Electronic supporting information (ESI)

Isomerisation of 1,4-dichlorobenzene using highly acidic alkali chloroaluminate melts

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1. Isomerisation of 1,4-dichlorobenzene (1,4-DCB) with acidic chloroaluminate melts (reactions in a glass flask)

The isomerization reactions were carried out in a three necked 250 ml flask equipped with a mechanical stirrer and a reflux condenser. In order to achieve a successful isomerization reaction, the respective chloroaluminate melts had to be prepared before adding the organic substrate. Therefore, the flask was preheated to 170 °C and purged with Argon. Afterwards the respective components of the acidic melt were added and the mixture was melted under gentle stirring in a time period of 5 minutes (for amounts and weights of the components, refer to table ST1) without further purging with inert gas. As 1,4-dichlorobenzene (1,4-DCB) exhibits a melting point of 53 °C, it was melted at 70 °C in a water bath and handled always with preheated equipment (at ca. 70°C). After the addition of 150.0 g (1.02 mol) of 1,4-dichlorobenzene to the melt, the resulting biphasic reaction system was stirred at 500 rpm for 24 h.

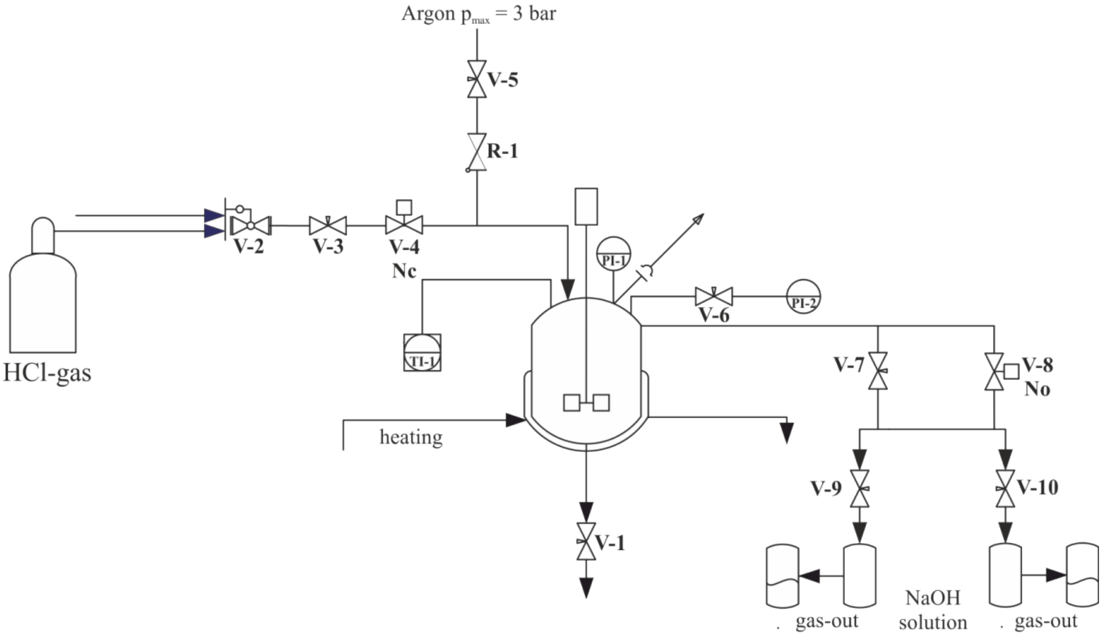
The procedure for the reference system ($AlCl_3$ and $AlCl_3*6\,H_2O$) had to be adjusted, due to the strong sublimation of $AlCl_3$ at 170 °C. Hence, the flask was preheated, purged with inert gas and 150.0 g (1.02 mol) of 1,4-dichlorobenzene were added to the flask. Afterwards, 24.95 g (187.1 mmol) of $AlCl_3$ and 4.11 g (17.0 mmol) of $AlCl_3*6\,H_2O$ were added to the solution. The reaction mixture was again stirred at 500 rpm for 24 h. For kinetic measurements, 1 ml samples were taken in the corresponding time intervals and dissolved in 5 ml dichloromethane. After extraction of each sample with 2 ml of water, the organic phase was separated and analysed by gas chromatography (GC).

Table ST1 Compositions of acidic melts (mol fraction of $AlCl_3$ $X = 0.67$) for the 1,4-DCB isomerization experiments in the glass flask. ([EMIM]Cl – 1-ethyl-3-methyl imidazolium chloride)

$X(AlCl_3) = 0.67$	$AlCl_3$	KCl	LiCl	NaCl	[EMIM]Cl
$AlCl_3$-LiCl	27.21 g (204.1 mmol)	--	4.32 g (101.2 mmol)	--	--
$AlCl_3$-LiCl-NaCl	27.21 g (204.1 mmol)	--	1.73 g (40.8 mmol)	3.58 g (61.2 mmol)	--
$AlCl_3$-[EMIM]Cl	27.21 g (204.1 mmol)	--	--	--	14.90 g (101.2 mmol)

2. Isomerisation of 1,4-dichlorobenzene with acidic chloroaluminate melts in a 500 ml glass autoclave

These experiments were carried out in a 500 ml glass *inertclave* form *büchi glas uster*©. The materials used in the autoclave were borosilicate glass 3.3, PTFE, PFA and PEEK in order to avoid corrosion due to the corrosive catalyst and hydrogen chloride. The autoclave was already equipped with the appropriate safety devices, like a bursting disc (see also Figure S1), but further adjustments were performed in order to ensure save handling of the hazardous hydrogen chloride (V-2). To regulate the hydrogen chloride volume flow, we used a PFA needle valve with a plug stem tip to ensure a leak-tight shutoff (V-3) (*Swagelok*©). In order to purge the autoclave we installed an additional argon gas inlet (V-5) secured by a flap valve (R-1). The temperature of the reaction mixture was measured by the aid of a *PT 100* temperature sensor (TI-1). The corresponding gas outlet was regulated by a needle valve (V-7) equivalent to (V-3). The excess of hydrogen chloride was neutralized in an aqueous 1 M solution of sodium hydroxide (replacement of the solution was realizede via (V-11) - indicator was added as optical validation of the neutralization reaction). In case of an unwanted state of the rig, the security shutdown procedure was automatically carried out as follows: closing of pneumatic regulated ball valve V-4 and opening of pneumatic regulated ball valve (V-9).



V-2: pressure regulator
V-3: needle valve
V-4: regulated ball valve normally closed
V-5/6/7: needle valve
V-8:regulated ball valve normally open
V-9/10: needle valve

R-1: flap valve
TI-1: temperature sensor
PI-1/2: pressure indicator

Figure S1 Flow sheet for the glass autoclave used in the isomerization of 1,4-dichlorobenzene with $AlCl_3$-LiCl and hydrogen chloride for catalyst recycling.

A) Preparation of the $AlCl_3$-LiCl melt, isomerisation experiments and separation of the organic product phase

The acidic chloroaluminate melt was prepared prior to the addition of the organic substrate to ensure complete formation of the melt prior to the catalytic experiment. Therefore, the autoclave was preheated at 170 °C and flushed with argon gas for 10 minutes. Afterwards, a mixture of 45.4 g (340 mmol) $AlCl_3$ and 7.21 g (170 mmol) LiCl was charged in the autoclave. The inert gas purging was stopped and the autoclave closed. During the melting process at 170 °C a certain amount of gaseous hydrogen chloride was formed. This over-pressure in the autoclave was released and subsequently the autoclave was opened again. Afterwards, 250 g (1.70 mol) of 1,4-DCB (liquid) were added. The autoclave was closed again and once the biphasic reaction mixture reached 170 °C, the mixture was stirred (400 rpm) for 4 h.

After this reaction time, the autoclave was cooled down to 60 °C. By this cooling the phases separated into a solid catalytic phase (lower one) and a liquid product phase (top phase). The product phase was isolated by pumping the organic layer out of the autoclave.

B) Recycling of the chloroaluminate melt $AlCl_3$-LiCl

In the recycling experiments we used the solid catalytic phase from experiment **A)**. 4.54 g (34 mmol) $AlCl_3$ were added to compensate the determined Al-leaching into the organic phase (further information see **(C)**). Afterwards, the autoclave was closed and heated to 170 °C. The resulting overpressure was released and the autoclave was opened. Then, 250 g (1.70 mol) of 1,4-dichlorobenzene were added. After closing the autoclave, hydrogen chloride gas was subsequently added until a pressure of 1 bar was reached. Once the biphasic reaction mixture reached 170 °C, the mixture was stirred (400 rpm) for 4 h. After 4 h of reaction time, the autoclave was cooled down to 60 °C. The phases separated at this temperature in a solid catalytic phase (lower one) and a liquid product phase (top phase). The organic product phase was isolated by pumping. The recycling could be repeated several times by following the above protocol.

C) Quantitation of $AlCl_3$ leached in the product phase with ICP-AES

Although the isomerisation reaction is biphasic with the $AlCl_3$-LiCl melt, a certain amount of $AlCl_3$ leaches into the organic phase. To quantify this amount owe used a Spectro ciros-ccp inductively coupled plasma atomic emission spectroscopy (ICP-AES). For this analysis, 2.00 g of the DCB phase was dissolved in 50 ml ethanol and the respective sample was analysed via ICP-AES. As a result, we determined that approximately 4 mol% of the Al from the original catalyst phase is leaching into the organic product phase. In contrast, lithium chloride, the other component of the acidic melt, remained completely in the catalytic phase. As also some minor sublimation of $AlCl_3$ occurred during the reaction, we decided to replace 4.54 g (34.0 mmol) $AlCl_3$ in the course of the recycling experiments (see also **B**).

2.1. Influence of hydrogen chloride on the catalytic isomerisation reaction

For the reaction under HCl pressure all steps were carried out as described in 2 **A)**, but 1 bar hydrogen chloride was added directly after addition of the 1,4 DCB. The rest of the procedure was kept the same.

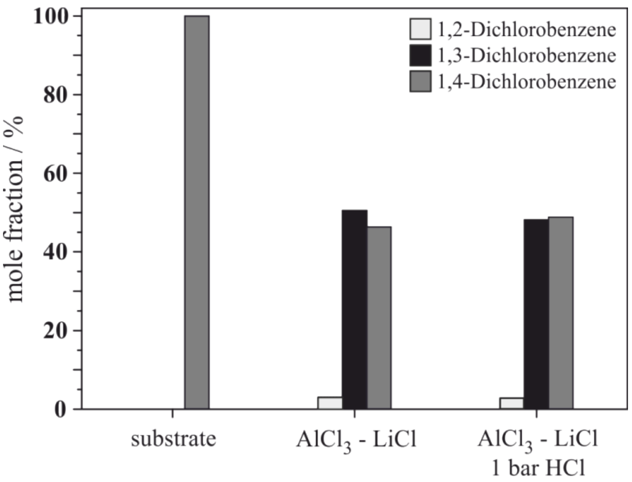


Figure S 2 Influence of hydrogen chloride during the isomerization of 1,4-dichlorobenzene with $AlCl_3$-LiCl in the autoclave; 170 °C, 4 h, 20 mol % $AlCl_3$ and 10 mol % LiCl, 250 g 1,4-DCB, 1 bar HCl.

2.2. Recycling of the $AlCl_3$-LiCl melt and replacing leached $AlCl_3$ without addition of hydrogen chloride

Also this experiment was carried out as described in 2 **A)**. After separation of the liquid product phase leached $AlCl_3$ was replaced as described in 2 **B)**. However, no hydrogen chloride gas was added prior to the recycling experiment.

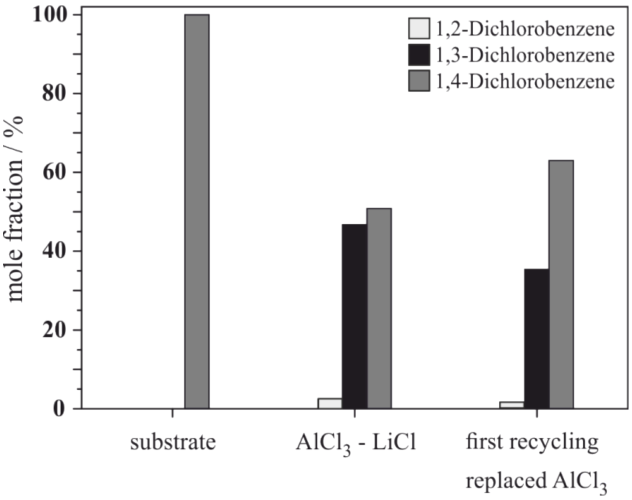


Figure S 3 Influence of the lack of hydrogen chloride on the first recycling reaction of the isomerisation of 1,4-dichlorobenzene with $AlCl_3$-LiCl in an autoclave; leached $AlCl_3$ has been replaced; 170 °C, 4 h, 20 mol % $AlCl_3$ and 10 mol % LiCl, 250 g 1,4-DCB; 4.54 g $AlCl_3$ added for the recycling experiment.

2.3. Recycling of the $AlCl_3$-LiCl melt: Addition of hydrogen chloride gas but without replacing the leached $AlCl_3$ before the recycling experiment

Also this isomerisation experiment was carried out as described in 2 **A)** and 2 **B)**. For the recycling experiment 1 bar of hydrogen chloride gas was used but no extra $AlCl_3$ was added to compensate the Al-leaching into the organic phase.

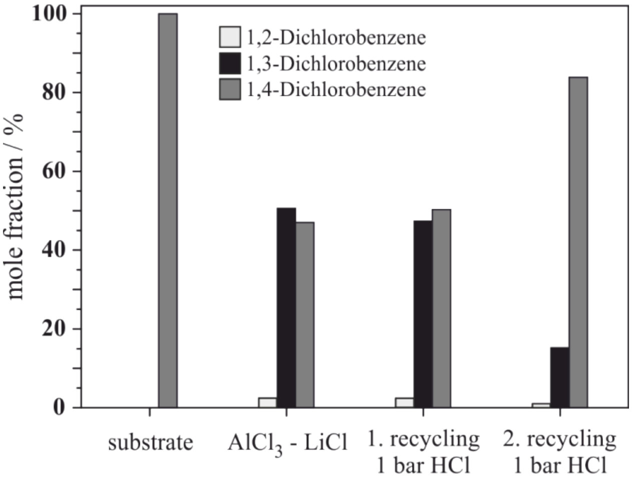


Figure S 4 Isomerisation of 1,4-dichlorobenzene with $AlCl_3$-LiCl in an autoclave and recycling of the melt with the use of hydrogen chloride but without adding extra $AlCl_3$; 170 °C, 4 h, 20 mol % AlCl3 and 10 mol % LiCl, 250 g 1,4-DCB, 1 bar HCl.

3. Product analysis using gas chromatography (GC)

In order to determine the ratio of the three DCB isomers gas chromatography (GC) was applied. Technical details about the used device have been summarized in Table ST3. The samples were prepared by dissolving 1 ml of the organic product phase in 5 ml dichloromethane and extraction with 1 ml water. The extraction with water is necessary to remove leached $AlCl_3$ from the organic phase before GC analysis. The respective retention times (Table ST4) of the DCB isomers were determined by comparison with the isolated substances 1,2-DCB, 1,3 DCB, and 1,4-DCB.

Table ST3 Details of the applied gas chromatographic analysis method.

	m/z
Modell	Varian CP 3900
Column	CP-WAX (FFAP), 50 m x 0.25 mm ID
Temperature program	Ramp from 40 °C to 190 °C in 10 K / min; 10 min iso at 190 °C (total: 20 min)
Carrier gases	He
Injector temperature	200 °C
Injected volume	1 µl
Split ratio	10
Column flow	2 ml/min
Detector	FID (H_2) (T = 300 °C)

Table ST4 Retention times of the dichlorobenzene isomers

substance	**Retention time / min**
1,3-dichlorobenzene	5.4
1,4-dichlorobenzene	5.7
1,2-dichlorobenzene	6.1

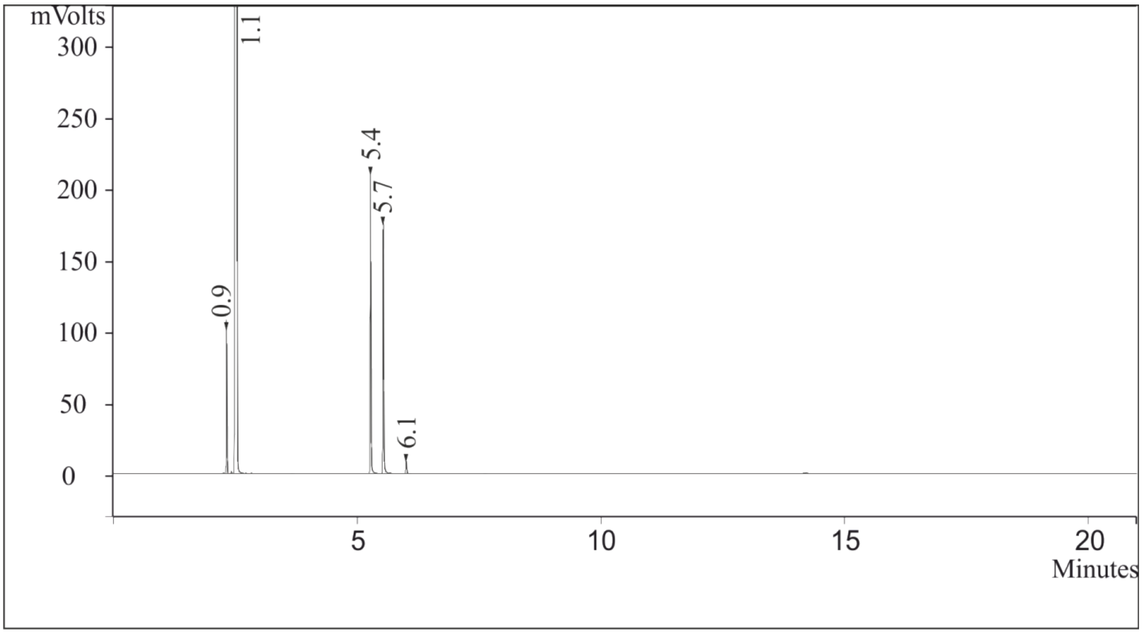


Figure S 5 Typical chromatogram of the DCB reaction mixture after 4 h reaction time in the autoclave. Retention times (5.4 min 1,3-DCB, 5.7 min 1,4-DCB, 6.1 min 1,2-DCB, solvents: cyclohexane 0.9 min; dichloromethane 1.1 min).

3. Isomerisation of 1-chloro-4-bromobenzene (BCB) with Lewis acidic chloroaluminate melts

The isomerisation reactions with 1-chloro-4-bromobenzene were (BCB) carried out in a three necked 250 ml flask equipped with a mechanical stirrer and a reflux condenser. In order to achieve a successful isomerisation reaction, the respective chloroaluminate melts had to be prepared prior to adding the organic compound. First, the flask was preheated to 170 °C under inert atmosphere. Afterwards the respective melt components (5.55 g (40 mmol) $AlCl_3$ and either 2.92 g (20 mmol) [EMIM]Cl or 0.85 g (20 mmol) LiCl mixture) were added under gentle stirring in a period of 5 minutes without further purging of the sample with inert gas. Then, 38.29 g (200 mmol) of the solid BCB were added to the melt.

The reaction mixture was stirred at 500 rpm for 24 h. For the kinetic measurements, 1 ml samples were taken at the corresponding time intervals and dissolved in 5 ml dichloromethane. After extraction of the organic sample phase with 2 ml of water, the organic phase was analysed by gas chromatography coupled with mass spectroscopy (GC-MS) (Table ST5). Note that a side reaction occurs during the isomerization of BCB which is not relevant in DCB isomerisation.[1] This reaction is an intermolecular halogene exchange, more precisely a bromine transfer between two different aromatic rings. Consequently, dibromochlorobenzenes and chlorobenzene are also identified by mass spectroscopy. The corresponding fraction of the yielded BCB isomers were calculated from the relative GC peak surface areas. (Figure S 6). The respective retention times of the product species were determined by comparison with reference substances for the three BCB isomeres and chlorobenzene (Table ST6). Typical chromatograms and spectra of the organic product phases after 23 h reaction time with the inorganic melt (Figure S 6) and the organic melt (Figure S 7) are pesented below. The results of the kinetic measurements of the BCB isomerisation reaction are depicted in Figure S11.

Table ST5 Applied GC-MS and analytic parameters.

	parameter
Modell	Varian 450-GC / Varian 220-MS
Column	Factor Four Capillary Column, VF-Wax ms, 30 m x 0.25 mm ID
Temperature program	Ramp 50 °C to 70 °C in 10 K / min and from 70 °C to 200 °C in 2 K / min; (total: 38 min)
Carrier gases	He
Injector temperature	220 °C
Injected volume	1 µl
Split ratio	5
Column flow	1 ml / min

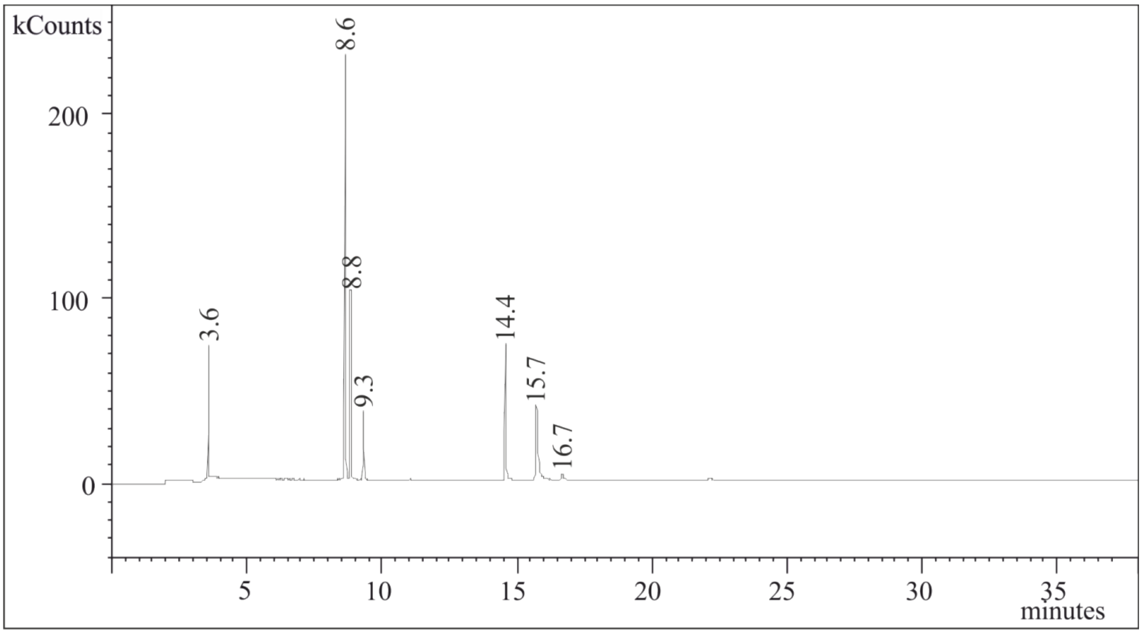


Figure S 6 GC-chromatogram of a typical reaction mixture of BCB isomerisation after 23 h at 170 °C with the inorganic $AlCl_3$-LiCl melt; retention times: 3.6 min chlorobenzene; 8.6 min 1-bromo-3-chlorobenzene; 8.8 min 1-bromo-4-chlorobenzene; 9.3 min 1-bromo-2-chlorobenzene; 14.4/15.7/16.7 dibromochlorobenzene isomers.

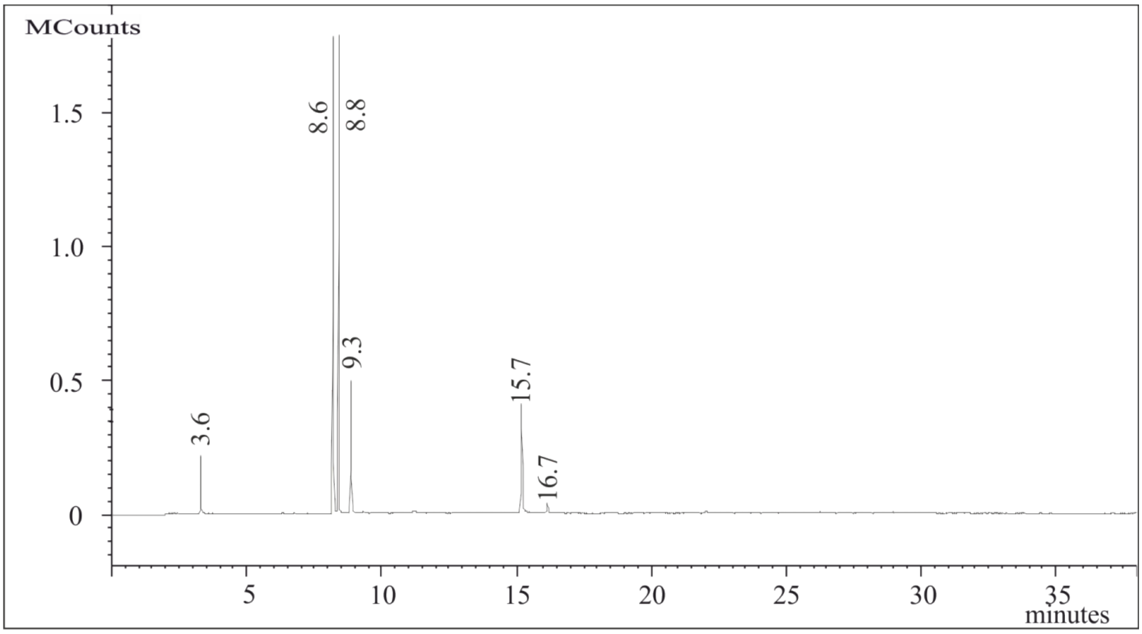


Figure S 7 GC-chromatogram of a typical reaction mixture of BCB isomerisation after 23 h at 170 °C with the organic $AlCl_3$-[EMIM]Cl melt; retention times: 3.6 min chlorobenzene; 8.6 min 1-bromo-3-chlorobenzene; 8.8 min 1-bromo-4-chlorobenzene; 9.3 min 1-bromo-2-chlorobenzene; 14.4/15.7/16.7 dibromochlorobenzene isomers.

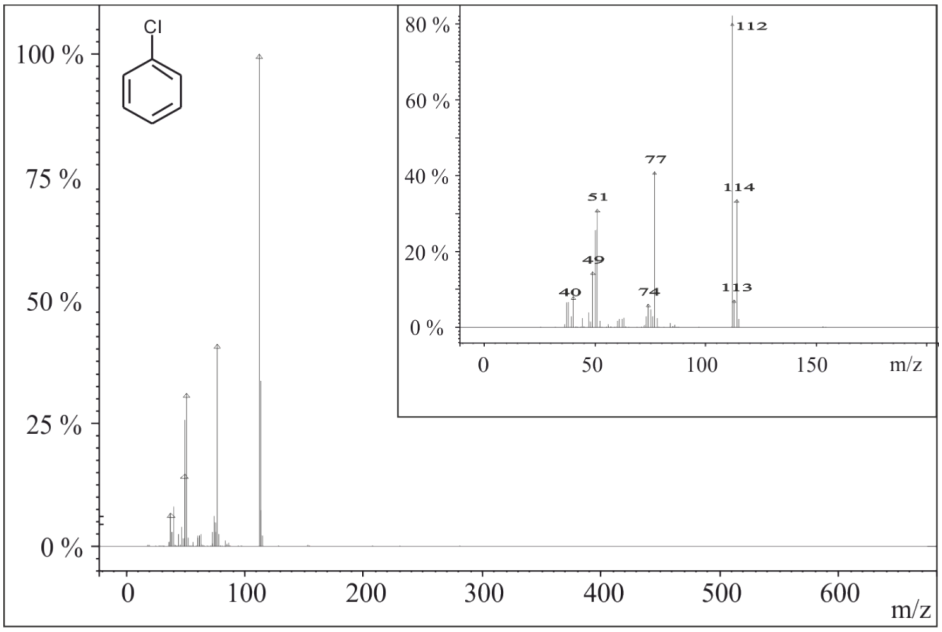


Figure S 8 Mass spectrum of chlorobenzene; retention time 3.6 min; m/z 112, 113, 114, 115.

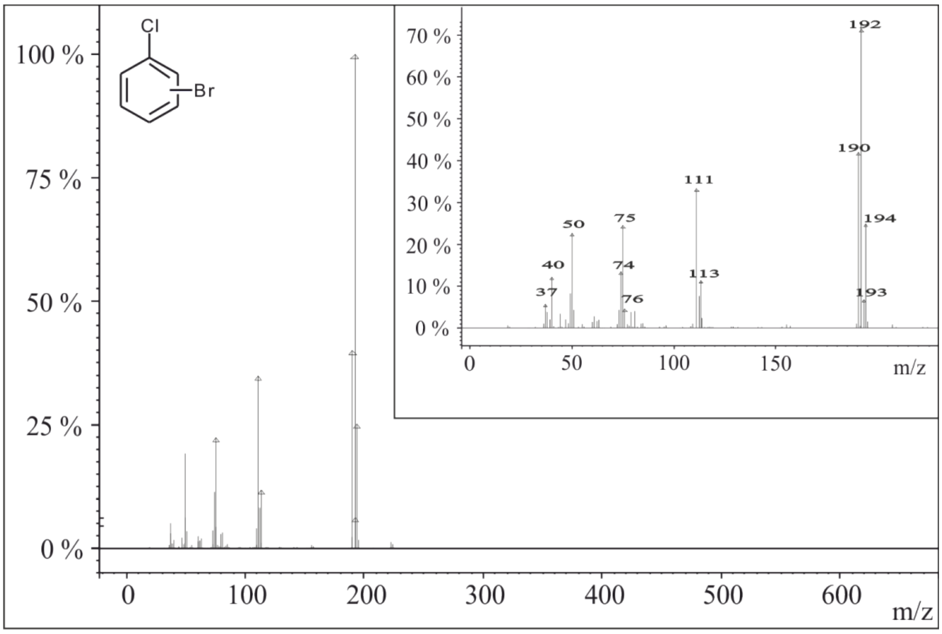


Figure S 9 Mass spectra, of bromochlorobenzenes; retention time 8.6, 8.8 and 9.3 min; m/z 190, 191, 192, 193, 194, 195.

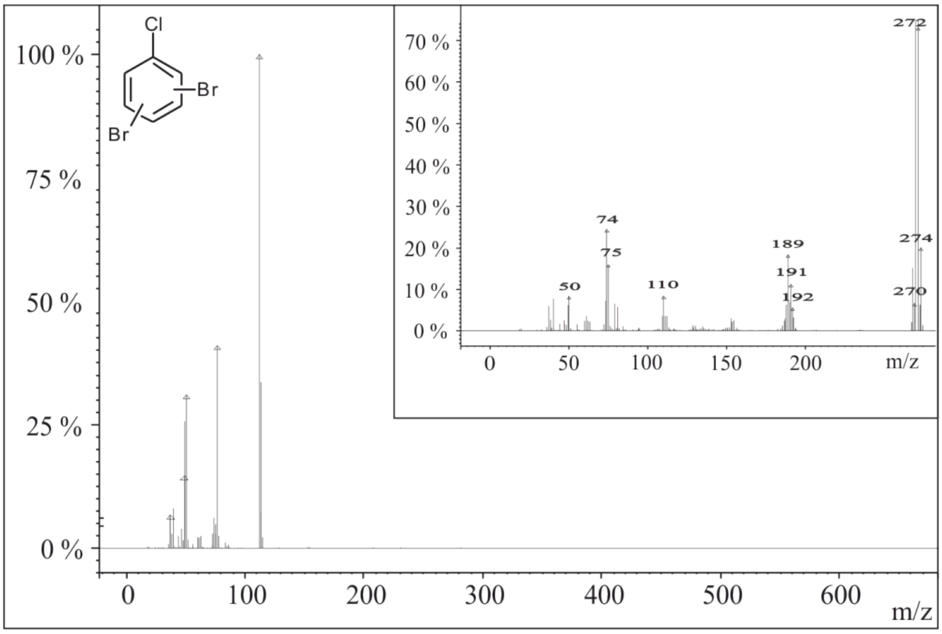


Figure S 10 Mass spectra of the dibromochlorobenzene; retention times: 14.7, 15.7 and 16.7 min; m/z 268, 269, 270, 271, 272, 273, 274.

Table ST6 GC retention times and m/z values of typical products of the BCB ismomerisation reaction.

	Retention time / min	**m/z**
chlorobenzene	3.6	112, 113, 114, 115
1-bromo-3-chlorobenzene	8.6	190, 191, 192, 193, 194, 195
1-bromo-4-chlorobenzene	8.8	
1-bromo-2-chlorobenzene	9.3	
Dibromo-chlorobenzene isomeres	14.4 / 15.7 / 16.7	268, 269, 270, 271, 272, 273, 274

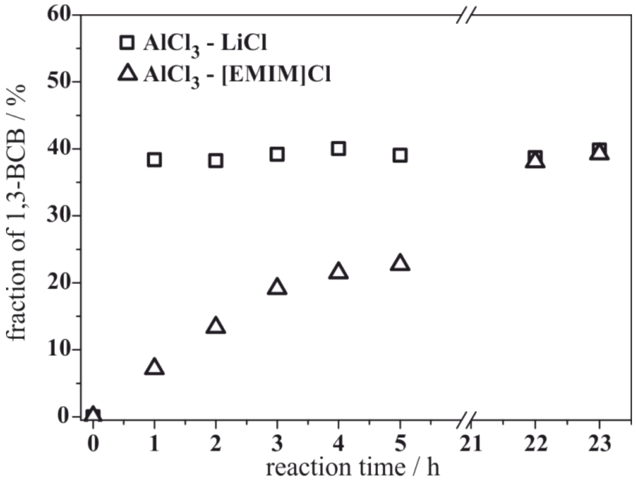


Figure S 11 Isomerisation of 1-bromo-4-chlorobenzene with acidic chloroaluminate melts. Comparison of the inorganic melt $AlCl_3$-LiCl and the organic melt $AlCl_3$-[EMIM]Cl; 170 °C, 23 h, 20 mol % $AlCl_3$ and 10 mol % LiCl / [EMIM]Cl, 38.3 g 1,4-BCB.

Literature ESI:

[1] G. A. Olah, W. S. Tolgyesi, R. E. A. Dear, The Journal of Organic Chemistry 1962, 27, 3455-3464.