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Reaction mechanisms in Ionic Liquids: Kinetics and mechanism of the reaction of *O*, *O*-diethyl *O*-(2,4-dinitrophenyl) phosphate triester with secondary alicyclic amines

Paulina Pavez*, Daniela Millán, Javiera Morales, Mabel Rojas, Daniel Céspedes,

José G. Santos.

Facultad de Química. Pontificia Universidad Católica de Chile. Casilla 306, Santiago 6094411, Chile.

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 S1: Pseudo-first-order rate constants *(k_{obsd})* for the reaction of **1** with the secondary alicyclic amines in [Bmim]BF_4 at 25ºC±0.1.

Piperidine		**Morpholine**	
10^3[Amine]/M	$10^3 k_{obsd}$/ s^{-1}	10^3[Amine]/M	$10^3 k_{obsd}$/ s^{-1}
4.32	1.87	8.69	1.41
5.62	7.79	9.78	1.87
6.92	10.3	10.9	2.26
9.51	20.9	12.2	2.59
12.1	33.9	13.9	2.95
14.7	48.2	15.2	3.59
17.3	59.5	17.4	4.58
-	-	19.6	4.88
-	-	21.7	6.05
1-(2-Hydroxyethyl)-piperazine		**1-Formylpiperazine**	
10^3[Amine]/M	$10^3 k_{obsd}$/ s^{-1}	10^3[Amine]/M	$10^3 k_{obsd}$/ s^{-1}
9.51	2.21	1.31	0.357
12.1	4.49	2.40	0.830
13.4	6.74	3.48	1.09
14.7	7.71	4.57	3.26
16.0	8.42	5.65	4.22
17.3	10.5	7.83	10.2
-	-	10.0	13.4
-	-	11.1	18.2
-	-	12.2	23.5
-	-	13.3	25.4
-	-	14.4	30.6

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 the secondary alicyclic amines in [Bmim]DCA at 25ºC±0.1.

Piperidine		**1-(2-Hydroxyethyl)-piperazine**	
10^3[Amine]/M	$10^3 k_{obsd}$/ s^{-1}	10^3[Amine]/M	$10^3 k_{obsd}$/ s^{-1}
1.73	0.960	2.17	3.08
4.32	2.60	3.50	5.56
6.29	5.26	4.35	7.67
9.51	7.66	8.70	13.9
12.1	9.85	15.2	23.0
14.7	11.3	-	-
21.7	15.8	-	-
Morpholine		**1-Formylpiperazine**	
10^3[Amine]/M	$10^3 k_{obsd}$/ s^{-1}	10^3[Amine]/M	$10^3 k_{obsd}$/ s^{-1}
0.870	0.413	0.870	0.129
2.20	1.13	2.17	0.335
3.50	1.87	3.48	0.524
8.70	4.46	4.35	0.657
15.2	8.32	8.70	1.78
22.0	11.9	13.0	3.29
		15.2	4.53
		21.7	7.73

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

Table S3: Pseudo-first-order rate constant (k_{obsd}), second-order rate constant (k_N^T), rate constant for nucleophilic attack at P (k_N^P) and rate constant for nucleophilic attack at aromatic C-1 (k_N^{Ar}) for the reaction of piperidine to 1 in [Bmim]BF_4 at the 20-40ºC range.

Temperature 20ºC±0.1		**Temperature 25ºC**±0.1		**Temperature 30ºC**±0.1	
10^3[Amine]/M	**$10^2 k_{obsd}$/ s^{-1}**	**10^3[Amine]/M**	**$10^2 k_{obsd}$/ s^{-1}**	**10^3[Amine], M**	**$10^2 k_{obsd}$/ s^{-1}**
6.92	1.13	4.32	0.192	6.92	1.44
9.51	1.95	6.92	1.03	9.51	2.64
14.7	4.30	9.51	2.09	12.1	3.90
17.3	5.15	12.1	3.39	14.7	5.86
21.7	6.54	14.7	4.82	17.3	6.50
-	-	17.3	5.95	21.7	7.85

Temperature 35ºC±0.1		**Temperature 40 ºC**±0.1	
10^3[Amine]/M	**$10^2 k_{obsd}$/ s^{-1}**	**10^3[Amine]/M**	**$10^2 k_{obsd}$/ s^{-1}**
6.92	1.61	6.92	1.74
9.51	3.11	9.51	3.65
12.1	4.80	12.1	5.45
14.7	6.52	14.7	6.60
17.3	7.71	17.3	9.20
21.7	9.02	21.7	10.8

T°±0.1	$k_N^T / M^{-1}s^{-1}$	$k_N^P / M^{-1}s^{-1}$	$k_N^{Ar} / M^{-1}s$
20	3.77	0.75	3.02
25	4.56	0.91	3.65
30	4.50	0.90	3.60
35	5.18	1.04	4.14
40	6.26	1.25	5.01

Table S4: Pseudo-first-order rate constant (k_{obsd}), second-order rate constant (k_N^T), rate constant for nucleophilic attack at P (k_N^P) and rate constant for nucleophilic attack at aromatic C-1 (k_N^{Ar}) for the reaction of piperidine to **1** in [Bmim]DCA at the 20-40ºC range.

Temperature 20ºC±0.1		**Temperature 25ºC**±0.1		**Temperature 30ºC**±0.1	
10^3[Amine]/M	**$10^2 k_{obsd}$/ s^{-1}**	**10^3[Amine]/M**	**$10^2 k_{obsd}$/ s^{-1}**	**10^3[Amine], M**	**$10^2 k_{obsd}$/ s^{-1}**
2.17	1.25	1.73	9.64	2.17	1.37
4.35	3.17	4.32	26.0	3.48	2.31
8.70	6.88	6.92	52.6	8.70	7.71
15.0	10.8	9.51	76.6	15.0	12.2
21.7	14.8	12.1	98.5	21.7	18.0
-	-	14.7	113	-	-
-	-	21.7	158	-	-

Temperature 35ºC±0.1		**Temperature 40 ºC**±0.1	
10^3[Amine]/M	**$10^2 k_{obsd}$/ s^{-1}**	**10^3[Amine]/M**	**$10^2 k_{obsd}$/ s^{-1}**
2.17	19.4	0.870	0.254
3.48	3.41	1.52	0.866
8.70	9.42	2.17	1.14
15.0	15.3	3.48	2.49
21.7	18.8	4.35	3.33
-	-	8.70	8.31

T°±0.1	k_N^P /$M^{-1}s^{-1}$
20	6.89
25	7.62
30	8.50
35	8.87
40	10.4

Table S5: Pseudo-first-order rate constant (k_{obsd}), second-order rate constant (k_N^T), rate constant for nucleophilic attack at P (k_N^P) and rate constant for nucleophilic attack at aromatic C-1 (k_N^{Ar}) for the reaction of piperidine to **1** in aqueous media at the 20-40ºC range.

Temperature 20ºC±0.1		**Temperature 25ºC**±0.1		**Temperature 30ºC**±0.1	
10^4[Amine]/M	**$10^4 k_{obsd}$/ s^{-1}**	**10^4[Amine]/M**	**$10^4 k_{obsd}$/ s^{-1}**	**10^4[Amine],M**	**$10^4 k_{obsd}$/ s^{-1}**
2.50	1.67	2.50	2.26	2.50	2.76
6.00	3.40	6.00	3.95	6.00	5.16
10.0	5.60	10.0	7.07	10.0	8.77
14.0	6.12	14.0	9.12	14.0	14.3
17.5	8.68	17.5	12.3	17.5	15.8
20.0	11.7	20.0	17.2	20.0	24.7

Temperature 35ºC±0.1		**Temperature 40 ºC**±0.1	
10^4[Amine]/M	**$10^4 k_{obsd}$/ s^{-1}**	**10^4[Amine]/M**	**$10^4 k_{obsd}$/ s^{-1}**
2.50	5.13	2.50	9.14
6.00	9.70	6.00	16.3
10.0	16.6	10.0	20.9
14.0	25.4	14.0	29.3
17.5	35.0	17.5	31.8
20.0	35.4	20.0	49.3

T°±0.1	$k_N^T / M^{-1}s^{-1}$	k_N^{Ar} /$M^{-1}s^{-1}$	k_N^P /$M^{-1}s^{-1}$
20	0.59	0.12	0.47
25	0.60	0.12	0.48
30	0.93	0.18	0.74
35	1.77	0.35	1.42
40	2.21	0.44	1.77

Figure S1: ^{31}P-NMR spectrum for the reaction of **1** with the secondary alicyclic amines in [Bmim]BF_4 at the 25ºC±0.1

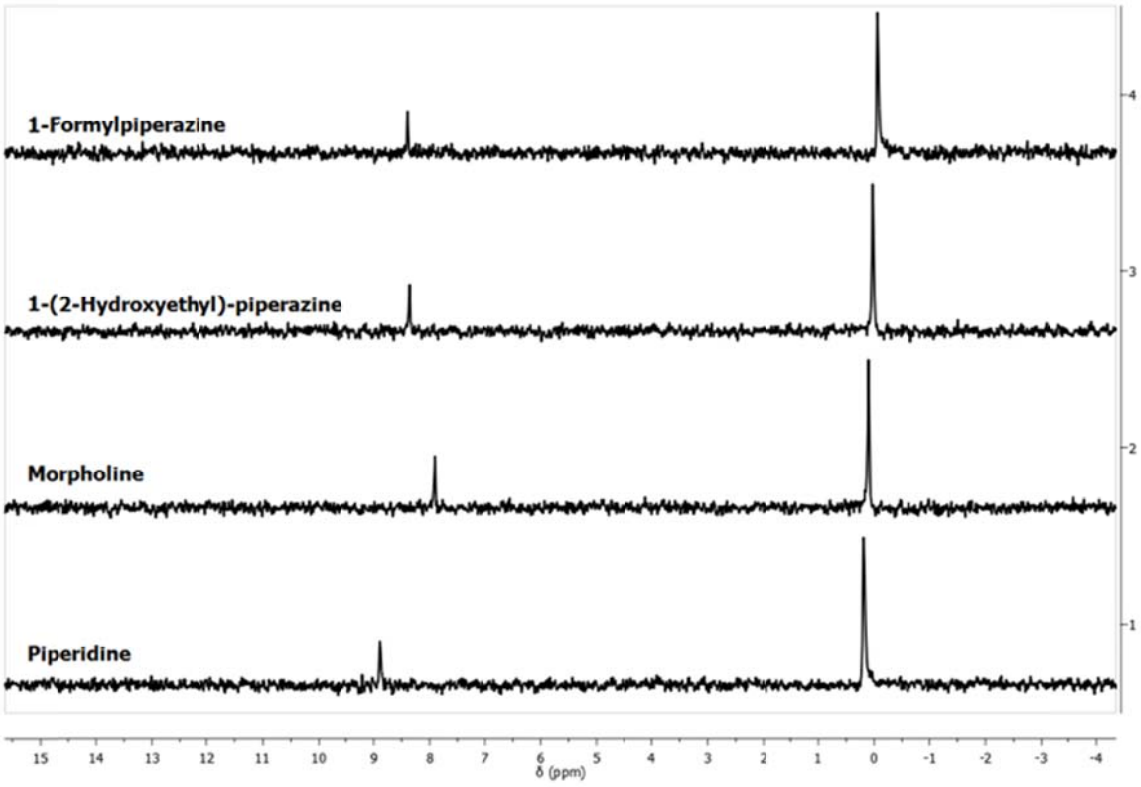


Figure S2: Plots k_{obsd}^{P} against amine concentration for the reaction of **1** with a) piperidine. b) morpholine and c) 1-(2-hydroxyethyl)piperazine in [Bmim]BF_4 at the 25ºC±0.1.

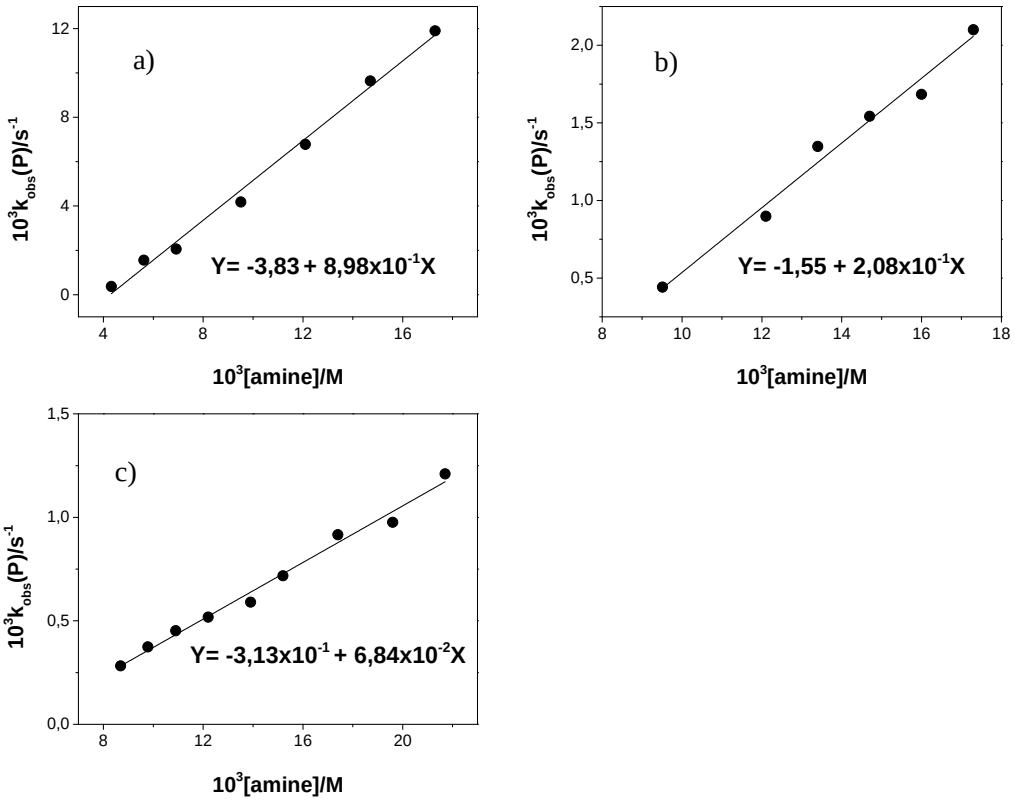


Figure S3: Plots k_{obsd}^{P} against amine concentration for the reaction of **1** with a) piperidine, b) 1-(2-hydroxyethyl)piperazine and c) Morpholine in [Bmim]DCA at the 25ºC±0.1

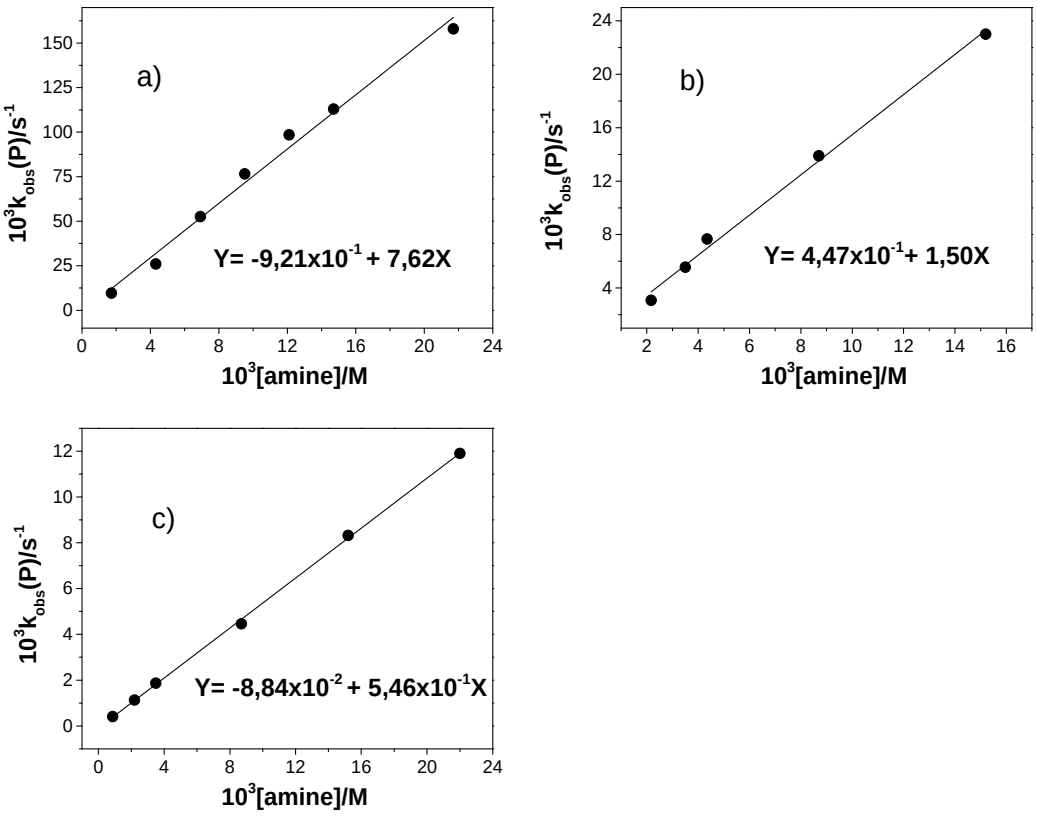


Figure S4. Linear plot of k_{obsd} *vs*. [Formylpiperazine]^2 in a) [Bmim]BF_4 and b) [Bmim]DCA.

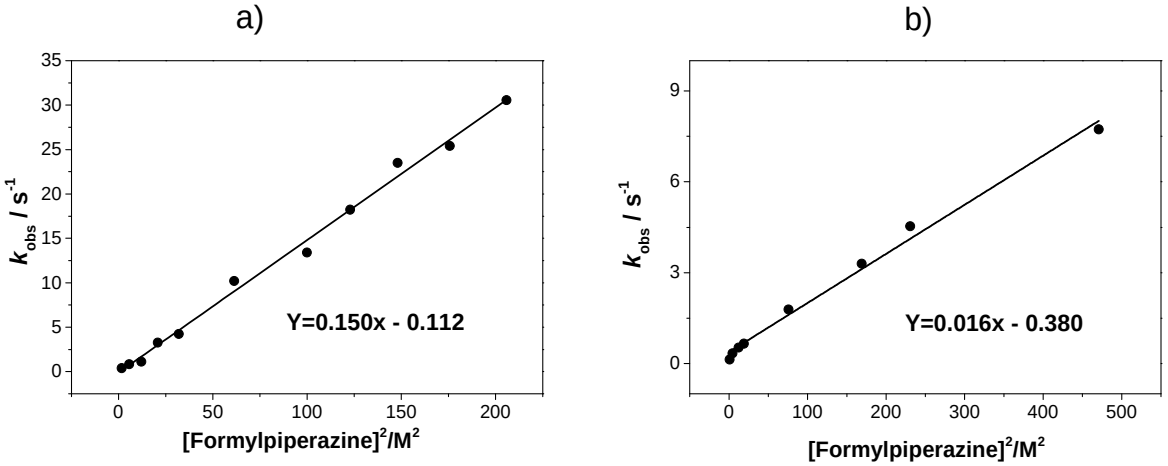


Figure S5: Double pK_a plot between pK_a values of SA amines in [Bmim]BF_4 and Water

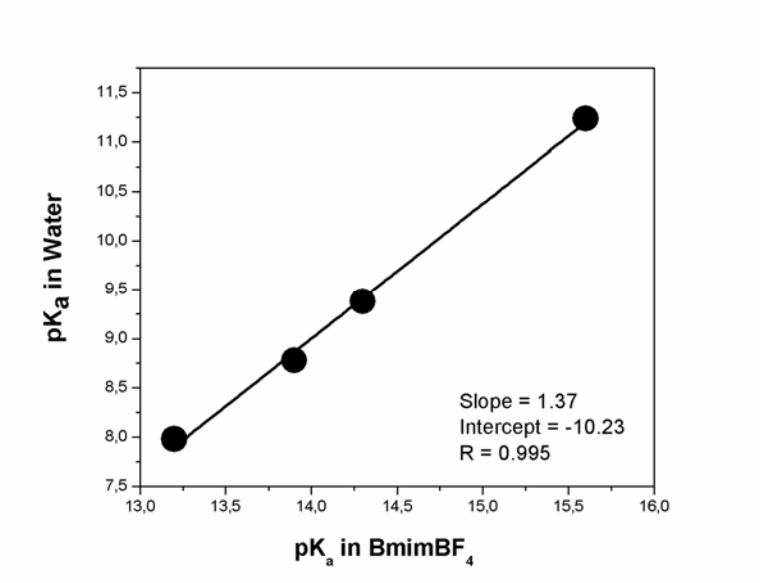


Figure S6: Arrhenius and Eyring plots for the reaction of **1** with piperidine in [Bmim]DCA.

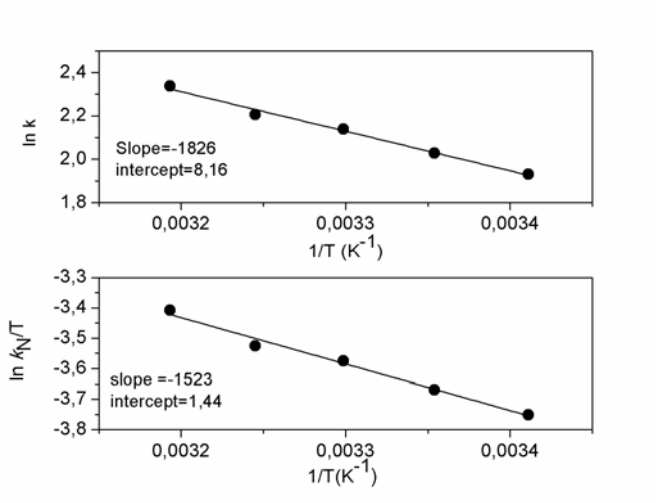


Figure S7: Arrhenius and Eyring plots for the reaction of **1** with piperidine in [Bmim]BF_4

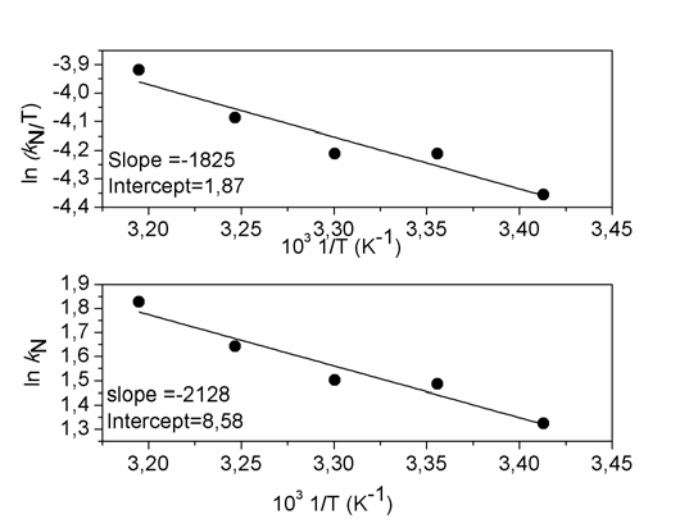


Figure S8: Arrhenius and Eyring plots for the reaction of **1** with piperidine in 44% w/w ethanol-water.

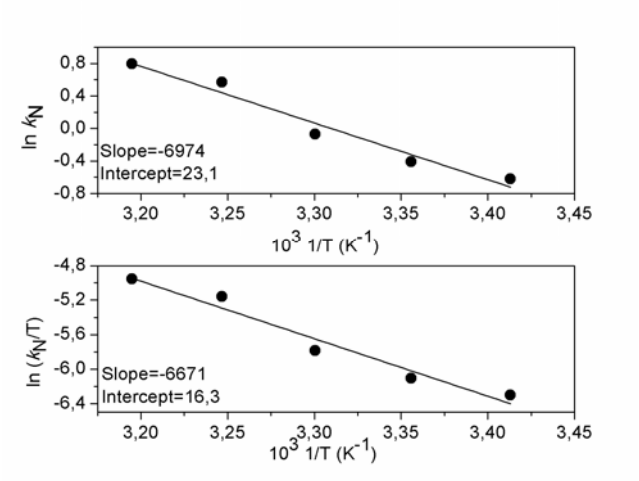
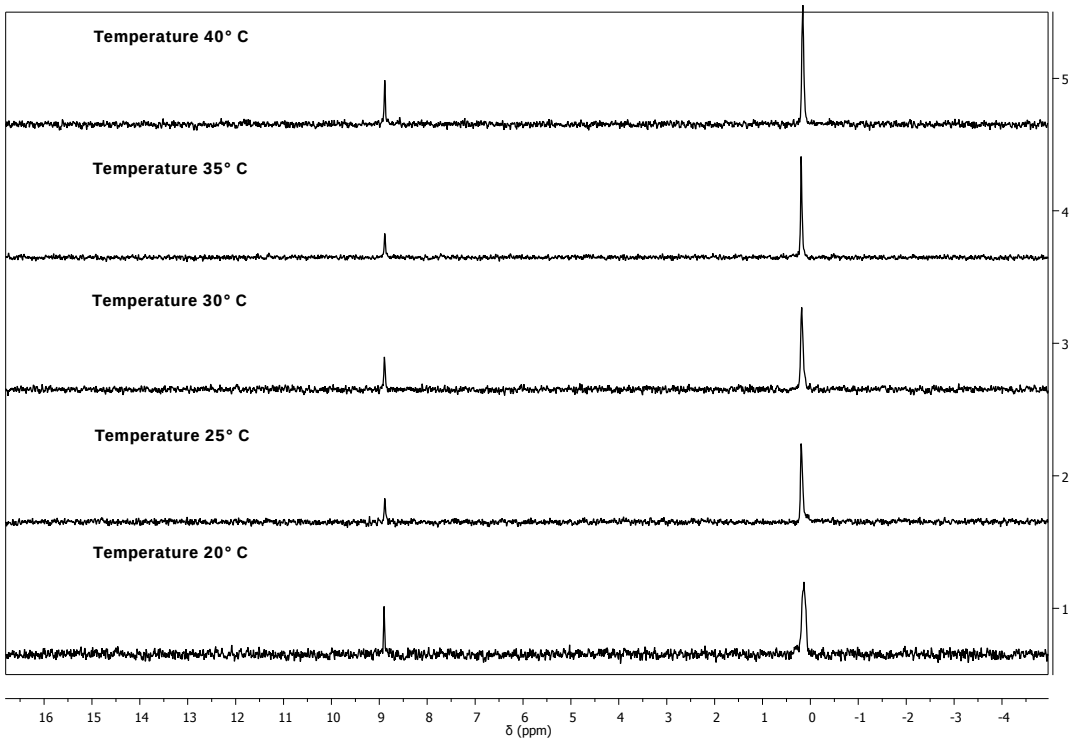


Figure S9. ^{31}P-NMR spectrum for the reaction of **1** with piperidine in [Bmim]BF_4 at the 20-40ºC ±0.1 range.



Kinetic Details. These were performed spectrophotometrically (diode array) in the range 300-500 nm, by following the appearance of products after at least four half- lives, by means of a Hewlett-Packard 8453 instrument. In a typical spectrophotometric measurement a quartz cuvette (light-path 0.2 cm) containing 500 μL of ionic liquid was thermostated at 25°C during 10 minutes. The concentration of substrate 1 on the cell was 1.8 x 10^{-4} M, whilst the range concentrations of SA amines were 9 x 10^{-4} to 2.2 x 10^{-2} M. The spectra were recorded at different reaction times and pseudo-first-order rate coefficients (k_{obsd}) were found for all reactions. Each sample was made in triplicate. The (k_{obsd}) values were obtained by means of the kinetic software of the spectrophotometer, at the wavelength where the greatest absorbance change was observed. The nucleophilic rate constants k_N^T were obtained as the slope of linear plots of k_{obsd} *vs*. free nucleophile concentration. For the reactions in [Bmim]BF_4, the separation of k_N^T into k_N^P (the nucleophilic rate constant at the phosphoryl center) and k_N^{Ar} (the nucleophilic rate constant at the C-1 aromatic carbon) was performed considering the quantitative product analysis (see below) an the fact that for parallel reactions $k_N^T = k_N^{Ar} + k_N^P$.

The activation parameters were determined at the same experimental conditions as above, at the 20-40ºC-temperature range, by using Arrhenius and Eyring equations. In these experimental conditions the product analysis shows that in [Bmim]BF_4 the relative attack to the phosphoryl center remains constant within the temperature range (20%, see Figure S5 in Supporting Information).