Supporting information

for

Zinc 8-aminotrihydroquinolines appended with pendant *N*-diphenylphosphinoethyl arms as exceptionally active catalysts for the ROP of ε-CL

Furong Cao,[a,b] Yun Wang,[a,b] Xing Wang,[a,b] Wenjuan Zhang,[a,*] Gregory A. Solan,[c,*] Rui Wang [a], Yanping Ma,[b] Xiang Hao,[b] Wen-Hua Sun[b,*]

[a] Beijing Key Laboratory of Clothing Materials R&D and Assessment, Beijing Engineering Research Center of Textile Nanofiber, School of Materials Science and Engineering, Beijing Institute of Fashion Technology, Beijing 100029, China. E-mail: zhangwj@bift.edu.cn.

[b] Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: whsun@iccas.ac.cn

[c] Department of Chemistry, University of Leicester, University Road, Leicester LE1 7RH, UK. E-mail: gas8@leicester.ac.uk.

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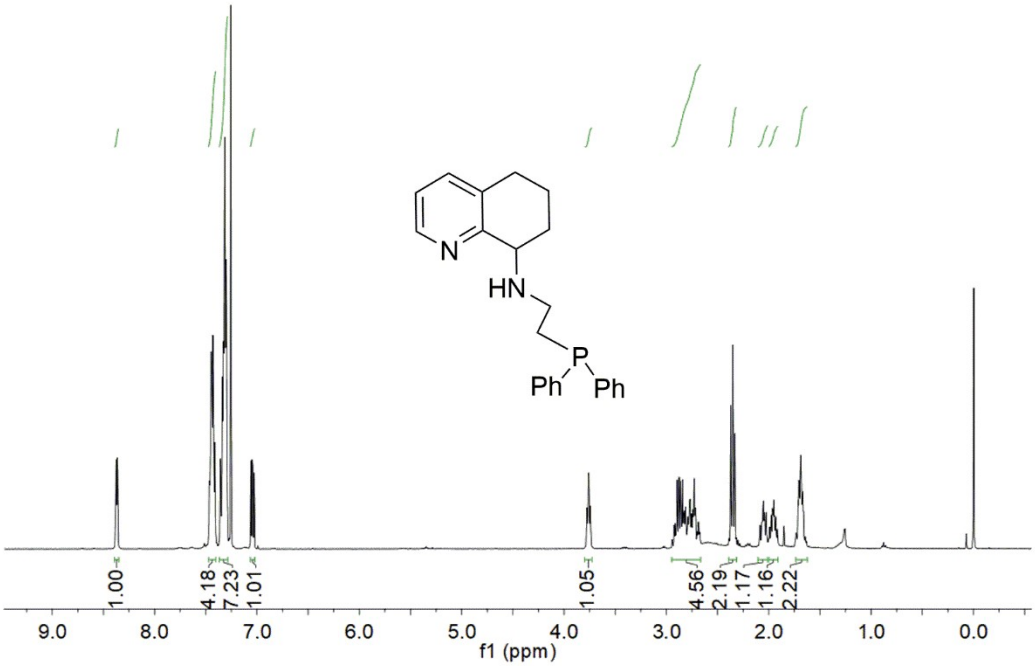


Figure S1(a) ^{1}H NMR spectrum of **L1**; recorded in $CDCl_3$ at 25 ^{o}C

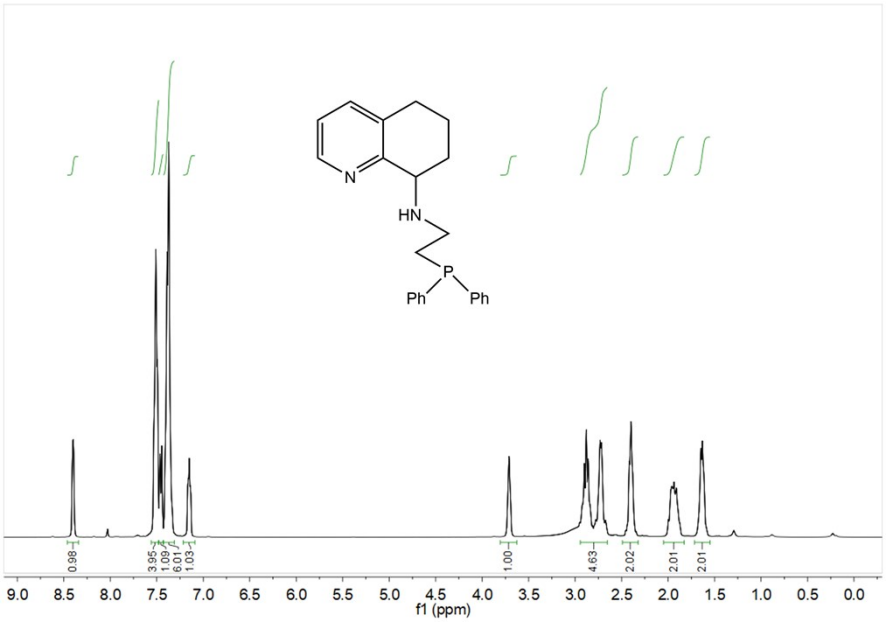


Figure S1(b) ^{1}H NMR spectrum of **L1**; recorded in C_3D_7NO at 25 ^{o}C

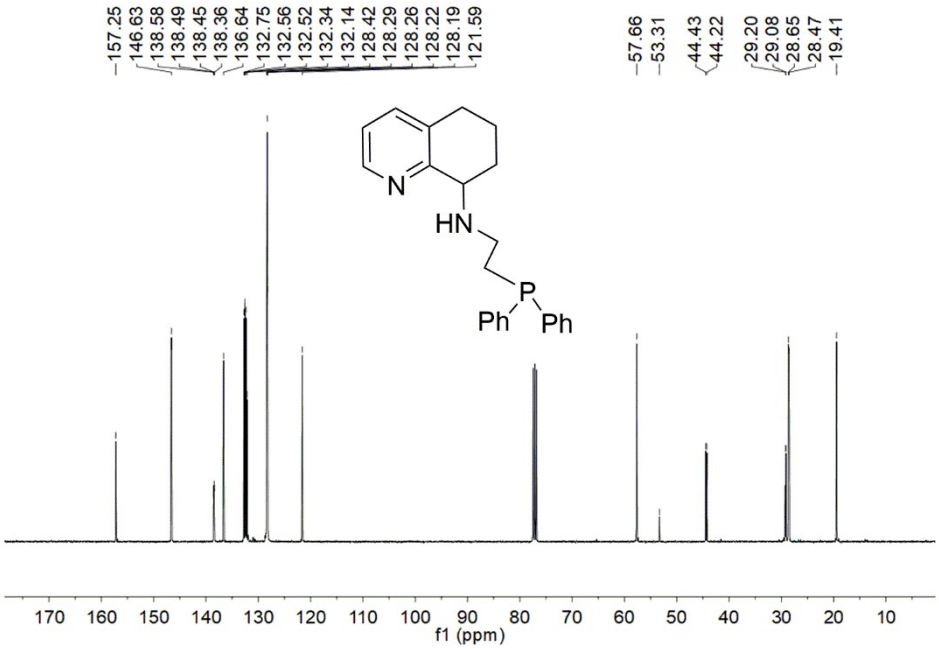


Figure S2 ^{13}C NMR spectrum of **L1**; recorded in $CDCl_3$ at 25 ^{o}C

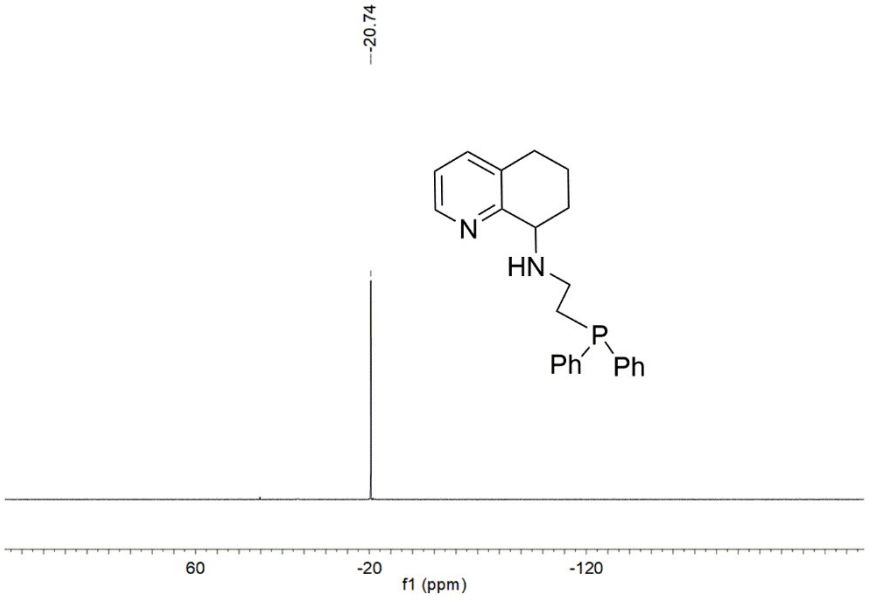


Figure S3 (a) ^{31}P NMR spectrum of **L1**; recorded in $CDCl_3$ at 25 ^{o}C

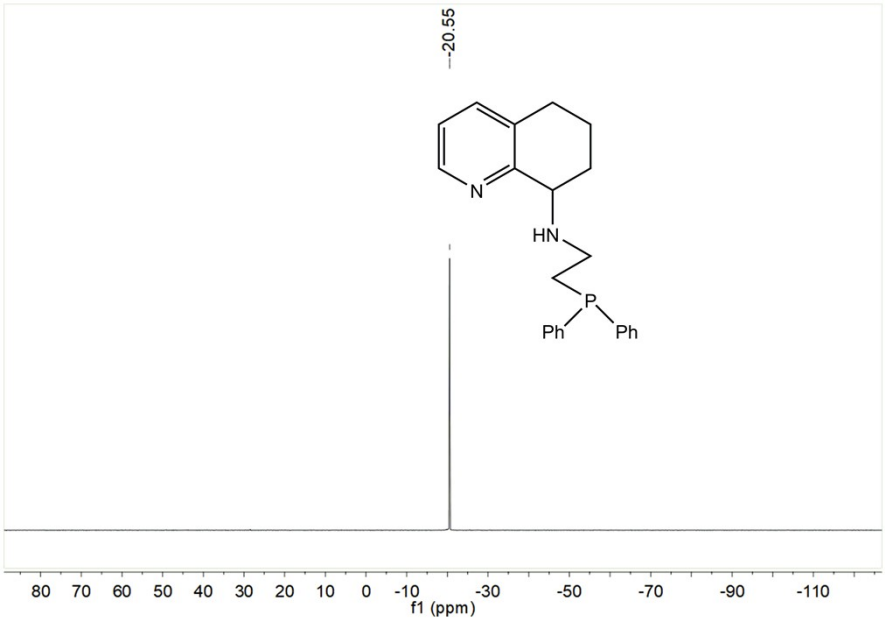


Figure S3(b) ^{31}P NMR spectrum of **L1**; recorded in C_3D_7NO at 25 ^oC

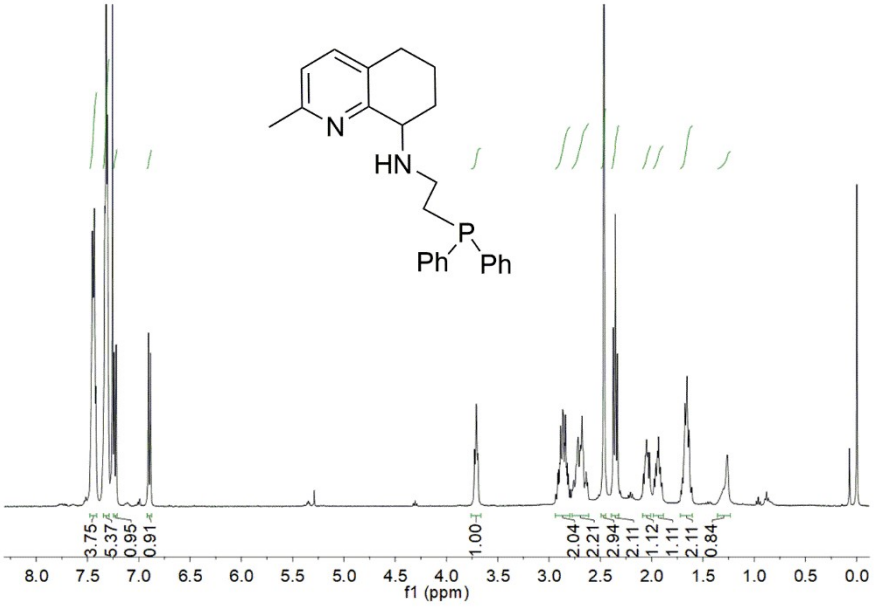


Figure S4(a) ^1H NMR spectrum of **L2**; recorded in $CDCl_3$ at 25 ^oC

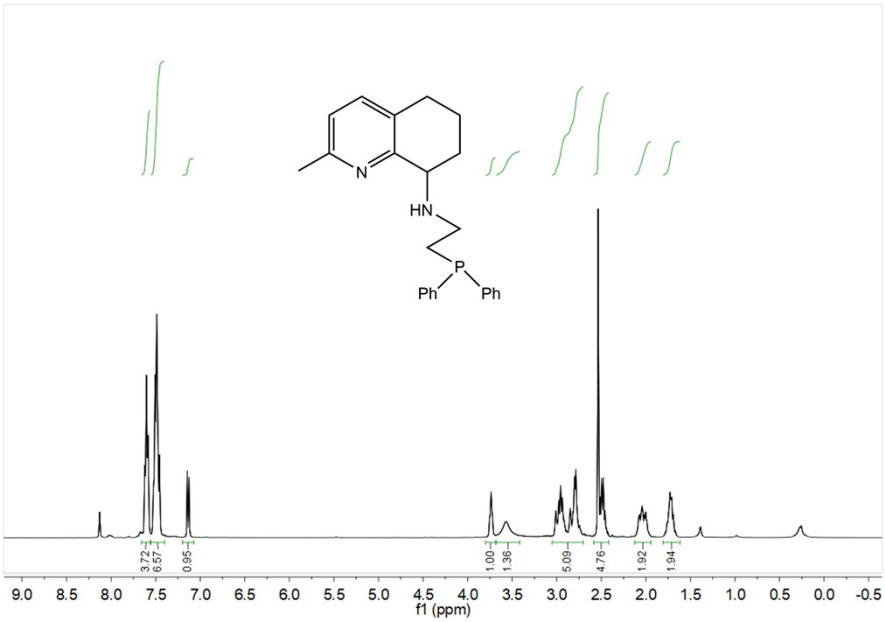


Figure S4 (b) ^{1}H NMR spectrum of **L2**; recorded in C_3D_7NO at 25 ^{o}C

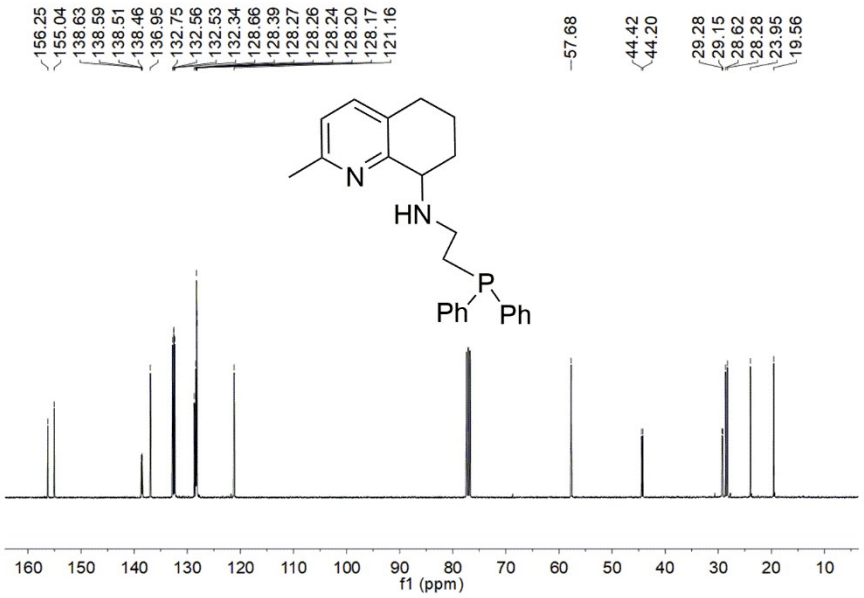


Figure S5 ^{13}C NMR spectrum of **L2**; recorded in $CDCl_3$ at 25 ^{o}C

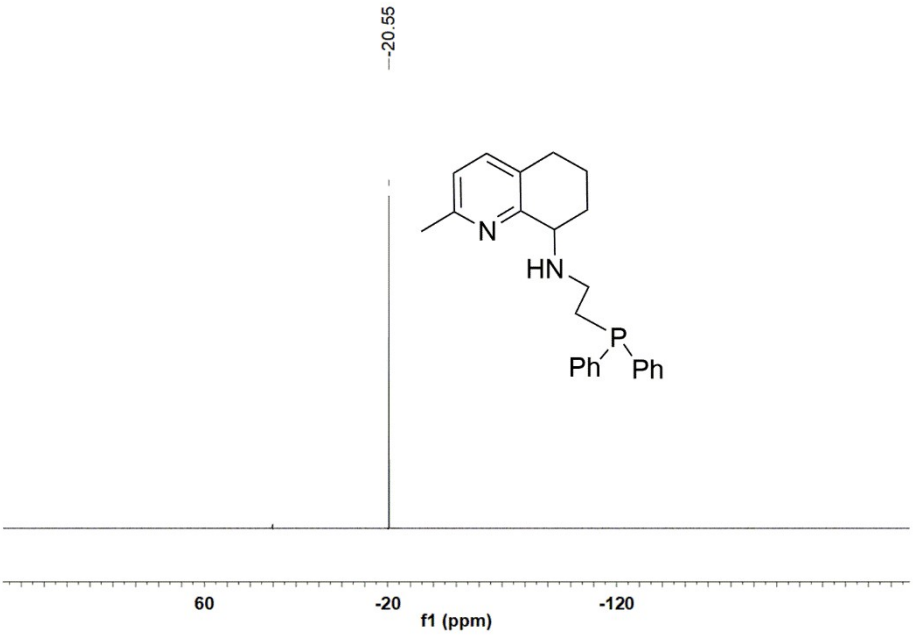


Figure S6 (a) ^{31}P NMR spectrum of **L2**; recorded in $CDCl_3$ at 25 ^{o}C

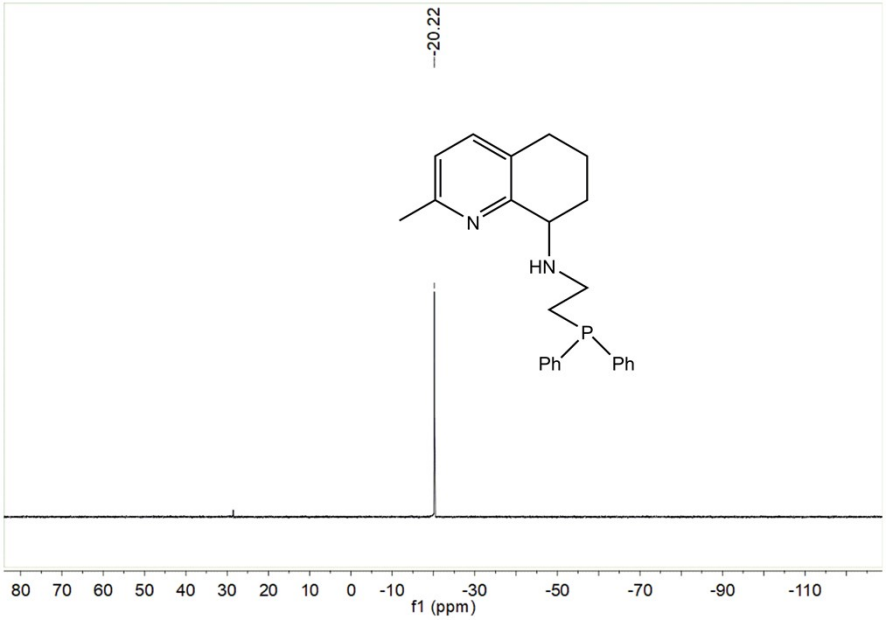


Figure S6 (b) ^{31}P NMR spectrum of **L2**; recorded in C_3D_7NO at 25 ^{o}C

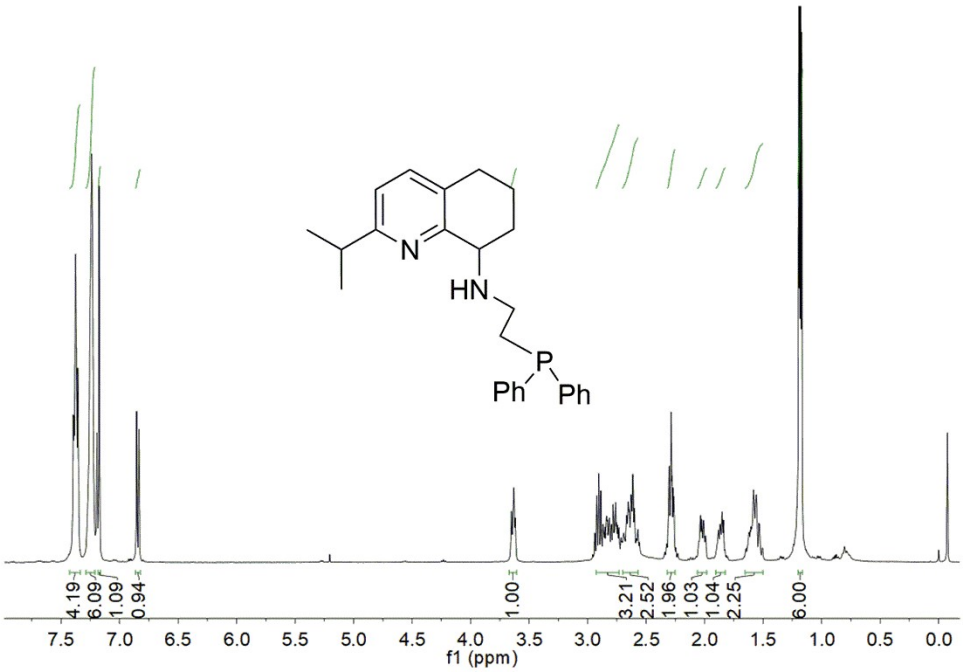


Figure S7(a) ^{1}H NMR spectrum of **L3**; recorded in $CDCl_3$ at 25 ^{o}C

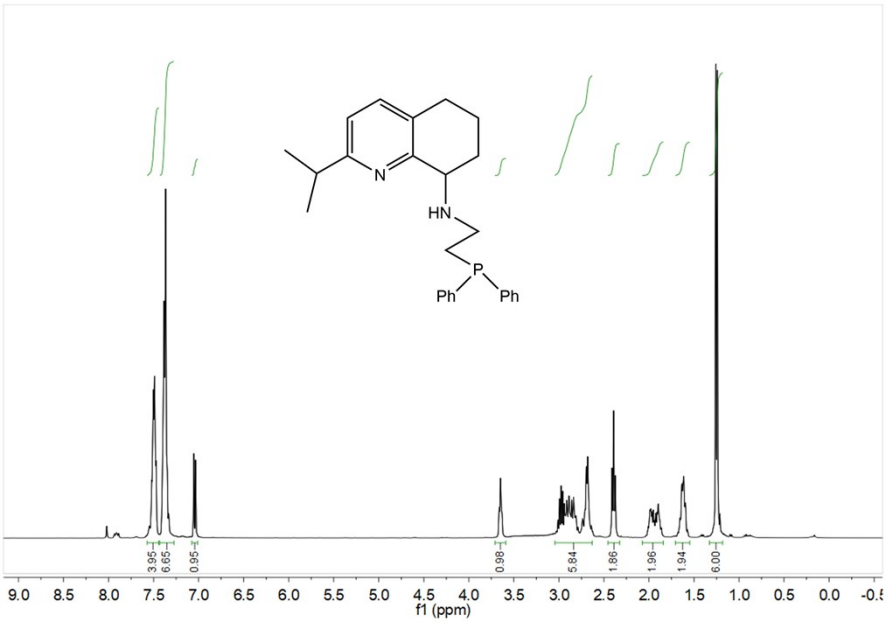


Figure S7 (b) ^{1}H NMR spectrum of **L3**; recorded in C_3D_7NO at 25 ^{o}C

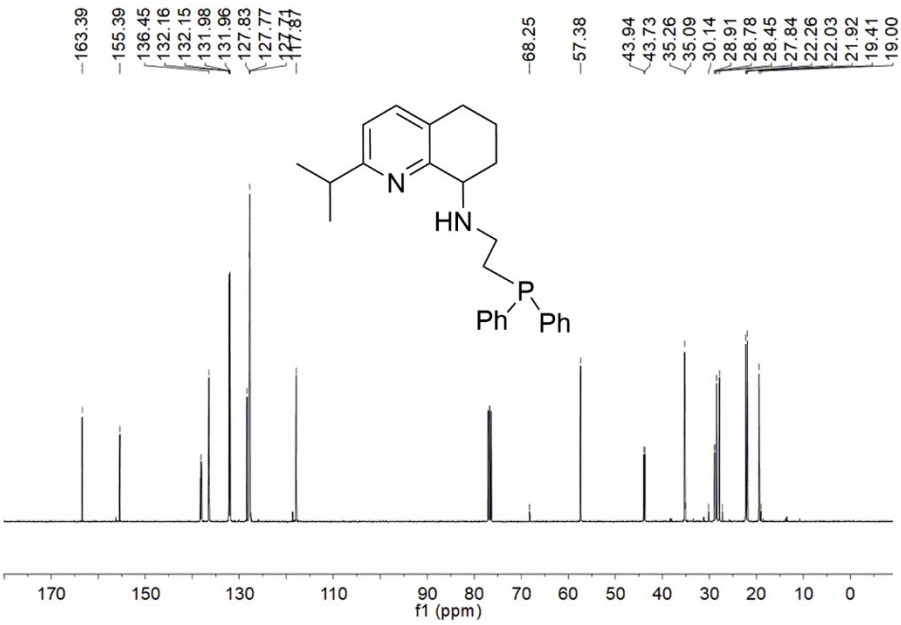


Figure S8 ^{13}C NMR spectrum of **L3**; recorded in $CDCl_3$ at 25 ^{o}C

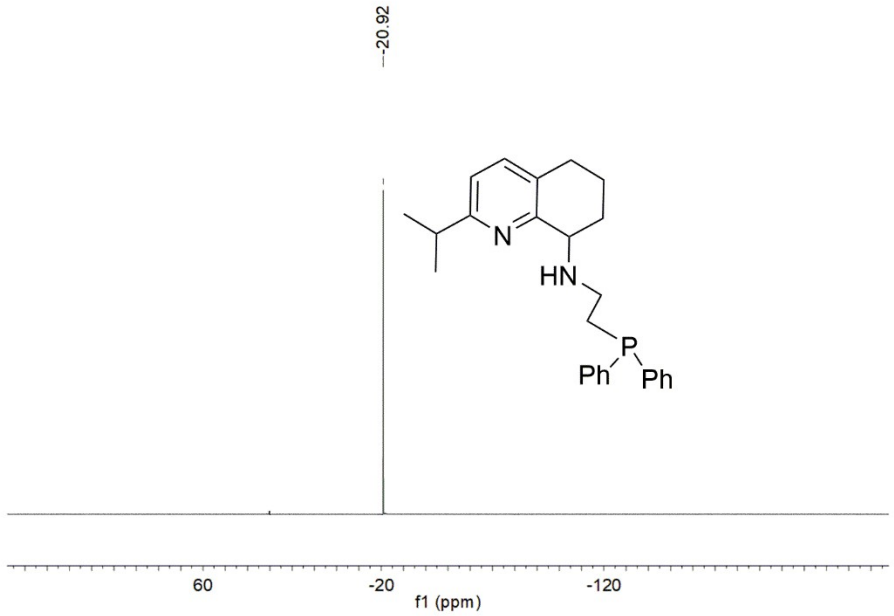


Figure S9(a) ^{31}P NMR spectrum of **L3**; recorded in $CDCl_3$ at 25 ^{o}C

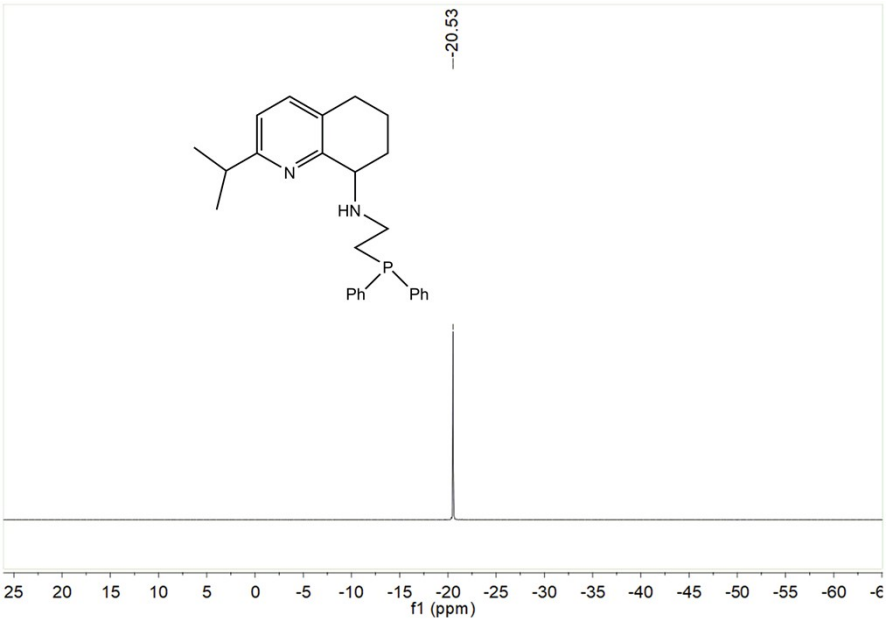


Figure S9 (b) ^{31}P NMR spectrum of **L3**; recorded in C_3D_7NO at 25 ^oC

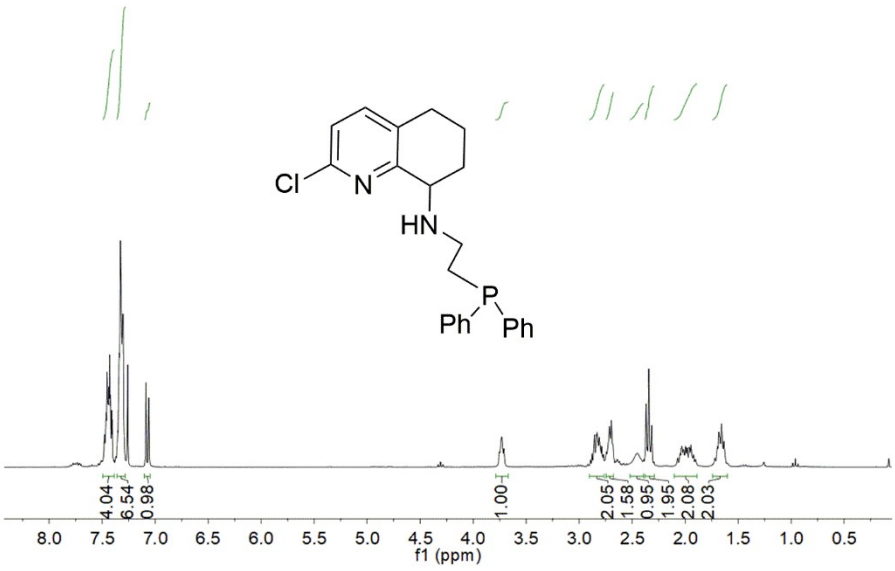


Figure S10(a) ^1H NMR spectrum of **L4**; recorded in $CDCl_3$ at 25 ^oC

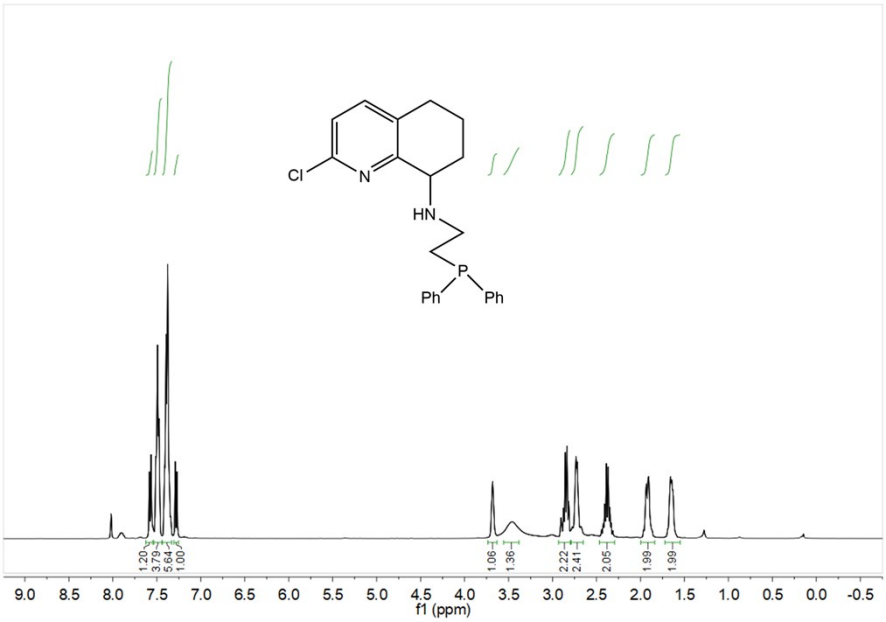
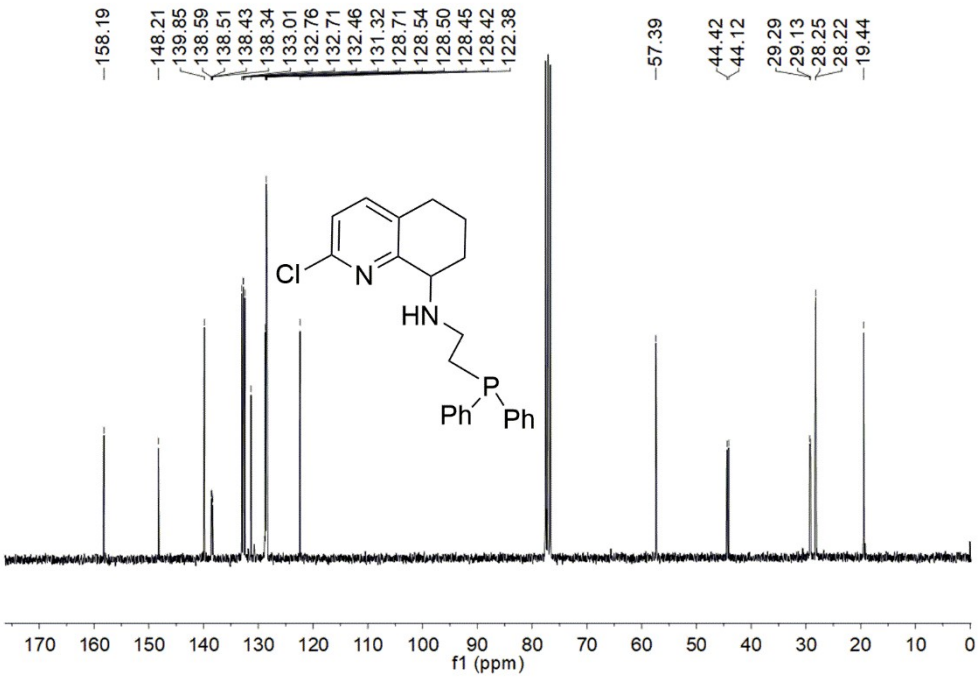


Figure S10 (b) ^{1}H NMR spectrum of **L4**; recorded in C_3D_7NO at 25 ^{o}C



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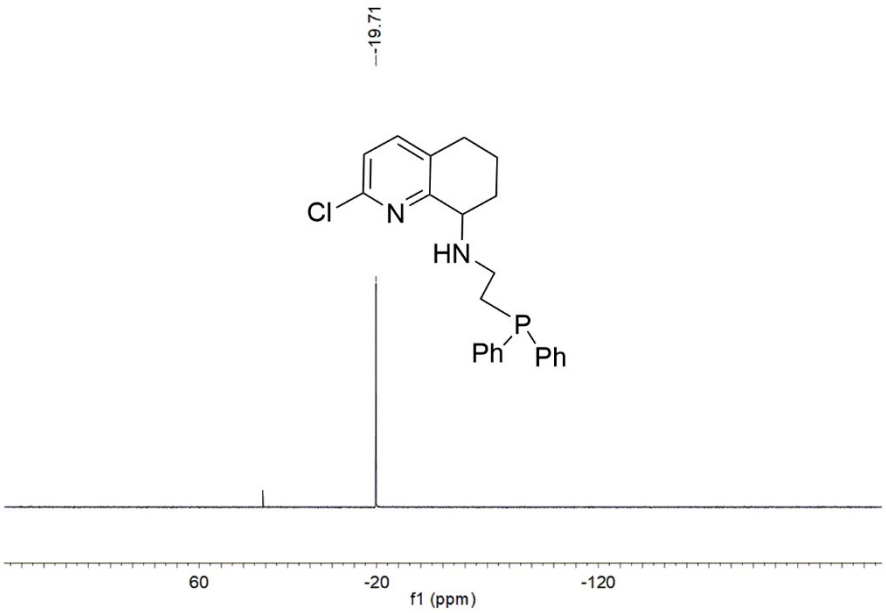


Figure S12(a) ^{31}P NMR spectrum of **L4**; recorded in $CDCl_3$ at 25 ^{o}C

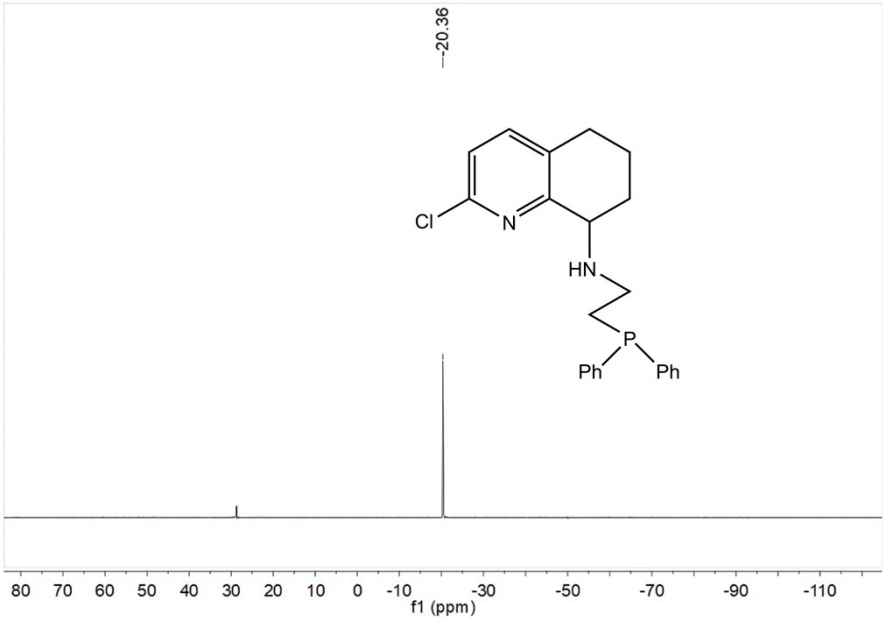


Figure S12 (b) ^{31}P NMR spectrum of **L4**; recorded in C_3D_7NO at 25 ^{o}C

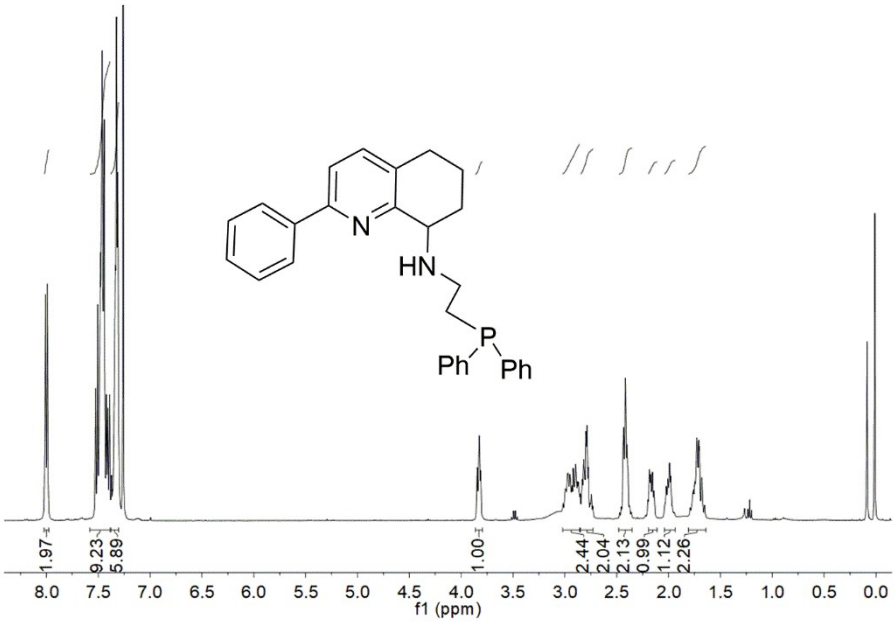


Figure S13(a) ^{1}H NMR spectrum of **L5**; recorded in $CDCl_3$ at 25 ^{o}C

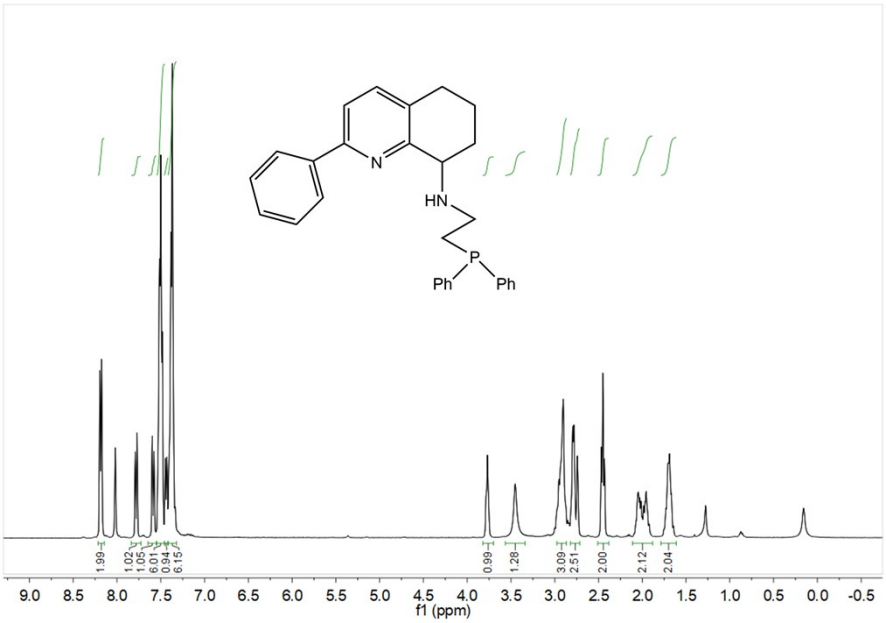


Figure S13 (b) ^{1}H NMR spectrum of **L5**; recorded in C_3D_7NO at 25 ^{o}C

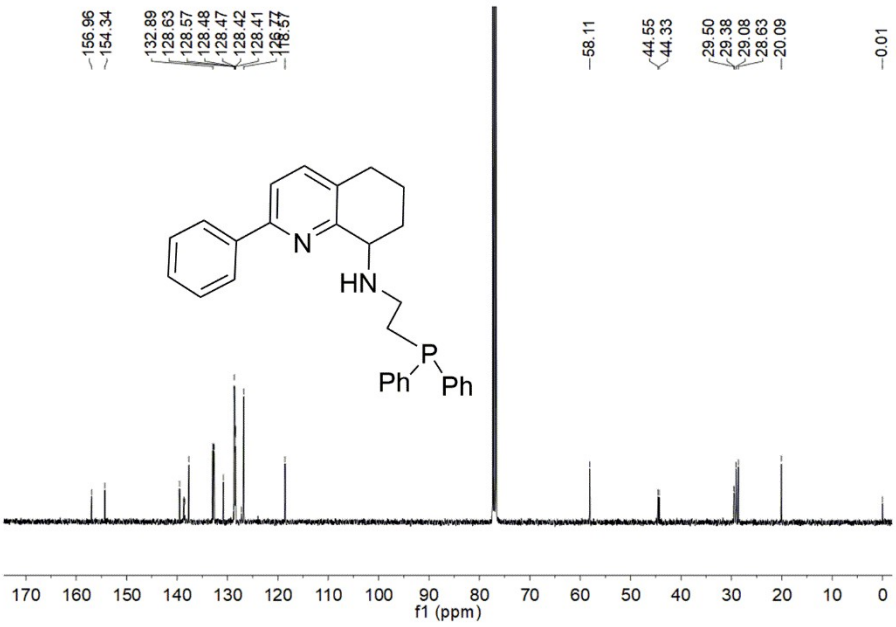


Figure S14 ^{13}C NMR spectrum of **L5**; recorded in $CDCl_3$ at 25 ^{o}C

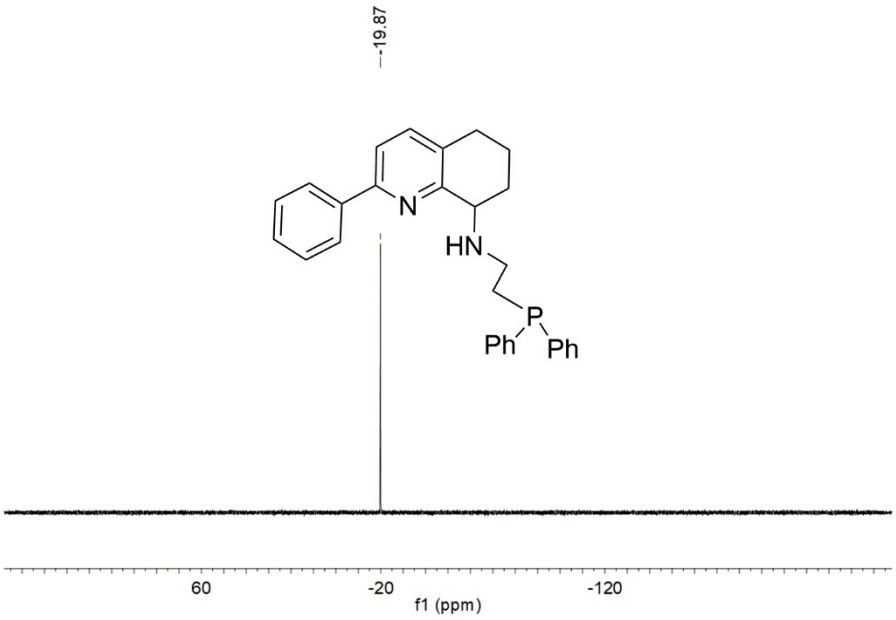


Figure S15(a) ^{31}P NMR spectrum of **L5**; recorded in $CDCl_3$ at 25 ^{o}C

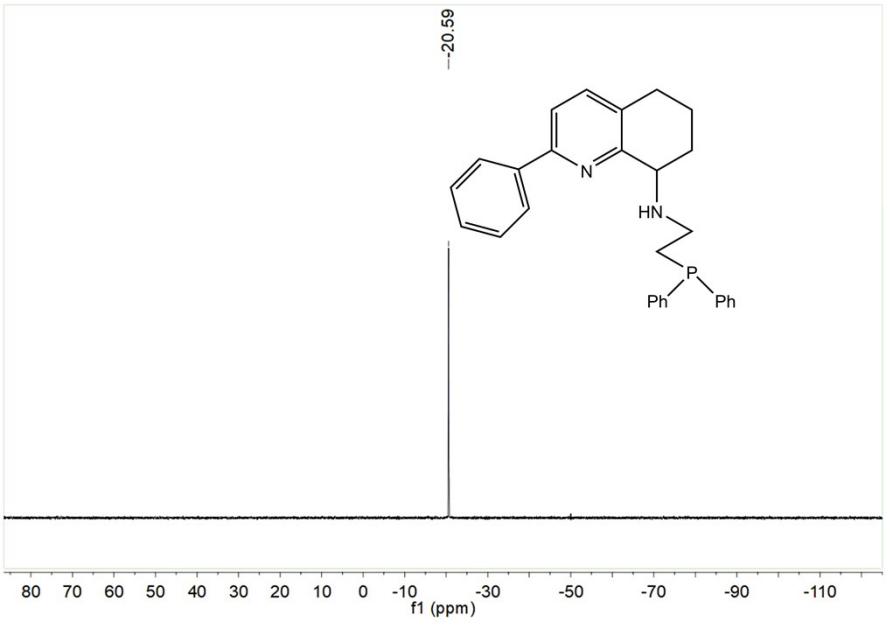


Figure S15 (b) ^{31}P NMR spectrum of **L5**; recorded in C_3D_7NO at 25 ^{o}C

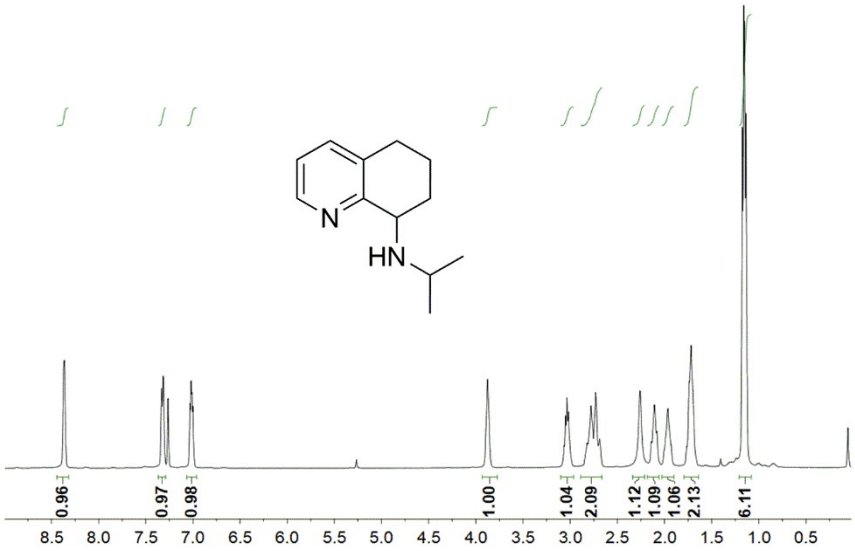


Figure S16 ^{1}H NMR spectrum of **L6**; recorded in $CDCl_3$ at 25 ^{o}C

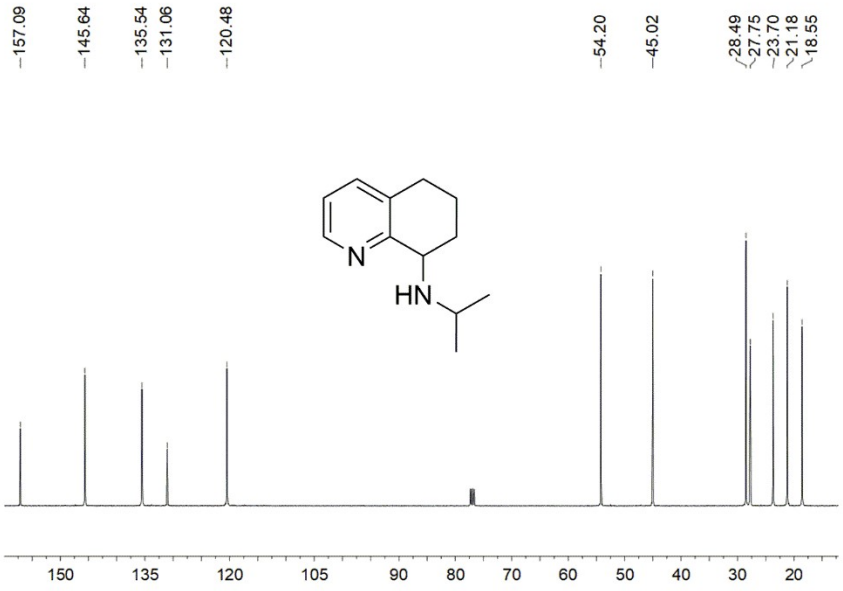


Figure S17 ^{13}C NMR spectrum of **L6**; recorded in $CDCl_3$ at 25 ^{o}C

2. $^{1}H/^{13}C/^{31}P$ NMR spectra of Zn1 – Zn7 (Figures S18 – S37)

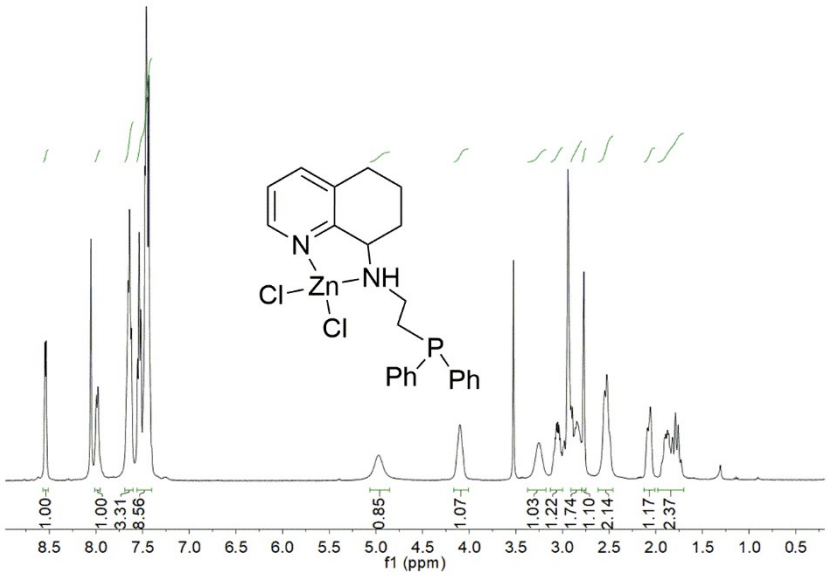


Figure S18 ^{1}H NMR spectrum of **Zn1**; recorded in C_3D_7NO at 25 °C

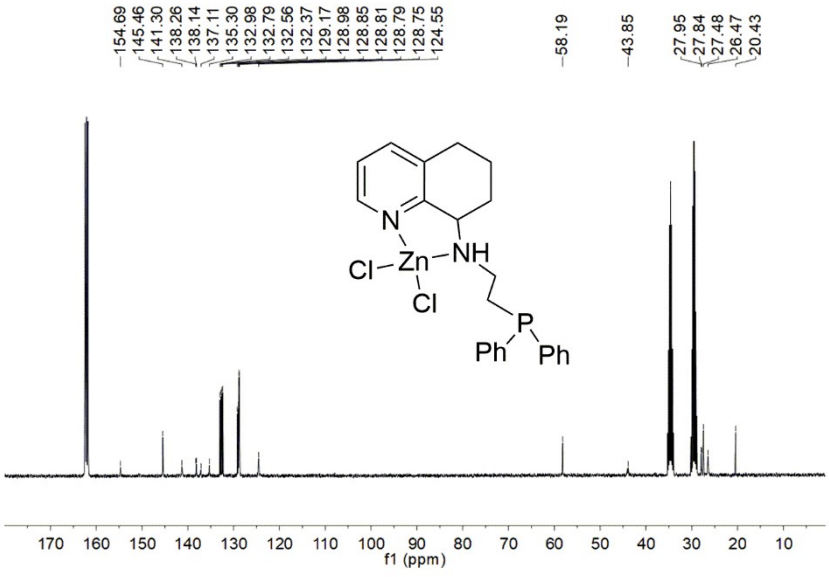


Figure S19 ^{13}C NMR spectrum of **Zn1**; recorded in C_3D_7NO at 25 °C

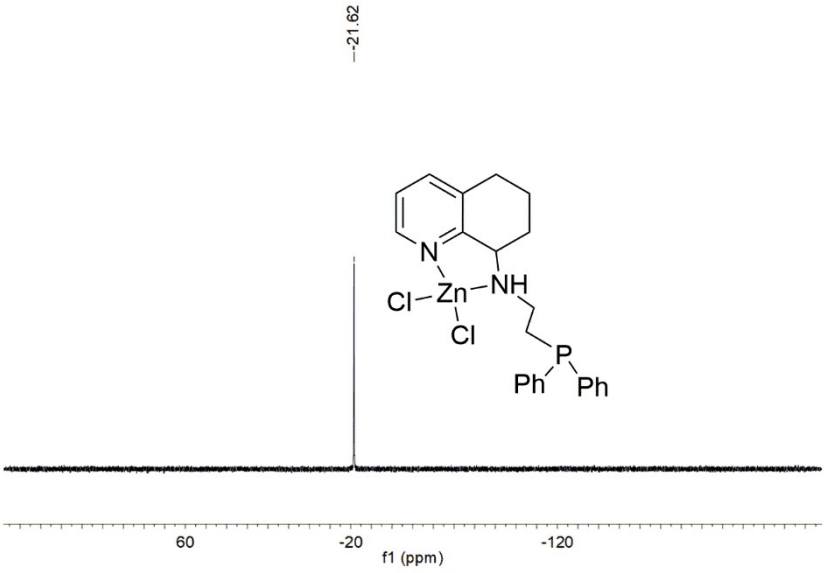


Figure S20 ^{31}P NMR spectrum of **Zn1**; recorded in C_3D_7NO at 25 ^{o}C

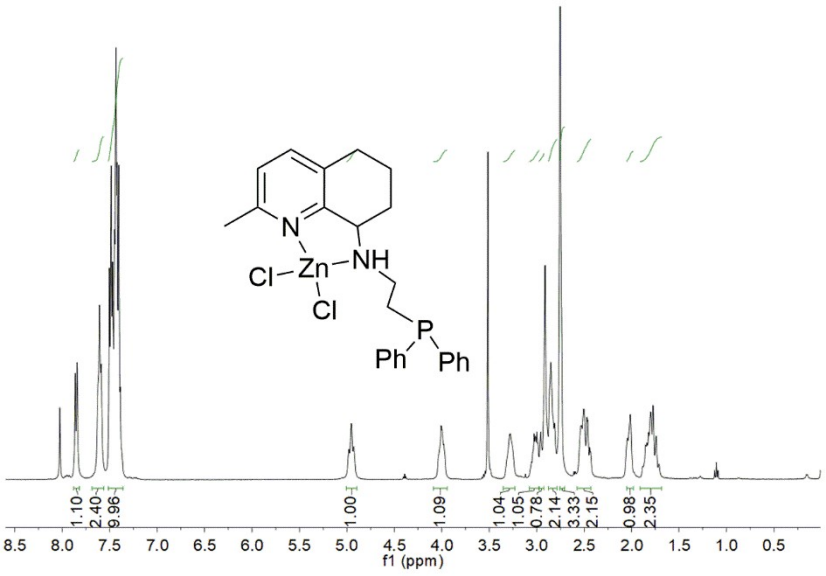


Figure S21 ^{1}H NMR spectrum of **Zn2**; recorded in C_3D_7NO at 25 ^{o}C

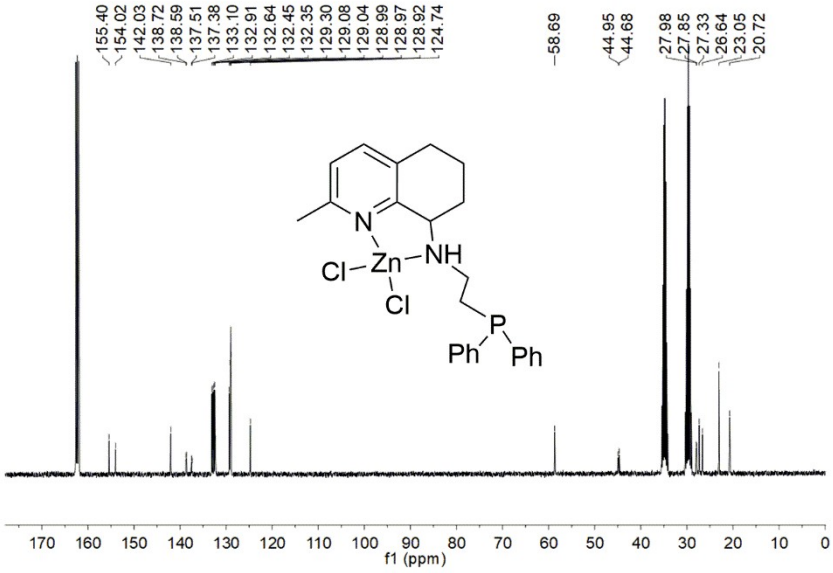


Figure S22 ^{13}C NMR spectrum of **Zn2**; recorded in C_3D_7NO at 25 ^{o}C

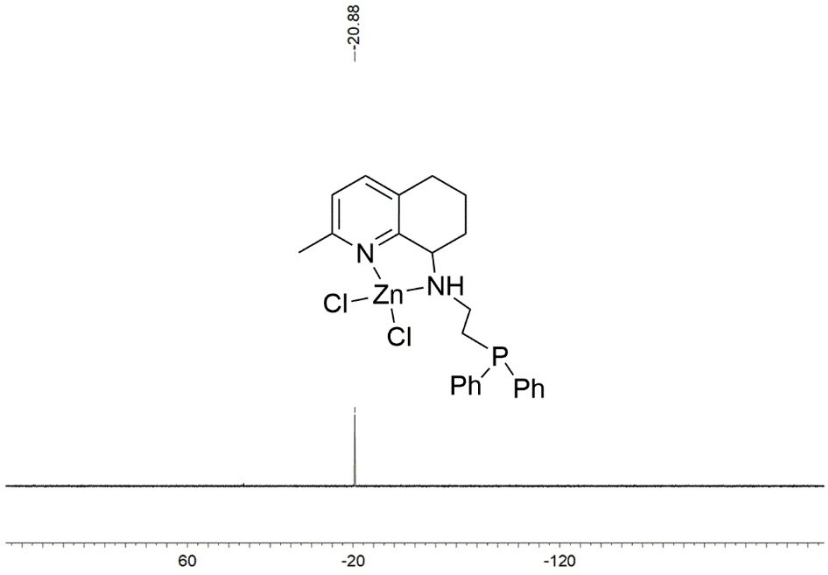


Figure S23 ^{31}P NMR spectrum of **Zn2**; recorded in C_3D_7NO at 25 ^{o}C

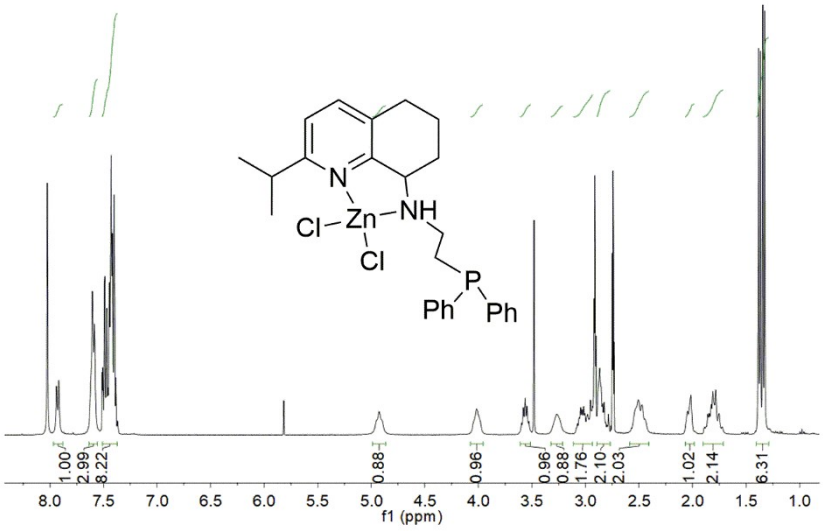


Figure S24 ^{1}H NMR spectrum of **Zn3**; recorded in C_3D_7NO at 25 ^{o}C

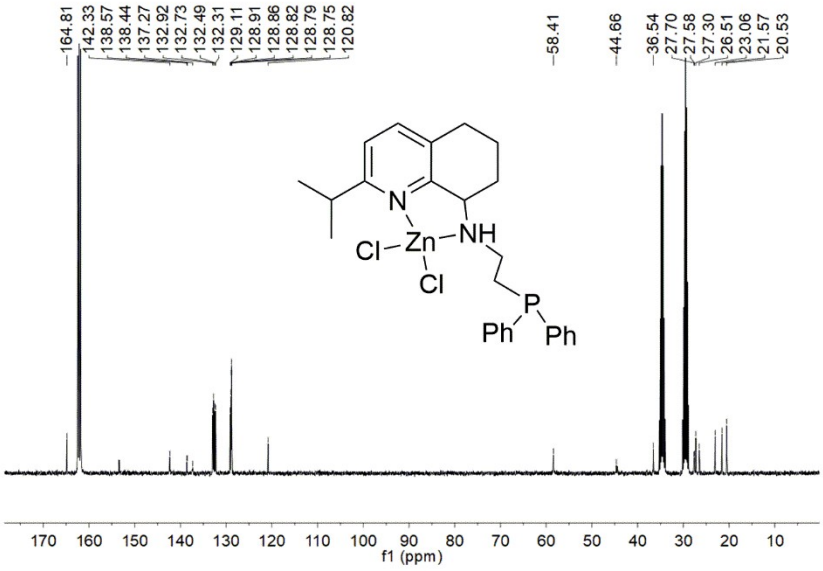


Figure S25 ^{13}C NMR spectrum of **Zn3**; recorded in C_3D_7NO at 25 ^{o}C

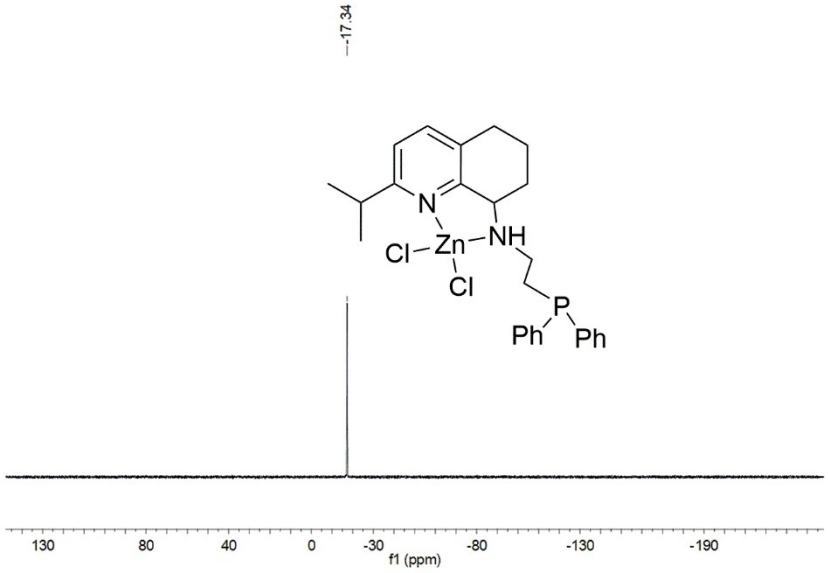


Figure S26 ^{31}P NMR spectrum of **Zn3**; recorded in C_3D_7NO at 25 ^{o}C

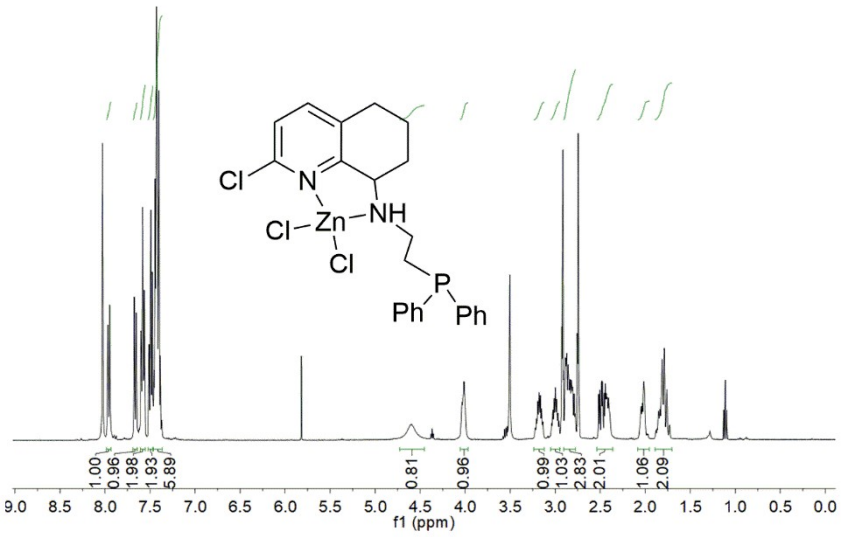


Figure S27 ^{1}H NMR spectrum of **Zn4**; recorded in C_3D_7NO at 25 ^{o}C

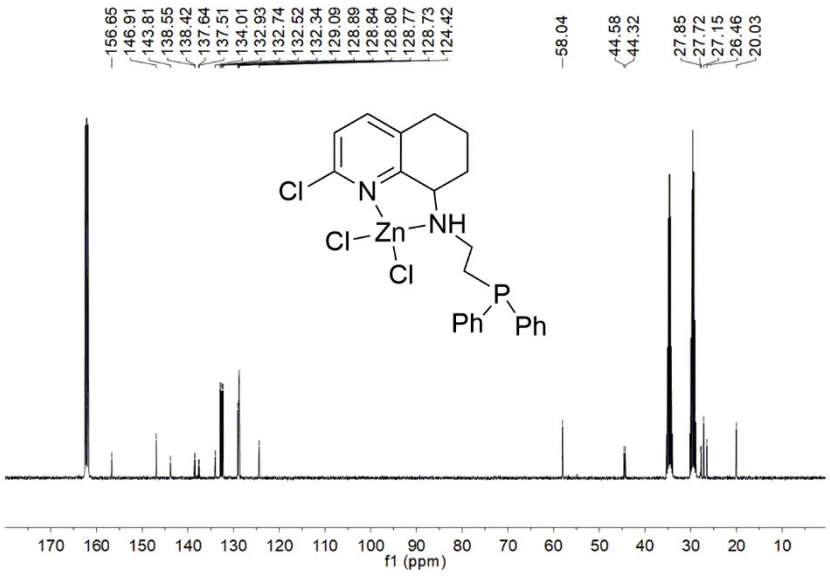


Figure S28 ^{13}C NMR spectrum of **Zn4**; recorded in C_3D_7NO at 25 ^{o}C

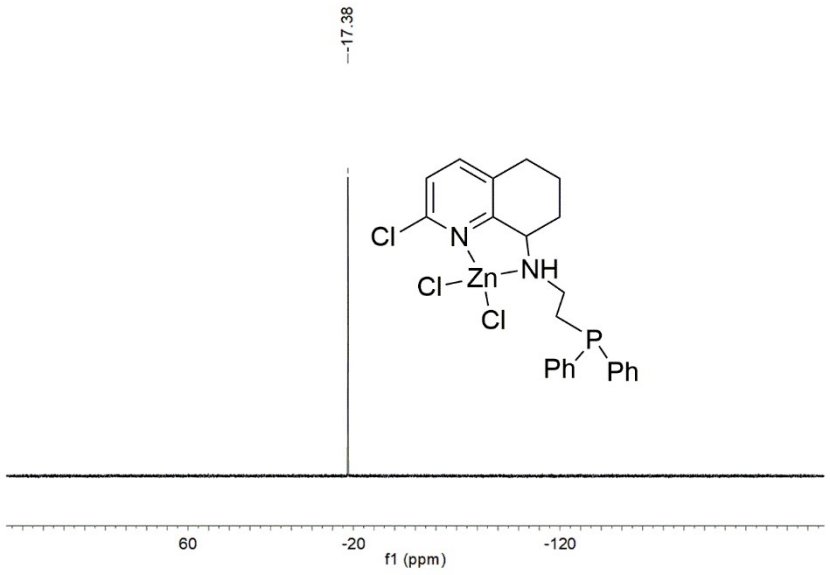


Figure S29 ^{31}P NMR spectrum of **Zn4**; recorded in C_3D_7NO at 25 ^{o}C

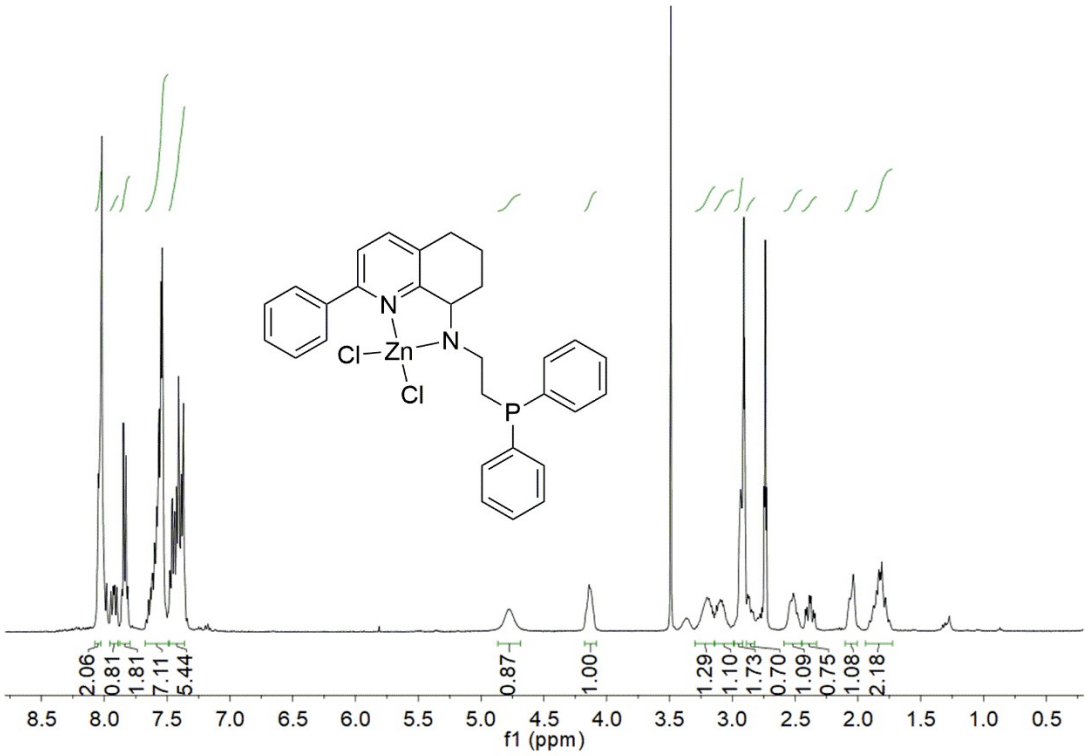


Figure S30 ^{1}H NMR spectrum of **Zn5**; recorded in C_3D_7NO at 25 ^{o}C

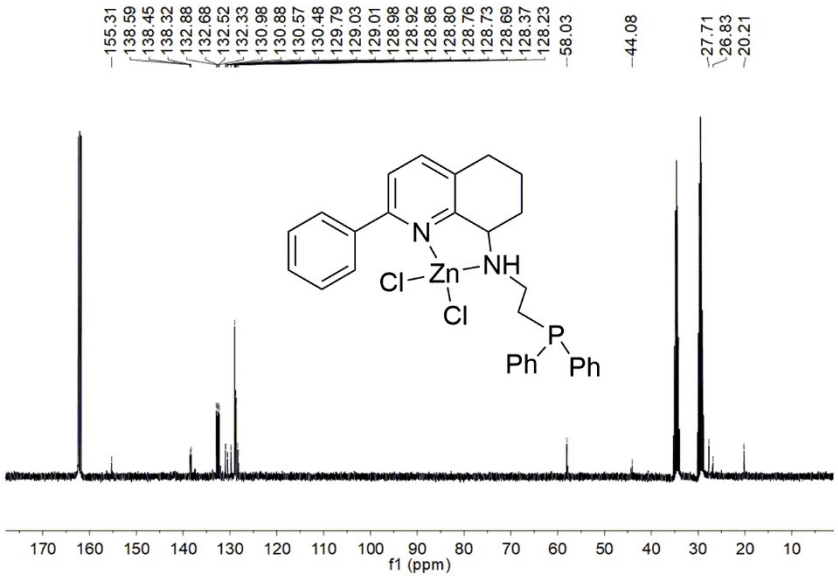


Figure S31 ^{13}C NMR spectrum of **Zn5**; recorded in C_3D_7NO at 25 ^{o}C

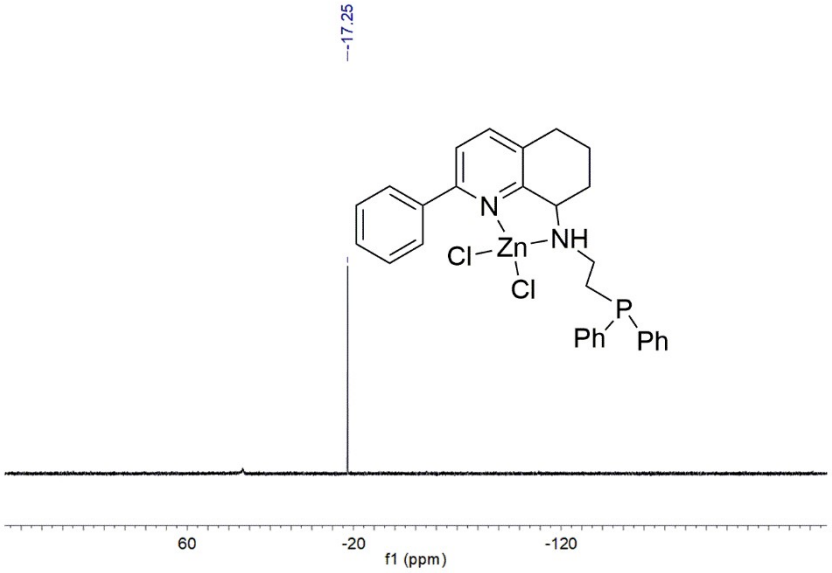


Figure S32 ^{31}P NMR spectrum of **Zn5**; recorded in C_3D_7NO at 25 ^{o}C

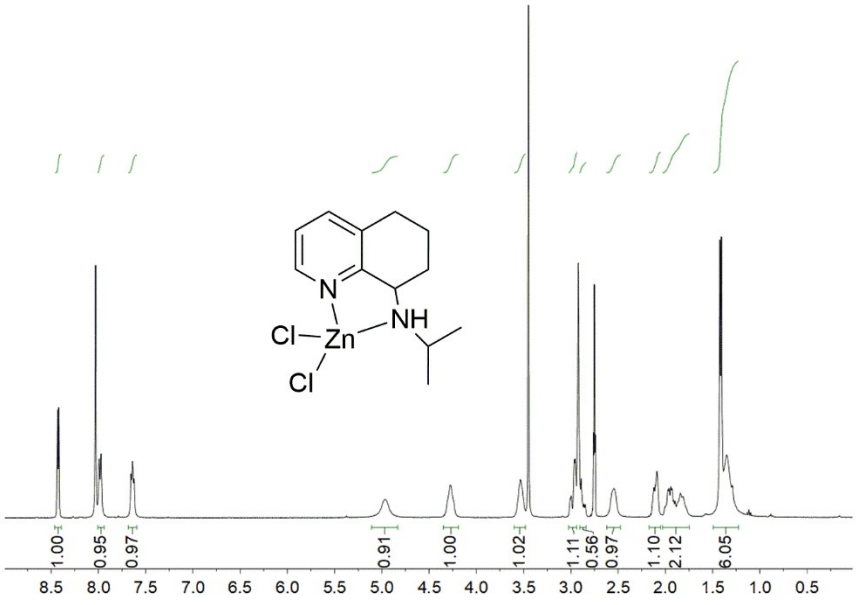


Figure S33 ^{1}H NMR spectrum of **Zn6**; recorded in C_3D_7NO at 25 ^{o}C

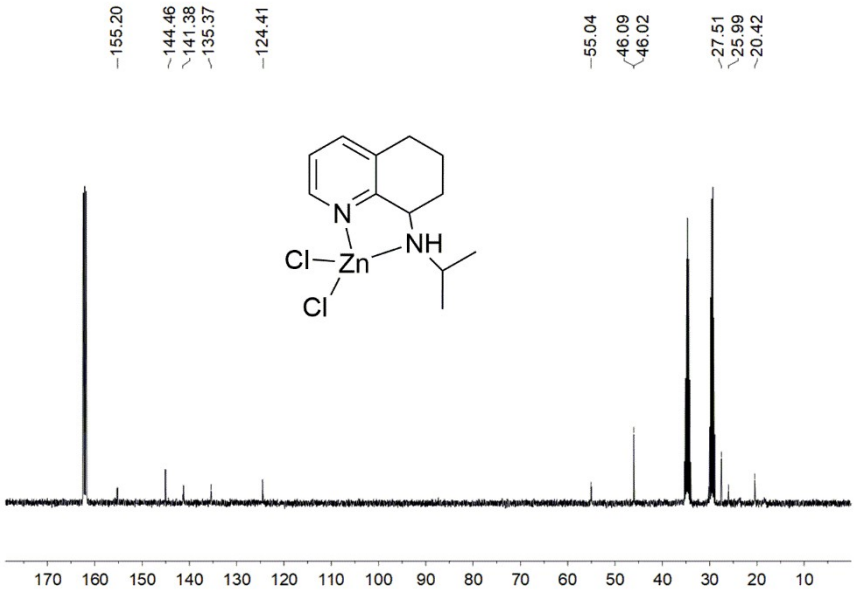


Figure S34 ^{13}C NMR spectrum of **Zn6**; recorded in C_3D_7NO at 25 °C

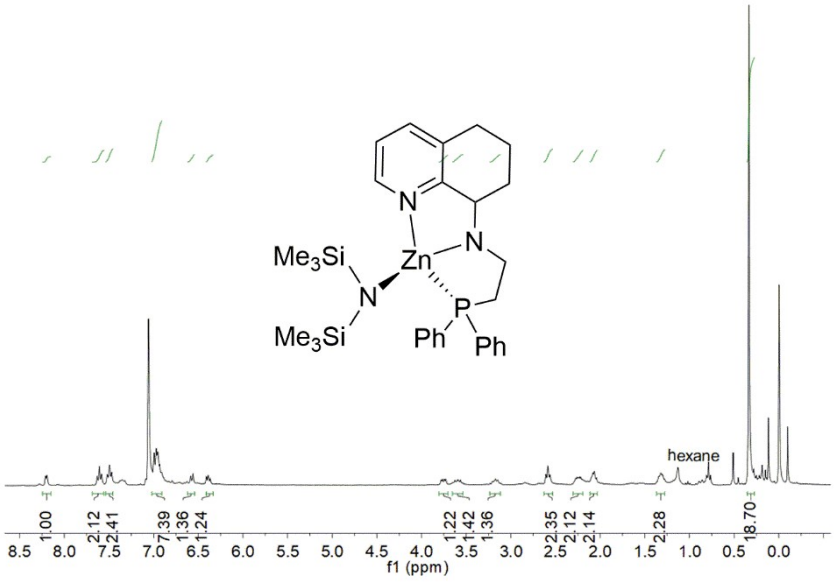


Figure S35 ^{1}H NMR spectrum of **Zn7**; recorded in C_6D_6 at 25 °C

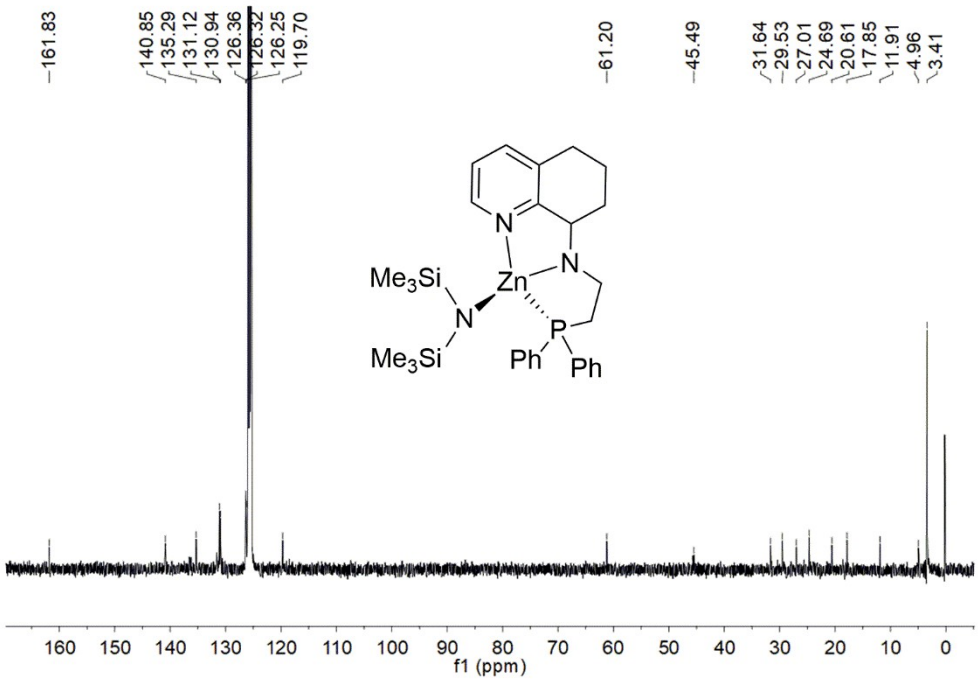


Figure S36 ^{13}C NMR spectrum of **Zn7**; recorded in C_6D_6 at 25 ^{o}C

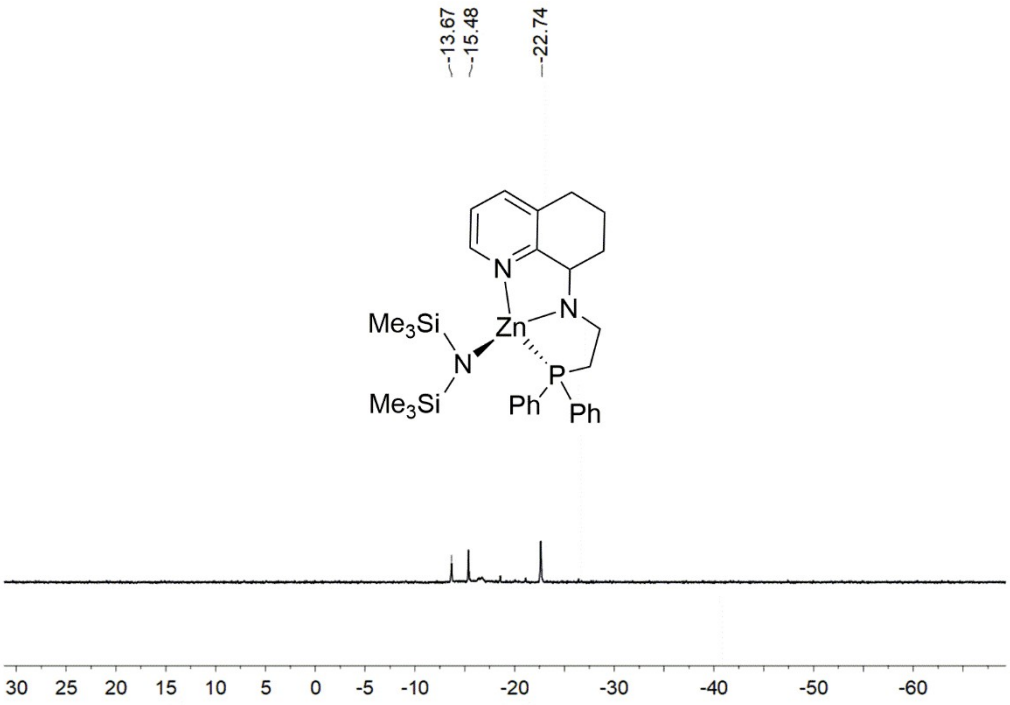


Figure S37 ^{31}P NMR spectrum of **Zn7**; recorded in C_6D_6 at 25 ^{o}C

3. Table SI-1 Comparison of the ^{31}P NMR chemical shifts for **L1 - L5** with those in **Zn1 - Zn5**

Compound	^{31}P NMR chemical shift (ppm, in $CDCl_3$)	^{31}P NMR chemical shift (ppm, in d_7-DMF)	Complex	^{31}P NMR chemical shift (ppm, in d_7-DMF)
L1 (H)	-20.74	-20.55	**Zn1**	-21.62
L2 (Me)	-20.55	-20.22	**Zn2**	-20.88
L3 (iPr)	-20.92	-20.53	**Zn3**	-17.34
L4 (Cl)	-19.71	-20.36	**Zn4**	-17.38
L5 (Ph)	-19.87	-20.59	**Zn5**	-17.25

Table SI-2 Ring opening polymerization of *rac*-LA and ε-CL using **Zn7** [a]

Entry	Monomer	[monomer]/[Zn]	t (min)	T (ºC)	Conv. (%) [b]
1	*rac*-LA	250:1	30	50	99
2	*rac*-LA	500:1	30	50	98
3	*rac*-LA	1000:1	30	50	93
4	ε-CL	1000:1	120	50	0

Conditions: 10 μmol zinc procatalyst 1.0 mL toluene; [b] Determined by ^{1}H NMR spectroscopy.

5. ^{1}H and ^{31}P NMR spectra of Zn1 + $2LiCH_2SiMe_3$ (Figure S38)

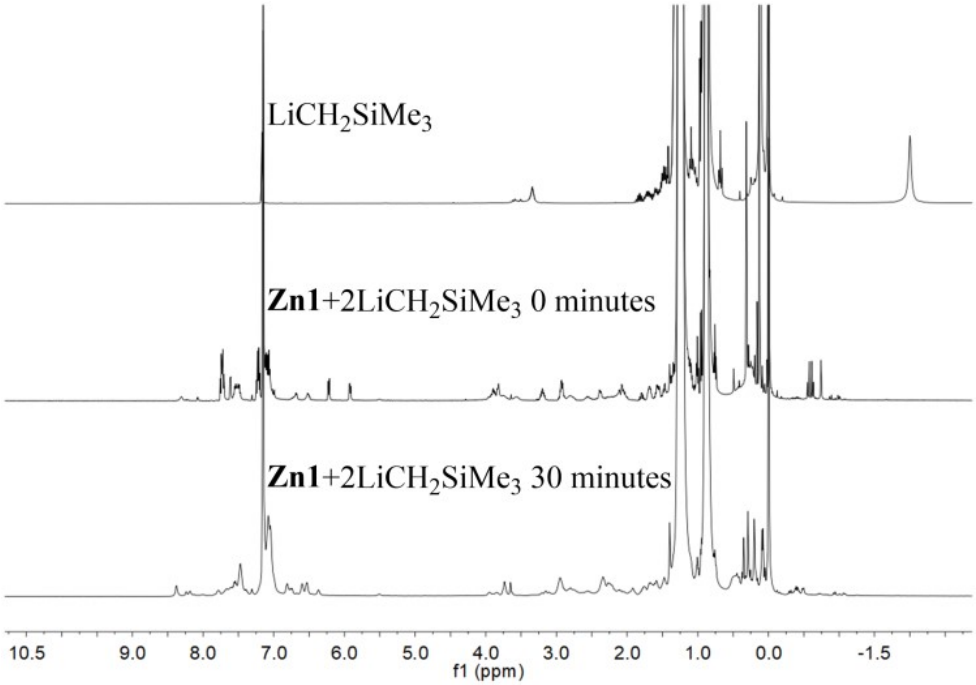


Figure S38a Stacked ^{1}H NMR spectra of $LiCH_2SiMe_3$ (top), **Zn1**+$2LiCH_2SiMe_3$ after 0 minutes (middle) and **Zn1**+$2LiCH_2SiMe_3$ after 30 minutes (bottom); all spectra recorded in C_6D_6 at 25 °C

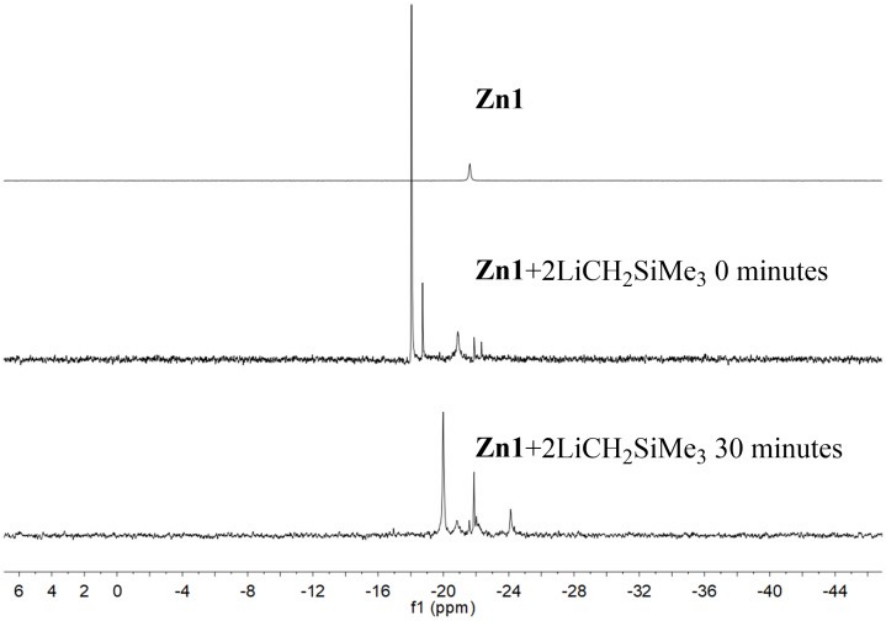


Figure S38b Stacked ^{31}P NMR spectra of **Zn1** (top), **Zn1**+$2LiCH_2SiMe_3$ after 0 minutes (middle) and **Zn1**+$2LiCH_2SiMe_3$ after 30 minutes (bottom); all spectra recorded in C_6D_6 at 25 °C

6. ^{1}H NMR spectra of Zn1 + 2LiN(SiMe$_3$)$_2$ (Figure S39)

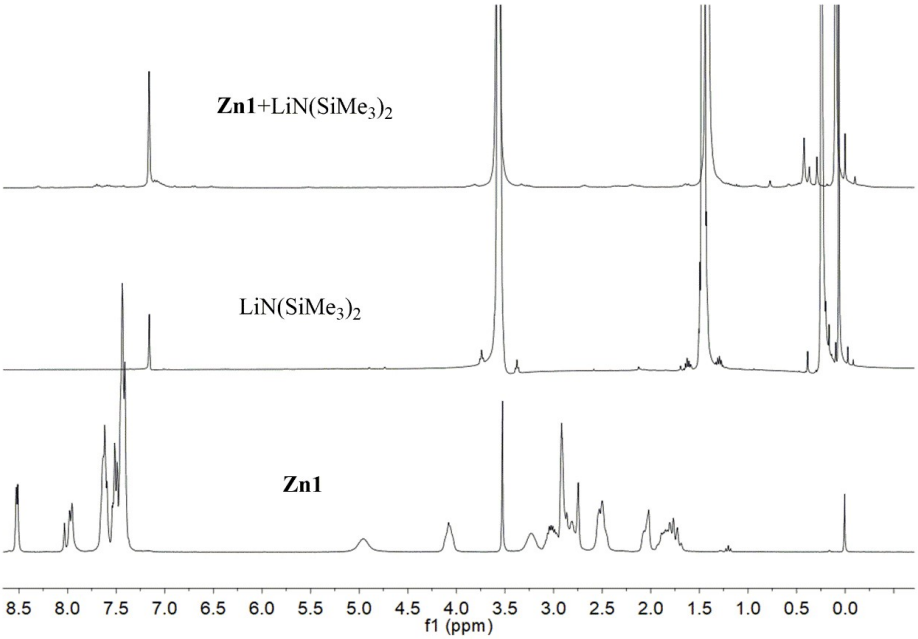


Figure S39 Stacked ^{1}H NMR spectra of **Zn1** + LiN(SiMe$_3$)$_2$ after 30 minutes (top, in C_6D_6 at 25 ^{o}C), LiN(SiMe$_3$)$_2$ (middle, in C_6D_6 at 25 ^{o}C) and **Zn1** (bottom, in C_3D_7NO at 25 ^{o}C)

7. ^{1}H NMR spectra of the PCLs obtained using Zn1/2LiN(SiMe$_3$)$_2$ ([Zn]) with different quenching solvents (Figures S40 - S42)

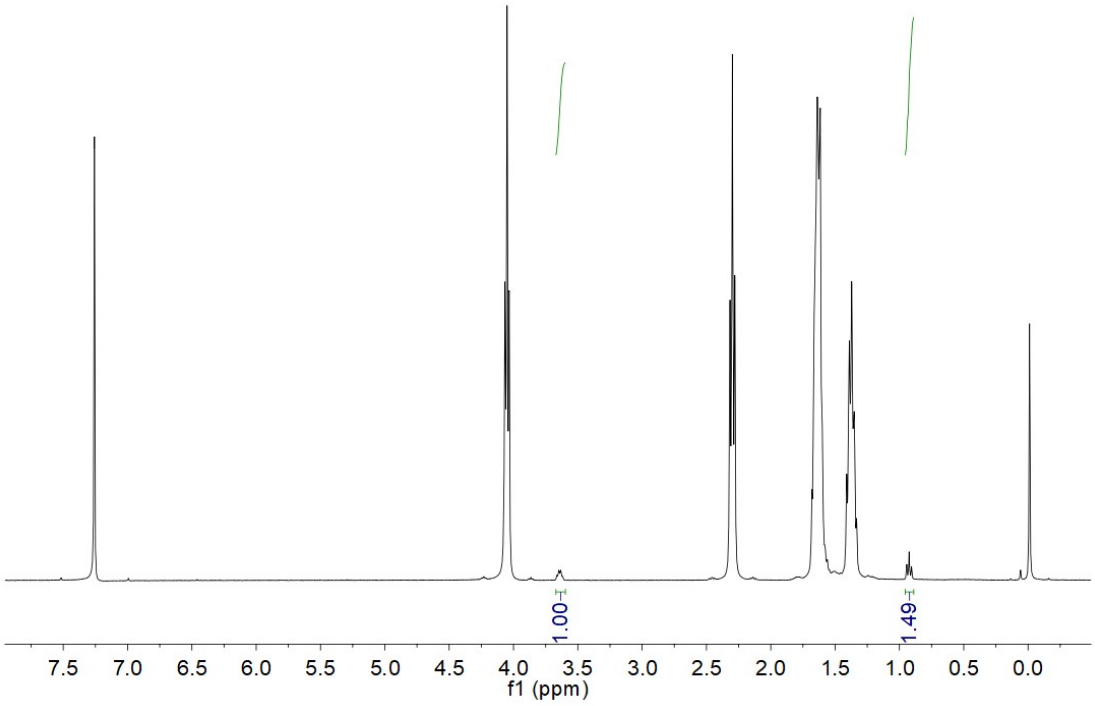


Figure S40 ^{1}H NMR spectrum of the PCL (run 6, Table 3) generated using **Zn1**/2LiN(SiMe$_3$)$_2$ ([Zn]) following quenching with *n*-butanol; recorded in $CDCl_3$ at 25 ^oC

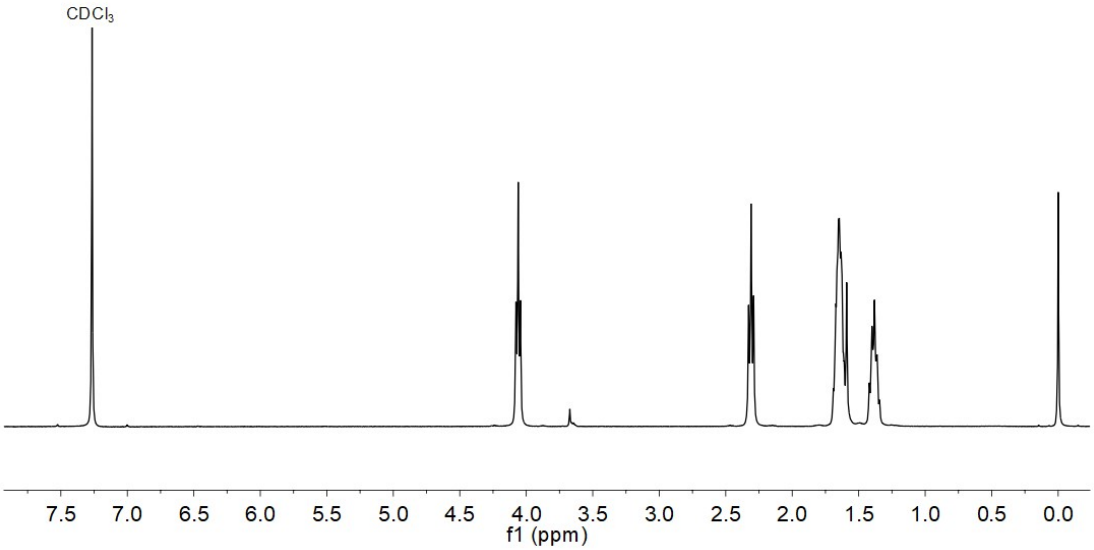


Figure S41 ^{1}H NMR spectrum of the PCL (run 6, Table 3) generated using **Zn1**/2LiN(SiMe$_3$)$_2$ ([Zn]) following quenching with methanol; recorded in $CDCl_3$ at 25 ^oC

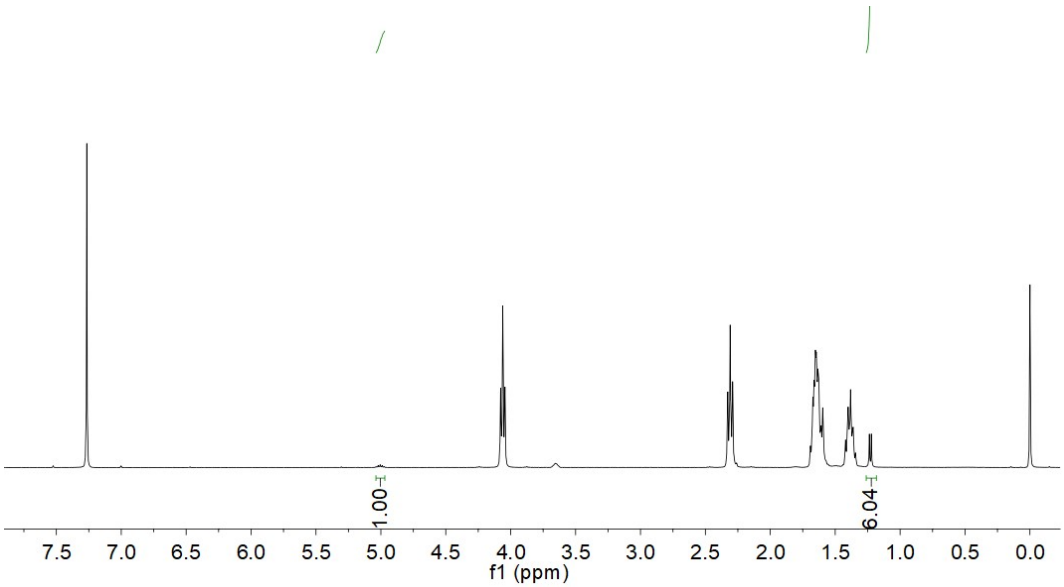


Figure S42 ^{1}H NMR spectrum of the PCL (run 6, Table 3) generated using **Zn1**/2LiN(SiMe$_3$)$_2$ ([Zn]) following quenching with *iso*-propanol; recorded in $CDCl_3$ at 25 ^oC

8. ^{1}H NMR and MALDI-TOF spectra for the PCL produced with Zn1/2LiN(SiMe$_3$)$_2$ ([Zn]) using a CL:[Zn]:BnOH molar ratio of 4000:1:1 (run 14, Table 3 & Figure S43)

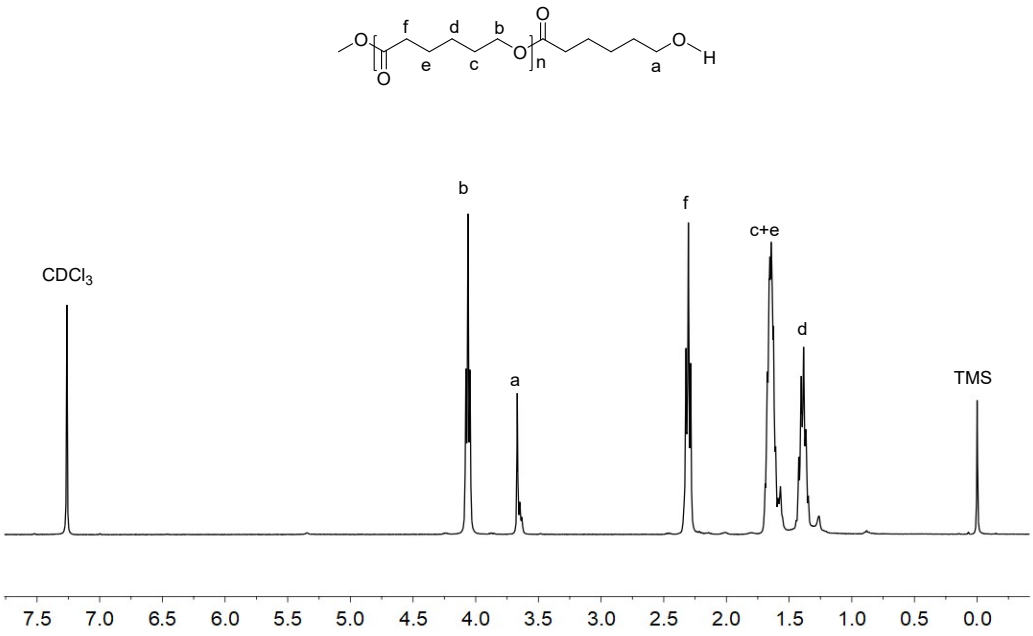


Figure S43a ^{1}H NMR spectrum of the PCL generated with **Zn1**/2LiN(SiMe$_3$)$_2$ ([Zn]) using a CL:[Zn]:BnOH molar ratio of 4000:1:1 (run 14, Table 3); recorded in $CDCl_3$, 25 ^{o}C.

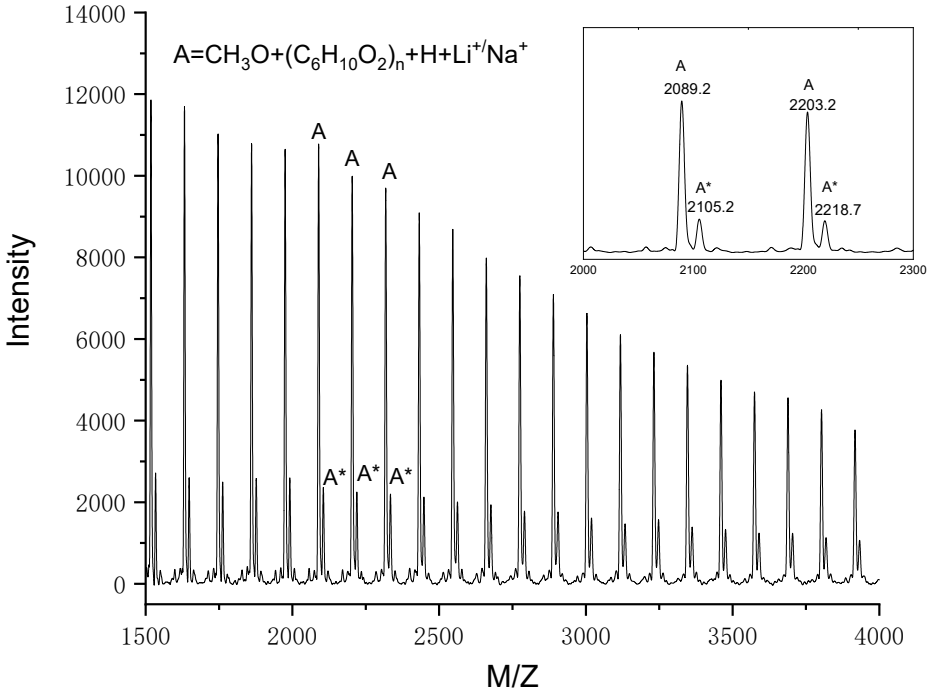
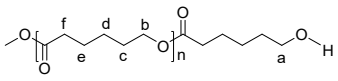


Figure S43b MALDI-TOF mass spectrum of the PCL generated with **Zn1**/2LiN(SiMe$_3$)$_2$ ([Zn]) using a CL:[Zn]:BnOH molar ratio of 4000:1:1 (run 14, Table 3).

9. ^{1}H NMR and MALDI-TOF spectra for the PCL produced with Zn1/2LiN(SiMe$_3$)$_2$ ([Zn]) using a CL:[Zn]:BnOH molar ratio of 5000:1:1 (run 15, Table 3 & Figure S44)



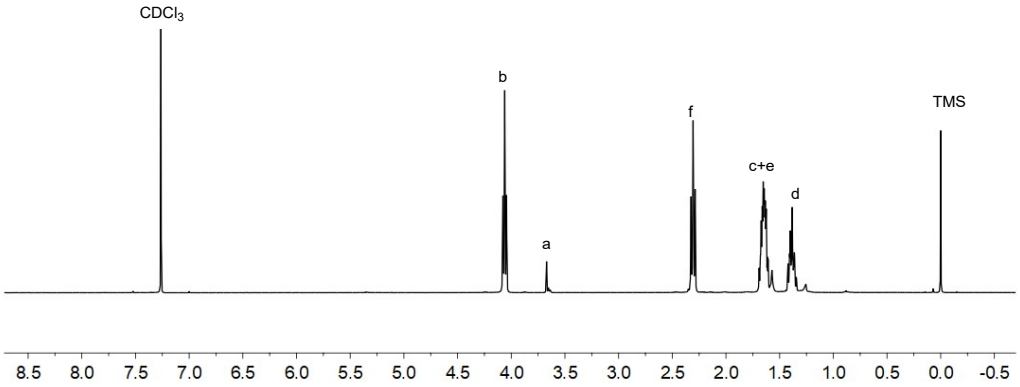


Figure S44a ^{1}H NMR spectrum of the PCL generated with **Zn1**/2LiN(SiMe$_3$)$_2$ ([Zn]) using a CL:[Zn]:BnOH molar ratio of 5000:1:1 (run 15, Table 3); recorded in $CDCl_3$, 25 ^{o}C.

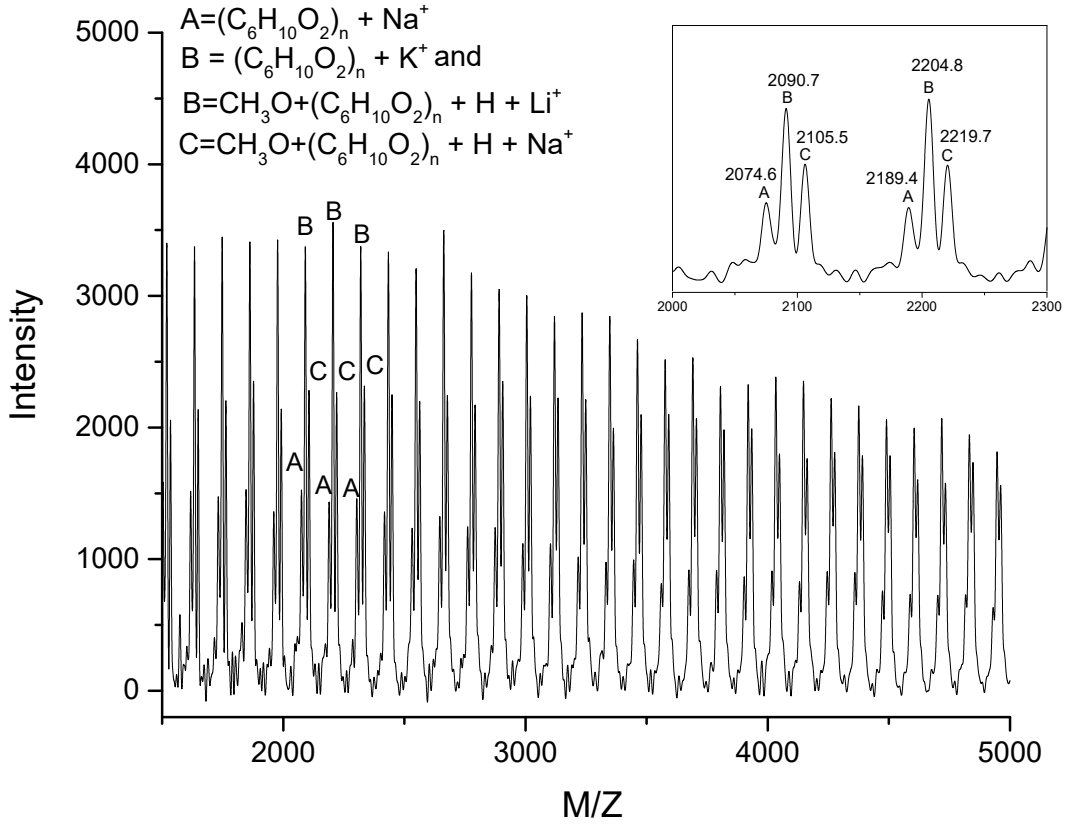


Figure S44b MALDI-TOF mass spectrum of the PCL generated with **Zn1**/2LiN(SiMe$_3$)$_2$ ([Zn]) using a CL:[Zn]:BnOH molar ratio of 5000:1:1 (run 15, Table 3).