Electronic Supplementary Material (ESI) for Dalton Transactions.

Ortho-phenyl dialkylphosphonium sulfonate compounds: two rotamers in equilibrium

Emmanuelle Martin-Mothes, Emmanuel Puig, Laure Vendier, Christian Bijani, Mary Grellier and Sébastien Bontemps*

CNRS, LCC (Laboratoire de Chimie de Coordination), 205 route de Narbonne, BP 44099, F-31077 Toulouse Cedex 4, France and Université de Toulouse, UPS, INPT, F-31077 Toulouse Cedex 4, France

Table of Contents

NMR and IR Spectra of compound 1

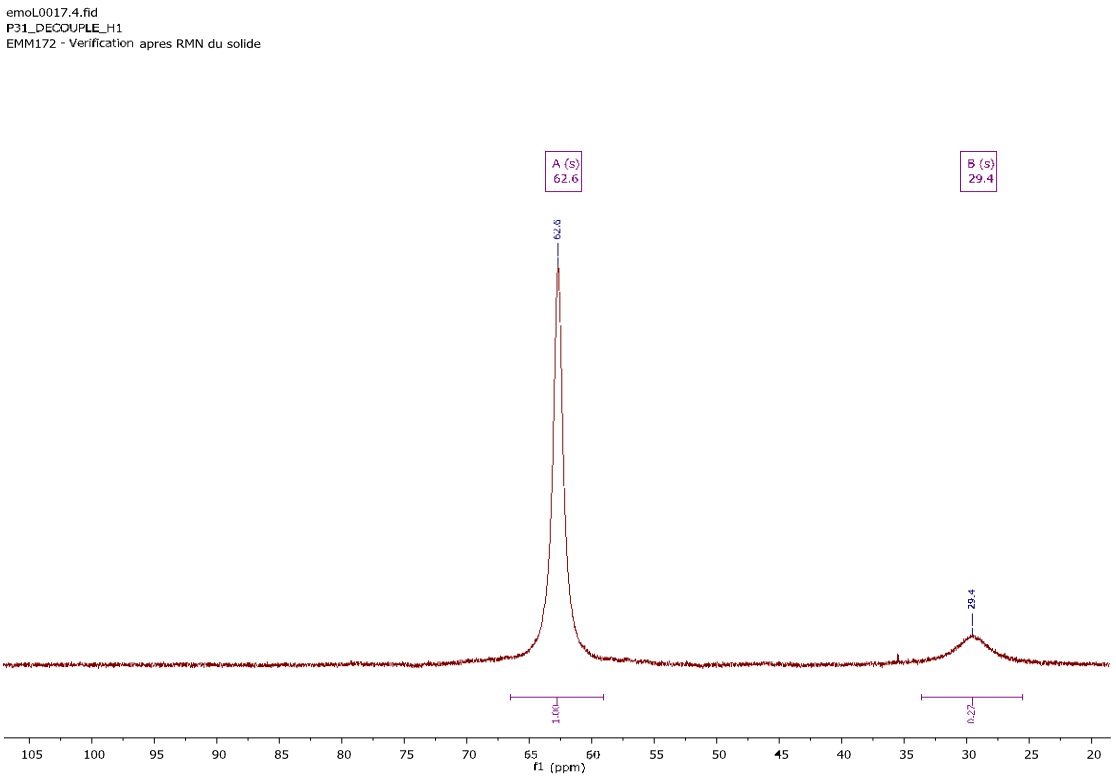


*Figure S1. $^{31}P\{^{1}H\}$ NMR spectrum for compound **1** at 298 K in CD_2Cl_2*

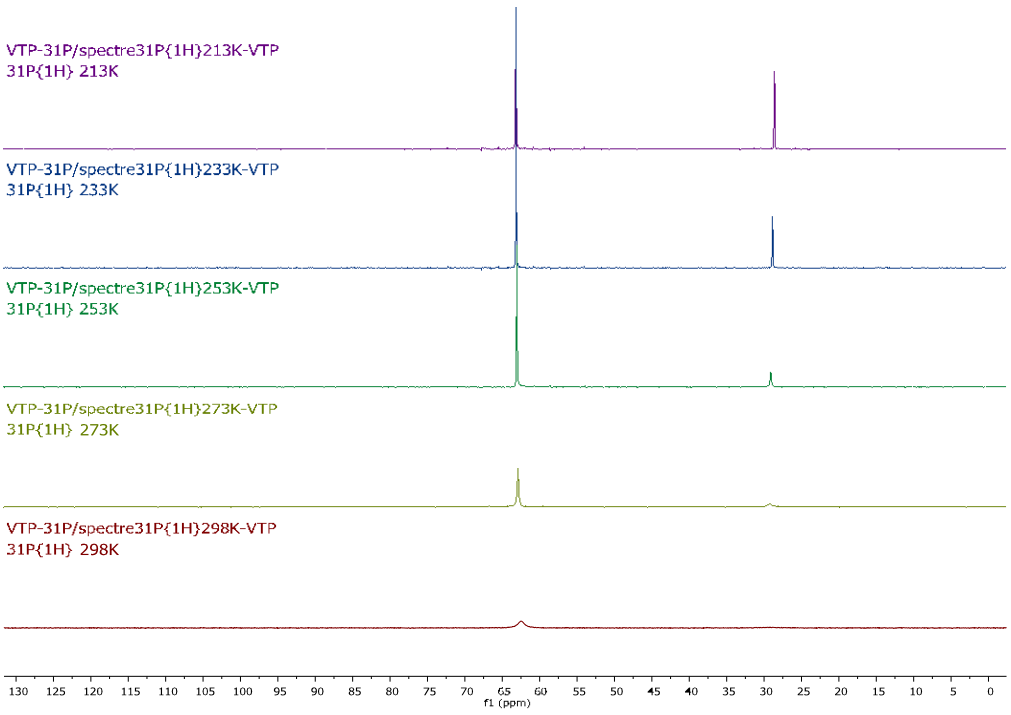


*Figure S2. Variable temperature $^{31}P\{^{1}H\}$ NMR spectra for compound **1** from 298 K to 213 K in CD_2Cl_2*

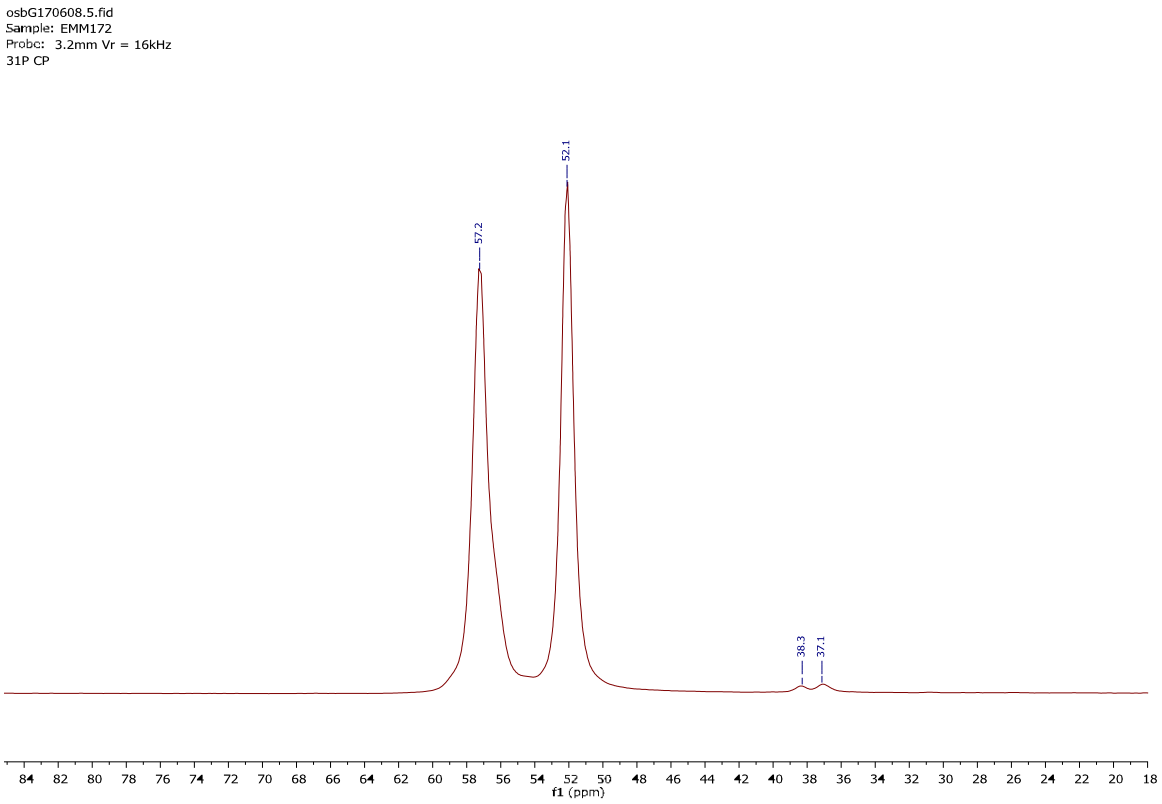


*Figure S3. Solid state CPMas ^{31}P NMR spectrum for compound **1***

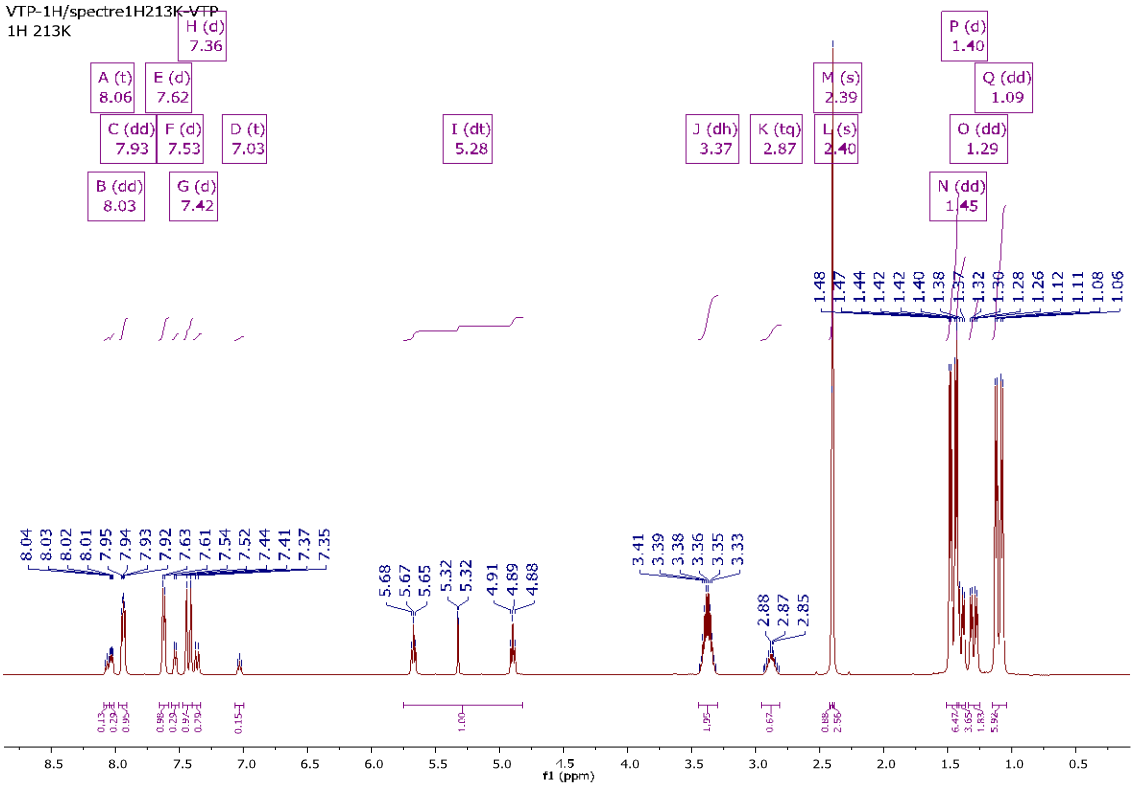


*Figure S4. ^{1}H NMR spectrum for compound **1** at 213 K in CD_2Cl_2*

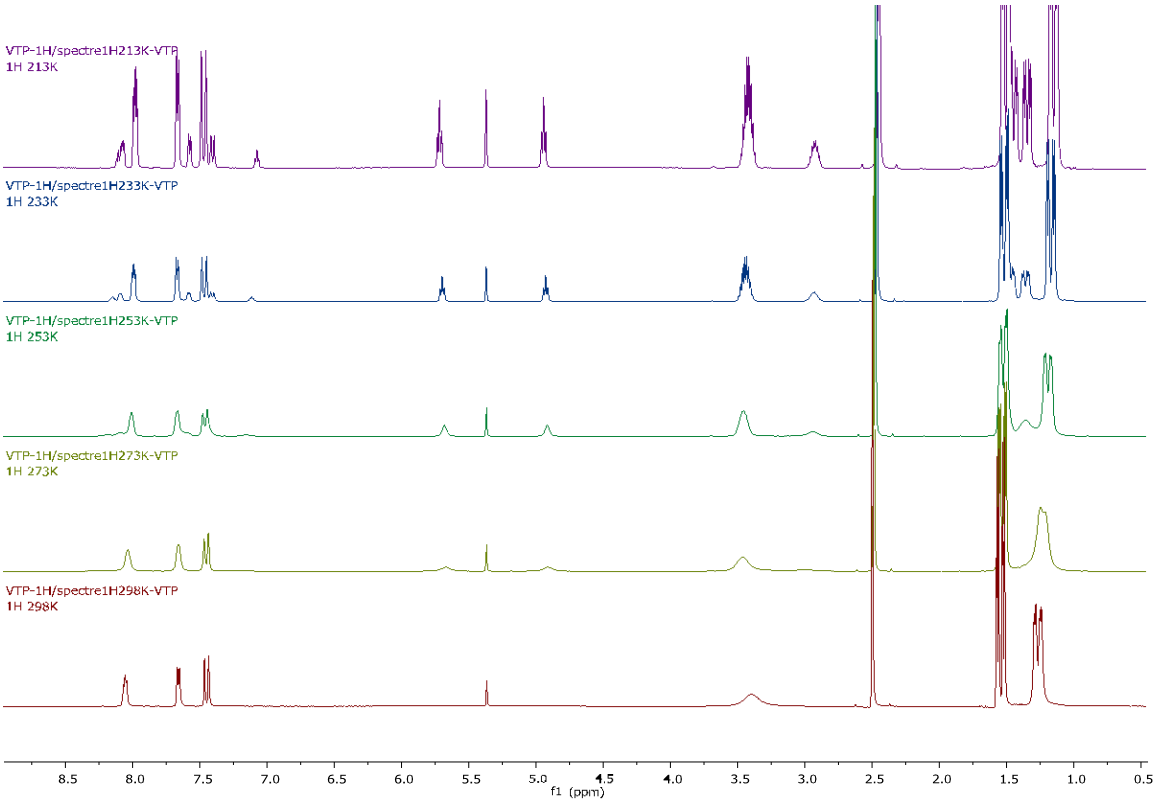


*Figure S5. Variable temperature ^{1}H NMR spectra for compound **1** from 298 K to 213 K in CD_2Cl_2*

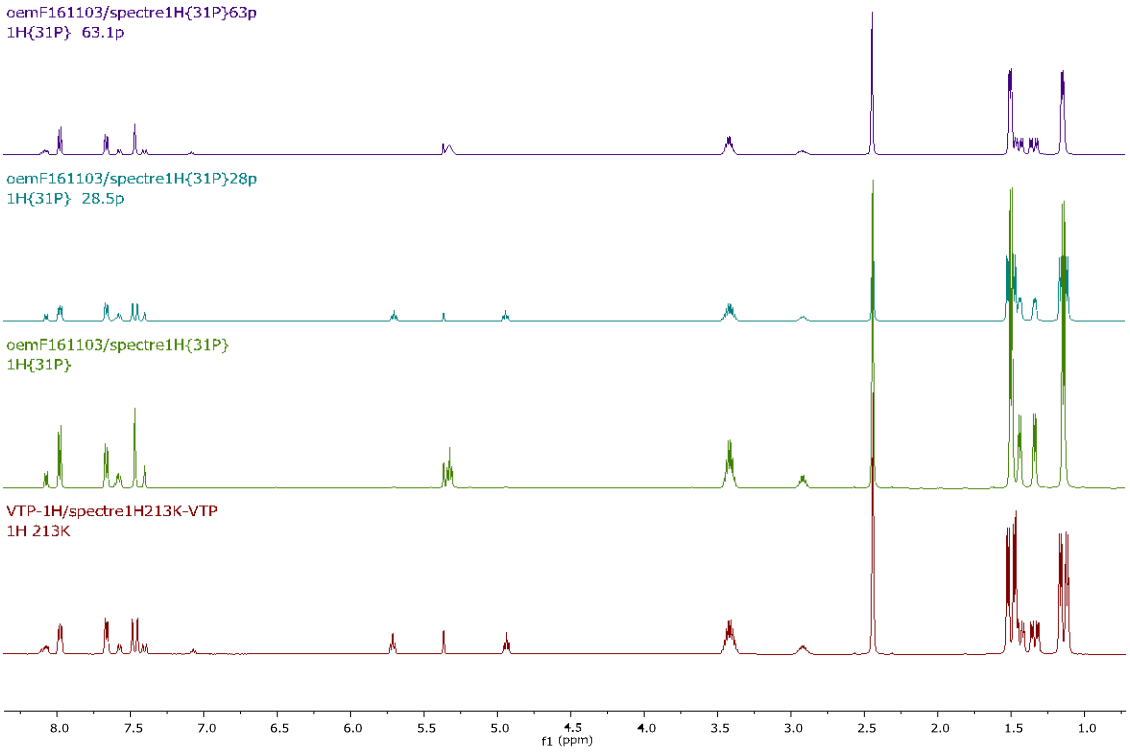


*Figure S6. ^{1}H NMR analysis of compound **1** at 213 K in CD_2Cl_2, from bottom to top: no ^{31}P decoupling, broad band ^{31}P decoupling, selective ^{31}P decoupling at 28 ppm, selective ^{31}P decoupling at 63 ppm.*

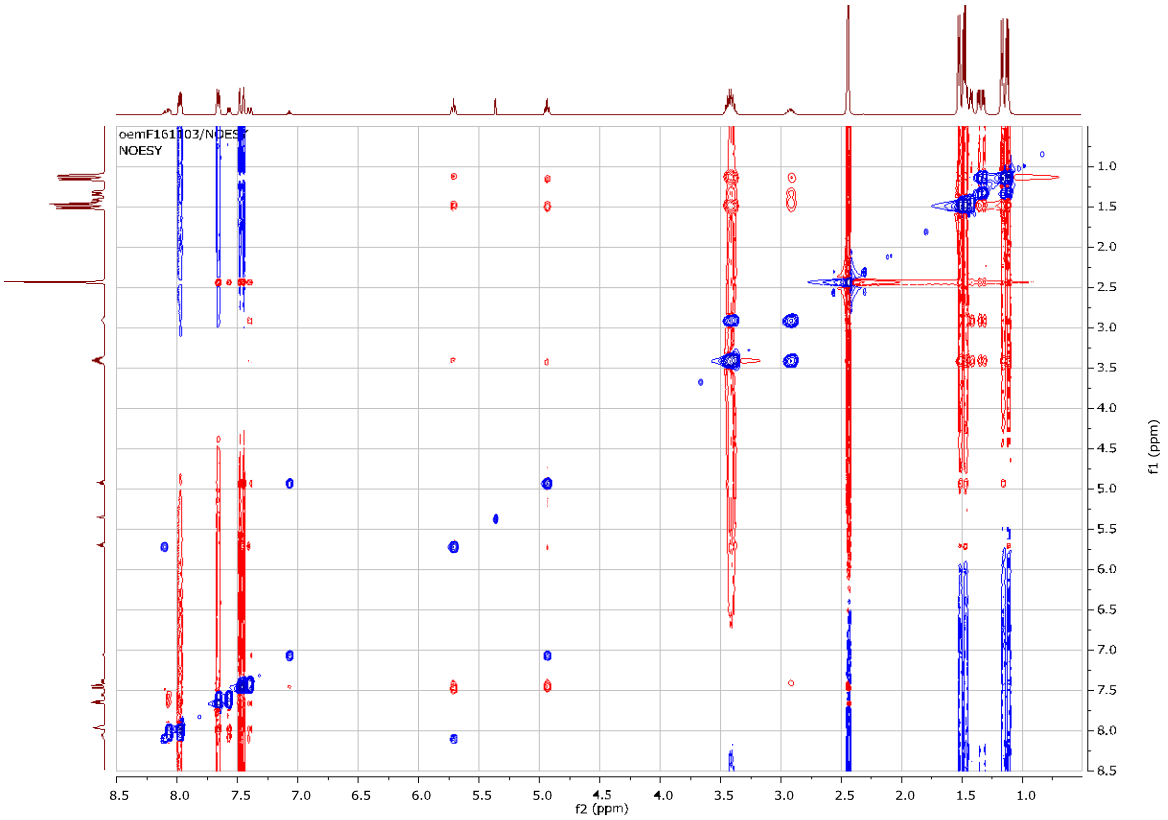


*Figure S7. NOESY $^1H/^1H$ spectrum for compound **1** at 213 K in CD_2Cl_2*

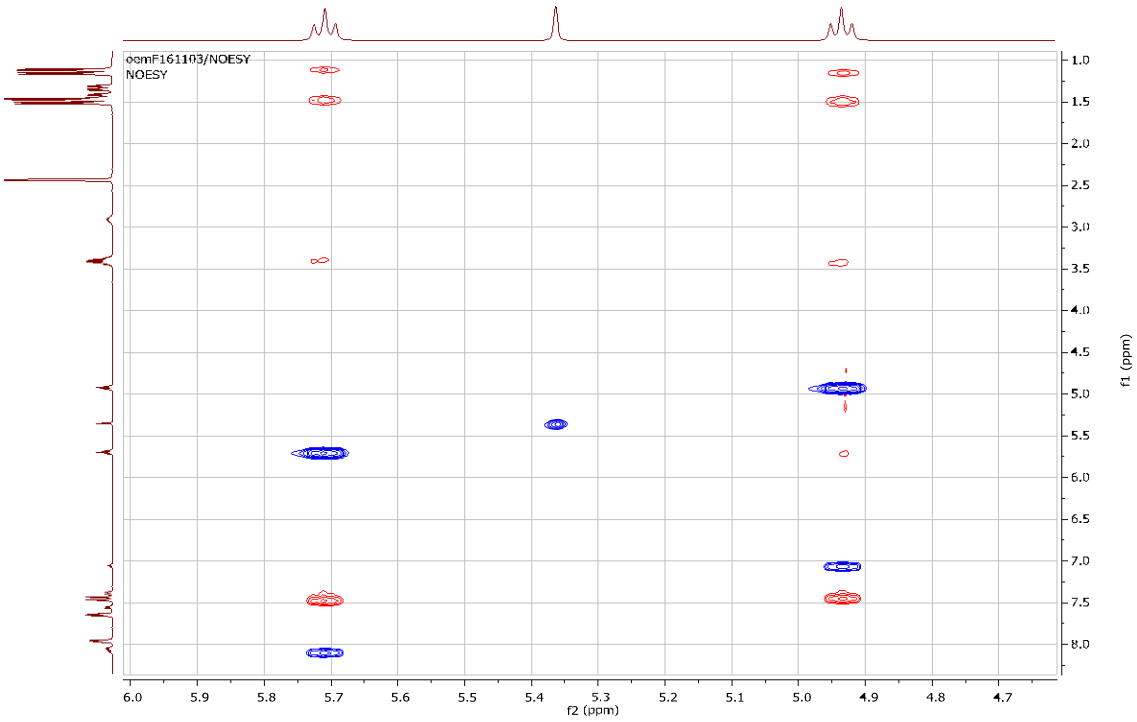


*Figure S8. NOESY $^1H/^1H$ spectrum for compound **1** at 213 K, zoom on H-P form 1 in CD_2Cl_2*

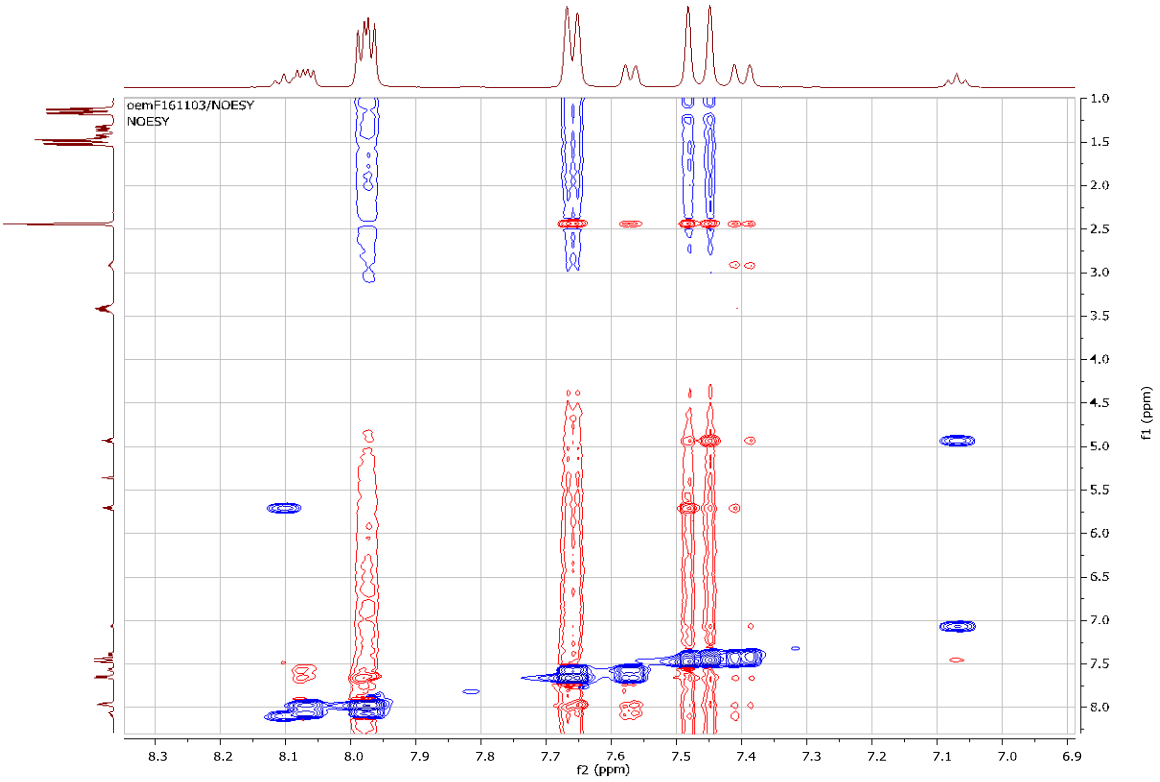


*Figure S9. NOESY $^{1}H/^{1}H$ spectrum for compound **1** at 213 K, zoom on H-P form 2 in CD_2Cl_2*

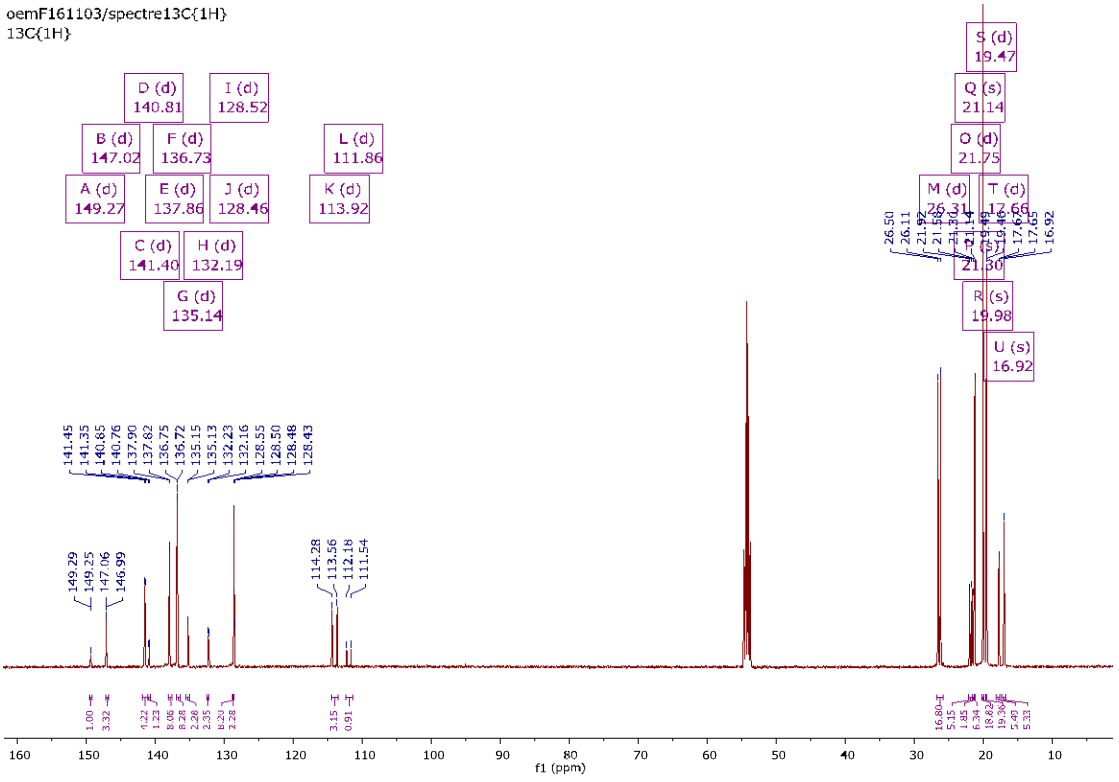


*Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1** at 213 K in CD_2Cl_2*

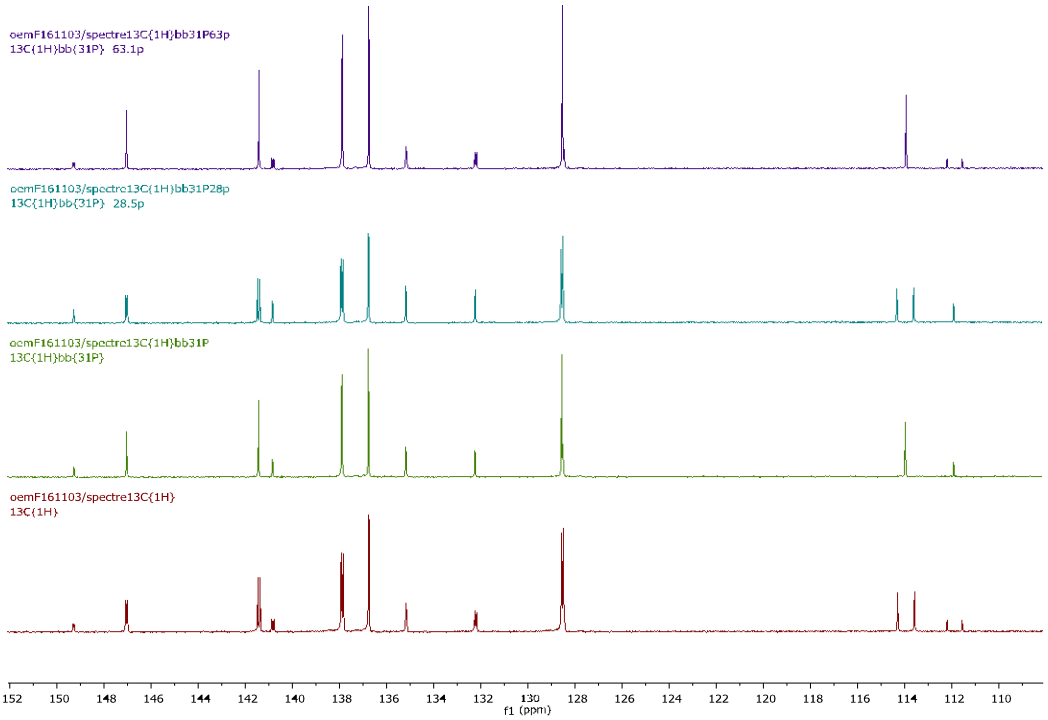


*Figure S11. $^{13}C\{^{1}H\}$ NMR analysis of compound **1** at 213 K in CD_2Cl_2, from bottom to top: no ^{31}P decoupling, broad band ^{31}P decoupling, selective ^{31}P decoupling at 28.5 ppm, selective ^{31}P decoupling at 63.1 ppm.*

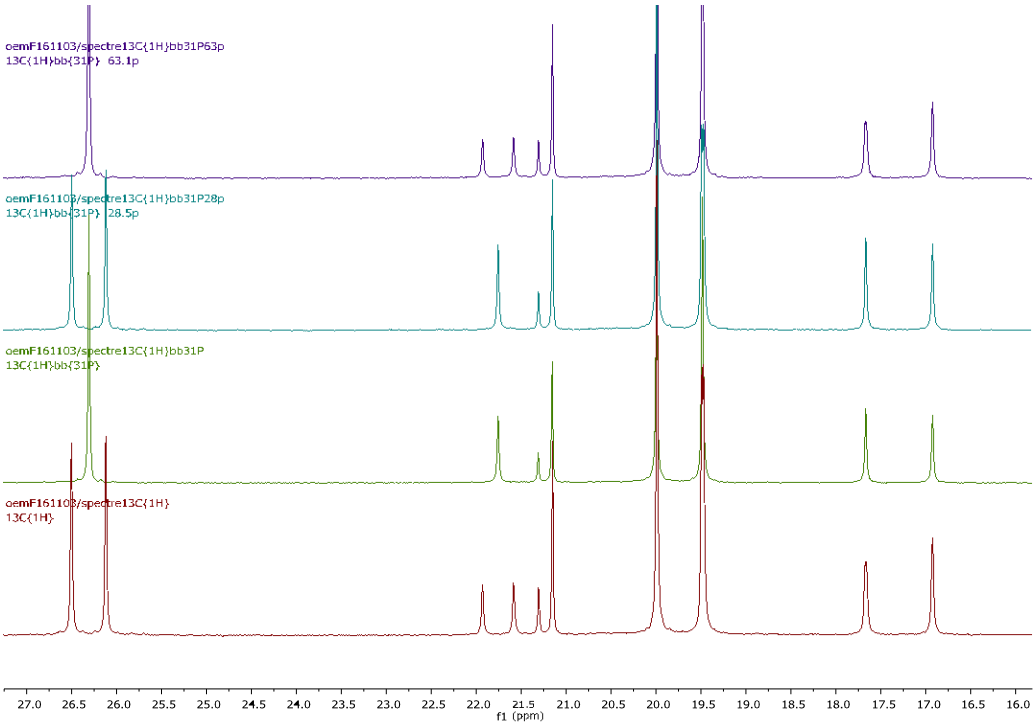


*Figure S12. $^{13}C\{^{1}H\}$ NMR analysis of compound **1** at 213 K in CD_2Cl_2, from bottom to top: no ^{31}P decoupling, broad band ^{31}P decoupling, selective ^{31}P decoupling at 28.5 ppm, selective ^{31}P decoupling at 63.1 ppm, 27.5 to 16.0 ppm window.*

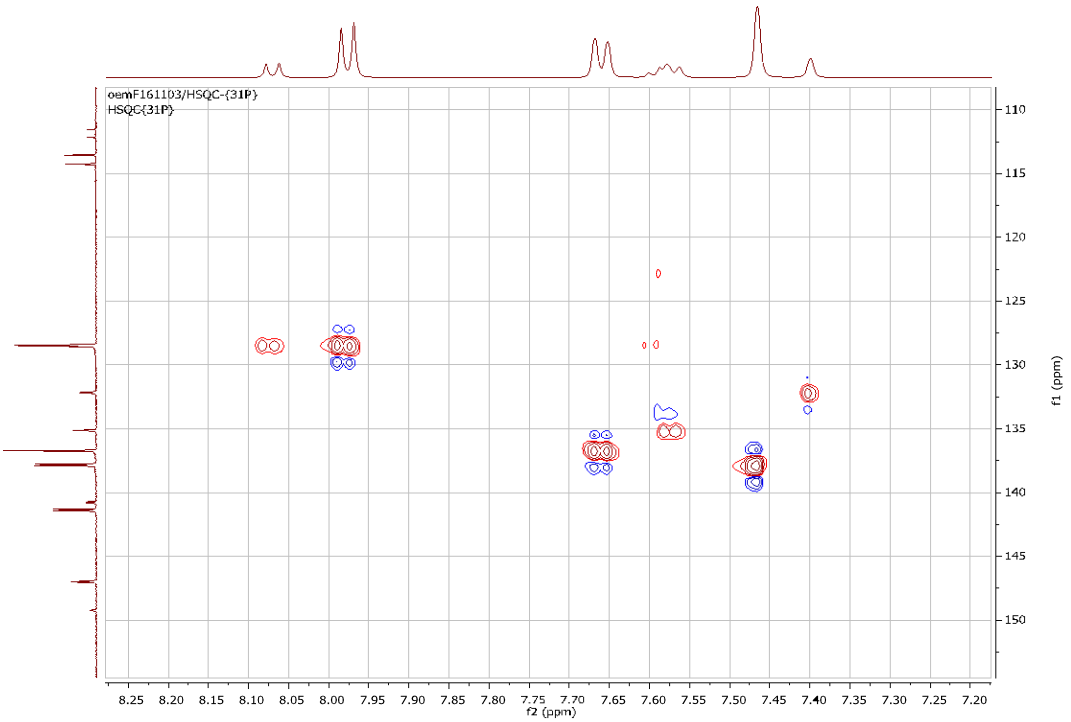


*Figure S13. ^{1}H / $^{13}C\{^{1}H\}$ NMR HSQC experiment at 213 K for compound **1**, zoom 1 in CD_2Cl_2*

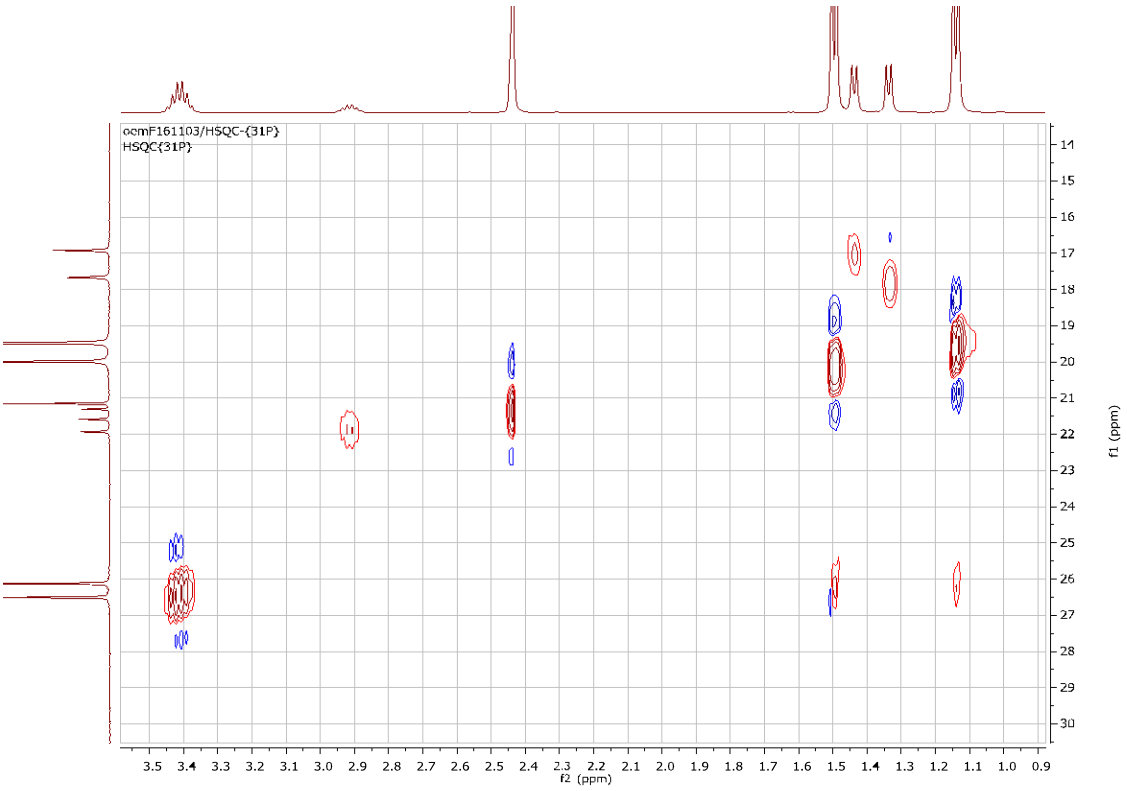


*Figure S14. ^{1}H / $^{13}C\{^{1}H\}$ NMR HSQC experiment at 213 K for compound **1**, zoom 2 in CD_2Cl_2*

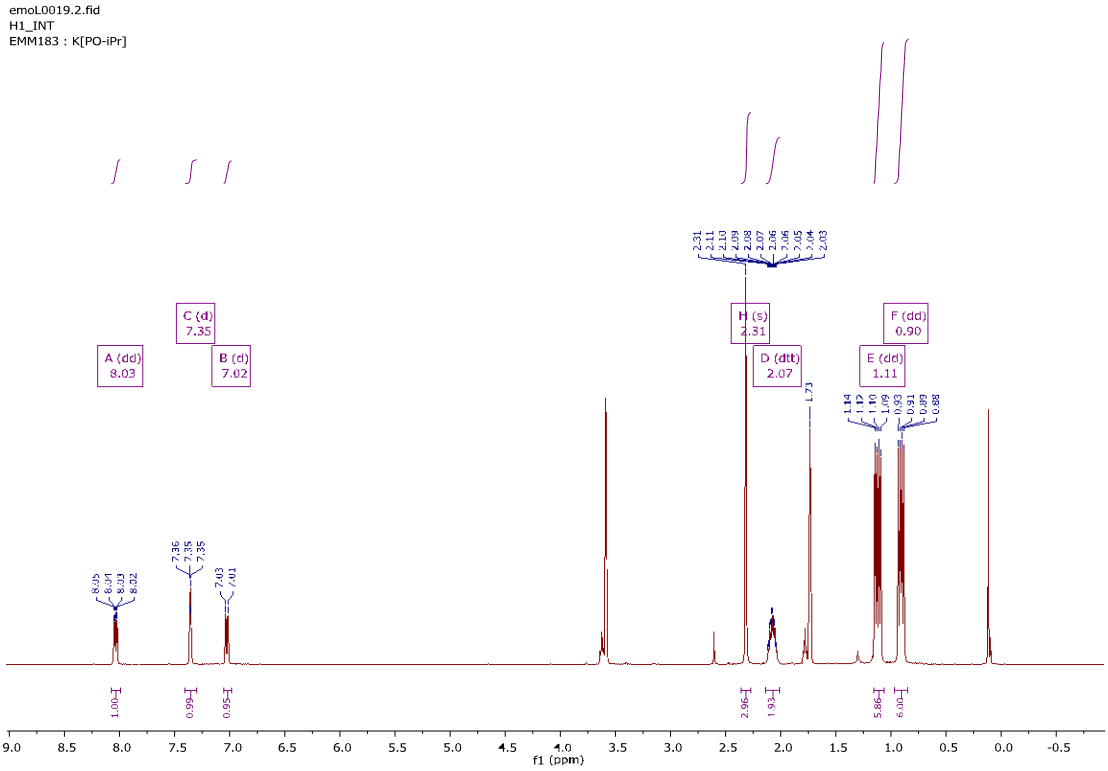


*Figure S15. [1]H NMR spectrum for compound **K[PO-iPr]** at 298 K in THF-d8*

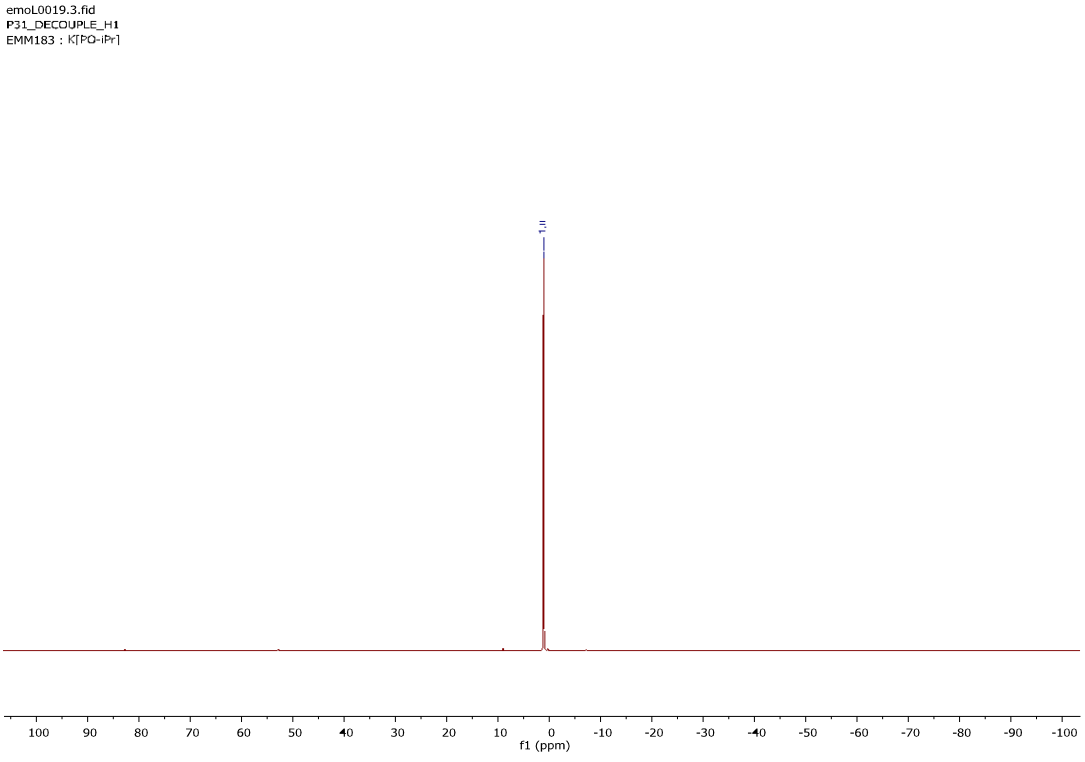


*Figure S16. [31]P{[1]H} NMR spectrum for compound **K[PO-iPr]** at 298 K in THF-d8*

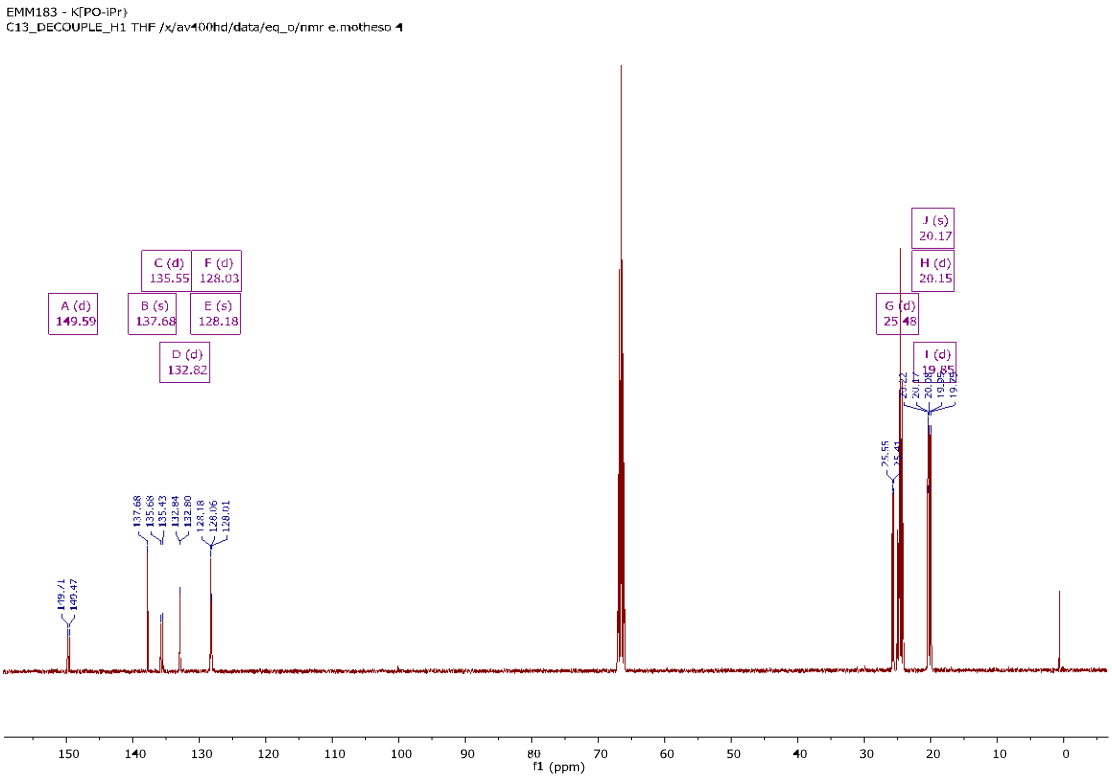


*Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum for compound **K[PO-iPr]** at 298 K in THF-d_8*

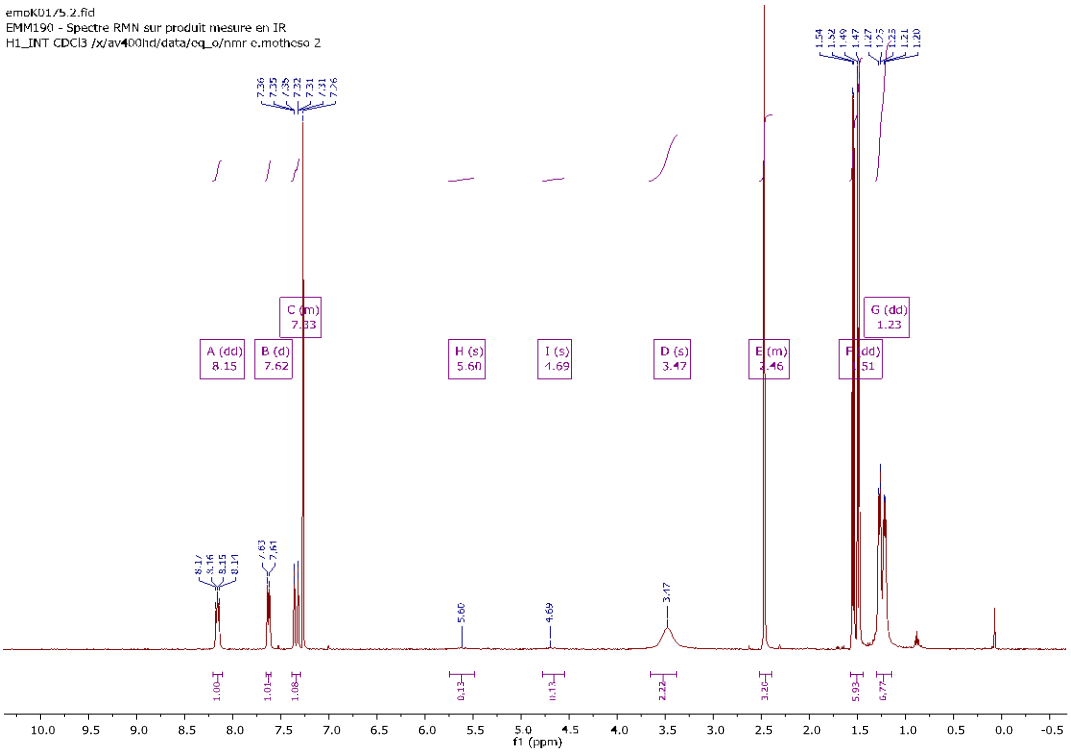


*Figure S18. ^{1}H NMR spectrum for compound **D[PO-iPr]** at 298 K in $CDCl_3$*

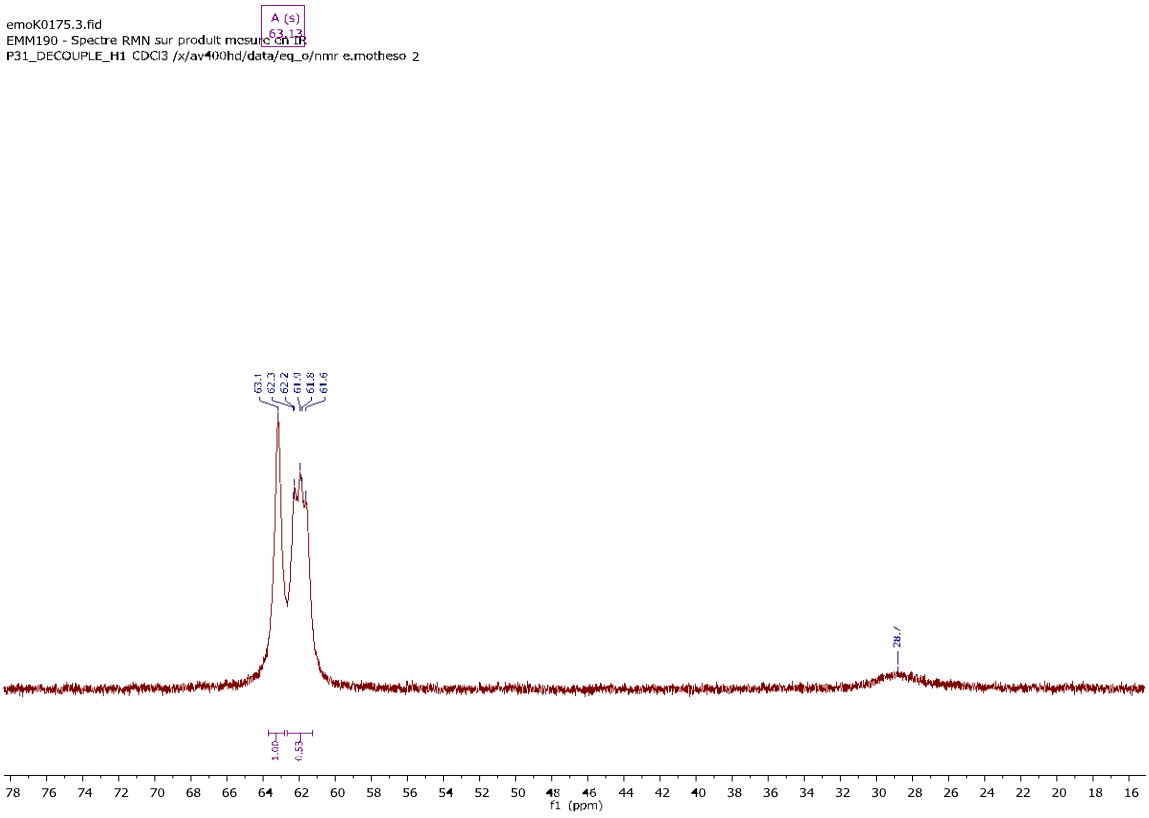
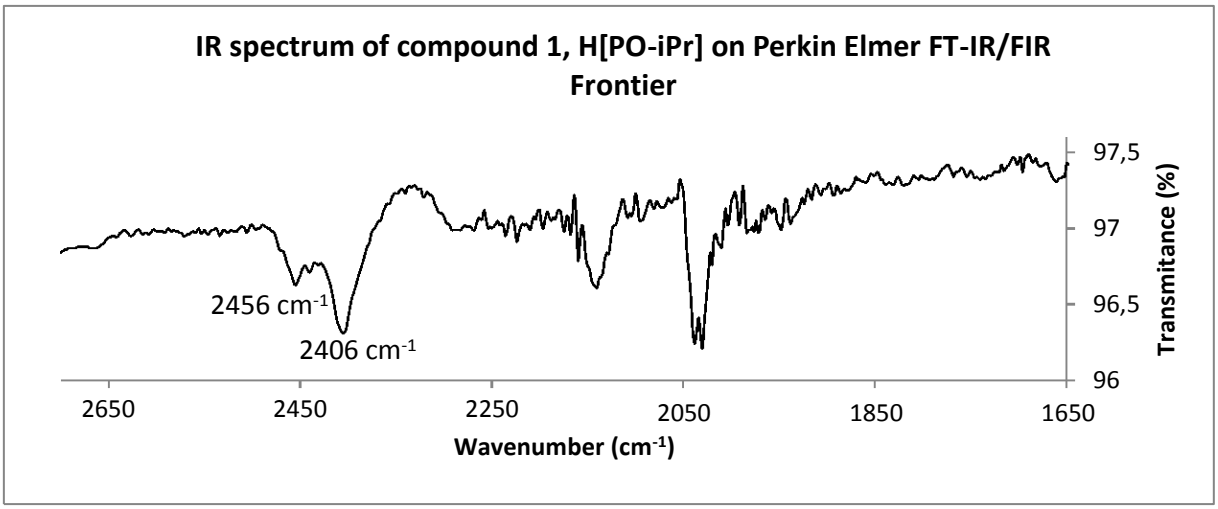
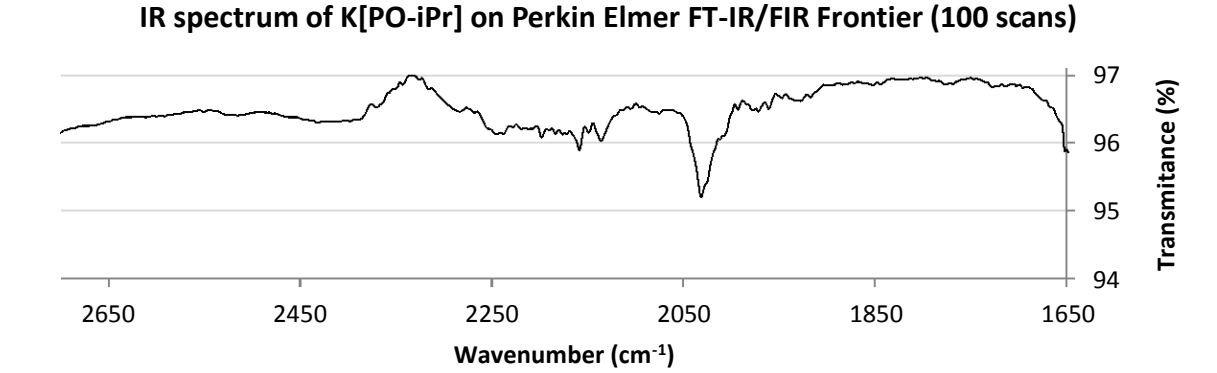


*Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum for compound **D[PO-iPr]** at 298 K in $CDCl_3$*





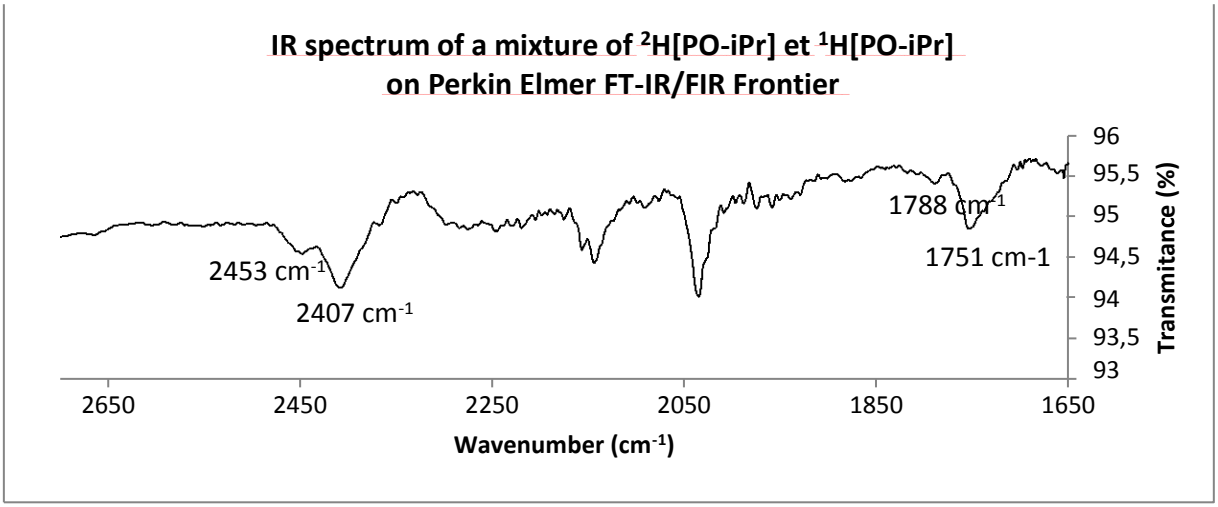


*Figure S20. Powder ATR IR for compound **1**.*

NMR and IR Spectra of compound 2

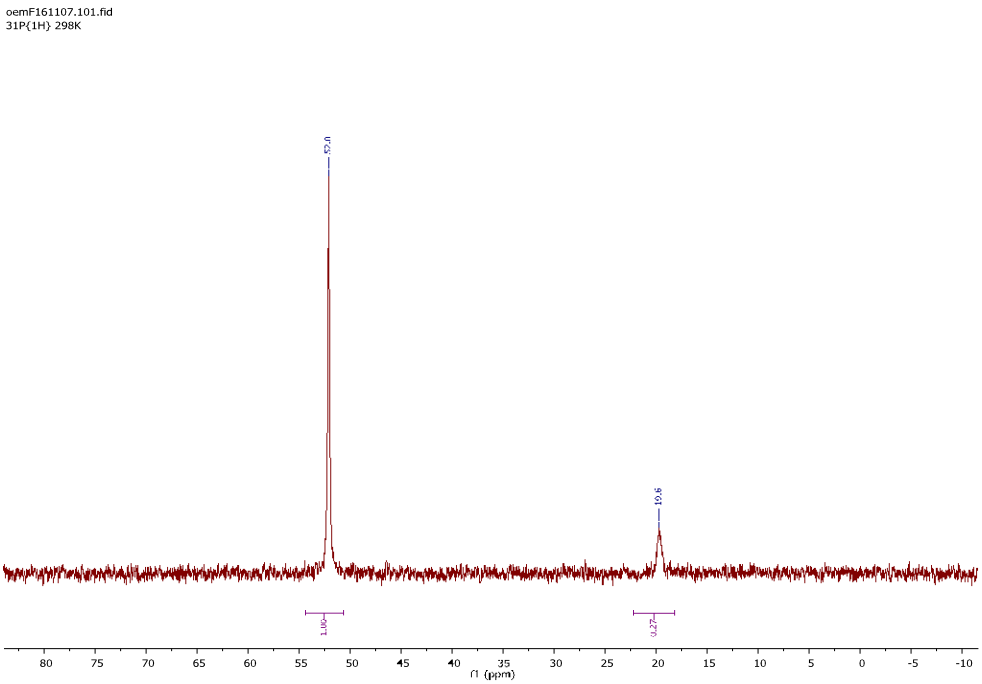


*Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum for compound **2** at 298 K in CD_2Cl_2*

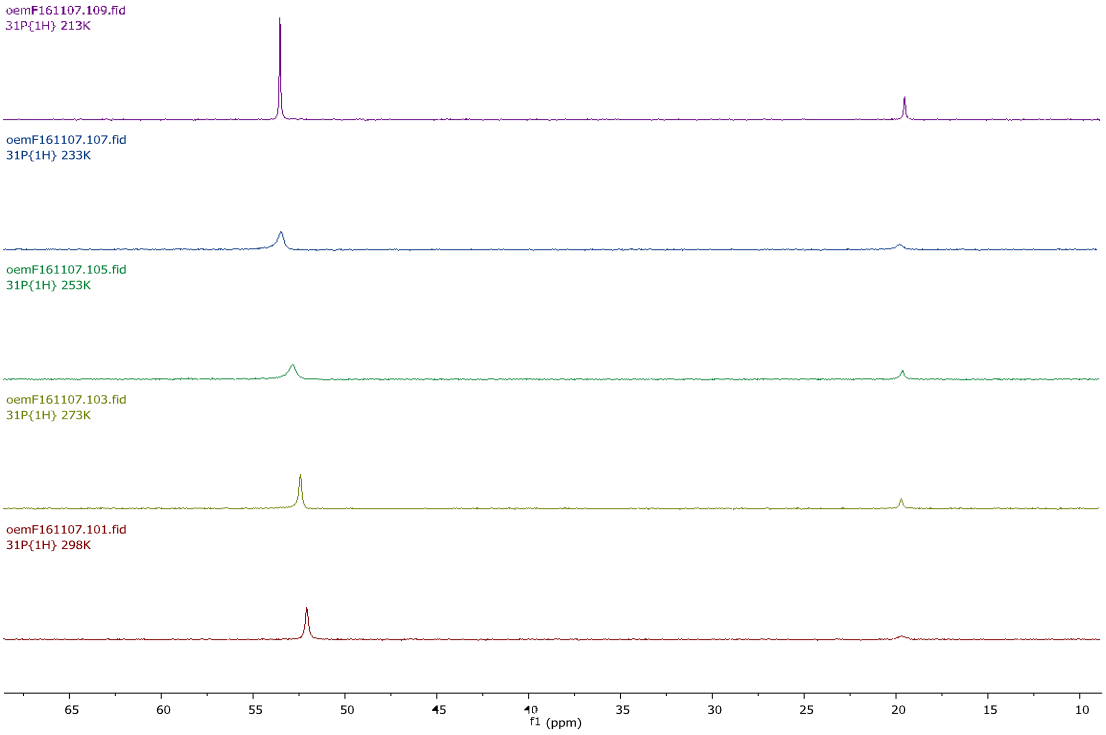


*Figure S22. Variable temperature $^{31}P\{^{1}H\}$ NMR spectra for compound **2** from 298 K to 213 K in CD_2Cl_2*

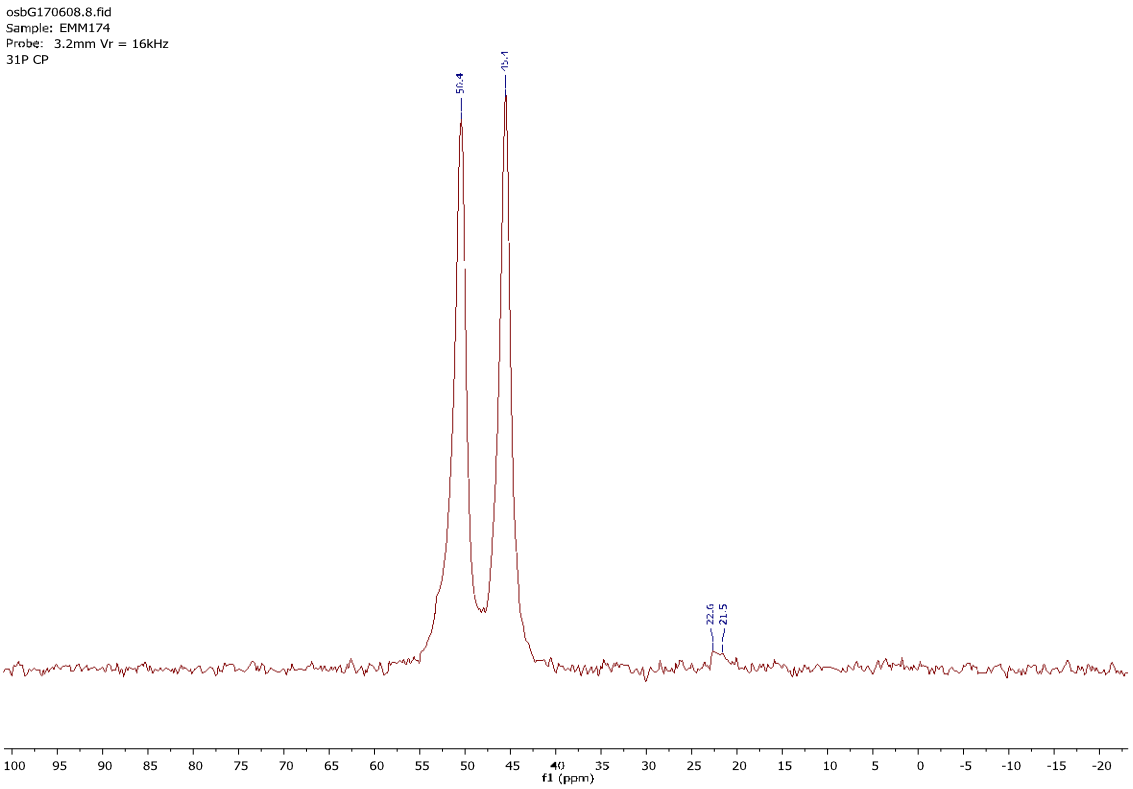


*Figure S23. Solid state CPMas [31]P NMR spectrum for compound **2***

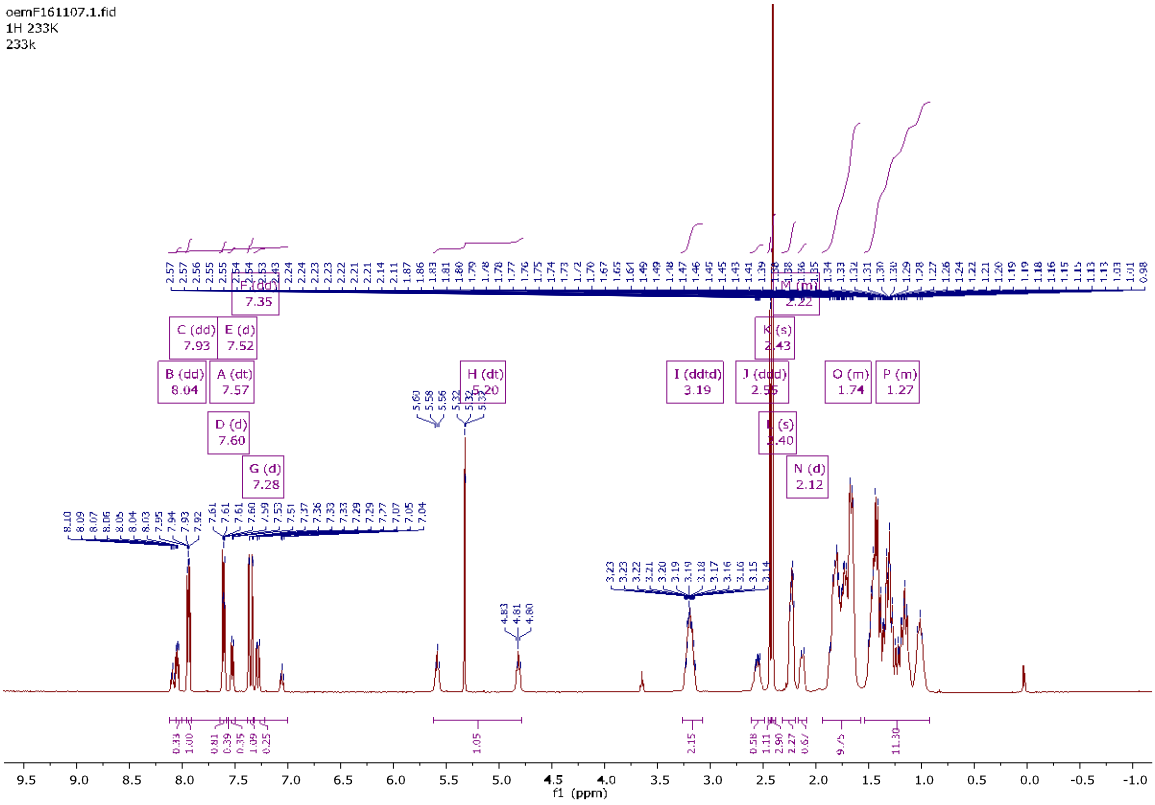


*Figure S24. [1]H NMR spectrum for compound **2** at 233 K in CD_2Cl_2*

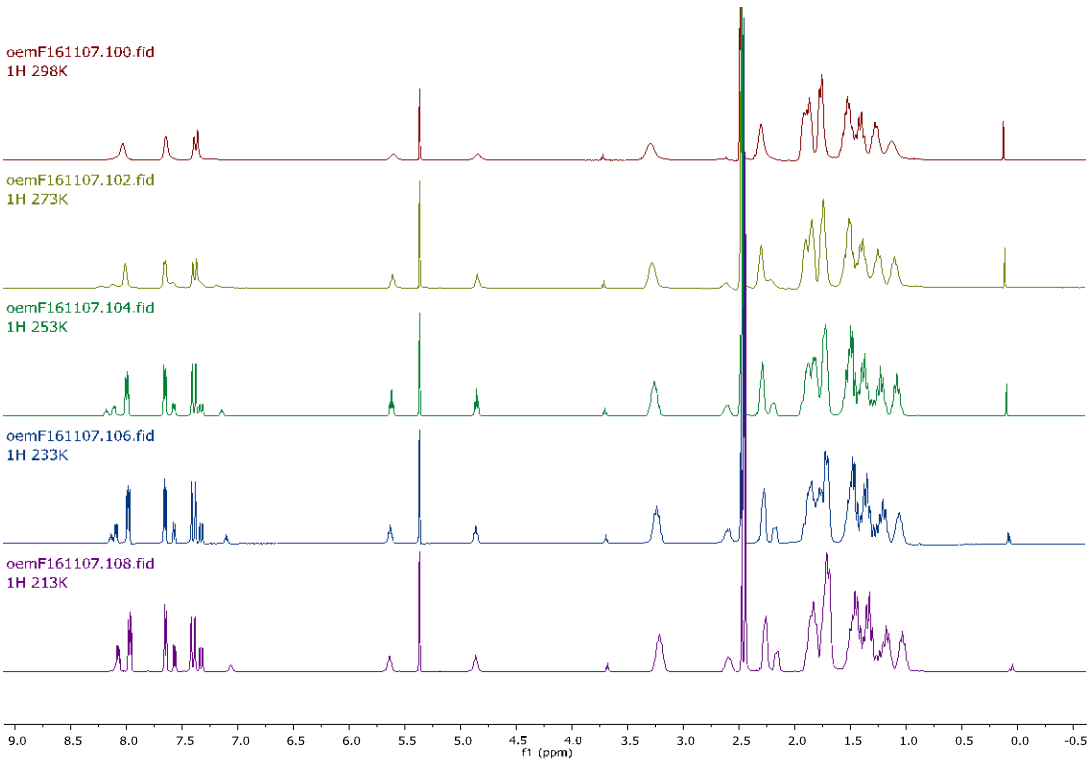


*Figure S25. Variable temperature ^1H NMR spectra for compound **2** from 298 K to 213 K in CD_2Cl_2*

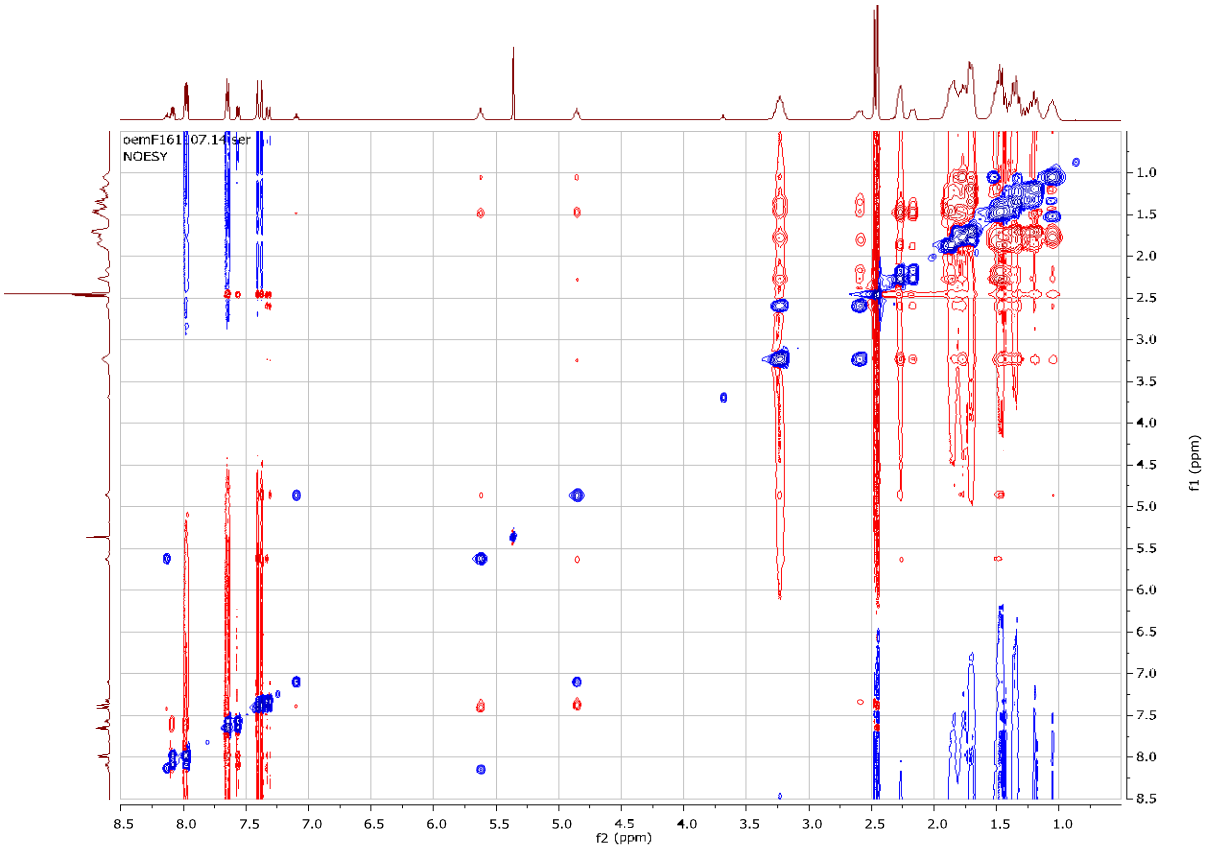


*Figure S26. NOESY $^1H/^1H$ spectrum for compound **2** at 233 K in CD_2Cl_2*

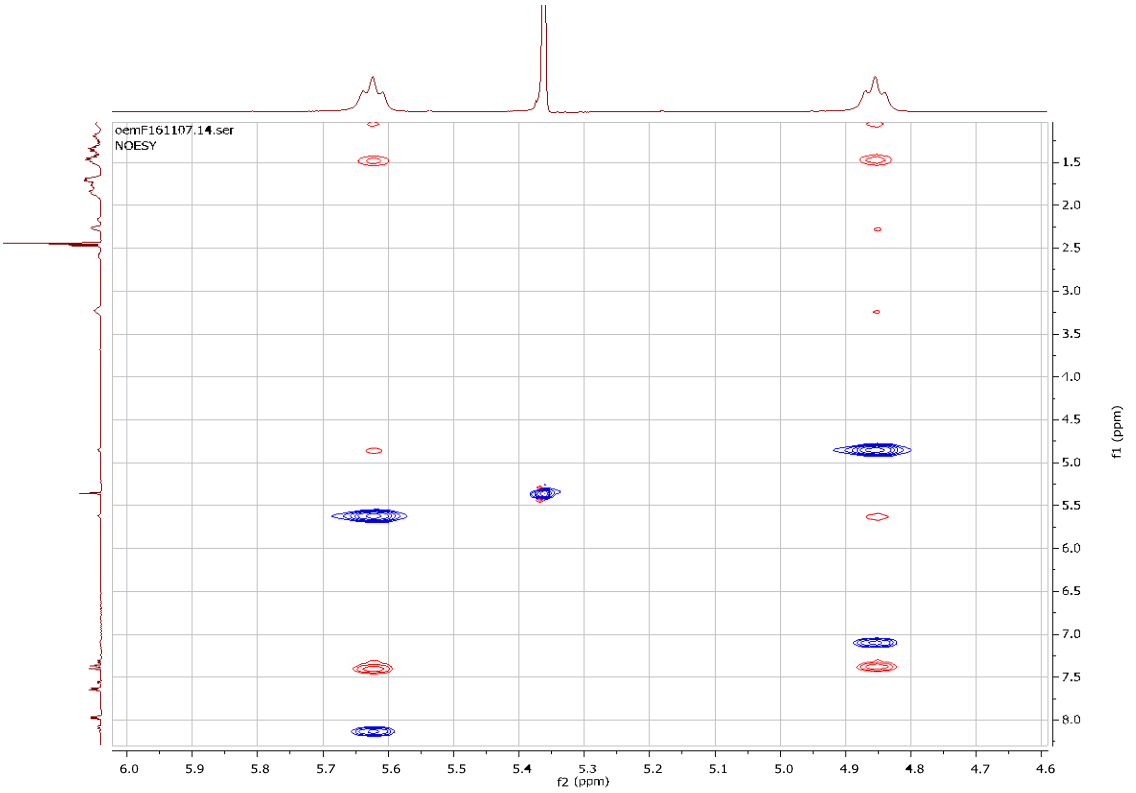


*Figure S27. NOESY $^{1}H/^{1}H$ spectrum for compound **2** at 233 K, zoom on H-P form 1 in CD_2Cl_2*

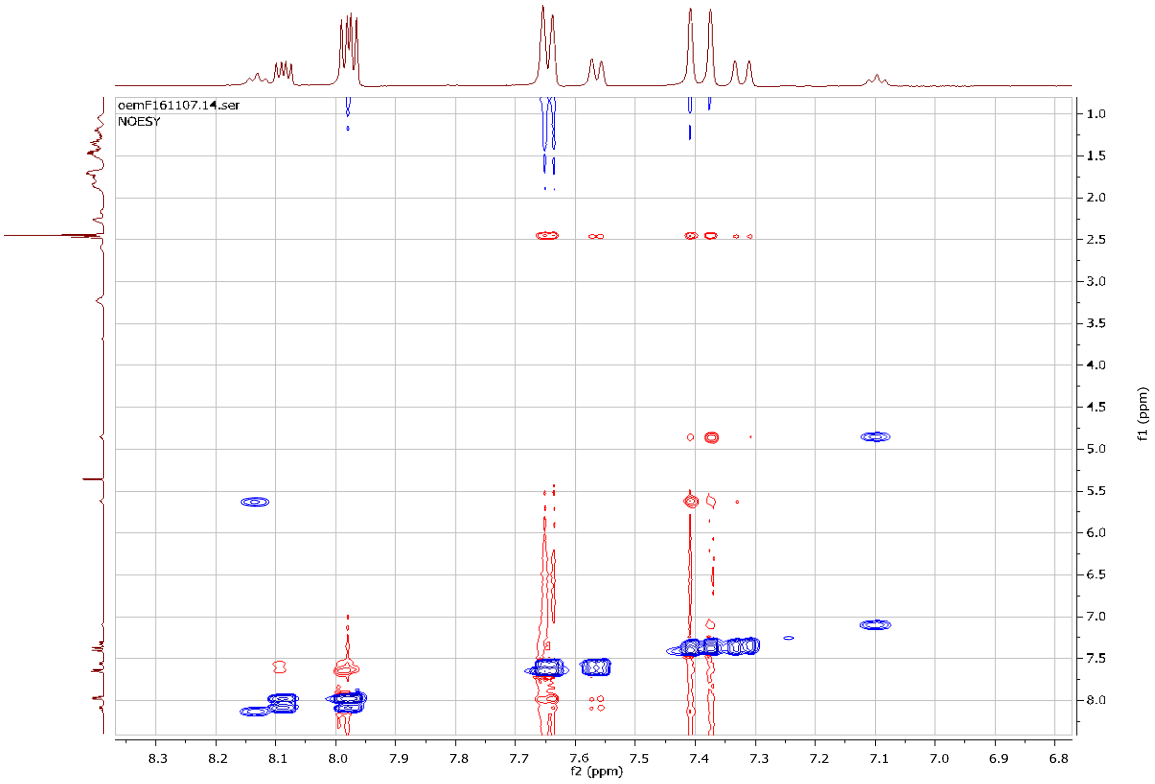


*Figure S28. NOESY $^{1}H/^{1}H$ spectrum for compound **2** at 233 K, zoom on H-P form 2 in CD_2Cl_2*

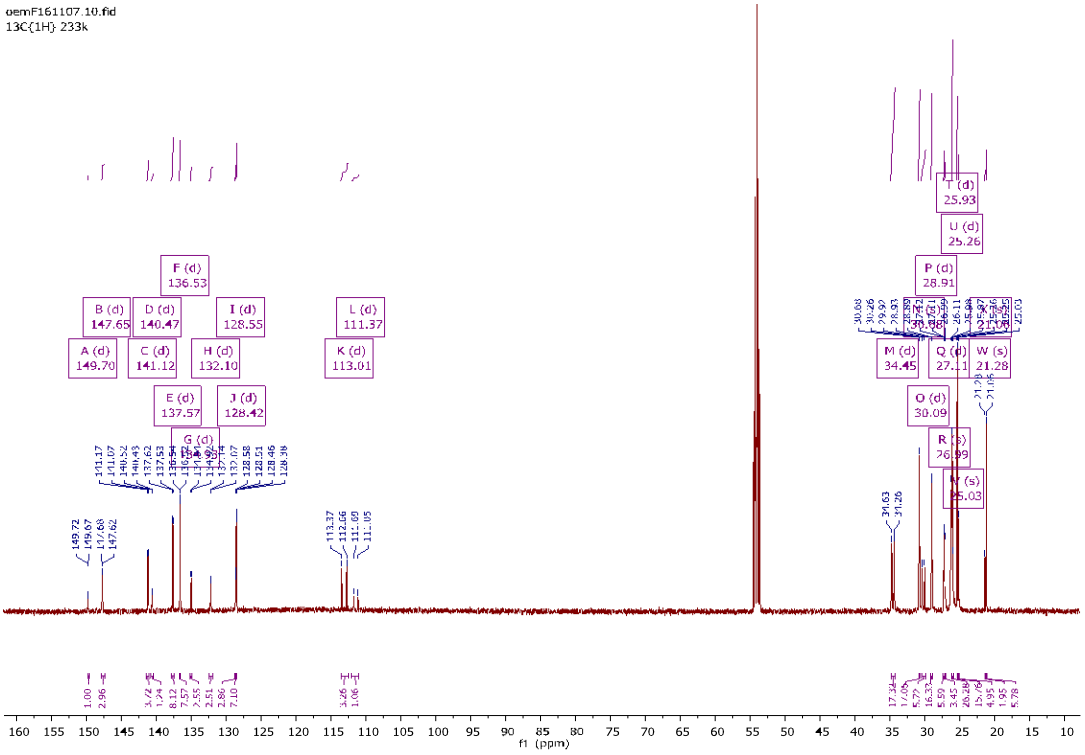


*Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2** at 213 K in CD_2Cl_2*

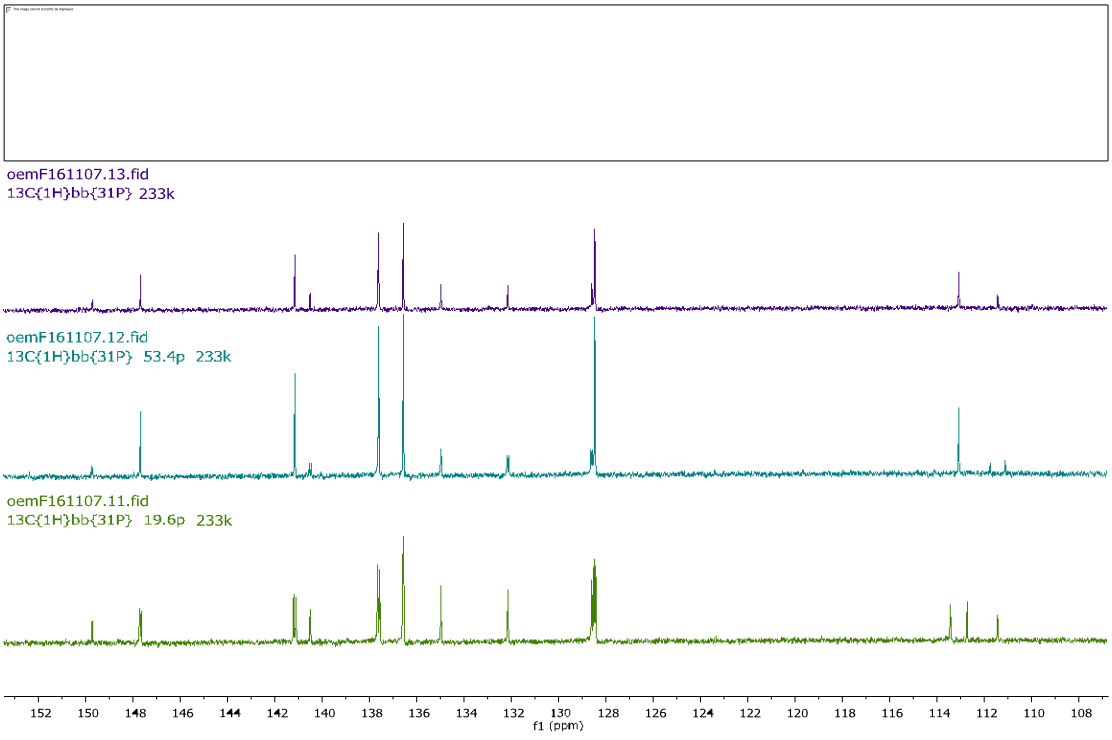


*Figure S30. $^{13}C\{^{1}H\}$ NMR analysis of compound **2** at 233 K in CD_2Cl_2, from top to bottom: no ^{31}P decoupling, broad band ^{31}P decoupling, selective ^{31}P decoupling at 53.4 ppm, selective ^{31}P decoupling at 19.6 ppm, 153 to 107 ppm window.*

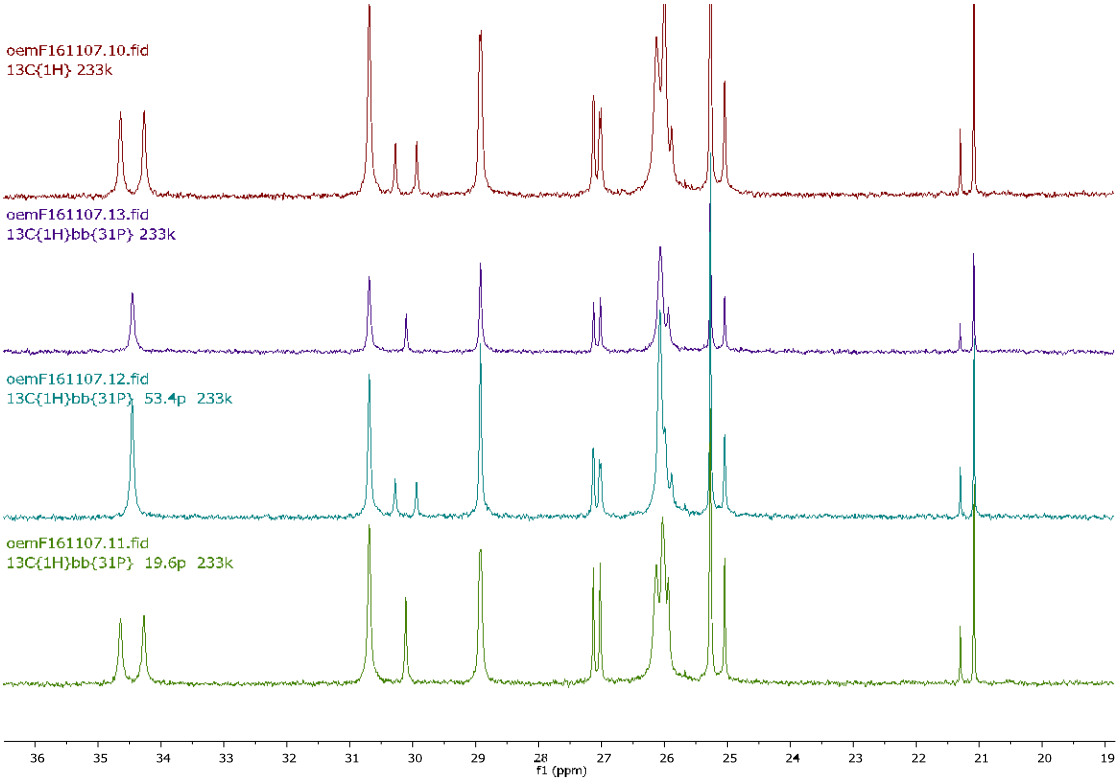


*Figure S31. $^{13}C\{^{1}H\}$ NMR analysis of compound **2** at 233 K in CD_2Cl_2, from top to bottom: no ^{31}P decoupling, broad band ^{31}P decoupling, selective ^{31}P decoupling at 53.4 ppm, selective ^{31}P decoupling at 19.6 ppm, 36 to 19 ppm window.*

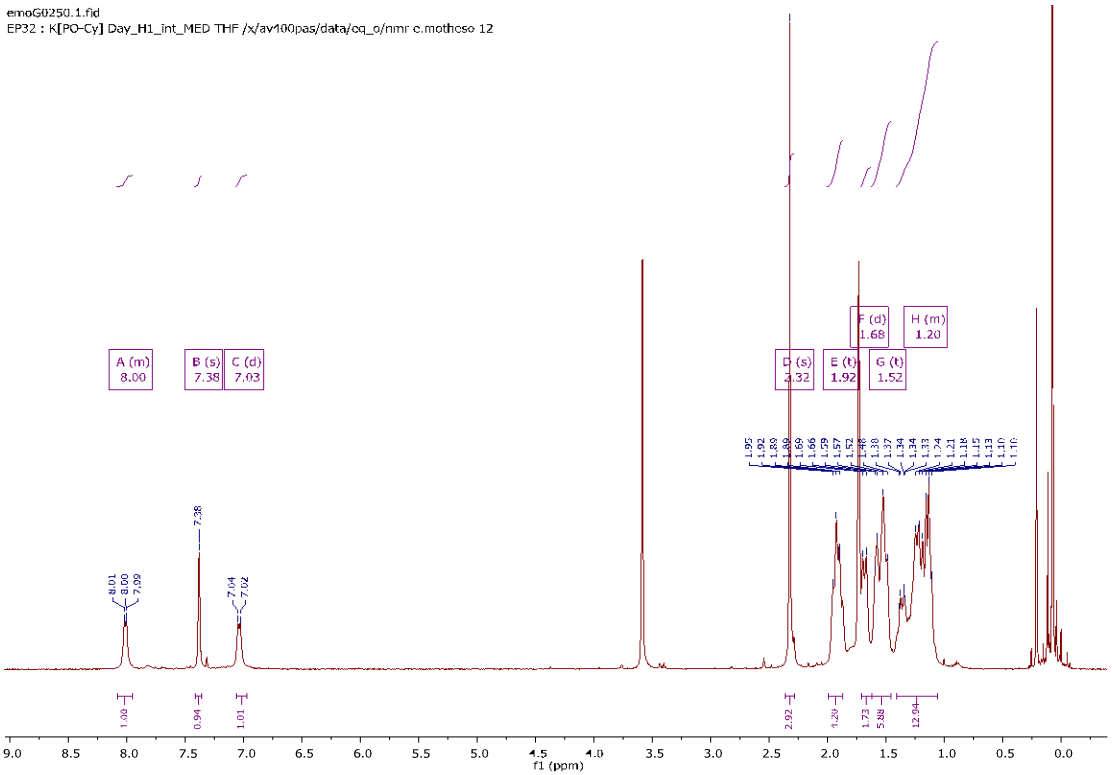


*Figure S32. ^{1}H NMR spectrum for compound **K[PO-Cy]** at 298 K in THF-d_8*

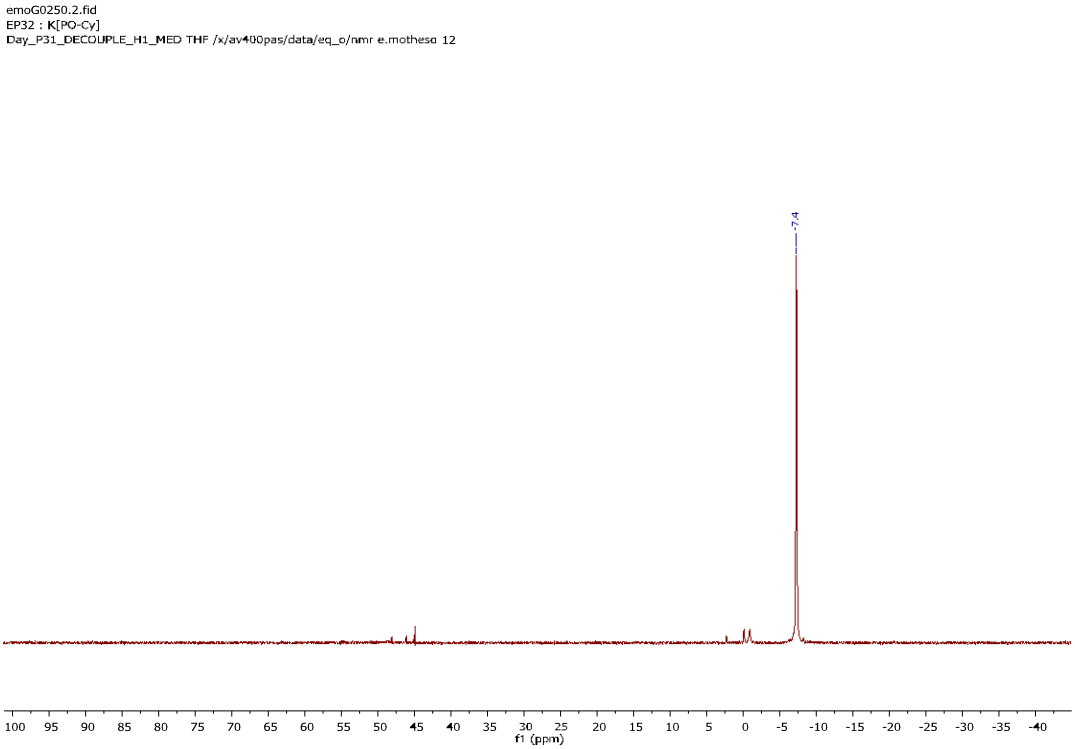


*Figure S33. $^{31}P\{^{1}H\}$ NMR spectrum for compound **K[PO-Cy]** at 298 K in THF-d_8*

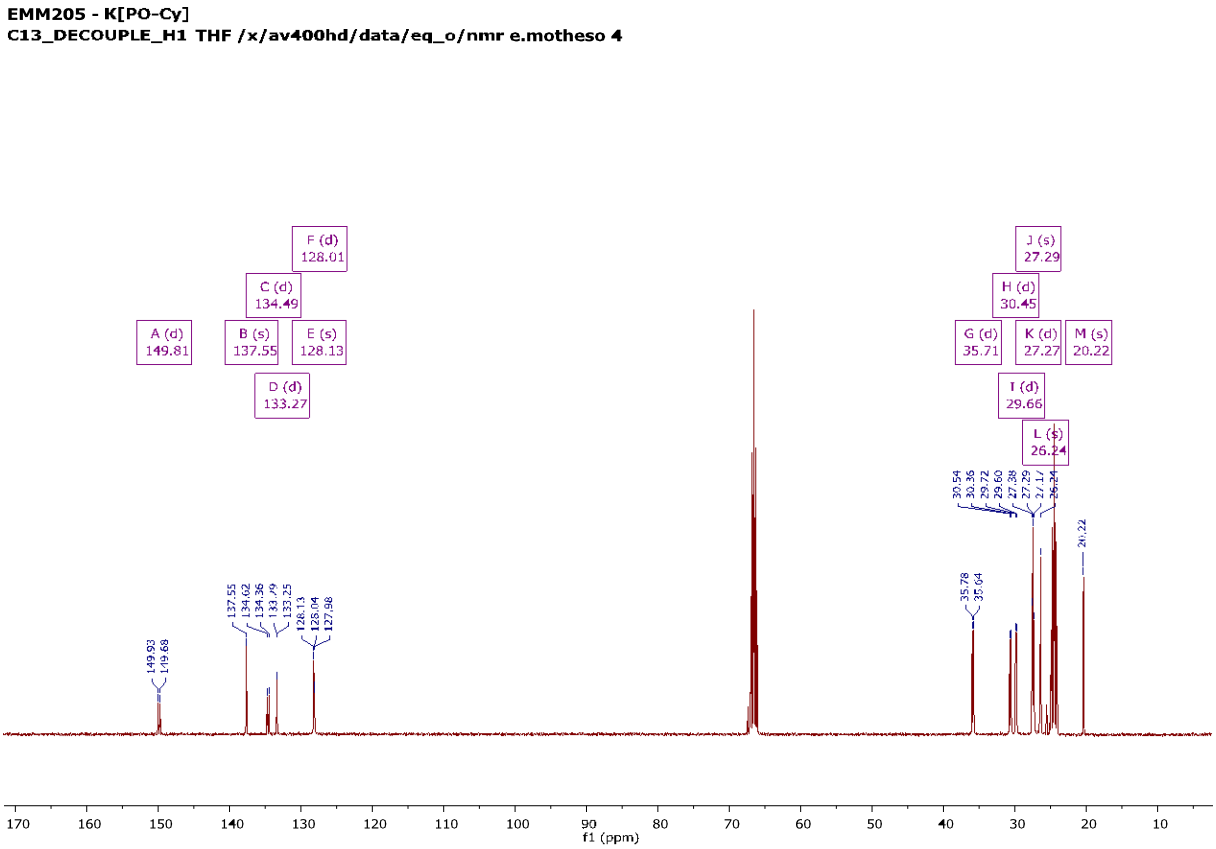


*Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum for compound **K[PO-Cy]** at 298 K in THF-d_8*

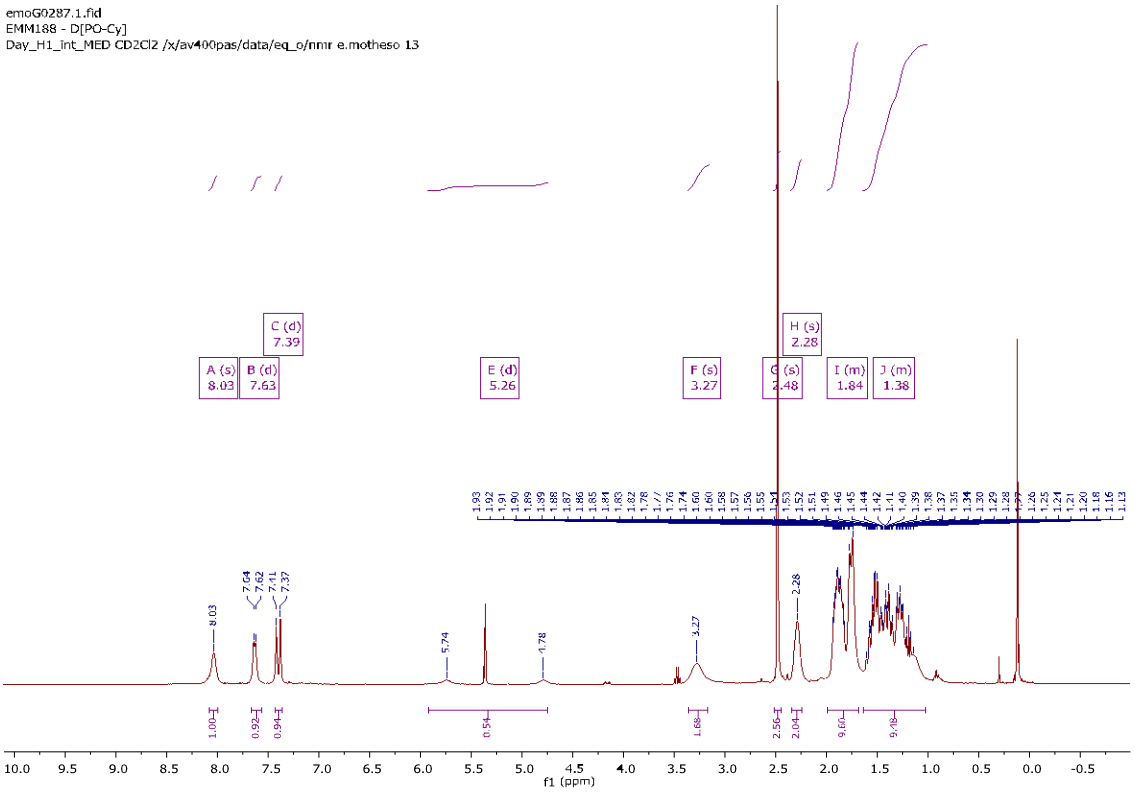


*Figure S35. ^{1}H NMR spectrum for compound **D[PO-Cy]** at 298 K in CD_2Cl_2*

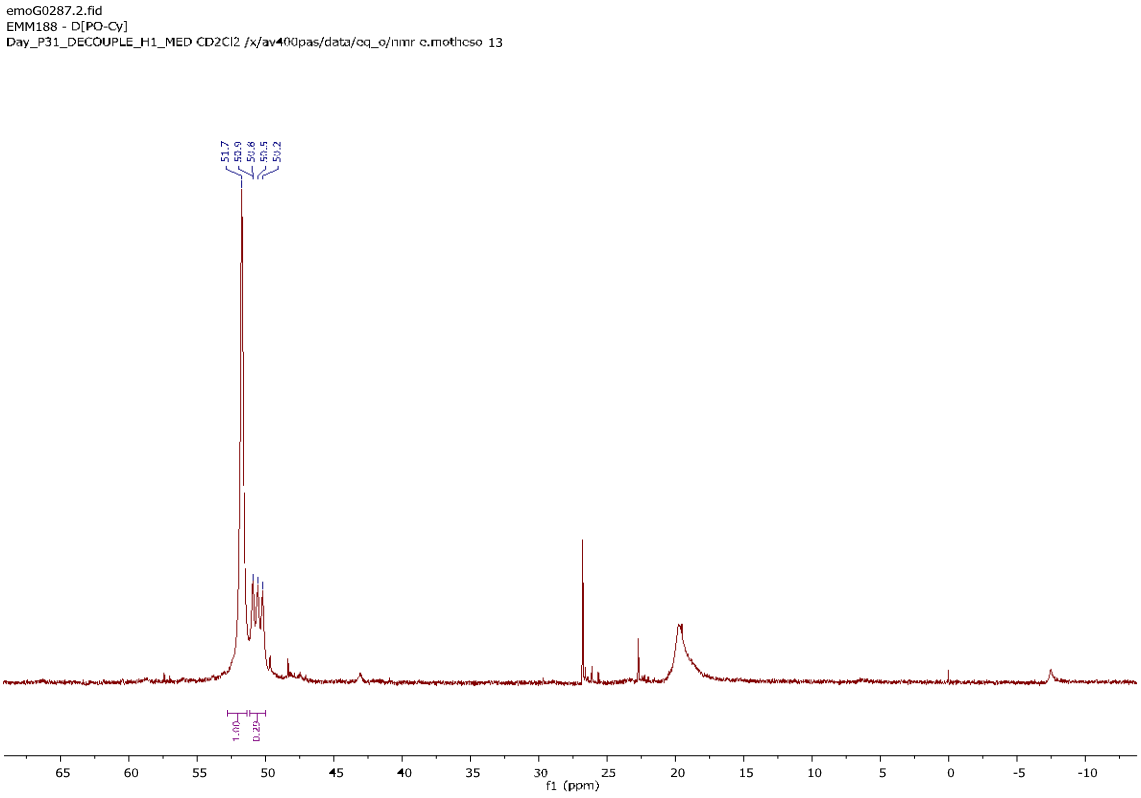
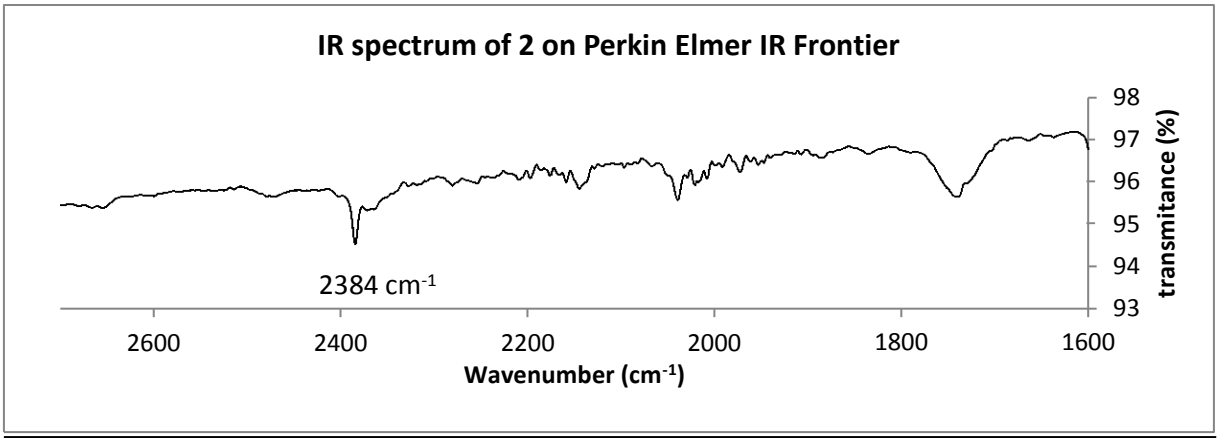
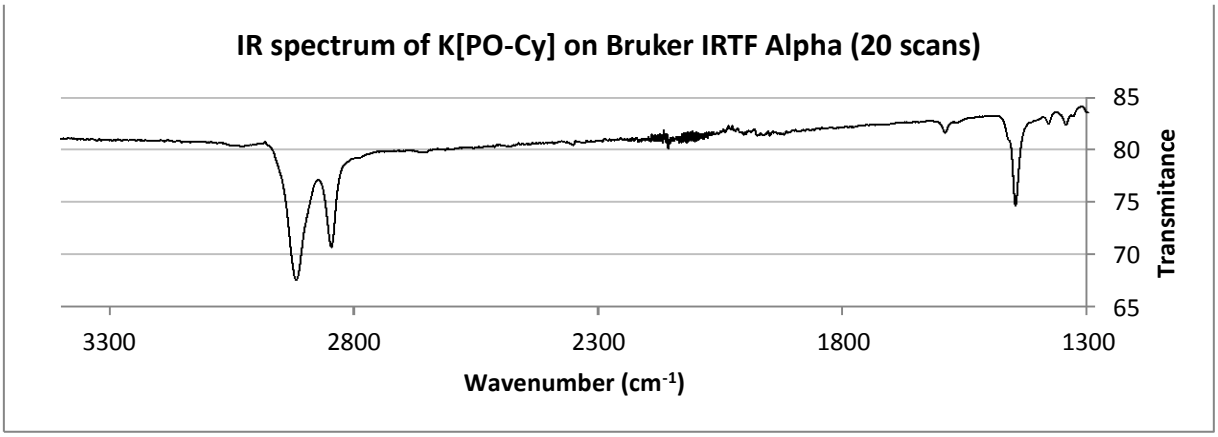


*Figure S36. $^{31}P\{^{1}H\}$ NMR spectrum for compound **D[PO-Cy]** at 298 K in CD_2Cl_2*





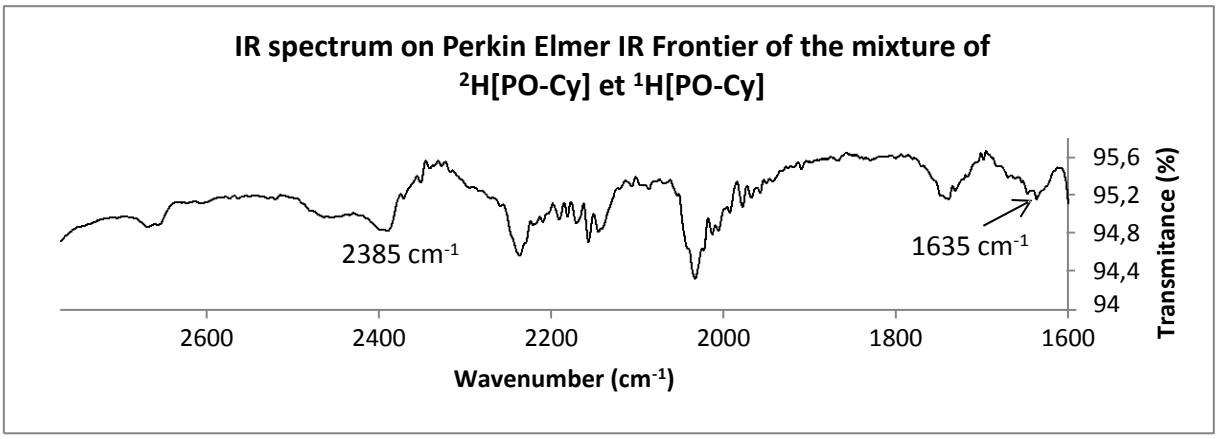


*Figure S37. Powder ATR IR for compound **2**.*

NMR and IR Spectra of compound 3

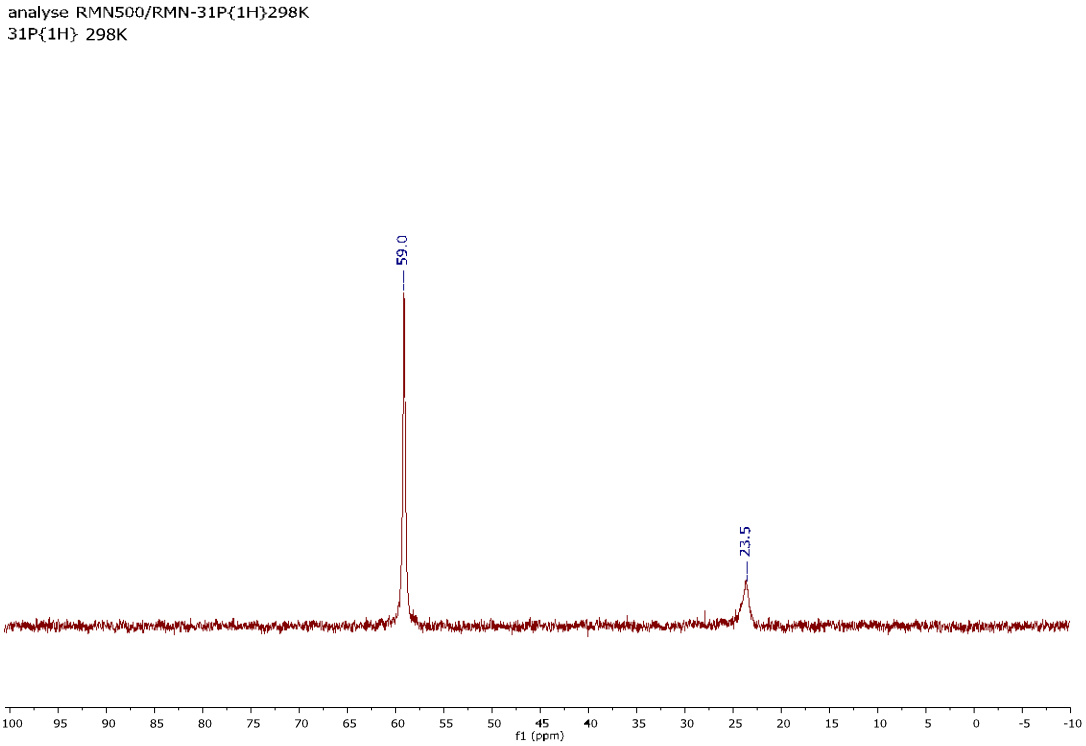


*Figure S38. $^{31}P\{^{1}H\}$ NMR spectra for compound **3** at 298 K in CD_2Cl_2*

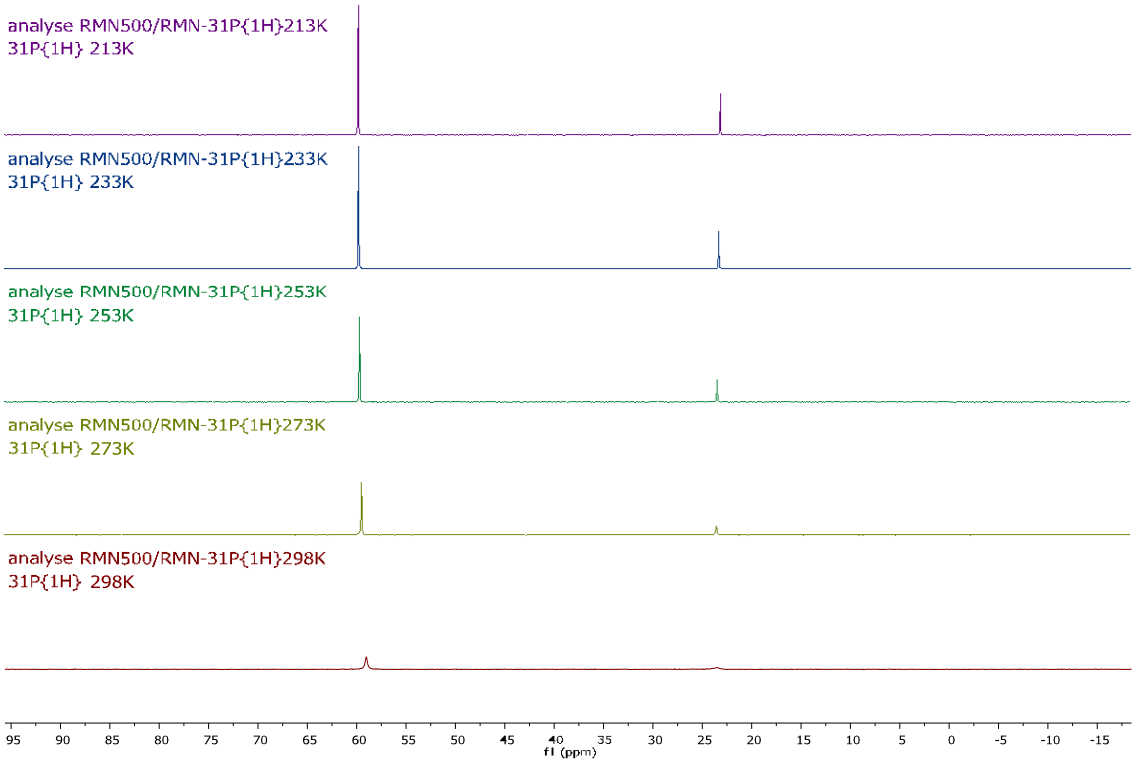


*Figure S39. Variable temperature $^{31}P\{^{1}H\}$ NMR spectra for compound **3** from 298 K to 213 K in CD_2Cl_2*

osbG170608.2.fid
Sample: EMM171
Probe: 3.2mm Vr = 16kHz
31P CP

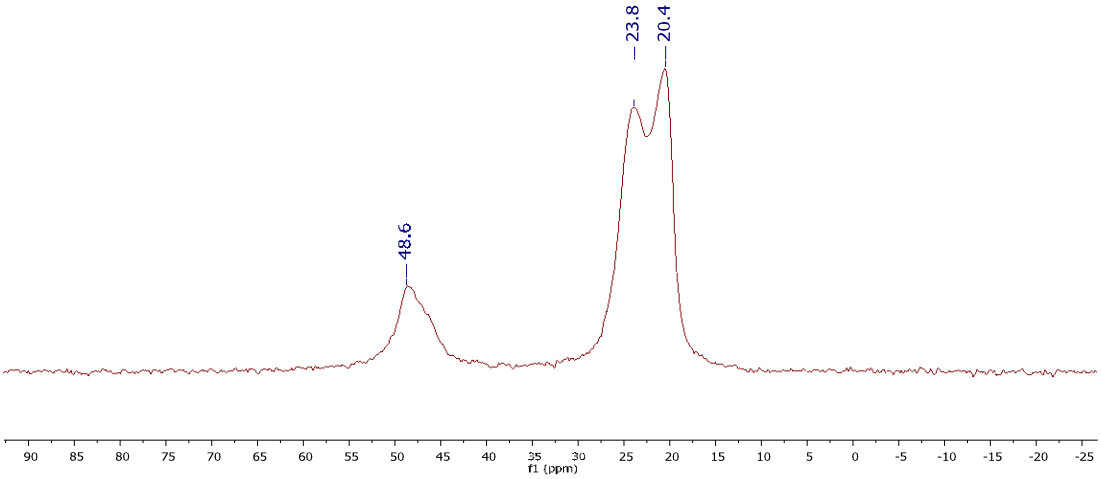


*Figure S40. Solid state CPMas ^{31}P NMR spectrum for compound **3***

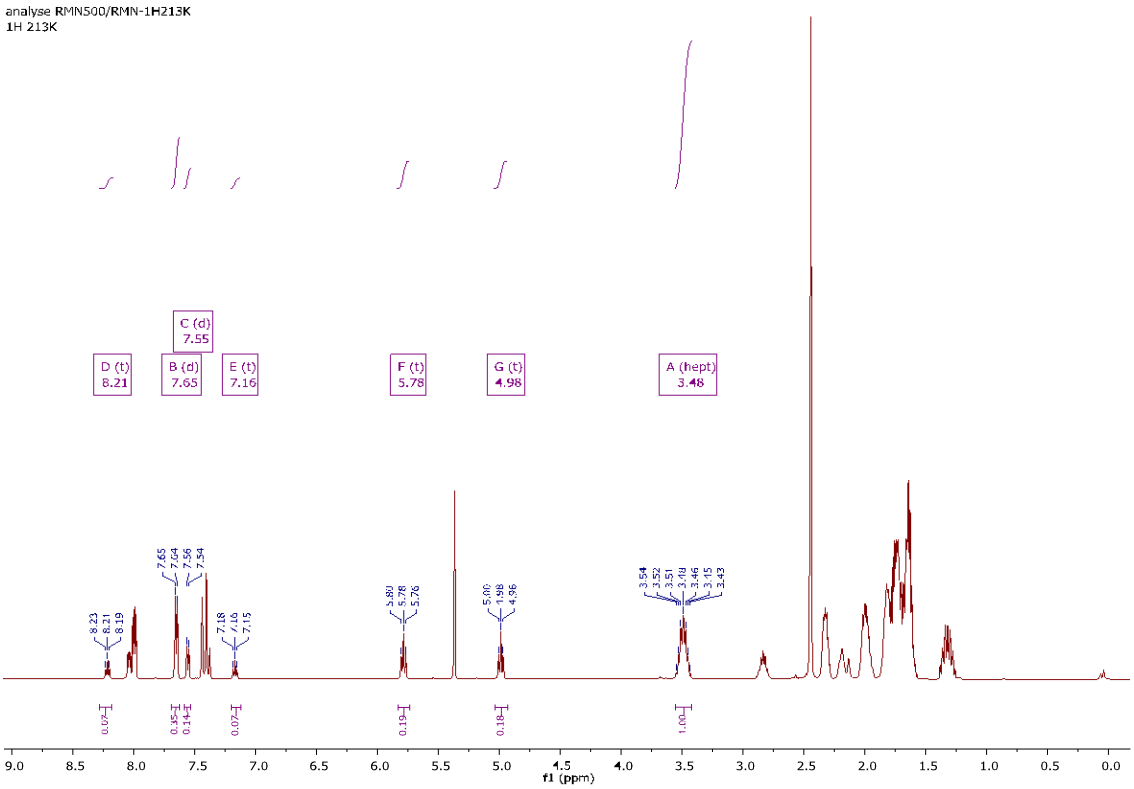


*Figure S41. ^{1}H NMR spectrum for compound **3** at 213 K in CD_2Cl_2*

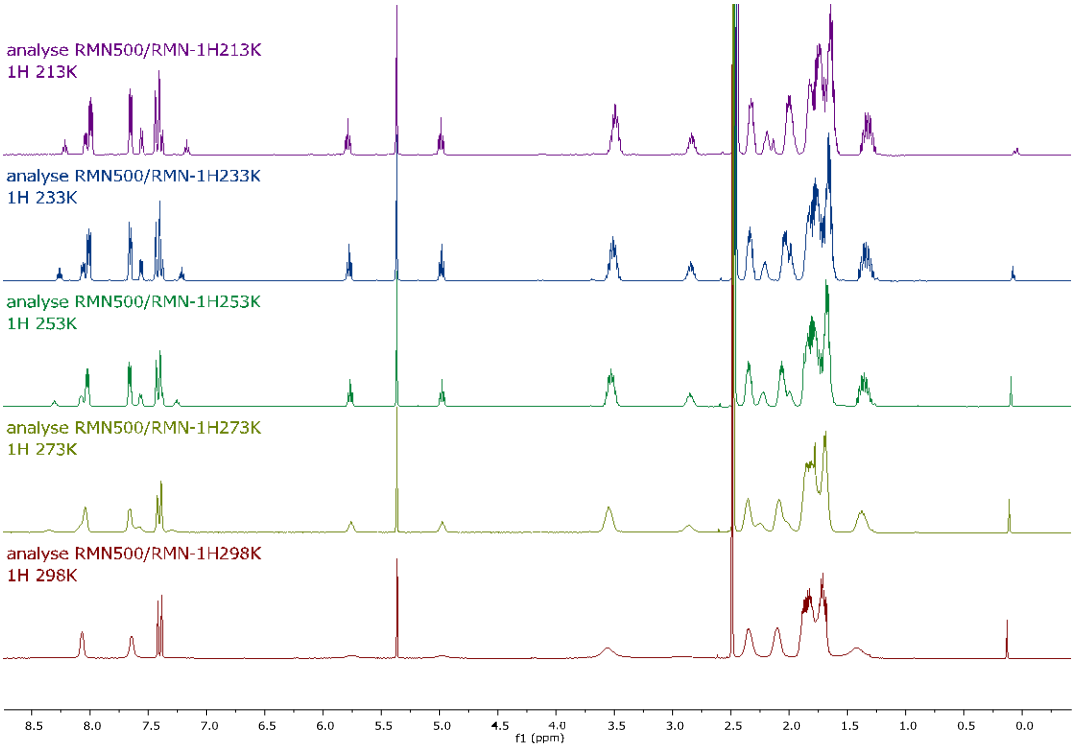


*Figure S42. Variable temperature ^{1}H NMR spectra for compound **3** from 298 K to 213 K in CD_2Cl_2*

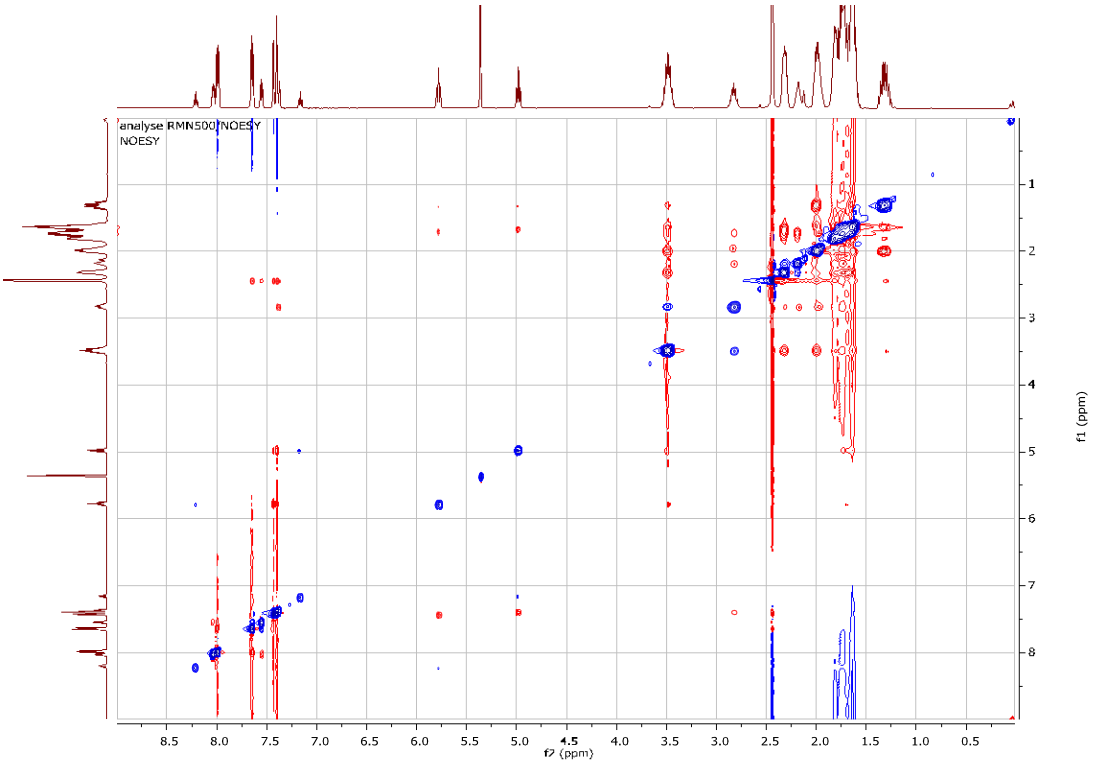


*Figure S43. NOESY ^{1}H/^{1}H spectrum for compound **3** at 213 K in CD_2Cl_2*

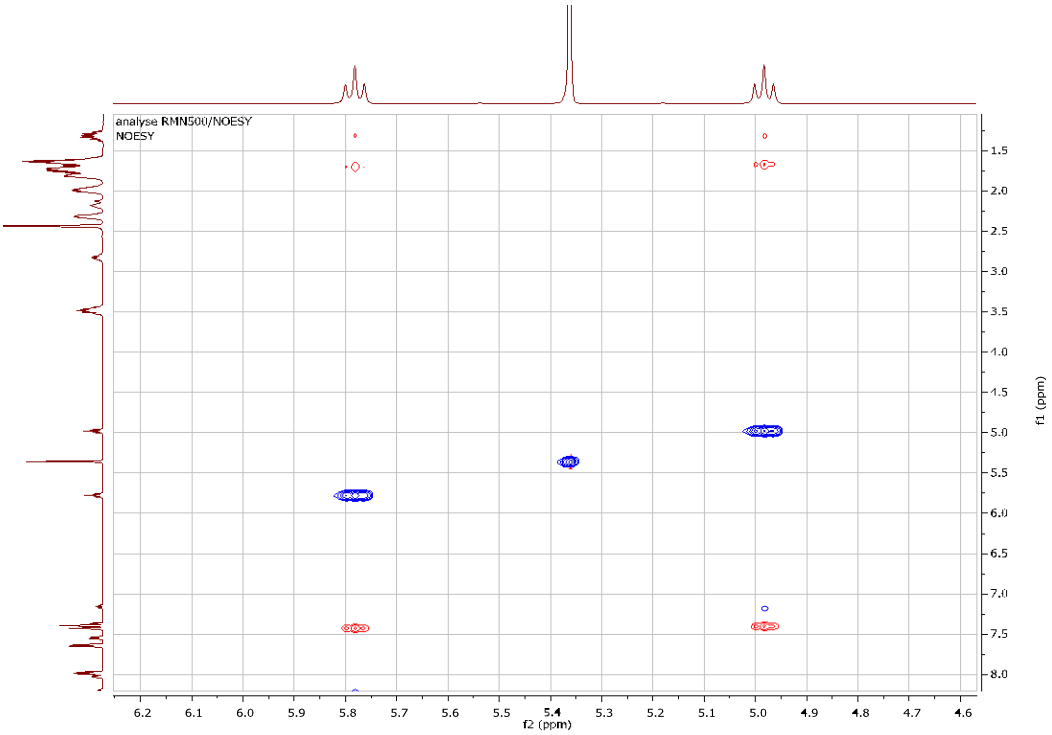


*Figure S44. NOESY $^1H/^1H$ spectrum for compound **3** at 213 K, zoom on H-P form 1 in CD_2Cl_2*

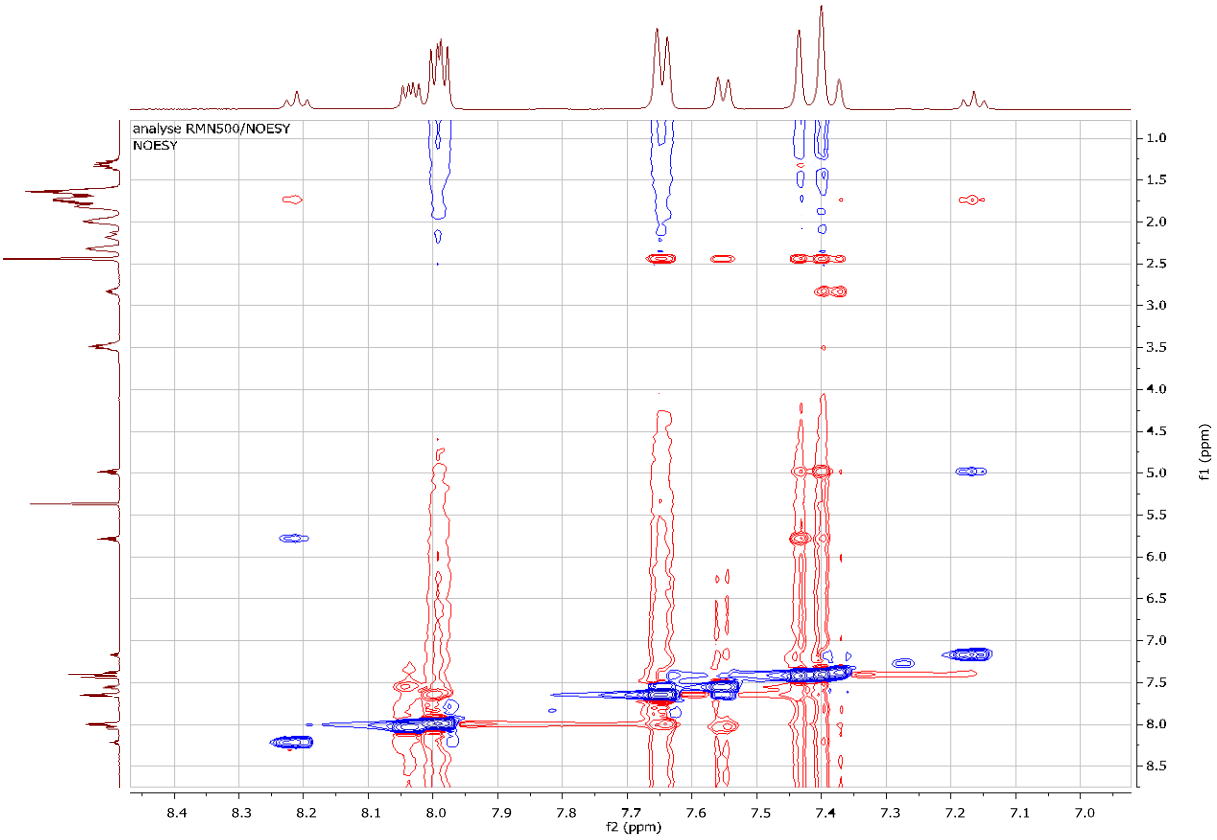


*Figure S45. NOESY $^1H/^1H$ spectrum for compound **3** at 213 K, zoom on H-P form 2 in CD_2Cl_2*

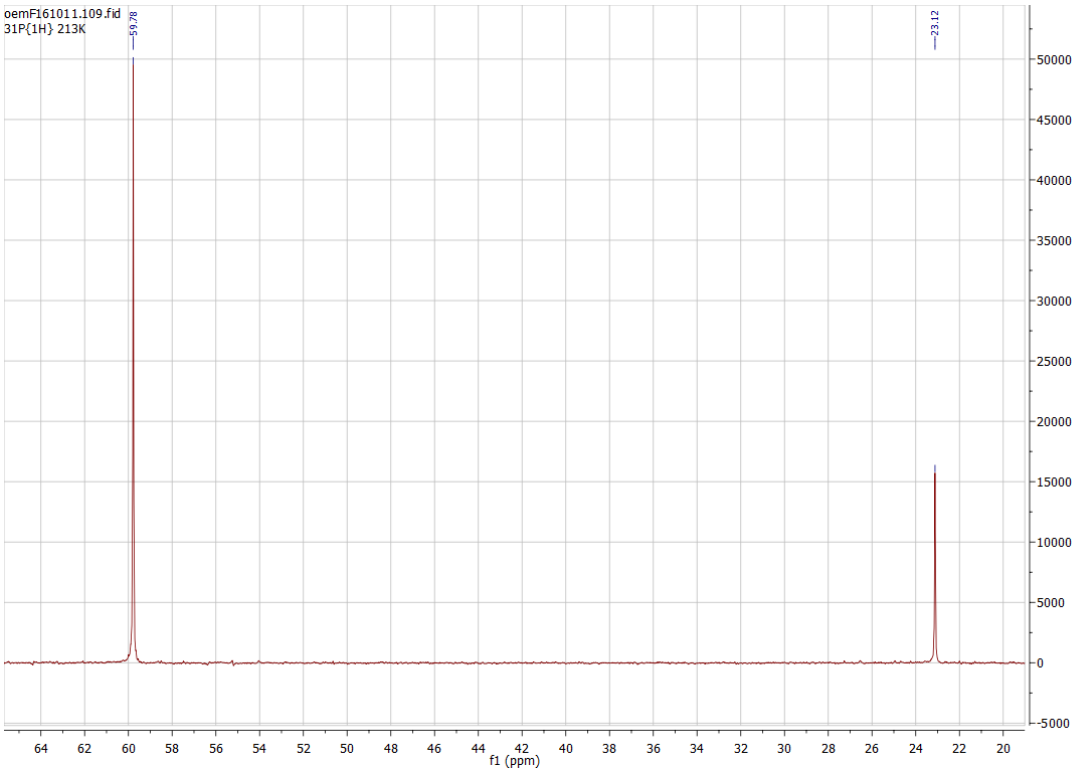


*Figure S46. $^{31}P\{^{1}H\}$ NMR spectra for compound **3** at 213 K in CD_2Cl_2*

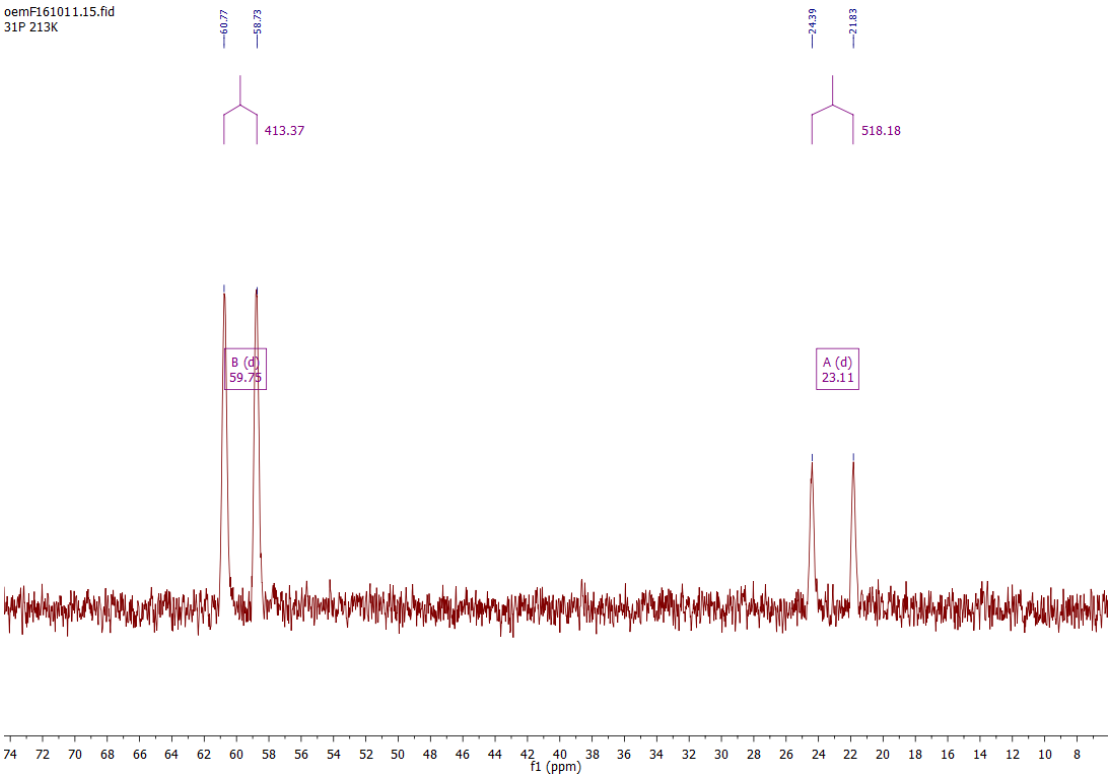


*Figure S47. ^{31}P NMR spectra for compound **3** at 213 K in CD_2Cl_2*

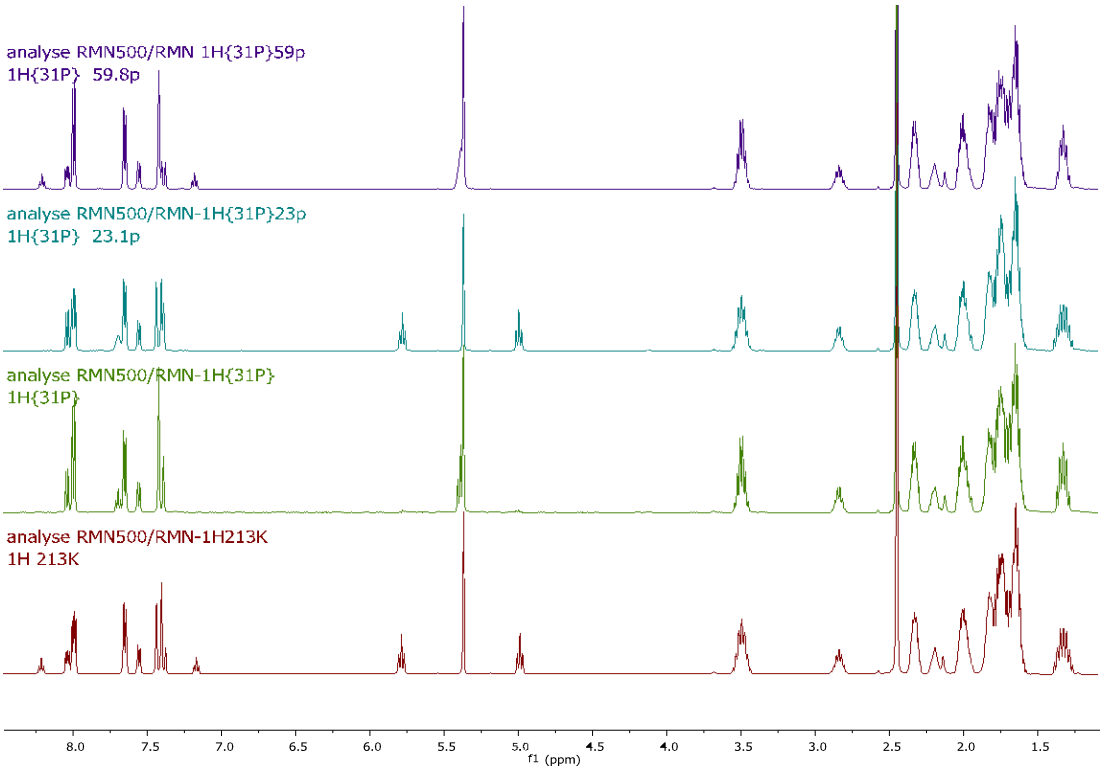


*Figure S48. ^{1}H NMR analysis of compound **3** at 213 K in CD_2Cl_2, from bottom to top: no ^{31}P decoupling, broad band ^{31}P decoupling, selective ^{31}P decoupling at 23 ppm, selective ^{31}P decoupling at 59 ppm.*

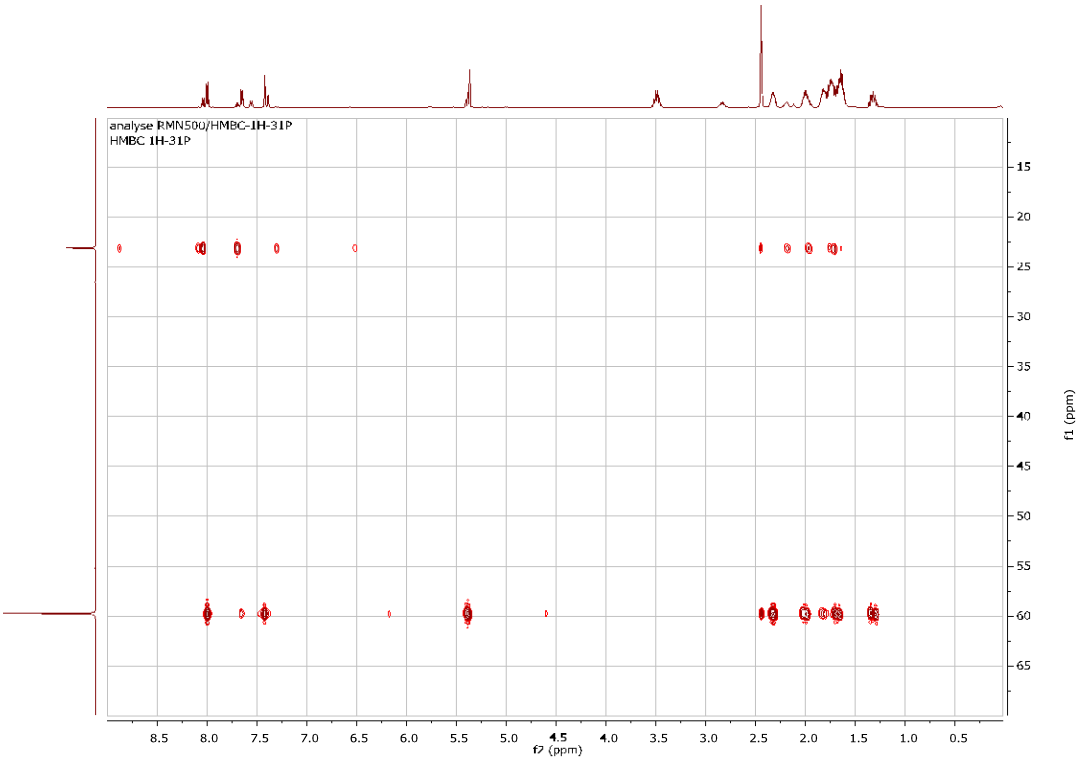


*Figure S49. ^{1}H / $^{31}P\{^{1}H\}$ NMR HMBC experiment at 213 K for compound **3** in CD_2Cl_2*

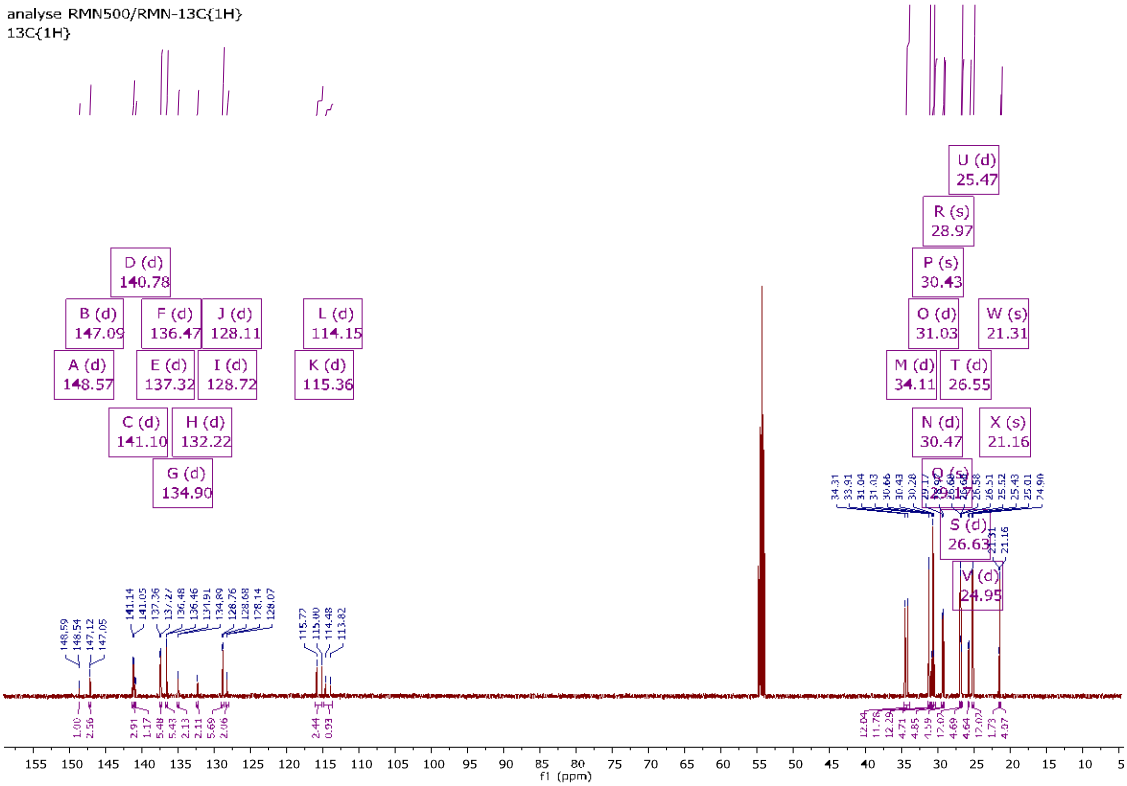


*Figure S50. $^{13}C\{^{1}H\}$ NMR spectrum at 213 K for compound **3** in CD_2Cl_2*

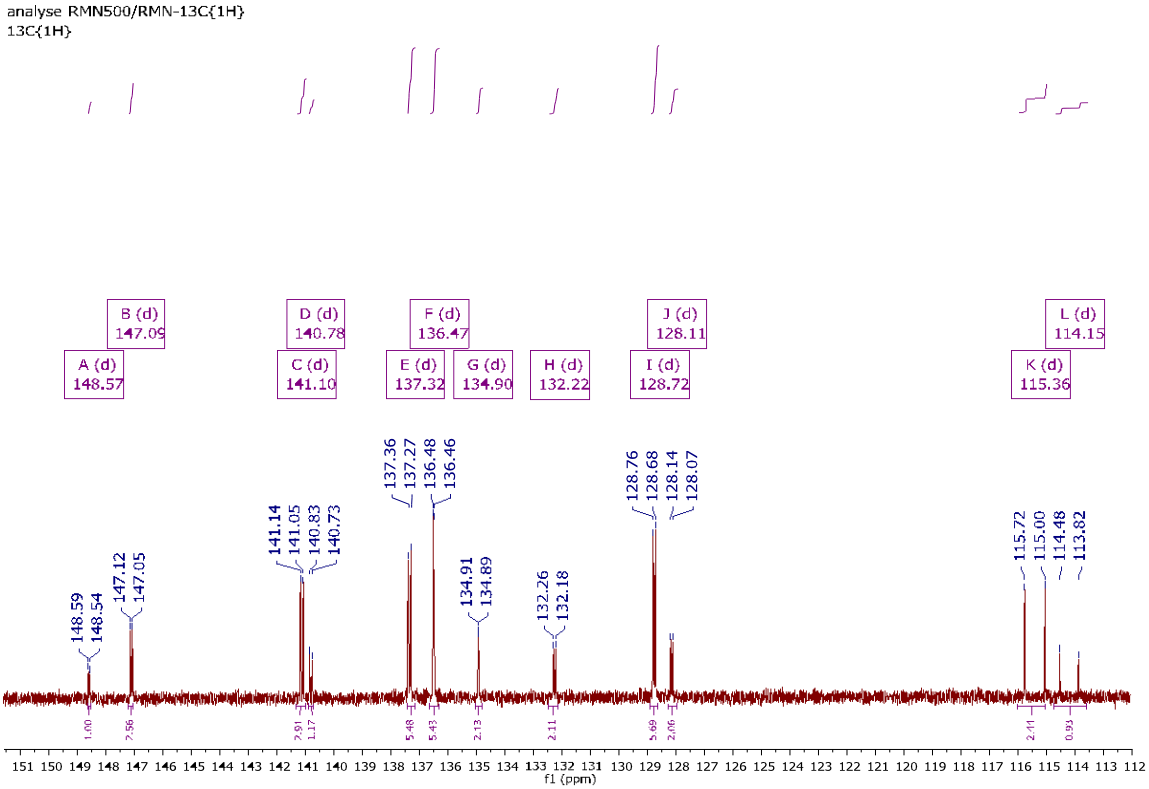


*Figure S51. $^{13}C\{^{1}H\}$ NMR spectrum at 213 K in CD_2Cl_2 for compound **3**, 152 to 112 ppm window.*

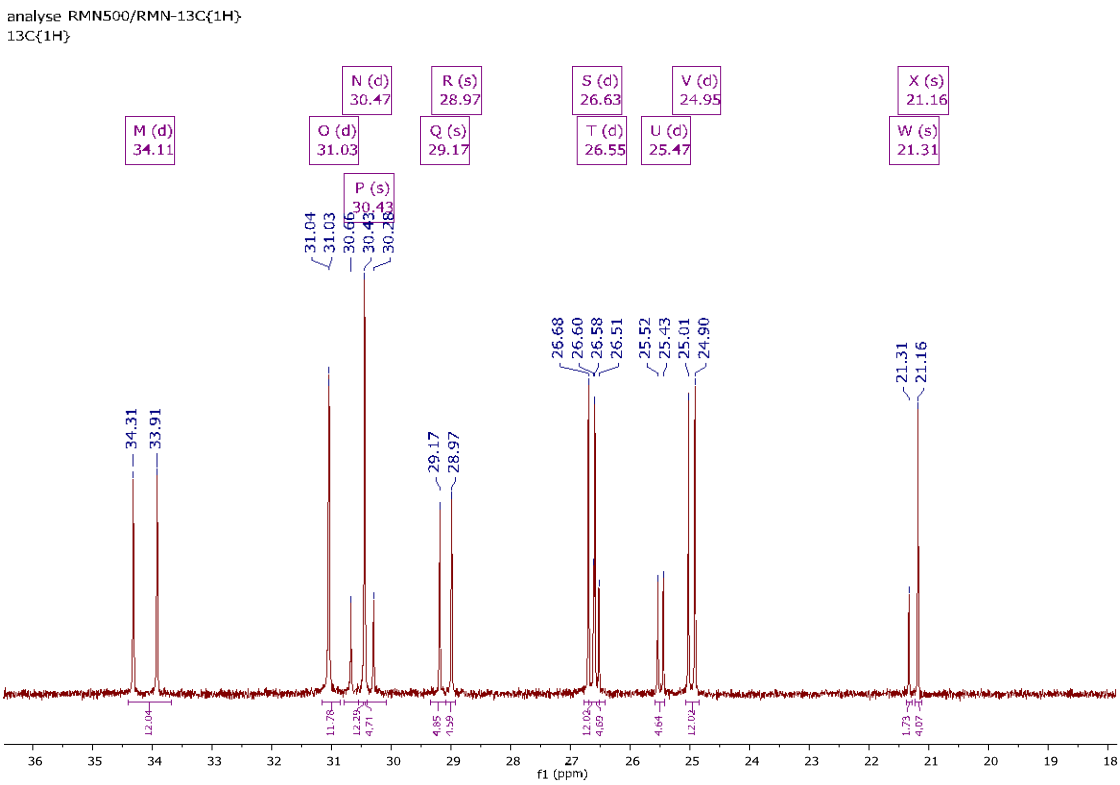


*Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum at 213 K in CD_2Cl_2 for compound **3**, 36 to 18 ppm window.*

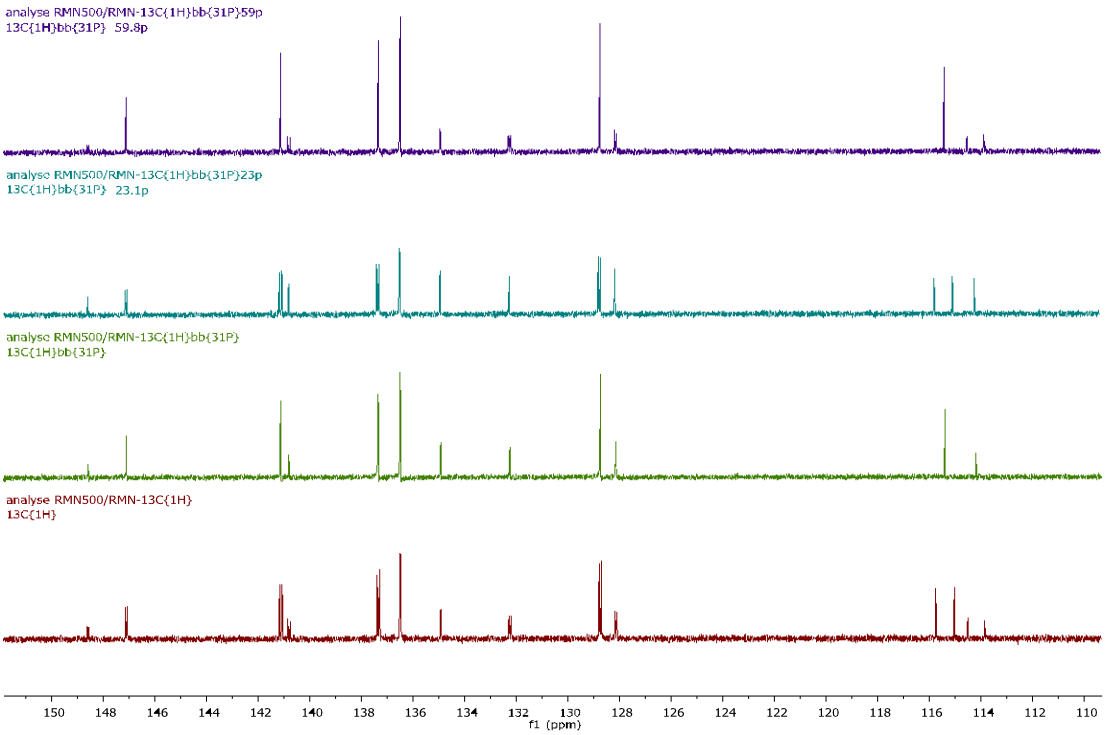


*Figure S53. $^{13}C\{^{1}H\}$ NMR analysis of compound **3** at 213 K in CD_2Cl_2, from bottom to top: no ^{31}P decoupling, broad band ^{31}P decoupling, selective ^{31}P decoupling at 23 ppm, selective ^{31}P decoupling at 59 ppm.*

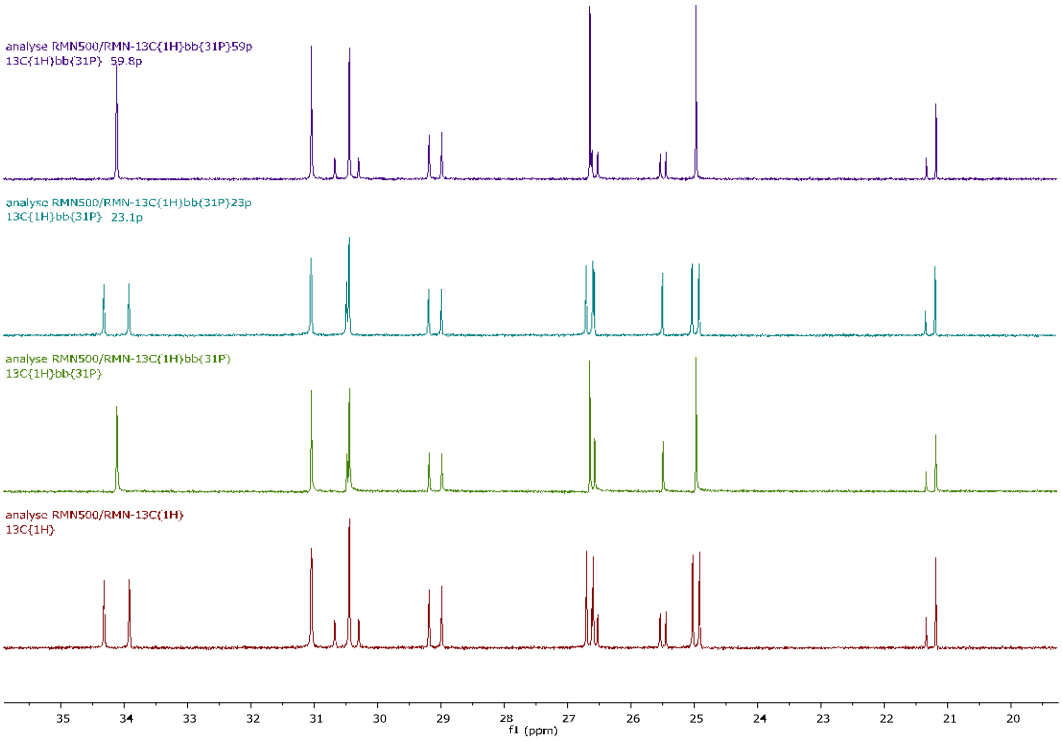


*Figure S54. $^{13}C\{^{1}H\}$ NMR analysis of compound **3** at 213 K in CD_2Cl_2, from bottom to top: no ^{31}P decoupling, broad band ^{31}P decoupling, selective ^{31}P decoupling at 23 ppm, selective ^{31}P decoupling at 59 ppm, 36 to 18 ppm window.*

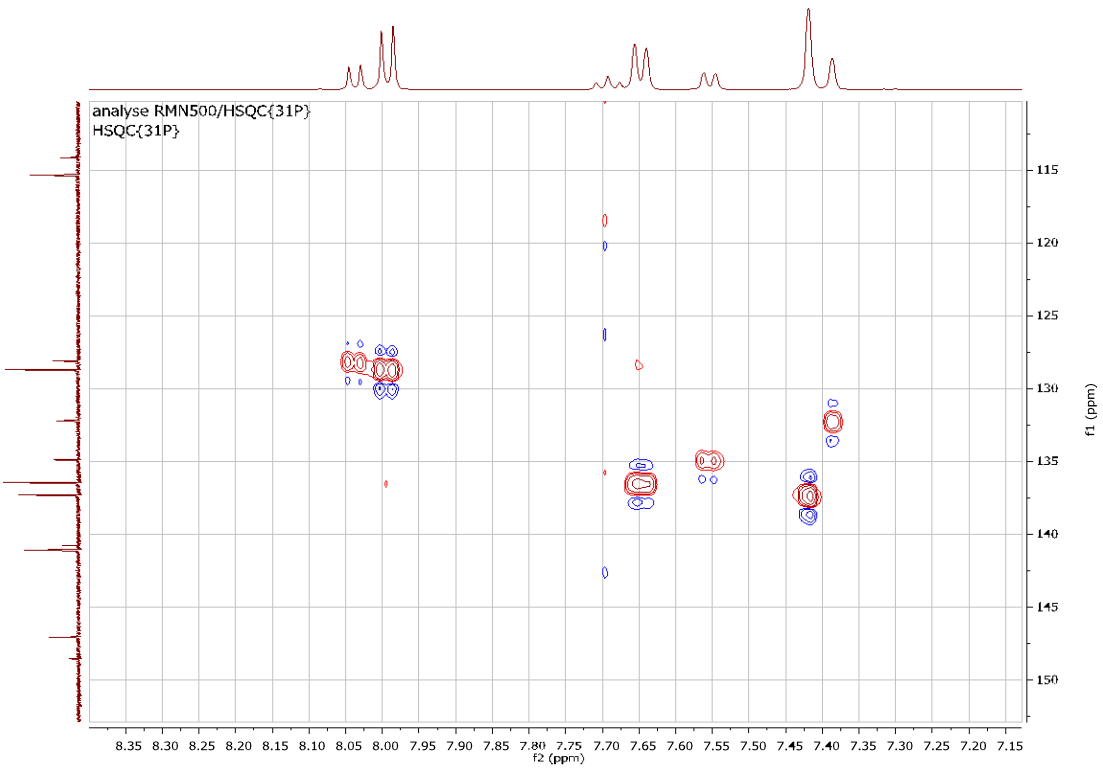


*Figure S55. ^{1}H / $^{13}C\{^{1}H\}$ NMR HSQC experiment at 213 K in CD_2Cl_2 for compound **3**.*

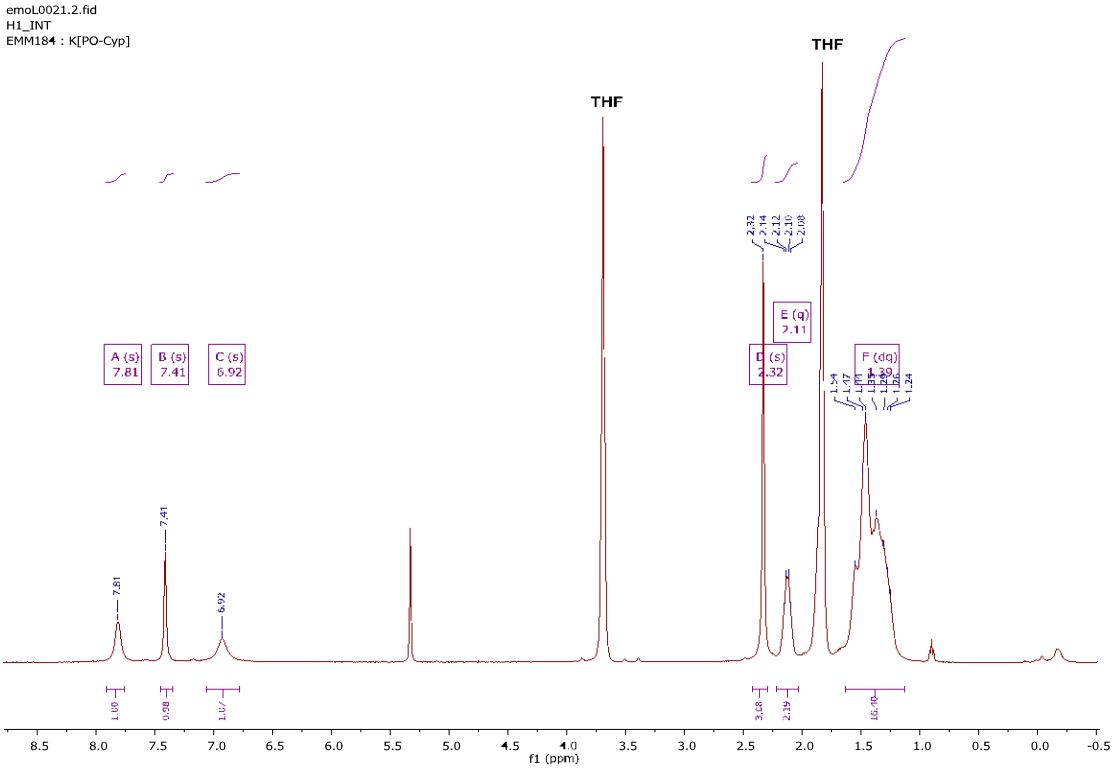


*Figure S56. ^{1}H NMR spectrum for compound **K[PO-Cyp]** at 298 K in CD_2Cl_2*

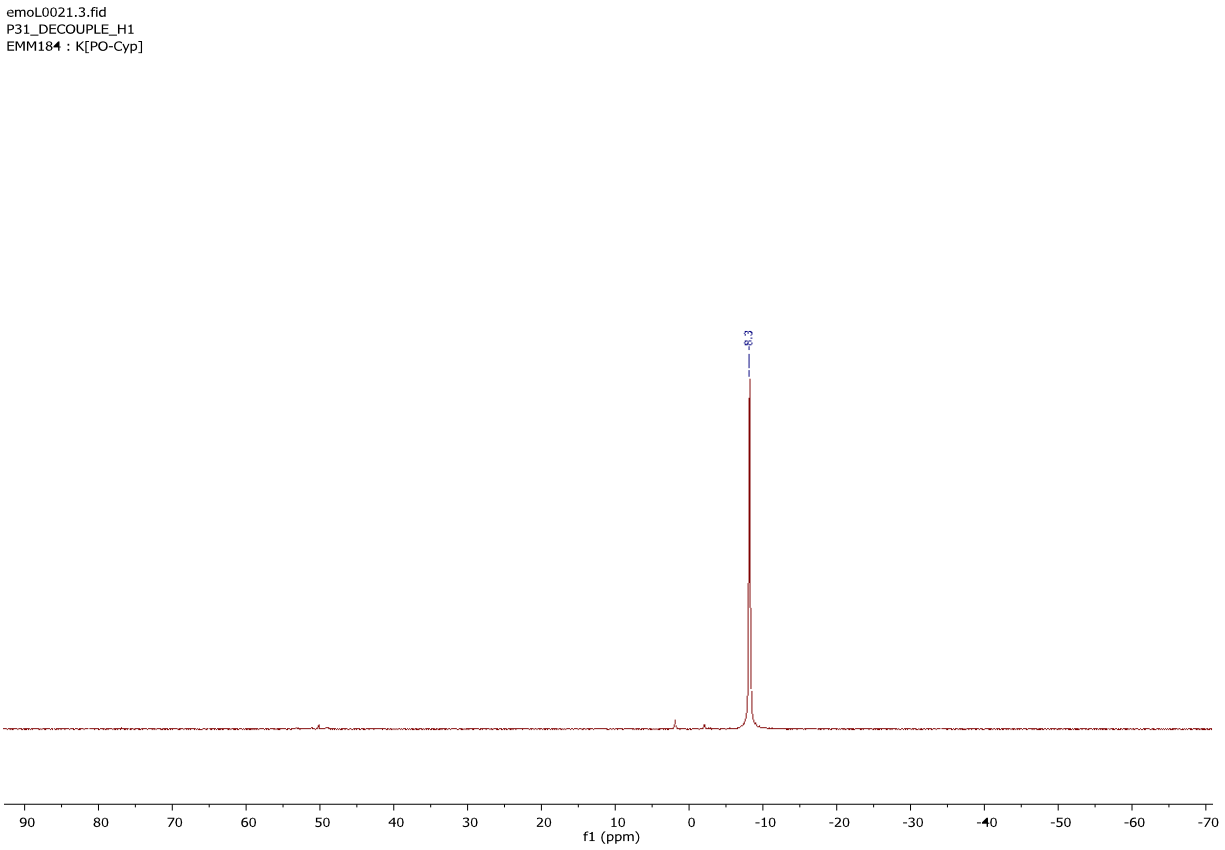


*Figure S57. $^{31}P\{^{1}H\}$ NMR spectrum for compound **K[PO-Cyp]** at 298 K in CD_2Cl_2*

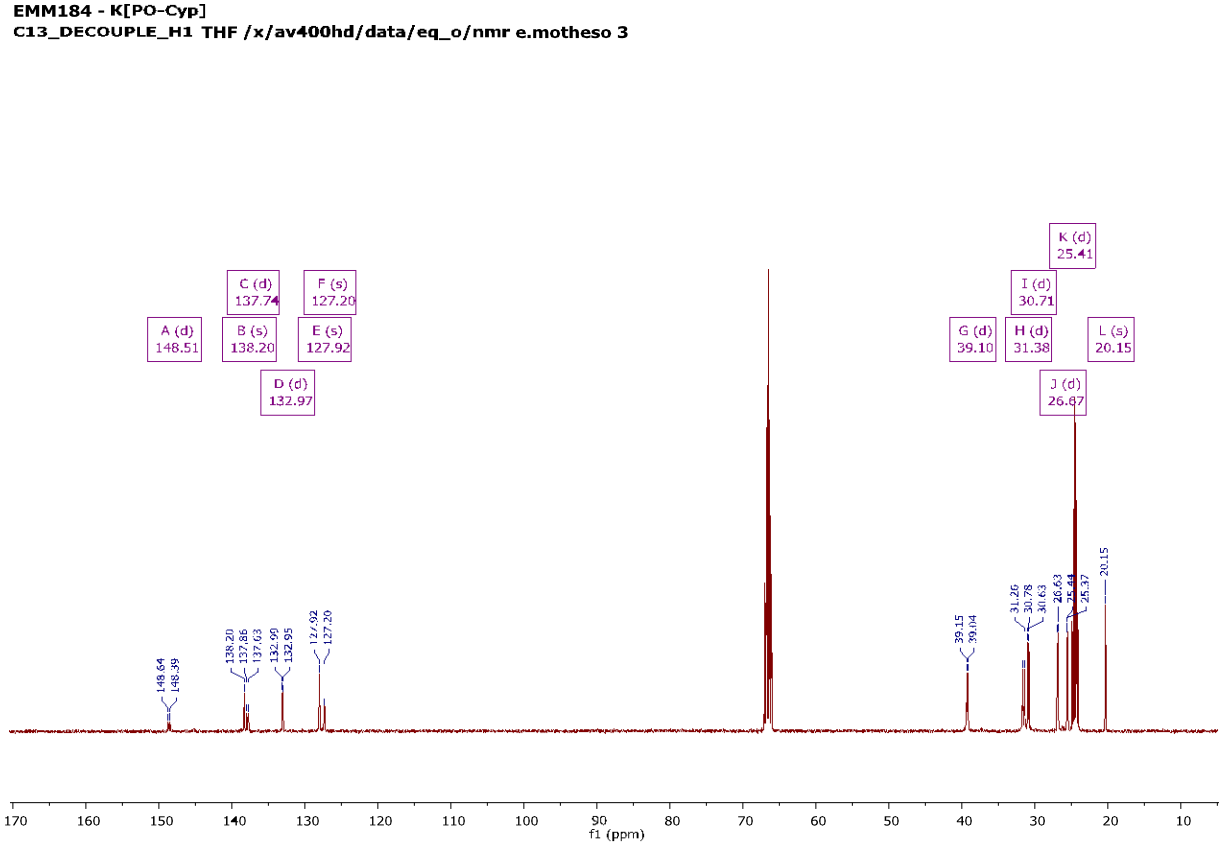
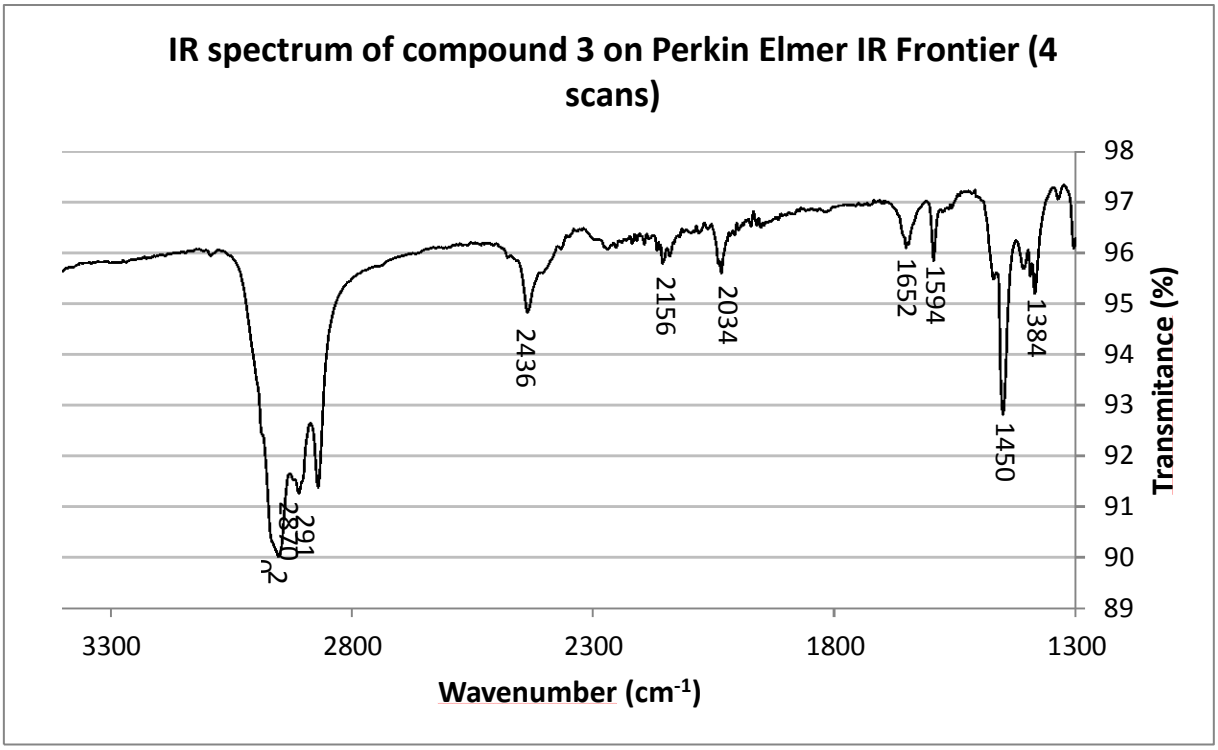


*Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum for compound **K[PO-Cyp]** at 298 K in THF-d_8*



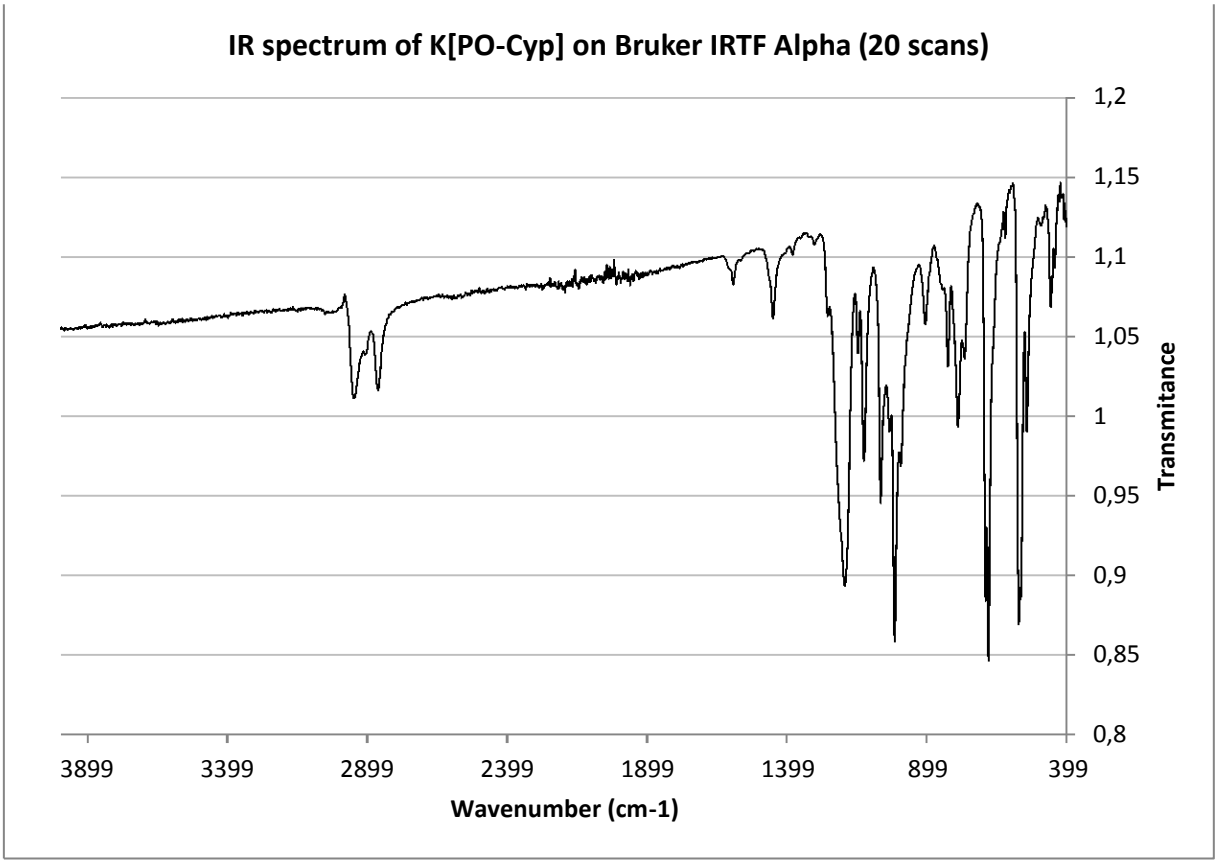


*Figure S59. Powder IR analysis for compound **3** and **K[PO-Cyp]**.*

NMR and IR Spectra of compound 4

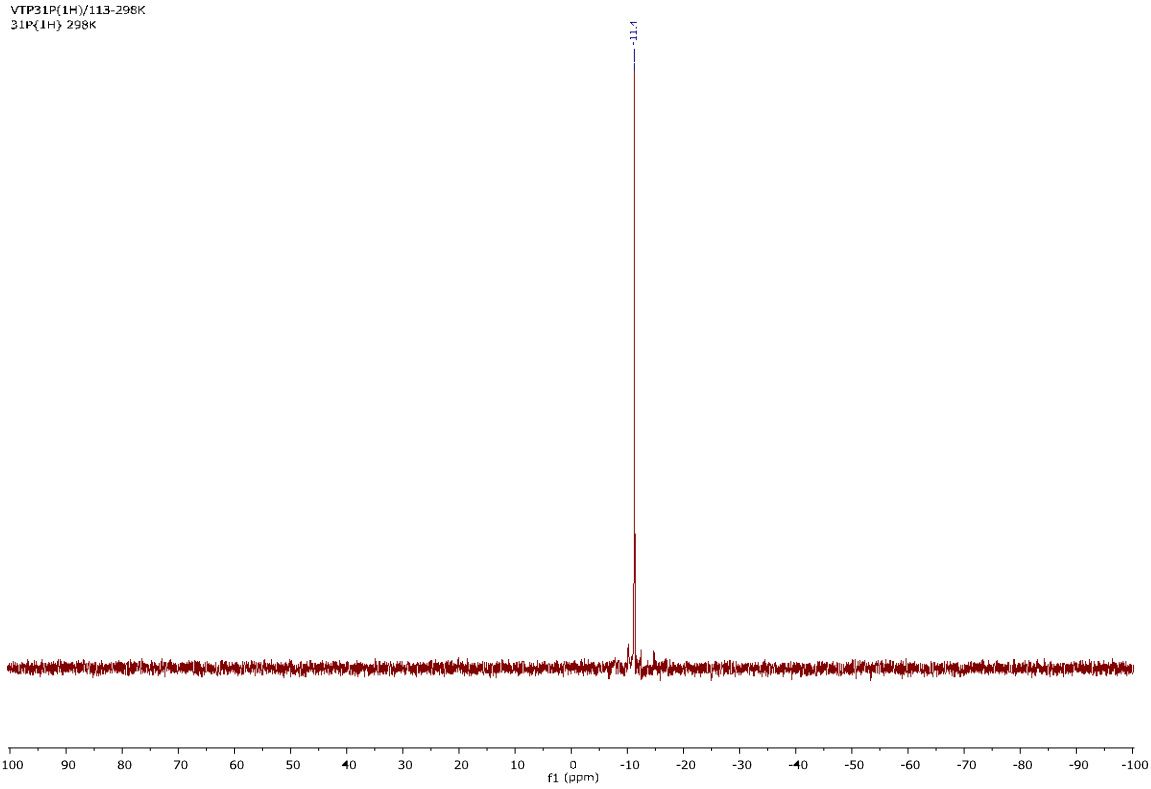


*Figure S60. $^{31}P\{^{1}H\}$ NMR spectra for compound **4** at 298 K in CD_2Cl_2*

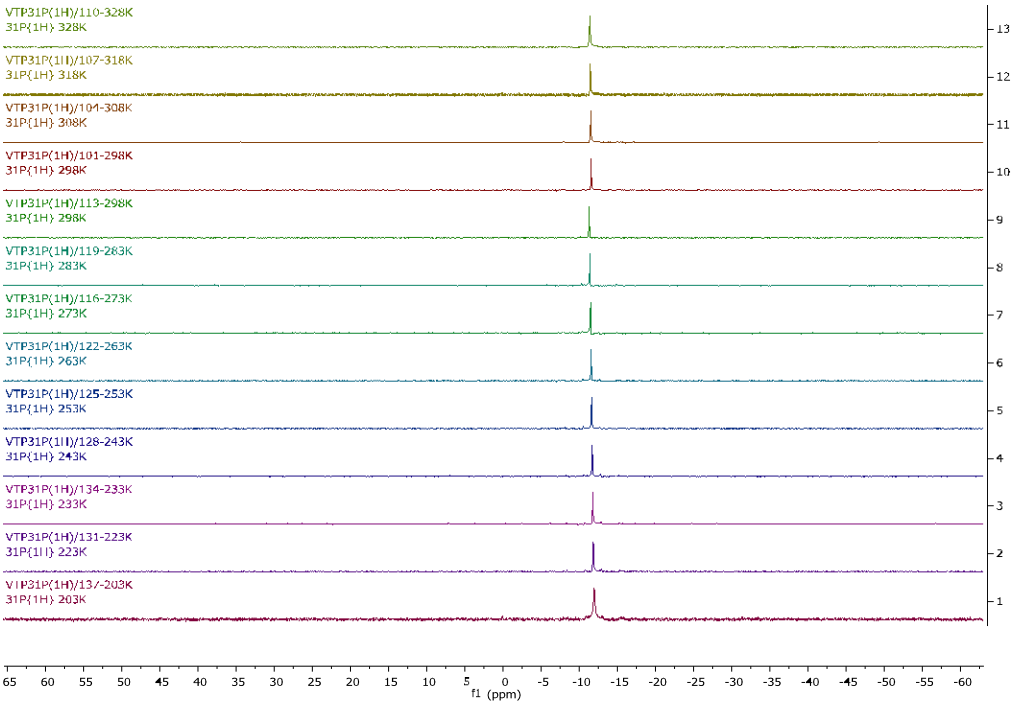


*Figure S61. Variable temperature $^{31}P\{^{1}H\}$ NMR spectra for compound **4** from 203 K to 328 K in CD_2Cl_2 (exp 1 to 9) and $CDCl_3$ (exp 10 to13)*

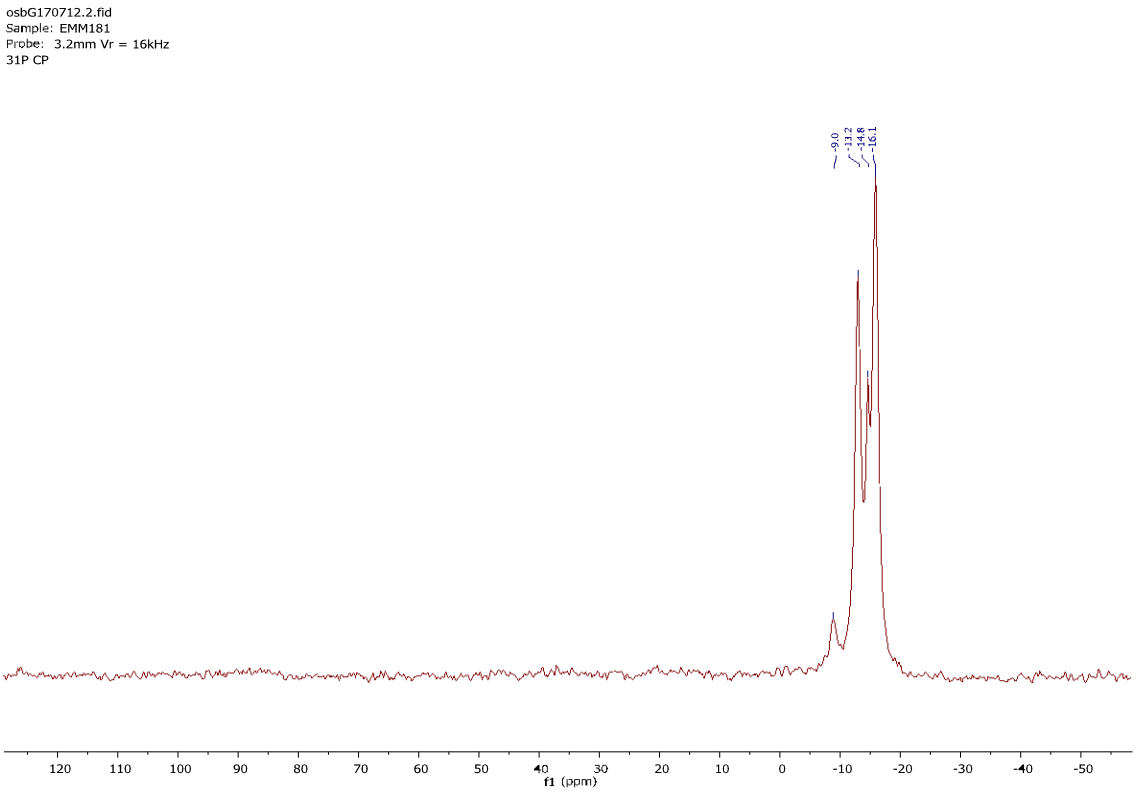


*Figure S62. Solid state CPMas [31]P NMR spectrum for compound **4***

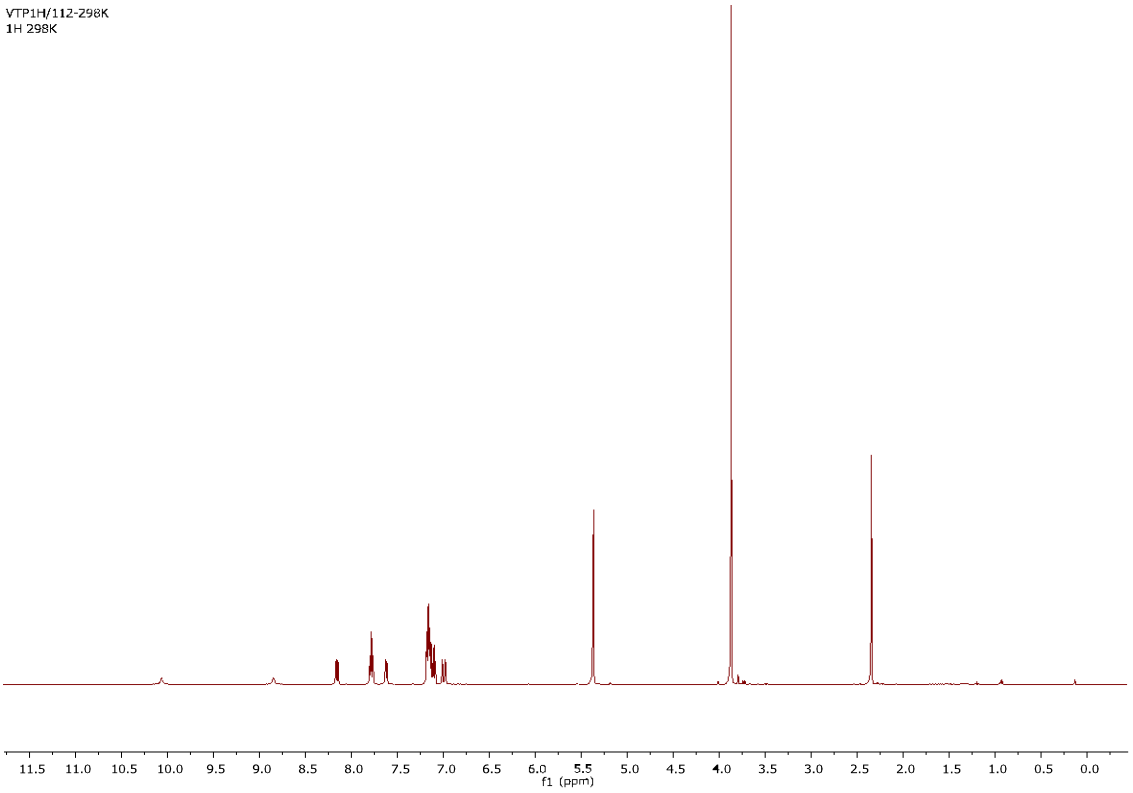


*Figure S63. [1]H NMR spectrum for compound **4** at 298 K in CD_2Cl_2*

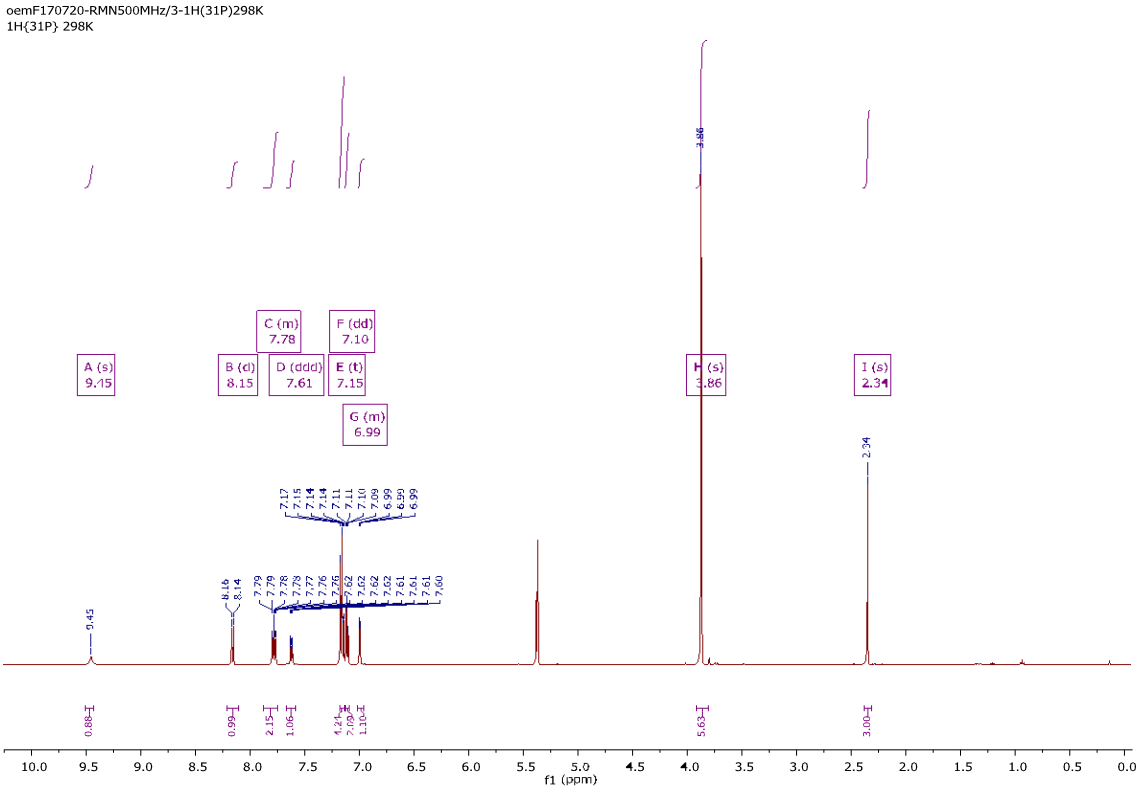


*Figure S64. $^{1}H\{^{31}P\}$ NMR spectrum for compound **4** at 298 K in CD_2Cl_2*

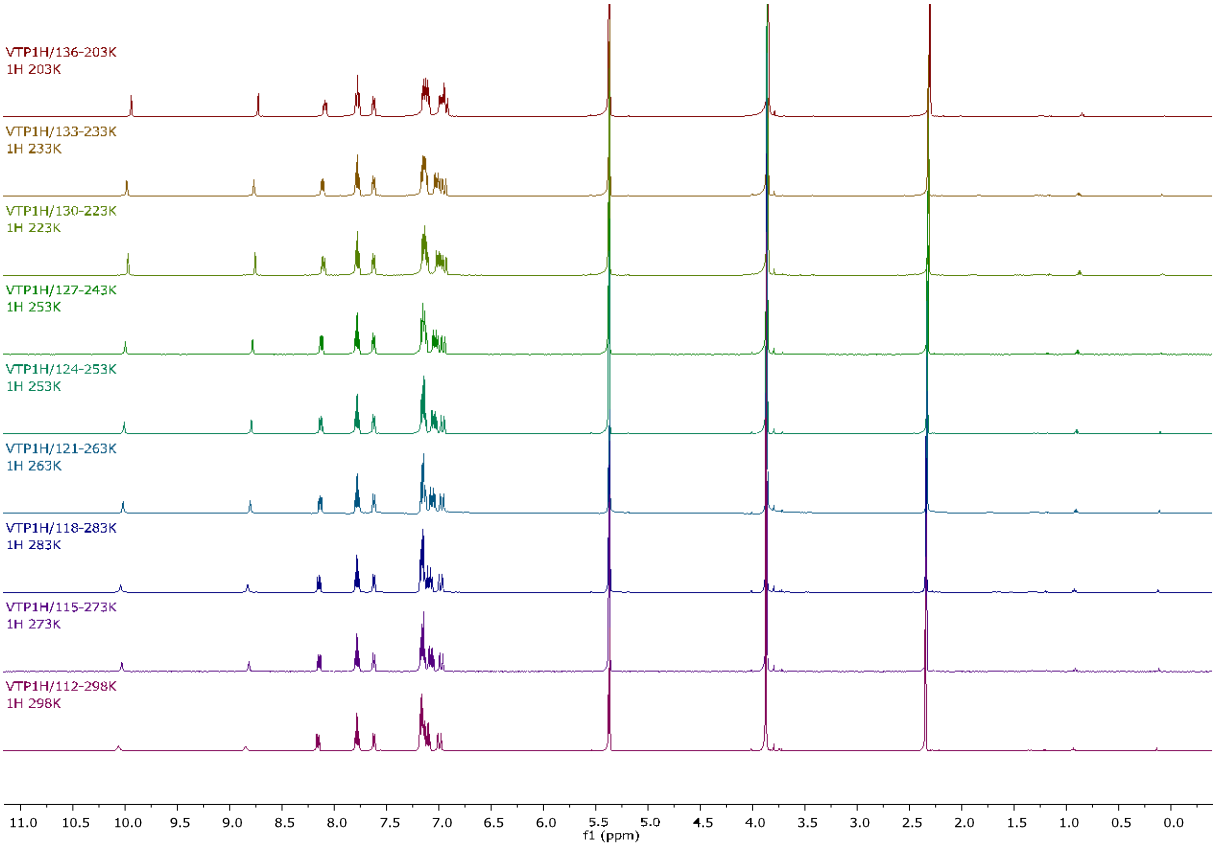


*Figure S65. Variable temperature ^{1}H NMR spectra for compound **4** from 203 K to 298 K in CD_2Cl_2*

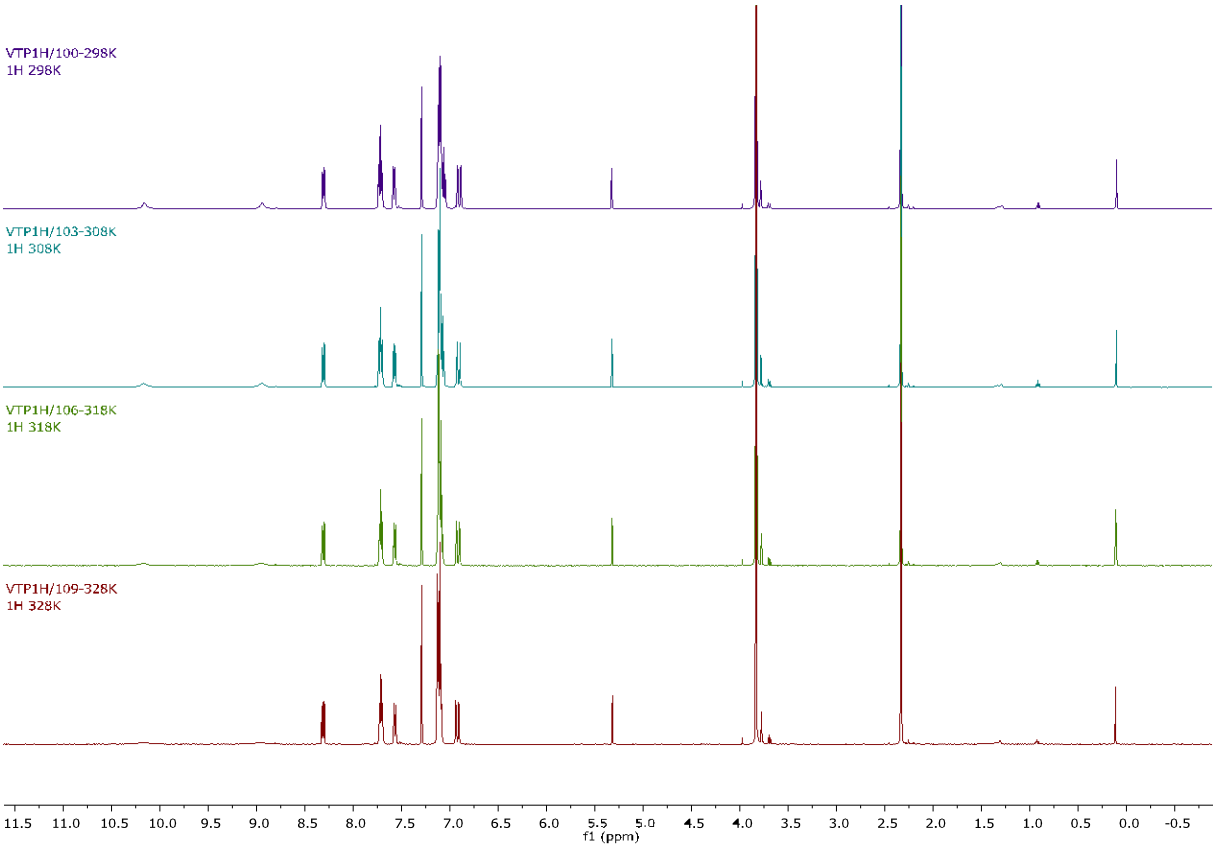


*Figure S66. Variable temperature ^{1}H NMR spectra for compound **4** from 298 K to 328 K in $CDCl_3$*

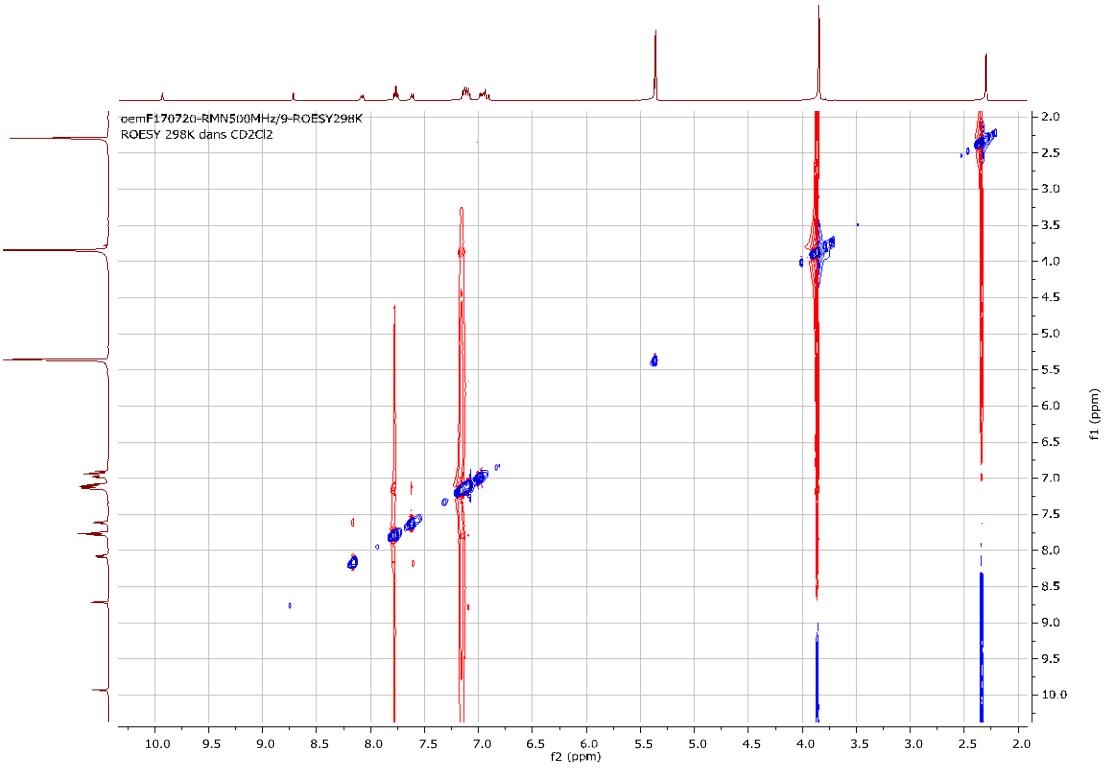


*Figure S67. NOESY $^{1}H/^{1}H$ spectrum for compound **4** at 298 K in CD_2Cl_2*

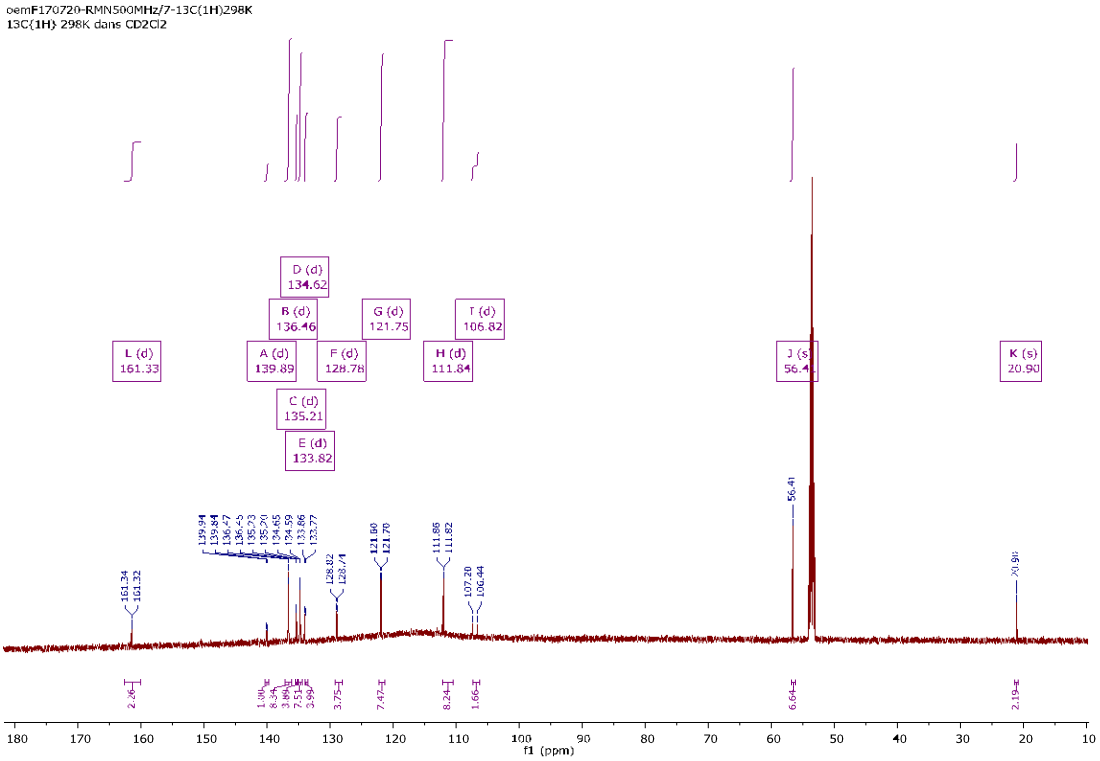


*Figure S68. $^{13}C\{^{1}H\}$ NMR spectrum at 298 K for compound **4** in CD_2Cl_2*

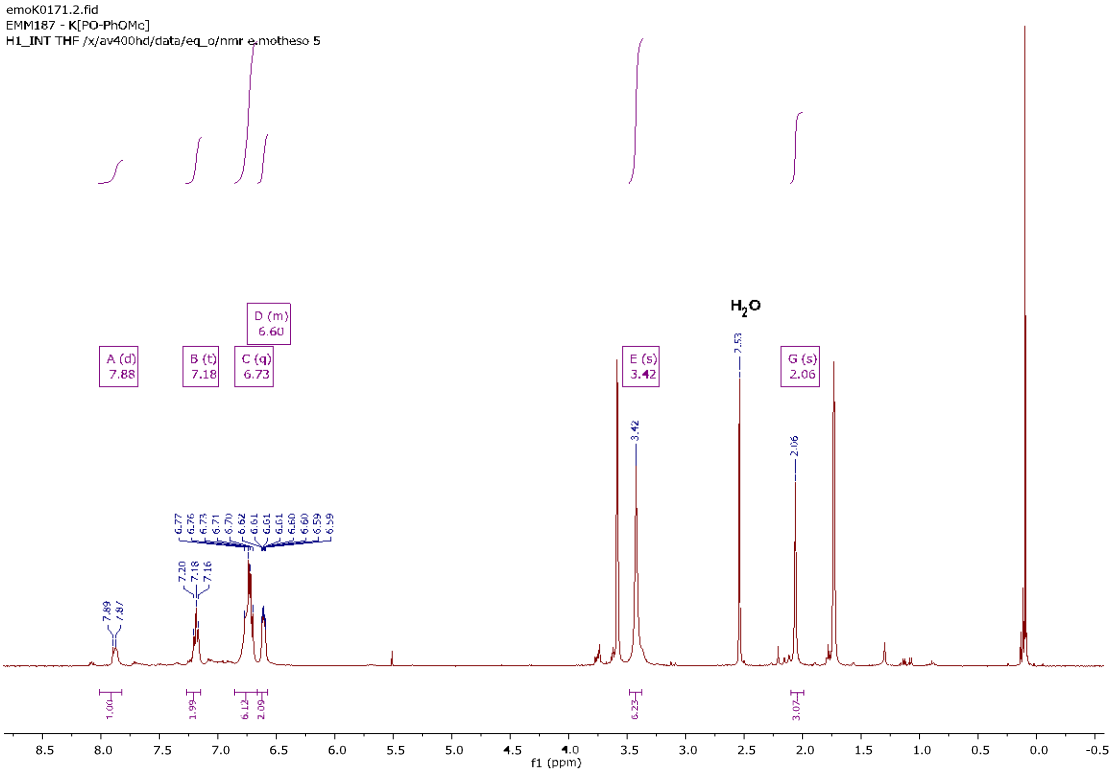


*Figure S69. ^{1}H NMR spectrum for compound **K[PO-OMe-Ph]** at 298 K in THF-d_8*

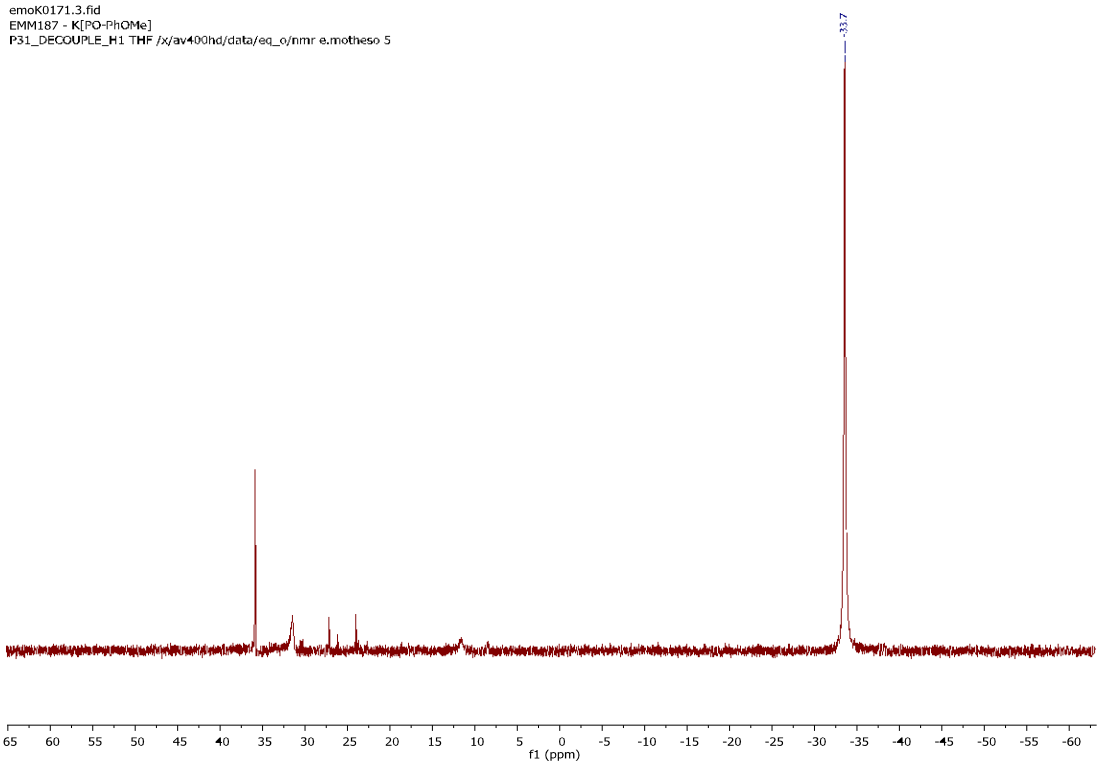


*Figure S70. $^{31}P\{^{1}H\}$ NMR spectrum for compound **K[PO-OMe-Ph]** at 298 K in THF-d_8*

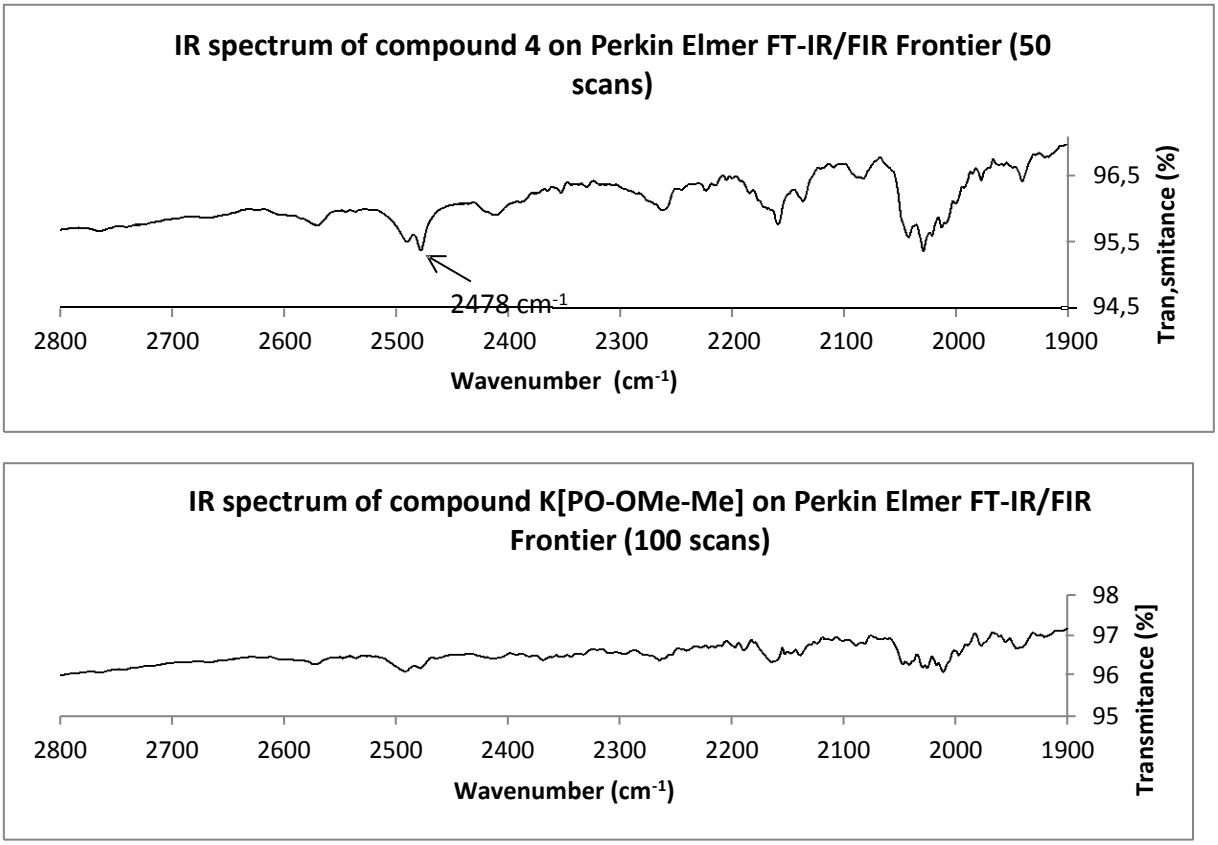


*Figure S71. Powder ATR IR for compound **4** and K[PO-OMe-Me]*

Dynamic exchange between the exo and endo form in solution for 1-3

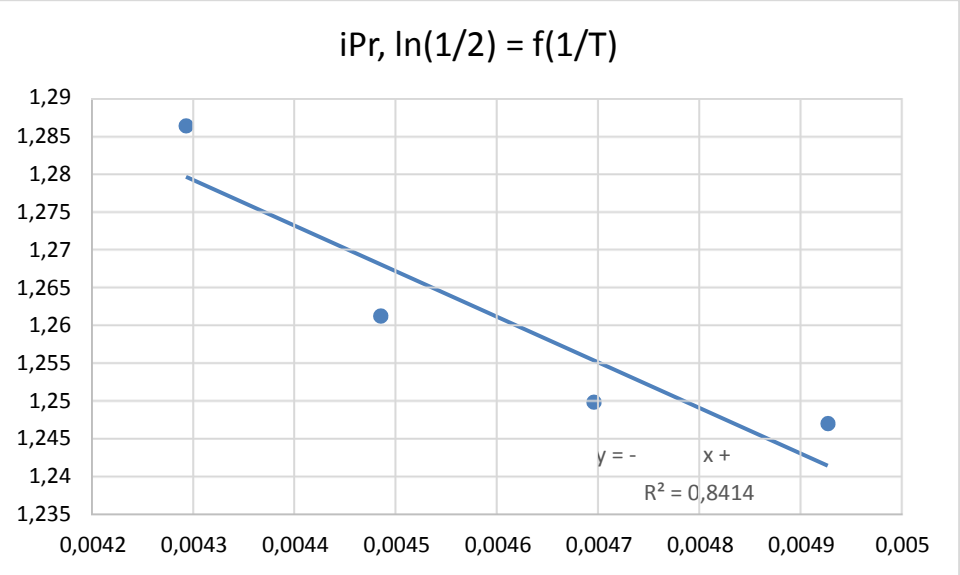
Thermodynamic data

The van't Hoff plot affords ΔG_0 according to the following equation:

$$\ln k = \frac{\Delta G}{RT} \quad (1)$$

Compound 1 H[PO-iPr]

T (K)	Integral Form 1	Integral Form 2	ln(1/2)	1/T
233	3,62	1	1,28647403	0,00429185
223	3,53	1	1,26129787	0,0044843
213	3,49	1	1,24990174	0,00469484
203	3,48	1	1,24703229	0,00492611



ΔH_0 = -(-60.315) * 8.31.10^{-3} = 501.21765 10^{-3} kJ.mol^{-1}

ΔS_0 = 1.5386*8.31.10^{-3} = 12.785766 J.mol^{-1}

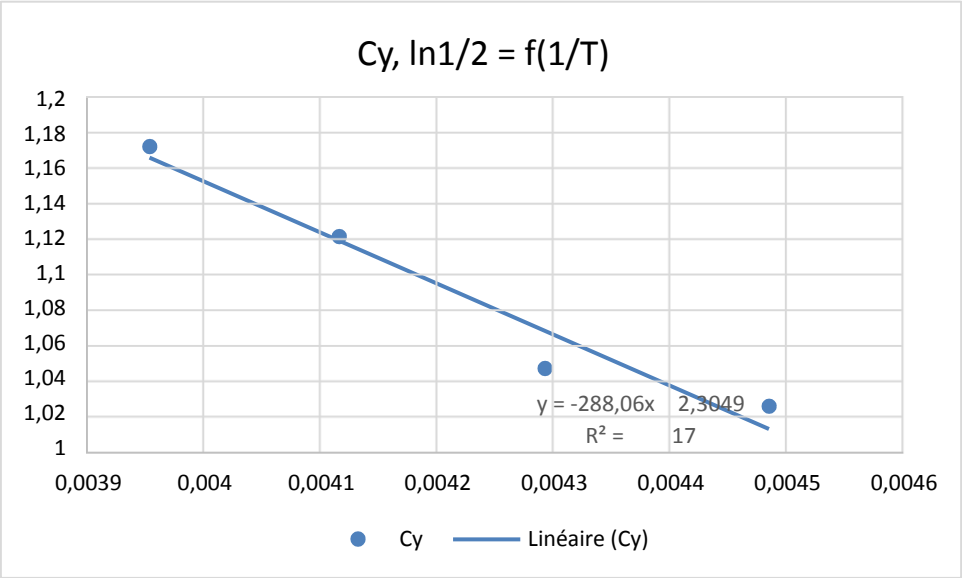
With $\Delta G_0 = \Delta H_0 - T\Delta S_0$

ΔG_0^{298} = -3.31 kJ.mol^{-1}

$\Delta G_0^{213.15}$ = -2.22 kJ.mol^{-1}

Compound 2 H[PO-Cy]

T (K)	Integral Form 1	Integral Form 2	ln(1/2)	1/T
253	3,23	1	1,17248214	0,00395257
243	3,07	1	1,12167756	0,00411523
233	2,85	1	1,04731899	0,00429185
223	2,79	1	1,0260416	0,0044843



$\Delta H_0 = 2393.8\ 10^{-3}$ kJ.mol^{-1}

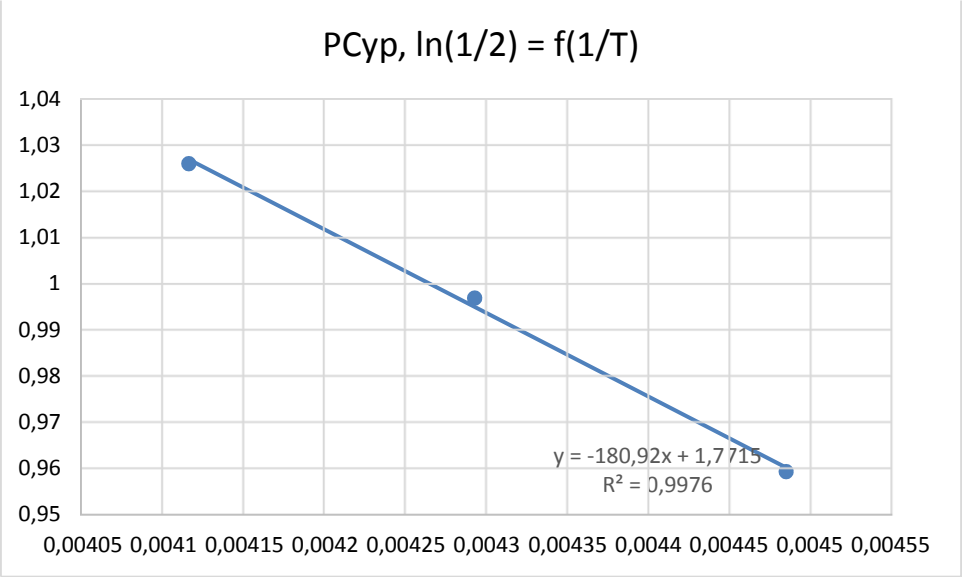
$\Delta S_0 = 19.15$ J.mol^{-1}

$\Delta G_0^{298} = -3.31$ kJ.mol^{-1}

$\Delta G_0^{213.15} = -1.69$ kJ.mol^{-1}

Compound 3 H[PO-Cyp]

T	Integral Form 1	Integral Form 2	ln(1/2)	1/T
243	2,79	1	1,0260416	0,00411523
233	2,71	1	0,99694863	0,00429185
223	2,61	1	0,95935022	0,0044843



$\Delta H_0 = 1503.45\ 10^{-3}$ kJ.mol^{-1}

$\Delta S_0 = 14.709$ J.mol^{-1}

$\Delta G_0^{298} = -2.88$ kJ.mol^{-1}

$\Delta G_0^{213.15} = -1.63$ kJ.mol^{-1}

Kinetic data

The activation parameters for the equilibrium have been determined according to equation (2), from the Eyring equation (1).

$$k = x\frac{k_B T}{h} e^{-\Delta G/RT} \qquad (1)$$

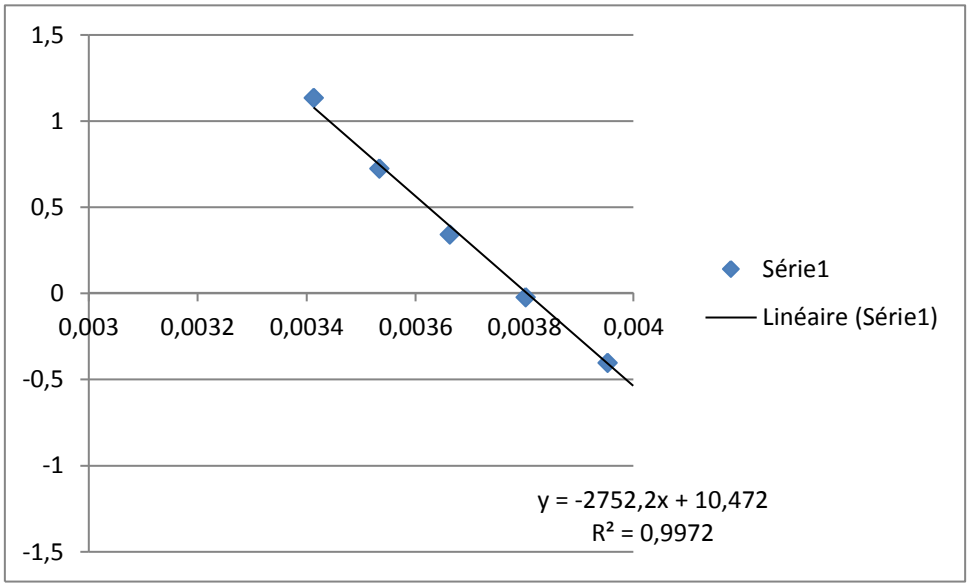
$$\log\frac{k}{T} = 10{,}32 - \frac{\Delta H}{4{,}58\,T} + \frac{\Delta S}{4{,}58} \qquad (2)$$

The rate constant k has been determined with DNMR software from Topspin 1.3

Compound 1 H[PO-iPr]

T (Kelvin)	k (s^{-1})
233	10
243	40
253	100
263	250
273	600
283	1500
293	4000

$\log\frac{k}{T} = f(\frac{1}{T})$ below



$$-\frac{\Delta H}{4{,}58} = -2752{,}2$$

$$\Delta H = 12605 \text{ cal/mol}$$

$$\frac{\Delta S}{4{,}58} + 10{,}32 = 10{,}47$$

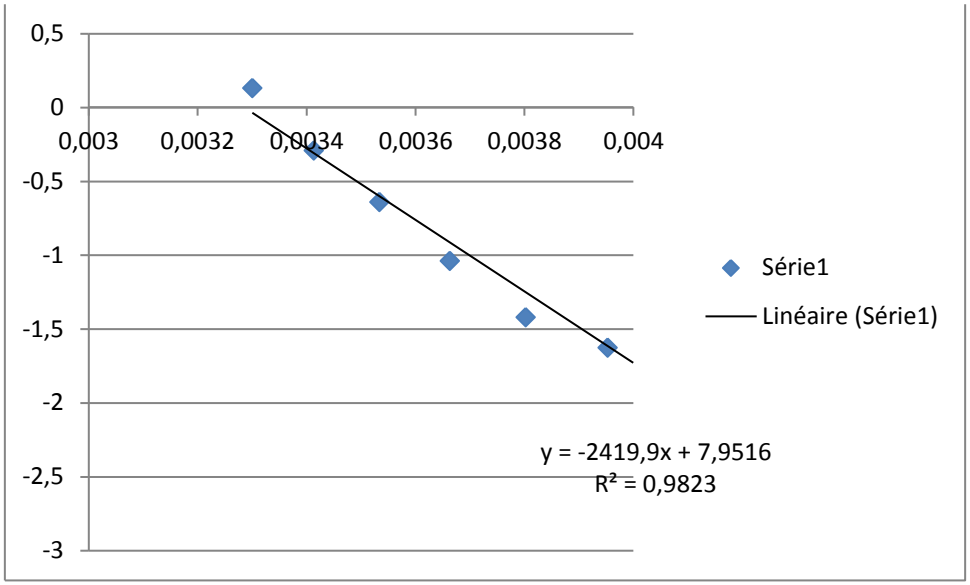
$$\Delta S = 0{,}69 \text{ cal/mol}$$

At 293 K: ΔG = 12605 – 293 (0,69) = 12,4 Kcal/mol = 51.9 KJ/mol

Compound 2 H[PO-Cy]

T (Kelvin)	k (s^{-1})
233	1
243	3
253	6
263	10
273	25
283	65
293	150
303	410

$\log \frac{k}{T} = f(\frac{1}{T})$ below



$$-\frac{\Delta H}{4{,}58} = -2419{,}9$$

$$\Delta H = 11083 \text{ cal/mol}$$

$$\frac{\Delta S}{4{,}58} + 10{,}32 = 7{,}95$$

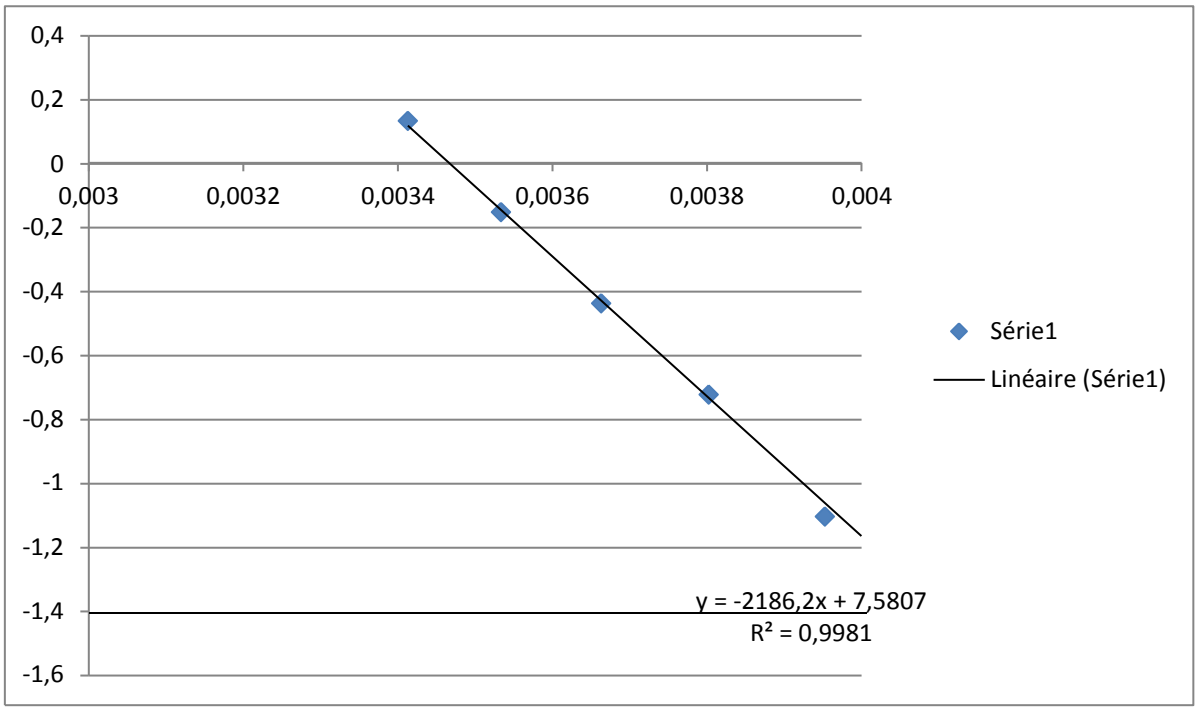
$$\Delta S = -10{,}85 \text{ cal/mol}$$

At 293 K: ΔG = 11083 – 293 (-10,85) = 14,3Kcal/mol = 59.8 KJ/mol

Compound 3 H[PO-Cyp]

T (Kelvin)	k (s^{-1})
243	10
253	20
263	50
273	100
283	200
293	400

$\log\frac{k}{T} = f(\frac{1}{T})$ below



$$-\frac{\Delta H}{4{,}58} = -2186{,}2$$

$$\Delta H = 10013 \text{ cal/mol}$$

$$\frac{\Delta S}{4{,}58} + 10{,}32 = 7{,}58$$

$$\Delta S = -12{,}55 \text{ cal/mol}$$

At 293 K: ΔG = 10013 – 293 (-12,55) = 13,7 Kcal/mol = 57.3 KJ/mol

X-Ray Analyses and Structural Figures

Data for **2** (CCDC 1846730), **3** (CCDC 1846732) and **4** (CCDC 1846731) were collected at low temperature (100 K) on a *Bruker Kappa Apex II* diffractometer using a microsource with a Mo-Kα radiation (λ = 0.71073Å) and equipped with an *Oxford Cryosystems Cryostream Cooler Device*.

The structures have been solved by Direct Methods using either SIR92 [1] or SHELXS97 [2], and refined by means of least-squares procedures on a F^2 with the aid either of the program SHELXL2016 [2] included in the softwares package WinGX version 1.63 [3] or with the software Crystals [4]. The Atomic Scattering Factors were taken from International tables for X-Ray Crystallography [5]. All hydrogens atoms were placed geometrically, and refined by using a riding model, except for the Hydrogen atom bonded to the Phosphorus atom which was located for each structure by Fourier differences. All non-hydrogens atoms were anisotropically refined. Drawing of molecules were performed with the program ORTEP32 [6] with 30% probability displacement ellipsoids for non-hydrogen atoms.

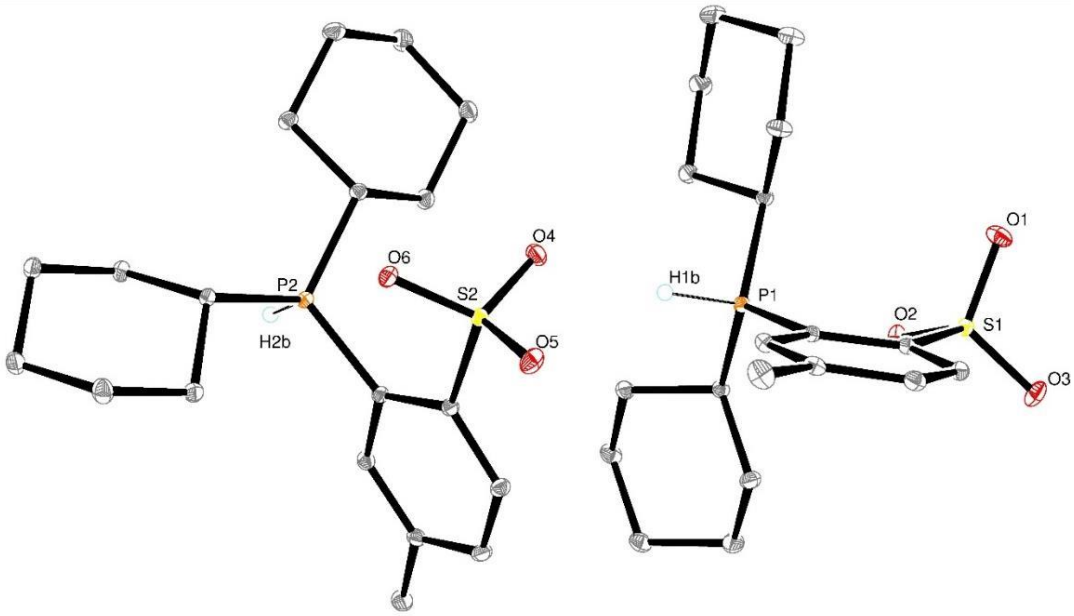


Figure S72. Molecular structure of ***2***

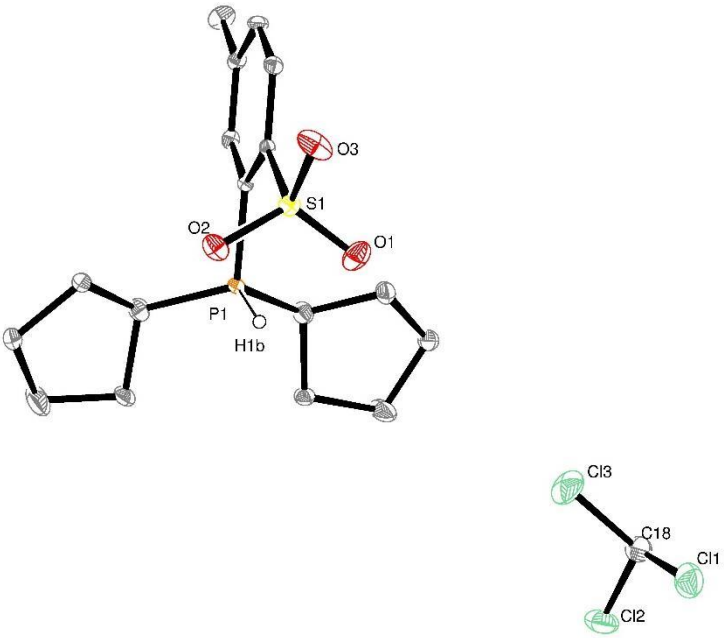


*Figure S73. Molecular structure of **3***

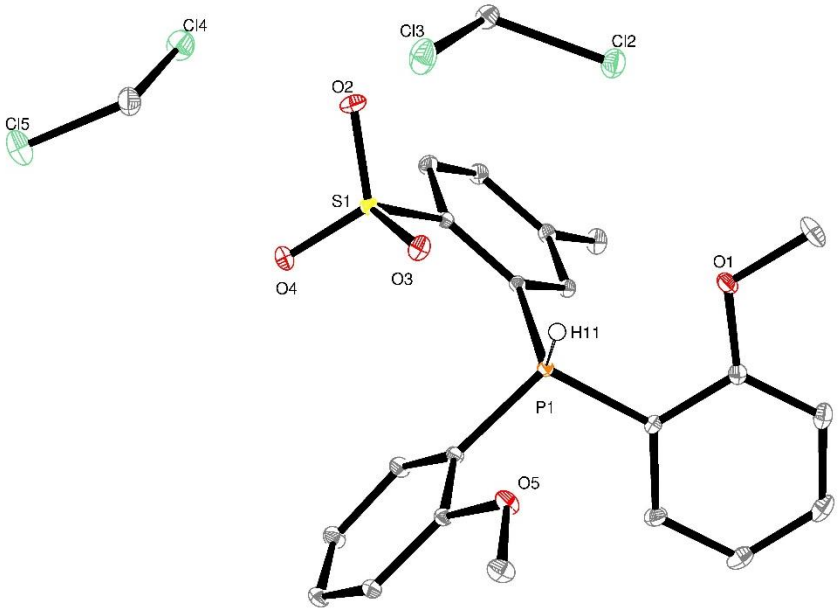


*Figure S74. Molecular structure of **4***

References

1. SIR92 - A program for crystal structure solution. A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr*. **1993**, *26*, 343-350.
2. WINGX - 1.63 Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-Ray Diffraction Data. L.Farrugia, *J. Appl. Crystallogr*.**1999**, *32*, 837 - 838.
3. SHELX&SHELXTL programms - G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr*., **2008**, *64*, 112-122.
4. CRYSTALS, P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Crystallogr.,* **2003**, *36*, 1487.
5. INTERNATIONAL tables for X-Ray crystallography, **1974**, Vol IV, Kynoch press, Birmingham, England.
6. ORTEP3 for Windows - L. J. Farrugia, *J. Appl. Crystallogr*. **1997**, *30*, 565.