Supporting Information

Integrated desulfurization of diesel by combination of metal-free oxidation and product removal by molecularly imprinted polymers

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Experimental Details

All reagents were obtained from commercial sources (*Sigma-Aldrich, or Alfa Aesar)*). Trihexyl(tetradecyl)phosphonium chloride was kindly donated by CYTEC. In all the experiments 30% aqueous solution of H_2O_2 was used. Amberlyst 15 and Aliquat 336® were purchased to Sigma-Aldrich. All the solvents were distilled before use. Flash chromatography was performed on *Merck* silica gel (40-63 mesh) by standard techniques or using a Teledyne Isco CombiFlash Automated Flash Chromatography System.

^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance II+ 300 and 400 MHz (UltraShield Magnet) and Bruker Avance II+ 500 (UltraShield Plus Magnet) spectrometers at room temperature.

Quantification of DBT, DBT-SO and DBT-SO_2 by Gas Chromatography (GC)

This analysis was performed on a Finnigan Focus gas chromatograph equipped with a SGE BP20(WAX) capillary column (25m × 0.22mm ×0.25µm; helium as carrier gas; injector at 250ºC, detector at 300ºC, oven at 160ºC) for 60 minutes. The retention times were 12 minutes for DBT, 48 minutes to DBTSO and 50 minutes to $DBTSO_2$.

To calibrate the column for the molecules under study, several samples with different proportions of the 3 compounds were analysed by GC, allowing to draw two calibration curves (figures S1 and S2).

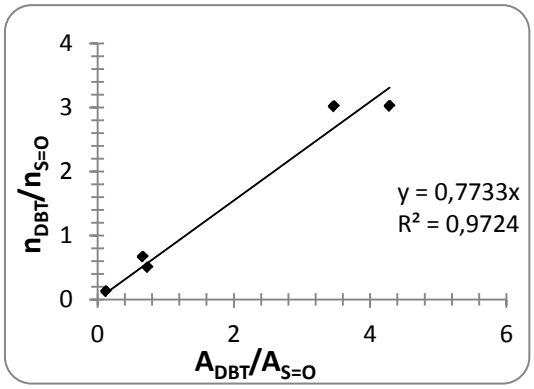

Figure S1.Calibration curve for the relation DBT/DBTSO.

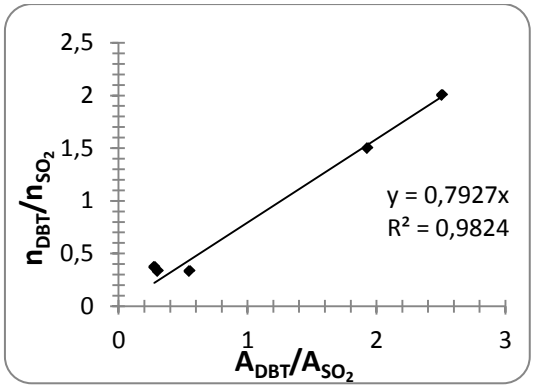

Figure S2.Calibration curve for the relation DBT/DBTSO$_2$.

From these curves, it is possible to determine the percentage of conversion of dibenzothiophene in each product, using the following equations.

$$conv_{S=O}\ (\%) = \frac{\frac{A_{S=O}}{0,7733}}{\frac{A_{S=O}}{0,7733}+\frac{A_{SO_2}}{0,7927}+A_{DBT}} \times 100$$

$$conv_{SO_2}\ (\%) = \frac{\frac{A_{SO_2}}{0,7927}}{\frac{A_{S=O}}{0,7733}+\frac{A_{SO_2}}{0,7927}+A_{DBT}} \times 100$$

Quantification of DBT, DBT-SO and DBT-SO$_2$ by High Pressure Liquid Chromatography (HPLC)

Optimized HPLC conditions were achieved using an analytical column Phenomenex Gemini-NX 110A C18 *5.0µm* NC (250x4.6mm) with a Shimadzu LC-20AT pump, flow *0.8mL/min*. Detection performed with a Merck/Hitachi 655A-22 Variable Wavelength UV monitor at *λ=230nm*. Manual injection with *20µL* loop was used. Mobile phase was water and methanol 60:40 for 20 minutes, increasing gradually to 0:100 for 30 minutes, and staying at this proportion for 20 minutes. Bidistilled water, filtered using a cellulose acetate membrane (0.45µm, 47MM), and commercial HPLC grade methanol were used.

Since diesel was not soluble in any of HPLC solvents suitable for this analysis, column chromatography was performed in the end of each reaction, to isolate the products of the reaction, which were then dissolved in acetonitrile and analysed by HPLC.

As presented in figure S3, the retention times for sulfoxide, sulfone and dibenzothiophene were 30, 32 and 49 minutes, respectively.

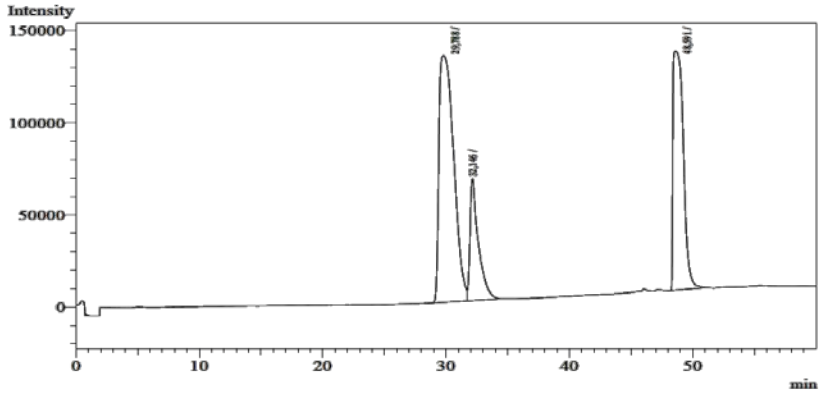

Figure S3.HPLC chromatogram of a solution with DBT and its sulfone and sulfoxide.

To calibrate the column for the molecules under study, several samples with known amounts of the three compounds were analysed, allowing 3 calibration curves to be drawn (figures S4, S5 and S6).

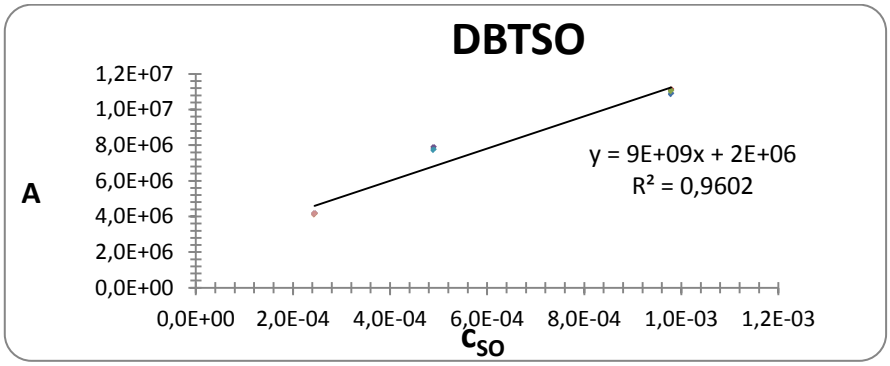

Figure S4. Calibration curve of DBTSO for HPLC (A-peack area; C_{SO} -DBTSO Molar concentration).

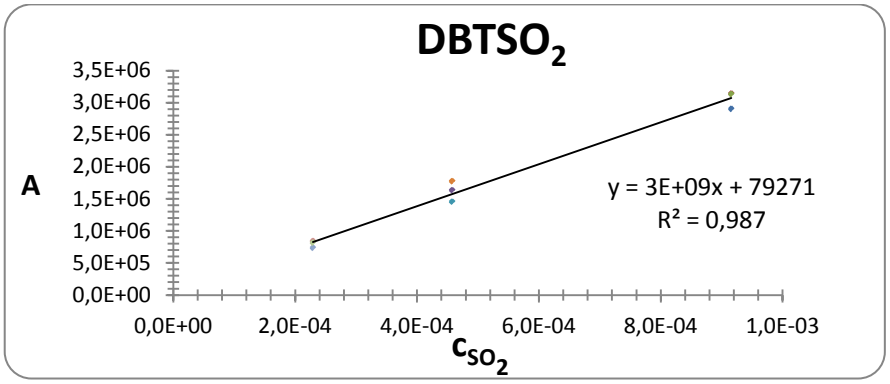

Figure S5. Calibration curve of $DBTSO_2$ for HPLC (A-peack area; C_{SO2}-$DBTSO_2$ Molar concentration).

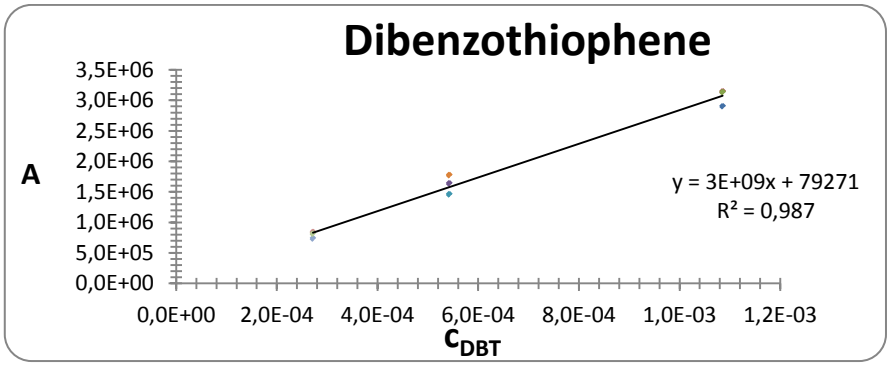

Figure S6. Calibration curve of DBT for HPLC (A-peack area; C_{DBT}-DBT Molar concentration).

Oxidation of dibenzothiophene in hexane (general procedure)

To a closed flask with a solution of dibenzothiophene in hexane was added a solution of *p*-TsOH in 4 equivalents of H_2O_2. After 24 hours stirring at 60ºC, the aqueous phase was removed and washed with CH_2Cl_2. The organic phase from the crude reaction, with a solid in suspension was added to the CH_2Cl_2 phase and the final mixture was evaporated. Final samples were dissolved in dichloromethane in order to be analysed GC (retention times: DBT – 12 min; DBTSO – 48 min; $DBTSO_2$– 50 min).

Table S. Oxidation of DBT to DBTSO and $DBTSO_2$ in hexane[a]

entry	***p*-TsOH** (mol%)			**T** (ºC)	**Conv. DBTSO** (%)[b]	**Conv. $DBTSO_2$** (%)[b]	**Total conv.** (%)[b]
1	10			60	-	13.7	13.7
2	20			60	1,7	16.1	17.8
3	30			60	-	39.0	39.0
4	30			60	-	6.7	6.7
5	40			60	-	20.4	20.4
6	50			60	-	15.2	15.2
7	30			RT	-	0.0	0.0
8	30			70 to 80	-	35.9	35.9
9	30			60	2.3	5.1	7.4

a) General procedure: DBT (1,35mmol) was dissolved in hexane (6mL, except for entry 9:1 mL) and added to a solution of H_2O_2 (4 equivalents) and *p*-TsOH, then stirred for 24 hours, in a closed reactor (except entry 4, performed in a round-bottom flask). b) Observed conversion by GLC to dibenzothiophene sulfoxide (DBTSO), dibenzothiophene sulfone ($DBTSO_2$) and total conversion (DBTSO + $DBTSO_2$).

Oxidation of dibenzothiophene in hexane with IL as co-solvent(general procedure)

To a closed flask with a solution of dibenzothiophene in hexane was added an amount of IL (Aliquat® or trihexyl(tetradecyl)phosphonium chloride $[P_{6,6,6,14}]Cl$) and a solution of 30 mol% of *p*-TsOH in 4 equivalents of H_2O_2. After 24 hours stirring at 60ºC, the aqueous phase was removed and cold hexane was added to the solid in suspension in the organic phase, to remove the ionic liquid. Hexane was decanted and the solid was dried in a rotaevaporator. Final samples were analysed GC.

Table S2. Oxidation of DBT to DBTSO and $DBTSO_2$ in hexane[a)].

entry		**Ionic Liquid** (g)	**Solvent**	**T** (ºC)	**Conv. DBTSO** (%)[b]	**Conv. $DBTSO_2$** (%)[b]	**Total conv.** (%)[b]
1		Aliquat® (1.1)	hexane	50	88.6	8.8	97.4
2		$[P_{6,6,6,14}]Cl$ (1.1)	hexane	50	86.3	8.1	94.4
3		Aliquat® (1.1)	hexane	65	87.8	11.0	98.8
4		Aliquat® (0.27)	DCE	65	79.7	19.3	99.0
5		$[P_{6,6,6,14}]Cl$ (0.26)	DCE	65	83.8	12.8	96.6

a) General procedure: DBT (2,71mmol)was dissolved in 3 mL of solvent, and added to a solution of H_2O_2 (4 equivalents), and 30 mol% of *p*-TsOH , after that the IL was added. The solution was stirred for 24 hours (except entry 3 - for 48 hours), in a closed reactor. b) Observed conversion by GLC to dibenzothiophene sulfoxide (DBTSO), dibenzothiophene sulfone ($DBTSO_2$) and total conversion (DBTSO + $DBTSO_2$).

Oxidation of dibenzothiophene in diesel

To a solution of dibenzothiophene in 3 ml of diesel were added 260,6 mg of Aliquat® and a solution of 30 mol% of *p*-TsOH in 4 equivalents of H_2O_2.

After 24 hours at 60ºC, the suspension was filtered; the solid was washed with hexane a then dried in rotaevaporator. Final sample was analysed GC.

Table S3. Oxidation of DBT to DBTSO and $DBTSO_2$ in diesel.

	***p*-TsOH (mol%)**	**Ionic Liquid (g)**	**Solvent (mL)**	**T (ºC)**	**Conv. DBTSO (%)[a]**	**Conv. $DBTSO_2$ (%)[a]**	**Total conv. (%)[a]**
	30	Aliquat® (0.26)	diesel (3)	50	63.1	35.8	98.9

a) Observed conversion by GLC to dibenzothiophene sulfoxide (DBTSO), dibenzothiophene sulfone ($DBTSO_2$) and total conversion (DBTSO + $DBTSO_2$).

Oxidation of dibenzothiophene in diesel using different promoters(general procedure)

To a solution of dibenzothiophene in diesel was added a solution of 30 mol% of *p*-TsOH in 4 equivalents of H_2O_2. In some cases, a phase-transfer catalyst was also added (30 mol%). After 24 hours at 60ºC, the oxidation products were isolated from diesel through column chromatography (hexane as eluent until diesel and DBT are eluted from the column; then, hexane-ethyl acetate (1:1) to remove DBTSO and $DBTSO_2$). The portion containing the isolated products was then analyzed by HPLC.

Table S4. Effect of the catalyst and PTCs for the oxidation of DBT in diesel.[a]

	Catalyst (30 mol%)	**PTC** (30 mol%)	**$DBTSO_2$** (%)[b]	**DBTSO** (%)[b]	**η(%)[b]**	
1	*p*-TsOH	---	15.2 17.0	4.6 5.3	19.8 22.3	21.1
2	Camphorsulfonic acid	---	9.4 9.1	5.8 5.5	15.2 14.6	14.9
3	dodecyl benzene sulfonic acid	---	8.6 8.8	7.7 8.5	16.3 17.2	16.8
4	Formic acid	---	0.8 0.8	6.3 6.1	7.1 6.9	7.0
5	Phosphoric acid	---	5.2 5.9	4.1 4.7	9.4 10.6	10.0
6	Amberlyst	---	12.8	3.8	16.6	16.6
7	---	---	1.5 2.1	0.0 0.0	1.5 2.1	1.8
8	*p*-TsOH	Aliquat®	12.8 13.4	7.9 8.3	20.7 21.7	21.2
9	*p*-TsOH	$[P_{6,6,6,14}]Cl$	11.2 10.8	9.9 11.0	21.0 21.8	21.4
10	*p*-TsOH	CHAPS	18,6 18,9	1,9 1,3	20,5 20,2	20,4
11	*p*-TsOH	SDS	25.0 24.7	4.2 4.2	29.2 28.9	29.1
12[c]	*p*-TsOH	---	25.0 24.7	4.9 4.7	29.9 29.4	29.7
13[d]	*p*-TsOH	---	14.9 18.4	9.6 8.1	24.5 26.5	25.5

a) General procedure: DBT (50.0 mg, 0.27mmol) was dissolved in diesel (10 mL), and added to a solution of H_2O_2 (4 equivalents), 30mol% of catalyst and 30mol% of phase-transfer catalyst (PTC), then stirredfor 24 hours at 60ºC, in a closed reactor. b) Observed yield by HPLC of $DBTSO_2$, DBTSO and total ($DBTSO_2$ + DBTSO), average of two independent analysis. c) After 24 h, more H2O2 (4 eq.), *p*-TsOH (30 mol%) was added and left under reaction for more 24 h (total time of 48 h). d) Was used H_2O_2 (8 equivalents).

MIP synthesis in supercritical carbon dioxide

Three MIPs were synthesized in $scCO_2$ in a 33 mL stainless steel rector equipped with sapphire windows at the tops. Methacrylic acid (MAA), 2-vinylpyridine (2Vpy) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) were used as functional monomers, ethylene glycol dimethacrylate (EGDMA) as cross-linker, azobisisobutyronitrile (AIBN) as initiator and $DBTSO_2$ as template, with a molar ratio of monomer/template/cross-linker of 1:5:25. Preliminary binding tests were performed to evaluate the static adsorption capacity of the synthesized polymers by adding 20 mg of polymeric to solutions of $DBTSO_2$, stirred at 50 rpm, with concentrations ranging from 0.019 to 0.116μg.mL^{-1}. MAA based MIP presented the best binding affinity and thus it was chosen in the selective removal of benzothiophene-based compounds from diesel. The polymerizations proceeded for 24h at 65ºC and 222 bar, under stirring, followed by the continuous wash of unreacted reagents and template with fresh $scCO_2$ for 1h. NIP (Non-imprinted polymer) were produced with the same protocol but without adding the template. The produced MIPs were obtained as dry, free-flowing powders in high yields (> 90 %, determined gravimetrically). All polymers present a similar morphology, showing discrete particles slightly agglomerated, consistent with other precipitation polymerizations in $scCO_2$. Polymers were obtained without residues of solvent and without the need of grinding and sieving as conventional MIPs.

MIPs and NIPs testing

Several tests were initially performed to understand the best way to use the polymer in the extraction process; these tests showed that the polymer would retain not only our target molecule (sulfone) but also the sulfoxide, probably due to the similarity between them or the fact that it was in template's sample as an impurity when polymerization occurred.

The sample was placed in a glass column (internal diameter = 1cm; length = 20cm) containing the polymer (200mg), and dragged with hexane. Dichloromethane or acetonitrile were then used to remove extracted compounds from the polymer. The final portion was analysed HPLC.

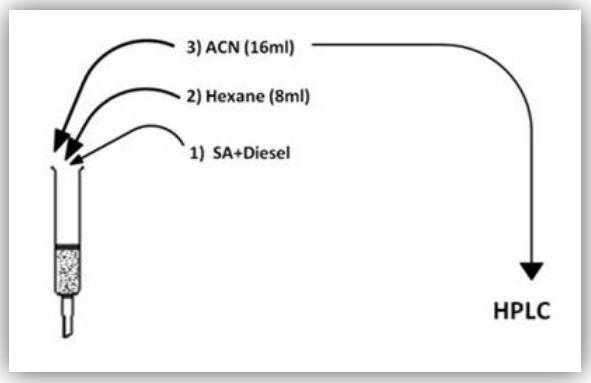

Figure S7.Method used for imprinted polymers testing.

Table S5 – Observed binding of $DBTSO_2$ in diesel by MIP and NIP.[a]

Entry	m($DBTSO_2$) (g)	V(diesel) (mL)	conc. (mM)	polymer	m($DBTSO_2$ ret.)[b] (mg)		$DBTSO_2$ ret. (%)		mg($DBTSO_2$)/g(pol.)
1	75.4	15	23.1	MIP	36.3 34.5	35.4	48,4 46,0	47,2	177.0
2	75.6	15	23.1	NIP	27.0 27.6	27.3	36,0 36,8	36,4	136.5
3	50.0	10	23.1	MIP	27.3 29.3	28.3	54,7 58,6	56,7	141.5
4	30.0	6	23.1	MIP	20.7 21.2	21.0	69,0 70,7	69,9	105.0
5	75.4	15	23.1	MIP	30.4 32.2	31.3	40,5 43,0	41,8	156.5
6c	75.0	15			31.5 34.0	32.8	42,0 45,3	43,7	164.0
7c	75.1	15			33.8 37.4	35.6	45,1 49,9	47,5	178.0

a) To MIP or NIP (200 mg) in a glass column was passed diesel containing $DBTSO_2$, and then washed successively with hexane and acetonitrile. b) Observed $DBTSO_2$ present in the acetonitrile fraction by HPLC (duplicate analysis). c) Observed results of reused MIP from the previously experiment.

HPLC chromatograms of MIPs and NIPs testing

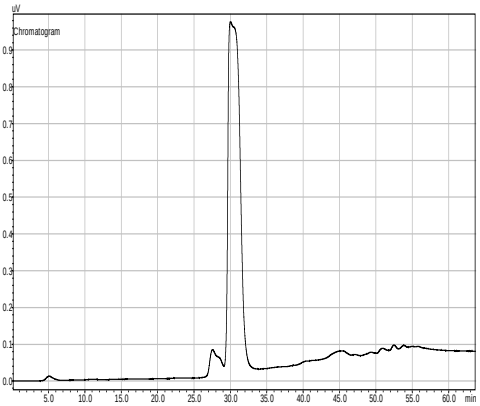

Figure S8. MIP testing.

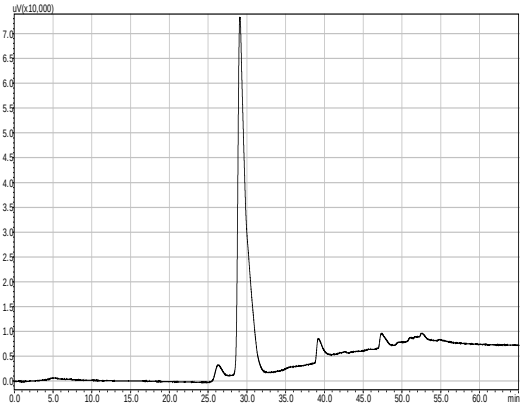

Figure S9. NIP testing.

Oxidation of dibenzothiophene in diesel followed by extraction with MIP

To a solution of 0.050g of dibenzothiophene (DBT) in 10 ml of diesel was added a solution of 30 mol% of *p*-TsOH in 4 equivalents of H_2O_2. After 24 hours at 60ºC, the reaction mixture was placed through a chromatography column containing the MIP (200 mg), and dragged with hexane (8 mL) followed by acetonitrile (16 mL) to remove binding compounds from the polymer. The acetonitrile fraction was analysed by HPLC providing 12.7 mg of $DBTSO_2$ (with 10.8% yield).

Table S5 – Observed results for the DBT oxidation in diesel followed by oxidized products removal using MIP.

	m(pol) (mg)	polymer	$DBTSO_2$ ret. (mg)[a]		η(%)		mg($DBTSO_2$)/g(pol)
1	200.0	**MIP**	6.0 6.6	6.3	10.3 11.3	10.8	31.5

a) Observed $DBTSO_2$ present in the acetonitrile fraction by HPLC (duplicate analysis).

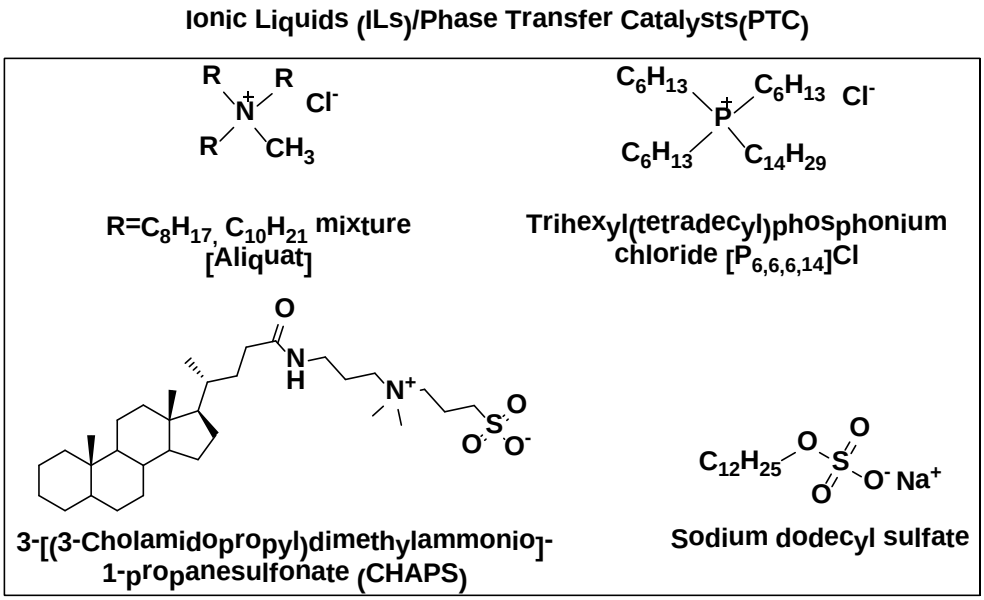

Figure S6. Structure of the used ILs/PTC.