Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Ionic Liquids: Anion effect on the reaction of *O*, *O*-diethyl *O*-(2,4-dinitrophenyl) phosphate triester with piperidine.

Paulina Pavez,[a]* Daniela Millán[a], Cristian Cocq[a], José G. Santos[a], Faruk Nome[b].

[a]Facultad de Química. Pontificia Universidad Católica de Chile. Casilla 306, Santiago 6094411, Chile. [b]INCT-Catálise, Departamento de Química, Universidade Federal de Santa Catarina, Florianópolis, SC, 88040-970, Brasil.

Author Information

∗Corresponding authors. Tel.: +56-02-23541743; fax: +56-02-26864744; e-mail: ppavezg@uc.cl

Present address: Facultad de Química, Pontificia Universidad Católica de Chile, Av. Vicuña Mackenna 4860, Santiago 6094411, Chile.

Electronic supplementary information

Table of contents	
Table S1: Pseudo-first-order rate constants *(k_{obsd})* for the reaction of **1** with piperidine in different ionic liquids at 25ºC.	
Table S2: Pseudo-first-order rate constants *(k_{obsd})* for the reaction of **1** with piperidine in organic solvents (COS) at 25ºC.	
Table S3: Relative products distribution (%) for the nucleophilic attack of piperidine to **1** in the solvent used.	
Table S4: π∗ Kamlet-Taft´s parameters (α, β, π∗)	
Table S5: Statistical data from the multiple regression procedure including α, β, π∗ Kamlet-Taft ´s parameters	
Figure S1: ^{31}P-NMR spectrum (400MHz) of *O,O*-diethyl piperidinophosphate diester (**2a**) obtained in the reaction of *O,O*-diethyl chlorophosphate with piperidine in [Bmim]BF_4.	
Figure S2: ^{31}P-NMR spectrum (400MHz) of *O,O*-diethyl phosphate acid (**2b**) obtained in the reaction of *O,O*-diethyl chlorophosphate with NaOH in [Bmim]BF_4.	
Figure S3: Figure S3: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in [Bmim]PF_6 at 25°C.	
Figure S4: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in [Bmim]NTf_2 at 25°C.	
Figure S5: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in [Bmim]OTf at 25°C	
Figure S6: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in [Em_2pAm]NTf_2 at25°C.	
Figure S7: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in [B_2mim]BF_4 at 25°C.	
Figure S8: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in [Bmpyrr]NTf_2 at 25°C.	
Figure S9: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in [Bmpyrr]OTf at 25°C.	
Figure S10: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in [B_2mim]NTf_2 at 25°C.	
Figure S11: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in H_2O (pH=pK_a) at 25°C.	
Figure S12: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in DMSO at 25°C.	
Figure S13: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in acetonitrile at 25°C.	
Figure S14: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in [Bmim]DCA at 25°C.	
Figure S15: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in [Bmpyrr]DCA at 25°C.	
Figure S16: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in [Bmpy]DCA at 25°C.	
Figure S17: Correlation between log k_N^{Ar} and the solvent hydrogen bond acceptor capacity (β) for a series of ionic liquids.	

Table S1: Pseudo-first-order rate constants *(k_{obsd})* for the reaction of **1** with piperidine in different ionic liquids at 25ºC.

[Bmim]BF_4		**[Bmim]PF_6**		**[Bmim]DCA**	
10^3[Amine]/M	10^3k_{obsd}/ s^{-1}	10^3[Amine]/M	10^3k_{obsd}/ s^{-1}	10^3[Amine]/M	10^3k_{obsd}/ s^{-1}
4.32	1.87	2.17	4.43	1.73	0.960
5.62	7.79	4.32	7.50	4.32	2.60
6.29	10.3	6.52	11.5	6.29	5.26
9.51	20.9	8.69	16.0	9.51	7.66
12.1	33.9	10.9	21.1	12.1	9.85
14.7	48.2	14.7	24.3	14.7	11.3
17.3	59.5	17.3	27.1	21.7	15.8
[Bmim]NTf_2		**[Bmim]OTf**		**[Em_2pAm]NTf_2**	
10^3[Amine]/M	10^3k_{obsd}/ s^{-1}	10^3[Amine]/M	10^3k_{obsd}/ s^{-1}	10^3[Amine]/M	10^3k_{obsd}/ s^{-1}
4.32	0.741	1.73	1.53	1.73	3.94
6.92	2.94	4.32	11.4	4.32	12.1
9.51	7.19	6.92	22.9	6.92	20.1
12.1	10.7	9.51	34.1	8.51	28.0
17.3	16.5	12.1	47.3	12.1	37.5
21.7	23.1	14.7	53.1	14.7	43.2
-	-	17.3	71.2	17.3	52.7
[B_2mim]BF_4		**[Bmpyrr]DCA**		**[Bmpyrr]NTf_2**	
10^3[Amine]/M	10^2k_{obsd}/ s^{-1}	10^3[Amine]/M	10^2k_{obsd}/ s^{-1}	10^3[Amine]/M	10^3k_{obsd}/ s^{-1}
2.17	4.74	1.73	0.679	6.92	2.08
4.35	5.33	4.32	3.27	9.51	4.83
6.52	7.11	6.92	5.09	12.1	9.16
8.70	7.72	9.51	7.43	14.7	11.0
10.9	8.51	12.1	9.15	17.3	16.5
14.1	10.0	14.7	10.4	21.7	23.1
17.4	11.5				

[Bmpyrr]OTf		**[Bm_2im]NTf_2**	
10^3[Amine]/M	10^3k_{obsd}/ s-1	10^3[Amine]/M	10^3k_{obsd}/ s^{-1}
1.73	2.75	1.73	0.262
4.32	12.2	4.32	6.43
6.92	25.3	6.92	14.2
9.51	37.8	9.51	22.6
12.1	49.8	12.1	29.8
14.7	52.8	14.7	35.7
17.3	72.8	17.3	47.2

Pseudo first-order rate constants were reproducible within a ± 5%

Table S2: Pseudo-first-order rate constants *(k_{obsd})* for the reaction of **1** with piperidine in organic solvents (COS) at 25ºC.

H_2O pH= pK_a		**DMSO**		**Acetonitrilo**	
10^3[Amine]/M	10^3k_{obsd}/ s^{-1}	10^3[Amine]/M	10^3k_{obsd}/ s^{-1}	10^3[Amine]/M	10^3k_{obsd}/ s^{-1}
1.73	1.95	1.73	1.15	1.73	2.90
4.32	3.71	4.32	2.49	4.32	6.78
6.92	7.40	6.92	4.88	6.29	11.5
9.51	12.0	9.51	7.32	9.51	16.2
12.1	15.9	12.1	8.50	12.1	21.4
14.7	18.1	14.7	10.5	14.7	26.3
17.3	21.1	17.3	11.9	17.3	29.8
-	-	21.7	14.6	21.7	37.9

Pseudo first-order rate constants were reproducible within a ± 5%

Table S3: Relative products distribution (%) for the nucleophilic attack of piperidine to **1** in the solvent used.

Solvent	**% S_N2(P)**	**% S_NAr**
H_2O	26	74
EtOH:H_2O (50% v/v)*	30	70
ACN	15	85
DMSO	49	51
[Bmim]BF_4	20	80
[Bmim]PF_6	6	94
[Bmim]DCA	100	0
[Bmim]OTf	31	69
[Bmim]NTf_2	8	92
[Bmpyrr]NTf_2	12	88
[Em2pAm]NTf_2	14	86
[B_2mim]NTf_2	10	90
[B_2mim]BF_4	15	85
[Bmpyrr]OTf	25	75
[Bmpyrr]DCA	100	0
[Bmpy]DCA	100	0

* ref 24

Table S4: π∗ Kamlet-Taft ´s parameters (α, β, π∗)

Solvente	π^*	α	β
[Bmim]BF_4	1.08	0.613	0.376
[Bmim]PF_6	1.03	0.634	0.209
[Bmim]DCA	1.13	0.464	0.708
[Bmim]NTf_2	1.09	0.940	0.230
[Bmim]OTf	1.01	0.625	0.464
[Em_2pAm]NTf_2	0.97	0.470	--
[Bm_2im]BF_4	1.08	0.400	0.360
[Bmpyrr]DCA	--	--	--
[Bmpyrr]NTf_2	0.971	0.409	0.243
[Bmpyrr]OTf	1.02	0.400	0.460
[Bm_2im]NTf_2	0.987	0.384	0.299
[Bmpy]DCA.	1.03	0.370	--
H_2O pH=pKa.	1.33	1.12	0.500
DMSO	1.00	0	0.760
Acetonitrilo	0.799	0.350	0.370
EtOH:H_2O	1.01	0.940	0.650

1. Chiappe, C.; Pomelli, C.; Rajamani, S. *J. Phys. Chem. B,* **2011,** *115*, 9653.

2. Jessop, P.; Jessop, D.; FU, D.; Phan, L. *Green Chem.* **2012,** 14, 1245.

Table S5: Statistical data from the multiple regression procedure including α, β, π∗ Kamlet-Taft ´s parameters

LSER equation	F[a]	R[b]	α	*β*	π*
3	31	0.92	-0.45(0.45)	3.68(0.56)	-0.04(1.69)
4	57	0.93	-0.45(0.33)	3.67(0.38)	
5	47	0.92		4.00(0.45)	-1.05(1.34)
6	160	0.95		3.79(0.29)	

[a] Statistical F. [b] Correlation coefficient. [c] Standart deviations are given in parentheses.

Figure S1: ^{31}P-NMR spectrum (400MHz) of *O,O*-diethyl piperidinophosphate diester (**2a**) obtained in the reaction of *O,O*-diethyl chlorophosphate with piperidine in [Bmim]BF_4.

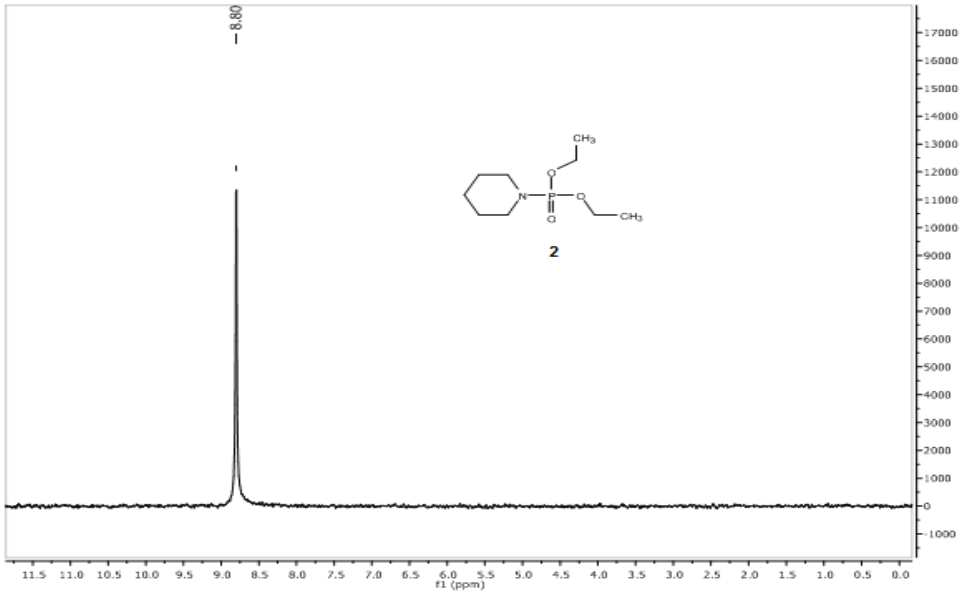

Figure S2: ^{31}P-NMR spectrum (400MHz) of *O,O*-diethyl phosphate acid (**2b**) obtained in the reaction of *O,O*-diethyl chlorophosphate with NaOH in [Bmim]BF_4.

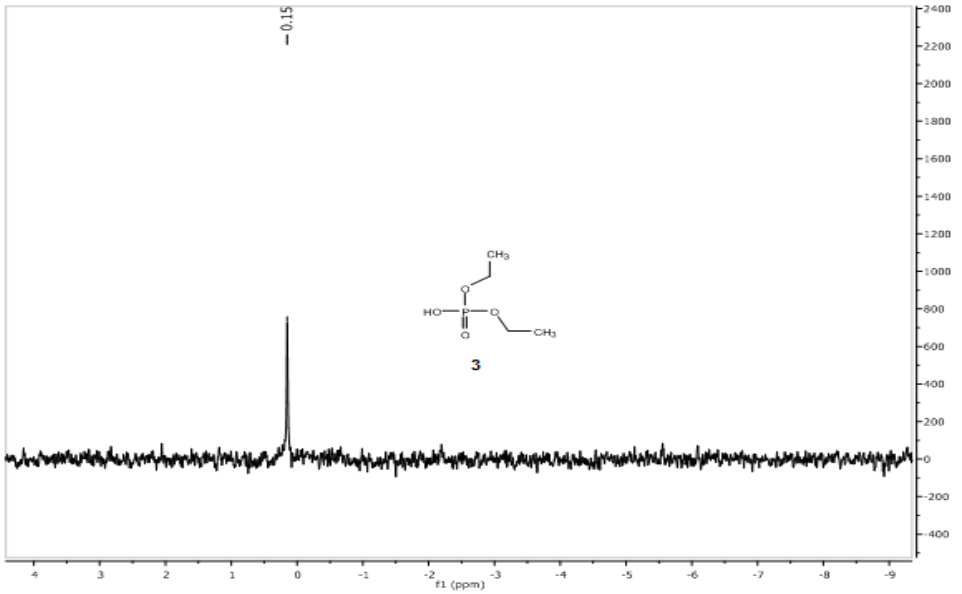

Figure S3: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in [Bmim]PF_6 at 25°C.

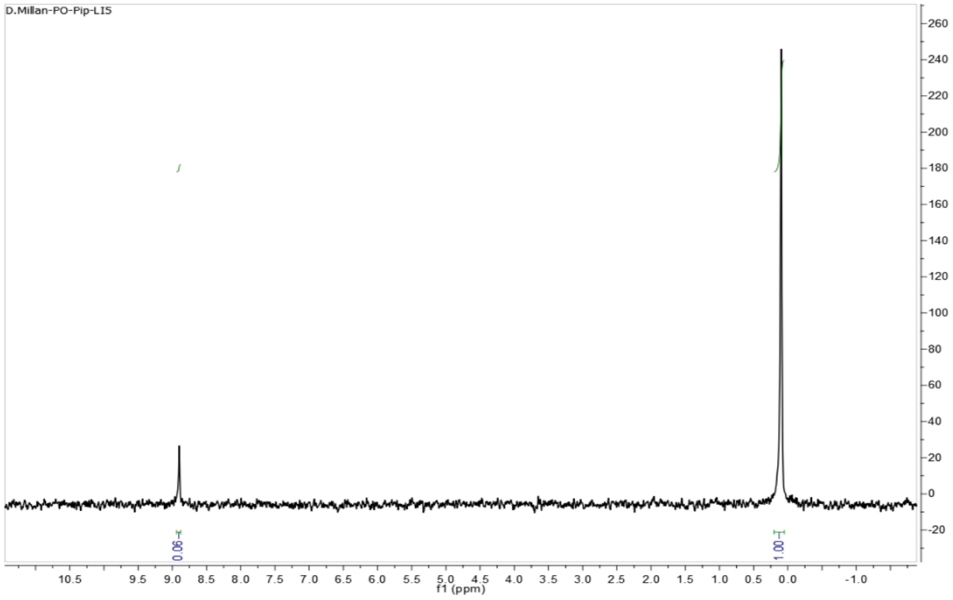

Figure S4: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in [Bmim]NTf_2 at 25°C.

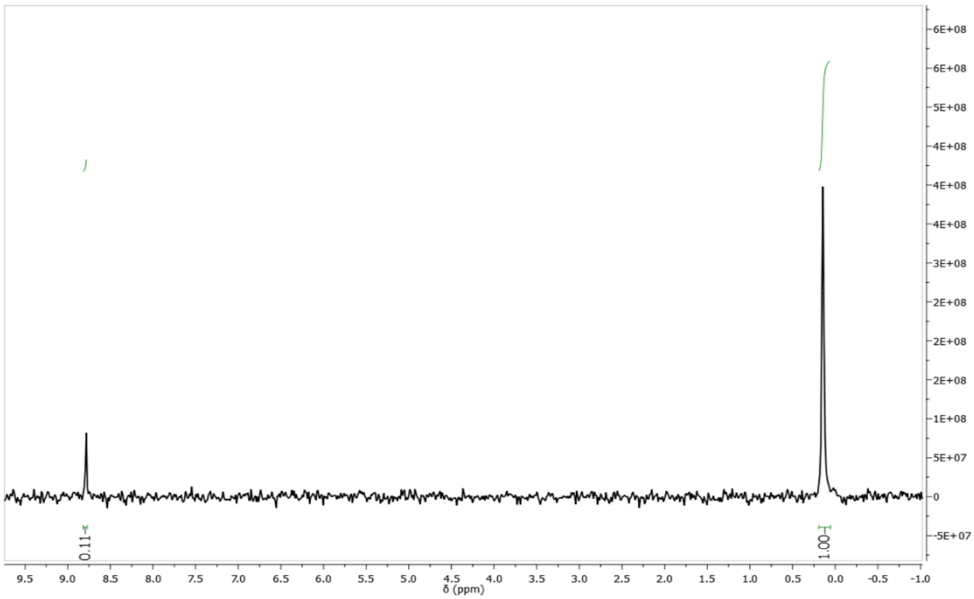

Figure S5: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in [Bmim]OTf at 25°C.

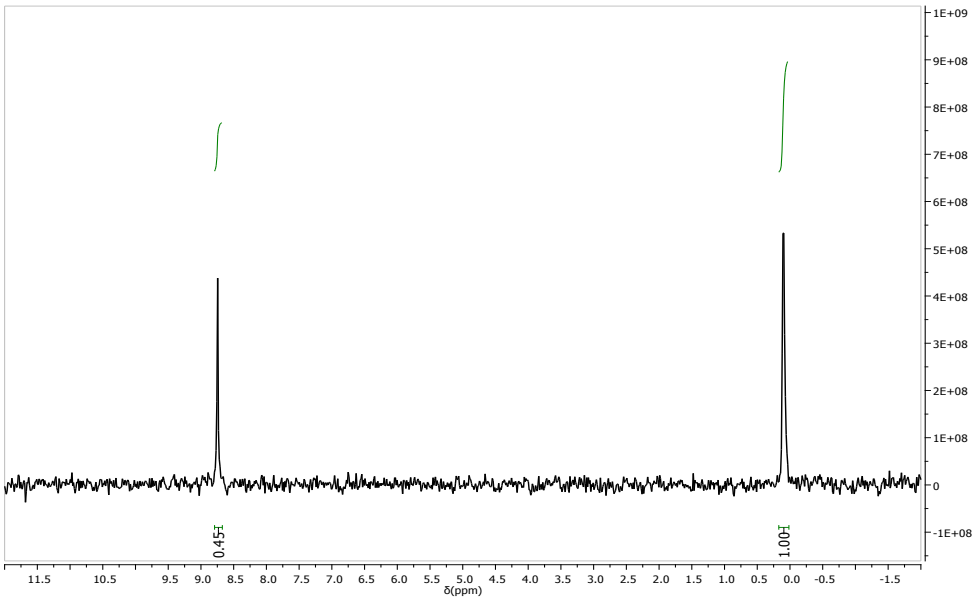

Figure S6: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in $[Em_2pAm]NTf_2$ at 25°C.

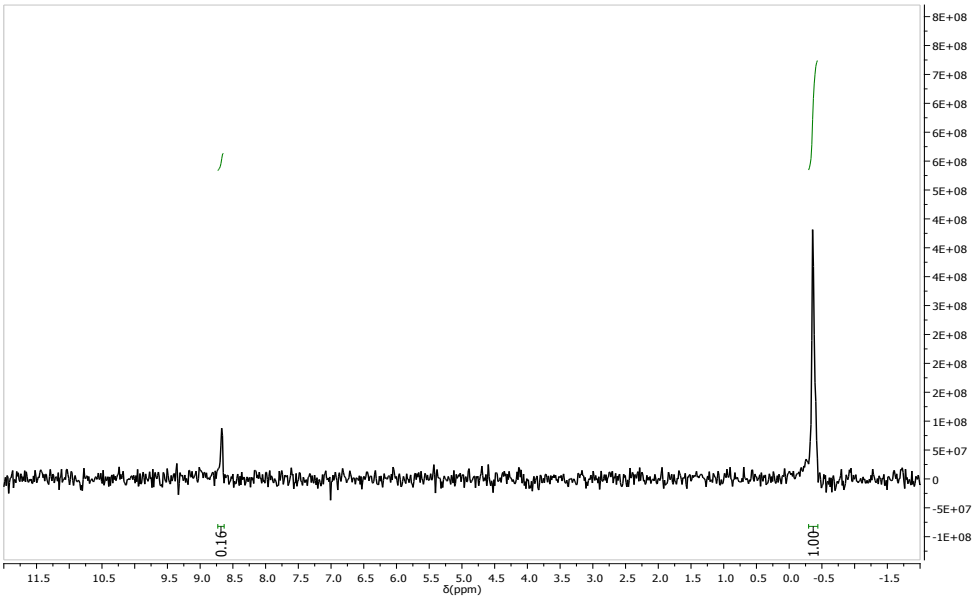

Figure S7: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in $[B_2mim]BF_4$ at 25°C.

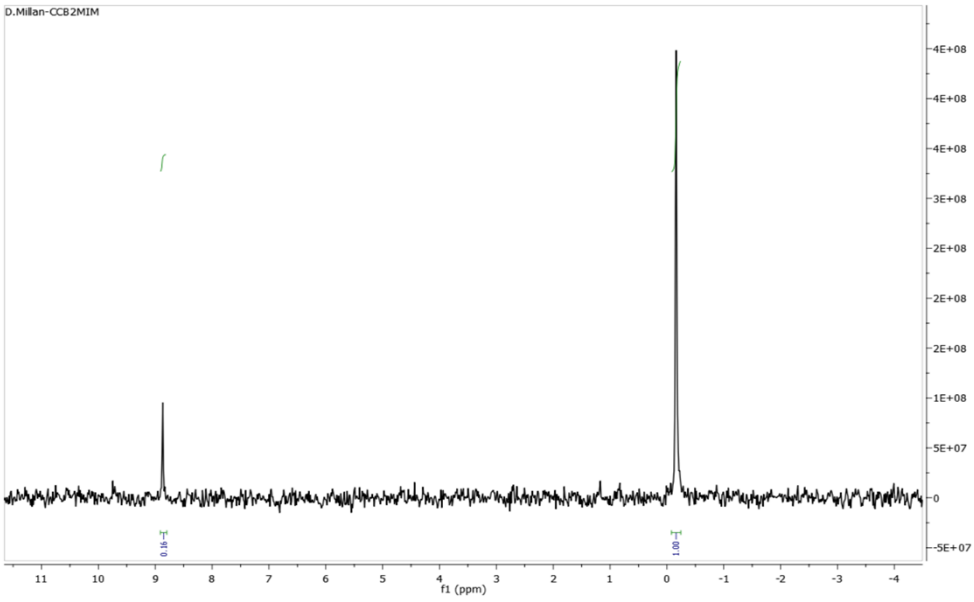

Figure S8: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in $[Bmpyrr]NTf_2$ at 25°C.

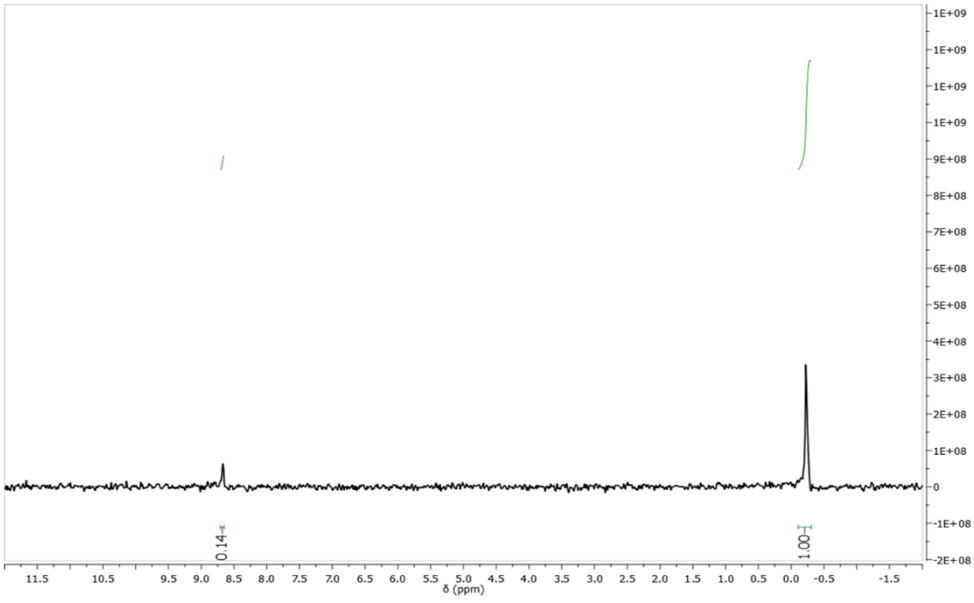

Figure S9: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in [Bmpyrr]OTf at 25°C.

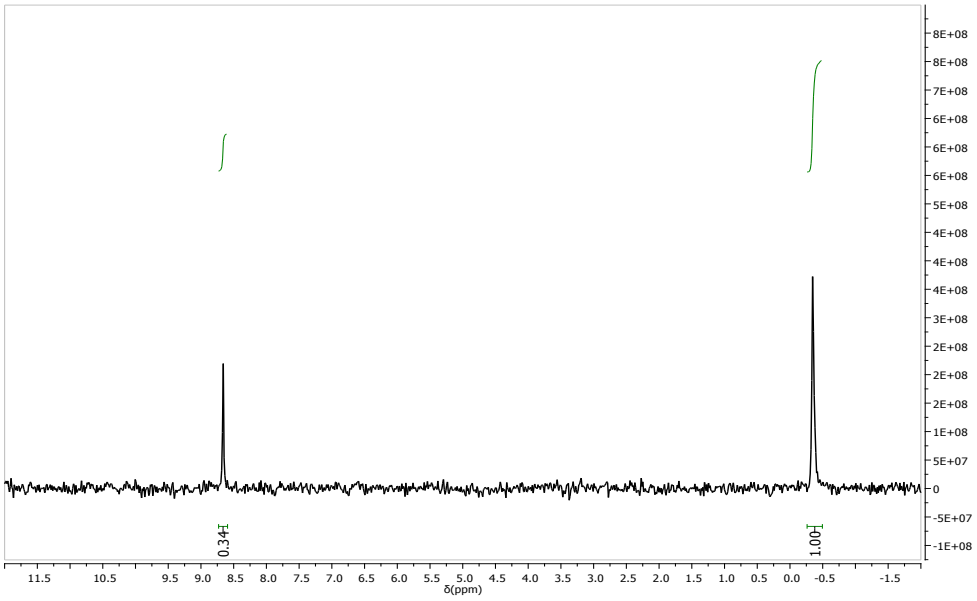

Figure S10: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in $[B_2mim]NTf_2$ at 25°C.

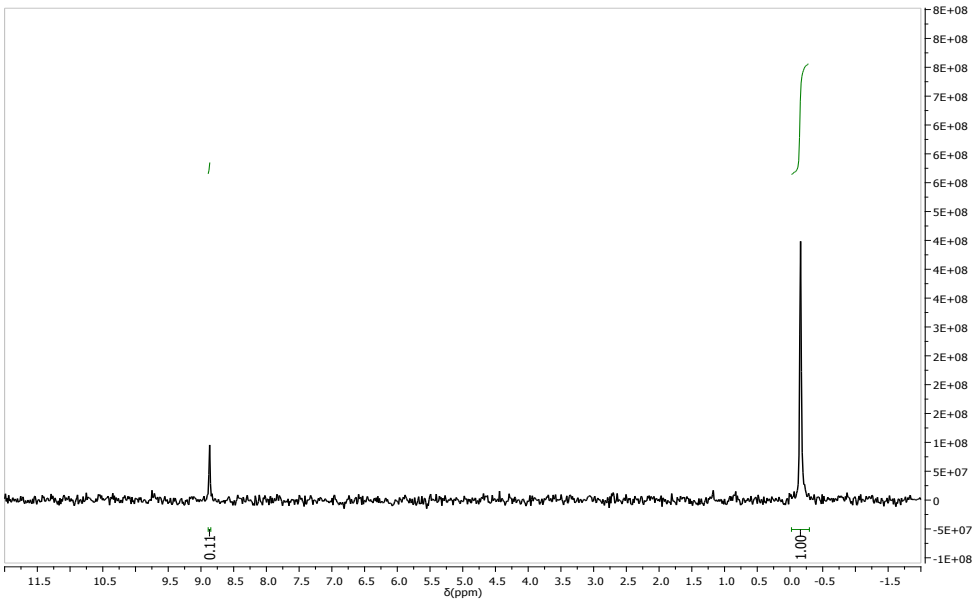

Figure S11: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in H_2O (pH=pK_a) at 25°C.

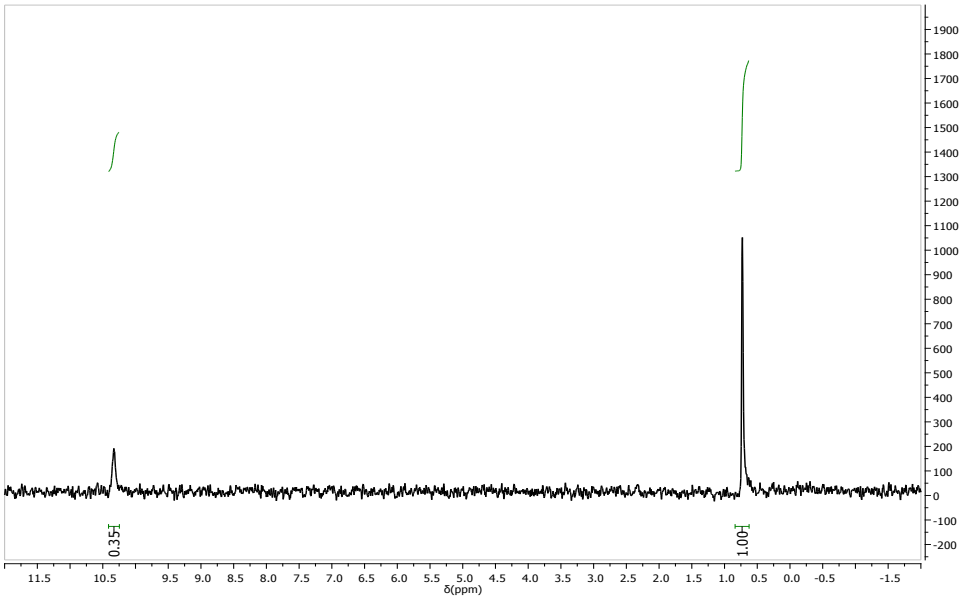

Figure S12: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in DMSO at 25°C.

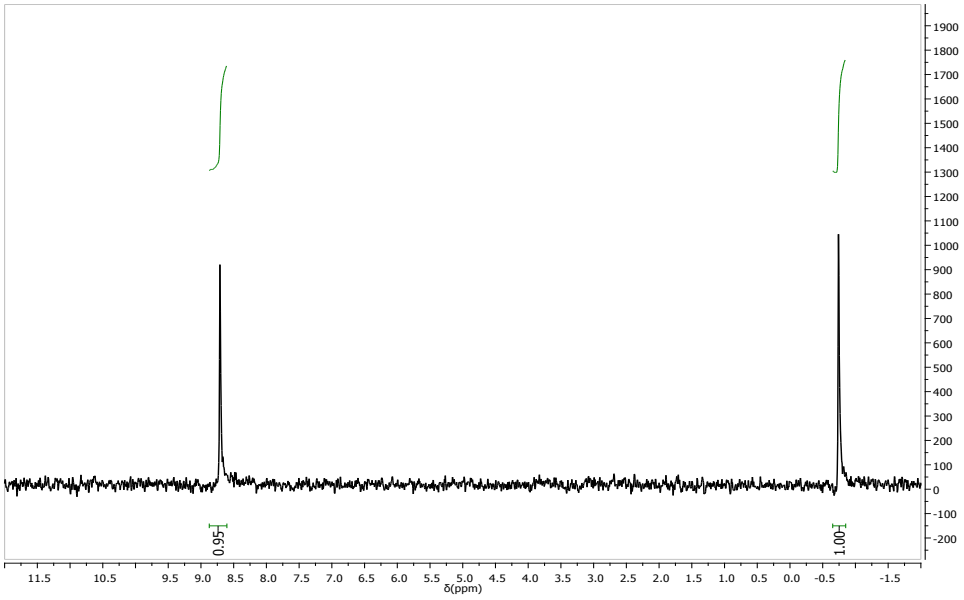

Figure S13: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in acetonitrile at 25°C

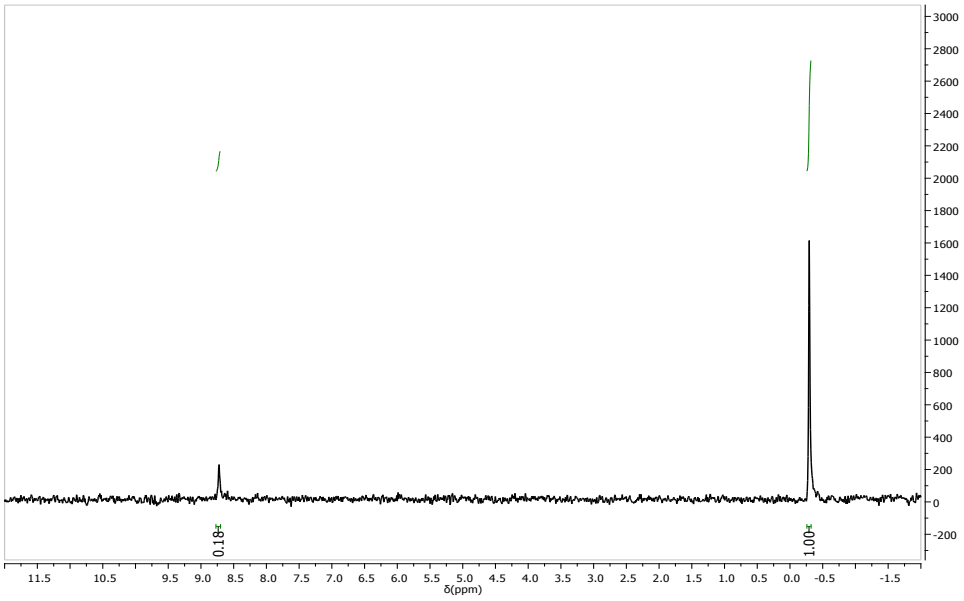

Figure S14: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in [Bmim]DCA at 25°C.

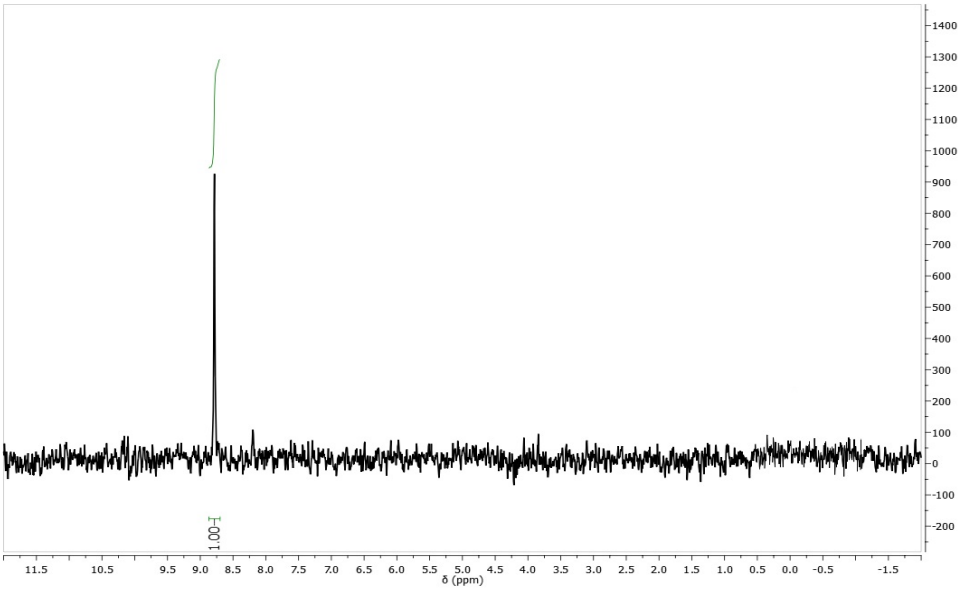

Figure S15: ^{31}P-NMR spectrum for the reaction of **1** with piperidine in [Bmpyrr]DCA at 25°C.

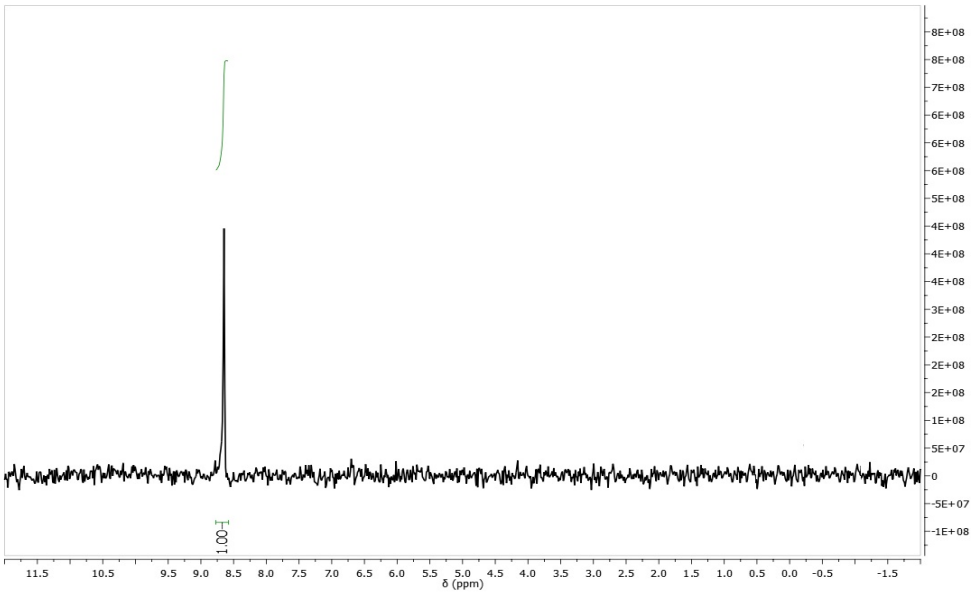

Figure S16: ^{31}P-NMR spectrum for the reaction of **1** with in [Bmpy]DCA at 25°C.

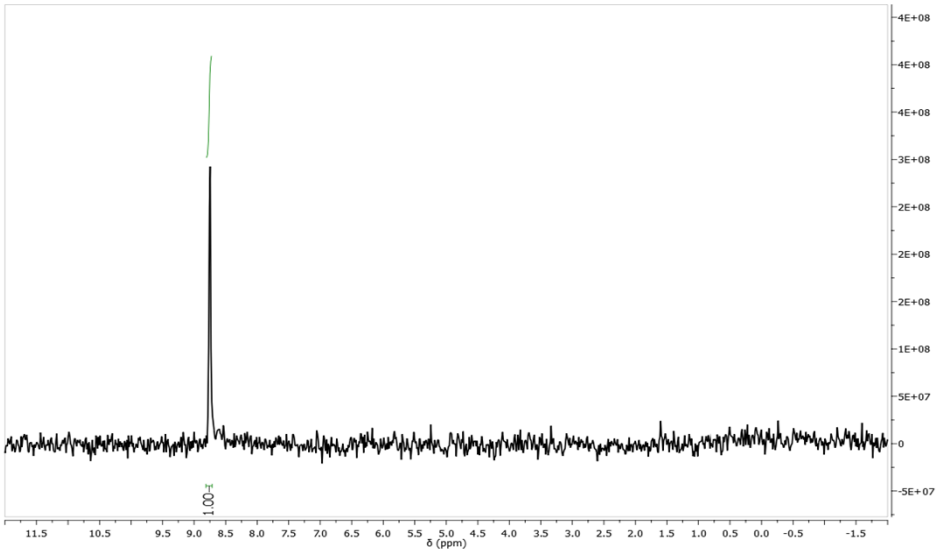

Figure S17: Correlation between log k_N^{Ar} and the solvent hydrogen bond acceptor capacity (β) for a series of ionic liquids.