Electronic Supporting Information

Verification of Stereospecific Dyotropic Racemisation of Enantiopure *d* and *l*-1, 2-Dibromo-1, 2-diphenylethane in Non-polar Media

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General experimental

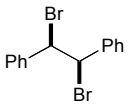
Reagents: All reagents were obtained from commercial sources and used as received.

Solvents: CH_2Cl_2 was dried by passing through a column of alumina beads. Extraction solvents and recrystallization solvents were used as received. MeOH and CH_2Cl_2 were HiPerSolv grade and EtOH was AnalaR grade. *n*-Hexane and *i*-PrOH for HPLC were HPLC grade.

Experimental techniques: Reactions were carried out in oven-dried glassware under an inert atmosphere of nitrogen, unless otherwise stated. Reaction temperatures were recorded as or bath temperatures. Analytical TLC was performed on Kieselgel 60 F254 pre-coated aluminium-backed plates and visualised by ultraviolet light (350 nm). Analytical and preparative chiral HPLC was performed on a CHIRALCEL OD-H column detecting at 238 nm. Retention times (t_R) are reported in minutes.

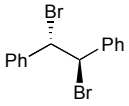
Characterisation: Melting points were obtained on a Reichert–Thermovar melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV400 spectrometer at 400 MHz and 100 MHz respectively. Chemical shifts (δ) are quoted in parts per million (ppm) and are referenced to the residual solvent resonance. Low resolution MS (EI^+) and GCMS, were recorded by the Imperial College Department of Chemistry Mass Spectrometry Service.

Experimental details and characterising data for bromides 1 and 2



dl-**1**

dl-1,2-Dibromo-1,2,-diphenylethane (**1**): Molecular bromine (0.12 mL, 2.3 mmol) in CH_2Cl_2 (0.9 mL) was added to a stirrer solution of *Z*-stilbene (0.41 g, 2.3 mmol) in CH_2Cl_2 (5.0 mL) at 0 ˚C and the reaction mixture stirred for 0.5 hours. The solid *meso* compound was filtered off, the filtrate washed with saturated aqueous Na_2SO_3 solution (15 mL), and the separated organics reduced in volume by half. The solids were filtered off, the filtrate concentrated to dryness and the crude solid was recrystallised from methanol to give the title compound (0.50 g, 1.5 mmol, 64 %) as a white crystalline solid: m.p. 100-102 ˚C (lit.[1] 100-110 ˚C). R_f (0.71, Et_2O:EtOAc. 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 10H), 5.50 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 128.6, 128.2, 59.2; MS (EI^+) *m/z* 342, 340, 338 (M^+).

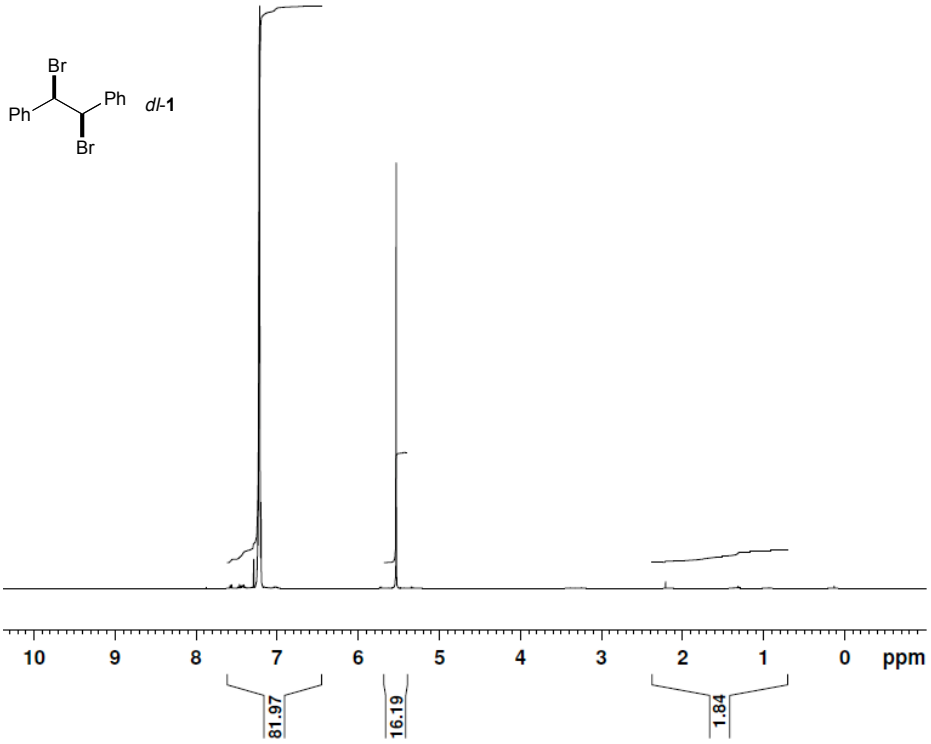


2

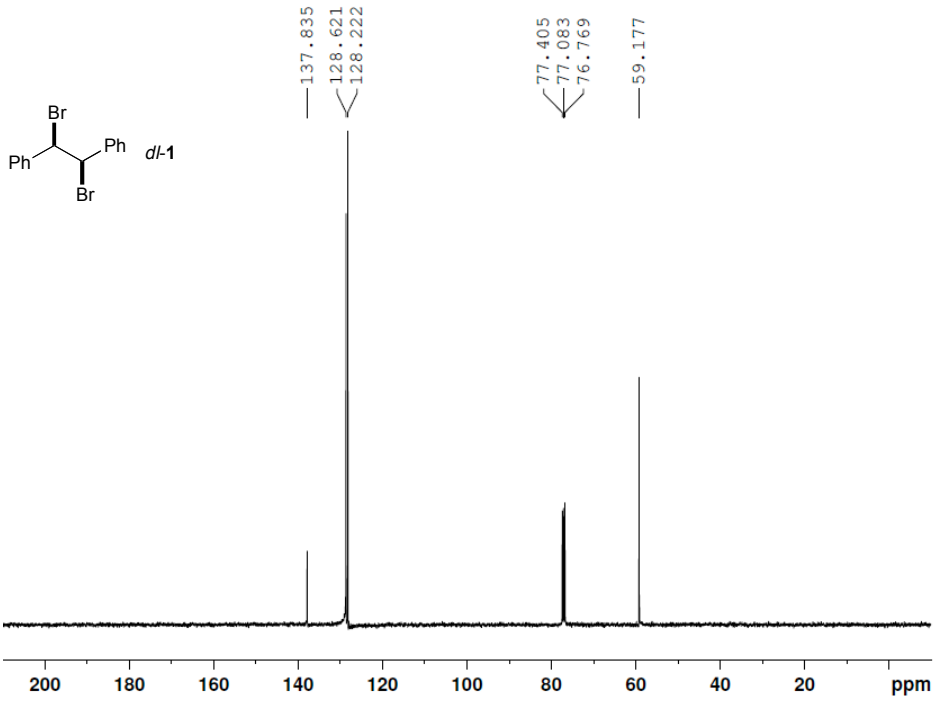
meso-1,2-Dibromo-1,2,-diphenylethane (**2**): Molecular bromine (0.12 mL, 2.3 mmol) in CH_2Cl_2 (0.9 mL) was added to a stirrer solution of *E*-stilbene (0.40 g, 2.2 mmol) in CH_2Cl_2 (5.0 mL) at 0 ˚C and the reaction mixture stirred for 0.5 hours. The resulting solid was collected by filtration and recrystallized from ethanol to yield the title compound (0.48 g, 1.4 mmol, 64%) as a white crystalline solid: m.p. 240-242 ˚C (lit.[1] 240 ˚C). R_f (0.82, Et_2O:EtOAc, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.35 (m, 10 H), 5.50 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 129.0, 128.8, 127.9, 56.1; MS (EI^+) *m/z* 342, 340, 338 (M^+).

^{1}H and ^{13}C NMR spectra for dibromides 1 and 2

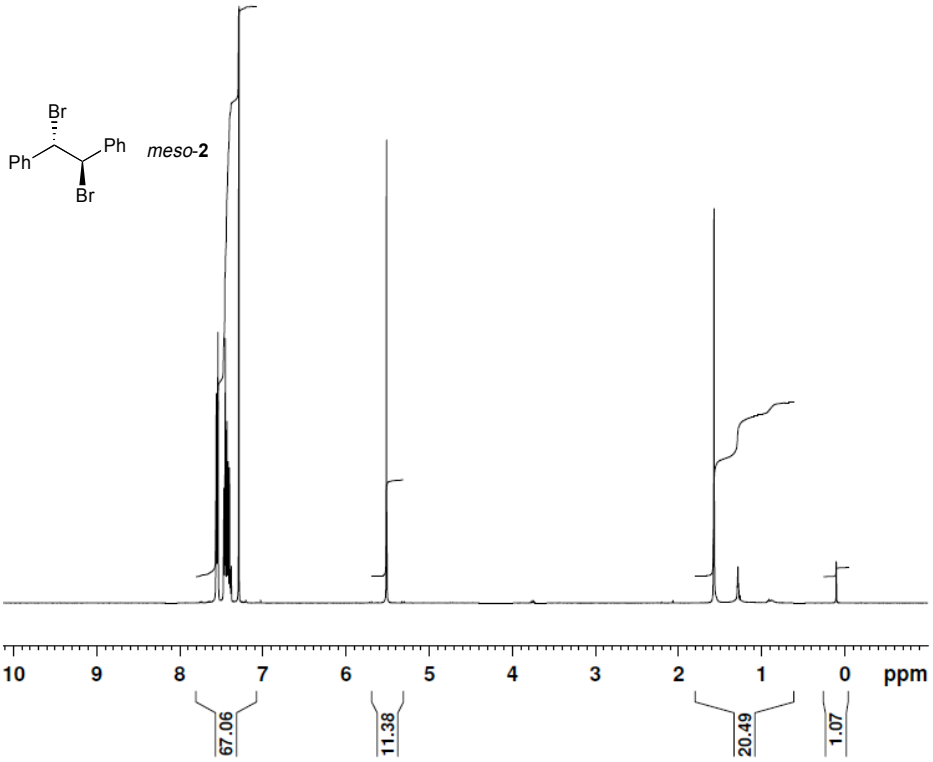
^{1}H NMR spectrum of *dl*-1,2-dibromo-1,2-diphenylethane (**1**) (400 MHz, $CDCl_3$)



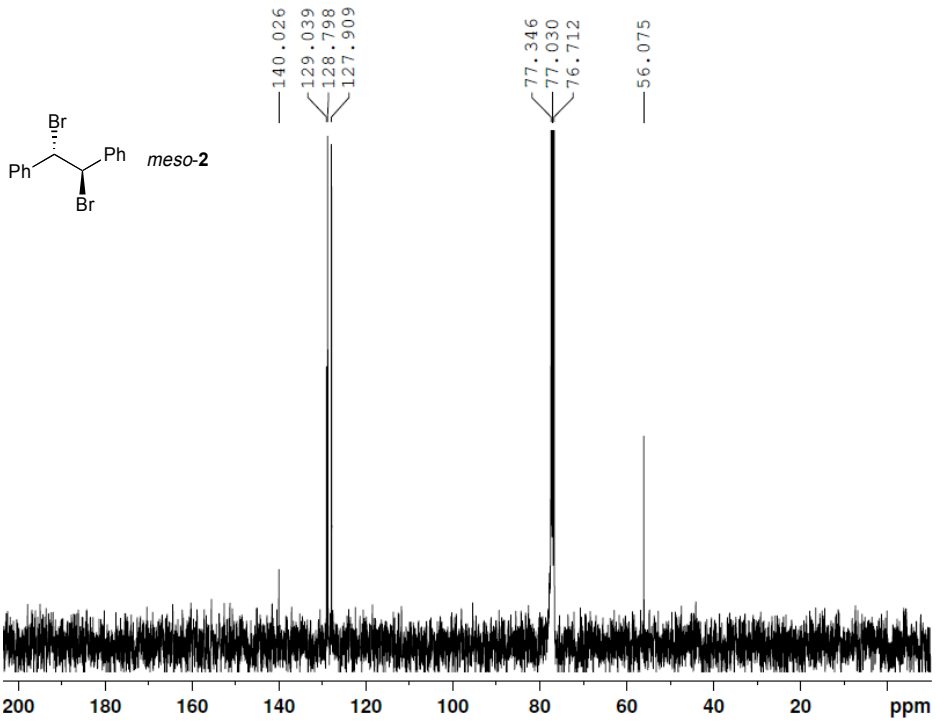
^{13}C NMR spectrum of *dl*-1,2-dibromo-1,2-diphenylethane (**1**) (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of *meso*-1,2-dibromo-1,2-diphenylethane (**2**) (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of *meso*-1,2-dibromo-1,2-diphenylethane (**2**) (100 MHz, $CDCl_3$)

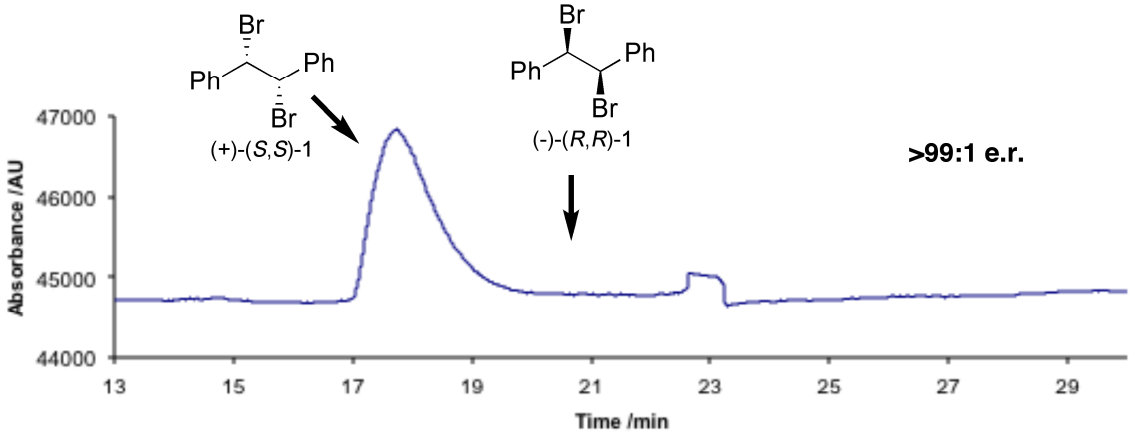


Separation of *d*- and *l*-1,2-dibromo-1,2-diphenylethane by chiral HPLC methods

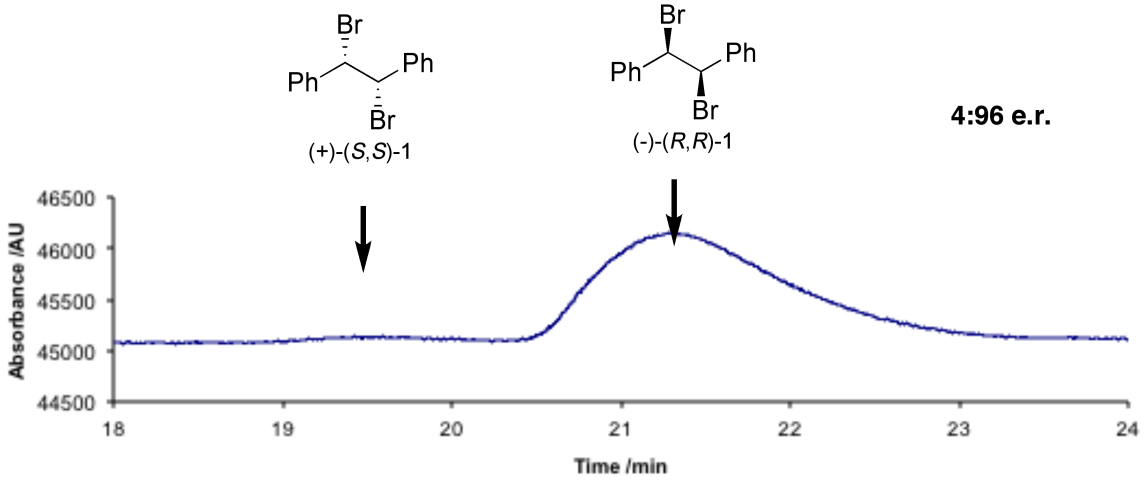
Chiral HPLC separation of *dl*-1 was performed using a CHIRALCEL OD-H column detecting at 238 nm. 200 runs gave:

(+)-*S*,*S*-1,2-dibromo-1,2-biphenylethane, 4.3 mg. HPLC (CHIRALCEL OD-H; 99.7:0.3 *n*-hexane:IPA; 1.0 mL/min) 100% ee; $[\alpha]^{23}_{D}$ +154.5 (*c* 0.21, EtOH).
(-)-*R*,*R*-1,2-dibromo-1,2-biphenylethane, 3.2 mg. HPLC (CHIRALCEL OD-H; 99.7:0.3 *n*-hexane:IPA; 1.0 mL/min) 91% ee; $[\alpha]^{23}_{D}$ -143.4 (*c* 0.21, EtOH), [lit.[2] -169 (*c* 0.635, EtOH)].

HPLC trace for separated (+)-*S*,*S*-1,2-dibromo-1,2-biphenylethane (*d*-**1**)



HPLC trace for separated (+)-*R*,*R*-1,2-dibromo-1,2-biphenylethane (*l*-**1**)



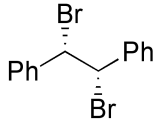
Evidently there is variability in the retention times in this system. This may be related to the very small mole fraction of IPA used as eluent.

Experimental details for Dyotropic Rearrangement of *d* and *l*-1

(+)-1,2-Dibromo-1,2-diphenylethane (4.2 mg, 0.012 mmol) in benzene (4.2 mL), and separately (–)-1,2-dibromo-1,2-diphenylethane (3.2 mg, 0.032 mmol) in benzene (3.2 mL), were heated to reflux for 312 hours. Samples for HPLC analysis were taken at 94, 118.25, 142, 167, 191.5, 263, 287.5 and 311.5 hours.

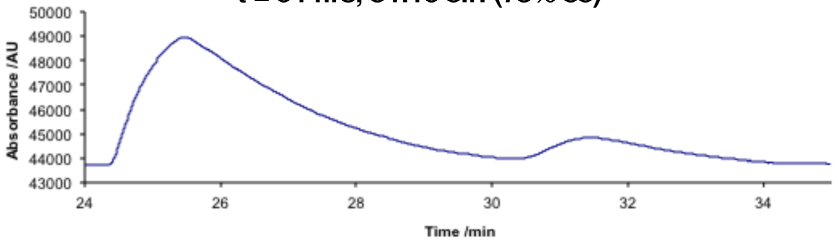
HPLC analysis of dyotropic rearrangements – selected traces of composition vs time – (+)-1 (lhs); (-)-1 (rhs)

Dyotropic rearrangement of:

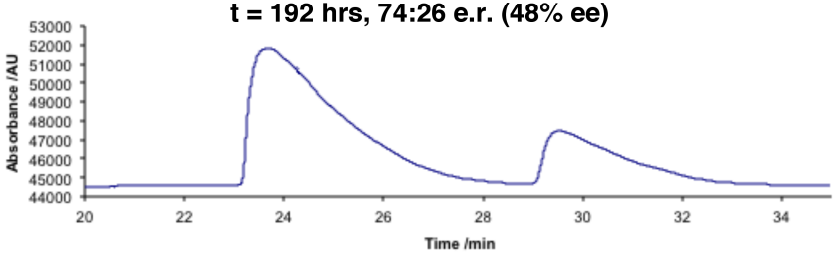


(+)-(*S*,*S*)-1

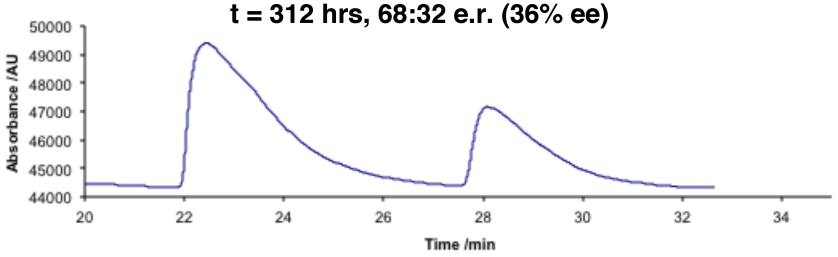
t = 94 hrs, 84:16 e.r. (78% ee)



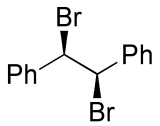
t = 192 hrs, 74:26 e.r. (48% ee)



t = 312 hrs, 68:32 e.r. (36% ee)

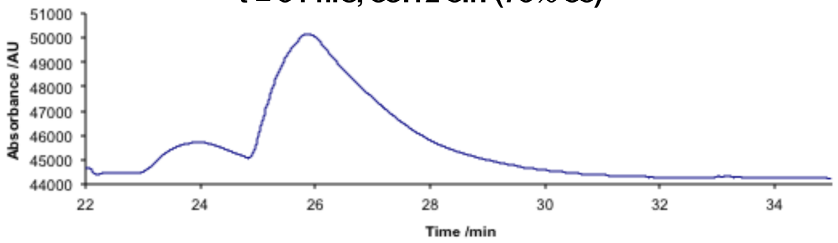


Dyotropic rearrangement of:

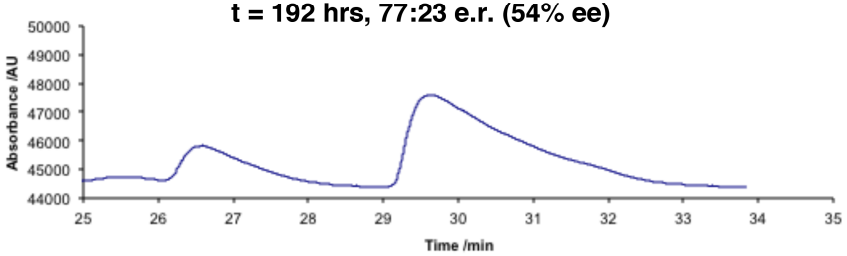


(-)-(*R*,*R*)-1

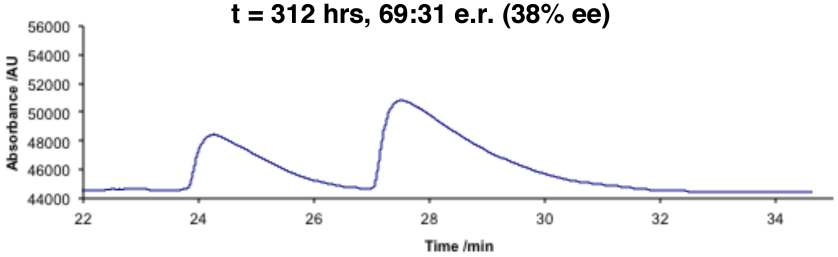
t = 94 hrs, 88:12 e.r. (76% ee)



t = 192 hrs, 77:23 e.r. (54% ee)

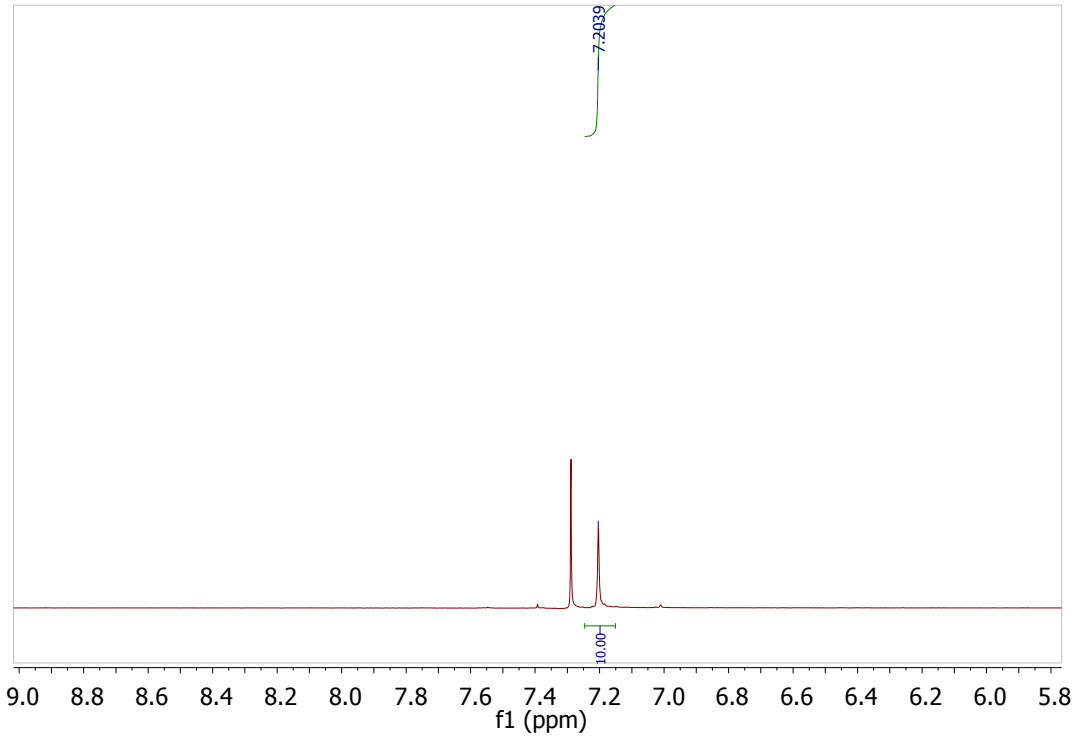


t = 312 hrs, 69:31 e.r. (38% ee)

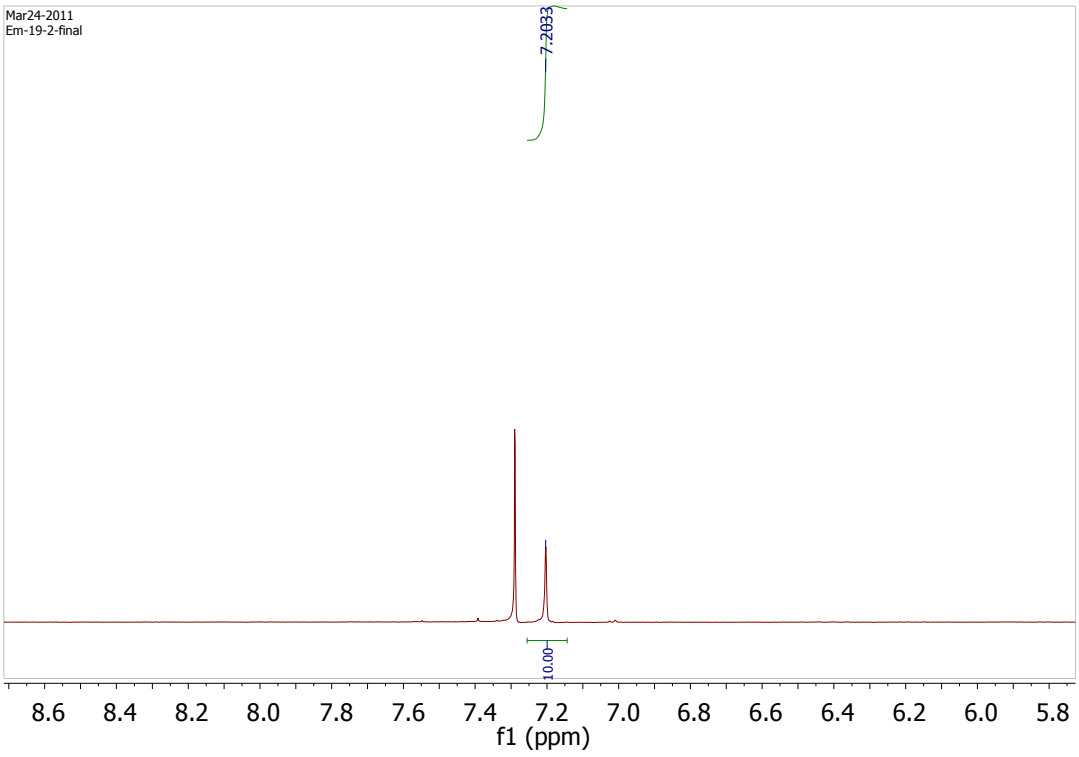


^{1}H NMR spectra post-dyotropic rearrangements

^{1}H NMR spectrum of *d*-1,2-dibromo-1,2-diphenylethane (**1**) (400 MHz, $CDCl_3$) post-dyotropic rearrangement



^{1}H NMR spectrum of *l*-1,2-dibromo-1,2-diphenylethane (**1**) (400 MHz, $CDCl_3$) post-dyotropic rearrangement



Kinetic analysis of dyotropic rearrangement.

For: $\mathbf{A} \underset{k_b}{\overset{k_a}{\rightleftharpoons}} \mathbf{B}$

$-d[A]/dt = k_a[A]-k_b[B]$ (*1*)

and if $\mathbf{[B]_0 = 0}$ then $[A]_0 = [A] + [B]$,

and so $-d[A]/dt = (k_a+k_b)[A]-k_b[A]_0$ (*2*)

At equilibrium:

$-d[A]/dt = 0$ *and* $[A] = [A]_{eq}$

and so: $k_b[A]_0 = (k_a+k_b)[A]_{eq}$ (*3*)

substituting (*3*) back into (*2*) gives:

$-d[A]/dt = (k_a+k_b)\{[A]-[A]_{eq}\}$ (*4*)

Rearrange (*4*) to integrate:

$$\int_0^t \frac{-1}{[A]-[A]_{eq}}.d[A] = \int_0^t (k_a+k_b).dt \quad (5)$$

and using: $\int 1/(a+bx).dx = [\ln(a+bx)]/b$ gives (*6*)

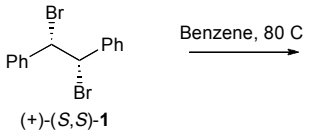
$$\ln\left(\frac{[A]_0-[A]_{eq}}{[A]_t-[A]_{eq}}\right) = (k_a+k_b)t \quad (6)$$

Since A and B are enantiomers,
then $k_a = k_b$, and $[A]_0 = 2[A]_{eq}$, gives (*7*):

$$\ln\left(\frac{[A]_{eq}}{[A]_t-[A]_{eq}}\right) = 2kt \quad (7)$$

This equation can be used to extract the rate constant (see ESI 12)

Data for dyotropic rearrangement of *d*-1 in benzene at 80˚C

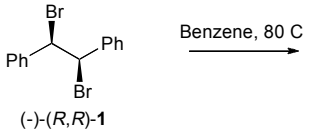


(+)-(*S*,*S*)-**1**

Time (hours)	Mole fraction *d*-1 (x)[a]	ln(0.5/ *x*-0.5)
0	100	0
94	0.84	0.37
118.25	0.83	0.43
142	0.80	0.51
167	0.77	0.61
191.5	0.74	0.72
263	-	-
287.5	0.71	0.86
312	0.68	1.00

[a] As determined by chiral HPLC

Data for dyotropic rearrangement of *l*-1 in benzene at 80˚C

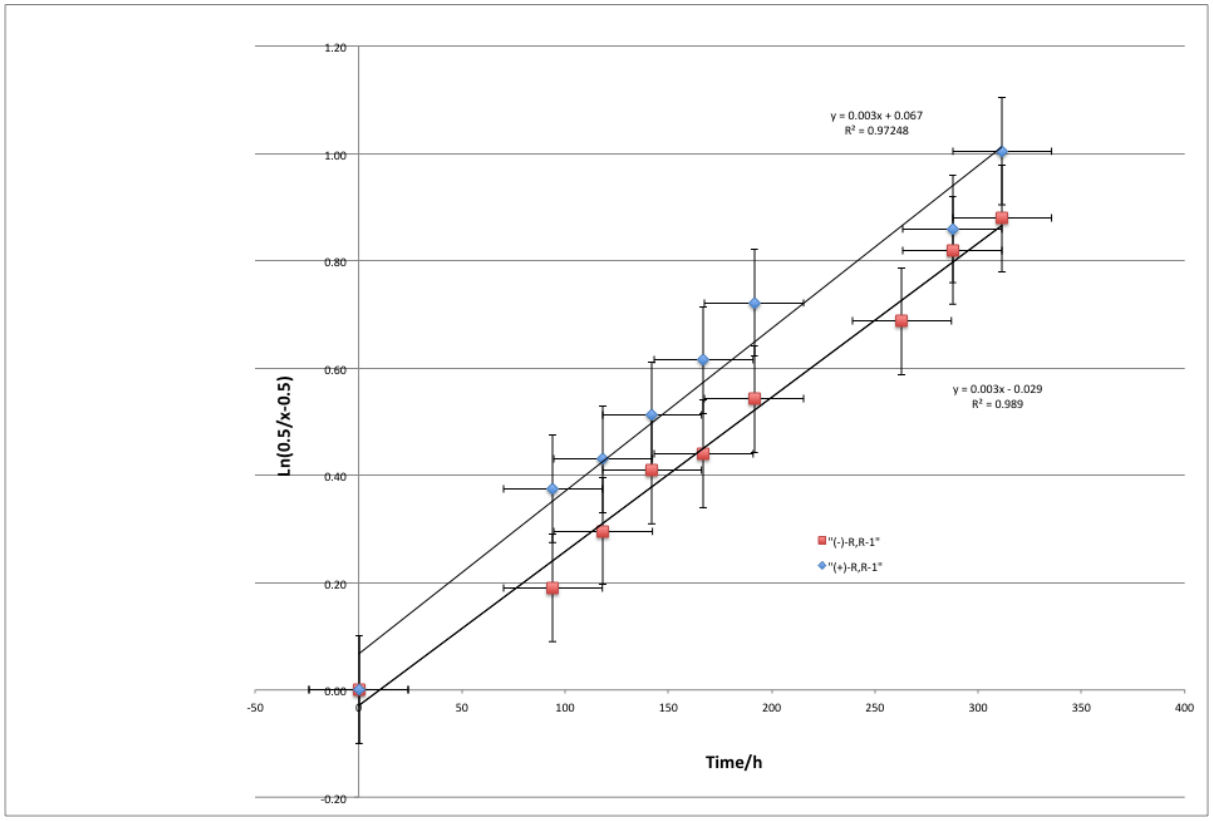


(-)-(*R*,*R*)-**1**

Time (hours)	Mole fraction *l*-1 (x)	ln(0.46/ *x*-0.5)
0	0.96	0.00
94	0.88	0.19
118.25	0.84	0.30
142	0.81	0.41
167	0.80	0.44
191.5	0.77	0.54
263	0.73	0.69
287.5	0.70	0.82
312	0.69	0.88

[a] As determined by chiral HPLC

Graphical extraction of rate constant for dyotropic rearrangement of *d*- and *l*-1 in benzene at 80C



Rate constant = 0.0015 ± 0.0002 s^{-1}.

References:

1. Amburgey-Peters, J. C.; Haynes, L. W. *J. Chem, Ed.* **2005**, *82*, 1051-1052.

2. Stoev, L.; Stefanovsky, Y. *Izvestiya po Khimiya* **1977**, *10*, 587-592.