Supporting Information

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S1 Materials and Methods

Unless otherwise indicated, all starting materials were obtained from commercial sources (Sigma-Aldrich, Alfa-Aeser, Roth, TCI, VWR or Fischer Chemical) and were used without further purification. Elemental analyses were carried out on a Vario Micro Cube System. All operations with air and moisture sensitive compounds were performed in a glove box under a dry argon atmosphere (MBraun 200B) or on a high vacuum line using Schlenk techniques.

The ^{1}H, ^{11}B, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on Bruker AVII 300 (300 MHz) and Bruker AV-II 600 (600 MHz). The chemical shifts are expressed in parts per million (ppm) with the residual solvent signal as internal standard for ^{1}H and ^{13}C NMR spectra. All other spectra were calibrated using external references. Coupling constants (*J*) are reported in Hertz (Hz) and splitting patterns are indicated as s (singlet), d (doublet), t (triplet), sept (septet), m (multiplet) and br (broad). ^{11}B, ^{13}C, ^{19}F and ^{31}P NMR spectra were measured broadband proton decoupled. Hexane, THF, and toluene were purified by distillation over sodium/benzophenone and chlorobenzene over CaH_2, respectively. Deuterated solvents were purified by stirring the degassed solvents with Na/K alloy overnight and were subsequently filtered and distilled under reduced pressure. All solvents were stored over molecular sieves (4 Å) in argon atmosphere prior to use. IDipp=P(TMS) (**2**),[3] [WCA-IDipp]ECl_2 (**1a**: E = P; **1b**: E = As)[4] and 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine[5] were prepared according to literature procedures.

The X-band EPR spectra were recorded on a Bruker EMX spectrometer. The samples were transferred into a 4 mm diameter quartz EPR tube (Wilmad 707-SQ-250M) and the spectra were simulated with EasySpin 5.2.2.[6]

S2 Synthetic Procedures

S2.1 WCA-IDipp-P(Cl)-P=IDipp (3a)

WCA-IDipp-PCl_3 (**1a**, 500 mg, 0.500 mmol, 1 eq.) was suspended in 15 mL hexane and IDipp=P(TMS) (**2**, 246 mg, 0.500 mmol, 1 eq.) dissolved in 5 mL hexane was added dropwise. The resulting dark green suspension was stirred for 3 d at room temperature. Afterwards the mixture was filtered and the remaining solid was washed with 5 × 5 ml hexane. Residual solvent was removed in vacou, yielding the product as a brown green solid (610 mg, 0.4396 mmol, 88%).

^{11}B-NMR (96 MHz; THF-d_8): δ = -15.2 (s, 1B) ppm.

^{19}F-NMR (282 MHz; THF-d_8): δ = -128.0- -134.0 (m), -161.6 (t), -166.5—167.1 (m) ppm.

^{31}P-NMR (203 MHz; THF-d_8): δ = 155.9 (d, $^1J(^{31}P, ^{31}P)$ = 405 Hz, 1P), 120.7 (d, $^1J(^{31}P, ^{31}P)$ = 370 Hz, 1P), -3.1 (d, $^1J(^{31}P, ^{31}P)$ = 405 Hz, 1P), -31.2 (d, $^1J(^{31}P, ^{31}P)$ = 370 Hz, 1P) ppm.

EA - Anal. calc. for $C_{72}H_{71}BClF_{15}N_4P_2$: C, 62.41; H, 5.17; N, 4.04. Found: C, 61.94; H, 5.13; N, 3.84.

UV/Vis (THF): λ_{max} = 441 nm.

S2.2 WCA-IDippAs(Cl)-P=IDipp (3b)

WCA-IDipp-$AsCl_3$ (**1b**, 300 mg, 0.287 mmol, 1 eq.) was suspended in 15 mL hexane and IDipp=P(TMS) (**2**, 141.4 mg, 0.287 mmol, 1 eq.) dissolved in 5 mL hexane was added dropwise. The resulting dark green suspension was stirred for 24 h at room temperature. Afterwards the mixture was filtered and the remaining solid was washed with 5 × 5 ml hexane. Residual solvent was removed in vacou, yielding the product as a brown green solid (349 mg, 0.244 mmol, 85%).

^{11}B-NMR (96 MHz; THF-d_8): δ = -15.3 (s, 1B) ppm.

^{19}F-NMR (282 MHz; THF-d_8): δ = -125.0- -135.0 (m), -161.1 (t), -165.0- -168.0 (m) ppm.

^{31}P-NMR (203 MHz; THF-d_8): δ = -9.2 (br s), -24.5 (s) ppm.

EA - Anal. calc. for $C_{72}H_{71}AsBClF_{15}N_4P$: C, 60.50; H, 5.01; N, 3.92. Found: C, 60.66; H, 5.069; N, 3.72.

UV/Vis (THF): λ_{max} =452 nm.

S2.3 [WCA-IDipp-P=P-IDipp][$GaCl_4$] (4a)

WCA-IDipp-P(Cl)-P=IDipp (**2a**, 300 mg, 0.216 mmol, 1 eq.) was dissolved in 10 mL toluene and $GaCl_3$ (38.1 mg, 0.216 mmol, 1 eq.) dissolved in 5 ml toluene was added dropwise. The resulting red suspension was stirred for 3 h at room temperature. Afterwards the supernatant solution was removed via decantation. Residual solvent was removed in vacuo and afterwards co-evaporation was performed with hexane in order to convert the resulting red oil into a solid. Subsequently, the red solid was washed with 4 × 2 mL hexane and the solvent was removed in vacuo yielding the product as a red-orange solid (242 mg, 0.155 mmol, 72%). In order to obtain a better purity, **4a** can be recrystallized from a chlorobenzene solution layered with hexane at ambient temperatures.

^{1}H-NMR (500 MHz; THF-d_8): δ = 8.54 (s, 2H, HC=CH), 7.96 (s, 1H, HC=CB), 7.72 (t, $^3J(^1H, ^1H)$ = 7.8 Hz, 2H, *p*-$Dipp_{NHC}$), 7.63 (t, $^3J(^1H, ^1H)$ = 7.8 Hz, 1H, *p*-$Dipp_{WCA\text{-}NHC}$), 7.56 (t, $^3J(^1H, ^1H)$ = 7.8 Hz, 1H, *p*-$Dipp_{WCA\text{-}NHC}$), 7.44 (d, $^3J(^1H, ^1H)$ = 7.9 Hz, 4H, *m*-$Dipp_{NHC}$), 7.34 (d, $^3J(^1H, ^1H)$ = 7.8 Hz, 2H, *m*-$Dipp_{WCA\text{-}NHC}$), 7.20 (d, $^3J(^1H, ^1H)$ = 7.2 Hz, 2H, *m*-$Dipp_{WCA\text{-}NHC}$), 2.70-2.63 (m, 2H, C$\underline{H}(CH_3)_{2\ WCA\text{-}NHC}$), 2.28-2.20 (m, 6H, C$\underline{H}(CH_3)_2$), 1.16 (d, $^3J(^1H, ^1H)$ = 6.7 Hz, 12H, CH(C$\underline{H_3}$)$_{2\ NHC}$), 1.08 (d, $^3J(^1H, ^1H)$ = 6.7 Hz, 6H, CH(C$\underline{H_3}$)$_{2\ WCA\text{-}NHC}$), 1.03 (d, $^3J(^1H, ^1H)$ = 6.8 Hz, 12H,

CH(C$\underline{H}_3$)$_{2\ NHC}$), 0.92 (d, ^3J(^{1}H, ^{1}H) = 6.8 Hz, 6H, CH(C$\underline{H}_3$)$_{2\ WCA\text{-}NHC}$), 0.87 (d, ^3J(^{1}H, ^{1}H) = 6.4 Hz, 6H, CH(C$\underline{H}_3$)$_{2\ WCA\text{-}NHC}$), 0.65 (d, ^3J(^{1}H, ^{1}H) = 6.7 Hz, 6H, CH(C$\underline{H}_3$)$_{2\ WCA\text{-}NHC}$) ppm.

^{11}B-NMR (96 MHz; THF-d_8): δ = -15.7 (s, 1B) ppm.

^{13}C-NMR (151 MHz; THF-d_8): δ = 160.26-159.55 (m, 1C, N-C-N$_{WCA\text{-}NHC}$, detected by HMBC), 149.69-149.55 (m, 3C, Ar^F), 149.23-148.55 (m, 1C, N-C-N$_{NHC}$), 148.41-148.13 (m, 1C, HC=$\underline{C}$B), 148.12-148.00 (m, 3C, Ar^F), 145.72 (s, 2C, *o*-Dipp$_{WCA\text{-}NHC}$), 144.69 (s, 4C, *o*-Dipp$_{NHC}$), 144.42 (s, 2C, *o*-Dipp$_{WCA\text{-}NHC}$), 140.14-139.95 (m, 3C, Ar^F), 140.0 (s, 1C, H$\underline{C}$=CB) 138.42-138.24 (m, 3C, Ar^F), 137.72-137.50 (m, 3C, Ar^F), 136.06-135.80 (m, 3C, Ar^F), 133.89 (s, 1C, *p*-Dipp$_{WCA\text{-}NHC}$), 133.02 (s, 2C, *p*-Dipp$_{NHC}$) 132.76 (s, 1C, *p*-Dipp$_{WCA\text{-}NHC}$), 132.02 (s, 1C, *ipso*-Dipp$_{WCA\text{-}NHC}$), 131.22 (m, 2C, HC=CH), 130.53-130.40 (m, 2C, *ipso*-Dipp$_{NHC}$), 130.30-130.04 (s, 1C, *ipso*-Dipp$_{WCA\text{-}NHC}$), 126.54 (s, 2C, *m*-Dipp$_{WCA\text{-}NHC}$) 125.66 (s, 4C, *m*-Dipp$_{NHC}$), 125.04 (s, 2C, *m*-Dipp$_{WCA\text{-}NHC}$), 29.51 (s, 4C, $\underline{C}$H(CH$_3$)$_{2\ NHC}$), 28.71 (s, 2C, $\underline{C}$H(CH$_3$)$_{2\ WCA\text{-}NHC}$), 28.06 (s, 2C, $\underline{C}$H(CH$_3$)$_{2\ WCA\text{-}NHC}$), 26.32 (s, 2C, CH($\underline{C}$H$_3$)$_{2\ WCA\text{-}NHC}$), 23.39 (s, 2C, CH($\underline{C}$H$_3$)$_{2\ WCA\text{-}NHC}$), 22.36 (s, 4C, CH($\underline{C}$H$_3$)$_{2\ NHC}$), 21.58 (s, 2C, CH($\underline{C}$H$_3$)$_{2\ WCA\text{-}NHC}$) ppm. One signal corresponding to CH($\underline{C}$H$_3$)$_{2\ WCA\text{-}NHC}$ and one signal corresponding to CH($\underline{C}$H$_3$)$_{2\ NHC}$ is overlayed with the residual solvent signal of the THF-d_8.

^{19}F-NMR (282 MHz; THF-d_8): δ = -124.9--132.6 (m, 6F), -164.0--164.8 (m, 6F), -167.8—168.9 (m, 6F) ppm.

^{31}P-NMR (203 MHz; THF-d_8): δ = 456.3 (d, ^1J(^{31}P, ^{31}P) = 552.3 Hz, 1P), 403.4 (d, ^1J(^{31}P, ^{31}P) = 556.7 Hz, 1P) ppm.

EA - Anal. calc. for $C_{72}H_{71}BCl_4F_{15}GaN_4P_2$: C, 55.38; H, 4.58; N, 3.59. Found: C, 54.98; H, 4.38; N, 3.19.

UV/Vis (THF): λ_{max} =465 nm.

S2.4 [WCA-IDipp-As=P-IDipp][GaCl$_4$] (4b)

WCA-IDipp-As(Cl)-P=IDipp (**2b**, 200 mg, 0.140 mg, 1 eq.) was dissolved in 5 mL toluene and $GaCl_3$ (33.5 mg, 0.140 mmol, 1 eq.) dissolved in 2 ml toluene was added dropwise. The resulting dark red suspension was stirred for 2 h at room temperature. Afterwards the supernatant solution was removed via decantation. Residual solvent was removed in vacuo and afterwards co-evaporation was performed with hexane in order to convert the resulting dark red oil into a solid. Subsequently, the solid was washed with 4 × 2 mL hexane and the solvent was removed in vacuo. The crude solid was recrystallized from a chlorobenzene solution layered with hexane at ambient temperatures yielding the product as red crystals (132 mg, 0.077 mmol, 55%).

^{1}H-NMR (600 MHz; THF-d_8): δ = 8.64 (s, 2H, HC=CH), 7.78 (s, 1H, HC=CB), 7.70 (t, ^3J(^{1}H,^{1}H) = 7.8 Hz, 2H, *p*-Dipp$_{NHC}$), 7.56-7.53 (m, 2H, *p*-Dipp$_{WCA\text{-}NHC}$), 7.45 (d, ^3J(^{1}H,^{1}H) = 7.8 Hz, 4H, *m*-Dipp$_{NHC}$), 7.29 (d, ^3J(^{1}H,^{1}H) = 7.8 Hz, 2H, *m*-Dipp$_{WCA\text{-}NHC}$), 7.22 (d, ^3J(^{1}H,^{1}H) = 7.5 Hz, 2H, *m*-Dipp$_{WCA\text{-}NHC}$), 2.74 (sept, ^3J(^{1}H,^{1}H) = 6.7 Hz, 2H, C$\underline{H}$(CH$_3$)$_{2\ WCA\text{-}NHC}$), 2.29-2.23 (m, 6H, C$\underline{H}$(CH$_3$)$_{2\ WCA\text{-}NHC}$ and C$\underline{H}$(CH$_3$)$_{2\ NHC}$), 1.19 (d, ^3J(^{1}H,^{1}H) = 6.7 Hz, 12H, CH(C$\underline{H}_3$)$_{2\ NHC}$), 1.08 (d, ^3J(^{1}H,^{1}H) = 6.7 Hz, 6H, CH(C$\underline{H}_3$)$_{2\ WCA\text{-}NHC}$), 1.05 (d, ^3J(^{1}H,^{1}H) = 6.8 Hz, 12H, CH(C$\underline{H}_3$)$_{2\ NHC}$), 0.91 (d, ^3J(^{1}H,^{1}H) = 6.8 Hz, 6H, CH(C$\underline{H}_3$)$_{2\ WCA\text{-}NHC}$), 0.88 (d, ^3J(^{1}H,^{1}H) = 6.7 Hz, 6H, CH(C$\underline{H}_3$)$_{2\ WCA\text{-}NHC}$), 0.72 (d, ^3J(^{1}H,^{1}H) = 6.7 Hz, 6H, CH(C$\underline{H}_3$)$_{2\ WCA\text{-}NHC}$).

^{11}B-NMR (96 MHz; THF-d_8): δ = -15.7 (s, 1B) ppm.

^{13}C-NMR (151 MHz; THF-d_8): δ = 157.19-155.84 (m, 1C, N-C-N$_{WCA\text{-}NHC}$, detected by HMBC), 154.15-154.05 (m, 1C, HC=$\underline{C}$B, detected by HMBC), 151.97-151.08 (m, 1C, N-C-N$_{NHC}$, detected by HMBC), 149.73-149.52 (m, 3C, Ar^F), 148.17-147.89 (m, 3C, Ar^F), 145.89 (s, 2C, *o*-Dipp$_{WCA\text{-}NHC}$), 144.72 (s, 6C, *o*-Dipp$_{WCA\text{-}NHC}$ and *o*-Dipp$_{NHC}$), 140.14-139.78 (m, 3C, Ar^F), 138.41-138.11 (m, 3C, Ar^F), 138.05 (s, 1C, H$\underline{C}$=CB, detected by HMBC) 137.69-137.49 (m, 3C, Ar^F), 136.07-

135.75 (m, 3C, Ar^F), 133.38 (s, 1C, *p*-$Dipp_{WCA-NHC}$), 133.26 (s, 2C, *p*-$Dipp_{NHC}$), 133.18-132.98 (m, 1C, *ipso*-$Dipp_{WCA-NHC}$), 132.51 (s, 1C, *p*-$Dipp_{WCA-NHC}$), 131.40 (s, 2C, HC=CH), 131.02 (s, 1C, *ipso*-$Dipp_{WCA-NHC}$), 130.61 (s, 2C, *ipso*-$Dipp_{NHC}$), 126.13 (s, 2C, *m*-$Dipp_{WCA-NHC}$), 126.02 (s, 4C, *m*-$Dipp_{NHC}$), 125.54 (s, 2C, *m*-$Dipp_{WCA-NHC}$), 29.45 (s, 4C, $\underline{C}H(CH_3)_{2\ NHC}$), 28.65 (s, 2C, $\underline{C}H(CH_3)_{2\ WCA-NHC}$), 27.99 (s, 2C, $\underline{C}H(CH_3)_{2\ WCA-NHC}$), 26.91 (s, 2C, $CH(\underline{C}H_3)_{2\ WCA-NHC}$), 23.23 (s, $CH(\underline{C}H_3)_{2\ WCA-NHC}$), 22.53 (s, $CH(\underline{C}H_3)_{2\ NHC}$), 21.63 (s, $CH(\underline{C}H_3)_{2\ WCA-NHC}$) ppm. One signal corresponding to $CH(\underline{C}H_3)_{2\ WCA-NHC}$ and one signal corresponding to $CH(\underline{C}H_3)_{2\ NHC}$ is overlayed with the residual solvent signal of the THF-d_8.
^{19}F-NMR (282 MHz; THF-d_8): δ = -126.1- -131.4 (m, 6F), -163.5- -164.1 (m, 6F), -168.0 - -168.4 (m, 6F) ppm.
^{31}P-NMR (203 MHz; THF-d_8): δ = 456.0 (s, 1P) ppm.
EA - Anal. calc. for $C_{72}H_{71}AsBCl_4F_{15}GaN_4P$: C, 53.86; H, 4.46; N, 3.49. Found: C, 53.70; H, 4.443; N, 3.20.
UV/Vis (THF): λ_{max} =472 nm.

S2.5 WCA-IDipp-PP-IDipp radical
WCA-IDipp-P(Cl)-P=IDipp (**2a**, 50 mg, 0.036 mmol, 1 eq.) was dissolved in 2 mL thf and 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (4 mg, 0.018 mmol, 0.5 eq.) dissolved in 2 mL thf was added dropwise. The dark blue green solution was stirred over night at room temperature and afterwards the thf was removed in vacuo. The resulting dark green solid was washed with 5 × 3 mL hexane and then recrystallized by layering a toluene solution with hexane at room temperature. After 5 d the supernatant solution was discarded and residual solvent was removed in vacuo, yielding the product as a dark green solid (22 mg, 0.016 mmol, 45%).
EA - Anal. calc. for $C_{72}H_{71}BF_{15}N_4P_2 \cdot$ toluene: C, 65.79; H, 5.52; N, 3.88. Found: C, 65.41; H, 5.024; N, 4.04.
UV/Vis (THF): λ_{max} = 614 nm.

S2.6 WCA-IDipp-AsP.IDipp radical
WCA-IDipp-As(Cl)-P=IDipp (**2b**, 50 mg, 0.035 mmol, 1 eq.) was dissolved in 2 mL thf and 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (4 mg, 0.017 mmol, 0.5 eq.) dissolved in 2 mL thf was added dropwise. The dark green solution was stirred over night at room temperature and afterwards the thf was removed in vacuo. The resulting dark green solid was washed with 5 × 3 mL hexane and then recrystallized by layering a DCM solution with hexane at room temperature. After 14 d the supernatant solution was discarded and residual solvent was removed in vacuo, yielding the product as a dark green solid (17 mg, 0.012 mmol, 35%).
EA - Anal. calc. for $C_{72}H_{71}AsBF_{15}N_4P$: C, 62.03; H, 5.13; N, 4.02. Found: C, 62.15; H, 5.095; N, 4.03.
UV/Vis (THF): λ_{max} =645 nm.

S3 Crystallographic details

Suitable single crystals were mounted on a hair or on a MiTiGen mount in perfluorinated inert oil. The intensity measurements were performed at 100 K on an Oxford Diffraction Nova A and a Rigaku XtaLAB Synergy S Single Source diffractometer using mirror-focussed Cu*K*α radiation. The diffractometer software CrysAlisPRO was employed.[1] Absorption corrections were based on multiscans. The structures were refined anisotropically on F^2 using SHELXL-2014/7 or -2018.[2] Hydrogen atoms were included using a riding model or rigid methyl groups. Further details are given in Table S1-6.

Solvent content: The chloride species **3a** and **3b** contain one non-coordinated benzene molecule; both are ordered. The diphosphene **4a** crystallizes with two molecules of chlorobenzene, which are formally ordered but display high *U* values. The diarsene **4a** contains one non-coordinated toluene molecule. The radical **5a** contains a thf molecule disordered over a special position, so the overall composition is half a solvate per asymmetric unit. The radical **5b** contains a chlorobenzene molecule disordered over a special position, so the overall composition is half a solvate per asymmetric unit.

Exceptions and special details: The solvent molecules in **4a**, **5a** and **5b** were refined using appropriate restraints to improve stability of refinement, but the dimensions are not entirely satisfactory and should be interpreted with caution.

Complete data have been deposited with the Cambridge Crystallographic Data Centre under the CCDC numbers 1942669-1942674 for compounds **3a**, **3b**, **4a**, **4b**, **5a** and **5b**. These data can be obtained free of charge from http://www.ccdc.cam.ac.uk/.

S3.1 (WCA-IDipp)P(Cl)P(IDipp)

Table S1. Crystallographic data for compound **3a.**

Compound	**3a**	
Identification code (CCDC)	1942669	
Empirical formula	$C_{75}H_{74}BClF_{15}N_4P_2$	
Formula weight	1424.58	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 13.5450(6) Å	□ = 99.475(4)°
	b = 14.3760(10) Å	β = 93.788(4)°
	c = 19.5043(8) Å	γ = 109.582(4)°
Volume	3499.3(3) Å^3	
Z	2	
Density (calculated)	1.352 Mg/m^3	
Absorption coefficient	1.657 mm^{-1}	
F(000)	1478	
Crystal habitus	irregular (orange)	
Crystal size	0.391 x 0.157 x 0.080 mm^3	
Theta range for data collection	3.329 to 76.204°	
Index ranges	-13<=h<=17, -18<=k<=17, -24<=l<=24	
Reflections collected	70864	
Independent reflections	14515 [R(int) = 0.0707]	
Completeness to theta = 67.684°	100.0 %	
Max. and min. transmission	0.985 and 0.951	
Data / restraints / parameters	14515 / 0 / 899	
Goodness-of-fit on F^2	1.038	
Final R indices [I>2sigma(I)]	R1 = 0.0579, wR2 = 0.1521	
R indices (all data)	R1 = 0.0773, wR2 = 0.1668	
Largest diff. peak and hole	0.692 and -0.440 e.Å^{-3}	

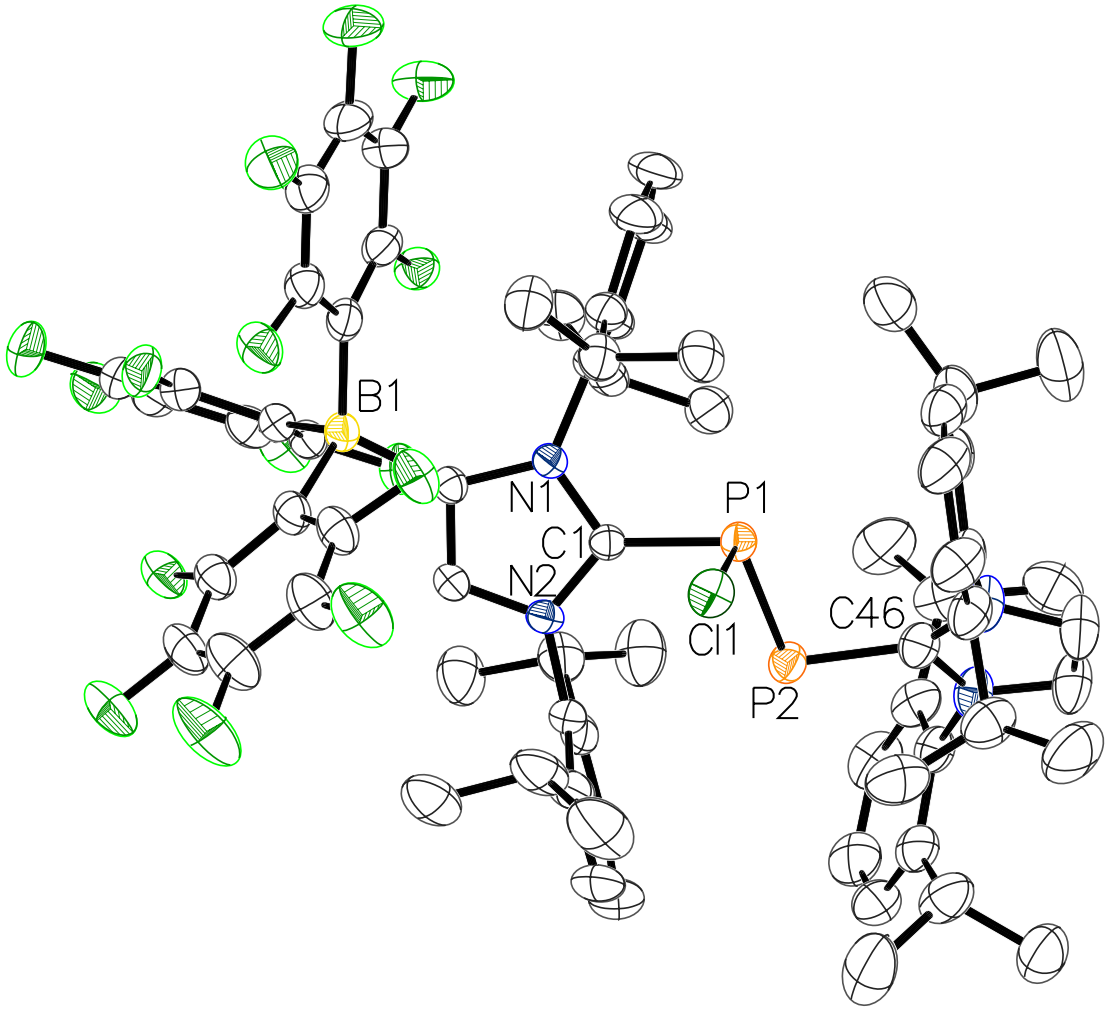

Figure S1a. Molecular structure of (WCA-IDipp)P(Cl)P(IDipp) (**3a**); thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and one co-crystallized benzene molecule are omitted for clarity.

S3.2 (WCA-IDipp)As(Cl)P(IDipp)

Table S2 Crystallographic data for compound **3b.**

Compound	**3b**	
Identification code (CCDC)	1942670	
Empirical formula	$C_{75}H_{74}AsBClF_{15}N_4P$	
Formula weight	1468.53	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 13.5035(8) Å	α= 99.868(4)°
	b = 14.3960(8) Å	β= 93.997(4)°
	c = 19.4613(8) Å	γ = 108.674(5)°
Volume	3499.4(3) $Å^3$	
Z	2	
Density (calculated)	1.394 Mg/m^3	
Absorption coefficient	1.966 mm^{-1}	
F(000)	1514	
Crystal habitus	plate (yellow)	
Crystal size	0.135 x 0.055 x 0.026 mm^3	
Theta range for data collection	3.311 to 76.706°	
Index ranges	-16<=h<=16, -18<=k<=18, -24<=l<=18	
Reflections collected	82893	
Independent reflections	14545 [R(int) = 0.1297]	
Completeness to theta = 67.684°	100.0 %	
Max. and min. transmission	0.996 and 0.986	
Data / restraints / parameters	14545 / 0 / 899	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0563, wR2 = 0.1329	
R indices (all data)	R1 = 0.0888, wR2 = 0.1555	
Largest diff. peak and hole	0.666 and -0.758 $e.Å^{-3}$	

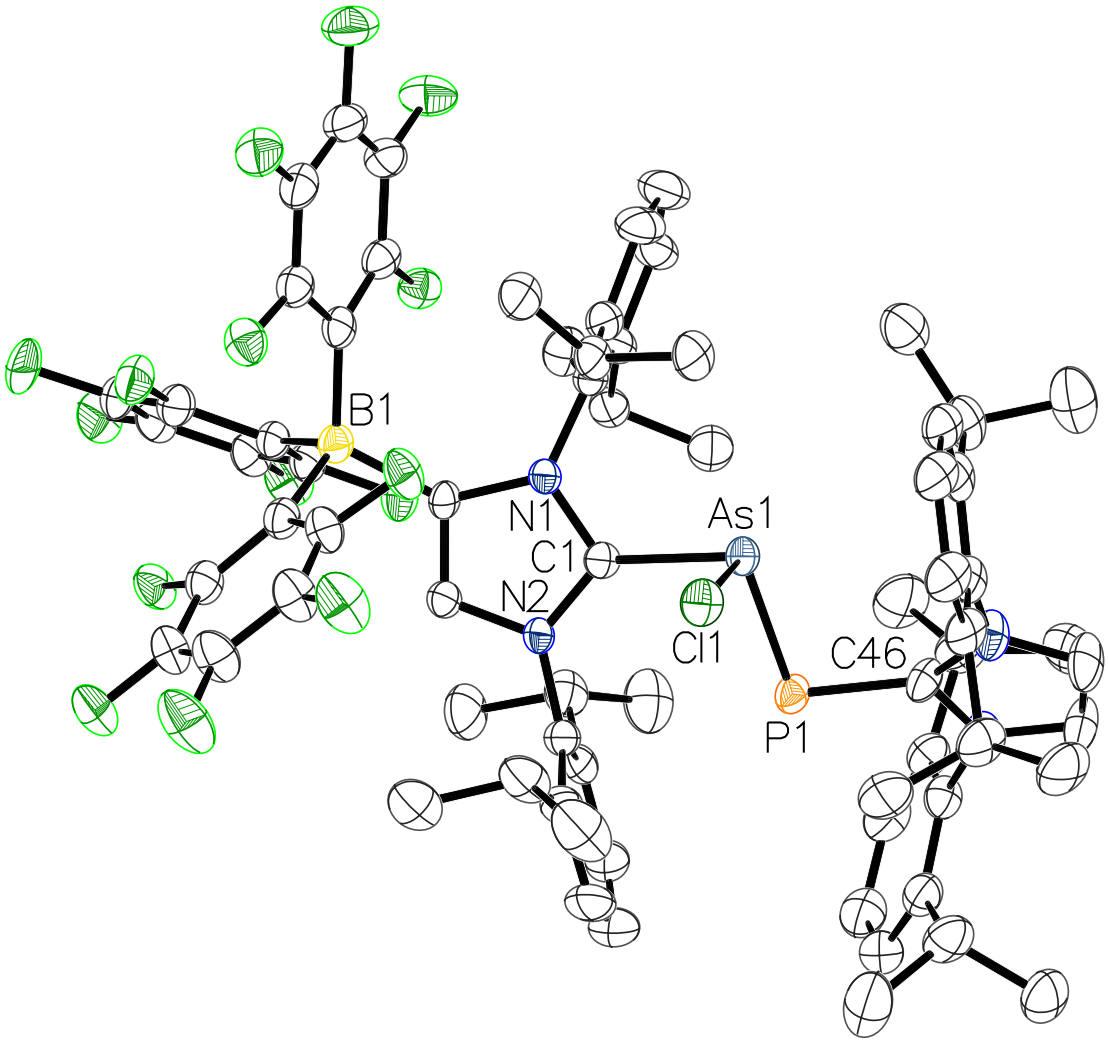

Figure S2. Molecular structure of (WCA-IDipp)As(Cl)P(IDipp) (**3b**); thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and one co-crystallized benzene molecule are omitted for clarity.

S3.3 [(WCA-IDipp)P=P(IDipp)][$GaCl_4$]

Table S3 Crystallographic data for compound **4a.**

Compound	**4a**	
Identification code (CCDC)	1942671	
Empirical formula	$C_{78}H_{76}BC_{l5}F_{15}GaN_4P_2$	
Formula weight	1674.14	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 10.6105(2) Å	α= 83.1200(10)°
	b = 14.4633(2) Å	β= 89.6020(10)°
	c = 26.9560(4) Å	γ = 72.833(2)°
Volume	3922.23(12) $Å^3$	
Z	2	
Density (calculated)	1.418 Mg/m^3	
Absorption coefficient	3.132 mm^{-1}	
F(000)	1716	
Crystal habitus	irregular (orange)	
Crystal size	0.329 x 0.237 x 0.189 mm^3	
Theta range for data collection	3.223 to 76.209°	
Index ranges	-12<=h<=13, -18<=k<=18, -33<=l<=33	
Reflections collected	161786	
Independent reflections	16378 [R(int) = 0.0815]	
Completeness to theta = 67.684°	100.0 %	
Max. and min. transmission	0.973 and 0.960	
Data / restraints / parameters	16378 / 271 / 1080	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0554, wR2 = 0.1541	
R indices (all data)	R1 = 0.0704, wR2 = 0.1688	
Largest diff. peak and hole	0.985 and -1.261 $e.Å^{-3}$	

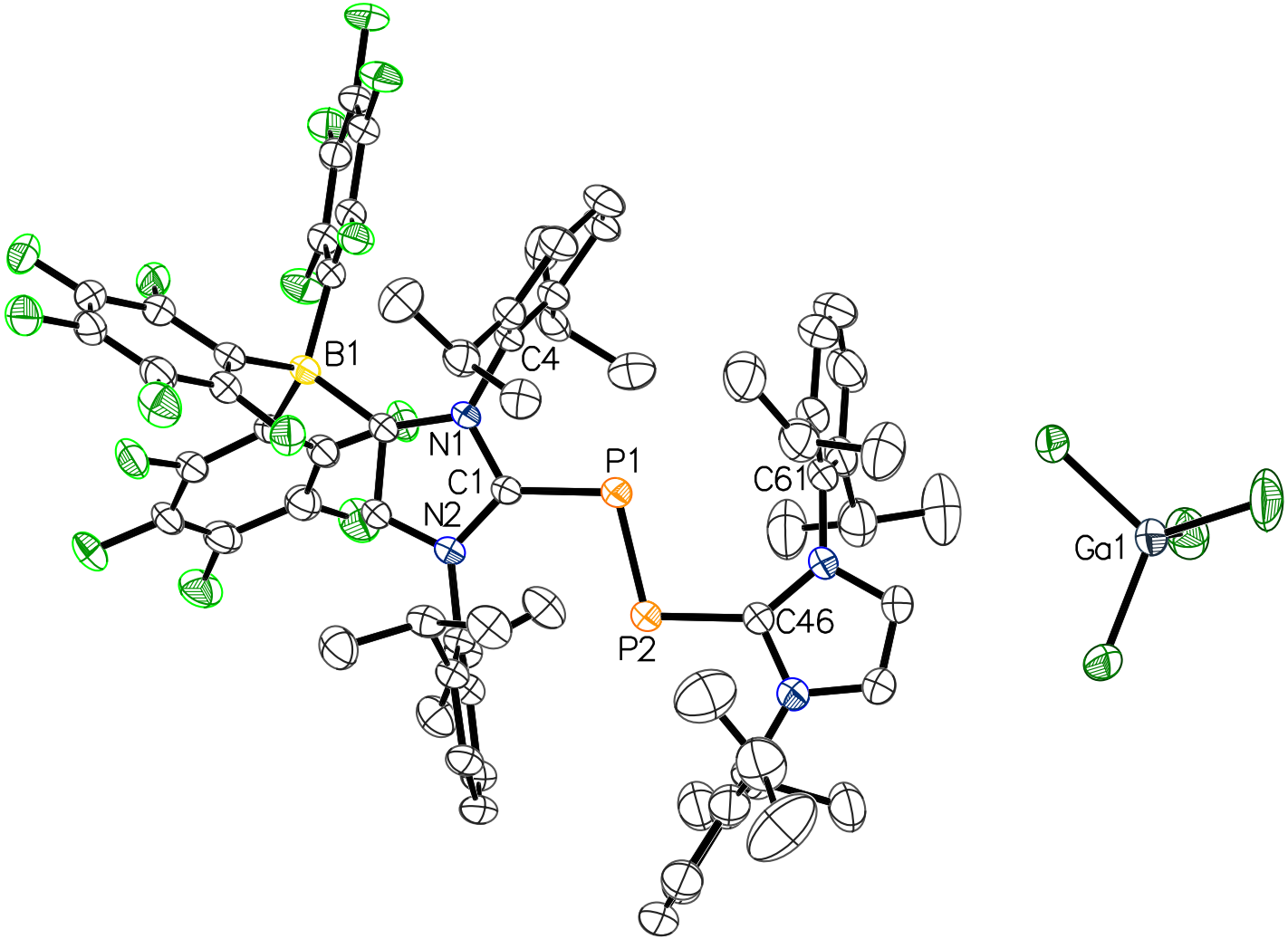

Figure S3. Molecular structure of [(WCA-IDipp)P=P-(IDipp)][$GaCl_4$] (**4a**); thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and two co-crystallized chlorobenzene molecules are omitted for clarity.

S3.4 [(WCA-IDipp)As=P(IDipp)][$GaCl_4$]

Table S4 Crystallographic data for compound **4b.**

Compound	**4b**	
Identification code (CCDC)	1942672	
Empirical formula	$C_{79}H_{79}AsBCl_4F_{15}GaN_4P$	
Formula weight	1697.68	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 13.8673(2) Å	α = 102.619(2)°
	b = 14.4035(2) Å	β = 96.156(2)°
	c = 21.4914(4) Å	γ = 110.132(2)°
Volume	3854.26(12) $Å^3$	
Z	2	
Density (calculated)	1.463 Mg/m^3	
Absorption coefficient	1.025 mm^{-1}	
F(000)	1736	
Crystal habitus	plate (orange)	
Crystal size	0.626 x 0.342 x 0.161 mm^3	
Theta range for data collection	2.529 to 31.121°	
Index ranges	-19<=h<=20, -20<=k<=20, -30<=l<=30	
Reflections collected	177241	
Independent reflections	21529 [R(int) = 0.0338]	
Completeness to theta = 25.242°	99.9 %	
Max. and min. transmission	1.000 and 0.165	
Data / restraints / parameters	21529 / 0 / 1022	
Goodness-of-fit on F^2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.1129	
R indices (all data)	R1 = 0.0494, wR2 = 0.1166	
Largest diff. peak and hole	2.650 and -1.151 $e.Å^{-3}$	

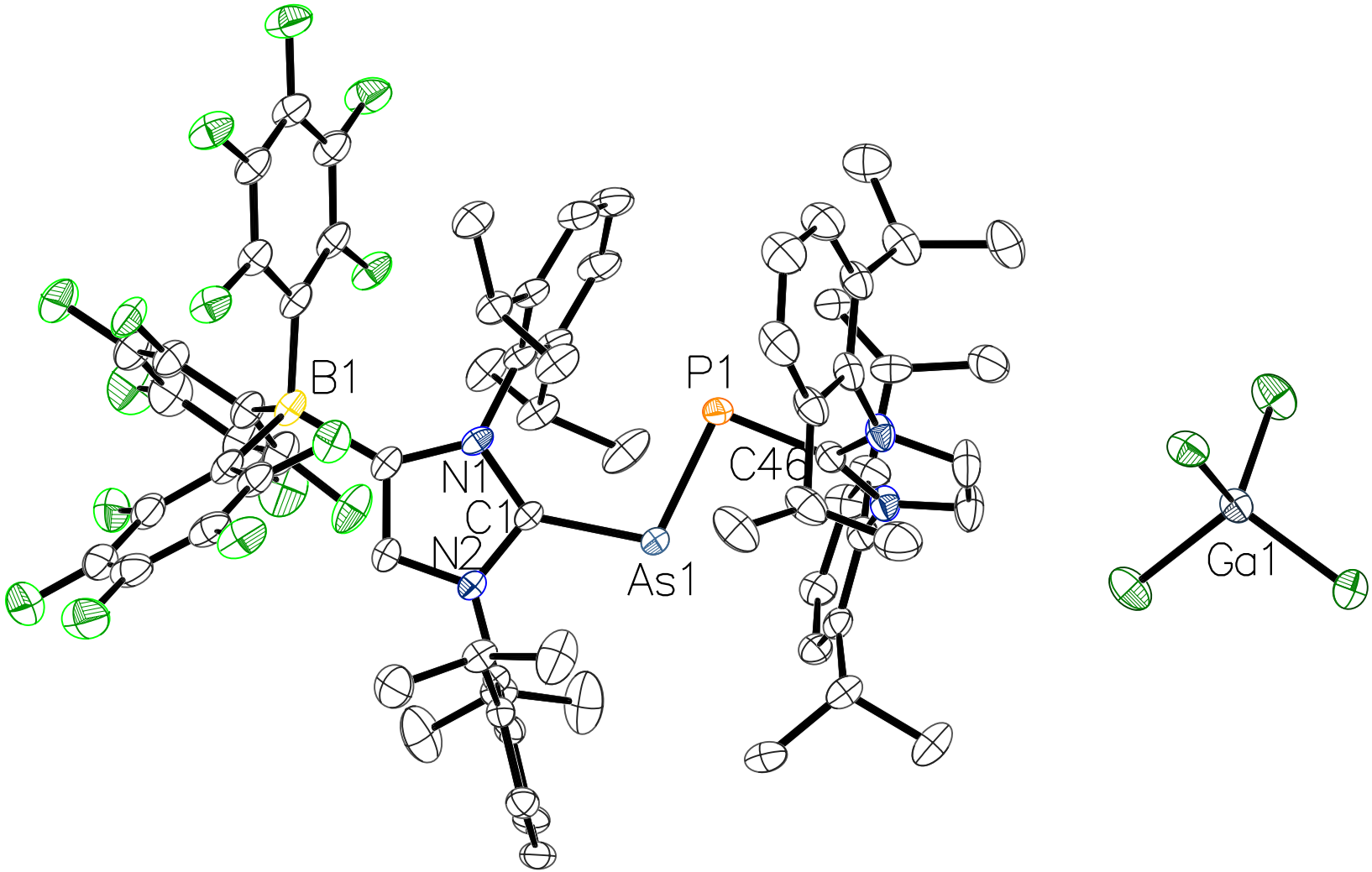

Figure S4. Molecular structure of [(WCA-IDipp)As=P(IDipp)][$GaCl_4$] (**4b**); thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and on co-crystallized toluene molecule are omitted for clarity.

S3.5 [(WCA-IDipp)PP(IDipp)]•

Table S5 Crystallographic data for compound **5a.**

Compound	**5a**	
Identification code (CCDC)	1942673	
Empirical formula	$C_{74}H_{75}BF_{15}N_4O_{0.50}P_2$	
Formula weight	1386.13	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 12.5253(2) Å	α = 105.855(2)°
	b = 15.4459(2) Å	β = 90.306(2)°
	c = 20.2657(2) Å	γ = 112.409(2)°
Volume	3460.20(10) Å^3	
Z	2	
Density (calculated)	1.330 Mg/m^3	
Absorption coefficient	1.319 mm^{-1}	
F(000)	1442	
Crystal habitus	irregular (red-green dichroic)	
Crystal size	0.298 x 0.252 x 0.147 mm^3	
Theta range for data collection	2.284 to 77.620°	
Index ranges	-15<=h<=15, -19<=k<=19, -25<=l<=25	
Reflections collected	144778	
Independent reflections	14569 [R(int) = 0.0416]	
Completeness to theta = 67.684°	100.0 %	
Max. and min. transmission	1.000 and 0.399	
Data / restraints / parameters	14569 / 66 / 908	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0466, wR2 = 0.1269	
R indices (all data)	R1 = 0.0487, wR2 = 0.1285	
Largest diff. peak and hole	0.638 and -0.603 e.Å^{-3}	

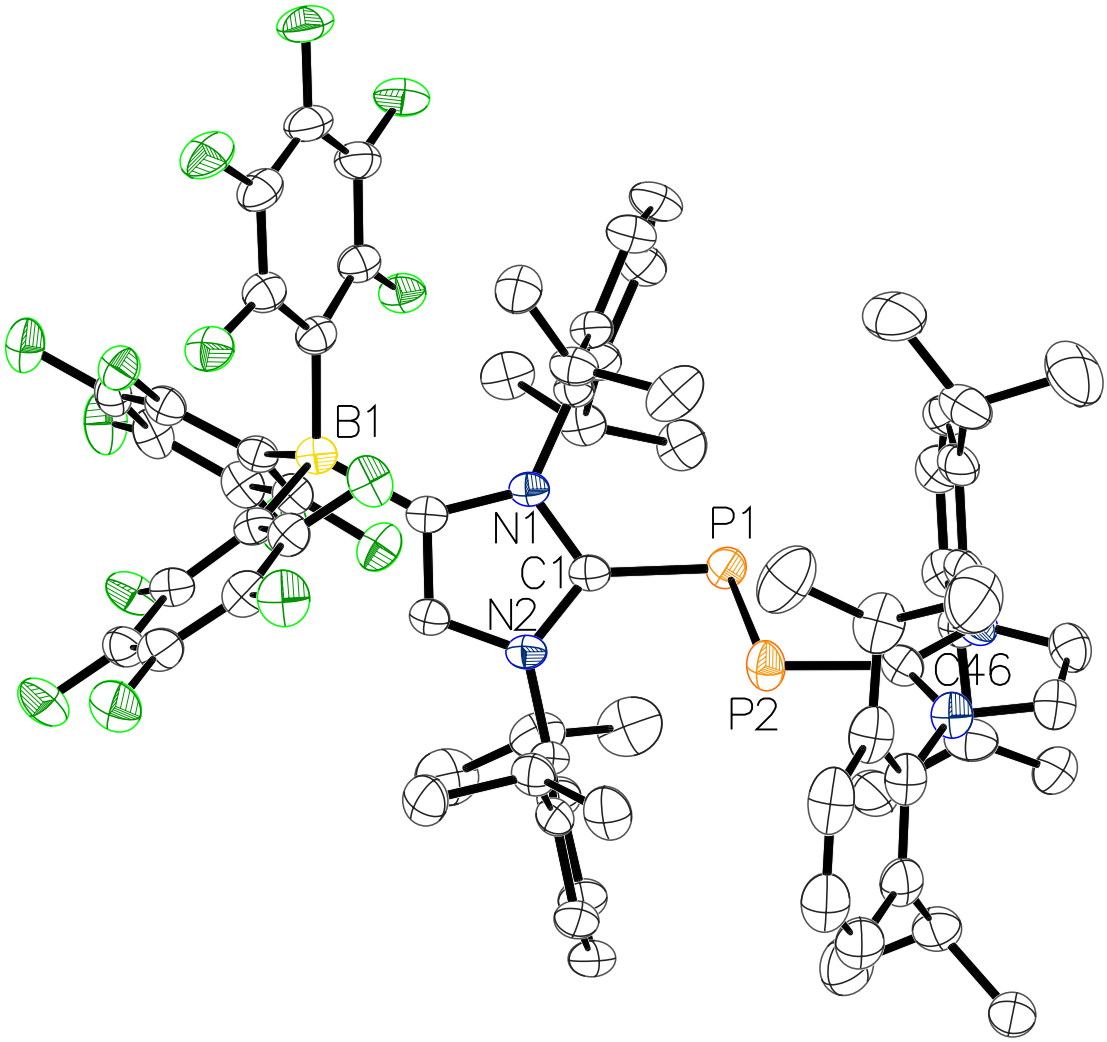

Figure S5. Molecular structure of [(WCA-IDipp)PP(IDipp)]• (**5a**); thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and one half co-crystallized thf molecule are omitted for clarity.

S3.6 [(WCA-IDipp)AsP(IDipp)]•

Table S6 Crystallographic data for compound **5b.**

Compound	**5b**	
Identification code (CCDC)	1942674	
Empirical formula	$C_{75}H_{73.50}AsBCl_{0.50}F_{15}N_4P$	
Formula weight	1450.30	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 12.4926(8) Å	α = 105.543(4)°
	b = 15.7024(10) Å	β = 90.831(4)°
	c = 20.2821(8) Å	γ = 112.950(6)°
Volume	3497.8(4) $Å^3$	
Z	2	
Density (calculated)	1.377 Mg/m^3	
Absorption coefficient	1.789 mm^{-1}	
F(000)	1496	
Crystal habitus	needle (green)	
Crystal size	0.175 x 0.041 x 0.032 mm^3	
Theta range for data collection	2.282 to 766.600°	
Index ranges	-14<=h<=14, -18<=k<=18, -18<=l<=24	
Reflections collected	36387	
Independent reflections	12081 [R(int) = 0.0677]	
Completeness to theta = 67.684°	99.3 %	
Max. and min. transmission	1.000 and 0.699	
Data / restraints / parameters	12081 / 161 / 926	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0675, wR2 = 0.1768	
R indices (all data)	R1 = 0.0938, wR2 = 0.1970	
Largest diff. peak and hole	1.391 and -0.622 $e.Å^{-3}$	

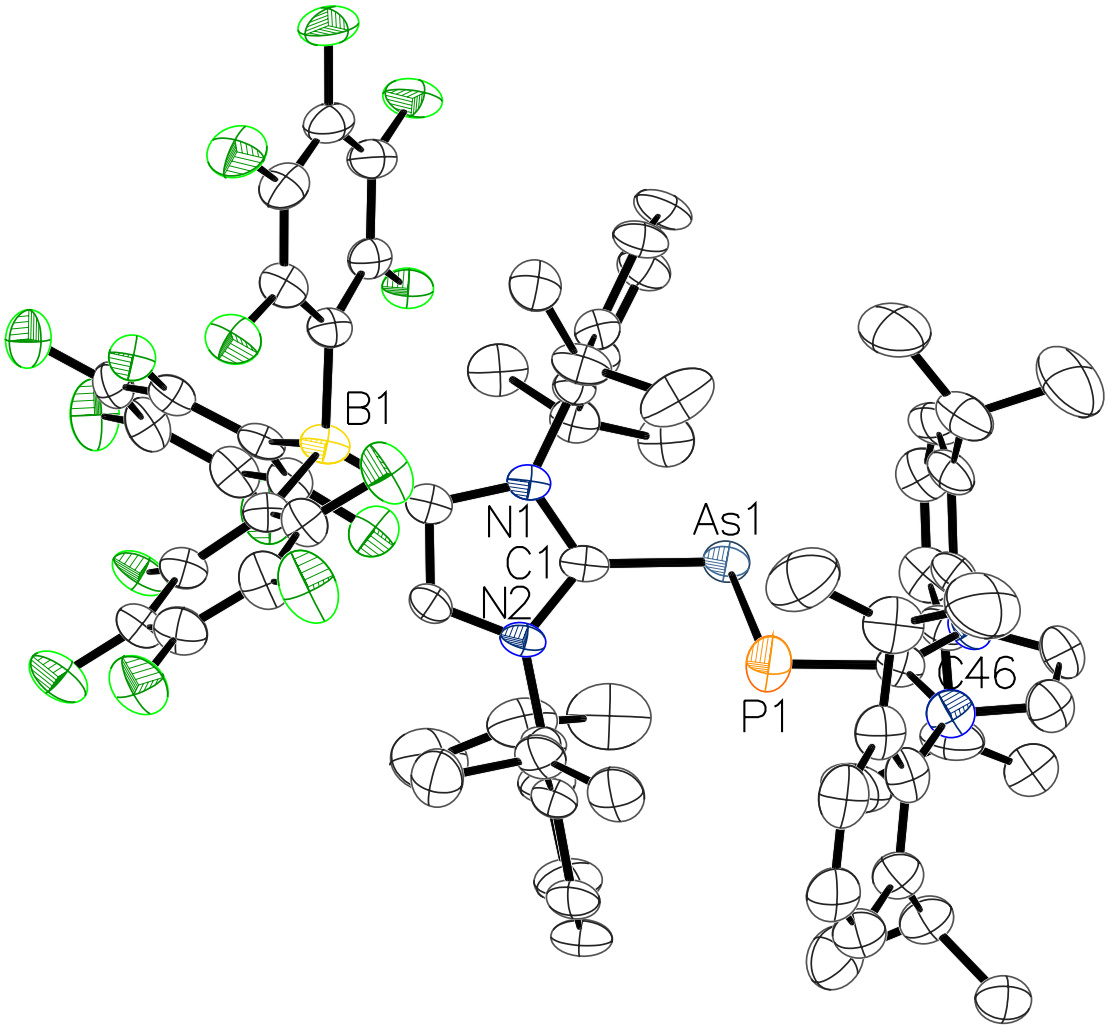

Figure S6. Molecular structure of [(WCA-IDipp)As=P(IDipp)]• (**5b**); thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and one half co-crystallized chlorobenzene moleculeare omitted for clarity.

S4 ^{1}H, ^{13}C, ^{11}B, ^{19}F and ^{31}P NMR spectra

S4.1 (WCA-IDipp)P(Cl)P(IDipp) (3a)

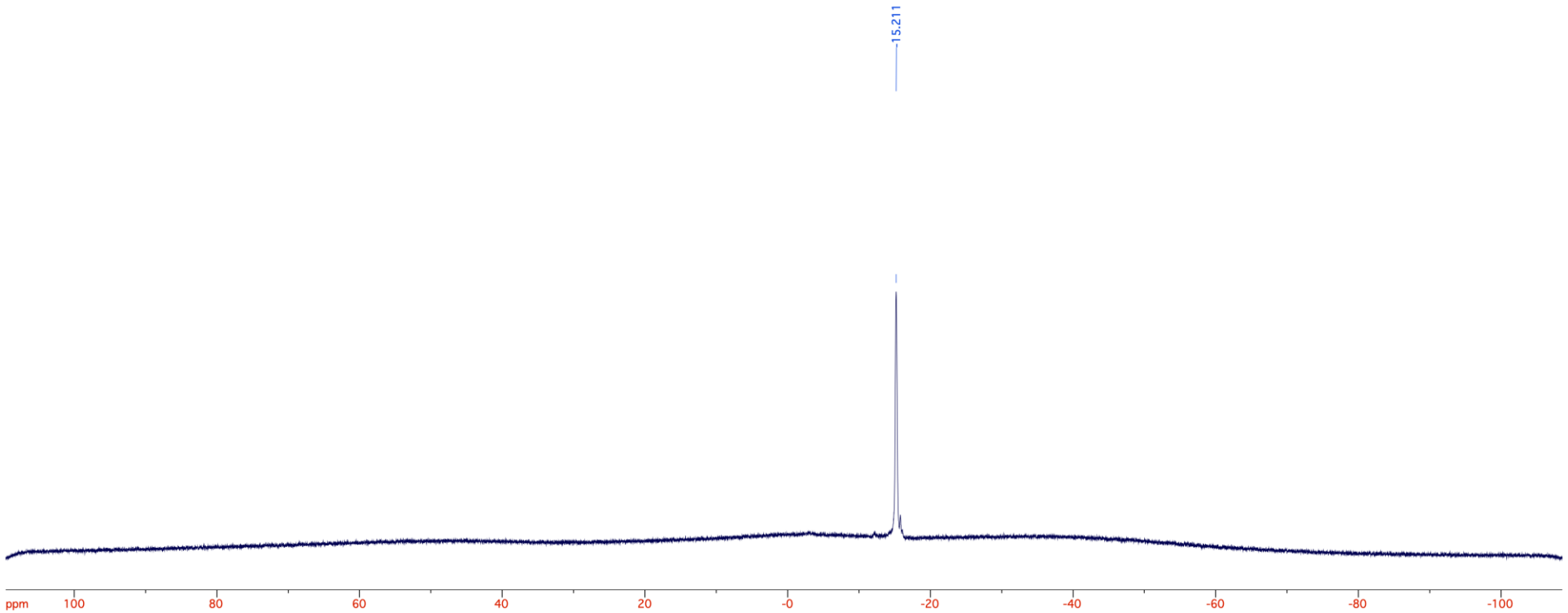

Figure S7. ^{11}B NMR spectrum (96 MHz, THF-d_8, 278 K) of (WCA-IDipp)P(Cl)P(IDipp) (**3a**).

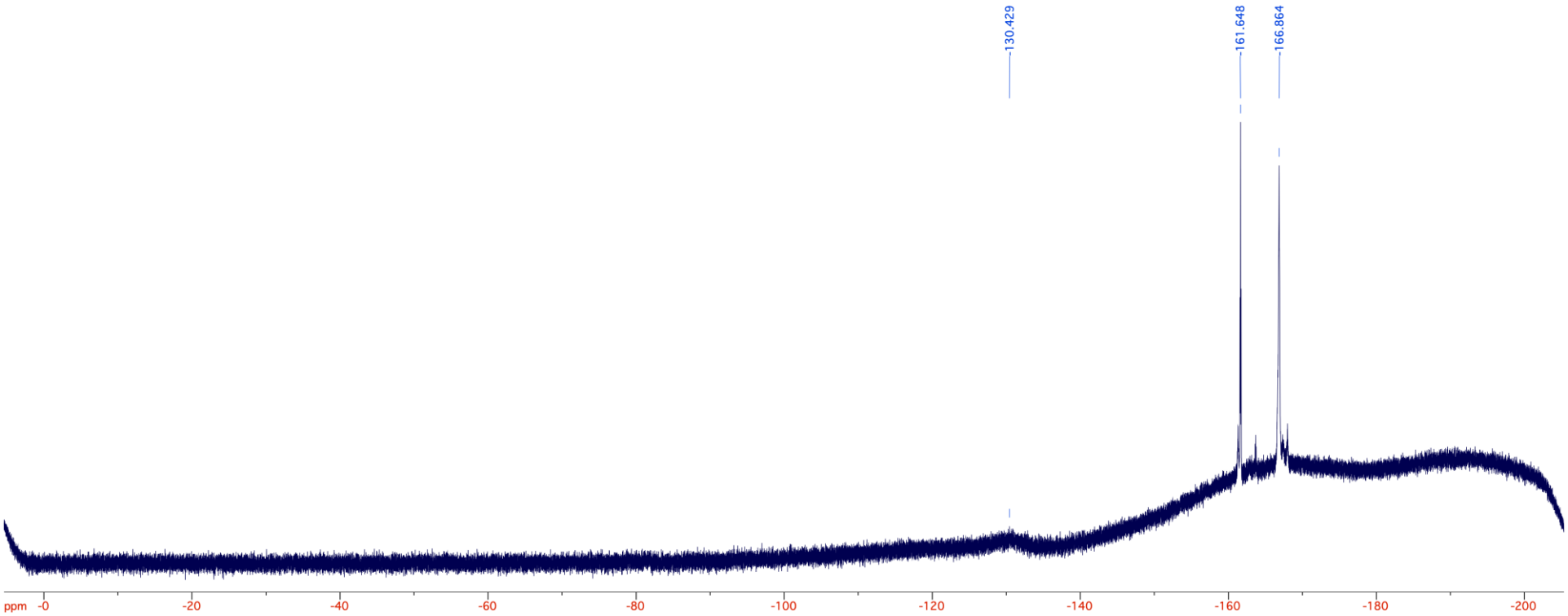

Figure S8. ^{19}F NMR spectrum (282 MHz, THF-d_8, 278 K) of (WCA-IDipp)P(Cl)P(IDipp) (**3a**).

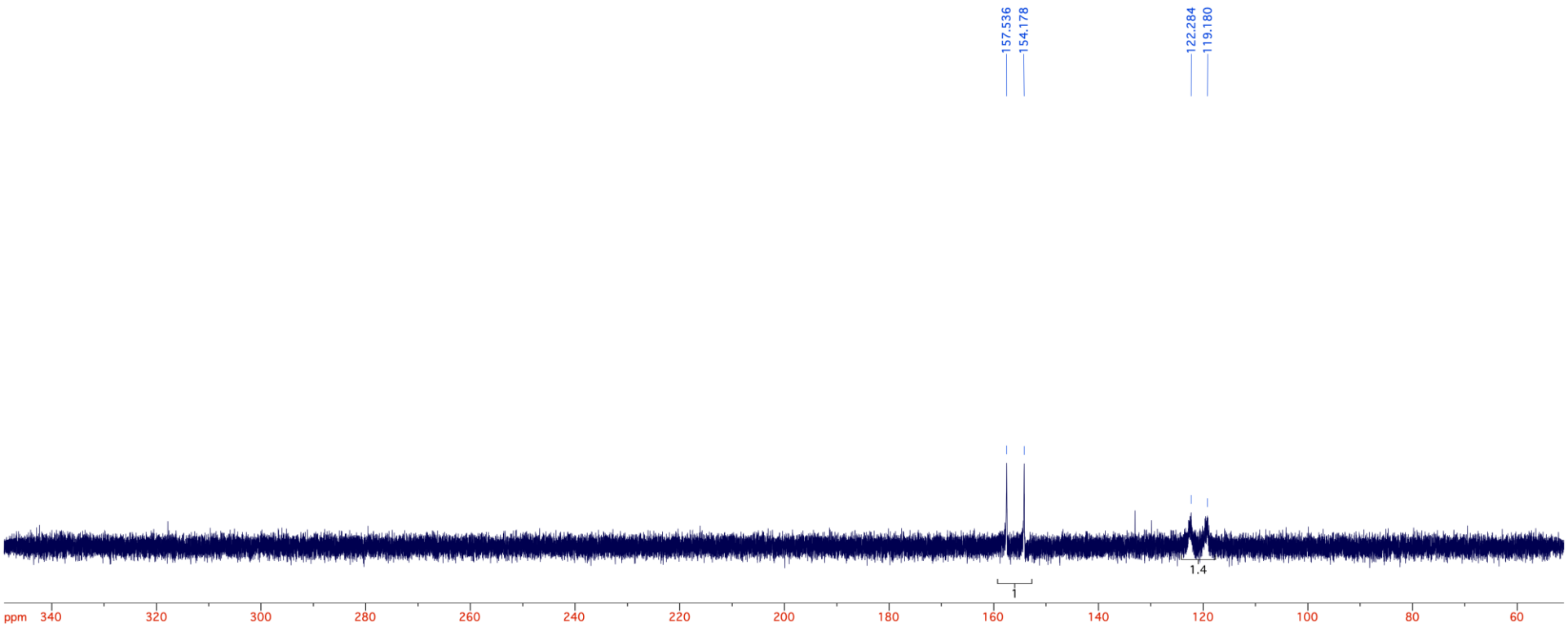

Figure S9. ^{31}P NMR spectrum (122 MHz, THF-d_8, 278 K) of (WCA-IDipp)P(Cl)P(IDipp) (**3a**).

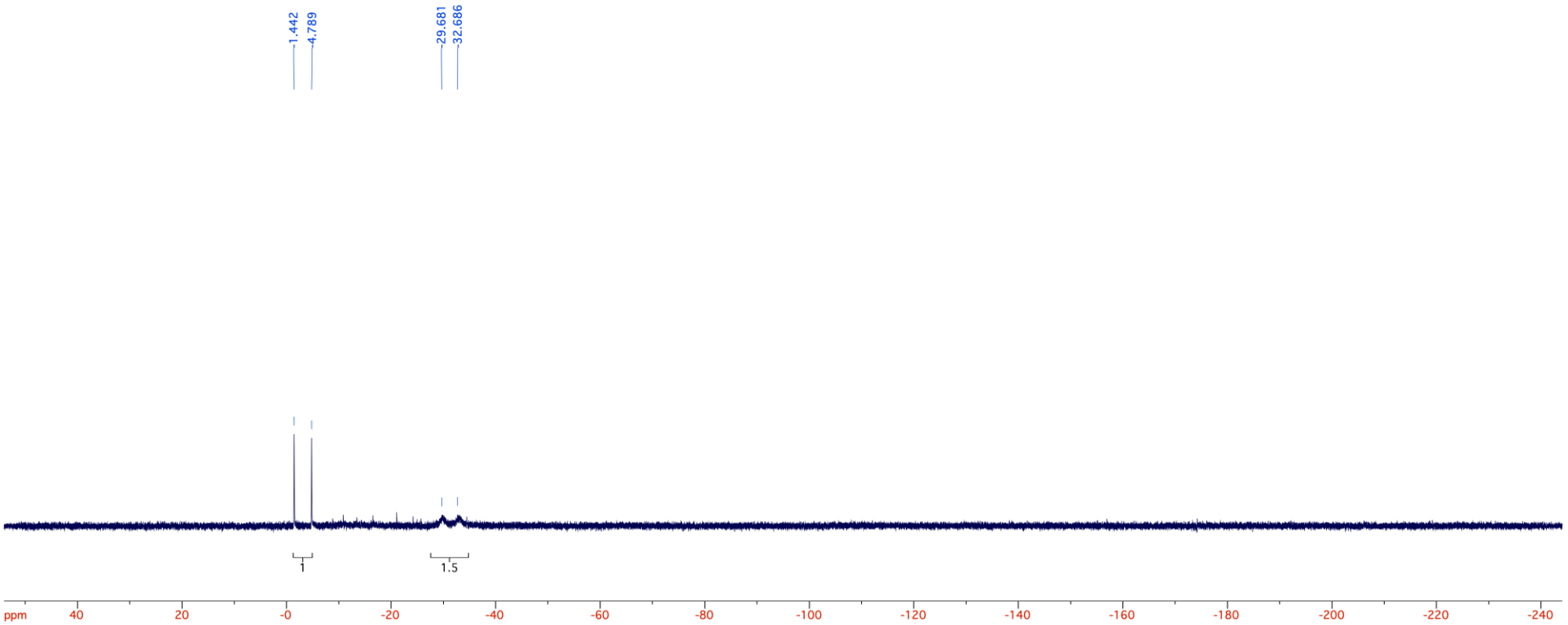

Figure S10. ^{31}P NMR spectrum (122 MHz, THF-d_8, 278 K) of (WCA-IDipp)P(Cl)P(IDipp) (**3a**).

S4.2 (WCA-IDipp)As(Cl)P(IDipp) (3b)

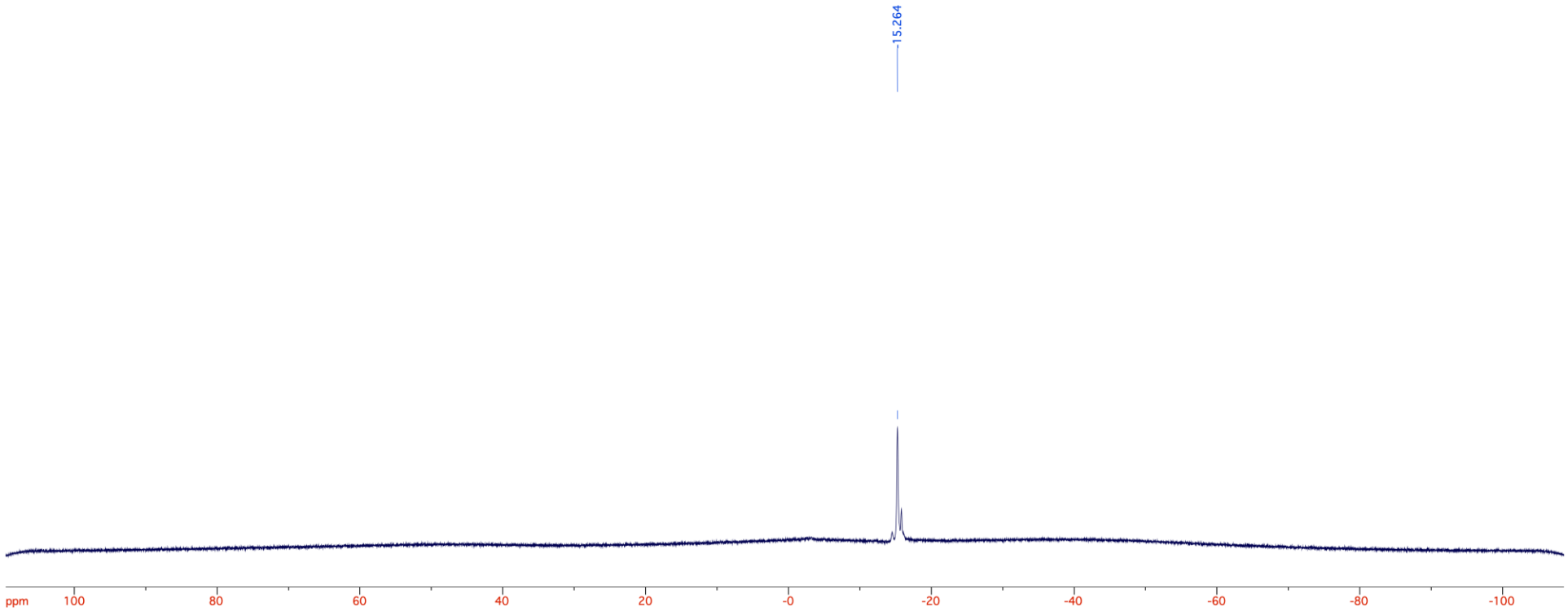

Figure S11. ^{11}B NMR spectrum (96 MHz, THF-d_8, 278 K) of (WCA-IDipp)As(Cl)P(IDipp) (**3b**).

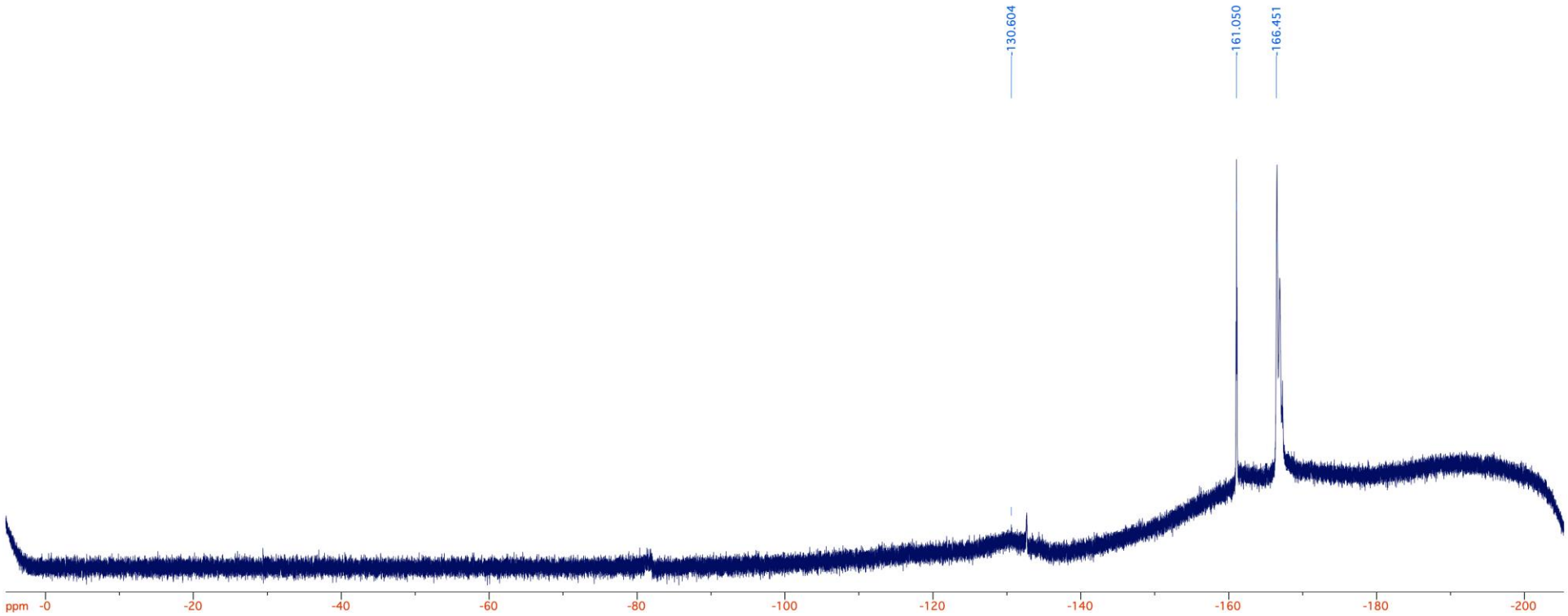

Figure S12. ^{19}F NMR spectrum (282 MHz, THF-d_8, 278 K) of (WCA-IDipp)As(Cl)P(IDipp) (**3b**).

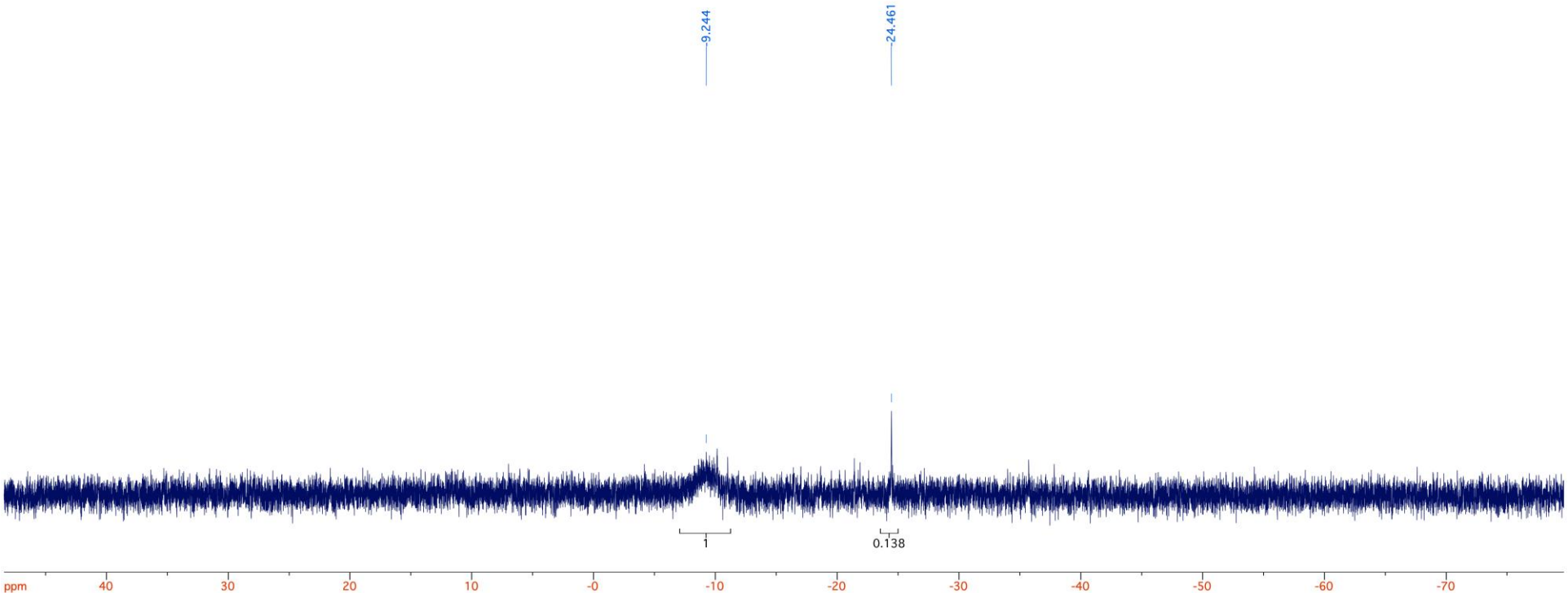

Figure S13. ^{31}P NMR spectrum (122 MHz, THF-d_8, 278 K) of (WCA-IDipp)As(Cl)P(IDipp) (**3b**).

S4.3 [(WCA-IDipp)P=P(IDipp)][$GaCl_4$] (4a)

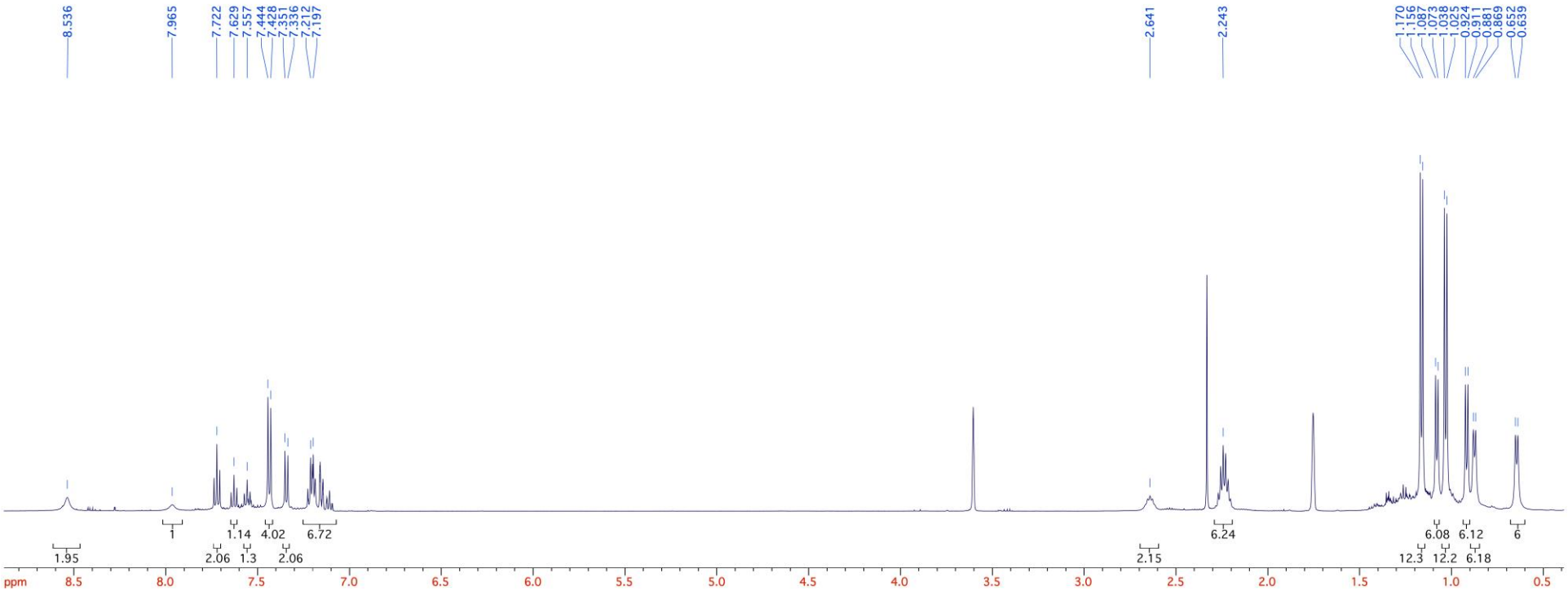

Figure S14. ^{1}H NMR spectrum (500 MHz, THF-d_8, 278 K) of [(WCA-IDipp)P=P(IDipp)][$GaCl_4$] (**4a**).

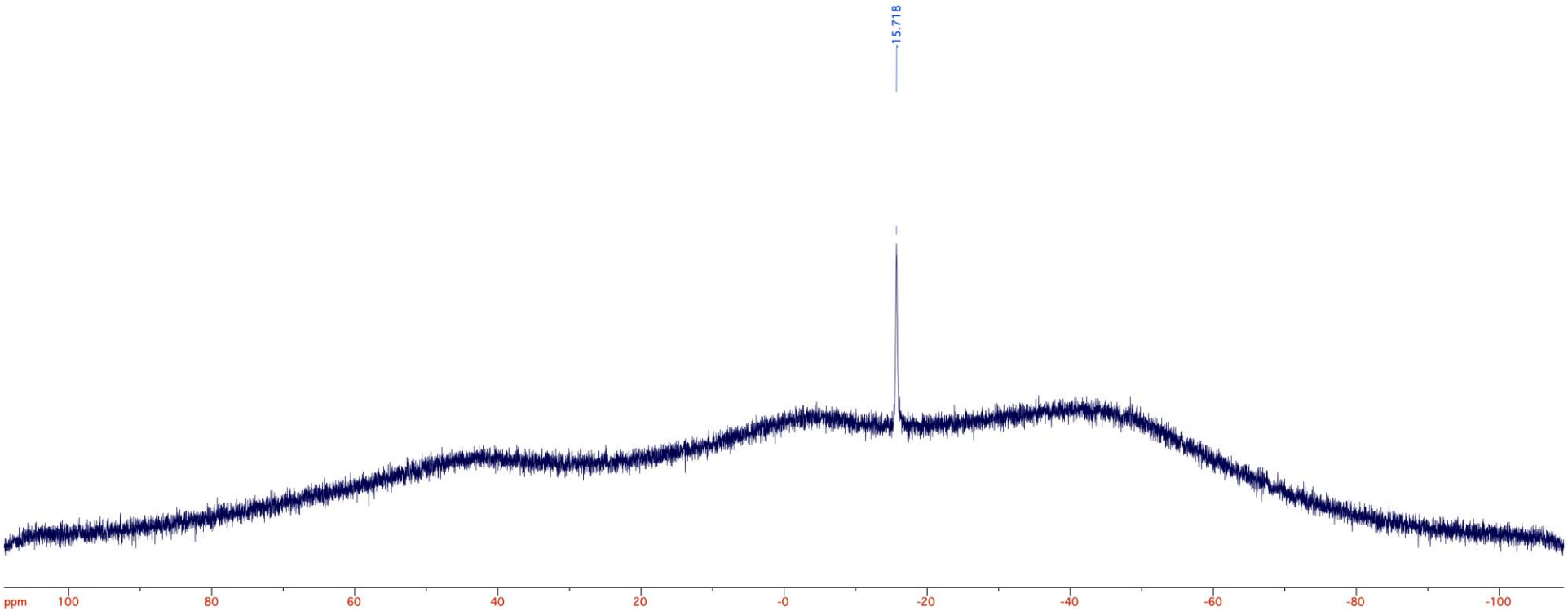

Figure S15. ^{11}B NMR spectrum (96 MHz, THF-d_8, 278 K) of [(WCA-IDipp)P=P(IDipp)][$GaCl_4$] (**4a**).

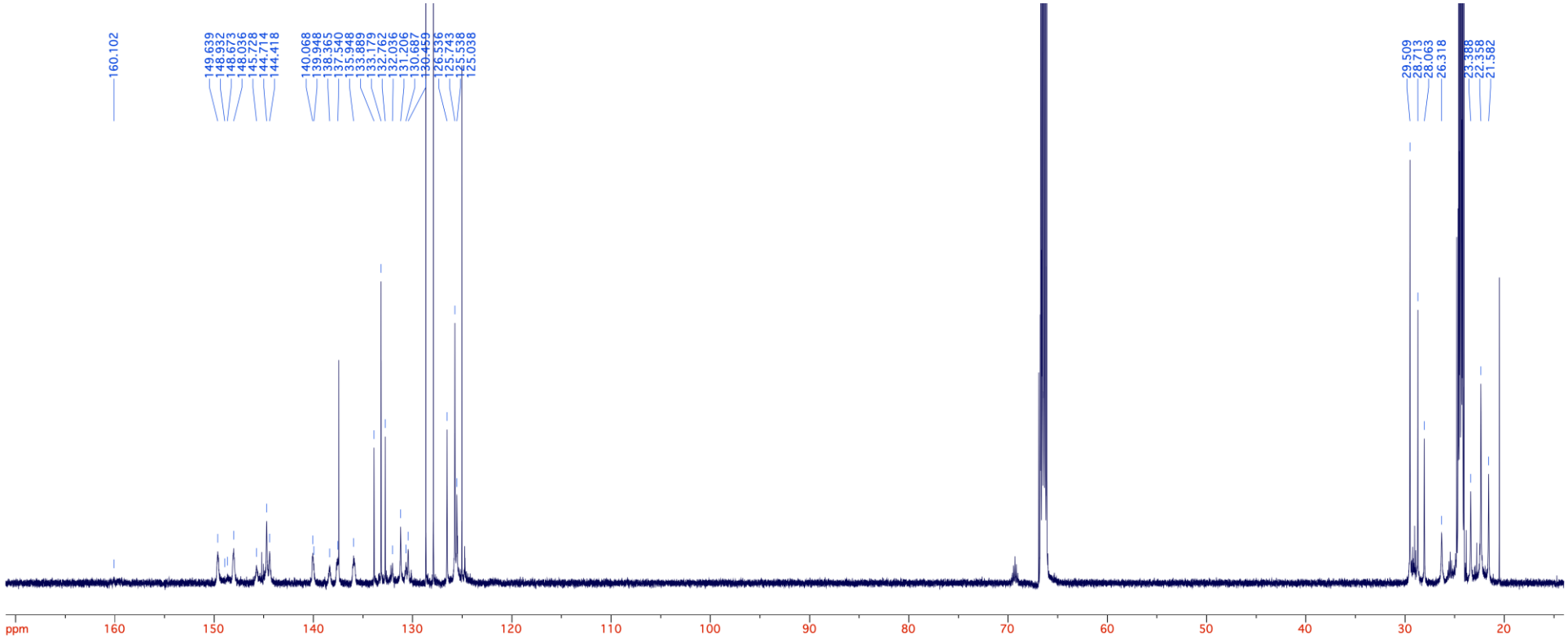

Figure S16. ^{13}C NMR spectrum (151 MHz, THF-d_8, 278 K) of [(WCA-IDipp)P=P(IDipp)][$GaCl_4$] (**4a**).

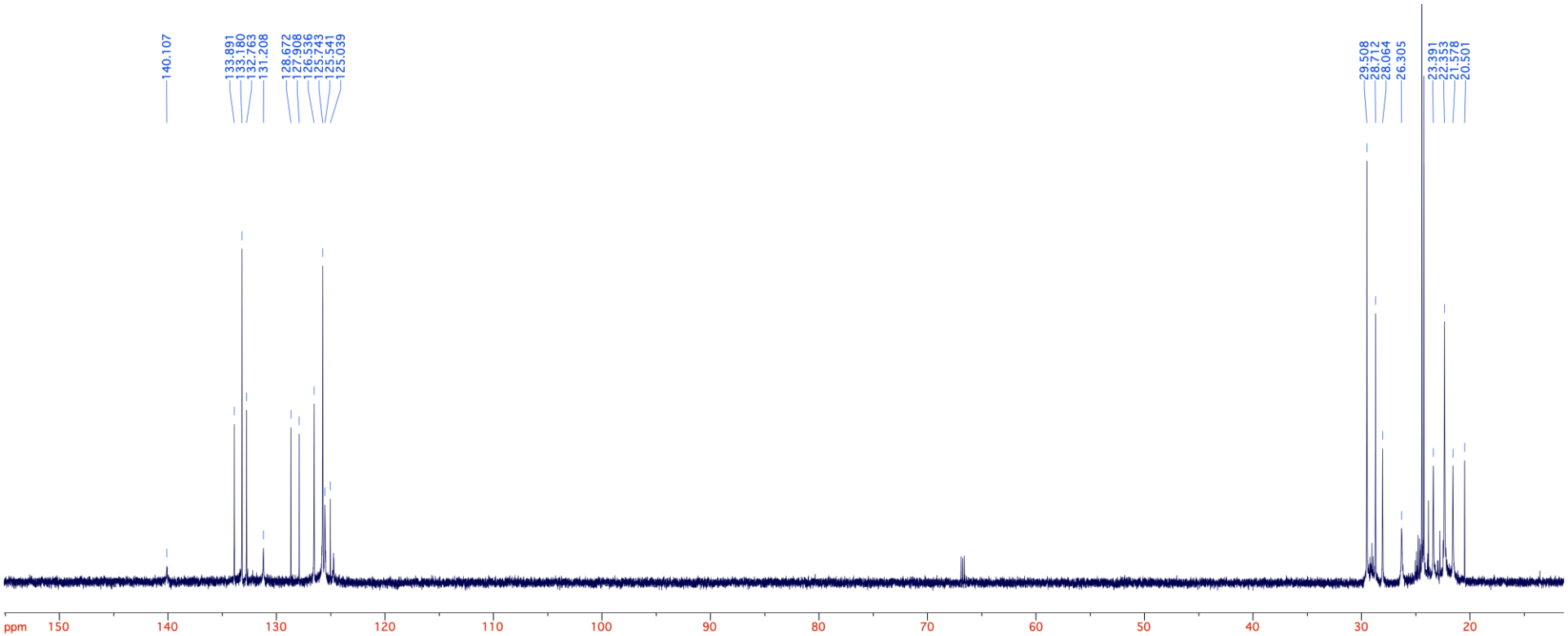

Figure S17. ^{13}C DEPT135 NMR spectrum (151 MHz, THF-d_8, 278 K) of [(WCA-IDipp)P=P(IDipp)][$GaCl_4$] (**4a**).

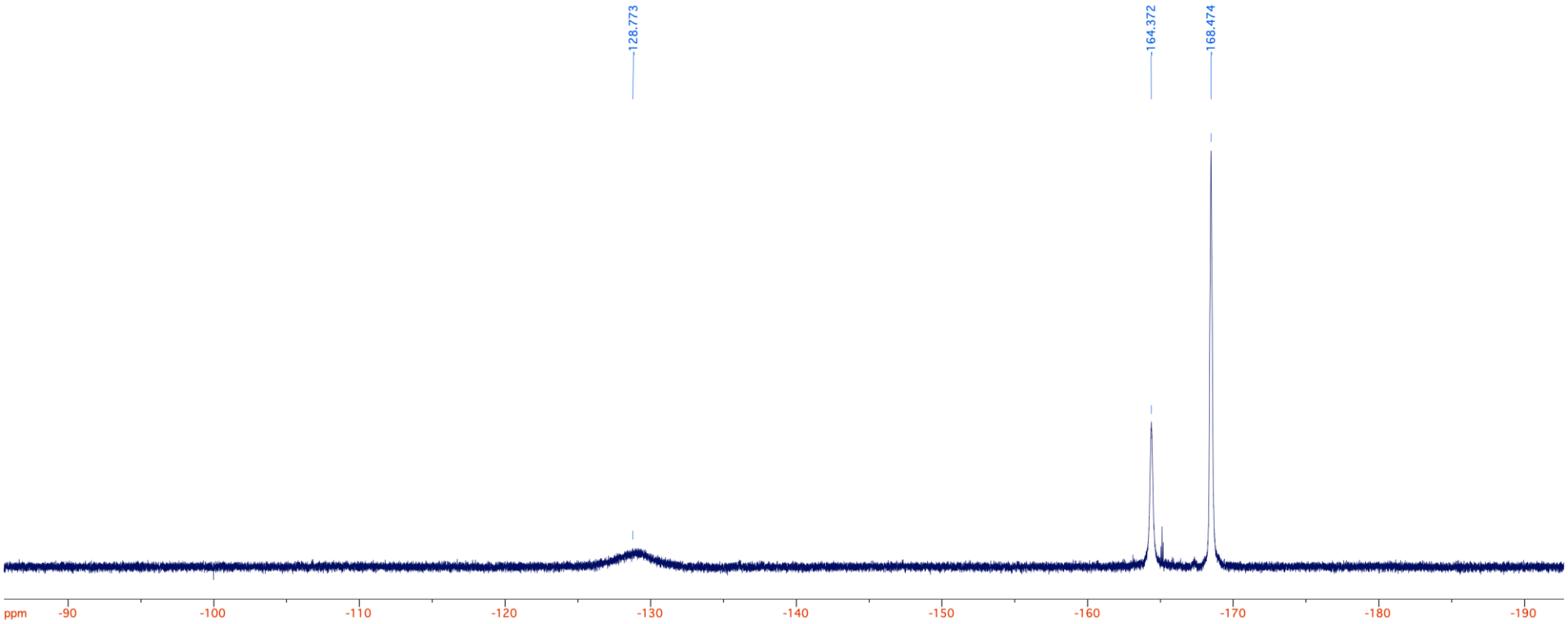

Figure S18. ^{19}F NMR spectrum (282 MHz, THF-d_8, 278 K) of [(WCA-IDipp)P=P(IDipp)][$GaCl_4$] (**4a**).

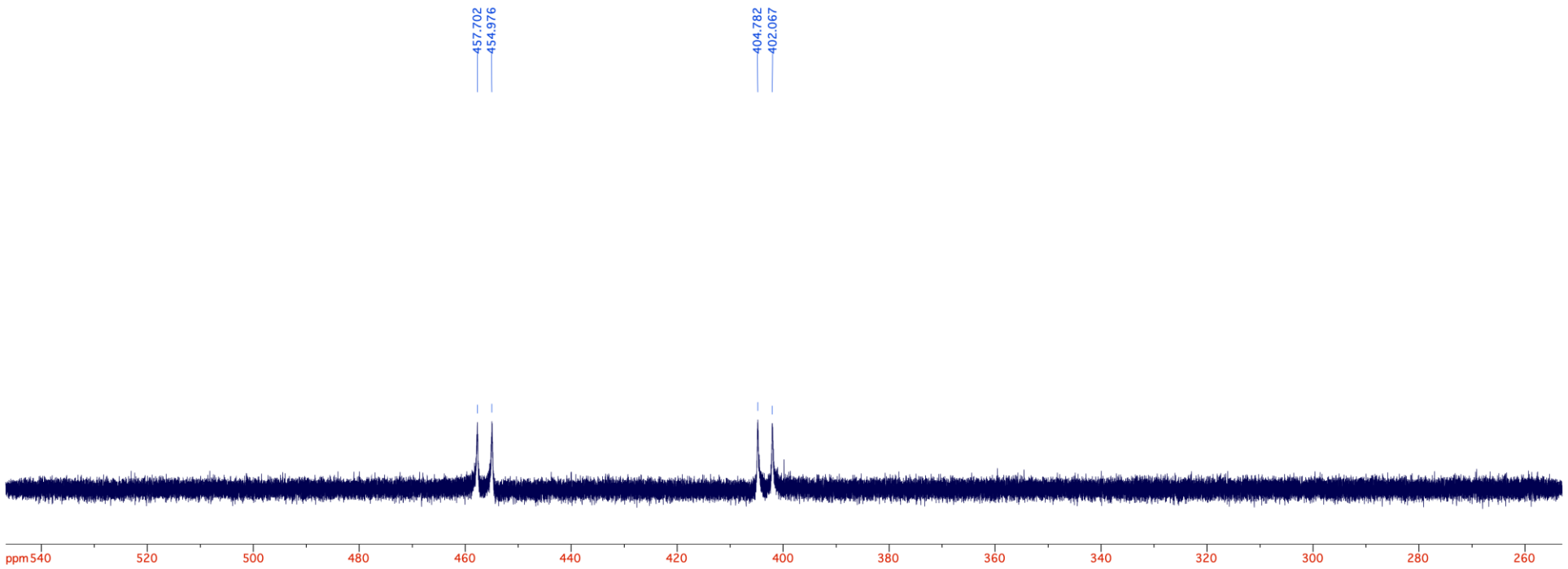

Figure S19. ^{31}P NMR spectrum (122 MHz, THF-d_8, 278 K) of [(WCA-IDipp)P=P(IDipp)][$GaCl_4$] (**4a**).

S4.3 [(WCA-IDipp)As=P(IDipp)][$GaCl_4$] (4b)

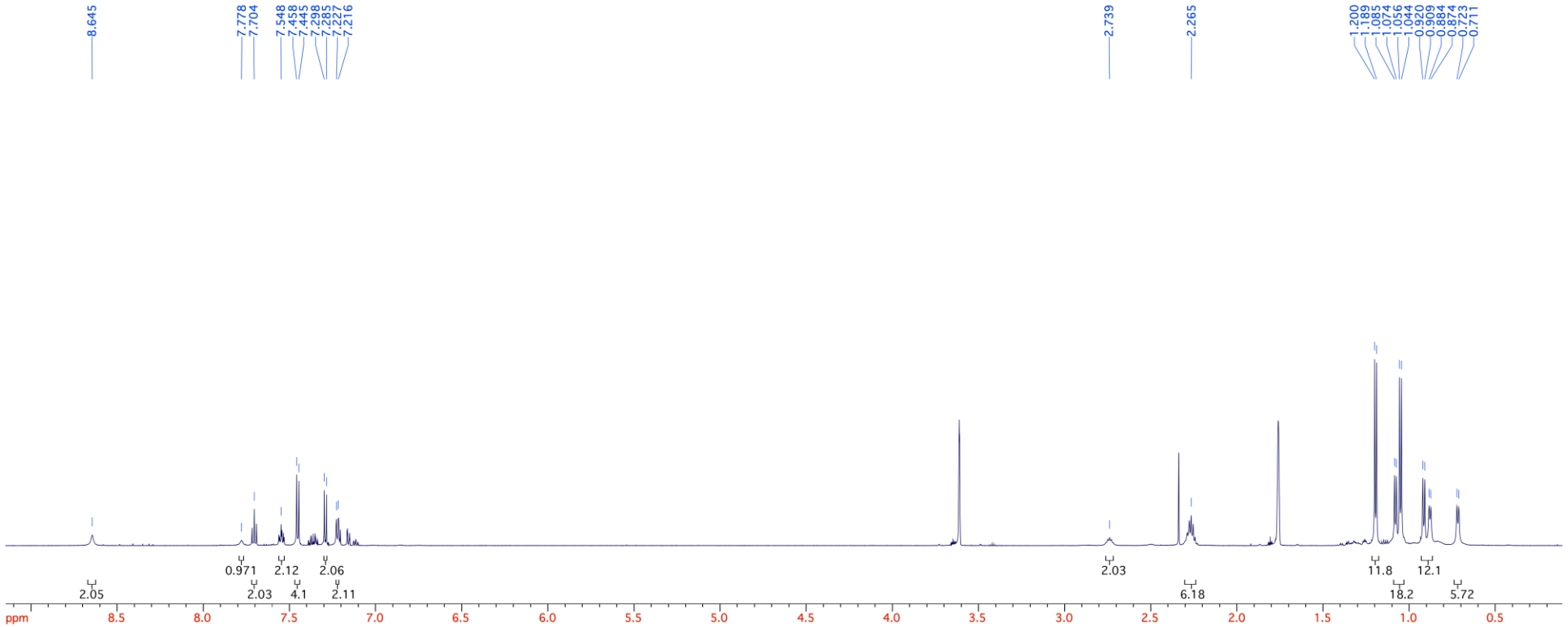

Figure S20. ^{1}H NMR spectrum (500 MHz, THF-d_8, 278 K) of [(WCA-IDipp)As=P(IDipp)][$GaCl_4$] (**4b**).

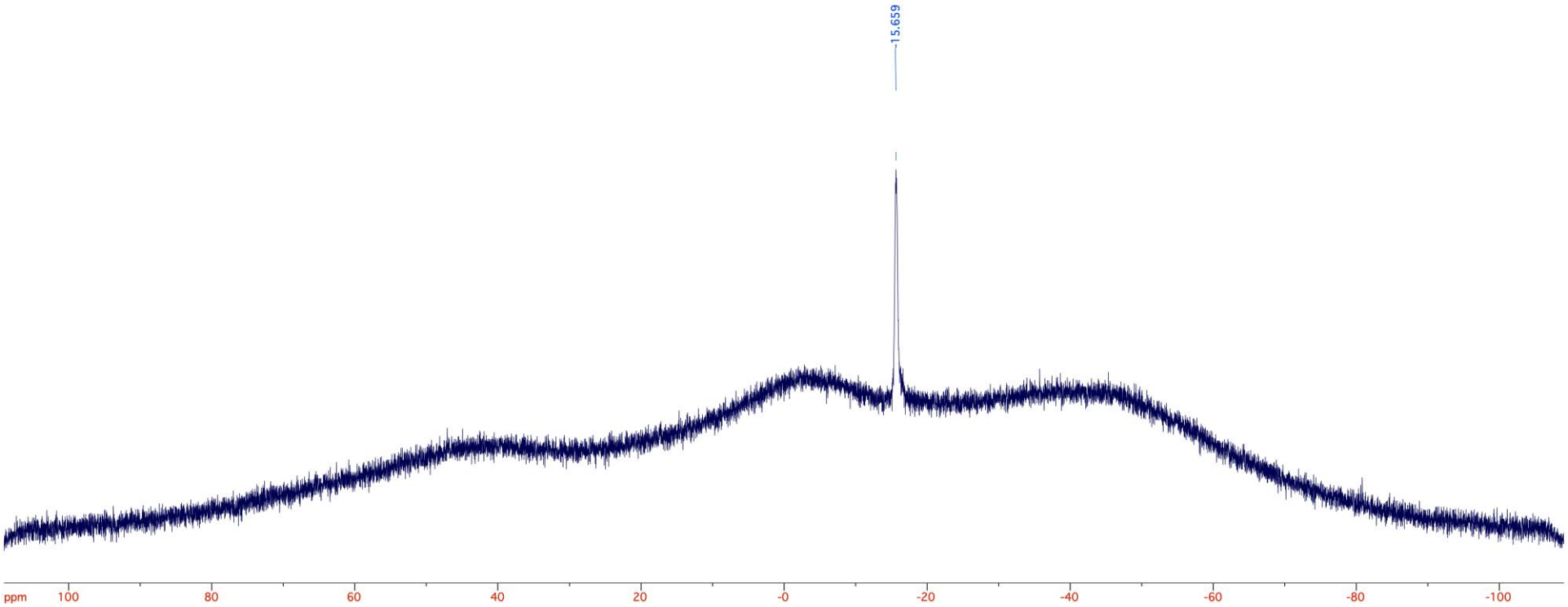

Figure S21. ^{11}B NMR spectrum (96 MHz, THF-d_8, 278 K) of [(WCA-IDipp)As=P(IDipp)][$GaCl_4$] (**4b**).

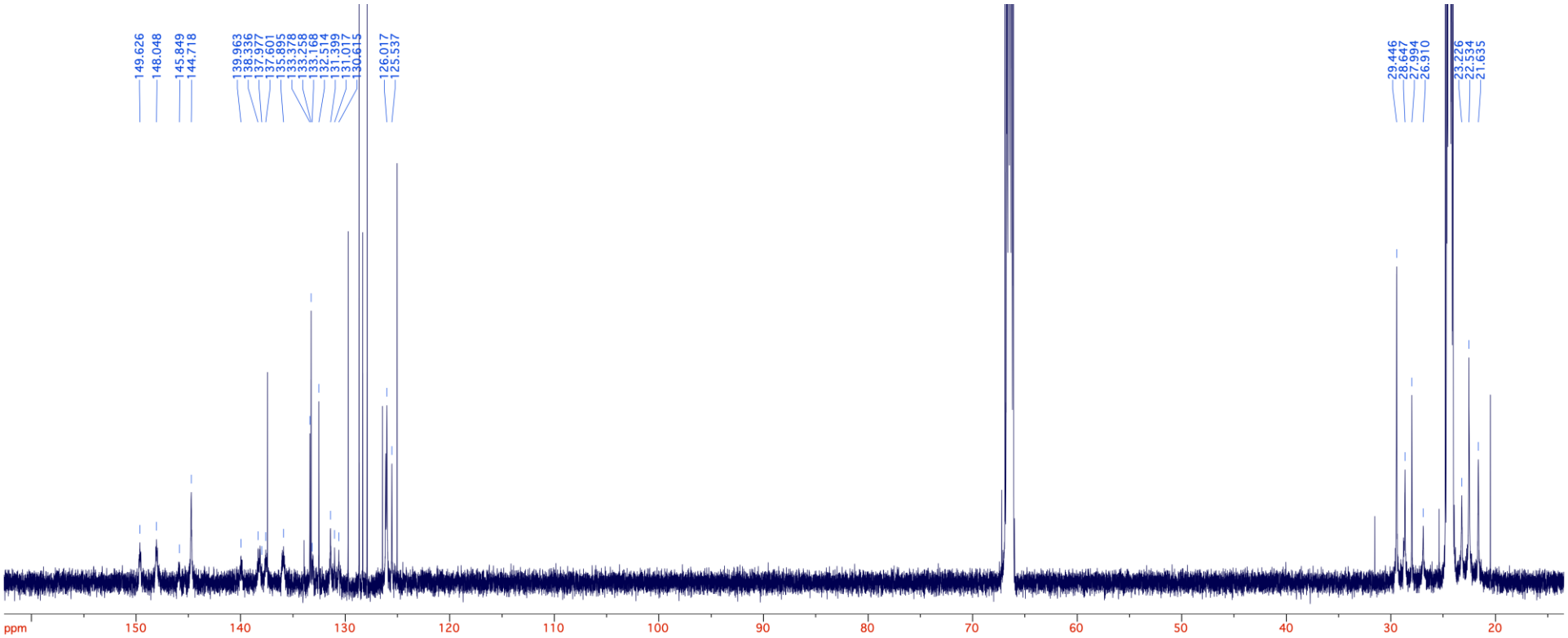

Figure S22. ^{13}C NMR spectrum (151 MHz, THF-d_8, 278 K) of [(WCA-IDipp)As=P(IDipp)][$GaCl_4$] (**4b**).

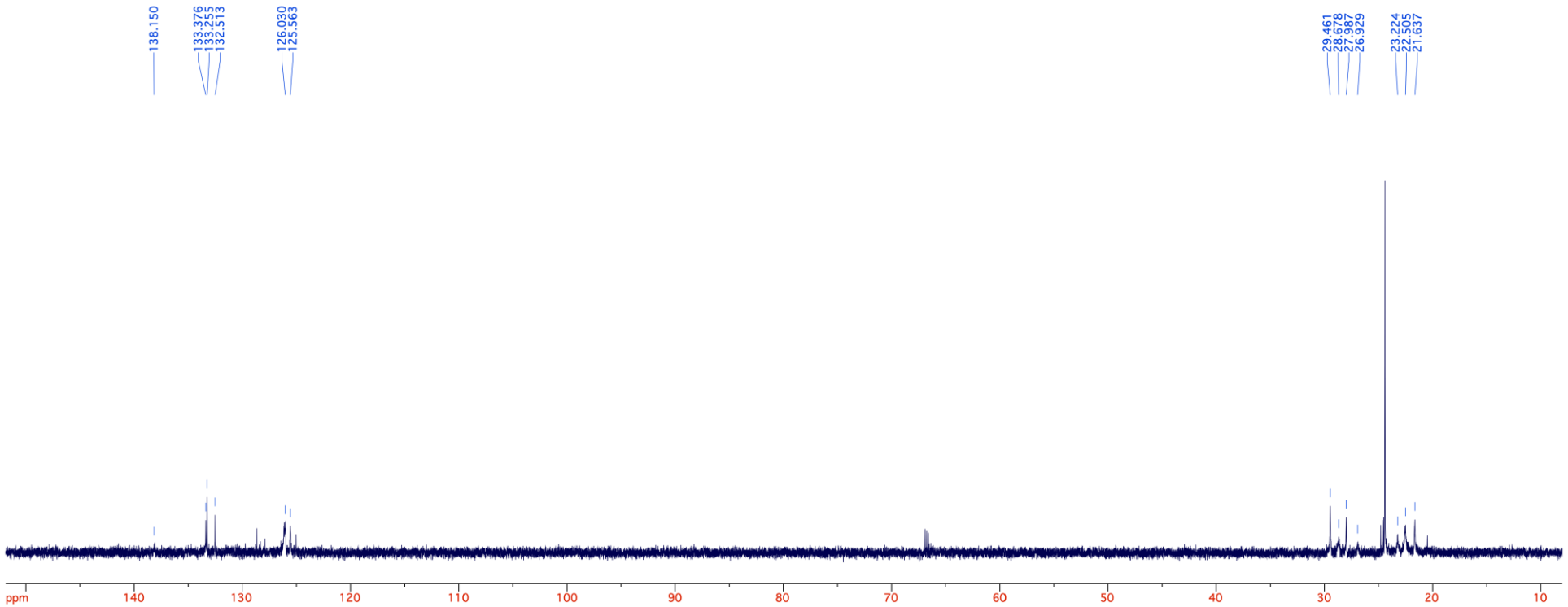

Figure S23. ^{13}C DEPT135 NMR spectrum (151 MHz, THF-d_8, 278 K) of [(WCA-IDipp)As=P(IDipp)][$GaCl_4$] (**4b**).

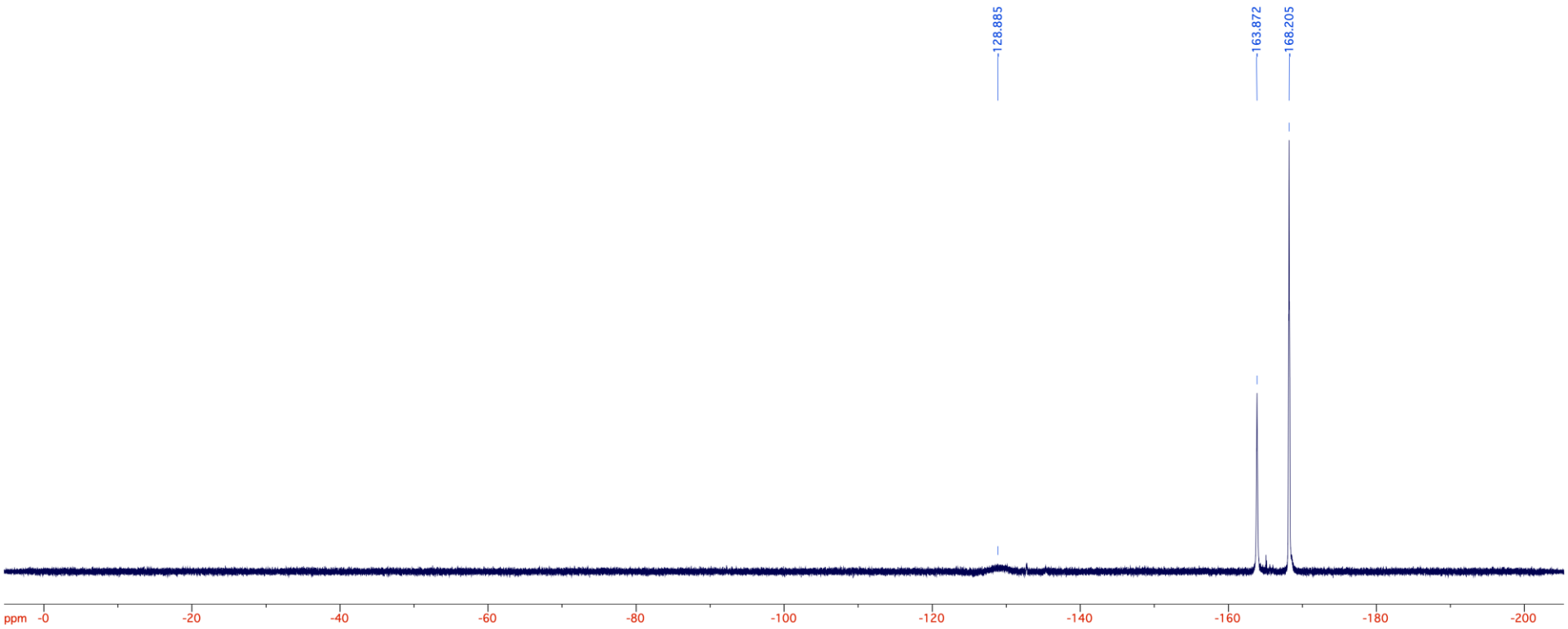

Figure S24. ^{19}F NMR spectrum (282 MHz, THF-d_8, 278 K) of [(WCA-IDipp)As=P(IDipp)][$GaCl_4$] (**4b**).

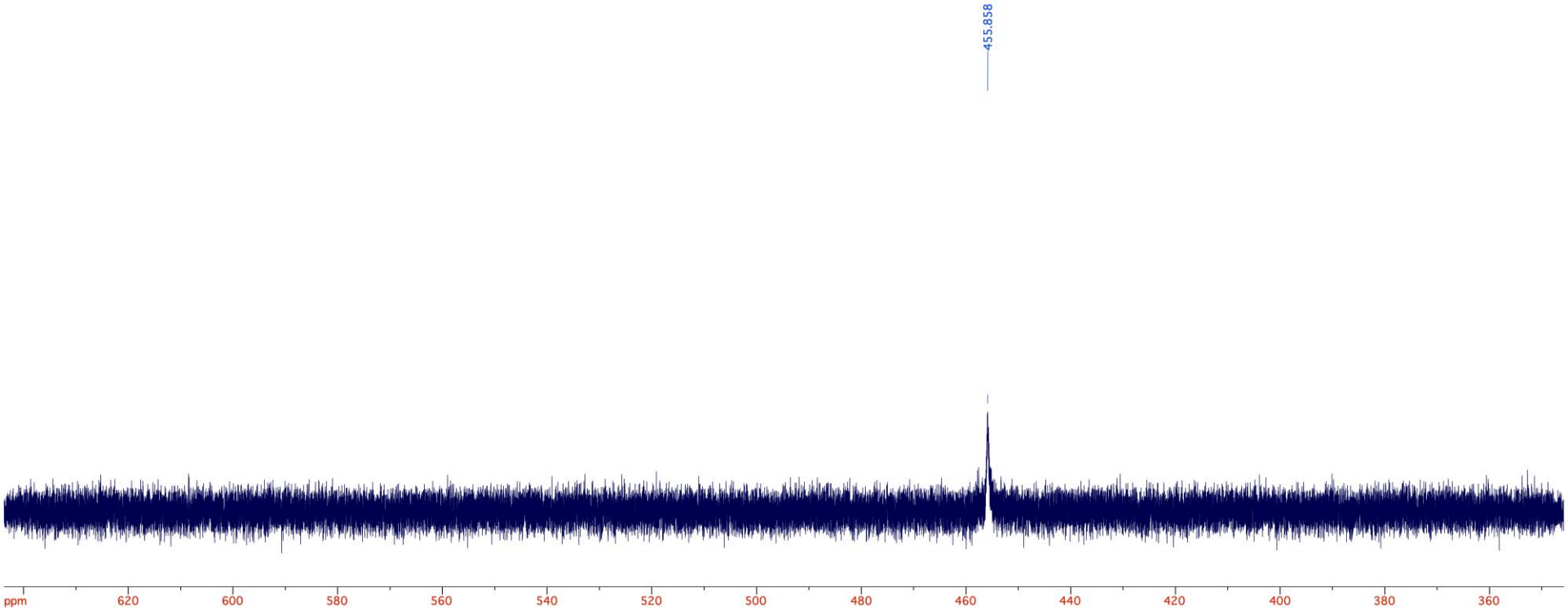

Figure S25. ^{31}P NMR spectrum (122 MHz, THF-d_8, 278 K) of [(WCA-IDipp)As=P(IDipp)][$GaCl_4$] (**4b**).

S5 X-Band EPR spectra

S5.1 [(WCA-IDipp)PP(IDipp)]• (5a)

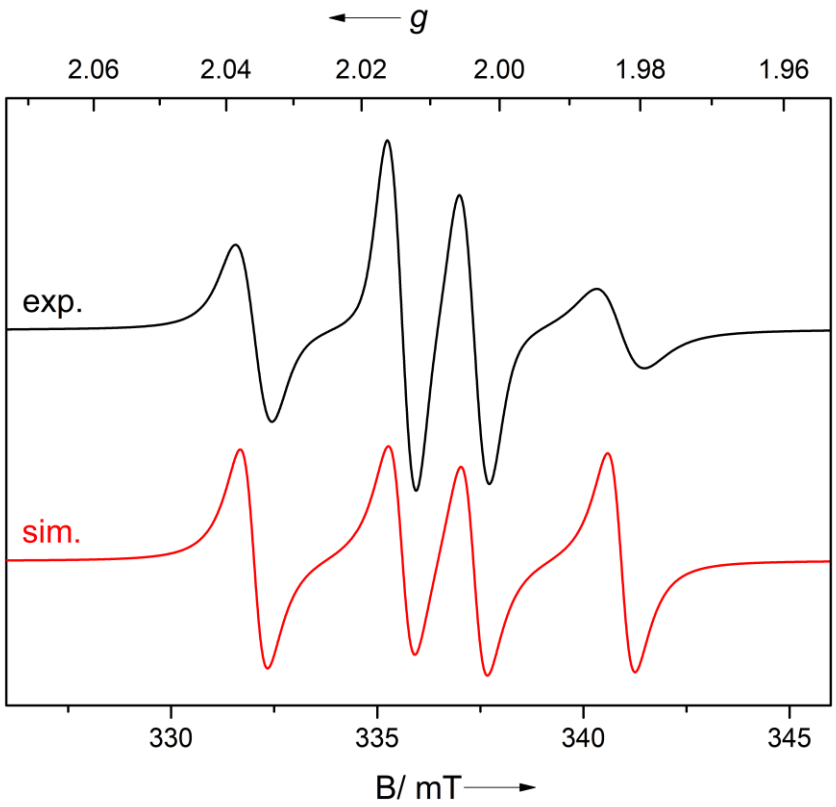

Figure S 26. Experimental (black) and simulated (red) X-band EPR spectrum (9.460444 GHz) of radical **5a** in thf solution at room temperature, displaying a g = 2.0087 with couplings of a(^{31}P1) = 53.5 G and a(^{31}P2) = 35.9 G. For the simulation a Lorentzian line broadening [0, 1.15] was used.

S5.1 [(WCA-IDipp)AsP(IDipp)]• (5b)

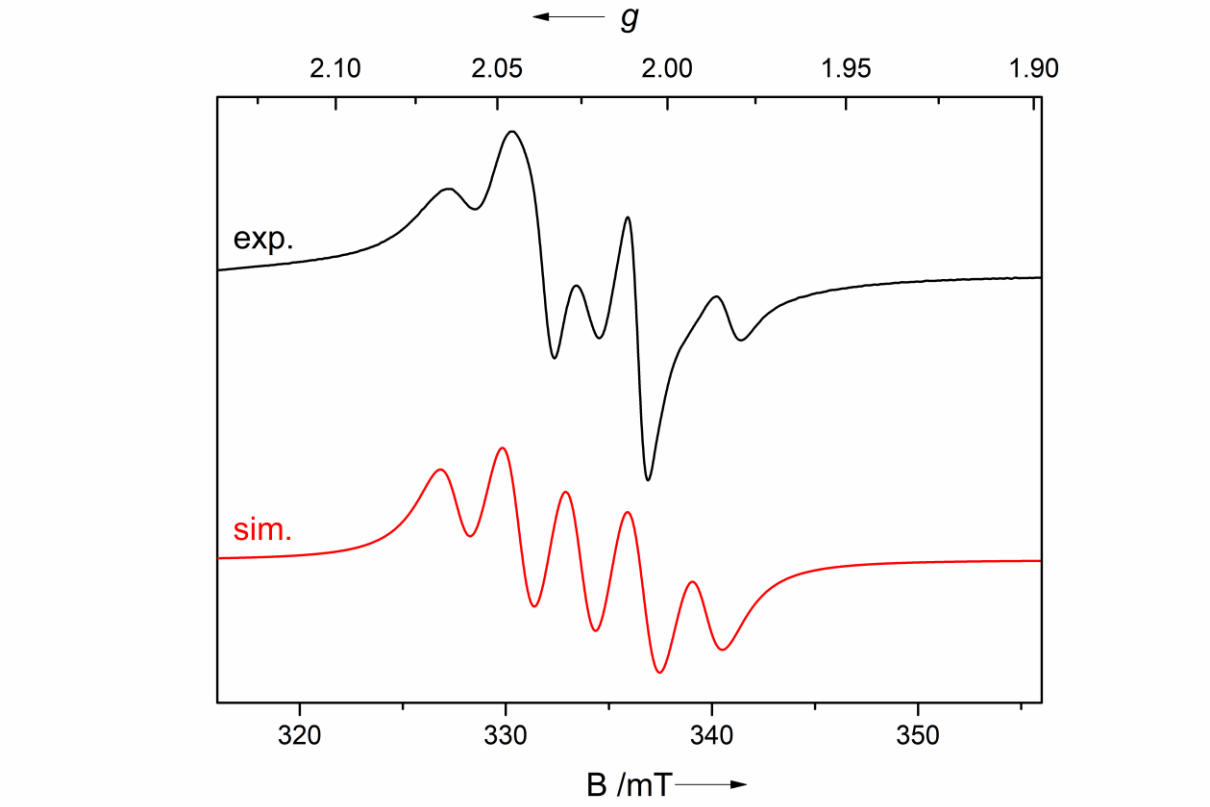

Figure S27. Experimental (black) and simulated (red) X-band EPR spectrum (9.456808 GHz) of radical **5b** in thf solution at room temperature, displaying a g = 2.0249 with couplings of a(^{31}P1) = 33.9 G and a(^{75}As) = 26.8 G. For the simulation a Lorentzian line broadening [0, 2.0] was used.

S6 Computational Details

All computations were performed using the density functional method B97-D (S. Grimme) as implemented in the Gaussian09 program.[7] For all main group elements (C, H, B, F, P and As) the all-electron triple-ζ basis set (6-311G**) was used.[8] Natural Bond Orbital (NBO) analysis (Wiberg Bond Index, WBI) was carried out using NBO version 3,[9] which is part of the Gaussian09 program package. For quantitative analysis of the spin density the free software *Muliwfn 3.6* was used.[10]

Table S7: Energies for all optimized structures

Compound	E_{0K}[a] [Ha]	E_{298K}[b] [Ha]	H_{298K}[b] [Ha]	G_{298K}[b] [Ha]
P_2 cation (**4a**)	-5207.408046	-5207.314306	-5207.313362	-5207.537450
As-P cation (**4b**)	-7103.041150	-7102.946329	-7102.945385	-7103.173142
P_2 radical (**5a**)	-5207.611732	-5207.517939	-5207.516995	-5207.740718
As-P radical (**5b**)	-7103.239316	-7103.144291	-7103.143347	-7103.373367

[a] DFT energy incl. ZPE.
[b] standard conditions T = 298.15 K and p = 1 atm.

S6.1 Electron Spin Density Distribution for [(WCA-IDipp)PP(IDipp)]• (5a)

Table S7. Electron Spin Density Distribution for Radical **5a**. Atom numbering according to given .mol file.

Electron Spin Density			
Atom	**Value**	**% of sum**	**% of sum abs.**
P1	0.48	**48.3**	47.8
P2	0.24	**24.0**	23.8
N18	**0.01**	**1.2**	**1.2**
N19	**0.01**	**1.2**	**1.2**
N20	**0.06**	**5.7**	**5.6**
N21	**0.05**	**4.9**	**4.9**
C25	**0.01**	**1.2**	**1.1**
C43	**0.04**	**3.6**	**3.6**
C57	**0.01**	**1.2**	**1.2**
C65	**0.02**	**2.5**	**2.4**

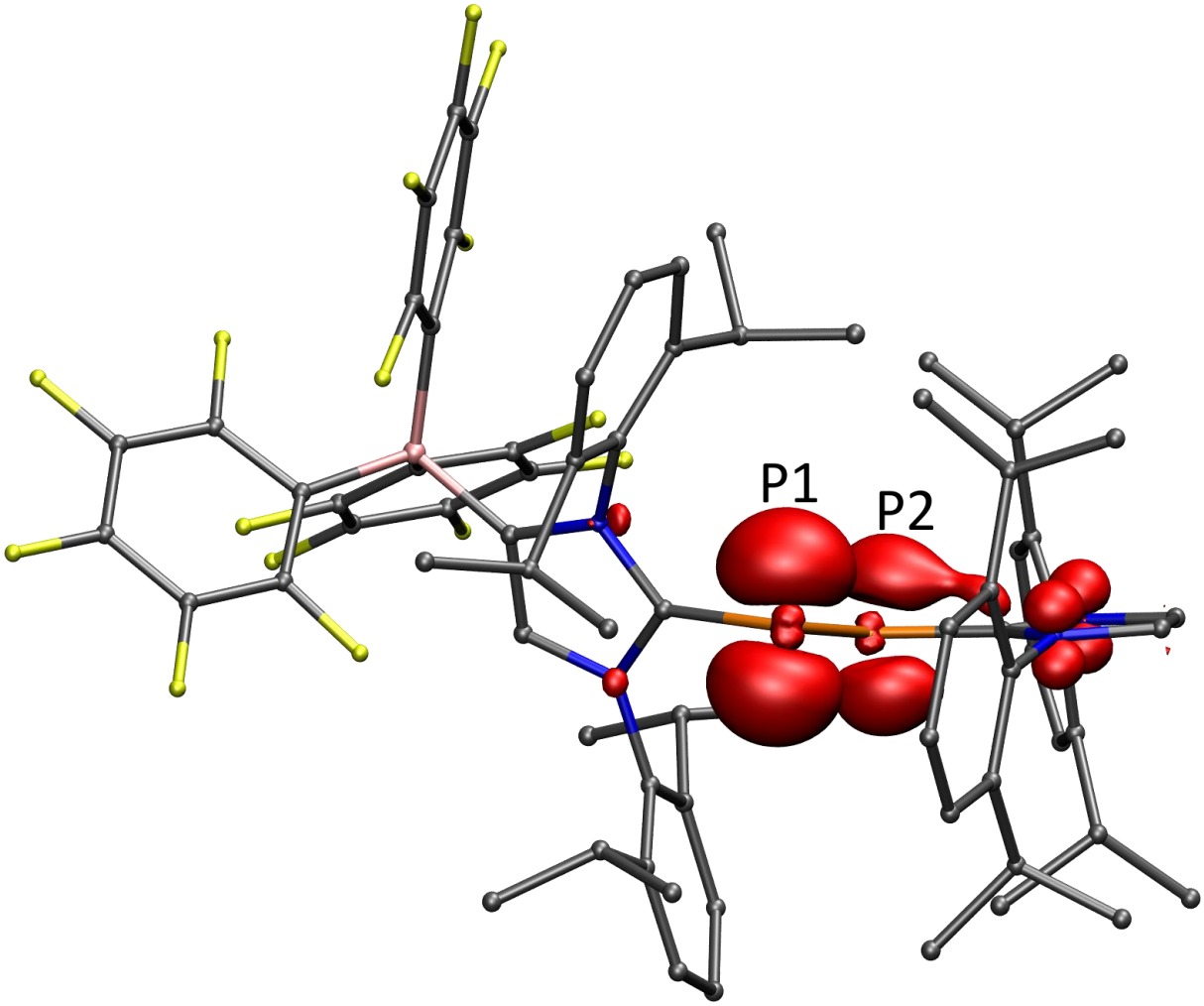

Figure S28. Plotted Spin density for radical **5a**.

S6.2 Electron Spin Density Distribution for [(WCA-IDipp)AsP(IDipp)]• (5b)

Table S8. Electron Spin Density Distribution for Radical **5b**. Atom numbering according to given .mol file.

Electron Spin Density			
Atom	**Value**	**% of sum**	**% of sum abs.**
As1	0.53	**53.4**	52.4
P2	0.21	**21.3**	20.9
N18	**0.01**	**1.3**	**1.2**
N19	**0.01**	**1.2**	**1.2**
N20	**0.05**	**4.9**	**4.8**
N21	**0.04**	**4.3**	**4.2**
C24	**0.01**	**1.1**	**1.1**
C102	**0.03**	**3.0**	**2.9**
C103	**0.01**	**1.2**	**1.2**
C105	**0.02**	**2.1**	**2.0**

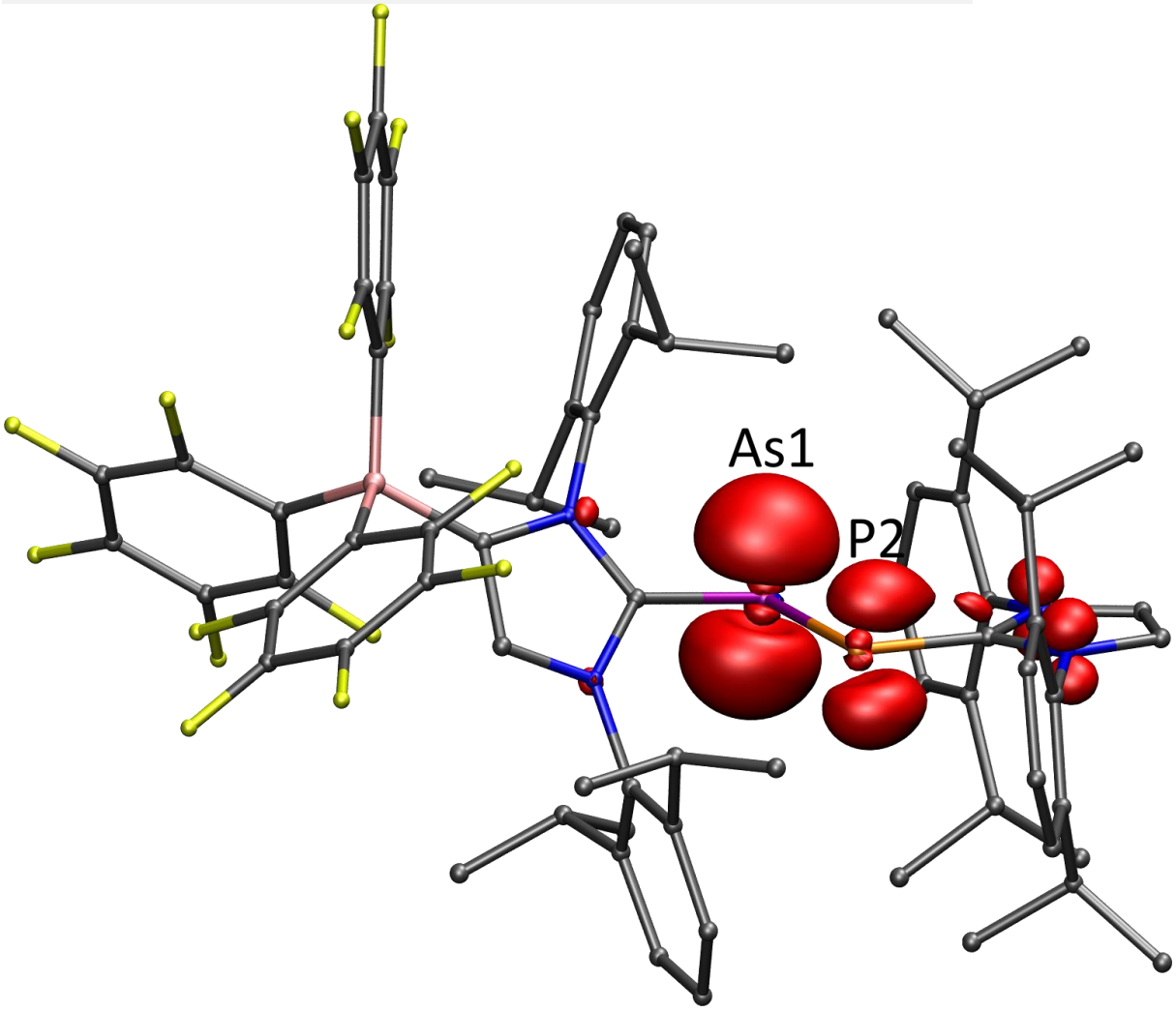

Figure S29. Plotted Spin Density for radical **5b**.

S6.3 Plot of the Single Occupied Molecular Orbitals (SOMO)

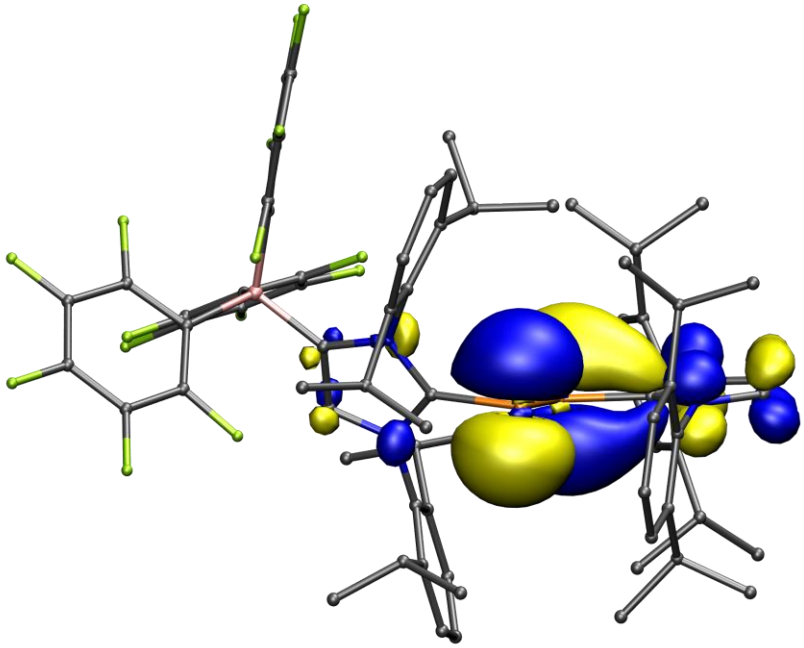

Figure S30. Plot of the Single Occupied Molecular Orbital of **5a**.

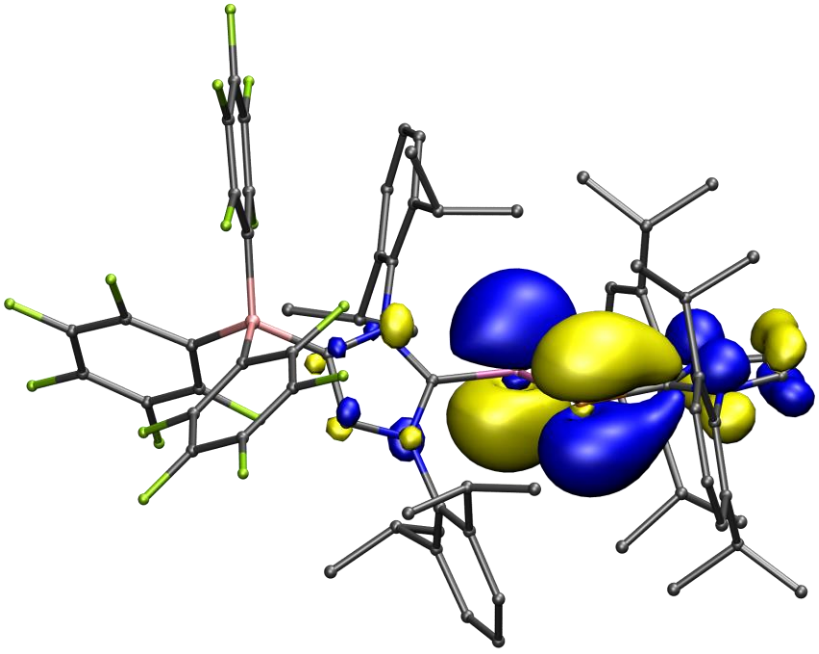

Figure S31. Plot of the Single Occupied Molecular Orbital of **5b**.

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