

## Shifting the equilibrium of methanol synthesis from CO<sub>2</sub> by *in situ* absorption using ionic liquid media

Jenny Reichert<sup>a)</sup>, Stephanie Maerten<sup>a)</sup>, Katharina Meltzer<sup>b)</sup>, Alexander Tremel<sup>b)</sup>, Manfred Baldauf<sup>b)</sup> Peter Wasserscheid<sup>a),c)</sup>, Jakob Albert<sup>\*a)</sup>

### Supporting information

#### a) Synthesis of non-commercial sorption agents

All reactions requiring tri-*n*-butylphosphine were carried out in protective atmosphere using standard Schlenck techniques. All reagents were commercial and used as received. All product purities were above 98,5 %.

##### [P<sub>1444</sub>][Me<sub>2</sub>PO<sub>4</sub>]

Tri-*n*-butylphosphine was mixed with the same amount of trimethylphosphate under nitrogen atmosphere and kept at 120 °C for 8 hours. The reaction mixture was then cooled to room temperature and washed with *n*-hexane: The solvent was removed in the rotary evaporator (yield 96 %).

##### [P<sub>2444</sub>][Et<sub>2</sub>PO<sub>4</sub>]

For the preparation of [P<sub>2444</sub>][Et<sub>2</sub>PO<sub>4</sub>] tri-*n*-butylphosphine was mixed with triethylphosphate under nitrogen atmosphere and kept at 120 °C for 8 hours. After cooling to room temperature the reaction mixture was washed with *n*-hexane. The remaining solvent was removed using a rotary evaporator reaching a yield of 94 %.

##### [P<sub>1444</sub>][OTf]

First, methyl triflate (MeOTf) is produced by the reaction of dimethyl sulfate (C<sub>2</sub>H<sub>6</sub>SO<sub>4</sub>) with trifluoromethanoic acid. For the synthesis of [P<sub>1444</sub>][OTf], MeOTf and tributylphosphine react at 0 °C. The reaction is carried out in the presence of a trifluoromethanoic acid. After 60 min the [P<sub>1444</sub>][OTf] yield was 89 %.

##### [N<sub>1888</sub>][NTf<sub>2</sub>]

[N<sub>1888</sub>][NTf<sub>2</sub>] was synthesized in an ion exchange reaction. An aqueous trioctylmethylammonium chloride solution was added to Li[NTf<sub>2</sub>] and water and stirred at room temperature for 3 hours. The product is then washed with water and dried aiming a yield of 95 %.

##### [P<sub>4444</sub>][NTf<sub>2</sub>]

After [P<sub>4444</sub>][Br] was completely dissolved in water Li[NTf<sub>2</sub>] was added and stirred for 2 hours. The content of the flask was then placed in a separating funnel with dichloromethane and

washed with water. The organic phase was isolated and the solvent was removed using a rotary evaporator. The remaining water was removed by keeping the product at 100 °C for 48 h. The yield was 94 %.

[P<sub>66614</sub>][NTf<sub>2</sub>]

[P<sub>66614</sub>]Br and Li[NTf<sub>2</sub>] were each dissolved in water. The prepared Li[NTf<sub>2</sub>] solution was added to the bromide solution in excess (1.1 M relative to the bromide salt). After the addition of dichloromethane, the organic phase was separated. It was washed three times with water. After the distillative separation of dichloromethane, the remaining liquid was dried under vacuum at 60 °C for 3 hours. In the end a yield of 87 % was reached.

### **b) Synthesis of non-commercial additives**

All reactions requiring tri-n-butylphosphine were carried out in protective atmosphere using standard Schlenck techniques. All reagents were commercial and used as received. The content of Li was determined by inductively coupled plasma – atom emission spectroscopy (ICP-AES) using a Ciros CCD (Spectro Analytical Instruments GmbH).

[P<sub>444</sub>(C<sub>2</sub>OH)][NTf<sub>2</sub>]

A 100 mL Schlenck flask equipped with a stirring bar and a reflux condenser was charged with 45,16 g of ClCH<sub>2</sub>CH<sub>2</sub>OH. Under stirring, 23,58 g of (Bu)<sub>3</sub>P were slowly added. The homogeneous solution was refluxed overnight. The resulting mixture was evaporated at the rotary evaporator and the resulting viscous liquid dissolved in 200 mL distilled water. The resulting pale brown solution was decolorized with black carbon under reflux and after cooling, carefully filtered. The obtained yellowish solution was transferred in a 500 mL bottle and 31,40 g of Li[NTf<sub>2</sub>] were added in small portion under vigorous stirring. After completing the addition, the whole mixture was vigorously stirred for 1 h. Then 200 mL of CH<sub>2</sub>Cl<sub>2</sub> were added. The stirring was continued for 15 min, then the biphasic mixture was transferred in a 500 mL separatory funnel. The lower organic phase was collected and washed with distilled water until the washing tested negative to Ag(NO<sub>3</sub>)-test for chloride. The organic phase was evaporated at the rotary evaporator and the product dried at 80 °C and 1 mbar overnight. 54,10 g of a pale yellow viscous liquid were obtained.

[P<sub>444</sub>(C<sub>3</sub>-2,3-OH)][NTf<sub>2</sub>]

A 100 mL Schlenck flask equipped with a stirring bar and a reflux condenser was charged with 27,78 g of ClCH<sub>2</sub>CH(OH)CH<sub>2</sub>OH and 49,75 g of (Bu)<sub>3</sub>P. The homogeneous solution was heated at 120 °C overnight. The resulting viscous liquid was dissolved in 200 mL distilled water. The obtained colorless solution was transferred in a 1 L bottle and a solution of 77.06 g

of Li[NTf<sub>2</sub>] in 300 mL distilled water was added under vigorous stirring. After completing the addition, the whole mixture was vigorously stirred for 1 h and then 200 mL of CH<sub>2</sub>Cl<sub>2</sub> were added. The stirring was continued for 15 min, then the biphasic mixture was transferred in a 1 L separatory funnel, the lower organic phase was collected and transferred in a 500 mL separatory funnel, where it was washed with distilled water until the washing tested negative to Ag(NO<sub>3</sub>)-test for chloride. The organic phase was evaporated at the rotary evaporator and the product dried at 80 °C and 1 mbar overnight. 134,70 g of a colorless viscous liquid were obtained.

#### [P(CH<sub>2</sub>OH)<sub>4</sub>][NTf<sub>2</sub>]

81,52 g of a aqueous solution of [(HOCH<sub>2</sub>)<sub>4</sub>P]<sub>2</sub>(SO<sub>4</sub>) (Aldrich, 70-75 % w/w) were diluted with 250 mL of ethanol in a 500 mL bottle. 88,16 g of LiNTf<sub>2</sub> were added in small portion under vigorous stirring to the solution. A white precipitate formed immediately. After completing the addition, the suspension was stirred at room temperature overnight. The resulting mixture was filtered, the filtrate collected and evaporated at the rotary evaporator yielding 86,50 g of a colorless viscous liquid.

**c) Simulation results for methanol yields in the investigated temperature range using Aspen Plus V8.8**

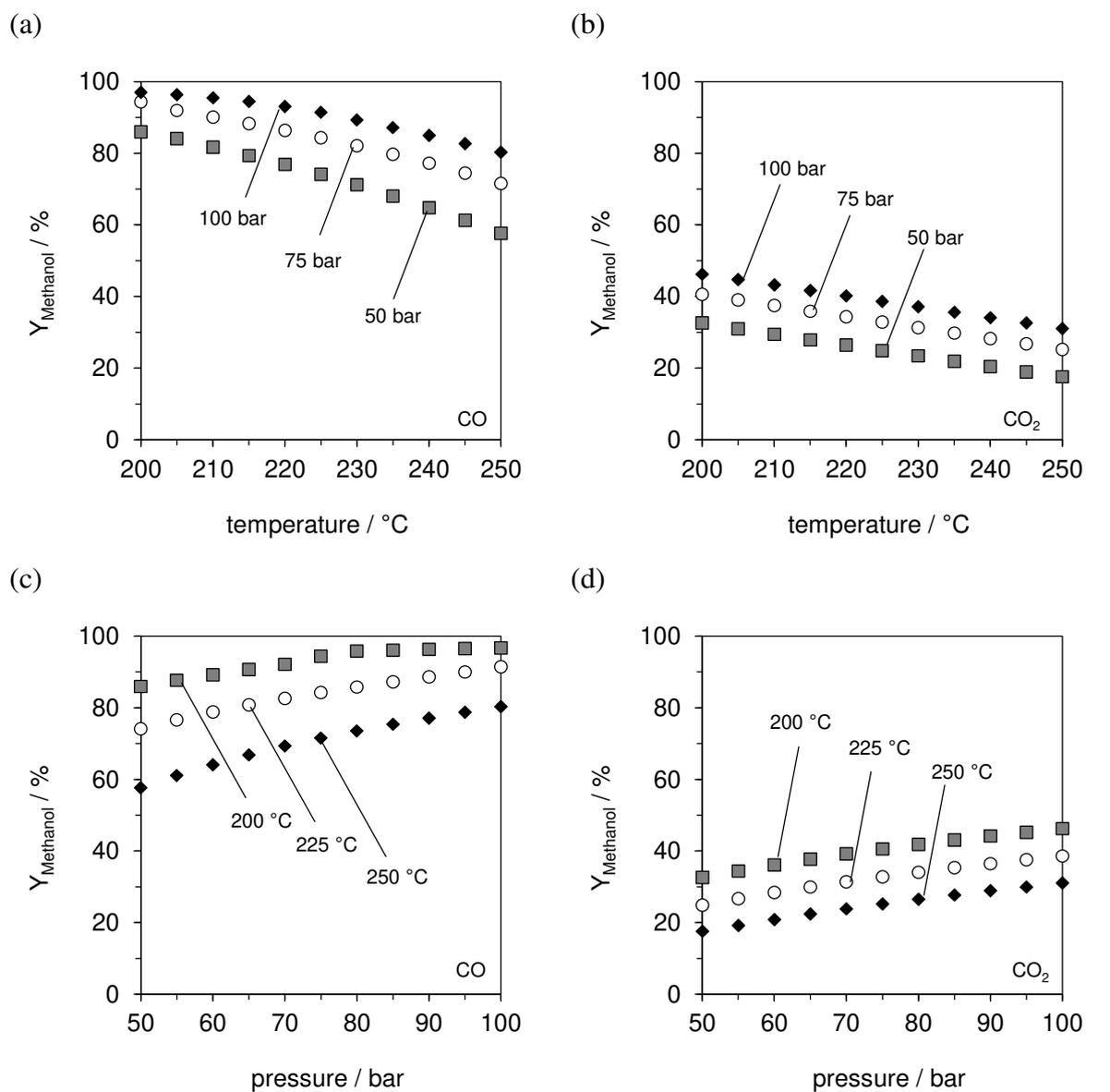


Figure S1: Simulated equilibrium methanol yields using Aspen Plus V8.8 (method SRK) for (a), (b)  $T = 200\text{-}250\text{ }^{\circ}\text{C}$ ,  $p$  ■ 50 bar, ○ 75 bar, ◆ 100 bar; (c), (d)  $p = 50\text{-}100$  bar,  $T =$  ■ 200 °C, ○ 225 °C, ◆ 250 °C.

### d) Thermal stability tests using thermogravimetric analysis for ionic liquids

Table S1: Mass decrease during thermogravimetric analysis at 250 °C of the ILs tested as sorbents.

Sorbent	Mass decrease at 250 °C / % h <sup>-1</sup>
[P <sub>2444</sub> ][Et <sub>2</sub> PO <sub>4</sub> ]	8.46
[P <sub>1444</sub> ][OTf]	5.97
[P <sub>1444</sub> ][Me <sub>2</sub> PO <sub>4</sub> ]	1.47
[EMIM][MeSO <sub>3</sub> ]	0.97
[P <sub>1444</sub> ][MeSO <sub>4</sub> ]	0.67
[EMIM][NTf <sub>2</sub> ]	0.54
[N <sub>1888</sub> ][NTf <sub>2</sub> ]	0.27
[P <sub>4444</sub> ][NTf <sub>2</sub> ]	0.28
[P <sub>66614</sub> ][NTf <sub>2</sub> ]	0.19
[P <sub>1444</sub> ][NTf <sub>2</sub> ]	0.06

### e) Solubility of an equimolar mixture of methanol and water in sorbents consisting of additives and the IL [P<sub>1444</sub>][NTf<sub>2</sub>].

Table S2: Solubility of methanol and water in sorbent consisting of additive and IL [P<sub>1444</sub>][NTf<sub>2</sub>] at room temperature.

Additive	Ratio additive in [P <sub>1444</sub> ][NTf <sub>2</sub> ] / wt. %	CH <sub>3</sub> OH loading / wt. %	H <sub>2</sub> O loading / wt. %
[P(C <sub>2</sub> OH) <sub>4</sub> ][NTf <sub>2</sub> ] pure	100	> 190	> 100
Li[NTf <sub>2</sub> ]	40	37.7	21.2
[P(C <sub>2</sub> OH) <sub>4</sub> ][NTf <sub>2</sub> ]	50	27.9	15.7
[P <sub>444</sub> C <sub>4</sub> S]	20.4	18.9	10.6
[P <sub>444</sub> (C <sub>3</sub> -2,3-OH)][NTf <sub>2</sub> ] pure	100	18.2	10.2
Li[NTf <sub>2</sub> ]	20	15.7	8.8
[P <sub>444</sub> C <sub>3</sub> S]	17.4	11.6	6.5
[P <sub>4444</sub> ] <sub>2</sub> [SO <sub>4</sub> ]	16.6	9.9	5.6
[P <sub>4444</sub> ] <sub>3</sub> [PO <sub>4</sub> ]	3.7	7.6	4.3
Mg[NTf <sub>2</sub> ] <sub>2</sub>	27.8	3.6	2.0
[P <sub>444</sub> (C <sub>2</sub> OH)][NTf <sub>2</sub> ] pure	100	3.3	1.9
[P <sub>444</sub> (C <sub>3</sub> -2,3-OH)][NTf <sub>2</sub> ]	50	3.2	1.8
Cs[NTf <sub>2</sub> ]	14.0	2.8	1.6
Co[NTf <sub>2</sub> ] <sub>2</sub>	24.2	-	0.1
[P <sub>444</sub> (C <sub>2</sub> OH)][NTf <sub>2</sub> ]	50	1.5	0.8
-	-	0.9	0.5

## f) Thermal stability tests using thermogravimetric analysis for additives

Table S3: Thermogravimetric analysis at 250 °C of compounds tested as additives.

Additive	Mass decrease at 250 °C / % h <sup>-1</sup>
Cs[NTf <sub>2</sub> ]	0.01
Co[NTf <sub>2</sub> ] <sub>2</sub>	0.02
Mg[NTf <sub>2</sub> ] <sub>2</sub>	0.02
Li[NTf <sub>2</sub> ]	0.02
[P <sub>444</sub> C <sub>4</sub> S]	0.10
[P <sub>444</sub> C <sub>3</sub> S]	0.14
[P <sub>444</sub> (C <sub>2</sub> OH)][NTf <sub>2</sub> ]	0.43
[P <sub>444</sub> (C <sub>3</sub> -2,3-OH)][NTf <sub>2</sub> ]	0.50
[P <sub>4444</sub> ] <sub>3</sub> [PO <sub>4</sub> ]	0.69
[P <sub>4444</sub> ] <sub>2</sub> [SO <sub>4</sub> ]	1.52
[P(C <sub>2</sub> OH) <sub>4</sub> ][NTf <sub>2</sub> ]	11.41

## g) Equilibrium methanol yields for methanol synthesis using different in-situ sorbent compositions

Table S4: Methanol yields in equilibrium for methanol synthesis with in-situ sorption applying different sorbent compositions using 100 mL sorbent and 5 g catalyst (Alfa Aesar for carbon source CO, Clariant for CO<sub>2</sub>) at 75 bar (H<sub>2</sub>:CO = 2:1, H<sub>2</sub>:CO<sub>2</sub> = 3:1), 250 °C, stirrer speed 200 rpm, 24 h.

Sorbent	Y <sub>MeOH</sub> (from CO)	Y <sub>MeOH</sub> (from CO <sub>2</sub> )
	/ %	/ %
Thermal oil	70.2	24.6
[P <sub>1444</sub> ][NTf <sub>2</sub> ]	81.1	25.3
7 % Li[NTf <sub>2</sub> ] in [P <sub>1444</sub> ][NTf <sub>2</sub> ]	82.7	48.6
20 % Li[NTf <sub>2</sub> ] in [P <sub>1444</sub> ][NTf <sub>2</sub> ]	85.1	57.6
30 % Li[NTf <sub>2</sub> ] in [P <sub>1444</sub> ][NTf <sub>2</sub> ]	86.2	60.0
40 % Li[NTf <sub>2</sub> ] in [P <sub>1444</sub> ][NTf <sub>2</sub> ]	87.8	63.3

## h) $^1\text{H-NMR}$ spectra of the sorbents and additives after synthesis

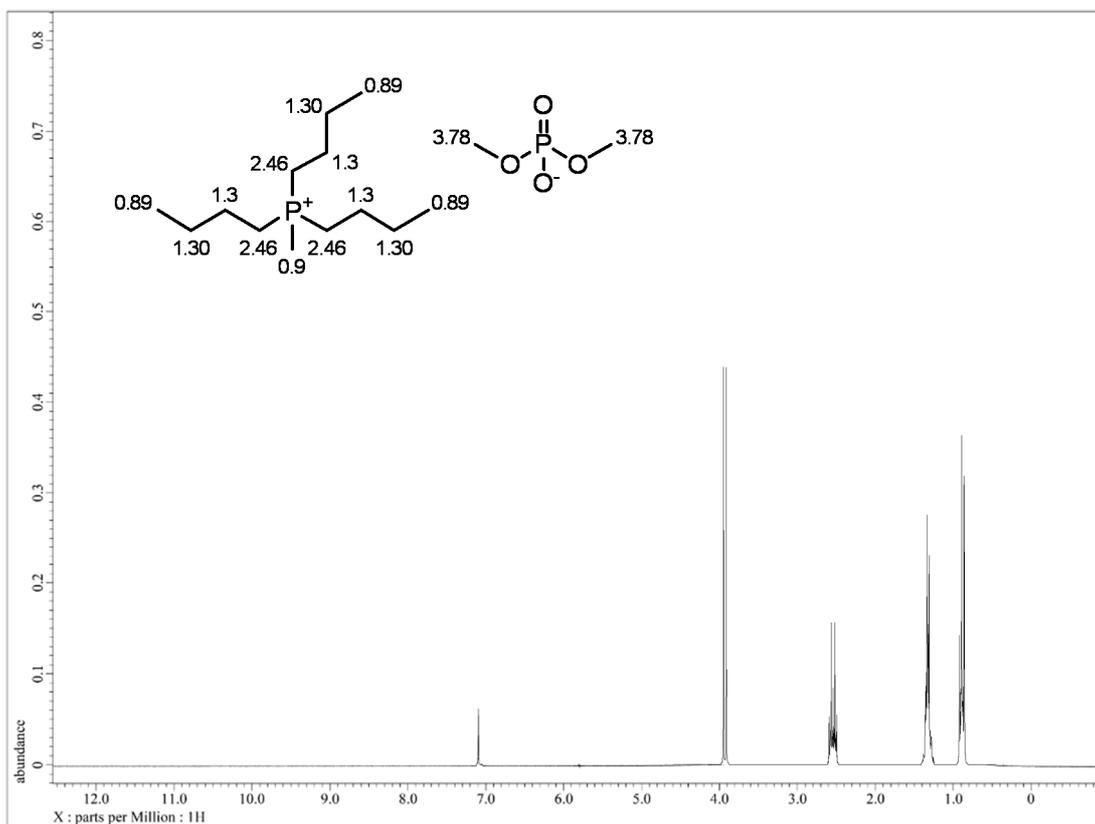


Figure S2:  $^1\text{H}$  NMR spectrum of  $[\text{P}_{1444}]\text{Me}_2\text{PO}_4$  in  $\text{CD}_3\text{OD}$  with external benzene standard.

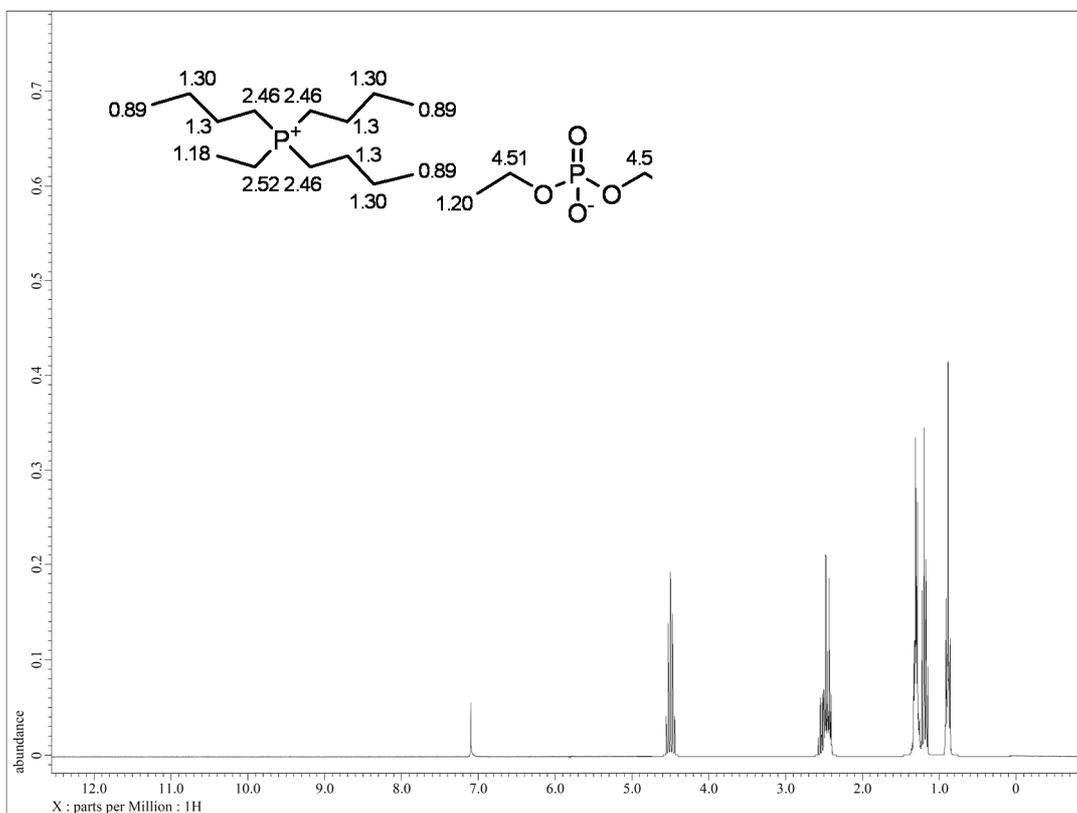


Figure S3:  $^1\text{H}$  NMR spectrum of  $[\text{P}_{2444}]\text{Et}_2\text{PO}_4$  in  $\text{CD}_3\text{OD}$ .

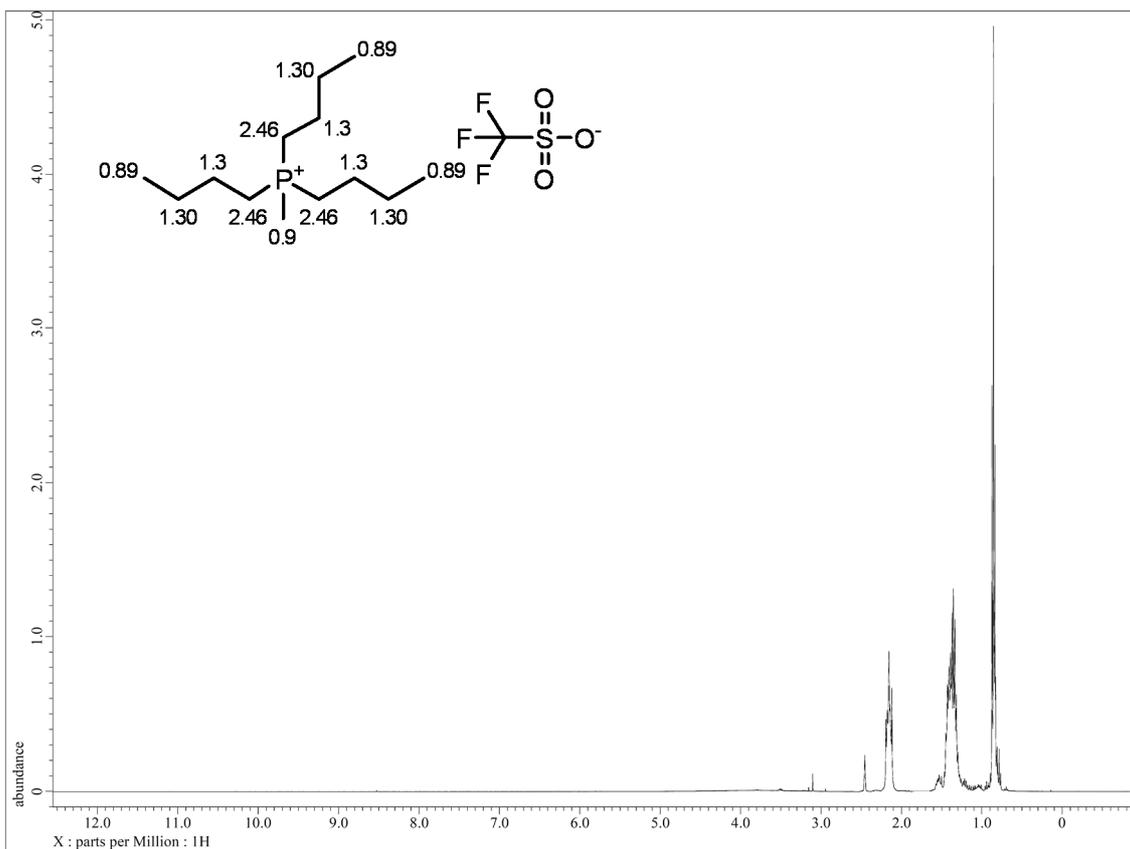


Figure S4:  $^1\text{H}$  NMR spectrum of  $[\text{P}_{1444}][\text{OTf}]$  in  $\text{CD}_3\text{OD}$ .

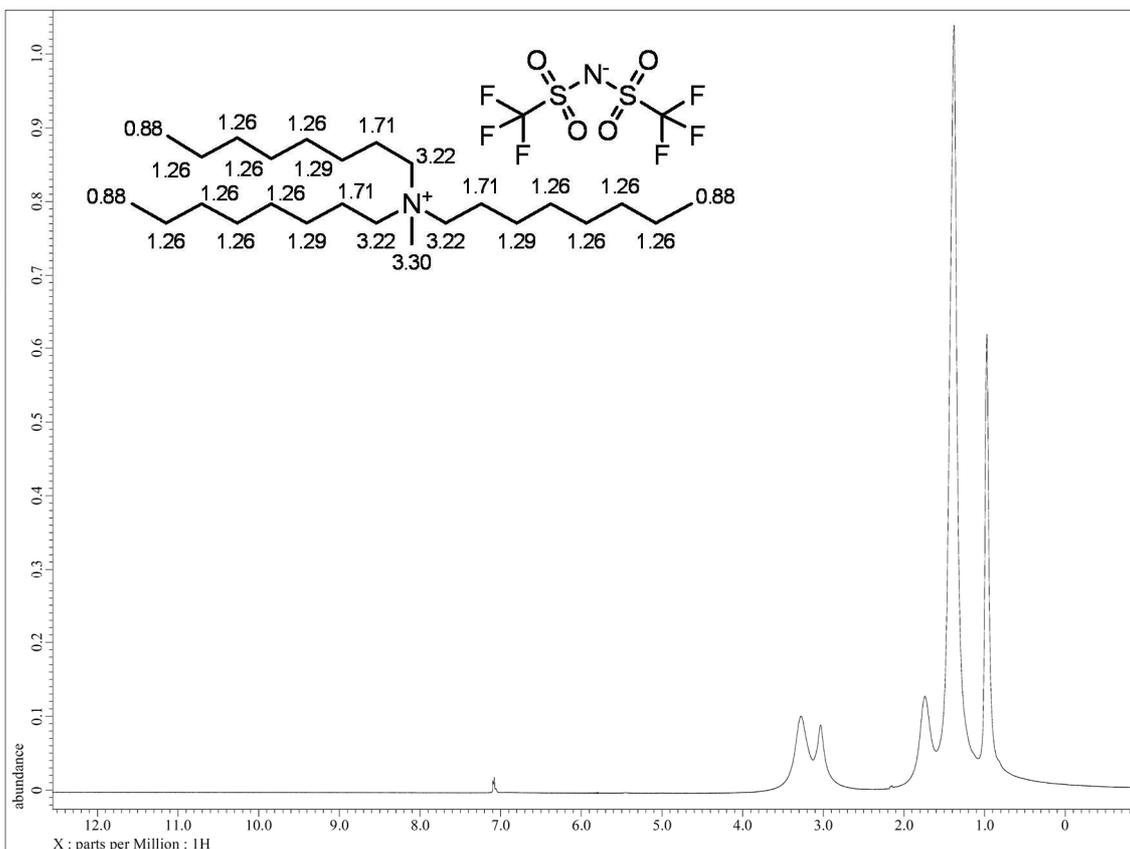


Figure S5:  $^1\text{H}$  NMR spectrum of  $[\text{N}_{1888}][\text{NTf}_2]$  in  $\text{CD}_3\text{OD}$ .

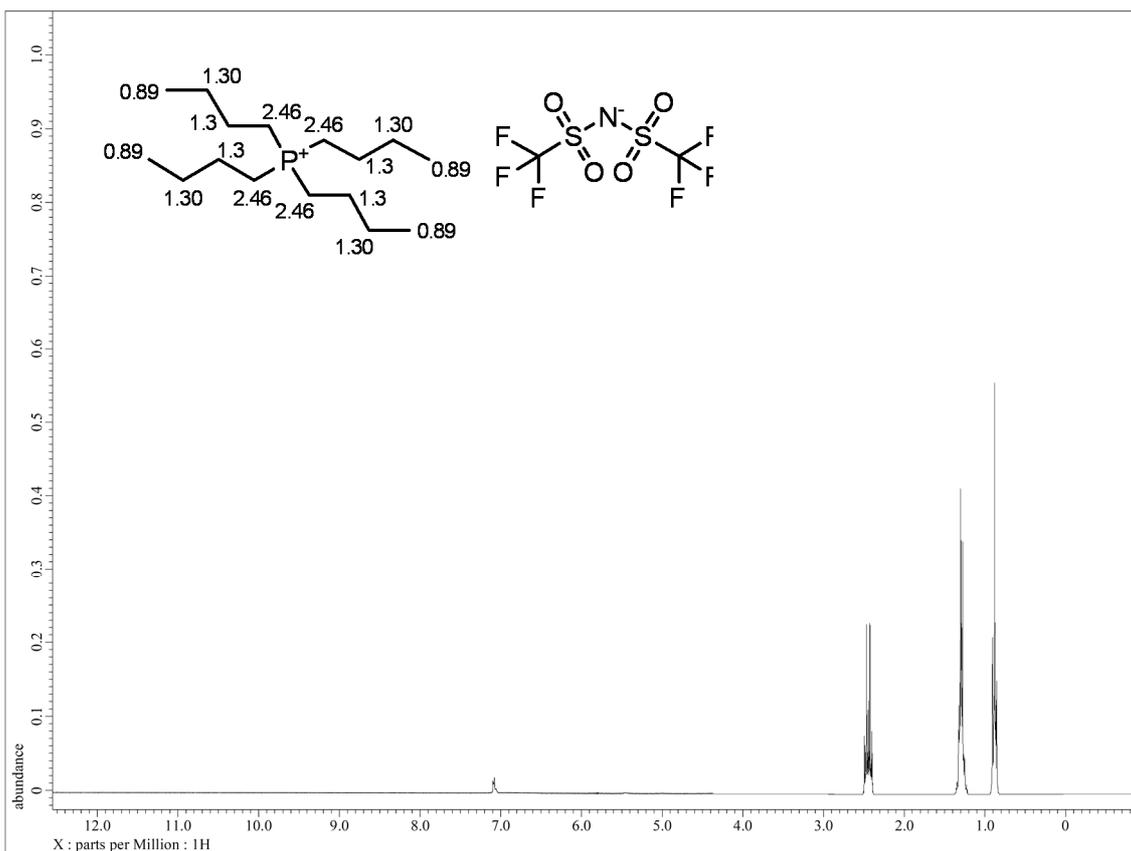


Figure S6:  $^1\text{H}$  NMR spectrum of  $[\text{P}_{444}][\text{NTf}_2]$  in  $\text{CD}_3\text{OD}$  with external benzene standard.

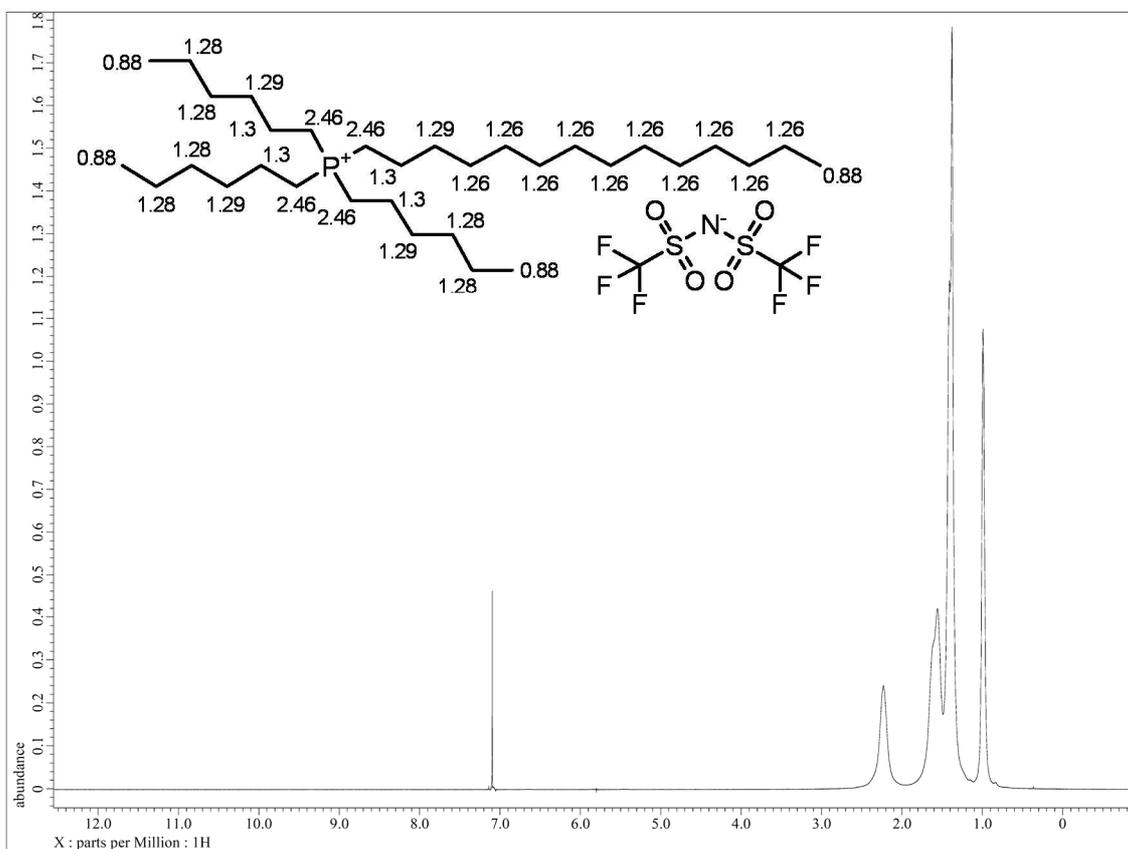


Figure S7:  $^1\text{H}$  NMR spectrum of  $[\text{P}_{66614}][\text{NTf}_2]$  in  $\text{CD}_3\text{OD}$  with external standard benzene.

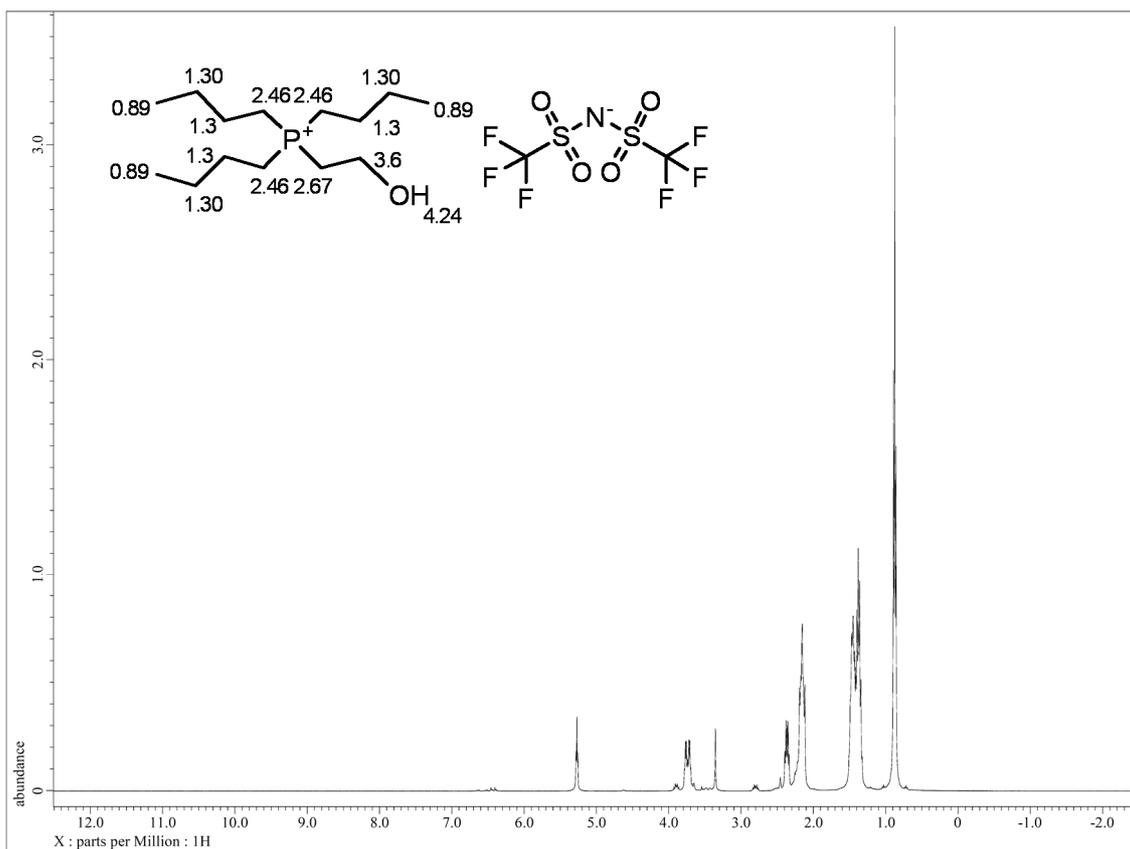


Figure S8:  $^1\text{H}$  NMR spectrum of  $[\text{P}_{444}(\text{C}_2\text{OH})][\text{NTf}_2]$  in  $\text{CD}_3\text{OD}$ .

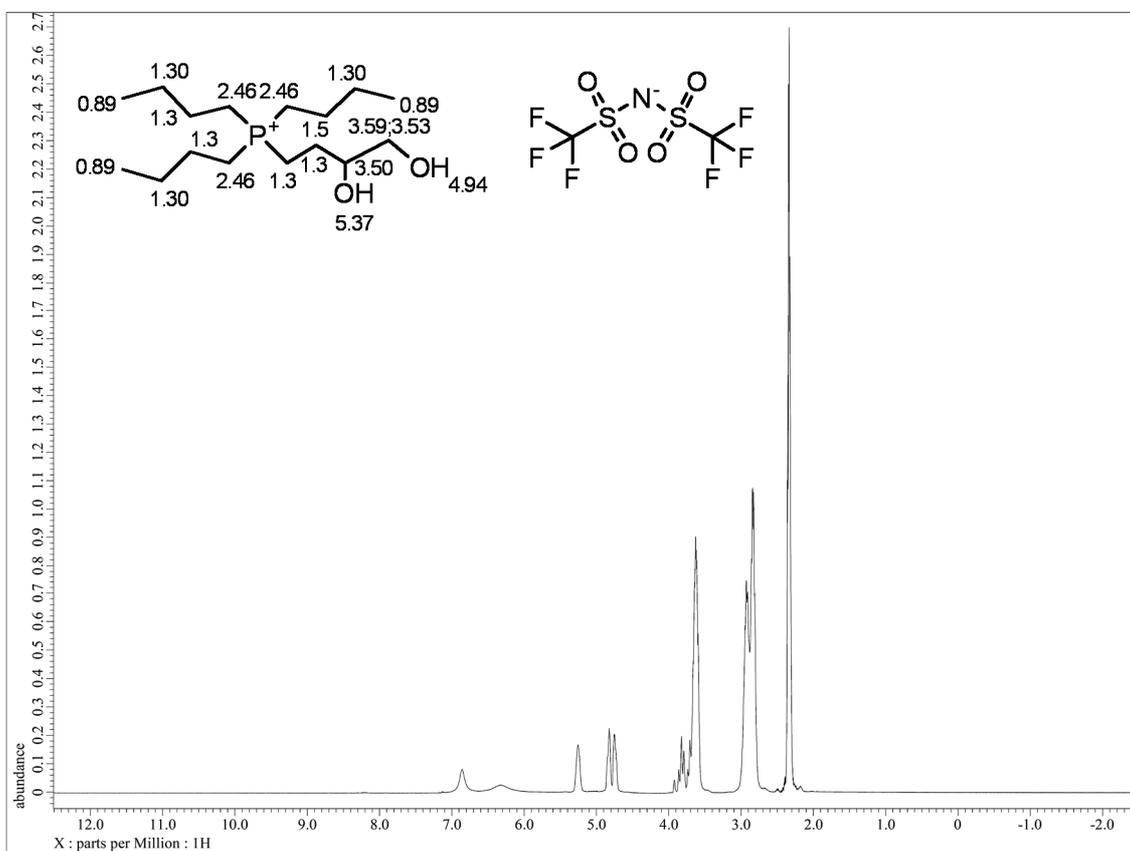


Figure S9:  $^1\text{H}$  NMR spectrum of  $[\text{P}_{444}(\text{C}_3-2,3\text{-OH})][\text{NTf}_2]$  in  $\text{CD}_3\text{OD}$ .

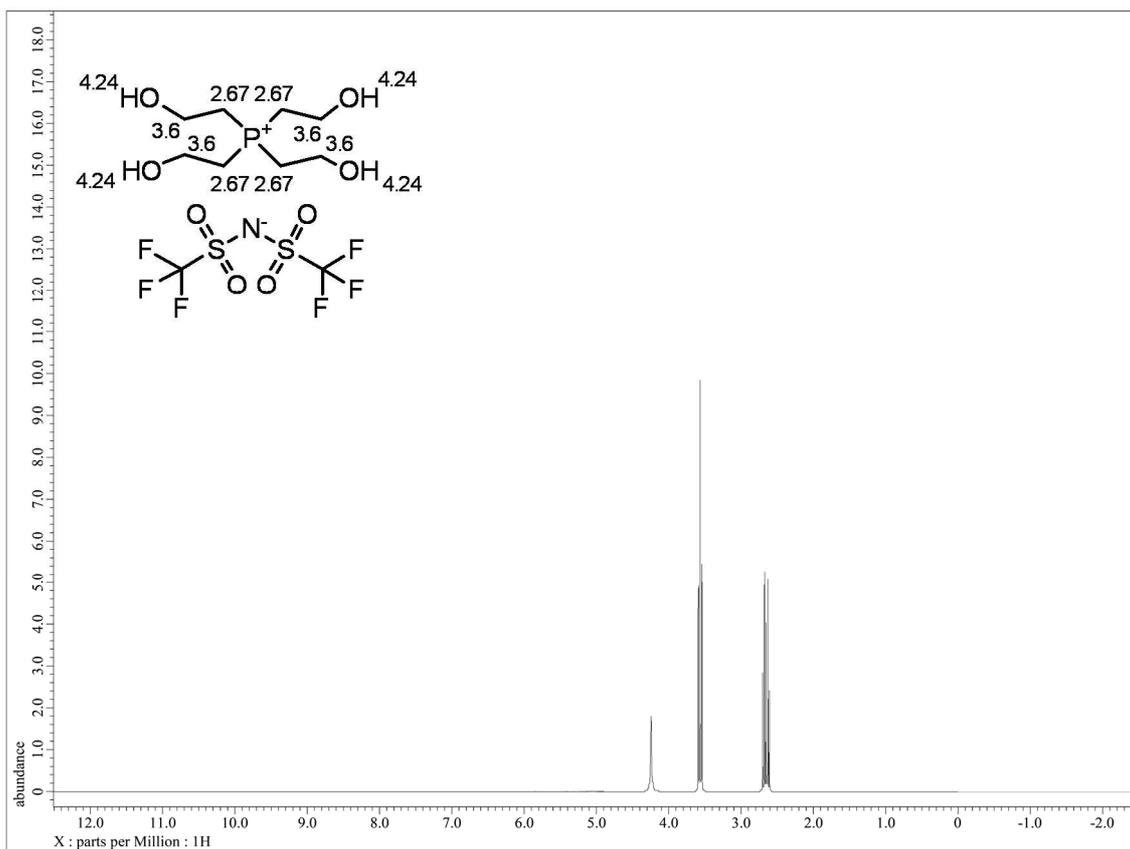


Figure S10:  $^1\text{H}$  NMR spectrum of  $[\text{P}(\text{CH}_2\text{OH})_4][\text{NTf}_2]$  in  $\text{CD}_3\text{OD}$ .