Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Material for

Lewis base-free thiophosphonium ion: a cationic sulfur atom transfer reagent

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1 Experimental procedures

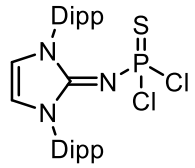
1.1 Synthetic Details

General remarks: All manipulations were performed under an inert atmosphere of dry argon, using standard Schlenk and drybox techniques. Dry and oxygen-free solvents were employed. All glassware was oven-dried at 150 °C prior to use. ^{1}H, ^{13}C, ^{19}F, ^{31}P, ^{77}Se, and ^{125}Te NMR spectra were recorded at 300 K on Agilent DD2 600, Bruker AVANCE I 400, Bruker AVANCE III 400 or Bruker AVANCE II 200 spectrometers. Chemical shifts are given in parts per million (ppm) relative to $SiMe_4$ (^{1}H, ^{13}C), CCl_3F (^{19}F), 85% H_3PO_4 (^{31}P), Me_2Se (^{77}Se), Me_2Te (90% in C_6D_6, ^{123}Te) and they were referenced to the residual solvent signals ($CDCl_3$: ^{1}H δ_H = 7.26, ^{13}C δ_C = 77.16; CD_2Cl_2: ^{1}H δ_H = 5.32, ^{13}C δ_C = 54.00; C_6D_6: ^{1}H δ_H = 7.16, ^{13}C δ_C = 128.06; CD_3CN: δ_H = 1.94, ^{13}C δ_C = 118.26) or internally by the instrument after locking and shimming to the deuterated solvent (^{19}F, ^{31}P, ^{77}Se, ^{125}Te). Chemical shifts (δ) are reported in ppm. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, p = pentet, sept = septet, m = multiplet, br = broad signal. Mass spectrometry was recorded using an Orbitrap LTQ XL (Thermo Scientific) spectrometer.

Safety remarks: The use of a burst shield is strongly recommended for all reactions that require heating of closed Schlenk flasks above the boiling point of the respective solvent!

Reagents and Handling: All compounds were purchased from commercial sources (Sigma Aldrich, Alfa Aesar, Tokyo Chemical Industry) and used as received, if not stated otherwise. The synthetic approach reported by Tamm was used to synthesize NIDippTMS (**1**).[1] The synthetic approach reported by Bergman was used to synthesize $NaBArF_{24}$.[2] The synthetic approach reported by Dielmann was used to synthesize [**5a**][$BArF_{24}$].[3] 2,6-Diisopropylaniline was obtained from Alfa Aesar (technical grade) and distilled. After distillation it still contained two isomeric impurities (2.1% and 0.6%, respectively, confirmed by GC-MS and ^{1}H NMR). These isomers are also found in the synthesized compounds bearing diisopropylphenyl substituents.

1.2 **Preparation of 2**



To a solution of **1** (5.51 mmol, 2.62 g, 1.00 eq.) in toluene (50 mL) $PSCl_3$ (16.5 mmol, 16.5 mL, 1 M in toluene, 3.00 eq.) was added at −78 °C. The reaction was warmed to room temperature and stirred for 16 h. The precipitate was filtered off and all volatiles were removed *in vacuo*. The product was obtained as a yellow solid.

Note: The filtered off precipitate contains the byproduct $[(R^1)_2PCl_2][Cl]$, which was also characterized (*vide infra*).

Yield: 73 % (4.03 mmol, 2.16 g).

^{1}H NMR (C_6D_6, 400 MHz, 300 K): δ (ppm) = 7.21 (t, $^3J_{HH}$ = 7.7 Hz, 4 H, *p*-Dipp), 7.09 (d, $^3J_{HH}$ = 7.7 Hz, 8 H, *m*-Dipp), 6.19 (s, 2 H, N-CH=CH-N), 2.94 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, Dipp-*i*Pr-C*H*), 1.45 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, Dipp-*i*Pr-CH_3), 1.06 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, Dipp-*i*Pr-CH_3).

^{13}C{^{1}H} NMR (C_6D_6, 101 MHz, 300 K): δ (ppm) = 146.9 (*o*-Dipp), 145.3 (d, $^2J_{CP}$ = 8 Hz, C2), 131.8 (*p*-Dipp), 131.1 (*i*-Dipp), 124.6 (*m*-Dipp), 117.9 (N-CH=CH-N), 29.3 (*i*Pr-*C*H), 25.4 (*i*Pr-*C*H_3), 23.4 (*i*Pr-*C*H_3).

^{31}P NMR (C_6D_6, 162 MHz, 300 K): δ (ppm) = 27.1.

HR MS(ESI): m/z calculated for $[C_{27}H_{37}Cl_2N_3PS]^+$ as $[M+H]^+$: 536.18174, found: 536.18206. Fitting isotope pattern: Yes.

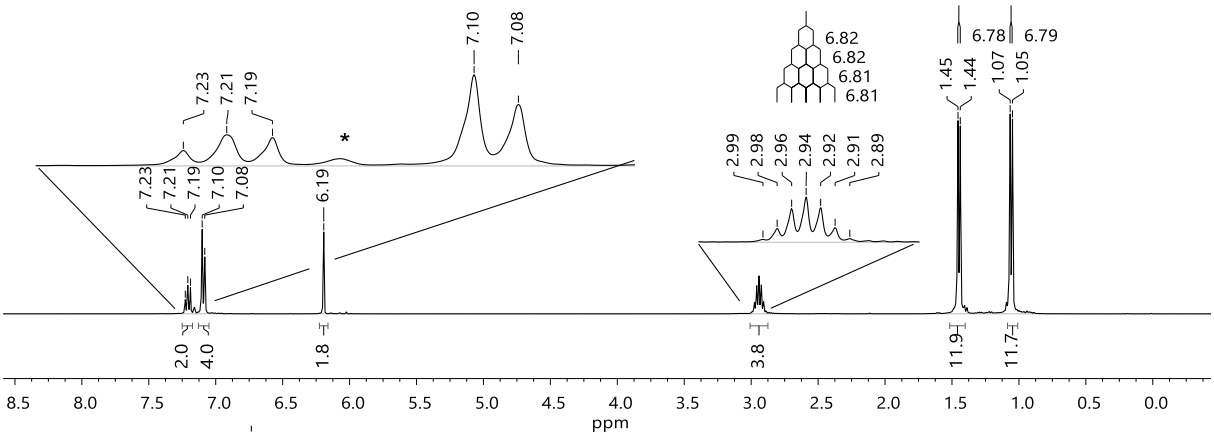


Figure S 1: ^{1}H NMR spectrum of **2** in C_6D_6. *solvent residue signal.

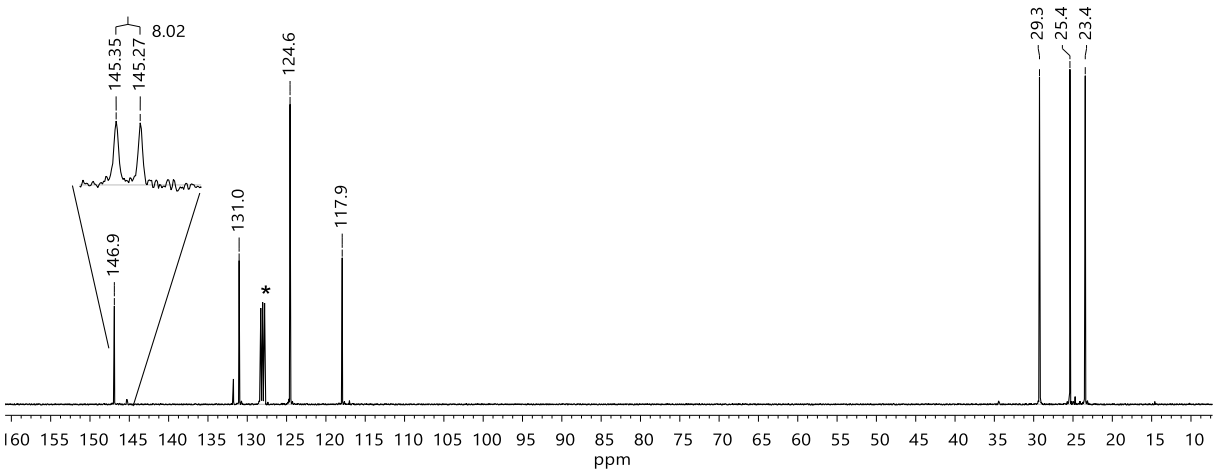


Figure S 2: $^{13}C\{^{1}H\}$ NMR spectrum of **2** in C_6D_6. *solvent residue signal.

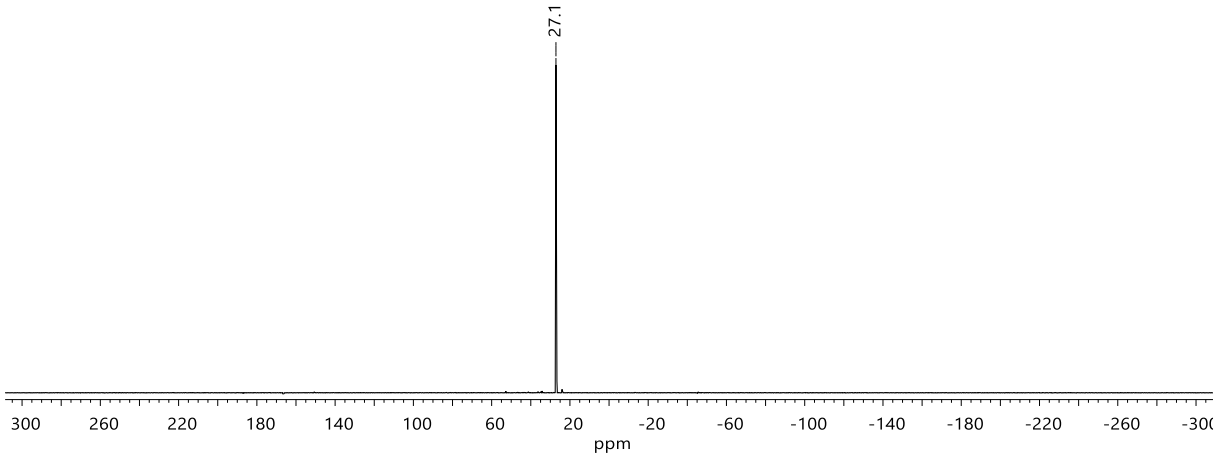
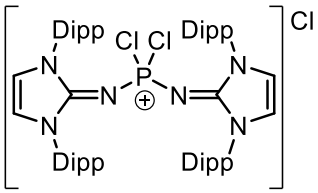


Figure S 3: ^{31}P NMR spectrum of **2** in C_6D_6.

2.1.1 Characterization of the byproduct $[(R^1)_2PCl_2][Cl]$



The compound forms as a byproduct in the synthesis of **2** (*vide supra*):

The precipitate from the synthesis of **2** was isolated and dried in vacuo. $[(R^1)_2PCl_2][Cl]$ was crystallized out of a concentrated THF/fluorobenzene solution. The mother liquor was pipetted off and the colourless crystals were dried *in vacuo*.

^{1}H NMR (CD_2Cl_2, 500 MHz, 300 K): δ (ppm) = 7.43 (t, $^3J_{HH}$ = 7.8 Hz, 4 H, *p*-Dipp), 7.20 (d, $^3J_{HH}$ = 7.8 Hz, 8 H, *m*-Dipp), 6.92 (s, 4 H, N-CH=CH-N), 2.29 (sept, $^3J_{HH}$ = 6.8 Hz, 8H, Dipp-*i*Pr-C*H*), 1.09 (d, $^3J_{HH}$ = 6.8 Hz, 24 H, Dipp-*i*Pr-CH_3), 1.00 (d, $^3J_{HH}$ = 6.8 Hz, 24 H, Dipp-*i*Pr-CH_3).

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 126 MHz, 300 K): δ (ppm) = 146.5 (*o*-Dipp), 143.8 (d, $^2J_{CP}$ = 14 Hz, N-C-N), 131.4 (*p*-Dipp), 130.7 (*i*-Dipp), 124.8 (*m*-Dipp), 119.6 (N-CH=CH-N), 29.3 (*i*Pr-*C*H), 25.8 (*i*Pr-*C*H_3), 23.0 (*i*Pr-*C*H_3).

^{31}P NMR (CD_2Cl_2, 162 MHz, 300 K): δ (ppm) = −44.19.

Single crystal X-ray diffraction: The compound was crystallized out of a concentrated THF/fluorobenzene solution of the crude product. A molecular structure was obtained (*vide infra*).

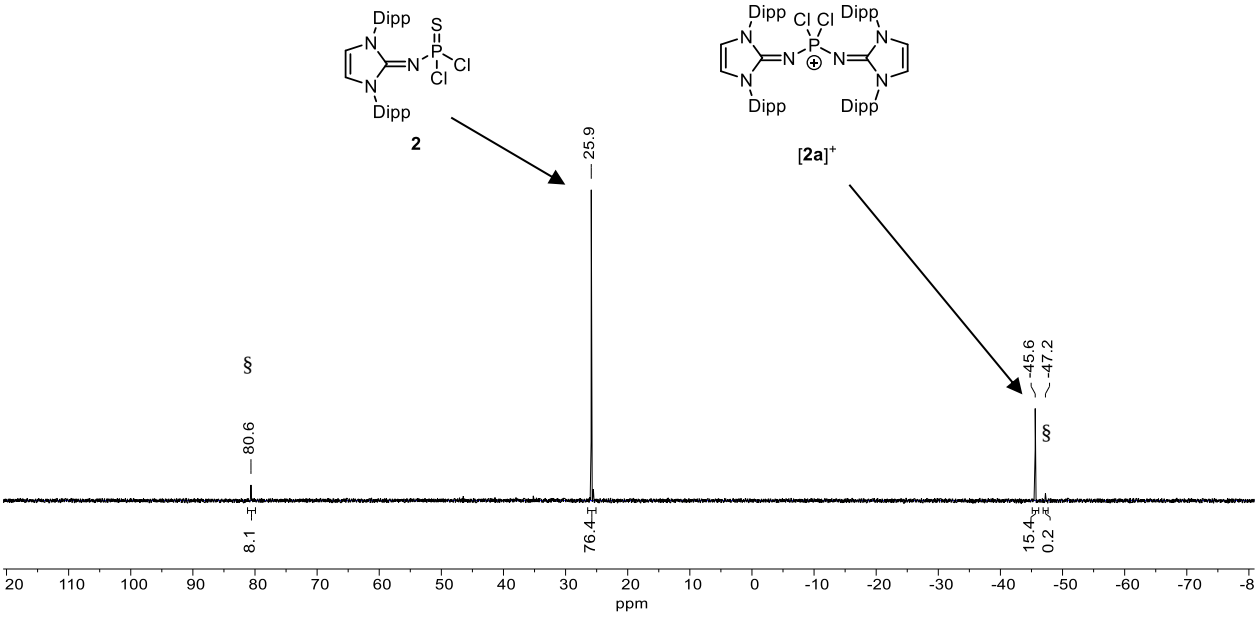


Figure S 4: $^{31}P\{^1H\}$ NMR spectrum of the dried reaction mixture (before filtering off the precipitate) in CD_3CN. The section signs (§) mark unidentified byproducts.

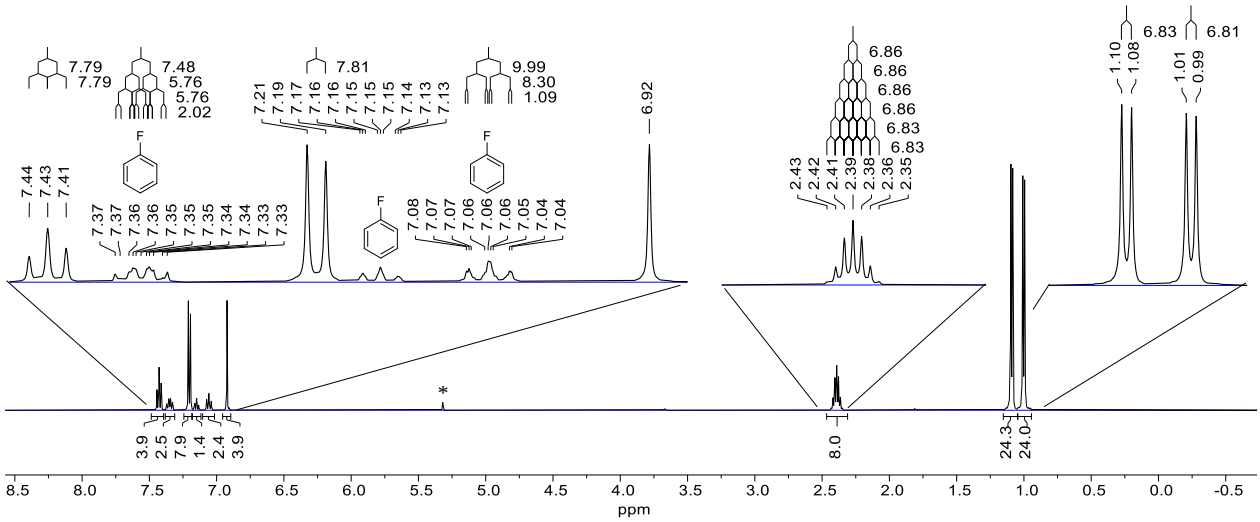


Figure S 5: ^{1}H NMR spectrum of $[(R^1)_2PCl_2][Cl]$ in CD_2Cl_2. *solvent residue signal.

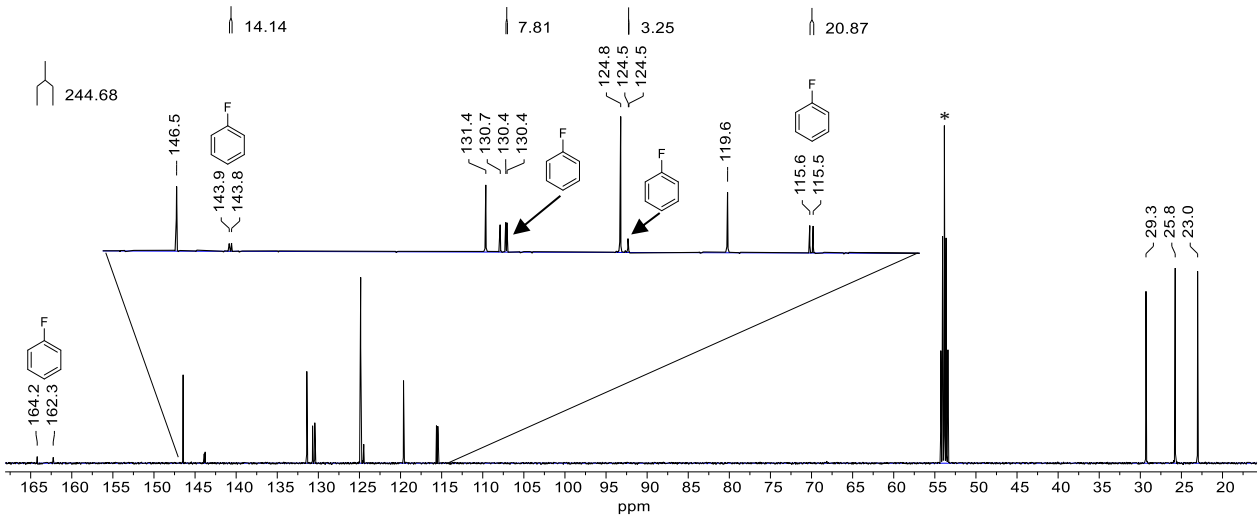


Figure S 6: $^{31}C\{^{1}H\}$ NMR spectrum of $[(R^1)_2PCl_2][Cl]$ in CD_2Cl_2.

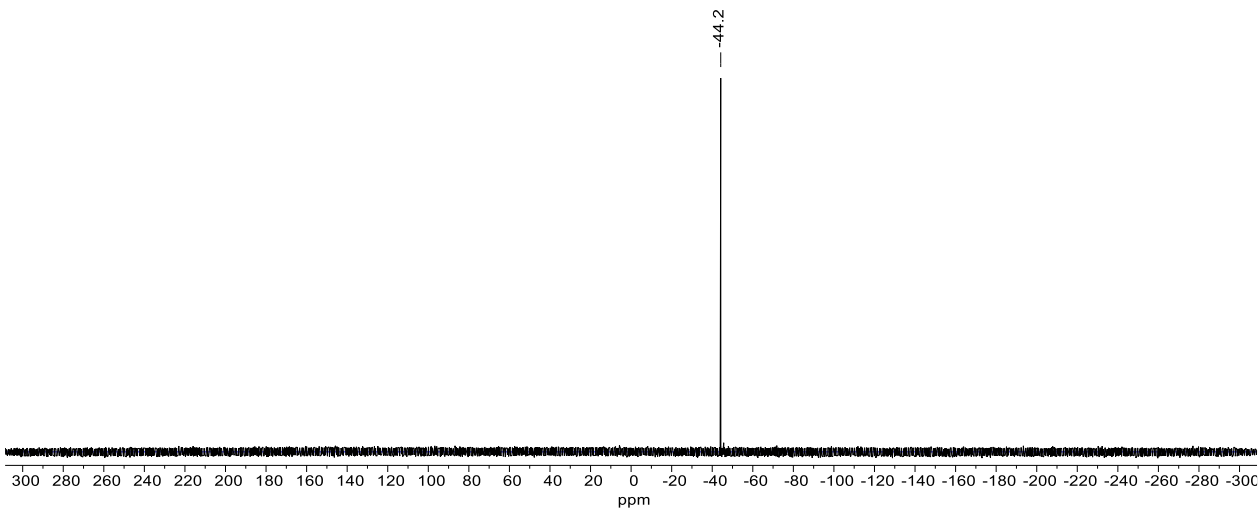
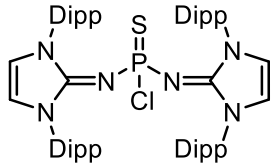


Figure S 7: $^{31}P\{^{1}H\}$ NMR spectrum of $[(R^1)_2PCl_2][Cl]$ in CD_2Cl_2.

1.3 **Preparation of 3**



1 (3.17 mmol, 1.51 g, 1.00 eq.) and **2** (3.17 mmol, 1.70 g, 1.00 eq.) were dissolved in toluene (30 mL). The solution was heated in a sealed Schlenk flask at 120 °C for 10 days. All volatiles were removed *in vacuo* and the product was obtained as a brown solid.

Yield: 97% (3.07 mmol, 2.77 g).

^{1}H NMR (C_6D_6, 400 MHz, 300 K): δ (ppm) = 7.23 (t, $^{3}J_{HH}$ = 7.7 Hz, 4 H, *p*-Dipp), 7.09 (d, $^{3}J_{HH}$ = 7.7 Hz, 8 H, *m*-Dipp), 6.03 (s, 4 H, N-CH=CH-N), 3.16 - 3.05 (m, 4 H, Dipp-*i*Pr-C*H*), 3.15 - 3.03 (m, 4 H, Dipp-*i*Pr-C*H*), 1.32 (d, $^{3}J_{HH}$ = 6.9 Hz, 24 H, Dipp-*i*Pr-CH_3), 1.10 (d, $^{3}J_{HH}$ = 6.9 Hz, 24 H, Dipp-*i*Pr-CH_3).

^{13}C{^{1}H} NMR (C_6D_6, 101 MHz, 300 K): δ (ppm) = 147.4 (*o*-Dipp), 147.3 (*o*-Dipp), 146.2 (d, $^{2}J_{CP}$ = 15 Hz, N-C-N), 134.0 (*p*-Dipp), 129.7 (*i*-Dipp), 124.0 (*m*-Dipp), 123.9 (*m*-Dipp), 116.9 (N-CH=CH-N), 29.0 (*i*Pr-*C*H), 29.0 (*i*Pr-*C*H), 25.5 (*i*Pr-*C*H_3), 25.5 (*i*Pr-*C*H_3), 23.9 (*i*Pr-*C*H_3), 23.8 (*i*Pr-*C*H_3).

^{31}P NMR (C_6D_6, 162 MHz, 300 K): δ (ppm) = 25.9.

Melting point: 252°C (decomposition).

Elemental analysis: calculated for $C_{54}H_{72}ClN_6PS$: C 71.77%, H 8.03%, N 9.30%. Found: C 72.10%, H 7.93%, N 9.08%.

Single crystal X-ray diffraction: Single crystals were obtained by cooling down a saturated solution of **3** in CH_2Cl_2 to −40 °C. A molecular structure was obtained (*vide infra*).

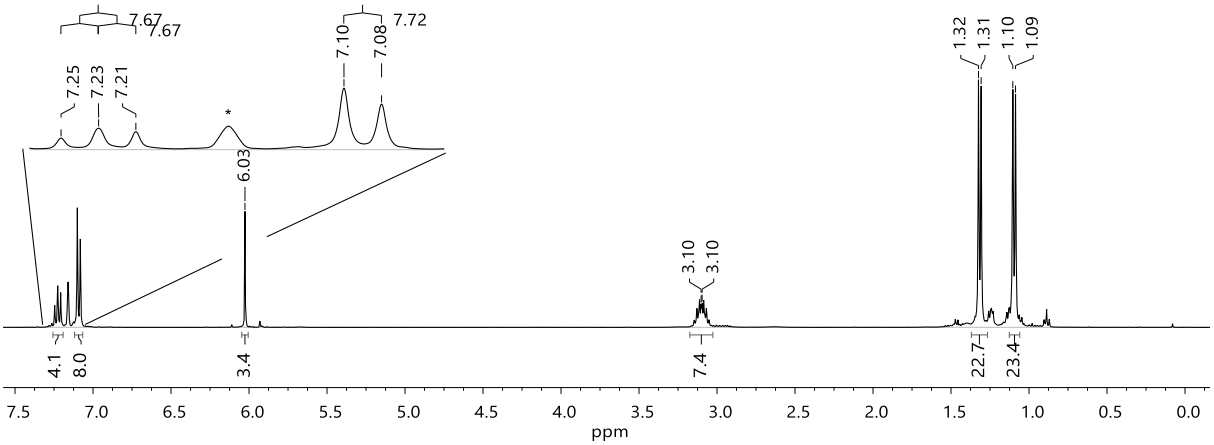


Figure S 8: ^{1}H NMR spectrum of **3** in C_6D_6. *solvent residue signal.

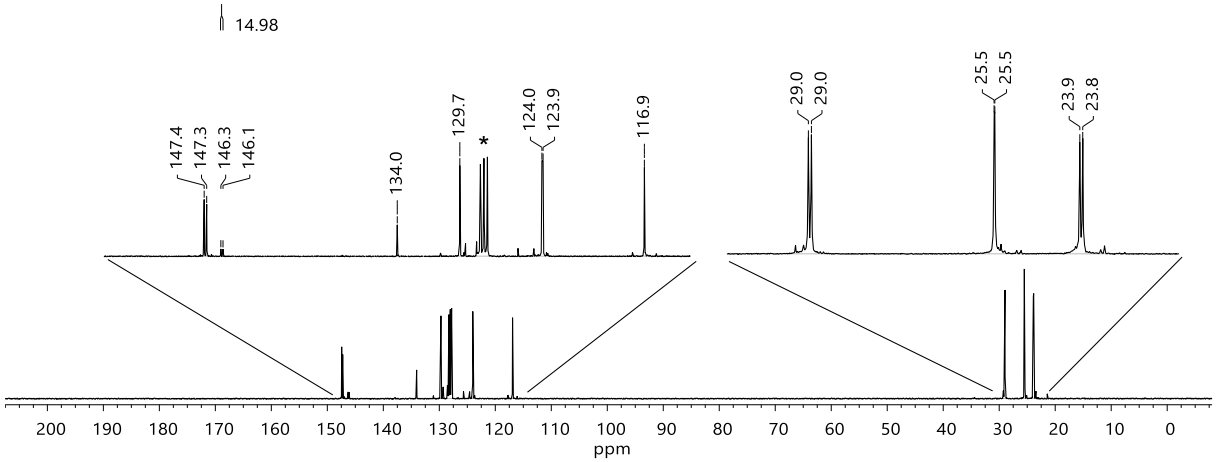


Figure S 9: $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6. *solvent residue signal.

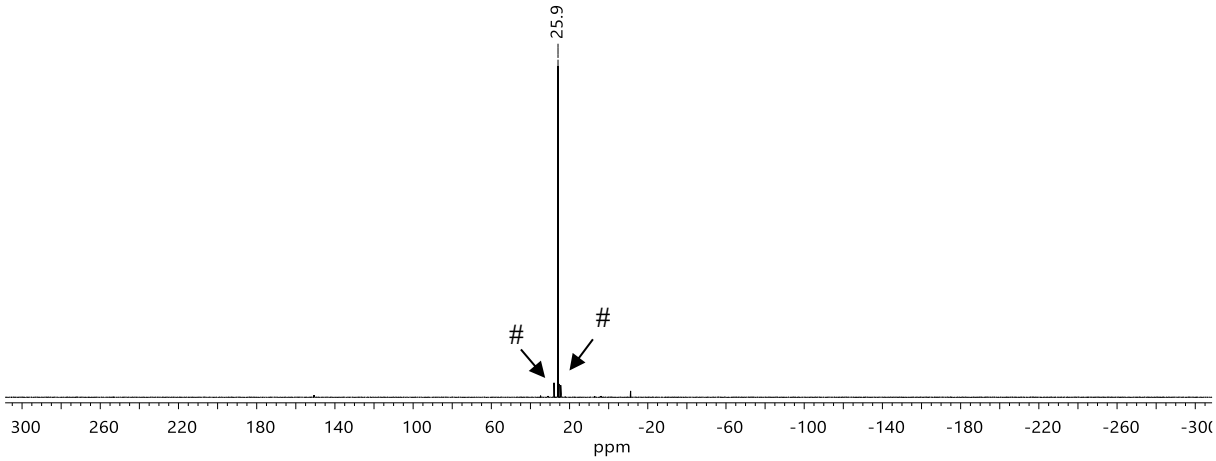
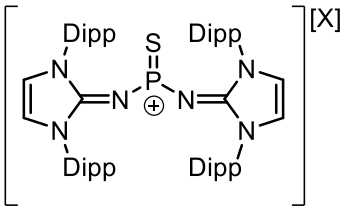


Figure S 10: ^{31}P NMR spectrum **3** in C_6D_6. The number signs (#) mark structural isomers within the Dipp-substituents (for more information see chapter 1.1).

1.4 **Preparation of [4][X] [(X = $BArF_{24}$ or OTf)**



3 (0.111 mmol, 100 mg, 1.00 eq.) was dissolved in CH_2Cl_2 and added to $NaBArF_{24}$ (0.111 mmol, 98 mg, 1.00 eq.) or AgOTf (0.111 mmol, 28 mg, 1.00 eq.). The reaction mixture was stirred at room temperature for 3 h. The precipitate was filtered off and all volatiles were removed *in vacuo*. The product was obtained as a beige solid for both anions.

Analytical data for [4][$BArF_{24}$]:

Yield: 91% (0.100 mmol, 174 mg).

^{1}H-NMR (CD_2Cl_2, 400 MHz, 300 K): δ (ppm) = 7.74 (m, 8 H, BAr^F_{24}; *ortho*), 7.57 (m, 4 H, BAr^F_{24}; *para*), 7.50 (t, $^3J_{HH}$ = 7.8 Hz, 4 H, *p*-Dipp), 7.18 (d, $^3J_{HH}$ = 7.8 Hz, 8 H, *m*-Dipp), 6.90 (s, 4 H, N-CH=CH-N), 2.38 (sept, $^3J_{HH}$ = 6.9 Hz, 8 H, Dipp-*i*Pr-C*H*), 1.09 (d, $^3J_{HH}$ = 6.9 Hz, 24 H, Dipp-*i*Pr-CH_3), 0.92 (d, $^3J_{HH}$ = 6.9 Hz, 24 H, Dipp-*i*Pr-CH_3).

^{13}C{^{1}H}-NMR (CD_2Cl_2, 101 MHz, 300 K): δ (ppm) = 162.2 (q, $^1J_{CB}$ = 50 Hz, BAr^F_{24}; ipso), 146.4 (*o*-Dipp), 146.4 (d, $^2J_{CP}$ = 13 Hz, N-C-N), 135.3 (BAr^F_{24}; *ortho*), 131.7 (*p*-Dipp), 129.9 (*i*-Dipp), 129.3 (qq, $^2J_{CF}$ = 31 Hz, $^4J_{CF}$ = 3 Hz, BAr^F_{24}; *meta*), 126.4 (q, $^1J_{CF}$ = 273 Hz, BAr^F_{24}; CF_3), 125.2 (*m*-Dipp), 119.6 (N-CH=CH-N), 117.9 (sept, $^3J_{CF}$ = 4 Hz, BAr^F_{24}; *para*), 29.3 (*i*Pr-*C*H), 25.3 (*i*Pr-*C*H_3), 23.35 (*i*Pr-*C*H_3).

^{11}B-NMR (CD_2Cl_2, 128 MHz, 300 K): δ (ppm) = −6.6.

^{19}F-NMR (CD_2Cl_2, 376 MHz, 300 K): δ (ppm) = −62.8.

^{31}P-NMR (CD_2Cl_2, 162 MHz, 300 K): δ (ppm) = 116.6.

HR-MS(ESI): m/z calculated for $[C_{54}H_{72}N_6PS]^+$ as $[M]^+$: 867.52713, found: 867.52751. Fitting isotope pattern: Yes.

Melting point: 230°C (decomposition).

Elemental analysis: calculated for $C_{86}H_{84}BF_{24}N_6PS$: C 59.66%, H 4.85%, N 4.89%. Found: C 59.11%, H 4.90%, N 4.86%.

Single crystal X-ray diffraction: Single crystals were obtained by cooling down a saturated solution of [**4**][$BArF_{24}$] in CH_2Cl_2 to −40 °C. A molecular structure was obtained.

Analytical data for [4][OTf]:

^{31}P-NMR (CD_3CN, 162 MHz, 300 K): δ (ppm) = 116.6.

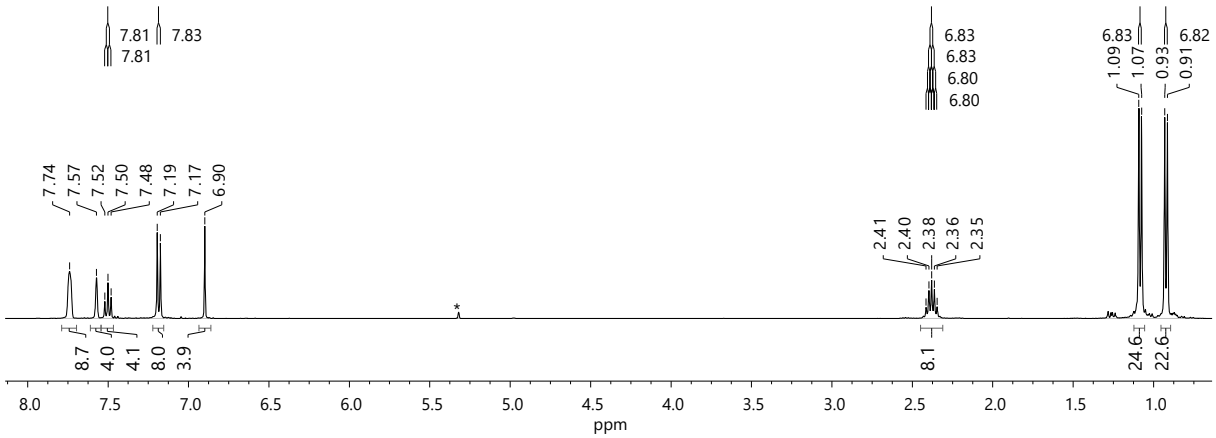


Figure S 11: ^{1}H NMR spectrum of [**4**][$BArF_{24}$] in CD_2Cl_2. *solvent residue signal.

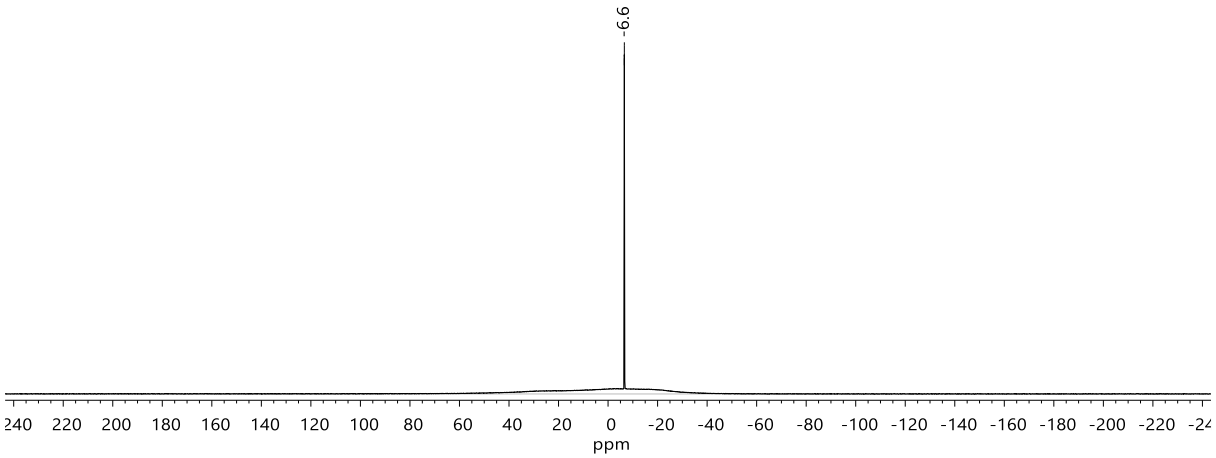


Figure S 12: ^{11}B NMR spectrum of [**4**][$BArF_{24}$] in CD_2Cl_2.

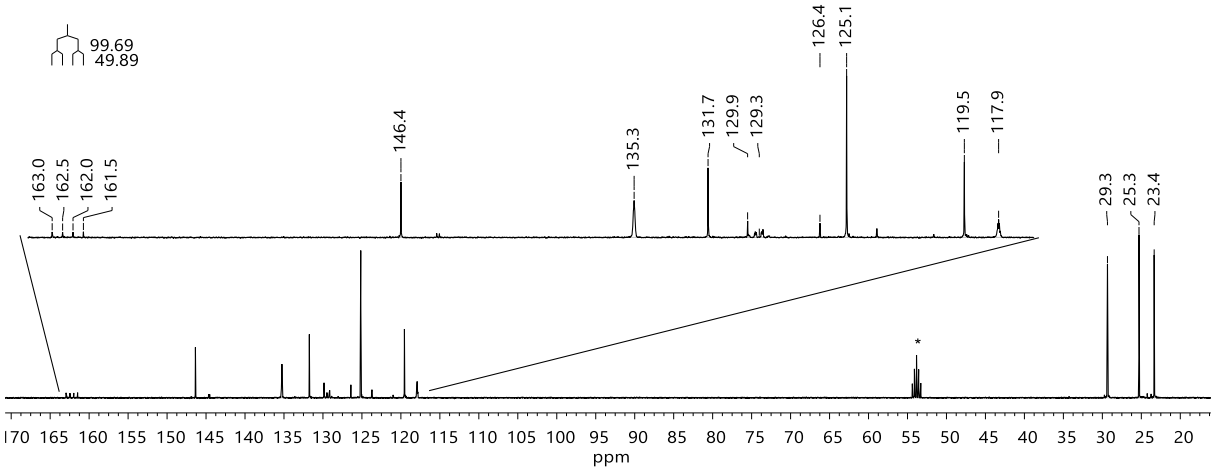


Figure S 13: ^{13}C{^{1}H} NMR spectrum of [**4**][$BArF_{24}$] in CD_2Cl_2. *solvent residue signal.

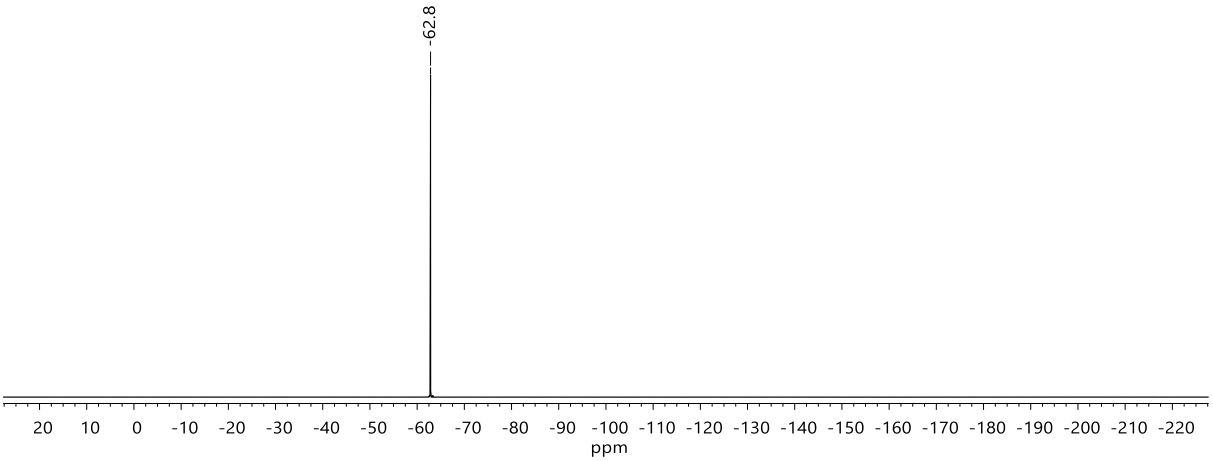


Figure S 14: ^{19}F NMR spectrum of [**4**][$BArF_{24}$] in CD_2Cl_2.

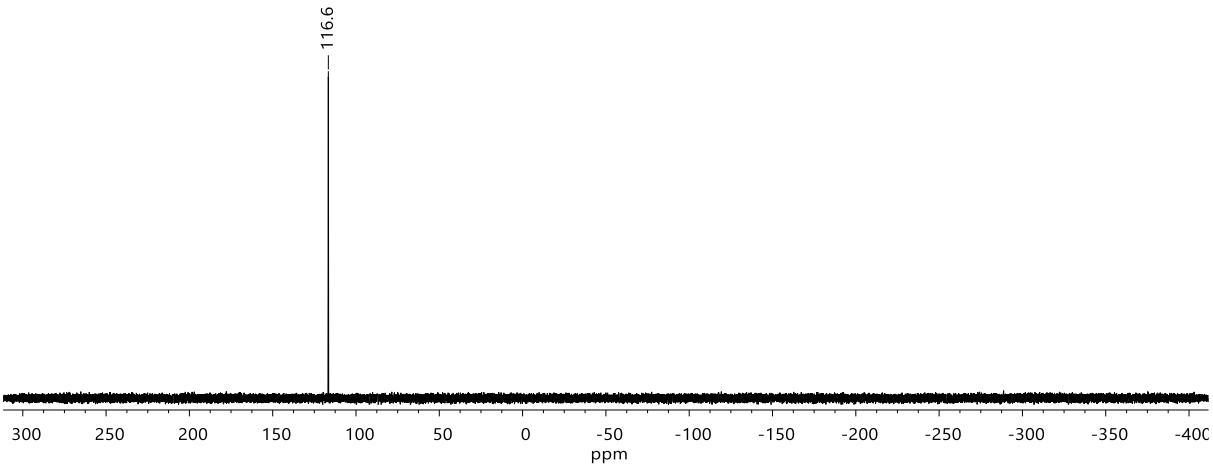


Figure S 15: ^{31}P NMR spectrum of [**4**][$BArF_{24}$] in CD_2Cl_2.

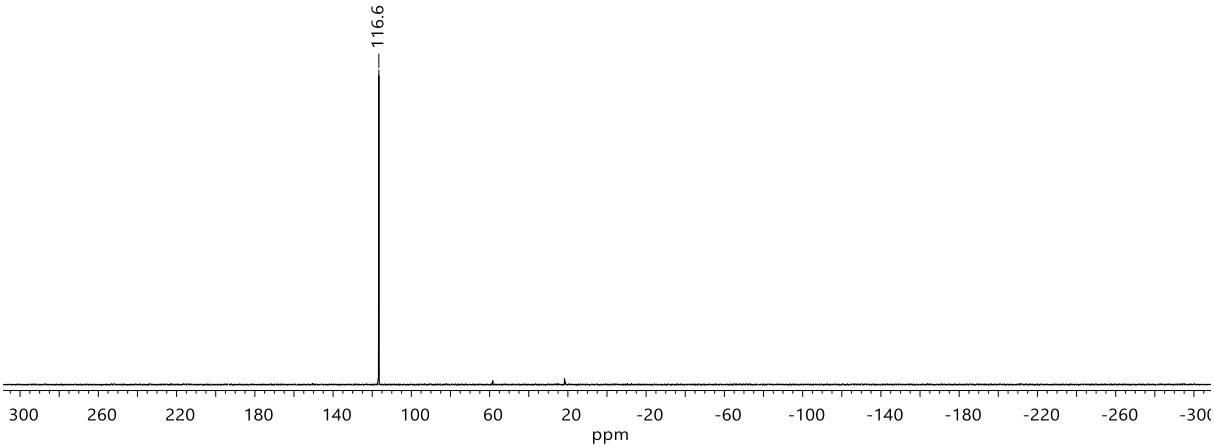
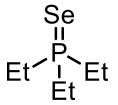


Figure S 16: ^{31}P NMR spectrum of [**4**][OTf] in CD_3CN.

1.5 **Preparation of $PSeEt_3$**



The synthesis was performed according to a modified literature procedure.[4]

Gray selenium (300 mg, 3.80 mmol, 1.00 eq.) and toluene (10 mL) were added to a Schlenk flask. The suspension was cooled to −78 °C and PEt_3 (560 µL, 3.80 mmol, 1.00 eq.) was added dropwise while stirring. The mixture was allowed to warm up to room temperature and stirred at 120 °C for 16 h. Afterwards, all volatiles were removed *in vacuo*. The obtained white solid was dissolved in 3 mL toluene and stored at –40 °C to afford colorless needles of $PSeEt_3$. The mother liquor was pipetted off and the crystals were dried *in vacuo*.

Yield: 78% (2.96 mmol, 584 mg).

^{1}H NMR (C_6D_6, 400 MHz, 300 K): δ (ppm) = 1.32 (dq, $^2J_{PH}$ = 11.3 Hz, $^3J_{HH}$ = 7.6 Hz, 6 H, CH_2), 0.85 (dt, $^3J_{PH}$ = 11.3 Hz, $^3J_{HH}$ = 7.6 Hz, 9 H, CH_3).

^{13}C{^{1}H} NMR (C_6D_6, 101 MHz, 300 K): δ (ppm) = 23.1 (d, $^1J_{PC}$ = 45 Hz, CH_2), 7.3 (d, $^2J_{PC}$ = 4 Hz, CH_3).

^{31}P NMR (C_6D_6, 162 MHz, 300 K): δ (ppm) = 43.2 (m).

^{31}P{^{1}H} NMR (C_6D_6, 162 MHz, 300 K): δ (ppm) = 43.2 ($^1J_{PSe}$ = 716 Hz, $^1J_{PC}$ = 45 Hz).

^{77}Se{^{1}H} NMR (C_6D_6, 76 MHz, 300 K): −426.0 (d, $^1J_{PSe}$ = 713 Hz).

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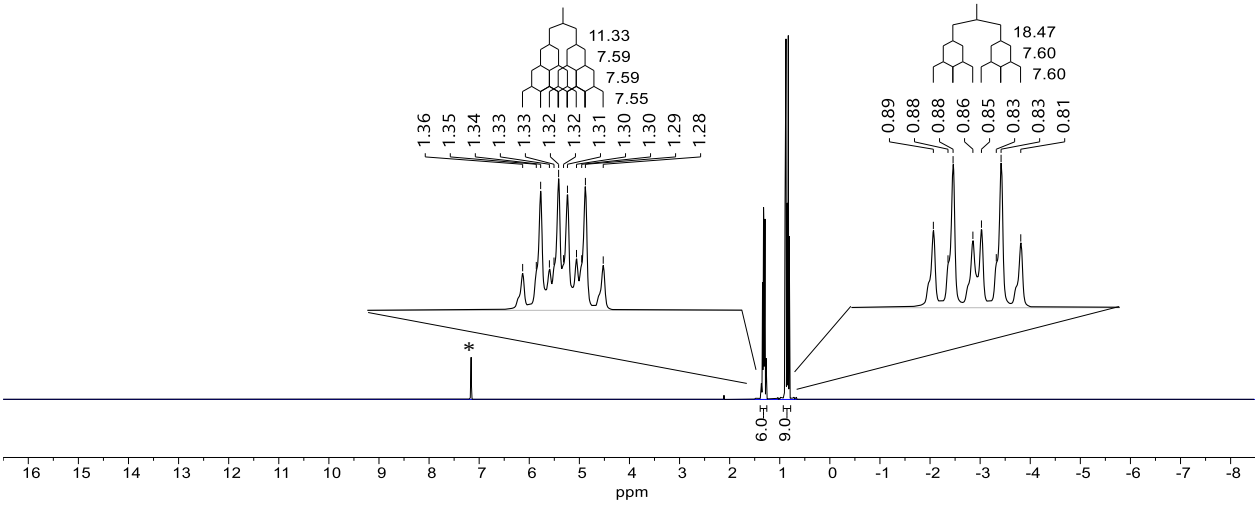


Figure S 17: ^{1}H NMR spectrum of $PSeEt_3$ in C_6D_6. *solvent residue signal.

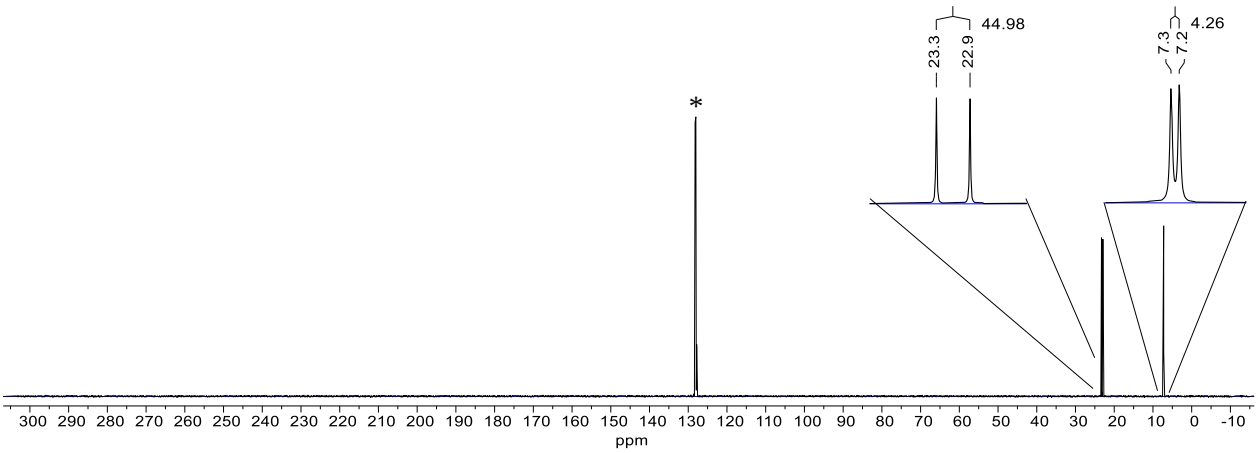


Figure S 18: $^{13}C\{^{1}H\}$ NMR spectrum of $PSeEt_3$ in C_6D_6. *solvent residue signal.

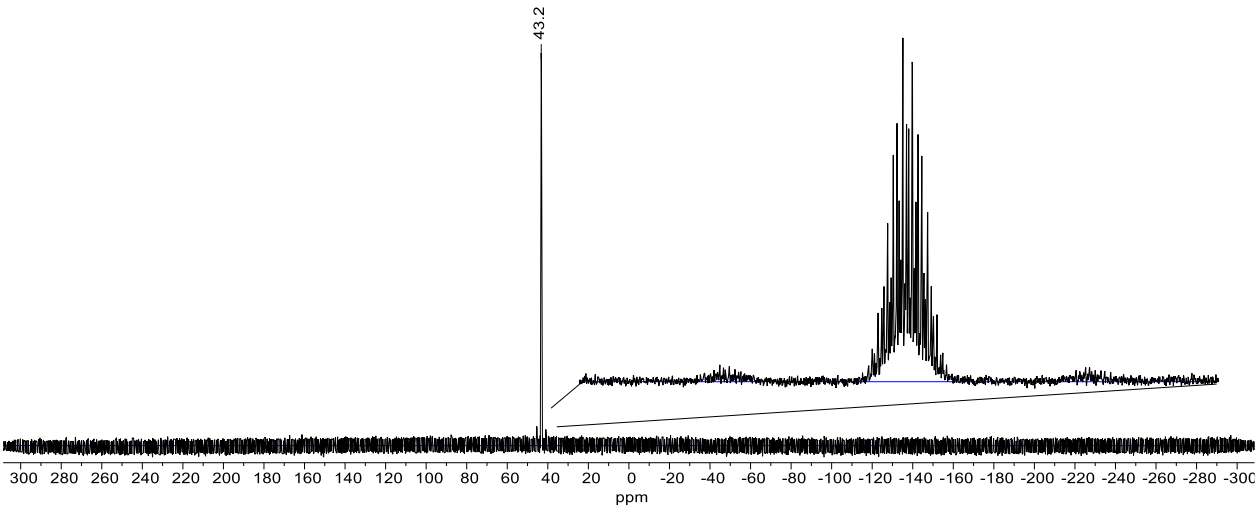


Figure S 19: ^{31}P NMR spectrum of $PSeEt_3$ in C_6D_6.

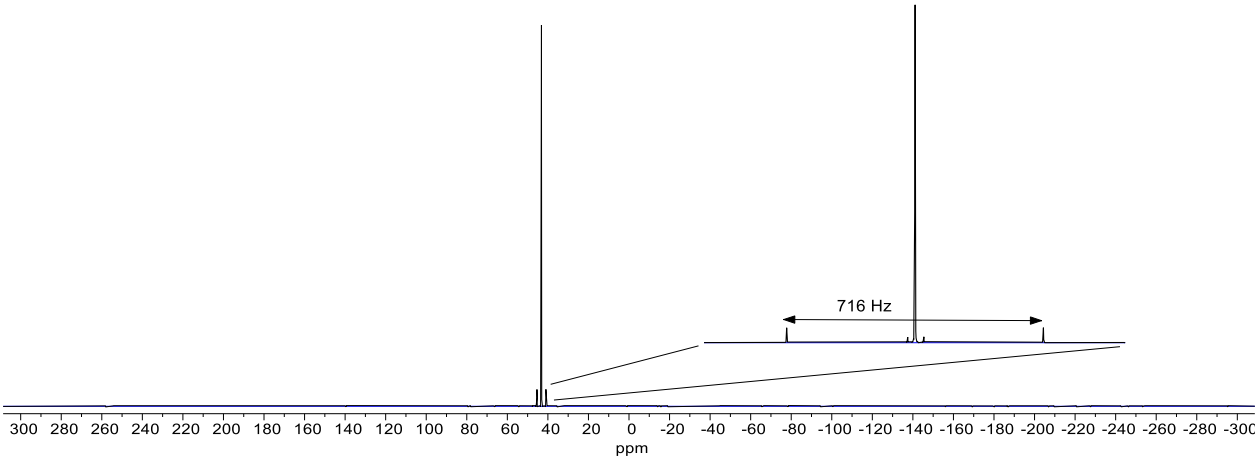


Figure S 20: $^{31}P\{^{1}H\}$ NMR spectrum of $PSeEt_3$ in C_6D_6.

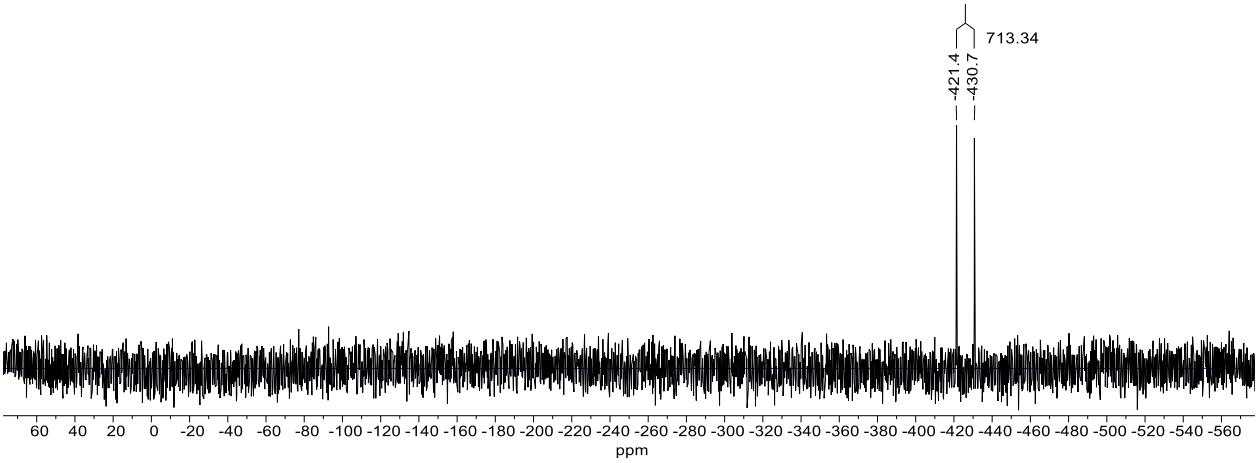
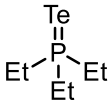


Figure S 21: $^{77}Se\{^{1}H\}$ NMR spectrum of $PSeEt_3$ in C_6D_6.

1.6 **Preparation of $PTeEt_3$**



The synthesis was performed according to a modified literature procedure.[4]

Gray tellurium (500 mg, 3.92 mmol, 1.00 eq.) and toluene (10 mL) were added to a Schlenk flask. The suspension was cooled to −78 °C and PEt_3 (577 µL, 3.92 mmol, 1.00 eq.) was added dropwise while stirring. The mixture was allowed to warm up to room temperature and stirred at 120 °C for 16 h. Afterwards, all volatiles were removed *in vacuo*. The resulting yellow solid was dissolved in 3 mL toluene. The solution was filtrated and stored at –40 °C to give $PTeEt_3$ as yellow needles. The mother liquor was pipetted off and the crystals were dried *in vacuo*.

Yield: 52% (2.05 mmol, 505 mg).

^{1}H-NMR (C_6D_6, 400 MHz, 300 K): δ (ppm) = 1.38 (dq, $^2J_{PH}$ = 11.5 Hz, $^3J_{HH}$ = 7.6 Hz, 6 H, CH_2), 0.76 (dt, $^3J_{PH}$ = 19.1 Hz, $^3J_{HH}$ = 7.6 Hz, 9 H, CH_3).

^{13}C{^{1}H}-NMR (C_6D_6, 101 MHz, 300 K):): δ (ppm) = 23.3 (d, $^1J_{PC}$ = 37 Hz, CH_2), 8.8 (d, $^2J_{PC}$ = 4 Hz, CH_3).

^{31}P NMR (C_6D_6, 162 MHz, 300 K): δ (ppm) = −2.5 (br).

^{125}Te NMR (C_6D_6, 126 MHz, 300 K): δ (ppm) = −870.1 (d, $^1J_{PTe}$ = 1747 Hz).

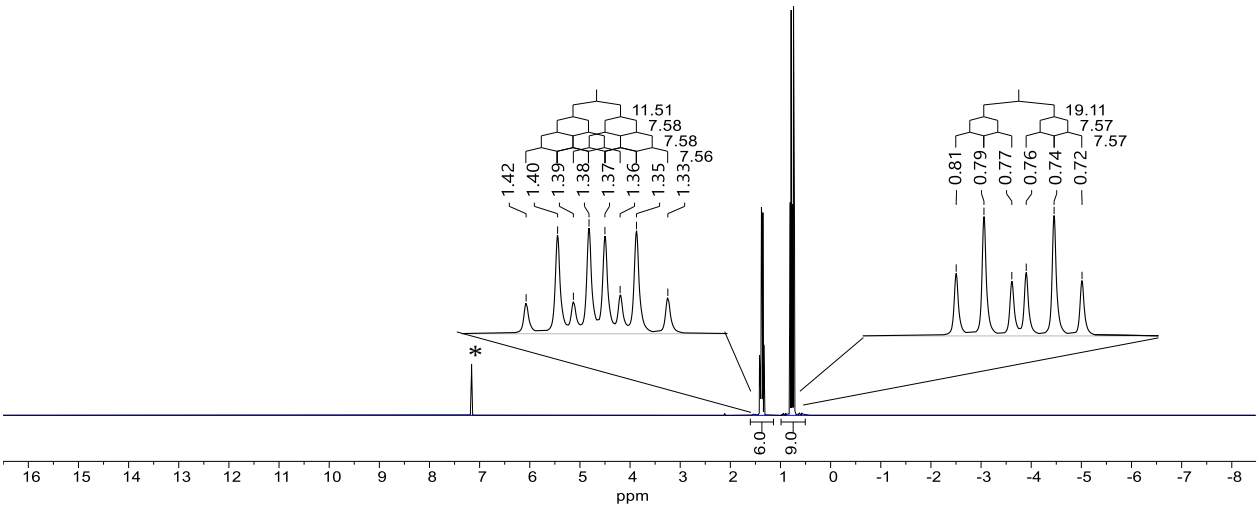


Figure S 22: ^{1}H NMR spectrum of $PTeEt_3$ in C_6D_6. *solvent residue signal.

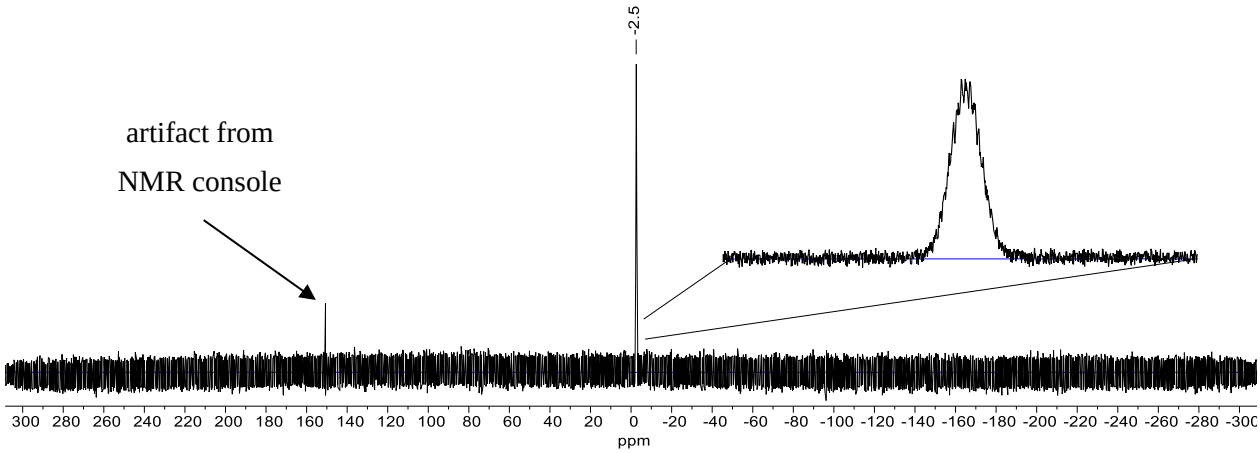


Figure S 23: ^{31}P NMR spectrum of $PTeEt_3$ in C_6D_6.

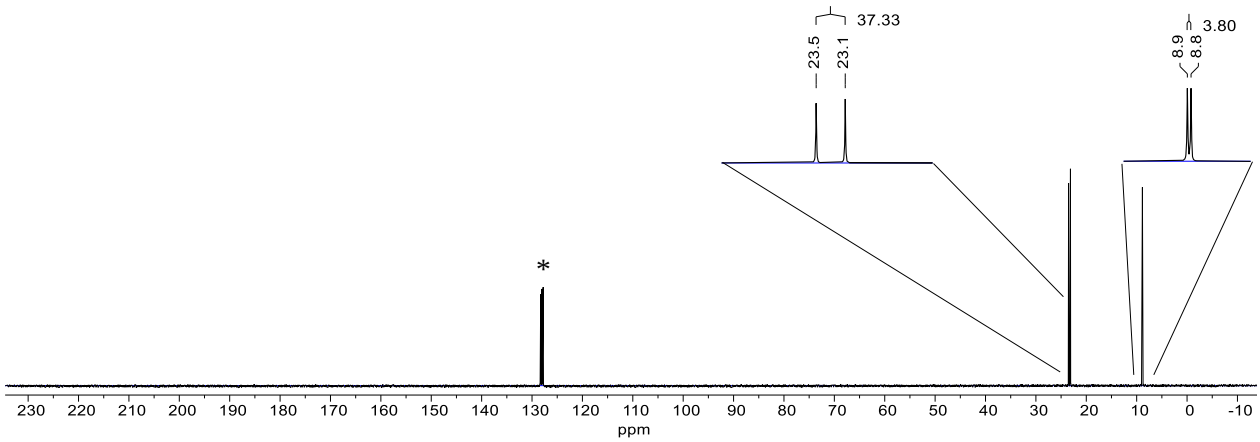


Figure S 24: $^{13}C\{^1H\}$ NMR spectrum of $PTeEt_3$ in C_6D_6. *solvent residue signal.

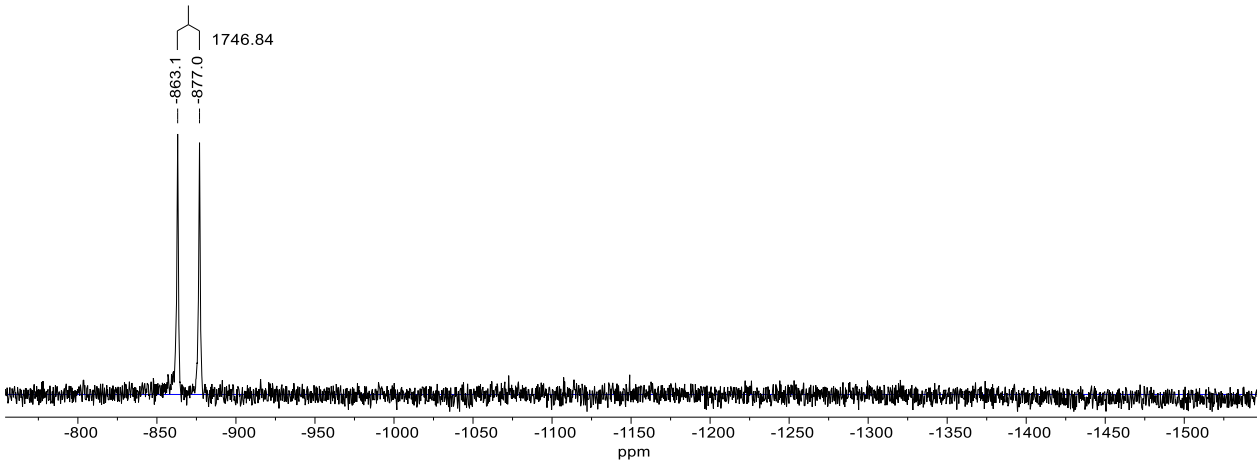
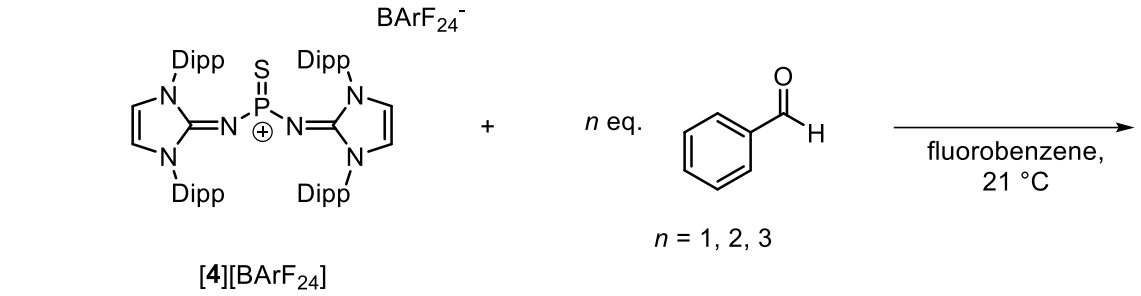


Figure S 25: ^{125}Te NMR spectrum of $PTeEt_3$ in C_6D_6.

1.7 **Reactivity of [4][BArF$_{24}$] with benzaldehyde**

[**4**][BArF$_{24}$] (50 mg, 29 µmol, 1.0 eq.) was dissolved in fluorobenzene (0.5 mL). Benzaldehyde (7.65% w/w in fluorobenzene, 39 mg, 29 µmol, 1.0 eq.) was added to the solution at 21 °C. After addition, the mixture was submitted for $^{31}P\{^{1}H\}$ NMR analysis (total reaction time approx. 1h). The addition of benzaldehyde (1.0 eq.) and subsequent $^{31}P\{^{1}H\}$ NMR measurement was repeated two additional times.



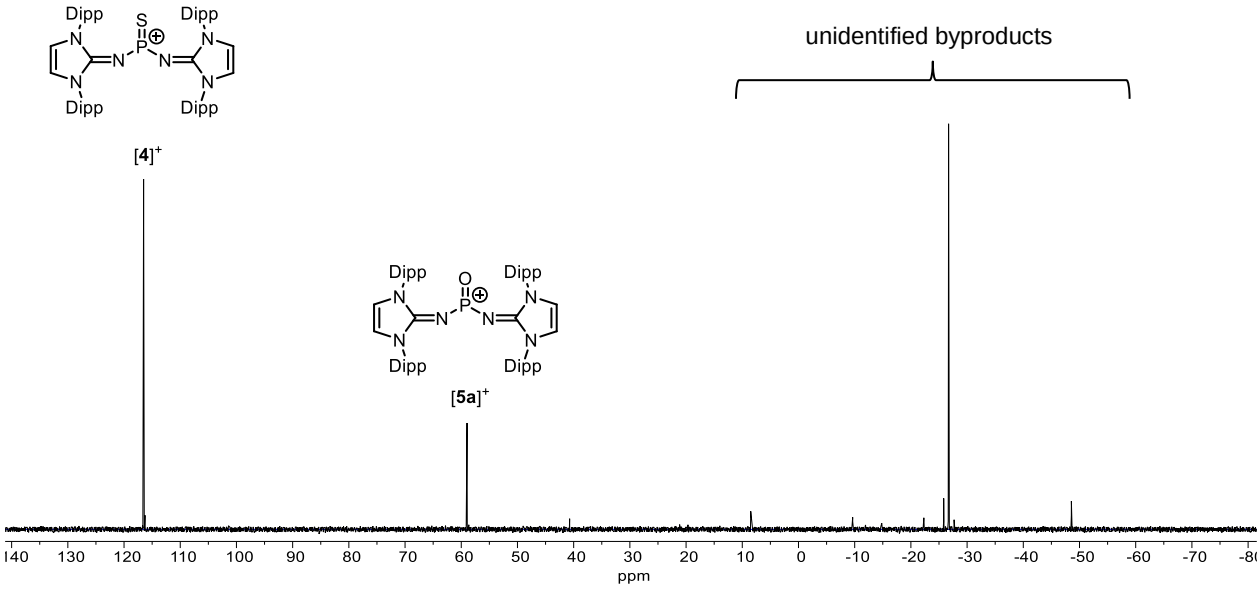


Figure S 26: $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of [**4**][BArF$_{24}$] and **one** equivalent of benzaldehyde in fluorobenzene.

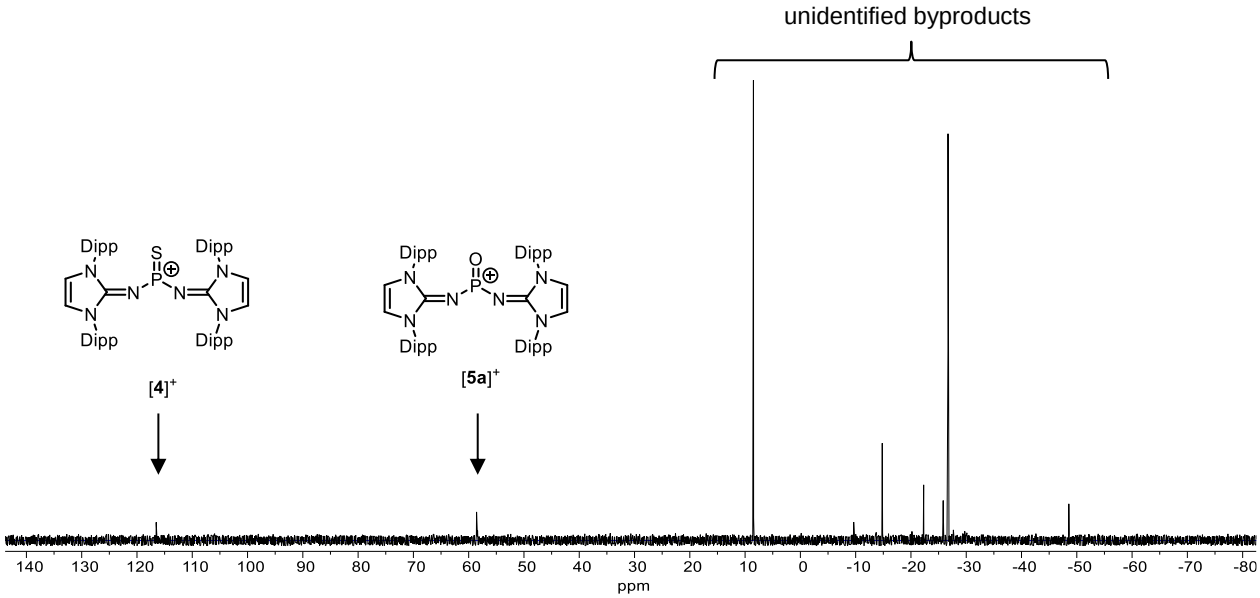


Figure S 27: $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of [**4**][$BArF_{24}$] and **two** equivalents of benzaldehyde in fluorobenzene.

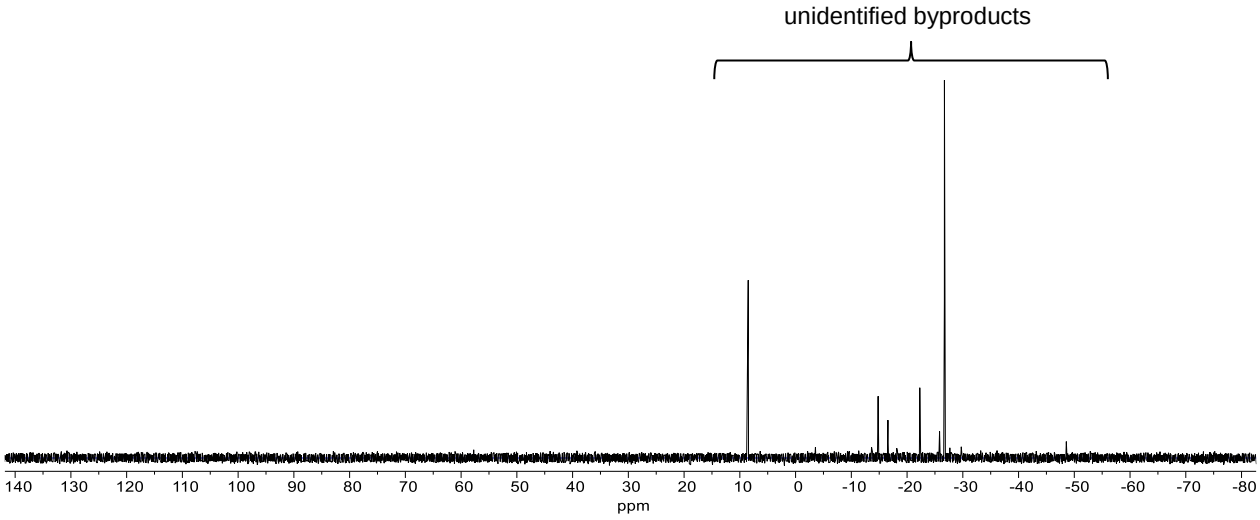
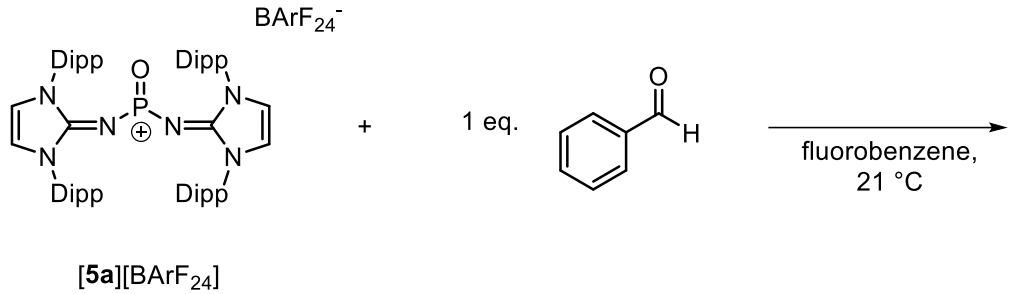


Figure S 28: $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of [**4**][$BArF_{24}$] and **three** equivalent of benzaldehyde in fluorobenzene.

1.8 **Reactivity of [5a][BArF$_{24}$] with benzaldehyde**

[**5a**][BArF$_{24}$] (30 mg, 18 µmol, 1.0 eq.) was dissolved in fluorobenzene (0.5 mL). Benzaldehyde (7.65% w/w in fluorobenzene, 24 mg, 18 µmol, 1.0 eq.) was added to the solution at 21 °C. After addition, the mixture was submitted for $^{31}P\{^{1}H\}$ NMR analysis (total reaction time approx. 1h).



[**5a**][BArF$_{24}$]

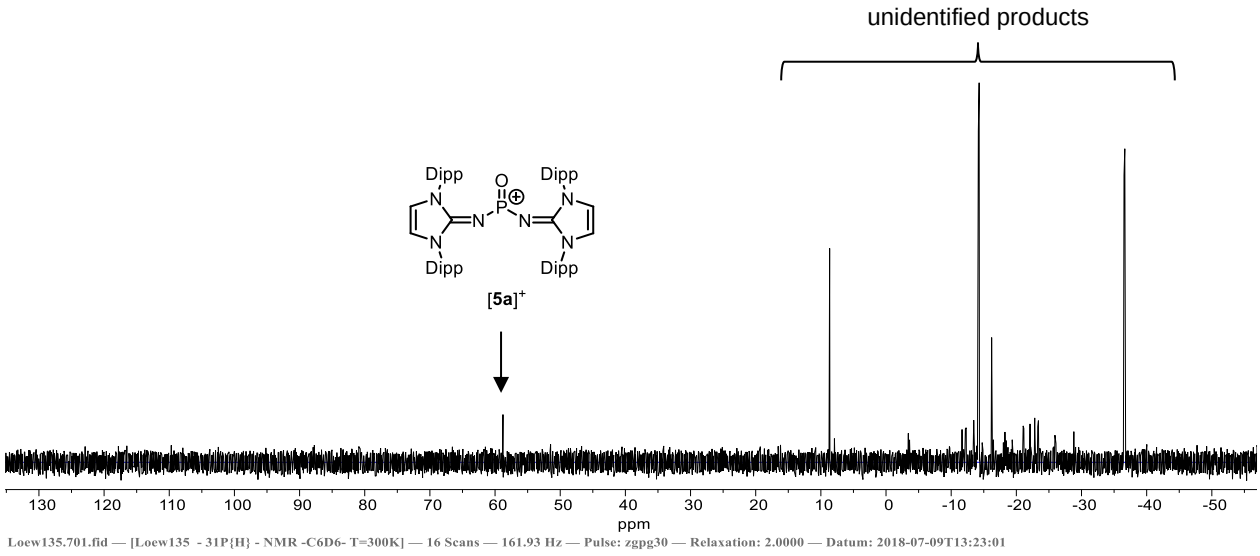
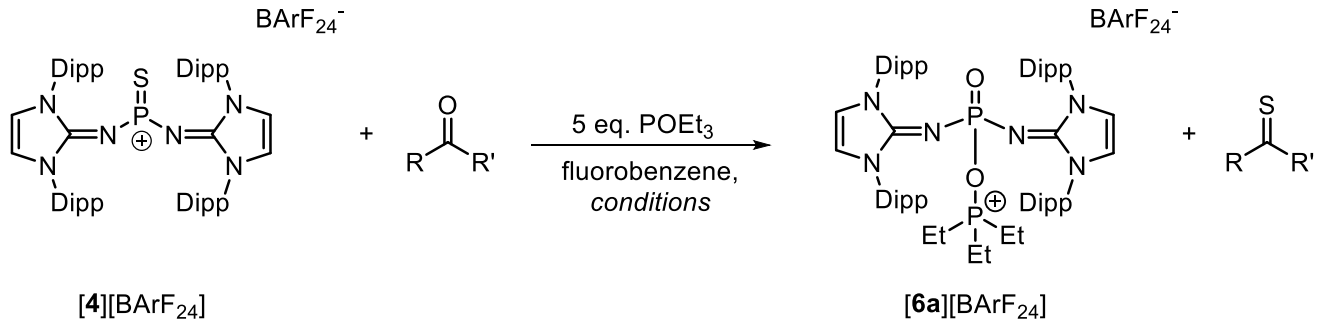


Figure S 29: $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of [**5a**][BArF$_{24}$] and benzaldehyde in fluorobenzene.

1.9 **Thionation reactions with $POEt_3$ as trapping reagent**

General procedure:

[**4**][$BArF_{24}$] (40 mg, 23 µmol, 1.0 eq.) and triethylphosphine oxide (15 mg, 0.12 mmol, 5.0 eq.) were dissolved in 0.3 mL of the solvent (*vide infra*). While stirring at room temperature, a stock solution of the carbonyl compound in fluorobenzene (23 µmmol, 1.0 eq.) was mixed with 0.2 mL solvent and added dropwise to the mixture. The mixture was immediately transferred into an NMR tube and submitted for NMR measurement.



[**4**][$BArF_{24}$] [**6a**][$BArF_{24}$]

For benzaldehyde:

Solvent: CD_2Cl_2

Stock solution: 7.65% w/w in fluorobenzene

For N-methyl-2-pyrollidinone:

Solvent: fluorobenzene

Stock solution: 1.93% w/w in fluorobenzene

1-methylpyrrolidine-2-thione was confirmed in a GC/MS analysis of the product mixture.

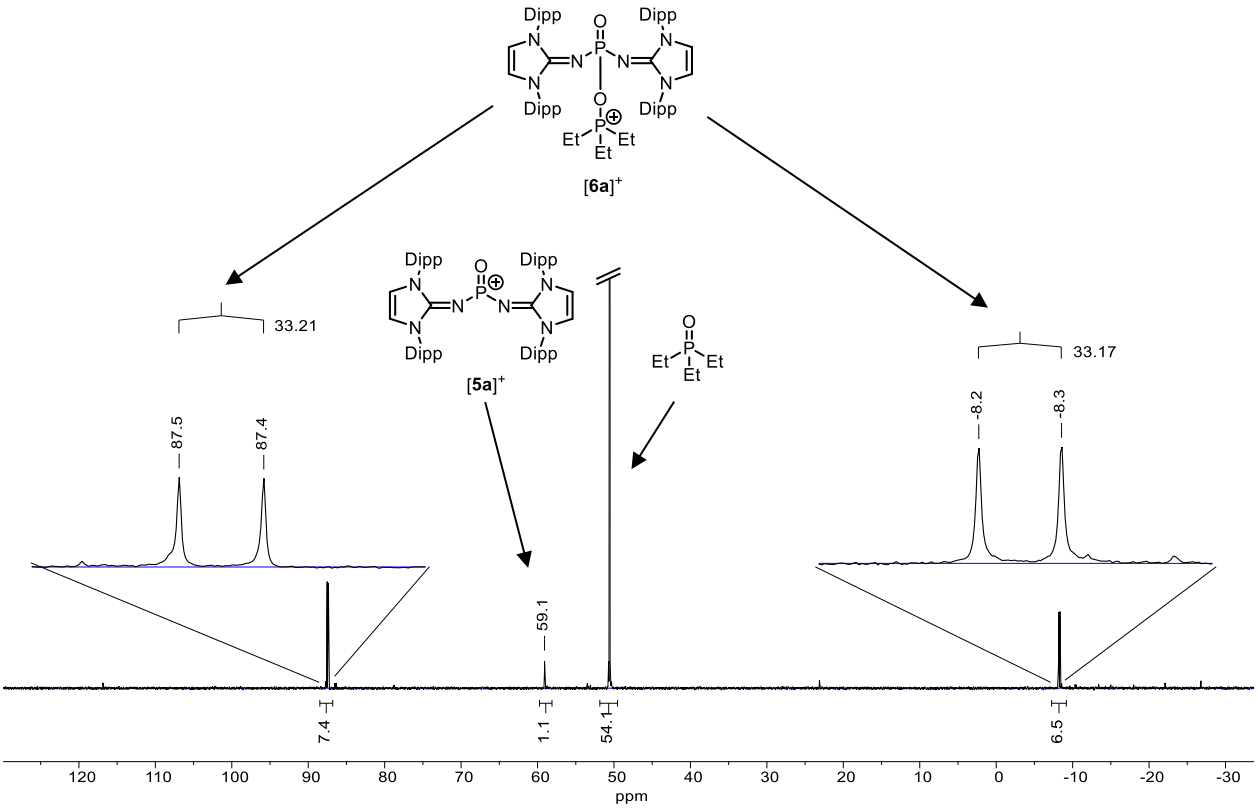


Figure S 30: $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of [**4**][$BArF_{24}$] and benzaldehyde in the presence of $POEt_3$ in fluorobenzene/CD_2Cl_2.

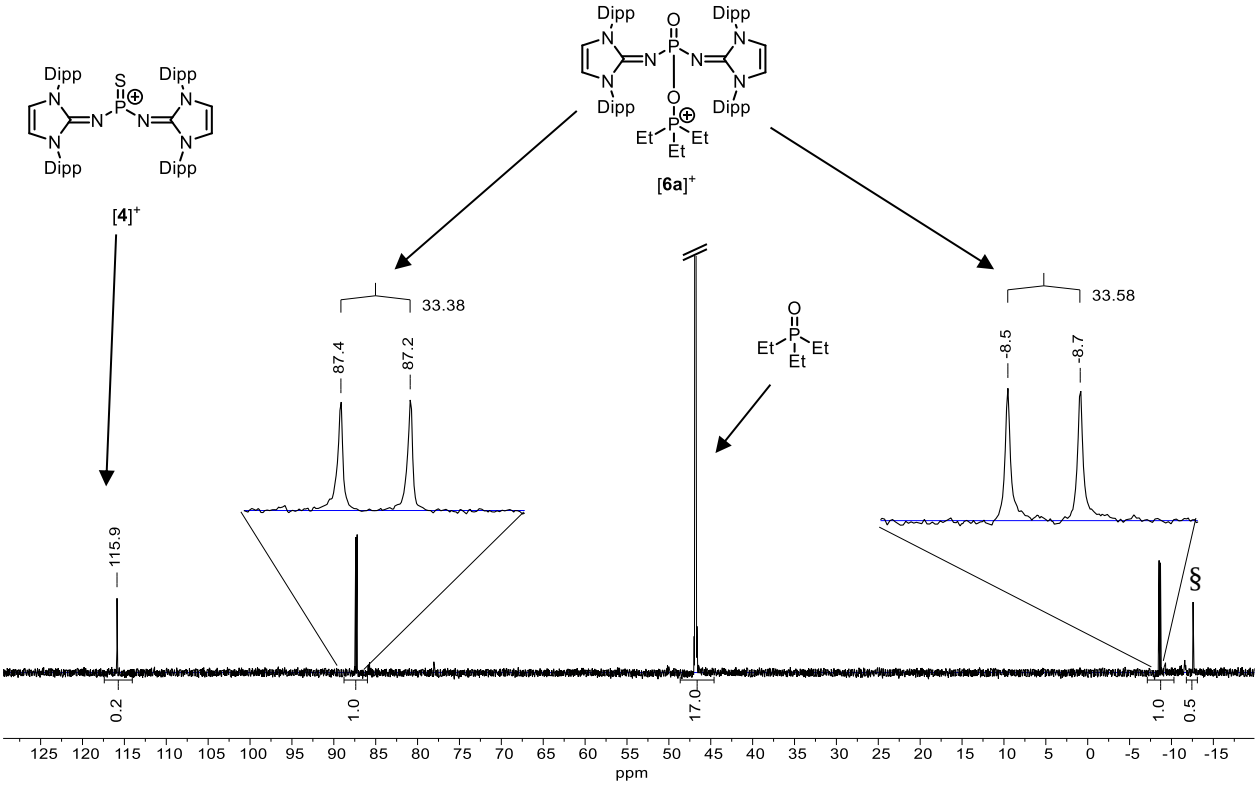
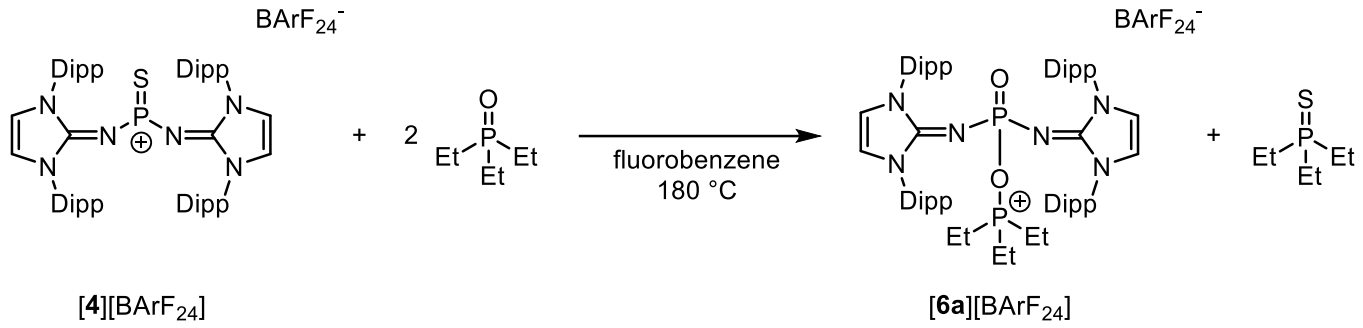


Figure S 31: $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of [**4**][$BArF_{24}$] and N-methylpyrrolidinone in the presence of $POEt_3$ in fluorobenzene/CD_2Cl_2. The section sign (§) marks an unidentified byproduct.

1.10 **Reaction of [4][BArF$_{24}$] with triethylphosphine oxide**

10.1.1 Starting from thiophosphonium salt [**4**][BArF$_{24}$]

Thiophosphonium salt [**4**][BArF$_{24}$] (65 mg, 37 µmol, 1.0 eq.) and triethylphosphine oxide (10 mg, 75 µmol, 2.0 eq.) were dissolved in fluorobenzene. The solution was heated in a sealed NMR tube at 180 °C for the given amount of time and afterwards analyzed via $^{31}P\{^{1}H\}$ NMR.



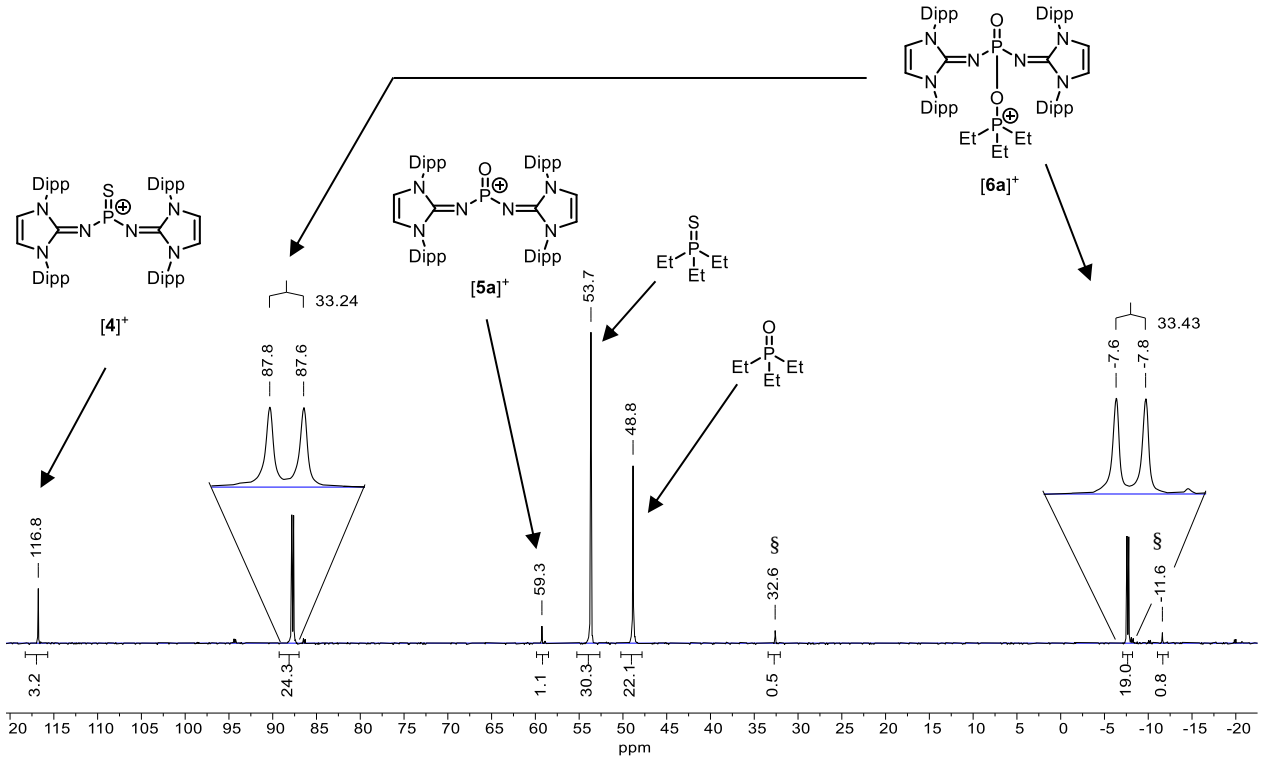


Figure S 32: $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of [**4**][BArF$_{24}$] and triethylphosphine oxide in fluorobenzene after heating at 180 °C for **14 h**. The section signs (§) mark unidentified byproducts.

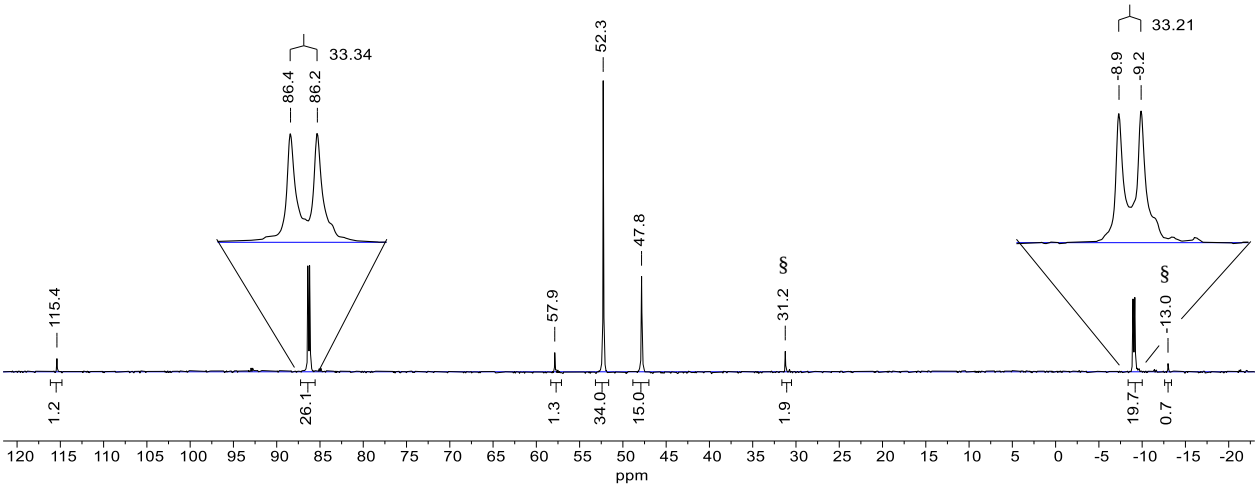
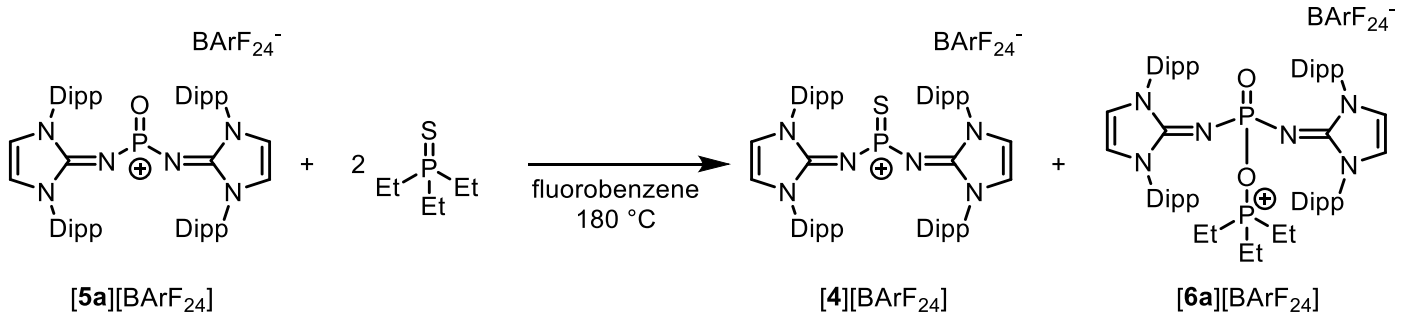


Figure S 33: $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of [**4**][$BArF_{24}$] and triethylphosphine oxide in fluorobenzene after heating at 180 °C for **29 h**. The section signs (§) mark unidentified byproducts.

Note: The conversion didn't significantly change upon further heating of the mixture.

10.1.2 Starting from oxophosphonium salt [**5a**][$BArF_{24}$]

Oxophosphonium salt [**5a**][$BArF_{24}$] (57 mg, 33 µmol, 1.0 eq.) and triethylphosphine sulfide (10 mg, 67 µmol, 2.0 eq.) were dissolved in fluorobenzene. The solution was heated in a Teflon-sealed NMR tube at 180 °C for the given amount of time and afterwards analyzed via $^{31}P\{^{1}H\}$ NMR.



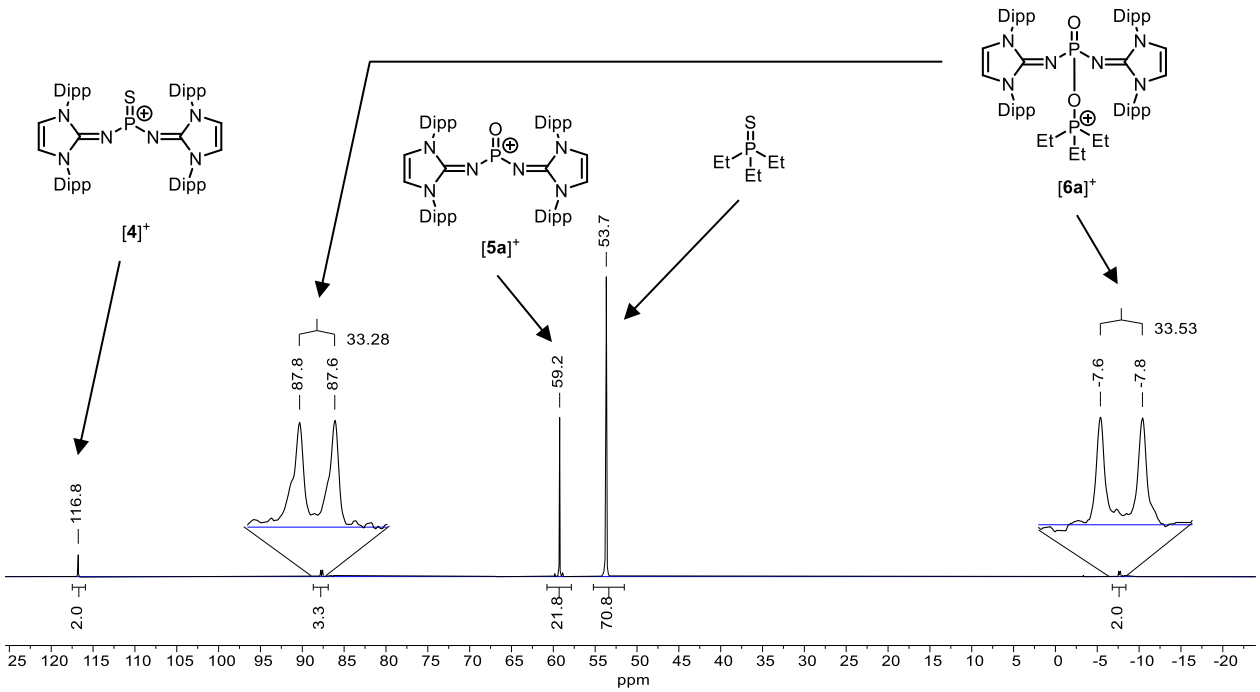


Figure S 34: $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of [**5a**][$BArF_{24}$] and triethylphosphine sulfide in fluorobenzene after heating at 180 °C for **14 h**.

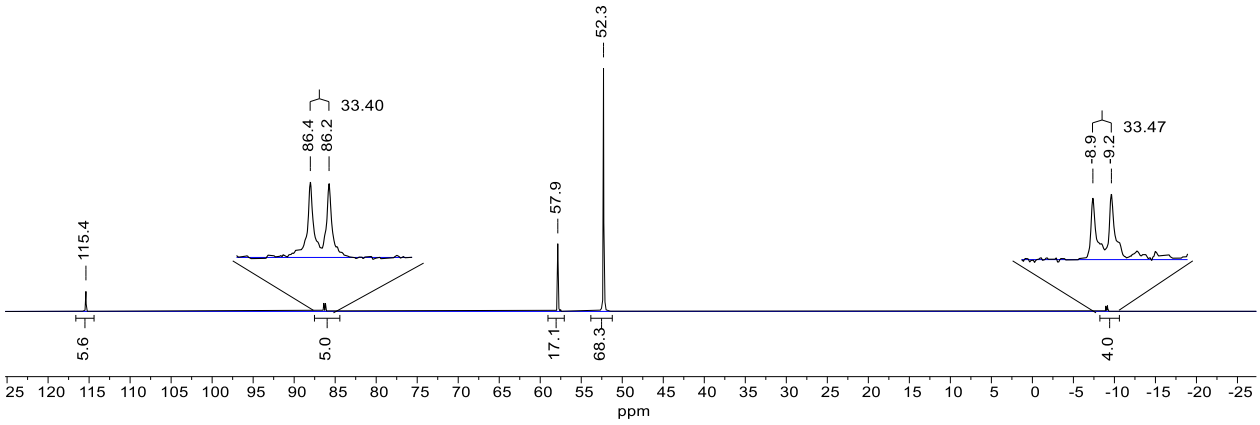


Figure S 35: $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of [**5a**][$BArF_{24}$] and triethylphosphine sulfide in fluorobenzene after heating at 180 °C for **29 h**.

Note: The conversion didn't significantly change upon further heating of the mixture.

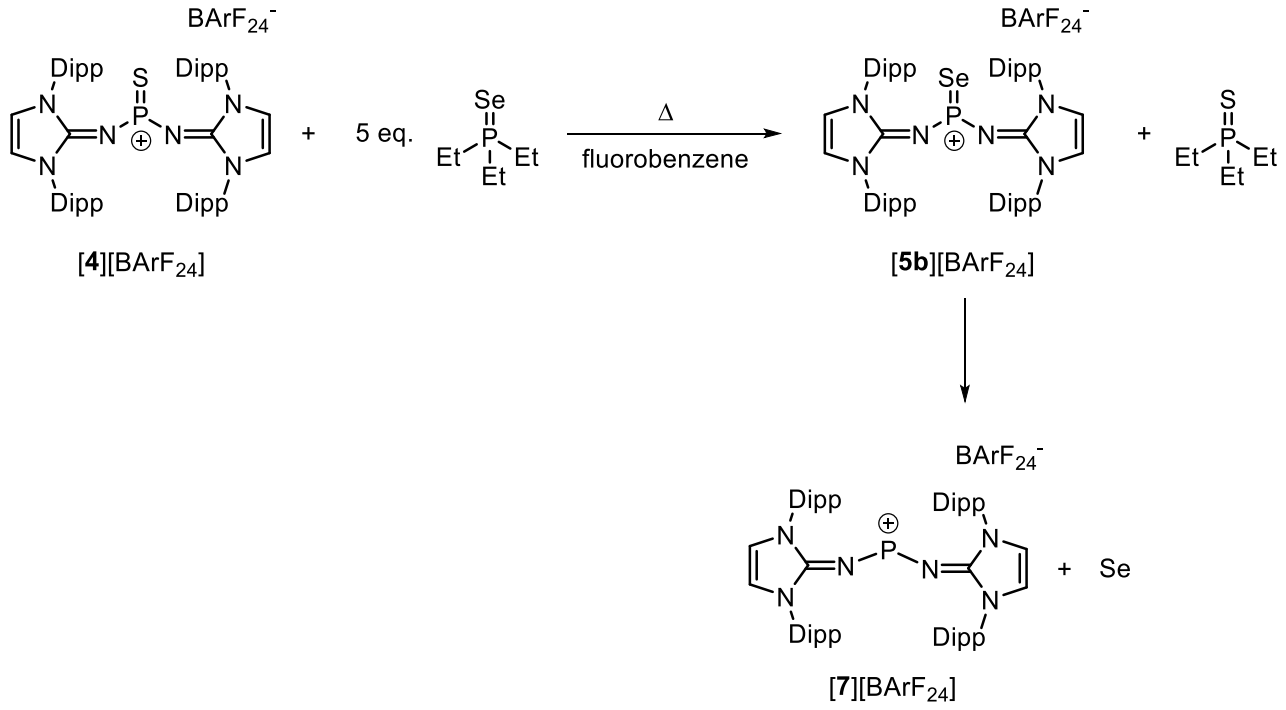
1.11 **Reaction of [4][BArF$_{24}$] with triethylphosphine chalcogenides**

11.1.1 General procedure

Thiophosphonium salt [**4**][BArF$_{24}$] (40 mg, 23 µmol, 1.0 eq.) and triethylphosphine chalcogenide (PSeEt$_3$ or PTeEt$_3$, 0.12 mmol, 5.0 eq.) were dissolved in fluorobenzene and heated at the given temperature for the given amount of time (*vide infra*). Afterwards, the reaction mixtures were analyzed by ^{31}P{^{1}H} NMR spectroscopy. The formation of a gray precipitate was observed in both mixtures. The precipitates were identified as the corresponding elemental chalcogenides by subsequent isolation of the precipitate and treatment with PEt$_3$, yielding PSeEt$_3$ and PTeEt$_3$, respectively (characterized via ^{1}H and ^{31}P NMR spectroscopy).

11.1.2 Reaction of [**4**][BArF$_{24}$] with PSeEt$_3$

The reaction was performed according to the general procedure. The mixture was gradually heated up (13 h at 120 °C, 14.5 h at 180 °C, 15.5 h at 190 °C and 63 h at 200 °C). After each heating period, the mixture was analyzed via ^{31}P{^{1}H} NMR spectroscopy.



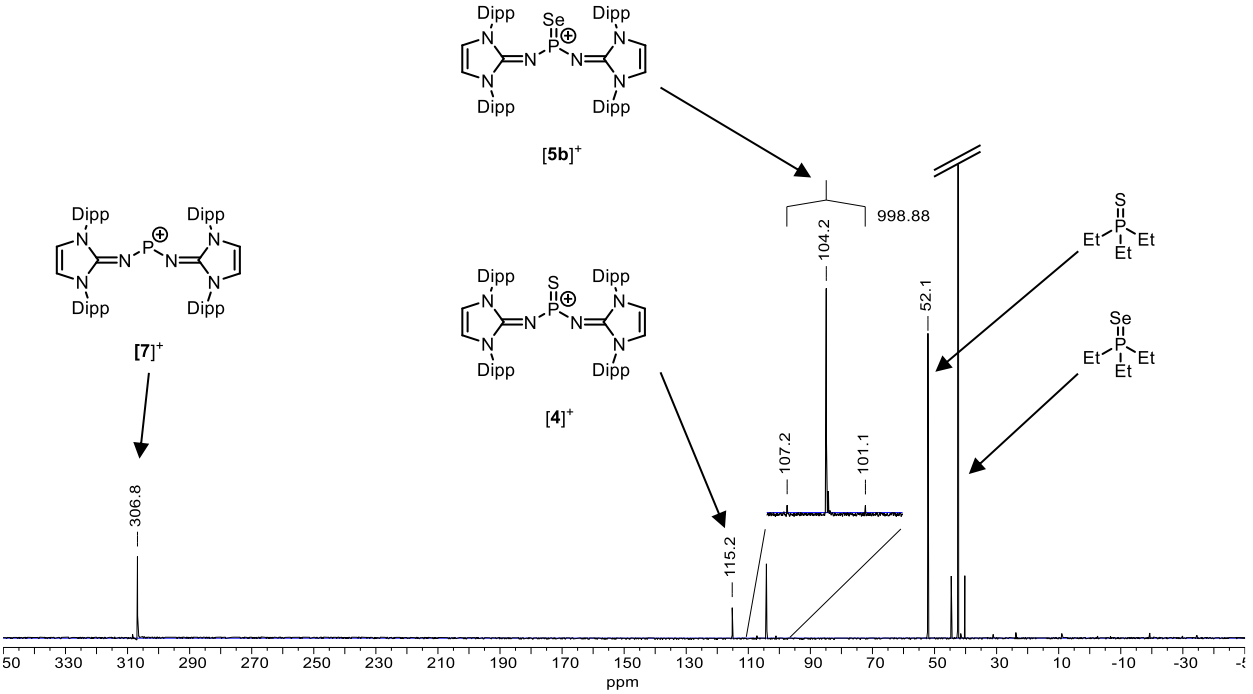


Figure S 36: $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of [**4**][$BArF_{24}$] and triethylphopsphine selenide in fluorobenzene after 63 h at 200 °C.

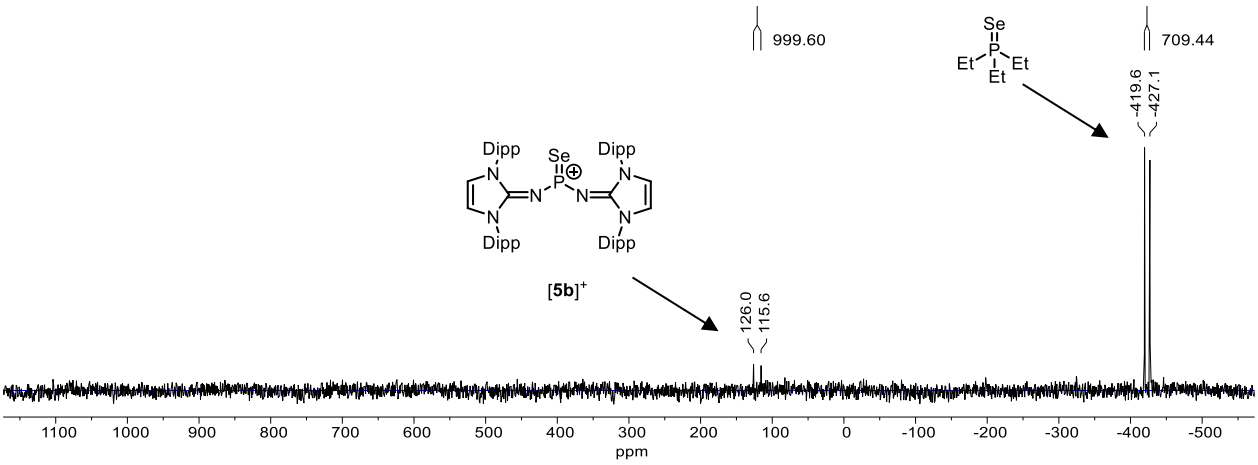


Figure S 37: $^{77}Se\{^{1}H\}$ NMR spectrum of the reaction of [**4**][$BArF_{24}$] and triethylphopsphine selenide in fluorobenzene after 63 h at 200 °C.

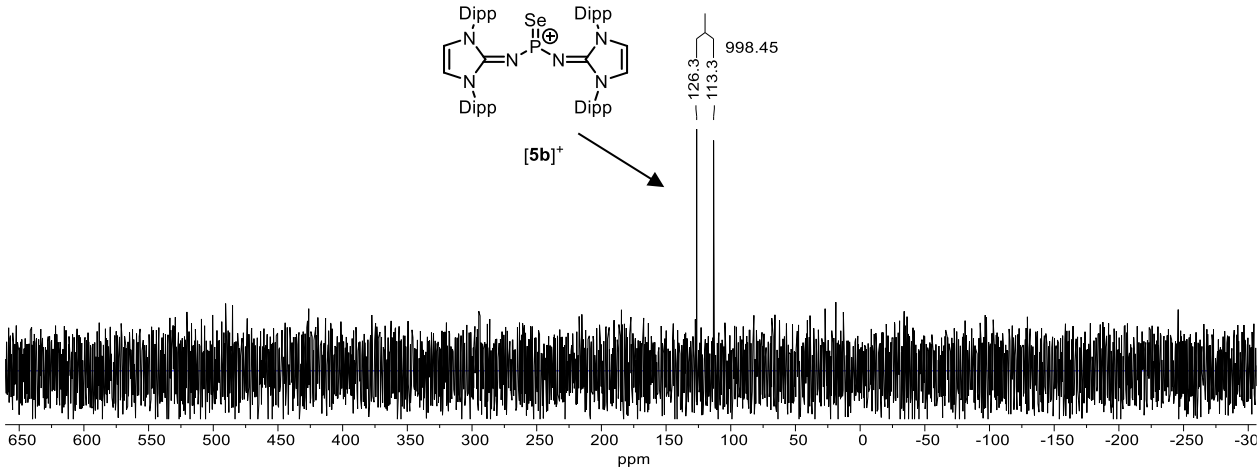
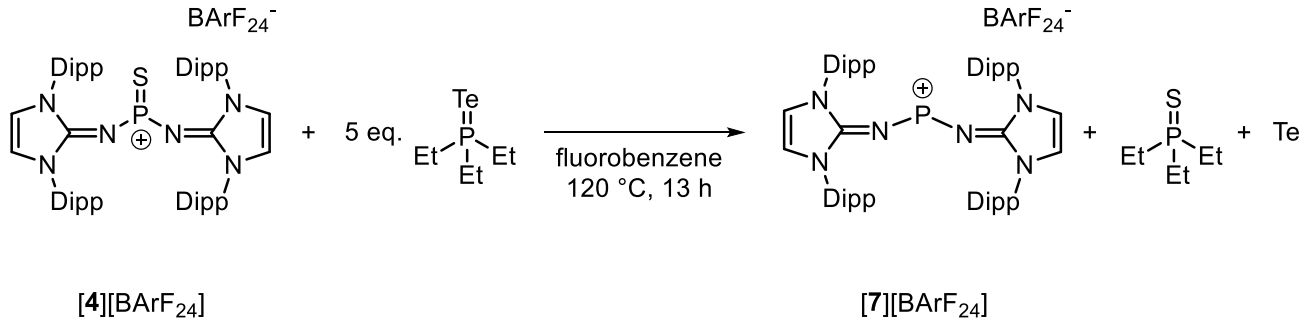


Figure S 38: $^{77}Se\{^{1}H\}$ NMR spectrum of the reaction of [**4**][$BArF_{24}$] and triethylphopsphine selenide after 63 h at 200 °C (decreased ppm window with increased number of scans).

11.1.3 Conditions for Et_3PTe

The reaction was performed according to the general procedure. The mixture was heated at 120 °C for 13 h.



[**4**][$BArF_{24}$] [**7**][$BArF_{24}$]

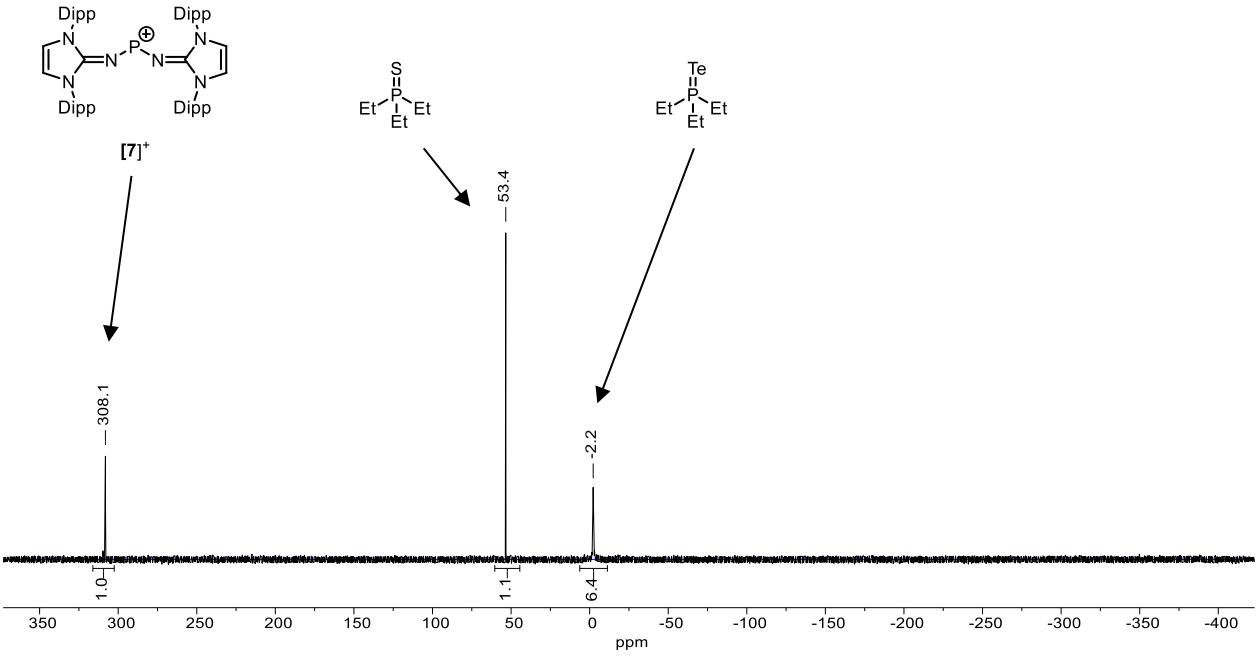


Figure S 39: $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of [**4**][$BArF_{24}$] and triethylphosphine telluride in fluorobenzene.

2 Computational details

2.1 General

The geometry optimizations and frequency calculations were performed with Gaussian09[5], using the B3LYP[6] functional with a dispersion correction (D3BJ)[7]. A triple zeta basis set (def2-TZVP)[8] was used in all calculations. The absence of any imaginary frequency with a magnitude greater than 11 cm^{-1} confirmed that each optimized structure is at a local minimum. Wiberg bond indices and natural bond orbital charges were obtained using the NBO program version 3.1 by F. Weinhold et al.[9] included in Gaussian09.

2.2 Optimized geometries of $[4]^+$ and $[5b]^+$

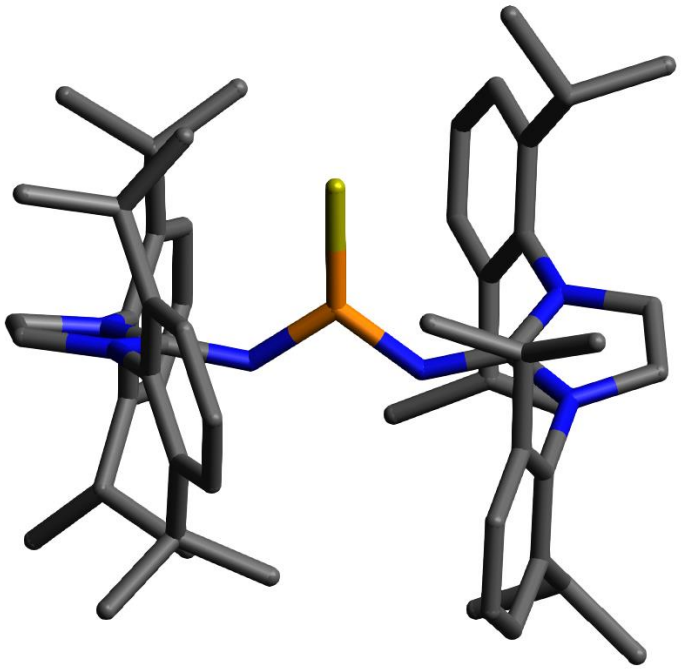


Figure S 40: Optimized geometry of $[\mathbf{4}]^+$.

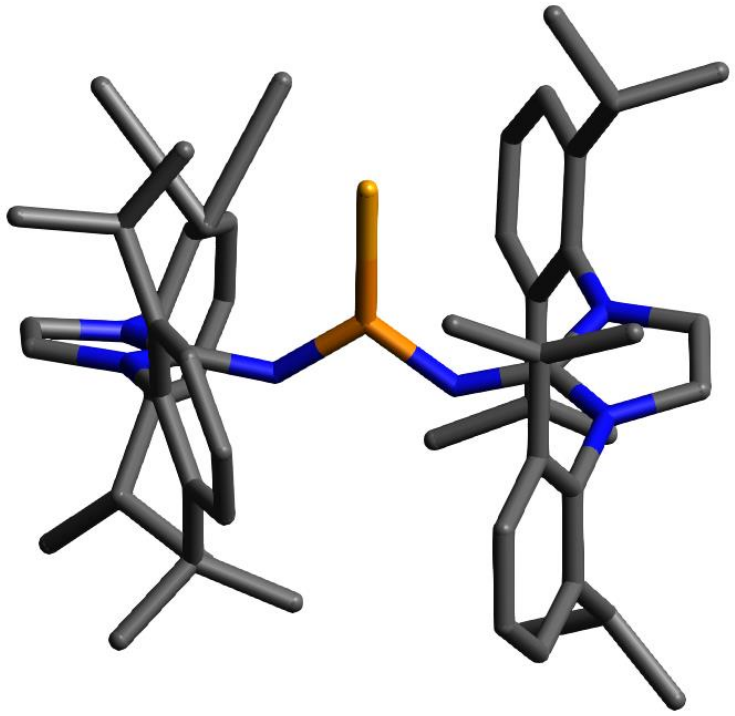


Figure S 41: Optimized geometry of [**5b**]$^+$.

2.3 Calculated Fluoride Ion Affinites (FIA) of [4]$^+$ and [5b]$^+$

The Fluoride Ion Afiinity (FIA) was calculated according to a procedure by Christe *et al*. with the experimentally determined FIA of COF_2 as reference compound.[10]

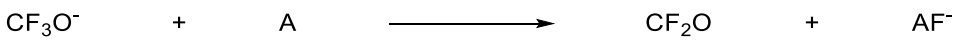


Table S 1: Calculated Fluoride Ion Affinities (FIA).

Lewis-Acid (A)	FIA [kJ/mol]
[**4**]$^+$	616
[**6a**]$^+$	614

2.4 **Molecular orbitals of [5a]$^+$, [4]$^+$ and [5b]$^+$**

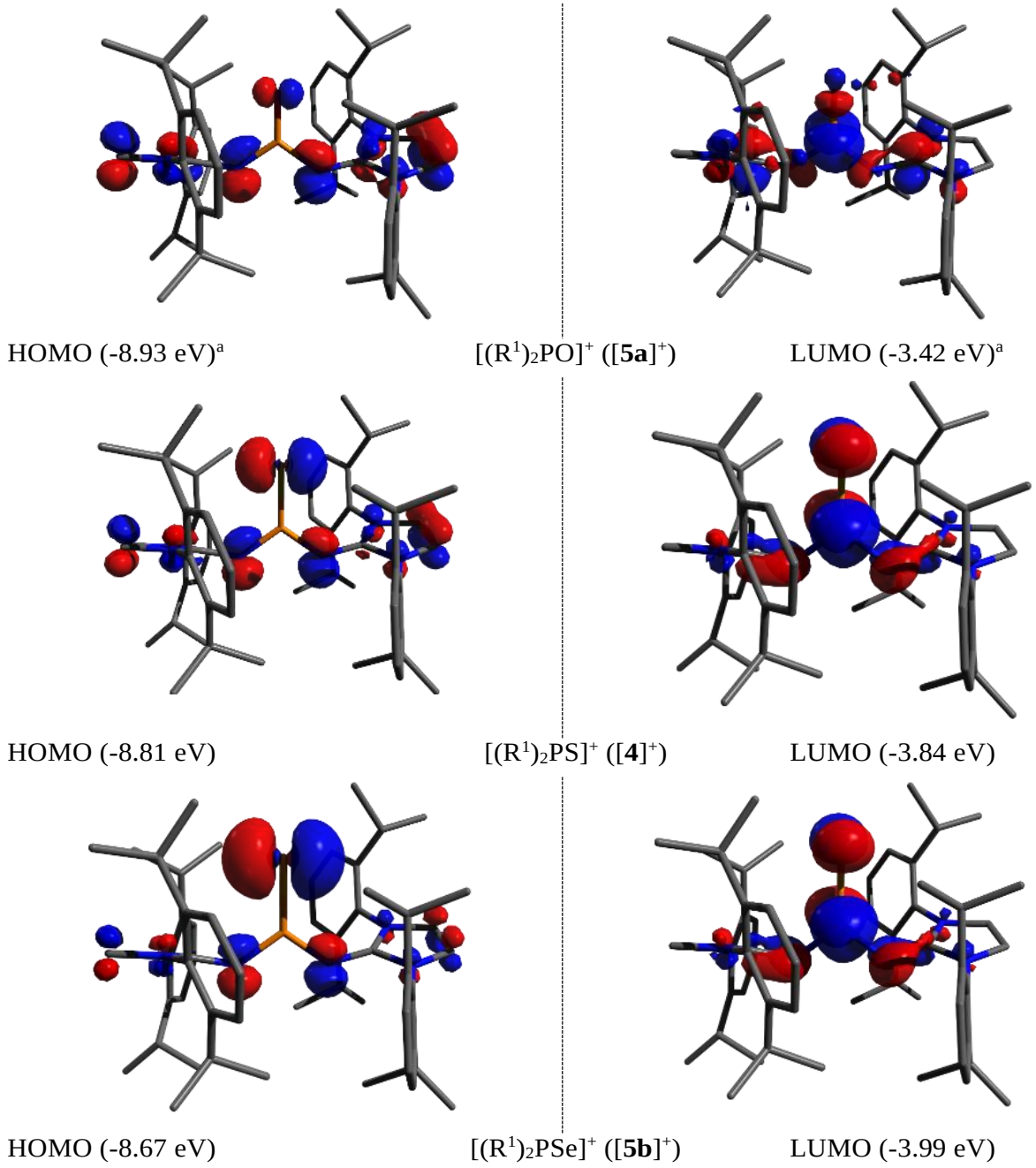


Figure S 42 Selected molecular orbitals of [**5a**]$^+$ (top),[3] [**4**]$^+$ (middle) and [**5b**]$^+$ (bottom) at the B3LYP-D3BJ/def2-TZVP level of theory (±0.05 isosurface). [a]literature data.[3]

2.5 **XYZ data of the optimized structures**

[**4**]$^+$ (-1989440.0362827)				[**4**][F] (-2052267.8771827)				[**5b**]$^+$ (-3246573.5924822)				[**5b**][F] (-3309403.4650131)			
S	0.12659	0.19178	-2.48448	S	-0.14429	-0.73967	-2.48920	Se	0.00005	0.00004	-2.53932	Se	0.01123	-0.72023	-2.49810
P	0.02704	0.04325	-0.58556	P	0.04535	-0.54044	-0.55611	P	0.00001	0.00001	-0.47896	P	0.12972	-0.50647	-0.39354
N	1.19728	-0.40442	0.35143	N	1.15146	0.49274	-0.01268	N	1.24807	-0.22280	0.43544	N	1.11216	0.62754	0.18044
N	-1.23504	0.32376	0.29284	N	-1.27687	-0.13330	0.24943	N	-1.24808	0.22279	0.43541	N	-1.25342	-0.22768	0.36042
C	2.34519	-0.99297	0.05079	C	2.38125	0.71289	-0.32463	C	2.47584	-0.62250	0.15023	C	2.30772	1.00489	-0.13265
N	3.56117	-0.46326	0.31287	N	2.97935	1.94939	-0.22201	N	3.58186	0.12870	0.35351	N	2.70004	2.31983	-0.08573
C	4.54568	-1.39464	0.01730	C	4.32865	1.85345	-0.54641	C	4.71124	-0.63749	0.10535	C	4.05168	2.43063	-0.38048
C	3.74873	0.85905	0.84372	C	2.28071	3.13156	0.18817	C	3.53404	1.48619	0.82562	C	1.83409	3.39194	0.29819
N	2.55414	-2.24946	-0.41904	N	3.38346	-0.14002	-0.72627	N	2.89631	-1.85400	-0.23637	N	3.44456	0.30189	-0.47426
C	3.92209	-2.50412	-0.42924	C	4.58066	0.56671	-0.85098	C	4.28789	-1.86761	-0.25213	C	4.51192	1.18872	-0.61615
C	1.52508	-3.20704	-0.73074	C	3.26818	-1.56903	-0.76636	C	2.03807	-2.98610	-0.47326	C	3.57772	-1.12880	-0.50504
C	-2.36537	0.95777	0.03302	C	-2.48650	-0.56698	0.32684	C	-2.47584	0.62250	0.15015	C	-2.41024	-0.79926	0.33661
N	-3.58553	0.43311	0.29265	N	-2.96040	-1.78257	0.75729	N	-3.58187	-0.12871	0.35336	N	-2.76847	-2.08281	0.68361
C	-4.56202	1.38970	0.06080	C	-4.35124	-1.76032	0.82185	C	-4.71123	0.63748	0.10516	C	-4.15407	-2.21042	0.64641
C	-3.77926	-0.89065	0.81677	C	-2.11005	-2.79467	1.30242	C	-3.53407	-1.48621	0.82544	C	-1.87901	-3.04265	1.27145
N	-2.56639	2.23974	-0.37286	N	-3.60750	0.19495	0.11093	N	-2.89630	1.85400	-0.23644	N	-3.59340	-0.15948	0.05704
C	-3.93191	2.51054	-0.34541	C	-4.75019	-0.53909	0.41395	C	-4.28787	1.86761	-0.25228	C	-4.66221	-1.02476	0.26007
C	-1.53466	3.20923	-0.63553	C	-3.57128	1.53450	-0.38836	C	-2.03803	2.98611	-0.47326	C	-3.69059	1.19558	-0.39546
C	3.81323	1.92906	-0.05505	C	1.45363	3.79028	-0.72762	C	3.34434	2.50871	-0.11091	C	0.93456	3.90326	-0.64189
C	3.82054	1.00939	2.23254	C	2.46003	3.58335	1.50637	C	3.63237	1.70792	2.20300	C	1.91506	3.87129	1.61209
C	3.97126	3.20224	0.48737	C	0.84112	4.96925	-0.30411	C	3.26873	3.80968	0.37960	C	0.14145	4.98019	-0.24960
C	3.76322	1.71624	-1.55609	C	1.23009	3.27446	-2.13604	C	3.27064	2.22174	-1.59851	C	0.82225	3.32642	-2.03844
C	4.05470	3.38640	1.85932	C	1.04135	5.46335	0.97362	C	3.37706	4.06639	1.73836	C	0.23895	5.51040	1.02665
C	3.97855	2.30384	2.72190	C	1.83520	4.77124	1.87468	C	3.55551	3.02889	2.63948	C	1.10815	4.95355	1.95305
C	3.68956	-0.16893	3.17960	C	3.21938	2.75216	2.52678	C	3.75927	0.56871	3.19747	C	2.77005	3.17428	2.65479
C	5.18450	1.68244	-2.13569	C	2.11541	4.03318	-3.13356	C	4.66543	2.33123	-2.23148	C	1.57313	4.20314	-3.04872
C	2.89866	2.75261	-2.27420	C	-0.24350	3.32405	-2.54095	C	2.26375	3.10934	-2.32967	C	-0.63279	3.10815	-2.45326
C	2.28909	-0.20781	3.80682	C	2.25234	1.78614	3.23116	C	2.40767	0.29236	3.87179	C	1.90876	2.17231	3.43935
C	4.77987	-0.17544	4.25539	C	3.98997	3.58833	3.54891	C	4.85774	0.81555	4.23567	C	3.49021	4.14130	3.59639
C	1.32785	-3.57368	-2.07109	C	3.19592	-2.21702	-2.00553	C	1.92981	-3.49279	-1.77785	C	3.75601	-1.77448	-1.73581
C	0.78768	-3.75681	0.32677	C	3.24718	-2.25684	0.45049	C	1.36546	-3.54850	0.62053	C	3.53951	-1.82292	0.71388
C	0.36913	-4.54971	-2.32900	C	3.09476	-3.60580	-1.99725	C	1.12339	-4.61315	-1.96016	C	3.90224	-3.16058	-1.71737
C	2.13072	-2.97595	-3.21122	C	3.25913	-1.44828	-3.30956	C	2.67138	-2.89203	-2.95771	C	3.82465	-1.02069	-3.05073
C	-0.37300	-5.11427	-1.30395	C	3.06717	-4.31292	-0.80488	C	0.43695	-5.18401	-0.90027	C	3.86424	-3.86905	-0.52891
C	-0.17441	-4.71240	0.00534	C	3.14593	-3.64508	0.40631	C	0.54984	-4.65081	0.37165	C	3.68418	-3.20542	0.67431
C	1.01302	-3.38870	1.78085	C	3.33694	-1.52960	1.77982	C	1.52117	-3.04798	2.04408	C	3.36154	-1.09875	2.03609
C	1.26319	-2.64765	-4.43144	C	2.37571	-2.05368	-4.40423	C	1.80333	-2.80604	-4.21812	C	3.11387	-1.75123	-4.19408
C	3.27574	-3.91271	-3.62530	C	4.70995	-1.34200	-3.79982	C	3.94805	-3.69008	-3.26553	C	5.28378	-0.74631	-3.44854
C	-0.26514	-2.83993	2.42111	C	2.26379	-1.98187	2.77634	C	0.17188	-2.66303	2.65719	C	2.61992	-1.92788	3.08501
C	1.56628	-4.58340	2.56804	C	4.74409	-1.66719	2.37697	C	2.25287	-4.08543	2.90592	C	4.71369	-0.61033	2.57410
C	-3.79345	-1.05011	2.20693	C	-1.66815	-2.64260	2.62320	C	-3.63247	-1.70799	2.20280	C	-1.60218	-2.93078	2.63898
C	-3.90378	-1.95354	-0.08204	C	-1.69593	-3.84294	0.48111	C	-3.34435	-2.50872	-0.11112	C	-1.30664	-4.02914	0.46032
C	-3.95698	-2.34354	2.69540	C	-0.81716	-3.61329	3.13862	C	-3.55564	-3.02896	2.63925	C	-0.74299	-3.87170	3.20216
C	-3.61827	0.11716	3.16034	C	-2.03226	-1.44295	3.46560	C	-3.75941	-0.56880	3.19730	C	-2.16205	-1.80730	3.49071
C	-4.09997	-3.41893	1.83145	C	-0.42202	-4.68769	2.35778	C	-3.37716	-4.06644	1.73811	C	-0.18807	-4.87863	2.42944
C	-4.07307	-3.22644	0.45907	C	-0.85089	-4.79668	1.04209	C	-3.26876	-3.80970	0.37936	C	-0.46598	-4.95406	1.07346
C	-3.84287	-1.75825	-1.58438	C	-2.14214	-3.91929	-0.96327	C	-3.27057	-2.22171	-1.59871	C	-1.56810	-4.07749	-1.03190
C	-4.78554	0.21987	4.14866	C	-2.67391	-1.86165	4.79046	C	-4.85792	-0.81566	4.23545	C	-2.87491	-2.33011	4.74205
C	-2.27010	0.04120	3.88689	C	-0.79882	-0.55988	3.67855	C	-2.40785	-0.29247	3.87169	C	-1.05932	-0.80337	3.85257
C	-2.67996	-2.54703	-2.19475	C	-1.05812	-4.46645	-1.89468	C	-2.26362	-3.10927	-2.32984	C	-0.33762	-4.50451	-1.83515
C	-5.17335	-2.12599	-2.25173	C	-3.44119	-4.72757	-1.08740	C	-4.66532	-2.33120	-2.23175	C	-2.76909	-4.97918	-1.34931
C	-1.36951	3.68298	-1.94631	C	-3.89699	1.73163	-1.73338	C	-1.92973	3.49284	-1.77783	C	-4.02498	1.43143	-1.73578
C	-0.76379	3.66557	0.44294	C	-3.18716	2.58473	0.45796	C	-1.36549	3.54848	0.62058	C	-3.45144	2.23237	0.51485
C	-0.39978	4.66031	-2.15192	C	-3.89180	3.03842	-2.21578	C	-1.12330	4.61321	-1.96007	C	-4.17798	2.75603	-2.13836
C	-2.22090	3.20084	-3.10612	C	-4.21784	0.57189	-2.65599	C	-2.67125	2.89212	-2.95775	C	-4.21498	0.30467	-2.73380
C	0.38335	5.12506	-1.10722	C	-3.53648	4.09786	-1.39731	C	-0.43691	5.18403	-0.90014	C	-3.96615	3.80059	-1.25322
C	0.20995	4.62514	0.17155	C	-3.17495	3.86967	-0.07911	C	-0.54984	4.65079	0.37177	C	-3.59035	3.53974	0.05408
C	-0.98169	3.21063	1.87382	C	-2.79508	2.38492	1.90854	C	-1.52127	3.04792	2.04411	C	-3.05077	1.98264	1.95499
C	-1.40416	2.95440	-4.37929	C	-3.31095	0.56107	-3.89134	C	-1.80315	2.80617	-4.21812	C	-3.39087	0.52263	-4.00661
C	-3.35018	4.19954	-3.40432	C	-5.70087	0.57298	-3.04877	C	-3.94790	3.69019	-3.26560	C	-5.69996	0.10858	-3.06712
C	-1.59943	4.34075	2.70818	C	-3.75428	3.11850	2.85129	C	-2.25301	4.08535	2.90594	C	-4.09888	2.53186	2.93018
C	0.30828	2.68709	2.50924	C	-1.34254	2.81771	2.13562	C	-0.17200	2.66296	2.65726	C	-1.65934	2.55387	2.24265
H	5.58701	-1.17493	0.15908	H	4.97294	2.71229	-0.53045	H	5.69980	-0.23299	0.21507	H	4.54825	3.38259	-0.39310
H	4.31067	-3.45277	-0.74452	H	5.49237	0.07295	-1.12899	H	4.83524	-2.75340	-0.50834	H	5.49574	0.84101	-0.86205
H	4.03130	4.05776	-0.17022	H	0.19420	5.50223	-0.98542	H	3.12334	4.63055	-0.30762	H	-0.56569	5.40065	-0.95094
H	4.17996	4.38386	2.26058	H	0.55927	6.38399	1.27852	H	3.31962	5.08565	2.09826	H	-0.38280	6.35046	1.31028
H	4.03631	2.46725	3.78904	H	1.95242	5.15018	2.88006	H	3.62638	3.24612	3.69612	H	1.14415	5.35296	2.95716
H	3.30764	0.74374	-1.74594	H	1.51974	2.22775	-2.16876	H	2.93107	1.19352	-1.72878	H	1.29089	2.34435	-2.04111

H	5.68855	2.63787	-1.97855	H	1.86153	5.09566	-3.15152	H	5.05499	3.34601	-2.13119	H	1.13715	5.20371	-3.09830
H	5.15437	1.48728	-3.20894	H	1.97949	3.63433	-4.14083	H	4.62209	2.08703	-3.29420	H	1.52202	3.76044	-4.04534
H	5.79053	0.90596	-1.66644	H	3.17209	3.94531	-2.87260	H	5.37610	1.65313	-1.75703	H	2.62534	4.30921	-2.77725
H	1.89783	2.79675	-1.85074	H	-0.86339	2.80486	-1.81365	H	1.28321	3.07099	-1.85928	H	-1.15817	2.49905	-1.72036
H	2.80561	2.48991	-3.32880	H	-0.37823	2.82805	-3.50146	H	2.15524	2.77077	-3.36066	H	-0.66820	2.57905	-3.40530
H	3.33425	3.75156	-2.22275	H	-0.60782	4.34837	-2.63592	H	2.58579	4.15142	-2.35999	H	-1.17143	4.05022	-2.56878
H	3.81063	-1.08456	2.59917	H	3.95242	2.14729	1.99309	H	4.03789	-0.33183	2.64898	H	3.53878	2.60205	2.13566
H	2.11596	0.67927	4.41868	H	1.52516	2.34470	3.82270	H	2.08826	1.15336	4.46149	H	1.14061	2.69539	4.01243
H	2.18822	-1.08433	4.44946	H	2.79905	1.12023	3.90301	H	2.48868	-0.56461	4.54309	H	2.52592	1.60247	4.13727
H	1.51444	-0.24742	3.04237	H	1.69754	1.18249	2.51507	H	1.63309	0.08422	3.13493	H	1.40696	1.47673	2.76777
H	5.77625	-0.13630	3.81310	H	4.65685	4.30188	3.06192	H	5.81663	1.02345	3.75898	H	4.08526	4.86862	3.04151
H	4.70798	-1.08461	4.85412	H	4.59325	2.93562	4.18226	H	4.97588	-0.06397	4.87018	H	4.15871	3.58791	4.25838
H	4.68120	0.67157	4.93567	H	3.31967	4.14603	4.20548	H	4.61699	1.65704	4.88661	H	2.79015	4.69097	4.22797
H	0.19323	-4.86388	-3.34782	H	3.02251	-4.13937	-2.93429	H	1.01861	-5.03544	-2.94922	H	4.03002	-3.69203	-2.64954
H	-1.11495	-5.86899	-1.52985	H	2.97794	-5.39181	-0.82210	H	-0.19280	-6.04755	-1.07008	H	3.96676	-4.94686	-0.54033
H	-0.76450	-5.15454	0.79599	H	3.11366	-4.20628	1.32933	H	0.00850	-5.10249	1.19110	H	3.64032	-3.77264	1.59255
H	2.56453	-2.03861	-2.85982	H	2.88846	-0.44189	-3.11335	H	2.95765	-1.87362	-2.69058	H	3.31459	-0.06737	-2.90905
H	0.92714	-3.55245	-4.93993	H	2.77763	-3.00184	-4.76918	H	1.61544	-3.79258	-4.64391	H	3.66270	-2.64311	-4.50397
H	1.84263	-2.06807	-5.15138	H	2.32889	-1.37173	-5.25505	H	2.31562	-2.21675	-4.97977	H	3.04583	-1.09342	-5.06243
H	0.38637	-2.06655	-4.15182	H	1.36244	-2.21097	-4.04053	H	0.84435	-2.33569	-4.00915	H	2.10522	-2.03661	-3.90330
H	3.94297	-4.14311	-2.79511	H	5.35352	-0.84814	-3.06992	H	4.61413	-3.75702	-2.40592	H	5.82677	-0.19145	-2.68462
H	3.87030	-3.45851	-4.41956	H	4.75514	-0.77063	-4.72929	H	4.49923	-3.22503	-4.08435	H	5.32206	-0.16880	-4.37448
H	2.87865	-4.85806	-3.99923	H	5.12102	-2.33545	-3.99213	H	3.69653	-4.70937	-3.56370	H	5.81530	-1.68598	-3.61425
H	1.76249	-2.60145	1.83150	H	3.16934	-0.47117	1.59707	H	2.13780	-2.15215	2.03616	H	2.74215	-0.22483	1.85422
H	-0.64766	-1.98285	1.87004	H	1.26955	-1.91406	2.34287	H	-0.34179	-1.92026	2.04989	H	1.68547	-2.31884	2.68544
H	-0.06619	-2.52409	3.44586	H	2.29717	-1.35241	3.66751	H	0.31929	-2.24369	3.65315	H	2.38722	-1.30051	3.94718
H	-1.05088	-3.59497	2.45314	H	2.42179	-3.01279	3.09642	H	-0.48445	-3.52807	2.75473	H	3.21966	-2.76612	3.44591
H	0.85283	-5.40865	2.59026	H	4.97673	-2.71305	2.58709	H	1.67766	-5.00893	2.98793	H	5.37590	-1.45498	2.77677
H	1.77258	-4.29195	3.59935	H	4.81865	-1.10902	3.31300	H	2.40724	-3.69623	3.91380	H	4.57538	-0.05605	3.50508
H	2.49249	-4.95474	2.12669	H	5.50346	-1.28557	1.69191	H	3.22739	-4.33552	2.48366	H	5.21393	0.04700	1.86209
H	-5.60365	1.17582	0.21005	H	-4.91068	-2.61124	1.16177	H	-5.69980	0.23298	0.21483	H	-4.63734	-3.13135	0.91228
H	-4.31372	3.47693	-0.61050	H	-5.73205	-0.11596	0.31276	H	-4.83522	2.75341	-0.50849	H	-5.67637	-0.71091	0.10270
H	-3.96985	-2.51182	3.76362	H	-0.46033	-3.52310	4.15917	H	-3.62657	-3.24622	3.69588	H	-0.49834	-3.80791	4.25399
H	-4.23167	-4.41567	2.23224	H	0.24266	-5.43573	2.77116	H	-3.31974	-5.08572	2.09798	H	0.47950	-5.60017	2.88344
H	-4.17987	-4.07551	-0.20225	H	-0.49878	-5.61760	0.43438	H	-3.12335	-4.63054	-0.30788	H	-0.00026	-5.72553	0.47734
H	-3.61464	1.03731	2.57557	H	-2.75805	-0.84009	2.92879	H	-4.03801	0.33176	2.64882	H	-2.90804	-1.27430	2.90222
H	-5.74019	0.30014	3.62676	H	-3.53519	-2.51077	4.62685	H	-5.81679	-1.02356	3.75871	H	-3.66443	-3.03669	4.48074
H	-4.66777	1.10034	4.78221	H	-3.00991	-0.98079	5.34187	H	-4.97609	0.06384	4.86997	H	-3.32596	-1.50148	5.29144
H	-4.83450	-0.65327	4.80081	H	-1.96289	-2.39839	5.42427	H	-4.61720	-1.65717	4.88637	H	-2.18271	-2.83584	5.41747
H	-2.20545	-0.85569	4.50508	H	-0.03948	-1.08471	4.26364	H	-2.08846	-1.15348	4.46137	H	-0.28749	-1.27764	4.46151
H	-2.14618	0.90682	4.54019	H	-1.07272	0.34862	4.21816	H	-2.48888	0.56448	4.54301	H	-1.47636	0.02831	4.42403
H	-1.44416	0.02398	3.17695	H	-0.36632	-0.27363	2.71768	H	-1.63323	-0.08431	3.13486	H	-0.59134	-0.40217	2.95507
H	-3.66131	-0.70184	-1.78440	H	-2.34697	-2.90076	-1.29753	H	-2.93101	-1.19346	-1.72893	H	-1.81184	-3.06493	-1.35516
H	-1.73367	-2.30329	-1.71493	H	-1.37437	-4.34124	-2.93095	H	-1.28312	-3.07091	-1.85939	H	-0.53040	-4.36002	-2.89870
H	-2.58506	-2.32380	-3.25847	H	-0.87748	-5.53119	-1.72963	H	-2.15508	-2.77067	-3.36081	H	-0.09786	-5.55929	-1.68133
H	-2.83615	-3.62067	-2.08938	H	-0.12141	-3.92470	-1.76501	H	-2.58565	-4.15136	-2.36019	H	0.52965	-3.90167	-1.57157
H	-5.40473	-3.18379	-2.11649	H	-3.28795	-5.75757	-0.75675	H	-5.05487	-3.34598	-2.13151	H	-2.57370	-6.00724	-1.03523
H	-5.12655	-1.92983	-3.32416	H	-3.77508	-4.75017	-2.12674	H	-4.62193	-2.08697	-3.29446	H	-2.96669	-4.98382	-2.42311
H	-6.00002	-1.54849	-1.83513	H	-4.24271	-4.29664	-0.48580	H	-5.37603	-1.65312	-1.75731	H	-3.67345	-4.64000	-0.84255
H	-0.24602	5.05366	-3.14654	H	-4.14337	3.22383	-3.25114	H	-1.01847	5.03552	-2.94911	H	-4.44163	2.97177	-3.16468
H	1.13731	5.87829	-1.29441	H	-3.52054	5.10466	-1.79541	H	0.19285	6.04758	-1.06989	H	-4.07635	4.82371	-1.58999
H	0.82766	4.99395	0.97827	H	-2.86846	4.69901	0.54442	H	-0.00854	5.10245	1.19125	H	-3.39981	4.36187	0.73077
H	-2.67051	2.24905	-2.81870	H	-4.02001	-0.35183	-2.11144	H	-2.95753	1.87370	-2.69066	H	-3.84761	-0.61349	-2.27611
H	-1.04333	3.88856	-4.81180	H	-3.47165	1.44271	-4.51460	H	-1.61523	3.79272	-4.64387	H	-3.72576	1.40267	-4.55911
H	-2.02968	2.47073	-5.13080	H	-3.52466	-0.31985	-4.50013	H	-2.31540	2.21690	-4.97981	H	-3.49358	-0.34133	-4.66600
H	-0.54613	2.31427	-4.18493	H	-2.26299	0.52362	-3.59769	H	-0.84418	2.33581	-4.00912	H	-2.33555	0.63654	-3.76408
H	-3.97638	4.39135	-2.53342	H	-6.34792	0.54659	-2.16952	H	-4.61402	3.75711	-2.40602	H	-6.29276	-0.08488	-2.17168
H	-3.98987	3.82296	-4.20402	H	-5.93275	-0.29530	-3.66871	H	-4.49906	3.22517	-4.08446	H	-5.83002	-0.73427	-3.74876
H	-2.93595	5.15670	-3.72586	H	-5.95265	1.46982	-3.61871	H	-3.69636	4.70948	-3.56373	H	-6.11010	0.99867	-3.54912
H	-1.69315	2.38862	1.87730	H	-2.86454	1.32158	2.14376	H	-2.13789	2.15209	2.03613	H	-2.99779	0.90796	2.11178
H	-0.92614	5.19708	2.77218	H	-3.71839	4.19835	2.69539	H	-1.67780	5.00884	2.98800	H	-4.18429	3.61754	2.85364
H	-1.80020	3.99424	3.72350	H	-3.48384	2.92292	3.89099	H	-2.40743	3.69611	3.91380	H	-3.81917	2.29188	3.95819
H	-2.53884	4.68651	2.27388	H	-4.78466	2.79243	2.69815	H	-3.22751	4.33544	2.48363	H	-5.08439	2.10450	2.73584
H	0.74443	1.88200	1.92061	H	-0.67188	2.26806	1.47805	H	0.34170	1.92020	2.04998	H	-0.91971	2.12469	1.56927
H	0.10219	2.30118	3.50807	H	-1.05087	2.62413	3.16907	H	-0.31946	2.24358	3.65321	H	-1.36397	2.32538	3.26797
H	1.05714	3.47297	2.60658	H	-1.21020	3.88392	1.94513	H	0.48432	3.52800	2.75487	H	-1.64403	3.63755	2.12495
				F	0.50745	-1.97125	0.00948					F	0.68251	-1.88860	0.21089

3 X-ray Diffraction Studies

General: Single-crystal X-ray diffraction data were collected on a Bruker AXS detector using Mo-K_α radiation (λ = 0.71073 Å). Crystals were selected under oil, mounted on glass capillaries and then immediately placed in a cold stream of N_2 on a diffractometer. The APEX2 software was used to operate the diffractometer.[11] Using Olex2,[12] the structures were solved with ShelXS or ShelXT structure solution program using and refined with the ShelXL refinement package using Least Squares minimisation.[13]

Ellipsoids are drawn at 50% probability and for clarity hydrogen atoms are omitted. If present, solvent molecules and disordered parts are shown for a complete structural depiction.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 2060578 ([$(R^1)_2PCl_2$][Cl]) 2057624 (**3**) and 2057623 ([**4**][$BArF_{24}$]). These data can be obtained free of charge via www.ccdc.cam.uk/data_request/cif (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

3.1 Crystal structure data of compound $[(R^1)_2PCl_2][Cl]$

CCDC deposition number	2060578
Empirical formula	$C_{66}H_{81}Cl_3F_2N_6P$
Formula weight	1133.68
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	12.4753(4)
b/Å	15.7403(5)
c/Å	17.5125(6)
α/°	70.944(2)
β/°	82.683(2)
γ/°	75.308(2)
Volume/Å^3	3140.38(18)
Z	2

ρ_{calc}g/cm^3	1.145
μ/mm^{-1}	0.181
F(000)	1994
Crystal size/mm^3	0.29 × 0.28 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.404 to 59.168
Index ranges	$-17 \le h \le 17$, $-28 \le k \le 28$, $-30 \le l \le 30$
Reflections collected	92726
Independent reflections	29960 [R_{int} = 0.0252, R_{sigma} = 0.0279]
Data/restraints/parameters	29960/60/1302
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0406, wR_2 = 0.1040
Final R indexes [all data]	R_1 = 0.0495, wR_2 = 0.1095
Largest diff. peak/hole / e Å^{-3}	0.55/-0.29

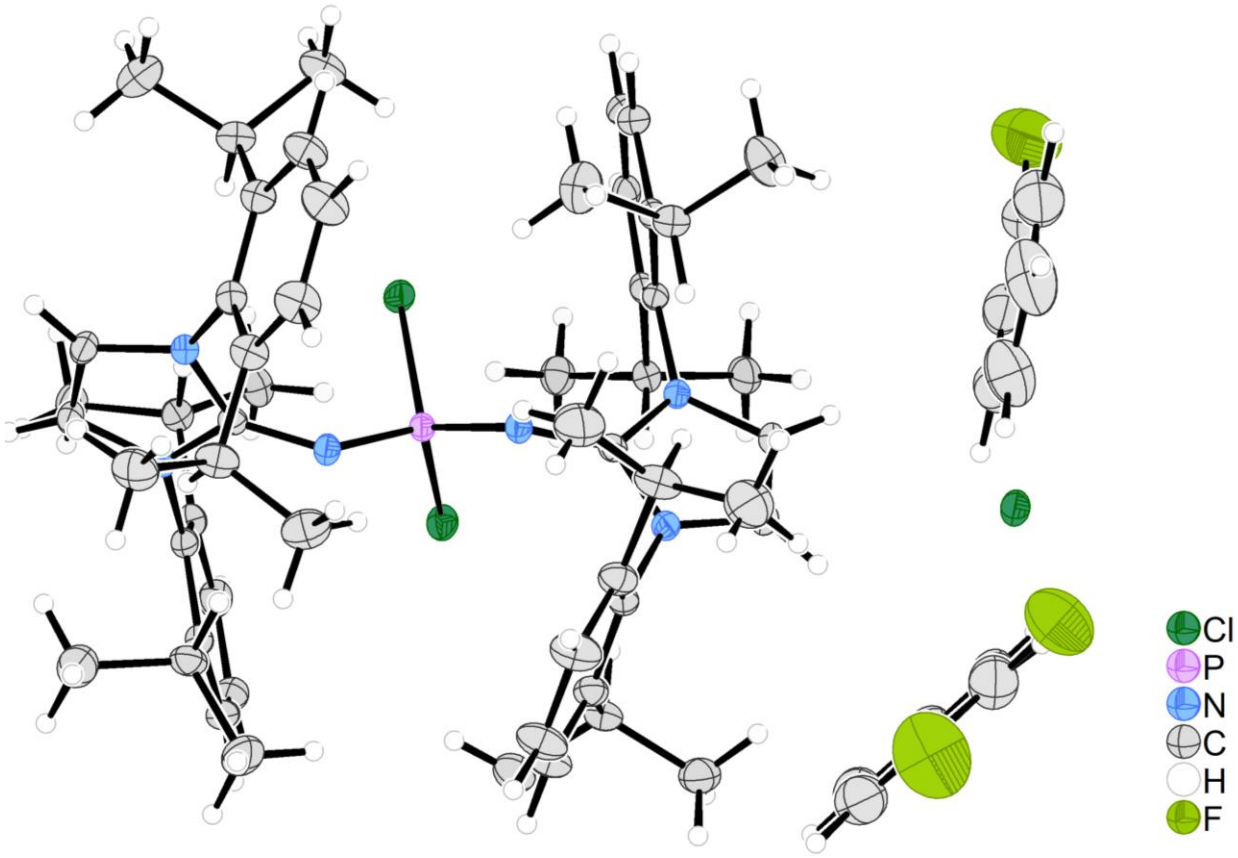


Figure S 43: Molecular view of $[(R^1)_2PCl_2][Cl]$ in the solid state. The asymmetric unit contains one molecule of $[(R^1)_2PCl_2][Cl]$ and two molecules of fluorobenzene. One of the latter has its fluorine atom disordered over two positions.

3.2 **Crystal structure data of compound 3**

CCDC deposition number	2057624
Empirical formula	$C_{55.5}H_{75.5}ClN_6PS$
Formula weight	925.19
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	12.5153(3)
b/Å	20.6933(4)
c/Å	21.8690(5)
α/°	97.8224(10)
β/°	104.4821(10)
γ/°	96.7163(11)
Volume/Å^3	5365.0(2)
Z	4

ρ_{calc}g/cm^3	1.145
μ/mm^{-1}	0.181
F(000)	1994
Crystal size/mm^3	0.29 × 0.28 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.404 to 59.168
Index ranges	-17 ≤ h ≤ 17, -28 ≤ k ≤ 28, -30 ≤ l ≤ 30
Reflections collected	92726
Independent reflections	29960 [R_{int} = 0.0252, R_{sigma} = 0.0279]
Data/restraints/parameters	29960/60/1302
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0406, wR_2 = 0.1040
Final R indexes [all data]	R_1 = 0.0495, wR_2 = 0.1095
Largest diff. peak/hole / e Å^{-3}	0.55/-0.29

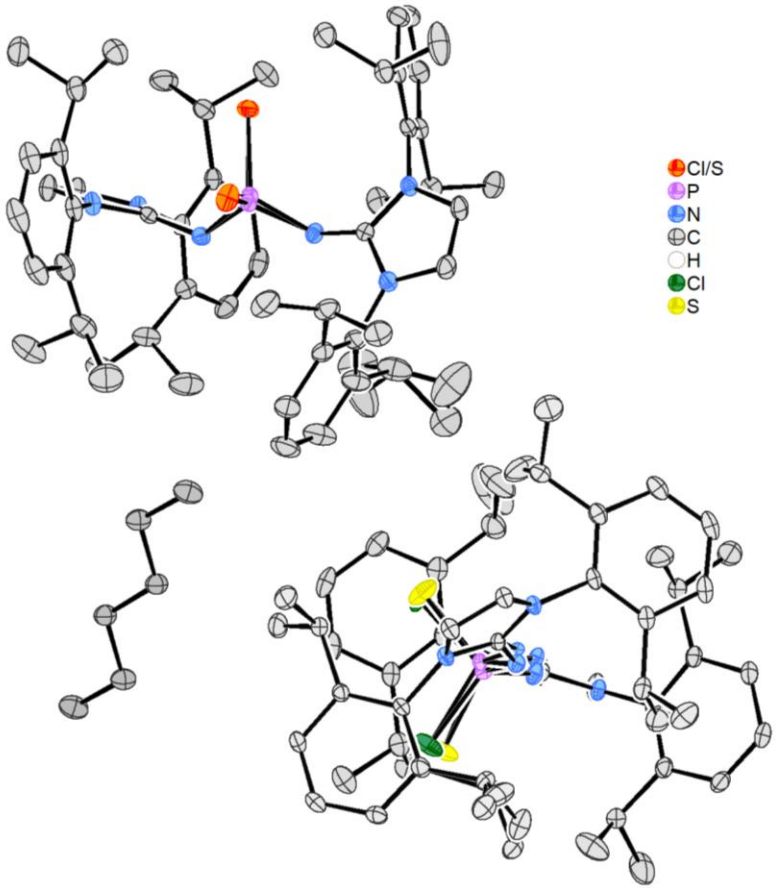


Figure S 44: Molecular view of **3** in the solid state. The asymmetric unit contains two molecules of **3** and half a molecule of hexane. In one molecule of **3**, the PSCl moiety is disordered over two positions with the Cl and the S atom alternately occupying the same positions. In the other molecule of **3**, the PN_2SCl moiety is disordered over two positions.

3.3 **Crystal structure data of compound [4][BArF$_{24}$]**

CCDC deposition number	2057623
Empirical formula	$C_{88}H_{88}BCl_4F_{24}N_6PS$
Formula weight	1901.28
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	12.5476(3)
b/Å	18.3022(4)
c/Å	20.6150(5)
α/°	83.0761(13)
β/°	77.4361(13)
γ/°	79.3360(12)
Volume/Å^3	4525.10(19)
Z	2

ρ_{calc}g/cm^3	1.395
μ/mm^{-1}	1.395
F(000)	0.269
Crystal size/mm^3	1956
Radiation	0.59 × 0.58 × 0.24
2Θ range for data collection/°	MoKα (λ = 0.71073)
Index ranges	2.918 to 59.238
Reflections collected	-17 ≤ h ≤ 17, -25 ≤ k ≤ 25, -28 ≤ l ≤ 28
Independent reflections	77013
Data/restraints/parameters	25293 [R_{int} = 0.0254, R_{sigma} = 0.0264]
Goodness-of-fit on F^2	25293/0/1142
Final R indexes [I>=2σ (I)]	1.005
Final R indexes [all data]	R_1 = 0.0450, wR_2 = 0.1178
Largest diff. peak/hole / e Å^{-3}	R_1 = 0.0528, wR_2 = 0.1239

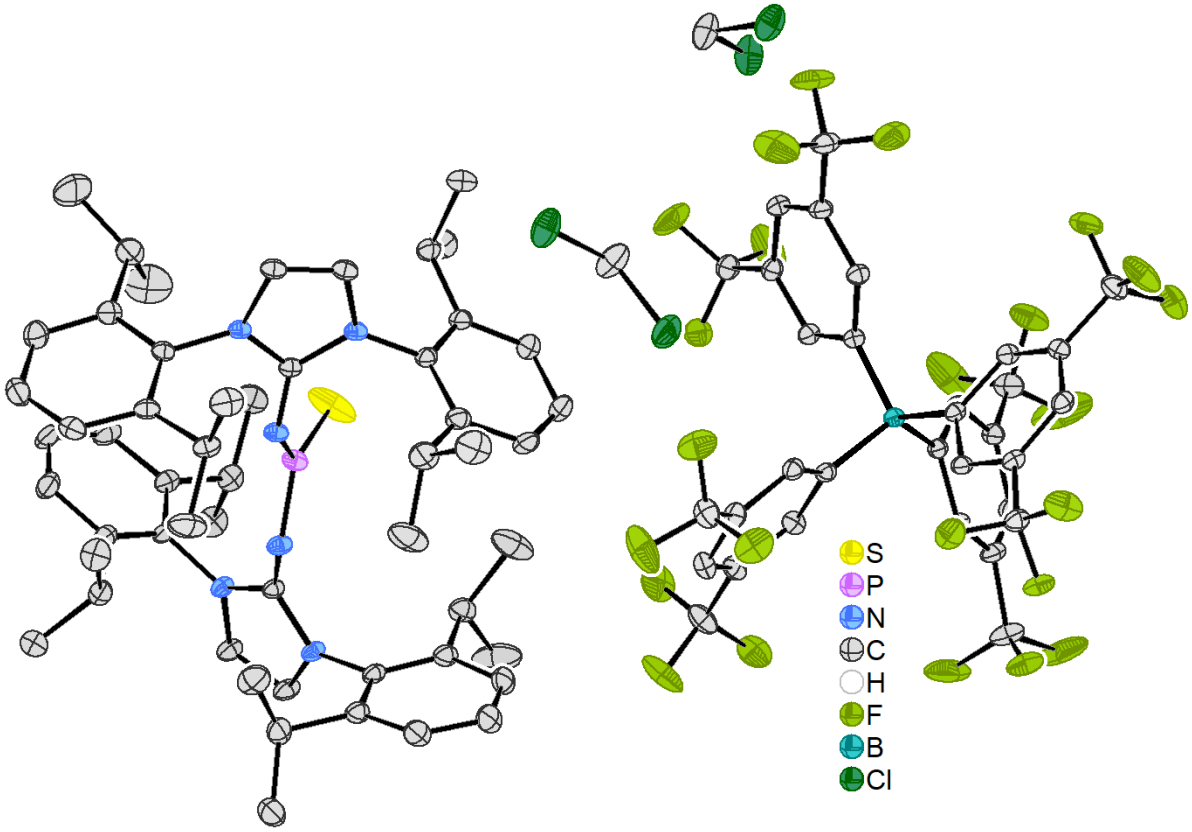


Figure S 45: Molecular view of [**4**][BArF$_{24}$] in the solid state. The asymmetric unit contains one molecule of [**4**][BArF$_{24}$] and two molecules of CH_2Cl_2.

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