

Supporting Information for:

**Solvent-Modulated Reactivity of  $\text{PCl}_3$  with Amines**

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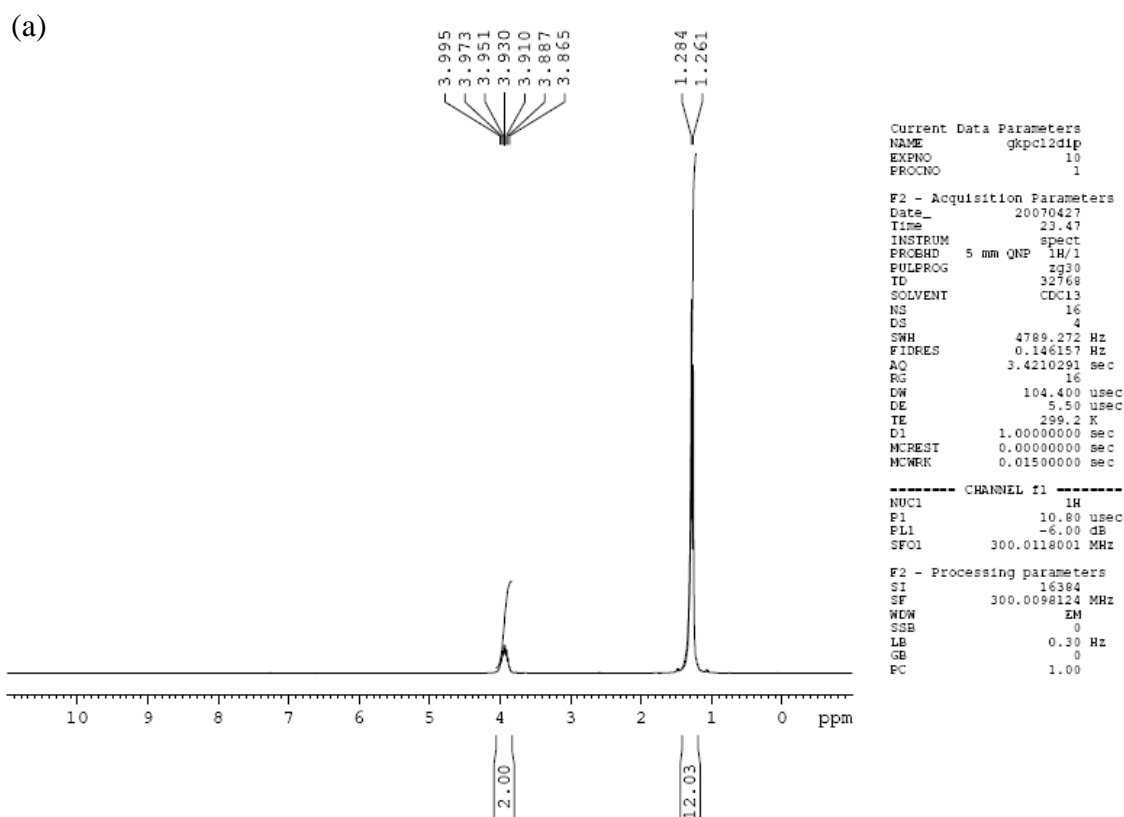
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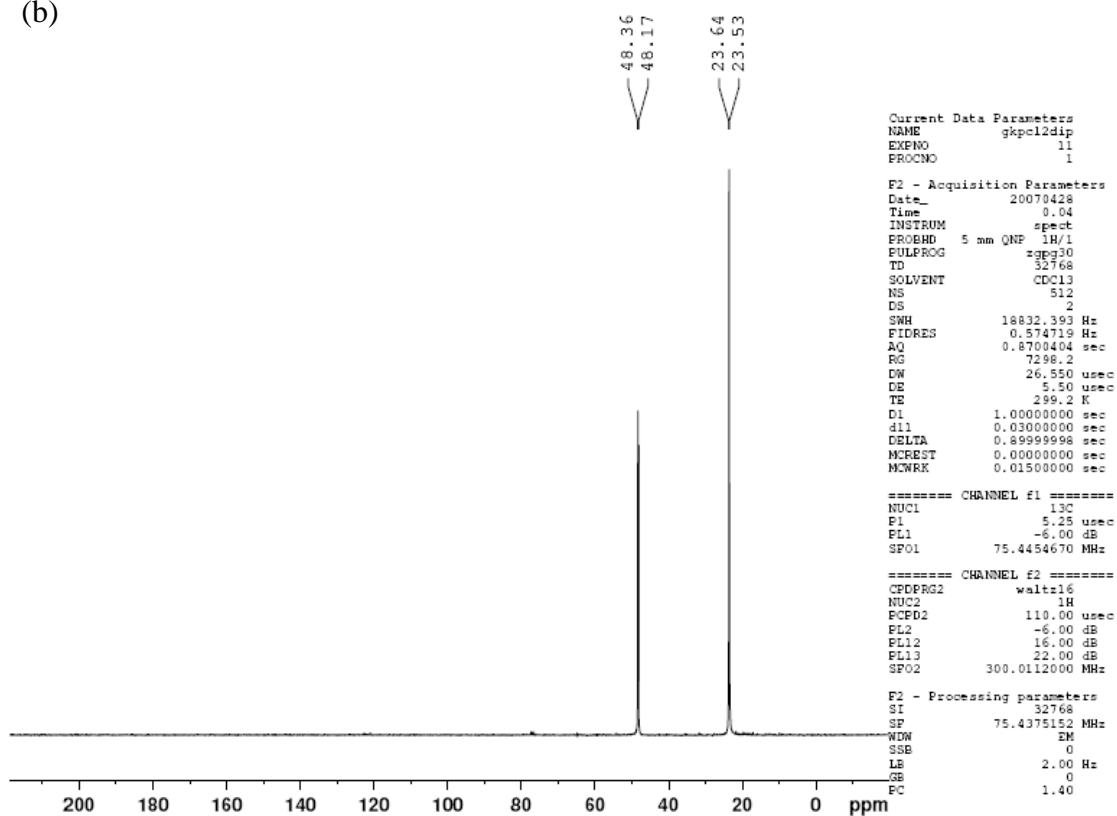
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**Figure S1**

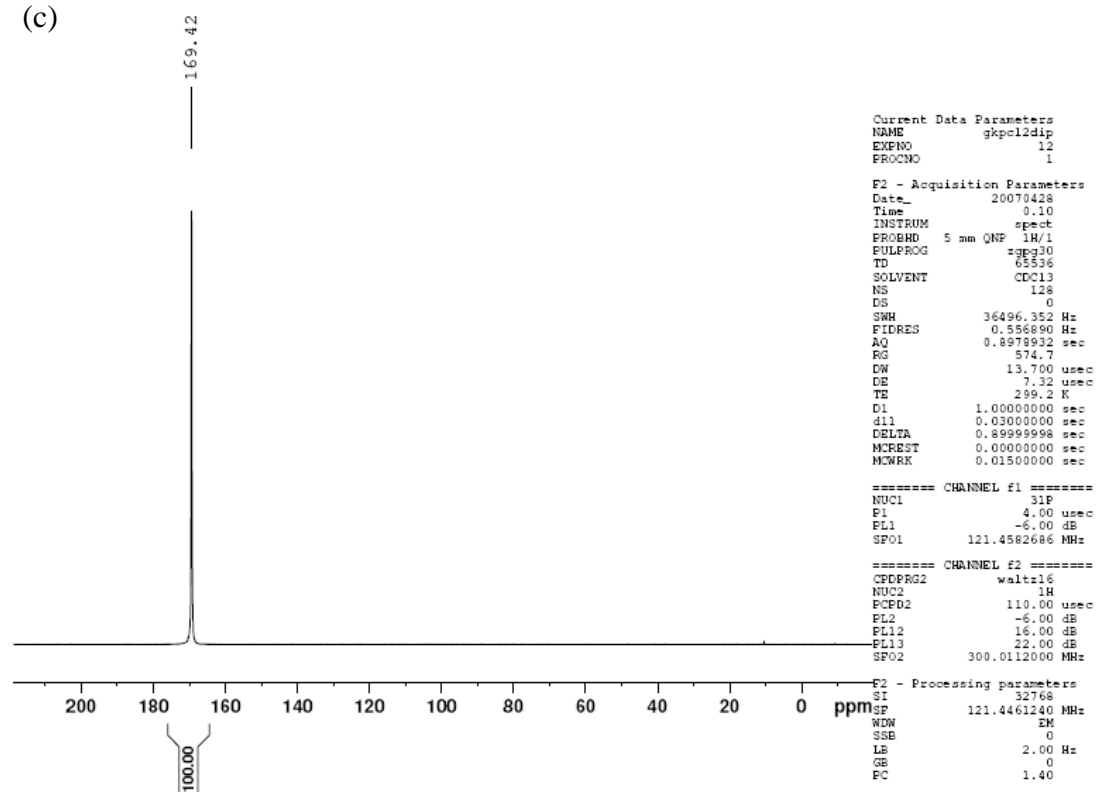
(a)  $^1\text{H}$  NMR, (b)  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR spectra following the reaction 0.4 mol of distilled diisopropylamine ( $56.10\text{ cm}^3$ ) and 0.4 mol of distilled ethyldiisopropylamine (Hünig's base,  $69.68\text{ cm}^3$ ) with 0.4 mol of  $\text{PCl}_3$  ( $34.90\text{ cm}^3$ ) in  $[\text{C}_4\text{mim}][\text{NTf}_2]$  under argon and subsequent isolation of dichloro diisopropylaminophosphine at  $20^\circ\text{C}$ .



(b)



(c)



**Figure S2** A comparison of the reaction mixture following the reaction of  $\text{PCl}_3$  (0.0008 mol) with diisopropylamine (0.0008 mol) in the presence of Hünig's base (0.0008 mol) and either 1.5  $\text{cm}^3$  (a) hexane (0.011 mol) or (b)  $[\text{C}_4\text{mpyr}][\text{NTf}_2]$  (0.005 mol) at 20 °C.

