Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Data

Orthogonality in Main Group Compounds: Direct One-step Synthesis of Air- and Moisture-stable Cyclophosphazanes by Mechanochemistry

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1. Experimental Procedures of Compounds 2-7

General Method and Materials

All reactions were prepared in an argon-filled glovebox into stainless steel grinder jars (10 mL) along with 10 mm stainless steel miller balls (one miller ball in a miller jar; weighed approximately 4.0153 g).[1] These jars were subsequently brought out of the glovebox and placed onto Retsch Mixer Mill MM400 machine and subjected to 30 Hz milling for respective reaction time. All manipulations were conducted using Schlenk techniques and glovebox under inert atmosphere of dry argon. All chemicals were purchased from Sigma-Aldrich, Merek and Alfa Aesar and were used as received. Solvents were distilled over sodium/benzophenone according to standard procedures. All solvents were degassed using freeze-pump-thaw cycles and stored over 4Å molecular sieves. Deuterated solvents were distilled from calcium hydride and degassed by three freeze-pump-thaw cycles and stored over 4Å molecular sieves prior to use. Compound **1** was prepared according to literature procedure.[2]

^{1}H, ^{13}C, ^{31}P-{^{1}H} NMR spectra were recorded using Bruker Avance III 400 (BBFO 400) spectrometers with thin -walled NMR tubes (Wilmad, 535-LPV-7). ^{1}H and ^{13}C NMR spectra were recorded in dried $CDCl_3$ or MeOD as an internal standard. ^{31}P-{^{1}H} NMR spectra were referenced to 85% H_3PO_4/D_2O as the external standard. ^{13}C and ^{31}P-{^{1}H} NMR spectra were acquired using broad band decoupling. For ^{1}H NMR spectroscopy, spectra were internally referenced to signal at a singlet at δ 7.26 ppm for $CDCl_3$ or a quintet at δ 3.31 ppm for MeOD, and for ^{13}C NMR spectroscopy, a triplet at δ 77.16 ppm for $CDCl_3$ or a septet at δ 49.00 ppm for MeOD. All reactions are monitored via ***in situ*** ^{31}P-{^{1}H} NMR.[3] ***In situ*** NMR was conducted by taking a spatula of reaction mixture (~ 5 mg) into NMR tube in the glovebox and dissolved in dried THF or toluene. X-ray crystallography studies were carried out using Bruker X8 CCD Diffractometer and/or Kruker Kappa CCD Diffractometer. The reflections were recorded and processed with Bruker SAINT software package which uses narrow-frame

algorithm. The structures were solved via direct methods with the SHELXTL software package and refined by full-matrix least-squares calculations on F2 with anisotropic displacements parameters assigned to all atoms. Infra-red spectroscopic studies were conducted by smearing Nujol mulls of the compounds between two sodium chloride windows in the glovebox, kept in a box of silica beads and transferred out of the glovebox. The preparation of samples was carried out in the glovebox. Samples were packed inside melting point capillary tubes to about 0.5cm in height. The tubes must be sealed with silicon grease to prevent oxidation and hydrolysis. Melting points of the samples was measured using standard melting point apparatus (Optimelt MPA100 Automated Melting Point System). Melting points reported were uncorrected. Fourier transform infrared (FT-IR) spectra were recorded using Shimadzu IR Prestige-21 FTIR spectrometer. Elemental analyses were performed using Euro Vector Euro EA Elemental Analyzer (CHNS). High-resolution ESI mass spectra were obtained using a Waters Q-Tof Premier.

Synthesis of $[(S)P(N^tBu)(OAd)]_2$ (2)*:* **1** (0.275 g, 1.0 mmol), 1-adamantanol (0.304 g, 2.0 mmol) and elemental sulfur (0.096 g, 3.0 mmol) were weighed and poured into a mechanochemical grinder reaction vessel along with Et_3N (0.28 cm^3, 2.0 mmol) and 10 mm stainless steel ball. The grinding frequency was set to 30 Hz and the vessel was subjected to grinding for 7.0 hours. Toluene was added and the reaction solution was filtered to remove excess unreacted sulfur. The solution was concentrated and left to crystallize at room temperature. Yield: 0.204 g (31 %); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.31 (d, $^4J_{P-H}$ = 2.4 Hz, 12H, OC(CH_2)$_3$), 2.20 (s, 6H, C***H***), 1.65 (s, 12H, CHCH_2), 1.63 (s, 18H, C(CH_3)$_3$); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 87.96 (d, $^2J_{P-C}$ = 7.1 Hz, O-***C***), 57.44 (s, ***C***(CH_3)$_3$), 44.00 (s, O-C-***C***H_2), 36.00 (s, **C**H_2), 31.66 (s, O-C-CH_2-***C***H), 30.32 (t, $^3J_{P-C}$ = 5.1 Hz, C(***C***H_3)$_3$); ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 39.52 (s); m.p. 241-242 ˚C; IR (mineral oil, NaC*l*) υ (cm^{-1}): 1051 (C-O), 988 (P-OC), 910 (P-OR), 760 (P=S); MS (EI) *m/z*: 571.27 $[M+1]^+$; Anal. Calcd for

$C_{28}H_{50}N_2O_3P_2S_2$: C, 57.12; H, 8.56; N, 4.76; S, 10.89. Found: C, 57.47; H, 8.12; N, 8.12; S, 10.84 %.

Synthesis of [(Se)P(N^{t}Bu)(OAd)]$_2$ (3)*:* **1** (0.275 g, 1.0 mmol), 1-adamantanol (0.304 g, 2.0 mmol) and elemental selenium (0.237 g, 3.0 mmol) were weighed and poured into a mechanochemical grinder reaction vessel along with Et_3N (0.28 cm^3, 2.0 mmol) and 10 mm stainless steel ball. The grinding frequency was set to 30 Hz and the vessel was subjected to grinding for 6.0 hours. Toluene was added and the reaction solution was filtered to remove excess unreacted selenium. The solution was concentrated and left to stand at room temperature to obtain colourless crystals. Yield: 0.352 g (62 %); ^{1}H NMR (CDC*l*$_3$, 400 MHz): δ 2.35 (s, 12H, OC(C***H***$_2$)$_3$), 2.21 (s, 6H, C***H***), 1.70 (s, 12H, C***H***$_2$), 1.65 (s, 18H, C(C***H***$_3$)$_3$); ^{13}C NMR (CDC*l*$_3$, 101 MHz): δ 89.89 (d, $^2J_{P\text{-}C}$ = 15.2Hz, PO-***C***), 58.35 (s, OC(***C***H$_2$)$_3$), 44.01 (t, $^2J_{P\text{-}C}$ = 2.0Hz, ***C***(CH$_3$)$_3$), 35.93 (s, ***C***H$_2$), 31.73 (s, ***C***H), 30.46 (t, $^3J_{P\text{-}C}$ = 4.5Hz, C(***C***H$_3$)$_3$); ^{31}P{^{1}H} NMR (CDC*l*$_3$, 162 MHz): δ 24.62 (s, $^1J_{P\text{-}Se}$ = 930.4Hz); m.p. 198-200 ˚C; IR (mineral oil, NaC*l*) υ (cm^{-1}): 1011 (P-OC), 897 (P=Se); MS (EI) *m/z*: 665.16 [M-1]$^+$; Anal. Calcd for $C_{28}H_{48}N_2O_2P_2Se_2$: C, 50.61; H, 7.28; N, 4.22. Found: C, 50.82; H, 7.74; N, 4.49 %.

Synthesis of [(S)P(N^{t}Bu)(NHAd)]$_2$ (4)*:* **1** (0.550 g, 2.0 mmol), 1-adamantamine (0.604 g, 4.0 mmol) and elemental sulfur (0.192 g, 6.0 mmol) were weighed and poured into a mechanochemical grinder reaction vessel along with Et_3N (0.56 cm^3, 4.0 mmol) and 10 mm stainless steel ball. The grinding frequency was set to 30 Hz and the vessel was subjected to grinding for 9.0 hours. THF was added and the reaction solution was filtered to remove excess unreacted sulfur. The filtrate was concentrated and equivolume of toluene was added. The resulting solution was left to crystallize at room temperature to give colourless crystals. Yield: 0.532 g (47 %); ^{1}H NMR (CDC*l*$_3$, 400 MHz): δ 2.97 (s, 2H, N-***H***), 2.09 (s, 18H, C***H*** and C***H***$_2$), 1.69 (s, 18H, C(C***H***$_3$)$_3$), 1.67 (br s, 12H, C***H***$_2$); ^{13}C NMR (CDC*l*$_3$, 101 MHz): δ 57.80 (s, N-***C***), 55.65 (t, $^2J_{P\text{-}C}$ = 2.0Hz, ***C***(CH$_3$)$_3$), 44.79 (s, C(***C***H$_2$)$_3$), 36.31 (s, **C**H$_2$), 30.37 (t, $^3J_{P\text{-}C}$ = 4.5Hz,

C(***C***H_3)$_3$), 30.06 (s, ***C***H); ^{31}P{^{1}H} NMR (CDC*l*$_3$, 162 MHz): δ38.53 (s); m.p. 258-259 ˚C; IR (mineral oil, NaC*l*) υ (cm^{-1}): 3379 (N-H), 758 (P=S); MS (EI) *m/z*: 568.30 [M+1]$^+$; Satisfactory C, H and N analysis could not be obtained.[4]

Synthesis of [(Se)P(N^{t}Bu)(AdNH)]$_2$ (5)*:* 1 (0.550 g, 2.0 mmol), 1-adamantamine (0.604 g, 4.0 mmol) and elemental selenium (0.474 g, 6.0 mmol) were weighed and poured into a mechanochemical grinder reaction vessel along with Et_3N (0.56 cm^3, 4.0 mmol) and 10 mm stainless steel ball. The grinding frequency was set to 30 Hz and the vessel was subjected to grinding for 10.0 hours. THF was added and the reaction solution was filtered to remove excess unreacted selenium. The filtrate was concentrated and equal volume of toluene was added. The resulting solution was left to crystallize at room temperature to give colourless crystals. Yield: 0.562 g (42 %); ^{1}H NMR (CDC*l*$_3$, 400 MHz): δ 3.29 (s, 2H, N-***H***), 2.11 (s, 18H, C***H*** and C***H***$_2$), 1.76 (s, 18H, C(C***H***$_3$)$_3$), 1.67 (s, 12H, C***H***$_2$); ^{13}C NMR (CDC*l*$_3$, 101 MHz): δ 58.75 (s, N-***C***), 56.76 (t, $^2J_{P\text{-}C}$ = 3.5 Hz, ***C***(CH$_3$)$_3$), 44.75 (s, C(***C***H$_2$)$_3$), 36.26 (s, **C**H$_2$), 30.45 (t, $^3J_{P\text{-}C}$ = 4.5 Hz, C(***C***H$_3$)$_3$), 30.05 (s, ***C***H); ^{31}P{^{1}H} NMR (CDC*l*$_3$, 162 MHz): δ23.45 (s, $^1J_{P\text{-}Se}$ = 873.2 Hz, $^2J_{P\text{-}P}$ = 25.9 Hz,); m.p. 256 ˚C; IR (mineral oil, NaC*l*) υ (cm^{-1}): 3366 (N-H), 899 (P=Se); MS (EI) *m/z*: 663.20 [M+1]$^+$; Anal. Calcd for $C_{28}H_{50}N_4P_2Se_2$: C, 50.76; H, 7.61; N, 8.46. Found: C, 51.07; H, 8.11; N, 8.11 %.

Synthesis of [(S)P(N^{t}Bu)*p*-NHPhCN]$_2$ (6)*:* 1 (0.275 g, 1.0 mmol), 4-aminobenzonitrile (0.236 g, 2.0 mmol) and elemental sulfur (0.096 g, 3.0 mmol) were weighed and poured into a mechanochemical grinder reaction vessel along with Et_3N (0.28 cm^3, 2.0 mmol) and 10 mm stainless steel ball. The grinding frequency was set to 30 Hz and the vessel was subjected to grinding for 6.0 hours. THF was added and the reaction solution was filtered to remove excess unreacted sulfur. The filtrate was then concentrated and left to crystallize at room temperature. Yield: 0.203 g (40 %); ^{1}H NMR (CDC*l*$_3$, 400 MHz):[5] δ 11.10 (br s, ***H***N(CH$_2$CH$_3$)$_3$C*l*), 7.66 (d, $^3J_{H\text{-}H}$ = 8.4 Hz, 4H, *m*-Ar***H***), 7.53 (d, $^3J_{H\text{-}H}$ = 8.4 Hz, 4H, *o*-Ar***H***), 3.77-3.73 (m, 2H, OC***H***$_2$

of THF), 3.11-3.04 (m, 6H, HN(C***H***$_2$CH$_3$)$_3$C*l*), 1.85 (m, 2H, C***H***$_2$ of THF), 1.60 (s, 18H, C(C***H***$_3$)$_3$), 1.38 (t, $^3J_{H\text{-}H}$ = 7.4Hz, 9H, HN(CH$_2$C***H***$_3$)$_3$C*l*); ^{13}C NMR (CDC*l*$_3$, 101 MHz): δ 145.02 (s, N-Ar***C***), 133.04 (s, *m*-Ar***C***), 121.13 (t, $^3J_{P\text{-}C}$ = 3.0 Hz, *o*-Ar***C***), 119.26 (s, ***C***≡N), 106.00 (s, Ar***C***-CN), 57.04 (s, ***C***(CH$_3$)$_3$), 46.45 (s, NH(***C***H$_2$CH$_3$)$_3$C*l*), 29.94 (t, $^3J_{P\text{-}C}$ = 4.5 Hz, C(***C***H$_3$)$_3$), 8.83 (s, NH(CH$_2$***C***H$_3$)$_3$C*l*); ^{31}P{^{1}H} NMR (CDC*l*$_3$, 162 MHz): δ 39.43 (s); m.p. 272˚C; IR (mineral oil, NaC*l*) υ (cm^{-1}): IR (mineral oil, NaC*l*) υ (cm^{-1}): 3235 (N-H), 2220 (C≡N), 1601 (N-H bending), 1508 (aromatic C=C); MS (EI) *m/z*: 503.14 [M+1]$^+$; Satisfactory C, H and N analysis could not be obtained.[4]

Synthesis of [(Se)P(N^{t}Bu)*p*-NHPhCN]$_2$ (7): 1 (0.275 g, 1.0 mmol), 4-aminobenzonitrile (0.236 g, 2.0 mmol) and elemental selenium (0.237 g, 3.0 mmol) were weighed and poured into a mechanochemical grinder reaction vessel along with Et$_3$N (0.28 cm^3, 2.0 mmol) and 10 mm stainless steel ball. The grinding frequency was set to 30 Hz and the vessel was subjected to grinding for 6.0 hours. THF was added and the reaction solution was filtered to remove excess unreacted selenium. THF was then removed and the resulting solid was dissolved in methanol and left to crystallize at room temperature. Yield: 0.388 g (65 %); ^{1}H NMR (MeOD, 400 MHz):[6] δ 7.65 (dd, $^3J_{H\text{-}H}$ = 8.8 Hz, $^4J_{P\text{-}H}$ = 14.0Hz, 8H, Ar***H***), 1.62 (s, 18H, C(C***H***$_3$)$_3$; ^{13}C NMR (MeOD, 101 MHz):[6] δ 145.90 (s, N-Ar***C***), 134.04 (s, *m*-Ar***C***), 122.88 (s, *o*-Ar***C***), 119.89 (s, ***C***≡N), 107.26 (s, Ar***C***-CN), 58.59 (s, ***C***(CH$_3$)$_3$), 30.35 (t, $^3J_{P\text{-}C}$ = 4.5 Hz, C(***C***H$_3$)$_3$); ^{31}P{^{1}H} NMR (CDC*l*$_3$, 162 MHz): δ30.09 (s); m.p. 232-233 ˚C; IR (mineral oil, NaC*l*) υ (cm^{-1}): 3287 (N-H), 2224 (C≡N), 1603 (N-H bending), 1508 (aromatic C=C), 897 (P=Se); MS (EI) *m/z*: 599.03 [M+1]$^+$; Satisfactory C, H and N analysis could not be obtained.[4]

2. $^{31}P\{^{1}H\}$ NMR Spectrum of compound 1 and *in situ*[3] $^{31}P\{^{1}H\}$ NMR Spectrum of reactions

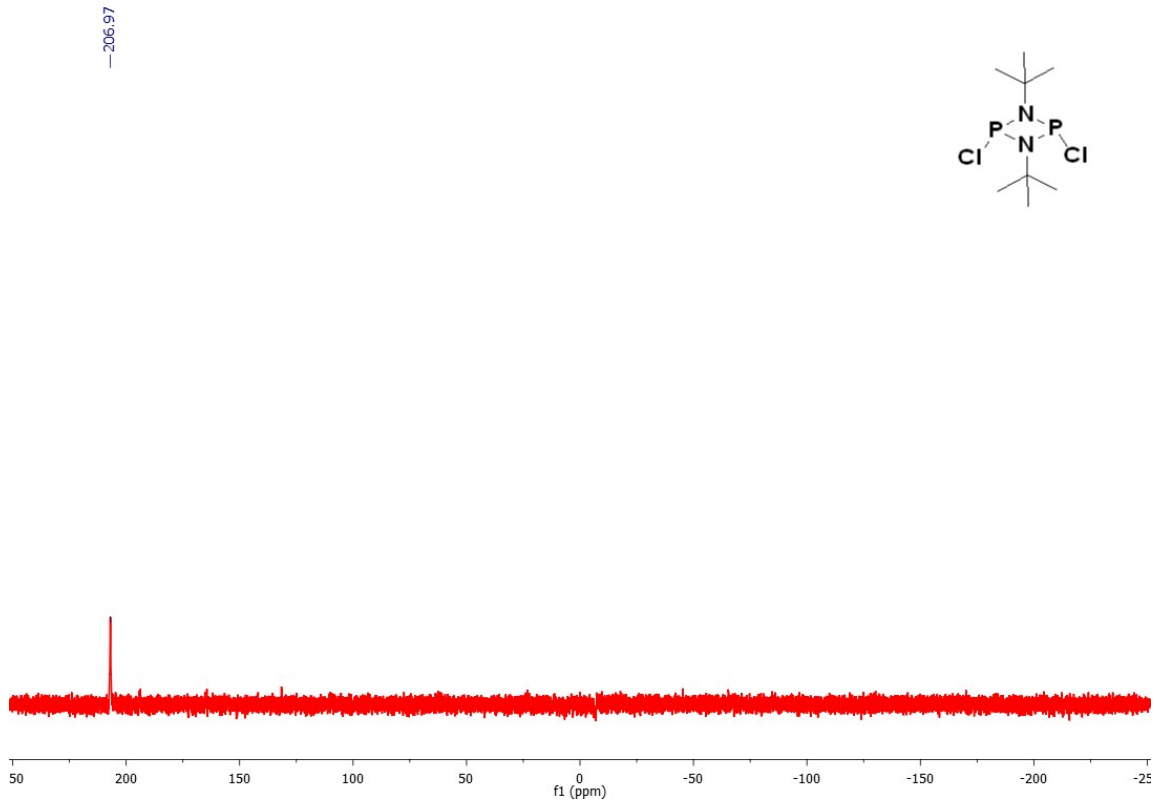


Figure S 1. $^{31}P\{^{1}H\}$ NMR spectrum of ***1***

The following spectrum supports the sole formation of one product in the reactions conducted. The formation of oxidised dichlorocyclodiphosphazanes, $[(E)P(\mu\text{-}N^{t}Bu)Cl]_2$ where E = S or Se, is not observed throughout the reactions. The $^{31}P\{^{1}H\}$ chemical shift of $[(S)P(\mu\text{-}N^{t}Bu)Cl]_2$ and $[(Se)P(\mu\text{-}N^{t}Bu)Cl]_2$ are reported to be δ 40.96 and 40.16, 22.7 and 22.1 ppm, respectively.[7,8] The oxidised dichlorocyclodiphosphazanes are obtained in mixture of *cis*- and *trans*- isomers.

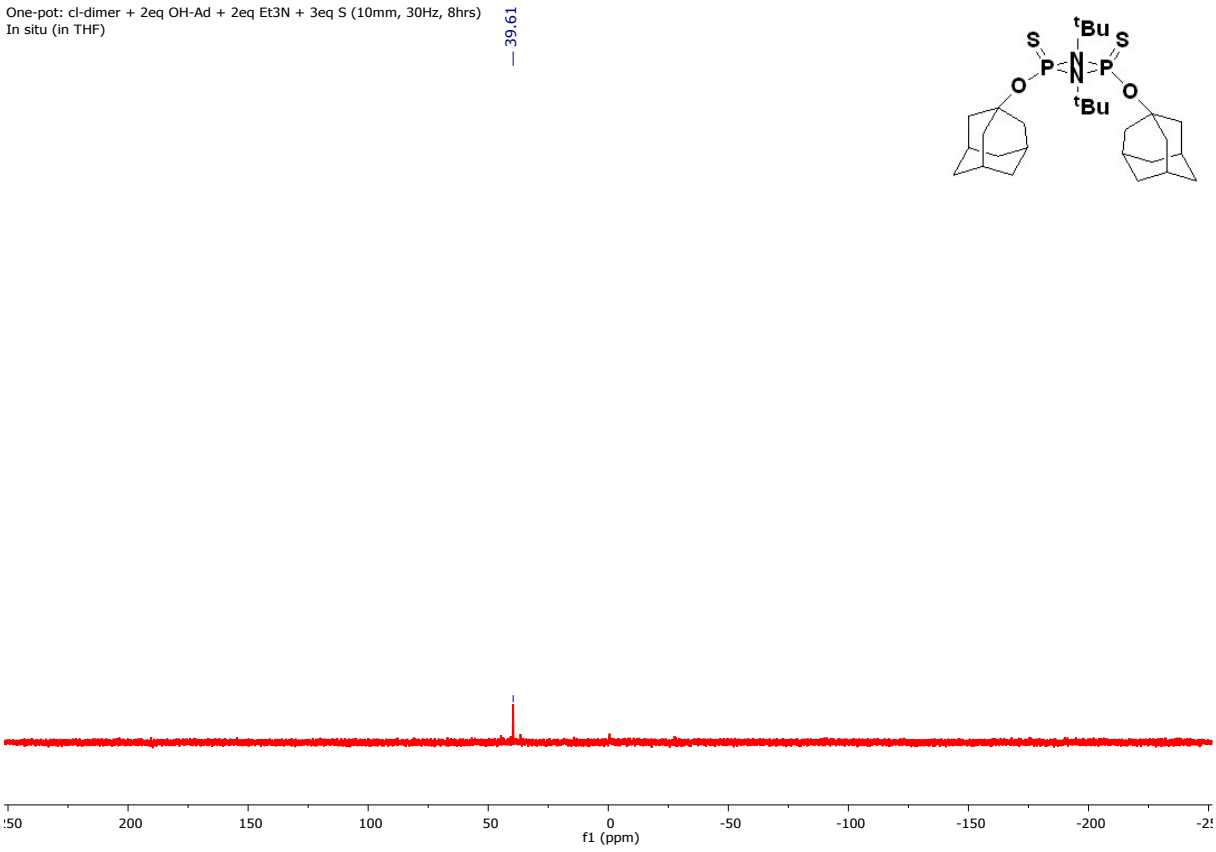


Figure S 2. in situ $^{31}P\{^{1}H\}$ NMR spectrum of reaction for ***2***

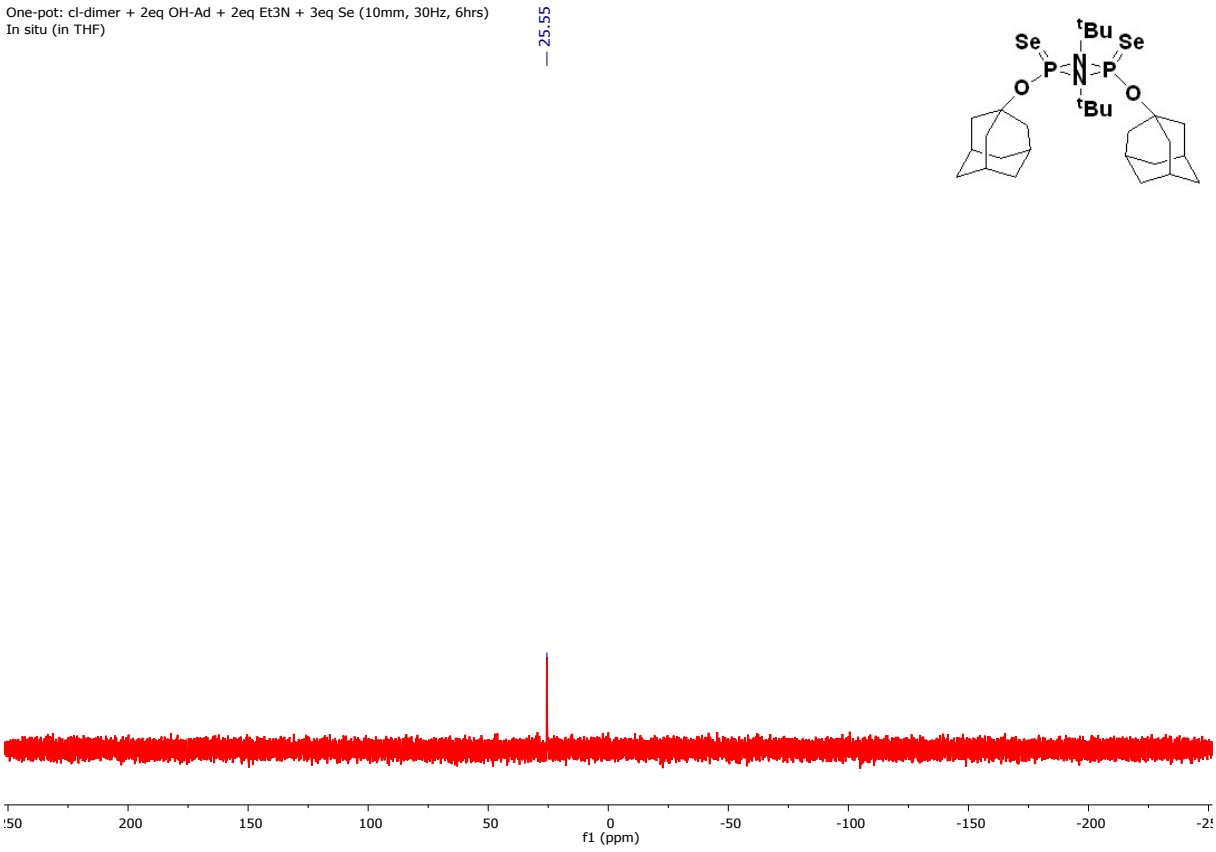


Figure S 3. ***In situ*** $^{31}P\{^{1}H\}$ NMR spectrum of reaction for ***3***

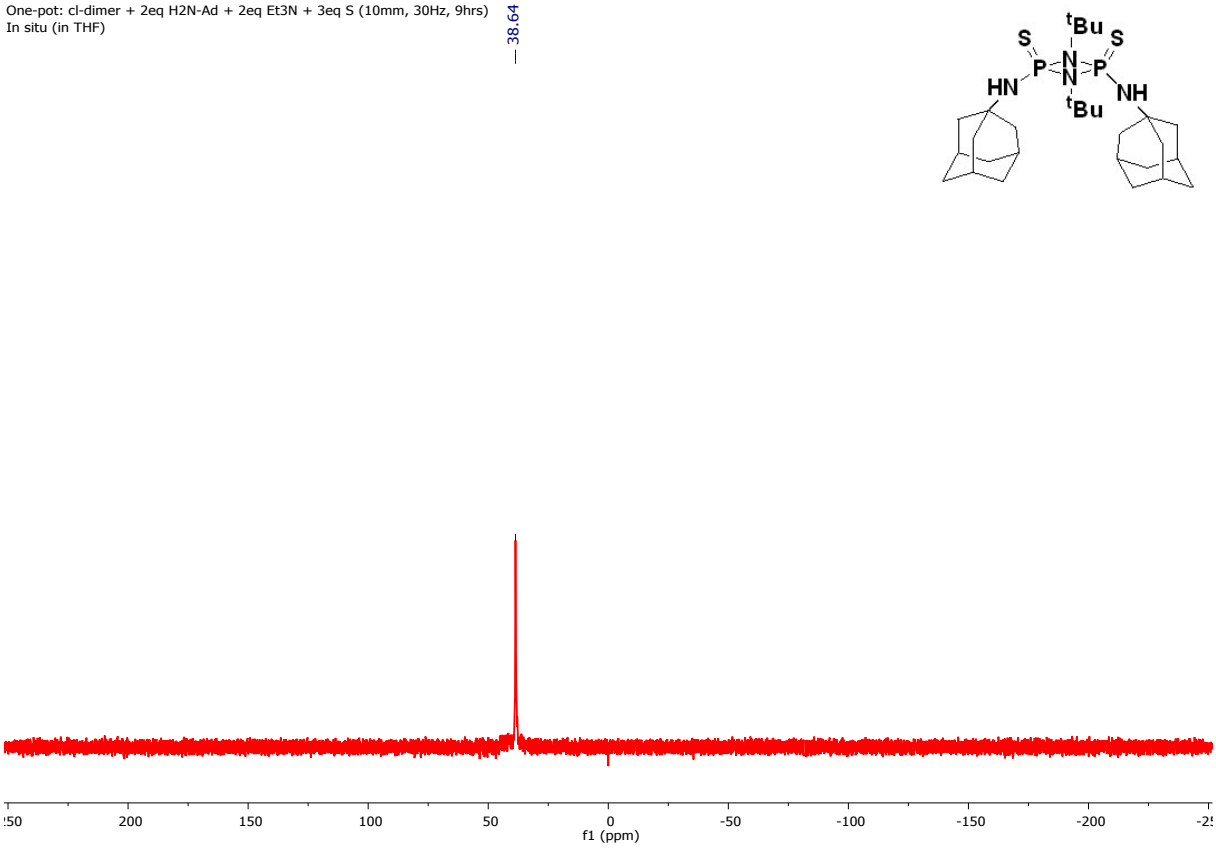


Figure S 4. ***In situ*** $^{31}P\{^{1}H\}$ NMR spectrum of reaction for ***4***

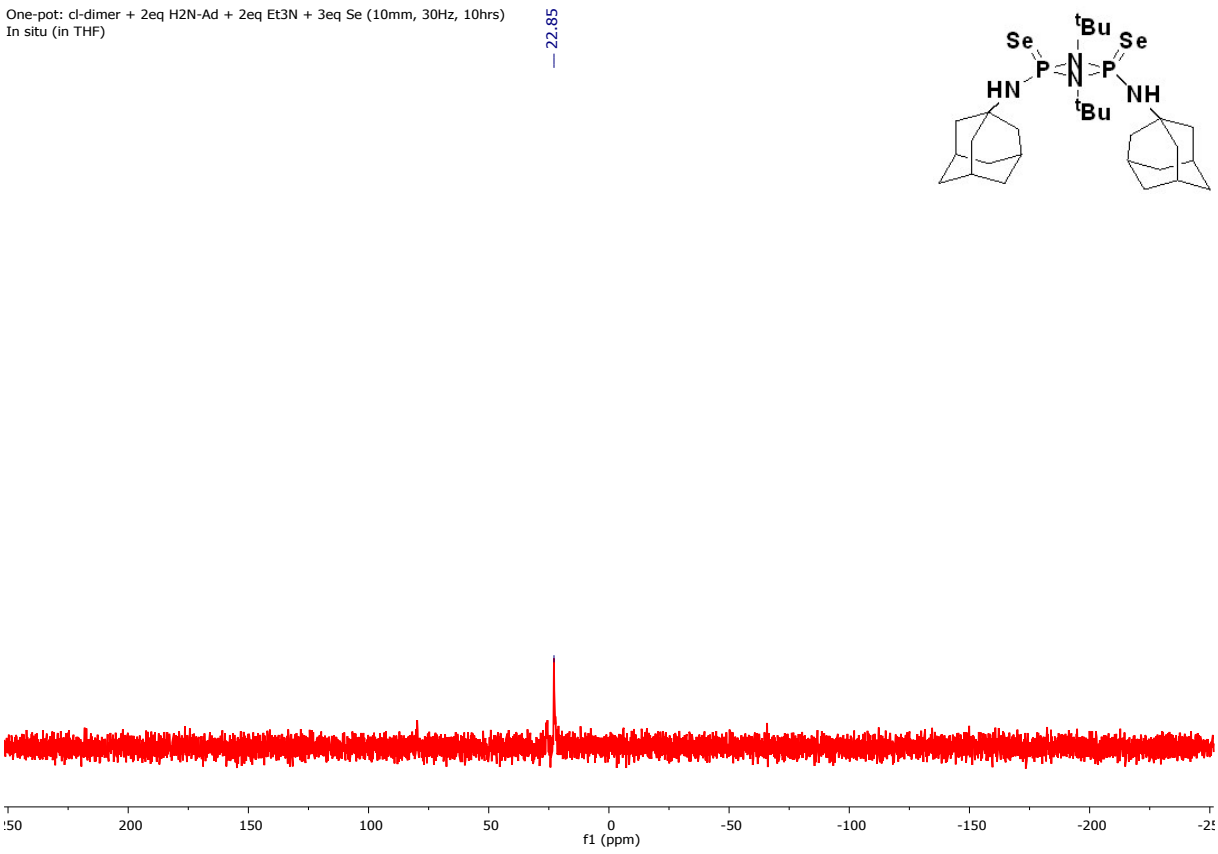


Figure S 5. ***<u>In situ</u>*** $^{31}P\{^{1}H\}$ NMR spectrum of reaction for ***5***

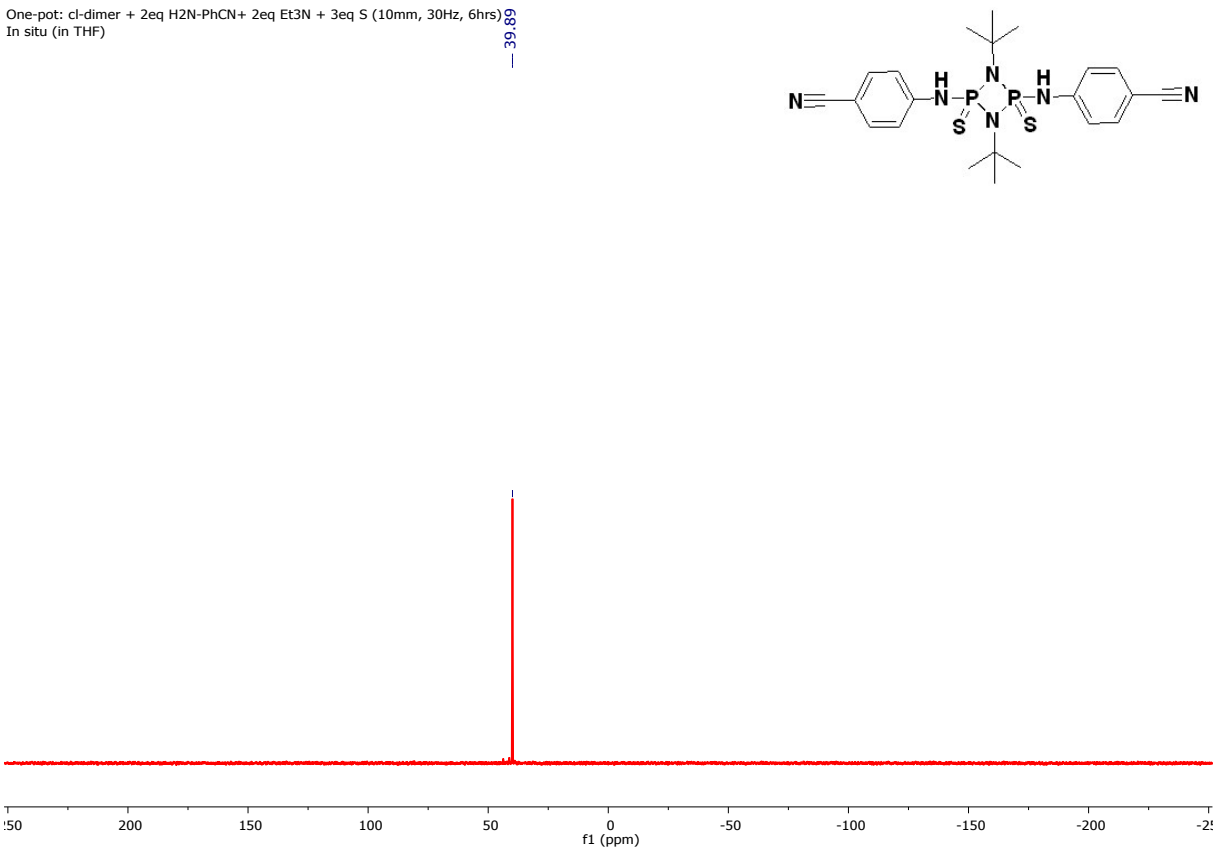


Figure S 6. ***<u>In situ</u>*** $^{31}P\{^{1}H\}$ NMR spectrum of reaction for ***6***

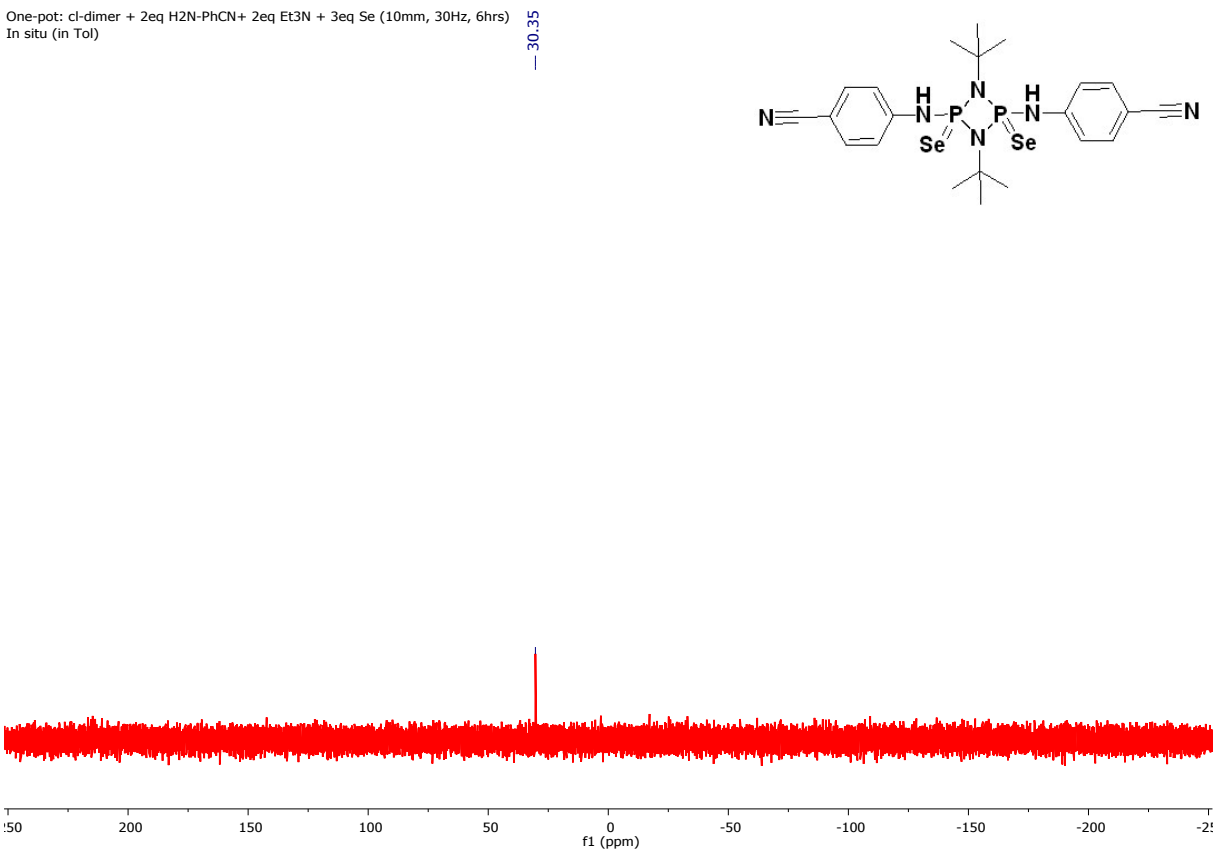


Figure S 7. ***In situ*** $^{31}P\{^{1}H\}$ NMR spectrum of reaction for ***7***

3. $^{31}P\{^{1}H\}$, ^{1}H and ^{13}C NMR Spectrum of Compounds 2-7

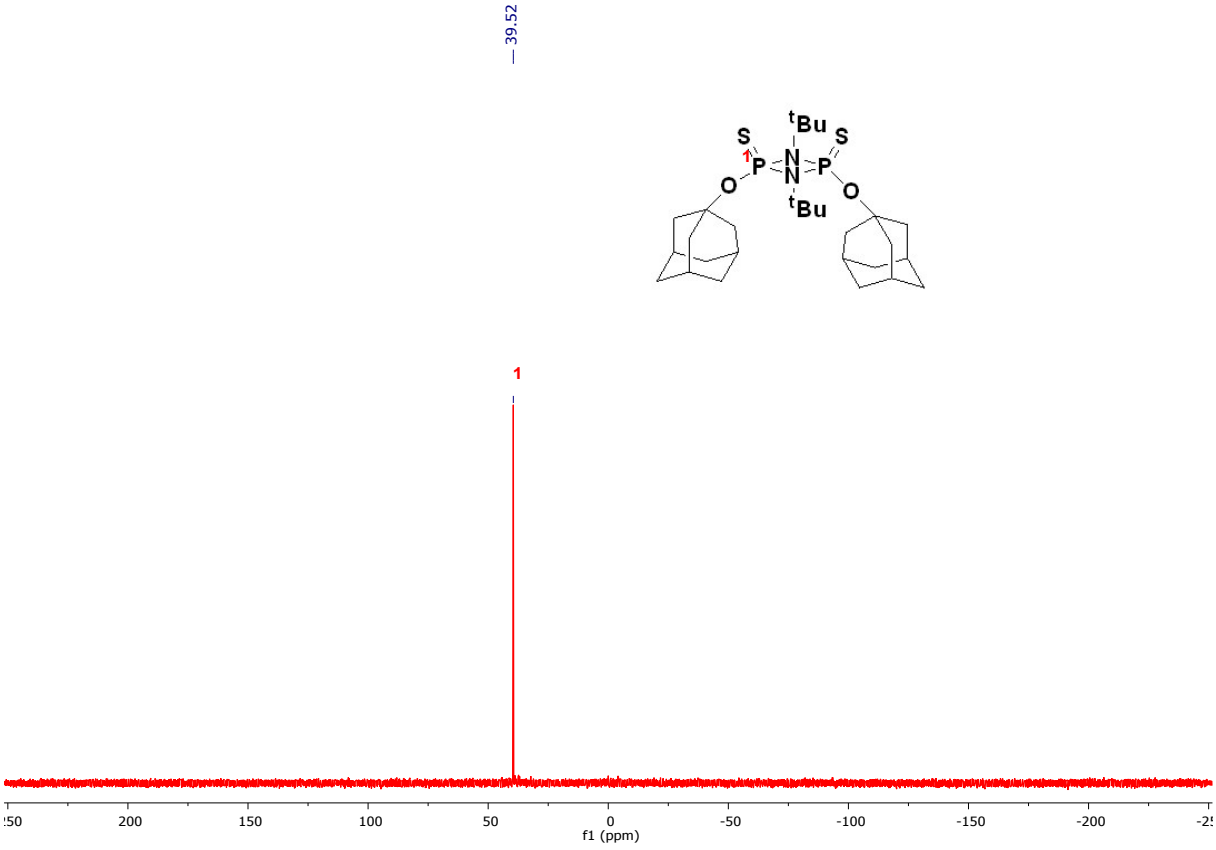


Figure S 8. $^{31}P\{^{1}H\}$ NMR spectrum of ***2***

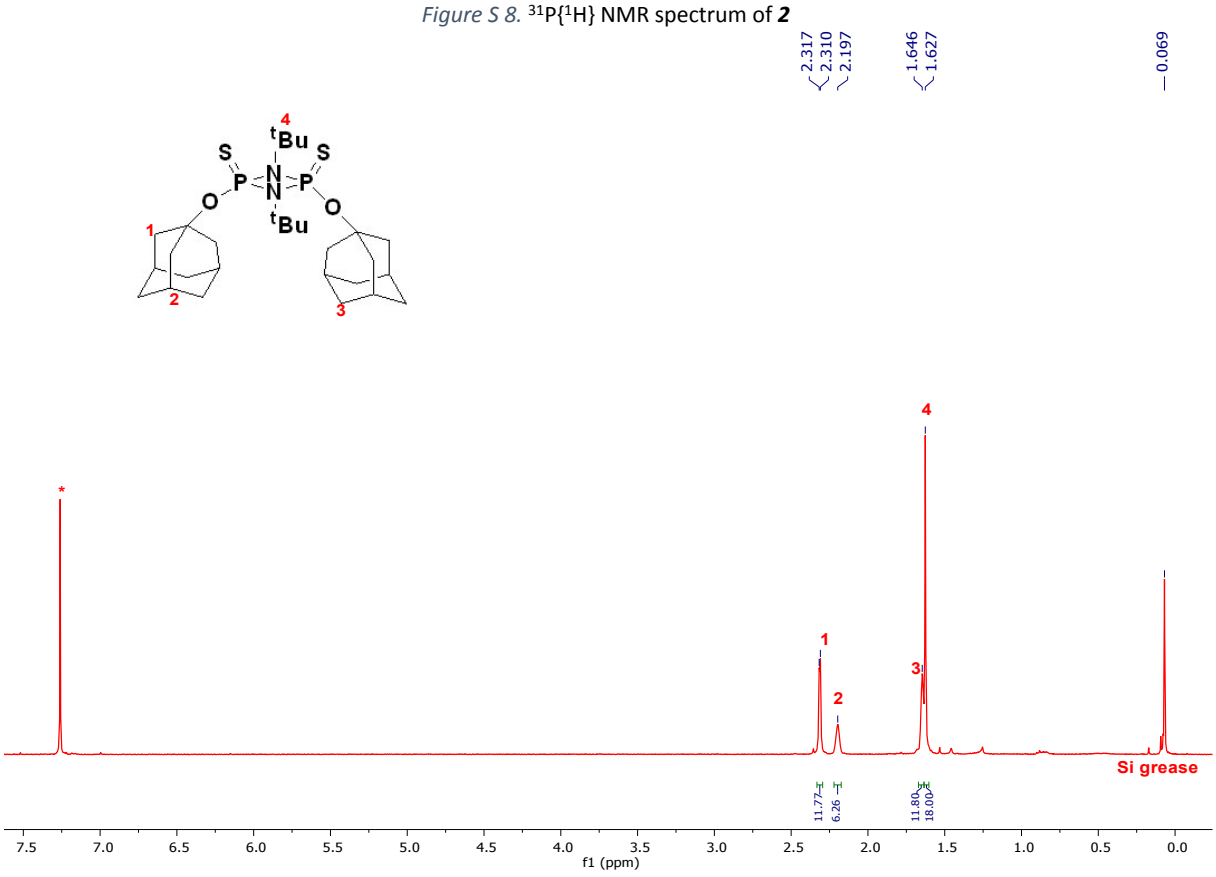


Figure S 9. ^{1}H NMR spectrum of ***2***

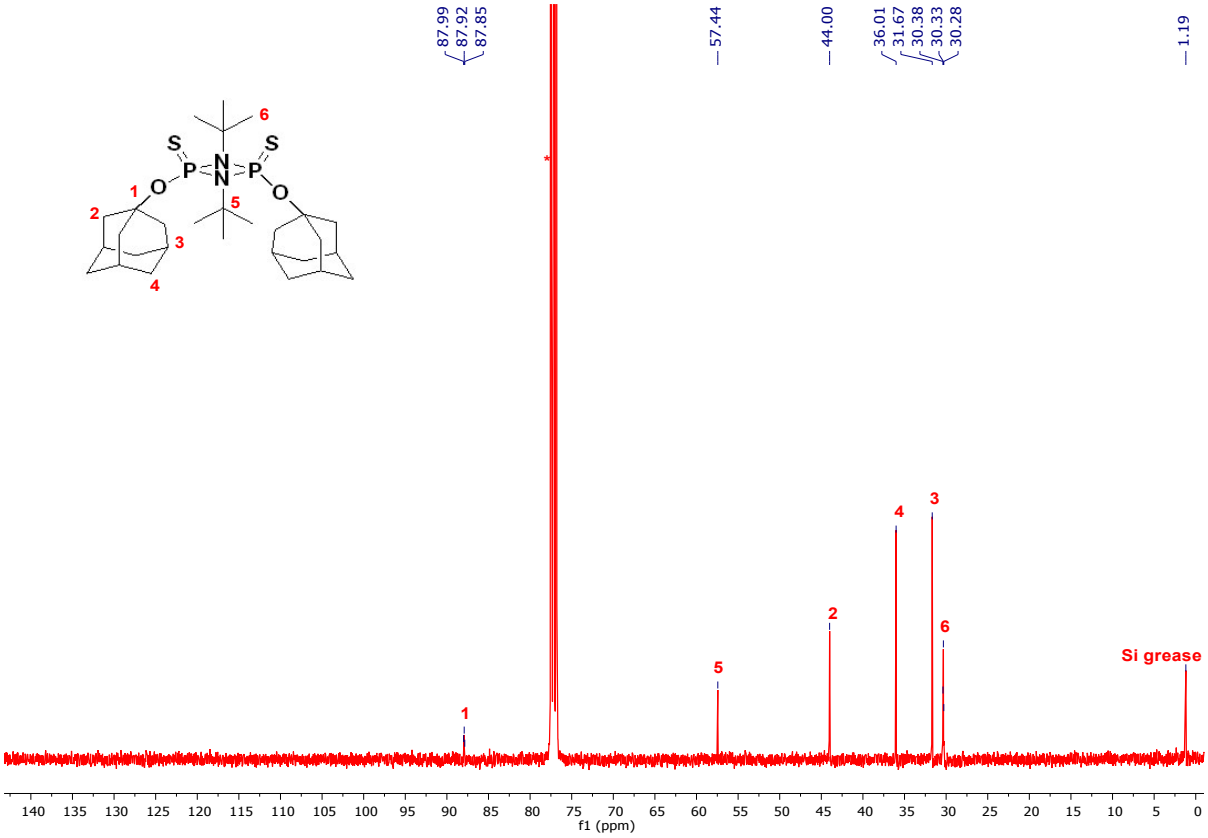


Figure S 10. ^{13}C NMR spectrum of ***2***

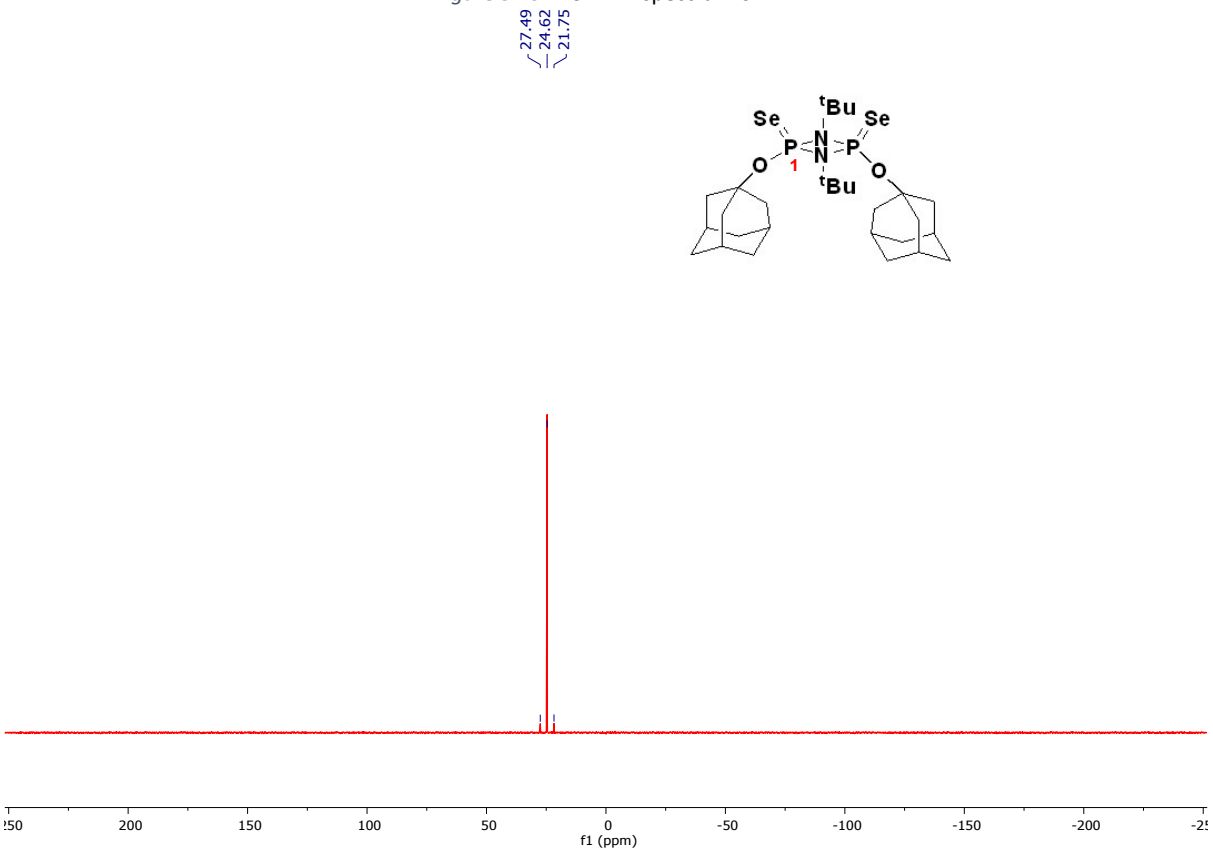


Figure S 11. $^{31}P\{^{1}H\}$ NMR spectrum of ***3***

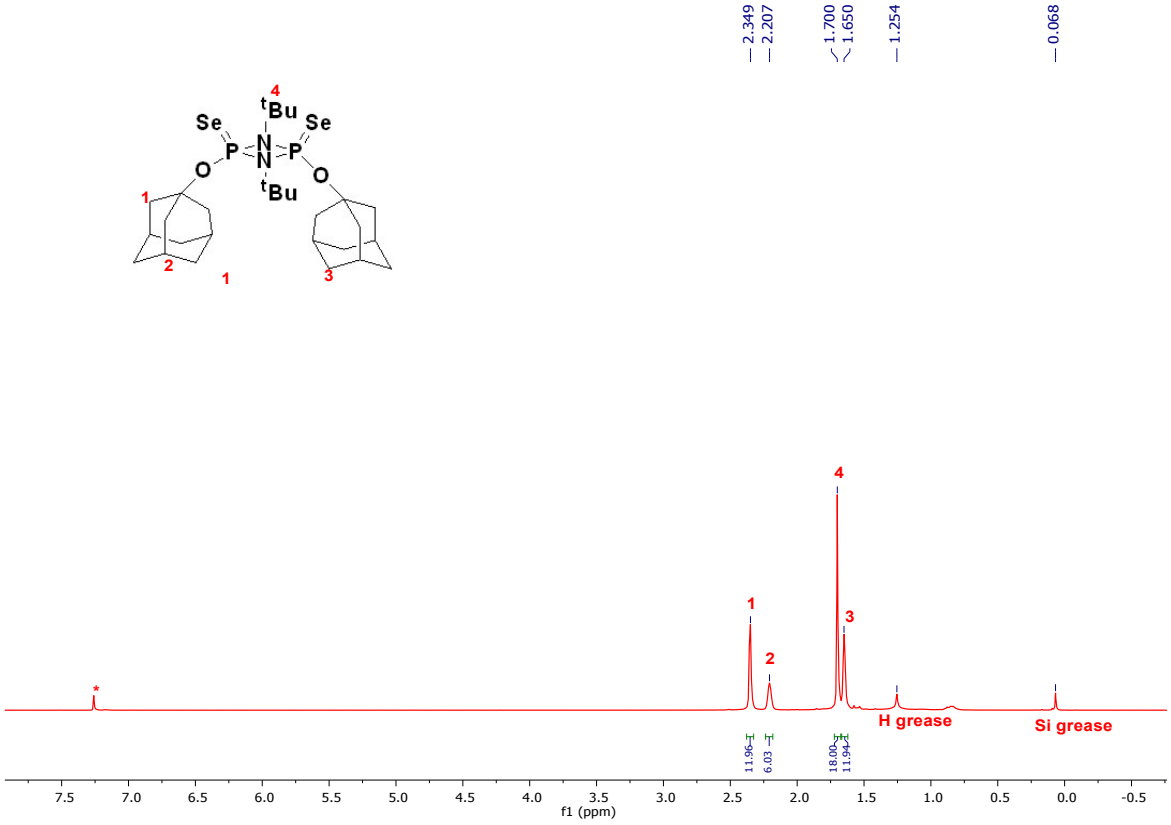


Figure S 12. ^{1}H NMR spectrum of ***3***

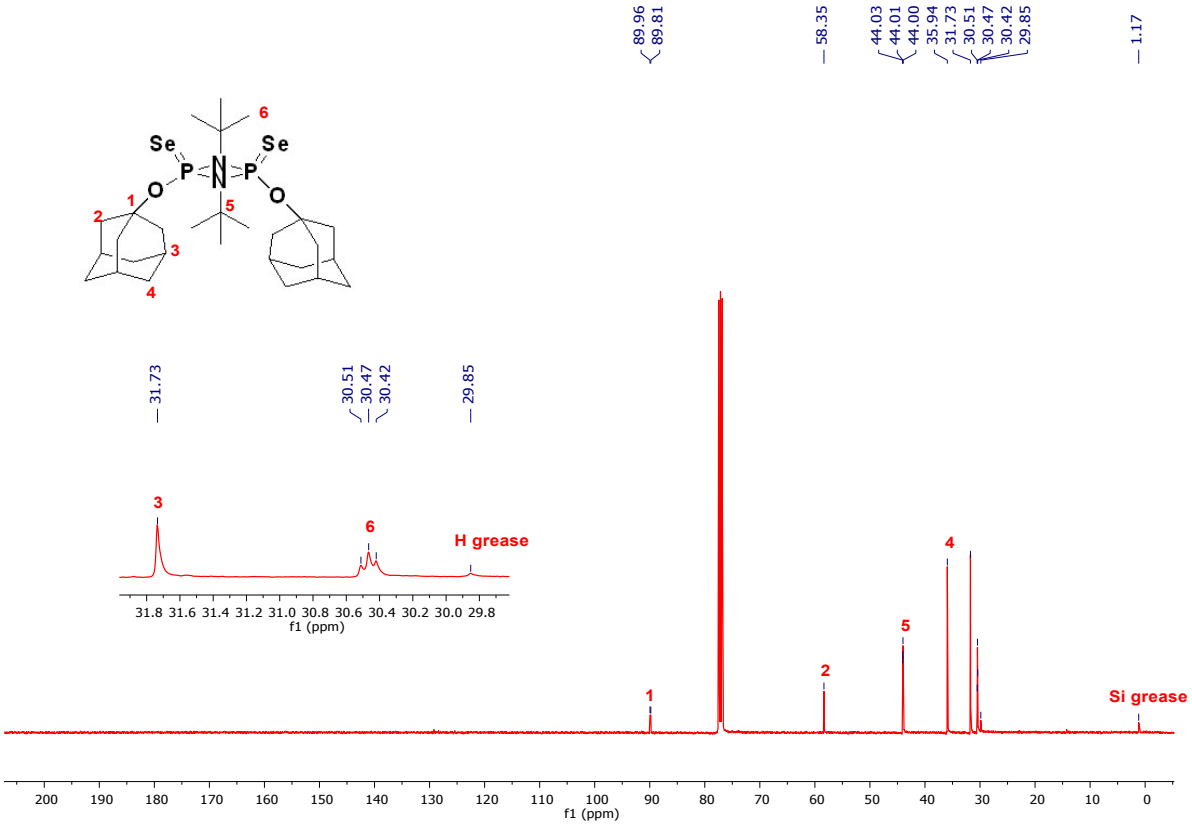


Figure S 13. ^{13}C NMR spectrum of ***3***

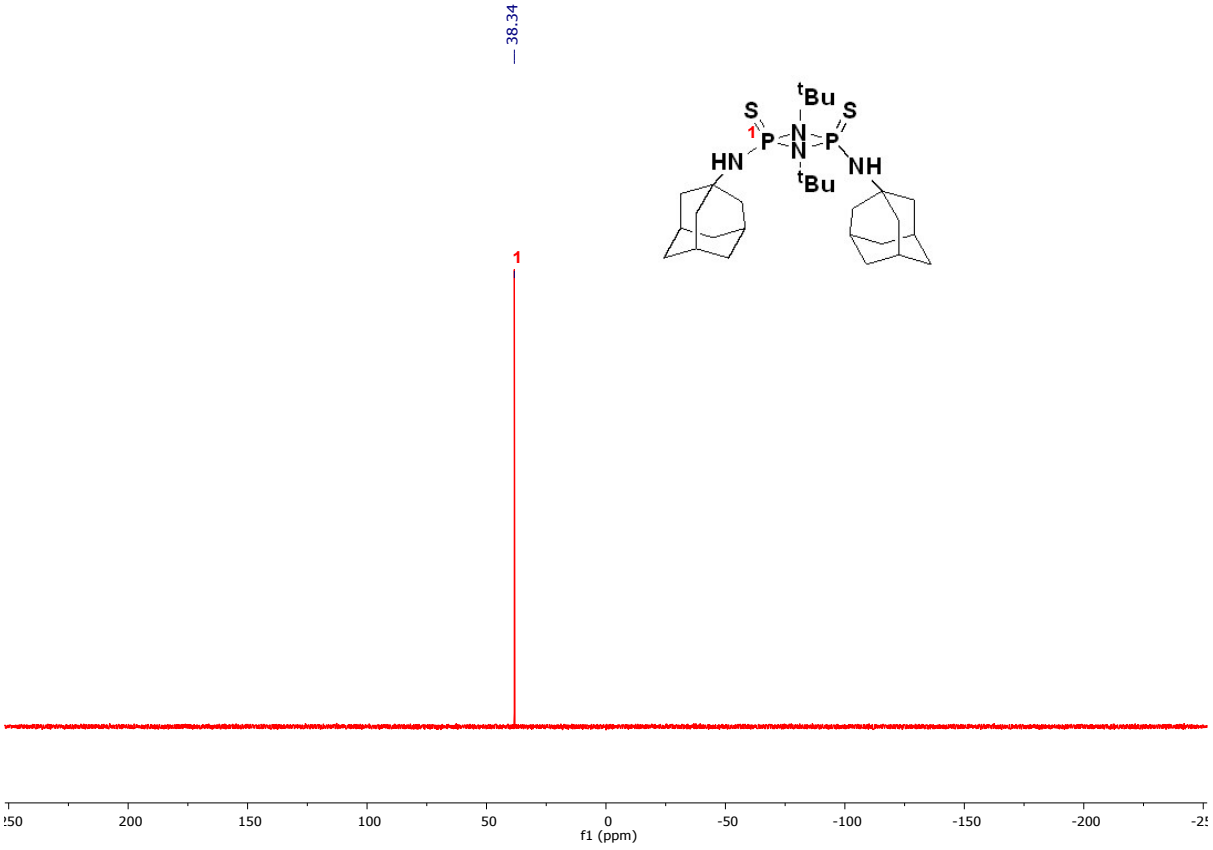


Figure S 14. $^{31}P\{^{1}H\}$ NMR spectrum of ***4***

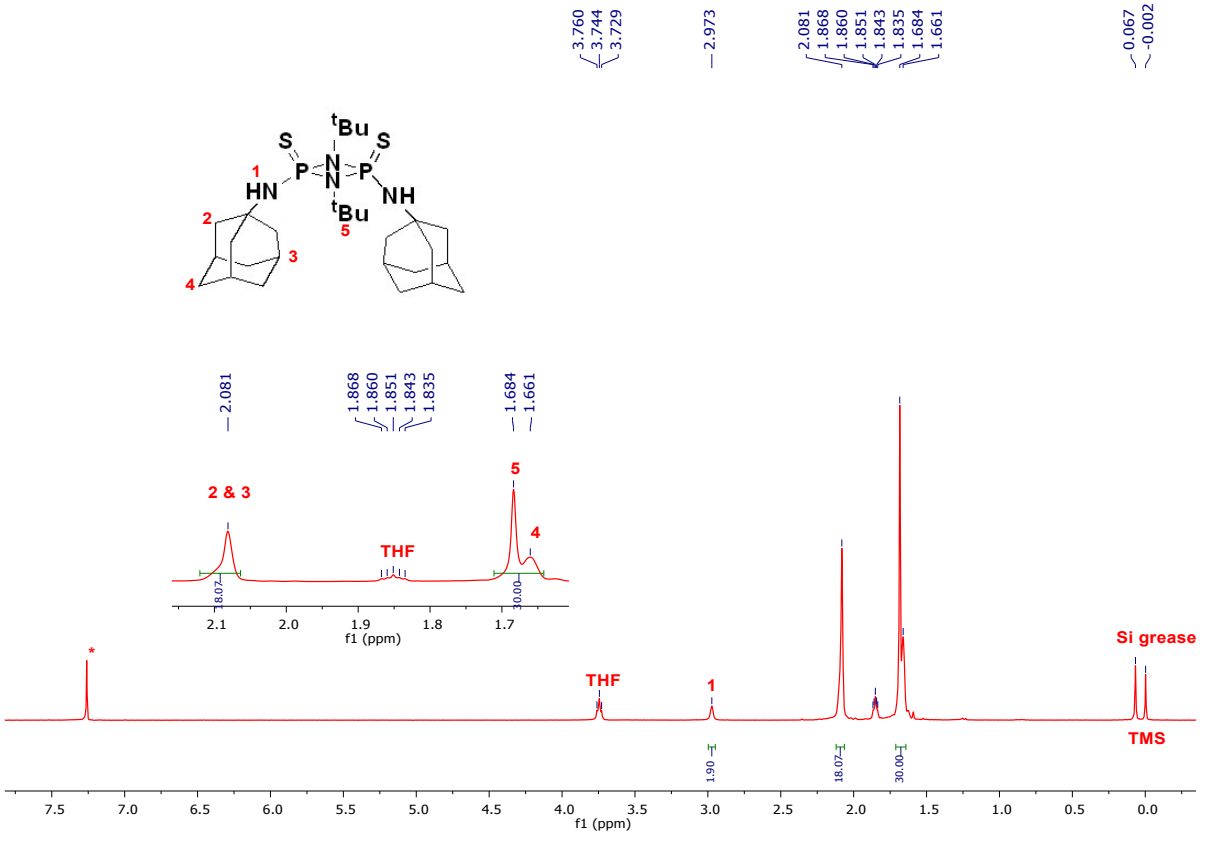


Figure S 15. ^{1}H NMR spectrum of ***4***

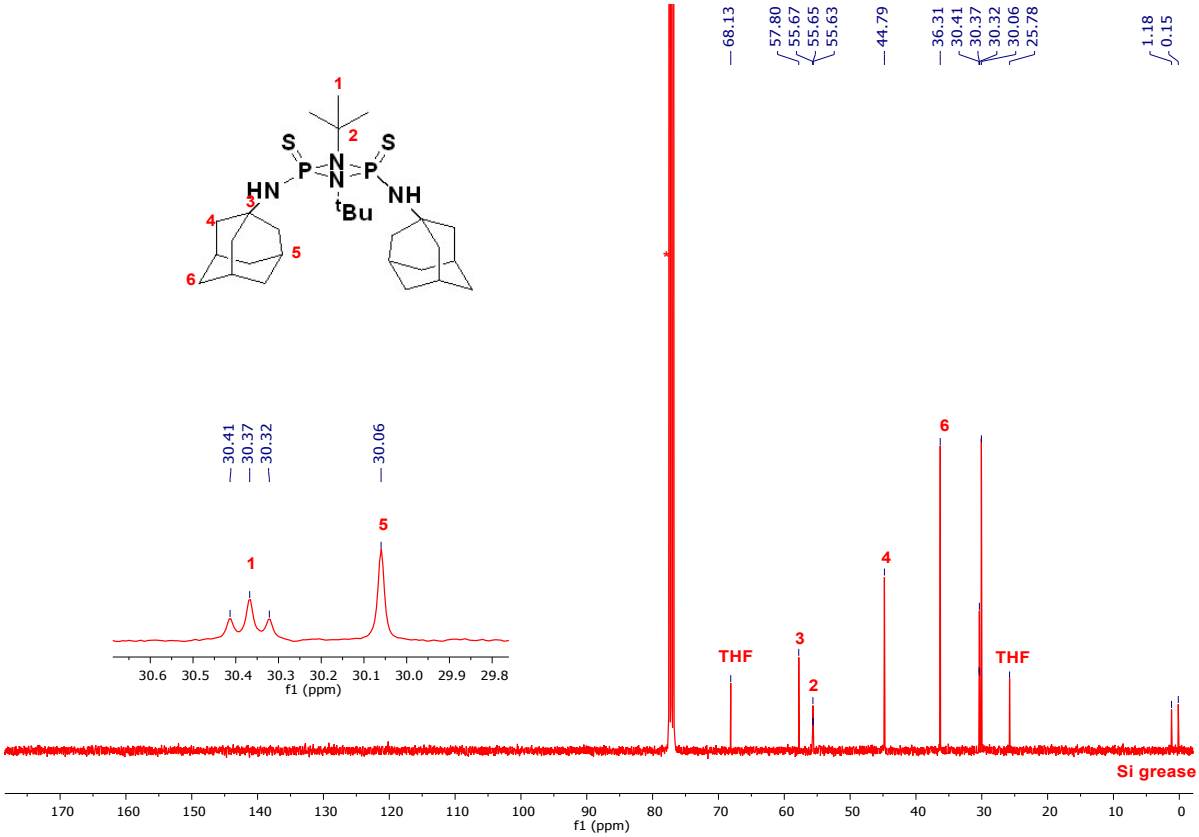


Figure S 16. ^{13}C NMR spectrum of ***4***

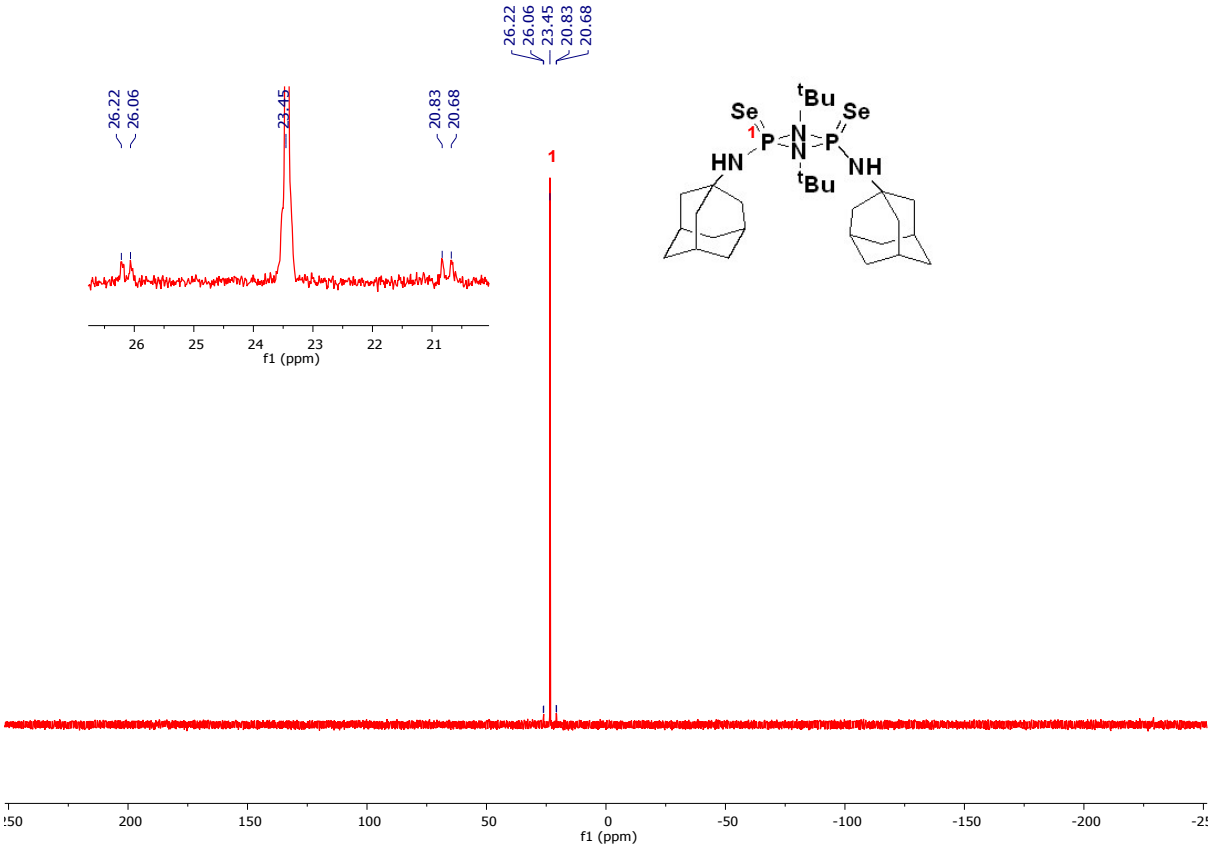


Figure S 17. ^{31}P{^{1}H} NMR spectrum of ***5***

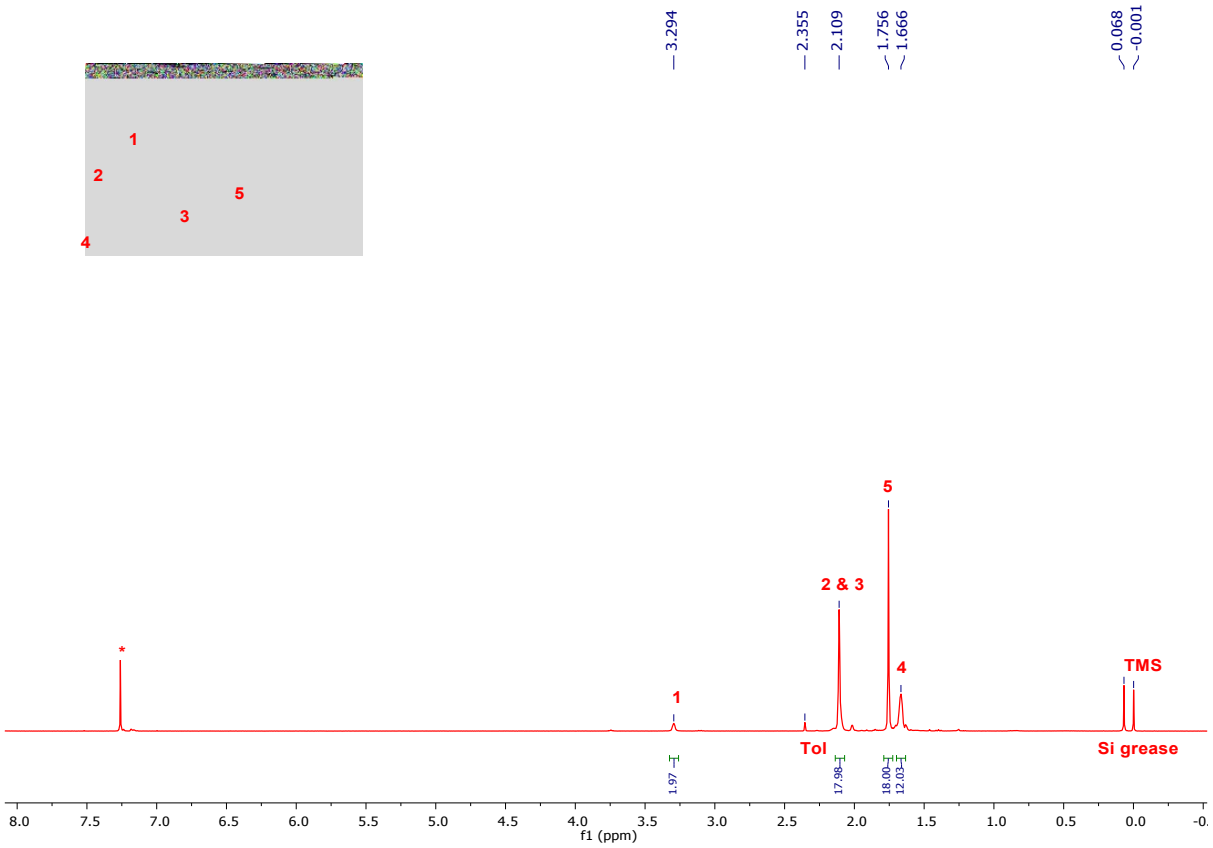


Figure S 18. ^{1}H NMR spectrum of ***5***

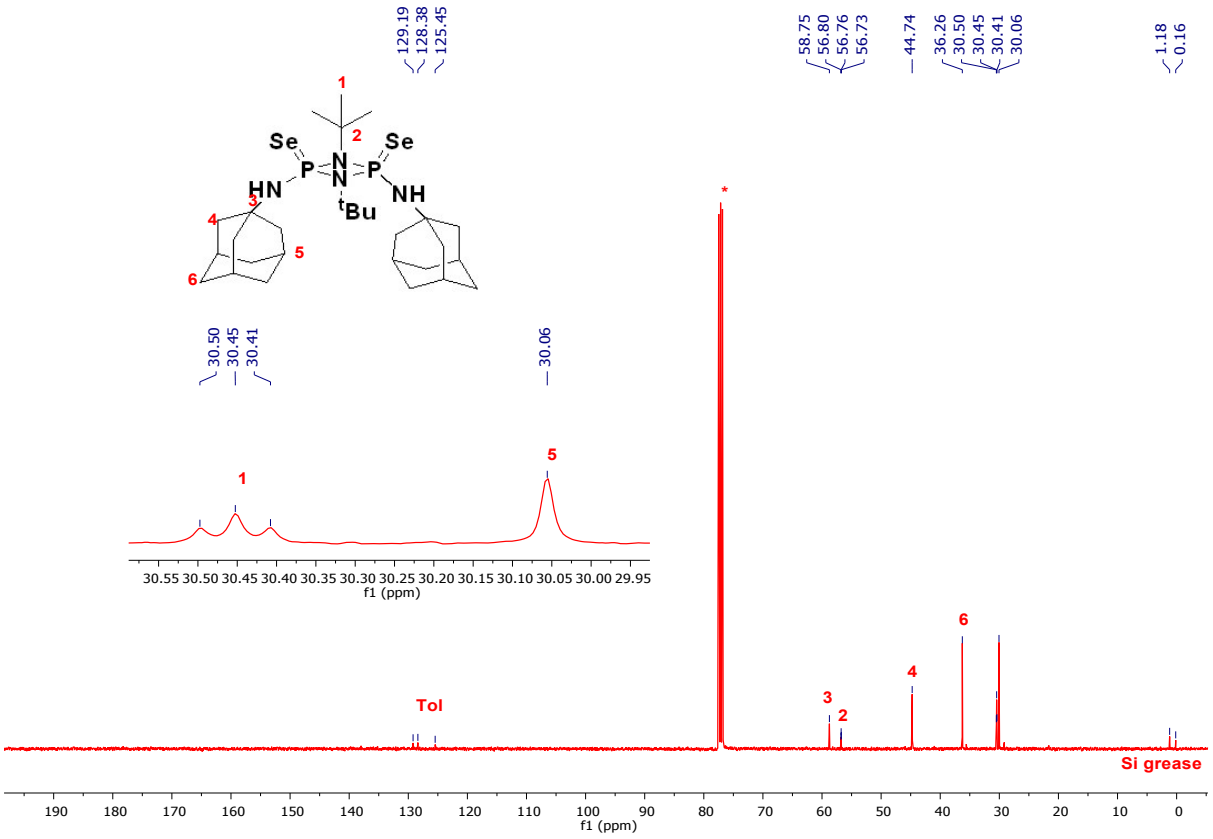


Figure S 19. ^{13}C NMR spectrum of ***5***

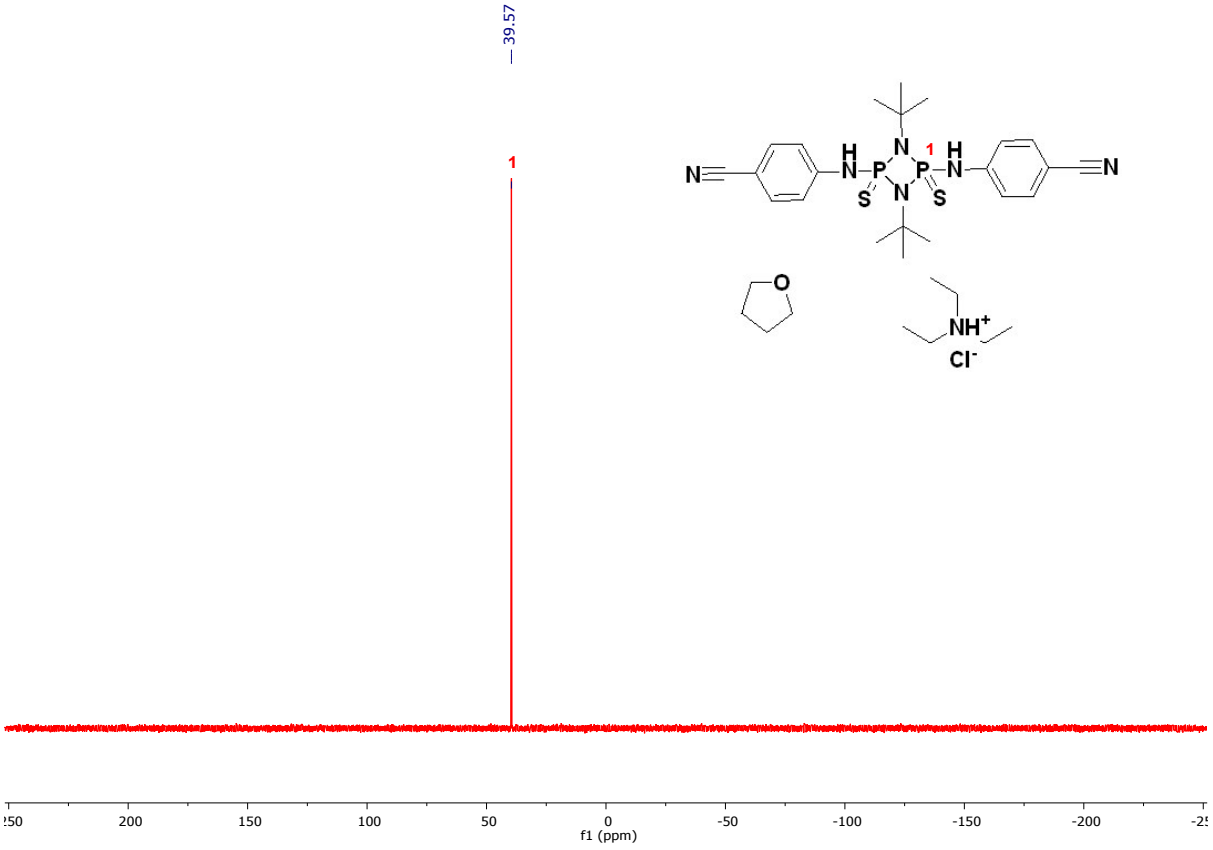


Figure S 20. $^{31}P\{^{1}H\}$ NMR spectrum of ***6***

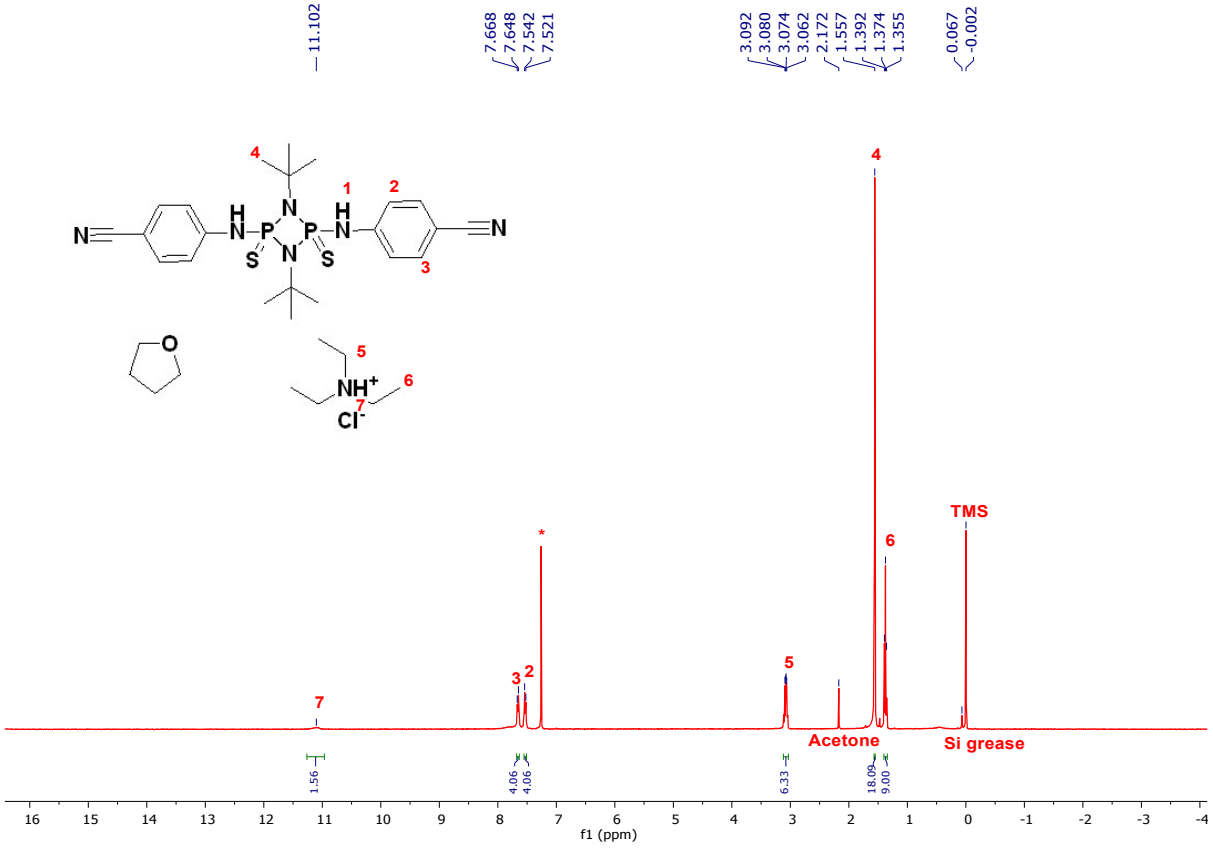


Figure S 21. ^{1}H NMR spectrum of ***6***

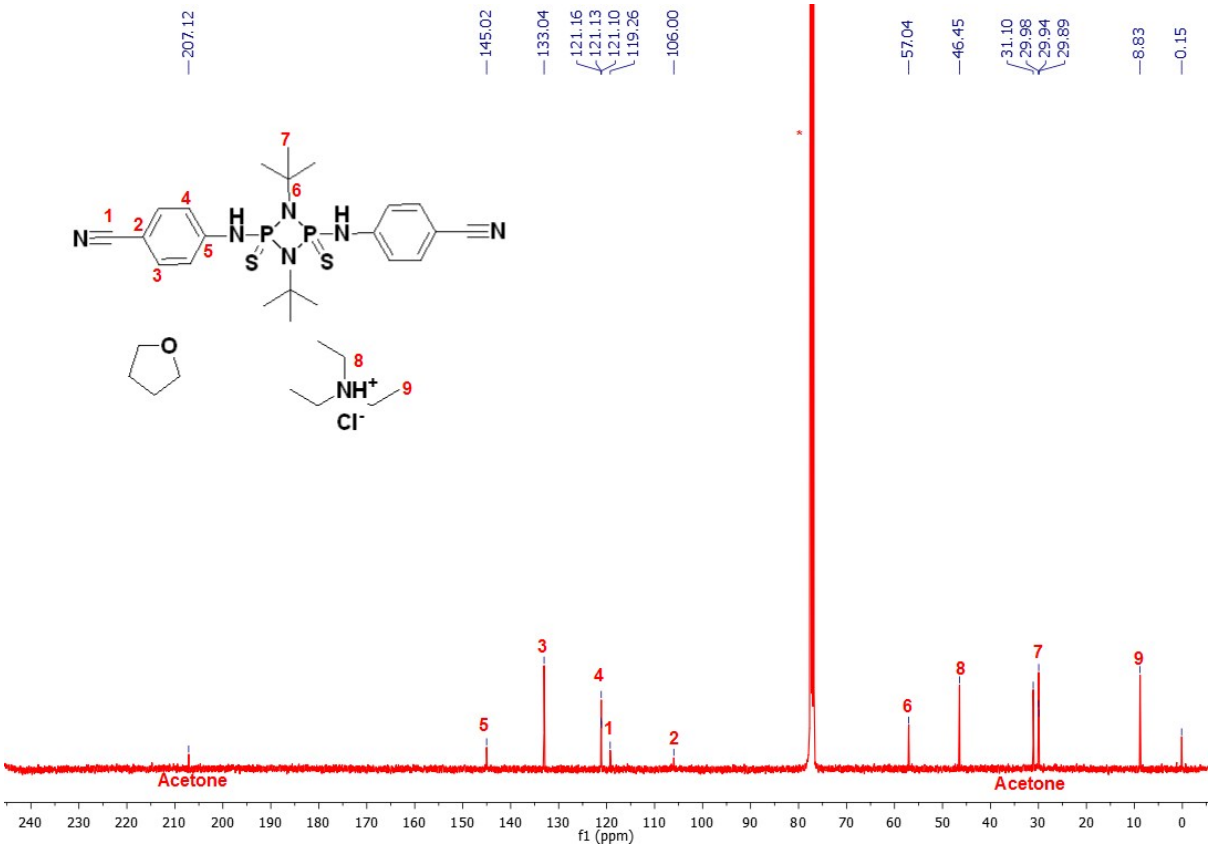


Figure S 22. ^{13}C NMR spectrum of ***6***

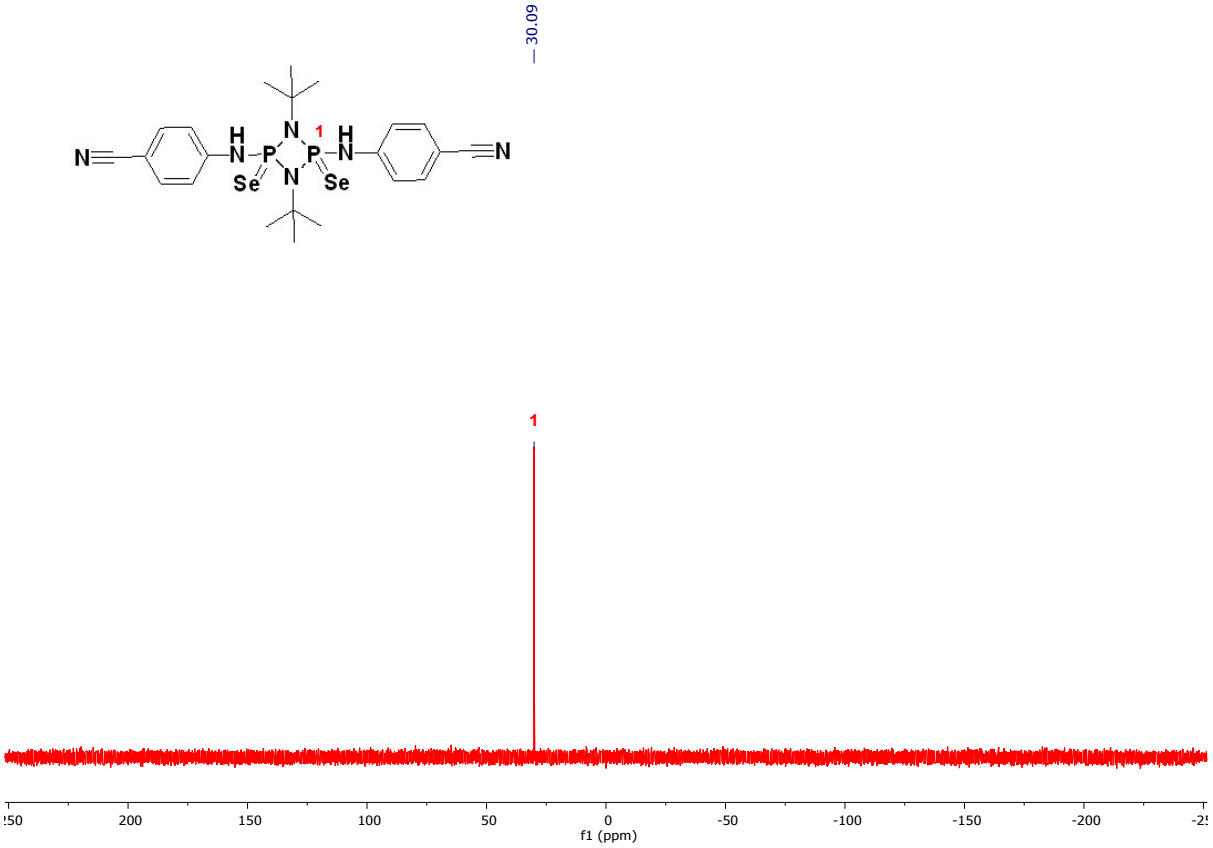


Figure S 23. ^{31}P{^{1}H} NMR spectrum of ***7***

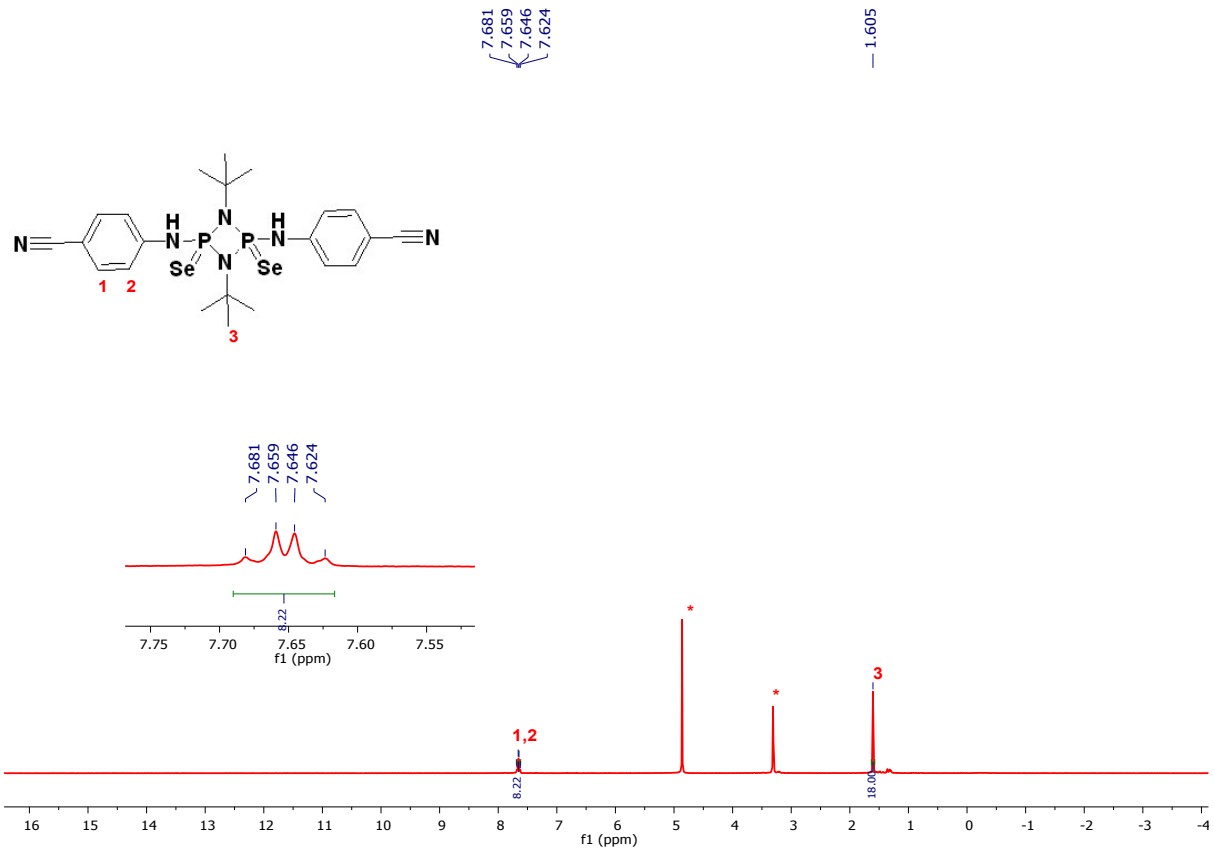


Figure S 24. ^{1}H NMR spectrum of ***7***

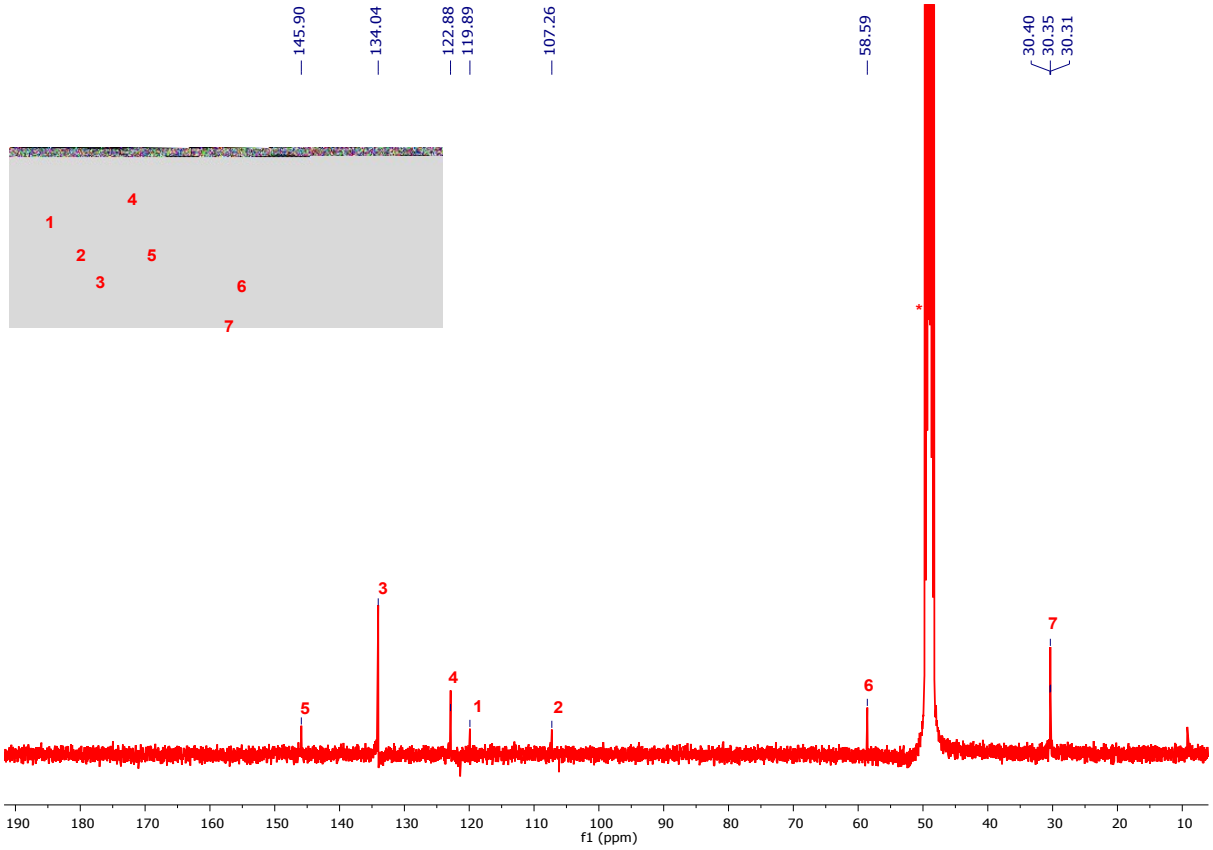


Figure S 25. ^{13}C NMR spectrum of ***7***

4. HRMS and IR Spectra

HRMS

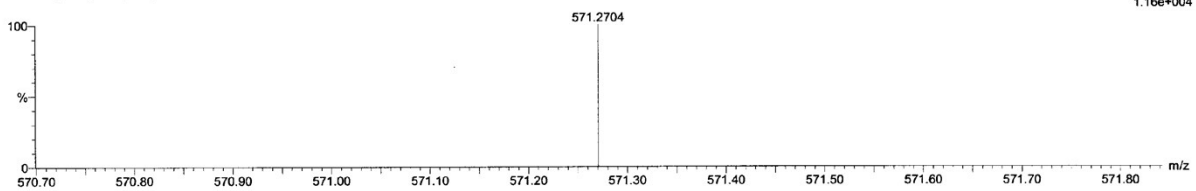
Elemental Composition Report

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
378 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 27-29 H: 47-50 N: 1-2 O: 1-5 F: 0-3 S: 1-3 51V: 0-1 P: 1-3

C28H48N2O2P2S2
SY272 8 (0.166) Cm (8:45)

1: TOF MS ES+
1.16e+004



Minimum:				-1.5			
Maximum:		5.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
571.2704	571.2711	-0.7	-1.2	6.5	25.6	0.0	C28 H49 N2 O2 S2 P2

2S-P2N2-20Ad.
MW: 570.77
Exact Mass: 570.26

Figure S 26. HRMS spectrum of **2**

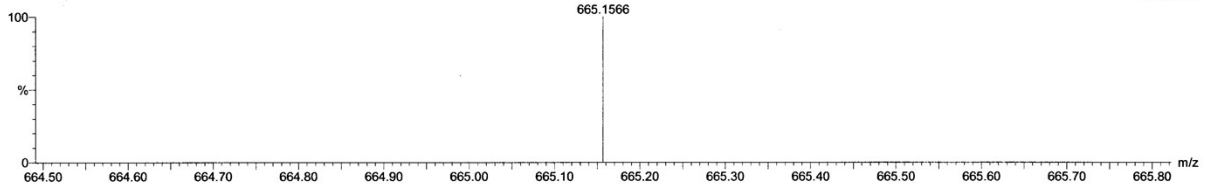
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
45 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 27-29 H: 47-50 N: 1-3 O: 1-2 P: 1-3 78Se: 0-1 80Se: 0-1

C28H48N2O2P2Se2
SY504 30 (0.628) Cm (22:57)

1: TOF MS ES+
6.22e+001



Minimum:				-1.5									
Maximum:		5.0	10.0	50.0									
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula						
665.1566	665.1608	-4.2	-6.3	8.5	15.9	0.0	C28	H49	N2	O2	P2	78Se	80Se

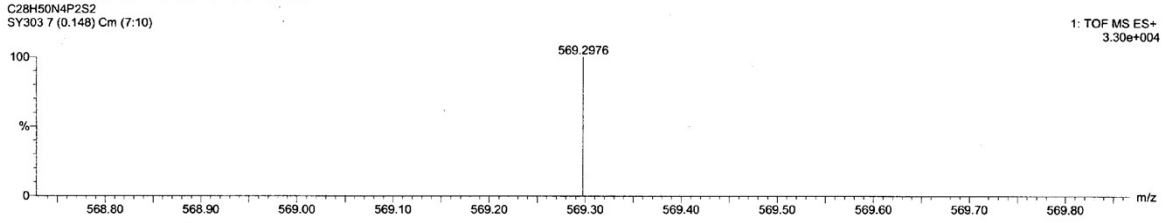
JSP-P2N2-20Ad.
mW. 664.57.
Exact mass 666.15

Figure S 27. HRMS spectrum of **3**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
5 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 27-29 H: 49-52 N: 3-5 P: 1-3 S: 1-2
C28H50N4P2S2
SY303 7 (0.148) Cm (7:10)



Minimum:				-1.5						
Maximum:		5.0	10.0	50.0						
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula			
569.2976	569.3030	-5.4	-9.5	6.5	29.6	0.0	C28	H51	N4	P2 S2

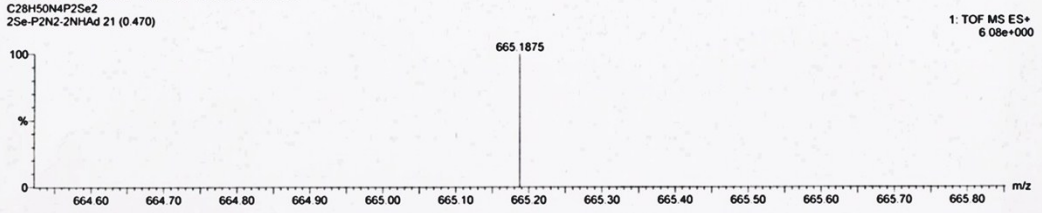
2S-P2N2-2NHAd
MW: 568.80
Exact Mass: 568.30

Figure S 28. HRMS spectrum of **4**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 28-28 H: 50-51 N: 4-4 P: 2-2 Se: 2-2
C28H50N4P2Se2
2Se-P2N2-2NHAd 21 (0.470)



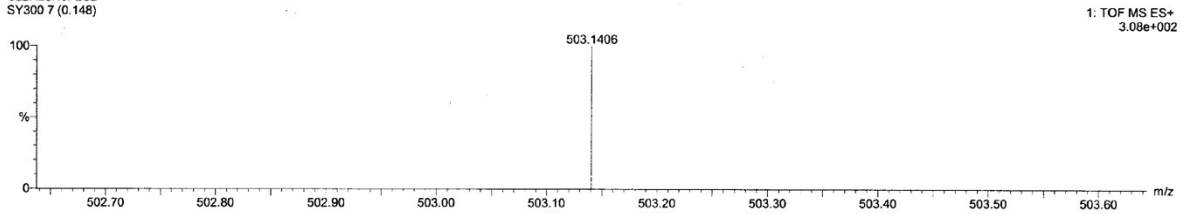
Minimum:				-1.5						
Maximum:		10.0	10.0	50.0						
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula			
665.1875	665.1919	-4.4	-6.6	8.5	17.5	0.0	C28	H51	N4	P2 Se2

Figure S 29. HRMS spectrum of **5**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 22-23 H: 28-30 N: 5-7 P: 1-2 S: 1-2
C22H28N6P2S2
SY300 7 (0.148)



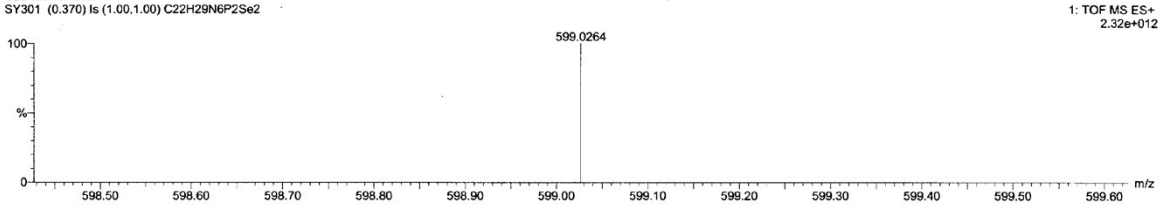
Minimum:				-1.5			
Maximum:		5.0	10.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
503.1406	503.1370	3.6	7.2	12.5	19.2	0.0	C22 H29 N6 P2 S2

Figure S 30. HRMS spectrum of **6**

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 30.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
8 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 21-23 H: 28-29 N: 5-6 P: 1-2 Se: 1-3
C22H28N6P2S2
SY301 (0.370) Is (1.00,1.00) C22H29N6P2Se2



Minimum:				-1.5			
Maximum:		5.0	30.0	50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
599.0264	599.0259	0.5	0.8	14.5	69.0	0.0	C22 H29 N6 P2 Se2

28e-P2N2-2NHPhCN
MW: 596.38
Exact mass: 598.02

Figure S 31. HRMS spectrum of **7**

IR

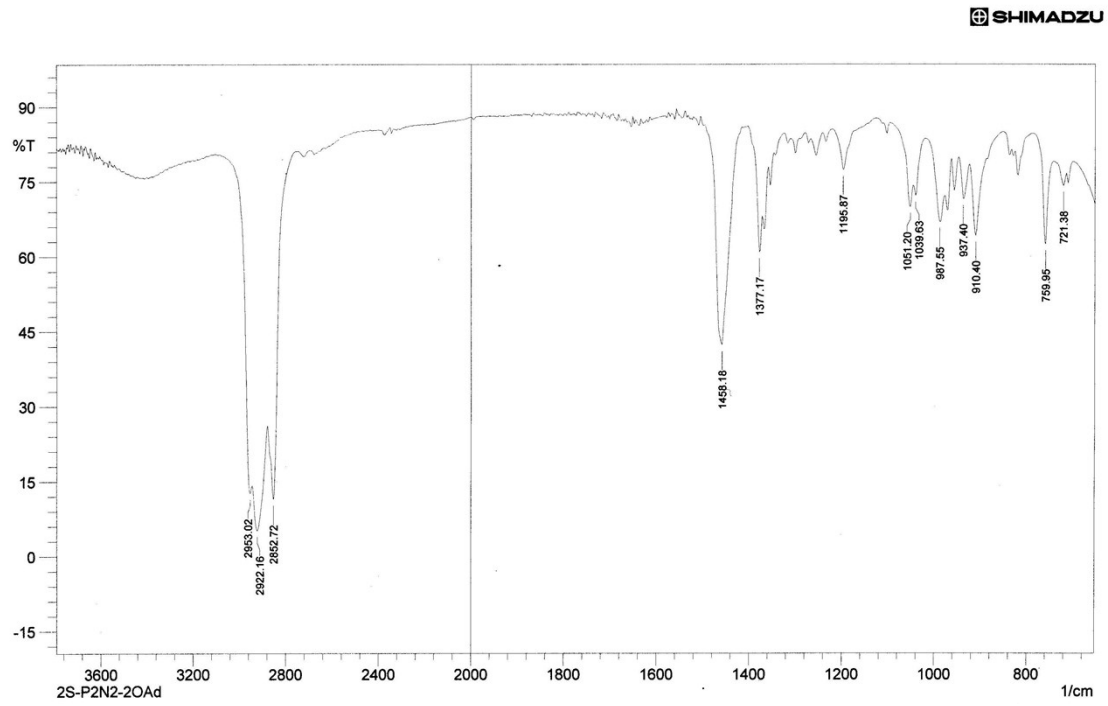


Figure S 32. IR spectrum of **2**

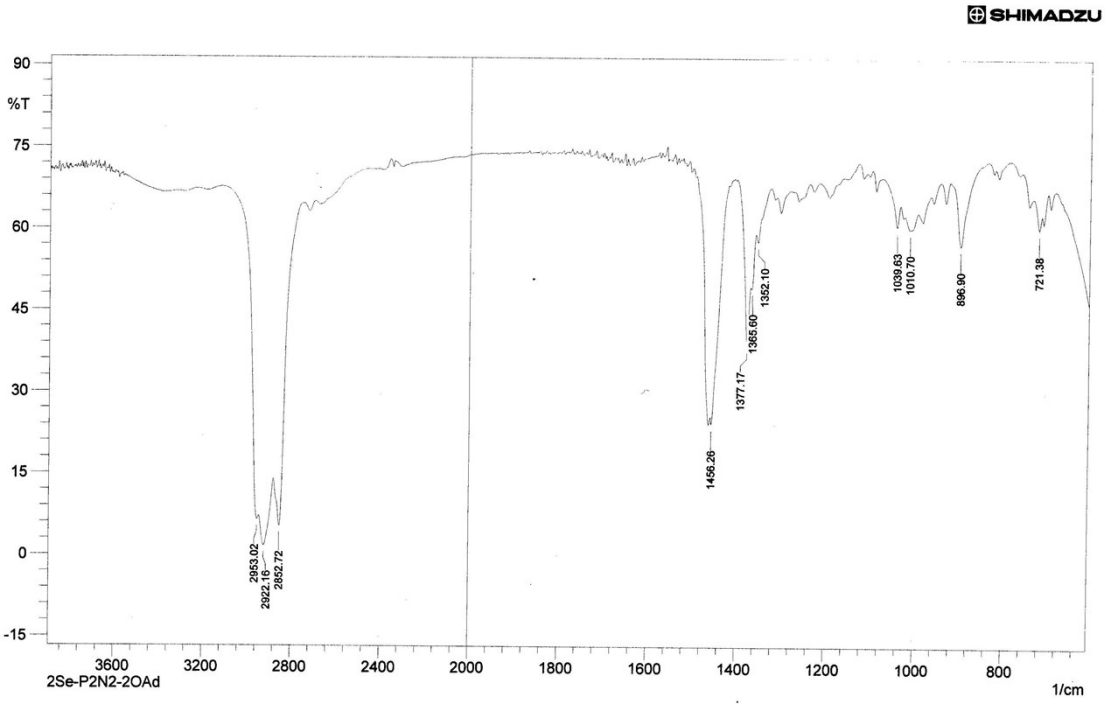


Figure S 33. IR spectrum of **3**

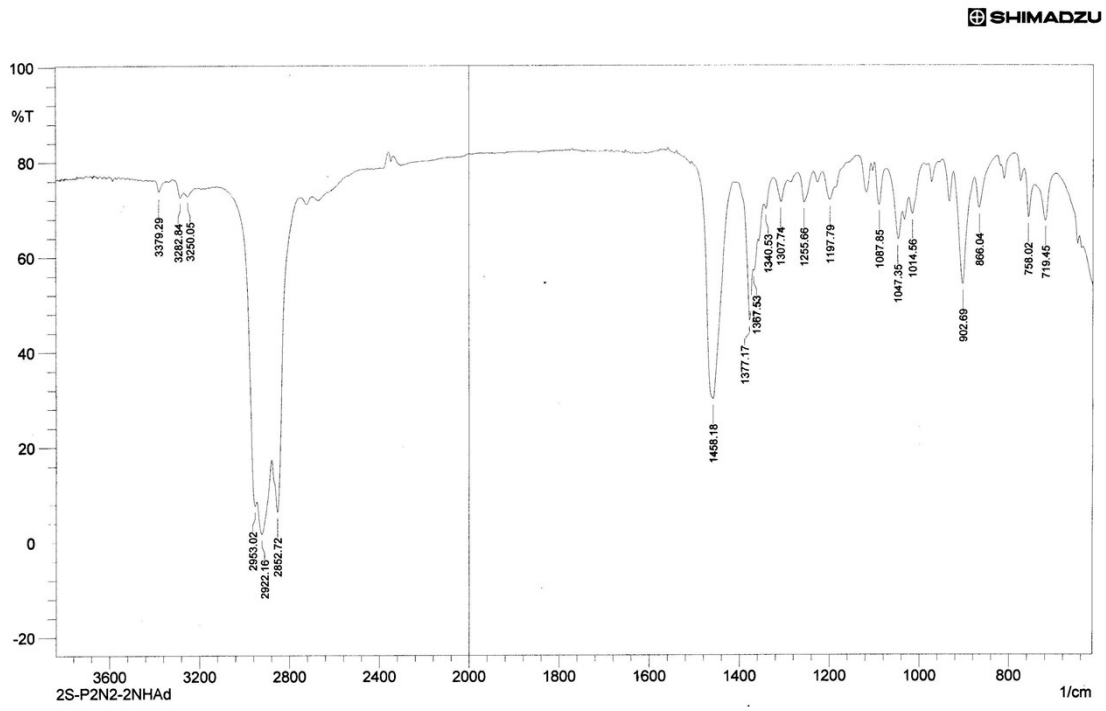


Figure S 34. IR spectrum of **4**

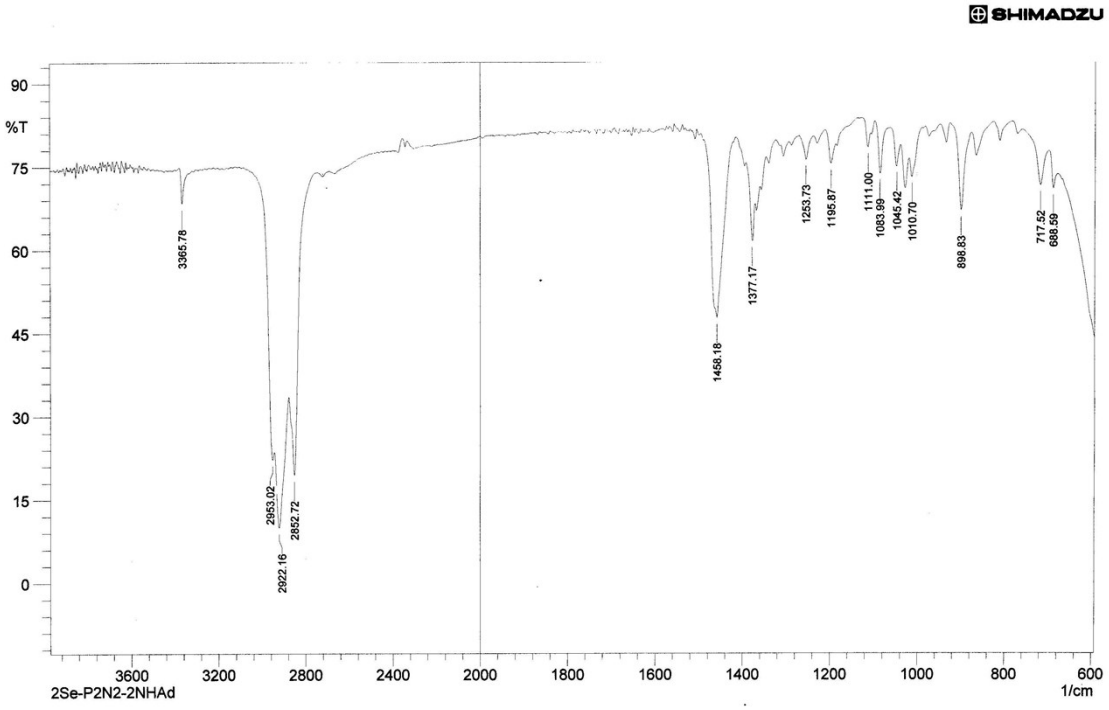


Figure S 35. IR spectrum of **5**

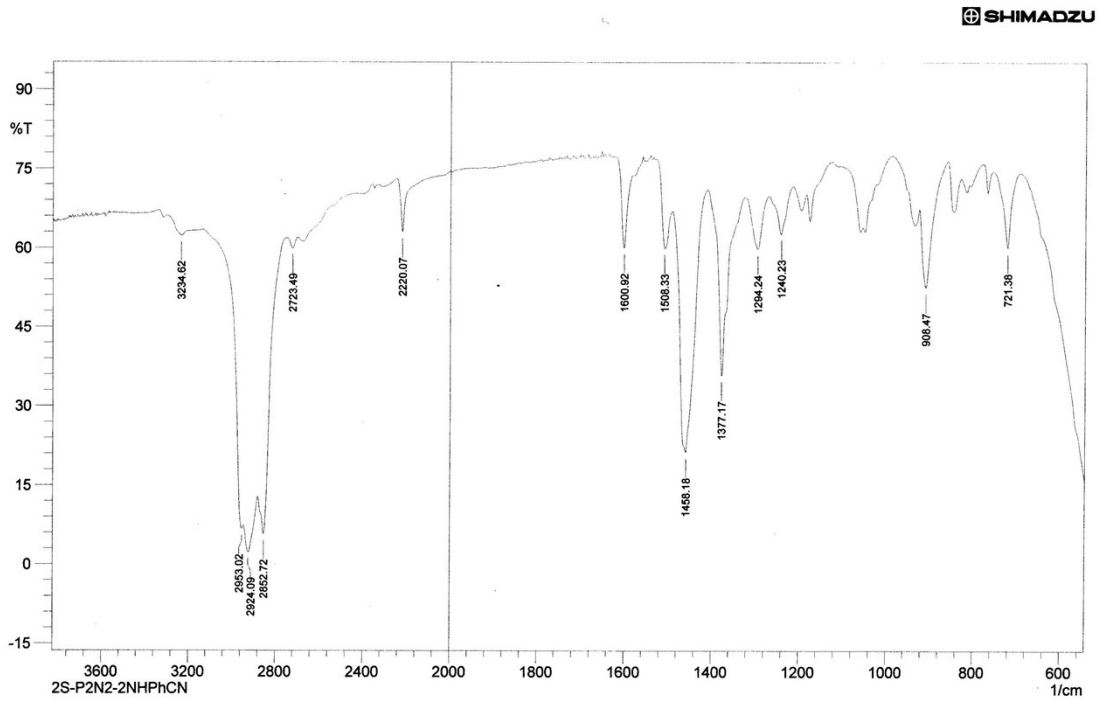


Figure S 36. IR spectrum of **6**

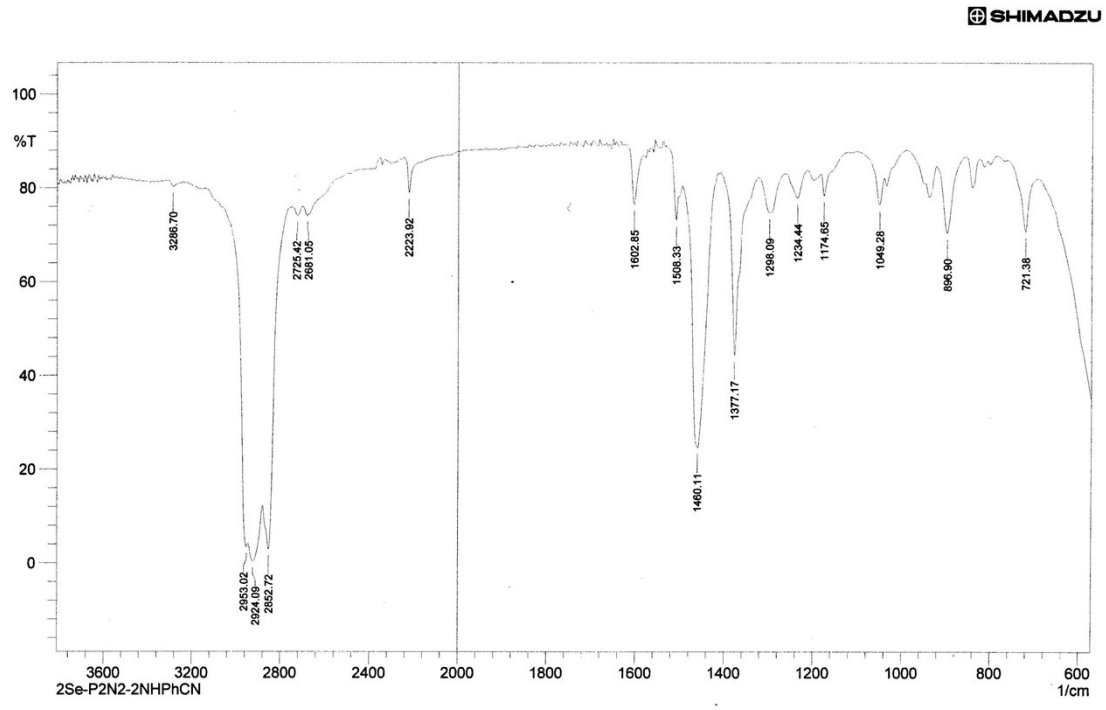


Figure S 37. IR spectrum of **7**

5. Air Stability Studies of Compound 2-7

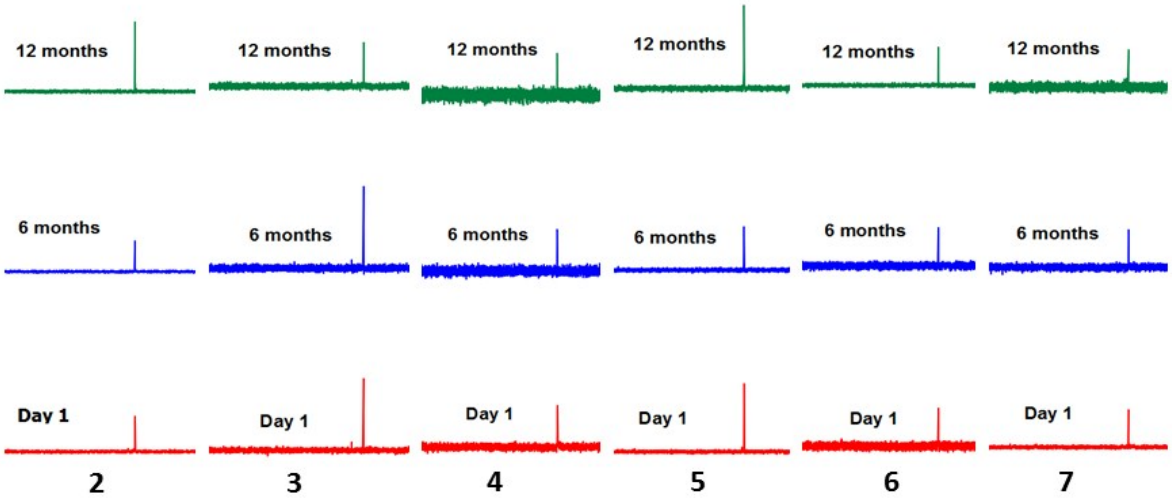


Figure S 38. Complied air-stability studies *via* $^{31}P\{^{1}H\}$ NMR spectrum of **2**-**7** over a period of 12 months

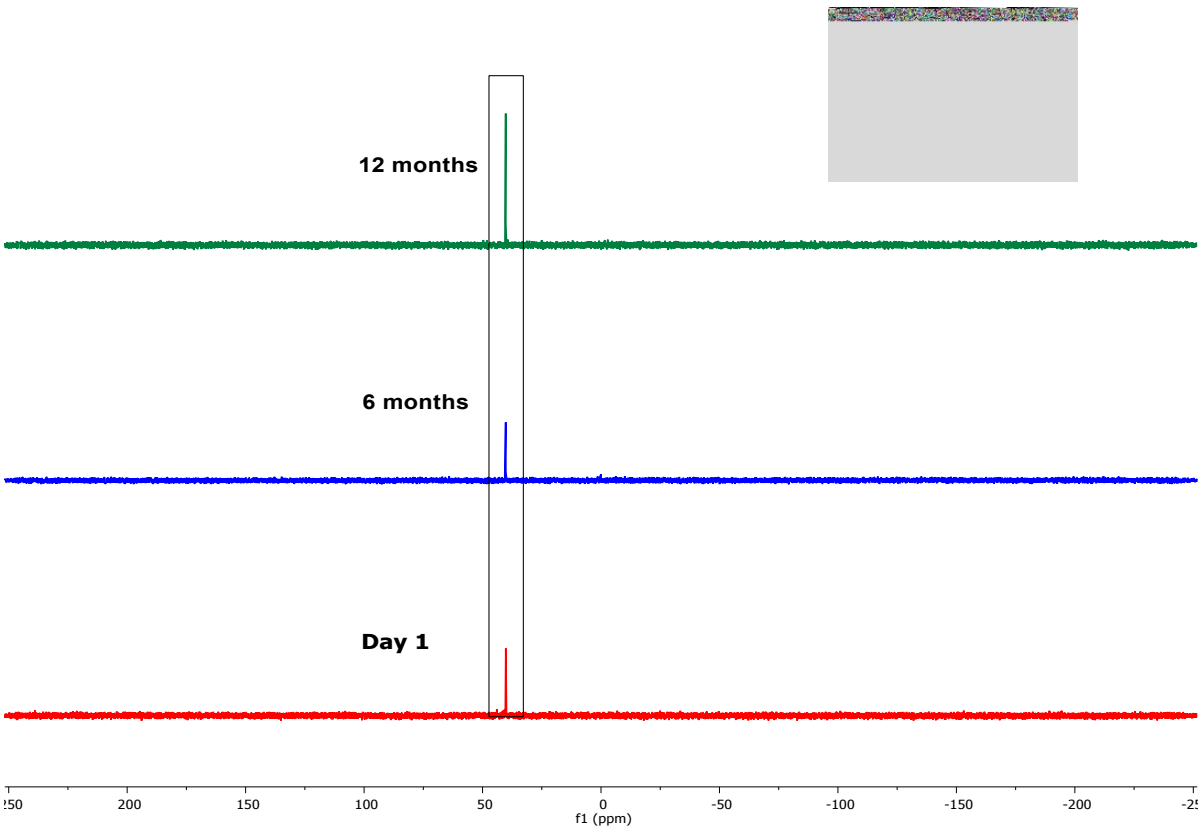


Figure S 39. Air-Stability Study for **2**. $^{31}P\text{-}\{^{1}H\}$ NMR spectrum of **2** on day 1, 6 and 12 months

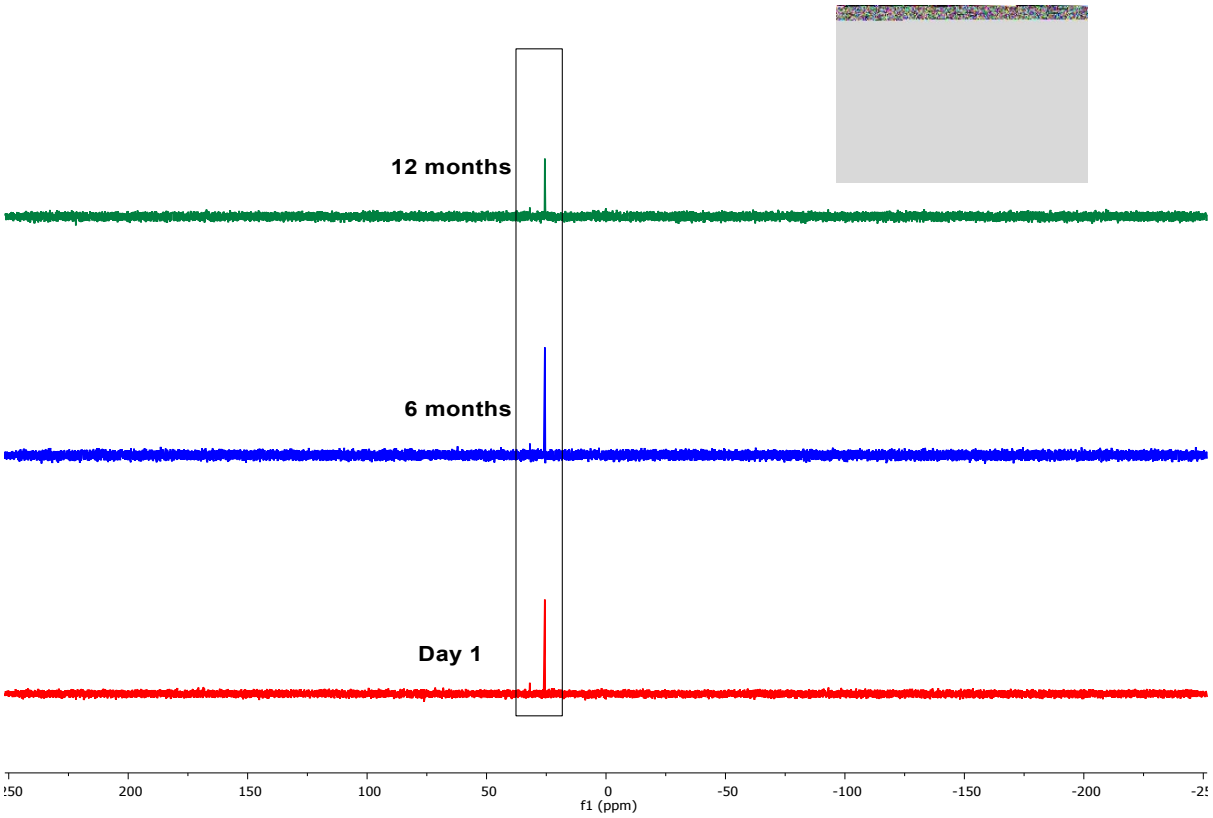


Figure S 40. Air-Stability Study for **3**. ^{31}P-{^{1}H} NMR spectrum of **3** on day 1, 6 and 12 months

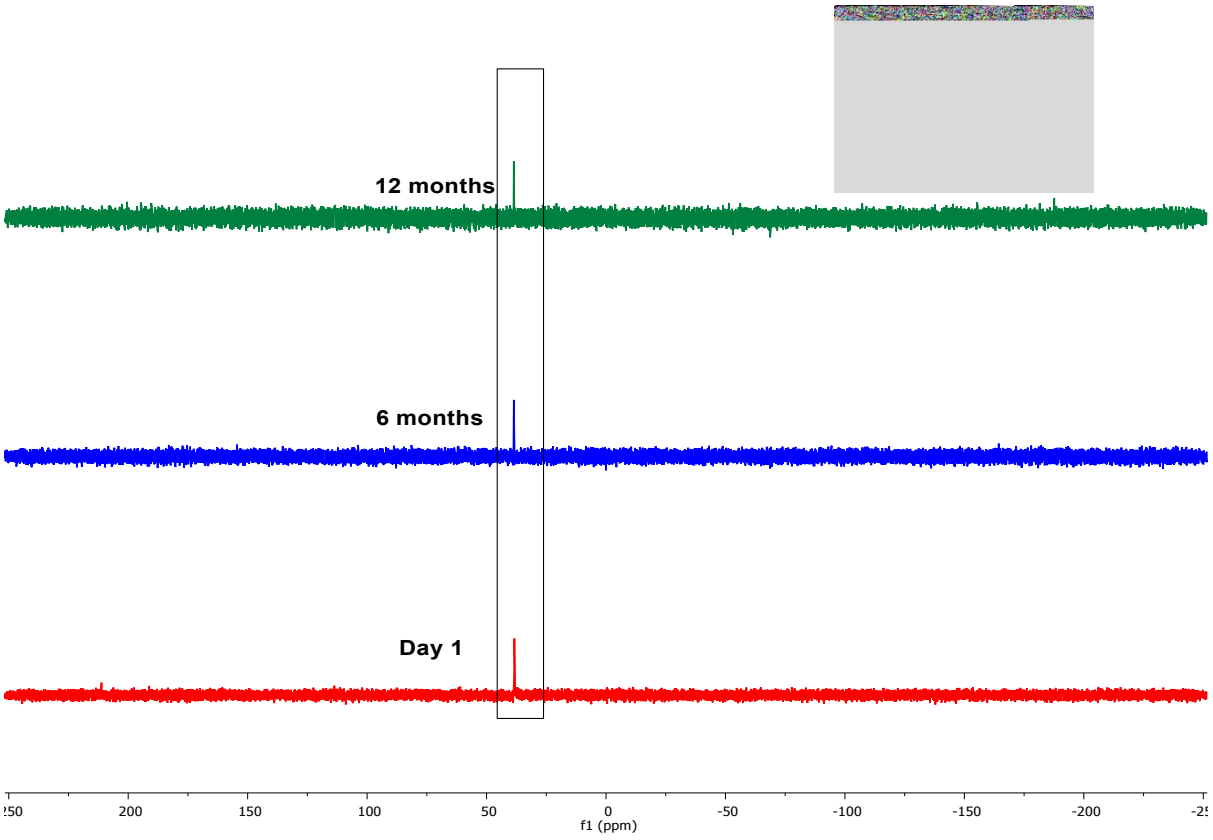


Figure S 41. Air-Stability Study for **4**. ^{31}P-{^{1}H} NMR spectrum of **4** on day 1, 6 and 12 months

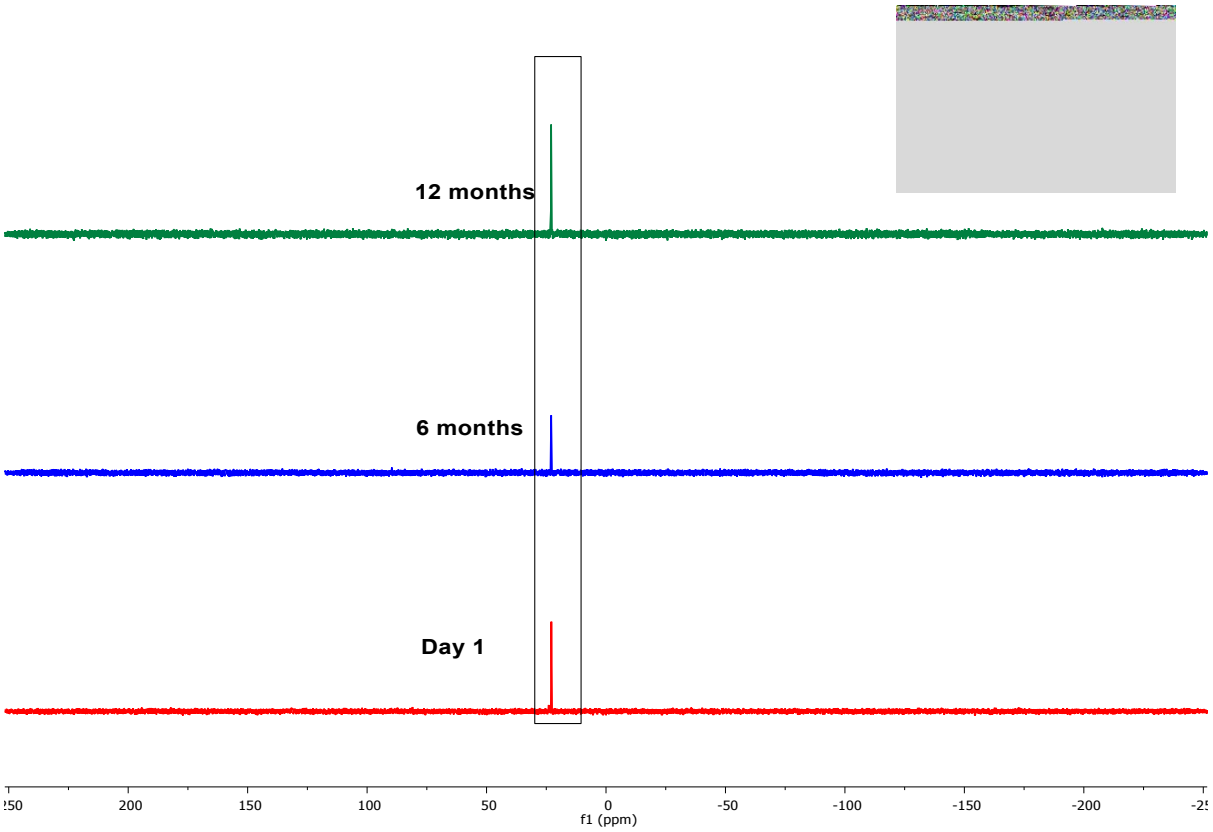


Figure S 42. Air-Stability Study for **5**. $^{31}P-\{^{1}H\}$ NMR spectrum of **5** on day 1, 6 and 12 months

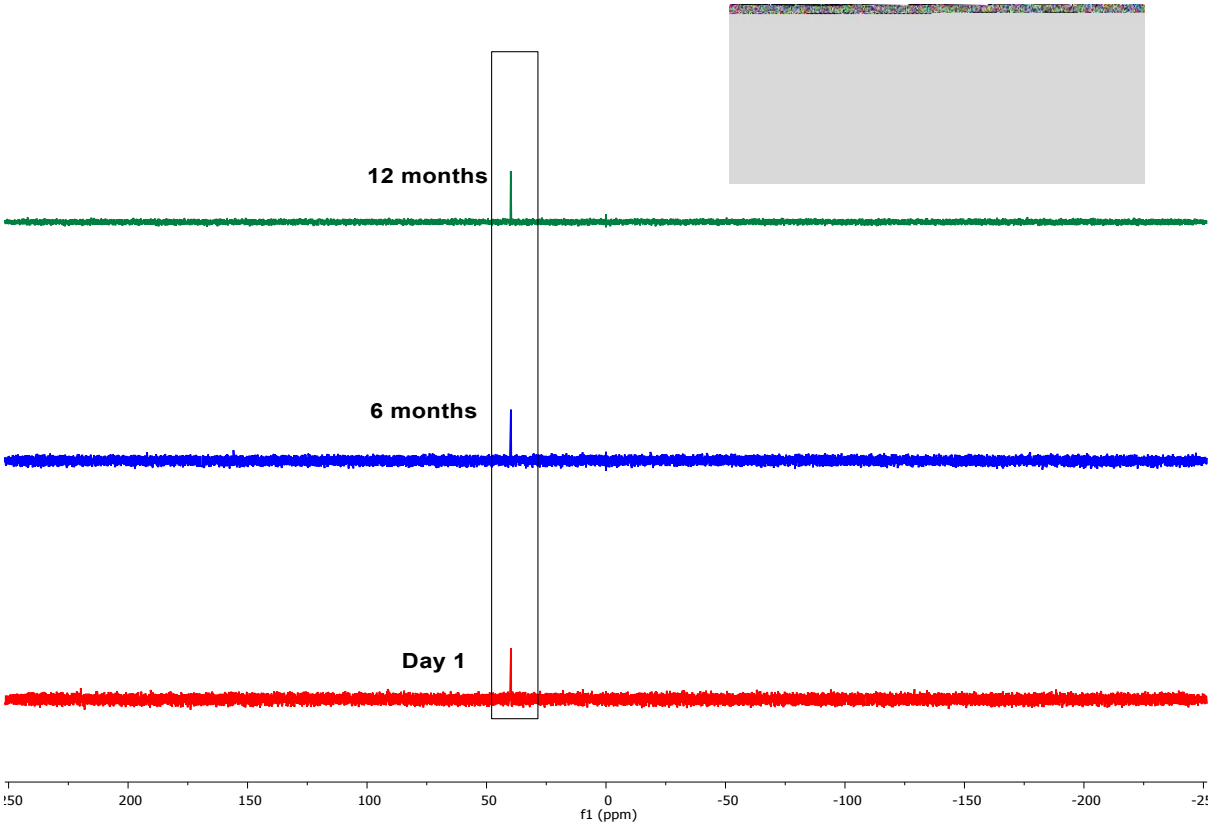


Figure S 43. Air-Stability Study for **6**. $^{31}P-\{^{1}H\}$ NMR spectrum of **6** on day 1, 6 and 12 months

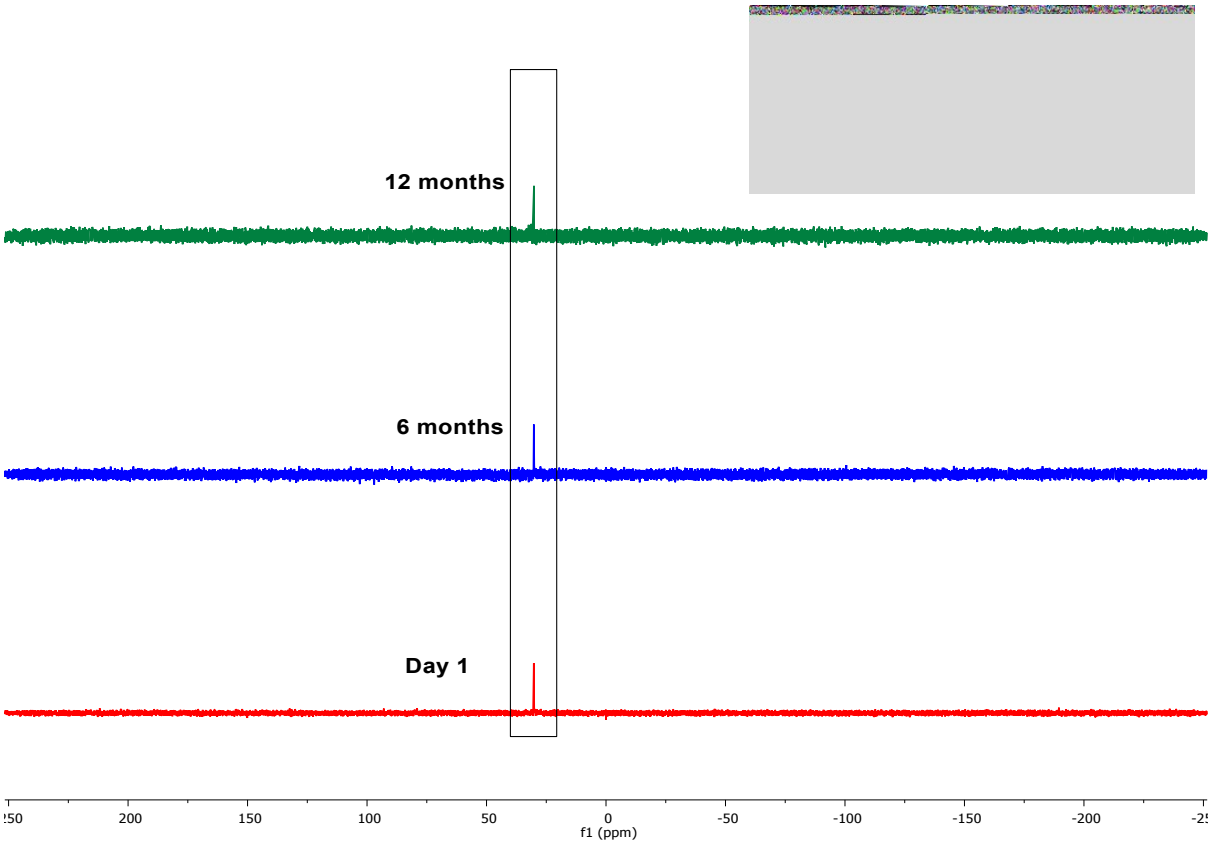


Figure S 44. Air-Stability Study for **7**. ^{31}P-{^{1}H} NMR spectrum of **7** on day 1, 6 and 12 months

6. Hydrolytic Studies of Compounds 2-7

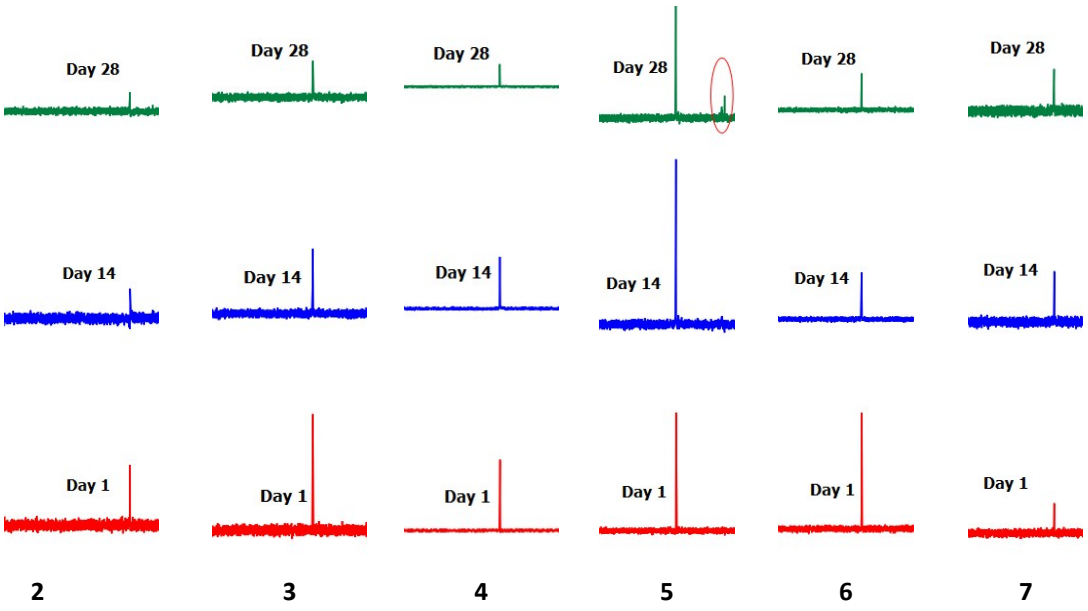


Figure S 45. Complied hydrolytic-stability studies *via* $^{31}P\{^{1}H\}$ NMR spectrum of **2**-**7** over a period of 1 month

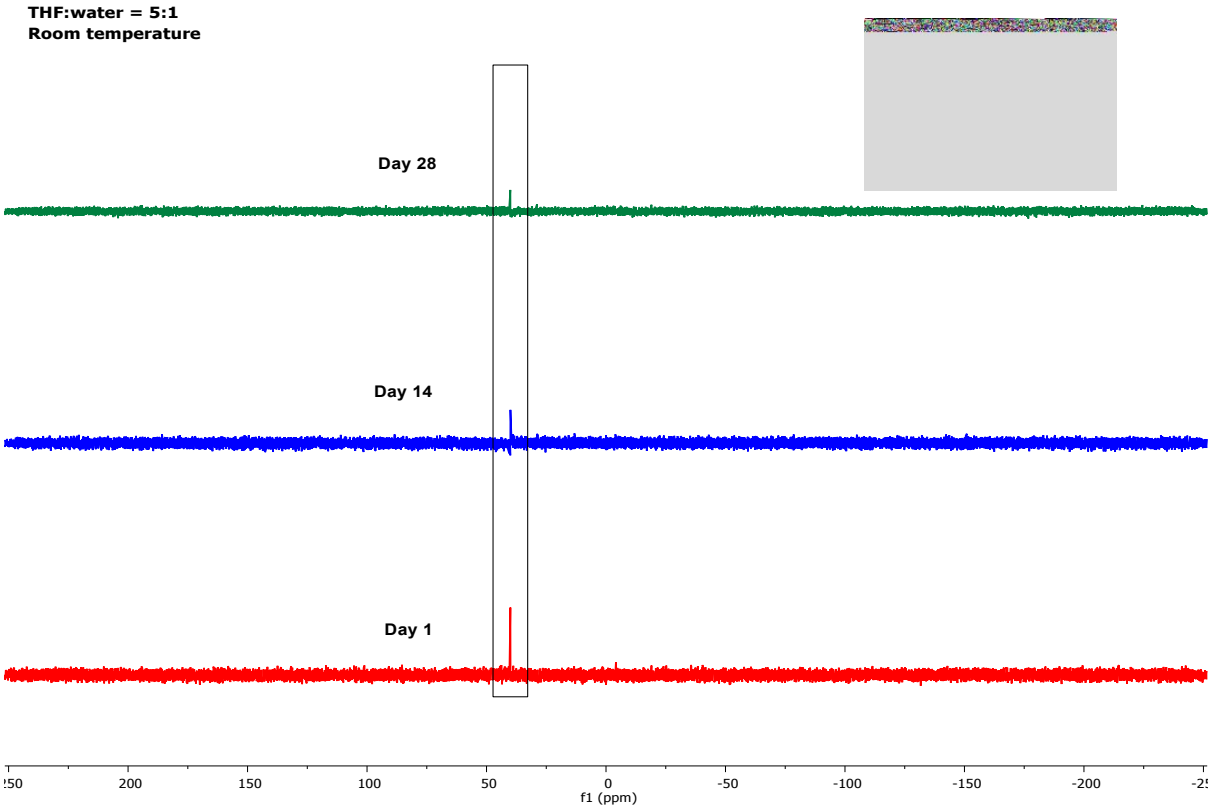


Figure S 46. Hydrolytic stability of **2** over the course of 1 month. 31P-{1H} NMR in THF:Water=5:1 on Day 1, 14 and 28.

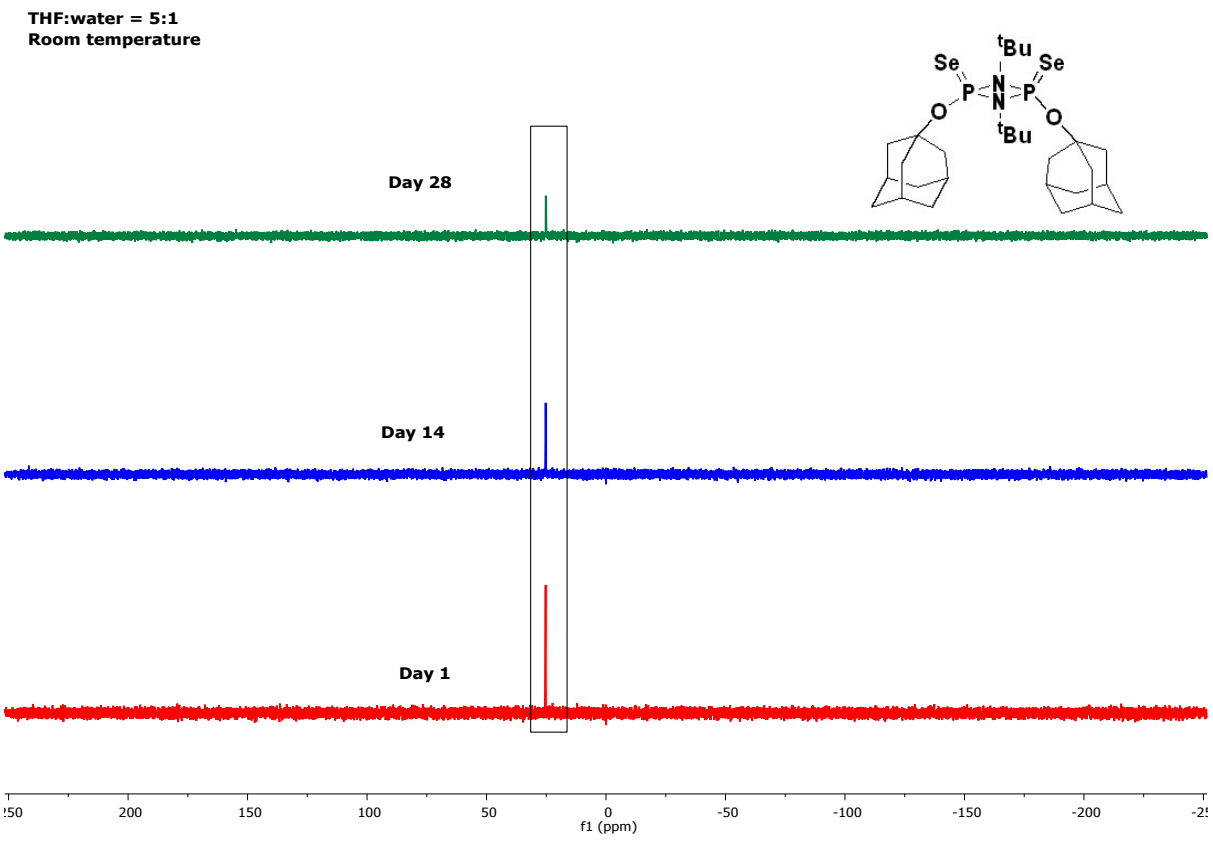


Figure S 47. Hydrolytic stability of **3** over the course of 1 month. 31P-{1H} NMR in THF:Water=5:1 on Day 1, 14 and 28.

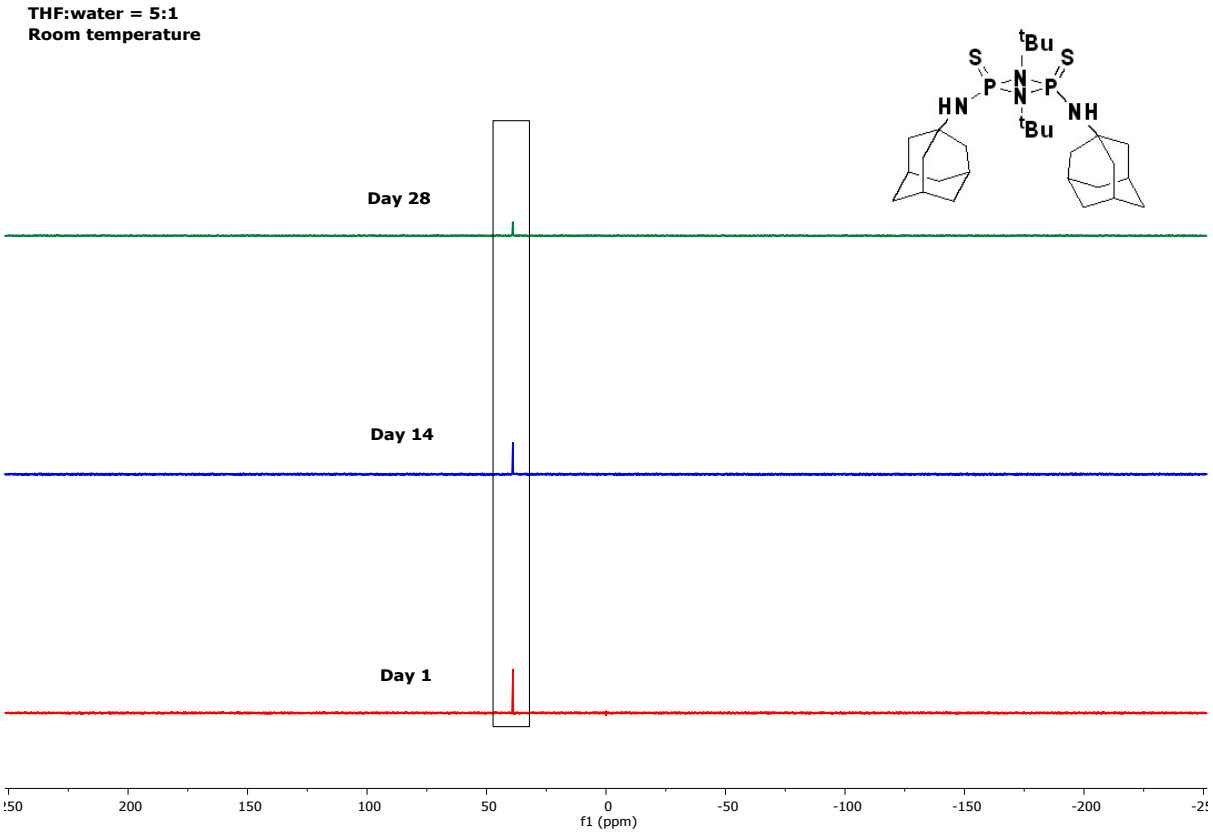


Figure S 48 Hydrolytic stability of **4** over the course of 1 month. 31P-{1H} NMR in THF:Water=5:1 on Day 1, 14 and 28.

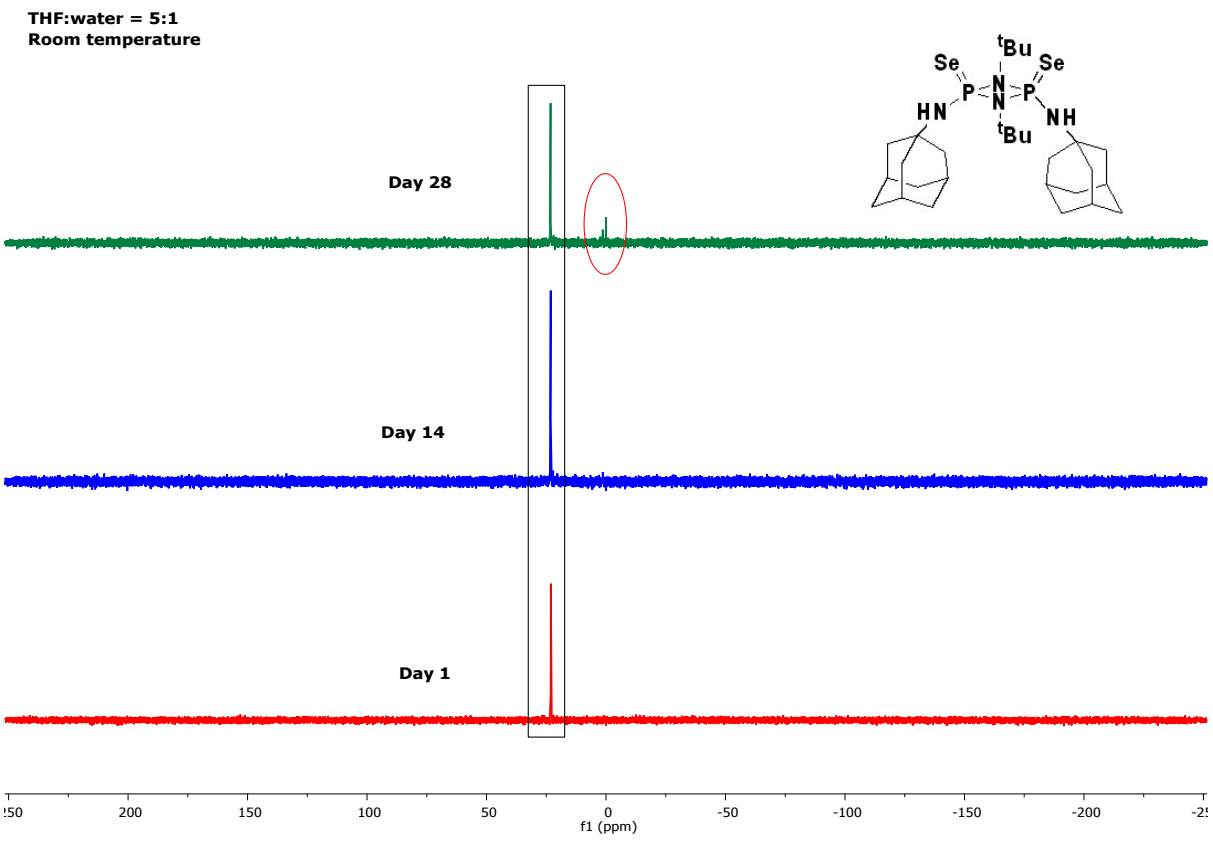


Figure S 49. Hydrolytic stability of **5** over the course of 1 month. 31P-{1H} NMR in THF:Water=5:1 on Day 1, 14 and 28.

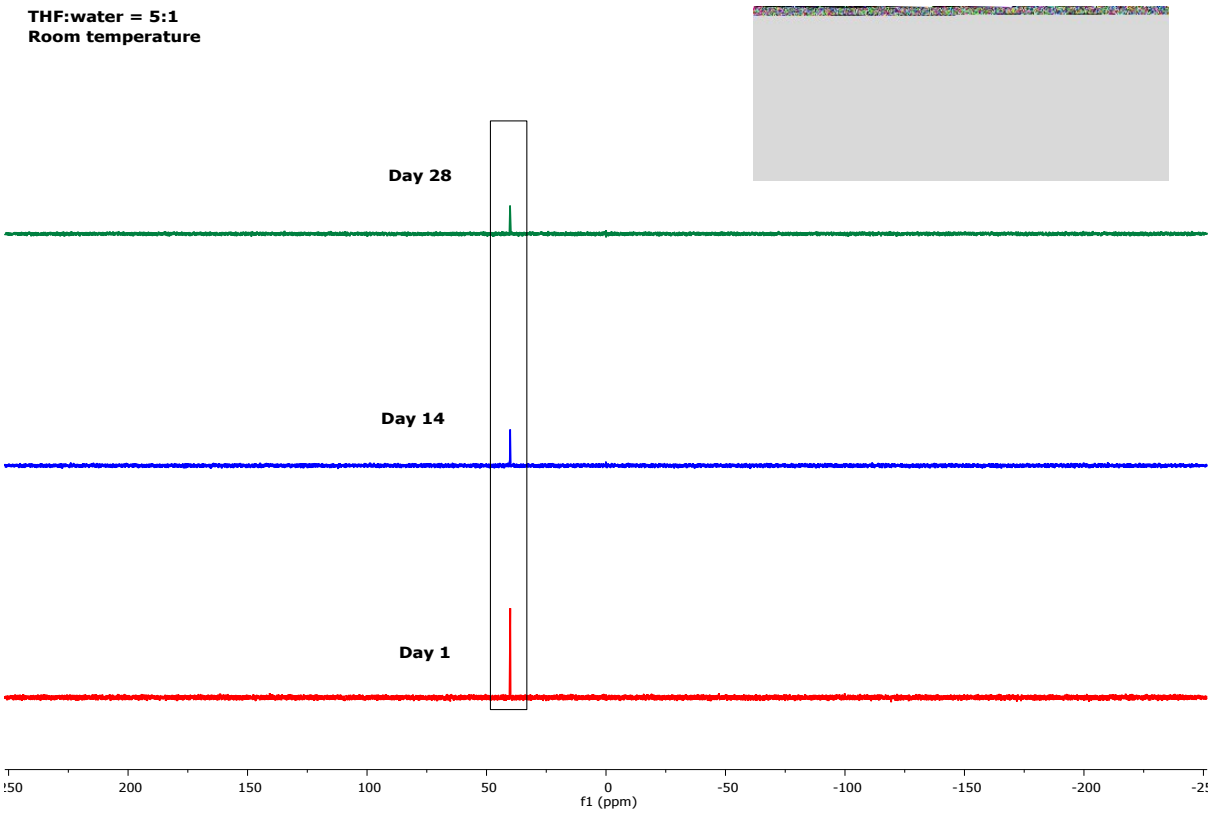


Figure S 50. Hydrolytic stability of **6** over the course of 1 month. 31P-{1H} NMR in THF:Water=5:1 on Day 1, 14 and 28.

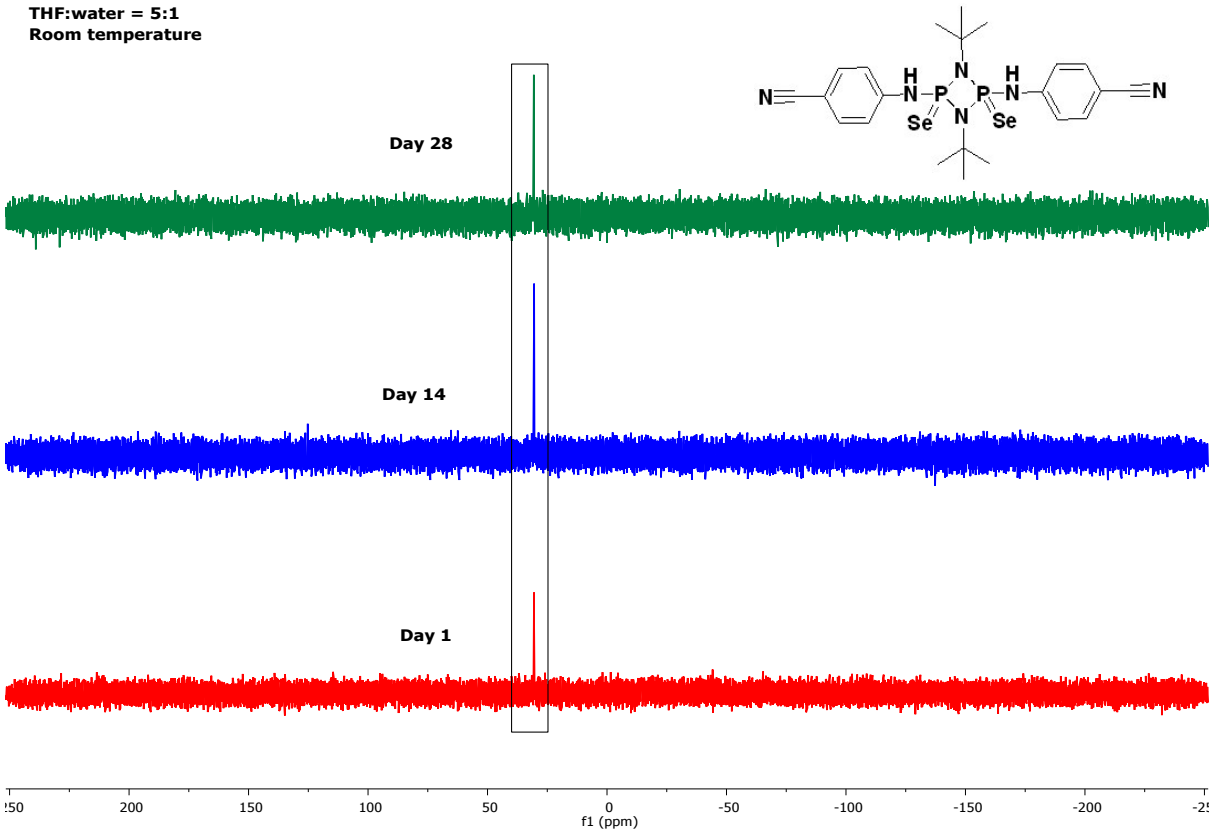


Figure S 51. Hydrolytic stability of **7** over the course of 1 month. 31P-{1H} NMR in THF:Water=5:1 on Day 1, 14 and 28.

7. X-ray Crystallographic Data (CCDC 1819730-1819735)

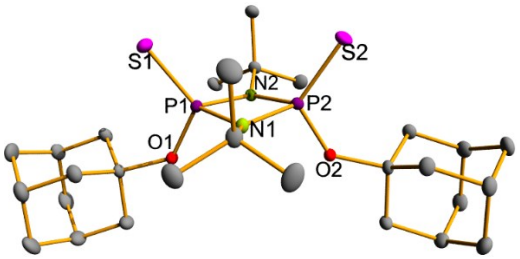


Figure S 52. ORTEP drawing of the molecular structure of **2** *in the crystal. Thermal ellipsoids with 50% probability at 153K. Hydrogen atoms and solvent toluene molecules are omitted for clarity. Selected Bond Lengths (Å): P1-S1 1.9293(7), P2-S2 1.9299(6), P1-N1 1.6863(15), P1-N2 1.6886(15), P2-N1 1.6886(15), P2-N2 1.6893(15), P1-O1 1.5804(13), P2-O2 1.5746(13); Selected Bond Angles (˚): N1-P1-N2 84.03(7), N1-P2-N2 83.94(7), P1-N1-P2 95.51(8), P1-N2-P2 95.40(8), O1-P1-N1 107.61(7), O1-P1-N2 106.80(7), O2-P2-N1 107.44(7), O2-P2-N2 107.40(7), N1-P1-S1 119.09(6), N2-P1-S1 119.21(6), N2-P2-S2 119.17 (6), N1-P2-S2 119.49(6), O1-P1-S1 115.58(5), O2-P2-S2 105.05(5).*

Empirical Formula	$C_{28}H_{48}N_2O_2P_2S_2$	Volume (Å^3)	2880.2(3)
Formula Weight	570.74 g/mol	Z	4
Temperature (K)	153(2)	Calculated Density (g/cm^3)	1.316
Wavelength (Å)	0.71073	μ, Abs. coeff. C(mm^{-1})	0.325
Crystal System	Monoclinic	F(000)	1232
Space Group	P 1 21/n 1	Crystal Size (mm)	0.180 x 0.220 x 0.420
Unit Cell Dimension, cell		2θ range (˚)	1.45 to 28.85
length (Å)	a = 15.8615(11)	Reflections collected	29542
	b = 6.9081(5)	Indep. Refl. (R_{int})	7507 [R(int) = 0.0900]
	c = 26.3622(17)	Larg. Diff. Peak and hole (eÅ^{-3})	0.681 and -0.436
angles (˚)	α = 90	R1, wR2 (I>2σ(I))	0.0478, 0.1160
	β = 94.360(2)	R1, wR2 (all data)	0.0620, 0.1263
	γ = 90		

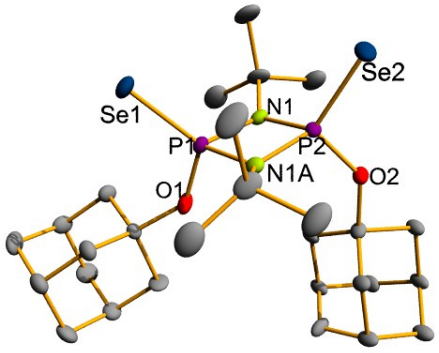


Figure S 53. ORTEP drawing of the molecular structure of **3** *in the crystal. Thermal ellipsoids with 50% probability at 153K. Hydrogen atoms are omitted for clarity. Selected Bond Lengths (Å): P1-Se1 2.079(3), P2-Se2 2.085(3), P1-N1 1.693(7), P2-N1 1.691(7), P1-O1 1.579(9), P2-O2 1.565(8); Selected Bond Angles (°): N1-P1-N1 84.1(4), N1-P2-N1 84.2(5), P1-N1-P2 95.7(3), O1-P1-Se1 115.6(3), O2-P2-Se2 106.6(3), Se1-P1-N1 120.4(2), Se2-P2-N1 119.9(2).*

Empirical Formula	$C_{28}H_{48}N_2O_2P_2Se_2$	Volume (Å^3)	1495.5(2)
Formula Weight	664.54 g/mol	Z	2
Temperature (K)	153(2)	Calculated Density (g/cm^3)	1.476
Wavelength (Å)	0.71073	μ, Abs. coeff. C(mm^{-1})	2.607
Crystal System	Monoclinic	F(000)	688
Space Group	P 1 21/m 1	Crystal Size (mm)	0.220 x 0.300 x 0.320
Unit Cell Dimension, cell		2θ range (°)	1.59 to 29.00
length (Å)	a = 10.7455(9)	Reflections collected	21674
	b = 10.8723(9)	Indep. Refl. (R_{int})	4140 [R(int) = 0.1484]
	c = 13.5836(12)	Larg. Diff. Peak and hole (eÅ^{-3})	1.565 and -1.848
angles (°)	α = 90	R1, wR2 (I>2σ(I))	0.0924, 0.2277
	β = 109.542(2)	R1, wR2 (all data)	0.1358, 0.2428
	γ = 90		

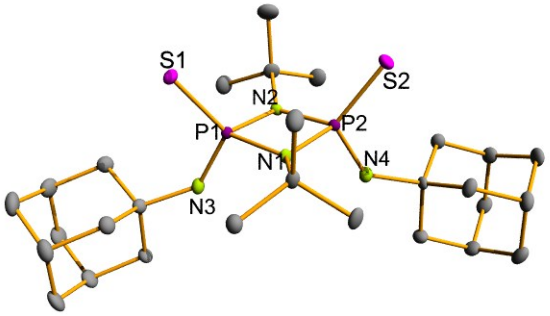


Figure S 54. ORTEP drawing of the molecular structure of **4** *in the crystal. Thermal ellipsoids with 50% probability at 100K. Hydrogen atoms and THF solvate molecule are omitted for clarity. Selected Bond Lengths (Å): P1-S1 1.9286(18), P2-S2 1.9321(17), P1-N1 1.704(4), P2-N1 1.679(4), P1-N2 1.694(4), P2-N2 1.696(4), P1-N3 1.638(4), P2-N4 1.628(4); Selected Bond Angles (˚): N1-P1-N2 82.9(2), N1-P2-N2 83.6(2), P1-N1-P2 96.7(2), P1-N2-P2 96.4(2), N1-P1-S1 117.66(16), N2-P2-S2 119.03(16), N1-P1-N3 110.2(2), N2-P2-N4 108.9(2).*

Empirical Formula	$C_{64}H_{112}N_8O_2P_4S_4$	Volume (Å^3)	6805.0(3)
Formula Weight	1277.73 g/mol	Z	4
Temperature (K)	100(2)	Calculated Density (g/cm^3)	1.247
Wavelength (Å)	0.71073	μ, Abs. coeff. C(mm^{-1})	0.282
Crystal System	Orthorhombic	F(000)	2768
Space Group	P n a 21	Crystal Size (mm)	0.100 x 0.140 x 0.220
Unit Cell Dimension, cell		2θ range (˚)	2.65 to 27.00
length (Å)	a = 24.3568(6)	Reflections collected	53479
	b = 9.8974(2)	Indep. Refl. (R_{int})	14773 [R(int) = 0.0449]
	c = 28.2283(6)	Larg. Diff. Peak and hole (eÅ^{-3})	1.964 and -0.659
angles (˚)	α = 90	R1, wR2 (I>2σ(I))	0.0597, 0.1503
	β = 90	R1, wR2 (all data)	0.0642, 0.1543
	γ = 90		

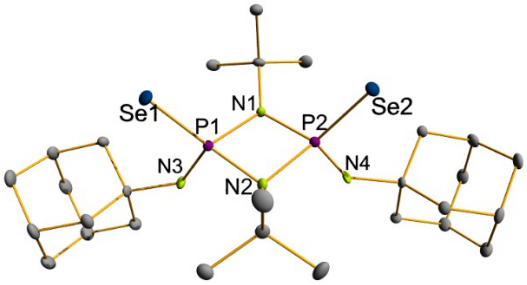


Figure S 55. ORTEP drawing of the molecular structure of **5** *in the crystal. Thermal ellipsoids with 50% probability at 103K. Hydrogen atoms and solvent toluene molecules are omitted for clarity. Selected Bond Lengths (Å): P1-Se1 2.0841(6), P2-Se2 2.0817(6), P1-N1 1.7004(17), P1-N2 1.6926(18), P2-N1 1.7003(18), P2-N2 1.6966(17), P1-N3 1.6384(18), P2-N4 1.6334(19); Selected Bond Angles (˚): N1-P1-N2 82.87(8), N1-P2-N2 82.75(8), P1-N1-P2 96.44(9), P1-N2-P2 96.88(9), N2-P1-N3 108.41(9), N2-P2-N4 108.22(9), N1-P1-Se1 118.84(7), N3-P1-Se1 113.96(7), N2-P2-Se2 120.65(7), N4-P2-Se2 113.09(7).*

Empirical Formula	$C_{28}H_{50}N_4P_2Se_2$	Volume (Å^3)	2960.58(17)
Formula Weight	662.58 g/mol	Z	4
Temperature (K)	103(2)	Calculated Density (g/cm^3)	1.487
Wavelength (Å)	0.71073	μ, Abs. coeff. C(mm^{-1})	2.631
Crystal System	Monoclinic	F(000)	1376
Space Group	P 1 21/n 1	Crystal Size (mm)	0.040 x 0.120 x 0.320
Unit Cell Dimension, cell		2θ range (˚)	1.44 to 31.11
length (Å)	a = 16.0802(6)	Reflections collected	40803
	b = 7.0317(2)	Indep. Refl. (R_{int})	9501 [R(int) = 0.0718]
	c = 26.2586(9)	Larg. Diff. Peak and hole (eÅ^{-3})	00562 and -0.471
angles (˚)	α = 90	R1, wR2 (I>2σ(I))	0.0388, 0.0706
	β = 94.340(2)	R1, wR2 (all data)	0.0701, 0.0790
	γ = 90		

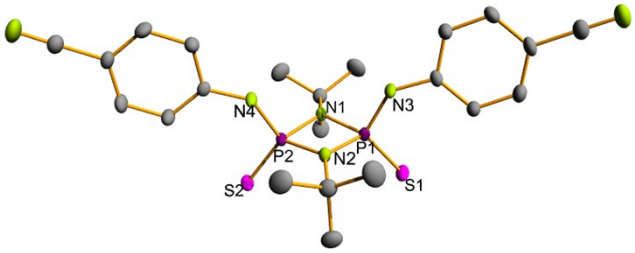


Figure S 56. ORTEP drawing of the molecular structure of **6** *in the crystal. Thermal ellipsoids with 50% probability at 153K. Hydrogen atoms, ammonium chloride and THF solvate molecules are omitted for clarity. Selected Bond Lengths (Å): P1-S1 1.9257(7), P2-S2 1.9193(7), P1-N1 1.6838(16), P1-N2 1.6843(17), P2-N1 1.6936(17), P2-N2 1.6855(17), P1-N3 1.6436(17), P2-N4 1.6460(17); Selected Bond Angles (°): N1-P1-N2 83.57(8), N1-P2-N2 83.24(8), P1-N1-P2 95.98(9), P1-N2-P2 96.26(9), N3-P1-N1 106.29(8), N3-P1-N2 108.53(9), N4-P2-N1 107.29(9), N4-P2-N2 107.19(9), N1-P1-S1 120.01(7), N2-P1-S1 120.05(6), N2-P2-S2 120.00(6), N1-P2-S2 120.06(6), N3-P1-S1 114.18(7), N4-P2-S2 114.63(6).*

Empirical Formula	$C_{32}H_{52}ClN_7OP_2S_2$	Volume (Å^3)	1903.1(2)
Formula Weight	712.31 g/mol	Z	2
Temperature (K)	153(2)	Calculated Density (g/cm^3)	1.243
Wavelength (Å)	0.71073	μ, Abs. coeff. C(mm^{-1})	0.329
Crystal System	Triclinic	F(000)	760
Space Group	P -1	Crystal Size (mm)	0.120 x 0.160 x 0.320
Unit Cell Dimension, cell		2θ range (°)	1.93 to 28.07
length (Å)	a = 9.1079(7)	Reflections collected	31949
	b = 11.4296(8)	Indep. Refl. (R_{int})	9229 [R(int) = 0.0585]
	c = 19.8336(15)	Larg. Diff. Peak and hole (eÅ^{-3})	0.371 and -0.441
angles (°)	α = 75.8067(18)	R1, wR2 (I>2σ(I))	0.0452, 0.1063
	β = 87.554(2)	R1, wR2 (all data)	0.0684, 0.1191
	γ = 72.0615(19)		

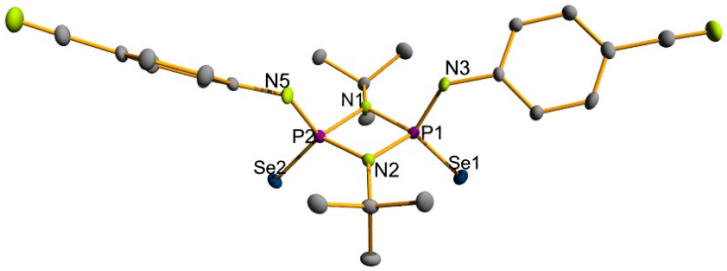


Figure S 57. ORTEP drawing of the molecular structure of **7** *in the crystal. Thermal ellipsoids with 50% probability at 100K. Hydrogen atoms and MeOH solvate molecules are omitted for clarity. Selected Bond Lengths (Å): P1-Se1 2.0741(11), P2-Se2 2.0788(10), P1-N1 1.677(3), P1-N2 1.688(3), P2-N1 1.690(3), P2-N2 1.684(3), P1-N3 1.660(3), P2-N5 1.652(3); Selected Bond Angles (°): N1-P1-N2 83.69(16), N1-P2-N2 83.45(17), P1-N1-P2 96.32(16), P1-N2-P2 96.15(17), N1-P1-N3 105.19(17), N2-P2-N5 104.41(17), N1-P1-Se1 121.55(12), N2-P2-Se2 122.41(12).*

Empirical Formula	$C_{24}H_{36}N_6O_2P_2Se_2$	Volume (Å^3)	2968.89(14)
Formula Weight	660.45 g/mol	Z	4
Temperature (K)	100(2)	Calculated Density (g/cm^3)	1.478
Wavelength (Å)	0.71073	μ, Abs. coeff. C(mm^{-1})	2.630
Crystal System	Orthorhombic	F(000)	1344
Space Group	P c a 21	Crystal Size (mm)	0.080 x 0.240 x 0.320
Unit Cell Dimension, cell		2θ range (°)	2.38 to 30.50
length (Å)	a = 21.6603(6)	Reflections collected	23446
	b = 9.7970(3)	Indep. Refl. (R_{int})	7914 [R(int) = 0.0585]
	c = 13.9906(3)	Larg. Diff. Peak and hole (eÅ^{-3})	0.550 and -0.620
angles (°)	α = 90	R1, wR2 (I>2σ(I))	0.0367, 0.0619
	β = 90	R1, wR2 (all data)	0.0599, 0.0693
	γ = 90		

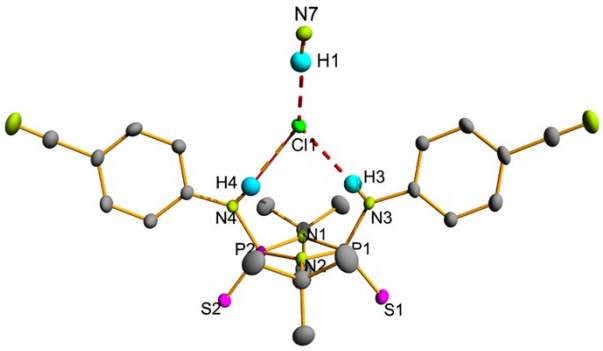


*Figure S 58. Interaction of chloride ion with the exocyclic NH protons and the proton of triethylammonium cation in the crystal structure of compound **6**. Only proton H1, H3 and H4 are shown for illustration of interaction. Ethyl groups of triethylammonium cation, hydrogen atoms and THF solvate molecules are omitted for clarity.*

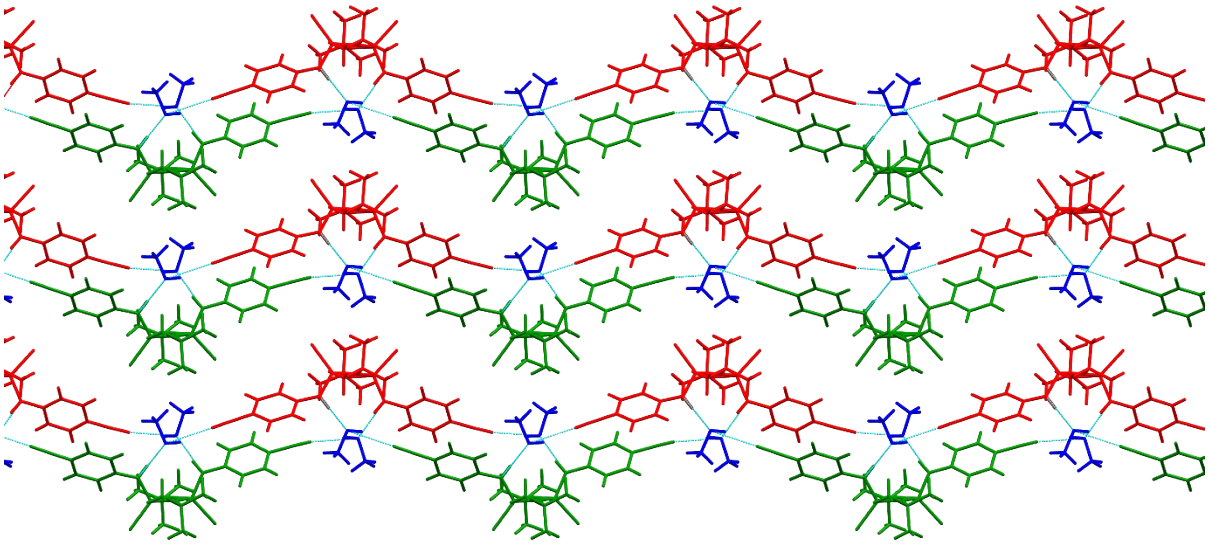


Figure S 59. Packing pattern of **7** with methanol solvate molecules

The methanol solvate molecules are represented in blue, while the molecules of compound **7** are in green and red, representing two independent liner chains. These two chains are packed in zig-zag manner and in opposite direction. Each pair of zig-zag chains then in turn form one layer and chain propagation is along the crystallographic c-axis. The hydrogen bonds between the molecules are shown in light blue dotted lines.

8. Solubility Studies

Cyclophosphazane-based compounds are known to be incompatible to protic solvents, particularly water. Upon oxidation of the phosphorus centers, the stability of these compounds can be enhanced. However, there is no publication with detailed studies on the air- and hydrolytic stability of such cyclophosph(V)azanes prior to our results published previously.[7]

In our earlier work, we have focused our studies on the series of oxidized derivatives bearing the same organic substituent i.e. *p*-OC_6H_4CN. While in this work, we have broadened the family of cyclophosph(V)azanes by including a few selected organic substituents. They are adamantanol (HOAd), adamantylamine (NH_2Ad) and 4-aminobenzonitrile (*p*-$NH_2C_6H_4CN$). Therefore, it is essential for us to refine our protocol so to standardize the solvent system used for the stability studies of these compounds.

We have established a standard protocol prior to the detailed studies of moisture-stability of compounds **2-7**. First, we commenced by determining the solubility of these compounds *i.e.* subjecting all the six synthesized compounds to different solvent systems (such as Acetone:water, THF:water) in different ratio of the solvents and monitor the prepared samples overtime (2 days). This is evident from this study that some of the synthesized compounds precipitated out after leaving to stand for a period of time.(Table S1) These precipitates can be re-dissolved upon addition of organic solvent and the corresponding NMR spectrum recorded reveal only resonance signals consistent to that of the compounds.

Acetone:water			Cpds	THF:water					
1:0	2:1	1:5		1:0	5:1	2:1	1:1	1:2	1:5
√	√	X	**2**	√	√	√	√	√	X
√	X	X	**3**	√	√	√	√	X	X
√	X	X	**4**	√	√	√	√	√	X
√	X	X	**5**	√	√	√	√	√	X
√	X	X	**6**	√	√	√	√	X	X
√	√	X	**7**	√	√	√	X	X	X

*Table S1 Solubility of compound **2-7** in different ratio and different solvent system*

From the table, we have identified that the solvent system of THF:water 5:1 as the best ratio for hydrolytic studies across the six compounds. Coincidentally, this ratio is also employed in our previous study, therefore allowing fair comparison across different sets of oxidized cyclodiphosphazanes.[7] Hence, NMR samples of compounds **2**-**7** in the ratio of THF:water 5:1 are prepared again for the hydrolytic studies as described the earlier section.(ESI section 5)

9. Comparison between one-pot solution and one-pot mechanochemical method

We have performed a solution one-pot test reaction using toluene, which is commonly use as a solvent in cyclophosphazane *i.e.* toluene. The figure below shows a comparison of in situ ^{31}P-{^{1}H} NMR spectrum of reactions (top: one-pot mechanochemical method (6 hours); bottom: one-pot solution-based (overnight *i.e.* 14 hours)) carried out for the synthesis of compound **7**. It can be observed in the in situ ^{31}P-{^{1}H} NMR spectrum for the solution-based method that the major resonance is at approximately δ 21 ppm along with minor peak at δ 31.90 ppm, the latter being likely compound **7**'s signal. This indicated that the sole formation of one product only observed using mechanochemical methods.

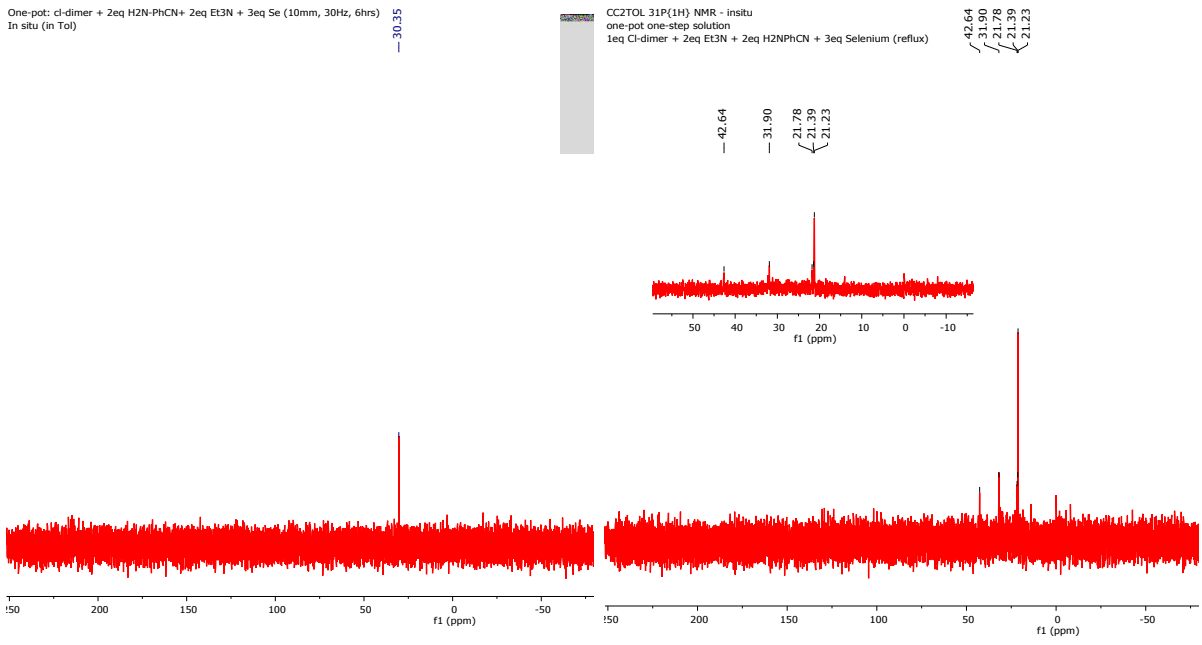


Figure S 60: Comparative between the one-pot mechanochemical route (left) and solution-based for the synthesis (right)

for compound **7**

10. References

(1) (a) Mechanochemistry is herein considered in the context of transformations conducted by bulk milling or grinding. This is an area of mechanochemical research that is distinct from also highly popular use of ultrasonic irradiation for transformations of mechanophores embedded in polymer chains, as well as studies of individual molecules using atomic force spectroscopy. (b) One-pot one-step reaction to generate oxide species is not possible due to the incompatibility of 1 with m-cpba (m-chloroperoxybenzoic acid) or pyridine-N-oxide which fume up immediately even in the argon-filled glovebox. While, other oxidizing agents such as t-butyl hydroperoxide, water and DMSO are not suitable due to the presence of water or the tendency of attaching moisture.

(2) R. Jefferson, J. F. Nixon, T. M. Painter, R. Keat and L. Stobbs*, J. Chem. Soc.*, *Dalton Trans*, 1973, 1414-1419.

(3) The term "**in situ** $^{31}P\{^{1}H\}$ NMR spectra" herein is considered as the $^{31}P\{^{1}H\}$ NMR spectra of crude reaction mixtures. Details of the preparation of these NMR samples: The grinding jars were brought into the inert argon-filled glovebox after the milling was completed. The crude (~0.5mg) of the reaction mixture was transferred into an NMR tube and dissolved into the corresponding deuterated solvent. The NMR spectrum was immediately recorded after bringing the NMR samples out of the glovebox.

(4) Satisfactory C, H and N analysis could not be obtained. This is a common problem in the analysis of phosph(III)azanes, see the following literatures. (a) Benson, C. G. M.; Vasilenko, V.; García-Rodríguez, R.; Bond, A. D.; González Calera, S.; Gade, L. H.; Wright, D. S. *Dalton Trans.*, 2015, **44**(32), 14242–14247. (b) Benson, C. G. M.; Plajer, A. J.; García-Rodríguez, R.; Bond, A. D.; Singh, S.; Gade, L. H.; Wright, D. S. *Chem. Commun.* 2016, **52** (62), 9683–9686.

(5) For compound **6**'s ^{1}H NMR: N-H protons are missing from the spectrum, this is likely attributed to its hydrogen-bonding to chloride ion.

(6) For compound **7**'s NMR: ^{1}H NMR: N-H protons are not detected, regardless of the use of deuterated solvents ($CDCl_3$, MeOD); NMR spectra were recorded again in attempt to obtain clearer NMR using MeOD after establishing that the compound is hydrolytic stable.

(7) Y. X. Shi, R. Z. Liang, K. A. Martin, N. Weston, S. Gonzalez-Calera, R. Ganguly, Y. Li, Y. Lu, A. J. M. Ribeiro, M. J. Ramos, P. A. Fernandes and F. García, *Inorg. Chem.*, 2015, **54**, 6423-6432.

(8) S. Gonzalez-Calera, D. J. Eisler, J. V. Morey, M. McPartlin, S. Singh and D. S. Wright, *Angew Chem. Int. Ed.*, 2008, **47**, 1111-1114.