Supporting Information

Masked P(III)/P(V) Frustrated Lewis Pair for C–H and X–H Bond Cleavage and Catalytic Hydroarylation of Alkenes

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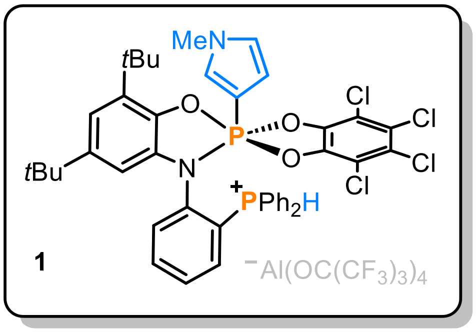
Contents

1. General Information

Unless stated otherwise, manipulations were carried out under a dry nitrogen atmosphere by using standard Schlenk techniques to prevent oxidation and hydrolysis of sensitive compounds. All solvents were rigorously dried by applying standard procedures, freshly degassed and stored over molecular sieve (3 Å resp. 4 Å) for at least two days prior to use. All glassware, syringes, magnetic stirring bars and needles were thoroughly dried. Commercially available chemicals were purchased and used as received. [**PNOPcat^{Cl}**][Al(OR^F)$_4$][1] was prepared according to reported literature procedures. Air or moisture-sensitive compounds were stored in a glove box and handled under N_2 atmosphere. Purity and identity of the compounds were confirmed by high-resolution multinuclear NMR spectroscopy, mass spectrometry, elemental analysis, and, where possible, X-ray diffraction analysis. **^{1}H**, **^{13}C{^{1}H}**, **^{19}F**, **^{31}P**, and **^{31}P{^{1}H} NMR** spectra were recorded at 295 K with a Bruker Avance II 400 or Bruker 2 Avance III 600 NMR spectrometer and referenced to the solvent in use. Chemical shifts are reported as dimensionless δ values in ppm, coupling constants *J* are given in Hertz (Hz). NMR standards were used as followed: (**^{1}H NMR**) CD_2Cl_2 = 5.32 ppm, $CDCl_3$ = 7.26 ppm; (**^{13}C{^{1}H} NMR**) CD_2Cl_2= 53.8 ppm, $CDCl_3$ = 77.2 ppm. Observed signal patterns are noted according to their multiplicities in the standard fashion (e.g. s = singlet, d = doublet, dd = doublets of doublets, etc.). Overlapping signals with indistinct shapes are described as m = multiplet. Electrospray ionization (ESI) mass spectra were obtained with a Bruker ApexQe FT-ICR instrument, M denotes the corresponding chemical formula of the cation.

2. Reactions of [PNOPcat^{Cl}][Al(OR^F)$_4$] with Different Substrates

2.1 C-H Deprotonation



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1

[**PNOPcat^{Cl}**][Al(OR^F)$_4$] (50 mg, 29 µmol, 1.0 eq) and *N*-methylpyrrole (2.4 mg, 29 µmol, 1.0 eq) were dissolved in CH$_2$Cl$_2$ (0.4 mL), which was stirred at room temperature overnight. Then *n*-pentane was introduced in the gas phase and allowed to diffuse into the solution at -40 °C for few days until white precipitate formed. The solvent was removed under reduced pressure. The product was washed with *n*-pentane and dried *in vacuo* to give the target compound as a white solid (30.5 mg, 16.9 µmol, 58%). Single crystals suitable for X-ray diffraction were grown by gas phase diffusion of *n*-pentane into the solution in CH$_2$Cl$_2$ at -40 °C.

^{1}H NMR (400 MHz, CDCl$_3$, 295K): δ [ppm] = 8.23 (d, J = 511.4 Hz, PPh$_2$***H***), 7.99 – 7.84 (m, 2H), 7.80 – 7.64 (m, 4H), 7.57 – 7.46 (m, 5H), 7.39 – 7.27 (m, 3H), 7.03 (d, J = 2.0 Hz, 1H), 6.84 (s, 1H), 6.58 (dt, J = 7.2, 2.6 Hz, 1H), 6.40 (s, 1H), 5.70 (s, 1H), 3.50 (s, 3H), 1.54 (s, 9H), 1.10 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, 295K): δ [ppm] = 146.0 (d, J = 4.6 Hz), 144.3 (s), 142.3 (d, J = 3.1 Hz), 140.7 (d, J = 3.5 Hz), 139.4 (d, J = 2.5 Hz), 138.4 (s), 136.5 (dd, J = 16.1, 3.2 Hz), 135.2 (d, J = 9.8 Hz), 134.0 (d, J = 11.6 Hz), 133.8 (s), 133.6 (d, J = 6.2 Hz), 133.5 (s), 133.1 (d, J = 11.7 Hz), 132.7 (d, J = 20.7 Hz), 131.7 (d, J = 7.7 Hz), 131.1 (d, J = 13.7 Hz), 131.0 (d, J = 13.8 Hz), 130.3 (d, J = 13.1 Hz), 126.5 (s), 125.4 (d, J = 19.2 Hz), 124.4 (s), 121.4 (q, J = 293.2 Hz, OC(***C***F$_3$)$_3$), 118.1 (s), 116.4 (d, J = 15.1 Hz), 114.5 (s), 113.7 (s), 113.2 (d, J = 17.8 Hz), 113.2 (d, J = 7.5 Hz), 112.2 (s), 110.5 (s), 106.0 (d, J = 10.5 Hz), 37.0 (s), 34.8 (s), 34.6 (s), 31.6 (s), 29.8 (s).

^{19}F NMR (377 MHz, CDCl$_3$, 295K): δ [ppm] = -75.4.

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, 295K): δ [ppm] = -2.6 (d, $^4J_{PP}$ = 3.2 Hz, ***P***Ph$_2$H), -33.3 (d, $^4J_{PP}$ = 3.3 Hz, O***P***N). *minor diastereomer:* -3.6 (d, $^4J_{PP}$ = 3.2 Hz, ***P***Ph$_2$H), -37.7 (d, $^4J_{PP}$ = 3.5 Hz, O***P***N).

^{31}P NMR (162 MHz, CDCl$_3$, 295K): δ [ppm] = -2.6 (d, $^1J_{PH}$ = 511.0 Hz, ***P***Ph$_2$H), -33.3 (s, O***P***N).

HRMS (ESI): [M]$^+$ = [C$_{43}$H$_{41}$Cl$_4$N$_2$O$_3$P$_2$]$^+$, calculated: 835.1341, found: 835.1329.

Elem. Anal. for C$_{59}$H$_{41}$AlCl$_4$F$_{36}$N$_2$O$_7$P$_2$ x 0.5 C$_5$H$_{12}$ calculated: C, 40.13; H, 2.57; N, 1.52; found: C, 40.13; H, 3.04; N, 1.68 (C$_5$H$_{12}$ content estimated from **^{1}H NMR** measurements).

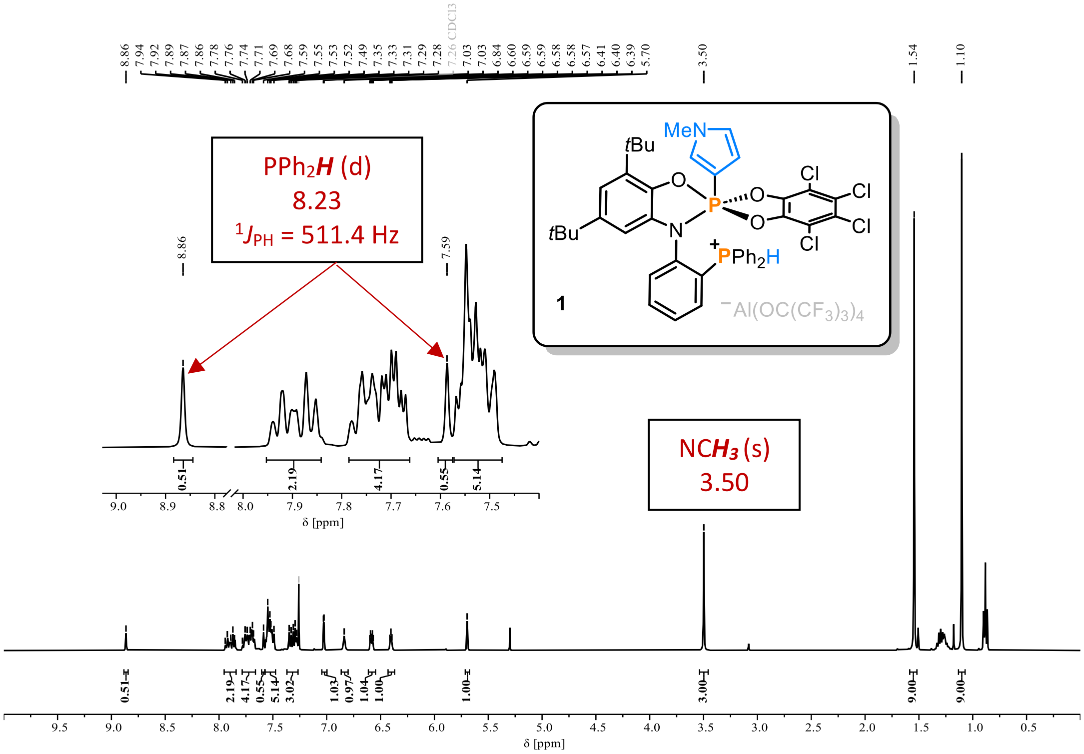


Figure S1: ^{1}**H NMR of 1** (400 MHz, CDCl$_3$, 295K).

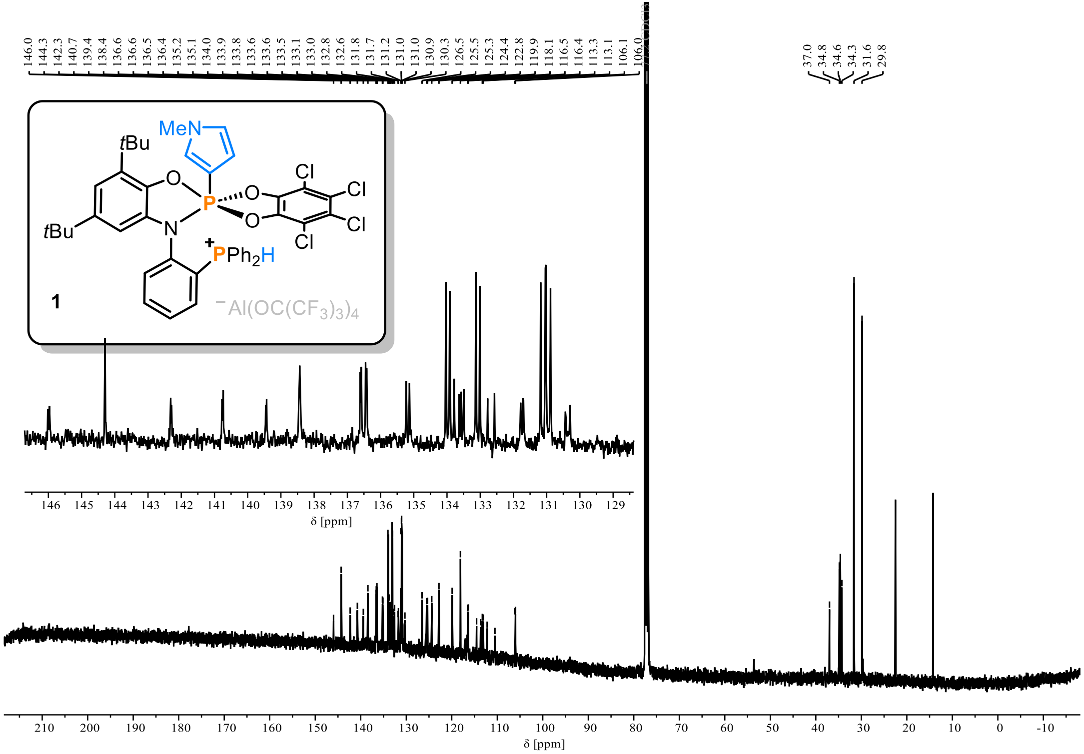


Figure S2: ^{13}**C{^{1}H} NMR of 1** (101 MHz, CDCl$_3$, 295K).

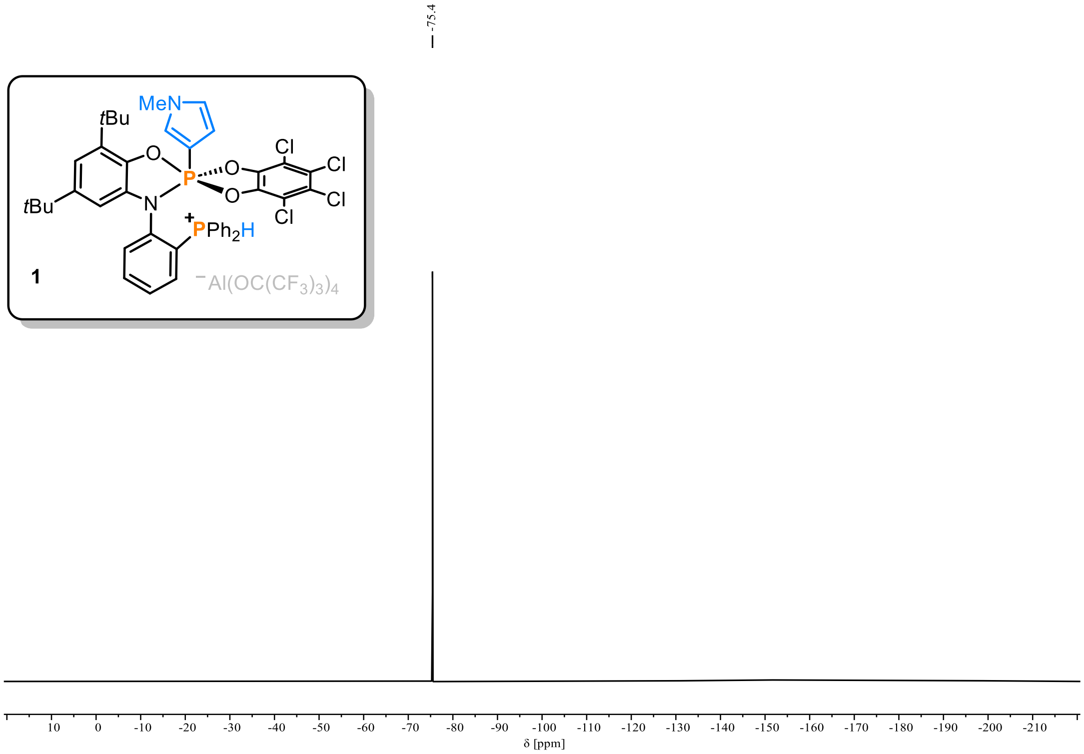


Figure S3: ^{19}**F NMR** of **1** (377 MHz, CDCl$_3$, 295K).

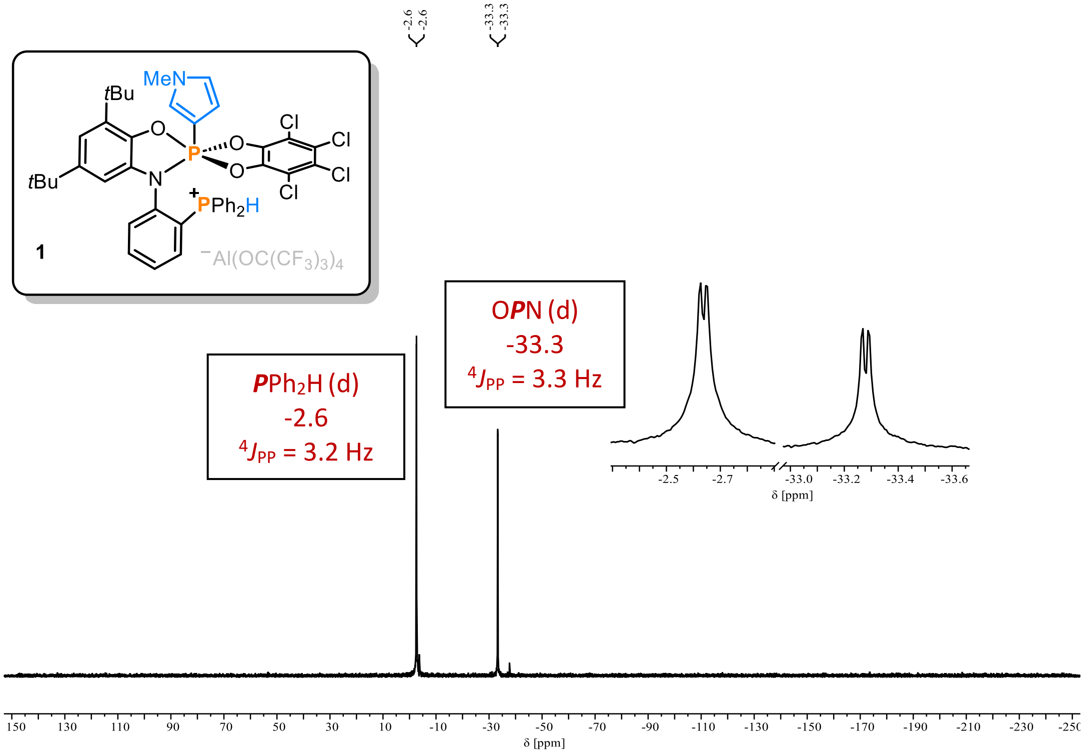


Figure S4: ^{31}**P{**^{1}**H} NMR** of **1** (162 MHz, CDCl$_3$, 295K), containing signals of minor diastereomer.

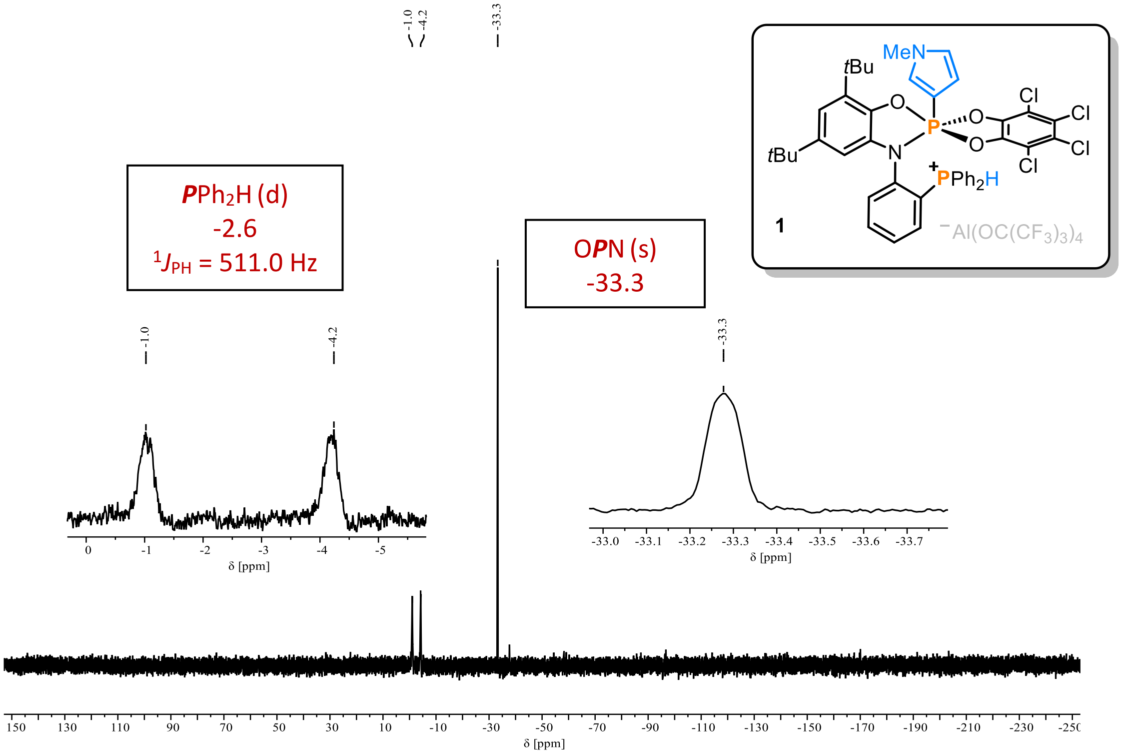


Figure S5: ^{31}P NMR of **1** (162 MHz, $CDCl_3$, 295K).

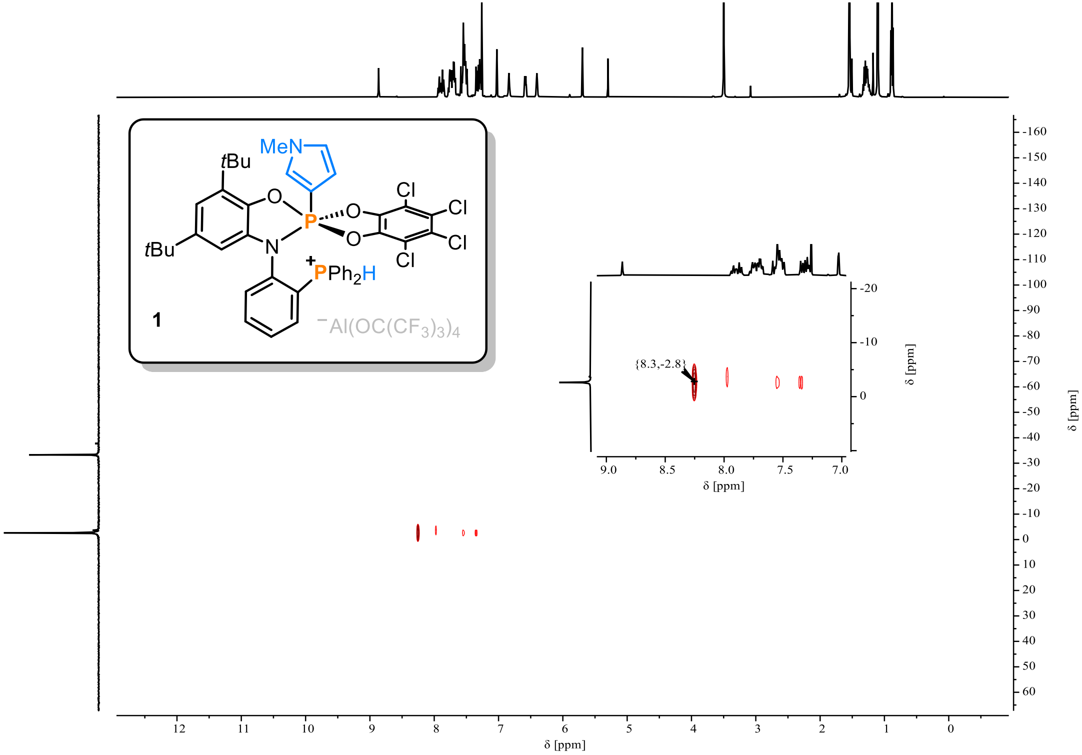
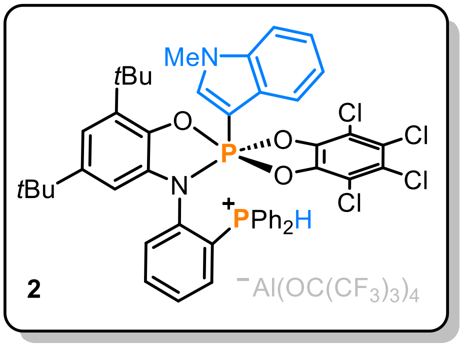


Figure S6: ^{1}H-^{31}P HMBC NMR of **1** ($CDCl_3$, 295K).



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2

[**PNOPcat**^{Cl}][Al(OR^F)$_4$] (50 mg, 29 µmol, 1.0 eq) and *N*-methylindole (3.8 mg, 29 µmol, 1.0 eq) were dissolved in CH_2Cl_2 (0.4 mL), which was stirred at room temperature overnight. Then *n*-pentane was introduced in the gas phase and allowed to diffuse into the solution at -40 °C for few days until light-pink solids precipitated out. The solvent was removed under reduced pressure. The product was washed with *n*-pentane and dried *in vacuo* to give the target compound as a white solid (26.1 mg, 14.1 µmol, 49%). Single crystals suitable for X-ray diffraction were grown by gas phase diffusion of *n*-pentane into the solution in CH_2Cl_2 at -40 °C.

^{1}H NMR (600 MHz, $CDCl_3$, 295K): δ [ppm] = 8.10 (d, J = 508.4 Hz, PPh$_2$***H***), 7.89 (t, J = 7.8 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.53 (td, J = 7.8, 3.5 Hz, 3H), 7.45 (dd, J = 13.9, 7.7 Hz, 2H), 7.35 – 7.26 (m, 6H), 7.23 – 7.14 (m, 3H), 7.13 (d, J = 2.0 Hz, 1H), 7.08 (dd, J = 15.2, 7.6 Hz, 2H), 5.88 (s, 1H), 3.70 (s, 3H), 1.53 (s, 9H), 1.19 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 295K): δ [ppm] = 145.5 (d, J = 3.9 Hz), 144.8 (s), 142.1 (d, J = 2.0 Hz), 140.6 (d, J = 4.0 Hz), 139.6 (d, J = 2.7 Hz), 138.4 (s), 138.2 (s), 136.6 (d, J = 2.7 Hz), 135.6 (d, J = 3.1 Hz), 135.4 (d, J = 9.8 Hz), 133.9 (d, J = 6.2 Hz), 133.2 (d, J = 12.0 Hz), 133.0 (d, J = 11.8 Hz), 131.7 (d, J = 7.6 Hz), 131.1 (d, J = 13.6 Hz), 130.6 (d, J = 13.4 Hz), 130.2 (d, J = 14.0 Hz), 128.8 (s), 128.6 (s), 126.7 (s), 124.8 (s), 124.2 (s), 123.1 (s), 122.0 (s), 121.4 (q, J = 293.6 Hz, OC(***C***F$_3$)$_3$), 118.4 (s), 116.6 (d, J = 16.6 Hz), 114.9 (s), 114.0 (s), 113.6 (d, J = 9.4 Hz), 112.0 (s), 111.0 (d, J = 2.2 Hz), 106.1 (d, J = 10.4 Hz), 105.5 (s), 102.7 (s), 35.0 (s), 34.8 (s), 33.8 (s), 31.6 (s), 29.9 (s).

^{19}F NMR (377 MHz, $CDCl_3$, 295K): δ [ppm] = -75.4.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 295K): δ [ppm] = -2.5 (s, ***P***Ph$_2$H), -30.3 (s, O***P***N).

^{31}P NMR (162 MHz, $CDCl_3$, 295K): δ [ppm] = -2.5 (d, $^1J_{PH}$ = 508.1 Hz, ***P***Ph$_2$H), -30.3 (s, O***P***N).

HRMS (ESI): $[M]^+ = [C_{47}H_{43}Cl_4N_2O_3P_2]^+$, calculated: 885.1498, found: 885.1481.

Elem. Anal. for $C_{63}H_{43}AlCl_4F_{36}N_2O_7P_2$ calculated: C, 40.80; H, 2.34; N, 1.51; found: C, 41.26; H, 2.84; N, 1.64.

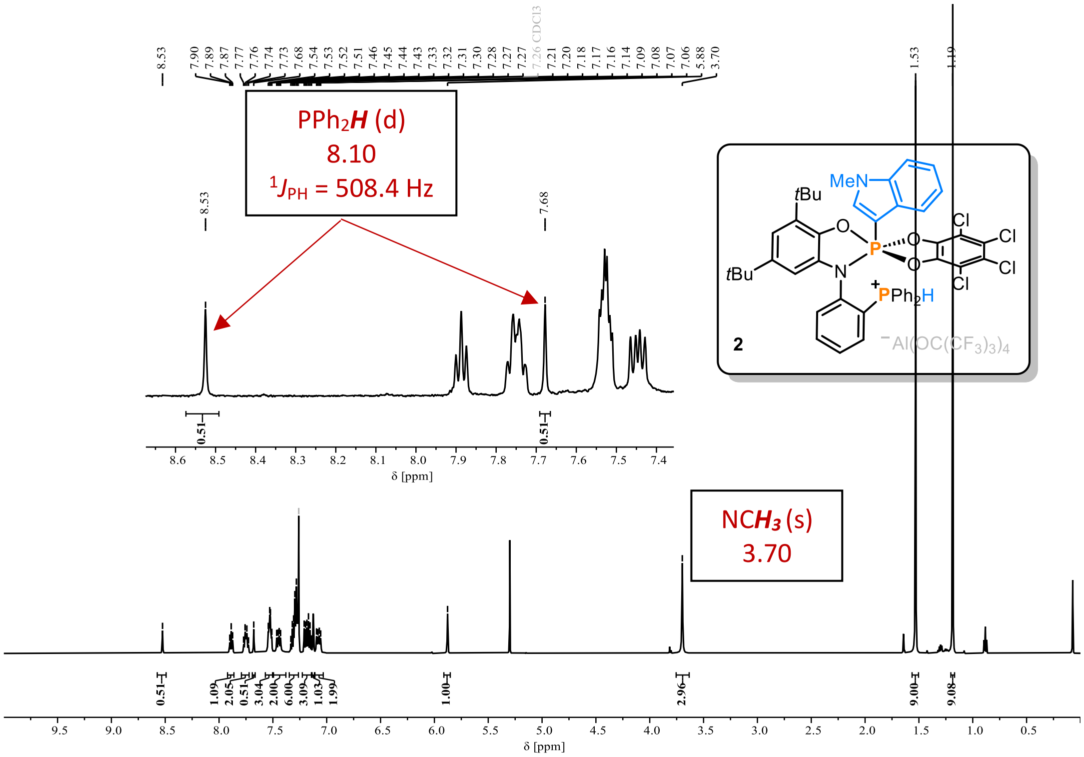


Figure S7: ^{1}H NMR of **2** (600 MHz, $CDCl_3$, 295K).

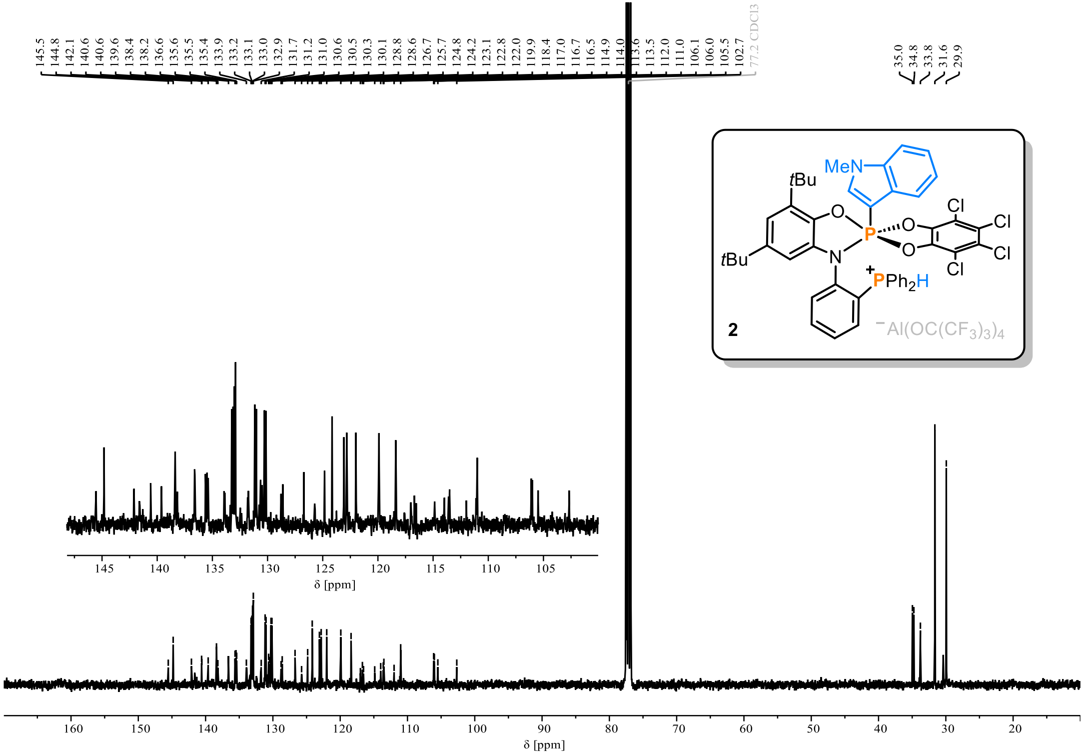


Figure S8: $^{13}C\{^{1}H\}$ NMR of **2** (101 MHz, $CDCl_3$, 295K).

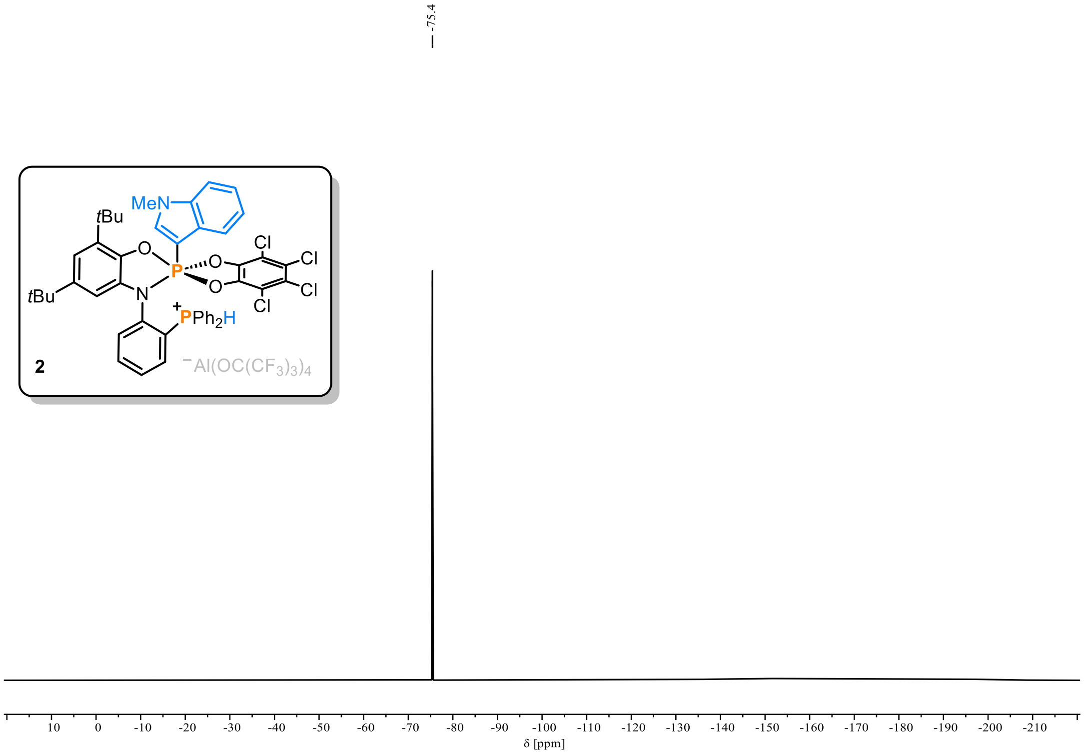


Figure S9: ^{19}**F NMR** of **2** (377 MHz, $CDCl_3$, 295K).

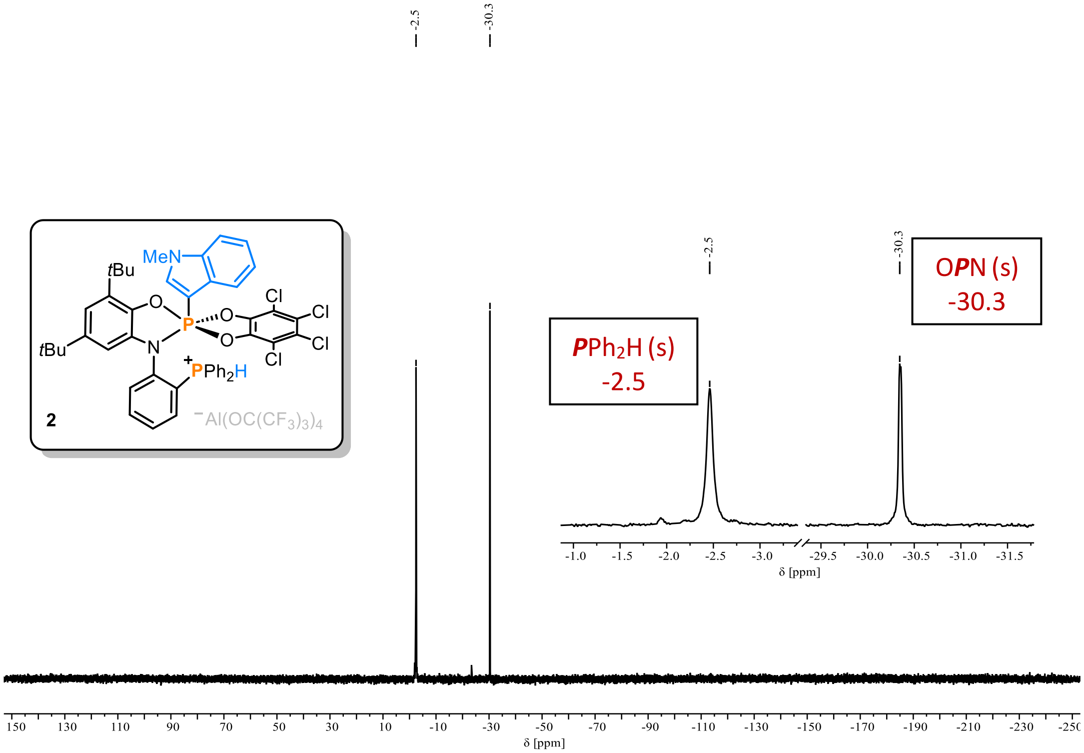


Figure S10: ^{31}**P{^{1}H} NMR** of **2** (162 MHz, $CDCl_3$, 295K).

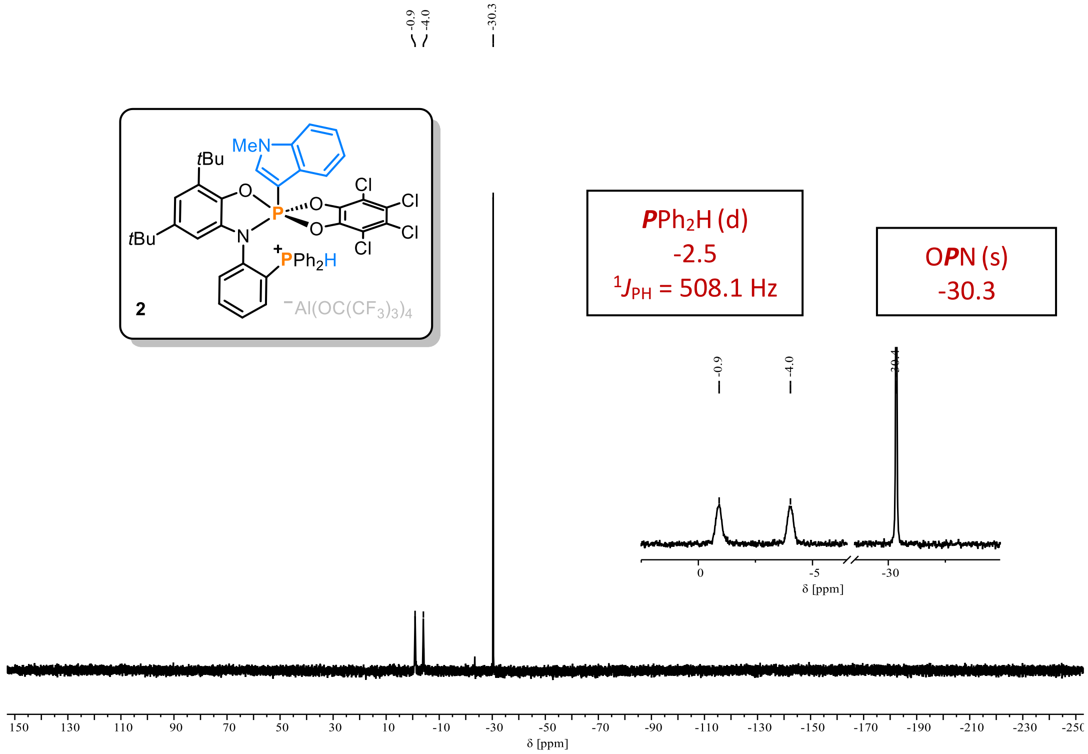


Figure S11: ^{31}**P NMR** of **2** (162 MHz, $CDCl_3$, 295K).

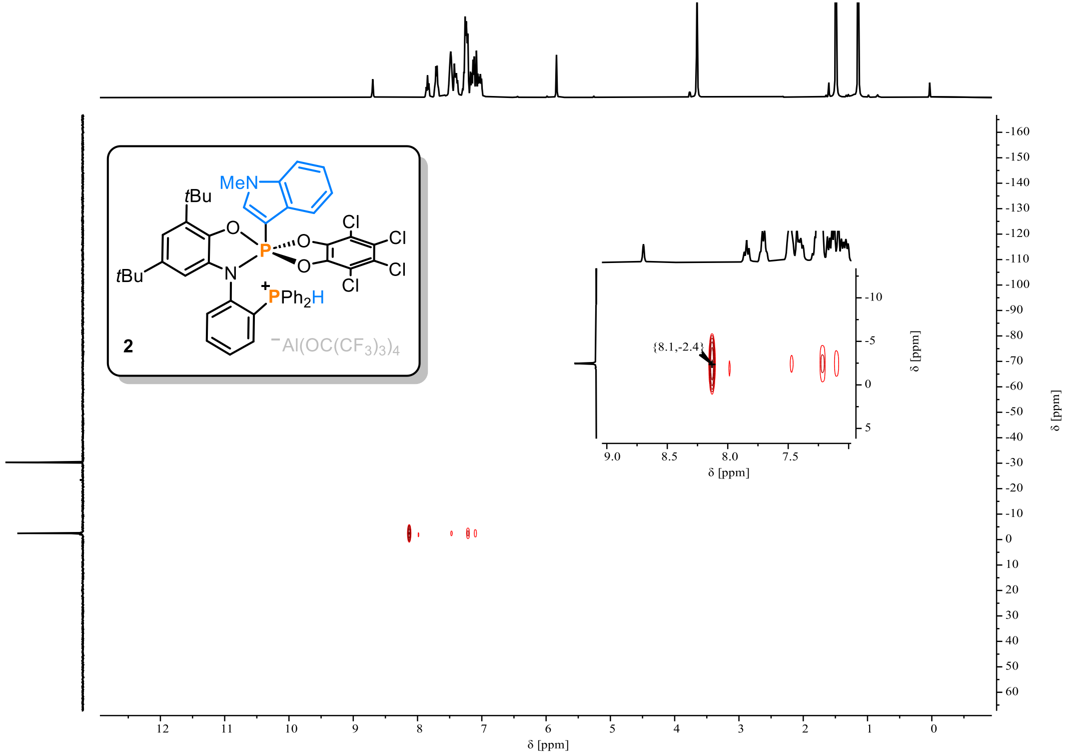
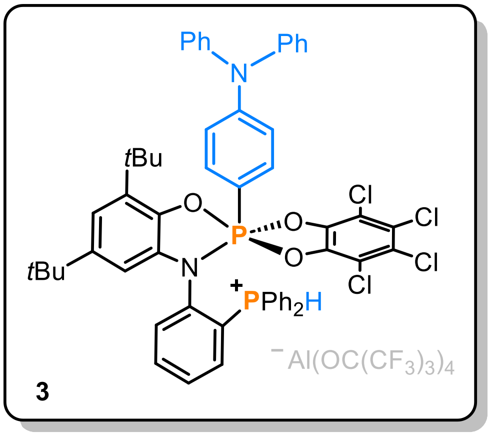


Figure S12: ^{1}**H-**^{31}**P HMBC NMR** of **2** ($CDCl_3$, 295K).



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[**PNOPcat**$^{\mathbf{Cl}}$][Al(OR^{F})$_4$] (50 mg, 29 µmol, 1.0 eq) and Ph_3N (7.1 mg, 29 µmol, 1.0 eq) were dissolved in toluene (0.4 mL), which was stirred at 100 °C for 4 days. The ^{31}**P{**^{1}**H} NMR** spectrum showed a set of diastereomers of product **3** in a ratio of 1:2.4 (**A**: **B**). After cooling the solution to room temperature, the solvent was removed under reduced pressure, and the resulting residue was dissolved in 0.3 mL of CH_2Cl_2. Then *n*-pentane was introduced in the gas phase and allowed to diffuse into the solution at -40 °C for few days until white solids precipitated out. The solvent was removed under reduced pressure. The product was washed with *n*-pentane and dried *in vacuo* to give **A** and **B** in a ratio of 3.8:1 as a white solid (32.3 mg, 16.4 µmol, 57%). Single crystals suitable for X-ray diffraction were grown by gas phase diffusion of *n*-pentane into the solution in $CHCl_3$ at -40 °C. The formation of enthalpically favored isomer **A**, as shown in the scXRD structure, occurs at lower temperature. At elevated temperature, the formation of entropically favored isomer **B** is observed.

^{1}**H NMR**: ***isomer A***: (600 MHz, $CDCl_3$, 295K) δ [ppm] = 8.03 (d, J = 506.1 Hz, PPh$_2$***H***), 7.90 (t, J = 7.8 Hz, 1H), 7.85 (t, J = 7.5 Hz, 1H), 7.80 (t, J = 7.9 Hz, 1H), 7.75 (td, J = 8.4, 2.5 Hz, 1H), 7.64 (dtd, J = 14.0, 7.1, 3.0 Hz, 4H), 7.54 (td, J = 15.3, 8.5 Hz, 2H), 7.49 – 7.38 (m, 4H), 7.33 (t, J = 7.8 Hz, 5H), 7.30 – 7.24 (m, 2H), 7.24 – 7.19 (m, 2H), 7.14 – 7.11 (m, 1H), 7.07 – 7.01 (m, 3H), 6.73 – 6.52 (m, 2H), 5.85 (t, J = 1.7 Hz, 1H), 1.50 (s, 9H), 1.15 (s, 9H). ***isomer B***: (400 MHz, $CDCl_3$, 295K) δ [ppm] = 8.13 (t, J = 7.9 Hz, 1H), 7.89 – 7.76 (m, 2H), 7.85 (d, J = 505.2 Hz, PPh$_2$***H***), 7.69 – 7.57 (m, 4H), 7.58 – 7.52 (m, 1H), 7.49 – 7.39 (m, 4H), 7.35 – 7.28 (m, 5H), 7.28 – 7.18 (m, 2H), 7.20 – 7.15 (m, 2H), 7.16 – 7.09 (m, 4H), 7.06 (dd, J = 8.5, 1.3 Hz, 2H), 6.95 – 6.79 (m, 2H), 6.05 (t, J = 1.6 Hz, 1H), 1.56 (s, 9H), 1.21 (s, 9H).

^{13}**C{**^{1}**H} NMR** (151 MHz, $CDCl_3$, 295K): δ [ppm] = 145.9, 145.8, 145.3, 145.1, 144.8, 142.2, 141.0, 139.5, 138.6, 136.9, 136.6, 135.9, 135.8, 135.3, 135.2, 134.1, 134.0, 133.6, 133.3, 133.2, 133.0, 131.9, 131.4, 131.3, 131.2, 131.0, 130.9, 130.2, 130.0, 126.8, 126.7, 126.7, 126.3, 124.8, 124.3, 122.3, 120.4, 118.5, 118.4, 117.9, 117.8, 116.5, 114.5, 113.9, 106.3, 104.9, 35.1, 34.9, 34.8, 34.7, 31.7, 31.6, 30.1, 29.7. These signals could not be reliably assigned due to an overlap of two diastereomer signals.

^{19}**F NMR** (377 MHz, $CDCl_3$, 295K): δ [ppm] = -75.4.

^{31}**P{**^{1}**H} NMR** (162 MHz, $CDCl_3$, 295K): δ [ppm] = ***isomer A***: -3.4 (d, $^{4}J_{PP}$ = 3.2 Hz, ***P***Ph$_2$H), -29.1 (d, $^{4}J_{PP}$ = 3.2 Hz, O***P***N). ***isomer B***: -1.8 (d, $^{4}J_{PP}$ = 1.8 Hz, ***P***Ph$_2$H), -23.7 (d, $^{4}J_{PP}$ = 1.8 Hz, O***P***N).

^{31}**P NMR** (162 MHz, $CDCl_3$, 295K): δ [ppm] = ***isomer A***: -3.4 (d, $^{1}J_{PH}$ = 507.1 Hz, ***P***Ph$_2$H), -29.1 (br, O***P***N). ***isomer B***: -1.7 (d, $^{1}J_{PH}$ = 505.0 Hz, ***P***Ph$_2$H), -23.7 (br, O***P***N).

HRMS (ESI): $[M]^+ = [C_{56}H_{49}Cl_4N_2O_3P_2]^+$, calculated: 999.1967, found: 999.1940.

Elem. Anal. for $C_{72}H_{49}AlCl_4F_{36}N_2O_7P_2$ x 1.0 C_5H_{12} calculated: C, 45.31; H, 3.01; N, 1.37; found: C, 45.63; H, 3.50; N, 1.64. (C_5H_{12} content estimated from **^{1}H NMR** measurements).

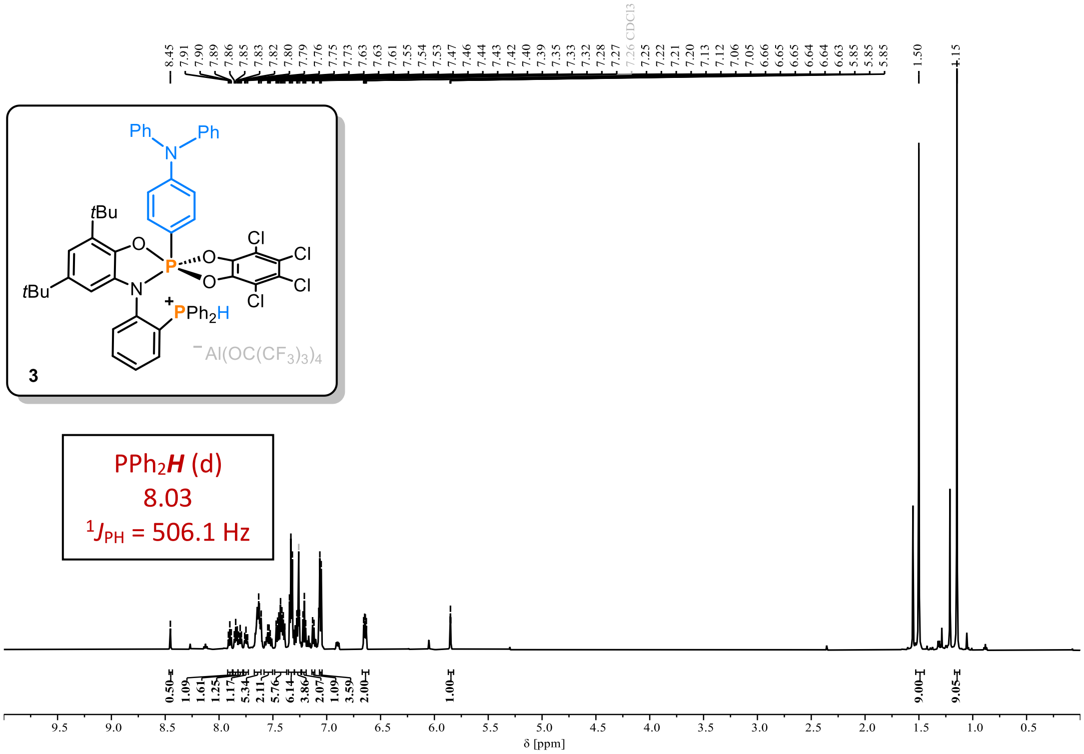


Figure S13: **^{1}H NMR** of **3** (600 MHz, CDCl$_3$, 295K) with only peaks for ***isomer A*** labeled.

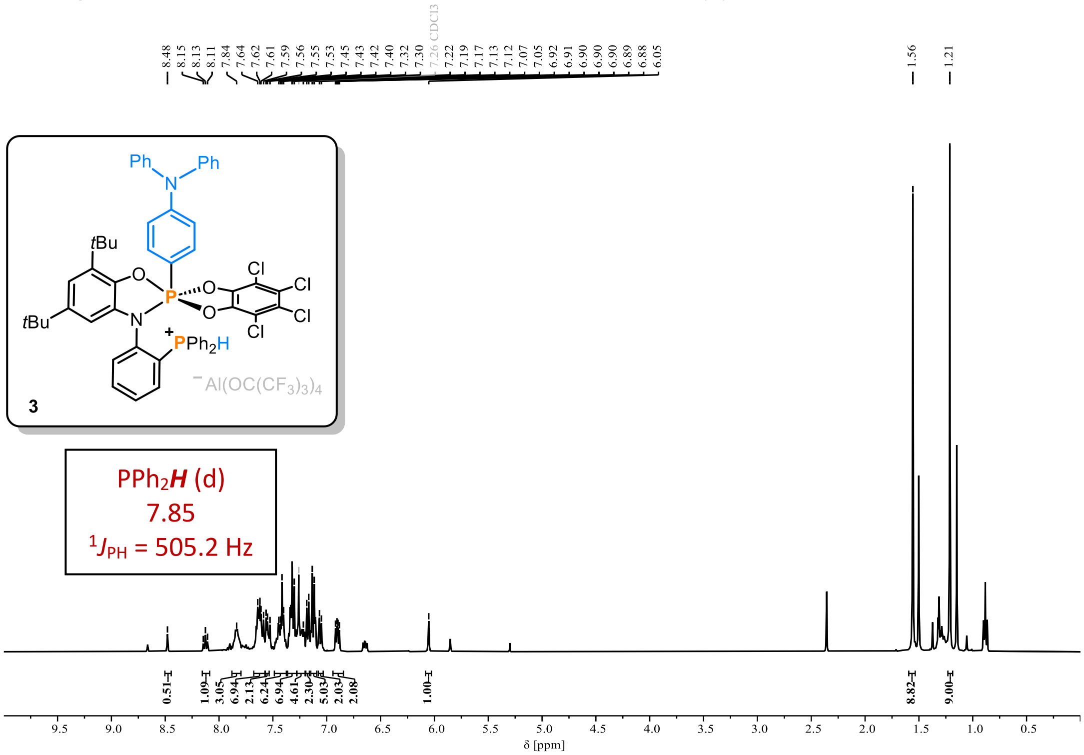


Figure S14: ^{1}**H NMR** of **3** (400 MHz, CDCl$_3$, 295K) with only peaks for ***isomer B*** labeled.

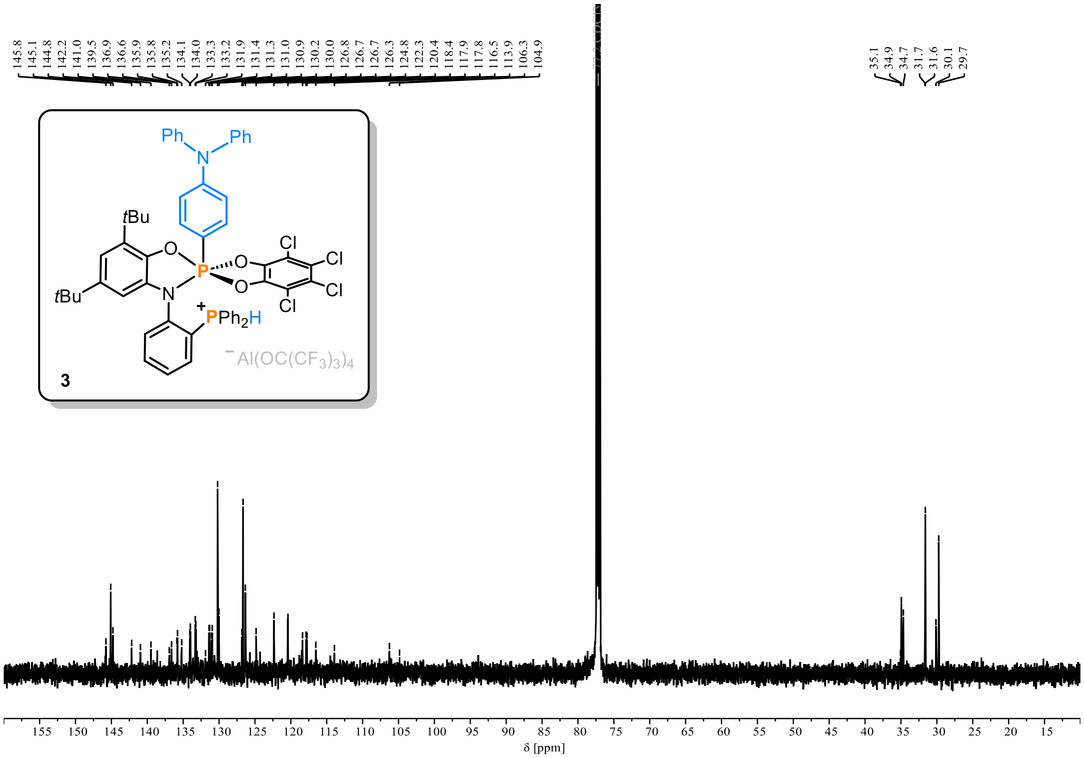


Figure S15: ^{13}**C NMR** of **3** (151 MHz, CDCl$_3$, 295K).

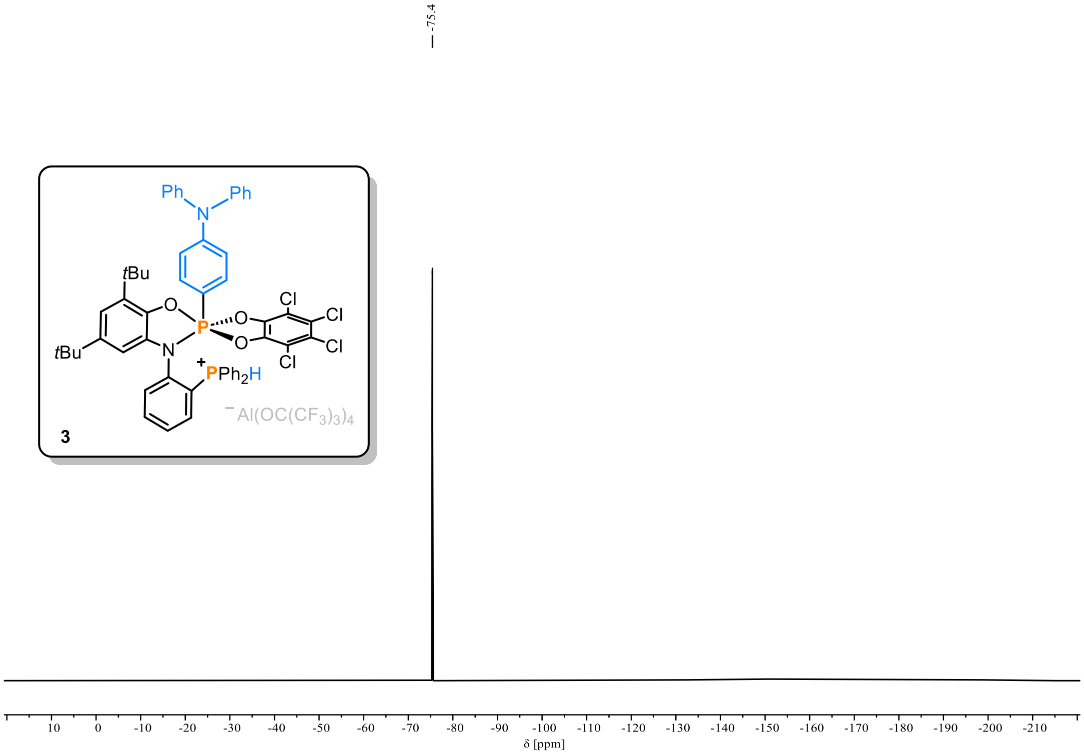
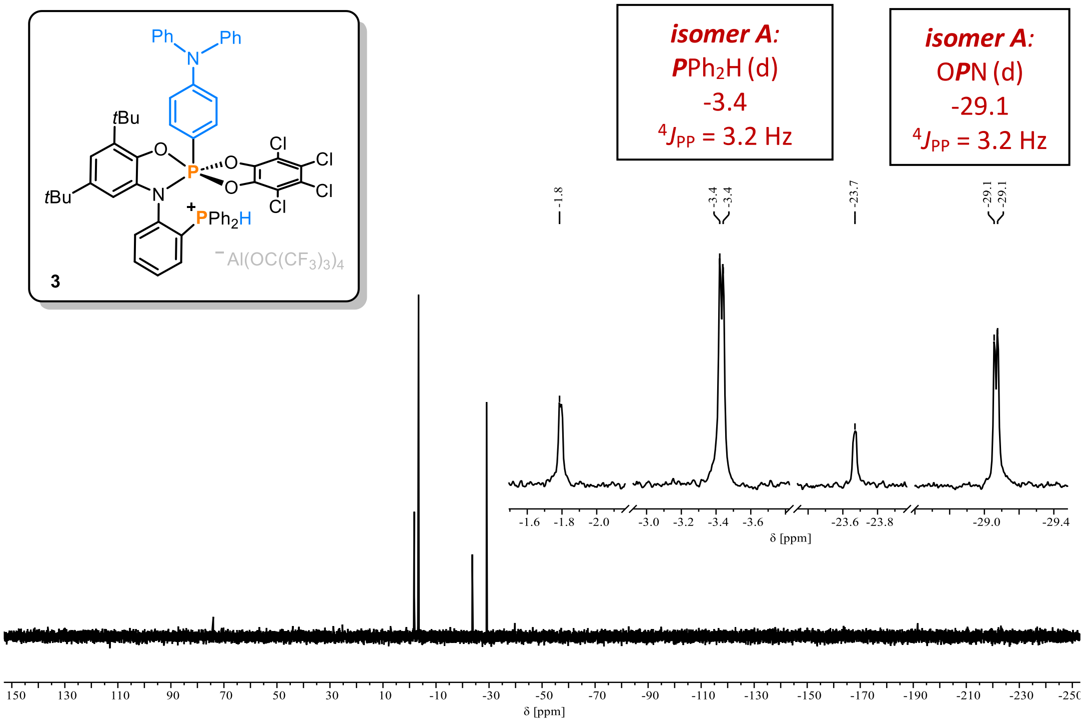


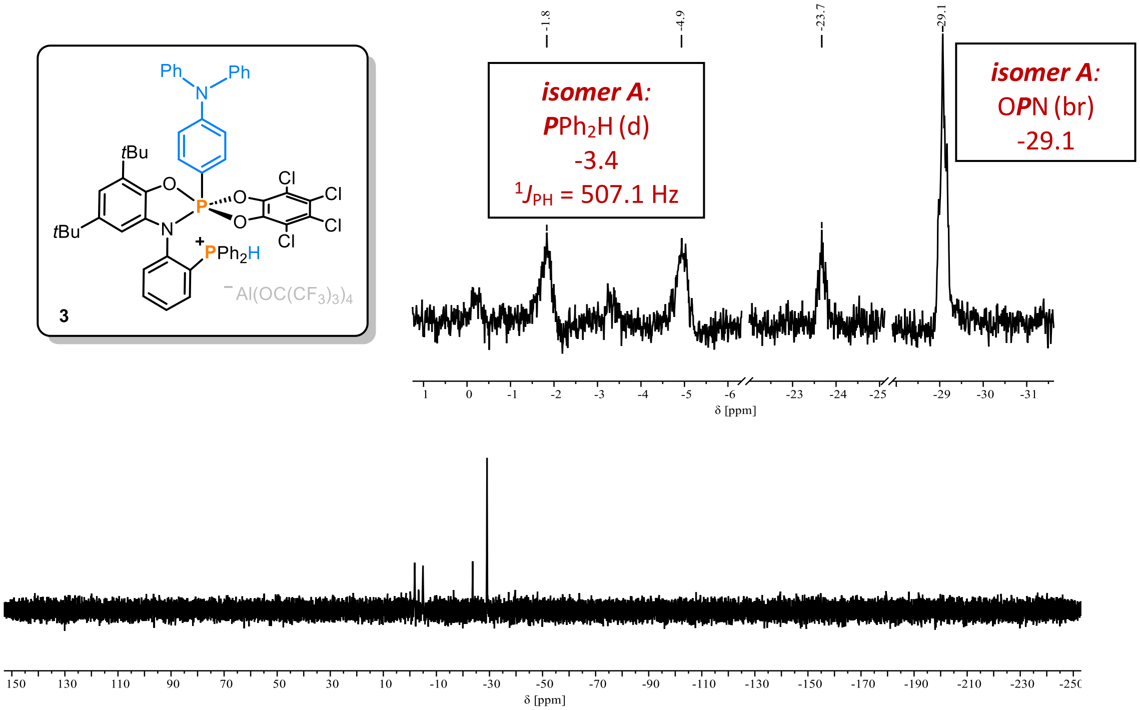
Figure S16: ^{19}**F NMR** of **3** (377 MHz, CDCl$_3$, 295K).



***isomer A*:**
***P*Ph$_2$H (d)**
-3.4
$^4J_{PP}$ = 3.2 Hz

***isomer A*:**
O*P*N (d)
-29.1
$^4J_{PP}$ = 3.2 Hz

Figure S17: **$^{31}P\{^1H\}$ NMR** of **3** (162 MHz, CDCl$_3$, 295K).



***isomer A*:**
***P*Ph$_2$H (d)**
-3.4
$^1J_{PH}$ = 507.1 Hz

***isomer A*:**
O*P*N (br)
-29.1

Figure S18: **^{31}P NMR** of **3** (162 MHz, CDCl$_3$, 295K).

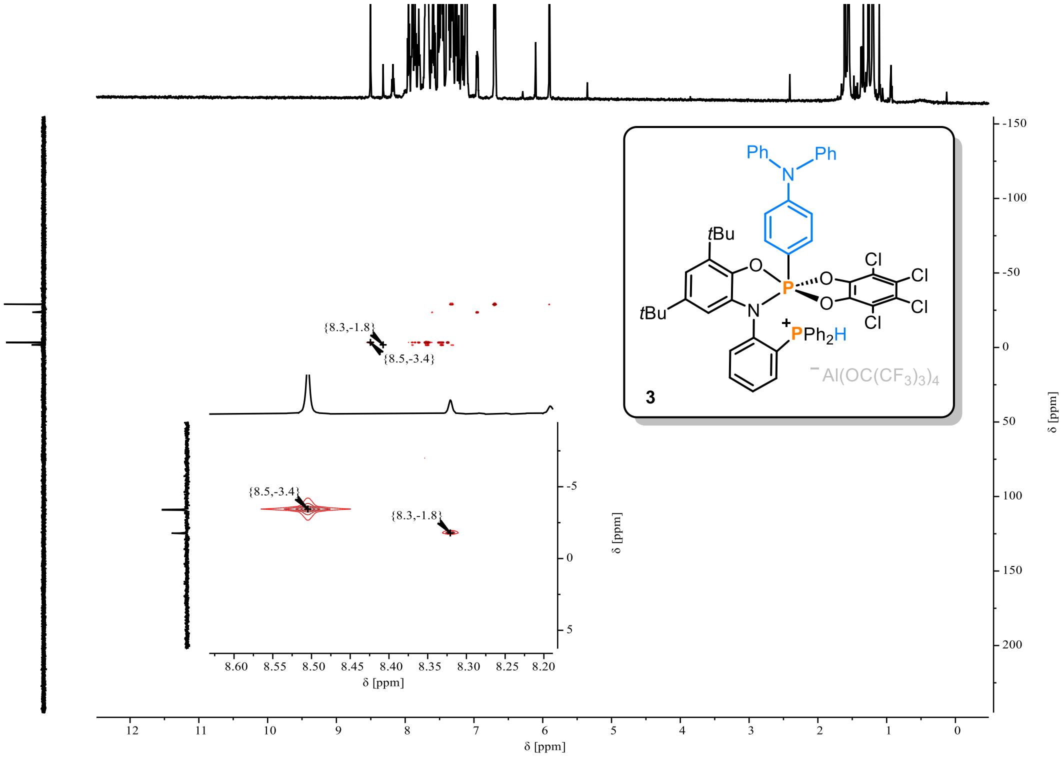
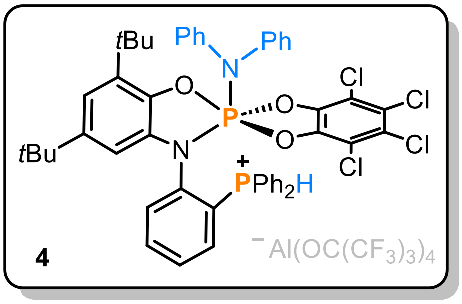


Figure S19: ^{1}H-^{31}P HMBC NMR of **3** ($CDCl_3$, 295K).

2.2 X-H Deprotonation



4

[**PNOPcat**^{Cl}][Al(OR^F)$_4$] (50 mg, 29 µmol, 1.0 eq) and Ph_2NH (4.9 mg, 29 µmol, 1.0 eq) were dissolved in CH_2Cl_2 (0.4 mL), which was stirred at room temperature overnight. Then *n*-pentane was introduced in the gas phase and allowed to diffuse into the solution at -40 °C for few days until white solids precipitated out. The solvent was removed under reduced pressure. The product was washed with *n*-pentane and dried *in vacuo* to give the target compound as a white solid (33 mg, 17.4 µmol, 60%). Single crystals suitable for X-ray diffraction were grown by gas phase diffusion of *n*-pentane into the solution in CH_2Cl_2 at -40 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 295K): δ [ppm] = 9.33 (d, J = 504.2 Hz, 1H, PPh$_2$***H***), 7.96 (q, J = 7.5 Hz, 2H), 7.85 – 7.68 (m, 7H), 7.63 (t, J = 7.7 Hz, 1H), 7.52 (dd, J = 15.0, 7.7 Hz, 2H), 7.38 (dd, J = 14.8, 7.8 Hz, 1H), 7.30 – 7.21 (t, J = 6.8 Hz, 1H), 7.11 (dt, J = 14.8, 7.2 Hz, 6H), 6.92 – 6.84 (m, 1H), 6.77 (d, J = 7.6 Hz, 4H), 5.93 (s, 1H), 1.11 (s, 9H), 0.92 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 295K): δ [ppm] = 146.7 (d, J = 3.8 Hz), 146.3 (d, J = 7.2 Hz), 144.7 (s), 141.0 (d, J = 5.4 Hz), 139.9 (s), 139.4 (d, J = 4.8 Hz), 138.4 (s), 137.2 (dd, J = 9.4, 3.1 Hz), 135.9 (d, J = 10.6 Hz), 134.3 (d, J = 11.8 Hz), 133.7 (d, J = 11.6 Hz), 133.5 (d, J = 9.1 Hz), 132.4 (d, J = 23.0 Hz), 131.5 (d, J = 14.4 Hz), 131.3 (d, J = 14.4 Hz), 131.0 (d, J = 7.3Hz), 130.5 (d, J = 13.3 Hz), 129.8 (s), 129.5 (s), 126.8 (s), 126.7 (s), 126.6 (d, J = 3.6 Hz), 125.1 (s), 121.4 (q, J = 291.9 Hz, OC(***C***F$_3$)$_3$), 121.2 (s), 118.3 (s), 118.1 (s), 117.0 (d, J = 3.5 Hz), 116.8 (d, J = 5.6 Hz), 116.3 (s), 116.1 (s), 113.6 (d, J = 29.2 Hz), 113.2 (d, J = 13.5 Hz), 112.7 (d, J = 29.6 Hz), 106.9 (d, J = 12.2 Hz), 34.8 (s), 34.2 (s), 31.5 (s), 29.0 (s).

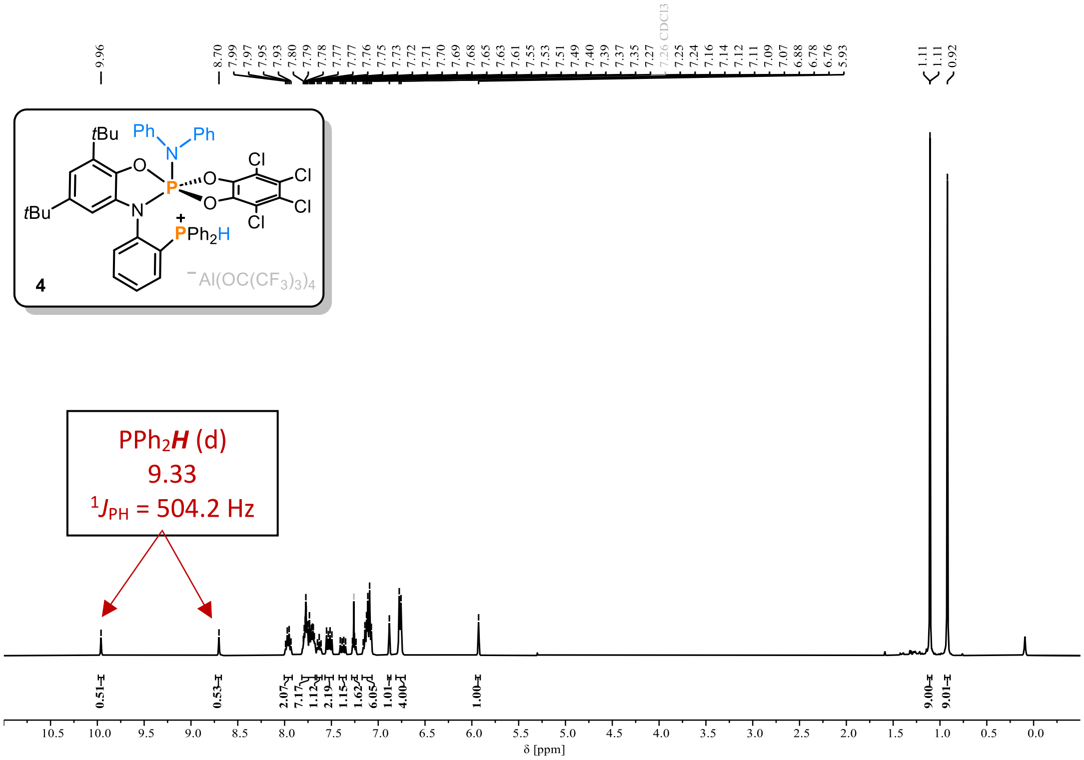
^{19}F NMR (377 MHz, $CDCl_3$, 295K): δ [ppm] = -75.4 (s).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 295K): δ [ppm] = -1.2 (d, $^4J_{PP}$ = 3.4 Hz, ***P***Ph$_2$H), -43.3 (d, $^4J_{PP}$ = 3.5 Hz, O***P***N).

^{31}P NMR (162 MHz, $CDCl_3$, 295K): δ [ppm] = -1.2 (d, $^1J_{PH}$ = 503.6 Hz, ***P***Ph$_2$H), -43.3 (br, O***P***N).

HRMS (ESI): $[M]^+ = [C_{50}H_{45}Cl_4N_2O_3P_2]^+$, calculated: 923.1654, found: 923.1646.

Elem. Anal. for $C_{66}H_{45}AlCl_4F_{36}N_2O_7P_2$ calculated: C, 41.88; H, 2.40; N, 1.48; found: C, 42.05; H, 2.83; N, 1.74.



PPh$_2$**H** (d)
9.33
$^1J_{PH}$ = 504.2 Hz

Figure S20: ^{1}**H NMR** of **4** (400 MHz, CDCl$_3$, 295K).

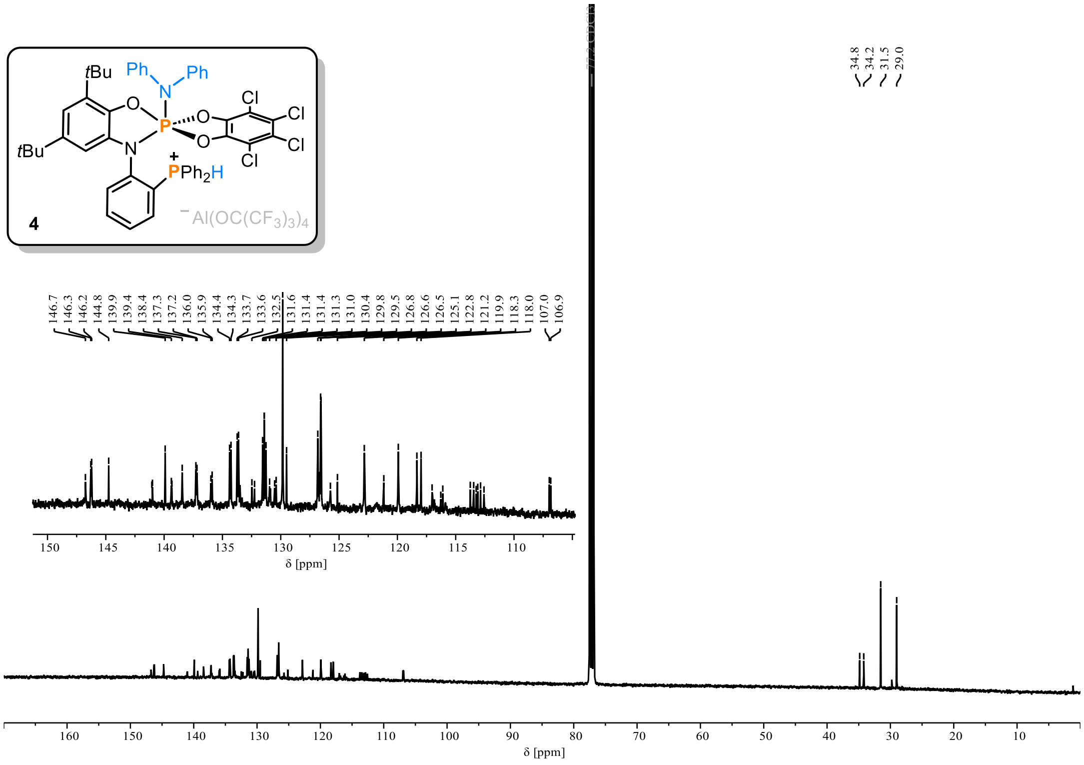


Figure S21: ^{13}**C{^{1}H} NMR** of **4** (101 MHz, CDCl$_3$, 295K).

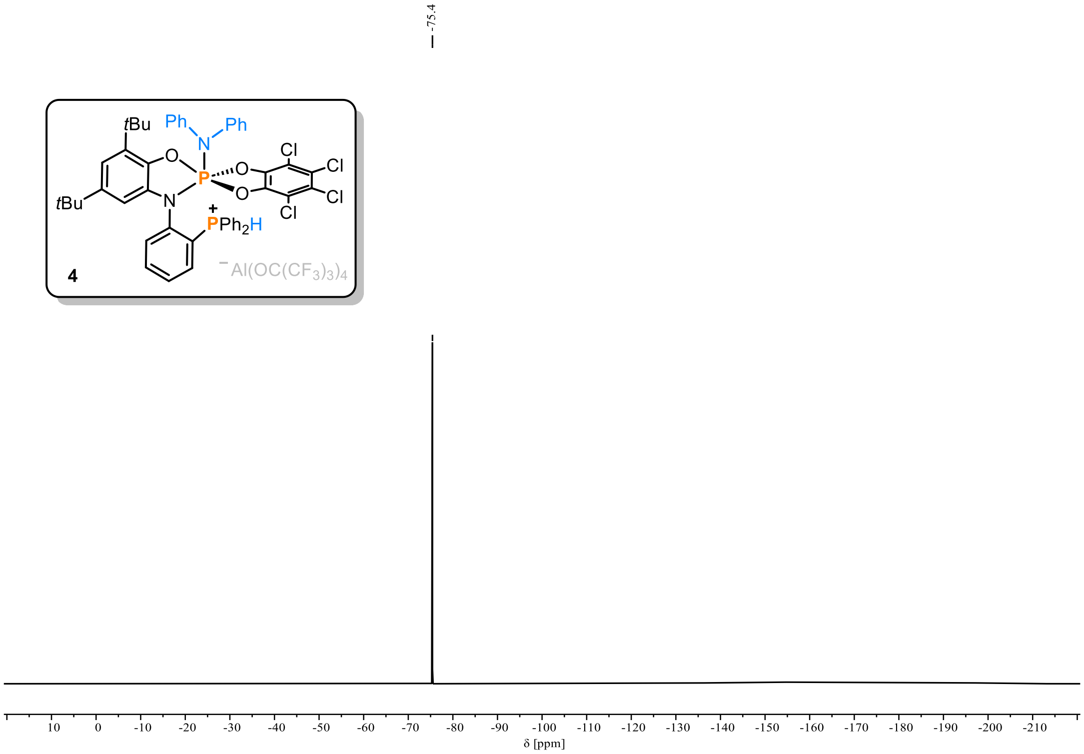


Figure S22: **^{19}F NMR** of **4** (377 MHz, $CDCl_3$, 295K).

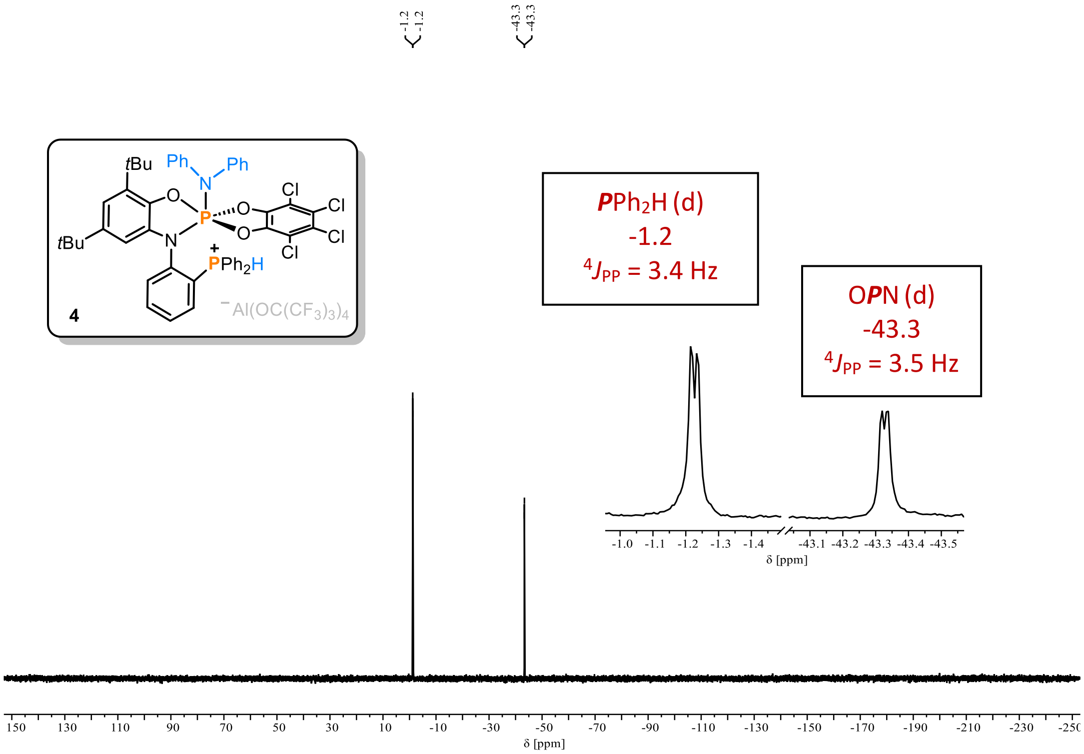


Figure S23: **^{31}P{^{1}H} NMR** of **4** (162 MHz, $CDCl_3$, 295K).

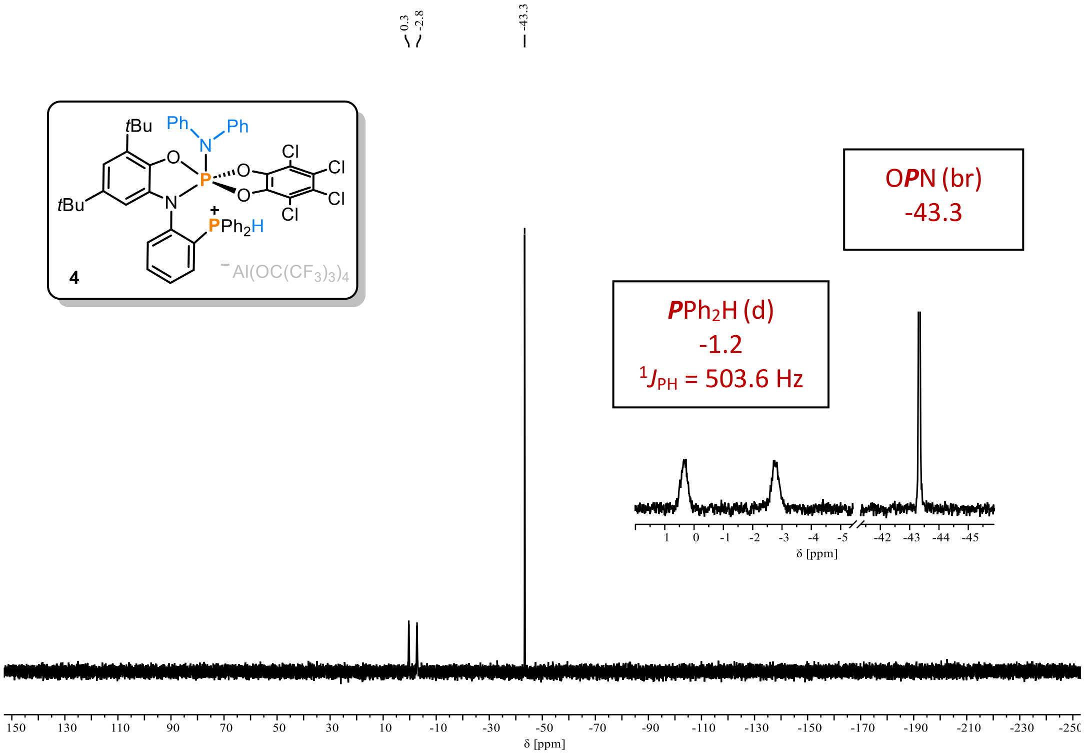


Figure S24: ^{31}**P NMR** of **4** (162 MHz, $CDCl_3$, 295K).

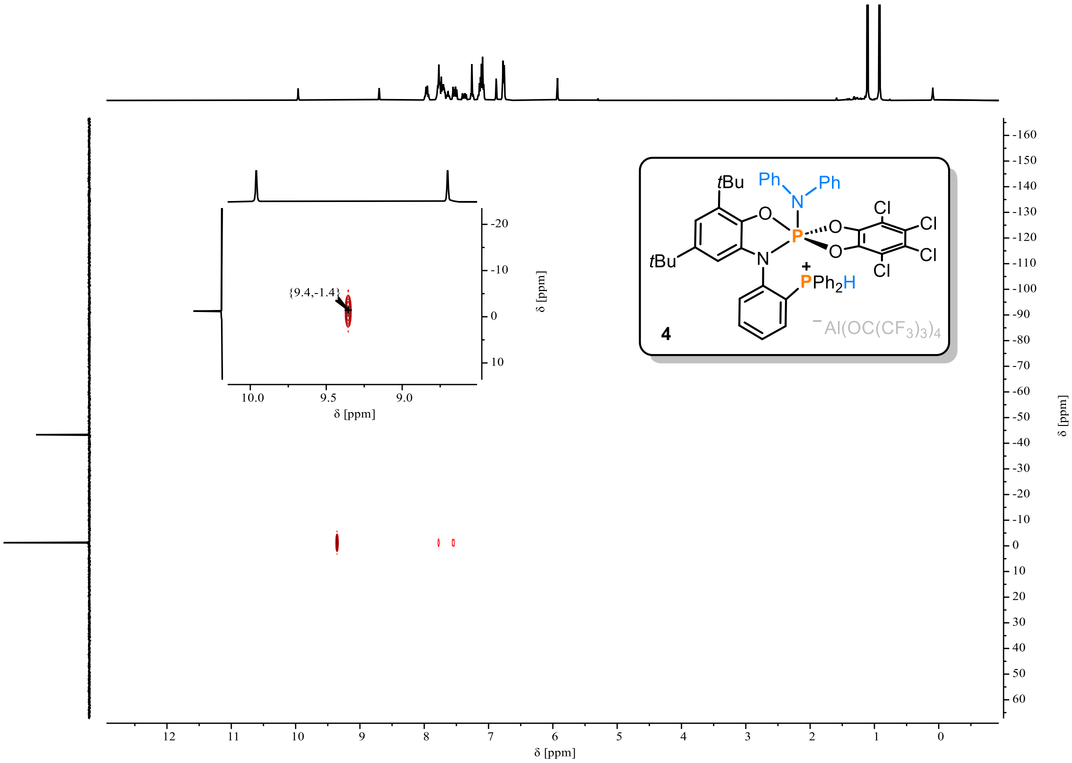
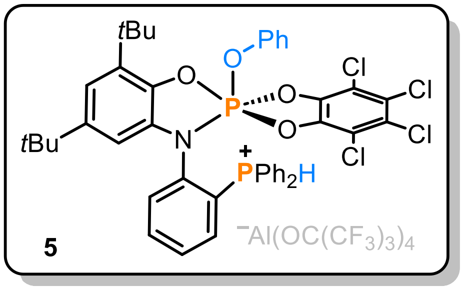


Figure S25: ^{1}**H-**^{31}**P HMBC NMR** of **4** ($CDCl_3$, 295K).



5

5

[**PNOPcat^{Cl}**][Al(OR^{F})$_4$] (50 mg, 29 μmol, 1.0 eq) and phenol (2.7 mg, 29 μmol, 1.0 eq) were dissolved in CH_2Cl_2 (0.4 mL), which was stirred at room temperature overnight. Then *n*-pentane was introduced in the gas phase and allowed to diffuse into the solution at -40 °C for few days until white solids precipitated out. Then removed the solvent under reduced pressure and the solid was washed with *n*-pentane and dried *in vacuo* to give a set of diastereomers of product **5** in an approximately 2.2:1 ratio as a white solid (40 mg, 22 μmol, 76%).

^{1}H NMR (400 MHz, $CDCl_3$, 295K): *major diastereomer*: *δ* [ppm] = 8.24 (t, *J* = 7.9 Hz, 1H), 8.05 – 7.68 (m, 5H), 7.75 (d, *J* = 503.8 Hz, PPh$_2$***H***), 7.68 – 7.48 (m, 4H), 7.38 (dd, *J* = 11.5, 3.4 Hz, 3H), 7.25 – 7.20 (m, 3H), 7.17 – 7.13 (m, 1H), 7.07 (t, *J* = 1.8 Hz, 1H), 6.89 – 6.78 (m, 2H), 6.19 (t, *J* = 1.8 Hz, 1H), 1.25 (s, 9H), 1.12 (s, 9H). *minor diastereomer*: *δ* [ppm] = 8.76 (d, *J* = 504.4 Hz, PPh$_2$***H***), 8.24 (t, *J* = 7.9 Hz, 1H), 8.05 – 7.68 (m, 5H), 7.68 – 7.48 (m, 4H), 7.38 (dd, *J* = 11.5, 3.4 Hz, 3H), 7.29 (d, *J* = 7.8 Hz, 3H), 7.19 – 7.13 (m, 1H), 6.98 (s, 1H), 6.58 (d, *J* = 7.9 Hz, 2H), 5.97 (s, 1H), 1.14 (s, 9H), 1.01 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 295K): *δ* [ppm] = 151.9, 151.7, 151.5, 151.4, 146.2, 145.5, 145.2, 140.8, 140.7, 139.7, 139.3, 139.2, 138.8, 138.3, 138.3, 137.3, 137.2, 137.1, 137.1, 136.3, 136.3, 136.2, 136.1, 134.8, 134.7, 134.6, 134.5, 134.1, 134.0, 133.8, 133.7, 133.4, 133.4, 132.9, 132.8, 132.4, 132.2, 132.1, 131.8, 131.8, 131.6, 131.6, 131.4, 131.3, 131.2, 131.1, 131.0, 130.9, 130.6, 130.6, 130.5, 130.5, 127.6, 127.2, 126.5, 126.5, 126.0, 125.5, 125.3, 123.1, 120.8, 120.8, 120.5, 120.5, 120.2, 119.3, 119.1, 117.3, 116.7, 116.3, 116.2, 116.1, 115.3, 115.3, 115.0, 114.9, 113.8, 113.5, 113.0, 112.9, 112.7, 112.1, 106.6, 106.4, 105.4, 105.3, 35.3, 35.1, 34.6, 34.5, 31.7, 31.6, 29.3, 29.2. The signals could not be reliably assigned due to an overlap of two diastereomer signals.

^{19}F NMR (376 MHz, $CDCl_3$, 295K): *δ* [ppm] = -75.4.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 295K): *δ* [ppm] = *major diastereomer*: -1.6 (d, $^{4}J_{PP}$= 2.3 Hz, ***P***Ph$_2$H), -40.1 (d, $^{4}J_{PP}$ = 2.3 Hz, O***P***N); *minor diastereomer*: -1.8 (d, $^{4}J_{PP}$= 2.6 Hz, ***P***Ph$_2$H), -41.0 (d, $^{4}J_{PP}$ = 2.3 Hz, O***P***N).

^{31}P NMR (162 MHz, $CDCl_3$, 295K): *δ* [ppm] = *major diastereomer*: -1.6 (d, $^{1}J_{PH}$ = 504.7 Hz, ***P***Ph$_2$H), -40.1 (br, O***P***N); *minor diastereomer*: -41.0 (br, O***P***N), The ***P***Ph$_2$H signal could not be reliably assigned due to low intensity and an overlap of signals.

HRMS (ESI): [M]$^{+}$ = [$C_{44}H_{40}Cl_4NO_4P_2$]$^{+}$, calculated: 848.1181, found: 848.1155. **Elem. Anal.** for $C_{60}H_{40}AlCl_4F_{36}NO_8P_2$ calculated: C, 39.65; H, 2.22; N, 0.77; found: C, 39.68; H, 2.78; N, 0.98.

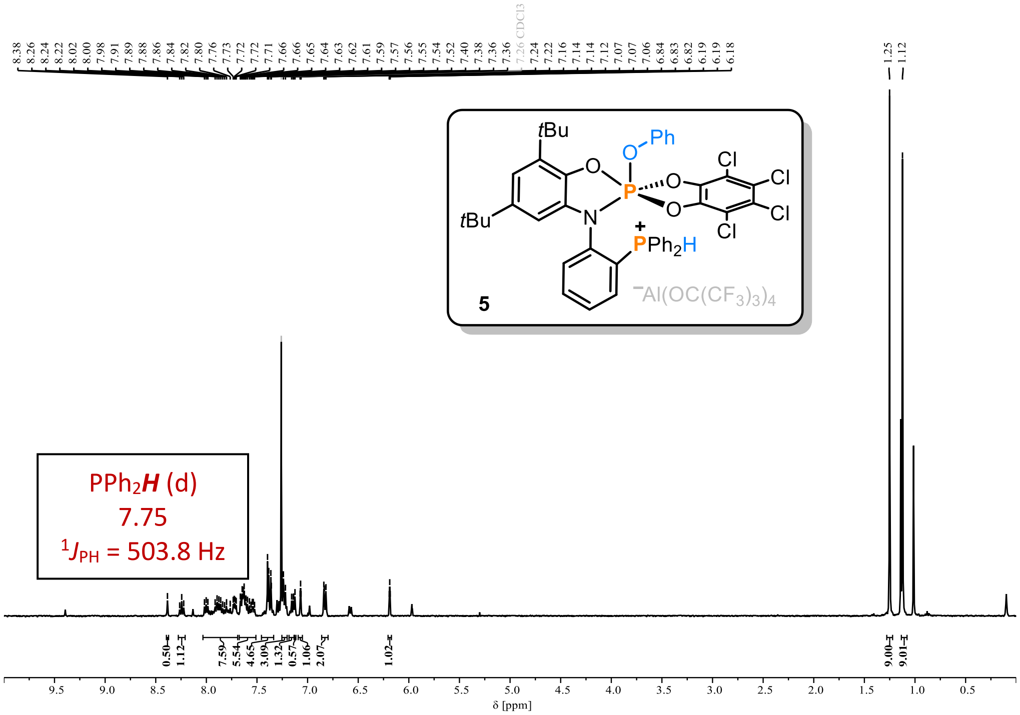


Figure S26: ^{1}**H NMR** of **5** (400 MHz, $CDCl_3$, 295K), only peaks for major diastereomer are labeled and integrated. Some of the integration are the sum of major and minor diastereomer signals.

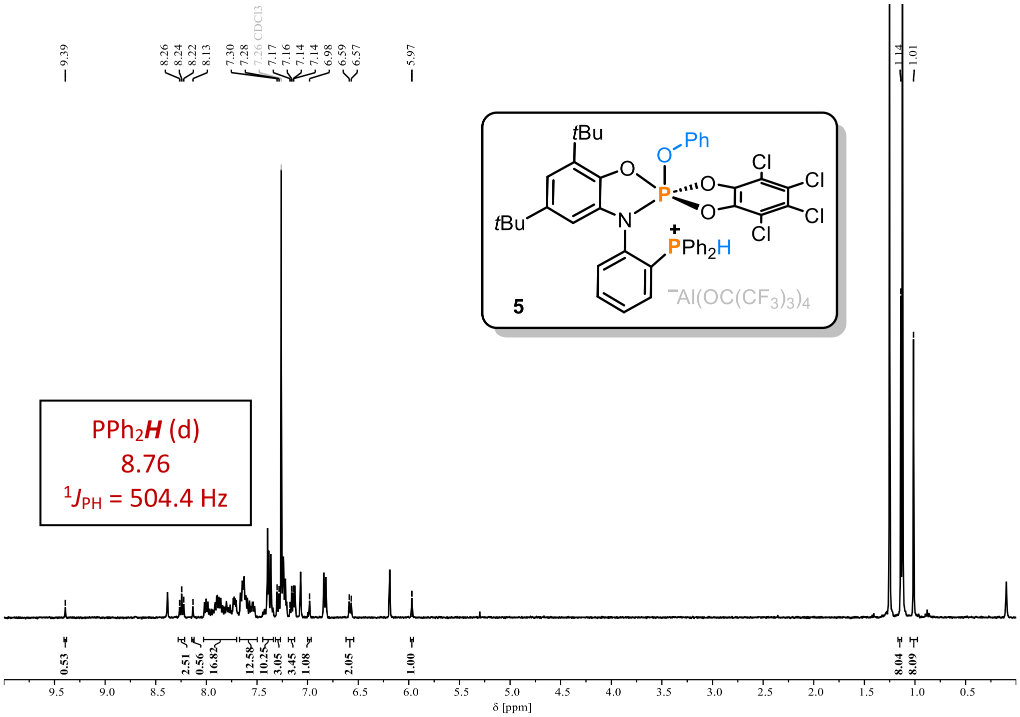


Figure S27: ^{1}**H NMR** of **5** (400 MHz, $CDCl_3$, 295K), only peaks for minor diastereomer are labeled and integrated. Some of the integration are the sum of major and minor diastereomer signals.

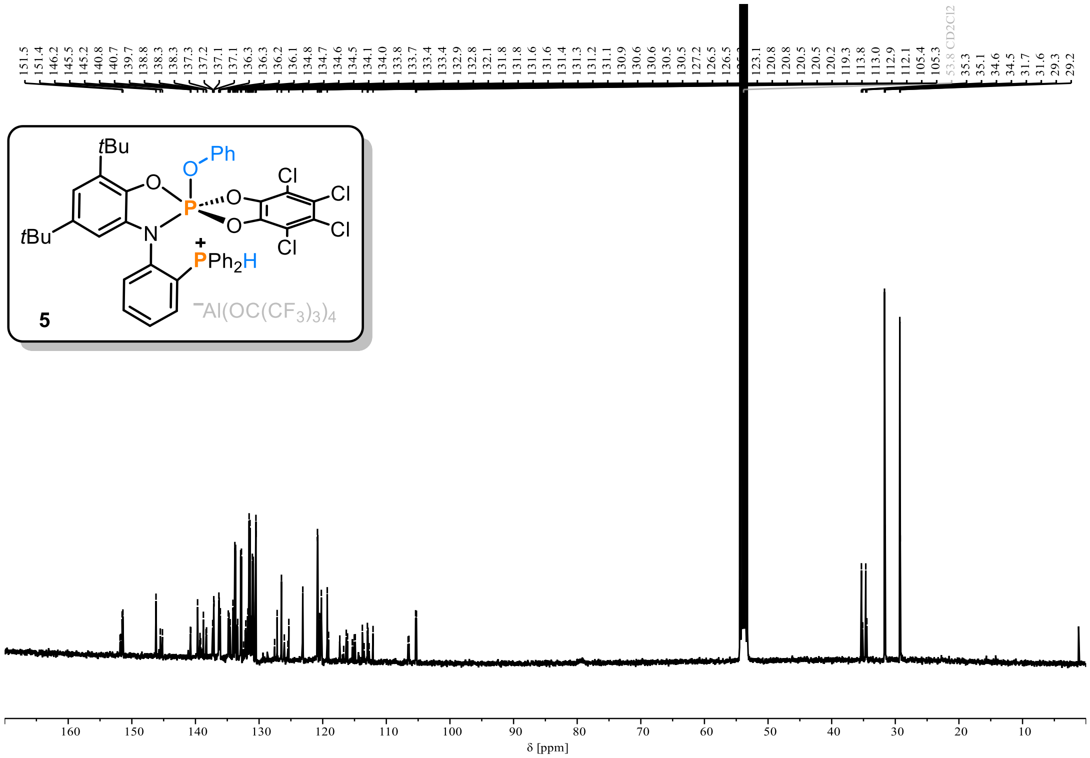


Figure S28: $^{13}C\{^{1}H\}$ **NMR** of **5** (101 MHz, CD_2Cl_2, 295K).

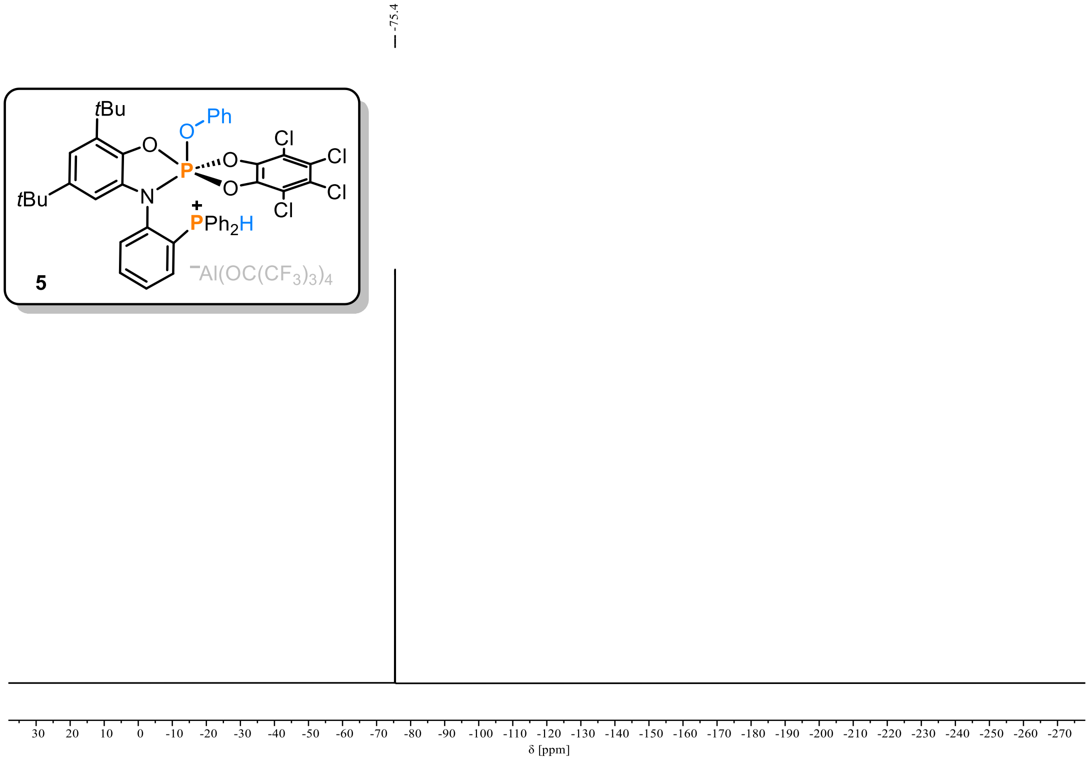


Figure S29: ^{19}F **NMR** of **5** (376 MHz, $CDCl_3$, 295K).

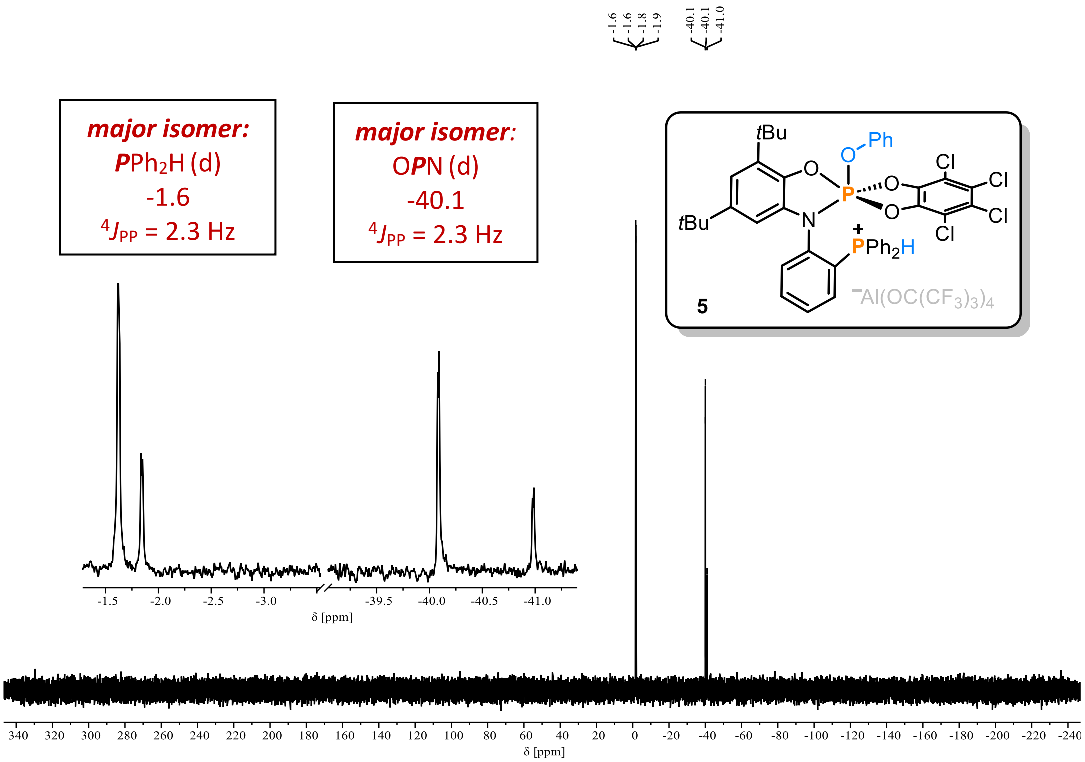


Figure S30: ^{31}**P{^{1}H} NMR** of **5** (162 MHz, CDCl$_3$, 295K).

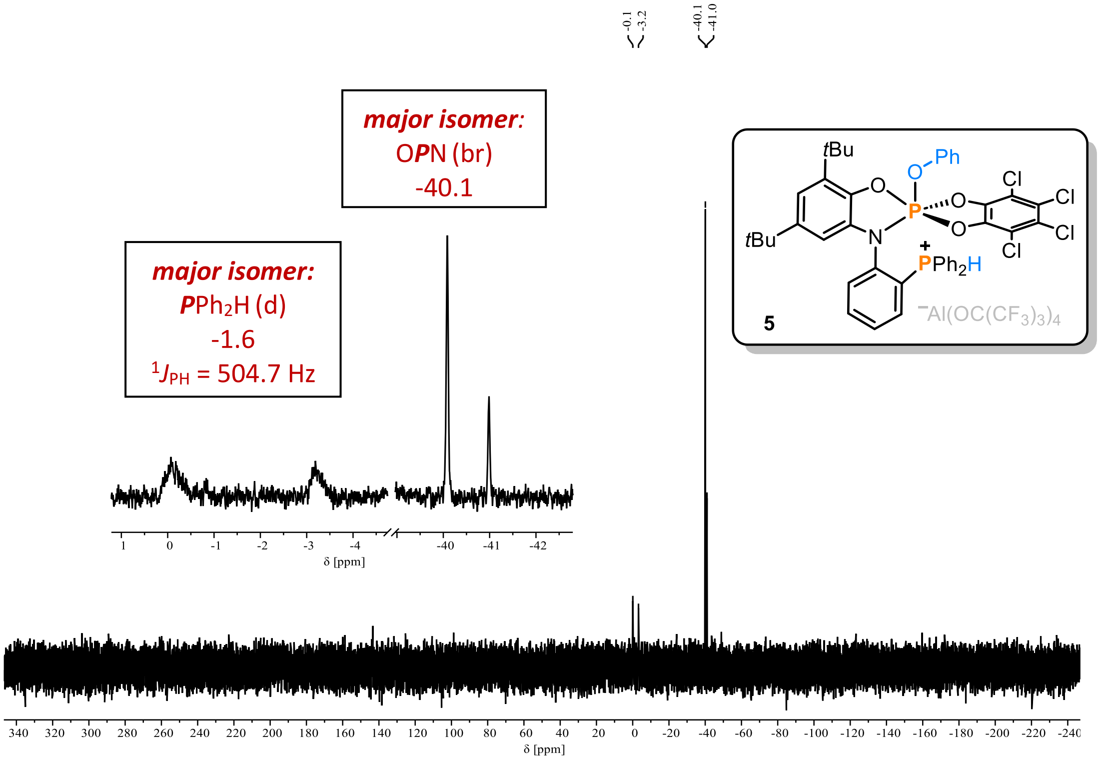


Figure S31: ^{31}**P NMR** of **5** (162 MHz, CDCl$_3$, 295K).

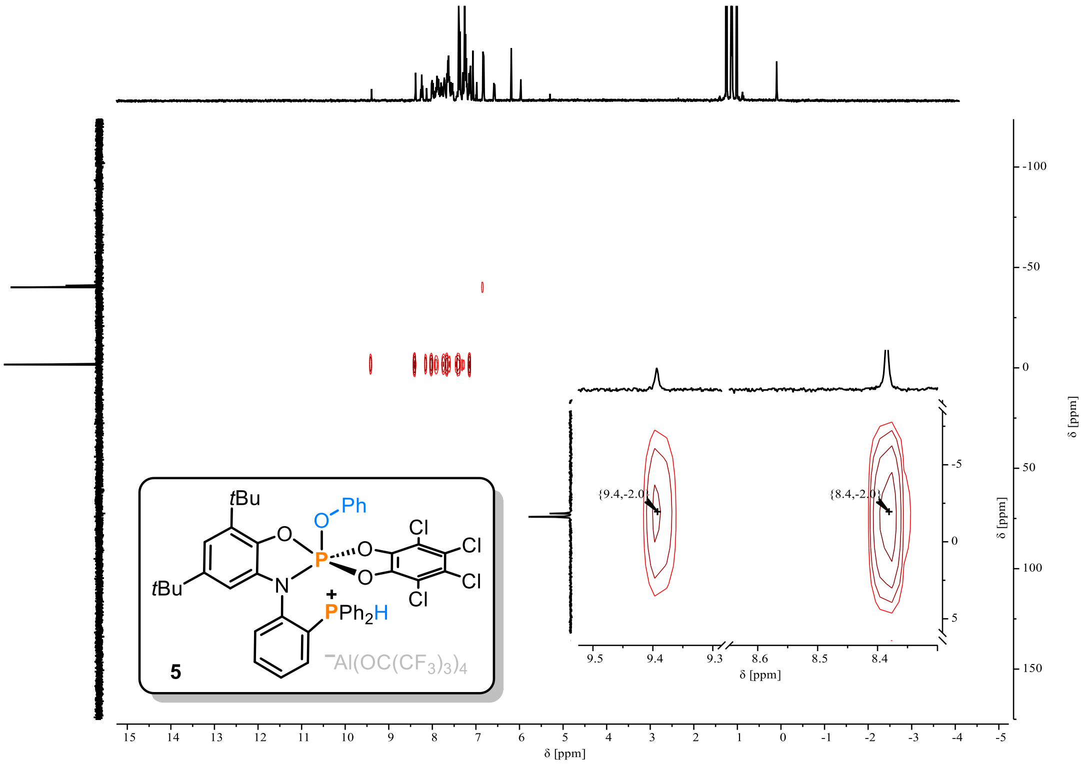


Figure S32: ^{1}H-^{31}P HMBC NMR of **5** (CDCl$_3$, 295K).

2.3 Reactions with Phenylacetylene and Benzaldehyde

2.3.1 Reaction investigations

[**PNOPcat**^{Cl}][Al(OR^F)$_4$] (50 mg, 29 µmol, 1.0 eq) and phenylacetylene (3.0 mg, 29 µmol, 1.0 eq) were dissolved in CH_2Cl_2 (0.4 mL). The affording colorless solution was probed by **^{31}P{^{1}H} NMR** (Figure S33), showing multiple products. The peaks for an isolable product, namely compound **6**, are labeled: δ [ppm] = 77.7 (br, ***P***Ph$_2$), 35.4 (br, O***P***N).

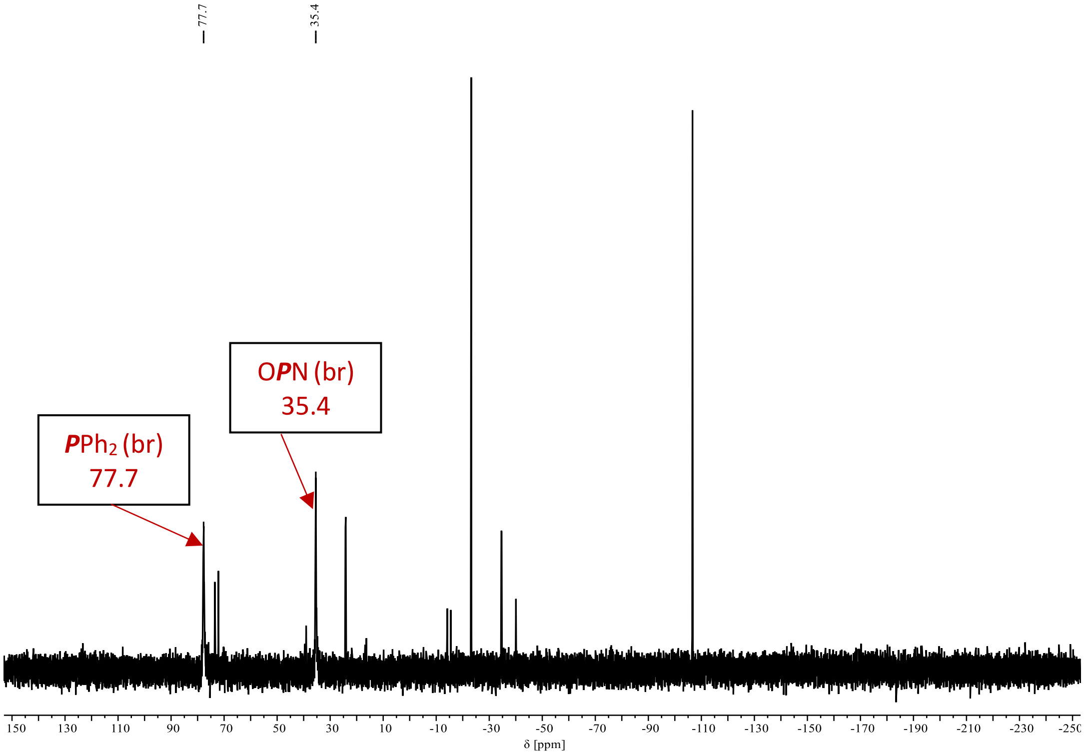


Figure S33: **^{31}P{^{1}H} NMR** (162 MHz, CH_2Cl_2, 295K) for the crude reaction mixture of [**PNOPcat**^{Cl}][Al(OR^F)$_4$] and phenylacetylene. Only peaks for isolated product (**6**) are labeled.

[**PNOPcat^{Cl}**][Al(OR^F)$_4$] (50 mg, 29 µmol, 1.0 eq) and benzaldehyde (3.0 mg, 29 µmol, 1.0 eq) were dissolved in CH_2Cl_2 (0.4 mL). The affording solution was probed by **^{31}P{^{1}H} NMR** (Figure S34), showing multiple products. The peaks for an isolable product, namely compound **7**, are labeled: δ [ppm] = 33.3 (s, ***P***Ph$_2$), 4.8 (s, O=***P***O).

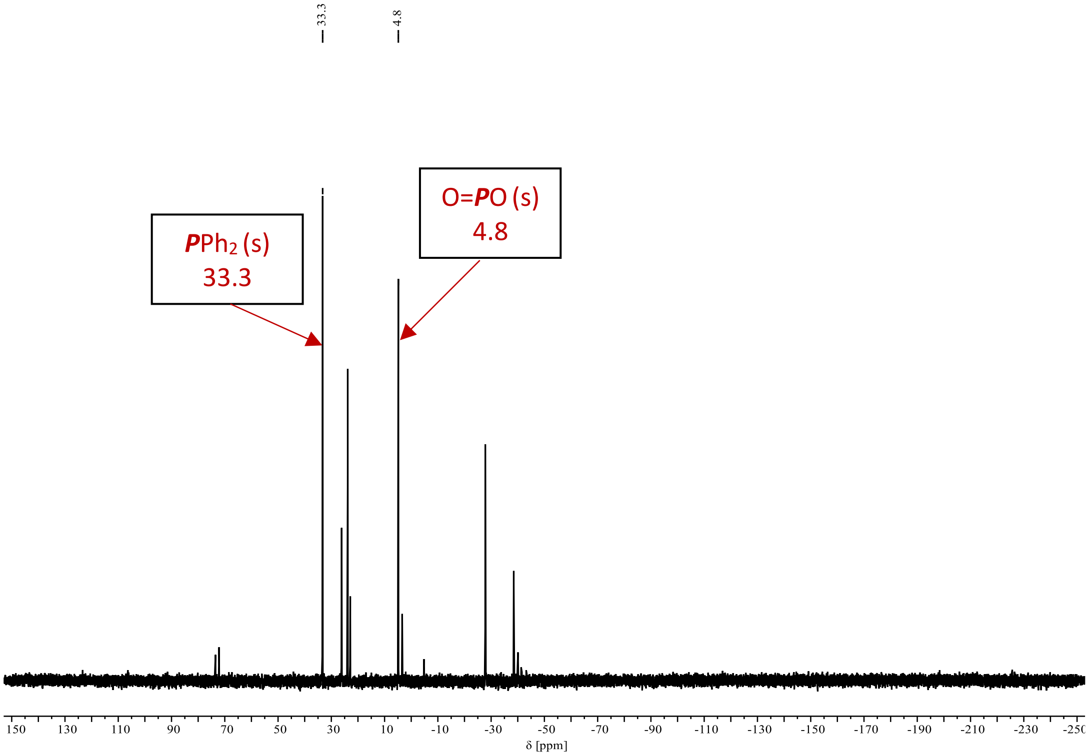
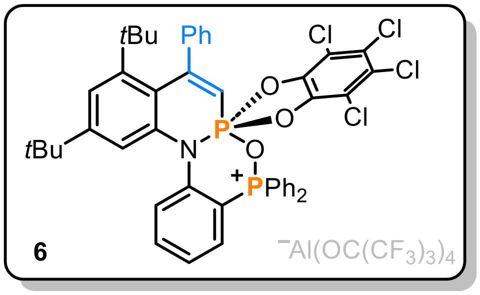


Figure S34: ^{31}P{^{1}H} NMR (162 MHz, CH_2Cl_2, 295K) for the crude reaction mixture of [**PNOPcat^{Cl}**][Al(OR^F)$_4$] and benzaldehyde. Only peaks for isolated product (**7**) are labeled.

2.3.2 Characterization



6

6

[**PNOPcat**$^{\mathrm{Cl}}$][Al(OR$^{\mathrm{F}}$)$_4$] (50 mg, 29 µmol, 1.0 eq) and phenylacetylene (3.0 mg, 29 µmol, 1.0 eq) were dissolved in CH_2Cl_2 (0.4 mL), which was stirred at room temperature overnight. Then *n*-pentane was introduced in the gas phase and allowed to diffuse into the solution at -40 °C for few days until white solids precipitated out. Then removed the solvent under reduced pressure. The product was washed with *n*-pentane and dried *in vacuo* to give the target compound as a white solid (16 mg, 8.8 µmol, 30%). Single crystals suitable for X-ray diffraction were grown by gas phase diffusion of *n*-pentane into the solution in CH_2Cl_2 at -40 °C.

^{1}H NMR (400 MHz, $CDCl_3$, 295K): δ [ppm] = 8.16 (br, 1H), 8.11 – 7.98 (m, 1H), 8.00 – 7.90 (m, 1H), 7.88 – 7.66 (m, 8H), 7.61 (dd, J = 11.1, 7.6 Hz, 1H), 7.55 – 7.41 (m, 6H), 7.31 – 7.18 (m, 1H), 6.47 (br, 1H), 6.28 (br, 1H), 6.26 (d, J = 21.5 Hz, 1H), 1.39 (s, 9H), 1.06 (s, 9H).

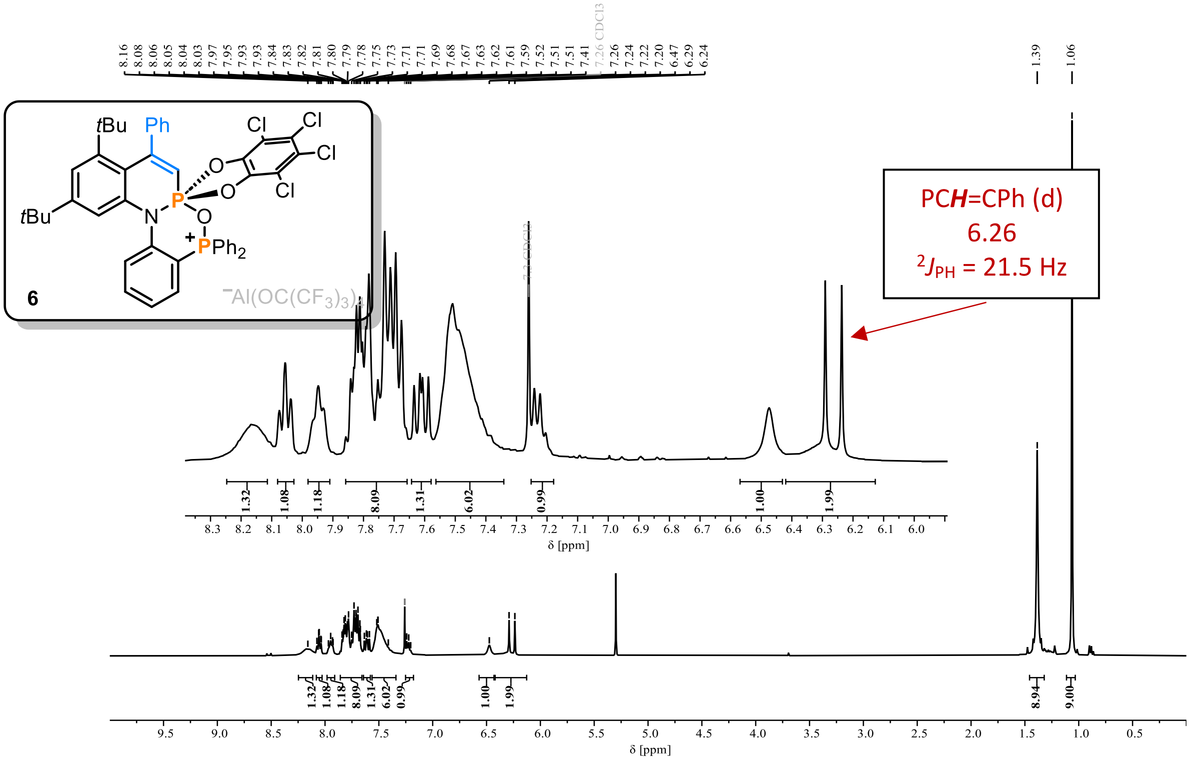
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 295K): δ [ppm] = 162.1 (d, J = 10.4 Hz), 153.6 (d, J = 2.7 Hz), 150.5 (s), 140.7 (d, J = 1.4 Hz), 140.5 (d, J = 2.1 Hz), 139.0 (br), 138.2 (d, J = 2.9 Hz), 137.6 (s), 137.4 (br), 137.0 (br), 135.5 (br), 134.1 (d, J = 13.2 Hz), 133.8 (d, J = 13.9 Hz), 132.7 (s), 131.2 (d, J = 15.6 Hz), 130.8 (d, J = 2.6 Hz), 130.7 (d, J = 3.0 Hz), 129.7 (s), 129.2 (d, J = 1.2 Hz), 129.1 (d, J = 3.4 Hz), 128.4 (d, J = 6.6 Hz), 127.6 (br), 125.4 (d, J = 14.5 Hz), 123.5 (br), 121.4 (q, J = 293.2 Hz, OC(***C***F$_3$)$_3$), 118.8 (s), 117.8 (s), 117.3 (s), 117.2 (s), 116.8 (s), 116.7 (s), 108.8 (s), 106.9 (s), 38.6 (s), 34.9 (s), 33.3 (s), 30.8 (s).

^{19}F NMR (377 MHz, $CDCl_3$, 295K): δ [ppm] = -75.5.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 295K): δ [ppm] =78.1 (br, ***P***Ph$_2$), 35.9 (br, O***P***N).

HRMS (ESI): $[M]^+ = [C_{46}H_{40}Cl_4NO_3P_2]^+$, calculated: 856.1232, found: 856.1195.

Elem. Anal. for $C_{62}H_{40}AlCl_4F_{36}NO_7P_2$ calculated: C, 40.79; H, 2.21; N, 0.77; found: C, 41.18; H, 2.84; N, 1.08.



PC*H*=CPh (d)
6.26
$^2J_{PH}$ = 21.5 Hz

Figure S35: ^{1}H NMR of **6** (400 MHz, $CDCl_3$, 295K).

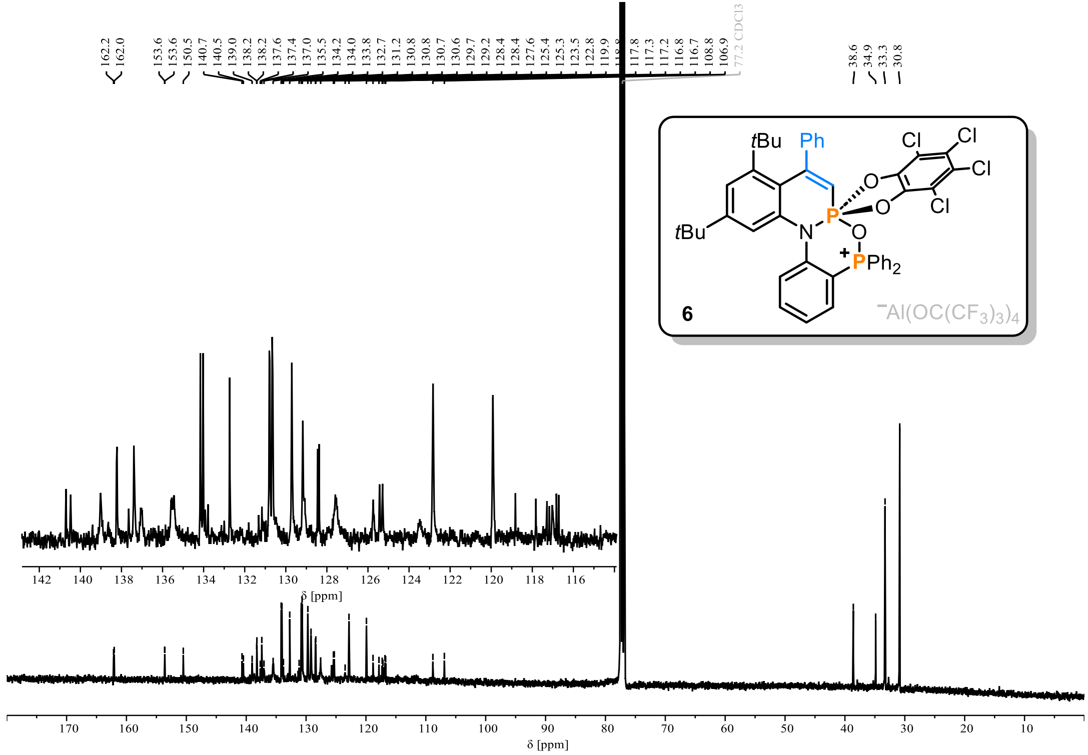


Figure S36: $^{13}C\{^1H\}$ NMR of **6** (101 MHz, $CDCl_3$, 295K).

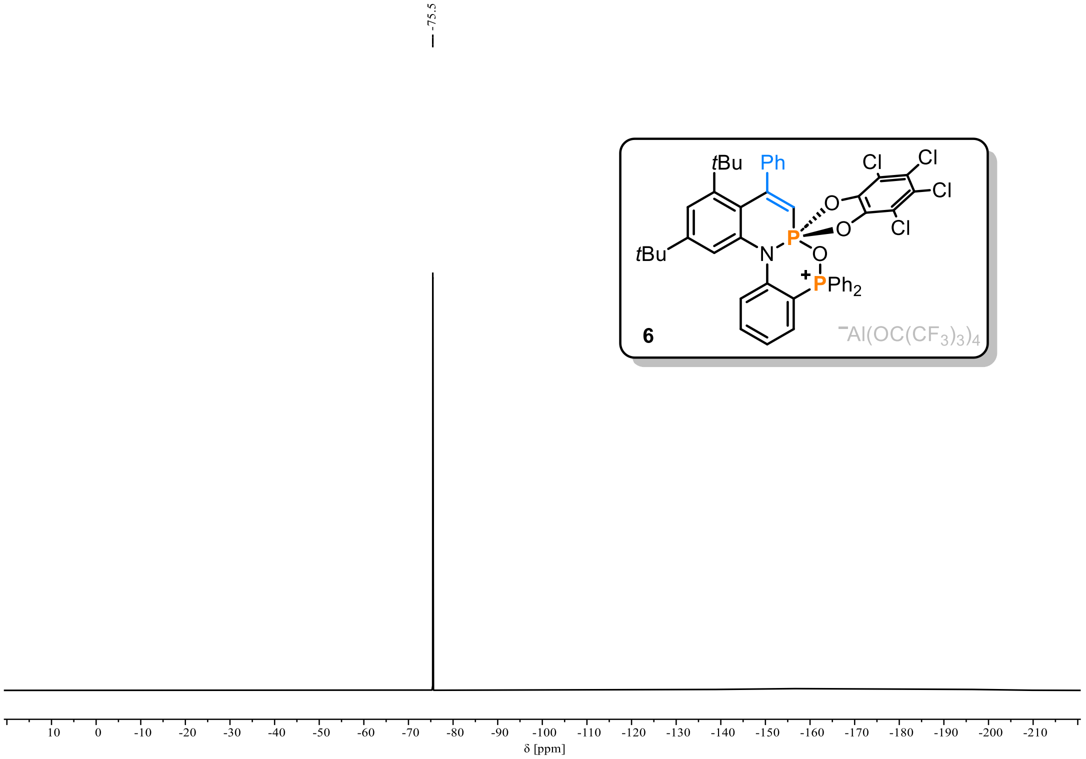


Figure S37: ^{19}**F NMR** of **6** (377 MHz, CDCl$_3$, 295K).

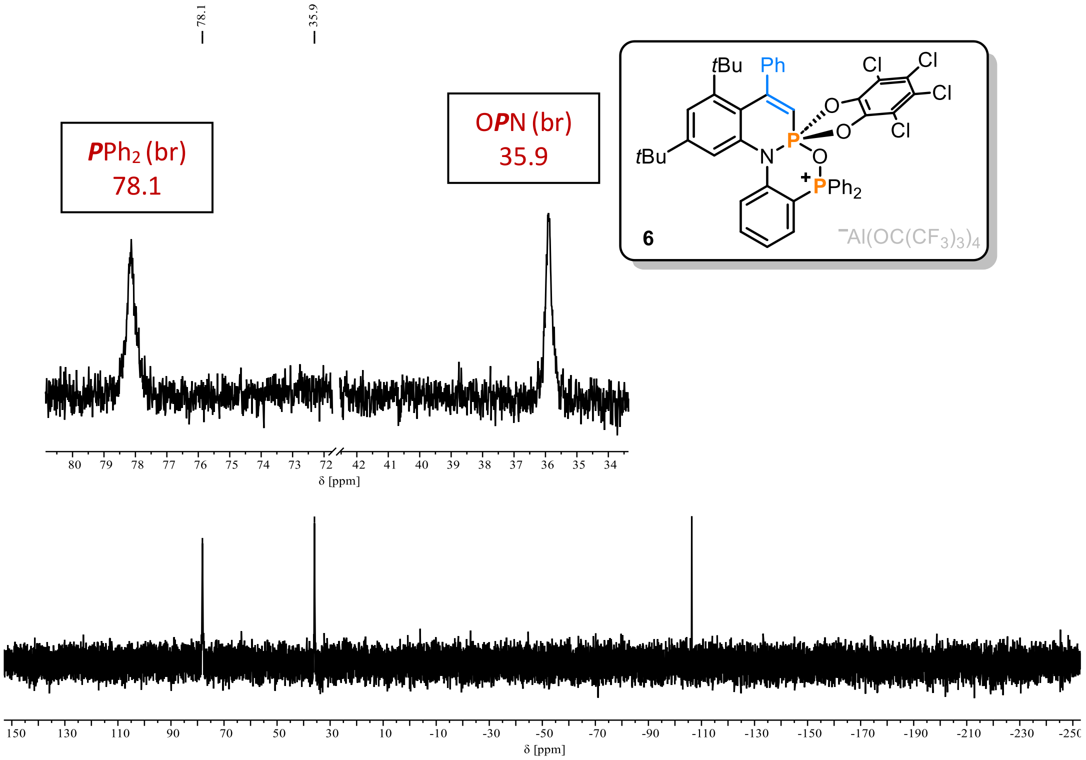


Figure S38: ^{31}**P{^{1}H} NMR** of **6** (162 MHz, CDCl$_3$, 295K), containing trace of impurities with a sharp peak.

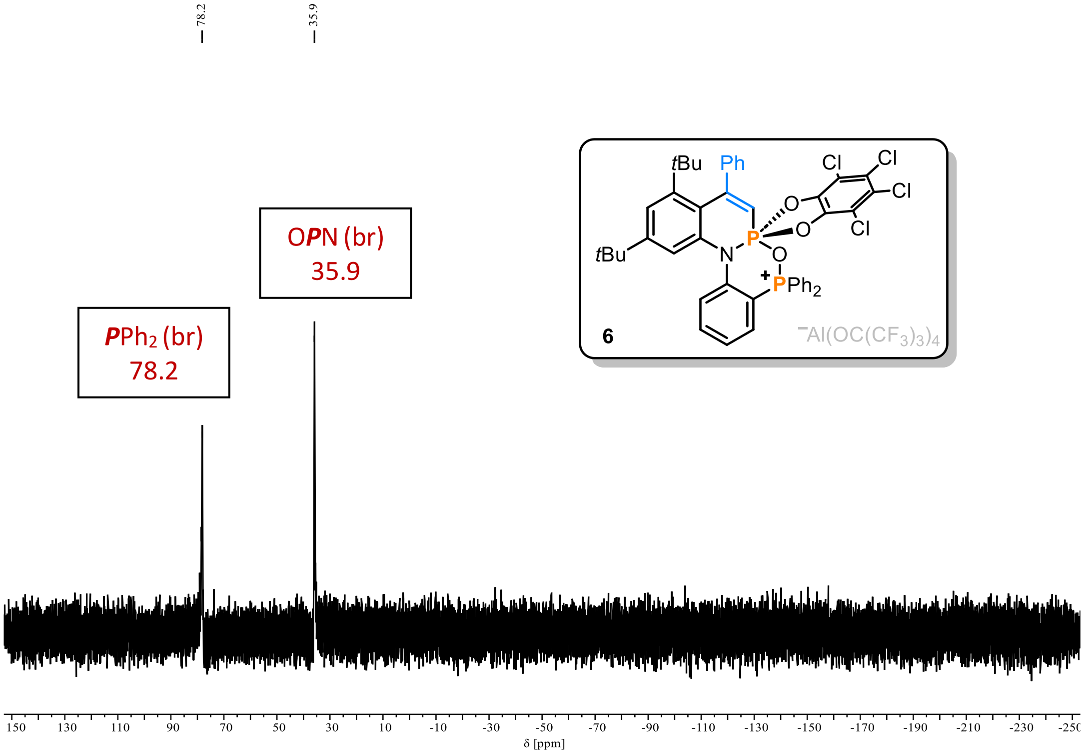


Figure S39: ^{31}**P NMR** of **6** (162 MHz, CDCl$_3$, 295K).

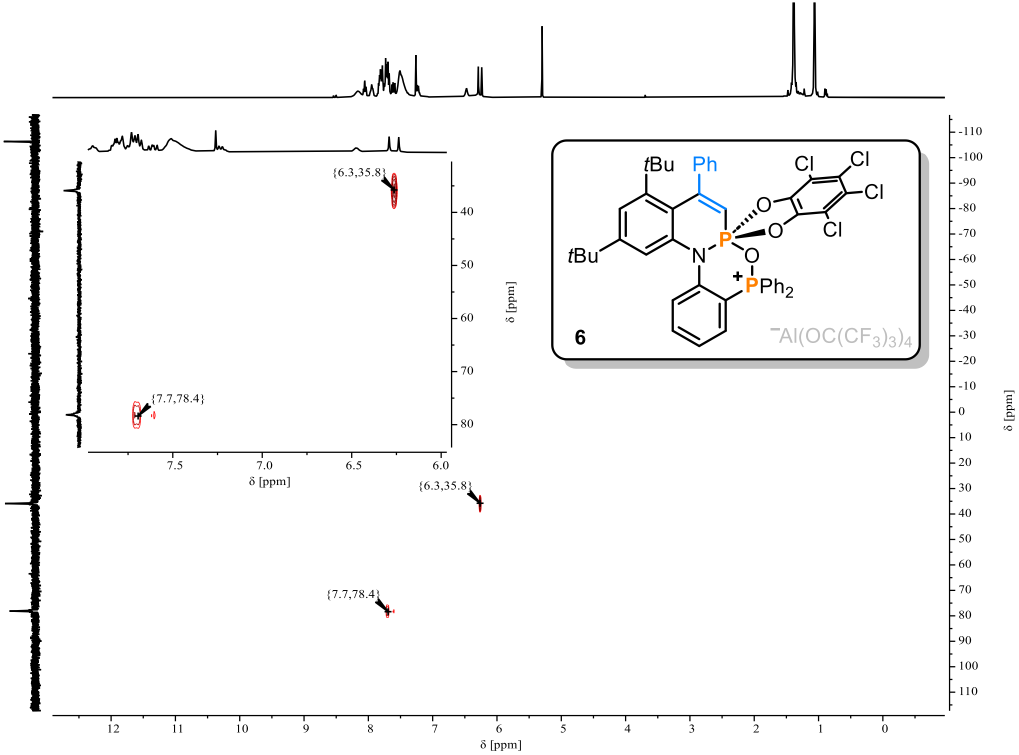
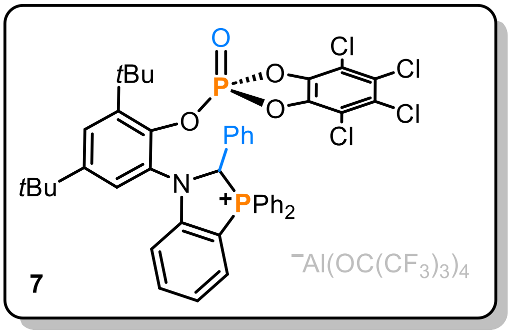


Figure S40: ^{1}**H-**^{31}**P HMBC NMR** of **6** (CDCl$_3$, 295K).



7

7

[**PNOPcat^{Cl}**][Al(OR^F)$_4$] (50 mg, 29 µmol, 1.0 eq) and benzaldehyde (3.0 mg, 29 µmol, 1.0 eq) were dissolved in CH_2Cl_2 (0.4 mL), which was stirred at room temperature overnight. Then *n*-pentane was introduced in the gas phase and allowed to diffuse into the solution at -40 °C for few days until white solids precipitated out. The solvent was removed under reduced pressure. The product was washed with *n*-pentane and dried *in vacuo* to give the target compound as a white solid (10 mg, 5.5 µmol, 19%). Single crystals suitable for X-ray diffraction were grown by gas phase diffusion of *n*-pentane into the solution in CH_2Cl_2 at -40 °C.

^{1}H NMR (400 MHz, CD_2Cl_2, 295K): δ [ppm] = 8.09 (dd, *J* = 13.0, 7.6 Hz, 2H), 7.91 (t, *J* = 8.6 Hz, 1H), 7.84 (t, *J* = 7.9 Hz, 1H), 7.77 – 7.68 (m, 4H), 7.50 – 7.43 (m, 2H), 7.41 – 7.36 (m, 2H), 7.30 – 7.19 (m, 3H), 7.11 (t, *J* = 7.4 Hz, 2H), 6.97 – 6.90 (m, 3H), 6.85 (dd, *J* = 8.9, 3.8 Hz, 1H), 6.76 (d, *J* = 9.1 Hz, 1H), 1.31 (s, 9H), 1.04 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 295K): δ [ppm] = 150.8, 147.9, 143.9, 139.1, 134.3, 134.2, 133.1, 133.0, 130.8, 130.6, 130.4, 130.3, 129.6, 125.7, 125.0, 122.9, 119.9, 117.3, 116.2, 35.3, 35.0, 30.9, 30.4. Signals were not fully included and reliably assigned due to low intensities.

^{19}F NMR (377 MHz, $CDCl_3$, 295K): δ [ppm] = -75.5.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 295K): δ [ppm] = 34.0 (s, ***P***Ph$_2$), 5.3 (s, O=***P***O).

HRMS (ESI): [M]$^+$ = [$C_{45}H_{40}Cl_4NO_4P_2$]$^+$, calculated: 860.1181, found: 860.1153.

Elem. Anal. for $C_{61}H_{40}AlCl_4F_{36}NO_8P_2$ x 0.5 C_5H_{12} calculated: C, 40.88; H, 2.49; N, 0.75; found: C, 40.93; H, 2.92; N, 0.97. (C_5H_{12} content estimated from **^{1}H NMR** measurements).

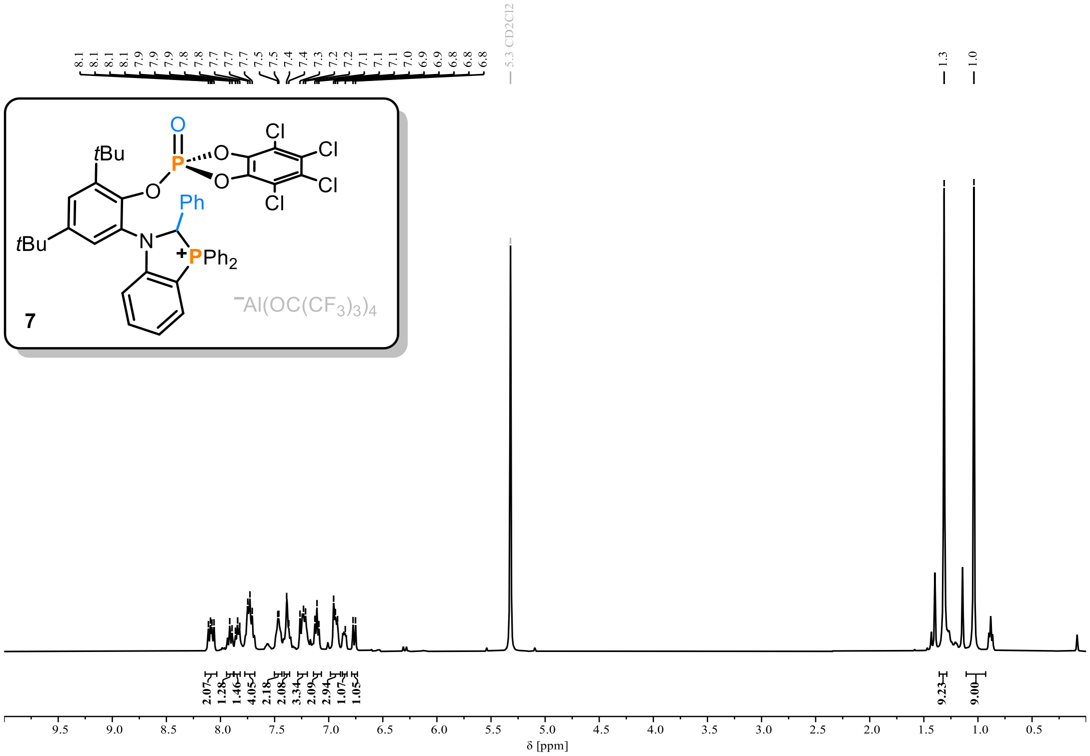


Figure S41: ^{1}**H NMR** of **7** (400 MHz, CD_2Cl_2, 295K).

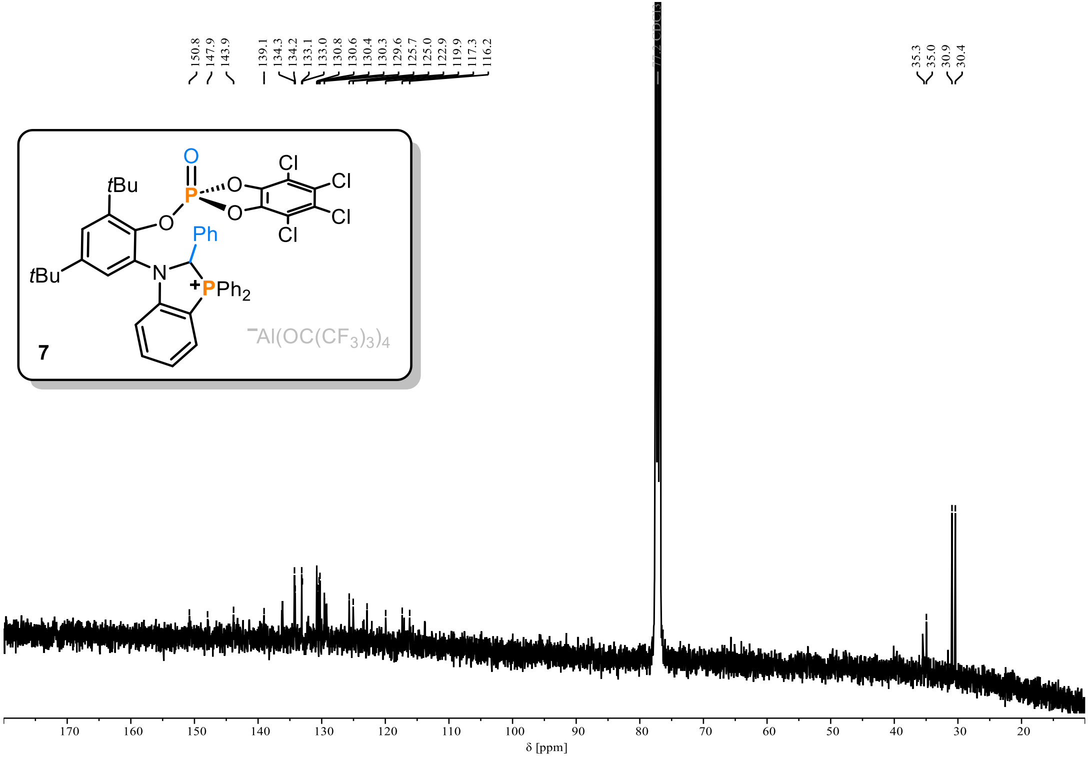


Figure S42: ^{13}**C NMR** of **7** (101 MHz, $CDCl_3$, 295K).

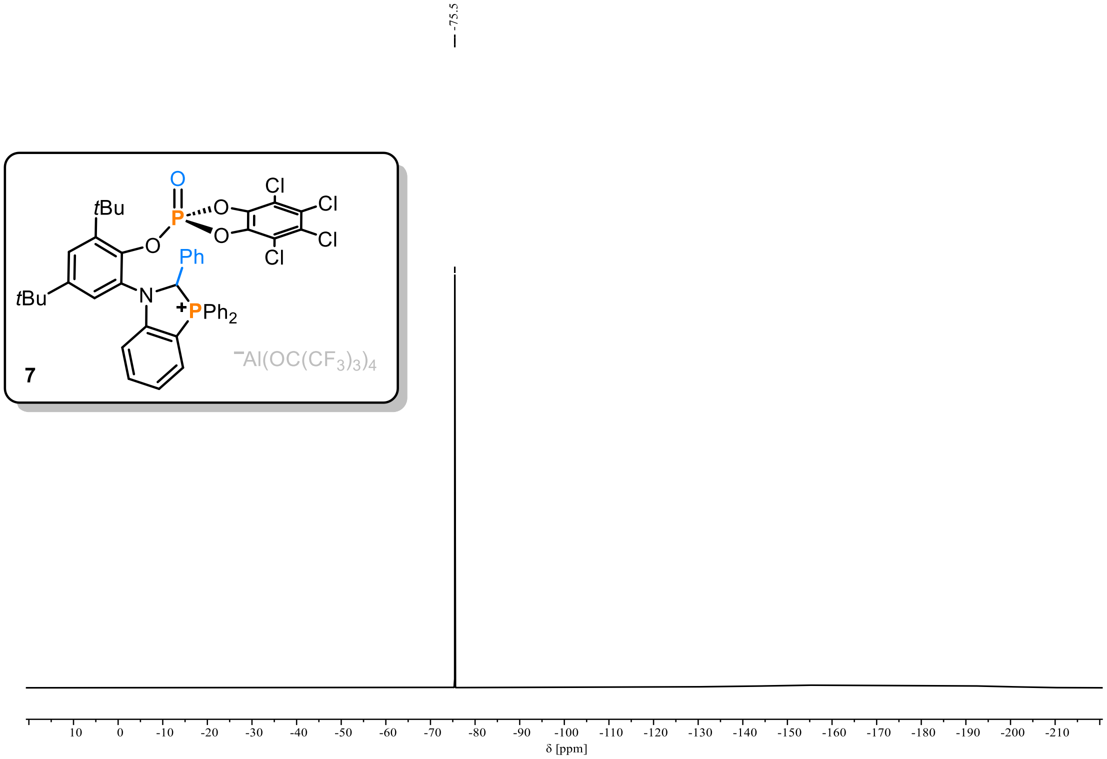


Figure S43: ^{19}F NMR of **7** (377 MHz, CDCl$_3$, 295K).

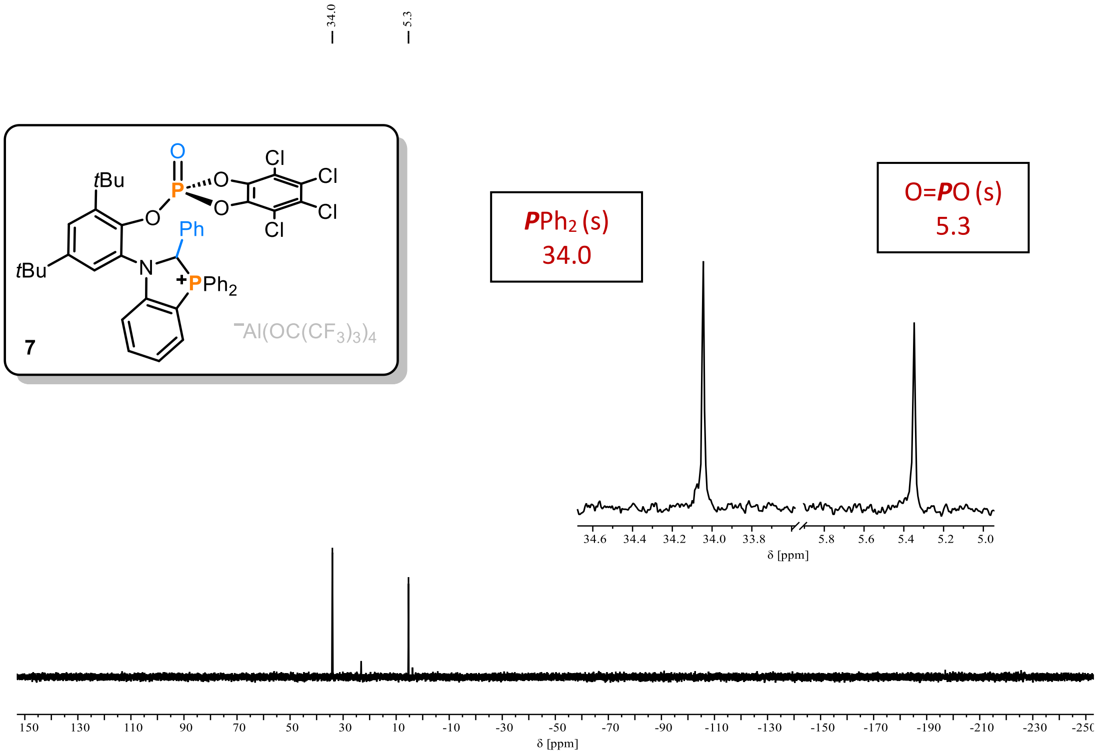


Figure S44: ^{31}P{^{1}H} NMR of **7** (162 MHz, CDCl$_3$, 295K).

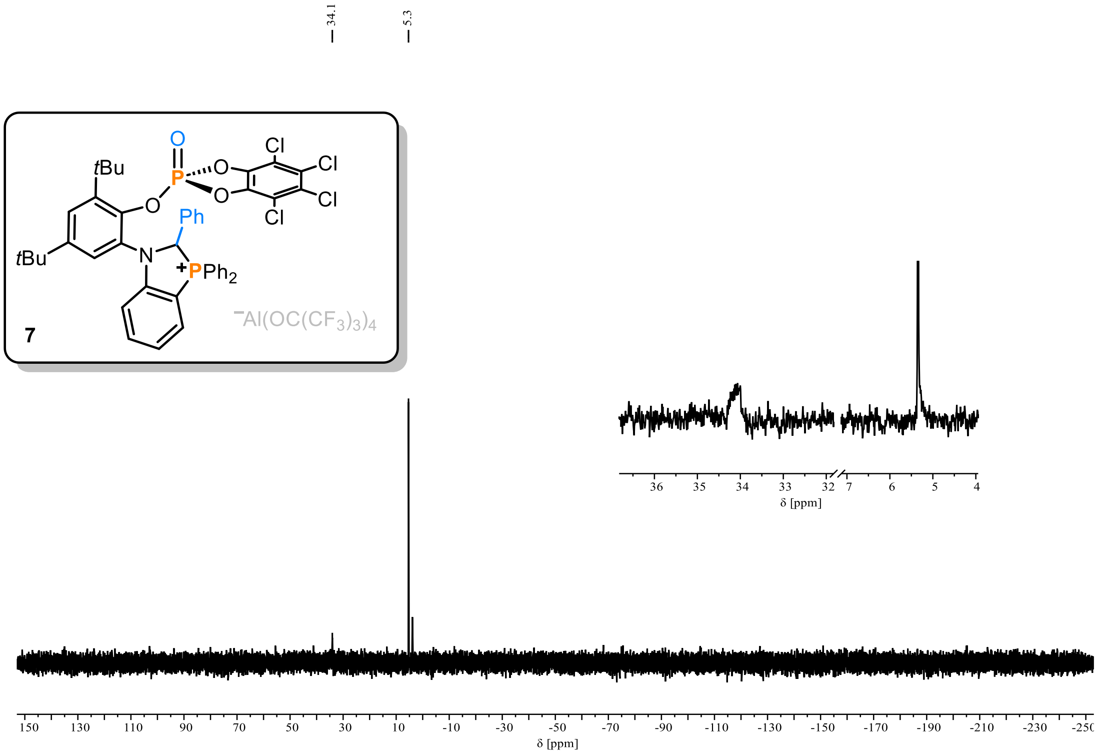


Figure S45: ^{31}**P NMR** of **7** (162 MHz, CDCl$_3$, 295K).

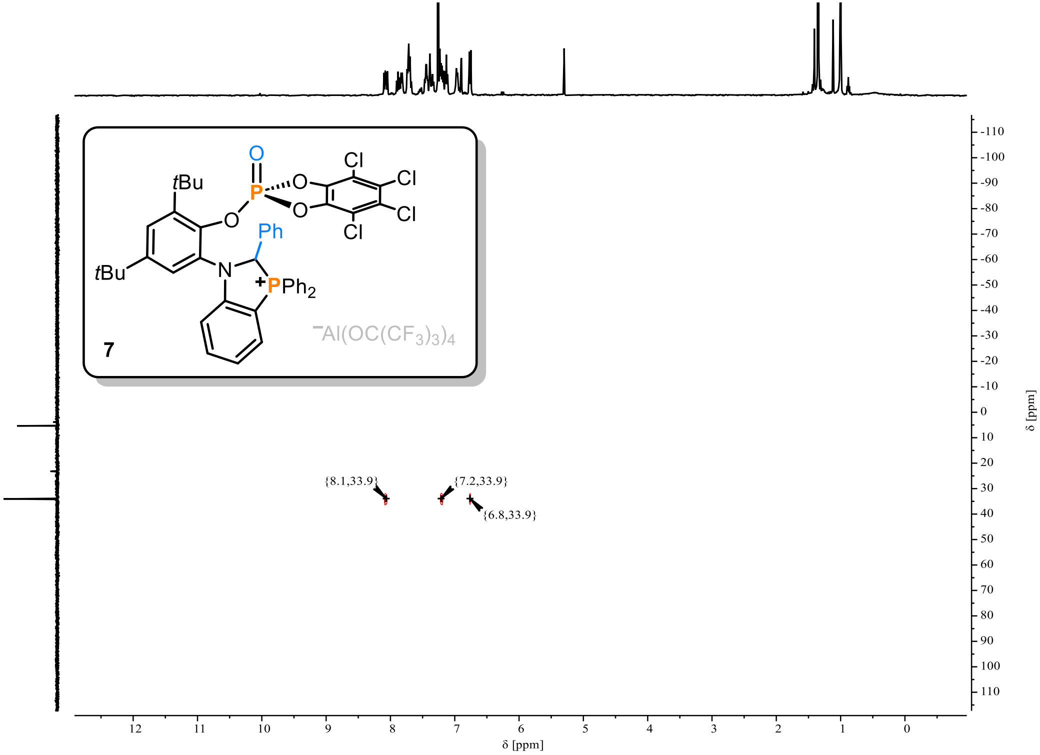


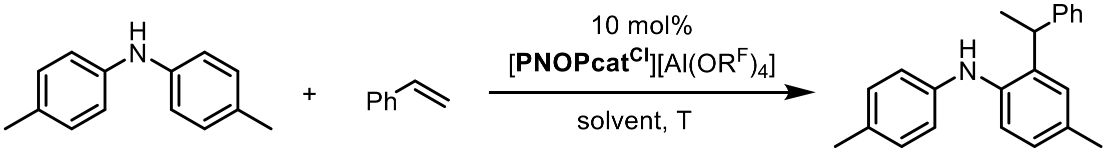
Figure S46: ^{1}**H-**^{31}**P HMBC NMR** of **7** (CDCl$_3$, 295K).

3. Catalytic Hydroarylation of Alkenes

3.1 Reaction Development

General procedure: di-*p*-tolylamine (x eq), styrene (10.4 mg, 0.1 mmol, 1.0 eq), **[PNOPcat^{Cl}][Al(OR^F)$_4$]** (17.2 mg, 0.01 mmol, 10 mol%), and solvent (0.3 mL) were charged in a J. Young type NMR tube. The reaction mixture was kept at the indicated temperature until **^{1}H NMR** showed the full consumption of alkene. Then, 1.0 eq cyclooctane was added as the internal standard to obtain the NMR yield. Isolated yields are shown in the brackets (Table S1).

Table S1. Development of hydroarylation of styrene with di-*p*-tolylamine.[a]



8b, x eq   **9a**, 1.0 eq   **10b**

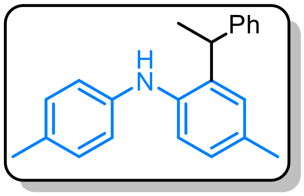
entry	x	T/°C	solvent	yield
1	1.0	80	$CDCl_3$	53%
2	1.0	80	CD_2Cl_2	54%
3	1.0	80	C_6D_6	63%
4	1.0	80	toluene	59% (49%)
5[b]	1.0	60	C_6D_6	55%
6[c]	1.0	100	C_6D_6	67%
7	2.0	80	C_6D_6	86%
8	3.0	80	C_6D_6	90%
9	**4.0**	**80**	**C_6D_6**	**95% (90%)**

[a]Conditions: 10 mol% **[PNOPcat^{Cl}][Al(OR^F)$_4$]**, styrene (1.0 eq), overnight at indicating temperature. Yields are determined by **^{1}H NMR** spectroscopy using cyclooctane as internal standard. [b]23 h heating at 60 °C, 16% of styrene remained. [C]6 h heating at 100 °C**.**

3.2 Substrate Scope

General procedure: arylamine **8** (0.4 mmol, 4.0 eq), alkene **9** (0.1 mmol, 1.0 eq), [**PNOPcat**^{Cl}][Al(OR^F)$_4$] (17.2 mg, 0.01 mmol, 10 mol%), and C_6H_6 (0.3 mL) were charged in a J. Young type NMR tube. The reaction mixture was kept at the indicated temperature until **^{1}H NMR** showed a full consumption of alkene. Then removed the solvent and the crude product was purified by preparative TLC using the indicated gradient of solvents to give the corresponding product **10**.

4-methyl-2-(1-phenylethyl)-*N*-(*p*-tolyl)aniline (10a)

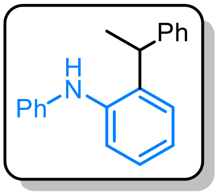


Starting from di-*p*-tolylamine (78.9 mg, 0.4 mmol, 4.0 eq), styrene (10.4 mg, 0.1 mmol, 1.0 eq), and [**PNOPcat**^{Cl}][Al(OR^F)$_4$] (17.2 mg, 0.01 mmol, 10 mol%), 27.2 mg of **10a** were obtained (90%) after 22 h at 80 °C. Preparative TLC using petroleum ether/ethyl acetate 30:1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$, 295K): δ [ppm] = 7.36 (t, J = 7.4 Hz, 2H), 7.32 – 7.21 (m, 4H), 7.16 (d, J = 8.1 Hz, 1H), 7.09 – 6.96 (m, 3H), 6.68 (d, J = 8.0 Hz, 2H), 4.43 (br, N***H***), 4.28 (q, J = 7.2 Hz, 1H), 2.42 (s, 3H), 2.31 (s, 3H), 1.66 (d, J = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 295K): δ [ppm] = 145.9, 142.5, 138.7, 136.7, 131.9, 129.9, 129.1, 128.9, 128.5, 127.7, 127.6, 126.5, 121.3, 116.8, 40.3, 22.0, 21.2, 20.7.

N-phenyl-2-(1-phenylethyl)aniline (10b)



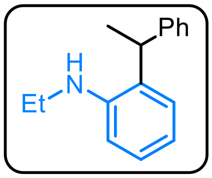
Starting from Ph_2NH (67.7 mg, 0.4 mmol, 4.0 eq), styrene (10.4 mg, 0.1 mmol, 1.0 eq), and [**PNOPcat**^{Cl}][Al(OR^F)$_4$] (17.2 mg, 0.01 mmol, 10 mol%), 18.4 mg of **10b** were obtained (67%) after 24 h at 80 °C. Preparative TLC using petroleum ether/ethyl acetate 30:1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$, 295K): δ [ppm] = 7.44 (dd, J = 7.7, 1.6 Hz, 1H), 7.31 (dd, J = 8.2, 6.8 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.23 – 7.14 (m, 5H), 7.08 (td, J = 7.4, 1.4 Hz, 1H), 6.83 (tt, J = 7.3, 1.0 Hz, 1H), 6.74 (dt, J = 7.7, 1.0 Hz, 2H), 5.18 (br, N***H***), 4.25 (q, J = 7.2 Hz, 1H), 1.63 (d, J = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 295K): δ [ppm] = 145.7, 144.4, 141.0, 136.3, 129.4, 129.0, 127.9, 127.6, 127.2, 126.6, 122.6, 120.6, 120.2, 116.9, 40.5, 22.0.

Data in agreement with: S. Wang, G. Force, R. Guillot, J.-F. Carpentier, Y. Sarazin, C. Bour, V. Gandon and D. Lebœuf, *ACS Cata.*, 2020, **10**, 10794-10802. [2]

N-ethyl-2-(1-phenylethyl)aniline (10c)

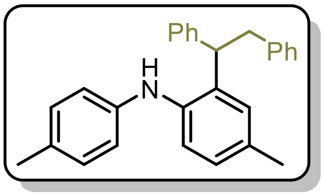


Starting from *N*-ethylaniline (48.5 mg, 0.4 mmol, 4.0 eq), styrene (10.4 mg, 0.1 mmol, 1.0 eq), and [**PNOPcat**$^{\mathbf{Cl}}$][Al(OR^{F})$_4$] (17.2 mg, 0.01 mmol, 10 mol%), 14.6 mg of **10c** were obtained (65%) after 18 h at 120 °C. Preparative TLC using petroleum ether/ethyl acetate 20:1 as eluent.

^{1}H NMR (400 MHz, CDCl$_3$, 295K): δ [ppm] = 7.37 – 7.23 (m, 3H), 7.24 – 7.13 (m, 4H), 6.80 (td, J = 7.4, 1.2 Hz, 1H), 6.63 (d, J = 8.0 Hz, 1H), 4.03 (q, J = 7.2 Hz, 1H), 3.32 (br, N***H***), 3.04 (dq, J = 11.5, 7.1 Hz, 1H), 2.95 (dq, J = 11.4, 7.1 Hz, 1H), 1.63 (d, J = 7.1 Hz, 3H), 1.03 (t, J = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, 295K): δ [ppm] = 146.2, 146.0, 129.2, 128.9, 127.6, 127.5, 127.0, 126.5, 117.0, 111.0, 40.2, 38.6, 22.2, 14.7.

2-(1,2-diphenylethyl)-4-methyl-*N*-(*p*-tolyl)aniline (10e)

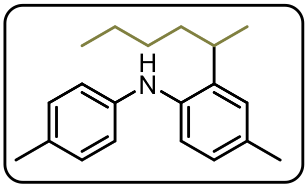


Starting from di-*p*-tolylamine (78.9 mg, 0.4 mmol, 4.0 eq), *cis*-stilbene (18.0 mg, 0.1 mmol, 1.0 eq), and [**PNOPcat**$^{\mathbf{Cl}}$][Al(OR^{F})$_4$] (17.2 mg, 0.01 mmol, 10 mol%), 32.3 mg of **10e** were obtained (86%) after 24 h at 120 °C. Preparative TLC using petroleum ether/ethyl acetate 30:1 as eluent.

^{1}H NMR (400 MHz, CDCl$_3$, 295K): δ [ppm] = 7.40 – 7.24 (m, 7H), 7.19 (d, J = 7.4 Hz, 2H), 7.14 (d, J = 8.1 Hz, 1H), 7.10 – 6.95 (m, 5H), 6.63 (d, J = 8.0 Hz, 2H), 4.72 (br, N***H***), 4.48 (t, J = 7.7 Hz, 1H), 3.49 – 3.31 (m, 2H), 2.42 (s, 3H), 2.34 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, 295K): δ [ppm] = 143.8, 142.8, 140.4, 138.8, 136.5, 132.3, 129.8, 129.4, 128.9, 128.8, 128.6, 128.4, 128.3, 127.8, 126.5, 126.2, 121.8, 116.5, 47.6, 42.2, 21.3, 20.7.

2-(hexan-2-yl)-4-methyl-*N*-(*p*-tolyl)aniline (10f)



Starting from di-*p*-tolylamine (78.9 mg, 0.4 mmol, 4.0 eq), 1-hexene (8.4 mg, 0.1 mmol, 1.0 eq), and [**PNOPcat**$^{\mathbf{Cl}}$][Al(OR^{F})$_4$] (17.2 mg, 0.01 mmol, 10 mol%), 16.9 mg of **10f** were obtained (60%) after 50 h at 120 °C. Preparative TLC using petroleum ether/ethyl acetate 40:1 as eluent.

^{1}H NMR (400 MHz, CDCl$_3$, 295K): δ [ppm] = 7.11 (dd, J = 8.1, 1.3 Hz, 1H), 7.07 (d, J = 1.9 Hz, 1H), 7.05 – 6.99 (m, 2H), 6.95 (dd, J = 8.0, 2.1 Hz, 1H), 6.82 – 6.65 (m, 2H), 5.19 (br, N***H***), 2.97 (qd, J = 7.0, 1.4 Hz, 1H), 2.34 (s, 3H), 2.28 (s, 3H), 1.70 – 1.45 (m, 2H), 1.33 – 1.24 (m, 3H), 1.26 – 1.13 (m, 1H), 1.21 (d, J = 6.9 Hz, 3H), 0.86 (td, J = 7.1, 1.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, 295K): δ [ppm] = 143.8, 140.7, 137.8, 133.1, 129.8, 128.7, 127.4, 127.1, 122.9, 116.2, 37.6, 32.9, 30.1, 23.0, 21.6, 21.3, 20.7, 14.2.

3.3 Controlled Experiments

3.3.1 Reversible reaction of Ph_2NH with [PNOPcat^{Cl}][Al(OR^F)$_4$]

10 mg **4** and 0.3 mL $CDCl_3$ were given into a J. Young type NMR tube. **^{31}P{^{1}H} NMR** showed two signals at -1.2 and -43.3 ppm. Then the solution was kept at 60 °C for 18 h and was probed by **^{31}P{^{1}H} NMR**. Resonance signals of **[PNOPcat^{Cl}][Al(OR^F)$_4$]** (-12.9 and -15.9 ppm) were observed. Upon standing the solution again at room temperature for several days, the resonance signals at -12.9 and -15.9 ppm diminished progressively (**Figure S47**).

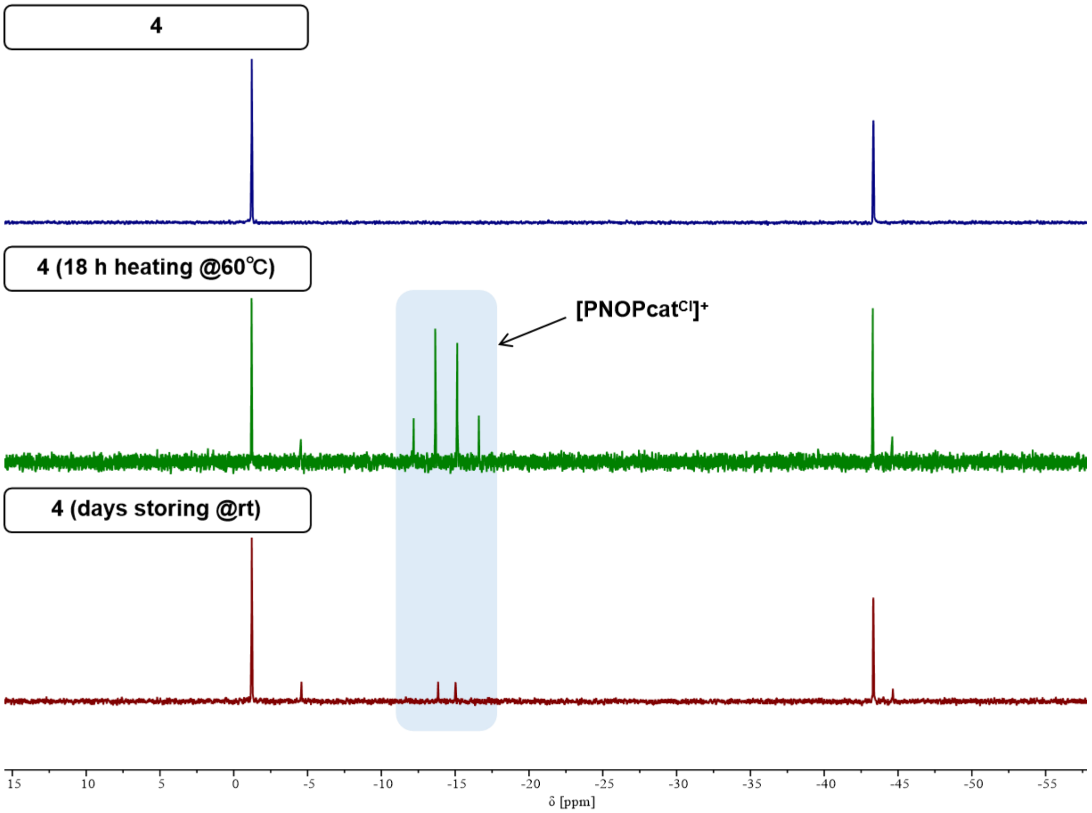


Figure S47: ^{31}P{^{1}H} NMR ($CDCl_3$, 295K) of **4** (up) and after 18 h heating at 60°C (middle) and after storing at room temperature again (down).

3.3.2 Reaction attempts of [PNOPcat^{Cl}][Al(OR^F)$_4$] with styrene

In a J. Young type NMR tube, **[PNOPcat^{Cl}][Al(OR^F)$_4$]** (10.0 mg, 5.8 µmol, 1.0 eq) and 3.0 eq styrene (1.8 mg, 17.4 µmol, 3.0 eq) were dissolved with 0.3 mL CD_2Cl_2. Then the solution was kept at 60 °C for 24 h and probed by multinuclear NMR. Only resonance signals of **[PNOPcat^{Cl}][Al(OR^F)$_4$]** were observed in ^{31}P{^{1}H} NMR (**Figure S48**). A side reaction was attributed to styrene polymerization, in line with some broad signals in ^{1}H NMR (**Figure S49**).

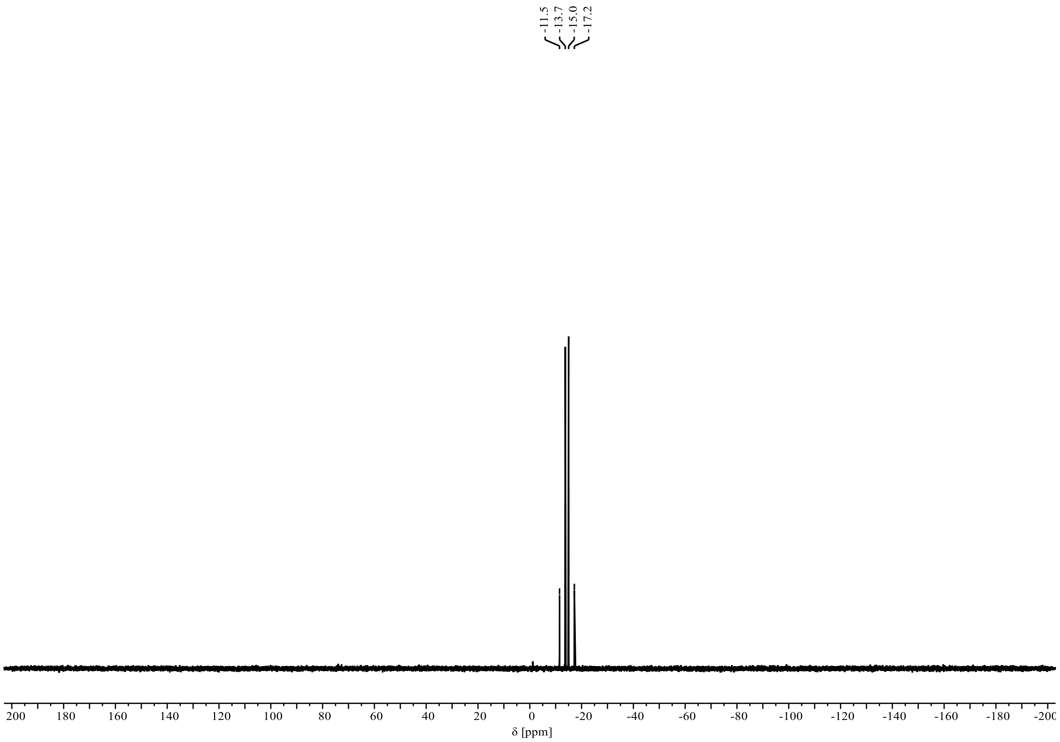


Figure S48: $^{31}P\{^{1}H\}$ **NMR** (CD_2Cl_2, 295K) of the mixture solution of **[PNOPcat^{Cl}][Al(OR^{F})$_4$]** and styrene after 24 h heating at 60 °C.

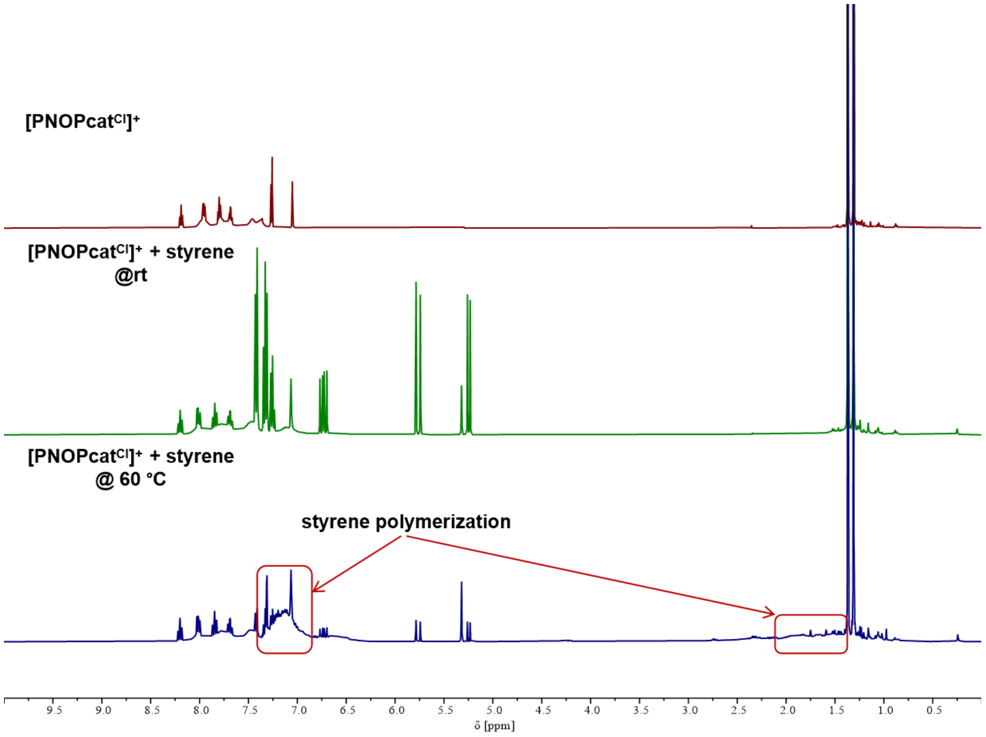


Figure S49: ^{1}H **NMR** (CD_2Cl_2, 295K) of **[PNOPcat^{Cl}][Al(OR^{F})$_4$]** (up) and its mixture solution with styrene at room temperature (middle), after 24 h heating at 60 °C (down).

3.4 Proposed Mechanisms

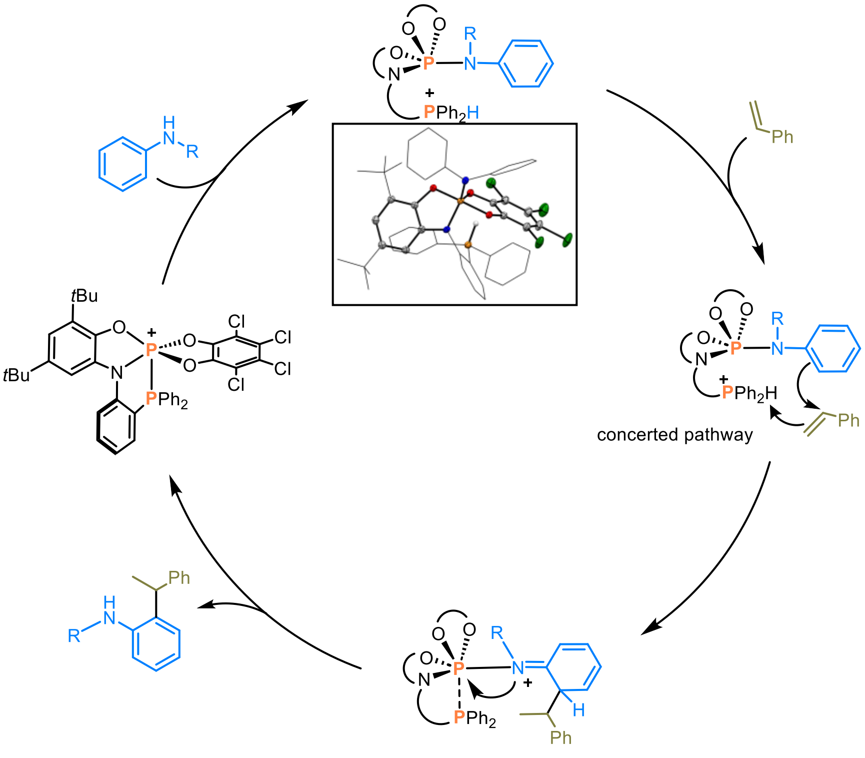


Figure S50: Plausible mechanism 1.

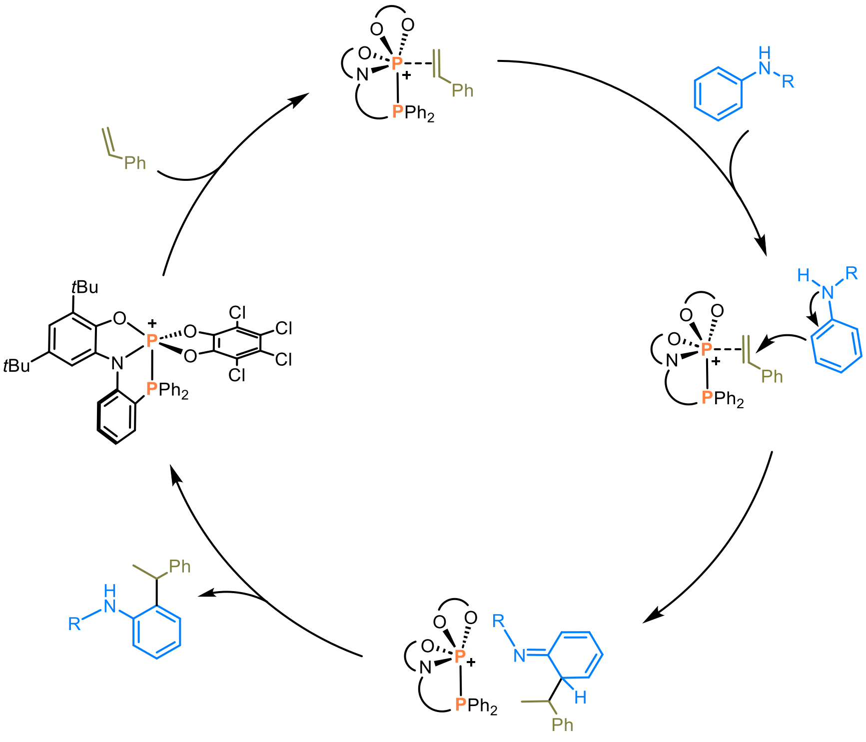


Figure S51: Plausible mechanism 2.

3.5 NMR Spectra

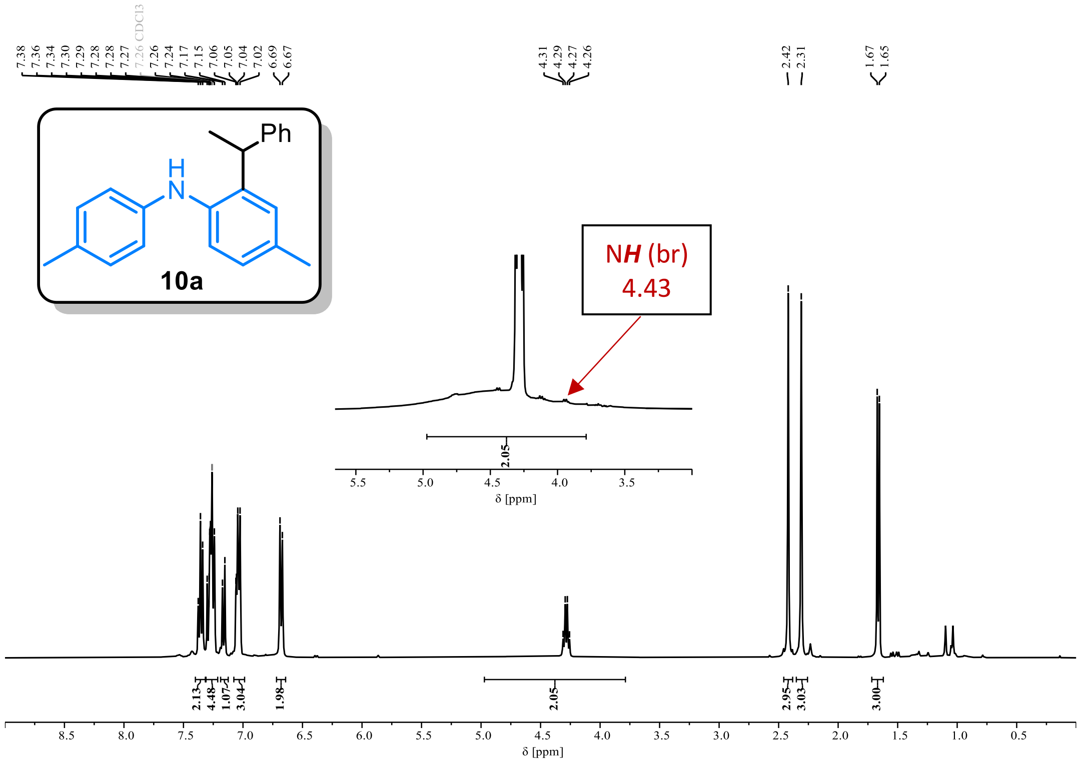


Figure S52: ^{1}**H NMR** of **10a** (400 MHz, CDCl$_3$, 295K).

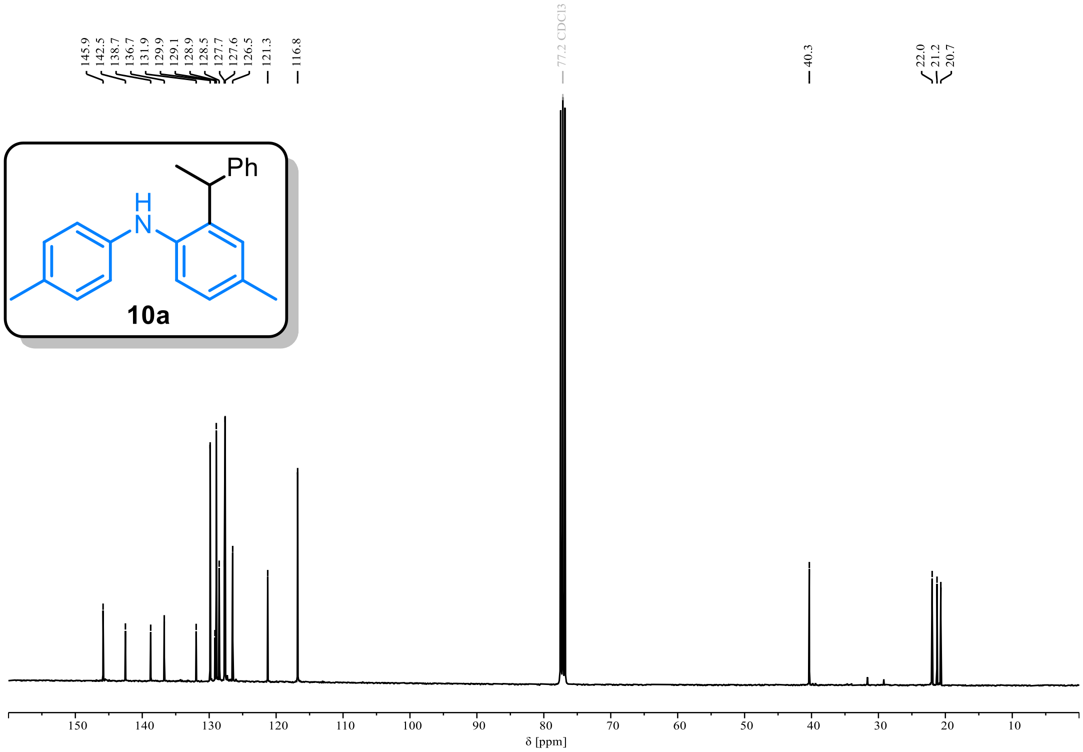


Figure S53: ^{13}**C{**^{1}**H} NMR** of **10a** (101 MHz, CDCl$_3$, 295K).

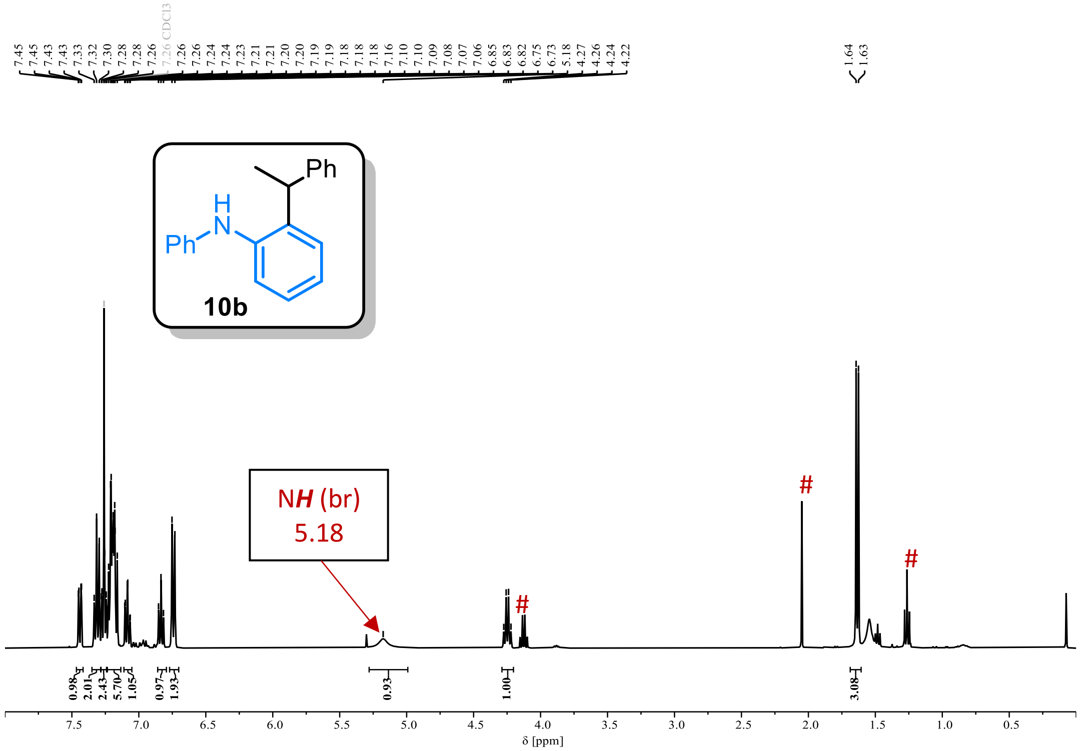


Figure S54: ^{1}**H NMR** of **10b** (400 MHz, $CDCl_3$, 295K). # denotes ethyl acetate.

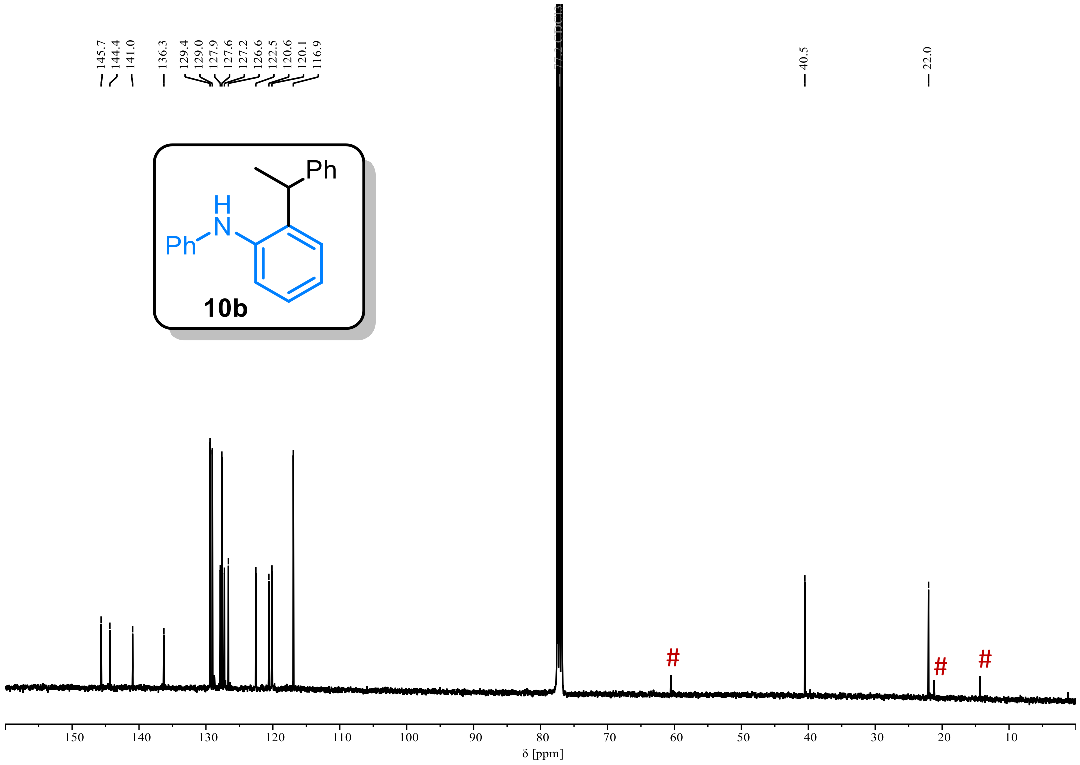


Figure S55: ^{13}**C{^{1}H} NMR** of **10b** (101 MHz, $CDCl_3$, 295K). # denotes ethyl acetate.

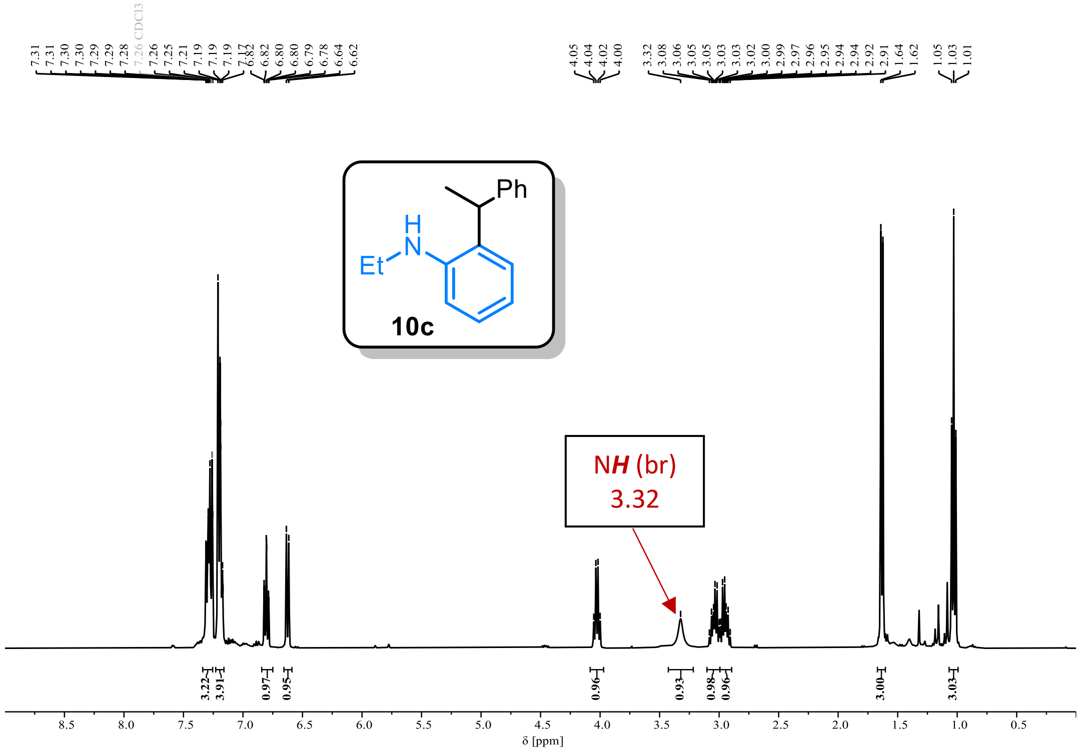


Figure S56: ^{1}**H NMR** of **10c** (400 MHz, $CDCl_3$, 295K).

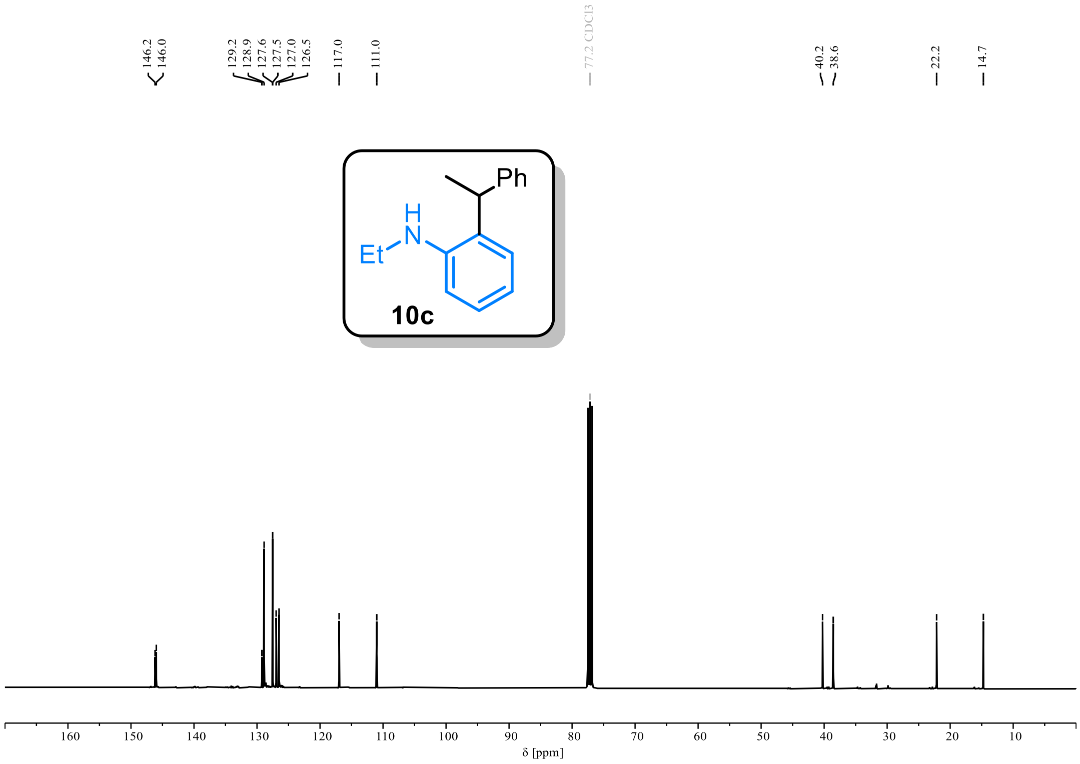


Figure S57: ^{13}**C{**^{1}**H} NMR** of **10c** (101 MHz, $CDCl_3$, 295K).

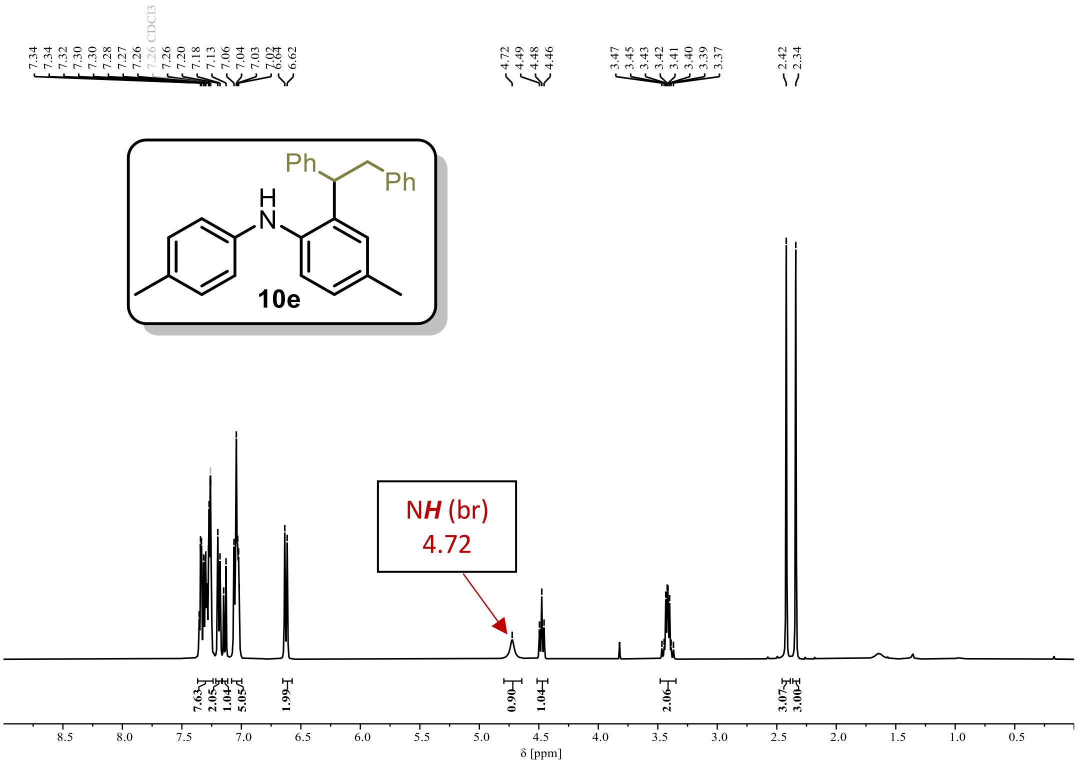


Figure S58: ^{1}**H NMR** of **10e** (400 MHz, $CDCl_3$, 295K).

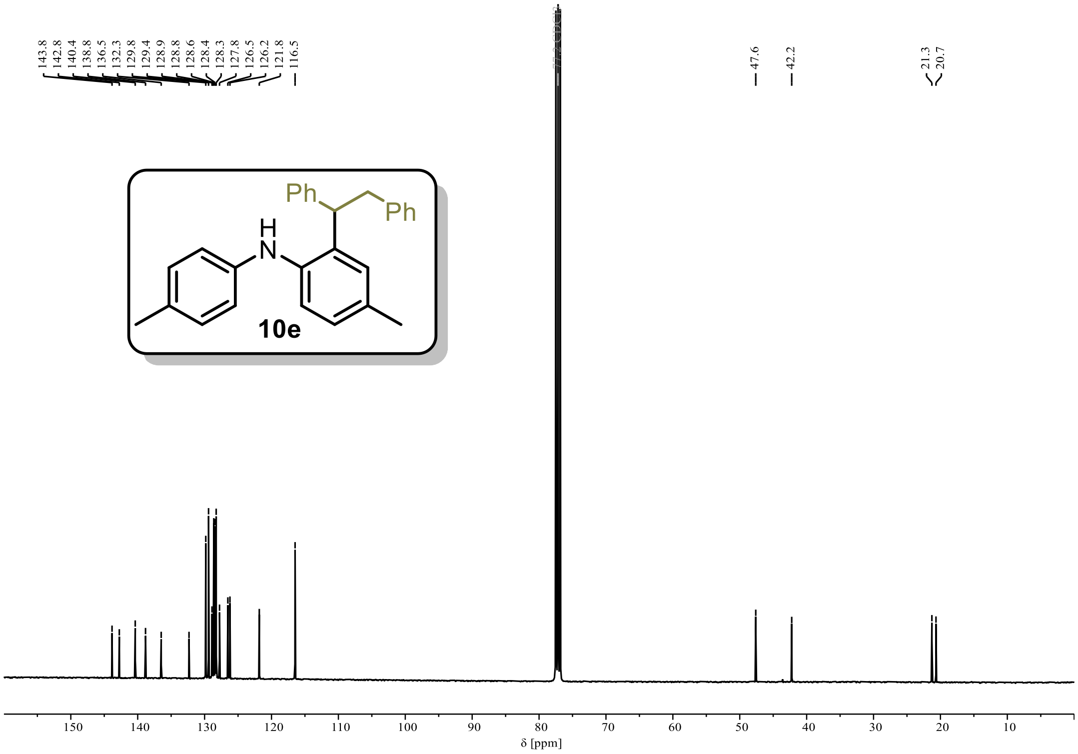


Figure S59: ^{13}**C{**^{1}**H} NMR** of **10e** (101 MHz, $CDCl_3$, 295K).

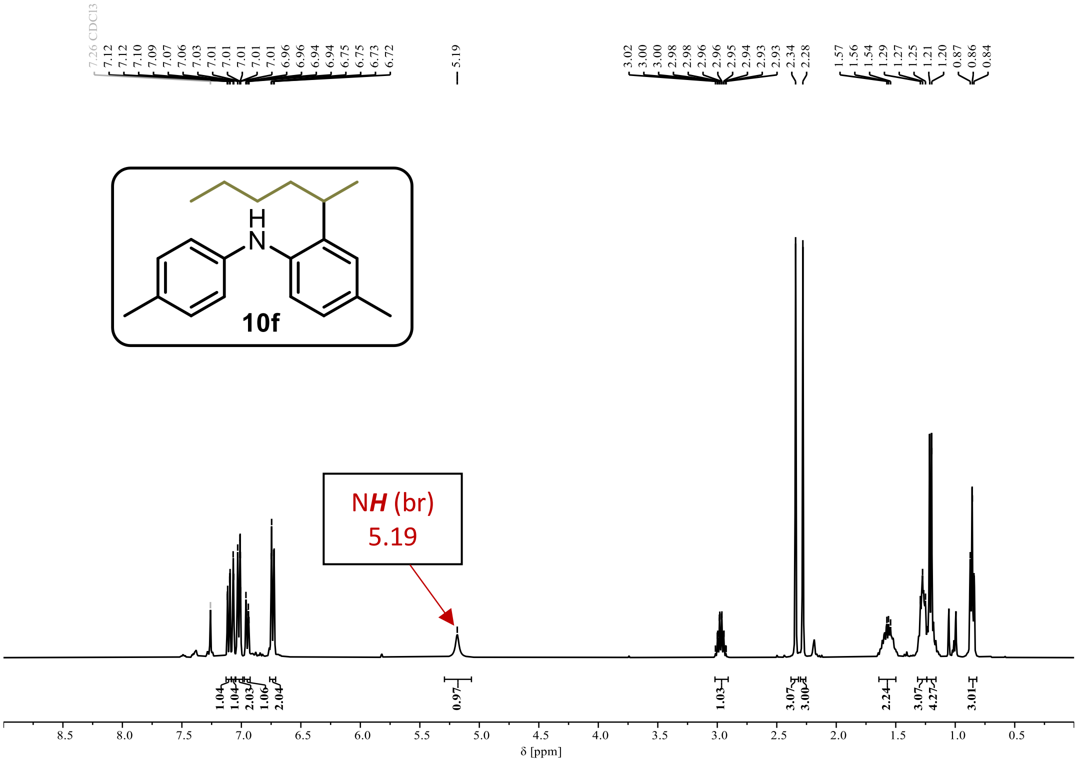


Figure S60: ^{1}H NMR of **10f** (400 MHz, $CDCl_3$, 295K).

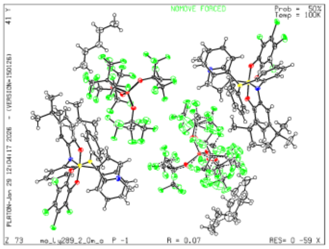
Figure S61: ^{13}C{^{1}H} NMR of **10f** (101 MHz, $CDCl_3$, 295K).

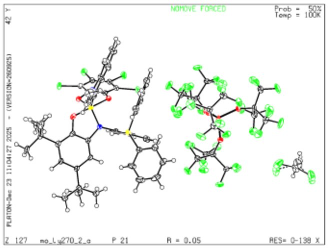
4. X-Ray Diffraction

4.1 General Information

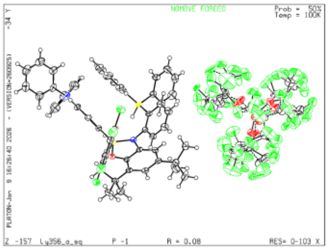
Suitable crystals were taken directly from the mother liquor, immersed in a perfluorinated ether oil and fixed on a cryo loop. The diffraction data were collected from a shock-cooled single crystal at 100 K on a Bruker D8 VENTURE dual wavelength Mo/Cu three-circle diffractometer with a microfocus sealed X-ray tube using mirror optics as monochromator and a Bruker PHOTON III detector. The diffractometer was equipped with an Oxford Cryostream 800 low temperature device and used MoK_{α} radiation ($\lambda = 0.71073$ Å). All data were integrated with SAINT and a multi-scan absorption correction using SADABS was applied.[3] The structures were solved by direct methods using SHELXT and refined by full-matrix least-squares methods against F^2 by SHELXL-2018/3.[4,5] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.[6] CCDC 2523825-2523830 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/structures. This report and the CIF file were generated using FinalCif.[7]

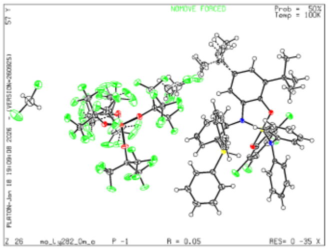
4.2 Crystal Data and Structures Refinement



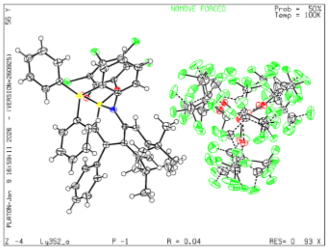


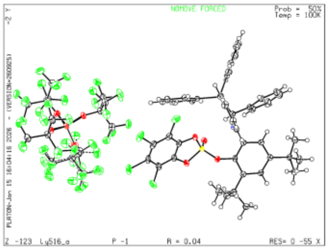
CCDC number	2523830	2523826
Compound name	**1**	**2**
Empirical formula	$C_{64}H_{53}AlCl_4F_{36}N_2O_7P_2$	$C_{64}H_{45}AlCl_6F_{36}N_2O_7P_2$
Formula weight	1876.80	1939.64
Temperature [K]	100(2)	100(2)
Crystal system	triclinic	monoclinic
Space group (number)	$P\bar{1}$ (2)	$P2_1$(4)
a [Å]	17.8277(10)	13.875(2)
b [Å]	19.8707(14)	15.431(2)
c [Å]	24.4861(16)	18.102(3)
α [°]	101.995(2)	90
β [°]	96.748(2)	102.687(4)
γ [°]	113.876(2)	90
Volume [Å^3]	7559.0(9)	3781.1(10)
Z	4	2
ρ_{calc} [gcm^{-3}]	1.649	1.704
μ [mm^{-1}]	0.352	0.423
F(000)	3768	1936
Crystal size [mm^3]	0.17×0.28×0.32	0.190×0.190×0.360
Crystal colour	colourless	colourless
Crystal shape	block	block
Radiation	MoKα (λ=0.71073 Å)	MoKα (λ=0.71073 Å)
2θ range [°]	3.84 to 57.70 (0.74 Å)	4.00 to 57.39 (0.74 Å)
Index ranges	$-24 \le h \le 24$ $-26 \le k \le 26$ $-33 \le l \le 33$	$-18 \le h \le 18$ $-20 \le k \le 20$ $-24 \le l \le 24$
Reflections collected	417840	161264
Independent reflections	39425 R_{int} = 0.1063 R_{sigma} = 0.0501	19500 R_{int} = 0.0546 R_{sigma} = 0.0303
Completeness to θ = 25.242° or 25.130°	100.0 %	99.8 %
Data / Restraints / Parameters	39425 / 23017 / 2647	19500 / 2946 / 1102
Absorption correction T_{min}/T_{max} (method)	0.6650 / 0.7458 (multi-scan)	0.6581 / 0.7452 (multi-scan)
Goodness-of-fit on F^2	1.049	1.046
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0665 wR_2 = 0.1646	R_1 = 0.0546 wR_2 = 0.1478
Final R indexes [all data]	R_1 = 0.1000 wR_2 = 0.1948	R_1 = 0.0575 wR_2 = 0.1507
Largest peak/hole [eÅ^{-3}]	1.47/−1.05	1.49/−0.73
Flack X parameter		0.010(13)





CCDC number	2523827	2523828
Compound name	**3**	**4**
Empirical formula	$C_{72}H_{49}AlCl_4F_{36}N_2O_7P_2$	$C_{68}H_{49}AlCl_8F_{36}N_2O_7P_2$
Formula weight	1968.85	2062.61
Temperature [K]	100(2)	100(2)
Crystal system	triclinic	triclinic
Space group (number)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
a [Å]	14.236(6)	14.2762(9)
b [Å]	15.548(7)	14.4839(8)
c [Å]	22.474(8)	20.6365(13)
α [°]	95.646(8)	101.344(2)
β [°]	101.943(7)	100.156(2)
γ [°]	105.755(8)	97.123(2)
Volume [Å^3]	4620(3)	4062.1(4)
Z	2	2
ρ_{calc} [gcm^{-3}]	1.415	1.686
μ [mm^{-1}]	0.292	0.463
F(000)	1972	2060
Crystal size [mm^3]	0.180×0.338×0.340	0.123×0.176×0.294
Crystal colour	colourless	colourless
Crystal shape	block	block
Radiation	MoKα (λ=0.71073 Å)	MoKα (λ=0.71073 Å)
2θ range [°]	4.28 to 50.40 (0.83 Å)	3.78 to 57.61 (0.74 Å)
Index ranges	$-16 \leq h \leq 17$ $-18 \leq k \leq 18$ $-26 \leq l \leq 26$	$-19 \leq h \leq 19$ $-19 \leq k \leq 19$ $-27 \leq l \leq 27$
Reflections collected	201831	268990
Independent reflections	16434 R_{int} = 0.0639 R_{sigma} = 0.0289	21168 R_{int} = 0.0794 R_{sigma} = 0.0315
Completeness to θ = 25.242° or 25.130°	98.8 %	99.9 %
Data / Restraints / Parameters	16434 / 11288 / 1635	21168 / 4571 / 1321
Absorption correction T_{min}/T_{max} (method)	0.6751 / 0.7452 (multi-scan)	0.6807 / 0.7458 (multi-scan)
Goodness-of-fit on F^2	1.040	1.062
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0802 wR_2 = 0.2020	R_1 = 0.0468 wR_2 = 0.1172
Final R indexes [all data]	R_1 = 0.0920 wR_2 = 0.2123	R_1 = 0.0620 wR_2 = 0.1275
Largest peak/hole [eÅ^{-3}]	1.06/−0.88	0.88/−1.09





CCDC number	2523829	2523825
Compound name	**6**	**7**
Empirical formula	$C_{62}H_{40}AlCl_4F_{36}NO_7P_2$	$C_{61}H_{40}AlCl_4F_{36}NO_8P_2$
Formula weight	1825.67	1829.66
Temperature [K]	100(2)	100(2)
Crystal system	triclinic	triclinic
Space group (number)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
a [Å]	12.020(3)	13.699(9)
b [Å]	14.217(3)	15.519(7)
c [Å]	21.016(4)	19.103(10)
α [°]	98.119(12)	104.595(14)
β [°]	96.587(15)	110.911(18)
γ [°]	92.642(13)	95.273(11)
Volume [Å^3]	3524.8(14)	3596(3)
Z	2	2
ρ_{calc} [gcm^{-3}]	1.720	1.690
μ [mm^{-1}]	0.374	0.368
F(000)	1820	1824
Crystal size [mm^3]	0.276×0.285×0.317	0.096×0.136×0.203
Crystal colour	yellow	colourless
Crystal shape	block	block
Radiation	MoKα (λ=0.71073 Å)	MoKα (λ=0.71073 Å)
2θ range [°]	4.15 to 54.39 (0.78 Å)	3.82 to 50.24 (0.84 Å)
Index ranges	$-15 \leq h \leq 15$ $-18 \leq k \leq 18$ $-26 \leq l \leq 27$	$-16 \leq h \leq 16$ $-18 \leq k \leq 18$ $-22 \leq l \leq 22$
Reflections collected	201053	122823
Independent reflections	15616 R_{int} = 0.0539 R_{sigma} = 0.0231	12830 R_{int} = 0.0638 R_{sigma} = 0.0326
Completeness to θ = 25.242° or 25.130°	99.4 %	99.7%
Data / Restraints / Parameters	15616 / 10298 / 1532	12830 / 4334 / 1151
Absorption correction T_{min}/T_{max} (method)	0.6334 / 0.7455 (multi-scan)	0.6901 / 0.7452 (multi-scan)
Goodness-of-fit on F^2	1.054	1.049
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0359 wR_2 = 0.0942	R_1 = 0.0375 wR_2 = 0.0880
Final R indexes [all data]	R_1 = 0.0423 wR_2 = 0.1011	R_1 = 0.0534 wR_2 = 0.0971
Largest peak/hole [eÅ^{-3}]	0.47/−0.31	0.23/-0.36

5. References

1 L. You, N. Ansmann and L. Greb, Inverting Palladium–Phosphorus Lewis Pair Formation: Phosphonium Acting as Z-Type Ligand, *Angew. Chem. Int. Ed.*, 2025, **64**, e202519355.

2 S. Wang, G. Force, R. Guillot, J.-F. Carpentier, Y. Sarazin, C. Bour, V. Gandon and D. Lebœuf, Lewis Acid/Hexafluoroisopropanol: A Promoter System for Selective *ortho*-C-Alkylation of Anilines with Deactivated Styrene Derivatives and Unactivated Alkenes, *ACS Cata.*, 2020, **10**, 10794-10802.

3 L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, Comparison of Silver and Molybdenum Microfocus X-ray Sources for Single-crystal Structure Determination, *J. Appl. Crystallogr.*, 2015, **48**, 3-10.

4 G. M. Sheldrick, SHELXT – Integrated Space-group and Crystal-structure Determination, *Acta Crystallogr. A: Found. Adv*, 2015, **71**, 3-8.

5 G. M. Sheldrick, Crystal Structure Refinement with SHELXL, *Acta Crystallogr. C: Struct. Chem.,* 2015, **71**, 3-8.

6 C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, The Cambridge Structural Database, *Acta Crystallogr. B B: Struct. Sci. Cryst. Eng. Mater*, 2016, **72**, 171-179.

7 D. Kratzert, *FinalCif*, https://dkratzert.de/finalcif.html, (last accessed 29 January 2026).