Supporting Information

Table S1 Percentage yields (as determined by ^{31}P NMR) of the reaction of **2** with each amine as a function of the ionic liquid and ratio of PCl_3:Amine:Hünigs base. This data has been used to produce Figures 1-3 in the main text.

Ionic Liquid or Molecular Solvent	Amine	Ratio (PCl_3:Amine:Hünigs)	Composition (%)					
			P(OR)(NR'$_2$)Cl **3a/b/c**	P(OR)$_2$(NR'$_2$) **4a/b/c**	P(NR'$_2$)Cl_2 **5a/b/c**	P(NR'$_2$)$_2$Cl **6a/b/c**	P(OR)$_3$ **7**	Hydrolysis
[C_4mim][NTf_2]	^{i}Pr$_2$NH	1:1:1	70	18			5	7
		1:2:0	72	12			4	12
	Morpholine	1:1:1	74		7	7	3	9
		1:2:0	74		7	7		12
	Et_2NH	1:1:1	77	8		7		8
		1:2:0	82	3	7			8
[C_4dmim][NTf_2]*	^{i}Pr$_2$NH	1:1:1	79	7	10			4
		1:2:0	87	4	7			2
	Morpholine	1:1:1	72			5		23
		1:2:0	73			10		15
	Et_2NH	1:1:1	79	11		5		5
		1:2:0	83		12			5
[C_4mpyrr][NTf_2]	^{i}Pr$_2$NH	1:1:1	52	20			20	8
		1:2:0	84	13				3
	Morpholine	1:1:1	83		3	3		9
		1:2:0	89			4		7
	Et_2NH	1:1:1	65	10		5		20
		1:2:0	85	8	4			3
[C_4mpip][NTf_2]	^{i}Pr$_2$NH	1:1:1†	61		5			12
		1:2:0	75	11	6			8
	Morpholine	1:1:1	46			9	23	22
		1:2:0	66			15		19
	Et_2NH	1:1:1	87	7		6		
		1:2:0	75		15			10
[C_4py][NTf_2]	^{i}Pr$_2$NH	1:1:1	75	15	3			7
		1:2:0	82	10	4			4
	Morpholine	1:1:1	61		17	14		8
		1:2:0	80		8	8		4
	Et_2NH	1:1:1	83	10		5		2
		1:2:0	83	3	13			1

*Remainder made up from **2** 22%.

Table S2 ^{31}P-NMR data for all compounds observed. Ionic liquid samples were transferred directly into the NMR tube with no addition of deuterated solvents. The ^{31}P-NMR chemical shifts were recorded in parts per million (ppm) relative to an external probe (sealed capillary inside the NMR tube sample) of triethylphosphonate ($PO(OEt)_3$) in $CDCl_3$ (solvent used for locking/shimming optimisation). Literature data is shown in parentheses.

	$^{i}Pr_2NH$ (**a**)	Morpholine (**b**)	Et_2NH (**c**)
PCl_3	220 (219)[1]		
$P(OR)Cl_2$ (**1**)	179 (179)[2]		
$P(OR)_2Cl$ (**2**)	164 (165)[2]		
$P(OR)_3$ (**7**)	139 (139)[2]		
P(OR)(NR'$_2$)Cl (**3**)	181 (179)[3]	169 (168)[3]	176 (176)[4]
$P(OR)_2$(NR'$_2$) (**4**)	148 (150)[5]	Not observed	147[6]
P(NR'$_2$)Cl_2 (**5**)	170 (170)[7]	158 (156)[8]	163 (162)[9]
P(NR'$_2$)$_2$Cl (**6**)	162 (140)[10]	150 (145)[11]	159 (154)[12]

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