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Anionic *N*-heterocyclic carbenes featuring weakly coordinating perfluoroalkylphosphorane moieties

Ludwig Zapf,[a] Udo Radius[a]* and Maik Finze[a]*

[a]*Institute of Inorganic Chemistry, Institute for Sustainable Chemistry & Catalysis with Boron (ICB), Julius-Maximilians Universität Würzburg, Am Hubland, 97074 Würzburg, Germany. E-mail: u.radius@uni-wuerzburg.de; maik.finze@uni-wuerzburg.de; Web: https://www.ak-radius.de; https://go.uniwue.de/finze-group.*

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1. General Synthetic Aspects

All reactions involving air-sensitive compounds were performed under an argon atmosphere using standard Schlenk line techniques in tubes equipped with PTFE stems (Rettberg, Göttingen and Young, London).

2. Analytical Instruments and Details

^{1}H, ^{13}C, ^{19}F, ^{31}P, and ^{77}Se NMR spectra were recorded at 25 °C in [D$_8$]THF, on a Bruker Avance 500 spectrometer, a Bruker Avance III 400 Nanobay, or a Bruker Avance Neo 400 spectrometer. NMR signals were referenced against TMS (^{1}H and ^{13}C with Ξ (^{13}C) = 25.145020 MHz), CCl_3F (Ξ (^{19}F) = 94.094011 MHz), H_3PO_4 (Ξ (^{31}P) = 40.480742 MHz), and Me_2Se in C_6D_6 (Ξ (^{77}Se) = 19.071513).[1] Chemical shifts were calibrated against the residual solvent signal, respectively (δ(^{1}H): [D$_7$]THF 3.58 and 1.72 ppm; δ(^{13}C): [D$_8$]THF 67.21 and 25.31 ppm.[2] IR spectra of the solid samples were recorded at room temperature with a Bruker Alpha-FT-IR spectrometer with an apodized resolution of 2 cm^{-1} in the attenuated total reflection (ATR) mode in the region of 4000–400 cm^{-1} using a setup with a diamond crystal. Raman spectra were measured at room temperature on a Bruker MultiRAM FT spectrometer with an apodized resolution of 2 cm^{-1} in the region of 4000–400 cm^{-1}. The samples were sealed in melting point capillaries and excited with the 1064 nm line of a Nd/YAG laser. Thermal analyses were performed with a DSC 204 F1 Phoenix (Netzsch) in the temperature range of –20 to 500 °C with a heating rate of 10 K min^{-1}. Elemental analyses (C, H, N) were performed either with a Euro EA3000 instrument (HEKA-Tech, Germany) or with an Elementar Vario MICRO cube instrument (Elementar Analysensysteme, Germany).

3. Chemicals

All standard chemicals were obtained from commercial sources and used without further purification except potassium hydride (suspension in mineral oil), which was washed with pentane and dried under vacuum. $(C_2F_5)_3PF_2$ was synthesized via electrochemical fluorination (ECF) starting from triethylphosphine as described in the literature.[3] Benzyl potassium,[4] potassium imidazolate,[5] and lithium imidazolate[6] were prepared as reported in the literature. Solvents were dried according to standard protocols[7] and stored under argon atmosphere in flasks with valves with PTFE stems (Rettberg, Göttingen and Young, London).

4. Syntheses

1-Methyl-3-(tris(pentafluoroethyl)difluorophosphorane)imidazole (1)

1-Methylimidazole (821 mg, 793 µL, 10.0 mmol) was dissolved in Et_2O (10 mL) and cooled to 0 °C. Under stirring, tris(pentafluoroethyl)difluorophosphorane (4.69 g, 2.59 mL 11.0 mmol) was added and the reaction mixture was warmed to room temperature. After stirring for 20 minutes, the solvent was distilled off under vacuum, and the solid residue was dried under vacuum. Yield: 4.86 g (9.56 mmol, 96% calculated for 1-methylimidazole).

^{1}H NMR (500.1 MHz, [D$_8$]THF): δ = 8.84 (s, 1H, NC*H*N), 7.53 (s, 1H, NC*H*CHN), 7.32 (m, 1H, NCHC*H*N), 3.89 ppm (s, 3H, CH_3).

^{13}C{^{1}H} NMR (125.8 MHz, [D$_8$]THF): δ = 141.2 (d, 1C, $^{2}J(^{31}\text{P},^{13}\text{C})$ = 12.5 Hz, N*C*N), 126.9 (d, 1C, $^{2}J(^{31}\text{P},^{13}\text{C})$ = 12.6 Hz, N*C*CN), 121.3 (s, 1C, NC*C*N), 120.7 (qm, 2C, $^{1}J(^{19}\text{F},^{13}\text{C})$ = 288.1 Hz, CF_3), 120.7 (qm, 1C, $^{1}J(^{19}\text{F},^{13}\text{C})$ = 288.1 Hz, CF_3), 118.3 (m, 2C, CF_2), 118.3 (m, 1C, CF_2), 35.6 ppm (s, 1C, CH_3).

^{13}C{^{19}F} NMR (125.8 MHz, [D$_8$]THF): δ = 141.2 (dm, 1C, $^{1}J(^{13}\text{C},^{1}\text{H})$ = 223.0 Hz, N*C*N), 126.9 (dm, 1C, $^{1}J(^{13}\text{C},^{1}\text{H})$ = 203.3 Hz, N*C*CN), 121.3 (dm, 1C, $^{1}J(^{13}\text{C},^{1}\text{H})$ = 198.8 Hz, NC*C*N), 120.7 (d, 2C, $^{3}J(^{31}\text{P},^{13}\text{C})$ = 31.8 Hz, CF_3), 120.7 (d, 2C, $^{3}J(^{31}\text{P},^{13}\text{C})$ = 25.1 Hz, CF_3), 118.3 (d, 2C, $^{2}J(^{31}\text{P},^{13}\text{C})$ = 237.2 Hz, CF_2), 118.3 (d, 1C, $^{2}J(^{31}\text{P},^{13}\text{C})$ = 143.1 Hz, CF_2), 35.6 ppm (q, 1C, $^{1}J(^{13}\text{C},^{1}\text{H})$ = 143.0 Hz, CH_3).

^{19}F NMR (470.6 MHz, [D$_8$]THF): δ = −79.8 (dtt, 3F, $^{3}J(^{31}\text{P},^{19}\text{F})$ = 19.7 Hz, $^{4}J(^{19}\text{F},^{19}\text{F})$ = 19.6 Hz, $^{3}J(^{19}\text{F},^{19}\text{F})$ = 6.9 Hz, CF_3), −80.5 (dtt, 6F, $^{3}J(^{31}\text{P},^{19}\text{F})$ = 15.7 Hz, $^{4}J(^{19}\text{F},^{19}\text{F})$ = 8.0 Hz, $^{3}J(^{19}\text{F},^{19}\text{F})$ = 7.6 Hz, CF_3), −94.0 (dm, 1F, $^{1}J(^{31}\text{P},^{19}\text{F})$ = 951 Hz, P*F*), −98.9 (dm, 1F, $^{1}J(^{31}\text{P},^{19}\text{F})$ = 945 Hz, P*F*), −112.5 (m, 4F, CF_2), −114.7 ppm (dm, 2F, $^{2}J(^{31}\text{P},^{19}\text{F})$ = 96 Hz, CF_2).

^{19}F{^{31}P} NMR (470.6 MHz, [D$_8$]THF): δ = −79.8 (m, 3F, CF_3), −80.5 (m, 6F, CF_3), −94.0 (m, 1F, P*F*), −98.9 (m, 1F, P*F*), −112.5 (m, 4F, CF_2), −114.7 ppm (m, 2F, CF_2).

^{31}P NMR (202.5 MHz, [D$_8$]THF): δ = −146.9 ppm (ddquintt, 1P, $^{1}J(^{31}\text{P},^{19}\text{F})$ = 951 Hz, $^{1}J(^{31}\text{P},^{19}\text{F})$ = 945 Hz, $^{2}J(^{31}\text{P},^{19}\text{F})$ = 104 Hz, $^{2}J(^{31}\text{P},^{19}\text{F})$ = 96 Hz, PF_2).

The vibrational spectra are depicted in Figure S57.

Elemental analysis: Calculated (%) for $C_{10}H_6F_{17}N_2P$, C 23.64, H 1.19, N 5.51; found, C 23.34, H 0.91, N 5.97.

Crystals of **1** suitable for an X-ray diffraction study were obtained by slow evaporation of a Et_2O solution.

Potassium 1,3-bis(tris(pentafluoroethyl)difluorophosphorane)imidazolate with 0.5 eq Et$_2$O (K2·(Et$_2$O)$_{0.5}$)

Potassium imidazolate (212 mg, 2.00 mmol) was suspended in Et_2O (20 mL) and cooled to −10 °C. Under stirring, tris(pentafluoroethyl)difluorophosphorane (1.79 g, 988 µL, 4.20 mmol) was added and the reaction mixture was warmed to room temperature. After stirring for 60 minutes, the solvent was distilled off under vacuum and, the solid residue was dried under vacuum. Yield: 1.97 g (1.98 mmol, 99% calculated for potassium imidazolate).

^{1}H NMR (500.1 MHz, [D$_8$]THF): δ = 8.39 (s, 1H, NC*H*N), 7.22 (s, 2H, NC*H*C*H*N), 3.37 (q, 2H, ^{3}*J*(^{1}H,^{1}H) = 7.0 Hz, $^{\mathrm{Et2O}}$C*H*$_2$), 1.10 ppm (t, 3H, ^{3}*J*(^{1}H,^{1}H) = 7.0 Hz, $^{\mathrm{Et2O}}$C*H*$_3$).

^{13}C{^{1}H} NMR (125.8 MHz, [D$_8$]THF): δ = 144.2 (m, 1C, N*C*N), 122.7 (m, 2C, N*CC*N), 120.9 (m, 1C, *C*F$_3$), 120.7 (qm, 2C, ^{1}*J*(^{19}F,^{13}C) = 287.5 Hz, *C*F$_3$), 118.7 (m, 1C, *C*F$_2$), 118.2 (m, 2C, *C*F$_2$), 66.3 (s, 1C, $^{\mathrm{Et2O}}$*C*H$_2$), 15.7 ppm (s, 1C, $^{\mathrm{Et2O}}$*C*H$_3$).

^{13}C{^{19}F} NMR (125.8 MHz, [D$_8$]THF): δ = 144.2 (dm, 1C, ^{1}*J*(^{13}C,^{1}H) = 221.8 Hz, N*C*N), 122.7 (dm, 2C, ^{1}*J*(^{13}C,^{1}H) = 204.2 Hz, N*CC*N), 120.9 (d, 1C, ^{3}*J*(^{31}P,^{13}C) = 24.7 Hz, *C*F$_3$), 120.7 (d, 2C, ^{3}*J*(^{31}P,^{13}C) = 32.1 Hz, *C*F$_3$), 118.7 (d, 1C, ^{2}*J*(^{31}P,^{13}C) = 241.8 Hz, *C*F$_2$), 118.2 (d, 2C, ^{2}*J*(^{31}P,^{13}C) = 237.4 Hz, *C*F$_2$), 66.3 (tm, 1C, ^{1}*J*(^{13}C,^{1}H) = 139.8 Hz, $^{\mathrm{Et2O}}$*C*H$_2$), 15.7 ppm (qt, 1C, ^{1}*J*(^{13}C,^{1}H) = 125.4 Hz, ^{3}*J*(^{13}C,^{1}H) = 2.5 Hz, $^{\mathrm{Et2O}}$*C*H$_2$).

^{19}F NMR (470.6 MHz, [D$_8$]THF): δ = −79.6 (m, 3F, C*F*$_3$), −80.5 (m, 6F, C*F*$_3$), −95.0 (dm, 1F, ^{1}*J*(^{31}P,^{19}F) ≈ 953 Hz, P*F*), −98.2 (dm, 1F, ^{1}*J*(^{31}P,^{19}F) ≈ 945 Hz, P*F*), −109.6 (m, 2F, C*F*$_2$), −114.5 (dm, 2F, ^{2}*J*(^{31}P,^{19}F) = 95 Hz, C*F*$_2$), −115.2 ppm (m, 2F, C*F*$_2$).

^{19}F{^{31}P} NMR (470.6 MHz, [D$_8$]THF): δ = −79.6 (m, 3F, C*F*$_3$), −80.5 (m, 6F, C*F*$_3$), −95.0 (m, 1F, P*F*), −98.2 (m, 1F, P*F*), −109.6 (m, 4F, C*F*$_2$), −114.5 (m, 2F, C*F*$_2$), −115.2 ppm (m, 2F, C*F*$_2$).

^{31}P NMR (202.5 MHz, [D$_8$]THF): δ = −147.1 ppm (ddquintt, 1P, ^{1}*J*(^{31}P,^{19}F) ≈ 953 Hz, ^{1}*J*(^{31}P,^{19}F) ≈ 945 Hz, ^{2}*J*(^{31}P,^{19}F) ≈ 104 Hz, ^{2}*J*(^{31}P,^{19}F) ≈ 96 Hz, *P*F$_2$).

The vibrational spectra are depicted in Figure S58.

Elemental analysis: Calculated (%) for $C_{17}H_8F_{34}KN_2O_{0.5}P_2$, C 20.52, H 0.81, N 2.81; found, C 20.05, H 0.81, N 2.81.

Tetraphenylphosphonium 1,3-bis(tris(pentafluoroethyl)difluorophosphorane)imidazolate ([PPh$_4$]2)

Lithium imidazolate (148 mg, 2.00 mmol) was suspended in Et$_2$O (10 mL) and cooled to −10 °C. Under stirring, tris(pentafluoroethyl)difluorophosphorane (1.79 g, 988 µL, 4.20 mmol) was added and the reaction mixture was warmed to room temperature. After stirring for 60 minutes solid tetraphenylphosphonium chloride (788 mg, 2.10 mmol) was added. The resulting suspension was stirred at room temperature for 16 hours whereupon the precipitated solid was filtered off. The solvent was distilled off under reduced pressure and the resulting solid residue was dried under vacuum. Yield: 2.27 g (1.80 mmol, 90% calculated for lithium imidazolate).

^{1}H NMR (500.1 MHz, [D$_8$]THF): δ = 8.40 (s, 1H, NC*H*N), 7.93 (m, 4H, $^{\mathrm{Ph}}$C*H*), 7.76 (m, 16H, $^{\mathrm{Ph}}$C*H*), 7.22 ppm (s, 2H, NC*H*C*H*N).

^{13}C{^{1}H} NMR (125.8 MHz, [D$_8$]THF): δ = 144.2 (m, 1C, N*C*N), 136.4 (d, 4C, ^{4}*J*(^{31}P,^{13}C) = 3.1 Hz, $^{\mathrm{Ph}}$*C*H), 135.7 (d, 8C, ^{3}*J*(^{31}P,^{13}C) = 10.4 Hz, $^{\mathrm{Ph}}$*C*H), 131.3 (d, 8C, ^{2}*J*(^{31}P,^{13}C) = 12.7 Hz, $^{\mathrm{Ph}}$*C*H), 122.6 (m, 2C, N*CC*N), 120.9 (m, 1C, *C*F$_3$), 120.7 (qm, 2C, ^{1}*J*(^{19}F,^{13}C) = 287.5 Hz, *C*F$_3$), 119.2 (d, 4C, ^{2}*J*(^{31}P,^{13}C) = 89.3 Hz, $^{\mathrm{Ph}}$*C*P), 118.7 (m, 1C, *C*F$_2$), 118.2 ppm (m, 2C, *C*F$_2$).

^{13}C{^{19}F} NMR (125.8 MHz, [D$_8$]THF): *δ* = 144.2 (dm, 1C, $^{1}J(^{13}\mathrm{C},^{1}\mathrm{H})$ = 221.8 Hz, N*C*N), 136.4 (dm, 4C, $^{1}J(^{13}\mathrm{C},^{1}\mathrm{H})$ = 163.2 Hz, $^{\mathrm{Ph}}$*C*H), 135.7 (dm, 8C, $^{1}J(^{13}\mathrm{C},^{1}\mathrm{H})$ = 165.2 Hz, $^{\mathrm{Ph}}$*C*H), 131.3 (dm, 8C, $^{1}J(^{13}\mathrm{C},^{1}\mathrm{H})$ = 165.9 Hz, $^{\mathrm{Ph}}$*C*H), 122.6 (dm, 2C, $^{1}J(^{13}\mathrm{C},^{1}\mathrm{H})$ = 202.3 Hz, N*CC*N), 120.9 (d, 1C, $^{3}J(^{31}\mathrm{P},^{13}\mathrm{C})$ = 24.7 Hz, *C*F$_3$), 120.7 (d, 2C, $^{3}J(^{31}\mathrm{P},^{13}\mathrm{C})$ = 32.1 Hz, *C*F$_3$), 119.2 (s, 4C, $^{\mathrm{Ph}}$*C*P), 118.7 (d, 1C, $^{2}J(^{31}\mathrm{P},^{13}\mathrm{C})$ = 241.8 Hz, *C*F$_2$), 118.2 ppm (d, 2C, $^{2}J(^{31}\mathrm{P},^{13}\mathrm{C})$ = 237.4 Hz, *C*F$_2$).

^{19}F NMR (470.6 MHz, [D$_8$]THF): *δ* = −79.6 (m, 3F, C*F*$_3$), −80.4 (m, 6F, C*F*$_3$), −95.0 (dm, 1F, $^{1}J(^{31}\mathrm{P},^{19}\mathrm{F})$ ≈ 953 Hz, P*F*), −98.2 (dm, 1F, $^{1}J(^{31}\mathrm{P},^{19}\mathrm{F})$ ≈ 945 Hz, P*F*), −109.6 (m, 2F, C*F*$_2$), −114.5 (dm, 2F, $^{2}J(^{31}\mathrm{P},^{19}\mathrm{F})$ = 95 Hz, C*F*$_2$), −115.2 ppm (m, 2F, C*F*$_2$).

^{19}F{^{31}P} NMR (470.6 MHz, [D$_8$]THF): *δ* = −79.6 (m, 3F, C*F*$_3$), −80.4 (m, 6F, C*F*$_3$), −95.0 (m, 1F, P*F*), −98.2 (m, 1F, P*F*), −109.7 (m, 4F, C*F*$_2$), −114.5 (m, 2F, C*F*$_2$), −115.2 ppm (m, 2F, C*F*$_2$).

^{31}P NMR (202.5 MHz, [D$_8$]THF): *δ* = 23.1 (m, 1P, *P*Ph$_4$) −147.1 ppm (ddquintt, 1P, $^{1}J(^{31}\mathrm{P},^{19}\mathrm{F})$ ≈ 953 Hz, $^{1}J(^{31}\mathrm{P},^{19}\mathrm{F})$ ≈ 945 Hz, $^{2}J(^{31}\mathrm{P},^{19}\mathrm{F})$ ≈ 104 Hz, $^{2}J(^{31}\mathrm{P},^{19}\mathrm{F})$ ≈ 96 Hz, *P*F$_2$).

^{31}P{^{1}H} NMR (202.5 MHz, [D$_8$]THF): *δ* = 23.1 (s, 1P, *P*Ph$_4$) −147.1 ppm (ddquintt, 1P, $^{1}J(^{31}\mathrm{P},^{19}\mathrm{F})$ ≈ 953 Hz, $^{1}J(^{31}\mathrm{P},^{19}\mathrm{F})$ ≈ 945 Hz, $^{2}J(^{31}\mathrm{P},^{19}\mathrm{F})$ ≈ 104 Hz, $^{2}J(^{31}\mathrm{P},^{19}\mathrm{F})$ ≈ 96 Hz, *P*F$_2$).

The vibrational spectra are depicted in Figure S59.

Elemental analysis: Calculated (%) for $C_{39}H_{23}F_{34}N_2P_3$, C 37.22, H 1.84, N 2.23; found, C 37.22, H 1.48, N 2.54.

Crystals of [PPh$_4$]**2** suitable for an X-ray diffraction study were obtained by slow evaporation of a Et$_2$O solution.

Potassium 1-methyl-3-(tris(pentafluoroethyl)difluorophosphorane)imidazoline-2-ylidenate with 0.5 eq THF (K3·THF$_{0.5}$)

1 (1.02 g, 2.00 mmol) and KH (120 mg, 3.00 mmol) were suspended in THF (5 mL) under vigorous stirring, resulting in immediate gas evolution. After 16 hours at room temperature excess KH was filtered off and the solvent was evaporated under reduced pressure. The resulting solid residue was dried under vacuum. Yield: 1.10 g (1.94 mmol, 97% calculated for **1**).

^{1}H NMR (500.1 MHz, [D$_8$]THF): *δ* = 7.13 (s, 1H, NC*H*CHN), 6.65 (m, 1H, NCHC*H*N), 3.65 (s, 3H, C*H*$_3$), 3.61 (m, 2H, THF^{2,5}*H*$_2$), 1.77 ppm (m, 2H, THF^{3,4}*H*$_2$).

^{13}C{^{1}H} NMR (125.8 MHz, [D$_8$]THF): *δ* = 218.1 (m, 1C, N*C*N), 125.6 (m, 1C, N*C*CN), 121.5 (m, 2C, *C*F$_3$), 121.4 (m, 1C, *C*F$_3$), 120.8 (m, 1C, *C*F$_2$), 119.5 (m, 2C, *C*F$_2$), 116.7 (s, 1C, NC*C*N), 68.2 (s, 1C, THF^{2,5}*C*), 37.8 (s, 1C, *C*H$_3$), 26.4 ppm (s, 1C, THF^{3,4}*C*).

^{13}C{^{19}F} NMR (125.8 MHz, [D$_8$]THF): *δ* = 218.1 (dm, 1C, $^{2}J(^{31}\mathrm{P},^{13}\mathrm{C})$ = 38.2 Hz, N*C*N), 125.6 (dm, 1C, $^{1}J(^{13}\mathrm{C},^{1}\mathrm{H})$ = 194.4 Hz, N*C*CN), 121.5 (d, 2C, $^{3}J(^{31}\mathrm{P},^{13}\mathrm{C})$ ≈ 49.5 Hz, *C*F$_3$), 121.4 (d, 1C, $^{3}J(^{31}\mathrm{P},^{13}\mathrm{C})$ ≈ 28.9 Hz, *C*F$_3$), 120.8 (d, 1C, $^{2}J(^{31}\mathrm{P},^{13}\mathrm{C})$ = 192.1 Hz, *C*F$_2$), 119.5 (d, 2C, $^{2}J(^{31}\mathrm{P},^{13}\mathrm{C})$ = 208.9 Hz, *C*F$_2$), 116.7 (dm, 1C, $^{1}J(^{13}\mathrm{C},^{1}\mathrm{H})$ = 188.9 Hz, NC*C*N), 68.2 (m, 1C, THF^{2,5}*C*), 37.8 (q, 1C, $^{1}J(^{13}\mathrm{C},^{1}\mathrm{H})$ = 138.1 Hz, *C*H$_3$), 26.4 ppm (m, 1C, THF^{3,4}*C*).

^{19}F NMR (470.6 MHz, [D$_8$]THF): δ = −79.1 (m, 3F, C*F*$_3$), −79.9 (m, 6F, C*F*$_3$), −96.0 (dq, 2F, ^{1}*J*(^{31}P,^{19}F) = 905 Hz, ^{3}*J*(^{19}F,^{19}F) = 135.9 Hz, P*F*$_2$), −110.0 (m, 2F, C*F*$_2$), −112.7 (m, 2F, C*F*$_2$), −113.0 ppm (dm, 2F, ^{2}*J*(^{31}P,^{19}F) = 92 Hz, C*F*$_2$).

^{19}F{^{31}P} NMR (470.6 MHz, [D$_8$]THF): δ = −79.1 (m, 3F, C*F*$_3$), −79.9 (m, 6F, C*F*$_3$), −96.0 (q, 2F, ^{3}*J*(^{19}F,^{19}F) = 135.9 Hz, P*F*$_2$), −110.0 (m, 2F, C*F*$_2$), −112.7 (m, 2F, C*F*$_2$), −113.0 ppm (m, 2F, C*F*$_2$).

^{31}P NMR (202.5 MHz, [D$_8$]THF): δ = −151.4 ppm (tquintt, 1P, ^{1}*J*(^{31}P,^{19}F) = 905 Hz, ^{2}*J*(^{31}P,^{19}F) = 92 Hz, ^{2}*J*(^{31}P,^{19}F) = 92 Hz, *P*F$_2$).

The IR spectrum is depicted in Figure S60.

Elemental analysis: Calculated (%) for $C_{12}H_9F_{17}KN_2O_{0.5}P$, C 24.75, H 1.56, N 4.81; found, C 24.88, H 1.17, N 5.15.

Crystals of [K**3**(THF)$_2$]$_2$ suitable for an X-ray diffraction study were obtained by slow diffusion of hexane into a THF solution.

Dipotassium 1,3-bis(tris(pentafluoroethyl)difluorophosphorane)imidazoline-2-ylidenate with 0.5 eq Et$_2$O and 0.5 eq toluene (K$_2$4·(Et$_2$O)$_{0.5}$,·(C$_7$H$_8$)$_{0.5}$)

K**2**·(Et$_2$O)$_{0.5}$ (507 mg, 0.509 mmol) and benzyl potassium (73.1 mg, 0.561 mmol) were dissolved in Et$_2$O (3 mL) under vigorous stirring. After 15 minutes at room temperature the solvent was evaporated under reduced pressure and the resulting solid residue was dried under vacuum. Yield: 514 mg (0.485 mmol, 95% calculated for K**2**·(Et$_2$O)$_{0.5}$).

^{1}H NMR (500.1 MHz, [D$_8$]THF): δ = 7.12 (m, 2.5H, $^{\text{C7H8}}$C*H*), 6.85 (s, 2H, NC*H*C*H*N), 3.37 (q, 2H, ^{3}*J*(^{1}H,^{1}H) = 7.0 Hz, $^{\text{Et2O}}$C*H*$_2$), 2.29 (m, 1.5H, $^{\text{C7H8}}$C*H*$_3$), 1.10 ppm (t, 3H, ^{3}*J*(^{1}H,^{1}H) = 7.0 Hz, $^{\text{Et2O}}$C*H*$_3$).

^{13}C{^{1}H} NMR (125.8 MHz, [D$_8$]THF): δ = 230.0 (m, 1C, N*C*N), 138.5 (s, 0.5C, $^{\text{C7H8}}$*C*CH$_3$), 129.7 (s, 1C, $^{\text{C7H8}}$*C*H), 128.9 (s, 1C, $^{\text{C7H8}}$*C*H), 126.0 (s, 1C, $^{\text{C7H8}}$*C*H), 121.9 (m, 2C, *C*F$_3$), 121.5 (m, 4C, *C*F$_3$), 121.0 (m, 2C, *C*F$_2$), 120.7 (s, 1C, N*C*CN), 119.5 (m, 4C, *C*F$_2$), 66.3 (s, 1C, $^{\text{Et2O}}$*C*H$_2$), 21.5 (s, 0.5C, $^{\text{C7H8}}$*C*H$_3$), 15.7 ppm (s, 1C, $^{\text{Et2O}}$*C*H$_3$).

^{13}C{^{19}F} NMR (125.8 MHz, [D$_8$]THF): δ = 230.0 (t, 1C, ^{2}*J*(^{31}P,^{13}C) = 44.0 Hz, N*C*N), 138.5 (m, 0.5C, $^{\text{C7H8}}$*C*CH$_3$), 129.7 (dm, 1C, ^{1}*J*(^{13}C,^{1}H) = 156.0 Hz, $^{\text{C7H8}}$*C*H), 128.9 (dm, 1C, ^{1}*J*(^{13}C,^{1}H) = 158.3 Hz, $^{\text{C7H8}}$*C*H), 128.9 (dm, 1C, ^{1}*J*(^{13}C,^{1}H) = 160.1 Hz, $^{\text{C7H8}}$*C*H), 121.9 (d, 2C, ^{3}*J*(^{31}P,^{13}C) = 25.5 Hz, *C*F$_3$), 121.5 (d, 4C, ^{3}*J*(^{31}P,^{13}C) = 28.7 Hz, *C*F$_3$), 121.0 (d, 2C, ^{2}*J*(^{31}P,^{13}C) ≈ 162.1 Hz, *C*F$_2$), 120.7 (dm, 1C, ^{1}*J*(^{13}C,^{1}H) ≈ 189 Hz, N*C*CN), 119.5 (d, 4C, ^{2}*J*(^{31}P,^{13}C) = 207.6 Hz, *C*F$_2$), 66.3 (tm, 1C, ^{1}*J*(^{13}C,^{1}H) = 139.8 Hz, $^{\text{Et2O}}$*C*H$_2$), 21.5 (qm, 0.5C, ^{1}*J*(^{13}C,^{1}H) = 125.8 Hz, $^{\text{C7H8}}$*C*H$_3$), 15.7 ppm (qt, 1C, ^{1}*J*(^{13}C,^{1}H) = 125.4 Hz, ^{3}*J*(^{13}C,^{1}H) = 2.5 Hz, $^{\text{Et2O}}$*C*H$_2$).

^{19}F NMR (470.6 MHz, [D$_8$]THF): δ = −79.0 (m, 6F, C*F*$_3$), −79.6 (m, 12F, C*F*$_3$), −95.9 (dm, 2F, ^{1}*J*(^{31}P,^{19}F) = 902 Hz, P*F*), −96.8 (dm, 2F, ^{1}*J*(^{31}P,^{19}F) = 902 Hz, P*F*), −109.6 (m, 4F, C*F*$_2$), −112.4 (m, 4F, C*F*$_2$), −112.9 ppm (dm, 4F, ^{2}*J*(^{31}P,^{19}F) = 92 Hz, C*F*$_2$).

^{19}F{^{31}P} NMR (470.6 MHz, [D$_8$]THF): δ = −79.0 (m, 6F, C*F*$_3$), −79.6 (m, 12F, C*F*$_3$), −95.9 (m, 2F, P*F*), −96.8 (m, 2F, P*F*), −109.6 (m, 4F, C*F*$_2$), −112.4 (m, 4F, C*F*$_2$), −112.9 ppm (m, 4F, C*F*$_2$).

^{31}P NMR (202.5 MHz, [D$_8$]THF): δ = −150.0 ppm (ddquintt, 2P, $^1J(^{31}P,^{19}F)$ ≈ 902 Hz, $^1J(^{31}P,^{19}F)$ ≈ 902 Hz, $^2J(^{31}P,^{19}F)$ ≈ 92 Hz, $^2J(^{31}P,^{19}F)$ ≈ 92 Hz, *P*F$_2$).

The IR spectrum is depicted in Figure S61.

Elemental analysis: Calculated (%) for $C_{20.5}H_{11}F_{34}K_2N_2O_{0.5}P_2$, C 22.81, H 1.03, N 2.60; found, C 22.58, H 0.96, N 2.91.

Crystals of [K(18c6)(THF)$_2$][{K(18c6)}**4**]·THF suitable for an X-ray diffraction study were obtained in the presence of 18-crown-6 (18c6) from a saturated THF solution.

Potassium 1-methyl-3-(tris(pentafluoroethyl)difluorophosphorane)imidazoline-2-ylidenate-selenium with 1 eq THF (K5·THF)

K**3**·THF$_{0.5}$ (291 mg, 0.500 mmol) and selenium (43.4 mg, 0.550 mmol) were suspended in THF (8 mL) and stirred at room temperature for 60 minutes. The reaction mixture was filtered, the solvent was distilled off under reduced pressure, and the solid residue was dried under vacuum. Yield: 328 mg (0.471 mmol, 94% calculated for K**3**·THF$_{0.5}$).

^{1}H NMR (500.1 MHz, [D$_8$]THF): δ = 7.13 (ddm, 1H, $^3J(^1H,^1H)$ = 2.5 Hz, $^4J(^{31}P,^1H)$ = 1.8 Hz, NC*H*CHN), 6.85 (dd, 1H, $^3J(^1H,^1H)$ = 2.5 Hz, $^3J(^{31}P,^1H)$ = 2.1 Hz, NCHC*H*N), 3.61 (m, 4H, THF^{2,5}*H*$_2$), 3.58 (s, 3H, C*H*$_3$), 1.77 ppm (m, 4H, THF^{3,4}*H*$_2$).

^{1}H{^{31}P} NMR (500.1 MHz, [D$_8$]THF): δ = 7.13 (dm, 1H, $^3J(^1H,^1H)$ = 2.5 Hz, NC*H*CHN), 6.85 (d, 1H, $^3J(^1H,^1H)$ = 2.5 Hz, NCHC*H*N), 3.61 (m, 4H, THF^{2,5}*H*$_2$), 3.58 (s, 3H, C*H*$_3$), 1.77 ppm (m, 4H, THF^{3,4}*H*$_2$).

^{13}C{^{1}H} NMR (125.8 MHz, [D$_8$]THF): δ = 161.4 (ddd, 1C, $^2J(^{31}P,^{13}C)$ = 6.1 Hz, $^3J(^{19}F,^{13}C)$ = 6.0 Hz, $^3J(^{19}F,^{13}C)$ = 6.0 Hz, N*C*N), 124.1 (m, 1C, N*C*CN), 121.5 (m, 1C, *C*F$_3$), 120.9 (m, 2C, *C*F$_3$), 119.8 (m, 1C, *C*F$_2$), 119.4 (m, 2C, *C*F$_2$), 118.0 (m, 1C, NC*C*N), 68.2 (s, 2C, THF^{2,5}*C*), 38.4 (s, 1C, *C*H$_3$), 26.4 ppm (s, 2C, THF^{3,4}*C*).

^{13}C{^{19}F} NMR (125.8 MHz, [D$_8$]THF): δ = 161.4 (m, 1C, N*C*N), 124.1 (dm, 1C, $^1J(^{13}C,^1H)$ = 199.7 Hz, N*C*CN), 121.5 (d, 1C, $^3J(^{31}P,^{13}C)$ = 24.8 Hz, *C*F$_3$), 120.9 (d, 2C, $^3J(^{31}P,^{13}C)$ = 31.5 Hz, *C*F$_3$), 119.8 (d, 1C, $^2J(^{31}P,^{13}C)$ = 147.1 Hz, *C*F$_2$), 119.4 (d, 2C, $^2J(^{31}P,^{13}C)$ = 234.4 Hz, *C*F$_2$), 118.0 (dm, 1C, $^1J(^{13}C,^1H)$ = 197.9 Hz, NC*C*N), 68.2 (m, 2C, THF^{2,5}*C*), 38.4 (q, 1C, $^1J(^{13}C,^1H)$ = 140.4 Hz, *C*H$_3$), 26.4 ppm (m, 2C, THF^{3,4}*C*).

^{19}F NMR (470.6 MHz, [D$_8$]THF): δ = −79.5 (tm, 3F, $^3J(^{19}F,^{19}F)$ = 38.9, C*F*$_3$), −79.8 (m, 6F, C*F*$_3$), −88.3 (ddm, 1F, $^1J(^{31}P,^{19}F)$ = 948 Hz, $^3J(^{19}F,^{19}F)$ = 105.5 Hz, P*F*), −90.2 (ddm, 1F, $^1J(^{31}P,^{19}F)$ = 979 Hz, $^3J(^{19}F,^{19}F)$ = 105.5 Hz, P*F*), −107.5 (dd, 2F, $^3J(^{19}F,^{19}F)$ = 286 Hz, $^2J(^{31}P,^{19}F)$ = 100 Hz, C*F*$_2$), −114.4 (dm, 2F, $^2J(^{31}P,^{19}F)$ = 84 Hz, C*F*$_2$), −115.6 ppm (ddm, 2F, $^3J(^{19}F,^{19}F)$ = 287 Hz, $^2J(^{31}P,^{19}F)$ = 112 Hz, C*F*$_2$).

^{19}F{^{31}P} NMR (470.6 MHz, [D$_8$]THF): δ = −79.5 (tm, 3F, $^3J(^{19}F,^{19}F)$ = 38.9, C*F*$_3$), −79.8 (m, 6F, C*F*$_3$), −88.3 (dm, 1F, $^3J(^{19}F,^{19}F)$ = 105.5 Hz, P*F*), −90.2 (dm, 1F, $^3J(^{19}F,^{19}F)$ = 105.5 Hz, P*F*), −107.5 (d, 2F, $^3J(^{19}F,^{19}F)$ = 286 Hz, C*F*$_2$), −114.4 (m, 2F, C*F*$_2$), −115.6 ppm (dm, 2F, $^3J(^{19}F,^{19}F)$ = 287 Hz, C*F*$_2$).

^{31}P NMR (202.5 MHz, [D$_8$]THF): δ = −146.7 ppm (ddttt, 1P, $^1J(^{31}P,^{19}F)$ = 979 Hz, $^1J(^{31}P,^{19}F)$ = 948 Hz, $^2J(^{31}P,^{19}F)$ = 112 Hz, $^2J(^{31}P,^{19}F)$ = 100 Hz, $^2J(^{31}P,^{19}F)$ = 84 Hz, *P*F$_2$).

^{77}Se{^{1}H} NMR (76.4 MHz, [D$_8$]THF): *δ* = 142.1 ppm (ddd, 1Se, ^{3}*J*(^{77}Se,^{31}P) = 70.8 Hz, ^{4}*J*(^{77}Se,^{19}F) = 9.7 Hz, ^{4}*J*(^{77}Se,^{19}F) = 9.7 Hz, C=Se).

The IR spectrum is depicted in Figure S62.

Elemental analysis: calculated (%) for $C_{14}H_{13}F_{17}KN_2OPSe$, C 24.12, H 1.88, N 4.02; found, C 24.34, H 1.33, N 5.12.

Crystals of $^{2}_{\infty}$[K**5**]·$C_6F_2H_4$ suitable for an X-ray diffraction study were obtained from a saturated $C_6F_2H_4$ solution.

Tetraethylammonium 1-methyl-3-(tris(pentafluoroethyl)difluorophosphorane)imidazoline-2-ylidenate-selenium ([Et$_4$N]5)

K**5**·THF (100 mg, 0.143 mmol) and tetraethylammonium chloride (26.2 mg, 0.158 mmol) were suspended in THF (5 mL) and stirred at room temperature for 16 hours. Insoluble KCl was filtered off, the solvent was distilled off under reduced pressure, and the solid residue was dried under vacuum. Yield: 92.5 mg (0.129 mmol, 84% calculated for K**5**·THF).

^{1}H NMR (500.1 MHz, [D$_8$]THF): *δ* = 7.09 (m, 1H, NC*H*CHN), 6.76 (m, 1H, NCHC*H*N), 3.55 (s, 3H, C*H*$_3$), 3.36 (m, 8H, C$^{\mathrm{Et}}$*H*$_2$), 1.30 ppm (m, 12H, C$^{\mathrm{Et}}$*H*$_3$).

^{19}F NMR (470.6 MHz, [D$_8$]THF): *δ* = −79.4 (tm, 3F, ^{3}*J*(^{19}F,^{19}F) = 38.8, C*F*$_3$), −79.8 (m, 6F, C*F*$_3$), −88.4 (ddm, 1F, ^{1}*J*(^{31}P,^{19}F) = 952 Hz, ^{3}*J*(^{19}F,^{19}F) = 106.4 Hz, P*F*), −90.3 (ddm, 1F, ^{1}*J*(^{31}P,^{19}F) = 979 Hz, ^{3}*J*(^{19}F,^{19}F) = 105.3 Hz, P*F*), −107.5 (dd, 2F, ^{3}*J*(^{19}F,^{19}F) = 286 Hz, ^{2}*J*(^{31}P,^{19}F) = 100 Hz, C*F*$_2$), −114.4 (dm, 2F, ^{2}*J*(^{31}P,^{19}F) ≈ 85 Hz, C*F*$_2$), −115.7 ppm (dm, 2F, ^{3}*J*(^{19}F,^{19}F) ≈ 285 Hz, C*F*$_2$).

^{31}P NMR (202.5 MHz, [D$_8$]THF): *δ* = −146.7 ppm (ddttt, 1P, ^{1}*J*(^{31}P,^{19}F) ≈ 980 Hz, ^{1}*J*(^{31}P,^{19}F) ≈ 950 Hz, ^{2}*J*(^{31}P,^{19}F) ≈ 110 Hz, ^{2}*J*(^{31}P,^{19}F) = 100 Hz, ^{2}*J*(^{31}P,^{19}F) ≈ 85 Hz, *P*F$_2$).

^{77}Se{^{1}H} NMR (76.4 MHz, [D$_8$]THF): *δ* = 160.9 ppm (dm, 1Se, ^{3}*J*(^{77}Se,^{31}P) = 76.4 Hz, C=Se).

Bis(trimethylphosphine)gold bis(1-methyl-3-(tris(pentafluoroethyl)difluorophosphorane)-imidazoline-2-ylidenate)-gold ([{($H_3C)_3P\}_2$Au]6)

K**3**·THF$_{0.5}$ (146 mg, 0.250 mmol) and Chloro(trimethylphosphine)gold (77.1 mg, 0.250 mmol) were dissolved in THF (5 mL) and stirred at room temperature for 2 hours. The precipitated solid was filtered off, the solvent was evaporated under reduced pressure, and the solid residue was dried under vacuum. Yield: 179 mg (0.112 mmol, 90% calculated for K**3**·THF$_{0.5}$).

^{1}H NMR (500.1 MHz, [D$_8$]THF): *δ* = 7.29 (m, 2H, NC*H*CHN), 6.95 (m, 2H, NCHC*H*N), 3.93 (s, 6H, C*H*$_3$), 1.56 ppm (d, 18H, ^{2}*J*(^{31}P,^{1}H) = 10.3 Hz, PC*H*$_3$).

^{1}H{^{31}P} NMR (500.1 MHz, [D$_8$]THF): *δ* = 7.29 (m, 2H, NC*H*CHN), 6.95 (m, 2H, NCHC*H*N), 3.93 (s, 6H, C*H*$_3$), 1.56 ppm (s, 18H, PC*H*$_3$).

^{13}C{^{1}H} NMR (125.8 MHz, [D$_8$]THF): *δ* = 193.1 (m, 2C, N*C*N), 126.2 (m, 2C, N*C*CN), 121.4 (m, 2C, *C*F$_3$), 121.2 (m, 4C, *C*F$_3$), 119.9 (m, 2C, *C*F$_2$), 118.8 (m, 4C, *C*F$_2$), 118.7 (m, 2C, NC*C*N), 38.3 (s, 2C, *C*H$_3$), 15.1 ppm (d, 6C, ^{1}*J*(^{31}P,^{13}C) = 32.4 Hz, P*C*H$_3$).

^{13}C{^{19}F} NMR (125.8 MHz, [D$_8$]THF): δ = 193.1 (m, 2C, N*C*N), 126.2 (dm, 2C, ^1J(^{13}C,^{1}H) = 198.0 Hz, N*C*CN), 121.4 (d, 2C, ^3J(^{31}P,^{13}C) = 24.8 Hz, *C*F$_3$), 121.2 (d, 4C, ^3J(^{31}P,^{13}C) = 31.0 Hz, *C*F$_3$), 119.9 (d, 2C, ^2J(^{31}P,^{13}C) = 149.9 Hz, *C*F$_2$), 118.8 (d, 4C, ^2J(^{31}P,^{13}C) = 228.6 Hz, *C*F$_2$), 118.7 (dm, 2C, ^1J(^{13}C,^{1}H) = 193.8 Hz, NC*C*N), 38.3 (q, 2C, ^1J(^{13}C,^{1}H) = 139.8 Hz, *C*H$_3$), 15.1 ppm (qdm, 6C, ^1J(^{13}C,^{1}H) = 131.1 Hz, ^1J(^{31}P,^{13}C) = 32.4 Hz, P*C*H$_3$).

^{19}F NMR (470.6 MHz, [D$_8$]THF): δ = −79.4 (tm, 6F, ^3J(^{19}F,^{19}F) = 33.8, C*F*$_3$), −79.6 (m, 12F, C*F*$_3$), −89.1 (ddm, 2F, ^1J(^{31}P,^{19}F) = 969 Hz, ^3J(^{19}F,^{19}F) = 98.6 Hz, P*F*), −90.8 (ddm, 2F, ^1J(^{31}P,^{19}F) = 931 Hz, ^3J(^{19}F,^{19}F) = 87.6 Hz, P*F*), −105.6 (dm, 4F, ^3J(^{19}F,^{19}F) = 289 Hz, C*F*$_2$), −114.0 (dm, 4F, ^2J(^{31}P,^{19}F) = 87 Hz, C*F*$_2$), −116.0 ppm (dm, 4F, ^3J(^{19}F,^{19}F) = 279 Hz, C*F*$_2$).

^{19}F{^{31}P} NMR (470.6 MHz, [D$_8$]THF): δ = −79.4 (tm, 6F, ^3J(^{19}F,^{19}F) = 33.8, C*F*$_3$), −79.6 (m, 12F, C*F*$_3$), −89.1 (dm, 2F, ^3J(^{19}F,^{19}F) = 98.6 Hz, P*F*), −90.8 (dm, 2F, ^3J(^{19}F,^{19}F) = 87.6 Hz, P*F*), −105.6 (d, 4F, ^3J(^{19}F,^{19}F) = 289 Hz, C*F*$_2$), −114.0 (m, 4F, C*F*$_2$), −116.0 ppm (dm, 4F, ^3J(^{19}F,^{19}F) = 279 Hz, C*F*$_2$).

^{31}P NMR (202.5 MHz, [D$_8$]THF): δ = 5.4 (s, 2P, *P*CH$_3$), −149.1 ppm (ddttt, 2P, ^1J(^{31}P,^{19}F) = 969 Hz, ^1J(^{31}P,^{19}F) = 931 Hz, ^2J(^{31}P,^{19}F) ≈ 110 Hz, ^2J(^{31}P,^{19}F) ≈ 100 Hz, ^2J(^{31}P,^{19}F) = 87 Hz, *P*F$_2$).

^{31}P{^{1}H} NMR (202.5 MHz, [D$_8$]THF): δ = 5.4 (s, 2P, *P*CH$_3$), −149.1 ppm (ddttt, 2P, ^1J(^{31}P,^{19}F) = 969 Hz, ^1J(^{31}P,^{19}F) = 931 Hz, ^2J(^{31}P,^{19}F) ≈ 110 Hz, ^2J(^{31}P,^{19}F) ≈ 100 Hz, ^2J(^{31}P,^{19}F) = 87 Hz, *P*F$_2$).

The IR spectrum is depicted in Figure S63.

Elemental analysis: calculated (%) for $C_{26}H_{28}Au_2F_{34}N_4P_4$, C 20.01, H 1.81, N 3.59; found, C 20.70, H 1.95, N 4.01.

Crystals of [{(H$_3$C)$_3$P}$_2$Au]**6** suitable for an X-ray diffraction study were obtained by slow diffusion of hexane into a THF solution.

Potassium triphenylphosphine-1,3-bis(tris(pentafluoroethyl)difluorophosphorane)imidazoline-2-ylidenate -gold (K7·(THF)$_2$)

K$_2$**4**·(Et$_2$O)$_{0.5}$,·(C$_7$H$_8$)$_{0.5}$ (161 mg, 0.150 mmol) and Chloro(triphenylphosphine)gold (74.2 mg, 0.150 mmol) were dissolved in THF (3 mL) and stirred at room temperature for 16 hours. The precipitated solid was filtered off, the solvent was evaporated under reduced pressure, and the solid residue was dried under vacuum. Yield: 212 mg (0.135 mmol, 91% calculated for K$_2$**4**·(Et$_2$O)$_{0.5}$,·(C$_7$H$_8$)$_{0.5}$).

^{1}H NMR (500.1 MHz, [D$_8$]THF): δ = 7.71−7.40 (m, 15H, ^{Ph}C*H*), 7.23 (s, 2H, NC*H*C*H*N), 3.61 (m, 8H, THF^{2,5}*H*$_2$), 1.77 ppm (m, 8H, THF^{3,4}*H*$_2$).

^{1}H{^{31}P} NMR (500.1 MHz, [D$_8$]THF): δ = 7.71−7.40 (m, 15H, ^{Ph}C*H*), 7.23 (s, 2H, NC*H*C*H*N), 3.61 (m, 8H, THF^{2,5}*H*$_2$), 1.77 ppm (m, 8H, THF^{3,4}*H*$_2$).

^{13}C{^{1}H} NMR (125.8 MHz, [D$_8$]THF): δ = 201.5 (m, 1C, N*C*N), 135.4 (d, 6C, ^2J(^{31}P,^{13}C) = 14.2 Hz, ^{Ph}*C*H), 131.9 (d, 3C, ^1J(^{31}P,^{13}C) = 54.9 Hz, ^{Ph}*C*H), 131.8 (d, 3C, ^4J(^{31}P,^{13}C) = 2.5 Hz, ^{Ph}*C*H), 129.6 (d, 6C, ^3J(^{31}P,^{13}C) = 11.4 Hz, ^{Ph}*C*H), 122.1 (m, 1C, N*C*CN), 121.5 (m, 2C, *C*F$_3$), 121.2 (m, 4C, *C*F$_3$), 120.0 (m, 2C, *C*F$_2$), 118.6 (m, 4C, *C*F$_2$), 68.2 (s, 4C, THF^{2,5}*C*), 26.4 ppm (s, 4C, THF^{3,4}*C*).

$^{13}C\{^{19}F\}$ NMR (125.8 MHz, [D$_8$]THF): δ = 201.5 (dm, 1C, $^2J(^{31}P,^{13}C)$ = 134.1 Hz, N*C*N), 135.4 (dm, 6C, $^1J(^{13}C,^1H)$ = 162.3 Hz, ^{Ph}*C*H), 131.9 (dm, 3C, $^1J(^{31}P,^{13}C)$ = 54.9 Hz, ^{Ph}*C*H), 131.8 (dm, 3C, $^1J(^{13}C,^1H)$ = 161.1 Hz, ^{Ph}*C*H), 129.6 (dm, 6C, $^1J(^{13}C,^1H)$ = 161.2 Hz, ^{Ph}*C*H), 122.1 (dm, 1C, $^1J(^{13}C,^1H)$ ≈ 199 Hz, N*CC*N), 121.5 (d, 2C, $^3J(^{31}P,^{13}C)$ = 24.9 Hz, *C*F$_3$), 121.2 (d, 4C, $^3J(^{31}P,^{13}C)$ = 32.0 Hz, *C*F$_3$), 120.0 (d, 2C, $^2J(^{31}P,^{13}C)$ = 148.8 Hz, *C*F$_2$), 118.6 (d, 4C, $^2J(^{31}P,^{13}C)$ = 231.9 Hz, *C*F$_2$), 68.2 (m, 4C, THF^{2,5}*C*), 26.4 ppm (m, 4C, THF^{3,4}*C*).

^{19}F NMR (470.6 MHz, [D$_8$]THF): δ = −79.3 (m, 6F, C*F*$_3$), −79.7 (m, 12F, C*F*$_3$), −88.0 (dd, 2F, $^1J(^{31}P,^{19}F)$ = 950 Hz, $^2J(^{19}F,^{19}F)$ = 96.3 Hz, P*F*), −89.8 (dd, 2F, $^1J(^{31}P,^{19}F)$ = 980 Hz, $^2J(^{19}F,^{19}F)$ = 96.3 Hz, P*F*), −104.6 (dm, 4F, $^2J(^{31}P,^{19}F)$ = 101.5 Hz, C*F*$_2$), −114.0 (dm, 4F, $^2J(^{31}P,^{19}F)$ = 91.2 Hz, C*F*$_2$), −116.5 ppm (m, 4F, C*F*$_2$).

$^{19}F\{^{31}P\}$ NMR (470.6 MHz, [D$_8$]THF): δ = −79.3 (m, 6F, C*F*$_3$), −79.7 (m, 12F, C*F*$_3$), −88.0 (d, 2F, $^2J(^{19}F,^{19}F)$ = 96.3 Hz, P*F*), −89.8 (d, 2F, $^2J(^{19}F,^{19}F)$ = 96.3 Hz, P*F*), −104.6 (m, 4F, C*F*$_2$), −114.0 (m, 4F, C*F*$_2$), −116.5 ppm (m, 4F, C*F*$_2$).

^{31}P NMR (202.5 MHz, [D$_8$]THF): δ = 37.5 (m, 1P, Ph$_3$*P*), −148.7 ppm (ddquintt, 2P, $^1J(^{31}P,^{19}F)$ ≈ 980 Hz, $^1J(^{31}P,^{19}F)$ ≈ 950 Hz, $^2J(^{31}P,^{19}F)$ ≈ 102 Hz, $^2J(^{31}P,^{19}F)$ ≈ 91 Hz, *P*F$_2$).

$^{31}P\{^1H\}$ NMR (202.5 MHz, [D$_8$]THF): δ = 37.5 (s, 1P, Ph$_3$*P*), −148.7 ppm (ddquintt, 2P, $^1J(^{31}P,^{19}F)$ ≈ 980 Hz, $^1J(^{31}P,^{19}F)$ ≈ 950 Hz, $^2J(^{31}P,^{19}F)$ ≈ 109 Hz, $^2J(^{31}P,^{19}F)$ ≈ 93 Hz, *P*F$_2$).

The IR spectrum is depicted in Figure S64.

Elemental analysis: calculated (%) for $C_{41}H_{33}AuF_{34}N_2O_2P_3$, C 31.55, H 2.13, N 1.80; found, C 31.85, H 2.01, N 2.54.

Crystals of $^1_\infty$[K**7**(NCCH$_3$)$_2$] suitable for an X-ray diffraction study were obtained by slow diffusion of hexane into a acetonitrile solution.

5. NMR Spectra

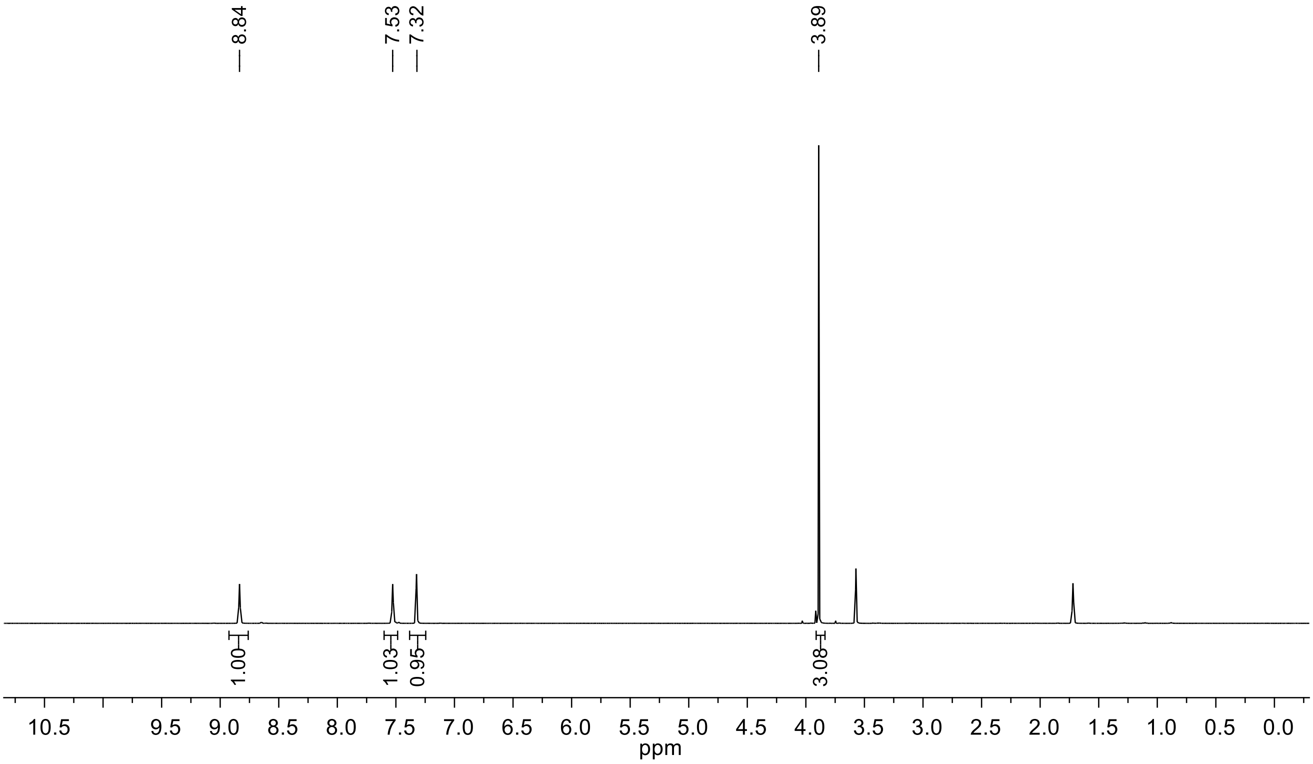

Figure S1. ^{1}H NMR spectrum of **1** in [D$_8$]THF.

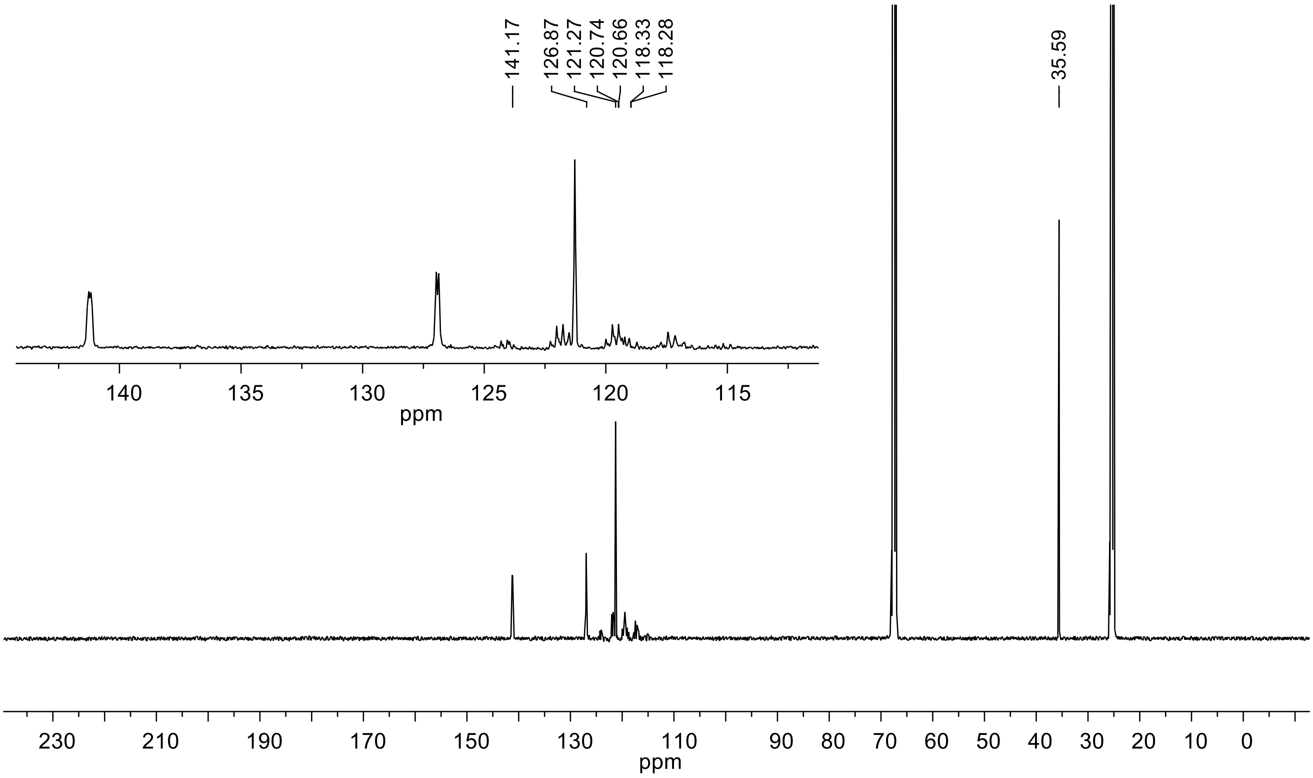

Figure S2. ^{13}C{^{1}H} NMR spectrum of **1** in [D$_8$]THF.

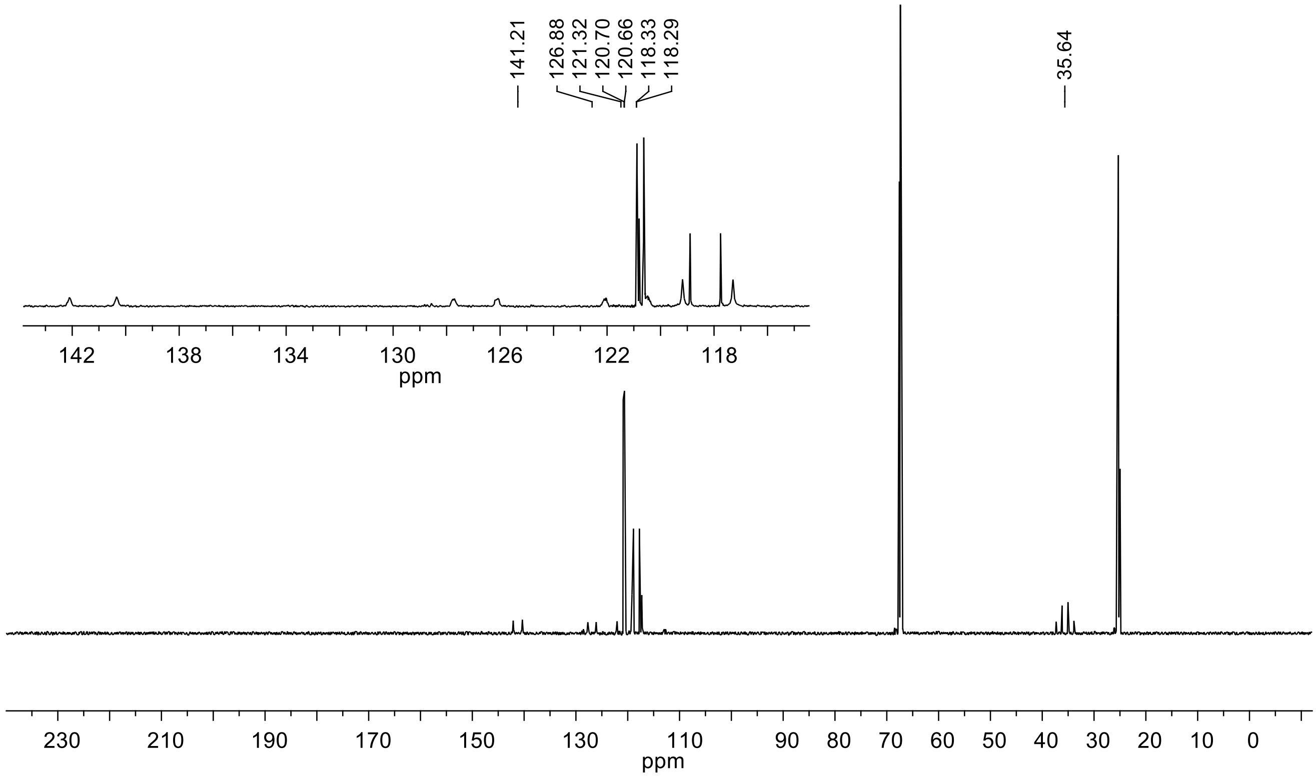

Figure S3. $^{13}C\{^{19}F\}$ NMR spectrum of **1** in [D$_8$]THF.

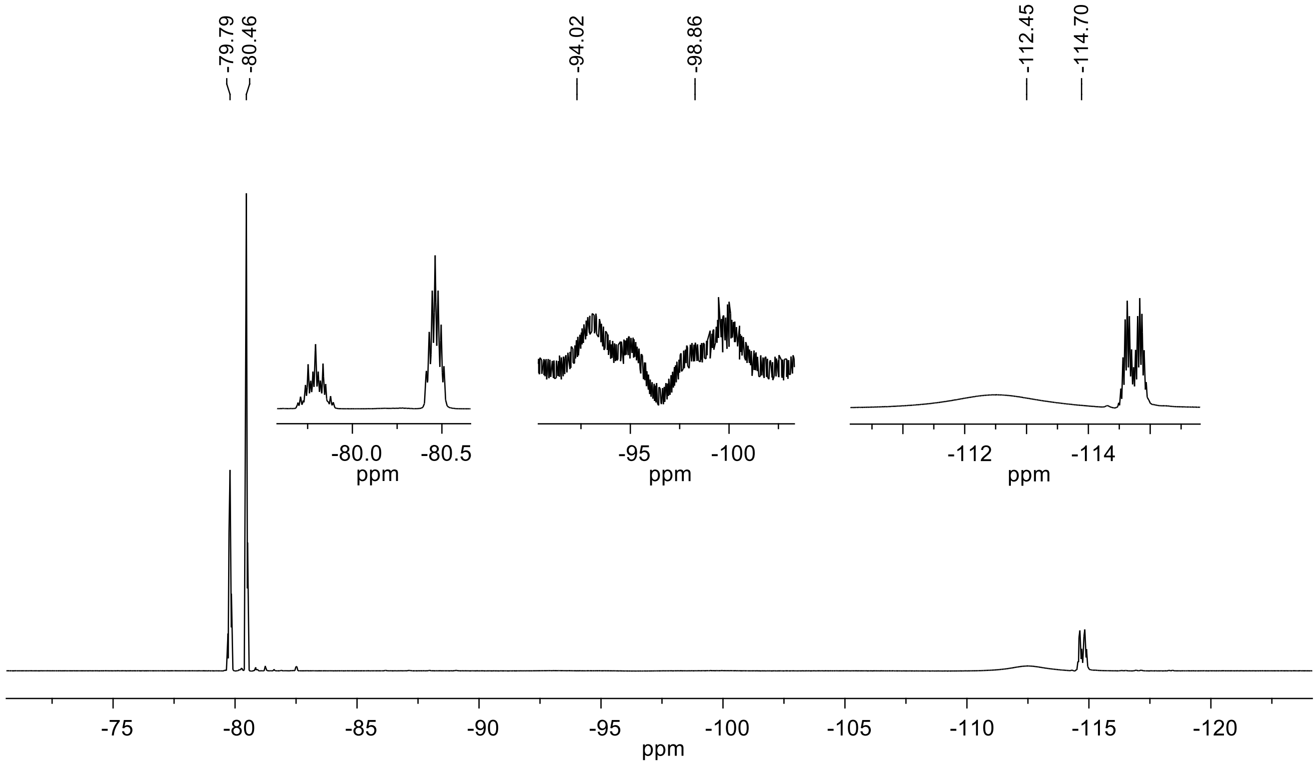

Figure S4. ^{19}F NMR spectrum of **1** in [D$_8$]THF.

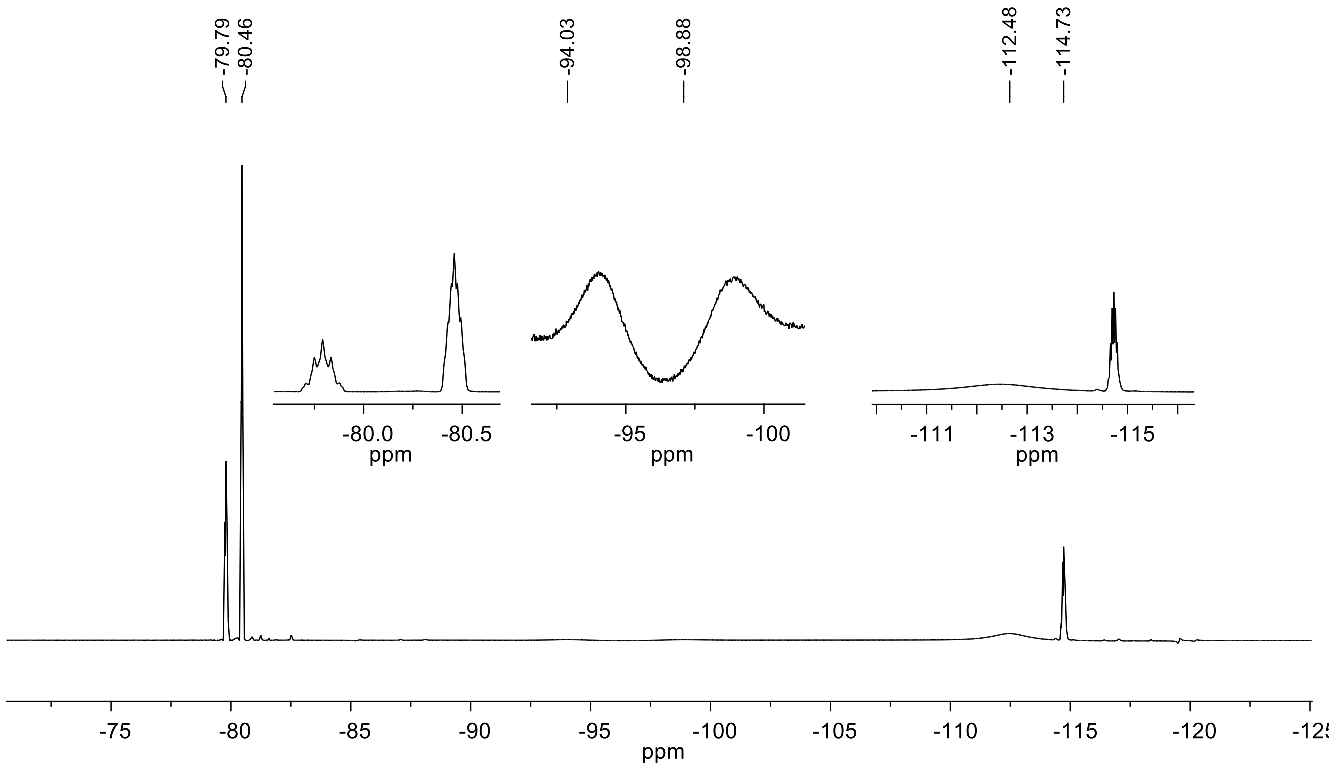

Figure S5. $^{19}F\{^{31}P\}$ NMR spectrum of **1** in [D$_8$]THF.

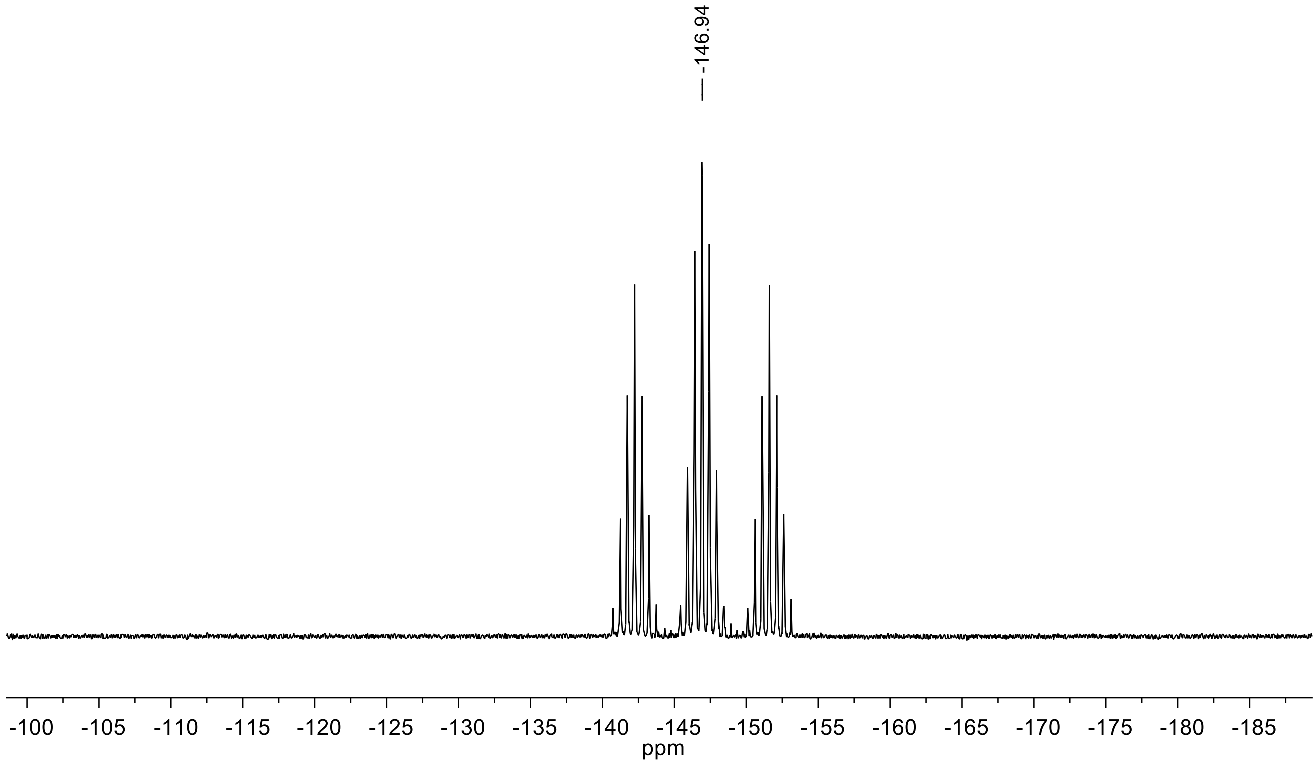

Figure S6. ^{31}P NMR spectrum of **1** in [D$_8$]THF.

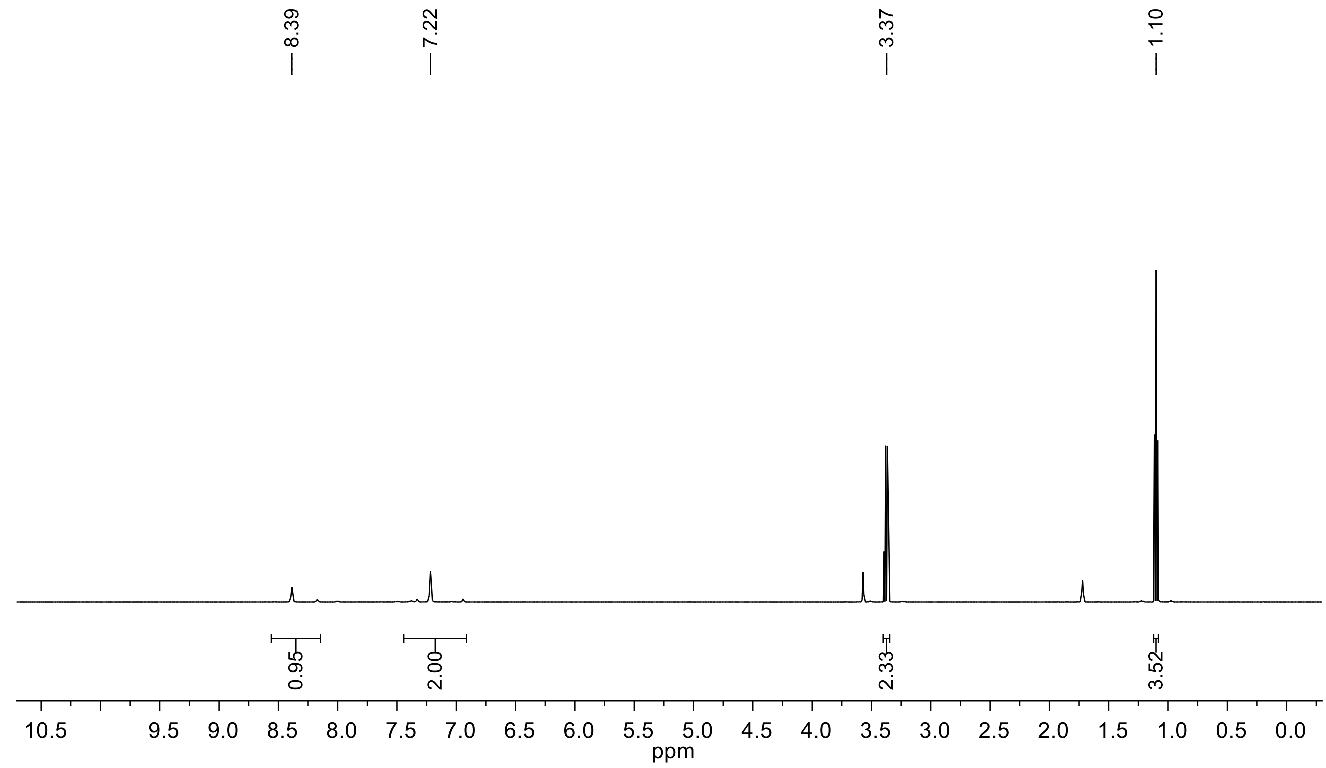

Figure S7. ^{1}H NMR spectrum of K**2**·$(Et_2O)_{0.5}$ in [D$_8$]THF.

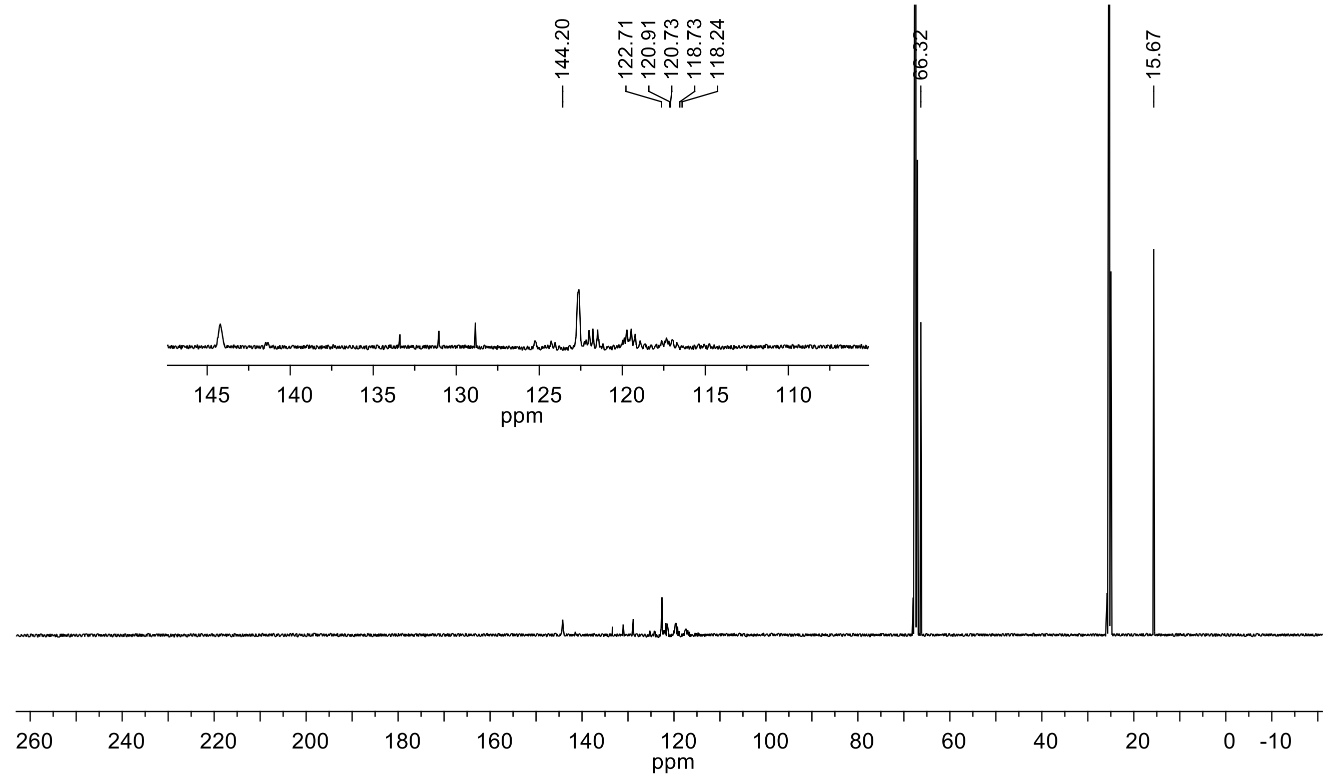

Figure S8. $^{13}C\{^1H\}$ NMR spectrum of K**2**·$(Et_2O)_{0.5}$ in [D$_8$]THF.

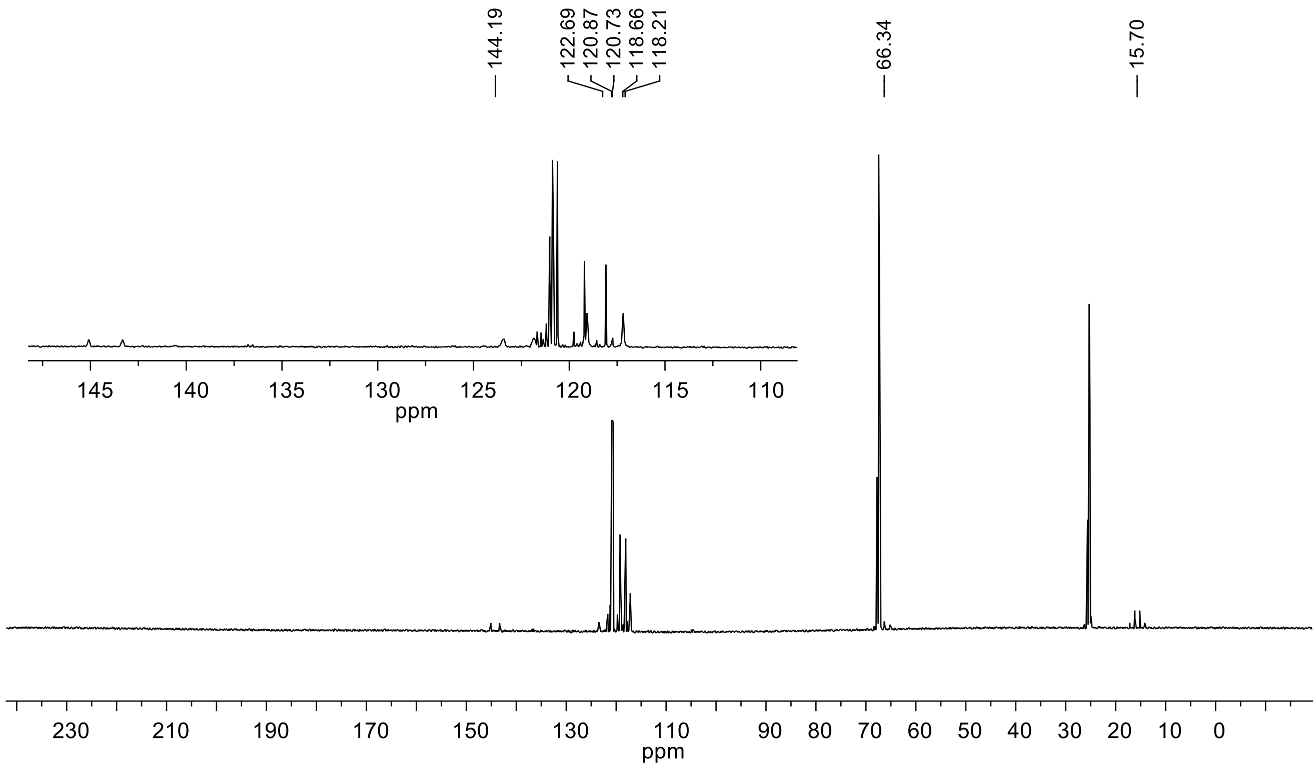

Figure S9. $^{13}C\{^{19}F\}$ NMR spectrum of K**2**·$(Et_2O)_{0.5}$ in [D$_8$]THF.

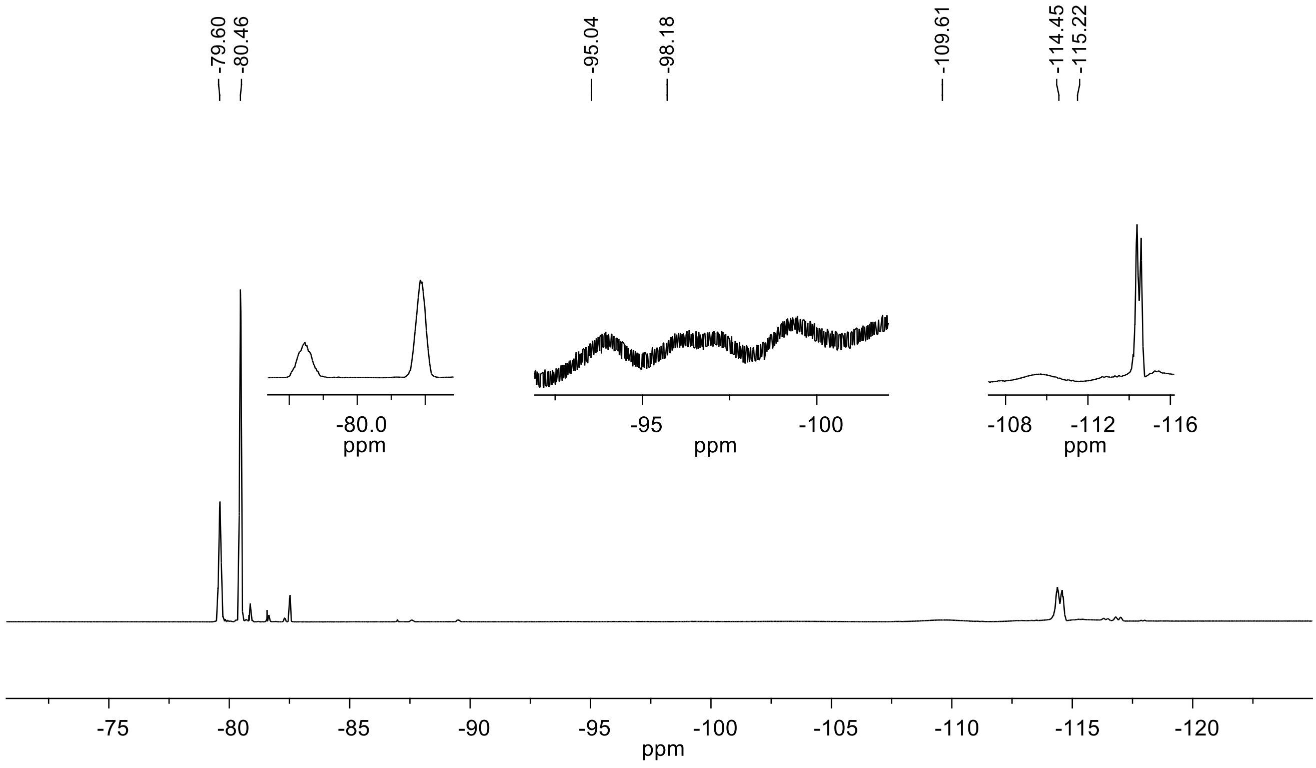

Figure S10. ^{19}F NMR spectrum of K**2**·$(Et_2O)_{0.5}$ in [D$_8$]THF.

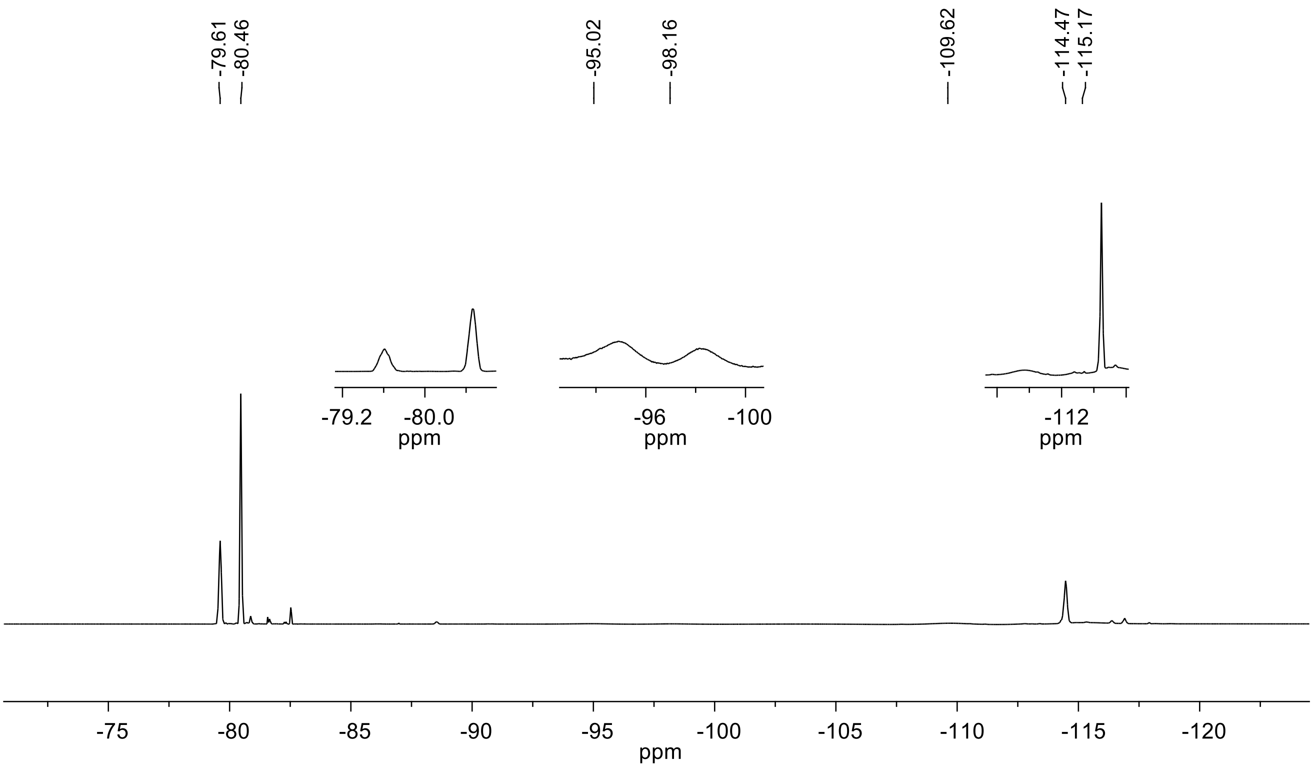

Figure S11. $^{19}F\{^{31}P\}$ NMR spectrum of K**2**·$(Et_2O)_{0.5}$ in $[D_8]$THF.

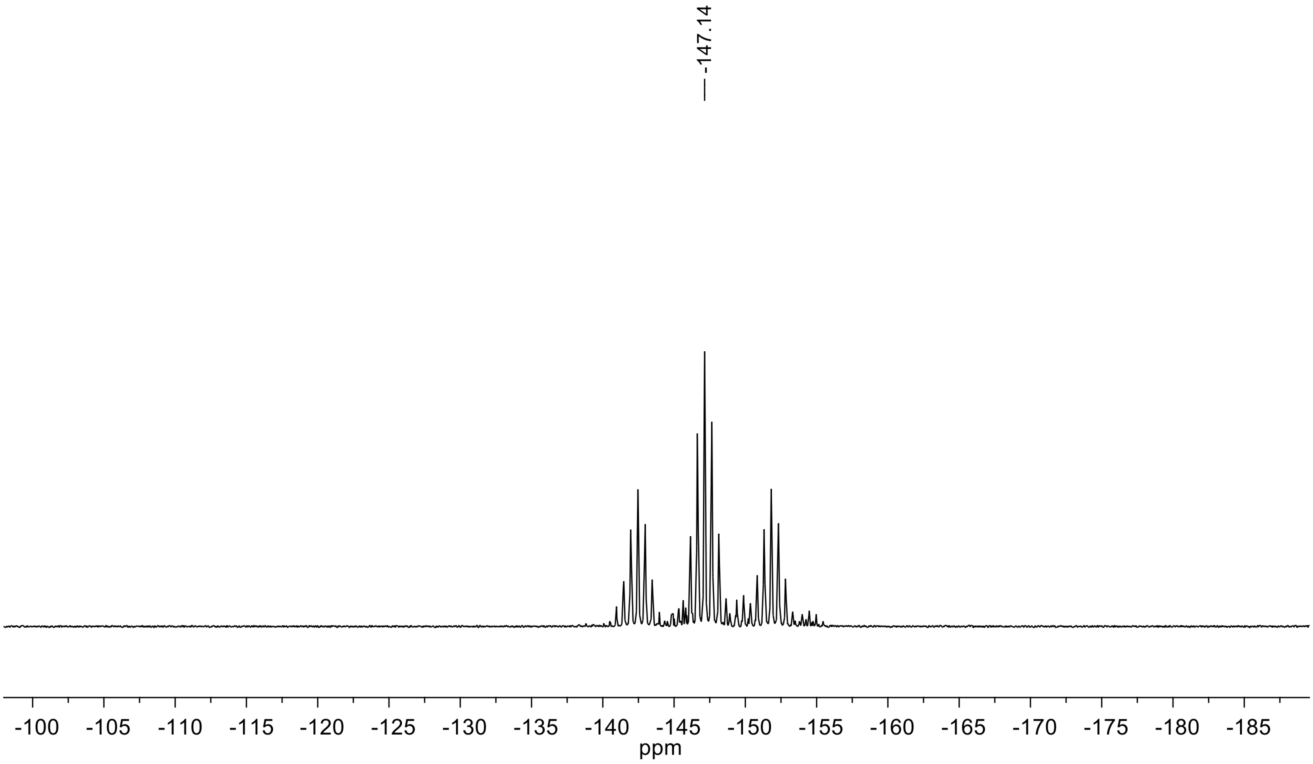

Figure S12. ^{31}P NMR spectrum of K**2**·$(Et_2O)_{0.5}$ in $[D_8]$THF.

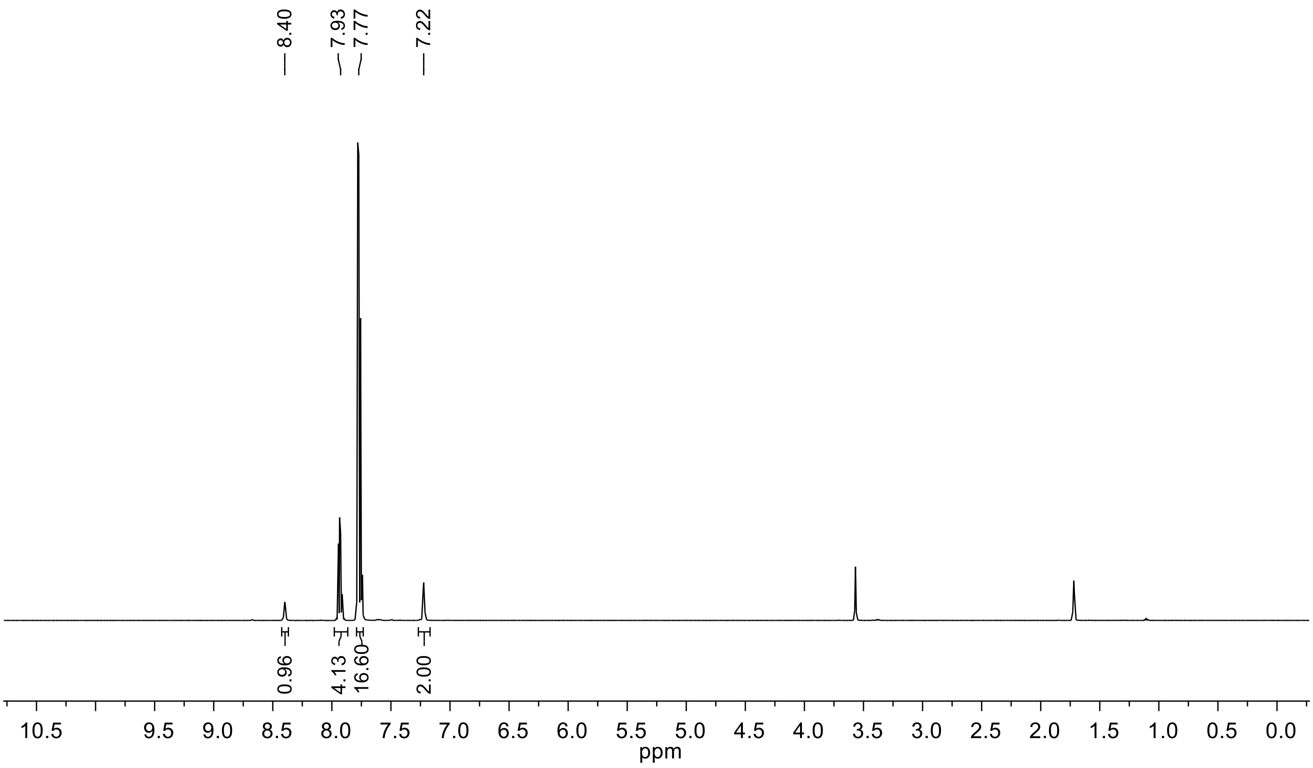

Figure S13. ^{1}H NMR spectrum of [PPh$_4$]**2** in [D$_8$]THF.

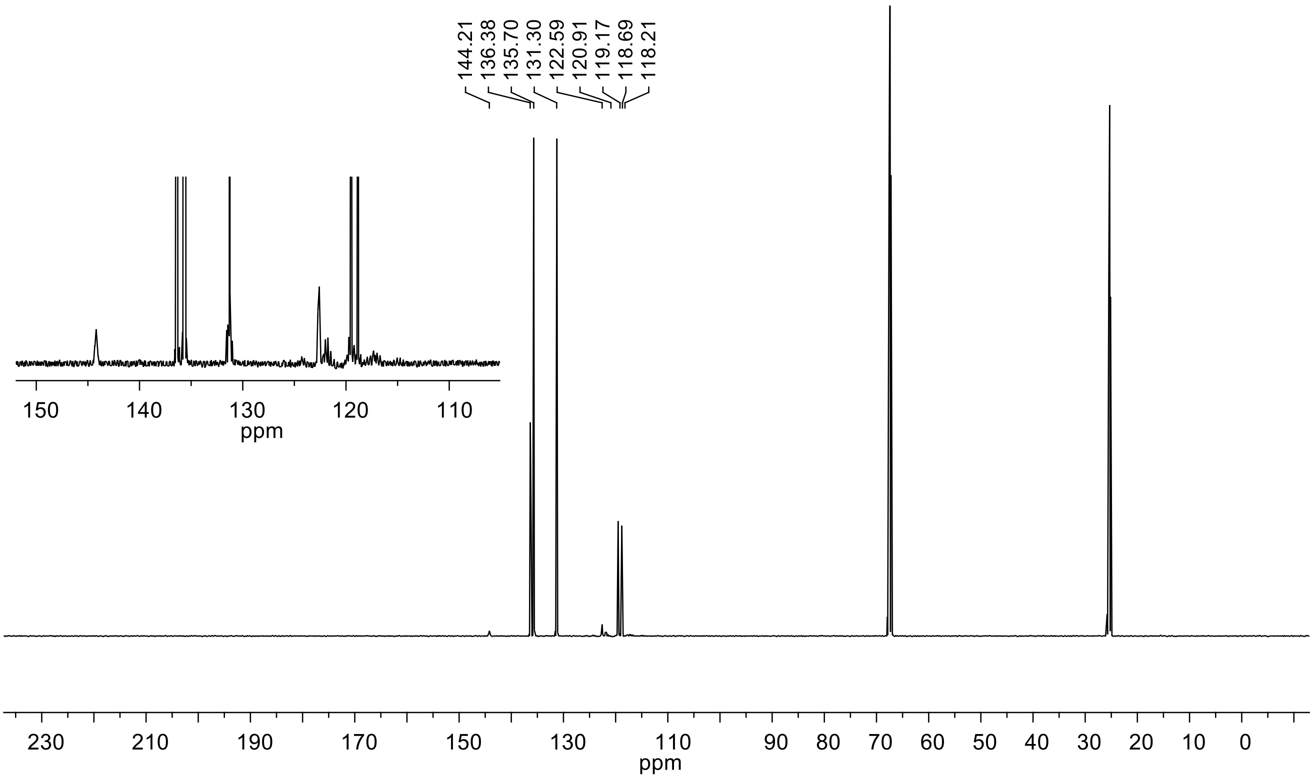

Figure S14. ^{13}C{^{1}H} NMR spectrum of [PPh$_4$]**2** in [D$_8$]THF.

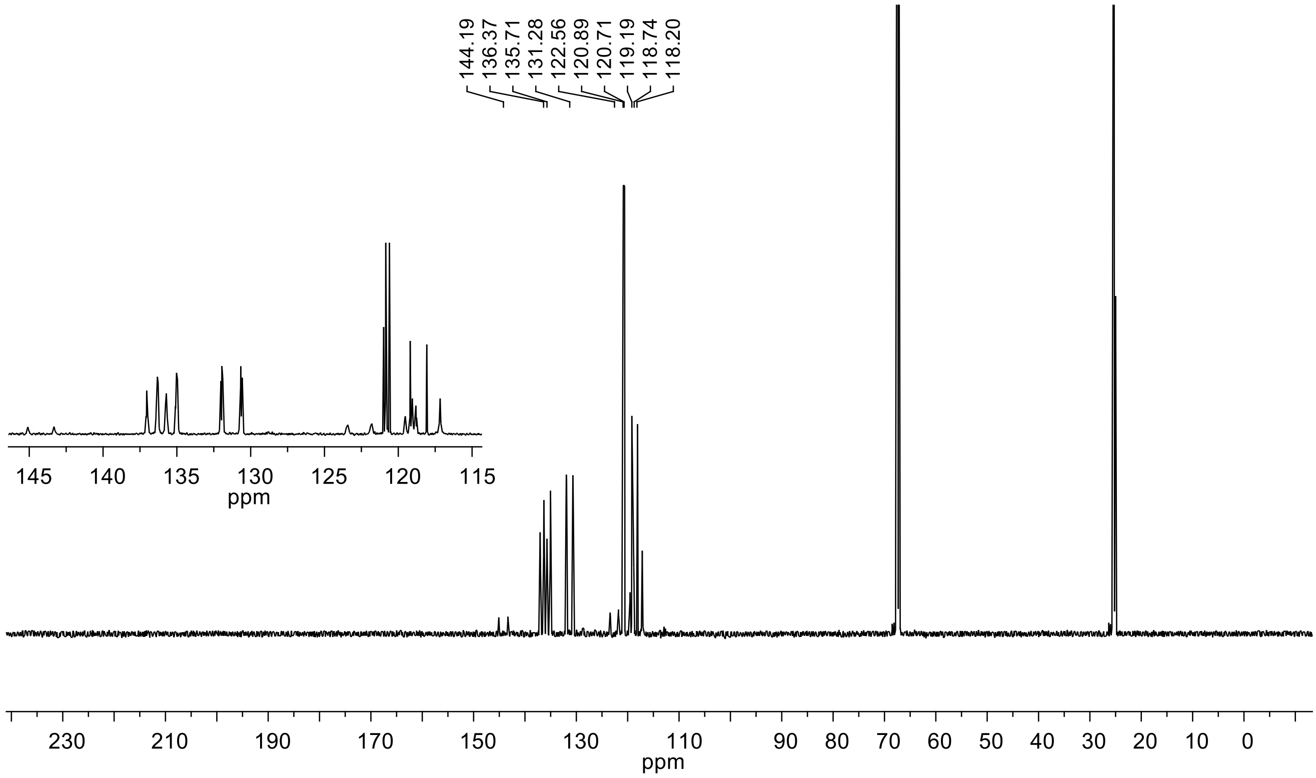

Figure S15. $^{13}C\{^{19}F\}$ NMR spectrum of [PPh$_4$]**2** in [D$_8$]THF.

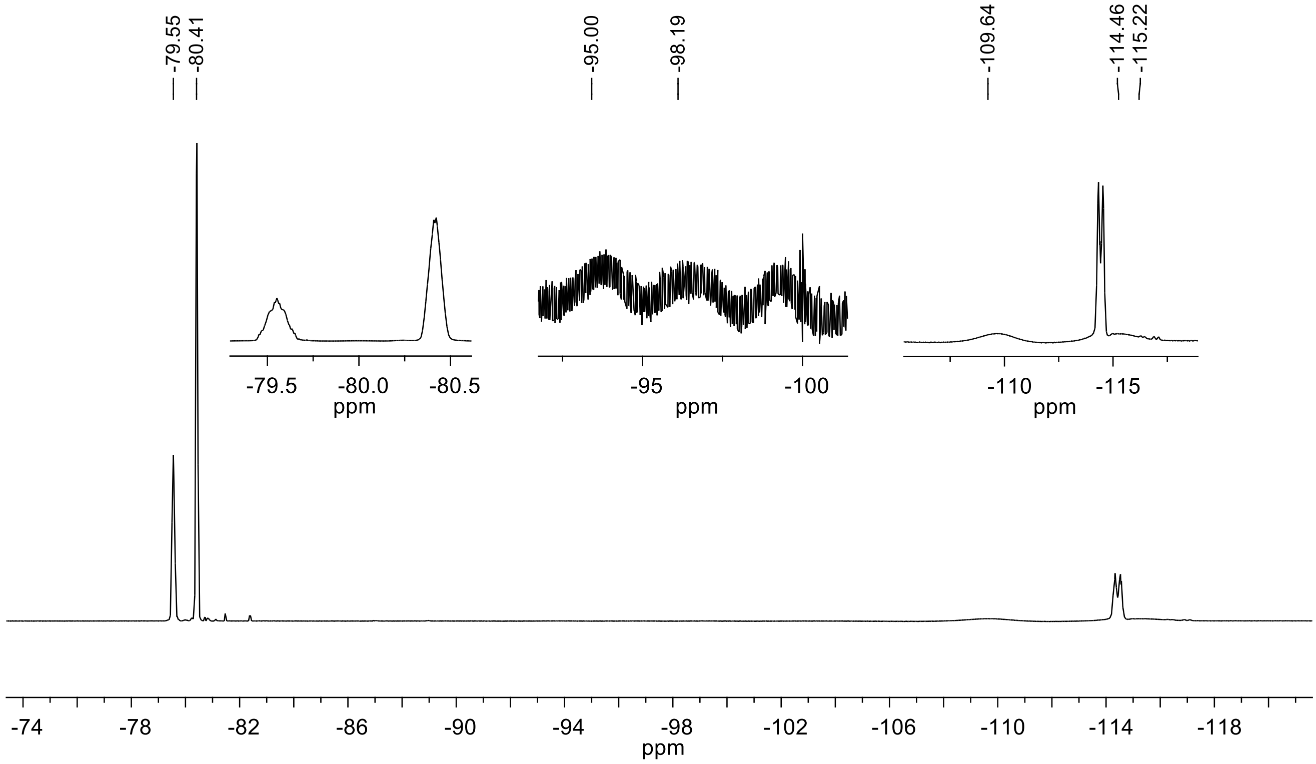

Figure S16. ^{19}F NMR spectrum of [PPh$_4$]**2** in [D$_8$]THF.

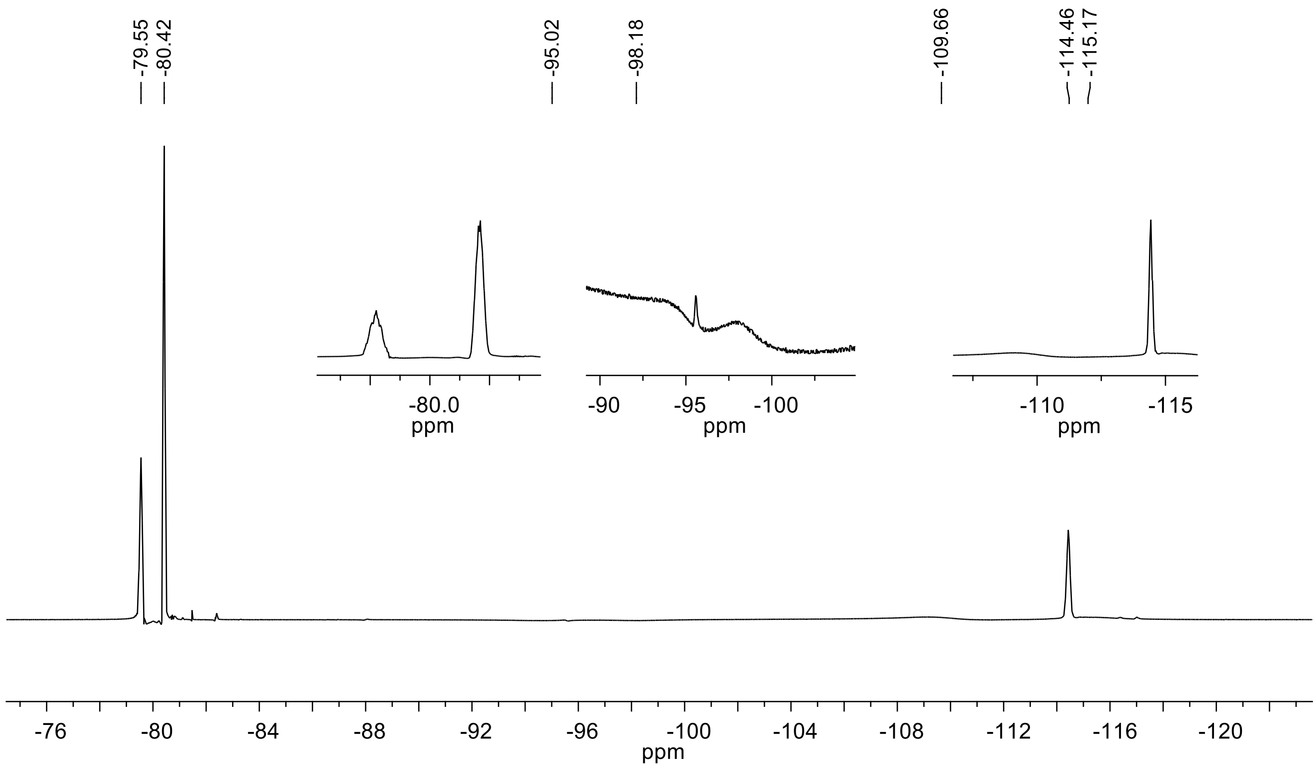

Figure S17. $^{19}F\{^{31}P\}$ NMR spectrum of [PPh$_4$]**2** in [D$_8$]THF.

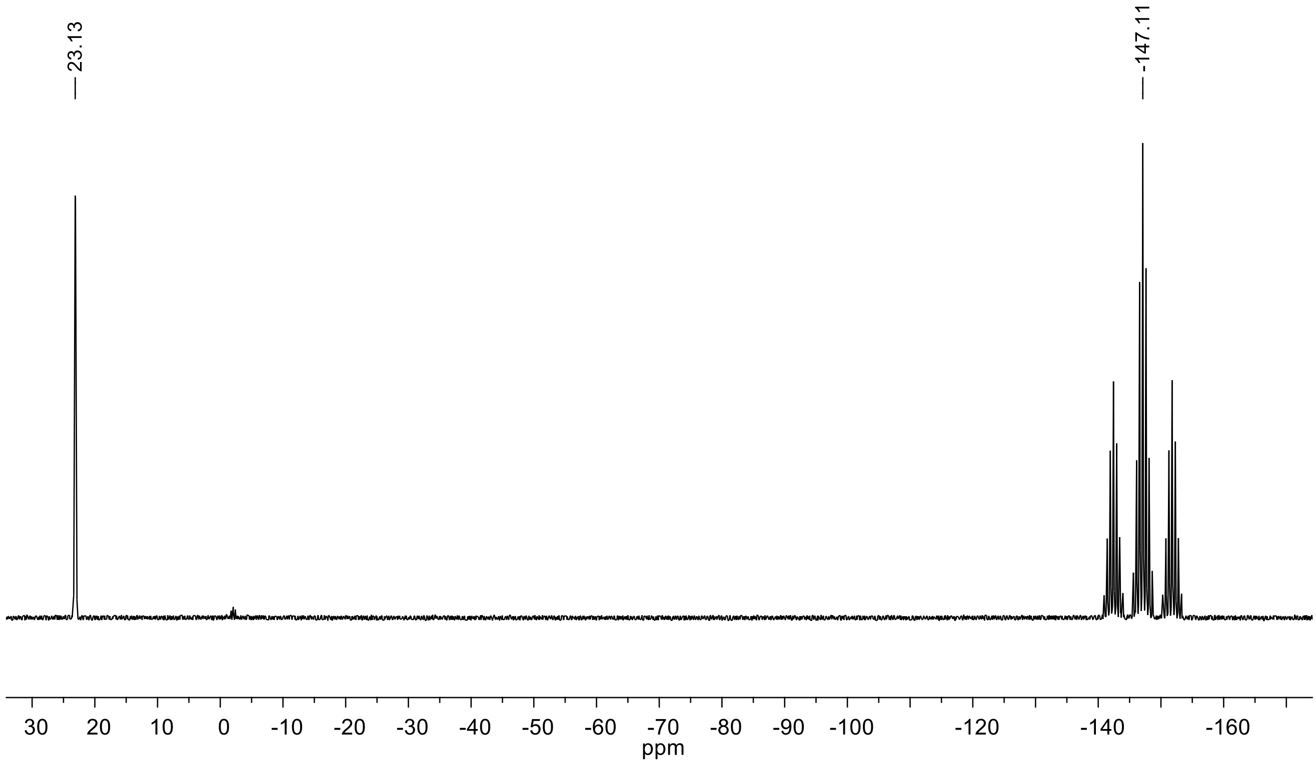

Figure S18. $^{19}F\{^{31}P\}$ NMR spectrum of [PPh$_4$]**2** in [D$_8$]THF.

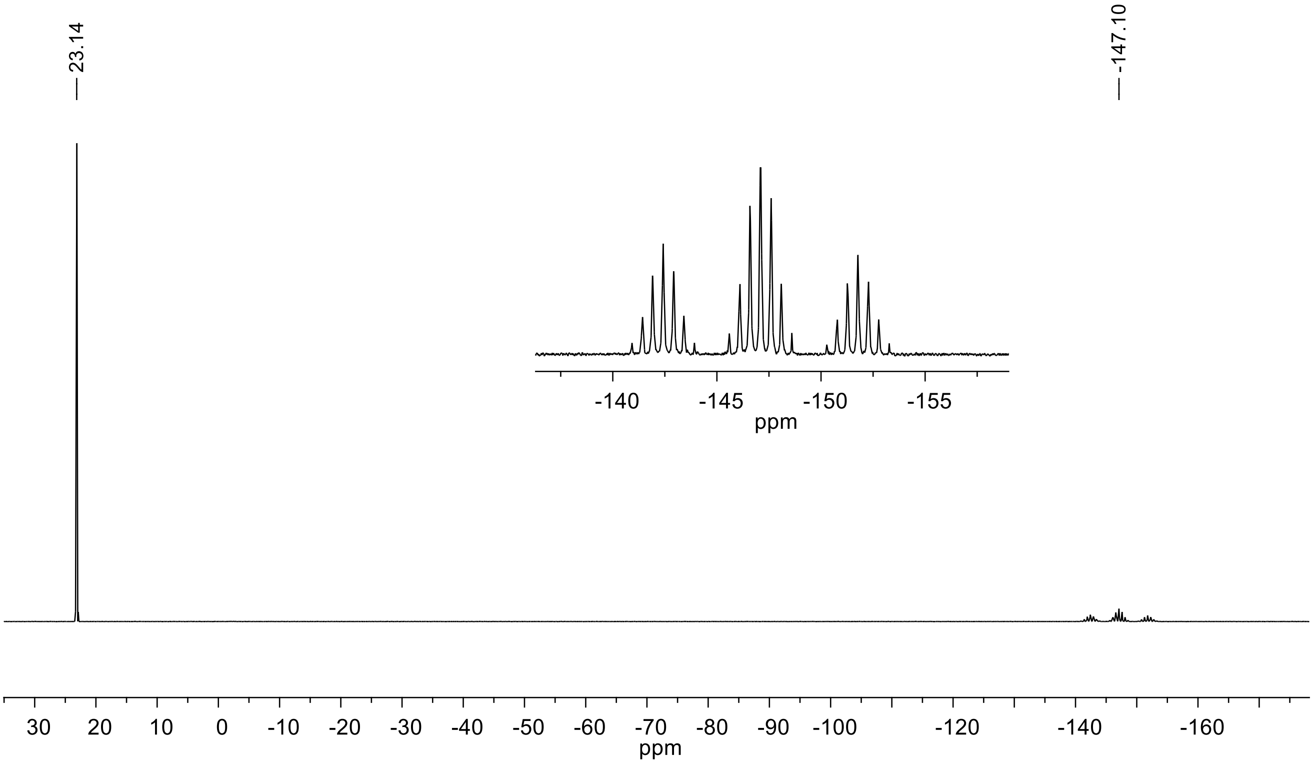

Figure S19. $^{31}P\{^1H\}$ NMR spectrum of [PPh$_4$]**2** in [D$_8$]THF.

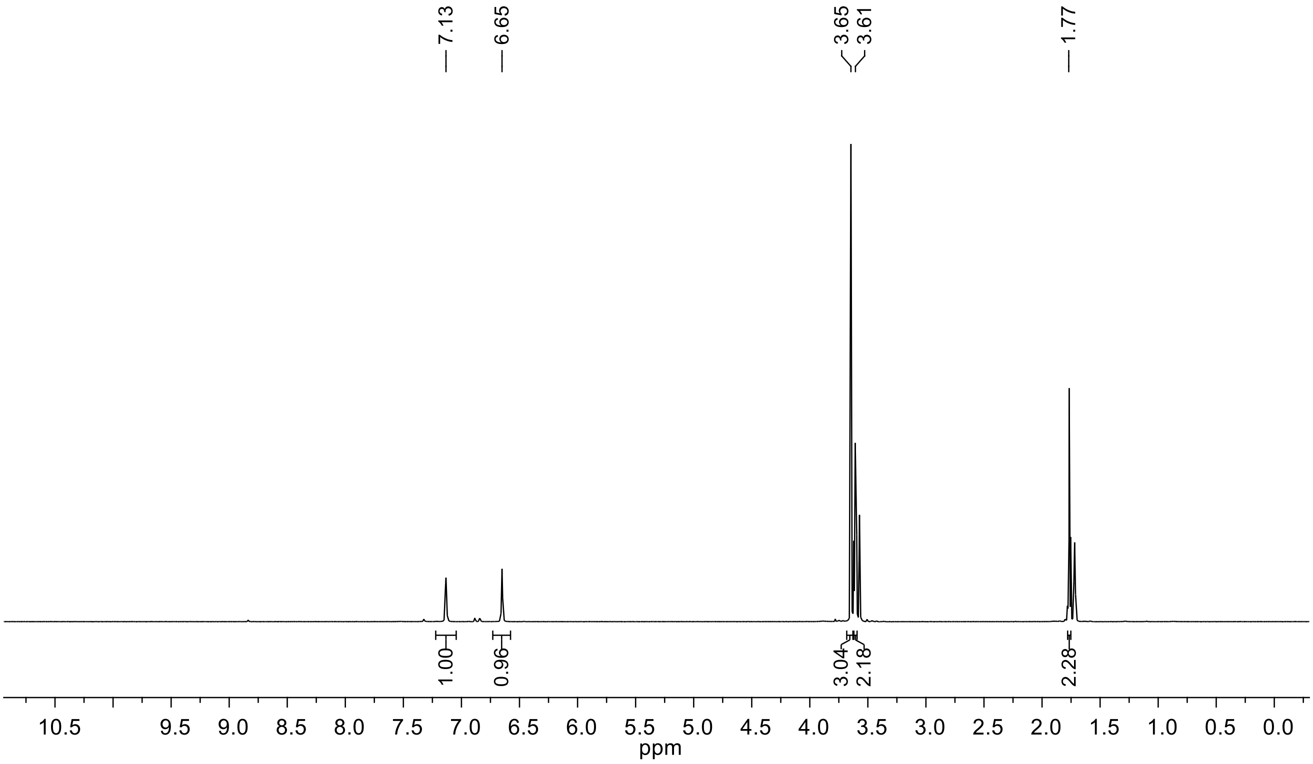

Figure S20. ^1H NMR spectrum of K**3**·THF$_{0.5}$ in [D$_8$]THF.

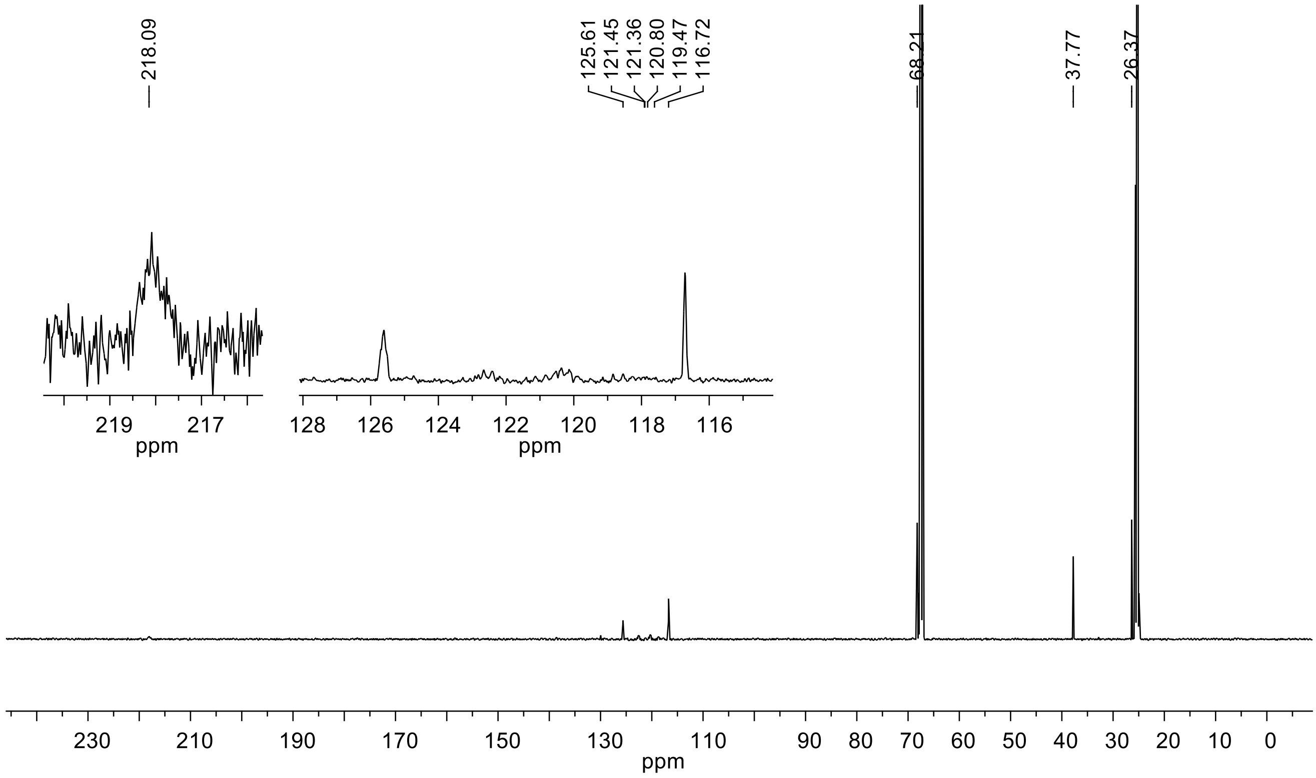

Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of K**3**·$THF_{0.5}$ in $[D_8]THF$.

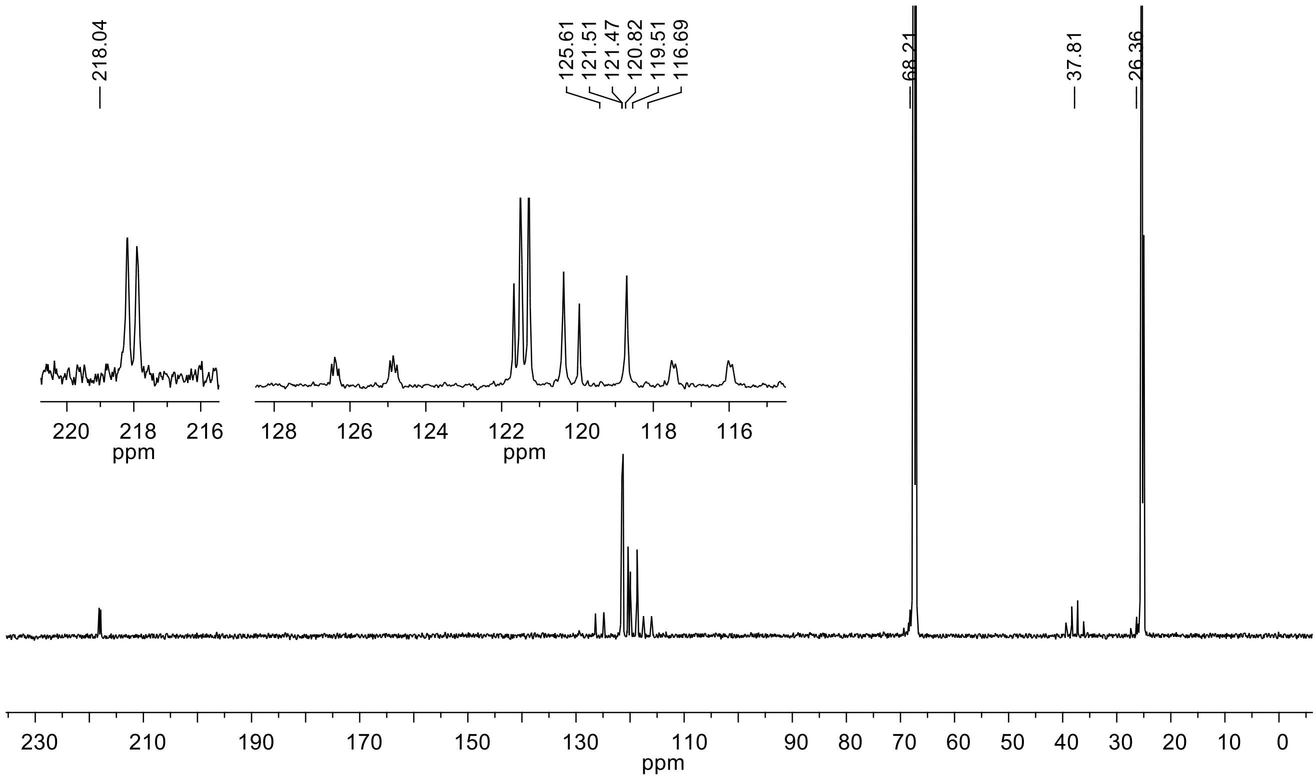

Figure S22. $^{13}C\{^{19}F\}$ NMR spectrum of K**3**·$THF_{0.5}$ in $[D_8]THF$.

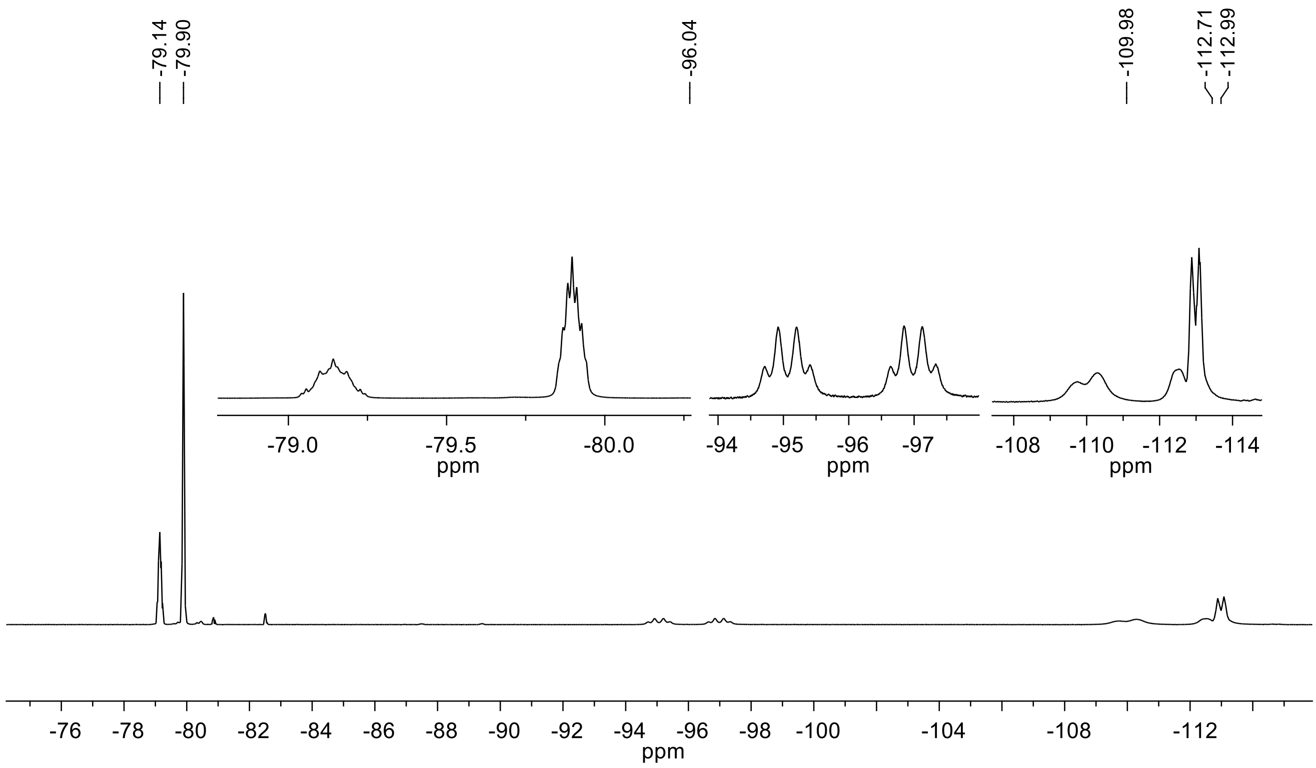

Figure S23. ^{19}F NMR spectrum of K**3**·THF$_{0.5}$ in [D$_8$]THF.

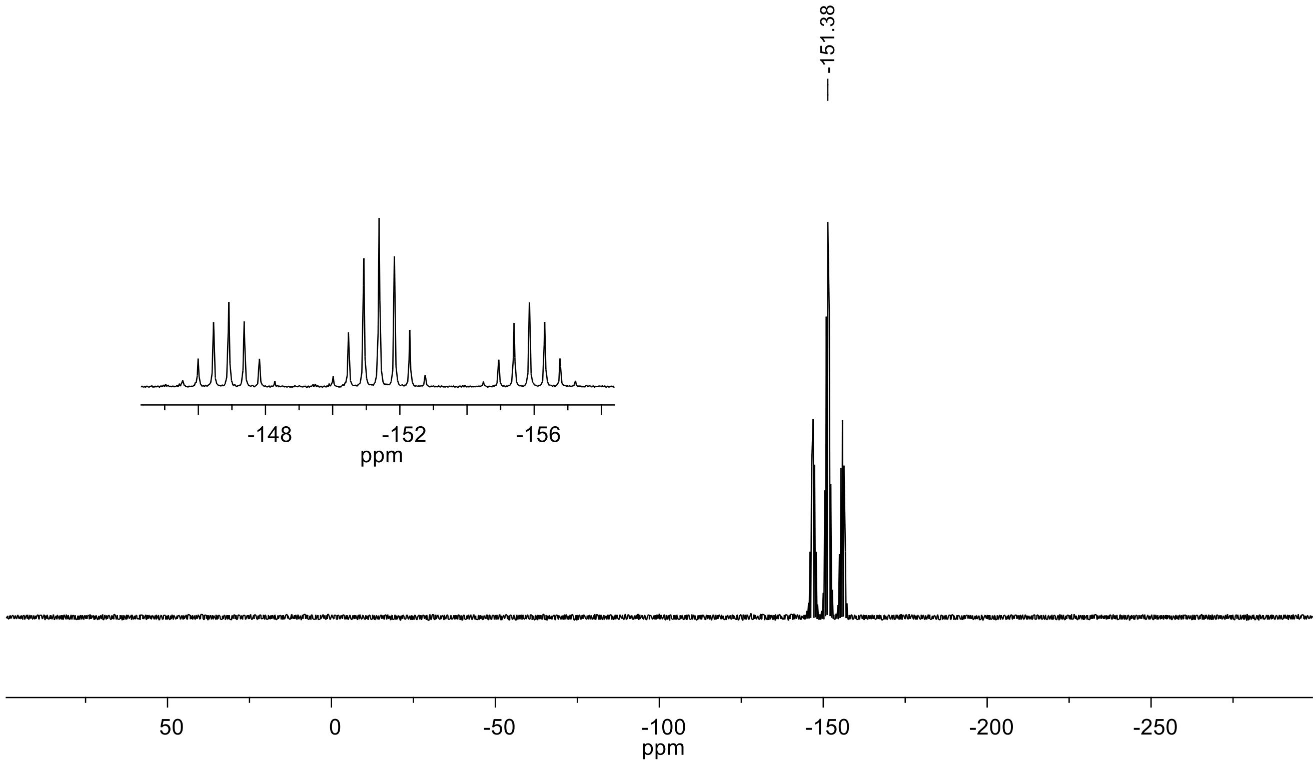

Figure S24. ^{31}P NMR spectrum of K**3**·THF$_{0.5}$ in [D$_8$]THF.

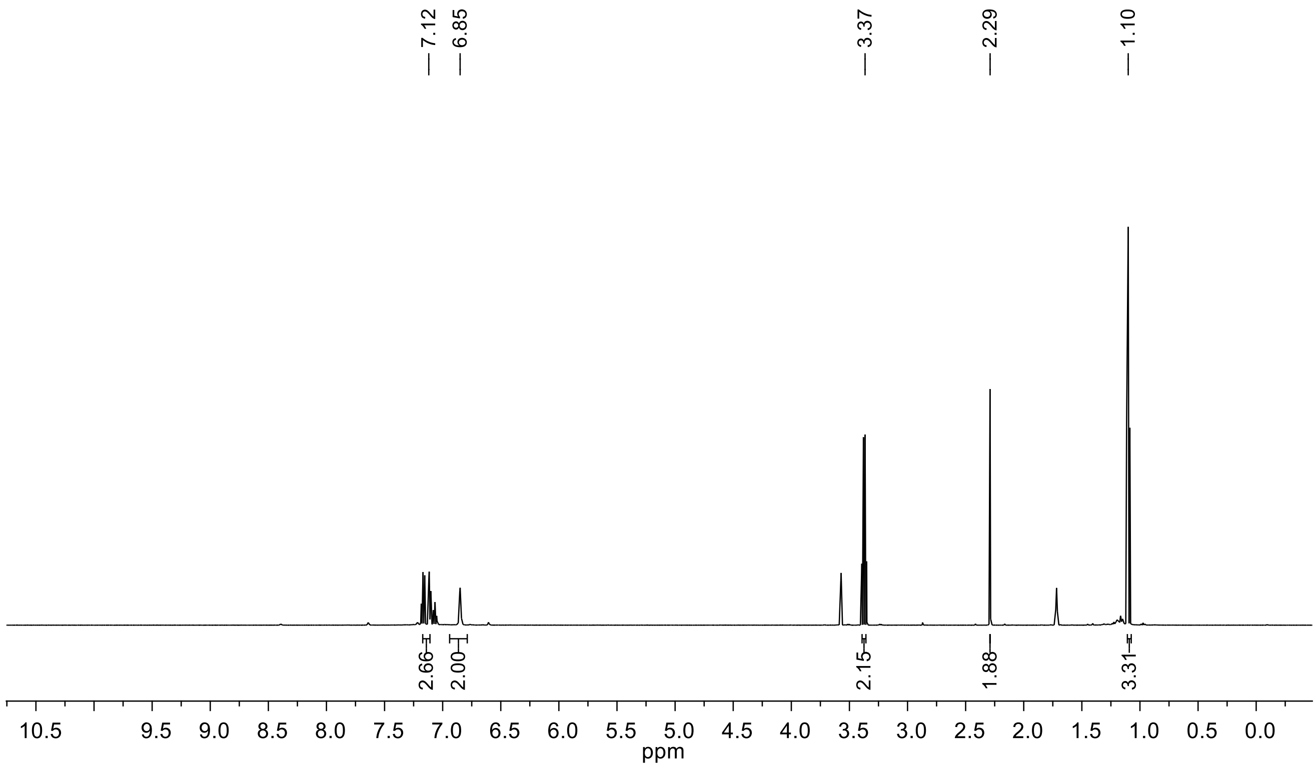

Figure S25. ^{1}H NMR spectrum of K_2**4**·$(Et_2O)_{0.5}$,$(C_7H_8)_{0.5}$ in [D$_8$]THF.

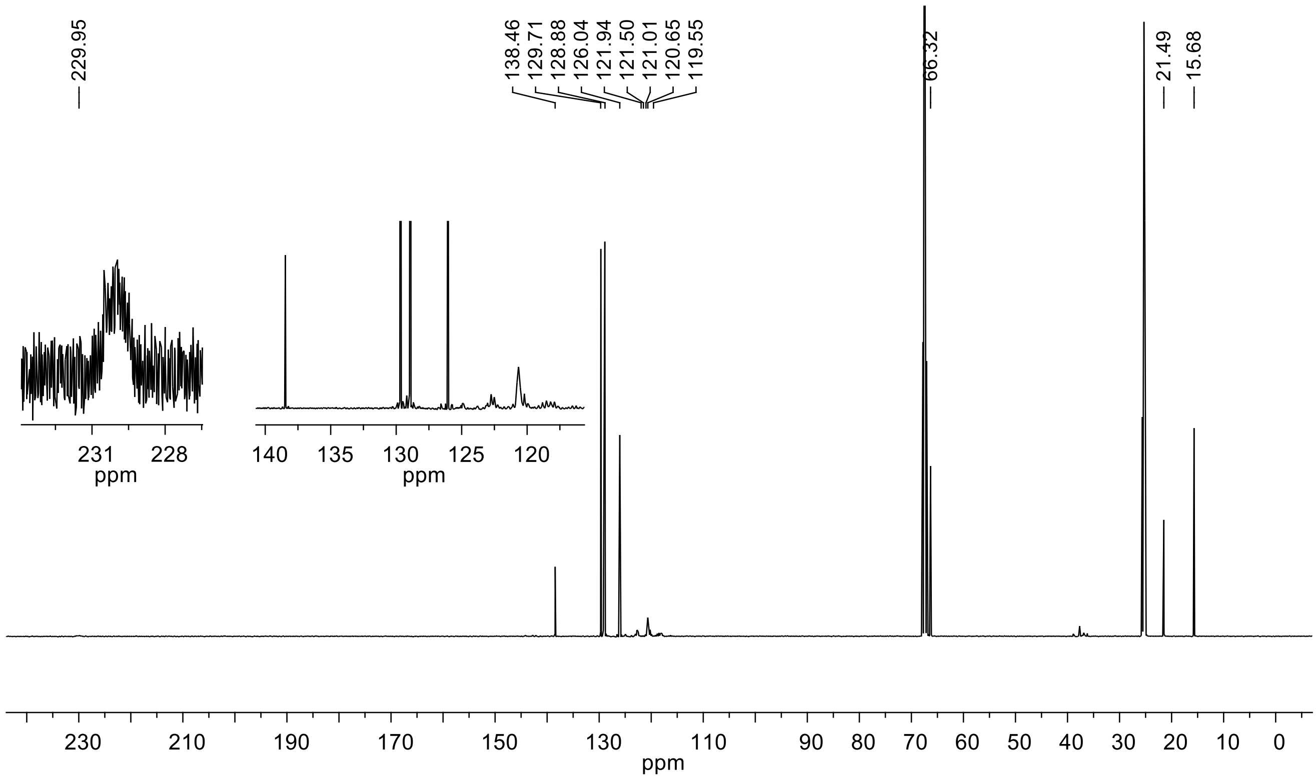

Figure S26. ^{13}C{^{1}H} NMR spectrum of K_2**4**·$(Et_2O)_{0.5}$,$(C_7H_8)_{0.5}$ in [D$_8$]THF.

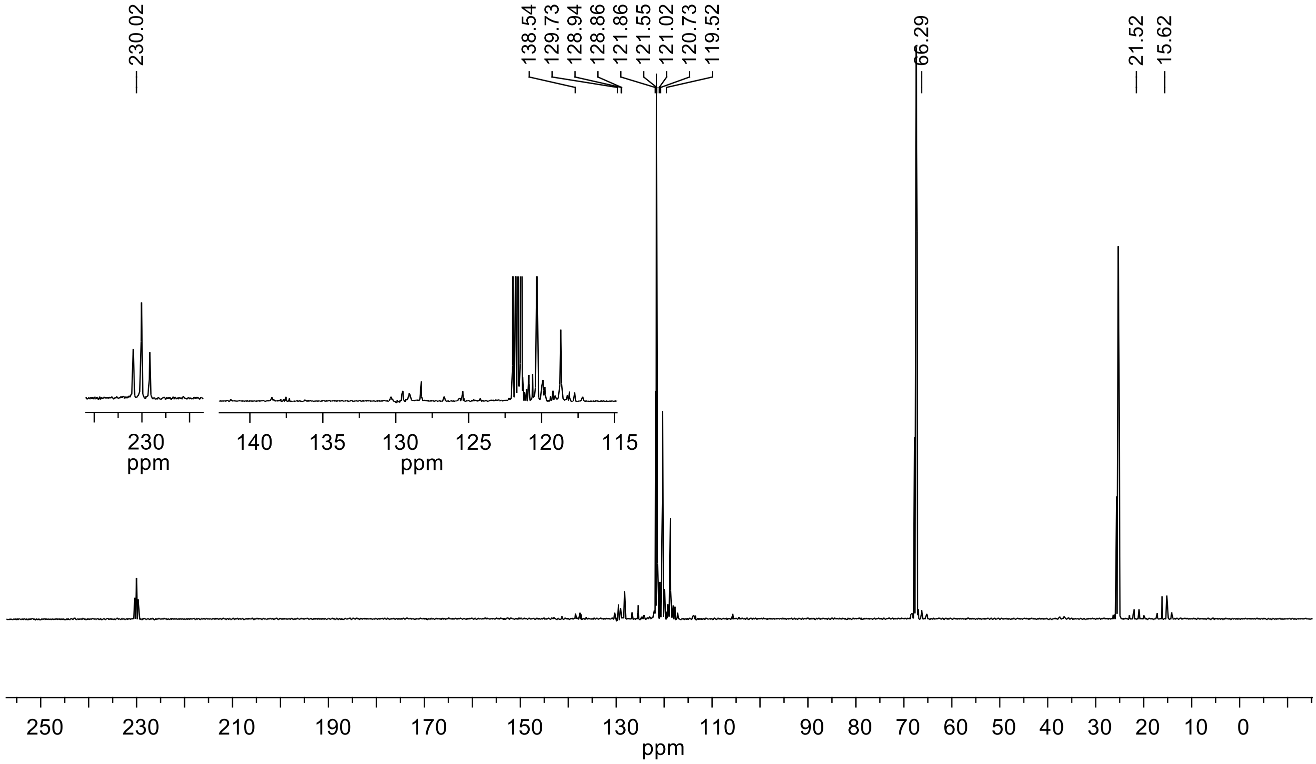

Figure S27. $^{13}C\{^{19}F\}$ NMR spectrum of K_2**4**$\cdot(Et_2O)_{0.5},(C_7H_8)_{0.5}$ in $[D_8]THF$.

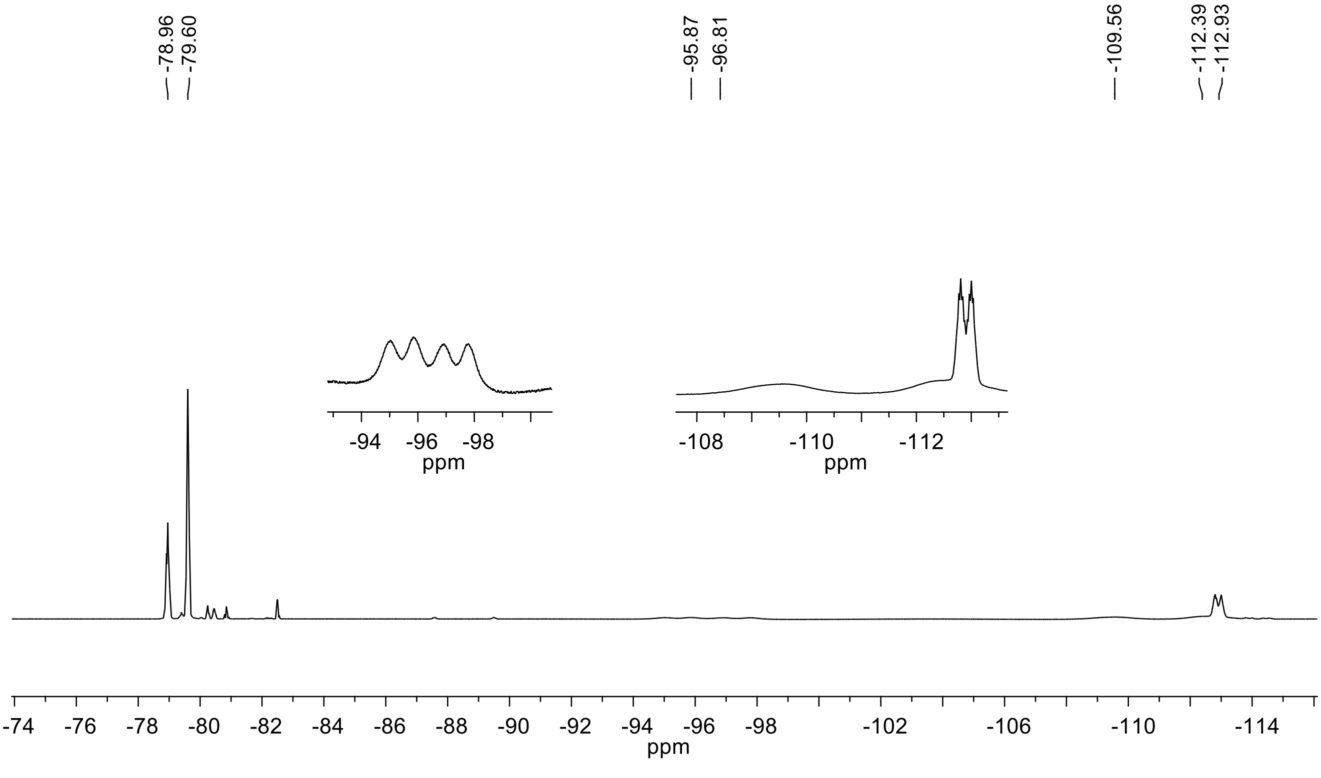

Figure S28. ^{19}F NMR spectrum of K_2**4**$\cdot(Et_2O)_{0.5},(C_7H_8)_{0.5}$ in $[D_8]THF$.

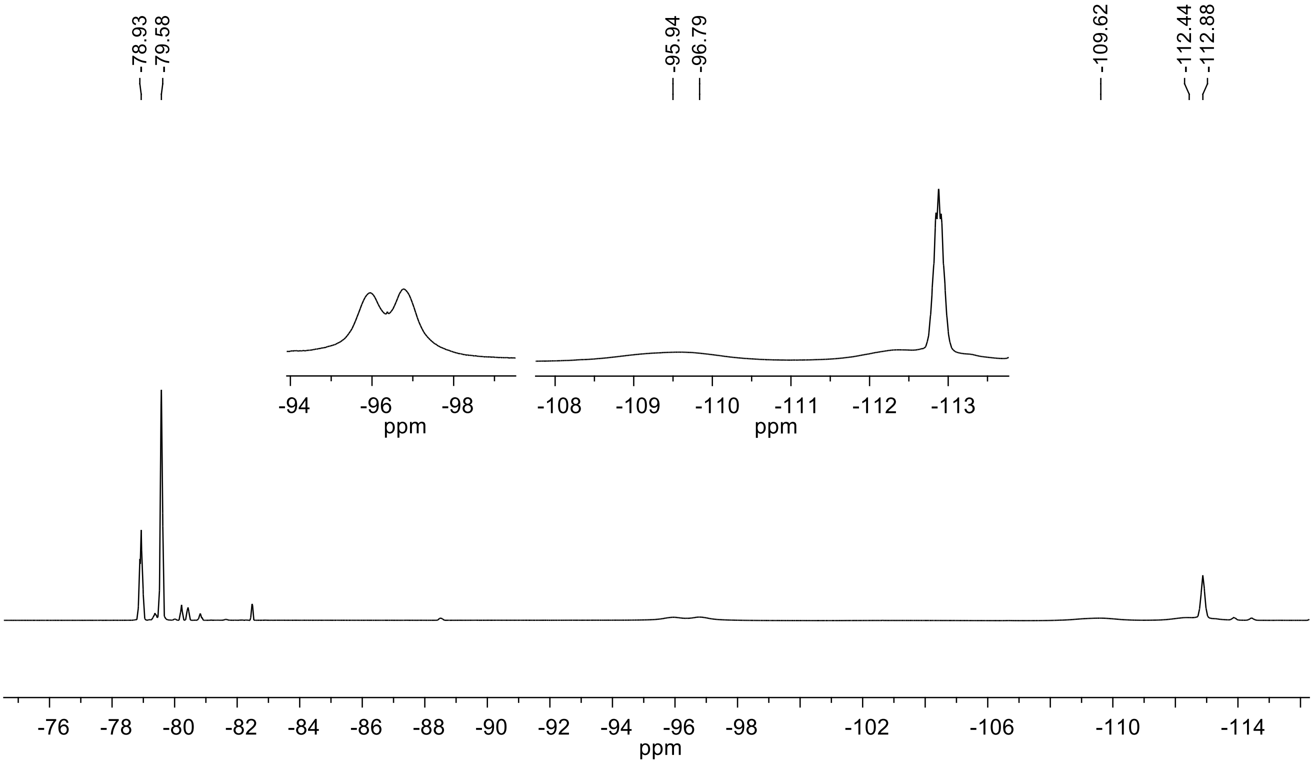

Figure S29. $^{19}F\{^{31}P\}$ NMR spectrum of K_2**4**·$(Et_2O)_{0.5}$,$(C_7H_8)_{0.5}$ in [D_8]THF.

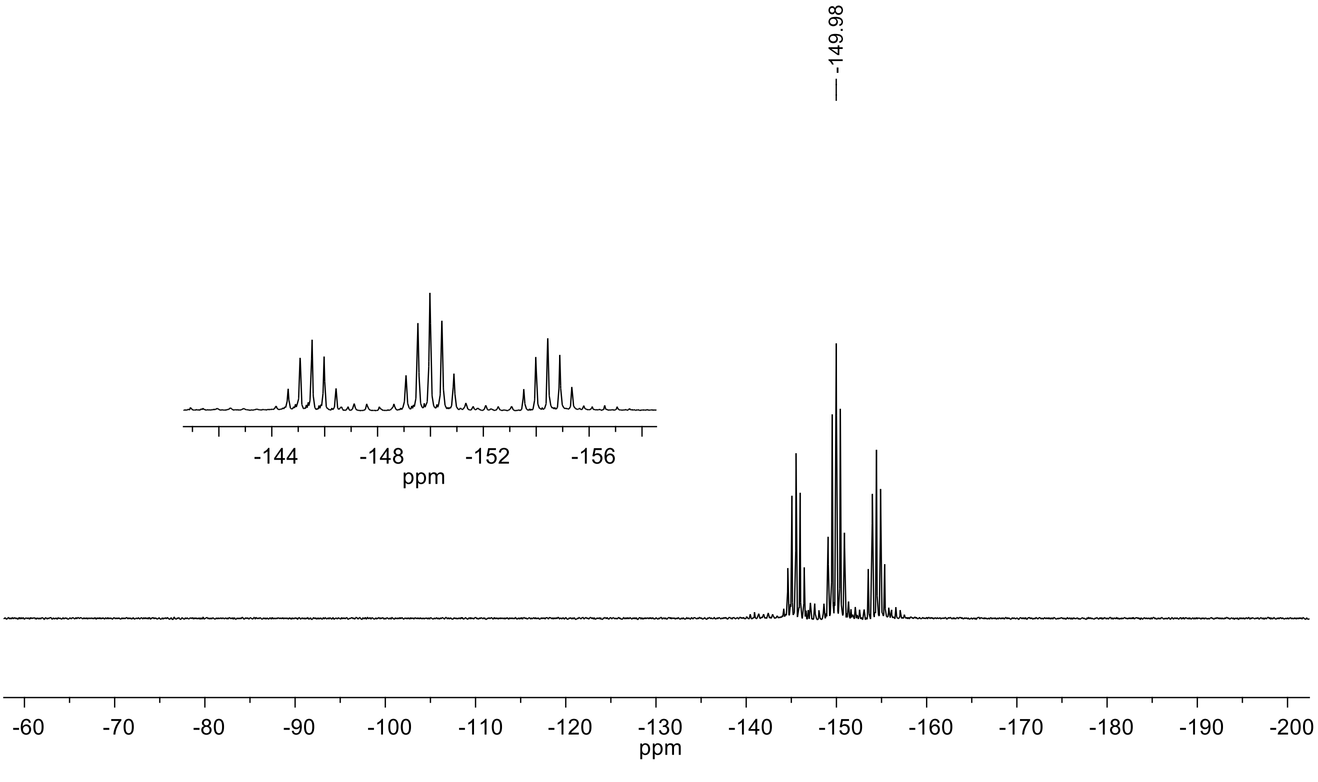

Figure S30. ^{31}P NMR spectrum of K_2**4**·$(Et_2O)_{0.5}$,$(C_7H_8)_{0.5}$ in [D_8]THF.

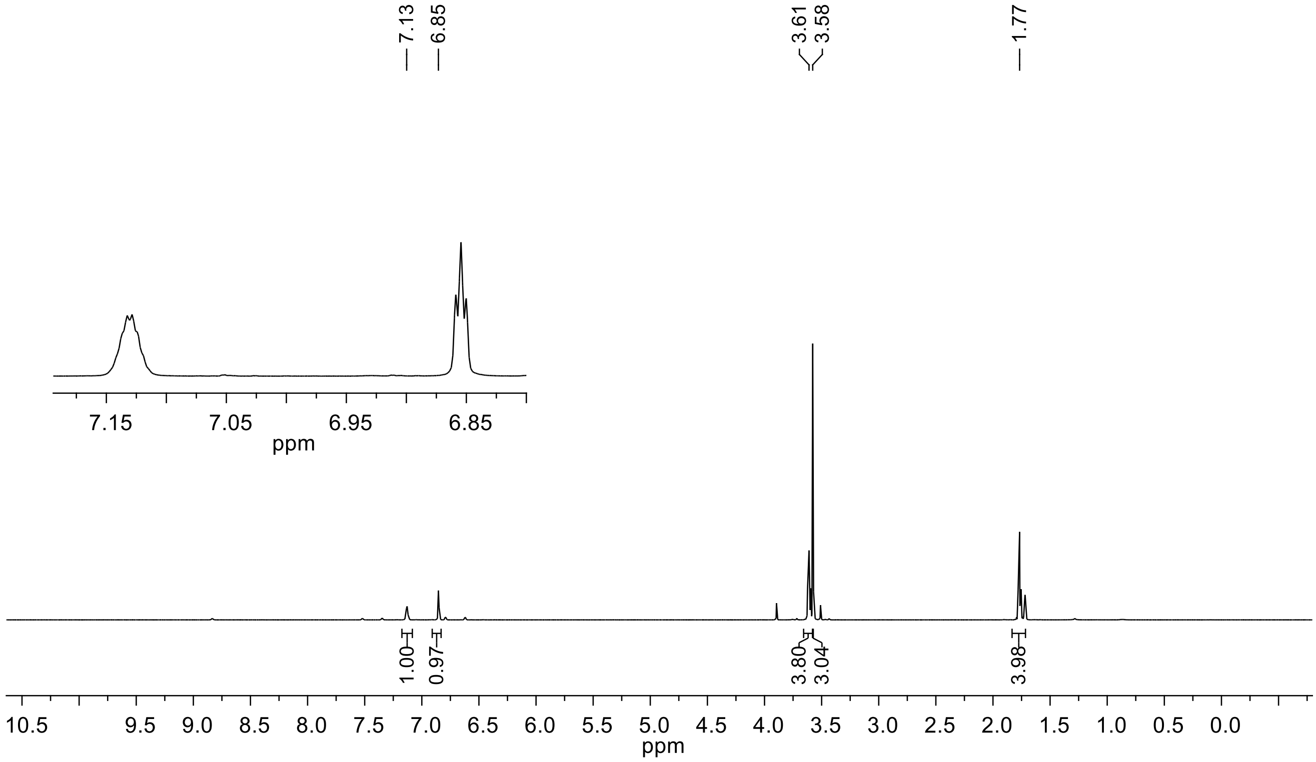

Figure S31. ^{1}H NMR spectrum of K**5**·THF in [D$_8$]THF.

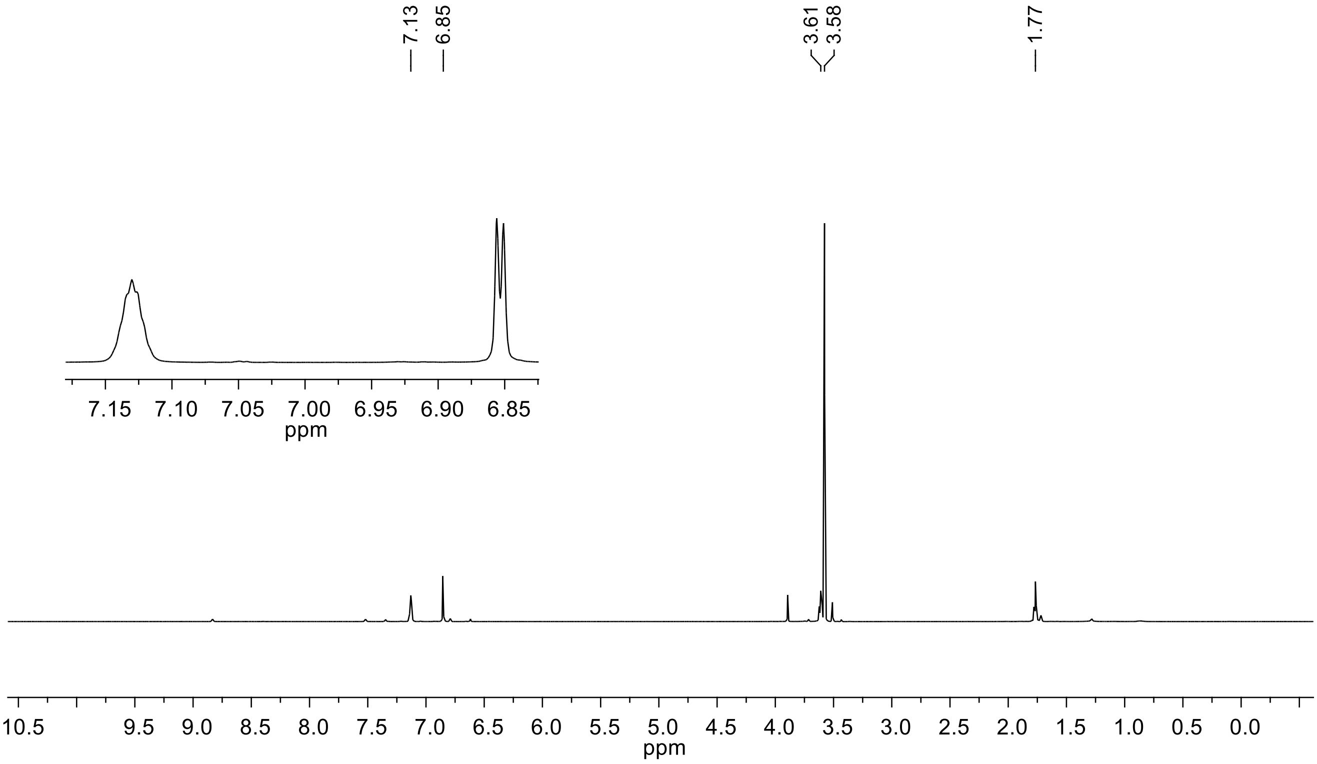

Figure S32. ^{1}H{^{31}P} NMR spectrum of K**5**·THF in [D$_8$]THF.

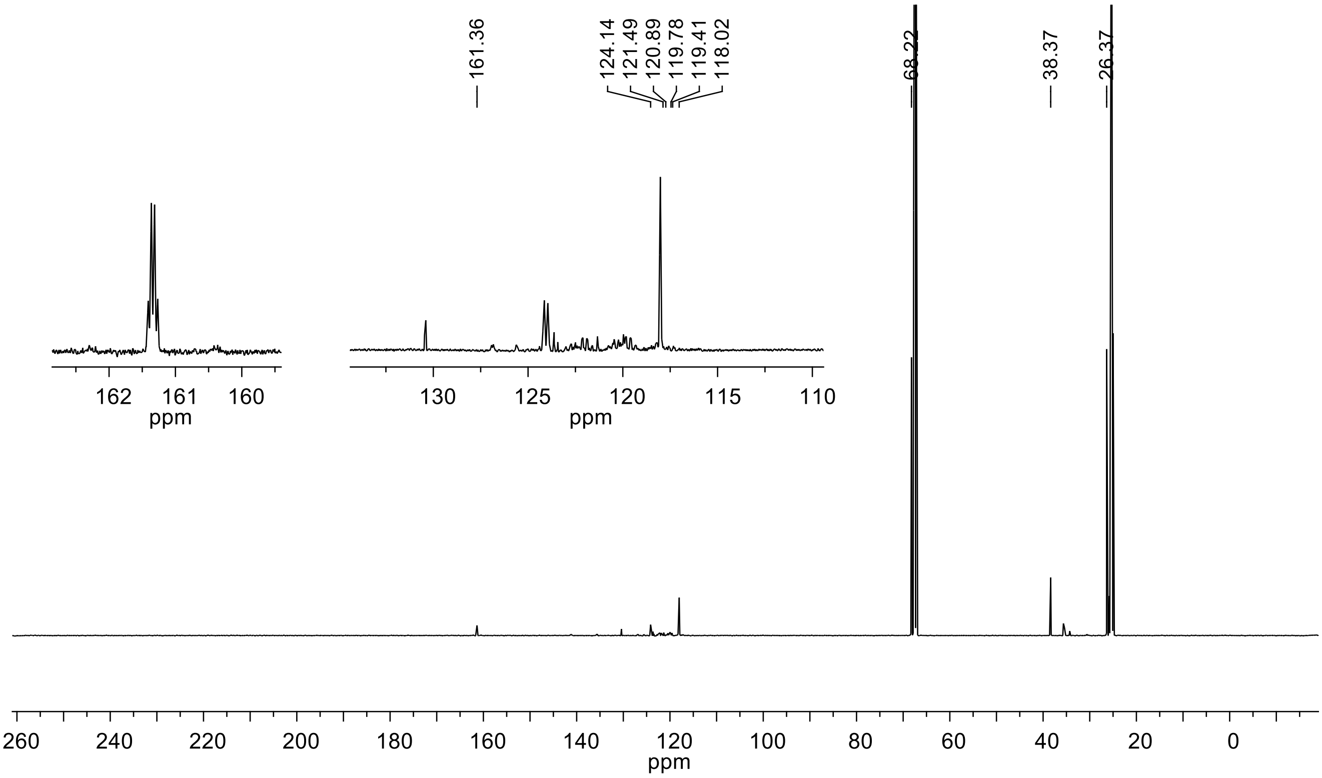

Figure S33. $^{13}C\{^1H\}$ NMR spectrum of K**5**·THF in [D$_8$]THF.

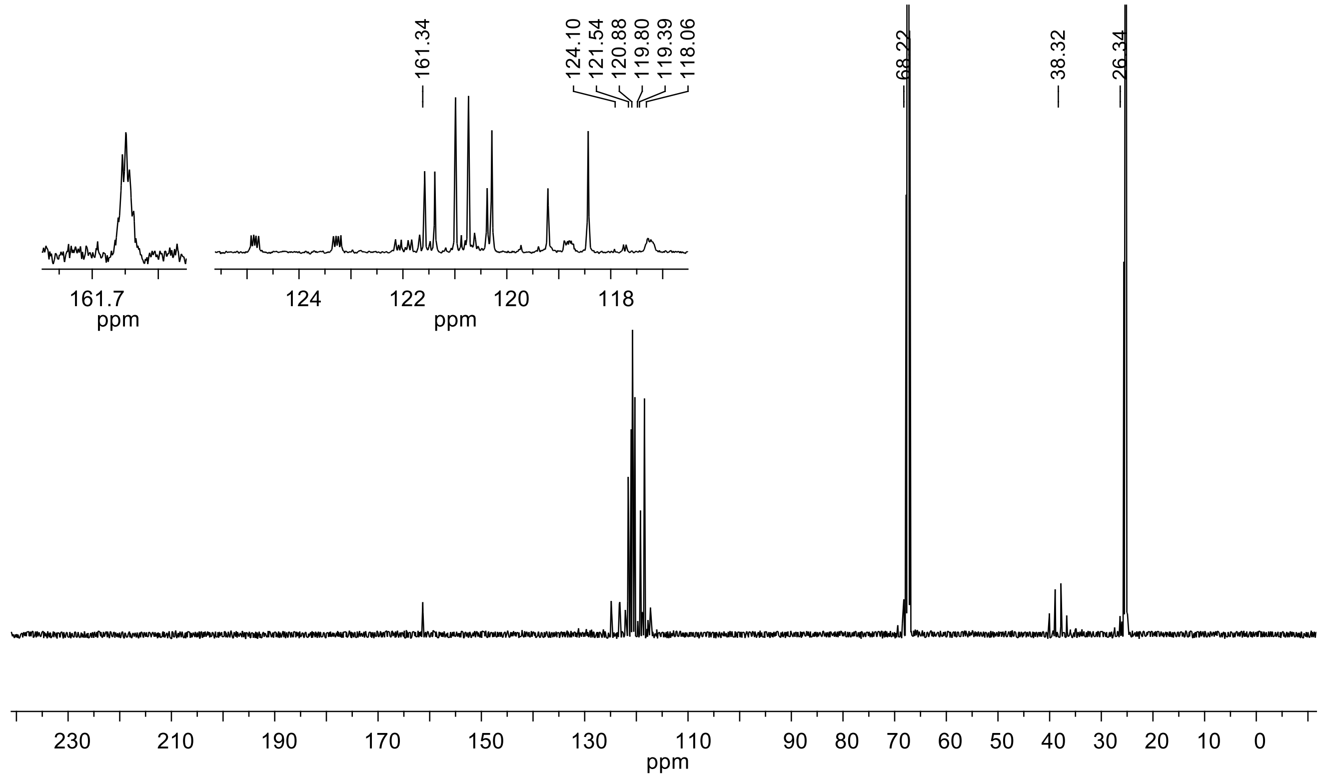

Figure S34. $^{13}C\{^{19}F\}$ NMR spectrum of K**5**·THF in [D$_8$]THF.

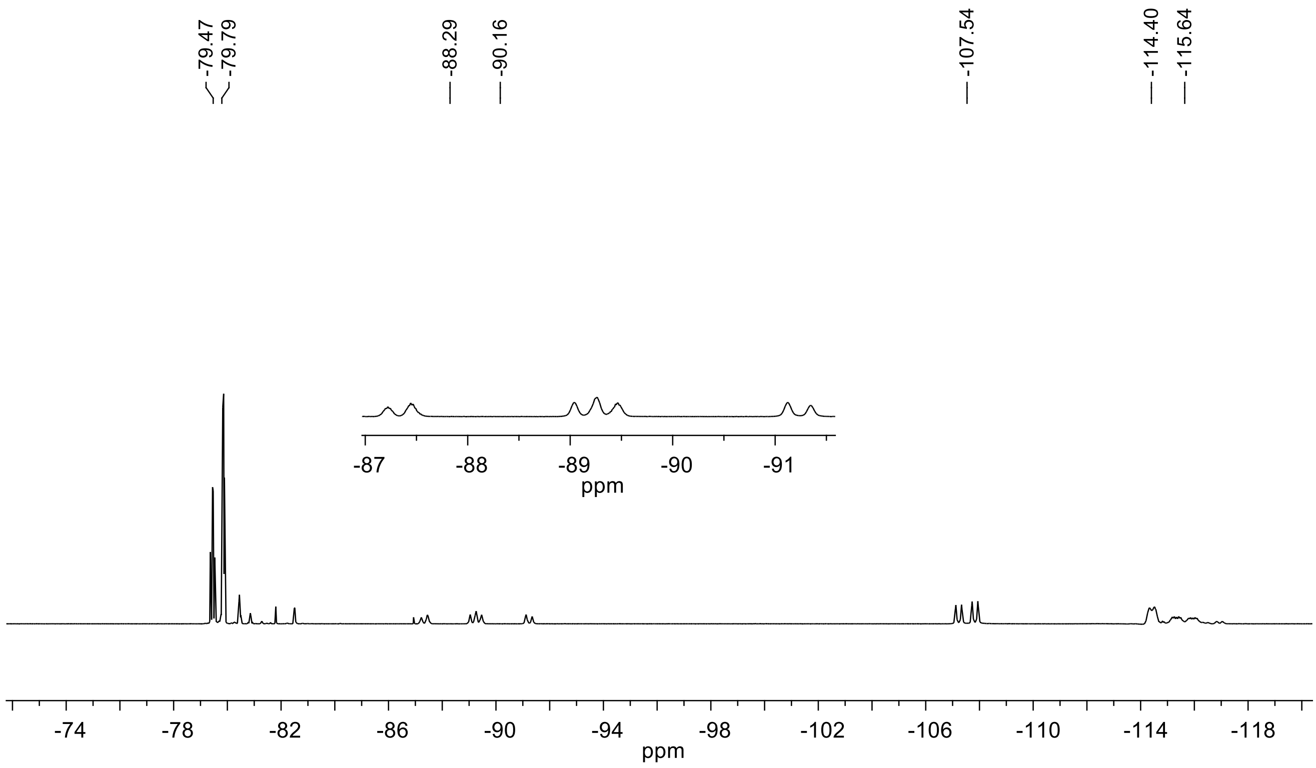

Figure S35. ^{19}F NMR spectrum of K**5**·THF in [D$_8$]THF.

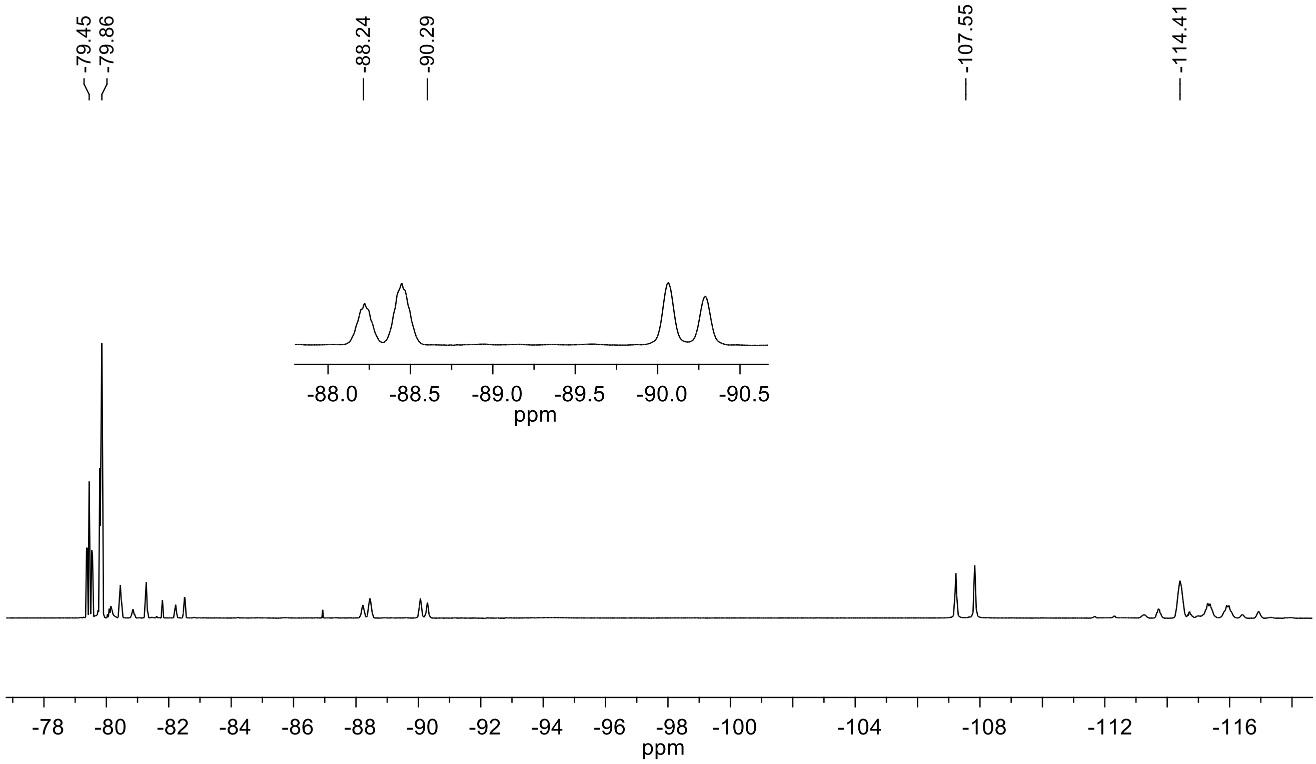

Figure S36. ^{19}F{^{31}P} NMR spectrum of K**5**·THF in [D$_8$]THF.

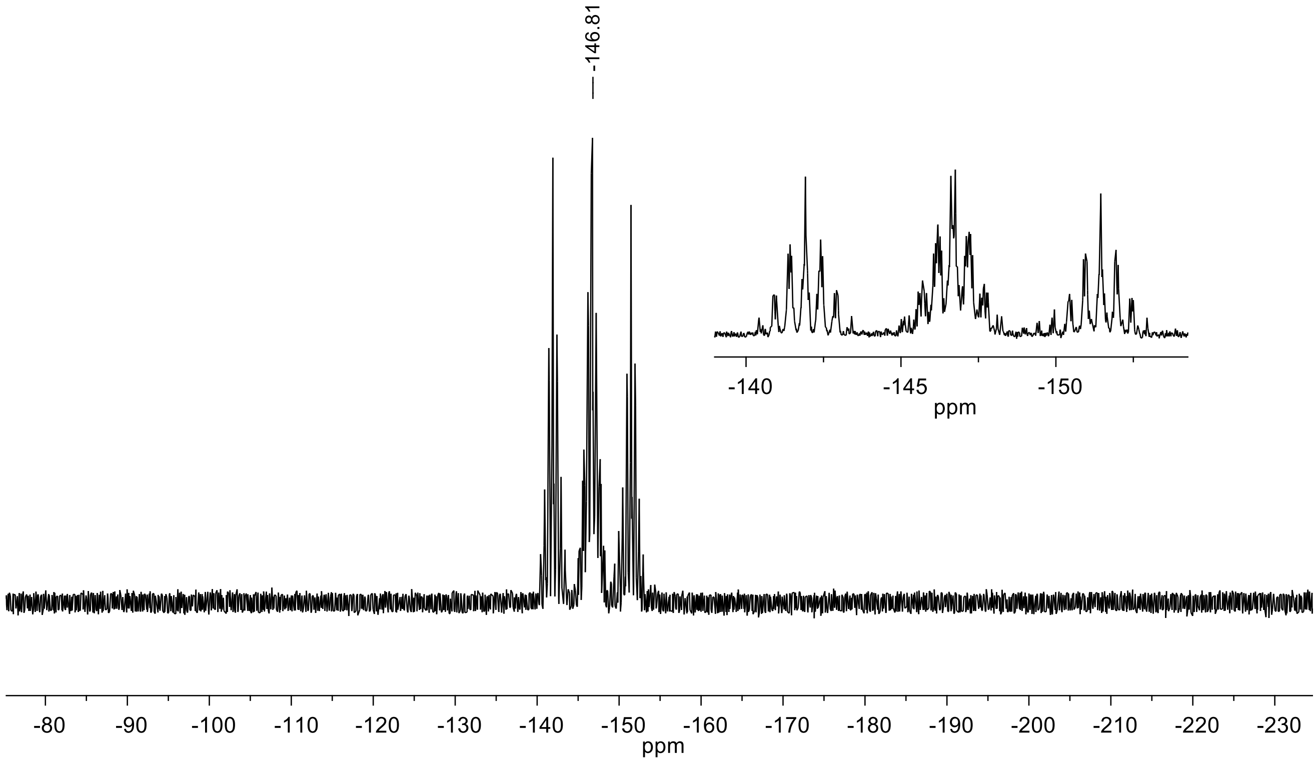

Figure S37. ^{31}P NMR spectrum of K**5**·THF in [D$_8$]THF.

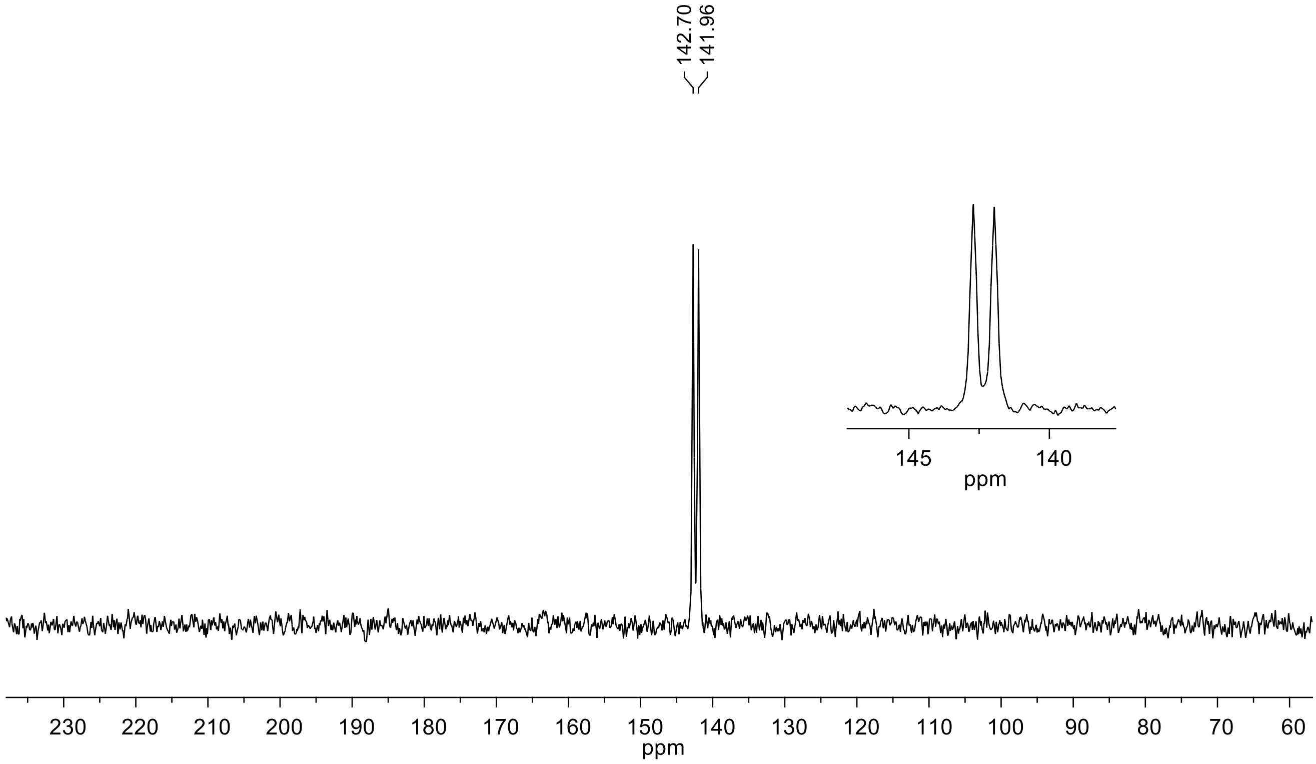

Figure S38. ^{77}Se NMR spectrum of K**5**·THF in [D$_8$]THF.

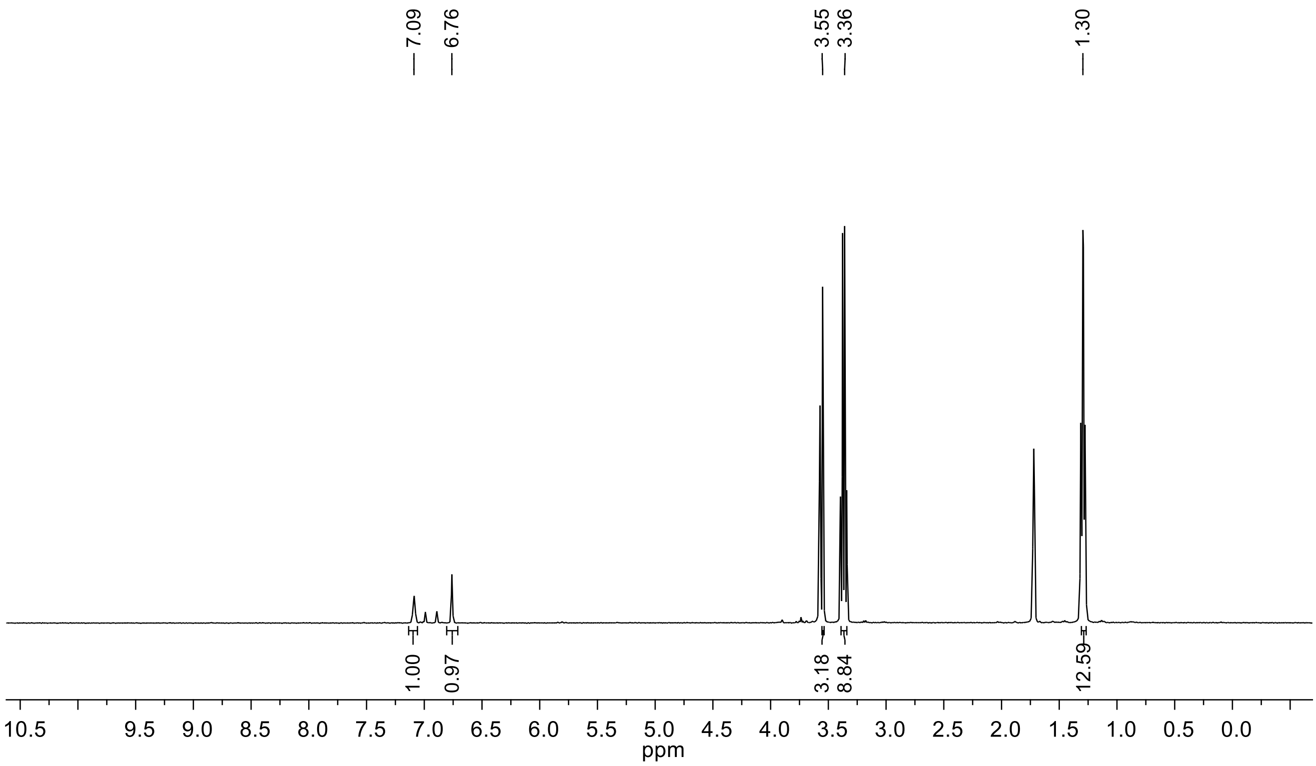

Figure S39. ^{1}H NMR spectrum of [Et$_4$N]**5** in [D$_8$]THF.

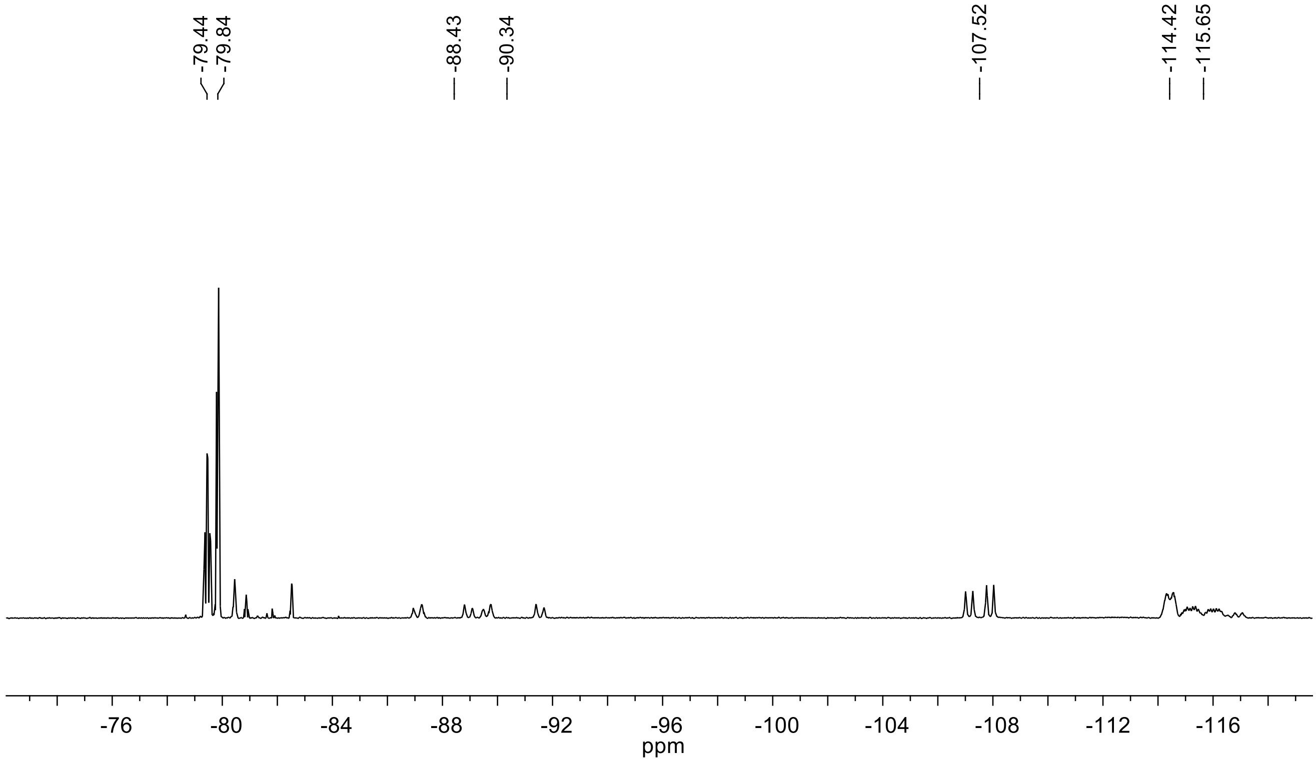

Figure S40. ^{19}F NMR spectrum of [Et$_4$N]**5** in [D$_8$]THF.

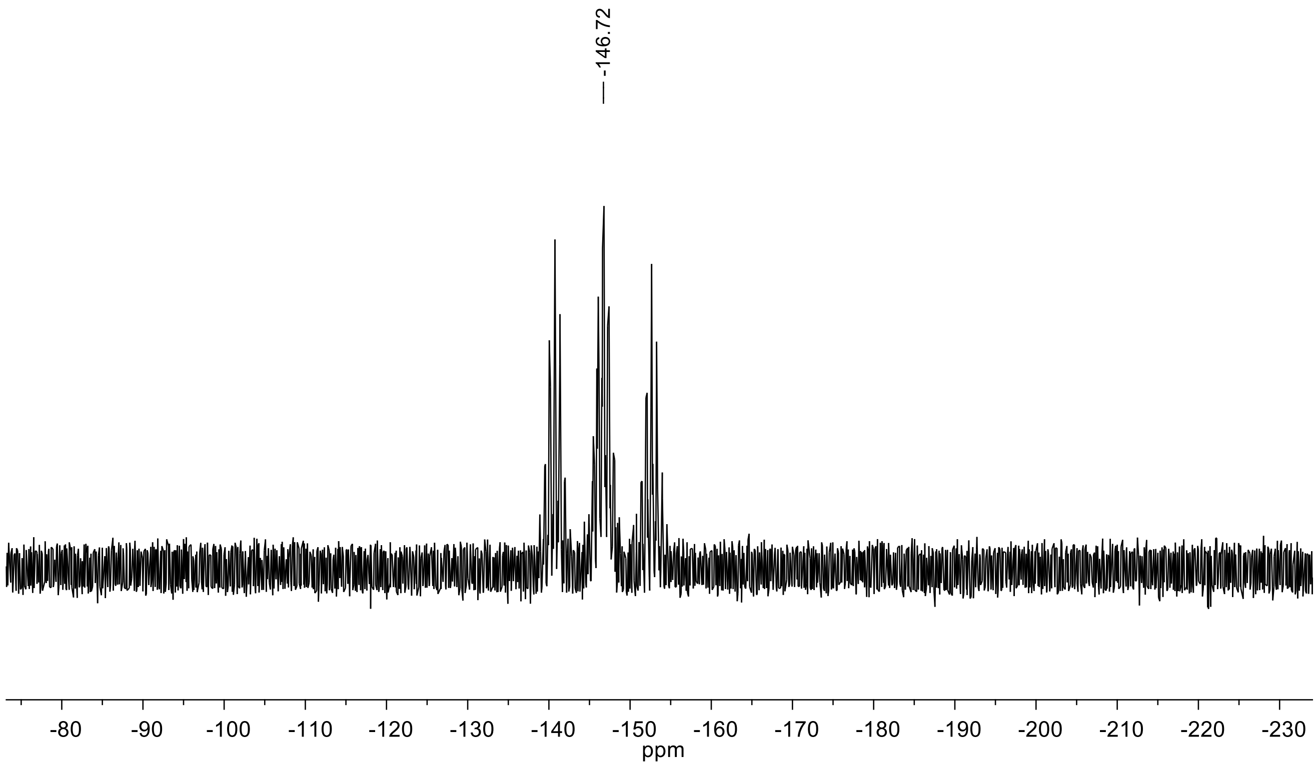

Figure S41. ^{31}P NMR spectrum of [Et$_4$N]**5** in [D$_8$]THF.

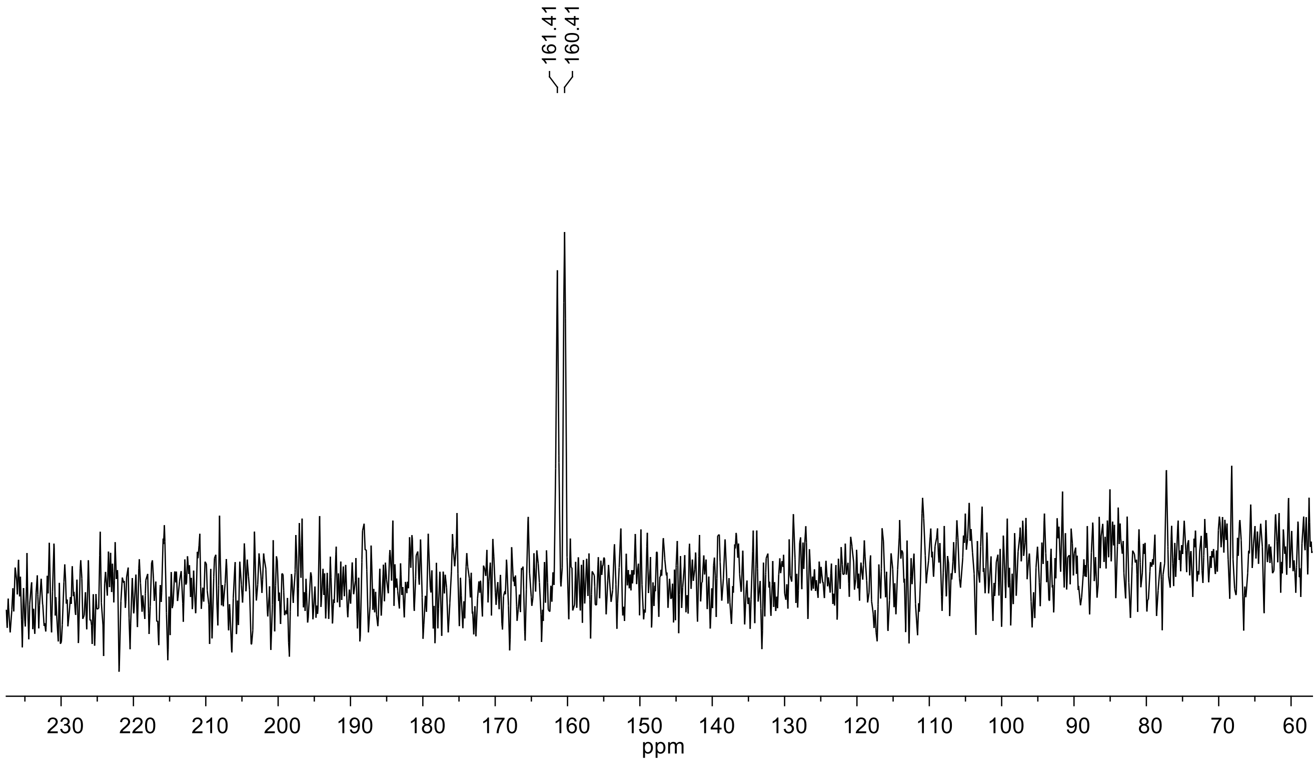

Figure S42. ^{77}Se NMR spectrum of [Et$_4$N]**5** in [D$_8$]THF.

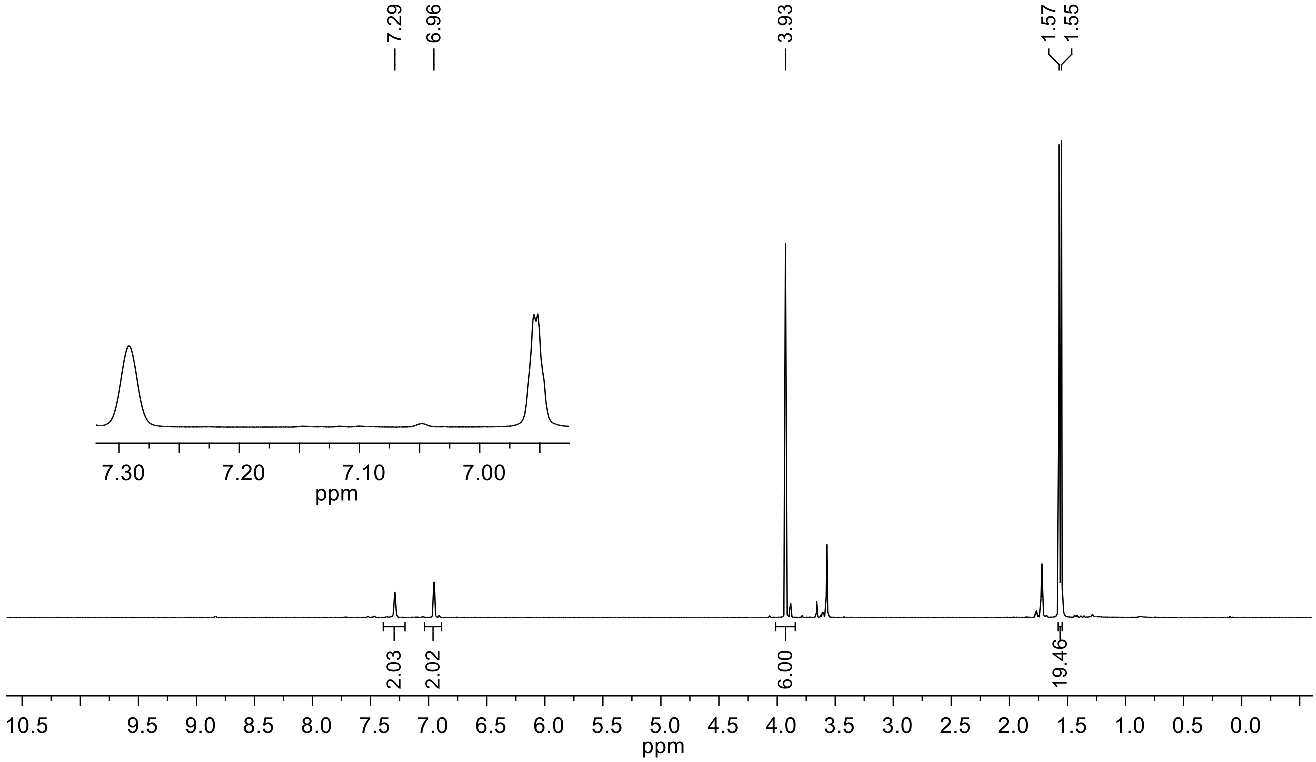

Figure S43. ^{1}H NMR spectrum of [{$(H_3C)_3P$}$_2$Au]**6** in [D$_8$]THF.

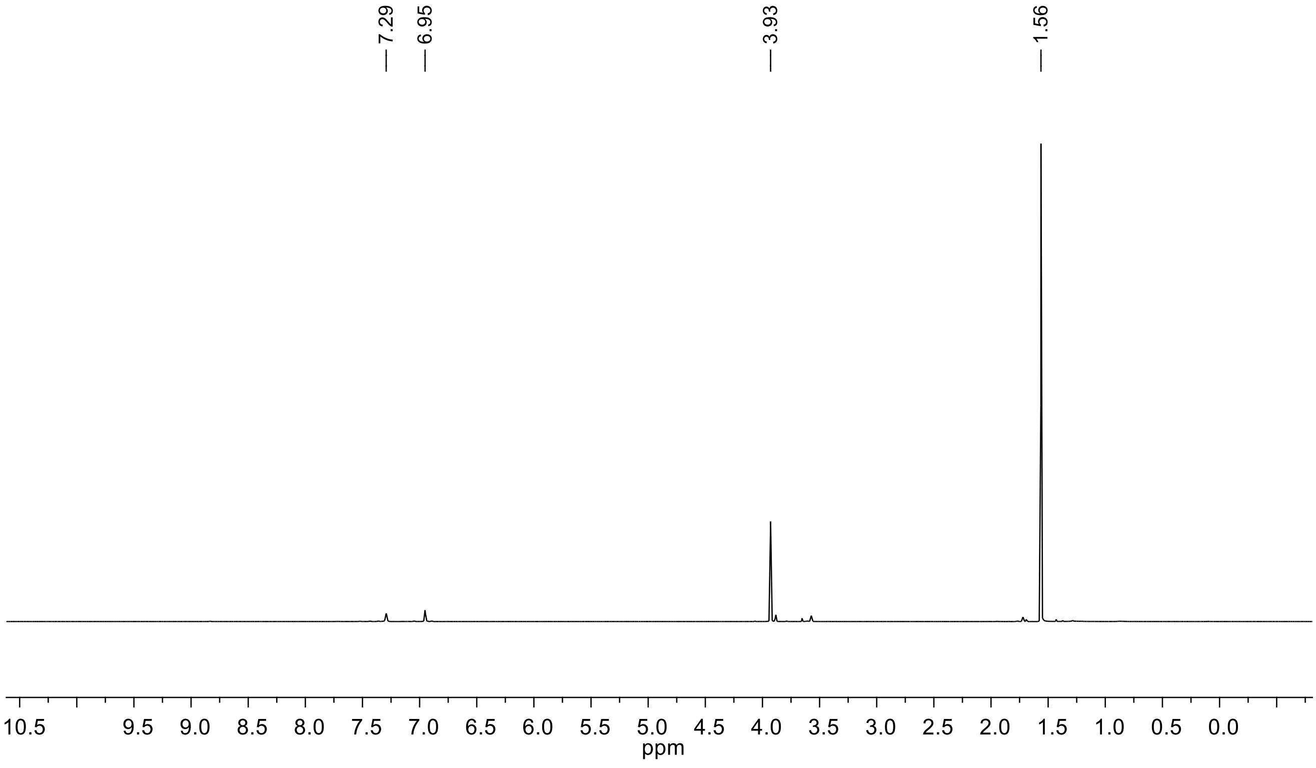

Figure S44. ^{1}H{^{31}P} NMR spectrum of [{$(H_3C)_3P$}$_2$Au]**6** in [D$_8$]THF.

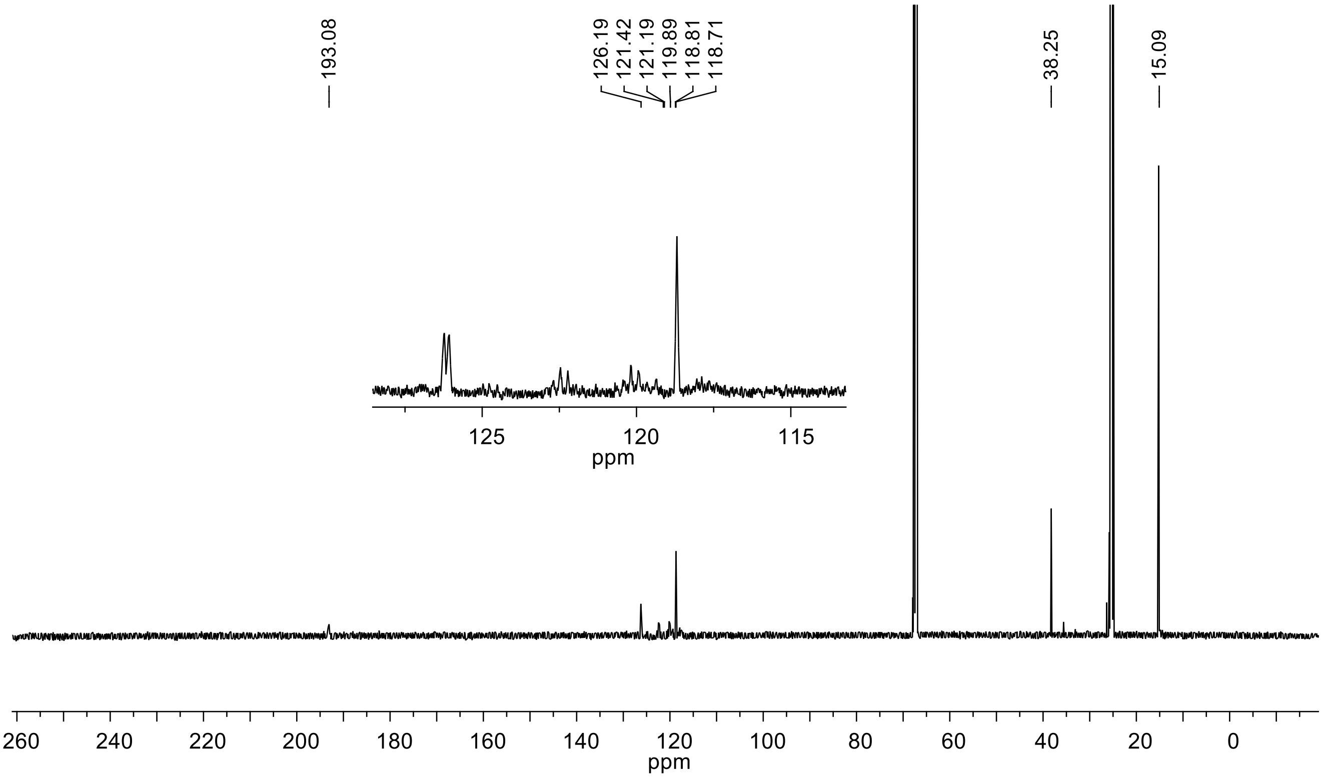

Figure S45. ^{13}C{^{1}H} NMR spectrum of [{($H_3C)_3P$}$_2$Au]**6** in [D_8]THF.

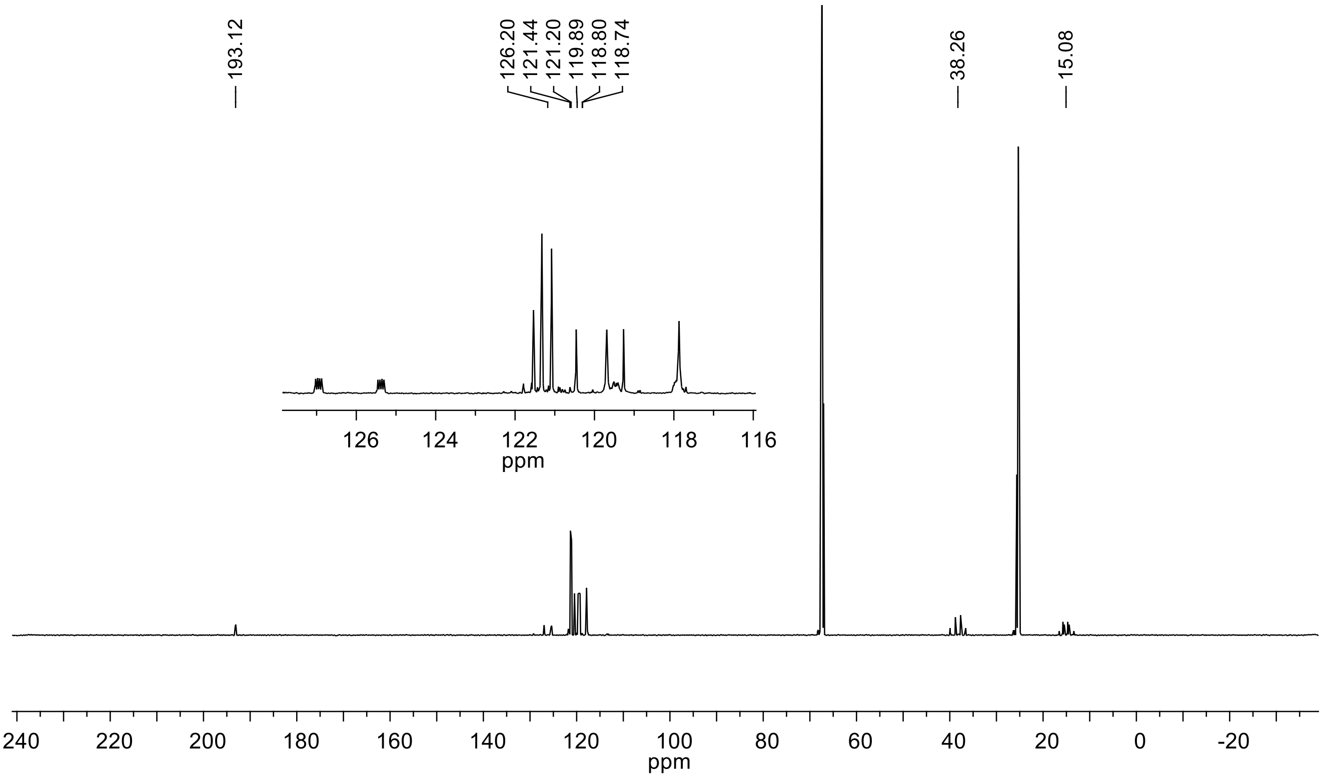

Figure S46. ^{13}C{^{19}F} NMR spectrum of [{($H_3C)_3P$}$_2$Au]**6** in [D_8]THF.

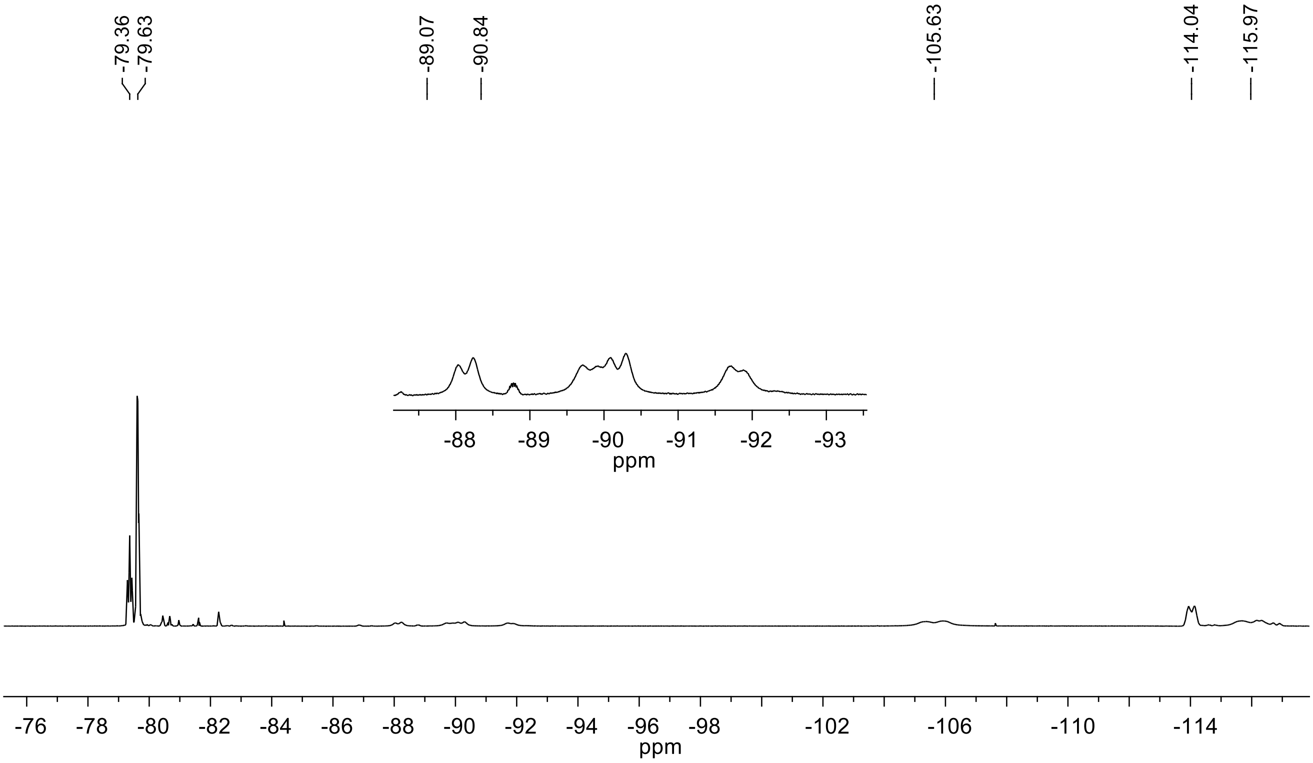

Figure S47. ^{19}F NMR spectrum of [{$(H_3C)_3P$}$_2$Au]**6** in [D_8]THF.

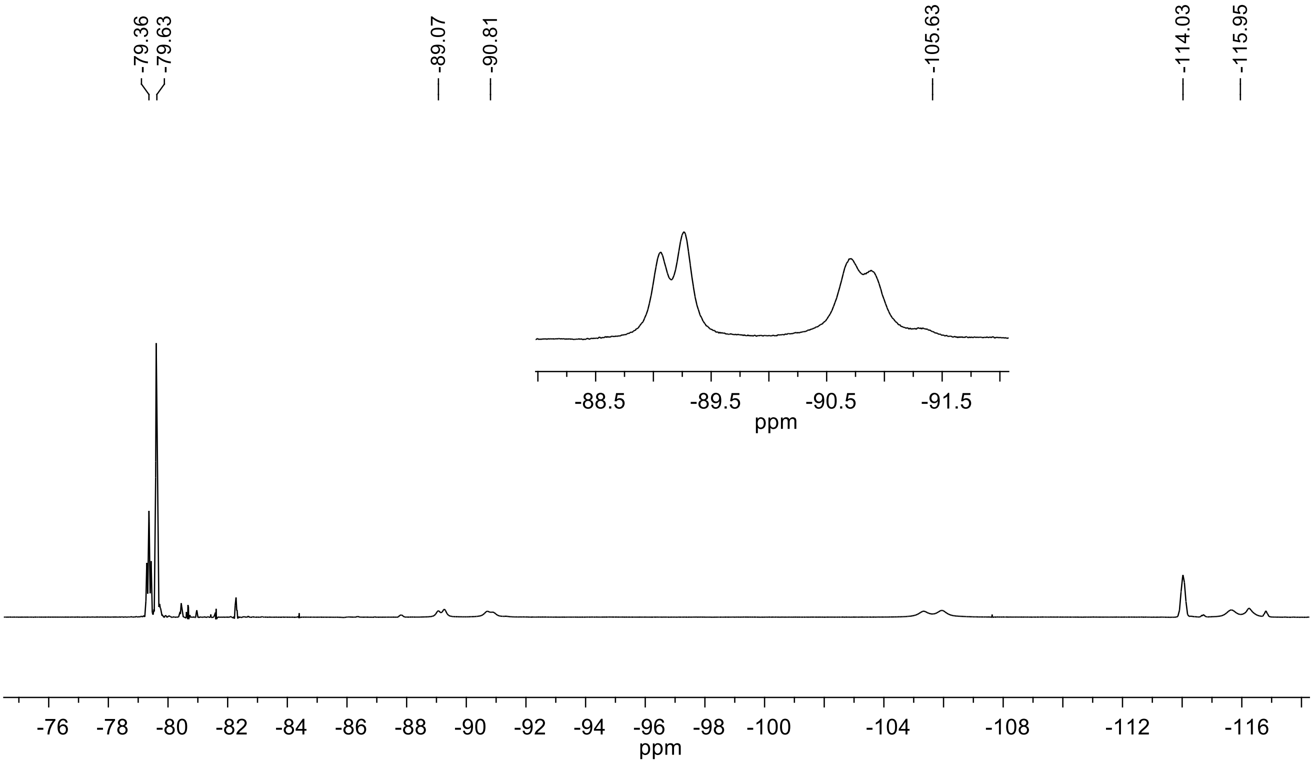

Figure S48. ^{19}F{^{31}P} NMR spectrum of [{$(H_3C)_3P$}$_2$Au]**6** in [D_8]THF.

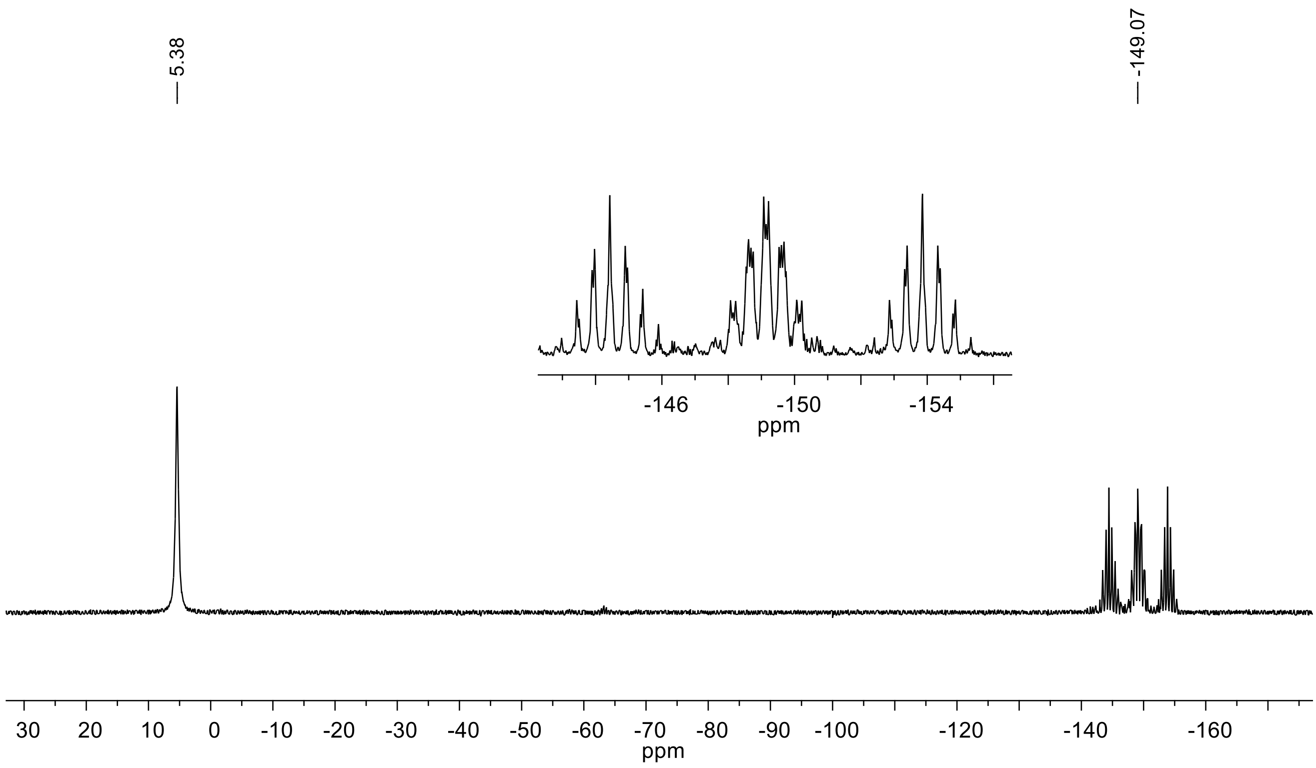

Figure S49. ^{31}P NMR spectrum of [{(H$_3$C)$_3$P}$_2$Au]**6** in [D$_8$]THF.

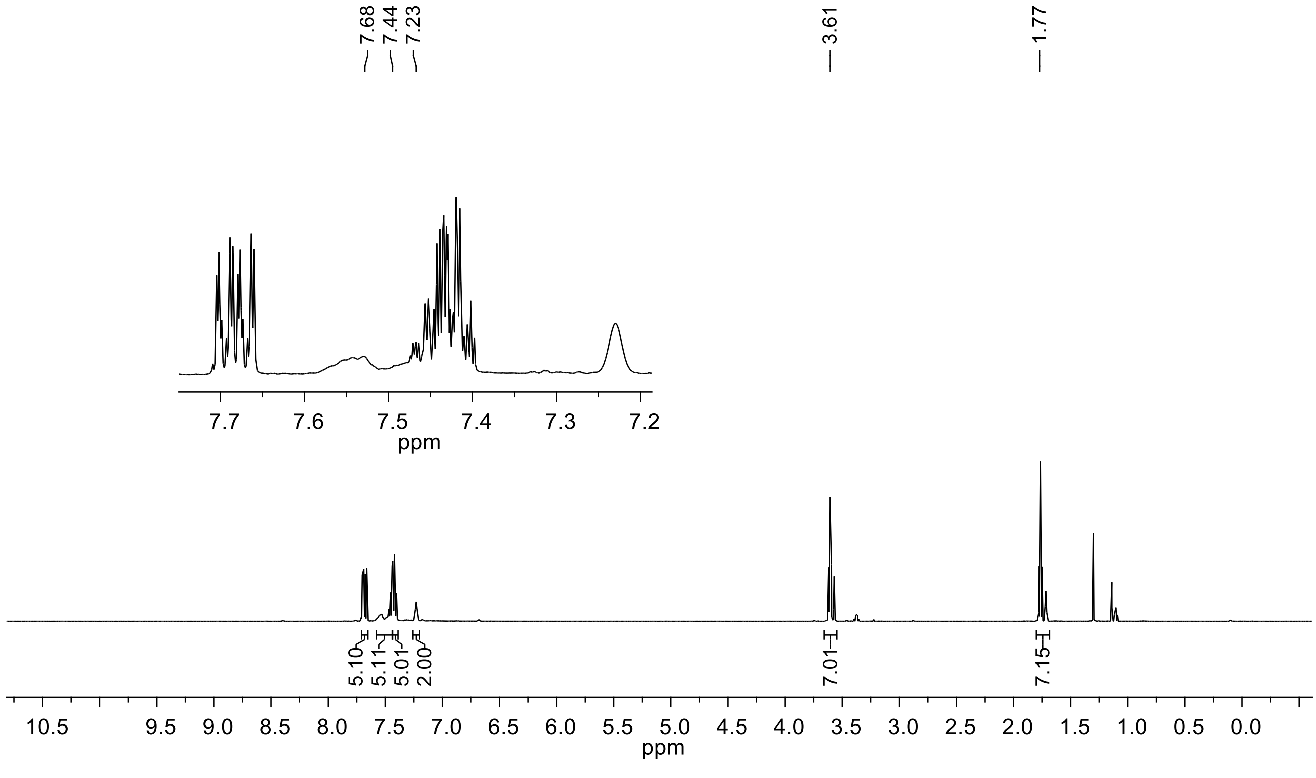

Figure S50. ^{1}H NMR spectrum of K**7**·(THF)$_2$ in [D$_8$]THF.

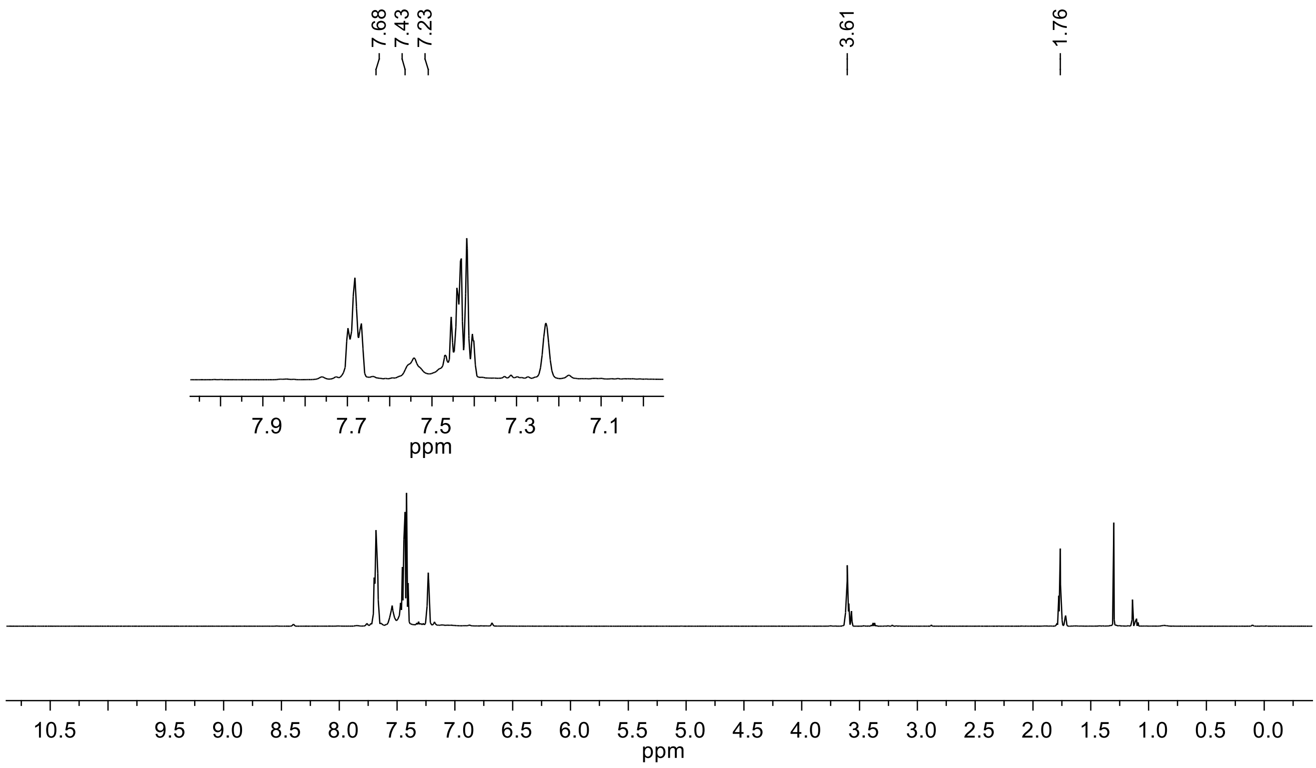

Figure S51. $^{1}H\{^{31}P\}$ NMR spectrum of K**7**·(THF)$_2$ in [D$_8$]THF.

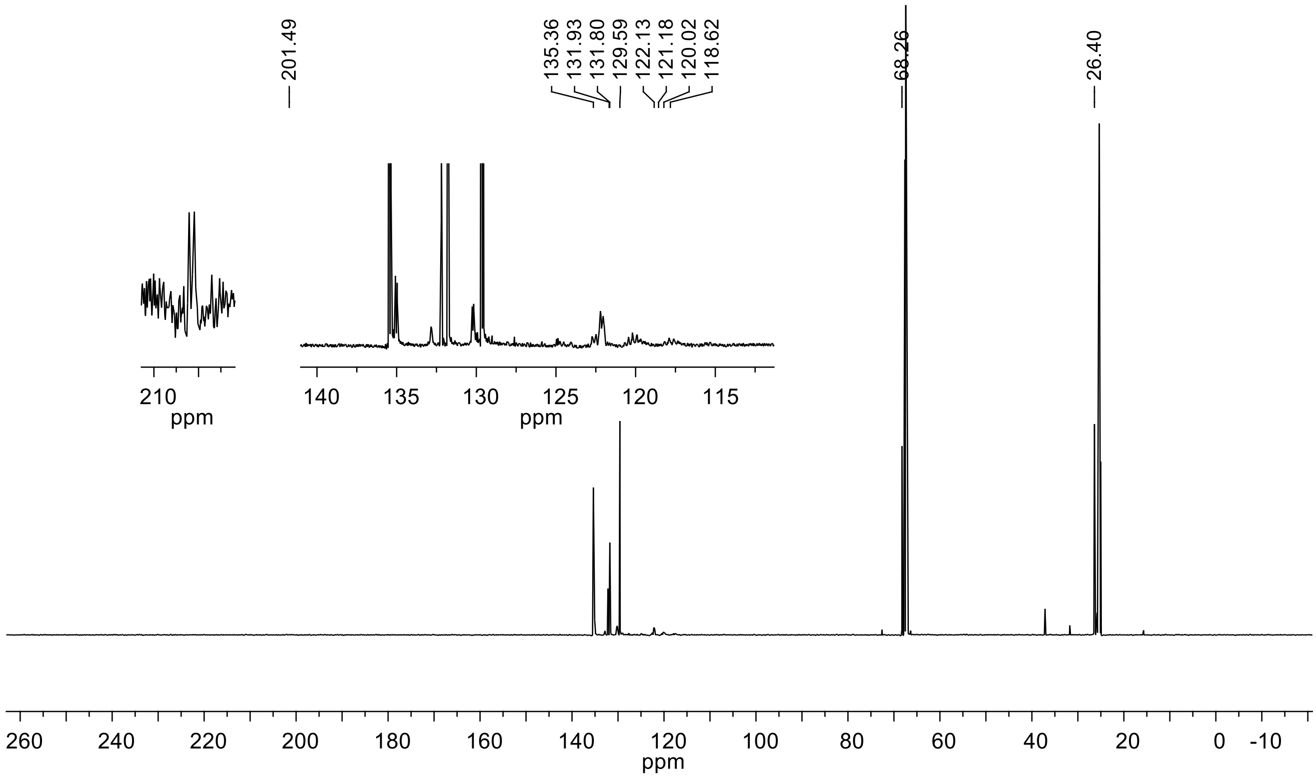

Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum of K**7**·(THF)$_2$ in [D$_8$]THF.

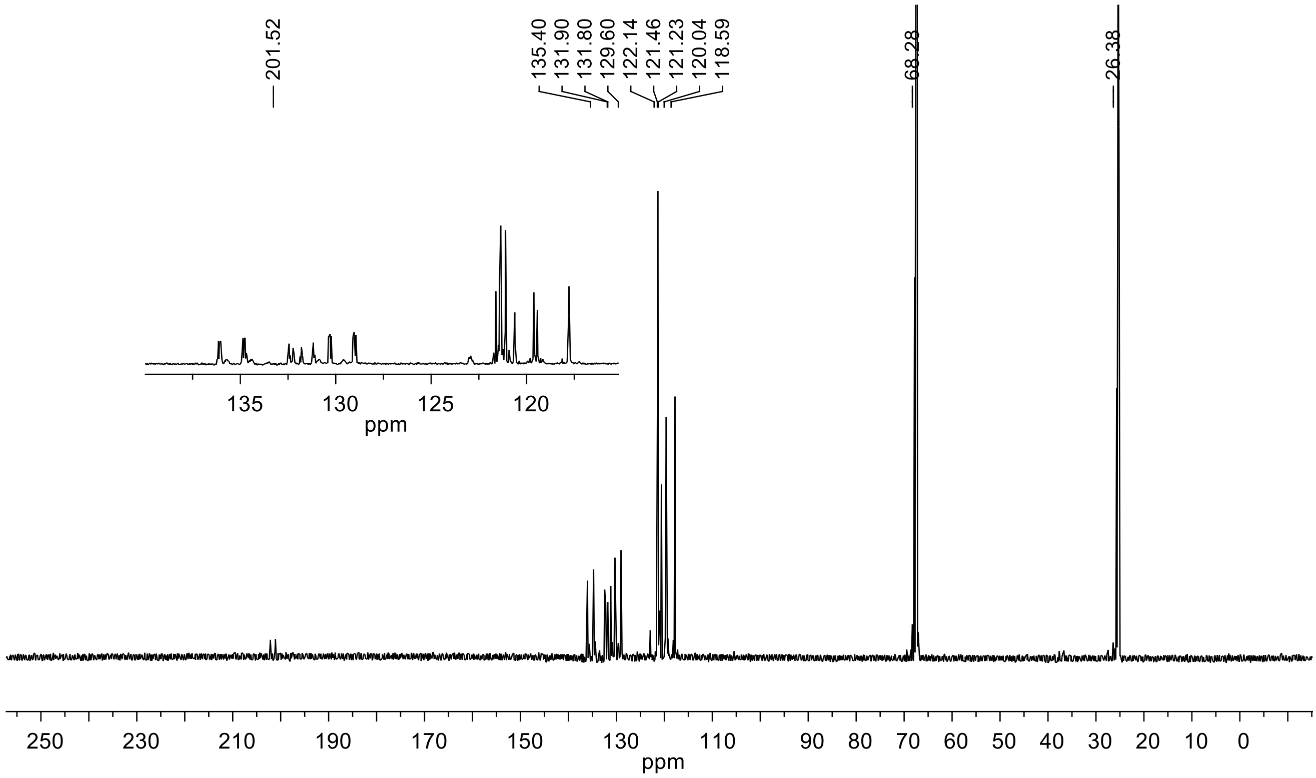

Figure S53. $^{13}C\{^{19}F\}$ NMR spectrum of K**7**·(THF)$_2$ in [D$_8$]THF.

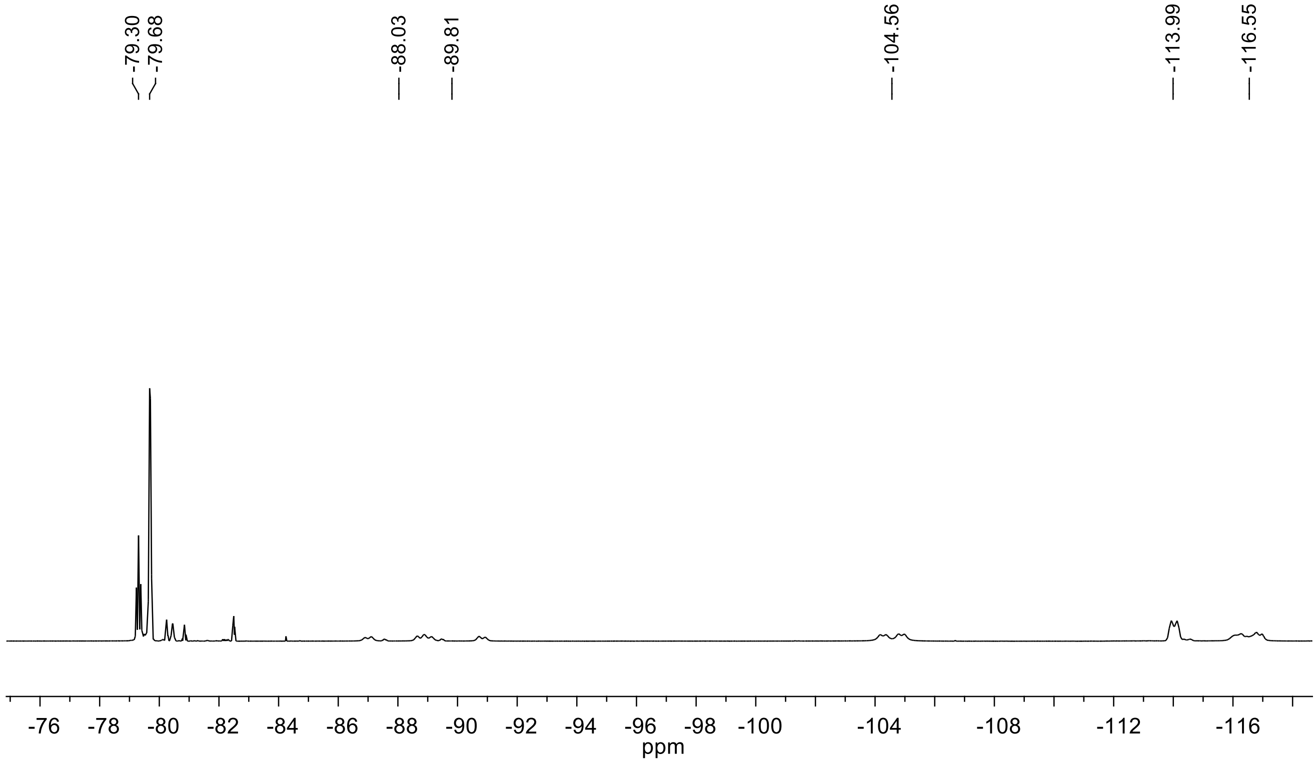

Figure S54. ^{19}F NMR spectrum of K**7**·(THF)$_2$ in [D$_8$]THF.

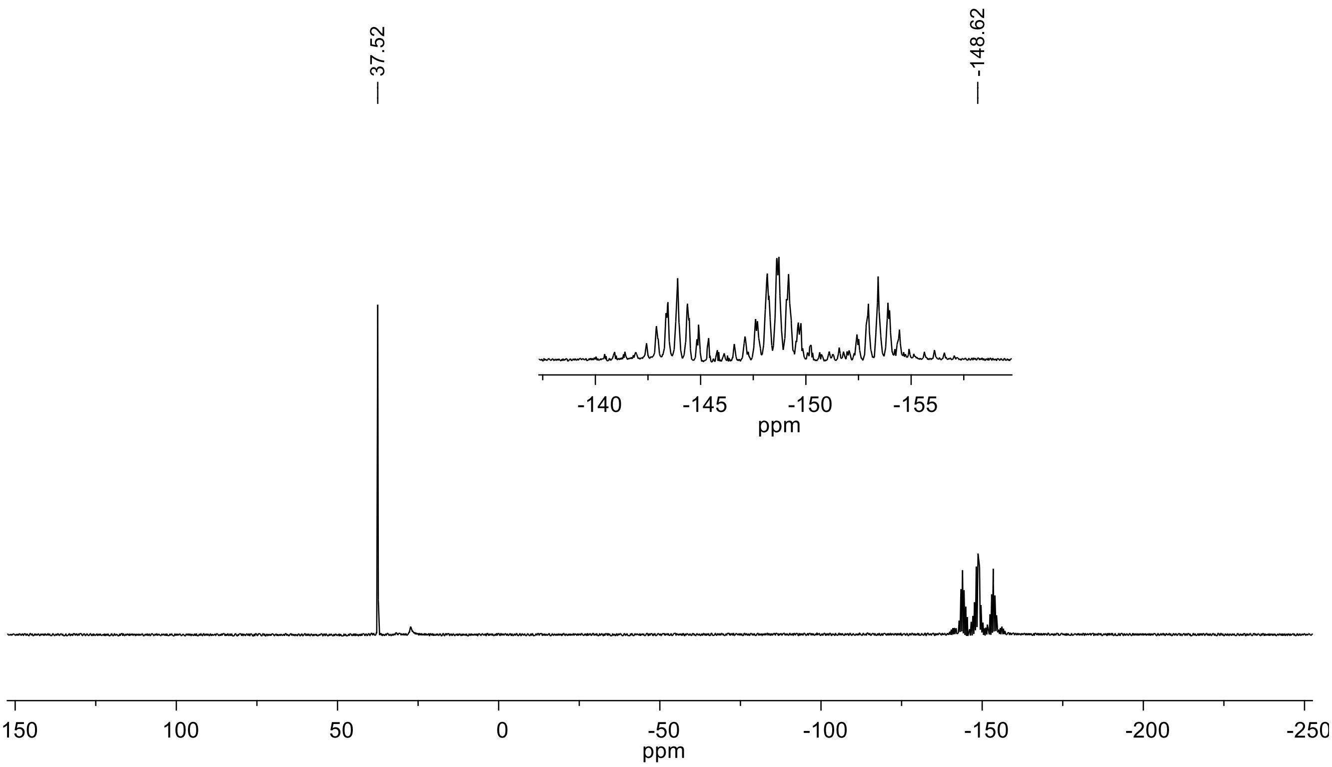

Figure S55. ^{31}P NMR spectrum of K**7**·(THF)$_2$ in [D$_8$]THF.

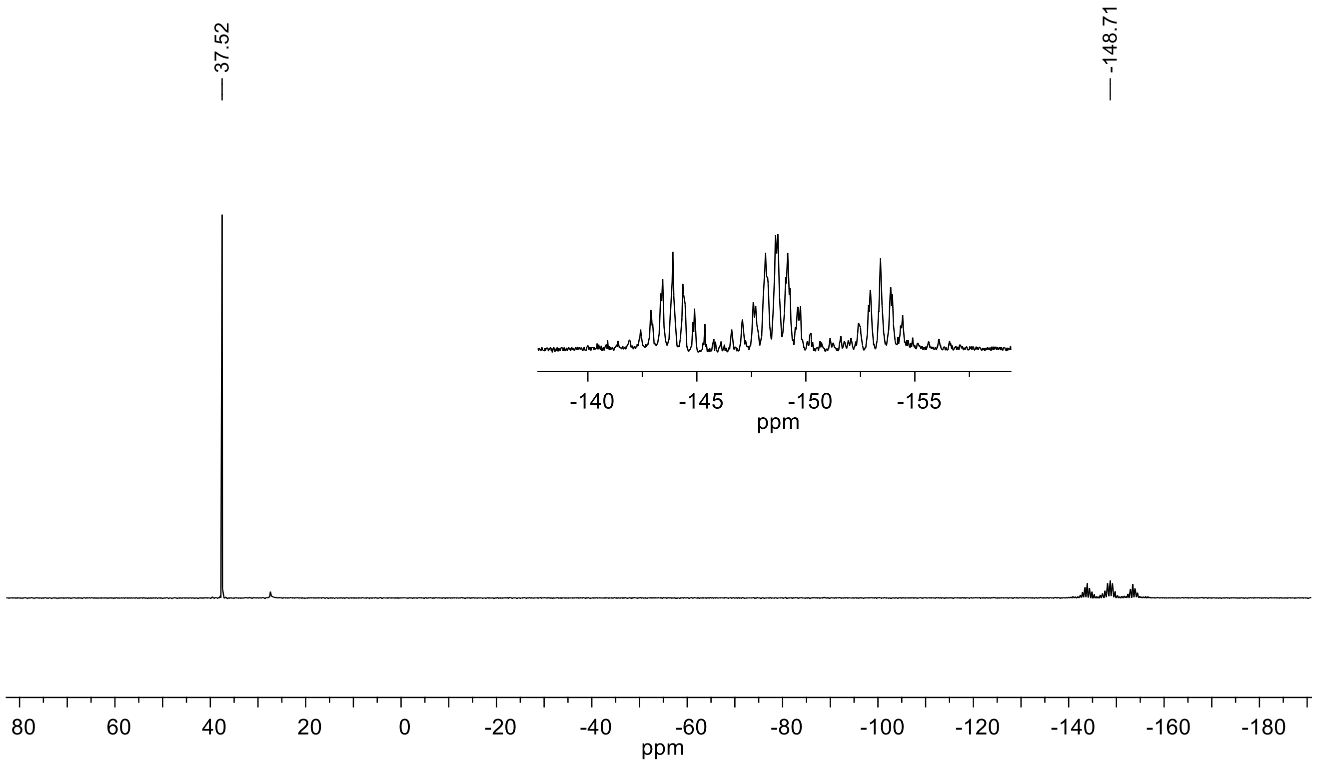

Figure S56. ^{31}P{^{1}H} NMR spectrum of K**7**·(THF)$_2$ in [D$_8$]THF.

6. Vibrational Spectra

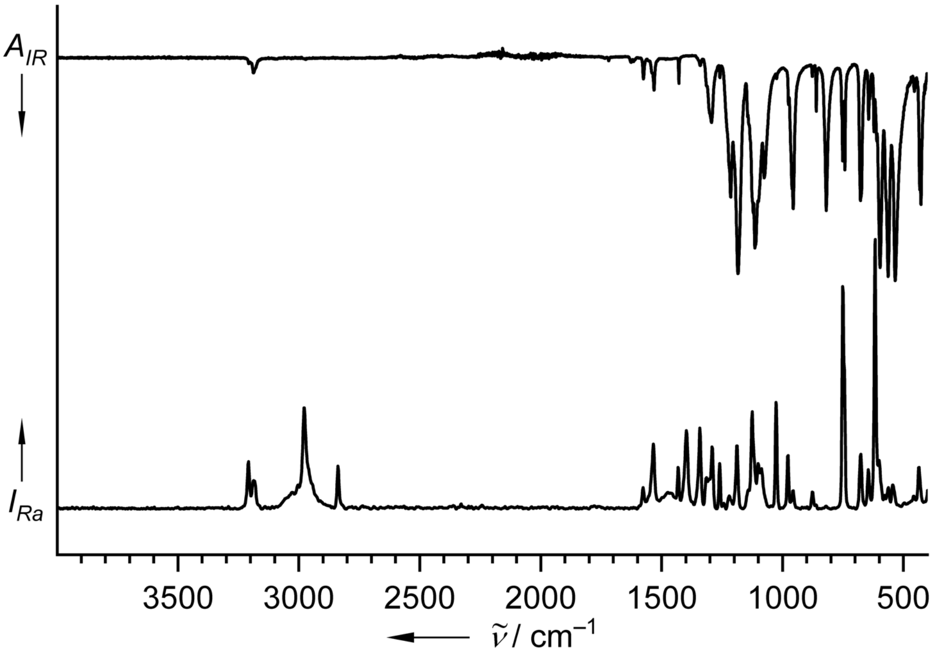

Figure S57. Vibrational spectra of **1** in the solid state.

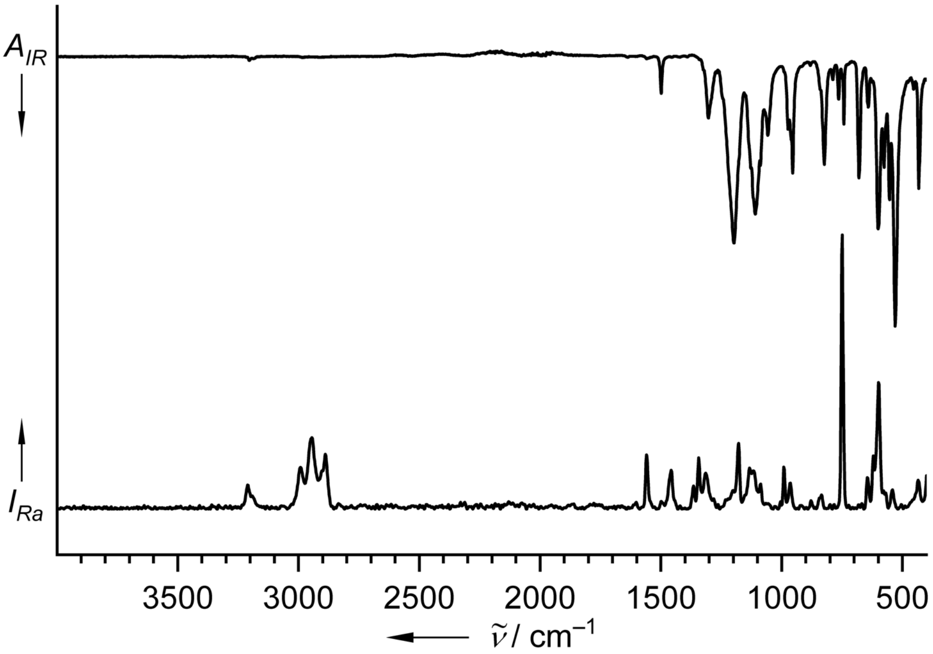

Figure S58. Vibrational spectra of K**2**·$(Et_2O)_{0.5}$ in the solid state.

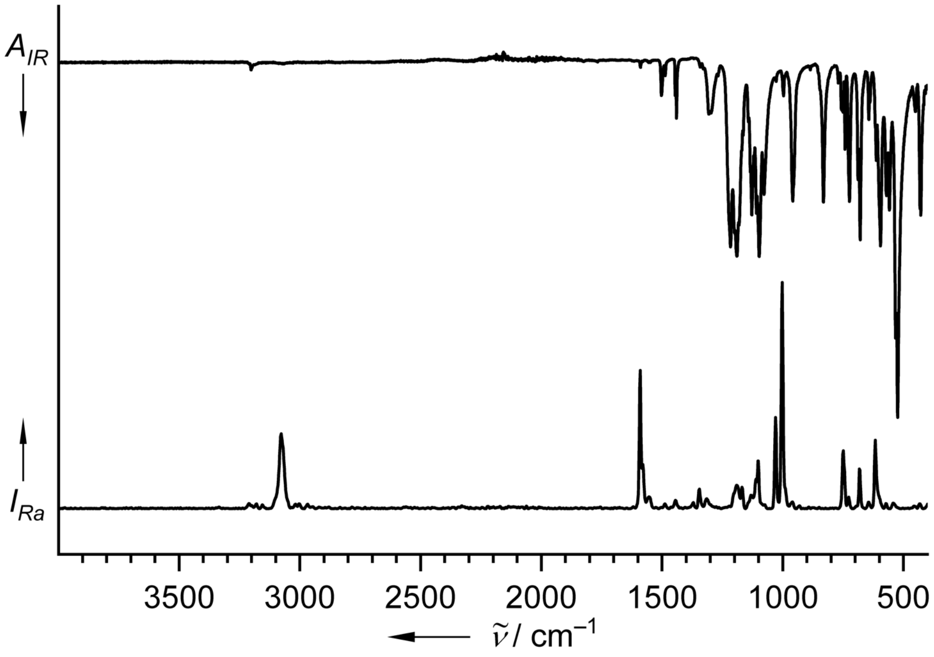

Figure S59. Vibrational spectra of [PPh$_4$]**2** in the solid state.

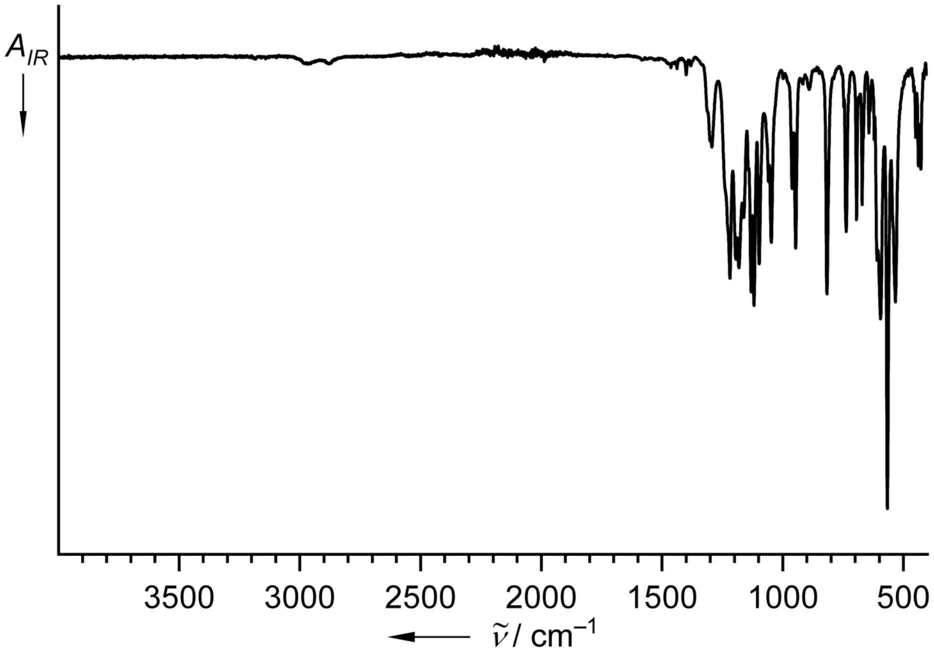

Figure S60. IR spectrum of K**3**·THF$_{0.5}$ in the solid state.

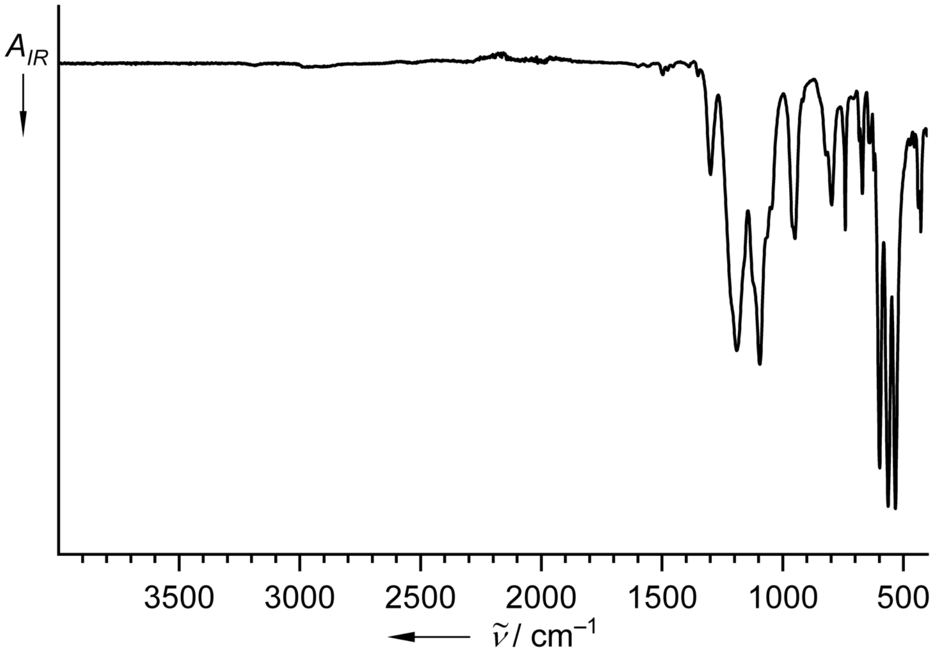

Figure S61. IR spectrum of K_2**4**$\cdot(Et_2O)_{0.5},\cdot(C_7H_8)_{0.5}$ in the solid state.

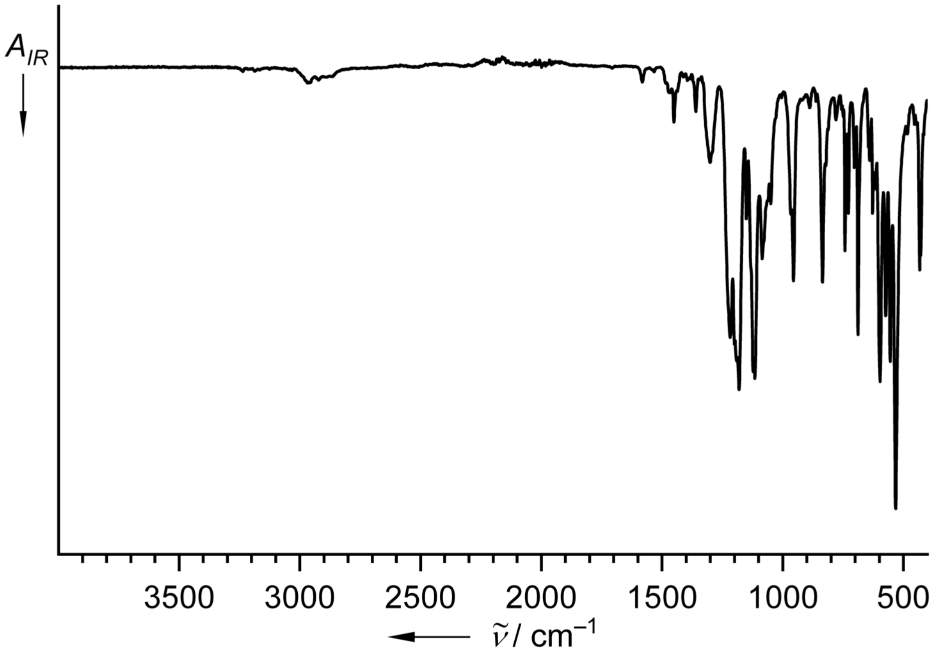

Figure S62. IR spectrum of K**5**$\cdot$THF in the solid state.

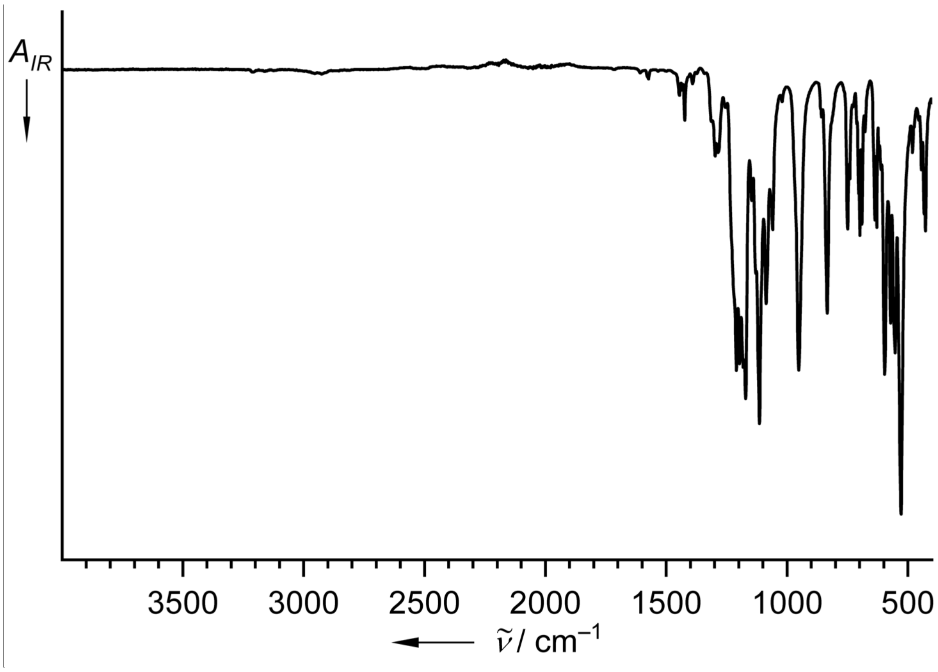

Figure S63. IR spectrum of [{$(H_3C)_3P$}$_2$Au]**6** in the solid state.

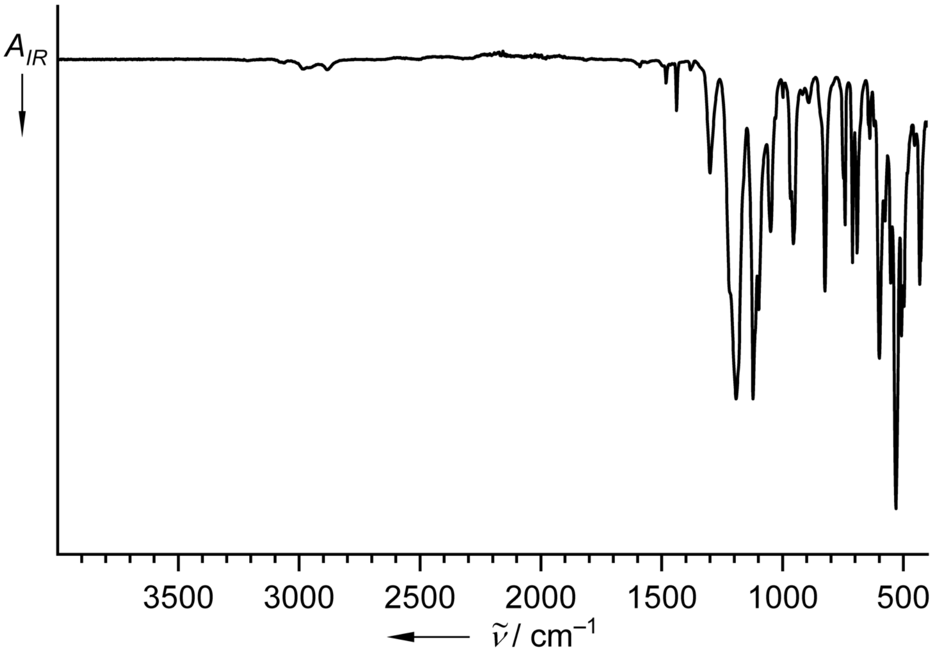

Figure S64. IR spectrum of K**7**·$(THF)_2$ in the solid state.

7. Crystal Structure Determination

Crystal data of **1**, [PPh$_4$]**2**, [K(18c6)(THF)$_2$][{K(18c6)}**4**]·THF, [[{(H$_3$C)$_3$P}$_2$Au]**6**], and $^{1}_{\infty}$[K**7**(NCCH$_3$)$_2$] were collected on a XtaLAB Synergy Dualflex diffractometer with a hybrid pixel array detector, using Cu$_{K\alpha}$ or Mo$_{K\alpha}$ radiation (micro-focus sealed X-ray tube, λ_{Cu} = 1.54184 Å, λ_{Mo} = 0.71073 Å). Crystal data of [K**3**(THF)$_2$]$_2$ and $^{2}_{\infty}$[K**5**]·C$_6$F$_2$H$_4$ were collected on a XtaLAB Synergy-R diffractometer with a hybrid pixel array detector, using Cu$_{K\alpha}$ radiation (rotating-anode X-ray tube, λ_{Cu} = 1.54184 Å).

The structures were solved by intrinsic phasing methods (SHELXT) and refinement is based on full-matrix least-squares calculations on F^2 (SHELXL).[8] All nonhydrogen atoms were refined anisotropically. Unless specified differently, for CH idealized bond lengths and angles were used. Calculations were carried out using the ShelXle graphical interface.[9] Molecular structure diagrams were drawn with the program Diamond 4.6.6.[10] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. Experimental details, crystal data, and CCDC numbers are summarized in Tables S1. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Additional refinement details for [K**3**(THF)$_2$]$_2$: The structure was refined as a two-component twin with occupancies of approximately 50 and 50%. The THF ligands are disordered over two positions. Thus, SIMU, RIGU, and SADI restraints were introduced to ensure a stable refinement of these ligands.

Additional refinement details for [K(18c6)(THF)$_2$][{K(18c6)}**4**]·THF: The structure was refined as a two-component inversion twin with occupancies of approximately 49 and 51%.

Additional refinement details for $^{2}_{\infty}$[K**5**]·C$_6$F$_2$H$_4$: Multiple disordered 1,2-difluorobenzene solvent contribution to the calculated structure factors was calculated and removed with the SQUEZZE routine as implemented in the Platon program.[11, 12]

The buried volumes (%V_{bur})[13, 14] of the free anionic NHC **3** was estimated to 41.5% or 38.9% from the structural data of [[{(H$_3$C)$_3$P}$_2$Au]**6**] and of the free dianionic NHC **4** to 47.0% from the structural data of [K**7**(THF)$_2$]$_2$ using the SambVca 2.1 web application[15] with the following parameters: bondi radii scaled by 1.17, sphere radius of 3.5 Å, Au1 atom as the center of the sphere, mesh spacing of 0.10, hydrogen atoms not included in the calculation. The corresponding steric maps are shown below (Figure S9).

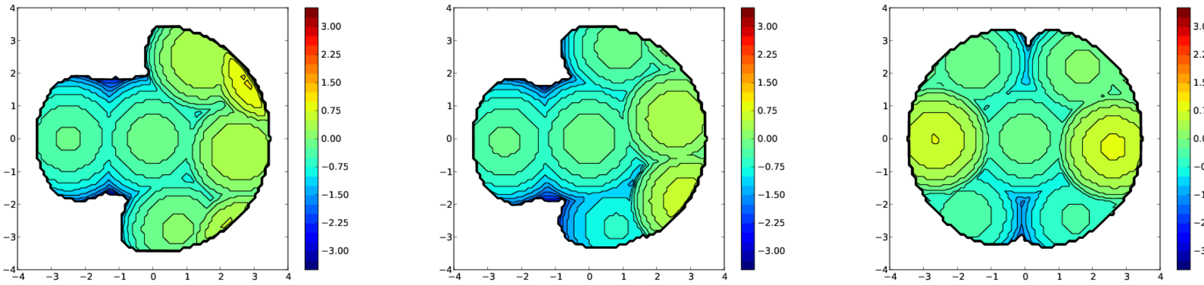

Figure S65. Steric maps of **3** from [[{(H$_3$C)$_3$P}$_2$Au]**6**] (left, middle) and of **4** from [K**7**(THF)$_2$]$_2$ (right). Selected bond lengths [pm] and angles [°] (mean value where applicable):

1

P1–N3 186.4(2), C^{Me}–N1 146.8(3), N1–C2 132.4(2), C2–N3 133.6(3), N3–C4 138.8(3), C4–C5 134.6(3), C5–N1 138.4(3), P1–F 162.3(1), P1−C 197.2(2), C^{F2}–F 136.2(3), C^{F2}–C^{F3} 155.0(3), C^{F3}–F 133.2(3), P1−N3−C2 125.1(1), H2−C2−N3 125.1(2), H2−C2−N1 125.1(2), C^{Me}–N1−C2 125.2(2).

[PPh$_4$]**2**

P1–N1 185.6(1), N1–C2 133.0(2), C5'–C5 134.8(2), C5–N1 139.1(2), P1–F 162.2(1), P1–C 197.2(2), C^{F2}–F 136.3(2), C^{F2}–C^{F3} 154.8(2), C^{F3}–F 133.1(2), P1−N1−C2 125.0(1), H2−C2−N1 124.5(1).

[K**3**(THF)$_2$]$_2$

P1–N3 180.2(3), C^{Me}–N1 146.1(6), N1–C2 135.2(5), C2–N3 139.5(5), N3–C4 140.1(5), C4–C5 134.5(7), C5–N1 138.3(6), P1–F 162.6(2), P1−C 197.6(4), C^{F2}–F 136.6(5), C^{F2}–C^{F3} 154.5(6), C^{F3}–F 133.1(6), K1···C2 300.8(4), K1'···C2 291.9(4), K1···O1^{THF} 269.7(11), K1···O2^{THF} 268.3(14), K1···F^{PF} 277.9(2), K1···F^{CF2} 268.5(3), K1'···F^{CF2} 280.3(3), P1−N3−C2 123.8(3), K1−C2−N3 121.0(2), K1−C2−N1 106.4(3), C^{Me}–N1−C2 122.5(4).

[K(18c4)(THF)$_2$][{K(18c6)}**4**]·THF

P1–N1 179.4(3), P2–N3 179.4(3), N1–C2 137.5(4), C2–N3 137.8(4), N3–C4 140.8(4), C4–C5 133.2(5), C5–N1 140.5(4), P–F 162.8(2), P–C 199.0(3), C^{F2}–F 136.4(4), C^{F2}–C^{F3} 154.7(5), C^{F3}–F 133.3(4), K1···C2 294.4(3), K1···O1^{18c6} 296.6(4), K1···F1^{PF} 288.5(2), K1···F2^{PF} 310.0(2), P1−N1−C2 124.7(2), K1−C2−N1 125.3(2), K1−C2−N3 130.4(2), P2−N3−C2 125.1(2), O1^{18c6}···K1···O1^{18c6} 111.4(1), 123.4(1), 162.1(1), K2···O2^{18c6} 279.8(3), K2···O^{THF} 274.3(3), O1^{18c6}···K1···O1^{18c6} 177.9(1), 178.4(1), 178.4(1).

$^{2}_{\infty}$[K**5**]·C$_6$F$_2$H$_4$

P1–N3 185.0(8), C^{Me}–N1 145.9(12), N1–C2 131.9(15), C2–N3 141.3(9), N3–C4 141.1(13), C4–C5 133.1(14), C5–N1 139.2(12), P1–F 161.5(5), P1−C 197.5(9), C^{F2}–F 136.5(11), C^{F2}–C^{F3} 154.8(14), C^{F3}–F 132.6(12), Se1−C2 187.9(9), K1···Se1 327.9(3), 331.1(2), 341.0(2), K1···F^{PF} 285.4(5), K1···F^{CF2} 261.5(5), 287.0(6), 304.5(5), K1···F^{CF3} 329.7(5), P1−N3−C2 132.6(6), Se1−C2−N3 131.0(7), Se1−C2−N1 120.9(7), C^{Me}–N1−C2 125.5(8).

[{(H$_3$C)$_3$P}$_2$Au]**6**

^{1}P1–^{1}N3 184.9(3), ^{2}P1–^{2}N3 183.5(3), ^{1}C^{Me}–^{1}N1 146.5(5), ^{1}C^{Me}–^{1}N1 146.(4), ^{1}N1–^{1}C2 134.5(4), ^{2}N1–^{2}C2 135.1(5), ^{1}C2–^{1}N3 138.1(4), ^{2}C2–^{2}N3 138.0(4), ^{1}N3–^{1}C4 139.9(3), ^{2}N3–^{2}C4 140.6(4), ^{1}C4–^{1}C5 134.1(5), ^{2}C4–^{2}C5 133.5(5), ^{1}C5–^{1}N1 138.3(3), ^{2}C5–^{2}N1 138.3(3), ^{1}P1–^{1}F 162.1(2), ^{2}P1–^{2}F 161.9(2), ^{1}P1–^{1}C 197.7(3), ^{2}P1–^{2}C 198.0(3), ^{1}C^{F2}–^{1}F 136.7(4), ^{2}C^{F2}–^{2}F 136.8(4), ^{1}C^{F2}–^{1}C^{F3} 155.1(5), ^{2}C^{F2}–^{2}C^{F3} 154.9(5), ^{1}C^{F3}–^{1}F 133.2(4), ^{2}C^{F3}–^{2}F 133.3(4), Au1–^{1}C2 204.1(3), Au1–^{2}C2 203.4(3), Au2–^{3}P2 229.9(1), Au2–^{4}P2 230.3(1), ^{1}P1−^{1}N3−^{1}C2 128.7(2), ^{2}P1−^{2}N3−^{2}C2 128.2(2), Au1−^{1}C2−^{1}N3 133.5(2), Au1−^{2}C2−^{2}N3 133.5(2), Au1−^{1}C2−^{1}N1 121.1(2), Au1−^{2}C2−^{2}N1 120.8(2), ^{1}C^{Me}−^{1}N1−^{1}C2 124.9(3), ^{2}C^{Me}−^{2}N1−^{2}C2 125.0(3), ^{1}C2−Au1−^{2}C2 177.8(1), ^{3}P2−Au1−^{4}P2 175.2(1).

$^{1}_{\infty}$[K**7**(NCCH$_3$)$_2$]:

P1–N1 185.4(3), P2−N3 185.2(3), N1–C2 136.4(4), C2–N3 135.8(4), N3–C4 140.1(3), C4–C5 132.5(4), C5–N1 139.2(4), P–F 162.3(2), P1−C 197.7(4), C$^{\mathrm{F2}}$−F 136.2(4), C$^{\mathrm{F2}}$−C$^{\mathrm{F3}}$ 154.9(5), C$^{\mathrm{F3}}$−F 133.0(5), Au1−C2 207.2(3), Au1−P3 226.4(1), K1···N1$^{\mathrm{MeCN}}$ 275.2(4), K1···N2$^{\mathrm{MeCN}}$ 276.4(4), K1···F$^{\mathrm{PF}}$ 313.8(2), K1···F$^{\mathrm{CF2}}$ 300.3(2), P1−N1−C2 130.3(2), Au1−C2−N1 125.5(2), Au1−C2−N3 127.1(2), P2−N3−C2 130.9(2).

Table S1. Selected Crystal Data and Details of the Refinement of the Crystal Structures of **1**, $[PPh_4]$**2**, [K**3**$(THF)_2]_2$, [K(18c6)$(THF)_2$][{K(18c6)}**4**]·THF, ${}^{2}_{\infty}$[K**5**]$\cdot C_6F_2H_4$, [[{$(H_3C)_3P$}$_2$Au]**6**], and [K**7**$(THF)_2]_2$

	1	$[PPh_4]$**2**	[K**3**$(THF)_2]_2$	[K(18c6)$(THF)_2$][{K(18c6)}**4**]·THF	${}^{2}_{\infty}$[K**5**]$\cdot C_6F_2H_4$	[[{$(H_3C)_3P$}$_2$Au]**6**],	${}^{1}_{\infty}$[K**7**$(NCCH_3)_2$]
Formula	$C_{10}H_6F_{17}N_2P$	$C_{39}H_{23}F_{34}N_2P_3$	$C_{36}H_{42}F_{34}K_2N_4O_4P_2$	$C_{51}H_{74}F_{34}K_2N_2O_{15}P_2$	$C_{20}H_{10}F_{34}K_2N_4P_2Se_2$	$C_{26}H_{28}Au_2F_{34}N_4P_4$	$C_{37}H_{23}AuF_{34}KN_4P_3$
M_W	508.14	1258.50	1380.87	1741.26	1250.38	1560.34	1498.57
T (K)	100.0(1)	100.0(3)	100.0(1)	100.0(1)	100.0(1)	100.0(1)	100.0(1)
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic	triclinic	triclinic
Space group	$P2_1/c$	$C2/c$	$P2_1/n$	$Pca2_1$	$P-1$	$P-1$	$P-1$
a (Å)	8.4857(1)	20.4078(2)	12.3654(2)	38.1996(3)	11.4047(4)	11.5040(2)	11.7802(1)
b (Å)	11.6205(1)	14.2097(1)	15.5068(2)	11.6120(1)	12.8031(5)	14.8392(3)	12.2669(1)
c (Å)	32.6317(1)	15.9722(1)	13.9007(2)	16.1595(1)	14.8702(9)	15.2026(3)	17.7907(2)
α	90	90	90	90	112.761(5)	108.414(2)	80.079(1)
β	90.467(1)	96.907(1)	95.834(1)	90	101.065(4)	102.734(2)	79.500(1)
γ	90	90	90	90	92.038(3)	110.562(2)	79.146(1)
Volume (Å^3)	3217.64(5)	4598.14(6)	2651.62(7)	7167.93(9)	1950.45(17)	2139.09(8)	2457.13(4)
Z	8	4	2	4	2	2	2
ρ (calcd) (Mg m^{-3})	2.098	1.818	1.730	1.613	2.129	2.423	2.025
μ (mm^{-1})	3.380	2.822	3.671	2.959	6.869	7.179	8.864
F(000)	1984	2488	1384	3552	1200	1472	1444
No. of collected reflections	70352	24669	28434	80375	37310	48999	103900
No. of unique reflections	6568	4808	5403	13209	7051	11227	10384
R(int)	0.0515	0.0282	0.0298	0.0505	0.1018	0.0529	0.0633
No. of parameters / restraints	543 / 0	353 / 0	464 / 588	956 / 1	582 / 0	639 / 0	723 / 0
$R1$ ($I > 2\sigma(I)$)	0.0399	0.0307	0.0583	0.0359	0.0906	0.0253	0.0283
$wR2$ (all)	0.1085	0.0794	0.1363	0.0798	0.2607	0.0567	0.0647
GOF on F^2	1.118	1.052	0.924	1.168	1.055	1.037	1.362
Largest diff. peak / hole / e Å^{-3}	0.634 / –0.388	0.326 / –0.432	1.027 / –0.700	0.393 / –0.287	1.965 / –1.281	1.007 / –1.398	1.437 / –1.163
CCDC no.	2252891	2252892	2252893	2252894	2252895	2252896	2252897

8. Quantum Chemical Calculations

Computational Details

Calculations were carried out using the TURBOMOLE V7.2 2017 program suite, a development of the University of Karlsruhe and the Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.[16, 17] Geometry optimizations were performed using (RI-)DFT calculations[18-20] on an m4 grid employing the D3BJ[21, 22] dispersion-corrected B3LYP[23-30] functional and a def2-TZVPP[31-35] basis set for all atoms. Solvent effects were considered by using the implicit solvent model COSMO (ε = infinite).[36-38]

Coordinates of the optimized structures

1,3-dimethyl-imidazoline-2-ylidene (IMe)

Energy = -304.7395511487

C	0.0000000	0.0000000	-0.9751333
N	0.0000000	-1.0601000	-0.1189333
C	0.0000000	-0.6760000	1.2134667
N	0.0000000	1.0601000	-0.1189333
C	0.0000000	0.6760000	1.2134667
H	0.0000000	1.3767000	2.0293667
H	0.0000000	-1.3767000	2.0293667
C	0.0000000	2.4382000	-0.5667333
H	-0.8878000	2.9617000	-0.2086333
H	0.8878000	2.9617000	-0.2086333
H	0.0000000	2.4315000	-1.6523333
C	0.0000000	-2.4382000	-0.5667333
H	0.8878000	-2.9617000	-0.2086333
H	-0.8878000	-2.9617000	-0.2086333
H	0.0000000	-2.4315000	-1.6523333

1-methyl-3-(tricyanoborane)imidazoline-2-ylidenate

Energy = -568.4580363821

C	-1.6473315	-0.7083085	-0.0016200
N	-2.4577111	-0.4406204	1.0625556
C	-3.6670138	0.1297550	0.6836462
N	-2.3915543	-0.2795890	-1.0652279
C	-3.6192771	0.2256446	-0.6643783
H	-4.3411324	0.6145944	-1.3597417
H	-4.4320975	0.4155930	1.3840298
C	-2.0829865	-0.7220335	2.4276969
H	-1.0921718	-1.1675276	2.4083303

H	-2.0551361	0.1927953	3.0255031
H	-2.7838431	-1.4208366	2.8917291
B	-1.9288829	-0.4367343	-2.5303719
C	-2.8855099	0.4264357	-3.4804556
C	-0.4367091	0.0858792	-2.7294475
C	-2.0296342	-1.9636307	-2.9963510
N	-3.5934488	1.0480983	-4.1442766
N	0.6258025	0.4890936	-2.9192246
N	-2.1306625	-3.0608085	-3.3345960

1,3-bis(tricyanoborane)imidazoline-2-ylidenate

Energy = -832.1552368060

C	-1.4822230	-0.3549693	-0.0001148
N	-2.3308549	-0.3517089	1.0780041
C	-3.6638051	-0.3579280	0.6788603
N	-2.3353837	-0.3643374	-1.0745815
C	-3.6666389	-0.3666235	-0.6697758
H	-4.4870993	-0.3739238	-1.3660828
H	-4.4813136	-0.3584374	1.3786599
B	-1.9311998	-0.3872354	-2.5478897
C	-2.5851183	0.8614971	-3.3305820
C	-0.3575016	-0.3387353	-2.7831008
C	-2.4989112	-1.7121118	-3.2706429
N	-3.0734873	1.7420978	-3.8933154
N	0.7514843	-0.3055118	-3.0951240
N	-2.9277518	-2.6480759	-3.7909718
B	-1.9201874	-0.3194333	2.5493595
C	-0.3466985	-0.3955133	2.7788195
C	-2.4606619	1.0225801	3.2612673
C	-2.5934348	-1.5482535	3.3469871
N	-2.8703119	1.9708620	3.7747162
N	0.7626745	-0.4493650	3.0865652
N	-3.0953759	-2.4145733	3.9198425

1-methyl-3-(tris(pentafluoroethyl)difluorophosphorane)imidazoline-2-ylidenate (3)

Energy = -2532.503751773

C	6.9367408	7.1696200	8.5158281
F	4.5545739	5.8713021	9.3627103
F	8.6774266	5.6225977	6.8897013
F	5.9268781	5.1288753	7.0406117
N	7.5189723	8.0024060	9.4069510

N	7.1776824	5.9197349	9.0476178
C	4.9062982	4.5504903	9.3067963
C	8.3476068	4.3432106	7.2440817
P	6.6349075	4.3697208	8.2961223
C	7.5122718	9.4504513	9.2886657
C	8.1090270	7.3257425	10.4688022
C	7.8957886	6.0155250	10.2434116
C	4.8055955	4.0733991	10.7857119
F	3.8662385	3.9461433	8.6602640
F	8.2137256	3.6824494	6.0564640
C	9.6529382	3.7832060	7.8824030
F	7.3195226	3.5124946	9.5233128
C	6.0794868	2.5712447	7.5510152
H	8.5263037	9.8407501	9.3718812
H	7.1033727	9.7114274	8.3171083
H	6.8972545	9.8968583	10.0707381
H	8.6193129	7.8259286	11.2729692
H	8.1926654	5.1654993	10.8226636
F	3.5612265	4.3193990	11.2488561
F	5.0298298	2.7662831	10.9358035
F	5.6595766	4.7386926	11.5736983
F	9.5668463	2.4935250	8.2152767
F	10.0004559	4.4760943	8.9741679
F	10.6662293	3.8988974	6.9974366
F	5.3335736	1.8992902	8.4791756
F	7.1850398	1.7868064	7.3725980
C	5.2753424	2.4363185	6.2192110
F	4.0829008	3.0352833	6.2729101
F	5.0525364	1.1256417	5.9752057
F	5.9334537	2.9267921	5.1657306

1,3-bis(tris(pentafluoroethyl)difluorophosphorane)imidazoline-2-ylidenate (4)

Energy = -4760.244816866

F	15.4491055	7.7054575	8.3703852
F	15.0311689	7.6321619	13.1406768
C	14.3499766	6.7527142	10.6647182
P	14.3716733	6.5950998	7.8583700
P	13.9066594	6.4886650	13.4274977
N	13.6705406	6.1301342	11.6776730
N	13.8460078	6.1748929	9.5300478
F	13.3156960	5.4989020	7.2274586

C	12.9767686	8.0421207	7.8418044
C	15.8151249	5.2040510	8.0209600
C	14.8741244	6.9741977	5.9311218
C	12.5006211	7.9169169	13.2707926
F	12.7813884	5.3559837	13.8340037
C	15.3813074	5.1223269	13.4526938
C	14.0812804	6.7978953	15.4244341
C	12.7625166	5.1857826	11.1743802
C	12.8707549	5.2143660	9.8399227
F	13.3171342	9.0755691	7.0120664
F	12.9005090	8.6078574	9.0812337
C	11.4983115	7.7058436	7.4893710
F	16.2997848	5.2084239	9.2967871
F	16.9008477	5.4913147	7.2394306
C	15.4978314	3.7052236	7.7437347
F	15.2865648	5.8182010	5.3270172
F	13.7606485	7.3437336	5.2272779
C	15.9559377	8.0316792	5.5454409
F	12.6926944	8.9270028	14.1735348
F	12.6070067	8.5208149	12.0515948
C	10.9910216	7.5517596	13.3786043
F	16.3151736	5.3850059	14.4177737
F	16.0737363	5.1870435	12.2787524
C	15.0469586	3.6103074	13.6106645
F	14.3996583	5.6195560	16.0422224
F	12.8660411	7.1376037	15.9527851
C	15.0755882	7.8437842	16.0210011
H	12.1286272	4.5843708	11.7931007
H	12.3470407	4.6416661	9.1022915
F	10.7564453	8.8333766	7.5593357
F	10.9730569	6.8329213	8.3561557
F	11.3466534	7.2140903	6.2566806
F	15.0987643	3.4731275	6.4899214
F	16.6129653	2.9690264	7.9461960
F	14.5599717	3.2380032	8.5748227
F	15.6321455	9.2681794	5.9328699
F	17.1605330	7.7474795	6.0477261
F	16.0823075	8.0572930	4.1991596
F	10.6555253	7.0277474	14.5606348
F	10.6241091	6.6929432	12.4209012
F	10.2495873	8.6700750	13.2172970

F	16.1931229	2.8949356	13.5746749
F	14.4418663	3.3207736	14.7659173
F	14.2748655	3.1702299	12.6111608
F	16.3452934	7.6148558	15.6771622
F	14.7748007	9.0964872	15.6664923
F	15.0126591	7.7869275	17.3707695

1-methyl-3-(tris(pentafluoroethyl)difluorophosphorane)imidazoline-2-ylidenate-selenium (5)

Energy = -4934.018998339

Se	9.1028276	-4.3902742	6.2705102
C	9.0140476	-6.1925223	5.7924760
F	11.3153611	-5.8974325	4.0813937
F	8.9538902	-4.6418027	3.3111554
F	11.3918452	-5.2918929	2.0058290
F	9.9635005	-3.4881200	0.8724264
C	10.8689247	-6.2369383	2.8368388
F	6.5831529	-5.7180856	4.3087030
N	8.9274693	-6.8416934	4.5778331
N	9.0223811	-7.1640623	6.7405133
P	8.8697949	-6.1805021	2.8255607
C	8.8440381	-4.1008120	0.4803957
C	11.6330468	-7.5533995	2.5034450
C	6.8828136	-6.0793696	3.0267675
C	8.8806482	-8.2160758	4.8253334
C	8.9380467	-8.4114808	6.1538098
C	9.0959271	-6.9493256	8.1759324
F	8.7811435	-7.7175426	2.2581140
C	8.8012991	-5.6057446	0.8976862
F	8.7953895	-4.0239137	-0.8667398
F	7.8067945	-3.4067209	0.9548214
F	12.9592279	-7.3225522	2.5813188
F	11.3809255	-8.0127808	1.2770069
F	11.3449125	-8.5204899	3.3829211
F	6.3625277	-5.0873266	2.2507544
C	5.9876895	-7.3279564	2.7647036
H	8.8123030	-8.9385692	4.0414911
H	8.9291042	-9.3163700	6.7328639
H	9.9615695	-6.3373798	8.4169355
H	9.1813412	-7.9203147	8.6554490
H	8.2007108	-6.4402546	8.5283376
F	9.8276397	-6.1906238	0.2117910

F	7.6693085	-6.0993643	0.3138694
F	6.0882395	-7.7979580	1.5207802
F	6.2764777	-8.3212181	3.6145078
F	4.6971824	-6.9919313	2.9642653

1,3-bis(tris(pentafluoroethyl)difluorophosphorane)imidazoline-2-ylidenate-selenium

Energy = -7161.745891743

Se	15.8519666	8.2708384	10.8203161
F	15.5476259	7.7842992	7.9562194
F	15.0762015	7.6796050	13.5722768
C	14.5441387	6.9439392	10.6860881
P	14.4355652	6.6484698	7.6909487
P	13.9461704	6.5310922	13.6077872
N	13.8741391	6.3342080	11.7325992
N	14.0553691	6.3801878	9.5204960
F	13.3237463	5.5044436	7.2960298
C	13.0391586	8.0782893	7.7076319
C	15.8682959	5.2676550	7.8823756
C	14.7280268	6.8184760	5.7011630
C	12.5590279	7.9582304	13.4169147
F	12.7938116	5.3704340	13.7722896
C	15.4021265	5.1613761	13.6005281
C	13.9091969	6.6262634	15.6229764
C	12.9824587	5.4054255	11.1954866
C	13.0909119	5.4334210	9.8666519
F	13.3109599	9.0308161	6.7683910
F	13.0861076	8.7339538	8.9003404
C	11.5302546	7.7343536	7.5222834
F	16.4479340	5.3959717	9.1082017
F	16.8768140	5.4853957	6.9887725
C	15.5410501	3.7476145	7.7734107
F	15.0799313	5.6033244	5.1828168
F	13.5462112	7.1260411	5.0863595
C	15.7621257	7.8217891	5.0985406
F	12.6672590	8.8772253	14.4202713
F	12.7935517	8.6562967	12.2709395
C	11.0430025	7.6038383	13.3429012
F	16.2465371	5.3412614	14.6578418
F	16.1765650	5.3413723	12.4948752
C	15.0730287	3.6381206	13.5909431
F	14.1762172	5.3908400	16.1446224

F	12.6432865	6.9144984	16.0508969
C	14.8292302	7.6040359	16.4211281
H	12.3425716	4.7979561	11.7960090
H	12.5586239	4.8538795	9.1456077
F	10.8146652	8.8785116	7.5533647
F	11.0796769	6.9571988	8.5126148
F	11.2622244	7.1326262	6.3617022
F	15.0293847	3.4008021	6.5903197
F	16.6801811	3.0424965	7.9377485
F	14.6916161	3.3577830	8.7293024
F	15.4806690	9.0931409	5.3947056
F	17.0131046	7.5738425	5.4948420
F	15.7406258	7.7115779	3.7519989
F	10.5945925	6.9716590	14.4297303
F	10.7657445	6.8501216	12.2741418
F	10.3326157	8.7452591	13.2234087
F	16.2292965	2.9415993	13.5940837
F	14.3709485	3.2427733	14.6550058
F	14.4012685	3.2870230	12.4896710
F	16.1287244	7.3898880	16.2022400
F	14.5718031	8.8864416	16.1500309
F	14.6119631	7.4242189	17.7425598

9. Evaluation of Steric Repulsion using the LAB-Rep Model

The calculation of $\%V_{bur\_all}$ for the adduct Se/**4** was done with the LAB-Rep Excel spreadsheet,[39] inserting the following input:
$\%V_{bur\_LA}$ = 24.2%, d_{LA} = 1.71 Å (derived for Se from the anion $[SeF_5]^-$)
$\%V_{bur\_LB}$ = 47.0%, d_{LB} = 2.04 Å (*vide supra*)
With the correction volume of $\%V_{cl}$ = 29.9% the result of $\%V_{bur\_all}$ is 101.1%

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