Supporting Information

for

Crystalline Phosphino-functionalized Mesoionic Olefins (p-MIOs)

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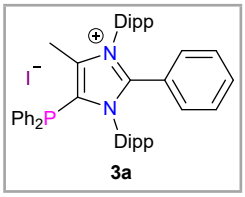
Materials and Methods

All syntheses and manipulations were carried out under an inert gas atmosphere (Ar or N_2) using standard *Schlenk* techniques or a glove box (MBraun LABMasterPro). Solvents were dried over appropriate drying agents, distilled, and stored over 3Å molecular sieve prior to use. Deuterated solvents were dried over appropriate drying agents, distilled, and stored inside a glove box. NMR spectra were recorded on a Bruker Avance III 500 or a Bruker Avance III 500 HD spectrometer. Chemical shifts (in δ, ppm) are referenced to the solvent residual signals [$CDCl_3$: ^{1}H, 7.26 ppm and ^{13}C, 77.7 ppm, C_6D_6: ^{1}H, 7.16 and ^{13}C, 128.06 ppm, CD_2Cl_2: ^{1}H, 5.32 ppm and ^{13}C, 53.8 ppm].[1] Nano-ESI mass spectra were recorded using an Esquire 3000 ion trap mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a nano-ESI source. Samples were dissolved in THF and introduced by static nano-ESI using *in-house* pulled glass emitters. Nitrogen served both as nebulizer as well as dry gas and was generated by a Bruker nitrogen generator NGM 11. Helium served as cooling gas for the ion trap. The mass axis was externally calibrated with ESI-L Tuning Mix (Agilent Technologies, Santa Clara, CA, USA) as a calibration standard. UV-vis spectra were recorded on an Agilent 8453 visible system. Melting points were measured with a Büchi B-545 Melting Point apparatus. Elemental analyses were carried out with a EURO EA Element Analyzer. LiHMDS, KHMDS (HMDS = $N(SiMe_3)_2$), and *n*BuLi (2.5 M in hexane) were used as received from the supplier (Sigma Aldrich). [$(Ph_2P)IPr^{Ph}$]Br **1**was synthesized according to the literature method.[2]

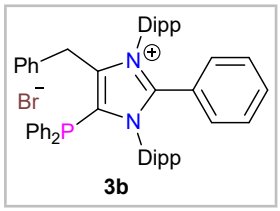


3a

Synthesis of 3a. To a 20 mL THF suspension of [$(Ph_2P)IPr^{Ph}$]Br (**1**) (1.0 g, 1.37 mmol) was added *n*BuLi (0.61 mL, 1.51 mmol) at −30 °C. The resulting green reaction mixture was stirred for 30 min at room temperature (rt) and then CH_3I (90 µL, 1.37 mmol) was added. The brown suspension was stirred overnight and then filtered through a plug of *Celite*. The residue over the *Celite* plug was extracted with 30 mL dichloromethane (DCM). The volatiles from the filtrate were removed under vacuum to obtain **3a** as an off-white solid. Yield: 1.04 g, 96% . M.p.: 235 °C (dec.). Elemental analysis (%) calculated for $C_{46}H_{52}N_2IP$ (790.8) **3a**: C 69.87, H 6.63, N 3.54; found: C 69.79, H 6.72, N 3.65. **^{1}H NMR (500 MHz, $CDCl_3$, 298 K):** 7.68 (t, *J* = 7.9 Hz, 1H, *p*-C_6H_3), 7.64 (t, *J* = 7.8 Hz, 1H, *p*-C_6H_3), 7.49 – 7.43 (m, 7H, C_6H_5), 7.41 (d, *J* = 7.9 Hz, 2H, *m*-C_6H_3), 7.32 (d, *J* = 7.8 Hz, 2H, *m*-C_6H_3), 7.26 – 7.18 (m, 6H, C_6H_5), 6.97 (d, *J* = 8.1 Hz, 2H, *o*-C_6H_5), 2.45–2.30 (m, 4H, C*H*Me_2), 1.57 (s, 3H, C*Me*), 1.26 (d, *J* = 6.8 Hz, 6H, CH*Me*$_2$), 1.04 (d, *J* = 6.8 Hz, 6H, CH*Me*$_2$), 0.95 (d, *J* = 6.7 Hz, 6H, CH*Me*$_2$), 0.89 (d, *J* = 6.7 Hz, 6H, CH*Me*$_2$) ppm. **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K):** 146.8 (N*C*N), 145.0, 144.5 (*i*-C_6H_3), 140.3, 140.2 (*i*-C_6H_5), 133.4, 133.2, 132.9, 132.1, 132.0 (*p*-C_6H_3/C_6H_5), 131.8 (d, $^1J_{PC}$ = 22.6 Hz), 130.9, 130.9, 130.4, 129.9, 129.8, 129.2, 129.0 (*o*/m- C_6H_5/C_6H_3), 128.1 (*C*Me), 126.3, 125.8 (C_6H_5/C_6H_3), 120.4 (*i*-

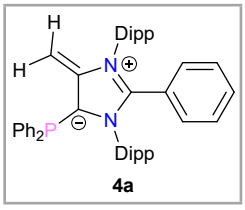
C_6H_5), 29.4 , 29.4 , 29.4 (*C*HMe$_2$), 24.4, 23.9, 23.9, 23.5, 23.2 (CH*Me*$_2$), 11.6 (C*Me*) ppm. **^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$, 298 K):** −34.4 ppm. **MS** (ESI pos.): [M−I]$^+$ = 663.4 m/z.

Synthesis of 3b. Compound **3b** was prepared by employing a similar method as described above for **3a** as an off-white solid in 70% (1.56 g) yield using **1** (2.0 g, 2.74 mmol), *n*BuLi (1.31 mL, 3.28 mmol), and PhCH$_2$Br (0.33 mL, 2.74 mmol). M.p.: 293 °C (dec.). Elemental analysis (%) calculated for $C_{52}H_{56}N_2BrP$ (819.9) **3b**: C 76.18, H 6.88, N 3.42; found: C 75.74, H 6.89, N 3.43. **^{1}H NMR (500 MHz, CDCl$_3$, 298 K):** 7.71 (t, *J* = 7.8 Hz, 2H, *p*-C$_6$*H*$_3$), 7.44 (t, *J* = 7.6 Hz, 1H, *p*-C$_6$*H*$_5$), 7.39 – 7.28 (m, 14H, C$_6$*H*$_5$/C$_6$*H*$_3$), 7.18 (t, *J* = 7.9 Hz, 2H, *m*-C$_6$*H*$_5$), 7.08 (t, *J* = 7.4 Hz, 1H, *p*-C$_6$*H*$_5$), 6.99 (t, *J* = 7.5 Hz, 2H, *m*-C$_6$*H*$_5$), 6.83 (d, *J* = 8.2 Hz, 2H, *o*-C$_6$*H*$_5$), 6.23 (d, *J* = 7.6 Hz, 2H, *o*-C$_6$*H*$_5$), 3.81 (s, 2H, CC*H*$_2$Ph), 2.55 (sept, *J* = 6.9 Hz, 2H, C*H*Me$_2$), 2.33 (sept, *J* = 6.8 Hz, 2H, C*H*Me$_2$), 1.01 (d, *J* = 6.7 Hz, 6H, CH*Me*$_2$), 0.90 (d, *J* = 6.7 Hz, 6H, CH*Me*$_2$), 0.80 (d, *J* = 6.8 Hz, 6H, CH*Me*$_2$), 0.74 (d, *J* = 6.7 Hz, 6H, CH*Me*$_2$) ppm. **^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, 298 K):** 146.9 (NCN),, 144.6, 144.4 (*i*-C$_6$H$_3$), 141.7, 141.6 (*i*-C$_6$H$_5$), 133.5, 133.3, 133.2, 133.0, 132.9 (*p*-C$_6$H$_3$/C$_6$H$_5$), 132.5 (d, $^1J_{PC}$ = 30.7 Hz), 130.7, 129.9, 129.8, 129.4, 129.4, 129.3, 129.3, 129.1, 128.5 (*o*/m- C$_6$H$_5$/C$_6$H$_3$), 127.7 (*C*CH$_2$), 127.5, 127.4, 126.4, 125.8 (C$_6$H$_5$/C$_6$H$_3$), 120.4 (*i*-C$_6$H$_5$), 29.7 (*C*H$_2$Ph), 29.5 , 29.5, 29.3 (*C*HMe$_2$), 23.7 , 23.5, 23.5, 23.5, 23.1 (CH*Me*$_2$) ppm. **^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$, 298 K):** −32.3 ppm. **MS** (ESI pos.): [M−Br]$^+$ = 739.4 *m*/*z*.



3b

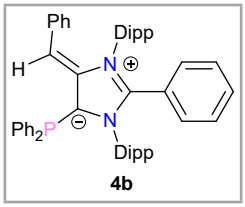
Synthesis of 4a. **3a** (1.04 g, 1.32 mmol) and KHMDS (0.32 g, 1.58 mmol) were suspended in 30 mL toluene at rt and stirred for one hour. The deep blue reaction mixture was filtered through a plug of Celite and the volatiles from the filtrate were removed under vacuum to obtain **4a** as a dark blue solid in 80 % (0.70 g) yield. Single crystals suitable for X-ray diffraction studies were obtained by a slow diffusion of *n*-hexane into a saturated benzene solution of **4a.** Elemental analysis (%) calculated for $C_{46}H_{52}N_2IP$ (662.9) **4a**: C 83.35, H 7.75, N 4.23; found: C 84.01, H 7.60, N 4.15. **^{1}H NMR (500 MHz, C$_6$D$_6$, 298 K):** 7.84 (t, *J* = 7.2 Hz, 4H, *m*-C$_6$*H*$_5$), 7.25 – 7.15 (m, 6H, C$_6$*H*$_5$), 7.15 – 7.11 (m, 2H, C$_6$*H*$_5$/C$_6$*H*$_3$), 7.08 (t, *J* = 7.4 Hz, 2H, C$_6$*H*$_5$/C$_6$*H*$_3$), 7.01 (d, *J* = 7.8 Hz, 2H, C$_6$*H*$_5$/C$_6$*H*$_3$), 6.95 (d, *J* = 7.6 Hz, 2H, C$_6$*H*$_5$/C$_6$*H*$_3$), 6.58 (t, *J* = 7.8 Hz, 2H, *m*-C$_6$*H*$_5$), 6.52 (t, *J* = 7.3 Hz, 1H, *p*-C$_6$H$_5$), 3.55 (sept, *J* = 7.2 Hz, 2H, C*H*Me$_2$), 3.46 (sept, *J* = 6.8 Hz, 2H, C*H*Me$_2$), 2.81 (d, *J* = 1.5 Hz, 1H, CC*H*$_2$), 2.45 (d, *J* = 1.5 Hz, 1H, CC*H*$_2$), 1.52 (d, *J* = 6.8 Hz, 6H, CH*Me*$_2$), 1.12 (d, *J* = 6.8, Hz, 12H, CH*Me*$_2$), 0.99 (d, *J* = 6.8 Hz, 6H, CH*Me*$_2$) ppm. **^{13}C{^{1}H} NMR (126 MHz, C$_6$D$_6$, 298 K):** 149.7 (*i*-C$_6$H$_3$), 147.0 (N*C*N), 146.0 (*i*-C$_6$H$_3$),137.6, 134.8, 134.8, 133.5, 133.1, 133.1, 132.3, 132.2, 130.2, 129.5, 128.1, 128.0, 127.4, 127.1 (C$_6$H$_5$/C$_6$H$_3$), 126.9 (*C*CH$_2$), 126.7, 126.0 (d, *J* = 30.6 Hz, *C*PPh$_2$) 125.0, 124.4 (*i*-C$_6$H$_5$), 96.8 (*C*PPh$_2$) 53.1 (C*C*H$_2$), 29.0, 28.5 (*C*HMe), 24.8, 24.3, 24.3 (CH*Me*), 23.2, 23.2 ppm. **^{31}P{^{1}H} NMR (202 MHz,**



4a

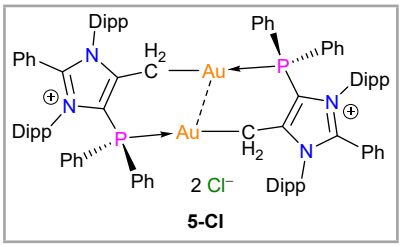
C_6D_6, 298 K): −30.2 ppm. **MS** (ESI pos.): $[M+H]^+$ = 663.4 *m/z*. **UV-vis (THF, λ [nm] (ε [L·mol^{-1}·cm^{-1}])):** 380 (202), 613 (322).

Synthesis of 4b. **4b** was prepared by employing a similar method as described above for **4a** and was isolated as a dark green solid in 73% (0.33 g) yield. Reagents used: **3b** (0.5 g, 0.61 mmol), KHMDS (0.13 g, 0.67 mmol). Single crystals suitable for X-ray diffraction studies were obtained by a slow diffusion of *n*-hexane into a saturated benzene solution of **4b**. Elemental analysis (%) calculated for $C_{52}H_{55}N_2P$ (739.00) **4b**: C 84.52, H 7.50, N 3.79; found: C 83.92, H 7.38, N 4.01. **^{1}H NMR (500 MHz, C_6D_6, 298 K):** 7.77 (t, *J* = 7.2 Hz, 4H, C_6H_5), 7.20 (t, *J* = 7.7 Hz, 1H, C_6H_3), 7.14 (d, *J* = 7.7 Hz, 4H, C_6H_5), 7.09 – 7.05 (m, 2H, C_6H_3/C_6H_5), 7.01 (d, *J* = 7.8 Hz, 2H, *m*-C_6H_3), 6.98 (d, *J* = 7.8 Hz, 2H, *m*-C_6H_3), 6.84 – 6.80 (m, 2H, C_6H_5), 6.72 (t, *J* = 7.6 Hz, 2H, C_6H_5), 6.60 –, 6.49 (m, 5H, C_6H_3/C_6H_5), 6.02 (s, 2H, C_6H_5), 4.70 (s, 1H, C*H*Ph), 3.57 (sept, *J* = 6.9 Hz, 2H,C*H*Me), 3.46 (sept, *J* = 6.7 Hz, 2H, C*H*Me), 1.22 (d, *J* = 6.8 Hz, 6H, CH*Me*), 1.08 (d, *J* = 6.8 Hz, 6H, CH*Me*), 1.00 (d, *J* = 6.9 Hz, 6H, CH*Me*), 0.95 (d, *J* = 6.8 Hz, 6H, CH*Me*) ppm. **^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 298 K):** −29.0 ppm. **MS** (ESI pos.): $[M+H]^+$ = 739.4 *m/z*. **UV-vis (THF, $\lambda_{max.}$ [nm] (ε [L·mol^{-1}·cm^{-1}])):** 365 (1690), 667 (516).



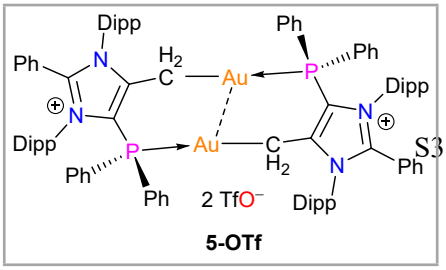
4b

Synthesis of 5-Cl. **4a** (0.25 g, 0.38 mmol) and (Me_2S)AuCl (0.11 g, 0.38 mmol) were suspended in 20 mL toluene at rt. The resulting colorless suspension was stirred at rt for 1h. The insoluble material was separated by filtration and then extracted with 25 mL DCM. The volatiles were removed under vacuum to obtain **5-Cl** as an off-white solid in 68% yield (0.23 g). Single crystals suitable for X-ray diffraction studies were obtained at rt by a slow diffusion of *n*-hexane into a saturated DCM solution of **5-Cl**. Elemental analysis (%) calculated for $C_{92}H_{102}N_4Au_2Cl_2P_2$ (1790.6) **5-Cl**: C 61.71, H 5.74, N 3.13; found: C 61.32, H 5.95, N 3.45. **^{1}H NMR (500 MHz, CD_2Cl_2, 298 K):** 7.94 – 7.81 (m, 8H, C_6H_5), 7.70 (t, *J* = 7.9 Hz, 2H, *p*-C_6H_3), 7.65 – 7.55 (m, 16H, C_6H_5), 7.37 (d, *J* = 7.8 Hz, 4H, *o*-C_6H_3), 7.06 (t, *J* = 7.9 Hz, 4H), 6.88 (d, *J* = 8.4 Hz, 4H, *o*-C_6H_5), 2.58 (sept, *J* = 6.8 Hz, 4H, C*H*Me), 2.47 (sept, *J* = 6.5 Hz, 4H, C*H*Me), 1.63 (s, 4H, CH_2-Au), 1.40 (d, *J* = 6.8 Hz, 12H, CH*Me*), 1.13 (d, *J* = 6.7 Hz, 12H, CH*Me*), 0.81 (d, *J* = 6.7 Hz, 12H, CH*Me*), 0.76 (d, *J* = 6.8 Hz, 12H, CH*Me*). **^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K):** 146.1 (NCN), 145.6 (*i*-C_6H_3), 134.1, 134.1, 134.0 (*o*-C_6H_5), 133.5, 132.9, 132.9, 132.9 (*p*-C_6H_5), 132.7 (*p*-C_6H_3), 130.5, 130.4, 130.3, 129.3 (C_6H_5/C_6H_3), 127.0 (*i*-C_6H_5), 126.9, 100.6 (*i*-C_6H_5), 30.0, 29.5 ($CHMe_2$), 25.5, 25.4, 24.1, 23.8, 23.5 (CH*Me*$_2$), 8.1 (CH_2). **MS** (ESI pos.): $[M-Cl]^+$ = 1753.7 *m/z*.



5-Cl

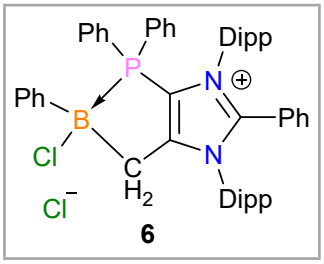
Synthesis of 5-OTf. **4a** (0.5 g, 0.75 mmol) and Me_2SAuCl were suspended in 20 mL toluene. The resulting suspension was stirred



5-OTf

overnight and then AgOTf (0.19 g,0.75 mmol) was added. The resulting suspension was filtrated through a plug of Celite and the residue over the Celite was extracted with 40 mL DCM. The volatiles were removed under vacuum to obtain **5-OTf** as a colourless solid in 61% (0.46 g) yield. Elemental analysis (%) calculated for $C_{94}H_{102}N_4Au_2F_6O_6P_2S_2$ (2017.9) **5-OTf**: C 55.95, H 5.10, N 2.78; found: C 55.35, H 4.92, N 3.10. **^{1}H NMR (500 MHz, CD_2Cl_2, 298 K):** 7.79–7.68 (m, 12H, C_6H_5/C_6H_3), 7.61 (d, J = 8.0 Hz, 2H, *m*-C_6H_3), 7.33–7.21 (m, 13H, C_6H_5/C_6H_3), 7.10 (t, J = 7.9 Hz, 4H, *p*-C_6H_3), 7.03 (br, 8H, C_6H_5/C_6H_3), 6.90 (d, J = 7.9 Hz, 2H, *m*-C_6H_3), 6.73 (d, J = 8.2 Hz, 4H, *o*-C_6H_5), 2.62 (sept, J = 6.9 Hz, 2H, C*H*Me$_2$), 2.47 (sept, J = 7.4 Hz, 2H, C*H*Me$_2$), 2.39 (sept, J = 6.7 Hz, 2H, C*H*Me$_2$), 2.33 (s, 2H, CH_2Au), 2.24 (br, 2H, C*H*Me$_2$), 2.08 (br, 2H, CH_2Au), 1.47 (d, J = 6.8 Hz, 6H, CH*Me*$_2$), 1.37 (d, J = 6.6 Hz, 6H, CH*Me*$_2$), 1.33 (d, J = 6.6 Hz, 6H, CH*Me*$_2$), 1.29 (d, J = 6.9 Hz, 6H, CH*Me*$_2$), 1.17 (d, J = 6.7 Hz, 6H, CH*Me*$_2$), 1.11 (d, J = 6.9 Hz, 6H, CH*Me*$_2$), 0.39 (d, J = 6.9 Hz, 6H, CH*Me*$_2$), 0.10 (d, J = 7.1 Hz, 6H, CH*Me*$_2$). **^{13}C{^{1}H} NMR (500 MHz, CD_2Cl_2, 298 K)**: 146.1 (N*C*N), 145.2, 144.2, 143.8, 143.5, 136.5, 136.3, 134.1, 133.4, 133.4, 133.2, 131.1, 131.0, 130.2, 130.1, 129.6, 129.5, 129.4, 129.3, 128.8, 128.7, 127.2, 127.0, 126.9, 126.5, 125.8, 123.0, 121.6 (*C*$_6$H$_5$, *C*$_6$H$_3$, *C*CH$_2$, *C*PPh$_2$),120.4 (*i*-*C*$_6$H$_5$), 31.2, 30.2, 30.0, 29.3, 26.3, 25.3 (*C*HMe), 24.9 (*C*H$_2$Au), 24.7 (*C*H$_2$Au), 24.2, 23.9, 23.6, 23.5, 22.8 (CH*Me*) ppm. **^{19}F NMR (471 MHz, CD_2Cl_2, 298 K)**: −78.7 ppm. **^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 298 K)**: 27.4 ppm. **MS** (ESI pos.): [M-OTf]$^+$ = 1867.5 *m*/*z*.

Synthesis of 6. To a 20 mL toluene solution of **4a** (1.0 g, 1.50 mmol) was added $PhBCl_2$ (0.19 mL, 1.50 mmol) at −40 °C. The resulting reaction mixture was brought to rt and stirred overnight. The colorless precipitate was isolated by filtration, washed with toluene (2x10 mL), and dried under vacuum to give **6** in 89% (1.31 g) yield. Single crystals suitable for X-ray diffraction studies were obtained by a slow diffusion of *n*-hexane into a saturated DCM solution of **6**. Elemental analysis (%) calculated for $C_{52}H_{56}N_2BCl_2P$ (980.5) **6**: C 71.05, H 6.27, N 2.86; found: C 70.71, H 6.35, N 2.96. **^{1}H NMR (500 MHz, $CDCl_3$, 298 K):** 7.95 (m, 2H, C_6H_5), 7.67 (m, 2H, *p*-C_6H_3), 7.57 (m, 2H, C_6H_5), 7.47 (m, 5H, C_6H_5), 7.40 (d, J = 7.8 Hz, 1H, *m*-C_6H_3), 7.35 (d, J = 7.8 Hz, 1H, *m*-C_6H_3), 7.30–7.26 (m, 5H, C_6H_5), 7.14–7.06 (m, 5H, C_6H_5/C_6H_3), 6.81 (m, 2H, C_6H_5/C_6H_3), 2.77 (sept, J = 6.8 Hz, 1H, C*H*Me$_2$), 2.70–2.62 (m, 2H, C*H*Me$_2$), 2.54 (sept, J = 6.8 Hz, 1H, C*H*Me$_2$), 2.35–2.24 (m, 2H, CH_2B), 1.50 (d, J = 6.8 Hz, 3H, CHMe$_2$), 1.36 (d, J = 6.7 Hz, 3H, CHMe$_2$), 1.29 (d, J = 6.7 Hz, 3H, CHMe$_2$), 1.02 (d, J = 6.8 Hz, 3H, CHMe$_2$), 0.90 (d, J = 6.8 Hz, 3H, CHMe$_2$), 0.82 (d, J = 6.8 Hz, 3H, CHMe$_2$), 0.47 (d, J = 6.7 Hz, 3H, CHMe$_2$), 0.36 (d, J = 6.7 Hz, 3H, CHMe$_2$) ppm. **^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 298 K)**: 145.6 (N*C*N), 145.0 (*i*-*C*$_6$H$_3$), 144.9 (*i*-*C*$_6$H$_3$), 144.6, 136.0, 135.9, 134.2, 133.6, 133.2, 132.2, 132.1, 131.2, 131.1, 130.6, 130.6, 130.0, 130.0, 129.9, 129.2, 128.7, 128.4, 127.9, 127.8, 126.8, 126.3, 125.4, 120.2 (*C*$_6$H$_5$, *C*$_6$H$_3$), 30.2, 29.8, 29.4, 29.3 (CH*Me*$_2$), 25.3, 25.1, 24.1, 23.9, 22.7



6

(CH*Me*$_2$) ppm. **^{11}B NMR (205 MHz, CDCl$_3$, 298 K):** 9.8 ppm. **^{31}P{^{1}H} NMR (202 MHz, CDCl$_3$, 298 K):** 4.3 ppm. **MS** (ESI pos.): $[M\text{-}Cl]^+$ = 785.4 *m*/*z*.

Plots of NMR Spectra

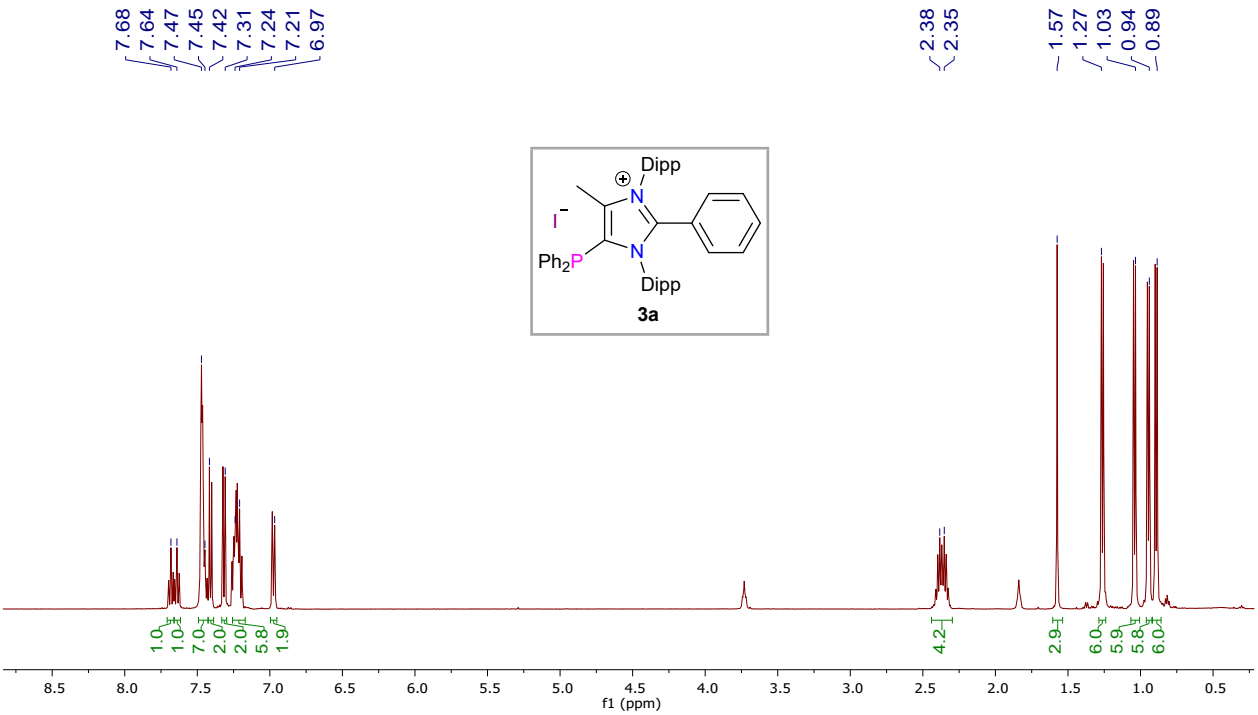


Figure S1. ^{1}H NMR (500 MHz, CDCl$_3$, 298 K) spectrum of **3a**.

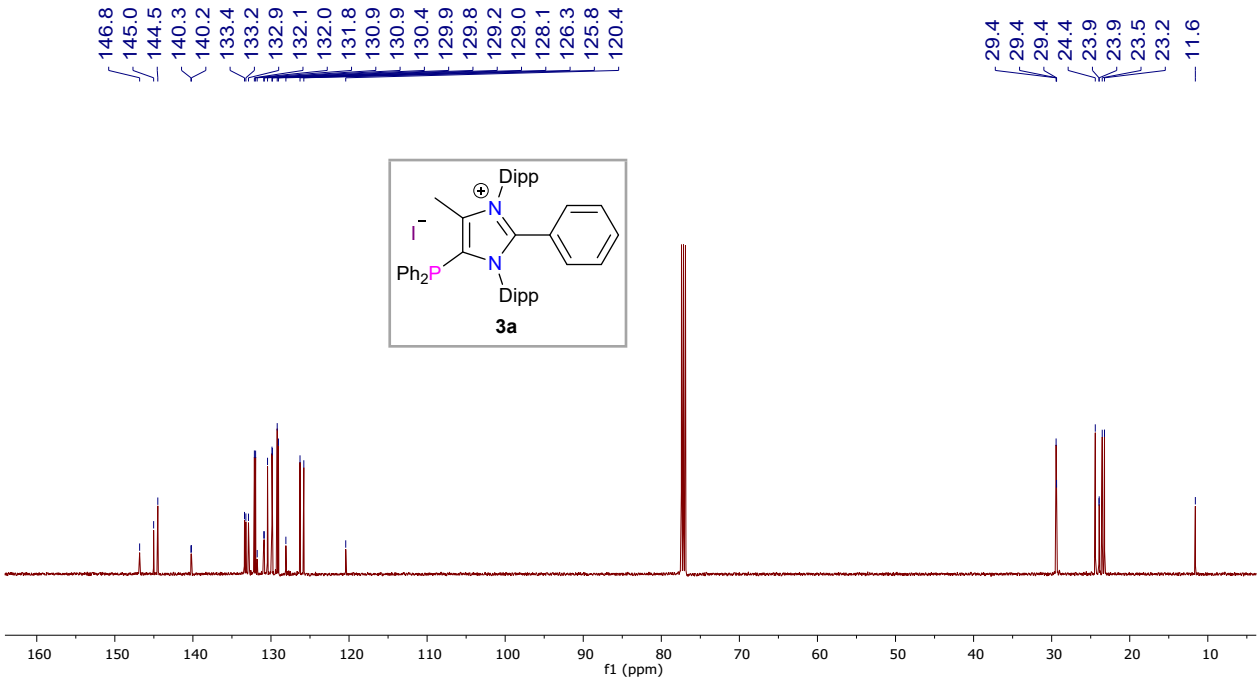


Figure S2. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **3a**.

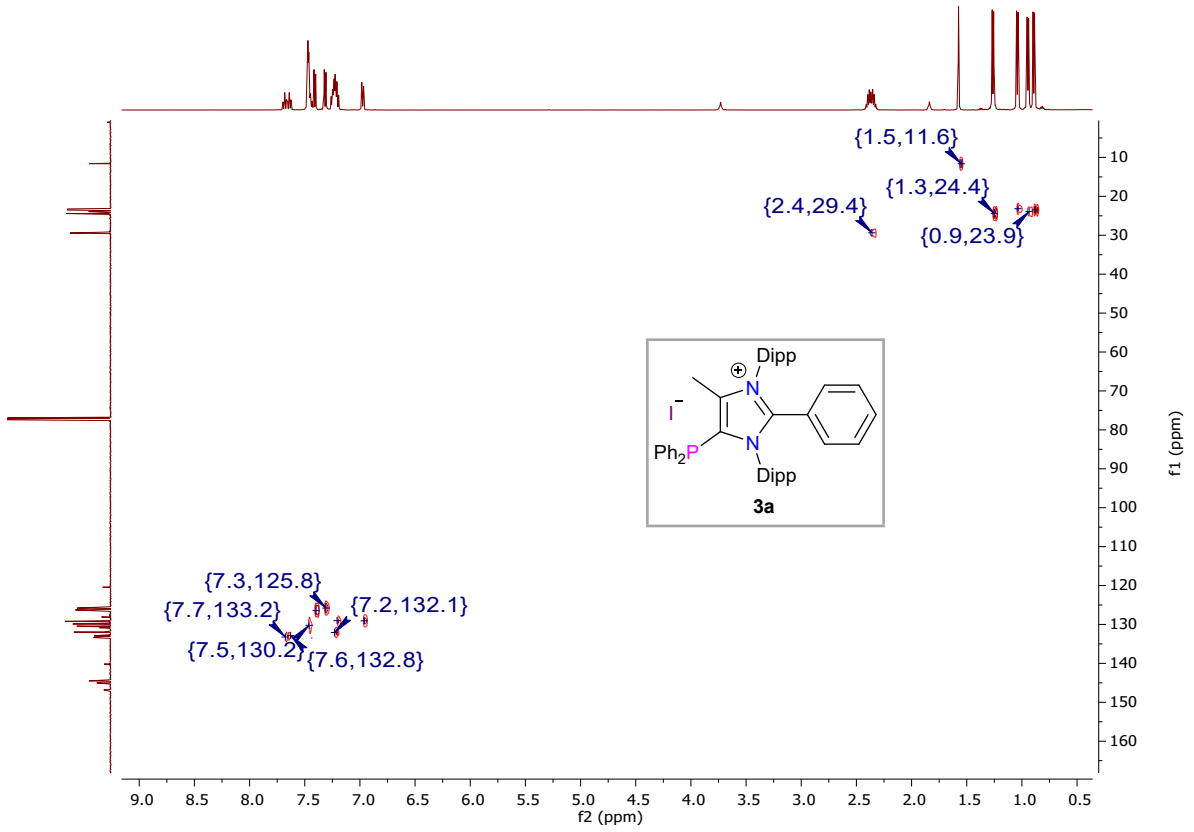


Figure S3. ^{1}H-^{13}C HMQC (500/126 MHz, $CDCl_3$, 298 K) spectrum of **3a**.

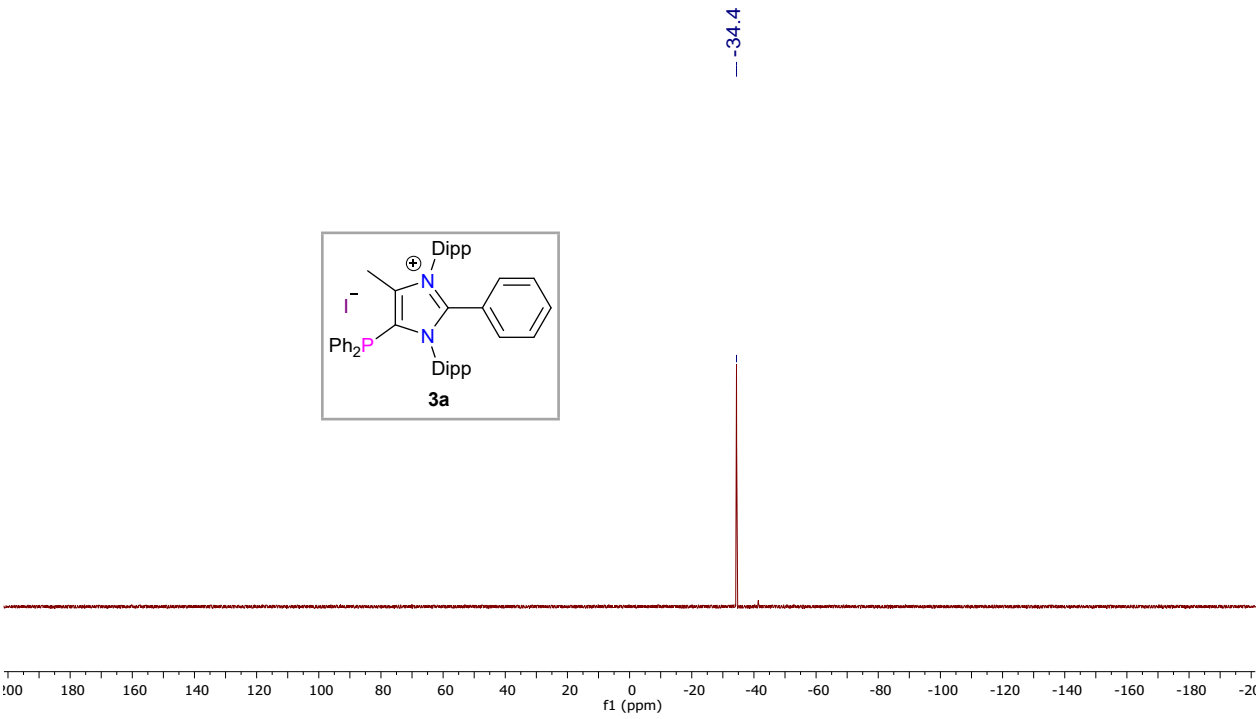


Figure S4. $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$, 298 K) spectrum of **3a**.

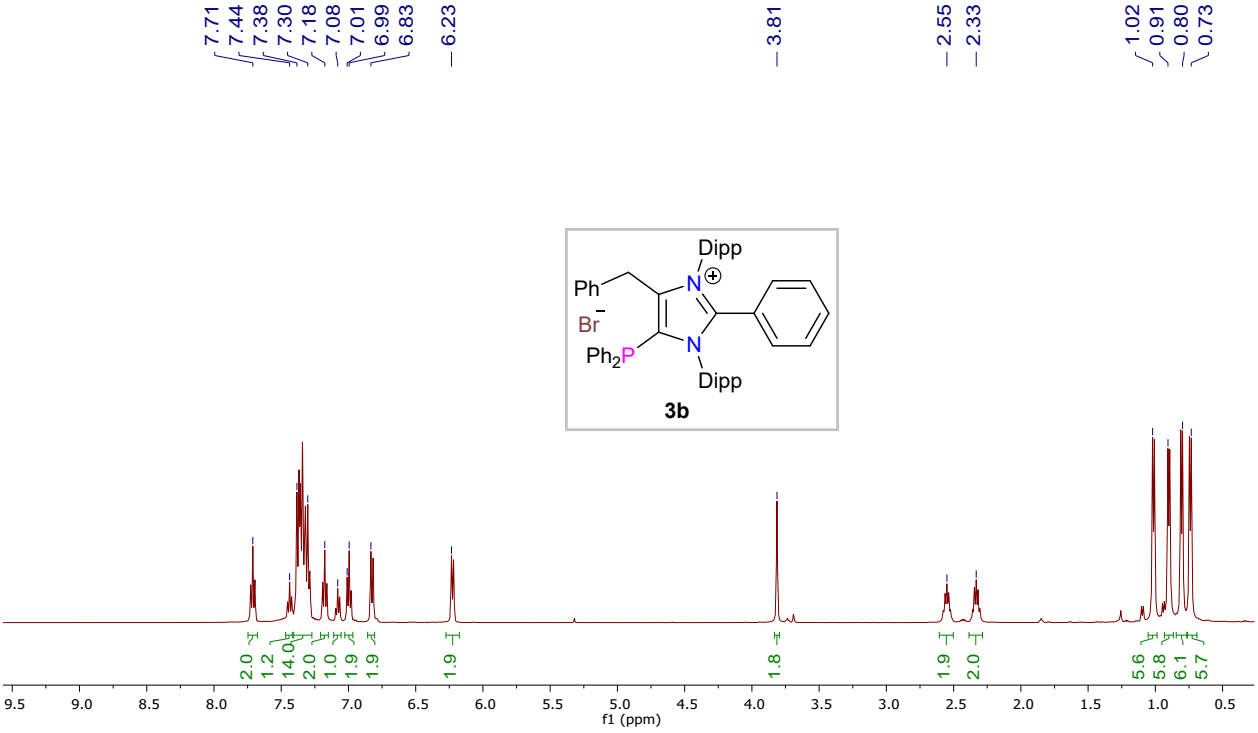


Figure S5. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **3b**.

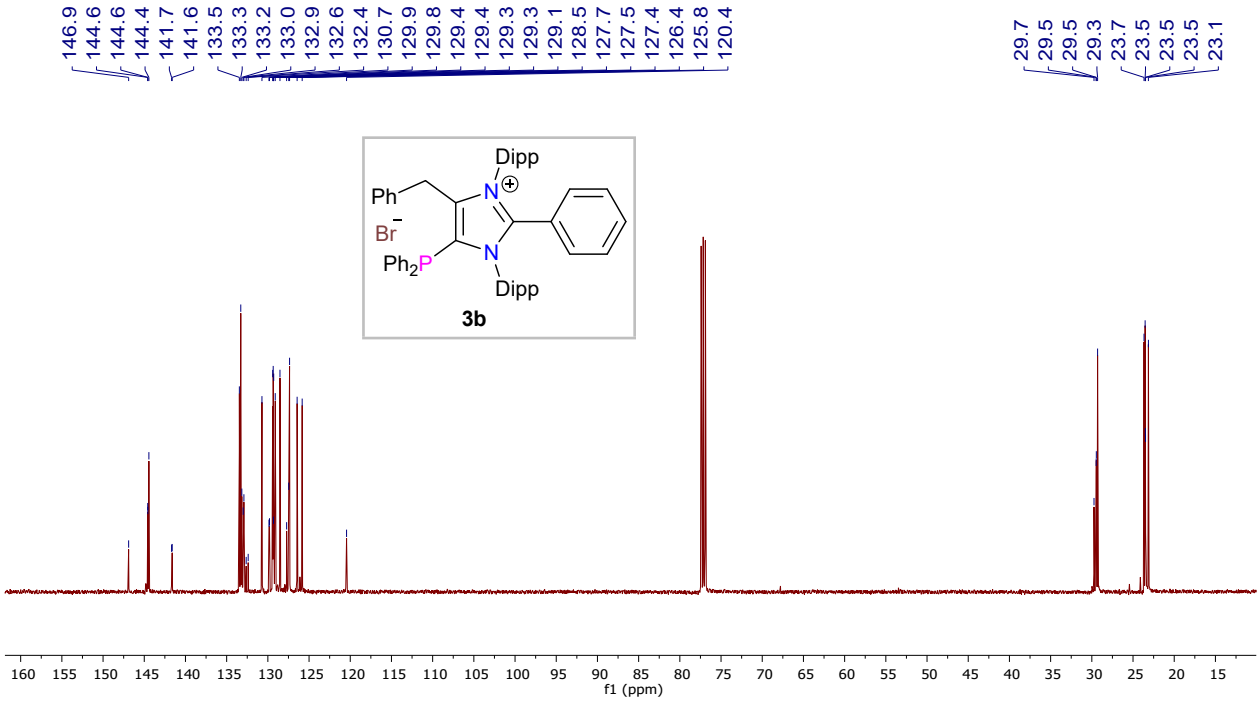


Figure S6. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 298 K) spectrum of **3b**.

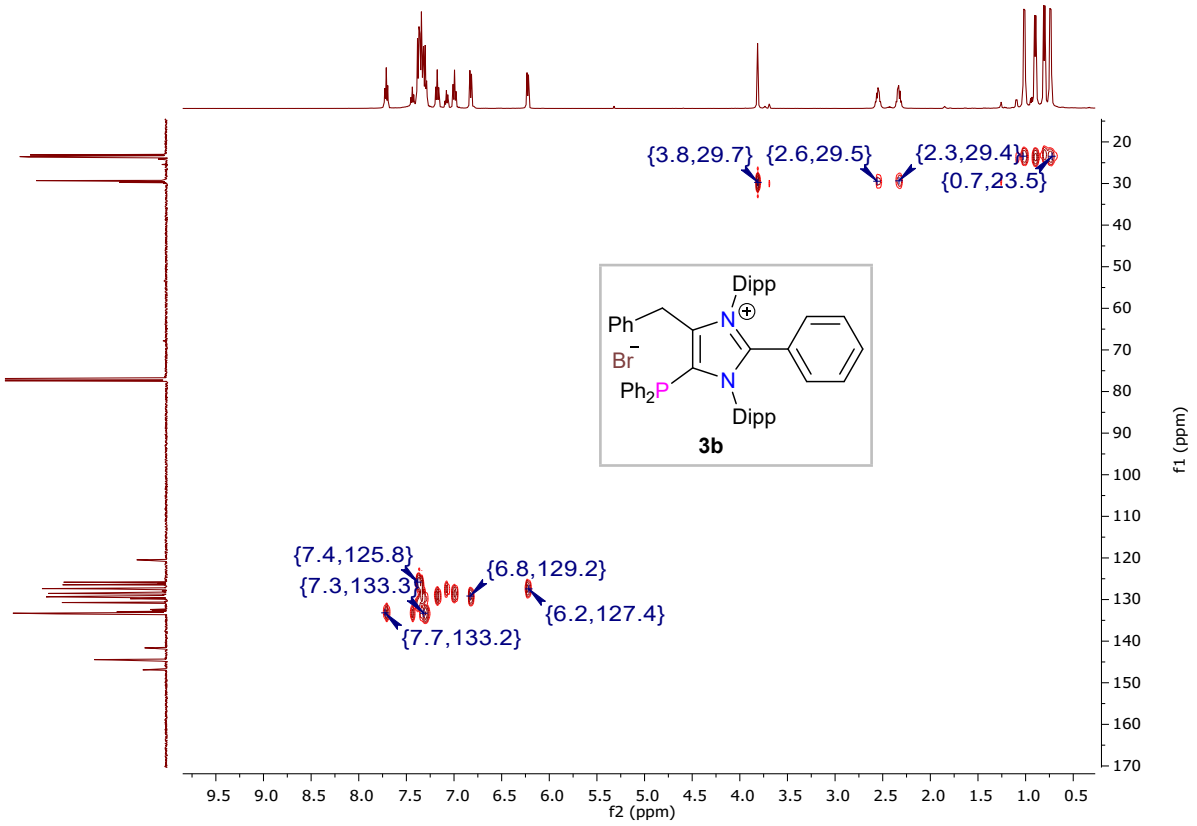


Figure S7. ^{1}H -^{13}C HMQC (500/126 MHz, $CDCl_3$, 298 K) spectrum of **3b**.

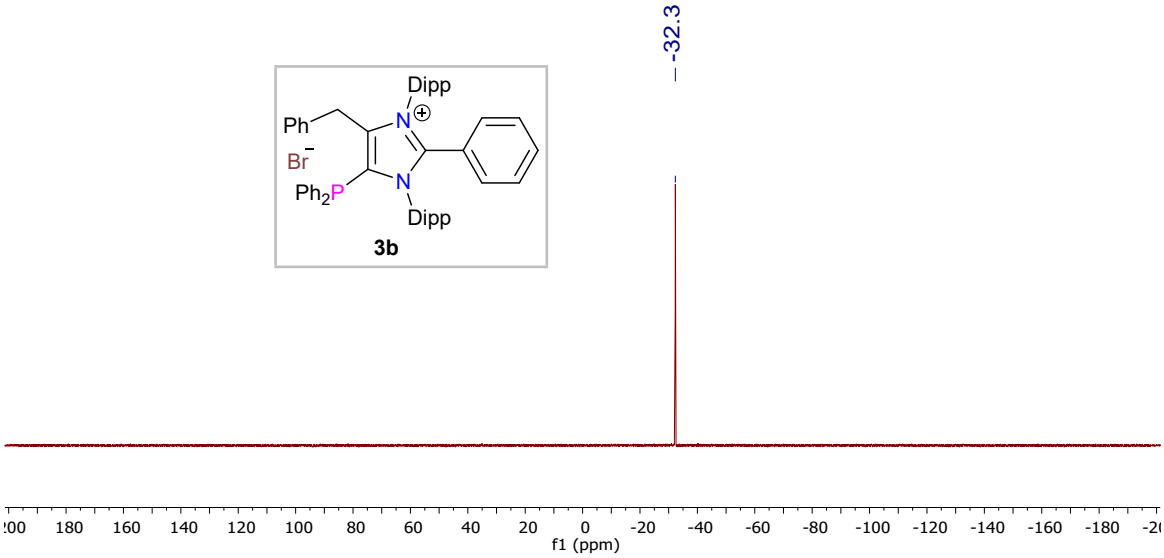


Figure S8. $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$, 298 K) spectrum of **3b**.

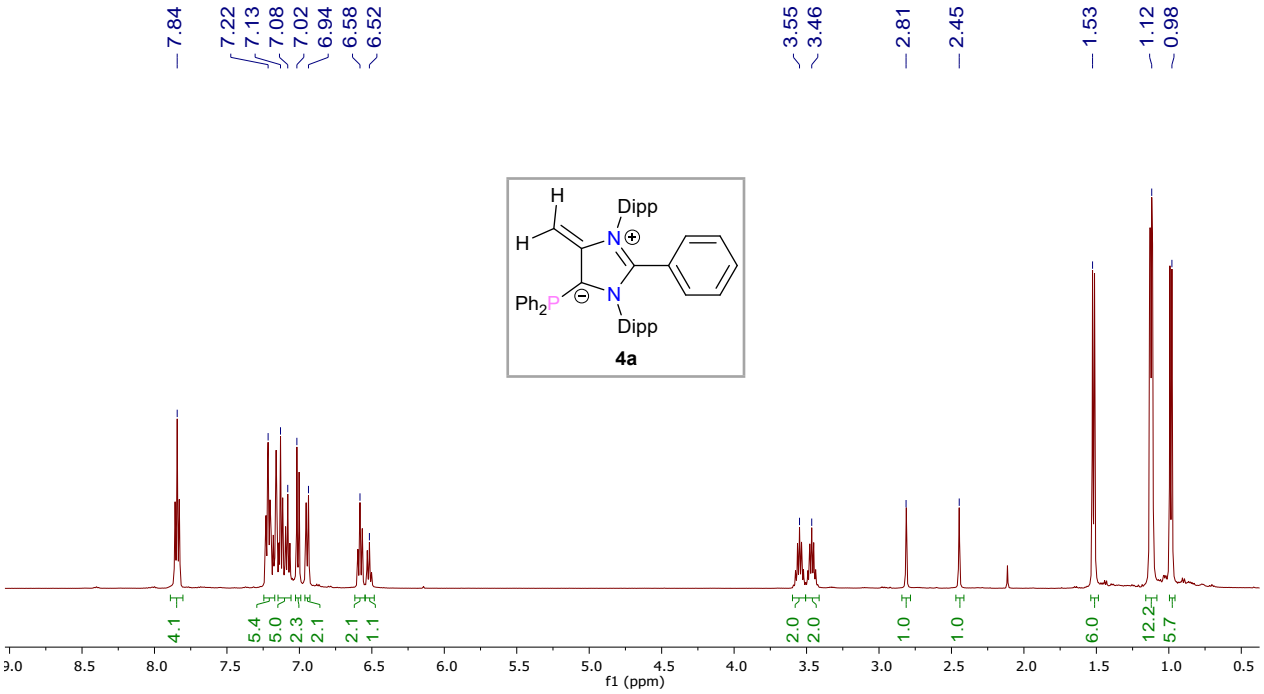


Figure S9. ^{1}H NMR (500 MHz, C_6D_6, 298 K) spectrum of **4a**.

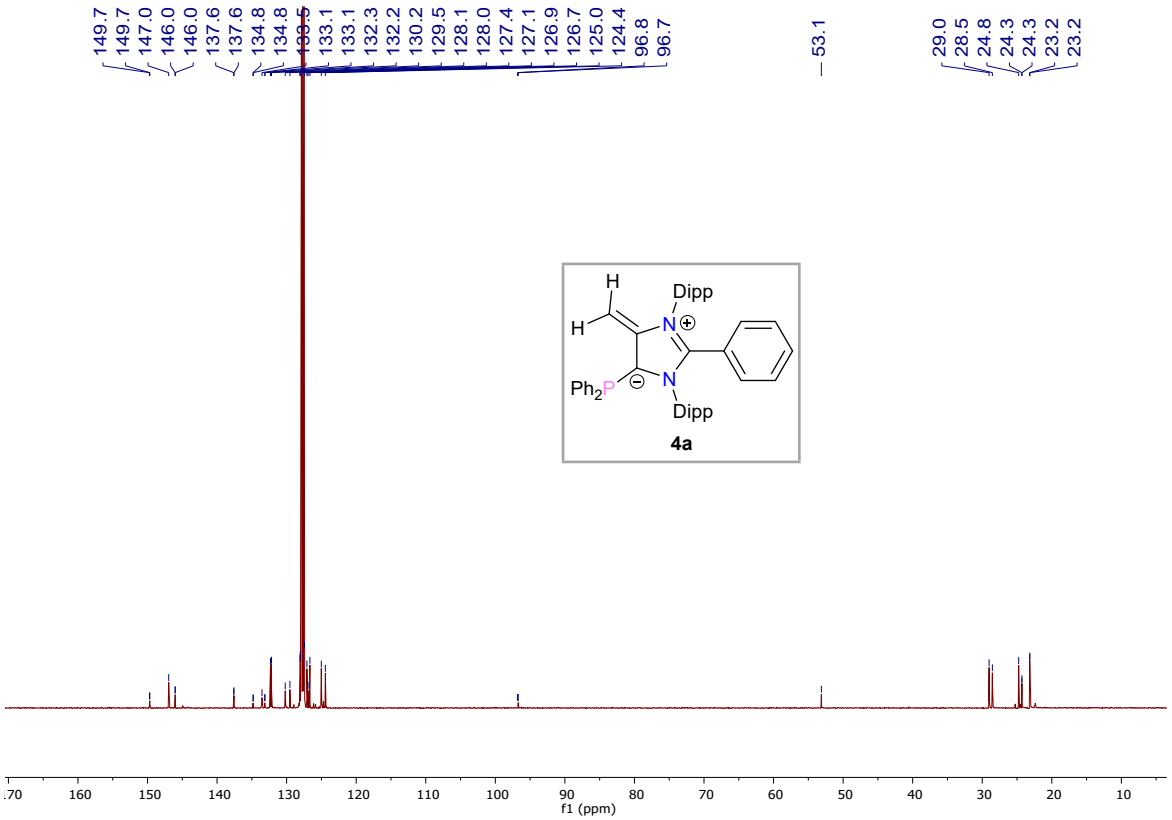


Figure S10. $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 298 K) spectrum of **4a**.

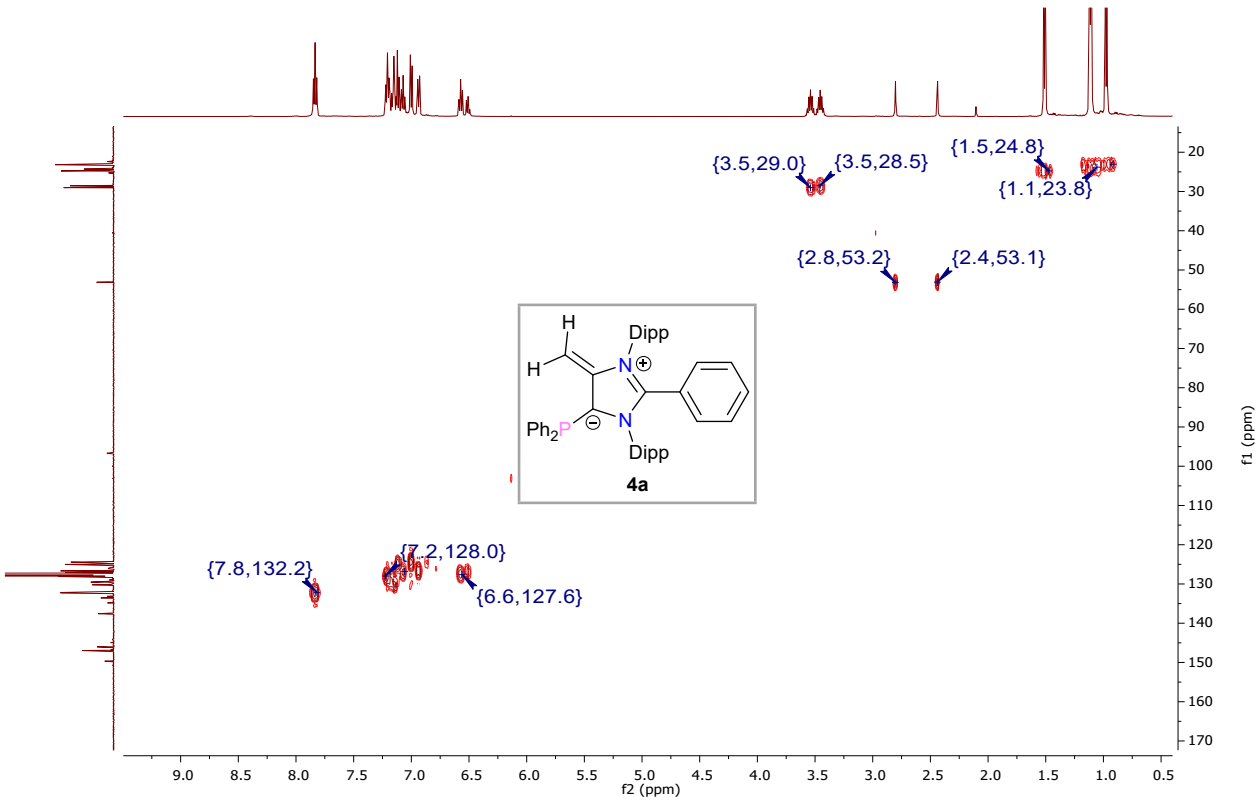


Figure S11. $^{1}H/^{13}C$ HMQC (500/126 MHz, C_6D_6, 298 K) spectrum of **4a**.

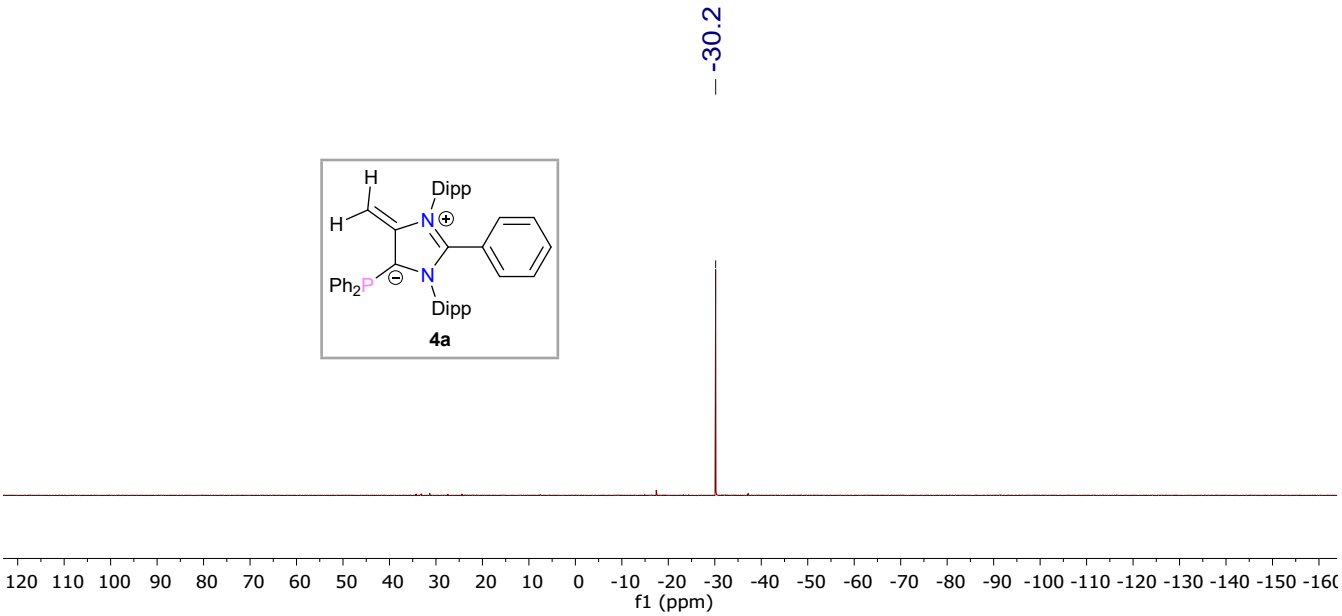


Figure S12. $^{31}P\{^{1}H\}$ NMR (500 MHz, C_6D_6, 298 K) spectrum of **4a**.

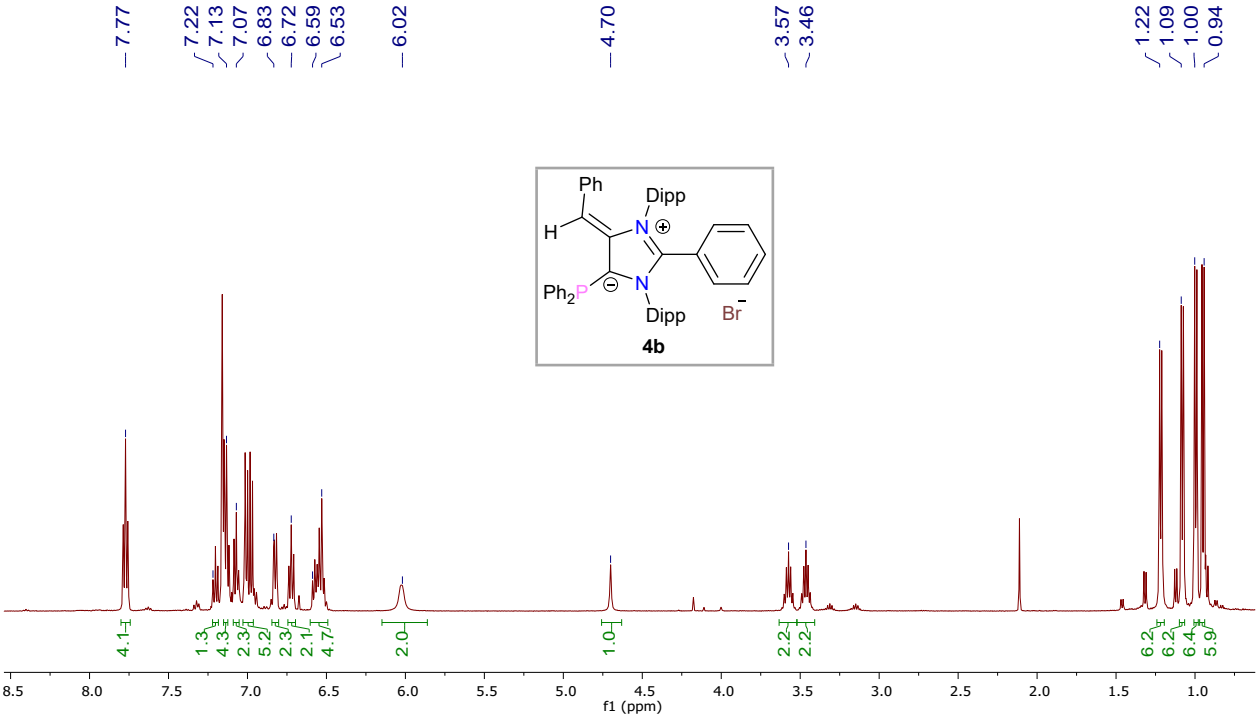


Figure S13. ^{1}H NMR (500 MHz, C_6D_6, 298 K) spectrum of **4b**.

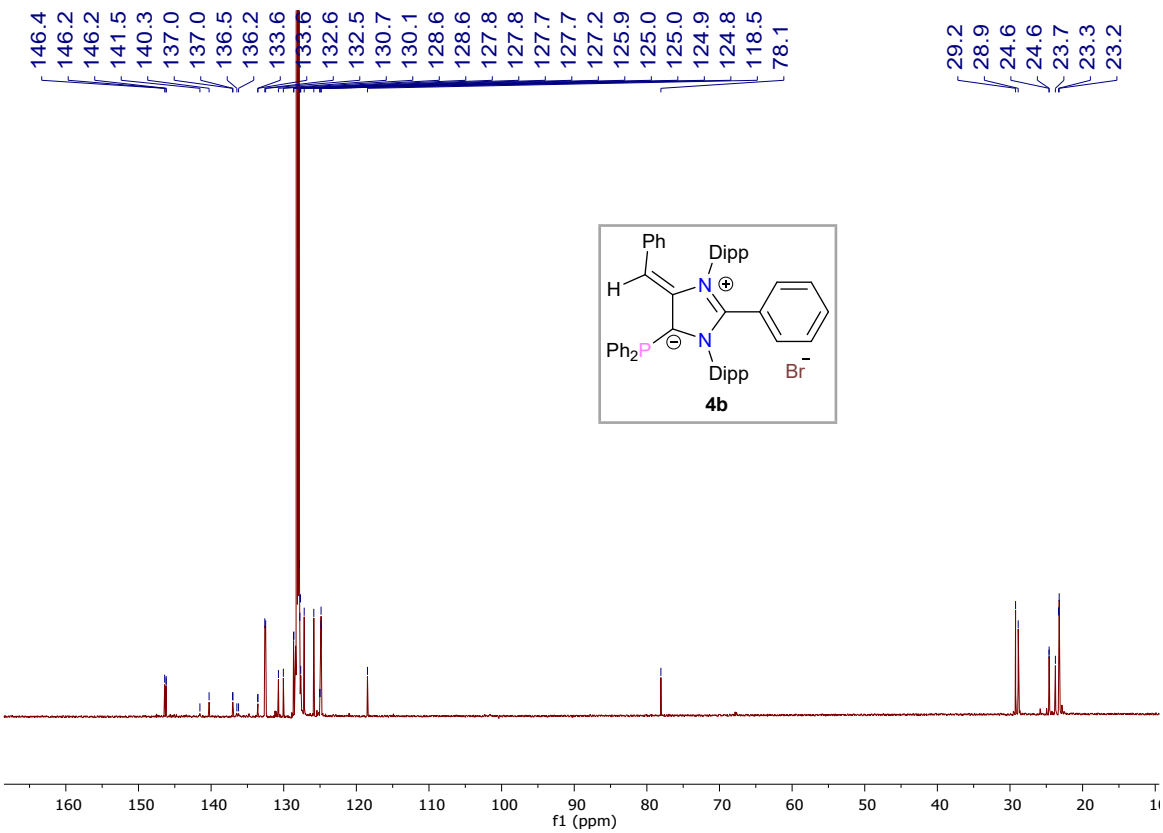


Figure S14. $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6, 298 K) spectra of **4b**.

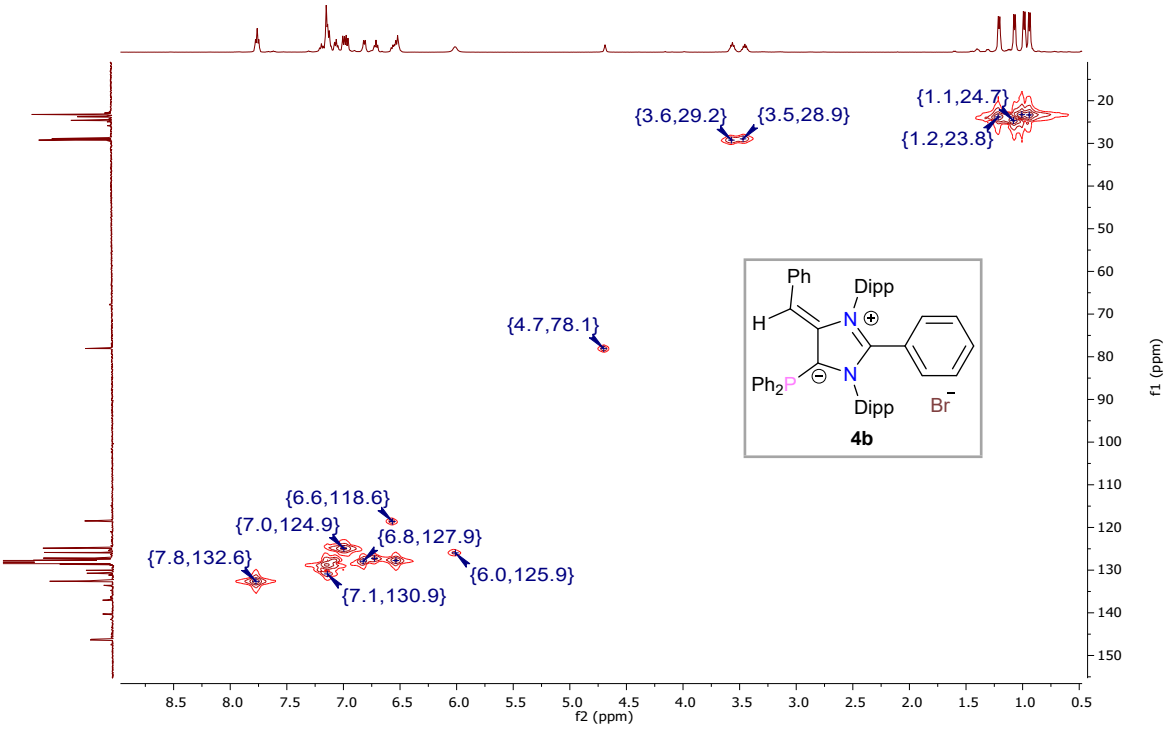


Figure S15. $^{1}H/^{13}C\{^{1}H\}$ NMR (600/151 MHz, C_6D_6, 298 K) spectrum of **4b**.

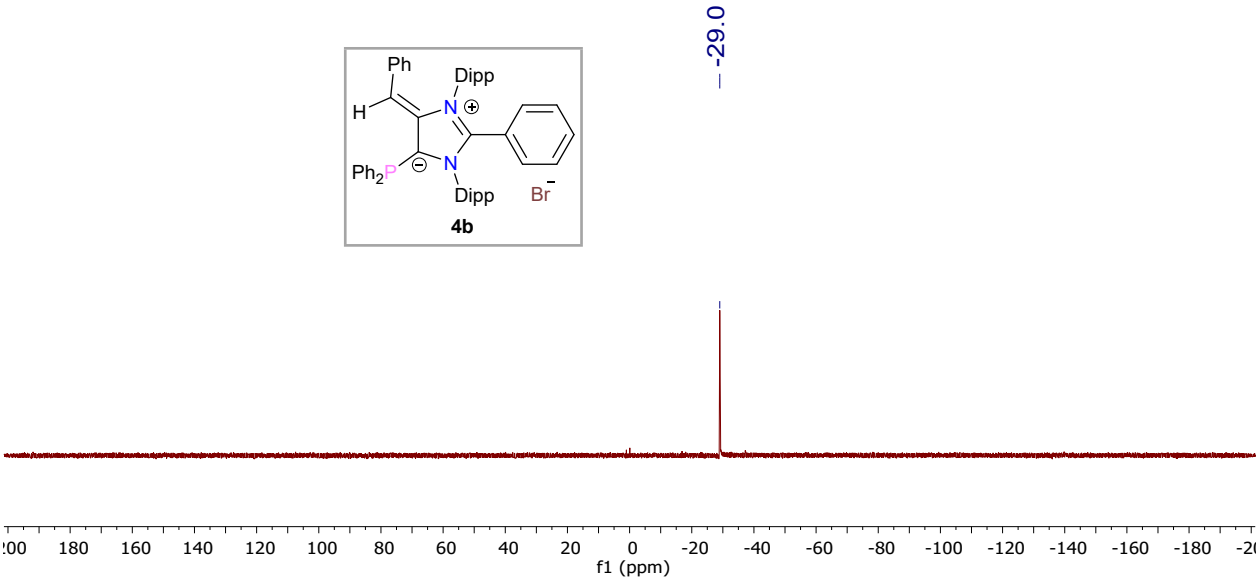


Figure S16. $^{31}P\{^{1}H\}$ NMR (500 MHz, C_6D_6, 298 K) spectrum of **4b**.

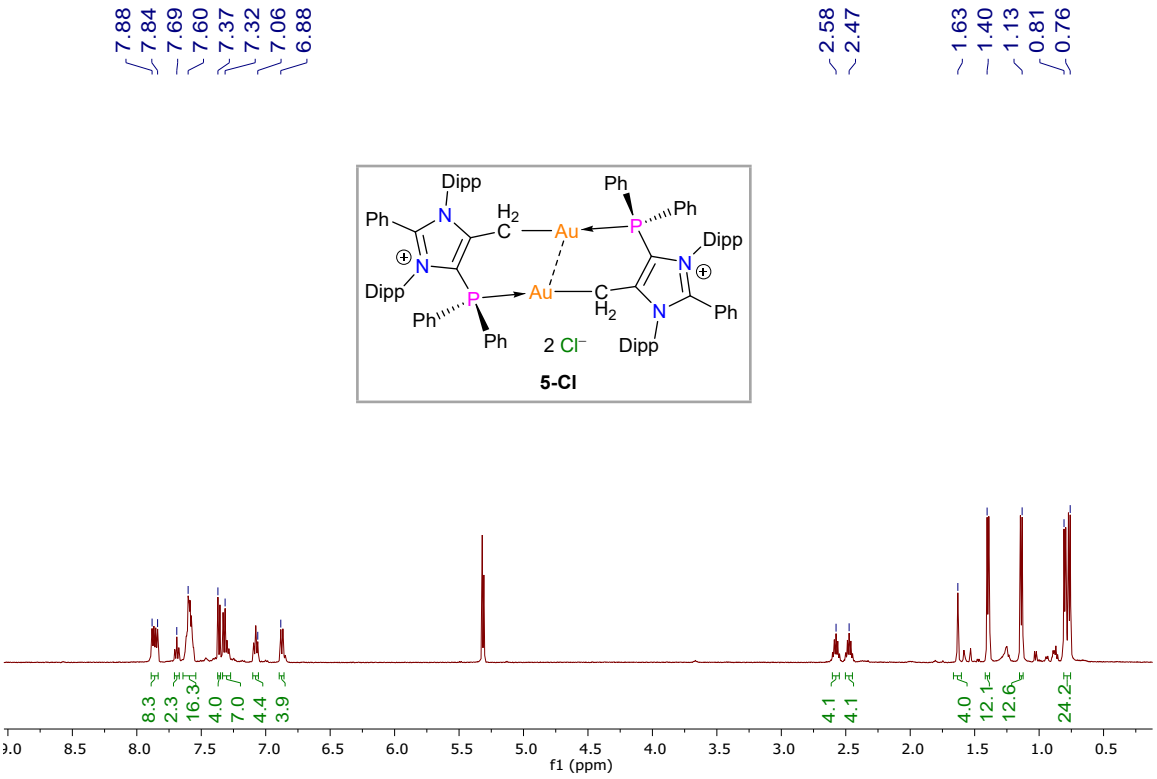


Figure S17. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) spectrum of **5-Cl**.

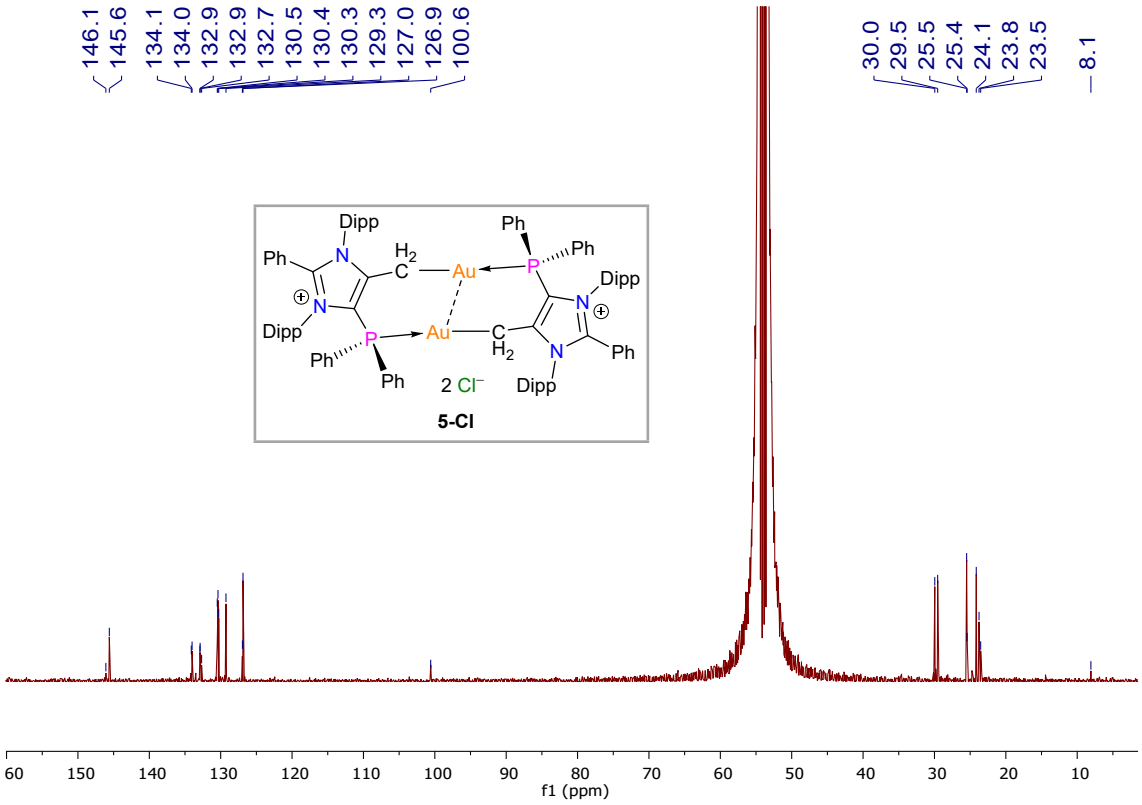


Figure S18. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 298 K) spectrum of **5-Cl**.

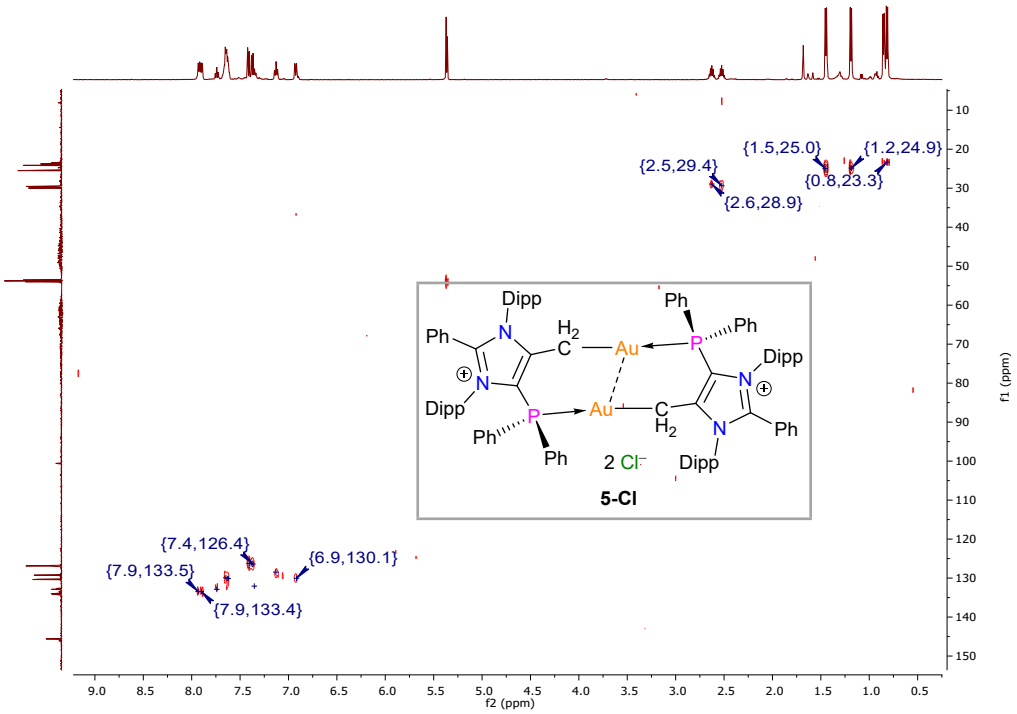


Figure S19. 1H-$^{13}C\{^{1}H\}$ NMR (500/126 MHz, CD_2Cl_2, 298 K) spectrum of **5-Cl**.

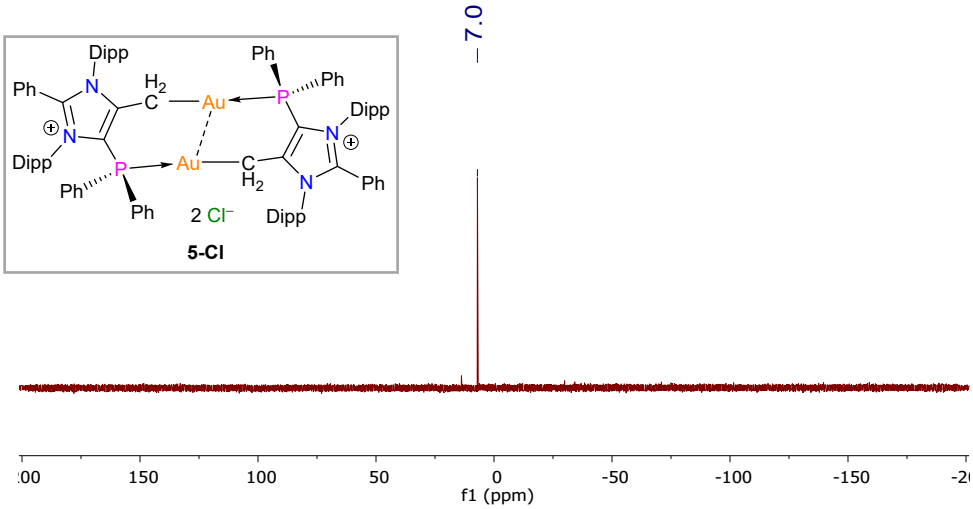


Figure S20. $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2, 298 K) spectrum of **5-Cl**.

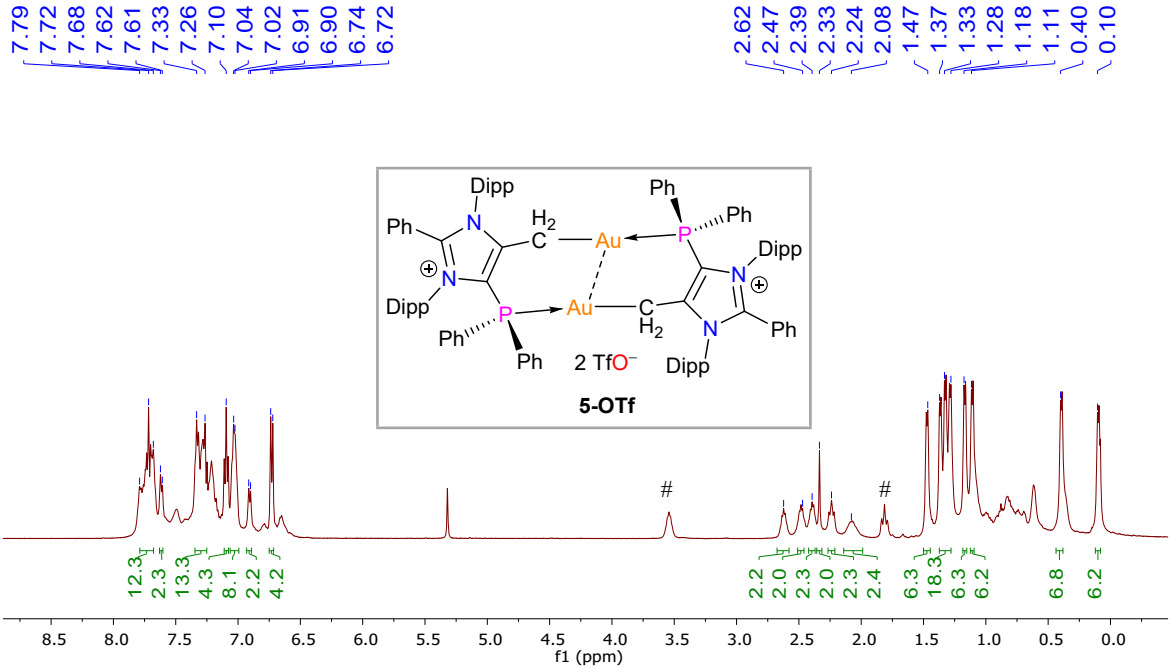


Figure S21. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) spectrum of **5-OTf**. #THF

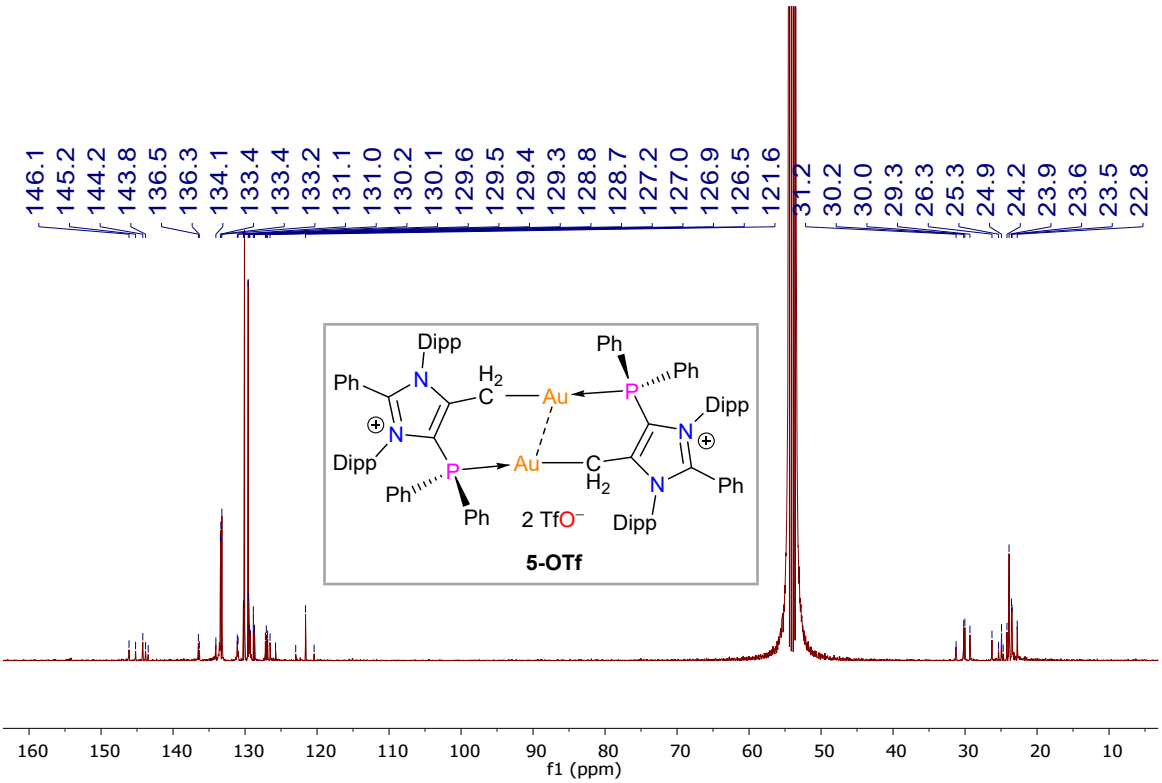


Figure S22. ^{13}C NMR (500 MHz, CD_2Cl_2, 298 K) spectra of **5-OTf**.

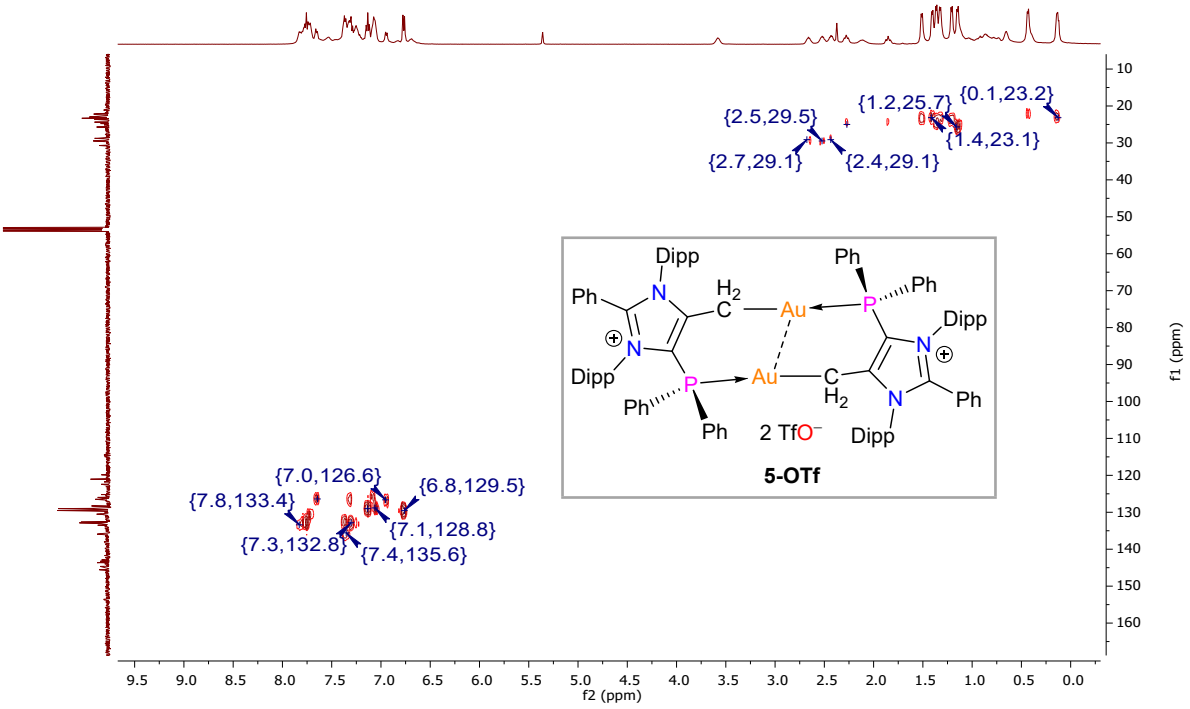


Figure S23. ^{1}H/^{13}C NMR (500/126 MHz, CD_2Cl_2, 298 K) spectrum of **5-OTf**.

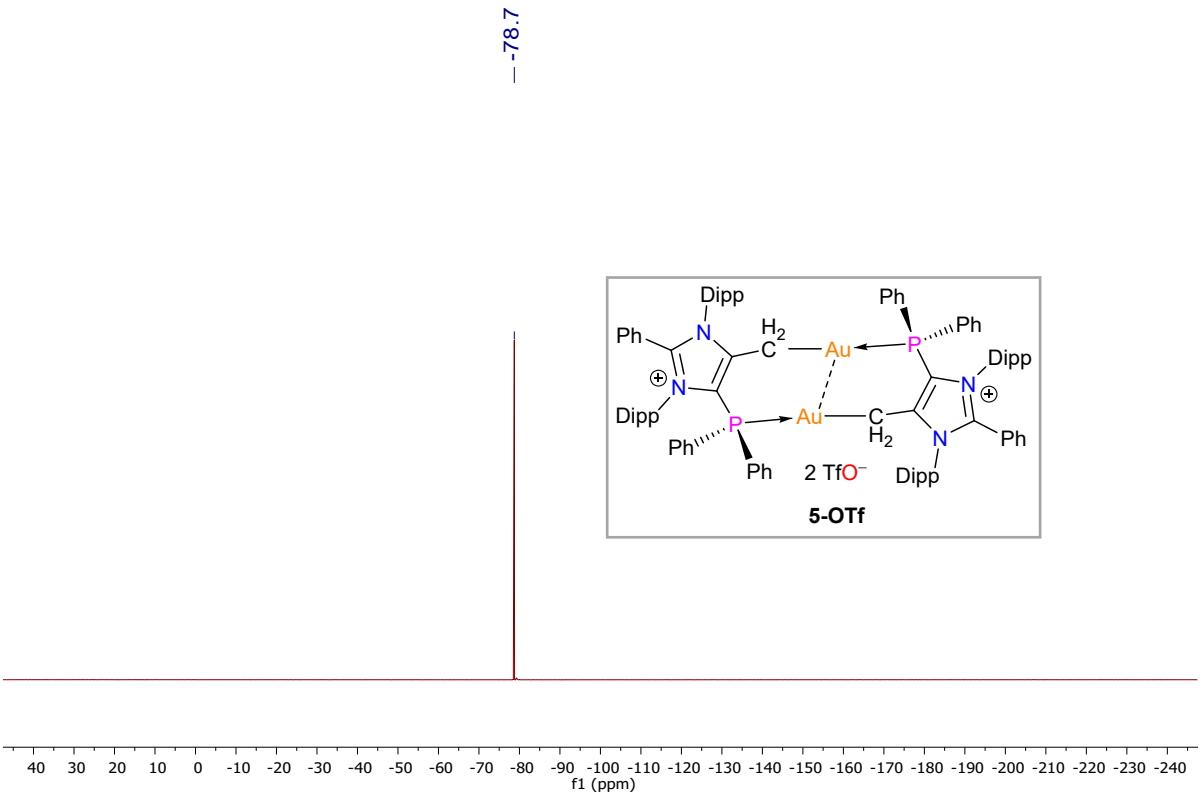


Figure S24. ^{19}F NMR (471 MHz, CD_2Cl_2, 298 K) spectrum of **5-OTf**.

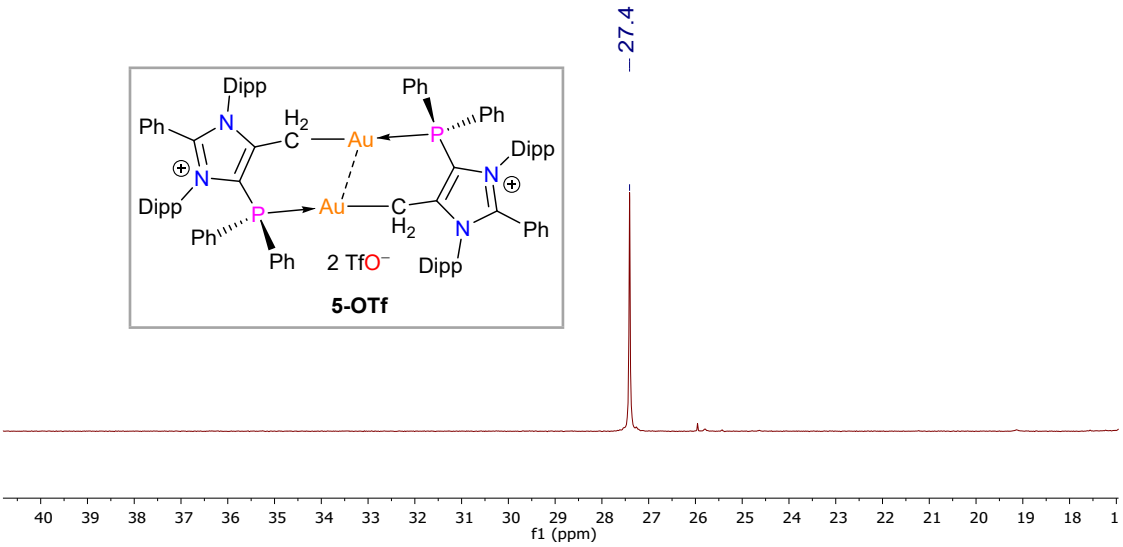


Figure S25. $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 298 K) spectrum of **5-OTf**.

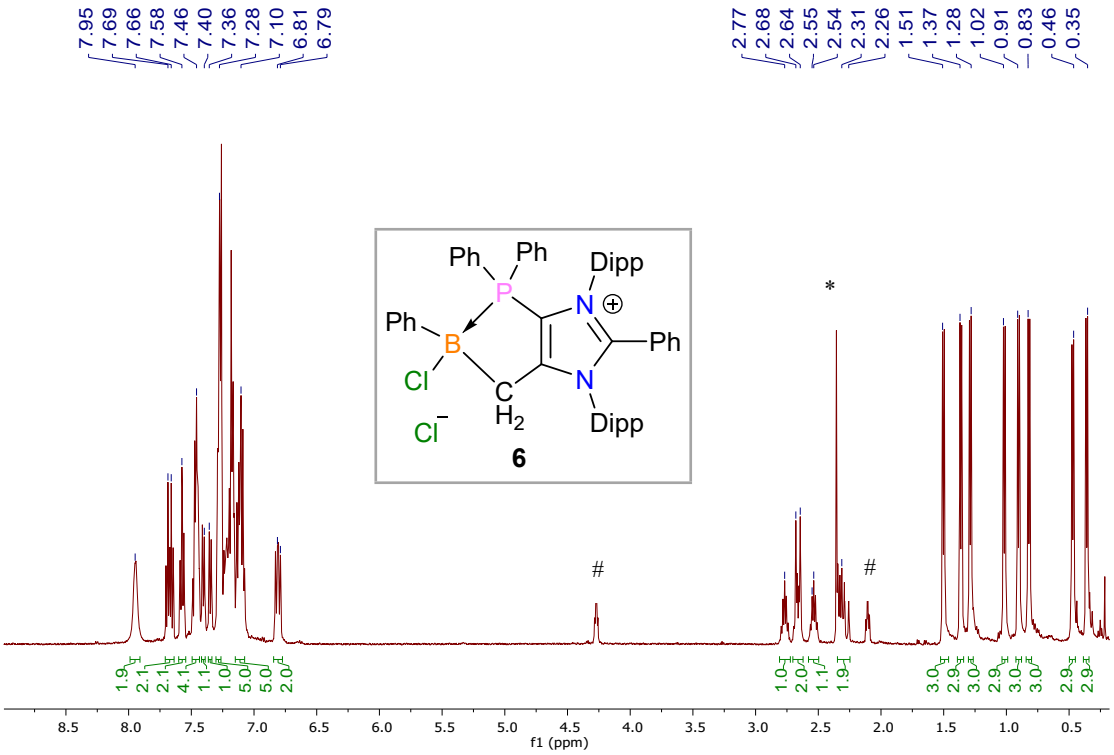


Figure S26. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **6**. #THF, *toluene.

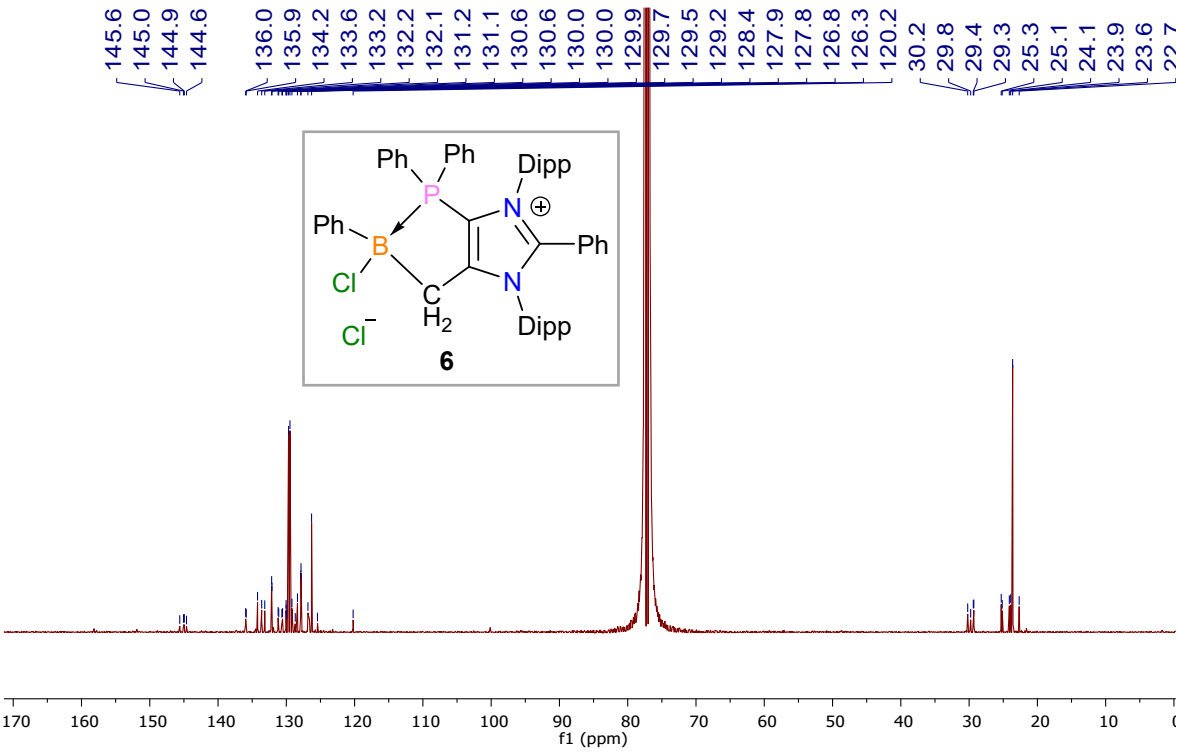


Figure S27. ^{13}C NMR (500 MHz, $CDCl_3$, 298 K) spectrum of **6**.

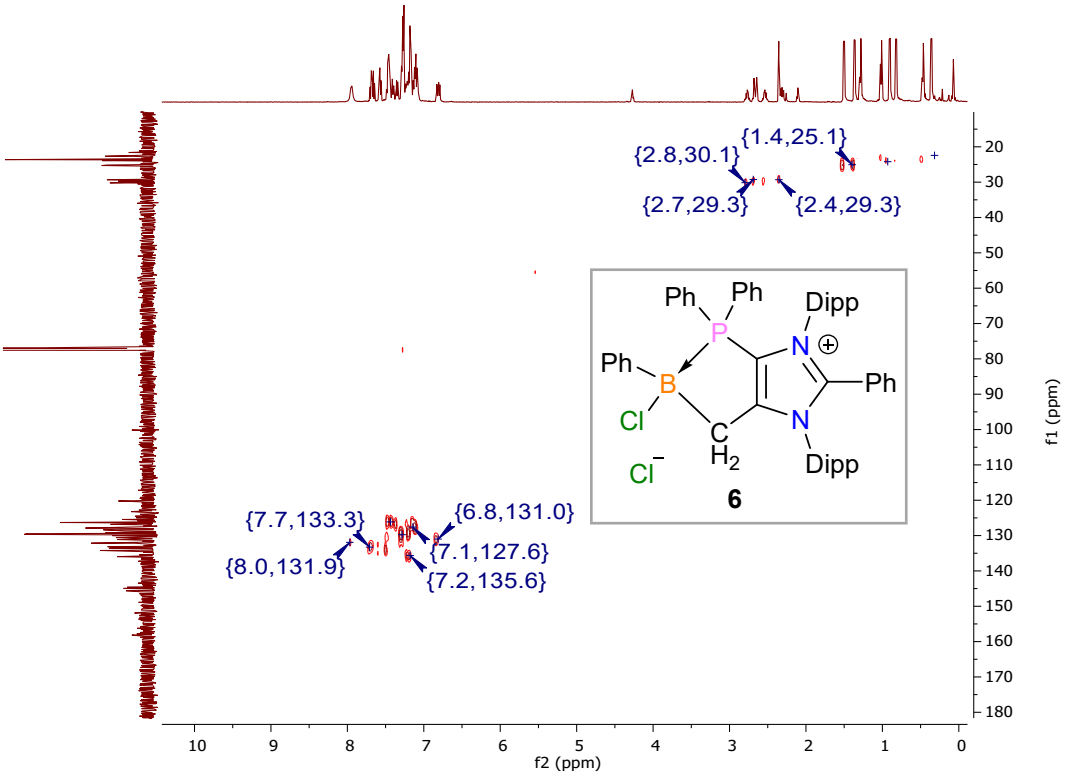


Figure S28. $^{1}H/^{13}C$ NMR (500/126 MHz, $CDCl_3$, 298 K) spectrum of **6**.

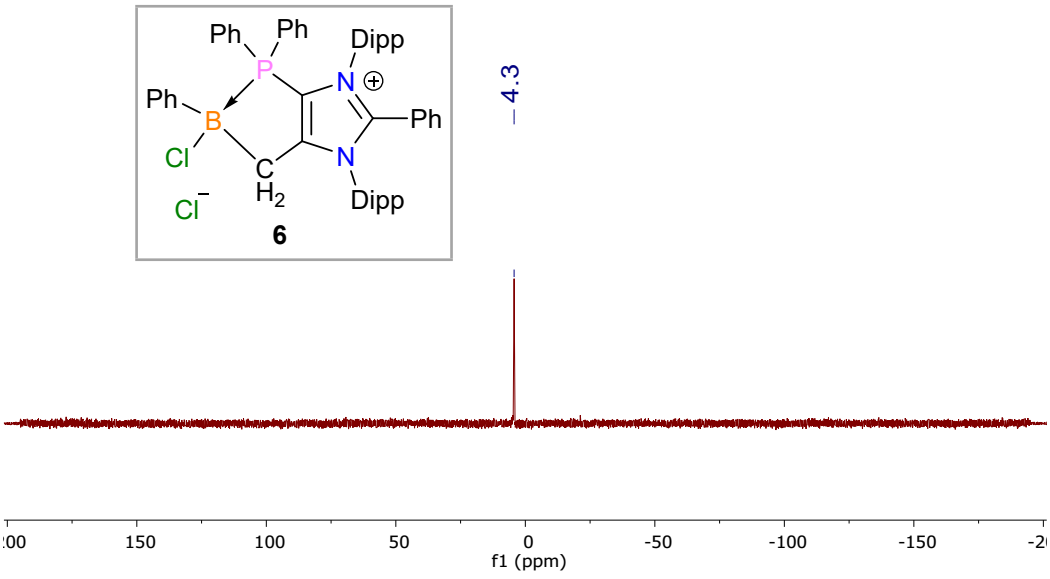


Figure S29. $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$, 298 K) spectrum of **6**.

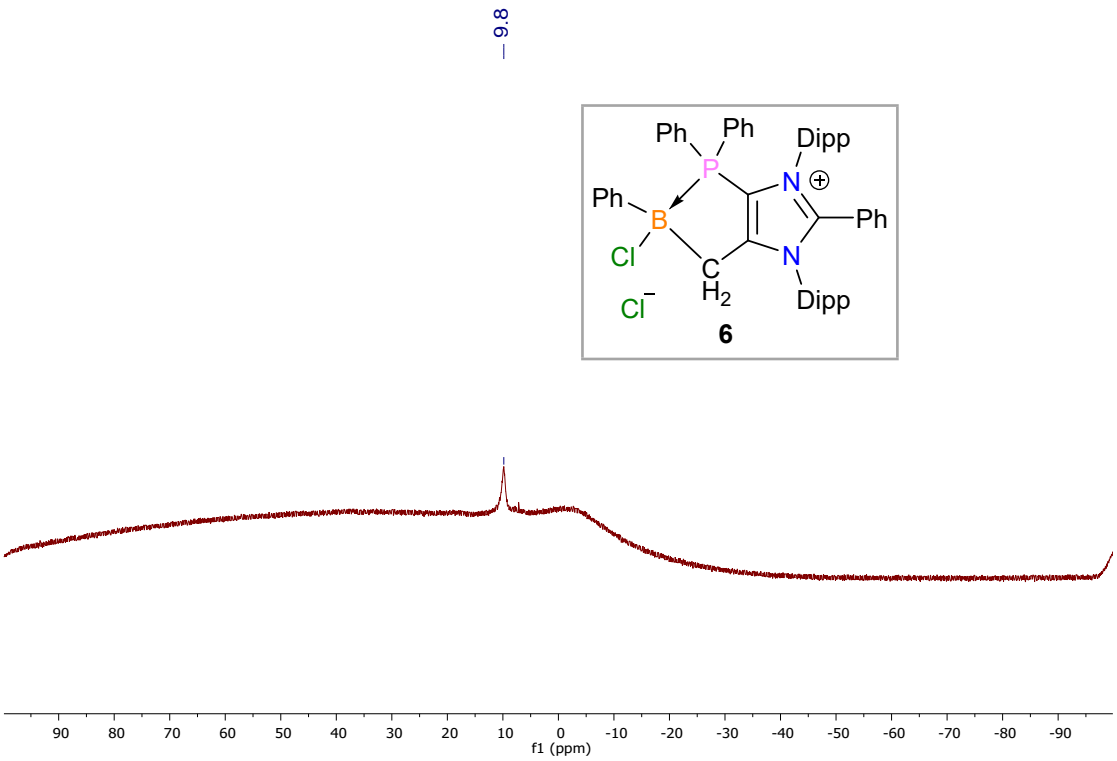


Figure S30. ^{11}B NMR (202 MHz, $CDCl_3$, 298 K) spectrum of **6**.

UV-vis Spectra

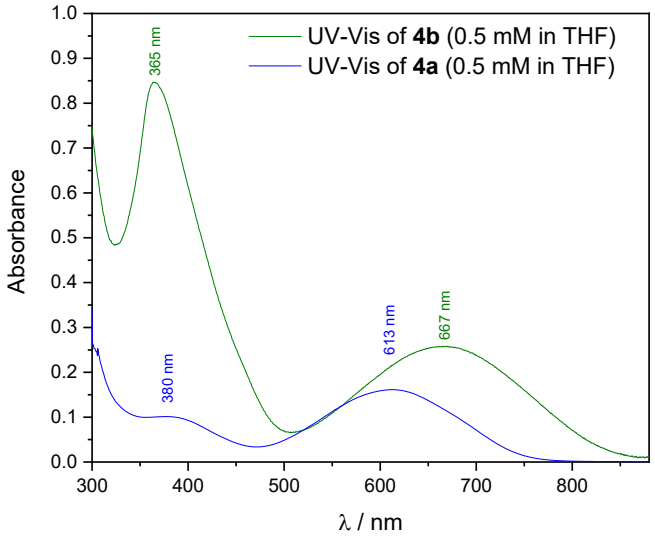


Figure S31. UV-Vis (298 K, THF) spectra of **4a** [λ_1 = 380 nm (202 $M^{-1}\cdot cm^{-1}$); λ_2 = 613 nm (322 $M^{-1}\cdot cm^{-1}$)] and **4b** [λ_1 = 365 nm (1690 $M^{-1}\cdot cm^{-1}$); λ_2 = 667 nm (516 $M^{-1}\cdot cm^{-1}$)].

Crystallographic Details

Single crystals were examined on a Rigaku Supernova diffractometer using Cu Kα (λ = 1.54184 Å) or Mo Kα (λ = 0.71073 Å) radiation. Using Olex2,[3] the structure was solved with the ShelXS[4] (**3b**) or ShelXT[5] (**3a**, **4a**, **5-Cl**) structure solution program using Intrinsic Phasing and refined with the ShelXL[6] refinement package using Least Squares minimization. For **3a** one chloroform solvent molecule is disordered over two sites (65:35). For **5-Cl** roughly disordered DCM molecules could been refined seriously, therefore a solvent mask was calculated and 234 electrons per unit cell were found in a volume of 1161\%A^3 in 1 void. This is roughly consistent with the presence of 5 DCM molecules per formula unit which account for 210.0 electrons. For **6** a molecule of DCM is disordered near an inversion center. The solvent was included using the fragment database of Olex2. The occupancy of this solvent molecule refines to 0.35(1).

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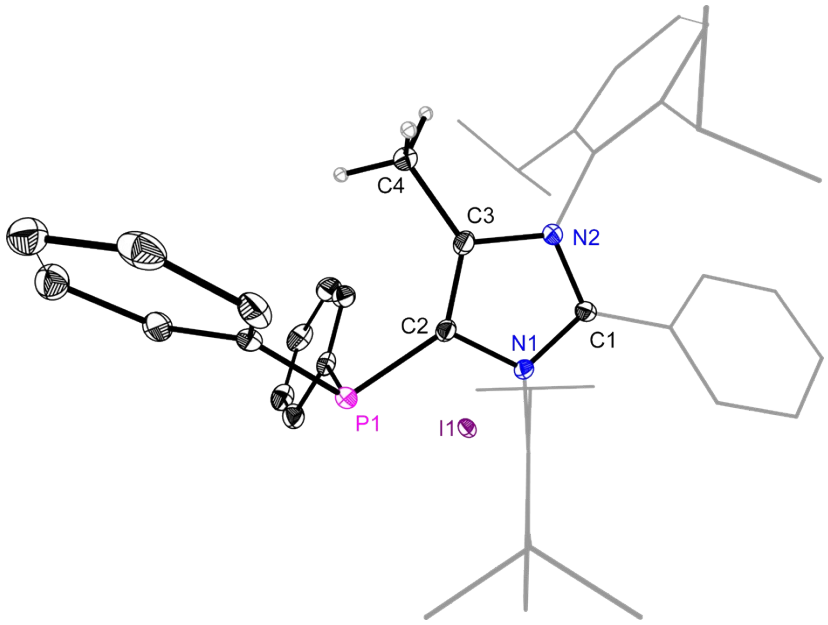

Figure S32. Solid-state structure of **3a**. Hydrogen atoms except for C4 were omitted for clarity. Selected bond lengths (Å) and angles (deg) for **3a**. C2−P1 1.832(3), C2−C3 1.364(4), C3−C4 1.487(5), C2−N1 1.405(4), C3−N2 1.389(4); C3−C2−P1 135.6(3), N2−C3−C4 120.5(3), C2−C3−C4 132.7(3), N2−C3−C2 106.8(3).

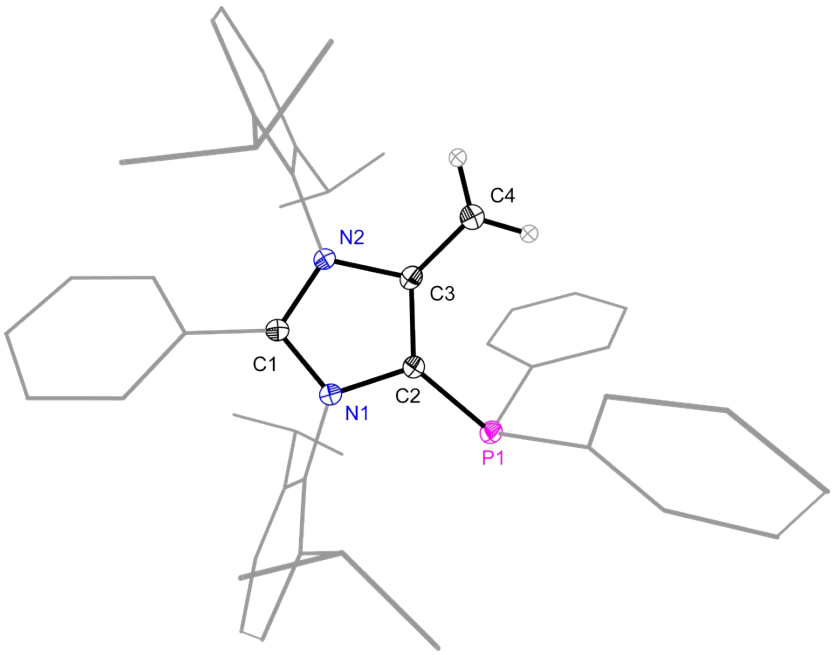

Figure S33. Solid-state structure of **4a**. Hydrogen atoms except for C4 were omitted for clarity. Selected bond lengths (Å) and angles (deg) for **4a**. C2−P1 1.771(1), C2−C3 1.436(2), C3−C4 1.358(2), C2−N1 1.411(1), C3−N2 1.423(1); C3−C2−P1 131.3(8), N2−C3−C4 123.1(1), C2−C3−C4 133.0(1), N2−C3−C2 103.9(1).

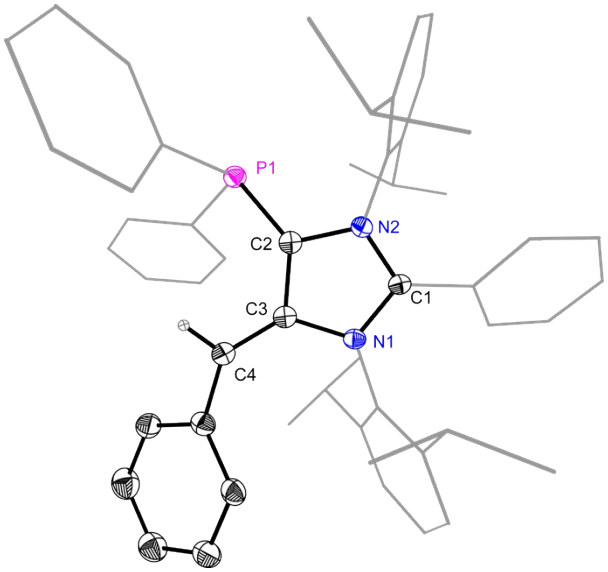

Figure S34. Solid-state structure of **4b**. Hydrogen atoms except for C4 were omitted for clarity. Selected bond lengths (Å) and angles (deg) for **4b**. C2−P1 1.790(2), C2−C3 1.435(3), C3−C4 1.375(3), C2−N1 1.403(2), C3−N2 1.430(2); C3−C2−P1 133.6(1), N2−C3−C4 131.2(2), C2−C3−C4 125.2(2), N2−C3−C2 103.6(2).

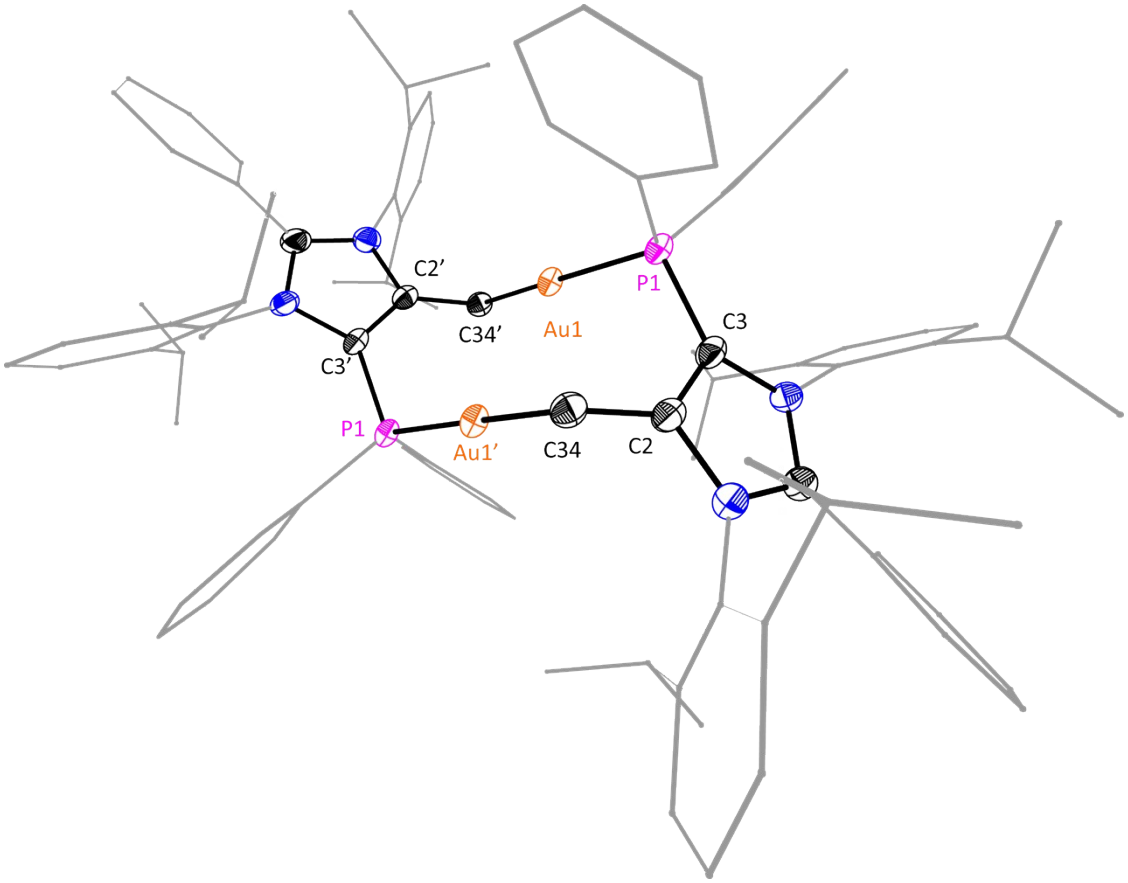

Figure S35. Solid-state structure of **5-Cl**. Hydrogen atoms and two counter anions chloride were omitted for clarity. Selected bond lengths (Å) and angles (deg) for **5-Cl**. Au1−Au1' 3.130(2), Au1−P1 2.284(1), C34−Au1 2.099(3), C3−P1 1.809(3), C2−C3 1.377(5), C2−C34 1.470(5); C34−Au1−P1 174.3(1), N2−C3−C4 131.2(2), C2−C3−C4 125.2(2), N2−C3−C2 103.6(2).

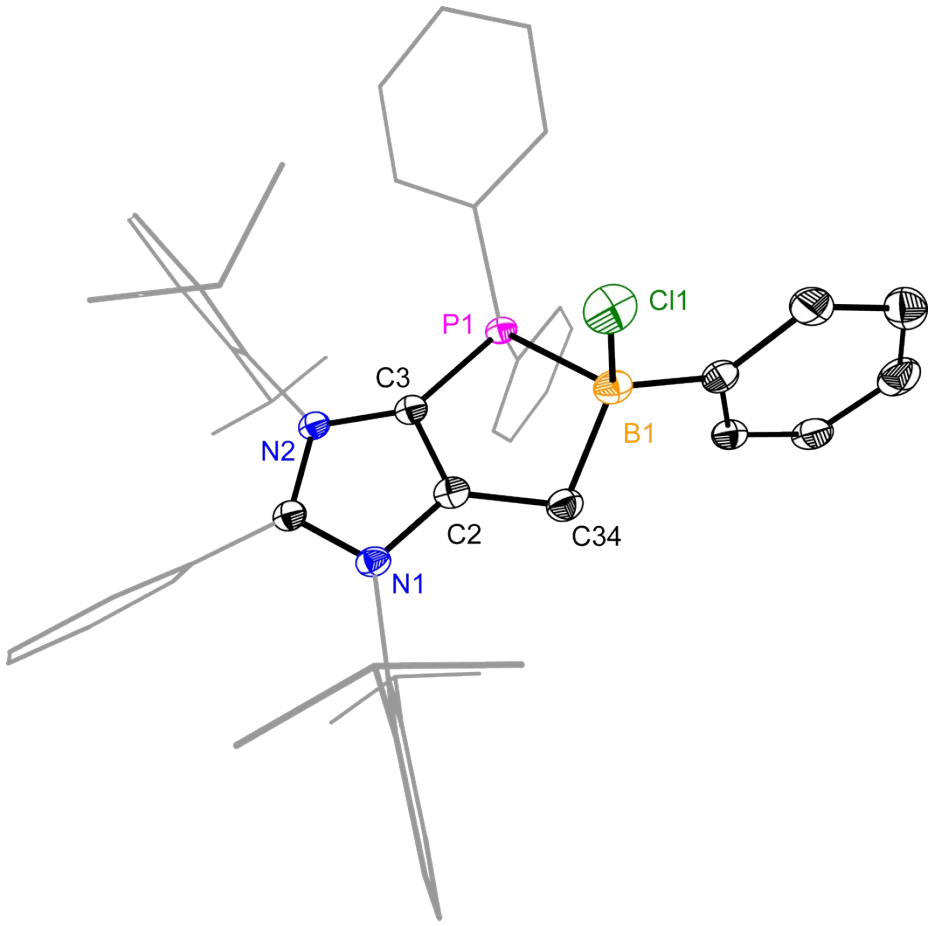

Figure S36. Solid-state structure of **6**. Hydrogen atoms and the counter anion were omitted for clarity. Selected bond lengths (Å) and angles (deg) for **6**: P1−C3 1.795(1), P1−B1 2.035(2), C2−C3 1.363(2), C2−C34 1.479(2), C34−B1 1.648(2), P1−B1 2.035(2), P1−C3 1.795(1); N1−C2−C34 130.3(1), C2−C3−P1 109.7(1), C34−B1−P1 98.6(1).

Table S1. Crystallographic details of **3a**, **4a**, and **4b**.

	3a (2x $CHCl_3$)	**4a**	**4b**
Empirical formula	$C_{48}H_{54}Cl_6IN_2P$	$C_{46}H_{51}N_2P$	$C_{52}H_{55}N_2P$
Formula weight	1029.50	662.85	738.95
Temperature/K	100.0(1)	100.0(1)	100.0(1)
Crystal system	monoclinic	orthorhombic	triclinic
Space group	$P2_1$	Pbca	P-1
a/Å	9.6946(3)	20.2225(4)	10.5080(7)
b/Å	23.0494(5)	18.7068(4)	10.6031(6)
c/Å	11.1709(3)	20.3020(4)	20.8200(14)
α/°	90	90	75.720(6)
β/°	100.423(3)	90	87.335(5)
γ/°	90	90	70.184(6)
Volume/Å^3	2454.99(11)	7680.2(3)	2113.2(3)
Z	2	8	2
ρ_{calc}g/cm^3	1.393	1.147	1.161
μ/mm^{-1}	1.045	0.105	0.846
F(000)	1052.0	2848.0	792.0
Crystal size/mm^3	0.269 × 0.196 × 0.148	0.309 × 0.246 × 0.098	0.127 × 0.061 × 0.012
Radiation/Å	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.122 to 60.066	4.99 to 65.754	8.772 to 148.958
Index ranges	-13 ≤ h ≤ 13, -32 ≤ k ≤ 32, -15 ≤ l ≤ 15	-28 ≤ h ≤ 30, -28 ≤ k ≤ 27, -28 ≤ l ≤ 30	-11 ≤ h ≤ 13, -13 ≤ k ≤ 12, -24 ≤ l ≤ 25
Reflections collected	52929	162835	15647
Independent reflections	14359 [R_{int} = 0.0367, R_{sigma} = 0.0394]	13820 [R_{int} = 0.0622, R_{sigma} = 0.0383]	8322 [R_{int} = 0.0385, R_{sigma} = 0.0570]
Reflections with $I > 2\sigma(I)$	13037	10265	6141
Data/restraints/parameters	14359/1/533	13820/0/646	8322/0/504
Goodness-of-fit on F^2	1.024	1.023	1.031
Final R indexes [$I > 2\sigma(I)$]	R_1 = 0.0363, wR_2 = 0.0743	R_1 = 0.0492, wR_2 = 0.1133	R_1 = 0.0467, wR_2 = 0.1007
Final R indexes [all data]	R_1 = 0.0425, wR_2 = 0.0778	R_1 = 0.0753, wR_2 = 0.1262	R_1 = 0.0736, wR_2 = 0.1134
Largest diff. peak/hole / e Å^{-3}	1.25/-0.87	0.42/-0.33	0.27/-0.29
Flack parameter	-0.063(4)		
CCDC number	2121789	2121790	2121791

Table S2. Crystallographic details of **5-Cl** and **6**.

	5-Cl x 5 CH_2Cl_2	**6**-PhBCl3x 0.35 CH_2Cl_2
Empirical formula	$C_{97}H_{112}Au_2Cl_{12}N_4P_2$	$C_{58.35}H_{61.7}B_2Cl_{4.71}N_2P$
Formula weight	2215.17	1010.44
Temperature/K	99.97(13)	100.01(10)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	12.5519(2)	11.6389(3)
b/Å	13.5059(3)	15.0221(5)
c/Å	17.4784(3)	15.9346(5)
α/°	95.2343(15)	83.088(3)
β/°	105.4602(15)	75.067(3)
γ/°	90.6853(15)	80.567(3)
Volume/Å^3	2841.87(9)	2646.59(14)
Z	1	2
ρ_{calc}g/cm^3	1.294	1.268
μ/mm^{-1}	2.928	2.944
F(000)	1114.0	1062.0
Crystal size/mm^3	0.37 × 0.171 × 0.135	0.18 × 0.079 × 0.033
Radiation/Å	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.116 to 65.78	5.76 to 153.898
Index ranges	-18 ≤ h ≤ 19, -20 ≤ k ≤ 19, -26 ≤ l ≤ 26	-14 ≤ h ≤ 14, -18 ≤ k ≤ 18, -20 ≤ l ≤ 20
Reflections collected	89437	51224
Independent reflections	19635 [R_{int} = 0.0551, R_{sigma} = 0.0434]	11005 [R_{int} = 0.0305, R_{sigma} = 0.0218]
Reflections with *I* > 2σ(*I*)	17539	10119
Data/restraints/parameters	19635/0/468	11005/22/640
Goodness-of-fit on F^2	1.036	1.072
Final R indexes [*I* > 2σ(*I*)]	R_1 = 0.0458, wR_2 = 0.1183	R_1 = 0.0367, wR_2 = 0.0947
Final R indexes [all data]	R_1 = 0.0512, wR_2 = 0.1228	R_1 = 0.0397, wR_2 = 0.0974
Largest diff. peak/hole / e Å^{-3}	4.49/-2.40	0.42/-0.40
CCDC number	2121792	2121793

Quantum-Chemical Calculations

Molecular structures **4a**, **4b**, and the dication (**5**)$^{2+}$ in free state have been optimized at the PBE0-D3BJ/def2-TZVP (for gold atoms dhf-TZVP basis set) level of theory implemented in Turbomole 7.4.1 program package.[7] The optimized structures are shown in Figures 37−39, the respective Cartesian coordinates are given in Tables 1 – 3. The integration grid was m4 and the SCF convergence criterion scfconv was 7. For (**5**)$^{2+}$ the optimization was repeated with m5 and scfconv=8, which confirmed the convergence of lengths of bonds with gold atoms at the 10^{-3} Å level. For the optimized structures the fractional occupation number weighted density (FOD) analysis[8] has been performed at the same level of theory in Orca 4.2.1 package.[9] These calculations were done for T_{el} = 10000 K, using RIJCOSX approximation and with TightSCF and Grid4 settings. The resulting N_{FOD} numbers were 2.71, 1.78 and 2.01 e for **5-Cl**, **4a** and **4b** respectively. The plots of FOD electron density are shown in Figures 40−42. Frontier molecular orbitals of **4a** and **4b** are given in Figures 43−44. At the same level of theory were also done TD-DFT calculations using TDA approximation and CPCM solution model for THF as implemented in Orca. In these calculations the integration grid was increased to Grid5.

Proton affinities of **4a** and **4b** have been calculated as

$$\mathrm{PA} = E_{\mathrm{Mol}} - E_{\mathrm{Mol\text{-}H^+}}$$

where E_{Mol} and $E_{Mol\text{-}H^+}$ are energies of the optimized structures of **4a** or **4b** and of the respective forms protonated at the exocyclic olefinic carbon atom. PA calculations have been done at the BLYP/def2-TZVPP level of theory without any corrections for dispersion interactions, for compatibility with earlier calculations.[10] This was done using Turbomole program package. The resulting PAs were 291.3 (**4a**) and 288.1 (**4b**) kcal/mol. The optimized Cartesian coordinates at the BLYP/def2-TZVPP level are provided in Tables 6 − 9.

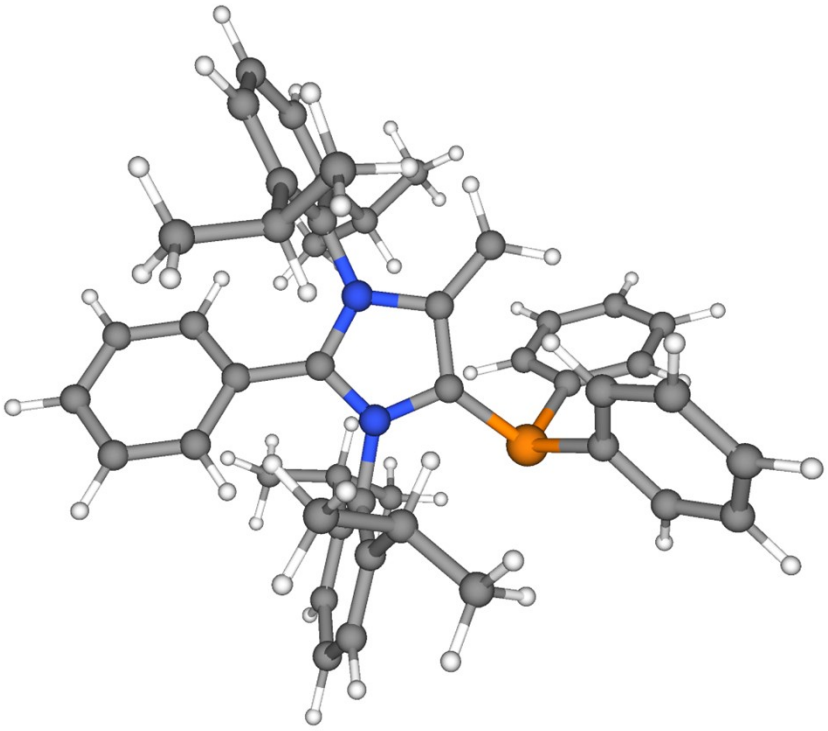

Figure S37. Optimized gas-phase molecular structure of **4a** at the PBE0-D3BJ/def2-TZVP level.

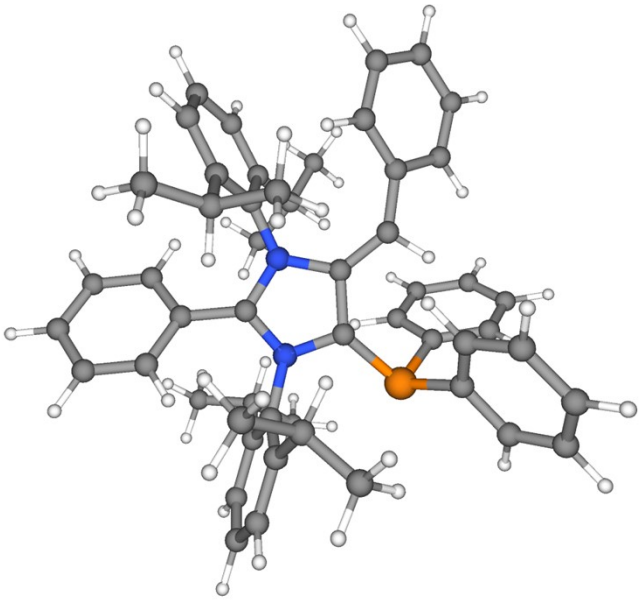

Figure S38. Optimized gas-phase molecular structure of **4b** at the PBE0-D3BJ/def2-TZVP level.

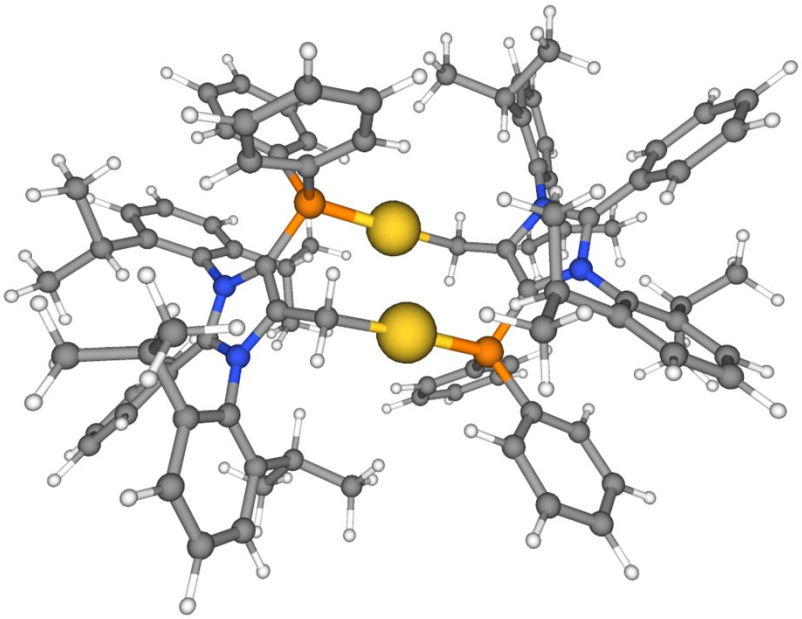

Figure S39. Optimized gas-phase molecular structure of $(\mathbf{5})^{2+}$ at the PBE0-D3BJ/dhf-TZVP level. Selected equilibrium parameters (Å) are: r(Au...Au) = 3.071, r(Au-P) = 2.306, r(Au-C) = 2.099.

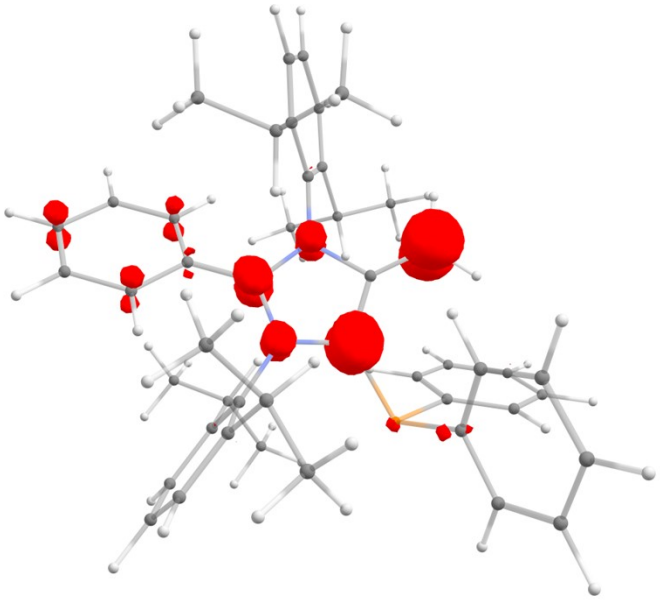

Figure S40. Isosurface (0.005 a.e., plotted in red) of FOD for **4a**.

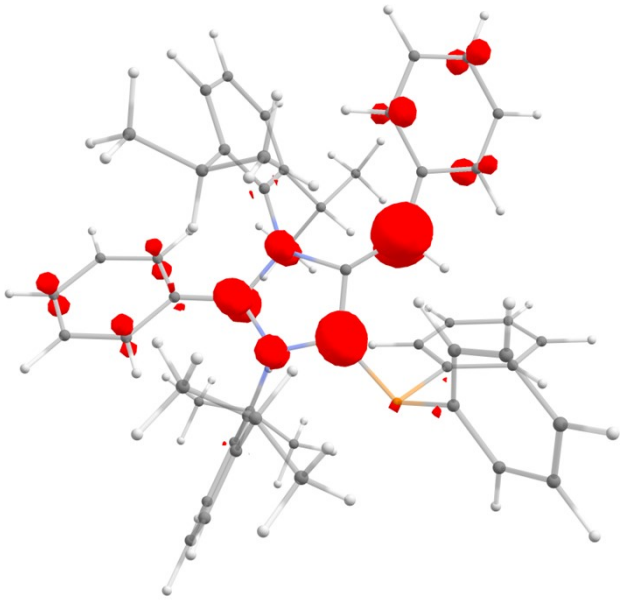

Figure S41. Isosurface (0.005 a.e., plotted in red) of FOD for **4b**.

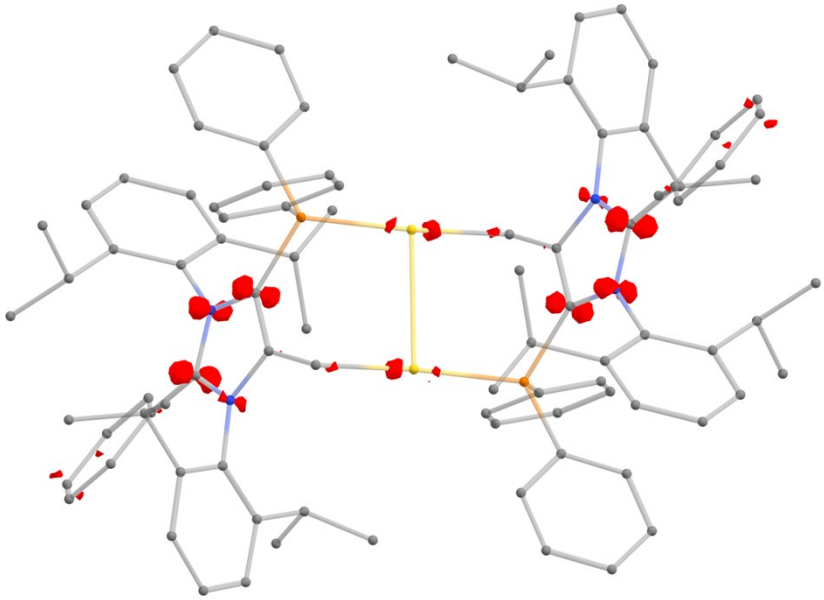

Figure S42. Isosurface (0.005 a.e., plotted in red) of FOD for $(\mathbf{5})^{2+}$. Hydrogen atoms are omitted for clarity.

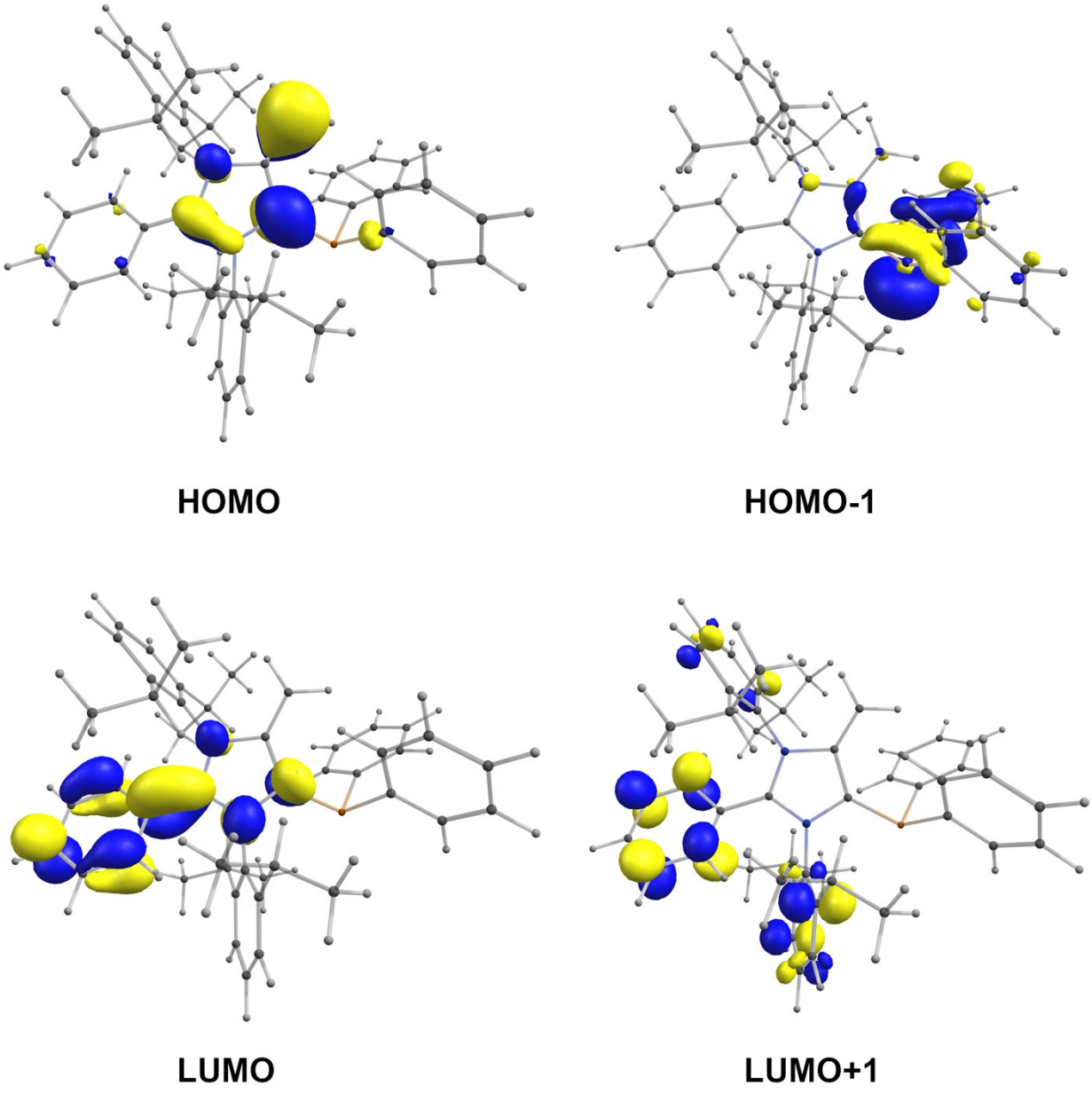

Figure S43. Frontier molecular orbitals of **4a** in PBE0-D3BJ/def2-TZVP calculation.

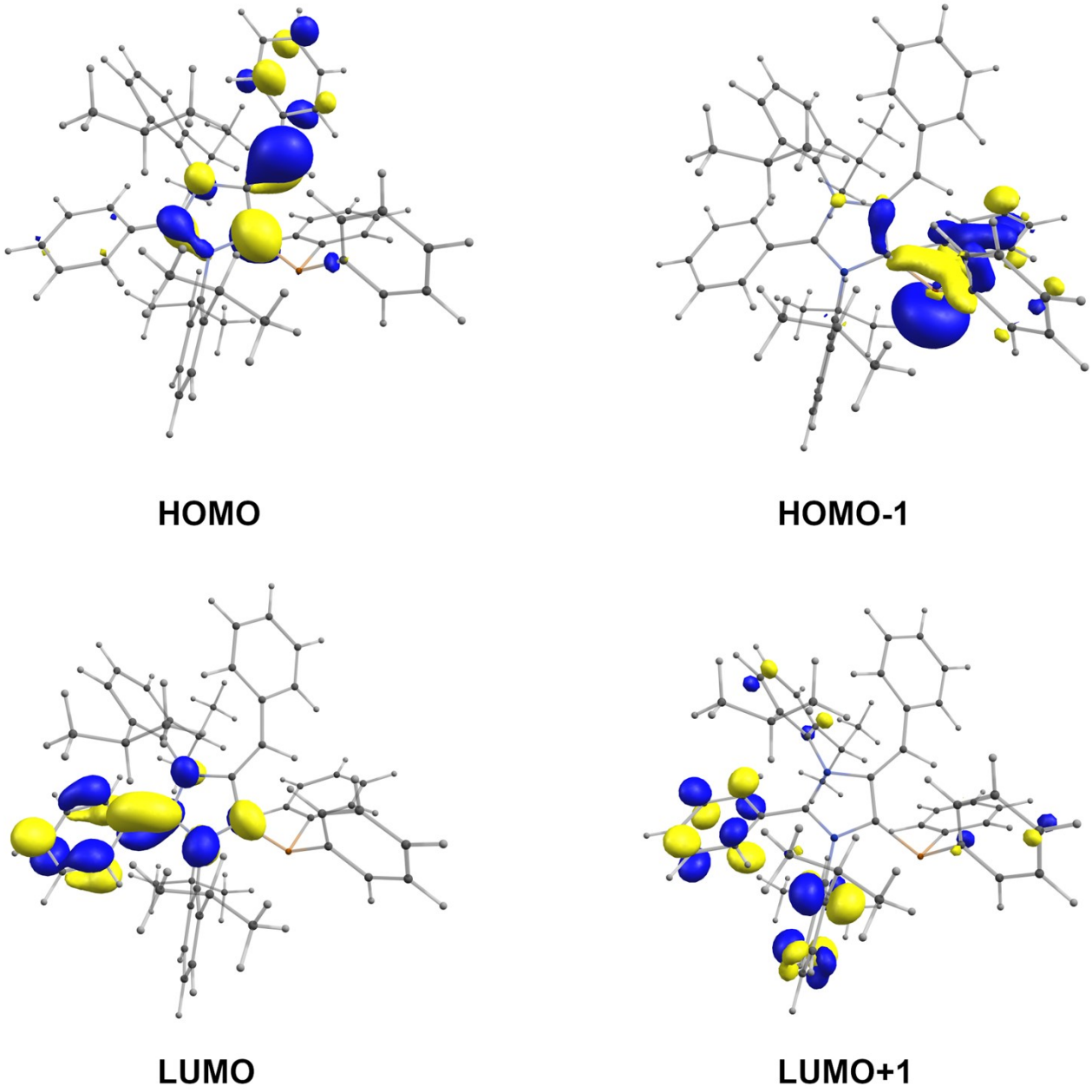

Figure S44. Frontier molecular orbitals of **4b** in PBE0-D3BJ/def2-TZVP calculation.

Table S3. Cartesian coordinates (Å) of atoms in **4a**, optimized at the PBE0-D3BJ/def2-TZVP level of theory.

P	0.3810703	5.5319418	6.9285202	C	1.0570892	7.9212674	8.1592434
N	1.8613641	3.4781037	5.8285677	C	1.8579174	0.5034138	7.7434785
N	1.6963721	1.7847580	7.1599754	C	0.7241577	-0.3054211	7.8906775
C	2.1605146	2.1874257	5.9409233	C	0.9032642	-1.5705887	8.4355634
C	1.1935677	3.9572340	6.9548712	C	2.1575975	-2.0064613	8.8305978
C	1.1479837	2.8721303	7.8861818	C	3.2546677	-1.1738983	8.7052678
C	0.7242717	2.7804537	9.1682961	C	3.1266832	0.1029253	8.1683522
C	2.7941372	1.3411651	4.9425404	C	-0.6491774	0.1546025	7.4515734
C	2.4681197	-0.0193617	4.8585454	C	-1.1042155	-0.5690260	6.1858625
C	3.0504567	-0.8337708	3.9043384	C	-1.6780809	-0.0015786	8.5655050
C	3.9755131	-0.3212034	3.0078986	C	4.3253219	1.0185729	8.0866087
C	4.3107932	1.0233068	3.0813577	C	4.7465860	1.4656695	9.4842792
C	3.7341726	1.8437931	4.0325238	C	5.4832419	0.3847096	7.3235386
C	2.1175415	4.2837875	4.6784890	H	1.0000774	4.7595358	1.5391649
C	1.2981364	4.1232216	3.5623492	H	1.7507993	-0.4480469	5.5409161
C	1.6119488	4.8633756	2.4277702	H	4.0202305	2.8833393	4.0630807
C	2.6866134	5.7334559	2.4220946	H	0.7708786	1.8442120	9.7037917
C	3.4554336	5.9021801	3.5620904	H	2.3137961	4.9311262	9.1249074
C	3.1846697	5.1866223	4.7217774	H	4.2800035	6.6046230	3.5517216
C	0.0903751	3.2166910	3.5717349	H	-1.2269649	4.5190040	2.4335108
C	0.1877391	2.1257508	2.5099396	H	0.0453969	2.7264378	4.5472445
C	-1.1881287	4.0360421	3.4133592	H	0.2900703	3.6386063	9.6559907
C	4.0350981	5.3727926	5.9600026	H	4.2284480	-1.5171386	9.0352781
C	5.3627740	4.6243596	5.8568129	H	0.0479175	-2.2262073	8.5511138
C	4.2720177	6.8468648	6.2677867	H	5.8715084	-0.4950834	7.8427892
C	-1.1862246	5.1195001	7.7801598	H	-0.5863393	1.2204346	7.2284768
C	-1.9563364	4.0787796	7.2611508	H	1.0950276	1.5312279	2.6301385
C	-3.1753584	3.7486369	7.8255972	H	5.0359434	1.4429356	2.3940689
C	-3.6542979	4.4598955	8.9177210	H	3.5476498	6.4011750	10.6740454
C	-2.8989883	5.4989993	9.4375361	H	4.0283974	1.9164104	7.5418258
C	-1.6732219	5.8268366	8.8747066	H	2.9190955	6.2987229	1.5268281
C	1.2520215	6.5412052	8.1815827	H	0.1950409	2.5542326	1.5043941
C	2.1571498	6.0037301	9.0949128	H	2.2772956	-2.9990986	9.2495315
C	2.8467506	6.8315952	9.9673533	H	2.7716278	-1.8801291	3.8632147
C	2.6379107	8.2039858	9.9448669	H	4.9220283	7.3165185	5.5250151
C	1.7376362	8.7481274	9.0408287	H	4.7545181	6.9493494	7.2418668

H	3.4831593	4.9544788	6.8041017	H	-1.3642597	0.5366609	9.4606600
H	6.3051490	1.0982989	7.2257853	H	3.9196798	1.9622914	9.9962138
H	-1.2514769	4.8154006	4.1753418	H	-1.5831821	3.5124616	6.4140746
H	0.3742060	8.3509850	7.4326902	H	-1.1577105	-1.6494592	6.3454497
H	5.1761595	0.0783616	6.3215521	H	-0.4294686	-0.3861906	5.3469548
H	-1.0844844	6.6290391	9.3041472	H	-1.8388929	-1.0510052	8.8261370
H	3.1790785	8.8482820	10.6283032	H	-2.6377730	0.4117144	8.2468920
H	-3.2594627	6.0563174	10.2949995	H	-2.0994329	-0.2248271	5.8929400
H	-4.6078248	4.2008974	9.3630363	H	5.0607297	0.6130697	10.0923256
H	1.5753480	9.8196649	9.0116474	H	5.9602480	4.7996256	6.7549167
H	4.4315185	-0.9612049	2.2621578	H	5.5857700	2.1635336	9.4235523
H	-0.6725758	1.4553300	2.5776487	H	5.2197587	3.5464568	5.7588653
H	3.3326959	7.4000075	6.3025713	H	5.9421078	4.9681326	4.9952150
H	-2.0664409	3.3917510	3.5029469	H	-3.7547135	2.9297958	7.4134080

Table S4. Cartesian coordinates (Å) of atoms in **4b**, optimized at the PBE0-D3BJ/def2-TZVP level of theory.

P	12.3181902	8.3200318	7.7563859	C	7.8647239	9.5681789	8.4269115
N	10.4954114	9.1549072	5.8812489	H	7.0453724	9.0086474	8.8630206
N	11.1610955	8.4333565	3.9490752	C	8.6649144	8.9647465	7.4632441
C	10.1188342	9.0269573	4.6133961	C	11.1584997	11.8183811	6.7847136
C	11.7647799	8.6374352	6.0951931	H	11.8131068	11.1221924	6.2564110
C	12.2544775	8.2091773	4.8212177	C	11.9894406	12.4642887	7.8882613
C	13.4943506	7.6745258	4.5852184	H	11.4365997	13.2574172	8.3980097
H	14.0362043	7.5440429	5.5137514	H	12.8904163	12.9101615	7.4621170
C	14.1756406	7.0604987	3.4626893	H	12.3015034	11.7298947	8.6317215
C	14.1285768	7.4684067	2.1219630	C	10.6902182	12.8698860	5.7806330
H	13.5461907	8.3328407	1.8406734	H	10.1957183	12.4212090	4.9169974
C	14.8325717	6.7956178	1.1364181	H	11.5457142	13.4417143	5.4128046
H	14.7586565	7.1400247	0.1103741	H	9.9908576	13.5718927	6.2432425
C	15.6304267	5.7046897	1.4465975	C	8.4209722	7.5306169	7.0604386
H	16.1783137	5.1819658	0.6714952	H	9.1449641	7.2734080	6.2838650
C	15.7270589	5.3072857	2.7753404	C	7.0261702	7.3308506	6.4764450
H	16.3534878	4.4643043	3.0467465	H	6.2543317	7.5285827	7.2247160
C	15.0191445	5.9715514	3.7578669	H	6.9033774	6.2988095	6.1390833
H	15.0858764	5.6369592	4.7881559	H	6.8498958	7.9916233	5.6261532
C	8.8183837	9.3772324	4.0553104	C	8.6695238	6.5961589	8.2418928
C	8.0981897	10.4850558	4.5222519	H	9.6695493	6.7425004	8.6548314
H	8.5115113	11.1171755	5.2925771	H	8.5738804	5.5537609	7.9280140
C	6.8491677	10.7881718	4.0134095	H	7.9453033	6.7726023	9.0413461
H	6.3191203	11.6517290	4.3975482	C	11.1368186	8.1528805	2.5565332
C	6.2817033	10.0042561	3.0196557	C	11.1132673	6.8179550	2.1429908
H	5.3030686	10.2446421	2.6219040	C	11.0493283	6.5751366	0.7755530
C	6.9865676	8.9107870	2.5404754	H	11.0443483	5.5543960	0.4161488
H	6.5610212	8.2835535	1.7660570	C	11.0126821	7.6171990	-0.1326076
C	8.2357919	8.5992389	3.0456856	H	10.9608050	7.4053776	-1.1944679
H	8.7535966	7.7371203	2.6554723	C	11.0617675	8.9304213	0.3050490
C	9.7027604	9.7241614	6.9260539	H	11.0508107	9.7337274	-0.4202221
C	10.0009210	11.0231673	7.3503016	C	11.1341818	9.2283765	1.6598030
C	9.1700493	11.5793011	8.3150247	C	11.1543611	5.6805291	3.1413029
H	9.3614394	12.5872219	8.6629393	H	11.7697416	6.0097459	3.9813111
C	8.1050975	10.8657152	8.8395363	C	9.7648449	5.3560782	3.6864596
H	7.4673453	11.3214923	9.5882217	H	9.3132141	6.2088165	4.1967613

H	9.8277314	4.5351290	4.4056288	C	15.3655294	10.3757059	9.5135551
H	9.0883358	5.0471688	2.8841539	H	15.7204082	10.5162987	10.5282121
C	11.8187114	4.4299695	2.5829543	C	15.9846402	11.0335047	8.4609888
H	11.1998122	3.9367744	1.8279009	H	16.8291052	11.6864915	8.6491042
H	11.9785841	3.7123160	3.3906569	C	15.5149343	10.8567660	7.1667417
H	12.7910963	4.6616578	2.1449239	H	15.9964898	11.3667368	6.3399477
C	11.2732968	10.6541569	2.1478707	C	14.4357499	10.0222161	6.9214634
H	10.6983888	10.7485273	3.0713503	H	14.0814733	9.8777846	5.9073147
C	10.7091183	11.6857367	1.1834106	C	13.0184506	6.6371468	7.5740306
H	11.2993023	11.7538770	0.2659412	C	12.2153084	5.6534792	6.9962634
H	10.7263021	12.6727648	1.6506706	H	11.2258844	5.9158004	6.6368355
H	9.6761156	11.4567923	0.9124121	C	12.6789258	4.3588319	6.8454062
C	12.7305813	10.9645999	2.4904458	H	12.0468015	3.6126894	6.3767680
H	13.1311636	10.2690850	3.2311236	C	13.9517303	4.0174576	7.2835009
H	12.8157485	11.9777648	2.8920273	H	14.3182499	3.0050426	7.1610527
H	13.3588302	10.9003441	1.5979076	C	14.7514170	4.9843897	7.8722909
C	13.8078182	9.3555397	7.9717249	H	15.7492839	4.7307512	8.2121247
C	14.2779427	9.5502324	9.2699545	C	14.2906667	6.2861981	8.0145995
H	13.7758352	9.0597547	10.0982585	H	14.9387392	7.0385726	8.4487731

Table S5. Cartesian coordinates (Å) of atoms in $(\mathbf{5})^{2+}$, optimized at the PBE0-D3BJ/dhf-TZVP level of theory.

Au	1.4911067	0.3546856	0.0949696	C	-1.8428297	-0.8145954	4.8424000
P	1.9069770	-0.8712311	-1.8135004	C	-2.4559916	-1.9139467	4.2215303
N	1.3685627	0.3927536	3.9361849	C	-3.5832795	-2.4319339	4.8436749
N	-0.6741742	-0.2530613	4.2266182	H	-4.0975066	-3.2743902	4.4025711
C	0.5600099	-0.3221495	4.7490590	C	-4.0680852	-1.8880391	6.0228953
C	0.6555345	0.8994183	2.8666871	H	-4.9496447	-2.3135554	6.4872496
C	-0.6548103	0.5208982	3.0663001	C	-3.4339606	-0.8118349	6.6076707
C	2.7374236	0.7370806	4.1902000	H	-3.8214253	-0.4000110	7.5316994
C	3.7429220	-0.1783894	3.8842537	C	-2.2994051	-0.2453756	6.0334982
C	5.0468937	0.1843863	4.2073780	C	-1.9319241	-2.5156805	2.9298395
H	5.8565328	-0.5057702	4.0036460	H	-1.7532130	-1.6903229	2.2299305
C	5.3265619	1.4099227	4.7829542	C	-0.5968480	-3.2448673	3.0816508
H	6.3492169	1.6691107	5.0297363	H	-0.6899483	-4.0937225	3.7635373
C	4.3072317	2.3124987	5.0361832	H	0.2043295	-2.6022265	3.4462926
H	4.5421390	3.2750087	5.4748105	H	-0.2876829	-3.6327964	2.1085140
C	2.9858217	1.9989248	4.7456106	C	-2.9262202	-3.4440109	2.2487661
C	3.4690115	-1.5155107	3.2364618	H	-2.5538785	-3.7057026	1.2563956
H	2.4107919	-1.5459553	2.9576417	H	-3.9060818	-2.9803467	2.1317388
C	3.7364856	-2.6672970	4.2027569	H	-3.0530172	-4.3760732	2.8049372
H	4.7914330	-2.7003246	4.4844011	C	-1.6241921	0.9126654	6.7396415
H	3.4892440	-3.6216650	3.7322515	H	-0.7231758	1.1866638	6.1860691
H	3.1491784	-2.5743043	5.1170680	C	-1.1964548	0.5122166	8.1513675
C	4.2862667	-1.6784491	1.9578675	H	-2.0663943	0.3467639	8.7904001
H	4.0569646	-0.8907376	1.2363333	H	-0.6050246	1.3104549	8.6045186
H	4.0762772	-2.6423102	1.4904075	H	-0.6005341	-0.4000788	8.1531817
H	5.3579476	-1.6463487	2.1626240	C	-2.5089195	2.1552028	6.8029789
C	1.8897512	3.0006869	5.0450496	H	-2.7227252	2.5639459	5.8147301
H	0.9356778	2.5775513	4.7207064	H	-2.0111504	2.9355210	7.3824984
C	1.7763900	3.2895260	6.5404633	H	-3.4627632	1.9408685	7.2894770
H	2.6998417	3.7209160	6.9322931	C	0.9625065	-1.0410670	5.9548600
H	1.5575220	2.3886360	7.1169769	C	0.3733590	-2.2663583	6.2806403
H	0.9735675	4.0070624	6.7241773	H	-0.3901489	-2.6913009	5.6485285
C	2.0978933	4.2942271	4.2613364	C	0.7642764	-2.9537320	7.4149762
H	3.0220853	4.7934033	4.5597618	H	0.2995955	-3.9040416	7.6470707
H	1.2742422	4.9857988	4.4506935	C	1.7428702	-2.4329475	8.2486123
H	2.1444646	4.1086433	3.1872875	H	2.0452225	-2.9726154	9.1377886

C	2.3292106	-1.2156874	7.9377061	C	-5.0468937	-0.1843863	-4.2073780
H	3.0889613	-0.7948001	8.5845656	H	-5.8565328	0.5057702	-4.0036460
C	1.9472327	-0.5247890	6.8021453	C	-5.3265619	-1.4099227	-4.7829542
H	2.4174815	0.4212907	6.5848509	H	-6.3492169	-1.6691107	-5.0297363
C	1.2921136	1.6066619	1.7680076	C	-4.3072317	-2.3124987	-5.0361832
H	2.2891871	1.9421614	2.0512735	H	-4.5421390	-3.2750087	-5.4748105
H	0.7008499	2.4645694	1.4512188	C	-2.9858217	-1.9989248	-4.7456106
C	3.5754137	-0.5649286	-2.4352888	C	-3.4690115	1.5155107	-3.2364618
C	4.3941756	0.3009096	-1.7143523	H	-2.4107919	1.5459553	-2.9576417
H	3.9997990	0.8052211	-0.8386999	C	-3.7364856	2.6672970	-4.2027569
C	5.7044570	0.5158952	-2.1116633	H	-4.7914330	2.7003246	-4.4844011
H	6.3359858	1.1882571	-1.5434528	H	-3.4892440	3.6216650	-3.7322515
C	6.2034874	-0.1313201	-3.2305262	H	-3.1491784	2.5743043	-5.1170680
H	7.2271534	0.0368958	-3.5429864	C	-4.2862667	1.6784491	-1.9578675
C	5.3954280	-1.0059025	-3.9455986	H	-4.0569646	0.8907376	-1.2363333
H	5.7855803	-1.5204718	-4.8152737	H	-4.0762772	2.6423102	-1.4904075
C	4.0919149	-1.2292238	-3.5442206	H	-5.3579476	1.6463487	-2.1626240
H	3.4781436	-1.9269096	-4.0950109	C	-1.8897512	-3.0006869	-5.0450496
C	1.7719683	-2.6679306	-1.6318900	H	-0.9356778	-2.5775513	-4.7207064
C	1.6039516	-3.5125415	-2.7268421	C	-1.7763900	-3.2895260	-6.5404633
H	1.5057805	-3.0995606	-3.7244832	H	-2.6998417	-3.7209160	-6.9322931
C	1.5293447	-4.8822162	-2.5411629	H	-1.5575220	-2.3886360	-7.1169769
H	1.3997791	-5.5364008	-3.3949924	H	-0.9735675	-4.0070624	-6.7241773
C	1.6164237	-5.4174794	-1.2625623	C	-2.0978933	-4.2942271	-4.2613364
H	1.5563700	-6.4897702	-1.1204403	H	-3.0220853	-4.7934033	-4.5597618
C	1.7696704	-4.5792372	-0.1683789	H	-1.2742422	-4.9857988	-4.4506935
H	1.8275187	-4.9949706	0.8307560	H	-2.1444646	-4.1086433	-3.1872875
C	1.8428845	-3.2072190	-0.3513859	C	1.8428297	0.8145954	-4.8424000
H	1.9400691	-2.5440252	0.5005421	C	2.4559916	1.9139467	-4.2215303
Au	-1.4911067	-0.3546856	-0.0949696	C	3.5832795	2.4319339	-4.8436749
P	-1.9069770	0.8712311	1.8135004	H	4.0975066	3.2743902	-4.4025711
N	-1.3685627	-0.3927536	-3.9361849	C	4.0680852	1.8880391	-6.0228953
N	0.6741742	0.2530613	-4.2266182	H	4.9496447	2.3135554	-6.4872496
C	-0.5600099	0.3221495	-4.7490590	C	3.4339606	0.8118349	-6.6076707
C	-0.6555345	-0.8994183	-2.8666871	H	3.8214253	0.4000110	-7.5316994
C	0.6548103	-0.5208982	-3.0663001	C	2.2994051	0.2453756	-6.0334982
C	-2.7374236	-0.7370806	-4.1902000	C	1.9319241	2.5156805	-2.9298395
C	-3.7429220	0.1783894	-3.8842537	H	1.7532130	1.6903229	-2.2299305

C	0.5968480	3.2448673	-3.0816508
H	0.6899483	4.0937225	-3.7635373
H	-0.2043295	2.6022265	-3.4462926
H	0.2876829	3.6327964	-2.1085140
C	2.9262202	3.4440109	-2.2487661
H	2.5538785	3.7057026	-1.2563956
H	3.9060818	2.9803467	-2.1317388
H	3.0530172	4.3760732	-2.8049372
C	1.6241921	-0.9126654	-6.7396415
H	0.7231758	-1.1866638	-6.1860691
C	1.1964548	-0.5122166	-8.1513675
H	2.0663943	-0.3467639	-8.7904001
H	0.6050246	-1.3104549	-8.6045186
H	0.6005341	0.4000788	-8.1531817
C	2.5089195	-2.1552028	-6.8029789
H	2.7227252	-2.5639459	-5.8147301
H	2.0111504	-2.9355210	-7.3824984
H	3.4627632	-1.9408685	-7.2894770
C	-0.9625065	1.0410670	-5.9548600
C	-0.3733590	2.2663583	-6.2806403
H	0.3901489	2.6913009	-5.6485285
C	-0.7642764	2.9537320	-7.4149762
H	-0.2995955	3.9040416	-7.6470707
C	-1.7428702	2.4329475	-8.2486123
H	-2.0452225	2.9726154	-9.1377886
C	-2.3292106	1.2156874	-7.9377061
H	-3.0889613	0.7948001	-8.5845656
C	-1.9472327	0.5247890	-6.8021453
H	-2.4174815	-0.4212907	-6.5848509
C	-1.2921136	-1.6066619	-1.7680076
H	-2.2891871	-1.9421614	-2.0512735
H	-0.7008499	-2.4645694	-1.4512188
C	-3.5754137	0.5649286	2.4352888
C	-4.3941756	-0.3009096	1.7143523
H	-3.9997990	-0.8052211	0.8386999
C	-5.7044570	-0.5158952	2.1116633
H	-6.3359858	-1.1882571	1.5434528
C	-6.2034874	0.1313201	3.2305262
H	-7.2271534	-0.0368958	3.5429864
C	-5.3954280	1.0059025	3.9455986
H	-5.7855803	1.5204718	4.8152737
C	-4.0919149	1.2292238	3.5442206
H	-3.4781436	1.9269096	4.0950109
C	-1.7719683	2.6679306	1.6318900
C	-1.6039516	3.5125415	2.7268421
H	-1.5057805	3.0995606	3.7244832
C	-1.5293447	4.8822162	2.5411629
H	-1.3997791	5.5364008	3.3949924
C	-1.6164237	5.4174794	1.2625623
H	-1.5563700	6.4897702	1.1204403
C	-1.7696704	4.5792372	0.1683789
H	-1.8275187	4.9949706	-0.8307560
C	-1.8428845	3.2072190	0.3513859
H	-1.9400691	2.5440252	-0.5005421

Table S6. TD-DFT absorption spectrum (vertical energy differences) of **4a**, wavelengths in nm, oscillator strengths via transition electric dipole moments and assignments.

600.3	0.214636262	94% HOMO → LUMO
480.3	0.011725976	87% HOMO → LUMO+1
462.0	0.006595443	88% HOMO → LUMO+2
448.4	0.026267124	93% HOMO → LUMO+3
442.2	0.004914607	16% HOMO → LUMO+4, 61% HOMO → LUMO+5, 19% HOMO → LUMO+6
425.4	0.020405467	72% HOMO → LUMO+4, 21% HOMO → LUMO+5
421.2	0.014269026	14% HOMO → LUMO+5, 79% HOMO → LUMO+6
405.7	0.010372680	87% HOMO → LUMO+7, 10% HOMO → LUMO+8
402.4	0.002201747	81% HOMO → LUMO+8
395.5	0.003137635	92% HOMO → LUMO+9
359.5	0.025697452	98% HOMO-1 → LUMO
310.1	0.044621077	95% HOMO → LUMO+10
302.6	0.001564499	94% HOMO → LUMO+11
285.4	0.065071493	59% HOMO-1 → LUMO+1, 31% HOMO-1 → LUMO+2
274.7	0.020384318	79% HOMO → LUMO+12, 12% HOMO → LUMO+13

Table S7. TD-DFT absorption spectrum (vertical energy differences) of **4b**, wavelengths in nm, oscillator strengths via transition electric dipole moments and assignments.

617.0	0.204737019	96% HOMO → LUMO
487.4	0.022177822	89% HOMO → LUMO+1
461.7	0.017895441	87% HOMO → LUMO+2
464.5	0.031290903	84% HOMO → LUMO+3
460.0	0.002163580	81% HOMO → LUMO+4, 15% HOMO → LUMO+5
424.9	0.032509538	39% HOMO → LUMO+5, 50% HOMO → LUMO+6
434.9	0.066358887	41% HOMO → LUMO+5, 45% HOMO → LUMO+6
410.9	0.008798134	97% HOMO → LUMO+7
394.6	0.004522373	39% HOMO → LUMO+8, 57% HOMO → LUMO+9
392.2	0.007067614	55% HOMO → LUMO+8, 41% HOMO → LUMO+9
347.0	0.262991470	64% HOMO → LUMO+10, 30% HOMO → LUMO+11
349.7	0.137823757	27% HOMO → LUMO+10, 67% HOMO → LUMO+11
355.8	0.032598370	97% HOMO-1 → LUMO
317.3	0.002068154	96% HOMO → LUMO+12
289.3	0.001000619	94% HOMO → LUMO+13

Table S8. Cartesian coordinates (Å) of atoms in **4a**, optimized at the BLYP/def2-TZVPP level of theory.

P	-1.2378237	2.5427554	0.4148774	C	0.2849359	-2.5876618	1.1533273
N	0.2300764	0.4644290	-0.7921528	C	-0.8247677	-3.4673688	1.2773419
N	0.0849276	-1.2902522	0.5420858	C	-0.6070155	-4.7127744	1.8881369
C	0.5344099	-0.8590882	-0.7030370	C	0.6505563	-5.0762443	2.3719852
C	-0.4227375	0.9297040	0.3776566	C	1.7175417	-4.1851553	2.2694279
C	-0.4605385	-0.1864076	1.2964133	C	1.5607260	-2.9215807	1.6743013
C	-0.8638195	-0.2804676	2.5985396	C	-2.2354256	-3.1184772	0.7806978
C	1.1471061	-1.7069693	-1.7341816	C	-2.7283006	-4.0854454	-0.3269139
C	0.7793482	-3.0726572	-1.8557446	C	-3.2578140	-3.0822780	1.9452985
C	1.3438572	-3.8958439	-2.8312827	C	2.7519913	-1.9577936	1.6473798
C	2.2985390	-3.3961641	-3.7244656	C	3.1142863	-1.4827430	3.0782605
C	2.6781945	-2.0517281	-3.6208134	C	3.9853261	-2.5635840	0.9332708
C	2.1197599	-1.2232881	-2.6471012	H	-0.7279349	1.9633534	-5.0656093
C	0.4912982	1.3072630	-1.9579375	H	0.0390601	-3.4943235	-1.1895490
C	-0.3882782	1.2338735	-3.0643788	H	2.4493421	-0.1948591	-2.5967992
C	-0.0740788	2.0037149	-4.1972157	H	-0.8158792	-1.2157058	3.1416222
C	1.0531282	2.8222193	-4.2286037	H	0.6885183	1.9867514	2.7448463
C	1.8839925	2.9039531	-3.1108123	H	2.7512648	3.5595666	-3.1404270
C	1.6260756	2.1597523	-1.9479077	H	-2.9412687	1.7616608	-4.2264759
C	-1.6646171	0.3858487	-3.0762598	H	-1.7465044	-0.1163612	-2.1059072
C	-1.6276011	-0.7146758	-4.1663865	H	-1.2817659	0.5797797	3.1039718
C	-2.9236425	1.2750777	-3.2429283	H	2.6891875	-4.4698020	2.6677352
C	2.5783674	2.3041105	-0.7506888	H	-1.4369836	-5.4092751	1.9882121
C	3.9746412	1.6845996	-1.0202265	H	4.3794258	-3.4334833	1.4738720
C	2.7396972	3.7862996	-0.3285534	H	-2.2002457	-2.1118796	0.3511824
C	-2.8769877	2.1799572	1.2342396	H	-0.7595926	-1.3717605	-4.0489594
C	-3.7354586	1.2414953	0.6270148	H	3.4243673	-1.6407641	-4.2984107
C	-5.0227267	1.0134632	1.1208368	H	1.8428419	3.5068191	4.3183925
C	-5.4902582	1.7280719	2.2314826	H	2.4558611	-1.0677979	1.0831272
C	-4.6509522	2.6647967	2.8428777	H	1.2790030	3.4060659	-5.1192076
C	-3.3577680	2.8877538	2.3515846	H	-1.5875334	-0.2774650	-5.1722519
C	-0.3706644	3.5663820	1.7096705	H	0.7951305	-6.0493415	2.8382176
C	0.5141263	3.0577016	2.6798046	H	1.0279380	-4.9356398	-2.8929936
C	1.1644356	3.9187958	3.5727242	H	3.2756755	4.3652203	-1.0914155
C	0.9399781	5.3003624	3.5178510	H	3.3179093	3.8490460	0.6013244
C	0.0664963	5.8198876	2.5549260	H	2.1375572	1.7717012	0.0986000
C	-0.5737273	4.9605618	1.6540016	H	4.7906099	-1.8199777	0.8748809

H	-2.9642161	2.0583705	-2.4782940	H	2.2535998	-1.0094622	3.5643715
H	-1.2329714	5.3765796	0.8923903	H	-3.3912534	0.6785680	-0.2382234
H	3.7415186	-2.8822051	-0.0865673	H	-2.8013628	-5.1163071	0.0423303
H	-2.7221522	3.6141213	2.8509470	H	-2.0650719	-4.0883714	-1.1994808
H	1.4454658	5.9660632	4.2151644	H	-3.3780080	-4.0726270	2.4038063
H	-4.9970483	3.2234385	3.7113021	H	-4.2403625	-2.7661836	1.5722692
H	-6.4935287	1.5535282	2.6155729	H	-3.7272270	-3.7852360	-0.6689451
H	-0.1081317	6.8930618	2.4963827	H	3.4431151	-2.3210100	3.7062284
H	2.7390222	-4.0396564	-4.4829079	H	4.6222137	1.8322454	-0.1463949
H	-2.5334303	-1.3321293	-4.1097373	H	3.9331742	-0.7523229	3.0394616
H	1.7713196	4.2648786	-0.1557280	H	3.9221625	0.6083715	-1.2161608
H	-3.8320562	0.6644887	-3.1597202	H	4.4626284	2.1615497	-1.8801454
H	-2.9489931	-2.3737063	2.7198114	H	-5.6632062	0.2782429	0.6358659

Table S9. Cartesian coordinates (Å) of atoms in **4a**-H^+, optimized at the BLYP/def2-TZVPP level of theory.

P	-1.2543220	2.6003447	0.3933664	C	2.5453404	2.4089791	-0.8353244
N	0.2288938	0.4777508	-0.8324179	C	3.9737554	1.8405515	-1.0446262
N	0.0775564	-1.2486983	0.5241829	C	2.6395653	3.9207146	-0.5016756
C	0.5288649	-0.8494723	-0.7112065	C	-2.8399563	2.2043811	1.2902777
C	-0.4330412	0.9315516	0.3396503	C	-3.8261531	1.4849911	0.5841638
C	-0.4975369	-0.1558322	1.1888135	C	-5.0796954	1.2400146	1.1536043
C	1.1935159	-1.7131177	-1.7103795	C	-5.3809891	1.7316134	2.4303783
C	0.7616197	-3.0435131	-1.9070389	C	-4.4175324	2.4638751	3.1319292
C	1.3803027	-3.8666187	-2.8497932	C	-3.1558292	2.6974188	2.5694261
C	2.4476313	-3.3865497	-3.6165195	C	-0.2902080	3.5769553	1.6389316
C	2.8865713	-2.0707707	-3.4334487	C	0.6736468	3.0698811	2.5285245
C	2.2674634	-1.2413104	-2.4960955	C	1.3446501	3.9215170	3.4152759
C	0.4938565	1.2955850	-2.0283043	C	1.0572181	5.2911091	3.4318100
C	-0.3743377	1.1580451	-3.1397382	C	0.1032016	5.8096388	2.5475631
C	-0.0560397	1.8847150	-4.2986875	C	-0.5560206	4.9624100	1.6511578
C	1.0621274	2.7141094	-4.3528343	C	0.2504584	-2.5732706	1.1352029
C	1.8769378	2.8569712	-3.2308605	C	-0.8638319	-3.4504519	1.2041095
C	1.6169777	2.1641897	-2.0364775	C	-0.6480760	-4.7088753	1.7898309
C	-1.6452461	0.3002367	-3.1385863	C	0.5990059	-5.0750240	2.2957284
C	-1.5959955	-0.8247600	-4.2031493	C	1.6645859	-4.1781304	2.2417467
C	-2.9072946	1.1796809	-3.3388682	C	1.5216258	-2.9040314	1.6671428

C	-2.2748399	-3.1050099	0.6999512	H	-1.2810829	5.3810914	0.9542484
C	-2.7365708	-4.0205185	-0.4642174	H	3.7396625	-2.8503132	-0.0446599
C	-3.3175390	-3.1697197	1.8479967	H	-2.4231414	3.2694972	3.1323550
C	2.7177722	-1.9440040	1.6827207	H	1.5771969	5.9504136	4.1233111
C	3.0595168	-1.5036894	3.1305107	H	-4.6440628	2.8572882	4.1209528
C	3.9623654	-2.5456940	0.9838415	H	-6.3610169	1.5546872	2.8679690
H	-0.6991650	1.8008981	-5.1712294	H	-0.1205140	6.8743236	2.5466624
H	-0.0664945	-3.4382097	-1.3338580	H	2.9301638	-4.0294344	-4.3491256
H	2.6278942	-0.2289026	-2.3774524	H	-2.4961394	-1.4482287	-4.1347877
H	0.9156630	2.0100136	2.5305535	H	1.6513738	4.3768964	-0.3930216
H	2.7331187	3.5249077	-3.2798551	H	-3.8135855	0.5688881	-3.2413383
H	-2.9219284	1.6322210	-4.3375015	H	-3.0192591	-2.5688962	2.7134579
H	-1.7387341	-0.1815322	-2.1576061	H	2.1998648	-1.0377744	3.6272750
H	2.6259267	-4.4684752	2.6582126	H	-3.6224202	1.1257751	-0.4227733
H	-1.4739413	-5.4130794	1.8540458	H	-2.7677202	-5.0723415	-0.1564642
H	4.3417308	-3.4230679	1.5207839	H	-2.0837551	-3.9463491	-1.3405868
H	-2.2667567	-2.0763214	0.3200885	H	-3.4614798	-4.1998041	2.1949557
H	-0.7219141	-1.4713848	-4.0728959	H	-4.2880632	-2.8011412	1.4952108
H	3.7165626	-1.6839198	-4.0201800	H	-3.7479486	-3.7382673	-0.7811085
H	2.0892133	3.5126970	4.0957058	H	3.3753836	-2.3567798	3.7428844
H	2.4452968	-1.0378715	1.1297041	H	4.6029430	2.0923228	-0.1821243
H	1.2910185	3.2614805	-5.2647778	H	3.8815768	-0.7774909	3.1209442
H	-1.5592212	-0.4103126	-5.2176337	H	3.9834716	0.7505094	-1.1509421
H	0.7368382	-6.0571231	2.7429760	H	4.4463555	2.2710191	-1.9358236
H	1.0217087	-4.8842635	-2.9861830	H	-5.8276957	0.6836599	0.5920257
H	3.1809059	4.4676221	-1.2825744	C	-1.0432417	-0.2640416	2.5773492
H	3.1851215	4.0626386	0.4383614	H	-2.1040841	-0.5406369	2.5711417
H	2.1190838	1.9073961	0.0408554	H	-0.5012912	-1.0200665	3.1536108
H	4.7706427	-1.8049200	0.9534403	H	-0.9629259	0.6938909	3.0935869
H	-2.9551064	1.9926435	-2.6057531				

Table S10. Cartesian coordinates (Å) of atoms in **4b**, optimized at the BLYP/def2-TZVPP level of theory.

P	0.9915036	-0.2478341	2.7435187	C	0.8353727	-0.4066612	-0.2451430
N	-0.9034265	0.5983830	0.8723757	C	2.0801613	-0.9840000	-0.4739386
N	-0.2689553	-0.1107043	-1.1280643	H	2.5579924	-1.1897008	0.4805423
C	-1.3038202	0.5128078	-0.4232382	C	2.9467694	-1.3765866	-1.5752072
C	0.3689945	0.0220126	1.0568255	C	2.8847383	-0.9588123	-2.9321733

H	2.1006497	-0.2888880	-3.2572140
C	3.8293121	-1.3741089	-3.8755042
H	3.7374588	-1.0208463	-4.9022350
C	4.8870551	-2.2200838	-3.5214105
H	5.6189646	-2.5381274	-4.2609686
C	4.9852916	-2.6383426	-2.1850846
H	5.8009862	-3.2912215	-1.8760600
C	4.0467291	-2.2266922	-1.2424420
H	4.1449346	-2.5675384	-0.2125573
C	-2.6164661	0.9059110	-0.9639537
C	-3.2977326	2.0696892	-0.5247331
H	-2.8449176	2.7189688	0.2114528
C	-4.5531088	2.4129568	-1.0281106
H	-5.0379605	3.3175939	-0.6658848
C	-5.1799881	1.6170123	-1.9948397
H	-6.1568016	1.8892189	-2.3886118
C	-4.5236278	0.4664434	-2.4471389
H	-4.9906649	-0.1722356	-3.1945313
C	-3.2691592	0.1158430	-1.9455045
H	-2.8004206	-0.7853141	-2.3158555
C	-1.6830217	1.2143060	1.9498699
C	-1.3863519	2.5495628	2.3298346
C	-2.1979759	3.1335947	3.3161062
H	-2.0035023	4.1579403	3.6252377
C	-3.2461600	2.4300968	3.9095975
H	-3.8626519	2.9085291	4.6685583
C	-3.4930685	1.1098446	3.5393987
H	-4.2996847	0.5628077	4.0222253
C	-2.7187110	0.4669819	2.5586926
C	-0.2417970	3.3816041	1.7293383
H	0.3625710	2.7226846	1.0969948
C	0.6920146	3.9415070	2.8323160
H	0.1840034	4.7007761	3.4403620
H	1.5678269	4.4164669	2.3739921
H	1.0479397	3.1522614	3.5005456
C	-0.7496856	4.5473824	0.8407712
H	-1.3229874	4.1950476	-0.0230931
H	0.1034956	5.1234755	0.4602421
H	-1.3868660	5.2351251	1.4117667
C	-3.0172369	-0.9986734	2.2263911
H	-2.3095032	-1.3236843	1.4554928
C	-4.4447900	-1.1913512	1.6556547
H	-5.2092009	-0.9263390	2.3971477
H	-4.6013125	-2.2423778	1.3806144
H	-4.6112423	-0.5774198	0.7646480
C	-2.8013594	-1.9051717	3.4657611
H	-1.7965183	-1.7812732	3.8834107
H	-2.9326529	-2.9596149	3.1909266
H	-3.5266543	-1.6763114	4.2568889
C	-0.3163136	-0.3849196	-2.5522601
C	-0.4629551	-1.7282440	-2.9906237
C	-0.5392551	-1.9557758	-4.3743498
H	-0.6503156	-2.9742425	-4.7397569
C	-0.4747939	-0.9069113	-5.2910662
H	-0.5381339	-1.1109895	-6.3584556
C	-0.3177250	0.4025572	-4.8381641
H	-0.2521725	1.2114941	-5.5625561
C	-0.2286049	0.6976156	-3.4677986
C	-0.5626757	-2.9289183	-2.0363738
H	-0.3577083	-2.5742807	-1.0219268
C	-1.9815506	-3.5574150	-2.0370837
H	-2.7518808	-2.8486956	-1.7128532
H	-2.0102410	-4.4151382	-1.3525833
H	-2.2568338	-3.9204133	-3.0358253
C	0.4924862	-4.0178516	-2.3559004
H	0.3002267	-4.4933668	-3.3264069
H	0.4555600	-4.8036357	-1.5908407
H	1.5046619	-3.6050391	-2.3708244
C	-0.0035695	2.1549229	-3.0388179
H	-0.0675379	2.2025990	-1.9471610
C	-1.0846691	3.1086389	-3.6057555
H	-1.0259911	3.1785908	-4.6992872
H	-0.9402805	4.1201454	-3.2048858
H	-2.0947657	2.7785913	-3.3417114
C	1.4128384	2.6530863	-3.4280306
H	2.1982485	2.0373258	-2.9769149

H	1.5535818	3.6873348	-3.0876970	H	2.9699322	1.1633792	0.8423406
H	1.5557272	2.6370805	-4.5161217	C	1.6124677	-2.0092784	2.7276467
C	2.5585390	0.7418289	2.9263890	C	0.7337759	-3.0334161	2.3201911
C	2.9943611	0.9766527	4.2473518	H	-0.2434419	-2.7767425	1.9165698
H	2.4303462	0.5596745	5.0813572	C	1.0995438	-4.3790544	2.4156239
C	4.1340118	1.7475410	4.5050441	H	0.4052573	-5.1500818	2.0852939
H	4.4551259	1.9109408	5.5324858	C	2.3509762	-4.7364740	2.9335592
C	4.8476087	2.3186514	3.4446462	H	2.6357433	-5.7839704	3.0102270
H	5.7304132	2.9242030	3.6414070	C	3.2316613	-3.7311518	3.3459094
C	4.4134471	2.1110498	2.1294126	H	4.2109212	-3.9923110	3.7441572
H	4.9620605	2.5515121	1.2984132	C	2.8687544	-2.3820044	3.2424933
C	3.2816473	1.3280333	1.8700013	H	3.5767100	-1.6200482	3.5575100

Table S11. Cartesian coordinates (Å) of atoms in **4b**-H^+, optimized at the BLYP/def2-TZVPP level of theory.

P	0.9658829	-0.5539389	2.6590750	C	-4.4204611	2.4792983	-1.1323437
N	-0.8512943	0.5176630	0.7766841	H	-4.8002218	3.4588960	-0.8514184
N	-0.3875833	-0.3673354	-1.1834544	C	-5.1709236	1.6460390	-1.9687452
C	-1.3320469	0.3502546	-0.4898255	H	-6.1404626	1.9695569	-2.3404519
C	0.4038902	-0.1374337	0.9173911	C	-4.6617680	0.3915150	-2.3203399
C	0.7049408	-0.6439701	-0.3361684	H	-5.2351816	-0.2721052	-2.9634826
C	1.9362680	-1.3557795	-0.8145012	C	-3.4149555	-0.0242966	-1.8483488
H	1.6482205	-2.1766410	-1.4783984	H	-3.0509916	-1.0010805	-2.1364740
C	3.0061362	-0.5197012	-1.5346048	C	-1.5053258	1.2877368	1.8453144
C	3.1698323	0.8598550	-1.3397953	C	-1.0531872	2.6117036	2.0951387
H	2.4718051	1.4081261	-0.7114174	C	-1.7411718	3.3426762	3.0780492
C	4.2269861	1.5505432	-1.9488213	H	-1.4337374	4.3627449	3.2931026
H	4.3364152	2.6207142	-1.7844703	C	-2.8079971	2.7907857	3.7867925
C	5.1329838	0.8716794	-2.7690447	H	-3.3226243	3.3819628	4.5414117
H	5.9530091	1.4070259	-3.2423479	C	-3.2058153	1.4785572	3.5384715
C	4.9704152	-0.5031160	-2.9832025	H	-4.0256672	1.0534999	4.1122343
H	5.6638798	-1.0416105	-3.6257687	C	-2.5685770	0.6907089	2.5659311
C	3.9166013	-1.1896976	-2.3722606	C	0.1182528	3.2869912	1.3592947
H	3.8043067	-2.2596969	-2.5433470	H	0.6659287	2.5155931	0.8056961
C	-2.6450200	0.8056565	-1.0026610	C	1.1218263	3.9381732	2.3444976
C	-3.1770278	2.0657219	-0.6499205	H	0.6878900	4.8149160	2.8395957
H	-2.6234163	2.7331656	-0.0044139	H	2.0087503	4.2797897	1.7978276

H	1.4478509	3.2372991	3.1177386
C	-0.3519308	4.3503065	0.3306786
H	-0.9475956	3.9193955	-0.4808824
H	0.5192797	4.8380962	-0.1235854
H	-0.9533623	5.1296172	0.8149333
C	-3.0402610	-0.7539127	2.3627826
H	-2.4303032	-1.2080838	1.5724550
C	-4.5191323	-0.8253282	1.9041700
H	-5.1938191	-0.4377310	2.6769363
H	-4.8032657	-1.8673932	1.7122599
H	-4.6913703	-0.2500944	0.9886143
C	-2.8306686	-1.5993125	3.6460482
H	-1.7894770	-1.5644144	3.9840180
H	-3.1003110	-2.6458205	3.4559819
H	-3.4642225	-1.2407738	4.4661851
C	-0.5222005	-0.8800883	-2.5580915
C	-0.8280248	-2.2597131	-2.7307880
C	-0.9936210	-2.7187960	-4.0473676
H	-1.2331381	-3.7654351	-4.2177602
C	-0.8638827	-1.8641313	-5.1414240
H	-1.0034772	-2.2463501	-6.1504196
C	-0.5469340	-0.5234345	-4.9405190
H	-0.4367951	0.1306679	-5.8015172
C	-0.3605678	0.0069937	-3.6517839
C	-1.0037475	-3.2713383	-1.5839018
H	-0.7379870	-2.7830083	-0.6398478
C	-2.4703995	-3.7602374	-1.4484104
H	-3.1640432	-2.9423746	-1.2254415
H	-2.5469757	-4.4907408	-0.6337071
H	-2.8128392	-4.2512079	-2.3672409
C	-0.0658129	-4.4964376	-1.7458227
H	-0.3471648	-5.1046820	-2.6131999
H	-0.1304248	-5.1368379	-0.8585145
H	0.9823323	-4.2037538	-1.8719260
C	-0.0015474	1.4924632	-3.5248075
H	0.1948201	1.7123177	-2.4687111
C	-1.1622610	2.4092555	-3.9923292
H	-1.3656029	2.2701090	-5.0610828
H	-0.8912860	3.4616306	-3.8425119
H	-2.0898556	2.2144534	-3.4460727
C	1.2876616	1.8345472	-4.3146921
H	2.1219524	1.1854983	-4.0345489
H	1.5812058	2.8726415	-4.1167580
H	1.1289973	1.7401474	-5.3955318
C	2.4151264	0.5002043	3.1107947
C	2.4495913	0.8925006	4.4652570
H	1.6320120	0.6133106	5.1278266
C	3.5232615	1.6370952	4.9675094
H	3.5362782	1.9259470	6.0163242
C	4.5706499	2.0142696	4.1197018
H	5.4033533	2.5978353	4.5065513
C	4.5440834	1.6367367	2.7709537
H	5.3581761	1.9229612	2.1079069
C	3.4785965	0.8799304	2.2706134
H	3.4897486	0.5838630	1.2263001
C	1.6876121	-2.2560015	2.4674703
C	0.7779149	-3.3243354	2.3111928
H	-0.2881195	-3.1208573	2.2227736
C	1.2232995	-4.6488291	2.2963497
H	0.5058323	-5.4588584	2.1804131
C	2.5852510	-4.9354815	2.4613645
H	2.9305324	-5.9670184	2.4651225
C	3.4938786	-3.8877683	2.6404682
H	4.5515764	-4.1004046	2.7823785
C	3.0514552	-2.5579743	2.6436991
H	3.7736958	-1.7603721	2.7927469
H	2.3976384	-1.8259081	0.0621979

References

1. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179.
2. a) N. K. T. Ho, B. Neumann, H.-G. Stammler, V. H. Menezes da Silva, D. G. Watanabe, A. A. C. Braga, R. S. Ghadwal, *Dalton Trans.* **2017**, *46*, 12027–12031; b) D. Rottschäfer, F. Ebeler, T. Strothmann, B. Neumann, H.-G. Stammler, A. Mix, R. S. Ghadwal, *Chem. Eur. J.* **2018**, *24*, 3716–3720.
3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst*. **2009**, *42*, 339–341.
4. G. M. Sheldrick, *Acta Cryst. A*, **2015**, *71*, 3–8.
5. G. M. Sheldrick, *Acta Cryst. A*, **2008**, *64*, 112–122.
6. G. M. Sheldrick, *Acta Cryst. C*, **2015**, *71*, 3–8.
7. S. G. Balasubramani, G. P. Chen, S. Coriani, M. Diedenhofen, M. S. Frank, Y. J. Franzke, F. Furche, R. Grotjahn, M. E. Harding, C. Hättig, A. Hellweg, B. Helmich-Paris, C. Holzer, U. Huniar, M. Kaupp, A. Marefat Khah, S. Karbalaei Khani, T. Müller, F. Mack, B. D. Nguyen, S. M. Parker, E. Perlt, D. Rappoport, K. Reiter, S. Roy, M. Rückert, G. Schmitz, M. Sierka, E. Tapavicza, D. P. Tew, C. van Wüllen, V. K. Voora, F. Weigend, A. Wodyński, J. M. Yu, *J. Chem. Phys.* **2020**, *152*, 184107.
8. C. A. Bauer, A. Hansen, S. Grimme, *Chem. Eur. J.* **2017**, *23*, 6150–6164.
9. F. Neese, *Wiley Interdiscip. Rev. Comput. Mol. Sci*. **2012**, *2*, 73–78.
10. (a) R. Schuldt, J. Kästner, S. Naumann, *J. Org. Chem.* **2019**, *84*, 2209–2218; (b) M. M. Hansmann, P. W. Antoni, H. Pesch, *Angew. Chem. Int. Ed.* **2020**, *59*, 5782–5787.