Supporting Information for:

**Solvent-Modulated Reactivity of PCl₃ with Amines**

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**Figure S1**

(a) ^1^H NMR, (b) ^1^3^C NMR and ^31^P NMR spectra following the reaction 0.4 mol of distilled diisopropylamine (56.10 cm³) and 0.4 mol of distilled ethyldiisopropylamine (Hünig’s base, 69.68 cm³) with 0.4 mol of PCl₃ (34.90 cm³) in [C₄mim][NTf₂] under argon and subsequent isolation of dichloro diisopropylaminophosphine at 20°C.
Figure S2 A comparison of the reaction mixture following the reaction of PCl₃ (0.0008 mol) with diisopropylamine (0.0008 mol) in the presence of Hünig’s base (0.0008 mol) and either 1.5 cm³ (a) hexane (0.011 mol) or (b) [C₄mpyrr][NTf₂] (0.005 mol) at 20 °C.