Electronic Supplementary Material (ESI) for Dalton Transactions.

General Synthetic Procedures

All manipulations were performed using standard Schlenk and glovebox techniques under an atmosphere of dry nitrogen. Solvents were dried over Na/benzophenone (tetrahydrofuran, pentanes, hexanes, diethyl ether, toluene, benzene-d6) or over calcium hydride (dichloromethane, acetonitrile, 1,2-difluorobenzene, dichloromethane-d2, chloroform-d) and distilled prior to use. Reaction glassware was baked in a 130 ^{o}C oven for at least 1 hour prior to use and assembled under nitrogen while hot.

Solution NMR spectroscopy

Nuclear magnetic resonance spectra are referenced to tetramethylsilane (^{1}H, ^{13}C), 85% H_3PO_4 (^{31}P), $CFCl_3$ (^{19}F), or $B(OMe)_3$ (^{11}B) on a Bruker AV-300 spectrometer or a Bruker AV-500 spectrometer with residual solvent used for chemical shift calibration. Samples for NMR spectroscopy were prepared and sealed inside the glovebox with Parafilm before removal into ambient atmosphere. Heteronuclear NMR experiments were run using a sealed capillary containing benzene-d6 placed within the NMR tube for solvent locking.

Vibrational spectroscopy

Infrared spectra were obtained on an Agilent Technologies Cary 630 FTIR instrument equipped with a ZnSe ATR module. Raman spectra were obtained on a Thermo Scientific Nicolet NXR 9650 FT-Raman Spectrometer instrument equipped with a 1064 nm Nd:YVO_4 laser and InGaAs detector.

Crystallography

Single crystals diffraction experiments were performed on a Bruker APEX-II CCD diffractometer. Reflections were integrated using the APEX II software and solved and refined using Olex2 software. Cambridge Structural Database # 1997647, 1997649

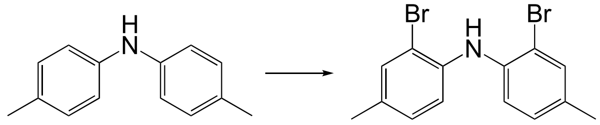
Commercial reagents

2-nitroaniline, 1-fluoro-2-nitrobenzene: Oakwood Chemicals, used as received
Bismuth(III) chloride, Silver(I) triflate: Oakwood Chemicals, purified by vacuum sublimation (10^{-2} mbar, 200 ^{o}C)
Triethylsilane, diisopropylchlorophosphine: Oakwood Chemicals, dried over activated molecular sieves
Triethylamine: Millipore Sigma, used after distillation under nitrogen
^{n}BuLi (1.6M/hexanes): Millipore Sigma, used as received
Triphenylmethylium Tetrakis(pentafluorophenyl)borate (Trityl Bar^{F}): Millipore Sigma, used as received

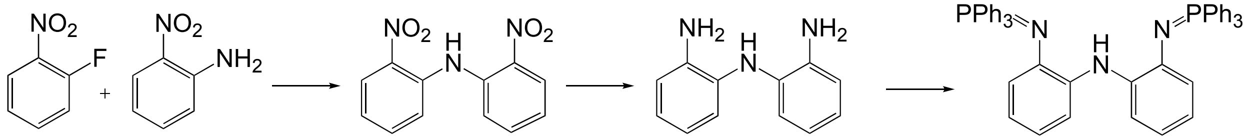
Starting materials

SM1: Bis(2-bromo-4-methylphenyl)amine was prepared by literature[1] and purified by crystallization from hot ethanol.

SM2: $HN(1,2\text{-}C_6H_4N{=}PPh_3)_2$ was prepared by literature procedure[2, 3] and purified by crystallization from DCM/pentane.



SM1



SM2

Syntheses and Characterization Data

Synthesis and characterization of 1

$HN(1,2-C_6H_4N=PPh_3)_2$ (0.9105 g, 1.26 mmol) and triethylamine (0.21 mL, 1.5 mmol) were combined in THF (5 mL). This mixture was then added slowly to a stirring solution of bismuth(III) chloride (0.3975 g, 1.26 mmol) at 0 ^{o}C in THF (5 mL), resulting in the immediate appearance of a white precipitate. The reaction was allowed to stir at room temperature for 18 h and the precipitated triethylammonium chloride was removed by filtration. Volatiles were removed under *vacuum*. The product was isolated as an orange powder after washing with acetonitrile (3 x 5mL). Crystals were grown from a 1:3 DCM/pentane solution.

Yield: 0.8089 g, 0.81 mmol (64.3%)

Elemental analysis: calcd. C 57.73, H 3.84, N 4.21; expt. C 55.93, H 3.93, N 4.41

^{1}H NMR (500 MHz, $CDCl_3$-d) δ 7.94 (dd, J = 12.5 Hz, 7.9 Hz, 12H, orthoC_{Ph}-H), 7.63 (t, J = 7.3 Hz, *overlapping*, 8H paraC_{Ph}-H and 2H Ar_{Hd}), 7.52 (td, J = 7.5 Hz, 2.8 Hz, 12H, metaC_{Ph}-H), 6.67 (t, J = 7.4 Hz, 2H, Ar_{Ha}), 6.23 (d, J = 7.7 Hz, 2H, Ar_{Hb}), 6.18 (t, J = 7.6 Hz, 2H, Ar_{Hc})

^{31}P {^{1}H} NMR (500 MHz, $CDCl_3$-d) δ 23.5 (s)

^{13}C {^{1}H} NMR (500 MHz, $CDCl_3$-d) δ 138.82 (C_Q), 134.15 (d, J_{CP} = 10.4 Hz, orthoC_{Ph}), 133.17 (paraC_{Ph}), 129.28 (d, J_{CP} = 12.4 Hz, metaC_{Ph}), 125.47 (Ar_C), 124.47 (Ar_C), 121.52 (Ar_{Cb}) 120.21 (Ar_{Cd}), 119.50 (Ar_{Ca}), 117.79 (Ar_{Cc})

Synthesis and characterization of 2a

Bis(2-bromo-4-methylphenyl)amine (11.912 g, 33.55 mmol) was dissolved in Et_2O (125 mL) and cooled to -78 ^{o}C. ^{n}BuLi (1.6 M, 69.20 mL) in hexane was added dropwise to a stirring solution over 5 minutes. In another vessel $^{i}Pr_2PCl$ (10.2409 g, 67.11 mmol) was dissolved in Et_2O (50 mL) and was added to the reaction mixture dropwise over 15 minutes at -78 ^{o}C resulting in the formation of a yellow precipitate. The reaction was allowed to warm to room temperature and left to stir for 2 hours which resulted in a homogenous yellow solution. $BiCl_3$ (10.5811 g, 33.55 mmol) was dissolved in Et_2O (50 mL) in a separate vessel and was added via cannula dropwise to the cooled reaction mixture at -78 ^{o}C, which resulted in a heterogenous red solution forming. The reaction was allowed to stir overnight at room temperature. Solvent was removed *in vacuo* before extracting the residue with CH_2Cl_2 leaving an orange supernatant and a white precipitate. The solid was removed by filtration, and the CH_2Cl_2 was removed under vacuum before recrystalizing the product from 1:2 CH_2Cl_2:Et_2O to obtain dark red crystals. (crystals can also be grown from thf/ether).

Yield: 15.3434g, 21.67 mmol (64.5%)

Elemental analysis: calcd. C 44.08, H 5.69, N 1.98; expt. C 43.93, H 5.13, N 1.91

^{1}H NMR (500 MHz, $CDCl_3$-d): δ 7.07-7.04 (m, 4H, C_{Ar}-H), 6.81 (dt, *J* = 6.8 Hz, 2.4 Hz, 2H, C_{Ar}-H) 3.22 (b, 1H, P$\underline{H}$), 3.22 (b, 1H, P$\underline{H}$), 2.73 (b, 1H, P$\underline{H}$), 2.04 (s, 6H, C_{Ar}-C$\underline{H}_3$), 1.37 (b, 24H,C_{iPr}-C$\underline{H}_3$)

^{13}C NMR: not obtained due to solubility

^{31}P {^{1}H} NMR (500 MHz, $CDCl_3$-d): δ 41.31 (s)

Synthesis and characterization of 2b

Compound **2a** (5.0018 g, 7.05 mmol) was dissolved in CH_2Cl_2 (50mL). The reaction vessel was covered in aluminum foil and AgOTf (3.9895 g, 15.53 mmol) was added to the stirring solution of **1** as a solid over 10 minutes. The red solution quickly converts to a dark purple solution and a white precipitate is observed after 5 minutes. The reaction is left to stir for 1.5 hours. The precipitate formed was removed by filtration, and the filtrate was dried under vacuum. Conversion by ^{31}P NMR is nearly quantitative, pure material can be isolated with extensive pentane/hexane washes or by recrystallization from 1:2 CH_2Cl_2:pentane.

^{13}C NMR spectra and elemental analysis could not be obtained due to thermal decomposition over time.

Yield: 3.8475g, 4.11 mmol (%)

^{1}H NMR (300 MHz, $CDCl_3$-d): δ 7.32 (dd, *J* = 8.4 Hz, 2.0 Hz, 2H, C_{Ar}-H), 7.13 (m, 2H, C_{Ar}-H), 6.97 (dt, *J* = 8.7 Hz, 2.2 Hz, 2H, C_{Ar}-H), 3.48 (m, 4H, P$\underline{H}$), 2.43 (s, 6H, C_{Ar}-C$\underline{H}_3$), 1.45 (m, 24H,C_{iPr}-C$\underline{H}_3$)

^{31}P {^{1}H} NMR (300 MHz, $CDCl_3$-d: δ 90.41 (s)

^{19}F NMR (300 MHz, $CDCl_3$-d): δ 77.06 (s)

Synthesis and characterization of 2c

Triethylsilane (0.2558 g, 2.20 mmol) in 1,2-difluorobenzene (5 mL) was added dropwise to a stirring solution of (triphenylmethyl)(tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) (1.8447 g, 2.00 mmol) in 1,2-difluorobenzene (5 mL). The solution becomes dark and brown after 15 minutes at which point it was added dropwise to a stirring solution of **2a** (0.7084g, 1.00 mmol) in 1,2-difluorobenzene (5 mL). The reaction was allowed to stir at room temperature for 2 hours which resulted in a dark green reaction mixture. The solution was dried under vacuum and the resulting black residue was washed with hexane (3 x 15mL) yielding a green powder.

This compound was not isolated. The available spectroscopic data are given below, limited by its thermal instability and high reactivity towards available deuterated solvents.

^{31}P {^{1}H} NMR (500 MHz, 1,2-PhF_2) δ 108.97 (s)
^{19}F NMR (500 MHz, 1,2-PhF_2) δ -132.87 (s, orthoC_{Ar}-F), -163.19 (s, metaC_{Ar}-F), -167.16 (s, paraC_{Ar}-F)
^{11}B NMR (500 MHz, 1,2-PhF_2) δ -16.64 (s)

Figure S1. ^{1}H NMR spectrum of **1** in $CDCl_3$.

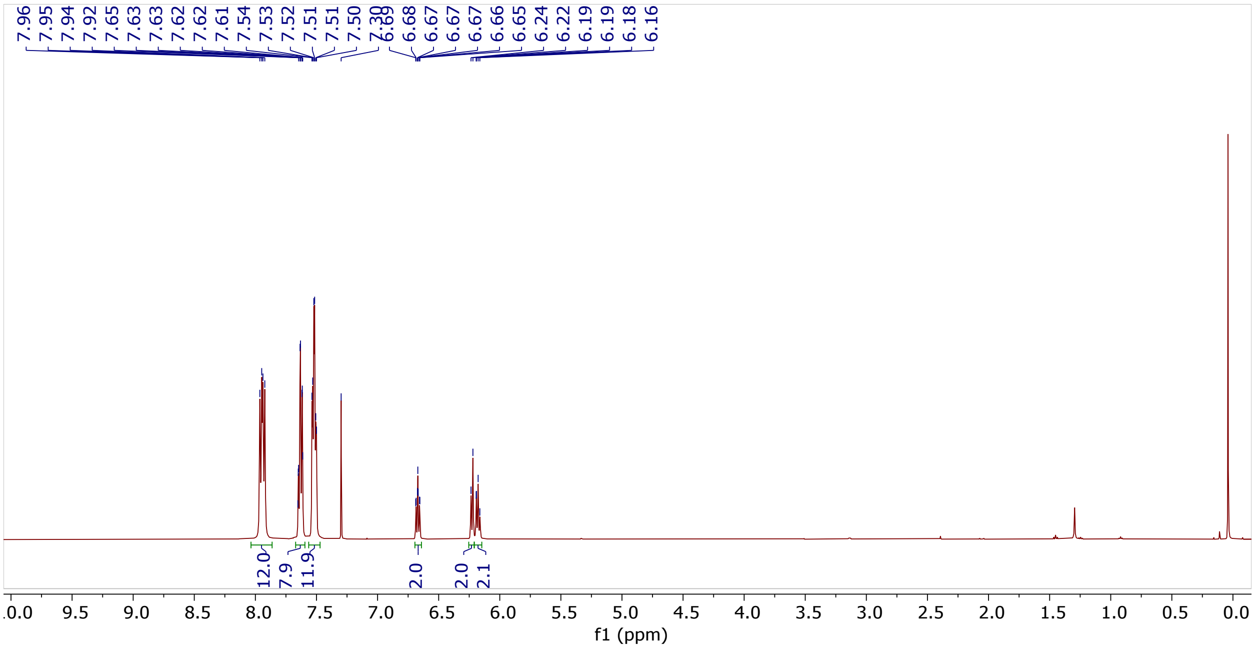


Figure S2. ^{13}C NMR spectrum of **1** in $CDCl_3$.

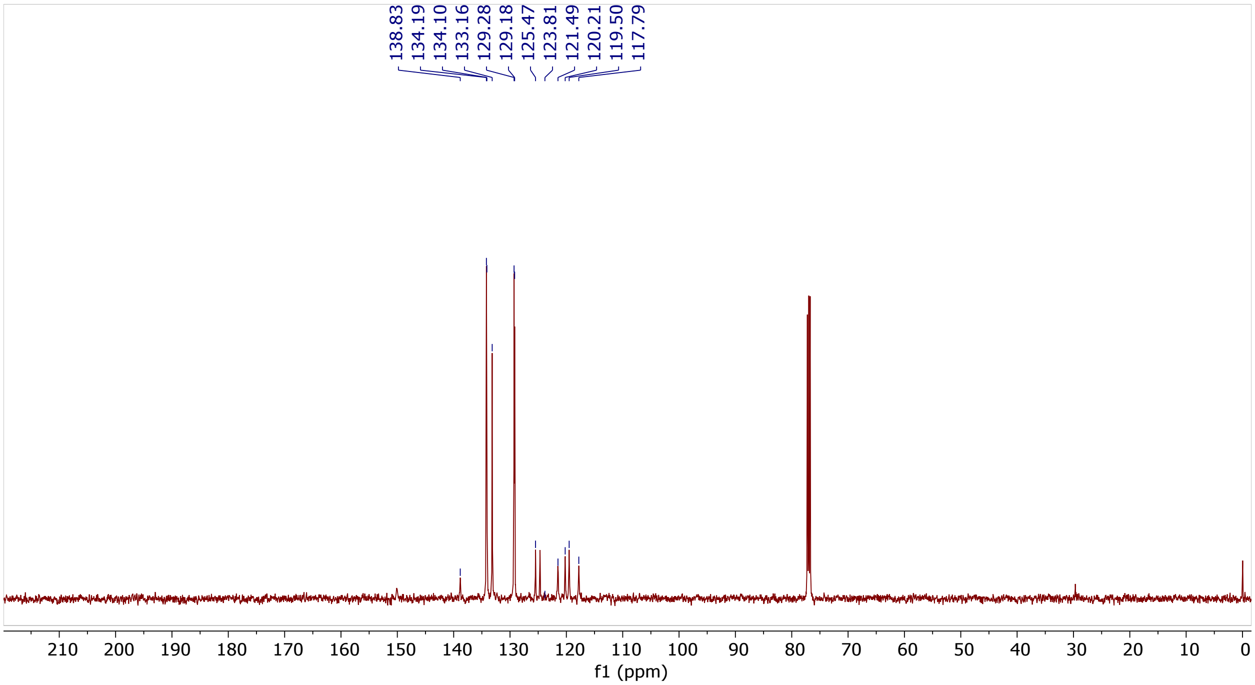


Figure S3. ^{31}P NMR spectrum of **1** in $CDCl_3$.

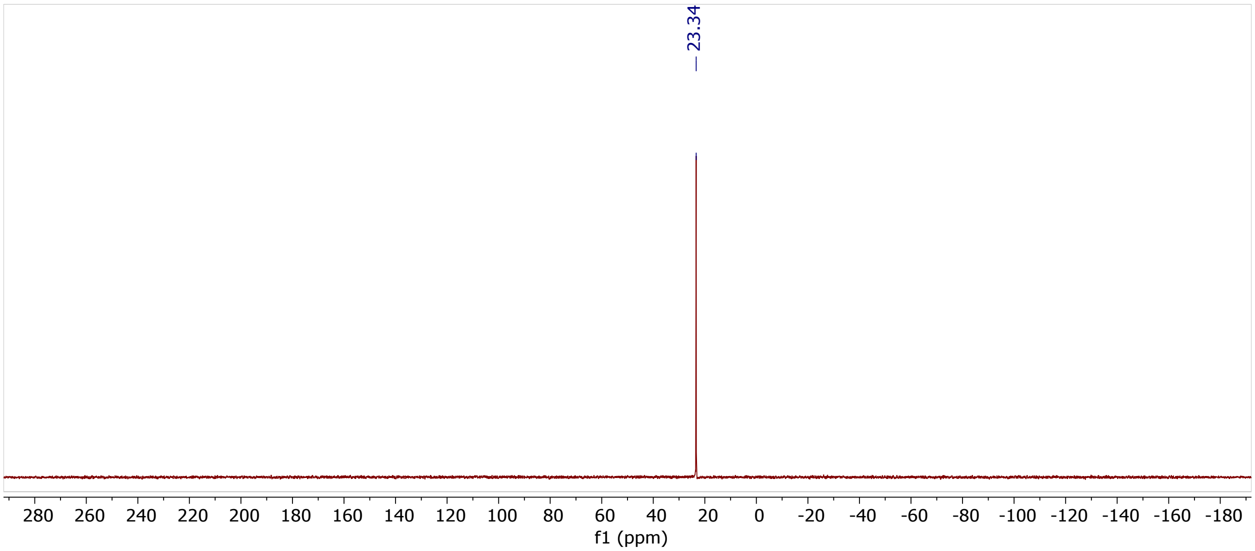


Figure S4. ^{1}H NMR spectrum of **2a** in $CDCl_3$. The peaks at 0.8 ppm and 1.5 ppm are due to traces of residual pentane in the deuterated solvent from the glovebox atmosphere.

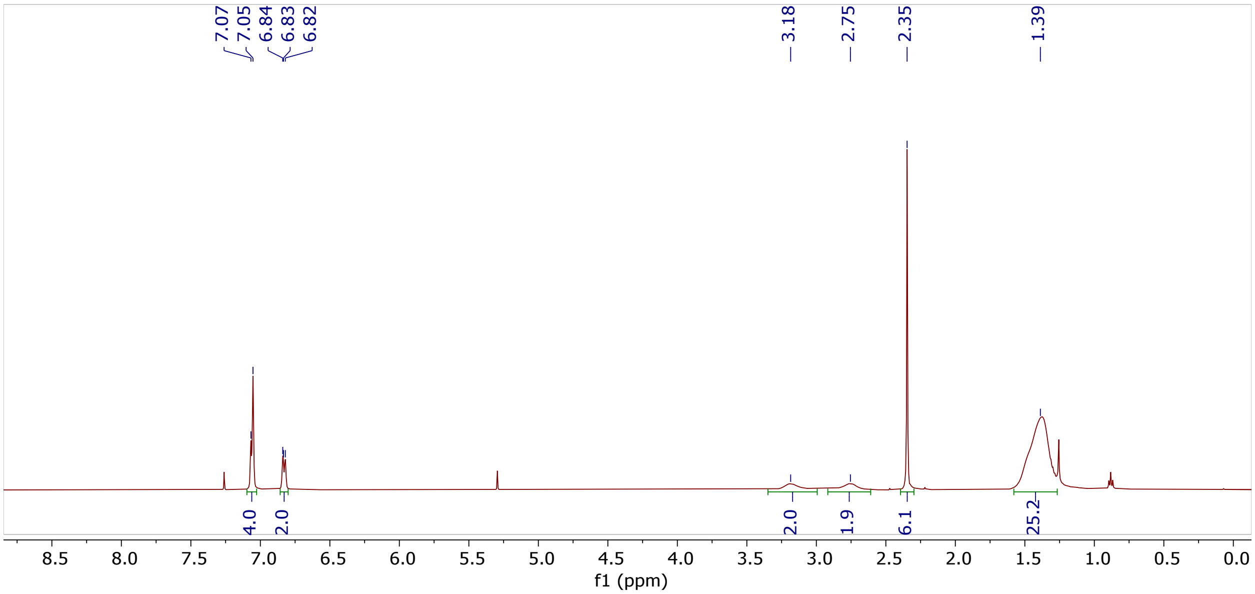


Figure S5. ^{31}P NMR spectrum of **2a** in $CDCl_3$.

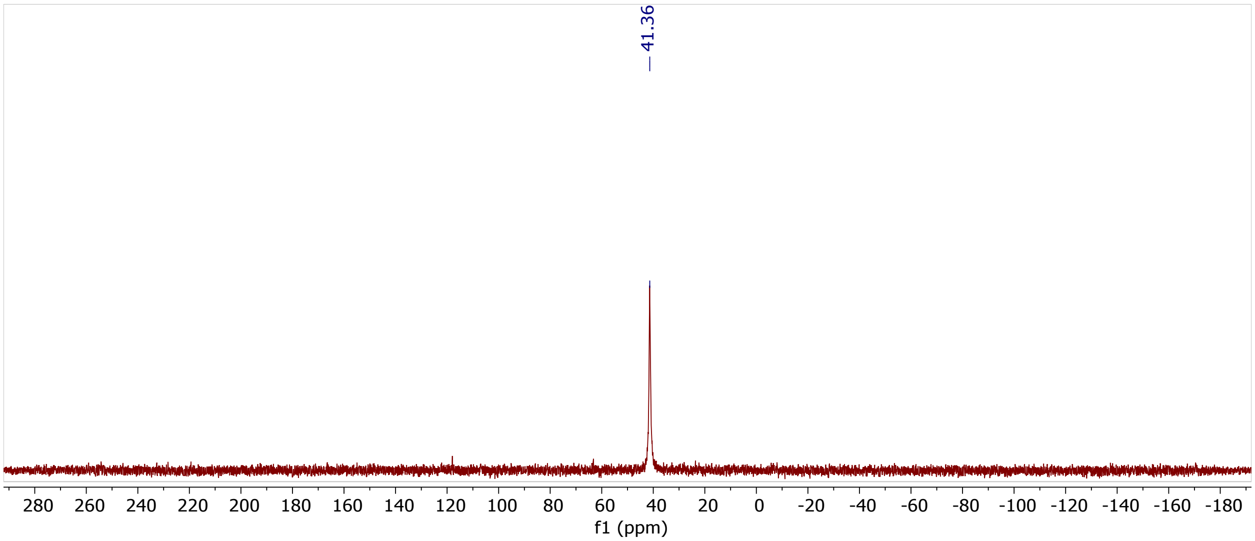


Figure S6. ^{1}H NMR spectrum of **2b** in $CDCl_3$. The peaks at 0.8 ppm, 1.5 ppm, and 5.4 ppm are due to trace residues of pentane and DCM in the deuterated solvent from the glovebox atmosphere.

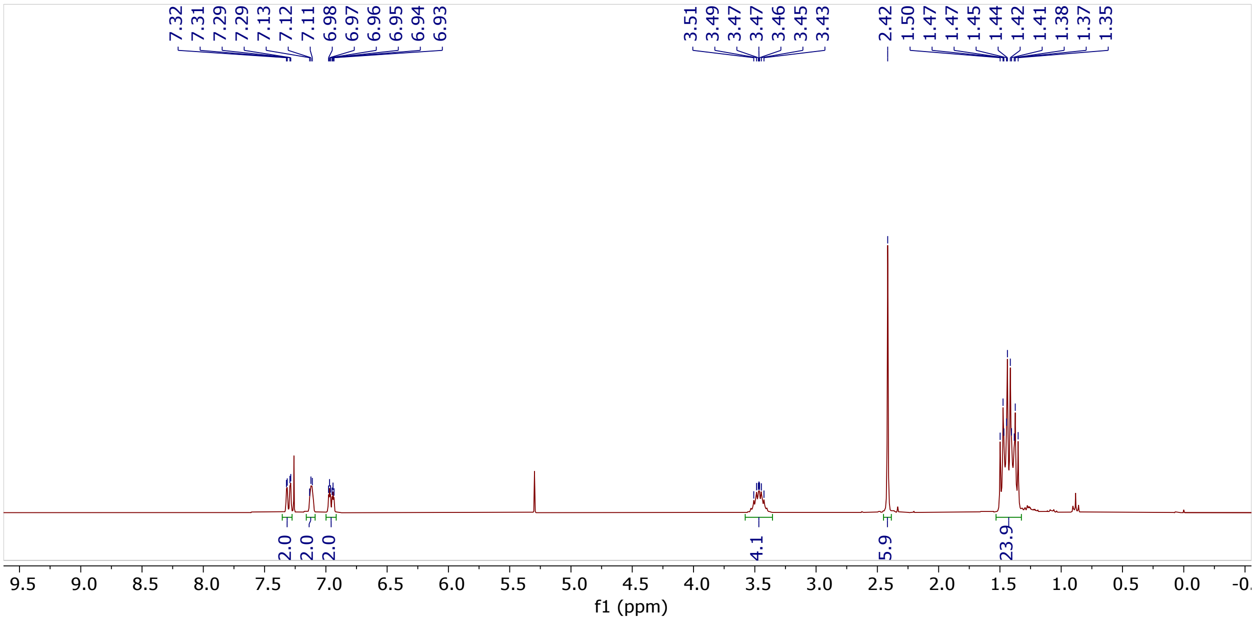


Figure S7. ^{31}P NMR spectrum of **2b** in $CDCl_3$.

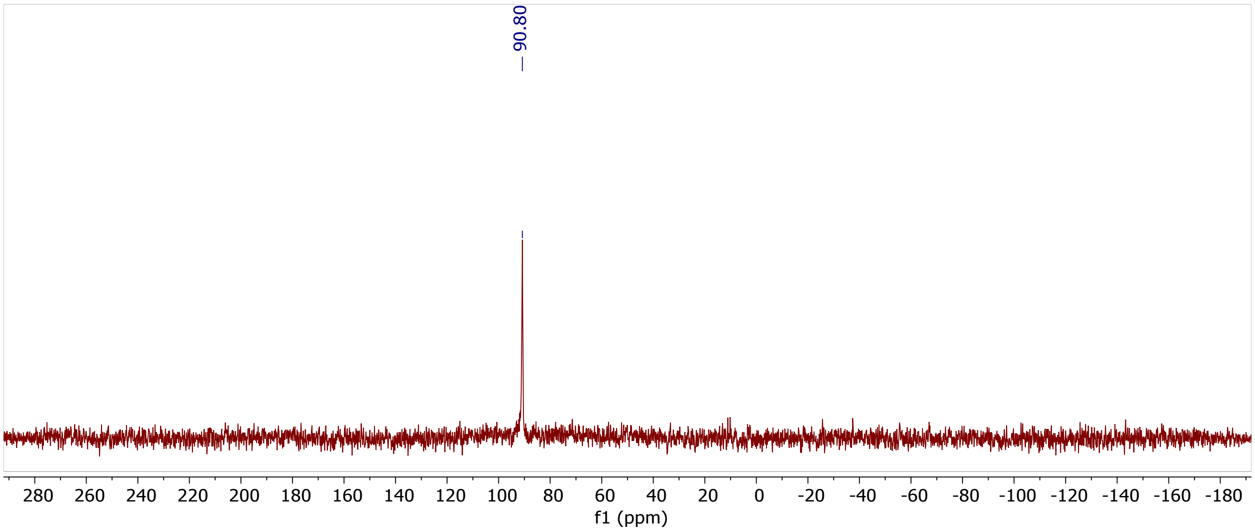


Figure S8. ^{19}F NMR spectrum of **2b** in $CDCl_3$.

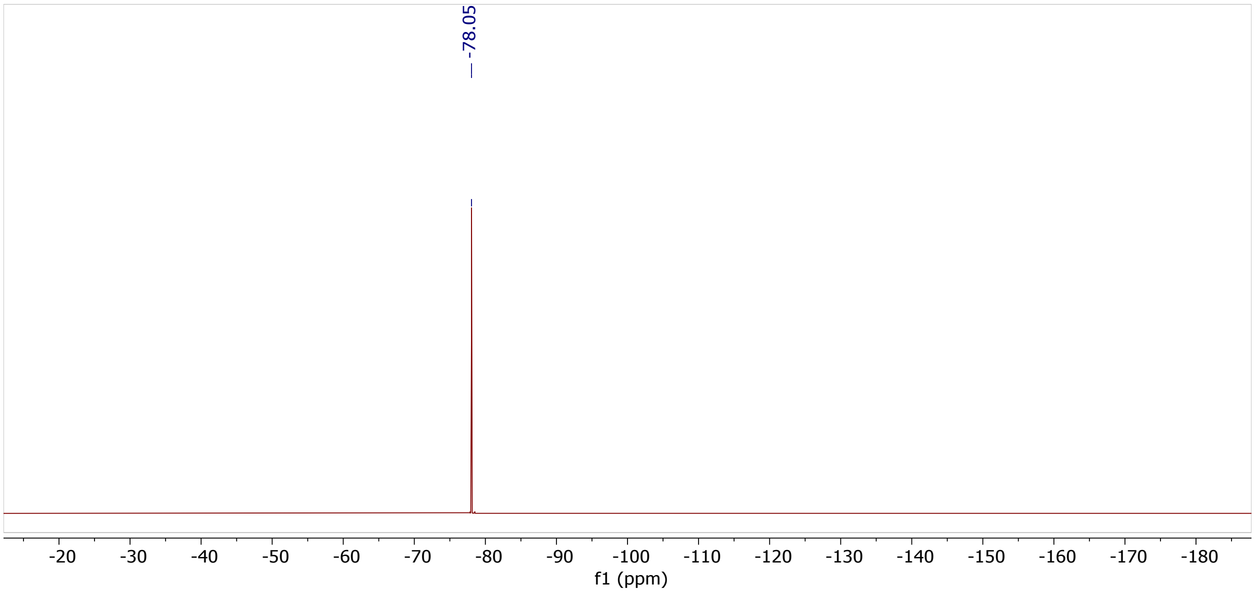


Figure S9. ^{31}P NMR spectrum of **2b** in DCM after few hours showing extensive thermal degradation and formation of **2a** (37.2 ppm) by solvent activation.

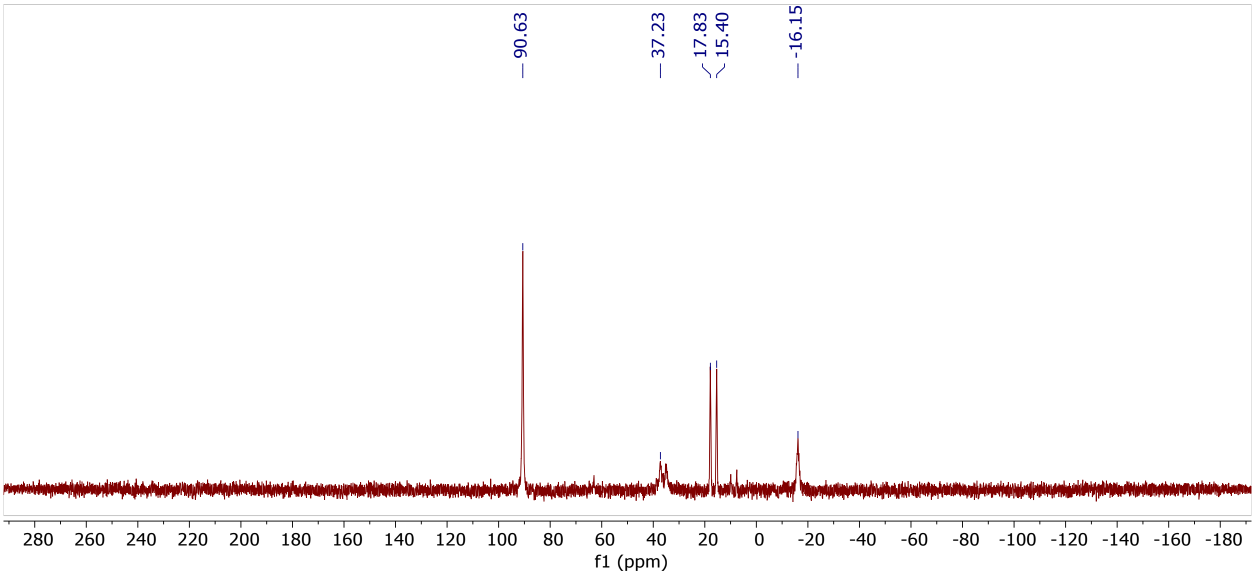


Figure S10. ^{31}P NMR spectrum of **2c** in *o,o*-difluorobenzene.

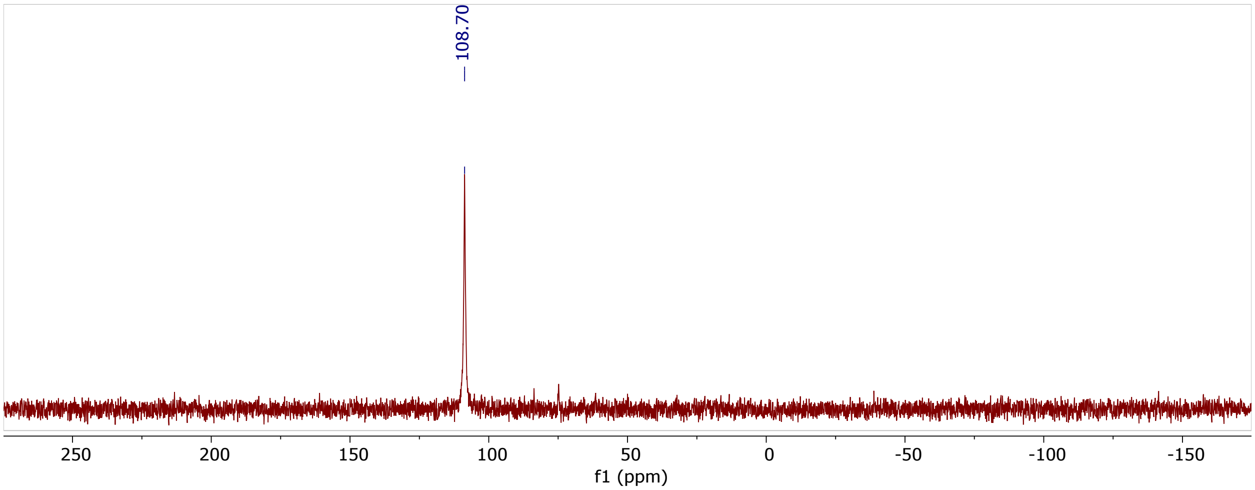


Figure S11. ^{11}B NMR spectrum of **2c** in *o,o*-difluorobenzene.

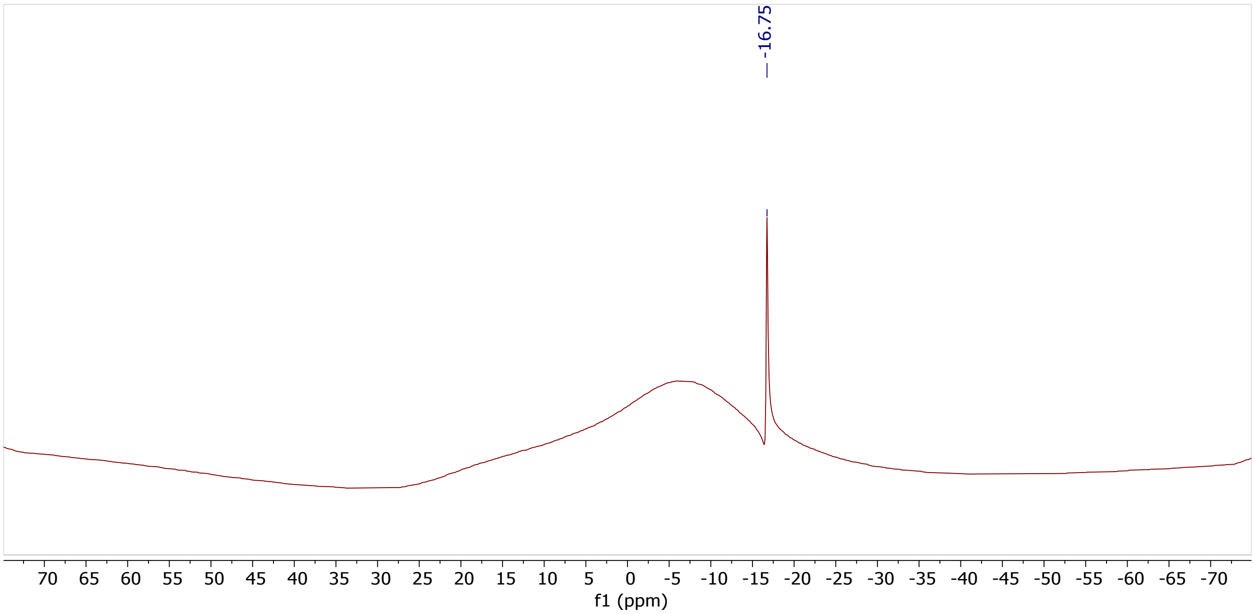


Figure S12. ^{19}F NMR spectrum of **2c** in DCM. Signals besides those of the $B(C_6F_5)_4$ anion are due to thermal decomposition in this solvent.

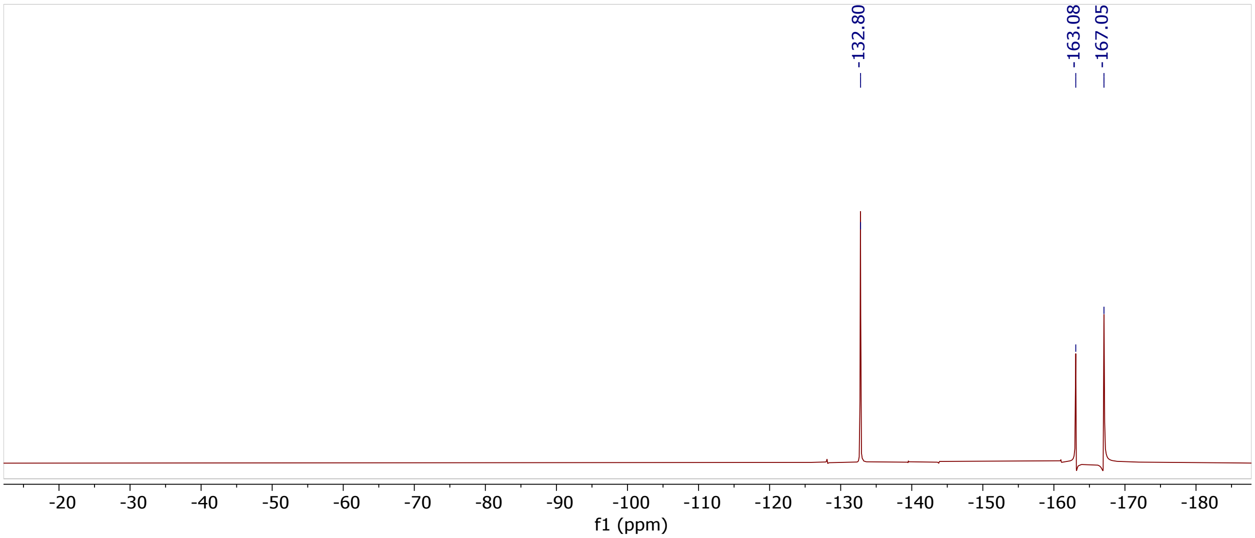


Figure S13 Variable temperature 31P NMR of **2a** in told-d_8.

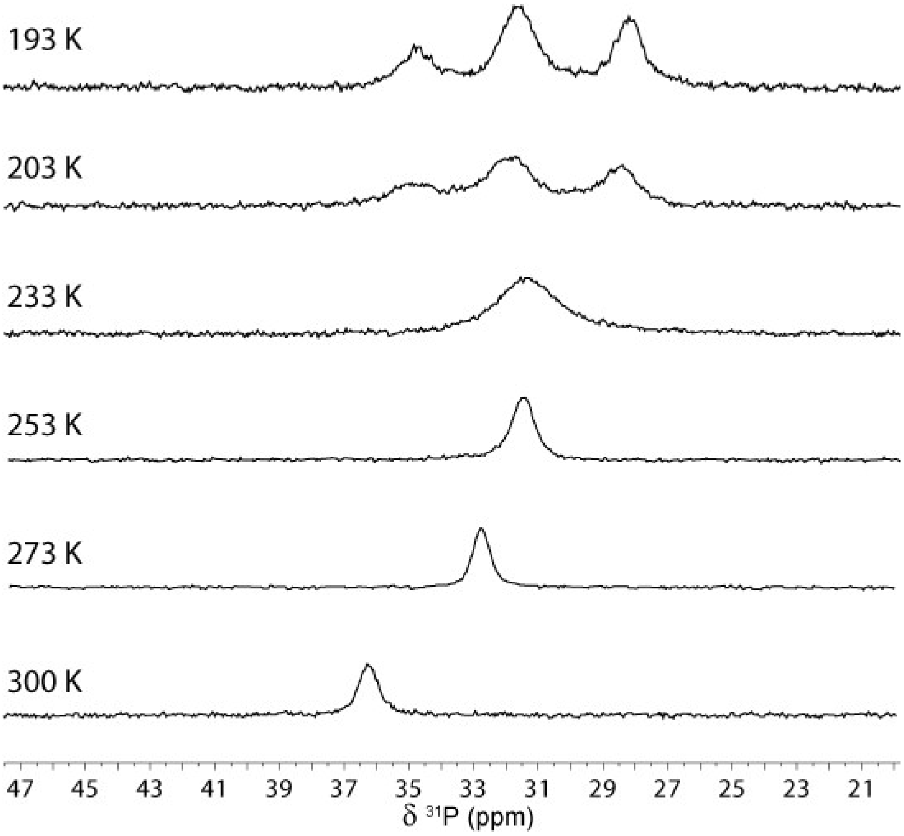
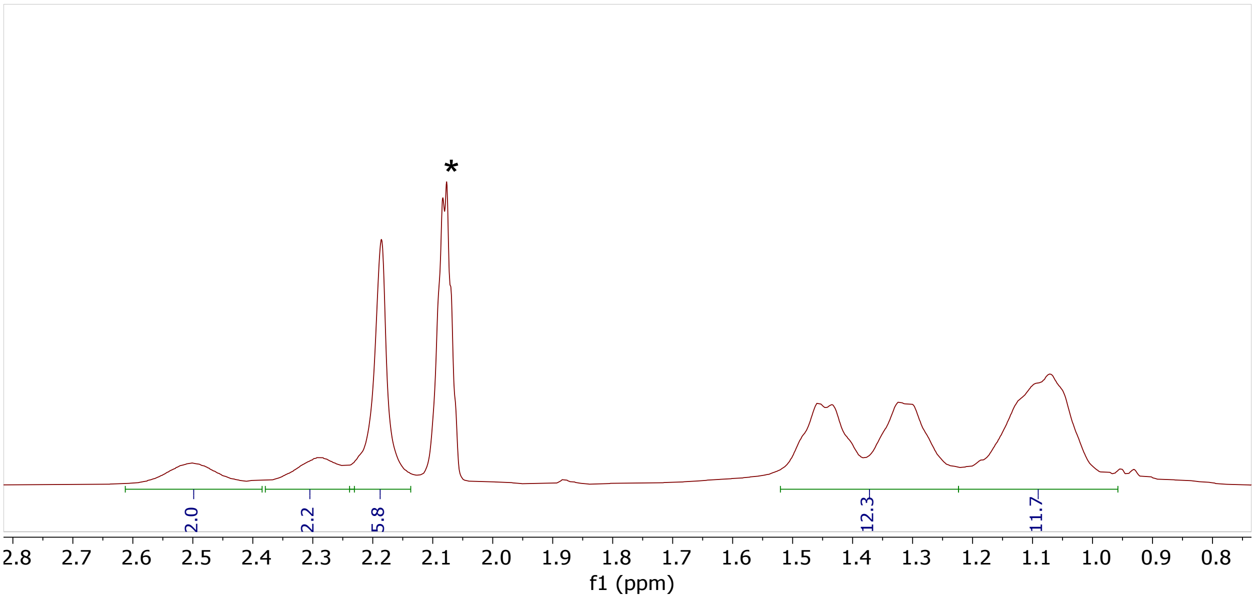


Figure S14 ^{1}H NMR of **2a** in the alkyl region in told-d_8 at 203 K. Asterisk denotes solvent signal.



Estimating $\Delta G^{\mp}$ at coalescence temperature (T_c)

$$\Delta G^{\mp} = RT_c\left[ln\frac{T_c k_b}{h} - \ln k\right] = RT_c\left[23.76 - \ln\frac{T_c}{k}\right] = RT_c\left[23.76 - \ln\frac{T_c}{2.22\Delta v}\right] = 58.76\ KJ\ mol^{-}$$

$R = 8.31\ J \cdot mol^{-1}$
$h = 6.62\ x10^{-34} J \cdot s$
$k_b = 1.38\ x10^{-34}\ m^2 \cdot Kg \cdot s^{-1} \cdot K^{-1}$

$\Delta v = 40.60\ Hz - 25.86\ Hz = 14.47\ Hz$
$T_c = 273\ K$
$k = \frac{\pi \Delta v}{\sqrt{2}} = 2.22\ \Delta v$

Assuming a transmission coefficient (κ) = 1
At coalescence temperature T = T_c

Figure S15. Solution of **2c** in THF in an *inverted* NMR tube showing gel formation by catalytic ring-opening polymerization of the solvent.

Figure S16. Calculated structure of **2a** at the B3LYP/cc-pVDZ//aug-cc-pVDZ(Bi) level. The two P-Bi bond lengths are 2.707 and 3.061 Å.

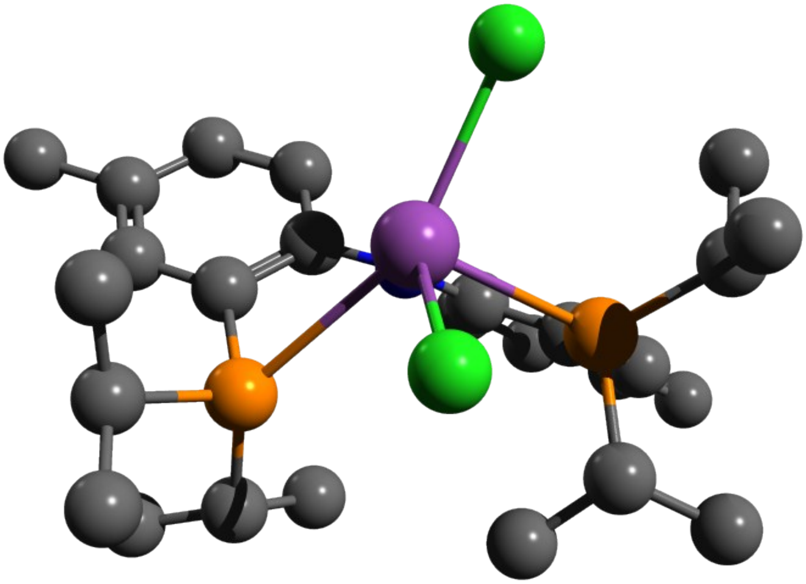
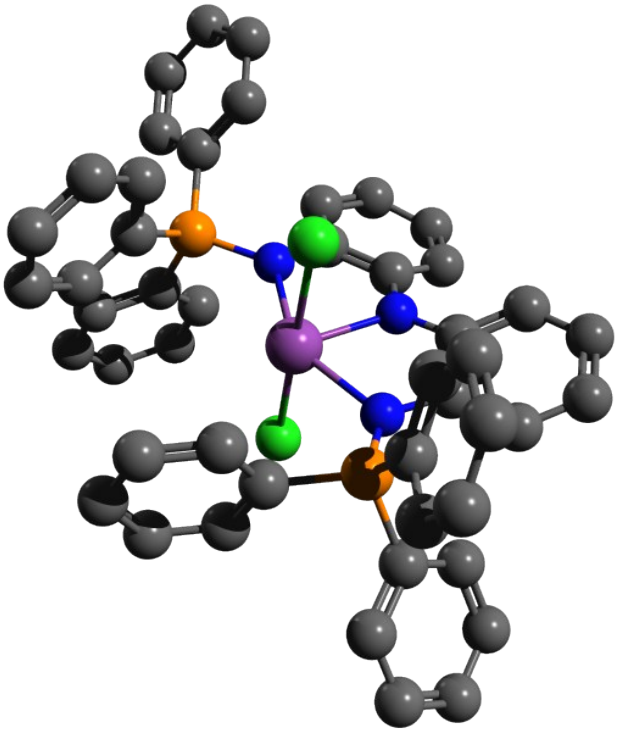


Figure S17. Calculated structure of **1** at the B3LYP/def2svp(d) level.



Computational Details

All calculations were performed using the Gaussian 16 Suite.[4] The B3LYP function was employed with Grimme's D3-BJ dispersion correction.[5] Geometries were optimized using the cc-pvdz basis set for non-Bi atoms and aug-cc-pvdz-PP + ECM60MDF at bismuth.[6] Cartesian coordinates are given below.

[PNP-Bi]$^{2+}$

Bi	-0.04062	-1.32791	-0.86824
P	1.78798	-0.66369	1.02599
P	-2.42046	-0.50828	-0.03277
N	0.17080	0.84482	-1.09128
C	-0.78570	1.71502	-0.51243
C	4.31958	1.89681	-1.00150
C	3.79666	0.96830	-0.09217
H	4.47328	0.50635	0.62906
C	-2.97438	2.15835	0.52834
H	-3.93478	1.78364	0.88294
C	2.43636	0.61275	-0.11067
C	1.56390	1.19827	-1.06199
C	-2.72013	3.52501	0.60542
C	3.44399	2.44135	-1.95786
H	3.83205	3.14390	-2.69853
C	-1.47202	3.96721	0.12609
H	-1.22885	5.03112	0.17515
C	2.09523	2.09084	-1.99953
H	1.43865	2.50706	-2.76467
C	-3.10975	-1.23063	1.54276
H	-3.10874	-2.30997	1.31056
C	-0.53578	3.09992	-0.42146
H	0.40919	3.50087	-0.78135
C	1.46540	0.08837	2.70978
H	0.89785	-0.68225	3.25606
C	3.01823	-2.05133	1.16766
H	3.91661	-1.58071	1.60215
C	-2.18077	-0.97117	2.72917
H	-1.16163	-1.34332	2.54269
H	-2.57069	-1.49477	3.61481
H	-2.12598	0.10088	2.96757
C	-2.02788	1.25307	-0.00269
C	5.77367	2.28264	-0.98131
H	5.88561	3.36231	-0.79208
H	6.24794	2.07522	-1.95353
H	6.33049	1.74085	-0.20477

C	0.63522	1.36620	2.58088
H	1.18296	2.13906	2.02177
H	0.42988	1.76004	3.58768
H	-0.32502	1.20031	2.07759
C	2.80185	0.34733	3.42245
H	3.38300	-0.56855	3.59646
H	2.58657	0.79236	4.40641
H	3.42110	1.06658	2.86530
C	-2.99397	-0.32725	-2.76265
H	-2.71116	0.73164	-2.68031
H	-3.75024	-0.41653	-3.55653
H	-2.11477	-0.90389	-3.10047
C	2.48576	-3.11811	2.13245
H	2.29589	-2.72419	3.14131
H	3.22655	-3.92614	2.22759
H	1.55341	-3.57135	1.75433
C	-4.55553	-0.79198	1.82087
H	-4.60375	0.25578	2.14867
H	-4.95357	-1.41050	2.63987
H	-5.22033	-0.92529	0.95587
C	-3.89676	-2.37757	-1.53225
H	-2.99388	-2.98410	-1.72055
H	-4.58477	-2.55360	-2.37296
H	-4.38617	-2.75595	-0.62363
C	-3.56761	-0.88377	-1.45450
H	-4.47710	-0.31319	-1.19473
C	3.37093	-2.62723	-0.20761
H	2.52181	-3.17982	-0.64517
H	4.19204	-3.35130	-0.09710
H	3.69760	-1.85521	-0.91915
C	-3.72703	4.49452	1.16336
H	-4.04272	5.21728	0.39393
H	-3.29691	5.07534	1.99459
H	-4.62512	3.98116	1.53382

2a

Bi	-0.11748	-1.32590	-0.63275
P	2.11682	-0.29103	1.18586
P	-2.39092	-0.15771	0.25751
Cl	-0.74609	-3.35019	1.02019
Cl	-1.14932	-1.72834	-3.03210
N	0.23241	1.03978	-0.65336
C	-0.70173	1.98828	-0.33598
C	4.27480	1.72699	-1.77162
C	3.94386	0.93692	-0.66694
C	-2.97617	2.56917	0.43371

C	2.61251	0.73759	-0.26659
C	1.55886	1.33781	-1.00764
C	-2.71122	3.93534	0.38764
C	3.22215	2.31531	-2.49455
C	-1.40995	4.31358	0.00053
C	1.89403	2.11761	-2.13227
C	-2.66810	-0.61487	2.05071
C	-0.44068	3.38812	-0.35007
C	2.35024	0.88554	2.64595
C	3.46389	-1.57834	1.36207
C	-1.49476	-0.12596	2.90126
C	-2.00851	1.60221	0.10061
C	5.70864	1.93667	-2.18889
C	1.48418	2.13300	2.44531
C	3.80890	1.26603	2.90907
C	-4.02433	0.15632	-2.02420
C	3.22156	-2.36816	2.65545
C	-4.00922	-0.13629	2.61444
C	-4.17223	-2.05405	-0.74730
C	-3.97148	-0.53584	-0.65909
C	3.44870	-2.50954	0.14309
C	-3.75619	4.96603	0.73118

1

N	-0.09699	2.17213	0.07158
C	-1.31690	2.77380	-0.12430
C	-2.46446	1.90650	-0.07558
C	-1.51786	4.12494	-0.47705
C	-3.75625	2.47319	-0.21677
C	-2.79014	4.64115	-0.65105
C	-3.91539	3.81849	-0.48527
C	1.10017	2.80374	0.30917
C	2.27883	1.98455	0.20362
C	1.25165	4.13451	0.75248
C	3.54903	2.58760	0.38447
C	2.50423	4.68429	0.96262
C	3.65883	3.91667	0.74328
N	-2.22367	0.59211	0.06305
N	2.08645	0.67453	-0.02368
Bi	-0.05610	-0.04468	-0.00330
P	3.44265	-0.42858	-0.10345
P	-3.30100	-0.35461	0.06602
C	4.85300	0.40057	-0.90085
C	6.15032	0.16200	-0.44642
C	4.63694	1.27442	-1.96633
C	7.23122	0.79770	-1.05694

C	5.71815	1.90964	-2.57780
C	7.01515	1.67154	-2.12322
C	2.97468	-1.89628	-1.07261
C	2.80652	-1.79549	-2.45393
C	2.78424	-3.12187	-0.43448
C	2.44735	-2.91995	-3.19677
C	2.42592	-4.24698	-1.17754
C	2.25732	-4.14619	-2.55846
C	3.91074	-0.93727	1.58016
C	4.15190	-2.28249	1.86069
C	4.02848	0.01769	2.58997
C	4.51007	-2.67265	3.15093
C	4.38771	-0.37230	3.88042
C	4.62838	-1.71723	4.16107
C	-2.63863	-2.04688	0.16540
C	-2.31072	-2.59589	1.40537
C	-2.45891	-2.79501	-0.99803
C	-1.80258	-3.89249	1.48175
C	-1.95155	-4.09238	-0.92171
C	-1.62325	-4.64115	0.31789
C	-4.40507	-0.12401	1.49440
C	-5.17449	-1.19037	1.96060
C	-4.48194	1.11872	2.12310
C	-6.02106	-1.01377	3.05483
C	-5.32798	1.29528	3.21828
C	-6.09760	0.22935	3.68413
C	-4.31949	-0.24794	-1.43854
C	-5.59719	-0.80794	-1.45708
C	-3.82278	0.39374	-2.57303
C	-6.37767	-0.72683	-2.61012
C	-4.60375	0.47582	-3.72618
C	-5.88097	-0.08444	-3.74494
Cl	-0.27030	0.07245	-2.73523
Cl	0.11156	-0.16051	2.72333

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