# Cationic 5-Phosphonio Substituted *N*-heterocyclic Carbenes

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## Supporting Information

**This PDF file includes:**

## S1 General remarks

General Considerations: All manipulations were performed in a Glovebox MB Unilab or using Schlenk techniques under an atmosphere of purified Argon. Dry, oxygen-free solvents ($CH_2Cl_2$, $CH_3CN$, $C_6H_5F$, $C_6H_4F_2$, distilled from $CaH_2$), $Et_2O$, THF, benzene (distilled from potassium/benzophenone), *n*-hexane (distilled from potassium) were employed. Deuterated benzene ($C_6D_6$) was purchased from Sigma-Aldrich and distilled from potassium. Anhydrous deuterated acetonitrile ($CD_3CN$), dichloromethane ($CD_2Cl_2$) and tetrahydrofurane (THF-$d_8$) were purchased from Sigma-Aldrich. All distilled and deuterated solvents were stored over molecular sieves (4 Å: $CH_2Cl_2$, $CD_2Cl_2$, $C_6H_5F$, $C_6H_4F_2$, benzene, $C_6D_6$, toluene, *n*-hexane, $Et_2O$, THF, THF-$d_8$; 3 Å: $CH_3CN$, $CD_3CN$). All glassware was oven-dried at 160 °C prior to use. NHC **8**[1], $Ph_2PCl$,[2] $Cy_2PCl$,[2] AuCl(tht),[3] CuBr(tht)[3] were prepared according to procedures given by literature. Reagents $Me_3SiOTf$, and MeOTf were purchased from Sigma Aldrich and degased and distilled for purification. $PPh_3$ and $Cy_3P$ were purchased from Sigma Aldrich and sublimed for purification. LDA, $XeF_2$, AgOTf, $[RhCl(cod)]_2$, $Ph_2PH$, $Cy_2PH$, *i*$Bu_2PH$, *t*$Bu_2PH$, were purchased form Apollo Scientific, Sigma Aldrich or abcr and used as received. NMR spectra were measured on a Bruker AVANCE III HD Nanobay ($^1$H (400.13 MHz), $^{13}$C (100.61 MHz), $^{31}$P (161.98 MHz) $^{19}$F (376.50 MHz)), 400 MHz UltraSield or on a Bruker AVANCE III HDX, 500 MHz Ascend ($^1$H (500.13 MHz), $^{13}$C (125.75 MHz), $^{31}$P (202.45 MHz) $^{19}$F (470.59 MHz)). All $^{13}$C NMR spectra were exclusively recorded with composite pulse decoupling. Reported numbers assigning atoms in the $^{13}$C spectra were indirectly deduced from the cross-peaks in 2D correlation experiments (HMBC, HSQC). Chemical shifts were referenced to $\delta_{TMS} = 0.00$ ppm ($^1$H, $^{13}$C) and $\delta_{H3PO4(85\%)} = 0.00$ ppm ($^{31}$P, externally). Chemical shifts ($\delta$) are reported in ppm. Coupling constants (*J*) are reported in Hz. Melting points were recorded on an electrothermal melting point apparatus (Büchi Switzerland, Melting point M-560) in sealed capillaries under Argon atmosphere 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 modus.

## S2 NMR spectra and additional figures

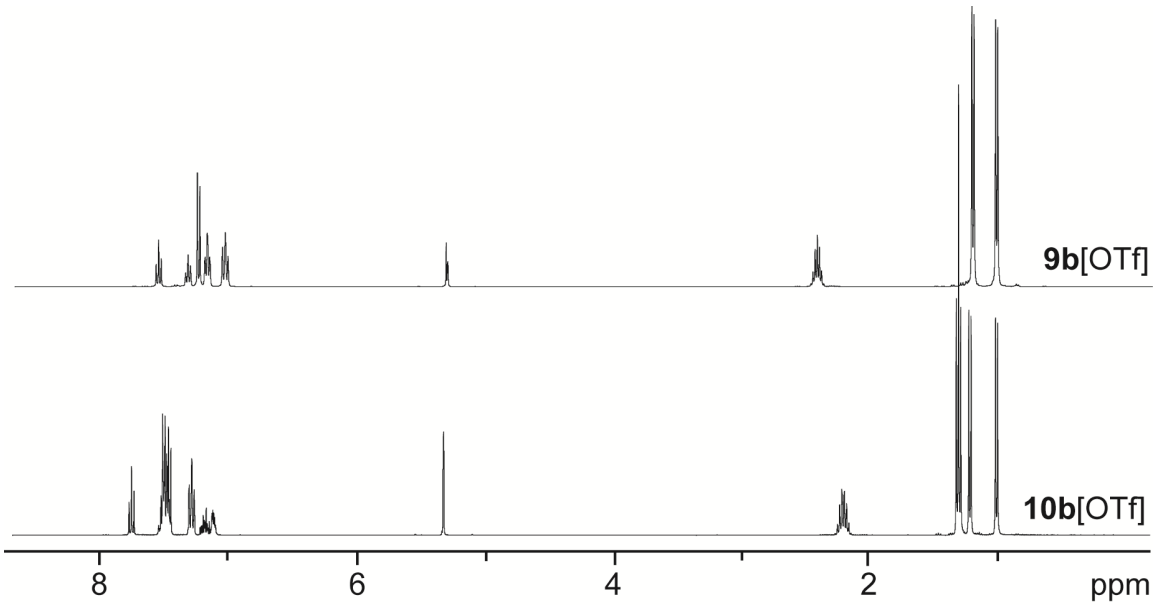



***Figure S2.1.*** $^{1}$H NMR spectra of **9b**$^{+}$ and **10b**$^{+}$ ($CD_2Cl_2$, 300 K).

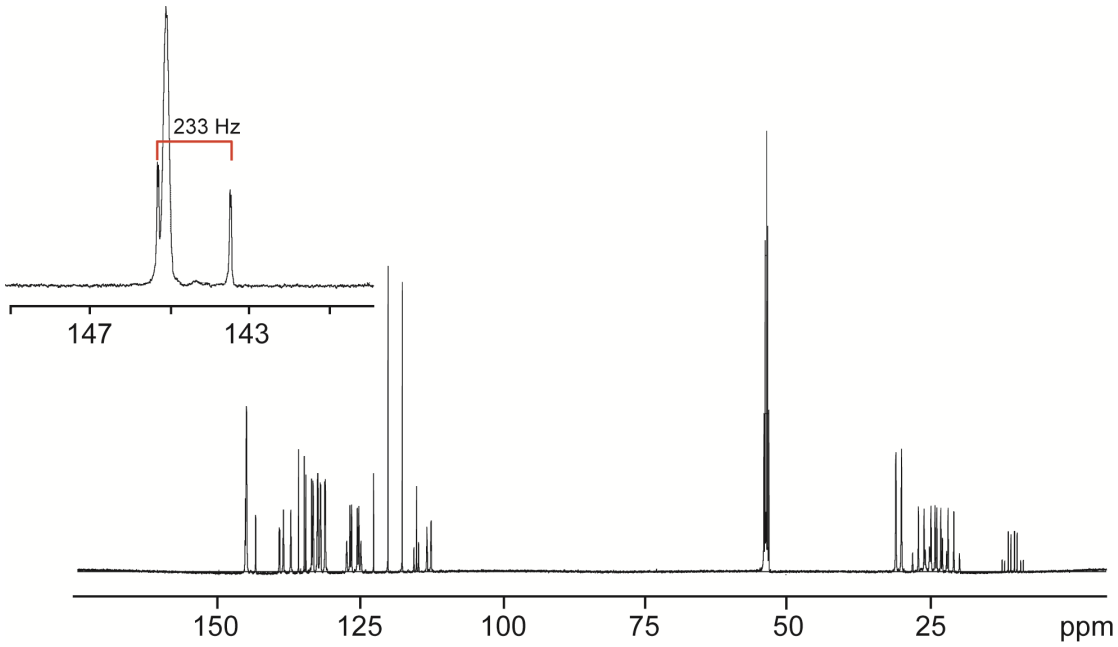



***Figure S2.2.*** $^{13}$C NMR spectrum of **17bH**$^{2+}$; Zoom in shows a doublet carbene C atom (δ(C) = 144.3 ppm; $^{1}J_{CH}$ = 233 Hz, $CD_2Cl_2$, 300 K).

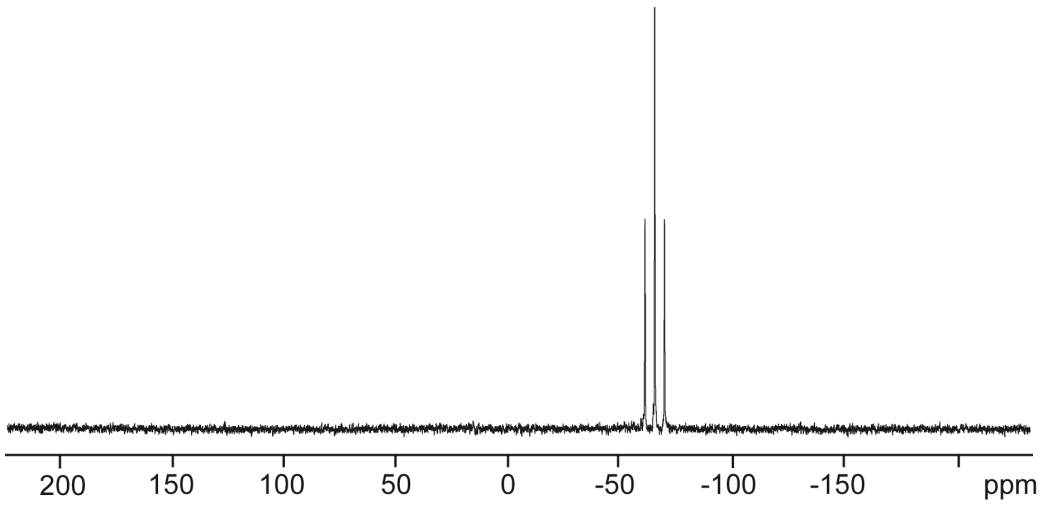



***Figure S2.3.*** $^{31}$P NMR spectrum of **25**[OTf] ($CD_3CN$, 300 K).

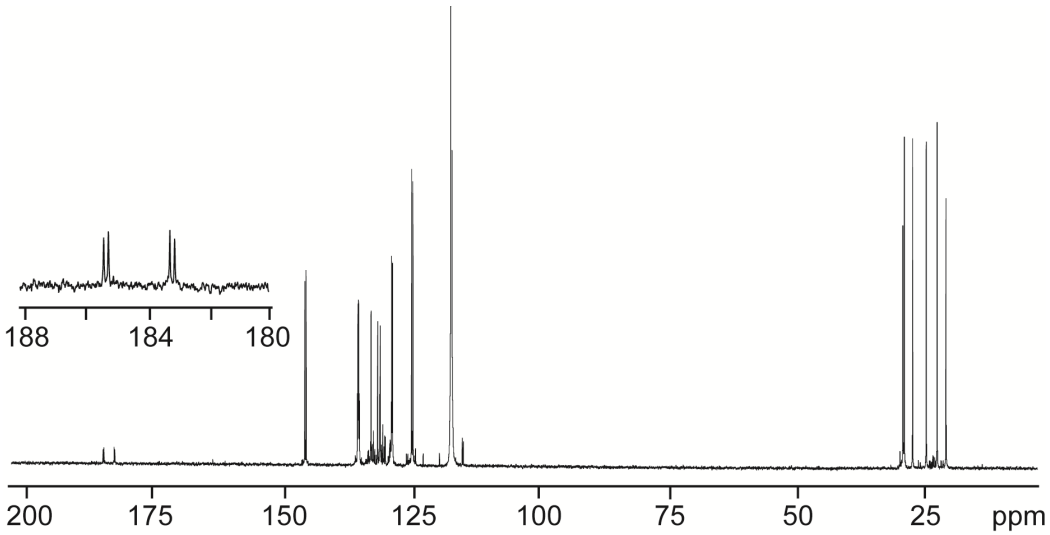



***Figure S2.4.*** $^{13}C\{H\}$ NMR spectrum of **25**[OTf]; Zoom in shows a doublet of doublets for the carbene C atom (δ(C) = 184.3 ppm; $^{1}J_{C\text{-}Ag109}$ = 232 Hz, $^{1}J_{C\text{-}Ag107}$ = 200 Hz; $CD_3CN$, 300 K).

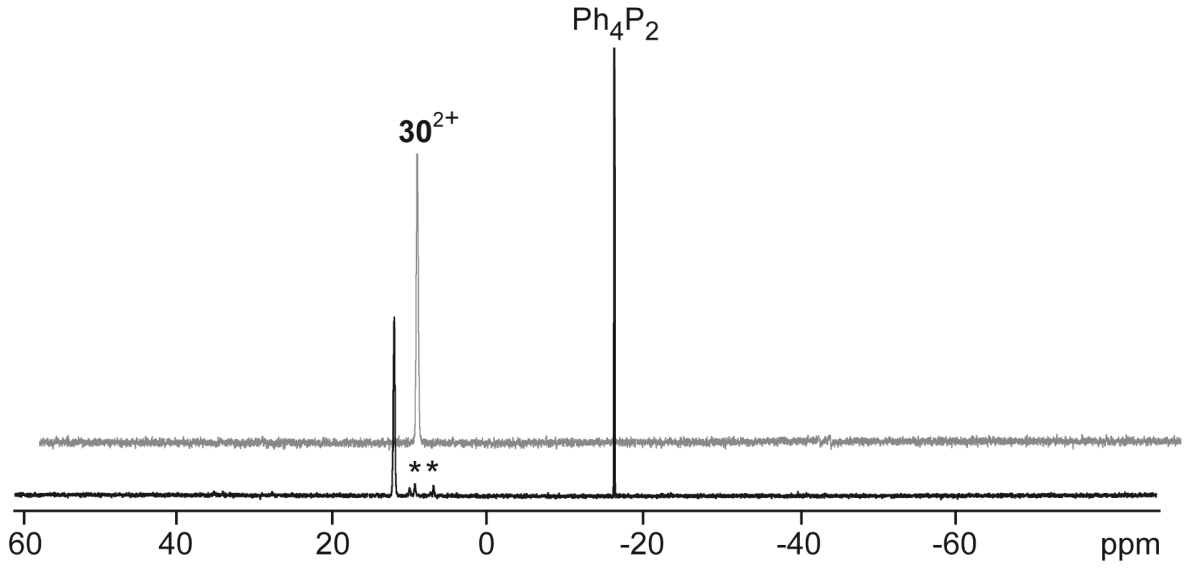



***Figure S2.5.*** $^{31}P$ NMR spectrum for the reaction of **17b**[OTf] with 2eq. $Ph_2PH$ after 30 h (1,2-dichloroethane, $C_6D_6$-capillary, 300 K). Small amounts of not identified sideproducts are marked with asterisks; isolated **30**$^{2+}$ (top).

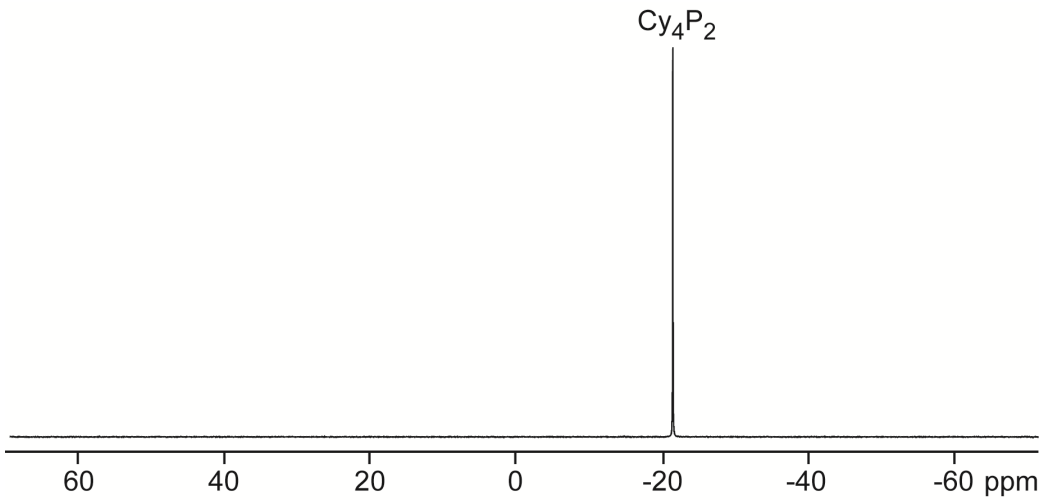



***Figure S2.6.*** $^{31}$P NMR spectrum of the isolated colorless precipitate from the reaction of **17b**[OTf] with 2eq. $Cy_2PH$ after 12 h ($C_6D_6$, 300 K).

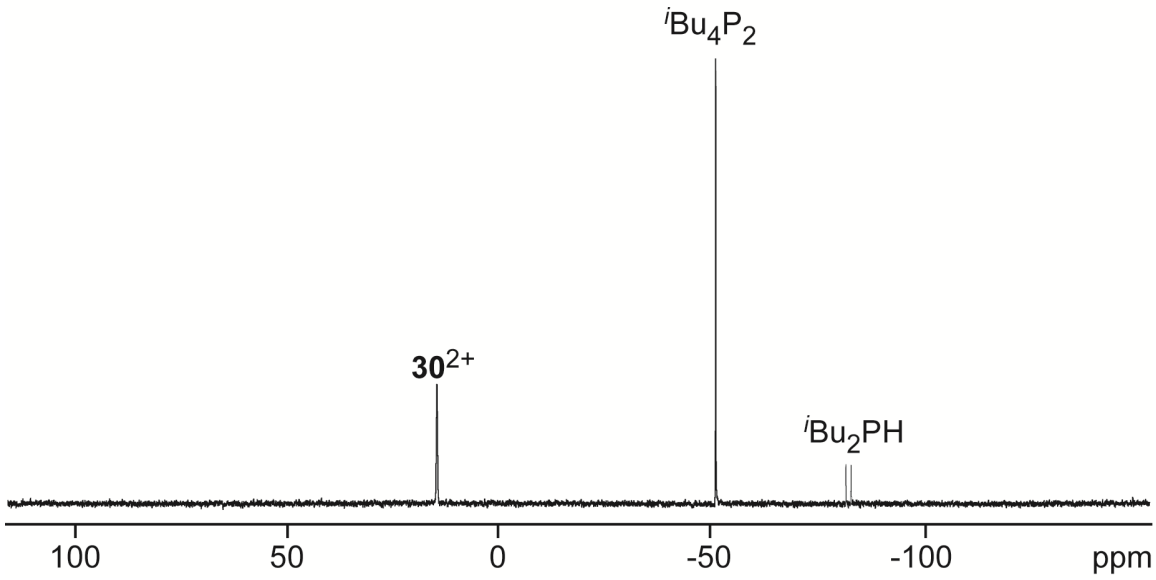



***Figure S2.7.*** $^{31}$P NMR spectrum for the reaction of 2 eq. $^{i}Bu_2PH$ with **17b**[OTf] after 12 h ($C_6D_6$, 300 K).

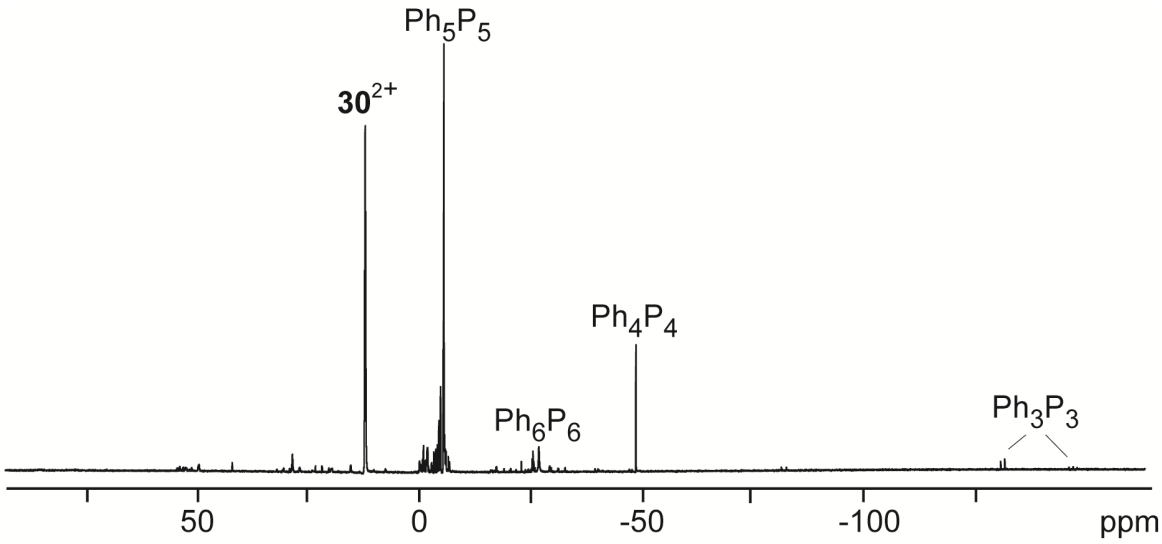



***Figure S2.8.*** $^{31}$P NMR spectrum for the reaction of **17b**[OTf] with 1eq. $PhPH_2$ after 24 h (1,2-dichloroethane, $C_6D_6$-capillary, 300 K). Dicationic **30**$^{2+}$, $Ph_3P_3$, $Ph_4P_4$, $Ph_5P_5$ and $Ph_6P_6$ are identified next to small amounts of of not identified sideproducts.

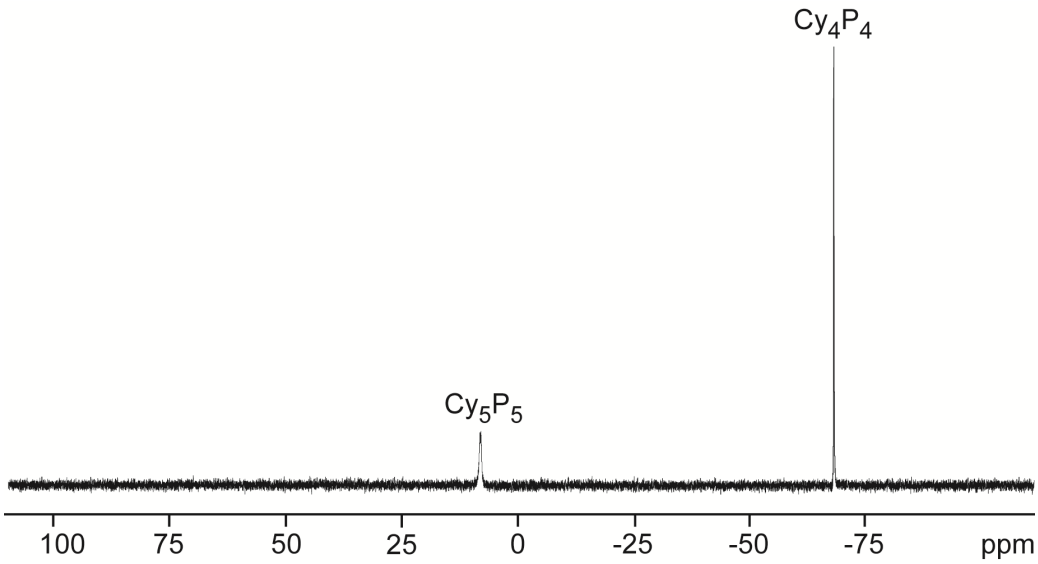



***Figure S2.9.*** $^{31}$P NMR spectrum of the isolated colorless precipitate from the reaction of **17b**[OTf] with 1eq. $CyPH_2$ after 24 h ($C_6D_6$, 300 K).

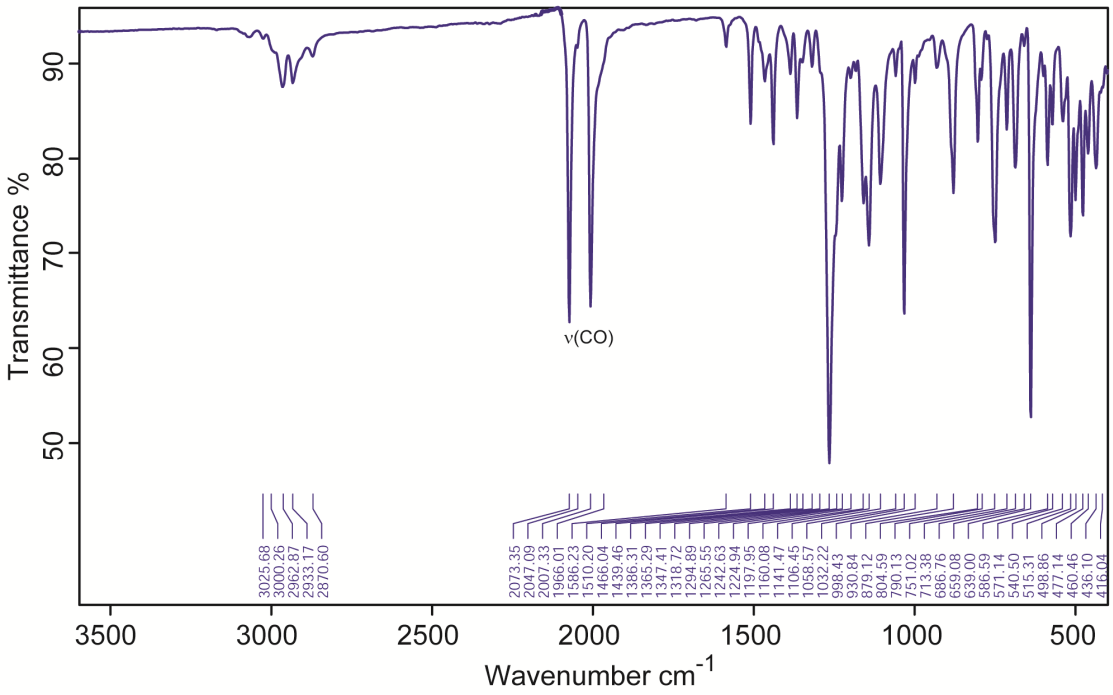



***Figure S2.10.*** IR spectrum of **24**[OTf] (neat, ATR, ambient temperature).

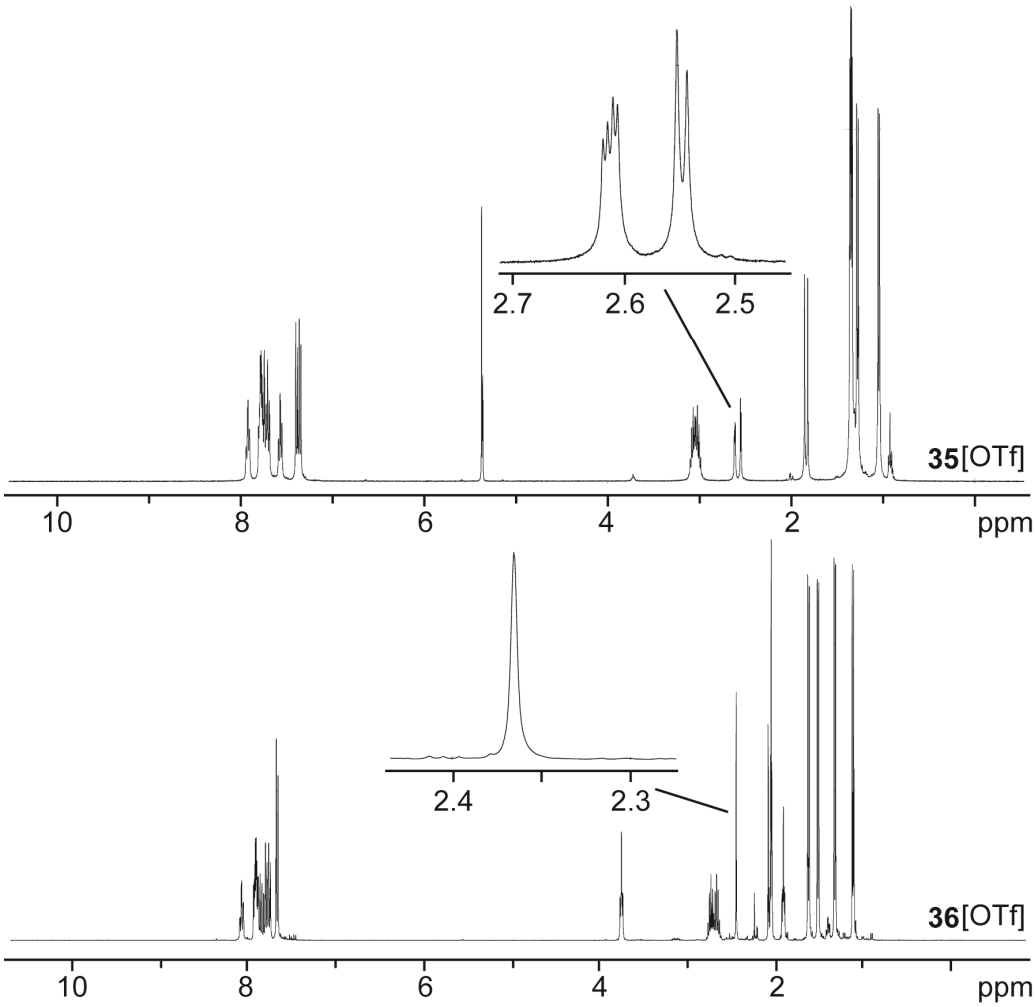



***Figure S2.11.*** $^{1}$H NMR spectra of **35**[OTf] ($CD_2Cl_2$, 300 K, top) and **36**[OTf] ($CD_3CN$, 300 K, bottom); zoom in displays the resonances which can be attributed to the $CH_2$-group attached to C1.

## S3 Experimental Details

### S3.1 Reaction of 9b[OTf] with 0.3 eq. of NHC 8

A solution of NHC **8** (18.0 mg, 0.039mmol) in *o*-$C_6H_4F_2$ (1 ml) was added to a solution of **9b**[OTf] (103 mg, 0.13 mmol) in *o*-$C_6H_4F_2$ (2 ml). The reaction mixture was stirred for 30 h. During this time the reaction mixture was investigated using multinuclear NMR spectroscopy. After removing of all volatiles *in vacuo* the residue was again dissolved in $CH_2Cl_2$. The collected NMR spectroscopical data revealed a quantitative formation to cation **10b**$^+$.

**$^{31}$P{$^1$H} NMR** ($CH_2Cl_2$, $C_6D_6$-capillary, in ppm)**:** $\delta$ = –29.12 (s).

### S3.2 Reaction of 17b[OTf] with trifluoromethanesulfonic acid

HOTf (6 mg, 0.04 mmol) was added to a stirred solution of **17b**[OTf] (30 mg, 0.04 mmol) in $C_6H_5F$ (2 ml). After 1 h the solvent was removed *in vacuo* and the crude material again dissolved in $CD_2Cl_2$ for NMR spectroscopic analysis. For the determination of the CH coupling constant see $^{13}$C NMR spectrum in figure S2.2.

**$^{31}$P{$^1$H} NMR** ($CH_2Cl_2$, $C_6D_6$-capillary, in ppm)**:** $\delta$ = 14.6 (s).

### S3.3 Reaction of 18b[OTf] with silver fluoride in a 1:1 stoichiometry

Silver fluoride was added (10 mg, 0.07 mmol) to a stirred solution of NHC **18b**[OTf] (60 mg, 0.07 mmol) in $C_6H_5F$ (1 ml). After 10 h the solvent was removed *in vacuo* and the residue again dissolved in $CD_3CN$. The multinuclear NMR spectroscopy revealed quantitative formation to **25**[OTf] (figures S2.3 and S2.4). Due to decomposition in solution, a full characterization could not be performed.

**$^{31}$P{$^1$H} NMR** ($CD_3CN$, in ppm): $\delta$ = –65.26 (t, $^1J_{PF}$ = 703 Hz).

### S3.4 Reaction of 17b[OTf] with diphenylphosphane ($Ph_2PH$) in a 1:2 stoichiometry

A solution of **17b**[OTf] (38 mg, 0.05 mmol) in 1,2-dichloroethane (2 ml) was added dropwise to a stirred solution of diphenylphosphane ($Ph_2PH$, 20 mg, 0.11 mmol) in 1,2-dichloroethane (1 ml). The reaction mixture was stirred for 30 h at ambient temperature. The collected NMR spectroscopical data revealed a quantitative conversion of **17b**$^+$ (figure S2.5).

**$^{31}$P NMR** ($C_2H_4Cl_2$, $C_6D_6$-capillary, in ppm): $\delta$ = –16.23 (s, $Ph_4P_2$), 12.10 (s, **30**$^{2+}$).

### S3.5 Reaction of 17b[OTf] with dicyclohexylphosphane ($Cy_2PH$) in a 1:2 stoichiometry

A solution of **17b**[OTf] (100 mg, 0.13 mmol) in $CH_3CN$ (1.5 ml) was added to a stirred solution of dicyclohexylphosphane ($Cy_2PH$, 52 mg, 0.26 mmol) in $CH_3CN$ (1.5 ml). The reaction mixture was stirred for 12 h at ambient temperature accompanied by the formation of a colorless precipitate. After filtration and drying *in vacuo*, $Cy_4P_2$ was isolated as colorless powder in quantitative yield (see figure S2.6).

**$^{31}$P NMR** ($C_6D_6$, in ppm): δ = –21.31 (s, $Cy_4P_2$).

### S3.6 Reaction of 17b[OTf] with diisobutylphosphane ($^{i}Bu_2PH$) in a 1:2 stoichiometry

A solution of **17b**[OTf] (107 mg, 0.14 mmol) in $CH_3CN$ (1.5 ml) was added to a solution of di-*iso*butylphosphane ($^{i}Bu_2PH$, 42 mg, 0.28 mmol) in $CH_3CN$ (1.5 ml). The reaction mixture was stirred for 10 h at ambient temperature. The collected NMR spectroscopical data revealed a quantitative formation of $^{i}Bu_4P_2$ (figure S2.7).

**$^{31}$P NMR** ($CH_3CN$, $C_6D_6$-capillary, in ppm): $\delta$ = –83.73 (d, $^{1}J_{PH}$ = –199 Hz, $^{i}Bu_2PH$), –52.41 (s, $^{i}Bu_4P_2$), 13.53(s, **30**$^{2+}$).

### S3.7 Reaction of 17b[OTf] with phenylphosphane ($PhPH_2$) in a 1:1 stoichiometry

A solution of **17b**[OTf] (38 mg, 0.05 mmol) in 1,2-dichloroethane (2 ml) was added dropwise to a stirred solution of phenylphosphane ($PhPH_2$, 5.5 mg, 0.05 mmol) in 1,2-dichloroethane (1 ml). The reaction mixture was stirred for 24 h at ambient temperature. The collected NMR spectroscopical data revealed a quantitative conversion of **17b**$^{+}$ (figure S2.8).

**$^{31}$P NMR** ($C_2H_4Cl_2$, $C_6D_6$-capillary, in ppm): $\delta$ = –147.2 (t, $Ph_3P_3$), –131.2 (d, $Ph_3P_3$), –49.0 (s, $Ph_4P_4$), –27.1 (s(br), unassigend), -25.7 (m, $Ph_6P_6$), –5.0 (m, $Ph_5P_5$), –1.1 (m, unassigned), –12.1 (s, **30**$^{2+}$), 28.72 (m, unassigend), 52.7 (m, unassigend).

### S3.8 Reaction of 17b[OTf] with cyclohexylphosphane ($CyPH_2$) in a 1:1 stoichiometry

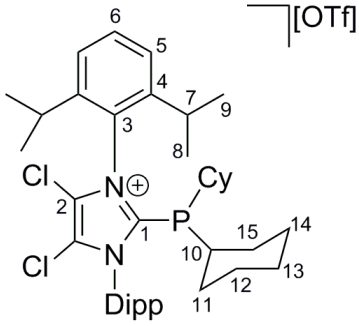
A solution of **17b**[OTf] (38 mg, 0.13 mmol) in 1,2-dichloroethane (1.5 ml) was added to a stirred solution of cyclohexylphosphane ($CyPH_2$, 5.5 mg, 0.13 mmol) in $CH_3CN$ (1.5 ml). The reaction mixture was stirred for 24 h at ambient temperature, accompanied by the formation of a colorless precipitate. The precipitate was filtered and washed with $CH_3CN$ (2 ml) and dried *in vacuo*. The collected NMR spectroscopical data revealed a clean and quantitative formation of $Cy_5P_5$ and $Cy_4P_4$ (figure S2.9).

**$^{31}$P NMR** ($C_6D_6$, in ppm): $\delta$ = –68.88 (s, $Cy_4P_4$), 7.66 (s, $Cy_5P_5$).

### S3.9 General procedure for the preparation of compounds [2-$PR_2$(4,5-Cl-$Im^{Dipp}$)][OTf] (R = Ph, Cy)

A solution of NHC **46** in $C_6H_5F$ was added dropwise to a stirred $C_6H_5F$ solution of $R_2PCl$ (R = Ph, Cy) and $Me_3SiOTf$ at ambient temperature. *n*-Hexane was added after 3 h which afforded a colorless precipitate. After filtration and washing with *n*-hexane the solid was dried *in vacuo*. Compounds **9a,b**[OTf] were obtained as colorless, moisture sensitive powders.

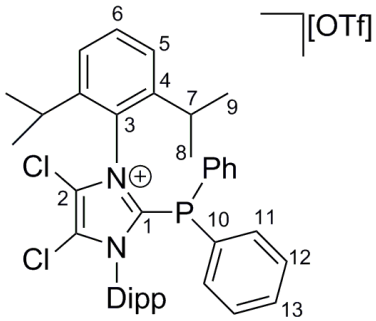
### S3.10 Characterization data of 9a[OTf]




**8**: 1.48 g, 3.22 mmol ($C_6H_5F$: 12 ml); $Cy_2PCl$: 749 mg, 3.22 mmol; $Me_3SiOTf$: 716 mg, 3.22 mmol, ($C_6H_5F$: 12 ml); *n*-hexane: 35 ml; **yield**: 4.59 g (91%); **mp**: 262-264 °C, **Raman** (60 mW, in $cm^{-1}$): $\nu$ = 3081(7), 3067(20), 2974(45), 2942(100), 2909(9), 2858(67), 2723(7), 1590(20), 1467(16), 1446(31), 1344(33), 1316(13), 1288(31), 1237(9), 1183(7), 1098(9), 1031(33), 985(13), 885(18), 851(7), 811(9), 754(13), 709(11), 606(13); **IR** (ATR, in $cm^{-1}$): $\nu$ = 2968(vw), 2931(w), 1573(vw), 1505(vw), 1465(w), 1387(vw), 1358(vw), 1309(vw), 1256(vs), 1223(w), 1178(vw), 1150(s), 1059(vw), 1029(vs), 994(vw), 933(vw), 850(w), 803(m), 762(w), 636(vs), 572(w), 543(vw), 516(m), 461(w), 434(vw); **$^1$H NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 0.87-0.91 (2H, m (br), H11a), 0.90-0.92 (2H, m, (br), H12a),

1.03-1.05 (2H, m (br), H13a), 1.13-1.15 (2H, m (br), H12b), 1.18-1.20 (2H, m (br), H15a), 1.24-1.26 (2H, m (br), H14a), 1.26 (12H, d, $^3J_{HH}$ = 6.69 Hz, H8), 1.47 (12H, d, $^3J_{HH}$ = 6.69 Hz, H9), 1.50-1.52 (2H, m (br), H11b), 1.57-1.59 (2H, m (br), H14b), 1.59-1.61 (2H, m (br), H13b), 1.70-1.72 (2H, m (br), H15b), 1.92-1.94 (2H, m (br), H10), 2.36 (4H, *pseudo* sept, $^3J_{HH}$ = 6.69 Hz, H7), 7.53 (4H, d, $^3J_{HH}$ = 7.91 Hz, H5), 7.76 (2H, d, $^3J_{HH}$ = 7.91 Hz, H6); **$^{13}$C{$^1$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 24.09 (4C, s, C9), 25.76 (2C, s, C13), 25.97 (4C, s, C8), 27.22 (2C, s, C11), 27.46 (2C, s, C15), 30.18 (4C, s, C7), 31.02 (2C, s, C12), 33.19 (2C, d, $^1J_{CP}$ = 20 Hz, C10), 33.54 (2C, s, C14), 121.63 (1C, q, $^1J_{CF}$ = 321 Hz, -$CF_3$), 126.28 (2C, d, $^3J_{CP}$ = 2 Hz C2), 126.84 (4C, s, C5), 129.95 (2C, s, C3), 146.21 (4C, s, C4), 155.42 (1C, d, $^1J_{CP}$ = 99 Hz, C1); **$^{19}$F{$^1$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = –78.86 (3F, s, -$CF_3$); **$^{31}$P{$^1$H} NMR** ($CD_2Cl_2$,in ppm): $\delta$ = 12.71 (s); **elemental analysis**: calcd. for $C_{40}H_{56}Cl_2F_3N_3O_3PS$: C: 59.8, H:7.0, N: 3.5, S: 4.0; found: C: 59.7, H: 6.7, N: 3.6, S: 4.0.

**S3.11 Characterization data of 9b[OTf]**



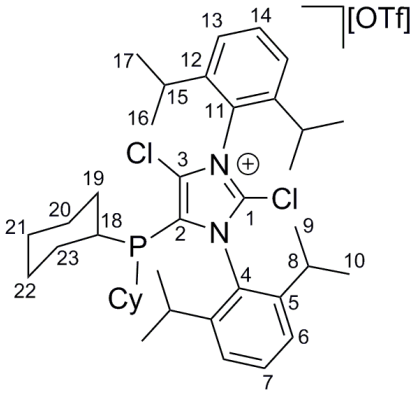

**8**: 1.84 g, 4.00 mmol ($C_6H_5F$: 8 ml); $Ph_2PCl$: 889 mg, 4.00 mmol; $Me_3SiOTf$: 882 mg, 4.00 mmol, ($C_6H_5F$: 8 ml); *n*-hexane: 32 ml; **yield**: 3.15 g (99%); **mp**: 224-226 °C; **Raman** (60 mW, in cm$^{-1}$): $\nu$ = 3061(100), 2971(32), 2940(50), 2914(21), 2870(31), 2771(7), 2722(11), 1585(46), 1562(21), 1468(18), 1443(21), 1368(7), 1346(57), 1317(25), 1280(46), 1240(14), 1186(7), 1164(14), 1102(10), 1049(10), 1031(50), 1000(39), 957(7), 886(18), 754(10), 735(7), 607(7), 573(7), 452(10); **IR** (ATR, in cm$^{-1}$): $\nu$ = 2968(vw), 2932(vw), 1560(w), 1463(w), 1436(vw), 1389(vw), 1365(w), 1313(vw), 1265(vs), 1224(w), 1180(vw), 1146(s), 1112(vw), 1087(vw), 1059(vw), 1030(s), 998(vw), 936(vw), 811(m), 766(vw), 754(vw), 743(m), 699(m), 654(vw), 636(vs), 571(w), 544(vw), 516(m), 498(w), 472(w), 454(m); **$^1$H NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 1.02 (12H, d, $^3J_{HH}$ = 6.71 Hz, H8), 1.21 (12H, d, $^3J_{HH}$ = 6.71 Hz, H9), 2.42 (4H, *pseudo* sept, $^3J_{HH}$ = 6.71 Hz, H7), 7.04 (2H, t, $^3J_{HH}$ = 7.79 Hz, H12), 7.04 (2H, t, $^3J_{HH}$ = 7.79 Hz, H14), 7.18 (2H, t, $^3J_{HH}$ = 7.79 Hz, H11), 7.19 (2H, t, $^3J_{HH}$ = 7.71 Hz, H15), 7.25 (4H, d, $^3J_{HH}$ = 7.69 Hz, H5), 7.34 (2H, t, $^3J_{HH}$ = 7.71 Hz,

H13), 7.56 (2H, t, $^{3}J_{HH}$ = 7.69 Hz, H6); **$^{13}$C{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 23.47 (4C, s, C8), 25.58 (4C, s, C9), 30.29 (4C, s, C7), 121.72 (1C, q, $^{1}J_{CF}$ = 321 Hz, -$CF_3$), 126.43 (4C, s, C5), 126.64 (2C, d, $^{3}J_{CP}$ = 3 Hz, C2), 128.23 (2C, d, $^{1}J_{CP}$ = 9 Hz, C10), 128.96 (2C, s, C3), 130.04 (2C, s, C11), 30.14 (2C, s, C15), 132.23 (2C, s, C13), 134.00 (2C, s, C6), 135.13 (2C, s, C14), 135.37 (2C, s, C12), 145.30 (2C, s, C3), 151.23 (2C, d, $^{1}J_{CP}$ = 80 Hz, C1); **$^{31}$P{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = –5.04 (s); **$^{19}$F{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = –78.72 (s); **elemental analysis**: calcd. for $C_{40}H_{44}Cl_2F_3N_2O_3PS$: C: 60.7, H: 5.6, N: 3.5, S: 4.0; found: C: 60.6, H: 5.4, N: 3.2, S: 4.0.

### S3.12 General procedure for the preparation of compounds [5-PR$_2$(2,4-Cl-Im$^{Dipp}$)][OTf] (R = Ph, Cy)

A solution of NHC **8** in *o*-$C_6H_4F_2$ was added dropwise to a stirred *o*-$C_6H_4F_2$ solution of $R_2PCl$ (R = Ph, Cy, *i*Pr) and $Me_3SiOTf$ at ambient temperature. After 12 h - 14 h *n*-hexane was added accompanied by the formation of a colorless precipitate. The precipitate was filtered, washed with *n*-hexane and dried in *vacuo*. Compounds **10a,b**[OTf] were obtained as colorless and moisture sensitive powders.

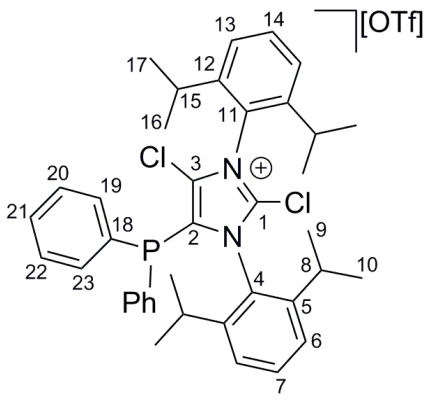
### S3.13 Characterization data of 10a[OTf]




**8**: 3.51 g, 7.62 mmol (*o*-$C_6H_4F_2$: 12 ml); $Cy_2PCl$: 1.48 g, 6.35 mmol; $Me_3SiOTf$: 1.42 g, 6.35 mmol, (*o*-$C_6H_4F_2$: 8 ml); *n*-hexane: 40 ml; **yield**: 4.71 g (92%); **mp**: 273-275 °C; **Raman** (60 mW, in cm$^{-1}$): $\nu$ = 3081(6), 3067(17), 3027(6), 2977(39), 2941(100), 2909(6), 2857(39), 2722(6), 2284(6), 1590(27), 1575(6), 1467(22), 1446(50), 1386(6), 1344(56), 1316(22), 1287(56), 1267(6), 1237(17), 1182(17), 1098(17), 1047(11), 1030(56), 985(22), 957(11), 884(33), 851(17), 810(22), 754(28), 734(11), 709(22), 663(6), 606(28), 573(6), 518(6), 459(11); **IR** (ATR, in cm$^{-1}$): $\nu$ = 2965(vw) 2928(w), 2852(vw), 1505(w), 1467(m), 1389(vw), 1367(vw), 1325(vw),

1262(vs), 1222(w), 1183(vw), 1145(w), 1059(vw), 1030(s), 936(vw), 850(vw), 808(w), 763(m), 679(vw), 654(vw), 636(vs), 570(vw), 516(m), 432(vw); **$^{1}$H NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 1.21 (6H, d, $^{3}J_{HH}$ = 6.83 Hz, H9), 1.23-1.25 (2H, m (br), H21a), 1.26-1.28 (2H, m (br), H22a), 1.26 (6H, d, $^{3}J_{HH}$ = 6.89 Hz, H16), 1.31 (6H, d, $^{3}J_{HH}$ = 6.89 Hz, H17), 1.32-1.34 (2H, m (br), H19a), 1.32-1.34 (2H, m (br), H20a), 1.32-1.34 (2H, m (br), H23a), 1.40 (6H, d, $^{3}J_{HH}$ = 6.83 Hz), 1.54-1.56 (2H, m (br), H22b), 1.73-1.75 (2H, m (br), H21b), 1.81-1.83 (2H, m (br), H23b), 1.82-1.84 (2H, m (br), H19b), 1.88-1.90 (2H, m (br), H20b) 2.16 (2H, *pseudo* sept, $^{3}J_{HH}$ = 6.89 Hz, H15), 2.20 (2H, *pseudo* sept, $^{3}J_{HH}$ = 6.83 Hz, H8), 2.29 (2H, m (br), H18), 7.48 (2H, d, $^{3}J_{HH}$ = 7.90 Hz, H6), 7.52 (2H, d, $^{3}J_{HH}$ = 7.94 Hz, H13), 7.74 (1H, t, $^{3}J_{HH}$ = 7.90 Hz, H7), 7.74 (1H, t, $^{3}J_{HH}$ = 7.94 Hz, H14); **$^{13}$C{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 23.87 (2C, s, C16), 24.11 (2C, s, C17), 24.15 (2C, s, C9), 25.05 (2C, s, C10), 26.20 (2C, s, C21), 27.36 (2C, d, $^{2}J_{CP}$ = 11 Hz, C19), 27.78 (2C, d, $^{2}J_{CP}$ = 11 Hz, C23), 30.19 (2C, d, $^{5}J_{CP}$ = 1 Hz, C8), 30.66 (2C, s, C15), 31.53 (2C, d, $^{3}J_{CP}$ = 7 Hz, C20), 31.67 (2C, d, $^{3}J_{CP}$ = 7 Hz, C22), 34.77 (2C, d, $^{1}J_{CP}$ = 15 Hz, C18), 121.62 (1C, q, $^{1}J_{CF}$ = 322 Hz, -$CF_3$), 126.02 (1C, s, C11), 126.39 (2C, s, C6), 126.59 (2C, s, C13), 131.38 (1C, d, $^{2}J_{CP}$ = 10 Hz, C3), 134.13 (1C, s, C7), 134.58 (1C, s, C14), 135.44 (1C, d, $^{1}J_{CP}$ = 50 Hz, C2), 136.90 (1C, s, C1), 145.38 (1C, d, $^{4}J_{CP}$ = 2Hz, C5), 145.94 (1C, s, C12); **$^{19}$F{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = –78.89 (3F, s, -$CF_3$); **$^{31}$P{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = –15.23 (s); **elemental analysis**: calcd. for $C_{40}H_{56}Cl_2F_3N_2O_3PS$: C: 59.7, H: 7.0, N: 3.5, S: 4.0; found: C: 59.9, H: 7.2, N: 3.5, S: 4.7.

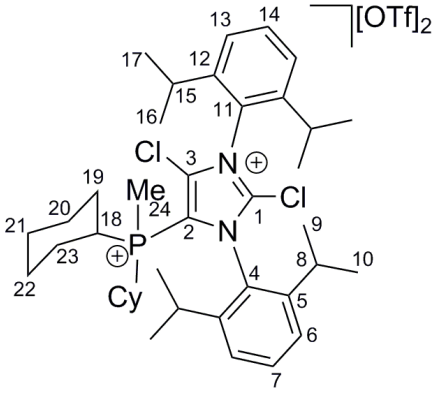
### S3.14 Characterization data of 10b[OTf]




**8**: 6.82 g, 14.80 mmol (*o*-$C_6H_4F_2$: 15 ml); $Ph_2PCl$: 2.52 g, 11.40 mmol; $Me_3SiOTf$: 2.53 g, 11.40 mmol, (*o*-$C_6H_4F_2$: 10 ml); *n*-hexane: 45 ml; **yield**: 8.72 g (97%); **mp**: 282-284 °C; **Raman** (60 mW, in $cm^{-1}$): $\nu$ = 3078(49), 3064(16), 3051(7), 2988(22), 2971(11), 2940(66), 2909(100), 2871(66), 2772(16), 2729(22), 1584(83), 1516(33), 1470(33), 1448(16), 1430(49), 1338(7), 1301(67), 1264(11), 1185(16), 1161(16), 1104(27), 1050(11), 1032(83), 998(91), 956(16), 930(7), 887(27), 753(33), 688(16), 618(16), 570(7), 492(7); **IR** (ATR, in $cm^{-1}$):

$\nu$ = 2962(vw), 2872(vw), 1514(w), 1467(w), 1389(vw), 1367(vw), 1347(vw), 1273(vw), 1259(vs), 1222(w), 1185(vw), 1164(m), 1138(vw), 1059(vw), 1028(s), 935(vw), 804(w), 754(w), 703(w), 703(vw), 661(vw), 635(s), 572(vw), 541(vw), 516(vw), 504(m), 493(vw), 432(vw), 412(vw); **$^1$H NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 1.00 (6H, d, $^3J_{HH}$ = 6.76 Hz, H9), 1.21 (6H, d, $^3J_{HH}$ = 6.76 Hz, H10); 1.29 (6H, d, $^3J_{HH}$ = H16), 1.31 (6H, d, $^3J_{HH}$ = 6.86 Hz, H17), 2.19 (2H, *pseudo* sept, $^3J_{HH}$ = 6.86 Hz, H15), 2.21 (2H, *pseudo* sept, $^3J_{HH}$ = 6.76 Hz, H8), 7.25-7.32 (4H, m, H20, 22), 7.42-7.56 (10H, m, H6, H13, H19, H21, H23), 7.75 (2H, t, $^3J_{HH}$ = 7.75 Hz, H7, H14); **$^{13}$C{$^1$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 22.98 (2C, d, $^6J_{CP}$ = 2 Hz, C9), 23.86 (2C, s, C16), 24.07 (2C, s, C17), 24.82 (2C, s, C10), 30.65 (2C, d, $^5J_{CP}$ = 2 Hz, H8), 30.72 (2C, s, C15), 121.72 (1C, q, $^1J_{CF}$ = 321 Hz, -$CF_3$), 126.03 (1C, s, C11), 126.39 (2C, s, C6), 126.54 (2C, s, C13), 127.65 (1C, d, $^3J_{CP}$ = 2 Hz, H4), 129.60 (2C, d, $^1J_{CP}$ = 8 Hz,C18), 130.40 (2C, s, C23), 130.48 (2C, s, C19), 131.65 (2C, s, C21), 132.66 (1C, d, $^2J_{CP}$ = 8 Hz, C3), 133.46 (2C, s, C20), 133.53 (2C, s, C22), 134.35 (1C, s, C7), 134.60 (1C, s, C14), 135.23 (1C, d, $^1J_{CP}$ = 37 Hz, C2), 136.96 (1C, s, C1), 145.88 (2C, s, C15), 145.95 (2C, d, $^4J_{CP}$ = 2 Hz, C5); **$^{31}$P{$^1$H}** ($CD_2Cl_2$, in ppm): $\delta$ = –28.98 (s); **$^{19}$F{$^1$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = –78.87 (s); **elemental analysis**: calcd. for $C_{40}H_{44}Cl_2F_3N_2O_3PS$: C: 60.7, H: 5.6, N: 3.5, S: 4.0; found: C: 60.6, H: 5.2, N: 3.0, S: 4.1.

### S3.15 Preparation of 14a[OTf]$_2$

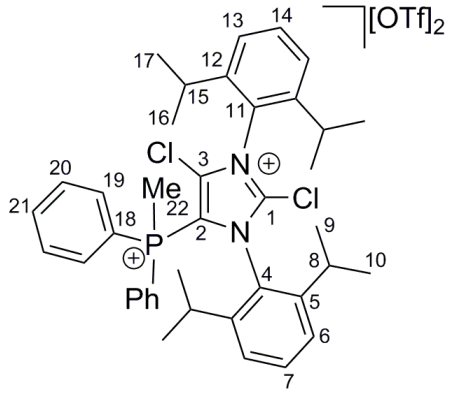



A solution of MeOTf (1.00 g, 6.10 mmol) in $CH_2Cl_2$ (3 ml) was slowly added to a solution of **10a**[OTf] (1.00 g, 1.22 mmol) in $CH_2Cl_2$ (10 ml). The reaction mixture was stirred for 36 h at ambient temperature. After the addition of *n*-hexane (25 ml) a beige precipitate was observed, filtered and washed with $C_6H_5F$ (10 ml). All volatiles were removed *in vacuo* and the product was isolated as colorless, moisture sensitive powder.

**Yield**: 800 mg (68%); **mp**: 270-272 °C; **Raman** (60 mW, in cm$^{-1}$): $\nu$ = 3076(40), 2991(19), 2947(59), 2922(14), 2898(35), 2871(22), 2861(8), 2779(5), 2733(11), 1600(8), 1586(16),

1514(19), 1471(29), 1447(48), 1424(37), 1397(8), 1334(19), 1305(22), 1286(14), 1271(11), 1234(11), 1223(8), 1182(14), 1102(16), 1048(22), 1030(100), 999(24), 959(11), 882(29), 851(5), 829(11), 793(5), 765(5), 752(27), 706(29), 609(11), 571(29), 518(11), 446(13); **IR** (ATR, in $cm^{-1}$): $\nu$ = 2969(vw), 2896(vw), 2861(vw), 1508(m), 1467(vw), 1450(m), 1394(vw), 1372(vw), 1345(vw), 1274(27), 1251(m), 1222(m), 1182(vw), 1142(m), 1101(vw), 1059(vw), 1028(vs), 908(vw), 876(vw), 845(vw), 810(m), 762(vs), 705(vw), 635(vs); **$^{1}$H NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 1.25 (6H, d, $^{3}J_{HH}$ = 6.68 Hz, H9), 1.25-1.28 (2H, m (br), H20a), 1.28 (6H, d, $^{3}J_{HH}$ = 6.84 Hz, H16), 1.30-1.34 (2H, m (br), H19a), 1.33 (6H, d, $^{3}J_{HH}$ = 6.84 Hz, H17), 1.47-1.49 (2H, m (br), H23a), 1.52-1.55 (2H, m (br), H21a), 1.52-1.55 (2H, m (br), H22a), 1.53 (6H, d, $^{3}J_{HH}$ = 6.68 Hz, H10), 1.76-1.80 (2H, m (br), H21b), 1.76-1.80 (2H, m (br), H22b), 1.85-1.89 (2H, m (br), H20b), 1.86 (3H, d, $^{2}J_{HP}$ = 12 Hz, H24), 1.87-1.91 (2H, m (br), H19b), 1.95-1.98 (2H, m (br), H23b), 2.11 (2H, *pseudo* sept, $^{3}J_{HH}$ = 6.84 Hz, H15), 2.33 (2H, *pseudo* sept, $^{3}J_{HH}$ = 6.68 Hz, H8), 3.26-4.01 (2H, m (br), H18), 7.56 (2H, d, $^{3}J_{HH}$ = 7.91 Hz, H13), 7.64 (2H, d, $^{3}J_{HH}$ = 7.84 Hz, H6), 7.83 (1H, t, $^{3}J_{HH}$ = 7.91 Hz, H14), 7.91 (1H, t ,$^{3}J_{HH}$ = 7.84 Hz, H7); **$^{13}$C{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 0.09 (1C, d, $^{1}J_{CP}$ = 48 Hz, C24), 24.01 (2C, s, C10), 24.10 (2C, s, C17), 24.22 (2C, s, C16), 25.12 (2C, d, $^{4}J_{CP}$ = 2 Hz, C21), 25.76 (2C, s, C9), 26.07 (2C, d, $^{2}J_{CP}$ = 15 Hz, C19), 26.61 (2C, $^{2}J_{CP}$ = 14 Hz, C23), 27.39 (2C, d, $^{3}J_{CP}$ = 4 Hz, C20), 27.95 (2C, d, $^{3}J_{CP}$ = 5 Hz, C22), 30.32 (2C, s, C8), 31.00 (2C, s, C15), 34.07 (2C, d, $^{1}J_{CP}$ = 37 Hz, C18), 116.98 (1C, d, $^{1}J_{CP}$ = 73 Hz, C2), 121.17 (2C, q, $^{1}J_{CF}$ = 321 Hz, -$CF_3$), 125.16 (1C, s, C11), 127.16 (2C, s, C13), 127.43 (1C, s, C4), 128.32 (2C, s, C6), 135.50 (1C, s, C14), 136.40 (1C, s, C7), 138.97 (1C, d, $^{2}J_{CP}$ = 10 Hz, C3), 142.62 (1C, d, $^{3}J_{CP}$ = 3 Hz, C1), 145.47 (2C, s, C12), 145.88 (2C, s, C5); **$^{19}$F{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = –78.76 (6F, s, -$CF_3$); **$^{31}$P{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 38.45 (s); **elemental analysis**: calcd. for $C_{42}H_{59}Cl_2F_6N_2O_6PS_2 \cdot 0.5CH_2Cl_2$: C: 50.5, H: 5.9, N: 2.8 S: 6.4; found: C: 50.3, H: 5.6, N: 2.8, S: 6.6.

**S3.16 Preparation of 14b[OTf]$_2$**

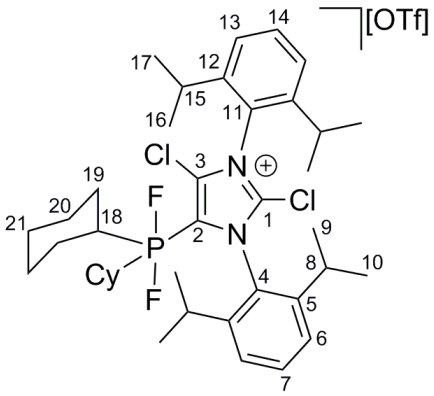



A solution of MeOTf (1.03 g, 6.30 mmol) in *o*-$C_6H_4F_2$ (3 ml) was slowly added to a solution of **10b**[OTf] (1.00 g, 1.26 mmol) in *o*-$C_6H_4F_2$ (10 ml). The reaction mixture was stirred for 48 h at 70 °C. After the addition of *n*-hexane (25 ml) a pale brown precipitate was observed, filtered and washed with $C_6H_5F$ (10 ml). All volatiles were removed *in vacuo* and the product was isolated as colorless, moisture sensitive powder.

**Yield**: 990 mg (79%); **mp**: 257-259 °C; **Raman** (60 mW, in $cm^{-1}$): ν = 3074(69), 3019(5), 2986(26), 2946(7), 2913(40), 2872(18), 2724(5), 1587(59), 1506(12), 1473(28), 1445(19), 1423(23), 1331(10), 1310(16), 1284(19), 1237(7), 1224(7), 1185(5), 1168(12), 1105(33), 1050(16), 1029(100), 998(75), 888(31), 755(27), 703(24), 612(21), 572(16), 518(5); **IR** (ATR, in $cm^{-1}$): ν = 2966(vw), 2911(vw), 2873(vw), 1586(vw), 1504(w), 1438(vw), 1391(vw), 1370(vw), 1286(vw), 1259(s), 1240(w), 1222(w), 1167(vw), 1143(m), 1109(vw), 1061(vw), 1026(vs), 995(vw), 936(vw), 908(m), 819(vw), 751(m), 722(vw), 682(w), 635(vs); **$^1$H NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 0.79 (6H, d, $^3J_{HH}$ = 6.68 Hz, H9), 1.11 (6H, d, $^3J_{HH}$ = 6.68 Hz, H10), 1.29 (6H, d, $^3J_{HH}$ = 6.82 Hz, H16), 1.44 (6H, d, $^3J_{HH}$ = 6.82 Hz, H17), 2.36 (2H, *pseudo* sept, $^3J_{HH}$ = 6.68 Hz, H8), 2.45 (2H, *pseudo* sept, $^3J_{HH}$ = 6.82 Hz, H15), 3.09 (3H, d, $^2J_{HP}$ = 14 Hz, H22), 7.28 (2H, d, $^3J_{HH}$ = 7.88 Hz, H6), 7.57 (2H, d, $^3J_{HH}$ = 7.92 Hz, H13), 7.59-7.66 (4H, m, H20), 7.67 (1H, t, $^3J_{HH}$ = 7.88 Hz, H7), 7.69-7.75 (4H, m, H19), 7.82 (1H, t, $^3J_{HH}$ = 7.92 Hz, H14), 7.90-7.96 (2H, m, H21); **$^{13}$C{$^1$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 13.30 (1C, d, $^1J_{CP}$ = 57 Hz, C22), 22.72 (2C, s, C9), 24.29 (2C, s, C17), 24.47 (2C, s, C16), 25.71 (2C, s, C10), 30.22 (2C, s, C8), 30.64 (2C, s, C15), 113.98 (2C, d, $^1J_{CP}$ = 92 Hz, C18), 117.16 (1C, d, $^1J_{CP}$ = 101 Hz, C2), 121.48 (2C, q, $^1J_{CF}$ = 321 Hz, -$CF_3$), 125.58 (1C, s, C11), 127.11 (2C, s, C13), 127.45 (1C, s, C4), 127.47 (2C, s, C6), 132.18 (4C, d, $^2J_{CP}$ = 14 Hz, C19), 134.17 (4C, d, $^3J_{CP}$ = 12 Hz, C20), 135.26 (1C, s, C14), 135.81 (1C, s, C7), 137.91 (2C, d, $^4J_{CP}$ = 3 Hz, C21), 139.69 (1C, d, $^2J_{CP}$ = 12 Hz, C3), 142.84 (1C, d, $^3J_{CP}$ = 5 Hz, C1), 146.51 (2C, s, C12), 146.58 (2C, s, C5); **$^{19}$F{$^1$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = –78.56 (s); **$^{31}$P{$^1$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 16.88 (s); **elemental**

**analysis**: calcd. for $C_{42}H_{47}Cl_2F_6N_2O_6PS_2$: C: 52.7, H: 4.9, N: 2.9, S: 6.7; found: C: 52.6, H: 4.9, N: 2.9, S: 7.1.

### S3.17 Preparation of 15a[OTf]

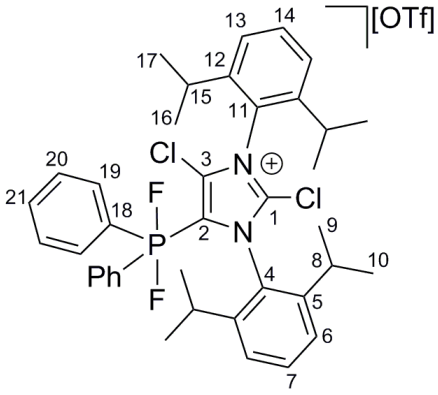



A solution of $XeF_2$ (2.78 g, 1.64 mmol) in $CH_2Cl_2$ (8 ml) was added dropwise to a solution of **10a**[OTf] (1.20 g, 1.50 mmol) in $CH_2Cl_2$ (8 ml). After stirring 12 h at ambient temperature *n*-hexane (20 ml) was added and a colorless precipitate was observed. The precipitate was filtered and washed with *n*-hexane (3 x 5 ml). All volatiles were removed *in vacuo* and the product was isolated as colorless and moisture sensitive powder.

**Yield:** 1.02 g (81%); **mp**: 165-167 °C; **Raman** (60 mW, in $cm^{-1}$): $\nu$ = 3070(43), 3035(5), 2995(6), 2976(9), 2940(57), 2918(8), 2901(35), 2871(30), 2856(48), 2770(13), 2723(11), 1600(12), 1586(26), 1469(30), 1445(74), 1427(22), 1392(8), 1349(21), 1332(9), 1302(100), 1275(17), 1222(18), 1183(17), 1104(30), 1049(39), 1032(91), 999(34), 960(17), 887(52), 854(9), 820(21), 771(7), 752(26), 737(13), 688(7), 609(34), 572(13), 549(17), 445(26), 373(27), 347(26), 317(17); **IR** (ATR, in $cm^{-1}$): ν = 2966(vw), 2928(w), 2854(vw), 1502(w), 1465(w), 1450(vw), 1390(vw), 1367(vw), 1349(vw), 1325(vw), 1287(vw), 1260(s), 1222(m), 1182(w), 1144(vs), 1060(vw), 1031(vs), 937(vw), 860(vw), 825(vw), 808(w), 771(m), 705(s), 657(w), 636(vs); **$^1$H NMR** ($CD_3CN$, in ppm): δ = 1.23 (6H, d, $^3J_{HH}$ = 6.68 Hz, H9), 1.30 (6H, d, $^3J_{HH}$ = 6.85 Hz, H16), 1.37 (6H, d, $^3J_{HH}$ = 6.85 Hz, H17), 1.46 (6H, d, $^3J_{HH}$ = 6.68 Hz, H10), 1.24-1.28(2H, m, H19), 1.25-1.29 (2H, m, H21), 1.46-1.52 (2H, m, H20), 1.71-1.76 (2H, m, H21), 1.82-1.85 (2H, m, H19), 1.83-1.87 (2H, m, H20), 2.21 (2H, *pseudo* sept, $^3J_{HH}$ = 6.85 Hz, H15), 2.25-2.35 (2H, m, H18), 2.41 (2H, *pseudo* sept, $^3J_{HH}$ = 6.68 Hz, H8), 7.51 (2H, d, $^3J_{HH}$ = 7.84 Hz, H6), 7.56 (2H, d, $^3J_{HH}$ = 7.84 Hz, H13), 7.75 (1H, t, $^3J_{HH}$ = 7.84 Hz, H7), 7.82 (1H, t, $^3J_{HH}$ = 7.84 Hz, H14); **$^{13}$C{$^1$H} NMR** ($CD_3CN$, in ppm): $\delta$ = 22.94 (2C, *pseudo* t, $^6J_{CP}$ = 1 Hz, C10), 23.51 (2C, s, C17), 23.73 (2C, s, C16), 24.90 (2C, s, C9), 25.72 (2C, d, $^4J_{CP}$ = 2 Hz, C21), 26.93 (4C, dt, $^2J_{CP}$ = 19 Hz, $^3J_{CF}$ = 2 Hz, C19), 28.07 (4C, dt, $^3J_{CP}$ = 4 Hz, $^4J_{CF}$ = 6 Hz, C20), 29.85 (2C, s, C8), 29.97 (2C, s, C15), 44.75 (2C, dt, $^1J_{CP}$ = 114 Hz,

$^{2}J_{CF}$ = 20 Hz, C18), 121.01 (1C, q, $^{1}J_{CF}$ = 321 Hz, -$CF_3$), 125.74 (2C, s, C6), 126.11 (2C, s, C13), 130.46 (2C, s, C4/11), 132.82 (1C, dt, $^{1}J_{CP}$ = 192 Hz, $^{2}J_{CF}$ = 48 Hz, C2), 133.18 (1C, s, C7), 134.05 (1C, dt, $^{2}J_{CP}$ = 48 Hz, $^{3}J_{CF}$ = 23 Hz, C3), 134.13 (1C, s, C14), 138.26 (1C, d, $^{3}J_{CP}$ = 9 Hz, C1), 145.23 (2C, s, C5), 145.41 (2C, s, C12); **$^{19}$F{$^{1}$H} NMR** ($CD_3CN$, in ppm): $\delta$ = –40.11 (2F, d, $^{1}J_{FP}$ = 721 Hz, -F1,2), –79.3 (3F, s, -$CF_3$); **$^{31}$P{$^{1}$H} NMR** ($CD_3CN$, in ppm): $\delta$ = –28.54 (t, $^{1}J_{PF}$ = 721 Hz); **elemental analysis**: calcd. for $C_{40}H_{56}Cl_2F_5N_2O_3PS$: C: 57.0, H: 6.7, N: 3.3, S: 3.8; found: C: 56.9, H: 6.5, N: 3.3, S: 4.5.

### S3.18 Preparation of 15b[OTf]

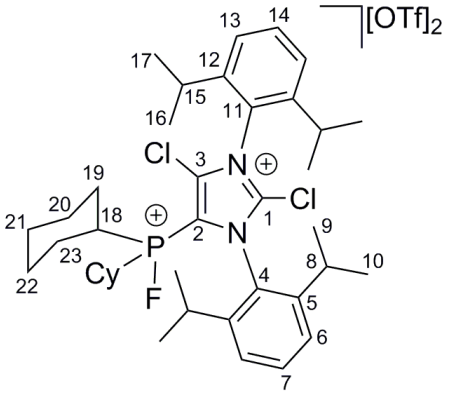



A solution of $XeF_2$ (1.21 g, 7.10 mmol) in $CH_2Cl_2$ (15 ml) was added dropwise to a solution of **10b**[OTf] (5.16 g, 6.50 mmol) in $CH_2Cl_2$ (10 ml). After stirring 3 h at ambient temperature, *n*-hexane was added and a colorless precipitate was observed. The precipitate was filtered and washed with *n*-hexane (30 ml). All volatiles were removed *in vacuo* and the product was isolated as colorless and moisture sensitive powder.

**Yield:** 4.82 g, (89%); **mp**: 241-243 °C; **Raman** (60 mW, in $cm^{-1}$): $\nu$ = 3084(37), 3068(24), 3036(5), 2975(48), 2939(41), 2909(51), 2870(44), 2767(8), 2722(16), 1591(68), 1519(10), 1466(29), 1445(17), 1429(32), 1389(5), 1338(13), 1301(44), 1277(19), 1237(13), 1222(6), 1205(7), 1171(11), 1151(6), 1102(29), 1050(6), 1034(65), 1002(100), 960(13), 887(29), 753(16), 708(19), 621(6), 608(14), 582(7), 523(6), 445(17); **IR** (ATR, in $cm^{-1}$): ν = 2971(vw), 2931(vw), 2871(vw), 2378(vw), 1588(vw), 1553(vw), 1516(w), 1466(w), 1444(vw), 1388(vw), 1367(vw), 1325(vw), 1265(vs), 1221(vw), 1184(vw), 1146(s), 1112(w), 1098(vw), 1059(vw), 1030(m), 999(vw), 936(vw), 808(w), 774(vw), 761(vw), 746(w), 730(w), 706(vw), 691(vw), 636(s), 582(vw), 553(s), 537(vw), 517(w), 464(vw); **$^{1}$H NMR** ($CD_3CN$, in ppm): δ = 1.00 (6H, d, $^{3}J_{HH}$ = 6.61 Hz, H9), 1.16 (6H, d, $^{3}J_{HH}$ = 6.61 Hz, H10), 1.26 (6H, d, $^{3}J_{HH}$ = 7.74 Hz, H16), 1.28 (6H, d, $^{3}J_{HH}$ = 6.74 Hz, H17), 2.20 (2H, *pseudo* sept, $^{3}J_{HH}$ = 6.74 Hz, H15), 2.37 (2H, *pseudo* sept, $^{3}J_{HH}$ = 6.61 Hz, H8), 7.37 (2H, d, $^{3}J_{HH}$ = 7.86 Hz, H6), 7.41-7.46 (4H, m, H20), 7.43-7.48

(1H, m, H14), 7.50 (2H, d, $^{3}J_{HH}$ = 7.88 Hz, H13), 7.57-7.64 (2H, m, H21), 7.70-7.80 (4H, m, H19), 7.71-7.76 (1H, m, H7); **$^{13}$C{$^{1}$H} NMR** ($CD_3CN$, in ppm): $\delta$ = 22.53 (2C, d, $^{6}J_{CP}$ = 1 Hz, C9), 23.98 (2C, s, C17), 24.16 (2C, s, C16), 25.36 (2C, s, C10), 30.41 (2C, s, C8), 30.47 (2C, s, C15), 122.01 (1C, q, $^{1}J_{CF}$ = 321 Hz, -$CF_3$), 125.94 (1C, s, C11), 126.41 (2C, s, C6), 126.61 (2C, s, C13), 129.69 (1C, s, C4), 129.97 (2C, dt, $^{1}J_{CP}$ = 24 Hz, $^{2}J_{CF}$ = 183 Hz, C18), 130.03 (4C, dt, $^{3}J_{CP}$ = 2 Hz,$^{4}J_{CF}$ = 17 Hz, C20), 130.98 (1C, dt, $^{2}J_{CP}$ = 5 Hz, $^{3}J_{CF}$ = 17 Hz, C3), 134.03 (1C, s, C14), 134.42 (1C, dt, $^{1}J_{CP}$ = 60 Hz, $^{2}J_{CF}$ = 226 Hz, C2), 134.58 (1C, s, C7), 134.71 (2C, dt, $^{4}J_{CP}$ = 2 Hz, $^{5}J_{CF}$ = 4 Hz, C21), 136.72 (4C, dt, $^{2}J_{CP}$ = 12 Hz, $^{3}J_{CF}$ = 14 Hz, C19), 137.33 (1C, d, $^{4}J_{CF}$ = 9 Hz, C1), 146.03 (2C, s, C12), 146.26 (2C, s, C5); **$^{19}$F{$^{1}$H} NMR** ($CD_3CN$, in ppm): $\delta$ = –39.9 (2F, d, $^{1}J_{FP}$ = 712 Hz, -F1,2), –78.9 (3F, s, -$CF_3$); **$^{31}$P{$^{1}$H} NMR** ($CD_3CN$, in ppm): $\delta$ = –64.9 (t, $^{1}J_{PF}$ = 712 Hz); **elemental analysis**: calcd. for $C_{40}H_{44}Cl_2F_5N_2O_3PS$: C: 57.9, H: 5.3, N: 3.4, S: 3.9; found: C: 57.6, H: 5.2, N: 3.3, S: 3.9.

### S3.19 Preparation of 16a[OTf]$_2$

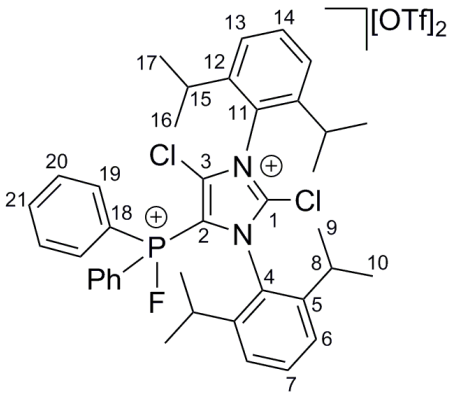



**15a**[OTf] (500 mg, 0.59 mmol) was dissolved in $C_6H_5F$ (4 ml) and an excess of $Me_3SiOTf$ (528 mg, 2.37 mmol) was added. The reaction mixture was stirred for 2 h accompanied by the formation of a colorless precipitate. After filtration the residue was washed with $C_6H_5F$ (3 x 3 ml). All volatiles were removed *in vacuo* and the product was isolated as colorless, very air and moisture sensitive powder

**Yield:** 521 mg, (91%); **mp**: 187-189 °C; **$^{1}$H NMR** ($CD_3CN$, in ppm): $\delta$ = 1.26 (6H, d, $^{3}J_{HH}$ = 6.76 Hz, H10), 1.29 (6H, d, $^{3}J_{HH}$ = 6.69 Hz, H17), 1.37 (6H, d, $^{3}J_{HH}$ = 6.69 Hz, H16), 1.47(6H, d, $^{3}J_{HH}$ = 6.76 Hz, H9), 1.39-1.51 (2H, m, H20), 1.45-1.54 (2H, m, H19), 1.55-1.62 (1H, m, H21), 1.84-2.22(2H, m, H20), 1.89-1.95 (2H, m, H23), 1.97-2.09 (1H, m, H21), 2.00-2.09 (2H, m, H23), 2.01-2.12 (2H, m, H19), 2.22-2.31 (2H, m, H22), 2.25 (2H, *pseudo* sept, $^{3}J_{HH}$ = 6.69 Hz, H15), 2.43 (2H, *pseudo* sept, $^{3}J_{HH}$ = 6.76 Hz, H8), 3.46 (2H, m, H18), 7.69 (4H, d, $^{3}J_{HH}$ = 8.01, H7, H14), 7.90 (2H, t, $^{3}J_{HH}$ = 8.01 Hz, H6, H13); **$^{13}$C{$^{1}$H} NMR** ($CD_3CN$, in ppm): $\delta$ = 24.11 (2C, d, $^{6}J_{CP}$ = 1 Hz, C9), 24.57 (2C, s, C16), 24.62 (2C, s, C17), 25.27 (2C, d,

$^3J_{CP}$ = 2 Hz, C20), 25.43 (2C, d, $^3J_{CP}$ = 1 Hz, C22), 25.74 (2C, s, C10), 26.07 (2C, s, C21), 26.27 (2C, dd, $^2J_{CP}$ = 5 Hz, $^3J_{CF}$ = 1 Hz, C23), 26.62 (2C, d, $^2J_{CP}$ = 14 Hz, C19), 30.92 (2C, s, C8), 31.39 (2C, s, C15), 37.87 (2C, dd, $^1J_{CP}$ = 40 Hz, $^2J_{CF}$ = 7 Hz, C18), 122.46 (2C, q, $^1J_{CF}$ = 319 Hz, -$CF_3$), 125.87 (1C, s, C11), 128.29 (2C, s, C14), 128.68 (2C, s, C7), 129.72 (1C, s, C4), 131.67 (1C, d, $^2J_{CP}$ = 9 Hz, C3), 136.35 (1C, s, C6), 136.47 (1C, s, C13), 140.33 (1C, dd, $^1J_{CP}$ = 22 Hz, $^2J_{CF}$ = 5 Hz, C2), 145.92 (1C, d, $^3J_{CP}$ = 5 Hz, C1), 146.84 (2C, d, $^4J_{CP}$ = 1 Hz, C5), 147.24 (2C, s, C12); **$^{19}$F{$^1$H} NMR** ($CD_3CN$, in ppm): $\delta$ = –149.69(d, $^1J_{FP}$ = 1027 Hz); **$^{31}$P{$^1$H} NMR** ($CD_3CN$, in ppm): $\delta$ = 122.11(d, $^1J_{PF}$ = 1027 Hz); **elemental analysis**: calcd. for $C_{41}H_{56}Cl_2F_7N_2O_6PS_2$: C: 50.7, H: 5.8, N: 2.9, S: 6.6; found: C: 50.7, H: 5.6, N: 3.1, S: 7.3.

### S3.20 Preparation of 16b[OTf]$_2$

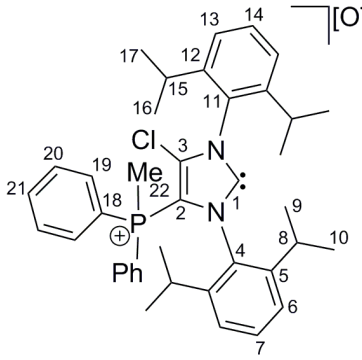



**15b**[OTf] (800 mg, 0.96 mmol) was dissolved in *o*-$C_6H_4F_2$ (5 ml) and an excess of $Me_3SiOTf$ (2.15 g, 9.67 mmol) was added. The reaction mixture was stirred for 48 h accompanied by the formation of a colorless precipitate. After filtration the residue was washed with *o*-$C_6H_4F_2$ (4 ml). All volatiles were removed *in vacuo* and the product was isolated as colorless, very air and moisture sensitive powder.

**Yield:** 661 mg, (72%); **mp**: decomp. 172-174 °C; **Raman** (80 mW, in $cm^{-1}$): ν = 3073(63), 3033(6), 2983(14), 2942(23), 2913(16), 2869(14), 2771(8), 1585(57), 1504(5), 1465(20), 1444(11), 1417(24), 1338(8), 1303(29), 1278(21), 1237(6), 1222(6), 1164(9), 1100(23), 1050(11), 1030(100), 999(63), 961(5), 909(6), 886(26), 756(25), 710(17), 683(7), 610(23), 574(11), 518(9); **IR** (ATR, $cm^{-1}$): $\nu$ = 3069(vw), 2871(vw), 1584(vw), 1501(m), 1464(vw), 1443(vw), 1390(vw), 1367(vw), 1329(vw), 1279(s), 1249(vs), 1220(w), 1164(w), 1150(w), 1113(vw), 1098(vw), 1060(vw), 1026(vs), 995(vw), 934(vw), 907(w), 806(m), 774(vw), 754(m), 734(m), 708(w), 690(vw), 679(vw), 656(vw), 635(vs), 573(w), 554(m), 519(s), 492(m), 433(vw); **$^1$H NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 0.93 (6H, d, $^3J_{HH}$ = 6.67 Hz, H9), 1.15 (6H, $^3J_{HH}$ = 6.67 Hz, H10), 1.25 (6H, d, $^3J_{HH}$ = 6.77 Hz, H17), 1.38 (6H, d, $^3J_{HH}$ = 6.77 Hz, H16), 2.45 (2H, *pseudo* sept, $^3J_{HH}$ = 6.77 Hz, H15), 2.51 (2H, *pseudo* sept, $^3J_{HH}$ = 6.67 Hz, H8), 7.38 (2H, d,

$^{3}J_{HH}$ = 7.86 Hz, H6), 7.54 (2H, d, $^{3}J_{HH}$ = 7.93 Hz, H13), 7.72-7.79 (2H, m, H7, H14), 7.80-7.86 (4H, m, H19), 8.02-8.10 (2H, m, H21), 8.11-8.15 (4H, m, H20); **$^{13}$C{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 22.71 (2C, d, $^{6}J_{CP}$ = 1 Hz, C9), 24.30 (2C, s, C16), 24.43 (2C, s, C17), 25.76 (2C, s, C10), 30.03 (2C, s, C8), 30.36 (2C, s, C15), 112.70 (2C, dd, $^{1}J_{CP}$ = 12 Hz, $^{2}J_{CF}$ = 115 Hz, C18), 117.72 (1C, dd, $^{1}J_{CP}$ = 142 Hz, $^{2}J_{CF}$ = 23 Hz, C2), 121.71 (2C, q, $^{1}J_{CF}$ = 322 Hz, -$CF_3$), 125.46 (1C, s, C11), 127.01 (2C, s, C13), 127.04 (1C, s, C4), 127.41 (2C, s, C6), 132.09 (4C, d, $^{3}J_{CF}$ = 16 Hz, C19), 135.05 (4C, dd, $^{3}J_{CP}$ = 3 Hz, $^{4}J_{CF}$ = 14 Hz, C20), 135.09 (1C, s, C14), 135.81 (1C, s, C7), 140.28 (2C, dd, $^{4}J_{CP}$ = 1 Hz, $^{5}J_{CF}$ = 3 Hz, C21), 142.56 (1C, dd, $^{2}J_{CP}$ = 3 Hz, $^{3}J_{CF}$ = 16 Hz, C3), 143.38 (1C, dd, $^{3}J_{CP}$ = 1 Hz, $^{4}J_{CF}$ = 8 Hz, C1), 146.82 (1C, s, C12), 147.09 (1C, s, C5); **$^{19}$F{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = -126.27 (1F, d, $^{1}J_{FP}$ = 996 Hz, F1); –78.79 (s, -$CF_3$); **$^{31}$P{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 70.6 (d, $^{1}J_{CP}$ = 996 Hz); **elemental analysis**: calcd. for $C_{41}H_{44}Cl_2F_7N_2O_6PS_2$: C: 51.3, H: 4.6, N: 2.9, S: 6.6; found: C: 50.9, H: 4.5, N: 2.9, S: 6.6.

### S3.21 Preparation of 17b[OTf]

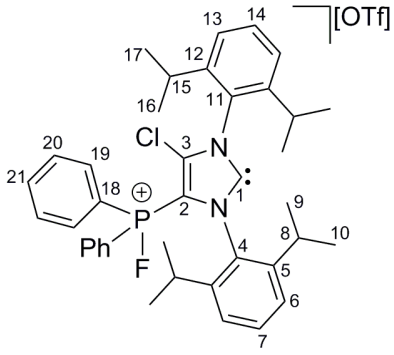



**14b**[OTf]$_2$ (505 mg, 0.53 mmol) and $PCy_3$ (148 mg, 0.53 mmol) were combined and suspended in $C_6H_5F$ (5 ml). The reaction mixture got clear after 5 min and the solvent was reduced after 1.5 h accompanied by the formation of a colorless precipitate. Benzene (6 ml) was added and the precipitate was filtered and washed with benzene (6 ml). All volatiles were removed *in vacuo* and the product was isolated as colorless, air and moisture sensitive powder.

**Yield**: 306 mg, (75%); **mp**: 177-179 °C; **IR** (ATR, in cm$^{-1}$): $\nu$ = 2957(vw), 2925(vw), 2867(vw), 1590(vw), 1510(w), 1386(vw), 1349(w), 1280(w), 1257(m), 1223(w), 1208(vw), 1152(s), 1110(m), 1060(vw), 1029(vs), 997(vw), 967(vw), 935(vw), 899(w), 883(w), 808(m), 764(vw), 749(s), 719(vw), 688(s), 636(vs), 572(vw), 538(vw), 516(s), 493(vw), 463(w), 433(w); **$^{1}$H NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 0.97 (6H, d, $^{3}J_{HH}$ = 6.83 Hz, H9), 1.11 (6H, d, $^{3}J_{HH}$ = 6.83 Hz, H10), 1.21 (6H, d, $^{3}J_{HH}$ = 6.87 Hz, H17), 1.27 (6H, d, $^{3}J_{HH}$ = 6.87 Hz, H16), 2.31 (3H, d, $^{2}J_{HP}$ = 14 Hz, H22),

2.53 (2H, *pseudo* sept, $^{3}J_{HH}$ = 6.83 Hz, H8), 2.67 (2H, *pseudo* sept, $^{3}J_{HH}$ = 6.87 Hz, H15), 7.26 (2H, d, $^{3}J_{HH}$ = 7.78 Hz, H6), 7.36 (2H, d, $^{3}J_{HH}$ = 7.79 Hz, H13), 7.47 (1H, t, $^{3}J_{HH}$ = 7.78 Hz, H7), 7.49 (1H, t, $^{3}J_{HH}$ = 7.79 Hz, H14), 7.69-7.75 (4H, m, H19), 7.72-7.80 (4H, m, H20), 7.77-7.85 (2H, m, H21); **$^{13}$C{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 9.91 (1C, d, $^{2}J_{CP}$ = 59 Hz, C22), 21.39 (2C, s, C9), 23.41 (2C, s, C16), 24.59 (2C, s, C17), 26.48 (2C, s, C10), 29.86 (2C, s, C15), 30.33 (2C, s, C8), 109.46 (1C, d, $^{1}J_{CP}$ = 108 Hz, C2), 118.7 (2C, d, $^{1}J_{CP}$ = 92 Hz, C18), 122.40 (1C, q, $^{1}J_{CF}$ = 323 Hz, -$CF_3$), 124.92 (2C, s, C13), 125.11 (2C, s, C6), 131.28 (1C, s, C14), 131.59 (4C, d, $^{2}J_{CP}$ = 14 Hz, C19), 132.07 (1C, s, C7), 133.79 (1C, s, C11), 134.08 (4C, d, $^{3}J_{CP}$ = 12 Hz, C20), 136.34 (2C, d, $^{4}J_{CP}$ = 3 Hz, C21), 136.42 (1C, s, C4), 137.08 (1C, d, $^{2}J_{CP}$ = 21 Hz, C3), 146.99 (2C, s, C12), 147.20 (2C, s, C5), 229.30 (1C, d, $^{3}J_{CP}$ = 5 Hz, C1); **$^{19}$F{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = –78.83 (s, -$CF_3$); **$^{31}$P{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 10.6 (s); **elemental analysis**: calcd. for $C_{41}H_{47}ClF_3N_2O_3PS$: C: 63.9, H: 6.1, N: 3.6, S: 4.2; found: C: 63.9, H: 6.0, N: 3.7, S: 4.4.

### S3.22 Preparation of 18b[OTf]




**16b**[OTf]$_2$ (250 mg, 0.26 mmol) and $PPh_3$ (69 mg, 0.26 mmol) were combined and suspended in $C_6H_5F$ (5 ml). The reaction mixture got clear after 10 min and the solvent was removed after 1 h. The crude product was extracted with toluene (15 ml) and precipitated with *n*-hexane (15 ml). The solid was filtered and dried *in vacuo*. The product was isolated as colorless, very air and moisture sensitive powder.

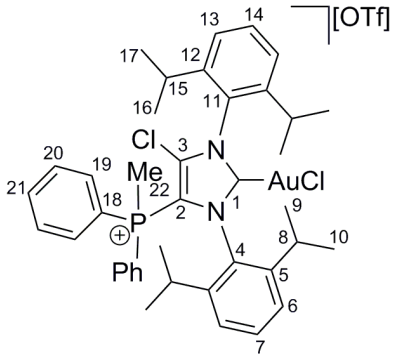
**Yield**: 110 mg, (55%); **mp**: 123-125 °C; **IR** (ATR, in cm$^{-1}$): $\nu$ = 2964(vw), 2870(vw), 1585(vw), 1531(vw), 1506(vw), 1466(vw), 1439(w), 1388(vw), 1367(vw), 1348(vw), 1273(vw), 1261(m), 1222(w), 1147(m), 1123(vw), 1060(vw), 1029(vs), 995(vw), 968(vw), 902(vw), 805(m), 756(w), 738(vw), 708(vw), 685(m), 636(vs), 615(vw), 592(w), 571(vw), 550(m), 532(vw), 513(s), 466(vw), 433(vw); **$^{1}$H NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 0.93 (6H, d, $^{3}J_{HH}$ = 6.84 Hz, H9), 1.13 (6H, d, $^{3}J_{HH}$ = 6.84 Hz, H10), 1.22 (6H, d, $^{3}J_{HH}$ = 6.76 Hz, H17), 1.28 (6H, d, $^{3}J_{HH}$ = 6.76 Hz, H16), 2.41 (2H, *pseudo* sept, $^{3}J_{HH}$ = 6.84 Hz, H8), 2.52 (2H, *pseudo* sept, $^{3}J_{HH}$ = 6.76 Hz, H15), 7.20 (2H, d,

$^{3}J_{HH}$ = 7.83 Hz, H6), 7.38 (2H, d, $^{3}J_{HH}$ = 7.88 Hz, H13), 7.48 (1H, t, $^{3}J_{HH}$ = 7.83 Hz, H7), 7.57 (1H, t, $^{3}J_{HH}$ = 7.88 Hz, H14), 7.65-7.73 (4H, m, H20), 7.82-7.89 (4H, m, H19), 8.05-8.12 (2H, m, H21); **$^{13}$C{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 21.64 (2C, s, C9), 23.53 (2C, s, C16), 24.94 (2C, s, C17), 26.26 (2C, s, C10), 29.84 (2C, s, C15), 30.18 (2C, s, C8), 107.87 (1C, dd, $^{1}J_{CP}$ = 143 Hz, $^{2}J_{CF}$ = 20 Hz, C2), 115.46 (2C, dd, $^{1}J_{CP}$ = 117 Hz, $^{2}J_{CF}$ = 14 Hz, C18), 121.61 (1C, q, $^{1}J_{CF}$ = 322 Hz, -$CF_3$), 124.73 (2C, s, C6), 125.05 (2C, s, C13), 131.72 (1C, s, C14), 132.02 (4C, d, $^{2}J_{CP}$ = 15 Hz, C19), 132.04 (1C, s, C7), 132.26 (1C, s, C11), 133.67 (4C, dd, $^{3}J_{CP}$ = 14 Hz, $^{4}J_{CF}$ = 1 Hz, C20), 134.80 (1C, d, $^{3}J_{CP}$ = 2 Hz, C4), 139.86 (2C, dd, $^{4}J_{CP}$ = 3 Hz, $^{5}J_{CF}$ = 1 Hz, C21), 140.59 (1C, dd, $^{2}J_{CP}$ = 30 Hz, $^{3}J_{CF}$ = 1 Hz, C3), 146.16 (2C, s, C12), 146.20 (2C, s, C5), 230.80 (1C, *pseudo* t, $^{3/4}J_{CP/F}$ = 4 Hz); **$^{19}$F{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = –78.79 (s, -$CF_3$), –128.22 (1F, d, $^{1}J_{FP}$ = 997 Hz, F1); **$^{31}$P{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 77.8 (d, $^{1}J_{CP}$ = 997 Hz); **elemental analysis**: calcd. for $C_{40}H_{44}ClF_4N_2O_3PS$: C: 61.9, H: 5.7, N: 3.6, S: 4.1; found: C: 61.1, H: 5.8, N: 3.3, S: 4.3.

### S3.23 General procedure for the preparation of transition metal complexes

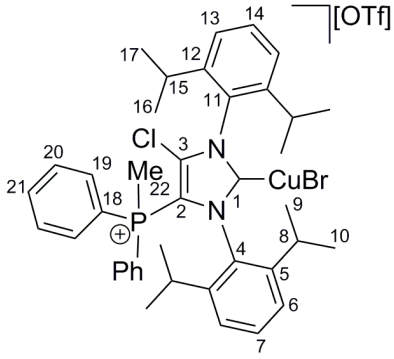
**14b**[OTf]$_2$ and $Cy_3P$ or **16b**[OTf]$_2$ and $PPh_3$ were suspended in THF at ambient temperature. After 10-30 minutes a suspension of the corresponding transition metal salt in THF was added to the clear reaction mixture. The reaction mixture was stirred for 4-6 h accompanied by a formation of a colorless precipitate which was filtered off, washed with THF and dried *in vacuo*. **19**[OTf] and **20**[OTf] were obtained as colorless, air-stable powder. **21**[OTf] and **22**[OTf]$_3$ were obtained as colorless, moisture sensitive powder. **23**[OTf] was obtained as yellow, moisture sensitive powder.

**S3.24 Characterization data of 19[OTf]**



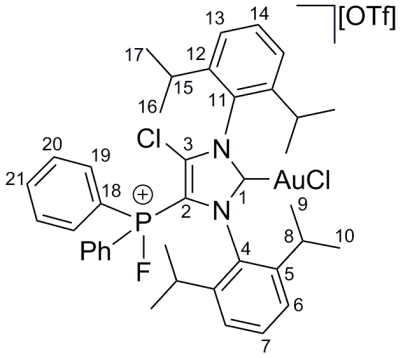

**14b**[OTf]$_2$ (400 mg, 0.42 mmol); $Cy_3P$ (117 mg, 0.42 mmol), THF (8 ml); AuCl(tht) (135 mg, 0.42 mmol), THF (5 ml); THF (8 ml); **yield**: 372 mg, (88%); **mp**: 300 °C (decomp.); **Raman** (40 mW, in cm$^{-1}$): ν = 3173(7), 3066(100), 3012(13), 2986(12), 2969(28), 2941(13), 2914(64), 2866(40), 2765(6), 2716(10), 1588(55), 1514(22), 1467(12), 1444(15), 1412(7), 1367(37), 1338(21), 1307(12), 1262(18), 1235(6), 1196(6), 1166(9), 1112(12), 1047(10), 1030(43), 999(44), 888(12), 754(9), 707(7), 693(11), 613(10); IR (ATR, in cm$^{-1}$): *ν* = 2966(vw), 2913(vw), 2866(vw), 1587(vw), 1513(m), 1465(vw), 1439(m), 1388(vw), 1364(vw), 1339(vw), 1273(vw), 1258(s), 1222(w), 1164(vw), 1114(m), 1059(vw), 1029(vs), 916(vw), 900(m), 805(m), 762(vw), 742(s), 723(vw), 685(m), 636(vs), 572(w), 543(vw), 516(s), 498(vw), 485(vw); **$^1$H NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 0.97 (6H, d, $^3J_{HH}$ = 6.79 Hz, H10), 1.28 (6H, d, $^3J_{HH}$ = 6.87 Hz, H17), 1.35 (6H, d, $^3J_{HH}$ = 6.87 Hz, H16), 1.38 (6H, d, $^3J_{HH}$ = 6.79 Hz, H9), 2.11 (3H, d, $^1J_{HP}$ = 14.01 Hz, H22), 2.39 (2H, *pseudo* sept, $^3J_{HH}$ = 6.79 Hz, H8), 2.42 (2H, *pseudo* sept, $^3J_{HH}$ = 6.87 Hz, H15), 7.44 (2H, d, $^3J_{HH}$ = 7.87 Hz, H6), 7.49 (2H, d, $^3J_{HH}$ = 7.87 Hz, H13), 7.59-7.69 (4H, m, H20), 7.67-7.72 (2H, m, H7, H14), 7.74-7.82 (4H, m, H19), 7.91-7.97 (2H, m, H21); **$^{13}$C{$^1$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 10.56 (1C, d, $^1J_{CP}$ = 59 Hz, C22), 22.52 (2C, s, C10), 23.67 (2C, s, C17), 24.80 (2C, s, C17), 27.00 (2C, s, C9), 30.04 (2C, s, C8), 30.48 (2C, s, C15), 112.46 (2C, d, $^1J_{CP}$ = 111 Hz, C18), 116.56 (1C, d, $^1J_{CP}$ = 93 Hz, C2), 122.21 (1C, q, $^1J_{CF}$ = 321 Hz, -$CF_3$), 126.45 (2C, s, C13), 127.24(2C, s, C6), 130.70 (1C, s, C11), 132.19 (4C, d, $^2J_{CP}$ = 14 Hz, C19), 132.98 (1C, s, C7), 133.61 (1C, s, C14), 134.09 (4C, d, $^3J_{CP}$ = 11 Hz, C20), 134.28 (1C, s, C7), 137.72 (2C, d, $^4J_{CP}$ = 3 Hz, C21), 138.97 (1C, d, $^2J_{CP}$ = 14 Hz, C3), 147.08 (2C, s, C12), 147.23 (2C, s, C5), 184.04 (1C, s, C1); **$^{19}$F{$^1$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = –79.24 (s, -$CF_3$); **$^{31}$P{$^1$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 14.08 (s); **elemental analysis**: calcd. for $C_{41}H_{47}Cl_2F_3N_2O_3PSAu$: C: 49.0, H: 4.7, N: 2.8, S:3.2; found: C: 49.0, H: 4.6, N: 2.8, S: 2.8.

**S3.25 Characterization data of 20[OTf]**



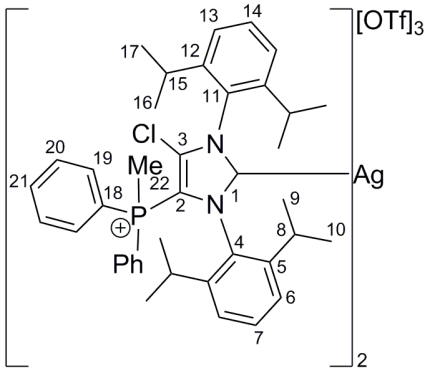

**14b**$[OTf]_2$ (500 mg, 0.52 mmol); $Cy_3P$ (147 mg, 0.52 mmol), THF (8 ml); CuBr(tht) (128 mg, 0.55 mmol), THF (5 ml); THF (8 ml); **yield**: 442 mg, 93%; **mp**: 278-280 °C (decomp.); **Raman** (40 mW, in $cm^{-1}$): ν = 3173(6), 3098(5), 3066(100), 3030(5), 3011(9), 2971(39), 2940(9), 2914(84), 2865(45), 2764(9), 2714(12), 2293(6), 2108(6), 1588(75), 1512(24), 1467(18), 1443(18), 1392(6), 1369(42), 1324(33), 1304(12), 1257(21), 1236(9), 1196(6), 1166(12), 1105(33), 1047(9), 1030(54), 999(55), 960(6), 887(18), 756(12), 733(6), 693(15), 613(9), 596(12), 573(6), 537(5), 517(6); **IR** (ATR, in $cm^{-1}$): *ν* = 2965(vw), 2912(vw), 1587(vw), 1508(w), 1464(vw), 1440(m), 1387(w), 1361(w), 1321(vw), 1303(vw), 1272(vw), 1258(vs), 1222(w), 1161(w), 1147(m), 1114(m), 1060(m), 1029(vs), 935(vw), 916(vw), 901(m), 807(m), 792(vw), 764(vw), 742(s), 724(vw), 686(vs), 572(w), 544(vw), 517(s), 498(w), 465(m), 430(w); **$^1$H NMR** ($CD_3CN$, in ppm): $\delta$ = 0.97 (6H, d, $^3J_{HH}$ = 6.68 Hz, H10), 1.28 (6H, d, $^3J_{HH}$ = 6.84 Hz, H17), 1.29 (6H, d, $^3J_{HH}$ = 6.68 Hz, H9), 1.30 (6H, d, $^3J_{HH}$ = 6.84 Hz, H16), 2.13 (3H, d, $^1J_{HP}$ = 13.88 Hz, H22), 2.40 (2H, *pseudo* sept, $^3J_{HH}$ = 6.68 Hz, H8), 2.44 (2H, *pseudo* sept, $^3J_{HH}$ = 6.84 Hz, H15), 7.41 (2H, d, $^3J_{HH}$ = 7.87 Hz, H6), 7.48 (2H, d, $^3J_{HH}$ = 7.85 Hz, H13), 7.59-7.65 (4H, m, H20), 7.64-7.69 (2H, m, H7, H14), 7.74-7.79 (4H, m, H19), 7.91-7.96 (2H, m, H21); **$^{13}$C{$^1$H} NMR** ($CD_3CN$, in ppm): $\delta$ = 10.55 (1C, d, $^1J_{CP}$ = 58 Hz, C22), 22.15 (2C, s, C10), 23.67 (2C, s, C17), 25.10 (2C, s, C16), 27.47 (2C, s, C9), 30.24 (2C, s, C8), 30.28 (2C, s, C15), 111.84 (2C, d, $^1J_{CP}$ = 110 Hz, C18), 116.75 (1C, d, $^1J_{CP}$ = 93 Hz, C2), 122.26 (1C, q, $^1J_{CF}$ = 321 Hz, -$CF_3$), 126.18 (2C, s, C13), 126.69(2C, s, C6), 130.87 (1C, s, C11), 132.11 (4C, d, $^2J_{CP}$ = 14 Hz, C19), 133.39 (1C, s, C4), 133.41 (1C, s, C7), 133.98 (1C, s, C14), 134.14 (4C, d, $^3J_{CP}$ = 11 Hz, C20), 137.39 (2C, d, $^4J_{CP}$ = 3 Hz, C21), 138.70 (1C, d, $^2J_{CP}$ = 15 Hz, C3), 147.09 (2C, s, C12), 147.11 (2C, s, C5), 189.51 (1C, s, C1); **$^{19}$F{$^1$H} NMR** ($CD_3CN$, in ppm): $\delta$ = –79.11 (s, -$CF_3$); **$^{31}$P{$^1$H} NMR** ($CD_3CN$, in ppm): $\delta$ = 13.12 (s); **elemental analysis**: calcd. for $C_{41}H_{47}ClBrF_3N_2O_3PSCu$: C: 53.8, H: 5.2, N: 3.1, S:3.5; found: C: 53.3, H: 5.3, N: 3.2, S: 3.4.

**S3.26 Characterization data of 21[OTf]**



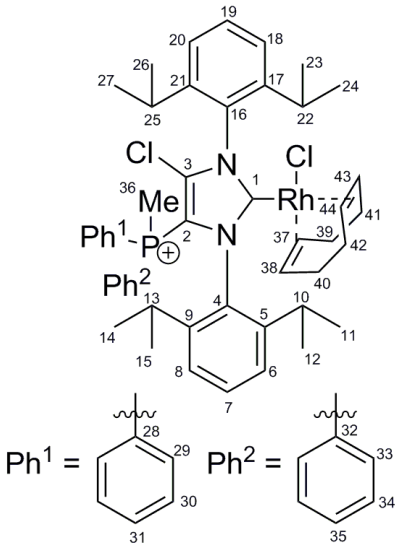

**16b**$[OTf]_2$ (120 mg, 0.12 mmol); $Ph_3P$ (33 mg, 0.12 mmol), THF (3 ml); AuCl(tht) (40 mg, 0.12 mmol), THF (2 ml); THF (3 ml); **yield**: 109 mg, (87%); **mp**: 136 °C (decomp.); **IR** (ATR, in $cm^{-1}$): $\nu$ = 2965(w), 2871(vw), 1586(vw), 1511(w), 1464(vw), 1440(m), 1382(vw), 1364(vw), 1340(vw), 1274(vw), 1265(vs), 1223(w), 1184(vw), 1156(w), 1145(vw), 1129(vw), 1118(vw), 1099(vw), 1061(w), 1030(vs), 996(vw), 927(m), 907(vw), 807(m), 782(vw), 764(vw), 743(s), 711(m), 688(vw), 676(vw), 636(vs), 603(vw), 572(w), 551(m), 533(m), 515(vs), 478(m), 430(w); **$^1$H NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 0.92 (6H, d, $^3J_{HH}$ = 6.80 Hz, H9), 1.35 (6H, d, $^3J_{HH}$ = 7.21 Hz, H16), 1.43 (6H, d, $^3J_{HH}$ = 7.21 Hz, H17), 1.45 (6H, d $^3J_{HH}$ = 6.80 Hz, H10), 2.38 (2H, *pseudo* sept, $^3J_{HH}$ = 6.80 Hz, H8), 2.43 (2H, *pseudo* sept, $^3J_{HH}$ = 7.21 Hz, H15), 7.34 (2H, d, $^3J_{HH}$ = 7.85 Hz, H6), 7.48 (2H, d, $^3J_{HH}$ = 7.91 Hz, H13), 7.68 (1H, t, $^3J_{HH}$ = 7.85 Hz, H7), 7.73 (1H, t, $^3J_{HH}$ = 7.91 Hz, H14), 7.80-7.88 (4H, m, H20), 7.91-7.99 (4H, m, H19), 8.14-8.21 (2H, m, H21); **$^{13}$C{$^1$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 22.52 (2C, s, C9), 23.77 (2C, s, C16), 24.74 (2C, s, C17), 26.65 (2C, s, C10), 30.24 (2C, s, C8), 30.35 (2C, s, C15), 110.58 (1C, dd, $^1J_{CP}$ = 146 Hz, $^2J_{CF}$ = 19 Hz, C2), 113.93 (2C, dd, $^1J_{CP}$ = 116 Hz, $^2J_{CF}$ = 14 Hz, C18), 125.88 (2C, s, C13), 125.98 (2C, s, C6), 129.69(1C, s, C11), 130.74 (1C, dd, $^2J_{CP}$ = 129 Hz, $^3J_{CF}$ = 14 Hz, C3), 131.86 (1C, d, $^3J_{CP}$ = 2Hz, C4), 132.14 (4C, d, $^2J_{CP}$ = 15 Hz, C19), 133.32 (1C, s, C14), 133.67 (1C, s, C7), 134.21 (4C, d, $^3J_{CP}$ = 13 Hz, C20), 140.28 (2C, s, C21), 146.11 (2C, s, C12), 146.23 (2C, s, C5), 186.46 (1C, s, C1); **$^{19}$F{$^1$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = –78.75 (s, -$CF_3$), –128.16 (1F, d, $^1J_{FP}$ = 1008 Hz, -PF); **$^{31}$P{$^1$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 78.97 (d, $^1J_{PF}$ = 1008 Hz); **elemental analysis**: calcd. for $C_{40}H_{44}AuCl_2F_4N_2O_3PS$: C: 47.7, H: 4.4, N: 2.8, S: 3.2; found: C: 47.9, H: 4.5, N: 2.8, S: 3.8.

**S3.27 Characterization data of 22[OTf]$_3$**




**14b**[OTf]$_2$ (220 mg, 0.23 mmol); $Cy_3P$ (65 mg, 0.23 mmol), THF (5 ml); AgOTf (58 mg, 0.23 mmol), THF (3 ml); THF (5 ml); **yield**: 193 mg, (82%); **mp**: 304 °C (decomp.); **Raman** (40 mW, in $cm^{-1}$): ν = 3069(68), 2987(14), 2965(16), 2939(18), 2908(25), 2866(19), 2846(9), 2765(9), 2721(11), 1588(75), 1520(31), 1467(22), 1442(19), 1392(10), 1370(37), 1320(21), 1297(25), 1258(13), 1223(9), 1168(16), 1108(44), 1048(15), 1031(100), 999(75), 984(9), 959(11), 887(25), 809(8), 753(26), 731(13), 692(25), 614(19), 595(12), 572(13), 518(10), 448(11), 405(10), 380(8); **IR** (ATR, in $cm^{-1}$): $\nu$ = 2968(vw), 2922(vw), 2875(vw), 1585(vw), 1516(w), 1463(vw), 1440(w), 1388(vw), 1363(vw), 1275(w), 1255(m), 1221(w), 1149(s), 1110(m), 1062(w), 1029(vs), 996(vw), 903(vw), 888(w), 807(w), 748(m), 720(w), 687(m), 636(vs), 571(w), 537(vw), 515(s), 497(vw), 462(vw), 433(w); **$^1$H NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 0.75 (6H, d, $^3J_{HH}$ = 6.70 Hz, H10), 0.83 (6H, d, $^3J_{HH}$ = 6.57 Hz, H17), 0.90 (6H, d, $^3J_{HH}$ = 6.57 Hz, H9), 1.16 (6H, d, $^3J_{HH}$ = 6.70 Hz, H16), 2.00 (3H, d, $^1J_{HP}$ = 13.41 Hz, H22), 2.10 (4H, *pseudo* sept, $^3J_{HH}$ = 6.79 Hz, H8, H15), 7.31 (4H, *pseudo* t, $^3J_{HH}$ = 7.87 Hz, H6, H13), 7.48-7.57 (4H, m, H20), 7.67-7.78 (2H, m, H7, H14), 7.67-7.78 (4H, m, H19), 7.87-7.93 (2H, m, H21); **$^{13}$C{$^1$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 9.19 (1C, d, $^1J_{CP}$ = 58 Hz, C22), 20.93 (2C, s, C9), 22.74 (2C, s, C16), 24.86 (2C, s, C17), 27.38 (2C, s, C10), 29.29 (2C, s, C8), 29.47 (2C, s, C15), 113.39 (2C, d, $^1J_{CP}$ = 107 Hz, C18), 115.16 (1C, d, $^1J_{CP}$ = 92 Hz, C2), 120.90 (2C, q, $^1J_{CF}$ = 322 Hz, -$CF_3$), 125.75 (2C, s, C13), 126.31(2C, s, C6), 129.76 (1C, s, C11), 131.35 (4C, d, $^2J_{CP}$ = 14 Hz, C19), 132.41 (1C, s, C4), 132.52 (4C, d, $^3J_{CP}$ = 12 Hz, C20), 134.19 (1C, s, C7), 133.03 (1C, s, C14), 136.79 (2C, d, $^4J_{CP}$ = 3 Hz, C21), 139.94 (1C, d, $^2J_{CP}$ = 15 Hz, C3), 145.40 (2C, s, C12), 145.42 (2C, s, C5), 183.68 (1C, d, $^1J_{CAg107}$ = 202 Hz, $^1J_{CAg109}$ = 234 Hz, C1); **$^{19}$F{$^1$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = –78.75 (s, -$CF_3$); **$^{31}$P{$^1$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 14.08 (s); **elemental analysis**: calcd. for $C_{83}H_{94}Cl_2F_9N_4O_9P_2S_3Ag$: C: 55.4, H: 5.3, N: 3.1, S:5.3; found: C: 54.9, H: 5.4, N: 2.9, S: 5.3.

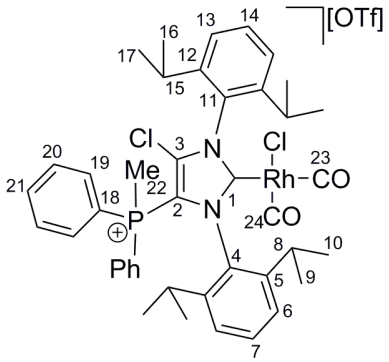
**S3.28 Characterization data of 23[OTf]**




**14b**$[OTf]_2$ (192 mg, 0.20 mmol); $Cy_3P$ (57 mg, 0.20 mmol), THF (5 ml); $[Rh(cod)Cl]_2$ (55 mg, 0.11 mmol), THF (2 ml); THF (6 ml); **yield**: 179 mg, (88%); **mp**: 199-201 °C (decomp.); **Raman** (40 mW, in $cm^{-1}$): ν = 3065(91), 3011(11), 2970(36), 2945(12), 2917(22), 2905(10), 2872(45), 2826(27), 1587(85), 1515(63), 1469(23), 1443(16), 1430(12), 1346(22), 1333(11), 1303(51), 1280(10), 1262(13), 1238(24), 1220(36), 1189(11), 1167(9), 1142(9), 1106(42), 1047(11), 1031(73), 998(100), 976(22), 954(17), 912(9), 883(17), 852(12), 809(12), 779(8), 754(13),. 733(12), 693(9), 615(10), 597(23), 573(27), 530(9), 505(10), 484(16); **IR** (ATR, in $cm^{-1}$): $\nu$ = 2968(vw), 2870(vw), 1586(vw), 1512(w), 1461(vw), 1440(w), 1388(vw), 1333(vw), 1286(m), 1252(m), 1219(w), 1152(vs), 1107(w), 1058(vw), 1031(s), 995(vw), 954(vw), 932(vw), 896(m), 851(vw), 803(vw), 753(vs), 690(m), 637(vs), 571(w), 546(vw), 516(m), 496(vw); **$^1$H NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 0.29 (3H, d, $^3J_{HH}$ = 6.79 Hz, H24), 0.91 (3H, d, $^3J_{HH}$ = 6.69 Hz, H26), 1.14 (3H, d, $^3J_{HH}$ = 6.69 Hz, H27), 1.16 (3H, d, $^3J_{HH}$ = 6.69 Hz, H11), 1.35-1.45 (8H, m, H12, H15, H42), 1.42 (3H, d, $^3J_{HH}$ = 6.90 Hz, H26), 1.55 (3H, d, $^3J_{HH}$ = 6.90 Hz, H23), 1.59-1.72 (2H, m, H39), 1.72-1.79 (4H, m, H40, H41), 1.85 (3H, d, $^2J_{HP}$ = 13 Hz, H36), 2.06 (1H, *pseudo* sept, $^3J_{HH}$ = 6.79 Hz, H25), 2.47 (1H, *pseudo* sept, $^3J_{HH}$ = 6.69 Hz, H13), 3.39 (2H, s(br), H37, H38), 3.50 (1H, *pseudo* sept, $^3J_{HH}$ = 6.69 Hz, H10), 3.68 (1H, *pseudo* sept, $^3J_{HH}$ = 6.69 Hz, H10), 4.45-4.54 (1H, m, H44), 4.79-4.88 (1H, m, H43), 7.39 (2H, d, $^3J_{HH}$ = 7.92 Hz, H8, H20), 7.43-7.53 (4H, m, H6, H18, H30), 7.59-7.66 (2H, m, H29), 7.61-7.70 (2H, m, H34), 7.65-7.70 (1H, m, H19), 7.79-7.86 (3H, m, H7, H33), 7.90-7.97 (2H, m, H31, H35); **$^{13}$C{$^1$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 9.99 (1C, d, $^1J_{CP}$ = 59 Hz, C36), 22.64 (1C, s, C24), 22.82 (1C, s, C26), 25.05 (1C, s, C14), 25.27 (1C, s, C27), 25.35 (1C, s, C11), 26.14 (1C, s, C15), 26.57 (1C, s, C42), 27.04 (1C, s, C12), 29.01 (1C, s, C23), 29.09 (1C, s, C12), 29.22 (1C, s, C25), 29.66 (1C, s, C10), 29.70 (1C, s, C13), 30.36 (1C, s, C40), 30.49 (1C, s, C39), 34.72 (1C, s, C41), 66.21 (1C, d, $^1J_{CRh}$ = 14 Hz, C38), 72.3 (1C, d, $^1J_{CRh}$ = 14 Hz, C37), 96.80 (1C, d, $^1J_{CRh}$ = 7 Hz, C44), 100.31 (1C, d, $^1J_{CRh}$ = 7 Hz, C43), 109.48 (1C, d, $^1J_{CP}$ = 114 Hz, C2), 115.88 (1C, d, $^1J_{CP}$ = 90 Hz, C28), 117.95

(1C, d, $^{1}J_{CP}$ = 93 Hz, C32), 120.82 (1C, q, $^{1}J_{CF}$ = 321 Hz, -$CF_3$), 124.48 (1C, s, C8), 125.70 (1C, s, C20), 126.65 (1C, s, C6), 127.74 (1C, s, C18), 131.02 (2C, d, $^{2}J_{CP}$ = 14 Hz, C29), 131.54 (2C, d, $^{2}J_{CP}$ = 14 Hz, C33), 131.79 (1C, s, C7), 132.01 (1C, s, C4), 132.65 (1C, s, C19), 132.99 (2C, d, $^{3}J_{CP}$ = 11 Hz, C30), 133.05 (2C, d, $^{3}J_{CP}$ = 11 Hz, C34), 133.34 (1C, s, C16), 136.26 (1C, d, $^{4}J_{CP}$ = 3 Hz, C31), 136.70 (1C, d, $^{4}J_{CP}$ = 3 Hz, C35), 140.20 (1C, d, $^{2}J_{CP}$ = 17 Hz, C16), 145.02 (1C, s, C9), 146.47 (1C, s, C21), 148.22 (1C, s, C17), 148.62 (1C, s, C5), 206.08 (1C, d, $^{1}J_{CRh}$ = 52 Hz, C1); **$^{19}$F{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = –78.99 (s, -$CF_3$); **$^{31}$P{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 13.34 (s); **elemental analysis**: calcd. for $C_{49}H_{59}RhCl_2F_3N_2O_3PS$: C: 57.6, H: 6.2, N: 2.7, S:3.1; found: C: 57.7, H: 5.9, N: 2.8, S: 4.0.

**S3.29 Preparation of 24[OTf]**

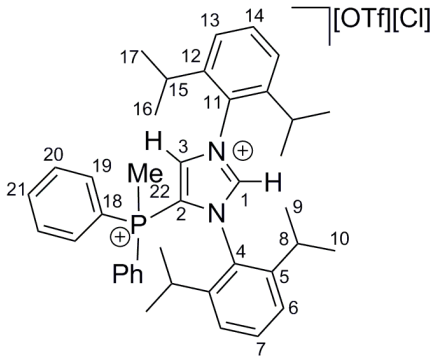



Carbon monoxide was bubbled for 45 min through a solution of **23**[OTf] (125 mg, 0.12 mmol) in $CH_2Cl_2$ (8 ml) accompanied by a color change from deep yellow to pale yellow. The solvent was reduced *in vacuo* and *n*-hexane (10mL) was added accompanied by the formation of a yellow precipitate. After filtration, all volatiles were removed *in vacuo*. **24**[OTf] was isolated as air and moisture sensitive, pale yellow powder. For CO stretching frequencies see IR spectrum in figure S2.10.

**Yield**: 99 mg, (86%); **mp**: 246-248 °C (decomp.); **Raman** (40 mW, in $cm^{-1}$): ν = 3072(77), 3062(61), 3026(23), 3006(20), 2971(30), 2963(28), 2937(73), 2915(61), 2869(35), 2079(67), 1997(100), 1587(76), 1572(17), 1510(30), 1467(15), 1442(21), 1366(40), 1350(38), 1317(28), 1295(38), 1273(11), 1244(31), 1228(22), 1183(8), 1168(9), 1107(23), 1046(21), 1029(81), 999(77), 982(16), 952(7), 883(23), 774(11), 754(17), 733(11), 714(9), 693(19), 658(7), 615(17), 600(19), 572(11), 539(15), 514(11), 491(15); **IR** (ATR, in $cm^{-1}$): $\nu$ = 2962(vw), 2933(vw), 2073(s), 2007(s), 1586(vw), 1510(w), 1466(vw), 1439(w), 1386(vw), 1365(w), 1318(vw), 1265(vs), 1224(w), 1160(w), 1141(w), 1106(m), 1058(vw), 1032(s), 930(vw), 879(m), 804(w), 751(s), 713(w), 686(m), 639(vs), 586(vw), 571(vw), 540(vw), 515(m), 498(vw), 477(w), 460(vw), 436(w); **$^{1}$H NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 0.95 (6H, d, $^{3}J_{HH}$ = 6.74 Hz, H10), 1.16 (6H,

d, $^{3}J_{HH}$ = 6.53 Hz, H16), 1.42 (6H, d, $^{3}J_{HH}$ = 6.74 Hz, H9), 1.48 (6H, d, $^{3}J_{HH}$ = 6.53 Hz, H17), 2.04 (3H, d, $^{3}J_{HP}$ = 13.61 Hz, H22), 2.76-2.88 (4H, m, H8, H15), 7.44 (2H, d, $^{3}J_{HH}$ = 7.82 Hz, H13), 7.48 (2H, $^{3}J_{HH}$ = 7.84 Hz, H6), 7.61-7.69 (5H, m, H14, H20), 7.71-7.76 (1H, m, H7), 7.73-7.79 (4H, m, H19), 7.88-7.94 (2H, m, H21); **$^{13}$C{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 9.59 (1C, d, $^{1}J_{CP}$ = 57 Hz, C22), 24.60 (2C, s, C17), 24.86 (2C, s, C10), 25.26 (2C, s, C16), 26.99 (2C, s, C9), 29.59 (2C, s, C8), 30.79 (2C, s, C15), 112.71 (2C, d, $^{1}J_{CP}$ = 110 Hz, C18), 117.25 (1C, d, $^{1}J_{CP}$ = 92 Hz, C2), 121.42 (1C, q, $^{1}J_{CF}$ = 320 Hz, -$CF_3$), 126.09 (2C, s, C13), 127.35 (2C, s, C6), 131.37 (1C, s, C11), 131.65 (4C, d, $^{2}J_{CP}$ = 14 Hz, C19), 132.75 (1C, s, C14), 133.37 (1C, s, C4), 133.39 (4C, d, $^{3}J_{CP}$ = 11 Hz, C20), 133.66 (1C, s, C7), 137.01 (2C, d, $^{4}J_{CP}$ = 3 Hz, C21), 140.09 (1C, dd, $^{2}J_{CP}$ = 15 Hz, $^{3}J_{CRh}$ = 2 Hz, C3), 146.75 (1C, s, C12), 147.13 (1C, s, C5), 182.06 (1C, d, $^{1}J_{CRh}$ = 72 Hz, C24), 183.37 (1C, d, $^{1}J_{CRh}$ = 55 Hz, C23), 194.97 (1C, d, $^{1}J_{CRh}$ = 48 Hz, C1); **$^{31}$P{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 14.3 (s); **$^{19}$F{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = –78.99 (s, -$CF_3$.

**S3.30 Preparation of 26[OTf][Cl]**

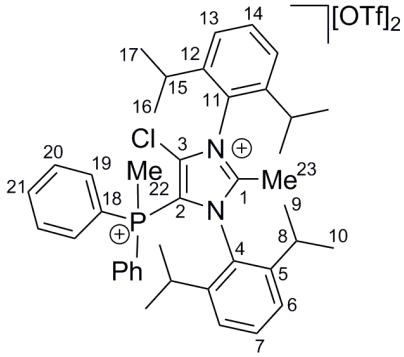



To a solution of $Ph_2PH$ (20 mg, 0.11 mmol) in 1,2-dichloroethane (1 ml) a solution of **17b**[OTf] (38 mg, 0.05 mmol) in 1,2-dichloroethane (2 ml) was added dropwise. The reaction mixture was stirred for 12 h at ambient temperature. *n*-Hexane was added (2 ml) followed by the formation of a colorless precipitate. The precipitate was filtered, washed with *n*-hexane and dried *in vacuo*.

**Yield**: not determined; **mp**: 199-201 °C; **$^{1}$H NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 0.45 (6H, d, $^{3}J_{HH}$ = 6.39 Hz, H10), 0.98 (6H, d, $^{3}J_{HH}$ = 6.39 Hz, H9), 1.16 (6H, d, $^{3}J_{HH}$ = 6.55 Hz, H17), 1.30 (6H, d, $^{3}J_{HH}$ = 6.55 Hz, H16), 1.94 (2H, *pseudo* sept, $^{3}J_{HH}$ = 6.39 Hz, H8), 2.42 (2H, *pseudo*, sept, $^{3}J_{HH}$ = 6.55 Hz, H15), 3.15 (3H, d, $^{2}J_{HP}$ = 14 Hz, H22), 7.17 (2H, d, $^{3}J_{HH}$ = 7.91 Hz, H6), 7.35 (2H, d, $^{3}J_{HH}$ = 7.82 Hz, H13), 7.45-7.56 (4H, m, H20), 7.52-7.64 (4H, m, H19), 7.56-7.66 (1H, m, H14), 7.56-7.61 (1H, m, H7), 7.79-7.85 (2H, m, H21), 10.69 (1H, s, H3), 11.66 (1H, s, H1); **$^{13}$C{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 12.17 (1C, d, $^{1}J_{CP}$ = 57 Hz, C22), 21.20 (2C, s, C10),

24.18 (2C, s, C16), 24.58 (2C, s, C17), 26.61 (2C, s, C9), 29.99 (2C, s, C15), 30.12 (2C, s, C8), 114.19 (2C, d, $^{1}J_{CP}$ = 92 Hz, C18), 118.76 (2C, d, $^{1}J_{CP}$ = 150 Hz, C2), 121.11 (1C, q, $^{1}J_{CF}$ = 321 Hz, -$CF_3$), 125.35 (2C, s, C13), 125.87 (2C, s, C6), 128.68 (1C, s, C4), 129.73 (1C, s, C11), 131.37 (4C, d, $^{3}J_{CP}$ = 14 Hz, C19), 132.97 (1C, s, C14), 134.27 (1C, s, C7), 134.46 (4C, d, $^{4}J_{CP}$ = 11 Hz, C20), 137.04 (2C, d, $^{5}J_{CP}$ = 3 Hz, C21), 141.07 (1C, d, $^{3}J_{CP}$ = 19 Hz, C3), 145.44 (2C, s, C12), 146.36 (2C, s, C5), 148.35 (1C, d, $^{4}J_{CP}$ = 4 Hz, C1); **$^{19}$F{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = –79.03 (s, -$CF_3$); **$^{31}$P{$^{1}$H} NMR** ($CD_2Cl_2$, in ppm): $\delta$ = 12.30 (s).

### S3.31 Preparation of 34[OTf]$_2$

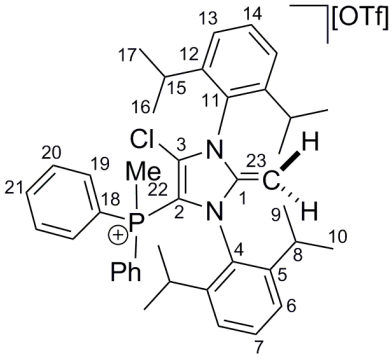



**14b**[OTf]$_2$ (500 mg, 0.52 mmol) and $Cy_3P$ (147 mg, 0.52 mmol) were combined and suspended in $C_6H_5F$ (8 ml). After 30 minutes MeOTf (103 mg, 0.62 mmol) in $C_6H_5F$ (2 ml) was added to the clear reaction mixture accompanied by a formation of a colorless precipitate. After 12 h the precipitate was filtered, washed with $C_6H_5F$ (6 ml) and dried *in vacuo*. The product was obtained as colorless, air-stable powder.

**Yield**: 466 mg, 96%; **mp**: 247-249 °C; **Raman** (40 mW, in cm$^{-1}$): ν = 3071(51), 3025(17), 2997(24), 2979(31), 2937(41), 2914(51), 2872(27), 1852(15), 1587(58), 1504(33), 1469(55), 1444(37), 1373(27), 1341(41), 1288(37), 1223(29), 1167(24), 1099(31), 1050(15), 1030(100), 999(76), 887(23), 813(15), 753(48), 722(36), 612(31), 572(26), 513(21), 451(19), 384(32), 348(41); **IR** (ATR, in cm$^{-1}$): $\nu$ = 2965(vw), 2904(vw), 1586(vw), 1511(vw), 1466(vw), 1439(w), 1391(vw), 1348(vw), 1268(w), 1251(m), 1223(w), 1162(vw), 1147(w), 1105(w), 1060(vw), 1028(vs), 996(vw), 934(vw), 904(m), 808(vw), 789(vw), 749(m), 723(vw), 686(m), 636(vs), 572(w), 540(vw), 517(w), 505(vw), 485(vw), 471(vw), 455(vw); **$^{1}$H NMR** ($CH_2Cl_2$, in ppm): $\delta$ = 0.88 (6H, d, $^{3}J_{HH}$ = 6.65 Hz, H10), 1.10 (6H, d, $^{3}J_{HH}$ = 6.65 Hz, H9), 1.33 (6H, d, $^{3}J_{HH}$ = 6.73 Hz, H16), 1.42 (6H, d, $^{3}J_{HH}$ = 6.73 Hz, H17), 2.38 (3H, s, H23), 2.91 (3H, d, $^{1}J_{HP}$ = 13.88 Hz, H22), 2.34 (2H, *pseudo* sept, $^{3}J_{HH}$ = 6.65 Hz, H8), 2.38 (2H, *pseudo* sept, $^{3}J_{HH}$ = 6.73 Hz, H15), 7.35 (2H, d, $^{3}J_{HH}$ = 7.94 Hz, H6), 7.59 (2H, d, $^{3}J_{HH}$ = 7.81 Hz, H13), 7.62-

7.69 (4H, m, H20), 7.71 (1H, t, $^{3}J_{HH}$ = 7.94 Hz, H7), 7.73-7.79 (4H, m, H19), 7.83 (1H, t, $^{3}J_{HH}$ = 7.81 Hz, H14), 7.91-7.97 (2H, m, H21); **$^{13}$C{$^{1}$H} NMR** ($CH_2Cl_2$, in ppm): $\delta$ = 12.31 (1C, d, $^{1}J_{CP}$ = 57 Hz, C22), 15.12 (1C, s, C23), 22.68 (2C, s, C9), 24.26 (2C, s, C16), 24.68 (2C, s, C17), 25.50 (2C, s, C10), 30.02 (2C, s, C8), 30.38 (2C, s, C15), 114.50 (2C, d, $^{1}J_{CP}$ = 92 Hz, C18), 114.81 (1C, d, $^{1}J_{CP}$ = 104 Hz, C2), 121.44 (1C, q, $^{1}J_{CF}$ = 321 Hz, -$CF_3$), 125.45 (1C, s, C11), 127.22 (2C, s, C6), 127.50 (2C, s, C13), 127.69 (1C, s, C4), 132.11 (4C, d, $^{2}J_{CP}$ = 14 Hz, C19), 133.86 (4C, d, $^{3}J_{CP}$ = 12 Hz, C20), 134.87 (1C, s, C14), 135.57 (1C, s, C7), 137.73 (2C, d, $^{4}J_{CP}$ = 3 Hz, C21), 139.05 (1C, d, $^{2}J_{CP}$ = 13 Hz, C3), 146.01 (2C, s, C12), 146.15 (2C, s, C5), 154.63 (1C, d, $^{3}J_{CP}$ = 4 Hz C1); **$^{19}$F{$^{1}$H} NMR** ($CH_2Cl_2$, in ppm): $\delta$ = –78.61 (s, -$CF_3$); **$^{31}$P{$^{1}$H} NMR** ($CH_2Cl_2$, in ppm): $\delta$ = 15.63 (s); **elemental analysis**: calcd. for $C_{43}H_{50}ClF_6N_2O_6PS$: C: 55.2, H: 5.4, N: 2.9, S:6.9; found: C: 54.9, H: 5.3, N: 2.9, S: 7.2.

### S3.32 Preparation of 35[OTf]

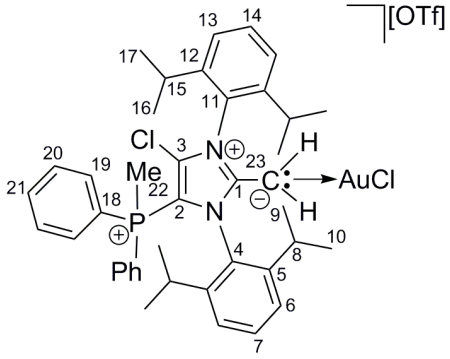



**34**$[OTf]_2$ (300 mg, 0.32 mmol) was suspended in THF (3 ml). LDA (147 mg, 0.52 mmol) was added accompanied by the formation of a clear yellow solution. The reaction mixture was stirred for 30 minuttes and the solvent was then removed in *vacuo*. The crude material was suspended in $CH_2Cl_2$ (2 ml), filtrated, and *n*-hexane was added to the filtrate until a yellow precipitate was observed. After filtration of the precipitate all volatiles were removed in *vacuo* and **35**[OTf] was isolated as yellow, air-sensitive powder.

**Yield**: 235 mg, 93%; **mp**: 156-158 °C (decomp.); **Raman** (40 mW, in $cm^{-1}$): ν = 3066(62), 3008(16), 2983(33), 2964(31), 2911(58), 2869(45), 1642(29), 1586(66), 1523(100), 1468(24), 1444(23), 1411(16), 1388(21), 1354(20), 1303(16), 1259(37), 1231(24), 1165(21), 1105(21), 1049(16), 1029(41), 997(45), 973(11), 887(14), 753(12), 720(13), 691(19), 610(21), 549(11), 480(16), 443(17), 394(26); **IR** (ATR, in $cm^{-1}$): $\nu$ = 2965(w), 2930(vw), 2870(vw), 1641(vs), 1586(vw), 1520(m), 1466(w), 1439(m), 1410(vw), 1387(w), 1365(vw), 1282(m), 1254(vs), 1223(m), 1192(vw), 1145(vs), 1106(m), 1060(vw), 1029(vs), 1009(vw), 971(vw), 937(vw), 897(s), 856(vw), 804(s), 745(vs), 717(w), 687(s), 636(vs), 609(w), 571(w), 538(vw), 511(vs),

473(w); **$^{1}$H NMR** ($CH_2Cl_2$, in ppm): $\delta$ = 1.00 (6H, d, $^{3}J_{HH}$ = 6.89 Hz, H9), 1.23 (6H, d, $^{3}J_{HH}$ = 6.89 Hz, H10), 1.31 (6H, d, $^{3}J_{HH}$ = 6.86 Hz, H16), 1.32 (6H, d, $^{3}J_{HH}$ = 6.86 Hz, H17), 1.80 (3H, d, $^{1}J_{HP}$ = 13.67 Hz, H22), 2.50 (1H, d, $^{2}J_{HH}$ = 3.65 Hz, H23a), 2.57 (1H, dd, $^{2}J_{HH}$ = 3.65 Hz, $^{5}J_{HP}$ = 1.64 Hz H23b), 2.98 (2H, *pseudo* sept, $^{3}J_{HH}$ = 6.86 Hz, H15), 3.02 (2H, *pseudo* sept, $^{3}J_{HH}$ = 6.89 Hz, H8), 7.30 (2H, d, $^{3}J_{HH}$ = 7.78 Hz, H6), 7.34 (2H, d, $^{3}J_{HH}$ = 7.78 Hz, H13), 7.56 (2H, t(br), $^{3}J_{HH}$ = 7.78 Hz, H7, H14), 7.63-7.71 (4H, m, H20), 7.70-7.76 (4H, m, H19), 7.83-7.91 (2H, m, H21); **$^{13}$C{$^{1}$H} NMR** ($CH_2Cl_2$, in ppm): $\delta$ = 10.37 (1C, d, $^{1}J_{CP}$ = 62 Hz, C22), 22.56 (2C, s, C9), 23.66 (2C, s, C16), 23.97 (2C, s, C17), 24.92 (2C, s, C10), 29.11 (2C, s, C8), 29.33 (2C, s, C15), 55.03 (1C, s, C23), 97.23 (1C, d, $^{1}J_{CP}$ = 127 Hz, C2), 118.65 (2C, d, $^{1}J_{CP}$ = 93 Hz, C18), 121.65 (1C, q, $^{1}J_{CF}$ = 322 Hz, -$CF_3$), 125.11 (2C, s, C13), 125.88 (2C, s, C6), 128.24 (1C, s, C11), 130.79 (4C, d, $^{2}J_{CP}$ = 14 Hz, C19), 131.18 (1C, s, C7), 131.31 (1C, s, C4), 131.50 (1C, s, C14), 132.44 (4C, d, $^{3}J_{CP}$ = 11 Hz, C20), 135.73 (1C, d, $^{2}J_{CP}$ = 15 Hz, C3), 135.80 (2C, d, $^{4}J_{CP}$ = 3 Hz, C21), 147.80 (2C, s, C12), 148.89 (2C, s, C5), 151.66 (1C, d, $^{3}J_{CP}$ = 6 Hz C1); **$^{19}$F{$^{1}$H} NMR** ($CH_2Cl_2$, in ppm): $\delta$ = –79.01 (s, -$CF_3$); **$^{31}$P{$^{1}$H} NMR** ($CH_2Cl_2$, in ppm): $\delta$ = 9.64 (s).

### S3.33 Preparation of 36[OTf]




**31**[OTf] (88 mg, 0.11 mmol) was dissolved in THF (1.5 ml), giving a clear yellow solution. AuCl(tht) (36 mg, 0.11 mmol) was added accompanied by the formation of a colorless precipitate. The reaction mixture was stirred for 3 h, filtered and washed with THF (2 ml). After removing all volatiles in *vacuo* **36**[OTf] was isolated as colorless solid.

**Yield**: 79 mg, 71%; **mp**: 171-173 °C (decomp.); **IR** (ATR, in cm$^{-1}$): $\nu$ = 2968(vw), 2904(vw), 1587(vw), 1522(m), 1478(w), 1441(w), 1391(w), 1368(vw), 1345(vw), 1322(vw), 1285(vs), 1254(s), 1223(w), 1182(vw), 1143(vs), 1103(m), 1058(vw), 1030(s), 1014(vw), 935(vw), 900(65), 839(vw), 810(m), 787(w), 748(vs), 718(w), 688(s), 637(vs), 571(w), 535(w), 516(m), 487(m), 469(m), 439(m); **$^{1}$H NMR** ($CD_3CN$, in ppm): $\delta$ = 1.04 (6H, d, $^{3}J_{HH}$ = 6.84 Hz, H9), 1.24 (6H, d, $^{3}J_{HH}$ = 6.68 Hz, H17), 1.43 (6H, d, $^{3}J_{HH}$ = 6.84 Hz, H10), 1.54 (6H, d, $^{3}J_{HH}$ = 6.68 Hz,

H16), 1.98 (3H, d, $^{1}J_{HP}$ = 13.71 Hz, H22), 2.36 (1H, s, H23), 2.58 (2H, *pseudo* sept, $^{3}J_{HH}$ = 6.68 Hz, H15), 2.65 (2H, *pseudo* sept, $^{3}J_{HH}$ = 6.84 Hz, H8), 7.58 (4H, d, $^{3}J_{HH}$ = 7.91 Hz, H6, H13), 7.65-7.72 (4H, m, H20), 7.75 (1H, t, $^{3}J_{HH}$ = 7.91 Hz, H14), 7.79 (1H, t, $^{3}J_{HH}$ = 7.91 Hz, H7), 7.79-7.86 (4H, m, H19), 7.95-8.02 (2H, m, H21); **$^{13}$C{$^{1}$H} NMR** ($CD_3CN$, in ppm): $\delta$ = 8.53 (1C, s, C23), 9.21 (1C, d, $^{1}J_{CP}$ = 57 Hz, C22), 23.02 (2C, s, C9), 23.65 (2C, s, C16), 24.27 (2C, s, C17), 25.87 (2C, s, C10), 29.29 (2C, s, C8), 29.68 (2C, s, C15), 108.21 (1C, d, $^{1}J_{CP}$ = 114 Hz, C2), 115.83 (2C, d, $^{1}J_{CP}$ = 93 Hz, C18), 121.52 (1C, q, $^{1}J_{CF}$ = 319 Hz, -$CF_3$), 126.23 (2C, s, C13), 126.39 (1C, s, C11), 127.15 (2C, s, C6), 127.92 (1C, s, C4), 131.22 (4C, d, $^{2}J_{CP}$ = 14 Hz, C19), 132.91 (4C, d, $^{3}J_{CP}$ = 12 Hz, C20), 133.12 (1C, s, C14), 133.80 (1C, s, C7), 136.68 (2C, d, $^{4}J_{CP}$ = 3 Hz, C21), 137.42 (1C, d, $^{2}J_{CP}$ = 15 Hz, C3), 146.14 (2C, s, C12), 146.57 (2C, s, C5), 168.72 (1C, d, $^{3}J_{CP}$ = 4 Hz C1); **$^{19}$F{$^{1}$H} NMR** ($CH_2Cl_2$, in ppm): $\delta$ = –79.30 (s, -$CF_3$); **$^{31}$P{$^{1}$H} NMR** ($CH_2Cl_2$, in ppm): $\delta$ = 14.30 (s).

## S4 Crystallographic Details

***Table S4.1***: Crystallographic data and details of the structure refinements of compounds **9b**[OTf], **10b**[OTf], **14b**$[OTf]_2$ and **15b**[OTf].

| | **9b**[OTf]·$C_6H_4F_2$ | **10b**[OTf]·$C_6H_4F_2$ | **14b**$[OTf]_2$ | **15b**[OTf]· 1.5 $CH_2Cl_2$ |
|---|---|---|---|---|
| formula | $C_{46}H_{48}Cl_2F_5N_2O_3PS$ | $C_{46}H_{48}Cl_2F_5N_2O_3PS$ | $C_{42}H_{47}Cl_2F_6N_2O_6PS_2$ | $C_{41.5}H_{47}Cl_5F_5N_2O_3PS$ |
| $M_r$ / g mol$^{-1}$ | 905.79 | 905.79 | 955.83 | 957.09 |
| color, habit | colorless block | colorless block | colorless stick | colorless block |
| crystal system | triclinic | monoclinic | monoclinic | triclinic |
| space group | *P*-1 | $P2_1/n$ | $P2_1/c$ | *P*-1 |
| *a* / Å | 12.4108(2) | 16.2304(11) | 14.924(13) | 12.8733(4) |
| *b* / Å | 12.7149(3) | 18.8946(12) | 15.476(13) | 13.2711(4) |
| *c* / Å | 14.6973(3) | 29.2339(18) | 20.278(18) | 15.8278(4) |
| $\alpha$ / ° | 106.9695(17) | 90 | 90 | 67.6070(10) |
| $\beta$ / ° | 91.5755(14) | 94.813(2) | 107.78(2) | 69.0530(10) |
| $\gamma$ / ° | 100.6970(16) | 90 | 90 | 75.4420(10) |
| *V* / Å$^3$ | 2171.47(7) | 8933.5(10) | 4460(7) | 2314.07(12) |
| *Z* | 2 | 8 | 4 | 1 |
| *T* / K | 153(2) | 100(2) | 153(2) | 173(2) |
| crystal size / mm$^3$ | 0.24x0.14x0.09 | 0.13x0.06x0.05 | 0.20x0.15x0.10 | 0.35x0.25x0.04 |
| $\rho_c$ / g cm$^{-3}$ | 1.385 | 1.347 | 1.4235 | 1.374 |
| F(000) | 944 | 3776 | 1987 | 990 |
| $\lambda_{XK\alpha}$ / Å | 0.71073 (X = Mo) | 0.71073 (X = Mo) | 0.71073 (X = Mo) | 0.71073 (X = Mo) |
| $\theta_{min}$ / ° | 2.139 | 2.50 | 1.50 | 2.547 |
| $\theta_{max}$ / ° | 34.970 | 26.30 | 29.14 | 28.34 |
| index range | −19 ≤ h ≤ 19<br>−19 ≤ k ≤ 20<br>−23 ≤ l ≤ 23 | −20 ≤ h ≤ 20<br>−23 ≤ k ≤ 23<br>−35 ≤ l ≤ 36 | −20 ≤ h ≤ 13<br>0 ≤ k ≤ 21<br>0 ≤ l ≤ 27 | −16 ≤ h ≤ 16<br>−17 ≤ k ≤ 17<br>−20 ≤ l ≤ 20 |
| $\mu$ / mm$^{-1}$ | 0.299 | 0.291 | 0.349 | 0.452 |
| absorption correction | multi-scan | multi-scan | multi-scan | multi-scan |
| refl. collected | 81346 | 188008 | 40162 | 39542 |
| refl. unique | 18665 | 19058 | 11957 | 10851 |
| $R_{int}$ | 0.0326 | 0.0560 | 0.0308 | 0.0213 |
| reflection obs. [F>3σ(F)] | 14138 | 15029 | 9119 | 8587 |
| residual density min / max / e Å$^{-3}$ | 0.926 / -0.613 | 0.508 / -0.538 | 0.754 / -0.603 | 0.759 / -0.777 |
| structure solution | Superflip | Superflip | Superflip | Superflip |
| parameters | 549 | 1164 | 558 | 613 |
| GOOF | 1.022 | 1.168 | 1.039 | 1.046 |
| $R_1$ [I>2σ(I)] | 0.0398 | 0.0689 | 0.0439 | 0.0459 |
| $wR_2$ | 0.0996 | 0.1567 | 0.1162 | 0.1341 |
| CCDC | 1450350 | 1450349 | 1450346 | 1450345 |

***Table S4.2***: Crystallographic data and details of the structure refinements of compounds **16b**[OTf]$_2$, **17b**[OTf], **19**[OTf] and **20**[OTf].

| | **16b**[OTf]$_2$ | **17b**[OTf] $\cdot$0.5 $C_6H_4F_2$ | **19**[OTf]$\cdot CH_2Cl_2$ | **20**[OTf]$\cdot 2CH_3CN$ |
|---|---|---|---|---|
| formula | $C_{41}H_{44}Cl_2F_7N_2O_6PS_2$ | $C_{44}H_{49}ClF_4N_2O_3PS$ | $C_{42}H_{49}AuCl_4F_3N_2O_3PS$ | $C_{45}H_{53}CuBrClF_3N_4O_3PS$ |
| $M_r$ / g mol$^{-1}$ | 959.79 | 828.33 | 1088.63 | 996.84 |
| color, habit | colorless block | colorless block | colorless stick | colorless block |
| crystal system | monoclinic | triclinic | monoclinic | monoclinic |
| space group | $P2_1/c$ | $P$-1 | $P2_1/n$ | $P2_1/n$ |
| $a$ / Å | 12.5233(17) | 10.5789(17) | 12.2965(3) | 12.0550(4) |
| $b$ / Å | 14.8180(18) | 14.667(3) | 28.6164(8) | 32.3002(11) |
| $c$ / Å | 24.220(2) | 15.965(3) | 12.7029(4) | 12.1453(5) |
| $\alpha$ / ° | 90 | 64.828(9) | 90 | 90 |
| $\beta$ / ° | 99.726(5) | 70.980(9) | 91.453(2) | 91.944(2) |
| $\gamma$ / ° | 90 | 85.838(9) | 90 | 90 |
| $V$ / Å$^3$ | 4430.0(9) | 2113.1(6) | 4468.5(2) | 4726.4(3) |
| $Z$ | 4 | 2 | 4 | 4 |
| $T$ / K | 153(2) | 123(2) | 100(2) | 173(2) |
| crystal size / mm$^3$ | 0.15x0.10x0.03 | 0.24x0.20x0.14 | 0.17x0.09x0.09 | 0.42x 0.38x0.12 |
| $\rho_c$ / g cm$^{-3}$ | 1.4390 | 1.302 | 1.618 | 1.401 |
| F(000) | 1987 | 870 | 2176 | 2056 |
| $\lambda_{XK\alpha}$ / Å | 0.71073 (X = Mo) | 0.71073 (X = Mo) | 0.71073 (X = Mo) | 0.71073 (X = Mo) |
| $\theta_{min}$ / ° | 2.20 | 2.55 | 2.39 | 2.34 |
| $\theta_{max}$ / ° | 23.87 | 26.40 | 31.49 | 27.47 |
| index range | $-15 \le h \le 16$<br>$-19 \le k \le 18$<br>$-28 \le l \le 31$ | $-13 \le h \le 13$<br>$-19 \le k \le 19$<br>$-20 \le l \le 20$ | $-17 \le h \le 18$<br>$-42 \le k \le 42$<br>$-18 \le l \le 18$ | $-16 \le h \le 16$<br>$-38 \le k \le 44$<br>$-12 \le l \le 16$ |
| $\mu$ / mm$^{-1}$ | 0.354 | 0.237 | 3.666 | 1.496 |
| absorption correction | multi-scan | multi-scan | multi-scan | multi-scan |
| refl. collected | 34337 | 42703 | 58502 | 36664 |
| refl. unique | 10051 | 9407 | 14898 | 13013 |
| $R_{int}$ | 0.0454 | 0.0617 | 0.0342 | 0.0325 |
| reflection obs. [F>3σ(F)] | 6672 | 7359 | 12616 | 9535 |
| residual density min / max / e Å$^{-3}$ | 1.4741 / -0.8423 | 0.702 / -0.783 | 2.359 / -3.849 | 0.509 / -0.904 |
| structure solution | Superflip | Superflip | ShelXT | ShelXT |
| parameters | 557 | 584 | 523 | 581 |
| GOOF | 1.027 | 1.025 | 1.081 | 1.026 |
| $R_1$ [I>2σ(I)] | 0.0541 | 0.0525 | 0.0393 | 0.0475 |
| $wR_2$ | 0.1432 | 0.1408 | 0.0956 | 0.1202 |
| CCDC | 1450348 | 1450347 | 1450351 | 1450352 |

***Table S4.3***: Crystallographic data and details of the structure refinements of compounds **21**[OTf], **22**$[OTf]_3$ and **23**[OTf].

| | **21**[OTf]·$CH_2Cl_2$ | **22**$[OTf]_3$· 1.5 $Et_2O$·$CH_3CN$ | **23**[OTf]·$Et_2O$ |
|---|---|---|---|
| formula | $C_{41}H_{46}AuCl_4F_4N_2O_3PS$ | $C_{91}H_{112}AgCl_2F_9N_5O_{10.5}P_2S_3$ | $C_{53}H_{69}Cl_2F_3N_2O_4PRhS$ |
| $M_r$ / g mol$^{-1}$ | 1092.59 | 1951.74 | 1091.94 |
| color, habit | colorless block | colorless needle | yellow block |
| crystal system | monoclinic | triclinic | triclinic |
| space group | $P2_1/n$ | $P$-1 | $P$-1 |
| $a$ / Å | 11.8603(6) | 17.14476(19) | 10.8203(3) |
| $b$ / Å | 28.3452(14) | 17.1735(3) | 14.3026(4) |
| $c$ / Å | 13.1731(6) | 18.09533(13) | 18.3756(2) |
| $\alpha$ / ° | 90 | 98.7772(11) | 71.9557(17) |
| $\beta$ / ° | 92.001(3) | 101.6430(8) | 88.5118(16) |
| $\gamma$ / ° | 90 | 97.9382(12) | 78.384(2) |
| $V$ / Å$^3$ | 4425.9(4) | 5078.06(12) | 2646.53(10) |
| $Z$ | 4 | 2 | 2 |
| $T$ / K | 100(2) | 100(2) | 100(2) |
| crystal size / mm$^3$ | 0.18x0.11x0.06 | 0.48x 0.11x0.06 | 0.14x 0.91x0.04 |
| $\rho_c$ / g cm$^{-3}$ | 1.640 | 1.276 | 1.370 |
| F(000) | 2176 | 2034 | 1140 |
| $\lambda_{XK\alpha}$ / Å | 0.71073 (X = Mo) | 1.54184 (X = Cu) | 1.54184 (X = Cu) |
| $\theta_{min}$ / ° | 2.352 | 3.2240 | 3.3170 |
| $\theta_{max}$ / ° | 31.212 | 76.4080 | 76.3330 |
| index range | −16 ≤ h ≤ 17<br>−41 ≤ k ≤ 41<br>−19 ≤ l ≤ 17 | −19 ≤ h ≤ 21<br>−21 ≤ k ≤ 21<br>−22 ≤ l ≤ 22 | −13 ≤ h ≤ 13<br>−17 ≤ k ≤ 17<br>−23 ≤ l ≤ 21 |
| $\mu$ / mm$^{-1}$ | 3.705 | 3.550 | 4.647 |
| absorption correction | multi-scan | gaussian | gaussian |
| refl. collected | 70316 | 57825 | 26966 |
| refl. unique | 14924 | 21098 | 10839 |
| $R_{int}$ | 0.0506 | 0.0543 | 0.0350 |
| reflection obs. [F>3σ(F)] | 11901 | 19184 | 9934 |
| residual density min / max / e Å$^{-3}$ | 1.525 / -1.763 | 1.910 / -1.482 | 1.827 / -1.013 |
| structure solution | ShelXT | ShelXT | ShelXT |
| parameters | 579 | 1378 | 615 |
| GOOF | 1.040 | 1.053 | 1.068 |
| $R_1$ [I>2σ(I)] | 0.0323 | 0.0771 | 0.0376 |
| $wR_2$ | 0.0697 | 0.2214 | 0.1086 |
| CCDC | 1450353 | 1450355 | 1450354 |

***Table S4.3***: Crystallographic data and details of the structure refinements of compounds **34**[OTf], **35**$[OTf]_2$ and **36**[OTf].

| | **34**[OTf]·0.5 $Et_2O$ | **35**$[OTf]_2$·2 $Et_2O$ | **36**[OTf]·$CH_3CN$ |
|---|---|---|---|
| formula | $C_{45}H_{55}ClF_6N_2O_{6.5}PS_2$ | $C_{50}H_{69}ClF_3N_2O_5PS$ | $C_{44}H_{52}AuCl_2F_3N_3O_3PS$ |
| $M_r$ / g mol$^{-1}$ | 972.45 | 933.55 | 1058.78 |
| color, habit | colorless block | yellow plate | colorless block |
| crystal system | orthorhombic | monoclinic | monoclinic |
| space group | $P2_12_12_1$ | $P2_1/c$ | $P2_1/c$ |
| $a$ / Å | 21.61588(4) | 18.0515(9) | 10.7069(2) |
| $b$ / Å | 21.61899(5) | 13.7825(6) | 21.3249(4) |
| $c$ / Å | 41.02783(8) | 20.6137(9) | 19.5715(5) |
| $\alpha$ / ° | 90 | 90 | 90 |
| $\beta$ / ° | 90 | 90.735(2) | 102.332(2) |
| $\gamma$ / ° | 90 | 90 | 90 |
| $V$ / Å$^3$ | 19172.86(7) | 5128.2(4) | 4365.52(16) |
| $Z$ | 16 | 4 | 4 |
| $T$ / K | 100(2) | 173(2) | 100(2) |
| crystal size / mm$^3$ | 0.49x0.30x0.24 | 0.31x 0.23x0.08 | 0.23x 0.13x0.12 |
| $\rho_c$ / g cm$^{-3}$ | 1.348 | 1.209 | 1.611 |
| F(000) | 8144 | 1992 | 2128 |
| $\lambda_{XK\alpha}$ / Å | 1.54184 (X = Cu) | 0.71073 (X = Mo) | 1.54184 (X = Cu) |
| $\theta_{min}$ / ° | 2.8650 | 2.256 | 3.0950 |
| $\theta_{max}$ / ° | 76.610 | 27.179 | 75.7480 |
| index range | −27 ≤ h ≤ 27<br>−27 ≤ k ≤ 27<br>−51 ≤ l ≤ 51 | −22 ≤ h ≤ 19<br>−17 ≤ k ≤ 16<br>−25 ≤ l ≤ 25 | −13 ≤ h ≤ 13<br>−16 ≤ k ≤ 26<br>−24 ≤ l ≤ 24 |
| $\mu$ / mm$^{-1}$ | 2.458 | 0.202 | 8.718 |
| absorption correction | multi-scan | gaussian | gaussian |
| refl. collected | 232073 | 50197 | 25208 |
| refl. unique | 40155 | 10485 | 9104 |
| $R_{int}$ | 0.0352 | 0.0299 | 0.0296 |
| reflection obs. [F>3σ(F)] | 40144 | 8088 | 8508 |
| residual density min / max / e Å$^{-3}$ | 0.950 / -0.525 | 1.104/ -0.807 | 2.016/ -1.303 |
| structure solution | ShelXT | ShelXT | ShelXT |
| parameters | 2406 | 589 | 533 |
| GOOF | 1.052 | 1.020 | 1.050 |
| $R_1$ [I>2σ(I)] | 0.0396 | 0.0621 | 0.0309 |
| $wR_2$ | 0.1073 | 0.1795 | 0.0757 |
| CCDC | 1469788 | 1469787 | 1469786 |

## S4.1 Structure solution and refinement

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 low temperature as indicated in tables S4.1-4.3 on either a Bruker Kappa APEX II diffractometer

using Mo $K_\alpha$ radiation ($\lambda = 0.71073$ Å) generated using a fine-focus sealed tube or on a Rigaku Oxford Diffraction SuperNova diffractometer using Cu $K_\alpha$ radiation ($\lambda = 1.54184$ Å) generated by a Nova micro-focus source. The data reduction and absorption correction was performed using Bruker SMART[4] and Bruker SADABS[5] or CrysAlisPro[6], respectively. For further crystal and data collection details see tables S4.1-4.3. Using Olex2[7], the structures were solved with the SHELXT package[8] by direct methods or with Superflip[9] Hydrogen atoms bonded to carbon atoms were added to the structure models on calculated positions using the riding model. Images of the Structures depicted were produced with Diamond[10] software.

Crystals of **22**$[OTf]_3 \cdot 1.5\ C_4H_{10}O \cdot CH_3CN$ loose solvent easily and were therefore handled below −20 °C at all times. It was also possible to crystallize **22**$[OTf]_3$ from THF, but disorder of the anions and of the 10 THF molecules per trication rendered satisfactory refinement impossible (Space group *Pbcn*, *a:* 25.3195(3), *b:* 18.4175(3), *c:* 26.8985(3); Ag on ½, 0.782, ¼).

Structures **10b**$[OTf] \cdot C_6H_4F_2$, **14b**$[OTf]_2$ and **15b**$[OTf] \cdot CH_2Cl_2$ exhibit very short Cl1–OTf distances of 2.6–2.8 Å causing checkCIF A and B alerts. This corresponds well to the calculated σ-hole of the phosphonio-imidazolium species **14b**$[OTf]_2$ supporting the close contact between cation and anion.

In some structures SIMU, DFIX or SADI restraints (**10b**$[OTf] \cdot C_6H_4F_2$, **15b**$[OTf] \cdot CH_2Cl_2$, **17b**$[OTf] \cdot 0.5\ C_6H_4F_2$, **20**$[OTf] \cdot 2\ CH_3CN$, **21**$[OTf] \cdot CH_2Cl_2$, **22**$[OTf]_3 \cdot 1.5\ C_4H_{10}O \cdot CH_3CN$) or an EADP constraint (**10b**$[OTf] \cdot C_6H_4F_2$) were employed in order to allow convergence of disordered solvent molecules or anions to a reasonable minimum.

## S5 Computational methods

### S5.1 General Considerations

The energies of all complexes included in this study were computed using either the DFT BP86[11]-D3[12] functional or the ab initio RI-MP2[13] method using the def2-TZVP[14] basis set. The calculations have been performed by using the program TURBOMOLE version 7.0.[15] The MEPS calculations have been performed at the ab-initio/DFT-D level by means of the SPARTAN software.[16]

### S5.2 Cartesian coordinates of the optimized compounds

***Table S5.2.1***: Reactants; Figure 5 (A); MP2-optimized.

| | | | |
|---|---|---|---|
| P | −3.4447061 | −1.3207040 | 0.0602280 |
| N | −0.6234714 | 1.4206168 | −0.1699352 |
| N | −0.6708394 | −0.7239636 | 0.0627691 |
| C | −1.9487706 | 1.0731119 | −0.1643669 |
| C | −1.9922659 | −0.3035571 | −0.0152928 |
| C | 0.1522868 | 0.3286036 | −0.0319869 |
| Cl | 1.8160333 | 0.2957711 | 0.0118706 |
| P | 4.9659910 | 0.2631353 | 0.0918405 |
| H | −0.2639074 | 2.3718358 | −0.2648722 |
| H | −0.3228378 | −1.6748089 | 0.1749143 |
| H | −3.4674387 | −2.2559064 | −0.9791316 |
| H | −4.5340377 | −0.4565456 | −0.0620975 |
| H | −3.5240259 | −2.0080540 | 1.2754055 |
| H | 5.6757216 | −0.9367344 | 0.2746413 |
| H | 5.6520811 | 1.0083482 | 1.0668143 |
| H | 5.7033305 | 0.7217519 | −1.0138850 |

***Table S5.2.2:*** Transition state (TS); Figure 5 (A); MP2-optimized.

| | | | |
|---|---|---|---|
| P | −3.0886144 | −1.7440454 | 0.0002855 |
| N | −0.3061452 | 1.0217152 | −0.0013735 |
| N | −0.3192255 | −1.1138892 | 0.0006910 |
| C | −1.6277668 | 0.6676420 | −0.0015134 |
| C | −1.6510577 | −0.7176846 | −0.0002025 |
| C | 0.5003242 | −0.0566307 | −0.0000411 |
| Cl | 2.5231110 | −0.0381252 | 0.0004868 |
| P | 4.8861277 | 0.0181032 | 0.0010212 |
| H | 0.0314205 | 1.9828628 | −0.0021871 |

| | | | |
|---|---|---|---|
| H | 0.0327463 | -2.0672595 | 0.0017076 |
| H | -3.1412836 | -2.5687672 | -1.1269916 |
| H | -4.1940595 | -0.8924470 | -0.0030733 |
| H | -3.1443984 | -2.5638287 | 1.1310166 |
| H | 5.5048475 | -1.2365079 | 0.0320349 |
| H | 5.4457191 | 0.6980163 | 1.0883274 |
| H | 5.4479135 | 0.6446582 | -1.1167883 |

***Table S5.2.3***: 15 lowest vibrations of the TS; MP2-optimized.

| # | | cm**(-1) | km/mol | IR | RAMAN |
|---|---|---|---|---|---|
| 1 | a | -420.29 | 0.00000 | YES | YES |
| 2 | | -0.00 | 0.00000 | - | - |
| 3 | | -0.00 | 0.00000 | - | - |
| 4 | | -0.00 | 0.00000 | - | - |
| 5 | | -0.00 | 0.00000 | - | - |
| 6 | | 0.00 | 0.00000 | - | - |
| 7 | | 0.00 | 0.00000 | - | - |
| 8 | a | 64.56 | 4.44479 | YES | YES |
| 9 | a | 72.40 | 3.65093 | YES | YES |
| 10 | a | 174.01 | 4.64993 | YES | YES |
| 11 | a | 190.63 | 0.03114 | YES | YES |
| 12 | a | 192.66 | 0.37189 | YES | YES |
| 13 | a | 217.62 | 5.84854 | YES | YES |
| 14 | a | 233.60 | 6.86201 | YES | YES |
| 15 | a | 239.36 | 3.26237 | YES | YES |

***Table S5.2.4***: Products (P); Figure 5 (A); MP2-optimized.

| | | | |
|---|---|---|---|
| P | -3.6459012 | -1.3705391 | 0.0016344 |
| N | -0.8012703 | 1.2850570 | -0.0027323 |
| N | -0.8624994 | -0.8225027 | 0.0010193 |
| C | -2.1277246 | 0.9761182 | -0.0024040 |
| C | -2.1886624 | -0.4039113 | 0.0000152 |
| C | 0.0324868 | 0.1962648 | -0.0006701 |
| Cl | 3.3928075 | 0.3471797 | 0.0016076 |
| P | 5.3390393 | 0.4998923 | 0.0007096 |
| H | -0.4602332 | 2.2395243 | -0.0044745 |
| H | -0.5561748 | -1.7864166 | 0.0026964 |
| H | -3.7482941 | -2.2045169 | -1.1149476 |
| H | -4.7321447 | -0.4960600 | -0.0023205 |
| H | -3.7510196 | -2.1975925 | 1.1231167 |
| H | 5.9243895 | -0.7651284 | 0.0255254 |
| H | 5.7698795 | 1.2106924 | 1.1200099 |
| H | 5.7721920 | 1.1673897 | -1.1440670 |

***Table S5.2.5***: Figure 5(B); DFT-optimized.

| | | | |
|---|---|---|---|
| Cl | -3.5887698 | 2.3940945 | 0.3138909 |
| P | -4.2051023 | -1.1552383 | 0.2359855 |
| N | -1.1169848 | 1.3853178 | 0.1909853 |
| N | -1.3468944 | -0.7855082 | 0.0443998 |
| C | -2.4791282 | 1.1265551 | 0.1677631 |
| C | -2.6497167 | -0.2473504 | 0.0709539 |
| C | -0.4505381 | 0.2128840 | 0.1164231 |
| Cl | 1.3089660 | 0.0830483 | 0.1990492 |
| P | 3.9995767 | 0.3232344 | 0.2707935 |
| C | -5.4244608 | -0.1363658 | -0.6008359 |
| C | -5.1515340 | 0.3566359 | -1.8904043 |
| C | -6.6547289 | 0.1268247 | 0.0194946 |
| C | -6.1165676 | 1.1097853 | -2.5542128 |
| H | -4.1868382 | 0.1651877 | -2.3643639 |
| C | -7.6126414 | 0.8841286 | -0.6564381 |
| H | -6.8609659 | -0.2447879 | 1.0236334 |
| C | -7.3455100 | 1.3729502 | -1.9378653 |
| H | -5.9098363 | 1.4967434 | -3.5519718 |
| H | -8.5689112 | 1.0949230 | -0.1778105 |
| H | -8.0966882 | 1.9664392 | -2.4594180 |
| C | -4.1889574 | -2.8012465 | -0.4936763 |
| C | -4.8087334 | -3.0189760 | -1.7366896 |
| C | -3.6331915 | -3.8810340 | 0.2172930 |
| C | -4.8527589 | -4.3089799 | -2.2665271 |
| H | -5.2709498 | -2.1979630 | -2.2825055 |
| C | -3.6743110 | -5.1604037 | -0.3274779 |
| H | -3.1658958 | -3.7258314 | 1.1875321 |
| C | -4.2828903 | -5.3764168 | -1.5684332 |
| H | -5.3401467 | -4.4782203 | -3.2265224 |
| H | -3.2337961 | -5.9911656 | 0.2228590 |
| H | -4.3219153 | -6.3821543 | -1.9875879 |
| C | 4.3376045 | 1.6782602 | 1.4399250 |
| C | 5.3641561 | 1.5983711 | 2.3943771 |
| C | 3.4877372 | 2.8017167 | 1.4331769 |
| C | 5.5432127 | 2.6270501 | 3.3221949 |
| H | 6.0281708 | 0.7337128 | 2.4082135 |
| C | 3.6862845 | 3.8325996 | 2.3503223 |
| H | 2.6792783 | 2.8803872 | 0.7020767 |
| C | 4.7095442 | 3.7471351 | 3.2998135 |
| H | 6.3457575 | 2.5560576 | 4.0569862 |
| H | 3.0377672 | 4.7080437 | 2.3233757 |
| H | 4.8595129 | 4.5545431 | 4.0171832 |
| C | 5.3202685 | -0.9045306 | 0.5077355 |
| C | 6.5428998 | -0.8326039 | -0.1796401 |
| C | 5.1024652 | -1.9373233 | 1.4348751 |

| | | | |
|---|---|---|---|
| C | 7.5365139 | -1.7811510 | 0.0676558 |
| H | 6.7161994 | -0.0361497 | -0.9047755 |
| C | 6.1038332 | -2.8766034 | 1.6860779 |
| H | 4.1464937 | -2.0016682 | 1.9593023 |
| C | 7.3202892 | -2.7994178 | 1.0013605 |
| H | 8.4851346 | -1.7223543 | -0.4669325 |
| H | 5.9339273 | -3.6732870 | 2.4110442 |
| H | 8.1005586 | -3.5366055 | 1.1928537 |
| C | 4.2383304 | 1.0083365 | -1.4024325 |
| C | 3.8338515 | 0.1978561 | -2.4797234 |
| C | 4.7484862 | 2.2893535 | -1.6601978 |
| C | 3.9505736 | 0.6571206 | -3.7908130 |
| H | 3.4303268 | -0.7991243 | -2.2874075 |
| C | 4.8505740 | 2.7501964 | -2.9754570 |
| H | 5.0701772 | 2.9253271 | -0.8350351 |
| C | 4.4543374 | 1.9378961 | -4.0407472 |
| H | 3.6461693 | 0.0172607 | -4.6199059 |
| H | 5.2539669 | 3.7450384 | -3.1681584 |
| H | 4.5427069 | 2.2997660 | -5.0654607 |
| C | -0.4940106 | 2.6776084 | 0.3812262 |
| C | -0.1043449 | 3.3962119 | -0.7589905 |
| C | -0.3137990 | 3.1124937 | 1.7054883 |
| C | 0.4685701 | 4.6541636 | -0.5316672 |
| C | 0.2437347 | 4.3853457 | 1.8681687 |
| C | 0.6219425 | 5.1483961 | 0.7632126 |
| H | 0.7928176 | 5.2558236 | -1.3809035 |
| H | 0.4000325 | 4.7760640 | 2.8737162 |
| H | 1.0556892 | 6.1375494 | 0.9134928 |
| C | -0.9463046 | -2.1778609 | -0.0172322 |
| C | -0.8466633 | -2.7724804 | -1.2906190 |
| C | -0.6244683 | -2.8208258 | 1.1917283 |
| C | -0.4136216 | -4.1019432 | -1.3222738 |
| C | -0.1929839 | -4.1510772 | 1.0911341 |
| C | -0.0899685 | -4.7813284 | -0.1464749 |
| H | -0.3251328 | -4.6159398 | -2.2780929 |
| H | 0.0741165 | -4.6959059 | 1.9970514 |
| H | 0.2527711 | -5.8151763 | -0.1989603 |
| C | -0.6467921 | 2.2428854 | 2.9077154 |
| H | -1.0801279 | 1.2959315 | 2.5444952 |
| C | -0.2724249 | 2.8509275 | -2.1671031 |
| H | -0.7096652 | 1.8413980 | -2.0983935 |
| C | -0.7045990 | -2.1412560 | 2.5529650 |
| H | -1.1274353 | -1.1320944 | 2.4174602 |
| C | -1.1575990 | -2.0009211 | -2.5669954 |
| H | -1.9426630 | -1.2628235 | -2.3281298 |
| C | -1.6970469 | 2.8989132 | 3.8181743 |

| | | | |
|---|---|---|---|
| H | −1.3215634 | 3.8352977 | 4.2524948 |
| H | −2.6185288 | 3.1321834 | 3.2656999 |
| H | −1.9492810 | 2.2290131 | 4.6528225 |
| C | 0.6362410 | 1.8764374 | 3.6758492 |
| H | 1.3618467 | 1.3734029 | 3.0222628 |
| H | 1.1262952 | 2.7716998 | 4.0820903 |
| H | 0.4002791 | 1.2091431 | 4.5163569 |
| C | −1.2484563 | 3.7160038 | −2.9835738 |
| H | −2.2279530 | 3.7903505 | −2.4896938 |
| H | −0.8605377 | 4.7359747 | −3.1130708 |
| H | −1.3938675 | 3.2868647 | −3.9848196 |
| C | 1.0899901 | 2.7039548 | −2.8648893 |
| H | 1.5681907 | 3.6802063 | −3.0219761 |
| H | 1.7800426 | 2.0845772 | −2.2762899 |
| H | 0.9672102 | 2.2327112 | −3.8496221 |
| C | 0.0832988 | −1.2254881 | −3.0584238 |
| H | 0.4625475 | −0.5089696 | −2.3198465 |
| H | 0.8989492 | −1.9254963 | −3.2870567 |
| H | −0.1545500 | −0.6701447 | −3.9764962 |
| C | −1.6993041 | −2.8914731 | −3.6932207 |
| H | −2.5243982 | −3.5268231 | −3.3485747 |
| H | −2.0647943 | −2.2672403 | −4.5197604 |
| H | −0.9153148 | −3.5408265 | −4.1067207 |
| C | −1.6338576 | −2.8955055 | 3.5200796 |
| H | −1.6936273 | −2.3611267 | 4.4776767 |
| H | −2.6563374 | −2.9826838 | 3.1277622 |
| H | −1.2598201 | −3.9071106 | 3.7290651 |
| C | 0.6976785 | −1.9792585 | 3.1714686 |
| H | 1.3748644 | −1.4304870 | 2.5055088 |
| H | 0.6324850 | −1.4309612 | 4.1210420 |
| H | 1.1459854 | −2.9605009 | 3.3815143 |
| C | −4.5785549 | −1.2285219 | 1.9979828 |
| H | −4.7254126 | −0.2052160 | 2.3675350 |
| H | −5.4775973 | −1.8346342 | 2.1649093 |
| H | −3.7337404 | −1.6806939 | 2.5274193 |

***Table S5.2.6***: Figure 5 (C); DFT-optimized.

| | | | |
|---|---|---|---|
| Cl | −3.4039265 | 1.9603728 | −0.4448624 |
| P | −4.2532281 | −1.4068075 | 0.1482304 |
| N | −0.9758572 | 0.7677222 | −0.4068301 |
| N | −1.3359253 | −1.3166693 | −0.0239840 |
| C | −2.3475816 | 0.6324634 | −0.2945769 |
| C | −2.6120547 | −0.7029936 | −0.0437805 |
| C | −0.3304217 | −0.4287642 | −0.2296235 |
| Cl | 2.4530769 | −0.0120573 | 0.0080837 |
| P | 4.3690428 | 0.6518114 | 0.2560292 |

| | | | |
|---|---|---|---|
| C | -5.1531452 | -0.2765506 | 1.2290707 |
| C | -6.4982677 | 0.0211844 | 0.9646618 |
| C | -4.5133421 | 0.2700629 | 2.3556513 |
| C | -7.2003599 | 0.8603987 | 1.8314068 |
| H | -6.9926373 | -0.3858046 | 0.0825950 |
| C | -5.2243975 | 1.1048290 | 3.2147864 |
| H | -3.4617231 | 0.0559211 | 2.5506911 |
| C | -6.5672169 | 1.3992603 | 2.9542430 |
| H | -8.2439751 | 1.0969265 | 1.6242095 |
| H | -4.7293582 | 1.5316358 | 4.0870643 |
| H | -7.1197316 | 2.0560841 | 3.6264842 |
| C | -5.0789437 | -1.5218422 | -1.4514209 |
| C | -4.7077002 | -0.6945011 | -2.5227305 |
| C | -6.1619767 | -2.4107199 | -1.5861259 |
| C | -5.4142713 | -0.7592301 | -3.7221815 |
| H | -3.8590370 | -0.0194390 | -2.4331266 |
| C | -6.8644351 | -2.4642277 | -2.7900829 |
| H | -6.4494590 | -3.0616073 | -0.7597460 |
| C | -6.4916373 | -1.6406181 | -3.8564975 |
| H | -5.1193159 | -0.1221903 | -4.5558964 |
| H | -7.7007474 | -3.1550688 | -2.8960080 |
| H | -7.0397965 | -1.6897116 | -4.7976707 |
| C | 4.3733497 | 1.7330423 | 1.6860645 |
| C | 4.2256737 | 1.1585138 | 2.9626405 |
| C | 4.4629355 | 3.1263504 | 1.5366995 |
| C | 4.1783090 | 1.9826416 | 4.0837462 |
| H | 4.1507932 | 0.0758884 | 3.0750168 |
| C | 4.4111215 | 3.9404591 | 2.6688987 |
| H | 4.5833680 | 3.5709051 | 0.5489543 |
| C | 4.2706475 | 3.3715489 | 3.9371852 |
| H | 4.0720468 | 1.5420702 | 5.0750408 |
| H | 4.4905371 | 5.0219710 | 2.5589272 |
| H | 4.2374999 | 4.0124252 | 4.8185560 |
| C | 4.8173529 | 1.5380696 | -1.2349885 |
| C | 6.0921186 | 1.3657434 | -1.7997415 |
| C | 3.8942587 | 2.4331119 | -1.8025719 |
| C | 6.4394552 | 2.1006810 | -2.9338410 |
| H | 6.8021756 | 0.6621972 | -1.3641049 |
| C | 4.2576192 | 3.1623405 | -2.9315353 |
| H | 2.8984572 | 2.5536334 | -1.3742468 |
| C | 5.5271349 | 2.9979058 | -3.4964296 |
| H | 7.4247691 | 1.9685370 | -3.3806754 |
| H | 3.5425788 | 3.8553549 | -3.3747102 |
| H | 5.8052002 | 3.5678269 | -4.3834320 |
| C | 5.4568202 | -0.7464380 | 0.5260091 |
| C | 5.2009016 | -1.9704187 | -0.1148236 |

| | | | |
|---|---|---|---|
| C | 6.6190623 | -0.5706234 | 1.2988452 |
| C | 6.1103652 | -3.0173161 | 0.0241040 |
| H | 4.2963365 | -2.1037298 | -0.7089543 |
| C | 7.5216222 | -1.6264997 | 1.4256170 |
| H | 6.8150676 | 0.3791245 | 1.7972945 |
| C | 7.2679466 | -2.8456689 | 0.7905676 |
| H | 5.9154219 | -3.9710239 | -0.4661299 |
| H | 8.4231289 | -1.4964355 | 2.0243838 |
| H | 7.9756230 | -3.6684652 | 0.8956818 |
| C | -0.2982805 | 2.0182030 | -0.6496293 |
| C | -0.0581741 | 2.8639729 | 0.4456489 |
| C | 0.0770349 | 2.3264498 | -1.9714040 |
| C | 0.5574373 | 4.0947471 | 0.1765122 |
| C | 0.6551172 | 3.5829873 | -2.1877057 |
| C | 0.8885209 | 4.4601333 | -1.1268572 |
| H | 0.7641663 | 4.7816918 | 0.9980673 |
| H | 0.9349139 | 3.8760281 | -3.1992813 |
| H | 1.3403394 | 5.4341072 | -1.3189526 |
| C | -1.0443093 | -2.7042576 | 0.2670431 |
| C | -0.7569140 | -3.5873736 | -0.7904468 |
| C | -1.0099576 | -3.0875486 | 1.6262184 |
| C | -0.4766284 | -4.9181709 | -0.4388798 |
| C | -0.7340623 | -4.4282870 | 1.9115483 |
| C | -0.4772279 | -5.3389255 | 0.8873403 |
| H | -0.2533795 | -5.6329757 | -1.2330370 |
| H | -0.7139811 | -4.7664677 | 2.9463152 |
| H | -0.2674889 | -6.3819354 | 1.1273148 |
| C | -0.4221567 | 2.4769799 | 1.8711492 |
| H | -0.9120311 | 1.4912735 | 1.8473058 |
| C | -0.1449219 | 1.3423539 | -3.1089071 |
| H | -0.1708348 | 0.3355862 | -2.6660631 |
| C | -1.1828950 | -2.0637189 | 2.7411499 |
| H | -1.9321584 | -1.3287564 | 2.4038020 |
| C | -0.6383330 | -3.2150657 | -2.2669629 |
| H | -0.6937824 | -4.1753084 | -2.8045254 |
| C | 0.8443075 | 2.3263846 | 2.7295343 |
| H | 1.5121251 | 1.5608142 | 2.3143894 |
| H | 1.4061298 | 3.2691801 | 2.7849701 |
| H | 0.5836376 | 2.0307134 | 3.7555069 |
| C | -1.4150517 | 3.4725539 | 2.4943660 |
| H | -0.9703000 | 4.4724466 | 2.5964004 |
| H | -2.3214898 | 3.5665930 | 1.8820149 |
| H | -1.7092259 | 3.1378889 | 3.4992953 |
| C | -1.5018278 | 1.5913054 | -3.7925736 |
| H | -2.3276383 | 1.5810846 | -3.0672242 |
| H | -1.5137131 | 2.5737608 | -4.2861879 |

| | | | |
|---|---|---|---|
| H | -1.6970531 | 0.8220568 | -4.5529595 |
| C | 0.9994151 | 1.3405189 | -4.1310873 |
| H | 1.0408575 | 2.2753097 | -4.7081180 |
| H | 1.9726544 | 1.1972455 | -3.6410086 |
| H | 0.8551692 | 0.5232449 | -4.8506584 |
| C | -1.6838606 | -2.6529070 | 4.0647697 |
| H | -0.9110187 | -3.2631958 | 4.5532044 |
| H | -1.9383007 | -1.8426245 | 4.7618649 |
| H | -2.5736075 | -3.2787991 | 3.9240720 |
| C | 0.1392757 | -1.3017435 | 2.9702444 |
| H | 0.9165425 | -1.9981586 | 3.3169435 |
| H | 0.4976967 | -0.8224674 | 2.0496796 |
| H | 0.0059887 | -0.5266181 | 3.7385871 |
| C | -1.7515559 | -2.3361986 | -2.8536807 |
| H | -2.7515478 | -2.7081363 | -2.5944610 |
| H | -1.6846933 | -1.2915775 | -2.5287050 |
| H | -1.6786300 | -2.3374885 | -3.9501362 |
| C | 0.7535380 | -2.6182980 | -2.5581094 |
| H | 1.5477546 | -3.3172042 | -2.2607952 |
| H | 0.8637006 | -2.4105496 | -3.6324449 |
| H | 0.8974846 | -1.6833378 | -1.9989195 |
| C | -4.1732822 | -3.0406031 | 0.9089636 |
| H | -3.6108156 | -3.7368174 | 0.2756472 |
| H | -3.6910094 | -2.9548671 | 1.8884396 |
| H | -5.2024493 | -3.3935914 | 1.0510728 |

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