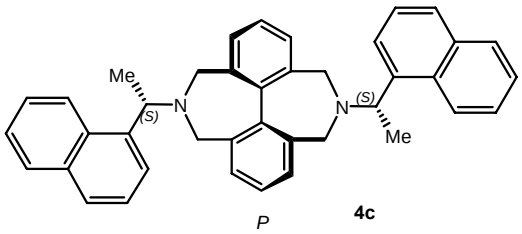
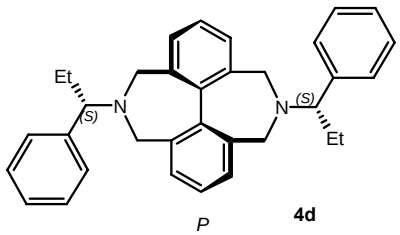
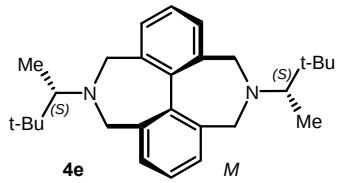


P **4c**

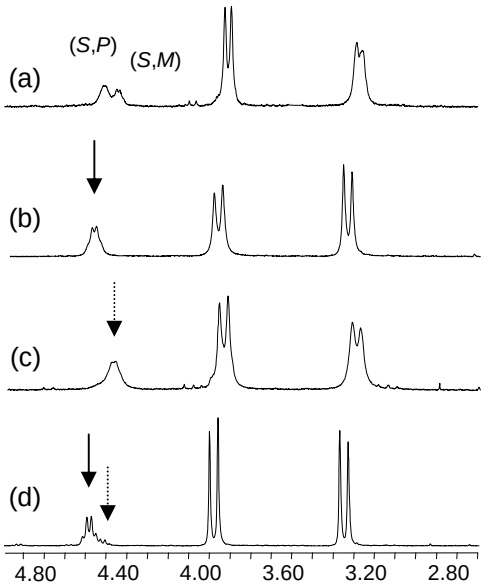


P **4d**

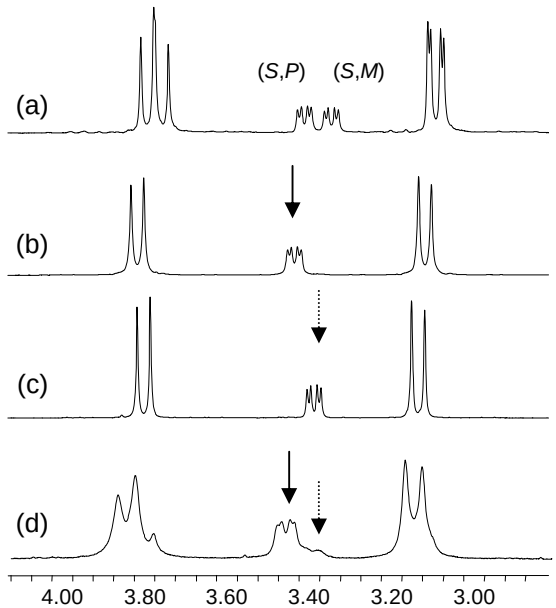


4e *M*

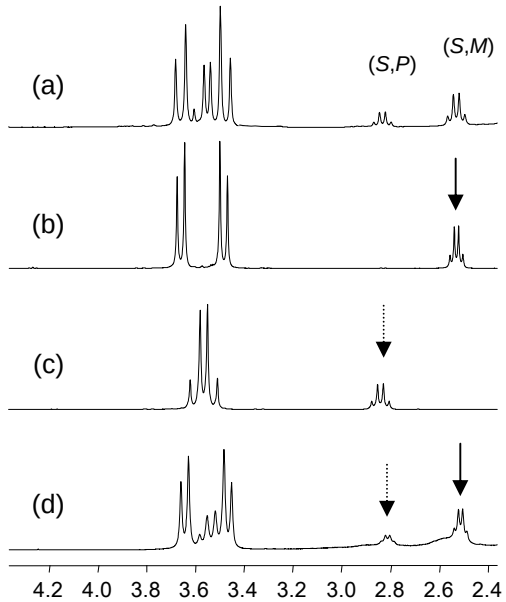
Ratios: (a) right after the synthesis; (b) first eluted (major) diastereomer; (c) second eluted (minor) diastereomer; (d) after 20 h at 80 °C (benzene)



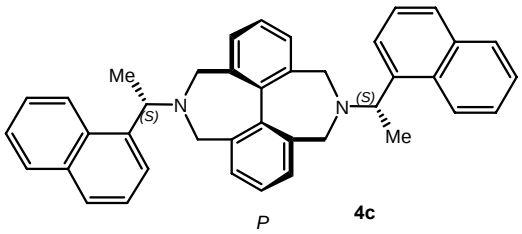
d.r. (*S*,*P*):(*S*,*M*) : (a) 1.4 : 1; (b) > 49 : 1; (c) > 1 : 49; (d) 4.3 : 1



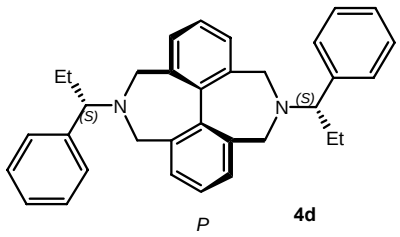
d.r. (*S*,*P*):(*S*,*M*) : (a) 1.1 : 1; (b) > 49 : 1; (c) > 1 : 49; (d) 4.2 : 1



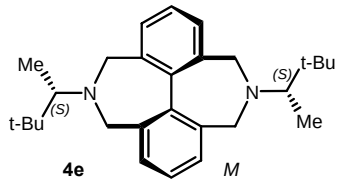
d.r. (*S*,*M*):(*S*,*P*) : (a) 2.4 : 1; (b) > 49 : 1; (c) > 1 : 49; (d) 2.5 : 1



P **4c**

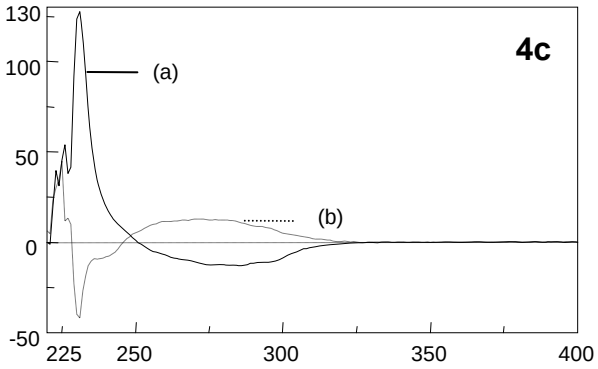


P **4d**

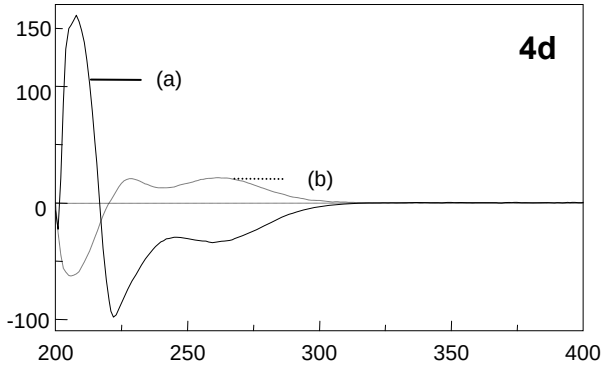


4e *M*

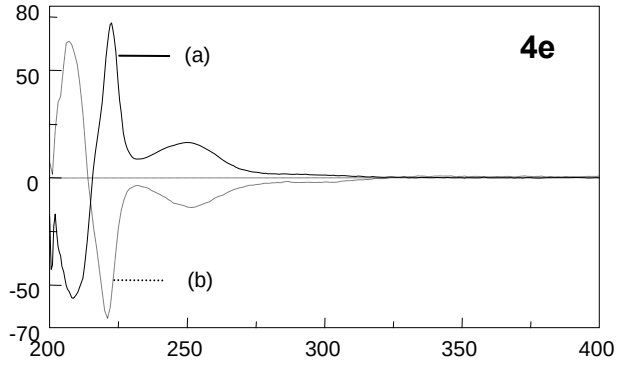
(a, plain) first eluted (major) diastereomer and (b, dashed) second eluted (minor) diastereomer



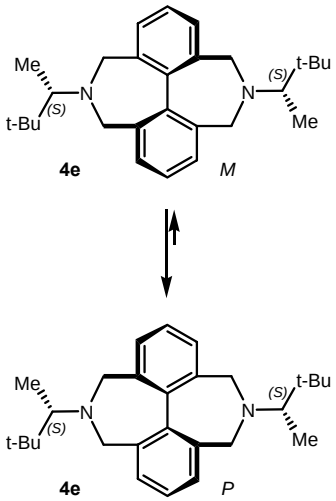
(*c* 1.10^{-5} M, CH_2Cl_2)



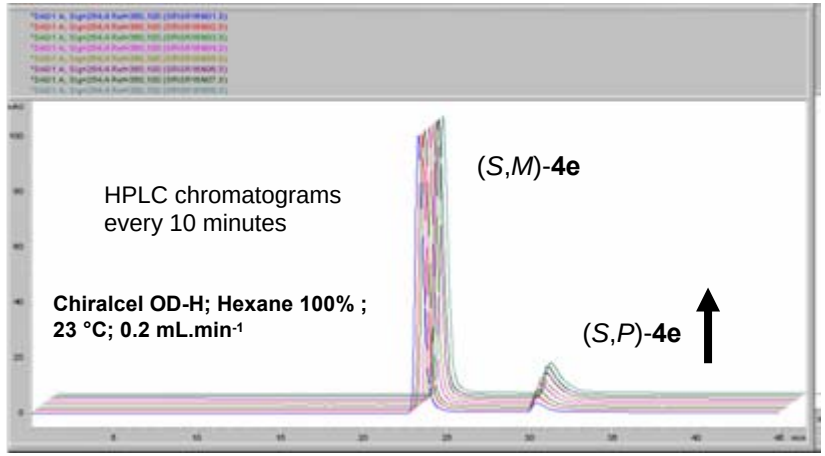
(*c* 1.10^{-5} M, MeOH)



(*c* 1.10^{-5} M, MeOH)



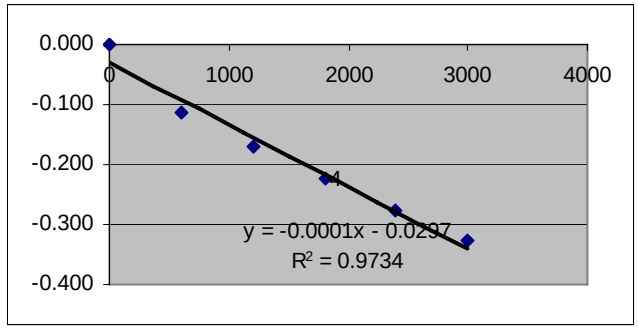
■ Experimental monitoring (HPLC) of the isomerisation (60 °C)

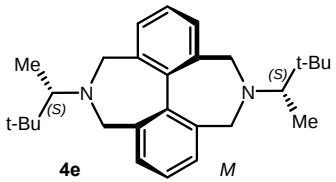


■ First-Order kinetics : ln ([a]/[ao]) = -k t [a] is the concentration of the major diastereomer
k is the kinetic constant and easily determined by the slope of the equation

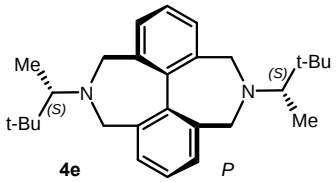
slope = -1.038E-04
DG = 107.308 kJ/mol
Température: 60 °C t1/2 = 6.68E+03 s 1.86 h
333.15 K R-square value = **0.97339**

Entrée	t [min]	t [s]	Maj	Min	d.e.	[a]/[a0]	ln ([a]/[ao])
0	0	0	100.00	0.00	100.00	1.00	0.000
1	10	600	94.60	5.40	89.20	0.89	-0.114
2	20	1200	92.16	7.84	84.32	0.84	-0.171
3	30	1800	90.02	9.98	80.04	0.80	-0.223
4	40	2400	87.93	12.07	75.86	0.76	-0.276
5	50	3000	86.01	13.99	72.02	0.72	-0.328



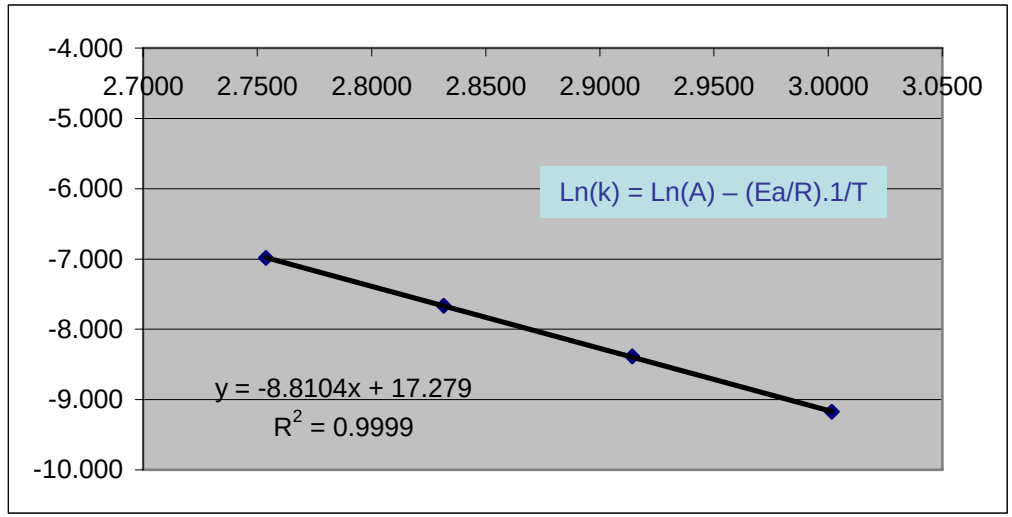


4e *M*



4e *P*

	T [K]	1000/T	k[s^{-1}]	ln(k)
60 °C	333	3.002	1.04E-04	-9.173
70 °C	343	2.914	2.28E-04	-8.386
80 °C	353	2.832	4.68E-04	-7.667
90 °C	363	2.754	9.25E-04	-6.986



Arrhenius Equation:

k = A.exp(-Ea/RT)
Ln(k) = Ln(A) – (Ea/R).1/T

Eyring Equation:

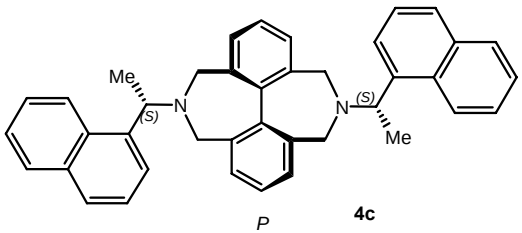
$\Delta H^{\neq}$ = Ea - RT
$\Delta S^{\neq}$ = R[Ln(h.A/$k_{B.}$T) - 1]
$\Delta G^{\neq}$ = $\Delta H^{\neq}$ - T$\Delta S^{\neq}$

ln(k)= f(1000/T)

slope=	-8.810	(- Ea/R)
intercept=	17.279	(Ln(A))

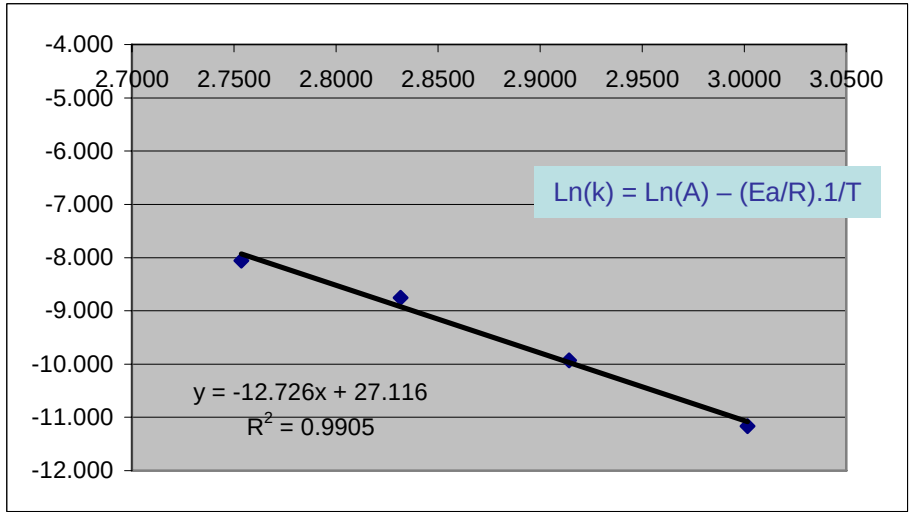
T	20	°C	
Ea	**73.479**	**kJ/mol**	**R^2 =** **0.999**
A	**3.19E+07**	**s^{-1}**	

$\Delta H^{\neq}$ = Ea-RT	16.994	kcal/mol
$\Delta S^{\neq}$ = R[ln(h.A/k.T)-1]	-26.178	cal/(mol.K)
$\Delta G^{\neq}$	24.668	kcal/mol



P **4c**

T [K]	1000/T	k [s^{-1}]	ln(k)
333	3.002	1.42E-05	-11.164
343	2.914	4.87E-05	-9.929
353	2.832	0.000158	-8.754
363	2.754	0.000316	-8.059



Arrhenius Equation:

$k = A.\exp(-Ea/RT)$
$Ln(k) = Ln(A) – (Ea/R).1/T$

Eyring Equation:

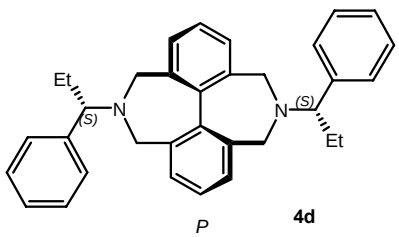
$\Delta H^{\neq} = Ea - RT$
$\Delta S^{\neq} = R[Ln(h.A/k_{B}.T) - 1]$
$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$

ln(k)= f(1000/T)

slope=	-12.726	(- Ea/R)
intercept=	27.116	(Ln(A))

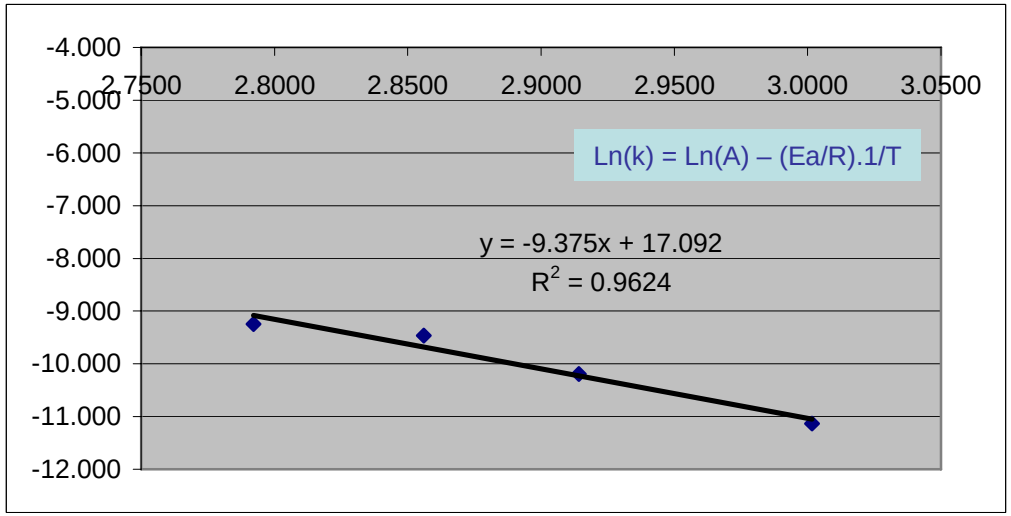
T	20	°C	
Ea	**106.138**	**kJ/mol**	**R^2 = 0.991**
A	**5.97E+11**	**s^{-1}**	

$\Delta H^{\neq}$ = Ea-RT	24.807	kcal/mol
$\Delta S^{\neq}$ = R[ln(h.A/k.T)-1]	-6.614	cal/(mol.K)
$\Delta G^{\neq}$	26.746	kcal/mol



P **4d**

T [K]	1000/T	k [s^{-1}]	ln(k)
333	3.002	1.46E-05	-11.133
343	2.914	3.74E-05	-10.194
350	2.856	7.74E-05	-9.466
358	2.792	9.63E-05	-9.248



Arrhenius Equation:

$k = A.\exp(-Ea/RT)$
$Ln(k) = Ln(A) – (Ea/R).1/T$

Eyring Equation:

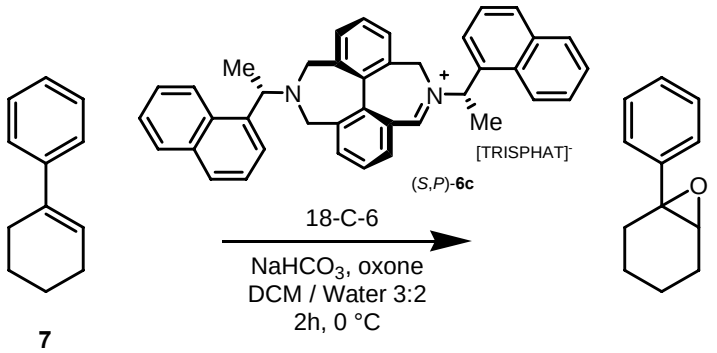
$\Delta H^{\neq} = Ea - RT$
$\Delta S^{\neq} = R[Ln(h.A/k_{B}.T) - 1]$
$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$

ln(k)= f(1000/T)

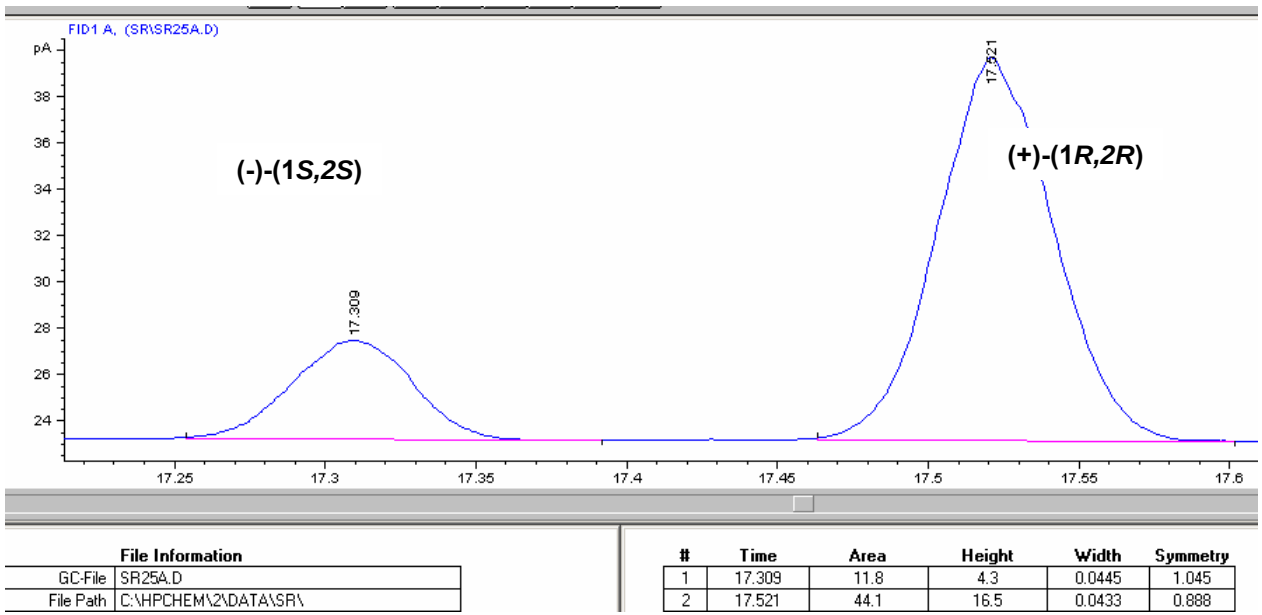
slope= -9.374959 (- Ea/R)
intercept= 17.09232 (Ln(A))

T 20 °C
Ea 78.187 kJ/mol **R^2 = 0.962**
A 2.64E+07 s^{-1}

$\Delta H^{\neq}$ = Ea-RT	18.120	kcal/mol
$\Delta S^{\neq}$ = R[ln(h.A/k.T)-1]	-26.550	cal/(mol.K)
$\Delta G^{\neq}$	25.903	kcal/mol



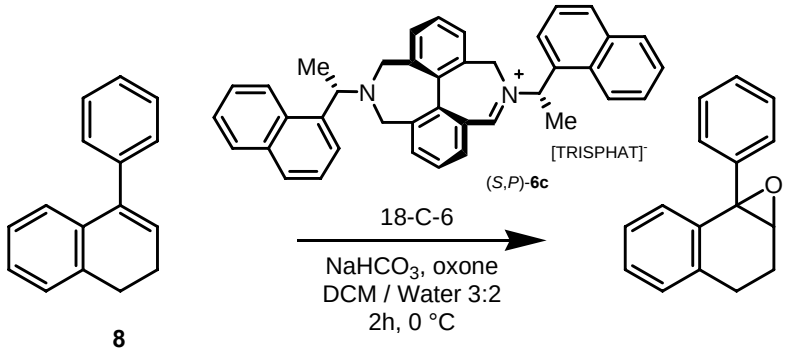
7



File Information	
GC-File	SR25A.D
File Path	C:\HPCHEM\2\DATA\SR\

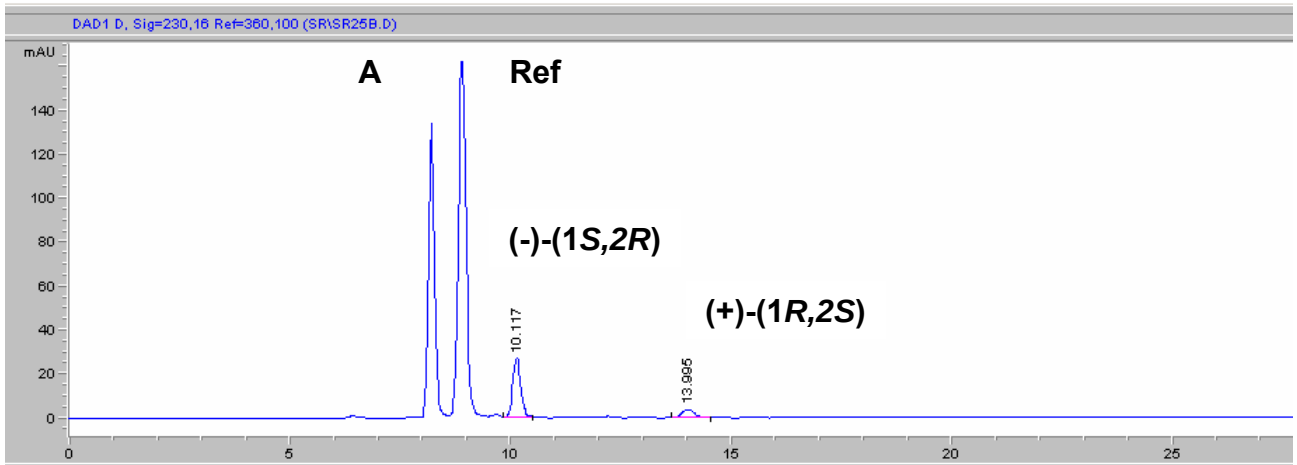
#	Time	Area	Height	Width	Symmetry
1	17.309	11.8	4.3	0.0445	1.045
2	17.521	44.1	16.5	0.0433	0.888

Determined by CSP-GC (Chiraldex Hydrodex β–3P), T_{inj} 250 °C, P = 0.842 bar;
Conditions: 80 °C, 5 min, then progression to 180 °C in 20 min, then 180 °C for 5 min.



8

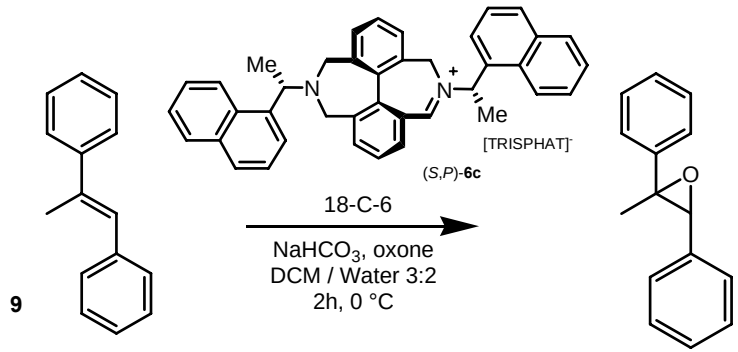
A: Alkene, Ref: naphthalene



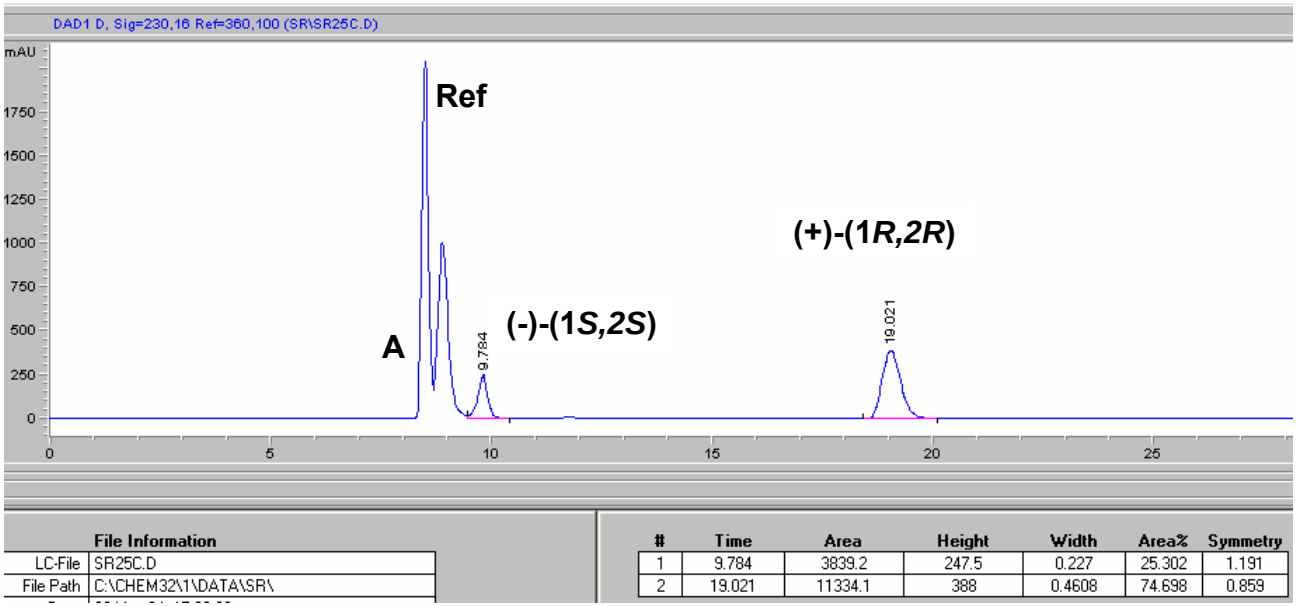
File Information	
LC-File	SR25B.D
File Path	C:\CHEM32\1\DATA\SR\

#	Time	Area	Height	Width	Area%	Symmetry
1	10.117	351.2	26.9	0.2021	83.726	0.899
2	13.995	68.3	3.6	0.2975	16.274	0.975

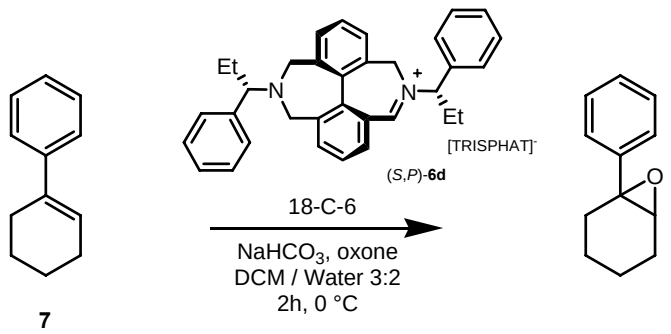
Determined by CSP-HPLC (Chiralcel OD-H); Hexane / iPrOH 95 : 5 ; 0.5 mL.min^{-1}



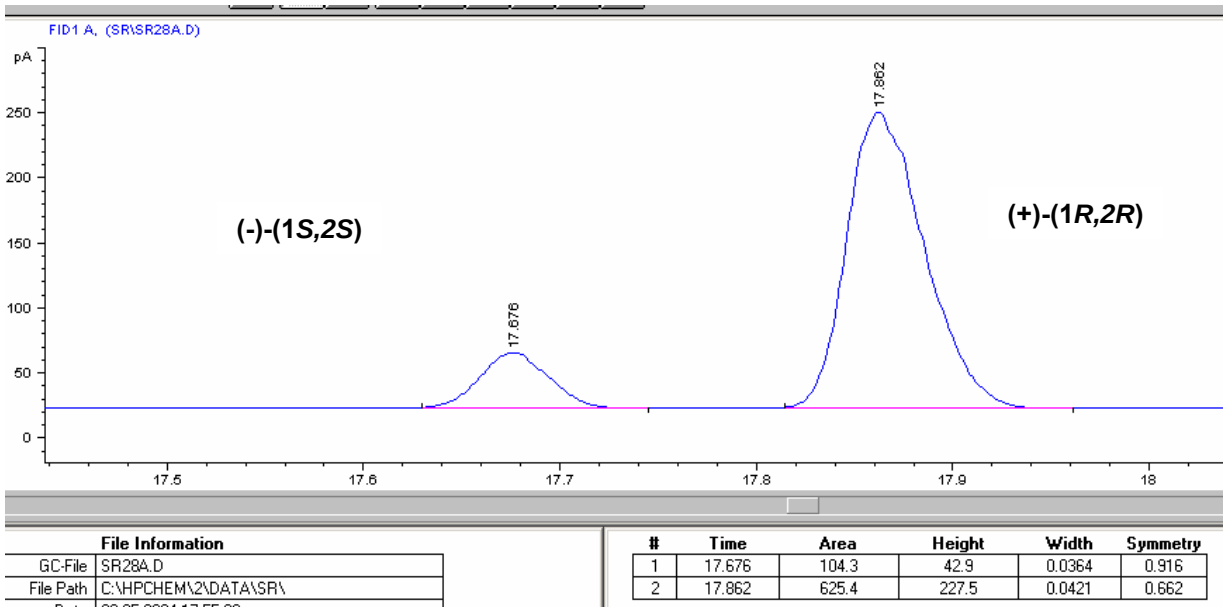
A: Alkene, Ref: naphthalene



Determined by CSP-HPLC (Chiralcel OD-H); Hexane / iPrOH 95 : 5 ; 0.5 mL.min^{-1}



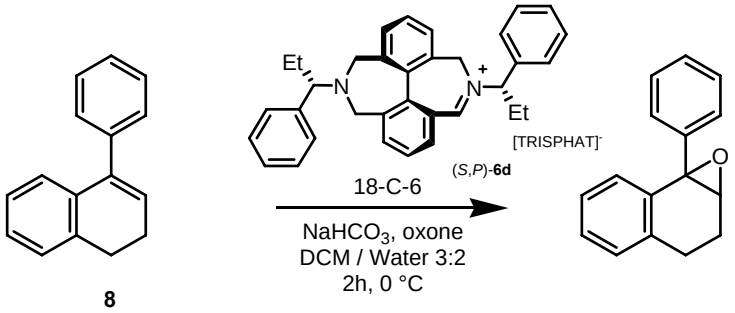
7



File Information	
GC-File	SR28A.D
File Path	C:\HPCHEM\2\DATA\SR\

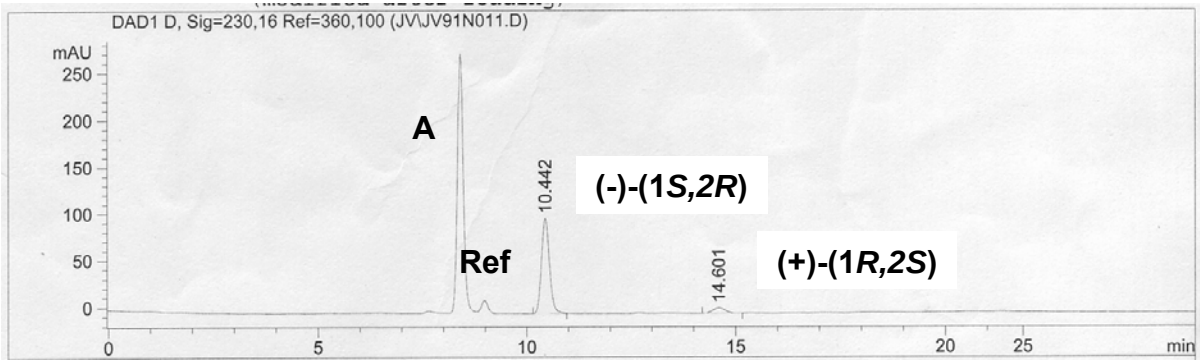
#	Time	Area	Height	Width	Symmetry
1	17.676	104.3	42.9	0.0364	0.916
2	17.862	625.4	227.5	0.0421	0.662

Determined by CSP-GC (Chiraldex Hydrodex β–3P), T_{inj} 250 °C, P = 0.842 bar;
Conditions: 80 °C, 5 min, then progression to 180 °C in 20 min, then 180 °C for 5 min.



8

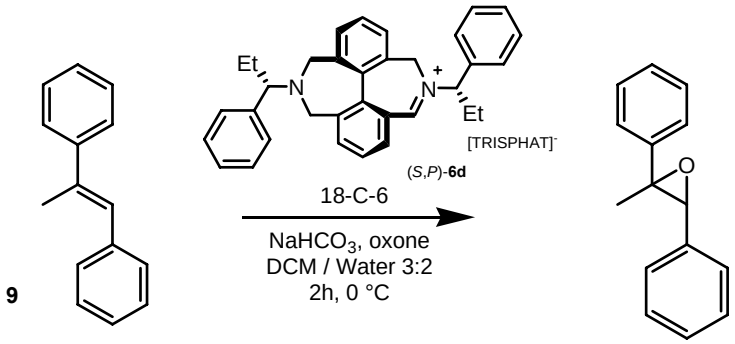
A: Alkene, Ref: naphthalene



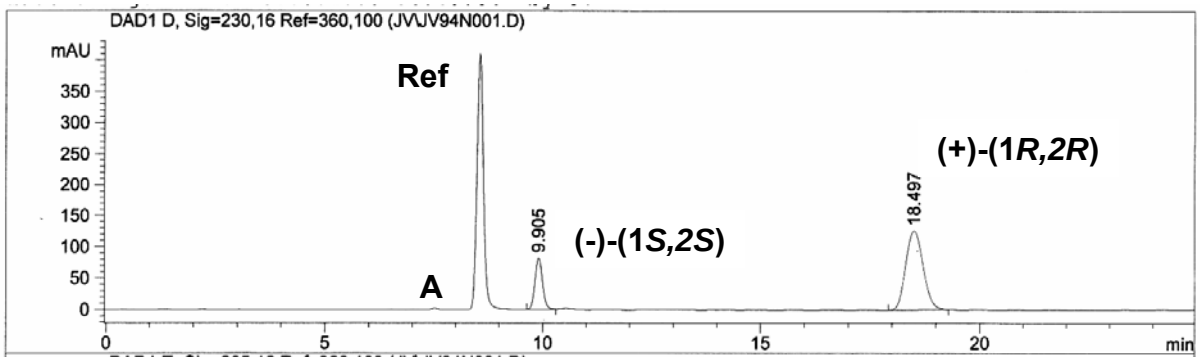
Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.442	BB	0.2070	1347.62756	101.43116	92.2391
2	14.601	PP	0.3161	113.38863	5.69863	7.7609
Totals :				1461.01620	107.12979	

Determined by CSP-HPLC (Chiralcel OD-H); Hexane / iPrOH 95 : 5 ; 0.5 mL.min^{-1}



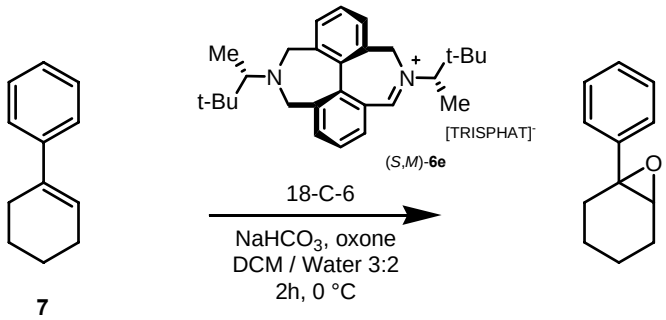
A: Alkene, Ref: naphthalene



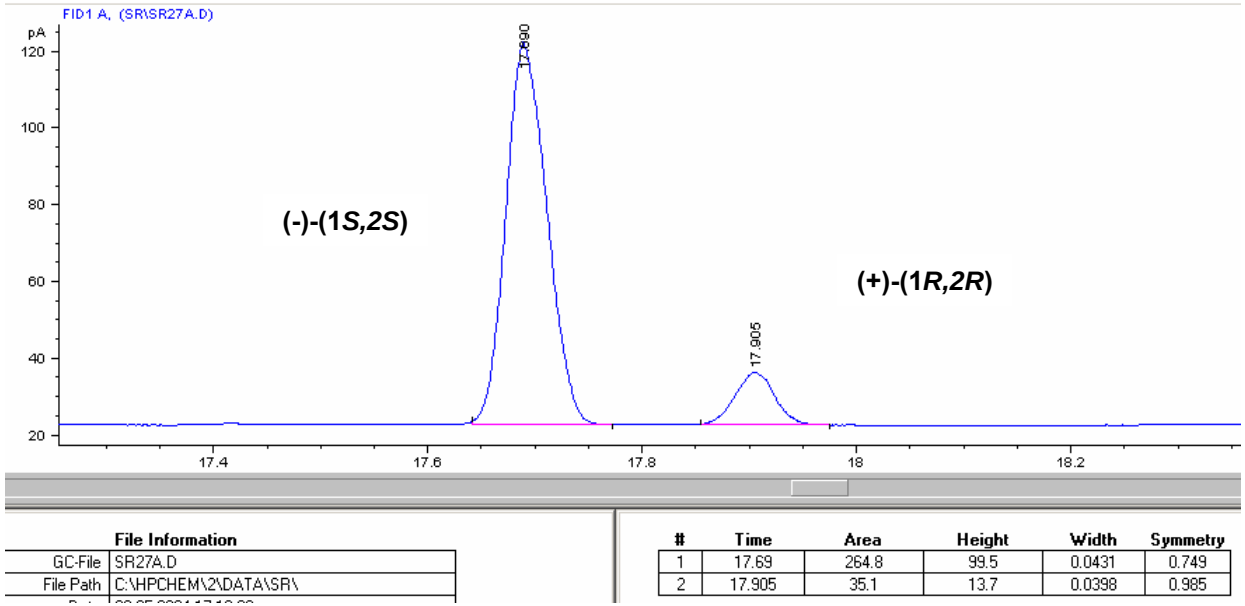
Signal 1: DAD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.905	BB	0.1896	994.71185	81.93610	22.3244
2	18.497	PB	0.4368	3460.99536	125.86764	77.6756
Totals :				4455.70721	207.80373	

Determined by CSP-HPLC (Chiralcel OD-H); Hexane / iPrOH 95 : 5 ; 0.5 mL.min^{-1}



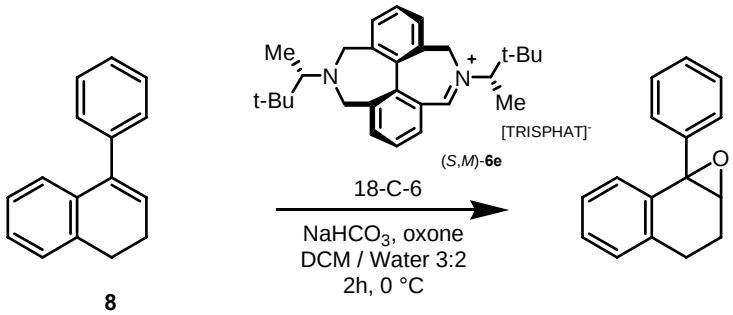
7



File Information	
GC-File	SR27A.D
File Path	C:\HPCHEM\2\DATA\SR\

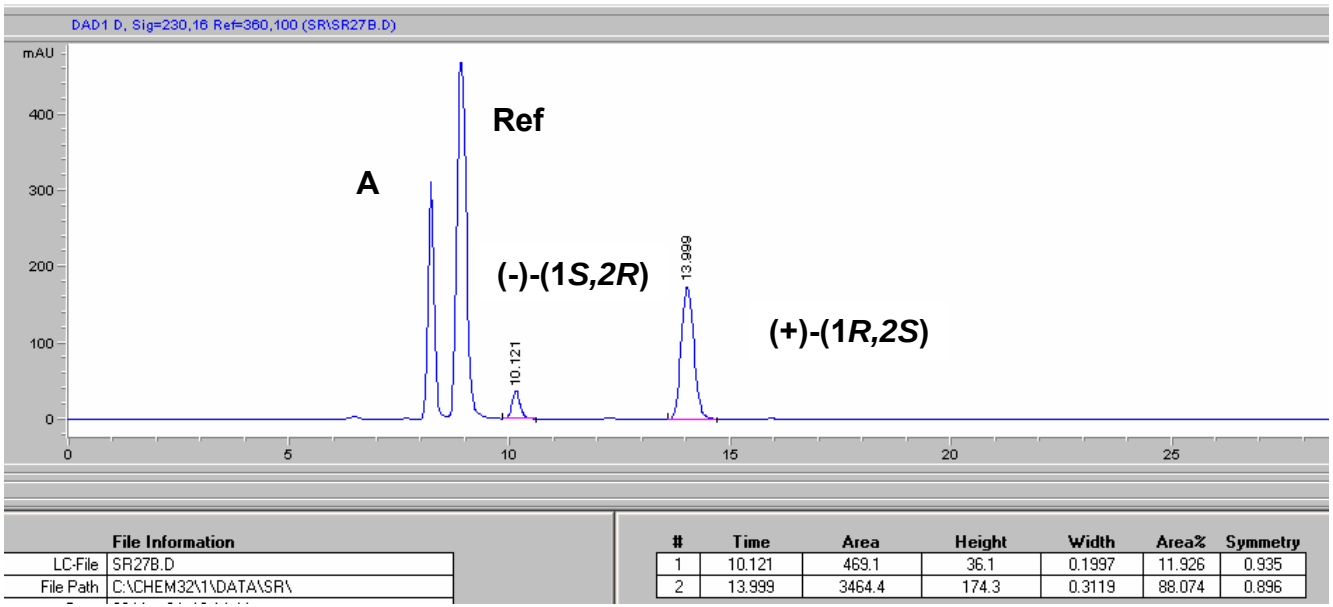
#	Time	Area	Height	Width	Symmetry
1	17.69	264.8	99.5	0.0431	0.749
2	17.905	35.1	13.7	0.0398	0.985

Determined by CSP-GC (Chiraldex Hydrodex β–3P), T_{inj} 250 °C, P = 0.842 bar;
Conditions: 80 °C, 5 min, then progression to 180 °C in 20 min, then 180 °C for 5 min.



8

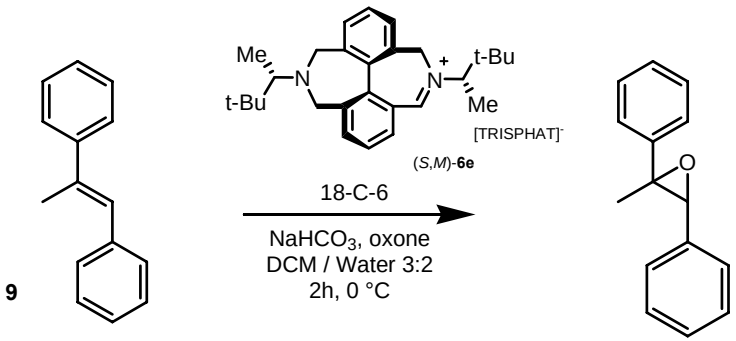
A: Alkene, Ref: naphthalene



File Information	
LC-File	SR27B.D
File Path	C:\CHEM32\1\DATA\SR\

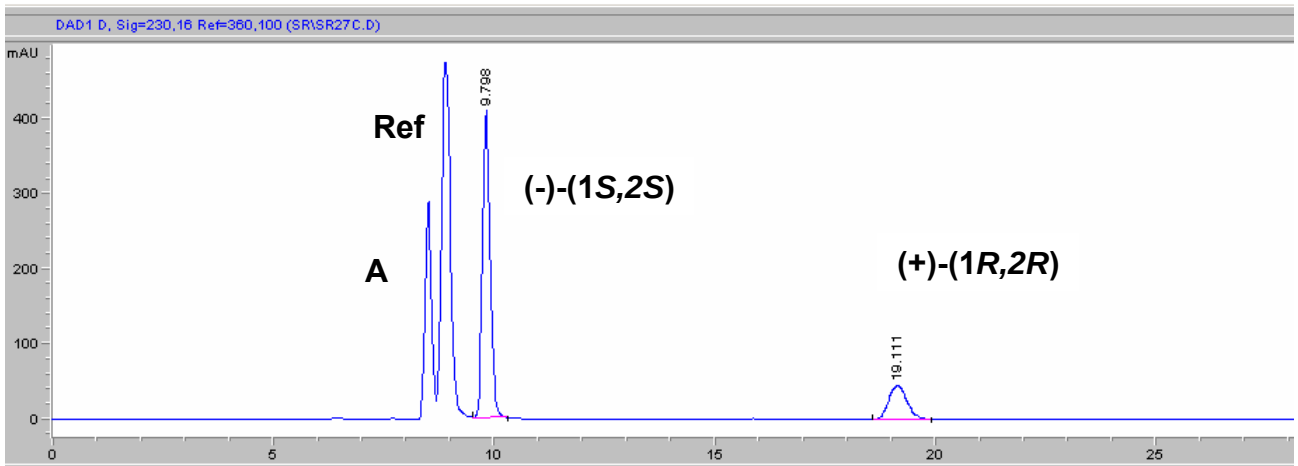
#	Time	Area	Height	Width	Area%	Symmetry
1	10.121	469.1	36.1	0.1997	11.926	0.935
2	13.999	3464.4	174.3	0.3119	88.074	0.896

Determined by CSP-HPLC (Chiralcel OD-H); Hexane / iPrOH 95 : 5 ; 0.5 mL.min^{-1}



9

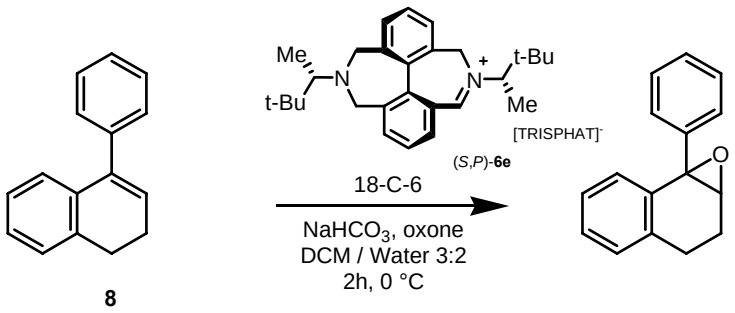
A: Alkene, Ref: naphthalene



File Information	
LC-File	SR27C.D
File Path	C:\CHEM32\1\DATA\SR\

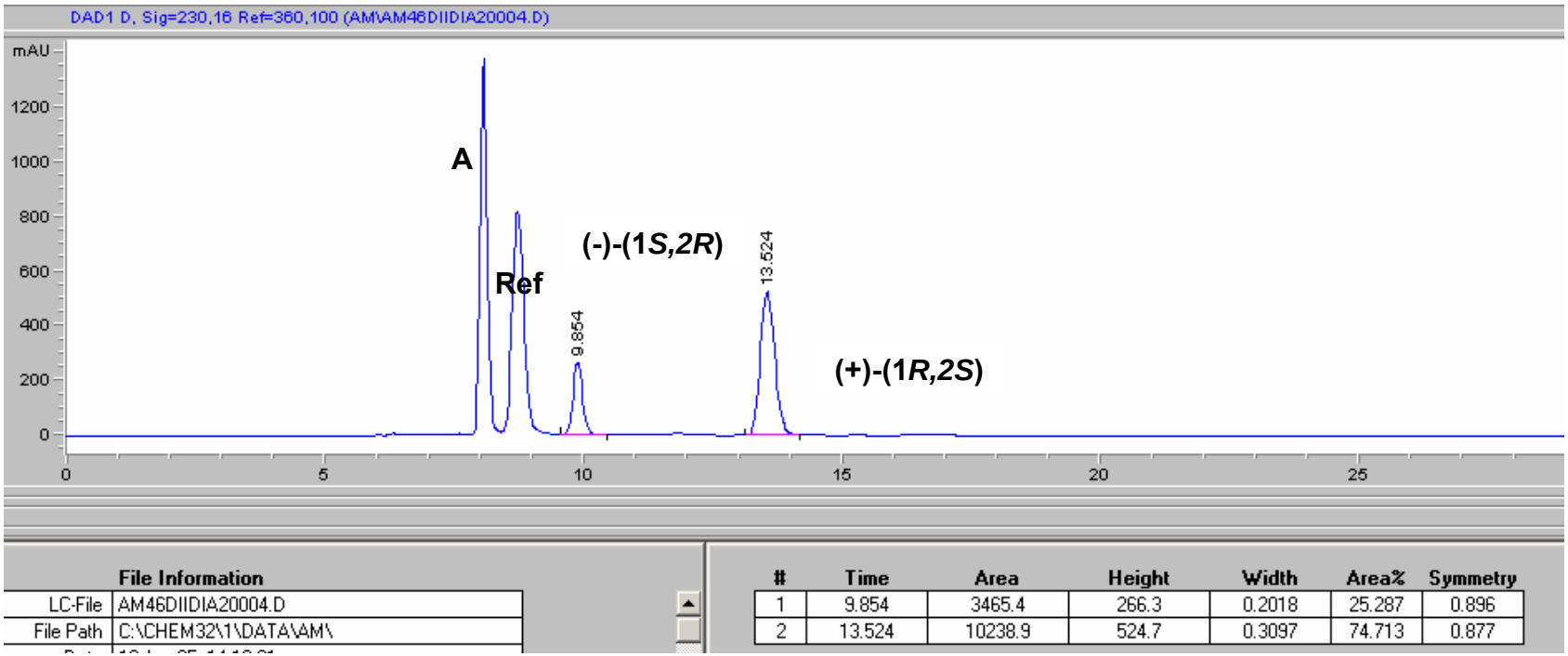
#	Time	Area	Height	Width	Area%	Symmetry
1	9.798	4953.8	409.5	0.1871	79.414	0.858
2	19.111	1284.1	45	0.4507	20.586	0.851

Determined by CSP-HPLC (Chiralcel OD-H); Hexane / iPrOH 95 : 5 ; 0.5 mL.min^{-1}



8

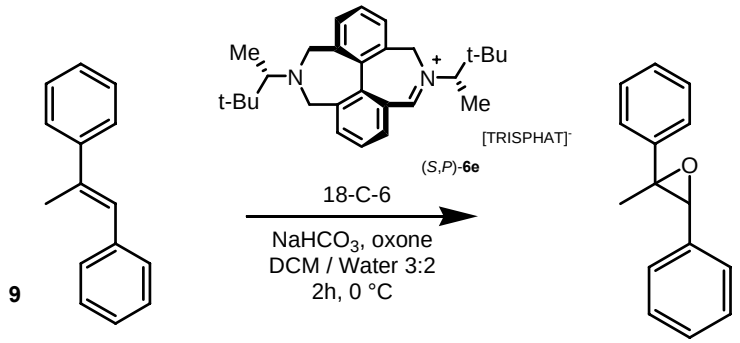
A: Alkene, Ref: naphthalene



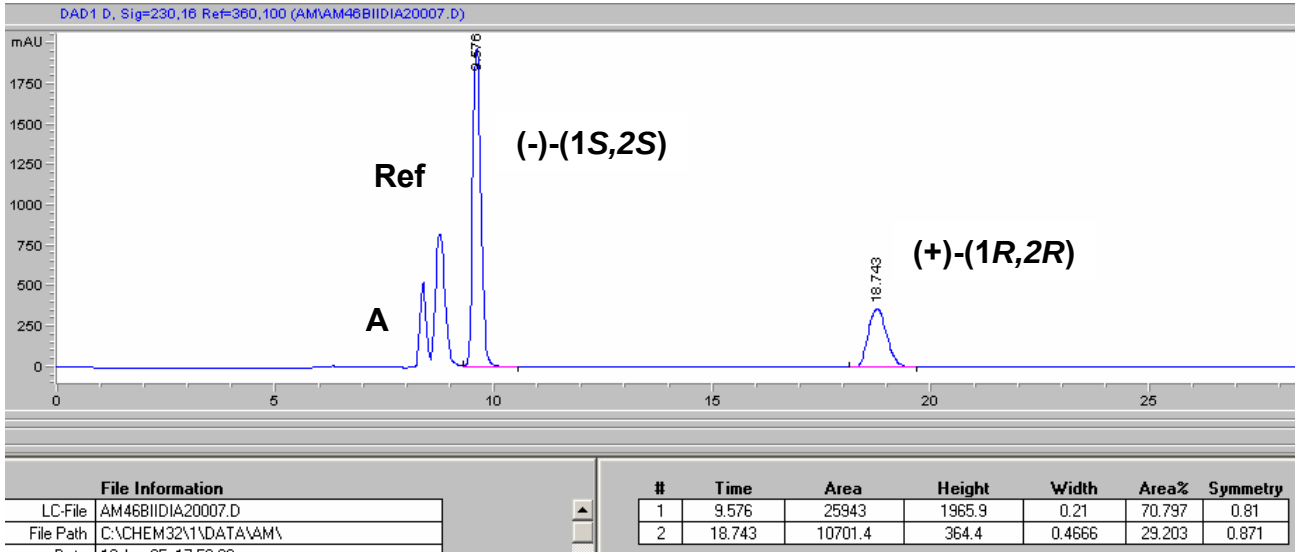
File Information	
LC-File	AM46DIIDIA20004.D
File Path	C:\CHEM32\1\DATA\AM\

#	Time	Area	Height	Width	Area%	Symmetry
1	9.854	3465.4	266.3	0.2018	25.287	0.896
2	13.524	10238.9	524.7	0.3097	74.713	0.877

Determined by CSP-HPLC (Chiralcel OD-H); Hexane / iPrOH 95 : 5 ; 0.5 mL.min^{-1}



A: Alkene, Ref: naphthalene



File Information	
LC-File	AM46BIIDIA20007.D
File Path	C:\CHEM32\1\DATA\AM\

#	Time	Area	Height	Width	Area%	Symmetry
1	9.576	25943	1965.9	0.21	70.797	0.81
2	18.743	10701.4	364.4	0.4666	29.203	0.871

Determined by CSP-HPLC (Chiralcel OD-H); Hexane / iPrOH 95 : 5 ; 0.5 mL.min^{-1}