Supporting Information

# Synthesis of metallophophaalkenes by reaction of organometallic nucleophiles with a phosphaethynolato-borane

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**Contents**

## 1. Experimental section

### 1.1. General synthetic methods

All reactions and product manipulations were carried out under an inert atmosphere of argon or dinitrogen using standard Schlenk-line or glovebox techniques (MBraun UNIlab glovebox maintained at <0.1 ppm $H_2O$ and <0.1 ppm $O_2$). [B]OCP and NaFp* were synthesized according to previously reported synthetic procedures.[1,2] Chlorotrimethylsilane and chloro(triphenylphosphine)gold(I) were purchased from Sigma Aldrich and used as received. Hexane (hex; Sigma Aldrich HPLC grade), and toluene (tol; Sigma Aldrich HPLC grade) were purified using an MBraun SPS-800 solvent system. $C_6D_6$ (Aldrich, 99.5%), was degassed prior to use. All dry solvents were stored under argon in gas-tight ampoules. Additionally chlorotrimethylsilane, $C_6D_6$, hexane, and toluene were stored over activated 3 Å molecular sieves.

**Additional characterization techniques:** NMR spectra were acquired on a Bruker AVIII 500 MHz NMR spectrometer ($^1H$ 500 MHz, $^{13}C$ 126 MHz) and Bruker AVIII 400 MHz NMR spectrometer ($^{31}P$ 162 MHz, $^{11}B$ 128 MHz). $^1H$ and $^{13}C$ NMR spectra were referenced to the most downfield solvent resonance ($^1H$ NMR $C_6D_6$: $\delta = 7.16$ ppm; $^{13}C$ NMR $C_6D_6$: $\delta = 188.06$ ppm). $^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ spectra were externally referenced to an 85% solution of $H_3PO_4$ in $H_2O$, and $BF_3 \cdot Et_2O$ in $C_6D_6$, respectively. Elemental analyses were carried out by Elemental Microanalyses Ltd. (Devon, U.K.). Samples (approx. 5 mg) were submitted in sealed Pyrex ampoules.

## 1.2. Compound syntheses

### *1.2.1. Synthesis of {[B](NaO)C=PFp*}$_2$ {Na[**1**]}$_2$*

[B]OCP (150 mg, 0.34 mmol) was added to a suspension of NaFp* (92 mg, 0.34 mmol) in toluene (2 mL). The solution darkened from light to dark orange. The solution was filtered to remove any excess NaFp*, concentrated to approximately 50% of the original volume and cooled overnight to yield {Na[**1**]}$_2$ as red crystals (195 mg, 80.6%) suitable for single crystal X-ray diffraction.

**CHN** Anal. Calcd. for $C_{39}H_{51}BFeN_2NaO_3P$: C, 65.38%; H, 7.18%; N, 3.91%. Found: C, 66.25%; H, 7.63%; N, 4.17%.

**$^1$H NMR** (500 MHz, $C_6D_6$): δ (ppm) 7.31 (br s, 6H; Ar*H*), 6.22 (s, 2H; (NC*H*)$_2$), 3.72 (br s, 4H; {C*H*(CH$_3$)$_2$}), 1.56 (br s, 26H; Cp* C*H*$_3$ and {CH(C*H*$_3$)$_2$}), 1.31 (d, $^3J_{H\text{–}H}$ = 7 Hz, 12H; {CH(C*H*$_3$)$_2$}).

**$^{13}$C{$^1$H} NMR** (126 MHz, $C_6D_6$): δ (ppm) 222.05 (s, br; *C*O), 146.58 (Ar*C*), 140.82 (Ar*C*), 126.63 (Ar*C*), 123.27 (Ar*C*), 118.44 ((N*C*H)$_2$), 94.93 (Cp**C*), 28.20 (*C*H(CH$_3$)$_2$), 25.85 (Cp**C*H$_3$), 23.52 (*C*H(CH$_3$)$_2$), 9.32 (CH(*C*H$_3$)$_2$), 9.27 (CH(*C*H$_3$)$_2$). Note: [B]*C*(O)PFp* not found, a small resonance at 145.79 ppm could be one half of the doublet with the other half obscured by the peak at 146.58 ppm.

**$^{11}$B{$^1$H} NMR** (128 MHz, $C_6D_6$): δ (ppm) 25.5 (s).

**$^{31}$P{$^1$H} NMR** (162 MHz, $C_6D_6$): δ (ppm) 188.6 (s).

**IR**: ν = 1899.7 cm$^{-1}$ ($\nu_{asym}$, C≡O), 1942.6 cm$^{-1}$ ($\nu_{sym}$, C≡O).

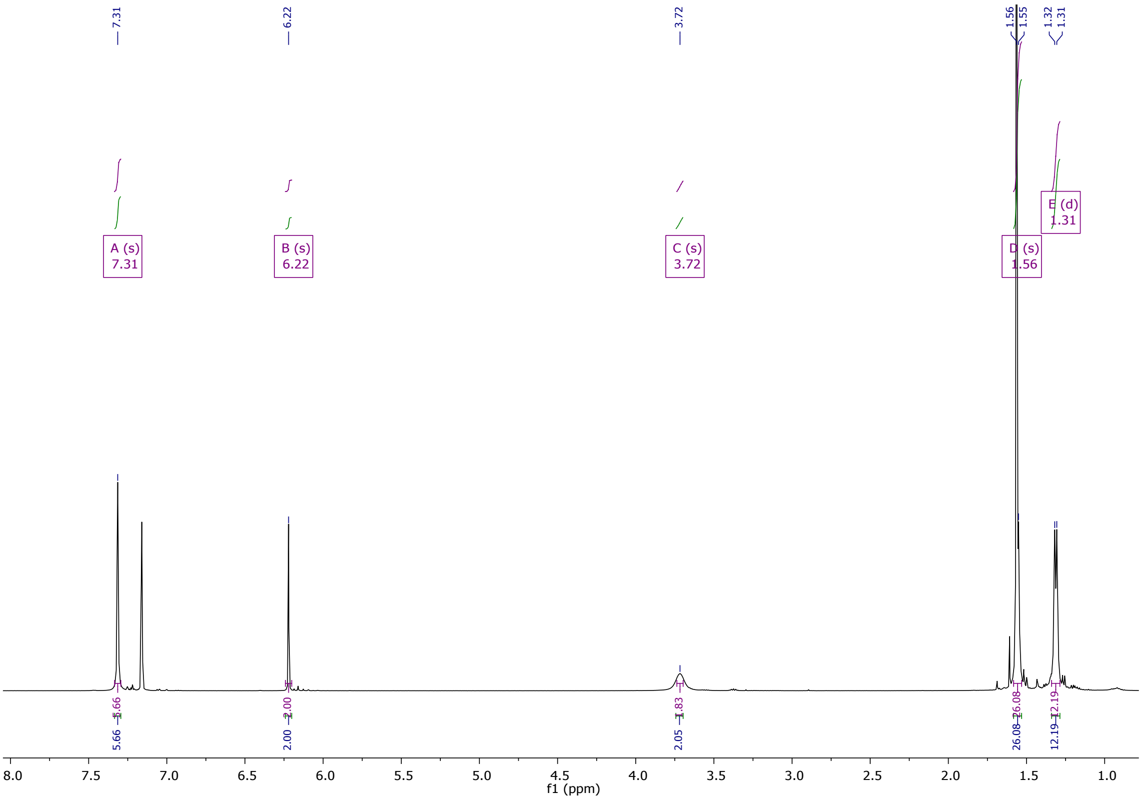

**Figure S1:** Room temperature $^1$H NMR of Na[**1**] in $C_6D_6$.

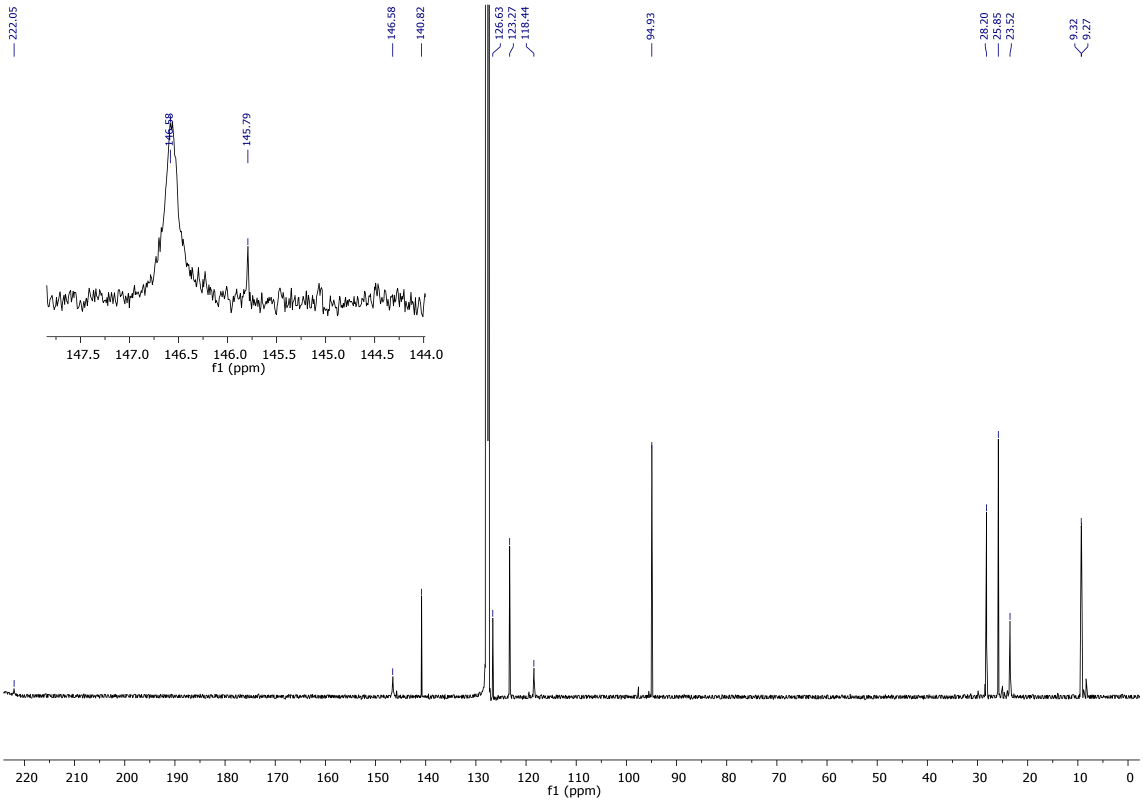

**Figure S2:** Room temperature $^{13}C\{^1H\}$ NMR of Na[**1**] in $C_6D_6$.

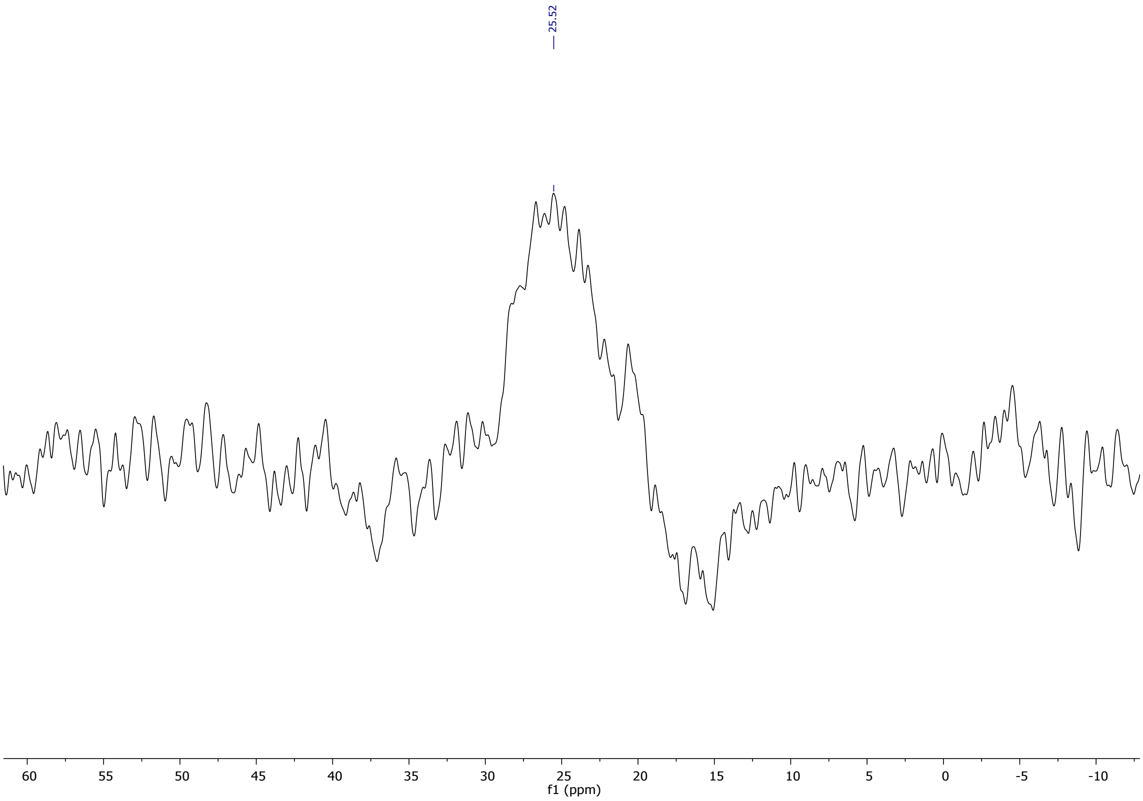

**Figure S3:** Room temperature $^{11}B\{^1H\}$ NMR of Na[**1**] in $C_6D_6$.

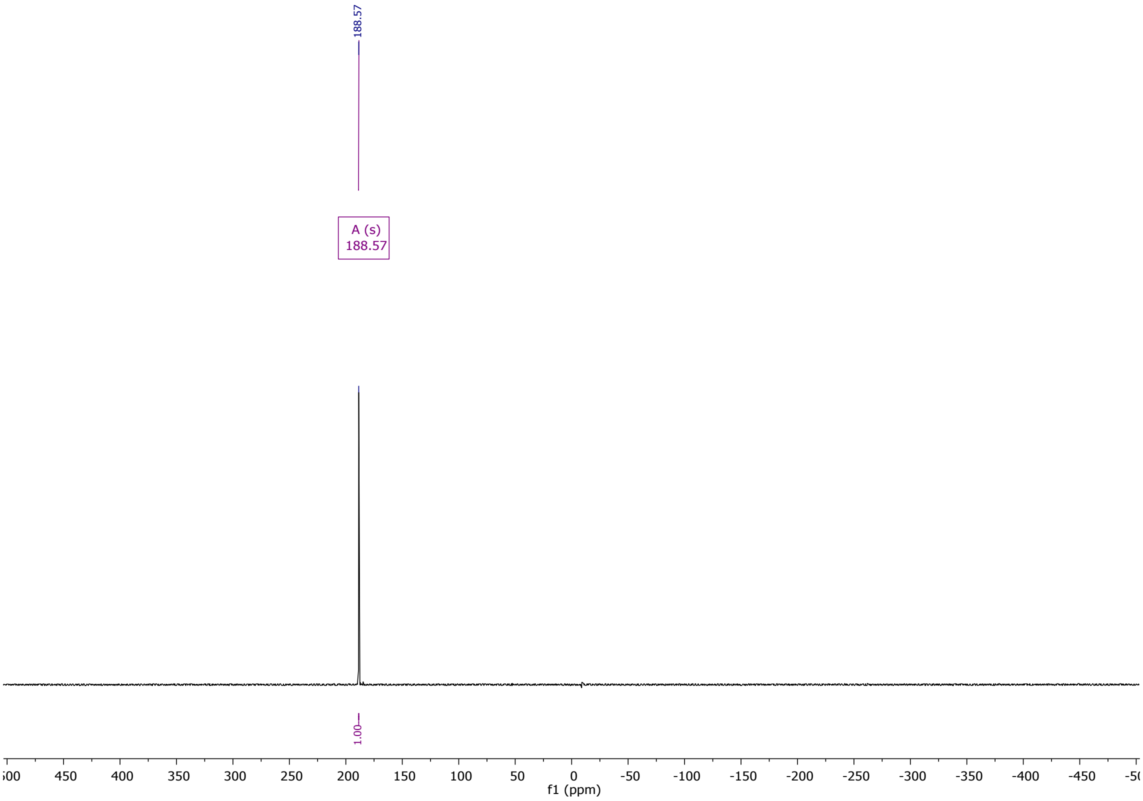

**Figure S4:** Room temperature $^{31}P\{^1H\}$ NMR of Na[**1**] in $C_6D_6$.

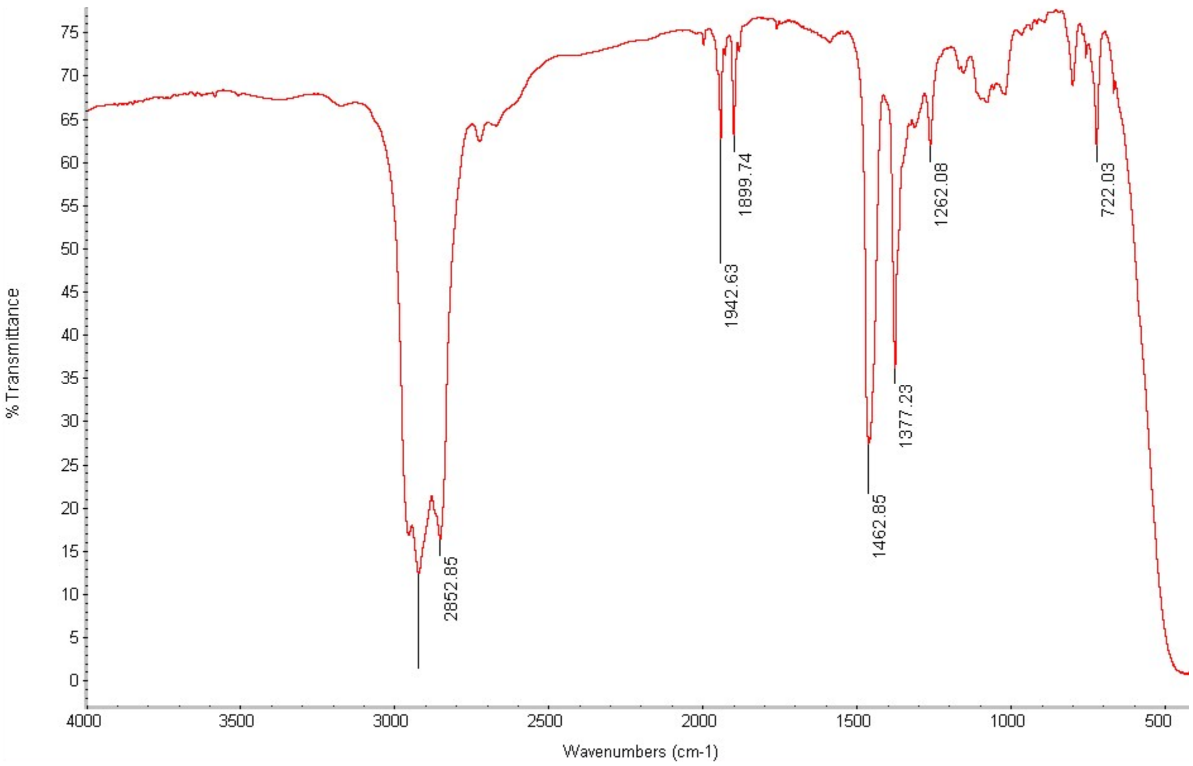

**Figure S5:** IR spectra of Na[**1**] in Nujol mull.

### *1.2.2. Synthesis of [B](Me$_3$SiO)C=PFp* (**2**)*

To a solution of Na[**1**] (100 mg, 0.14 mmol) in toluene (2 mL) was added trimethylsilyl chloride (18.3 mg, 0.17 mmol; 1.2 equivalents). A precipitate immediately formed and both the $^1$H and $^{31}$P NMR spectra revealed quantitative conversion to [B](Me$_3$SiO)C=PFp*. The solution was filtered and the solvent removed under reduced pressure, yielding an orange powder (91 mg, 85.0%). Recrystallisation from hexane yielded red crystals of [B](Me$_3$SiO)C=PFp* (**2**) suitable for X-ray diffraction.

**CHN** Anal. Calcd. for $C_{42}H_{60}BFeN_2O_3PSi$: C, 65.80%; H, 7.89%; N, 3.65%. Found: C, 65.35%; H, 7.61%; N, 3.99%.

**$^1$H NMR** (500 MHz, $C_6D_6$): δ(ppm) 7.27–7.20 (m, 6H; Ar*H*), 6.38 (s, 2H; (NC*H*)$_2$), 3.69 (sept, $^3J_{H\text{–}H}$ = 7 Hz, 4H; {C*H*(CH$_3$)$_2$}), 1.45 (d, $^3J_{H\text{–}H}$ = 7 Hz, 12H; {CH(C*H*$_3$)$_2$}), 1.40 (s, 15H; Cp* C*H*$_3$), 1.25 (d, $^3J_{H\text{–}H}$ = 7 Hz, 12H; {CH(C*H*$_3$)$_2$}), 0.15 (s, 9H; SiMe$_3$).

**$^{13}$C{$^1$H} NMR** (126 MHz, $C_6D_6$): δ (ppm) 217.04 (s, br; *C*O), 146.19 (d, $^1J_{C\text{–}P}$ = 33 Hz; [B]*C*(O)PFp*), 145.92 (Ar*C*), 140.72 (Ar*C*), 127.03 (Ar*C*), 124.00 (Ar*C*), 120.14 ((N*C*H)$_2$), 95.92(Cp**C*), 28.67 (*C*H(CH$_3$)$_2$), 26.36 (*C*H(CH$_3$)$_2$), 23.34 (Cp**C*H$_3$), 9.33 (CH(*C*H$_3$)$_2$), 1.15 (Si*C*H$_3$).

**$^{11}$B{$^1$H} NMR** (128 MHz, $C_6D_6$): δ(ppm) 23.3 (s, br).

**$^{31}$P{$^1$H} NMR** (162 MHz, $C_6D_6$): δ(ppm) 350.6 (s).

**IR**: $\nu$ = 1946.7 cm$^{-1}$ ($\nu_{asym}$, C≡O), 1993.7 cm$^{-1}$ ($\nu_{sym}$, C≡O).

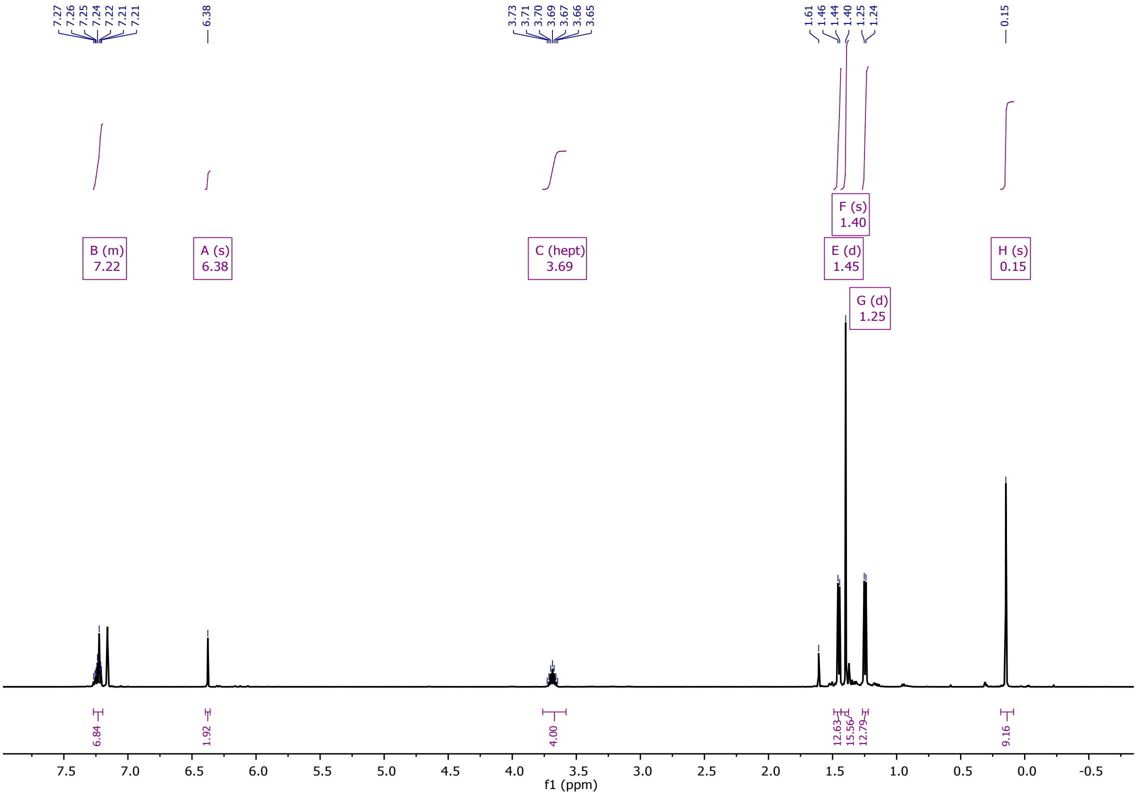

**Figure S6:** Room temperature $^1$H NMR spectrum of **2** in $C_6D_6$.

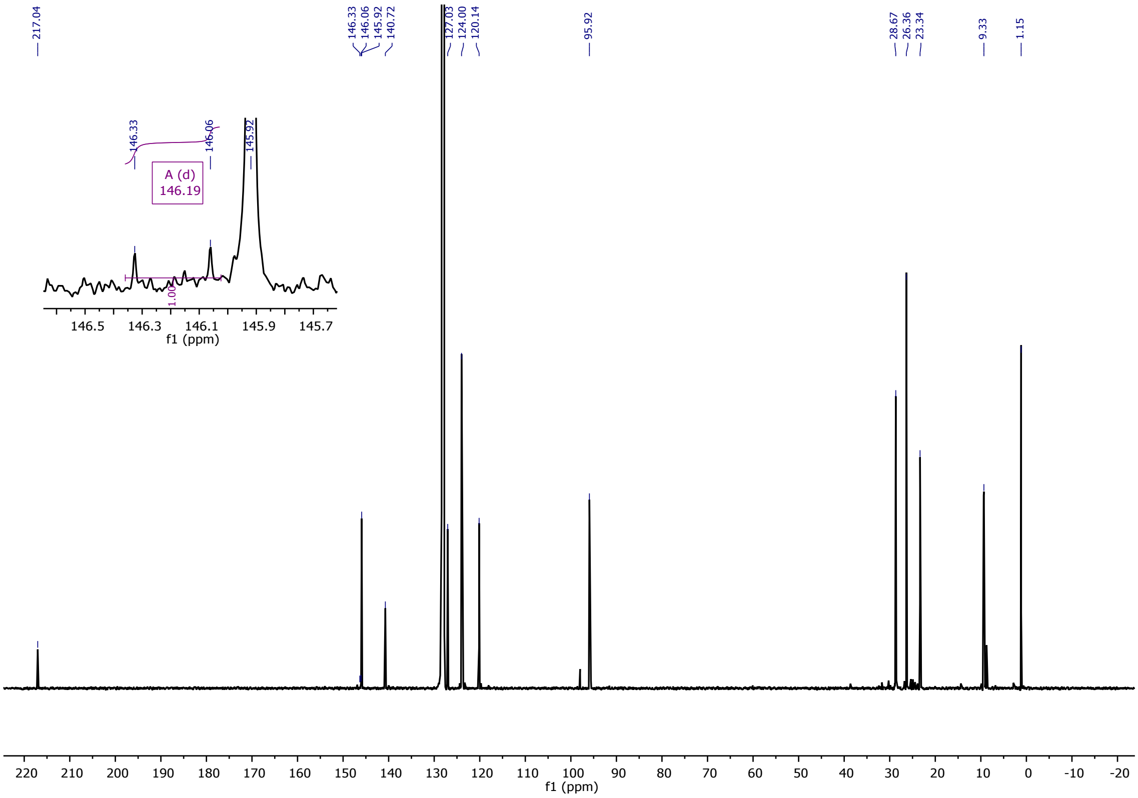

**Figure S7:** Room temperature $^{13}C\{^1H\}$ NMR spectrum of **2** in $C_6D_6$.

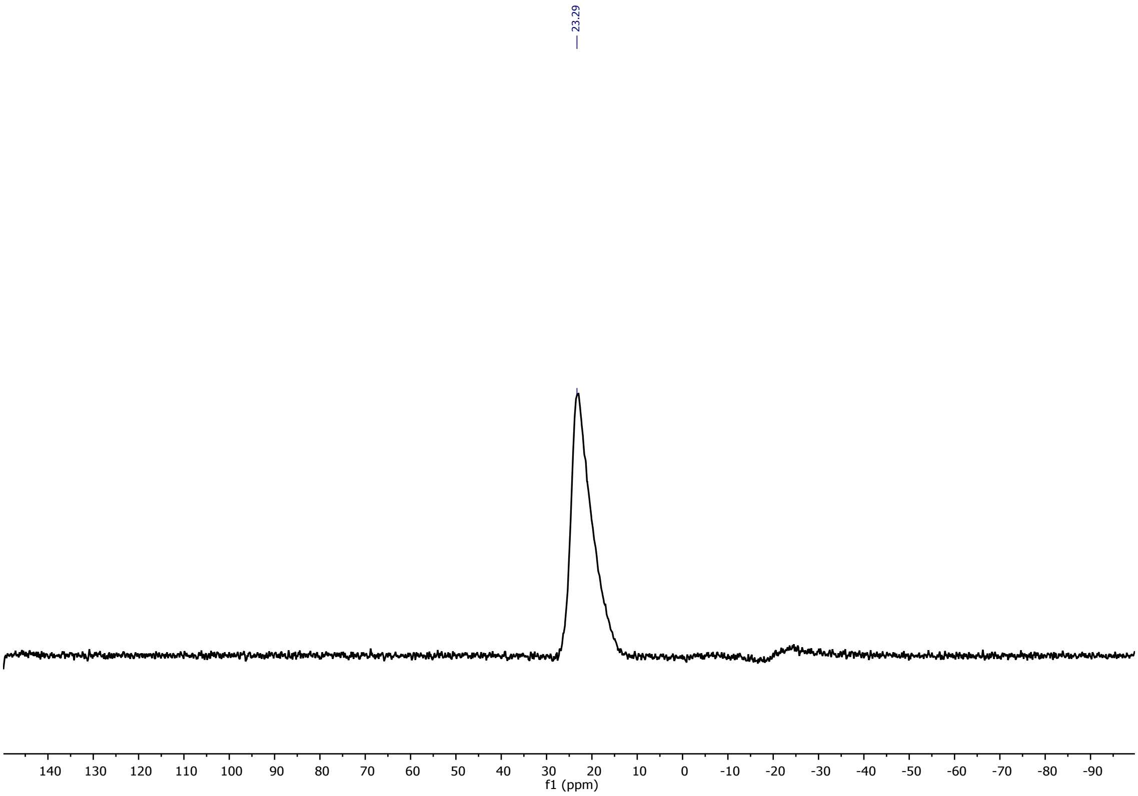

**Figure S8:** Room temperature $^{11}B\{^1H\}$ NMR spectrum of **2** in $C_6D_6$.

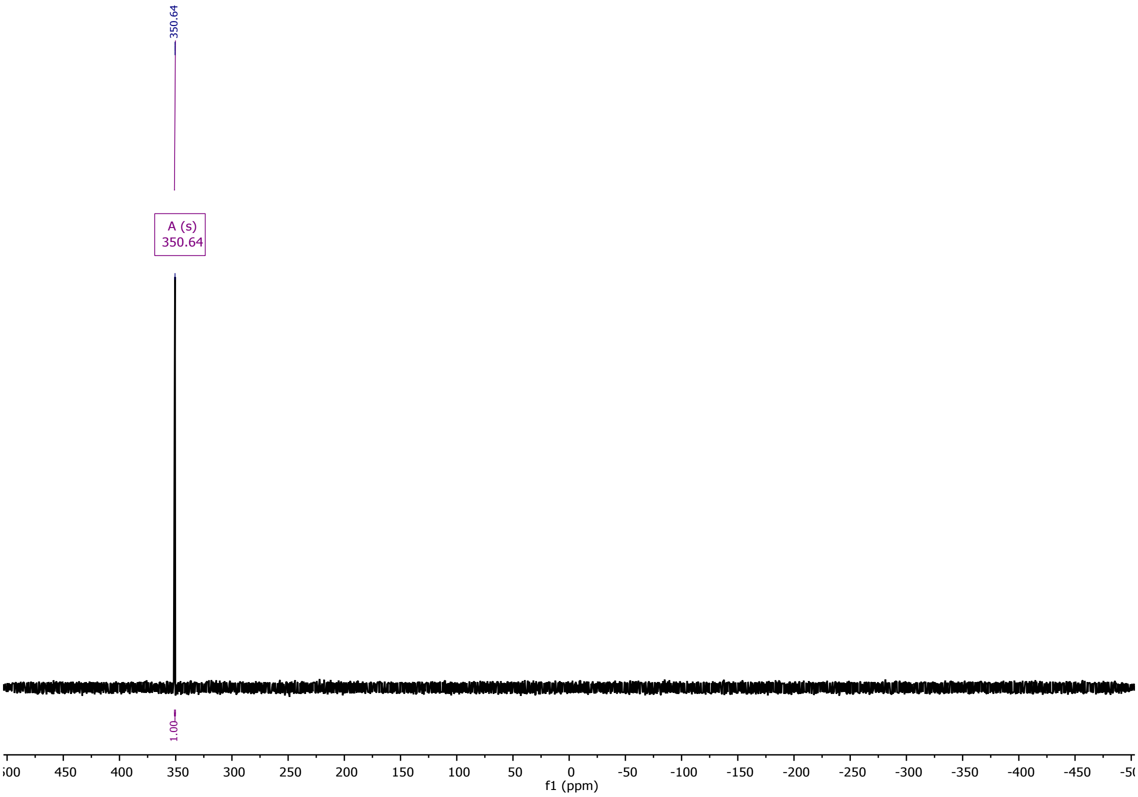

**Figure S9:** Room temperature $^{31}P\{^1H\}$ NMR spectrum of **2** in $C_6D_6$.

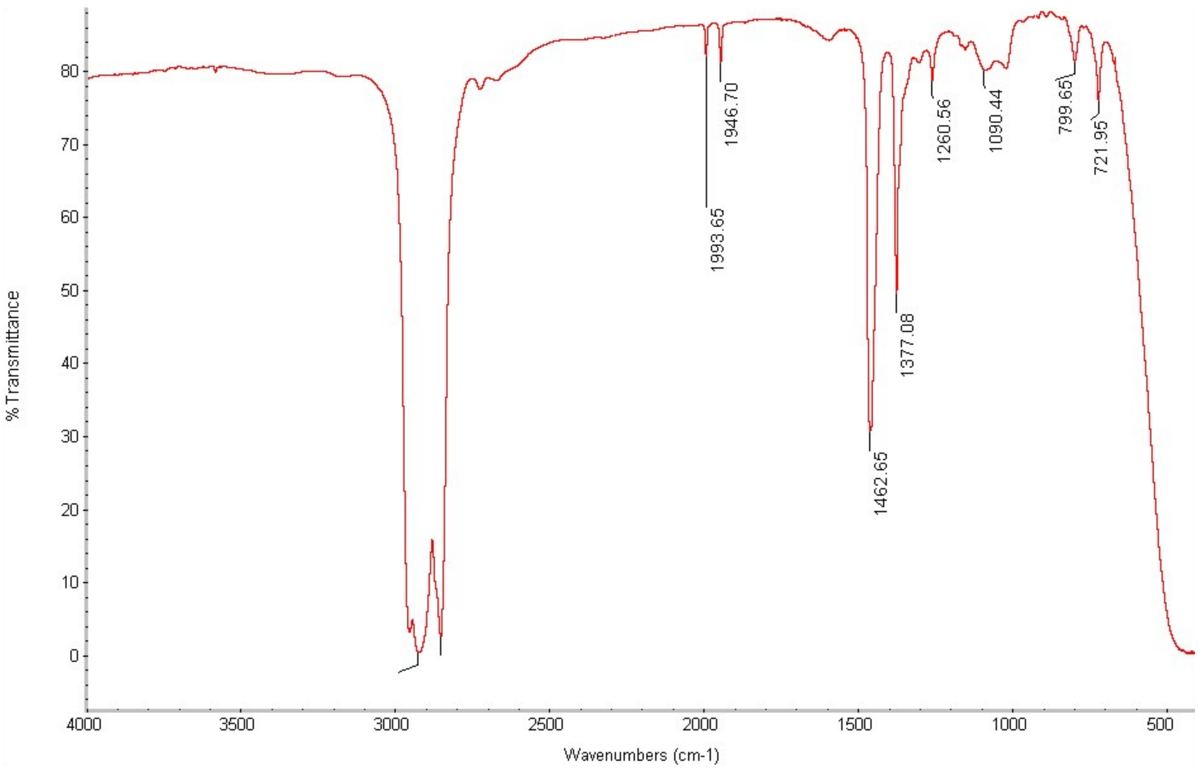

**Figure S10:** IR spectra of **2** in Nujol mull.

### *1.2.3. Synthesis of (PPh$_3$)AuP{C(O)[B]}Fp* (**3**)*

To a solution of Na[**1**] (100 mg, 0.14 mmol) in toluene (2 mL) was added chloro(triphenylphosphene)gold(I) (69 mg, 0.14 mmol). The suspension was sonicated for 30 minutes, after which the NMR spectra showed complete consumption of the starting material. The solution was filtered, and the solvent removed under reduced pressure. The resulting orange oil was washing with hexane and recrystallised from toluene yielding analytically pure orange crystals suitable for X-ray diffraction (87 mg, 60.1%).

**CHN** Anal. Calcd. for $C_{57}H_{66}AuBFeN_2O_3P_2$: C, 59.39%; H, 5.77%; N, 2.43%. Found: C, 58.91%, H5.34 %; N 2.40 %.

**$^1$H NMR** (500 MHz, $C_6D_6$): δ(ppm) 7.65–7.56 (m, 6H; Ar*H*), 7.28–7.18 (m, 6H; Ar*H*), 7.11–6.99 (m, 9H; Ar*H*), 6.26 (s, 2H; (NCH)$_2$), 3.57 (sept, $^3J_{H–H}$ = 7 Hz, 4H; C*H*(CH$_3$)$_2$), 1.47 (s, 15H; Cp* CH$_3$), 1.39 (d, $^3J_{H–H}$ = 7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.19 (d, $^3J_{H–H}$ = 7 Hz, 12H, CH(C*H*$_3$)$_2$).

**$^{13}$C{$^1$H} NMR** (126 MHz, $C_6D_6$): δ(ppm) 218.85 (s, br; *C*O), 146.38 (Ar*C*), 140.68 (Ar*C*), 138.40 (d, $^1J_{C–P}$ = 127.9 Hz; [B]*C*(O)PFp*), 134.75 (d, $^2J_{C–P}$= 14 Hz; P(Ph)$_3$ Ar*C*), 131.80 (d, $^1J_{C–P}$= 46 Hz; P(Ph)$_3$ Ar*C*), 131.21 (Ar*C*), 129.23 (d, $^3J_{C–P}$= 11 Hz; P(Ph)$_3$ Ar*C*), 127.21(Ar*C*), 123.38 (Ar*C*), 119.55 ((N*C*H)$_2$), 94.65 (Cp**C*), 30.23 (unknown impurity), 28.98 (*C*H(CH$_3$)$_2$), 26.00 (*C*H(CH$_3$)$_2$), 24.32 (Cp**C*H$_3$), 9.71(CH(*C*H$_3$)$_2$).

**$^{11}$B{$^1$H} NMR** (128 MHz, $C_6D_6$): δ(ppm) 21.8.

**$^{31}$P{$^1$H} NMR** (162 MHz, $C_6D_6$): δ(ppm) 98.8 (d, $^2J_{P–P}$= 102 Hz), 43.3 (d, $^2J_{P–P}$ = 102 Hz).

**IR**: $\nu$ = 1954.8 cm$^{-1}$ ($\nu_{asym}$, C≡O), 2003.2 cm$^{-1}$ ($\nu_{sym}$, C≡O).

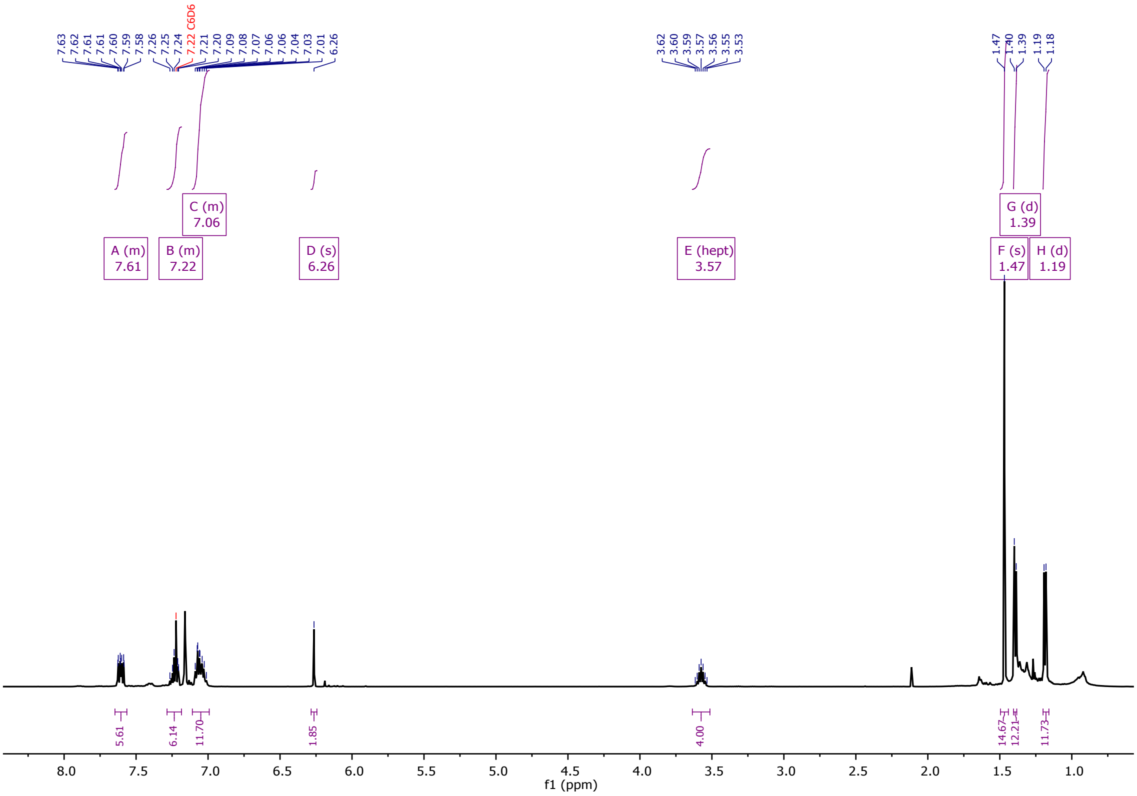

**Figure S11:** Room temperature $^{1}$H NMR spectrum of **3** in $C_6D_6$.

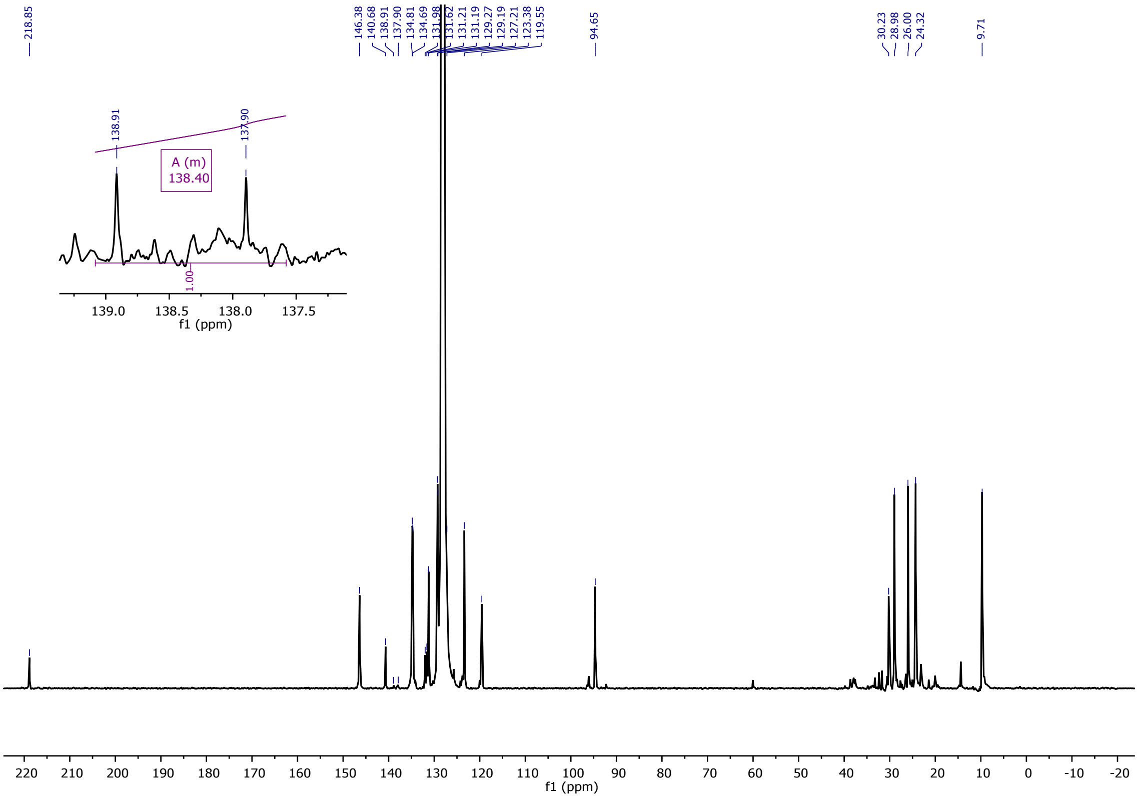

**Figure S12:** Room temperature $^{13}C\{^{1}H\}$ NMR spectrum of **3** in $C_6D_6$.

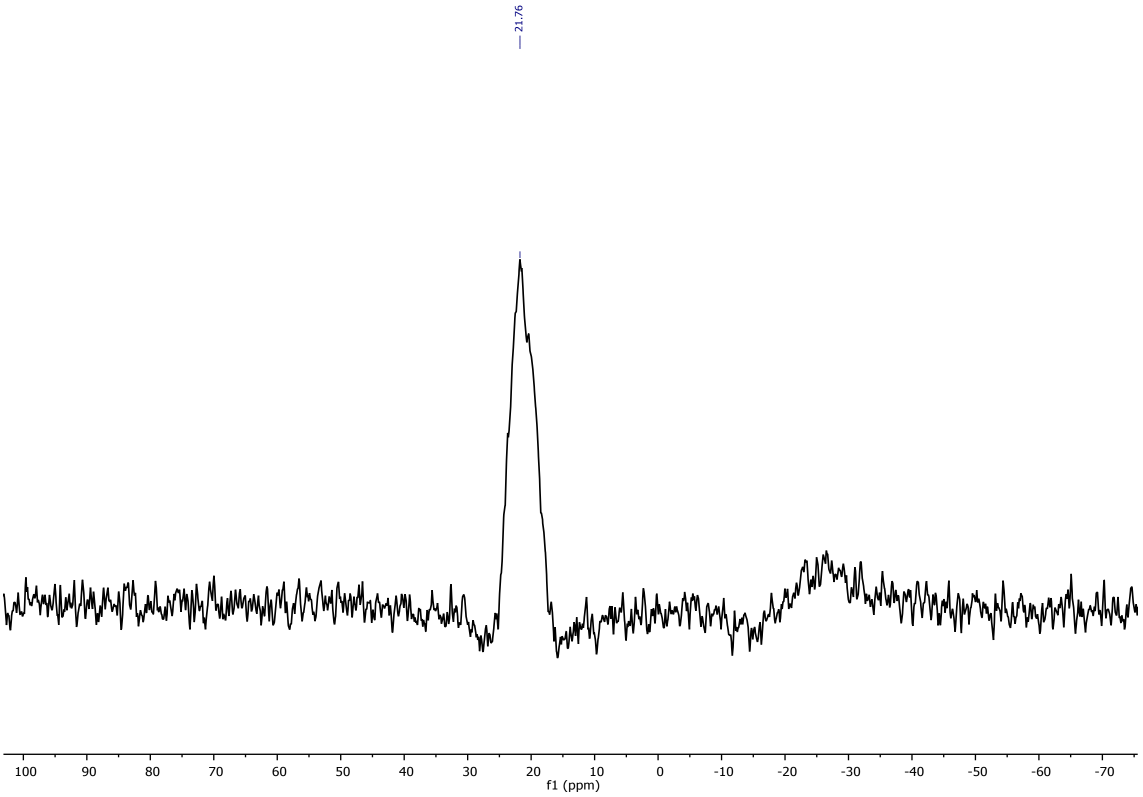

**Figure S13:** Room temperature $^{11}B\{^1H\}$ NMR spectrum of **3** in $C_6D_6$.

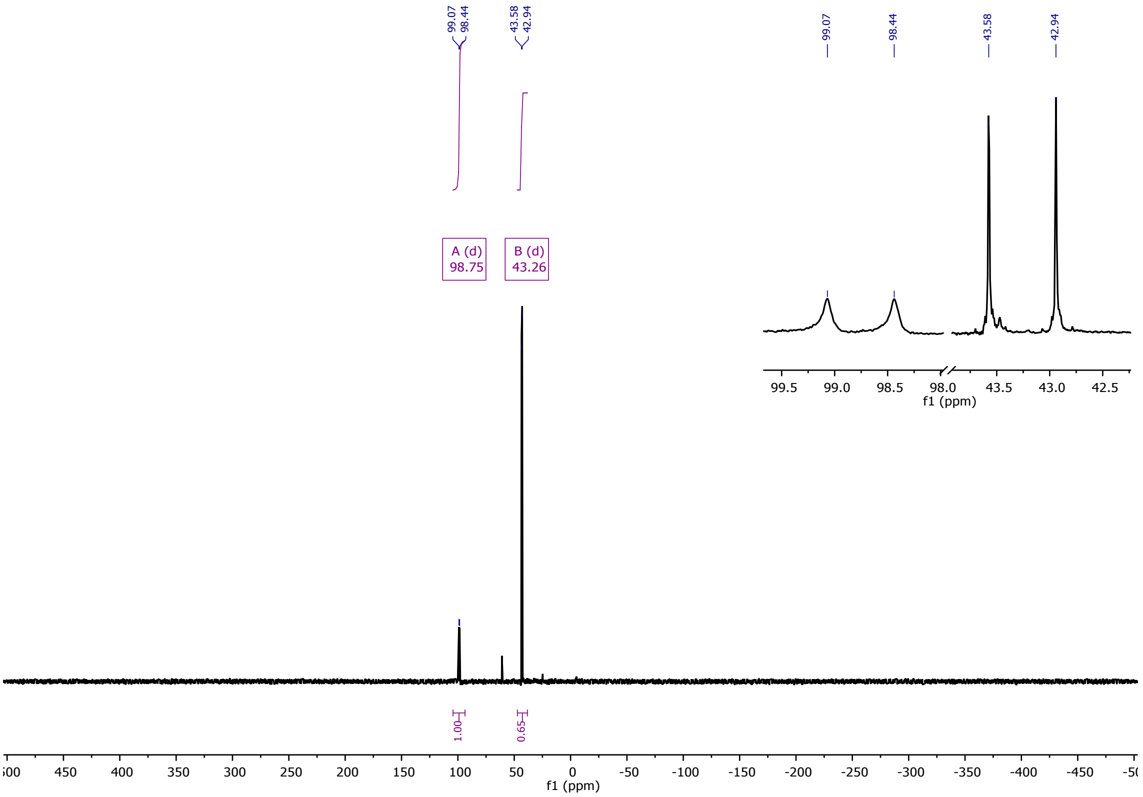

**Figure S14:** Room temperature $^{31}P\{^1H\}$ NMR spectrum of **3** in $C_6D_6$.

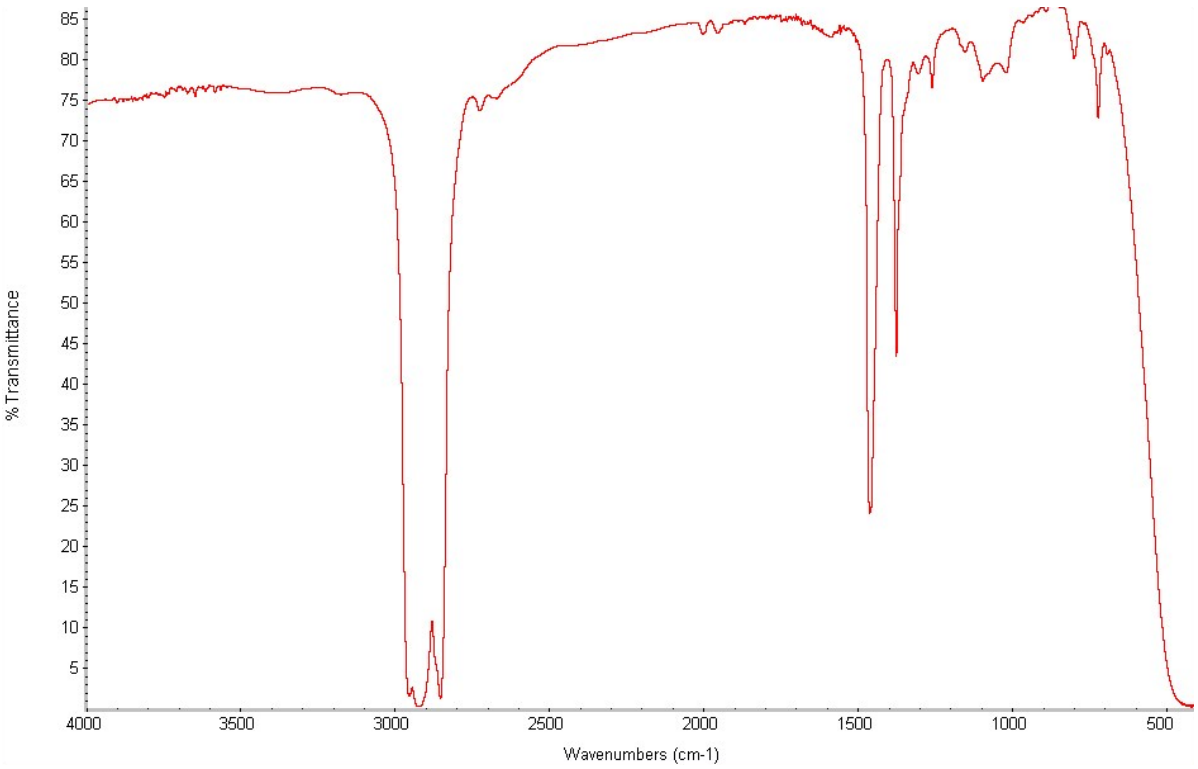

**Figure S15:** IR spectra of **3** in Nujol mull.

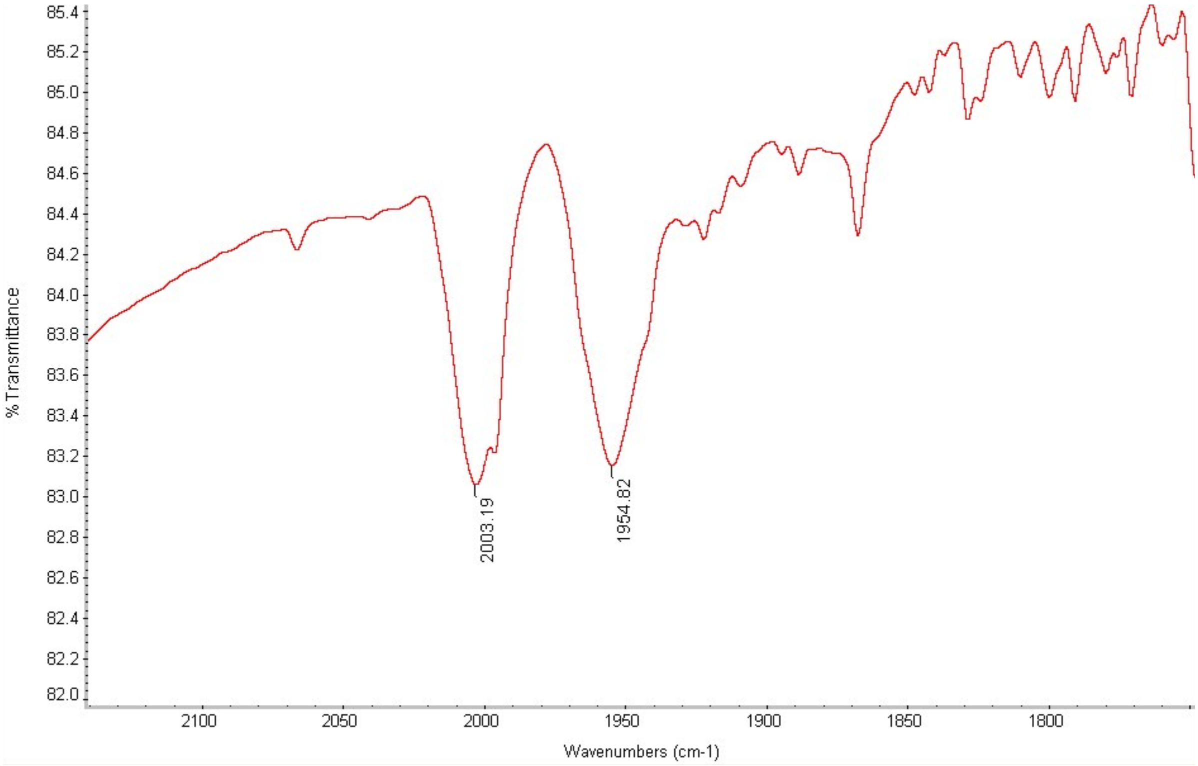

**Figure S16:** Enhanced view of carbonyl region of Figure S15.

## 2. Single Crystal X-ray diffraction Data

Single-crystal X-ray diffraction data were collected using either an Oxford Diffraction Supernova dual-source diffractometer equipped with a 135 mm Atlas CCD area detector. Crystals were selected under Paratone-N oil, mounted on micromount loops and quench-cooled using an Oxford Cryosystems open flow $N_2$ cooling device. Data were collected at 150 K using mirror monochromated Cu $K_\alpha$ radiation ($\lambda$ = 1.5418 Å; Oxford Diffraction Supernova) and processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro).[3] Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro suite. Structures were subsequently solved using direct methods and refined on $F^2$ using the SHELXL package.[4]

**Table S1.** Selected X-ray data collection and refinement parameters for (Na[**1**])$_2$, **2**·0.25hex, and **3**.

| | (Na[**1**])$_2$ | **2** | **3** |
|---|---|---|---|
| Formula | $C_{87}H_{123}B_2Fe_2N_4Na_2O_6P_2$ | $C_{43.5}H_{63.5}BFeN_2O_3PSi$ | $C_{57}H_{66}AuBFeN_2O_3P_2$ |
| CCDC | 1911021 | 1911022 | 1911023 |
| Fw [g mol$^{-1}$] | 1562.13 | 788.18 | 1152.68 |
| Crystal system | triclinic | triclinic | triclinic |
| Space group | *P*–1 | *P*–1 | *P*–1 |
| *a* (Å) | 12.4481(4) | 12.6726(7) | 12.5793(6) |
| *b* (Å) | 16.8150(7) | 14.4208(6) | 12.6322(5) |
| *c* (Å) | 22.2412(11) | 25.6379(10) | 17.8449(6) |
| α (°) | 96.817(4) | 78.827(4) | 86.392(3) |
| β (°) | 94.522(3) | 86.973(4) | 73.088(4) |
| γ (°) | 107.257(4) | 78.977(4) | 81.048(4) |
| *V* (Å$^3$) | 4382.4(3) | 4511.1(4) | 2679.5(2) |
| *Z* | 2 | 4 | 2 |
| Radiation, λ (Å) | Mo Kα, 0.71073 | Cu Kα, 1.54184 | Cu Kα, 1.54184 |
| Temp (K) | 150(2) | 150(2) | 150(2) |
| $\rho_{calc}$ (g cm$^{-3}$) | 1.184 | 1.161 | 1.429 |
| μ (mm$^{-1}$) | 0.429 | 3.556 | 8.145 |
| Reflections collected | 35282 | 39615 | 28840 |
| Independent reflections | 15427 | 18631 | 11081 |
| Parameters | 975 | 963 | 617 |
| R(int) | 0.0424 | 0.0476 | 0.0453 |
| R1/wR2,[a] I ≥ 2σI (%) | 5.05/10.25 | 5.38/13.81 | 3.96/9.55 |
| R1/wR2,[a] all data (%) | 8.12/11.31 | 7.17/15.56 | 4.83/9.93 |
| GOF | 1.042 | 1.039 | 1.029 |

$R1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$; $wR2 = \{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F_o^2)^2\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.0412 and 0.36 for (Na[**1**])$_2$, 0.0725 and 1.76 for **2**, and 0.0493 and 4.07 for **3**.

## 3. References

1 D. W. N. Wilson, A. Hinz and J. M. Goicoechea, *Angew. Chem. Int. Ed.* 2018, **57**, 2188–2193.

2 J. R. Green. Sodium Dicarbonylcyclopentadienylferrate in *Encycl. Reagents Org. Synth.*, John Wiley & Sons, Ltd, Chichester, UK, 2001.

3 *CrysAlisPro*, Agilent Technologies, Version 1.171.35.8.

4 (a) G. M. Sheldrick in SHELXL97, *Programs for Crystal Structure Analysis (Release 97-2)*, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998; (b) G. M. Sheldrick, *Acta Crystallogr. Sect. A* 1990, **46**, 467−473; (c) G. M. Sheldrick, *Acta Crystallogr. Sect. A* 2008, **64**, 112−122.