mmol) was added to the reaction flask. After the reaction mixture was stirred at room temperature for 3 h, the reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (150 mL), then washed with water (50 mL × 3). The organic layer was dried with MgSO<sub>4</sub> and then concentrated with rotary evaporator to give the crude product as solid. This product was dissolved in 20 mL CH<sub>3</sub>OH and then SOCl<sub>2</sub> (2.0 mL) was added to this reaction solution dropwise. After the reaction mixture was stirred at room temperature for 12 h, the reaction solution was concentrated with rotary evaporator to remove CH<sub>3</sub>OH and SOCl<sub>2</sub>. The residue was extracted with EtOAc (100 mL). The organic phase was washed with water (30 mL × 3), dried with MgSO<sub>4</sub>, concentrated with rotary evaporator to give the crude product as solid which was immediately subjected to flash column chromatography (SiO<sub>2</sub>, eluent: EtOAc/Petroleum ether = 1/4) to yield the corresponding product (15 mg),  $[\alpha]^{20}_D$  +28.7 (c 0.75,

$\text{CHCl}_3$ ).  $^1\text{H}$  NMR (300 MHz, TMS,  $\text{CDCl}_3$ ):  $\delta$  2.39 (3H, s), 3.56 (3H, s), 5.06 (1H, d,  $J$  = 7.2 Hz), 5.68 (1H, d,  $J$  = 7.2 Hz), 7.19-7.26 (7H, m), 7.62 (2H, d,  $J$  = 8.4 Hz).

Other aza-Baylis-Hillman adducts were treated in the same procedures as those described above.

*Typical reaction procedure for the aza-Baylis-Hillman reaction of N-sulfonated imines **1** with 2-cyclopenten-1-one in the presence of chiral phosphine Lewis base **LB13** (10 mol%).*

To *N*-(*p*-chlorobenzylidene)-*p*-toluenesulfinamide **1e** (147 mg, 0.5 mmol) and **LB13** (17.0 mg, 0.05 mmol) in 1.0 mL of THF was added cyclopent-2-en-1-one (42  $\mu\text{L}$ , 41.0 mg, 0.5 mmol). The reaction mixture was stirred at -78 °C (1 h) to room temperature for 12 h. The solvent was removed under reduced pressure and residue was purified by flash chromatography (eluent: EtOAc/petroleum ether = 1/2) to give the corresponding aza-Baylis-Hillman adduct **7a** (178 mg, 93%).

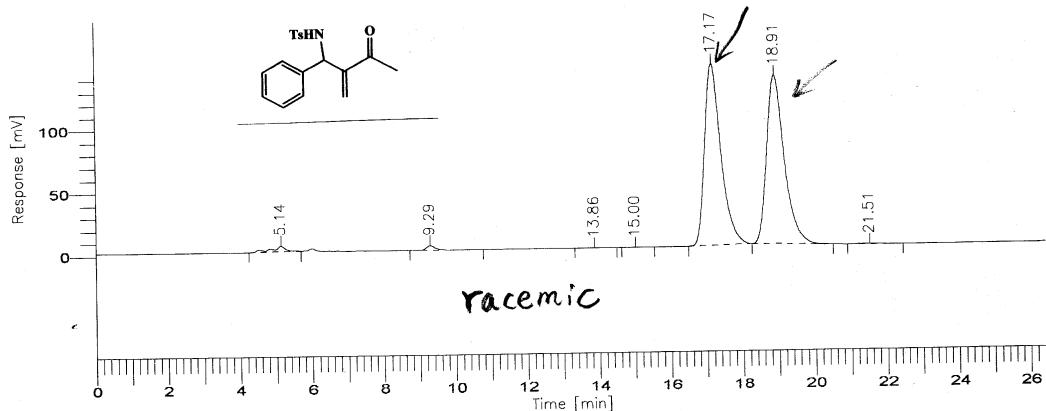
***N*-(4-Chlorophenyl)-(5-oxocyclopent-1-enyl)-methyl]-4-methylbenzenesulfonamide 7a:** a colorless solid.  $[\alpha]^{20}_{\text{D}} -6.5$  (c 1.23,  $\text{CHCl}_3$ ). mp. 184-186 °C. 178 mg, 93%. IR ( $\text{CHCl}_3$ ):  $\nu$  3408, 1675 (C=O), 1610, 1390, 1100, 1010, 700  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, 300 MHz):  $\delta$  2.14-2.53 (4H, m,  $\text{CH}_2$ ), 2.36 (3H, s, Me), 5.28 (1H, d,  $J$  = 8.6 Hz, NH), 6.08 (1H, d,  $J$  = 8.6 Hz, CH), 7.14 (2H, d,  $J$  = 8.6 Hz, Ar), 7.21 (2H, d,  $J$  = 8.3 Hz, Ar), 7.22 (2H, d,  $J$  = 8.6 Hz, Ar), 7.37 (1H, t,  $J$  = 2.6 Hz, =CH), 7.61 (2H, d,  $J$  = 8.3 Hz, Ar).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 75 MHz):  $\delta$  21.46, 26.80, 34.88, 54.64, 127.25, 127.71, 128.12, 128.63, 129.35, 133.63, 137.09, 142.94, 143.42, 160.90, 208.35. MS (EI):  $m/e$  294 ( $\text{M}^+ - 81$ , 0.60), 220 ( $\text{M}^+ - 155$ , 100). Anal. Calcd. for  $\text{C}_{19}\text{H}_{18}\text{ClNO}_3\text{S}$ : requires C, 60.71; H, 4.83; N, 3.73%. Found: C, 60.54; H, 4.84; N, 3.42%. Chiral HPLC: TBB column (reversed phase column);  $\lambda$  = 254 nm; eluent: Hexane/Isopropanol = 80/20 (0.1% HOAc); Flow rate: 1.0 mL/min., ee% = 63%.

## References.

- 1) Love, B. E.; Raje, P. S.; Williams, T. C. *Synlett* **1994**, 493.
- 2) Uozumi, Y.; Tanahashi, A.; Lee, S.-Y.; Hayashi, T. *J. Org. Chem.* **1993**, 58, 1945-1948.

## 9) Chiral HPLC analyses.

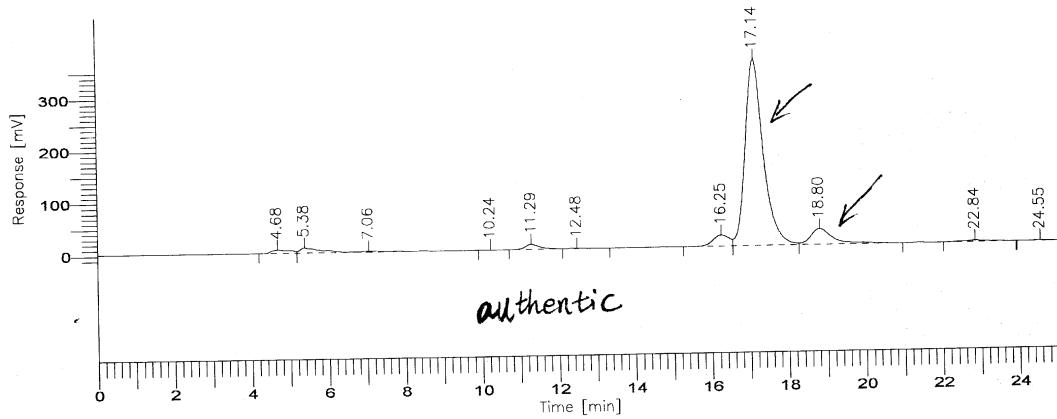
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2	9.292	63800.50	3567.81	0.68	0.00	BB	17.8823
3	13.862	4411.00	149.49	0.05	0.00	BB	29.5060
4	15.000	5361.00	217.58	0.06	0.00	BB	24.6390
5	17.172	4567581.00	144949.32	48.88	0.00	BB	31.5116
6	18.914	4570412.50	134562.96	48.91	0.00	BB	33.9649
7	21.512	12574.00	354.87	0.13	0.00	BB	35.4325
				9344557.00	288316.23	100.00	0.00

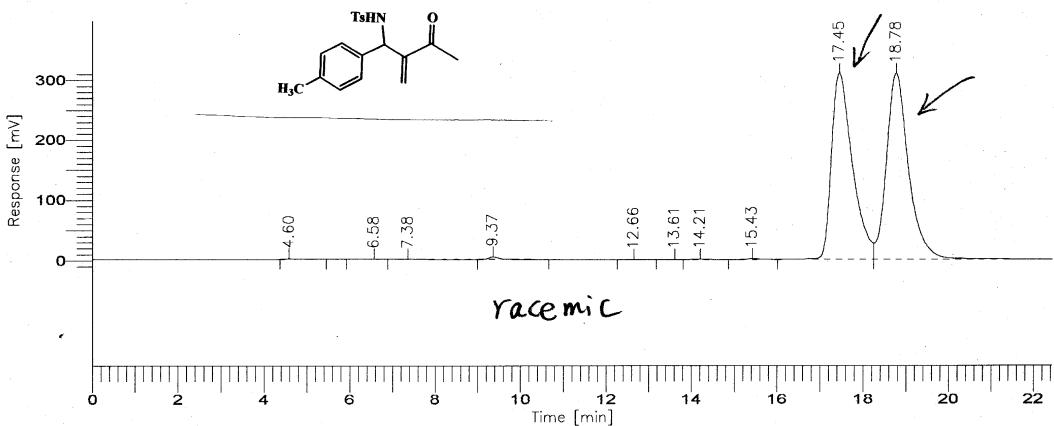
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Instrument : 970A\_-0 Rack/Vial: 0/0 Operator: DIN  
Sample Amount : 1.0000 Dilution Factor : 1.00



Peak #	Time [min]	Area [UV*sec]	Height [uV]	Area [%]	Norm. [%]	Area BL	Area/Height [sec]
1	4.683	220414.66	6315.55	1.54	0.00	BV	34.9003
2	5.380	370115.94	9453.58	2.58	0.00	VE	39.1509
3	7.058	66707.00	1598.81	0.47	0.00	EB	41.7229
4	10.236	6371.36	204.62	0.04	0.00	BV	31.1371
5	11.292	225373.59	9082.76	1.57	0.00	VV	24.8133
6	12.480	17980.55	538.92	0.13	0.00	VB	33.3641
7	16.250	597178.00	20432.85	4.17	0.00	BV	29.2264
8	17.135	11612851.64	356911.10	81.05	0.00	VV	32.5371
9	18.804	1123070.36	29038.65	7.84	0.00	VB	38.6750
10	22.842	83903.00	1965.66	0.59	0.00	BB	42.6844
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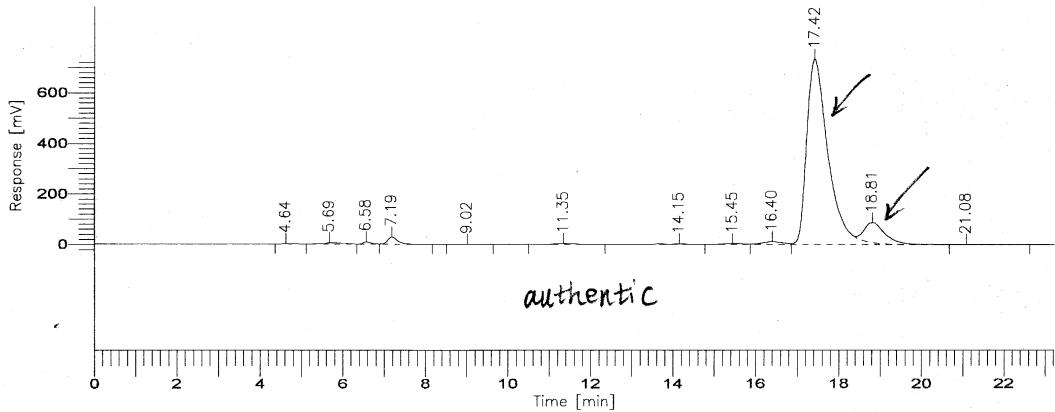
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 Sample Amount : 1.0000 Dilution Factor : 1.00



Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height
1	4.597	21526.50	982.64	0.10	0.00	BB	21.9068
2	6.581	5019.57	224.97	0.02	0.00	BV	22.3118
3	7.375	9163.70	224.65	0.04	0.00	VV	40.7901
4	9.366	70593.73	4287.23	0.32	0.00	VB	16.4660
5	12.658	3347.00	123.29	0.02	0.00	BB	27.1477
6	13.612	5782.56	296.74	0.03	0.00	BV	19.4872
7	14.208	19801.94	733.74	0.09	0.00	VB	26.9877
8	15.433	31489.79	1162.62	0.14	0.00	BV	27.0852
9	17.453	10528695.15	311299.20	48.27	0.00	VV	33.8218
10	18.775	11117701.06	311671.06	50.97	0.00	VB	35.6713
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21813121.00 631006.14 100.00 0.00							

Chiral AD column; 254 nm; Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min

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Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height
1	4.635	39914.36	1435.02	0.13	0.00	BV	27.8146
2	5.685	185104.65	5122.91	0.61	0.00	VV	36.1327
3	6.577	109306.20	8734.86	0.36	0.00	VV	12.5138
4	7.192	433475.68	27899.81	1.42	0.00	VB	15.5369
5	9.016	11252.00	510.50	0.04	0.00	BB	22.0410
6	11.347	89841.86	3041.78	0.29	0.00	BV	29.5359
7	14.153	74577.88	945.26	0.24	0.00	VV	78.8967
8	15.445	126752.39	3741.20	0.42	0.00	VV	33.8801
9	16.398	361655.14	10542.08	1.19	0.00	VV	34.3059
10	17.415	26280355.30	736810.54	86.11	0.00	VE	35.6677
11	18.808	2770434.00	79997.29	9.08	0.00	EV	34.6316
12	21.075	35986.23	749.86	0.12	0.00	VB	47.9908
				30518655.69	879531.11	100.00	0.00

**M****Individual Sample Report**

Reported by User: System

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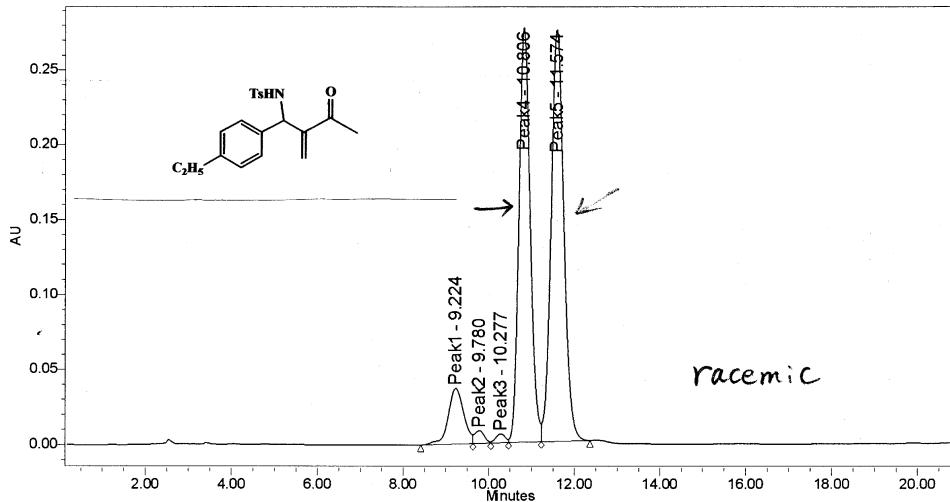
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Run Time 30.00 Minutes

Date Processed 6/20/02 2:27:18 PM

Current Date 6/20/02



Chiral TBB column; 254 nm; Hexane/Isopropanol = 95/5; Flow rate: 0.7 mL/min

**Peak Results**

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2	9.780	Peak2	132088	8418	VV	1.11	1.40		
3	10.277	Peak3	89114	5814	VV	0.75	0.96		
4	10.806	Peak4	5061510	277135	VV	42.64	45.93		
5	11.574	Peak5	5655739	275021	VB	47.65	45.58		

**M**

## Individual Sample Report

Reported by User: System

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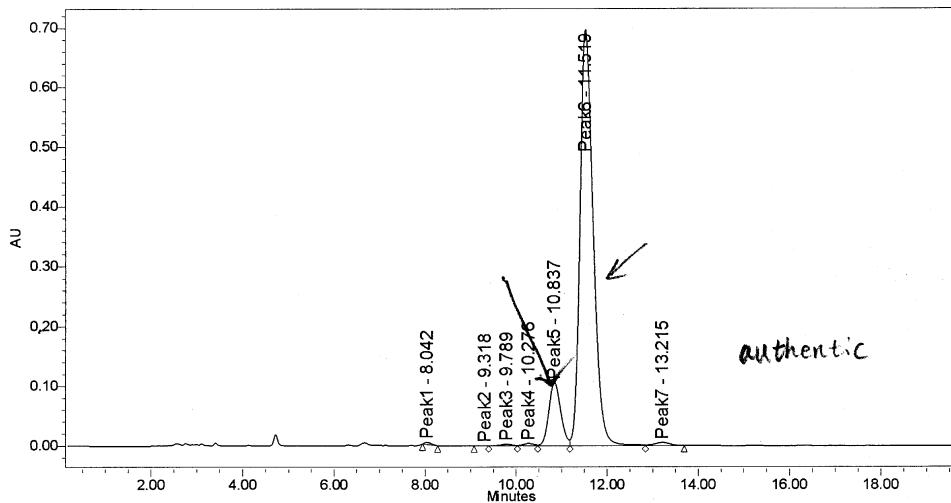
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Run Time 30.00 Minutes

Date Processed 6/20/02 3:40:13 PM

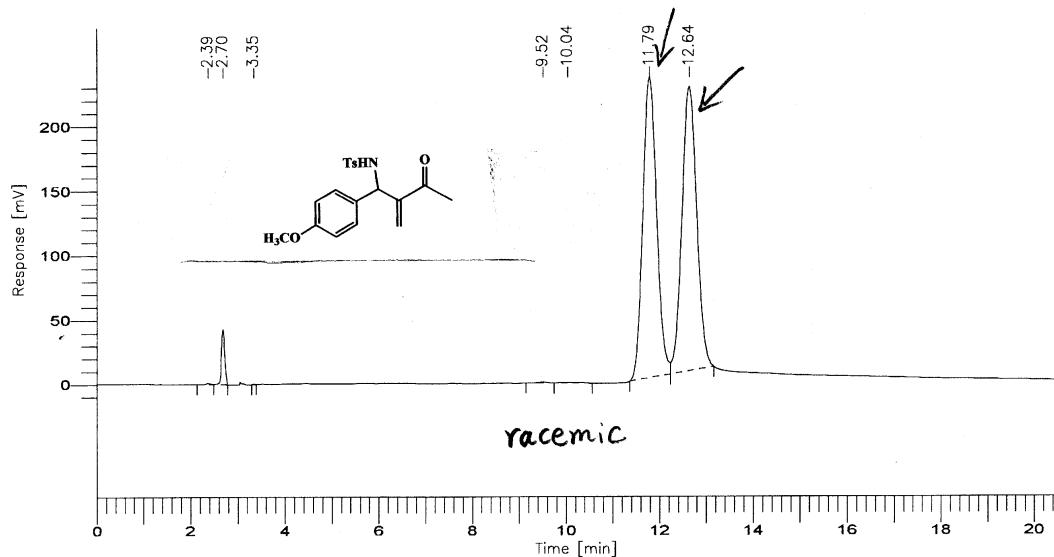
Current Date 6/20/02



### Peak Results

	RT	Name	Area	Height	Int Type	% Area	% Height	Amount	Units
1	8.042	Peak1	36572	3675	BB	0.22	0.45		
2	9.318	Peak2	8459	698	BV	0.05	0.09		
3	9.789	Peak3	52021	2741	VV	0.32	0.33		
4	10.276	Peak4	61517	3778	VV	0.38	0.46		
5	10.837	Peak5	1911955	106274	VV	11.73	12.96		
6	11.519	Peak6	14103127	697821	VV	86.52	85.07		
7	13.215	Peak7	126777	5263	VB	0.78	0.64		

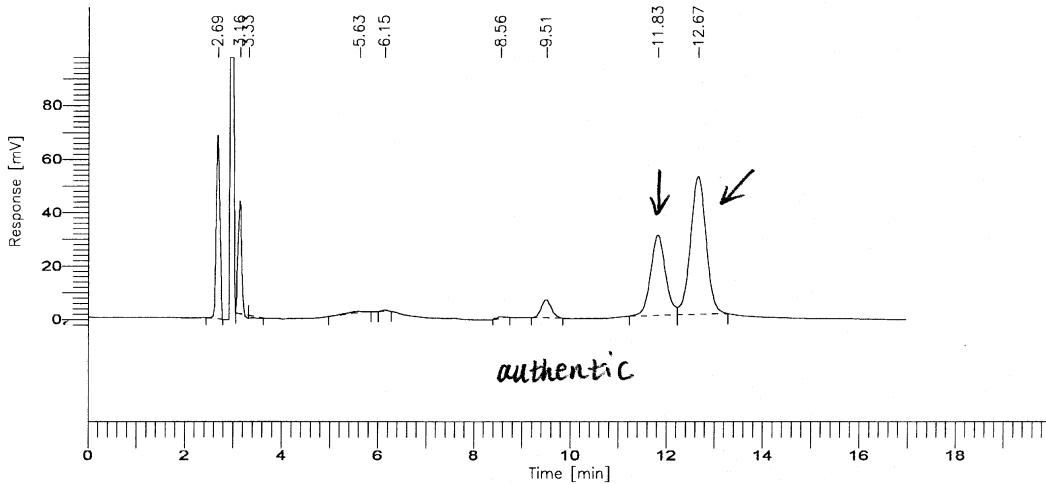
Software Version: 4.1<2F12>  
 Date: 02-1-14 1:50  
 Sample Name : XuII-83a-1  
 Data File : D:\HPLC\CSP\_708.RAW Date: 02-1-11 8:51  
 Sequence File: D:\HPLC\CSP.SEQ Cycle: 1 Channel : A  
 Instrument : 900A\_-0 Rack/Vial: 0/0 Operator:  
 Sample Amount : 1.0000 Dilution Factor : 1.00



Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Area/Height [sec]	BL
1	2.388	6544.96	988.63	0.07	0.00	6.6202	BV
2	2.700	208722.54	42956.88	2.11	0.00	4.8589	VB
3	3.353	1647.00	412.40	0.02	0.00	3.9937	BB
4	9.516	12441.60	858.47	0.13	0.00	14.4928	BV
5	10.042	22065.40	733.61	0.22	0.00	30.0780	VB
6	11.788	4788064.00	233154.98	48.34	0.00	20.5360	*BV
7	12.637	4864999.00	220286.59	49.12	0.00	22.0849	*VB
				9904484.50	499391.55	100.00	0.00

Chiral TBB column; 220 nm; Hexane/Isopropanol/TBME = 75/5/20; Flow rate: 0.7 mL/min

Software Version: 4.1<2F12>  
 Date: 02-1-14 2:22  
 Sample Name : CLH-011212-2  
 Data File : D:\HPLC\CSP\_709.RAW Date: 02-1-11 9:18  
 Sequence File: D:\HPLC\CSP.SEQ Cycle: 1 Channel : A  
 Instrument : 900A - 0 Rack/Vial: 0/0 Operator:  
 Sample Amount : 1.0000 Dilution Factor : 1.00



Peak #	Time [min]	Area [uv.sec]	Height [uv]	Area [%]	BL	Norm Area [%]	Component Name
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1	2.694	369354.50	69367.25	14.60	BB	0.00	
2	3.155	215433.88	42742.86	8.51	BV	0.00	
3	3.333	7534.88	-996.76	0.30	VB	0.00	
4	5.629	21060.50	613.53	0.83	BB	0.00	
5	6.149	4828.00	583.04	0.19	BB	0.00	
6	8.564	8679.50	687.98	0.34	BB	0.00	
7	9.507	97211.50	6679.23	3.84	BB	0.00	
8	11.828	644231.32	29965.63	25.46	BV	0.00	
9	12.666	1162339.18	51718.62	45.93	VB	0.00	

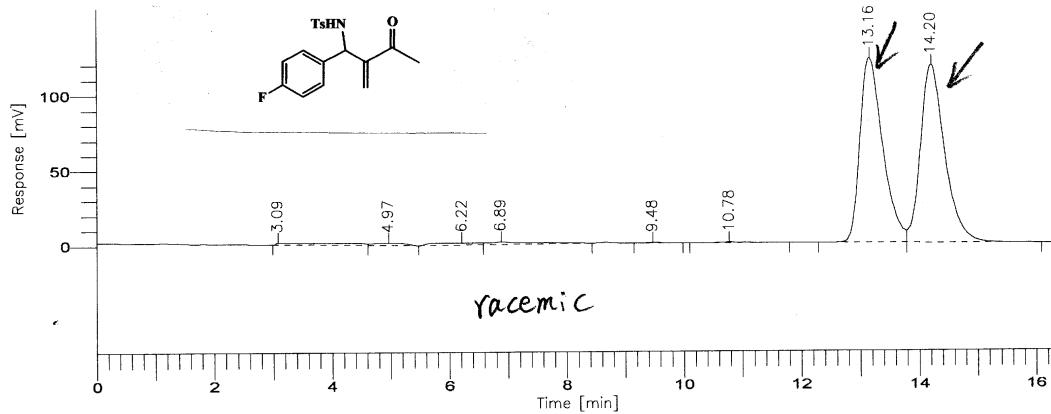
2530673.26 201361.37 100.00 0.00

#### Missing Component Report

Component Expected Retention (Calibration File)

All components were found

Software Version: 4.1<2F12>  
 Date: 02-2-6 14:54  
 Sample Name : Clh-020128-1  
 Data File : C:\C\CS6\_001.RAW Date: 02-2-6 14:20  
 Sequence File: C:\C\CS6.SEQ Cycle: 1 Channel : A  
 Instrument : 970A - 0 Rack/Vial: 0/0 Operator: DIN  
 Sample Amount : 1.0000 Dilution Factor : 1.00



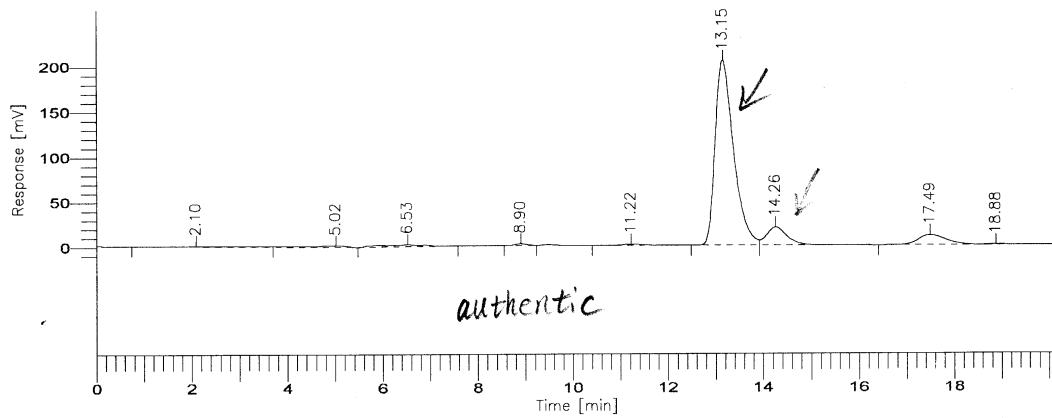
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height [sec]
1	3.089	122147.51	1199.34	1.72	1.72	BV	101.8453
2	4.968	66716.99	1716.92	0.94	0.94	VB	38.8584
3	6.220	94632.14	1634.08	1.33	1.33	BV	57.9115
4	6.890	95124.86	1787.67	1.34	1.34	VB	53.2116
5	9.475	5843.00	262.84	0.08	0.08	BB	22.2303
6	10.775	16333.00	484.82	0.23	0.23	BB	33.6891
7	13.156	3310954.63	123322.37	46.59	46.59	BV	26.8480
8	14.204	3395276.37	118570.24	47.77	47.77	VB	28.6351
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7107028.50 248978.29 100.00 100.00							

Chiral AD column; 254 nm; Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min

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Software Version: 4.1<2F12>  
 Date: 02-2-6 15:09  
 Sample Name : Clh-020124-5  
 Data File : C:\C\CS6\_002.RAW Date: 02-2-6 14:44  
 Sequence File: C:\C\CS6.SEQ Cycle: 1 Channel : A  
 Instrument : 970A - 0 Rack/Vial: 0/0 Operator: DIN  
 Sample Amount : 1.0000 Dilution Factor : 1.00

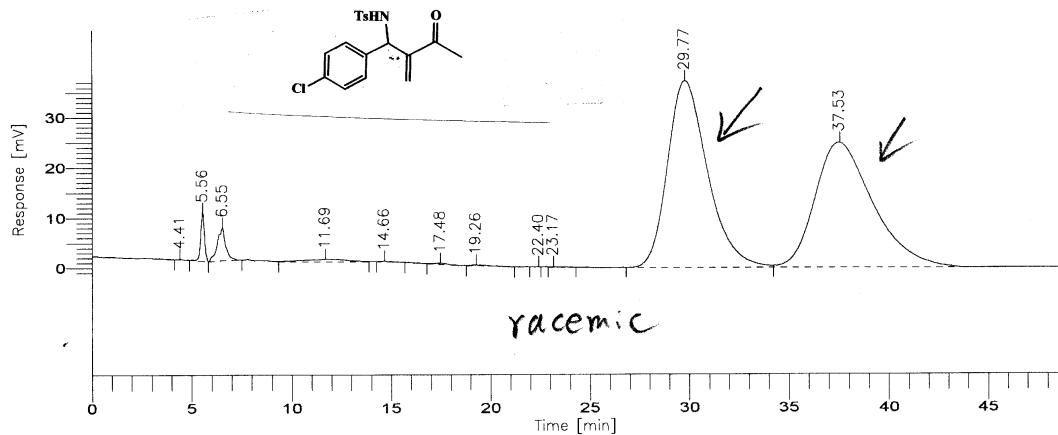
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Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height
1	2.096	101741.99	542.13	1.43	1.43	BV	187.6723
2	5.017	144526.01	1995.97	2.03	2.03	VB	72.4088
3	6.528	170059.00	2428.28	2.39	2.39	BB	70.0327
4	8.904	32783.50	1909.94	0.46	0.46	BB	17.1647
5	11.217	51047.50	1385.81	0.72	0.72	BB	36.8359
6	13.148	5539547.67	205418.99	77.83	77.83	BV	26.9671
7	14.256	594397.33	20412.35	8.35	8.35	VB	29.1195
8	17.488	458474.81	11409.03	6.44	6.44	BE	40.1853
9	18.875	25155.69	660.41	0.35	0.35	EB	38.0908
				7117733.50	246162.92	100.00	100.00

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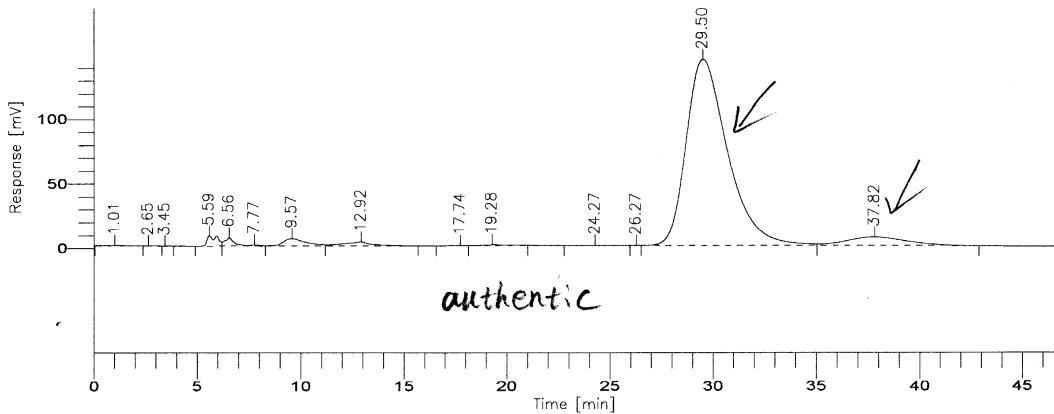
Software Version: 4.1<2F12>  
 Date: 02-1-11 18:14  
 Sample Name : CIh-011216-1  
 Data File : C:\C\CS5\_796.RAW Date: 02-1-11 16:38  
 Sequence File: C:\C\CS5.SEQ Cycle: 1 Channel : A  
 Instrument : 970A\_-\_0 Rack/Vial: 0/0 Operator: DIN  
 Sample Amount : 1.0000 Dilution Factor : 1.00



Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height
1	4.414	3628.35	165.91	0.03	0.00	BV	21.8692
2	5.559	131982.65	9730.09	1.23	0.00	VB	13.5644
3	6.552	198023.00	6651.04	1.85	0.00	BB	29.7732
4	11.689	80765.00	574.69	0.75	0.00	BB	140.5355
5	14.664	9387.00	215.22	0.09	0.00	BB	43.6167
6	17.475	9121.00	288.66	0.09	0.00	BB	31.5976
7	19.264	13976.50	206.69	0.13	0.00	BB	67.6219
8	22.401	1674.00	100.04	0.02	0.00	BB	16.7339
9	23.166	5550.00	140.34	0.05	0.00	BB	39.5474
10	29.773	5227929.00	37485.69	48.80	0.00	BV	139.4647
11	37.533	5030429.00	25030.02	46.96	0.00	VB	200.9758
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10712465.50 80588.38 100.00 0.00							

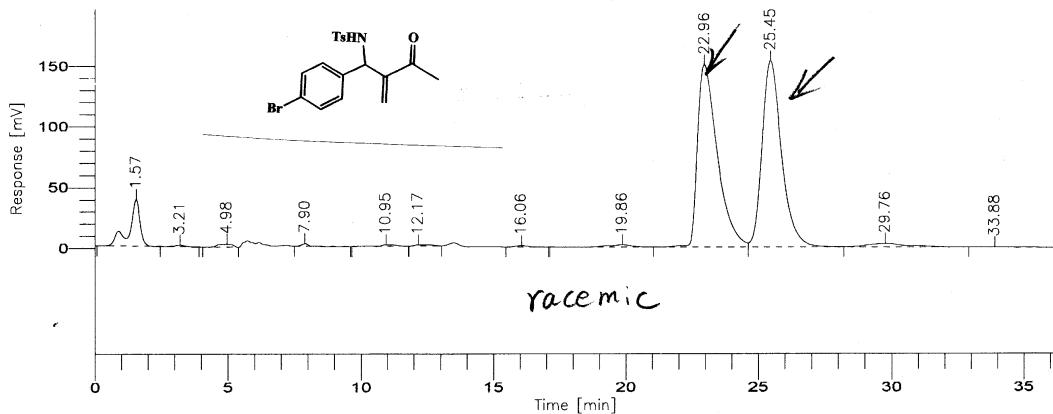
Chiral AS column; 254 nm; Hexane/Isopropanol = 65/35; Flow rate: 0.7 mL/min

Software Version: 4.1<2F12>  
Date: 02-1-11 18:23  
Sample Name : CIh-011216-1  
Data File : C:\C\CS5\_797.RAW Date: 02-1-11 17:34  
Sequence File: C:\C\CS5.SEQ Cycle: 1 Channel : A  
Instrument : 970A\_-0 Rack/Vial: 0/0 Operator: DIN  
Sample Amount : 1.0000 Dilution Factor : 1.00



Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL	Area/Height [sec]
1	1.010	18869.00	245.49	0.08	0.00	BB	76.8623
2	2.653	4217.50	143.29	0.02	0.00	BB	29.4342
3	3.450	2405.00	125.57	0.01	0.00	BB	19.1532
4	5.589	269706.13	7890.94	1.16	0.00	BV	34.1792
5	6.555	202731.03	6380.28	0.87	0.00	VE	31.7746
6	7.767	29253.00	959.04	0.13	0.00	EV	30.5025
7	9.566	449392.31	5873.22	1.94	0.00	VV	76.5155
8	12.921	330234.53	3283.68	1.43	0.00	VB	100.5683
9	17.738	21853.19	388.25	0.09	0.00	BV	56.2864
10	19.276	54703.81	686.85	0.24	0.00	VB	79.6445
11	24.269	25487.00	324.53	0.11	0.00	BB	78.5345
12	26.265	2593.03	111.86	0.01	0.00	BV	23.1803
13	29.499	20302421.94	145261.92	87.61	0.00	VV	139.7642
14	37.815	1459094.03	7008.57	6.30	0.00	VB	208.1870

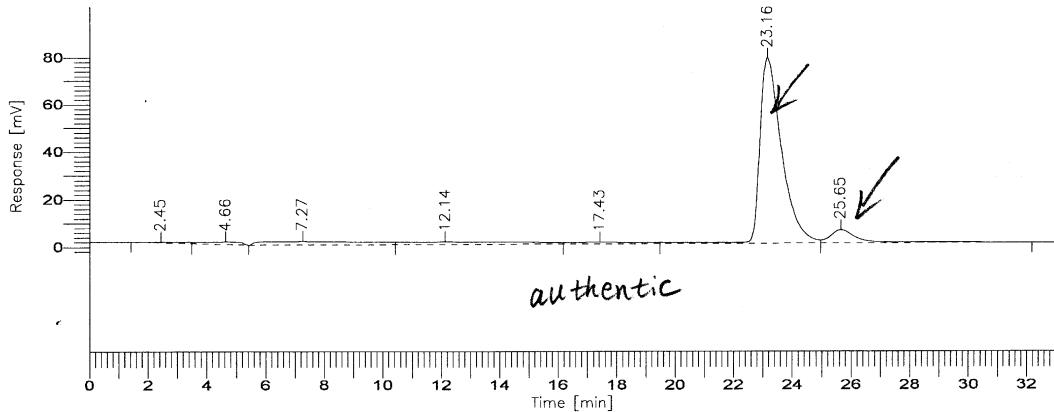
Software Version: 4.1<2F12>  
 Date: 02-2-7 14:58  
 Sample Name : Clh-020124-1b  
 Data File : C:\C\CS6\_012.RAW Date: 02-2-7 13:50  
 Sequence File: C:\C\CS6.SEQ Cycle: 1 Channel : A  
 Instrument : 970A\_-0 Rack/Vial: 0/0 Operator: DIN  
 Sample Amount : 1.0000 Dilution Factor : 1.00



Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Area BL [sec]	Area/Height
1	1.568	1123900.93	38808.74	6.37	6.37	BV	28.9600
2	3.212	43516.57	1391.27	0.25	0.25	VB	31.2784
3	4.975	107772.00	2690.49	0.61	0.61	BB	40.0566
4	7.895	41494.00	2334.07	0.24	0.24	BB	17.7775
5	10.950	62285.00	1349.53	0.35	0.35	BB	46.1531
6	12.169	44111.00	1107.71	0.25	0.25	BB	39.8219
7	16.055	38189.00	1208.99	0.22	0.22	BB	31.5875
8	19.863	130378.45	1937.57	0.74	0.74	BV	67.2897
9	22.956	7806409.98	150985.99	44.23	44.23	VV	51.7029
10	25.445	7861998.98	154239.24	44.54	44.54	VV	50.9728
11	29.755	364406.62	3230.58	2.06	2.06	VV	112.7992
12	33.883	25905.47	270.41	0.15	0.15	VB	95.8001
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17650368.00 359554.59 100.00 100.00							

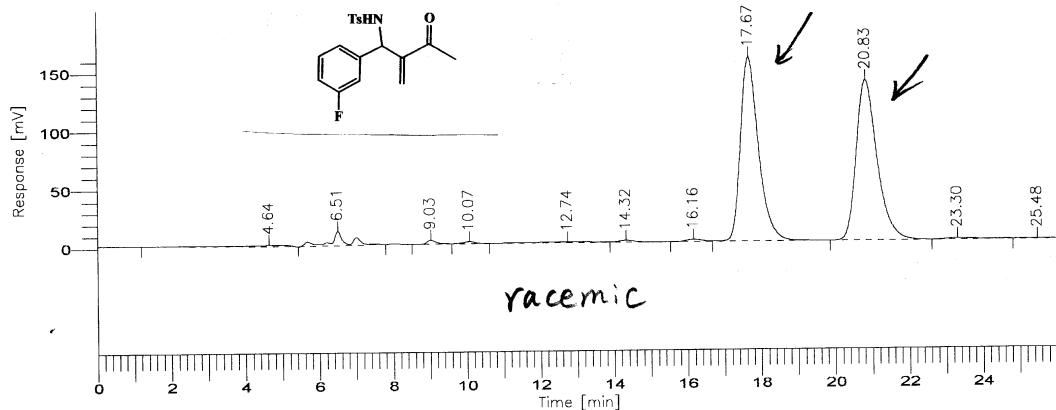
Chiral AD column; 254 nm; Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min

Software Version: 4.1<F12>  
Date: 02-2-7 15:09  
Sample Name : Clh-020124-3  
Data File : C:\C\CS6\_013.RAW Date: 02-2-7 14:31  
Sequence File: C:\C\CS6.SEQ Cycle: 1 Channel : A  
Instrument : 970A\_-0 Rack/Vial: 0/0 Operator: DIN  
Sample Amount : 1.0000 Dilution Factor : 1.00



Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL	Area/Height [sec]
1	2.450	42962.63	354.33	0.78	0.78	BV	121.2506
2	4.656	107871.37	1264.31	1.96	1.96	VB	85.3206
3	7.272	400068.47	1647.60	7.27	7.27	BV	242.8184
4	12.142	344949.41	1251.80	6.27	6.27	VV	275.5624
5	17.433	138499.99	840.61	2.52	2.52	VV	164.7618
6	23.157	4077731.44	78397.83	74.14	74.14	VV	52.0133
7	25.651	388013.69	5575.48	7.05	7.05	VB	69.5929
		5500097.00	89331.96	100.00	100.00		

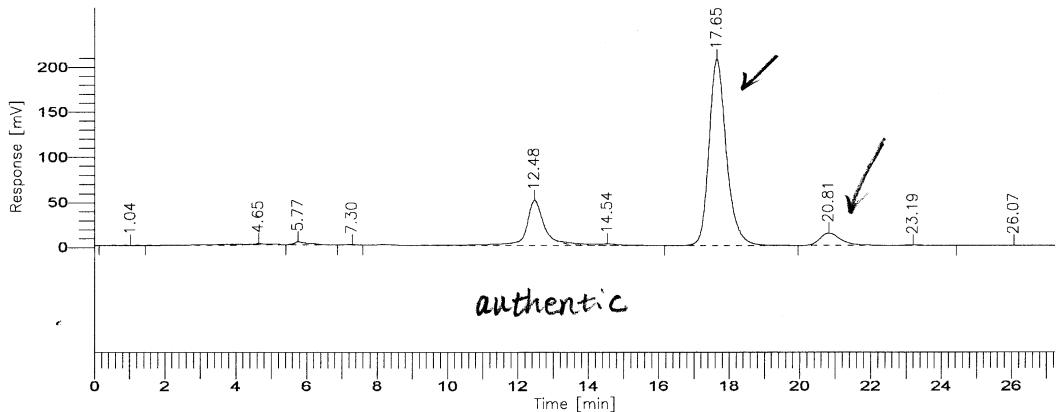
Software Version: 4.1<2F12>  
 Date: 02-2-7 15:36  
 Sample Name : CIh-020127-2  
 Data File : C:\C\CS6\_014.RAW Date: 02-2-7 15:08  
 Sequence File: C:\C\CS6.SEQ Cycle: 1 Channel : A  
 Instrument : 970A - 0 Rack/Vial: 0/0 Operator: DIN  
 Sample Amount : 1.0000 Dilution Factor : 1.00



Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. [%]	Area BL [sec]	Area/Height
1	4.644	173361.00	1620.28	1.48	1.48	BB	106.9943
2	6.508	372656.00	12356.96	3.18	3.18	BB	30.1576
3	9.028	59439.94	3346.53	0.51	0.51	BV	17.7617
4	10.071	48153.26	1989.24	0.41	0.41	VV	24.2069
5	12.742	113739.07	816.01	0.97	0.97	VV	139.3847
6	14.319	53849.22	1736.26	0.46	0.46	VB	31.0145
7	16.163	64888.97	2114.89	0.55	0.55	BV	30.6819
8	17.672	5366501.03	158098.25	45.79	45.79	VB	33.9441
9	20.831	5390931.10	137618.12	46.00	46.00	BV	39.1731
10	23.297	62933.38	1113.10	0.54	0.54	VV	56.5387
11	25.475	12458.53	288.02	0.11	0.11	VB	43.2564
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11718911.50 321097.65 100.00 100.00							

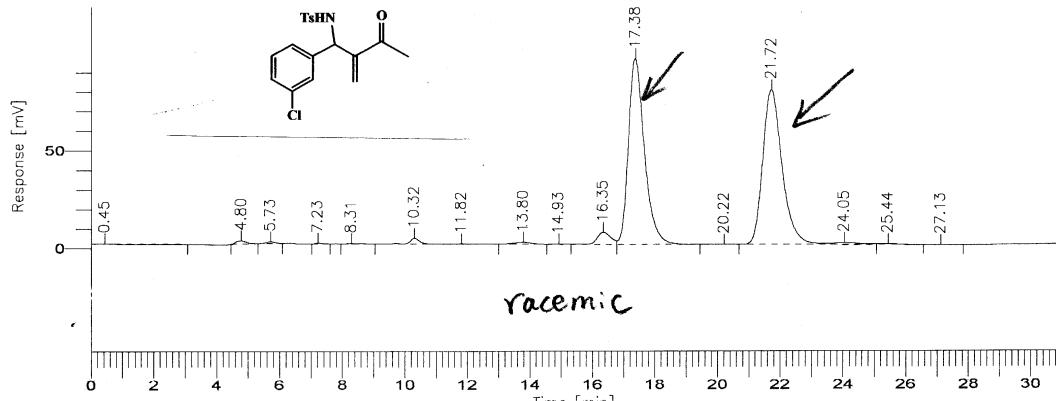
Chiral AD column; 254 nm; Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min;

Software Version: 4.1<F12>  
Date: 02-2-7 16:12  
Sample Name : CIh-011226-1  
Data File : C:\C\CS6\_015.RAW Date: 02-2-7 15:41  
Sequence File: C:\C\CS6.SEQ Cycle: 1 Channel : A  
Instrument : 970A\_0 Rack/Vial: 0/0 Operator: DIN  
Sample Amount : 1.0000 Dilution Factor : 1.00



Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. [%]	Area BL	Area/Height [sec]
1	1.042	6809.89	144.33	0.07	0.07	BV	47.1822
2	4.649	178936.58	1840.93	1.79	1.79	VV	97.1988
3	5.766	115750.96	3842.81	1.16	1.16	VV	30.1214
4	7.303	13274.07	660.21	0.13	0.13	VB	20.1060
5	12.475	1759926.00	50222.24	17.65	17.65	BE	35.0428
6	14.543	170080.00	1769.20	1.71	1.71	EB	96.1337
7	17.649	7093541.50	207025.08	71.15	71.15	BB	34.2642
8	20.810	576477.00	13996.93	5.78	5.78	BE	41.1860
9	23.192	34053.00	580.24	0.34	0.34	EB	58.6883
10	26.067	20569.50	195.77	0.21	0.21	BB	105.0701
		9969418.50	280277.75	100.00	100.00		

Software Version: 4.1<2F12>  
 Date: 02-2-20 14:20  
 Sample Name : CIh-020127-1  
 Data File : C:\C\CS6\_027.RAW Date: 02-2-20 13:48  
 Sequence File: C:\C\CS6.SEQ Cycle: 1 Channel : A  
 Instrument : 970A - 0 Rack/Vial: 0/0 Operator: DIN  
 Sample Amount : 1.0000 Dilution Factor : 1.00

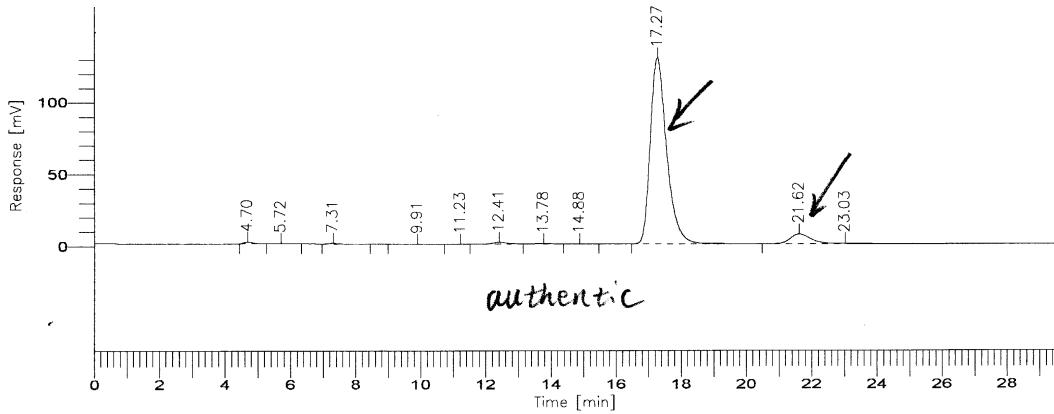


Chiral AD column; 254 nm; Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height [sec]
1	0.450	1985.00	242.20	0.03	0.03	BB	8.1959
2	4.799	47625.89	1879.13	0.65	0.65	BV	25.3447
3	5.726	23514.11	1057.87	0.32	0.32	VB	22.2277
4	7.233	8050.50	558.91	0.11	0.11	BB	14.4038
5	8.308	6399.50	156.23	0.09	0.09	BB	40.9628
6	10.316	62006.00	3004.74	0.85	0.85	BE	20.6360
7	11.819	7916.00	145.53	0.11	0.11	EB	54.3946
8	13.804	37406.00	966.32	0.51	0.51	BB	38.7097
9	14.928	5863.37	224.13	0.08	0.08	BV	26.1604
10	16.353	184257.84	6257.64	2.53	2.53	VV	29.4453
11	17.377	3387719.79	95530.50	46.53	46.53	VB	35.4622
12	20.217	6250.25	131.96	0.09	0.09	BV	47.3647
13	21.724	3400916.60	79579.04	46.71	46.71	VE	42.7363
14	24.050	75938.47	1200.76	1.04	1.04	EV	63.2419
15	25.442	22508.68	488.55	0.31	0.31	VB	46.0721
16	27.125	2585.00	63.59	0.04	0.04	BB	40.6539

7280943.00 191487.10 100.00 100.00

Software Version: 4.1<2F12>  
Date: 02-2-20 14:54  
Sample Name : CIh-020124-4  
Data File : C:\C\CS6\_028.RAW Date: 02-2-20 14:25  
Sequence File: C:\C\CS6.SEQ Cycle: 1 Channel : A  
Instrument : 970A - 0 Rack/Vial: 0/0 Operator: DIN  
Sample Amount : 1.0000 Dilution Factor : 1.00



Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL	Area/Height [sec]
1	4.703	31466.45	1359.64	0.64	0.64	BV	23.1433
2	5.723	11474.05	305.92	0.23	0.23	VB	37.5073
3	7.311	9973.00	469.80	0.20	0.20	BB	21.2283
4	9.908	3394.28	62.66	0.07	0.07	BV	54.1730
5	11.225	728.24	22.06	0.01	0.01	VV	33.0140
6	12.412	32226.59	1140.28	0.66	0.66	VV	28.2620
7	13.775	7824.38	227.82	0.16	0.16	VB	34.3453
8	14.883	2630.50	86.77	0.05	0.05	BB	30.3160
9	17.271	4519630.00	129673.50	91.87	91.87	BB	34.8539
10	21.619	282869.91	6716.24	5.75	5.75	BE	42.1173
11	23.025	17214.09	354.19	0.35	0.35	EB	48.6010

4919431.50 140418.86 100.00 100.00

\*\*\*\*\* MODEL 1022 RUNLOG for run: CH-2\_80 \*\*\*\*\*

Run terminated manually on Channel A.

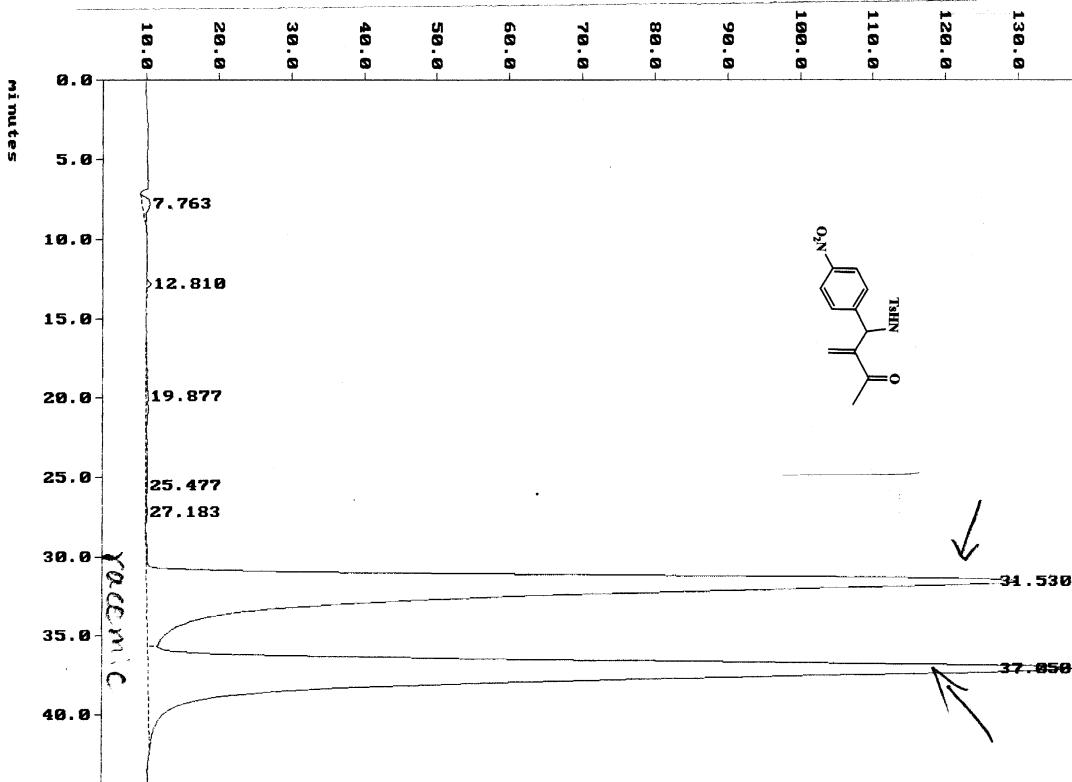
File : CH-2_80.D01	c1h-011203-2-rac	1
Run : 01		Type : Sample
Path : C:\CH-3		Inst : 1022 LC Plus
Collection : 11:42:33 Dec 19 2001	Method : LCTEST	[ 09:05:42 Dec 19 2001 ]
Integration: 11:42:33 Dec 19 2001	Method : LCTEST	[ 09:05:42 Dec 19 2001 ]
Report : 12:27:05 Dec 19 2001	Method : LCTEST	[ 09:05:42 Dec 19 2001 ]

PERCENT ( AREA )

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	7.763	630000	1.0747		0.2983	0.4302
2	12.810	92570	0.5960		0.0438	0.2386
3	19.877	560484	0.2899	T	0.2654	0.1161
4	25.477	396750	0.1942	T	0.1879	0.0778
5	27.183	116224	0.1646	V	0.0550	0.0659
6	31.530	104104648	120.0704	T	49.3004	48.0627
7	37.050	105263080	127.4302		49.8490	51.0088

7 Peaks > Area Reject      211163760 Total Area  
 7 Peaks > Height Reject      249.820 Total Height

Chiral OJ column; 254 nm; Hexane/Isopropanol = 60/40; Flow rate: 0.7 mL/min



\*\*\*\*\* MODEL 1022 RUNLOG for run: CH-2\_81 \*\*\*\*\*

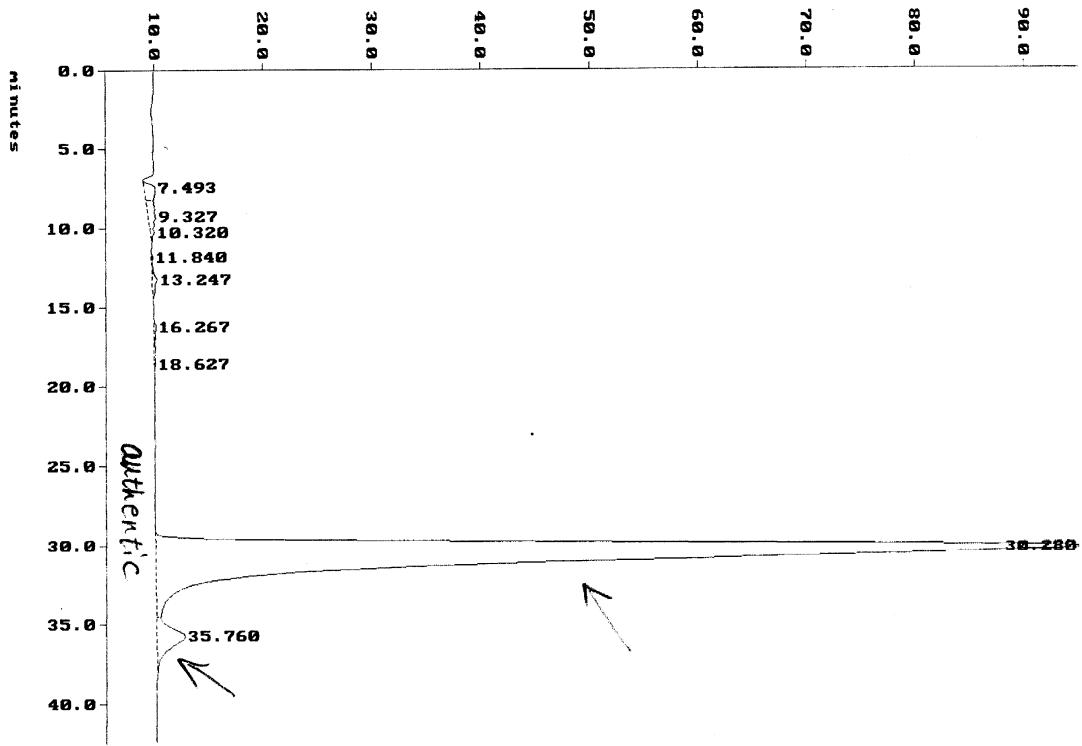
Run terminated manually on Channel A.

### PERCENT ( AREA )

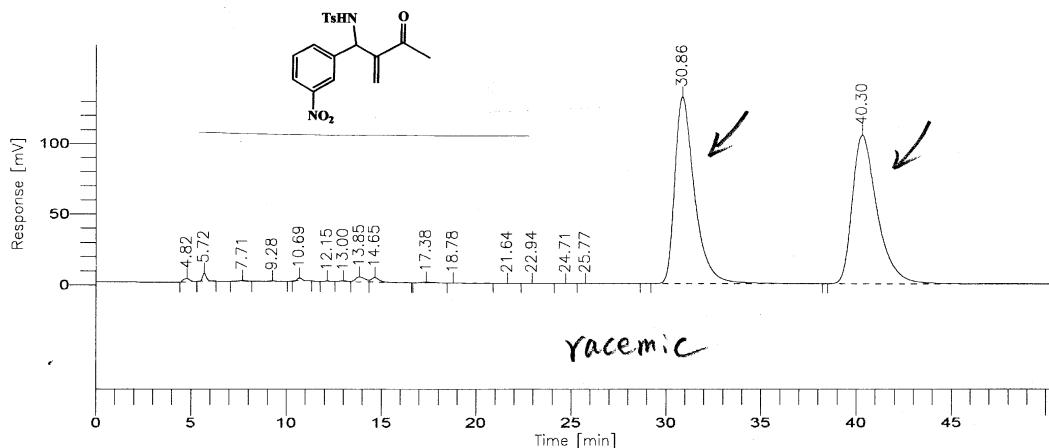
Pk #	RT	Area	Height	BC	Area	Percent	Height	Percent
1	7.493	586162	1.0311	T	0.8400		1.1390	
2	9.327	638695	0.6778	T	0.9153		0.7487	
3	10.320	111232	0.3343		0.1594		0.3693	
4	11.840	39645	0.1452	T	0.0568		0.1604	
5	13.247	260713	0.4739	V	0.3736		0.5235	
6	16.267	91699	0.1909	T	0.1314		0.2109	
7	18.627	121980	0.0963	V	0.1748		0.1064	
8	30.280	65697184	84.9662	T	94.1490		93.8546	
9	35.760	2232676	2.6138		3.1996		2.8873	

9 Peaks > Area Reject 69779984 Total Area  
9 Peaks > Height Reject 90.530 Total Height

(CH-2\_81.D01) M0



Software Version: 4.1<2F12>  
 Date: 02-2-20 10:25  
 Sample Name : CIh-020128-2  
 Data File : C:\C\CS6\_023.RAW Date: 02-2-20 8:49  
 Sequence File: C:\C\CS6.SEQ Cycle: 1 Channel : A  
 Instrument : 970A\_-0 Rack/Vial: 0/0 Operator: DIN  
 Sample Amount : 1.0000 Dilution Factor : 1.00

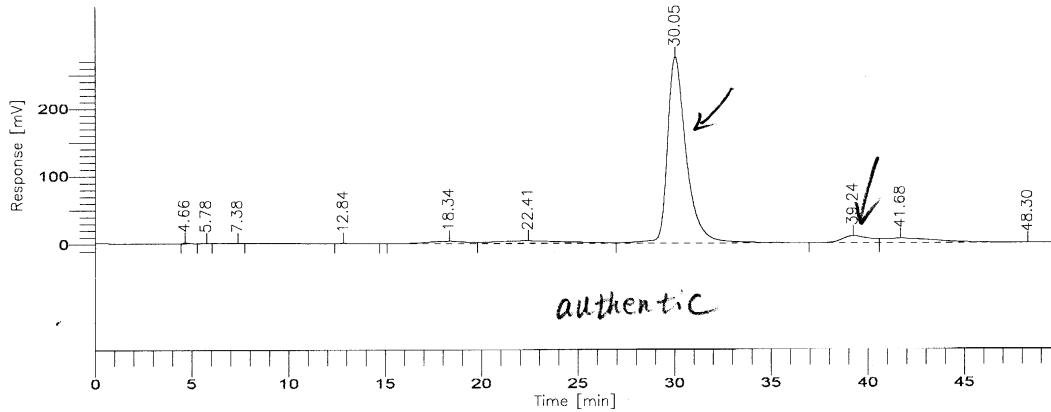


Chiral AD column; 254 nm; Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height [sec]
1	4.815	57461.50	2323.33	0.29	0.29	BB	24.7324
2	5.715	83107.00	5746.56	0.42	0.42	BB	14.4621
3	7.714	21665.70	776.36	0.11	0.11	BV	27.9067
4	9.275	17830.30	284.57	0.09	0.09	VB	62.6561
5	10.691	41826.50	2278.50	0.21	0.21	BB	18.3570
6	12.150	6507.97	203.48	0.03	0.03	BV	31.9829
7	12.997	18098.34	507.82	0.09	0.09	VV	35.6391
8	13.847	124342.00	3655.05	0.63	0.63	VV	34.0192
9	14.650	96082.76	3316.47	0.49	0.49	VB	28.9714
10	17.383	32088.49	634.93	0.16	0.16	BV	50.5387
11	18.783	5376.51	139.56	0.03	0.03	VB	38.5255
12	21.642	1729.00	47.64	0.01	0.01	BB	36.2915
13	22.942	4563.82	65.07	0.02	0.02	BV	70.1320
14	24.708	5790.52	115.33	0.03	0.03	VV	50.2100
15	25.767	5501.66	84.13	0.03	0.03	VB	65.3929
16	30.864	9563171.00	132464.37	48.80	48.80	BB	72.1943
17	40.304	9510121.00	105260.35	48.53	48.53	BB	90.3486

19595264.07 257903.53 100.00 100.00

Software Version: 4.1<2F12>  
 Date: 02-2-20 10:41  
 Sample Name : CIh-020128-3b  
 Data File : C:\C\CS6\_024.RAW Date: 02-2-20 9:49  
 Sequence File: C:\C\CS6.SEQ Cycle: 1 Channel : A  
 Instrument : 970A\_-0 Rack/Vial: 0/0 Operator: DIN  
 Sample Amount : 1.0000 Dilution Factor : 1.00



Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL	Area/Height [sec]
1	4.657	21835.00	1205.40	0.10	0.10	BB	18.1142
2	5.775	4555.81	144.74	0.02	0.02	BV	31.4757
3	7.382	4905.69	147.83	0.02	0.02	VB	33.1845
4	12.835	13338.00	507.63	0.06	0.06	BB	26.2752
5	18.336	535721.87	3783.28	2.36	2.36	BV	141.6027
6	22.408	1078311.51	3837.06	4.75	4.75	VV	281.0254
7	30.048	18730707.45	275699.04	82.45	82.45	VV	67.9390
8	39.242	1033535.39	10278.68	4.55	4.55	VV	100.5513
9	41.675	1281466.37	6443.84	5.64	5.64	VE	198.8670
10	48.303	14034.41	149.58	0.06	0.06	EB	93.8260

22718411.50 302197.08 100.00 100.00

## 色谱分析报告

样品名称: 分析谱图

样品文件名: clh041121-1.che

样品批号:

分析者:

分析日期: 2004-11-29

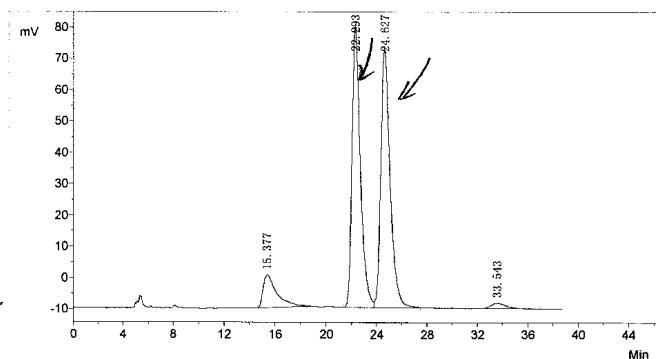
分析时间: 14:58

色谱柱:

流动相:

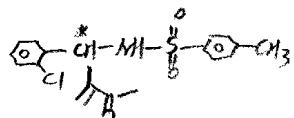
流速:

检测波长:



*racemic*

No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	15.377	10386.7	765601.4	8.3131
2	2	Unknown	22.293	89683.2	4128990.5	44.8335
3	3	Unknown	24.627	82508.6	4190339.6	45.4996
4	4	Unknown	33.543	1601.0	124688.3	1.3539
Total			184179.5	9209619.8	100.0000	

AD column  $\lambda: 254 \text{ nm}$ Hexane/isopropanol: 80/20  $0.7 \text{ mL/min}$

## 色谱分析报告

样品名称: 分析谱图

样品文件名: clh041121-4.che

样品批号:

分析者:

分析日期: 2004-11-29

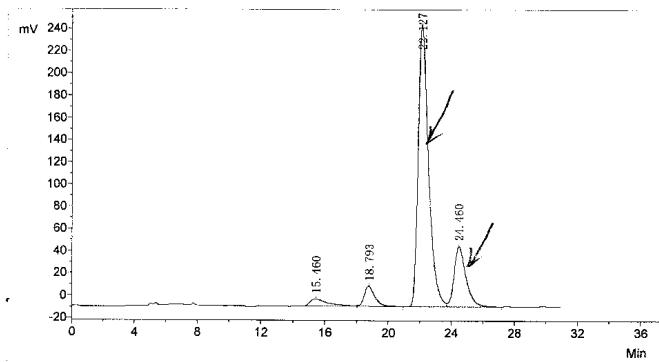
分析时间: 15:37

色谱柱:

流动相:

流速:

检测波长:



*authentic*

No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	15.460	6293.0	458532.9	2.9481
2	2	Unknown	18.793	17367.1	779885.4	5.0142
3	3	Unknown	22.127	253509.2	11537546.7	74.1795
4	4	Unknown	24.460	53590.9	2777590.0	17.8582
Total			330760.4	15553555.0	100.0000	

ee% 61%

## 色谱分析报告

样品名称: 分析谱图

样品文件名: clh-041118-5.che

样品批号:

分析者:

分析日期: 2004-12-01

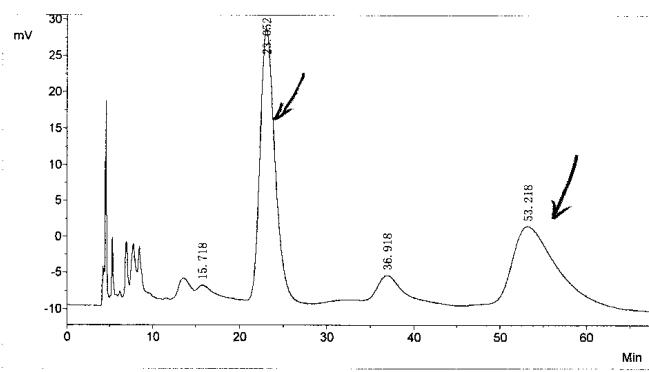
分析时间: 09:05

色谱柱:

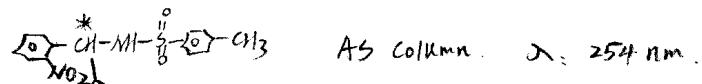
流动相:

流速:

检测波长:

*racemic*

序号	峰号	组份名	保留时间	峰高	峰面积	面积百分比(%)
1	1	Unknown	15.718	888.6	79477.4	0.9105
2	2	Unknown	23.052	37528.2	4446731.0	50.9433
3	3	Unknown	36.918	3367.1	564733.9	6.4698
4	4	Unknown	53.218	10724.3	3637834.0	41.6763
合计:				52508.2	8728776.3	100.0000



Hexane/isopropanol: 60/40  $0.7 \text{ mL/min}$

## 色谱分析报告

样品名称:分析谱图

样品文件名:clh-041121-2.che

样品批号:

分析者:

分析日期:2004-12-01

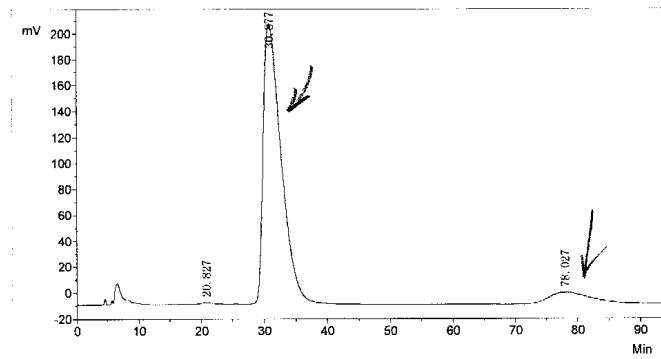
分析时间:10:36

色谱柱:

流动相:

流速:

检测波长:



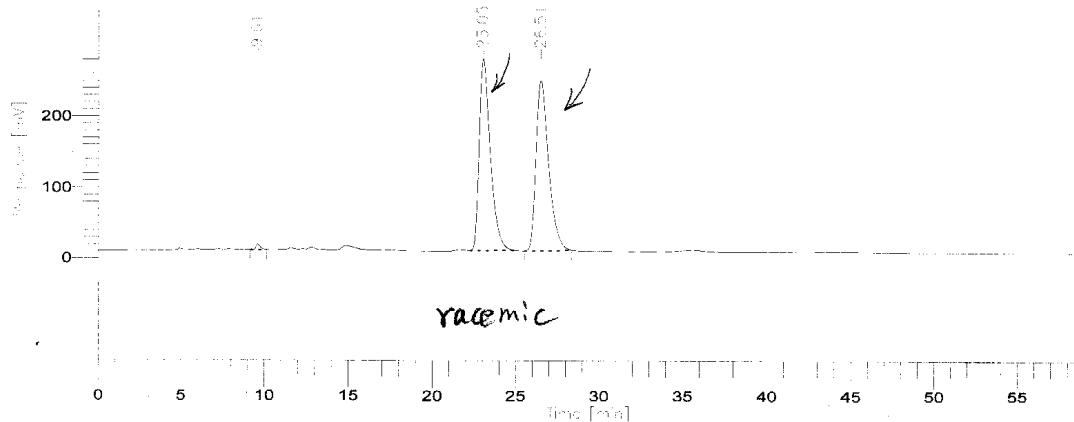
*authentic*

序号	峰号	组份名	保留时间	峰高	峰面积	面积百分比(%)
1	1	Unknown	20.827	1210.5	150526.4	0.3219
2	2	Unknown	30.877	216316.5	42608124.6	91.1258
3	3	Unknown	78.027	8889.5	3998814.1	8.5522
合计:				226416.5	46757465.1	100.0000

*ee% 84%*

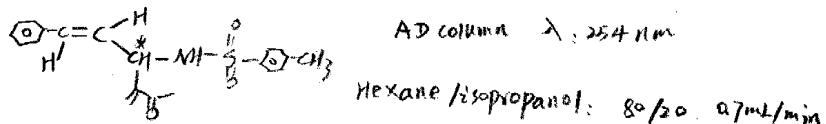
*The prolonged retention time is due to the supplement  
of eluent.*

Software Version: 4.1<2F12>  
 Date: 04-12-3 13:4'  
 Sample Name : clh041\_24-2  
 Data File : D:\TC4\DATA\CAO\CAP\_070M.RAW Date: 04-12-2 11:20  
 Sequence File: D:\TC4\DATA\CAO\CAP.SEQ Cycle: 1 Channel : A  
 Instrument : 970A - 0 Rack/Vial: 0/0 Operator:  
 Sample Amount : 1.0000 Dilution Factor : 1.00

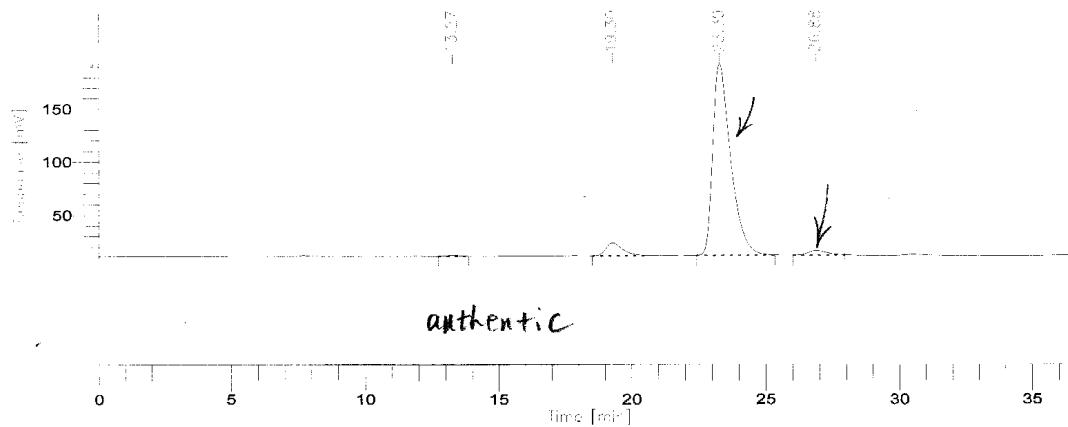


## REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height
1	9.612	137717.00	7970.27	0.54	0.00	BB	17.2788
2	23.046	12564581.00	269608.13	49.54	0.00	BB	46.6031
3	26.506	12658723.00	239901.29	49.91	0.00	BB	52.7664
25361021.00			517479.68	100.00	0.00		



Software Version: 4.1<2F12>  
 Date: 04-12-3 13:46  
 Sample Name : clh-041126-3  
 Data File : D:\TC4\DATA\CAO\CAP\_070N.RAW Date: 04-12-2 13:51  
 Sequence File: D:\TC4\DATA\CAO\CAP.SEQ Cycle: 1 Channel : A  
 Instrument : 970A - 0 Rack/Vial: 0/0 Operator:  
 Sample Amount : 1.0000 Dilution Factor : 1.00

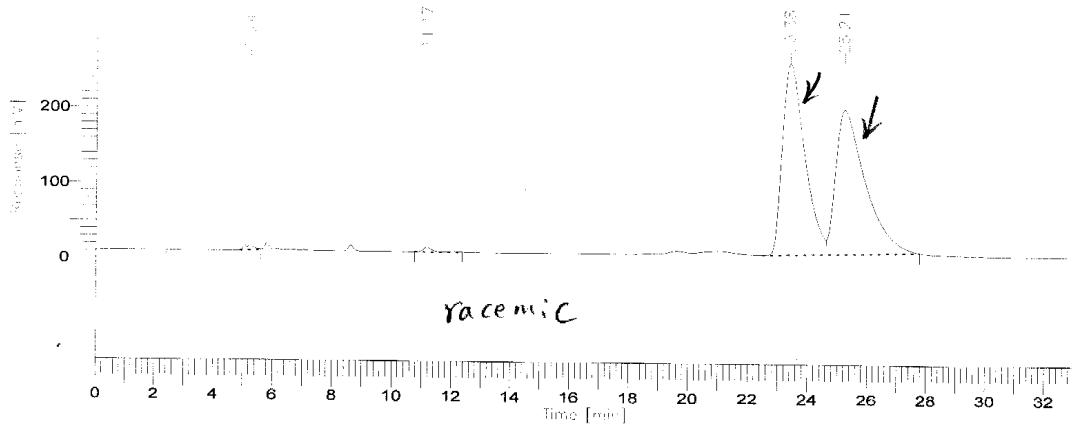


## REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height
1	13.271	35813.50	1331.05	0.39	0.00	BB	26.9063
2	19.298	519463.50	12211.10	5.72	0.00	BB	42.5403
3	23.297	8319116.00	180633.33	91.65	0.00	BB	46.0553
4	26.879	202843.00	4311.87	2.23	0.00	BB	47.0429
<hr/>							
9077236.00 198487.34 100.00 0.00							

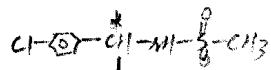
ee% 95%

Software Version: 4.1<2F12>  
 Date: 04-12-3 13:43  
 Sample Name : clh041126-3  
 Data File : D:\TC4\DATA\CAO\CAP\_070U.RAW Date: 04-12-3 11:36  
 Sequence File: D:\TC4\DATA\CAO\CAP.SEQ Cycle: 1 Channel : A  
 Instrument : 970A - 0 Rack/Vial: 0/0 Operator:  
 Sample Amount : 1.0000 Dilution Factor : 1.00



## REPORT

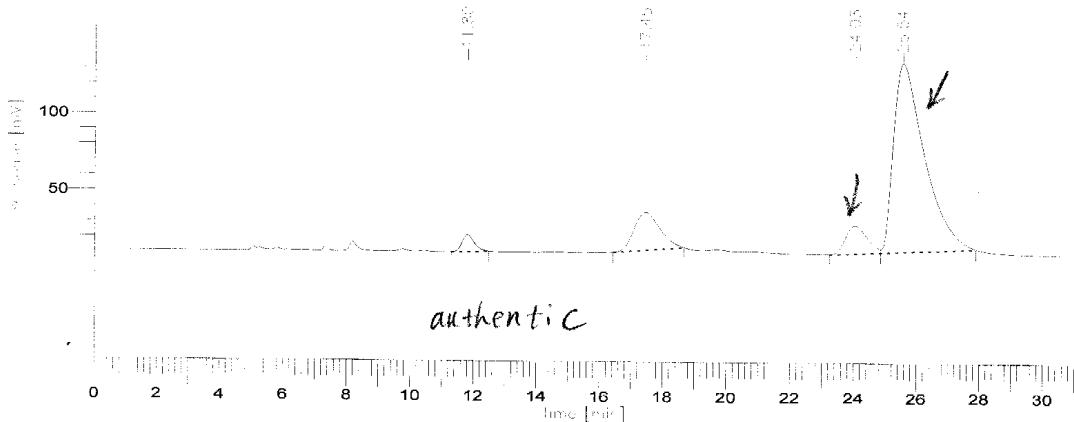
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL	Area/Height [sec]
1	5.240	137027.50	7433.01	0.51	0.00	BB	18.4350
2	11.168	144321.00	6068.88	0.54	0.00	BB	23.7805
3	23.384	13228442.07	253822.58	49.30	0.00	BV	52.1169
4	25.206	13321416.93	191764.10	49.65	0.00	VB	69.4677
				26831207.50	459088.58	100.00	0.00



OD column  $\lambda = 254 \text{ nm}$

Hexane/isopropanol = 85/15  $\text{cm}^2/\text{min}$

Software Version: 4.1<2F12>  
 Date: 04-12-3 13:44  
 Sample Name : clh041126-2  
 Data File : D:\TC4\DATA\CAO\CAP\_070T.RAW Date: 04-12-3 11:04  
 Sequence File: D:\TC4\DATA\CAO\CAP.SEQ Cycle: 1 Channel : A  
 Instrument : 970A\_-0 Rack/Vial: 0/0 Operator:  
 Sample Amount : 1.0000 Dilution Factor : 1.00

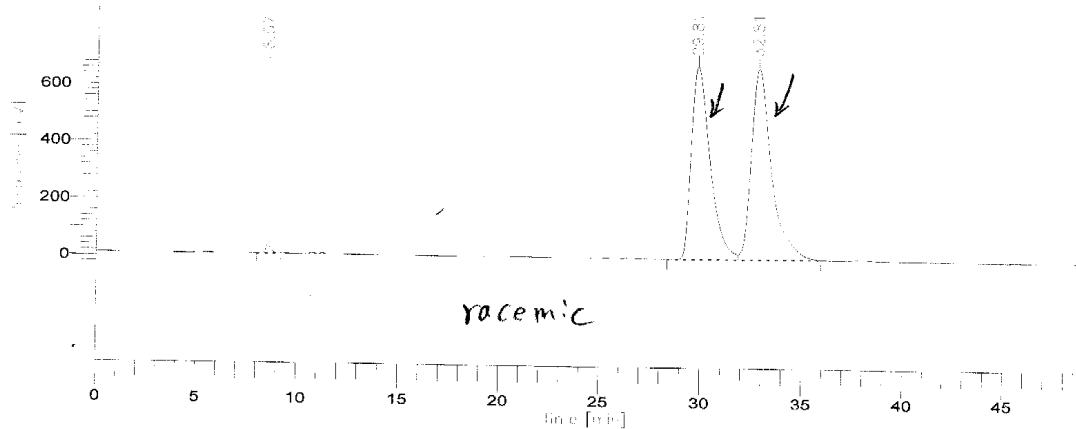


## REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height
1	11.798	292325.50	10926.49	2.66	0.00	BB	26.7538
2	17.453	1391490.50	24554.74	12.67	0.00	BB	56.6689
3	24.028	854731.30	18105.05	7.78	0.00	BV	47.2095
4	25.540	8440841.70	123100.64	76.88	0.00	VB	68.5686
				10979389.00	176686.93	100.00	0.00

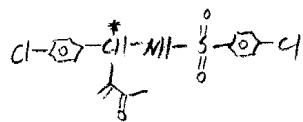
ee% 82%

Software Version: 4.1<2F12>  
 Date: 04-12-1 16:34  
 Sample Name : clh041117-2  
 Data File : D:\TC4\DATA\CAO\CAP\_070J.RAW Date: 04-12-1 13:31  
 Sequence File: D:\TC4\DATA\CAO\CAP.SEQ Cycle: 1 Channel : A  
 Instrument : 970A - 0 Rack/Vial: 0/0 Operator:  
 Sample Amount : 1.0000 Dilution Factor : 1.00



## REPORT

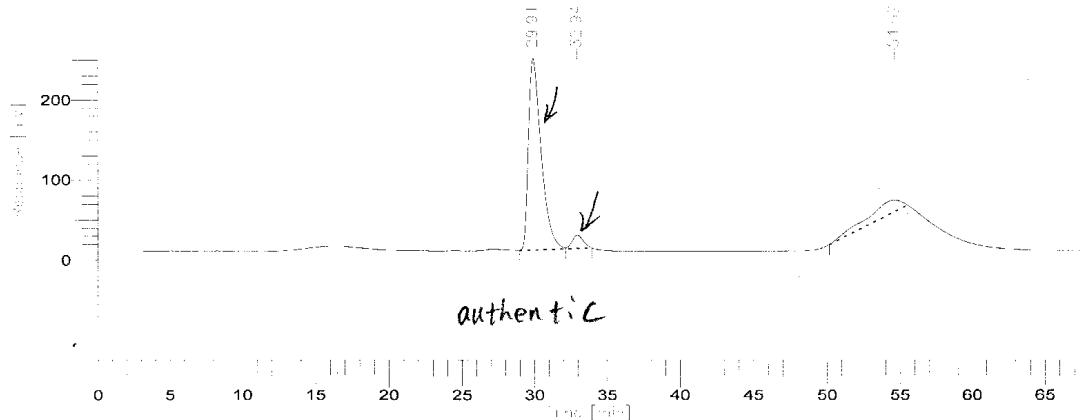
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height [sec]
1	8.568	541713.00	31531.93	0.60	0.00	BB	17.1798
2	29.808	43536715.55	677744.91	48.22	0.00	BV	64.2376
3	32.809	46209287.45	671643.83	51.18	0.00	VB	68.8003
		90287716.00	1.38e+06	100.00	0.00		



AD column  $\lambda = 254 \text{ nm}$

Hexane / Isopropanol = 80/20 0.7 mL/min.

Software Version: 4.1<2F12>  
Date: 04-12-1 16:34  
Sample Name : clh041121-3  
Data File : D:\TC4\DATA\CAO\CAP\_070K.RAW Date: 04-12-1 14:24  
Sequence File: D:\TC4\DATA\CAO\CAP.SEQ Cycle: 1 Channel : A  
Instrument : 970A - 0 Rack/Vial: 0/0 Operator:  
Sample Amount : 1.0000 Dilution Factor : 1.00



## REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area %	Norm. Area [%]	BL [sec]	Area/Height
1	29.905	14607469.64	238500.25	79.90	0.00	BV	61.2472
2	32.943	877471.36	16544.08	4.80	0.00	VB	53.0384
3	54.618	2796717.00	14652.20	15.30	0.00	BB	190.8735
18281658.00			269696.54	100.00	0.00		

89%

## 色谱分析报告

样品名称:分析谱图

样品文件名:clh-041118-3..che

样品批号:

分析者:

分析日期:2004-12-06

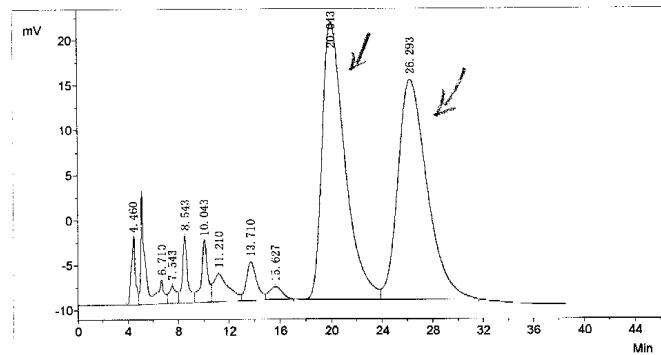
分析时间:08:46

色谱柱:

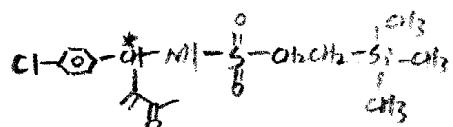
流动相:

流速:

检测波长:

*racemic*

No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	4.460	7411.2	168216.1	1.7962
2	2	Unknown	6.710	2508.3	348520.4	3.7214
3	3	Unknown	7.543	1922.9	76420.2	0.8160
4	4	Unknown	8.543	7432.8	215348.2	2.2994
5	5	Unknown	10.043	6733.7	240646.7	2.5696
6	6	Unknown	11.210	3081.0	253677.4	2.7087
7	7	Unknown	13.710	4276.6	241179.1	2.5753
8	8	Unknown	15.627	1404.0	99080.8	1.0580
9	9	Unknown	20.043	30666.1	3818174.9	40.7696
10	10	Unknown	26.293	24391.3	3903987.3	41.6859
Total			89827.8	9365251.1	100.0000	

AS column .  $\lambda$ : 254 nm

Hexane / isopropanol . 80/20, 0.7 mL/min

## 色谱分析报告

样品名称: 分析谱图

样品文件名: clh-041118-1.che

样品批号:

分析者:

分析日期: 2004-12-06

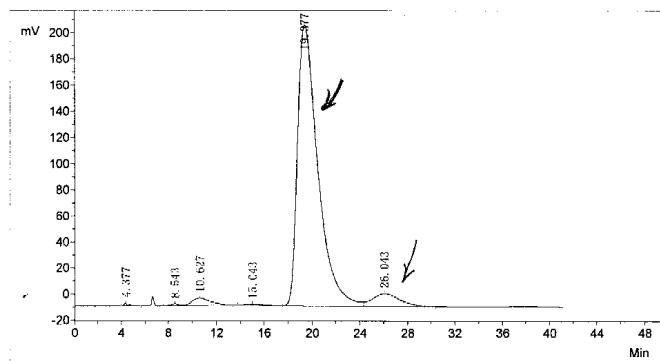
分析时间: 09:27

色谱柱:

流动相:

流速:

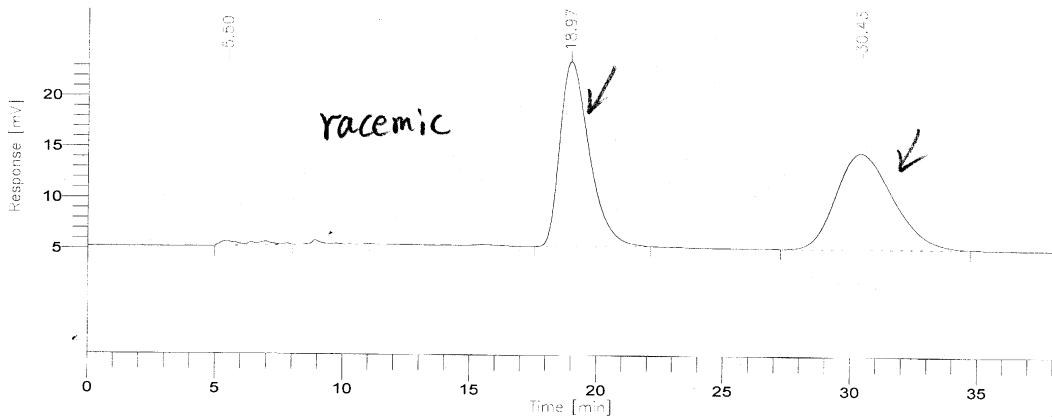
检测波长:

*authentic*

No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1	Unknown	4.377	2289.5	56174.3	0.2025
2	2	Unknown	8.543	1423.1	72629.4	0.2619
3	3	Unknown	10.627	5806.9	597418.4	2.1539
4	4	Unknown	15.043	753.0	91433.0	0.3296
5	5	Unknown	19.377	215183.4	25379391.5	91.5004
6	6	Unknown	26.043	9631.8	1539864.6	5.5517
Total				235087.7	27736911.2	100.0000

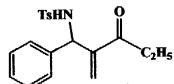
*ee: 89%*

Software Version: 4.1<2F12>  
 Date: 02-11-13 15:45  
 Sample Name : xu6-93a  
 Data File : D:\TC4\DATA\CAO\CAO\_336K.RAW Date: 02-11-13 15:04  
 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



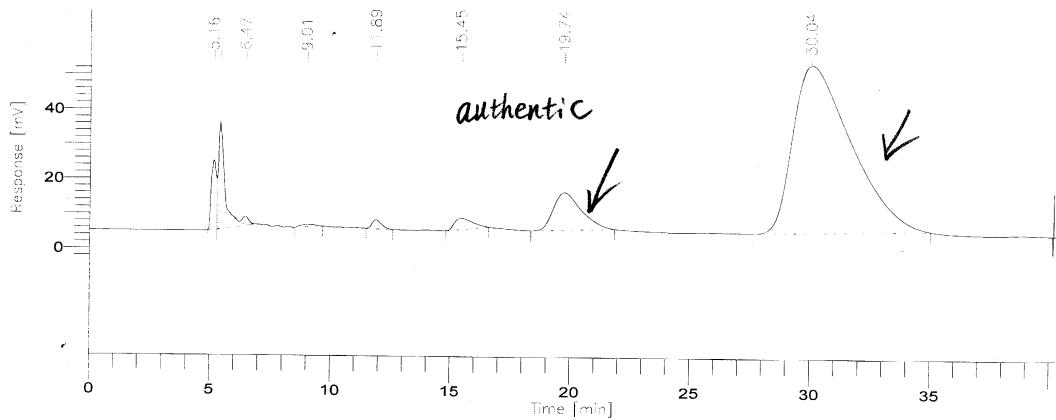
## REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height [sec]
1	5.499	48551.00	506.05	1.62	0.00	BB	95.9405
2	18.973	1470911.00	18236.94	49.09	0.00	BB	80.6556
3	30.426	1476820.50	9459.31	49.29	0.00	BB	156.1235
2996282.50				28202.30	100.00	0.00	



Chiral OJ column; 254 nm; Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min

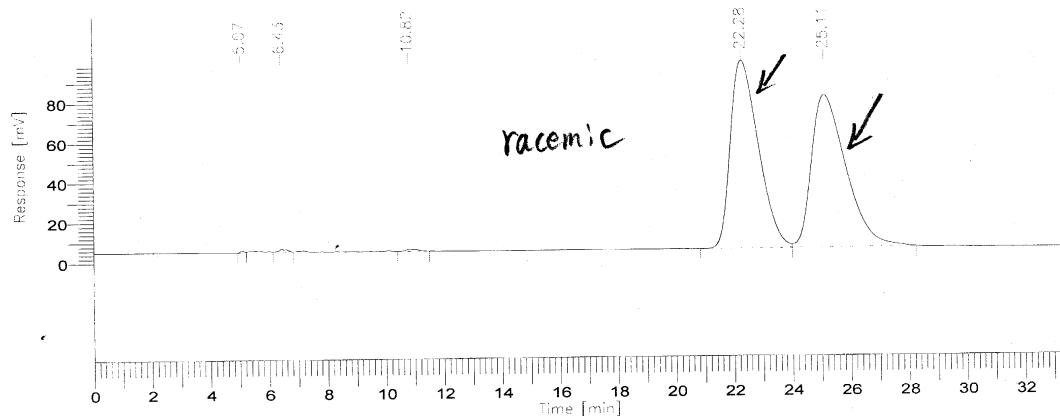
Software Version: 4.1<2F12>  
 Date: 02-11-13 16:25  
 Sample Name : clh-021028-1  
 Data File : D:\TC4\DATA\CAO\CAO\_336L.RAW Date: 02-11-13 15:43  
 Sequence File: D:\TC4\DATA\CAO\CAO.SEQ Cycle: 1 Channel : A  
 Instrument : 970A - 0 Rack/Vial: 0/0 Operator: CAO  
 Sample Amount : 1.0000 Dilution Factor : 1.00



## REPORT

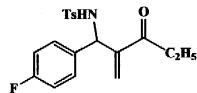
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [uV]	Norm. Area [%]	BL [sec]	Area/Height [sec]
1	5.156	295609.01	19847.66	2.89	0.00	BV	14.8939
2	5.411	568651.24	30691.47	5.56	0.00	VE	18.5280
3	6.470	46202.50	2307.49	0.45	0.00	EB	20.0229
4	9.007	26876.50	653.00	0.26	0.00	BB	41.1585
5	11.887	70992.00	2645.95	0.69	0.00	BB	26.8304
6	15.446	170551.50	3229.59	1.67	0.00	BB	52.8090
7	19.741	882103.50	10752.01	8.63	0.00	BB	82.0408
8	30.044	8160263.50	48239.85	79.84	0.00	BB	169.1602
				10221249.75	118367.02	100.00	0.00

Software Version: 4.1<2F12>  
 Date: 02-9-12 15:14  
 Sample Name : xu7-25rac  
 Data File : D:\TC4\DATA\CAO\CAO\_325J.RAW Date: 02-9-12 14:38  
 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



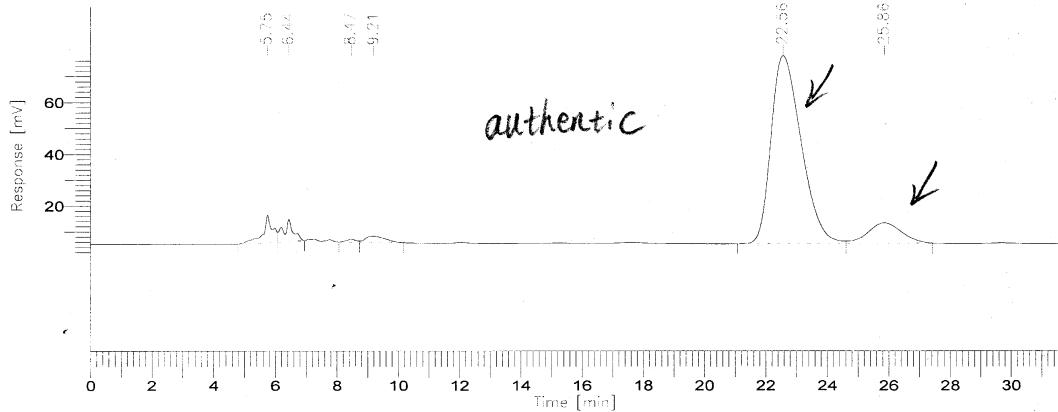
## REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height
1	5.070	6838.50	886.23	0.05	0.00	BB	7.7164
2	6.426	24324.00	1330.65	0.19	0.00	BB	18.2797
3	10.819	31799.25	1013.36	0.25	0.00	BB	31.3802
4	22.277	6312439.89	93852.81	49.96	0.00	BV	67.2589
5	25.114	6258705.11	76149.64	49.54	0.00	VB	82.1896
<hr/>							
12634106.75 173232.69 100.00 0.00							



Chiral AS column; 254 nm; Hexane/Isopropanol = 75/25; Flow rate: 0.7 mL/min

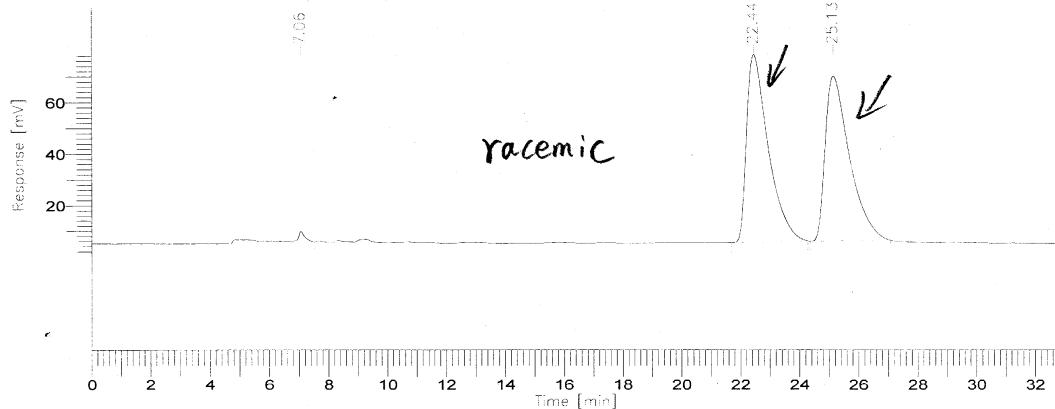
Software Version: 4.1<2F12>  
Date: 02-9-12 15:47  
Sample Name : clh-020902-1  
Data File : D:\TC4\DATA\CAO\CAO\_325K.RAW Date: 02-9-12 15:13  
Sequence File: D:\TC4\DATA\CAO\CAO.SEQ Cycle: 1 Channel : A  
Instrument : 970A - 0 Rack/Vial: 0/0 Operator: CAO  
Sample Amount : 1.0000 Dilution Factor : 1.00



## REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area	Norm. Area [%]	BL	Area/Height [sec]
1	5.750	234828.24	10603.55	3.83	0.00	BV	22.1462
2	6.442	192976.26	8653.00	3.15	0.00	VB	22.3017
3	8.470	24133.14	1106.44	0.39	0.00	BV	21.8115
4	9.210	106182.36	2400.97	1.73	0.00	VB	44.2247
5	22.564	4963017.14	72631.01	81.00	0.00	BV	68.3319
6	25.856	606309.86	7921.67	9.89	0.00	VB	76.5382
6127447.00				103316.65	100.00		0.00

Software Version: 4.1<2F12>  
 Date: 02-7-18 14:41  
 Sample Name : CLH020711-1  
 Data File : D:\TC4\DATA\CAO\CAO\_318B.RAW Date: 02-7-18 13:49  
 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

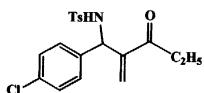


## REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height
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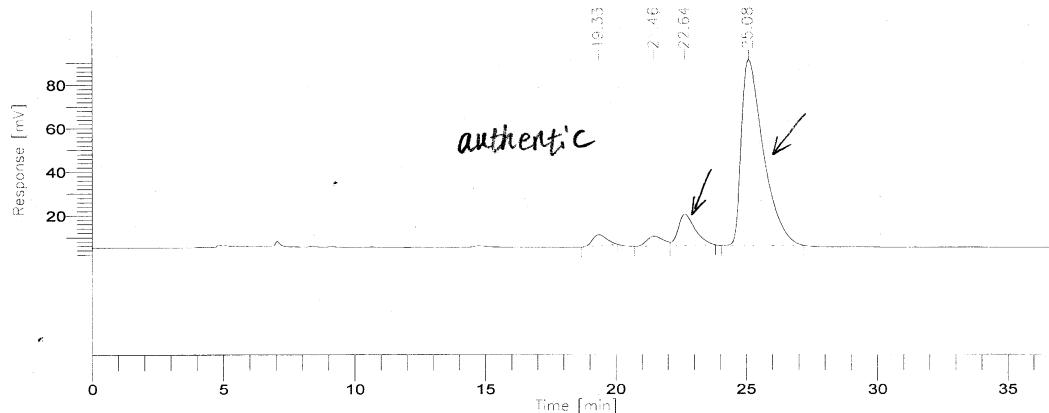
1	7.060	59139.00	4018.10	0.79	0.00	BB	14.7181
2	22.437	3728348.00	72731.23	49.97	0.00	BB	51.2620
3	25.129	3673762.00	64002.77	49.24	0.00	BB	57.4000

7461249.00 140752.10 100.00 0.00



Chiral OD column; 254 nm; Hexane/Isopropanol = 90/10; Flow rate: 0.7 mL/min

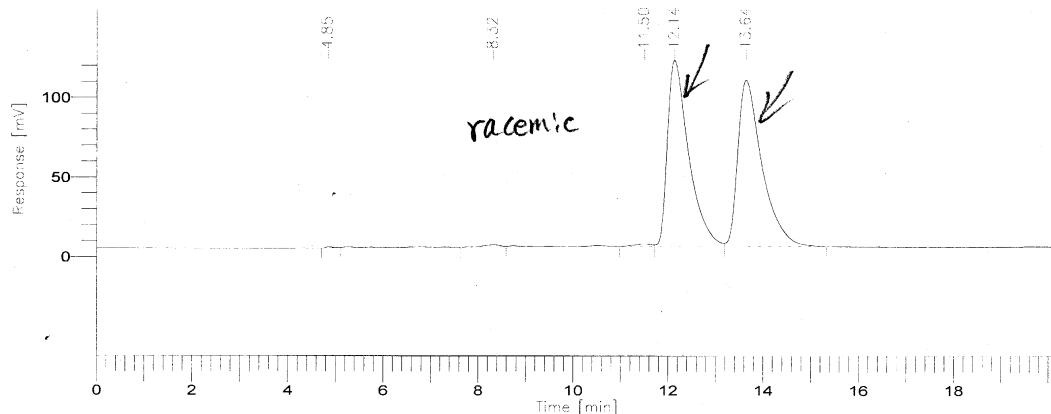
Software Version: 4.1<F12>  
Date: 02-7-18 15:09 .  
Sample Name : CLH02@711-2  
Data File : D:\TC4\DATA\CAO\CAO\_318C.RAW Date: 02-7-18 14:24  
Sequence File: D:\TC4\DATA\CAO\CAO.SEQ Cycle: 1 Channel : A  
Instrument : 970A - 0 Rack/Vial: 0/0 Operator: CAO  
Sample Amount : 1.0000 Dilution Factor : 1.00



## REPORT

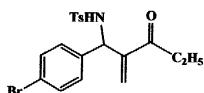
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL	Area/Height [sec]
1	19.334	200504.75	5196.35	3.30	0.00	BB	38.5857
2	21.456	208223.80	4589.50	3.43	0.00	BV	45.3696
3	22.636	644865.70	14380.75	10.62	0.00	VB	44.8423
4	25.075	5020049.25	85065.89	82.65	0.00	BB	59.0137
		6073643.50	109232.49	100.00	0.00		

Software Version: 4.1<2F12>  
 Date: 02-10-28 8:56  
 Sample Name : CLH-021017-1  
 Data File : D:\TC4\DATA\CAO\CAO\_332Z.RAW Date: 02-10-28 8:34  
 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



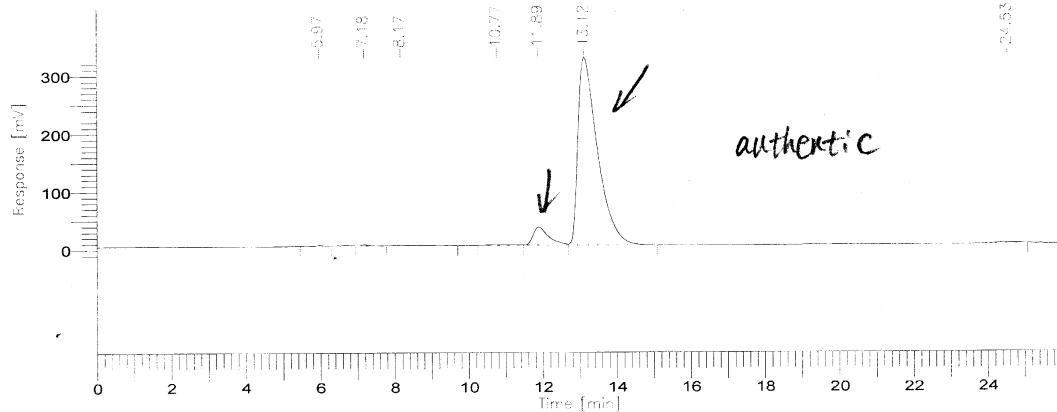
## REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height [sec]
1	4.849	7532.75	667.15	0.10	0.00	BB	11.2909
2	8.322	29499.00	1211.55	0.40	0.00	BB	24.3482
3	11.504	37859.62	1582.38	0.51	0.00	BV	23.9258
4	12.137	3647147.24	116877.36	49.09	0.00	VV	31.2049
5	13.644	3707567.64	104368.51	49.90	0.00	VB	35.5238
<hr/>							
7429606.25 224706.95 100.00 0.00							



Chiral OD column; 254 nm; Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min

Software Version: 4.1<2F12>  
 Date: 02-10-28 10:46  
 Sample Name : ~~044~~-020902-2  
 Data File : D:\TC4\DATA\CAO\CAO\_333.RAW Date: 02-10-28 9:08  
 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



## REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Area BL [sec]	Area/Height
1	5.968	18978.50	1106.60	0.15	0.00	BB	17.1502
2	7.183	21742.25	1808.10	0.17	0.00	BB	12.0249
3	8.166	47669.00	903.50	0.37	0.00	BB	52.7601
4	10.766	61610.98	1238.58	0.47	0.00	BV	49.7431
5	11.887	918187.70	31404.98	7.05	0.00	VV	29.2370
6	13.123	11895625.25	323399.39	91.36	0.00	VB	36.7831
7	24.533	56284.50	927.96	0.43	0.00	BB	60.6543

13020098.19 360789.11 100.00 0.00

\*\*\*\*\* MODEL 1022 RUNLOG for run: CH-10\_74 \*\*\*\*\*

Run terminated manually on Channel A.

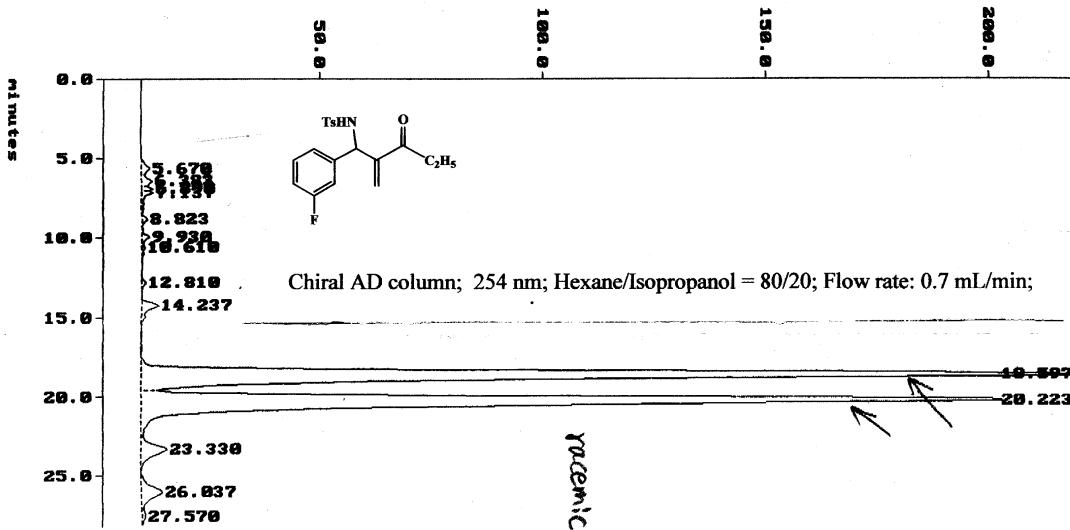
File : CH-10\_74.D01 CLH-021017-2 1  
 Run : 01 Type : Sample  
 Path : C:\CH-4 Inst : 1022 LC Plus  
 Collection : 15:24:58 Oct 28 2002 Method : LCTEST [ 08:32:07 Oct 28 2002 ]  
 Integration: 15:24:58 Oct 28 2002 Method : LCTEST [ 08:32:07 Oct 28 2002 ]  
 Report : 15:53:12 Oct 28 2002 Method : LCTEST [ 08:32:07 Oct 28 2002 ]

## PERCENT ( AREA )

Pk #	RT	Area	Height BC	Area Percent	Height Percent
1	5.670	605543	1.8701 T	0.3909	0.4331
2	6.383	643947	2.3053 T	0.4157	0.5339
3	6.890	366386	2.6089 T	0.2365	0.6042
4	7.137	635849	2.4478 T	0.4104	0.5669
5	8.823	307088	1.2723 T	0.1982	0.2946
6	9.930	426170	1.6912 T	0.2751	0.3916
7	10.610	206264	0.6554	0.1331	0.1518
8	12.810	200710	0.8164 V	0.1296	0.1891
9	14.237	1258708	3.7429	0.8125	0.8668
10	18.597	72048928	209.5836 T	46.5062	48.5349
11	20.223	72784216	193.7442 T	46.9808	44.8668
12	23.330	2734614	5.7432 V	1.7651	1.3300
13	26.037	2409932	4.6375 T	1.5556	1.0739
14	27.570	294919	0.7017	0.1904	0.1625

14 Peaks > Area Reject 154923280 Total Area  
 14 Peaks > Height Reject 431.820 Total Height

(CH-10\_74.D01) MU



\*\*\*\*\* MODEL 1022 RUNLOG for run: CH-10\_75 \*\*\*\*\*

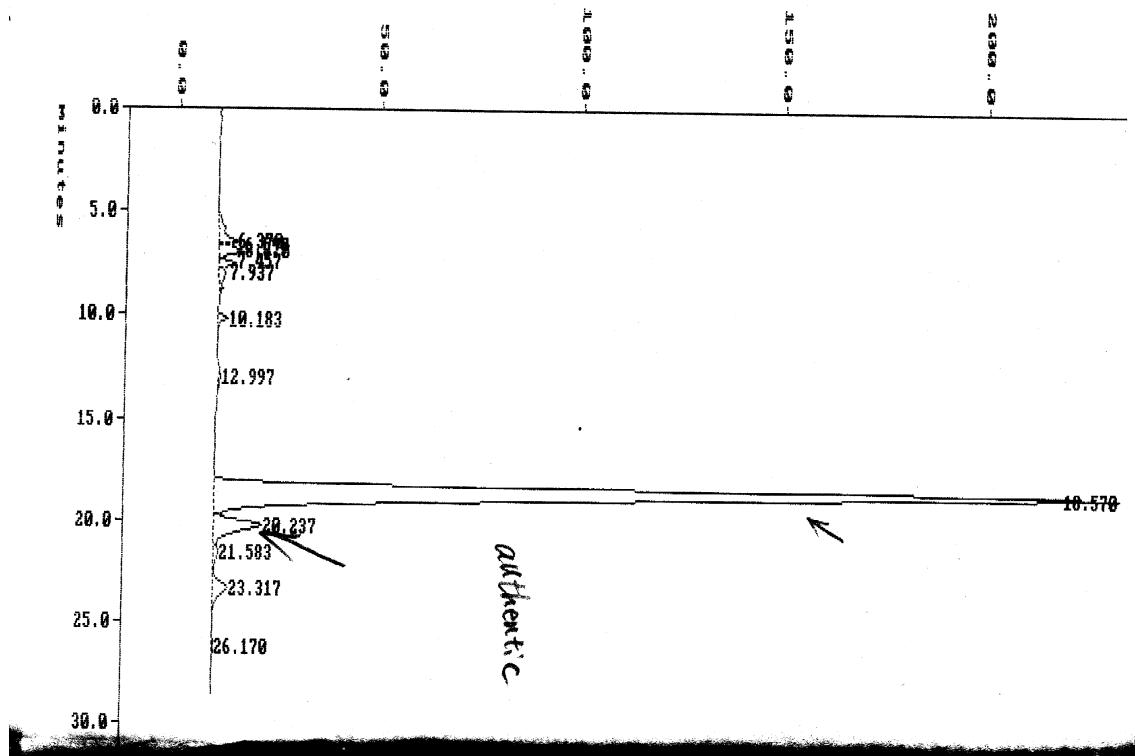
Run terminated manually on Channel A.

File : CH-10\_75.D01 CLH-020904-2 1  
 Run : 01 Type : Sample  
 Path : C:\CH-4 Inst : 1022 LC Plus  
 Collection : 15:54:34 Oct 28 2002 Method : LCTEST [ 08:32:07 Oct 28 2002 ]  
 Integration: 15:54:34 Oct 28 2002 Method : LCTEST [ 08:32:07 Oct 28 2002 ]  
 Report : 16:23:09 Oct 28 2002 Method : LCTEST [ 08:32:07 Oct 28 2002 ]

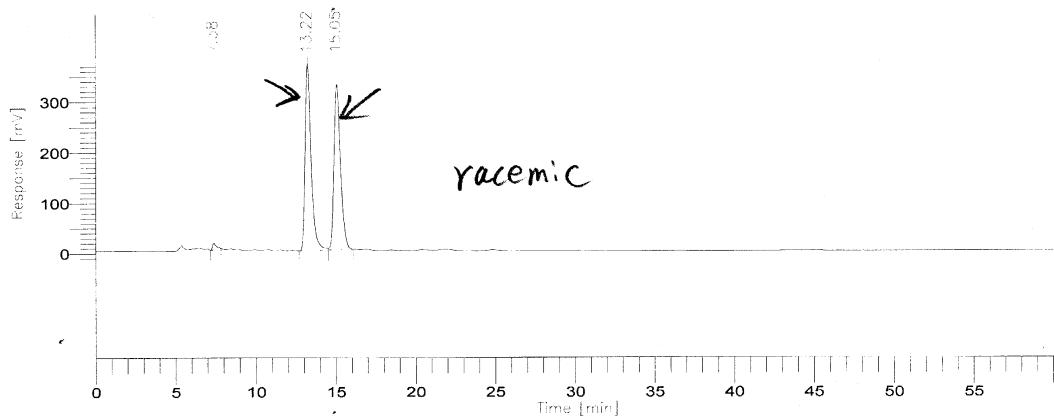
## PERCENT ( AREA )

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	6.370	1393106	4.4452	T	1.5894	1.6853
2	6.597	411710	3.7984	T	0.4697	1.4401
3	6.870	1115813	6.2625	T	1.2730	2.3743
4	7.457	716390	4.1048	T	0.8173	1.5562
5	7.937	722789	1.7122		0.8246	0.6492
6	10.183	454464	2.4933		0.5185	0.9453
7	12.997	172489	0.3488		0.1968	0.1323
8	18.570	75683376	223.6976	T	86.3458	84.8091
9	20.237	4624341	11.9977	T	5.2758	4.5486
10	21.583	515731	1.0646	T	0.5884	0.4036
11	23.317	1715914	3.5986		1.9577	1.3643
12	26.170	125374	0.2421		0.1430	0.0918

12 Peaks > Area Reject 87651496 Total Area  
 12 Peaks > Height Reject 263.766 Total Height

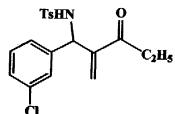


Software Version: 4.1<2F12>  
 Date: 02-11-1 13:09  
 Sample Name : clh021017-3  
 Data File : D:\TC4\DATA\CAO\CAO\_334C.RAW Date: 02-11-1 12:07  
 Sequence File: D:\TC4\DATA\CAO\CAO.SEQ Cycle: 1 Channel : A  
 Instrument : 970A - 0 Rack/Vial: 0/0 Operator: CAO  
 Sample Amount : 1.0000 Dilution Factor : 1.00



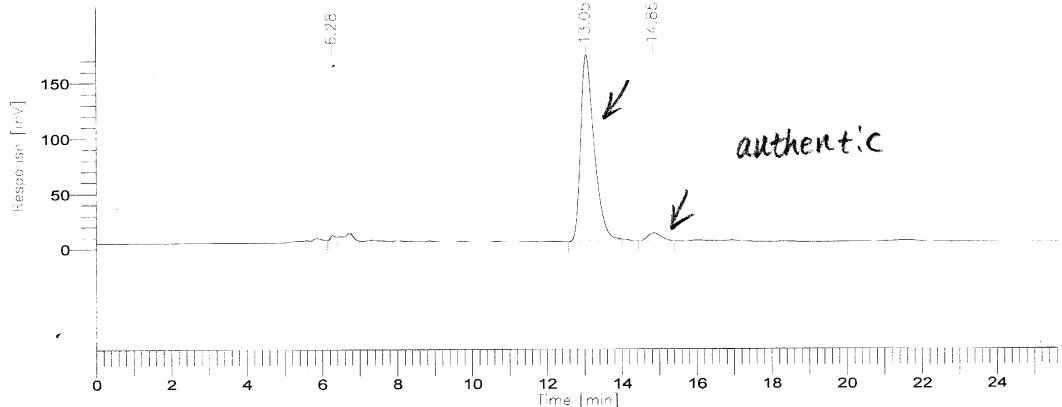
## REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. [%]	Area BL [sec]	Area/Height
1	7.377	235971.50	13953.57	1.22	0.00	BB	16.9112
2	13.221	9759184.69	370799.40	50.43	0.00	BV	26.3193
3	15.050	9358378.56	328265.02	48.35	0.00	VB	28.5086
			19353534.75	713017.99	100.00	0.00	



Chiral AD column; 254 nm; Hexane/Isopropanol = 75/25; Flow rate: 0.7 mL/min

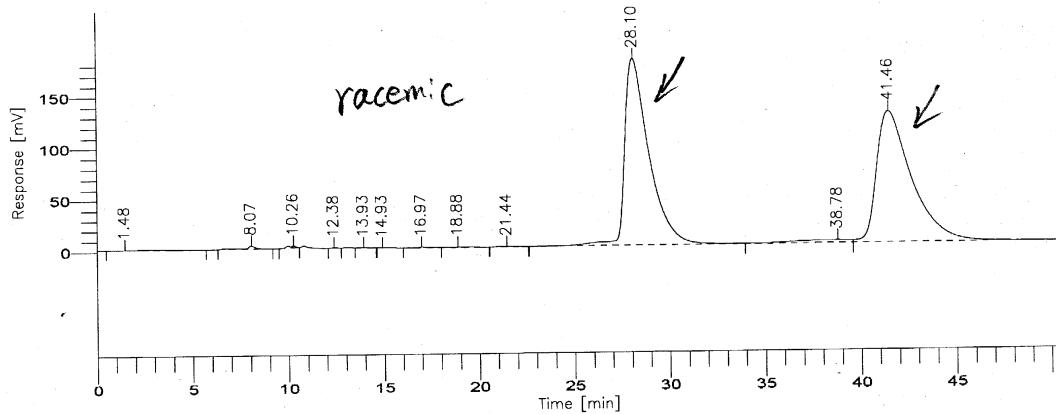
Software Version: 4.1<2F12>  
Date: 02-11-1 13:38  
Sample Name : clh020904-3  
Data File : D:\TC4\DATA\CAO\CAO\_334D.RAW Date: 02-11-1 13:11  
Sequence File: D:\TC4\DATA\CAO\CAO.SEQ Cycle: 1 Channel : A  
Instrument : 970A - 0 Rack/Vial: 0/0 Operator: CAO  
Sample Amount : 1.0000 Dilution Factor : 1.00



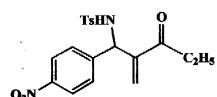
## REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height
1	6.278	22493.75	3013.73	0.51	0.00	BB	7.4638
2	13.052	4184217.50	167407.00	95.31	0.00	BB	24.9943
3	14.849	183408.00	7238.32	4.18	0.00	BB	25.3385
				4390119.25	177659.05	100.00	0.00

Software Version: 4.1<2F12>  
 Date: 02-12-10 14:22  
 Sample Name : CIh-021127-1  
 Data File : C:\C\CS7\_823.RAW Date: 02-12-10 12:12  
 Sequence File: C:\C\CS7.SEQ Cycle: 1 Channel : A  
 Instrument : 970A - 0 Rack/Vial: 0/0 Operator: DIN  
 Sample Amount : 1.0000 Dilution Factor : 1.00

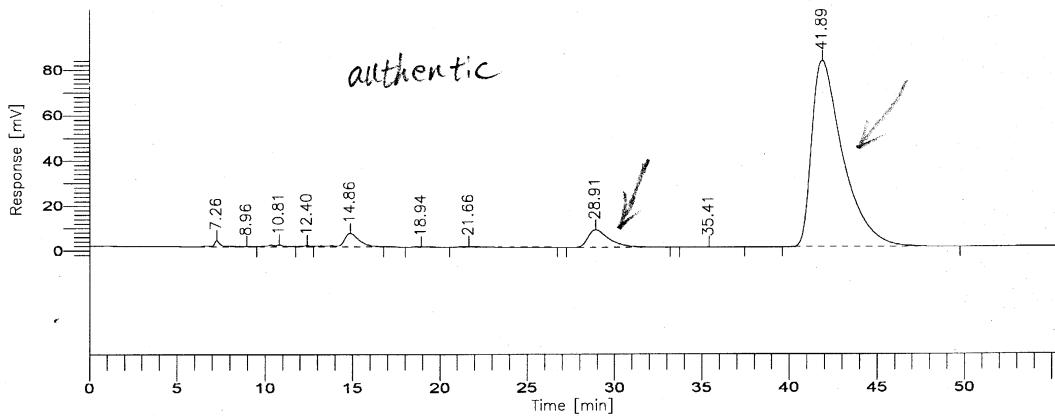


Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height [sec]
1	1.478	56781.00	585.64	0.17	0.00	BB	96.9561
2	8.066	133200.00	3104.22	0.40	0.00	BB	42.9093
3	10.263	59914.00	1789.23	0.18	0.00	BB	33.4860
4	12.379	5883.00	308.65	0.02	0.00	BB	19.0604
5	13.925	11719.50	425.14	0.04	0.00	BB	27.5660
6	14.925	5454.00	221.85	0.02	0.00	BB	24.5841
7	16.971	23319.21	611.70	0.07	0.00	BV	38.1219
8	18.883	40410.29	518.79	0.12	0.00	VB	77.8928
9	21.442	21111.50	356.88	0.06	0.00	BB	59.1555
10	28.102	16134743.06	181520.07	48.35	0.00	BV	88.8868
11	38.775	603223.66	2826.02	1.81	0.00	VV	213.4532
12	41.456	16276863.78	127593.65	48.77	0.00	VB	127.5680
<hr/>							
33372623.00 319861.84 100.00 0.00							



Chiral AS column; 254 nm; Hexane/Isopropanol = 60/40; Flow rate: 0.7 mL/min

Software Version: 4.1<F12>  
Date: 02-12-10 14:21  
Sample Name : CIh-021130-1  
Data File : C:\C\CS7\_824.RAW Date: 02-12-10 13:07  
Sequence File: C:\C\CS7.SEQ Cycle: 1 Channel : A  
Instrument : 970A -0 Rack/Vial: 0/0 Operator: DIN  
Sample Amount : 1.0000 Dilution Factor : 1.00



Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL	Area/Height [sec]
1	7.255	70610.77	2662.45	0.62	0.00	BE	26.5210
2	8.958	9179.00	175.58	0.08	0.00	EV	52.2782
3	10.807	45347.54	812.13	0.40	0.00	VV	55.8380
4	12.401	16895.65	548.28	0.15	0.00	VV	30.8157
5	14.864	357539.05	5890.42	3.14	0.00	VB	60.6984
6	18.942	15754.00	216.78	0.14	0.00	BB	72.6736
7	21.658	29363.50	370.44	0.26	0.00	BB	79.2657
8	28.912	648608.50	7802.77	5.69	0.00	BB	83.1254
9	35.408	7097.00	56.04	0.06	0.00	BB	126.6333
10	41.885	10203371.00	82623.34	89.47	0.00	BB	123.4926
		11403766.00	101158.24	100.00	0.00		

\*\*\*\*\* MODEL 1022 RUNLOG for run: "CH-4\_23 \*\*\*\*\*  
Run terminated manually on Channel A.

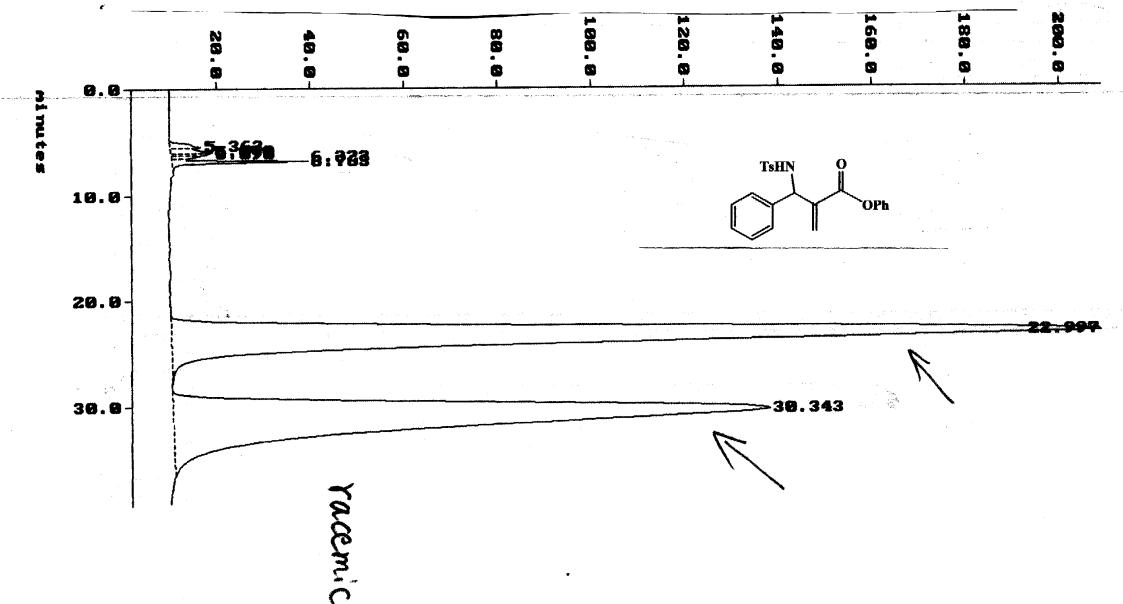
File : CH-4\_23.D01 c1h-020327-1rac 1  
Run #: 01 Type : Sample  
Path : C:\CH-4 Inst : 1022 LC Plus  
Collection : 14:29:21 Apr 05 2002 Method : LCTEST [ 14:27:14 Apr 05 2002 ]  
Integration: 14:29:21 Apr 05 2002 Method : LCTEST [ 14:27:14 Apr 05 2002 ]  
Report : 15:08:37 Apr 05 2002 Method : LCTEST [ 14:27:14 Apr 05 2002 ]

PERCENT ( AREA )

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	5.363	1507345	6.6354	T	0.3823	1.7085
2	5.870	1987307	8.9505	T	0.5041	2.3045
3	6.090	1093435	8.7491	T	0.2773	2.2527
4	6.323	967669	8.1028	T	0.2454	2.0863
5	6.763	3860688	29.2076		0.9792	7.5203
6	22.997	194846432	198.9774		49.4213	51.2321
7	30.343	189992784	127.7616		48.1903	32.8957

7 Peaks > Area Reject 394255648 Total Area  
7 Peaks > Height Reject 388.384 Total Height

Chiral AS column; 254 nm; Hexane/Isopropanol = 60/40; Flow rate: 0.7 mL/min



10. The following table summarizes the results of the study. The first column lists the variables, the second column lists the estimated coefficients, and the third column lists the standard errors.

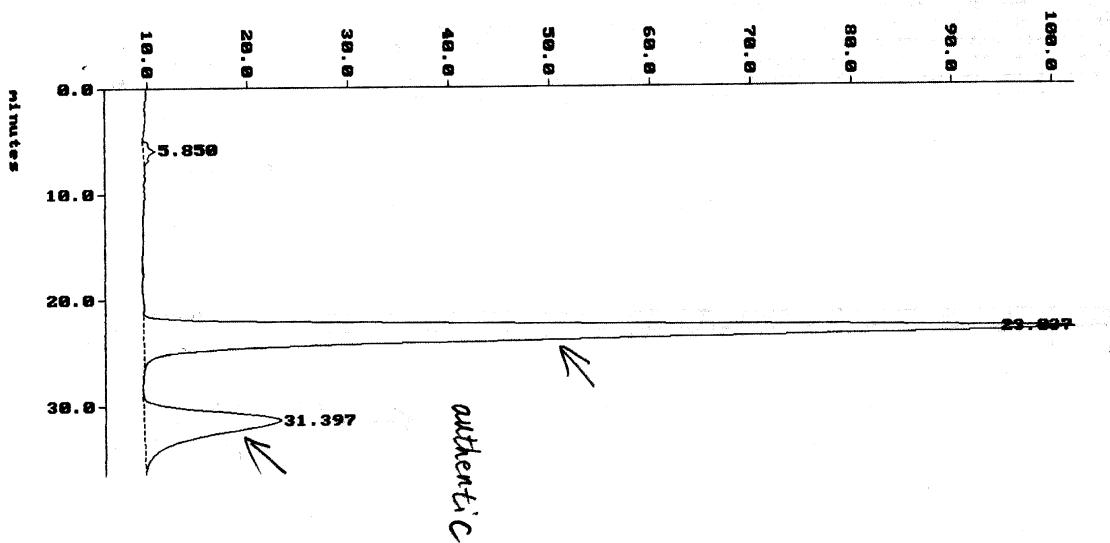
File : CH-4\_24.D01 c1h-020403-1 1  
Run : 01 Type : Sample  
Path : C:\CH-4 Inst : 1022 LC Plus  
Collection : 15:09:23 Apr 05 2002 Method : LCTEST [ 14:27:14 Apr 05 2002 ]  
Integration: 16:11:56 Apr 05 2002 Method : LCTEST [ 14:27:14 Apr 05 2002 ]  
Report : 16:12:03 Apr 05 2002 Method : LCTEST [ 14:27:14 Apr 05 2002 ]

**PERCENT ( AREA )**

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	5.850	672909	1.2107		0.6534	1.1266
2	23.037	82516096	92.5702		80.1239	86.1470

3 Peaks > Area Reject 102985640 Total Area  
3 Peaks > Height Reject 107 456 Total Height

(CH-4 24.091) 54



File : CH-4\_83.D01

CLH-020401-2

1  
Type : Sample

Run : 01

Inst : 1022 LC Plus

Path : C:\CH-4

[ 12:24:56 Apr 23 2002 ]

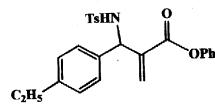
Collection : 12:25:13 Apr 23 2002 Method : LCTEST [ 12:24:56 Apr 23 2002 ]

Integration: 12:25:13 Apr 23 2002 Method : LCTEST [ 12:24:56 Apr 23 2002 ]

Report : 13:55:54 Apr 23 2002 Method : LCTEST [ 12:24:56 Apr 23 2002 ]

## PERCENT ( AREA )

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	5.377	1467177	6.8092	T	0.2488	1.2128
2	5.910	4832543	30.2538	T	0.8196	5.3884
3	6.090	3429993	26.4726	T	0.5817	4.7149
4	6.383	1847208	15.3153	T	0.3133	2.7277
5	6.663	2962692	11.5187		0.5025	2.0515
6	8.817	218286	0.8897		0.0370	0.1585
7	15.883	233993	0.4016		0.0397	0.0715
8	18.897	288685728	303.6220	T	48.9589	54.0766
9	26.243	285971392	166.1834		48.4986	29.5981

9 Peaks > Area Reject 589649024 Total Area  
9 Peaks > Height Reject 561.466 Total Height

Chiral AS column; 254 nm; Hexane/Isopropanol = 60/40; Flow rate: 0.7 mL/min

File : CH-4\_82.D01

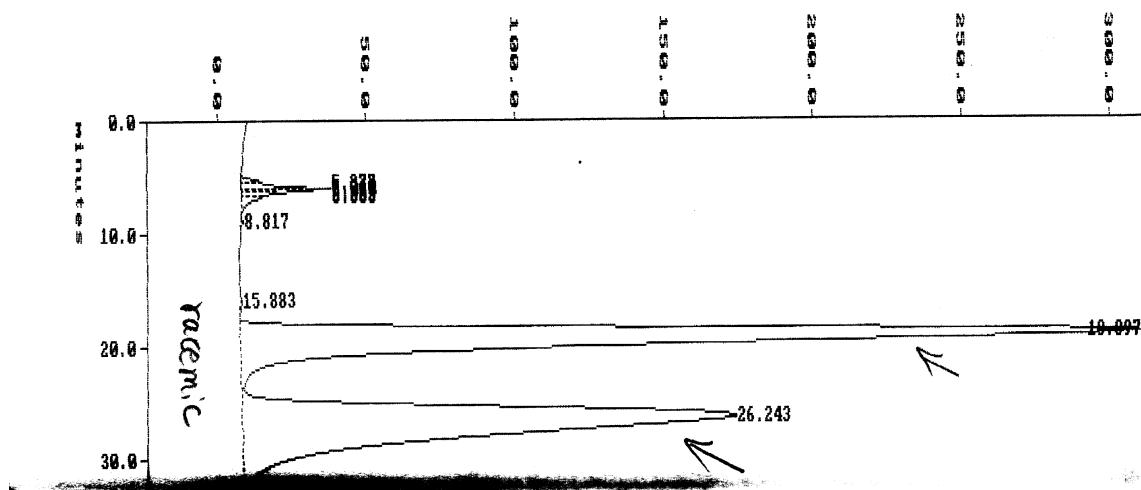
CLH-020401-2

4  
Type : Sample

Run : 01

Collection : 12:25:13 Apr 23 2002 Method : LCTEST [ 12:24:56 Apr 23 2002 ]

(CH-4\_83.D01) mU



\*\*\*\*\* MODEL 1022 RUNLOG for run: CH-4\_84 \*\*\*\*\*  
Run terminated manually on Channel A

File : CH-4\_84.D01  
Run : 01

c1h-020408-3

1

Ran : 01  
Path : C:

Type : Sample

Collection : 1

0 APR 23 2002 1

Integration: 14:09:49 Apr 23 2002 Method : LCTEST [ 14:00:10 Apr 23 2002 ]

Report : 14:43:12 Apr 23 2002 Method : LCTEST [14:00:10 Apr 23 2002]

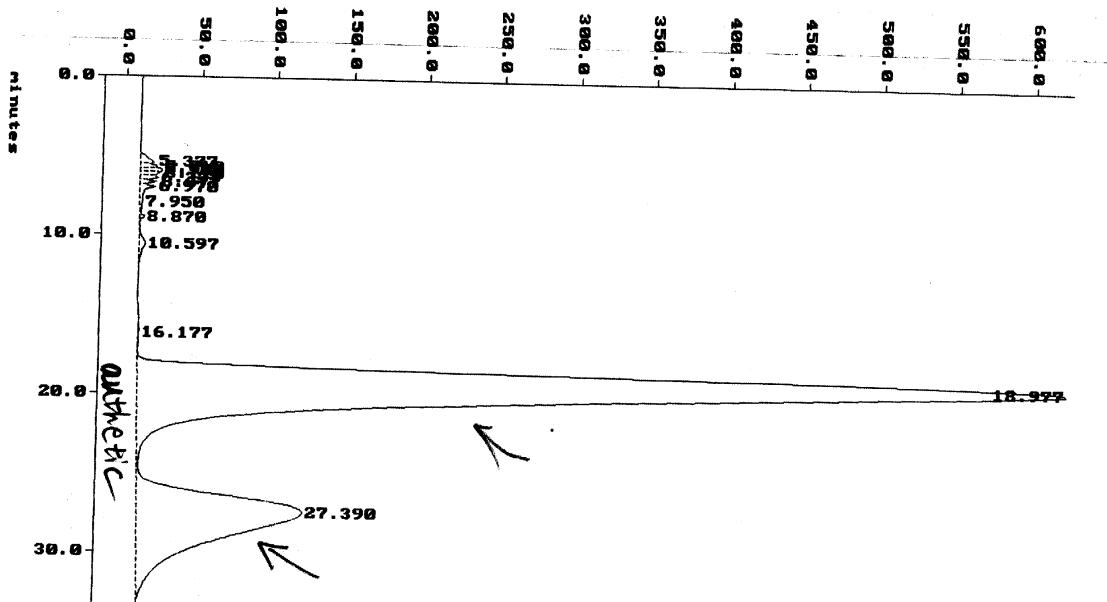
[ 11:00:18 Apr 25 2002 ]

### PERCENT ( AREA )

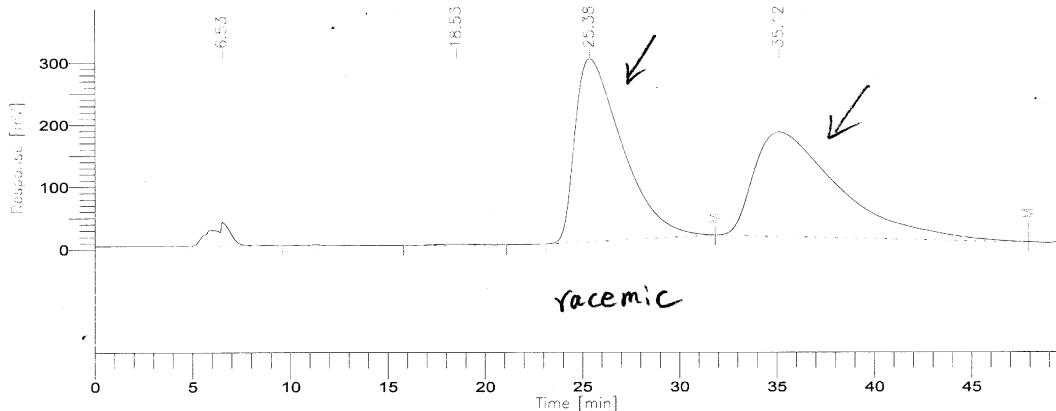
Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	5.377	1787904	8.5642	T	0.2081	1.0557
2	5.710	1583629	10.8709	T	0.1843	1.3401
3	5.903	1612966	14.1475	T	0.1877	1.7440
4	6.110	1918561	13.7141	T	0.2233	1.6906
5	6.377	1525503	12.1592	T	0.1775	1.4989
6	6.677	1130233	10.6742	T	0.1315	1.3158
7	6.970	2092175	10.2165	T	0.2435	1.2594
8	7.950	667534	1.8913	T	0.0777	0.2331
9	8.870	533902	3.1232	T	0.0621	0.3850
10	10.597	2197537	3.6957		0.2557	0.4556
11	16.177	147555	0.2874	V	0.0172	0.0354
12	18.977	645286784	612.5268	T	75.0957	75.5067
13	27.390	198801984	109.3505		23.1357	13.4797

13 Peaks > Area Reject 859286272 Total Area  
13 Peaks > Height Reject 811.221 Total Height

(CH-4\_84.D01) MU

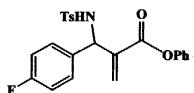


Software Version: 4.1<2F12>  
 Date: 02-4-8 15:28  
 Sample Name : CLH-020325-2  
 Data File : D:\TC4\DATA\CAO\CAO\_298N.RAW Date: 02-4-8 14:34  
 Sequence File: D:\TC4\DATA\CAO\CAO.SEQ Cycle: 1 Channel : A  
 Instrument : 970A - 0 Rack/Vial: 0/0 Operator: CAO  
 Sample Amount : 1.0000 Dilution Factor : 1.00



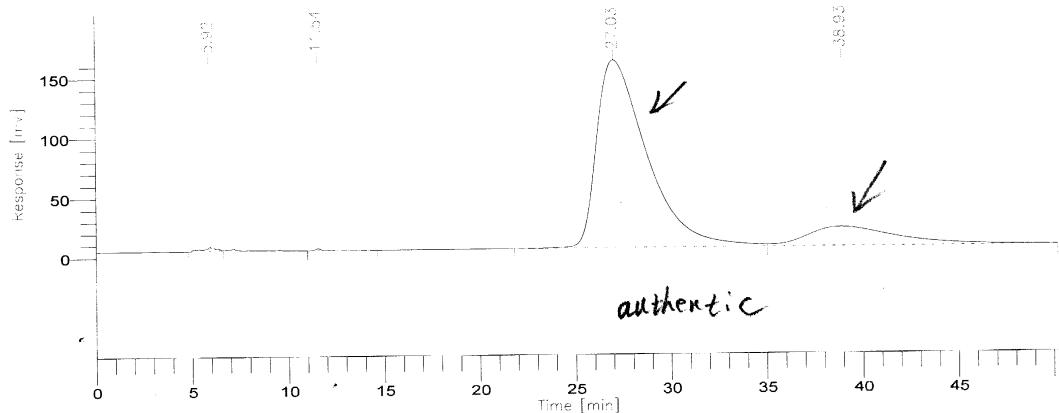
## REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height [sec]
1	6.526	2884731.50	38834.32	2.79	0.00	BB	74.2830
2	18.529	284640.50	1779.20	0.28	0.00	BB	159.9826
3	25.376	49621045.50	293623.12	48.02	0.00	*BB	168.9957
4	35.124	50550991.50	167028.75	48.92	0.00	*BB	302.6484
<hr/>							
1.03e+08 501265.39 100.00 0.00							



Chiral AS column; 254 nm; Hexane/Isopropanol = 60/40; Flow rate: 0.7 mL/min

Software Version: 4.1<2F12>  
Date: 02-4-8 14:36  
Sample Name : CLH-020402-2  
Data File : D:\TC4\DATA\CAO\CAO\_298M.RAW Date: 02-4-8 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



## REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height [sec]
1	5.922	150029.00	3315.15	0.44	0.00	BB	45.2556
2	11.542	37910.25	1609.46	0.11	0.00	BB	23.5546
3	27.026	28824931.08	157175.34	84.05	0.00	BV	183.3935
4	38.930	5282390.92	15998.64	15.40	0.00	VB	330.1776
				34295261.25	178098.59	100.00	0.00

\*\*\*\*\* MODEL 1022 RUNLOG for run: CH-2\_69 \*\*\*\*\*

Run terminated manually on Channel A.

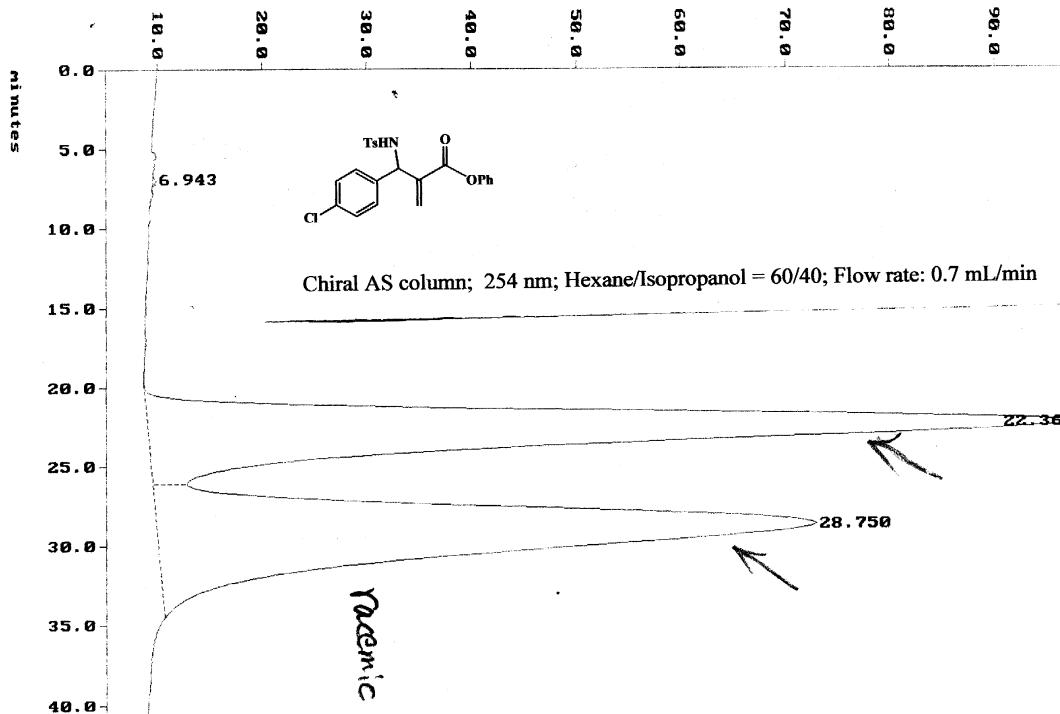
File : CH-2\_69.D01 CLH-020222-1RAC 1  
 Run : 01 Type : Sample  
 Path : C:\CH-4 Inst : 1022 LC Plus  
 Collection : 10:57:00 Feb 27 2002 Method : LCTEST [ 09:00:53 Feb 27 2002 ]  
 Integration: 10:57:00 Feb 27 2002 Method : LCTEST [ 09:00:53 Feb 27 2002 ]  
 Report : 11:37:48 Feb 27 2002 Method : LCTEST [ 09:00:53 Feb 27 2002 ]

PERCENT ( AREA )

Pk #	RT	Area	Height BC	Area Percent	Height Percent
1	6.943	51106	0.2929	0.0212	0.1924
2	22.363	120358472	88.8895 T	49.9949	58.3831
3	28.750	120331888	63.0697	49.9839	41.4245

3 Peaks > Area Reject 240741472 Total Area  
 3 Peaks > Height Reject 152.252 Total Height

(CH-2\_69.D01) mV



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

Run terminated manually on Channel A.

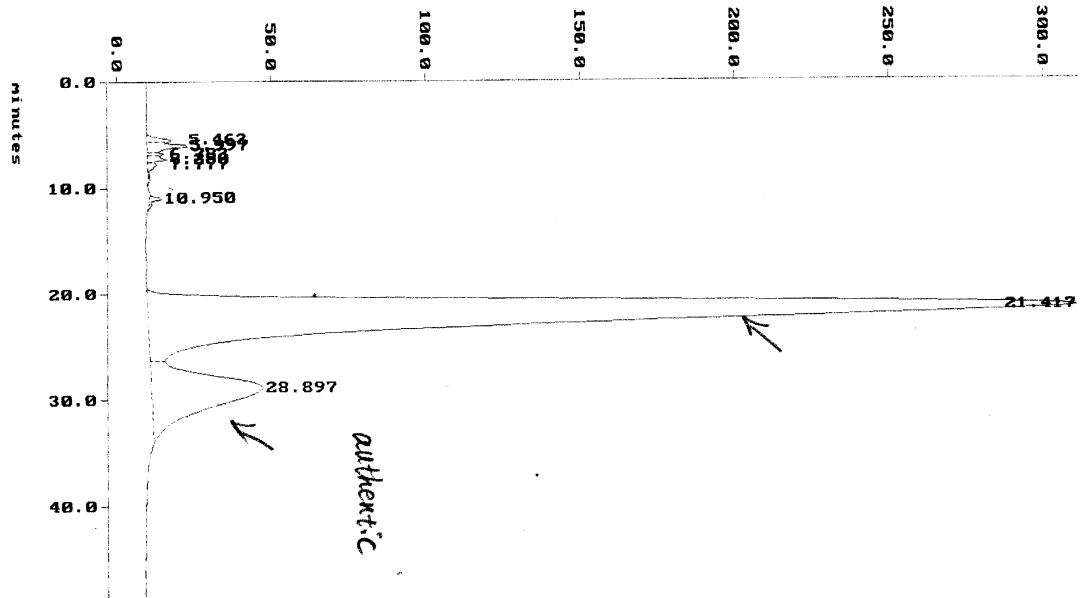
File : CH-2_70.D01	CLH-020222-1	Type : Sample
Run : 01		Inst : 1022 LC Plus
Path : C:\CH-4		[ 11:42:27 Feb 27 2002 ]
Collection : 11:43:48 Feb 27 2002	Method : LCTEST	[ 11:42:27 Feb 27 2002 ]
Integration: 11:43:48 Feb 27 2002	Method : LCTEST	[ 11:42:27 Feb 27 2002 ]
Report : 12:32:52 Feb 27 2002	Method : LCTEST	[ 11:42:27 Feb 27 2002 ]

PERCENT ( AREA )

Pk #	RT	Area	Height BC	Area Percent	Height Percent
1	5.463	1734638	7.8163 T	0.3484	2.0714
2	5.997	4561207	13.0837 T	0.9160	3.4674
3	6.783	901958	5.3914 T	0.1811	1.4288
4	7.250	1517485	6.4555 T	0.3048	1.7108
5	7.777	1458817	3.1311	0.2930	0.8298
6	10.950	947739	3.7852	0.1903	1.0031
7	21.417	412550144	301.3998 T	82.8509	79.8757
8	28.897	74271008	36.2730	14.9156	9.6129

8 Peaks > Area Reject 497943008 Total Area  
 8 Peaks > Height Reject 377.336 Total Height

(CH-2\_70.D01) MU



\*\*\*\*\* MODEL 1022 RUNLOG for run: CH-4\_19 \*\*\*\*\*

Run terminated manually on Channel A.

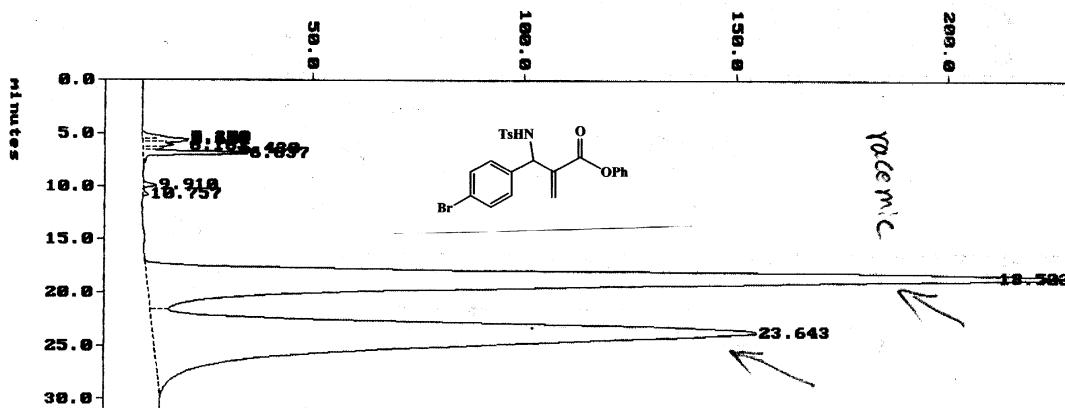
File : CH-4_19.D01	CLH-020325-1RAC	1
Run : 01		Type : Sample
Path : C:\CH-4		Inst : 1022 LC Plus
Collection : 10:42:59 Apr 05 2002	Method : LCTEST	[ 08:34:20 Apr 05 2002 ]
Integration: 10:42:59 Apr 05 2002	Method : LCTEST	[ 08:34:20 Apr 05 2002 ]
Report : 11:14:02 Apr 05 2002	Method : LCTEST	[ 08:34:20 Apr 05 2002 ]

PERCENT ( AREA )

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	5.370	1070154	6.1315	T	0.2508	1.4555
2	5.603	1375728	10.8069	T	0.3224	2.5653
3	6.163	1879251	7.4256	T	0.4405	1.7627
4	6.430	833186	6.9361	T	0.1953	1.6465
5	6.837	3859981	24.6374		0.9047	5.8484
6	9.910	554166	3.1509	T	0.1299	0.7480
7	10.757	209852	1.1501		0.0492	0.2730
8	18.523	204789120	218.6062	T	47.9985	51.8927
9	23.643	212085824	142.4211		49.7087	33.8079

9 Peaks > Area Reject      426657280 Total Area  
 9 Peaks > Height Reject      421.266 Total Height

(CH-4\_19.D01) mU



Chiral AS column; 254 nm; Hexane/Isopropanol = 60/40; Flow rate: 0.7 mL/min

\*\*\*\*\* MODEL 1022 RUNLOG for run: CH-4\_20 \*\*\*\*\*  
Run terminated manually on Channel A.

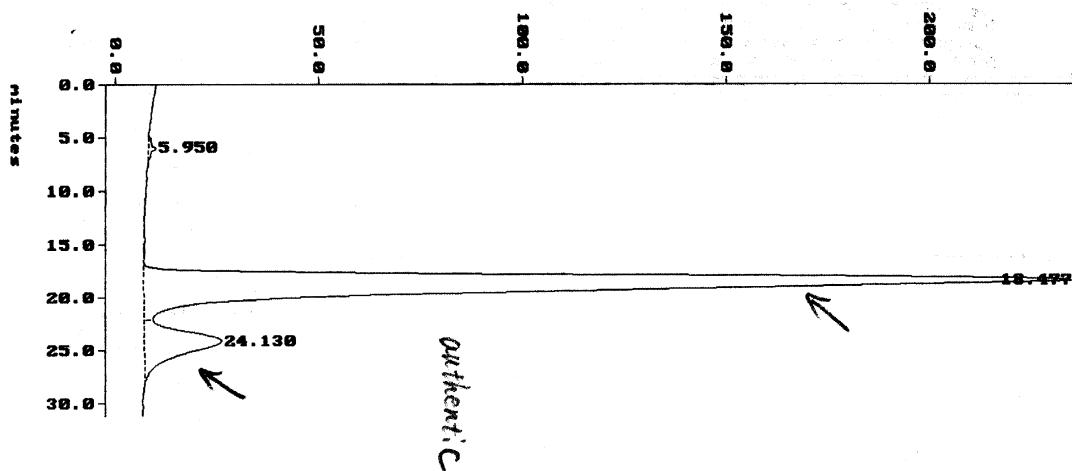
File : CH-4\_20.D01 CLH-020402-1  
Run : 01 Type : Sample  
Path : C:\CH-4 Inst : 1022 LC Plus  
Collection : 11:16:04 Apr 05 2002 Method : LCTEST [ 08:34:20 Apr 05 2002 ]  
Integration: 11:16:04 Apr 05 2002 Method : LCTEST [ 08:34:20 Apr 05 2002 ]  
Report : 11:47:13 Apr 05 2002 Method : LCTEST [ 08:34:20 Apr 05 2002 ]

## PERCENT ( AREA )

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	5.950	1002395	1.7843		0.4209	0.7154
2	18.477	210003536	228.6074	T	88.1886	91.6577
3	24.130	27124164	19.0227		11.3905	7.6269

3 Peaks > Area Reject 238130096 Total Area  
3 Peaks > Height Reject 249.414 Total Height

(CH-4\_20.D01) mV



\*\*\*\*\* MODEL 1022 RUNLOG for run: CH-4\_89 \*\*\*\*\*

Run terminated manually on Channel A.

File : CH-4\_89.D01

c1h020404-1

1

Run : 01

Type : Sample

Path : C:\CH-4

Inst : 1022 LC Plus

Collection : 10:28:29 Apr 24 2002 Method : LCTEST [ 08:26:35 Apr 24 2002 ]

Integration: 10:28:29 Apr 24 2002 Method : LCTEST [ 08:26:35 Apr 24 2002 ]

Report : 11:29:50 Apr 24 2002 Method : LCTEST [ 08:26:35 Apr 24 2002 ]

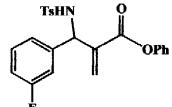
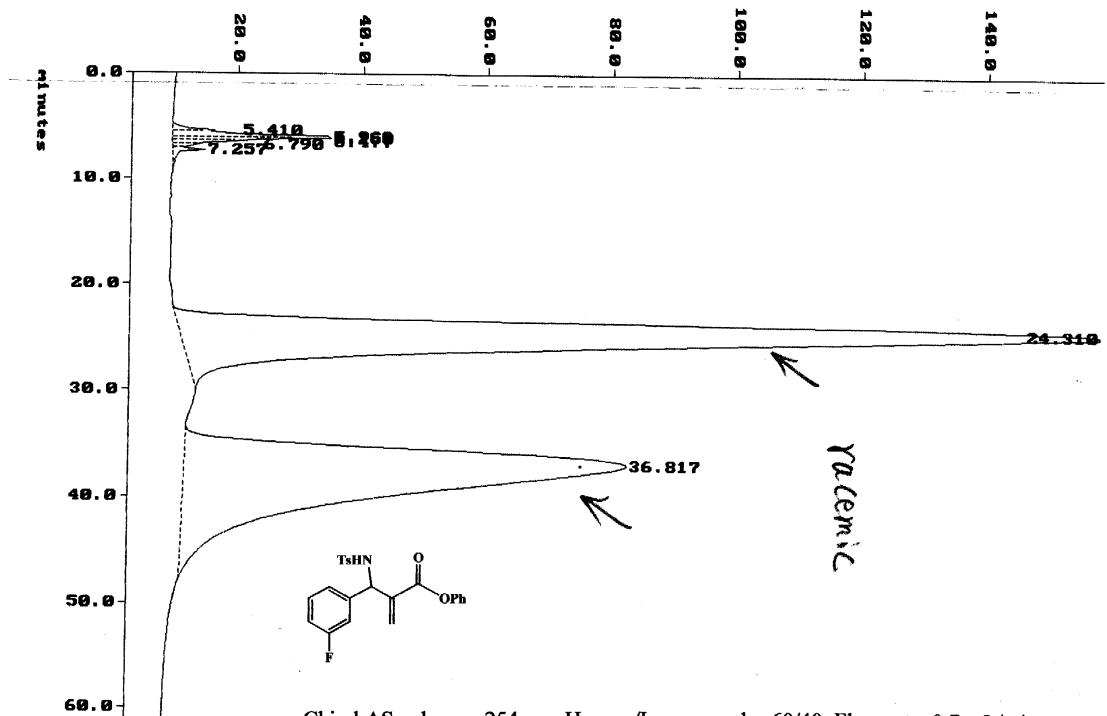
PERCENT ( AREA )

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	5.410	1064672	6.6150	T	0.2527	2.1919
2	5.963	3960745	25.2920	T	0.9401	8.3807
3	6.150	3604448	26.4334	T	0.8555	8.7590
4	6.477	1737144	13.6411	T	0.4123	4.5201
5	6.790	928588	6.5903	T	0.2204	2.1838
6	7.257	1146407	5.1832		0.2721	1.7175
7	24.310	209525584	147.2854		49.7295	48.8044
8	36.817	199362976	70.7468		47.3175	23.4426

8 Peaks > Area Reject 421330560 Total Area

8 Peaks > Height Reject 301.787 Total Height

(CH-4\_89.D01) MU



\*\*\*\*\* MODEL 1022 RUNLOG for run: CH-4\_91 \*\*\*\*\*  
Run terminated manually on Channel A.

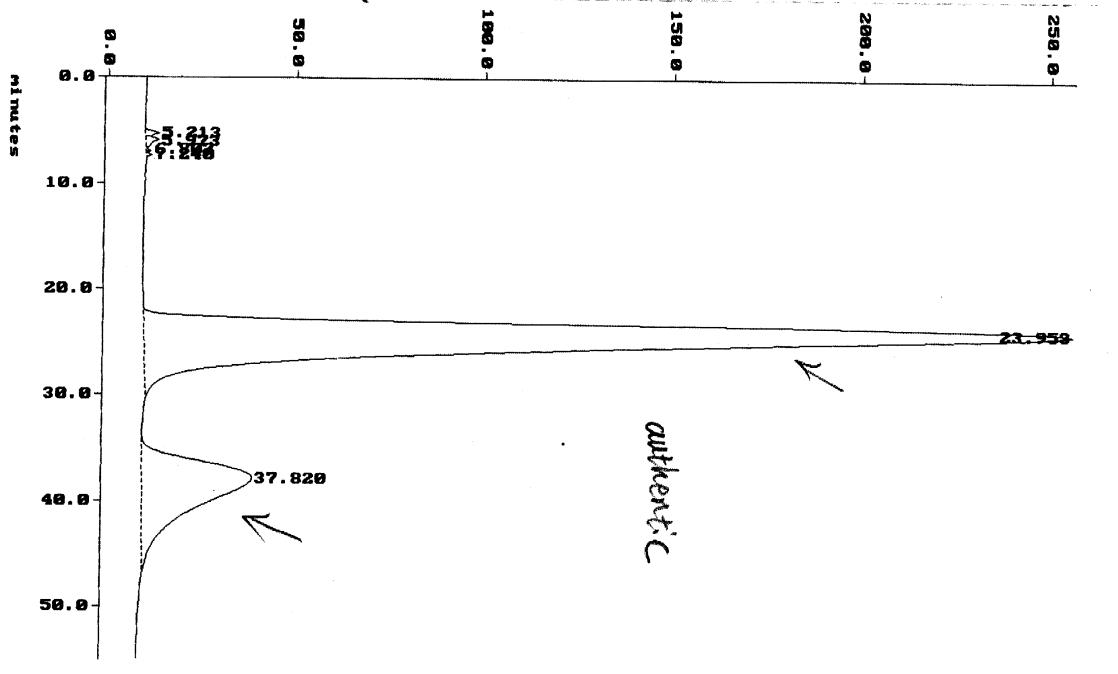
File : CH-4\_91.D01 c1h020409-1 1  
Run : 02 Type : Sample  
Path : C:\CH-4 Inst : 1022 LC Plus  
Collection : 12:39:47 Apr 24 2002 Method : LCTEST [ 08:26:35 Apr 24 2002 ]  
Integration: 12:39:47 Apr 24 2002 Method : LCTEST [ 08:26:35 Apr 24 2002 ]  
Report : 13:34:46 Apr 24 2002 Method : LCTEST [ 08:26:35 Apr 24 2002 ]

## PERCENT ( AREA )

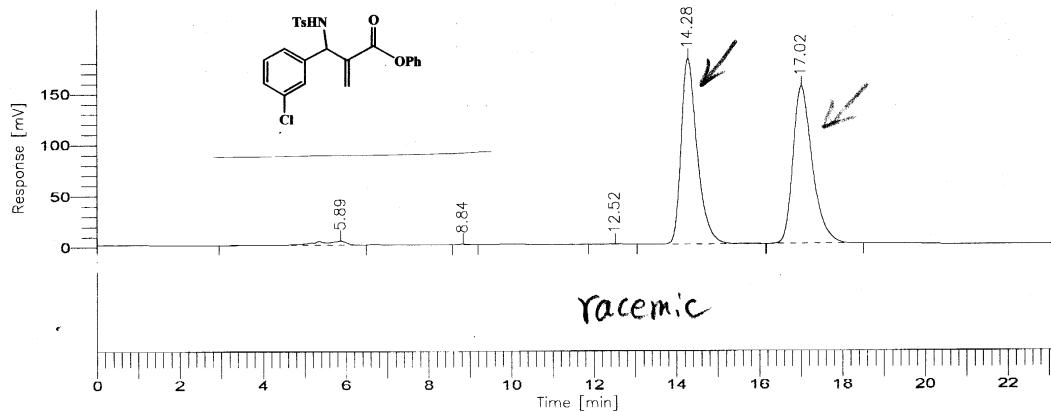
Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	5.213	762690	3.5996	T	0.1667	1.2607
2	5.973	1215805	3.6327	T	0.2657	1.2723
3	6.807	135291	1.1163	T	0.0296	0.3910
4	7.240	269152	1.5383		0.0588	0.5388
5	23.953	371439808	246.3103		81.1789	86.2676
6	37.820	83734400	29.3217		18.3003	10.2696

6' Peaks > Area Reject 457557152 Total Area  
6 Peaks > Height Reject 285.519 Total Height

(CH-4\_91.D01) mU

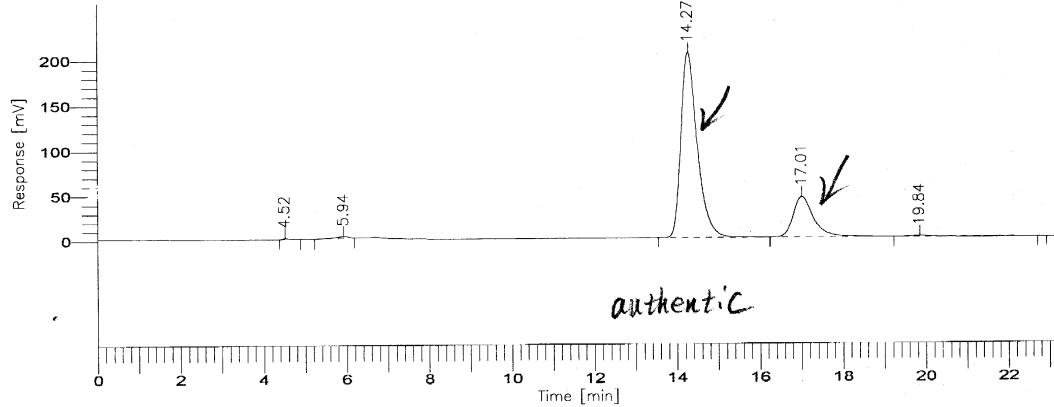


Software Version: 4.1<2F12>  
 Date: 02-4-30 14:58  
 Sample Name : CIh-020404-2  
 Data File : C:\C\CS6\_490.RAW Date: 02-4-30 14:34  
 Sequence File: C:\C\CS6.SEQ Cycle: 1 Channel : A  
 Instrument : 970A - 0 Rack/Vial: 0/0 Operator: DIN  
 Sample Amount : 1.0000 Dilution Factor : 1.00



Chiral AD column; 254 nm; Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min

Software Version: 4.1<F12>  
Date: 02-4-30 14:59  
Sample Name : CIh-020409-2  
Data File : C:\C\CS6\_489.RAW Date: 02-4-30 12:51  
Sequence File: C:\C\CS6.SEQ Cycle: 1 Channel : A  
Instrument : 970A\_-0 Rack/Vial: 0/0 Operator: DIN  
Sample Amount : 1.0000 Dilution Factor : 1.00



Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL	Area/Height [sec]
1	4.524	19634.50	1245.22	0.27	0.00	BB	15.7679
2	5.941	48484.00	2253.25	0.66	0.00	BB	21.5174
3	14.270	5627817.00	205739.98	76.99	0.00	BB	27.3540
4	17.010	1524198.65	44977.87	20.85	0.00	BV	33.8877
5	19.840	61349.35	1276.39	0.84	0.00	VB	48.0649
6	23.655	27963.50	700.45	0.38	0.00	BB	39.9221
		7309447.00	256193.16	100.00	0.00		

## \*\*\*\*\* MODEL 1022 RUNLOG for run: CH-4\_21 \*\*\*\*\*

Run terminated manually on Channel A.

File : CH-4\_21.D01

CLH-020401

1

Run : 01

Type : Sample

Path : C:\CH-4

Inst : 1022 LC Plus

Collection : 11:50:36 Apr 05 2002 Method : LCTEST [ 08:34:20 Apr 05 2002 ]

Integration: 11:50:36 Apr 05 2002 Method : LCTEST [ 08:34:20 Apr 05 2002 ]

Report : 13:14:05 Apr 05 2002 Method : LCTEST [ 08:34:20 Apr 05 2002 ]

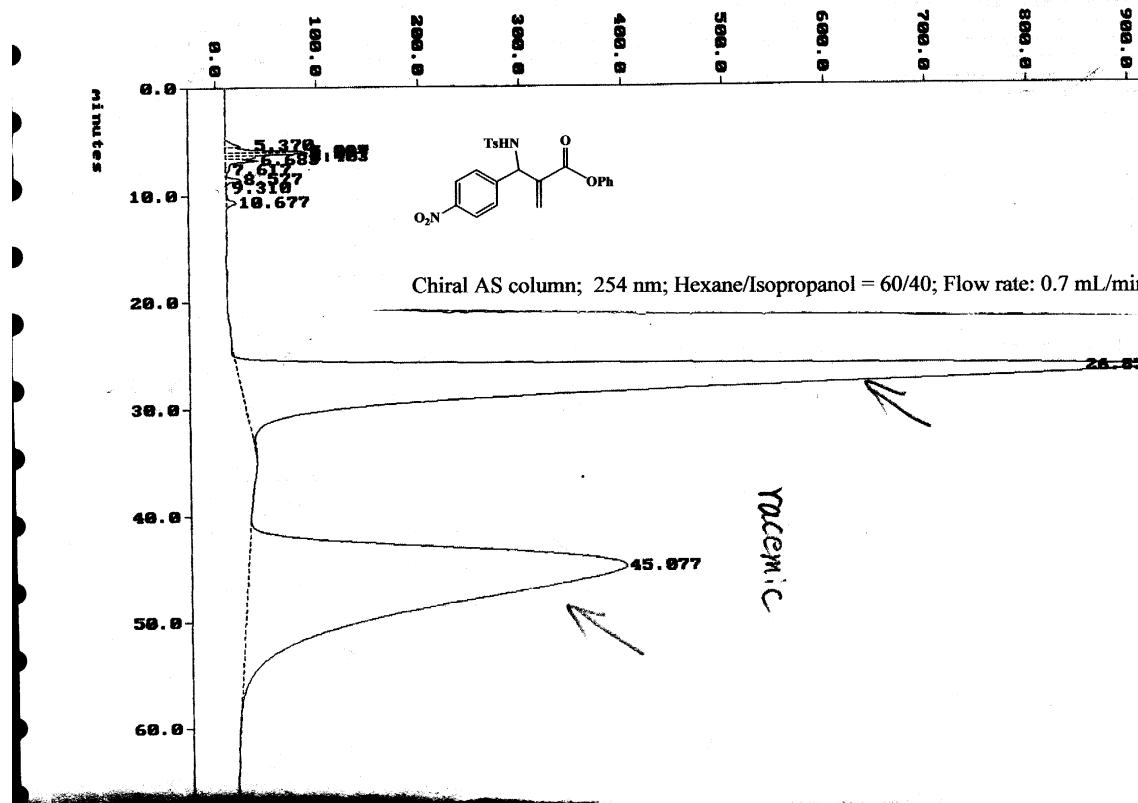
## PERCENT ( AREA )

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	5.370	2988154	14.4941	T	0.1094	0.9335
2	5.937	10696973	74.1197	T	0.3916	4.7738
3	6.097	10076943	80.9734	T	0.3689	5.2152
4	6.403	4522935	38.1301	T	0.1656	2.4558
5	6.683	5597046	32.3234	T	0.2049	2.0818
6	7.617	1135518	3.8634	T	0.0416	0.2488
7	8.577	3346026	15.4829	T	0.1225	0.9972
8	9.310	284490	1.0999	T	0.0104	0.0708
9	10.677	3066653	10.2347		0.1123	0.6592
10	26.850	1354969216	908.6471	T	49.6084	58.5224
11	45.077	1334648704	373.2791		48.8644	24.0415

11 Peaks &gt; Area Reject 2731332608 Total Area

11 Peaks &gt; Height Reject 1552.648 Total Height

(CH-4\_21.D01) mV



\*\*\*\*\* MODEL 1022 RUNLOG for run: CH-4\_22 \*\*\*\*\*  
Run terminated manually on Channel A.

File : CH-4\_22.D01 CLH-020403-2 1  
Run : 01 Type : Sample  
Path : C:\CH-4 Inst : 1022 LC Plus  
Collection : 13:23:48 Apr 05 2002 Method : LCTEST [ 08:34:20 Apr 05 2002 ]  
Integration: 13:23:48 Apr 05 2002 Method : LCTEST [ 08:34:20 Apr 05 2002 ]  
Report : 14:25:18 Apr 05 2002 Method : LCTEST [ 08:34:20 Apr 05 2002 ]

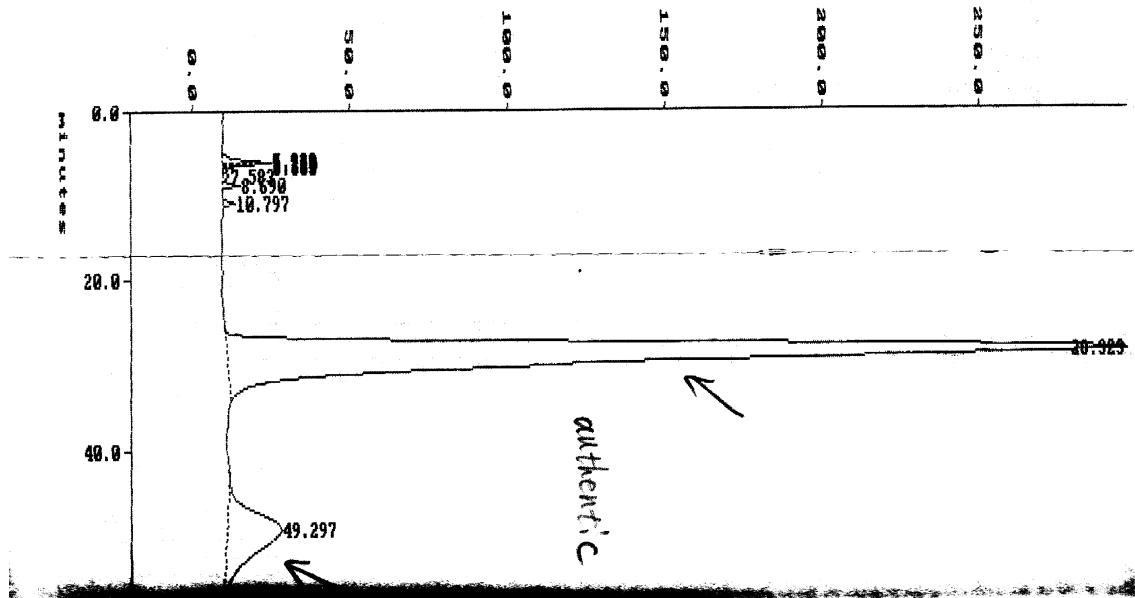
## PERCENT ( AREA )

Pk #	RT	Area	Height BC	Area Percent	Height Percent
1	5.923	2051842	12.8097 T	0.4380	3.6389
2	6.110	1906791	15.5147 T	0.4070	4.4073
3	6.397	659967	5.5285 T	0.1409	1.5705
4	6.683	627638	3.1440 T	0.1340	0.8931
5	7.583	801011	1.8923 T	0.1710	0.5375
6	8.690	1108410	5.6532	0.2366	1.6059
7	10.797	969875	3.9255	0.2070	1.1151
8	28.323	402712192	286.3254	85.9636	81.3366
9	49.297	57630416	17.2318	12.3019	4.8950

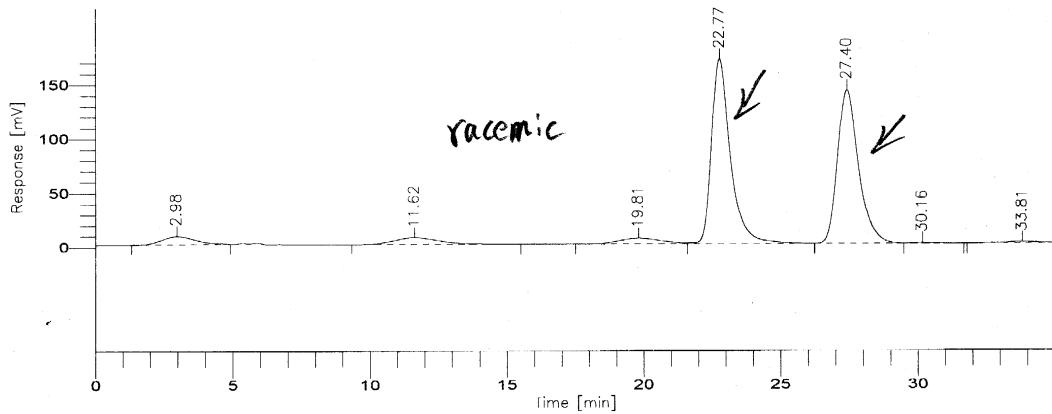
9 Peaks > Area Reject 468468160 Total Area  
9 Peaks > Height Reject 352.025 Total Height

File : CH-4\_22.D01 CLH-020403-2 1  
Run : 01 Type : Sample  
Collection : 13:23:48 Apr 05 2002 Method : LCTEST [ 08:34:20 Apr 05 2002 ]

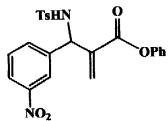
(CH-4\_22.D01) MU



Software Version: 4.1<2F12>  
 Date: 02-4-30 10:01  
 Sample Name : CIh-020408-1  
 Data File : C:\C\CS6\_486.RAW Date: 02-4-30 9:24  
 Sequence File: C:\C\CS6.SEQ Cycle: 1 Channel : A  
 Instrument : 970A - 0 Rack/Vial: 0/0 Operator: DIN  
 Sample Amount : 1.0000 Dilution Factor : 1.00

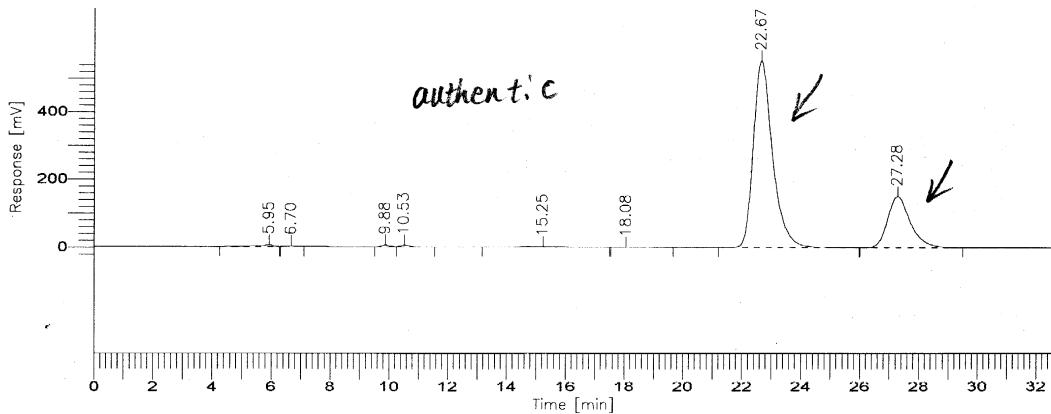


Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height
1	2.984	652828.00	7657.58	3.65	0.00	BB	85.2525
2	11.618	777056.00	6527.47	4.34	0.00	BB	119.0439
3	19.808	574679.35	5332.99	3.21	0.00	BV	107.7593
4	22.768	8187533.15	171224.02	45.73	0.00	VB	47.8177
5	27.404	7576931.90	142198.15	42.32	0.00	BV	53.2843
6	30.164	46845.10	732.96	0.26	0.00	VB	63.9125
7	33.808	89186.50	1213.73	0.50	0.00	BB	73.4813
<hr/>							
17905060.00 334886.90 100.00 0.00							



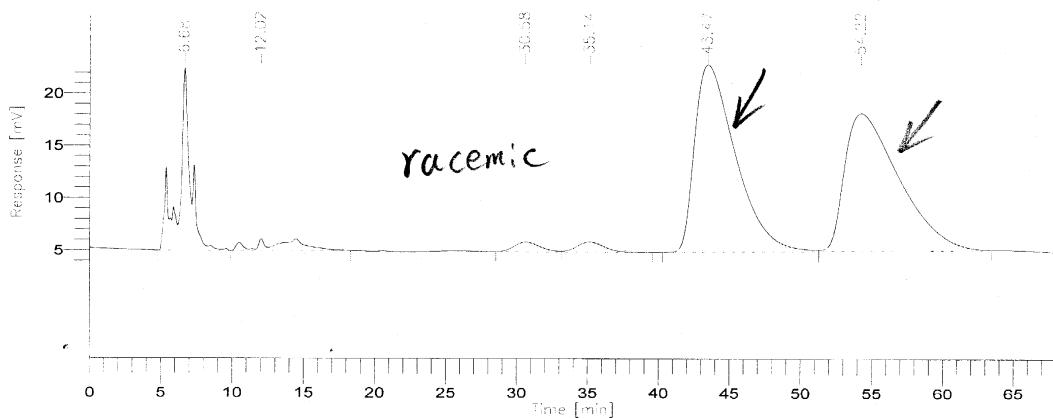
Chiral AD column; 254 nm; Hexane/Isopropanol = 80/20; Flow rate: 0.7 mL/min

Software Version: 4.1<2F12>  
 Date: 02-4-30 10:39  
 Sample Name : CIh-020408-2  
 Data File : C:\C\CS6\_487.RAW Date: 02-4-30 10:05  
 Sequence File: C:\C\CS6.SEQ Cycle: 1 Channel : A  
 Instrument : 970A - 0 Rack/Vial: 0/0 Operator: DIN  
 Sample Amount : 1.0000 Dilution Factor : 1.00



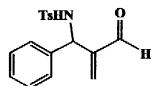
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height
1	5.950	202355.00	4971.37	0.60	0.00	BB	40.7041
2	6.698	17784.00	1250.06	0.05	0.00	BB	14.2265
3	9.883	85359.23	4803.19	0.25	0.00	BV	17.7713
4	10.530	102619.27	5284.45	0.31	0.00	VB	19.4191
5	15.250	101195.00	826.07	0.30	0.00	BB	122.5024
6	18.075	17979.00	290.64	0.05	0.00	BB	61.8590
7	22.670	25019878.50	554413.25	74.59	0.00	BB	45.1286
8	27.283	7994166.00	150802.39	23.83	0.00	BB	53.0109
-----							
		33541336.00	722641.42	100.00	0.00		

Software Version: 4.1<2F12>  
 Date: 02-11-20 15:42  
 Sample Name : clh021114-1  
 Data File : D:\TC4\DATA\CAO\CAO\_337S.RAW Date: 02-11-20 14:33  
 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



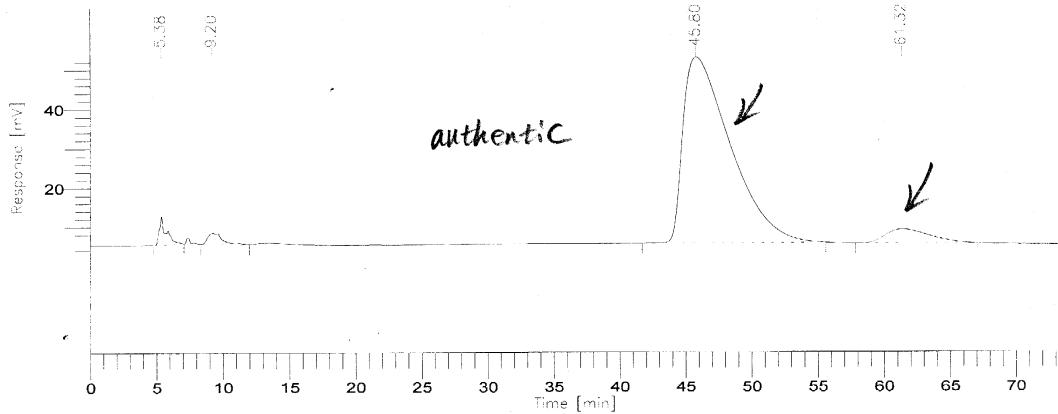
## REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height
1	6.677	963410.00	17472.28	11.27	0.00	BB	55.1394
2	12.016	205241.00	1133.24	2.40	0.00	BB	181.1107
3	30.580	119203.58	949.78	1.39	0.00	BV	125.5061
4	35.142	132628.67	991.78	1.55	0.00	VB	133.7281
5	43.466	3606504.16	17943.63	42.20	0.00	BV	200.9908
6	54.217	3519212.34	13207.66	41.18	0.00	VB	266.4524
				8546199.75	51698.36	100.00	0.00



Chiral AS column; 254 nm; Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min

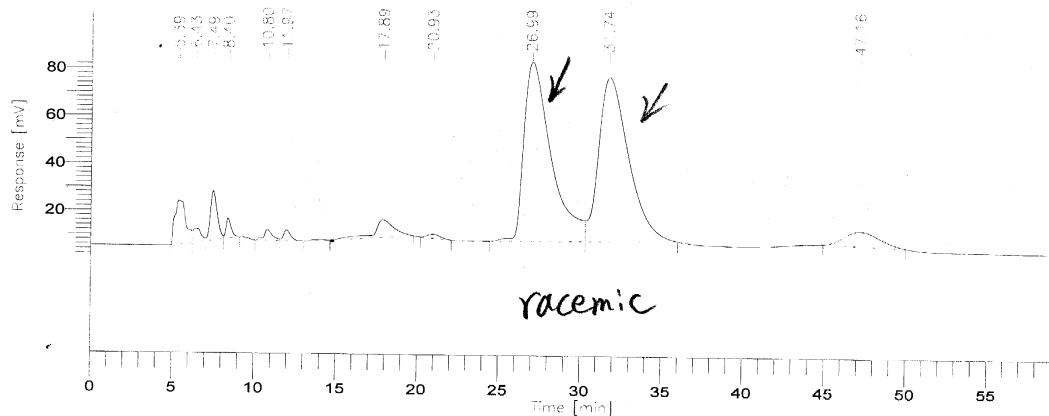
Software Version: 4.1<2F12>  
Date: 02-11-21 15:45  
Sample Name : CLH-021113-1  
Data File : D:\TC4\DATA\CAO\CAO\_338A.RAW Date: 02-11-21 14:30  
Sequence File: D:\TC4\DATA\CAO\CAO.SEQ Cycle: 1 Channel : A  
Instrument : 970A\_-0 Rack/Vial: 0/0 Operator: CAO  
Sample Amount : 1.0000 Dilution Factor : 1.00



## REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL	Area/Height [sec]
1	5.377	271729.50	7449.61	2.06	0.00	BB	36.4757
2	9.200	225251.50	2866.70	1.70	0.00	BB	78.5751
3	45.804	11860565.50	47373.86	89.70	0.00	BB	250.3610
4	61.321	864715.50	3610.28	6.54	0.00	BB	239.5149
		13222262.00	61300.46	100.00	0.00		

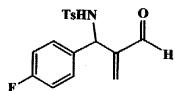
Software Version: 4.1<2F12>  
 Date: 02-11-14 16:25  
 Sample Name : clh-021106-1  
 Data File : D:\TC4\DATA\CAO\CAO\_336Q.RAW Date: 02-11-14 14:22  
 Sequence File: D:\TC4\DATA\CAO\CAO.SEQ Cycle: 1 Channel : A  
 Instrument : 970A - 0 Rack/Vial: 0/0 Operator: CAO  
 Sample Amount : 1.0000 Dilution Factor : 1.00



## REPORT

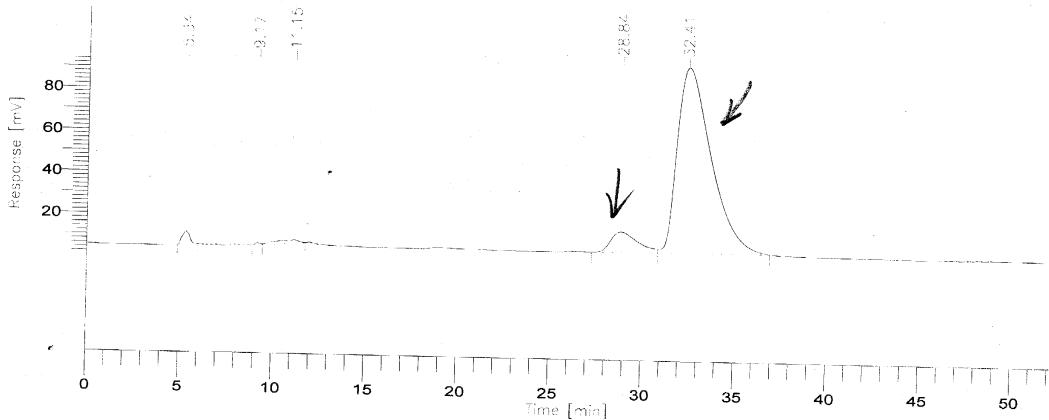
Peak #	Time [min.]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height
1	5.385	871555.57	18526.04	4.04	0.00	BV	47.0449
2	6.425	198782.90	5826.55	0.92	0.00	VV	34.1168
3	7.494	606461.10	20864.73	2.81	0.00	VV	29.0663
4	8.403	188592.43	8642.34	0.87	0.00	VB	21.8219
5	10.800	165296.39	4798.19	0.77	0.00	BV	34.4498
6	11.973	133708.61	4583.84	0.62	0.00	VB	29.1696
7	17.889	642915.50	7533.25	2.98	0.00	BB	85.3437
8	20.925	94503.25	1755.71	0.44	0.00	BB	53.8263
9	26.994	8847408.10	75729.52	41.01	0.00	BV	116.8291
10	31.735	8889327.90	69370.00	41.20	0.00	VB	128.1437
11	47.158	937833.50	6264.34	4.35	0.00	BB	149.7099

21576385.25 223894.49 100.00 0.00



Chiral OJ column; 254 nm; Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min

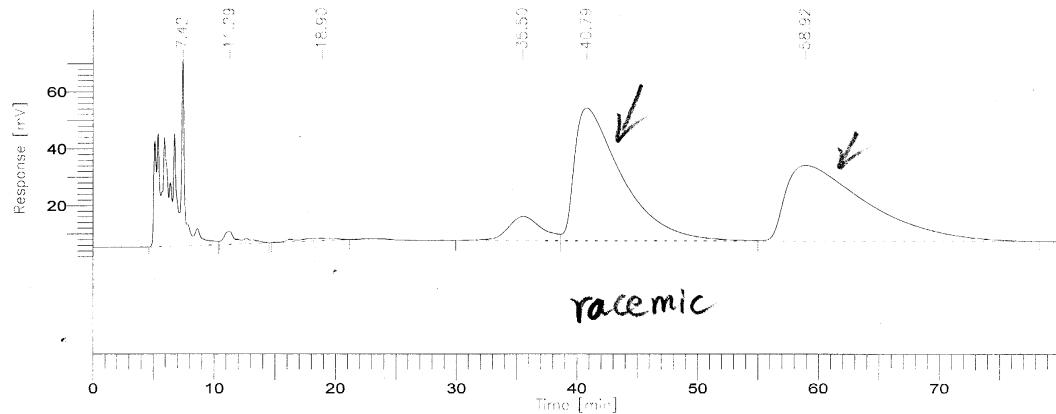
Software Version: 4.1<2F12>  
Date: 02-11-14 16:25  
Sample Name : clh021105-1  
Data File : D:\TC4\DATA\CAO\CAO\_336R.RAW Date: 02-11-14 15:27  
Sequence File: D:\TC4\DATA\CAO\CAO.SEQ Cycle: 1 Channel : A  
Instrument : 970A - 0 Rack/Vial: 0/0 Operator: CAO  
Sample Amount : 1.0000 Dilution Factor : 1.00



## REPORT

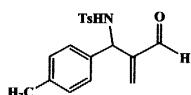
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height
1	5.335	183259.00	6528.73	1.44	0.00	BB	28.0696
2	9.173	22245.52	1258.79	0.18	0.00	BV	17.6722
3	11.149	148747.48	1651.72	1.17	0.00	VB	90.0560
4	28.839	1004207.93	9815.55	7.90	0.00	BV	102.3079
5	32.413	11345763.57	88609.73	89.31	0.00	VB	128.0420
				12704223.50	107864.52	100.00	0.00

Software Version: 4.1<2F12>  
 Date: 02-11-22 10:14  
 Sample Name : CLH-021111-1  
 Data File : D:\TC4\DATA\CAO\CAO\_338D.RAW Date: 02-11-22 8:41  
 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



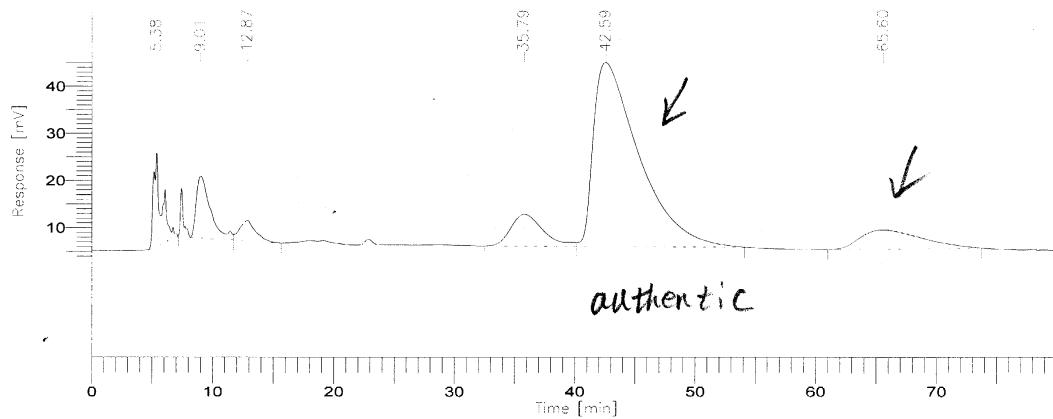
## REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height [sec]
1	7.423	4702730.89	65670.44	14.55	0.00	BV	71.6111
2	11.293	401016.88	4331.25	1.24	0.00	VB	92.5868
3	18.902	191619.00	762.45	0.59	0.00	BB	251.3195
4	35.498	1626695.22	8477.44	5.03	0.00	BV	191.8853
5	40.785	12830647.09	46811.55	39.70	0.00	VV	274.0915
6	58.924	12565264.69	26793.15	38.88	0.00	VB	468.9730
<hr/>							
32317973.77 152846.27 100.00 0.00							



Chiral AS column; 254 nm; Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min

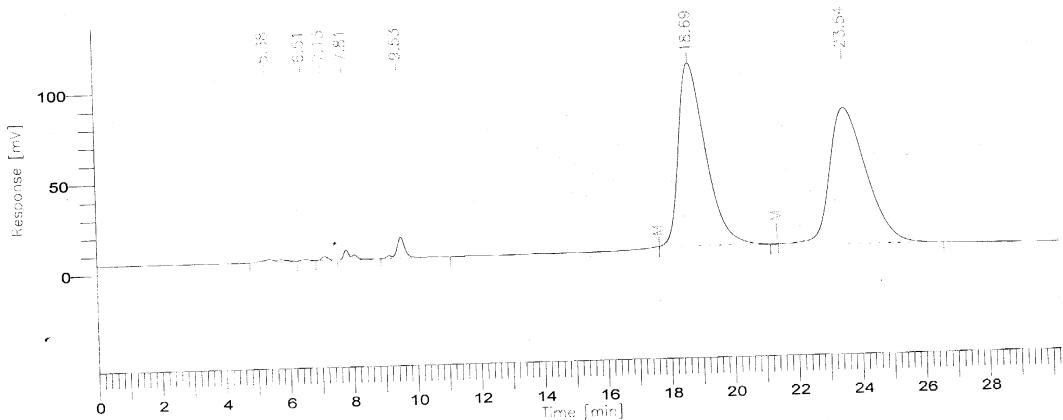
Software Version: 4.1<2F12>  
Date: 02-11-22 13:19  
Sample Name : CLH-021112-1  
Data File : D:\TC4\DATA\CAO\CAO\_338E.RAW Date: 02-11-22 10:05  
Sequence File: D:\TC4\DATA\CAO\CAO.SEQ Cycle: 1 Channel : A  
Instrument : 970A - 0 Rack/Vial: 0/0 Operator: CAO  
Sample Amount : 1.0000 Dilution Factor : 1.00



## REPORT

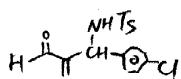
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height
1	5.384	883602.75	19716.45	5.75	0.00	BB	44.8155
2	9.011	1068402.85	13083.45	6.95	0.00	BV	81.6606
3	12.868	391182.15	4373.75	2.55	0.00	VB	89.4386
4	35.791	1272535.05	6788.80	8.28	0.00	BV	187.4464
5	42.585	10311585.95	39081.39	67.12	0.00	VB	263.8490
6	65.600	1434488.00	4042.06	9.34	0.00	BB	354.8908
				15361796.75	87085.90	100.00	0.00

Software Version: 4.1<2F12>  
 Date: 02-8-20 15:05  
 Sample Name : xu7-33  
 Data File : D:\TC4\DATA\CAO\CAO\_320L.RAW Date: 02-8-20 14:33  
 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

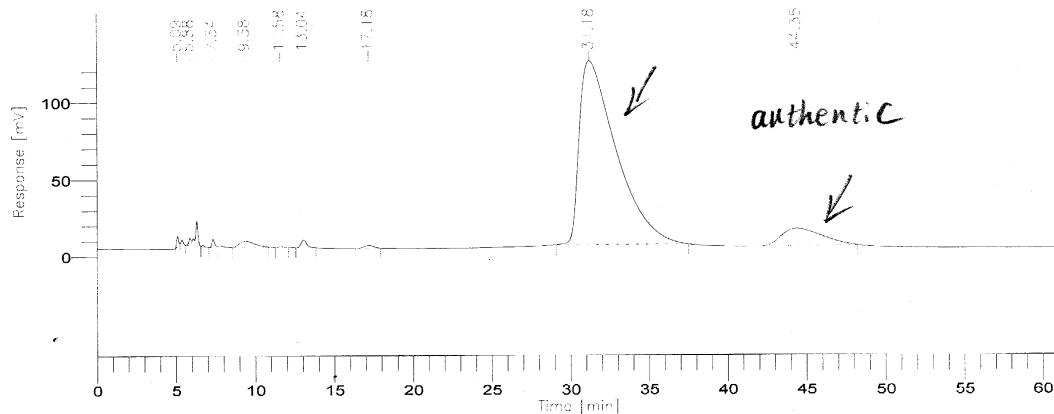


## REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height
1	5.380	74650.22	1836.05	0.60	0.00	BV	40.6582
2	6.506	21314.67	1086.44	0.17	0.00	VV	19.6189
3	7.131	36386.92	2329.80	0.29	0.00	VV	15.6180
4	7.812	100991.80	5585.90	0.82	0.00	VB	18.0798
5	9.531	226083.90	11795.75	1.83	0.00	*BB	19.1665
6	18.685	5961474.51	100833.33	48.20	0.00	BB	59.1221
7	23.536	5946104.50	74807.49	48.08	0.00		79.4854
-----							
12367006.51 198274.76 100.00 0.00							



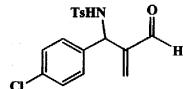
Software Version: 4.1<2F12>  
 Date: 02-11-1 11:14  
 Sample Name : clh021024-1  
 Data File : D:\TC4\DATA\CAO\CAO\_334B.RAW Date: 02-11-1 10:08  
 Sequence File: D:\TC4\DATA\CAO\CAO.SEQ Cycle: 1 Channel : A  
 Instrument : 970A - 0 Rack/Vial: 0/0 Operator: CAO  
 Sample Amount : 1.0000 Dilution Factor : 1.00



## REPORT

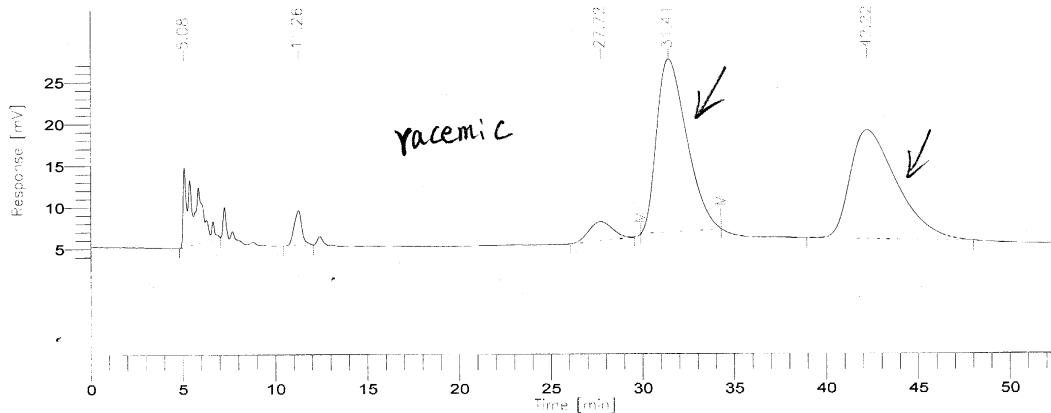
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. [%]	Area BL [sec]	Area/Height
1	5.089	59784.50	6987.33	0.27	0.00	BB	8.5561
2	5.879	53426.61	4895.02	0.24	0.00	BV	10.9145
3	6.319	202176.89	16296.93	0.90	0.00	VB	12.4058
4	7.337	60505.75	5276.52	0.27	0.00	BB	11.4670
5	9.379	283558.50	4256.99	1.27	0.00	BB	66.6102
6	11.581	15558.50	739.52	0.07	0.00	BB	21.0386
7	13.038	136525.50	5342.68	0.61	0.00	BB	25.5538
8	17.176	79453.50	1975.34	0.36	0.00	BB	40.2227
9	31.180	19466699.50	119139.92	87.10	0.00	BB	163.3936
10	44.354	1991303.50	11167.77	8.91	0.00	BB	178.3080

22348992.75 176078.02 100.00 0.00



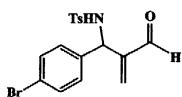
Chiral AS column; 254 nm; Hexane/Isopropanol =70/30; Flow rate: 0.7 mL/min

Software Version: 4.1<2F12>  
 Date: 02-11-12 11:07  
 Sample Name : clh021106-2  
 Data File : D:\TC4\DATA\CAO\CAO\_336A.RAW Date: 02-11-12 9:52  
 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



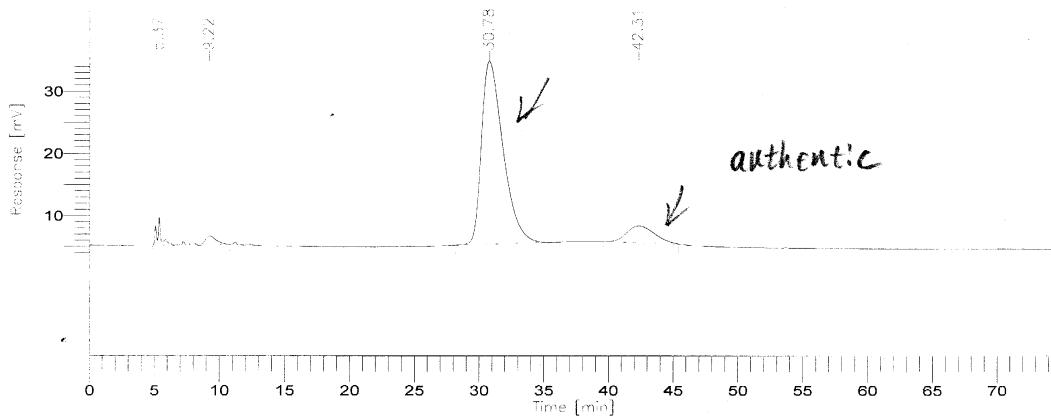
## REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	Area BL [sec]	Area/Height
1	5.084	440208.50	9653.51	8.11	0.00	BB	45.6009
2	11.258	124078.75	4208.20	2.29	0.00	BB	29.4850
3	27.715	206129.00	2304.34	3.80	0.00	BB	89.4525
4	31.413	2359614.00	20737.56	43.46	0.00	*BB	113.7845
5	42.217	2298793.50	13033.20	42.34	0.00	BB	176.3798
<hr/>							
5428823.75 49936.82 100.00 0.00							



Chiral AS column; 254 nm; Hexane/Isopropanol = 70/30; Flow rate: 0.7 mL/min

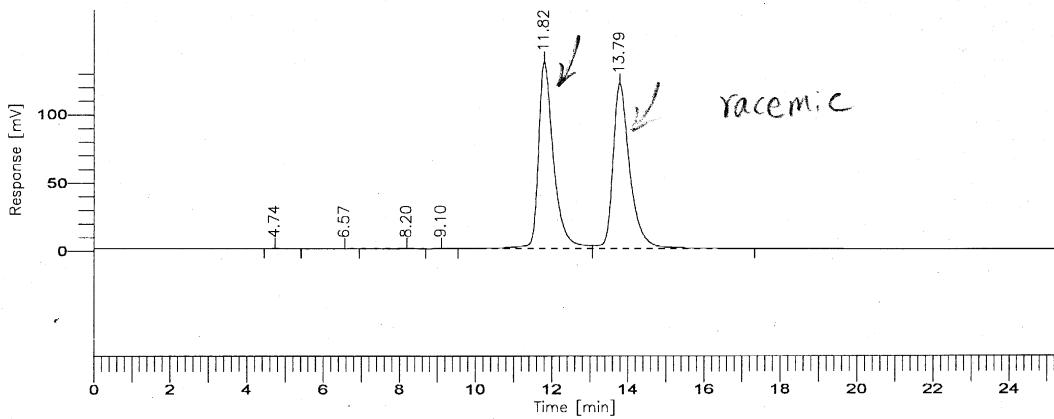
Software Version: 4.1<2F12>  
 Date: 02-11-12 14:23  
 Sample Name : clh021105-2  
 Data File : D:\TC4\DATA\CAO\CAO\_336B.RAW Date: 02-11-12 10:46  
 Sequence File: D:\TC4\DATA\CAO\CAO.SEQ Cycle: 1 Channel : A  
 Instrument : 970A - 0 Rack/Vial: 0/0 Operator: CAO  
 Sample Amount : 1.0000 Dilution Factor : 1.00



## REPORT

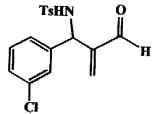
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area	Norm. [%]	Area BL [sec]	Area/Height
1	5.374	109268.00	4610.18	2.72	0.00	BB	23.7014
2	9.220	88120.25	1485.99	2.19	0.00	BB	59.3006
3	30.781	3413239.25	29435.68	84.89	0.00	BB	115.9558
4	42.311	410094.00	2718.97	10.20	0.00	BB	150.8268
				4020721.50	38250.83	100.00	0.00

Software Version: 4.1<2F12>  
 Date: 02-12-10 11:12  
 Sample Name : XU-7-43  
 Data File : C:\C\CS7\_821.RAW Date: 02-12-10 10:44  
 Sequence File: C:\C\CS7.SEQ Cycle: 1 Channel : A  
 Instrument : 970A - 0 Rack/Vial: 0/0 Operator: DIN  
 Sample Amount : 1.0000 Dilution Factor : 1.00



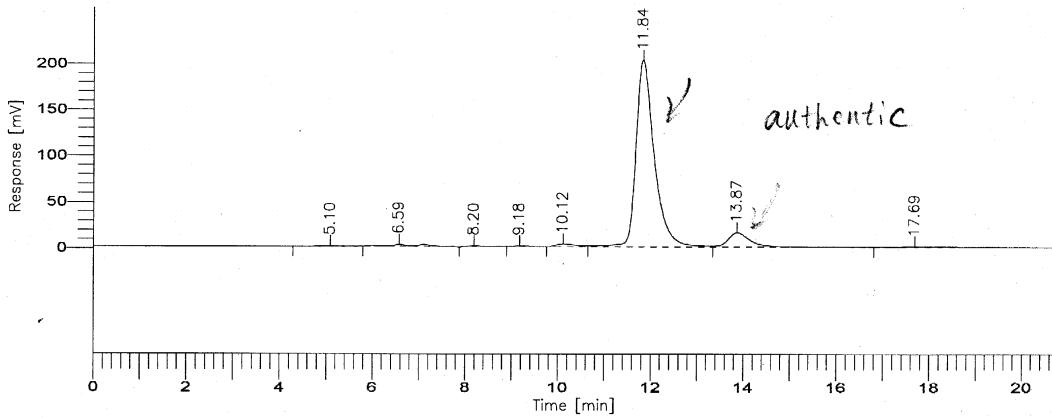
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height
1	4.744	5875.50	296.55	0.08	0.00	BB	19.8129
2	6.569	2524.77	85.05	0.03	0.00	BV	29.6861
3	8.203	8543.19	388.44	0.11	0.00	VV	21.9933
4	9.104	11322.32	420.83	0.15	0.00	VV	26.9047
5	11.815	3809674.85	137140.97	50.25	0.00	VV	27.7793
6	13.794	3743459.87	121043.88	49.38	0.00	VB	30.9265

7581400.50 259375.72 100.00 0.00



Chiral OD column; 254 nm; Hexane/Isopropanol = 65/35; Flow rate: 0.7 mL/min

Software Version: 4.1<2F12>  
Date: 02-12-10 11:33  
Sample Name : CIh-021126-2  
Data File : C:\C\CS7\_822.RAW Date: 02-12-10 11:11  
Sequence File: C:\C\CS7.SEQ Cycle: 1 Channel : A  
Instrument : 970A - 0 Rack/Vial: 0/0 Operator: DIN  
Sample Amount : 1.0000 Dilution Factor : 1.00

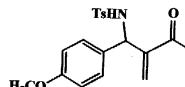
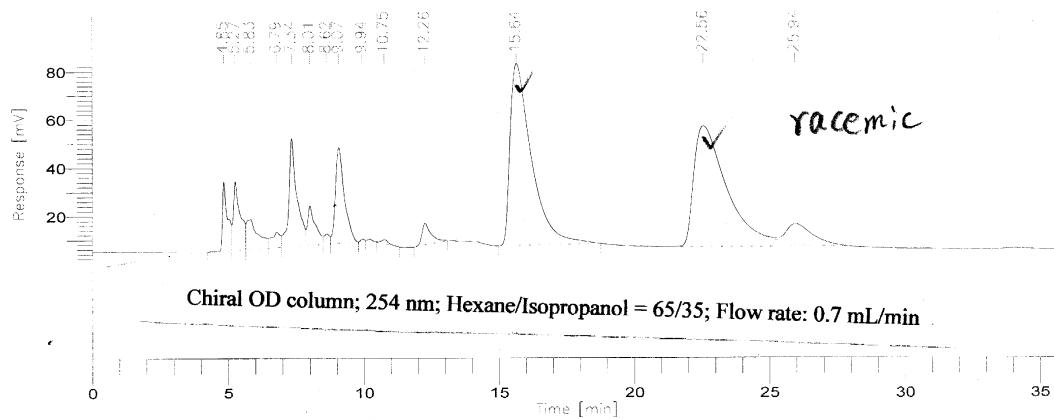


Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height
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1	5.100	38722.30	797.88	0.59	0.00	BV	48.5317
2	6.587	141447.83	2622.68	2.15	0.00	VV	53.9325
3	8.203	30387.59	887.34	0.46	0.00	VV	34.2457
4	9.183	31951.31	820.95	0.48	0.00	VV	38.9198
5	10.122	103305.12	3238.33	1.57	0.00	VV	31.9007
6	11.842	5611140.37	203736.03	85.10	0.00	VV	27.5412
7	13.874	565896.24	15779.03	8.58	0.00	VV	35.8638
8	17.687	71049.98	613.95	1.08	0.00	VB	115.7263

6593900.74	228496.20	100.00	0.00
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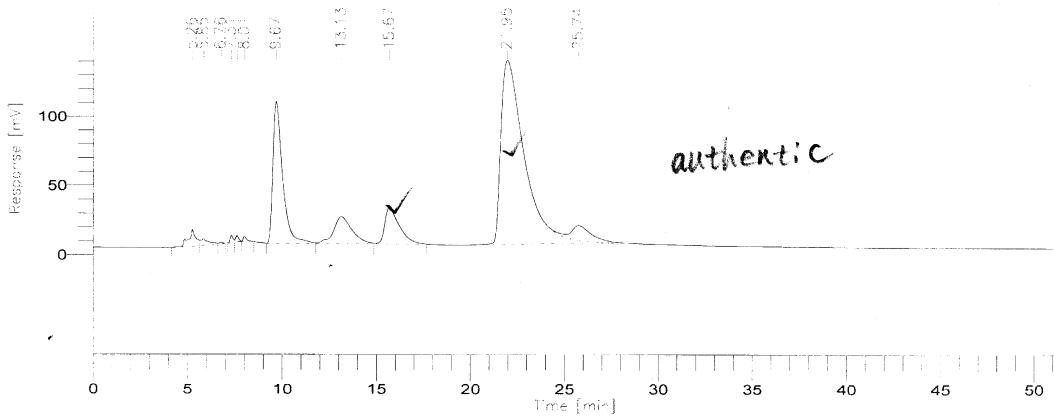
Software Version: 4.1<2F12>  
 Date: 02-11-19 14:18  
 Sample Name : clh021111-2  
 Data File : D:\TC4\DATA\CAO\CAO\_337H.RAW Date: 02-11-19 13:40  
 Sequence File: D:\TC4\DATA\CAO\CAO.SEQ Cycle: 1 Channel : A  
 Instrument : 970A - 0 Rack/Vial: 0/0 Operator: CAO  
 Sample Amount : 1.0000 Dilution Factor : 1.00



## REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL [sec]	Area/Height [sec]
1	4.848	383819.04	28806.10	2.95	0.00	BV	13.3242
2	5.269	525181.40	28676.21	4.03	0.00	VV	18.3142
3	5.830	373873.46	12535.25	2.87	0.00	VV	29.8258
4	6.785	148350.47	6526.06	1.14	0.00	VV	22.7320
5	7.338	956148.46	44978.10	7.34	0.00	VV	21.2581
6	8.008	334770.02	16451.38	2.57	0.00	VV	20.3490
7	8.623	63049.68	4256.85	0.48	0.00	VV	14.8113
8	9.074	922158.21	39698.23	7.08	0.00	VB	23.2292
9	9.943	6578.00	783.36	0.05	0.00	BB	8.3972
10	10.751	29489.50	1698.53	0.23	0.00	BB	17.3617
11	12.256	211993.75	9120.90	1.63	0.00	BB	23.2426
12	15.641	4149788.00	75610.31	31.85	0.00	BB	54.8839
13	22.560	4239330.34	50054.31	32.53	0.00	BE	84.6946
14	25.942	686463.16	9430.96	5.27	0.00	EB	72.7883
				13030993.50	328626.57	100.00	0.00

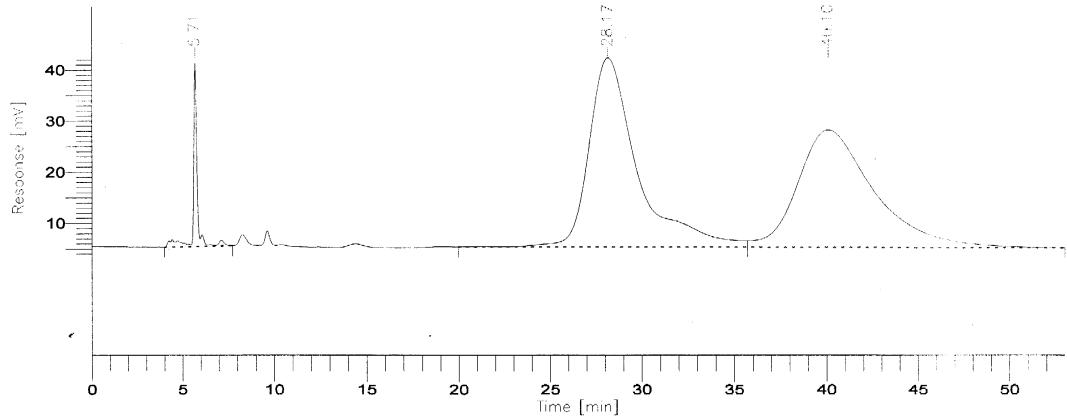
Software Version: 4.1<2F12>  
Date: 02-11-19 15:11  
Sample Name : clh021112-2  
Data File : D:\TC4\DATA\CAO\CAO\_337I.RAW Date: 02-11-19 14:17  
Sequence File: D:\TC4\DATA\CAO\CAO.SEQ Cycle: 1 Channel : A  
Instrument : 970A\_-0 Rack/Vial: 0/0 Operator: CAO  
Sample Amount : 1.0000 Dilution Factor : 1.00



## REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]	Norm. Area [%]	BL	Area/Height [sec]
1	5.260	325234.01	12054.41	1.66	0.00	BV	26.9805
2	5.847	135127.83	4757.15	0.69	0.00	VV	28.4052
3	6.760	14599.66	1188.38	0.07	0.00	VB	12.2854
4	7.314	59524.77	5627.00	0.30	0.00	BV	10.5784
5	7.608	58594.23	4803.04	0.30	0.00	VB	12.1994
6	8.008	47154.50	3902.79	0.24	0.00	BB	12.0822
7	9.670	3683873.36	102930.24	18.81	0.00	BV	35.7900
8	13.133	1347006.87	19615.53	6.88	0.00	VV	68.6704
9	15.674	1413132.27	26242.27	7.22	0.00	VB	53.8495
10	21.951	11631908.00	133057.99	59.40	0.00	BE	87.4198
11	25.736	865001.00	10929.25	4.42	0.00	EB	79.1455

Software Version: 4.1<2F12>  
Date: 04-4-9 14:43  
Sample Name : clh040330-2  
Data File : D:\TC4\DATA\CAO\CAP\_0520.RAW Date: 04-4-9 12:51  
Sequence File: D:\TC4\DATA\CAO\CAP.SEQ Cycle: 1 Channel : A  
Instrument : 970A - 0 Rack/Vial: 0/0 Operator:  
Sample Amount : 1.0000 Dilution Factor : 1.00



#### REPORT

Peak #	Time [min]	Area uV*sec	Height uV	Area [%]	Norm Area [%]	BL	Area/Height [s]
1	5.707	507409.50	36058.84	3.64	0.00	BB	14.07
2	28.173	6800672.11	37077.70	48.79	0.00	BV	183.42
3	40.096	6630039.39	22947.49	47.57	0.00	VB	288.92
13938121.00			96084.03	100.00	0.00		

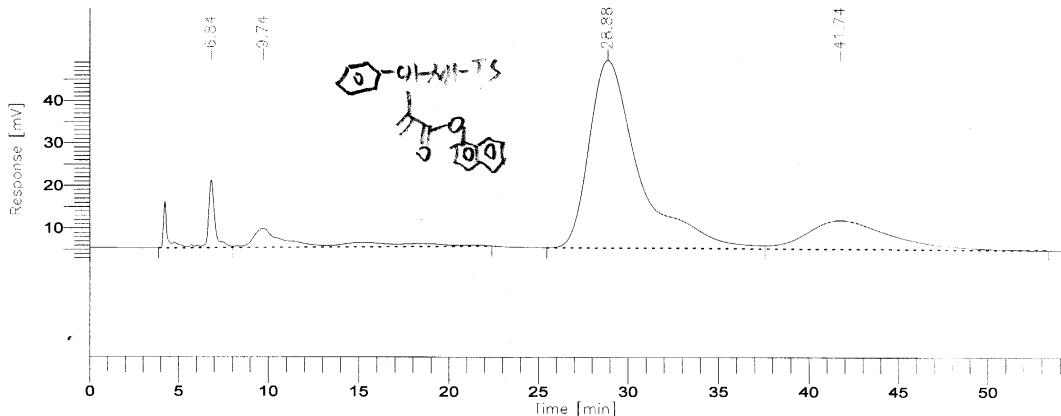
Missing Component Report  
Component                      Expected Retention (Calibration File)

All components were found

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Software Version: 4.1<2F12>  
 Date: 04-4-9 14:42  
 Sample Name : clh040401-2  
 Data File : D:\TC4\DATA\CAO\CAP\_052P.RAW Date: 04-4-9 13:47  
 Sequence File: D:\TC4\DATA\CAO\CAP.SEQ Cycle: 1 Channel : A  
 Instrument : 970A - 0 Rack/Vial: 0/0 Operator:  
 Sample Amount : 1.0000 Dilution Factor : 1.00

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## REPORT

Peak #	Time [min]	Area uV*sec	Height uV	Area %	Norm Area %	BL [s]	Area/Height [s]
1	6.841	586428.76	15891.61	4.82	0.00	BV	36.90
2	9.740	784538.24	4462.79	6.45	0.00	VB	175.80
3	28.879	8542706.36	44189.42	70.28	0.00	BV	193.32
4	41.735	2241809.64	6800.54	18.44	0.00	VB	329.65
				12155483.00	71344.35	100.00	0.00

### Missing Component Report

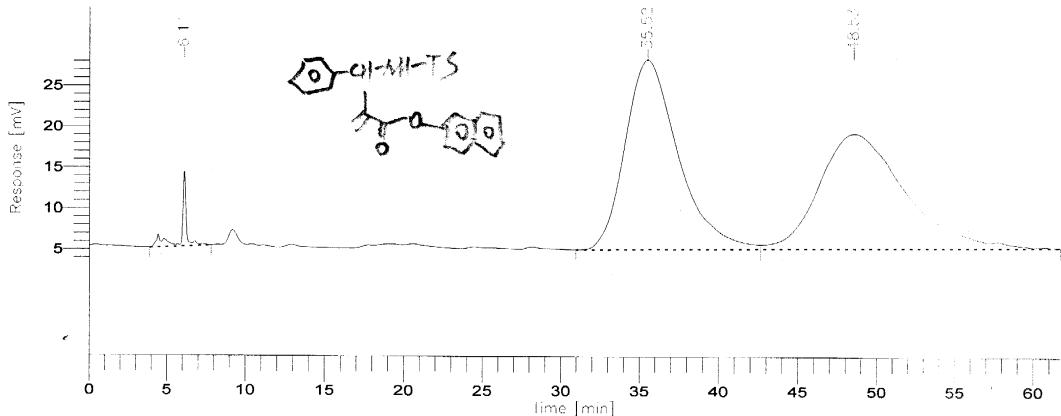
Component	Expected Retention (Calibration File)
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All components were found

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Software Version: 4.1<2F12>  
 Date: 04-4-9 11:12  
 Sample Name : clh-040330-1  
 Data File : D:\TC4\DATA\CAO\CAP\_052M.RAW Date: 04-4-9 10:09  
 Sequence File: D:\TC4\DATA\CAO\CAP.SEQ Cycle: 1 Channel : A  
 Instrument : 970A - 0 Rack/Vial: 0/0 Operator:  
 Sample Amount : 1.0000 Dilution Factor : 1.00

---



## REPORT

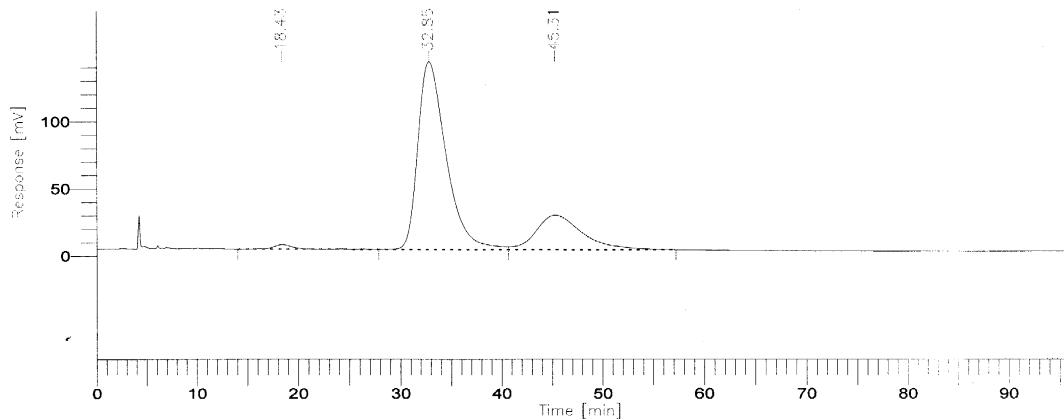
Peak #	Time [min]	Area uV*sec	Height uV	Area [%]	Norm Area [%]	BL	Area/Height [s]
1	6.114	187586.00	9076.29	1.71	0.00	BB	20.67
2	35.523	5423734.99	23174.05	49.45	0.00	BV	234.04
3	48.530	5356939.51	14015.88	48.84	0.00	VB	382.20
		10968260.50	46266.22	100.00	0.00		

### Missing Component Report

Component                      Expected Retention (Calibration File)

All components were found

Software Version: 4.1<2F12>  
Date: 04-4-9 12:51  
Sample Name : clh-040401-1  
Data File : D:\TC4\DATA\CAO\CAP\_052N.RAW Date: 04-4-9 11:13  
Sequence File: D:\TC4\DATA\CAO\CAP.SEQ Cycle: 1 Channel : A  
Instrument : 970A - 0 Rack/Vial: 0/0 Operator:  
Sample Amount : 1.0000 Dilution Factor : 1.00



## REPORT

Peak #	Time [min]	Area uV*sec	Height uV	Area [%]	Norm Area [%]	BL [s]	Area/Height
1	18.427	491849.76	3373.75	1.38	0.00	BV	145.79
2	32.848	27028876.79	139375.40	75.67	0.00	VV	193.93
3	45.305	8196364.95	25774.68	22.95	0.00	VB	318.00
			35717091.50	168523.82	100.00	0.00	

## Missing Component Report

Component                              Expected Retention (Calibration File)

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All components were found

**M**

# Individual Sample Report

Reported by User: System

Project Name: PDA\_996

SampleName LP4-78-T5

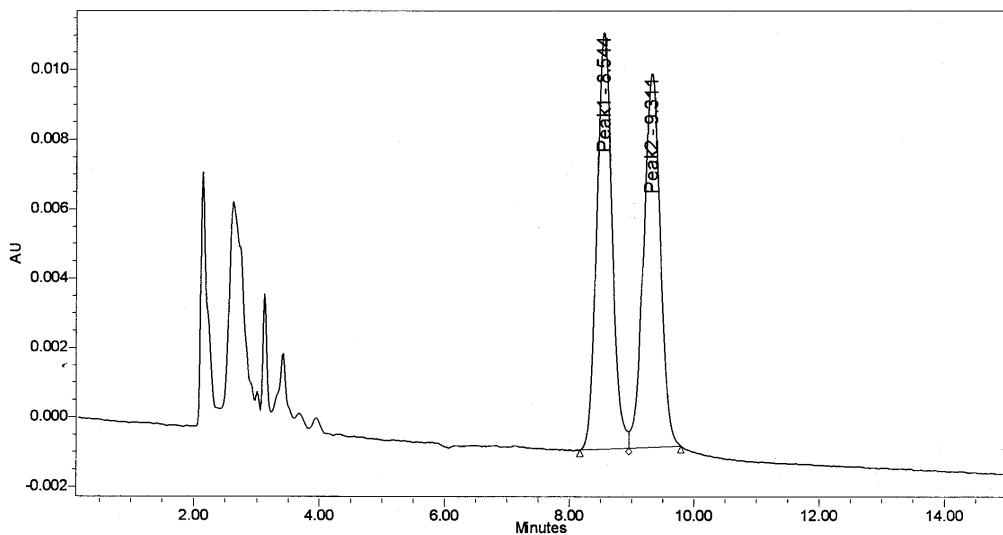
Processed Channel Descr. PDA 254.0 nm

Date Acquired 5/24/02 9:00:53 AM

Run Time 15.00 Minutes

Date Processed 5/24/02 9:32:21 AM

Current Date 5/24/02

**Peak Results**

	RT	Name	Area	Height	Int Type	% Area	% Height	Amount	Units
1	8.544	Peak1	203981	12014	BV	50.34	52.72		
2	9.311	Peak2	201209	10773	VB	49.66	47.28		

**M****Individual Sample Report**

Reported by User: System

Project Name: PDA\_996

SampleName LP5-79

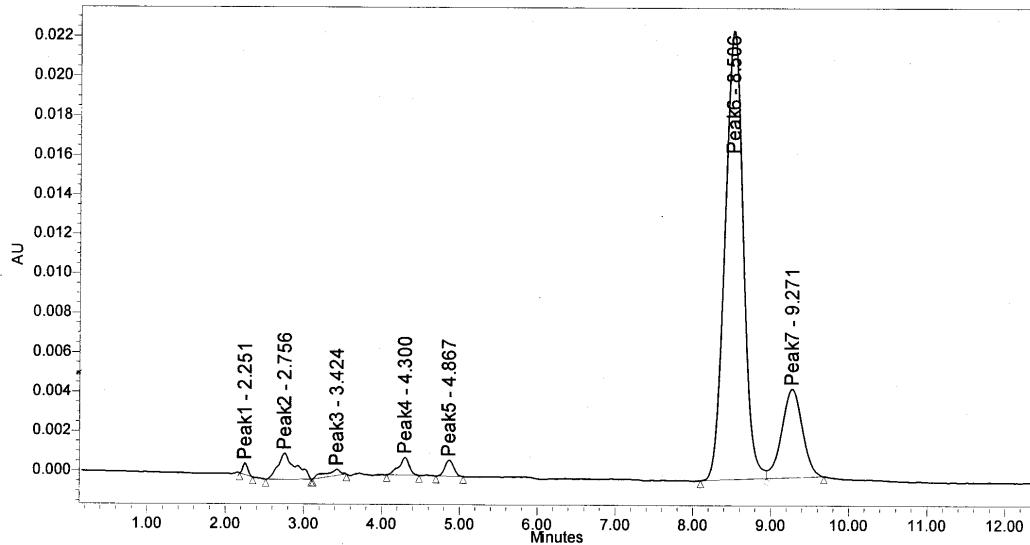
Processed Channel Descr. PDA 254.0 nm

Date Acquired 5/24/02 9:17:09 AM

Run Time 15.00 Minutes

Date Processed 5/24/02 9:33:49 AM

Current Date 5/24/02

**Peak Results**

	RT	Name	Area	Height	Int Type	% Area	% Height	Amount	Units
1	2.251	Peak1	2567	585	BB	0.52	1.88		
2	2.756	Peak2	20841	1331	BB	4.19	4.27		
3	3.424	Peak3	4445	307	BB	0.89	0.98		
4	4.300	Peak4	8333	899	BB	1.68	2.88		
5	4.867	Peak5	6506	823	BB	1.31	2.64		
6	8.506	Peak6	371458	22750	BV	74.76	72.94		
7	9.271	Peak7	82704	4493	VB	16.65	14.41		

Report Method: A\_report\_Full\_1

Printed 1:09:27 PM 5/24/02

Page: 1 of 1

The chiral HPLC chart of optically active **7a**.

Chiral HPLC: TBB column (reversed phase column);  $\lambda = 254$  nm; eluent: Hexane/Isopropanol = 80/20 (0.1% HOAc); Flow rate: 1.0 mL/min.

10)  $^1\text{H}$  NMR charts.

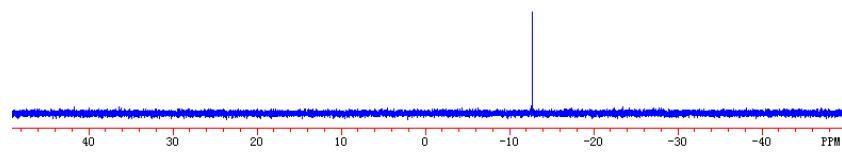


Figure SI-1. The  $^{31}\text{P}$  NMR chart of **LB2** (MOP) in  $\text{CDCl}_3$ .

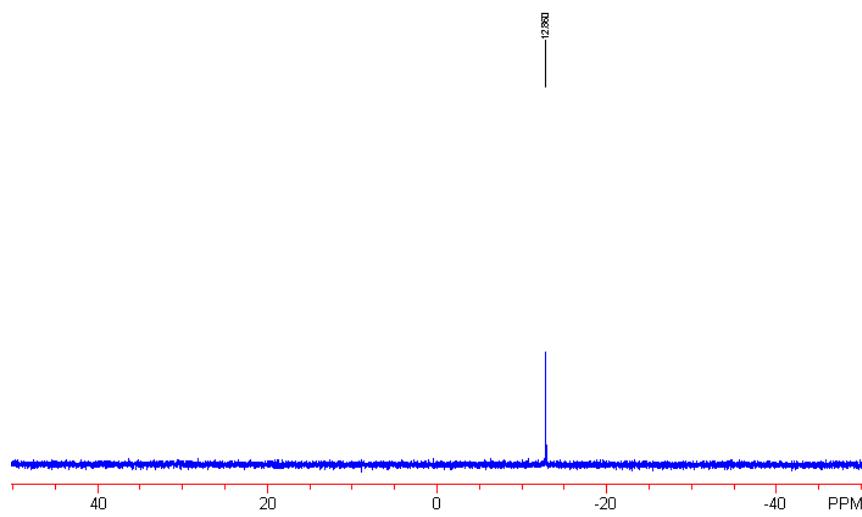


Figure SI-2. The  $^{31}\text{P}$  NMR chart of **LB2** (MOP) with MVK (molar ratio= 1:5) in  $\text{CDCl}_3$ .

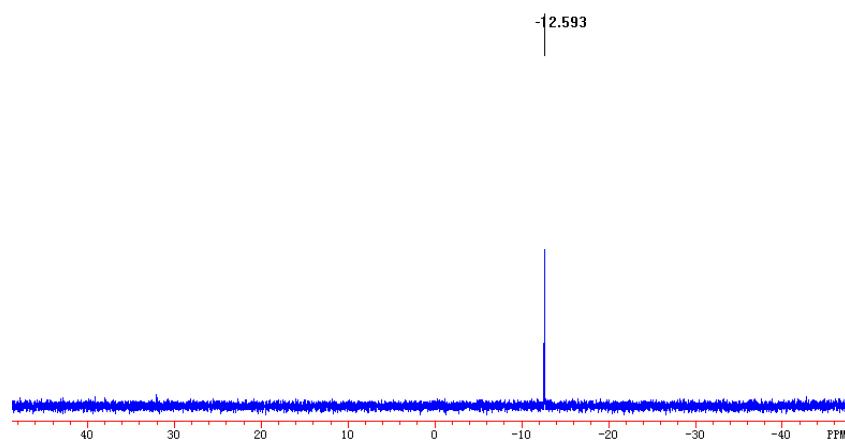


Figure SI-3. The  $^{31}\text{P}$  NMR chart of **LB2** (MOP) with MVK and imine in  $\text{CDCl}_3$ .

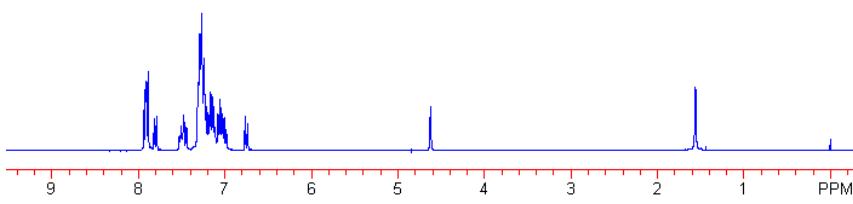


Figure SI-4. The  $^1\text{H}$  NMR chart of **LB1** in  $\text{CDCl}_3$ .

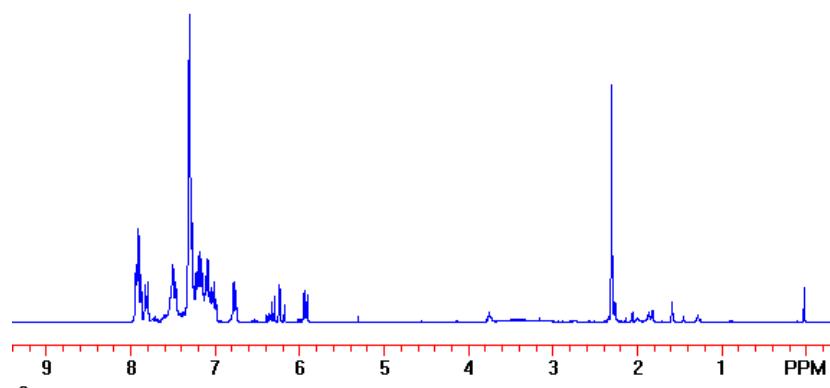


Figure SI-5. The  $^1\text{H}$  NMR chart of **LB1** with MVK in  $\text{CDCl}_3$ .