Electronic Supporting Information

This PDF file includes:

Experimental Section

General Considerations.

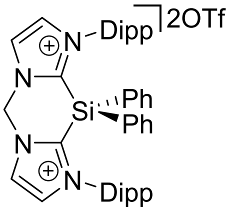
All experiments and manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk techniques or in an MBraun inert atmosphere dry box containing an atmosphere of purified nitrogen. Solvents were dried by standard methods and freshly distilled prior to use. The starting materials (bis)NHC,[1] Ph_3SiOTf,[2] $Ph_2Si(OTf)_2$,[2] $[(dioxane)_nNaOCP]$[3,4] and IPr (IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene)[5] were prepared according to literature procedures. All other reagents were purchased from Sigma Aldrich, Alfa-Aesar, abcr or TCI Chemicals and, if applicable, distilled prior to use. ^{1}H, ^{13}C, ^{19}F, ^{29}Si and ^{31}P NMR spectra were recorded on Bruker Avance II 200, Avance II 400, Avance III 500 or Avance III 700 spectrometers with residual solvent signals as internal reference (^{1}H, ^{13}C). Data for ^{1}H NMR spectroscopy are reported as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q =quartet, m = multiplet, dm = doublet of multiplets, b = broad, sept = septet), coupling constant (Hz), assignment. Data for ^{13}C, ^{19}F, ^{29}Si and ^{31}P NMR are reported in terms of chemical shift (δ ppm). Chemical shifts were referenced to δTMS = 0.00 ppm (^{1}H, ^{13}C), δH_3PO_4(85%) = 0.00 ppm (^{31}P), $\delta CFCl_3$ = 0.00 ppm (^{19}F), and δTMS = 0.00 ppm (^{29}Si). Assignments of individual resonances were performed using 2D NMR techniques (HMBC, HSQC, HH-COSY) when necessary. High-resolution mass spectra (HRMS) were obtained on a LTQ Orbitrap XL (ESI). Melting point samples were sealed in a glass capillary under nitrogen.

Single-Crystal X-ray Structure Determinations.

Crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data were collected on an Oxford Diffraction SuperNova, Single source at offset, Atlas at 150 K (Cu-Kα radiation, λ = 1.54184 Å). The structures were solved by direct methods or using the SHELXT program[6] and refined on F^2 with the SHELX-2014[7] software package. The positions of the H atoms were calculated and considered isotropically according to a riding model. CCDC 1866468-1866471 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223336033.

Synthetic Procedures

Synthesis of Compound 7[OTf]$_2$

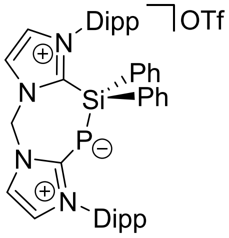


7[OTf]$_2$

A solid mixture of $Ph_2Si(OTf)_2$ (3.60 g, 7.49 mmol, 1.00 equiv) and bis(NHC) (3.51 g, 7.49 mmol, 1.00 equiv) was cooled to -78 °C. At this temperature Et_2O (150 mL) was added and the resulting suspension was stirred for 30 min. It was then allowed to warm to ambient temperature and stirred for another 30 min. The liquid phase was separated by decantation, the residue was washed with *n*-hexane (2 x 20 mL) and dried under vacuum to afford 5.95 g of the product as an off-white powder (Yield: 84 %). Single crystals qualified for X-Ray diffraction analysis were grown from a concentrated CH_3CN solution at ambient temperature.

m.p.: 230 °C (decomp.).
^{1}H NMR (500 MHz; CD_3CN) δ 8.37 (2H, d, $^3J_{HH}$ = 1.8 Hz, C***H***NCH_2), 7.92 (2H, d, $^3J_{HH}$ = 1.8 Hz, C***H***NDipp), 7.51 (2H, t, $^3J_{HH}$ = 7.5 Hz, *p*-Ph), 7.34 (2H, t, $^3J_{HH}$ = 7.8 Hz, *p*-Dipp), 7.28 (4H, t, $^3J_{HH}$ = 7.8 Hz, *m*-Ph), 7.21 (2H, s, C***H***$_2$), 7.17 (4H, d, *J* = 7.1 Hz, *o*-Ph), 7.08 (4H, d, *J* = 7.8 Hz, *m*-Dipp), 2.24 (4H, sept, $^3J_{HH}$ = 6.7 Hz, C***H***$(CH_3)_2$), 0.91 (12H, d, $^3J_{HH}$ = 6.7 Hz, CH(C***H***$_3$)$_2$), 0.77 (12H, d, $^3J_{HH}$ = 6.7 Hz, CH(C***H***$_3$)$_2$).
^{13}C NMR (101 MHz; CD_3CN) δ 146.1 (s, *o*-Dipp), 144.1 (s, N***C***N), 137.7 (s, *o*-Ph), 134.5 (s, *p*-Ph), 133.4 (s, *p*-Dipp), 132.3 (s, *i*-Dipp), 130.8 (s, ***C***HNC_6H_3*i*Pr_2) , 130.2 (s, *m*-Ph), 128.1 (s, ***C***$HNCH_2$), 125.6 (s, *m*-Dipp), 122.1 (q, $^1J_{CF}$ = 320 Hz, ***C***F_3) , 118.9 (s, *i*-Ph), 64.2 (s, ***C***H_2), 29.2 (s, ***C***$H(CH_3)_2$), 26.8 (s, CH(***C***H_3)$_2$), 21.6 (s, CH(***C***H_3)$_2$).
^{19}F NMR (188 MHz; CD_3CN) δ –79.2 (s).
^{29}Si NMR (79 MHz; CD_3CN) δ –36.7 (s).
HRMS (ESI+): m/z 325.1895 (Calcd for $[M\text{-}2OTf]^{2+}$: 325.1897).

Synthesis of Compound 8[OTf]



8[OTf]

To a stirred mixture of **7**[OTf]$_2$ (4.50 g, 4.74 mmol, 1.00 equiv) and ([Na(OCP)·(dioxane)$_{4.0}$] (2.06 g, 4.74 mmol, 1.00 equiv) was added DCM (150 mL) whereupon the reaction mixture turned red-brown and evolution of gas occured. After stirring for 1 h the mixture was filtered and the filtrate was concentrated *in vacuo* before adding *n*-Hexane (60 mL). The precipitate was separated by decantation and dried under vacuum to afford 3.35 g of the product as a yellowish solid (Yield: 85 %). Single crystals qualified for X-Ray diffraction analysis were grown from a concentrated CH_3CN solution at –25 °C.

m.p.: 138 °C.

^{1}H NMR (500 MHz; CD_2Cl_2) δ 8.73 (1H, d, $^3J_{HH}$ = 1.8 Hz, C*H*N), 7.95 (1H, s, C*H*N), 7.55 – 7.63 (2H, m, Ar-*H*), 7.48 (3H, m, Ar-*H*), 7.40 – 7.33 (3H, m, Ar-*H*), 7.31 (1H, d, $^3J_{HH}$ = 1.9 Hz, C*H*N), 7.26 (1H, d, $^3J_{HH}$ = 7.8 Hz, Ar-*H*), 7.12 (3H, m, Ar-*H*), 7.05 (2H, m, Ar-*H*), 6.86 – 6.89 (2H, m, Ar-*H* + C*H*$_2$), 6.84 (1H, d, $^3J_{HH}$ = 2.1 Hz, C*H*N), 6.73 (1H, d, $^3J_{HH}$ = 7.4 Hz, Ar-*H*), 6.31 (1H, d, $^2J_{HH}$ = 14.7 Hz, C*H*$_2$), 2.34 – 2.54 (4H, m, C*H*(CH$_3$)$_2$), 1.38 (3H, d br, $^3J_{HH}$ = 6.7 Hz, C*H*$_3$), 1.33 (3H, d br, $^3J_{HH}$ = 6.7 Hz, C*H*$_3$), 1.29 (3H, d br, $^3J_{HH}$ = 6.7 Hz, C*H*$_3$), 1.12 – 1.15 (6H, m, C*H*$_3$), 1.06 – 1.09 (6H, m, C*H*$_3$), 0.88 – 0-90 (3H, d br, $^3J_{HH}$ = 6.7 Hz, C*H*$_3$).

^{13}C NMR (125.79 MHz; CD_2Cl_2) δ 170.8 (d, $^1J_{CP}$ = 103.1 Hz, N$_2$*C*–P), 151.8 (s, N$_2$*C*–Si), 147.7 (s, Ar), 147.0 (s, Ar), 146.6 (s, Ar), 145.1 (s, Ar), 138.8 (s, Ar), 136.7 (s, Ar), 134.6 (s, Ar), 132.7 (s, Ar), 132.0 (s, Ar), 131.6 (s, Ar), 131.2 (s, Ar), 131.0 (s, Ar), 129.6 (s, Ar), 129.5 (s, ***C***HN), 128.2 (s, Ar), 128.0 (s, Ar), 127.8 (s, *C*HN), 125.3 (s, Ar), 124.5 (s, Ar), 124.1 (s, Ar), 122.1 (s, ***C***HN), 122.0 (s, ***C***HN), 121.2 (q, $^1J_{CF}$ = 320 Hz, ***C***F$_3$), 59.9 (s, ***C****H*$_2$), 29.0 (s, ***C***H(CH$_3$)$_2$), 28.5 (s, ***C***H(CH$_3$)$_2$), 26.7 (s, ***C***H(CH$_3$)$_2$), 26.2 (s, ***C***H(CH$_3$)$_2$), 25.1 (s, ***C***H$_3$), 24.7 (s, ***C***H$_3$), 24.6 (s, ***C***H$_3$), 24.2 (s, ***C***H$_3$), 23.2 (s, ***C***H$_3$), 22.3 (s, ***C***H$_3$), 21.5 (s, ***C***H$_3$).

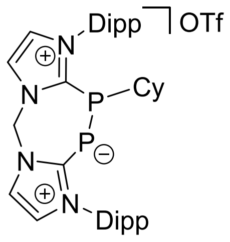
^{19}F NMR (188 MHz; CD_2Cl_2) δ –79.2 (s).

^{29}Si NMR (79 MHz; CD_2Cl_2) δ –16.0 (d, $^1J_{SiP}$.= 85 Hz).

^{31}P NMR (79 MHz; CD_2Cl_2) δ –161.4 (s).

HRMS (ESI+): m/z 681.3523 (Calcd for [M-OTf]$^+$: 681.3537).

Synthesis of Compound 9[OTf]



9[OTf]

To a stirred solution of **8**[OTf] (300 mg, 0.361 mmol, 1.00 equiv) in DCM (10 mL) was added $\mathrm{CyPCl_2}$ (56 µL, 0.36 mmol, 1.0 equiv). The resulting mixture was stirred for 30 min, concentrated to approximately 1 mL and *n*-Pentane (10 mL) was added, which led to precipitation of a yellow solid. The liquid phase was decanted and the residue washed with *n*-pentane (2 x 7 mL) before drying under vacuum. This afforded 235 mg of the product as a yellow solid (Yield: 85%). Single crystals qualified for X-Ray diffraction analysis were grown from a concentrated $\mathrm{CH_2Cl_2}$/toluene solution at ambient temperature.

<u>m.p.:</u> 200 °C.

^{1}<u>H NMR</u> (700 MHz, $\mathrm{CD_2Cl_2}$) δ 8.59 (d, $^3J_{\mathrm{HH}}$ = 2.0 Hz, 1H, NC*H*), 7.94 (s, 1H, NC*H*), 7.55 (t, $^3J_{\mathrm{HH}}$ = 7.8 Hz, 1H, *p*-Dipp), 7.49 (t, $^3J_{\mathrm{HH}}$ = 7.8 Hz, 1H, *p*-Dipp), 7.33 (dd, $^3J_{\mathrm{HH}}$ = 7.8, $^4J_{\mathrm{HH}}$ 1.3 Hz, 1H, *m*-Dipp), 7.31 – 7.25 (m, 5H, 3 x *m*-Dipp + 1 x $\mathrm{N_2C}H_2$ + 1 x NC*H*), 6.86 (d, $^3J_{\mathrm{HH}}$ = 2.0, 1H, NC*H*), 6.49 (d, $^2J_{\mathrm{HH}}$ = 14.5 Hz, 1H, $\mathrm{N_2C}H_2$), 2.53 (sept, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 1H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 2.41 (m, 2H, 2 x $\mathrm{C}H\mathrm{(CH_3)_2}$), 2.19 (sept, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 1H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 2.16 – 2.10 (m, 2H, P-C*H* + Cy-$\mathrm{C}H_2$), 1.81 – 1.58 (m, 4H, 2 x Cy-$\mathrm{C}H_2$), 1.32 – 1.27 (m, 5H, $\mathrm{CH_3}$ + Cy-$\mathrm{C}H_2$), 1.25 (d, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 3H, $\mathrm{CH_3}$), 1.22 (d, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 3H, $\mathrm{CH_3}$),1.21 – 1.16 (m, 2H, Cy-$\mathrm{C}H_2$), 1.15 (d, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 3H, $\mathrm{CH_3}$), 1.14 (d, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 3H, $\mathrm{CH_3}$), 1.11 (d, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 3H, $\mathrm{CH_3}$), 1.09 (d, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 3H, $\mathrm{CH_3}$), 0.99 (d, $^3J_{\mathrm{HH}}$ = 6.9 Hz, 3H, $\mathrm{CH_3}$), 0.93 – 0.90 (m, 1H, Cy-$\mathrm{C}H_2$).

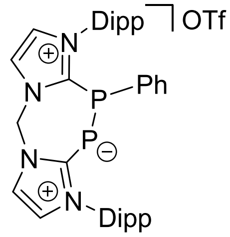
^{13}<u>C NMR</u> (176 MHz, $\mathrm{CD_2Cl_2}$) δ 169.21 (dd, $^1J_{\mathrm{CP}}$ = 145.2, $^2J_{\mathrm{CP}}$ = 10.6 Hz, $\mathrm{N_2}C$-P), 151.46 (dd, $^1J_{\mathrm{CP}}$ = 76.2, $^2J_{\mathrm{CP}}$ = 7.4 Hz, $\mathrm{N_2}C$-PCy), 147.17 (s, *o*-Dipp), 146.98 (s, *o*-Dipp), 146.96 (s, *o*-Dipp), 145.40 (s, *o*-Dipp), 132.06 (s, *p*-Dipp), 131.72 (s, *i*-Dipp), 131.50 (s, *i*-Dipp), 131.31 (s, *p*-Dipp), 125.91 (CH, d, $^3J_{\mathrm{CP}}$ = 2.5 Hz, NC*H*), 125.85 (s, *m*-Dipp), 125.21 (s, *m*-Dipp), 125.08 (s, N*C*H), 124.80 (s, , *m*-Dipp), 122.91 (CH, d, $^3J_{\mathrm{CP}}$ = 5.3 Hz, NC*H*), 121.79 (d, $^3J_{\mathrm{CP}}$ = 2.9 Hz, NC*H*), 121.17 (quart, $^1J_{\mathrm{CF}}$ = 320.1 Hz, $\mathrm{CF_3}$), 59.53 (s, $\mathrm{N_2CH_2}$), 45.08 (d, $^1J_{\mathrm{CP}}$ = 22.5 Hz, P*C*H), 32.02 (d, $^2J_{\mathrm{CP}}$ = 11.2 Hz, Cy-$C\mathrm{H_2}$), 29.05 (s, $C\mathrm{H(CH_3)_2}$), 29.01 (s, $C\mathrm{H(CH_3)_2}$), 28.98 (s, $C\mathrm{H(CH_3)_2}$), 28.83 (s, Cy-$C\mathrm{H_2}$), 27.10 (d, $^3J_{\mathrm{CP}}$ = 10.4 Hz, Cy-$C\mathrm{H_2}$), 26.9 (d, $^2J_{\mathrm{CP}}$ = 16.6 Hz, Cy-$C\mathrm{H_2}$), 26.45 (s, $\mathrm{CH_3}$), 26.25 (s, Cy-$C\mathrm{H_2}$), 25.65 (s, $\mathrm{CH_3}$), 25.01 (s, $\mathrm{CH_3}$), 24.74 (s, $\mathrm{CH_3}$), 23.88 (d, J = 2.9 Hz, $\mathrm{CH_3}$), 23.09 (d, J_{PC} = 2.5 Hz, $\mathrm{CH_3}$), 22.88 (d, J_{PC} = 3.2 Hz, $\mathrm{CH_3}$), 22.78 (s, $\mathrm{CH_3}$).

^{19}<u>F NMR</u> (188 MHz, $\mathrm{CD_2Cl_2}$) δ -78.9 (s).

^{31}<u>P NMR</u> (81 MHz, $\mathrm{CD_2Cl_2}$) δ -66.5 (d, $^1J_{\mathrm{PP}}$ = 453.5 Hz), -97.5 (d, $^1J_{\mathrm{PP}}$ = 453.5 Hz).

<u>HRMS</u> (ESI+): m/z 613.3577 (Calcd for $[\mathrm{M\text{-}OTf}]^+$: 613.3583).

Synthesis of Compound 10[OTf]



10[OTf]

To a stirred solution of **8**[OTf] (200 mg, 0.241 mmol, 1.00 equiv) in DCM (7 mL) was added $PhPCl_2$ (33 µL, 0.24 mmol, 1.0 equiv). The resulting mixture was stirred for 30 min, concentrated to approximately 1 mL and *n*-Pentane (8 mL) was added, which led to precipitation of a yellow solid. The liquid phase was decanted and the residue washed with *n*-pentane (2 x 7 mL) before drying under vacuum. This afforded 150 mg of the product as a yellow solid (Yield: 82%). Single crystals qualified for X-Ray diffraction analysis were grown from a concentrated CH_2Cl_2/*n*-Pentane solution at ambient temperature.

^{1}H NMR (200 MHz; CD_2Cl_2) δ 8.67 (1H, d, $^{3}J_{HH}$ = 2.0 Hz, C*H*N), 7.90 (1H, s, C*H*N), 7.51 – 7.67 (4H, m, Ph + Dipp), 7.32 – 7.46 (15H, m, Ph + Dipp + C*H*N), 6.82 – 6.90 (2H, m, C*H*N + C*H*$_2$), 5.92 (1H, d, $^{2}J_{HH}$ = 14.3 Hz, C*H*$_2$), 2.39 – 2.51 (3H, m, C*H*(CH_3)$_2$), 2.21 – 2.32 (1H, sept, $^{3}J_{HH}$ = 6.7 Hz, C*H*(CH_3)$_2$), 1.23 – 1.29 (12H, m, C*H*$_3$), 1.05 – 1.17 (12H, m, C*H*$_3$).

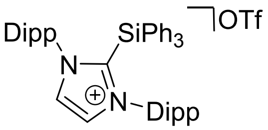
^{19}F NMR (188 MHz; CD_2Cl_2) δ –79.2 (s).

^{31}P NMR (81 MHz; CD_2Cl_2) δ –65.0 (d, $^{1}J_{PP}$ = 478.8 Hz), –102.4 (d, $^{1}J_{PP}$.= 478.8 Hz).

HRMS (ESI+): m/z 607.3109 (Calcd for [M-OTf]$^{+}$: 607.3114).

Note: Compound **10[OTf]** slowly decomposes in CH_2Cl_2 and CD_2Cl_2 and ^{1}H NMR spectra always showed the formation of the protonated bis(NHC) ligand [bis(NHC)·2HOTf]. This material was used without further purification for growing single crystals suitable for X-Ray structure analysis and investigation of the ^{31}P NMR shifts. Attempts to obtain pure material by recrystallisation afforded crystalline mixtures of **10[OTf]** and [bis(NHC)·2HOTf].

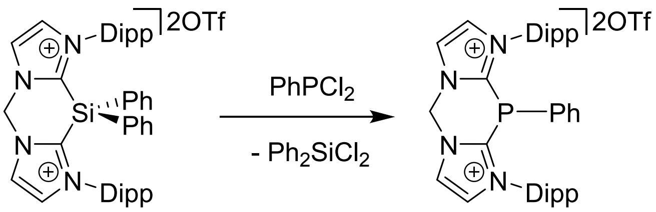
Synthesis of IPrSiPh3[OTf]



To a mixture of Ph_3SiOTf (252 mg, 0.617 mmol, 1.00 equiv) and IPr (240 mg, 0.617 mmol, 1.00 equiv) was added diethyl ether (7mL) at -60 °C. The mixture was allowed to warm to ambient temperature and stirred for 1 h what led to formation of a colourless precipitate. Subsequently, the supernatant was decanted and the solid residue was washed with diethyl ether (2 x 10 mL). Drying under vacuum afforded 445 mg of the product as white microcrystalline solid (Yield: 90 %).

m.p.: 205 °C.
^{1}H NMR (700 MHz, CD_2Cl_2) δ 7.91 (s, 2H, NC*H*), 7.43 – 7.29 (m, 5H, *p*-Ph + *p*-Dipp), 7.17 (t, $^3J_{HH}$ = 7.7 Hz, 6H, *m*-Ph), 7.04 (d, $^3J_{HH}$ = 7.8 Hz, 4H, *m*-Dipp), 7.02 – 7.00 (d, $^3J_{HH}$ = 7.7 Hz, 6H, *o*-Ph), 2.54 (sept, $^3J_{HH}$ = 6.7 Hz, 4H, C*H*(CH_3)$_2$), 1.11 (d, $^3J_{HH}$ = 6.8 Hz, 12H, C*H*$_3$), 0.86 (d, $^3J_{HH}$ = 6.7 Hz, 12H, C*H*$_3$).
^{13}C NMR (176 MHz, CD_2Cl_2) δ 150.95 (s, N_2*C*), 145.41 (s, *o*-Dipp), 136.88 (s, *o*-Ph), 132.92 (s, *p*-Dipp), 132.86 (s, *i*-Dipp), 131.52 (s, *p*-Ph), 131.12 (s, NCH), 128.78 (s, *m*-Ph), 127.31 (s, *i*-Ph), 125.29 (s, *m*-Dipp), 121.39 (q, $^1J_{CF}$ = 321.3 Hz, *C*F_3), 29.83 (s, *C*H(CH_3)$_2$), 26.77 (s, *C*H_3), 21.63 (s, *C*H_3).
^{19}F NMR (188 MHz, CD_2Cl_2) δ –78.92 (s).
^{29}Si NMR (139 MHz, CD_2Cl_2) δ –22.24 (s).
HRMS (ESI+): m/z 647.3802 (Calcd for [M-OTf]$^+$: 647.3816).

Synthesis of bis(NHC)(PPh)[OTf]$_2$ from 7[OTf]$_2$

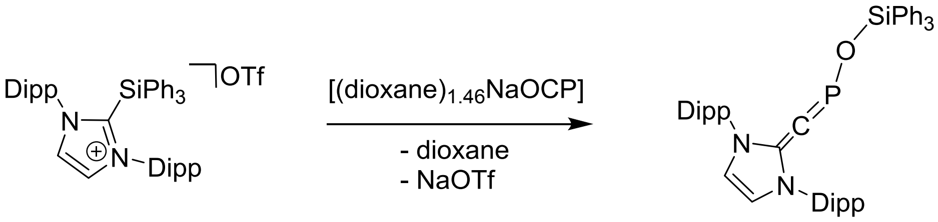


Scheme S1: Synthesis of bis(NHC)(PPh)[OTf]$_2$ starting from 7[OTf]$_2$

A solution of **7**[OTf]$_2$ (85 mg, 0.089 mmol, 1.0 equiv) and PhPCl$_2$ (12 µL, 0.089 mmol, 1.0 equiv) in *o*-$C_6H_4F_2$ was stirred at 55 °C for three days. After cooling to ambient temperature the mixture was concentrated under vacuum and subsequent addition of *n*-Pentane led to formation of an off-white precipitate. The supernatant was decanted and the solid residue was washed with *n*-Pentane (5 mL). Drying under vacuum afforded 64 mg of the product as an off-white solid (Yield: 83 %).

^{1}H and ^{31}P NMR spectra were in agreement with the ones that were previously reported.[8]

Synthesis of IPr=C=P-OSiPh3 from IPrSiPh3[OTf]



Scheme S2: Synthesis of IPr=C=P-OSiPh3 from IPrSiPh3[OTf]

THF (0.5 mL) was added to a mixture of [IPrSiPh$_3$][OTf] (25mg, 0.031 mmol, 1.0 equiv) and [(dioxane)$_{1.46}$NaOCP] (6.6 mg, 0.031 mmol, 1.0 equiv). After stirring the resulting suspension at ambient temperature for 12 h, all volatiles were removed under vacuum. The residue was extracted with C_6D_6 (0.5 mL) and filtered into an NMR tube.

^{1}H, ^{13}C and ^{31}P NMR spectra were in agreement with those previously reported.[9]

NMR and other spectra

Spectra of compound 7[OTf]$_2$

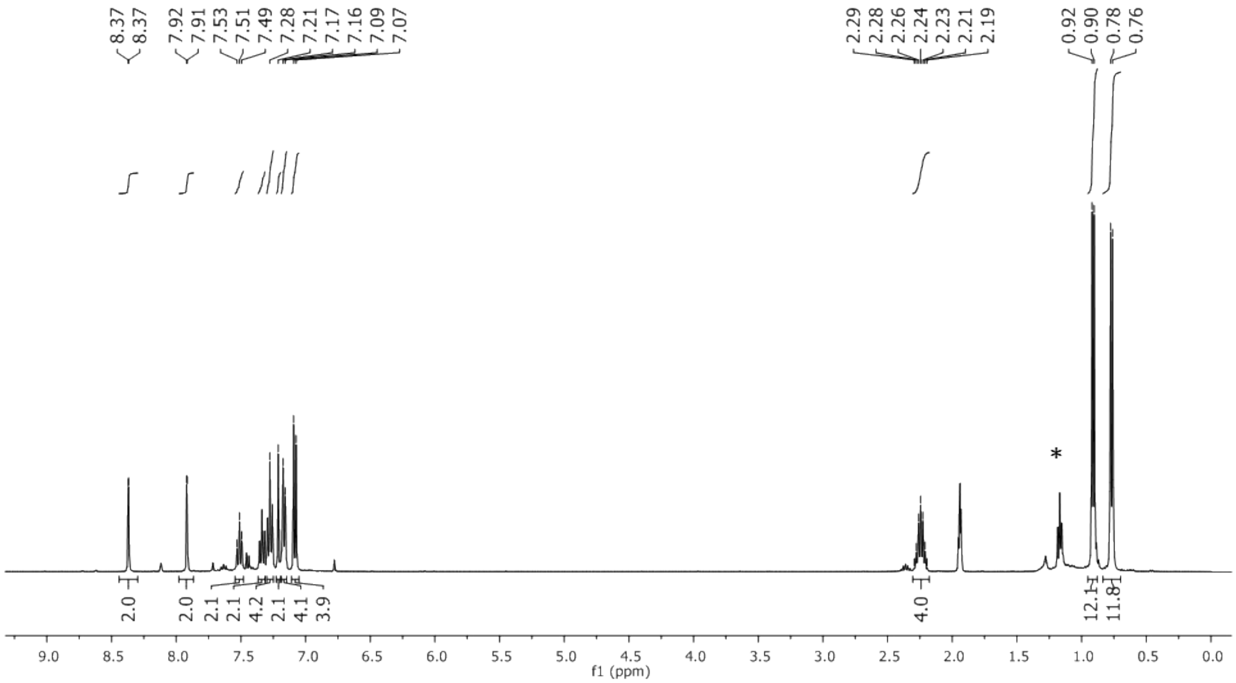


Figure S1. ^{1}H NMR spectrum of **7[OTf]$_2$** in CD_3CN. *Hexane.

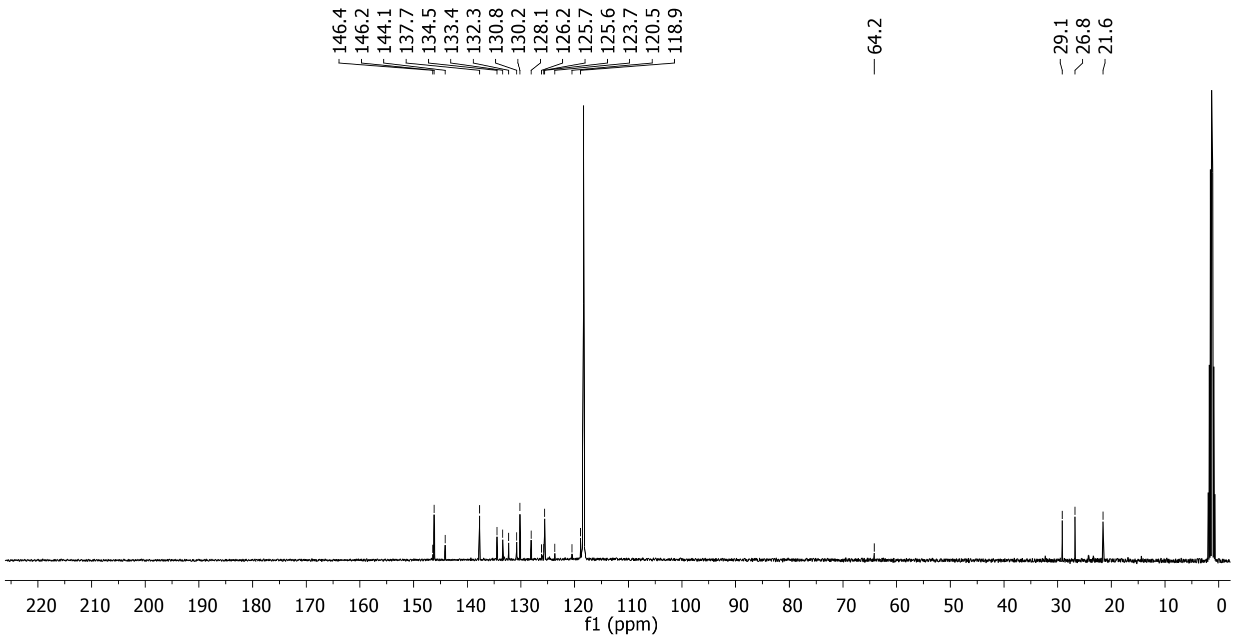


Figure S2: ^{13}C NMR spectrum of **7[OTf]$_2$** in CD_3CN.

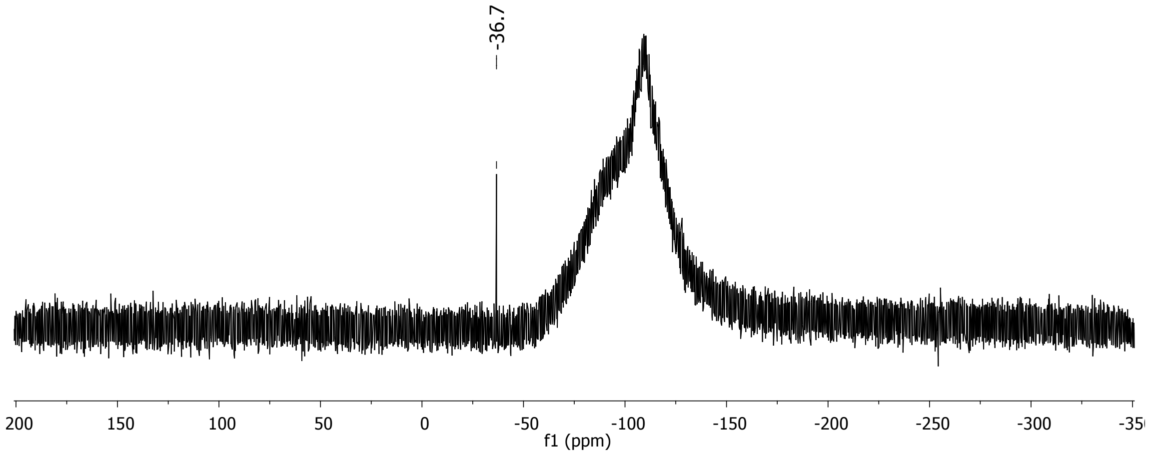


Figure S3: ^{29}Si NMR spectrum of **7[OTf]$_2$** in CD_3CN.

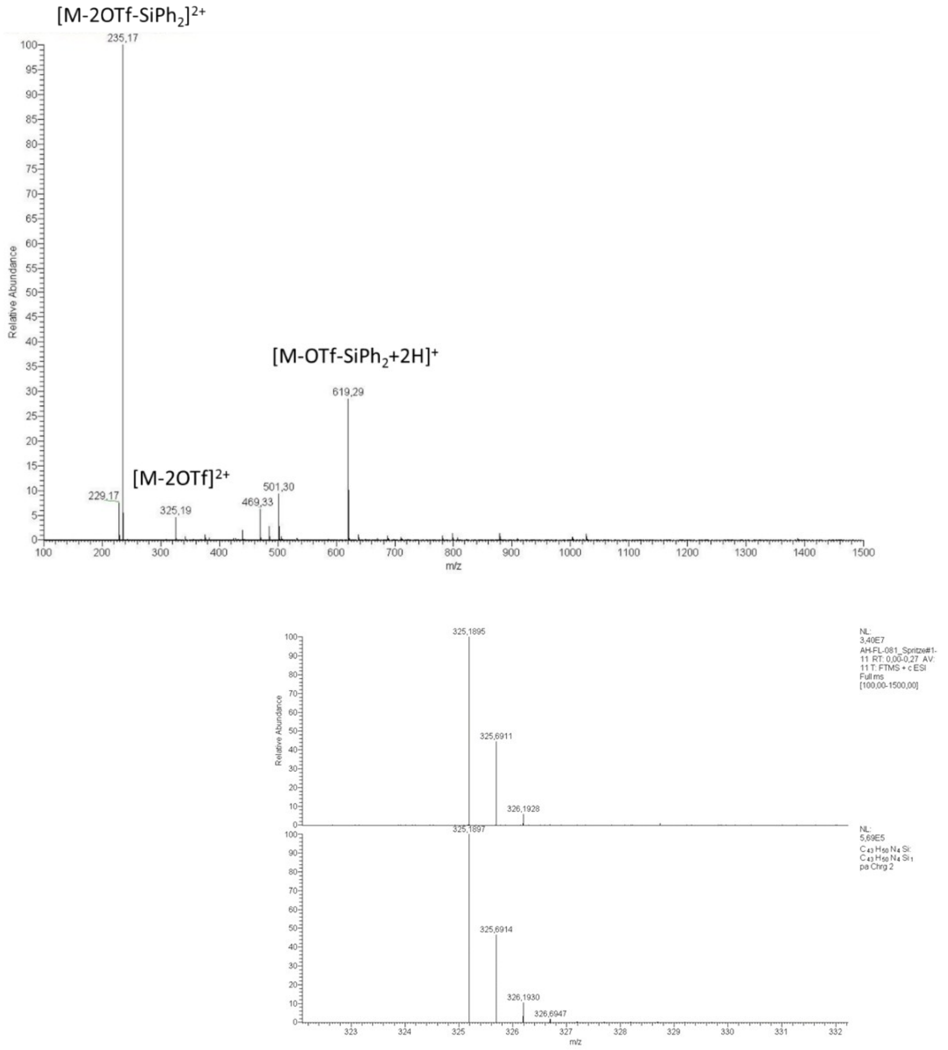


Figure S4: HRMS (ESI$^+$) of [$C_{45}H_{50}F_6N_4O_6S_2Si$] (**7[OTf]$_2$**) and zoom into the [M-2OTf]$^{2+}$-peak region (top) in comparison to the calculated isotopic pattern for [$C_{43}H_{50}N_4Si$]$^{2+}$ (bottom).

Spectra of compound 8[OTf]

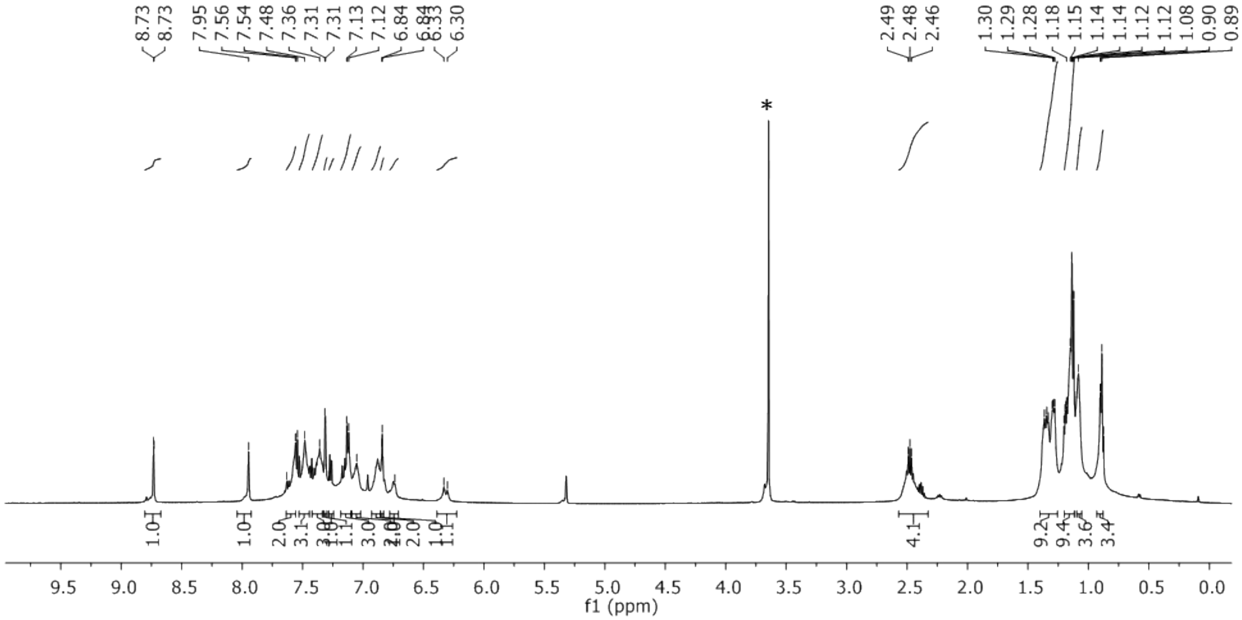


Figure S5: ^{1}H NMR spectrum of **8**[OTf] in CD_2Cl_2. *Dioxane.

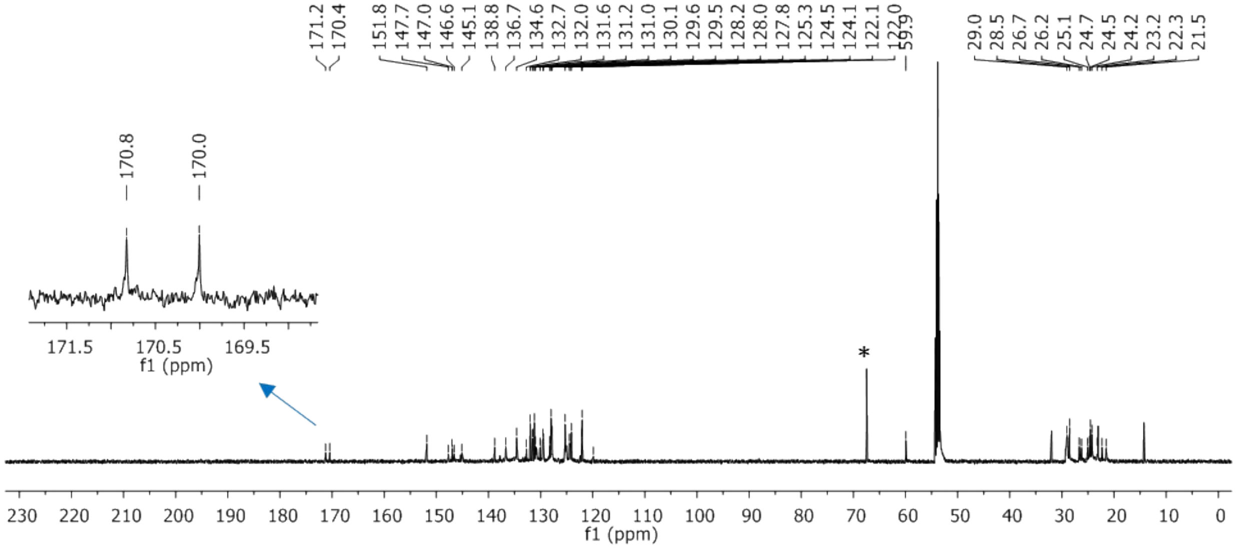


Figure S6: ^{13}C NMR spectrum of **8**[OTf] in CD_2Cl_2. *Dioxane.

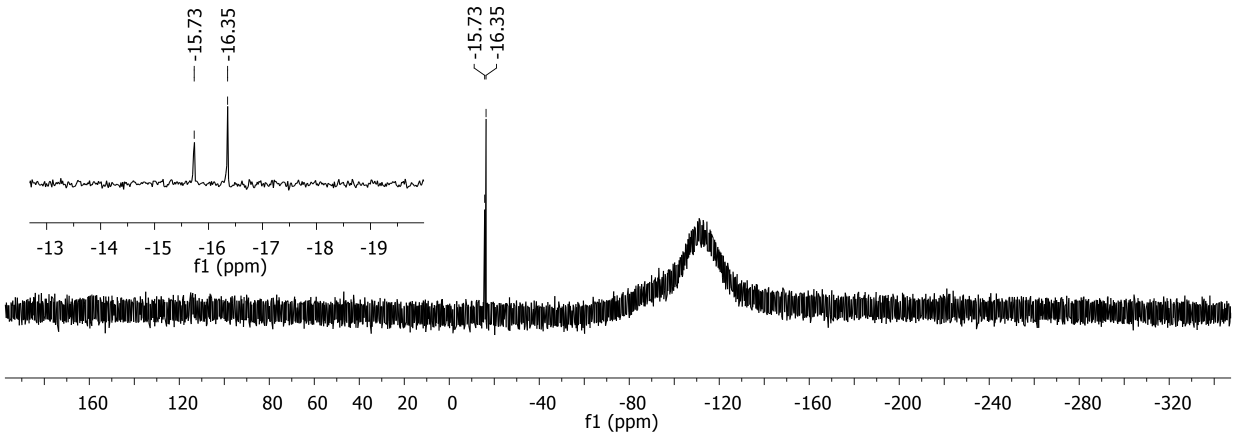


Figure S7: ^{29}Si NMR spectrum of **8**[OTf] in CD_2Cl_2.

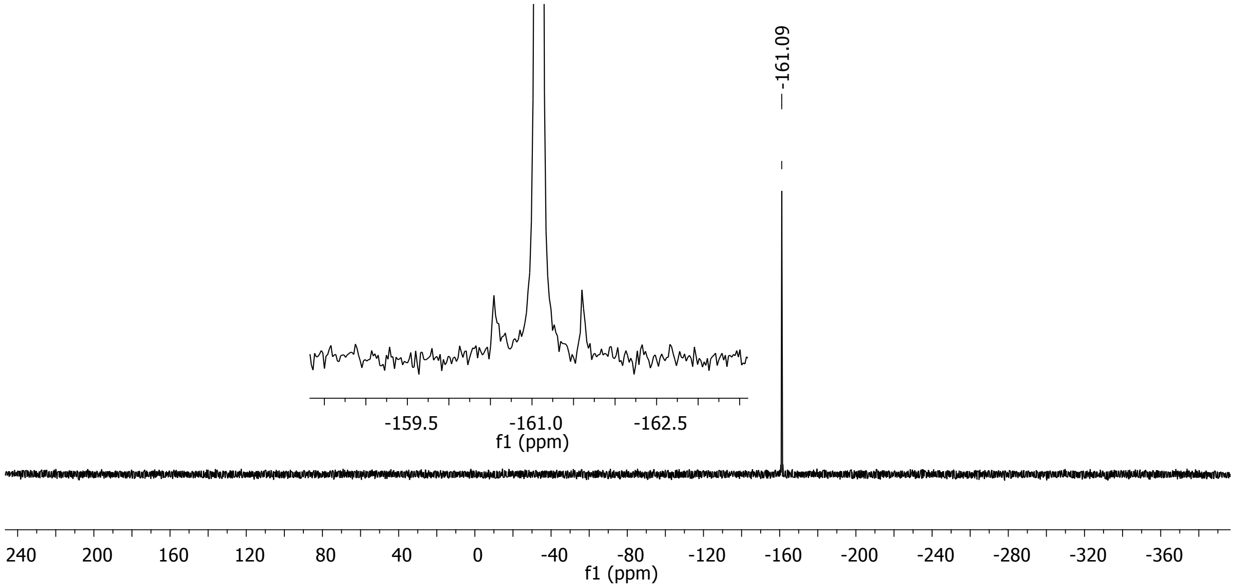


Figure S8: $^{31}P\{^1H\}$ NMR spectrum of **8**[OTf] in CD_2Cl_2.

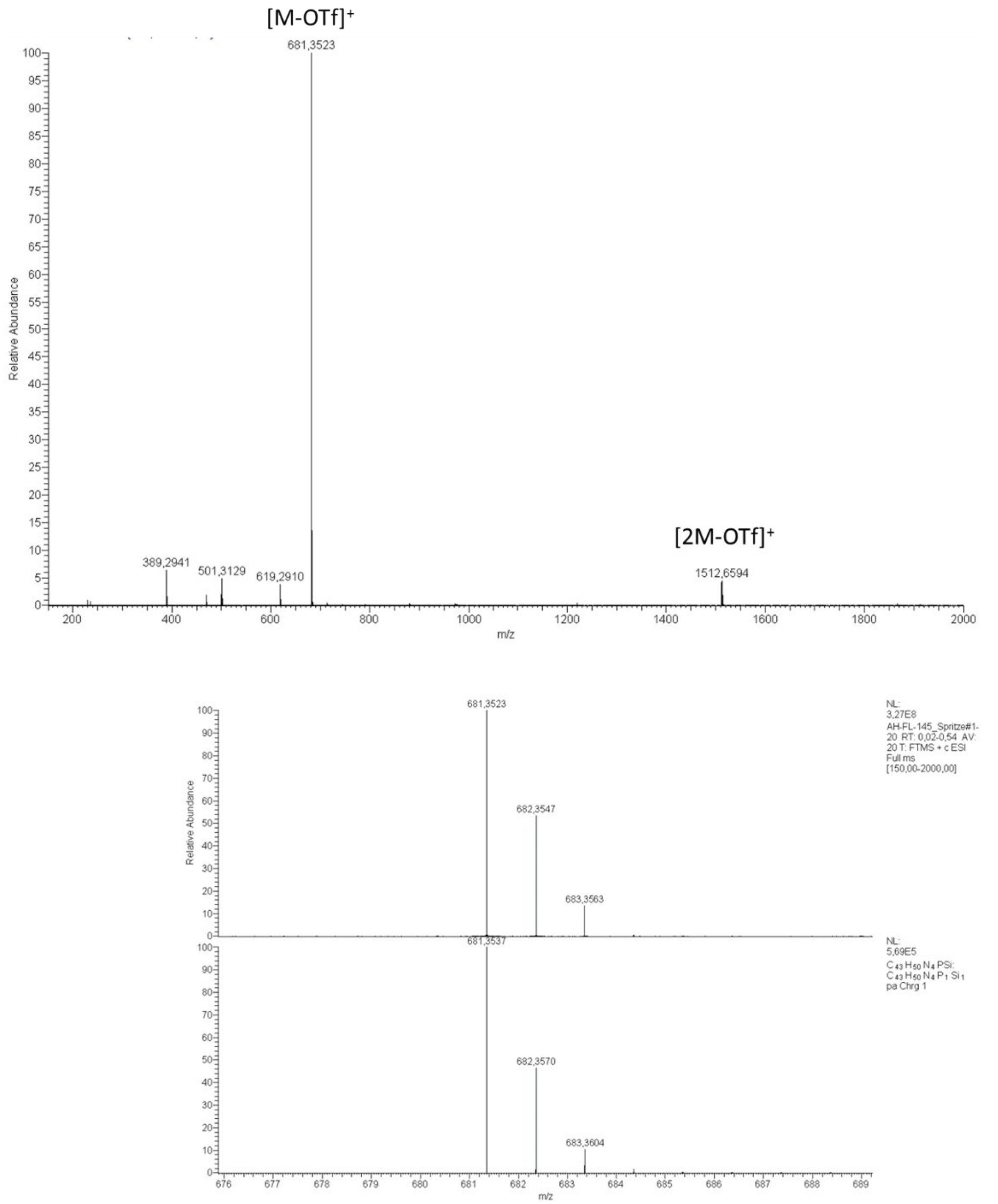


Figure S9: HRMS (ESI$^+$) of [$C_{44}H_{50}F_3N_4O_3PSSi$] (**8**[OTf]) and zoom into the [M-OTf]$^+$-peak region (top) in comparison to the calculated isotopic pattern for [$C_{43}H_{50}N_4PSi$]$^+$ (bottom).

Spectra of Compound 9[OTf]

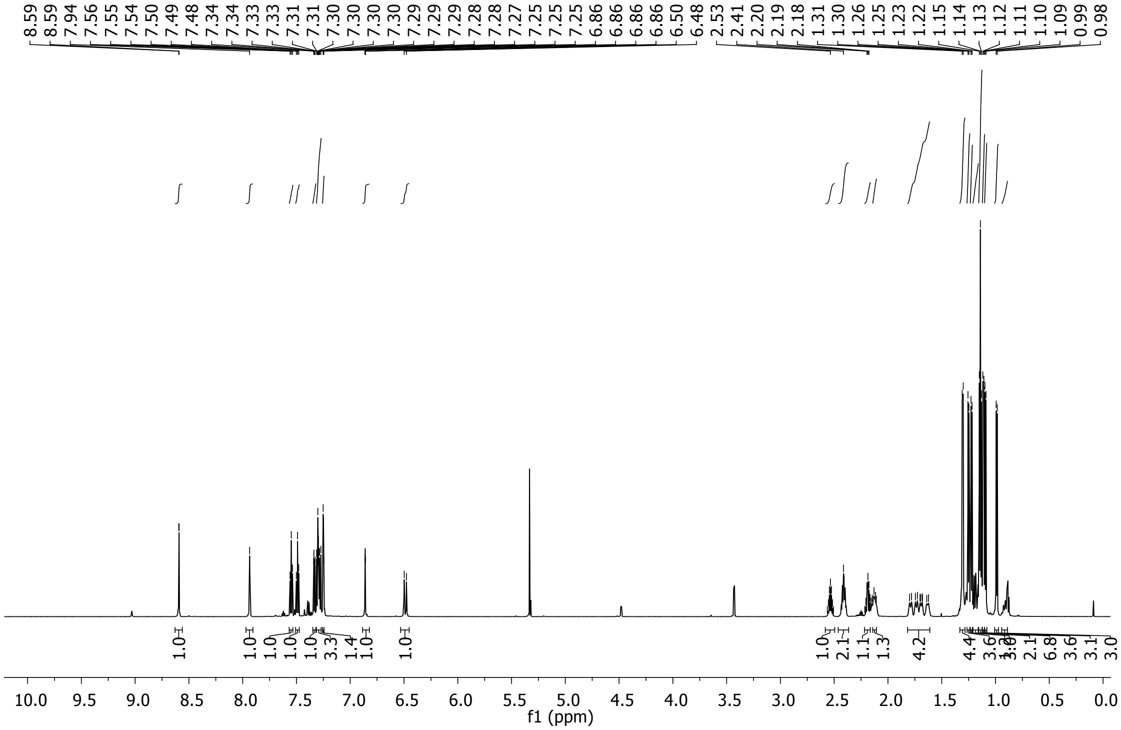


Figure S10: ^{1}H NMR spectrum of **9**[OTf] in CD_2Cl_2.

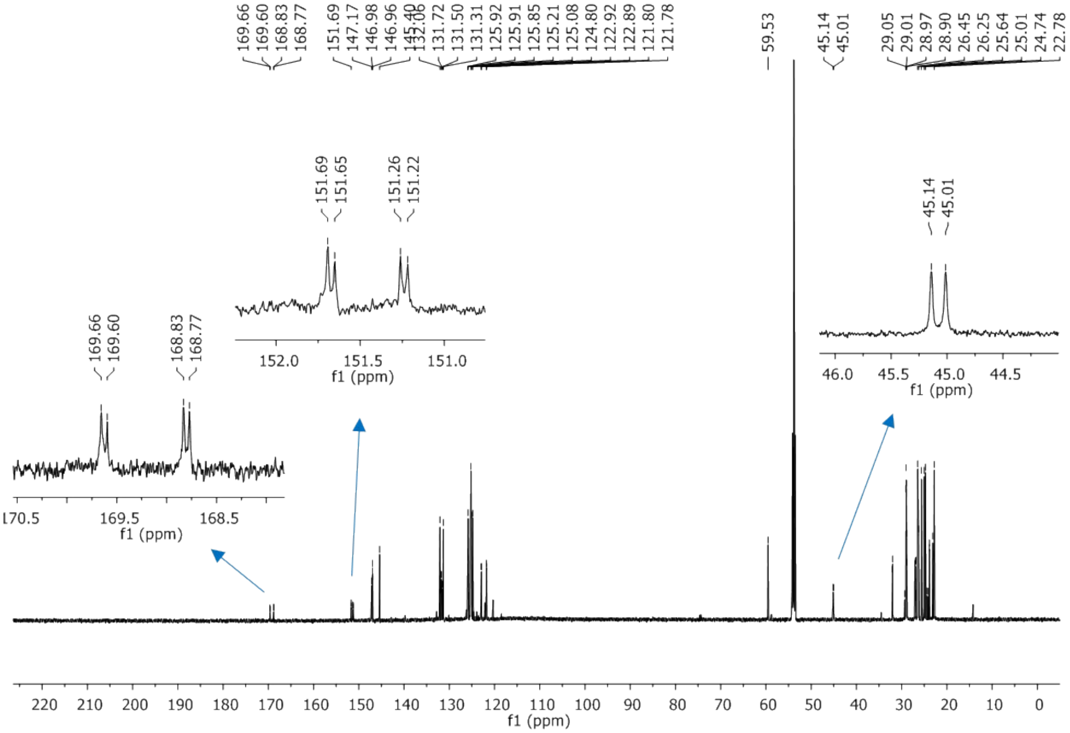


Figure S11: ^{13}C NMR spectrum of **9**[OTf] in CD_2Cl_2.

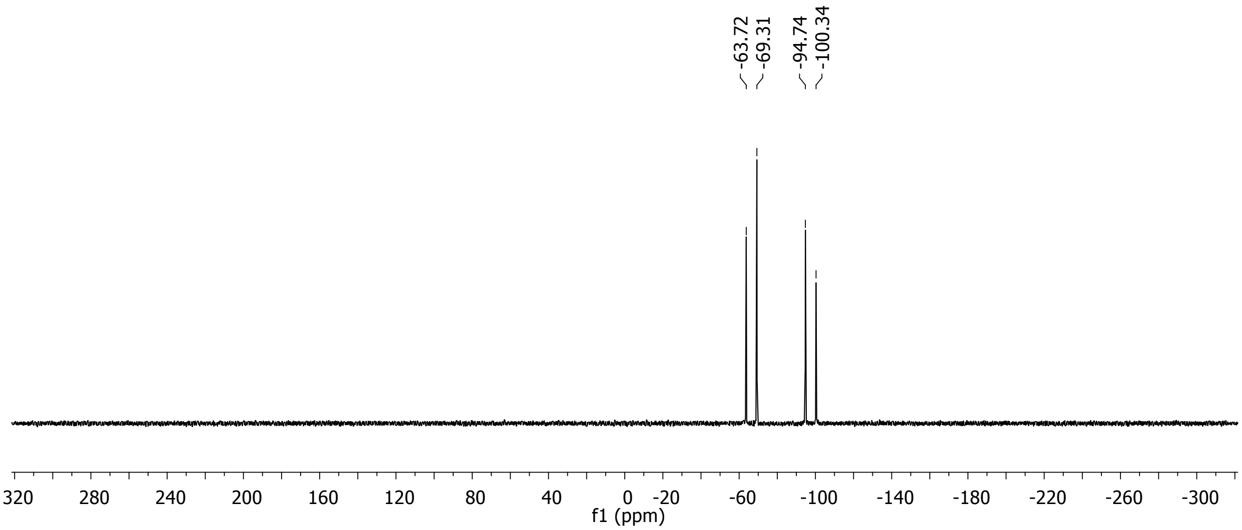


Figure S12: $^{31}P\{^{1}H\}$ NMR spectrum of **9**[OTf] in CD_2Cl_2.

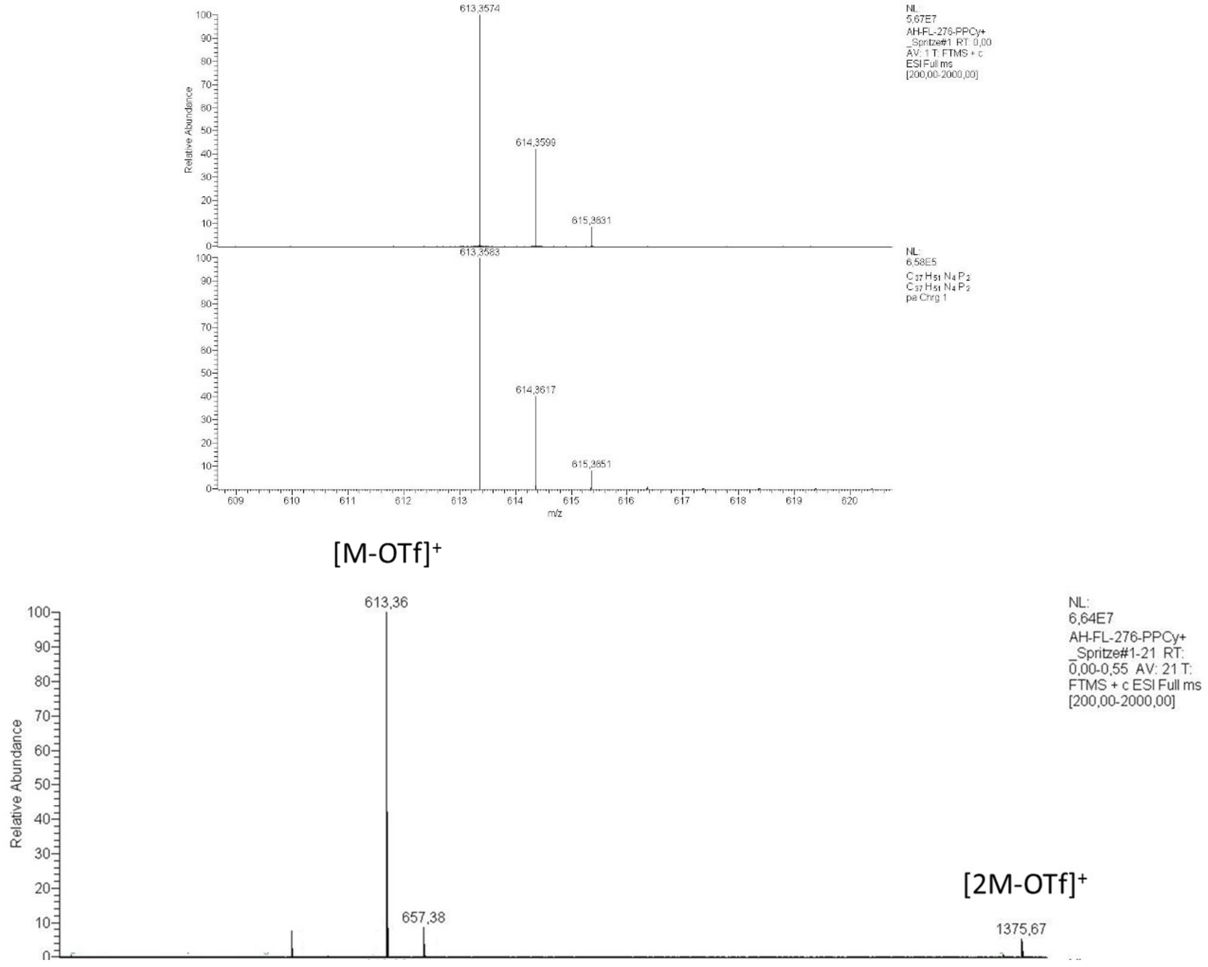


Figure S13: HRMS (ESI$^+$) of [$C_{38}H_{51}F_3N_4O_3P_2S$] (**9**[OTf]) and zoom into the [M-OTf]$^+$-peak region (top) in comparison to the calculated isotopic pattern for $C_{37}H_{51}N_4P_2$ (bottom).

Spectra of compound 10[OTf]

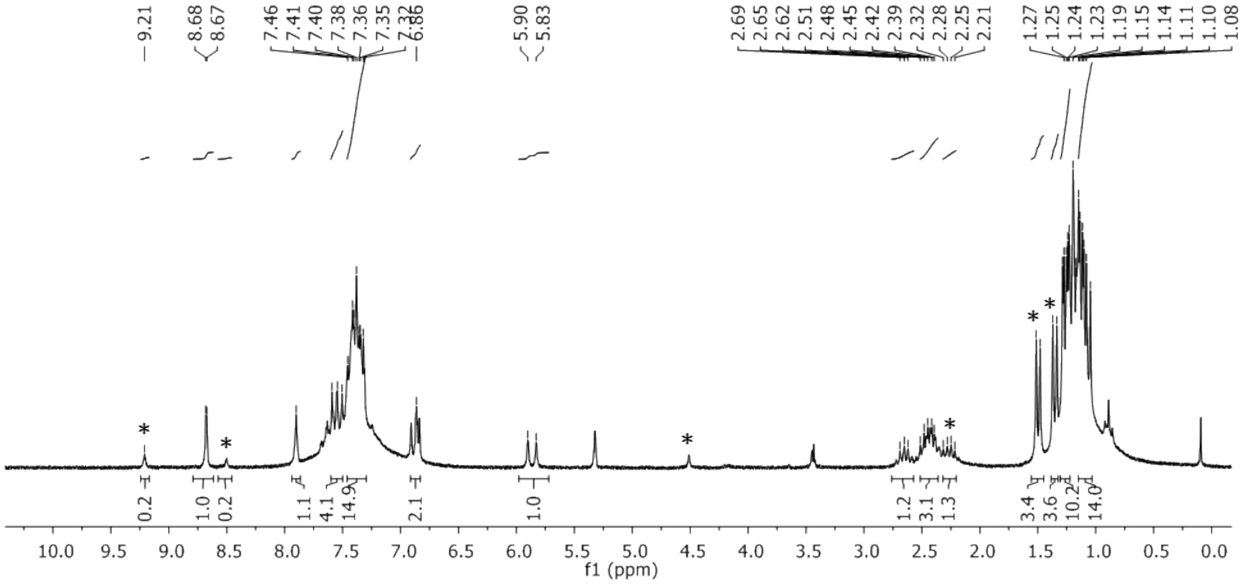


Figure S14: ^{1}H NMR spectrum of **10**[OTf] in CD_2Cl_2. * [bis(NHC)·2HOTf]

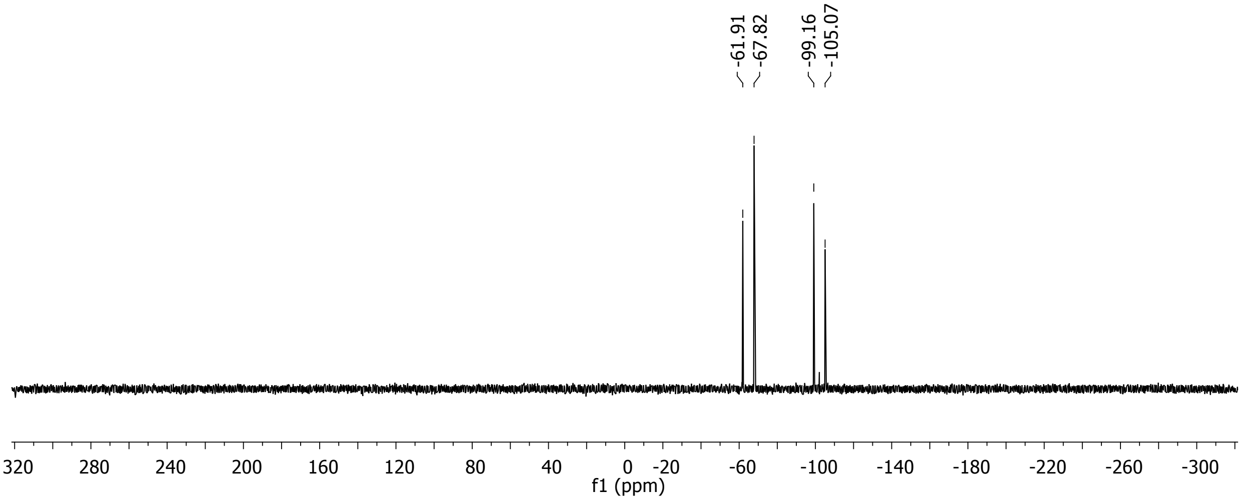


Figure S15: $^{31}P\{^1H\}$ NMR spectrum of **10**[OTf] in CD_2Cl_2.

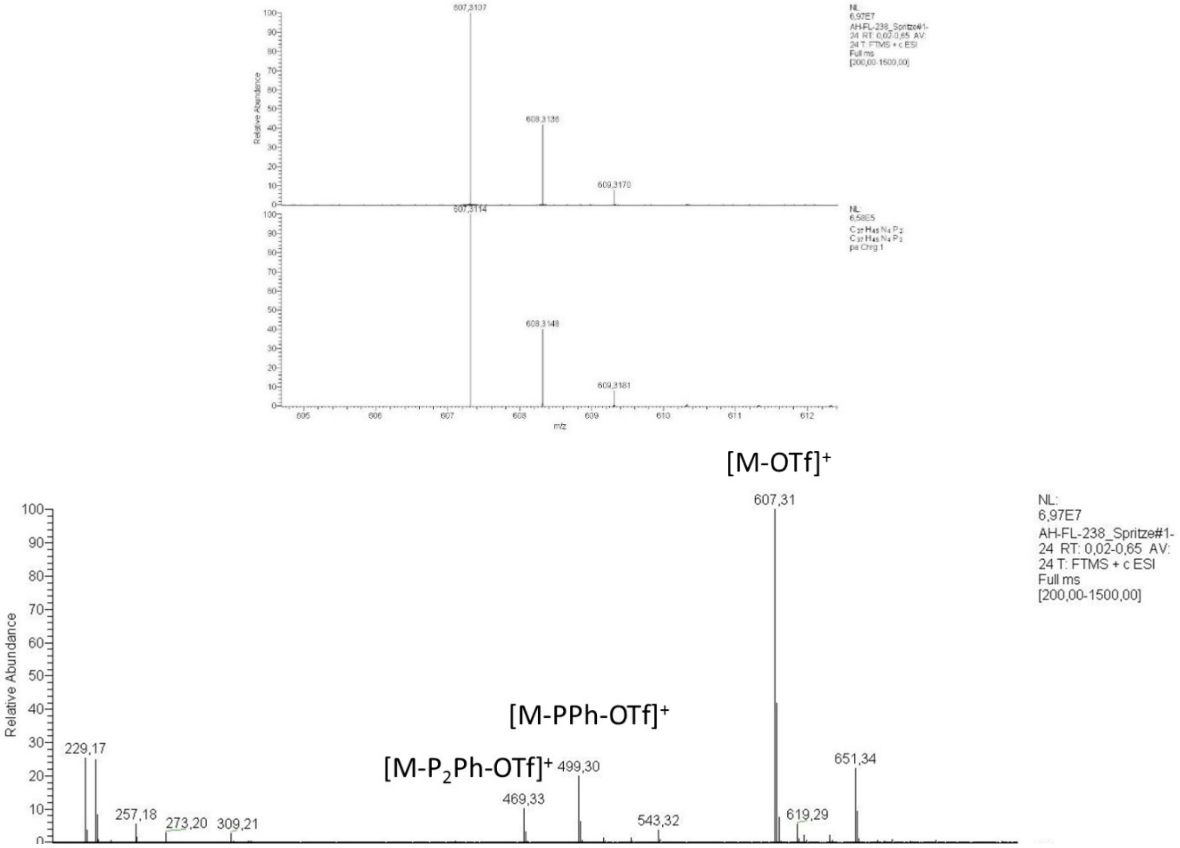


Figure S16: HRMS (ESI$^+$) of [$C_{38}H_{46}F_3N_4O_3P_2S$] (**10**[OTf]) and zoom into the [M-OTf]$^+$-peak region (top) in comparison to the calculated isotopic pattern for [$C_{37}H_{46}N_4P_2$]$^+$ (bottom).

Spectra of [IPrSiPh$_3$][OTf]

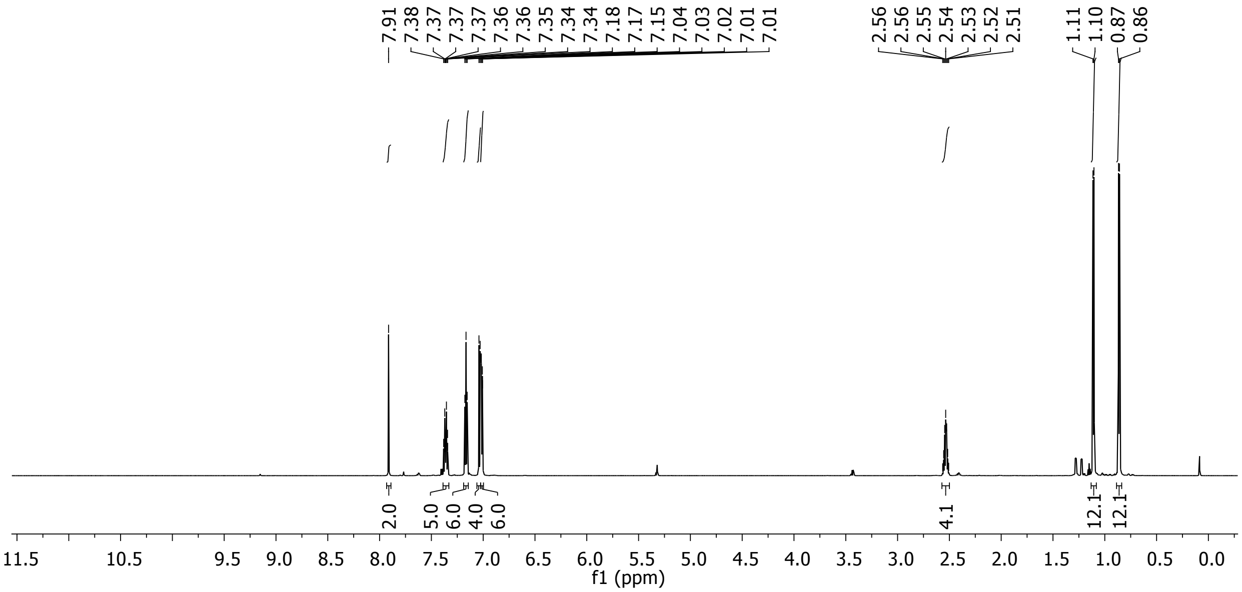


Figure S17: ^1H NMR spectrum of IPrSiPh$_3$[OTf] in CD$_2$Cl$_2$.

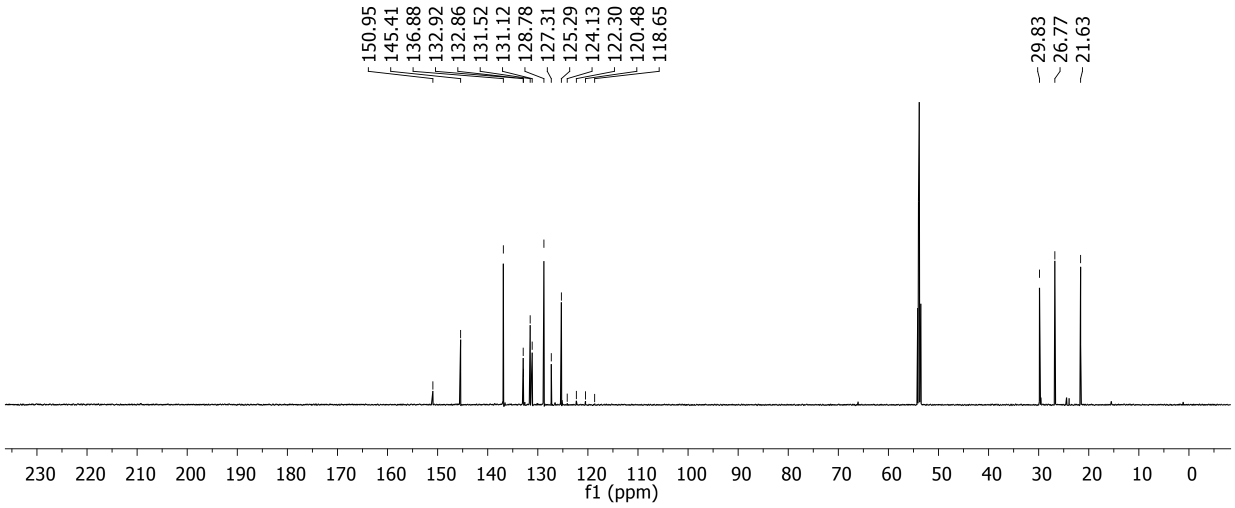


Figure S18: ^{13}C NMR spectrum of IPrSiPh$_3$[OTf] in CD$_2$Cl$_2$.

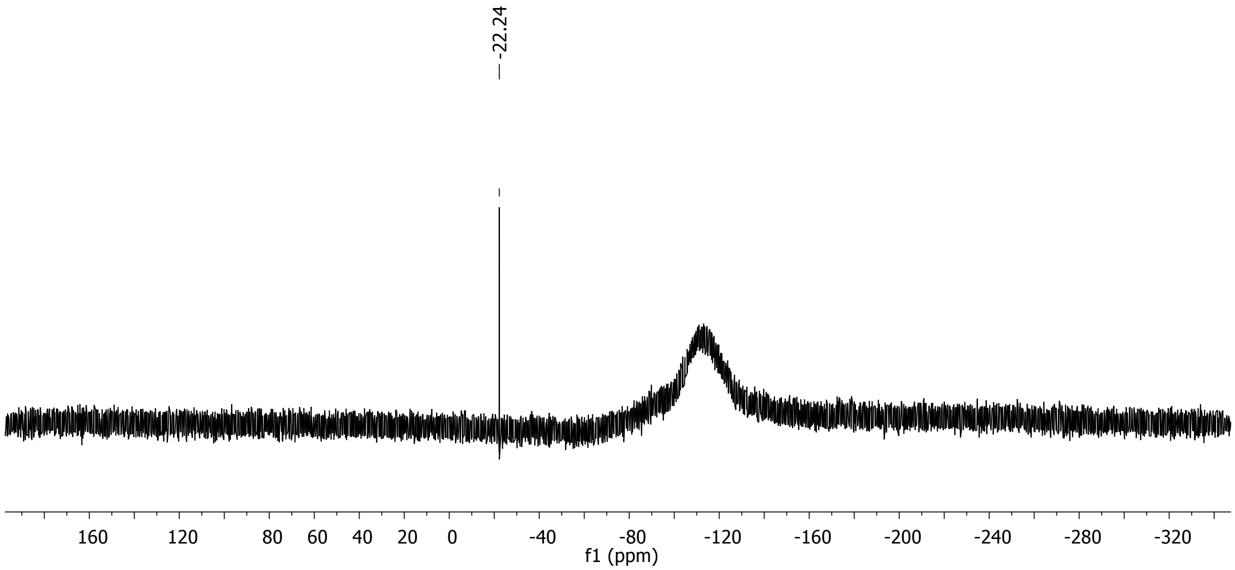


Figure S19: ^{29}Si NMR spectrum of IPrSiPh$_3$[OTf] in CD$_2$Cl$_2$.

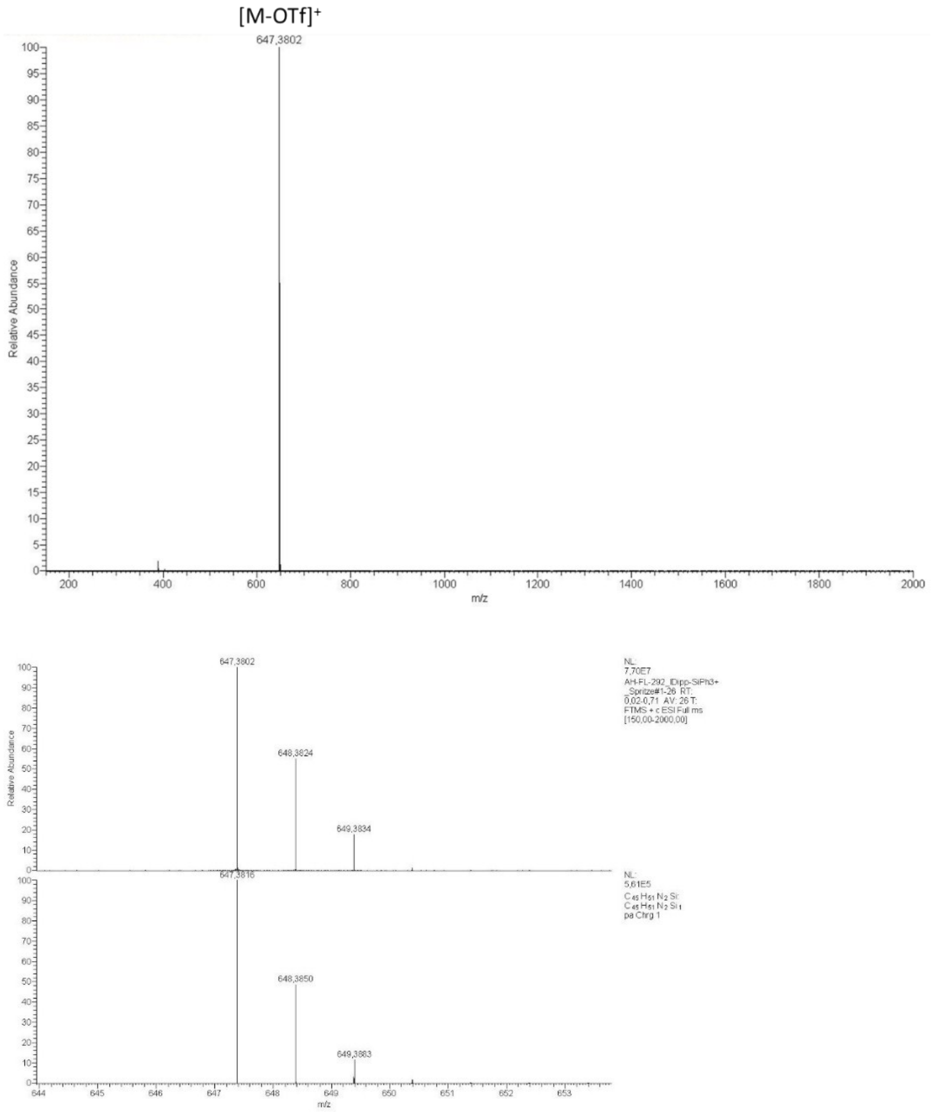


Figure S20: HRMS (ESI$^+$) of [$C_{46}H_{51}F_3N_2O_3SSi$] (IPrSiPh$_3$[OTf]) and zoom into the [M-OTf]$^+$-peak region (top) in comparison to the calculated isotopic pattern for $C_{45}H_{51}N_2Si$ (bottom).

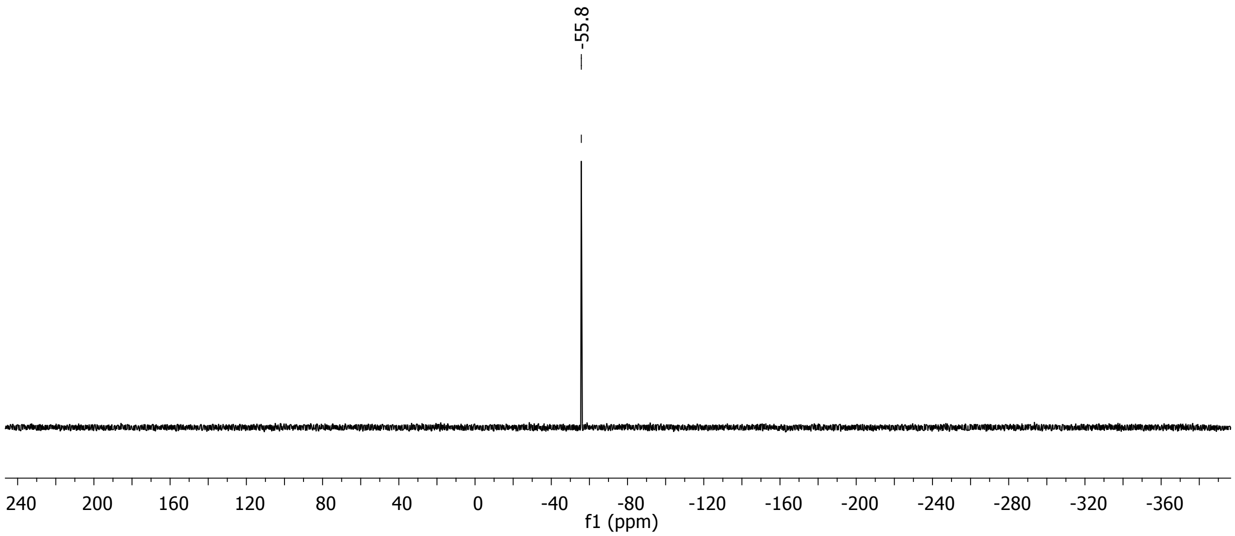


Figure S21: $^{31}P\{^1H\}$ NMR spectrum of bis(NHC)(PPh)[OTf$_2$] generated from **7**[OTf$_2$] and $PhPCl_2$ in CD_2Cl_2.

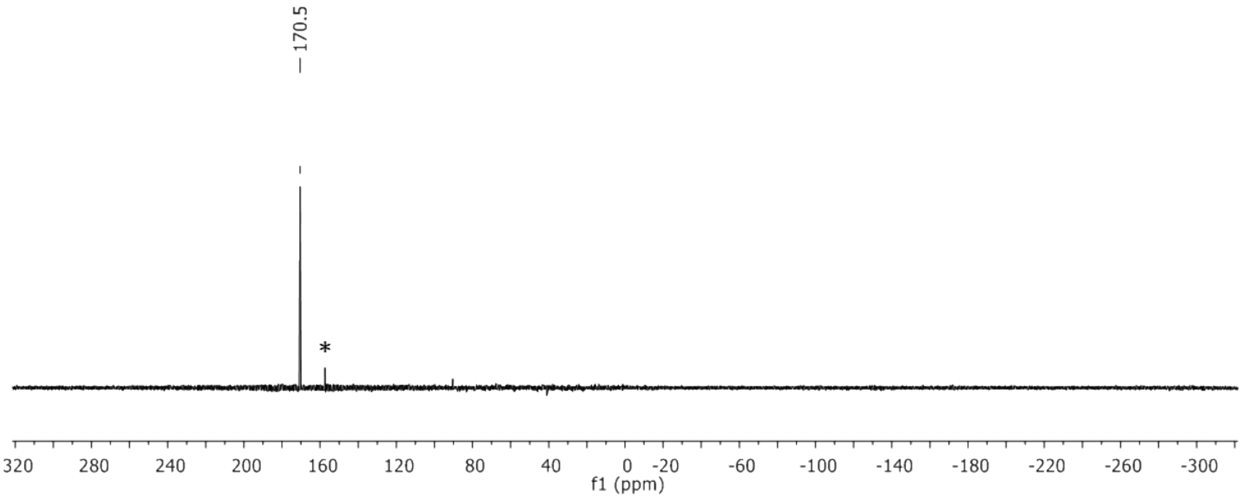


Figure S22: $^{31}P\{^1H\}$ NMR spectrum of IPr=C=P-O-SiPh$_3$ generated from [IPrSiPh$_3$][OTf] and NaOCP in C_6D_6. *Small amount of unidentified byproduct.

Crystallographic Details

Table S1. Crystallographic data of **7**[OTf]$_2$·2CH$_3$CN.

CCDC No.	1866468	
Empirical formula	C39.20 H44.80 F4.80 N4.80 O4.80 S1.60 Si0.80	
Formula weight	824.96	
Temperature	149.97(11) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 12.86820(10) Å	α= 90°.
	b = 24.1210(2) Å	β= 97.4150(10)°.
	c = 17.0410(2) Å	γ = 90°.
Volume	5245.19(9) Å^3	
Z	5	
Density (calculated)	1.306 Mg/m^3	
Absorption coefficient	1.769 mm^{-1}	
F(000)	2160	
Crystal size	0.398 x 0.160 x 0.102 mm^3	
Theta range for data collection	3.193 to 69.997°.	
Index ranges	-15<=h<=15, -29<=k<=18, -20<=l<=20	
Reflections collected	20333	
Independent reflections	9914 [R(int) = 0.0196]	
Completeness to theta = 69.997°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.59107	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9914 / 19 / 674	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R1 = 0.0375, wR2 = 0.0946	
R indices (all data)	R1 = 0.0444, wR2 = 0.1009	
Largest diff. peak and hole	0.398 and -0.372 e.Å^{-3}	

Table S2. Crystallographic data of **8**[OTf]·CH_3CN.

CCDC No.	1866469	
Empirical formula	C46 H53 F3 N5 O3 P S Si	
Formula weight	872.05	
Temperature	150.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 20.7909(2) Å	α= 90°.
	b = 9.61130(10) Å	β= 105.5340(10)°.
	c = 23.6415(2) Å	γ = 90°.
Volume	4551.66(8) Å^3	
Z	4	
Density (calculated)	1.273 Mg/m^3	
Absorption coefficient	1.693 mm^{-1}	
F(000)	1840	
Crystal size	0.176 x 0.160 x 0.150 mm^3	
Theta range for data collection	2.517 to 69.992°.	
Index ranges	-22<=h<=25, -11<=k<=11, -24<=l<=28	
Reflections collected	17708	
Independent reflections	8607 [R(int) = 0.0197]	
Completeness to theta = 69.992°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.69744	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8607 / 19 / 583	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0550, wR2 = 0.1425	
R indices (all data)	R1 = 0.0607, wR2 = 0.1486	
Largest diff. peak and hole	0.948 and -0.610 e.Å^{-3}	

Table S3. Crystallographic data of **9**[OTf]·$C_6H_5CH_3$·CH_2Cl_2.

CCDC No.	1866470	
Empirical formula	C33.09 H43.64 Cl0.73 F2.18 N2.91 O2.18 P1.45 S0.73	
Formula weight	652.67	
Temperature	150.01(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	I 2/a	
Unit cell dimensions	a = 21.3898(4) Å	α= 90°.
	b = 14.7759(2) Å	β= 108.989(2)°.
	c = 32.3467(7) Å	γ = 90°.
Volume	9666.9(3) Å^3	
Z	11	
Density (calculated)	1.233 Mg/m^3	
Absorption coefficient	2.168 mm^{-1}	
F(000)	3800	
Crystal size	0.222 x 0.148 x 0.120 mm^3	
Theta range for data collection	2.889 to 69.978°.	
Index ranges	-25<=h<=26, -18<=k<=17, -39<=l<=30	
Reflections collected	18470	
Independent reflections	9078 [R(int) = 0.0326]	
Completeness to theta = 69.978°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.19449	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9078 / 28 / 667	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2sigma(I)]	R1 = 0.0567, wR2 = 0.1510	
R indices (all data)	R1 = 0.0725, wR2 = 0.1674	
Largest diff. peak and hole	0.722 and -0.510 e.Å^{-3}	

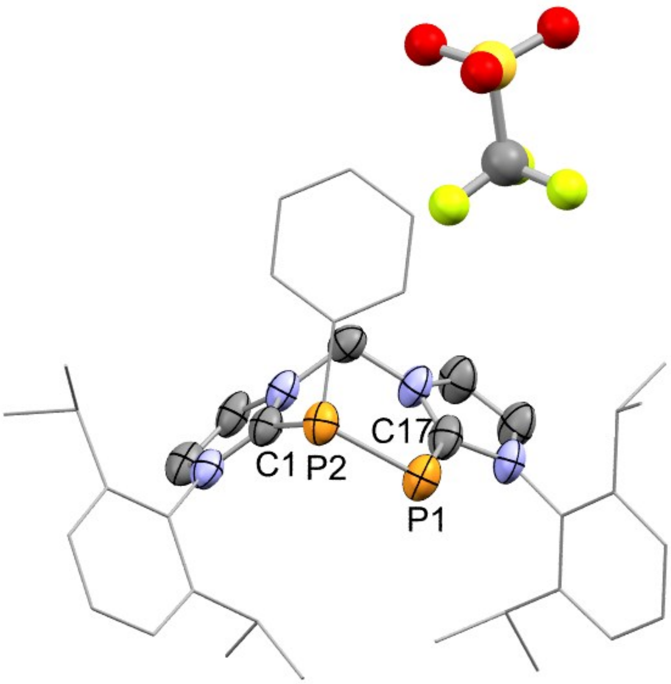


Figure S23: Molecular structure of **10**[OTf] in the crystal, (hydrogen atoms are omitted for clarity and thermal ellipsoids are displayed at 50% probability); selected experimental bond lengths in Å and angles in °; P1–P2 2.1561(18), P1–C17 1.802(6), P2–C1 1.825(5), C17–P1–P2 107.19(17), C1–P2–P1 100.09(15).

Table S4. Crystallographic data of **10**[OTf].

CCDC No.	1866471	
Empirical formula	C38 H45 F3 N4 O3 P2 S	
Formula weight	756.78	
Temperature	150.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.2894(6) Å	α= 95.680(7)°.
	b = 11.9054(10) Å	β= 101.636(6)°.
	c = 18.4338(15) Å	γ = 92.537(6)°.
Volume	1982.6(3) Å^3	
Z	2	
Density (calculated)	1.268 Mg/m^3	
Absorption coefficient	1.944 mm^{-1}	
F(000)	796	
Crystal size	0.356 x 0.094 x 0.068 mm^3	

Theta range for data collection	3.739 to 69.997°.
Index ranges	-11<=h<=8, -14<=k<=14, -22<=l<=22
Reflections collected	13380
Independent reflections	7469 [R(int) = 0.1021]
Completeness to theta = 69.997°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.63397
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7469 / 0 / 468
Goodness-of-fit on F^2	0.982
Final R indices [I>2sigma(I)]	R1 = 0.0800, wR2 = 0.1842
R indices (all data)	R1 = 0.1454, wR2 = 0.2505
Largest diff. peak and hole	0.475 and -0.365 e.Å^{-3}

References

[1] Y. Xiong, S. Yao, S. Inoue, J. D. Epping, M. Driess, *Angew. Chem. Int. Ed.* **2013**, *52*, 7147–7150.

[2] S. A. Weicker, D. W. Stephan, *Chem. Eur. J.* **2015**, *21*, 13027–13034.

[3] F. F. Puschmann, D. Stein, D. Heift, C. Hendriksen, Z. A. Gal, H.-F. Grützmacher, H. Grützmacher, *Angew. Chem.* **2011**, *123*, 8570–8574.

[4] F. F. Puschmann, D. Stein, D. Heift, C. Hendriksen, Z. A. Gal, H.-F. Grützmacher, H. Grützmacher, *Angew. Chem. Int. Ed.* **2011**, *50*, 8420–8423.

[5] L. Jafarpour, E. D. Stevens, S. P. Nolan, *J. Organomet. Chem.* **2000**, *606*, 49–54.

[6] G. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3–8.

[7] G. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8.

[8] M. Mehta, T. C. Johnstone, J. Lam, B. Bagh, A. Hermannsdorfer, M. Driess, D. W. Stephan, *Dalt. Trans.* **2017**, *46*, 14149–14157.

[9] Z. Li, X. Chen, Y. Li, C. Y. Su, H. Grützmacher, *Chem. Commun.* **2016**, *52*, 11343–11346.