Supporting Information.

Hyun M. Jung, Jeong H. Koh, Mahn-J. Kim* and Jaiwook Park*

Concerted Catalytic Reactions

for Conversion of Ketones or Enol Acetates to Chiral Acetates

Experimental:

General. All reactions and manipulations were performed under argon using standard Schlenk techniques. Toluene was distilled from sodium benzophenone ketyl under argon. Complex **5** ($((C_6H_5)_4C_4CO)_2H(\mu\text{-}H)(CO)_4Ru_2$) was prepared according to a literature procedure.[1] Novozym 435 (*C. antarctica* lipase B) was a generous gift from Novo Nordisk, Korea. 4-Chlorophenyl acetate was prepared according to a literature procedure.[2] Ketones **2a-d**, **2f**, and **2h** were commercially available and used without further purification. Ketones **2e** and **2g** were prepared according to literature procedures from the corresponding alcohols.[3] Euol acetates **1a-h** were prepared according to literature procedures.[4]

General procedure for conversion of ketones to chiral acetates: In a 50 mL flask equipped with a grease-free high-vacuum stopcock, 4'-methoxyacetophenone (**2b**) (150 mg, 1.00 mmol), $(Ph_4C_4CO)_2H(\mu\text{-}H)(CO)_4Rn_2$ (**5**) (22 mg, 0.020 mmol), 2,6-dimethylheptan-4-ol (268 μL, 1.50 mmol), 4-chloropheuyl acetate (510 mg, 2.99 mmol), and Novozym 435 (30 mg) were mixed in toluene (3.2 mL). The mixture was degassed with sonication under vacuum, and the flask was filled with argon. The resulting suspension was heated at 70 °C for 44 h. The reaction mixture was filtered and separated on silica gel (ethyl acetate/hexane 1:8) to give a mixture (274 mg) of chiral acetate **4b** (91 % yield, 99 % ee) and 4-chlorophenyl acetate (1.00 : 0.55 ratio determined by ^{1}H NMR).

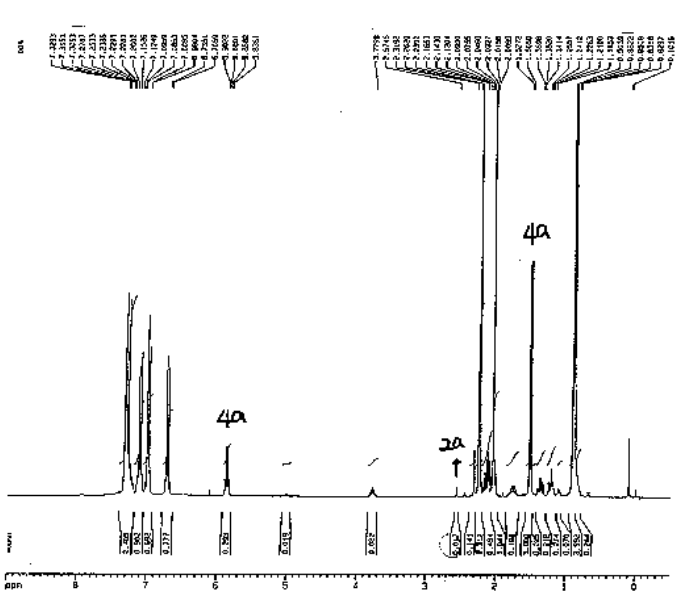
General procedure for conversion of enol acetates to chiral acetates: In a 50 mL flask equipped with a grease-free high-vacuum stopcock, $(Ph_4C_4CO)_2H(\mu\text{-}H)(CO)_4Ru_2$ (**5**) (22 mg, 0.020 mmol), Novozym 435 (28 mg), 2,6-dimethylheptan-4-ol (268 μL,

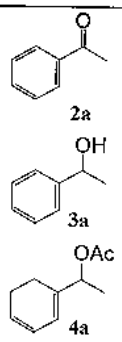
1.50 mmol), and 1-phenylethenyl acetate (**1a**) (162 mg, 1.00 mmol) were mixed in toluene (3.2 mL). The resulting suspension was degassed with sonication under vacuum, and the flask was filled with argon. The suspension was heated at 70 °C for 42 h. The reaction mixture was separated on silica gel (ethyl acetate/hexane 1:8) to give chiral acetate **4a** (139 mg, 85 % yield). The enantiomeric excess was measured by HPLC equipped with a chiral column (R,R) Whelk-O1 (99 %ee).

1. Shvo, Y.; Menashe, N. *Organometallics* **1991**, *10*, 3885.
2. Persson, B. A.; Larsson, A. L. E.; Ray, M. L.; Bäckvall, J.–E. *J. Am. Chem. Soc.* **1999**, *121*, 1645.
3. Almeda, M. L. S.; Beller, M.; Wang, G.-Z.; Bäckvall, J.-E. *Chem. Eur. J.* **1996**, *2*, 1533.
4. Larock, R. C. *Comprehensive Organic Transformations*; VCH: New York, 1989, p. 743.

Spectral data for Tables 1 and 2.

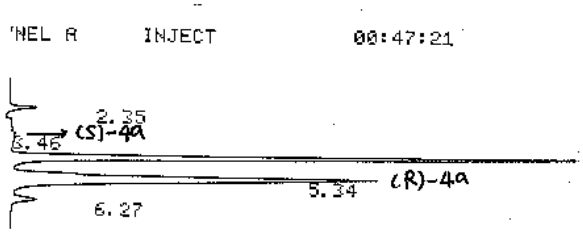
Crude ^{1}H NMR spectra for determination of reaction conversion of **2a** : **Entry 1** in **Table 1**.





3a : not detected.
(2,6-dimethyl-4-heptanol, 2,6-dimethyl-4-heptanone, 4-chlorophenyl acetate, 4-chlorophenol and toluene are shown on spectra)

HPLC analysis for determination of enantiomeric excess of **4a** : **Entry 1** in **Table 1**.



00:47:21

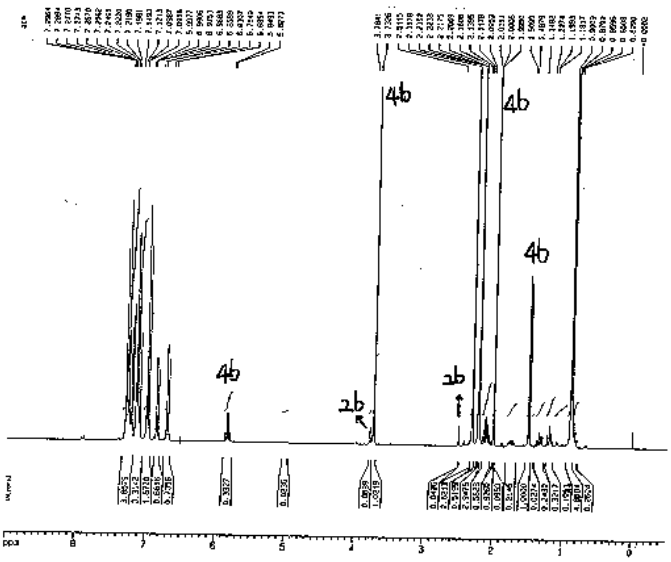
FILE 1. METHOD 0. RUN 2 INDEX 2

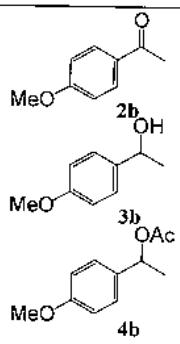
PEAK#	AREA%	RT	AREA	BC
1	1.705	2.35	3827	01
2	0.359	3.46	805	01
3	46.978	4.45	105470	01
4	48.298	5.34	108434	02
5.	2.66	6.27	5973	03
AL	100.		224509	

Condition :
(R,R) Whelk-O1, Merk eluent hexane/iPrOH 95:5, 1.0 ml/min.

Retention time :
(*S*)-**4a** (3.46 min),
(*R*)-**4a** (5.34 min).

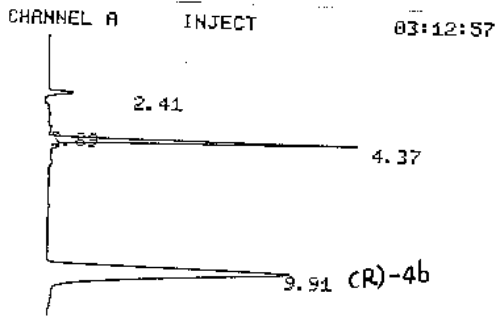
Crude ^{1}H NMR spectra for determination of reaction conversion of **2b** : **Entry 2** in **Table 1.**





3b : not detected.
(2,6-dimethyl-4-heptanol, 2,6-dimethyl-4-heptanone, 4-chlorophenyl acetate, 4-chlorophenol and toluene are shown on spectra)

HPLC analysis for determination of enantiomeric excess of **4b** : **Entry 2** in **Table 1.**



03:1

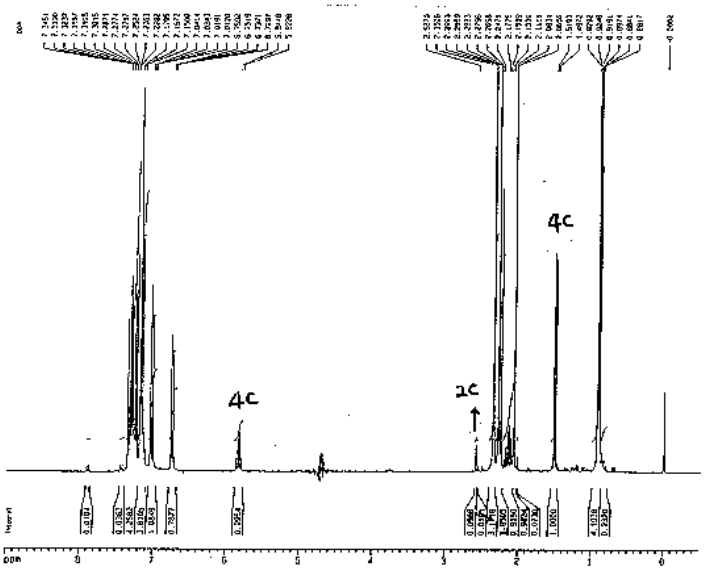
FILE 1. METHOD 0. RUN 10 INJ

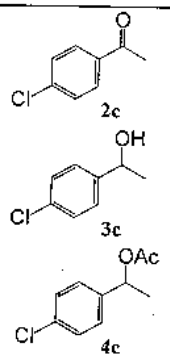
PEAK#	AREA%	RT	AREA	BC
1	2.108	2.41	3295	01
2	0.147	3.89	230	01
3	24.715	4.37	38624	01
4	73.029	9.91	114126	01
TOTAL	100.		156275	

Condition :
(R,R) Whelk-O1, Merk eluent hexane/iPrOH 95:5, 1.0 ml/min.

Retention time :
(*S*)-**4b** (4.56 min)/ not detected,
(*R*)-**4b** (9.91min).

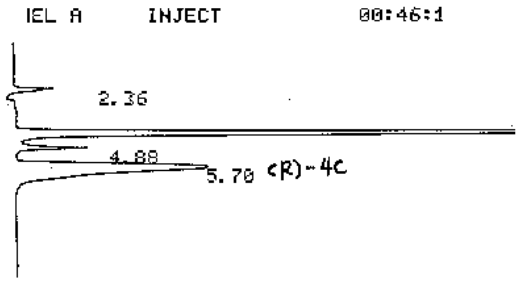
Crude ^{1}H NMR spectra for determination of reaction conversion of **2c** : **Entry 3** in **Table 1**.





3c : not detected.
(2,6-dimethyl-4-heptanol, 2,6-dimethyl-4-heptanone, 4-chlorophenyl acetate, 4-chlorophenol and toluene are shown on spectra)

HPLC analysis for determination of enantiomeric excess of **4c** : **Entry 3** in **Table 1**.



00:4

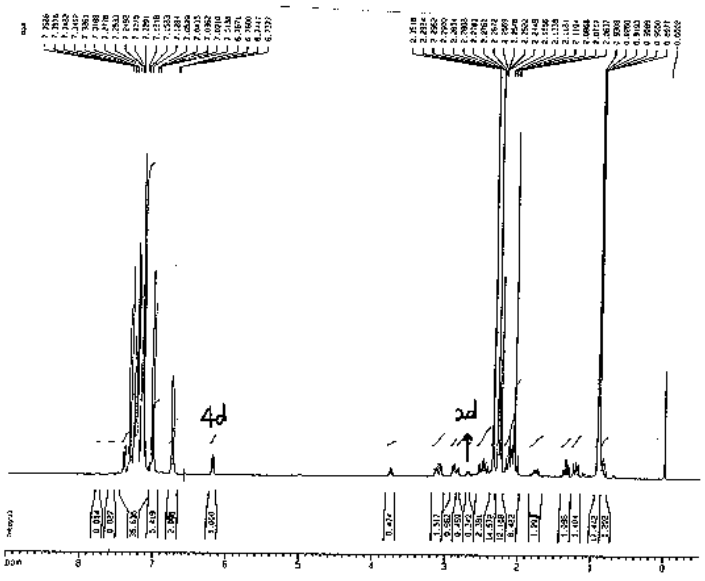
FILE 1. METHOD 0. RUN 2 INDI

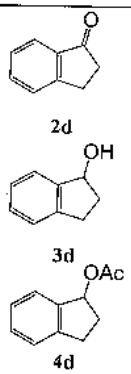
PEAK#	AREA%	RT	AREA	BC
1	2.254	2.36	5919	01
2	57.678	4.2	151433	08
3	3.321	4.88	8719	05
4	36.747	5.7	96478	01
AL	100.		262549	

Condition :
(R,R) Whelk-O1, Merk eluent hexane/iPrOH 95:5, 1.0 ml/min.

Retention time :
(*S*)-**4c** (3.54 min)/not detected
(*R*)-**4c** (5.70 min).

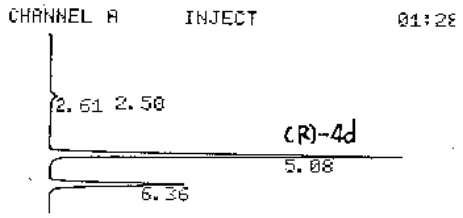
Crude ^{1}H NMR spectra for determination of reaction conversion of **2d** : **Entry** 4 in **Table 1**.





3d : not detected.
(2,6-dimethyl-4-heptanol, 2,6-dimethyl-4-heptanone, 4-chlorophenyl acetate, 4-chlorophenol and toluene are shown on spectra)

HPLC analysis for determination of enantiomeric excess of **4d** : **Entry** 4 in **Table 1**.



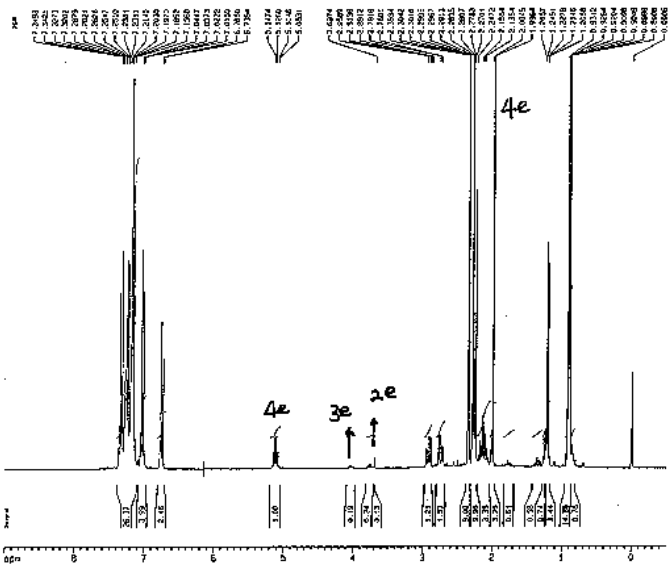
FILE 1. METHOD 0. RUN 3

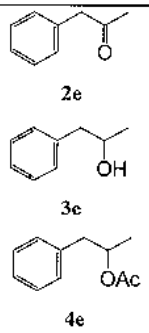
PEAK#	AREA%	RT	AREA
1	0.292	2.5	232
2	0.512	2.61	407
3	68.965	5.08	54866
4	30.232	6.36	24
TL	100.		79

Condition :
(R,R) Whelk-O1, Merk
eluent hexane/iPrOH 99:1,
1.0 ml/min.

Retention time :
(*S*)-**4d** (5.32min)/not detected
(*R*)-**4d** (5.08 min).

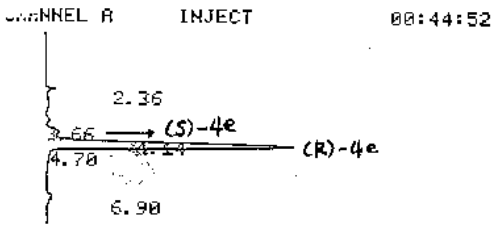
Crude ^{1}H NMR spectra for determination of reaction conversion of **2e** : **Entry** 5 in **Table** 1.





(2,6-dimethyl-4-heptanol, 2,6-dimethyl-4-heptanone, 4-chlorophenyl acetate, 4-chlorophenol and toluene are shown on spectra)

HPLC analysis for determination of enantiomeric excess of 4e: **Entry** 5 in **Table** 1.



00:44:

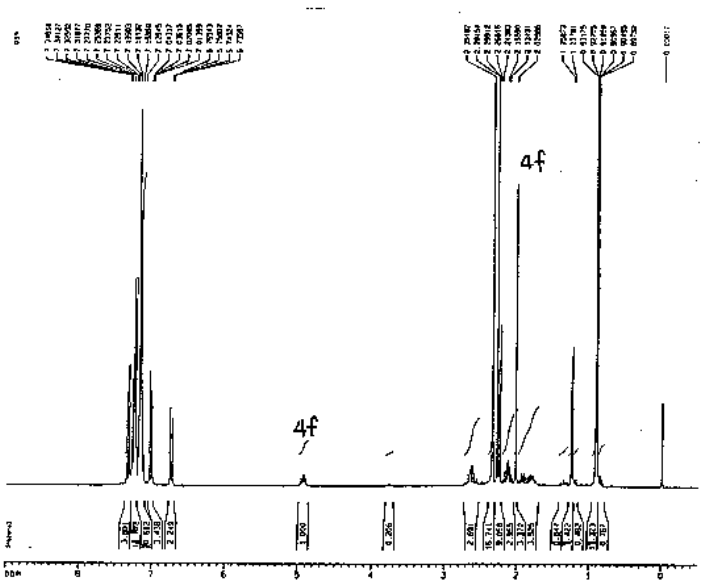
FILE 1. METHOD 0. RUN 2 IHDE

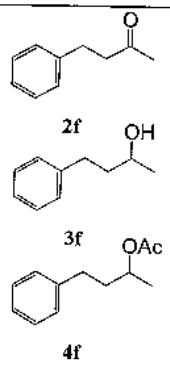
PEAK#	AREA%	RT	AREA	BC
1	0.593	2.36	455	01
2	0.909	3.66	697	02
3	4.813	4.14	3690	02
4	92.541	4.7	70949	03
5	1.144	6.9	877	01
AL	100.		76668	

Condition :
(R,R) Whelk-O1, Merck. eluent hexane/iPrOH 99:1, 1.0 ml/min.

Retention time :
(*S*)-**4e** (4.14 min),
(*R*)-**4e** (4.70 min)

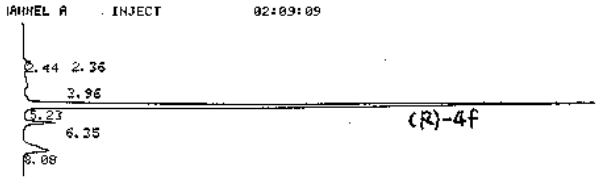
Crude ^{1}H NMR spectra for determination of reaction conversion of **2f** : **Entry 6** in **Table 1**.





2f : not detected,
3f : not detected.
(2,6-dimethyl-4-heptanol, 2,6-dimethyl-4-heptanone, 4-chlorophenyl acetate, 4-chlorophenol and toluene are shown on spectra)

HPLC analysis for determination of enantiomeric excess of **4f** : **Entry 6** in **Table 1**.



02:09:09 CH= "A" PS= 1.

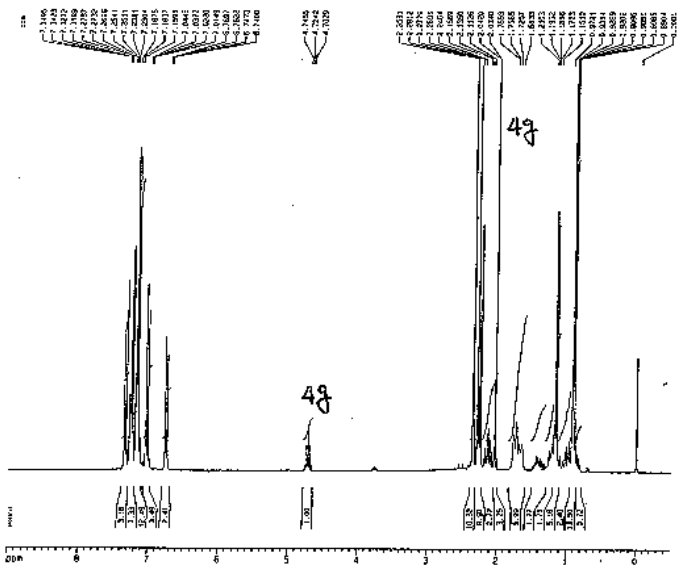
FILE 1. METHOD 0. RUN 6 INDEX 6

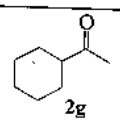
PEAK#	AREA%	RT	AREA	BC
1	0.141	2.36	338	02
2	0.332	2.44	797	03
3	1.171	2.96	2813	01
4	87.085	5.23	209188	02
5	4.064	6.34	9762	03
6	7.207	8.08	17313	01
TAL	100.		240211	

Condition :
(R,R) Whelk-O1, Merck.
eluent hexane/iPrOH 99:1, 1.0 ml/min.

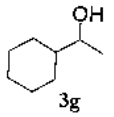
Retention time :
(*S*)-**4f** (4.96 min)/not detected
(*R*)-4f (5.23 min)

Crude ^{1}H NMR spectra for determination of reaction conversion of **2g** : **Entry** 7 in **Table 1**.

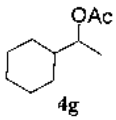




2g



3g



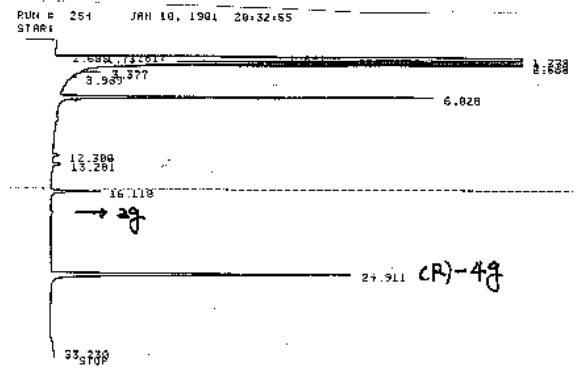
4g

2g : not resolved

3g : not detected.

(2,6-dimethyl-4-heptanol, 2,6-dimethyl-4-heptanone, 4-chlorophenyl acetate, 4-chlorophenol and toluene are shown on spectra)

GC analysis for determination of reaction conversion and enantiomeric excess of **4g**: **Entry** 7 in **Table 1**.



Closing signal file M:\SIGNAL .BNA

RUN# 254 JAN 10, 1901 20:32:55

SIGNAL FILE: M:\SIGNAL.BNA
AREAX

RT	AREA	TYPE	WIDTH	AREA%
1.617	49710	PV	.012	.02798
1.641	206223	VV	.014	.11614
1.688	6880	VB	.012	.00383
1.737	31293	PH	.011	.01761
1.779	92946752	>BHH	.182	52.31962
2.279	59074464	>BHH	.116	33.25293
2.588	15902584	BHB	.064	8.95154
3.372	122117	TBP	.087	.06874
3.969	31732	TPB	.037	.01786
6.028	3908718	BB	.153	2.20021
12.380	119864	BP	.266	.06747
13.281	154905	PB	.259	.08720
16.118	587710	BB	.184	.33082
24.911	4481261	BB	.226	2.52249
33.238	27798	PV	.668	.01564

TOTAL AREA=1.776SE+08
MUL FACTOR=1.0000E+00

Condition :

Chiraldex B-PH, Alltech, Initial temp. 60 °C (10 min), increase temp. rate 2 °C/min, final temp. 85 °C.

Retention time :

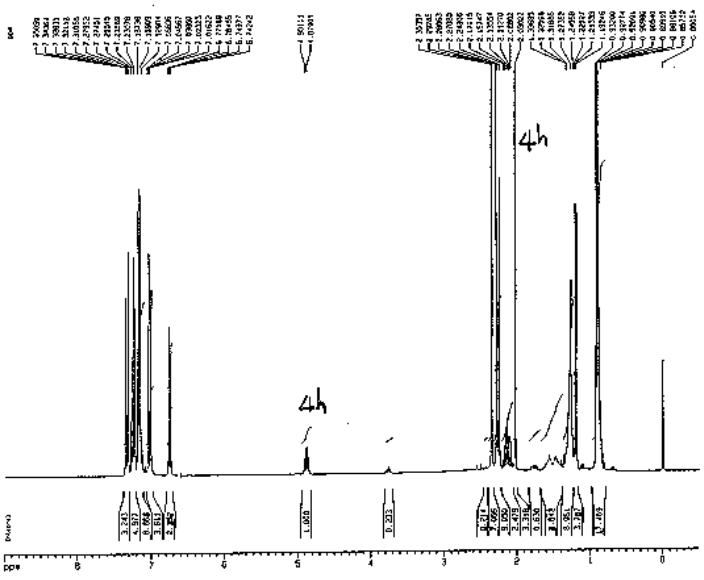
(*S*)-**4g** (24.51 min)/ not detected

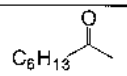
(*R*)-**4g** (24.91 min),

3g (30.65 min)/not detected,

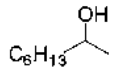
2g (18.45 min),

Crude ^{1}H NMR spectra for determination of reaction conversion of **2h** : **Entry 8** in **Table 1**.

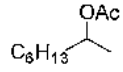




2h



3h



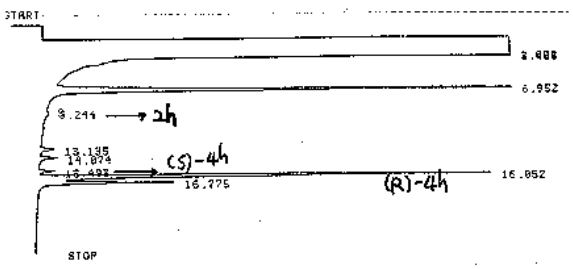
4h

2h : not detected.

3h : not resolved.

(2,6-dimethyl-4-heptanol, 2,6-dimethyl-4-heptanone, 4-chlorophenyl acetate, 4-chlorophenol and toluene are shown on spectra)

GC analysis for determination of reaction conversion and enantiomeric excess of **4h**: **Entry 8** in **Table1**.




```
Closing signal file M:SIGNAL   .BNC

RUN#   248          JAN 10, 1901  13:36:32

SIGNAL FILE: M:SIGNAL.BNC
AREA%
      RT        AREA TYPE  WIDTH       AREA%
   1.602  954498568 >SHB  1.870   95.791778
   3.465    2823726  TBB   .093     .28338
   6.952   18595488  TBB   .243    1.866521
   9.244      73278  BV    .211     .00735
  13.135     508080  BV    .291     .05099
  14.074     618875  VB    .275     .06211
  16.492     474271  BV    .225     .04760
  16.052   14981528  VV    .250    1.49047
  16.775    3987289  VB    .225     .40017

TOTAL AREA=9.9643E+08
MIN FACTOR=1.0000E+00
```

Condition :

Chiraldex B-PH, Alltech.

Initial temp. 60 °C (10 min), increase temp. rate 2 °C/min, final temp. 85 °C.

Retention time :

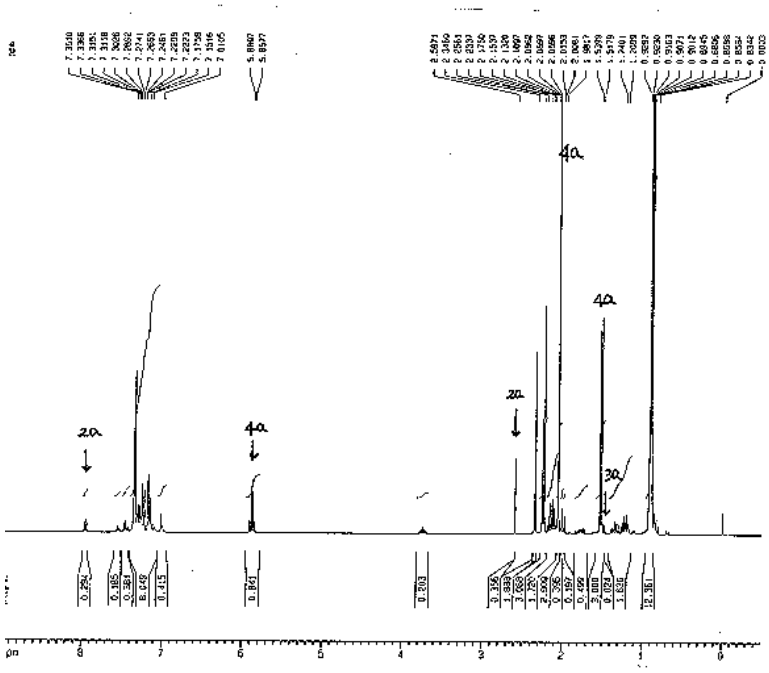
(*S*)-**4h** (15.49 min),

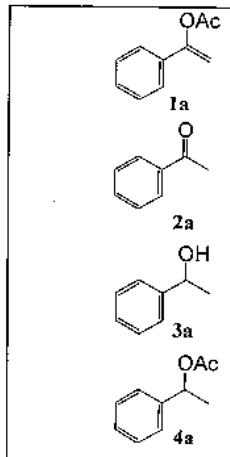
(*R*)-**4h** (16.05 min),

3h (18.85 min)/not detected,

2h (9.24 min),

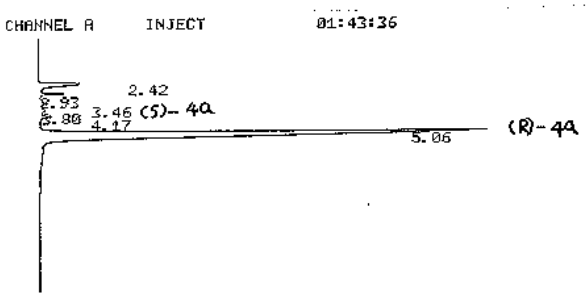
Crude ^{1}H NMR spectra for determination of reaction conversion of **1a** : **Entry** 1 in **Table** 2.





1a : not detected.
(2,6-dimethyl-4-heptanol, 2,6-dimethyl-4-heptanone and toluene are shown on spectra)

HPLC analysis for determination of enantiomeric excess of **4a** : **Entry** 1 in **Table** 2.



01:43:36 CH= "R" PS= 1.

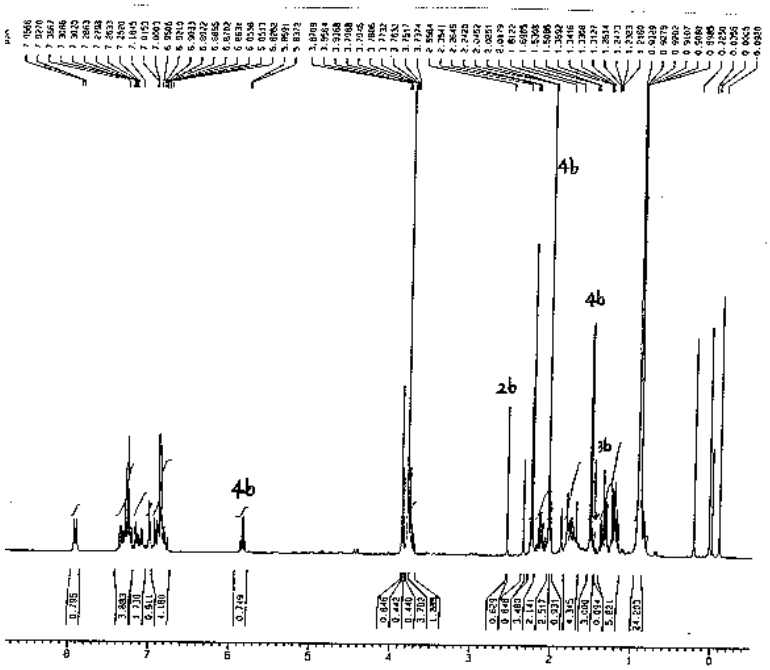
FILE 1. METHOD 0. RUN 4 INDEX 4

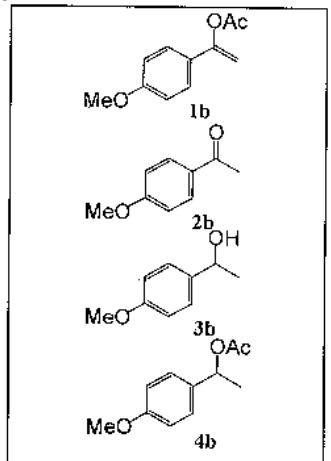
PEAK#	AREA%	RT	AREA	BC
1	4.522	2.42	7934	01
2	1.207	2.93	2117	01
3	0.837	3.46	1468	02
4	0.804	3.8	1410	02
5	0.979	4.17	1717	03
6	91.652	5.06	160809	01
TOTAL	100.		175455	

Condition :
(R,R) Whelk-O1, Merk eluent hexane/iPrOH 95:5, 1.0 ml/min.

Retention time :
(*S*)-**4a** (3.46 min),
(*R*)-**4a** (5.06 min).

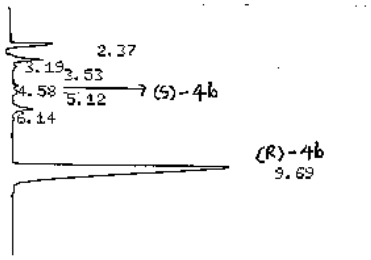
Crude ^{1}H NMR spectra for determination of reaction conversion of **1b** : **Entry 2** in **Table 2**.





1b : not detected.
(2,6-dimethyl-4-heptanol, 2,6-dimethyl-4-heptanone and toluene are shown on spectra)

HPLC analysis for determination of enantiomeric excess of **4b** : **Entry 2** in **Table 2**.



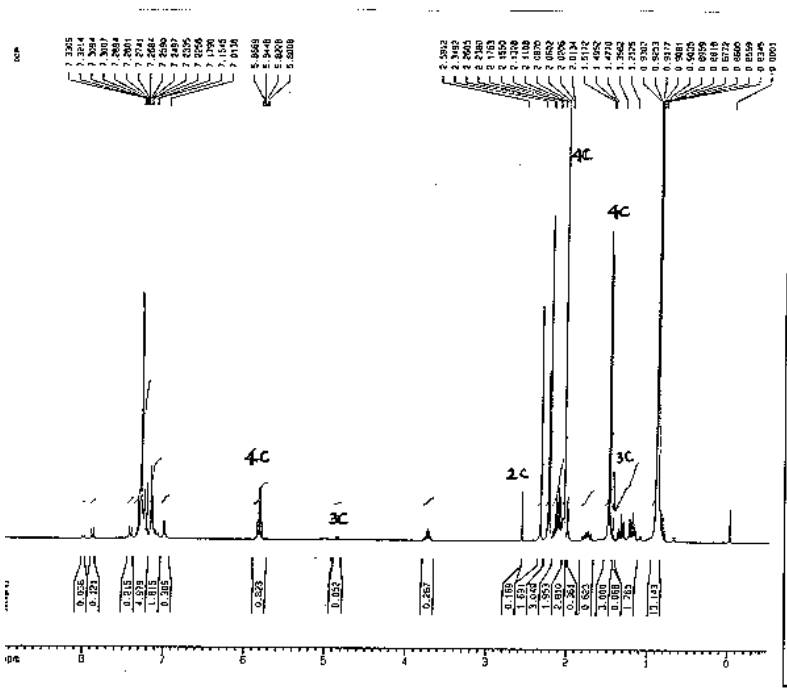
FILE 1. METHOD 0. RUN 2

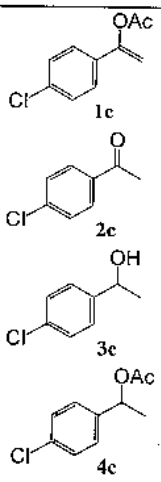
PEAK#	AREA%	RT	AREA	BC
1	4.417	2.37	7355	01
2	4.374	3.19	7283	01
3	0.312	3.53	519	01
4	0.813	4.58	1354	02
5	1.295	5.12	2157	03
6	3.099	6.14	5160	01
7	85.69	9.69	142686	01
L	100.		166514	

Condition :
(R,R) Whelk-O1, Merk eluent hexane/iPrOH 95:5, 1.0 ml/min.

Retention time :
(*S*)-**4b** (4.58 min),
(*R*)-**4b** (9.69 min).

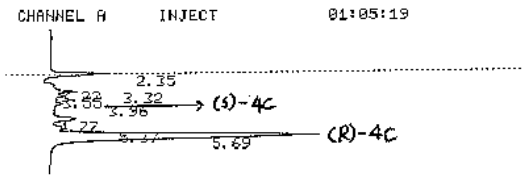
Crude ^{1}H NMR spectra for determination of reaction conversion of **1c** : **Entry 3** in **Table 2**.





1c : not detected.
(2,6-dimethyl-4-heptanol, 2,6-dimethyl-4-heptanone and toluene are shown on spectra)

HPLC analysis for determination of enantiomeric excess of **4c** : **Entry 3** in **Table 2**.



01:05:19

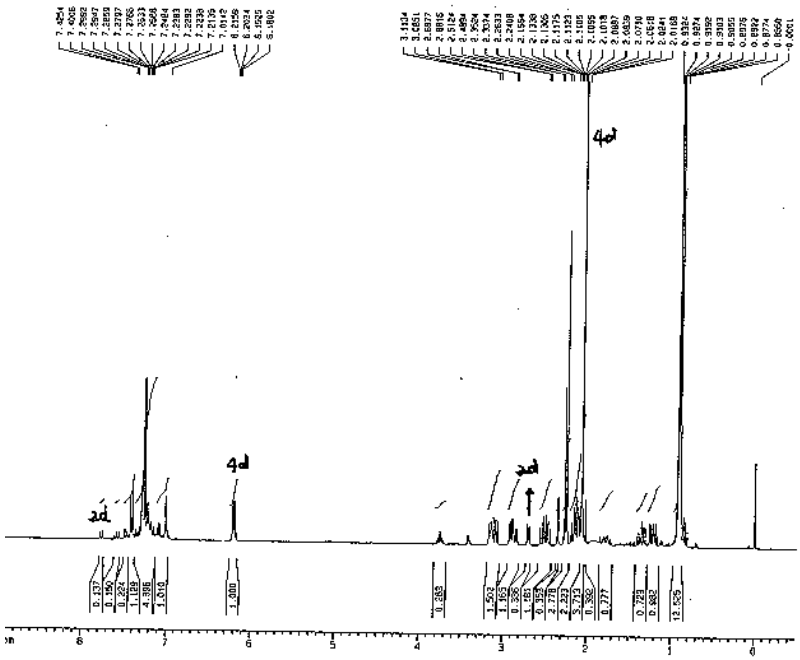
FILE 1. METHOD 0. RUN 2 INDEX 2

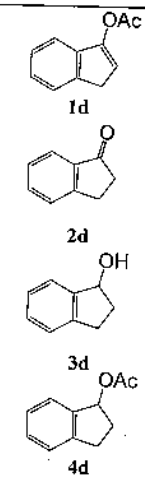
PEAK#	AREA%	RT	AREA	BC
1	7.9	2.35	11238	01
2	2.725	3.22	3877	02
3	3.147	3.32	4477	02
4	1.294	3.55	1837	03
5	0.91	3.96	1294	01
6	4.654	4.77	6620	02
7	2.489	5.37	3541	02
8	76.883	5.69	109369	03
TOTAL	100.		142253	

Condition :
(R,R) Whelk-O1, Merk eluent hexane/iPrOH 95:5, 1.0 ml/min.

Retention time :
(*S*)-**4c** (3.55 min),
(*R*)-**4c** (5.69 min).

Crude ^{1}H NMR spectra for determination of reaction conversion of **1d** : **Entry 4** in **Table 2**.



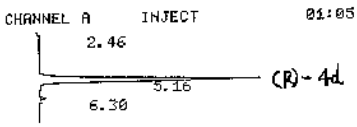


1d : not detected.

3d : not detected.

(2,6-dimethyl-4-heptanol, 2,6-dimethyl-4-heptanone and toluene are shown on spectra)

HPLC analysis for determination of enantiomeric excess of **4d** : **Entry 4** in **Table 2**.



01:05:30

FILE 1. METHOD 0. RUN 2 INDEX 2

PEAK#	AREA%	RT	AREA	BC
1	0.323	2.46	193	01
2	96.701	5.16	57868	01
3	2.976	6.3	1781	01
TOTAL	100.		59842	

Condition :

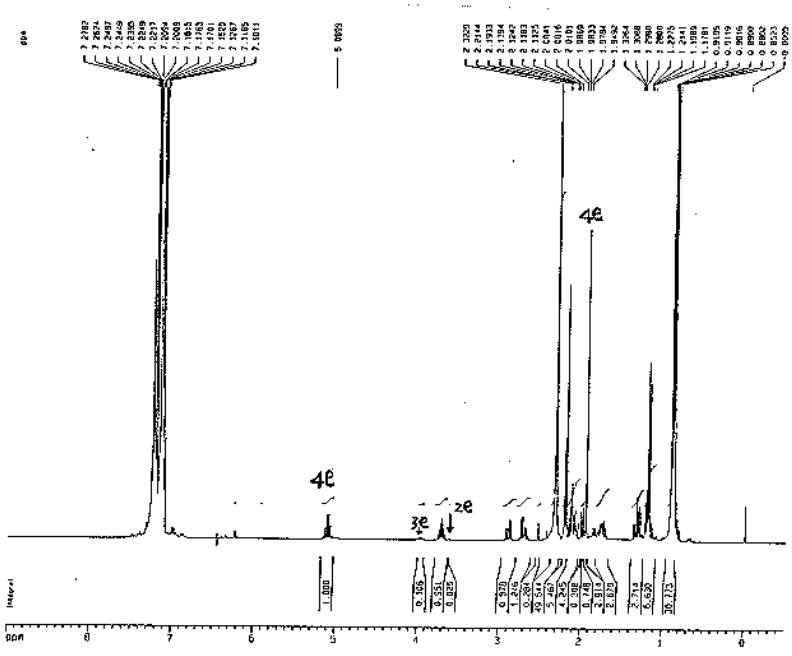
(R,R) Whelk-O1, Merk eluent hexane/iPrOH 99:1, 1.0 ml/min.

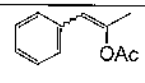
Retention time :

(*S*)-**4d** (5.32min)/not detected

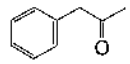
(*R*)-**4d** (5.16 min).

Crude ^{1}H NMR spectra for determination of reaction conversion of **1e** : **Entry 5** in **Table 2**.

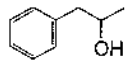




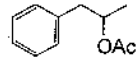
1e



2e



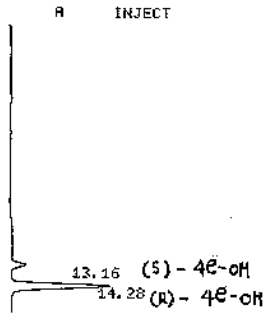
3e



4e

1e : not detected.
(2,6-dimethyl-4-heptanol, 2,6-dimethyl-4-heptanone and toluene are shown on spectra)

HPLC analysis for determination of enantiomeric excesses of **4e** : **Entry 5** in **Table 2**.
(after hydrolysis to alcohol)

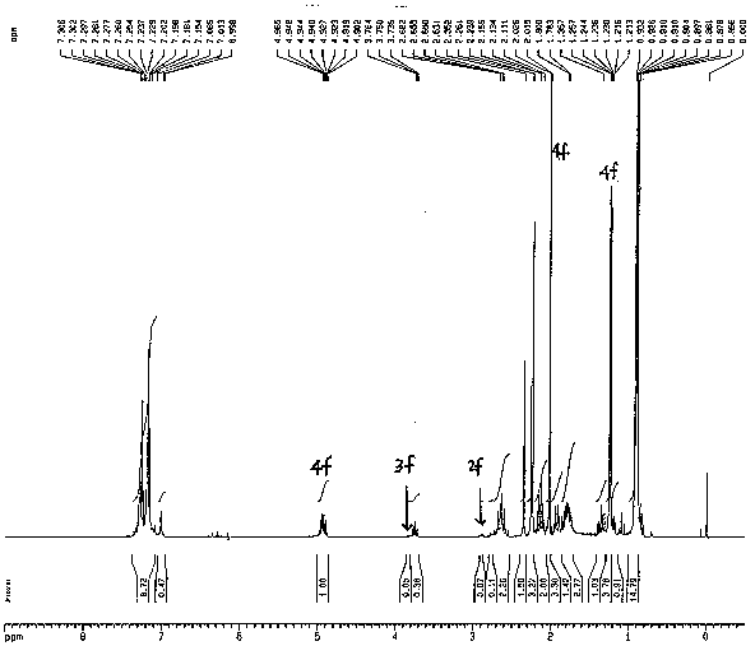


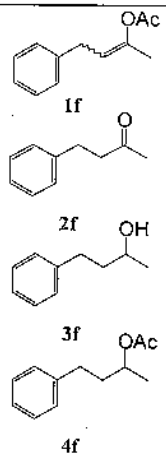
FILE 1.	METHOD 0.	RUN 1	
PEAK#	AREA%	RT	AREA BC
1	10.619	13.16	4606 01
2	89.381	14.28	38768 01
TOTAL	100.		43374

Condition :
Chiralcel OD, Daicel eluent hexane/iPrOH 98:2, 1.0 ml/min.

Retention time :
(*S*)-**4e-OH** (13.16 min),
(*R*)-**4e-OH** (14.28 min)

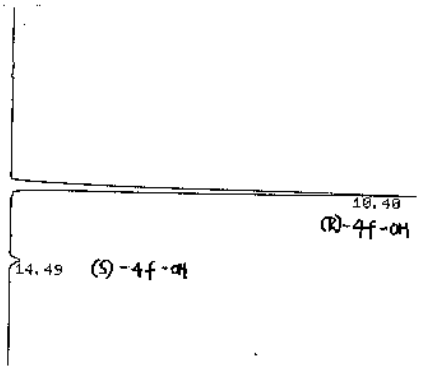
Crude ^{1}H NMR spectra for determination of reaction conversion of **1f** : **Entry 6** in **Table 2**.





1f : not detected.
(2,6-dimethyl-4-heptanol, 2,6-dimethyl-4-heptanone and toluene are shown on spectra)

HPLC analysis for determination of enantiomeric excess of **4f** : **Entry 6** in **Table 2**.
(after hydrolysis to alcohol)



01:04:36

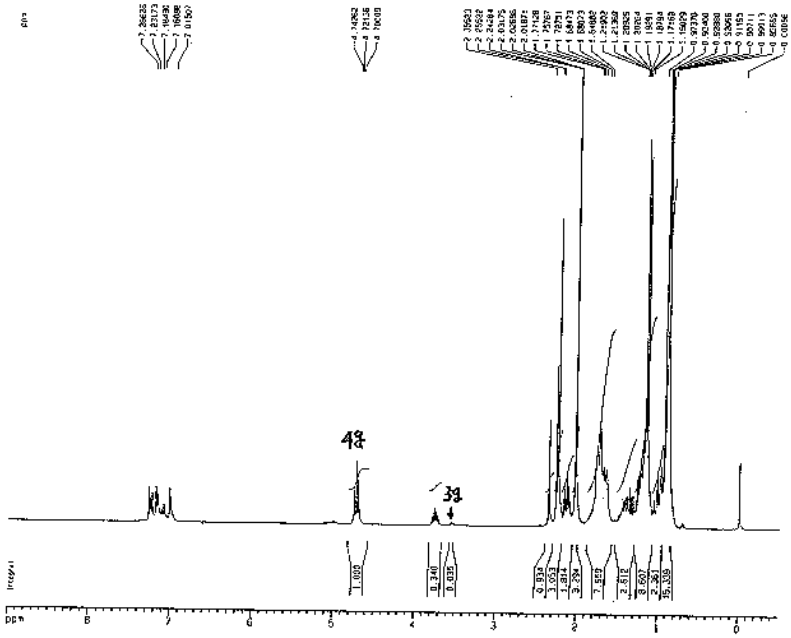
FILE 1. METHOD 0. RUN 1 INDEX 1

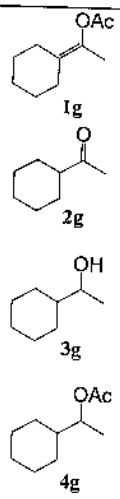
PEAK#	AREA%	RT	AREA BC
1	96.926	10.4	124733 01
2	3.074	14.49	3956 01
	100.		128689

Condition :
Chiralcel OD, Daicel
eluent hexane/iPrOH 95:5,
1.0 ml/min.

Retention time :
(*S*)-**4f-OH** (14.49 min),
(*R*)-**4f-OH** (10.40 min)

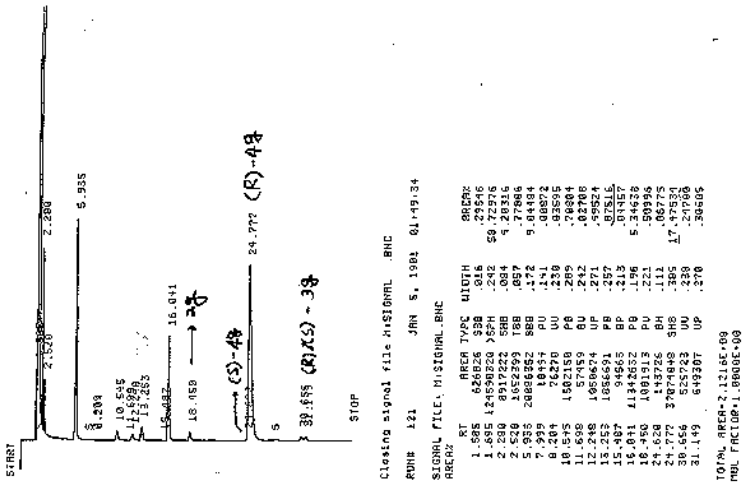
Crude ^{1}H NMR spectra for determination of reaction conversion of **1g** : **Entry 7** in **Table 2**.





1g : not detected.
2g : not resolved.
(2,6-dimethyl-4-heptanol, 2,6-dimethyl-4-heptanone and toluene are shown on spectra)

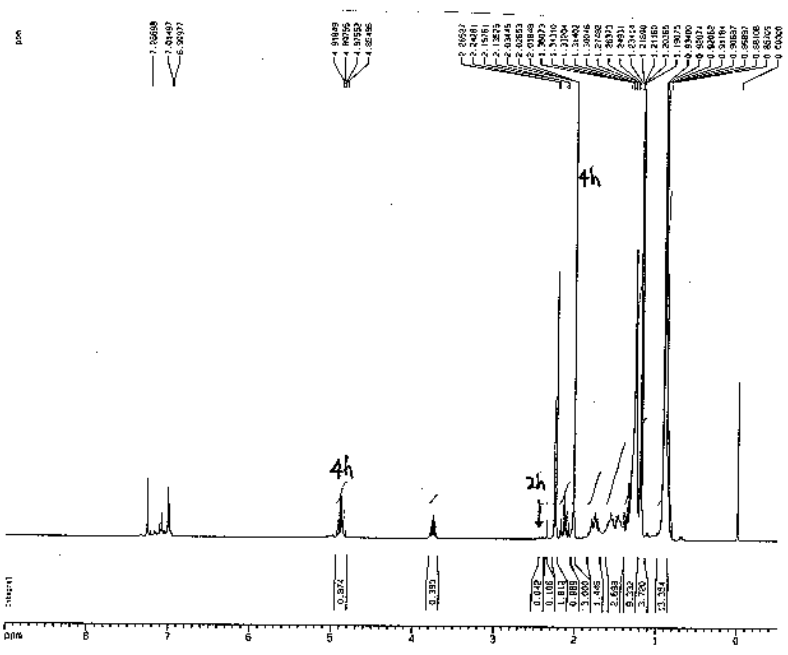
GC analysis for determination of reaction conversion and enantiomeric excess of **4g**: **Entry 7** in **Table 2**.

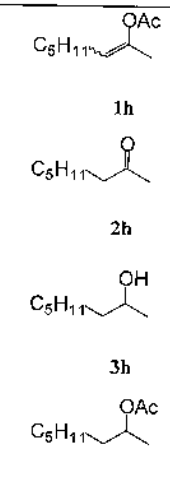


Condition :
Chiraldex B-PH, Alltech.
Initial temp. 60 °C (10 min), increase temp. rate 2 °C/min, final temp. 85 °C.

Retention time :
(*S*)-**4g** (24.62 min),
(*R*)-**4g** (24.78 min),
(*S*)/(*R*)-**3g** (30.66, 31.15 min)
2g (18.45 min),
1g (25.46, 27.90 min)/ not detected.

Crude ^{1}H NMR spectra for determination of reaction conversion of **1h** : **Entry 8** in **Table 2**.



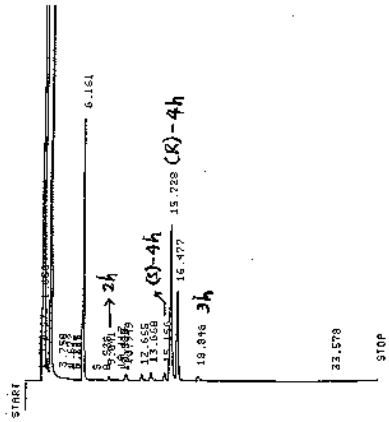


1h : not detected.

3h : not resolved.

(2,6-dimethyl-4-heptanol, 2,6-dimethyl-4-heptanone and toluene are shown on spectra)

GC analysis for determination of reaction conversion and enantiomeric excess of **4h**: **Entry 8** in **Table 2**.



RUN# 143 JAN 5, 1981 22:20:55

SIGNAL FILE: M:SIGNAL.BNC
AREAX

RT	AREA	TYPE	WIDTH	AREA%
1.578	2642	PB	.085	.00101
1.658	513853	BPB	.012	.19524
1.672	184459	TBB	.010	.07020
1.769	120512840	>SPH	.234	45.86141
2.211	28463	TBB	.024	.00893
2.575	83279912	>SH6	.162	31.69217
2.758	9639	TB6	.054	.00367
4.672	5668	TBV	.010	.00216
5.161	9847	TVP	.026	.00327
5.263	3422	TPP	.025	.00130
5.335	6630	TPV	.033	.00252
6.161	22753928	SPB	.159	8.66140
8.538	24749	VV	.163	.00942
9.041	508140	VV	.196	.19833
10.112	9456	PB	.006	.00360
10.425	1271	PB	.006	.00052
10.588	19745	BV	.109	.00751
10.949	972121	VB	.274	.37185
12.665	843152	PB	.254	.32087
12.688	1156262	BB	.241	.44007
15.166	939298	PV	.208	.35757
15.729	20091744	VV	.233	7.64600
16.477	9626950	VB	.195	3.66358
18.846	774080	PV	.271	.29458
33.578	502807	PV	1.442	.19135

TOTAL AREA=2.6277E+08

Condition :

Chiraldex B-PH, Alltech. Initial temp. 60 °C (10 min), increase temp. rate 2 °C/min, final temp. 85 °C.

Retention time :

(*S*)-**4h** (15.17 min),

(*R*)-**4h** (15.73 min)

3h (18.85 min)

2h (9.04 min),

1h (15.90, 18.89, 20.38 min)/ not detected.