

1,3-Dipolar Cycloaddition Reactions of Triflatophosphanes to Functionalized Azaphospholium salts and Azaphospholes

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1. General remarks, materials and methods

Manipulations were performed in a Glovebox MB Unilab or using Schlenk techniques under an atmosphere of purified nitrogen or argon, respectively. All glassware was oven-dried at 160 °C prior to use.

Dry, oxygen-free **solvents** (CH₂Cl₂, C₆H₅F, *o*-C₆H₄F₂, EtOAc, CHCl₃, NEt₃, CH₃CN, MeNO₂, C₂H₄Cl₂ (distilled from CaH₂), *n*-hexane, *n*-pentane, THF, Et₂O, Toluene, Benzene (distilled from potassium)) were employed. All distilled and deuterated solvents were stored over 4 Å molecular sieves (except CD₃CN and CH₃CN). Compounds **11**[OTf]¹, **30**[OTf]¹, **22**[OTf]² and **23**[OTf]³ were synthesized according to literature procedures. Additional reagents were obtained from commercial sources and used as received.

NMR spectra were measured on a Bruker *AVANCE III HD Nanobay 400 MHz UltraSield* (¹H (400.13 MHz), ¹³C (100.61 MHz), ³¹P (161.98 MHz) ¹⁹⁵Pt (86.01 MHz)) or on a Bruker *AVANCE III HDX, 500 MHz Ascend* (¹H (500.13 MHz), ¹³C (125.75 MHz), ³¹P (202.45 MHz)). All ¹³C NMR spectra were exclusively recorded with composite pulse decoupling. Reported numbers assigning atoms in the ¹³C spectra were indirectly deduced from the cross-peaks in 2D correlation experiments (HMBC, HSQC). Chemical shifts were referenced to δ_{TMS} = 0.00 ppm (¹H, ¹³C), δ_{H₃PO₄(85%)} = 0.00 ppm (³¹P) and δ_{K₂PtCl₆} = 0.00 ppm (¹⁹⁵Pt). Chemical shifts (δ) are reported in ppm. Coupling constants (*J*) are reported in Hz.

Simultaneous thermal analysis (STA) was conducted with a *STA 8000* apparatus (Perkin Elmer) under helium gas flow (20 mL/min) and a heating rate of 20 K/min. The “decomposition” temperature was obtained from 5 % weight loss and is disclosed as **T₉₅**.

Melting points were recorded on an electrothermal melting point apparatus (Büchi Switzerland, Melting point M-560) in sealed capillaries under Argon atmosphere or were deduced from STA measurements and are uncorrected.

Infrared (IR) and **Raman** spectra were recorded at ambient temperature using a *Bruker Vertex 70* instrument equipped with a RAM II module (Nd-YAG laser, 1064 nm). The Raman intensities are reported in percent relative to the most intense peak and are given in parenthesis. An ATR unit (diamond) was used for recording IR spectra. The intensities are reported relative to the most intense peak and are given in parenthesis using the following abbreviations: vw = very weak, w = weak, m = medium, s = strong, vs = very strong.

Elemental analyses were performed on a *Vario MICRO cube* Elemental Analyzer by Elementar Analysatorsysteme GmbH in CHNS mode.

Sample preparation for optical spectroscopy was conducted with a host matrix PMMA and the respective compound. Both were dissolved in chloroform with a doping concentration of 5 wt%. Films were prepared via spin-coating by dropping 180 µL blended solutions onto 1-inch quartz substrates with a spin speed of 1200 rpm and spin time of 60 s, and then annealed at 80 °C for 2 min. Solutions were prepared in chloroform at a concentration of 10⁻⁴ mol/L.

Optical spectroscopy. Absorption spectra were collected using a UV-vis-NIR 3600 double beam spectrophotometer (Shimadzu). Steady-state and delayed spectra were recorded using a 275 nm

M275L4 LED, 340 nm M340L4 LED or a 365 nm M365L2 LED (Thorlabs), a Spectrometer CAS 140CT-151 (Instrument Systems) and a TGP3122 pulse generator (AIM-TTI Instruments), the latter was acquired shortly after the trigger pulse and LED light off in nitrogen atmosphere. Photoluminescence quantum yields (PLQYs) were recorded using a setup consisting of a 340 nm LED (M340L4) as the excitation source, a calibrated integrating sphere (Labsphere RTC-060-SF), and an array spectrometer (CAS140CT, Instrument Systems). The PLQY values were determined based on the method proposed by de Mello⁴ et al. and improved by F. Fries⁵ et al. For fluorescence QYs, samples were measured in ambient atmosphere. Nitrogen atmosphere was purged to remove oxygen for the measurement of delayed spectra and phosphorescence PLQYs.

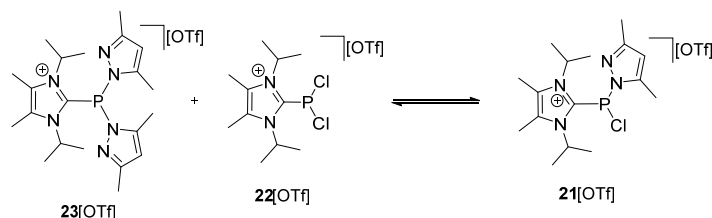
Electrochemical (EC) measurements such as cyclic voltammetry (CV), square wave voltammetry (SWV) and chronoamperometry (CA) were performed in a Glovebox Pure Lab HE GP-1 SR (Innovative Technology, USA) in an atmosphere of purified nitrogen (< 0.1 ppm O₂; < 0.1 ppm H₂O). The glovebox was equipped with military grade BNC feedthroughs in a custom-made gas tight flange for low noise electrical connection of the electrochemical cells inside. EC cells were connected to a PGSTAT302 (Metrohm Autolab, Utrecht, The Netherlands) $E = \pm 10$ V, $U = \pm 35$ V. NOVA Software (Metrohm Autolab) Version 1.11.2 was used to control the potentiostat and magnetic stirring. Data analysis of the electrochemical data was performed using OriginPro 2019 (OriginLab Cooperation, Northampton, MA, USA).

EC measurements were performed in 10 mL electrochemical cells using platinum disk electrodes (1,6 mm diameter, ALS Co. Ltd., Japan) as working electrodes. The electrodes were polished with 1 μ m Diamond polishing paste and then 0.05 μ m polishing alumina on separate polishing pads prior to use. A Pt wire coil (200 mm length, 0.5 mm width) was used as counter electrode without separation. A reference electrode consisting of a silver wire in a solution of 0.01 M AgNO₃ in 0.1 M [Bu₄N][OTf] supporting electrolyte solution in CH₂Cl₂ and separated from the substrate solution by a Vycor Frit was used. Ferrocene was used to reference the potentials obtained in CV and SWV experiments to a potential of $E_{1/2} = 0$ V according to IUPAC convention.

[*n*-Bu₄N][OTf] was pre-dried at least 5 times by dissolving in CH₂Cl₂ and evaporating the solvent to high vacuum at 80 °C. Final drying and removal of HOTf traces was achieved by dissolving in dry benzene and refluxing this solution in a Soxhlet apparatus for 5 days with vacuum activated molecular sieves in the extraction thimble renewed every day. Prior to each measurement the electrolyte stock solution is passed through a Pasteur pipette with an activated (1·10⁻³ mbar, 350 °C, 24 h) aluminum oxide bed (D = 5 mm; L = 70 mm) in the glove box before the substrate is added.

2. Synthetic details and characterization data

2.1. Scrambling reactions of $L_cPCl_2[OTf]$ and $L_cP(Pyrr)_2[OTf]$



Scheme S 1: Scrambling reaction between **23[OTf]** and **22[OTf]** to **21[OTf]**.

23[OTf] (15.4 mg, 0.028 mmol, 1.0 equiv.), **22[OTf]** (12 mg, 0.028 mmol, 1.0 equiv.) are dissolved in 0.3 mL of CH_2Cl_2 and stirred at room temperature. In the time between preparing the sample and measuring the ^{31}P NMR spectrum an equilibrium between the three species **23[OTf]**, **22[OTf]** and **21[OTf]** has established, that did not change even after three days of consecutive stirring.

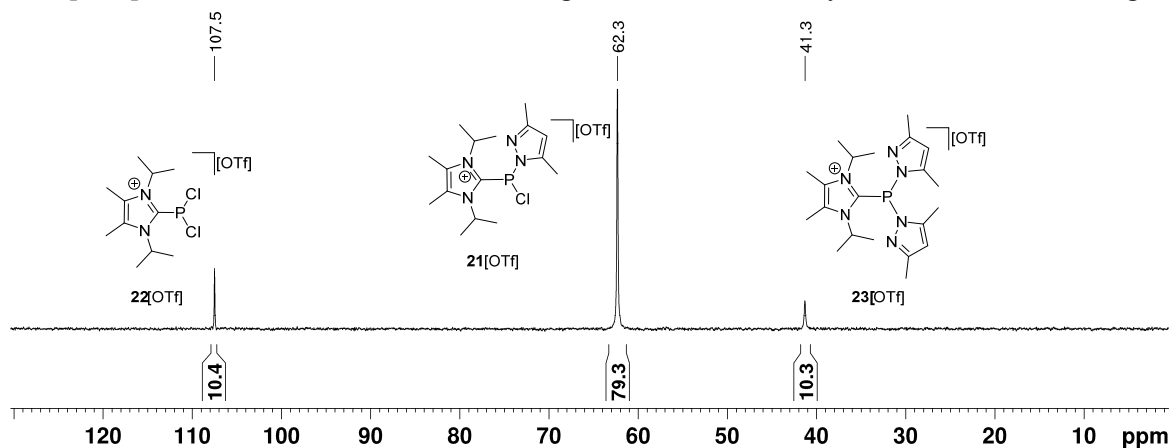
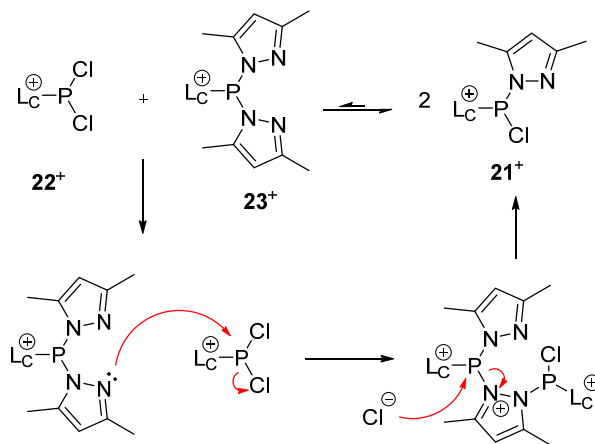


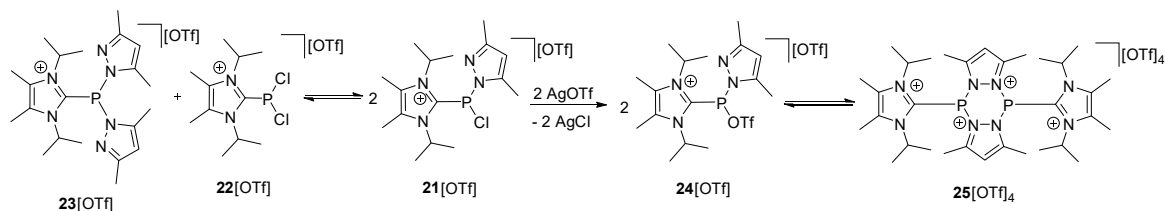
Figure S 1: ^{31}P NMR spectrum of the reaction of **22[OTf]** and **23[OTf]** in CH_2Cl_2 after stirring for 3 days. (300 K, C_6D_6 ref.)

Mechanistically, we assume that first a nucleophilic attack of the pyrazole N atom in **23⁺** at the P atom of **22⁺**, leading to the formation of a chloride anion. In a subsequent second nucleophilic attack the free chloride anion attacks at the central P atom and **21⁺** is formed, respectively.



Scheme S 2: Proposed Mechanism of the scrambling of **22⁺** and **23⁺** to **21⁺**.

2.2. Scrambling reactions of 23[OTf] and 22[OTf] in the presence of two equivalents of AgOTf



Scheme S 3: Reaction of *in situ* formed 21[OTf] with AgOTf to 24[OTf] and 25[OTf]₄.

22[OTf] (30 mg, 0.07 mmol, 1.0 equiv.), 23[OTf] (38.9 mg, 0.07 mmol, 1.0 equiv.) and AgOTf (39.4 mg, 0.153 mmol, 2.2 equiv.) are suspended in 2 mL of CH₂Cl₂ and stirred at room temperature for 4 h. The resulting suspension is filtered and the filtrate used for NMR-studies. For high temperature NMR-studies the solvent was removed and the residue dissolved in *o*-C₆H₄Cl₂. The obtained ³¹P{ }-NMR spectrum shows two sharp peaks ($\delta = 86.4$ ppm, $\delta = 34.7$ ppm; for *o*-C₆H₄Cl₂: $\delta = 78.3$ ppm, $\delta = 26.9$ ppm; **Figure S 2**) which are attributed to an equilibrium, resulting from the dimerization of 24[OTf] by coordination of the pyrazole N atom to the electrophilic P atom. This equilibrium can be slightly shifted by heating the sample. At higher temperature (350 K) the integral of the resonance with a chemical shift of 26.9 ppm decreases. This behaviour can be reversed by cooling the sample again.

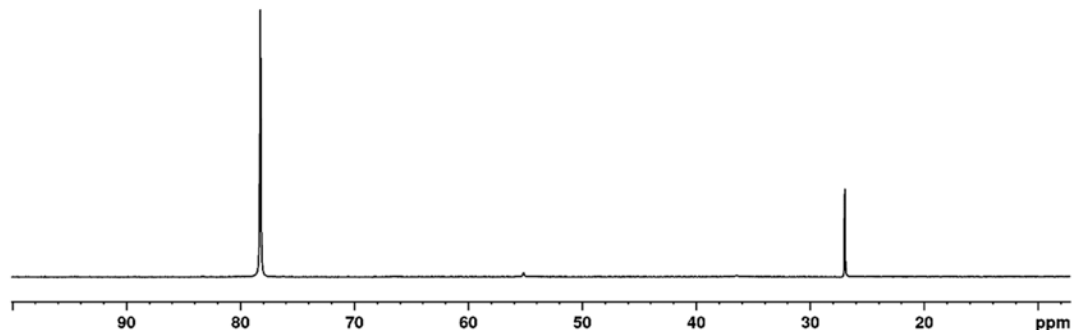


Figure S 2: ³¹P{ }-NMR spectrum of a mixture of 22[OTf], 23[OTf] and two equivalents of AgOTf in *o*-C₆H₄Cl₂ after stirring for 4 h. (300 K, C₆D₆ reference)

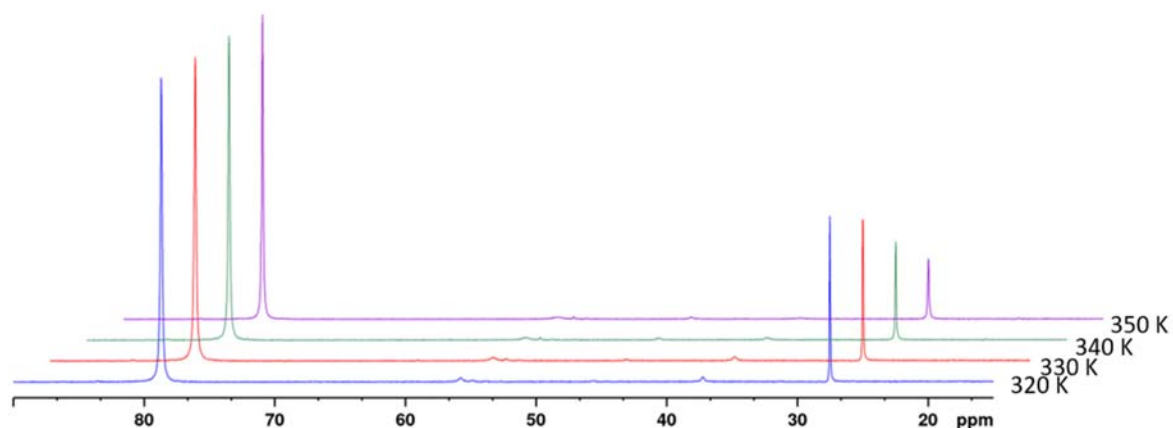


Figure S 3: Variable temperature $^{31}\text{P}\{-}$ -NMR spectra of a mixture of **22**[OTf], **23**[OTf] and two equivalents of AgOTf in *o*- $\text{C}_6\text{H}_4\text{Cl}_2$ after stirring for 4 h. (300 K, C_6D_6 reference)

To further underline this interpretation we investigated the reaction mixture in $^{31}\text{P}\{-}^{31}\text{P}\{-}$ -EXSY (Exchange Spectroscopy) NMR-experiments which revealed a chemical exchange between both resonances of **24**[OTf] and **25**[OTf]₄.

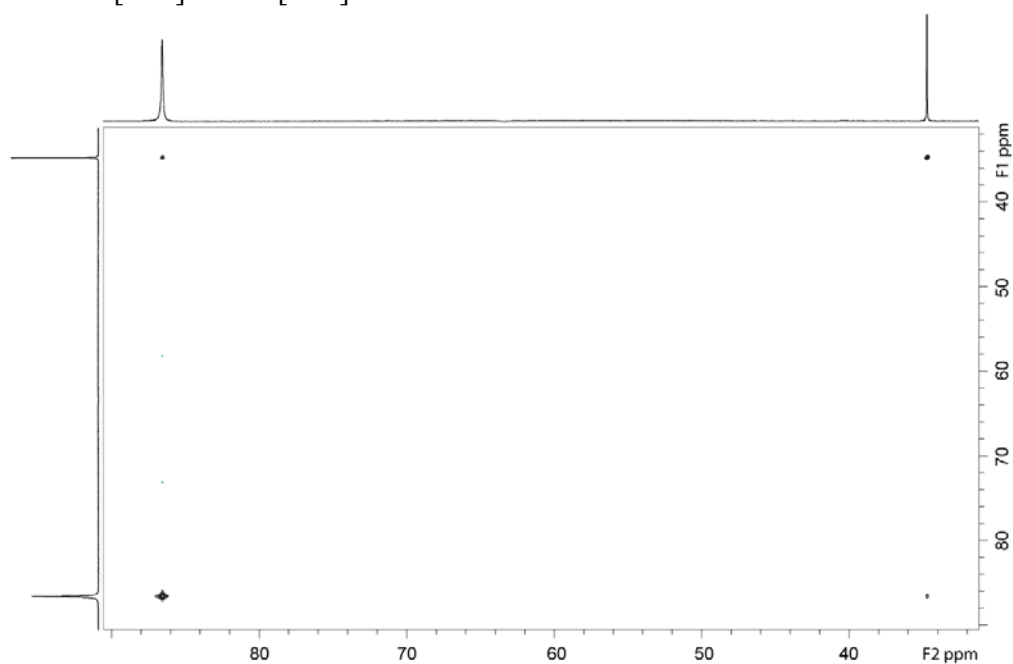


Figure S 4: $^{31}\text{P}\{-}^{31}\text{P}\{-}$ -EXSY NMR-spectrum of a mixture of **22**[OTf], **23**[OTf] and two equivalents of AgOTf in CH_2Cl_2 after stirring for 4 h. (300 K, C_6D_6 reference)

By slow diffusion of n-pentane in to a CH_2Cl_2 solution of **24**[OTf] at $-30\text{ }^\circ\text{C}$, single crystals suitable for X-Ray diffraction were obtained.

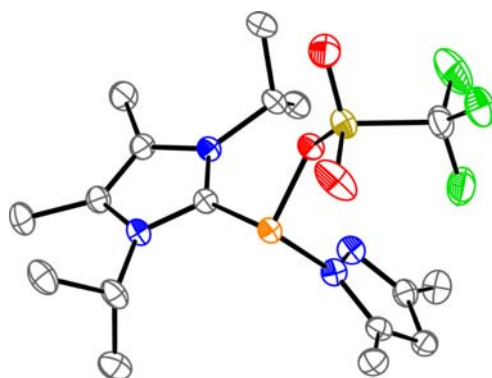
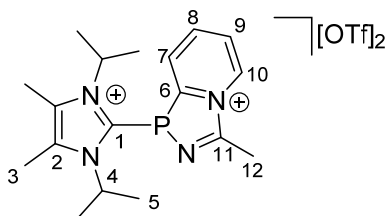


Figure S 5: Molecular structure of 24^+ in $24[\text{OTf}]\cdot\text{CH}_2\text{Cl}_2$; thermal ellipsoids are displayed at 50 % probability level, solvate molecules, hydrogen atoms and counterions are omitted for clarity

2.3. Cycloaddition reactions of 6[OTf] with Nitriles and (Thio)-Cyanates

2.3.1. Synthesis of 9a[OTf]₂



11[OTf] (300 mg, 0.630 mmol, 1.0 equiv.) and silver triflate (162 mg, 0.630 mmol, 1.0 equiv.) are suspended in 3 mL of CH₃CN and stirred at 40 °C for 2 h in a microwave oven. The resulting solid is filtered off and 3 mL of Et₂O are added to the solution, resulting in the formation of a colourless precipitate. By filtration and washing with Et₂O, **9a[OTf]₂** is obtained as a colourless, air

and moisture sensitive solid. Suitable crystals for X-ray diffraction analysis can be obtained by slow diffusion of Et₂O to a CH₃CN solution at -30 °C.

Yield: 320 mg (81 %); **m.p.** 229 °C (decomp.); **Raman**(80 mW, 200 scans, 298 K, cm⁻¹): 3100 (8), 3072 (9), 2990 (27), 2949 (51), 1657 (28), 1606 (35), 1558 (13), 1464 (28), 1448 (25), 1400 (33), 1383 (16), 1368 (21), 1271 (56), 1226 (20), 1193 (18), 1151 (35), 1075 (80), 1037 (100), 887 (18), 804 (15), 755 (38), 709 (13), 604 (11), 573 (23), 558 (13), 544 (17), 519 (20), 348 (33), 313 (41), 291 (16), 269 (18); **IR** (ATR, 298 K, cm⁻¹): 3137 (vw), 3071 (vw), 3002 (vw), 2962 (vw), 1655 (w), 1605 (w), 1465 (w), 1412 (w), 1398 (w), 1376 (w), 1257 (vs), 1222 (s), 1192 (w), 1167 (w), 1140 (vs), 1115 (m), 1089 (w), 1029 (s), 802 (w), 778 (w), 753 (w), 634 (vs); **¹H NMR** (CD₃CN, 298 K, in ppm) δ = 1.39 (6H, d, ³J_{HH} = 6.24 Hz, H5), 1.57 (6H, d, ³J_{HH} = 6.88 Hz, H5), 2.41 (6H, s, H3), 3.13 (3H, d, J_{HH} = 7.32 Hz, H12), 4.12 (2H, s(br), H4), 8.40 (1H, m, H9), 8.79 (1H, m, H8), 8.86 (1H, d, ³J_{HH} = 7.88 Hz, H7), 9.63 (1H, m, H10); **¹³C{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = 11.40 (2C, s, C3), 21.25 (2C, s(br), C5), 18.78 (1C, d, ³J_{CP} = 3 Hz, C12), 21.61 (2C, s(br), C5), 55.21 (1C, s, C4), 55.31 (1C, s, C4), 122.05 (2C, q, ¹J_{CF} = 320 Hz, OTf), 127.70 (1C, d, ¹J_{CP} = 48 Hz, C1), 129.43 (1C, s, C9), 131.36 (1C, d, ²J_{CP} = 11 Hz, C7), 136.70 (2C, s, C2), 142.85 (1C, d, ³J_{CP} = 3 Hz, C10), 147.04 (1C, d, ³J_{CP} = 6 Hz, C8), 158.74 (1C, d, ¹J_{CP} = 29 Hz, C6), 163.04 (1C, m, C11); **¹⁹F{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = -79.2 (s); **³¹P{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = 21.6 (s); **elemental analysis:** calculated for C₂₀H₂₇F₆N₄O₆PS₂: N 8.91, C 38.22, H 4.33, S 10.20; found: N 8.81, C 38.40, H 3.99, S 10.19.

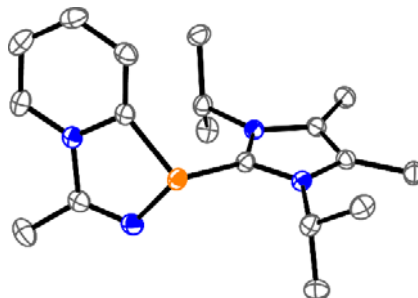


Figure S 6: Molecular structure of **9a²⁺** in **9a[OTf]₂**; thermal ellipsoids are displayed at 50 % probability level, hydrogen atoms and counterions are omitted for clarity.

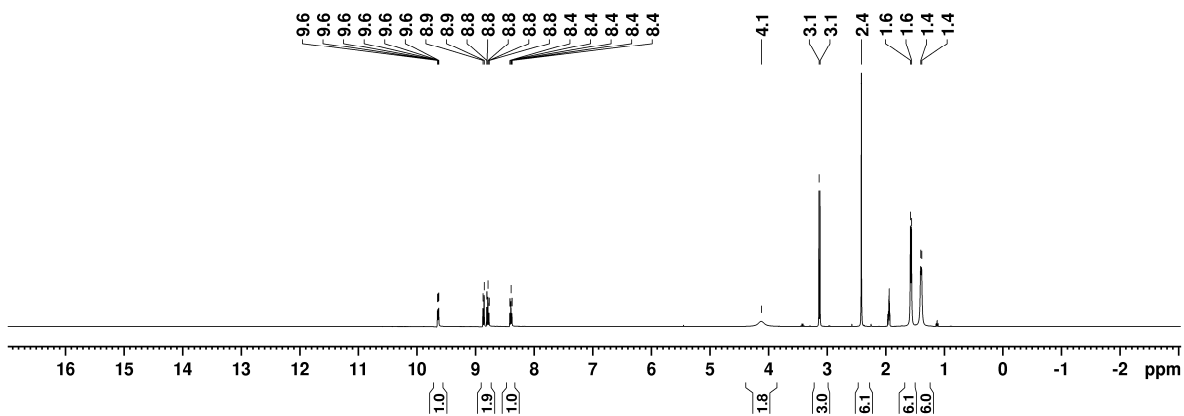


Figure S 7: ^1H NMR spectrum of $9\mathbf{a}[\text{OTf}]_2$ in CD_3CN .

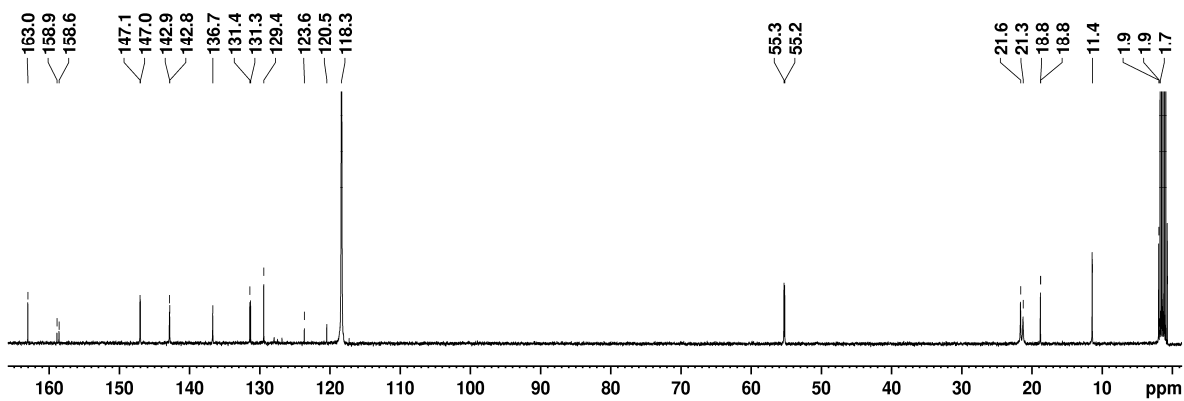


Figure S 8: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $9\mathbf{a}[\text{OTf}]_2$ in CD_3CN .

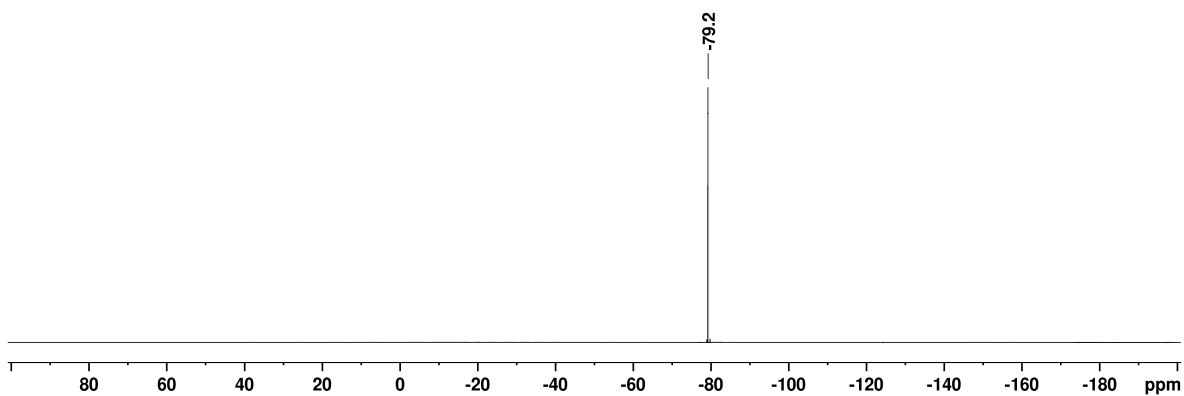


Figure S 9: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of $9\mathbf{a}[\text{OTf}]_2$ in CD_3CN .

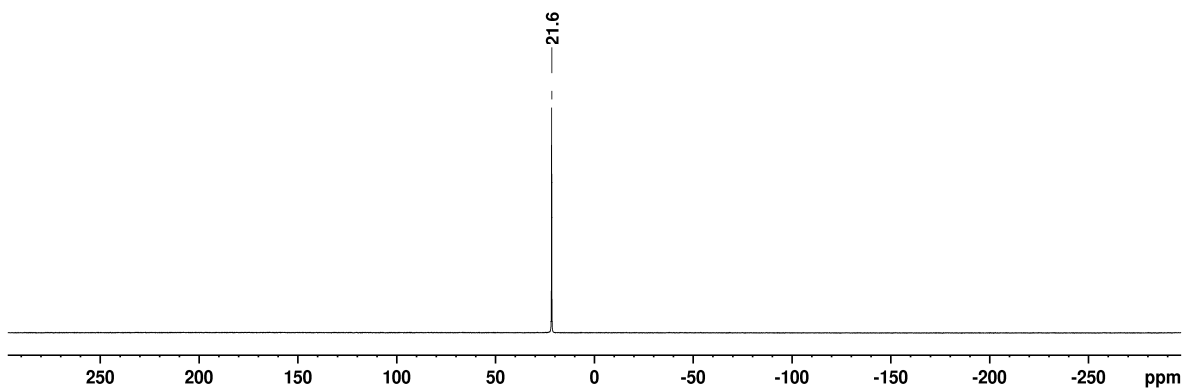
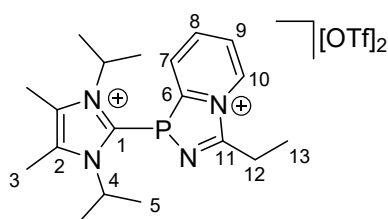


Figure S 10: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **9a**[OTf]₂ in CD₃CN.

2.3.2. Synthesis of **9b**[OTf]₂



11[OTf] (300 mg, 0.630 mmol, 1.0 equiv.) and silver triflate (162 mg, 0.630 mmol, 1.0 equiv.) are suspended in 3 mL of EtCN and stirred at 40 °C for 2 h in a microwave oven. The resulting solid is filtered off and 3 mL of Et₂O are added to the solution, resulting in the formation of a colourless precipitate. By filtration and washing with Et₂O, **9b**[OTf]₂ is obtained as a colorless, air

and moisture sensitive solid. Suitable crystals for X-ray diffraction analysis can be obtained by slow diffusion of Et₂O to a CH₃CN solution at –30 °C.

Yield: 166 mg (41 %); **m.p.** 208 °C (decomp.); **Raman** (20 mW, 200 scans, 298 K, cm⁻¹): 3009 (29), 2998 (43), 2984 (43), 2948 (100), 2934 (100), 2902 (29), 2888 (29), 2203 (29), 2185 (29), 2158 (29), 2146 (43), 2137 (43), 2113 (29), 2097 (29), 2076 (29), 2062 (29), 1602 (14), 1505 (43), 1457 (29), 1443 (14), 1403 (29), 1387 (29), 1352 (14), 1295 (14), 1273 (71), 1224 (14), 1149 (29), 1087 (29), 1073 (57), 1055 (29), 1034 (57), 758 (29), 283 (29), 259 (71), 249 (71), 226 (71), 204 (57), 189 (57), 179 (57), 169 (57); **IR** (ATR, 298 K, cm⁻¹): 3133 (vw), 3095 (vw), 3005 (vw), 2954 (vw), 1639 (vw), 1603 (w), 1462 (w), 1415 (w), 1400 (w), 1377 (w), 1272 (vs), 1246 (vs), 1222 (vs), 1151 (vs), 1117 (m), 1091 (w), 1073 (w), 1028 (vs), 830 (w), 798 (w), 782 (m), 754 (w), 634 (vs); **¹H NMR** (CD₃CN, 298 K, in ppm) δ = 1.40 (6H, d, ³J_{HH} = 5.92 Hz, H5), 1.52 (3H, t, ³J_{HH} = 7.06 Hz, H13), 1.57 (6H, d, ³J_{HH} = 6.84 Hz, H5), 2.41 (6H, s, H3), 3.28-3.66 (2H, m, H12), 4.12 (2H, s(br), H4), 8.39 (1H, m, H9), 8.78 (1H, m, H8), 8.84 (1H, d, ³J_{HH} = 7.72 Hz, H7), 9.63 (1H, m, H10); **¹³C{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = 8.77 (1C, s, C13), 10.38 (2C, s, C3), 20.25 (2C, s, C5), 20.61 (2C, s, C5), 24.70 (1C, s, C12), 54.15 (1C, s, C4) 54.26 (1C, s, C4), 121.06 (2C, q, ¹J_{CF} = 320 Hz, OTf), 126.73 (1C, d, ¹J_{CP} = 52 Hz, C1), 128.45 (1C, s, C9), 130.46 (1C, d, ²J_{CP} = 11.53 Hz, C7), 135.69 (2C, s, C2), 141.29 (1C, d, ³J_{CP} = 2.39 Hz, C10), 146.14 (1C, d, ³J_{CP} = 6.18 Hz, C8), 158.08 (1C, d, ¹J_{CP} = 28.95 Hz, C6), 166.06 (1C, s, C11); **¹⁹F{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = -79.3 (s); **³¹P{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = 22.6 (s); **elemental analysis:** calculated for C₂₁H₂₉F₆N₄O₆PS₂: N 8.72, C 39.25, H 4.55, S 9.98; found: N 8.70, C 39.23, H 4.33, S 9.99.

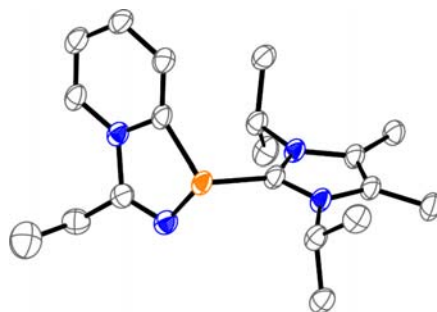


Figure S 11: Molecular structure of **9b**²⁺ in **9b**[OTf]₂; thermal ellipsoids are displayed at 50 % probability level, hydrogen atoms and counterions are omitted for clarity.

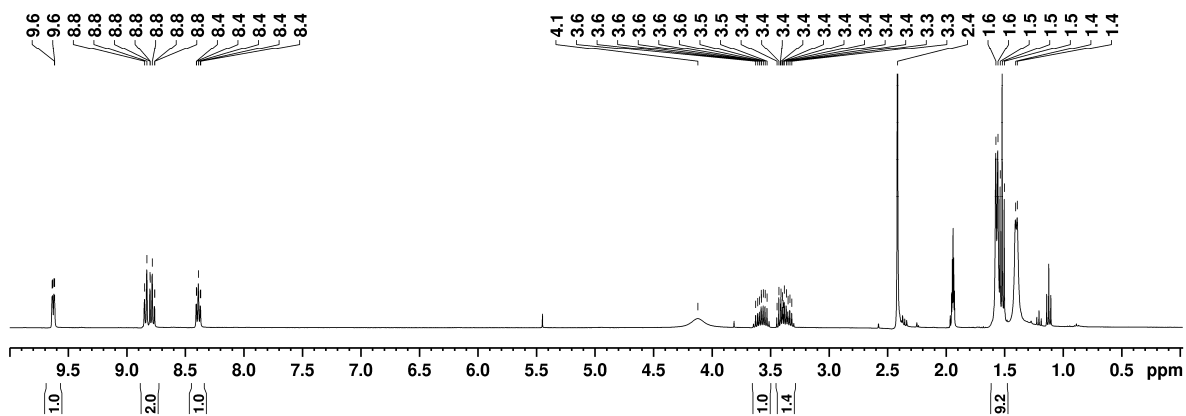


Figure S 12: ^1H NMR spectrum of **9b**[OTf] $_2$ in CD_3CN .

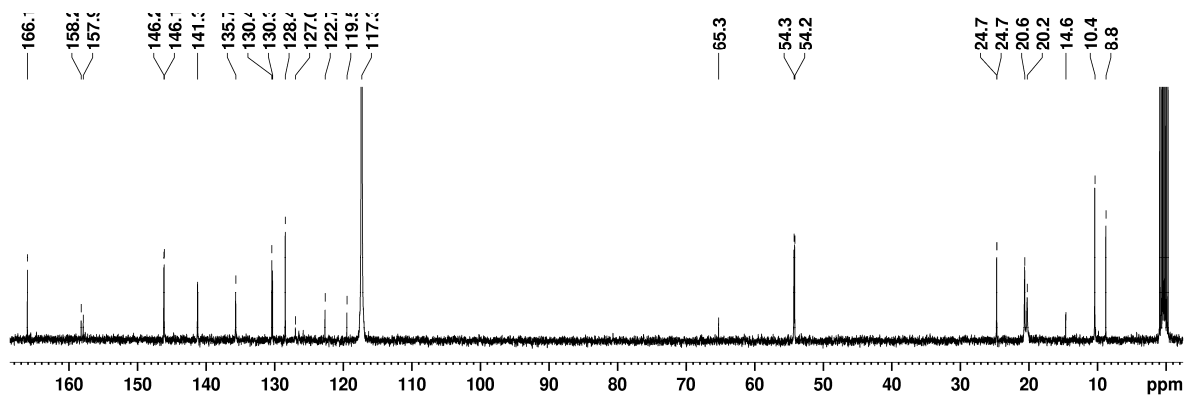


Figure S 13: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **9b**[OTf] $_2$ in CD_3CN .

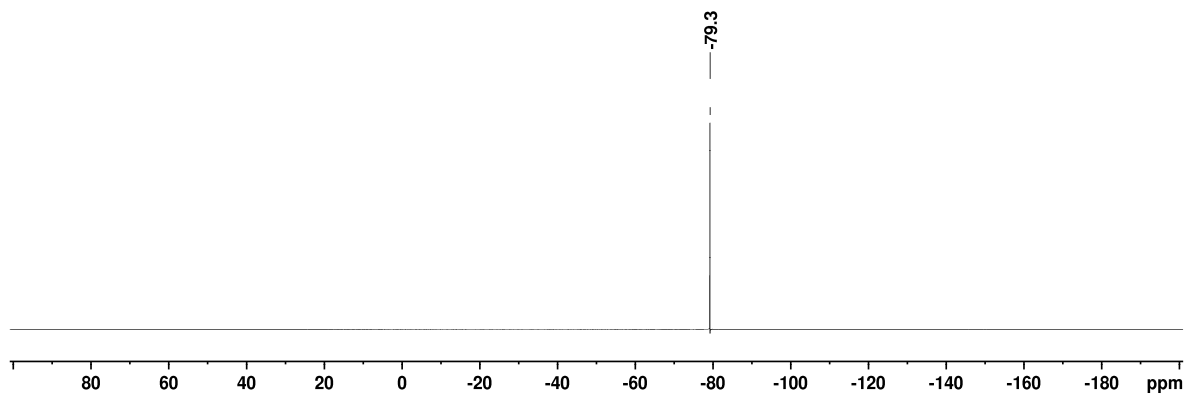


Figure S 14: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **9b**[OTf] $_2$ in CD_3CN .

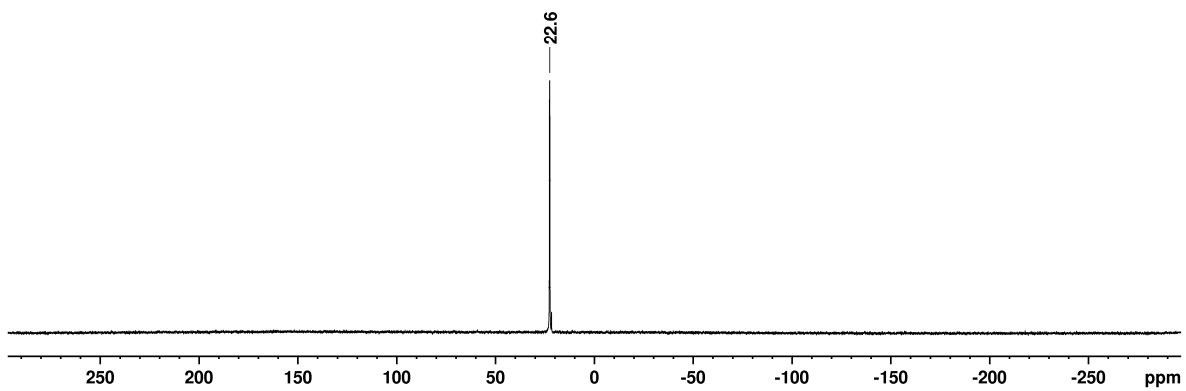
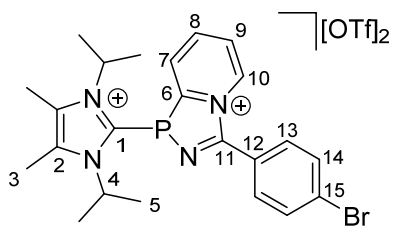


Figure S 15: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **9b**[OTf]₂ in CD₃CN.

2.3.3. Synthesis of **9c**[OTf]₂



11[OTf] (200 mg, 0.422 mmol, 1.0 equiv.), silver triflate (108 mg, 0.422 mmol, 1.0 equiv.) and 4-bromobenzonitrile (83 mg, 0.430 mmol, 1.0 equiv.) are suspended in 3 mL of C₂H₄Cl₂ and stirred for 2 h. The resulting solid is filtered off and all volatiles are removed *in vacuo*. By washing with Et₂O and filtration, **9c**[OTf]₂ is obtained as a colourless, air and moisture sensitive solid.

solid.

Yield: 266 mg (82 %); **m.p.** 125 °C (decomp.); **Raman** (80 mW, 200 scans, 298 K, cm⁻¹): 1623 (31), 1599 (100), 1555 (27), 1542 (18), 1454 (25), 1380 (12), 1276 (11), 1196 (22), 1096 (13), 1067 (12), 1045 (12), 1033 (14), 935 (14), 806 (18), 419 (23), 174 (14); **IR** (ATR, 298 K, cm⁻¹): 1625 (vw), 1599 (vw), 1587 (vw), 1461 (w), 1399 (w), 1378 (vw), 1254 (s), 1222 (s), 1149 (s), 1100 (m), 1071 (w), 1027 (vs), 942 (w), 903 (vw), 839 (w), 788 (w), 754 (w), 712 (vw), 675 (w), 635 (vs), 572 (m), 547 (w), 516 (s), 500 (m), 452 (w), 427 (w); **¹H NMR** (CD₂Cl₂, 298 K, in ppm) δ = 1.55 (6H, d, ³J_{HH} = 6.60 Hz, H5), 1.65 (6H, d, ³J_{HH} = 6.60 Hz, H5), 2.47 (6H, s, H3), 4.47 (2H, s(br), H4), 7.89 (2H, d, ³J_{HH} = 8.52 Hz, H13), 7.99 (2H, d, ³J_{HH} = 8.50 Hz, H14), 8.33 (1H, m, H9), 8.75 (1H, m, H8), 9.36 (1H, d, ³J_{HH} = 7.84 Hz, H7), 9.44 (1H, d, ³J_{HH} = 9.43 Hz, H10); **¹³C{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = 10.99 (2C, s, C3), 20.98 (2C, s, C5), 21.05 (2C, s, C5), 55.06 (1C, s, C4), 55.17 (1C, s, C4), 120.04 (2C, q, ¹J_{CF} = 319 Hz, OTf), 124.73 (1C, s, C15), 128.59 (1C, s(br), C1), 129.22 (1C, s, C9), 131.94 (1C, d, ²J_{CP} = 13 Hz, C7), 131.98 (1C, s, C12), 132.15 (2C, s, C14), 133.11 (2C, s, C13), 134.89 (2C, s, C2), 142.69 (1C, s, C10), 145.70 (1C, d, ³J_{CP} = 6 Hz, C8), 157.90 (1C, d, ¹J_{CP} = 33 Hz, C6), 160.13 (1C, s, C11); **¹⁹F{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = -78.6 (s); **³¹P{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = 27.0 (s); **elemental analysis:** calculated for C₂₅H₂₈BrF₆N₄O₆PS₂·0.25 Et₂O·MeCN: N 8.45, C 40.56, H 4.07, S 7.73; found: N 8.43, C 40.72, H 3.48, S 9.54. We found repeatable inconclusive results for the sulphur value in the elemental analysis of this compound and therefore abstain of any further analysis.

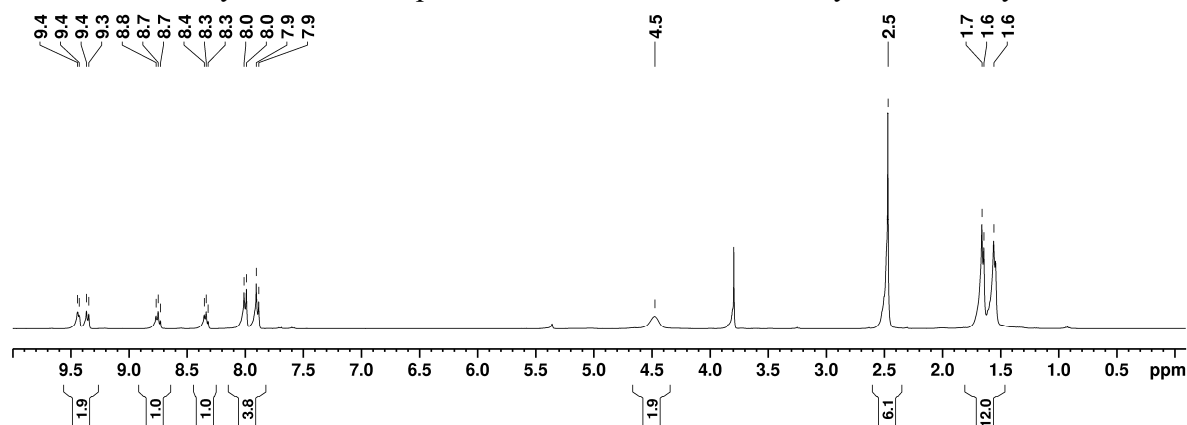


Figure S 16: ¹H NMR spectrum of **9c**[OTf]₂ in CD₂Cl₂.

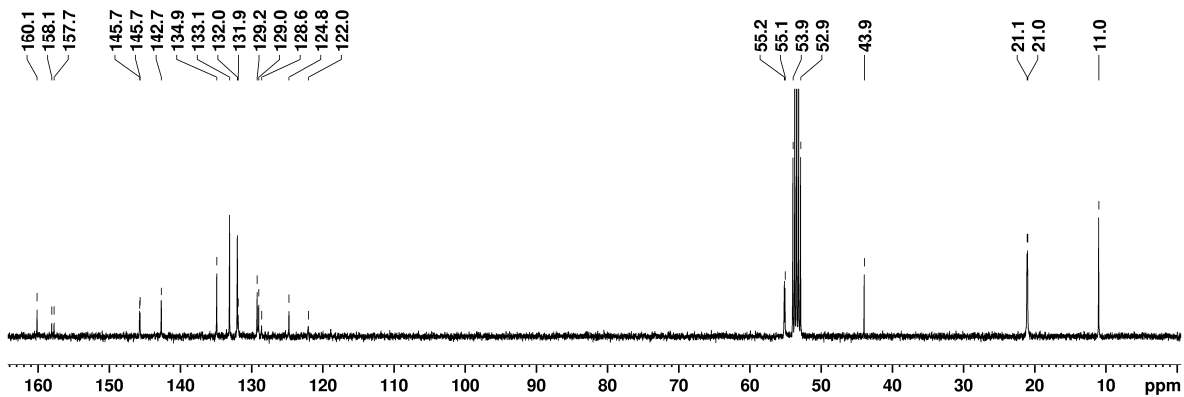


Figure S 17: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **9c**[OTf] $_2$ in CD_2Cl_2 .

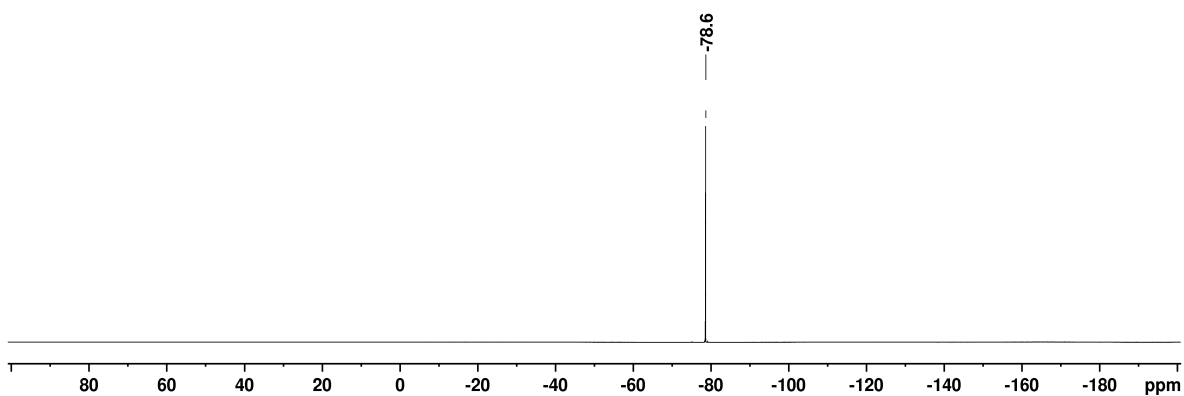


Figure S 18: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **9c**[OTf] $_2$ in CD_2Cl_2 .

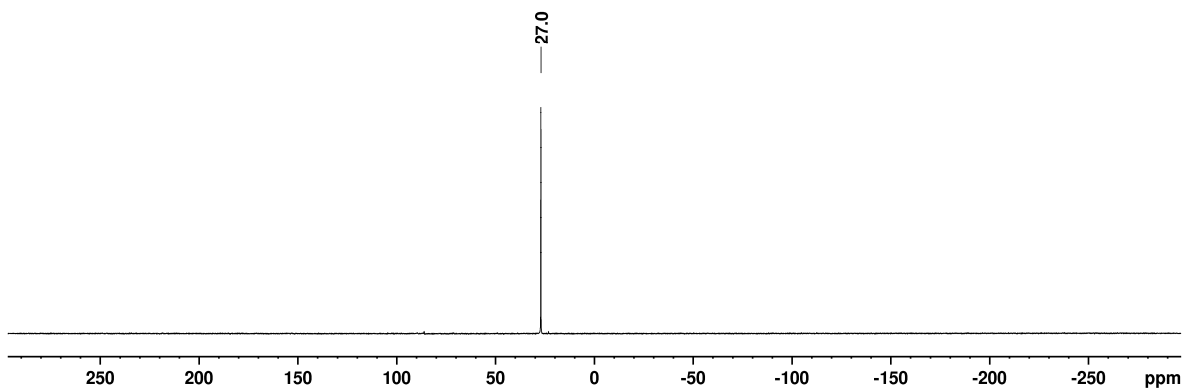
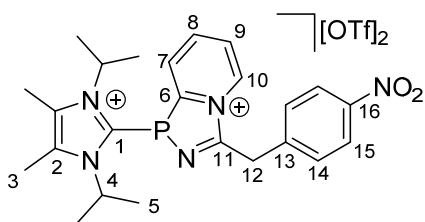


Figure S 19: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **9c**[OTf] $_2$ in CD_2Cl_2 .

2.3.4. Synthesis of **9d**[OTf]₂



11[OTf] (300 mg, 0.630 mmol, 1.0 equiv.), silver triflate (162 mg, 0.630 mmol, 1.0 equiv.) and 4-nitrophenylacetonitrile (112 mg, 0.690 mmol, 1.1 equiv.) are suspended in 3 mL of C₂H₄Cl₂ and stirred at 40 °C for 2 h in a microwave oven. The resulting solid is filtered off and 3 mL of Et₂O are added to the solution, resulting in the formation of a colourless precipitate.

By filtration and washing with Et₂O, **9d**[OTf]₂ is obtained as a colourless, air and moisture sensitive solid. Suitable crystals for X-ray diffraction analysis can be obtained by slow diffusion of Et₂O to a CH₃CN solution at -30 °C.

Yield: 390 mg (82 %); **m.p.** 211 °C (decomp.); **Raman**(80 mW, 200 scans, 298 K, cm⁻¹): 3085 (11), 2950 (18), 2920 (14), 1637 (15), 1603 (45), 1402 (18), 1353 (100), 1267 (33), 1149 (17), 1133 (26), 1114 (24), 1076 (37), 1035 (42), 862 (20), 756 (22), 573 (16), 350 (21), 314 (18); **IR** (ATR, cm⁻¹): 3112 (vw), 2977 (vw), 1635 (vw), 1600 (w), 1524 (w), 1461 (w), 1406 (w), 1396 (w), 1377 (vw), 1354 (m), 1301 (w), 1275 (s), 1256 (vs), 1224 (m), 1146 (s), 1116 (m), 1091 (w), 1075 (w), 1028 (vs), 979 (vw), 924 (vw), 905 (vw), 887 (vw), 861 (vw), 842 (w), 808 (w), 787 (w), 755 (w), 738 (w), 711 (vw), 695 (vw), 661 (vw), 633 (vs); **¹H NMR** (CD₃CN, 298 K, in ppm) δ = 1.39 (6H, s(br), H5), 1.54 (6H, m, H5), 2.39 (6H, s, H3), 2.40 (6H, s, H3), 4.14 (2H, s,(br), H4), 4.75 (1H, ddd, ²J_{HH} = 18.57 Hz, ⁴J_{HH} = 2.94 Hz, D_{HH} = 6.06 Hz, H12a) 5.02 (1H, dd, ²J_{HH} = 18.55 Hz, ⁴J_{HH} = 13.45 Hz, H12b), 7.51 (4H, d, ³J_{HH} = 2.0 Hz, H14/15), 8.45 (1H, m, H9), 8.83 (2H, m, H7/8), 9.78 (1H, m, H10); **¹³C{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = 11.41 (2C, s, C3), 21.22 (2C, s, C5), 21.69 (2C, s, C5), 37.81 (1C, s, C12), 55.25 (1C, s, C4), 55.34 (1C, s, C4), 121.77 (2C, q, ¹J_{CF} = 317 Hz, OTf), 126.98 (1C, s, C13), 127.16 (1C, d, ¹J_{CP} = 44 Hz, C1), 129.55 (1C, s, C9), 131.38 (1C, d, ²J_{CP} = 12 Hz, C7), 131.89 (4C, s, C14/15), 136.95 (3C, s, C2), 142.27 (1C, m, C10), 145.69 (1C, s, C16), 147.38 (1C, d, ³J_{CP} = 7 Hz, C8), 159.19 (1C, d, ¹J_{CP} = 29 Hz, C7), 165.77 (1C, d, ²J_{CP} = 4 Hz, C11); **¹⁹F{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = -79.3 (s); **³¹P{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = 22.1 (s); **elemental analysis:** calculated for C₂₆H₃₀F₆N₅O₈PS₂: N 9.34, C 41.66, H 4.03, S 8.55; found: N 9.16, C 41.58, H 3.87, S 8.54.

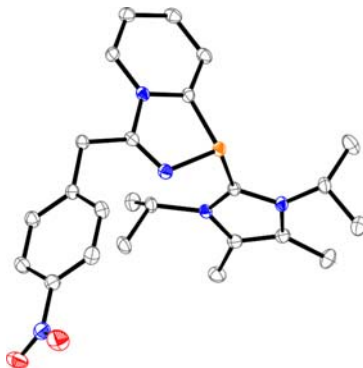


Figure S 20: Molecular structure of **9d**²⁺ in **9d**[OTf]₂; thermal ellipsoids are displayed at 50 % probability level, hydrogen atoms and counterions are omitted for clarity.

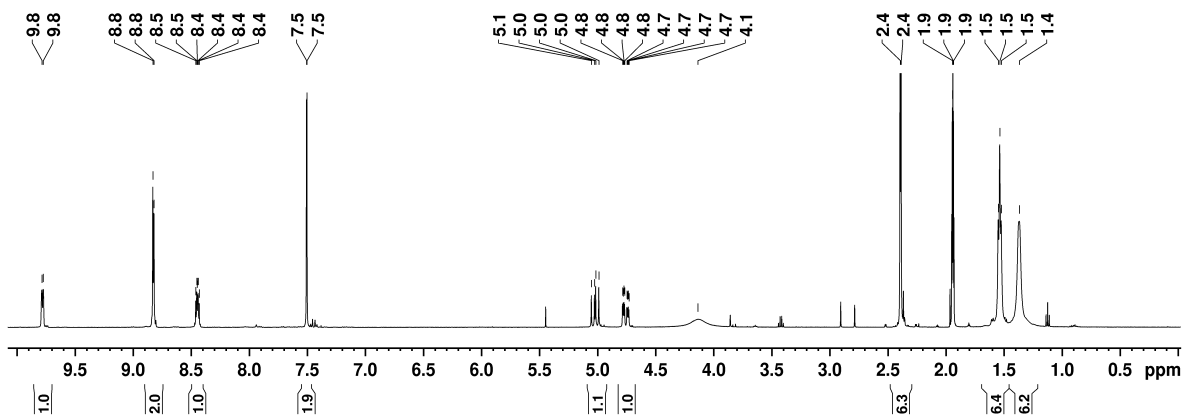


Figure S 21: ^1H NMR spectrum of $9\text{d}[\text{OTf}]_2$ in CD_3CN .

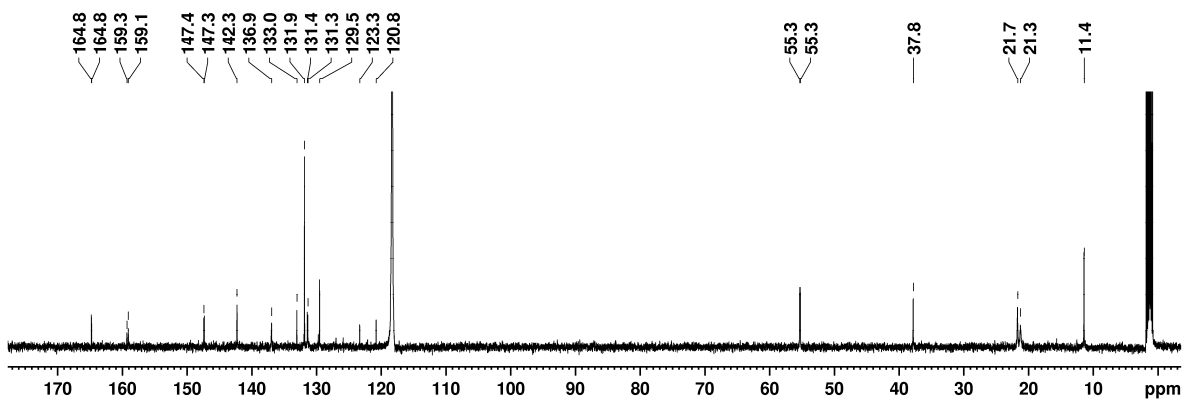


Figure S 22: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $9\text{d}[\text{OTf}]_2$ in CD_3CN .

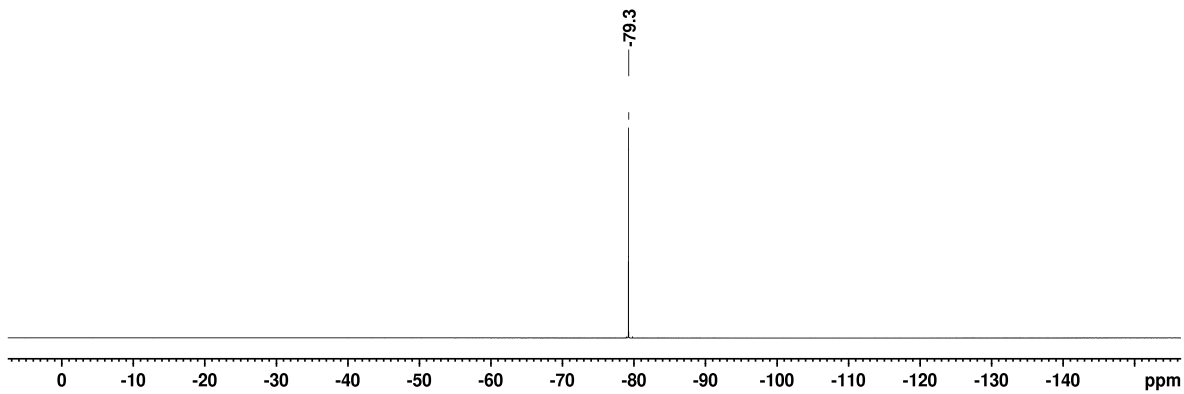


Figure S 23: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of $9\text{d}[\text{OTf}]_2$ in CD_3CN .

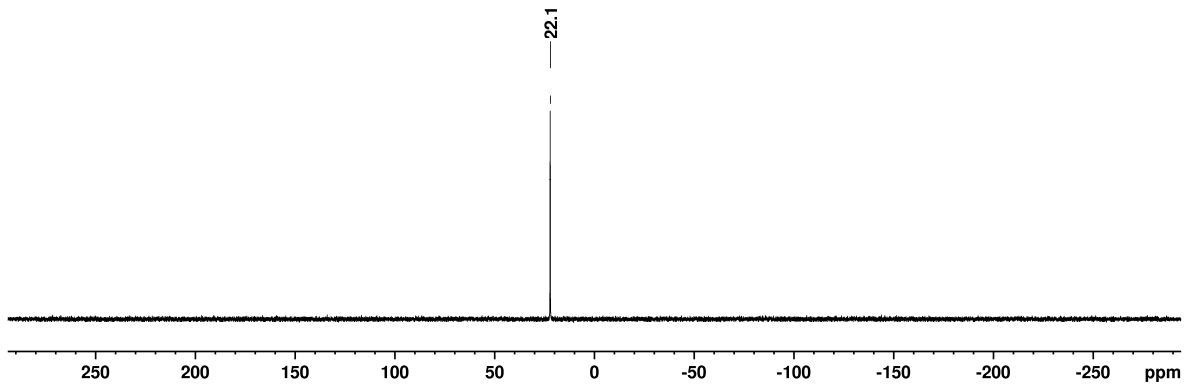
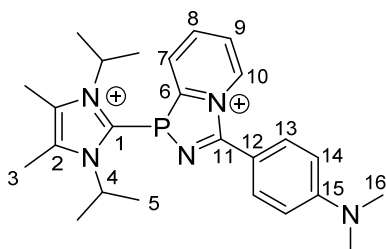


Figure S 24: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $9\text{d}[\text{OTf}]_2$ in CD_3CN .

2.3.5. Synthesis of **9e**[OTf]₂



11[OTf] (200 mg, 0.422 mmol, 1.0 equiv.), silver triflate (108 mg, 0.422 mmol, 1.0 equiv.) and 4-(dimethylamino)benzotrile (62 mg, 0.430 mmol, 1.0 equiv.) are suspended in 3 mL of C₂H₄Cl₂ and stirred at 40 °C for 2 h in a microwave oven. The resulting solid is filtered off and 3 mL of Et₂O are added to the solution, resulting in the formation of a deep red precipitate. By filtration and washing with Et₂O, **9e**[OTf]₂ is obtained as a red,

air and moisture sensitive solid. Suitable crystals for X-ray diffraction analysis can be obtained by vapour diffusion of Et₂O to a CH₃CN solution at -30 °C.

Yield: 261 mg (84 %); **m.p.** 153 °C; **Raman** (80 mW, 200 scans, 298 K, cm⁻¹): 1623 (31), 1599 (100), 1555 (27), 1542 (18), 1454 (25), 1380 (12), 1276 (11), 1196 (22), 1096 (13), 1067 (12), 1045 (12), 1033 (14), 935 (14), 806 (18), 419 (23), 174 (14); **IR** (ATR, 298 K, cm⁻¹): 1596 (m), 1529 (w), 1458 (vw), 1442 (w), 1430 (vw), 1401 (vw), 1379 (w), 1276 (s), 1258 (s), 1244 (s), 1223 (s), 1194 (m), 1149 (s), 1094 (w), 1067 (w), 1028 (vs), 934 (w), 828 (w), 803 (m), 753 (w), 741 (w), 679 (w), 635 (vs), 572 (w), 548 (w), 516 (m); **¹H NMR** (CD₂Cl₂, 298 K, in ppm) δ = 1.50 (6H, d, ³J_{HH} = 6.72 Hz, H5), 1.60 (6H, d, ³J_{HH} = 6.72 Hz, H5), 2.42 (6H, s, H3), 3.15 (6H, s, H16), 4.39 (2H, s(br), H4), 6.91 (2H, s(br), H13), 7.99 (2H, d, ³J_{HH} = 8.62 Hz, H14), 8.34 (1H, m, H9), 8.67 (1H, m, H8), 9.32 (1H, d, ³J_{HH} = 7.92 Hz, H7), 9.70 (1H, d, ³J_{HH} = 5.68 Hz, H10); **¹³C{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = 10.97 (2C, s, C3), 21.20 (4C, s, C5), 40.1 (2C, s, C16), 54.60 (1C, s, C4), 54.71 (1C, s, C4), 111.90 (2C, s, C14), 114.98 (1C, s, C12), 120.63 (2C, q, ¹J_{CF} = 319 Hz, OTf), 129.03 (1C, s, C9), 129.80 (1C, d, ¹J_{CP} = 54 Hz, C1), 132.11 (1C, d, ²J_{CP} = 12 Hz, C7), 132.52 (2C, s, C13), 134.70 (2C, s, C2), 142.72 (1C, s, C10), 145.27 (1C, d, ³J_{CP} = 6 Hz, C8), 154.03 (1C, s, C15), 158.65 (1C, d, ¹J_{CP} = 34 Hz, C6), 161.39 (1C, s(br), C11); **¹⁹F{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = -78.8 (s); **³¹P{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = 27.7 (s); **elemental analysis:** calculated for C₂₆H₃₀F₆N₅O₈PS₂·0.2 C₅H₁₂: N 9.00, C 43.20, H 4.51, S 8.24; found: N 9.23, C 43.29, H 4.84, S 8.66.

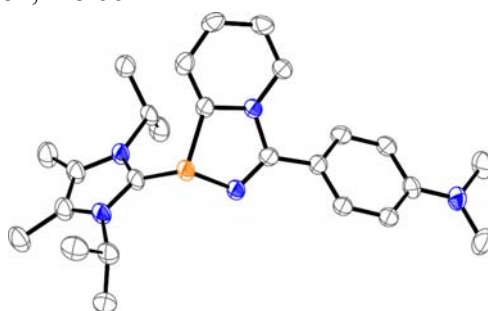


Figure S 25: Molecular structure of **9e**²⁺ in **9e**[OTf]₂·0.25 MeCN; thermal ellipsoids are displayed at 50 % probability level, hydrogen atoms, solvate molecules and counterions are omitted for clarity.

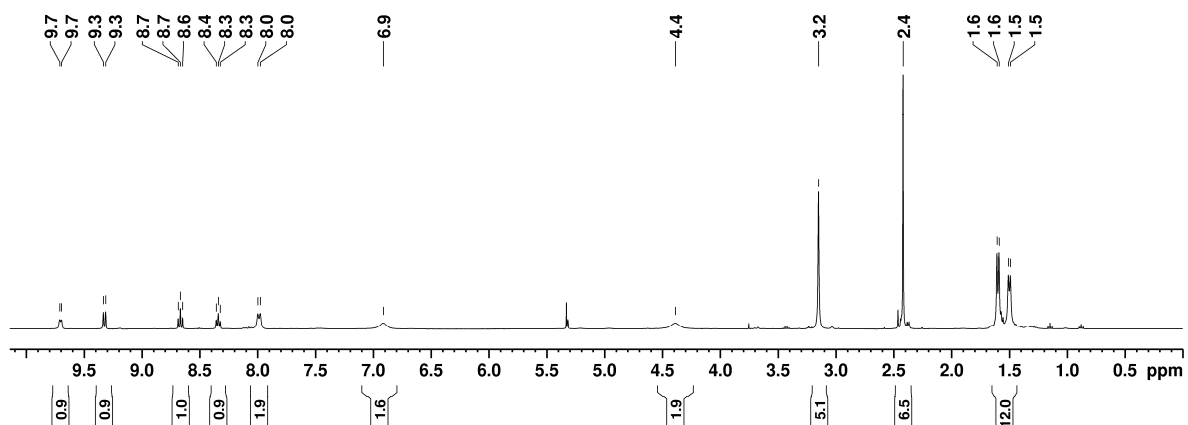


Figure S 26: ^1H NMR spectrum of $9\text{e}[\text{OTf}]_2$ in CD_2Cl_2 .

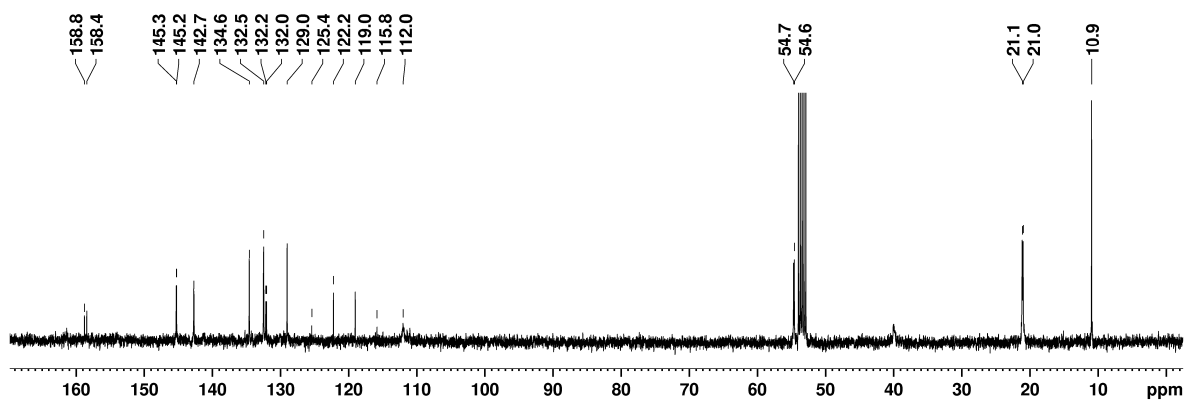


Figure S 27: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $9\text{e}[\text{OTf}]_2$ in CD_2Cl_2 .

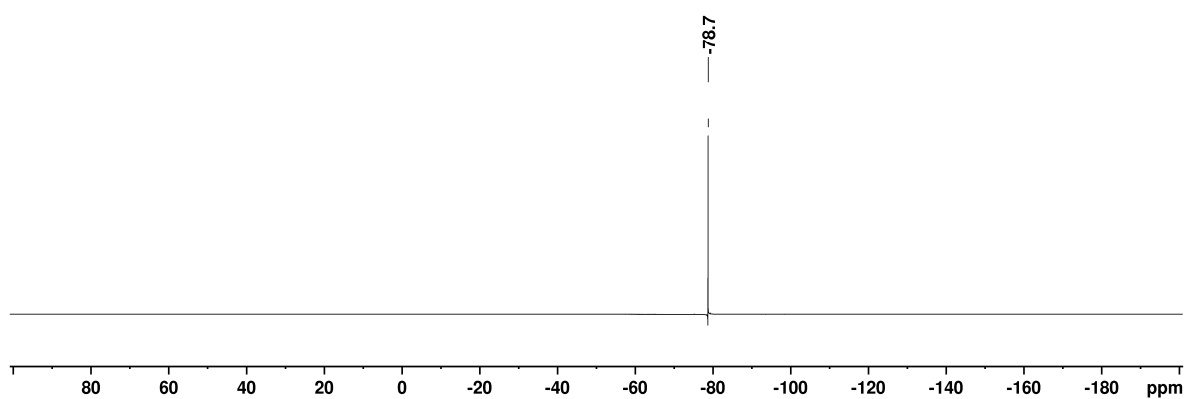


Figure S 28: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of $9\text{e}[\text{OTf}]_2$ in CD_2Cl_2 .

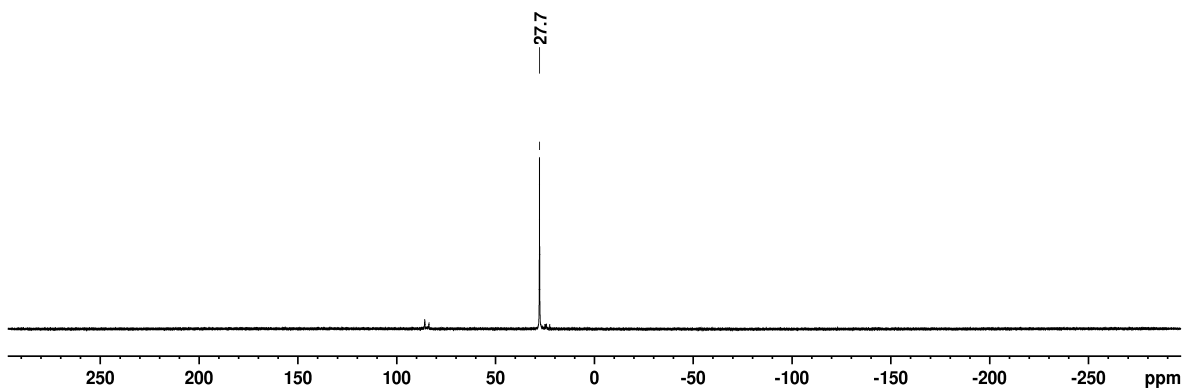
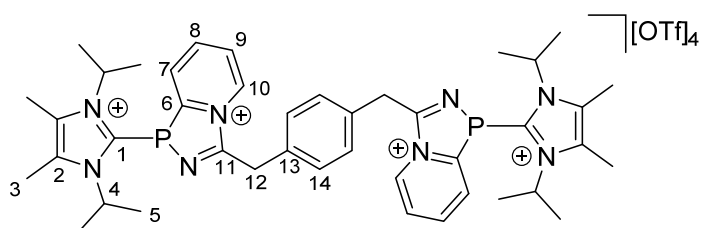


Figure S 29: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $9\mathbf{e}[\text{OTf}]_2$ in CD_2Cl_2 .

2.3.6. Synthesis of $\mathbf{9f[OTf]_4}$



$\mathbf{11[OTf]}$ (300 mg, 0.630 mmol, 1.0 equiv.), silver triflate (162 mg, 0.630 mmol, 1.0 equiv.) and 1,4-phenylenediacetonitrile (50 mg, 0.32 mmol, 0.5 equiv.) are suspended in 3 mL of $\text{C}_2\text{H}_4\text{Cl}_2$ and stirred for 36 h.

The resulting solid is filtered off and 3 mL of Et_2O are added to the solution, resulting in the formation of a colorless precipitate. By filtration and washing with Et_2O , $\mathbf{9f[OTf]_4}$ is obtained as a colorless, air and moisture sensitive solid. Suitable crystals for X-ray diffraction analysis can be obtained by slow diffusion of Et_2O to a CH_3CN solution at $-30\text{ }^\circ\text{C}$.

Yield: 280 mg (67 %); **m.p.** $154\text{ }^\circ\text{C}$ (decomp.); **Raman** (60 mW, 100 scans, cm^{-1}): 3084 (29), 3065 (29), 3010 (29), 2995 (29), 2980 (29), 2972 (29), 2945 (57), 2915 (29), 2884 (29), 1650 (29), 1640 (29), 1622 (29), 1600 (43), 1461 (29), 1270 (29), 1137 (43), 1072 (71), 1036 (100), 886 (14), 839 (14), 756 (29), 621 (29), 600 (29), 583 (43), 562 (43), 545 (29), 537 (43), 526 (29), 517 (43), 500 (29), 349 (43); **IR** (ATR, 298 K, cm^{-1}): 3101 (vw), 1635 (vw), 1597 (vw), 1520 (vw), 1462 (vw), 1408 (vw), 1377 (vw), 1257 (vs), 1224 (w), 1155 (m), 1091 (vw), 1071 (vw), 1030 (s), 903 (vw), 815 (w), 786 (vw), 756 (vw), 730 (vw), 706 (vw), 637 (vs); **$^1\text{H NMR}$** (CD_3CN , 298 K, in ppm) δ = 1.37 (12H, d, $^3J_{\text{HH}} = 5.72\text{ Hz}$, H5), 1.54 (12H, m, H5), 2.38 (6H, s, H3), 2.39 (6H, s, H3), 4.13 (4H, s, (br), H4), 4.76 (2H, ddd, $^2J_{\text{HH}} = 18.54\text{ Hz}$, $^4J_{\text{HH}} = 1.99\text{ Hz}$, $D_{\text{HH}} = 6.01\text{ Hz}$, H12a), 5.02 (2H, dd, $^2J_{\text{HH}} = 18.59\text{ Hz}$, $^4J_{\text{HH}} = 13.38\text{ Hz}$, H12b), 7.58 (4H, d, $^3J_{\text{HH}} = 1.56\text{ Hz}$, H14), 8.44 (2H, dt, $^3J_{\text{HH}} = 9.54\text{ Hz}$, $^4J_{\text{HH}} = 2.45\text{ Hz}$, H9), 8.83 (4H, m, H7/8), 9.79 (2H, m, H10); **$^{13}\text{C}\{^1\text{H}\}$ NMR** (CD_3CN , 298 K, in ppm): δ = 10.40 (4C, s, C3), 20.22 (4C, s, C5), 20.69 (4C, s, C5), 36.79 (2C, s, C12), 54.23 (1C, s, C4), 54.33 (1C, s, C4), 121.04 (4C, q, $^1J_{\text{CF}} = 320\text{ Hz}$, OTf), 126.19 (2C, d, $^1J_{\text{CP}} = 47\text{ Hz}$, C1) 128.49 (2C, s, C9), 130.36 (2C, d, $^2J_{\text{CP}} = 11\text{ Hz}$, C7), 130.84 (4C, s, C14), 132.03 (2C, s, C13), 135.91 (4C, s, C2), 141.32 (2C, s, C10), 146.32 (2C, d, $^3J_{\text{CP}} = 6\text{ Hz}$, C8), 158.16 (2C, d, $^1J_{\text{CP}} = 28\text{ Hz}$, C6), 163.79 (2C, d, $^2J_{\text{CP}} = 4\text{ Hz}$, C11); **$^{19}\text{F}\{^1\text{H}\}$ NMR** (CD_3CN , 298 K, in ppm): δ = -79.2 (s) ; **$^{31}\text{P}\{^1\text{H}\}$ NMR** (CD_3CN , 298 K, in ppm): δ = 22.1 (s) ; **elemental analysis:** calculated for $\text{C}_{46}\text{H}_{56}\text{F}_{12}\text{N}_8\text{O}_{12}\text{P}_2\text{S}_4$: N 8.42, C 41.51, H 4.24, S 9.63; found: N 8.38, C 41.34, H 3.80, S 9.64.

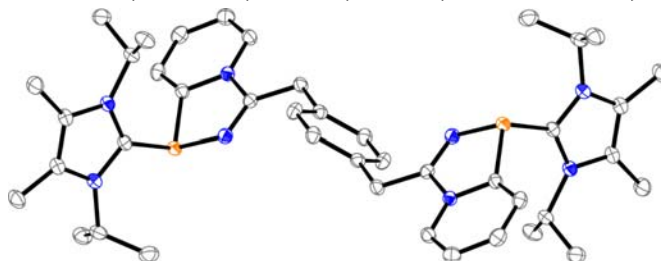


Figure S 30: Molecular structure of $\mathbf{9f}^{4+}$ in $\mathbf{9f[OTf]_4} \cdot 2\text{ MeCN}$; thermal ellipsoids are displayed at 50% probability level, hydrogen atoms, solvate molecules and counterions are omitted for clarity.

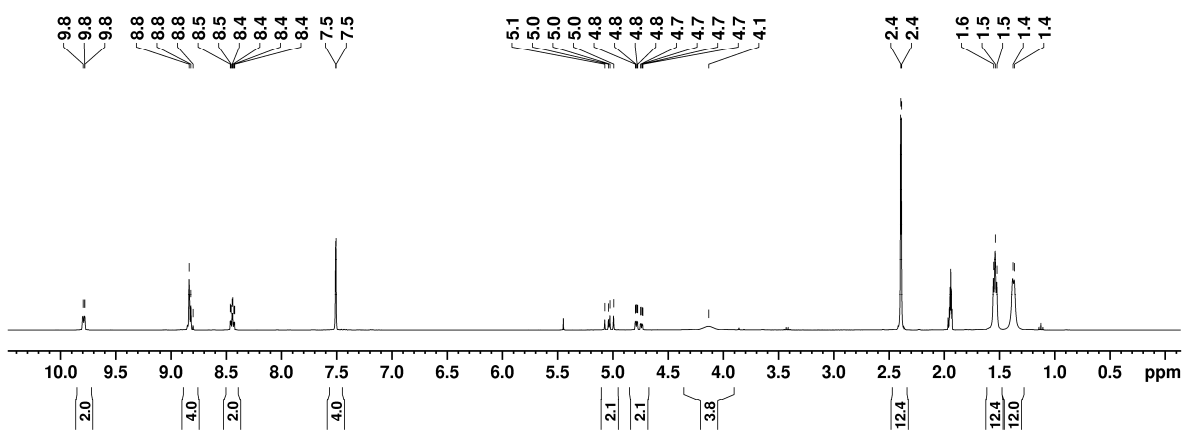


Figure S 31: ^1H NMR spectrum of $9\text{f}[\text{OTf}]_4$ in CD_3CN .

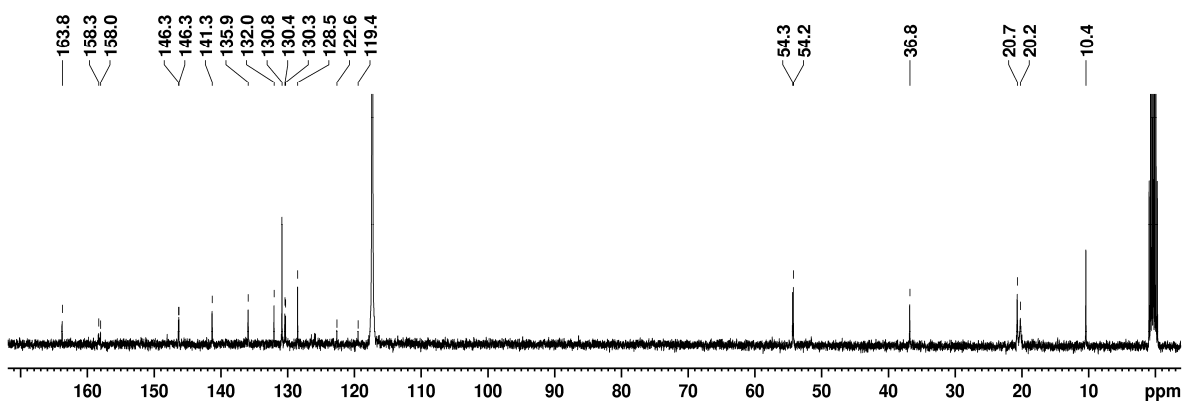


Figure S 32: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $9\text{f}[\text{OTf}]_4$ in CD_3CN .

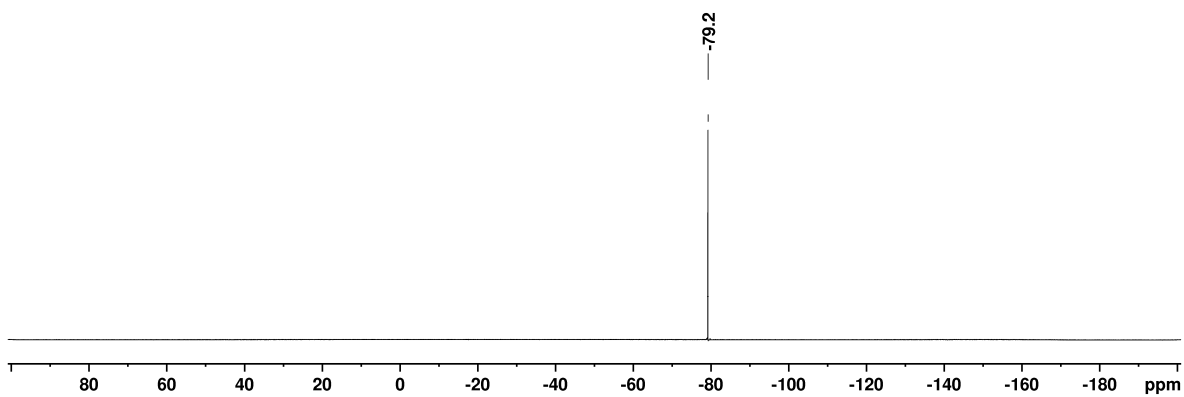


Figure S 33: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of $9\text{f}[\text{OTf}]_4$ in CD_3CN .

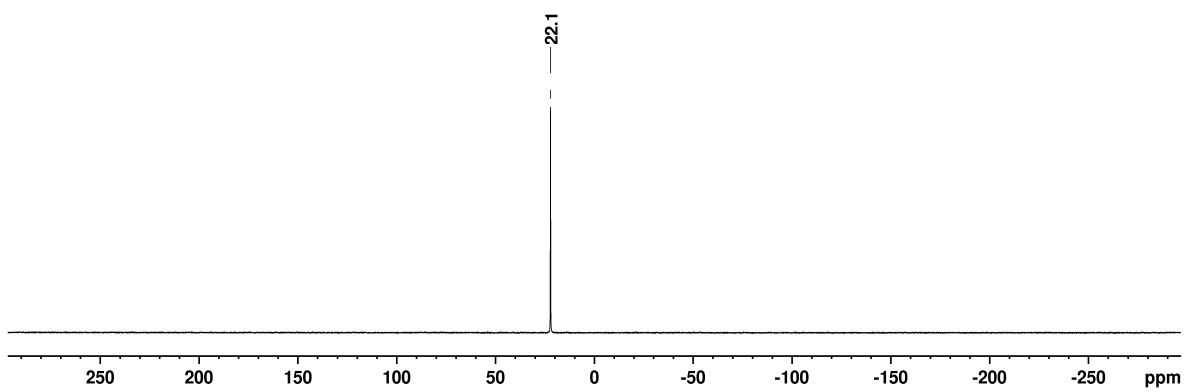
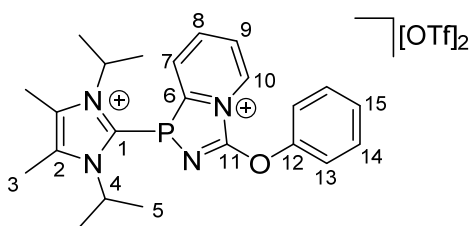


Figure S 34: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **9c**[OTf]₄ in CD₃CN.

2.3.7. Synthesis of **12**[OTf]₂



11[OTf] (1.000 g, 2.110 mmol, 1.0 equiv.) and silver triflate (542 mg, 2.110 mmol, 1.0 equiv.) are suspended in 10 mL of CH₂Cl₂ and phenylcyanate (20 % in CH₂Cl₂, 1.508 g, 2.532 mmol, 1.2 equiv.) is added. After stirring overnight, the resulting solid is filtered off and the solvent removed *in vacuo*. The remaining solid

is suspended in *n*-pentane and stirred overnight. By filtration and washing with *n*-pentane, **12**[OTf]₂ is obtained as a colourless, air and moisture sensitive solid. Suitable crystals for X-ray diffraction analysis can be obtained by slow diffusion of *n*-pentane to a CH₂Cl₂ solution at -30 °C.

Yield: 1.301 g (87 %); **m.p.** 190 °C (decomp.); **Raman:** No Raman spectrum could be obtained due to strong fluorescence of the sample; **IR** (ATR, 298 K, cm⁻¹): 1658 (w), 1601 (vw), 1580 (vw), 1487 (vw), 1419 (vw), 1378 (vw), 1302 (m), 1264 (s), 1247 (vs), 1224 (m), 1152 (s), 1097 (w), 1029 (vs), 925 (w), 903 (vw), 820 (vw), 783 (vw), 765 (m), 734 (w), 686 (w), 672 (vw), 635 (vs), 598 (vw), 573 (w), 548 (vw), 516 (m), 493 (w), 452 (vw); **¹H NMR** (CD₂Cl₂/CD₃CN, 298 K, in ppm) δ = 1.41 (6H, d, ³J_{HH} = 5.3 Hz, H5), 1.59 (6H, d, ³J_{HH} = 6.8 Hz, H5), 2.40 (6H, s, H3), 4.31 (2H, s(br), H4), 7.45 (1H, m, H15), 7.57 (4H, m, H14/H14), 8.44 (1H, m, H9), 8.84 (1H, m, H8), 9.06 (1H, m, H7), 9.83 (1H, m, H10); **¹³C{¹H} NMR** (CD₂Cl₂/CD₃CN, 298 K, in ppm): δ = 10.8 (1C, s, C3), 14.9 (1C, s, C3), 20.6 (2C, s, C5), 21.0 (2C, s, C5), 54.7 (2C, s, C4), 120.7 (2C, q, ¹J_{CF} = 320 Hz, OTf), 120.7 (2C, s, C13/C14), 128.2 (1C, s, C15), 128.5 (1C, s, C9), 128.5 (1C, d, ¹J_{CP} = 64 Hz, C1), 130.4 (2C, s, C13/C14), 131.0 (1C, d, ²J_{CP} = 10 Hz, C7), 135.2 (2C, s, C2), 140.9 (1C, s, C10), 147.1 (1C, d, ³J_{CP} = 6 Hz, C8), 151.5 (1C, s, C11), 152.0 (1C, s, C12), 159.3 (1C, d, ¹J_{CP} = 35 Hz, C6); **¹⁹F{¹H} NMR** (CD₂Cl₂/CD₃CN, 298 K, in ppm): δ = -79.0 (s); **³¹P{¹H} NMR** (CD₂Cl₂/CD₃CN, 298 K, in ppm): δ = 14.5 (s); **elemental analysis:** calculated for C₂₅H₂₉F₆N₄O₇PS₂: N 7.93, C 42.50, H 4.14, S 9.07; found: N 7.95, C 42.63, H 4.07, S 9.38.

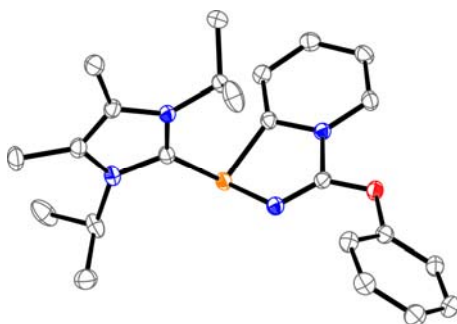


Figure S 35: Molecular structure of **12**²⁺ in **12**[OTf]₂; thermal ellipsoids are displayed at 50 % probability level, hydrogen atoms and counterions are omitted for clarity.

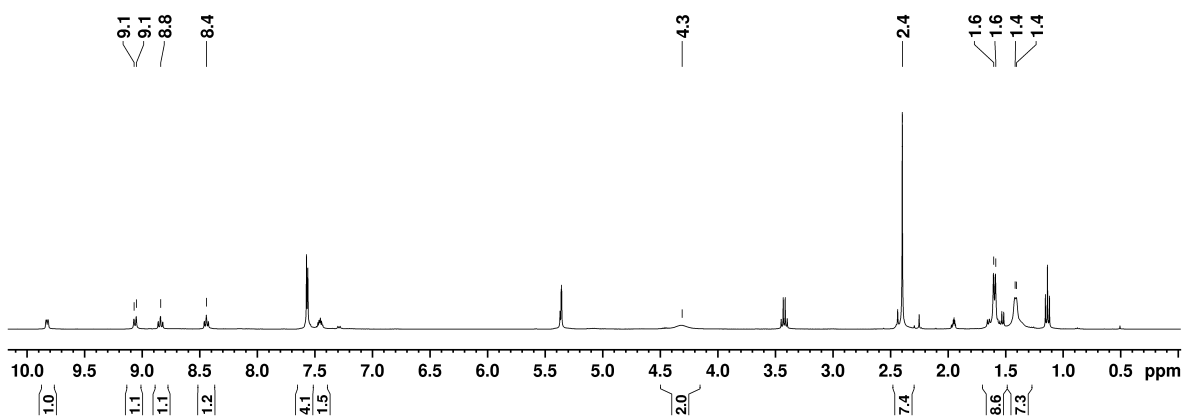


Figure S 36: ^1H NMR spectrum of $12[\text{OTf}]_2$ in $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$.

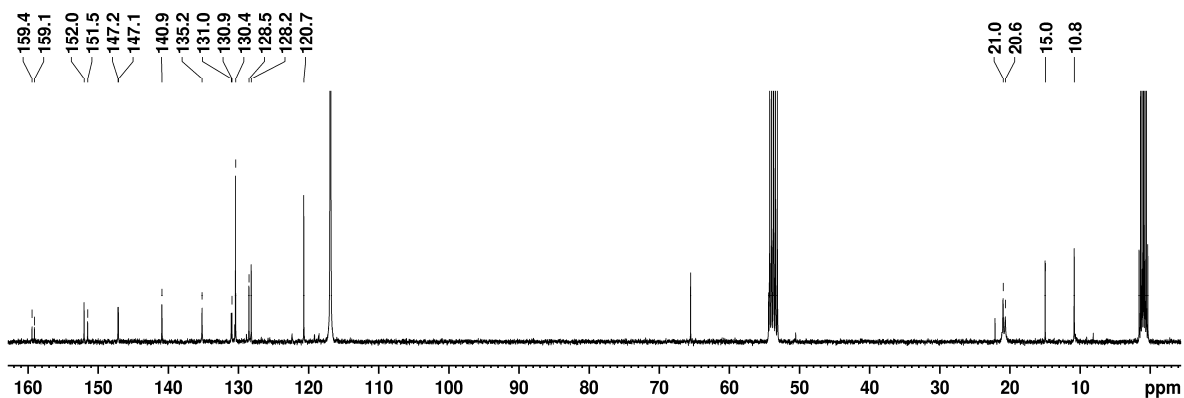


Figure S 37: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $12[\text{OTf}]_2$ in $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$.

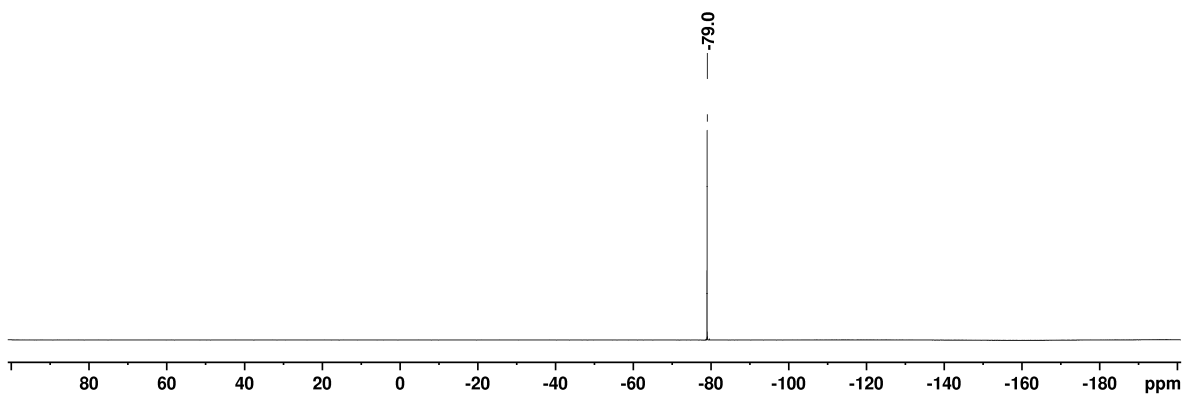


Figure S 38: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of $12[\text{OTf}]_2$ in $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$.

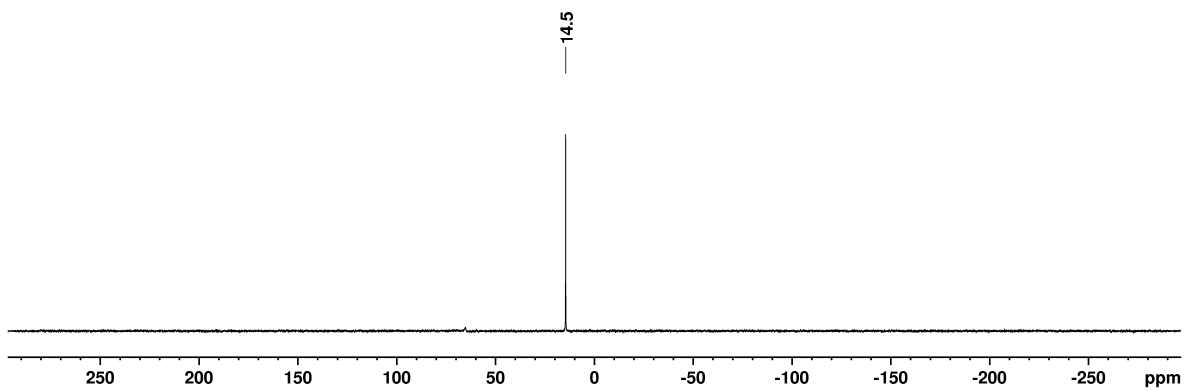
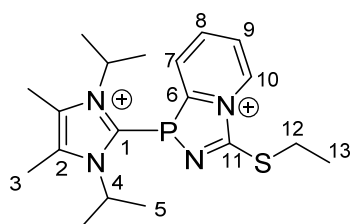


Figure S 39: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\mathbf{12}[\text{OTf}]_2$ in $\text{CD}_2\text{Cl}_2/\text{CD}_3\text{CN}$.

2.3.8. Synthesis of **13**[OTf]₂



11[OTf] (1.000 g, 2.110 mmol, 1.0 equiv.) and silver triflate (542 mg, 2.110 mmol, 1.0 equiv.) are suspended in 10 mL of CH₂Cl₂ and ethylthiocyanate (220.6 mg, 2.532 mmol, 1.2 equiv.) is added. After stirring overnight, the resulting solid is filtered off and the solvent removed *in vacuo*. The remaining solid is suspended in *n*-pentane

and stirred overnight. By filtration and washing with *n*-pentane, **13**[OTf]₂ is obtained as a green, air and moisture sensitive solid.

Yield: 1.210 g (85 %); **m.p.** 82 °C; **Raman** (100 mW, 200 scans, 298 K, cm⁻¹): 2989 (6), 2942 (18), 1606 (17), 1579 (7), 1544 (12), 1463 (11), 1405 (8), 1269 (20), 1226 (5), 1123 (9), 1077 (19), 1045 (19), 1034 (31), 887 (6), 756 (11), 707 (5), 574 (8), 547 (5), 349 (15), 313 (16), 80 (100); **IR** (ATR, 298 K, cm⁻¹): 1604 (w), 1575 (w), 1542 (w), 1460 (w), 1400 (vw), 1253 (vs), 1222 (s), 1147 (s), 1027 (vs), 979 (m), 788 (w), 754 (w), 724 (w), 635 (vs), 572 (m), 545 (w), 516 (s), 491 (m); **¹H NMR** (CD₂Cl₂, 298 K, in ppm) δ = 1.50 (6H, d, ³J_{HH} = 6.6 Hz, H5), 1.66 (3H, t, ³J_{HH} = 7.4 Hz, H13), 1.67 (6H, d, ³J_{HH} = 6.9 Hz, H5), 2.47 (6H, s, H3), 3.61 (2H, q, ³J_{HH} = 7.4 Hz, H12), 4.28 (2H, s(br), H4), 8.46 (1H, m, H9), 8.77 (1H, m, H8), 9.36 (1H, m, H7), 9.64 (1H, m, H10); **¹³C{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = 11.0 (2C, s, C3), 13.6 (1C, s, C13), 20.9 (2C, s, C5), 21.2 (2C, s, C5), 29.4 (1C, s, C12), 54.5 (1C, s, C4), 54.6 (1C, s, C4), 120.6 (2C, q, ¹J_{CF} = 321 Hz, CF3), 129.0 (1C, s, C9), 131.8 (1C, d, ²J_{CP} = 11 Hz, C7), 134.9 (2C, s, C2), 136.7 (1C, d, ¹J_{CP} = 66 Hz, C1), 140.6 (1C, d, ³J_{CP} = 3 Hz, C10), 146.2 (1C, d, ³J_{CP} = 6 Hz, C8), 157.9 (1C, d, ¹J_{CP} = 35 Hz, C6), 162.8 (1C, d, ³J_{CP} = 6 Hz, C11); **¹⁹F{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = -78.8 (s); **³¹P{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = 27.9 (s); **elemental analysis:** calculated for C₂₁H₂₉F₆N₄O₆PS₃: N 8.31, C 37.39, H 4.33, S 14.26; found: N 8.27, C 37.38, H 4.20, S 14.26.

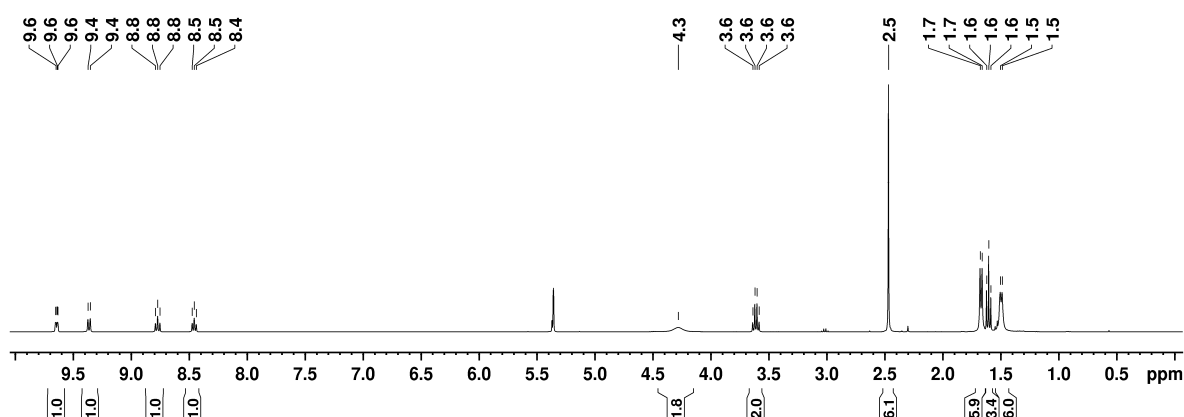


Figure S 40: ¹H NMR spectrum of **13**[OTf]₂ in CD₂Cl₂.

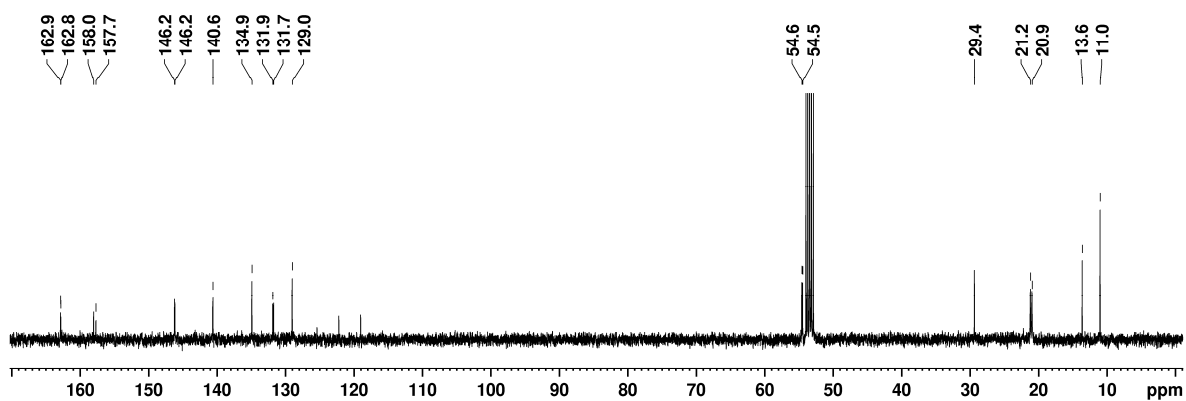


Figure S 41: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $^{13}\text{[OTf]}_2$ in CD_2Cl_2 .

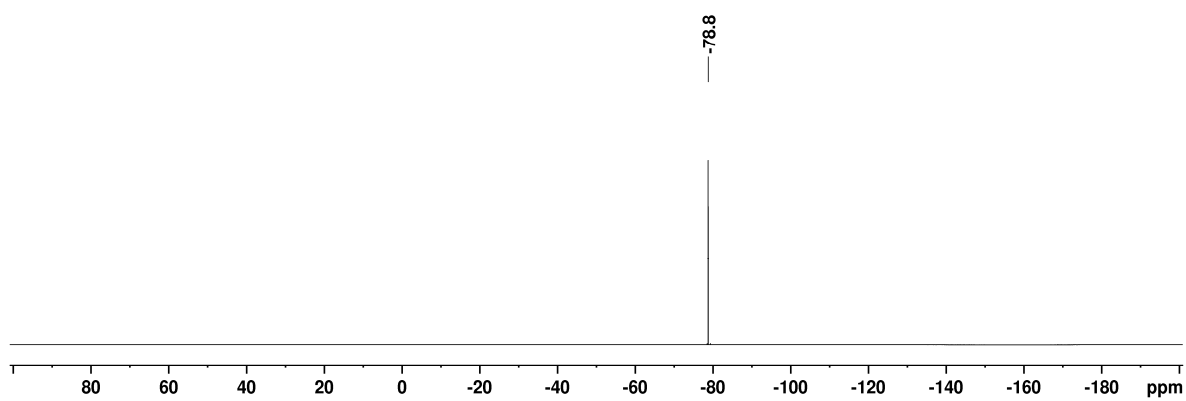


Figure S 42: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of $^{13}\text{[OTf]}_2$ in CD_2Cl_2 .

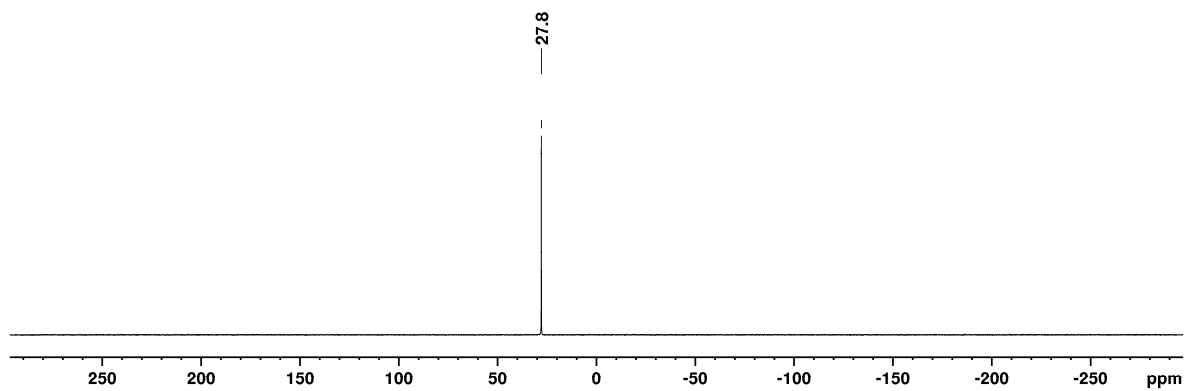
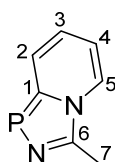


Figure S 43: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $^{13}\text{[OTf]}_2$ in CD_2Cl_2 .

2.4. Chemical Reductions towards Diazaphospholes

2.4.1. Synthesis of **14** by reduction of **9a**[OTf]₂



9a[OTf]₂ (1.1 g, 1.750 mmol, 1.0 equiv.) and KC₈ (521 mg, 3.854 mmol, 2.2 equiv) are cooled to -78 °C and cold THF (-78 °C, 25 mL) is added. The solution is slowly thawed to room temperature overnight. The solvent is removed *in vacuo* and the residue is taken up in CH₂Cl₂/Et₂O 1:1 (25 mL). After filtration over silica (~6 cm; 1.5 cm Ø) with CH₂Cl₂/Et₂O 1:1 as eluent and subsequent removal of the solvent *in vacuo*, **14** is obtained as a yellow crystalline air sensitive solid.

Yield: 164 mg (62 %); **m.p.** 72 °C; **T₉₅:** 130°C; **Raman:** No Raman spectrum of the sample could be obtained due to strong fluorescence of the sample; **IR** (ATR, 298 K, cm⁻¹): 1617 (m), 1518 (m), 1491 (m), 1449 (m), 1433 (m), 1413 (m), 1377 (m), 1314 (m), 1300 (s), 1260 (m), 1160 (m), 1062 (m), 1010 (m), 825 (s), 739 (vs), 702 (s), 603 (s), 574 (m), 525 (m), 515 (m), 496 (s), 409 (s); **¹H NMR** (CD₂Cl₂, 298 K, in ppm) δ = 2.77 (3H, s, H7), 6.81 (2H, m, H3/H4), 7.99 (1H, m, H2), 8.11 (1H, m, H5); **¹³C{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = 16.7 (1C, d, ³J_{CP} = 3 Hz, C7), 114.4 (1C, d, ⁴J_{CP} = 2 Hz, C4), 118.2 (1C, d, ³J_{CP} = 17 Hz, C3), 124.6 (1C, d, ²J_{CP} = 10 Hz, C2), 126.0 (1C, s, C5), 145.2 (1C, d, ²J_{CP} = 14 Hz, C6), 168.7 (1C, d, ¹J_{CP} = 65 Hz, C1); **³¹P{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = 150.4 (s); **elemental analysis:** calculated for C₇H₇N₂P: N 18.66, C 56.01, H 4.70; found: N 18.38, C 56.04, H 4.31.

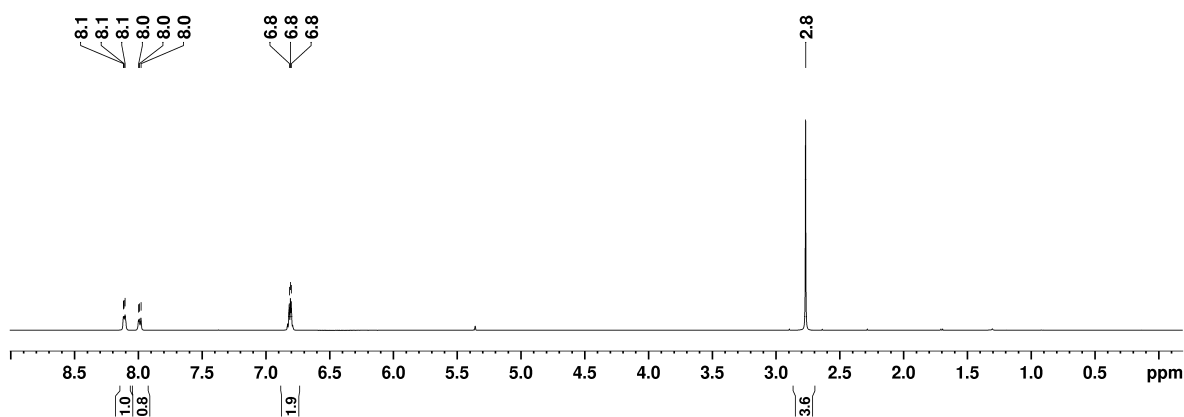


Figure S 44: ¹H NMR spectrum of **14** in CD₂Cl₂.

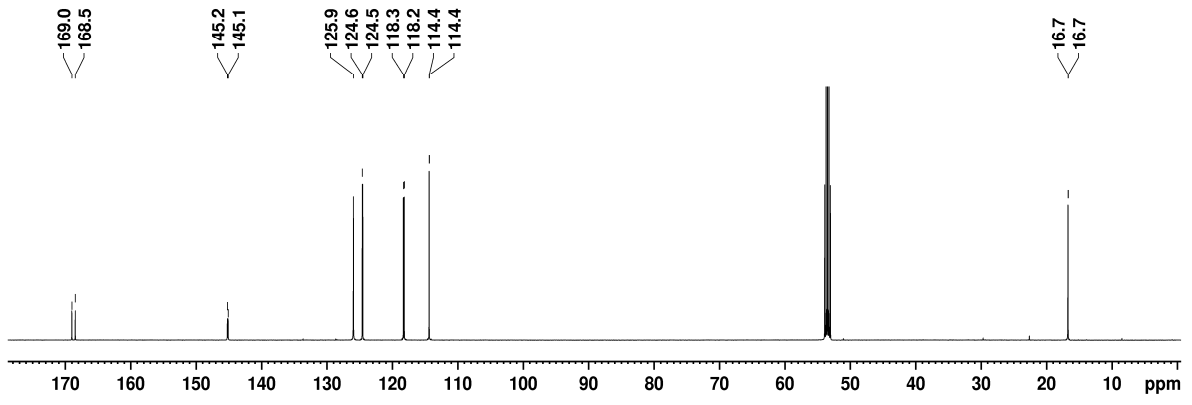


Figure S 45: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **14** in CD_2Cl_2 .

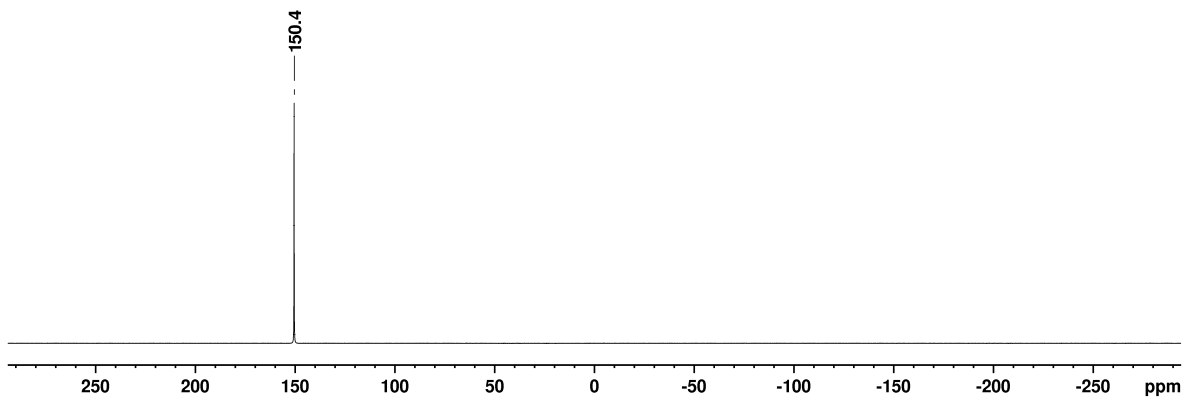
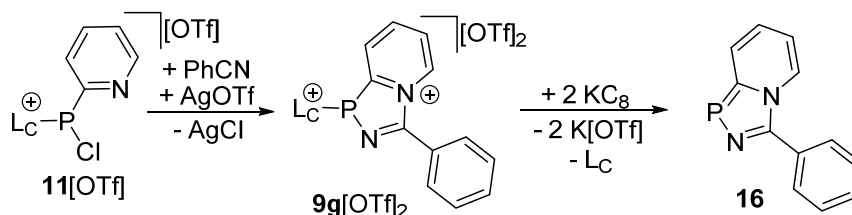


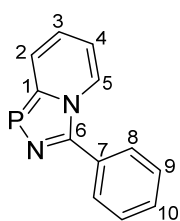
Figure S 46: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **14** in CD_2Cl_2 .

2.4.2. Synthesis of **16** by reduction of **9g**[OTf]₂



For the synthesis of **16**, the corresponding diazaphospholium salt **9g**[OTf]₂ was synthesized and used without further purification.

11[OTf] (1.000 g, 2.110 mmol, 1.0 equiv.) and silver triflate (542 mg, 2.110 mmol, 1.0 equiv.) are suspended in 10 mL of CH₂Cl₂ and benzonitrile (435 mg, 4.220 mmol, 2.0 equiv.) is added. After stirring overnight, the resulting solid is filtered off and the solvent removed *in vacuo*. The remaining solid is suspended in *n*-pentane/Et₂O 1:1 and stirred overnight. By filtration and washing with *n*-pentane, **9g**[OTf]₂ is obtained as an orange, air and moisture sensitive solid, which was used without further purification.



9g[OTf]₂ (1.187 g, 1.719 mmol, 1.0 equiv.) and KC₈ (456 mg, 3.438 mmol, 2.0 equiv) are cooled to -78 °C and cold THF (-78 °C, 35 mL) is added. The solution is slowly thawed to room temperature overnight. The solvent is removed *in vacuo* and the residue is taken up in CH₂Cl₂/Et₂O 1:1 (25 mL). After filtration over silica (~6 cm; 1.5 cm Ø) with CH₂Cl₂/Et₂O 1:1 as eluent and subsequent removal of the solvent *in vacuo*, **16** is obtained as a yellow crystalline air sensitive solid. Suitable crystals for X-ray diffraction analysis can be obtained by cooling a saturated *n*-pentane solution of **16** to -30 °C.

Yield: 163 mg (45 %); **m.p.** 111 °C; **T₉₅:** 177 °C; **Raman:** No Raman spectrum of the sample could be obtained due to strong fluorescence of the sample; **IR** (ATR, 298 K, cm⁻¹): 1616 (w), 1510 (m), 1463 (w), 1438 (m), 1409 (w), 1319 (m), 1296 (m), 1264 (w), 1182 (m), 1169 (w), 1123 (m), 1072 (w), 1063 (m), 1008 (m), 954 (m), 936 (w), 924 (w), 824 (m), 767 (s), 745 (vs), 724 (m), 712 (s), 698 (vs), 650 (s), 615 (m), 575 (m), 516 (m), 496 (s), 480 (s), 418 (s); **¹H NMR** (CD₂Cl₂, 298 K, in ppm) δ = 6.72 (1H, t, ³J_{HH} = 7.1 Hz, H4), 6.85 (1H, dd, ³J_{HH} = 6.4 Hz, ³J_{HH} = 8.9 Hz, H3), 7.58 (3H, m, H9/H10), 7.74 (2H, m, H8), 8.05 (1H, dd, ³J_{HH} = 8.9 Hz, ⁴J_{HH} = 1.0 Hz, H2), 8.51 (1H, m, H5); **¹³C{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = 114.6 (1C, d, ⁴J_{CP} = 2 Hz, C4), 119.2 (1C, d, ³J_{CP} = 17 Hz, C3), 124.6 (1C, d, ²J_{CP} = 10 Hz, C2), 126.8 (1C, s, C5), 128.9 (4C, s, C8), 129.5 (1C, s, C9), 132.2 (1C, d, ³J_{CP} = 4 Hz, C7), 147.8 (1C, d, ²J_{CP} = 13 Hz, C6), 169.4 (1C, d, ¹J_{CP} = 67 Hz, C1); **³¹P{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = 155.1 (s); **elemental analysis:** calculated for C₁₂H₉N₂P: N 13.20, C 67.93, H 4.28; found: N 13.19, C 67.70, H 3.93.

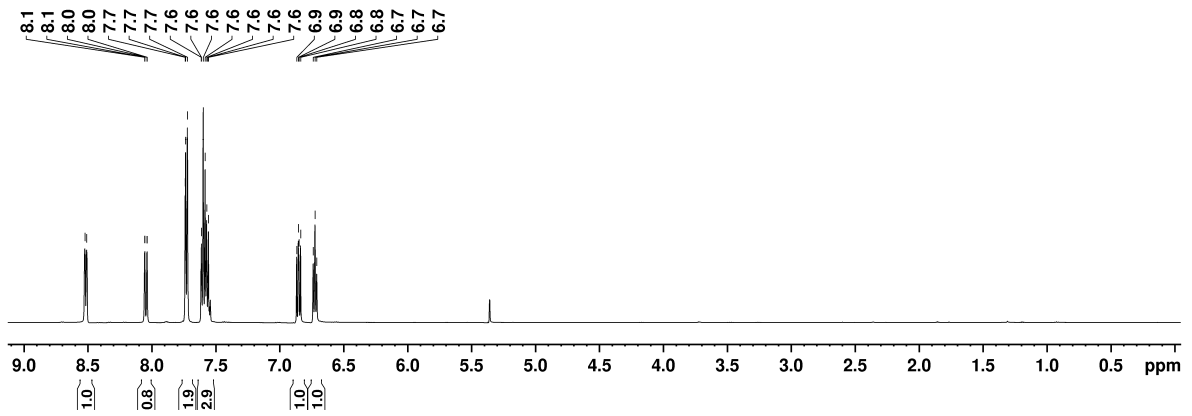


Figure S 47: ^1H NMR spectrum of **16** in CD_2Cl_2 .

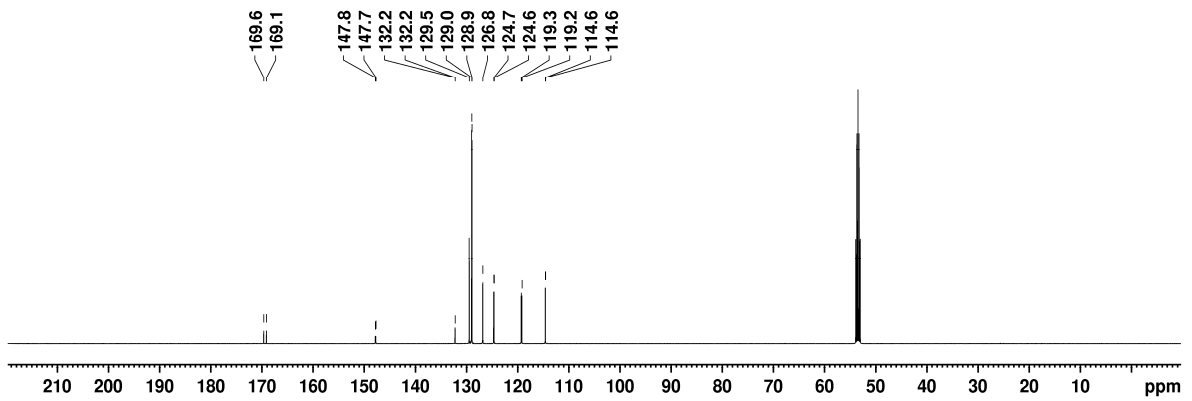


Figure S 48: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **16** in CD_2Cl_2 .

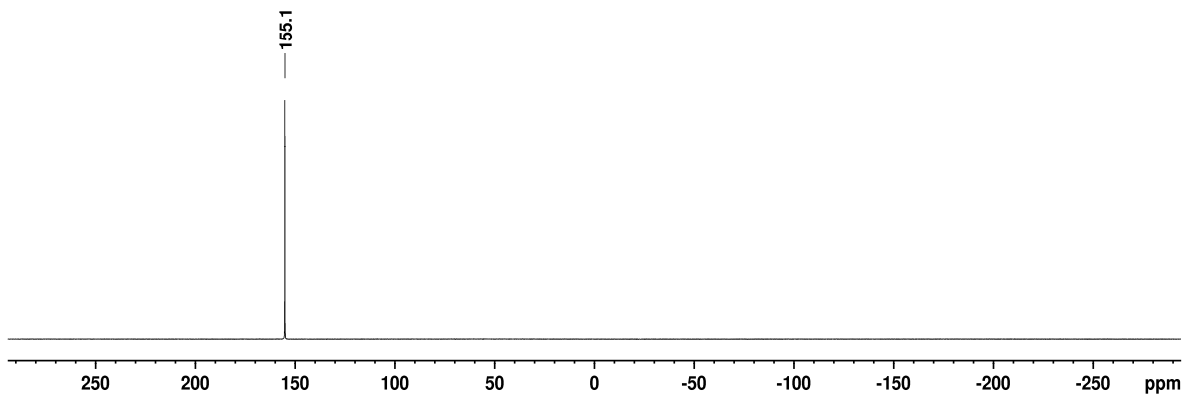
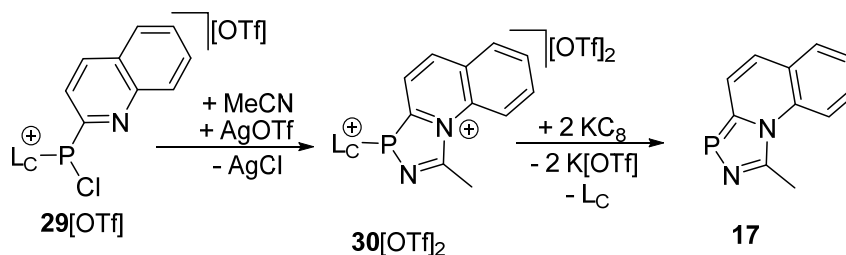


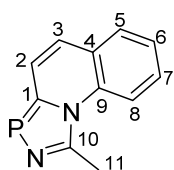
Figure S 49: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **16** in CD_2Cl_2 .

2.4.3. Synthesis of **17** by reduction of **30**[OTf]₂



For the synthesis of **17**, the corresponding diazaphospholium salt **31**[OTf]₂ was synthesized and used without further purification.

30[OTf] (1.500 g, 2.863 mmol, 1.0 equiv.) and silver triflate (736 mg, 2.863 mmol, 1.0 equiv.) are suspended in 10 mL of CH₂Cl₂ and after 5 min 5 mL of MeCN are added. After stirring for three days at room temperature, the resulting solid is filtered off and the solvent removed *in vacuo*. The remaining solid is suspended in Et₂O and stirred for 30 min. By filtration and washing with Et₂O, **31**[OTf]₂ is obtained as colorless, air and moisture sensitive solid, which was used without further purification.



31[OTf]₂ (1.88 g, 2.77 mmol, 1.0 equiv.) and KC₈ (768 mg, 5.679 mmol, 2.05 equiv) are cooled to -78 °C and cold THF (-78 °C, 40 mL) is added. The solution is slowly thawed to room temperature overnight. The solvent is removed *in vacuo* and the residue is taken up in CH₂Cl₂/Et₂O 1:1 (25 mL). After filtration over silica (~6 cm; 1.5 cm Ø) with CH₂Cl₂/Et₂O 1:1 as eluent and subsequent removal of the solvent *in vacuo*, **17** is obtained as a yellow crystalline air sensitive solid.

Yield: 238 mg (43 %); **m.p.** n.d.; **T₉₅:** n.d.; **Raman:** No Raman spectrum of the sample could be obtained due to strong fluorescence of the sample; **IR** (ATR, 298 K, cm⁻¹): 1603 (m), 1556 (m), 1483 (m), 1445 (m), 1435 (s), 1370 (m), 1322 (s), 1299 (s), 1228 (m), 1215 (s), 1173 (m), 1137 (m), 1102 (s), 1030 (m), 987 (m), 937 (m), 847 (s), 823 (s), 785 (vs), 753 (vs), 689 (s), 660 (m), 592 (m), 584 (m), 557 (m), 522 (m), 493 (vs); **¹H NMR** (CD₂Cl₂, 298 K, in ppm) δ = 3.24 (3H, s, H11), 7.03 (1H, d, ³J_{HH} = 9.1 Hz, H3), 7.51 (1H, m, H6), 7.59 (1H, m, H7), 7.74 (2H, m, H2/H5), 8.42 (1H, d, ³J_{HH} = 8.7 Hz, H8); **¹³C{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = 24.6 (1C, d, ³J_{CP} = 5 Hz, C11), 117.5 (1C, s, C8), 120.6 (1C, d, ³J_{CP} = 20 Hz, C3), 121.8 (1C, d, ²J_{CP} = 14 Hz, C2), 125.8 (1C, s, C6), 127.0 (1C, d, ³J_{CP} = 3 Hz, C9), 127.7 (1C, d, ⁵J_{CP} = 2 Hz, C7), 128.6 (1C, d, ⁵J_{CP} = 2 Hz, C5), 135.9 (1C, s, C4), 150.6 (1C, d, ²J_{CP} = 15 Hz, C10), 170.3 (1C, d, ¹J_{CP} = 58 Hz, C1); **³¹P{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = 155.5 (s); **elemental analysis:** calculated for C₁₁H₉N₂P: N 13.99, C 66.00, H 4.53; found: N 14.03, C 65.88, H 4.30

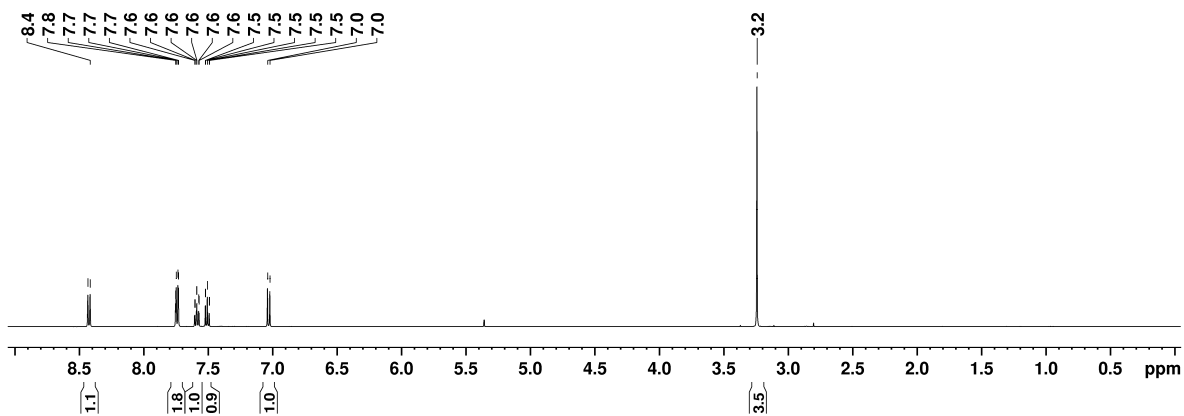


Figure S 50: ^1H NMR spectrum of **17** in CD_2Cl_2 .

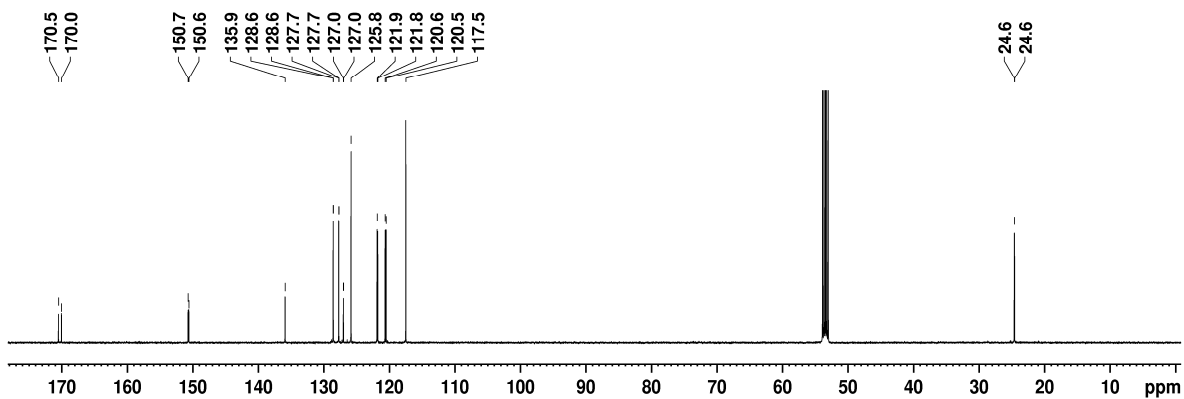


Figure S 51: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **17** in CD_2Cl_2 .

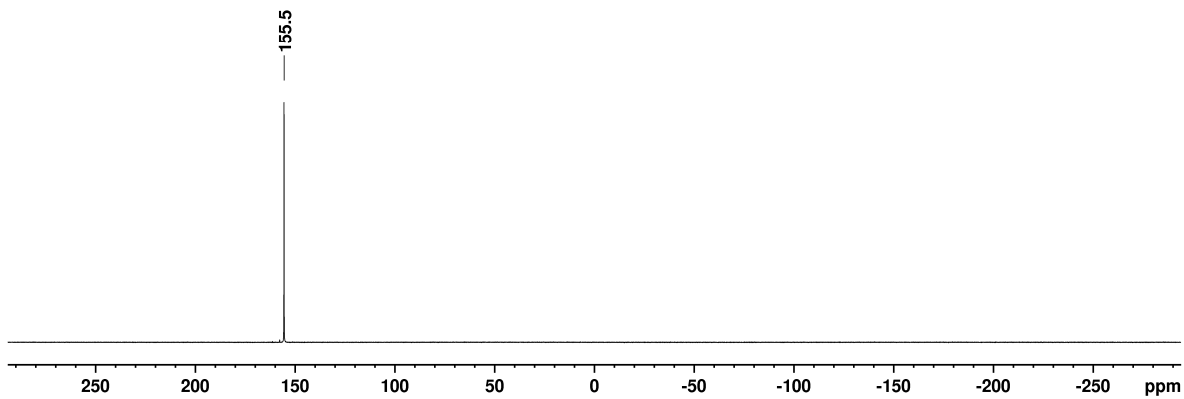
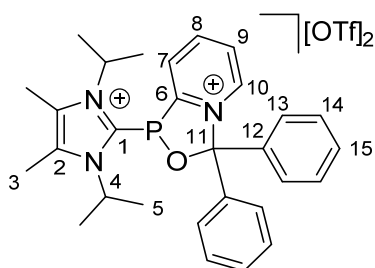


Figure S 52: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **17** in CD_2Cl_2 .

2.5. Cycloaddition Reactions of 6[OTf] with other Dipolarophiles

2.5.1. Synthesis of 18a[OTf]₂



11[OTf] (300.0 mg, 0.630 mmol, 1.0 equiv.), silver triflate (162.6 mg, 0.630 mmol, 1.0 equiv.) and benzophenone (127.0 mg, 0.697 mmol, 1.1 equiv.) are suspended in 10 mL of CH₂Cl₂ and stirred for 6 h. The resulting solid is filtered off and the solvent removed *in vacuo*. The remaining solid is suspended in *n*-pentane and stirred overnight. By filtration and washing with *n*-pentane, **18a[OTf]₂** is obtained as a colourless, air and moisture sensitive solid. Suitable crystals for X-ray diffraction analysis can be obtained by slow diffusion of *n*-pentane to a CH₂Cl₂ solution at -30°C.

Yield: 368 mg (76 %); **m.p.** 182 °C (decomp.); **Raman** (100 mW, 200 scans, 298 K, cm⁻¹): 3074 (14), 2989 (8), 2948 (14), 1600 (22), 1567 (6), 1450 (7), 1404 (6), 1271 (15), 1225 (5), 1189 (7), 1153 (6), 1088 (5), 1033 (37), 1003 (25), 886 (5), 756 (13), 700 (12), 618 (9), 575 (14), 349 (30), 313 (32), 286 (28), 87 (100); **IR** (ATR, 298 K, cm⁻¹): 1598 (vw), 1470 (w), 1450 (w), 1399 (vw), 1257 (s), 1221 (s), 1146 (s), 1027 (s), 900 (w), 786 (w), 753 (m), 697 (m), 634 (vs), 572 (m), 516 (s); **¹H NMR** (CD₂Cl₂, 298 K, in ppm) δ = 1.37 (6H, d, ³J_{HH} = 6.9 Hz, H5), 1.56 (6H, d, ³J_{HH} = 6.9 Hz, H5), 2.37 (6H, s, H3), 4.76 (2H, m, H4), 7.18 (2H, m, H13), 7.44 (2H, m, H13), 7.50 (6H, m, H14/H15), 8.57 (1H, m, H9), 8.81 (1H, m, H8), 9.15 (1H, d, ³J_{HH} = 6.1 Hz, H10), 9.40 (1H, d, ³J_{HH} = 7.4 Hz, H7); **¹³C{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = 10.9 (4C, s, C5), 20.9 (1C, s, C3), 21.0 (1C, s, C3), 54.3 (1C, s, C4), 54.4 (1C, s, C4), 114.1 (1C, d, ²J_{CP} = 13 Hz, C11), 120.6 (2C, q, ¹J_{CF} = 321 Hz, CF3), 127.1 (1C, s, C13), 128.3 (1C, s, C13), 129.7 (2C, s, C14/15), 129.9 (2C, s, C14/15), 131.4 (1C, s, C9), 131.7 (1C, s, C14/15), 132.1 (1C, s, C14/15), 132.6 (2C, s, C2), 133.1 (1C, d, ³J_{CP} = 1 Hz, C12), 133.3 (1C, d, ²J_{CP} = 15 Hz, C7), 136.2 (1C, d, ³J_{CP} = 4 Hz, C12), 139.3 (1C, d, ¹J_{CP} = 103 Hz, C1), 144.4 (1C, s, C10), 147.1 (1C, d, ³J_{CP} = 2 Hz, C8), 150.1 (1C, d, ¹J_{CP} = 49 Hz, C6); **¹⁹F{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = -78.8 (s); **³¹P{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = 65.8 (s); **elemental analysis:** calculated for C₃₁H₃₄F₆N₃O₇PS₂·0.25 CH₂Cl₂: N 5.31, C 47.46, H 4.40, S 8.11; found: N 5.52, C 47.23, H 4.18, S 8.16.

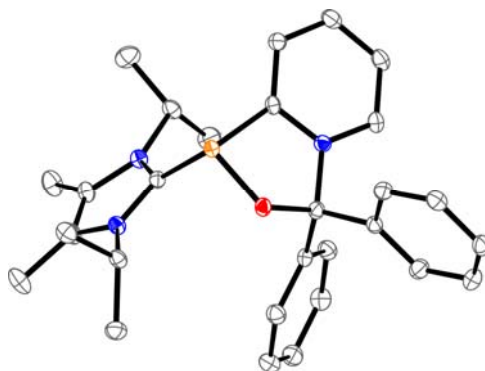


Figure S 53: Molecular structure of $18a^{2+}$ in $18a[OTf]_2 \cdot CH_2Cl_2$; thermal ellipsoids are displayed at 50 % probability level, hydrogen atoms, solvent molecules and counterions are omitted for clarity.

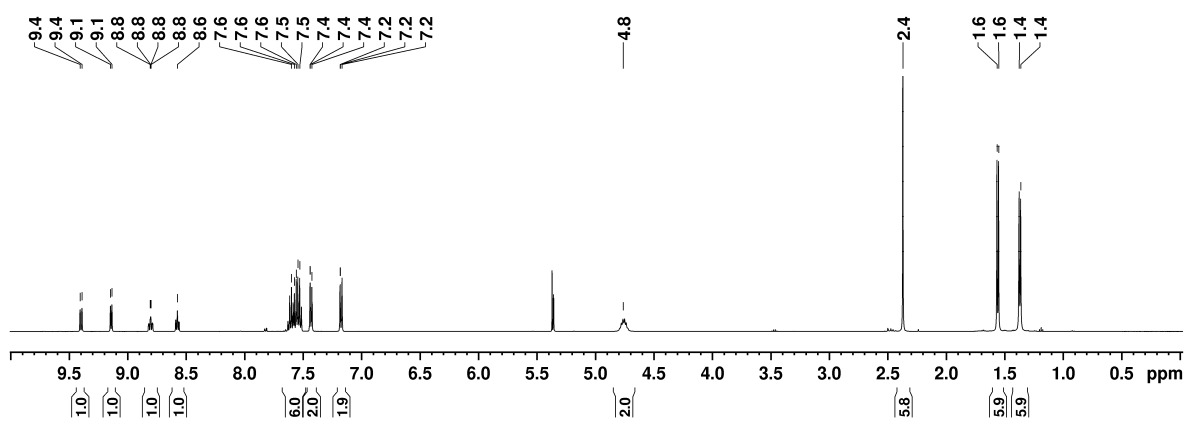


Figure S 54: 1H NMR spectrum of $18a[OTf]_2$ in CD_2Cl_2 .

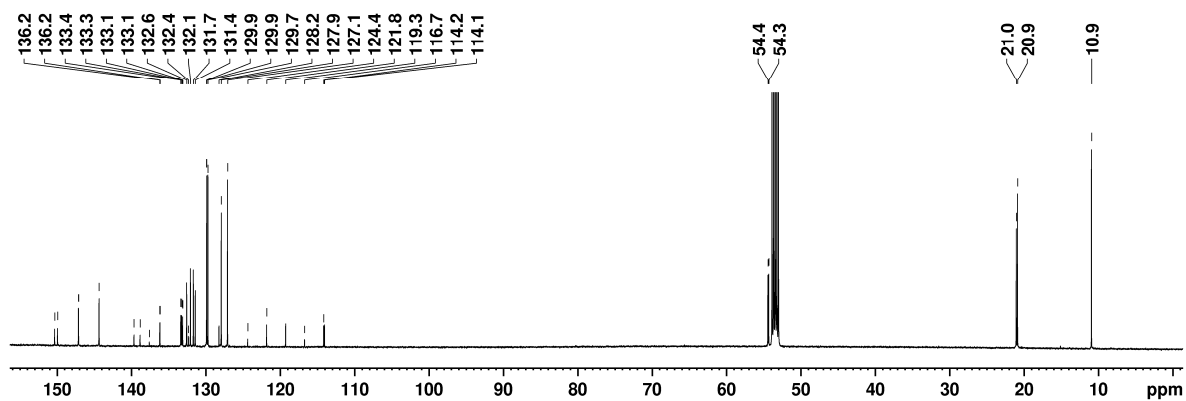


Figure S 55: $^{13}C\{^1H\}$ NMR spectrum of $18a[OTf]_2$ in CD_2Cl_2 .

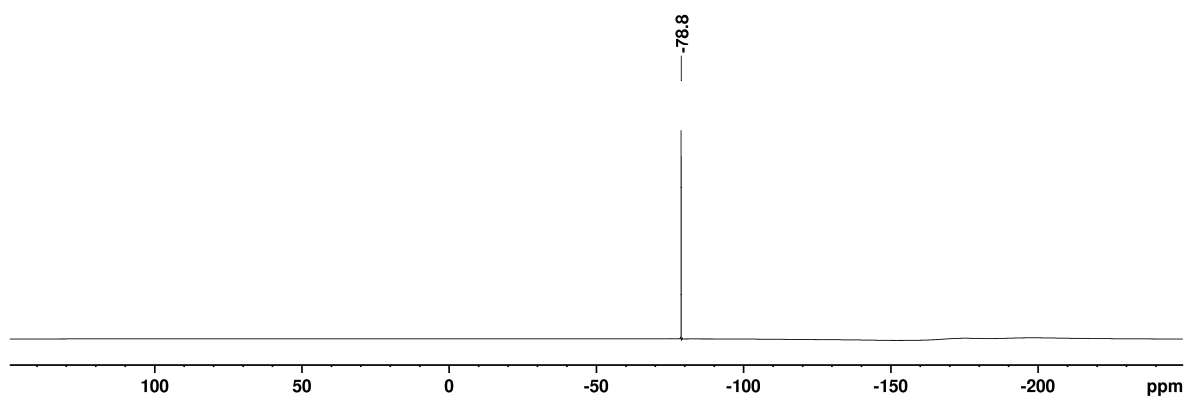


Figure S 56: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **18a**[OTf] $_2$ in CD_2Cl_2 .

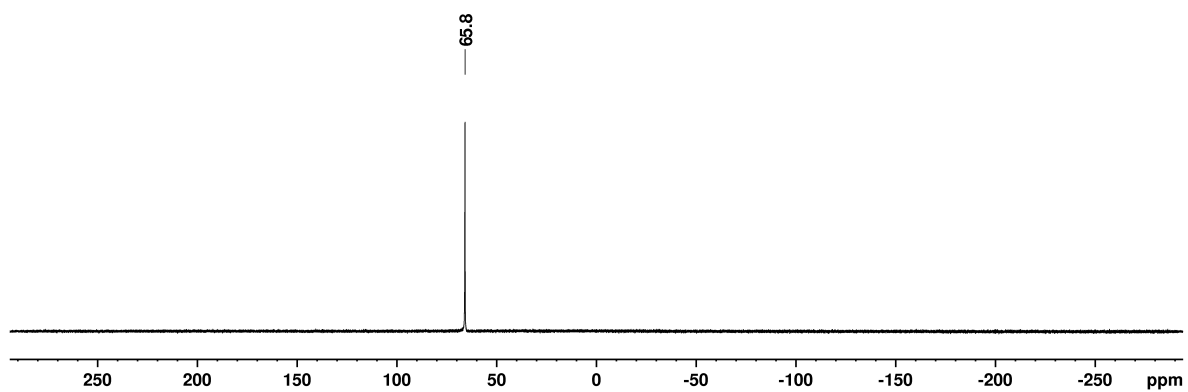
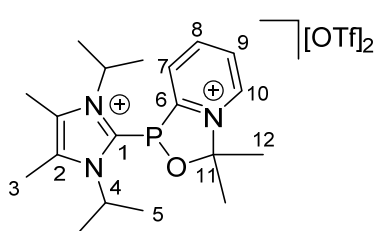


Figure S 57: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **18a**[OTf] $_2$ in CD_2Cl_2 .

2.5.2. Synthesis of **18b**[OTf]₂



11[OTf] (150.0 mg, 0.316 mmol, 1.0 equiv.), silver triflate (85.3 mg, 0.316 mmol, 1.0 equiv.) and acetone (300.0 mg, 5.165 mmol, 16.3 equiv.) are suspended in 6 mL of CH₂Cl₂ and stirred for 6 h. The resulting solid is filtered off and the solvent removed *in vacuo*. The remaining solid is suspended in *n*-pentane and stirred overnight. By filtration and washing with *n*-pentane, crude **18b**[OTf]₂ is obtained. After several recrystallizations from CH₂Cl₂/*n*-pentane **18b**[OTf]₂ was obtained as a colourless, air and moisture sensitive solid.

Yield: 52 mg (25 %); **m.p.** 222 °C; **Raman** (80 mW, 100 scans, 298 K, cm⁻¹): 3082 (19), 3003 (33), 2993 (33), 2948 (58), 2895 (17), 2886 (17), 1608 (33), 1564 (22), 1469 (28), 1460 (31), 1449 (31), 1438 (28), 1404 (28), 1375 (22), 1280 (53), 1224 (28), 1157 (22), 1145 (19), 1107 (28), 1087 (19), 1034 (100), 988 (19), 890 (25), 755 (42), 701 (31), 574 (33), 538 (25), 515 (25); **IR** (ATR, 298 K, cm⁻¹): 1607 (vw), 1400 (vw), 1264 (s), 1248 (s), 1221 (m), 1205 (w), 1156 (m), 1104 (w), 1026 (s), 984 (w), 944 (vw), 857 (w), 787 (w), 777 (w), 755 (vw), 739 (vw), 633 (vs), 573 (w), 537 (vw), 514 (m), 483 (w); **¹H NMR** (CD₂Cl₂, 298 K, in ppm) δ = 1.55 (12H, m, H5), 2.07 (3H, s, H12), 2.14 (3H, s, H12), 2.46 (6H, s, H3), 4.84 (2H, m, H4), 8.45 (1H, m, H9), 8.71 (1H, m, H8), 9.24 (1H, d, ³J_{HH} = 7.9 Hz, H7), 9.81 (1H, d, ³J_{HH} = 6.1 Hz, H10); **¹³C{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = 11.0 (2C, s, C3), 20.9 (4C, s, C5), 27.0 (1C, s, C12), 29.4 (1C, d, ³J_{CP} = 3 Hz, C12), 53.9 (1C, s, C4), 54.0 (1C, s, C4), 111.2 (1C, d, ²J_{CP} = 14 Hz, C11), 120.6 (2C, q, ¹J_{CF} = 320 Hz, CF3), 131.3 (1C, s, C9), 132.7 (1C, d, ²J_{CP} = 14 Hz, C7), 132.8 (2C, s, C2), 139.2 (1C, d, ¹J_{CP} = 103 Hz, C1), 142.9 (1C, s, C10), 146.2 (1C, d, ³J_{CP} = 1 Hz, C8), 150.1 (1C, d, ¹J_{CP} = 49 Hz, C6); **¹⁹F{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = -78.9 (s); **³¹P{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = 71.8 (s); **elemental analysis:** calculated for C₂₁H₃₀F₆N₃O₇PS₂: N 6.51, C 39.07, H 4.68, S 9.93; found: N 6.27, C 38.85, H 4.81, S 10.50.

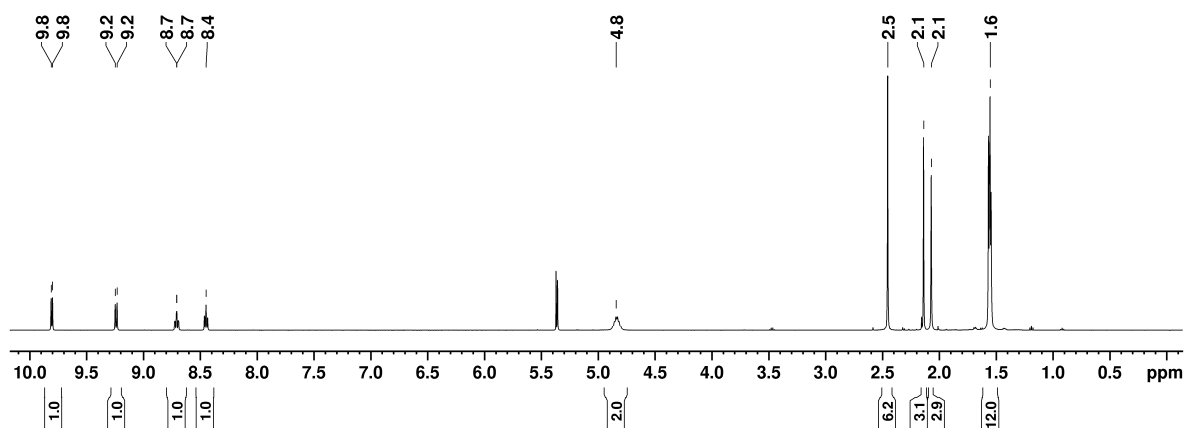


Figure S 58: ¹H NMR spectrum of **18b**[OTf]₂ in CD₂Cl₂.

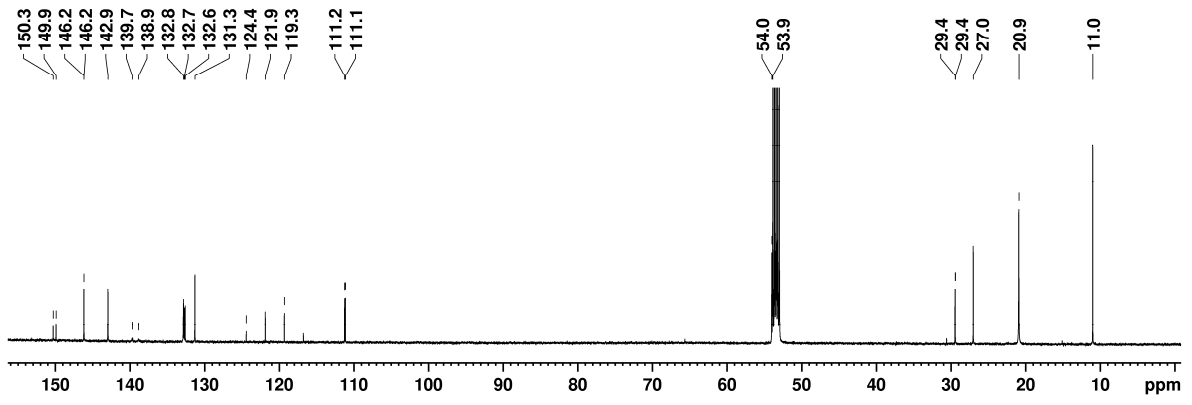


Figure S 59: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **18b**[OTf]₂ in CD₂Cl₂.

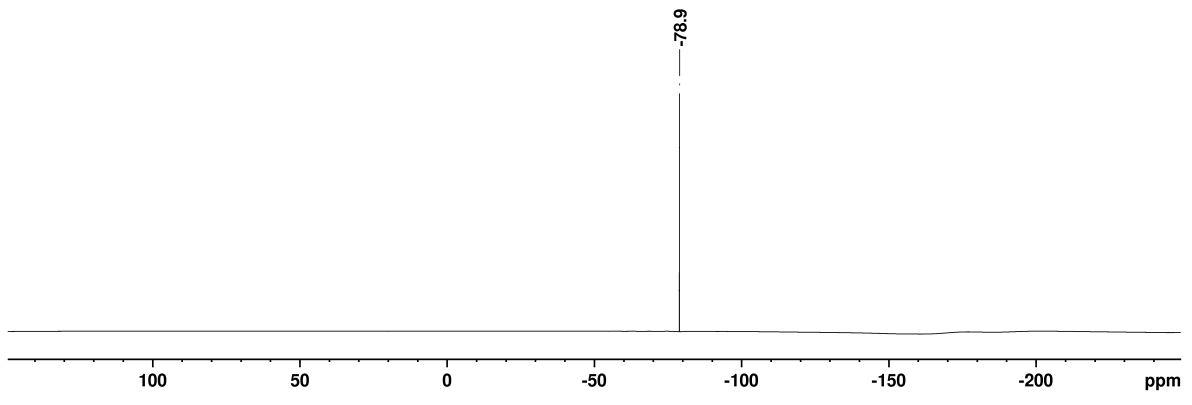


Figure S 60: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **18b**[OTf]₂ in CD₂Cl₂.

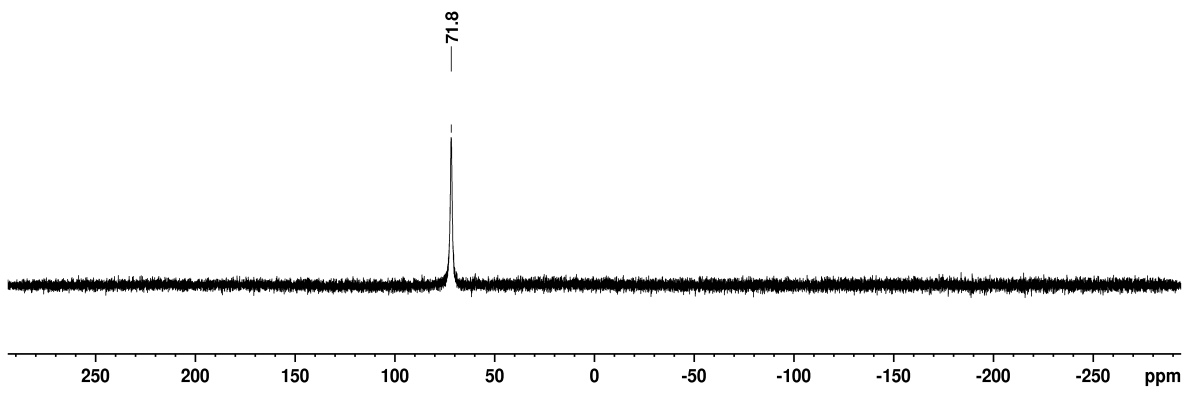
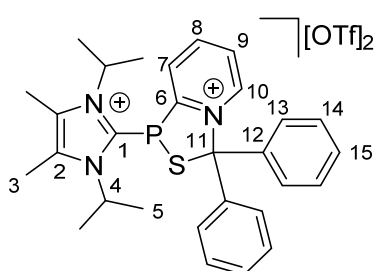


Figure S 61: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **18b**[OTf]₂ in CD₂Cl₂.

2.5.3. Synthesis of **19**[OTf]₂



11[OTf] (300.0 mg, 0.630 mmol, 1.0 equiv.), silver triflate (162.6 mg, 0.630 mmol, 1.0 equiv.) and thiobenzophenone (150.0 mg, 0.758 mmol, 1.2 equiv.) are suspended in 10 mL of CH₂Cl₂ and stirred for 6 h. The resulting solid is filtered off and the solvent removed *in vacuo*. The remaining solid is recrystallized from CH₂Cl₂ and Et₂O. By filtration and washing with *n*-pentane, **19**[OTf]₂ is obtained as a yellow, air and moisture

sensitive solid. Suitable crystals for X-ray diffraction analysis can be obtained by slow diffusion of *n*-pentane to a CH₂Cl₂ solution at -30 °C.

Yield: 433 mg (87 %); **m.p.** 207 °C (decomp.); **Raman** (100 mW, 200 scans, 298 K, cm⁻¹): 3095 (24), 3077 (47), 3067 (37), 2990 (38), 2948 (46), 1611 (57), 1599 (73), 1562 (46), 1462 (46), 1446 (45), 1414 (47), 1405 (47), 1392 (43), 1366 (55), 1305 (37), 1276 (87), 1224 (42), 1193 (38), 1173 (43), 1159 (55), 1104 (39), 1048 (52), 1032 (100), 1000 (57), 889 (33), 800 (30), 756 (37), 713 (26), 697 (26), 680 (34), 637 (25), 618 (29), 589 (24), 574 (29), 552 (26), 522 (39), 504 (26), 464 (25), 450 (28), 404 (29), 378 (26), 349 (35), 313 (32), 289 (25), 270 (25), 250 (24); **IR** (ATR, 298 K, cm⁻¹): 1610 (vw), 1599 (vw), 1473 (vw), 1453 (vw), 1432 (vw), 1410 (vw), 1383 (vw), 1263 (vs), 1253 (vs), 1222 (m), 1155 (s), 1138 (m), 1118 (w), 1087 (vw), 1028 (vs), 1000 (vw), 906 (vw), 890 (vw), 798 (vw), 776 (w), 749 (m), 733 (vw), 711 (vw), 693 (m), 635 (vs), 572 (w), 551 (vw), 516 (s), 501 (w), 449 (w), 419 (vw); **¹H NMR** (CD₃CN, 298 K, in ppm) δ = 1.43 (6H, d, ³J_{HH} = 5.1 Hz, H5), 1.65 (6H, d, ³J_{HH} = 7.9 Hz, H5), 2.46 (6H, s, H3), 4.94 (2H, s(br), H4), 7.14 (2H, d, ³J_{HH} = 6.6 Hz, H13), 7.35 (2H, d, ³J_{HH} = 7.5 Hz, H13), 7.54 (2H, m, H14/H15), 7.62 (3H, m, H14/H15), 7.69 (1H, m, H14/H15), 8.14 (1H, m, H9), 8.43 (1H, d, ³J_{HH} = 7.9 Hz, H7), 8.55 (1H, d, ³J_{HH} = 7.6 Hz, H10), 8.66 (1H, m, H8); **¹³C{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = 11.4 (2C, s, C3), 20.8 (2C, s, C5), 21.5 (2C, s, C5), 55.1 (1C, s, C4), 55.3 (1C, s, C4), 98.0 (1C, d, ²J_{CP} = 2 Hz, C11), 122.1 (2C, q, ¹J_{CF} = 320 Hz, CF3), 128.7 (2C, d, ⁴J_{CP} = 1 Hz, C13), 130.2 (1C, s, C9), 130.4 (2C, s, C14/C15), 131.1 (2C, s, C14/C15), 131.4 (2C, s, C13), 132.0 (1C, s, C12), 132.9 (1C, d, ²J_{CP} = 11 Hz, C7), 133.3 (2C, s, C14/C15), 136.1 (1C, d, ³J_{CP} = 2 Hz, C12), 136.6 (2C, s(br), C2), 136.7 (1C, s, C12), 146.4 (1C, s, C10), 147.2 (1C, d, ³J_{CP} = 2 Hz, C8), 156.2 (1C, d, ¹J_{CP} = 42 Hz, C6); **¹⁹F{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = -79.3 (s); **³¹P{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = -15.1 (s); **elemental analysis:** calculated for C₃₁H₃₄F₆N₃O₇PS₂·0.3 CH₂Cl₂: N 5.18, C 46.34, H 4.30, S 11.86; found: N 5.50, C 45.90, H 4.12, S 12.31.

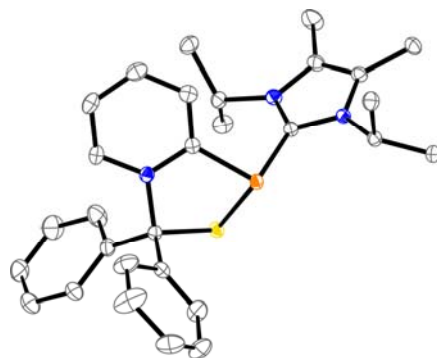


Figure S 62: Molecular structure of 19^{2+} in $19[OTf]_2$; thermal ellipsoids are displayed at 50 % probability level, hydrogen atoms and counterions are omitted for clarity.

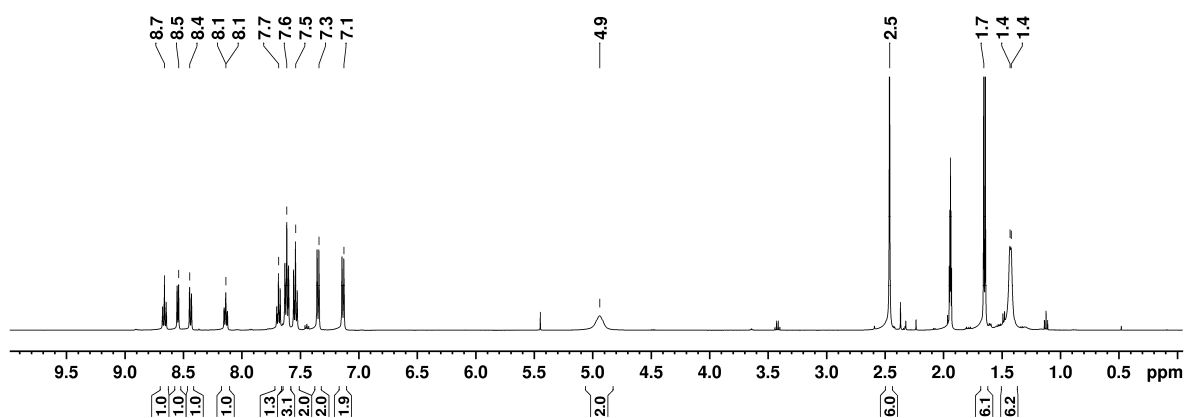


Figure S 63: 1H NMR spectrum of $19[OTf]_2$ in CD_3CN .

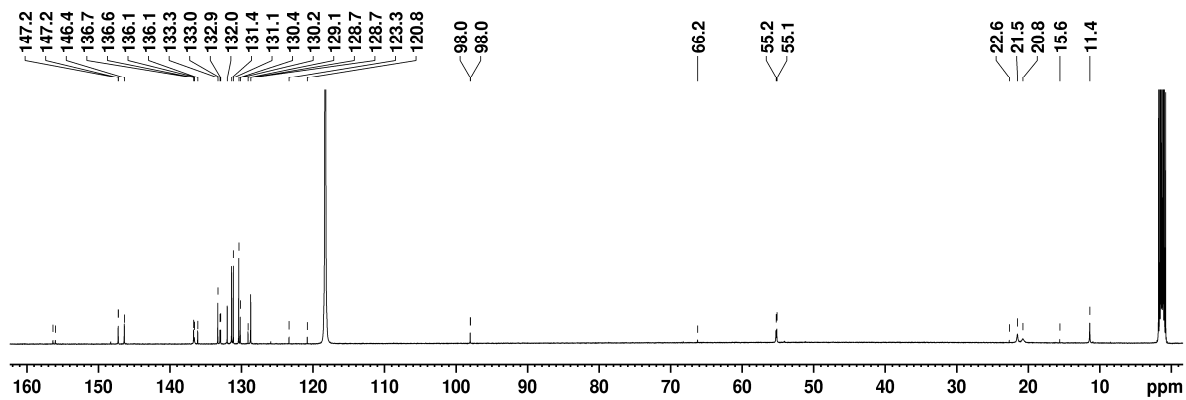


Figure S 64: $^{13}C\{^1H\}$ NMR spectrum of $19[OTf]_2$ in CD_3CN .

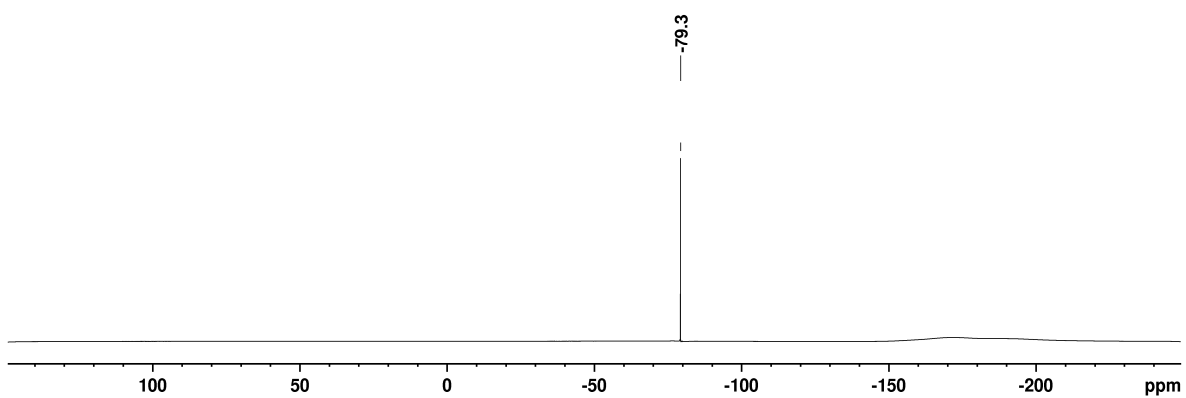


Figure S 65: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of $19[\text{OTf}]_2$ in CD_3CN .

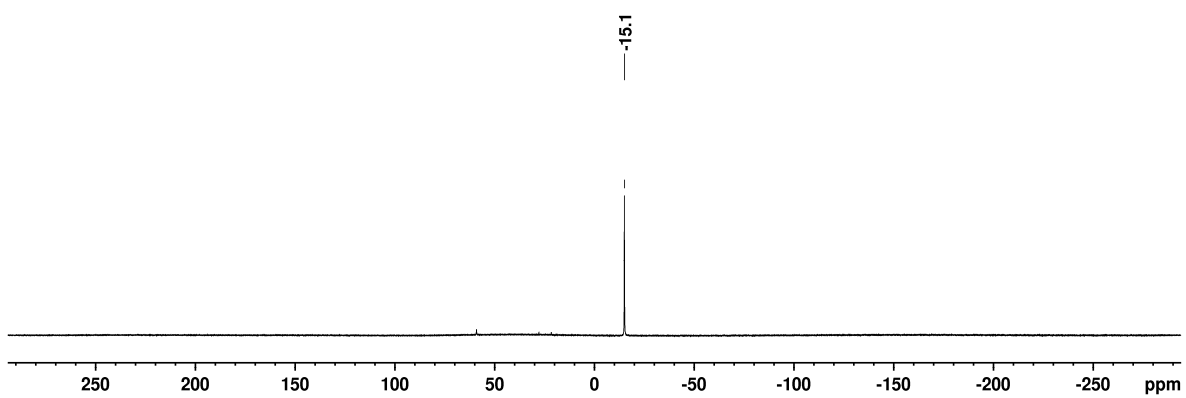
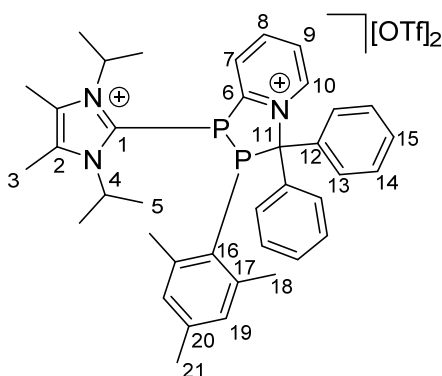


Figure S 66: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $19[\text{OTf}]_2$ in CD_3CN .

2.5.4. Synthesis of **20**[OTf]₂



11[OTf] (184.0 mg, 0.388 mmol, 1.0 equiv.), silver triflate (100.0 mg, 0.389 mmol, 1.0 equiv.) and MesP=CPh₂ (123.0 mg, 0.389 mmol, 1.0 equiv.) are suspended in 5 mL of 1,2-C₂H₄Cl₂ and stirred for 4 h. The resulting solid is filtered off and *n*-pentane is added to precipitate the product. By filtration and washing with *n*-pentane, **20**[OTf]₂ is obtained as a pale yellow, air and moisture sensitive solid. Suitable crystals for X-ray diffraction analysis can be obtained by slow diffusion of *n*-pentane to a 1,2-C₂H₄Cl₂ solution at -30 °C.

Yield: 251 mg (88 %); **m.p.** 217 °C (decomp.); **Raman** (80 mW, 200 scans, 298 K, cm⁻¹): 3075 (41), 2979 (44), 2950 (51), 2918 (49), 1605 (88), 1559 (26), 1461 (31), 1446 (29), 1400 (38), 1357 (48), 1288 (51), 1269 (100), 1152 (57), 1108 (35), 1052 (84), 1032 (95), 1003 (56), 882 (25), 842 (49), 755 (37), 675 (37), 570 (36), 518 (29), 507 (33), 385 (31), 348 (36), 312 (41), 287 (34), 273 (31); **IR** (ATR, 298 K, cm⁻¹): 2976 (vw), 1600 (vw), 1473 (w), 1448 (vw), 1428 (vw), 1398 (vw), 1378 (vw), 1260 (vs), 1223 (m), 1146 (s), 1089 (vw), 1052 (vw), 1029 (vs), 904 (vw), 849 (vw), 780 (w), 761 (w), 753 (w), 738 (w), 729 (w), 707 (w), 694 (w), 635 (vs); **¹H NMR** (CD₃CN, 298 K, in ppm) δ = 1.38 (3H, s(br), H1), 1.51 (3H, d, ³J_{HH} = 7.00 Hz, H1), 1.55 (3H, d, ³J_{HH} = 6.90 Hz, H1), 1.58 (3H, d, *D*_{HH} = 6.88 Hz, H18), 1.76 (3H, s(br), H1), 2.18 (3H, d, *D*_{HH} = 1.56 Hz, H18), 2.25 (3H, s, H21), 2.46 (6H, s, H4), 4.99 (1H, m, H2), 5.53 (1H, s(br), H2), 6.00 (2H, m, H15), 6.85 (1H, s, H19), 6.93 (1H, d, *D*_{HH} = 6.88 Hz, H19), 7.26 (2H, m, H14), 7.50 (2H, m, H13), 7.63 (2H, m, H13), 7.79 (2H, m, H14), 7.97 (1H, m, H9), 8.15 (1H, d, *D*_{HH} = 6.52 Hz, H10), 8.38 (1H, m, H7), 8.57 (1H, m, H8); **¹³C{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = 11.38 (2C, s, C4), 21.12 (1C, s, C21), 21.57 (4C, s, C1), 24.20 (1C, d, ³J_{CP} = 29.58 Hz, C18), 26.42 (1C, s, C18), 55.33 (1C, s, C2), 55.58 (1C, s, C2), 121.73 (1C, m, C16), 127.22 (2C, s, C15), 129.71 (2C, s, C14), 130.42 (1C, d, ⁴J_{CP} = 1.39 Hz, C9), 130.59 (1C, s, C11), 131.12 (1C, s, C19), 131.13 (2C, s, C13), 132.68 (2C, s, C14), 132.74 (2C, s, C13), 133.76 (1C, d, ²J_{CP} = 12.68 Hz, C7), 135.51 (2C, s, C3), 138.04 (1C, s, C12), 138.23 (1C, s, C12), 144.68 (1C, s, C20), 146.84 (1C, d, ³J_{CP} = 3.03 Hz, C8), 147.76 (1C, d, ³J_{CP} = 1.39 Hz, C10), 148.33 (2C, s, C17), 158.79 (1C, m, C6); **¹⁹F{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = -79.3 (s); **³¹P{¹H} NMR** (CD₃CN, 298 K, in ppm): δ(P_A) = -51.0, δ(P_B) = 29.7, ¹J_{AB} = -170 Hz; **elemental analysis:** calculated for C₄₀H₄₅ClF₆N₃O₆P₂S₂: N 4.65, C 53.15, H 5.02, S 7.09; found: N 4.50, C 53.43, H 4.78, S 7.02.

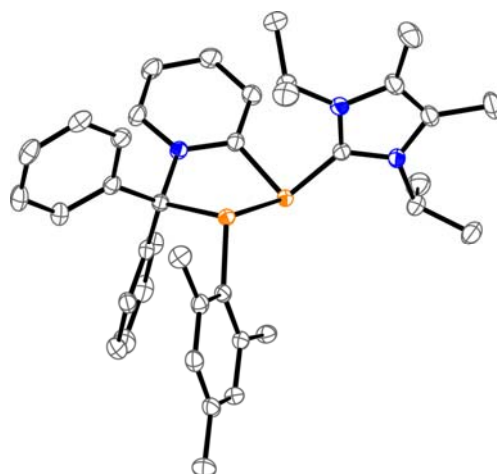


Figure S 67: Molecular structure of 20^{2+} in $20[OTf]_2 \cdot 2 C_2H_4Cl_2$; thermal ellipsoids are displayed at 50 % probability level, hydrogen atoms, solvent molecules and counterions are omitted for clarity.

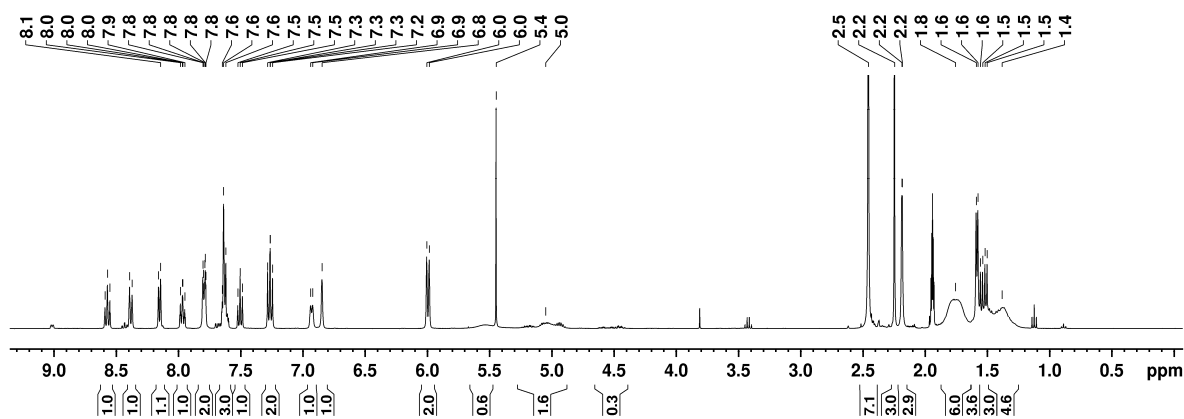


Figure S 68: 1H NMR spectrum of $20[OTf]_2$ in CD_3CN .

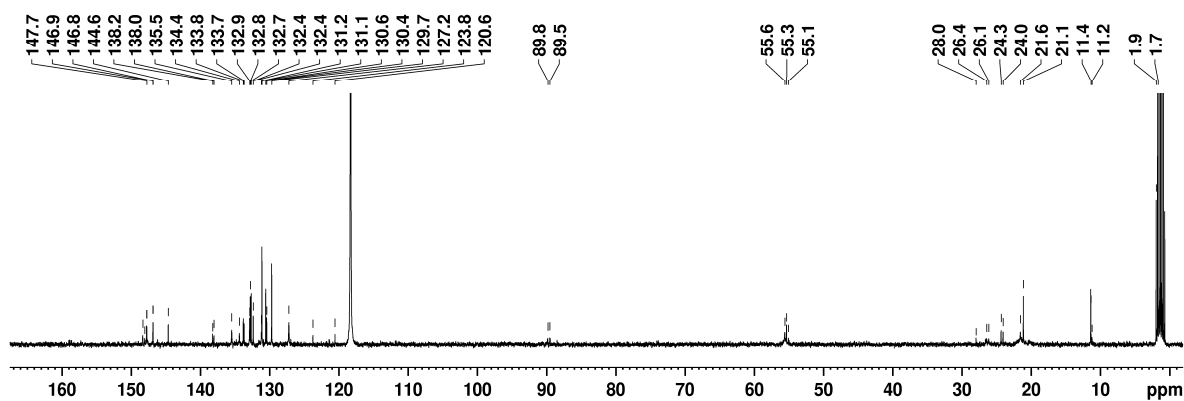


Figure S 69: $^{13}C\{^1H\}$ NMR spectrum of $20[OTf]_2$ in CD_3CN .

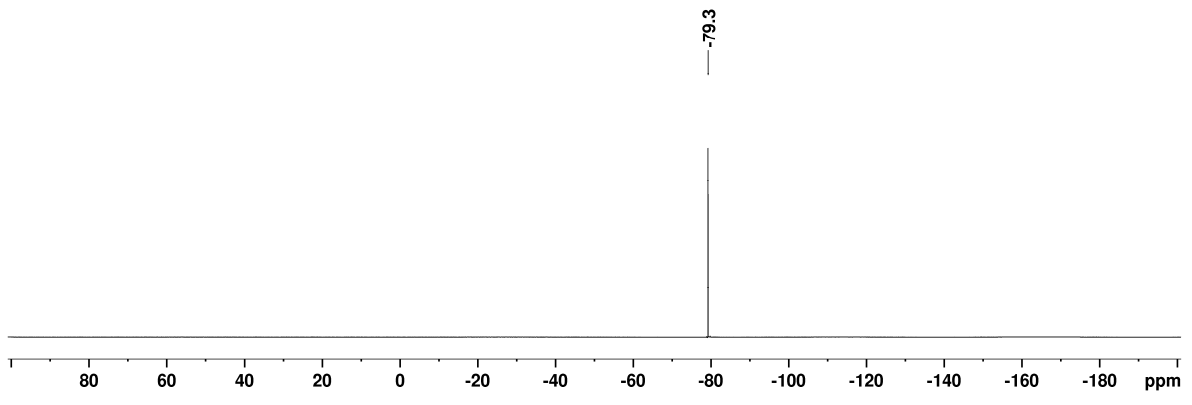


Figure S 70: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of $20[\text{OTf}]_2$ in CD_3CN .

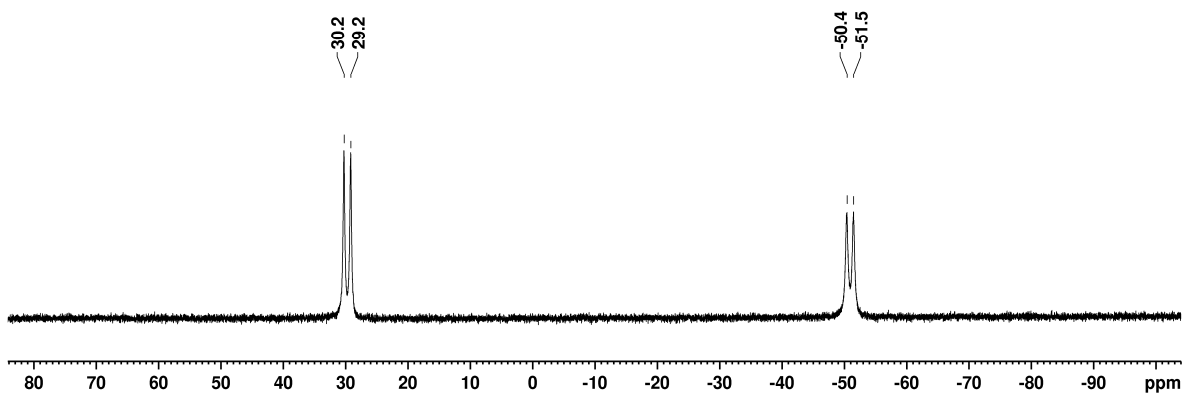
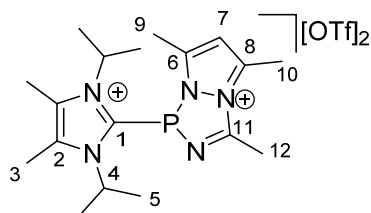


Figure S 71: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $20[\text{OTf}]_2$ in CD_3CN .

2.6. Cycloaddition reactions of 24[OTf] with nitriles

2.6.1. Synthesis of 26a[OTf]₂



22[OTf] (60 mg, 0.139 mmol, 1.0 equiv.), **23**[OTf] (76.6 mg, 0.139 mmol, 1.0 equiv.) and silver triflate (78.6 mg, 0.306 mmol, 2.2 equiv.) are suspended in 3 mL of CH₂Cl₂ and stirred for 2 h under exclusion of light. The resulting solid is filtered off and the solvent removed *in vacuo*. After addition of 2 mL of CH₃CN the reaction mixture is stirred overnight. By adding Et₂O, filtration and

washing with Et₂O, **26a**[OTf]₂ is obtained as a colorless, air and moisture sensitive solid. Suitable crystals for X-ray diffraction analysis can be obtained by diffusion of Et₂O to a CH₃CN solution at -30 °C.

Yield: 148 mg (82 %); **m.p.** 180 °C; **Raman** (100 mW, 500 scans, 298 K, cm⁻¹): 3130 (9), 2996 (32), 2944 (61), 2752 (12), 2413 (12), 2244 (12), 2219 (12), 2186 (12), 2158 (12), 2125 (13), 2077 (13), 2061 (13), 1628 (44), 1603 (39), 1551 (26), 1466 (58), 1407 (36), 1386 (46), 1338 (39), 1310 (24), 1271 (64), 1224 (34), 1194 (24), 1152 (31), 1120 (21), 1080 (35), 1032 (100), 979 (20), 908 (19), 887 (28), 792 (20), 755 (47), 702 (23), 648 (20), 633 (21), 615 (22), 579 (38), 565 (32), 544 (25), 533 (23), 518 (22), 457 (28), 428 (29), 403 (22), 348 (40), 313 (47), 278 (28); **IR** (ATR, 298 K, cm⁻¹): 1627 (w), 1603 (vw), 1552 (vw), 1465 (vw), 1415 (w), 1398 (w), 1380 (w), 1337 (w), 1255 (vs), 1221 (s), 1196 (w), 1148 (vs), 1119 (m), 1094 (w), 1079 (m), 1048 (vw), 1029 (vs), 999 (w), 908 (vw), 887 (vw), 862 (vw), 822 (w), 792 (w), 776 (w), 754 (w), 663 (vw), 635 (vs), 587 (w), 572 (m), 565 (m), 544 (w), 533 (w), 516 (s), 457 (w), 428 (m); **¹H NMR** (CD₃CN, 298 K, in ppm) δ = 1.56 (6H, d, ³J_{HH} = 6.18 Hz, H5), 1.66 (6H, d, ³J_{HH} = 6.78 Hz, H5), 2.46 (6H, s, H3), 2.54 (3H, d, ³J_{HH} = 2.25 Hz, H10), 2.88 (3H, d, ³J_{HH} = 2.50 Hz, H9), 2.97 (3H, d, ³J_{HH} = 5.13 Hz, H12), 4.65 (2H, s(br), H4), 6.92 (1H, s, H7); **¹³C{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = 10.65 (2C, s, C3), 12.78 (1C, s, C10), 12.84 (1C, d, ³J_{CP} = 1 Hz, C9), 19.10 (1C, d, ³J_{CP} = 6 Hz, C12), 20.30 (2C, s, C1), 20.81 (2C, s, C5), 53.67 (2C, d, ³J_{CP} = 13 Hz, C4), 118.25 (1C, d, ³J_{CP} = 4 Hz, C7), 121.07 (2C, q, ¹J_{CF} = 321 Hz, OTf), 128.98 (1C, d, ¹J_{CP} = 83 Hz, C1), 136.40 (2C, s, C3), 149.32 (1C, d, ²J_{CP} = 4 Hz, C6), 155.79 (1C, d, ³J_{CP} = 5 Hz, C8), 157.35 (1C, s, C11); **¹⁹F{¹H} NMR** (CD₃CN, 330K, in ppm): δ = -79.2 (s); **³¹P{¹H} NMR** (CD₃CN, 330K, in ppm): δ = 62.7 (s); **elemental analysis:** calculated for C₂₀H₃₀F₆N₅O₆PS₂: N 10.85, C 37.21, H 4.68, S 9.93; found: N 10.68, C 36.73, H 4.87, S 10.32.

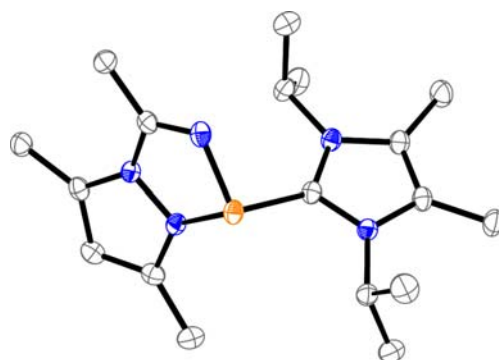


Figure S 72: Molecular structure of $26a^{2+}$ in $26a[OTf]_2 \cdot CH_2Cl_2$; thermal ellipsoids are displayed at 50 % probability level, hydrogen atoms, solvate molecules and counterions are omitted for clarity.

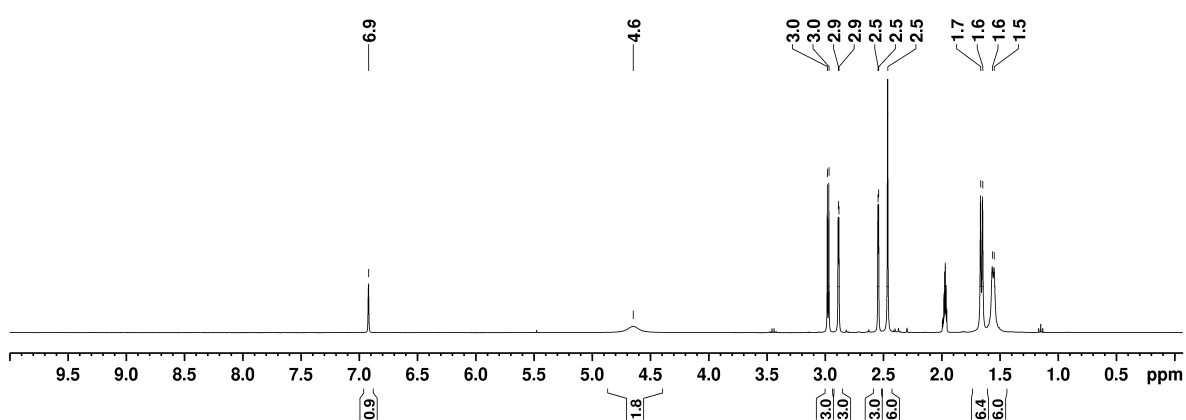


Figure S 73: 1H NMR spectrum of $26a[OTf]_2$ in CD_3CN .

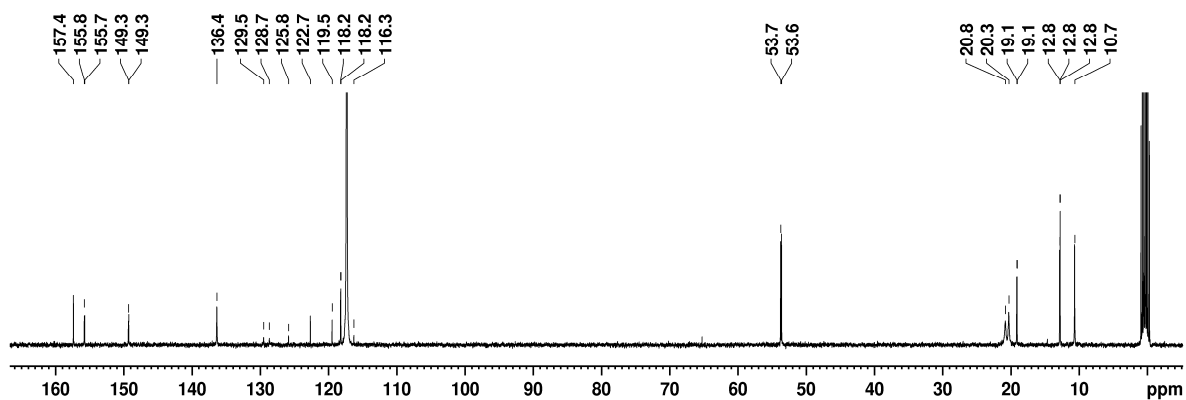


Figure S 74: $^{13}C\{^1H\}$ NMR spectrum of $26a[OTf]_2$ in CD_3CN .

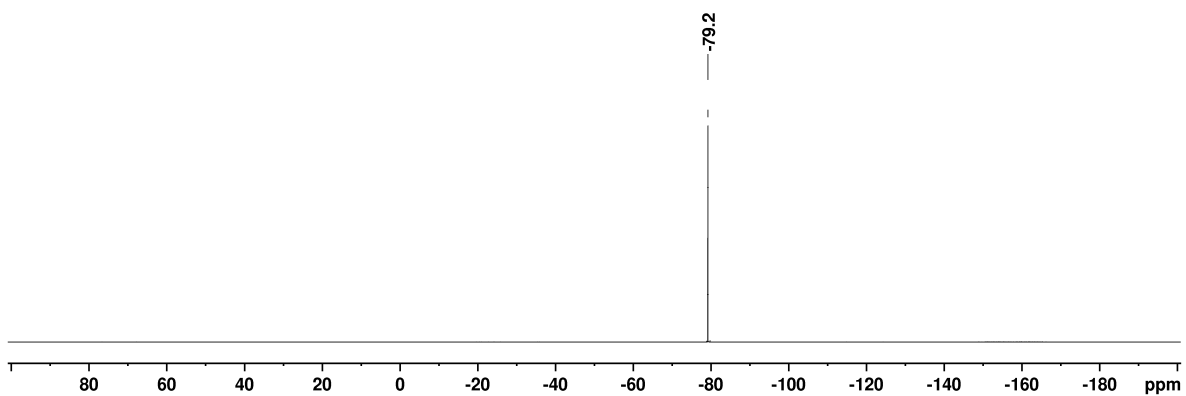


Figure S 75: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **26a**[OTf] $_2$ in CD_3CN .

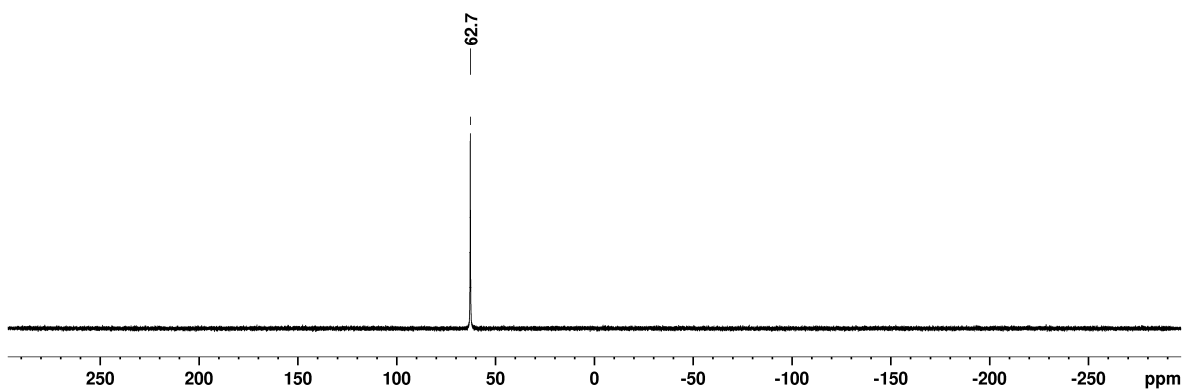
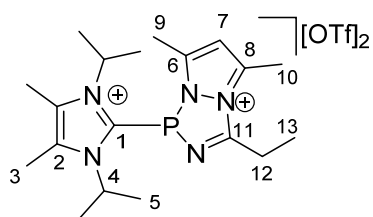


Figure S 76: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **26a**[OTf] $_2$ in CD_3CN .

2.6.2. Synthesis of **26b**[OTf]₂



22[OTf] (60 mg, 0.139 mmol, 1.0 equiv.), **23**[OTf] (76.6 mg, 0.139 mmol, 1.0 equiv.) and silver triflate (78.6 mg, 0.306 mmol, 2.2 equiv.) are suspended in 3 mL of CH₂Cl₂ and stirred for 2 h under exclusion of light. The resulting solid is filtered off and the solvent removed *in vacuo*. After addition of 2 mL of EtCN the reaction mixture is stirred overnight. By adding Et₂O, filtration and

washing with Et₂O, **26b**[OTf]₂ is obtained as a colorless, air and moisture sensitive solid. Suitable crystals for X-ray diffraction analysis can be obtained by diffusion of Et₂O to a CH₃CN solution at -30 °C.

Yield: 62 mg (34 %); **m.p.** 161 °C; **Raman** (100 mW, 200 scans, 298 K, [cm⁻¹]): Raman (100 mW, 200 scans, 298 K, cm⁻¹): 2995 (32), 2945 (66), 1631 (32), 1608 (44), 1550 (30), 1466 (61), 1411 (41), 1386 (40), 1364 (37), 1339 (39), 1271 (71), 1256 (39), 1226 (43), 1153 (34), 1086 (35), 1032 (100), 888 (34), 791 (27), 755 (50), 592 (41), 574 (49), 543 (31), 456 (37), 443 (36), 349 (52), 315 (50), 275 (35), 225 (34); **IR** (ATR, 298 K, cm⁻¹): 2949 (vw), 1611 (vw), 1550 (vw), 1463 (vw), 1412 (vw), 1399 (vw), 1379 (vw), 1337 (vw), 1266 (w), 1255 (w), 1222 (w), 1149 (w), 1119 (vw), 1105 (vw), 1085 (vw), 1028 (m), 1002 (vw), 972 (vw), 837 (vw), 789 (vw), 754 (vw), 635 (m), 572 (w), 532 (vw), 516 (w), 445 (w); **¹H NMR** (CD₃CN, 298 K, in ppm) δ = 1.45 (3H, t, ³J_{HH} = 7.02 Hz, H13), 1.56 (6H, d, ³J_{HH} = 5.92 Hz, H5), 1.66 (6H, d, ³J_{HH} = 6.96 Hz, H5), 2.47 (6H, s, H3), 2.54 (3H, d, ³J_{HH} = 2.20 Hz, H10), 2.88 (3H, d, ³J_{HH} = 2.56 Hz, H9), 3.22 (1H, dqd, ²J_{HH} = 19.38 Hz, ³J_{HH} = 11.75, *D*_{HH} = 3.16 Hz, H12), 3.41 (1H, m, H12), 4.65 (2H, s(br), H4), 6.92 (1H, s, H7); **¹³C{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = 8.41 (1C, s, C13), 10.64 (2C, s, C3), 12.75 (1C, s, C10), 13.10 (1C, s, C9), 20.28 (2C, s, C5), 20.85 (2C, s, C5), 26.09 (1C, d, ³J_{CP} = 5 Hz, C12), 53.54 (1C, s, C4), 53.68 (1C, s, C4), 118.22 (1C, d, ³J_{CP} = 4 Hz, C7), 121.09 (2C, q, ¹J_{CF} = 320 Hz, OTf), 129.60 (1C, s(br), C1), 136.38 (2C, s, C2), 149.05 (1C, d, ²J_{CP} = 4 Hz, C6), 155.47 (1C, d, ³J_{CP} = 4 Hz, C8), 161.76 (1C, s, C11); **¹⁹F{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = -79.3 (s); **³¹P{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = 64.4 (s); **elemental analysis:** calculated for C₂₁H₃₂F₆N₅O₆PS₂: N 10.62, C 38.24, H 4.89, S 9.72; found: N 10.55, C 38.01, H 4.89, S 10.25.

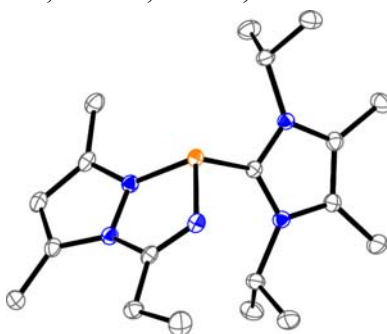


Figure S 77: Molecular structure of **26b**²⁺ in **26b**[OTf]₂; thermal ellipsoids are displayed at 50 % probability level, hydrogen atoms, solvate molecules and counterions are omitted for clarity.

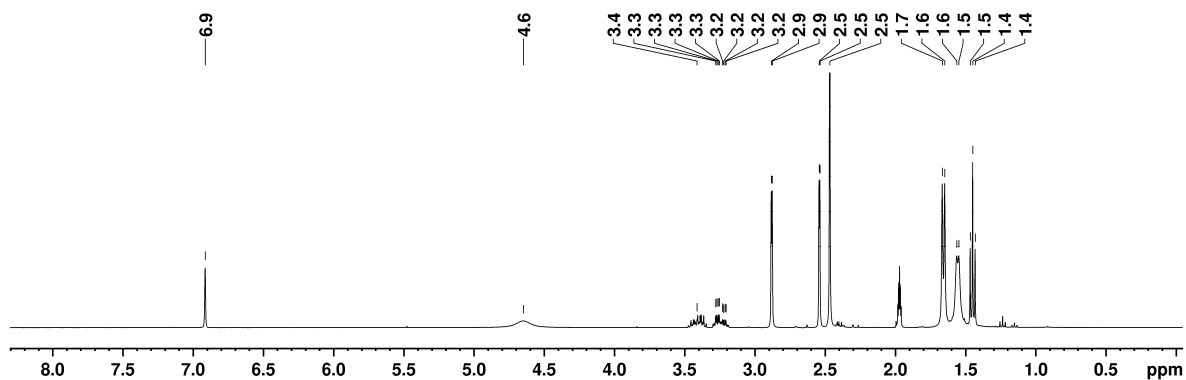


Figure S 78: ¹H NMR spectrum of **26b**[OTf]₂ in CD₃CN.

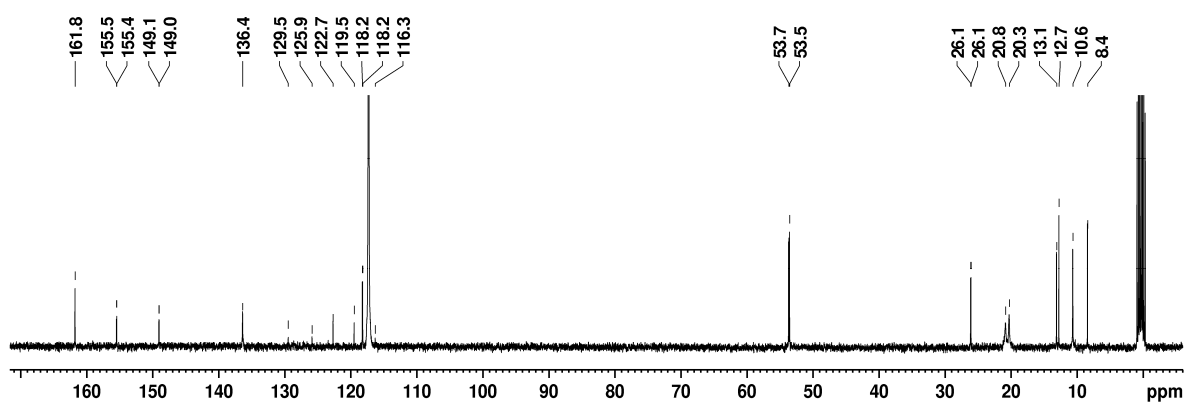


Figure S 79: ¹³C{¹H} NMR spectrum of **26b**[OTf]₂ in CD₃CN.

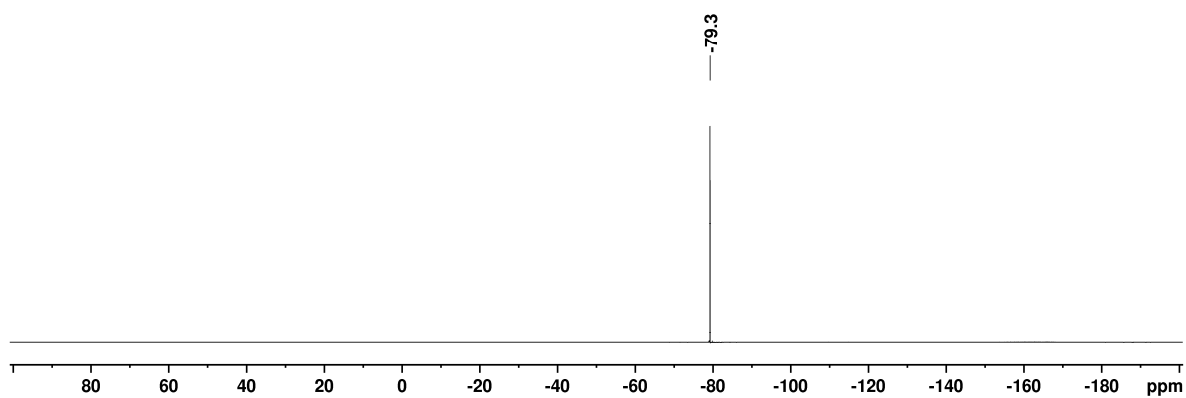


Figure S 80: ¹⁹F{¹H} NMR spectrum of **26b**[OTf]₂ in CD₃CN.

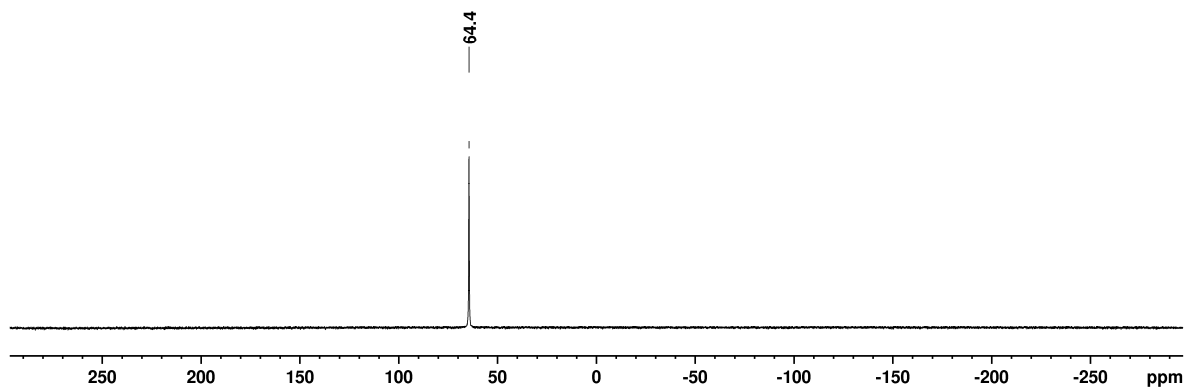
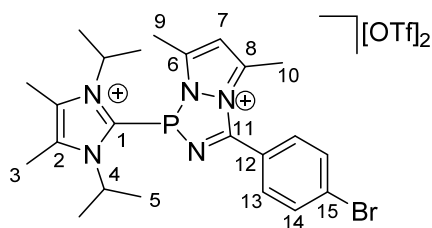


Figure S 81: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **26b**[OTf]₂ in CD₃CN.

2.6.3. Synthesis of **26c**[OTf]₂



22[OTf] (60 mg, 0.139 mmol, 1.0 equiv.), **23**[OTf] (76.6 mg, 0.139 mmol, 1.0 equiv.) and silver triflate (78.6 mg, 0.306 mmol, 2.2 equiv.) are suspended in 3 mL of CH₂Cl₂ and stirred for 2 h under exclusion of light. The resulting solid is filtered off and the solvent removed *in vacuo*. A solution of 4-bromobenzonitrile (61 mg, 0.335 mmol, 2.3 equiv.) in 2 mL

C₆H₅F is added and stirred overnight. By filtration and washing with C₆H₅F and Et₂O, **26c**[OTf]₂ is obtained as a colorless, air and moisture sensitive solid. Suitable crystals for X-ray diffraction analysis can be obtained by slow diffusion of Et₂O to a CH₃CN solution at –30 °C.

Yield: 178 mg (81 %); **m.p.** 159 °C; **Raman** (100 mW, 500 scans, 298 K, cm⁻¹): 3073 (14), 3000 (20), 2946 (38), 2747 (10), 2562 (11), 2231 (11), 2158 (10), 2112 (11), 2061 (11), 1614 (62), 1600 (100), 1563 (27), 1541 (31), 1457 (34), 1401 (30), 1384 (30), 1364 (22), 1325 (22), 1260 (44), 1223 (24), 1186 (35), 1150 (27), 1071 (28), 1031 (50), 959 (17), 886 (19), 831 (19), 806 (18), 756 (27), 695 (20), 685 (21), 639 (18), 625 (22), 584 (25), 574 (24), 551 (22), 518 (18), 456 (21), 436 (21), 410 (25), 348 (30), 313 (32), 271 (24); **IR** (ATR, 298 K, cm⁻¹): 1600 (w), 1562 (vw), 1541 (vw), 1486 (vw), 1457 (vw), 1404 (w), 1386 (vw), 1364 (vw), 1327 (vw), 1297 (w), 1258 (vs), 1241 (s), 1235 (s), 1221 (s), 1149 (s), 1092 (w), 1070 (w), 1025 (vs), 958 (w), 904 (vw), 851 (vw), 831 (vw), 798 (w), 784 (w), 774 (w), 754 (w), 725 (vw), 686 (w), 665 (vw), 635 (vs), 607 (w), 573 (w), 550 (w), 538 (w), 516 (m), 474 (w), 450 (m), 434 (w), 412 (w); **¹H NMR** (CD₃CN, 298 K, in ppm) δ = 1.53 (6H, d, ³J_{HH} = 6.40 Hz, H5), 1.59 (6H, d, ³J_{HH} = 6.96 Hz, H5), 2.43 (6H, s, H3), 2.54 (3H, d, ³J_{HH} = 2.24 Hz, H10), 3.00 (3H, d, ³J_{HH} = 2.52 Hz, H9), 4.79 (1H, dd, ²J_{HH} = 18.64 Hz, ³J_{HH} = 3.17, H12), 4.97 (1H, dd, ²J_{HH} = 18.83 Hz, ³J_{HH} = 10.50, H12), 4.65 (2H, s(br), H4), 6.97 (1H, s, H7), 7.71 (2H, d, ³J_{HH} = 8.76, H14), 8.29 (2H, d, ³J_{HH} = 8.80, H15); **¹³C{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = 10.66 (2C, s, C3), 12.81 (1C, s, C10), 13.23 (1C, s, C9), 20.24 (2C, s, C5), 20.85 (2C, s, C5), 37.78 (1C, d, ³J_{CP} = 5 Hz, C12), 53.64 (1C, s, C4), 53.78 (1C, s, C4), 118.40 (1C, d, ³J_{CP} = 4 Hz, C7), 121.06 (2C, q, ¹J_{CF} = 320 Hz, OTf), 123.80 (2C, s, C15), 129.20 (1C, s(br), C1), 131.80 (2C, s, C14), 136.57 (2C, s, C2), 139.60 (1C, s, C16), 148.00 (1C, s, C13), 149.18 (1C, s(br), C6), 155.85 (1C, d, ³J_{CP} = 5 Hz, C8), 158.74 (1C, s, C11); **¹⁹F{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = -79.2 (s); **³¹P{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = 64.3 (s); **elemental analysis:** calculated for C₂₅H₃₁BrF₆N₅O₆PS₂: N 8.90, C 38.18, H 3.97, S 8.15; found: N 9.52, C 37.72, H 3.95, S 8.11.

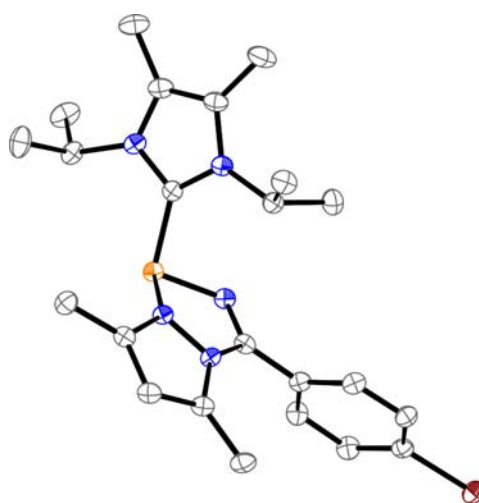


Figure S 82: Molecular structure of $26c^{2+}$ in $26c[OTf]_2 \cdot MeCN$; thermal ellipsoids are displayed at 50 % probability level, hydrogen atoms, solvate molecules and counterions are omitted for clarity.

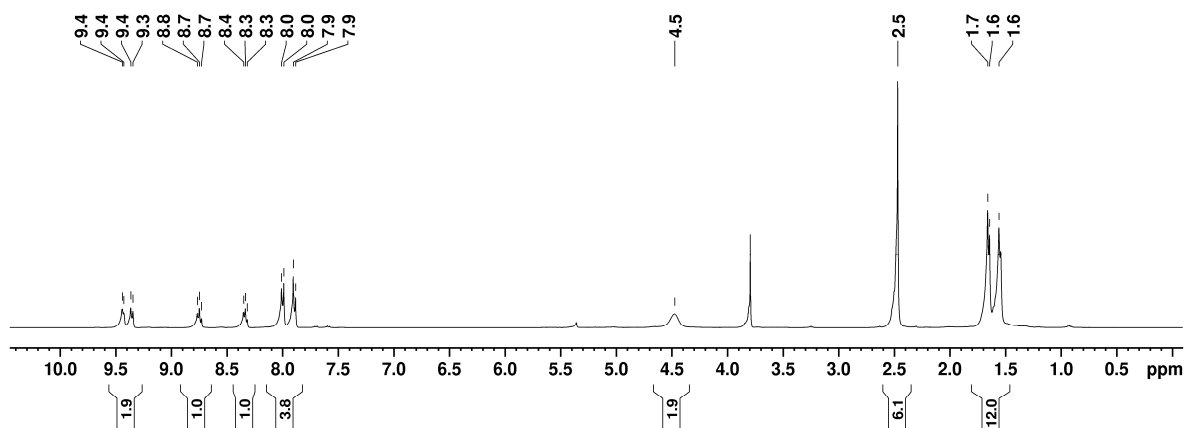


Figure S 83: 1H NMR spectrum of $26c[OTf]_2$ in CD_3CN .

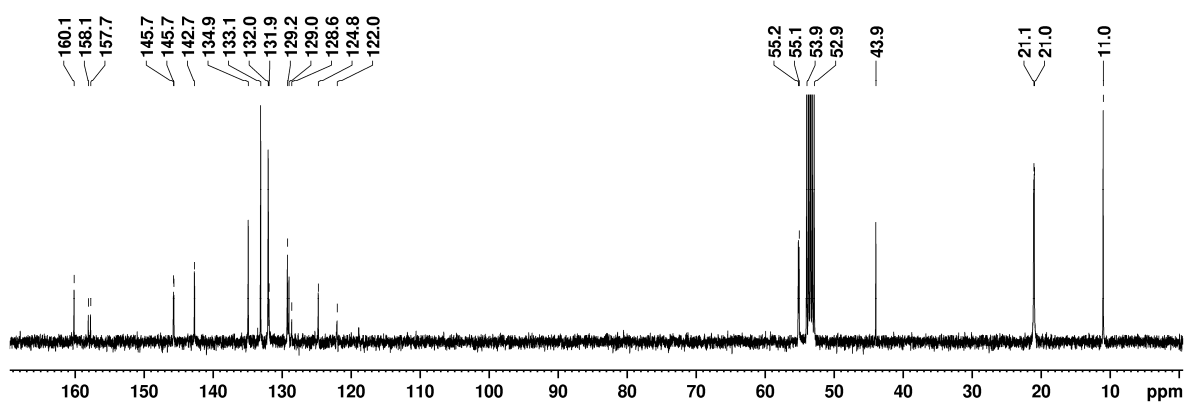


Figure S 84: $^{13}C\{^1H\}$ NMR spectrum of $26c[OTf]_2$ in CD_3CN .

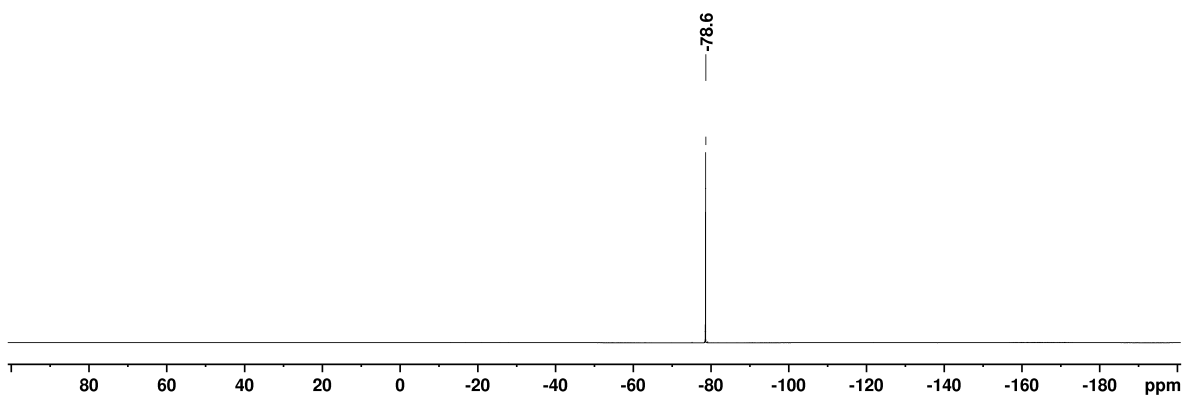


Figure S 85: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **26c**[OTf] $_2$ in CD_3CN .

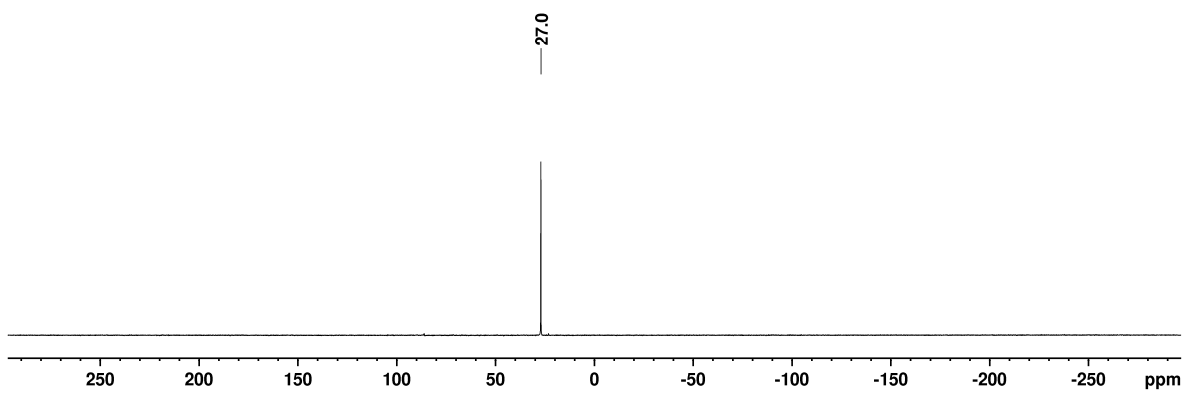
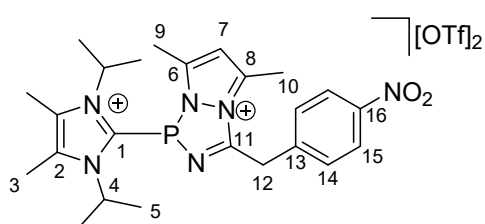


Figure S 86: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **26c**[OTf] $_2$ in CD_3CN .

2.6.4. Synthesis of **26d**[OTf]₂



22[OTf] (60 mg, 0.139 mmol, 1.0 equiv.), **23**[OTf] (76.6 mg, 0.139 mmol, 1.0 equiv.) and silver triflate (78.6 mg, 0.306 mmol, 2.2 equiv.) are suspended in 3 mL of CH₂Cl₂ and stirred for 2 h under exclusion of light. The resulting solid is filtered off and the solvent removed *in vacuo*. A solution of 4-nitrophenylacetonitrile (50 mg, 0.309

mmol, 2.2 equiv.) in 2 mL C₆H₅F is added and the mixture is stirred overnight. By filtration and washing with CH₂Cl₂ and *n*-pentane, **26d**[OTf]₂ is obtained as a colorless, air and moisture sensitive solid.

Yield: 166 mg (78 %); **m.p.** 168 °C (decomp.); **Raman** (80 mW, 200 scans, 298 K, cm⁻¹): 2995 (18), 2944 (29), 1603 (55), 1461 (47), 1404 (42), 1384 (42), 1352 (100), 1264 (52), 1112 (48), 1034 (57), 862 (43), 757 (42), 574 (41), 350 (39), 315 (39); **IR** (ATR, 298 K, cm⁻¹): 1602 (vw), 1526 (vw), 1461 (vw), 1410 (vw), 1379 (vw), 1352 (w), 1256 (s), 1224 (w), 1149 (m), 1100 (w), 1029 (s), 840 (w), 795 (vw), 776 (vw), 753 (w), 636 (s), 571 (w), 540 (vw), 517 (w), 484 (vw), 440 (w); **¹H NMR** (CD₃CN, 298 K, in ppm) δ = 1.53 (6H, d, ³J_{HH} = 6.40 Hz, H5), 1.59 (6H, d, ³J_{HH} = 6.96 Hz, H5), 2.43 (6H, s, H3), 2.54 (3H, d, ³J_{HH} = 2.24 Hz, H10), 3.00 (3H, d, ³J_{HH} = 2.52 Hz, H9), 4.79 (1H, dd, ²J_{HH} = 18.64 Hz, ³J_{HH} = 3.17, H12), 4.97 (1H, dd, ²J_{HH} = 18.83 Hz, ³J_{HH} = 10.50, H12), 4.65 (2H, s(br), H4), 6.97 (1H, s, H7), 7.71 (2H, d, ³J_{HH} = 8.76, H14), 8.29 (2H, d, ³J_{HH} = 8.80, H15); **¹³C{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = 10.66 (2C, s, C3), 12.81 (1C, s, C10), 13.23 (1C, s, C9), 20.24 (2C, s, C5), 20.85 (2C, s, C5), 37.78 (1C, d, ³J_{CP} = 5 Hz, C12), 53.64 (1C, s, C4), 53.78 (1C, s, C4), 118.40 (1C, d, ³J_{CP} = 4 Hz, C7), 121.06 (2C, q, ¹J_{CF} = 320 Hz, OTf⁻), 123.80 (2C, s, C15), 129.20 (1C, s(br), C1), 131.80 (2C, s, C14), 136.57 (2C, s, C2), 139.60 (1C, s, C16), 148.00 (1C, s, C13), 149.18 (1C, s(br), C6), 155.85 (1C, d, ³J_{CP} = 5 Hz, C8), 158.74 (1C, s, C11); **¹⁹F{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = -79.2 (s); **³¹P{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = 64.3 (s); **elemental analysis:** calculated for C₂₆H₃₃F₆N₆O₈PS₂: N 10.96, C 40.73, H 4.34, S 8.36; found: N 10.97, C 40.92, H 4.15, S 8.78.

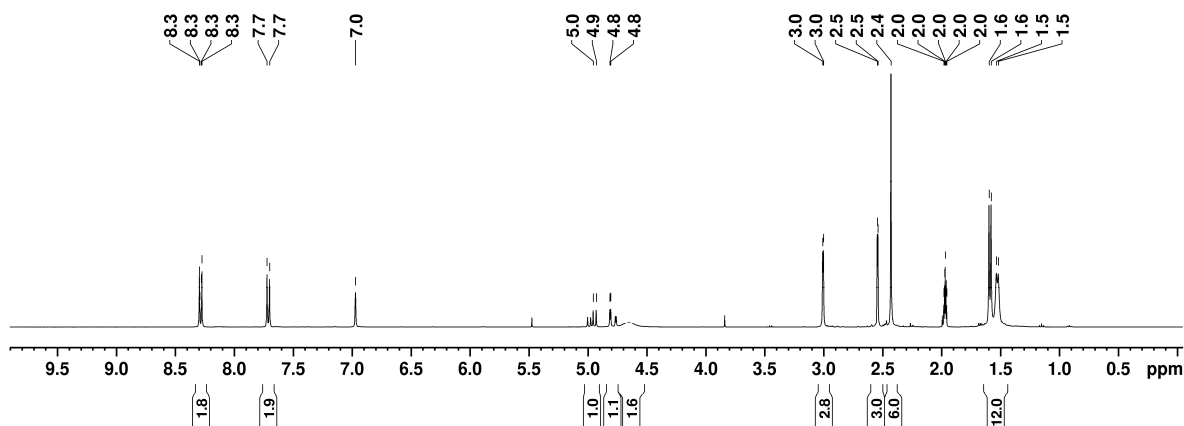


Figure S 87: ¹H NMR spectrum of **26d**[OTf]₂ in CD₃CN.

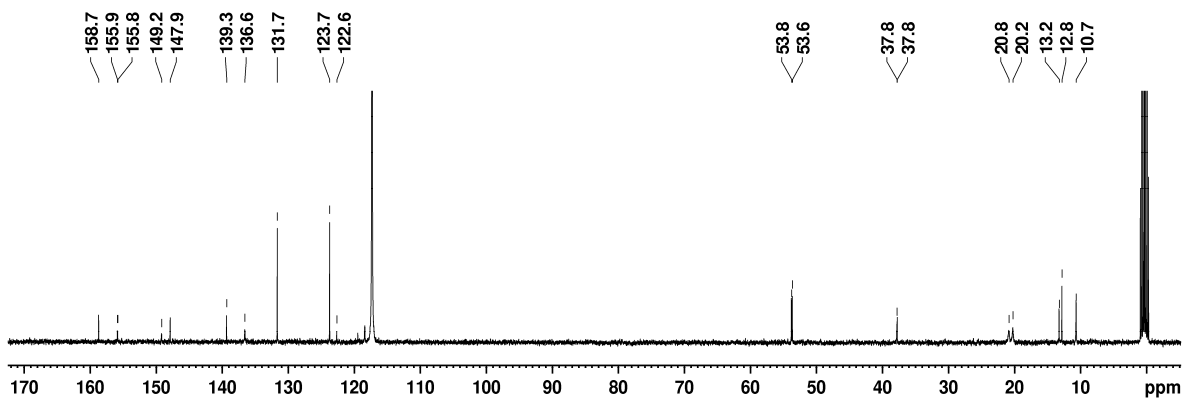


Figure S 88: ¹³C{¹H} NMR spectrum of 26d[OTf]₂ in CD₃CN.

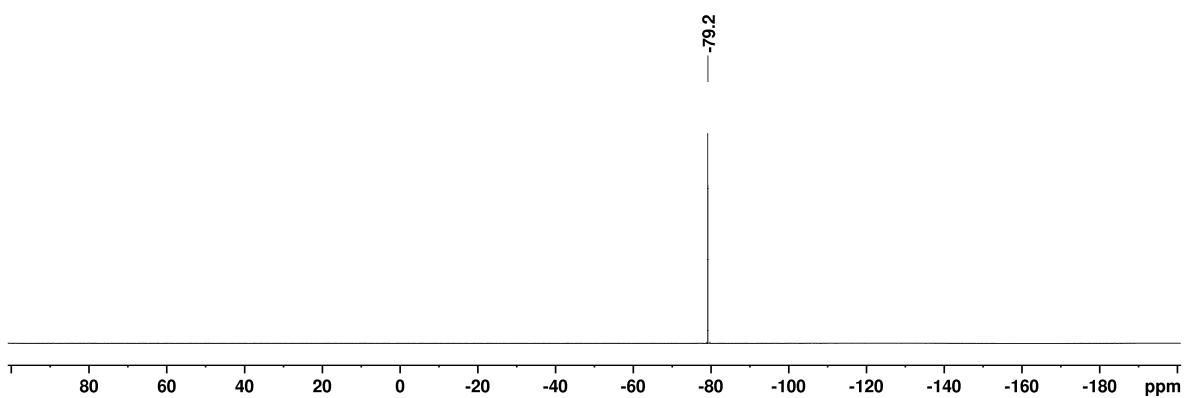


Figure S 89: ¹⁹F{¹H} NMR spectrum of 26d[OTf]₂ in CD₃CN.

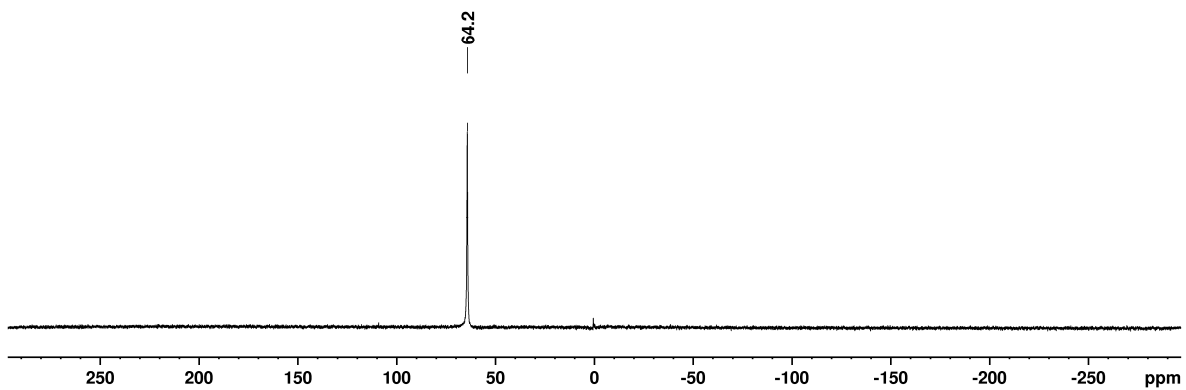
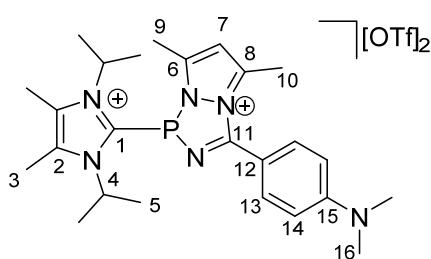


Figure S 90: ³¹P{¹H} NMR spectrum of 26d[OTf]₂ in CD₃CN.

2.6.5. Synthesis of **26e**[OTf]₂



22[OTf] (60 mg, 0.139 mmol, 1.0 equiv.), **23**[OTf] (76.6 mg, 0.139 mmol, 1.0 equiv.) and silver triflate (78.6 mg, 0.306 mmol, 2.2 equiv.) are suspended in 3 mL of CH₂Cl₂ and stirred for 2 h under exclusion of light. The resulting solid is filtered off and the solvent removed *in vacuo*. A solution of 4-(dimethylamino)benzonitrile (49 mg, 0.334 mmol, 2.4 equiv.) in 3.5 mL C₆H₅F is added and stirred overnight. By filtration and washing with C₆H₅F and *n*-pentane, **26e**[OTf]₂ is obtained as a colorless, air and moisture sensitive solid. Suitable crystals for X-ray diffraction analysis can be obtained by slow diffusion of Et₂O to a CH₃CN solution at -30 °C.

Yield: 194 mg (93 %); **m.p.** 134 °C (decomp.); **Raman** : No Raman spectrum of the sample could be obtained due to strong fluorescence of the sample; **IR** (ATR, 298 K, cm⁻¹): 1602 (w), 1584 (m), 1546 (w), 1526 (m), 1494 (vw), 1448 (w), 1403 (w), 1377 (w), 1328 (vw), 1317 (vw), 1254 (vs), 1223 (s), 1197 (s), 1163 (s), 1151 (s), 1114 (w), 1088 (w), 1028 (vs), 956 (vw), 940 (w), 901 (vw), 830 (w), 804 (m), 789 (w), 767 (w), 755 (w), 736 (vw), 698 (vw), 635 (vs), 610 (vw), 573 (m), 546 (vw), 517 (m), 479 (m), 448 (m), 416 (w); **¹H NMR** (CD₂Cl₂, 298 K, in ppm) δ = 1.60 (6H, s (br), H5), 1.70 (6H, s (br), H5), 2.48 (6H, s, H3), 2.58 (3H, s, H10), 2.71 (3H, s, H9), 3.17 (6H, s, H16), 4.93 (2H, s (br), H4), 6.81 (1H, s, H7), 6.86 (2H, d, ³J_{HH} = 8.20 Hz, H14), 7.79 (2H, d, ³J_{HH} = 8.16 Hz, H13); **¹³C{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = 11.19 (2C, s, C3), 13.62 (1C, d, ³J_{CP} = 2 Hz, C9), 15.20 (1C, s, C10), 20.87-22.00 (4C, m, C5), 39.89 (2C, s, C16), 53.44 (2C, s, C4), 111.39 (2C, s, C14), 118.88 (1C, d, ³J_{CP} = 3 Hz, C7), 120.69 (2C, q, ¹J_{CF} = 321 Hz, OTf-), 130.01 (1C, d, ³J_{CP} = 8 Hz, C12), 131.89 (2C, s, C13), 132.14 (1C, d, ¹J_{CP} = 87 Hz, C1), 135.21 (2C, s, C2), 152.51 (1C, d, ³J_{CP} = 4 Hz, C8), 154.57 (1C, s, C15), 156.60 (1C, s, C11), 158.33 (1C, d, ²J_{CP} = 8 Hz, C6); **¹⁹F{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = -78.7 (s); **³¹P{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = 69.9 (s); **elemental analysis:** calculated for C₂₇H₃₈F₆N₆O₆PS₂: N 11.18, C 43.14, H 5.10, S 8.53; found: N 10.99, C 42.48, H 4.76, S 8.31.

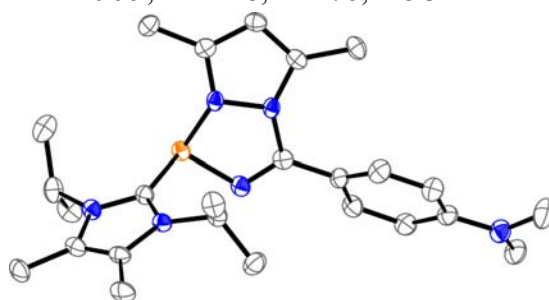


Figure S 91: Molecular structure of **26e**²⁺ in **26e**[OTf]₂·MeCN; thermal ellipsoids are displayed at 50 % probability level, hydrogen atoms, solvate molecules and counterions are omitted for clarity.

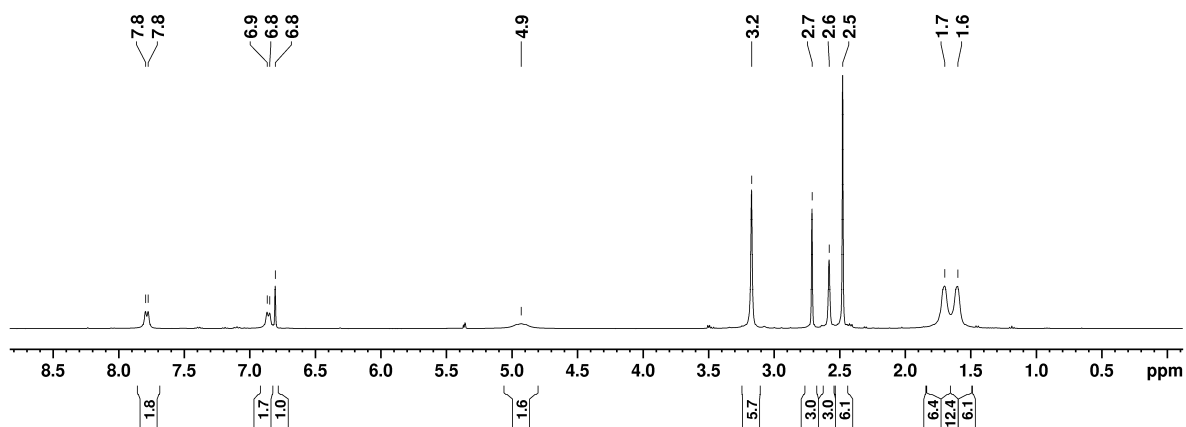


Figure S 92: ^1H NMR spectrum of $26\text{e}[\text{OTf}]_2$ in CD_2Cl_2 .

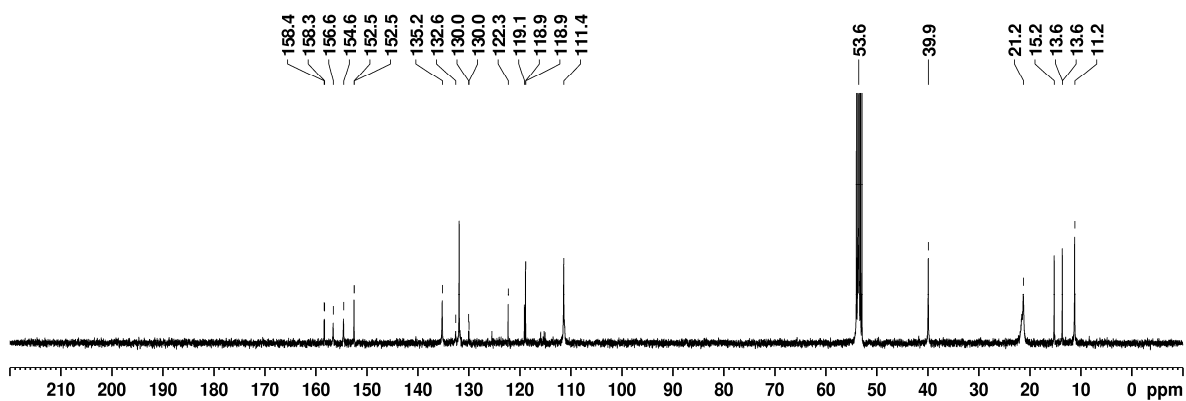


Figure S 93: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $26\text{e}[\text{OTf}]_2$ in CD_2Cl_2 .

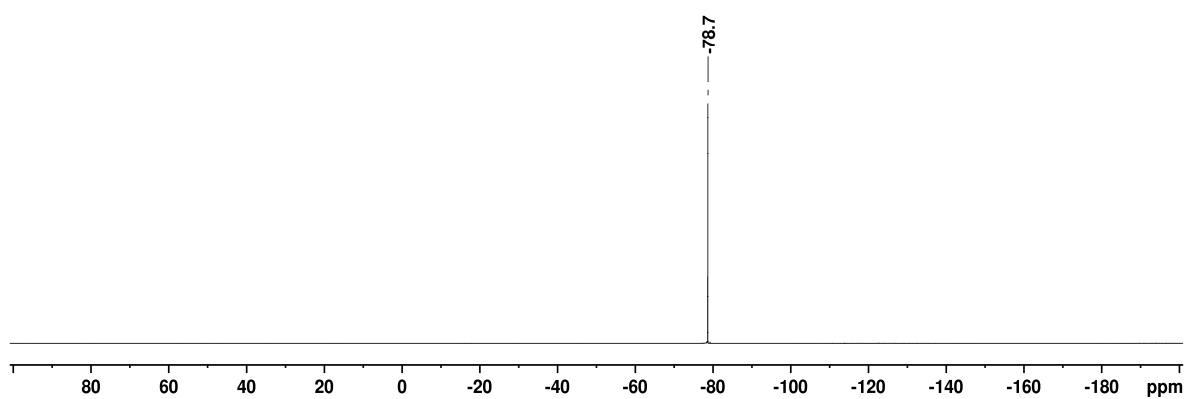


Figure S 94: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of $26\text{e}[\text{OTf}]_2$ in CD_2Cl_2 .

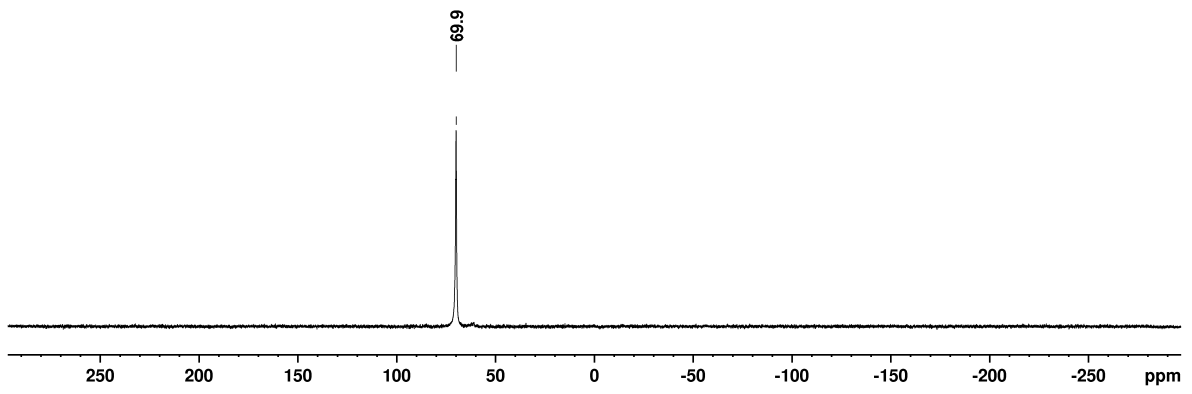
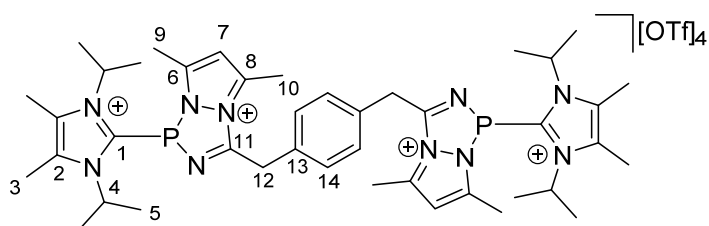


Figure S 95: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $26\text{e}[\text{OTf}]_2$ in CD_2Cl_2 .

2.6.6. Synthesis of **26f**[OTf]₄



22[OTf] (60 mg, 0.139 mmol, 1.0 equiv.), **23**[OTf] (76.6 mg, 0.139 mmol, 1.0 equiv.) and silver triflate (78.6 mg, 0.306 mmol, 2.2 equiv.) are suspended in 3 mL of CH₂Cl₂ and stirred for 2 h under exclusion of light.

The resulting solid is filtered off and the solvent removed *in vacuo*. A solution of 1,4-phenylenediacetonitrile (22 mg, 0.139 mmol, 1.0 equiv.) in 2 mL C₆H₅F is added and stirred for 2 d. By filtration and washing with CH₂Cl₂ and *n*-pentane, **26f**[OTf]₄ is obtained as a colorless, air and moisture sensitive solid. Suitable crystals for X-ray diffraction analysis can be obtained by slow diffusion of Et₂O to a CH₃CN solution at -30 °C.

Yield: 107 mg (56 %); **m.p.** 202 °C; **Raman:** No Raman spectrum of the sample could be obtained due to strong fluorescence of the sample; **IR** (ATR, 298 K, cm⁻¹): 1613 (w), 1544 (w), 1458 (vw), 1404 (w), 1329 (vw), 1256 (vs), 1224 (s), 1151 (s), 1111 (w), 1098 (w), 1090 (w), 1056 (vw), 1029 (vs), 999 (w), 901 (vw), 865 (vw), 826 (w), 809 (w), 793 (w), 768 (w), 753 (w), 636 (vs), 572 (m), 563 (w), 538 (w), 517 (m), 500 (m), 475 (w), 443 (m), 412 (w); **¹H NMR** (CD₃CN, 298 K, in ppm) δ = 1.47 – 1.64 (24H, m, H5), 2.42 – 2.45 (12H, m, H3), 2.53 (7H, s, H10), 2.99 (6H, s(br), H9), 4.54 – 4.87 (8H, m, H4/H12), 6.95 (2H, s, H7), 7.50 (4H, d, ⁴J_{HH} = 2.10 Hz, H14); **¹³C{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = 10.66 (4C, s, C3), 12.78 (2C, s, C10), 13.32 (2C, s, C9), 19.81–21.31 (8C, m, C5), 37.81 (4C, d, ³J_{CP} = 5 Hz, C12), 53.65 (4C, d, ³J_{CP} = 14 Hz, C4), 118.33 (2C, s, C7), 121.12 (4C, q, ¹J_{CF} = 321 Hz, OTf), 128.67 (2C, d, ¹J_{CP} = 86 Hz, C1), 130.77 (4C, s, C14), 131.76 (4C, s, C13), 136.54 (4C, s, C2), 149.24 (2C, s, C6), 155.62 (2C, s, C8), 159.74 (2C, d, ²J_{CP} = 3 Hz, C11); **¹⁹F{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = -79.2 (s); **³¹P{¹H} NMR** (CD₃CN, 298 K, in ppm): δ = 64.0 (s); **elemental analysis:** calculated for C₄₆H₆₂F₁₂N₁₀O₁₂P₂S₄: N 10.26, C 40.47, H 4.58, S 9.39; found: N 10.37, C 40.25, H 4.76, S 9.31.

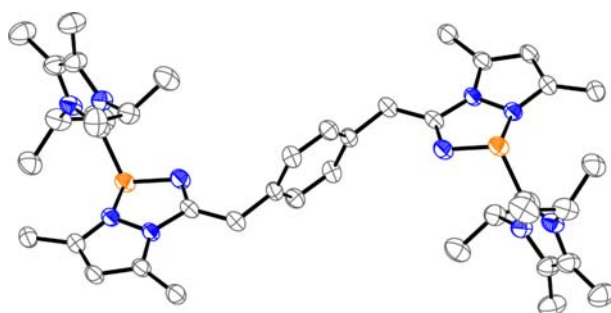


Figure S 96: Molecular structure of **26f**⁴⁺ in **26f**[OTf]₄; thermal ellipsoids are displayed at 50 % probability level, hydrogen atoms and counterions are omitted for clarity.

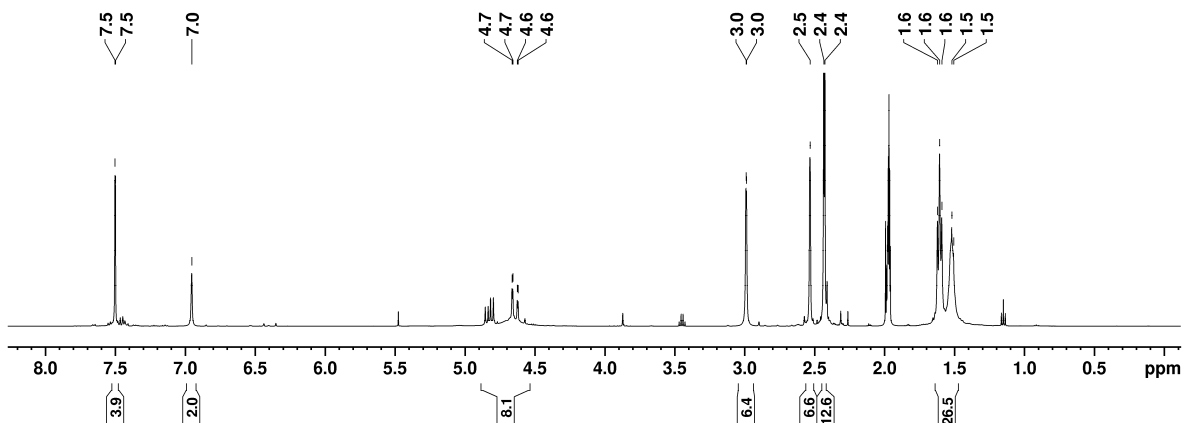


Figure S 97: ^1H NMR spectrum of $26\text{f}[\text{OTf}]_4$ in CD_3CN .

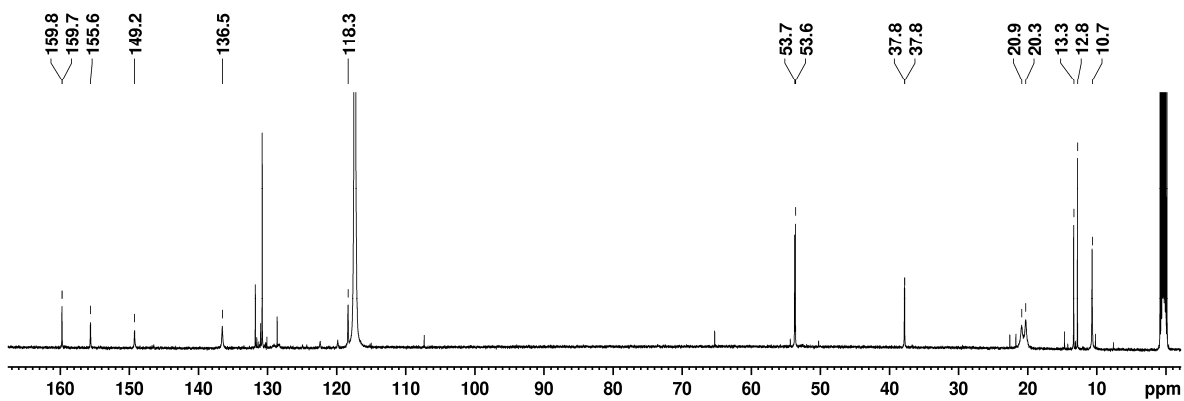


Figure S 98: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $26\text{f}[\text{OTf}]_4$ in CD_3CN .

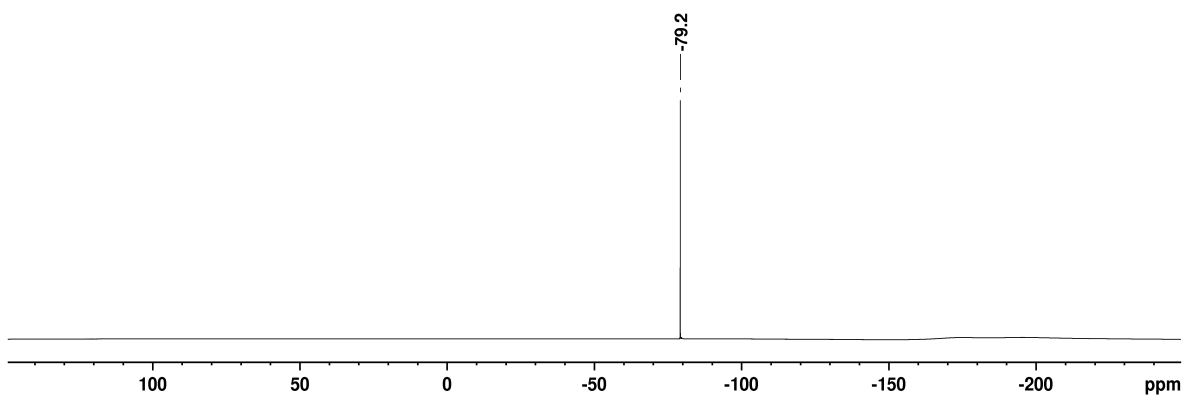


Figure S 99: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of $26\text{f}[\text{OTf}]_4$ in CD_3CN .

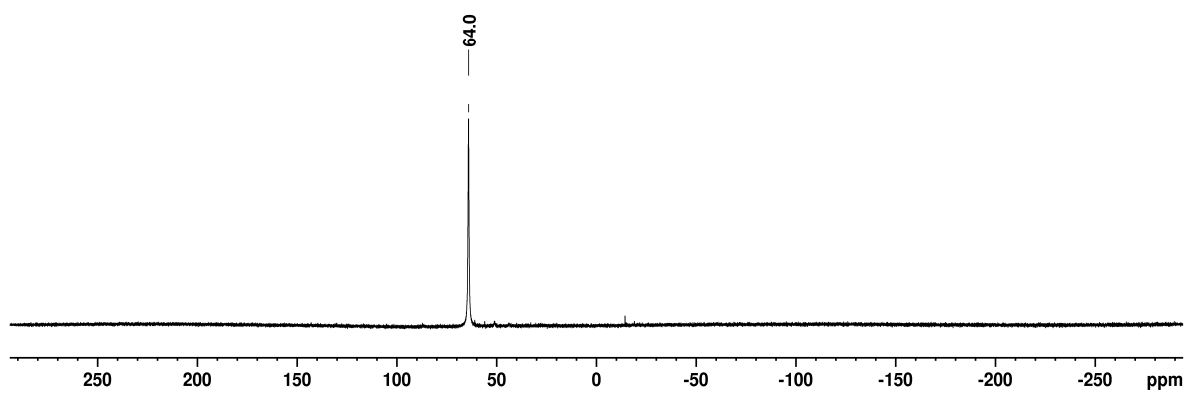
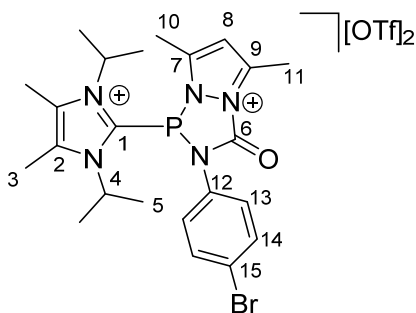


Figure S 100: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **26f**[OTf]₄ in CD₃CN.

2.7. Additional Cycloadditions of 24[OTf]

2.7.1. Synthesis of 27[OTf]



22[OTf] (60 mg, 0.139 mmol, 1.0 equiv.), **23[OTf]** (76.6 mg, 0.139 mmol, 1.0 equiv.) and silver triflate (78.6 mg, 0.306 mmol, 2.2 equiv.) are suspended in 3 mL of CH₂Cl₂ and stirred for 2 h under exclusion of light. The resulting solid is filtered off and the solvent removed *in vacuo*. A solution of 4-bromophenylisocyanate (82.6 mg, 0.417 mmol, 3.0 equiv.) in 2 mL CH₂Cl₂ is added and the mixture is heated to 70 °C in a microwave oven for 1 h. After the addition of *n*-pentane, a colorless solid forms. The solid is recrystallized from CH₂Cl₂ and *n*-pentane to afford **27[OTf]₂** as a colorless, air and moisture sensitive solid. Suitable crystals for X-ray diffraction analysis can be obtained by slow diffusion of *n*-pentane to a CH₂Cl₂ solution at -30 °C.

The solid is recrystallized from CH₂Cl₂ and *n*-pentane to afford **27[OTf]₂** as a colorless, air and moisture sensitive solid. Suitable crystals for X-ray diffraction analysis can be obtained by slow diffusion of *n*-pentane to a CH₂Cl₂ solution at -30 °C.

Yield: 100 mg (67 %); **m.p.** 160 °C (decomposition); **Raman** (200 mW, 500 scans, 298 K, cm⁻¹): 3075 (20), 2987 (31), 2941 (100), 2888 (15), 2875 (16), 1791 (22), 1585 (51), 1544 (15), 1464 (29), 1385 (20), 1342 (11), 1295 (25), 1248 (38), 1088 (15), 1032 (62), 881 (11), 755 (22), 680 (13), 586 (27), 572 (18), 519 (9), 347 (18), 313 (16), 177 (31); **IR** (ATR, 298 K, cm⁻¹): 2940 (vw), 1787 (w), 1592 (vw), 1543 (vw), 1489 (vw), 1463 (w), 1398 (w), 1381 (w), 1341 (w), 1246 (vs), 1222 (s), 1152 (s), 1108 (m), 1089 (m), 1072 (w), 1027 (vs), 900 (vw), 839 (w), 807 (w), 789 (w), 755 (w), 737 (vw), 717 (w), 704 (vw), 666 (vw), 635 (vs), 590 (m), 573 (m), 548 (w), 515 (s), 480 (m), 449 (m); **¹H NMR** (CD₂Cl₂, 298 K, in ppm) δ = 1.41-1.82 (12H, s, H5), 2.53 (6H, s, H3), 2.76 (3H, s, H11), 2.96 (3H, s, H10), 4.91 (2H, s (br., FWHM = 75 Hz), H4), 6.90 (1H, s, H8), 7.38-7.45 (2H, m, H13), 7.70-7.76 (2H, m, H14); **¹³C{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = 11.61 (2C, s, C3), 12.20 (1C, s, C10), 12.87 (1C, s, C11), 21.49 (4C, s(br.), C5), 53.88 (2C, s, C4), 116.92 (1C, s, C8), 120.53 (2C, q, ¹J_{CF} = 320 Hz, OTf), 124.69 (1C, s, C15), 128.34 (2C, s, C13), 130.49 (1C, d, ²J_{CP} = 15 Hz, C12), 131.41 (1C, d, ¹J_{CP} = 101 Hz, C1), 134.00 (2C, s, C14), 138.03 (2C, s, C2), 143.00 (1C, s, C6), 154.89 (1C, s, C7), 159.05 (1C, d, ²J_{CP} = 9 Hz, C9); **¹⁹F{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = -78.8 (s); **³¹P{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = 48.0 (s); **elemental analysis:** calculated for C₂₅H₃₁BrF₆N₅O₇PS₂ · MeCN · 3 CH₂Cl₂: N 7.65, C 32.81, H 3.67, S 5.84; found: N 8.07, C 32.35, H 4.10. We found repeatable inconclusive results for the sulphur value in the elemental analysis of this compound and therefore abstain of any further analysis.

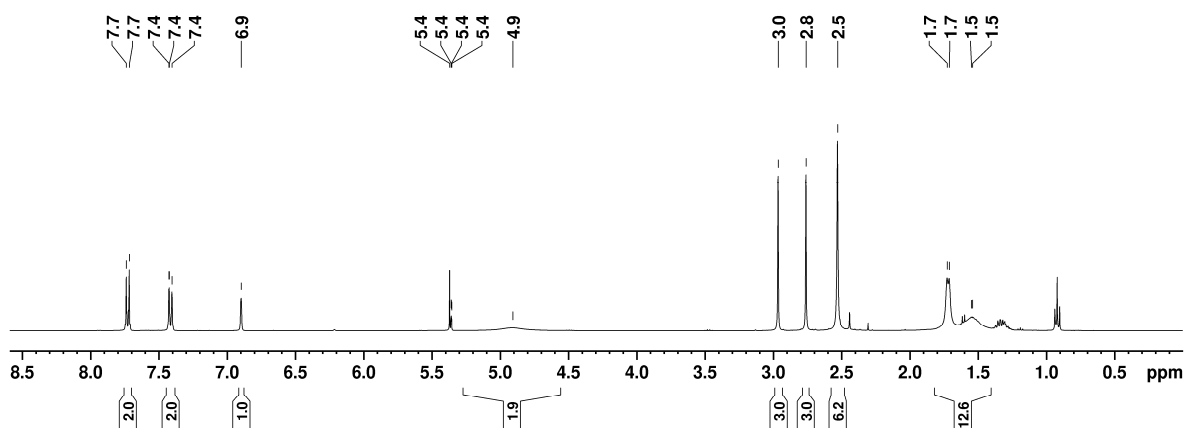


Figure S 101: ^1H NMR spectrum of $27[\text{OTf}]_2$ in CD_2Cl_2 .

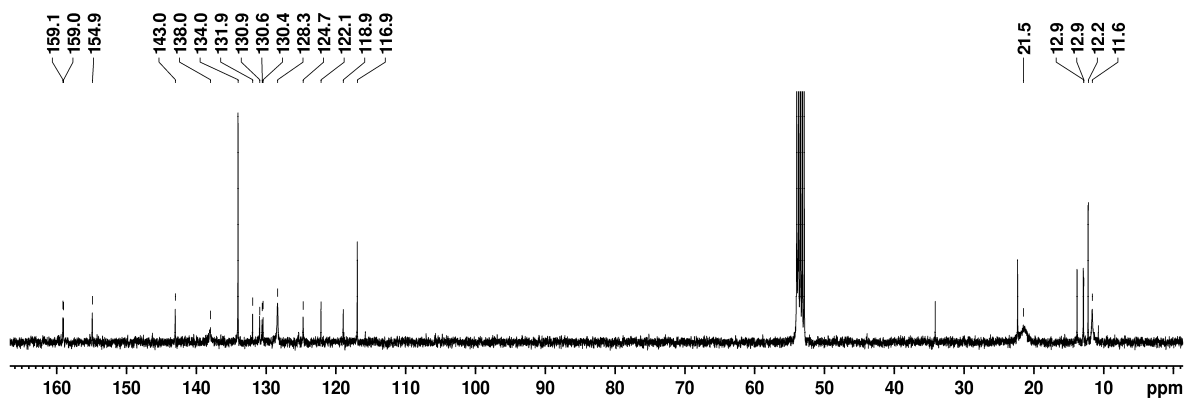


Figure S 102: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $27[\text{OTf}]_2$ in CD_2Cl_2 .

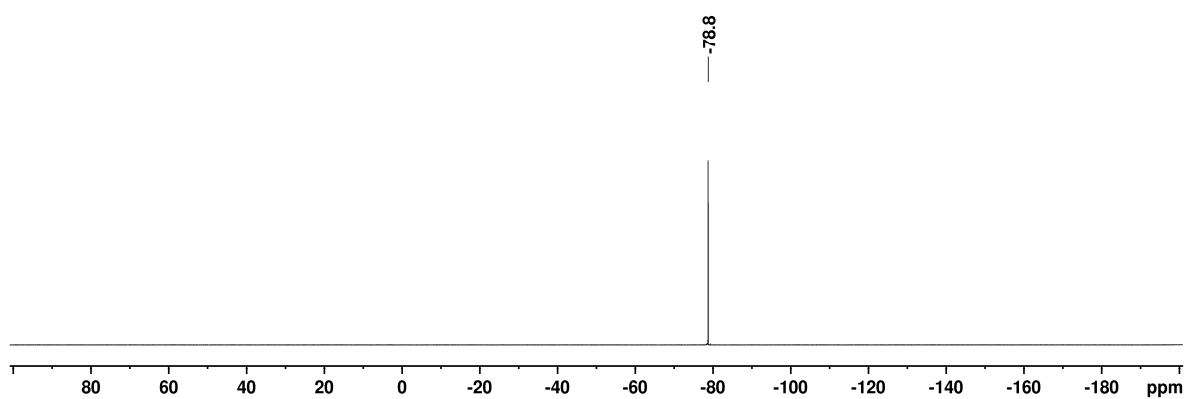


Figure S 103: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of $27[\text{OTf}]_2$ in CD_2Cl_2 .

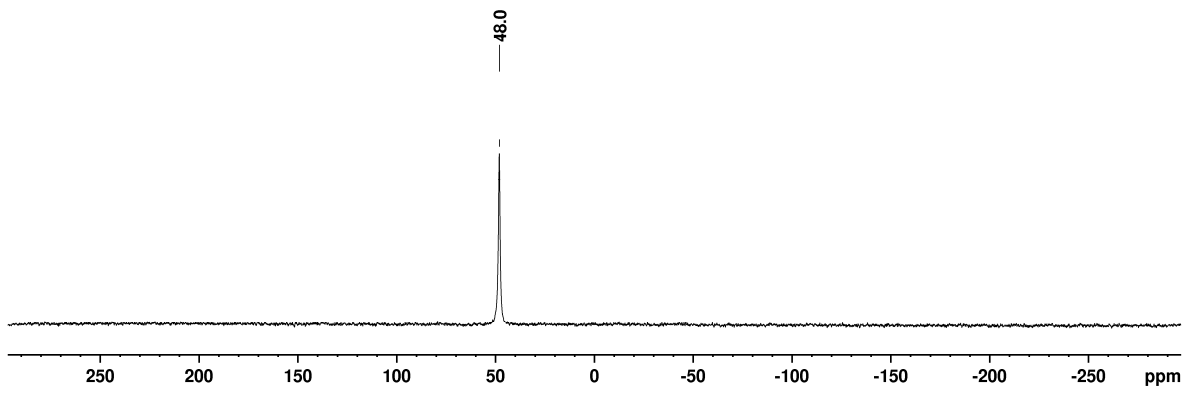
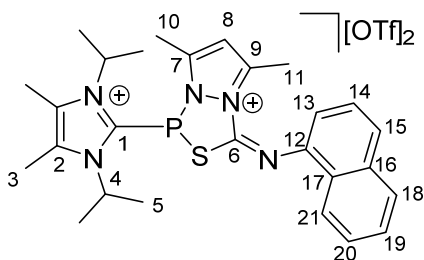


Figure S 104: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $27[\text{OTf}]_2$ in CD_2Cl_2 .

2.7.2. Synthesis of **28**[OTf]



22[OTf] (60 mg, 0.139 mmol, 1.0 equiv.), **23**[OTf] (76.6 mg, 0.139 mmol, 1.0 equiv.) and silver triflate (78.6 mg, 0.306 mmol, 2.2 equiv.) are suspended in 3 mL of CH₂Cl₂ and stirred for 2 h under exclusion of light. The resulting solid is filtered off and the solvent removed *in vacuo*. A solution of 1-naphthylisothiocyanate (109 mg, 0.556 mmol, 4.0 equiv.) in 4 mL C₆H₅F is added and the mixture is stirred for 64 h at room temperature. The formed suspension is filtered and the obtained solid is recrystallized from CH₂Cl₂ and *n*-pentane to afford **28**[OTf]₂ as a pale yellow, air and moisture sensitive solid. Suitable crystals for X-ray diffraction analysis can be obtained by slow diffusion of *n*-pentane to a CH₂Cl₂ solution at -30 °C.

Yield: 147 mg (67 %); **m.p.** 167 °C (decomposition); **Raman** (100 mW, 500 scans, 298 K, cm⁻¹): 3064 (10), 2999 (13), 2945 (21), 2749 (10), 2306 (13), 2265 (13), 2245 (13), 2221 (13), 2207 (13), 2184 (13), 2158 (13), 2112 (14), 2061 (14), 1648 (99), 1642 (100), 1604 (30), 1573 (97), 1509 (41), 1457 (38), 1438 (34), 1397 (41), 1378 (69), 1342 (36), 1262 (39), 1226 (50), 1151 (28), 1080 (34), 1047 (27), 1033 (38), 1022 (34), 925 (23), 883 (25), 816 (25), 792 (25), 755 (31), 716 (27), 697 (23), 666 (24), 625 (26), 589 (31), 573 (29), 547 (32), 530 (41), 514 (38), 488 (29), 457 (31), 411 (27); **IR** (ATR, 298 K, cm⁻¹): 1640 (vw), 1603 (vw), 1588 (vw), 1576 (vw), 1546 (vw), 1455 (vw), 1410 (w), 1398 (vw), 1380 (w), 1359 (vw), 1337 (vw), 1304 (w), 1264 (vs), 1233 (s), 1219 (vs), 1186 (w), 1151 (s), 1082 (m), 1031 (s), 1020 (vs), 981 (vw), 925 (w), 904 (w), 882 (vw), 832 (w), 810 (m), 790 (m), 754 (w), 634 (vs), 590 (w), 572 (m), 548 (w), 516 (s), 487 (w), 473 (w), 436 (w), 411 (w); **¹H NMR** (CD₂Cl₂, 298 K, in ppm) δ = 1.60 (13H, *pseudo t*, ³*J*_{HH} = 7.05 Hz, H5), 2.45 (6H, s, H3), 2.74 (3H, d, ⁴*J*_{PH} = 1.55 Hz, H11), 3.10 (3H, d, ⁵*J*_{HP} = 1.16 Hz, H10), 5.22-5.38 (2H, m, H4), 6.93 (1H, s, H8), 7.30 (1H, d, ³*J*_{HH} = 7.32 Hz, Naphthyl), 7.61 (3H, m, Naphthyl), 7.93 (3H, m, Naphthyl); **¹³C{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = 11.29 (2C, s, C3), 13.53 (1C, d, ³*J*_{CP} = 8 Hz, C11), 14.82 (1C, s, C10), 13.53 (2C, s, C5), 21.14 (2C, s, C5), 53.52 (2C, s, C4), 114.77 (1C, s, Naphthyl), 117.50 (1C, d, ³*J*_{CP} = 1 Hz, C8), 120.40 (2C, q, ¹*J*_{CF} = 321 Hz, OTf-), 122.24 (1C, s, Naphthyl), 125.53 (1C, s, Naphthyl), 126.91 (1C, s, Naphthyl), 127.13 (1C, s, Naphthyl), 127.44 (1C, s, Naphthyl), 128.32 (1C, s, Naphthyl), 128.47 (1C, s, Naphthyl), 133.76 (1C, d, ¹*J*_{CP} = 104 Hz, C1), 134.35 (1C, s, Naphthyl), 135.26 (1C, s, C2), 141.98 (1C, s, Naphthyl), 142.59 (1C, d, ²*J*_{CP} = 2 Hz, C6), 151.75 (1C, d, ³*J*_{CP} = 2 Hz, C7), 156.19 (1C, d, ²*J*_{CP} = 10 Hz, C9); **¹⁹F{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = -78.8 (s); **³¹P{¹H} NMR** (CD₂Cl₂, 298 K, in ppm): δ = 25.6 (s); **elemental analysis:** calculated for C₂₉H₃₄F₆N₅O₆PS₃ · 1 MeCN · 1.5 CH₂Cl₂: N 8.77, C 40.74, H 4.21, S 10.04; found: N 8.45, C 40.57, H 4.87. We found repeatable inconclusive results for the sulphur value in the elemental analysis of this compound and therefore abstain of any further analysis.

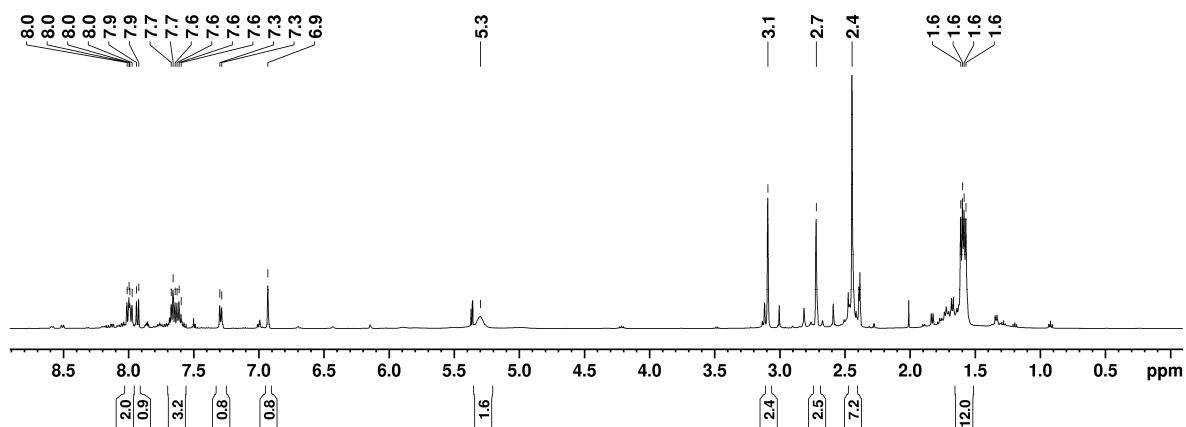


Figure S 105: ^1H NMR spectrum of $28[\text{OTf}]_2$ in CD_2Cl_2 .

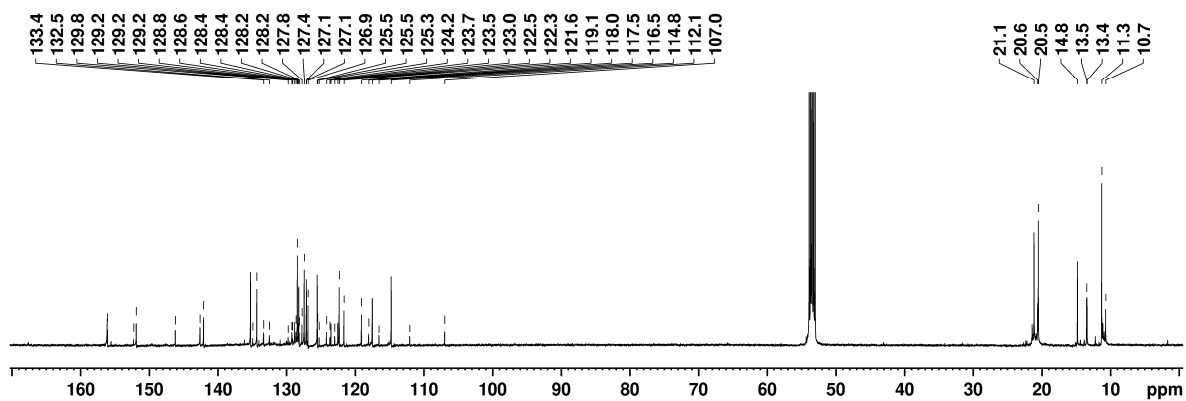


Figure S 106: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $28[\text{OTf}]_2$ in CD_2Cl_2 .

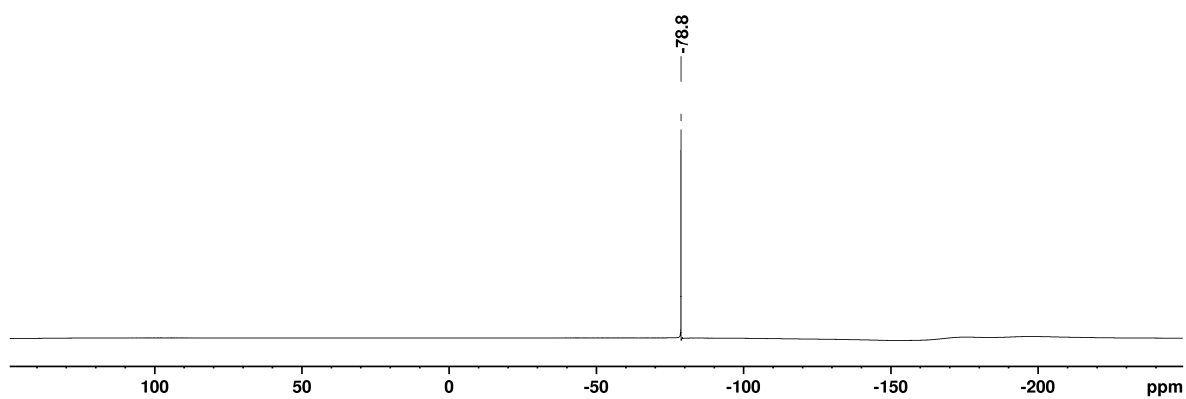


Figure S 107: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of $28[\text{OTf}]_2$ in CD_2Cl_2 .

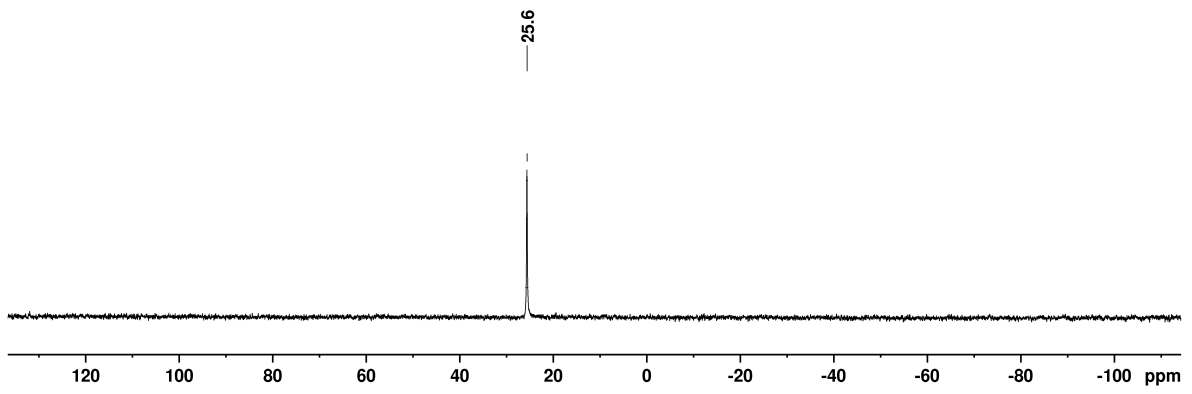


Figure S 108: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **28**[OTf]₂ in CD₂Cl₂.

2.8. Additional Experiments

2.8.1. Comparison of reducing agents

9g[OTf]₂ (50 mg, 0.07 mmol, 1.0 equiv.) and the corresponding reducing agent KC₈ (21 mg, 0.15 mmol, 2.1 equiv) or Zn (13 mg, 0.2 mmol, excess) are cooled to -40 °C and cold THF (-40 °C, 2 mL) is added. The corresponding reaction mixture is slowly thawed to room temperature overnight. An aliquot was taken from each of the reaction mixtures for the NMR investigation.

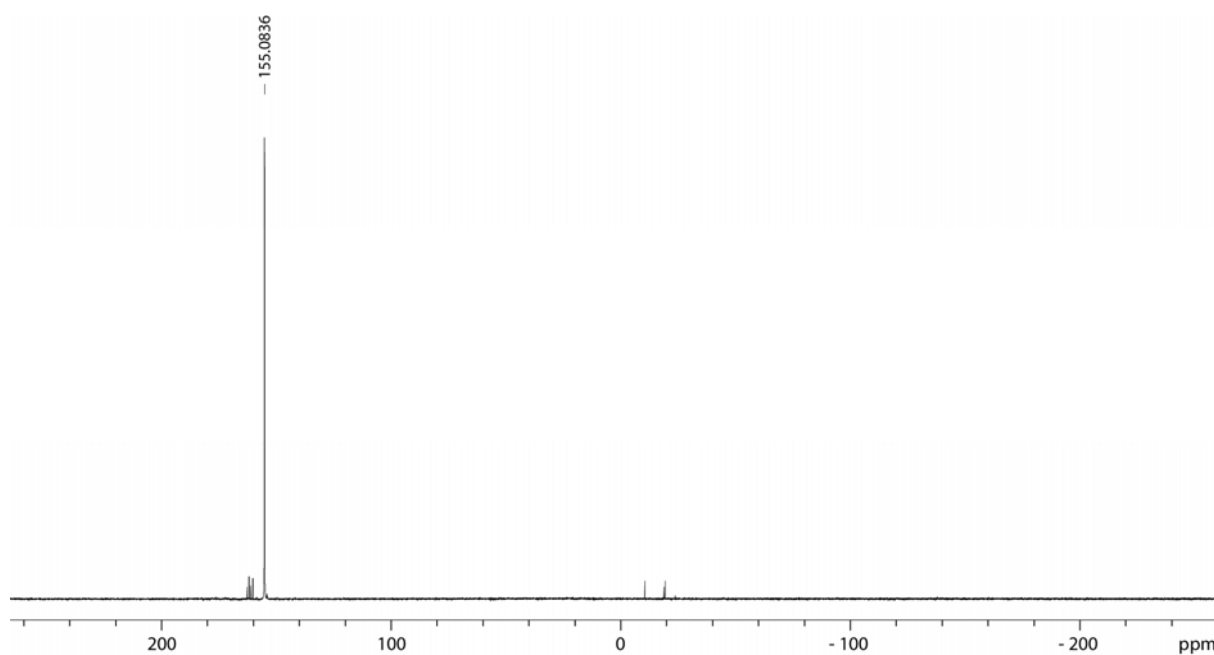


Figure S 109: ³¹P NMR spectrum of the reaction of **9g**[OTf]₂ with KC₈ in THF (300 K, C₆D₆ ref.)

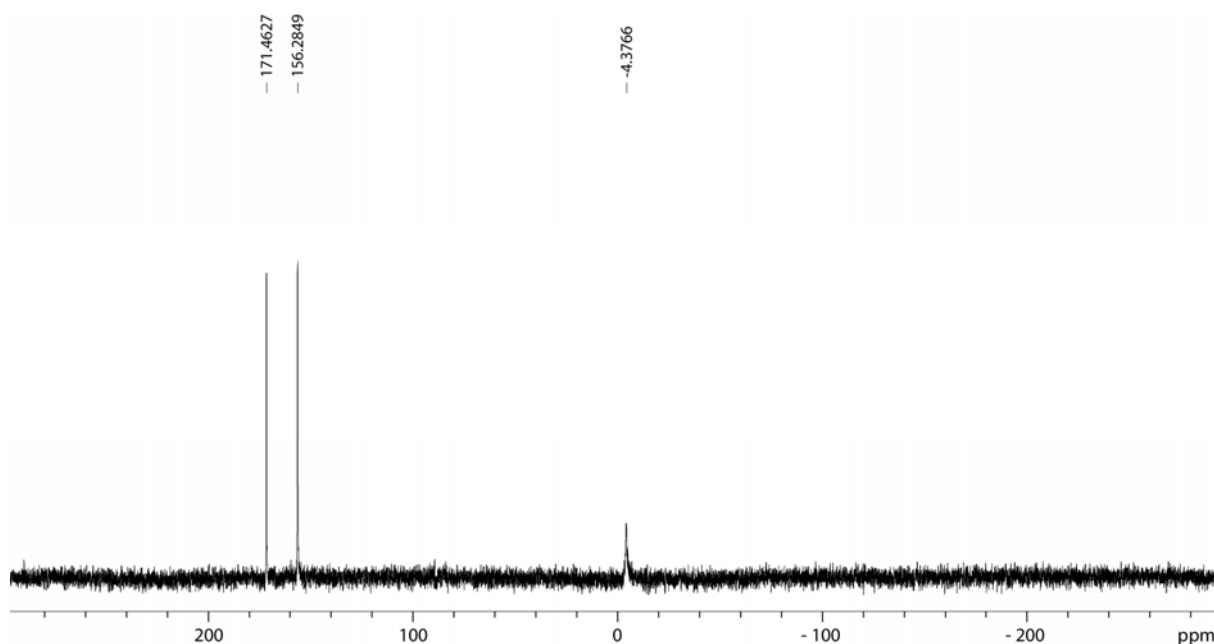


Figure S110: ^{31}P NMR spectrum of the reaction of **9g**[OTf]₂ with Zn in THF (300 K, C₆D₆ ref.)

2.8.2. Scope of Dipolarophiles

During the investigations numerous dipolarophiles were tested in the [3+2]-cycloaddition reaction with triflatophosphane **6**[OTf]. In the following table reaction conditions and outcome of small scale test-reactions are given. The reactions were conducted by mixing **11**[OTf] (50 mg, 0.105 mmol, 1 equiv.) with AgOTf (27 mg, 0.105 mmol, 1 equiv.) with 1.1 equiv of dipolarophile in CH₂Cl₂. It should be noted, that despite a positive outcome of the reaction, judged by ^{31}P NMR, none of the products could be successfully isolated to date.

Table S 1: Scope of investigated dipolarophiles.

Dipolarophile	Conditions	Outcome
N,1,1-triphenylmethanimine	Stirred at r.t. over night	No reaction
CO ₂	J-Young NMR tube, 2 bar, r.t. over night	No reaction
CS ₂	Stirred at r.t. over night	No reaction
NaOCP	Added in THF, stirred at r.t. over night	Mixture of products
tBu-C≡P (in HMDS)	Stirred at r.t. over night	Mixture of products
1-isothiocyanatonaphthalene	Stirred at r.t. over night	Mixture of products
ethynyltrimethylsilane	Stirred at r.t. over night	Mixture of products

2.8.3. Electrochemical Investigation of **9a**[OTf]₂

The first scan of the CV (**Figure S 110**, dashed black line) shows a non-reversible reduction process of the substrate at $E_p = -0.86$ V (vs. $E_{1/2}(\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+)$) and an additional process at $E_p = -1.95$ V (vs. $E_{1/2}(\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+)$). The SWV measurement of the compound reveals its formal potential of $E = -0.80$ V (vs. $E_{1/2}(\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+)$). Interestingly, the second scan CV (**Figure S 110**, black line) shows an oxidation process at $E_p = 0.44$ V (vs. $E_{1/2}(\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+)$), which is only observed after the previous reduction. These observations are similar to our previous findings (cf. Ref. ¹).

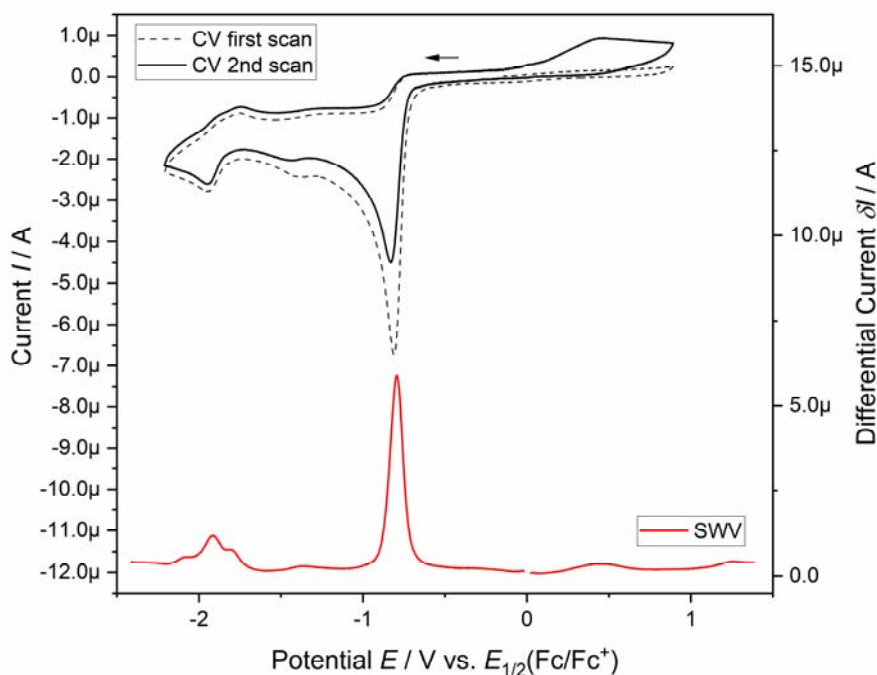


Figure S 110: CV first (dashed black) and second scan (black), SWV measurement (red) of **9a**[OTf]₂ (2.0 mM) in CH₂Cl₂ with 0.1 M [Bu₄N][OTf] supporting electrolyte with a 1.6 mm Pt disk electrode at a scan rate of $\nu = 0.1$ V/s. The arrow indicates the scan direction for CV experiments.

2.8.4. Side-Reaction in the synthesis of **18b**[OTf]₂

Using acetone in a reaction with **11**[OTf], the oxazaphosphole **18b**[OTf]₂ was obtained, after several recrystallizations, in 25 % yield. An extended work-up procedure was necessary to isolate a pure sample of **18b**[OTf]₂. Reason for this is the slow formation of **32**[OTf]₂ as side product (see **Figure S 111**). A proposed mechanism for the formation of **32**²⁺ is depicted in **Figure S 1112**. Intermediary formed LEWIS-acid-base adduct **33**²⁺, which undergoes nucleophilic attack of prop-1-en-2-ol, the enol-tautomer of acetone. Hence, this reaction can be classified as LEWIS-induced aldol-addition. Despite all efforts, **32**[OTf]₂ could not be isolated. However, from a reaction solution, colorless crystals of **32**[OTf]₂ were obtained, which were subsequently analyzed by sc-XRD.

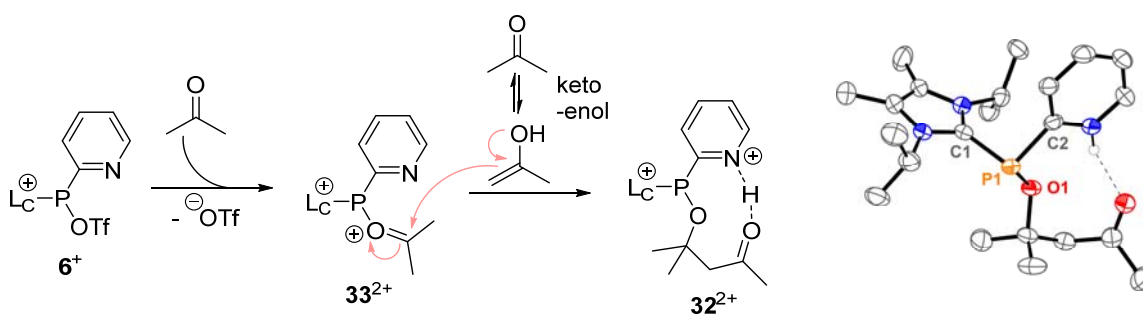
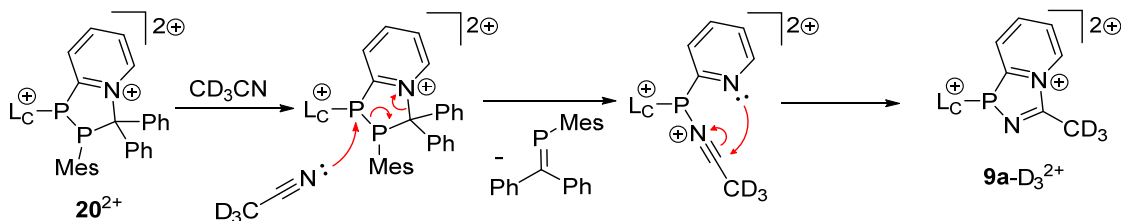


Figure S 111: Proposed mechanism for the formation of **32**²⁺ via an aldol-type addition of acetone and molecular structure of **32**²⁺ in **32**[OTf]₂ (right). Hydrogen atoms and counterions are omitted for clarity, thermal ellipsoids are displayed at 50 % probability, selected bond lengths in Å and angles in (°): P1-C1 1.844(5), P1-O1 1.622(4), P1-C2 1.836(5), C1-P1-O1 77.9(2), C1-P1-C2 82.0(2), C2-P1-O1 85.0(2).

The molecular structure of **32**²⁺ is depicted in **Figure S 1112** and proves the structural connectivity of **32**²⁺. Additionally, it reveals the anticipated pyramidal bonding environment on the phosphorus atom. The P1–C1 bond length (1.844(5) Å) is in range of known imidazoliumyl-substituted phosphanes. Notably, the pyridyl-substituent accepts the free proton which is formed in the addition reaction and the so formed pyridinium-salt forms a hydrogen bond to the carbonyl-oxygen atom.

2.8.5. Slow Formation of **9a**[OTf]₂ from **20**[OTf]₂ in MeCN Solution



Scheme S 4: Proposed mechanism for the formation of **9a-D₃**²⁺ from **20**²⁺.

20[OTf]₂ undergoes slow conversion to **9a-D₃**[OTf]₂ when dissolved in CD₃CN (see **Scheme S 4**). To gain a deeper understanding of this conversion, a solution of **20**[OTf]₂ in CD₃CN was prepared and observed by ³¹P NMR over two weeks.

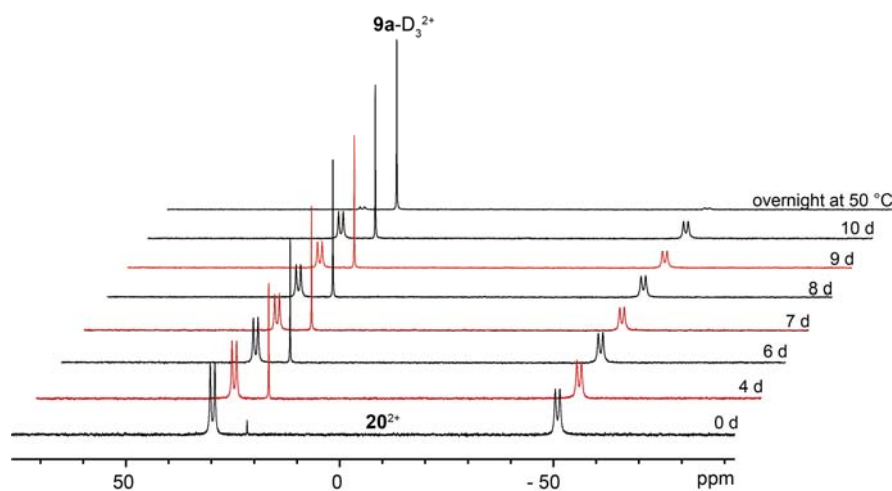


Figure S 112: ³¹P NMR spectra stack of the reaction of **20**[OTf]₂ with CD₃CN over two weeks at room temperature (CD₃CN, 300 K).

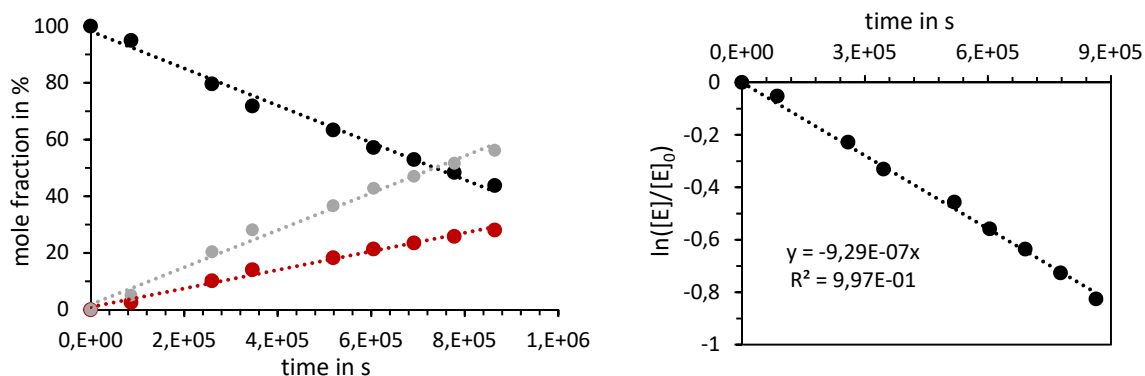


Figure S 113: Kinetic analysis of the reaction of **18**[OTf]₂ with CD₃CN: *Right:* Plot of molar fractions (from ³¹P NMR) vs. time **20**²⁺, **9a**²⁺, **9a**²⁺ + MesP=CPh₂; *Left:* Plot of ln([E]/[E]₀) vs. time.

As depicted in **Figure S 112**, **20**[OTf]₂ reacts with CD₃CN over a time span of approximately ten days to reach a conversion of 56 %. In **Figure S 1134** a rough kinetic analysis of the reaction is depicted. As two reactants are participating, one would expect the reaction to proceed as a reaction of second order. However, due to the large excess of CD₃CN that is present, the reaction should rather be described as pseudo-first order. The appropriate rate law is therefore:

$$[E] = [E]_0 e^{-[C]_0 k t} \quad (1)$$

Where:

[E] is the concentration of **20**[OTf]₂, [E]₀ at the beginning of the reaction

[C] the concentration of CD₃CN, [C]₀ at the beginning of the reaction

k is the second order reaction rate constant

t is the time in days

Assuming the concentration of CD₃CN to be constant, one can simplify the rate law as:

$$[E] = [E]_0 e^{-k' t} \quad (2)$$

With *k'* being the pseudo-first order rate constant. Resolving the formula, by employing the natural logarithm gives:

$$\ln\left(\frac{[E]}{[E]_0}\right) = -k' t \quad (3)$$

Plotting the natural logarithm of [E]/[E]₀ vs. the reaction time gives an approximation for the reaction rate constant *k'*, as can be seen in **Figure S 113**. As the reaction reached 56 % conversion in roughly 10 days, *k'* is expectedly low with 9.29x10⁻⁷ s⁻¹. By heating the reaction mixture to 50 °C, full conversion is reached overnight.

2.8.6. Attempted Cycloaddition of **24**[OTf] with Phenylacetylene

22[OTf] (60 mg, 0.139 mmol, 1.0 equiv.), **23**[OTf] (76.6 mg, 0.139 mmol, 1.0 equiv.) and silver triflate (78.6 mg, 0.306 mmol, 2.2 equiv.) are suspended in 3 mL of CH₂Cl₂ and stirred for 2 h under exclusion of light. The resulting solid is filtered off and the solvent removed *in vacuo*. After the addition of phenylacetylene (42.6 mg, 0.417 mmol, 1.5 equiv.) the reaction mixture is stirred overnight.

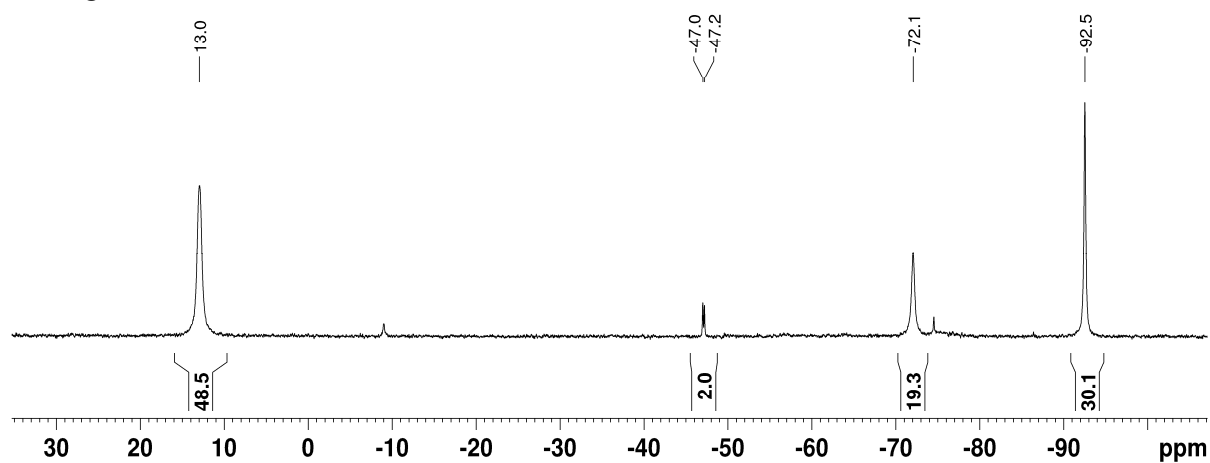


Figure S 1145: ³¹P NMR spectra stack of the reaction of **24**[OTf]₂ with 1.5 equiv. of phenylacetylene. (CH₂Cl₂, C₆D₆-ref., 300 K)

3. Computational Investigations

3.1. Theoretical Methods used for Mechanistic Studies

The geometries and energies of all systems included in this study were fully optimized at the RI-PBE0-D3/def2-TZVP level of theory without symmetry constrains. The calculations have been performed by using the program TURBOMOLE version 7.7.⁶ For the calculations we have used the PBE0⁷ functional, def2-TZVP⁸ basis set and the D3 correction for dispersion.⁹ In order to reproduce solvent effects, we have used the conductor-like screening model COSMO,¹⁰ which is a variant of the dielectric continuum solvation models. The minimum nature of the complexes and compounds have been confirmed by doing frequency calculations. The transition states only present one negative frequency that corresponds to the movement of atoms connecting the starting with the final product.

3.1.1. Cartesian Coordinates

Starting point

P	1.1181520	-1.0102171	0.5176404
N	-0.0692107	1.4407200	-0.5410264
N	0.6040635	-0.0238219	-1.9985174
N	-0.3249207	-1.6162047	1.1429072
N	-1.4663385	-0.8675834	1.2699001
C	0.4588702	0.2132383	-0.6805070
C	-0.2445847	1.9952202	-1.7865976
C	0.1743685	1.0699980	-2.7071713
C	-0.4332326	2.0667798	0.7566453
H	-0.3679844	1.2521228	1.4678180
C	0.5615685	3.1465142	1.1404586
H	1.5816047	2.7623884	1.1465324
H	0.3280938	3.4932551	2.1482382
H	0.5183138	4.0124080	0.4788011
C	-1.8819135	2.5195536	0.7757085
H	-2.0544820	3.4422114	0.2248758
H	-2.1588690	2.7049155	1.8147218
H	-2.5354972	1.7351988	0.3921414
C	1.1548376	-1.2841679	-2.5482570
H	1.2267059	-1.9456688	-1.6813697
C	2.5608056	-1.0786621	-3.0804507
H	2.5837304	-0.4216947	-3.9501702
H	2.9712297	-2.0426419	-3.3841229
H	3.2133109	-0.6583288	-2.3130130
C	0.2025504	-1.9424940	-3.5303029
H	-0.8106135	-1.9923576	-3.1276703
H	0.5442591	-2.9627460	-3.7103147
H	0.1766214	-1.4345391	-4.4928506

C	-0.8080080	3.3390973	-2.0610793
H	-1.8999024	3.3267973	-2.0466097
H	-0.4954648	3.6698447	-3.0502551
H	-0.4674627	4.0820657	-1.3433108
C	0.1450054	1.1848137	-4.1853192
H	1.0365435	0.7703850	-4.6519795
H	0.0852353	2.2345678	-4.4678561
H	-0.7270594	0.6821240	-4.6094606
C	-0.4745673	-2.8731150	1.7095206
C	-1.7453978	-2.9088761	2.1913891
H	-2.2165994	-3.7388175	2.6937796
C	-2.3207769	-1.6413021	1.8960338
C	0.6044896	-3.8903545	1.7349310
H	0.9274454	-4.1625444	0.7269447
H	0.2382451	-4.7907715	2.2255742
H	1.4814801	-3.5354393	2.2816791
C	-3.6932455	-1.1762909	2.2135718
H	-3.8693434	-1.2089340	3.2911244
H	-4.4383706	-1.8221149	1.7435274
H	-3.8434754	-0.1553082	1.8651105
O	1.5874977	0.1698003	1.6379916
S	2.5519101	-0.1248316	2.8671656
C	1.2967314	0.0984790	4.2138556
O	2.9329730	-1.4940883	2.8495509
O	3.4726152	0.9442032	2.9522151
F	0.3501760	-0.8160516	4.0841466
F	1.8998392	-0.0392539	5.3722986
F	0.7580475	1.3025200	4.1214132

TS1 (stepwise)

P	1.2396094	-0.6039289	0.5994755
N	-0.1566590	1.7622227	-0.3797505
N	0.9123779	0.5823152	-1.8612078
N	-0.1350085	-1.3220582	1.2699203
N	-1.3563554	-0.7232804	1.3917649
C	0.5498842	0.6323906	-0.5643202
C	-0.2489512	2.4310316	-1.5757711
C	0.4303615	1.6899392	-2.5086683
C	-0.6861101	2.2308732	0.9254076
H	-0.5492861	1.3835959	1.5867700
C	0.1239619	3.4023374	1.4521418
H	1.1875591	3.1656098	1.4840065
H	-0.2018614	3.6170543	2.4711756
H	-0.0140141	4.3116729	0.8670054
C	-2.1815831	2.4809228	0.8708037
H	-2.4474127	3.3979994	0.3476624
H	-2.5441382	2.5743423	1.8959056
H	-2.6937021	1.6352411	0.4111887
C	1.7964267	-0.4666612	-2.4288937
H	1.7310693	-1.2852113	-1.7133583
C	3.2273819	0.0372628	-2.4759934
H	3.3381790	0.8888724	-3.1493927

H	3.8772670	-0.7610517	-2.8373999
H	3.5766105	0.3355020	-1.4851953
C	1.2978905	-1.0156420	-3.7528622
H	0.2255573	-1.2042581	-3.7229003
H	1.7935613	-1.9722974	-3.9233815
H	1.5372469	-0.3706818	-4.5963884
C	-0.9841988	3.6995817	-1.7984802
H	-2.0574760	3.5247758	-1.8997943
H	-0.6386473	4.1666178	-2.7192146
H	-0.8325715	4.4132324	-0.9919662
C	0.6242871	1.9972029	-3.9461456
H	1.6624366	1.8737201	-4.2527897
H	0.3462796	3.0317417	-4.1378960
H	0.0042635	1.3642146	-4.5830273
C	-0.1478414	-2.6114218	1.7661880
C	-1.4163194	-2.8202425	2.2172188
H	-1.7882056	-3.7164857	2.6886536
C	-2.1296531	-1.6178253	1.9613990
C	1.0362181	-3.5037622	1.7558740
H	1.3659391	-3.7083126	0.7341146
H	0.7784821	-4.4506283	2.2286205
H	1.8788823	-3.0695143	2.2988639
C	-3.5526086	-1.3229382	2.2644230
H	-3.7410363	-1.3952733	3.3380313
H	-4.2141151	-2.0394469	1.7716471
H	-3.8145601	-0.3195263	1.9315828
O	1.6234324	0.5834665	1.7585181
S	2.7233267	0.3756055	2.8798770
C	1.5867173	0.3721842	4.3448008
O	3.2845776	-0.9256006	2.7636040
O	3.5001958	1.5559766	2.9405659
F	0.7861987	-0.6793959	4.2766546
F	2.3172395	0.3108461	5.4356968
F	0.8590870	1.4756224	4.3487721
N	-0.5036285	-2.5553805	-1.5222278
C	-1.3832380	-3.2871794	-1.4207448
C	-2.4884902	-4.2113815	-1.2849092
H	-2.6753839	-4.4034717	-0.2273166
H	-3.3873882	-3.7882717	-1.7354511
H	-2.2520639	-5.1528446	-1.7828870

Final Product

P	0.9026903	0.0913033	0.6644699
N	-0.5991170	1.6798629	-1.3129798
N	0.9786379	0.3836903	-2.0547504
N	-0.5925323	-0.7289056	1.2321381
N	-0.8440377	-0.2488628	2.4827455
N	0.6174457	1.3308977	1.7728368
C	0.3022165	0.7511818	-0.9473885
C	-0.4777257	1.9263090	-2.6573297
C	0.5187763	1.1019717	-3.1255736
C	-1.5419984	2.3010103	-0.3597860

H	-1.4484570	1.6832825	0.5302100
C	-1.1060121	3.7106595	-0.0040163
H	-0.0886321	3.7133411	0.3881769
H	-1.7702642	4.1068162	0.7659403
H	-1.1570018	4.3847399	-0.8597292
C	-2.9824193	2.1981618	-0.8298200
H	-3.2151159	2.8938921	-1.6341421
H	-3.6359954	2.4445419	0.0083239
H	-3.2238963	1.1852675	-1.1576575
C	2.0491835	-0.6548855	-2.0534960
H	1.9694808	-1.1427108	-1.0790404
C	3.4204740	-0.0147182	-2.1368427
H	3.5940836	0.4871217	-3.0901274
H	4.1747095	-0.7946442	-2.0238716
H	3.5666801	0.7062044	-1.3303078
C	1.8000195	-1.7351396	-3.0900031
H	0.7618087	-2.0724499	-3.0753591
H	2.4257476	-2.5900666	-2.8309137
H	2.0600878	-1.4281688	-4.1021000
C	-1.2926111	2.8919867	-3.4336100
H	-2.2677517	2.4766305	-3.6974302
H	-0.7801746	3.1391848	-4.3620733
H	-1.4548595	3.8218541	-2.8910823
C	1.0118327	0.9764369	-4.5179769
H	2.0958510	0.8858968	-4.5586550
H	0.7317467	1.8602966	-5.0889437
H	0.5797370	0.1082992	-5.0198789
C	-1.2132999	-1.9066388	1.0924107
C	-1.8954073	-2.1584271	2.2813079
H	-2.5035998	-3.0229512	2.4920080
C	-1.6279997	-1.1233632	3.1561341
C	-1.1300737	-2.7164767	-0.1373269
H	-1.1912522	-2.0878627	-1.0283935
H	-1.9371815	-3.4463948	-0.1626712
H	-0.1668864	-3.2351875	-0.1482827
C	-2.0546205	-0.9653556	4.5635278
H	-1.1897890	-0.9617109	5.2302222
H	-2.6874705	-1.8072882	4.8370840
H	-2.6203594	-0.0466170	4.7251476
C	-0.1310325	0.9451131	2.7293913
C	-0.3051857	1.6564135	4.0131585
H	-1.3568383	1.8505255	4.2304647
H	0.2414998	2.5944665	3.9627959
H	0.1080792	1.0544753	4.8264597
S	2.3547629	-2.4823052	1.9276276
C	1.8602698	-4.0607416	2.7458610
O	1.8204864	-2.6423663	0.5742836
O	3.7776926	-2.4190404	2.0315326
O	1.6115462	-1.4776330	2.6926609
F	0.5286589	-4.2232976	2.6572306
F	2.1861377	-4.0522928	4.0295857
F	2.4392556	-5.0953325	2.1578235

TS(concerted)

P	-0.5180023	-0.7610942	1.0505516
N	0.9039269	1.3933275	-0.3423259
N	2.1463662	-0.1762529	0.4965201
N	-1.8958634	-0.4230437	-0.0081012
N	-3.0286143	-0.0772338	0.6449402
N	-1.1082015	0.8317136	2.0617070
C	0.8749474	0.2191231	0.3172543
C	2.2150112	1.7286158	-0.6077553
C	2.9962403	0.7408388	-0.0769644
C	-0.2774315	2.2412536	-0.6205733
H	-1.1225658	1.6190432	-0.3485294
C	-0.2919804	3.4645015	0.2827639
H	-0.1710573	3.1814533	1.3282146
H	-1.2540017	3.9685490	0.1729511
H	0.4823934	4.1852554	0.0227746
C	-0.4183174	2.5835948	-2.0940741
H	0.2810554	3.3536651	-2.4153818
H	-1.4254726	2.9683756	-2.2614328
H	-0.2887009	1.7046913	-2.7257031
C	2.5391416	-1.3882012	1.2587641
H	1.6004129	-1.7922587	1.6360806
C	3.3821115	-1.0276162	2.4682362
H	4.3898596	-0.7127596	2.1993796
H	3.4724871	-1.9156394	3.0953376
H	2.9112462	-0.2423324	3.0625166
C	3.1620161	-2.4447268	0.3667650
H	2.5698697	-2.5954439	-0.5346957
H	3.1755992	-3.3873673	0.9137394
H	4.1876573	-2.2065157	0.0858015
C	2.6659730	2.9250176	-1.3610393
H	2.4940119	2.8133088	-2.4338302
H	3.7341251	3.0674981	-1.2086230
H	2.1703517	3.8367445	-1.0329817
C	4.4781068	0.6616262	-0.0806825
H	4.8342447	-0.3542731	-0.2310874
H	4.9019736	1.0356018	0.8538796
H	4.8755300	1.2683717	-0.8925996
C	-2.1625410	-0.6574404	-1.3276810
C	-3.5115906	-0.4509111	-1.4940287
H	-4.0572316	-0.5253832	-2.4215286
C	-4.0177404	-0.0932621	-0.2347648
C	-1.1655327	-1.0058434	-2.3688631
H	-0.1668745	-0.6439244	-2.1305035
H	-1.4837803	-0.5716227	-3.3172519
H	-1.0956026	-2.0844992	-2.5001784
C	-5.4170488	0.2368917	0.1325885
H	-6.0805630	-0.5831356	-0.1487204
H	-5.7599958	1.1288083	-0.3969733
H	-5.5220549	0.4005898	1.2034593
C	-2.2639132	0.9840805	2.2289424
C	-3.4349667	1.4771317	2.9278903

H	-4.0401849	2.0966236	2.2661843
H	-3.1036195	2.0643935	3.7863405
H	-4.0341065	0.6325972	3.2724198
S	-0.4240652	-3.5714203	0.4866884
O	-0.0449330	-2.2007864	-0.1132487
O	-1.8113660	-3.6101634	0.8146806
O	0.5572551	-4.0019187	1.4286009
C	-0.1915811	-4.6321673	-1.0149779
F	-1.1124097	-4.3509788	-1.9278622
F	-0.3092587	-5.8918393	-0.6506826
F	1.0092562	-4.4332315	-1.5423265

TS2 (stepwise)

P	-0.8547507	-1.3519923	1.4824979
N	0.4514280	1.0096414	0.4150815
N	1.7405568	-0.6949628	0.8625706
N	-2.1873962	-1.0563219	0.4197641
N	-3.3015277	-0.3919013	0.8167335
N	-1.5845603	-0.3519143	2.8053260
C	0.4608089	-0.2468372	0.9144849
C	1.7168534	1.3565005	0.0480260
C	2.5350664	0.2760774	0.3357261
C	-0.7618734	1.8624052	0.3468730
H	-1.5730483	1.1958857	0.6260816
C	-0.7001845	2.9759657	1.3793687
H	-0.4998445	2.5831417	2.3780023
H	-1.6629974	3.4894277	1.3965573
H	0.0568472	3.7246752	1.1505247
C	-1.0449656	2.3340279	-1.0680764
H	-0.3470337	3.0962277	-1.4094823
H	-2.0420582	2.7761276	-1.0889975
H	-1.0340199	1.5020699	-1.7745233
C	2.1822307	-2.0287529	1.3633173
H	1.2494660	-2.5573888	1.5695138
C	2.9284876	-1.8880447	2.6781882
H	3.8877221	-1.3839763	2.5640951
H	3.1283557	-2.8848594	3.0737424
H	2.3375007	-1.3433154	3.4167345
C	2.9218213	-2.8199011	0.3002346
H	2.3828470	-2.8221057	-0.6491026
H	3.0018759	-3.8532169	0.6406636
H	3.9342323	-2.4586438	0.1304248
C	2.1224939	2.6366761	-0.5774169
H	1.9729874	2.6064557	-1.6599418
H	3.1817645	2.8149407	-0.3995804
H	1.5742048	3.4882292	-0.1833591
C	3.9930343	0.1738008	0.0922104
H	4.5104847	-0.3586134	0.8864873
H	4.4261614	1.1704567	0.0266591
H	4.1996515	-0.3365338	-0.8517472
C	-2.3697095	-1.6122296	-0.8207919
C	-3.6346922	-1.2641231	-1.2142666

H	-4.1140394	-1.5300596	-2.1434432
C	-4.1906445	-0.5122585	-0.1564375
C	-1.3146773	-2.4069004	-1.4934144
H	-0.4528368	-1.7885339	-1.7616741
H	-1.7071401	-2.8431298	-2.4105863
H	-0.9660109	-3.2295553	-0.8603522
C	-5.5486553	0.0742298	-0.0627464
H	-6.3036728	-0.7150217	-0.0779114
H	-5.7441653	0.7241253	-0.9178442
H	-5.6730899	0.6552902	0.8498460
C	-2.6922606	0.0333554	2.9135536
C	-3.8522982	0.5982760	3.5429053
H	-4.1614546	1.5006851	3.0128218
H	-3.5940330	0.8343811	4.5804402
H	-4.6655223	-0.1315456	3.5237430
C	1.3032955	-0.4666326	-4.7012204
F	0.9960236	0.7666520	-5.0973600
F	2.3225483	-0.9040304	-5.4249836
F	0.2493575	-1.2519901	-4.9325673
S	1.7147230	-0.4794570	-2.9049470
O	0.4850670	0.0092106	-2.2864368
O	1.9858701	-1.8678990	-2.6055967
O	2.8326873	0.4261907	-2.7752290

3.2. Theoretical Methods used for Electronic Structure Analysis

Material simulations were performed at the density functional theory (DFT) and time-dependent DFT (TD-DFT) level of theory using the Gaussian16.^{1,11} The long-range corrected hybrid functional CAM-B3LYP¹² was used in combination with the 6-311G** basis set,¹³ which has shown especially qualitative agreement with experiments for organic molecules including azaphopholes.^{1,14} Simulated absorption spectra were constructed by using Gaussian functions with a broadening of 15 meV and a systematic empirical energy shift of -400 meV resembling the broadening and absorption energies of the experimental absorption features in PMMA films (cf. **Figure 4b**). To evaluate the aromaticity of the molecules, NICS(1)_{zz} values¹⁵ and plots of the anisotropy of the current induced density (ACID)¹⁶ are calculated and depicted in **Figure S 1156**.

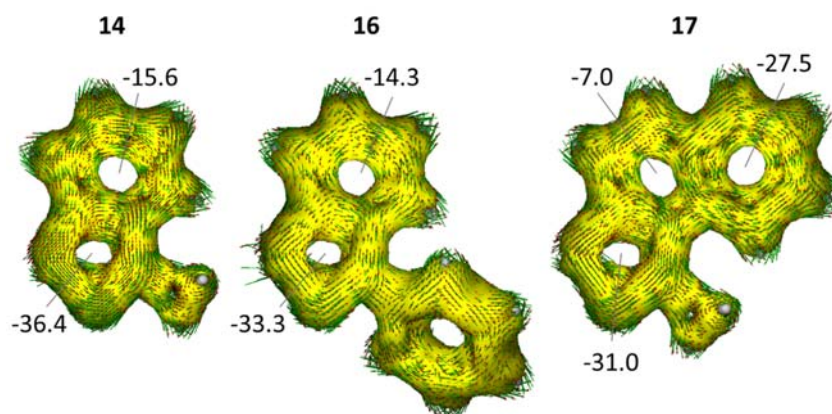


Figure S 1156: Anisotropy of the induced current plots (ACID) with NICS(1)_{zz} values of the diazaphosphole rings.

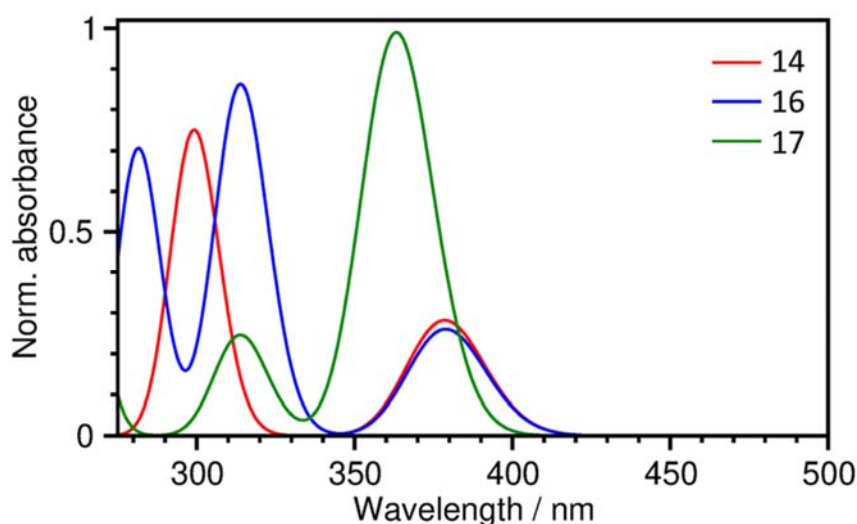


Figure S 1167: Simulated absorption spectra of the compounds diluted in PMMA (vacuum spectra empirically shifted in energy by -400 meV to match the experimental spectra depicted in **Figure 4b** in the main manuscript).

4. Photophysical Characterization

Aside from the absorption and emission spectra in PMMA shown in **Figure 4** in the main manuscript, spectroscopic analysis was also performed for **14**, **16**, and **17** in solution in chloroform (10^{-4} mol/L) as presented in **Figure S 1178**. Their photophysical characteristics are also summarized in **Table S 1**.

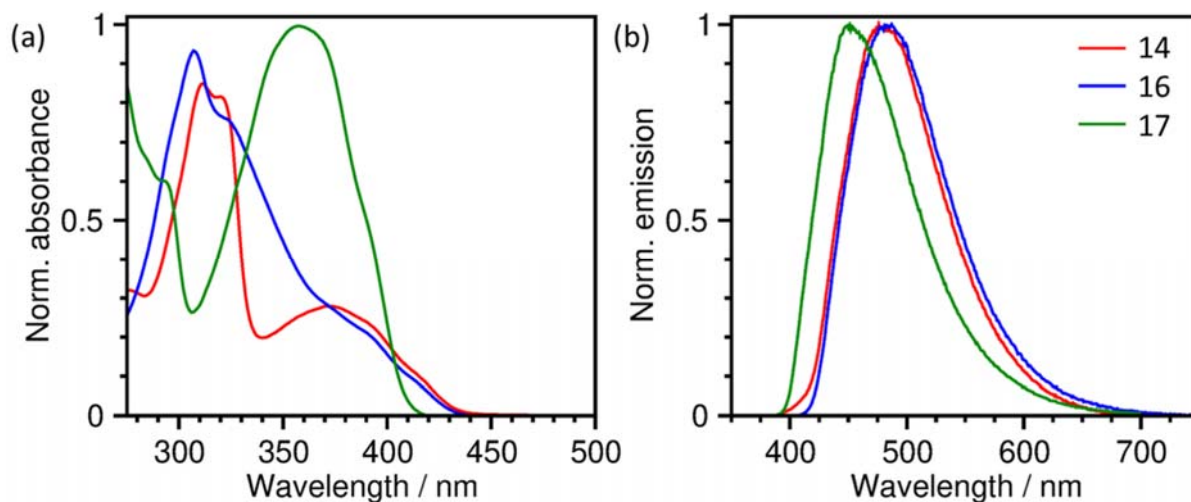


Figure S 1178: a) Normalized absorption spectra (relative to the absorption maximum of **17**) and b) normalized emission spectra of the newly synthesized diazaphospholes in chloroform solutions ($\lambda_{exc} = 340$ nm).

Table S 1: Photophysical characteristics of **14**, **16**, and **17** in diluted chloroform and PMMA films ($\lambda_{exc} = 340$ nm). The fluorescence quantum yield Φ_{FL}^{film} was measured in nitrogen atmosphere.

Compound	λ_{abs}^{sol} in nm	λ_{em}^{sol} in nm	Φ_{FL}^{sol} in %	λ_{abs}^{film} in nm	λ_{em}^{film} in nm	Φ_{FL}^{film} in %
14	310, 372	476	33.1	310, 360	470	37.0
16	307	480	6.5	304	470	9.2
17	272, 358	451	25.2	270, 358	457	14.9

5. X-ray Diffraction Refinements

5.1. General remarks

Suitable single crystals were coated with Paratone-N oil or Fomblin Y25 PFPE oil, mounted using a glass fiber and frozen in the cold nitrogen stream. X-ray diffraction data were collected at 100 K on a Rigaku Oxford Diffraction SuperNova diffractometer using either Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$) generated by micro-focus sources. The data reduction and absorption correction was performed using CrysAlisPro¹⁷, respectively. Using Olex2¹⁸, the structures were solved with SHELXT¹⁹ by direct methods and refined with SHELXL²⁰ by least-square minimization against F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions using the riding model. Images of the structures were produced with the Olex2 software.

5.2. Crystallographic data

Compound	9a[OTf] ₂	9b[OTf] ₂	9d[OTf] ₂	9e[OTf] ₂ ·0.25 MeCN	9f[OTf] ₄ ·2 MeCN
Empirical formula	C ₂₀ H ₂₇ F ₆ N ₄ O ₆ PS ₂	C ₂₁ H ₂₉ F ₆ N ₄ O ₆ PS ₂	C ₂₆ H ₃₀ F ₆ N ₅ O ₈ PS ₂	C ₁₁₀ H ₁₃₉ F ₂₄ N ₂₁ O ₂₄ P ₄ S ₈	C ₅₀ H ₆₂ F ₁₂ N ₁₀ O ₁₂ P ₂ S ₄
Formula weight [g/mol]	628.54	642.57	749.64	2975.77	1413.27
Temperature [K]	100.01(10)	100.03(12)	100.0(2)	100.01(10)	99.9(2)
Crystal system	triclinic	triclinic	triclinic	triclinic	monoclinic
Space group	P-1	P-1	P-1	P-1	P ₂ /c
a [Å]	8.0317(2)	7.8065(4)	10.0358(2)	13.6839(5)	14.2530(2)
b [Å]	12.2262(3)	12.1707(4)	11.58762(19)	14.3106(8)	13.4174(2)
c [Å]	13.7991(3)	14.9023(5)	15.5946(2)	18.0682(8)	16.3574(2)
α [°]	81.406(2)	79.352(3)	95.6498(12)	100.014(4)	90
β [°]	89.124(2)	86.084(4)	107.2800(15)	108.083(4)	90.1710(10)
γ [°]	83.879(2)	79.364(3)	110.3810(17)	92.247(4)	90
Volume [Å³]	1332.18(6)	1366.73(10)	1581.42(5)	3295.8(3)	3128.15(7)
Z	2	2	2	1	2
ρ_{calc} [g/cm³]	1.567	1.561	1.574	1.499	1.500
μ [mm⁻¹]	3.174	3.107	2.841	2.674	2.783
F(000)	648.0	664.0	772.0	1542.0	1460.0
Crystal size [mm³]	0.179 × 0.134 × 0.109	0.297 × 0.121 × 0.118	0.297 × 0.204 × 0.098	0.166 × 0.099 × 0.041	0.4 × 0.178 × 0.059
Radiation (λ in Å)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	Cu Kα (λ = 1.54184)	CuKα (λ = 1.54184)
2θ range for data collection [°]	6.478 to 152.982	6.038 to 153.932	6.092 to 153.54	5.246 to 136.498	6.202 to 153.17
Index ranges	-10 ≤ h ≤ 9, -15 ≤ k ≤ 12, -16 ≤ l ≤ 17	-9 ≤ h ≤ 7, -13 ≤ k ≤ 15, -18 ≤ l ≤ 18	-12 ≤ h ≤ 6, -13 ≤ k ≤ 14, -19 ≤ l ≤ 19	-16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -21 ≤ l ≤ 16	-17 ≤ h ≤ 17, -16 ≤ k ≤ 16, -12 ≤ l ≤ 20
Reflections collected	12715	12626	15338	38344	17844
Independent reflections	5524 [R _{int} = 0.0203, R _{sigma} = 0.0280]	5671 [R _{int} = 0.0360, R _{sigma} = 0.0383]	6601 [R _{int} = 0.0221, R _{sigma} = 0.0268]	12075 [R _{int} = 0.0484, R _{sigma} = 0.0468]	6508 [R _{int} = 0.0270, R _{sigma} = 0.0309]
Data/restraints/parameters	5524/22/432	5671/144/405	6601/0/439	12075/661/1026	6508/0/413
Goodness-of-fit on F²	1.045	1.058	1.043	1.092	1.030
Final R indexes (I >= 2σ (I))	R ₁ = 0.0294, wR ₂ = 0.0745	R ₁ = 0.0580, wR ₂ = 0.1614	R ₁ = 0.0327, wR ₂ = 0.0847	R ₁ = 0.0711, wR ₂ = 0.1721	R ₁ = 0.0377, wR ₂ = 0.0997
Final R indexes (all data)	R ₁ = 0.0315, wR ₂ = 0.0762	R ₁ = 0.0613, wR ₂ = 0.1656	R ₁ = 0.0337, wR ₂ = 0.0857	R ₁ = 0.0854, wR ₂ = 0.1808	R ₁ = 0.0411, wR ₂ = 0.1029
Largest diff. peak/hole [e/Å³]	0.30/-0.34	0.60/-0.75	0.52/-0.52	0.74/-0.69	0.52/-0.38
CCDC Number	2406454	2406467	2406457	2406468	2406456

Compound	12[OTf] ₂	16	18a[OTf] ₂ ·2 MeCN	19[OTf] ₂	20[OTf] ₂ ·2 C ₂ H ₄ Cl ₂
Empirical formula	C ₂₅ H ₂₉ F ₆ N ₄ O ₇ PS ₂	C ₁₂ H ₉ N ₃ P	C ₃₂ H ₃₆ Cl ₂ F ₆ N ₃ O ₇ PS ₂	C ₃₁ H ₃₄ F ₆ N ₃ O ₆ PS ₃	C ₄₄ H ₅₃ Cl ₄ F ₆ N ₃ O ₆ P ₂ S ₂
Formula weight [g/mol]	706.61	212.18	854.63	785.76	1101.75
Temperature [K]	100.00(10)	104.94(16)	100.00(10)	100.00(10)	99.98(10)
Crystal system	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic
Space group	Pbca	P2 ₁	P-1	P2 ₁ /c	P2 ₁ /n
a [Å]	14.45510(10)	6.64810(10)	8.85260(10)	18.75880(9)	10.68480(10)
b [Å]	15.32030(10)	7.88450(10)	10.52490(10)	11.36633(5)	41.6981(4)
c [Å]	27.6597(2)	9.99350(10)	19.7674(2)	16.43311(7)	11.29480(10)
a [°]	90	90	93.5370(10)	90	90
β [°]	90	104.510(2)	97.1010(10)	97.0303(4)	90.2940(10)
γ [°]	90	90	92.4710(10)	90	90
Volume [Å³]	6125.42(7)	507.121(12)	1821.78(3)	3477.50(3)	5032.17(8)
Z	8	2	2	4	4
ρ_{calc} [g/cm³]	1.532	1.390	1.558	1.501	1.454
μ [mm⁻¹]	2.859	2.094	3.824	3.098	4.132
F(000)	2912.0	220.0	880.0	1624.0	2280.0
Crystal size [mm³]	0.08 × 0.06 × 0.03	0.21 × 0.13 × 0.09	0.236 × 0.183 × 0.113	0.14 × 0.12 × 0.04	0.167 × 0.157 × 0.073
Radiation (λ in Å)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	CuKα (λ = 1.54184)
2θ range for data collection [°]	6.392 to 153.788	9.14 to 153.29	4.516 to 153.62	4.746 to 153.416	4.238 to 144.258
Index ranges	-18 ≤ h ≤ 17, -19 ≤ k ≤ 18, -21 ≤ l ≤ 34	-8 ≤ h ≤ 8, -9 ≤ k ≤ 8, -11 ≤ l ≤ 12	-11 ≤ h ≤ 10, -13 ≤ k ≤ 12, -24 ≤ l ≤ 24	-23 ≤ h ≤ 23, -14 ≤ k ≤ 14, -17 ≤ l ≤ 20	-13 ≤ h ≤ 13, -51 ≤ k ≤ 51, -13 ≤ l ≤ 12
Reflections collected	73709	4624	20485	41338	55532
Independent reflections	6454 [R _{int} = 0.0492, R _{sigma} = 0.0222]	1885 [R _{int} = 0.0175, R _{sigma} = 0.0201]	7547 [R _{int} = 0.0216, R _{sigma} = 0.0214]	7284 [R _{int} = 0.0302, R _{sigma} = 0.0217]	9911 [R _{int} = 0.0328, R _{sigma} = 0.0220]
Data/restraints/parameters	6454/0/412	1885/1/136	7547/0/484	7284/192/494	9911/120/660
Goodness-of-fit on F²	1.033	1.073	1.038	1.046	1.049
Final R indexes (I ≥ 2σ (I))	R ₁ = 0.0303, wR ₂ = 0.0756	R ₁ = 0.0236, wR ₂ = 0.0631	R ₁ = 0.0348, wR ₂ = 0.0894	R ₁ = 0.0273, wR ₂ = 0.0680	R ₁ = 0.0382, wR ₂ = 0.1005
Final R indexes (all data)	R ₁ = 0.0361, wR ₂ = 0.0791	R ₁ = 0.0241, wR ₂ = 0.0635	R ₁ = 0.0353, wR ₂ = 0.0898	R ₁ = 0.0298, wR ₂ = 0.0697	R ₁ = 0.0413, wR ₂ = 0.1032
Largest diff. peak/hole [e/Å³]	0.34/-0.36	0.16/-0.17	0.51/-0.56	0.32/-0.39	1.31/-0.59
Flack parameter	-	-0.009(10)	-	-	-
CCDC Number	2406459	2406453	2406455	2406460	2406458

Compound	24[OTf]·CH ₂ Cl ₂	26a[OTf] ₂ ·CH ₂ Cl ₂	26b[OTf] ₂	26c[OTf] ₂ ·MeCN	26e[OTf] ₂ ·MeCN
Empirical formula	C ₁₉ H ₂₉ Cl ₂ F ₆ N ₄ O ₆ PS ₂	C ₂₁ H ₃₂ Cl ₂ F ₆ N ₅ O ₆ PS ₂	C ₂₁ H ₃₂ F ₆ N ₅ O ₆ PS ₂	C ₂₇ H ₃₄ BrF ₆ N ₆ O ₆ PS ₂	C ₂₉ H ₄₀ F ₆ N ₇ O ₆ PS ₂
Formula weight [g/mol]	689.45	730.50	659.60	827.60	791.77
Temperature [K]	100.0(3)	100.0(2)	100.0(2)	100.01(10)	100.01(10)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	P2 ₁ /n	P2 ₁ /c	P2 ₁ /c	P-1	P2 ₁ /n
a [Å]	12.6759(2)	15.45123(18)	14.15063(9)	11.23858(13)	16.0067(3)
b [Å]	14.42555(18)	16.9704(2)	17.01045(11)	12.5586(2)	9.56675(19)
c [Å]	16.7660(2)	12.17720(15)	12.22371(7)	13.81121(16)	24.2375(6)
α [°]	90	90	90	103.8546(12)	90
β [°]	106.2654(15)	102.4422(12)	97.3287(5)	98.6579(10)	95.874(2)
γ [°]	90	90	90	103.2718(12)	90
Volume [Å³]	2943.08(7)	3118.03(7)	2918.31(3)	1797.97(4)	3692.04(14)
Z	4	4	4	2	4
ρ_{calc} [g/cm³]	1.556	1.556	1.501	1.529	1.424
μ [mm⁻¹]	4.557	4.347	2.934	3.773	2.435
F(000)	1416.0	1504.0	1368.0	844.0	1648.0
Crystal size [mm³]	0.354 × 0.253 × 0.159	0.242 × 0.148 × 0.032	0.25 × 0.147 × 0.137	0.373 × 0.203 × 0.065	0.368 × 0.037 × 0.027
Radiation (λ in Å)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2θ range for data collection [°]	7.784 to 152.77	5.858 to 153.806	6.298 to 153.098	6.754 to 153.24	6.332 to 153.168
Index ranges	-15 ≤ h ≤ 15, -18 ≤ k ≤ 13, -21 ≤ l ≤ 20	-19 ≤ h ≤ 19, -21 ≤ k ≤ 21, -15 ≤ l ≤ 10	-17 ≤ h ≤ 17, -21 ≤ k ≤ 16, -15 ≤ l ≤ 10	-13 ≤ h ≤ 14, -15 ≤ k ≤ 15, -17 ≤ l ≤ 12	-19 ≤ h ≤ 17, -12 ≤ k ≤ 9, -29 ≤ l ≤ 30
Reflections collected	21315	37436	16449	17302	20334
Independent reflections	6082 [R _{int} = 0.0247, R _{sigma} = 0.0208]	6513 [R _{int} = 0.0327, R _{sigma} = 0.0165]	6076 [R _{int} = 0.0170, R _{sigma} = 0.0185]	7459 [R _{int} = 0.0305, R _{sigma} = 0.0347]	7664 [R _{int} = 0.0364, R _{sigma} = 0.0396]
Data/restraints/parameters	6082/0/499	6513/0/443	6076/0/401	7459/0/506	7664/0/471
Goodness-of-fit on F²	1.059	1.063	1.047	1.034	1.071
Final R indexes (I >= 2σ (I))	R ₁ = 0.0335, wR ₂ = 0.0878	R ₁ = 0.0348, wR ₂ = 0.0979	R ₁ = 0.0281, wR ₂ = 0.0684	R ₁ = 0.0360, wR ₂ = 0.0951	R ₁ = 0.0471, wR ₂ = 0.1193
Final R indexes (all data)	R ₁ = 0.0347, wR ₂ = 0.0887	R ₁ = 0.0357, wR ₂ = 0.0987	R ₁ = 0.0292, wR ₂ = 0.0692	R ₁ = 0.0372, wR ₂ = 0.0964	R ₁ = 0.0561, wR ₂ = 0.1254
Largest diff. peak/hole [e/Å³]	0.37/-0.46	0.35/-0.50	0.27/-0.37	0.87/-0.86	0.59/-0.49
CCDC Number	2406464	2406462	2406469	2406465	2406470

Compound	26f[OTf] ₄	27[OTf] ₂ ·2 CH ₂ Cl ₂	28[OTf] ₂
Empirical formula	C ₄₆ H ₆₂ F ₁₂ N ₁₀ O ₁₂ P ₂ S ₄	C ₂₇ H ₃₅ BrCl ₄ F ₆ N ₅ O ₇ PS ₂	C ₂₉ H ₃₄ F ₆ N ₅ O ₆ PS ₃
Formula weight [g/mol]	1365.23	972.40	789.76
Temperature [K]	100.01(10)	100.01(10)	100.01(10)
Crystal system	monoclinic	triclinic	monoclinic
Space group	P2 ₁ /c	P-1	P2 ₁
a [Å]	16.3693(9)	9.8199(3)	12.16963(7)
b [Å]	13.6681(4)	11.6251(3)	21.08792(14)
c [Å]	15.2188(7)	18.7271(5)	13.73006(9)
α [°]	90	91.327(2)	90
β [°]	116.992(7)	98.488(2)	90.8006(5)
γ [°]	90	106.588(2)	90
Volume [Å³]	3034.1(3)	2021.62(10)	3523.23(4)
Z	2	2	4
ρ_{calc} [g/cm³]	1.494	1.597	1.489
μ [mm⁻¹]	2.846	5.838	3.076
F(000)	1412.0	984.0	1632.0
Crystal size [mm³]	0.26 × 0.122 × 0.02	0.421 × 0.06 × 0.045	0.146 × 0.049 × 0.046
Radiation (λ in Å)	Cu Kα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2θ range for data collection [°]	8.866 to 136.492	4.782 to 153.91	6.438 to 153.456
Index ranges	-19 ≤ h ≤ 19, -16 ≤ k ≤ 15, -17 ≤ l ≤ 18	-12 ≤ h ≤ 10, -13 ≤ k ≤ 14, -23 ≤ l ≤ 23	-12 ≤ h ≤ 15, -25 ≤ k ≤ 26, -15 ≤ l ≤ 17
Reflections collected	15387	22076	38763
Independent reflections	5479 [R _{int} = 0.0582, R _{sigma} = 0.0642]	8432 [R _{int} = 0.0413, R _{sigma} = 0.0392]	14269 [R _{int} = 0.0266, R _{sigma} = 0.0312]
Data/restraints/parameters	5479/10/427	8432/272/632	14269/1/917
Goodness-of-fit on F²	1.041	1.034	1.040
Final R indexes (I>=2σ (I))	R ₁ = 0.0815, wR ₂ = 0.2288	R ₁ = 0.0561, wR ₂ = 0.1540	R ₁ = 0.0302, wR ₂ = 0.0776
Final R indexes (all data)	R ₁ = 0.1056, wR ₂ = 0.2513	R ₁ = 0.0598, wR ₂ = 0.1586	R ₁ = 0.0311, wR ₂ = 0.0784
Largest diff. peak/hole [e/Å³]	0.74/-0.62	1.07/-1.09	0.29/-0.34
Flack parameter	-	-	-0.008(8)
CCDC Number	2406466	2406463	2406461

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