Electronic Supporting Information

# Redox-Responsive Phosphonite Gold Complexes in Hydroamination Catalysis

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## TOC of the Supporting Information:

# S1. Experimental details

## S1.1 General methods and instrumentation

All manipulations were performed under an argon atmosphere using standard Schlenk techniques.[S1] All solvents were freshly distilled under argon from sodium/benzophenone (THF, toluene, hexane, diethyl ether) or $CaH_2$ (acetonitrile, triethyl amine) prior to use. $C_6D_6$ and thf-$d_8$ were vacuum transferred from potassium/benzophenone into thoroughly dried glassware equipped with Young teflon valves. Air sensitive compounds were stored and weighed in glove boxes (Braun MB150 G-I and Unilab system). Solution NMR spectra were recorded using Bruker Avance instruments operating at $^1H$ Larmor frequencies of 300 or 400 MHz; chemical shifts are given relative to TMS for $^{13}C$ and $^1H$, or to $H_3PO_4$ for $^{31}P$. Coupling constants *J* are given in Hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as s, d, t, q, m, dd, dt, td, or ddd for singlets, doublets, triplets, quartetts, multiplets, doublets of doublets, doublets of triplets, triplets of doublets or doublet of doublets of doublets, respectively. The abbreviation br. is given for broadened signals. NMR samples were prepared in oven-dried 5 mm NMR tubes and sealed under argon. Unless otherwise stated, standard Bruker software routines (TOPSPIN) were used for the 1D and 2D NMR measurements. IR spectra were recorded on a Bruker Alpha FT-IR spectrometer using the ATR technique (attenuated total reflection) on bulk material, and the data are quoted in wavenumbers ($cm^{-1}$). The intensities of the absorption bands are indicated as vs (very strong), s (strong), m (middle), w (weak), vw (very weak). Mass spectra and elemental analyses were recorded by the institutional technical laboratories of the Karlsruhe Institute of Technology (KIT).

Cyclic voltammetry measurements were performed with a suitable potentiostat and an electrochemical cell within a glovebox. We used a freshly polished Pt disk working electrode, a Pt wire as counter electrode, and a Ag wire as (pseudo) reference electrode and $\{[nBu_4N][Al(OC(CF_3)_3)_4]\}$ (0.01 M) as electrolyte. Potentials were calibrated against the $Fc/Fc^+$ couple (internal standard: $Fc^*/Fc^{*+}$).

## S1.2 Starting materials

The amines, alkynes and the metal precursors were purchased from commercial sources and used as received. Commercial dichlorophenyl phosphine and dichloro-*tert*-butyl phosphine were degassed before usage. Dichloro-1,3-di(1,3,5-trimethylphenyl)phenyl phosphine[S2] and 1,1'-ferrocenediol[S3] were prepared according to literature procedures. The conducting salt $[NBu_4][Al\{OC(CF_3)_3\}_4]$ was purchased from Iolitec and used without further purification. The [3]ferrocenophanes **2** and **3** were described in the literature before[S3,S4], however, their synthesis and complementary characterisation are added for completeness.

**FcO$_2$PTer (1):** A stirred solution of 1,1'-ferrocenediol (763 mg, 3.5 mmol) and triethyl amine (1.2 mL, 8.75 mmol) in 20 mL THF was cooled to -78°C and then a solution of dichloro-1,3-di(1,3,5-trimethylphenyl)phenyl phosphine (1.452 g, 3.5 mmol) in 20 mL THF was added dropwise. The mixture was stirred for 1 hour at -78°C and slowly warmed to room temperature overnight. The solid was filtered off and the dried filtrate quickly purified at air by silica gel column chromatography with ethyl acetate as eluent. Single crystals were isolated from saturated solutions in hexane at -20°C. **Isolated yield** 1.304 g, 66%. **Decomp.** >196°C. **Elemental analysis** ($C_{34}H_{33}FeO_2P$, %) calc. (found): C 72.86 (72.81), H 5.94 (6.058). **$^1$H NMR** (300.1 MHz, $C_6D_6$, ppm): $\delta$ = 2.23 (s, 12 H, o-MesCH$_3$), 2.23 (s, 6 H, p-MesCH$_3$), 3.59-3.63 (m, 4 H, 3,4-CpH ), 3.75-3.77 (m, 2 H, 2,5-CpH ), 3.87- 3.89 (m, 2 H, 2,5-CpH), 6.90 (m, 4 H, m-MesH), 6.93 (dd, $^3J_{H,H}$ = 7.6 Hz, $^4J_{P,H}$ = 2.3 Hz, 2 H, m-ArH ), 7.23 (ddd, $^3J_{H,H}$ = 7.8 Hz, $^3J_{H,H}$ = 7.3 Hz, $^5J_{P,H}$ = 0.8 Hz, 1 H, p-ArH ). **$^{13}$C NMR** (75.5 MHz, $C_6D_6$, ppm): $\delta$ = 21.2 (s, p-MesC H$_3$), 21.5 (d, $^5J_{P,C}$ = 0,8 Hz, o-MesC$_3$), 60.4 (d, $^3J_{P,C}$= 7.6 Hz, 2,5-CpC ), 65.1 (s, 2,5-CpC ), 65.2 (s, 3,4-CpC), 66.4 (s, 3,4-CpC), 111.8 (d, $^2J_{P,C}$ = 1.2 Hz, i-CpC), 128.0 (s, m- MesC ), 129.9 (d, $^3J_{P,C}$ = 3.0 Hz, m-ArC ), 132.5 (s, p-ArC ), 135.7 (d, $^1J_{P,C}$ = 26.9 Hz, i-ArC), 136.6 (s, p-MesC), 136.9 (d, $^4J_{P,C}$ = 1.9 Hz, o-MesC), 139.1 (d, $^3J_{P,C}$ = 6.4Hz, i-MesC), 147.7 (d, $^2J_{P,C}$ = 23.3 Hz, o-ArC). **$^{31}$P NMR** (121.5 MHz, $C_6D_6$, ppm): $\delta$ = 183.8 (s). **ESI-MS** m/z calc. for $C_{34}H_{33}FeO_2P$ [M]: 560.156, found 560.156 (100.0 %). **IR** (solid, ATR, cm$^{-1}$) ν = 2915(vw), 2167(vw), 2044(vw), 2022(vw), 1983(vw), 1610(vw), 1561(vw), 1448(m), 1372(w), 1236(m), 1182(vw), 1119(vw), 1022 (w), 932 (m), 847 (m), 811 (w), 795 (vs), 756 (m), 731 (m), 657 (m), 634 (m), 617 (m), 589 (w), 556 (w), 521 (m), 508 (m), 487 (w), 475 (w), 464 (w), 441 (w), 427 (w), 415 (m), 404 (w), 395 (w).

**FcO$_2$PPh (2):**[S4] A stirred solution of 1,1'-ferrocenediol (1.090 g, 5.0 mmol) and triethyl amine (1.7 mL, 12.5 mmol) in 40 mL THF was cooled to -78°C and then a solution of dichlorophenyl phosphine (895 mg, 5.0 mmol) in 30 mL THF was added dropwise. The mixture was stirred for 1 hour at -78°C and slowly warmed to room temperature overnight. The solid was filtered off over Celite® and the filtrate dried *in vacuo*. Pure, yellow **2** was obtained after crystallization from a toluene/hexane mixture at room temperature. **Elemental analysis** ($C_{16}H_{13}FeO_2P$, %) calc. (found): C 59.30 (59.37), H 4.04 (3.963). **IR** (solid, ATR, cm$^{-1}$) ν = 3099 (vw), 1449 (s), 1375 (w), 1234 (s), 1212 (m), 1105 (w), 1026 (m), 931 (vs), 852 (w), 836 (w), 790 (vs), 753 (s), 704 (vs), 690 (s), 649 (s), 630 (s), 613 (m), 521 (s), 506 (vs), 486 (vs), 453 (m), 439 (m), 416 (vs).

**$FcO_2P^tBu$ (3):**$^{S3}$ A stirred solution of 1,1'-ferrocenediol (545 mg, 2.5 mmol) and triethyl amine (0.9 mL, 6.25 mmol) in 20 mL THF was cooled to -78°C and then a solution of dichloro-*tert*-butyl phosphine (397 mg, 2.5 mmol) in 20 mL THF was added dropwise. The mixture was stirred for 1 hour at -78°C and slowly warmed to room temperature overnight. The solid was filtered off over Celite® and the filtrate dried *in vacuo*. Pure, yellow **3** was obtained after crystallization from a saturated hexane solution at -20°C. **Elemental analysis** ($C_{14}H_{17}FeO_2P$, %) calc. (found): C 55.29 (55.69), H 5.63 (5.523). **$^{31}$P NMR** (121.5 MHz, $C_6D_6$, ppm): δ = 201.1 (s). **IR** (solid, ATR, cm$^{-1}$) ν = 3732 (vw), 3101 (vw), 2948 (vw), 2157 (vw), 2023 (vw), 1969 (vw), 1449 (s), 1375 (w), 1361 (w), 1235 (s), 1028 (m), 931 (vs), 839 (w), 808 (m), 789 (vs), 747 (s), 705 (vw), 691 (vw), 668 (s), 649 (m), 637 (w), 621 (m), 552 (vw), 518 (m), 504 (vs), 440 (w), 422 (w), 393 (vw).

**$FcO_2$PTerAuCl (4):** A solution of [Au(tht)Cl] (128 mg, 0.4 mmol) and **1** (224 mg, 0.4 mmol) in 20 mL THF was stirred for 5 days, filtered through Celite® and then dried *in vacuo*. Pure **4** was isolated as yellow single crystals from toluene/hexane solutions at room temperature. **Isolated yield:** 206 mg, 65 %. **Decomp.** 134-140°C. **Elemental analysis** [$C_{34}H_{33}AuClFeO_2P \cdot 1/5\ (C_6H_{14})$] calc. (found): C 52.19 (52.19), H 4.45 (4.137). **$^1$H NMR** (300.1 MHz, $C_6D_6$, ppm): δ = 2.07 (s, 12 H, o-$MesCH_3$), 2.38 (s, 6 H, p-$MesCH_3$), 3.49 (t, 4 H, $^3J_{H,H}$ = 2.0 Hz, 3,4-CpH ), 3.54-3.55 (m, 2 H, 2,5- CpH ), 5.17-5.19 (m, 2 H, 2,5-CpH ), 6.72 (dd, $^3J_{H,H}$ = 7.6 Hz, $^4J_{P,H}$ = 4.4 Hz, 2 H, m-ArH ), 6.97 (s, 4 H, m-MesH ), 7.06 (td, $^3J_{H,H}$ = 7.6 Hz, $^5J_{P,H}$ = 1.4 Hz, 1 H, p-ArH ). **$^{13}$C NMR** (75.5 MHz, $C_6D_6$, ppm): δ = 21.2 (s, o-$MesCH_3$), 21.4 s, p-$MesCH_3$), 62.6 (d, $^3J_{P,C}$ = 4.2 Hz, 2,5-CpCH), 64.7 (d, $^3J_{P,C}$ = 1.4 Hz, 2,5-CpCH), 65.8 (d, $^4J_{P,C}$ = 1.0 Hz, 3,4-CpCH), 68.7 (s, 3,4-CpCH), 109.1 (d, $^2J_{P,C}$ = 9.8 Hz, i-CpC), 128.1 (d, $^1J_{P,C}$ = 85.4Hz, i-ArC), 129.2 (s, m-MesCH), 131.5 (d, $^3J_{P,C}$ = 8.9 Hz, m-ArCH), 134.4 (d, $^4J_{P,C}$ = 1.9 Hz, p-ArCH), 136.5 (s, o -MesC ), 137.9 (d, $^3J_{P,C}$ = 7.1 Hz, i -MesC ), 138.5 (s, p -MesC ), 148.5 (d, $^2J_{P,C}$ = 17.2 Hz, o-ArC ). **$^{31}$P NMR** (121.5 MHz, $C_6D_6$), ppm): δ = 147.8 (s). **ESI-MS** m/z calc. for $C_{34}H_{33}AuClFe_2P$ [M]: 792.0922, found 792.0903 (6,7 %). **IR** (solid, ATR, cm$^{-1}$) ν = 2918 (vw), 2213 (vw), 2125 (vw), 2000 (vw), 1972 (vw), 1899 (vw), 1609 (vw), 1565 (vw), 1439 (s), 1373 (w), 1228 (w), 1183 (vw), 1123(vw), 1054(vw), 1028(w), 929(s), 866(vw), 847(vs), 832(m), 810(m), 796(m), 754(vw), 734(w), 656(s), 630(s), 586(w), 513(m), 492(s), 460(w), 435 (vw), 425 (vw), 413 (m), 380 (w).

**$FcO_2$PPhAuCl (5):** To a solution of [Au(tht)Cl] (160 mg, 0.5 mmol) in 10 mL THF a solution of **2** (162 mg, 0.5 mmol) in 10 mL THF was added at 0°C and stirred for 1 hour at room temperature. The mixture was filtered through Celite® and then dried *in vacuo*. Pure **5** was isolated as yellow single crystals from toluene/hexane solutions at room temperature. **Isolated yield:** 191 mg, 69 %. **Decomp.** 175-182°C. **Elemental analysis** [$C_{16}H_{13}AuClFeO_2P$] calc. (found): C 34.53 (34.61), H 2.35 (2.483). **$^1$H NMR** (300,1 MHz, $C_6D_6$, ppm): δ = 3.55 (td, $^3J_{H,H}$ = 2.7 Hz, $^4J_{H,H}$ = 1.4 Hz, 2 H, 3,4-CpH ), 3.64 (td, $^3J_{H,H}$ = 2.8 Hz, $^3J_{H,H}$ = 1.5 Hz, 2 H, 3,4-CpH ), 3.96-3.98 (m, 2 H, 2,5-CpH), 5.08 (dt, $^3J_{H,H}$ =

2.7 Hz, $^{3}J_{H,H}$ = 1.4 Hz, 2 H, 2,5-CpH), 6.91-6.97 (m, 2 H, m-PhH), 7.01-7.05 (m, 1 H, p-PhH), 7.60-7.68 (m, 2 H, o-PhH). **$^{13}$C NMR** (75.5 MHz, $C_6D_6$, ppm): $\delta$ = 62.4 (d, $^{3}J_{P,C}$ = 4.4Hz, 2,5-CpCH), 65.0 (d, $^{3}J_{P,C}$ = 2.0 Hz, 2,5-CpCH), 66.3 (s, 3,4-CpCH), 68.8 (s, 3,4-CpCH), 109.3 (d, $^{2}J_{P,C}$ = 9.7 Hz, i-CpC), 129.1 (d, $^{2}J_{P,C}$ = 14.1 Hz, m-PhC), 131.0 (d, $^{1}J_{P,C}$ = 87.4 Hz, i-PhC), 132.1 (d, $^{3}J_{P,C}$ = 19.9 Hz, o-PhC), 134.4 (d, $^{4}J_{P,C}$ = 2.4 Hz, p-PhC H). **$^{31}$P NMR** (121.5 MHz, $C_6D_6$, ppm): $\delta$ = 146.3 (s). **ESI-MS** m/z calc. for $C_{16}H_{13}AuClFeO_2P$ [M]: 555.9357, found 555.9348 (8.3 %). **IR** (solid, ATR, cm$^{-1}$) $\nu$ = 3100 (vw), 2157 (vw), 1960 (vw), 1439 (m), 1374 (vw), 1225 (m), 1120 (w), 1030 (w), 929 (s), 839 (m), 815 (s), 754 (m), 730 (m), 705 (w), 690 (m), 651 (m), 631 (m), 615 (m), 511 (vs), 487 (vs), 469 (m), 441 (w), 412 (w).

**$FcO_2P^tBuAuCl$ (6):** To a solution of [Au(tht)Cl] (160 mg, 0.5 mmol) in 10 mL THF a solution of **3** (152 mg, 0.5 mmol) in 10 mL THF was added at 0°C and stirred for 1 hour at room temperature. The mixture was filtered through Celite® and then dried *in vacuo*. Pure **6** was isolated as yellow single crystals from toluene/hexane solutions at room temperature. **Isolated yield:** 182 mg, 68 %. **Decomp.** 186-193°C. **Elemental analysis** [$C_{14}H_{17}AuClFeO_2P$] calc. (found): C 31.34 (31.79), H 3.19 (3.113). **$^{1}$H NMR** (300.1MHz, $C_6D_6$, ppm): $\delta$ = 0.88 (d, $^{3}J_{P,H}$ = 18.7 Hz, 9 H, $^{t}BuCH_3$), 3.53 (td, $^{3}J_{H,H}$ = 2.7 Hz, $^{4}J_{H,H}$ = 1.4 Hz, 2 H, 3,4-CpH ), 3.60 (td, $^{3}J_{H,H}$ = 2.8 Hz, $^{4}J_{H,H}$ = 1.5 Hz, 2 H, 3,4-CpH ), 3.87-3.90 (m, 2 H, 2,5-CpH ), 4.97 (dt, $^{3}J_{H,H}$ = 2.7 Hz, $^{4}J_{H,H}$= 1.4 Hz, 2 H, 2,5-CpH). **$^{13}$C NMR** (75.5 MHz, $C_6D_6$, ppm): $\delta$ = 22.6 (d, $^{2}J_{P,C}$ = 7.0 Hz, $^{t}BuCH_3$), 35.2 (d, $^{1}J_{P,C}$ = 49.9 Hz, i-$^{t}$BuC), 62.2 (d, $^{3}J_{P,C}$= 4.0 Hz, 2,5-CpC H), 64.8 (d, $^{3}J_{P,C}$ = 1.6 Hz, 2,5-CpC H), 66.0 (s, 3,4-CpC H), 68.6 (s, 3,4-CpC H), 109.9 (d, $^{2}J_{P,C}$ = 11.5 Hz,i-CpC). $^{31}$P NMR (121.5 MHz, $C_6D_6$), ppm): $\delta$ = 167.0 (s). **ESI-MS** m/z calc. for $C_{14}H_{17}AuClFeO_2P$ [M]: 535.9670, found 535.9661 (13.2 %). **IR** (solid, ATR, cm$^{-1}$) $\nu$ = 2122(vw), 2016 (vw), 1994 (vw), 1444 (m), 1374 (vw), 1236 (w), 1030 (w), 932 (s), 852 (s), 826 (w), 806 (m), 678 (s), 642 (w), 630 (m), 616 (m), 509 (vs), 491 (m), 448 (m), 428 (w), 393 (w).

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[S2] C. Overländer, J. J. Tirrée, M. Nieger, E. Niecke, C. Moser, S. Spirk and R. Pietschnig, *Appl. Organomet. Chem.*, 2007, **21**, 46–48.

[S3] M. Herberhold and H.-D. Brendel, *J. Organomet. Chem.*, 1993, **458**, 205–209.

[S4] M. Herberhold, A. Hofmann and W. Milius, *J. Organomet. Chem.*, 1998, **555**, 187–200.

## S2. X-Ray crystallography

Crystal data collection and processing parameters are given below. In order to avoid degradation, single crystals were mounted in perfluoropolyalkyletheroil on top of the edge of an open Mark tube and then brought into the cold nitrogen stream of a low- temperature device (Oxford Cryosystems Cryostream unit) so that the oil solidified. Diffraction data were measured using a Stoe IPDS II diffractometer and graphite-monochromated Mo$K_{\alpha}$ (0.71073 Å) radiation. The structures were solved by dual-space direct methods with SHELXT,[S5] followed by full-matrix least-squares refinement using SHELXL-2014/7.[S6] All non-hydrogen atoms were refined anisotropically, with organic hydrogen atoms placed in calculated positions using a riding model. Absorption corrections were applied for compounds **3**-**6** (multi-scan). Crystallographic data, data collection, and refinement details are summarized in Table S2-1. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1898143-1898147. Copies of the data can be obtained from https://summary.ccdc.cam.ac.uk/structure-summary-form.

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[S5] G. M. Sheldrick, *Acta Cryst. Sect. A*, 2015, **71**, 3–8.

[S6] G. M. Sheldrick, *Acta Cryst. Sect. C*, 2015, **71**, 3–8.

Table S2-1 Crystallographic data, data collection and refinement details for **1**, **3-6**.

| Compound | **1** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|
| Empirical formula | $C_{34}H_{33}FeO_2P$ | $C_{14}H_{17}FeO_2P$ | $C_{34}H_{33}AuClFeO_2P$ | $C_{16}H_{13}AuClFeO_2P$ | $C_{14}H_{17}AuClFeO_2P$ |
| *M* | 560.42 | 304.09 | 792.84 | 556.50 | 536.51 |
| Crystal system | Monoclinic | Triclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | $P2_1/n$ | $P$-1 | $P2_1/c$ | $P$–1 | $P2_1/n$ |
| $a$ /pm | 1620.9(3) | 907.80(18) | 800.90(16) | 733.60(15) | 1337.4(3) |
| $b$ /pm | 788.80(16) | 1033.4(2) | 2536.6(5) | 905.30(18) | 1297.2(3) |
| $c$ /pm | 2150.0(4) | 1446.8(3) | 1480.3(3) | 14.901(3) | 1822.3(4) |
| $\alpha$ /° | | 82.74(3) | | 98.89(3) | |
| $\beta$ /° | 98.26(3) | 89.87(3) | 102.49(3) | 95.82(3) | 91.65(3) |
| $\gamma$ /° | | 82.00(3) | | 106.42(3) | |
| $V$ /·$10^6$ pm$^3$ | 2720.4(10) | 1333.1(5) | 2936.2(11) | 926.8(4) | 3160.2(1) |
| $\mu$ /mm$^{-1}$ | 0.644 | 1.241 | 5.661 | 8.920 | 10.459 |
| $D_{calcd}$ /g cm$^{-3}$ | 1.368 | 1.515 | 1.794 | 1.994 | 2.255 |
| Crystal dim. /mm$^3$ | 0.2 × 0.1 × 0.05 | 0.2 × 0.2 × 0.15 | 0.4 × 0.4 × 0.3 | 0.4 × 0.2 × 0.1 | 0.25 × 0.25 × 0.05 |
| $Z$ | 4 | 4 | 4 | 2 | 8 |
| $T$ /K | 200 | 200 | 200 | 200 | 200 |
| $2\theta_{\max}$ /° | 52.00 | 54.00 | 55.00 | 56.564 | 54.00 |
| Refls. measured | 23780 | 21197 | 30466 | 16741 | 49558 |
| Refls. unique | 5350<br>($R_{int}$ = 0.0756) | 5828<br>($R_{int}$ = 0.0852) | 6745<br>($R_{int}$ = 0.0692) | 4590<br>($R_{int}$ = 0.0449) | 6902<br>($R_{int}$ = 0.0740) |
| Param./restraints | 350 / 0 | 331 / 0 | 368 / 0 | 200 / 0 | 368 / 0 |
| $R1$ [$I \geq 2\sigma(I)$] | 0.0522 | 0.0433 | 0.0285 | 0.0250 | 0.0315 |
| $wR2$ (all data) | 0.1644 | 0.1245 | 0.0769 | 0.0658 | 0.0768 |
| max./min. res. elec. dens. /e ·$10^{-6}$ pm$^{-3}$ | 0.41 / –0.44 | 0.63 / –0.61 | 1.05 / –1.22 | 0.90 / –0.82 | 1.65 / –1.11 |
| CCDC | 1898143 | 1898144 | 1898145 | 1898146 | 1898147 |

Table S2-2 Selected distances [pm], bond lengths [pm] and angles [°] of **1** and **3**-**6**. Values of the second molecule in the asymmetric unit are given in square brackets; α, δ and τ describe the angles [°] explained in figure S2-1.

| | **1** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|
| Fe1···P1 | 337.6(9) | 331.3(10) [330.8(11] | 339.5(6) | 337.9(12) | 338.4(7) [338.8(8)] |
| Fe1···Au1 | – | – | 418.6(9) | 423.2(12) | 426.4(10) [416.6(8)] |
| P1–O1 | 165.8(3) | 166.7(4) [166.7(4)] | 161.5(2) | 161.5(2) | 160.5(4) [160.9 (3)] |
| P1–O2 | 166.1(4) | 167.1(5) [167.0(5)] | 161.1(2) | 161.3(2) | 160.7(3) [161.6(3)] |
| P1-C1$_R$ | 182.6(4) | 183.9(6) [184.1(5)] | 181.5(3) | 178.5(4) | 181.5(5) [180.7(5)] |
| Au1–P1 | – | – | 220.7(7) | 220.1(5) | 221.4(5) [221.1(4)] |
| Au1–Cl1 | – | – | 227.6(7) | 228.1(5) | 228.6(5) [227.8(4)] |
| O1-P1-O2 | 101.5(8) | 100.8(18) [100.6(18)] | 106.38(12) | 105.62(13) | 107.19(18) [105.98(19)] |
| O1-P1-C1$_R$ | 96.1(9) | 99.2(16) [99.0(16)] | 99.76(14) | 101.23(15) | 101.9(2) [102.0(2)] |
| O2-P1-C1$_R$ | 96.9(8) | 97.9(17) [97.9(17)] | 102.39(14) | 101.48(14) | 100.7(2) [100.7(2)] |
| P1-Au1-Cl1 | – | – | 175.9(11) | 178.5(22) | 177.6(7) [174.8(7)] |
| α | 12.3 | 11.3 [11.2] | 12.2 | 11.9 | 11.5 [11.5] |
| δ | 170.7(10) | 171.4(21) [171.5(21)] | 171.7(14) | 172.2(19) | 171.8(9) [172.1(9)] |
| τ | 0.7 | 0.4 [0.2] | 0.4 | 1.1 | 1.4 [3.0] |

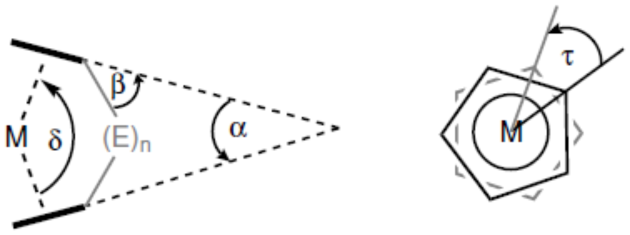

Figure S2-1 Important structural parameters of [n]metallocenophanes.

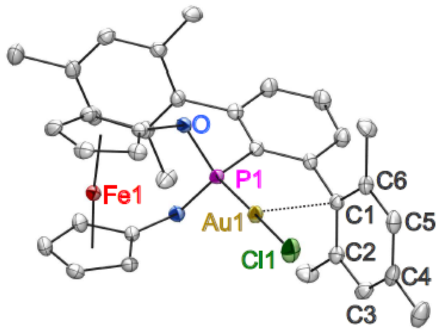

Figure S2-2 Molecular structure of **4**. Displacement ellipsoids drawn at 30% probability; H-atoms are omitted for clarity.

Table S2-3 Additional atom distances [pm] for **4**.

| | |
|---|---|
| Au1···C1 | 308.0(5) |
| Au1···C2 | 313.5(6) |
| Au1···C3 | 355.3(6) |
| Au1···C4 | 388.1(6) |
| Au1···C5 | 384.9(6) |
| Au1···C6 | 350.4(6) |

# S3. Electrochemistry

The electrochemical properties of the title compounds (**1-6**) were probed with the aid of cyclic voltammetry in order to determine if the coordinated metal fragment has an influence on the redox-potential of the iron atom.

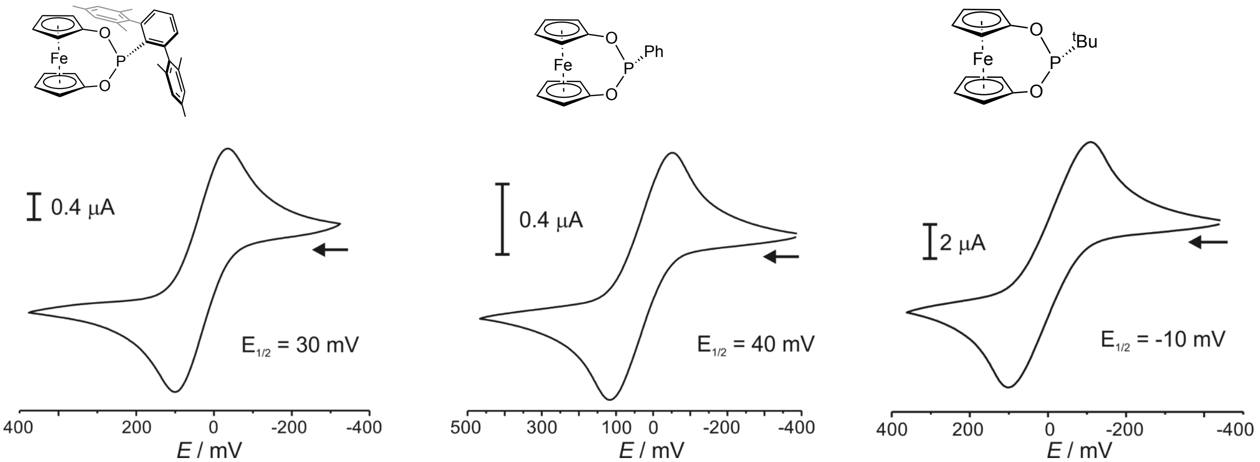

Figure S3-1: Cyclic voltammograms of **1** (left), **2** (middle), **3** (right) in $CH_2Cl_2$ at a scan rate of 250 mV/s at room temperature vs $Fc/Fc^+$ (internal standard $Fc^*/Fc^{*+}$). **1:** Pt/$[NBu_4][Al\{OC(CF_3)_3\}_4]$/Ag, **2, 3:** [NBu4]$[PF_6]$. Only one cycle is shown.

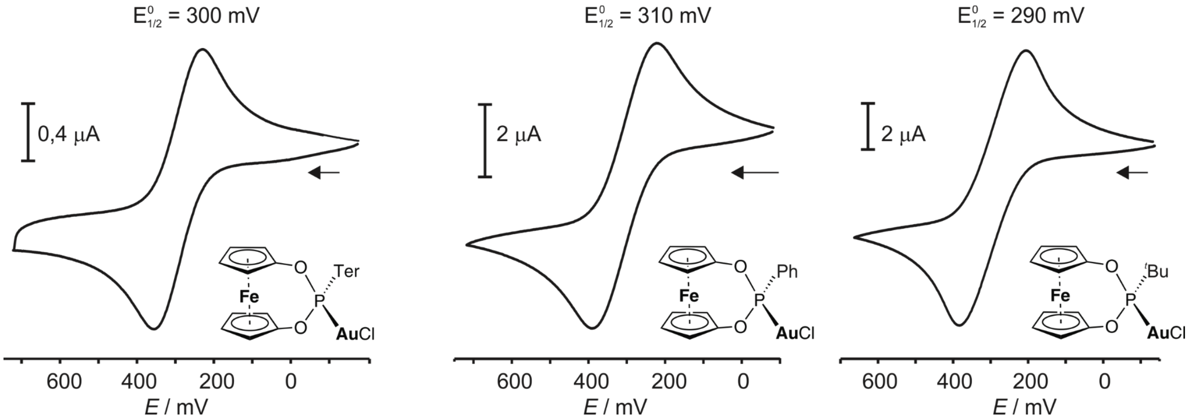

Figure S3-2: Cyclic voltammograms of **4** (left), **5** (middle), **6** (right) in $CH_2Cl_2$ at a scan rate of 250 mV/s at room temperature vs $Fc/Fc^+$ (internal standard $Fc^*/Fc^{*+}$), Pt/$[NBu_4][Al\{OC(CF_3)_3\}_4]$/Ag. Only one cycle is shown.

**Table S3-1.** Half-wave potentials, peak potential differences and corresponding $i_{pc}/i_{pa}$ values of **1**-**6** in $CH_2Cl_2$ *vs.* $Fc/Fc^+$ (internal standard $Fc^*/Fc^{*+}$), v = 250 mVs$^{-1}$, Pt/[$NBu_4$][Al{$OC(CF_3)_3$}$_4$]/Ag.

| Compound | $E^0_{1/2}$ [V] | $\Delta E_p$ [V] | $i_{pc}/i_{pa}$ |
|---|---|---|---|
| **1** | 0.03 | 0.14 | 1.0 |
| **2** | 0.04 | 0.15 | 1.0 |
| **3** | -0.01 | 0.21 | 1.0 |
| **4** | 0.30 | 0.12 | 1.0 |
| **5** | 0.31 | 0.17 | 1.0 |
| **6** | 0.29 | 0.18 | 1.0 |

# S4. NMR-spectra

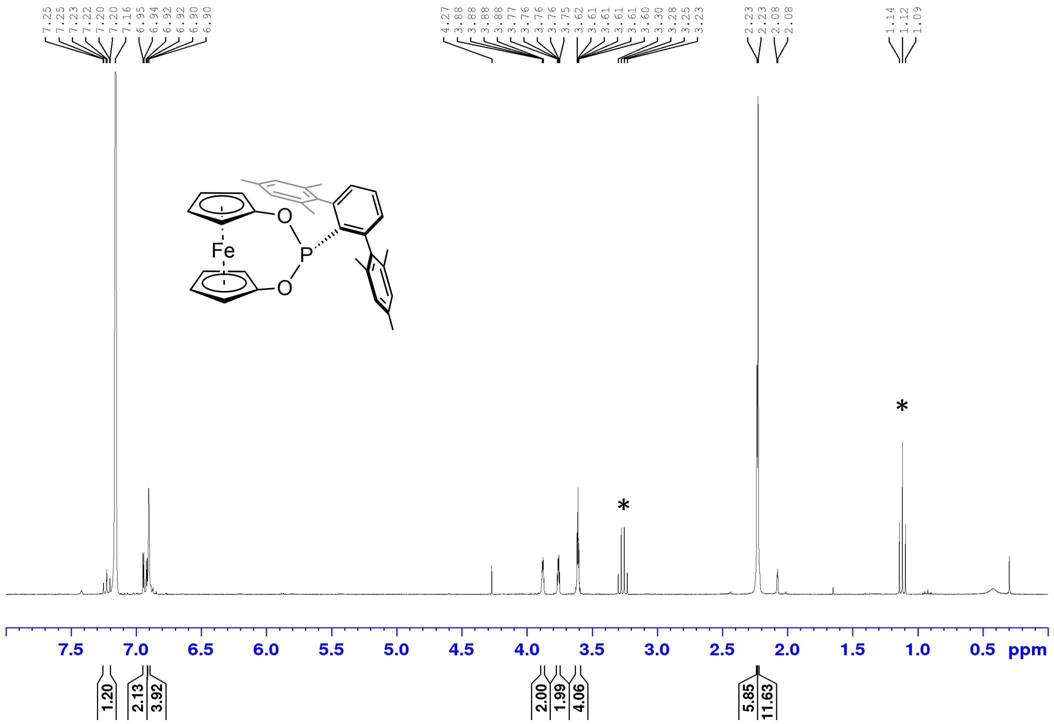

Figure S4-1: $^1$H NMR spectrum of **1** in $C_6D_6$. The signals marked with * correspond to diethyl ether impurities.

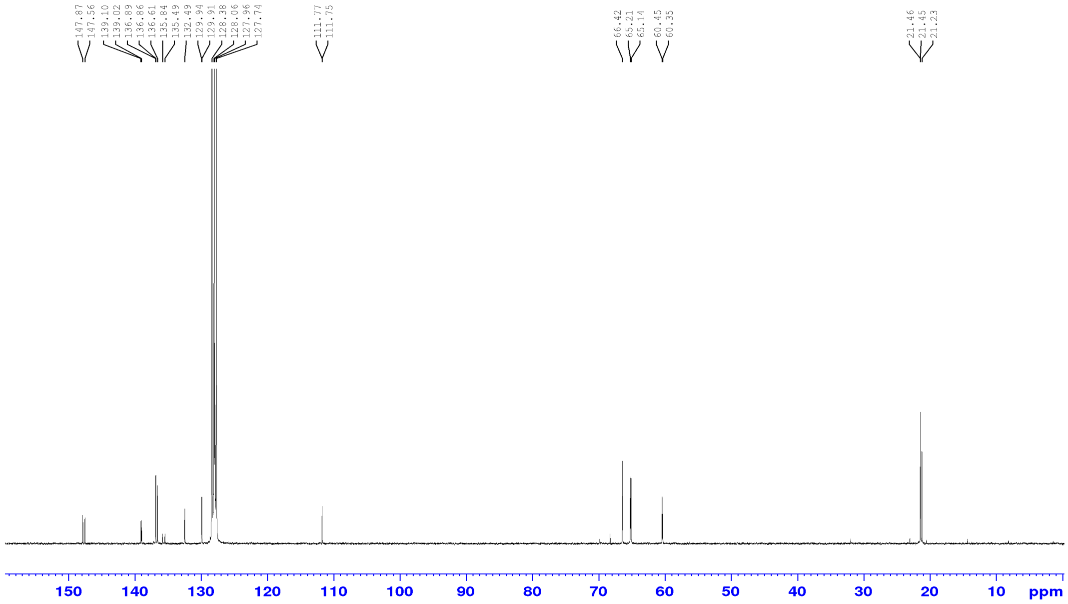

Figure S4-2 $^{13}$C NMR spectrum of **1** in $C_6D_6$.

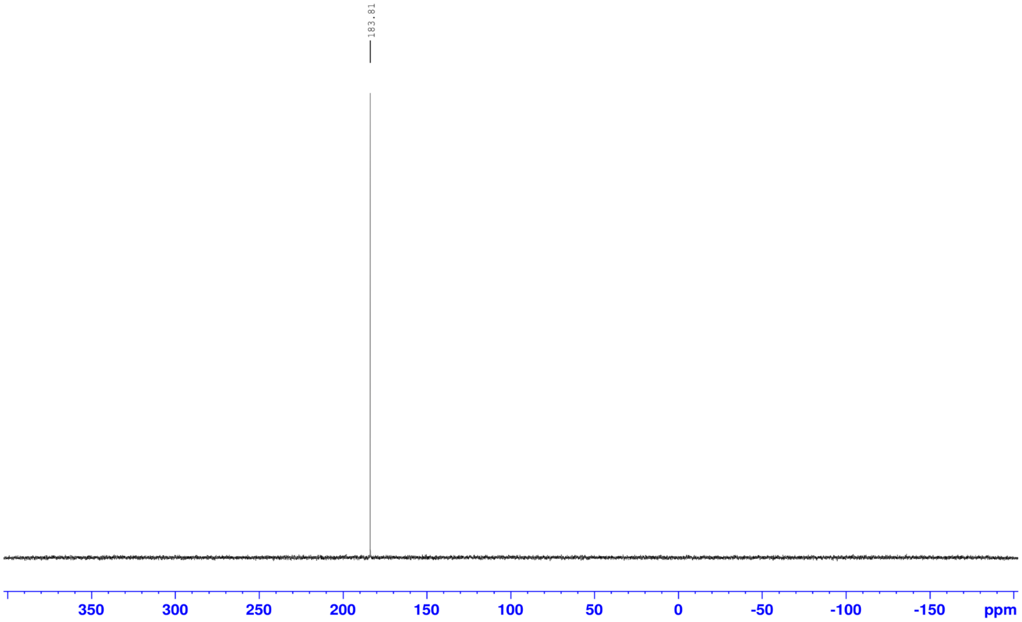

Figure S4-3: $^{31}$P NMR spectrum of **1** in $C_6D_6$.

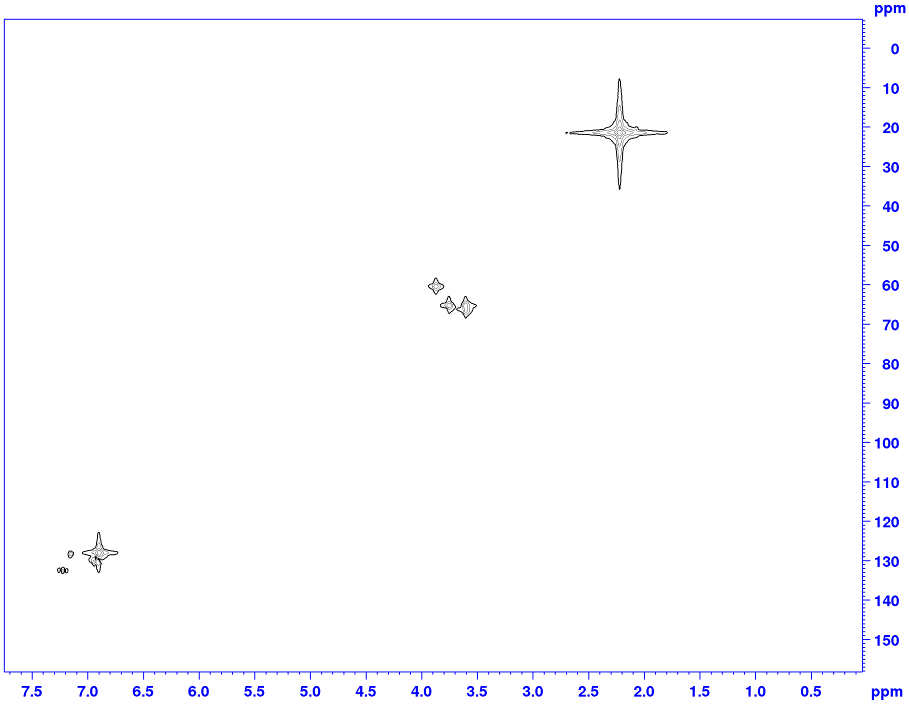

Figure S4-4: $^{1}$H/$^{13}$C-HMQC NMR spectrum of **1** in $C_6D_6$.

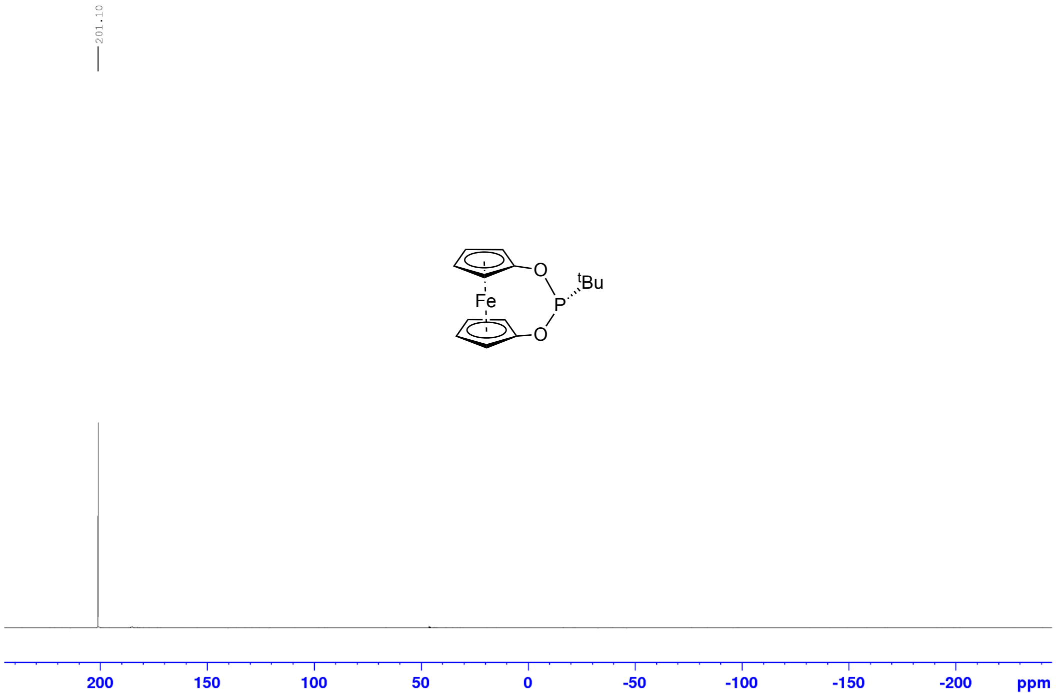

Figure S4-5 $^{31}$P NMR spectrum of **3** in $C_6D_6$. The respective $^{1}$H and $^{13}$C NMR spectra have already been published by Herberhold and coworkers (see reference [S3]).

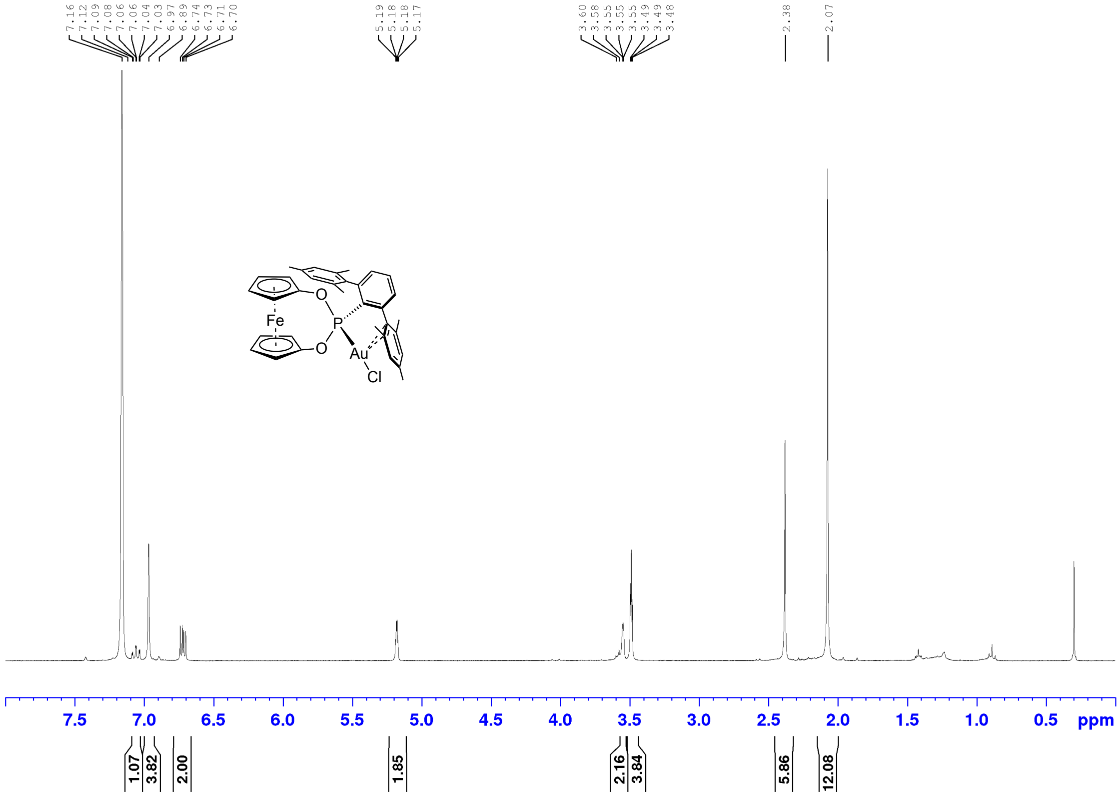

Figure S4-6: $^{1}$H NMR spectrum of **4** in $C_6D_6$.

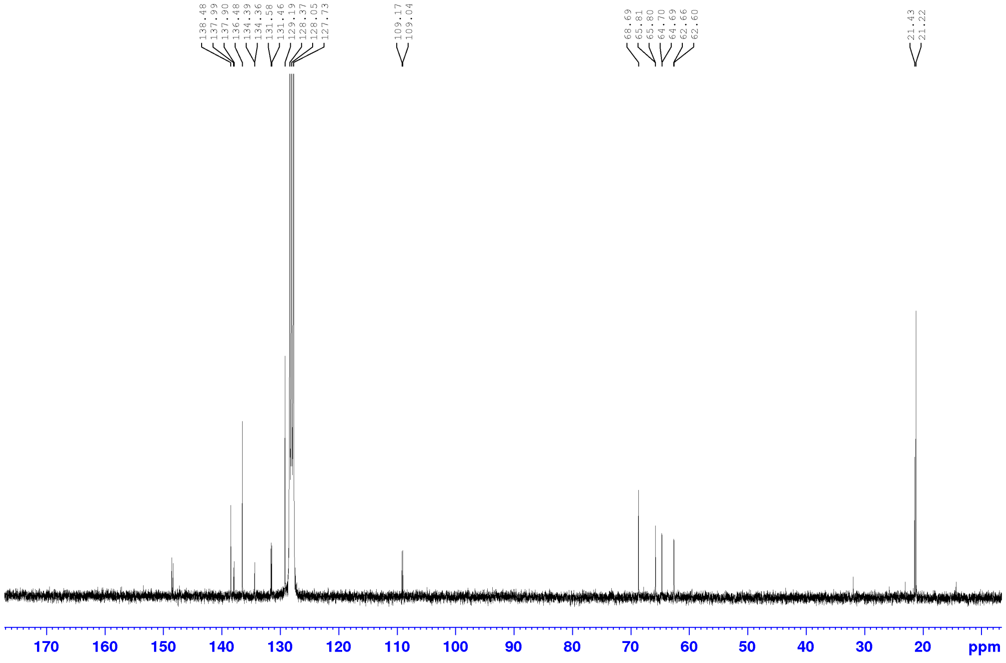

Figure S4-7: $^{13}$C NMR spectrum of **4** in $C_6D_6$.

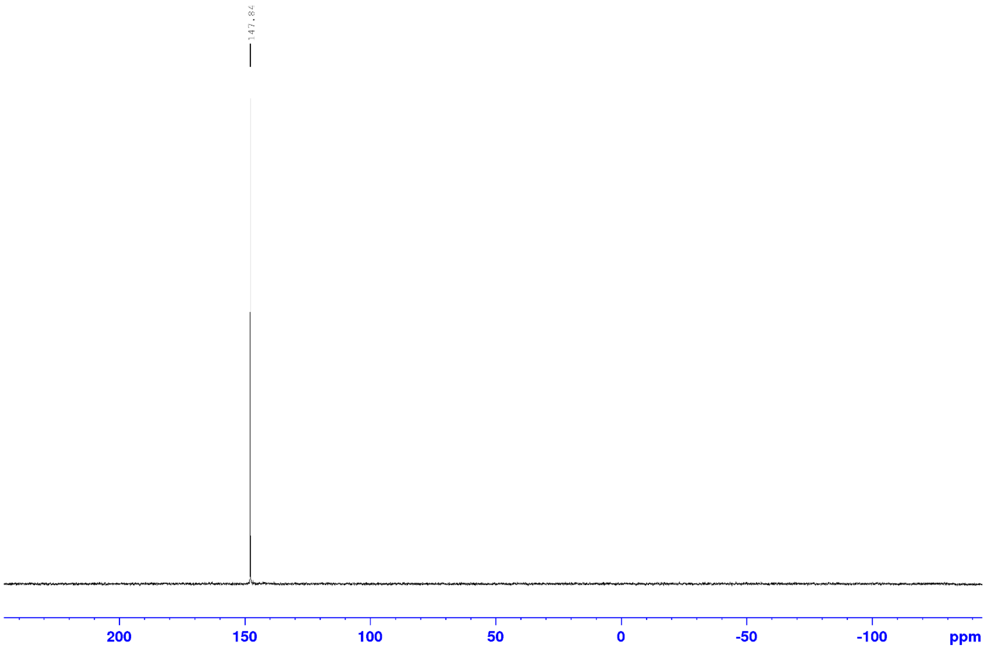

Figure S4-6: $^{31}$P NMR spectrum of **4** in $C_6D_6$.

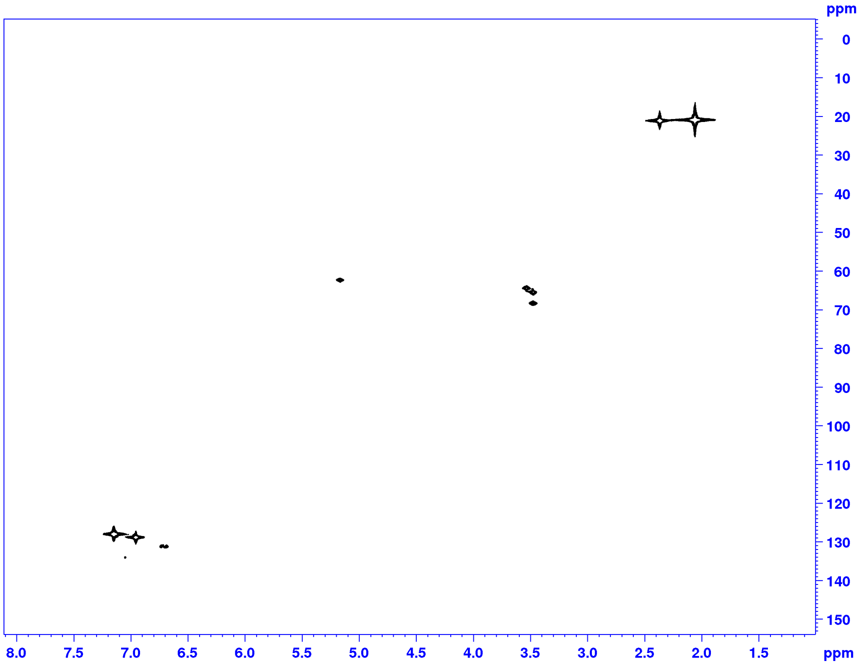

Figure S4-7: $^{13}C/^{1}H$ HMQC NMR spectrum of **4** in $C_6D_6$.

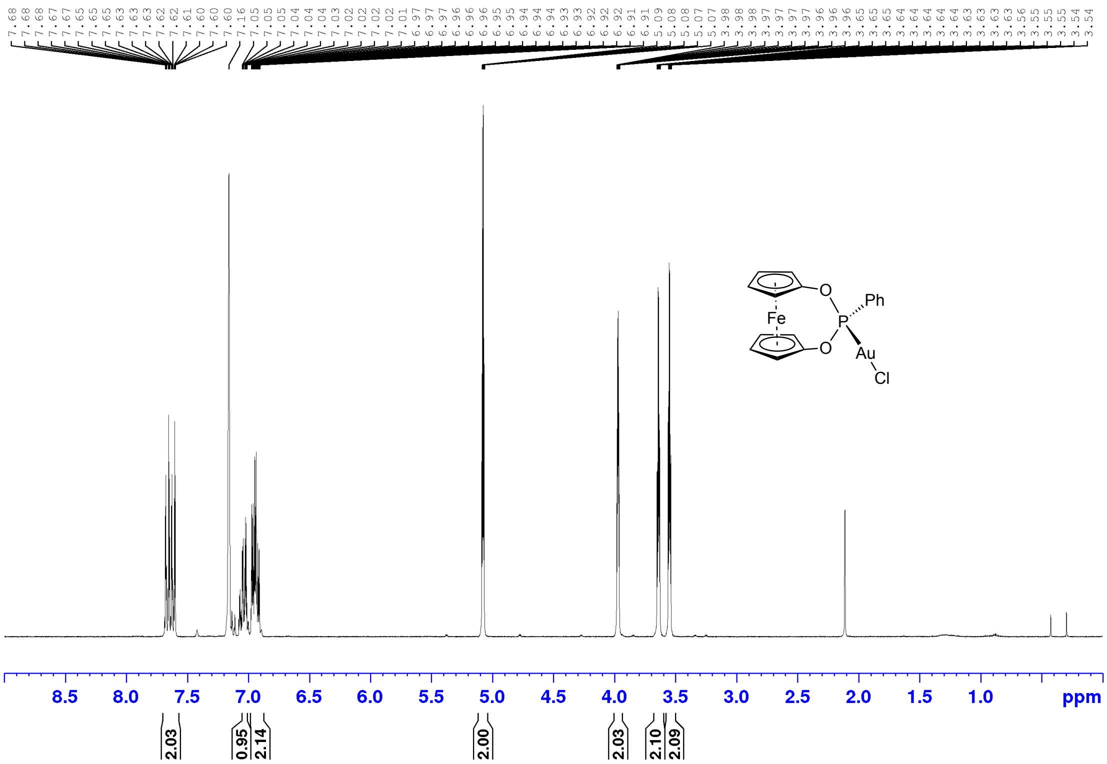

Figure S4-8: $^{1}$H NMR spectrum of **5** in $C_6D_6$.

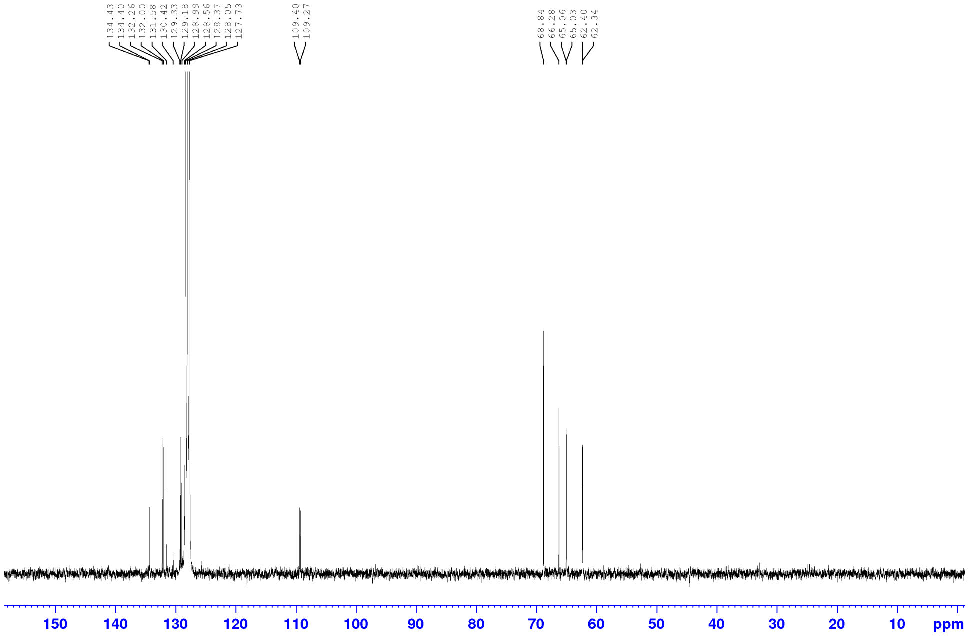

Figure S4-9: $^{13}$C NMR spectrum of **5** in $C_6D_6$.

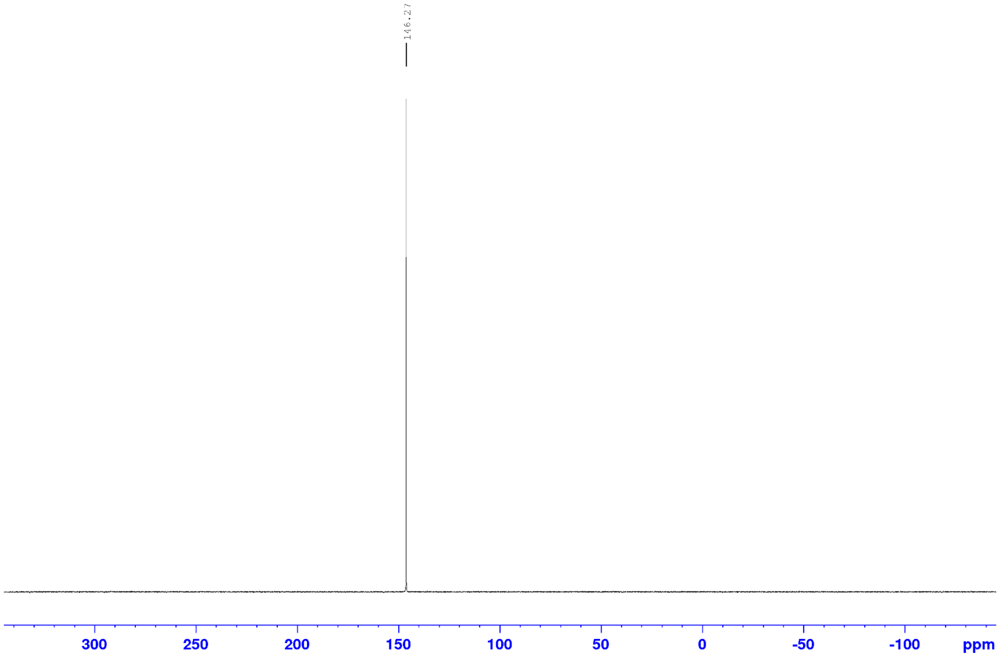

Figure S4-10: $^{32}$P NMR spectrum of **5** in $C_6D_6$.

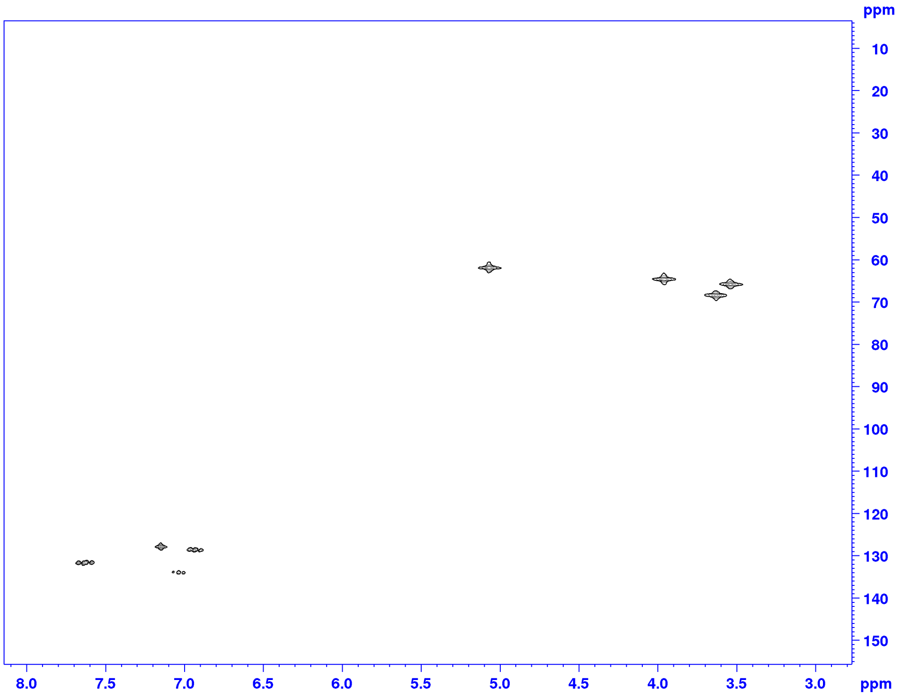

Figure S4-11: $^{13}$C/$^{1}$H HMQC NMR spectrum of **5** in $C_6D_6$.

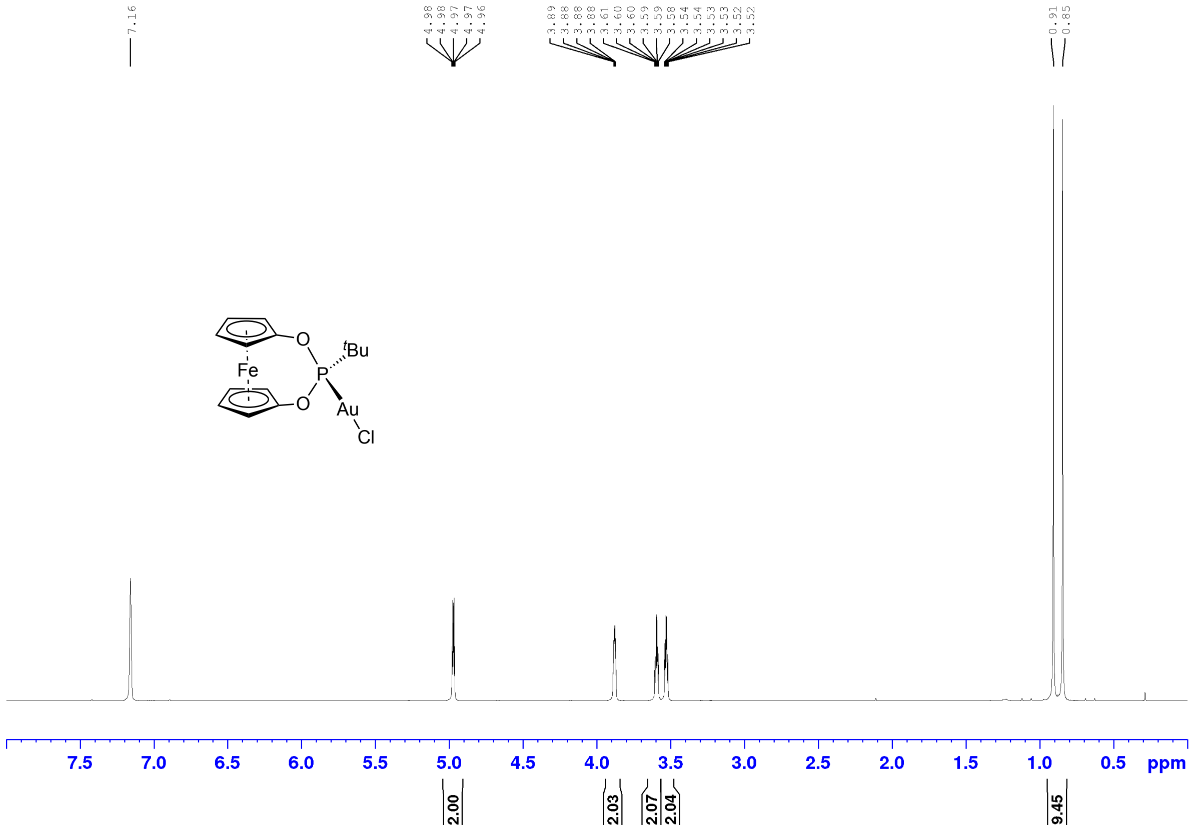

Figure S4-12: $^1$H NMR spectrum of **6** in $C_6D_6$.

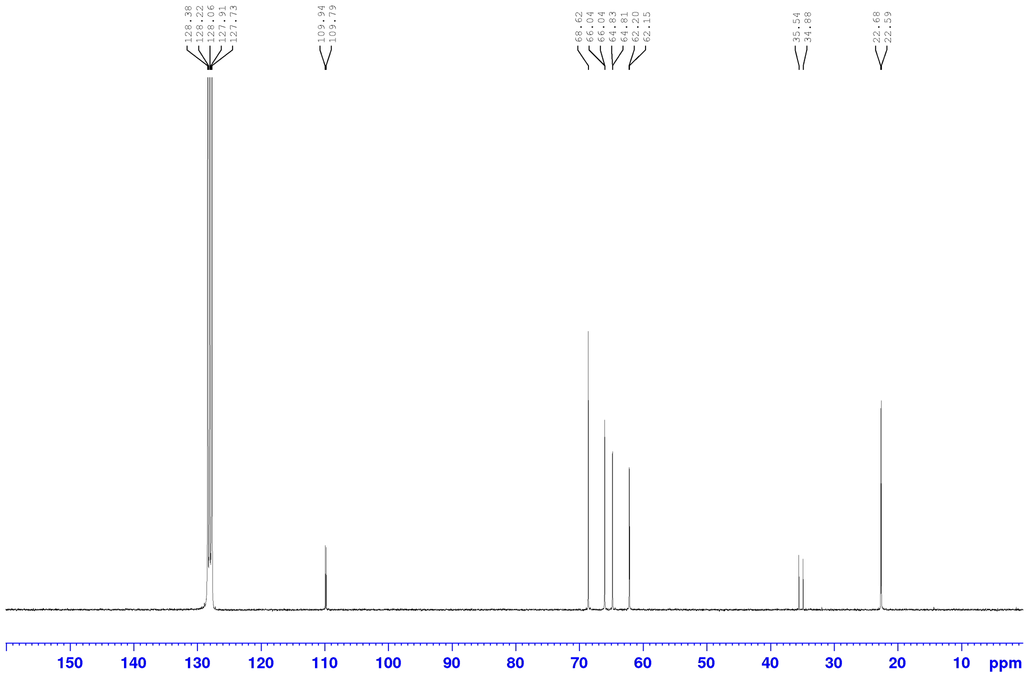

Figure S4-13: $^{13}$C NMR spectrum of **6** in $C_6D_6$.

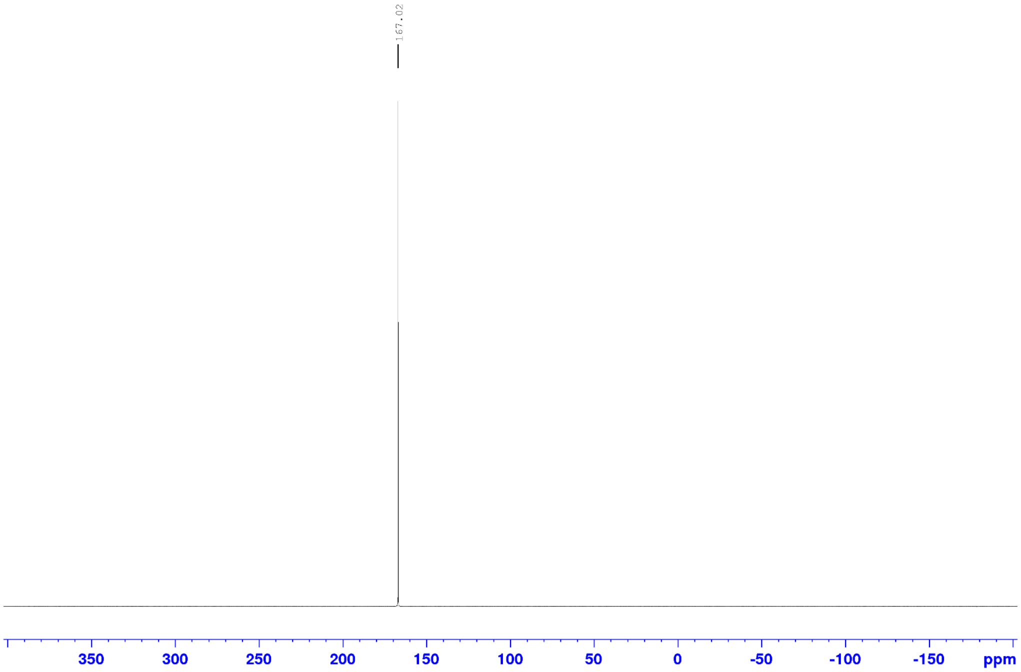

Figure S4-14: $^{31}$P NMR spectrum of **6** in $C_6D_6$.

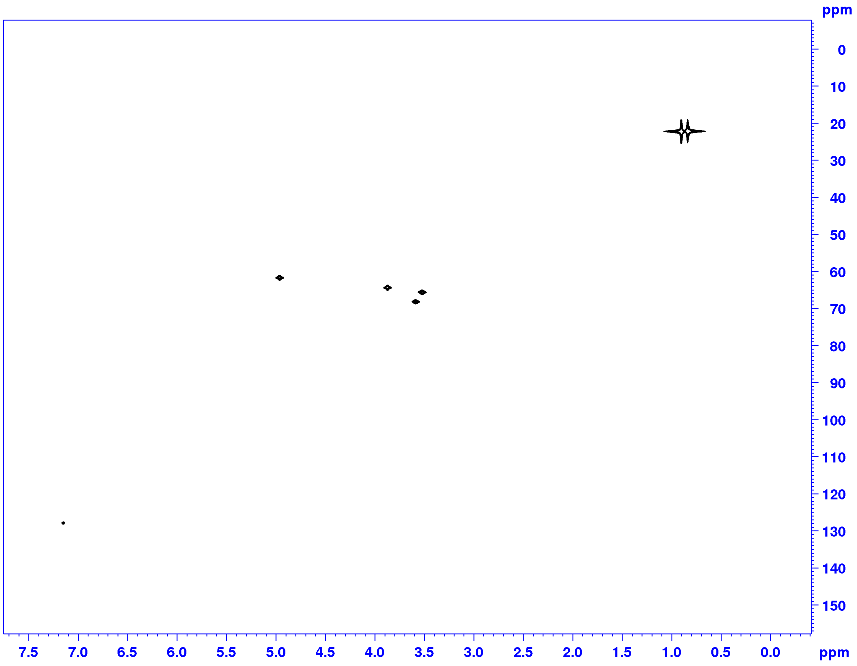

Figure S4-15: $^{13}$C/$^{1}$H HMQC NMR spectrum of **6** in $C_6D_6$.

# S5. Hydroamination catalysis

**General procedure used to measure the kinetics of the hydroamination of terminal alkynes and primary alkynes at room temperature:** Inside a glovebox, stock solutions of the respective pure alkynes and amines in a 1 : 1.1 mixture as well as the catalyst stock solutions in $C_6D_6$ were prepared. A screw-cap NMR tube was then charged with the substrate mixture, 1,3,5-trimethoxybenzene (internal NMR-standard), $NaBAr^F$ (chloride scavenger) and 0.4 mL $C_6D_6$. Then, the neutral point $^1H$ NMR measurement was conducted. Afterwards, the NMR tube was equipped with 0.05 mL of the catalyst stock solution and the catalysis started right away. After 15 minutes, the first $^1H$ NMR-spectrum was measured and subsequently every 20 minutes for the 'fast' catalyses or every hour for the 'slower' catalyses $^1H$ NMR spectra were recorded to follow the consumption of the respective alkyne. The measurements with the oxidized catalyst were performed analogously, but with addition of the oxidation reagent $[FeCp(C_5H_4COMe)][Al\{OC(CF_3)_3\}_4]$ in slight excess regarding to the used amount of catalyst to the catalysis mixture.[S4-1] We have furthermore tested for various substrates the possible catalytic activity of the oxidation reagent. Control reactions without any Au complex but pure oxidation reagent gave zero hydroamination.

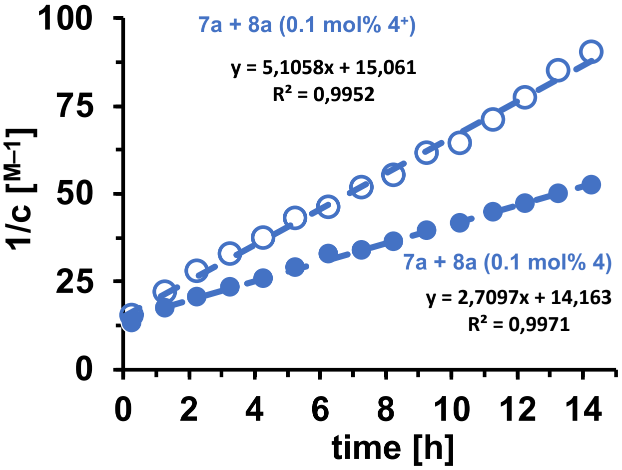

Figure S5-1: Second order rate plot for the reaction of aniline (**7a**) with phenyl acetylene (**8a**) in the presence of 0.1 mol% **4** or **4**$^+$ up to high conversion (81% for **4** and 89% for **4**$^+$).

[S4-1] Synthesis of acetylferrocenium salts: P. Carty, M. F. A. Dove, *J. Organomet. Chem.* **1971**, *28*, 125.