Supporting Information for:

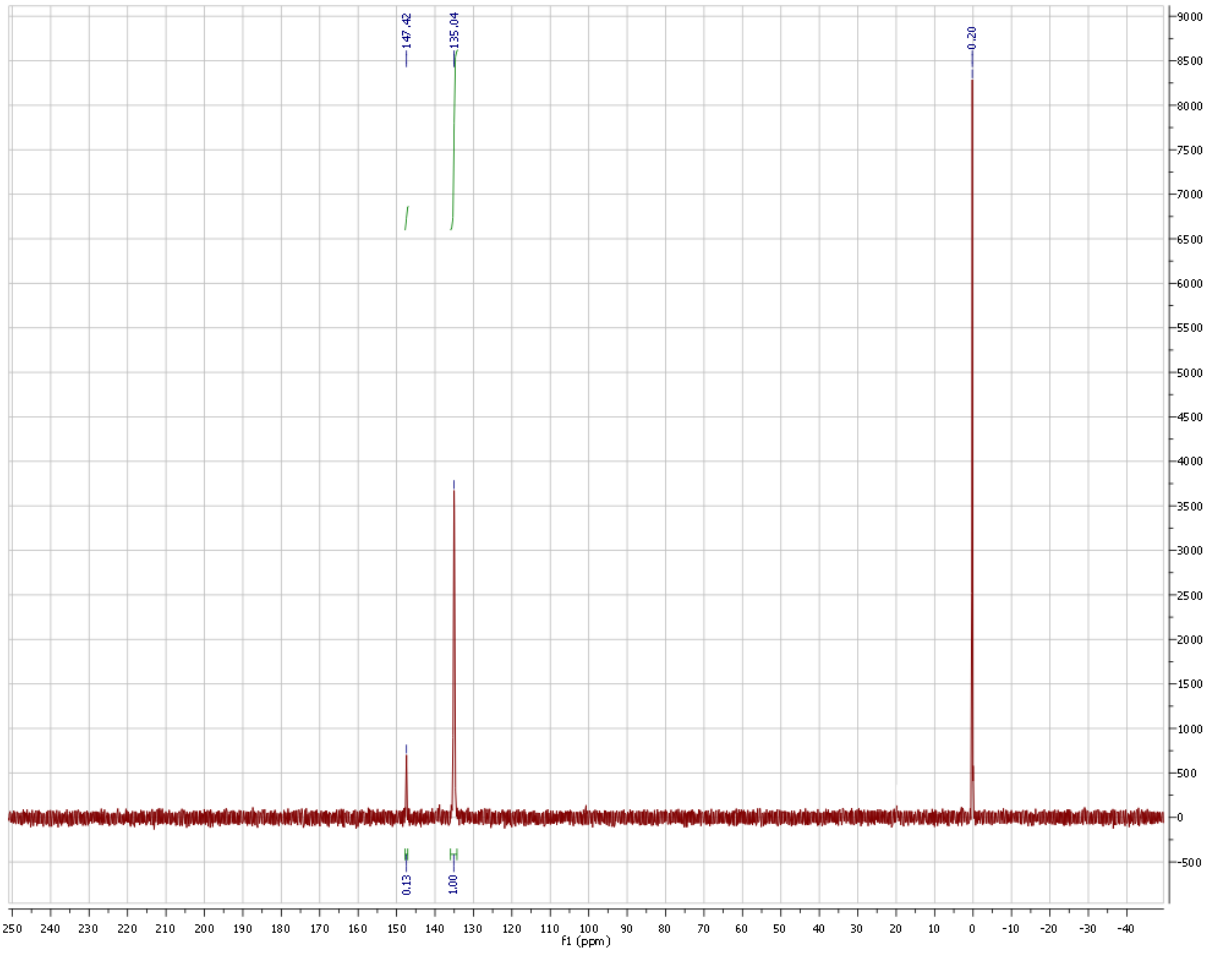
Exploiting the use of ionic liquids to access phosphorodiamidites

Kerri Crossey,[a] Christopher Hardacre,[a,]* Marie E. Migaud,[b,]* and Sarah E. Norman[a]

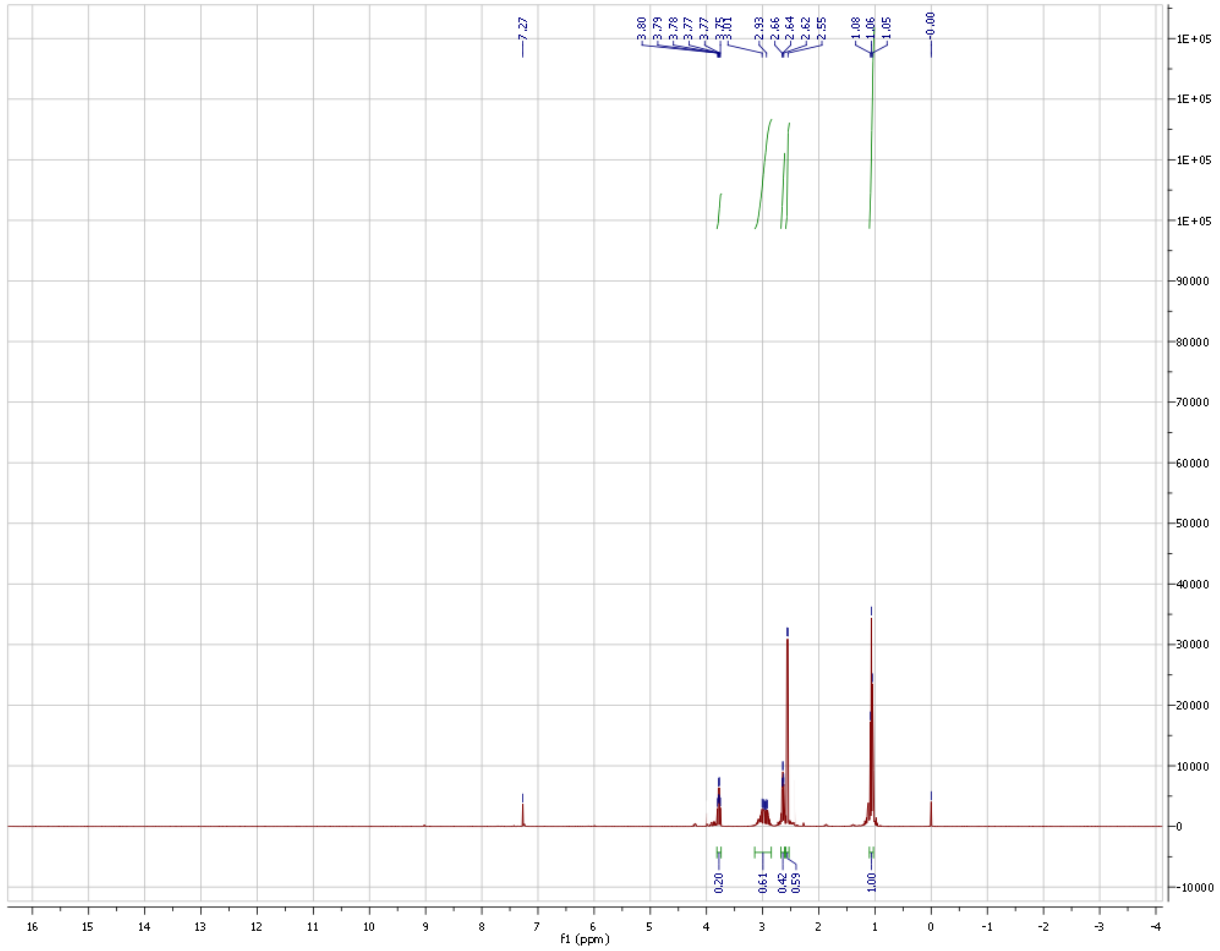
[a] *QUILL and School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast, Northern Ireland, BT9 5AG. Fax: +442890874687; E-mail: c.hardacre@qub.ac.uk*
[b] *School of Pharmacy, 97 Lisburn Road, Queen's University Belfast, Belfast, BT9 7BL. Fax: +; E-mail:m.migaud@qub.ac.uk*

Figure S1
(a) ^{31}P NMR, (b) ^{1}H NMR and (c) ^{13}C NMR spectra of 2-cyanoethyl-*N,N,N',N'*-ethylmethylphosphoramidite, **3b**, following extraction with diethyl ether. The ^{31}P- NMR chemical shifts for all spectra were recorded in parts per million (ppm) relative to an external probe using a sealed capillary containing triethylphosphonate ($PO(OEt)_3$) in d_6-DMSO (solvent used for locking/shimming optimization) inside the NMR tube. The $PO(OEt)_3$ probe was referenced to 0.2 ppm. The ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ referenced to 0.00 ppm using TMS for the ^{1}H NMR and 77.0 ppm for the ^{13}C NMR.

(a)



(b)



(c)

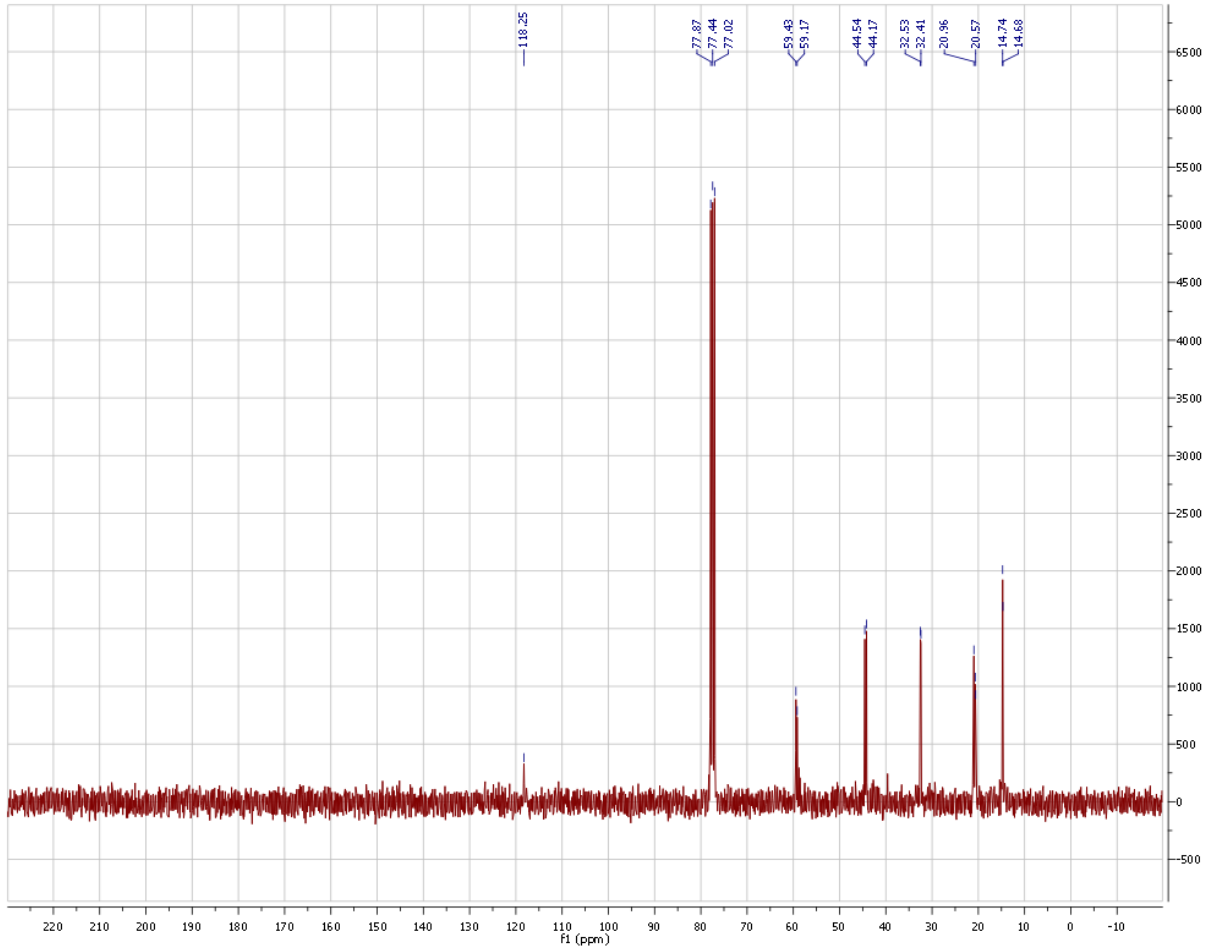
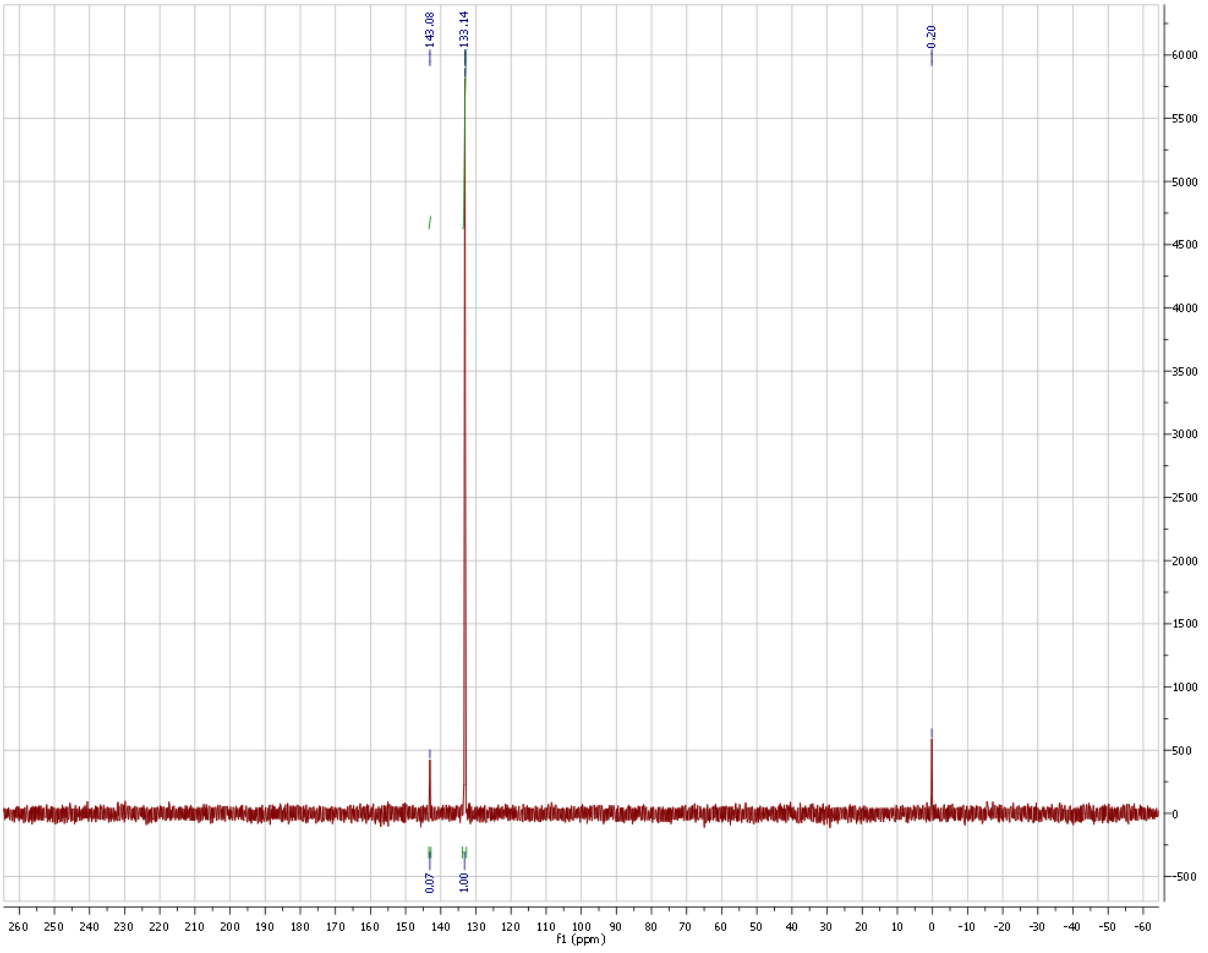


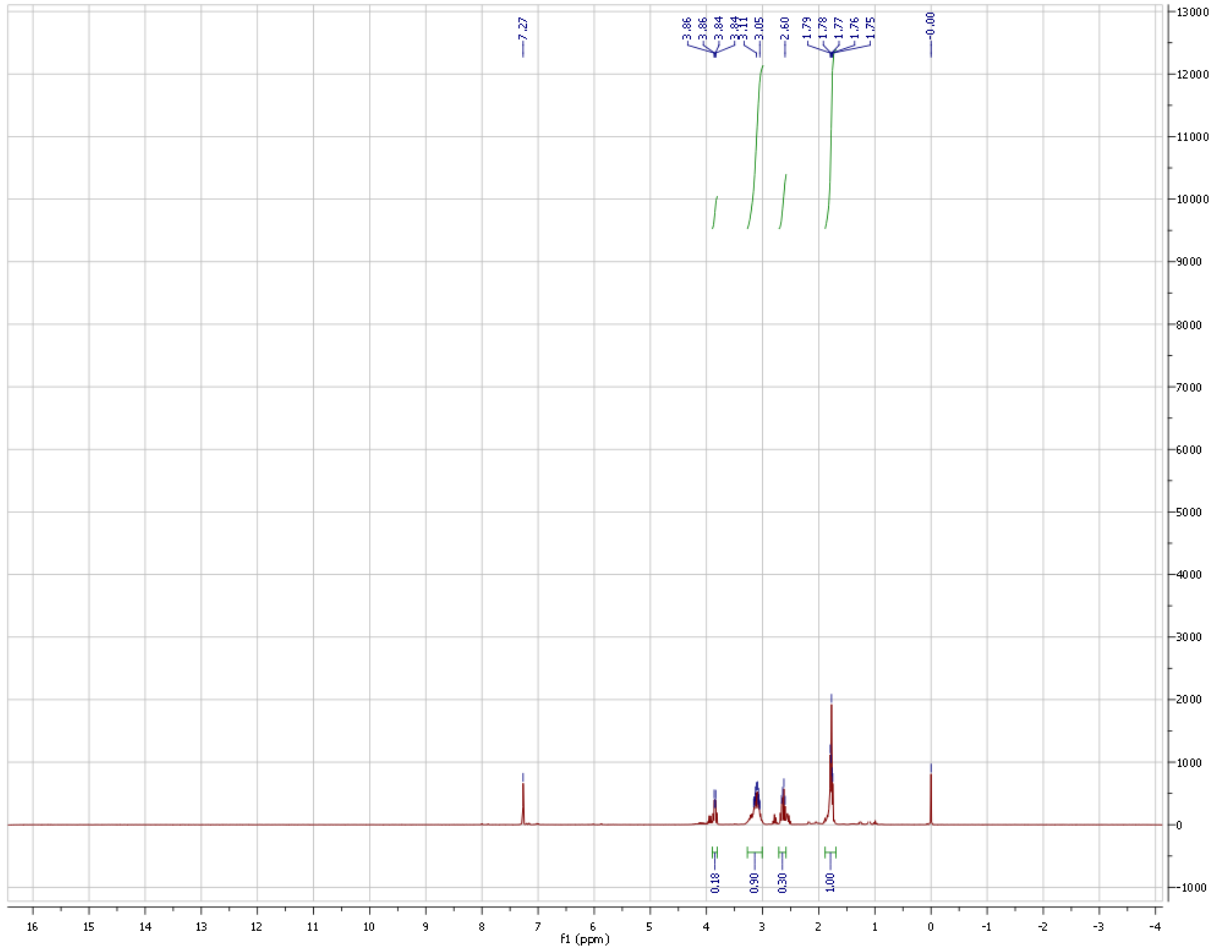
Figure S2

(a) ^{31}P NMR, (b) ^{1}H NMR and (c) ^{13}C NMR spectra of bis-(pyrrolidino)-2-cyanoethoxyphosphite, **3d**, following extraction with diethyl ether. The ^{31}P- NMR chemical shifts for all spectra were recorded in parts per million (ppm) relative to an external probe using a sealed capillary containing triethylphosphonate ($PO(OEt)_3$) in DMSO (solvent used for locking/shimming optimization) inside the NMR tube. The $PO(OEt)_3$ probe was referenced to 0.2 ppm. The ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ referenced to 0.00 ppm using TMS for the ^{1}H NMR and 77.0 ppm for the ^{13}C NMR.

(a)



(b)



(c)

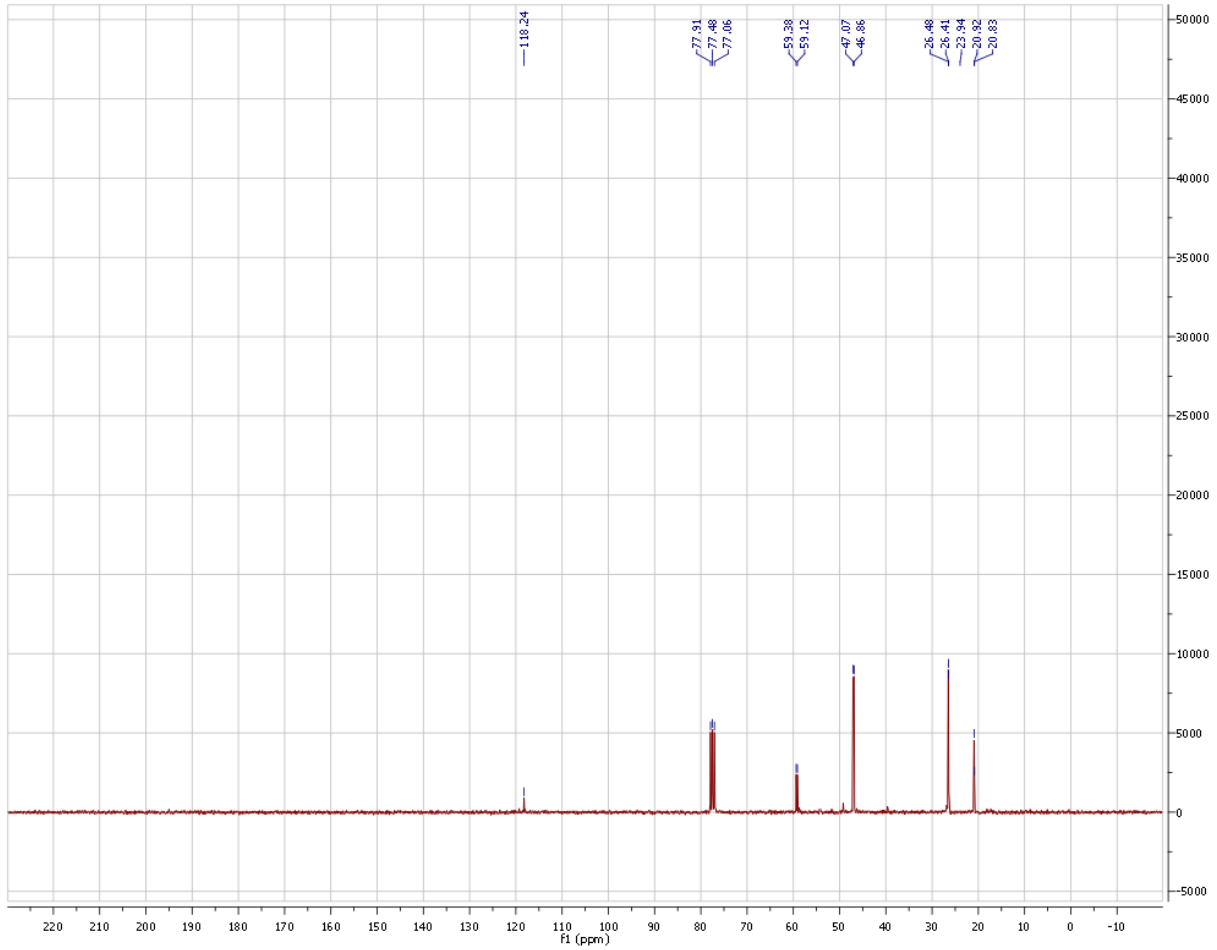
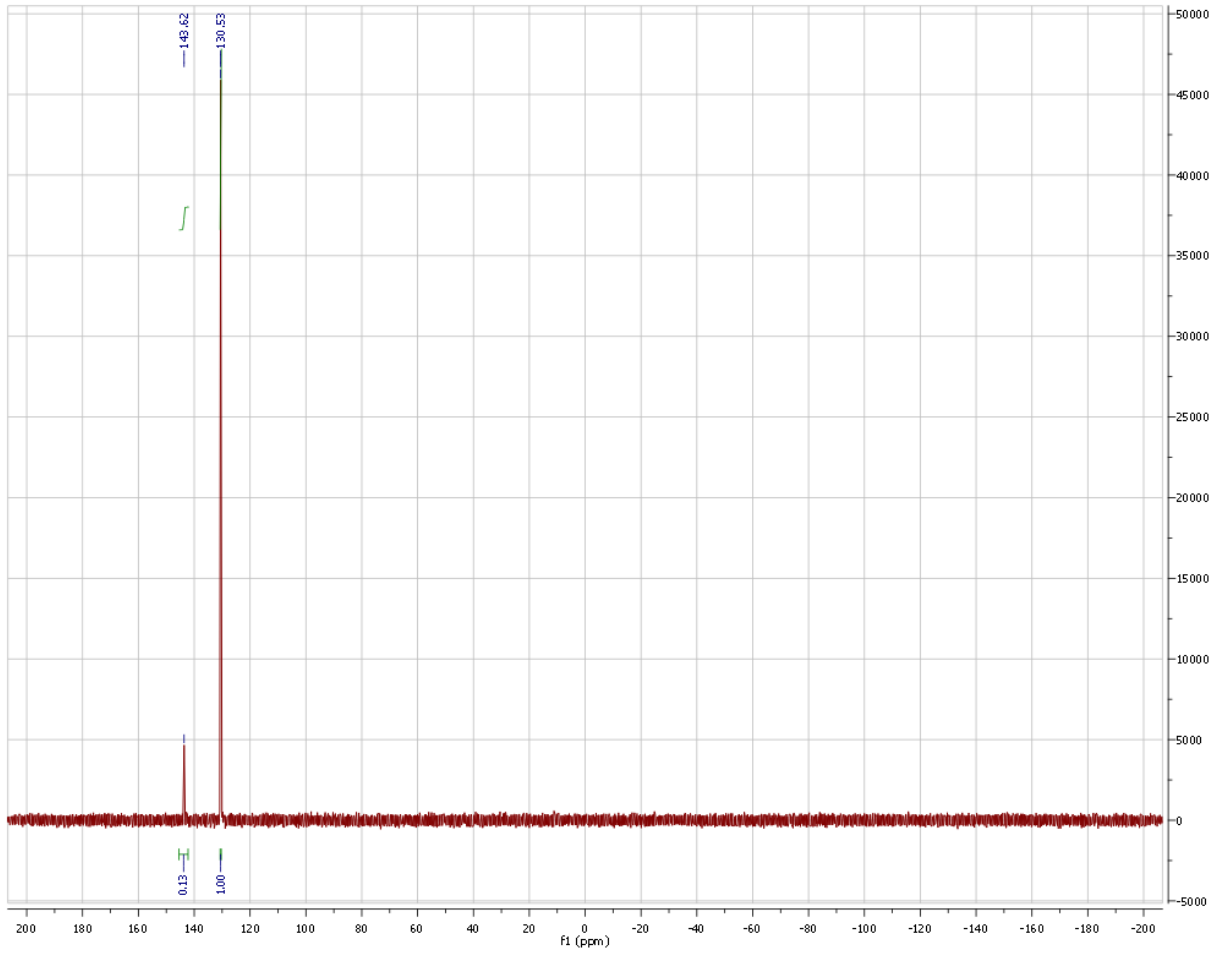


Figure S3

(a) ^{1}H NMR, (b) ^{13}C NMR and (c) ^{31}P NMR spectra following the large scale synthesis of bis-(morpholino)-2-cyanoethoxyphosphite, **3c**. The ^{31}P NMR, ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ referenced to 0.00 ppm using TMS for the ^{1}H NMR and 77.0 ppm for the ^{13}C NMR.

(a)



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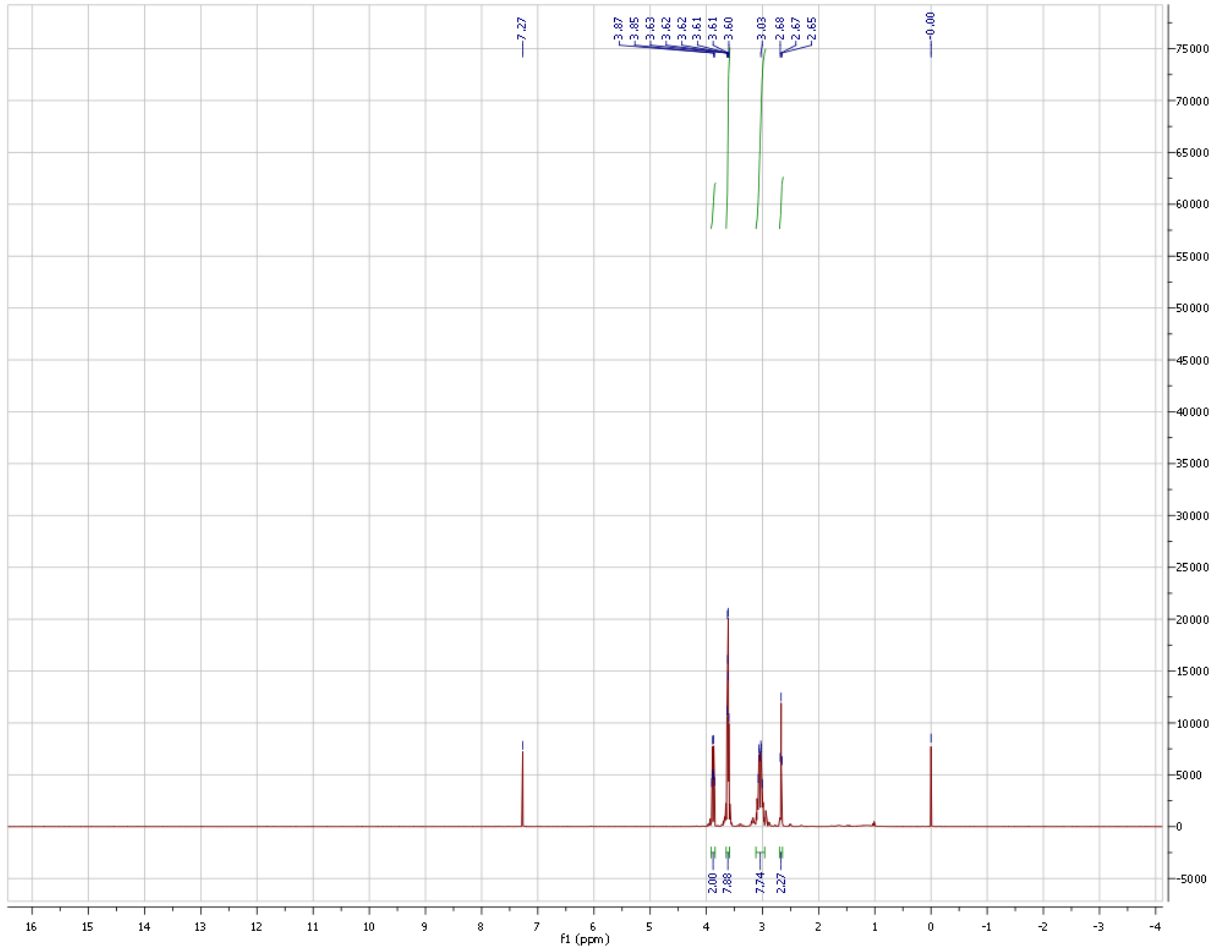


(c)

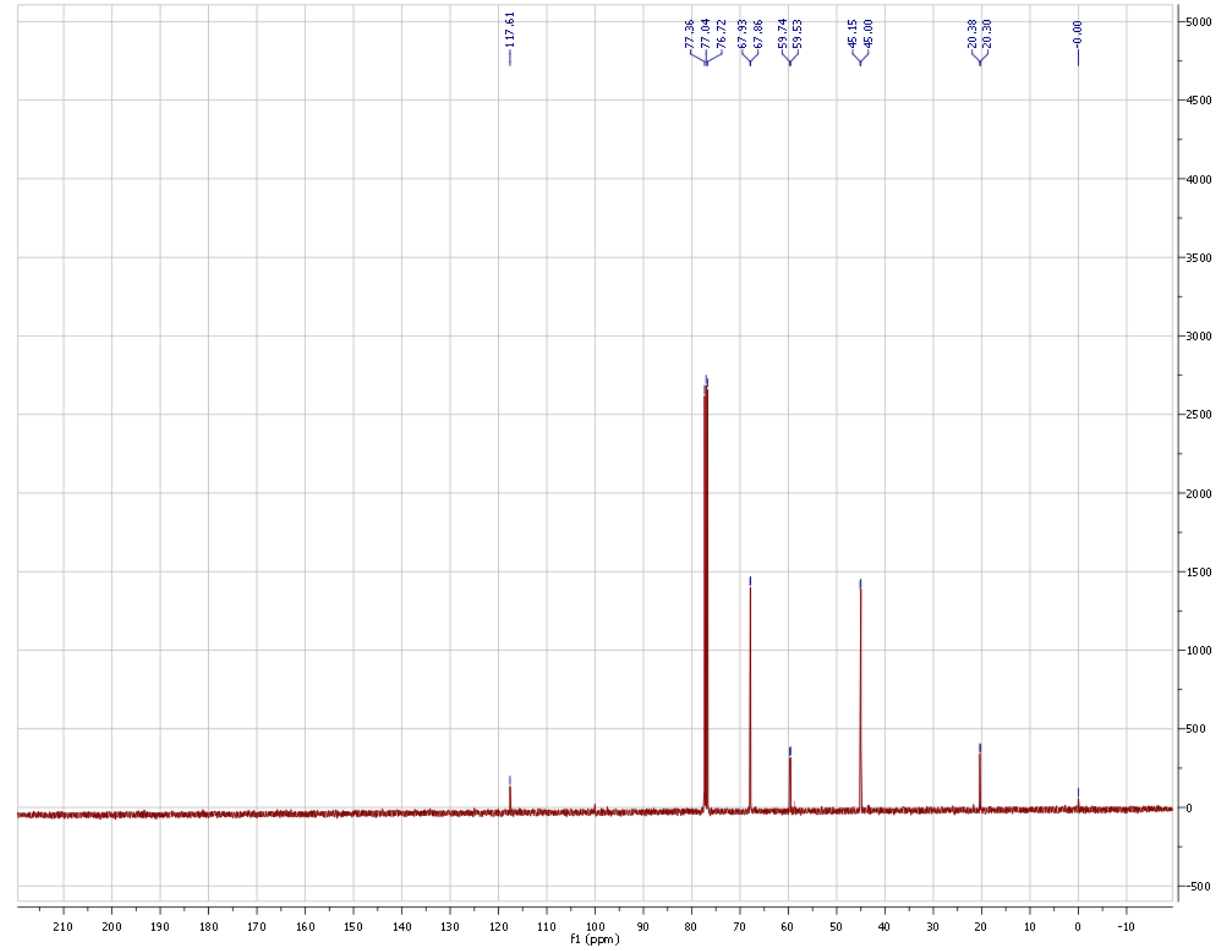
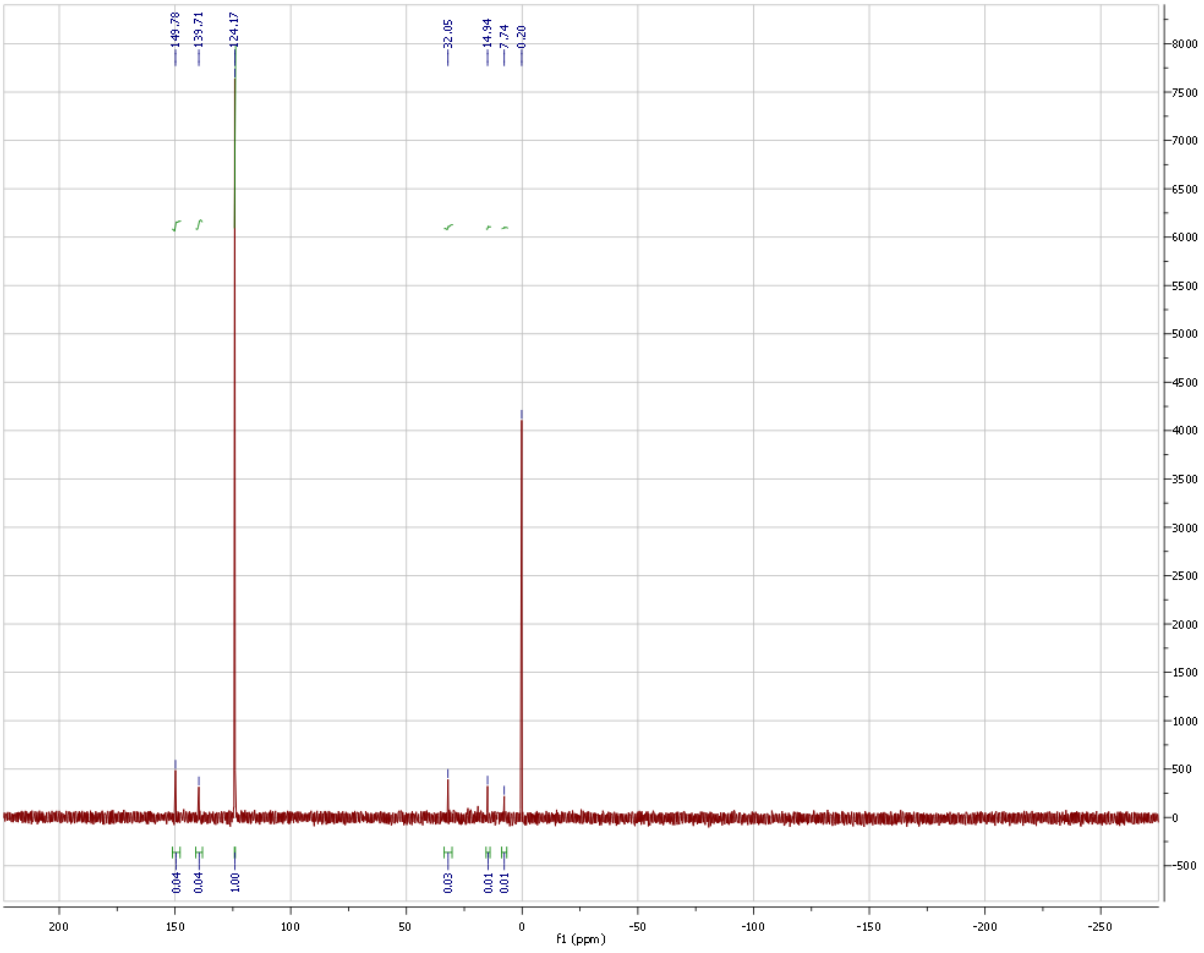


Figure S4

(a) ^{31}P NMR spectra of *N*,*N*,*N'*,*N'*-tetraisopropylphosphoramidite, **3a**, as obtained from Aldrich and (b)^{31}P NMR spectra of *N*,*N*,*N'*,*N'*-tetraisopropylphosphoramidite, **3a**, following synthesis in [C_4mpyrr][NTf_2] and subsequent distillation.. The ^{31}P- NMR chemical shifts were recorded in parts per million (ppm) relative to an external probe using a sealed capillary containing triethylphosphonate ($PO(OEt)_3$) in DMSO (solvent used for locking/shimming optimization) inside the NMR tube. The $PO(OEt)_3$ probe was referenced to 0.2 ppm.

(a)



(b)

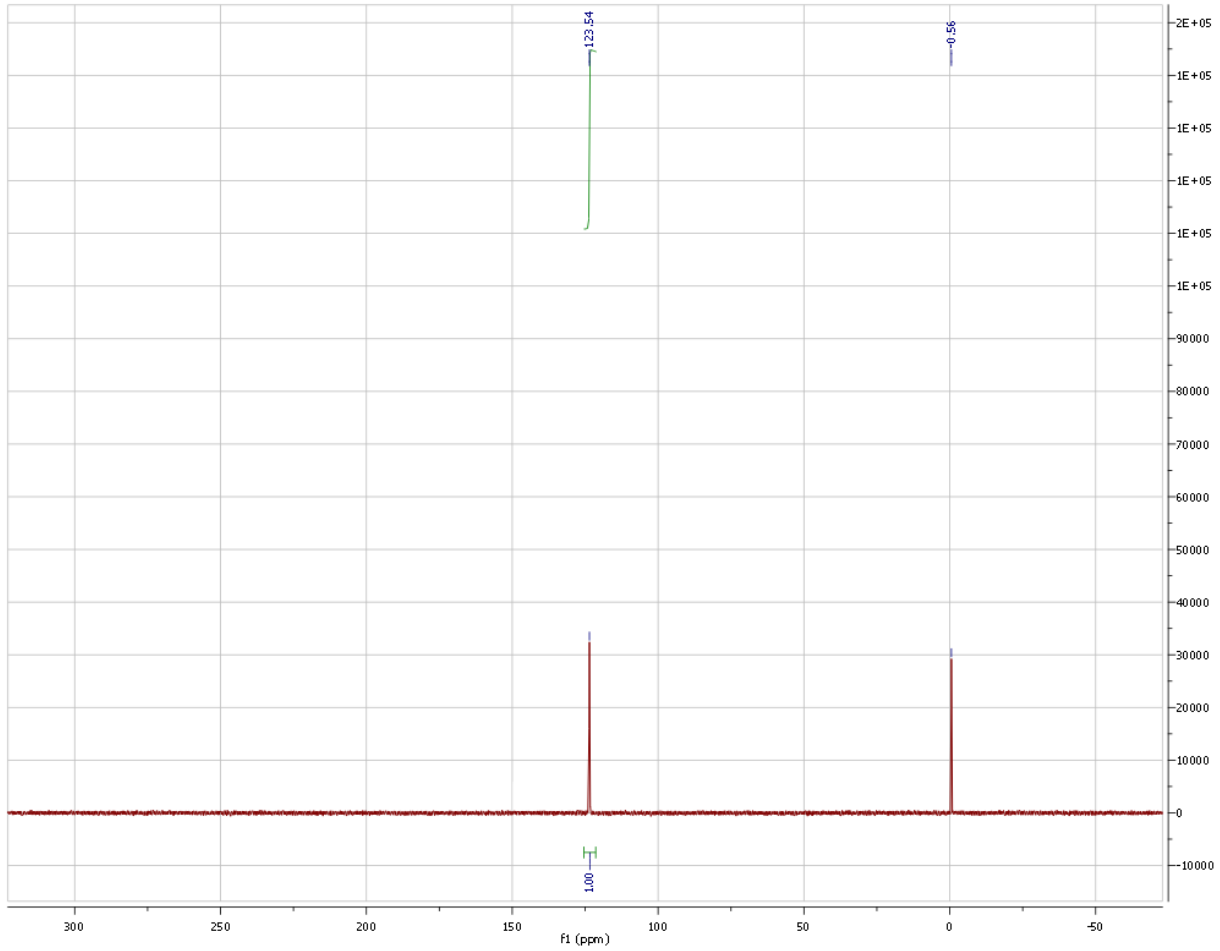


Table S5

^{31}P NMR data for the compounds observed. The ^{31}P-NMR chemical shifts were recorded in parts per million (ppm) relative to an external probe (sealed capillary inside the NMR tube) of triethylphosphonate ($PO(OEt)_3$ in d_6-DMSO (solvent used for locking/shimming optimisation. Literature data is shown in parentheses.

	$^{i}Pr_2NH$ (**a**)	EtMeNH (**b**)	Morpholine (**c**)	Pyrrolidine (**d**)
PCl_3	220(219)[1]			
$P(OR)Cl_2$ (**1**)	179(179)[2]			
$P(OR)_2Cl$ (**2**)	164 (165)[2]			
$P(OR)(NR'_2)_2$ (**3**)	123 (123)[3]	135[4]	131(131)[5]	133[4]
$P(OR)_2(NR'_2)$ (**4**)	149(150)[6]	146[4]	142[4]	143[4]
$P(O)(R)(NR'_2)_2$ (**6**)*	33[6]	31[6]	30[6]	29[6]
$P(OR)(NR'_2)Cl$ (**7**)	181(179)[7]	Not observed	Not observed	Not observed

*The corresponding *N,N,N',N'*-tetraethylphosphonic diamide derivative is reported at 31.9 ppm.[8]

4a LRMS (ES, M + Na^+) calculated for $C_{12}H_{22}N_3O_2PNa$ 294.13, found 294.13

4b LRMS (ES, M + H^+) calculated for $C_9H_{17}N_3O_2P$ 230.10, found 230.11

4c LRMS (ES, M + H^+) calculated for $C_{10}H_{17}N_3O_3P$ 258.10, found 258.10

4d LRMS (ES, M + H^+) calculated for $C_{10}H_{17}N_3O_2P$ 242.10, found 242.14

References

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