Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary information

Proton transfer vs. oligophosphine formation by P–C/P–H σ-bond metathesis: decoding the competing Brønsted and Lewis type reactivity of imidazolio-phosphines

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General conditions

Unless otherwise stated, all manipulations were carried out under an inert atmosphere of purified argon or nitrogen, either using flame-dried glassware and standard Schlenk techniques, or in gloveboxes. THF, *n*-pentane, *n*-hexane, benzene and diethyl ether were distilled from NaK alloy, and CH_2Cl_2 and CH_3CN from CaH_2, and stored in Schlenk-flasks under inert conditions. C_6D_6 and THF-D_8 were refluxed over NaK alloy for 72 h and CD_3CN over CaH_2 for 48 h, followed by distillation and storage over molecular sieves in a glovebox. Reaction monitoring experiments were carried out using NMR-tubes with a PTFE screw. Imidazolio-phosphides **4b-e** were prepared as described.[1]
NMR spectra were acquired on Bruker Avance 250 (^{1}H: 250.0 MHz, ^{11}B: 80.3 MHz, ^{13}C: 62.9 MHz, ^{19}F: 235.4 MHz, ^{31}P: 101.2 MHz) or Bruker Avance 400 (^{1}H: 400.1 MHz, ^{11}B: 128.4 MHz, ^{13}C: 100.5 MHz, ^{15}N 40.6: MHz, ^{31}P: 161.9 MHz) NMR spectrometers at 293 - 296 K if not stated otherwise. ^{1}H Chemical shifts were referenced to TMS using the signals of the residual protons of the deuterated solvent (δ^1H = 7.27 ($CDCl_3$), 7.15 (C_6D_6), 5.34 (CD_2Cl_2), 1.96 (CD_3CN), 1.73 (THF-D_8)) as secondary reference. Spectra of heteronuclei were referenced using the Ξ-scale[2] using $BF_3{\cdot}OEt_2$ (Ξ = 32.083974 MHz, ^{11}B), TMS (Ξ = 25.145020 MHz, ^{13}C), $MeNO_2$ (Ξ = 10.136767 MHz, ^{15}N), $CFCl_3$ (Ξ = 94.094011 MHz, ^{19}F), and 85 % H_3PO_4 (Ξ = 40.480747 MHz, ^{31}P) as secondary references. Coupling constants are generally given as absolute values unless stated otherwise. Spectra of mixtures or of single components giving rise to higher order splitting patterns were analysed by spectral simulation, which was performed using the DAISY spectrum simulation module in the Bruker TopSpin software. In simulations of higher order spectra comprising splitting patterns that are sensitive to the relative signs of coupling constants, the values of $^1J_{PP}$ were assumed to be negative. FTIR-spectra were recorded on a Thermo Scientific Nicolet iS5 spectrometer equipped with an iD5 attenuated total reflectance (ATR) unit under nitrogen atmosphere. Elemental analyses were performed with an Elementar Micro Cube elemental analyser. Mass spectra were obtained using Bruker Daltonics Microtof-Q (Electron spray ionization (ESI) at 0.4 bar, 200° C, dry gas flow 4.0 l min^{-1} with a set capillary of 4500 V, end plate offset -450 V in positive mode and at 1.0 bar, set capillary 2200 V in negative mode) or Varian MAT 711 (EI at 70 eV) mass spectrometers. Melting and decomposition temperatures were determined on a Büchi B-545 melting point apparatus in sealed capillaries under argon.

Synthetic procedures

Synthesis of imidazolio-phosphine iodides (1b-e)[I]

General procedure: A 50 ml round-bottomed Schlenk flask was charged the appropriate imidazolio-phosphide **4b-e** (500 mg, 1.2 – 3.9 mmol, 1 equiv.) The material was dissolved in toluene (at least 10 mL). The solution was cooled to -78 °C with a dry ice/*i*PrOH bath. Aqueous hydroiodic acid (67% soln, > 1.5 eq.) was rapidly added with a glass pipette under vigorous stirring. The water solidified immediately and melted eventually when the mixture was allowed to warm up to rt. The solvents were removed under reduced pressure. Toluene (10 mL) was added and the resulting yellowish slurry was stirred until a colourless precipitate formed. The solvent was again removed under reduced pressure. The remaining solid was dissolved in CH_2Cl_2 (5 mL) and the product precipitated by addition of Et_2O. The colourless solid was collected by filtration through a G4 glass frit and washed with *n*-pentane (5 mL). Colourless single crystals were grown from CH_2Cl_2/Et_2O (**1b**[I], **1e**[I]) or MeCN/*n*-pentane/Et_2O(**1c**[I], **1d**[I]).
1,3-Bis(2,6-diisopropylphenyl)-2-phosphino-imidazolium iodide 1b[I]: Yield 630 mg (97%). ^{1}H NMR (CD_3CN, 400 MHz): δ = 1.24 (12 H, d, $^3J_{HH}$ = 6.9 Hz, *i*Pr-CH_3), 1.27 (12 H, d, $^3J_{HH}$ = 6.9 Hz, *i*Pr-CH_3) 2.29 (4 H, sept, $^3J_{HH}$ = 6.9 Hz, *i*Pr-CH), 3.55 (2 H, d, $^1J_{PH}$ = 227 Hz, PH_2), 7.63 (6 H, m, *m*/*p*-CH), 8.05 (2 H, s, NCH). ^{13}C{^{1}H} NMR (CD_3CN, 100.6 MHz): δ = 22.3 (d, $^6J_{PC}$ = 1.7 Hz, *i*Pr-CH_3), 23.8 (s, *i*Pr-CH_3), 29.0 (s, *i*Pr-CH), 125.5 (s, *m*-CH), 127.9 (s, NCH), 130.4 (s, *i*-C), 132.6 (s, *p*-C), 145.2 (s, *o*-C), 147.8 (d, $^1J_{PC}$ = 40.4 Hz, CP). ^{15}N NMR (HMBC, CD_3CN, 40.6 MHz): δ -187.6 (2 N, s, NCN). ^{31}P NMR (CD_3CN, 161.9 MHz): δ -165.6 (1 P, t, $^1J_{PH}$ = 227 Hz, PH_2). ATR-IR: ṽ/cm^{-1} = 3160 (w), 3133 (vw), 3027 (vw/br), 2963 (s), 2926 (m), 2869 (m), 2360 (w), 2324 (br), 1594 (w), 1547 (m), 1459 (s/br), 1388 (m), 1367 (m), 1328 (m), 1276 (w), 1256 (w), 1208 (m), 1180 (m), 1134 (w), 1117 (w), 1060 (m), 1037 (w/br), 979 (w), 952 (w), 936 (m), 840 (m/br), 810 (vs), 759 (vs), 687 (m), 637 (w). $C_{27}H_{38}IN_2P \cdot 0.5MeCN$ (569.01 g mol^{-1}): calcd. C 59.10 H 7.00 N 6.15, found C 58.79 H 6.84 N 6.10.
1,3-Bis(2,4,6-trimethylphenyl)-2-phosphino-imidazolium iodide 1c[I]: Yield 649 mg (94%). ^{1}H NMR (CD_3CN, 250 MHz): δ = 2.06 (12 H, s, *o*-CH_3), 2.39 (6 H, s, *p*-CH_3), 3.57 (2 H, d, $^1J_{PH}$ = 227 Hz, PH_2), 7.22 (4 H, s, *m*-CH), 7.87 (2 H, s, NCH). ^{13}C{^{1}H} NMR (CD_3CN, 62.8 MHz): δ = 16.7 (s, *o*-CH_3), 20.3 (s, *p*-CH_3), 126.84 (s, NCH), 126.84 (s, NCH), 130 (s, *m*-CH), 131.1 (s, *i*-C), 134.6 (s, *o*-C), 134.7 (s, *o*-C), 142.1 (s, *p*-C), 146 (d, $^1J_{PC}$ = 40.4 Hz, NCN). ^{31}P NMR (CD_3CN, 101.2 MHz): δ = -170.4 (t, $^1J_{PH}$ = 227 Hz, PH_2). ATR-IR: ṽ/cm^{-1} = 3144 (m), 3070 (m/br), 2974 (m), 2916 (m), 2246 (w/br), 1606 (m), 1552 (m), 1484 (s), 1456 (m), 1383 (m), 1237 (s), 1173 (vw), 1040 (s), 1135 (m), 1013 (w), 932 (m), 868 (w), 852 (s), 836 (w), 757 (m), 732 (m), 684 (vs). $C_{21}H_{26}IN_2P \cdot 0.5MeCN$ (484.85 g mol^{-1}): calcd. C 54.50 H 5.72 N 7.22, found: C 54.23 H 5.69 N 7.32.
1,3-Diisopropyl-2-phosphino-imidazolium iodide 1d[I]: Yield 813 mg (96%). ^{1}H NMR (CD_3CN, 400 MHz): δ = 1.51 (12 H, d, $^3J_{HH}$ = 6.7 Hz, *i*Pr-CH_3), 4.13 (2 H, d, $^1J_{PH}$ = 227 Hz, PH_2), 4.91 (2 H, dsept, $^3J_{HH}$ = 6.7 Hz, $^4J_{PH}$ = 2.6 Hz, *i*Pr-

CH), 7.72 (2 H, s, NCH). ^{13}C{^{1}H} NMR (CD$_3$CN, 100.6 MHz): δ = 21.9 (s, *i*Pr-CH$_3$), 53.1 (s, *i*Pr-CH), 120.5 (s, NCH), 139.9 (PC). ^{31}P NMR (CD$_3$CN, 161.9 MHz): δ = -174.5 (dt, $^{1}J_{PH}$ = 227 Hz, $^{4}J_{PH}$ = 2.6 Hz, PH$_2$). ATR-IR: $\tilde{\nu}$/cm^{-1} = 3170 (w), 3069 (br), 2972 (m), 2959 (m), 2871 (m), 2322 (w/br), 1559 (m), 1452 (s), 1424 (w), 1412 (w), 1389 (m), 1369 (w), 1352 (w), 1207 (vs), 1188 (m), 1134 (s), 1078 (m), 1050 (m), 941 (w), 888 (s), 841 (s), 746 (vs), 667 (vs). $C_9H_{18}IN_2P$ (312.13 g mol^{-1}): calcd. C 34.63 H 5.81 N 8.97, found C 34.53 H 5.64 N: 9.00.

1,3-Dimethyl-2-phosphino-imidazolium iodide 1e[I]: Yield 940 mg (94%). ^{1}H NMR (CD$_3$CN, 400 MHz): δ = 3.86 (6 H, s, NCH$_3$), 3.98 (2 H, d, $^{1}J_{PH}$ = 226 Hz, PH$_2$), 7.50 (2 H, d, $^{4}J_{PH}$ = 0.5 Hz, NCH). ^{13}C{^{1}H} NMR (CD$_3$CN, 100.6 MHz): δ = 37.2 (d, $^{3}J_{PC}$ = 4.5 Hz, NCH$_3$), 125.4 (s, NCH), 142.7 (m, PC). ^{15}N NMR (^{1}H,^{15}N HMBC, CD$_3$CN, 40.6 MHz): δ = -197.9. ^{31}P NMR (CD$_3$CN, 161.9 MHz): δ = -176.1 (t, $^{1}J_{PH}$ = 226 Hz, PH$_2$). ATR-IR: $\tilde{\nu}$/cm^{-1} = 3087 (s), 3060 (s), 2263 (br), 1647 (w), 1571 (m), 1505 (m), 1469 (w), 1430 (s), 1407 (m), 1350 (m), 1247 (vs), 1110 (s), 1057 (w), 1036 (m), 842 (s), 777 (vs), 730 (w), 628 (vs). $C_5H_{10}IN_2P$ (256.02 g mol^{-1}): calcd. C 23.46 H 3.94 N 10.94, found C 23.47 H 3.92 N 19.92.

Synthesis of imidazolio-phosphine tetrafluoroborates (1b,d)[BF$_4$]

General procedure: A solution of 500 mg of the appropriate imidazolio-phosphide (**4b**,**d**, 1.2 – 2.7 mmol, 1 equiv.) in toluene (at least 10 mL) was prepared in a 50 ml round-bottomed Schlenk flask and cooled to -78° C under vigorous stirring. Ice-cold ethereal HBF$_4$ (54% soln. in Et$_2$O, 1.5 equiv.) was added quickly under vigorous stirring. The stirred reaction mixture was allowed to warm to rt while stirring was maintained. The solvents were removed under reduced pressure and the residue dissolved in CH$_2$Cl$_2$ (10 mL). Addition of Et$_2$O (at least 10 mL) under vigorous stirring produced a colourless precipitate, which was collected by filtration through a G4 glass frit and washed with *n*-pentane (5 mL). Colourless single crystals were grown from CH$_2$Cl$_2$/Et$_2$O solutions.

1,3-Bis(2,6-diisopropylphenyl)-2-phosphino-imidazolium tetrafluoroborate 1b[BF$_4$]: yield 580 mg (96%). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ = 1.27 (12 H, d, $^{3}J_{HH}$ = 6.9 Hz, *i*Pr-CH$_3$), 1.28 (12 H, d, $^{3}J_{HH}$ = 6.9 Hz, *i*Pr-CH$_3$), 2.29 (4 H, sept, $^{3}J_{HH}$ = 6.9 Hz, *i*Pr-CH), 3.57 (2 H, d, $^{1}J_{PH}$ = 220 Hz, PH$_2$), 7.59 (6 H, m, *m*/*p*-CH), 7.93 (2 H, s, NCH). ^{11}B NMR (CD$_2$Cl$_2$, 128.4 MHz): δ = -1.22 (s, BF$_4$). ^{31}P NMR (CD$_2$Cl$_2$, 161.9 MHz): δ = -165.6 (t, $^{1}J_{PH}$ = 220 Hz, PH$_2$). ATR-IR: $\tilde{\nu}$/cm^{-1} = 3174 (w), 2966 (m), 2930 (w/br), 2874 (w), 2323 (vw/br), 1596 (vw), 1553 (w), 1462 (m/br), 1390 (w), 1369 (w), 1350 (vw), 1327 (w), 1302 (vw), 1280 (w), 1257 (vw), 1211 (w), 1185 (vw), 1048 (vs/br), 1033 (vs/br), 953 (vw), 936 (w), 858 (w/br), 808 (m), 760 (s), 686 (m), 637 (w), 577 (vw). (+)-ESI HRMS: m/e = 421.2767 (calcd. for $[C_{27}H_{38}N_2P]^+$ 421.2767). (-)-ESI HRMS: m/e = 126.9031 (calcd. for $[BF_4]^-$ 126.9039). $C_{27}H_{38}BF_4N_2P$ (508.83 g mol^{-1}): calcd. C 63.79 H 7.53 N 5.51, found C 63.69 H 7.54 N 5.36.

1,3-Diisopropyl-2-phosphino-imidazolium tetrafluoroborate 1d[BF$_4$]: Yield 710 mg (96%). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ = 1.57 (12 H, d, $^{3}J_{HH}$ = 6.7 Hz, *i*Pr-CH$_3$), 4.16 (2 H, d, $^{1}J_{PH}$ = 223 Hz, PH$_2$), 4.91 (2 H, dsept, $^{3}J_{HH}$ = 6.7 Hz, $^{4}J_{PH}$ = 2.6 Hz, *i*Pr-CH), 7.62 (2 H, m, NCH). ^{11}B NMR (CD$_2$Cl$_2$, 128.4 MHz): δ = -1.28 (s, BF$_4$). ^{11}B NMR (CD$_2$Cl$_2$, 128.4 MHz, 213 K): δ = -1.33 (quint, $^{1}J_{BF}$ = 1.1 Hz, BF$_4$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100.6 MHz): δ = 22.4 (s, *i*Pr-CH$_3$), 53.5 (s, *i*Pr-CH), 121.7 (s, NCH), 138.8 (d, $^{1}J_{PC}$ = 41.4 Hz, PC). ^{31}P NMR (CD$_2$Cl$_2$, 161.9 MHz): δ = -177 (dt, $^{1}J_{PH}$ = 223 Hz, PH$_2$). ATR-IR: $\tilde{\nu}$/cm^{-1} = 3176 (w), 3152 (w), 3110 (vw), 2976 (w/br), 2943 (w), 2344 (vw/br), 1623 (vw), 1564 (w), 1458 (m/br), 1414 (m), 1376 (w), 1396 (m), 1353 (vw), 1317 (vw), 1286 (w), 1215 (s), 1187 (m), 1141 (w), 1099 (m), 1035 (vs/br), 888 (s), 833 (s), 756 (s), 677 (s), 666 (m), 563 (w). (+)-ESI HRMS: m/e = 185.1191 (calcd. for $[C_9H_{18}N_2P]^+$ 185.1202). $C_9H_{18}BF_4N_2P$ (272.03 g mol^{-1}): calcd. C 39.74 H 6.67 N 10.30, found C 39.49 H 6.82 N 10.31.

Synthesis of imidazolio-methylphosphine iodides (2b-e)[I]

General procedure: A solution of the appropriate imidazolio-phosphide **4b-e** (500 mg, 1.2 to 3.9 mmol, 1 equiv.) in MeCN (40 mL) was prepared in a 100 ml round-bottomed Schlenk flask. The solution was stirred vigorously, and freshly distilled MeI (1 equiv.) was added quickly at rt. Stirring was continued until the colour changed from light yellow to colourless (< 15 min). The solvent was removed under reduced pressure and the remaining colourless solid suspended in toluene (20 mL) and sonicated in an ultrasonic bath. The crude product was collected by filtration through a G4 glass frit, washed with *n*-pentane (10 mL) and dried under reduced pressure. Colourless single crystals were grown from CH$_2$Cl$_2$/Et$_2$O (**2b[I]**) or from MeCN at -8 °C (**2e[I]**), respectively.

1,3-Bis(2,6-diisopropylphenyl)-2-methylphosphino-imidazolium iodide 2b[I]: Yield 640 mg (96%). Mp. 383.2(5) °C. ^{1}H NMR (*o*-C$_6$H$_4$F$_2$, 400 MHz): δ = 1.10 (3 H, dd, $^{3}J_{HH}$ = 7.7 Hz, $^{2}J_{PH}$ = 4.5 Hz, PCH$_3$), 1.34 (6 H, d, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr-CH$_3$), 1.37 (6 H, d, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr-CH$_3$), 1.39 (6 H, d, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr-CH$_3$), 1.43 (6 H, d, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr-CH$_3$), 2.53 (2 H, sept, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr-CH), 2.58 (2 H, sept, $^{3}J_{HH}$ = 6.9 Hz, *i*Pr-CH), 4.10 (1 H, dq, $^{1}J_{PH}$ = 235 Hz, $^{3}J_{HH}$ = 7.7 Hz, PH), 7.44 (2 H, d, $^{3}J_{HH}$ = 7.8 Hz, *m*-CH), 7.46 (2 H, d, $^{3}J_{HH}$ = 7.8 Hz, *m*-CH), 7.67 (2 H, t, $^{3}J_{HH}$ = 7.8 Hz, *p*-CH), 8.52 (2 H, s, NCH). ^{13}C{^{1}H} NMR (*o*-C$_6$H$_4$F$_2$, 100.6 MHz): δ = 0.39 (d, $^{1}J_{PC}$ = 15.2 Hz, PCH$_3$), 21.1 (d, $^{6}J_{PC}$ = 2.4 Hz, *i*Pr-CH$_3$), 21.2 (d, $^{6}J_{PC}$ = 2.4 Hz, *i*Pr-CH$_3$), 23.8 (s, *i*Pr-CH$_3$), 24.2 (s, *i*Pr-CH$_3$), 28.6 (s, *i*Pr-CH), 28.7 (d, $^{5}J_{PC}$ = 1.8 Hz, *i*Pr-CH), 124.6 (s, *m*-CH), 124.8 (s, *m*-CH), 128.3 (m, NCH), 129.2 (s, *i*-C), 132.2 (s, *p*-CH), 144.5 (m, *o*-C), 145.1 (m, *o*-C), 150.2 (d, $^{1}J_{PC}$ = 40.8 Hz, PC). ^{15}N NMR (HMBC, *o*-C$_6$H$_4$F$_2$, 40.6 MHz): δ = -190.1. ^{31}P NMR (*o*-C$_6$H$_4$F$_2$, 161.9 MHz): δ = -96.5 (dm, $^{1}J_{PH}$ = 235 Hz). ATR-IR: $\tilde{\nu}$/cm^{-1} = 3157 (w), 2960 (m), 2926 (m/br), 2868 (m), 2325 (w/br), 1594 (vw), 1544 (m), 1451 (s/br), 1426 (m), 1379 (w), 1368 (m), 1359 (w), 13253 (w), 1275 (w), 1204 (m), 1184 (w), 1137 (vw), 1118 (w), 1061 (m), 1043 (w), 1004 (w), 977 (vw), 938 (w), 911 (m), 684 (m), 802 (s), 755 (vs), 732 (vw), 711 (w), 682 (w), 635 (w). $C_{28}H_{40}IN_2P$ (562.51g mol^{-1}): calcd. C 59.79 H 7.17 N 4.98, found C 59.72 H 7.22 N 4.88.

1,3-Bis(2,4,6-trimethylphenyl)-2-methylphosphino-imidazolium iodide 2c[I]: not isolated, characterised by NMR spectroscopy. ^{1}H NMR (CH_2Cl_2, 250 MHz): δ = 1.03 (3 H, dd, $^{3}J_{HH}$ = 7.8 Hz, $^{2}J_{PH}$ = 4.3 Hz, PCH_3), 2.07 (6 H, s, *o*-CH_3), 2.12 (6 H, s, *o*-CH_3), 2.39 (6 H, s, *p*-CH_3), 4.00 (dq, $^{1}J_{PH}$ = 234 Hz, $^{3}J_{HH}$ = 7.8 Hz, PH), 7.15 (4 H, m, *m*-CH), 7.94 (2 H, s, NCH). ^{31}P NMR (CH_2Cl_2,101.2 MHz): δ = -99.7 (dq, $^{1}J_{PH}$ = 234 Hz, $^{2}J_{PH}$ = 4.1 Hz).

1,3-Diisopropyl-2-methylphosphino-imidazolium iodide 2d[I]: not isolated, identified by ^{31}P NMR spectroscopy. ^{31}P NMR ($CDCl_3$, 101.2 MHz): δ = -114.5 (dq, $^{1}J_{PH}$ = 238 Hz, $^{2}J_{PH}$ = 4.6 Hz).

1,3-Dimethyl-2-methylphosphino-imidazolium iodide 2e[I]: yield 1.03 (98%) of >94% purity. ^{1}H NMR (CD_3CN, 400 MHz): δ = 1.41 (3 H, dd, $^{3}J_{HH}$ = 7.7 Hz, $^{2}J_{PH}$ = 4.4 Hz, PCH_3), 3.93 (6 H, s, NCH_3), 4.50 (1 H, dq, $^{1}J_{PH}$ = 236 Hz, $^{3}J_{HH}$ = 7.7 Hz, PH), 7.55 (2 H, s, NCH). ^{13}C{^{1}H} NMR (CD_3CN, 100.6 MHz): δ = 1.35 (d, $^{1}J_{PC}$ = 10.9 Hz, PCH_3), 38.0 (d, $^{3}J_{PC}$ = 5.5 Hz, NCH_3), 125.4 (s, NCH), 147.1 (NCN). ^{31}P NMR (CD_3CN, 161.9 MHz): δ = -114.1 (broad d, $^{1}J_{PH}$ = 236 Hz).

General synthesis of secondary imidazolio-alkylphosphine tetrafluoroborates (2b-e)[BF_4], (5b-e)[BF_4]

A 100 ml round-bottomed Schlenk flask was charged with the appropriate imidazolio-phosphide (**4b**-**e**, 1.00 g, 2.4 to 3 mmol, 1 equiv.) and [Me_3O][BF_4] (1.04 equiv.) or [Et_3O][BF_4] (1.05 equiv.), respectively. Acetonitrile (minimum 40 mL per gram of imidazolio-phosphide; working in higher dilution gave less by-products) was added under vigorous stirring. Stirring was continued for additional 15 min at rt and the solvent then removed under reduced pressure to afford a solid residue (a yellowish oil obtained at this point was stirred in a sufficient volume of toluene until a colourless solid separated which was collected by removing the supernatant solution with a cannula or by filtration through a G4 glass frit). The crude solid was dissolved in CH_2Cl_2 (dcm) and the solution filtered through a G4 glass frit. The solvent was removed from the filtrates under reduced pressure and the remaining solid residues were purified by repeated fractional crystallization. Single crystals were grown by slow evaporation of a concentrated solution in CH_2Cl_2 (**2c**[BF_4]) or from CH_2Cl_2/Et_2O (**5b**[BF_4]).

1,3-Bis(2,6-diisopropylphenyl)-2-methylphosphino-imidazolium tetrafluoroborate 2b[BF_4]: 1.22 g (93%), mp. 380 °C. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 0.96 (3 H, dd, $^{3}J_{HH}$ = 7.8 Hz, $^{2}J_{PH}$ = 4.5 Hz, PCH_3), 1.24 (6 H, d, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr-CH_3), 1.27 (6 H, d, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr-CH_3), 1.30 (6 H, d, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr-CH_3), 1.33 (6 H, d, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr-CH_3), 2.30 (2 H, sept, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr-CH), 2.35 (2 H, sept, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr-CH), 4.03 (1 H, dq, $^{1}J_{PH}$ = 234 Hz, $^{3}J_{HH}$ = 7.8 Hz, PH), 7.45 (2 H, dd, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 1.2 Hz, *m*-CH), 7.47 (2 H, dd, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 1.2 Hz, *m*-CH), 7.69 (2 H, t, $^{3}J_{HH}$ = 7.9 Hz, *p*-CH), 7.85 (2 H, s, NCH). ^{11}B NMR (CD_2Cl_2, 128.4 MHz): δ = -1.24 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.6 MHz): δ = 1.14 (d, $^{1}J_{PC}$ = 15.5 Hz, PCH_3), 22.40 (s, *i*Pr-CH_3), 22.43 (s, ^{i}Pr-CH_3), 24.9 (s, ^{i}Pr-CH_3), 25.2 (s, ^{i}Pr-CH_3), 29.3 (s, ^{i}Pr-CH), 29.4 (s, ^{i}Pr-CH), 125.3 (s, *m*-CH), 125.5 (s, *m*-CH), 127.9 (s, NCH), 130.0 (s, *i*-C), 132.8 (s, *p*-C), 144.8 (s, *o*-C), 145.4 (s, *o*-C), 151.3 (d, $^{1}J_{PC}$ = 50.7 Hz, PC). ^{15}N NMR (HMBC, CD_2Cl_2, 40.6 MHz): δ = -189.2. ^{19}F NMR (CD_2Cl_2, 235.2 MHz): δ = -152.5 (q, $^{1}J_{BF}$ = 0.7 Hz, BF_4). ^{31}P NMR (CD_2Cl_2, 161.9 MHz): δ = -96.5 (dq, $^{1}J_{PH}$ = 234 Hz, $^{2}J_{PH}$ = 4.6 Hz). (+)-ESI HRMS: m/e = 435.2935 (calcd. for $[C_{27}H_{38}N_2P]^+$ 435.2924.

1,3-Bis(2,4,6-trimethylphenyl)-2-methylphosphino-imidazolium tetrafluoroborate 2c[BF_4]: Yield 1.17 g (90%), mp. 211° C. ^{1}H NMR (CD_2Cl_2, 250 MHz): δ = 1.01 (3 H, dd, $^{3}J_{HH}$ = 7.8 Hz, $^{2}J_{PH}$ = 4.3 Hz, PCH_3), 2.07 (6 H, s, *o*-CH_3), 2.12 (6 H, s, *o*-CH_3), 2.41 (6 H, s, *p*-CH_3), 3.98 (1 H, dq, $^{1}J_{PH}$ = 233 Hz, $^{3}J_{HH}$ = 7.8 Hz, PH), 7.15 (2 H, m, *m*-CH), 7.17 (2 H, m, *m*-CH), 7.74 (2 H, s, NCH). ^{11}B NMR (CD_2Cl_2, 80.2 MHz): δ = -1.27 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2, 62.8 MHz): δ = 1.14 (d, $^{1}J_{PC}$ = 14.8 Hz, PCH_3), 17.2 (d, $^{5}J_{PC}$ = 1.5 Hz, *o*-CH_3), 17.3 (d, $^{5}J_{PC}$ = 4.0 Hz, *o*-CH_3), 21.9 (s, *p*-CH_3), 127.0 (d, $^{3}J_{PC}$ = 1.5 Hz, NCH), 130.2 (s, *m*-CH), 130.3 (s, *m*-CH), 130.7 (s, *i*-C), 134.0 (s, *o*-C), 134.5 (s, *o*-C), 142.4 (s, *p*-C), 149.7 (d, $^{1}J_{PC}$ = 50.2 Hz, PC). ^{19}F NMR (CD_2Cl_2, 235.2 MHz): δ = -152.8 (q, $^{1}J_{FB}$ = 1 Hz, BF_4). ^{31}P NMR (CD_2Cl_2, 101.2 MHz): δ = -99.8 (dq, $^{1}J_{PH}$ = 234 Hz, $^{2}J_{PH}$ = 4.3 Hz). ATR-IR: ṽ/cm^{-1} = 3135 (w), 2920 (w), 2323 (vw/br), 1606 (w), 1552 (w), 1486 (m), 1451 (m), 1385 (w), 1285 (w), 1236 (w), 1285 (vw), 1236 (m), 1173 (vw), 1089 (w), 1048 (vs/br), 1034 (s), 983 (w), 933 (w), 898 (w), 868 (m/br), 773 (w), 758 (w), 709 (w), 679 (vw). (+)-ESI HRMS: m/e = 351.1985 (calcd. for $[C_{22}H_{28}N_2P]^+$ 351.1985). (-)-ESI MS: m/e = 87.0 $[BF_4]^-$. $C_{22}H_{28}BF_4N_2P$ (581.40 mol^{-1}): calcd. C 60.29 H 6.44 N 6.39, found C 60.21 H 6.49 N: 6.51.

1,3-Dimethyl-2-methylphosphino-imidazolium tetrafluoroborate 2e[BF_4]: not isolated. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 1.43 (3 H, dd, $^{3}J_{HH}$ = 7.7 Hz, $^{2}J_{PH}$ = 4.7 Hz, PCH_3), 3.96 (6 H, s, NCH_3), 4.52 (1 H, dq, $^{1}J_{PH}$ = 234 Hz, $^{3}J_{HH}$ = 7.7 Hz, PH), 7.53 (2 H, d, $^{4}J_{PH}$ = 0.6 Hz, NCH). ^{11}B NMR (CD_2Cl_2, 128.4 MHz): δ = -1.20 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.6 MHz): δ = 1.61 (d, $^{1}J_{PC}$ = 11.5 Hz, PCH_3), 37.0 (d, $^{3}J_{PC}$ = 5.9 Hz, NCH_3), 125.7 (d, $^{3}J_{PC}$ = 0.9 Hz, NCH), 146.5 (d, $^{1}J_{PC}$ = 48.5 Hz, PC). ^{15}N NMR (HMBC, CD_3CN, 40.6 MHz): δ = -203.5. ^{31}P NMR (CD_2Cl_2, 161.9 MHz): δ = -115.0 (dq, $^{1}J_{PH}$ = 234 Hz, $^{2}J_{PH}$ = 4.7 Hz).

1,3-Bis(2,6-diisopropylphenyl)-2-ethylphosphino-imidazolium tetrafluoroborate 5b[BF_4]: 1.17 g (92%), mp. 377.5° C. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 0.86 (3 H, dt, $^{3}J_{PH}$ = 19.0 Hz, $^{3}J_{HH}$ = 7.6 Hz, $PCCH_3$), 1.15 (1 H, dddt, $^{2}J_{HH}$ = 13.8 Hz, $^{3}J_{HH}$ = 9.9 Hz, $^{2}J_{PH}$ = 11.3 Hz, $^{3}J_{HH}$ = 7.8 Hz, PCH_2), 1.24 (6 H, d, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr-CH_3), 1.26 (6 H, d, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr-CH_3), 1.31 (6 H, d, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr-CH_3), 1.33 (6 H, d, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr-CH_3), 1.65 (1 H, dddt, $^{2}J_{HH}$ = 13.8 Hz, $^{3}J_{HH}$ = 6.7 Hz, $^{2}J_{PH}$ = 6.0 Hz, $^{3}J_{HH}$ = 7.8 Hz, PCH_2), 2.29 (2 H, sept, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr-CH), 2.37 (2 H, sept, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr-CH), 3.80 (1 H, ddd, $^{1}J_{PH}$ = 231 Hz, $^{3}J_{HH}$ = 9.9 Hz, $^{3}J_{HH}$ = 6.7 Hz, PH), 7.45 (2 H, dd, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ =

1.3 Hz, *m*-CH), 7.47 (2 H, dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.3 Hz, *m*-CH), 7.69 (2 H, t, $^3J_{HH}$ = 7.7 Hz, *p*-CH), 7.85 (2 H, s, NCH). ^{11}B NMR (CD_2Cl_2, 128.4 MHz): δ = -1.21 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.6 MHz): δ = 11.7 (d, $^1J_{PC}$ = 13.0 Hz, PCH_2), 12.3 (d, $^2J_{PC}$ = 13.9 Hz, $PCCH_3$), 22.36 (d, $^6J_{PC}$ = 2.2 Hz, *i*Pr-CH_3), 22.38 (d, $^6J_{PC}$ = 1.8 Hz, *i*Pr-CH_3), 25.1 (s, *i*Pr-CH_3), 25.4 (s, *i*Pr-CH), 29.3 (s, *i*Pr-CH), 29.4 (d, $^5J_{PC}$ = 1.9 Hz, *i*Pr-CH), 125.3 (s, *m*-CH), 125.5 (s, *m*-CH), 128.04 (d, $^3J_{PC}$ = 1.7 Hz, NCH), 130.2 (s, *i*-C), 132.7 (s, *p*-C), 144.8 (s, *o*-C), 145.5 (s, *o*-C), 151.1 (d, $^1J_{PC}$ = 51.5 Hz, PC). ^{15}N NMR (HMBC, CD_2Cl_2, 40.6 MHz): δ = -189.3. ^{19}F NMR (CD_2Cl_2, 235.4 MHz): δ = -152.5 (q, $^1J_{BF}$ = 0.9 Hz, BF_4). ^{31}P NMR (CD_2Cl_2, 161.9 MHz): δ = -80.6 (dddq, $^1J_{PH}$ = 231 Hz, $^3J_{PH}$ = 19.0 Hz, $^2J_{PH}$ = 11.5 Hz, $^2J_{PH}$ = 6.5 Hz). ATR-IR: $\tilde{\nu}$/cm^{-1} = 3169 (w), 3143 (vw), 2965 (m/br), 2930 (m), 2872 (m), 2321 (w), 1548 (m), 1450 (m/br), 1389 (w), 1367 (m), 1328 (m), 1278 (w), 1211 (w), 1095 (m), 1048 (vs/br), 1035 (vs/br), 981 (w), 953 (w), 936 (w), 883 (w), 812 (s), 760 (s), 720 (w), 681 (w), 634 (w). (+)-ESI HRMS: m/e = 449.3070 (calcd. for $[C_{29}H_{42}N_2P]^+$ 449.3080). (-)-ESI MS: m/e = 87.0 $[BF_4]^-$. $C_{29}H_{42}BF_4N_2P$ (536.44g mol^{-1}): calcd. C 64.93 H 7.89 N: 5.22, found C 64.84 H 7.92 N: 5.19.

1,3-Bis(2,4,6-trimethylphenyl)-2-ethylphosphino-imidazolium tetrafluoroborate 5c[BF$_4$]: not isolated. ^{1}H NMR (MeCN, 250 MHz): δ = 0.82 (3 H, dt, $^3J_{PH}$ = 17.4 Hz, $^3J_{HH}$ = 7.5 Hz, $PCCH_3$), 1.24 (1 H, m, PCH_2), 1.58 (1 H, m, PCH_2), 2.03 (6 H, s, *o*-CH_3), 2.08 (6 H, s, *o*-CH_3), 2.37 (6 H, s, *p*-CH_3), 3.77 (1 H, dt, $^1J_{PH}$ = 234 Hz, $^3J_{HH}$ = 7.9 Hz, PH), 7.18 (4 H, s, *m*-CH), 7.79 (2 H, s, NCH). ^{11}B NMR (MeCN, 80.2 MHz) δ = -1.31 (s). ^{31}P NMR (MeCN, 101.2 MHz): δ = -80.0 (dddq, $^1J_{PH}$ = 231 Hz, $^3J_{PH}$ = 17.4 Hz, $^2J_{PH}$ = 11.7 Hz, $^2J_{PH}$ = 4.3 Hz).

1,3-Diisopropyl-2-ethylphosphino-imidazolium tetrafluoroborate 5d[BF$_4$]: ^{1}H NMR (MeCN, 250 MHz): δ = 1.09 (3 H, m, $PCCH_3$), 1.45 (6 H, d, $^3J_{HH}$ = 6.7 Hz, *i*Pr-CH_3), 1.49 (6 H, d, $^3J_{HH}$ = 6.7 Hz, *i*Pr-CH_3), 1.84 (2 H, m, PCH_2), 4.45 (1 H, dt, $^1J_{PH}$ = 234 Hz, $^3J_{HH}$ = 7.1 Hz, PH), 4.91 (2 H, m, *i*Pr-CH), 7.67 (2 H, s, NCH). ^{11}B NMR (MeCN, 80.2 MHz): δ = -1.26 (s). ^{31}P NMR (MeCN, 101.2 MHz): δ = -97.2 (br dq, $^1J_{PH}$ = 234 Hz, $^3J_{PH}$ = 17.4 Hz).

1,3-Dimethyl-2-ethylphosphino-imidazolium tetrafluoroborate 5e[BF$_4$]: not isolated. ^{1}H NMR (CH_2Cl_2, 250 MHz): δ = 1.14 (3 H, dt, $^3J_{HH}$ = 16.2 Hz, $^3J_{HH}$ = 7.6 Hz, $PCCH_3$), 1.93 (2 H, m, PCH_2), 3.98 (6 H, s, NCH_3), 4.46 (1 H, dt, $^1J_{PH}$ = 234 Hz, $^3J_{HH}$ = 7.0 Hz, PHEt), 7.56 (2 H, s, NCH). ^{11}B NMR (MeCN, 80.2 MHz) δ = -1.26 (s). ^{31}P NMR (CH_2Cl_2, 101.2 MHz): δ = -95.3 (1 P, dddq, $^1J_{PH}$ = 234 Hz, $^2J_{PH}$ = 2.9 Hz, $^2J_{PH}$ = 5.1 Hz, $^3J_{PH}$ = 15.9 Hz).

Synthesis of 1,3-Bis(2,6-diisopropylphenyl)-imidazolium-2-yl-alkylphosphides

Imidazolio-phosphine tetrafluoroborate (1.60 g, 3.06 mmol (**2b**[BF$_4$]) or 2.98 mmol (**5e**[BF$_4$]), 1 equiv.) was dispersed in THF (80 mL) under vigorous stirring. After the suspension was cooled to -78° C, an ice-cold solution of *t*-BuLi (1.7 M in n-pentane, 1 equiv.) was added slowly while stirring was maintained. When the addition was complete, the light yellow suspension had turned into a deep red solution, which was allowed to warm to rt. After stirring for additional 15 min, the solvent was removed under reduced pressure and the crude product extracted into toluene (100 mL) under sonication in an ultra sound bath. The resulting suspension was filtered through a G4 glass frit. The solvent was removed and the yellow residue extracted with *n*-pentane (50 mL). After filtration over celite and reduction of the volume of the filtrates under reduced pressure, the products were obtained as yellow solids by fractional crystallization from the concentrated solutions at -30° C. The synthesis can also be carried out using imidazolio-phosphine iodides instead of the tetrafluoroborates as starting materials.

1,3-Bis(2,6-diisopropylphenyl)-imidazolium-2-yl-ethylphosphide 6b. Yield: 0.78 g (1.73 mmol, 58%), mp. 160 °C (dec.). ^{1}H NMR (C_6D_6, 400 MHz): δ = 0.94 (3 H, dt, $^3J_{PH}$ = 20.9 Hz, $^3J_{HH}$ = 7.8 Hz, $PCCH_3$), 1.18 (12 H, d, $^3J_{HH}$ = 6.9 Hz, *i*Pr-CH_3), 1.31 (2 H, dq, $^2J_{PH}$ = 5.3 Hz, $^3J_{HH}$ = 7.8 Hz, PCH_2), 1.47 (12 H, broad d, *i*Pr-CH_3), 6.10 (2 H, s, NCH), 7.16 (6 H, m, *m/p*-CH). ^{1}H NMR (CD_3CN, 400 MHz): δ = 0.53 (3 H, dt, $^3J_{PH}$ = 21.4 Hz, $^3J_{HH}$ = 7.9 Hz, $PCCH_3$), 0.92 (2 H, dq, $^2J_{PH}$ = 5.3 Hz, $^3J_{HH}$ = 7.9 Hz, PCH_2), 1.18 (12 H, d, $^3J_{HH}$ = 6.9 Hz, *i*Pr-CH_3), 1.31 (12 H, d, $^3J_{HH}$ = 6.9 Hz, *i*Pr-CH_3), 3.00 (4 H, sept., $^3J_{HH}$ = 6.9 Hz, *i*Pr-CH), 6.75 (2 H, s, NCH), 7.35 (6 H, m, *m/p*-CH). ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz): δ = 9.74 (d, $^1J_{PC}$ = 33.1 Hz, PCH_2), 14.8 (d, $^2J_{PC}$ = 37.3 Hz, $PCCH_3$), 23.0 (broad, *i*Pr-CH_3), 24.3 (s, *i*Pr-CH_3), 28.6 (s, *i*Pr-CH), 119.2 (s, NCH), 123.9 (s, *m*-CH), 129.6 (s, *p*-CH), 147.4 (s, *i*-C), 174.1 (d, $^1J_{PC}$ = 99.8 Hz, PC). ^{13}C{^{1}H} NMR (CD_3CN, 100.6 MHz): δ = 8.84 (d, $^1J_{PC}$ = 31.3 Hz, PCH_2), 13.9 (d, $^2J_{PC}$ = 38.4 Hz, $PCCH_3$), 22.11 (br s, *i*Pr-CH_3), 22.13 (br s, *i*Pr-CH_3), 23.7 (s, *i*Pr-CH_3), 28.5 (s, *i*Pr-CH), 120.1 (s, NCH), 123.8 (s, *m*-CH), 129.6 (s, *p*-CH), 134.6 (s, *i*-C), 147.40 (d, $^1J_{PC}$ = 1.8 Hz, *o*-C), 173.4 (d, $^1J_{PC}$ = 97.6 Hz, PC). ^{15}N NMR (HMBC, CD_3CN, 40.6 MHz): δ = -228.5. ^{31}P NMR (C_6D_6, 161.9 MHz): δ = 37.3 (broad q, $^3J_{PH}$ = 20.4 Hz). ^{31}P NMR (CD_3CN, 161.9 MHz): δ = -43.3 (1 P, tq, $^3J_{PH}$ = 21.2 Hz, $^2J_{PH}$ = 5.3 Hz). $C_{29}H_{41}N_2P$ (590.76 g mol^{-1}): calcd. C 77.64 H 9.21 N 6.24, found C 75.73 H 9.15 N 6.52.

1,3-Bis(2,6-diisopropylphenyl)-imidazolium-2-yl-methylphosphide 8b. Yield: 0.68 g (1.99 mmol, 65%). ^{1}H NMR (THF-d_8, 400 MHz): δ = 0.42 (3 H, d, $^2J_{PH}$ = 3.4 Hz, PCH_3), 1.19 (12 H, d, $^3J_{HH}$ = 6.9 Hz, *i*Pr-CH_3), 1.35 (12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr-CH_3), 3.10 (4 H, broad-s, *i*Pr-CH), 6.71 (2 H, s, NCH), 7.27 (6 H, m, *m/p*-CH). ^{13}C{^{1}H} NMR (THF-d_8, 100.6 MHz): δ = 0.96 (d, $^1J_{PC}$ = 38.9 Hz, PCH_3), 22.4 (broad s, *i*Pr-CH_3), 23.7 (s, *i*Pr-CH_3), 28.4 (s, *i*Pr-CH), 119.7 (broad s, NCH), 123.4 (broad s, *m*-CH), 129.2 (s, *p*-CH), 134.7 (broad s, *o*-C), 147.3 (s, *i*-C), 174.5 (d, $^1J_{PC}$ = 100.2 Hz, PC). ^{15}N NMR (HMBC, THF-d_8, 40.6 MHz): δ = -80.96. ^{31}P NMR (THF-d_8, 161.9 MHz): δ = -61.4 (broad s). ATR-IR: $\tilde{\nu}$/cm^{-1} = 3076 (m), 2959 (m), 2865 (m), 1663 (vw), 1589 (w), 1541 (w), 1466 (m, br), 1425 (vw), 1396 (m), 1382 (vw), 1360 (vw), 1332 (vs), 1299 (w), 1269 (m), 1208 (m), 1179 (w), 1116 (m), 1087 (w), 1062 (m), 936 (m), 885 (m), 804 (s), 770 (m), 760 (s), 714 (m), 679 (m), 658 (w). $C_{28}H_{39}N_2P$ (576.74 g mol^{-1}): calcd. C 77.38 H 9.05 N 6.45, found: C 79.73 H 9.31 N 6.64.

Synthesis of tertiary imidazolio-dialkylphosphine tetrafluoroborates (19a-c)[BF$_4$]

A 100 ml round-bottomed Schlenk flask was charged with the appropriate imidazolio-phosphide (**6b** or **8b**, 800 mg, approx. 1.8 mmol, 1 equiv.) and Meerwein salt ([R$_3$O][BF$_4$], approx. 1.9 mmol, 1.05 equiv.). MeCN (30 mL) was added under vigorous stirring. The mixture was stirred for 15 min. at rt and the solvent then removed under reduced pressure. The remaining solid was treated with toluene (20 mL) and the resulting suspension filtered through a G4 glass frit. The crude products remained as colourless solids. Colourless single crystals of **19a**[BF$_4$], **19c**[BF$_4$] were grown from a CH$_2$Cl$_2$/Et$_2$O. **19c**[BF$_4$] could be prepared by treatment of either **6b** or **8b** with the appropriate Meerwein salt.

1,3-Bis(2,6-diisopropylphenyl)-2-dimethylphosphino-imidazolium tetrafluoroborate 19a[BF$_4$]: yield 0.96 g (1.78 mmol, 97%). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ = 0.92 (6 H, d, $^{3}J_{\mathrm{PH}}$ = 5.2 Hz, PCH$_3$), 1.24 (12 H, d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, *i*Pr-CH$_3$), 1.36 (12 H, d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, *i*Pr-CH$_3$), 2.39 (4 H, sept, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, *i*Pr-CH), 7.57 (6 H, m, *m*/*p*-CH), 7.72 (2 H, s, NCH). ^{11}B NMR (CD$_2$Cl$_2$, 128.4 MHz): δ = -1.27 (s). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100.6 MHz): δ = 9.83 (d, $^{1}J_{\mathrm{PC}}$ = 13.9 Hz, PCH$_3$), 22.1 (d, $^{6}J_{\mathrm{PC}}$ = 2.0 Hz, *i*Pr-CH$_3$), 25.4 (s, *i*Pr-CH$_3$), 29.4 (d, $^{5}J_{\mathrm{PC}}$ = 1.6 Hz, *i*Pr-CH), 125.1 (s, *m*-CH), 128.2 (d, $^{3}J_{\mathrm{PC}}$ = 2 Hz, NCH), 130.6 (s, *o*-C), 132.7 (s, *p*-CH), 145.2 (d, $^{3}J_{\mathrm{PC}}$ = 0.6 Hz, *i*-C), 151.9 (d, $^{1}J_{\mathrm{PC}}$ = 71.1 Hz, PC). ^{15}N NMR (HMBC, CD$_2$Cl$_2$, 40.6 MHz) δ = -189.4. ^{31}P NMR (CD$_2$Cl$_2$, 161.9 MHz): δ = -30.0 (sept, $^{2}J_{\mathrm{PH}}$ = 5.2 Hz). (+)-ESI HRMS: m/e = 449.3085 (calcd. for [C$_{29}$H$_{42}$N$_2$P]$^{+}$ 449.3080). C$_{29}$H$_{42}$BF$_4$N$_2$P (536.44 g mol^{-1}): calcd. C 64.93 H 7.89 N 5.22, found: C 65.07 H 7.75 N 5.14.

1,3-Bis(2,6-diisopropylphenyl)-2-diethylphosphino-imidazolium tetrafluoroborate 19b[BF$_4$]: not isolated. ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ = 0.87 (6 H, dt, $^{3}J_{\mathrm{PH}}$ = 18.3 Hz, $^{3}J_{\mathrm{HH}}$ = 7.7 Hz, PCCH$_3$), 1.23 (12 H, d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, *i*Pr-CH$_3$), 1.36 (12 H, d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, *i*Pr-CH$_3$), 1.29-1.44 (4 H, m, PCH$_2$), 2.38 (4 H, sept, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, *i*Pr-CH), 7.44 (4 H, d, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz, *m*-CH), 7.68 (2 H, t, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz, *p*-CH), 7.72 (2 H, s, NCH). ^{11}B NMR (CD$_2$Cl$_2$, 128.4 MHz) δ = -1.22 (s). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100.6 MHz) δ 10.4 (d, $^{2}J_{\mathrm{PC}}$ = 19.3 Hz, CCH$_3$), 15.3 (d, $^{1}J_{\mathrm{PC}}$ = 13.6 Hz, PCH$_2$), 21.9 (d, $^{6}J_{\mathrm{PC}}$ = 1.5 Hz, *i*Pr-CH$_3$), 25.6 (s, ^{i}Pr-CH$_3$), 29.5 (d, $^{5}J_{\mathrm{PC}}$ = 1.4 Hz, *i*Pr-CH), 125.1 (s, *m*-CH), 128.5 (d, $^{3}J_{\mathrm{PC}}$ = 2.2 Hz, NCH), 130.8 (s, *i*-CH), 132.6 (s, *p*-CH), 145.2 (d, $^{4}J_{\mathrm{PC}}$ = 1.4 Hz, *o*-C), 151.4 (d, $^{1}J_{\mathrm{PC}}$ = 71.6 Hz, PC). ^{15}N NMR (HMBC, CD$_2$Cl$_2$, 40.6 MHz): δ = -187.6. ^{31}P NMR (CD$_2$Cl$_2$, 161.9 MHz): δ = -12.5 (quint sept, $^{3}J_{\mathrm{PH}}$ = 18.4 Hz, $^{2}J_{\mathrm{PH}}$ = 3.7 Hz,).

1,3-Bis(2,6-diisopropylphenyl)-2-ethylmethylphosphino-imidazolium tetrafluoroborate 19c[BF$_4$]: Yield 0.92 g (1.67 mmol, 94%), mp. 246 °C (dec.). ^{1}H NMR (CD$_2$Cl$_2$, 400 MHz): δ 0.84 (3 H, dt, $^{3}J_{\mathrm{PH}}$ = 19.1 Hz, $^{3}J_{\mathrm{HH}}$ = 7.7 Hz, PCCH$_3$), 0.89 (3 H, d, $^{2}J_{\mathrm{PH}}$ = 5.1 Hz, PCH$_3$), 1.23 (6 H, d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, *i*Pr-CH$_3$), 1.24 (6 H, d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, *i*Pr-CH$_3$), 1.30 (1 H, ddq, $^{2}J_{\mathrm{HH}}$ = 13.4 Hz, $^{3}J_{\mathrm{HH}}$ = 7.7 Hz, $^{2}J_{\mathrm{PH}}$ = 6.0 Hz, PCH$_2$), 1.358 (6 H, d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, *i*Pr-CH$_3$), 1.363 (6 H, d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, *i*Pr-CH$_3$), 1.41 (1 H, ddq, $^{2}J_{\mathrm{HH}}$ = 13.4 Hz, $^{3}J_{\mathrm{HH}}$ = 7.7 Hz, $^{2}J_{\mathrm{PH}}$ = 5.9 Hz, PCH$_2$), 2.37 (2 H, sept, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, *i*Pr-CH), 2.40 (2 H, sept, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, ^{i}Pr-CH), 7.44 (4 H, d, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz, *m*-CH), 7.68 (2 H, t, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz, *p*-CH), 7.73 (2 H, s, NCH). ^{11}B NMR (CD$_2$Cl$_2$, 128.4 MHz) δ -1.22 (1 B, s, BF$_4$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 100.6 MHz): δ = 6.13 (d, $^{1}J_{\mathrm{PC}}$ = 16.2 Hz, PCH$_3$), 9.42 (d, $^{2}J_{\mathrm{PC}}$ = 19.2 Hz, PCCH$_3$), 17.9 (d, $^{1}J_{\mathrm{PC}}$ = 11.3 Hz, PCH$_2$), 22.0 (d, $^{6}J_{\mathrm{PC}}$ = 2 Hz, *i*Pr-CH$_3$), 22.1 (s, $^{6}J_{\mathrm{PC}}$ = 1.5 Hz, *i*Pr-CH$_3$), 25.4 (s, ^{i}Pr-CH$_3$), 25.5 (s, ^{i}Pr-CH$_3$), 29.4 (d, $^{5}J_{\mathrm{PC}}$ = 1 Hz, *i*Pr-CH), 29.5 (d, $^{5}J_{\mathrm{PC}}$ = 2 Hz, *i*Pr-CH), 125.0 (s, *m*-CH), 125.1 (s, *m*-CH), 128.4 (d, $^{3}J_{\mathrm{PC}}$ = 1.9 Hz, NCH), 130.7 (d, $^{3}J_{\mathrm{PC}}$ = 0.5 Hz, *i*-CH), 132.6 (s, *p*-CH), 145.1 (d, $^{3}J_{\mathrm{PC}}$ = 0.6 Hz, *o*-C), 145.2 (d, $^{3}J_{\mathrm{PC}}$ = 0.6 Hz, *o*-C), 151.2 (d, $^{1}J_{\mathrm{PC}}$ = 70.8 Hz, PC). ^{15}N NMR (HMBC, CD$_2$Cl$_2$, 40.6 MHz): δ = -188.3. ^{31}P NMR (CD$_2$Cl$_2$, 161.9 MHz): δ = -24.1 (tqq, $^{3}J_{\mathrm{PH}}$ = 19.1 Hz, $^{2}J_{\mathrm{PH}}$ = 5.8 Hz, $^{2}J_{\mathrm{PH}}$ = 4.8 Hz). ATR-IR: $\tilde{\nu}$/cm^{-1} = 3172 (w), 3142 (vw), 2964 (m), 2932 (m), 2883 (w), 1553 (w), 1459 (m/br), 1451 (m/br), 1421 (m), 1389 (w), 1365 (w), 1328 (w), 1277 (vw), 1209 (w), 1096 (m), 1049 (vs/br), 1035 (vs/br), 978 (w), 848 (w), 935 (w), 890 (m), 814 (s), 772 (m), 762 (m), 740 (w), 710 (m), 637 (w). C$_{30}$H$_{44}$BF$_4$N$_2$P (550.46 g mol^{-1}): calcd. C 65.46 H 8.06 N 5.09, found C 65.19 H 8.13 N 5.23. (+)-ESI HRMS: m/e = 463.3237 (calcd. for [C$_{29}$H$_{42}$N$_2$P]$^{+}$ 463.3237). (-)-ESI HRMS: m/e = 87.0 ([BF$_4$]$^{-}$).

Synthesis of tertiary imidazolio-dialkylphosphine iodides (19a,c)[I]

1,3-Bis(2,6-diisopropylphenyl)-2-dimethylphosphino-imidazolium iodide 19a[I]: Iodomethane (150 µL, 2.40 mmol) was added quickly to a vigorously stirred solution of **4b** (500 mg, 1.19 mmol) in *o*-difluorobenzene (20 mL) in a 100 ml round-bottomed Schlenk flask that had previously been cooled to -30 °C. After 2 h, Hünig's base (EtN*i*Pr$_2$, 200 µL, 1.19 mmol) was added. The solution was stirred for 30 more min and allowed to warm to rt. Characterisation of the solution by ^{1}H, and ^{31}P{^{1}H} NMR spectroscopy revealed the presence of a mixture of **19a**$^{+}$ (70% of the integrated signal intensity in the ^{31}P{^{1}H} NMR spectrum) beside further undisclosed by-products. After one week, **19a**$^{+}$ and (PMe)$_5$ (67 and 28% of the integrated signal intensity) were detected as the main phosphorus-containing species.

1,3-Bis(2,6-diisopropylphenyl)-2-ethylmethylphosphino-imidazolium iodide 19c[I]: Iodomethane (29 µl, 0.47 mmol) was added quickly to a vigorously stirred solution of **6b** (200 mg, 0.46 mmol) in acetonitrile (10 mL) in a 50 ml round-bottomed Schlenk flask. The reaction mixture was stirred for 10 min. at rt. Formation of **19c**[I] as the only phosphorus-containing product was identified in situ by NMR spectroscopy. ^{1}H NMR (MeCN, 250 MHz): δ = 0.78 (3 H, dt, $^{3}J_{\mathrm{PH}}$ = 19.0 Hz, $^{3}J_{\mathrm{HH}}$ 7.7 Hz, PCCH$_3$), 0.86 (3 H, d, $^{2}J_{\mathrm{PH}}$ = 4.9 Hz, PCH$_3$), 1.34 (2 H, m, PCH$_2$). ^{31}P NMR (MeCN, 101.2 MHz): δ -25.3 (quint sept, $^{3}J_{\mathrm{PH}}$ = 18.3 Hz, $^{2}J_{\mathrm{PH}}$ = 3.7 Hz).

Synthesis of cyclic oligophosphines

The following procedure is based on **4d**, but can also be carried out with other imidazolio-phosphides.
In a 100 ml round-bottomed Schlenk flask, **4d** (200 mg, 1.09 mmol) was dissolved in MeCN (25 mL). A solution of the appropriate trialkyloxonium tetrafluoroborate (17 ml of a solution prepared from 2.00 mmol $[R_3O][BF_4]$ in 30 mL of MeCN, 1.13 mmol, 1.04 equiv.) was added dropwise over 10 min under vigorous stirring. After 30 min, the solvent was removed under reduced pressure. The remaining yellow slurry was extracted into toluene and the extract filtered through a G4 glass frit. Removal of the solvent under reduced afforded the cyclic oligophosphines as yellow oils that were characterised by NMR spectroscopy and MS. Recrystallization of the solid extraction residue from CH_2Cl_2/Et_2O afforded **7d**$[BF_4]$ (no yield determined).
Pentamethyl-cyclopentaphosphine. $^{31}P\{^1H\}$ NMR (C_6D_6, 101.2 MHz): ABB'CC' pattern, δ = 18.4 (P^A), 17.3 (P^B), 16.3 (P^C), J_{AB} = -250.0 Hz, J_{AC} = 22.9 Hz, J_{BC} = -235.8 Hz, $J_{BB'}$ = -2.2 Hz, $J_{CC'}$ = -308.3 Hz, $J_{BC'}$ = -8.8 Hz. HRMS (EI, 70 eV): m/e = 229.9864 (calcd. for $[C_5H_{15}P_5]^+$ 229.9862, $[M^{+\cdot}]$].
Pentaethyl-cyclopentaphosphine. $^{31}P\{^1H\}$ NMR (C_6D_6, 161.9 MHz): ABB'CC' pattern, δ = 19.8 (P^A), 14.2 (P^B), 13.4 (P^C), J_{AB} = -259.2 Hz, J_{AC} = 21.8 Hz, J_{BC} = -244.4 Hz, $J_{BB'}$ = -3.8 Hz, $J_{CC'}$ = -315.6 Hz, $J_{BC'}$ = -9.4 Hz.

Synthesis of dimethylphosphine

A 50 ml round-bottomed Schlenk flask was loaded with **19a**$[BF_4]$ (400 mg, 0.75 mmol) and $LiAlH_4$ (30 mg, 0.83 mmol) and cooled with liq. N_2. Freshly dried CD_3CN (8 mL) was condensed onto the solid mixture, which was then allowed to warm to rt and stirred for 1 h. Then, 5 mL of the solution were distilled at 50° C into a second Schlenk flask cooled by liq. N_2. Characterisation of the distillate by NMR spectroscopy showed the formation of a mixture of Me_2PH (74% by integration of the ^{31}P NMR signals), Me_2PD (20%) and Me_4P_2 (6%).
Me_2PH/Me_2PD. ^1H NMR (CD_3CN, 250 MHz): δ = 1.11 (6 H, dd, $^2J_{PH}$ = 2.8 Hz, $^3J_{HH}$ = 7.7 Hz, PCH_3), 3.14 (1 H, dq, $^1J_{PH}$ = 194.7 Hz, $^3J_{HH}$ = 7.7 Hz, PH). $^{13}C\{^1H\}$ NMR (CD_3CN, 62.8 MHz): δ 5.47 (d, $^1J_{PC}$ = 9.5 Hz, PCH_3). ^{31}P NMR (CD_3CN, 101.2 MHz): δ = -99.1 (dsept, $^1J_{PH}$ = 194.7 Hz, $^2J_{PH}$ = 2.8 Hz, PH), -100.8 (t sept, $^1J_{PD}$ = 30.2 Hz, $^2J_{PH}$ = 2.8 Hz, PD).
P_2Me_4. ^1H NMR (CD_3CN, 250 MHz): δ = 1.13 (12 H, m, PCH_3). ^{31}P NMR (CD_3CN, 101.2 MHz): δ = -59.3 (m).

Synthesis of ethylmethylphosphine

A 50 ml round-bottomed Schlenk flask was loaded with **19a**$[BF_4]$ (300 mg, 0.55 mmol) and MeCN (8 mL). After the solid had dissolved, a solution of $LiAlH_4$ (0.25 ml of a 2.4 M solution in THF, 0.60 mmol) was rapidly added under vigorous stirring. After 30 min, 5 mL of this solution was distilled from the reaction mixture into a second round-bottomed Schlenk flask cooled with liq. N_2. Characterisation of the distillate by NMR spectroscopy showed the formation of a mixture of Et(Me)PH (86% by integration of the ^{31}P NMR signals) and two unidentified side products (14%) and the absence of any B- and Al-containing components.
Et(Me)PH. ^1H NMR (^1H,^{31}P HMQC, MeCN, 250 MHz): δ 1.07 (6 H, q, $^3J_{PH}$ = 6.9 Hz, $PCCH_3$), 3.00 (1 H, dsext, $^1J_{PH}$ = 194 Hz, $^3J_{HH}$ = 8 Hz, PH). ^{31}P NMR (MeCN, 101.2 MHz): δ = -77.2 (dq, $^1J_{PH}$ = 195 Hz, $^3J_{PH}$ = 14 Hz).

Reaction monitoring studies

Reactions of imidazolio-phosphine iodides or tetrafluoroborates with triethyl amine

Typical procedures.
(a) Triethyl amine (25.0 µl, 0.18 mmol) was added to a vigorously stirred solution of **1b**[I] (100 mg, 0.18 mmol) in MeCN (7.5 mL) in a 50 ml Schlenk flask. A precipitate formed, and the supernatant solution was analysed by recording ^1H, $^{31}P\{^1H\}$, ^{31}P, and ^1H,^{31}P HMQC NMR spectra after specific points in time (10 min, 1 h, 2 d). Signal assignment was aided by spectral simulation where necessary, and the identification of known compounds verified by comparison of the results with literature data. In this and all other reactions, the $^{31}P\{^1H\}$ NMR spectra disclosed the formation of P_3H_5 as reaction intermediate, and of P_2H_4, and occasionally PH_3 as final products. The ^1H NMR spectra disclosed formation of the appropriate imidazolium ion **7b**$^+$ (^1H NMR (MeCN, 250 MHz): δ = 1.17 (12 H, d, $^3J_{HH}$ = 6.8 Hz, *i*Pr-CH_3), 1.23 (12 H, d, $^3J_{HH}$ = 6.8 Hz, *i*Pr-CH_3), 2.38 (4 H, sept, $^3J_{HH}$ = 6.7 Hz, *i*Pr-CH), 7.54 (6 H, m, m/p-CH), 7.86 (2 H, d, $^4J_{HH}$ = 1.4 Hz, 4,5-NCH), 9.16 (1 H, t, $^4J_{HH}$ = 1.4 Hz, 2-NCH)) or its congeners. Selected $^{31}P\{^1H\}$ NMR spectra are shown in Figures S1. A summary of the results is described in the main text.

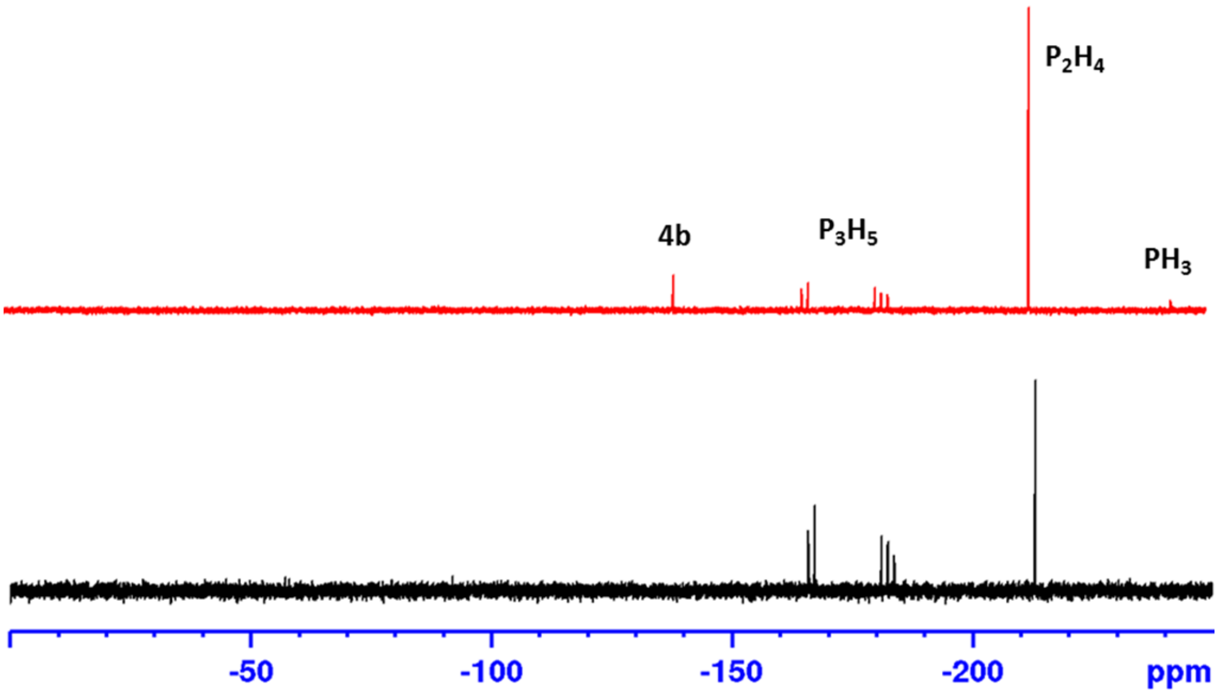


Figure S1: $^{31}P\{^{1}H\}$ NMR spectra recorded during the reaction of **1b**[I] with NEt_3 (1 equiv., red trace) and **1d**[I] with NEt_3 (ca. 10 mol-%, black trace) with signal assignments.

(b) A solution prepared by dissolving **1d**[BF_4] (13 mg, 50 µmol) in CD_2Cl_2 (0.6 mL) in an NMR tube with PTFE screw was cooled to -78 °C. Et_3N (2.2 µl, 20 µmol) was added, the mixture shaken vigorously (< 3 min) to ensure mixing, and then subjected to characterisation by NMR spectroscopy at -60 °C. A selected $^{31}P\{^{1}H\}$ NMR spectrum is shown in Figure S2. ^{1}H NMR spectra disclosed formation of **7d**$^{+}$ (^{1}H NMR (MeCN, 250 MHz): δ = 1.48 (12 H, d, $^{3}J_{HH}$ = 6.7 Hz, *i*Pr-CH_3), 4.56 (2 H, sept, $^{3}J_{HH}$ = 6.7 Hz, ^{i}Pr-CH), 7.45 (2 H, br s, 4,5-NCH), 8.68 (1 H, br s, 2-NCH).

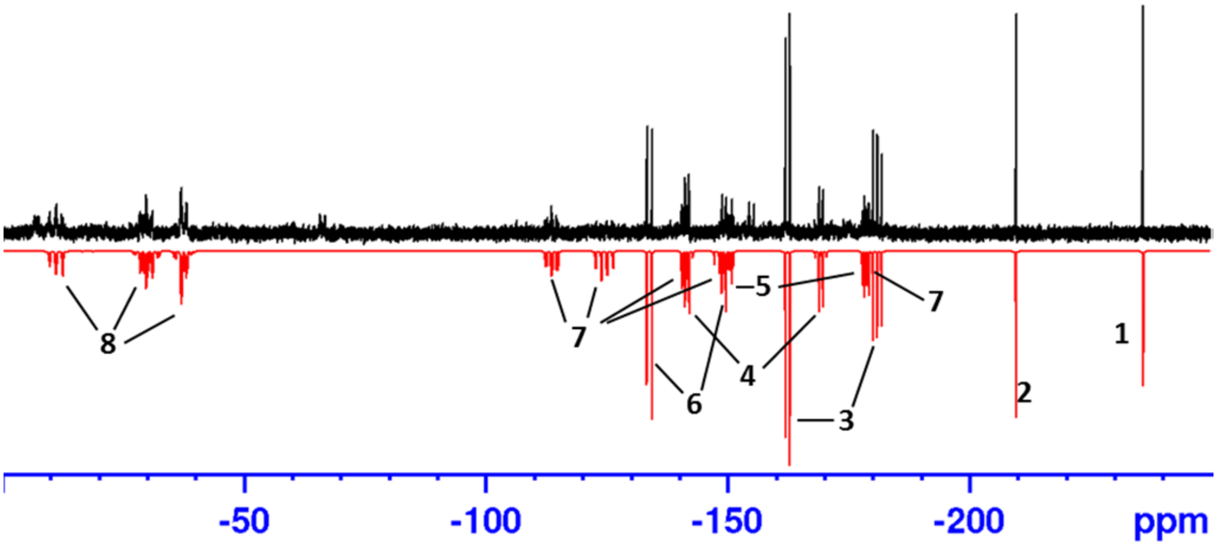


Figure S2: 161.9 MHz $^{31}P\{^{1}H\}$ NMR spectrum recorded during reaction of **1d**[I] with NEt_3 (40 mol-%) after 1 h reaction time at -60 °C (black trace) and result of a spectral simulation as superposition of the spin systems 1 – 8 (red trace). Spin systems and assignments (signs of all ^{1}J couplings assumed to be negative: 1 – PH_3 ($\delta^{31}P$ -235.95); 2 – P_2H_4 ($\delta^{31}P$ -209.7); 3 – P_3H_5 (A_2B system, $\delta^{31}P$ -162.4 (A), -181.0 (B), J_{AB} = 145 Hz); 4 – dl-P_4H_6 (AA'BB' system, $\delta^{31}P$ -141.7 (A), -169.3 (B), $J_{AA'}$ = -145.1 Hz, J_{AB} = -156.1 Hz, $J_{AB'}$ = +21.8 Hz, $J_{BB'}$ = 5 Hz); 5 – meso-P_4H_6 (AA'BB' system, $\delta^{31}P$ -149.3 (A), -178.8 (B), $J_{AA'}$ = -128.7 Hz, J_{AB} = -154.2 Hz, $J_{AB'}$ = +14 Hz, $J_{BB'}$ = ±9 Hz); 6 – iso-P_4H_6 (A_3B system, $\delta^{31}P$ -133.9 (A), -148.9 (B), J_{AB} = -176.9 Hz); 7 – P_5H_7 (ABCDE system, $\delta^{31}P$ -150.3 (A), -124.5 (B), -113.7 (C), -178.5 (D), -141.3 (E), J_{AB} = -189.1 Hz, J_{AC} = 43.6 Hz, J_{AD} = 5.8 Hz, J_{AE} = 49.7 Hz, J_{BC} = -200.4 Hz, J_{BD} = 28.6 Hz, J_{BE} = -191.7 Hz, J_{CD} = -173.4 Hz, J_{CE} = 35.9 Hz); 8 – P_5H_5 (ABB'CC' system, $\delta^{31}P$ -11.2 (A), -29.8 (B), -37.5 (C), J_{AB} = -224.8 Hz, J_{AC} = 33.1 Hz, J_{BC} = -226.7 Hz, $J_{BC'}$ = 27.2 Hz, $J_{BB'}$ = 45.2 Hz, $J_{CC'}$ = -237.3 Hz).

(c) In a 50 ml Schlenk flask, **5b**[BF_4] (100 mg, 0.19 mmol) was dissolved in MeCN (7 mL). Et_3N (26 µl, 0.19 mmol) was added under vigorous stirring. Samples taken from the reaction mixture after 10 min and 11 h were analysed by NMR spectroscopy. Selected $^{31}P\{^1H\}$ NMR spectra are shown in Figure S3. The ^1H NMR spectra disclosed formation of **7b**$^+$.

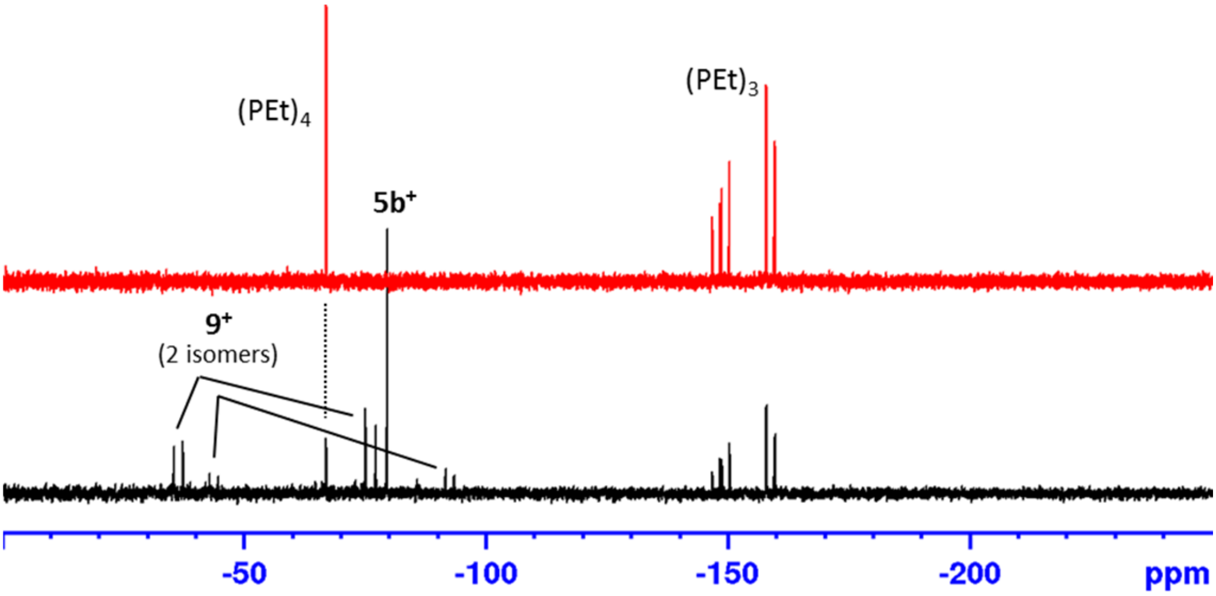


Figure S3: 101 MHz $^{31}P\{^1H\}$ NMR spectra recorded during reaction of **5b**[BF_4] with NEt_3 (1 equiv.) shortly after mixing (black trace) and after ca. 10 h (red trace) with spectral assignments.

Reactions of imidazolio-phosphine iodides with anion bases

Typical procedures:

(a) A 50 ml Schlenk flask was charged with **1d**[BF_4] (100 mg, 0.37 mmol) and *t*-BuOK (41 mg, 0.37 mmol). MeCN (7.5 mL) was added under vigorous stirring. Precipitates formed were allowed to settle and the supernatant solution was subjected to characterisation by NMR spectroscopy at various reaction times (10 min, 2 h, 18 h). Analysis of the spectra disclosed formation of a mixture of **7d**$^+$, **4d**, P_3H_5 (transient), P_2H_4 and PH_3 (follow-up product). Selected $^{31}P\{^1H\}$ NMR spectra are shown in Figures 2 and S4.

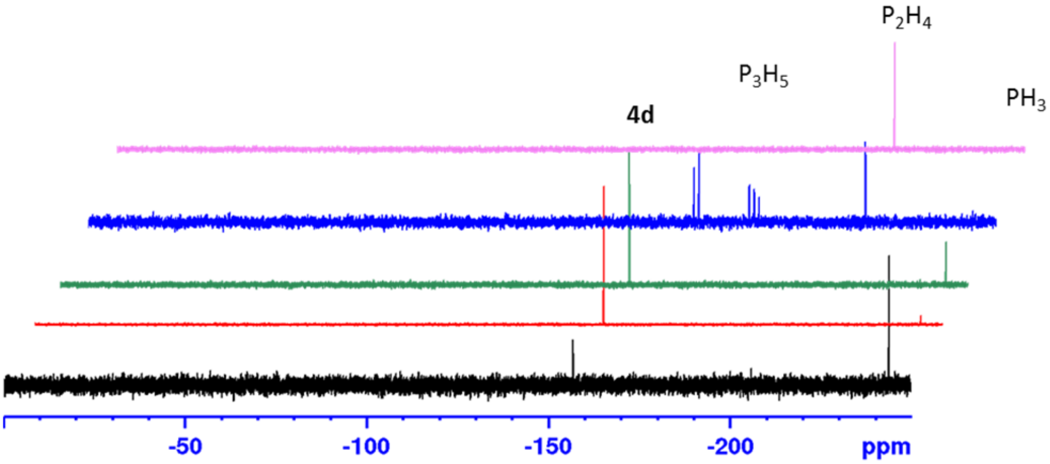


Figure S4: 101 MHz $^{31}P\{^1H\}$ NMR spectra recorded during reactions of **1d**[I] with KH (blue trace), KHMDS (red trace), *t*-BuOK (green trace), NEt_3 (blue trace - 1 h reaction time, purple trace – 1 d reaction time). Chemical shifts: δ -243.9 (PH_3), -213.1 (P_2H_4), -156.7 (**4d**), -162.4 (P_3H_5), -181.0 (P_3H_5).

(b) A solid mixture of **5b**[BF_4] (100 mg, 0.19 mmol) and *t*-BuOK (21 mg, 0.19 mmol) in a 50 ml round-bottomed Schlenk flask was dissolved under vigorous stirring in MeCN (7 mL). The reaction mixture was subjected to NMR characterisation after 30 min, 24 h, and 48 h. Quantitative deprotonation of the starting material to afford **6b** and $(PEt)_n$ occurred immediately, and transformation of $(PEt)_{3,4}$ into $(PEt)_5$ was observed with increasing reaction time. Analogous experiments were carried out using KHMDS, LDA, or KH as anion bases and **2b**[BF_4] as phosphorus source. Selected $^{31}P\{^1H\}$ NMR spectra are shown in Figure 2 in the main text.

Reactions of imidazolio-phosphine tetrafluoroborates with imidazolio-phosphides

(a) A NMR tube with PTFE screw was charged with **1d**[BF$_4$] (10 mg, 37 µmol) and **4d** (6.8 mg, 37 µmol). The reactants were dissolved by adding CD$_3$CN (0.6 mL) and vigorously agitating the mixture for 3 min. NMR spectra were recorded at -30 °C and after 25 h at rt. The solution was stockpiled with another batch of **1d**[BF$_4$] (10 mg, 40 µmol) and analysed by NMR spectroscopy. Selected ^{31}P{^{1}H} NMR spectra are shown in Figure S5.

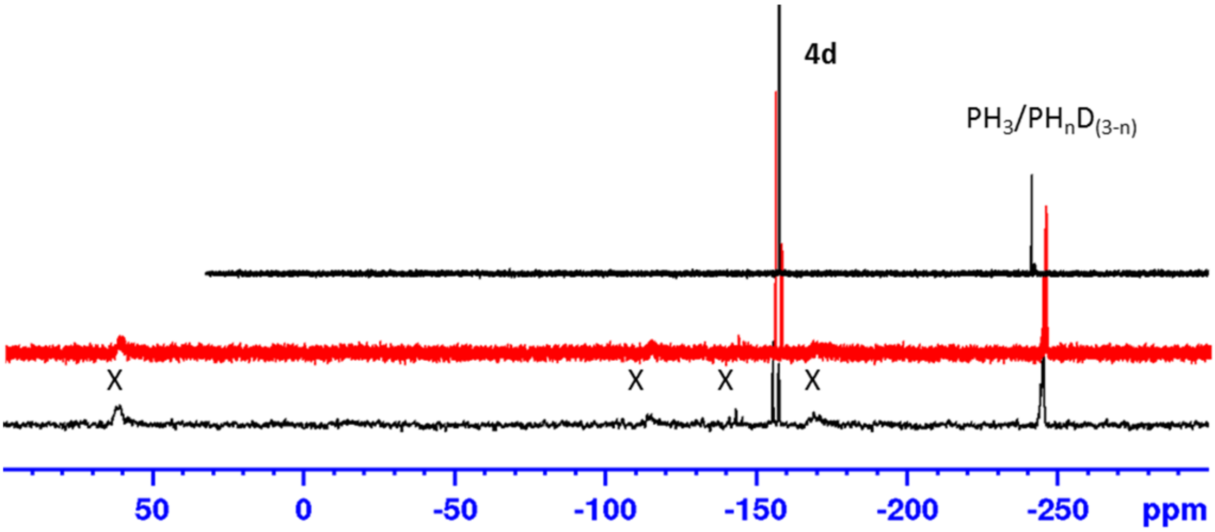


Figure S5: 161.9 MHz ^{31}P{^{1}H} NMR spectra recorded during reaction of **1d**[BF$_4$] with **4d** (a) at -30 °C shortly after mixing (top trace); (b) at rt 24 h after addition of a further batch of **1d**[BF$_4$] (centre trace); (c) as in (b) but processed with a stronger exponential apodizaton to highlight broad lines. Note that H/D-exchange of **4d** and PH$_3$ with the solvent leads to the appearance of signals of deuterated isotopomers of these species. The broad lines marked with X are assigned to yet unidentified soluble polyphosphorus compounds.

(b) A NMR tube with PTFE screw was charged with **1b**[BF$_4$] (20 mg, 39 µmol) and **4d** (2.2 mg, 12 µmol). The reactants were dissolved by adding CD$_2$Cl$_2$ (0.6 mL) and vigorously agitating the mixture for 3 min. NMR spectra were recorded directly after mixing and after further 25 h at rt (Figure S6). The solution was stockpiled with another batch of **1d**[BF$_4$] (20 mg, 39 µmol) and analysed by NMR spectroscopy. The spectral data disclosed that **1b**$^+$ had been fully consumed at both stages, and that formation of **4b**, PH$_3$, P$_2$H$_4$ and P$_3$H$_5$ was observed.
Mixtures of **1d**[BF$_4$]/**4b** and **1b**[BF$_4$]/**4b** reacted in the same manner.

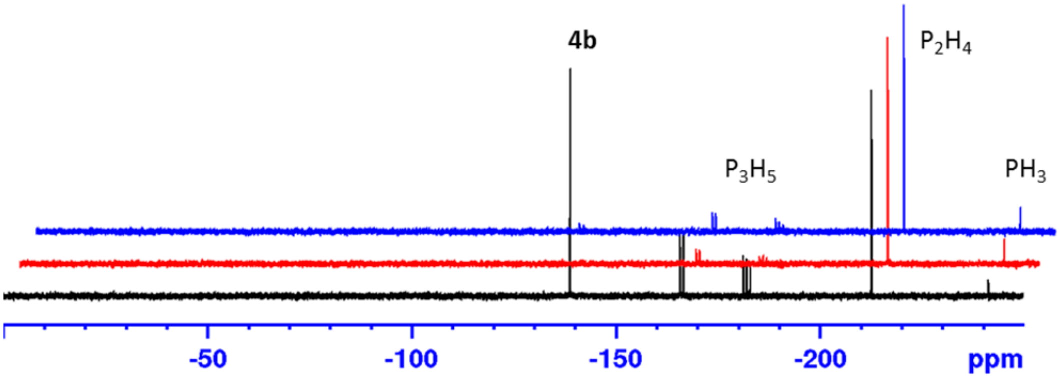


Figure S6: 161.9 MHz ^{31}P{^{1}H} NMR spectra recorded during reaction of **1b**[BF$_4$] with **4d** (a) shortly after mixing (black trace); (b) after 24 h at rt (red trace), and (c) after addition of a further batch of **1b**[BF$_4$] (blue trace).

(c) Several portions of **5b**[BF$_4$] (see Table) were added to a solution of **6b** (8 mg, 18 µmol) in CD$_3$CN (0.7 mL) in a NMR tube with PTFE screw. NMR characterisation was carried out before the first and then after each single addition of reagent. Selected ^{31}P{^{1}H} NMR spectra are shown in Figures S7-S9.

Entry	amount **5b**[BF$_4$] added	Ratio **5b**[BF$_4$]:**6b**
1	3 mg, 6 µmol	0.3:1
2	3 mg, 6 µmol	0.7:1
3	3 mg, 6 µmol	1:1
4	10 mg, 18 µmol	2:1
5	19 mg, 36 µmol	4:1

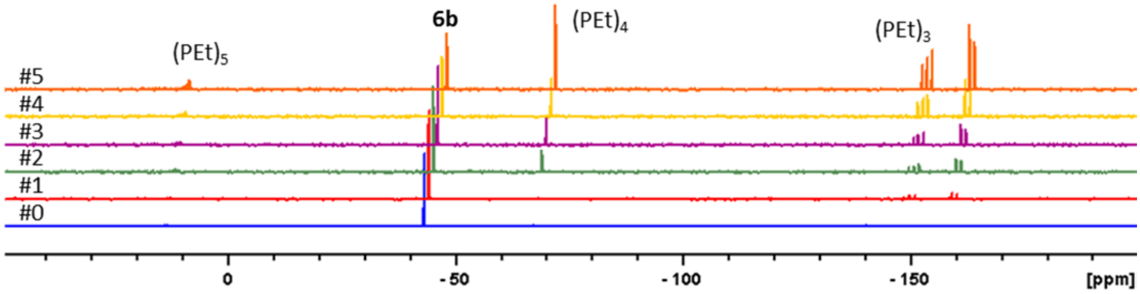


Figure S7: Stacked plot representation of 161.9 MHz $^{31}P\{^1H\}$ NMR spectra recorded during reaction of **6b** with different quantities of **5b**[BF$_4$] (traces refer to the entries in the table; trace #0 is the spectrum of pure **6b**.

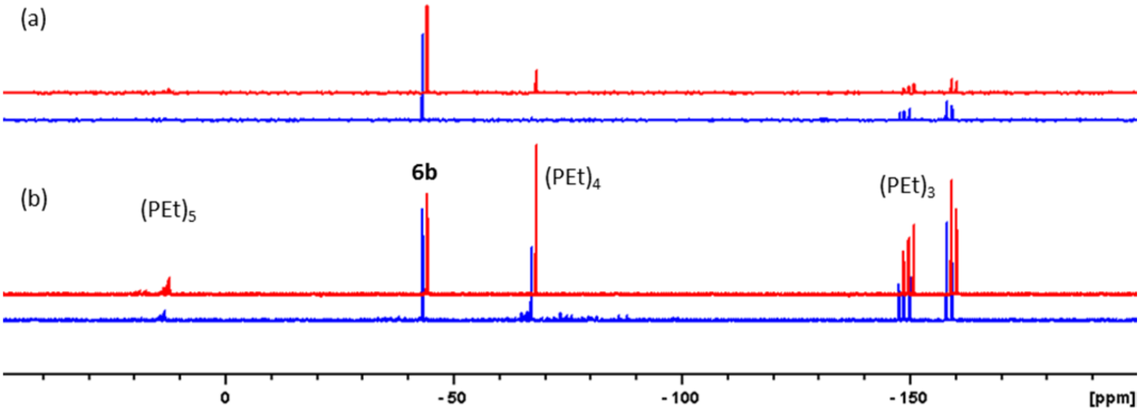


Figure S8: Stacked plot representation of the 161.9 MHz $^{31}P\{^1H\}$ NMR spectra recorded after stockpiling a reacting mixture of **6b**/**5b**[BF$_4$] with additional **5b**[BF$_4$]. The amounts of reagents added are specified in entries (a) #2 and (b) #5 of the table. Comparing blue (recorded directly after mixing) and red traces (after an additional 24 h) allow observe the effects of ring dismutation and identify transient intermediates (in (b), see also Figure S9).

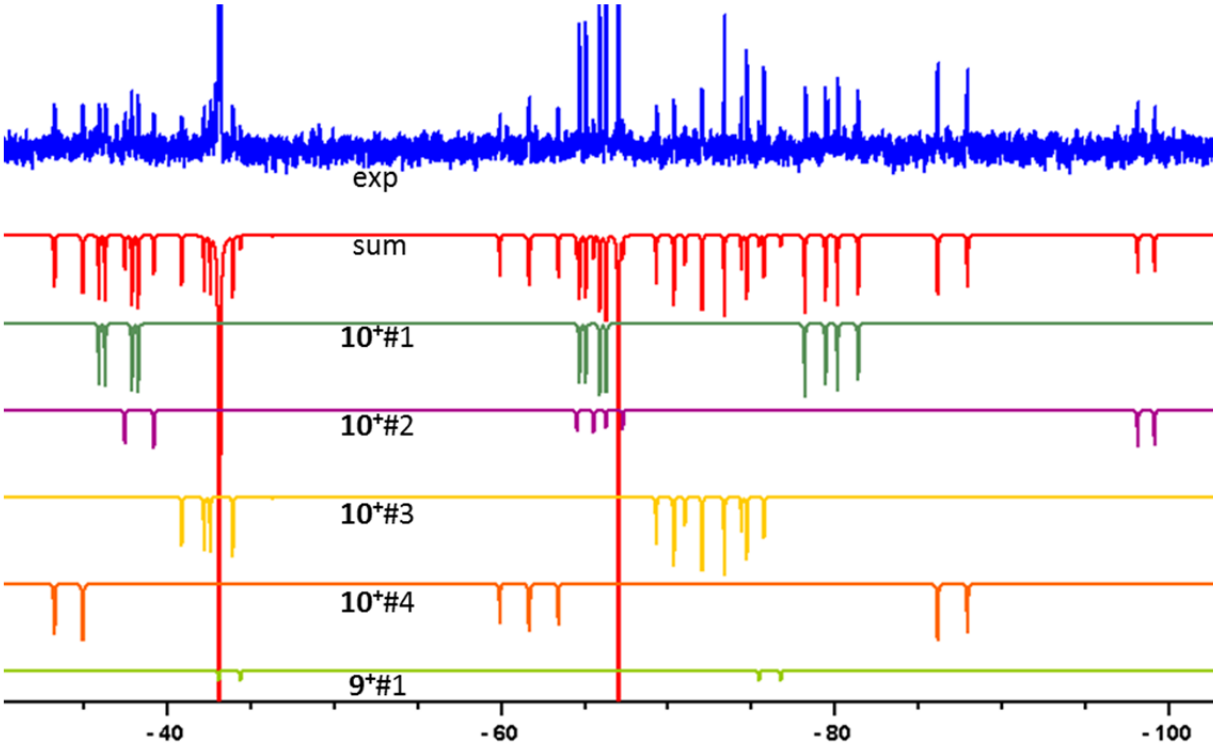


Figure S9: Expansion of the spectrum of Figure S8 (blue trace) and result of a spectral simulation (red trace). The simulation was obtained as a superposition of the singlet resonances attributable to **6b** and (PEt)$_4$ with AX and AMX/ABX-type patterns attributable to individual stereoisomers of **9**$^+$ and **10**$^+$, which are displayed separately in the remaining traces. One of the stereoisomers of **9**$^+$ was not observable. Spectral parameters obtained from the simulation: **10**$^+$#1: δ^{31}P -37.2(P^A), -65.6 (P^M), -79.8 (P^X), J_{AM} = 60.9 Hz, J_{AX} = 319.0 Hz, J_{MX} = 199.3 Hz; **10**$^+$#2: δ^{31}P -38.4(P^A), -66.0 (P^M), -98.7 (P^X), J_{AM} = 282.1 Hz, J_{AX} = 2.0 Hz, J_{MX} = 162.7 Hz; **10**$^+$#3: δ^{31}P -42.5(P^X), -70.8 (P^A), -74.6

(P^B), J_{AX} = -286.0 Hz, J_{BX} = +226.5 Hz, J_{AB} = ±167.3 Hz; **10**$^+$#4: δ^{31}P -34.2(P^A), -61.8 (P^M), -87.1 (P^X), J_{AM} = 278.0 Hz, J_{AX} = 4.4 Hz, J_{MX} = 279.3 Hz; **9**$^+$#1: δ^{31}P -43.8(P^A), -76.2 (P^X), J_{AX} = 210.9 Hz.

(d) Several portions of **5b**[BF_4] (see Table) were subsequently added to a solution of **4b** (30 mg, 71 µmol) in CD_3CN (0.7 mL) in a NMR tube with PTFE screw. NMR characterisation was carried out before the first and then after each single addition of reagent, and it was ensured that the reaction had gone to completion before further reagent was added. Selected $^{31}P\{^1H\}$ NMR spectra are shown in Figures S10-12. The signals of **4b**/**4b**-D_1 (the latter arising from H/D-exchange with the solvent after extended reaction times) and, after addition of the first portion of reagent, **6b** were constantly visible. Di- and triphosphines attributable to **12**, **13** were detected as intermediates which decayed eventually to leave $(EtP)_n$ (n = 4,5) and **7b**$^+$ (verified by ^{1}H NMR spectroscopy) as final products.

Entry	amount **5b**[BF_4] added	Ratio **5b**[BF_4]/**4b**
1	13 mg, 24 µmol	0.33:1
2	13 mg, 24 µmol	0.67:1
3	38 mg, 71 µmol	1.67:1
4	38 mg, 71 µmol	2.67:1
5	13 mg, 24 µmol	3:1

A similar experiment was also carried out starting with an initial ratio of **5b**[BF_4]/**4b** 3:1.

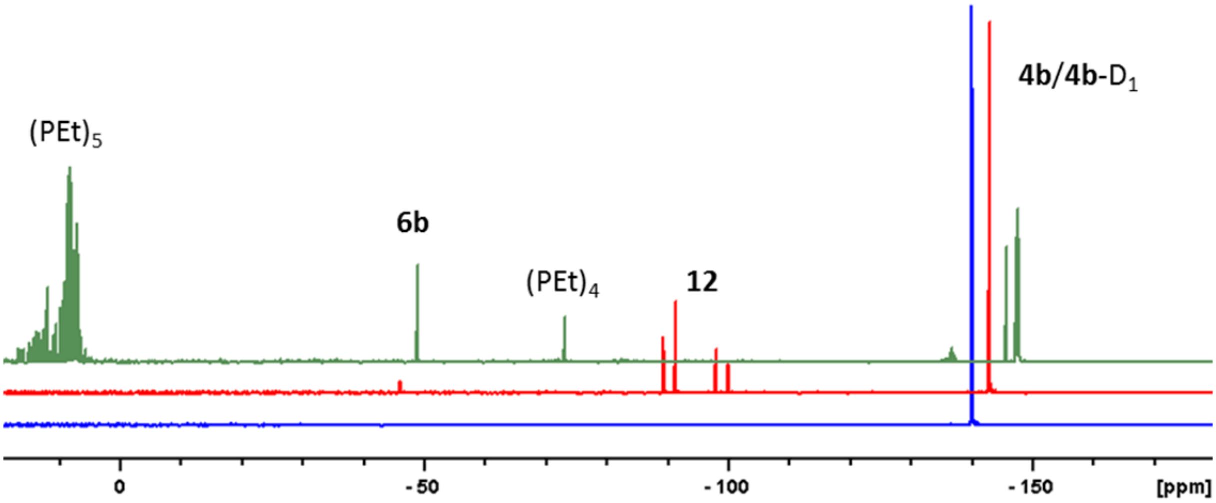


Figure S10: 101.9 MHz $^{31}P\{^1H\}$ NMR spectra recorded for monitoring the reaction of **4b** with **5b**[BF_4] in CD_3CN. (a) pure **4b**; (b) directly after addition of 0.33 equivs. of **5b**[BF_4]; (c) after addition of altogether 3 equivs. of **5b**[BF_4] and 2 weeks.

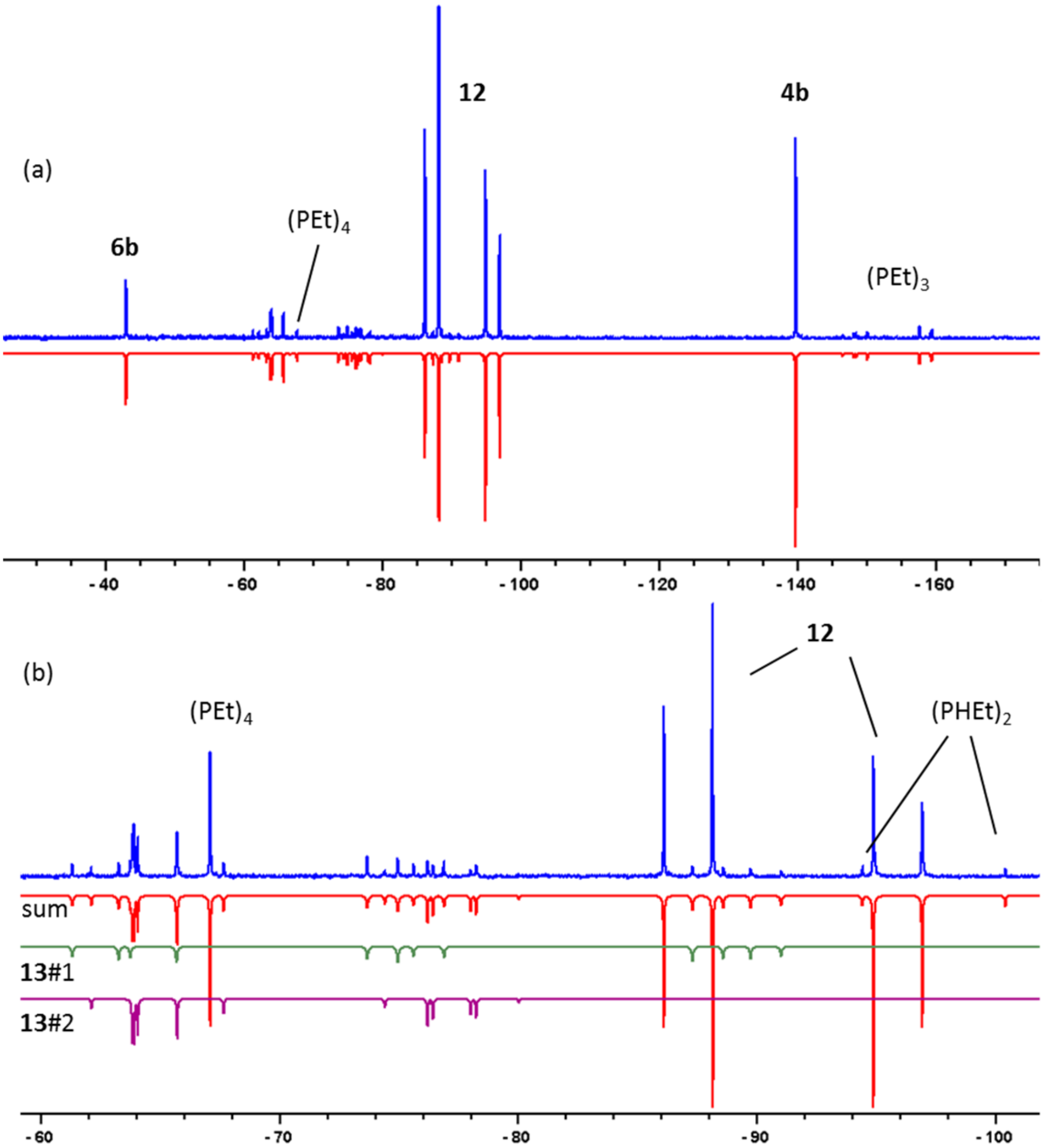


Figure S11: 101.9 MHz $^{31}P\{^1H\}$ NMR spectra recorded during monitoring the reaction of **4b** with **5b**[BF_4] in CD_3CN. (a) Spectrum recorded directly after addition of 1 equiv. of **5b**[BF_4] to establish a total ratio of **4b**:**5b**[BF_4] of 1:1.67; (b) expansion of a spectrum recorded after allowing the solution to equilibrate for 9 h. The blue and red traces show the experimental spectra and the result of a simulation as a multicomponent mixture. The green and purple traces in (b) display the simulated AMX/ABX patterns attributed to the two diastereomers of **13**. Spectral parameters: **12**: $\delta^{31}P$ = -87.3, -95.8, J = 207.2 Hz; **13**#1: $\delta^{31}P$ = -63.7 (P^A), -75.3 (P^M), -89.1 (P^X), J_{AM} = 195.5 Hz, J_{AX} = 248.8, J_{MX} = 127.6 Hz; **13**#2: $\delta^{31}P$ = -63.6 (P^A), -65.3 (P^B), -77.1 (P^X), J_{AM} = ±200.5 Hz, J_{AX} = +51.5, J_{MX} = -254.1 Hz.

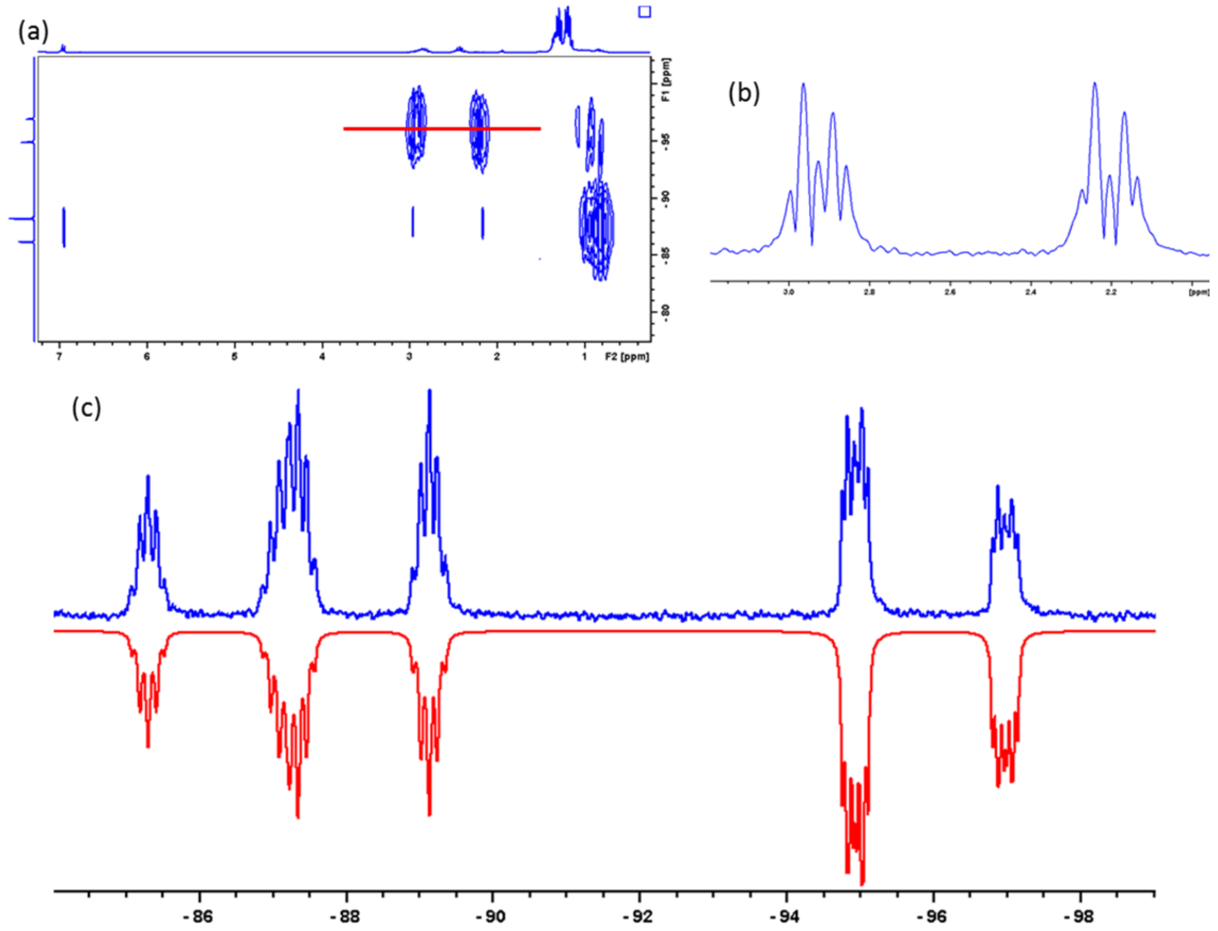


Figure S12: Expansions of the NMR spectra of a reaction mixture prepared from **4b** and **5b**[BF_4] (1:0.67) in CD_3CN showing the signals attributable to **12**. (a) The 2D $^1H,^{31}P$ HMQC spectrum reveals attachment of a hydrogen, an imidazole group and a single CH_2 group showing coupling to both P-atoms. (b) 2D cross section along the red line drawn in (a). The splitting pattern reveals coupling via $^1J_{PH}$, $^2J_{PH}$ and $^3J_{HH}$ to an adjacent CH_2-group, verifying the presence of a P(H)Et-unit. (c) The ^{31}P NMR spectrum (blue trace) and its simulation (red trace) as an ABHKNX$_3$-pattern (A, B = ^{31}P; H, K, N, X = ^1H) confirm the presence of a P–PHEt moiety and allow rule out the presence of a second Et-substituent. Spectral parameters: $\delta^{31}P = -87.3$ (P^A), -95.8 (P^B), $^1J_{AB} = 207.2$ Hz, $^1J_{AH} = 182.9$ Hz, $^2J_{AK} = -1.9$ Hz, $^2J_{AN} = 12.5$ Hz, $^3J_{AX} = 10.9$ Hz, $^2J_{BH} = 17.3$ Hz, $^3J_{BK} = 9.2$ Hz, $^3J_{BN} = 6.1$ Hz.

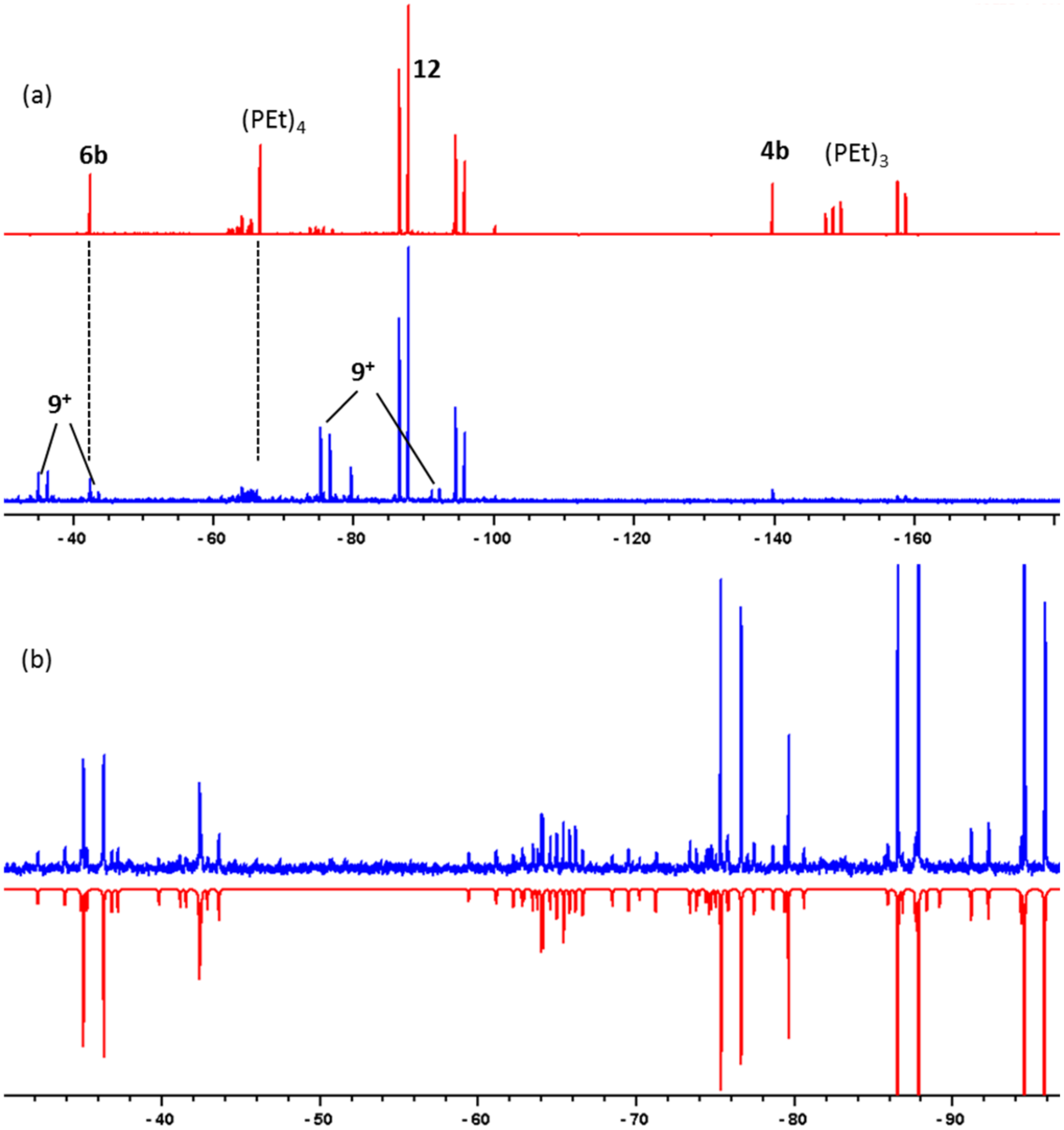


Figure S13: (a) 161.9 MHz $^{31}P\{^1H\}$ NMR spectra of a reaction mixture prepared from **4b** and **5b**[BF_4] (1:3) in CD_3CN shortly after mixing (blue trace) and after 6 h (red trace). (b) Expansion of the lower trace of (a) and result of a spectral simulation (red trace). The displayed region contains signals attributable to **6b**, (PEt)$_4$, (EtPH)$_2$ and trace amounts of **5b**$^+$ (all singlets), two diastereomers of **9**$^+$ and **12** (AX patterns), and finally **10**$^+$ (3 of 4 diastereomers) and **13** (2 diastereomers, all ABX/AMX patterns). Simulation parameters for the AX and AMX/ABX spin systems differ insignificantly from those given in Figures S9, S11. Comparison of the spectra displayed in (a) allowed identify **5b**$^+$, **9**$^+$ and **10**$^+$ as short-lived species whose signals disappeared at the expense of those of (PEt)$_n$.

(e) A solution of **6b** (5 mg, 0.01 mmol) in CD_3CN (0.7 mL) in a NMR tube with PTFE screw was cooled to -40 °C. After addition of **5b**$[BF_4]$ (30 mg, 0.56 mmol), the mixture was immediately frozen in liq. N_2. NMR characterisation at -35 °C was carried out after liquefaction at -40 °C and homogenisation by vigorous shaking. Selected $^{31}P\{^1H\}$ NMR spectra are shown in Figure S14.

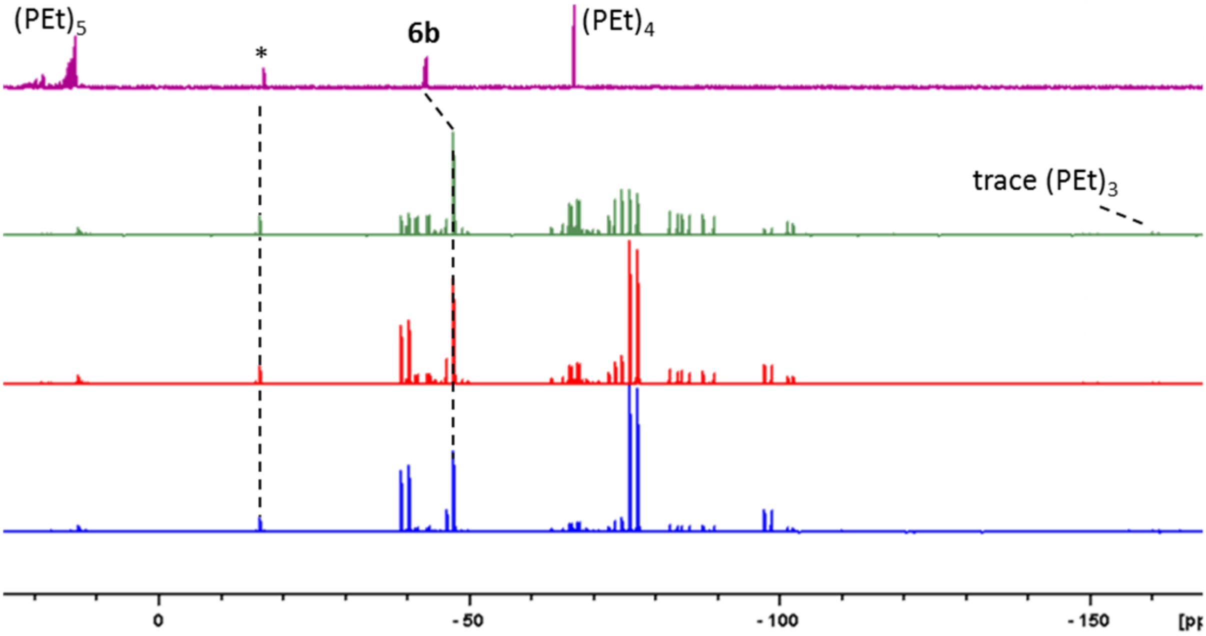


Figure S14: 161.9 MHz $^{31}P\{^1H\}$ NMR spectra of a reaction mixture prepared from **6b** and **5b**$[BF_4]$ (1:5.6) in CD_3CN recorded at -35 °C shortly after mixing (blue trace), after 1 h (red trace) and 6 h (green trace), and after ageing for 2 d at rt (purple trace). The last two spectra are identical to those displayed in Figure 4. The analysis of the spectra was derived from spectral simulations (see Figure 4) and allowed identify $(PEt)_n$ (n = 3-5) beside transient components attributed as **9**$^+$, **10**$^+$. Simulation parameters for the AX and AMX/ABX spin systems (in the spectra recorded at -35 °C): **9**$^+$#1: $\delta^{31}P$ -39.9(P^A), -76.6 (P^X), J_{AX} = 205.9 Hz; **9**$^+$#2: $\delta^{31}P$ -47.1(P^A), -98.3 (P^X), J_{AX} = 184.5 Hz; **10**$^+$#1: $\delta^{31}P$ -42.7(P^A), -67.1 (P^M), -84.0 (P^X), J_{AM} = 60.4 Hz, J_{AX} = 311.0 Hz, J_{MX} = 201.3 Hz; **10**$^+$#2: $\delta^{31}P$ -45.6(P^A), -69.7 (P^M), -101.9 (P^X), J_{AM} = 278.9 Hz, J_{AX} = 2.0 Hz, J_{MX} = 152.2 Hz; **10**$^+$#3: $\delta^{31}P$ -47.8 (P^X), -73.9 (P^A), -75.6 (P^B), J_{AX} = -277.7 Hz, J_{BX} = +238.6 Hz, J_{AB} = ±164.6 Hz; **10**$^+$#4: $\delta^{31}P$ -40.9 (P^A), -65.2 (P^M), -88.7 (P^X), J_{AM} = 278.6 Hz, J_{AX} = 1.7 Hz, J_{MX} = 290.9 Hz. Note that the chemical shifts and J_{PP} coupling constants differ from those given in Figure S9, indicating a temperature dependence of these data that is not uncommon for phosphines.

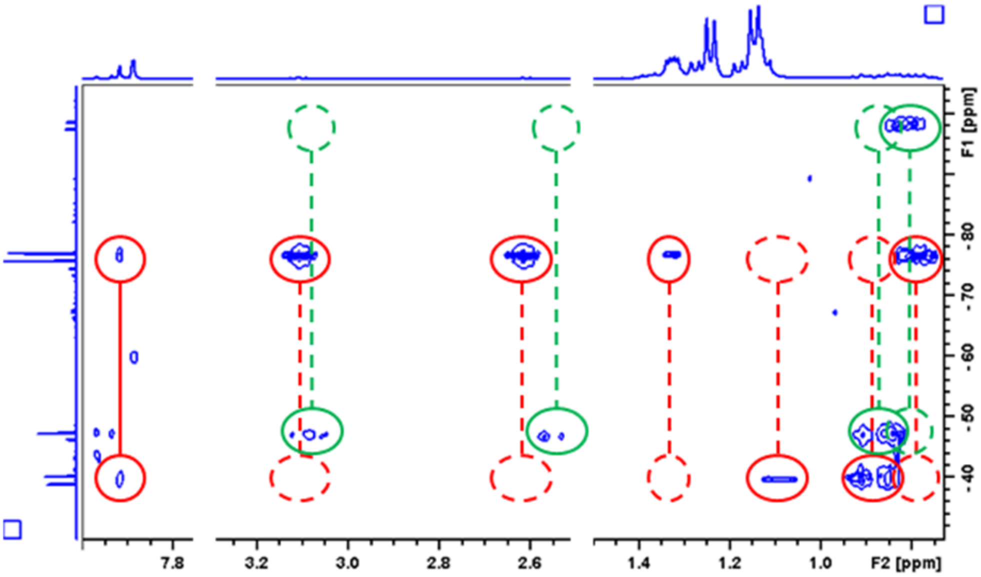


Figure S15: Expansion of a $^1H,^{31}P$ HMQC NMR spectrum of a reaction mixture prepared from **6b** and **5b**$[BF_4]$ (1:5.6) in CD_3CN recorded at -35 °C shortly after mixing showing the correlations involving the imidazole-, PH- and Et-protons of **9**$^+$#1 (marked in red) and **9**$^+$#2 (marked in green). The mutually exclusive P-Et correlations reveal the presence of two distinguishable Et-groups in each isomer.

Crystallographic studies

X-ray diffraction data were collected on a Bruker diffractometer equipped with a Kappa Apex II Duo CCD-detector and a KRYO-FLEX cooling device with Mo-K_α radiation (λ = 0.71073 Å) at 130(2) K for **1b**[I], **1c**[I], **1d**[I], **1e**[I], **2b**[I] and at 135(2) K for **1b**[BF_4], **2c**[BF_4], **5b**[BF_4], **8b**, **19a**[BF_4], **19c**[BF_4], and with Cu-$K_{\alpha 1}$ radiation (λ = 1.5406 Å) at 135(2) K for **6b**. The structures were solved with direct methods (SHELXS-2014[3]) and refined with a full-matrix least squares scheme on F^2 (SHELXL-2014[3]). Semi-empirical or numerical absorption corrections were applied. Non-hydrogen atoms were refined anisotropically and hydrogen atoms except those bound to phosphorus using a riding model. Phosphorus-bound hydrogen atoms were refined isotropically.

One *i*Pr group and the iodide anion of **1b**[I] were disordered. The refinement was carried out using a general RIGU restraint and further restraints (SADI) and constraints (EADP) for the disordered *i*Pr-moiety, and a riding model for all hydrogen atoms. Refinement with the listed atoms showed residual electron density in 8 voids due to heavily disordered solvent molecules (one MeCN and one H_2O per void), which could not be refined with split atoms. Therefore, the option "SQUEEZE" of the program package PLATON[4] was used to create a *hkl*-file that accounted for the residual electron density in the void areas. As a consequence, the atoms list and unit card do not agree.

In **1b**[BF_4], restraints (SADI, RIGU) were used for refining the atoms of a solvent molecule (CH_2Cl_2) that was disordered about a mirror plane (s.o.f.= 0.50).

The PH_2-moieties of **1c**[I] were disordered over two positions. Based on a s.o.f. of 0.600(3) determined from and isotropic refinement with an EADP constraint for the pair of P-atoms, the occupancies were fixed to 0.60 and 0.40, respectively, during the anisotropic refinement. Moreover, restraints (SADI for the C-P distances and the geometry of the PH_2-moiety (1,2 and 1,3 distances, C---H, P-H and H---H) and RIGU for the solvent (MeCN) were used.

In case of **1e**[I], refinement was carried out using constraints (ISOR) and a general RIGU restraint because of the bad quality of the data and a possible disorder perpendicular to the CNCCN-plane.

In **2b**[I], one of two solvent molecules (MeCN) was disordered over 2 positions with occupancies of 0.5 about the center of symmetry. Restraints (SADI, RIGU) were used for the refinement of the solvent molecules.

For **2c**[BF_4], the P(H)Me moieties of both crystallographically independent cations and one anion were disordered. The disordered C and F atoms were refined isotropically. Moreover, the refinement was carried out using a general RIGU restraint and additional constraints (EADP) and restraints (SIMU, SADI) for the disordered moieties. A common occupancy factor was calculated for the 3 different disordered moieties and afterwards fixed to 0.75.

The P(H)Et-unit and one *i*Pr-moiety of **5b**[BF_4] were disordered. The disordered atoms were refined isotropically using constraints (EADP) and restraints (SADI). Restraints (RIGU, SADI) were used in the refinement of the BF_4 anions.

In **6b**, four *i*Pr-groups were disordered. In addition to using a general RIGU restraint, the disordered atoms were refined isotropically using constraints (EADP) and restraints (SADI).

The P(Me)Et-moiety in **19c**[BF_4] was disordered over two positions. The disordered atoms were refined isotropically using constraints (EADP) and restraints (SADI).

Further details are given in the cif-files.

CCDC-1992147 to 1992153 and 1992155 to 1992158 (see Table S1 for further details) contain the crystallographic data for this paper, which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data for (**1b**-**e**)[I], **1b**[BF_4], **2b**[I], **2c**[BF_4], **5c**[BF_4], **6b**, **8b**, (**19a**,**c**)[BF_4].

	1b[I]	**1c**[I]	**1d**[I]	**1e**[I]	**1b**[BF_4]	**2b**[I]
CSD	1992155	1992151	1992147	1992146	1992157	1992150
sum formula	$C_{27}H_{38}IN_2P$, 0.5 C_2H_3N, 0.5 H_2O	$C_{21}H_{26}IN_2P$, 0.5 C_2H_3N	$C_9H_{18}IN_2P$	$C_5H_{10}IN_2P$	$C_{27}H_{38}BF_4N_2P$, CH_2Cl_2	$C_{28}H_{40}IN_2P$, 2 C_2H_3N
M / g mol^{-1}	578.00	484.83	312.12	256.02	593.30	644.60
T	130(2)	130(2)	130(2)	130(2)	135(2)	130(2)
wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
space group	Fdd2	$P2_1/c$	$P2_1/m$	Pmmn	Cmca	Pbcn
a / Å	30.490(2)	17.8150(8)	9.2450(5)	8.4133(14)	16.2797(11)	21.5771(13)
b / Å	32.625(2)	19.1134(9)	7.4965(4)	7.1479(11)	19.2139(11)	14.8112(8)
c / Å	12.8127(8)	14.7481(7)	10.4442(6)	7.5050(11)	20.2982(14)	21.4093(11)
α / °	90	90	90	90	90	90
β / °	90	114.254(2)	115.069(3)	90	90	90
γ / °	90	90	90	90	90	90
V / Å^3	12745.1(14)	4578.5(4)	655.65(6)	451.33(12)	1444.49(12)	6842.0(7)
Z	16	8	2	2	8	8
ρ_{calcd} / g cm^{-3}	1.205	1.407	1.581	1.884	1.241	1.252
F(000)	4768	1960	308	244	2496	2672
crystal size / mm^3	0.376 x 0.146 x 0.130	0.489 x 0.421 x 0.266	0.635 x 0.512 x 0.280	0.111 x 0.097 x 0.081	0.506 x 0.220 x 0.124	0.195 x 0.167 x 0.055
Θ-range / °	1.834 to 28.308	1.645 to 33.170	2.153 to 33.265	2.714 to 25.014	1.922 to 26.423	1.668 to 26.403
μ_{abs} / mm^{-1}	1.074	1.478	2.530	3.653	0.298	1.007
Refl. Collected	63973	81625	17628	4551	42948	53388
Refl. Unique	7918	17413	2681	447	3384	7008
Refl. Obsd. ($I > 2\sigma(I)$)	7380	13044	2559	409	2523	4801
$R_{int.}$	0.0264	0.0304	0.0253	0.0645	0.0466	0.0473
Compl. to Θ = 25.242°	0.997	0.999	1	0.959	0.999	1
Absorp. corr.	Semi-empirical from equivalents	Numerical	Numerical	Numerical	Semi-empirical from equivalents	Numerical
Max. / min. transm.	0.7457 / 0.6459	0.7353 / 0.5919	0.3096 / 0.1110	0.8917 / 0.5327	0.7433 / 0.7253	0.9728 and 0.8868
Data/restraints/parameters	7918 / 236 / 287	17413 / 85 / 533	2681 / 0 / 78	447 / 45 / 38	3384 / 14 / 196	7008 / 37 / 376
GoF (F^2)	1.106	1.010	1.188	1.288	1.030	1.015
R [$I>2\sigma(I)$]	0.0647	0.0323	0.0194	0.0639	0.0699	0.0383
wR2 (all data)	0.1944	0.0830	0.0496	0.1480	0.2139	0.0861

Table S1, continued.

	2c[BF$_4$]	**5b**[BF$_4$]	**6b**	**8b**	**19a**[BF$_4$]	**19c**[BF$_4$]
CSD	1992156	1992152	1992148	1992149	1992153	1992158
sum formula	$C_{22}H_{28}BF_4N_2P$	$C_{29}H_{42}BF_4N_2P$	$C_{29}H_{41}N_2P$	$C_{28}H_{39}N_2P$	$C_{29}H_{42}BF_4N_2P$	$C_{30}H_{44}BF_4N_2P$
M / g mol^{-1}	438.24	536.42	448.61	434.58	536.42	550.45
T	135(2)	135(2)	135(2)	135(2)	135(2)	135(2)
wavelength	0.71073 Å	0.71073 Å	1.5406 Å	0.71073 Å	0.71073 Å	0.71073 Å
crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
space group	$P2_1/n$	$P2_1/n$	Pna21	P21/n	Pnma	P21/n
a / Å	10.6034(5)	9.4999(3)	40.4446(12)	10.3552(6)	18.5540(5)	9.6514(5)
b / Å	27.3731(13)	19.6312(7)	10.7492(3)	7.0047(4)	19.0734(6)	19.5693(9)
c / Å	16.1467(7)	16.2528(6)	12.5916(3)	37.0995(19)	8.1713(2)	16.5413(7)
α / °	90	90	90	90	90	90
β / °	91.181(2)	100.794(2)	90	97.948(3)	90	101.591(2)
γ / °	90	90	90	90	90	90
V / Å^3	4685.6(4)	2977.43(18)	5474.2(3)	2665.2(3)	2891.72(14)	3060.5(2)
Z	8	4	8	4	4	4
ρ_{calcd} / g cm^{-3}	1.242	1.197	1.089	1.083	1.232	1.195
F(000)	1840	1144	1952	944	1144	1176
crystal size / mm^3	0.639 x 0.503 x 0.194	0.814 x 0.566 x 0.418	0.126 x 0.101 x 0.037	0.118 x 0.049 x 0.032	0.591 x 0.430 x 0.422	0.472 x 0.368 x 0.287
Θ-range / °	1.464 to 28.334	2.075 to 30.590	2.185 to 66.619	1.986 to 25.376	2.136 to 30.659	1.632 to 28.339
μ_{abs} / mm^{-1}	0.159	0.137	1.003	0.119	0.141	0.135
Refl. Collected	41082	60555	22897	29169	37631	64438
Refl. Unique	11552	9063	7792	4877	4562	7592
Refl. Obsd. (I > 2σ(I))	7251	6733	6627	2988	3607	5433
$R_{int.}$	0.0377	0.0353	0.0392	0.0940	0.0327	0.0507
Compl. to Θ = 25.242°	1	0.999	0.967	1	1	1
Absorp. corr.	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. / min. transm.	0.7457 / 0.6995	0.7461 / 0.7143	0.8642 and 0.7731	0.8620 and 0.8100	0.7461 and 0.7100	0.7373 and 0.7134
Data/restraints/parameters	11552 / 721 / 562	9063 / 70 / 35	7792 / 1084 / 565	4877 / 0 / 281	4562 / 0 / 176	7592 / 6 / 340
GoF (F^2)	1.036	1.041	1.033	1.001	1.049	1.032
R [I>2σ(I)]	0.0944	0.0594	0.0449	0.0528	0.0430	0.0521
wR2 (all data)	0.2697	0.1690	0.1085	0.1174	0.1223	0.1366

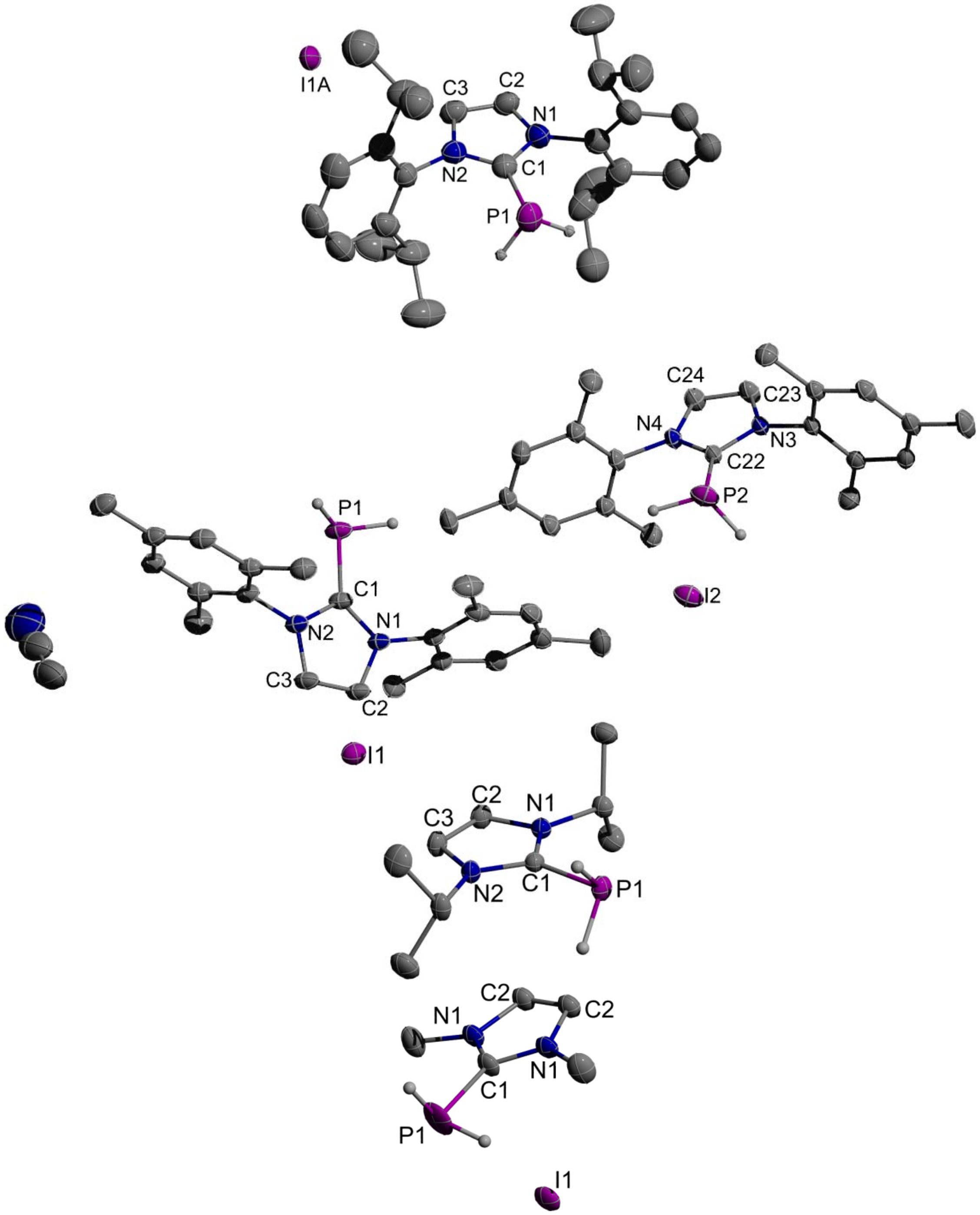


Figure S16. Representation of the molecular structures of **1b**[I] to **1e**[I] (from top to bottom) in the crystal. Hydrogen atoms (except those bound to phosphorous) are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Where parts of molecules are disordered, only the major part is shown.

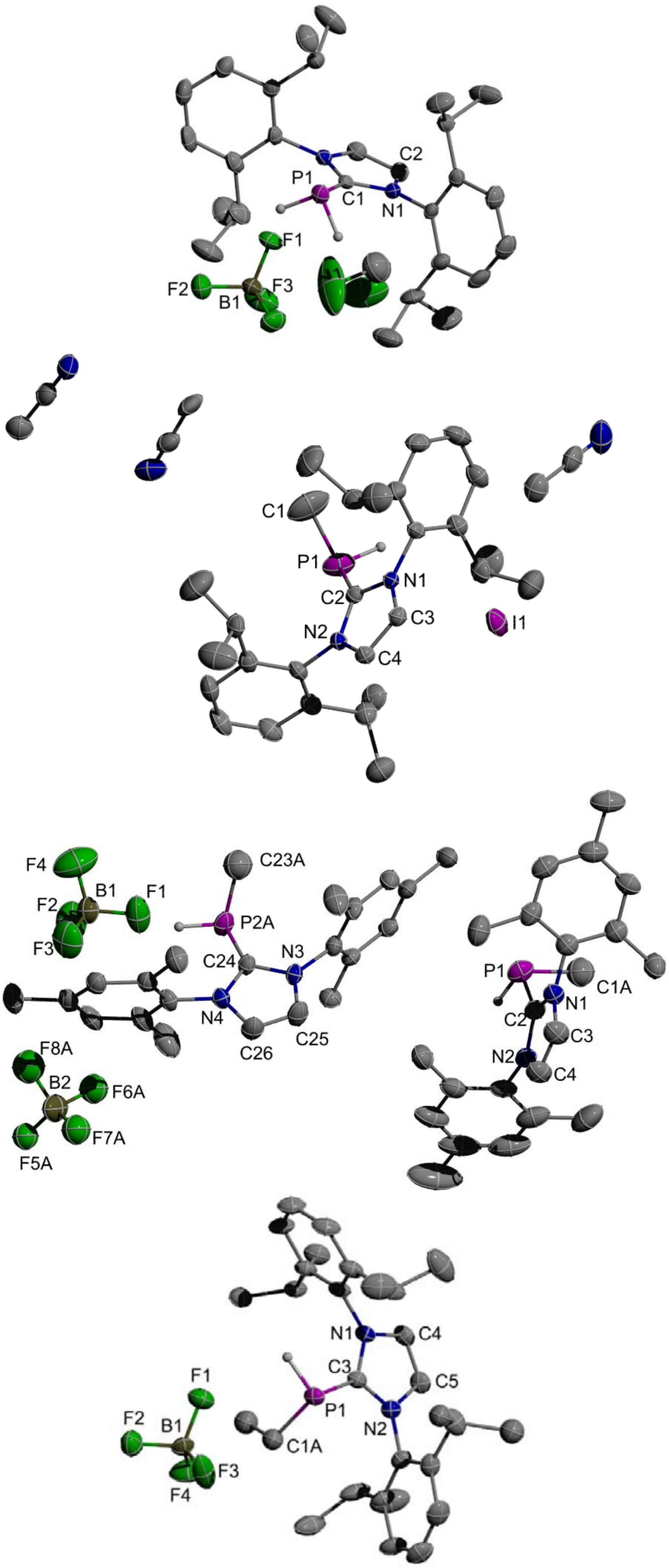
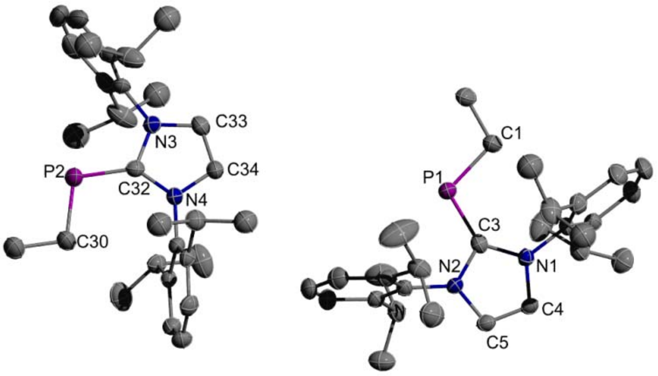
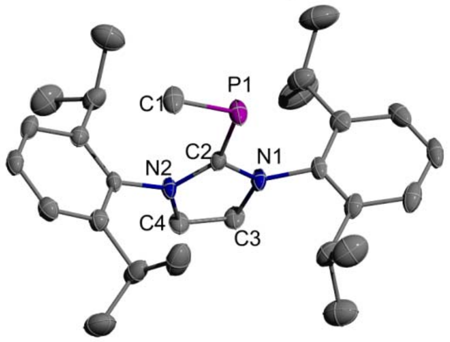
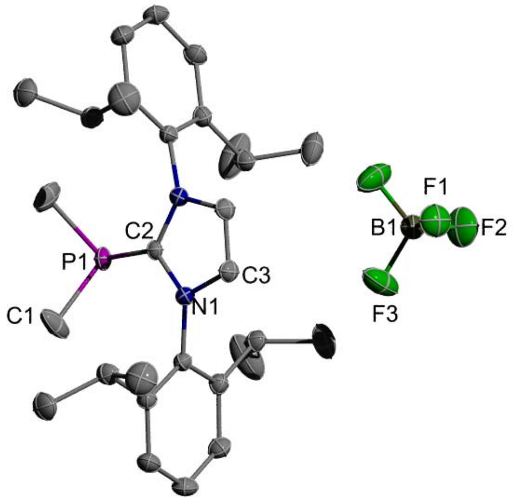


Figure S16 (continued)**.** Representation of the molecular structures of **1b**[BF$_4$], **2b**[I], **2c**[BF$_4$], to **5b**[BF$_4$] (from top to bottom) in the crystal.







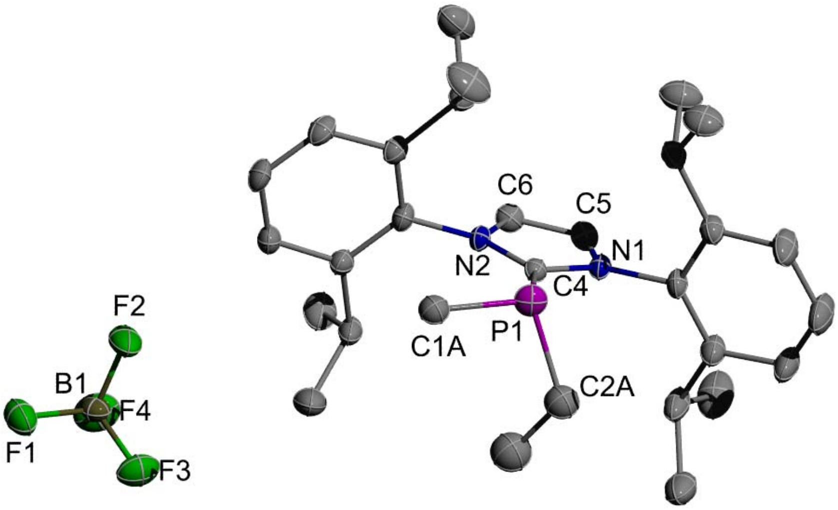


Figure S16 (continued)**.** Representation of the molecular structures of **6b**, **8b**, **19a**[BF_4], to **19c**[BF_4] (from top to bottom) in the crystal.

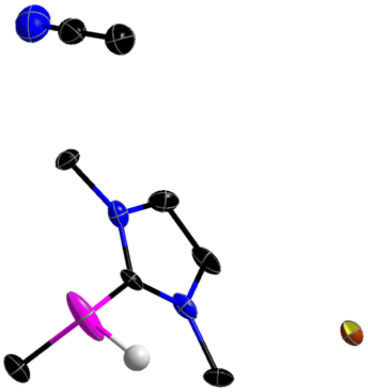


Figure S17. Molecular structure of one of three crystallographically independent ion pairs of **2e**[I] and the incorporated solvent molecule in crystalline solvate **2e**[I]·1/3 MeCN. Hydrogen atoms (except the one bound to phosphorous) are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Metric parameters are not discussed due to bad data quality, but the structure proves the salt-like structure of the compound.

NMR data

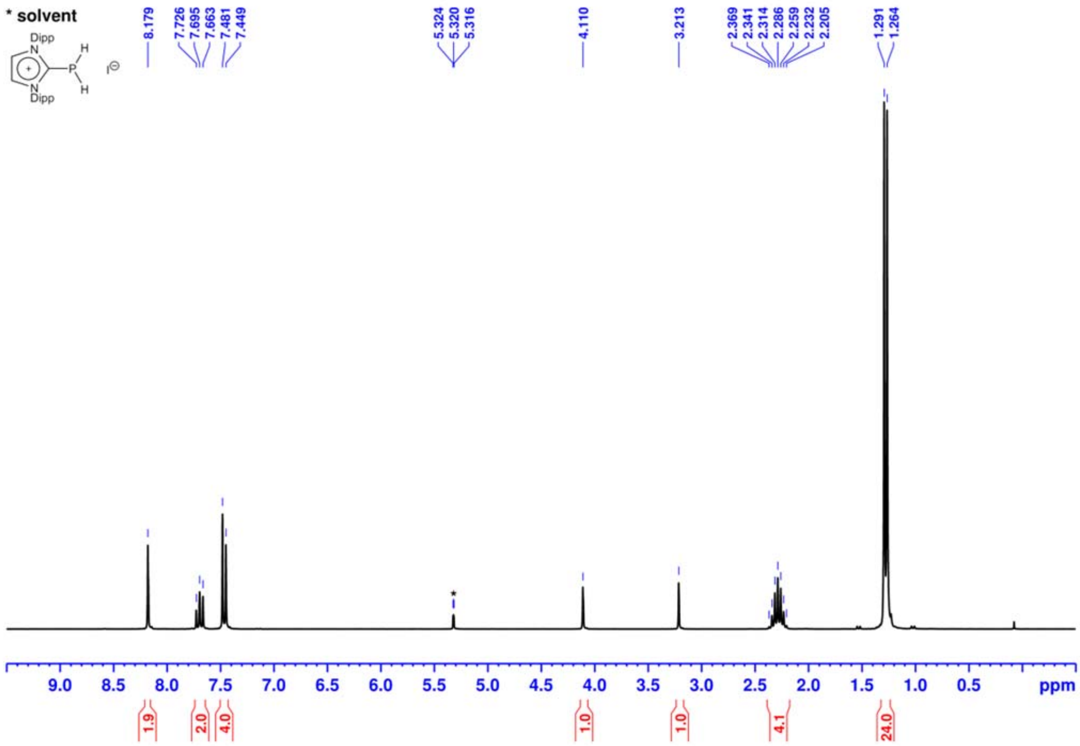


Figure S18. ^{1}H NMR spectrum (CD_2Cl_2, 250 MHz) of **1b**[I].

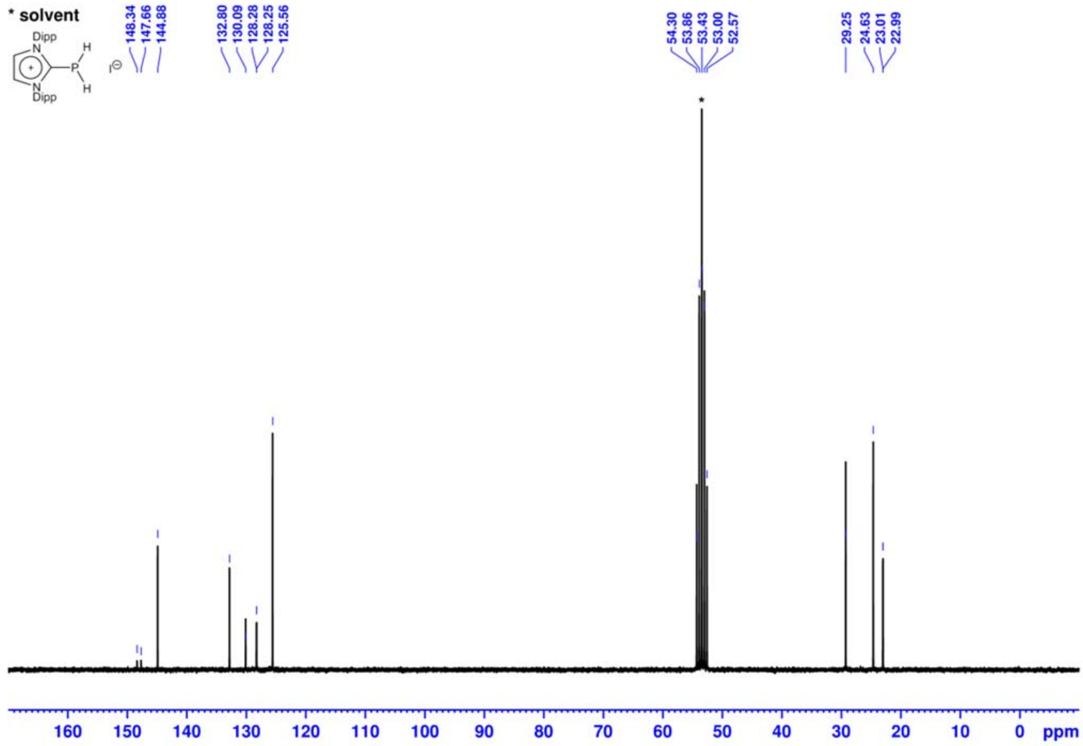


Figure S19. **^{13}C{^{1}H} NMR** spectrum (CD_2Cl_2, 62.8 MHz) of **1b**[I].

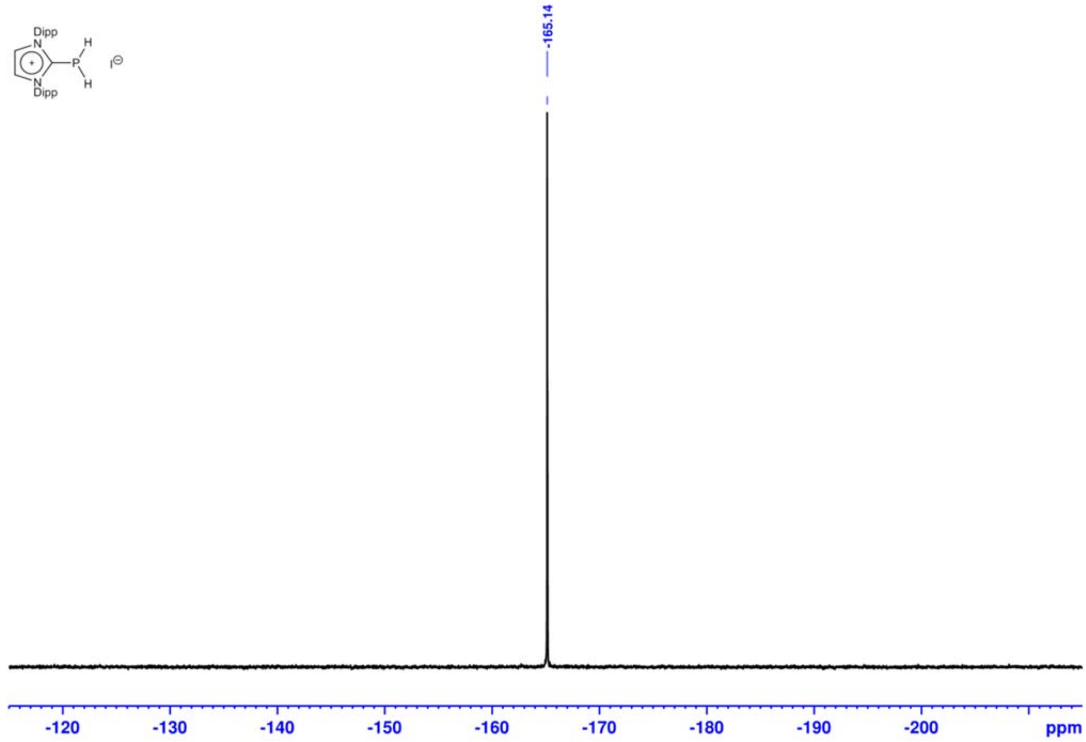


Figure S20. ^{31}P{^{1}H} NMR spectrum (CD_2Cl_2, 101.2 MHz) of **1b**[I].

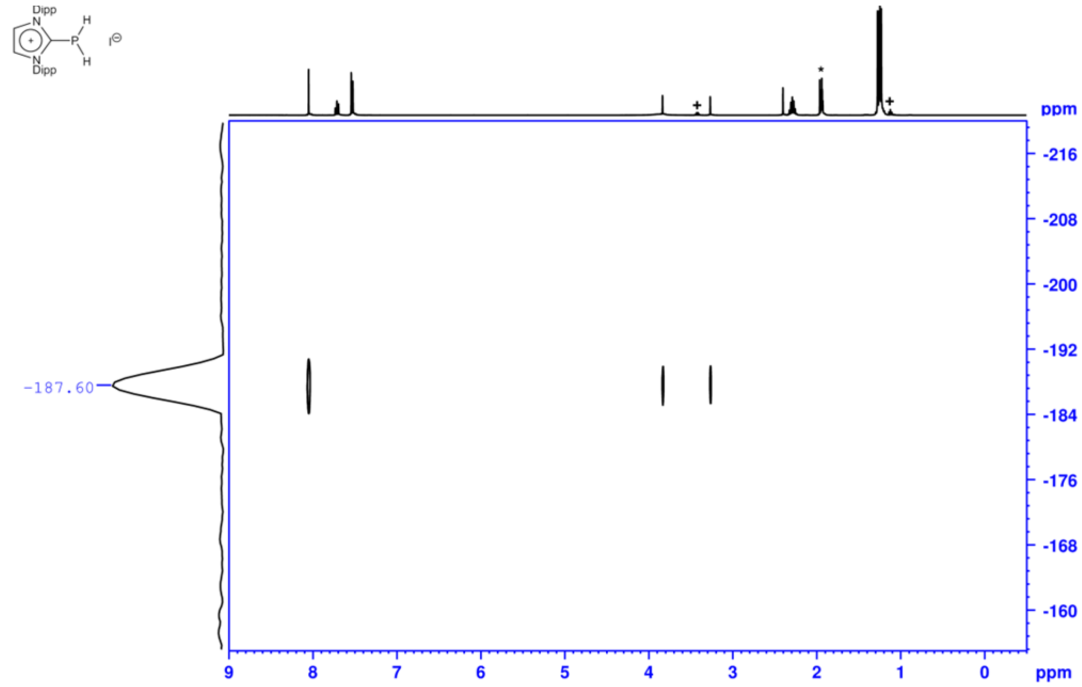


Figure S21. ^{1}H, ^{15}N{^{1}H} HMBC NMR spectrum (CD$_3$CN, 400 MHz, 40.6 MHz) of **1b**[I].

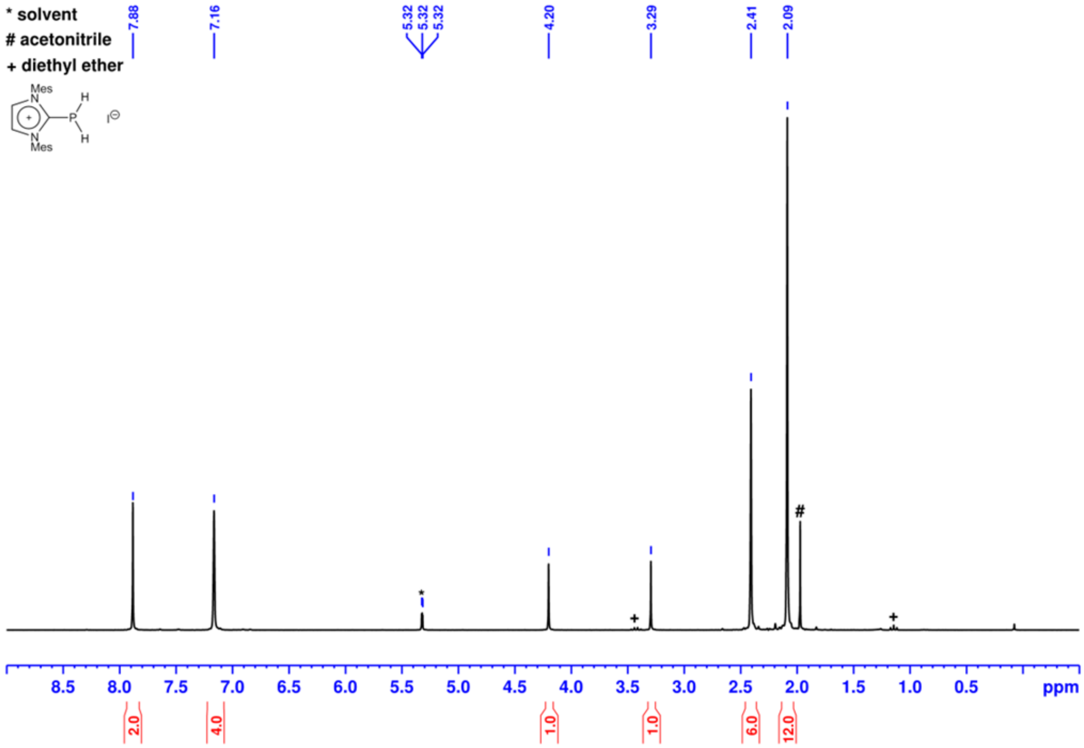


Figure S22. ^{1}H NMR spectrum (CD$_2$Cl$_2$, 250 MHz) of **1c**[I].

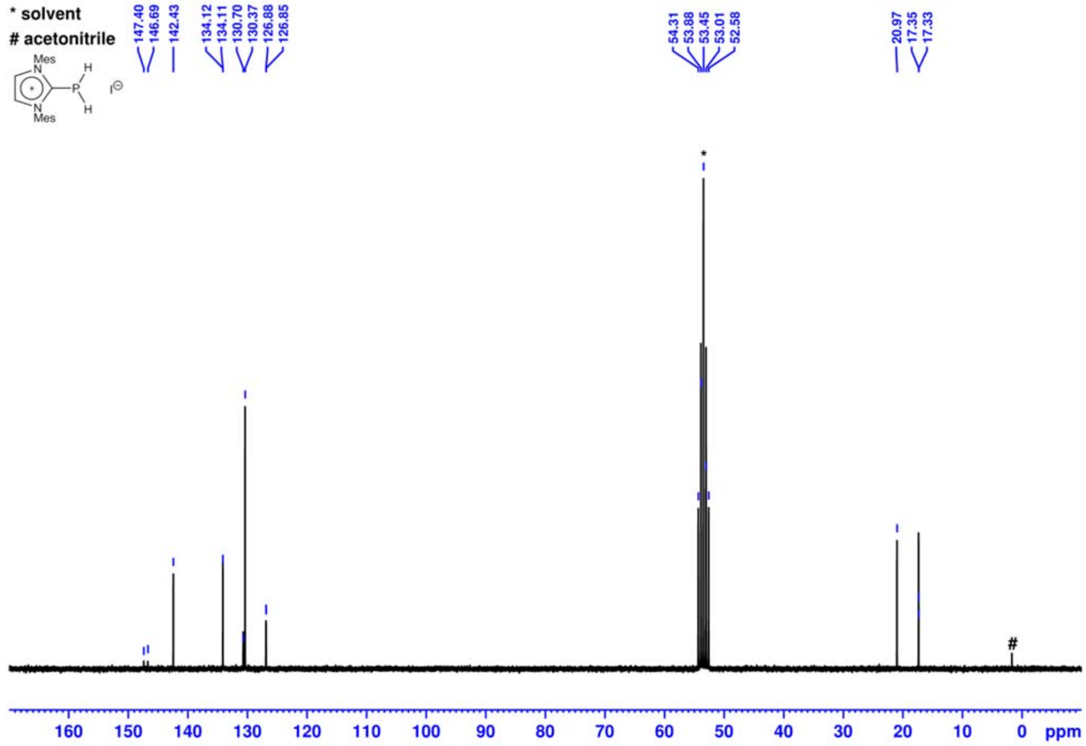


Figure S23. $^{13}C\{^1H\}$ NMR spectrum (CD_2Cl_2, 62.8 MHz) of **1c**[I].

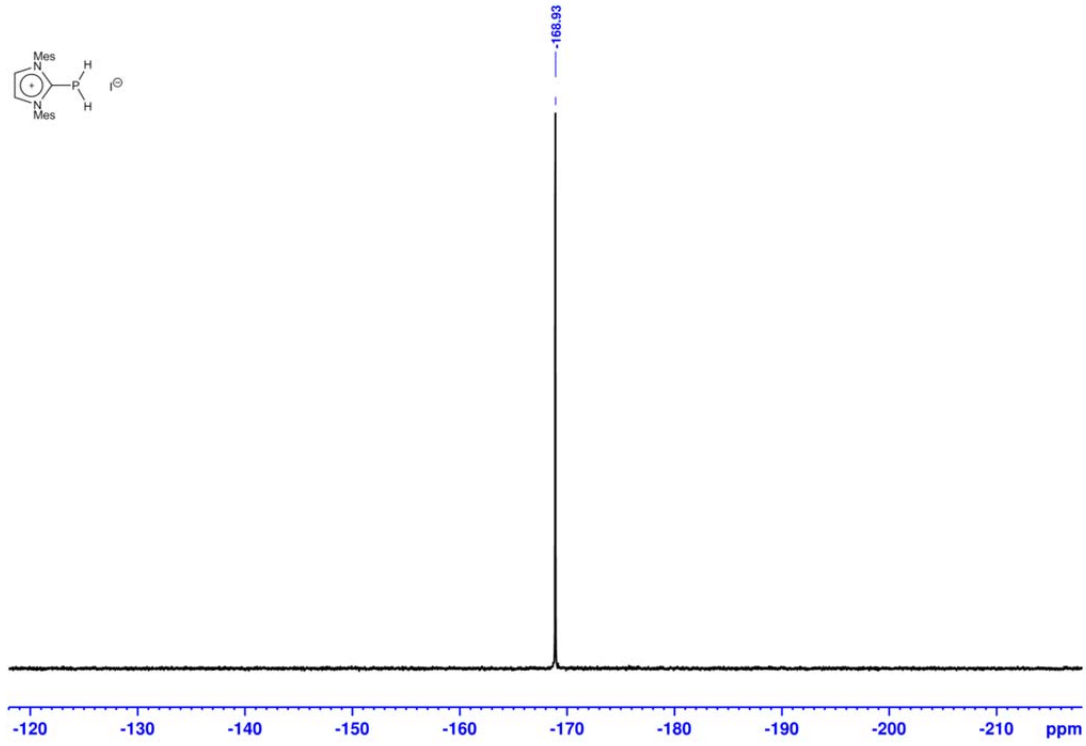


Figure S24. $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2, 101.2 MHz) of **1c**[I].

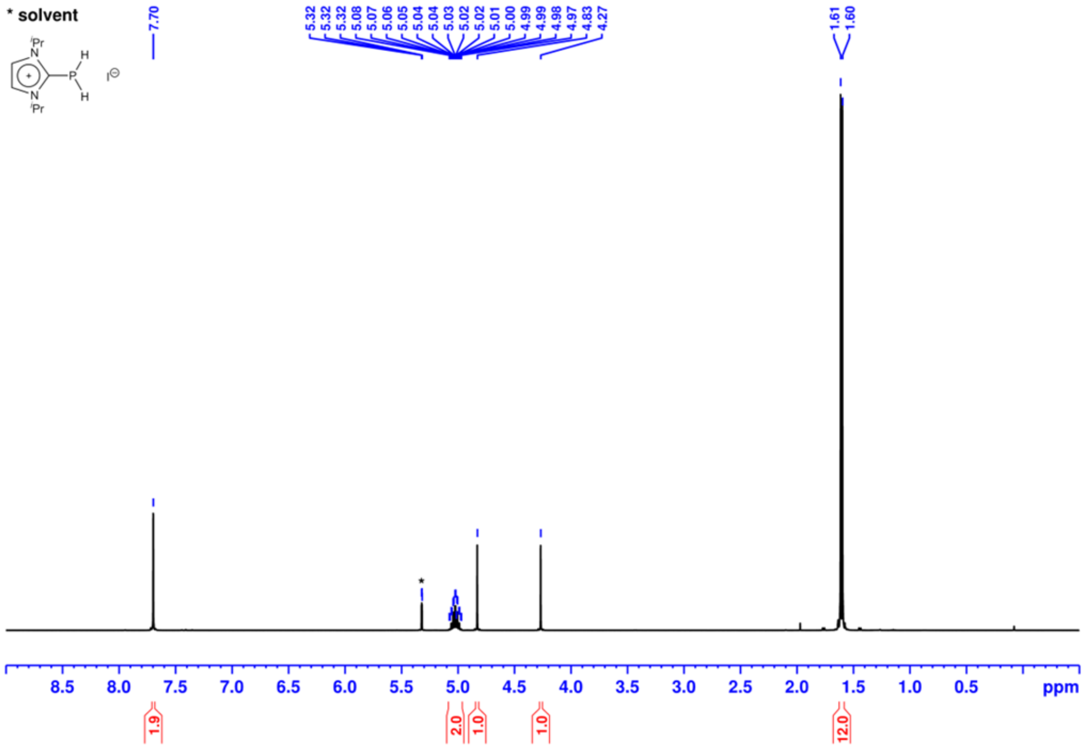


Figure S25. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz) of **1d**[I].

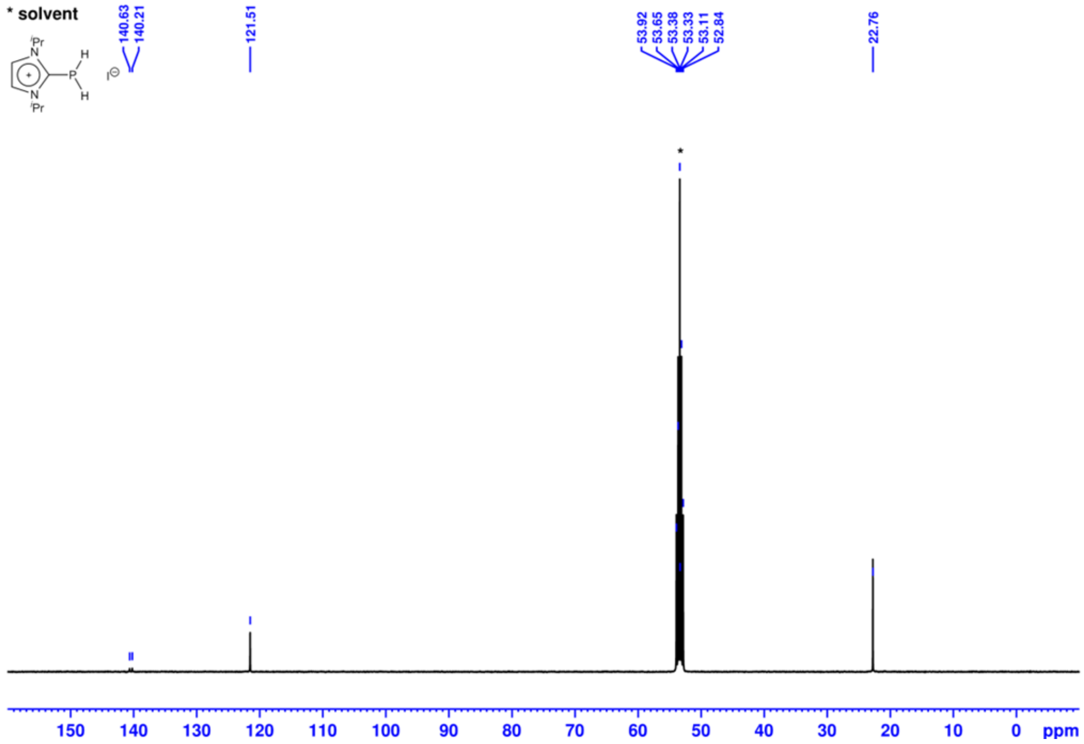


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100.6 MHz) of **1d**[I].

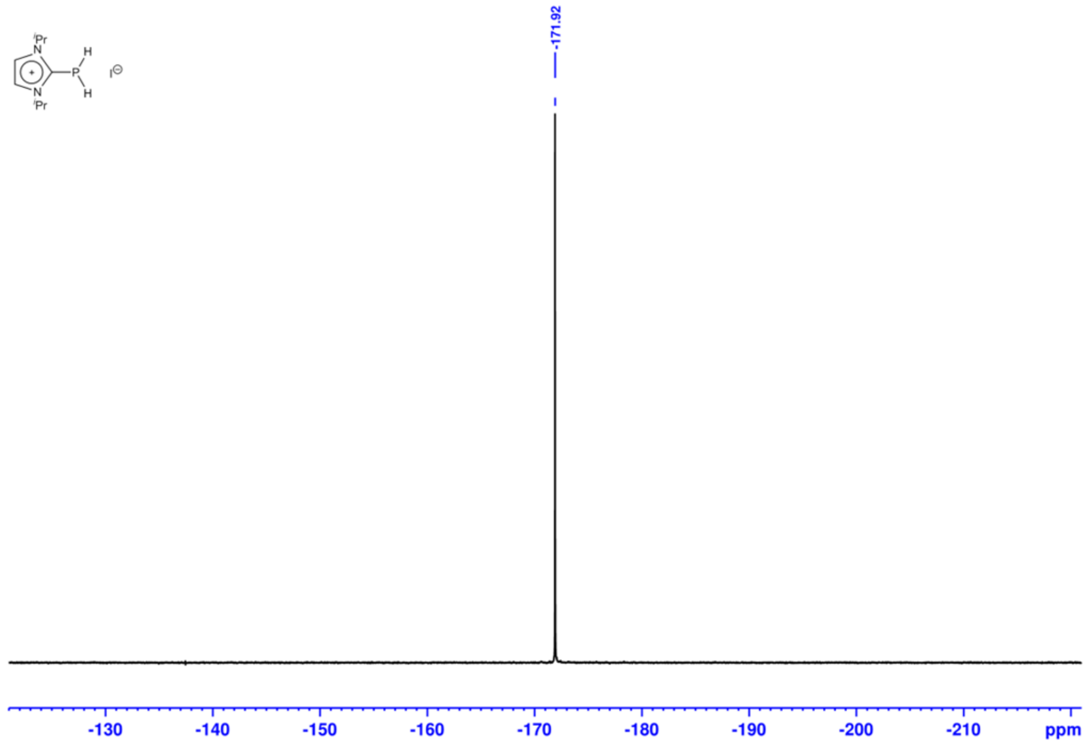


Figure S27. ^{31}P{^{1}H} NMR spectrum (CD$_2$Cl$_2$, 161.9 MHz) of **1d**[I].

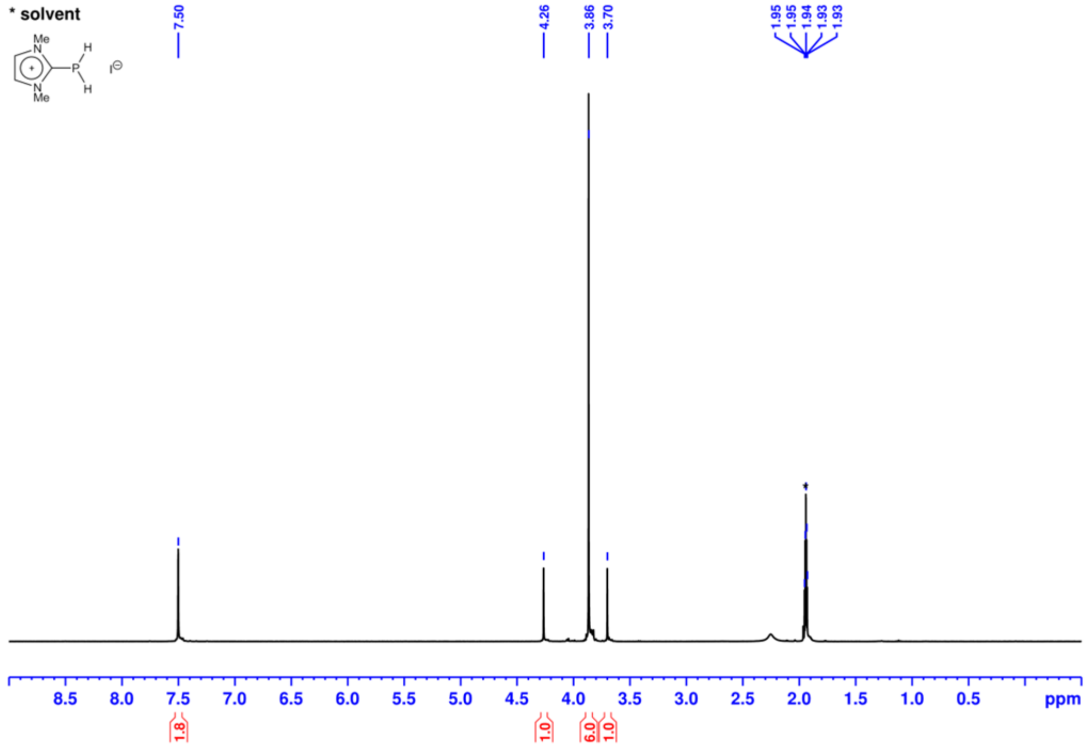


Figure S28. ^{1}H NMR spectrum (CD$_3$CN, 400 MHz) of **1e**[I].

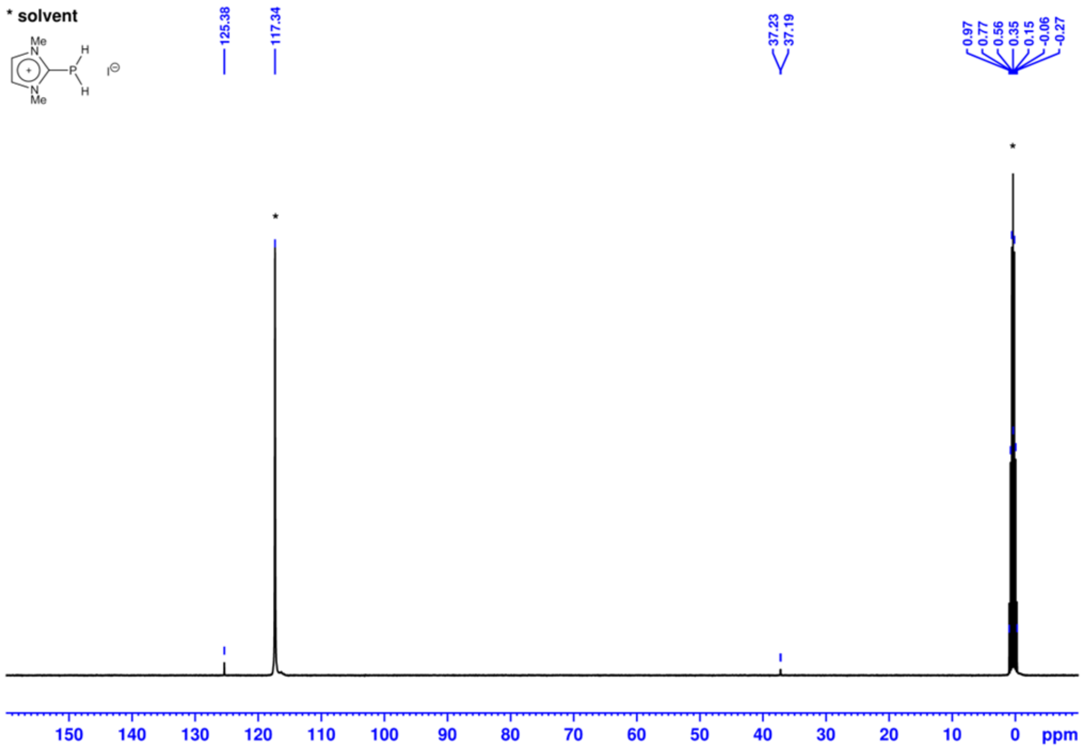


Figure S29. ^{13}**C{^{1}H} NMR** spectrum (CD$_3$CN, 100.6 MHz) of **1e**[I].

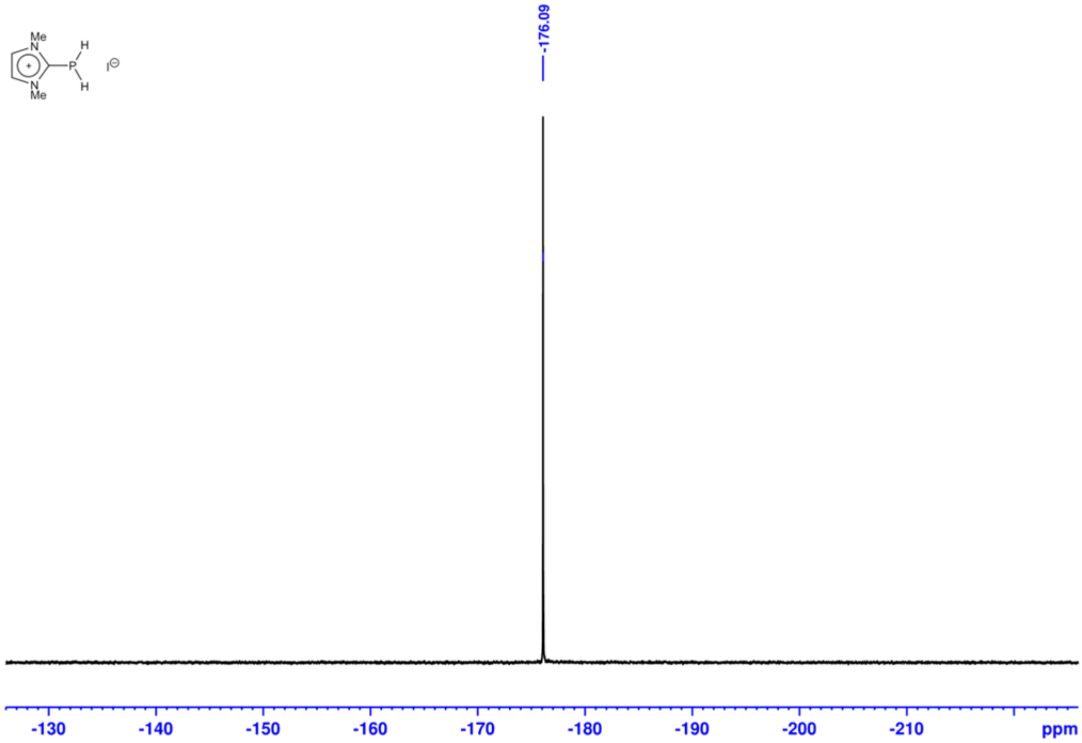


Figure S30. ^{31}P{^{1}H} NMR spectrum (CD$_3$CN, 161.9 MHz) of **1e**[I].

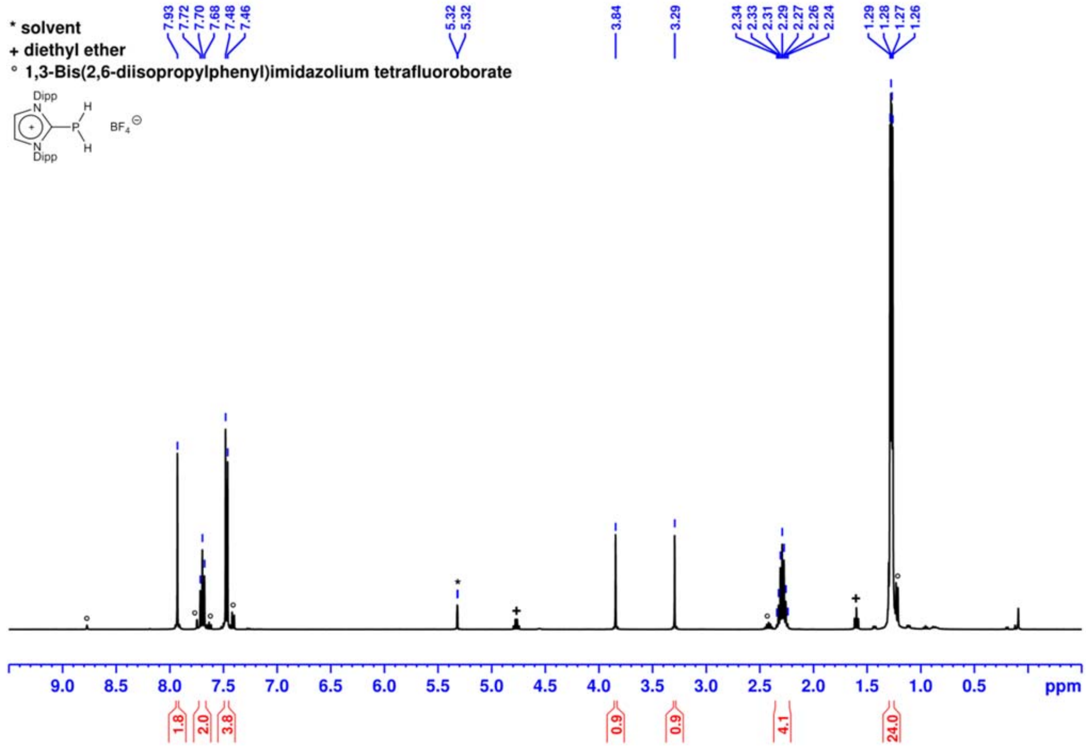


Figure S31. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz) of **1b**[BF_4].

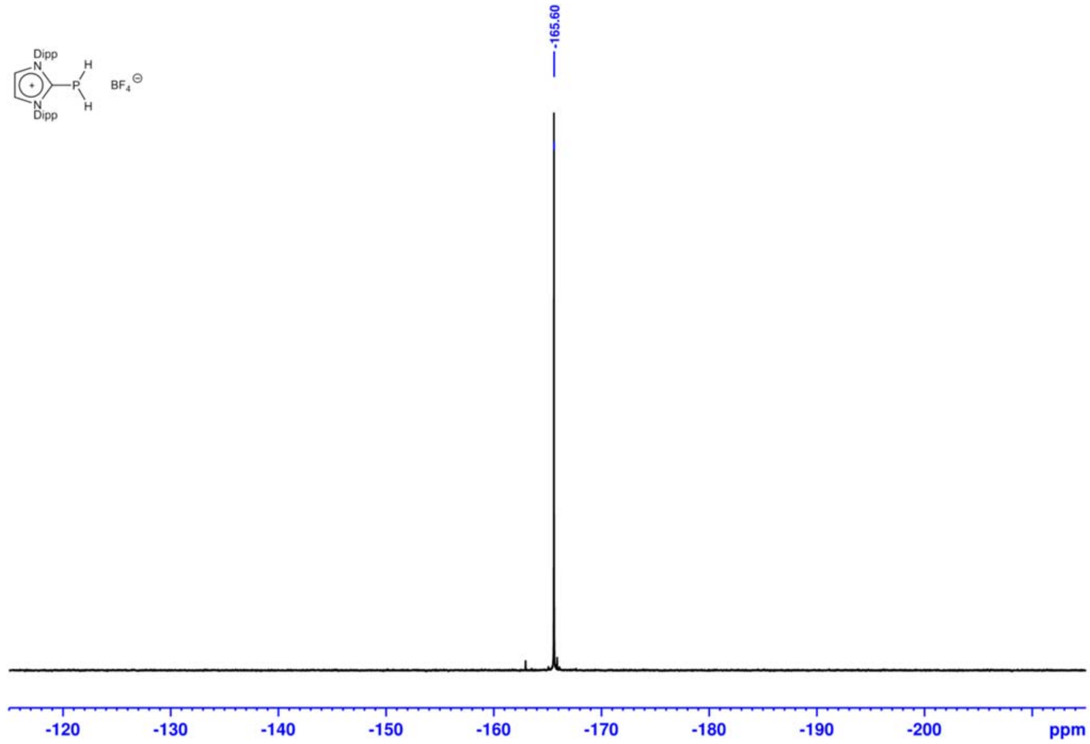


Figure S32. $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2, 161.9 MHz) of **1b**[BF_4].

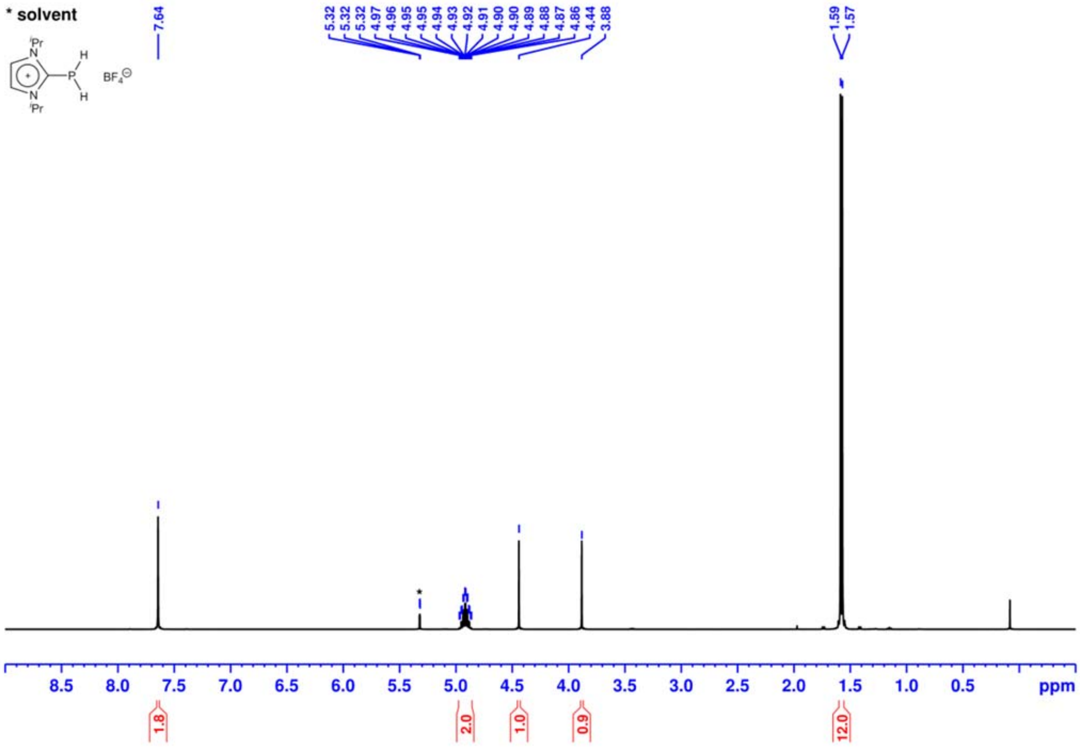


Figure S33. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz) of **1d**[BF_4].

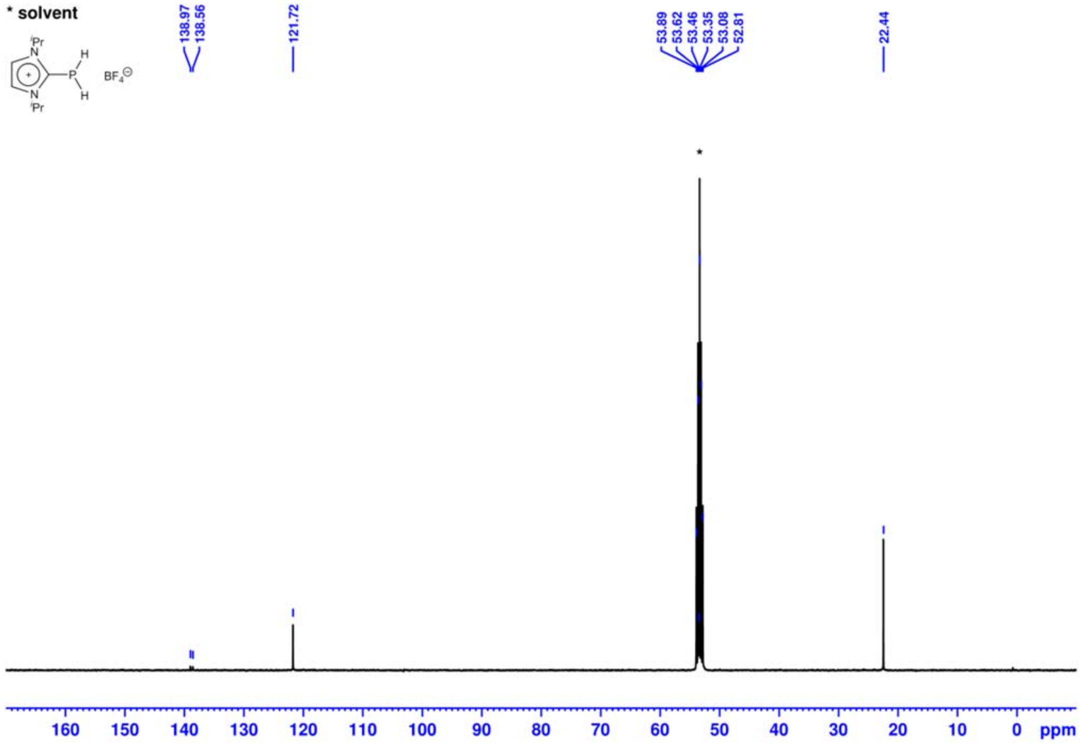


Figure S34. $^{13}C\{^1H\}$ NMR spectrum (CD_2Cl_2, 100.6 MHz) of **1d**[BF_4].

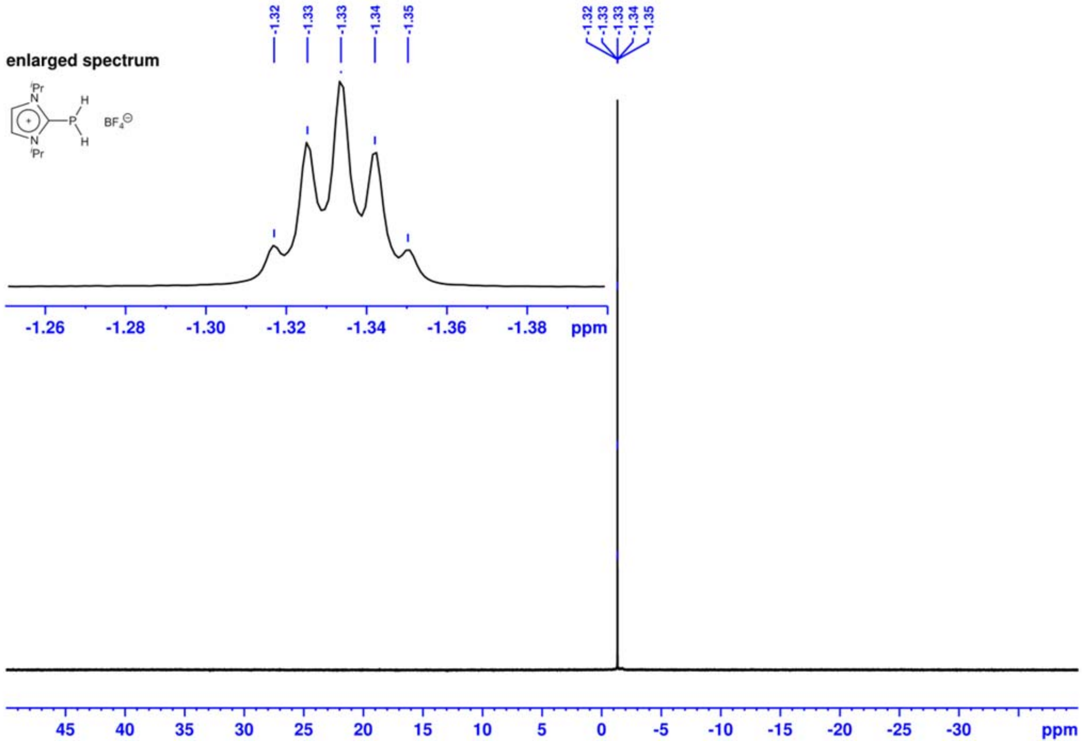


Figure S35. $^{11}B\{^{1}H\}$ NMR (CD_2Cl_2, 128.4 MHz, 213 K) spectrum of **1d**[BF_4] showing $^{11}B,^{19}F$ spin coupling.

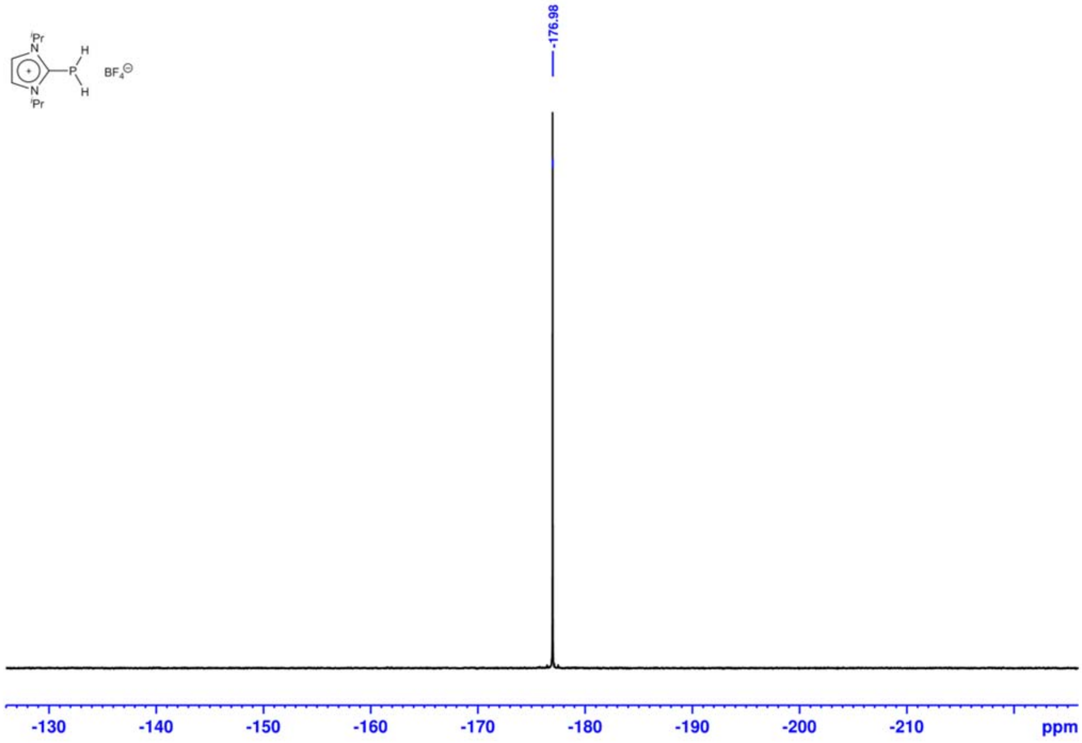


Figure S36. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 161.9 MHz) of **1d**[BF_4].

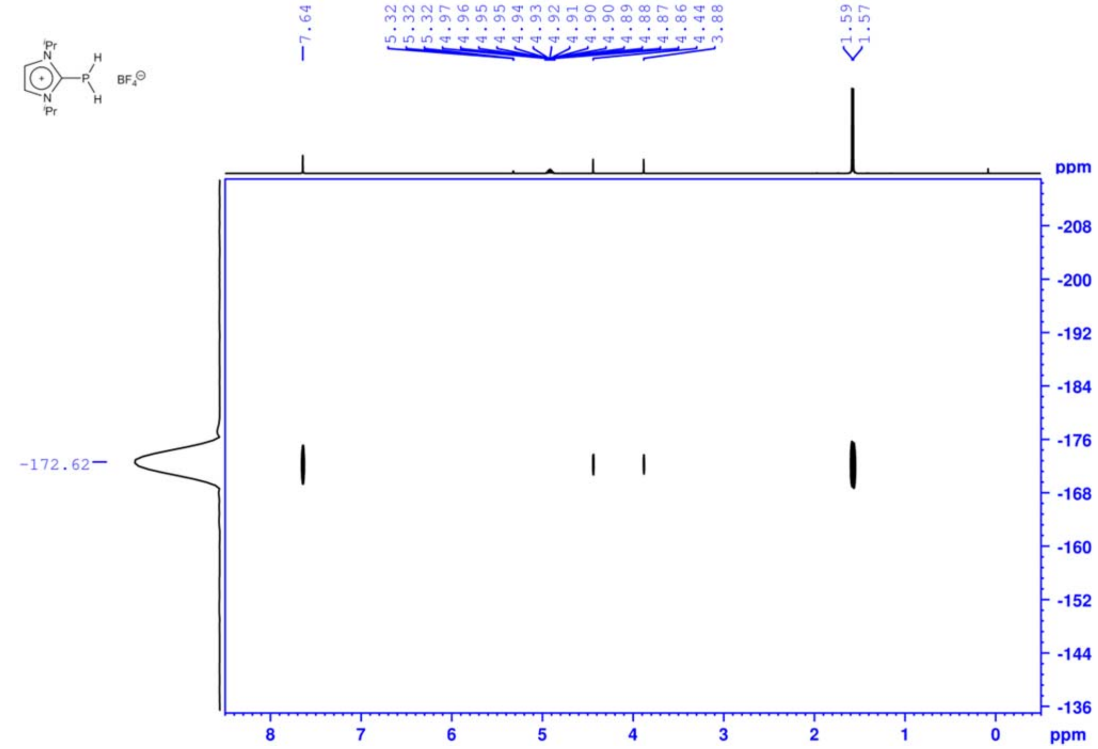


Figure S37. ^{1}H,^{15}N{^{1}H} HMBC NMR spectrum (CD_2Cl_2, 400 / 40.6 MHz) of **1d**[BF_4].

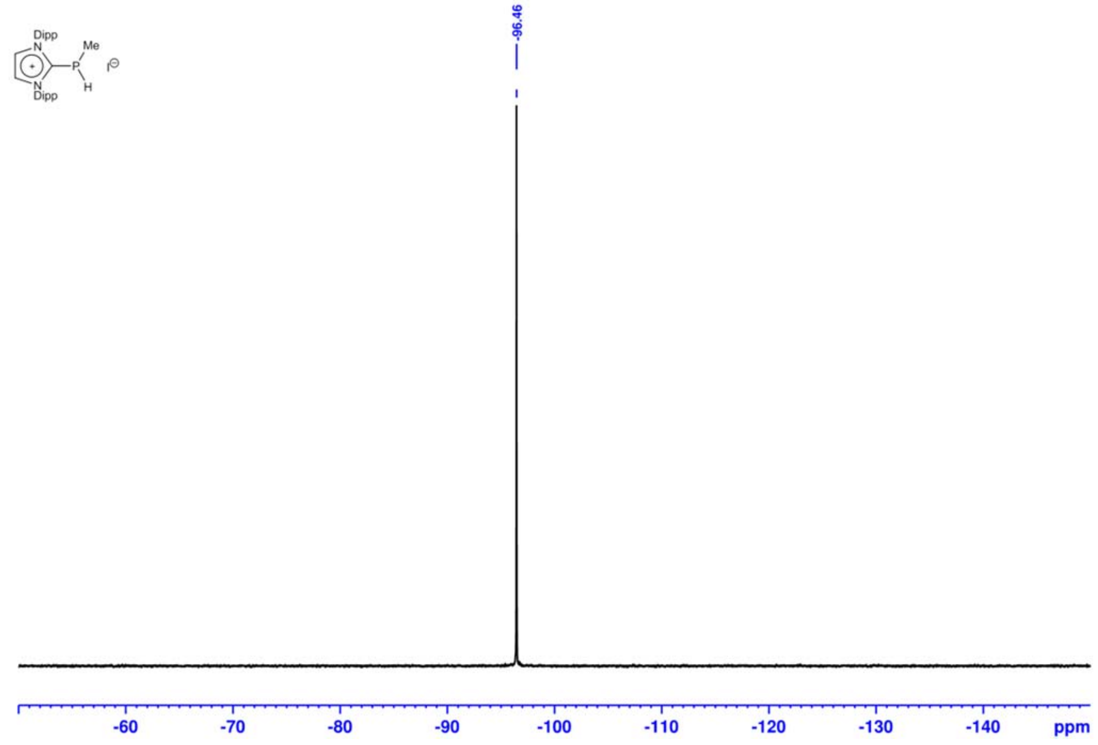


Figure S38. ^{31}P{^{1}H} NMR spectrum (o-$C_6H_4F_2$, 161.9 MHz) of **2b**[I] (reaction mixture).

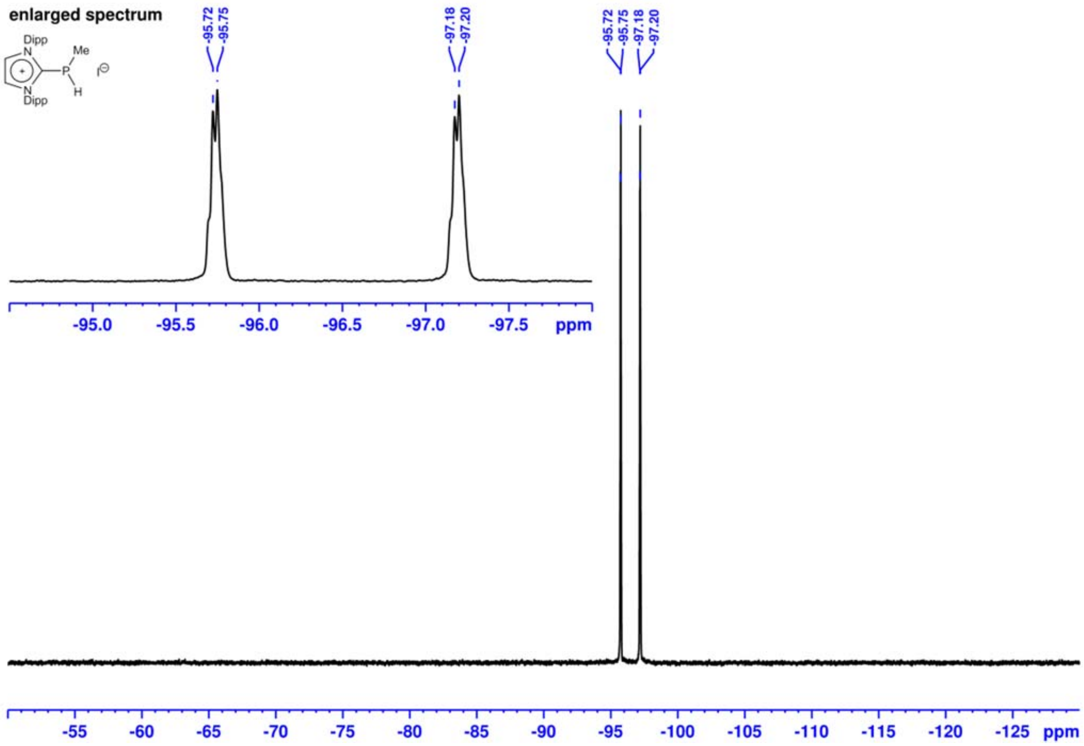


Figure S39. ^{31}P NMR spectrum (*o*-$C_6H_4F_2$, 161.9 MHz) of **2b**[I] (reaction mixture).

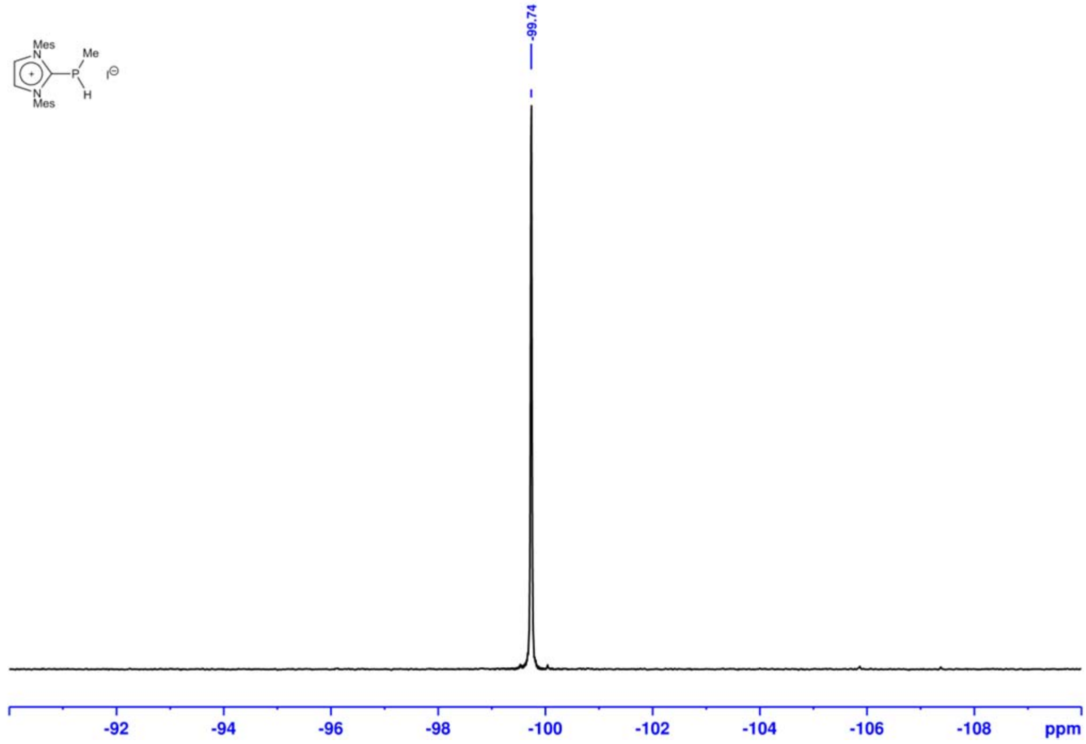


Figure S40. ^{31}P{^{1}H} NMR spectrum (CH_2Cl_2, 101.2 MHz) of **2c**[I] (reaction mixture).

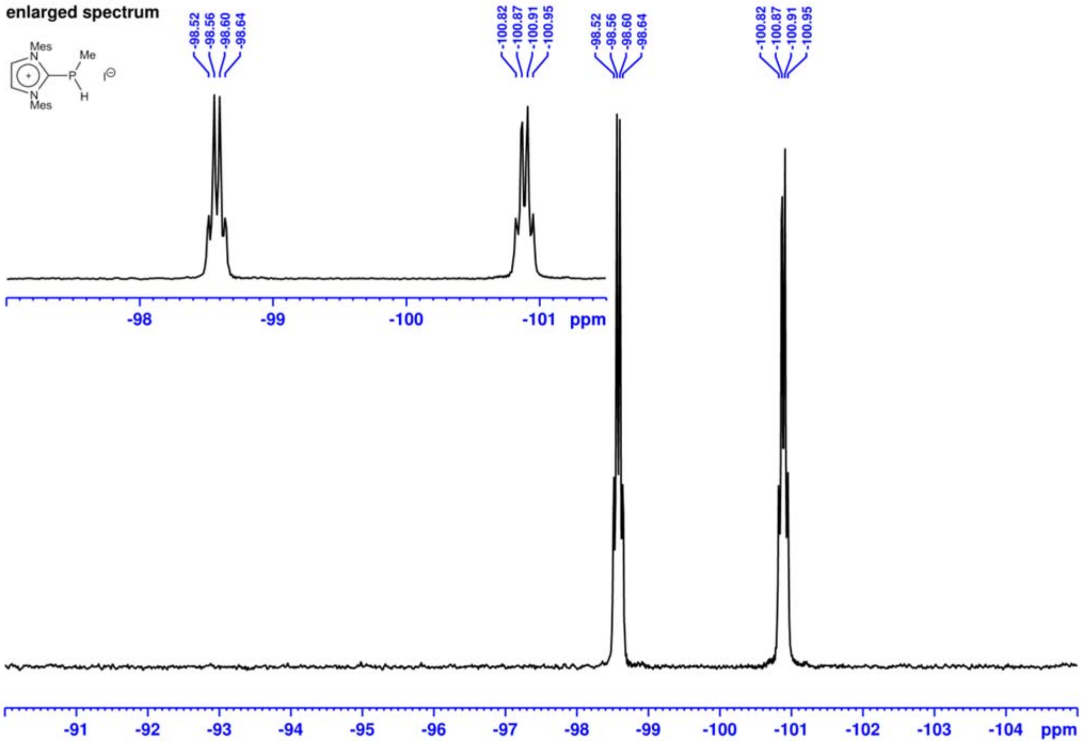


Figure S41. ^{31}P NMR spectrum (CH_2Cl_2, 101.2 MHz) of **2c**[I] (reaction mixture).

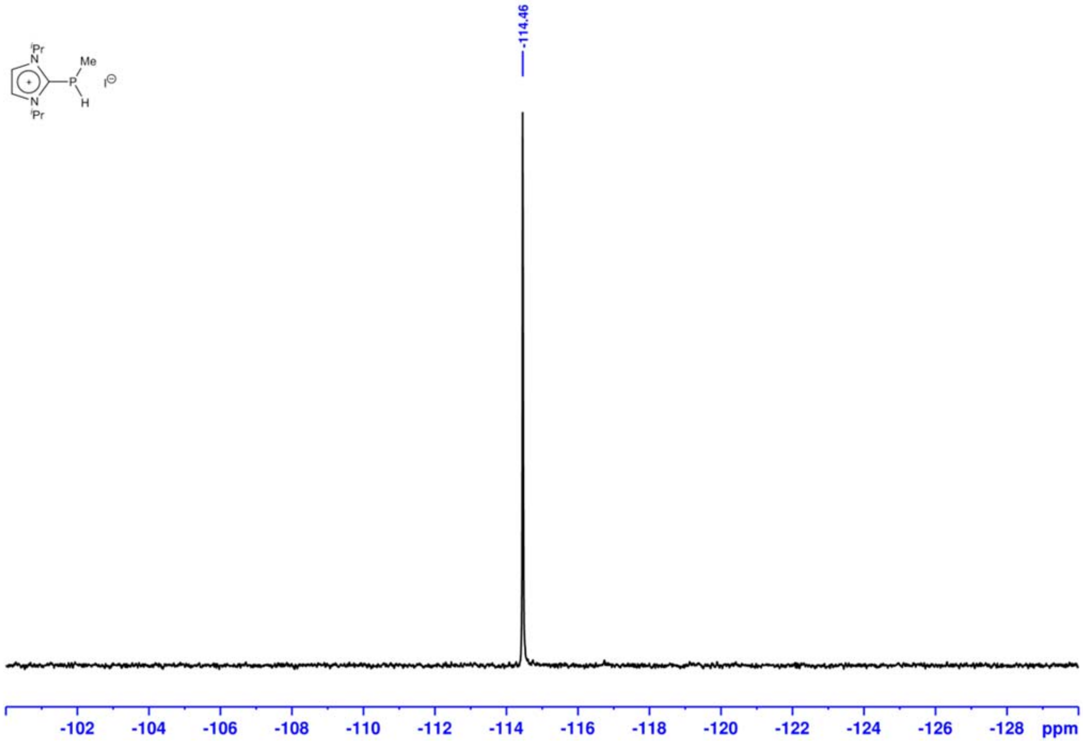


Figure S42. ^{31}P{^{1}H} NMR spectrum (MeCN, 101.2 MHz) of **2d**[I] (reaction mixture).

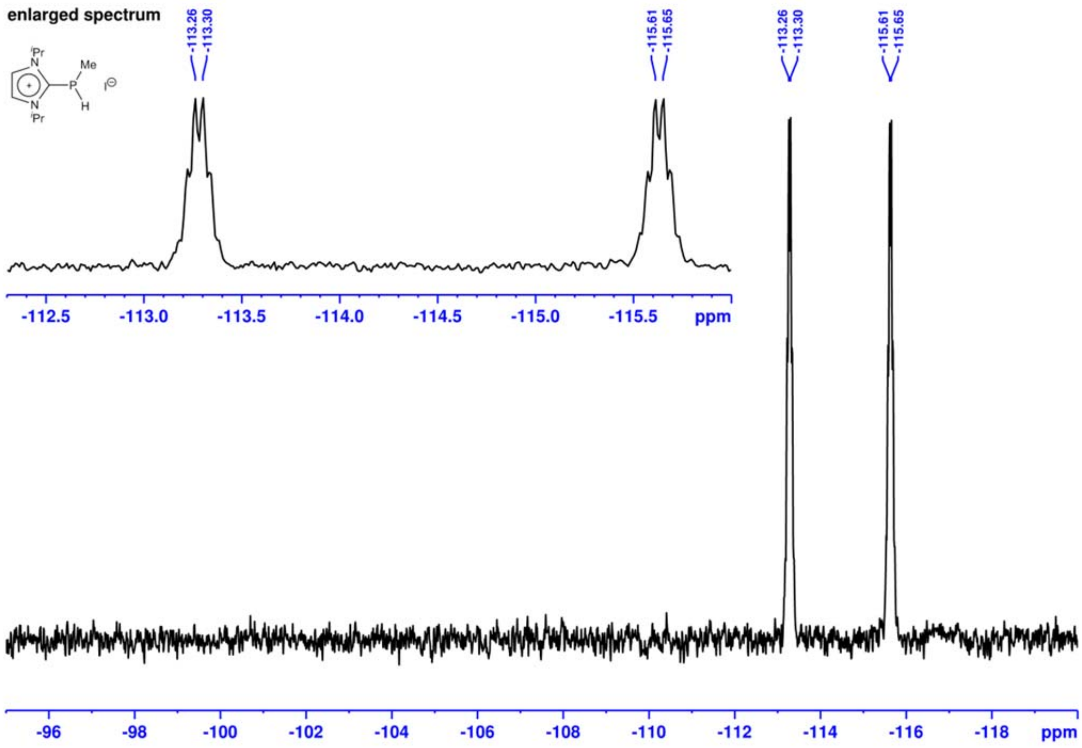


Figure S43. ^{31}P NMR spectrum (MeCN, 101.2 MHz) of **2d**[I].

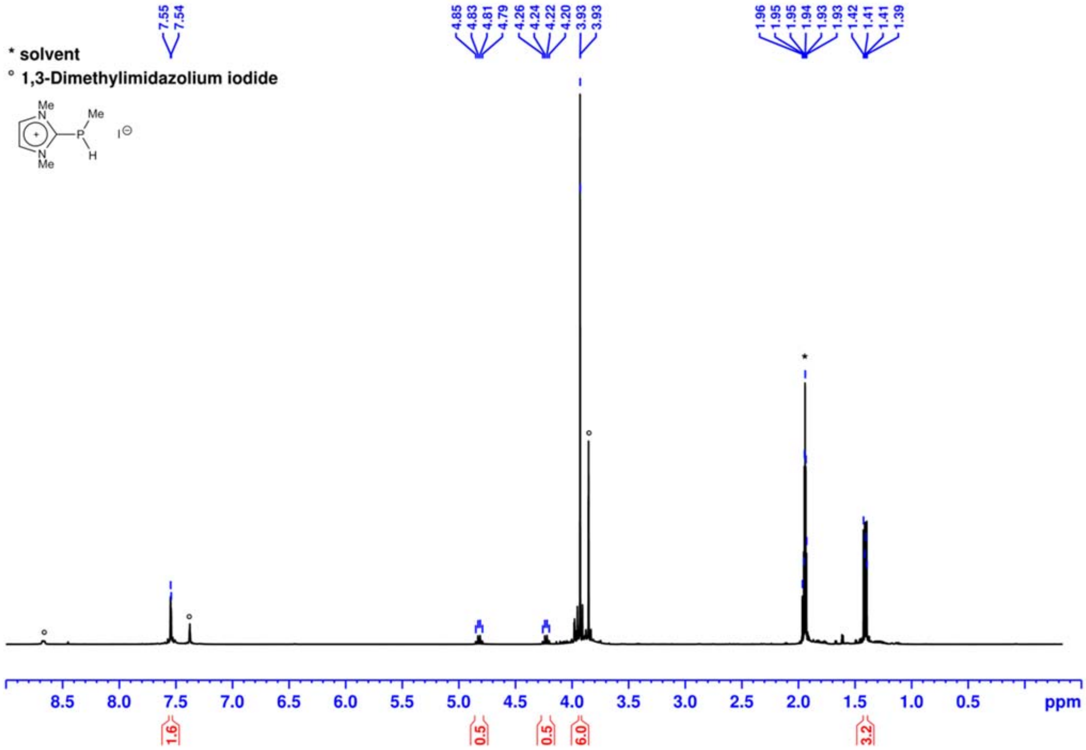


Figure S44. ^{1}H NMR spectrum (CD_3CN, 400 MHz) of **2e**[I].

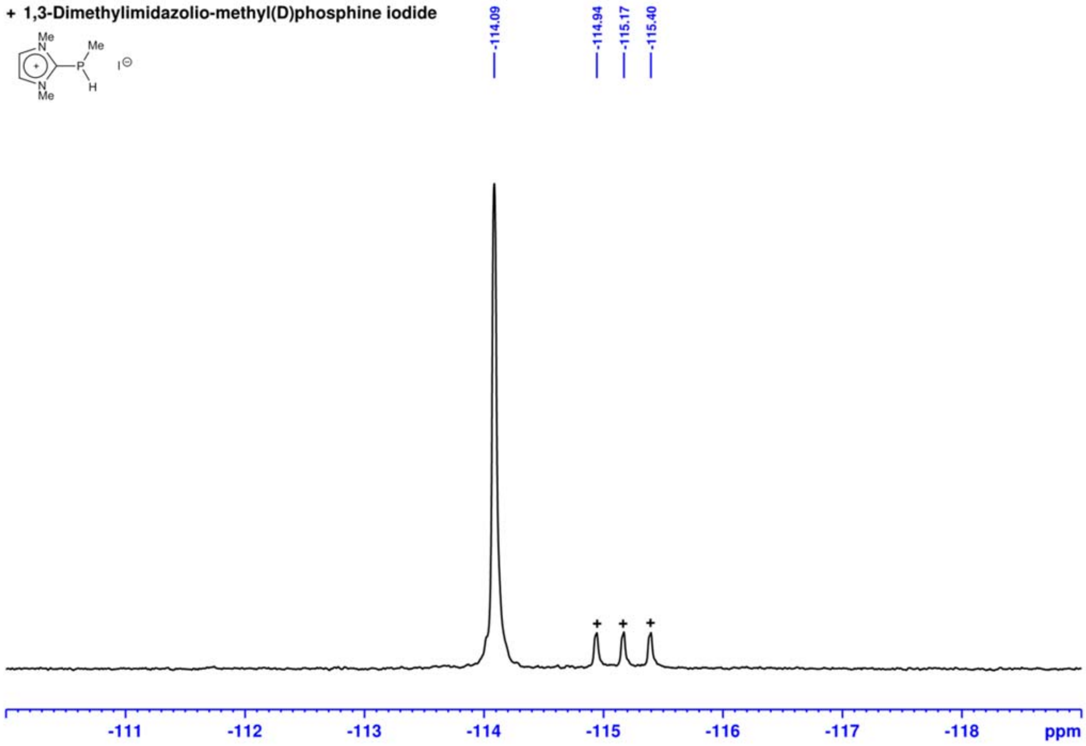


Figure S45. $^{31}P\{^1H\}$ NMR spectrum (CD_3CN, 161.9 MHz) of **2e**[I].

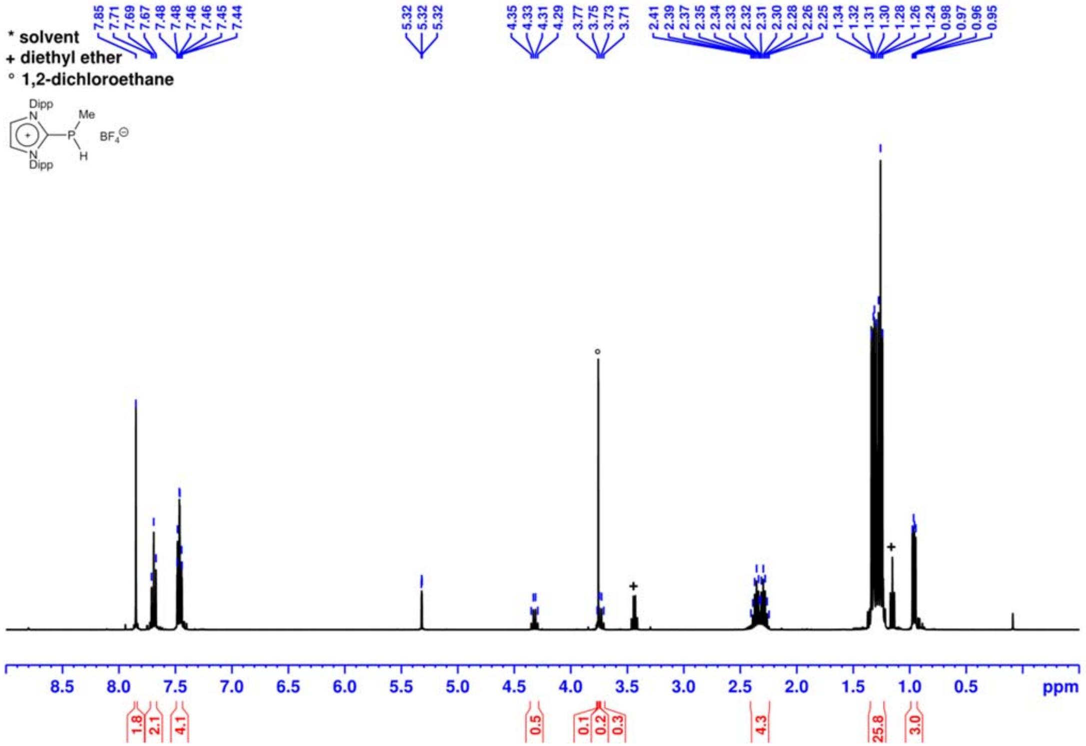


Figure S46. ^1H NMR spectrum (CD_2Cl_2, 400 MHz) of **2b**[BF_4].

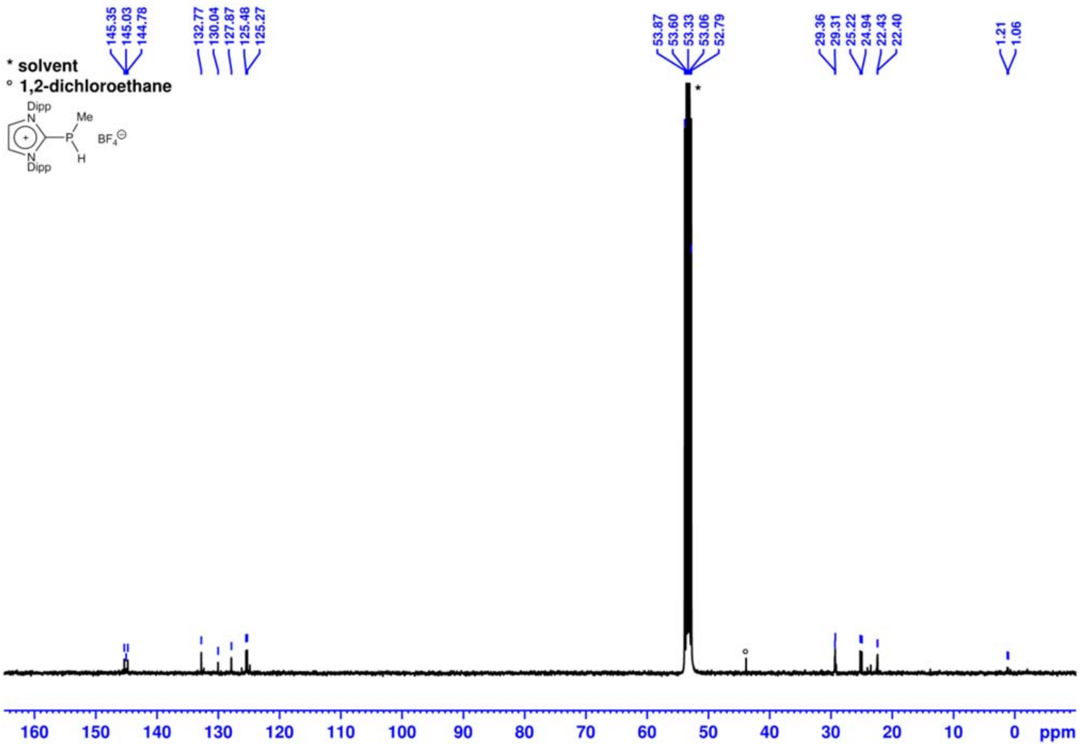


Figure S47. $^{13}C\{^1H\}$ NMR spectrum (CD_2Cl_2, 100.6 MHz) of **2b**[BF_4].

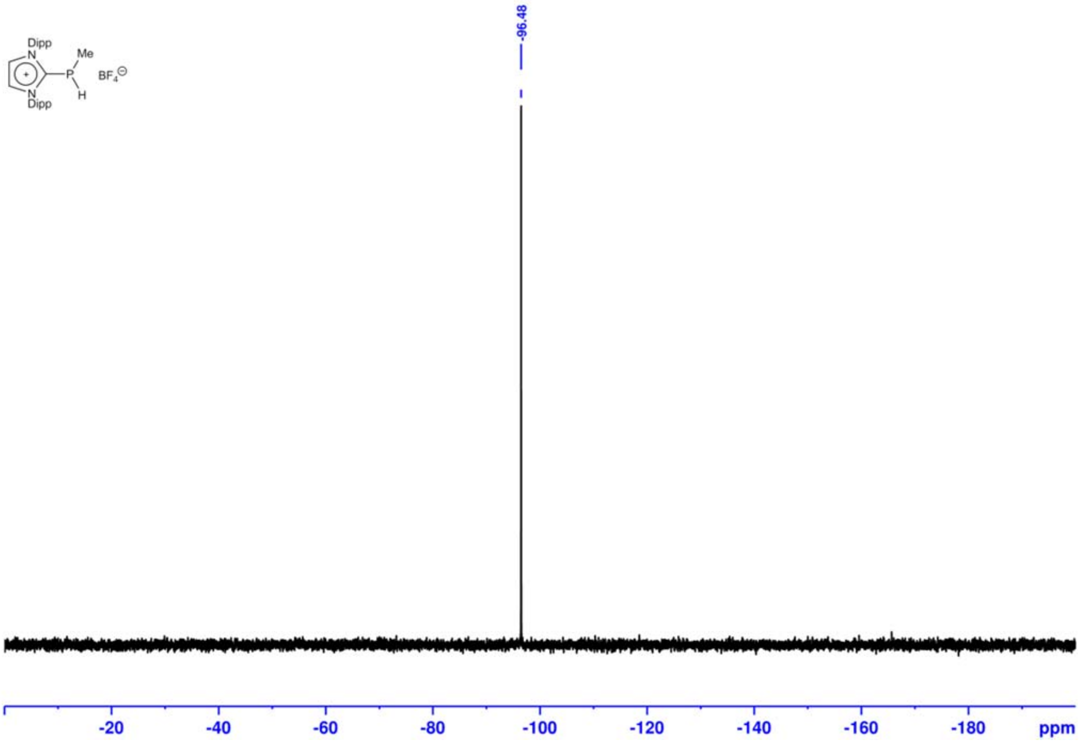


Figure S48. $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2, 161.9 MHz) of **2b**[BF_4].

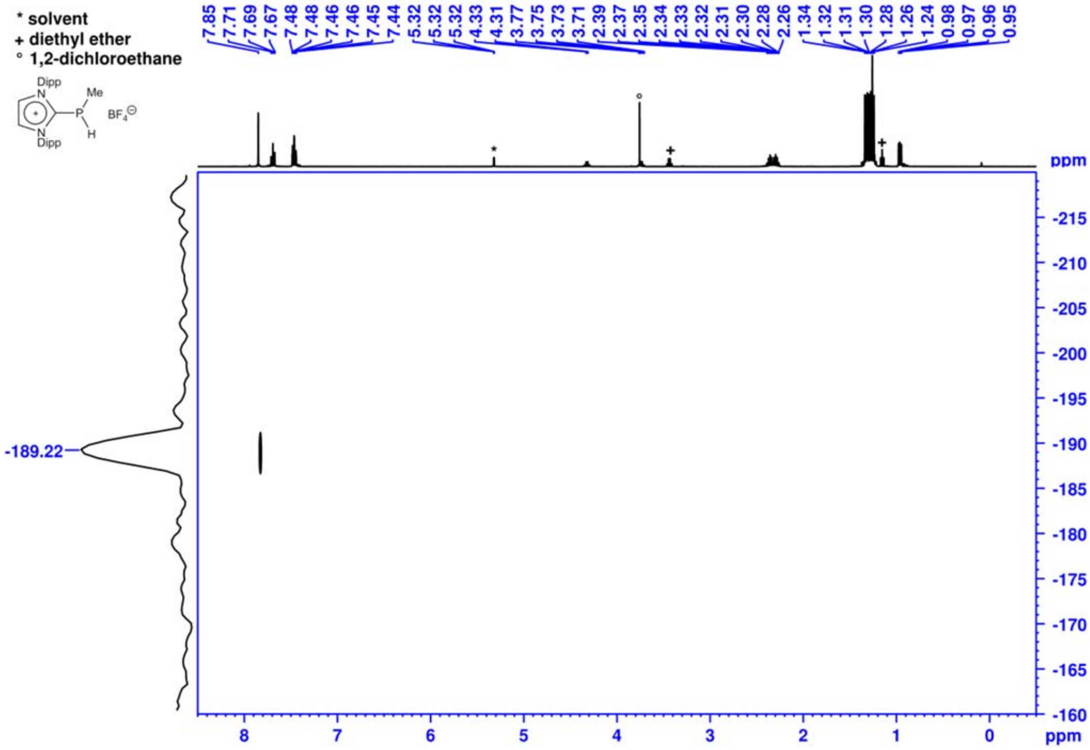


Figure S49. $^{1}H,^{15}N$ HMBC NMR spectrum (CD_2Cl_2, 400 / 40.6 MHz) of **2b**[BF_4].

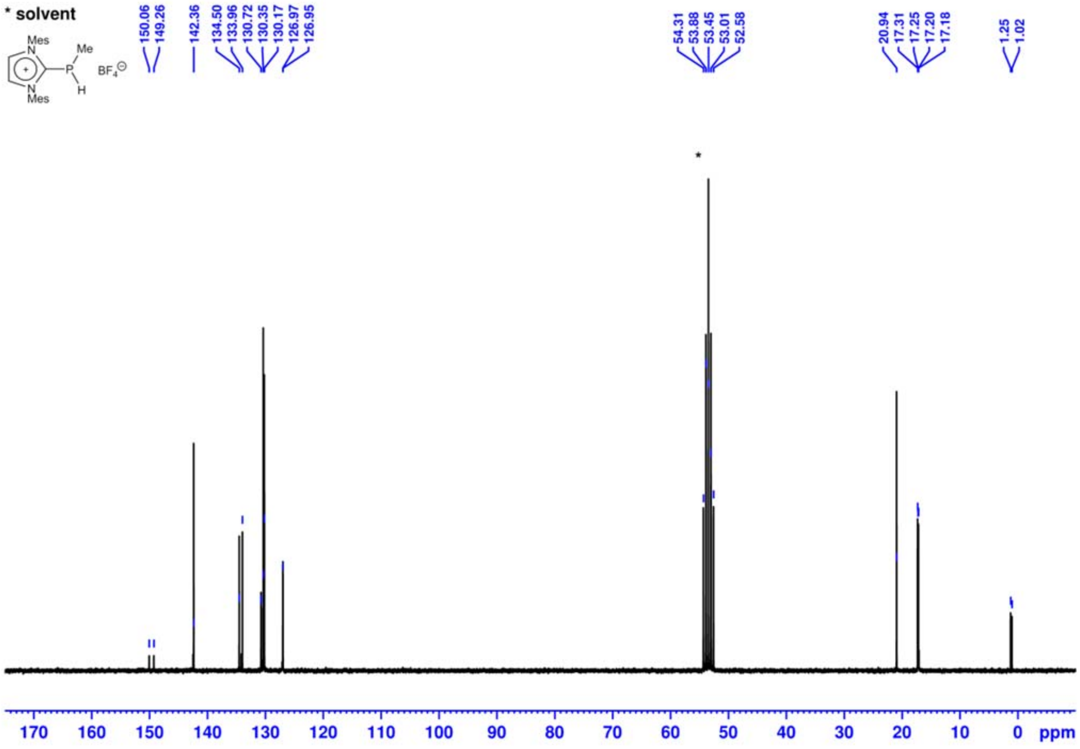


Figure S50. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 62.8 MHz) of **2c**[BF_4] (crude product).

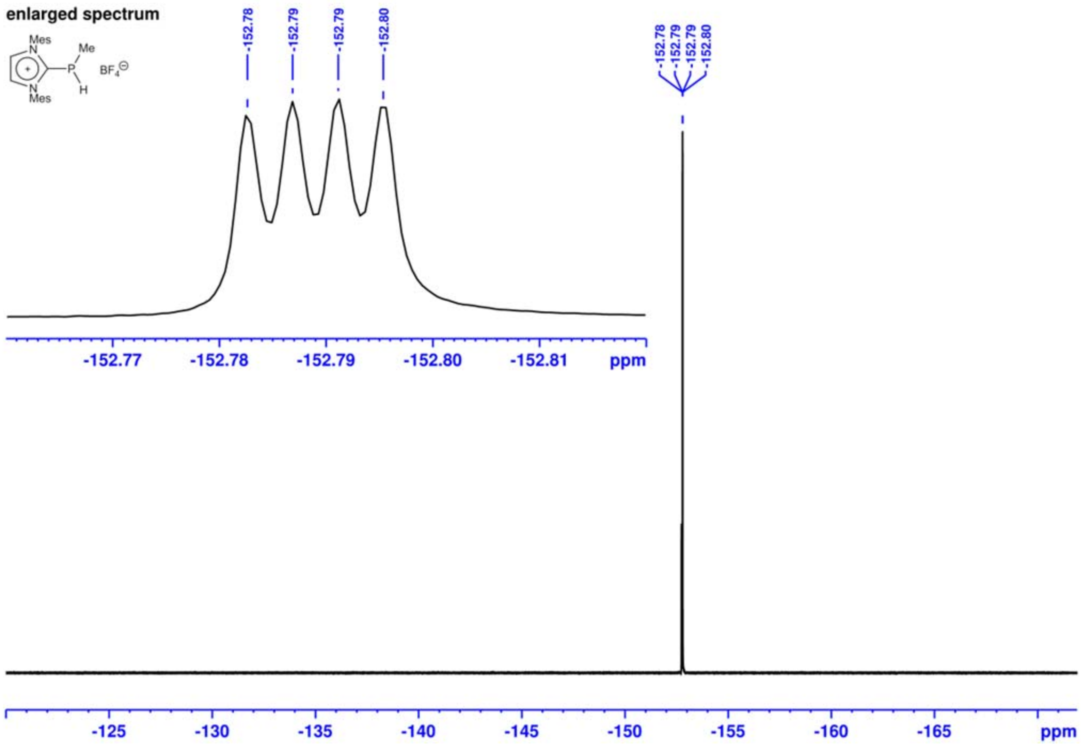


Figure S51. ^{19}F NMR spectrum (CD_2Cl_2, 235.3 MHz) of **2c**[BF_4] (crude product).

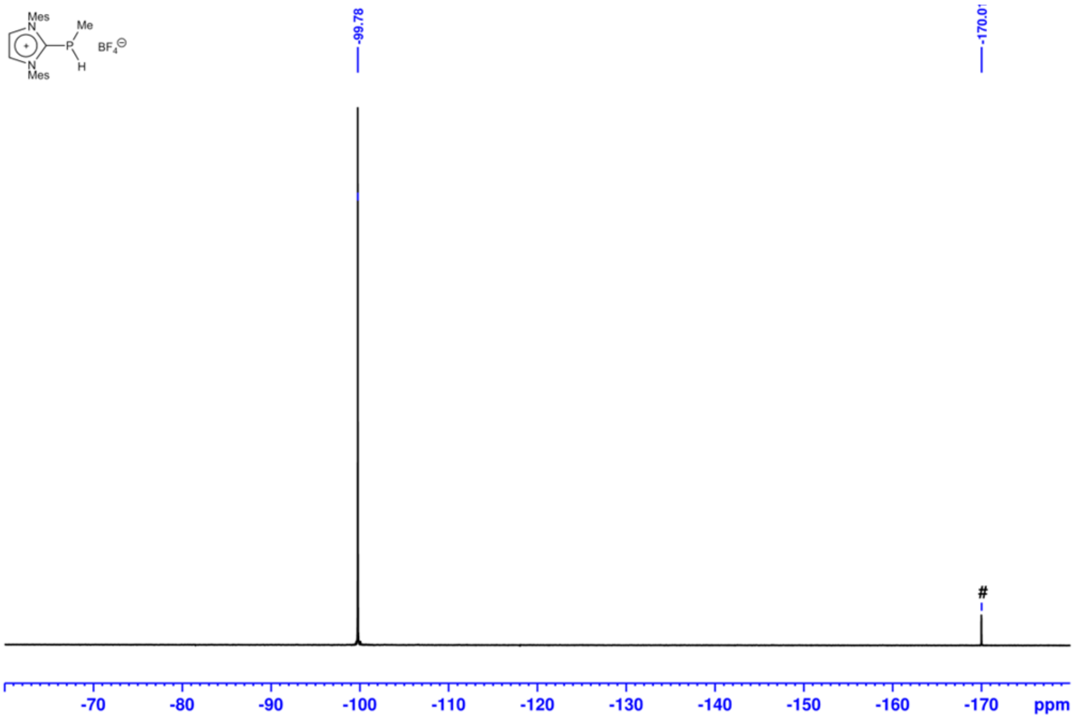


Figure S52. ^{31}P{^{1}H} NMR spectrum (CD_2Cl_2, 101.2 MHz) of **2c**[BF_4] (crude product; # denotes the signal of **1c**$^{+}$ present as an impurity).

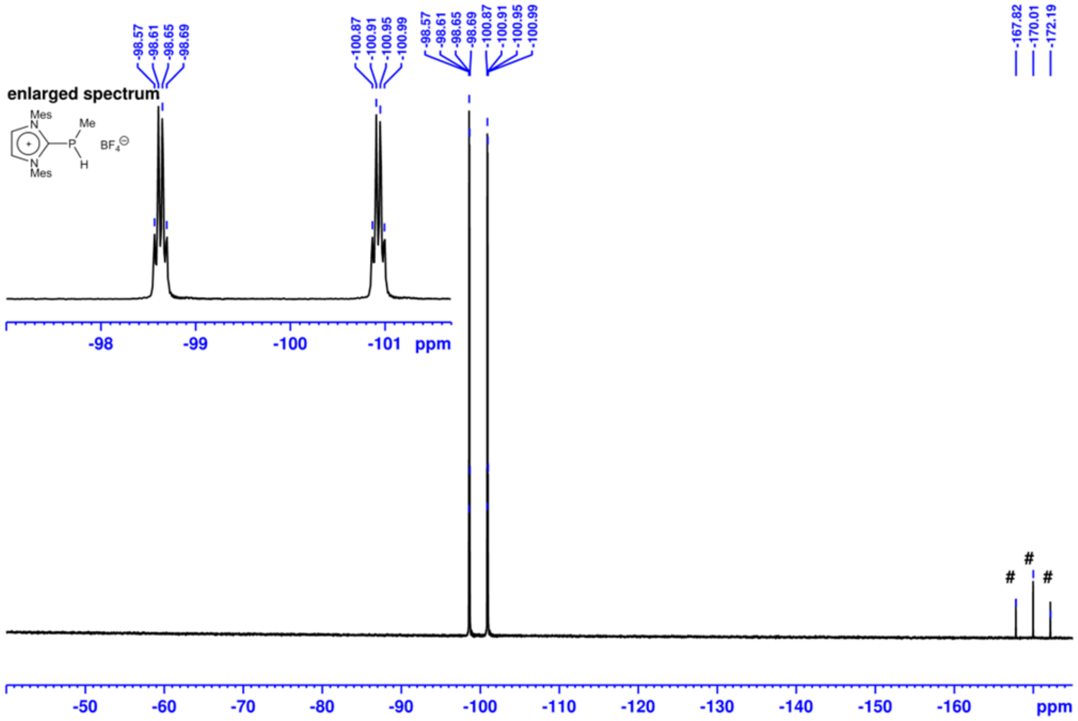


Figure S53. ^{31}PNMR spectrum (CD_2Cl_2, 101.2 MHz) of **2c**[BF_4] (crude product; # denotes the signal of **1c**$^+$ present as an impurity).

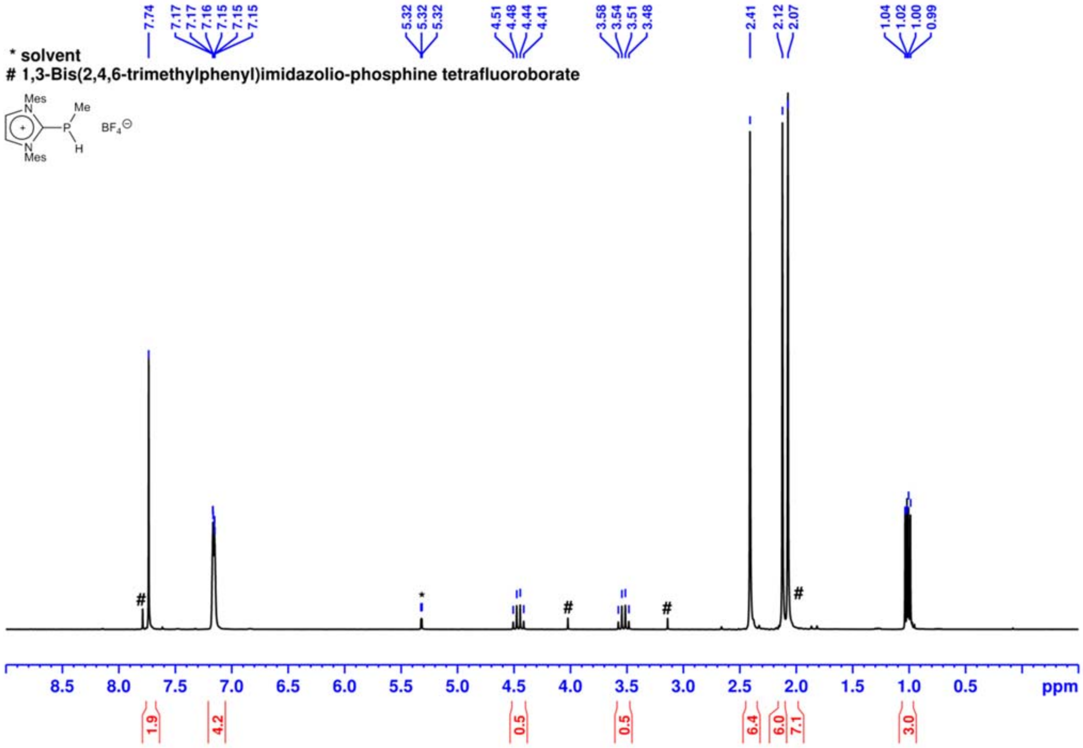


Figure S54. ^{1}H NMR spectrum (CD_2Cl_2, 250 MHz) of **2d**[BF_4] (crude product).

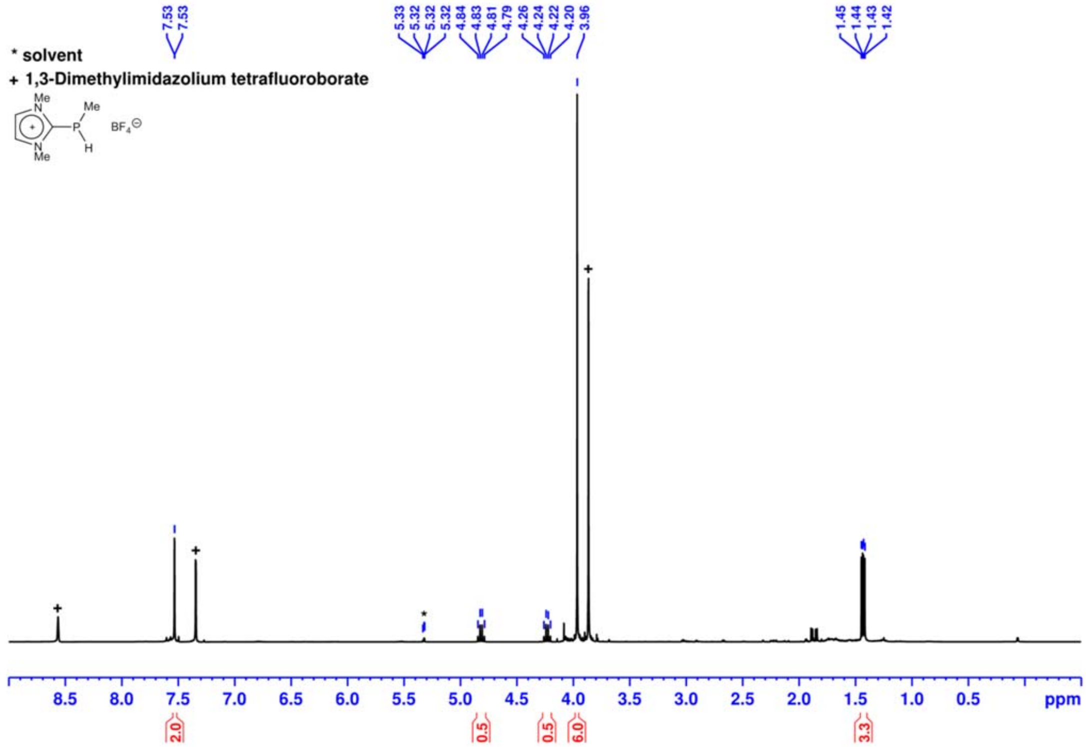


Figure S55. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz) of **2e**[BF_4].

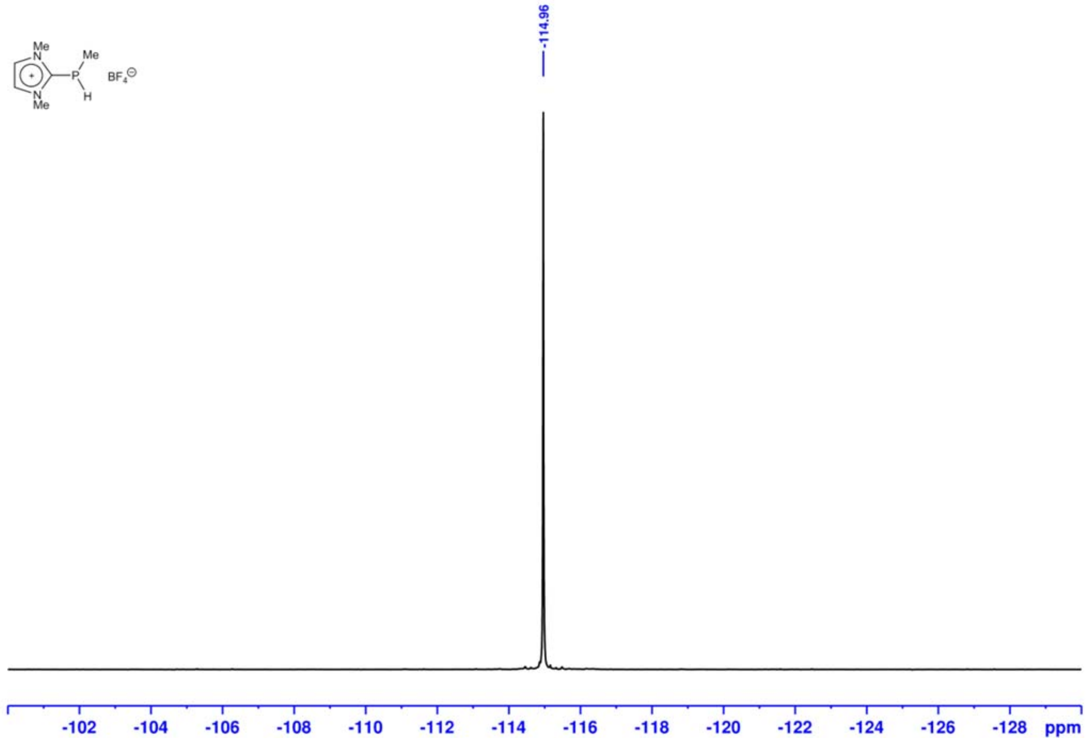


Figure S56. $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2, 400 MHz) of **2e**[BF_4].

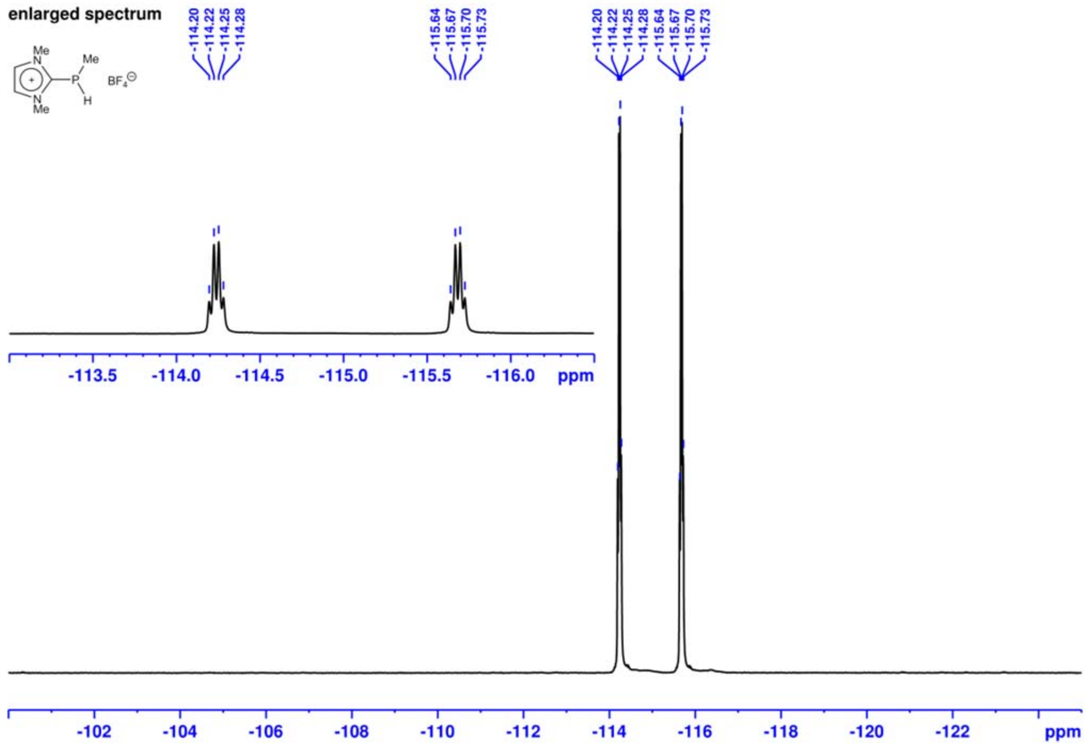


Figure S57. ^{31}P NMR spectrum (CD_2Cl_2, 400 MHz) of **2e**[BF_4].

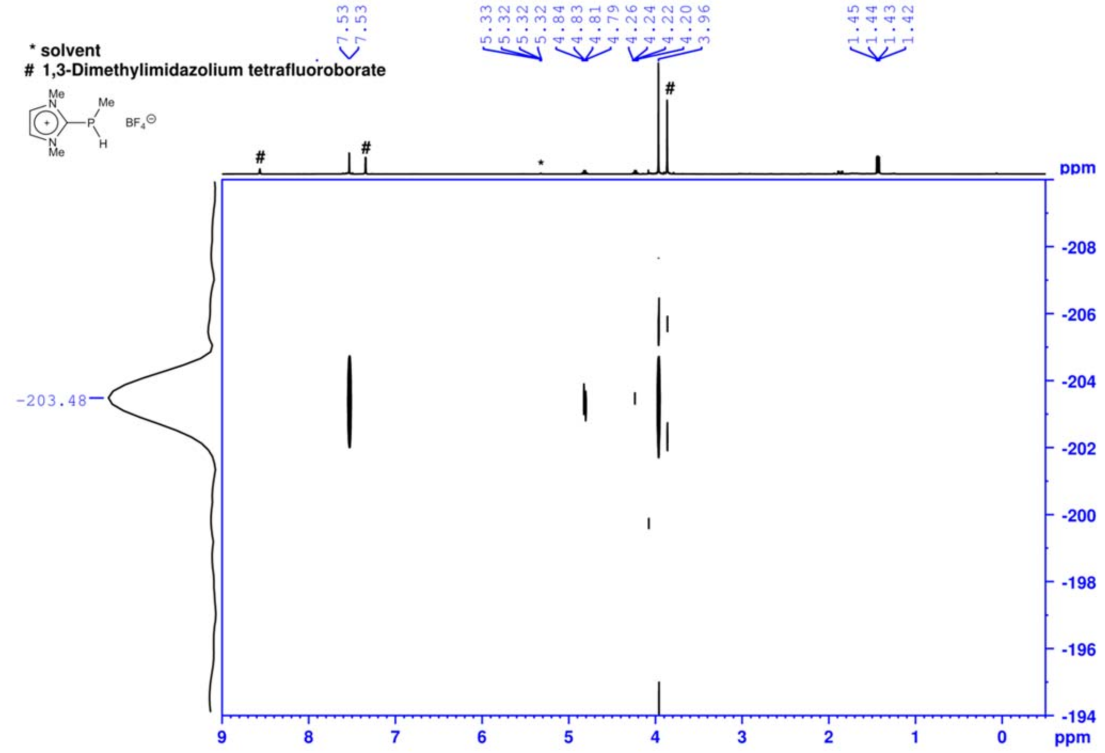


Figure S58. $^{1}H,^{15}N\{^{1}H\}$ HMBC NMR spectrum (CD_2Cl_2, 400 / 40.6 MHz) of **2e**[BF_4].

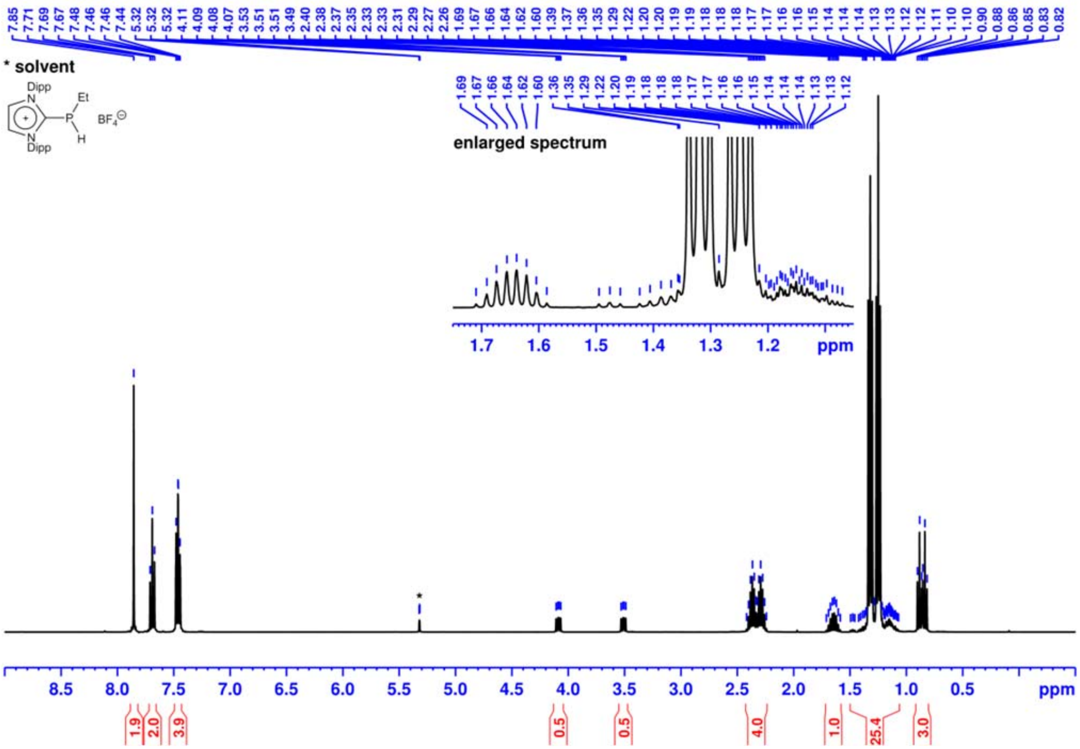


Figure S59. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz) of **5b**[BF_4].

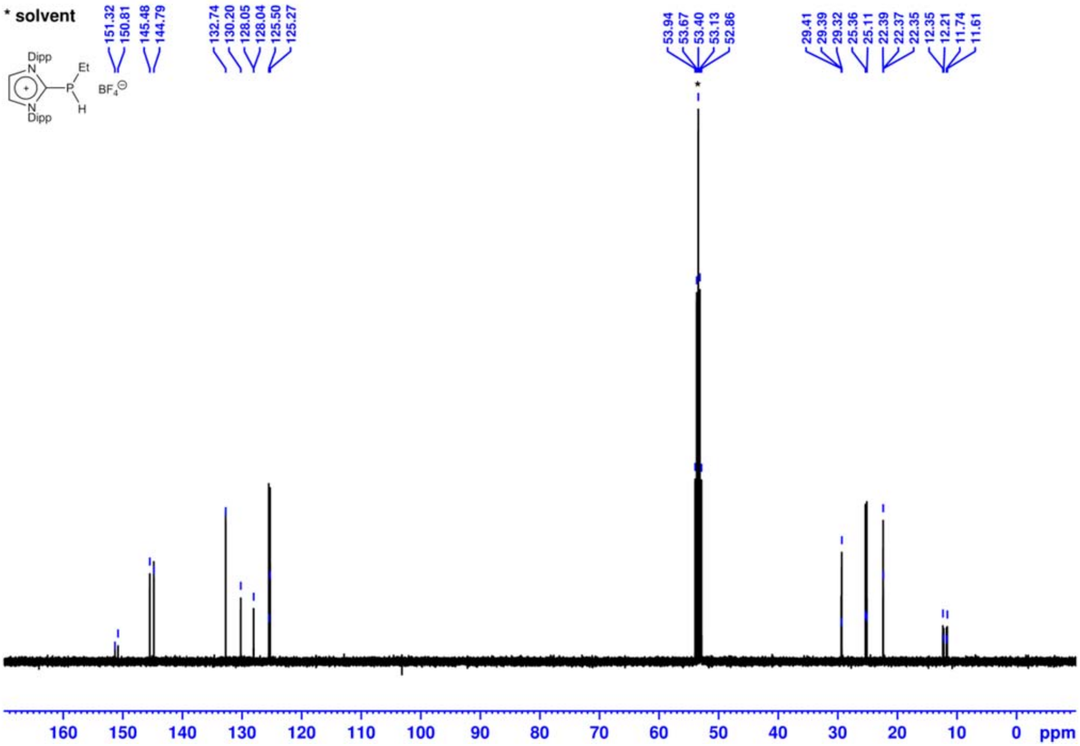


Figure S60. $^{13}C\{^1H\}$ NMR spectrum (CD_2Cl_2, 100.6 MHz) of **5b**[BF_4].

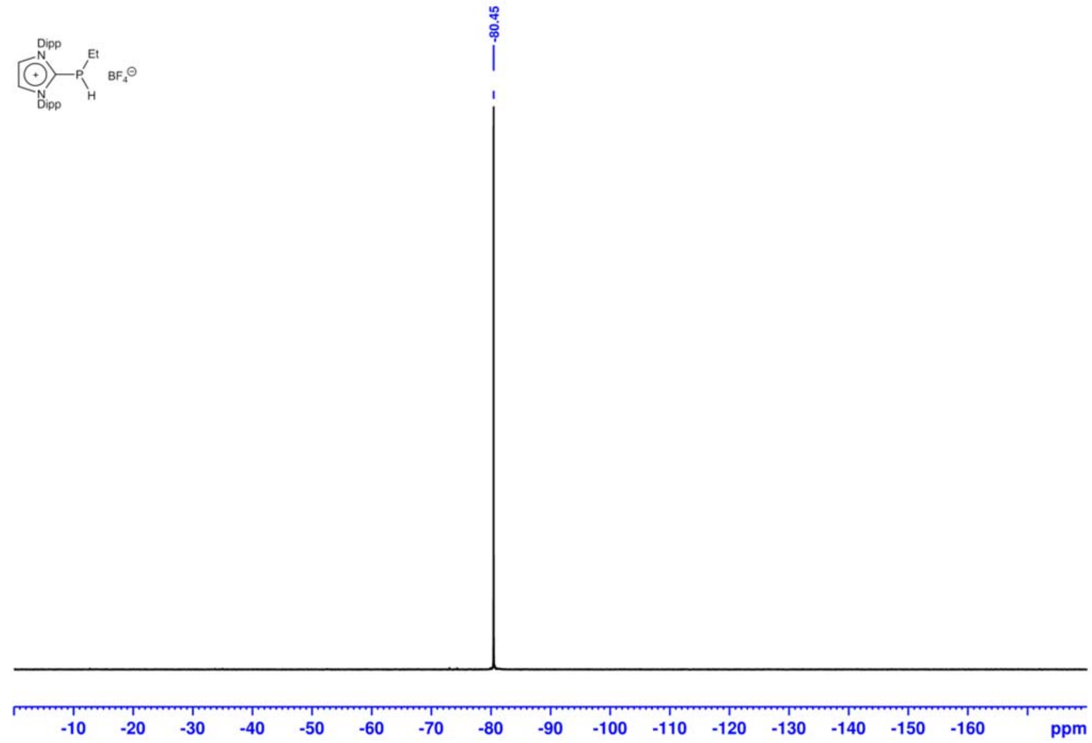


Figure S61. $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2, 161.9 MHz) of **5b**[BF$_4$].

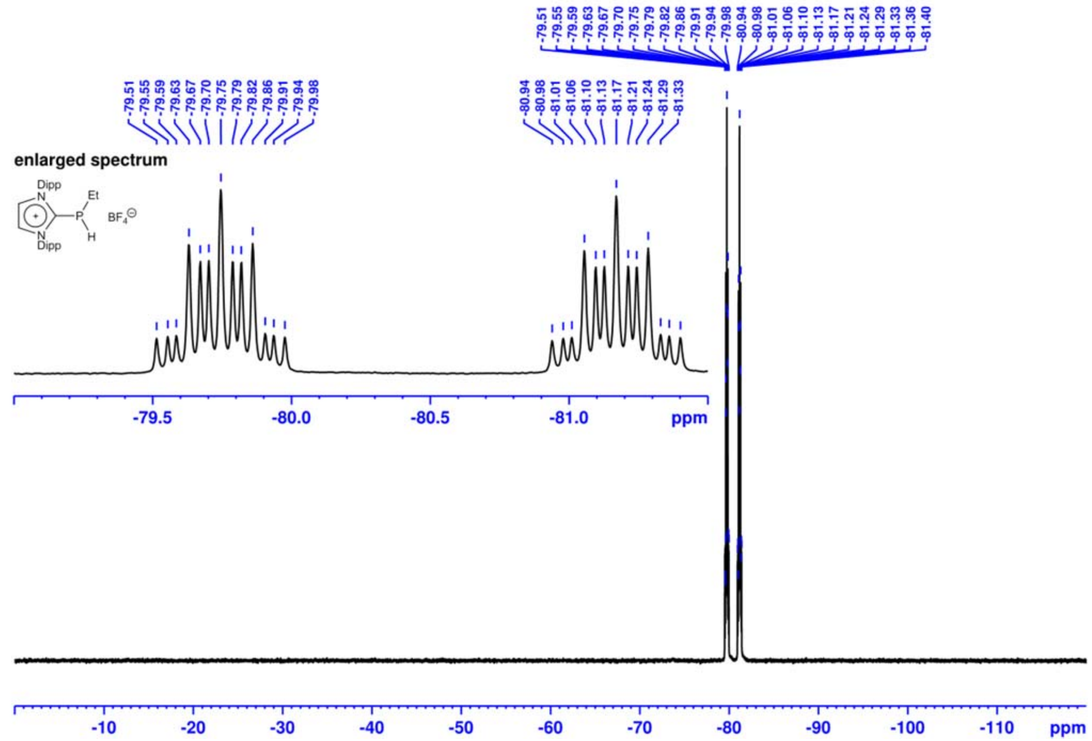


Figure S62. ^{31}P NMR spectrum (CD_2Cl_2, 161.9 MHz) of **5b**[BF$_4$].

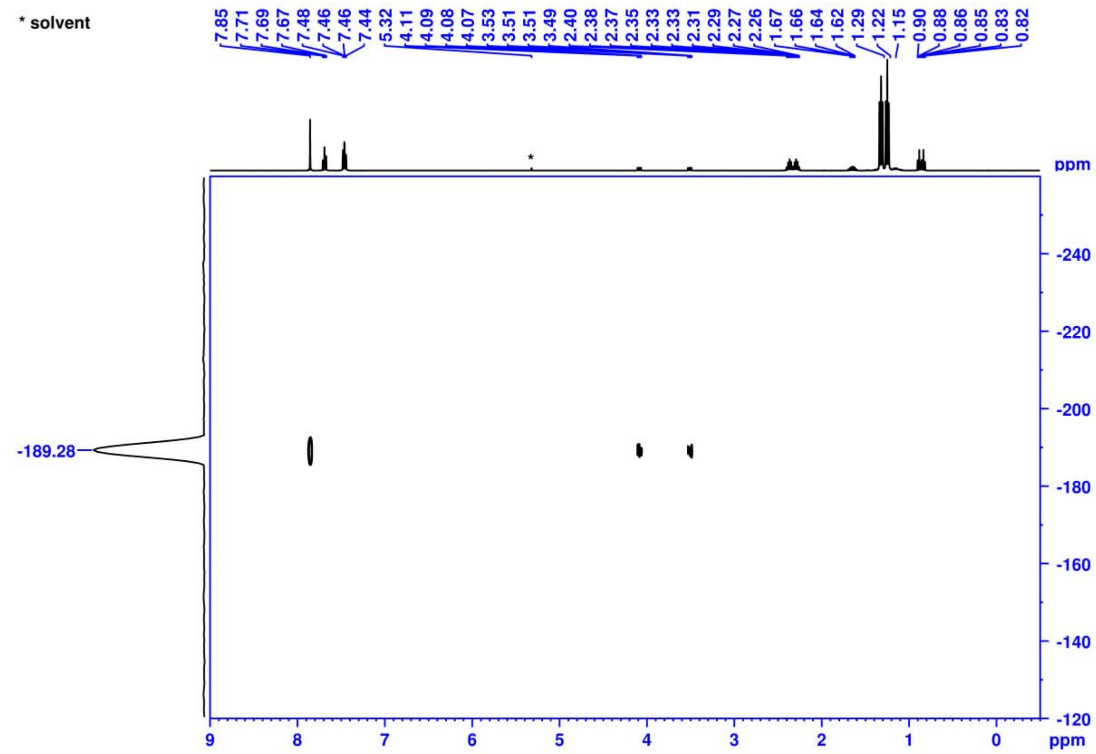


Figure S63. ^{1}H,^{15}N HMBC NMR spectrum (CD_2Cl_2, 400 / 40.6 MHz) of **5b**[BF_4].

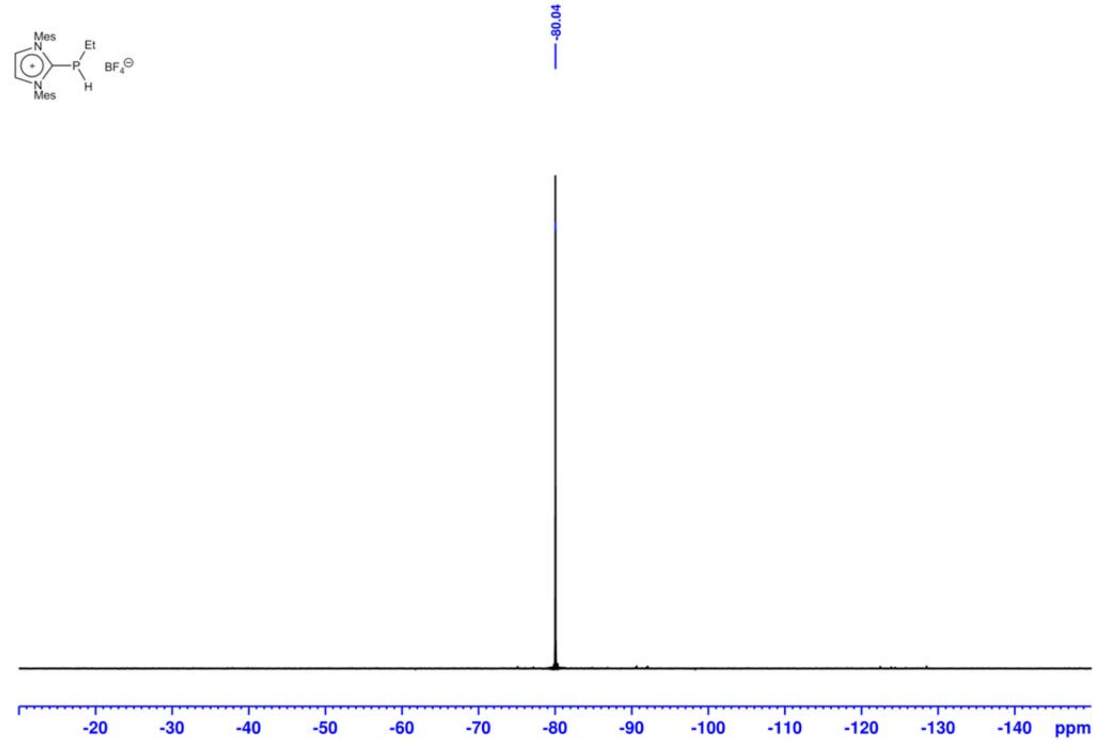


Figure S64. ^{31}P{^{1}H} NMR spectrum (MeCN, 101.2 MHz) of **5c**[BF_4] (reaction mixture).

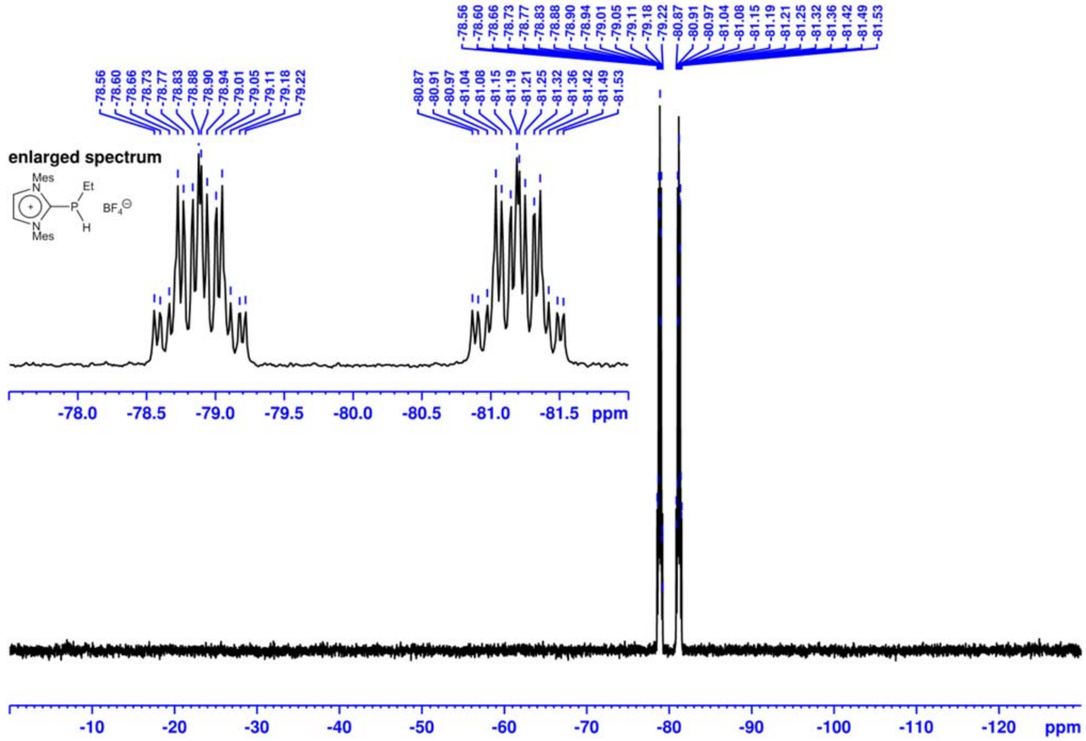


Figure S65. ^{31}P NMR spectrum (MeCN, 101.2 MHz) of **5c**[BF$_4$] (reaction mixture).

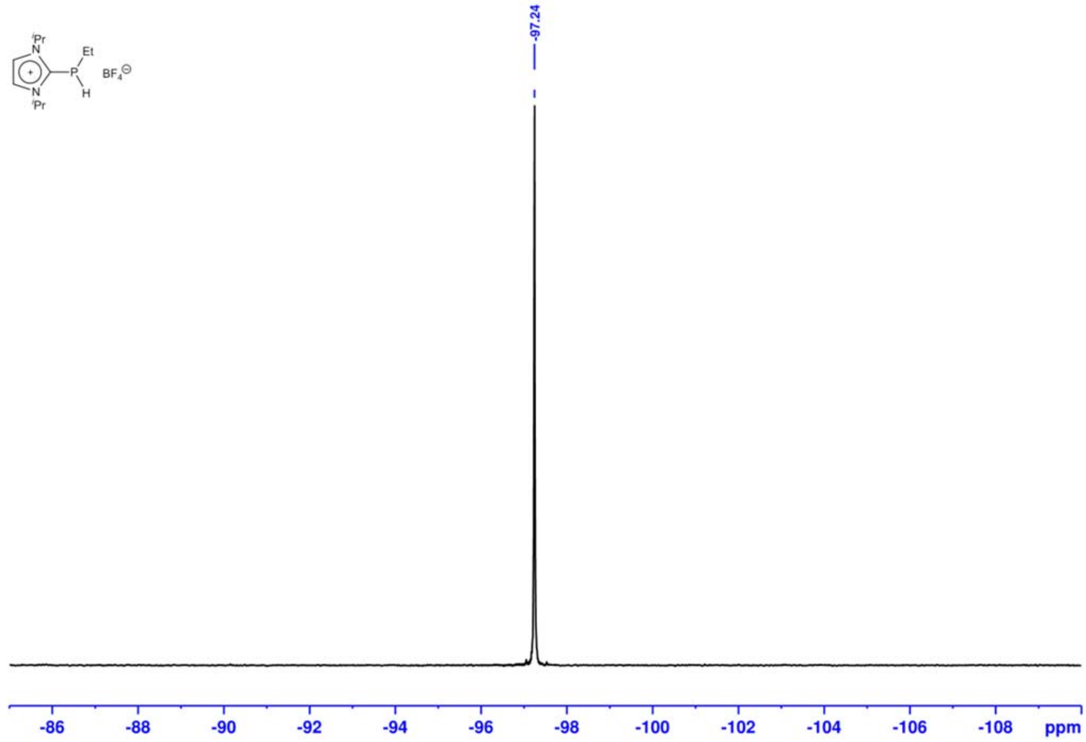


Figure S66. ^{31}P{^{1}H} NMR spectrum (MeCN, 101.2 MHz) of **5d**[BF$_4$] (reaction mixture).

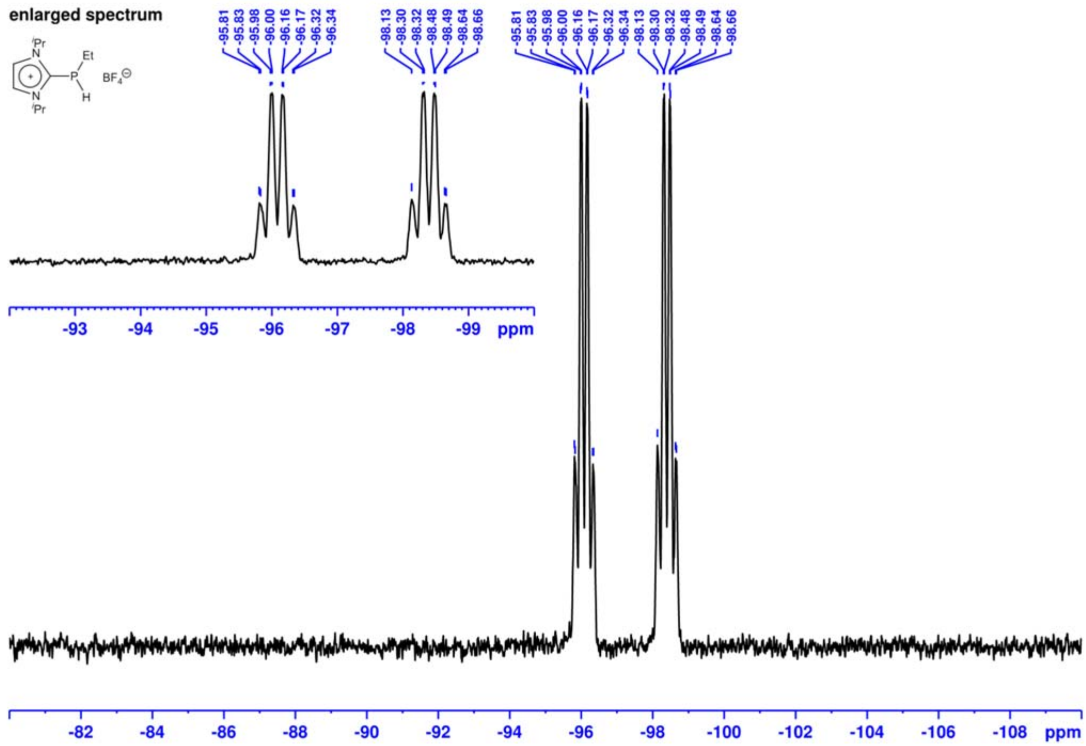


Figure S67. ^{31}P NMR spectrum (MeCN, 101.2 MHz) of **5d**[BF$_4$] (reaction mixture).

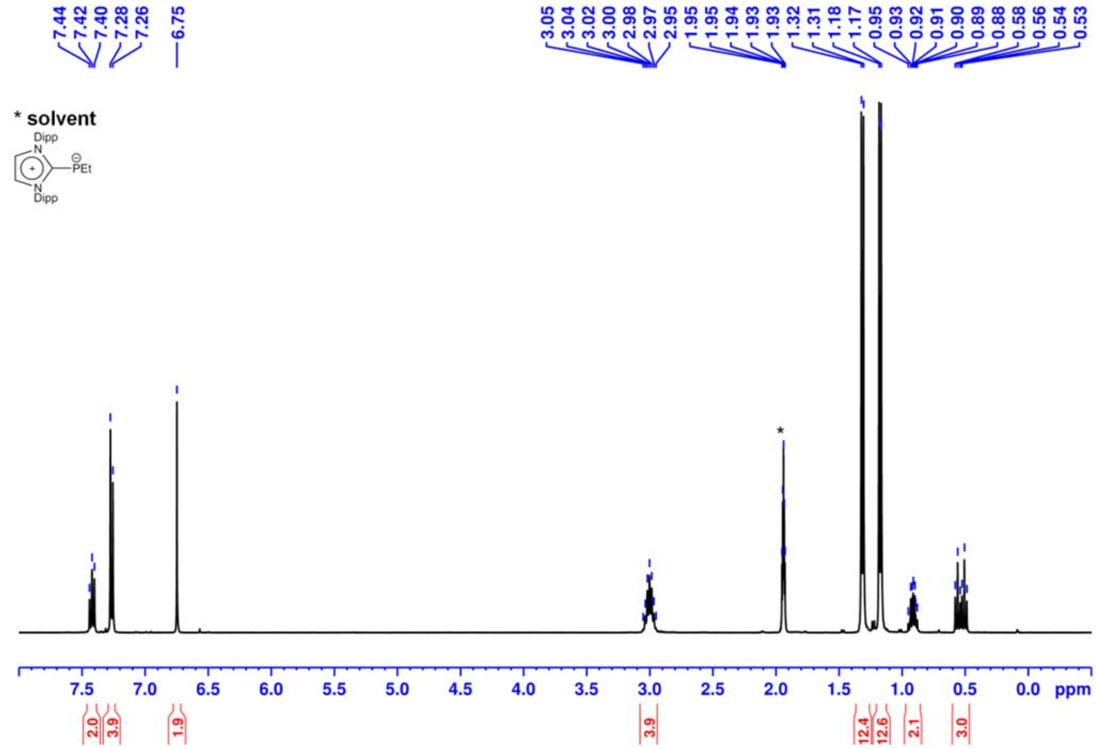


Figure S68. ^{1}H NMR spectrum (CD$_3$CN, 400 MHz) of **6b**.

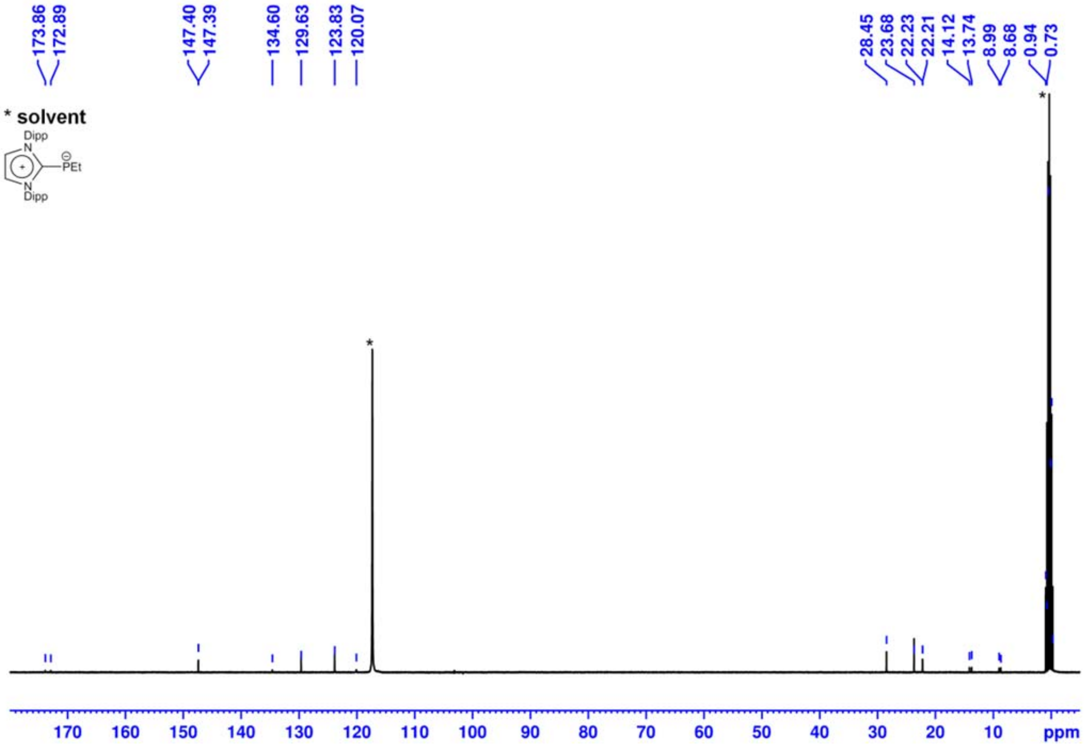


Figure S69. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3CN, 100.6 MHz) of **6b**.

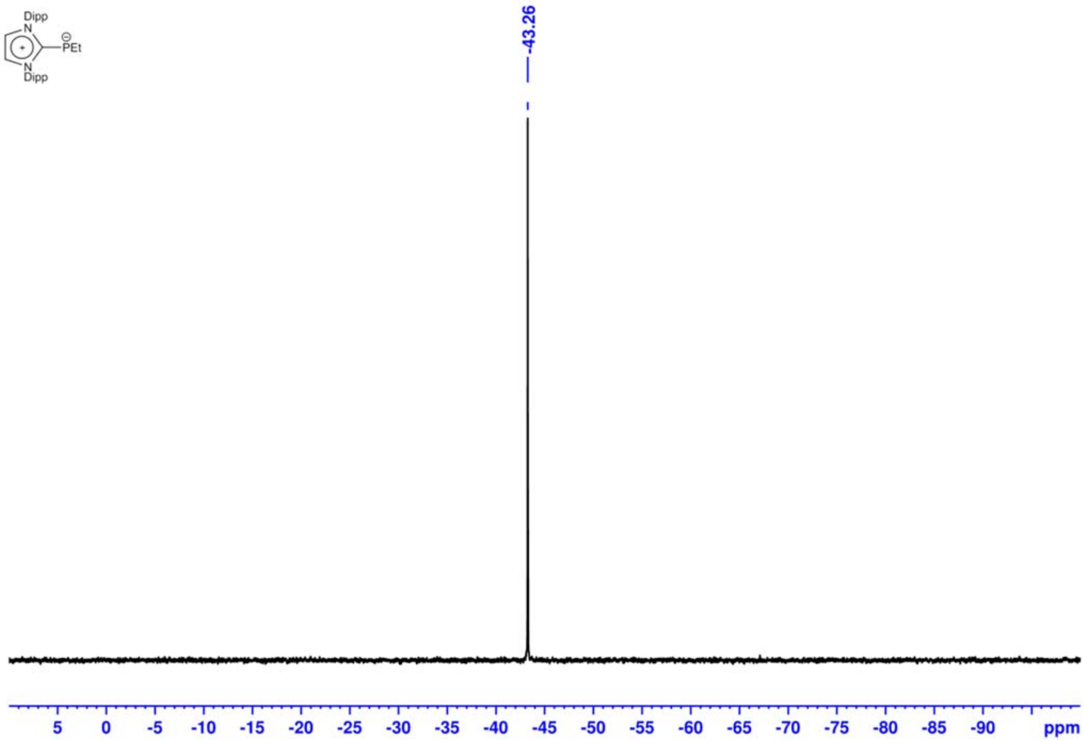


Figure S70. $^{31}P\{^{1}H\}$ NMR spectrum (CD_3CN, 161.9 MHz) of **6b**.

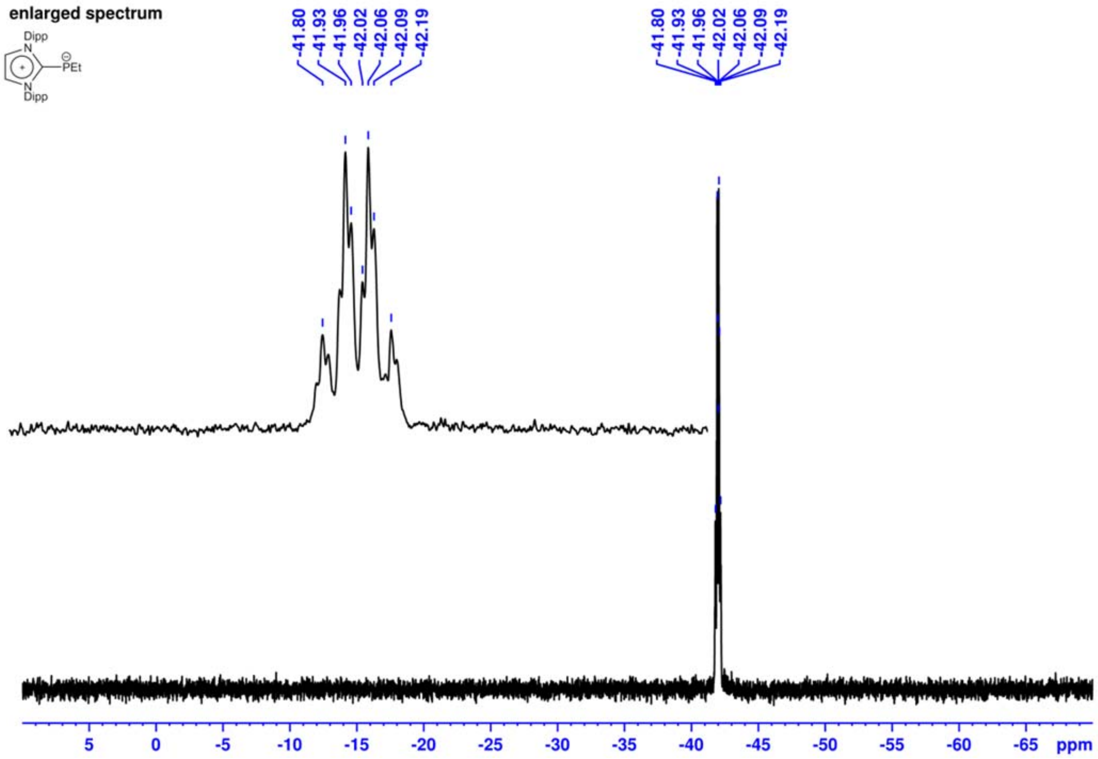


Figure S71. ^{31}P NMR spectrum (CD_3CN, 161.9 MHz) of **6b**.

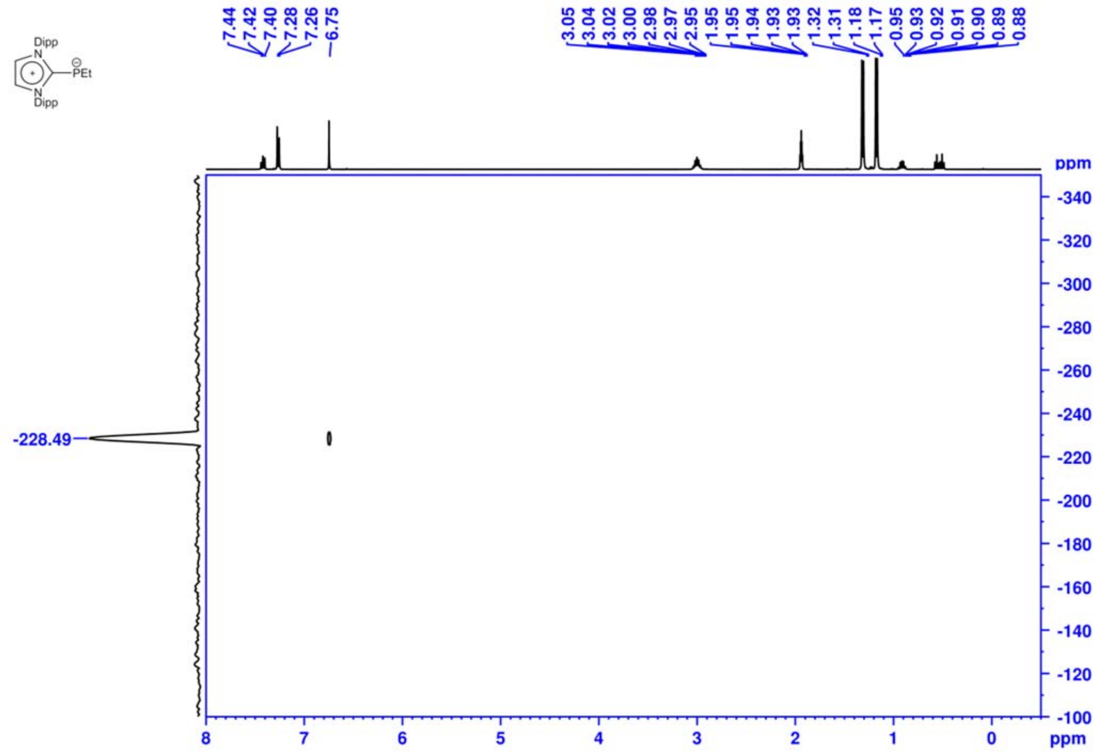


Figure S72. ^{1}H, ^{13}N HMBC NMR spectrum (thf-d_8, 400 / 40.6 MHz) of **6b**.

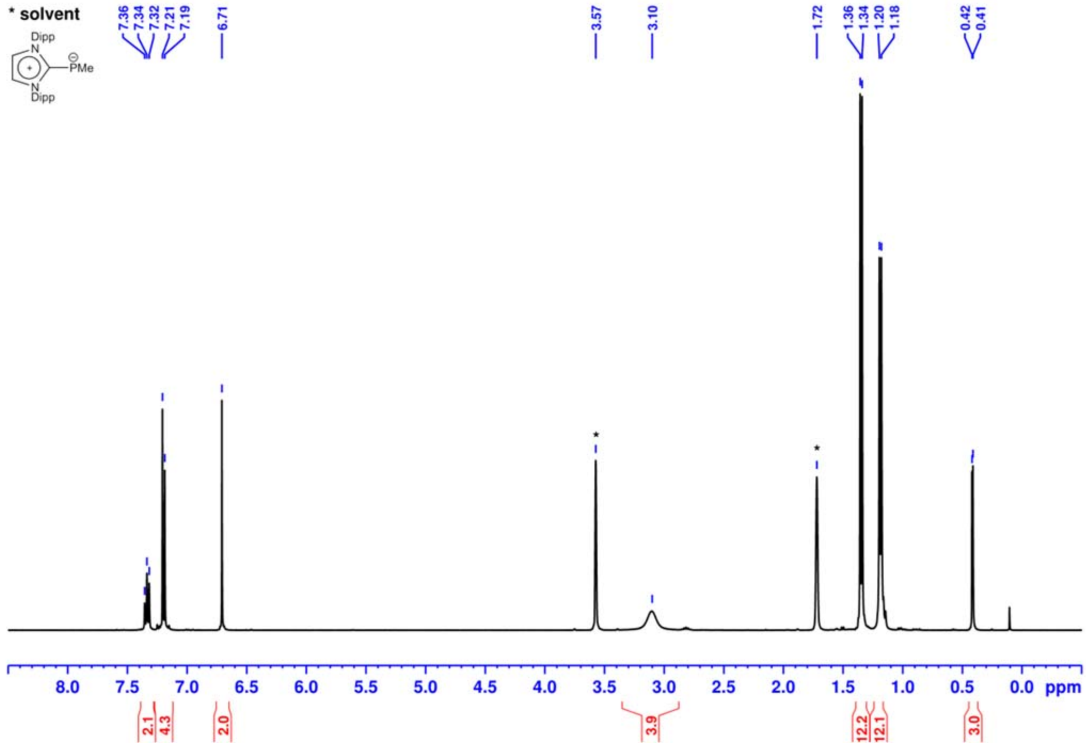


Figure S73. ^{1}H NMR spectrum (thf-d_8, 400 MHz) of **8b**.

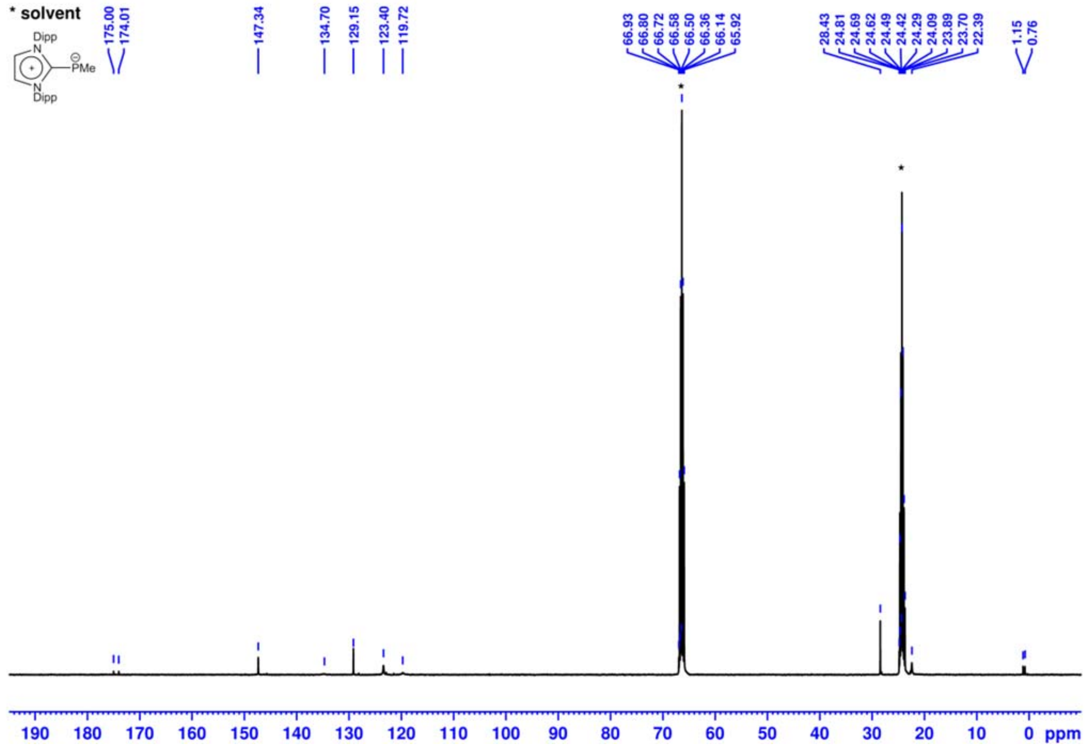


Figure S74. ^{13}C{^{1}H} NMR spectrum (thf-d_8, 100.6 MHz) of **8b**.

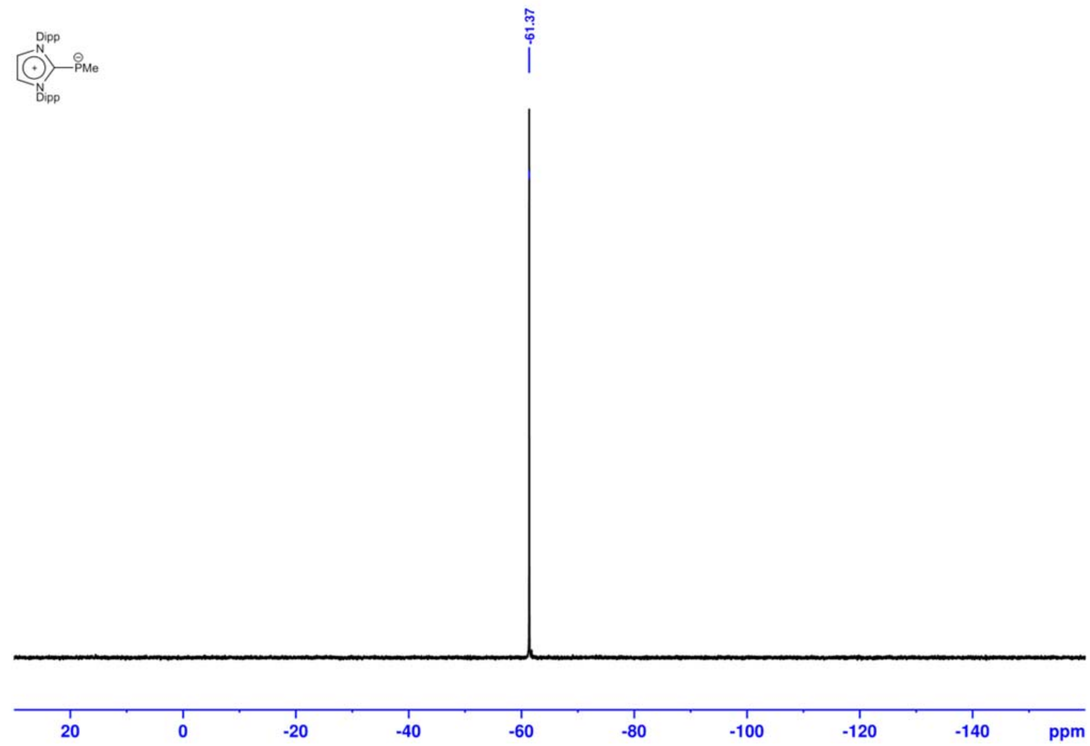


Figure S75. $^{31}P\{^{1}H\}$ NMR spectrum (thf-d_8, 161.9 MHz) of **8b**.

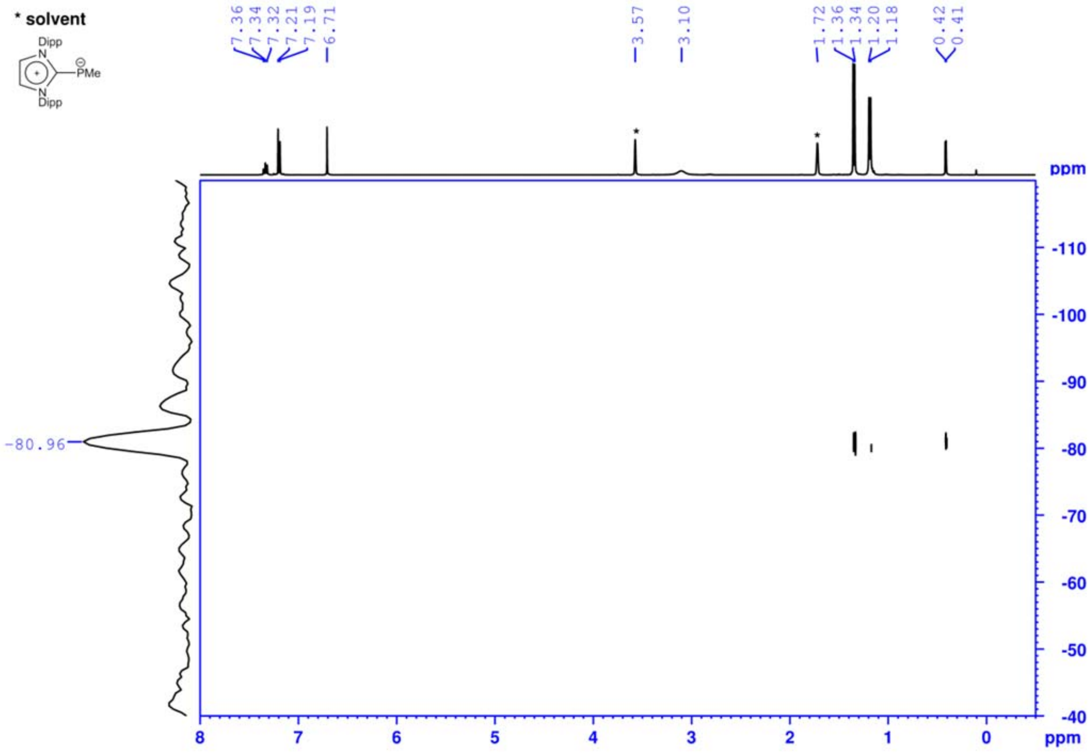


Figure S76. $^{1}H,^{13}N$ HMBC NMR spectrum (thf-d_8, 400 / 40.6 MHz) of **8b**.

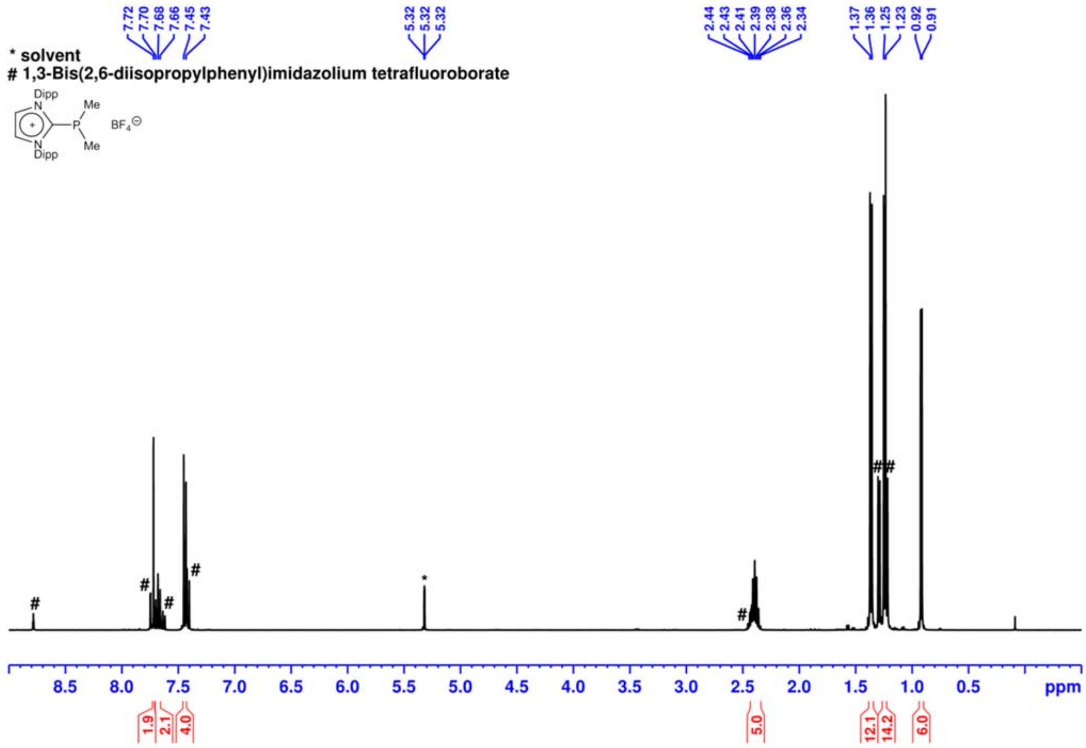


Figure S77. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz) of **19a**[BF_4].

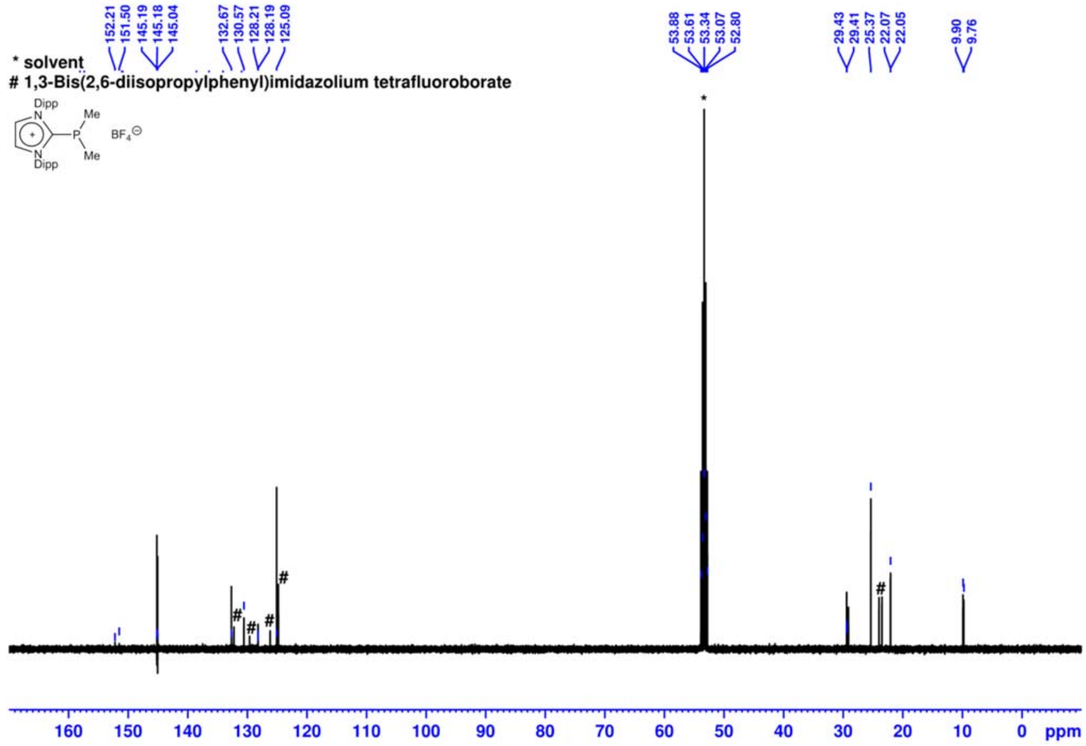


Figure S78. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100.6 MHz) of **19a**[BF_4].

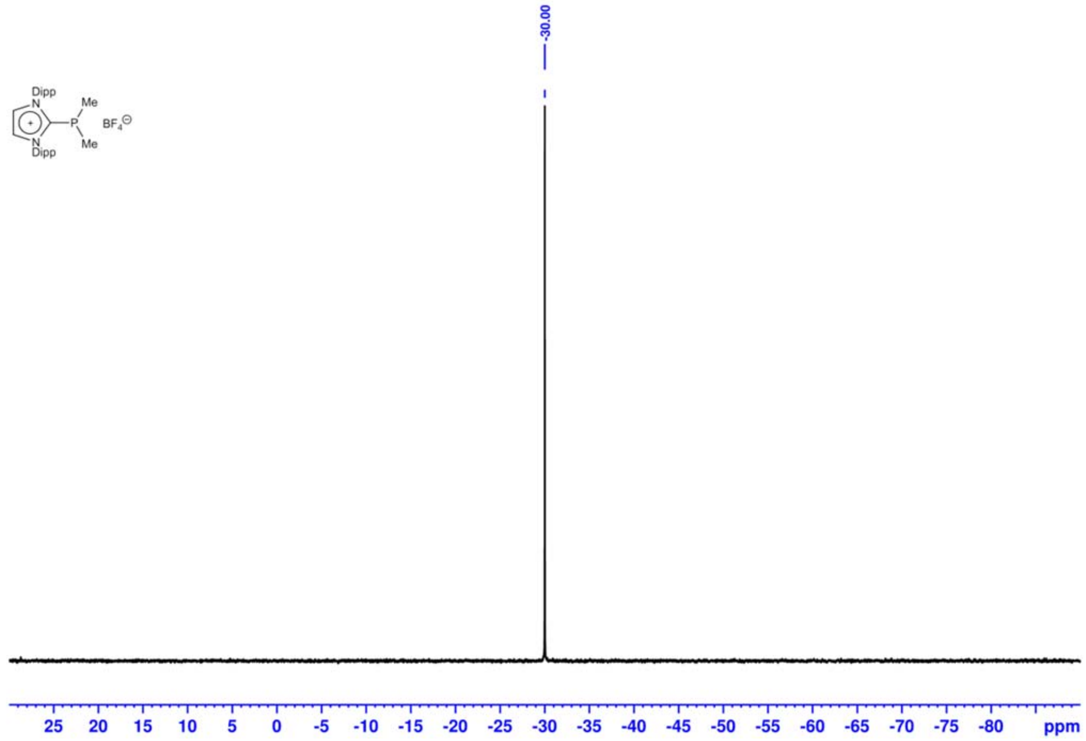


Figure S79. $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2, 161.9 MHz) of **19a**[BF_4].

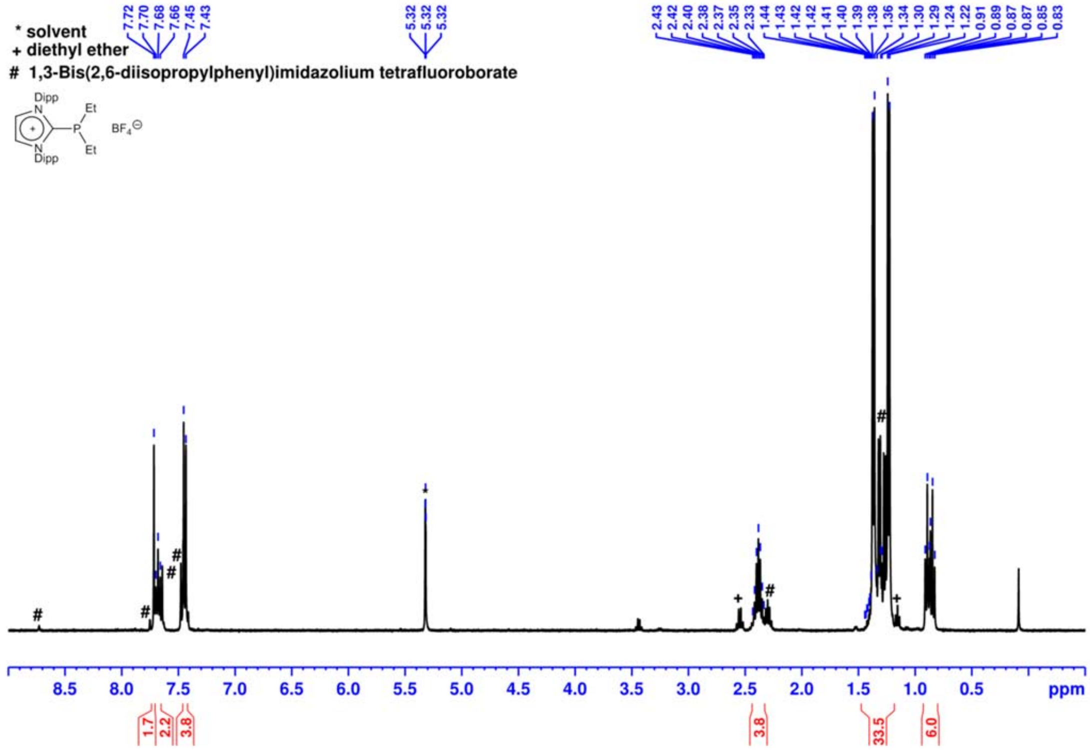


Figure S80. ^1H NMR spectrum (CD_2Cl_2, 400 MHz) of **19b**[BF_4].

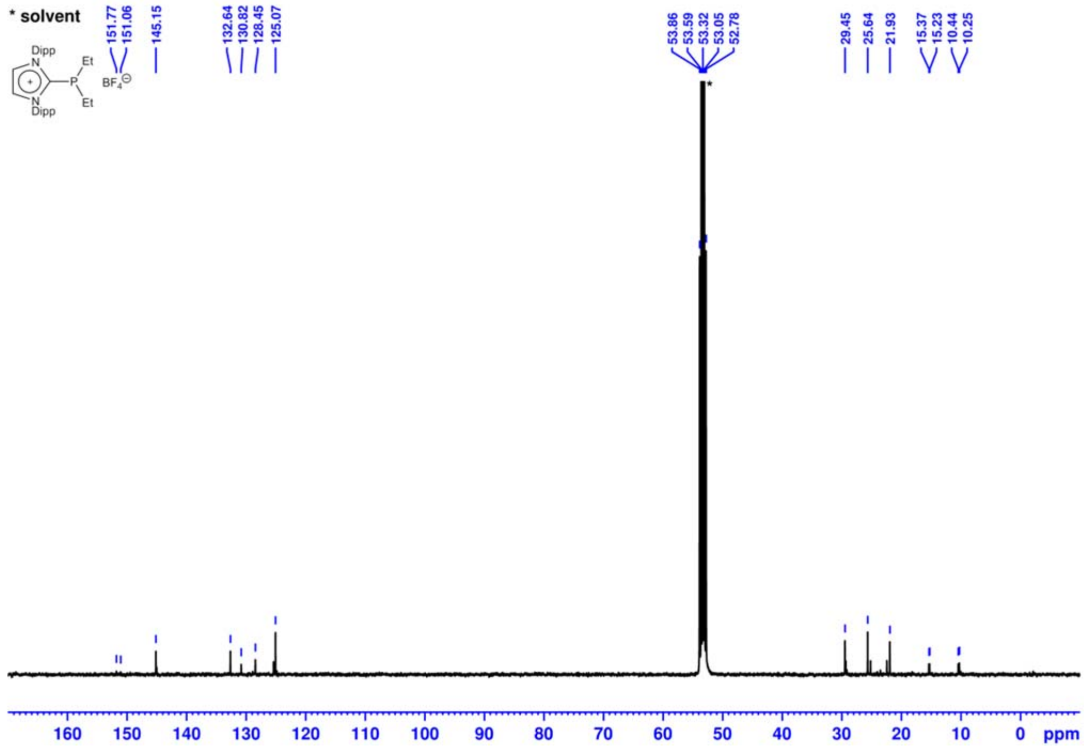


Figure S81. $^{13}C\{^1H\}$ NMR spectrum (CD_2Cl_2, 100.6 MHz) of **19b**[BF$_4$].

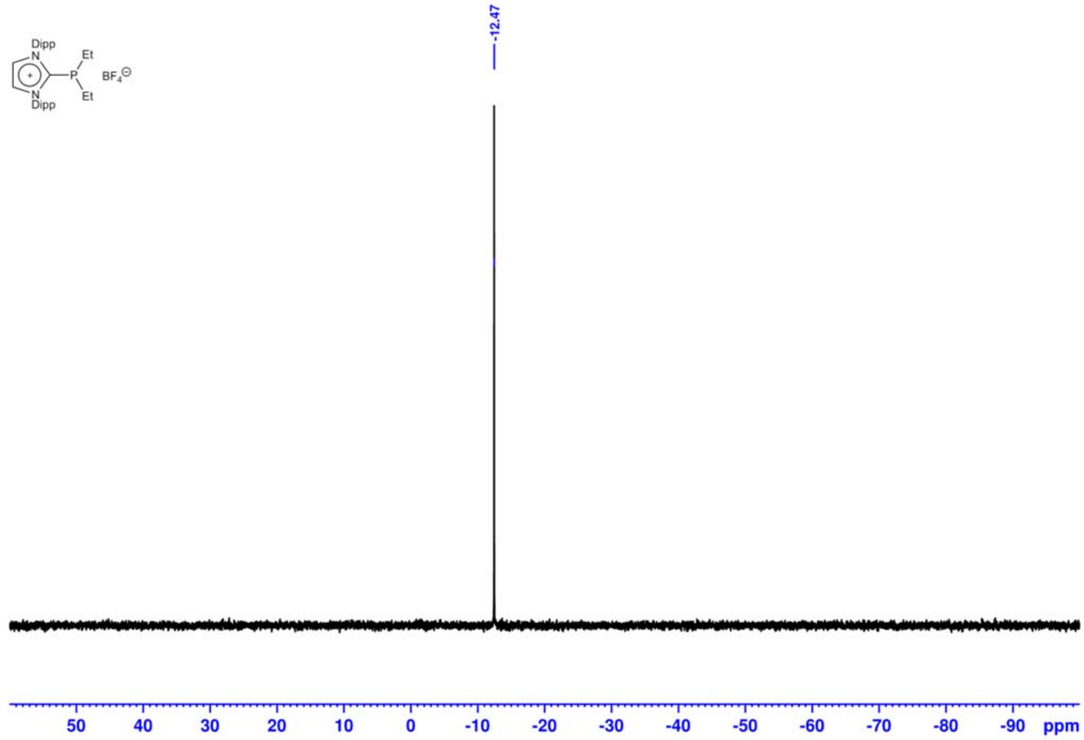


Figure S82. $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2, 161.9 MHz) of **19b**[BF$_4$].

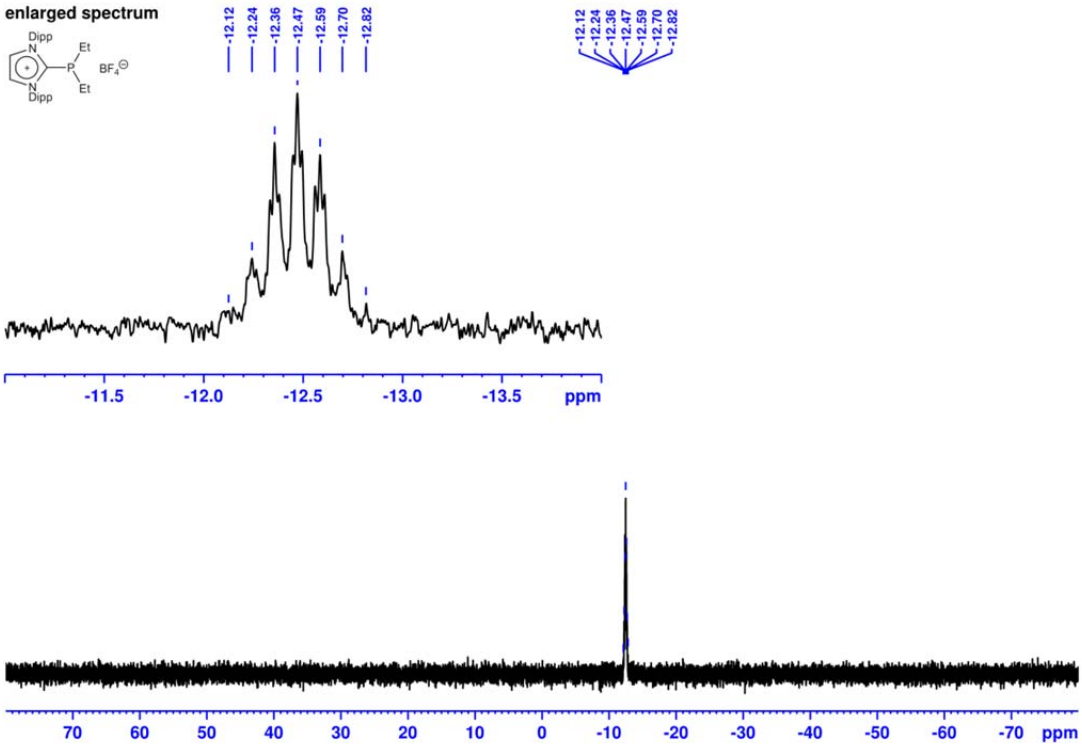


Figure S83. ^{31}P NMR spectrum (CD_2Cl_2, 161.9 MHz) of **19b**[BF_4].

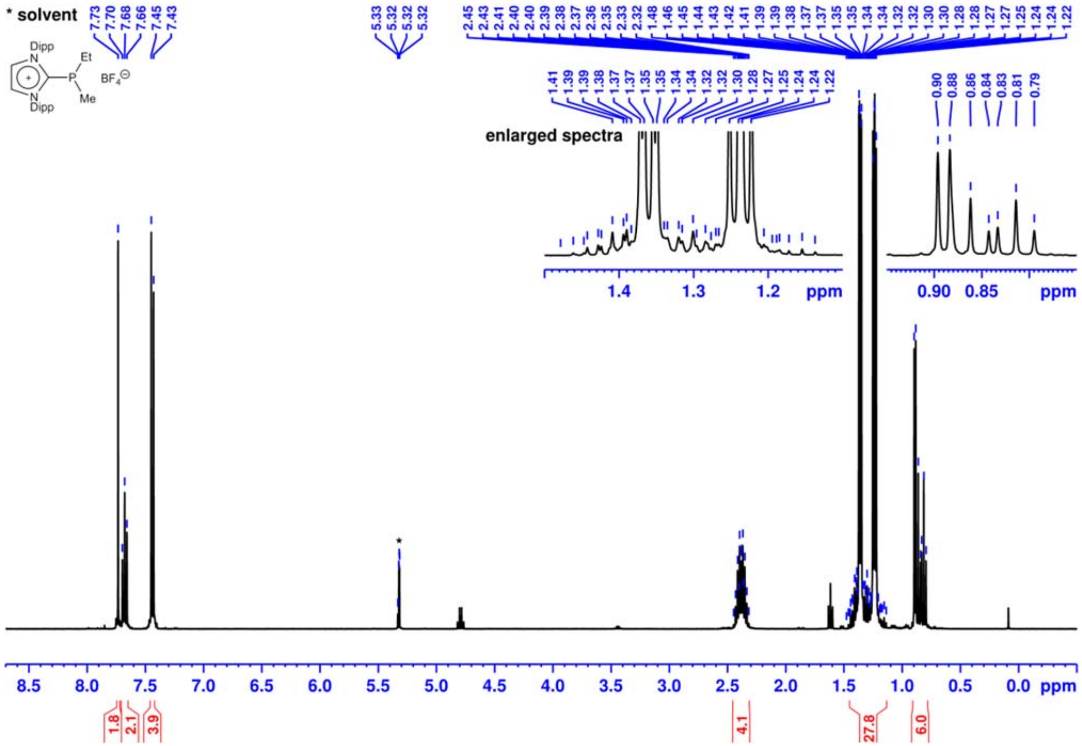


Figure S84. ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz) of **19c**[BF_4].

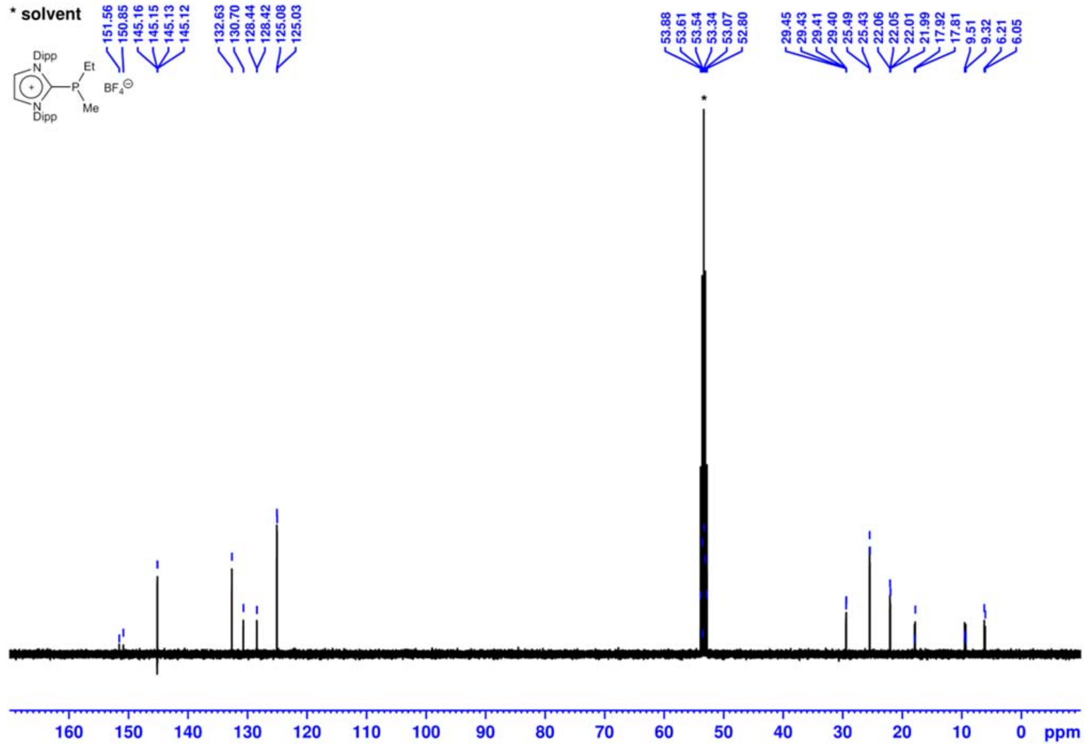


Figure S85. ^{13}C{^{1}H} NMR spectrum (CD$_2$Cl$_2$, 100.6 MHz) of **19c**[BF$_4$].

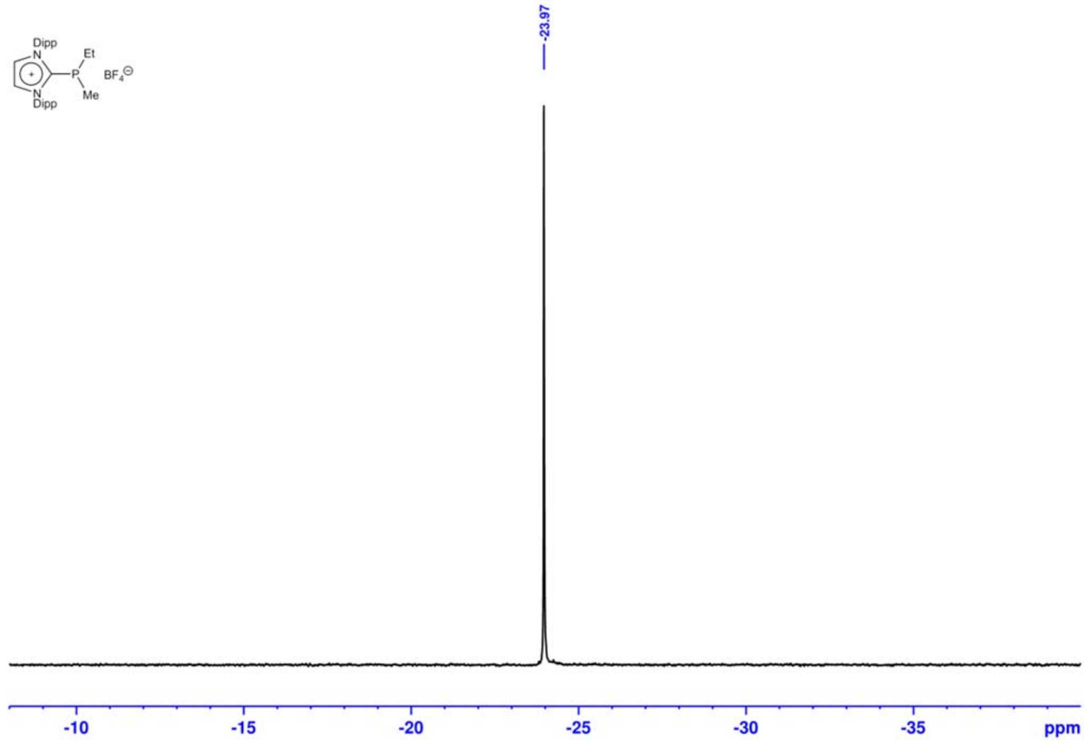


Figure S86. ^{31}P{^{1}H} NMR spectrum (CD$_2$Cl$_2$, 161.9 MHz) of **19c**[BF$_4$].

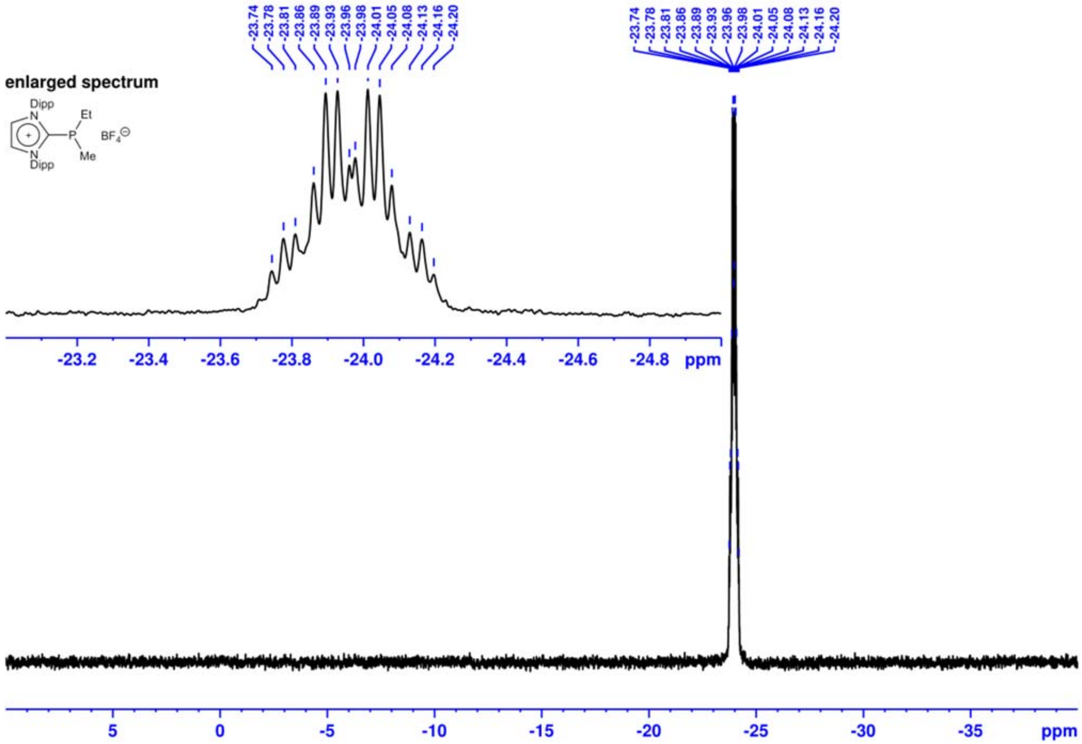


Figure S87. ^{31}P NMR spectrum (CD_2Cl_2, 161.9 MHz) of **19c**[BF_4].

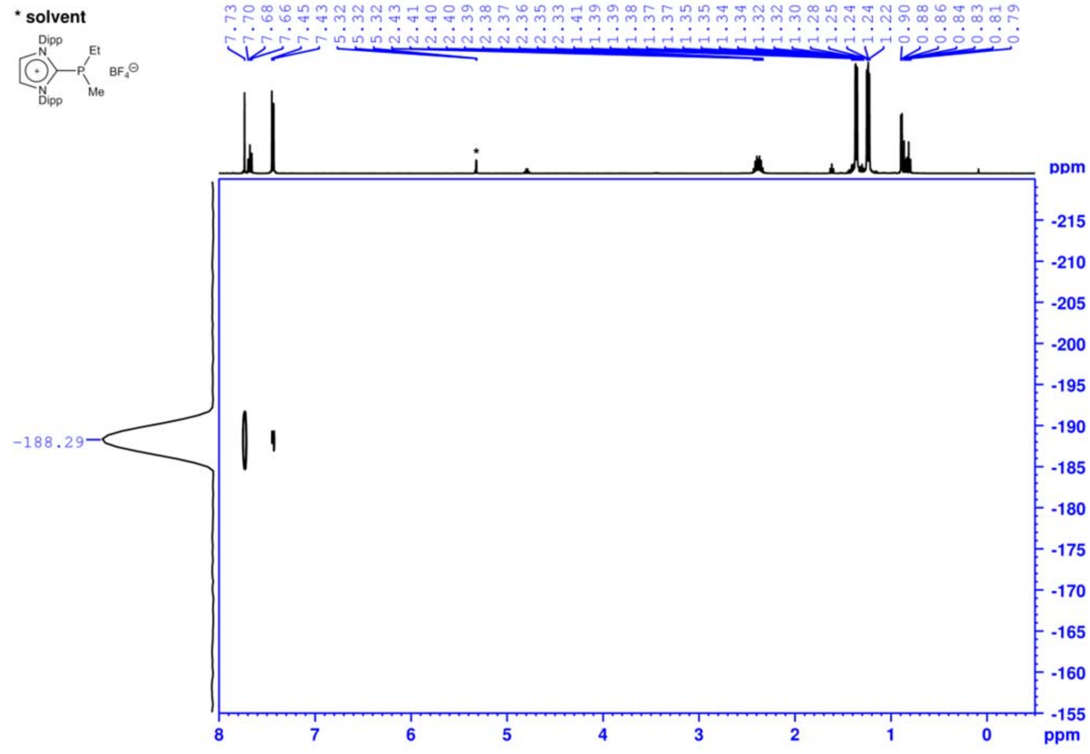


Figure S88. ^{1}H,^{15}N HMBC NMR spectrum (CD_2Cl_2, 400 / 40.6 MHz) of **19c**[BF_4].

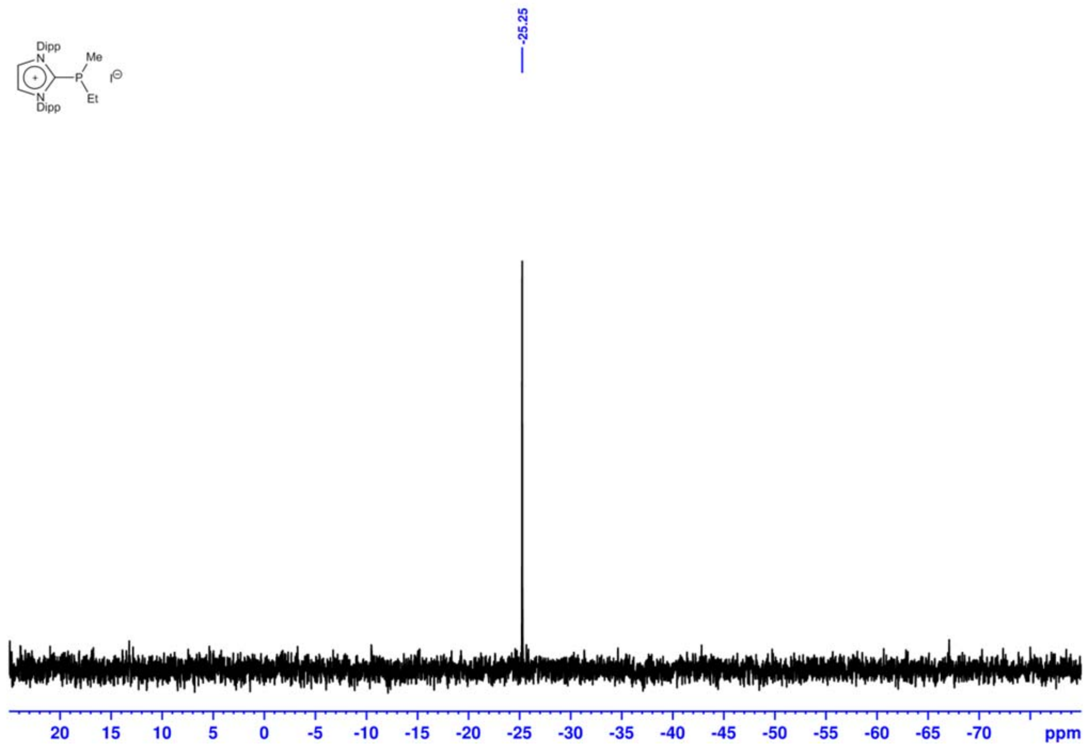


Figure S89. $^{31}P\{^1H\}$ NMR spectrum (MeCN, 101.2 MHz) of **19c**[I] (reaction mixture).

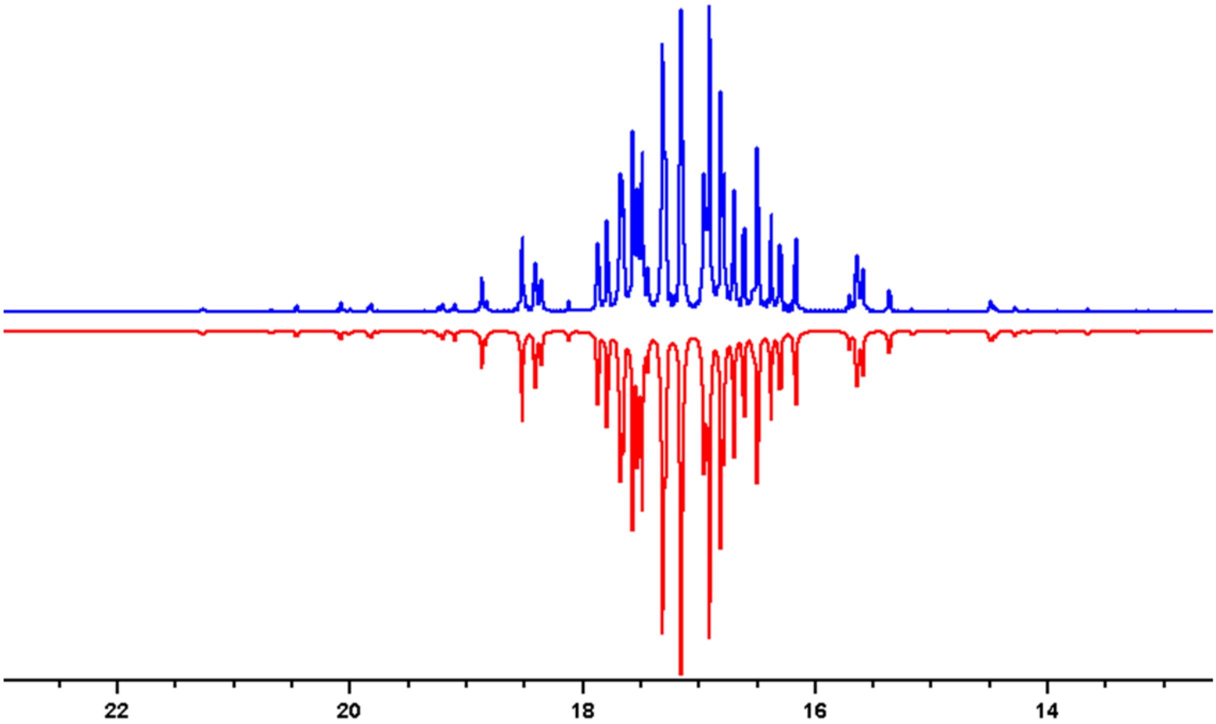


Figure S90. $^{31}P\{^1H\}$ NMR spectrum (C_6D_6, 101.2 MHz) of pentamethyl-cyclopentaphosphine (blue trace) and result of a spectral simulation (red trace).

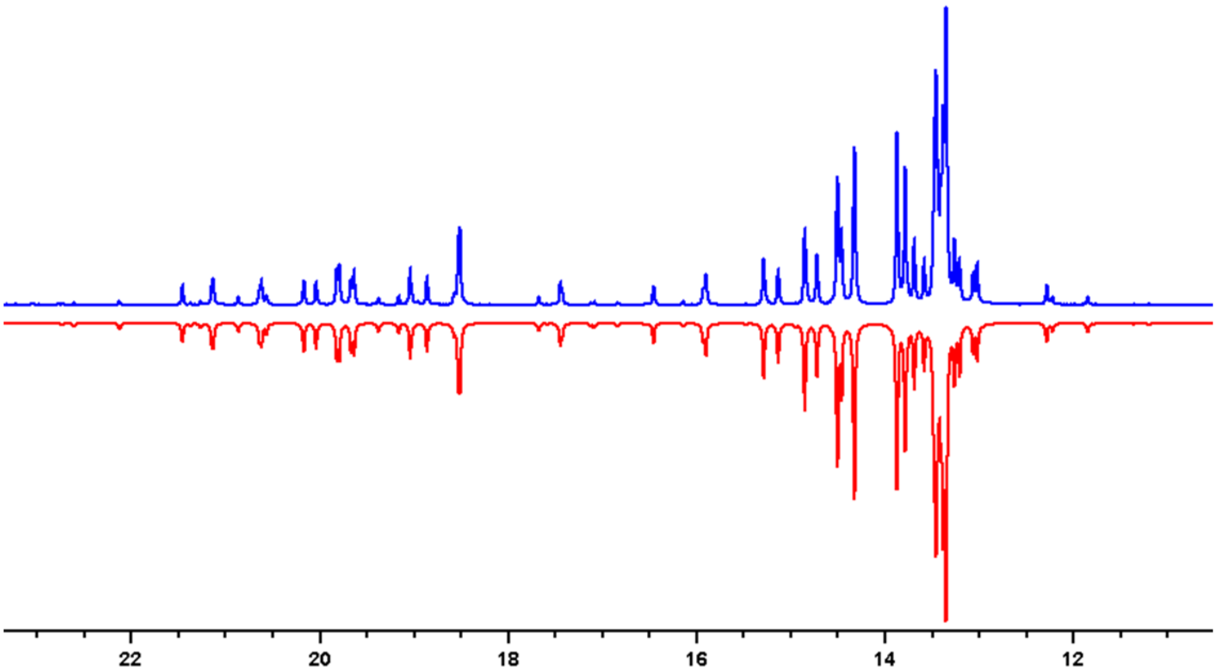


Figure S91. $^{31}P\{^1H\}$ NMR spectrum (MeCN, 161.9 MHz) of pentaethyl-cyclopentaphosphine (blue trace) and result of a spectral simulation (red trace).

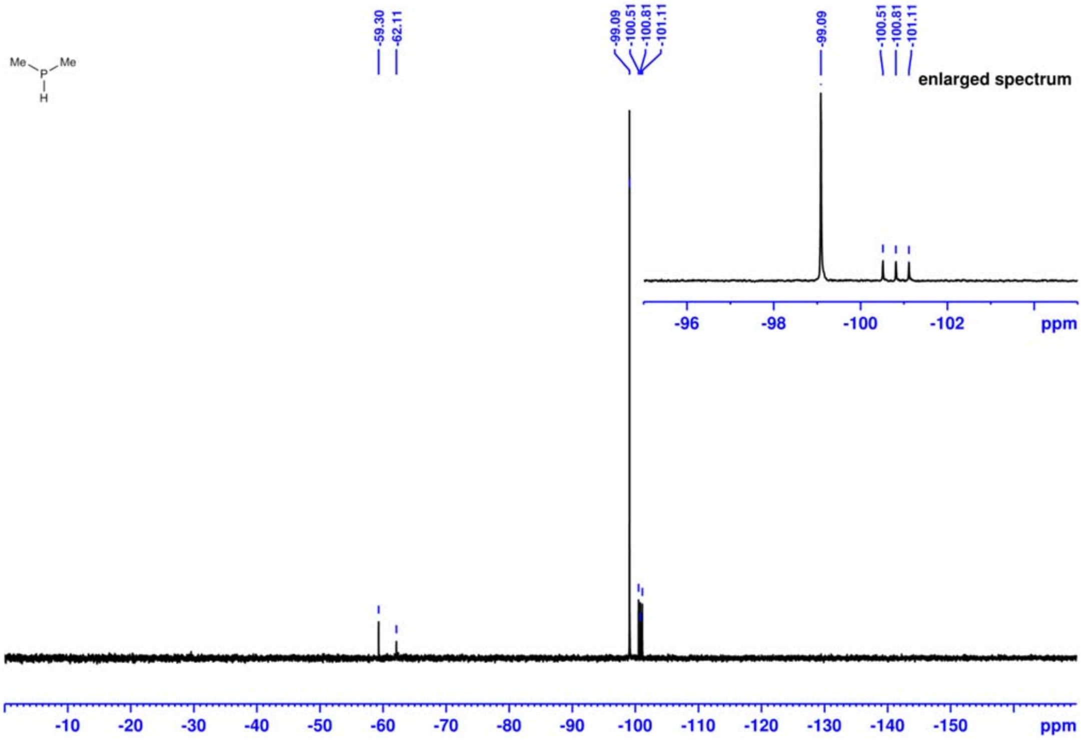


Figure S92. $^{31}P\{^1H\}$ NMR spectrum (CD_3CN, 101.2 MHz) of a distilled solution of Me_2PH. Signals at -100.8 and -59.3 ppm are attributable to Me_2PD (arising from isotope exchange with the solvent) and Me_4P_2, respectively.

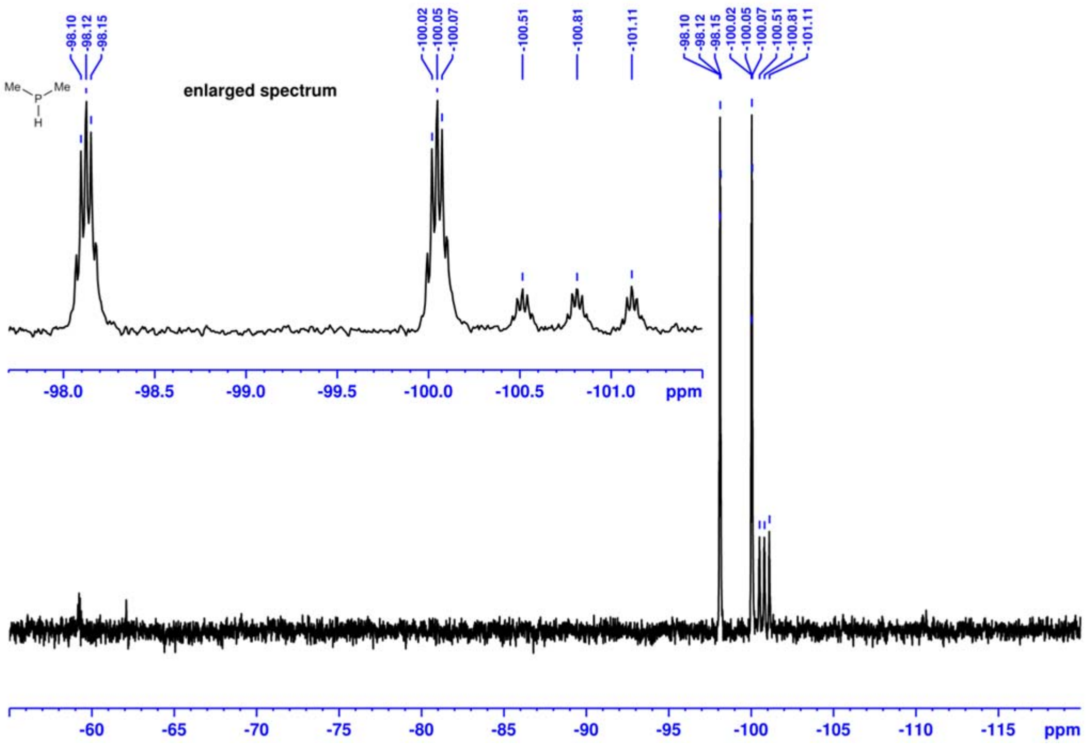


Figure S93. ^{31}P NMR spectrum (CD_3CN, 101.2 MHz) of a distilled solution of Me_2PH. Signals at -100.8 and -59.3 ppm are attributable to Me_2PD (arising from isotope exchange with the solvent) and Me4P2, respectively.

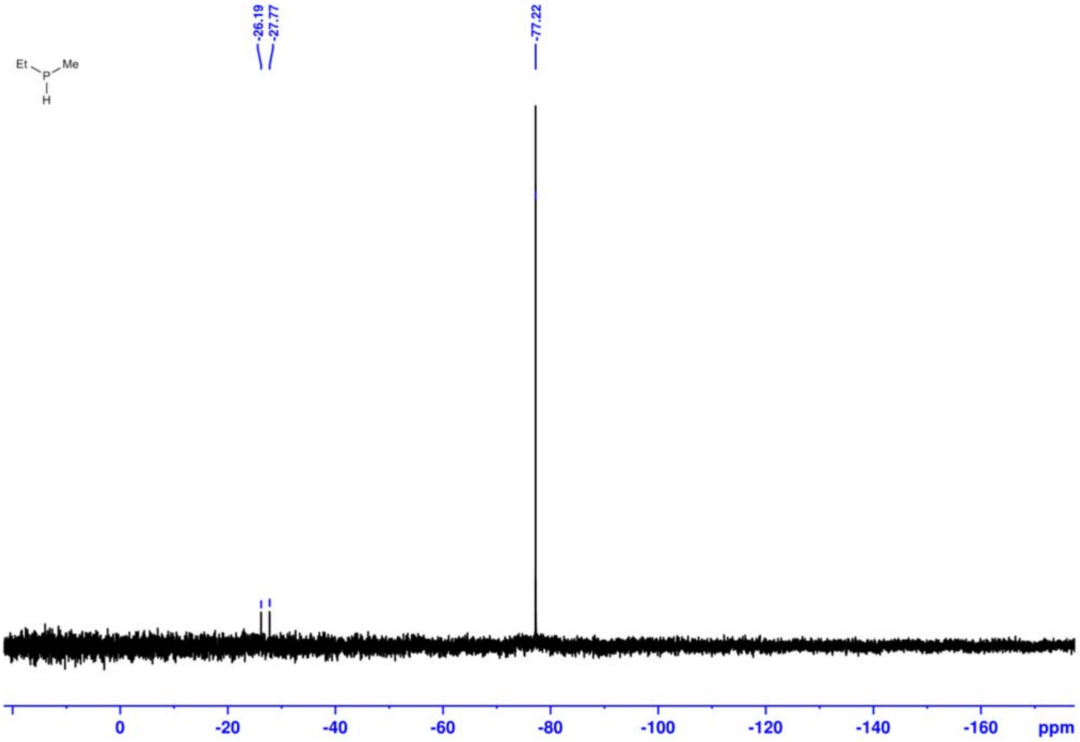


Figure S94. ^{31}P{^{1}H} NMR spectrum (MeCN, 101.2 MHz) of a distilled solution of Me(Et)PH.

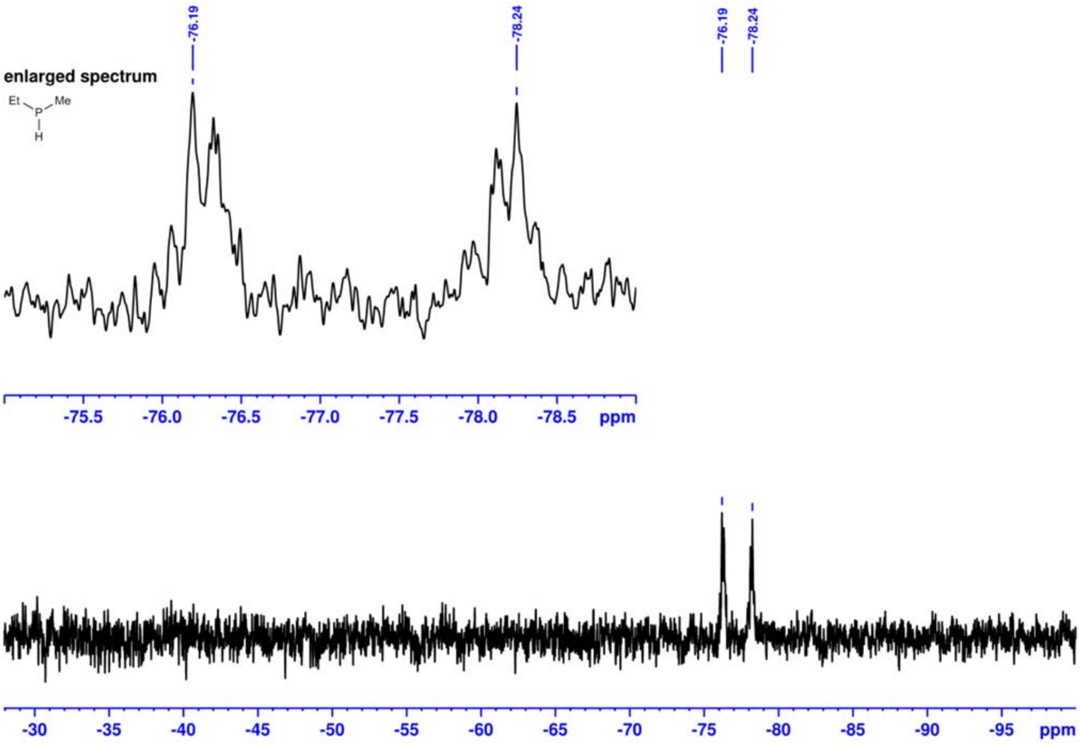


Figure S95. ^{31}P NMR spectrum (MeCN, 101.2 MHz) of a distilled solution of Me(Et)PH.

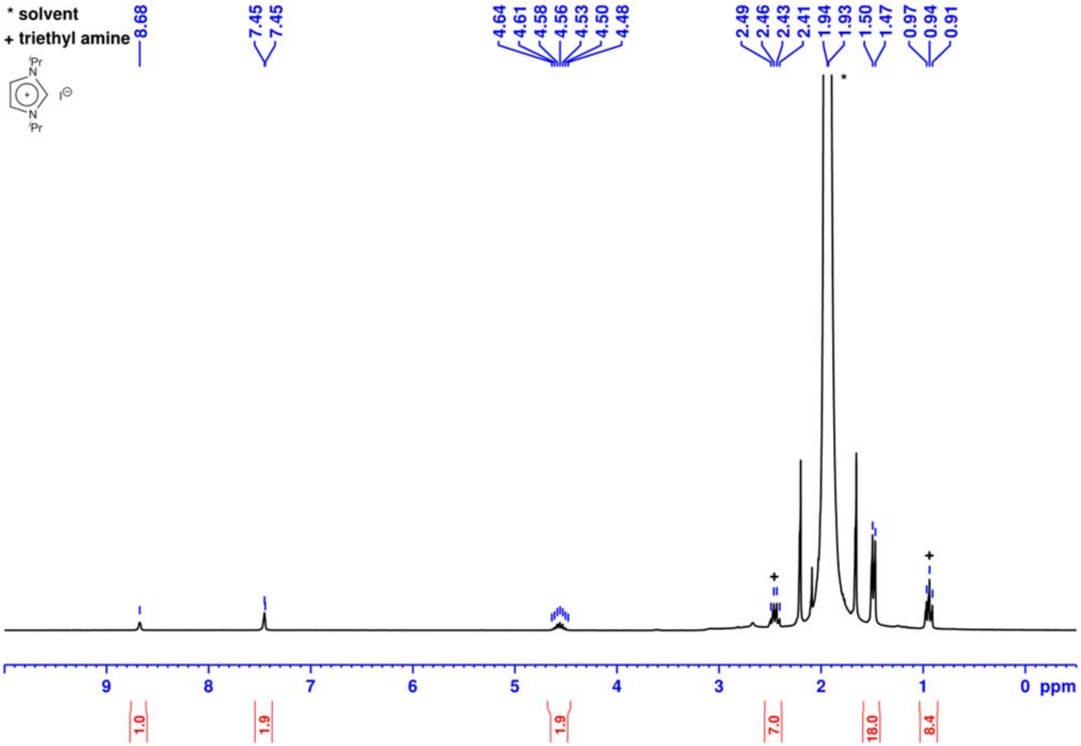


Figure S96. ^{1}H NMR spectrum (MeCN, 250 MHz) of a reaction mixture prepared from **1b**[I] and triethyl amine (1:1) showing the signals of **7b**$^{+}$ formed as by-product.

IR spectra

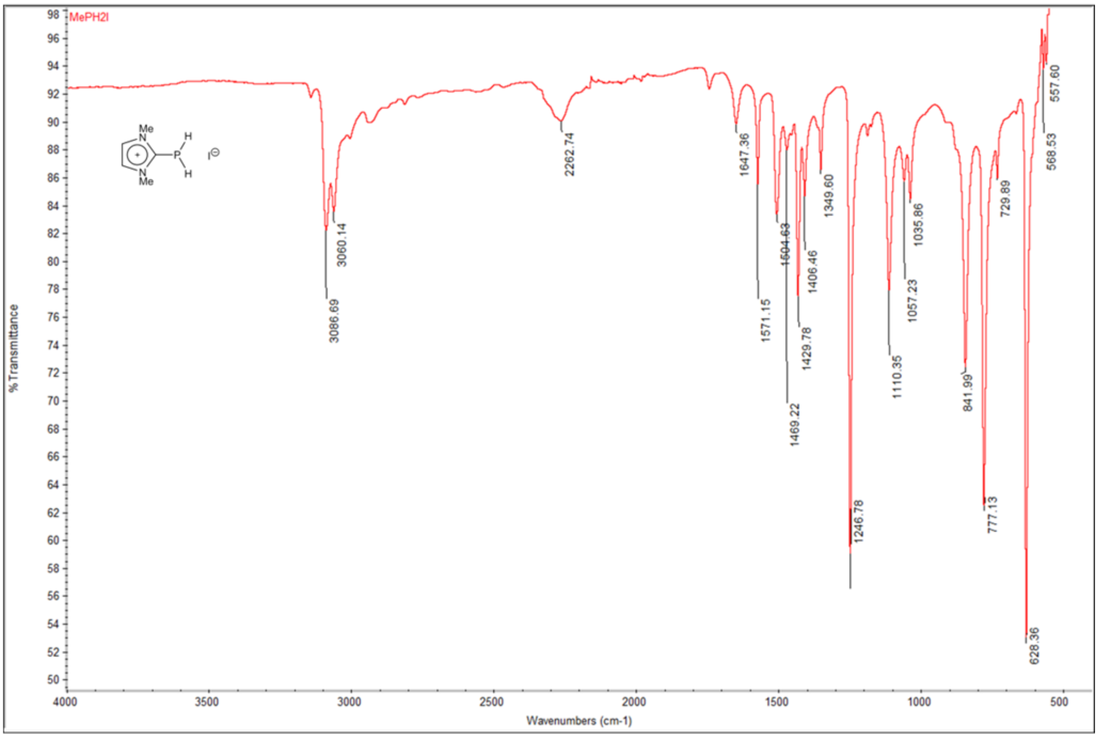


Figure S97. ATR-IR spectrum of **1e**[I].

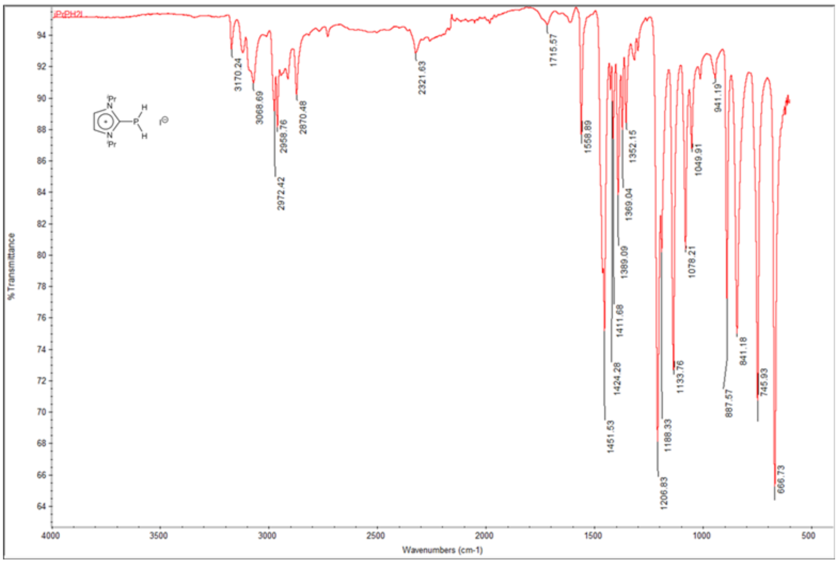


Figure S98. ATR-IR spectrum of **1d**[I].

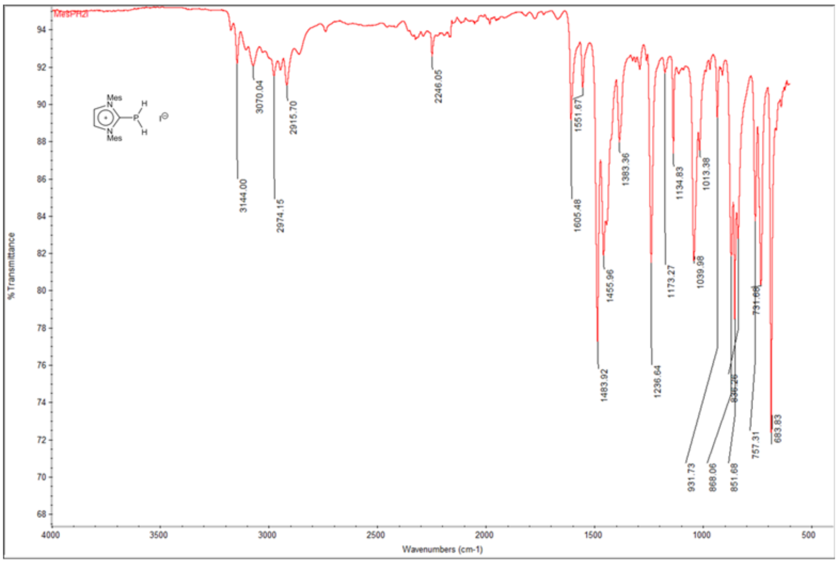


Figure S99. ATR-IR spectrum of **1c**[I].

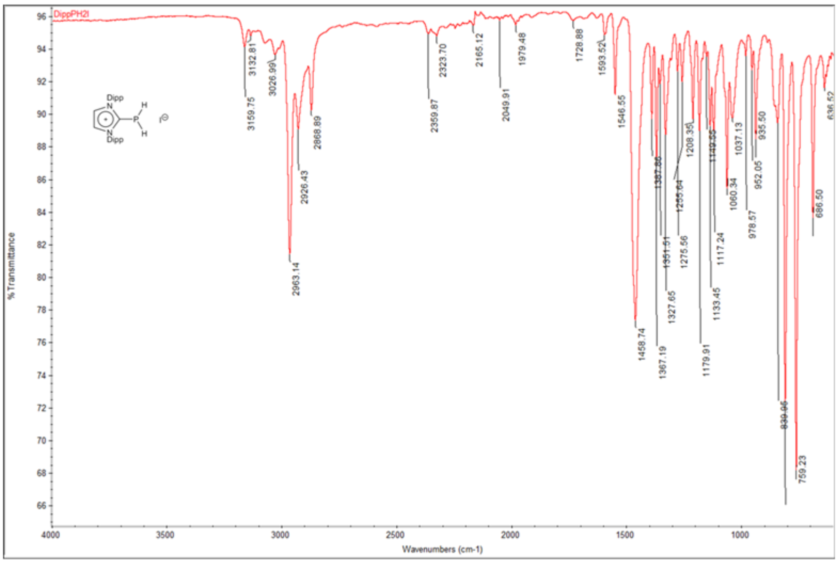


Figure S100. ATR-IR spectrum of **1b**[I].

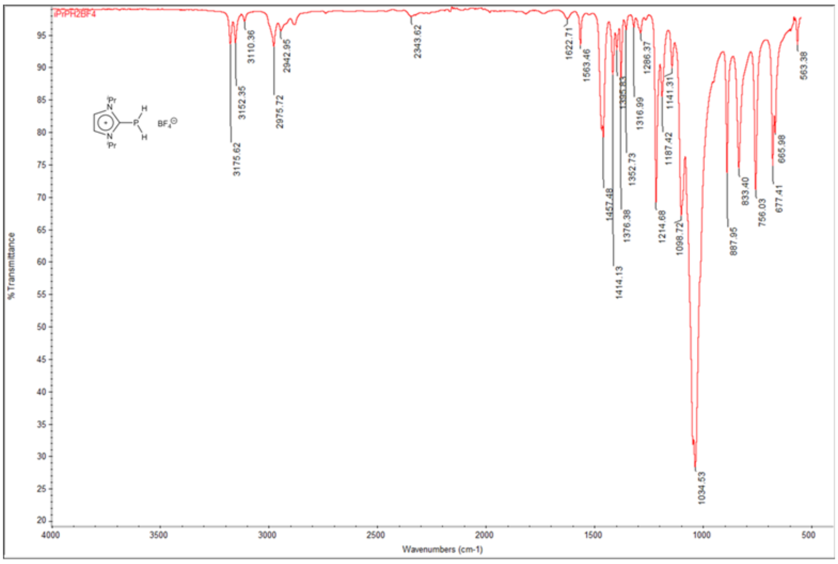


Figure S101. ATR-IR spectrum of **1d**[BF_4].

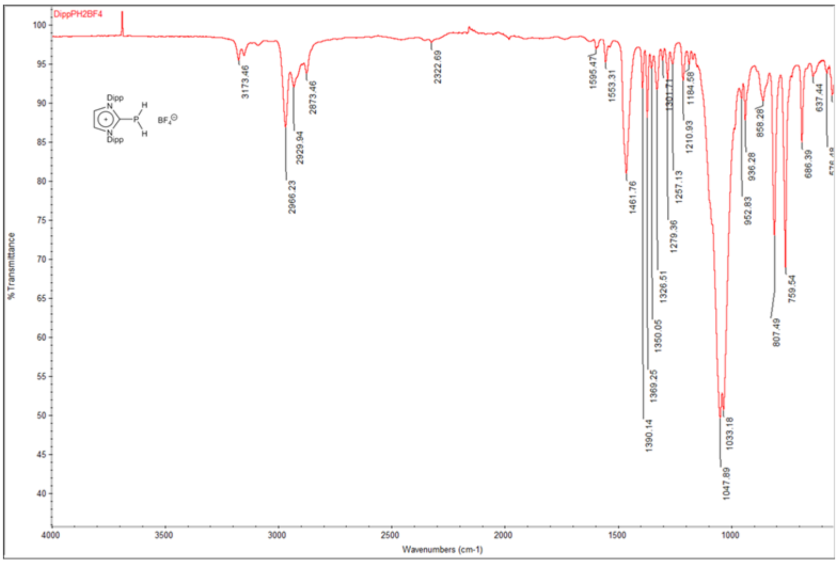


Figure S102. ATR-IR spectrum of **1b**[BF_4].

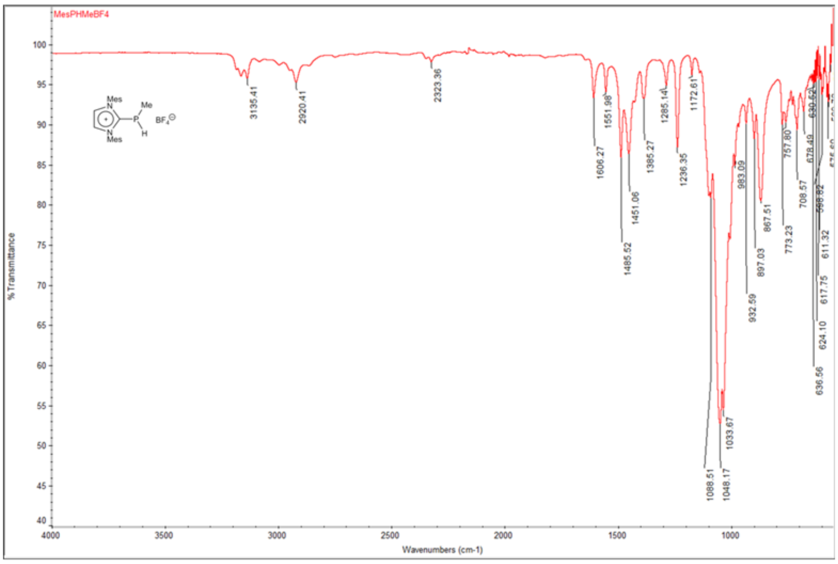


Figure S103. ATR-IR spectrum of **1c**[BF_4].

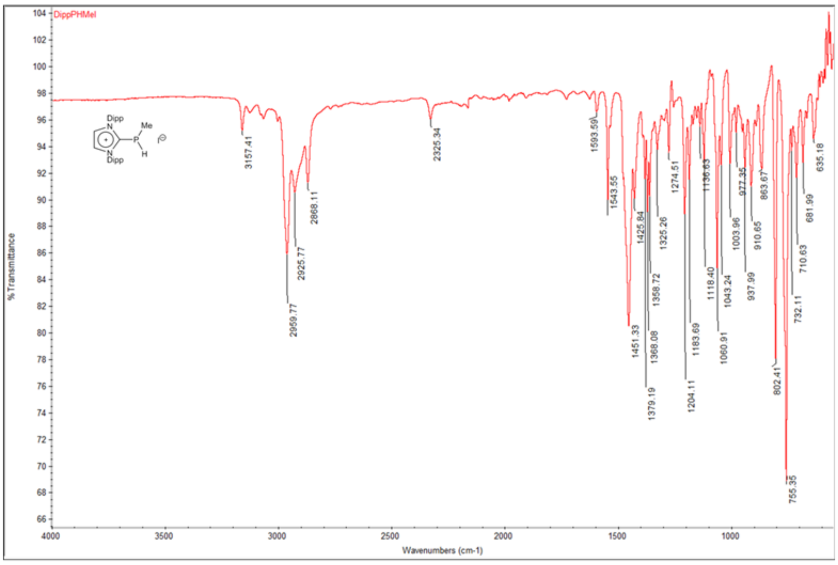


Figure S104. ATR-IR spectrum of **2b**[I].

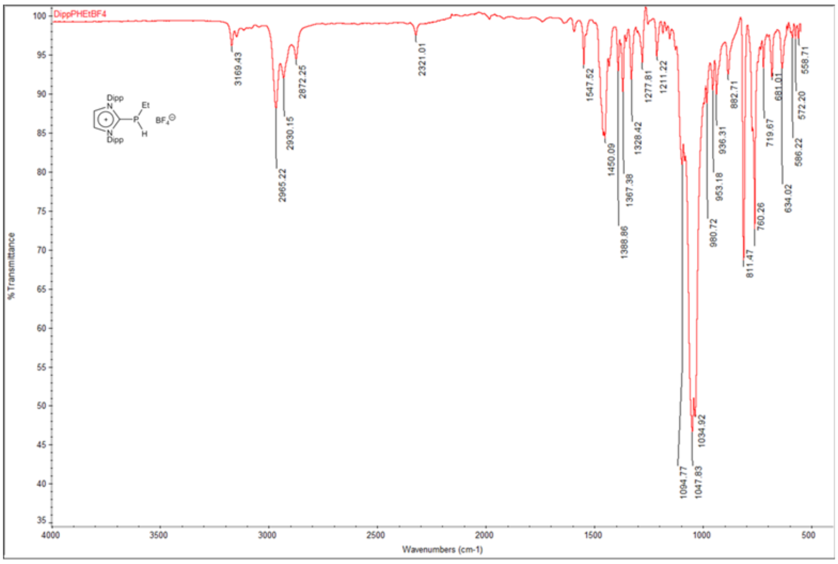


Figure S105. ATR-IR spectrum of **5b**[BF$_4$].

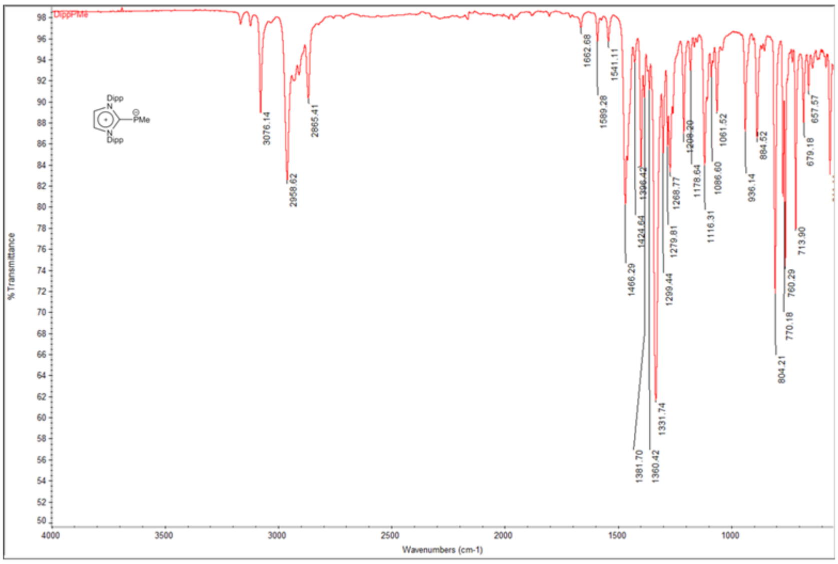


Figure S106. ATR-IR spectrum of **8b**.

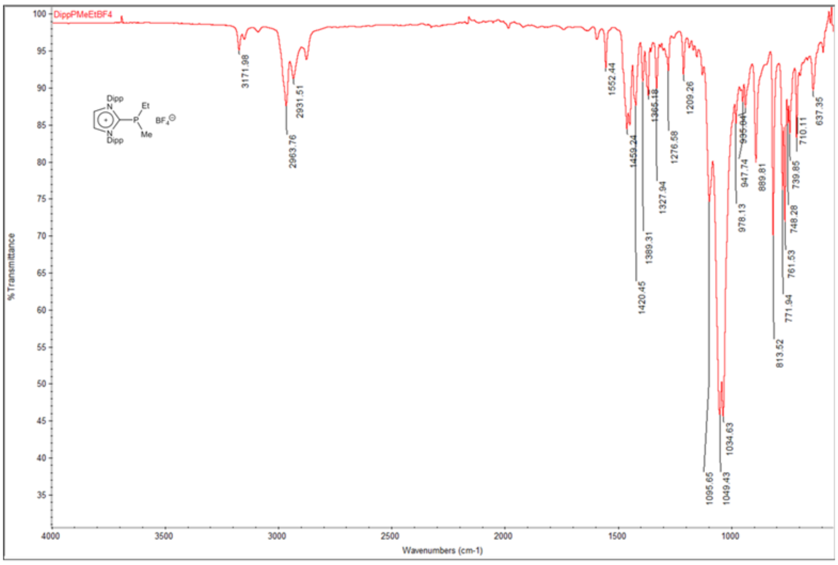


Figure S107. ATR-IR spectrum of **19c**[BF$_4$].

Mass spectra

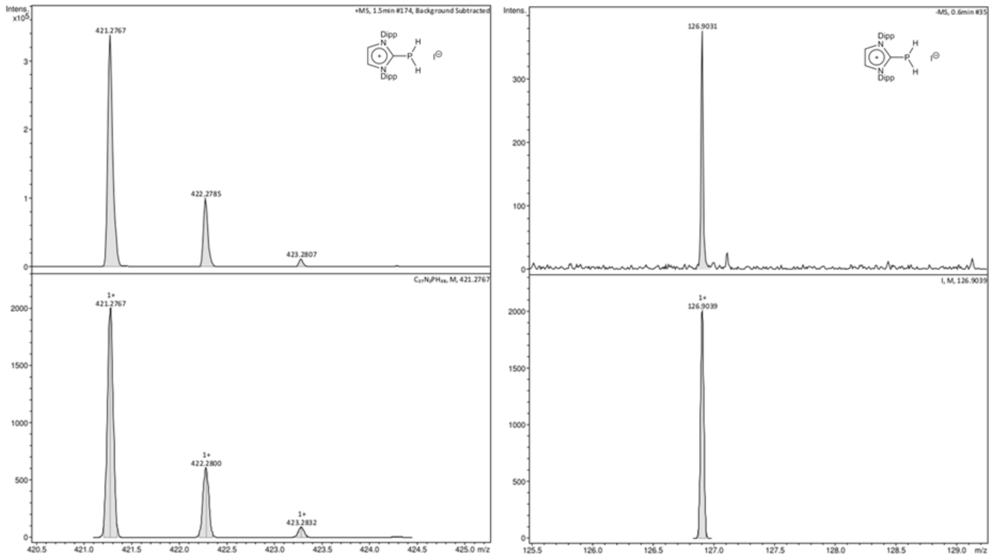


Figure S108. HR (+)- and (-)-ESI-MS of the **1b**[I] (top) and calculated isotope patterns (bottom).

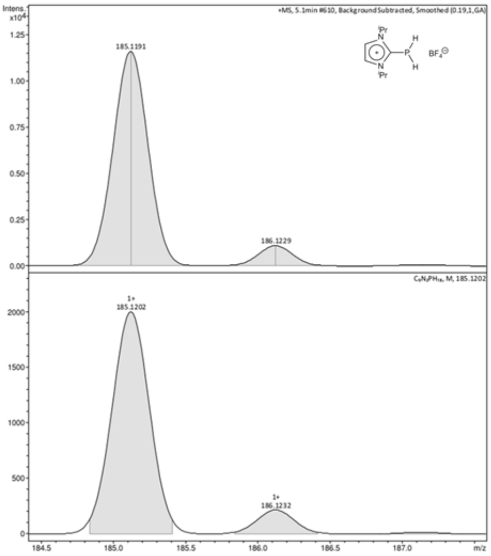


Figure S109. HR (+)-ESI-MS of **1b**[BF$_4$] (top) and calculated isotope patterns (bottom).

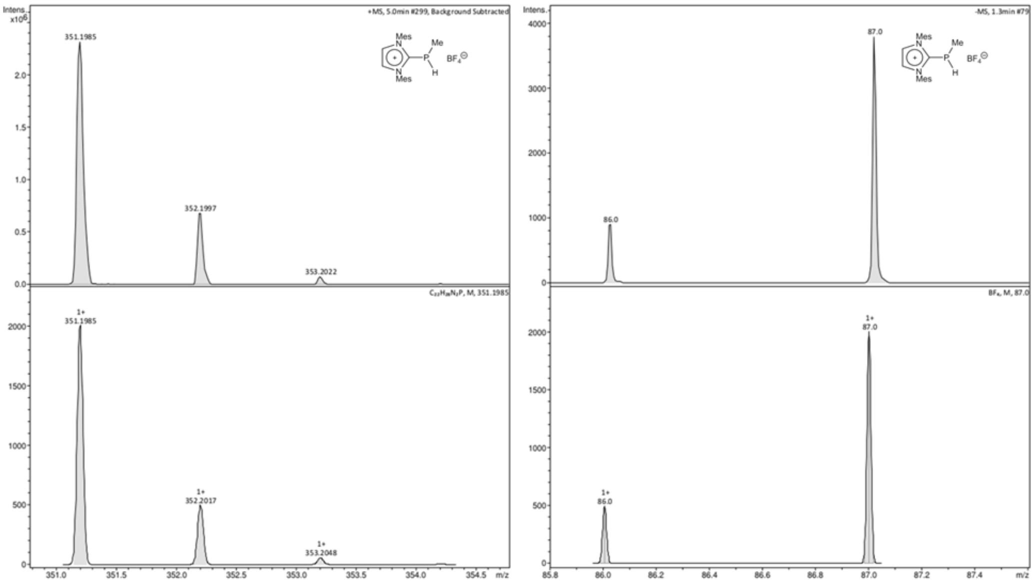


Figure S110. HR (+)- and (-)-ESI-MS of **2c**[BF$_4$] (top) and calculated isotope patterns (bottom).

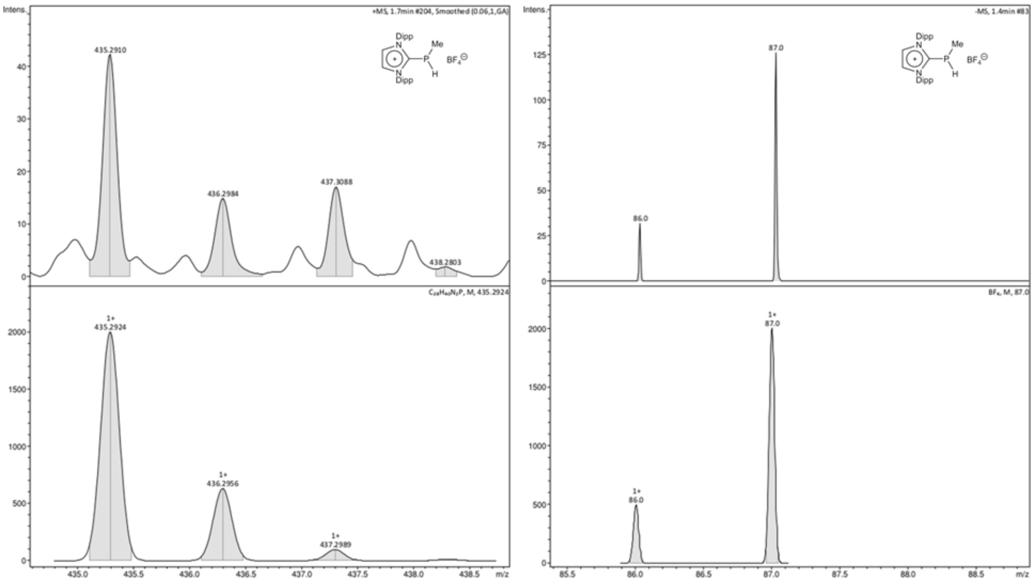


Figure S111. HR (+)- and (-)-ESI-MS of **2c**[BF$_4$] (top) and calculated isotope patterns (bottom).

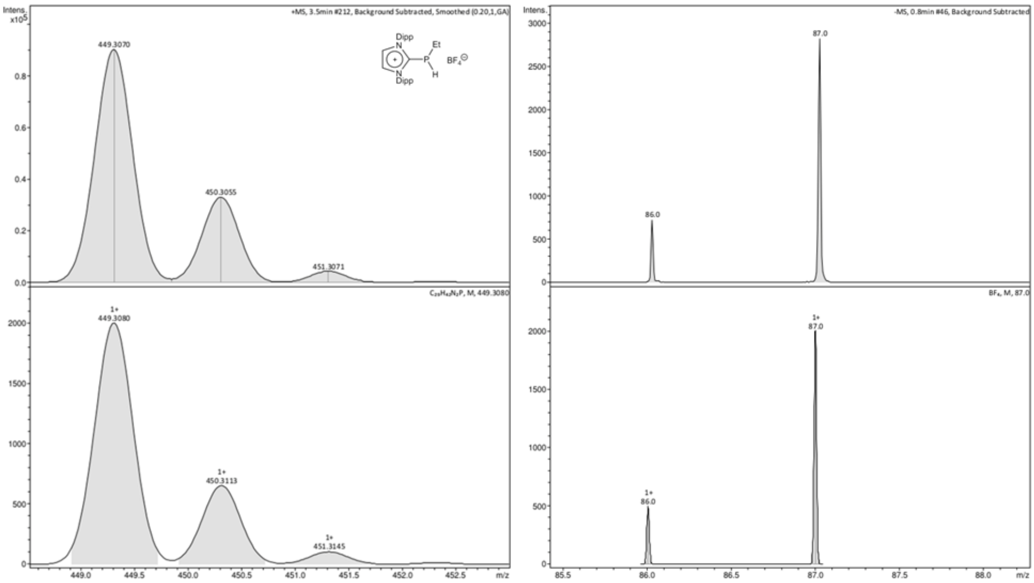


Figure S112. HR (+)- and (-)-ESI-MS of **5b**[BF$_4$] (top) and calculated isotope patterns (bottom).

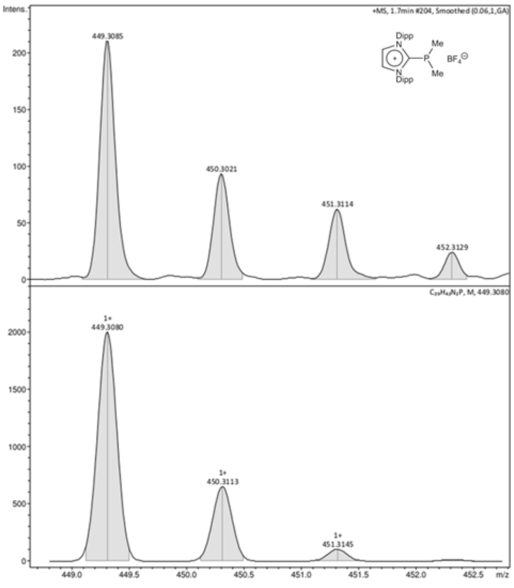


Figure S113. HR (+)-ESI-MS of **19a**[BF$_4$] (top) and calculated isotope patterns (bottom).

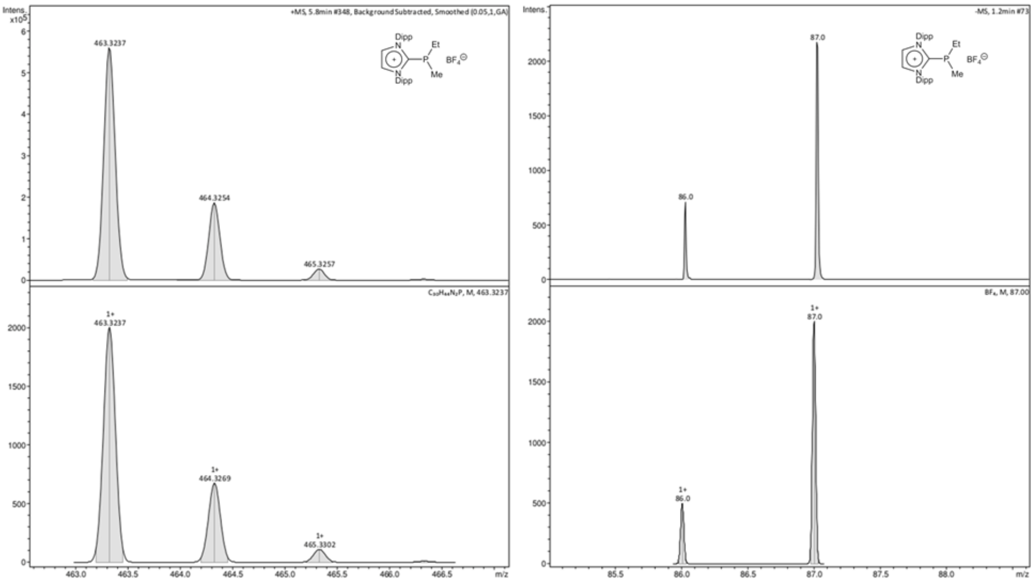


Figure S114. HR (+)- and (-)-ESI-MS of **19c**[BF_4] (top) and calculated isotope patterns (bottom).

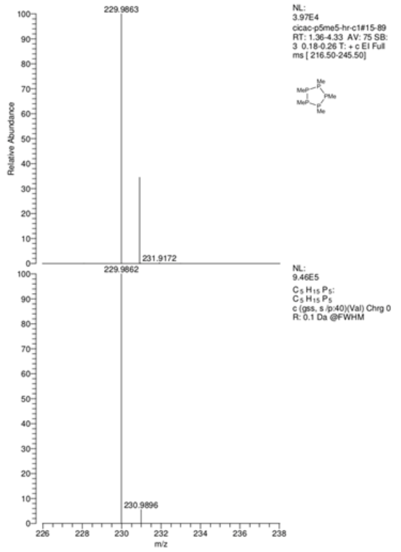


Figure S115. HRMS (EI, 70 eV) of pentamethyl-cyclopentaphosphine (top) and calculated isotope pattern (bottom).

Compuational Studies

General remarks. All computations were performed with the Gaussian 16[5] program package. DFT calculations were carried out using the B3LYP functional[6] with Weigend's and Ahlrichs' def2-svp and def2-tzvp basis sets[7] on an ultrafine grid for numerical integration, Grimme's D3BJ formalism[8] to include dispersion effects, and a polarizable continuum model (PCM) with the solvent parameters for THF to simulate solvation effects. The molecular structures were established by full energy optimization at the PCM-B3LYP-D3BJ/def2-svp level with starting geometries obtained by pre-optimization at the B3LYP-D3BJ/def2-svp level. Harmonic vibrational frequency calculations were finally out at the same level to identify the stationary points obtained as local minima (only positive normal modes) or transition states (one imaginary normal mode). Electronic energies were recalculated at the final geometries at the PCM-B3LYP-D3BJ/def2-tzvp level. Standard Gibbs free energies ΔG_0 (for p=1 bar and T=298K) were computed using these energies with the corrections obtained with the smaller basis sets.

In case of the condensation of **4e** with **1e**$^+$, all attempts to locate a TS with the correct number of imaginary modes failed when the PCM model was used. However, a TS search in the gas phase produced a structure with a single imaginary mode and a very similar geometry. The PCM-B3LYP-D3BJ/def2-tzvp energy of this state is only 0.3 kcal mol^{-1} above that of TS2. Moreover, we were able to locate a TS for the condensation of **4e** with (**15-P$_1$**)$^+$, viz. the homologue of **1e**$^+$, both in gas phase and PCM calculations, and found that the resulting molecular geometries exhibit core structure that are very similar to each other and to the gas phase geometry of TS2. We therefore presume that the PCM-optimised geometry of TS2 does not represent a higher order TS and wrong number of imaginary modes points to a technical problem in the solvation modeling.

Relaxed potential energy scans (PES) were carried out at the B3LYP-D3BJ/def2-svp level because the attempted inclusion of solvation effects led in several cases to failure of the optimization runs. Comparison of the geometries at stationary points on the energy hypersurface that had been located with or without inclusion of solvation effects revealed no fundamental differences, suggesting that the neglect of solvation effects in the PES does not cause severe errors.

Table S2. Computed energies and Gibbs free enthalpies (in Hartree) and number of imaginary normal modes (NImag).

Compound a)	E b)	Zpe correction c)	ΔG correction c)	ΔG^0_{298} d)	NImag
P-free imidazolium compounds					
7e$^+$	-305.432019	0.140577	0.109736	-305.322283	0
16e	-304.941878	0.126212	0.094986	-304.846892	0
Imidazolio-monophosphines/phosphides					
1e$^+$	-647.414041	0.148029	0.115153	-647.298888	0
4e	-646.957532	0.137490	0.104075	-646.853457	0
Imidazolio-diphosphines/phosphides					
14-P$_1$	-988.950410	0.147918	0.111096	-988.839314	0
(15-P$_1$)$^+$	-989.410566	0.158981	0.122527	-989.288039	0
Imidazolio-triphosphines/phosphides					
14-P$_2$	-1330.944168	0.158042	0.118083	-1330.826085	0
(15-P$_2$)$^+$	-1331.406833	0.168329	0.126551	-1331.280282	0
18-H	-1330.935113	0.158352	0.118268	-1330.816845	0
Imidazolio-tetraphosphines/phosphides					
14-P$_3$	-1672.950224	0.168968	0.125916	-1672.824308	0
(15-P$_3$)$^+$	-1673.405793	0.179020	0.136483	-1673.269310	0
17-P$_3$	-1672.925438	0.167992	0.127560	-1672.797878	0
18-PH$_2$	-1672.937206	0.168689	0.125274	-1672.811932	0
Imidazolio-pentaphosphines/phosphides					
14-P$_4$	-2014.944560	0.179064	0.132315	-2014.812245	0
(15-P$_4$)$^+$	-2015.402537	0.190382	0.145292	-2015.257245	0
Imidazolium-free P$_n$-compounds					
P_2H_4	-685.172620	0.034992	0.009044	-685.163576	0
P_3H_3	-1025.968999	0.029260	0.001485	-1025.967514	0
P_3H_5	-1027.167269	0.045167	0.014925	-1027.152344	0
P_4	-1365.585453	0.006232	-0.020172	-1365.605625	0
P_4H_4	-1367.966859	0.040050	0.009222	-1367.957637	0
P_5H_5	-1709.985519	0.050551	0.016194	-1709.969325	0
Transition states					
TS1	-1294.373726	0.283042	0.232742	-1294.140984	1
TS2	-1294.339586 e)	0.286626	0.239696	-1294.099890	2 e)
TS3	-2661.872978	0.312416	0.252591	-2661.620387	1
TS4	-1978.344814	0.303968	0.245195	-1978.099619	1
TS5	-1672.926003	0.169137	0.128029	-1672.797974	1
TS6	-3003.872499	0.322269	0.259127	-3003.613372	1

a) data for species that may form several diastereomers refer to the most stable isomer. b) Calculated at the PCM-B3LYP-D3BJ/def2-tzvp//PCM-B3LYP-D3BJ/def2-svp level of theory. c) Frequency analysis carried out at the PCM-B3LYP-D3BJ/def2-svp level of theory. d) Sum of the two previous columns. d) A TS search at the B3LYP-D3BJ/def2-svp converged to a proper TS with NImag = 1 and a PCM-B3LYP-D3BJ/def2-tzvp energy of -1294.33912492 Hartree only 0.3 kcal mol^{-1} above that of TS2.

Table S3. Computed (at the PCM-B3LYP-D3BJ/def2-svp level) Cartesian atomic coordinates (in Å)

7e$^+$			
C	-0.3071029137	2.0576854866	-0.0203540409
N	1.0356993933	2.3849439031	-0.0333717548
C	1.7515137313	1.2552478607	-0.0002305176
N	0.9110453889	0.2149776263	0.0336083712
C	-0.3854472939	0.693883427	0.0217413308
H	2.8368103528	1.1928818711	-0.0006917727
C	1.2974426389	-1.1946475437	0.0760734952
C	1.5809830949	3.7410307742	-0.0763772876
H	-1.2460433158	0.0315248116	0.0440251313
H	2.390792741	-1.2645266882	0.0757848621
H	0.8962157836	-1.7112053976	-0.8054108359
H	0.9002196638	-1.6560342824	0.9893976048
H	-1.0861848834	2.8142614826	-0.0419123168
H	2.6751411004	3.6852233862	-0.0762925093
H	1.2417587704	4.3004127126	0.8050075073
H	1.2390177474	4.24459857	-0.9897812672

16			
C	0.6805778639	1.2383312038	-0.0000551742
N	1.0651566571	-0.0966554773	0.0000211305
C	0.000000129	-0.9532155904	0.0000439957
N	-1.0651566133	-0.0966557732	-0.0000067619
C	-0.6805781875	1.2383310264	-0.0000637393
C	-2.4485671943	-0.5360788991	0.0000209644
C	2.4485673445	-0.5360782592	-0.0000221795
H	-1.391376088	2.0612021503	-0.0000945696
H	-2.4582925019	-1.6324389509	0.0000547747
H	-2.976830512	-0.1699913311	-0.8941893805
H	-2.9768135135	-0.1699372649	0.8942194046
H	1.3913755285	2.0612025324	-0.0000875362
H	2.4582929922	-1.632438188	0.0004899302
H	2.9769719847	-0.169539071	0.8939173501
H	2.9766721151	-0.170388108	-0.8944912091

1e$^+$			
C	1.7600180777	6.5699076967	-0.4644413142
N	1.7128673928	5.2790824395	-0.9553792973
C	1.6748958618	4.4092467475	0.0757831476
N	1.6762443172	5.136677849	1.2125341945
C	1.7370499468	6.4805094034	0.8964837503
P	1.4344490593	2.5882390465	-0.0478722678
C	1.6364984581	4.5912674305	2.5672666138
C	1.7199237398	4.9156185305	-2.3703680158
H	2.3818825627	2.4075241338	-1.0943883605
H	1.7580501324	7.2507162892	1.6616371725
H	0.8120441241	3.8715094114	2.6579853053
H	1.4680000485	5.4154575726	3.2685591977
H	2.5888428198	4.0977565799	2.8063844887
H	1.8050209744	7.433515313	-1.1211591003
H	2.6810079126	4.4558829869	-2.6399064735
H	1.5728942186	5.8247572578	-2.9631087434
H	0.9008145047	4.2154330629	-2.582032159
H	2.3462248489	2.2702052489	0.9975968613

4e			
P	0.31245898	2.05933115	0.00000499
C	0.02330345	0.31103552	-0.00001258
N	1.02970685	-0.62564006	-0.00001395
N	-1.14311967	-0.41651218	-0.00000988
C	0.49497241	-1.90797093	0.00000470
C	2.43414566	-0.28281601	0.00000612
C	-0.85597791	-1.77912794	0.00000451
C	-2.47095039	0.15697887	0.00000700
H	-1.07323499	2.39959633	-0.00003592
H	1.12469682	-2.79258690	0.00000680
H	2.68304614	0.31502802	-0.89189285
H	3.03108782	-1.20293188	-0.00013225
H	2.68309629	0.31479432	0.89204895
H	-1.64055239	-2.52982991	0.00000580
H	-2.62284446	0.78368716	0.89265413
H	-3.20839613	-0.65497254	-0.00000406
H	-2.62285344	0.78371673	-0.89261713

(15-P$_1$)$^+$			
C	0.6993816611	-1.9622954208	-0.1177625408
C	-0.6515170343	-1.8468021209	0.0458486823
N	-0.9408807578	-0.4984579869	0.1017271589
C	0.202723081	0.2115140332	-0.0312896518
N	1.2078100543	-0.6825308407	-0.1711343076
C	-2.2823261472	0.0536825179	0.2834144007
P	0.4566662425	2.0293416287	-0.1099037015
C	2.6226999556	-0.3419073357	-0.2988051135
H	-0.9189326699	2.3534891827	0.0045760235
H	1.3334456211	-2.8399009281	-0.2013804525
H	2.727509578	0.5423381894	-0.9409199985
H	3.1489483963	-1.1871266143	-0.7560824779
H	3.0503789633	-0.1294330422	0.690861138
H	-1.4249677021	-2.6050432422	0.123751675
H	-2.295171605	0.7218444546	1.154036659
H	-2.9732054586	-0.7778294644	0.4588247731
H	-2.5975262486	0.6000150093	-0.6152210513
P	1.1360061347	2.3160418309	2.0256664696
H	1.337906519	3.7154321136	1.8447497078
H	-0.1553335832	2.4605080358	2.6112726075

14-P$_1$			
C	0.6872531892	-1.9244579724	-0.1822019311
C	-0.6710653126	-1.9136678876	-0.2267020839
N	-1.0752547712	-0.6082945408	0.0011683326
C	0.0150469531	0.207871281	0.1729084106
N	1.1022684924	-0.6205698518	0.0467262841
C	-2.4546283364	-0.1635930936	0.0631805806
P	-0.1132675546	1.9913631594	0.3575416515
C	2.4857761388	-0.1853982795	-0.0220337728
H	1.3938023158	-2.7410671517	-0.2970343344
H	2.5185563186	0.7948635695	-0.5202664774
H	3.0574845134	-0.9151615403	-0.6102182209
H	2.9328971601	-0.0884446981	0.9764904785
H	-1.3824613181	-2.7178043083	-0.3897487657
H	-2.5346955788	0.6206691395	0.8302017481
H	-3.0961560071	-1.0160908754	0.3207663822
H	-2.7813280913	0.2593782612	-0.8993660792
P	1.4955285041	2.3008478445	1.8662235854
H	2.3332531344	3.2518914341	1.1938741677
H	0.8171822503	3.3196675105	2.6050380442

Table S3. Continued

$(15\text{-}P_2)^+$			
C	2.0926007904	2.1147695083	2.9617818722
N	1.6722000309	1.8244282502	1.6831652296
C	1.3433231199	0.5132385437	1.6034724685
N	1.5562825466	-0.0201686101	2.8287028287
C	2.0144128157	0.9562879245	3.6834911027
C	1.6221805501	2.7886003163	0.5846759901
P	0.7154622948	-0.4509011395	0.1661200273
P	-1.3229506716	0.556327916	0.0706991439
P	-2.1392434972	-0.5187462006	1.8763065396
C	1.3011361853	-1.4065328071	3.2211938572
H	1.3283100035	0.3776809383	-0.8153961765
H	2.4144794126	3.1105479439	3.2519851038
H	2.4298807952	2.5885812311	-0.132143046
H	1.7476161293	3.7932673221	1.0026798225
H	0.649454991	2.7251363433	0.081197447
H	2.2488721981	0.7500286146	4.7234507245
H	0.2690233219	-1.5051002169	3.5838418258
H	2.0075133485	-1.6816772779	4.0127075409
H	1.4476320285	-2.0610545341	2.3541327915
H	-1.7851548541	-0.3230420449	-0.9531406941
H	-3.3809001128	0.1799258275	1.8589745987
H	-2.6413444267	-1.6790048486	1.2201840025

$14\text{-}P_2$			
N	2.0463576191	2.0840815922	1.7073293017
C	1.1651975134	1.0863230732	1.366107719
N	1.0625309072	0.3051374189	2.4885227781
C	1.8518181275	0.8195496783	3.5055444468
C	2.4774419968	1.9211155023	3.0123375741
P	0.4803118751	0.9345149897	-0.2916165444
P	-1.6799698901	0.5327296955	0.0279747202
P	-1.8658330861	-1.7406256619	-0.0064574846
C	0.362555543	-0.9617273654	2.5626919024
C	2.4607330535	3.1613403488	0.8273930974
H	3.1810597427	2.6055589502	3.4766251614
H	3.2700024355	2.8376551755	0.1551428976
H	2.8107241052	4.0051332663	1.4356662616
H	1.6000538731	3.4615097976	0.2120758572
H	1.9022923016	0.354394571	4.4855201795
H	-0.7100442286	-0.8244473641	2.7581075542
H	0.8033551524	-1.5640835121	3.3667727721
H	0.471189477	-1.4869177873	1.6035707746
H	-1.7713147386	0.6725114153	1.446129041
H	-3.2579940324	-1.7822637954	-0.3478917027
H	-1.4547917474	-1.7981069888	-1.3725833071

$(15\text{-}P_3)^+$			
C	1.7487204444	2.4577076984	2.1100993442
N	1.8214697091	1.6598248909	0.986774039
C	1.3864723957	0.4148714853	1.2935731235
N	1.0587963597	0.4242518488	2.6052064374
C	1.2622374158	1.6835605648	3.1241176907
C	2.2953681768	2.1165639749	-0.3195193923
P	1.3343023606	-1.0905777509	0.2424580447
P	-0.9066109355	-1.2240902022	-0.0110683693
P	-1.2576769655	0.6583065792	-1.2061840125
C	0.5103849509	-0.7101535055	3.3431423963
H	1.6863985205	-0.4119997143	-0.9541565959
H	2.0479564924	3.5013137484	2.0959146421
H	3.2353779921	1.614264853	-0.5833296992
H	2.4675464813	3.1965558223	-0.2616423408
H	1.534332611	1.915011332	-1.0845192892
H	1.0456813706	1.9232843866	4.1607554256
H	-0.5686452601	-0.7965968917	3.1552038708
H	0.6897262684	-0.5532659494	4.4124796184
H	1.0136902683	-1.6323442656	3.0234619406
H	-0.7663255877	-2.0977720015	-1.1316223789
H	-2.5996617608	0.3158318826	-1.5503692986
P	-1.6769592588	1.9159228777	0.6200458575
H	-1.8499714729	3.129324636	-0.1080787647
H	-3.070095576	1.6490297003	0.7455887106

$14\text{-}P_3$			
C	2.0564599625	2.2339607405	2.8273258489
N	1.1722412748	1.8462893144	1.8320855077
C	1.0190472274	0.486444068	1.8387496801
N	1.8356453971	0.0385721291	2.8435213934
C	2.4817362384	1.1026429174	3.4498579409
C	0.5957758027	2.7547082515	0.8566775192
P	0.1025505217	-0.6369955915	0.7616124714
P	-1.7780292722	0.4902043444	0.5595088271
P	-2.0922543345	1.224804011	-1.5793651776
C	1.9959241729	-1.3550368832	3.2198740012
H	0.4066953698	-0.0271937633	-1.7874497541
H	2.3055048658	3.2765564143	3.0006781289
H	0.5885096769	2.2630517523	-0.1249339504
H	1.2159846589	3.6584923424	0.8053522057
H	-0.4332227084	3.0327444534	1.1228233169
H	3.1778978826	0.9621548199	4.2712155005
H	1.0182168413	-1.8538434227	3.158055879
H	2.3820747813	-1.4053859739	4.2455712439
H	2.6934875566	-1.8701973468	2.5421958382
H	-2.5664866937	-0.6736686129	0.3220144132
H	-1.4385238879	2.4802328258	-1.4016611662
P	-0.4765875338	0.3784875748	-2.8537431034
H	-1.0820838	-0.910105365	-2.9676415644

Table S3. Continued

(15-P$_4$)$^+$			
N	-3.4890234112	-0.9518877103	-0.1037861115
C	-4.5473642298	-0.3552073123	-0.7516880441
C	-4.3165761941	0.9918588628	-0.7352695356
N	-3.1180752149	1.1897593169	-0.0854611603
C	-2.6130840366	-0.0046629883	0.303401825
C	-2.49548625	2.4938539159	0.1344932879
P	-1.0492865889	-0.3847309374	1.2000498538
P	0.362342912	0.0261299649	-0.5395964631
P	2.22343376	-0.0136833763	0.7546037638
P	3.6230328854	-0.2185257064	-1.0153482024
C	-3.3215326635	-2.3956889488	0.0575491342
H	-0.9217712444	0.9179420339	1.7548816861
H	-4.9038962113	1.8170543891	-1.1268574274
H	-2.4765732209	2.7312198128	1.2062010303
H	-3.0877060713	3.2499012217	-0.3920727426
H	-1.4741133682	2.4897663275	-0.2682268674
H	-5.3710387255	-0.9298004899	-1.1645641626
H	-2.7602971636	-2.8062672672	-0.7932584028
H	-4.3123551361	-2.8615583285	0.104751809
H	-2.7778407278	-2.5971683985	0.9881932174
H	0.4562922195	-1.3622050112	-0.864189454
H	2.3193042194	1.4127543231	0.7745311049
P	5.5113503183	0.0919341335	0.198050122
H	3.674166809	-1.6419498043	-0.8907196551
H	6.362162071	-0.1736346268	-0.9193948555
H	5.5259972636	1.5028686042	-0.0267227499

14-P$_4$			
C	2.3086365383	1.1392445693	3.4305011797
C	1.6551265311	2.2451721807	2.9872086396
N	0.8134845038	1.8419371101	1.9606262122
C	0.9139383882	0.4879592116	1.7707358592
N	1.8430222388	0.067111268	2.687639674
C	0.0565494025	2.7585674714	1.1273486113
P	0.1852583116	-0.6284610752	0.556203509
P	-1.8638219081	0.2109591125	0.4961212027
P	-1.9973180999	0.6892196413	-1.7148989721
P	-3.979419018	1.7068650153	-1.980468607
C	2.2694994052	-1.3097532918	2.8600169869
P	-4.3956159718	2.5614414353	0.0780539995
H	1.7158379062	3.2811957693	3.306670926
H	0.1137299271	2.416446558	0.0845562255
H	0.502981634	3.7579732145	1.2056990125
H	-0.9990177333	2.803978747	1.4276652893
H	3.0536258787	1.0187663587	4.2111753401
H	1.395820483	-1.9682328538	2.748513341
H	2.706208008	-1.4250344795	3.8600450105
H	3.0161492895	-1.5923760508	2.1022946064
H	-2.5361561293	-1.0366498431	0.3174124418
H	-1.280208228	1.9189262355	-1.612752072
H	-4.7315315905	0.5086951762	-1.7820754216
H	-5.2576337389	3.5915907422	-0.4216773178
H	-3.2466850282	3.4094027776	0.0437473234

P$_3$H$_5$			
P	0.2157827691	0.6897885278	0.12262974
P	2.243243573	-0.1900318962	-0.3613639552
P	0.1052160606	-0.1689728424	2.2064991116
H	0.7456784736	1.9731719966	0.4574528292
H	0.9346725476	0.78064219	2.8738604915
H	-1.1111674653	0.4991279902	2.5409382863
H	1.6982081543	-1.4138777468	-0.8574790079
H	2.2987388871	0.4070257807	-1.6593594956

P$_2$H$_4$			
P	0.2174356373	0.6977824669	0.1215613671
P	2.2381306273	-0.1686386088	-0.3577225621
H	0.1557816344	0.121520246	1.425504806
H	-0.6091570697	-0.3055157577	-0.4679103797
H	1.8486284095	-1.5080516251	-0.6603782905
H	2.217790761	0.2496682789	-1.7218169408

P$_3$H$_3$			
P	2.3437851152	-1.3374349604	-0.5674734971
P	2.1192480833	0.7338866375	0.3102150687
P	1.3590290895	0.2912860082	-1.751209186
H	3.6210124345	-1.12823621	-1.1720391711
H	3.3624609463	1.2545080554	-0.1629584584
H	0.0489183313	-0.0463945307	-1.2893937562

P$_4$			
P	-0.0059696809	-0.0042212018	-0.0103397906
P	-0.0059696809	-0.0042212018	2.2103397906
P	1.9171952501	-0.0042212018	1.1
P	0.6350852961	1.8089560836	1.1

P$_5$H$_5$			
P	-1.6173778345	0.4859893039	0.1521558892
P	0.2424021095	-0.5747595273	0.9443353523
P	1.518022569	-0.9981758852	-0.8286340799
P	0.1934151187	-0.8770759309	-2.6157154783
P	-1.3804080954	0.5967874815	-2.0589180654
H	-2.4319387026	-0.6827091711	0.1002384225
H	-0.4855825502	1.7057097577	-2.0509118953
H	-0.5767925752	-2.0317967011	-2.2917471578
H	2.0140861349	0.3301565579	-0.9710983021
H	-0.3288091742	-1.8808058854	0.9575553147

P$_4$H$_4$			
P	2.3099173921	-1.3338596316	-0.5218201128
P	2.1184071221	0.7833468048	0.2889378138
P	1.0981418861	1.422841481	-1.6415216401
P	1.5176965531	-0.6274191467	-2.5342551879
H	1.0157011595	-1.7179212241	-0.0538731312
H	3.4150442626	1.1662704686	-0.17320385
H	-0.1996699988	1.0459727309	-1.1777031581
H	2.8130876233	-0.249412483	-3.0038787337

Table S3. Continued

18-PH$_2$			
C	1.5794219333	2.525738602	1.8924551344
N	1.8497199983	1.6207743068	0.8815257799
C	1.5298650826	0.3688812621	1.292856721
N	1.0415995842	0.4930712259	2.5529952752
C	1.0635393614	1.8191363769	2.9371900779
C	2.411360523	1.9757781667	-0.4185731782
P	1.6031002741	-1.2024922013	0.3944255631
P	-0.7751867526	-1.114633135	-0.1952947094
P	-1.2330347315	0.832605325	-0.9630857017
C	0.4799096232	-0.5993550144	3.3356634458
H	2.1284929528	-0.6187676972	-0.7896773642
H	1.7681491098	3.5883669427	1.7773350351
H	3.3777450134	1.4731936737	-0.5646678627
H	2.5612907099	3.061222073	-0.4408148067
H	1.7055451974	1.6894939588	-1.2084479048
H	0.7035480051	2.1430749353	3.9085637137
H	-0.5583335385	-0.7833845674	3.024534757
H	0.507668753	-0.3270161098	4.3972731251
H	1.0773047261	-1.5070034238	3.175649826
H	-0.4374367822	-1.7455292257	-1.4363541121
P	-2.0259138181	1.5553958839	0.9871121857
H	-1.3361085909	2.8061982751	1.106768741
H	-3.232501634	2.1937033665	0.5468592588

18-H			
C	1.5230060945	1.9433933529	2.8274411983
C	1.148228421	1.4857774183	1.601026933
N	1.3012276388	0.1100298495	1.6135087567
C	1.7997825945	-0.2844202819	2.8128823124
N	1.9164698557	0.8424308553	3.5655570754
C	1.0236628763	-0.7673854541	0.4834801351
P	2.1176726327	-1.9407421486	3.4500851862
P	-0.2214904545	-2.392189488	4.1581395365
P	-1.5971707212	-1.0934128505	3.1898632714
C	2.3492397361	0.8613835632	4.9541635863
H	1.9568207733	-2.5849823314	2.1948404555
H	0.7700771716	2.0139479289	0.7314033106
H	1.9577275427	-1.2007896314	0.0967769685
H	0.5463565083	-0.1737836824	-0.3044980137
H	0.3372235437	-1.5622284334	0.7973121162
H	1.5373392578	2.9481728755	3.2384836758
H	1.5608750876	0.4560973262	5.6054099856
H	2.5664966489	1.8954882727	5.2453388105
H	3.2559913877	0.2508058205	5.0670979332
H	0.0277027837	-1.5832826552	5.3118737656
H	-1.9367763792	-2.0912693063	2.2121850011

TS1			
N	-3.9318721177	-0.7315447245	1.2140500874
C	-2.832423924	-1.4086748299	0.7864104329
N	-2.7820391562	-2.552568322	1.5214578979
C	-3.8485810453	-2.593895293	2.4038817328
C	-4.5676779975	-1.4547323297	2.2126604821
P	-1.6258852969	-1.0016169897	-0.4914661832
C	-1.7542003755	-3.5742068168	1.3802796296
C	-4.3885965175	0.5475524168	0.6924798862
P	0.8764048851	-0.371410516	1.8915372655
C	2.1047403697	-0.0433150893	0.611690488
N	2.6968496184	1.1203148055	0.2302075365
C	3.6004151889	0.8720753436	-0.7927331147
C	3.5636270399	-0.4642863508	-1.0459990679
N	2.637746036	-1.0160183694	-0.176389412
C	2.4408522707	2.4269940397	0.8165413059
C	2.2799722371	-2.4251644396	-0.0960878142
H	-2.058083782	0.3441399355	-0.6484890739
H	-3.9996305029	-3.4245259313	3.0865727485
H	-1.7009621417	-3.9113319699	0.3346459139
H	-2.0126478464	-4.4254544896	2.0202143577
H	-0.7755740092	-3.177699536	1.6848478044
H	-5.4711140985	-1.0950155954	2.6956243488
H	-3.6511651936	1.3353362635	0.9021889542
H	-5.3369271106	0.8037267951	1.1783489745
H	-4.5454794697	0.4798537166	-0.3932230957
H	0.5604018424	0.9968417282	2.1163495253
H	4.1098980979	-1.067595564	-1.7646340856
H	4.1859699794	1.6656777023	-1.2467896816
H	2.6239348675	2.3986644126	1.8998792894
H	3.11813391	3.1548450756	0.3555119465
H	1.4015067268	2.7349628761	0.6340477681
H	2.4208715814	-2.7903994901	0.9318180678
H	1.2323693292	-2.5719720137	-0.3938412892
H	2.929239267	-2.9930437267	-0.7720321347
H	-0.3822816632	-0.658929814	0.700772514

TS2			
N	-1.6407047742	0.2802011201	0.539602808
C	-1.2490378581	1.4813436486	1.0325437967
N	-1.3507521502	2.3674996569	0.009973581
C	-1.8266521194	1.7254370177	-1.1159353258
C	-2.0018274642	0.4129433714	-0.7855222455
P	-0.595108969	1.7068447054	2.7130035667
C	-0.9898691408	3.7790604949	0.0777318603
C	-1.6670533433	-0.9683752699	1.2970282745
P	1.7457706459	1.6326679811	1.9823468136
C	1.9463144777	2.5332538415	3.8540606534
N	2.0348953316	1.9489032776	5.0710875866
C	2.1589283509	2.9091083357	6.0626185977
C	2.1390374873	4.1205699493	5.437933604
N	2.0087474683	3.8644869851	4.0820577031
C	2.030043359	0.5091980023	5.3061265504
C	1.9204377721	4.8944024401	3.0538286731
H	-0.7170777911	3.1251171393	2.7123534049
H	-1.9985370501	2.2501610893	-2.0509603441
H	-1.7000313733	4.3290789373	0.710082535
H	-1.0121844234	4.1926308462	-0.936554132
H	0.0240350561	3.874700378	0.4867078925
H	-2.349313808	-0.4282292397	-1.3775895298
H	-0.6548196684	-1.3877139566	1.3751706273
H	-2.3215007288	-1.6794189032	0.7798871161
H	-2.0582550131	-0.7730175985	2.3039847615
H	1.2484476923	0.4408467542	1.2489588631
H	2.2069473589	5.1290766771	5.835907448
H	2.2489360255	2.6522590969	7.1142956921
H	1.340659607	0.0279320098	4.6021454659
H	3.037401323	0.0908267448	5.1694359391
H	1.6926609044	0.3175648531	6.3318772602
H	2.0951556619	4.426790251	2.0781286857
H	0.9256593922	5.363237575	3.0659482615
H	2.6847418007	5.6611505178	3.2354534175
H	2.8255409609	0.8190252703	2.4719441376

Table S3. Continued

TS6			
N	-3.85828402	-0.33733247	-1.02360822
C	-3.41240684	-1.06162448	0.05353126
N	-3.53668793	-0.21866635	1.12852366
C	-4.03749584	1.01049866	0.72210529
C	-4.23883525	0.93703515	-0.61794756
P	-2.81524388	-2.73195835	0.17081243
C	-3.14296581	-0.57338441	2.47404144
C	-3.89528349	-0.82257019	-2.38563201
P	-0.5437165	0.62024132	-1.3730262
P	-0.52814416	1.50206663	0.56478618
P	2.81407352	1.88686609	0.71189401
P	2.82931567	1.55068104	-1.42501069
P	3.32951091	0.06697412	1.72818918
C	2.80645806	-1.20744567	0.51892386
N	1.66896963	-1.94713849	0.6006727
C	1.59651417	-2.83096552	-0.45678155
C	2.72196228	-2.646609	-1.20610016
N	3.45918561	-1.65489494	-0.58893508
C	0.66983675	-1.85005105	1.65750403
C	4.78290134	-1.22698411	-1.02354697
H	0.74694735	-3.49408206	-0.59111668
H	0.63303634	-0.81413617	2.01438606
H	0.94008639	-2.50942202	2.49519606
H	-0.30671002	-2.14537788	1.2469949
H	3.05674161	-3.13090202	-2.11855748
H	4.72883524	-0.808334	-2.03599449
H	5.46827946	-2.08612726	-1.007249
H	5.13465823	-0.45647344	-0.32681672
H	1.02062431	1.78603882	0.77203032
H	1.43702607	0.90520921	-1.58222095
H	2.31100524	2.84728133	-1.73194122
P	-0.8607994	3.67220722	0.07862389
H	-0.39404686	-0.72002518	-0.89458191
H	-2.89829387	-2.97827388	-1.23125661
H	-4.60559973	1.67698636	-1.32225501
H	-4.19803344	1.82448648	1.42182578
H	-2.8785777	-1.05342737	-2.73899385
H	-4.51065851	-1.73256331	-2.45355613
H	-4.32746227	-0.0445874	-3.02643896
H	-3.65027819	-1.49977498	2.7862377
H	-2.05478546	-0.73024821	2.52506635
H	-3.41886329	0.23992614	3.1558887
H	-2.26865883	3.53214161	-0.11148517
H	-0.57660967	3.62434374	-1.32235107

TS3			
C	-2.5960004366	-1.1196394963	-0.5197388951
N	-1.3729689966	-1.6873409132	-0.6910830455
C	-1.1081597956	-2.5753938081	0.3317010257
C	-2.1995723142	-2.5718711175	1.1509799261
N	-3.1079390765	-1.6826689189	0.6095675894
C	-0.468245846	-1.4255601712	-1.8029134254
C	-4.4502598592	-1.462227799	1.1322878879
P	-3.3650648658	0.0985540066	-1.652167458
P	-3.0361233589	1.9481559105	-0.6034409405
P	-2.8821138941	1.5501519659	1.5175318849
P	0.3273344373	2.0297698807	-0.6731589718
P	0.5689129626	1.1409040738	1.2435734865
P	2.9599100112	-2.2364492755	-0.2049234969
C	3.4923531758	-0.5484439159	-0.0272705891
N	3.628644309	0.3241797525	-1.0763016924
C	4.086145965	1.5544137703	-0.6239826438
C	4.2425678863	1.4532451931	0.7198472968
N	3.8776538309	0.1610051539	1.081958421
C	3.2975323975	-0.0074863206	-2.4447883237
C	3.8740603317	-0.3551672002	2.4331260545
H	-0.1595241458	-3.1009568233	0.3965610187
H	-0.5425384154	-0.3683176476	-2.0830737439
H	-0.743015105	-2.0450262147	-2.6689317705
H	0.5530023452	-1.66579073	-1.4764809236
H	-2.4042738176	-3.1192899075	2.0662286419
H	-4.3958320717	-1.0673560928	2.1542869331
H	-5.0060091684	-2.4106152601	1.1243586695
H	-4.9489881389	-0.7322351271	0.4832018261
H	-1.281202558	2.1405035704	-0.7713383845
H	-1.4038103809	1.1121146365	1.5777994702
H	-2.5302242762	2.8966574833	1.8459954075
H	0.416037095	3.3826178372	-0.2157862845
H	0.5692175251	-0.1983645445	0.7457845137
H	3.0093114653	-2.5171317075	1.1921036898
H	4.5648093444	2.1843151895	1.4546236714
H	4.2495694178	2.3888183703	-1.2987771929
H	2.852044778	-0.6287219067	2.7375400141
H	4.5159409152	-1.2461870862	2.5074387078
H	4.2526008496	0.4206545092	3.1093977377
H	3.8247447863	-0.9247667216	-2.7506674362
H	2.2141090555	-0.1693571452	-2.549803593
H	3.5994826344	0.8196965399	-3.0983030466

Table S3. Continued

TS4			
N	-4.1984038696	-3.0426803604	6.1525294984
C	-4.0434085198	-1.9645308117	5.3440061817
N	-4.6091181643	-2.3449202751	4.1723330852
C	-5.1044098787	-3.6401843567	4.2385758479
C	-4.8429028191	-4.0846955137	5.498376469
C	-4.6832258877	-1.4990569869	2.9913374641
C	-3.7337568285	-3.1057235962	7.5282648562
P	-3.4463061207	1.1613325761	6.106029689
P	-3.7421801368	0.7891261999	8.2709911694
P	-4.5182186945	2.7358003369	9.0826072299
P	-2.8251583414	4.0998804226	8.4052606167
C	-1.3558089699	2.9897600508	8.5175643798
N	-0.4782703317	2.8229659603	7.4994815085
C	0.5176545857	1.9555669401	7.884843041
C	0.2585773355	1.5956074312	9.1780578044
N	-0.8917799467	2.2503948823	9.5559956863
C	-0.5823120348	3.4339719686	6.1728918638
C	-1.5418104261	2.0793583763	10.852321172
H	-2.5987531968	4.6814103041	9.6892415328
H	0.7987581119	0.9377091485	9.8530109813
H	-2.0963971973	2.9883082927	11.1109957912
H	-0.7732385728	1.896289512	11.6130707027
H	-2.236097739	1.2281423043	10.8023886341
H	1.3292540232	1.6744082692	7.2199681801
H	0.3641215837	3.2718981098	5.6444343147
H	-0.7696806744	4.5099121221	6.2728592613
H	-1.4131269697	2.9563721885	5.6305207658
H	-5.328136315	3.1129061921	7.9684461105
H	-5.0403673918	0.1926260332	8.318781243
H	-3.6395822677	-0.3642614739	5.7214952193
H	-4.7782457528	1.5721034586	5.7880248099
H	-5.5917238963	-4.1301253098	3.3995856735
H	-5.0569463548	-5.0385916312	5.9734173446
H	-4.2161636696	-0.5345276694	3.2217797298
H	-4.147867448	-1.9632401179	2.1496277893
H	-5.7311390921	-1.3322245996	2.7003129233
H	-2.9680441484	-3.8877361114	7.6440893612
H	-3.2968566618	-2.1362832828	7.7969752589
H	-4.5706043215	-3.3225599833	8.2090898095

TS5			
C	1.2871427002	0.4804688973	1.1469805618
N	0.9845425991	-0.0365194101	2.3661317124
C	1.0020883019	0.9660788087	3.3170385101
C	1.3531595325	2.1156034979	2.6801809691
N	1.5375909205	1.8014568214	1.3445488867
C	0.4969914723	-1.386237638	2.6055326746
C	1.7752360182	2.7768586283	0.2938393045
P	1.3666569198	-0.5138959098	-0.3879289084
P	-0.9075537878	-0.7368576556	-0.7660447473
P	-1.8751205297	0.806187355	0.6482096911
P	-3.6418406513	-0.3502689276	1.1113353283
H	1.6155465582	0.6060359252	-1.2262893393
H	1.4834186978	3.12501231	3.0579013791
H	2.6577191636	2.5025898918	-0.3000616552
H	1.9479424616	3.7549988103	0.7586124484
H	0.8929915162	2.8394228655	-0.360935494
H	0.7580765779	0.7757206221	4.3575934725
H	-0.5897913313	-1.4333716874	2.421369749
H	0.7102156003	-1.660952405	3.6463419335
H	1.0125772448	-2.0863380906	1.9348299708
H	-3.0716751008	-0.7205270663	2.3841281291
H	-0.9419664378	-1.7773104393	0.1970726687
H	-2.3721114466	1.5460847962	-0.4721022454

Table S4. Computed Gibbs free enthalpies (in kcal mol^{-1} at the) of reactions involving $\mathbf{2e}^{+}$.

Reaction [a)]	ΔG^{0}_{298} [b)]
$\underset{\mathbf{2e}^{+}}{{}^{Me}\mathrm{nhc}^{(+)}\text{-P(H)Me}} + \underset{\mathbf{8e}}{{}^{Me}\mathrm{nhc}^{(+)}\text{-PMe}^{(-)}} \rightarrow \underset{\mathbf{8e}}{{}^{Me}\mathrm{nhc}^{(+)}\text{-PMe}^{(-)}} + \underset{\mathbf{2e}^{+}}{{}^{Me}\mathrm{nhc}^{(+)}\text{-P(H)Me}}$	0.0
$\underset{\mathbf{2e}^{+}}{{}^{Me}\mathrm{nhc}^{(+)}\text{-P(H)Me}} + \underset{\mathbf{8e}}{{}^{Me}\mathrm{nhc}^{(+)}\text{-PMe}^{(-)}} \rightarrow {}^{Me}\mathrm{nhc}^{(+)}\text{-PMe-P(H)Me} + {}^{Me}\mathrm{nhc}$	+2.7
$\underset{\mathbf{2e}^{+}}{{}^{Me}\mathrm{nhc}^{(+)}\text{-P(H)Me}} + \underset{\mathbf{16e}}{{}^{Me}\mathrm{nhc}} \rightarrow \underset{\mathbf{8e}}{{}^{Me}\mathrm{nhc}^{(+)}\text{-PMe}} + \underset{\mathbf{7e}^{+}}{{}^{Me}\mathrm{nhcH}^{(+)}}$	-9.0
$2\ \underset{\mathbf{2e}^{+}}{{}^{Me}\mathrm{nhc}^{(+)}\text{-P(H)Me}} \rightarrow {}^{Me}\mathrm{nhc}^{(+)}\text{-PMe-P(H)Me} + \underset{\mathbf{7e}^{+}}{{}^{Me}\mathrm{nhcH}^{(+)}}$	0.0
$\underset{\mathbf{2e}^{+}}{{}^{Me}\mathrm{nhc}^{(+)}\text{-P(H)Me}} + \underset{\mathbf{4e}}{{}^{Me}\mathrm{nhc}^{(+)}\text{-PH}^{(-)}} \rightarrow {}^{Me}\mathrm{nhc}^{(+)}\text{-P}^{(-)}\text{-P(H)Me} + \underset{\mathbf{2e}^{+}}{{}^{Me}\mathrm{nhcH}^{(+)}}$	-4.6
$\underset{\mathbf{2e}^{+}}{{}^{Me}\mathrm{nhc}^{(+)}\text{-P(H)Me}} + {}^{Me}\mathrm{nhc}^{(+)}\text{-P}^{(-)}\text{-P(H)Me} \rightarrow \underset{\mathbf{8e}}{{}^{Me}\mathrm{nhc}^{(+)}\text{-PMe}^{(-)}} + {}^{Me}\mathrm{nhc}^{(+)}\text{-PH-P(H)Me}$	+7.0

a) ${}^{Me}\mathrm{nhc}^{(+)}$ = 1,3-dimethylimidazol-2ylium. b) calculated from PCM-B3LYP-D3BJ/def2-tzvp//PCM-B3LYP-D3BJ/def2-svp energies and Gibbs free enthalpy corrections obtained from a frequency analysis carried out at the PCM-B3LYP-D3BJ/def2-svp level of theory.

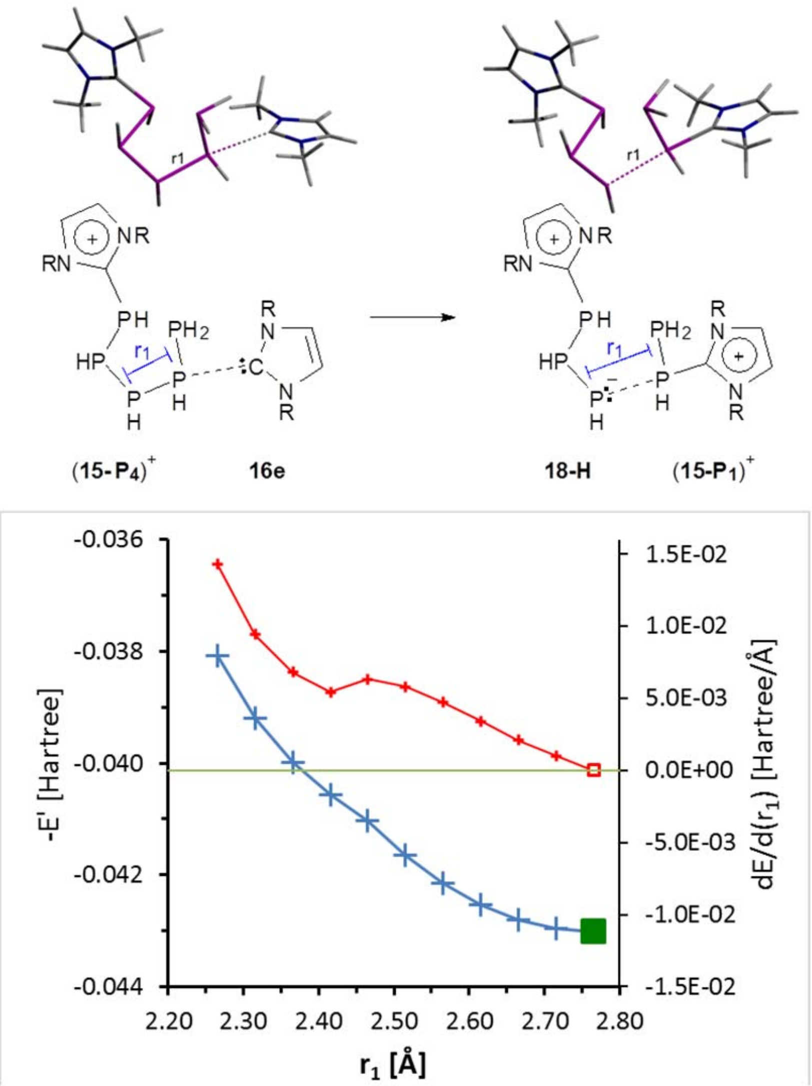


Figure S116. Plot of the reduced electronic energy E' = E + 2319 Hartree (blue) and its derivative dE'/dr$_1$ (red) vs. r$_1$ for a relaxed potential energy scan (PES) of the NHC-induced fragmentation of (**15-P$_4$**)$^+$ to furnish a van-der-Waals complex between **18-H** and (**15-P$_1$**)$^+$. The P–P distance r$_1$ was used as the reaction coordinate and the final state (denoted with green or red squares) was identified as a local minimum with zero energy gradient. The free energy ΔG^0_{298} of the reaction (**15-P$_4$**)$^+$ + 16e → **18-H** + (**15-P$_1$**)$^+$ was computed as -0.1 kcal mol^{-1} at the PCM-B3LYP-3DBJ/def2-tzvp//PCM-B3LYP-3DBJ/def2-svp level of theory.

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