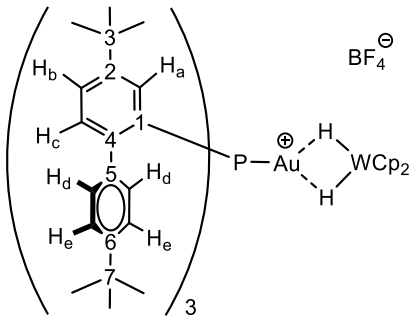
Supporting Information

1. Synthetic procedures

General Considerations. All preparations and manipulations were performed by using standard Schlenk and glovebox techniques, under an atmosphere of argon and of high purity nitrogen, respectively. All solvents were dried, stored over 4 Å molecular sieves, and degassed prior to use. CD_2Cl_2 was dried over CaH_2 and distilled under argon. *n*-pentane (C_5H_{12}) were distilled under nitrogen over sodium. [P(2-(4,4'-di-tertbutylbiphenylyl))$_3$AuNCMe][BF_4], and Cp_2MoH_2 were synthesised as reported in literature.[1,2] Cp_2WH_2 was used as received from commercial suppliers. Solution NMR spectra were recorded with Bruker AVANCE NEO-400, AVANCE III-400 and AVANCE NEO-500 spectrometers. Spectra were referenced to external $SiMe_4$ (δ = 0 ppm) by using the residual proton solvent peaks as internal standards (^{1}H NMR experiments), or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments), while ^{31}P was referenced to H_3PO_4. The following abbreviations and their combinations are used: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet. Spectral assignments were made by routine one- and two-dimensional NMR experiments (^{1}H, ^{13}C, ^{13}C{^{1}H}, ^{31}P{^{1}H}, COSY, NOESY, HSQC and HMBC) where appropriate. For elemental analyses a LECO TruSpec CHN elementary analyser was utilized.

Compound 1



In the glovebox, [P(2-(4,4'-di-tertbutylbiphenylyl))$_3$AuNCMe][BF_4] (20 mg, 0.017 mmol) was dissolved in 1 mL of CH_2Cl_2 and added into a solution (1 mL) of Cp_2WH_2 (6 mg, 0.019 mmol) in CH_2Cl_2. The yellow reaction mixture was stirred for 5 min, filtered and layered with *n*-pentane, thus affording complex **1** as yellow crystals. The yellow crystals were collected and dried in vacuo overnight. Yield: 18 mg (74%)

Anal. Calcd. $C_{70}H_{87}AuBF_4WP$: C, 58.92; H, 6.15. **Found:** C, 58.76; H, 6.17

^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C) δ: 7.66 (d, 3H, $^3J_{HH}$ = 7.7 Hz, H_b), 7.47 (d, 3H, $^3J_{PH}$ = 12.3 Hz, H_a), 7.39 (m, 3H, H_c), 7.21 (d, 6H, $^3J_{HH}$ = 7.7 Hz, H_e), 6.96 (d, 2H, $^3J_{HH}$ = 7.7 Hz, H_d), 4.20 (s, 10H, Cp), 1.24 (s, 27H, ^{t}Bu), 1.16 (s, 27H, ^{t}Bu), –11.08 (d+dd, 2H, $^2J_{PH}$ = 29.6 Hz, $^1J_{WH}$ = 74.0 Hz, Au(μ-H)$_2$W) ppm.

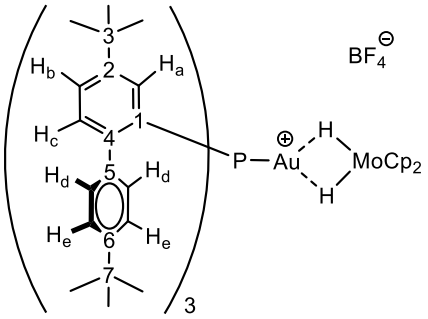
^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 25 °C) δ: 46.1 ppm.

^{19}F{^{1}H} NMR (376 MHz, CD_2Cl_2, 25 °C) d: –153.1 (s, $^{10}BF_3$), –153.2 (s, $^{11}BF_3$) ppm.

^{13}C{^{1}H} NMR (125 MHz, CD2Cl2, 25 °C) d: 151.1 (br, C_6 + C_2), 143.2 (d, $^2J_{PC}$ = 16 Hz, C_4), 139.1 (br, C_5), 135.0

(br, CH_a), 134.9 (br, CH_c), 130.7 (d, $^1J_{PC}$ = 51 Hz, C_1), 129.9 (s, CH_d), 128.3 (s, CH_b), 125.6 (s, CH_e), 77.5 (s, Cp), 35.0 (s, C_3), 34.8 (s, C_7), 31.4 (s, ^{t}Bu), 31.1 (s, ^{t}Bu) ppm.

Compound 2



In the glovebox, [P(2-(4,4̓-di-tertbutylbiphenylyl))$_3$AuNCMe][BF_4] (20 mg, 0.017 mmol) was dissolved in 1 mL of CH_2Cl_2 and added into a 1 mL solution of Cp_2MoH_2 (4 mg, 0.017 mmol) in CH_2Cl_2. The yellow reaction mixture was stirred for 5 min, filtered and layered with *n*-pentane, thus affording complex **2** as yellow crystals. The yellow crystals were collected and dried in vacuo overnight. Yield: 20 mg (88%)

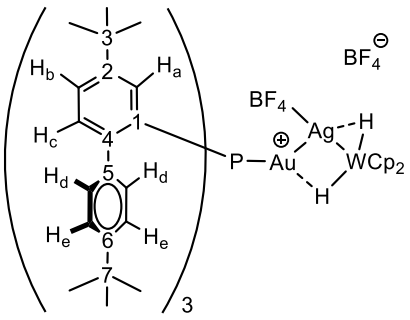
Anal. Calcd. $C_{70}H_{87}AuBF_4MoP$: C, 62.78; H, 6.55. **Found:** C, 62.70; H, 6.62**^{1}H NMR** (500 MHz, CD_2Cl_2, 25 °C) δ: 7.67 (d, 3H, $^3J_{HH}$ = 7.8 Hz, H_b), 7.48 (d, 3H, $^3J_{PH}$ = 12.0 Hz, H_a), 7.40 (m, 3H, H_c), 7.21 (d, 6H, $^3J_{HH}$ = 7.9 Hz, H_e), 6.97 (d, 2H, $^3J_{HH}$ = 7.9 Hz, H_d), 4.23 (s, 10H, Cp), 1.23 (s, 27H, ^{t}Bu), 1.17 (s, 27H, ^{t}Bu), –9.35 (d, 2H, $^2J_{PH}$ = 37.8 Hz, Au(μ-H)$_2$Mo) ppm.

^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 25 °C) δ: 36.4 ppm.

^{19}F{^{1}H} NMR (376 MHz, CD_2Cl_2, 25 °C) d: –153.2 (s, $^{10}BF_3$), –153.3 (s, $^{11}BF_3$) ppm.

^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, 25 °C) d: 151.3 (s, C_6), 151.2 (br, C_2), 143.2 (d, $^2J_{PC}$ = 16 Hz, C_4), 139.1 (d, $^3J_{PC}$ = 5 Hz, C_5), 135.1 (d, $^2J_{PC}$ = 9 Hz, CH_a), 134.8 (d, $^2J_{PC}$ = 6 Hz, CH_c), 130.7 (d, $^1J_{PC}$ = 52 Hz, C_1), 129.9 (s, CH_d), 128.5 (s, CH_b), 125.7 (s, CH_e), 81.2 (s, Cp), 35.1 (s, C_3), 34.9 (s, C_7), 31.4 (s, ^{t}Bu), 31.1 (s, ^{t}Bu) ppm.

Compound 3



Compound **1** (20 mg, 0.014 mmol) and $AgBF_4$ (5 mg, 0.026 mmol) were dissolved in CD_2Cl_2 (0.6 mL) in a small glass vial. The yellow reaction mixture was rapidly filtered through a short pad of Celite affording complex **3** in quantitative spectroscopic yield. Complex **3** was characterised in situ at –80 °C. Crystals suitable

for X-ray diffraction were grown by slow diffusion of pentane in a concentrated dichloromethane solution of complex **3** at –30 °C.

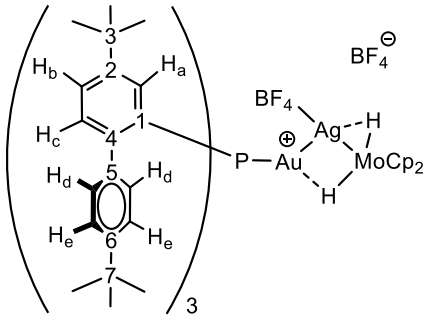
^{1}H NMR (400 MHz, CD_2Cl_2, 0 °C) δ: 7.74 (br, 3H, H_b), 7.45 (br, 6H, H_a, H_c), 7.38 (br, 6H, H_e), 7.07 (br, 6H, H_d), 4.69 (s, 10H, Cp), 1.26 (s, 27H, ^{t}Bu), 1.15 (s, 27H, ^{t}Bu), –12.50 (br, 2H, Au(μ-H)W, Ag(μ-H)W) ppm. **^{1}H NMR** (400 MHz, CD_2Cl_2, –80 °C) δ: 7.67 (br, 3H, H_b), 7.54 (br, 6H, H_a, H_c), 7.39 (br, 6H, H_e), 7.05 (br, 3H, H_e), 6.37 (br, 3H, H_e), 4.62 (s, 5H, Cp), 4.54 (s, 5H, Cp), 1.17 (s, 27H, ^{t}Bu), 1.06 (s, 27H, ^{t}Bu), –12.16 (d, 1H, $^2J_{PH}$ = 38.6 Hz, Au(μ-H)W), –13.26 (d, 1H, $^1J_{AgH}$ = 77.2 Hz, Ag(μ-H)W) ppm.

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, –80 °C) δ: 53.7 ppm.

^{19}F{^{1}H} NMR (376 MHz, CD_2Cl_2, –80 °C) d: –149.8 (br) ppm.

^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, –80 °C) d: 151.7 (s, C_6), 150.7 (br, C_2), 140.8 (d, $^2J_{PC}$ = 16 Hz, C_4), 138.9 (br, C_5), 134.3 (br, CH_a), 134.0 (br, CH_c), 129.3 (br, CH_d), 128.4 (d, $^1J_{PC}$ = 50 Hz, C_1), 128.3 (br, CH_d), 127.9 (br, CH_e), 126.9 (br, CH_e), 120.8 (br, CH_b), 80.5 (s, Cp), 80.3 (s, Cp), 34.3 (s, C_3), 34.2 (s, C_7), 30.5 (s, ^{t}Bu), 30.0 (s, ^{t}Bu) ppm

Compound 4



Compound **2** (20 mg, 0.015 mmol) and $AgBF_4$ (6 mg, 0.030 mmol) were dissolved in CD_2Cl_2 (0.6 mL) in a small glass vial. The yellow reaction mixture was rapidly filtered through a short pad of Celite affording complex **4** in quantitative spectroscopic yield. Complex **4** was characterised in situ at –80 °C.

^{1}H NMR (400 MHz, CD_2Cl_2, 0 °C) δ: 7.75 (br, 3H, H_b), 7.46 (br, 6H, H_a, H_c), 7.38 (br, 6H, H_e), 7.07 (br, 6H, H_d), 4.72 (s, 10H, Cp), 1.26 (s, 27H, ^{t}Bu), 1.16 (s, 27H, ^{t}Bu), –11.79 (d, 2H, $J_{average}$ = 27.2 Hz, Au(μ-H)Mo, Ag(μ-H)Mo) ppm. **^{1}H NMR** (400 MHz, CD_2Cl_2, –80 °C) δ: 7.68 (br, 3H, H_b), 7.54 (br, 6H, H_a, H_c), 7.40 (br, 6H, H_e), 7.06 (br, 3H, H_d), 6.35 (br, 3H, H_d), 4.62 (s, 5H, Cp), 4.56 (s, 5H, Cp), 1.16 (s, 27H, ^{t}Bu), 1.06 (s, 27H, ^{t}Bu), –11.98 (d, 1H, $^2J_{PH}$ = 53.4 Hz, Au(μ-H)Mo), –12.30 (d, 1H, $^1J_{AgH}$ = 78.9 Hz, Ag(μ-H)W) ppm.

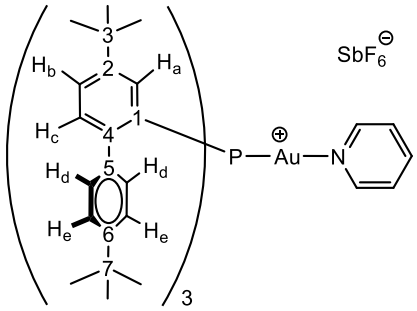
^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, –80 °C) δ: 41.0 ppm.

^{19}F{^{1}H} NMR (376 MHz, CD_2Cl_2, –80 °C) d: –149.8 (br) ppm.

^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, –80 °C) d: 152.0 (s, C_6), 150.8 (br, C_2), 140.8 (d, $^2J_{PC}$ = 17 Hz, C_4), 138.7 (br, C_5), 134.4 (br, CH_a), 133.8 (br, CH_c), 129.4 (br, CH_d), 128.3 (br, CH_d), 127.8 (d, $^1J_{PC}$ = 53 Hz, C_1), 127.7

(br, CH_e), 126.9 (br, CH_e), 121.0 (br, CH_b), 83.8 (br, Cp), 34.3 (s, C_3), 34.2 (s, C_7), 30.5 (s, ^{t}Bu), 30.0 (s, ^{t}Bu) ppm.

Compound 5



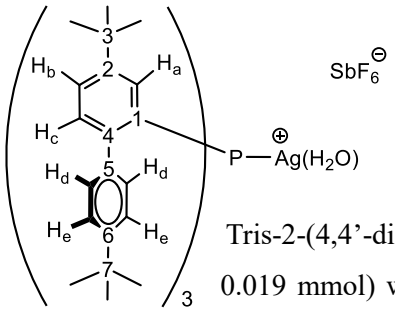
P(2-(4,4`-di-tertbutylbiphenylyl))$_3$AuCl (20 mg, 0.019 mmol) and 1 eq. of $AgSbF_6$ were added into a small glass vial and dissolved in CH_2Cl_2 (1 mL). A small excess of pyridine (1.1 eq.) was added, and the reaction mixture was stirred for 5 min. After this time, the reaction mixture was filtered over Celite and the solvent was removed under vacuum. The crude solid was washed with pentane (3 x 5 mL) and dried under vacuum yielding complex **5** as a colourless solid. Yield: 18 mg (70%). Crystals suitable for X-ray diffraction of complex **5** were grown by slow diffusion of pentane in a concentrated chloroform solution.

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ: 7.98 (m, 2H, *o*-py), 7.75 (ddd, 3H, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 2.3 Hz, $^5J_{HH}$ = 1.7 Hz, H_b), 7.52 (dd, 3H, $^3J_{PH}$ = 12.6 Hz, $^4J_{HH}$ = 2.0 Hz, H_a), 7.5 (tt, 1H, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.2 Hz, *p*-py), 7.43 (dd, 3H, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 5.6 Hz, H_c), 7.11 (d, 6H, $^3J_{HH}$ = 8.4 Hz, H_e), 7.02 (m, 2H, *m*-py), 6.71 (br, 6H, H_d), 1.28 (s, 27H, ^{t}Bu), 1.07 (s, 27H, ^{t}Bu) ppm.

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, 25 °C) δ: 5.1 ppm.

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 25 °C) δ: 151.4 (s, C_6), 151.1 (d, $^3J_{PC}$ = 8 Hz, C_2), 150.0 (s, *m*–py), 143.9 (d, $^2J_{PC}$ = 15 Hz, C_4), 141.6 (s, *o*-py), 138.2 (d, $^3J_{PC}$ = 7 Hz, C_5), 133.2 (d, $^3J_{PC}$ = 9 Hz, CH_a), 132.8 (d, $^3J_{PC}$ = 6 Hz, CH_c), 129.4 (s, CH_d), 128.9 (s, CH_b), 127.5 (d, $^1J_{PC}$ = 65 Hz, C_1), 126.0 (s, *p*-py), 125.1 (s, CH_e), 35.0 (s, C_3), 34.5 (s, C_7), 31.2 (br, ^{t}Bu) ppm.

Compound 6



Tris-2-(4,4'-di-tert-butylbiphenylyl)phosphine (16 mg, 0.019 mmol) and $AgSbF_6$ (7 mg, 0.019 mmol) were added into a small glass vial and dissolved in CH_2Cl_2 (1 mL) in the presence of a small excess of water (1.1 eq.). The reaction mixture was filtered over Celite and the solvent was

removed under vacuum thus yielding complex **6** as a colourless solid. Crystals suitable for X-ray diffraction were grown by slow diffusion of pentane in a concentrated dichloromethane solution of complex **6**.

^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C) δ: 7.70 (ddd, 3H, $^{3}J_{HH}$ = 8.1 Hz, $^{4}J_{HH}$ = 2.2 Hz, $^{5}J_{HH}$ = 1.0 Hz, H_b), 7.55 (dd, 3H, $^{3}J_{PH}$ = 9.4 Hz, $^{4}J_{HH}$ = 2.0 Hz, H_a), 7.40 (dd, 3H, $^{3}J_{HH}$ = 8.4 Hz, $^{4}J_{HH}$ = 5.8 Hz, H_c), 7.26 (d, 6H, $^{3}J_{HH}$ = 8.2 Hz, H_e), 6.70 (br, 6H, H_d), 1.28 (s, 27H, ^{t}Bu), 1.28 (s, 27H, ^{t}Bu) ppm.

^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 25 °C) δ: –19.5 (d + d, $^{1}J_{107AgP}$ = 625 Hz, $^{1}J_{109AgP}$ = 722 Hz) ppm.

^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, 25 °C) δ: 152.2 (s, C_6), 152.0 (d, $^{3}J_{PC}$ = 5 Hz, C_2), 143.5 (d, $^{2}J_{PC}$ = 22 Hz, C_4), 138.1 (d, $^{3}J_{PC}$ = 10 Hz, C_5), 133.1 (br, CH_c), 132.3 (d, $^{3}J_{PC}$ = 9 Hz, CH_a), 128.9 (s, CH_d), 128.4 (d, $^{1}J_{PC}$ = 50.7 Hz, C_1), 126.1 (s, CH_e), 117.1 (br, CH_b), 35.2 (s, C_3), 35.0 (s, C_7), 31.4 (s, ^{t}Bu), 31.3 (s, ^{t}Bu) ppm.

2. NMR data

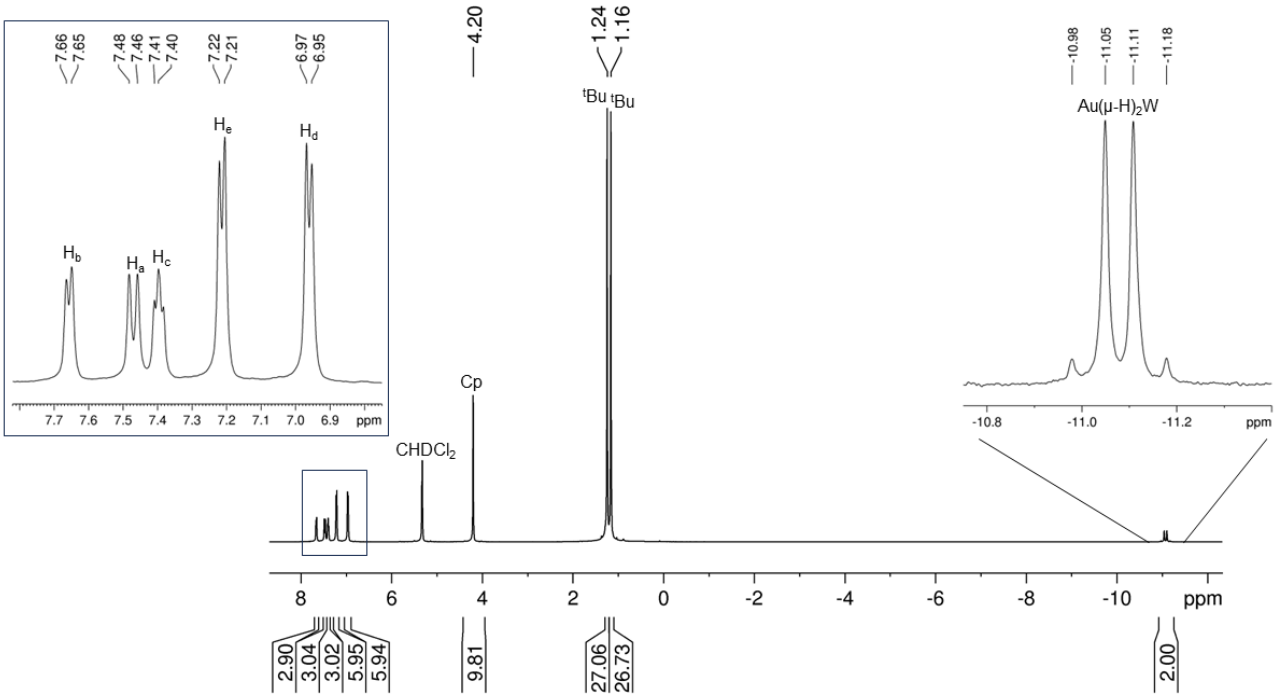


Figure S1. ^{1}H NMR (CD_2Cl_2, 500 MHz, 25 °C) spectrum of **1**.

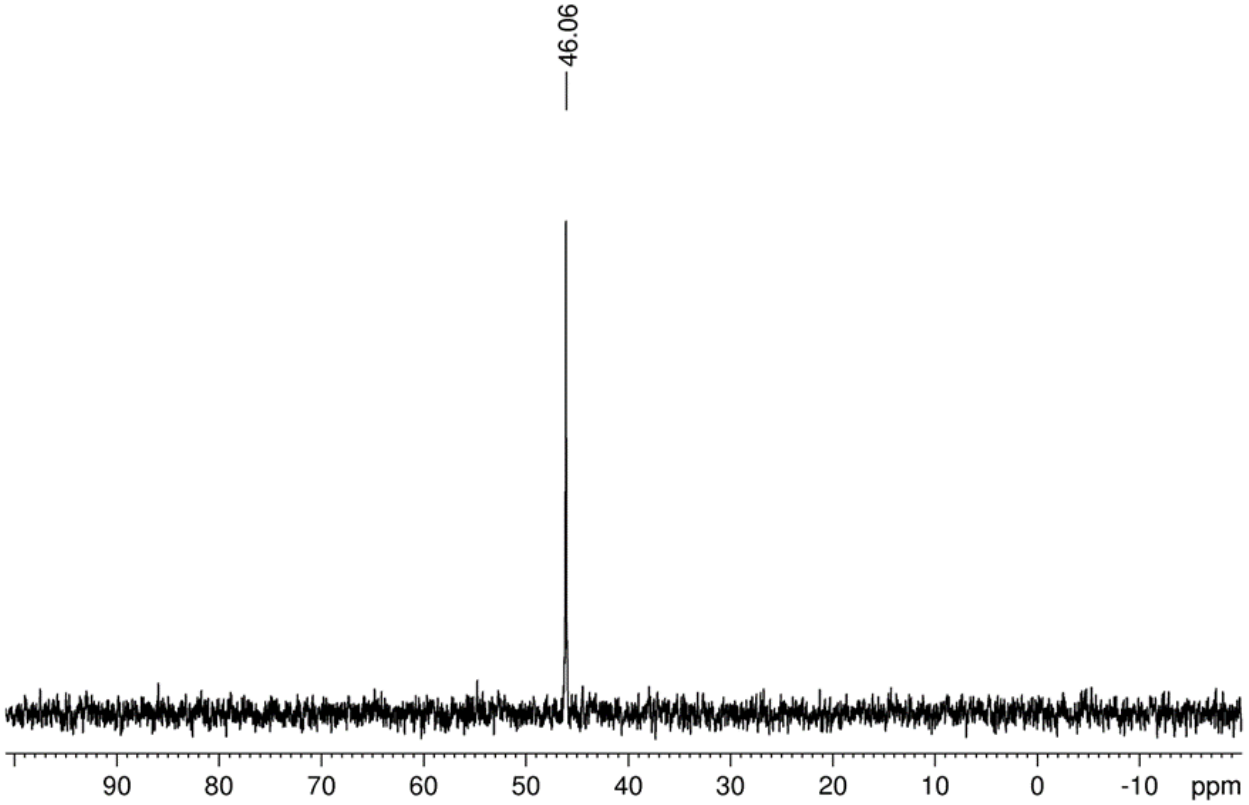


Figure S2. $^{31}P\{^{1}H\}$ (CD_2Cl_2, 202 MHz, 25 °C) NMR spectrum of **1**.

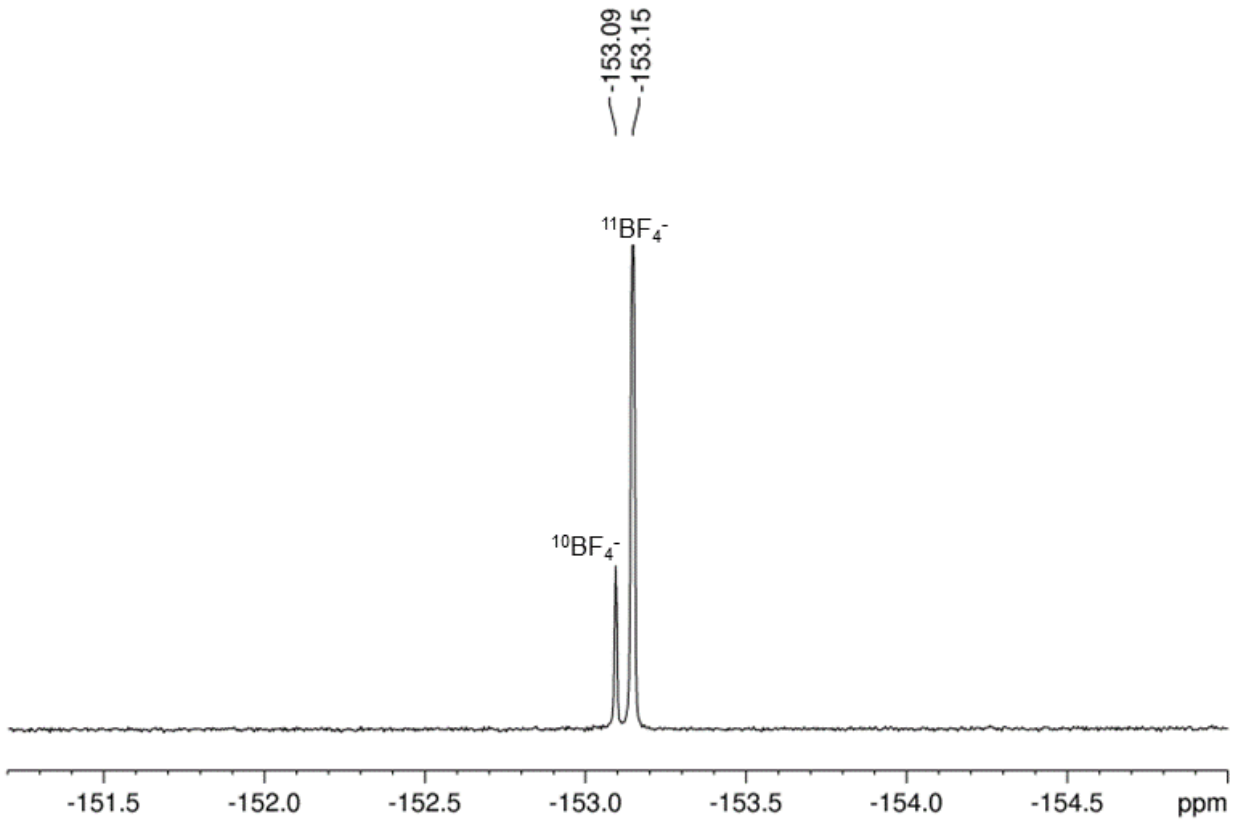


Figure S3. $^{19}F\{^{1}H\}$ (CD_2Cl_2, 376 MHz, 25 °C) NMR spectrum of **1**.

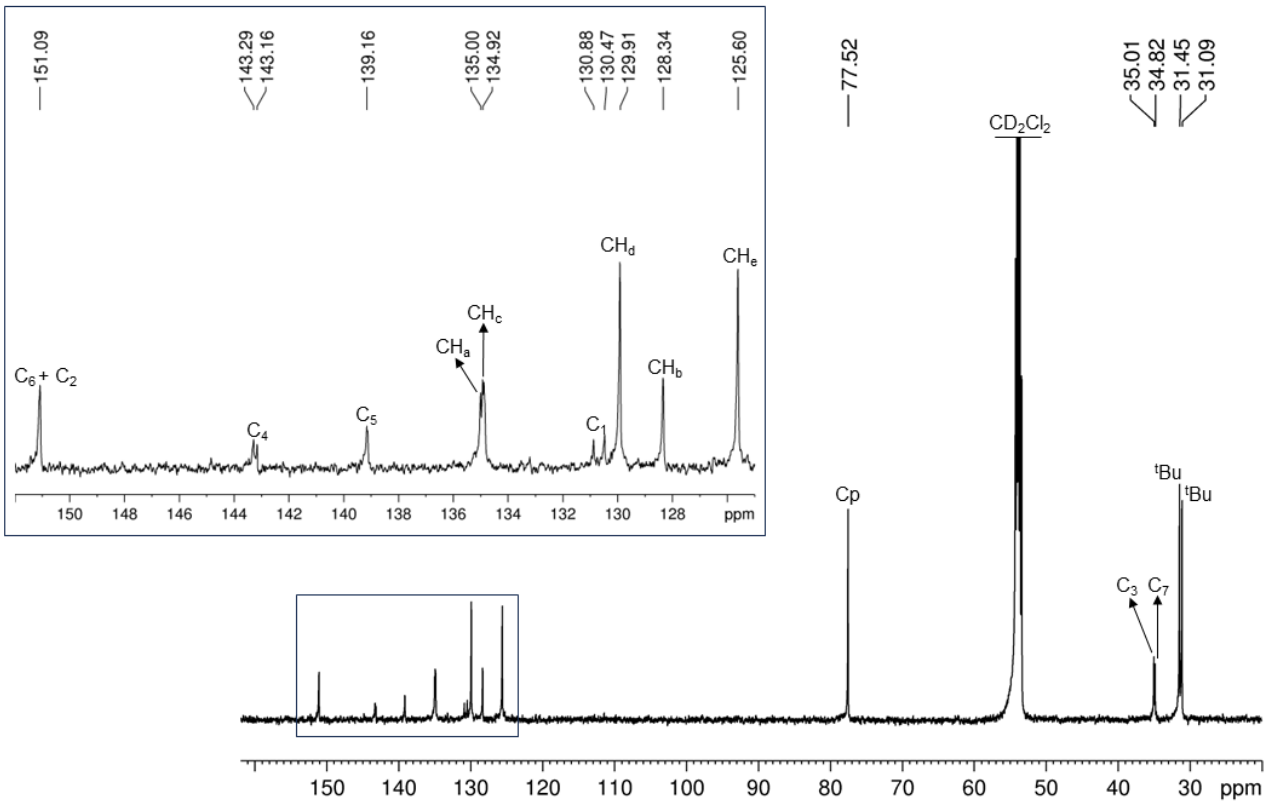


Figure S4. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 125 MHz, 25 °C) spectrum of **1**.

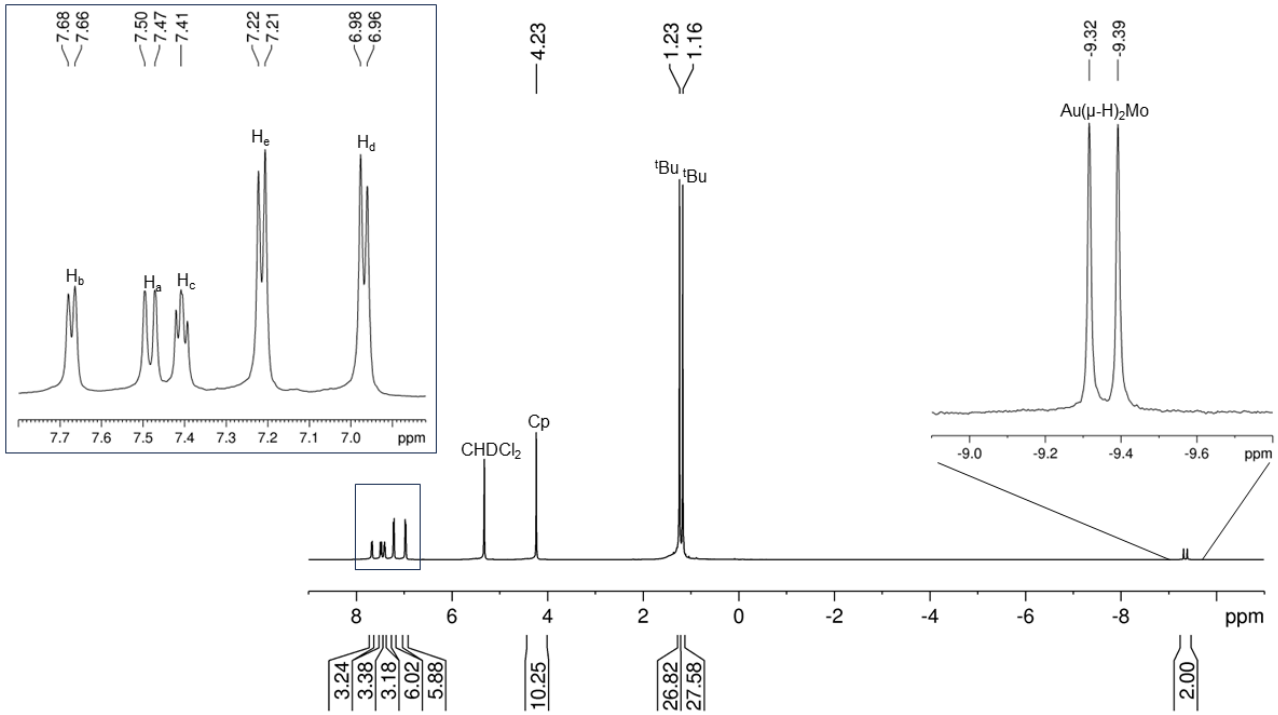


Figure S5. ^{1}H NMR (CD_2Cl_2, 500 MHz, 25 °C) spectrum of **2**.

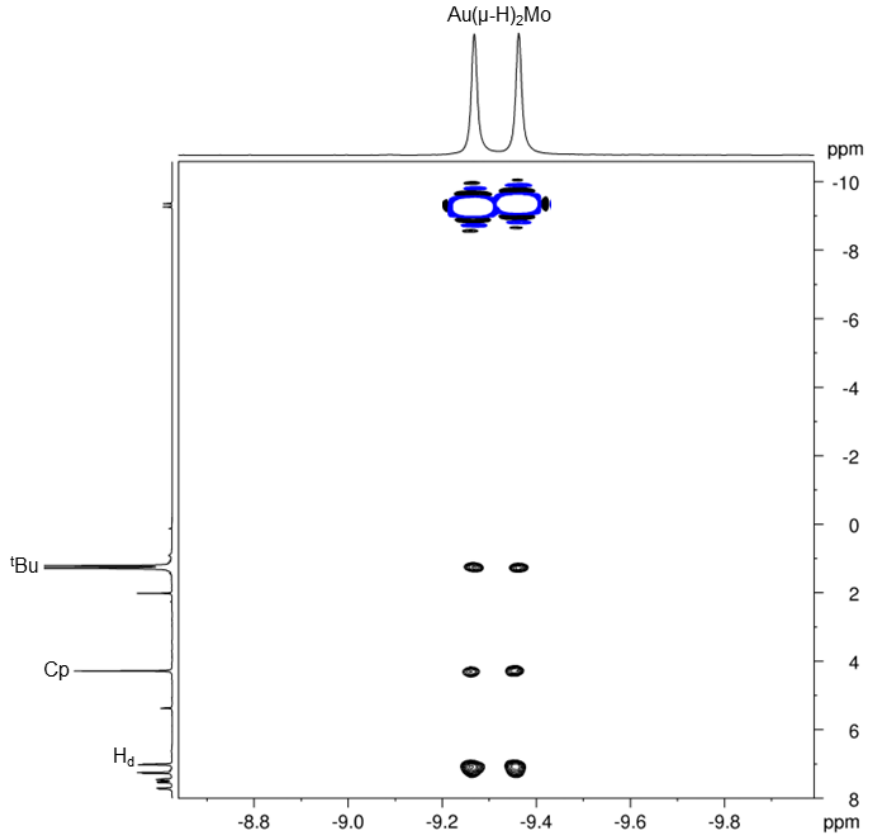


Figure S6. ^{1}H NOESY NMR (CD_2Cl_2, 500 MHz, 25 °C) spectrum of **2**.

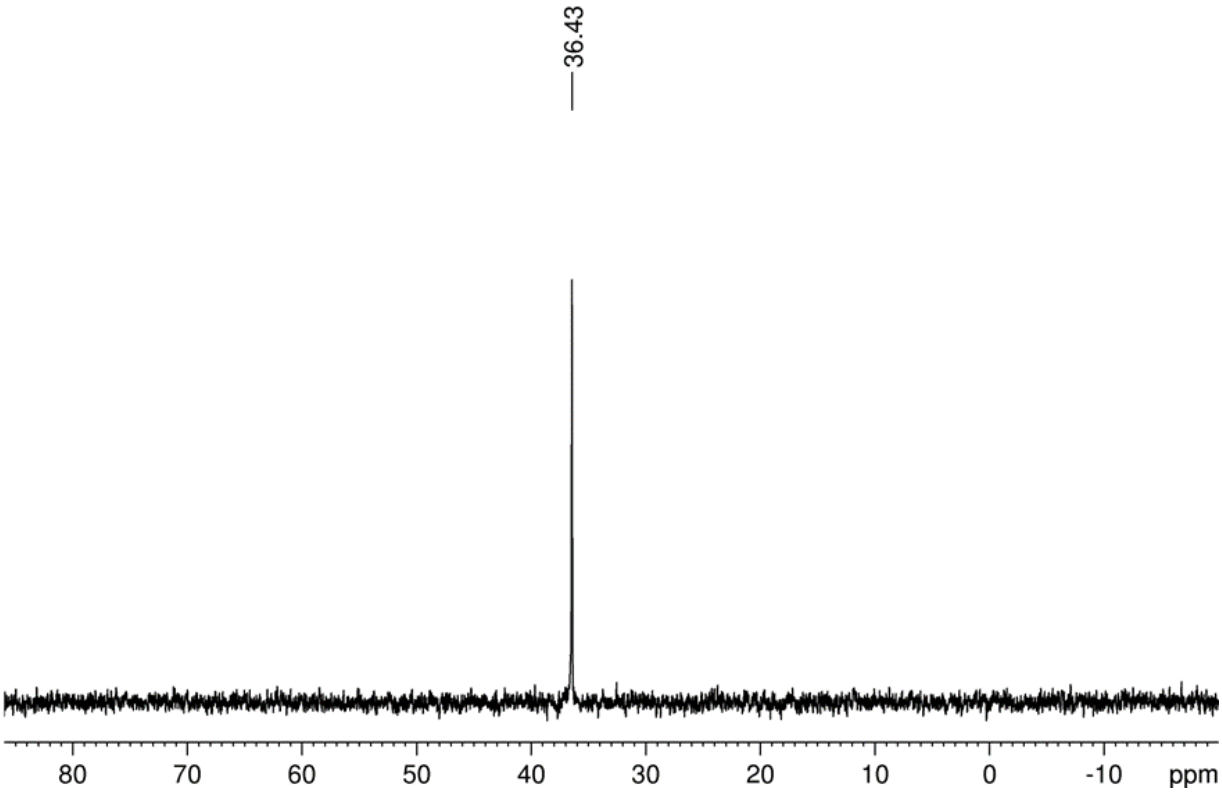


Figure S7. $^{31}P\{^{1}H\}$ (CD_2Cl_2, 202 MHz, 25 °C) NMR spectrum of **2**.

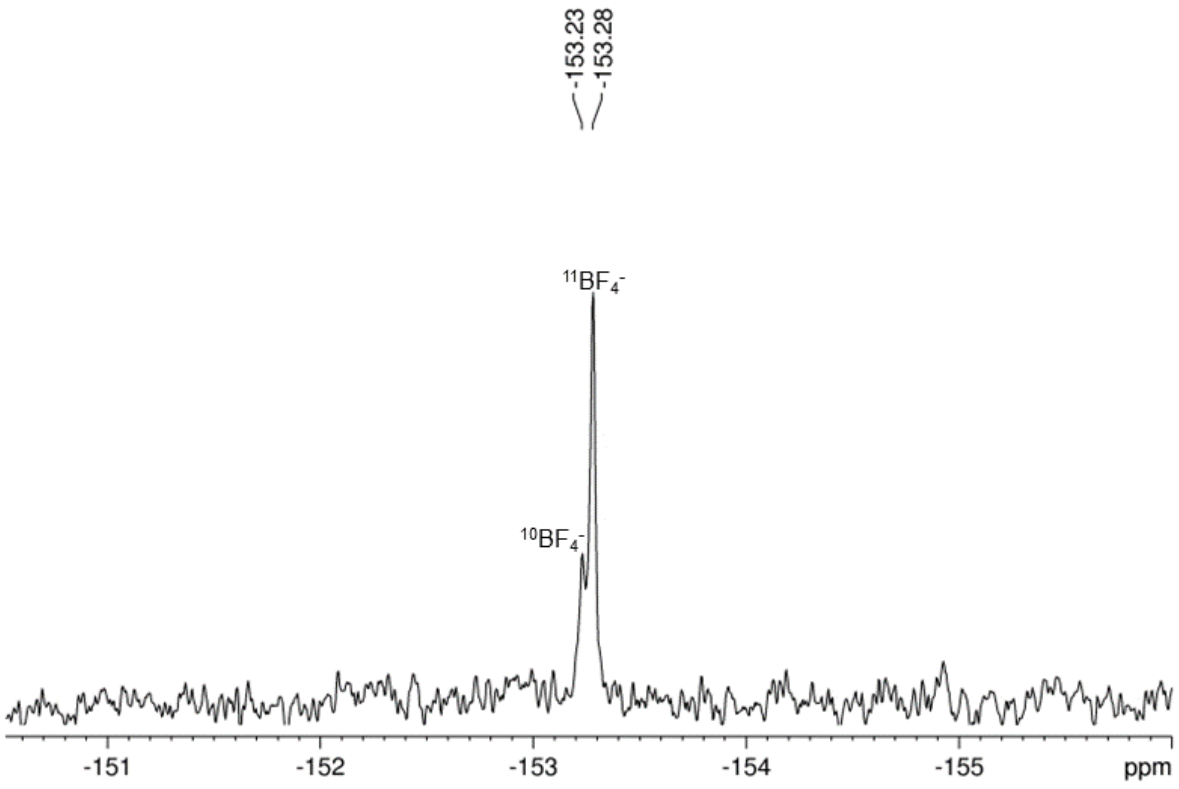


Figure S8. $^{19}F\{^{1}H\}$ (CD_2Cl_2, 376 MHz, 25 °C) NMR spectrum of **2**.

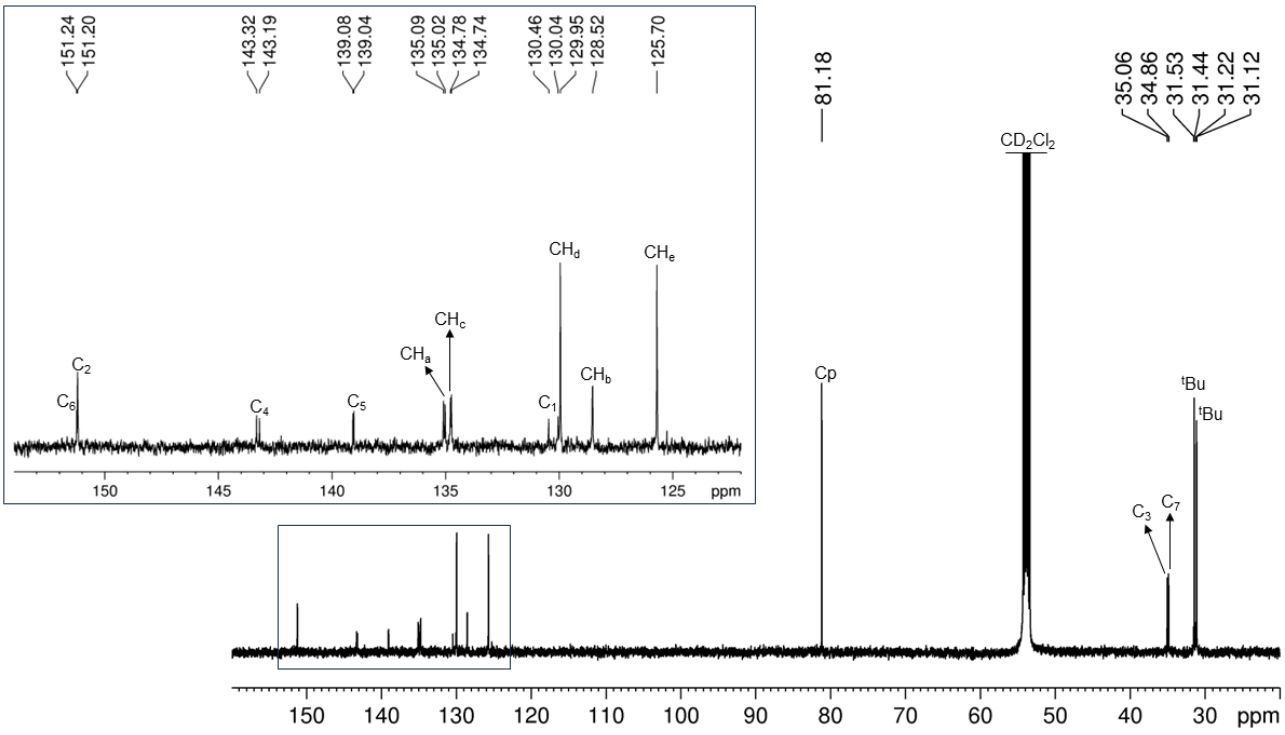


Figure S9. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 125 MHz, 25 °C) spectrum of **2**.

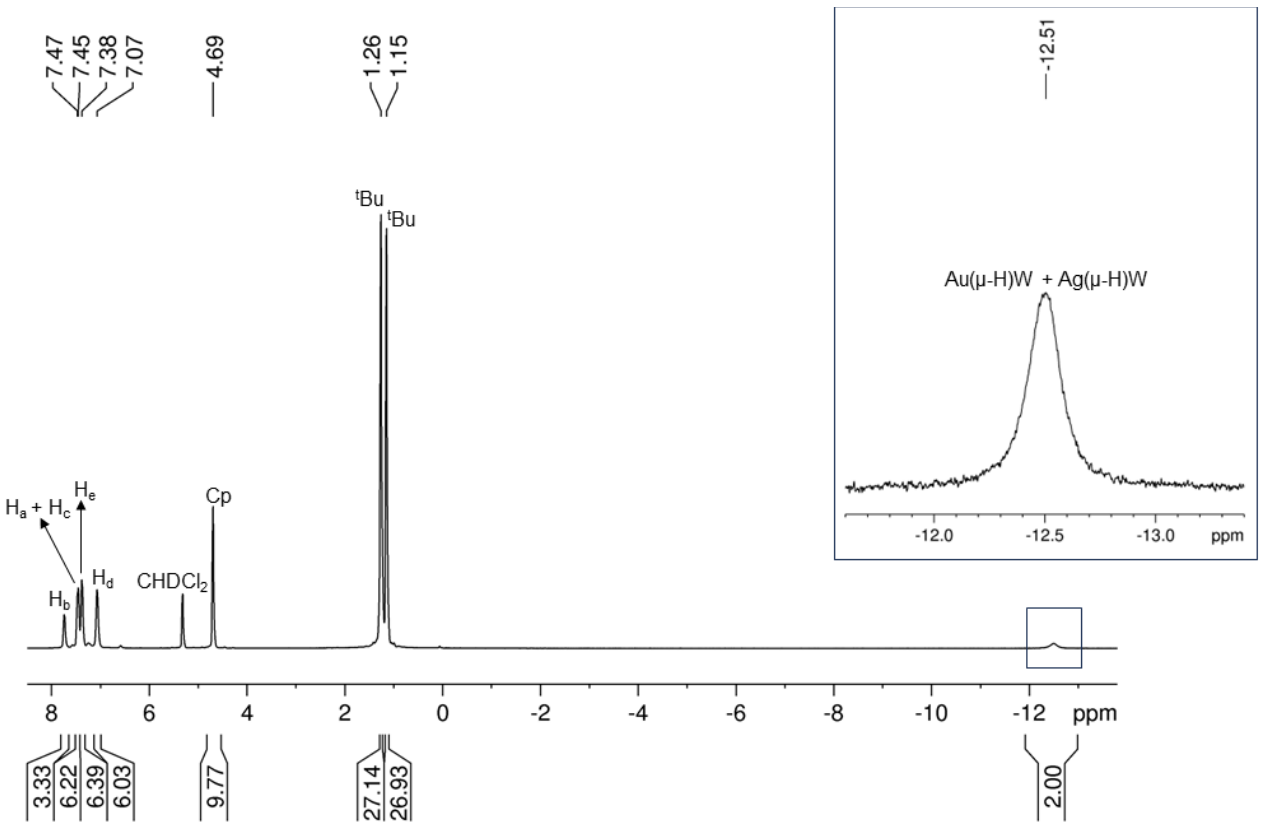


Figure S10. ^{1}H NMR (CD_2Cl_2, 400 MHz, 0 °C) spectrum of **3**.

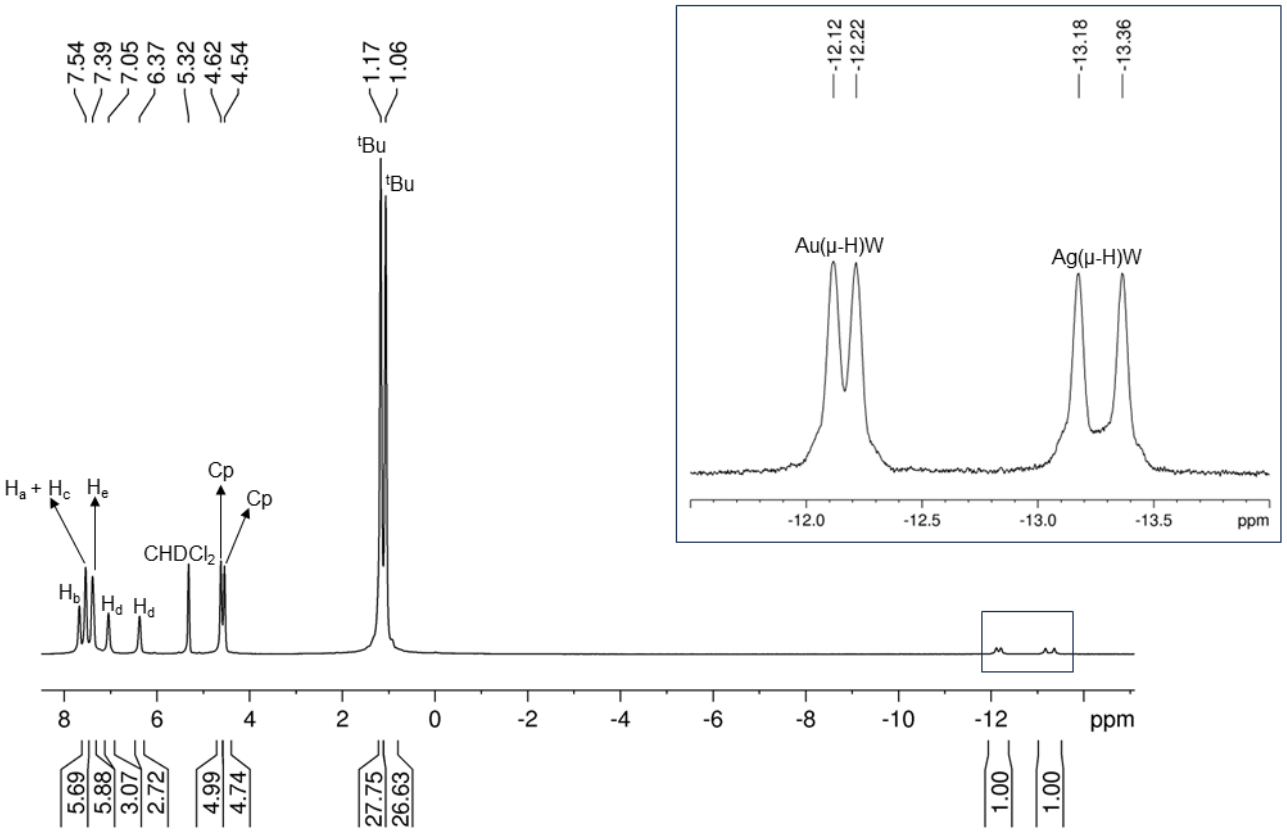


Figure S11. ^{1}H NMR (CD_2Cl_2, 400 MHz, –80 °C) spectrum of **3**

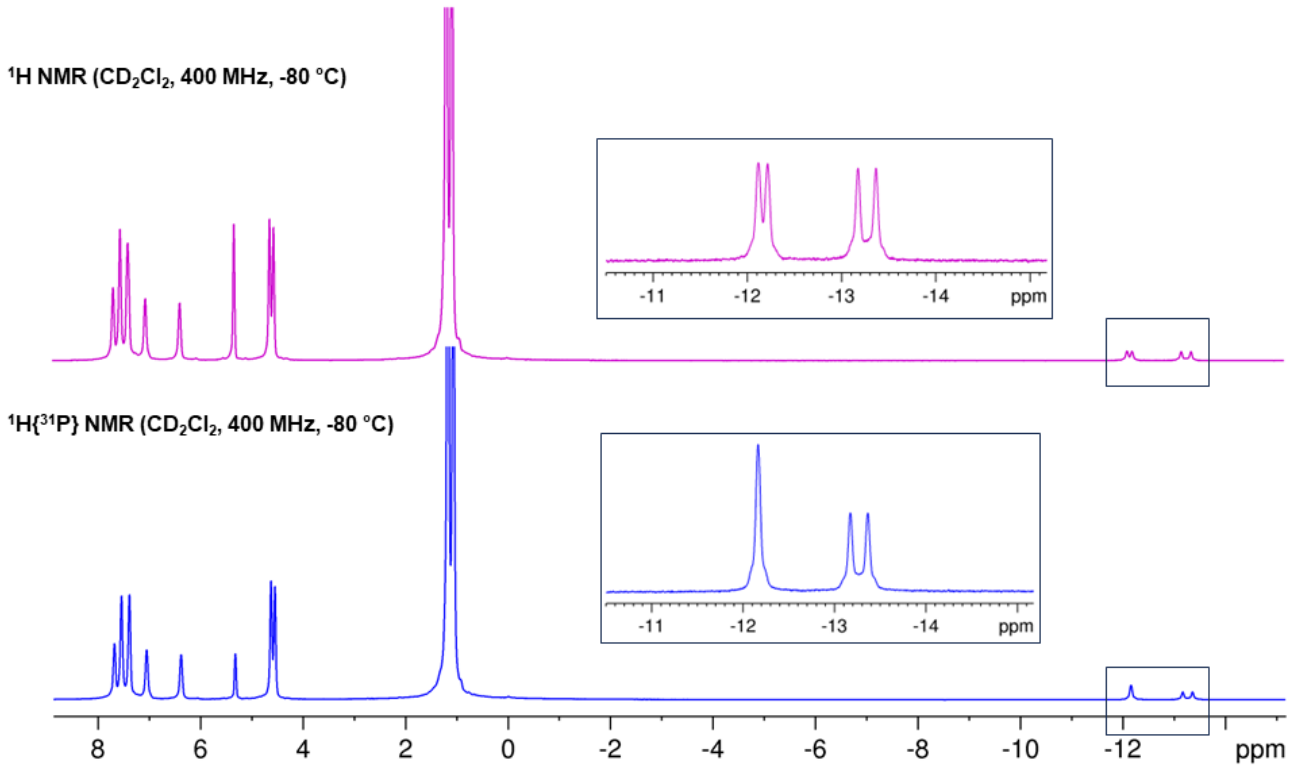


Figure S12. Top: ^{1}H NMR (CD_2Cl_2, 400 MHz, –80 °C) spectrum of **3**, bottom: ^{1}H{^{31}P} NMR (CD_2Cl_2, 400 MHz, –80 °C) spectrum of **3**.

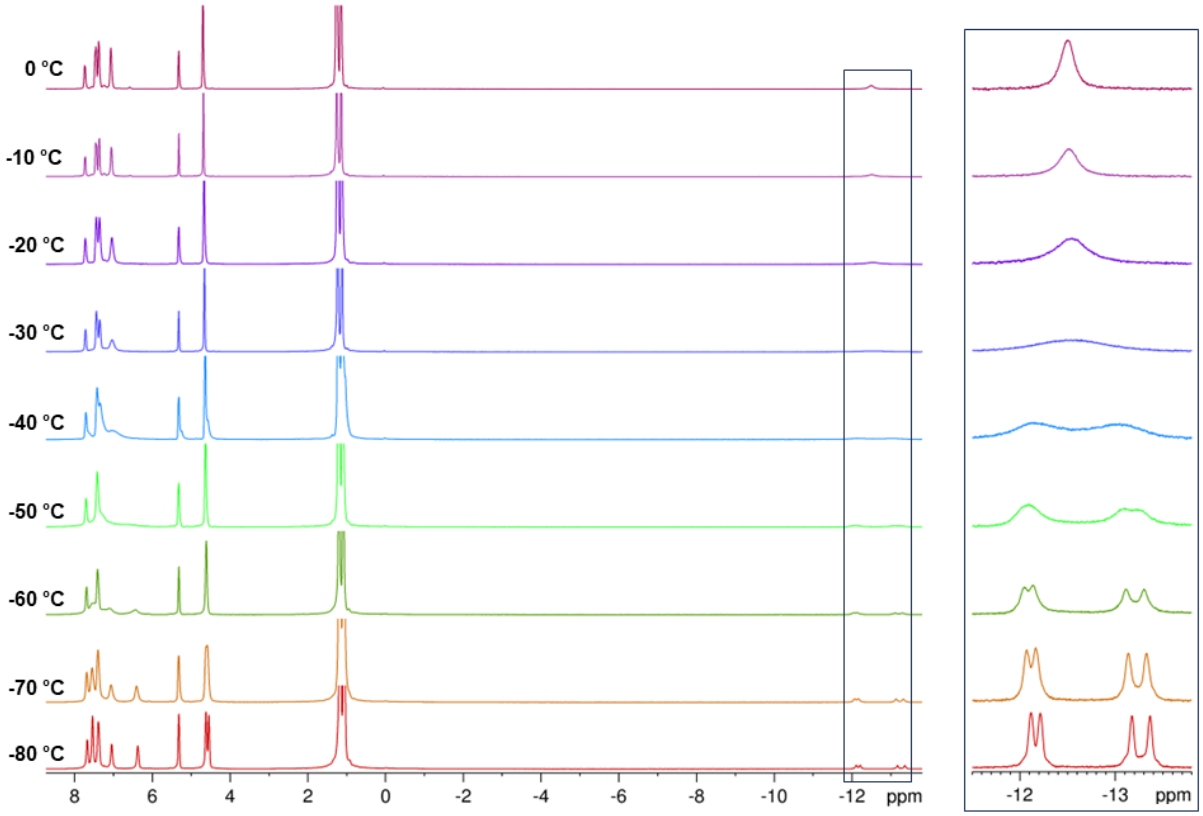


Figure S13. Variable temperature ^{1}H NMR spectra of complex **3**.

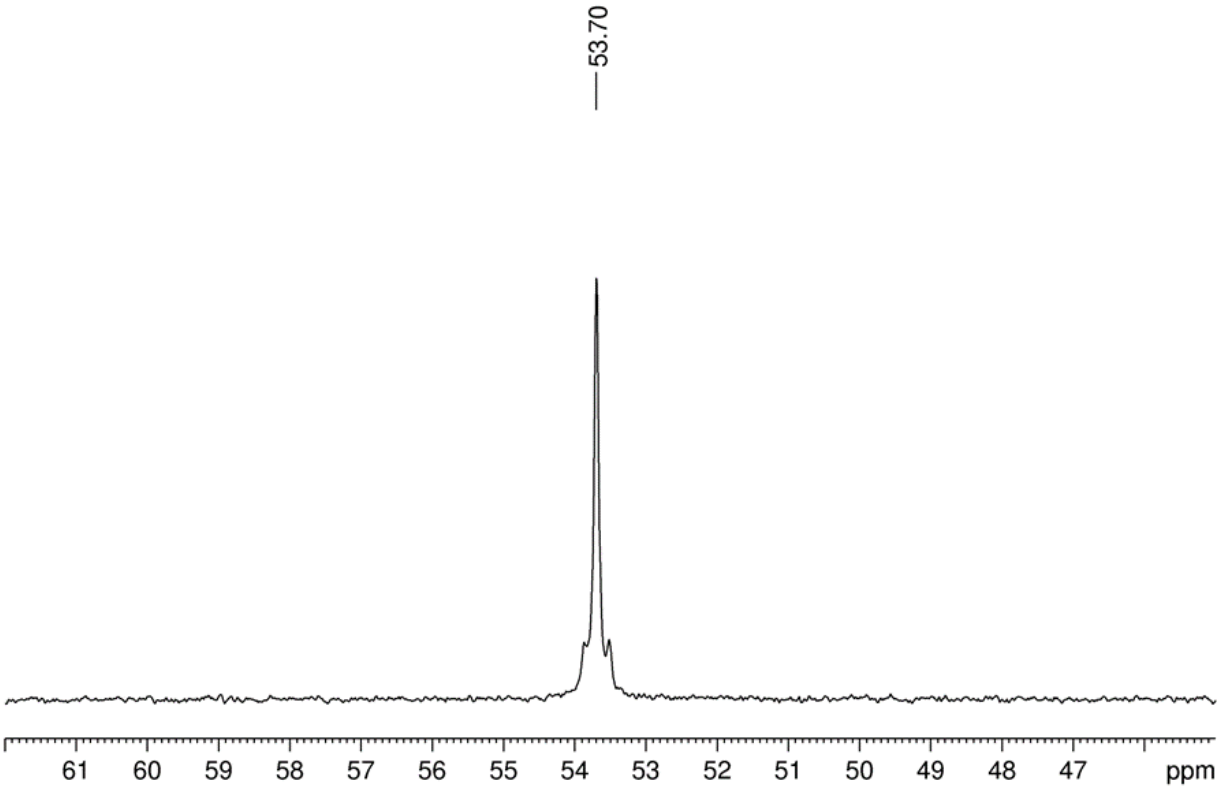


Figure S14. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 162 MHz, –80 °C) spectrum of **3**.

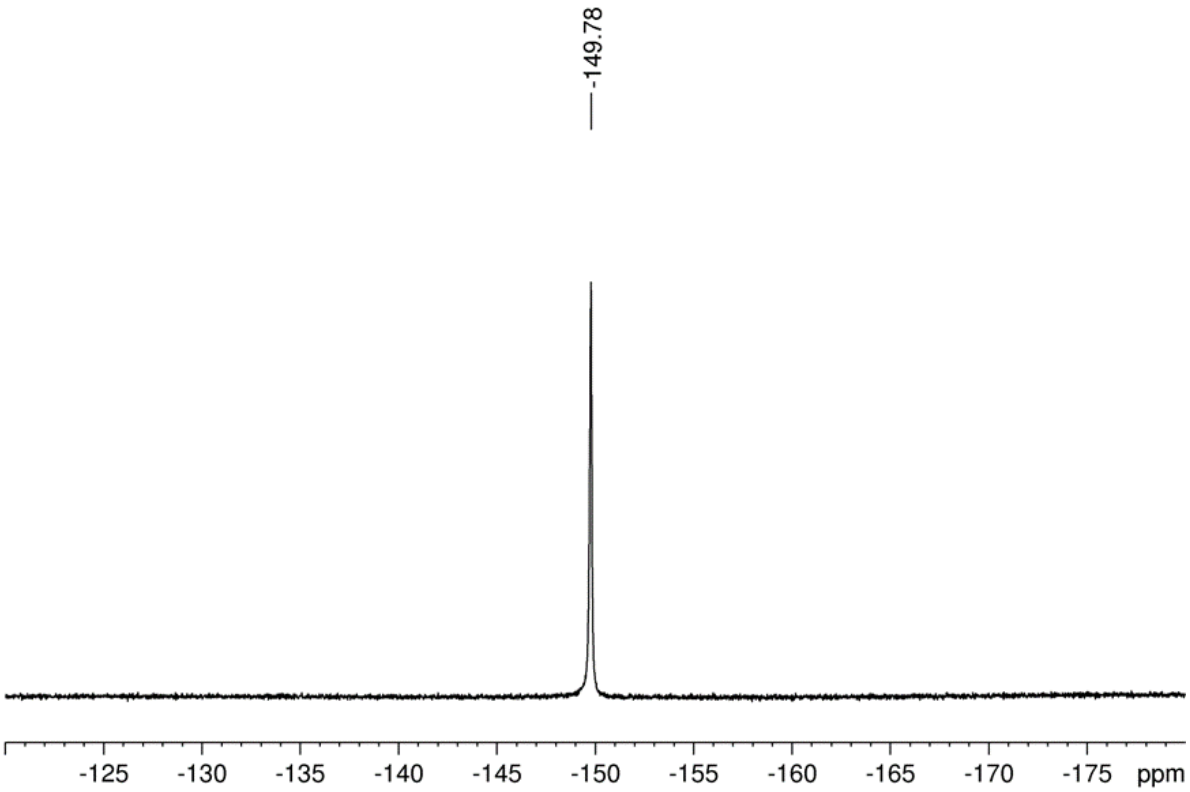


Figure S15. $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2, 376 MHz, –80 °C) spectrum of **3**.

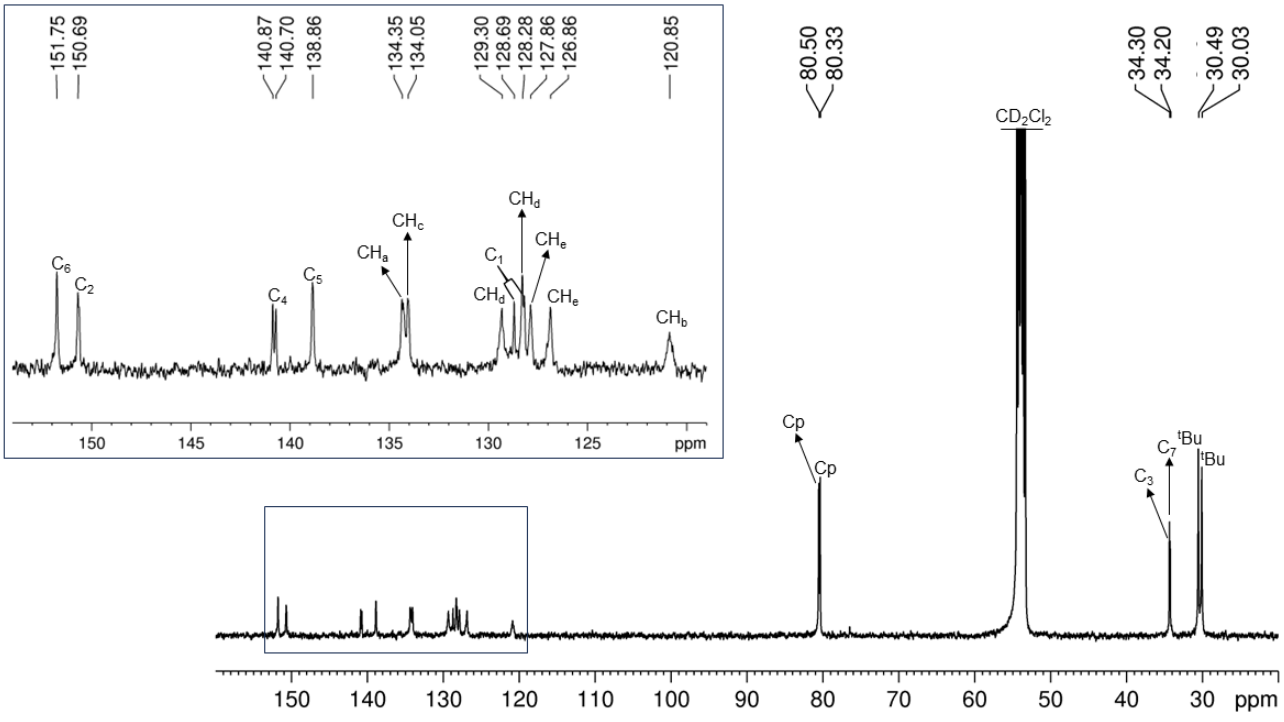


Figure S16. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 100 MHz, –80 °C) spectrum of **3**.

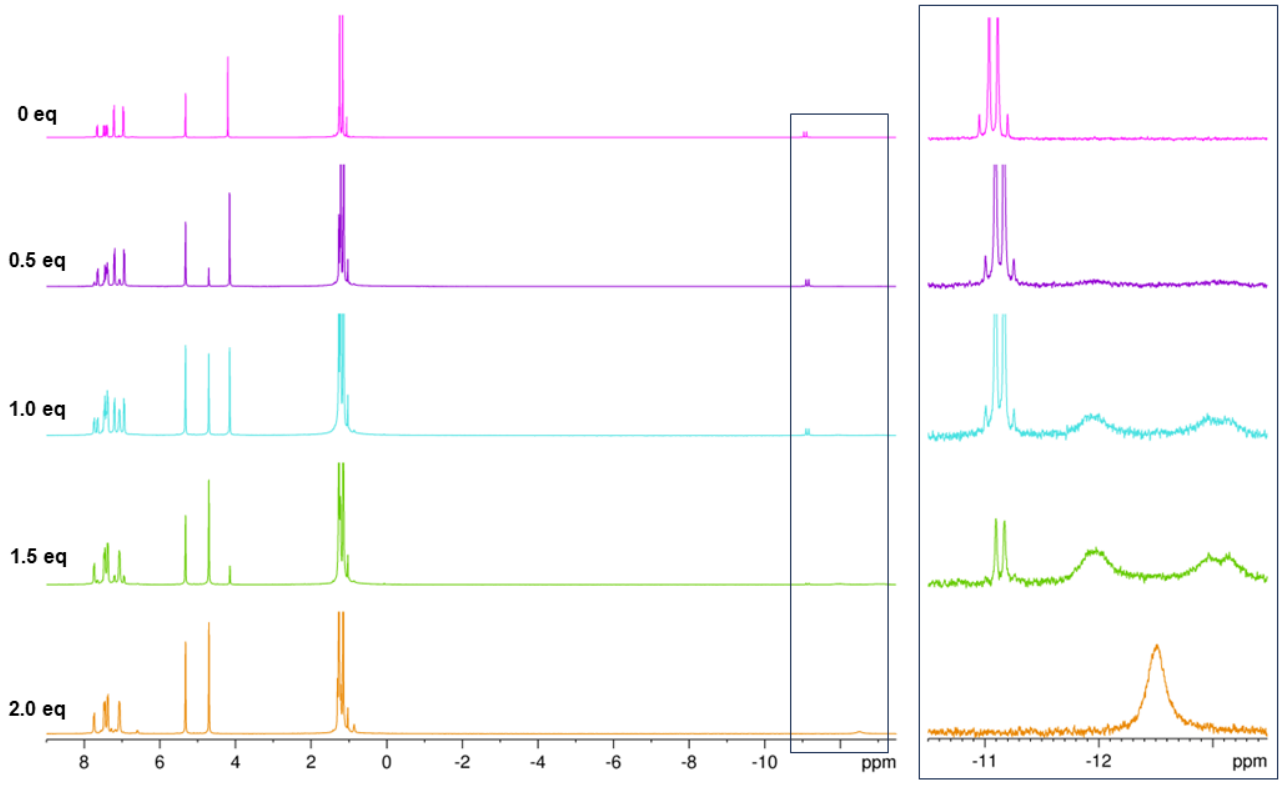


Figure S17. Stacked ^{1}H NMR (CD_2Cl_2, 400 MHz, 0 °C) spectra of consecutive additions of $AgBF_4$ to complex **1**.

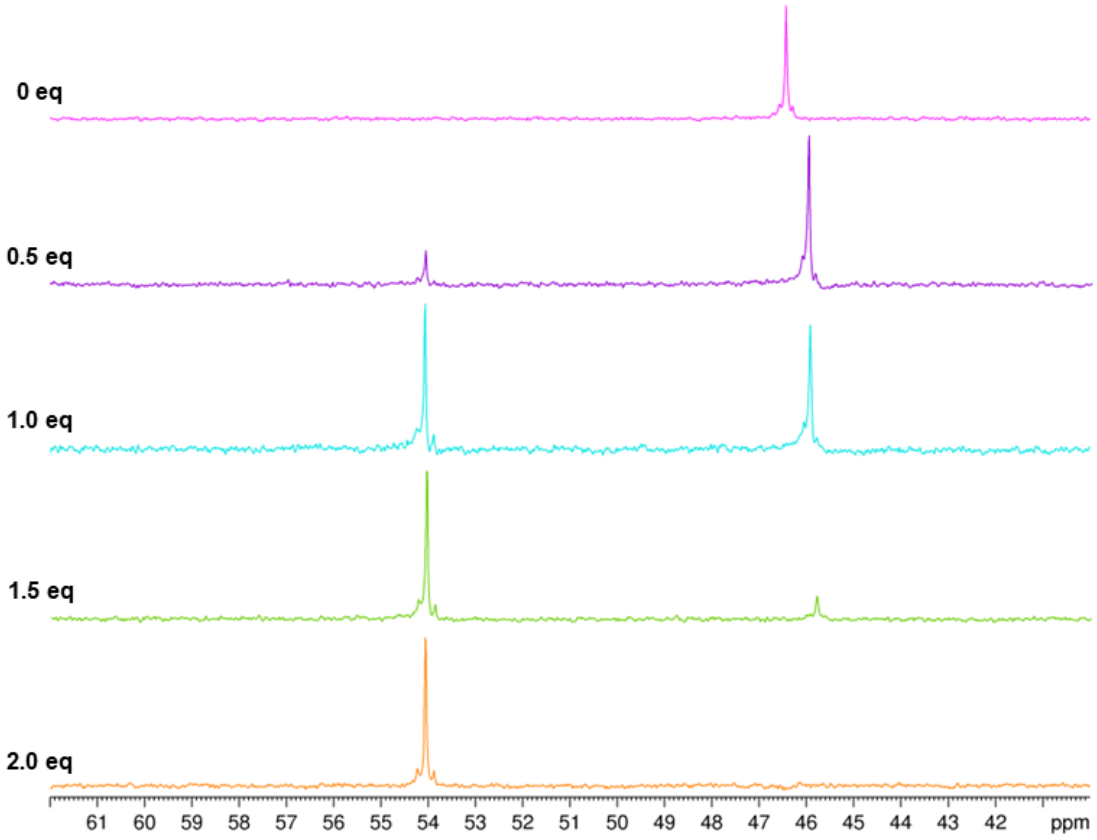


Figure S18. Stacked $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 162 MHz, 0 °C) spectra of consecutive additions of $AgBF_4$ to complex **1**.

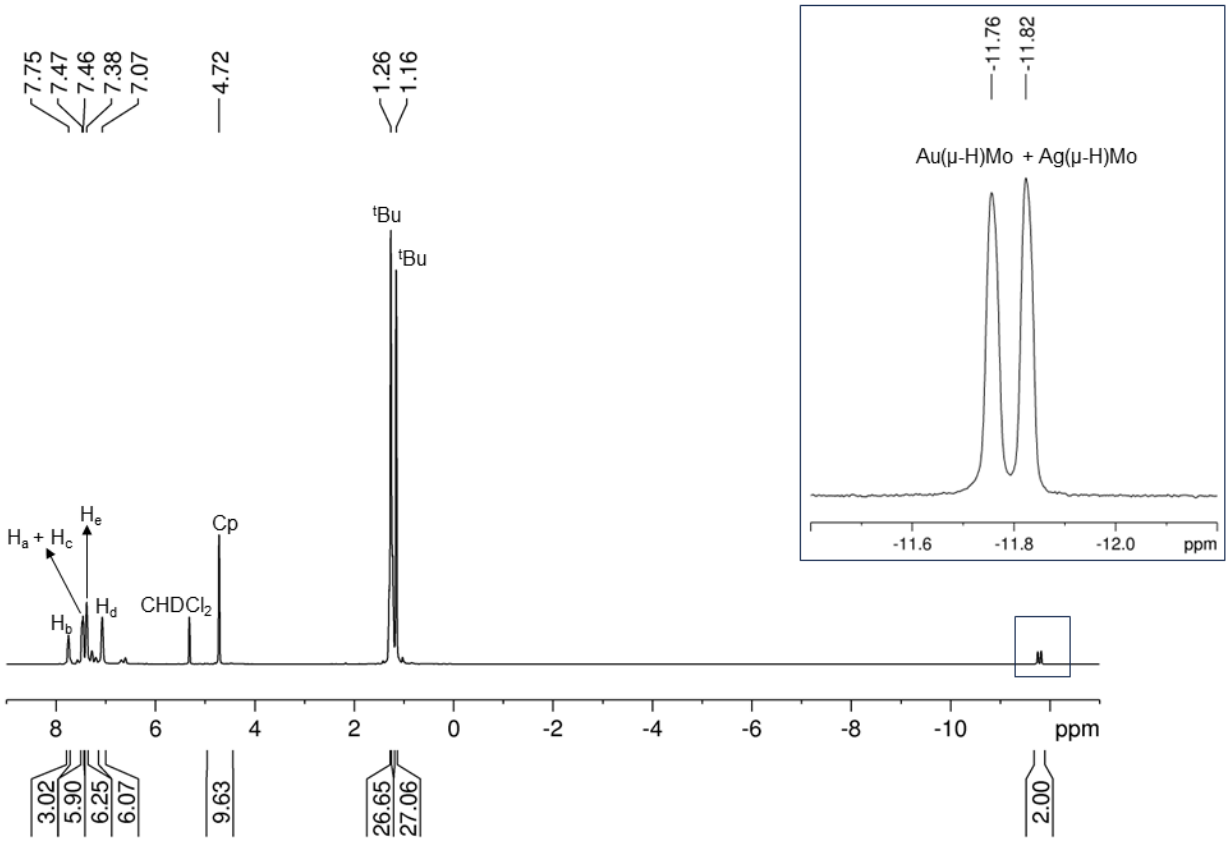


Figure S19. ^{1}H NMR (CD_2Cl_2, 400 MHz, 0 °C) spectrum of **4**.

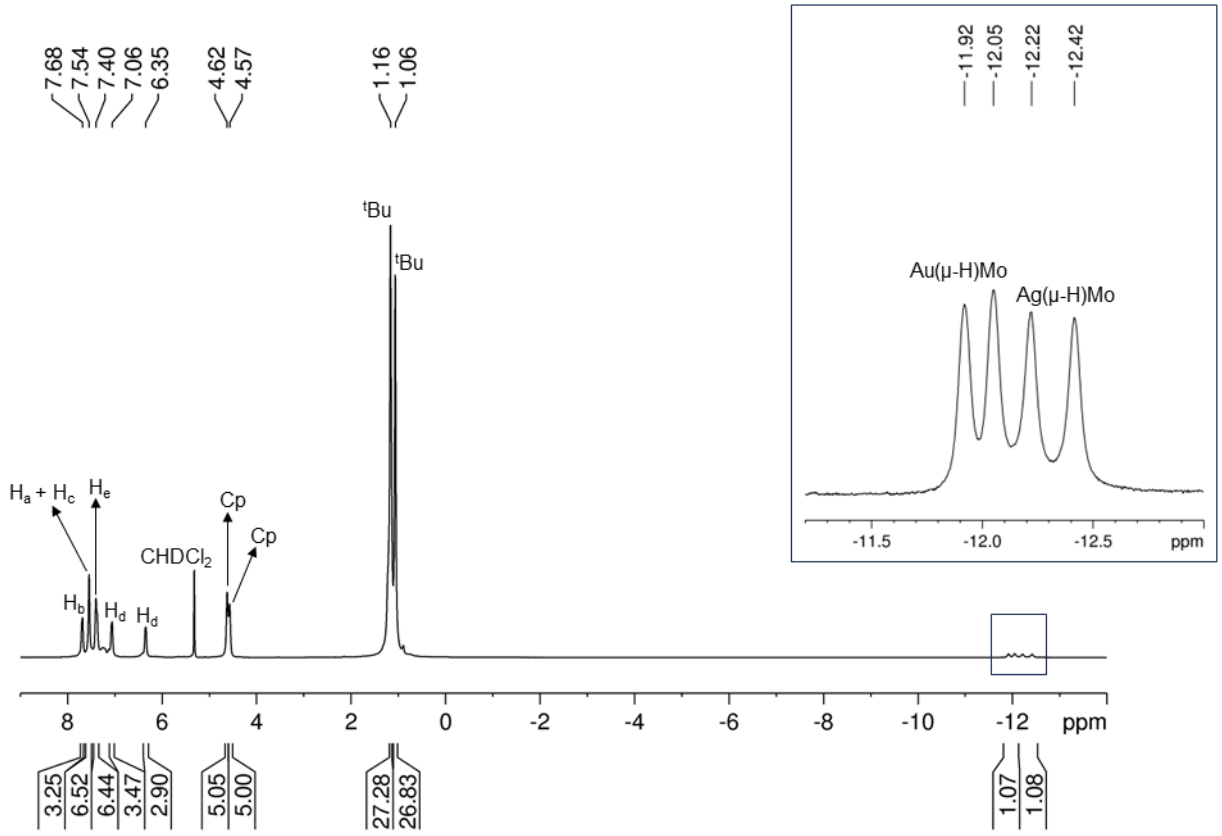


Figure S20. ^{1}H NMR (CD_2Cl_2, 400 MHz, –80 °C) spectrum of **4**.

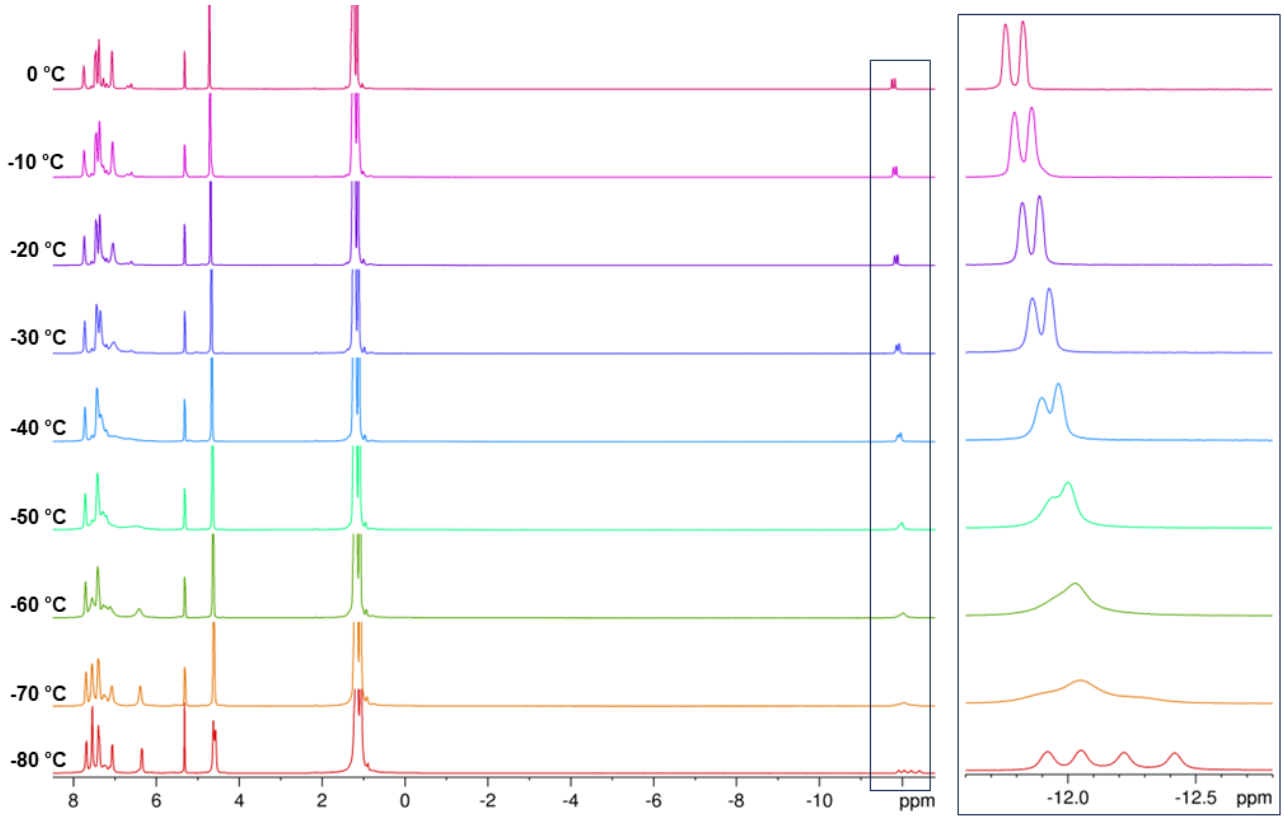


Figure S21. Variable temperature ^{1}H NMR spectra of complex **4** in CD_2Cl_2.

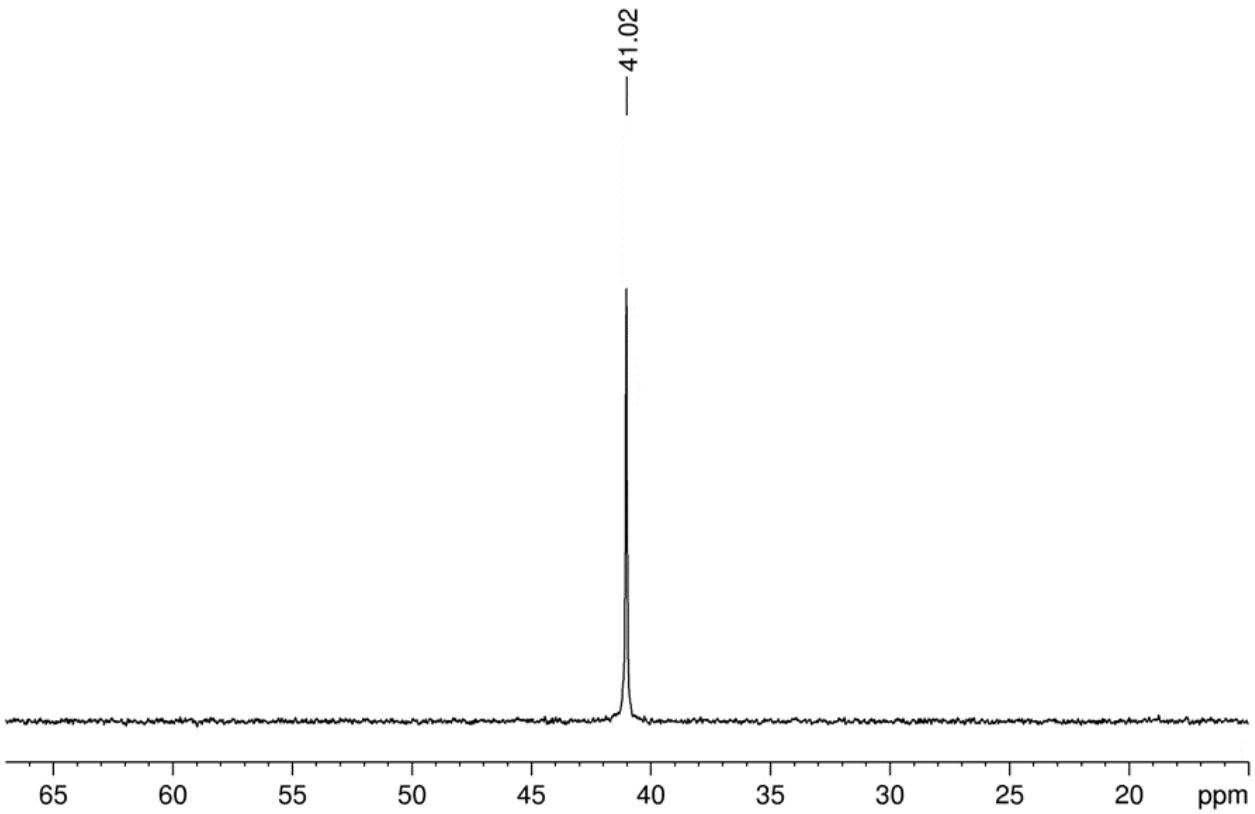


Figure S22. $^{31}P\{^{1}H\}$ (CD_2Cl_2, 162 MHz, –80 °C) NMR spectrum of **4**.

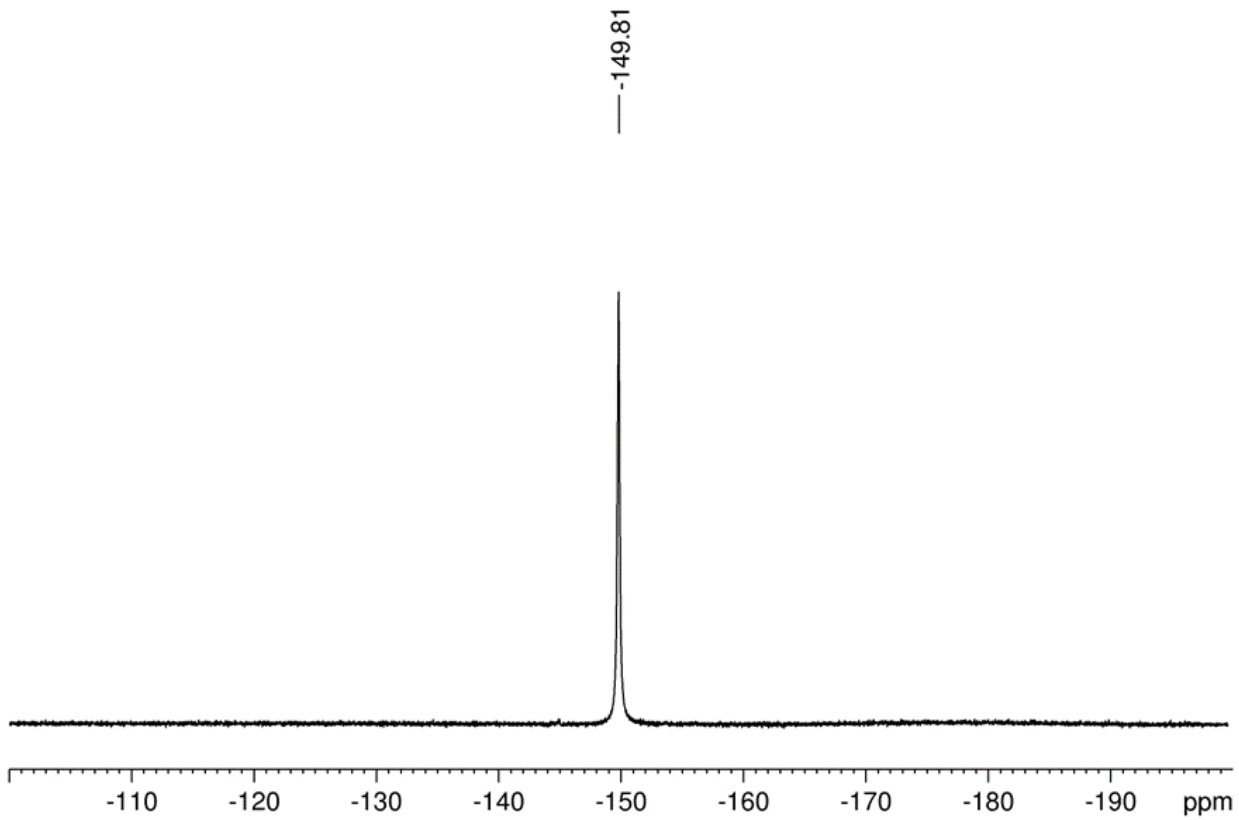


Figure S23. $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2, 376 MHz, –80 °C) spectrum of **4**.

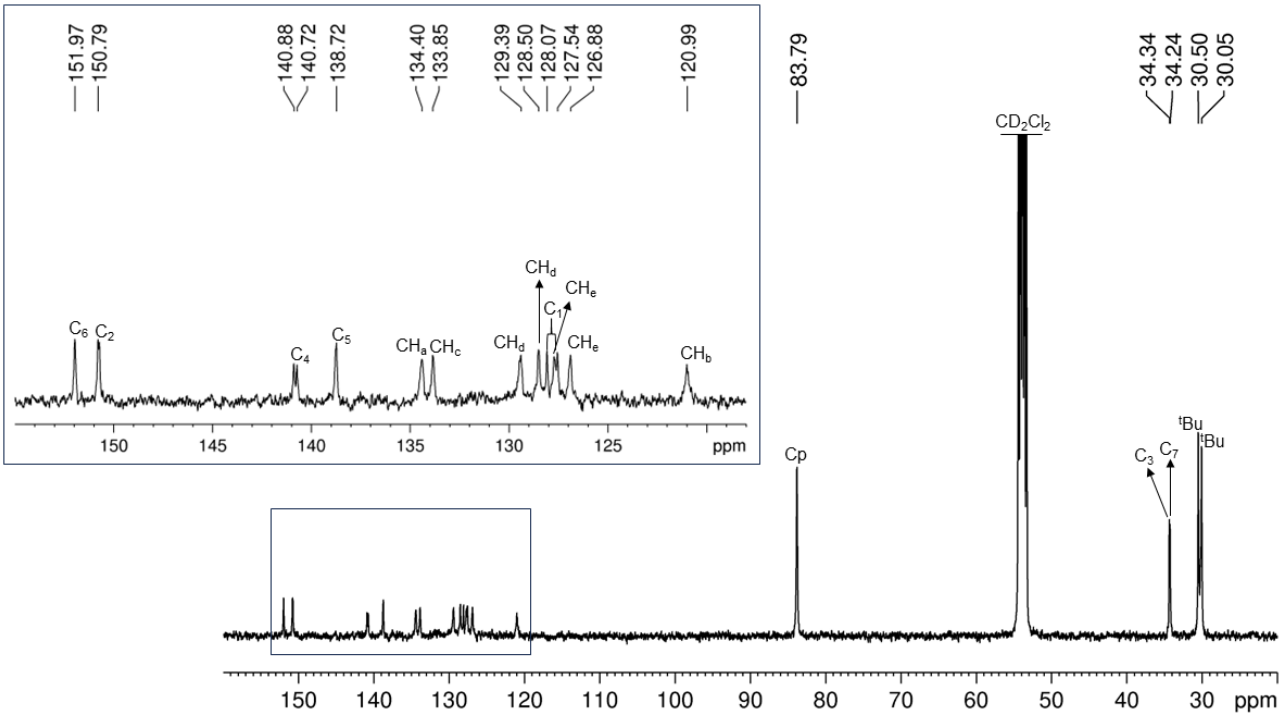


Figure S24. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 100 MHz, –80 °C) spectrum of **4**.

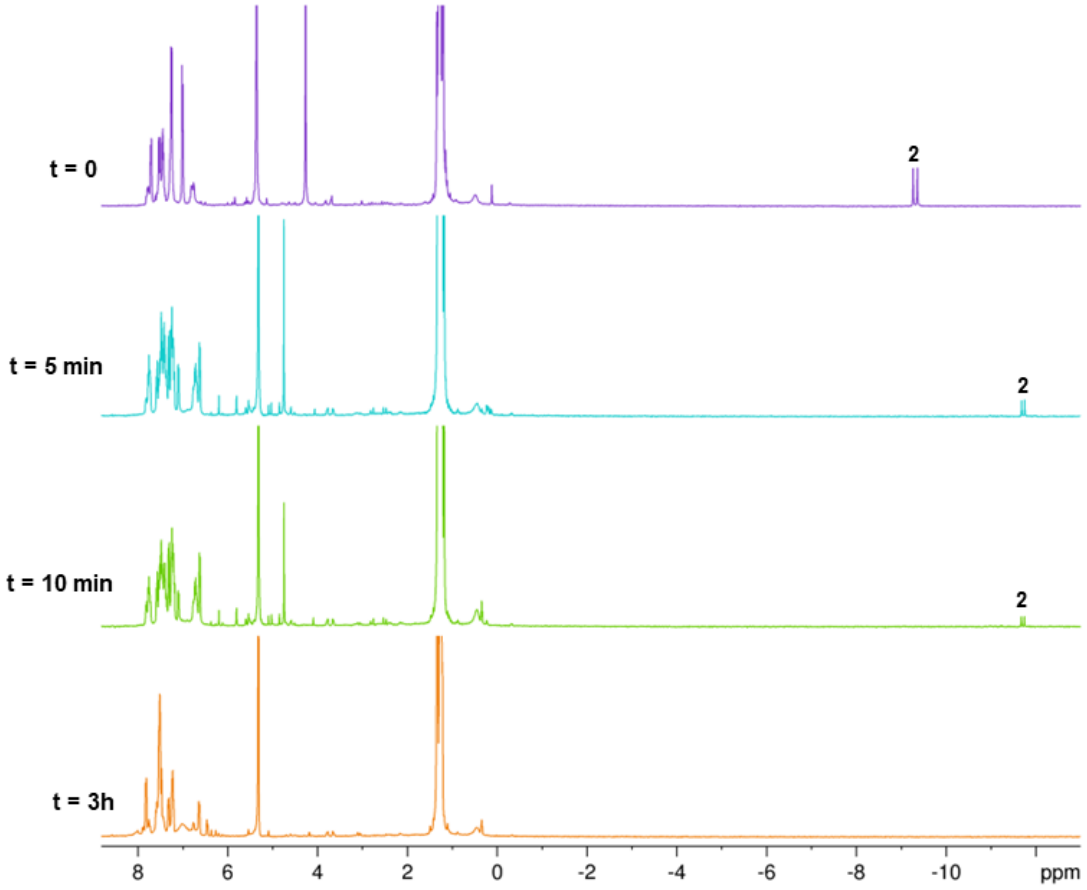


Figure S25. Stacked ^{1}H NMR (CD_2Cl_2, 400 MHz, 25 °C) spectra of the reaction of **2** with $AgBF_4$ (2 eq.).

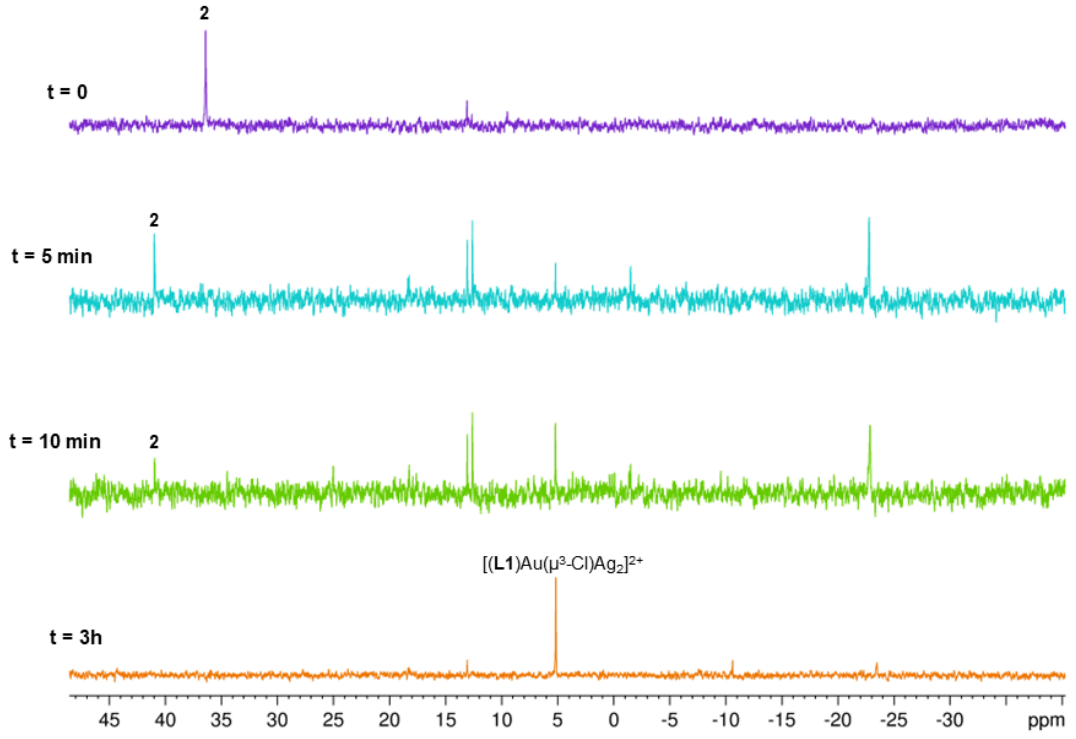


Figure S26. Stacked $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 162 MHz, 25 °C) spectra of the reaction of **2** with $AgBF_4$ (2 eq.)

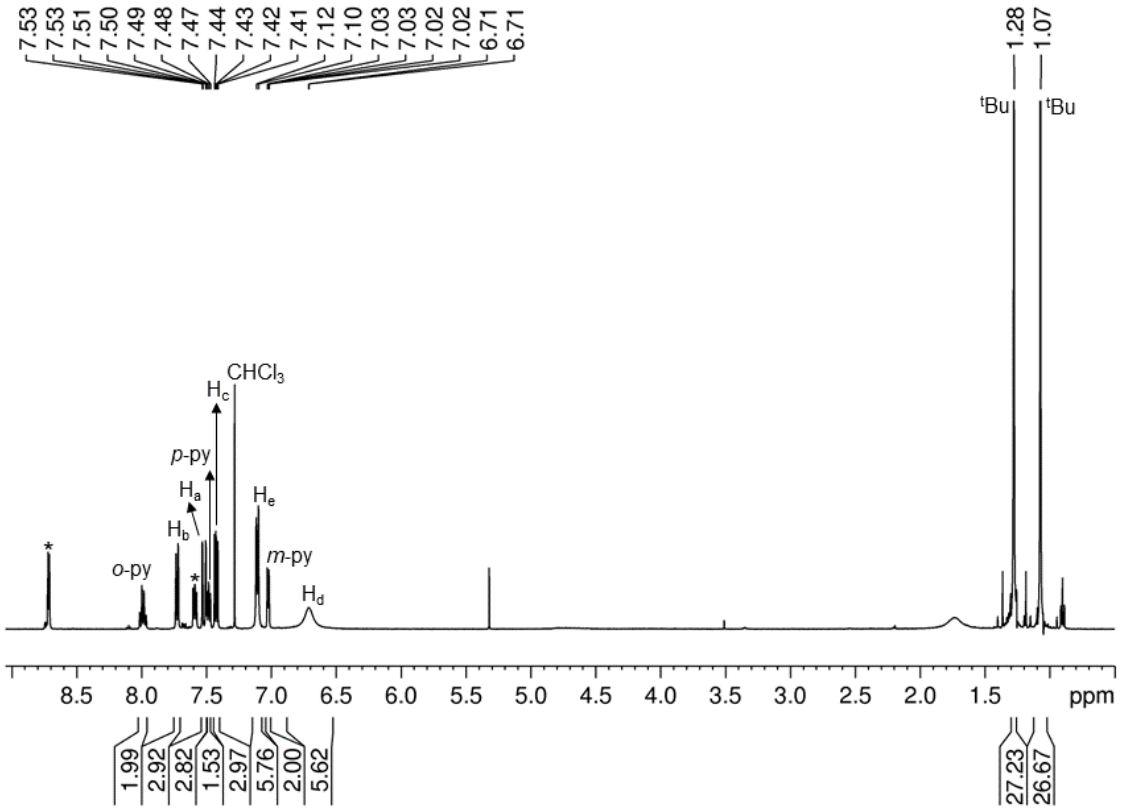


Figure S27. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C) spectrum of **5** (*by-product of the reaction assigned as **[Ag(py)$_2$][SbF$_6$]**, see X-Ray section Table S2).

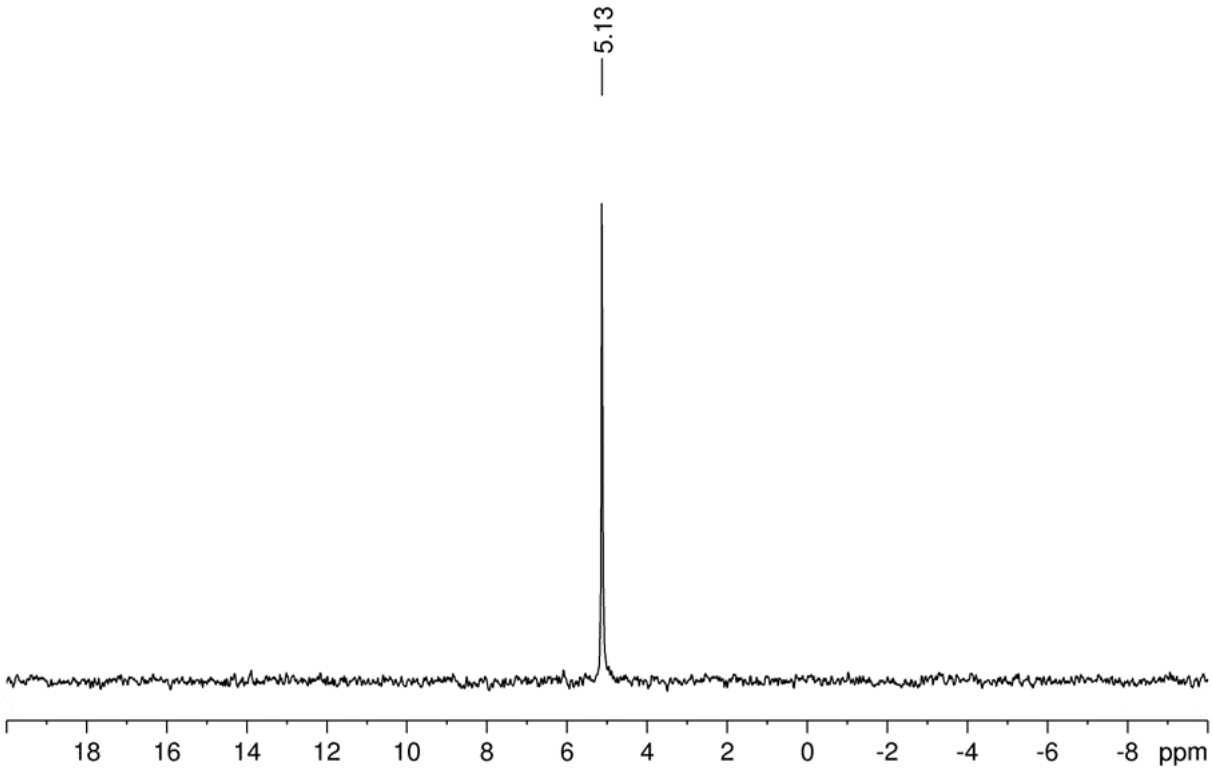


Figure S28. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz, 25 °C) spectrum of **5**.

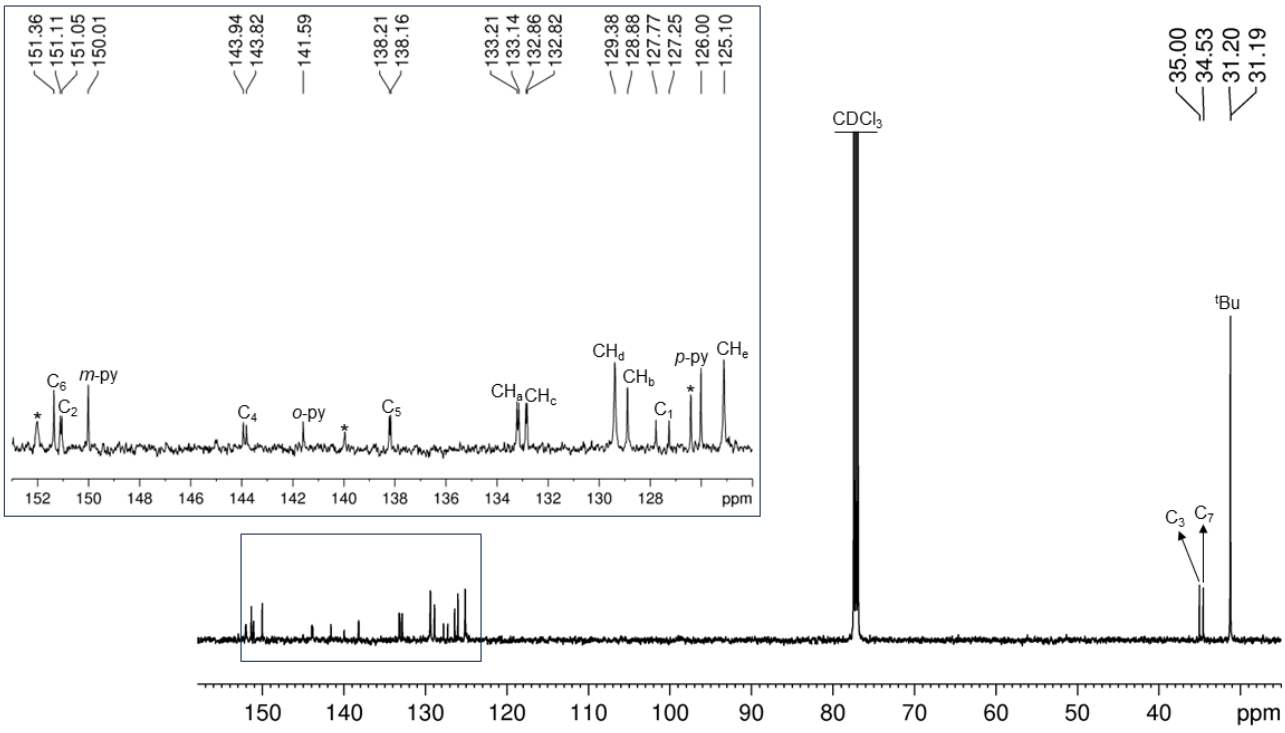


Figure S29. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz, 25 °C) spectrum of **5**.

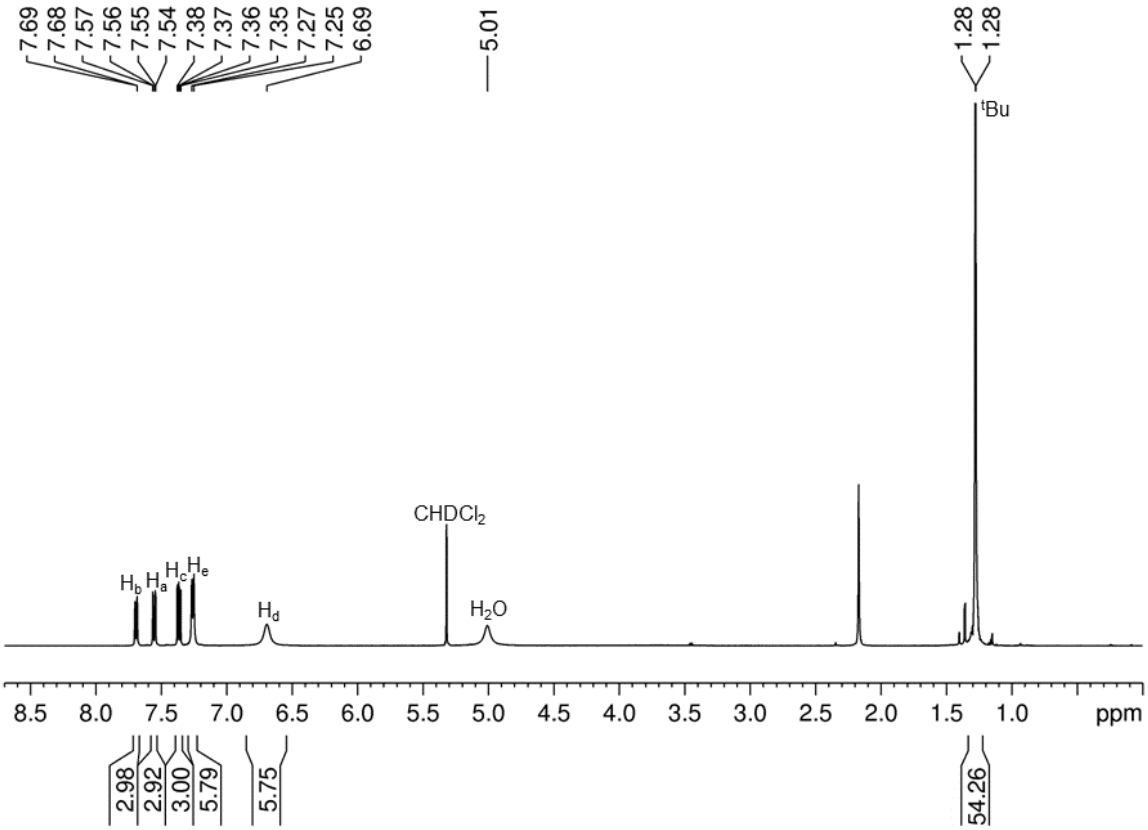


Figure S30. ^{1}H NMR (CD_2Cl_2, 500 MHz, 25 °C) spectrum of **6**.

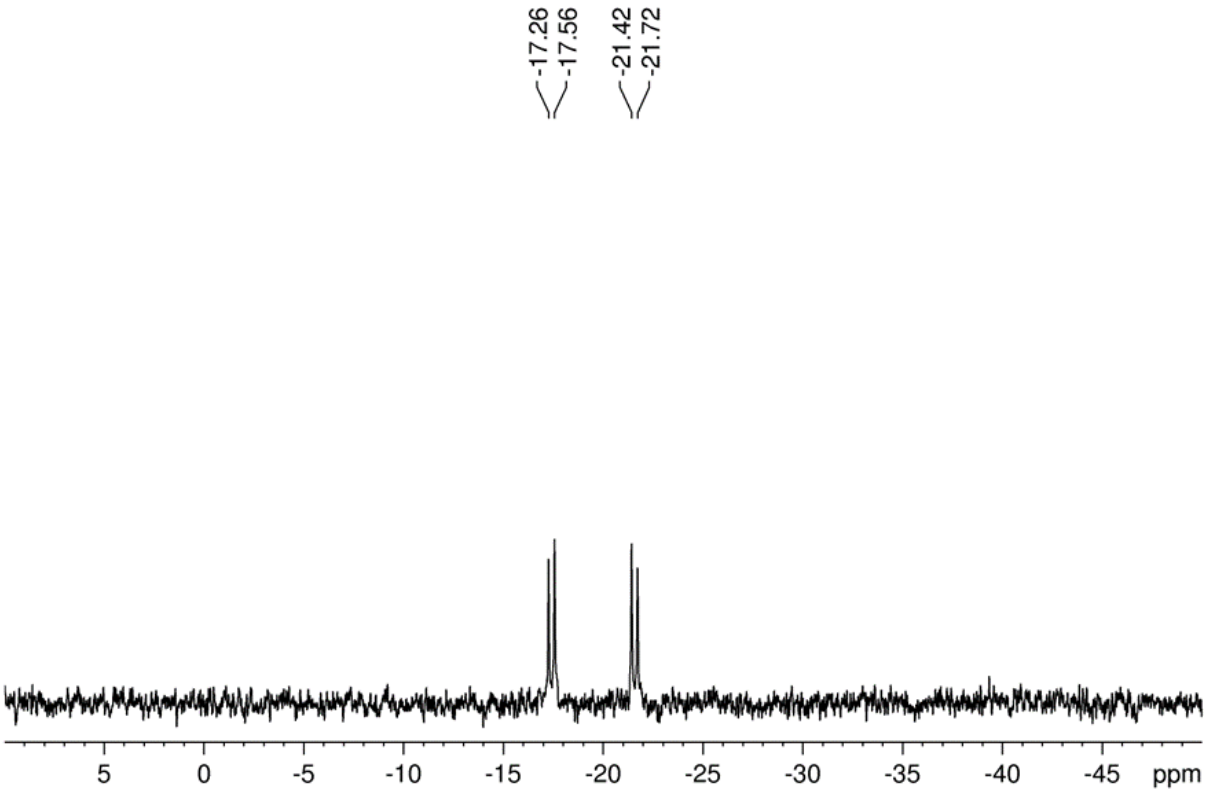


Figure S31. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 202 MHz, 25 °C) spectrum of **6**.

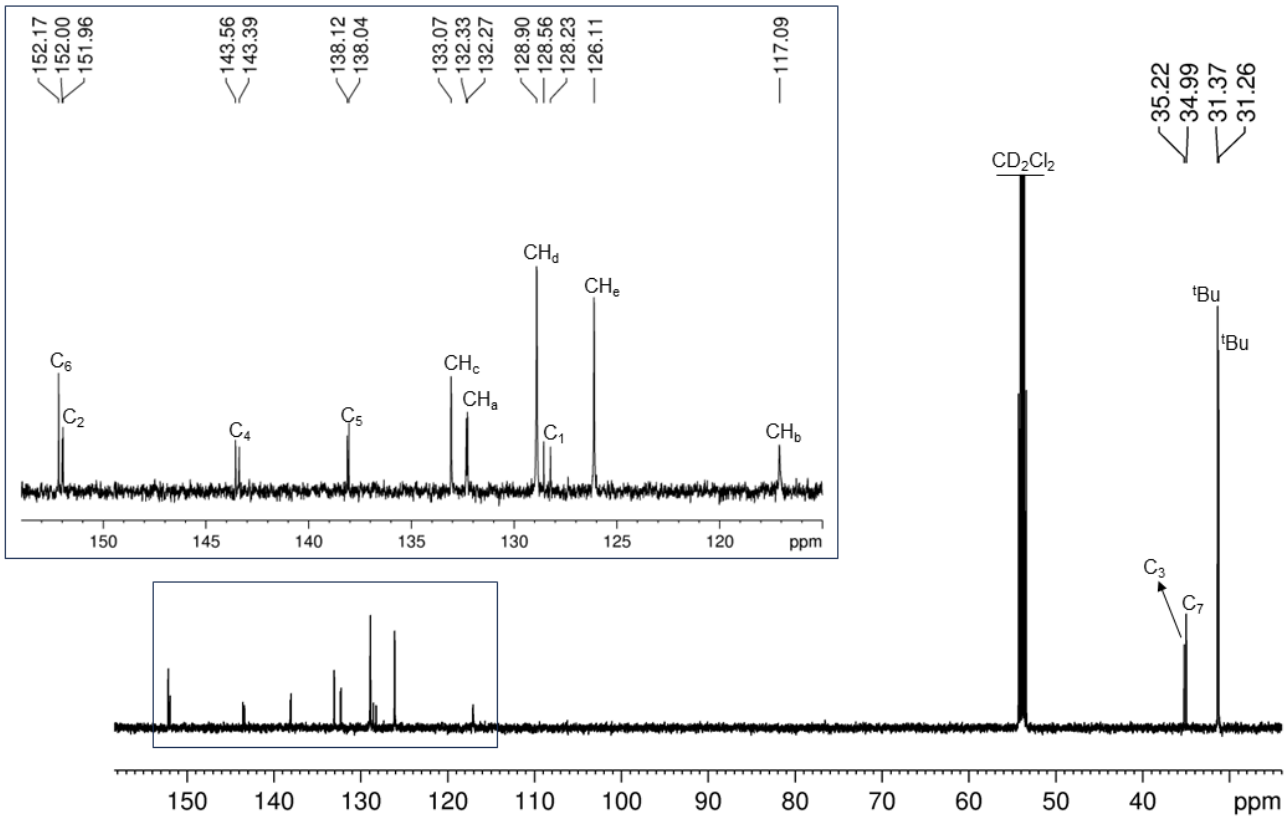


Figure S32. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 125 MHz, 25 °C) spectrum of **6**.

3. Photolysis Experiments

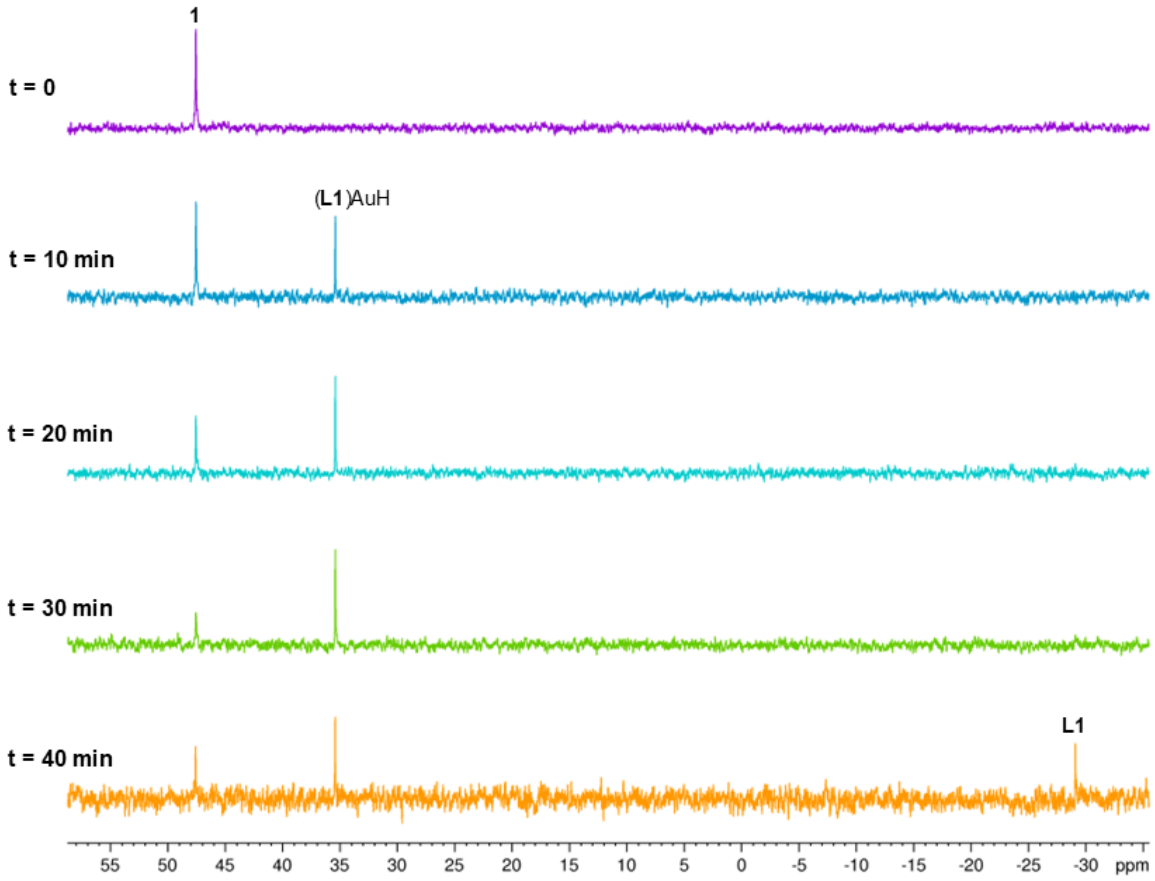


Figure S33 Stacked $^{31}P\{^{1}H\}$ NMR (THF-*d*8, 162 MHz, 25 °C) of **1** at different irradiation times with UV light.

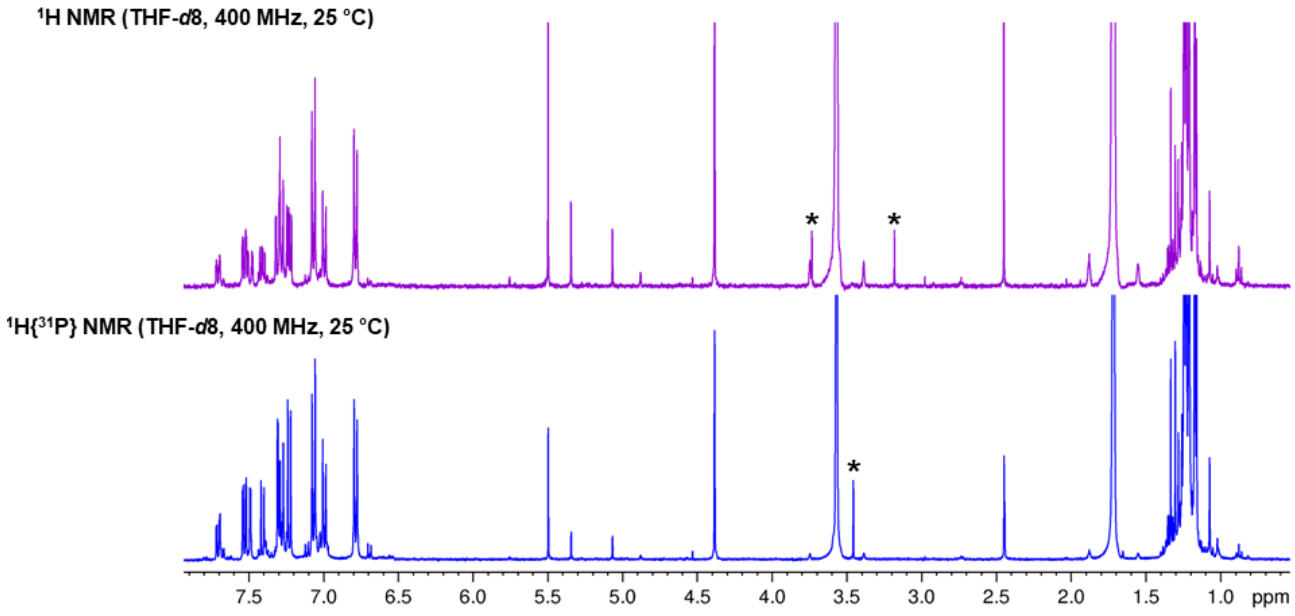


Figure S34 ^{1}H NMR (top) and $^{1}H\{^{31}P\}$ NMR (bottom) spectrum of **1** after 20 minutes of irradiation highlighting the hydride signal of the LAuH compound.

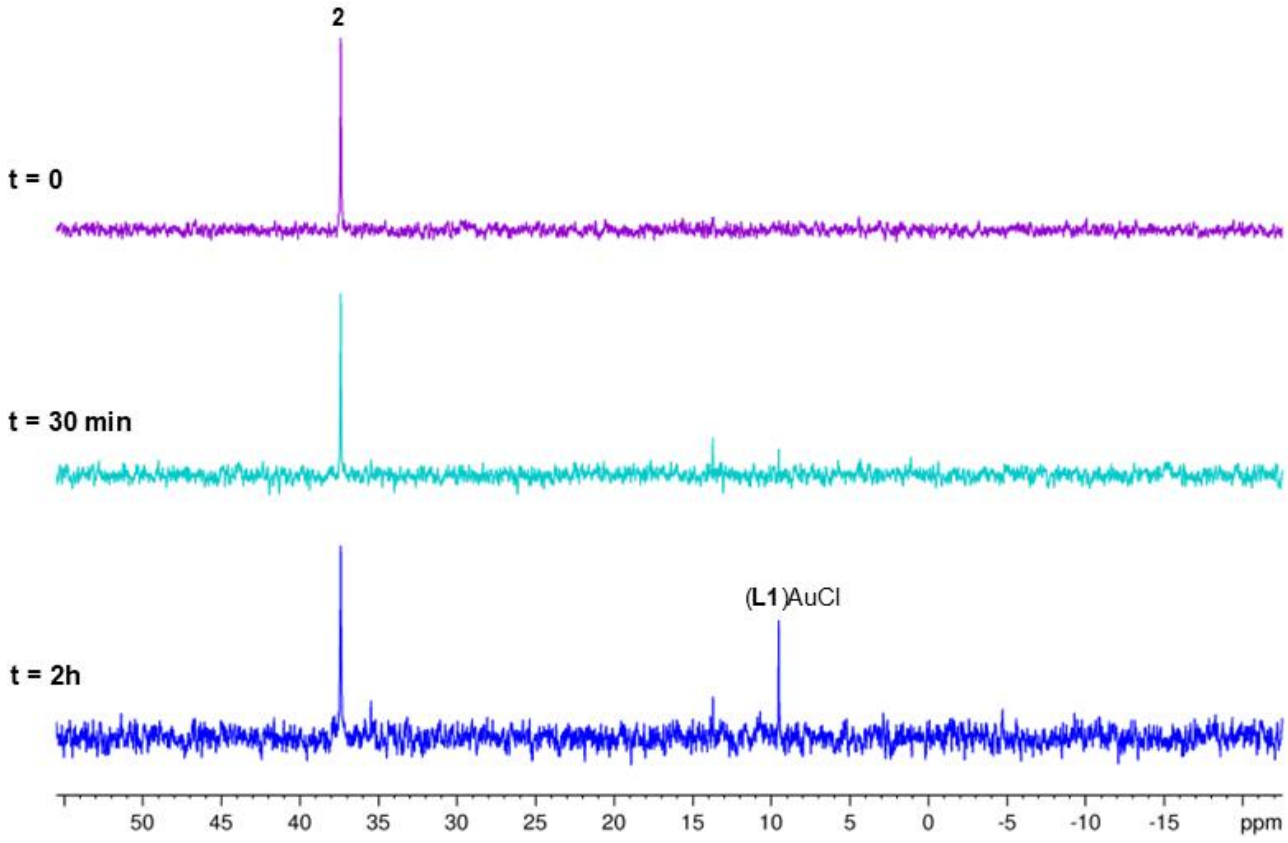


Figure S35 Stacked $^{31}P\{^{1}H\}$ NMR (THF-*d*8, 162 MHz, 25 °C) of **2** at different irradiation times with UV light.

4. *In situ* NMR reactions

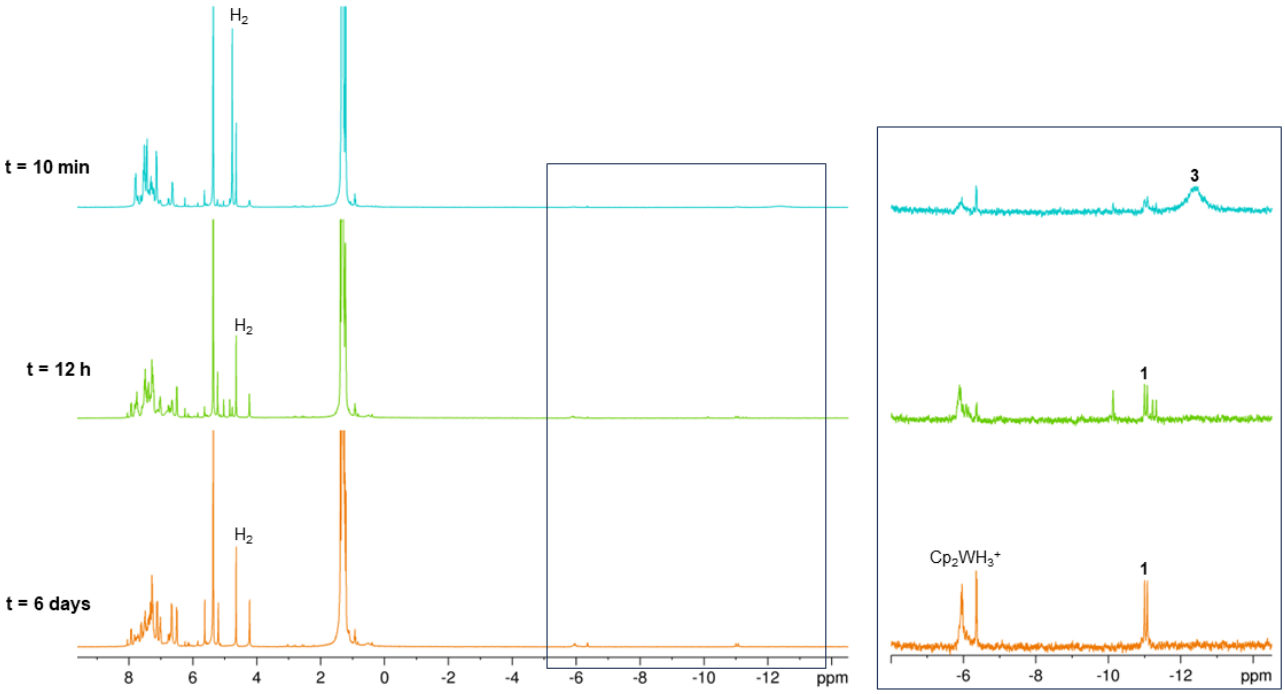


Figure S36. Stacked ^{1}H NMR (CD_2Cl_2, 400 MHz, 25 °C) spectra of the reaction between **3** and H_2 over the time.

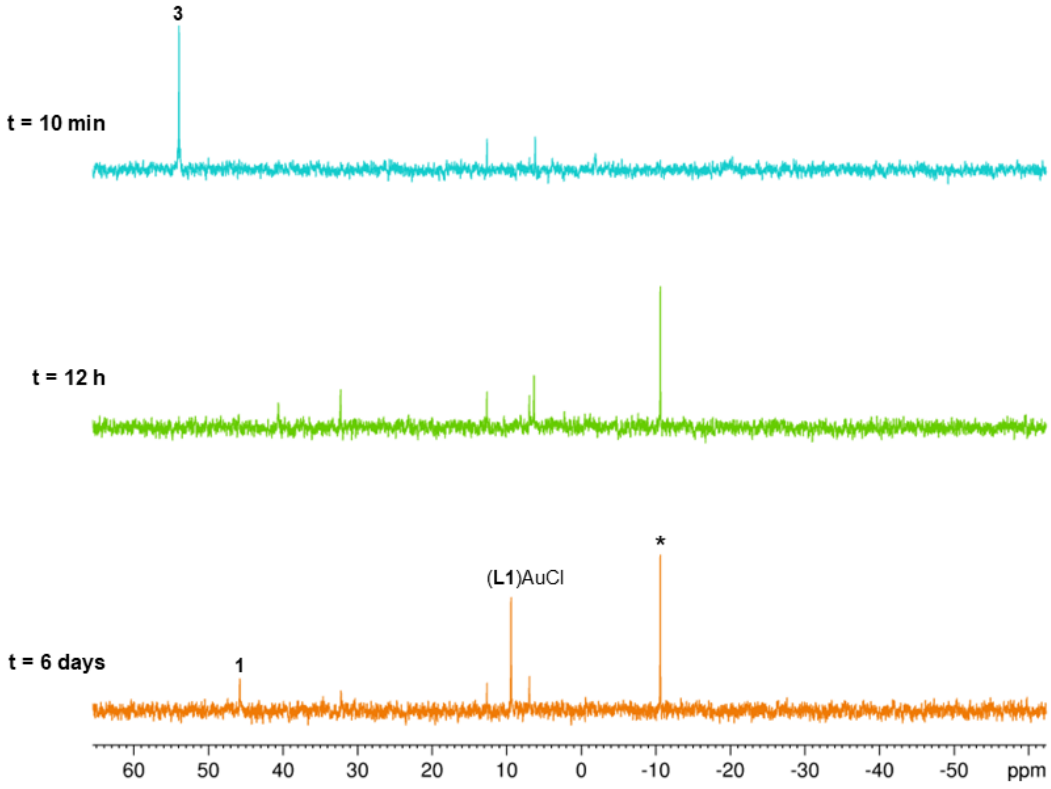


Figure S37. Stacked $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 162 MHz, 25 °C) spectra of the reaction between **3** and H_2 over the time (*major product).

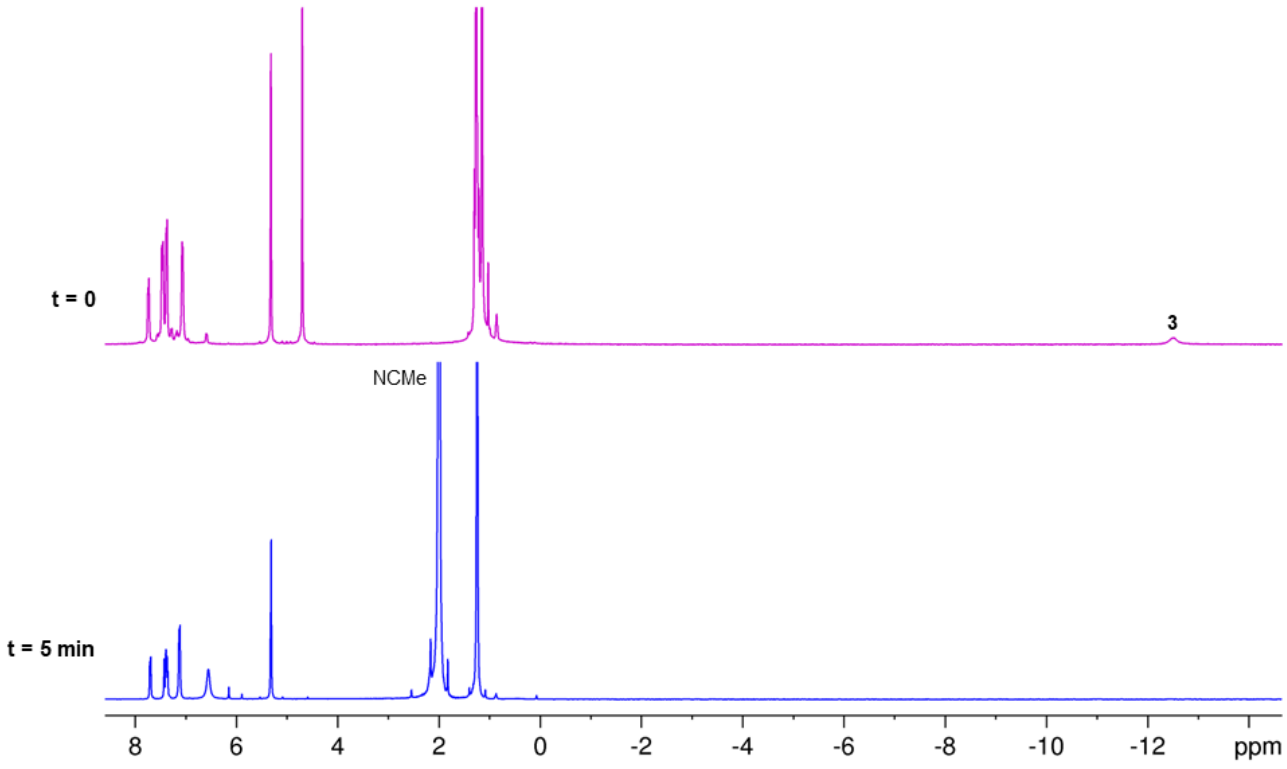


Figure S38. Stacked ^{1}H NMR (CD_2Cl_2, 400 MHz) spectra of top: **3** (0° C) and bottom: **3** + MeCN (25 °C).

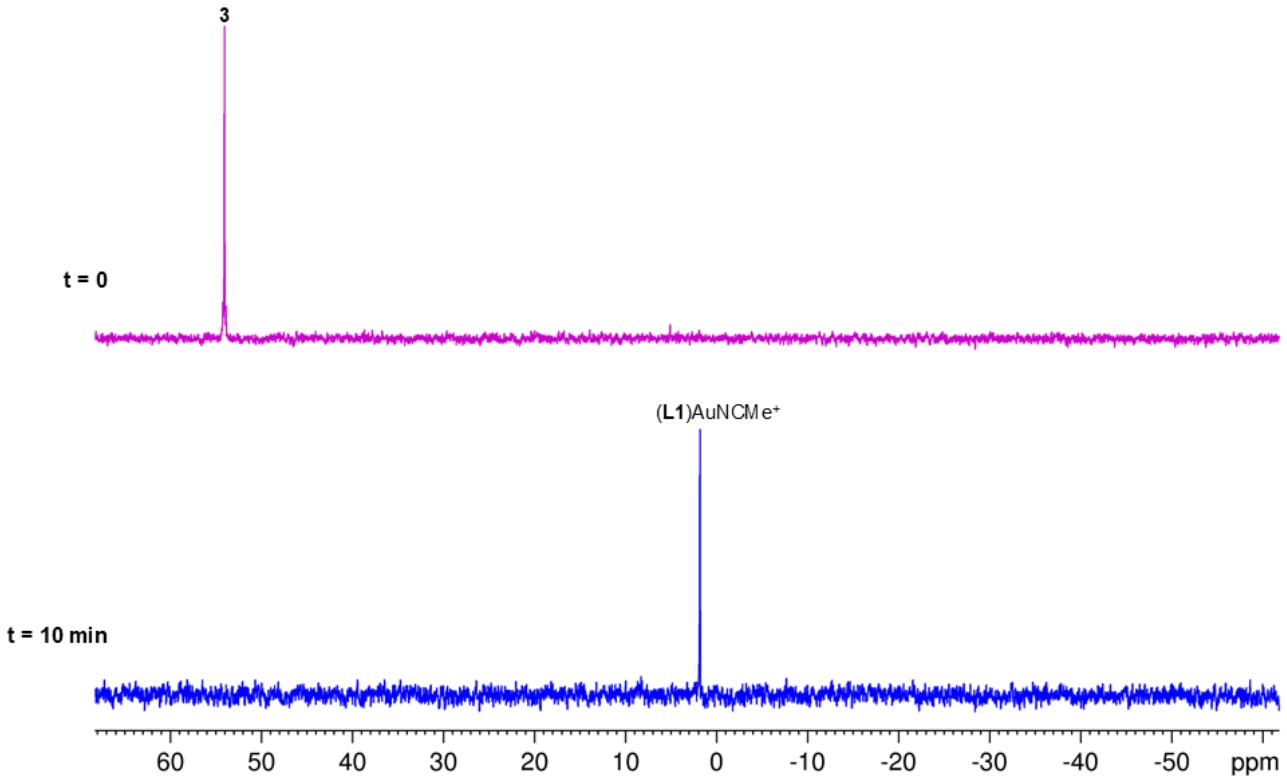


Figure S39. Stacked $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 162 MHz) spectra of top: **3** (0° C) and bottom: **3** + MeCN (25 °C).

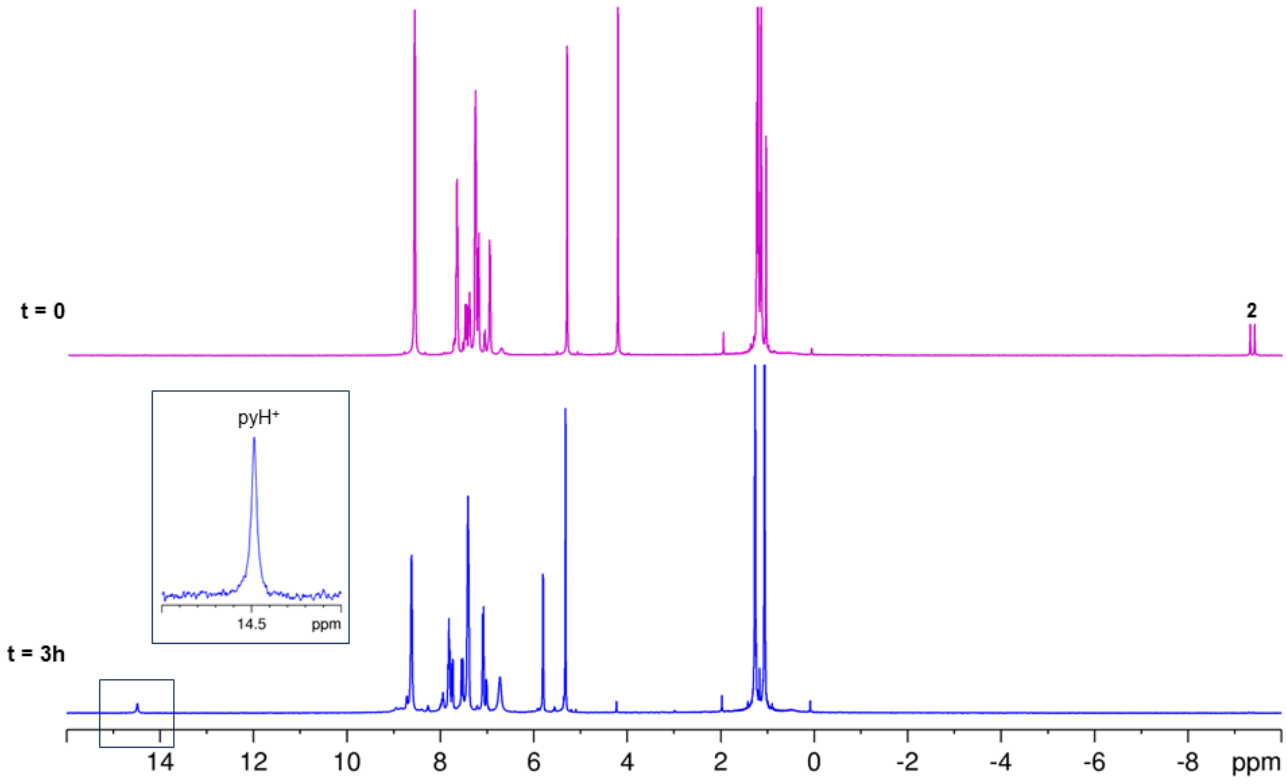


Figure S40. Stacked ^{1}H NMR (CD_2Cl_2, 400 MHz, 25 °C) spectra of top: **2** + py and bottom: **2** + py + $AgBF_4$.

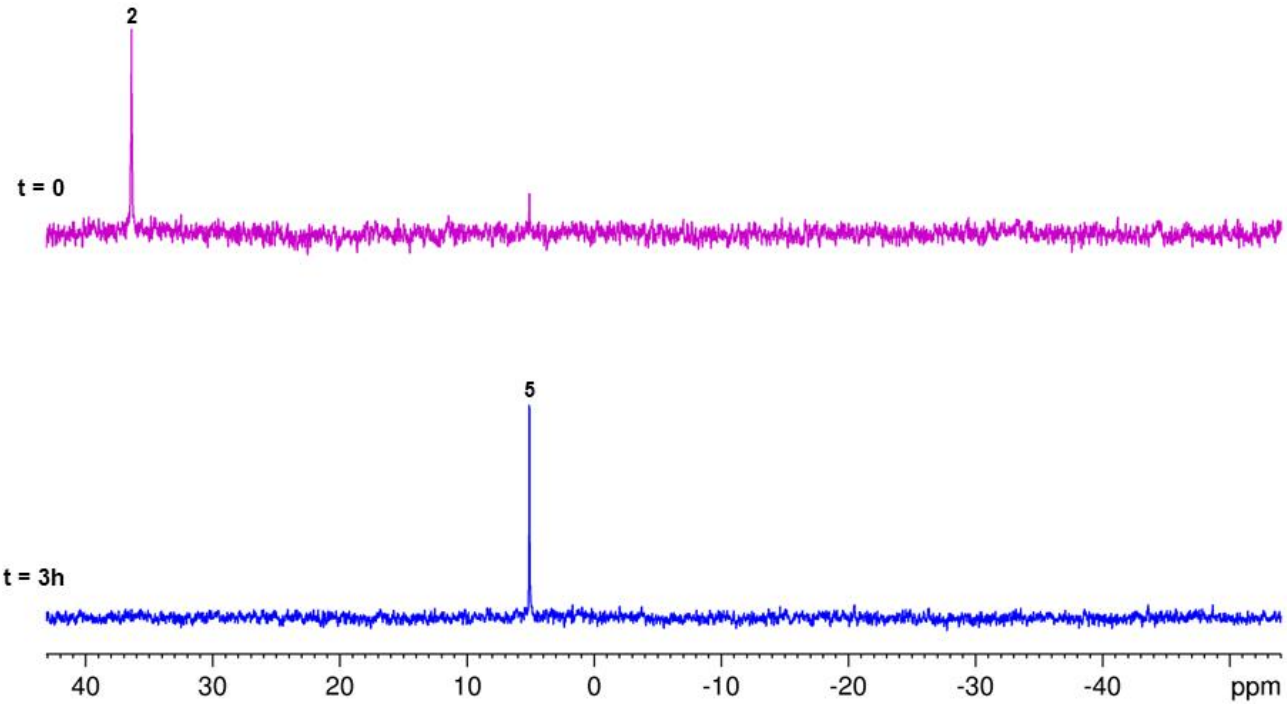


Figure S41. Stacked $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 162 MHz, 25 °C) spectra of top: **2** + py and bottom: **2** + py + $AgBF_4$.

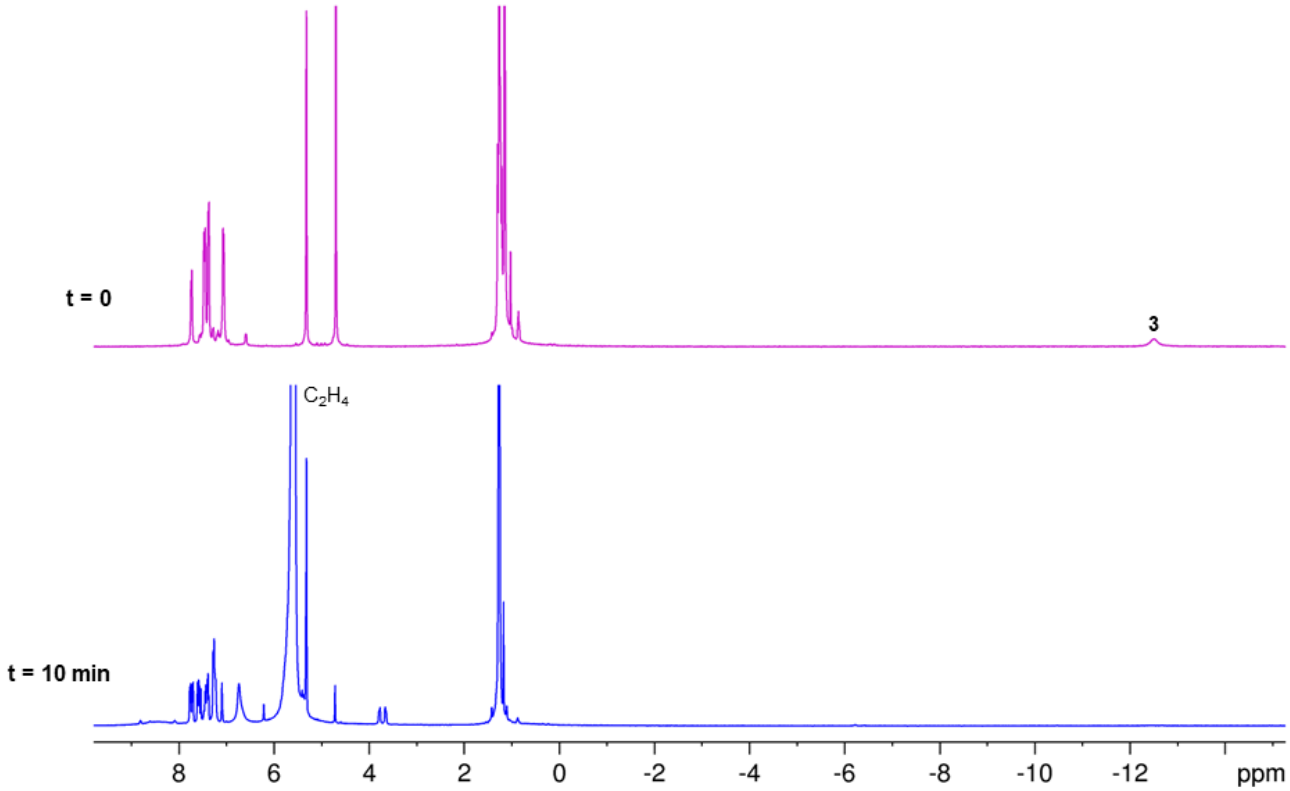


Figure S42. Stacked ^{1}H NMR (CD_2Cl_2, 400 MHz) spectra of top: **3** (0° C) and bottom: **3** + C_2H_4 (25 °C).

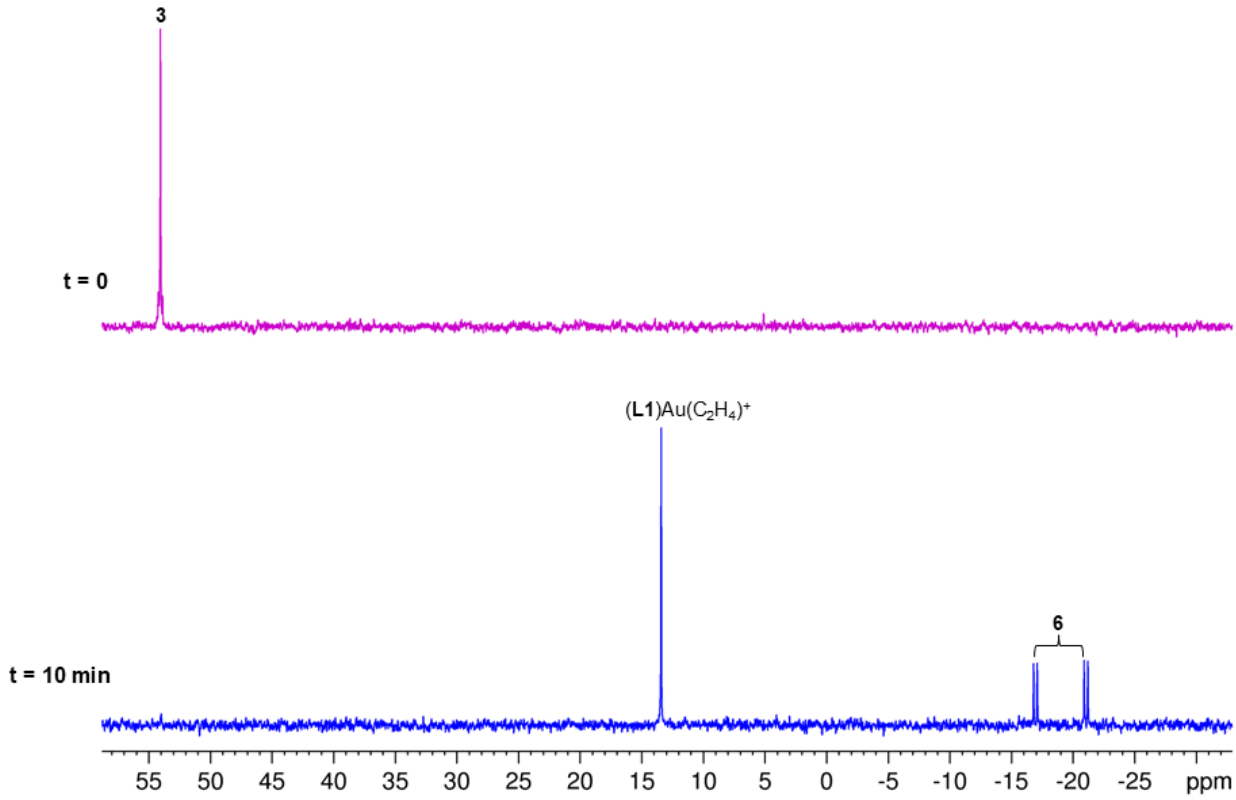


Figure S43. Stacked $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 162 MHz) spectra of top: **3** (0° C) and bottom: 3 + C_2H_4 (25 °C).

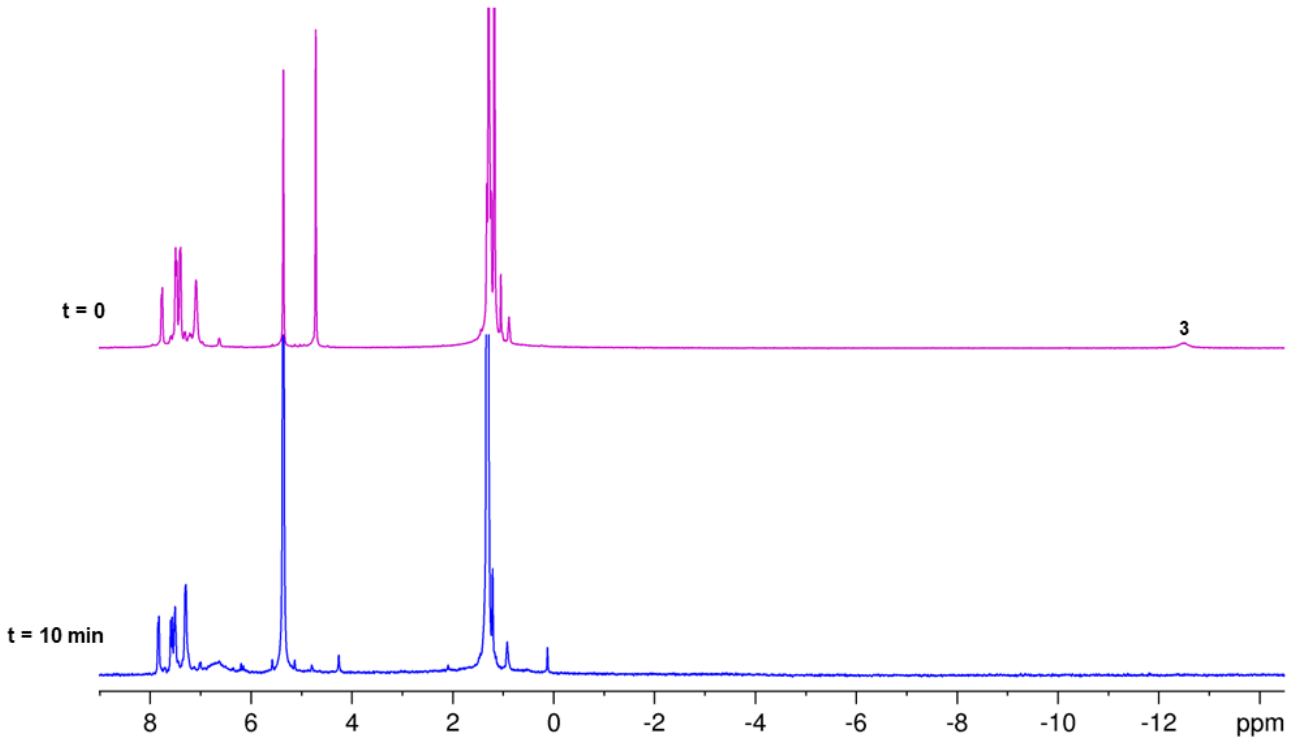


Figure S44. Stacked ^{1}H NMR (CD_2Cl_2, 400 MHz) spectra of top: **3** (0° C) and bottom: **3** + CO (25 °C).

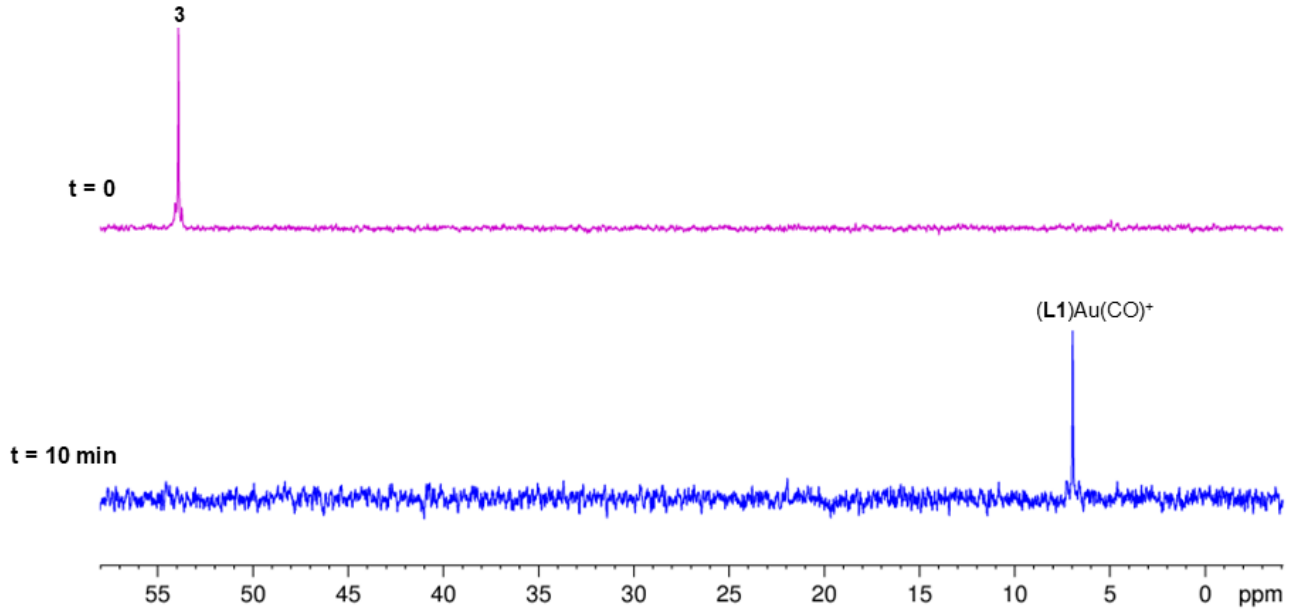


Figure S45. Stacked $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 162 MHz) spectra of top: **3** (0° C) and bottom: **3** + CO (25 °C).

5. Conformational analysis details

5.1 Computational details

Calculations were performed at the DFT level with the Gaussian 09 (Revision D.01) program.[3] The hybrid functional PBE0[4] was used throughout the computational study, and dispersion effects were accounted for by using Grimme's D3 parameter set with Becke−Johnson (BJ) damping at the optimization stage.[5] Geometry optimizations were carried out without geometry constraints, using the 6-31G(d,p)[6–8] basis set to represent the C, H, N, O and P atoms and the Stuttgart/Dresden Effective Core Potential and its associated basis set (SDD)[9] to describe the Au, Ag and W atoms. Bulk solvent effects (dichloromethane) were included at the optimization stage with the SMD continuum model.[10]

5.2 Cartesian coordinates and energies for all the species discussed in the text

3 E(RPBE1PBE) = -3832.15790932

Au	-0.229383000	0.644516000	-0.247008000
W	-3.045290000	0.961775000	-0.791895000
Ag	-2.625881000	-1.961882000	-0.220103000
P	1.984581000	0.071799000	-0.033371000
F	-2.464681000	-3.167844000	1.931506000
C	2.339659000	-1.328891000	1.092890000
C	1.656645000	-1.535878000	2.305691000
C	0.701871000	-0.589692000	2.927407000
C	-0.501341000	-1.061312000	3.473209000
H	-0.796365000	-2.094181000	3.316574000
C	-1.329633000	-0.223704000	4.208328000
H	-2.248548000	-0.637919000	4.612024000
C	-1.005977000	1.124020000	4.430484000
C	0.171283000	1.598894000	3.845216000
H	0.472085000	2.632050000	3.982599000
C	1.013631000	0.760683000	3.115393000
H	1.951539000	1.156969000	2.741382000
C	-1.886863000	1.986473000	5.333859000
C	-1.444906000	3.450616000	5.341293000
H	-0.433136000	3.572868000	5.741724000
H	-2.121508000	4.032768000	5.975469000
H	-1.471722000	3.886708000	4.335925000
C	-1.783547000	1.433823000	6.764540000
H	-2.138539000	0.399659000	6.818864000

H	-2.392193000	2.036683000	7.448109000
H	-0.747697000	1.455131000	7.120014000
C	-3.353314000	1.931006000	4.884081000
H	-3.480197000	2.371325000	3.890312000
H	-3.975676000	2.498556000	5.584818000
H	-3.739234000	0.907725000	4.853238000
C	1.939696000	-2.721855000	3.002924000
H	1.425194000	-2.905589000	3.941949000
C	2.873599000	-3.640604000	2.549734000
H	3.052524000	-4.538428000	3.134878000
C	3.594908000	-3.417310000	1.369684000
C	4.637663000	-4.422039000	0.890041000
C	5.299004000	-3.987144000	-0.419397000
H	6.040199000	-4.735411000	-0.717774000
H	5.820226000	-3.028722000	-0.315780000
H	4.573408000	-3.895872000	-1.235443000
C	3.300121000	-2.256284000	0.662281000
H	3.810668000	-2.067133000	-0.274187000
C	3.136560000	1.364028000	0.564247000
C	2.845765000	2.741497000	0.517638000
C	1.689515000	3.345316000	-0.181231000
C	1.473027000	3.167855000	-1.551558000
H	2.115480000	2.493926000	-2.113377000
C	0.486518000	3.896213000	-2.218118000
H	0.380872000	3.759752000	-3.289674000
C	-0.326922000	4.811154000	-1.541829000
C	-2.744439000	5.433753000	-1.644295000
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H	-3.500154000	6.040556000	-2.155911000
H	-2.778978000	5.686717000	-0.579677000
C	-1.409220000	5.458602000	-3.749741000
H	-0.441403000	5.647744000	-4.225860000
H	-2.138483000	6.139685000	-4.200204000
H	-1.717584000	4.438138000	-3.998277000
C	-0.977171000	7.170652000	-2.009168000
H	-0.951967000	7.420277000	-0.944122000
H	-1.709715000	7.828096000	-2.490749000
H	0.008647000	7.392113000	-2.431989000
C	-0.144109000	4.932737000	-0.156230000

H	-0.767345000	5.618689000	0.411239000
C	0.847525000	4.227186000	0.509911000
H	0.988162000	4.369987000	1.578182000
C	3.721459000	3.607473000	1.183761000
H	3.513311000	4.673614000	1.159759000
C	4.849915000	3.149417000	1.854806000
H	5.485718000	3.871701000	2.355585000
C	5.164885000	1.789039000	1.881149000
C	7.211156000	2.298211000	3.282884000
H	7.602344000	3.019017000	2.556833000
H	8.066180000	1.840080000	3.790254000
H	6.633888000	2.846292000	4.035277000
C	7.263408000	0.460191000	1.604117000
H	8.132307000	0.032717000	2.116656000
H	7.629090000	1.133438000	0.821295000
H	6.724596000	-0.362521000	1.122639000
C	5.888316000	0.226268000	3.684220000
H	5.241082000	0.728512000	4.411387000
H	6.743847000	-0.195353000	4.223437000
H	5.324330000	-0.606109000	3.250089000
C	4.287283000	0.924034000	1.225861000
H	4.492889000	-0.139984000	1.255821000
C	2.644271000	-0.482769000	-1.653094000
C	3.846367000	0.099249000	-2.063448000
H	4.313287000	0.829083000	-1.412085000
C	4.485266000	-0.216770000	-3.265906000
C	5.608068000	1.980266000	-3.652186000
H	4.868504000	2.256853000	-4.411534000
H	6.552571000	2.476686000	-3.900849000
H	5.269597000	2.374209000	-2.688250000
C	6.839850000	0.115276000	-2.520897000
H	6.521397000	0.473797000	-1.536979000
H	7.802322000	0.585208000	-2.752037000
H	6.996611000	-0.966894000	-2.454290000
C	6.353153000	-0.003649000	-4.960703000
H	6.546065000	-1.081711000	-4.974552000
H	7.300313000	0.505063000	-5.166814000
H	5.663763000	0.233207000	-5.778288000
C	3.865437000	-1.165227000	-4.075958000

H	4.313340000	-1.469969000	-5.015584000
C	2.664166000	-1.750515000	-3.690613000
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H	0.073940000	1.815420000	-4.235160000
C	2.149124000	6.154025000	-3.082885000
H	2.221888000	5.673302000	-4.063354000
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H	1.153799000	6.602878000	-2.996269000
C	2.369311000	5.926062000	-0.615680000
H	1.408879000	6.430559000	-0.464168000
H	3.148273000	6.695082000	-0.623963000
H	2.557702000	5.274733000	0.241355000
C	3.802419000	4.545821000	-2.108169000
H	4.027927000	3.862030000	-1.283166000

H	4.560299000	5.336936000	-2.102175000
H	3.896255000	4.006237000	-3.056570000
C	2.978824000	-1.360660000	-2.832310000
H	2.310355000	-2.163368000	-3.104360000
C	2.630195000	0.027626000	-2.740028000
H	1.658088000	0.451902000	-2.938320000
C	3.810467000	0.760319000	-2.418279000
H	3.876002000	1.829808000	-2.283145000
C	4.363840000	-1.468338000	-2.537234000
H	4.941911000	-2.382064000	-2.528699000
C	4.655379000	-2.279360000	0.317793000
H	5.250414000	-2.953435000	-0.282785000
C	4.023745000	-0.459187000	1.581813000
H	4.028269000	0.494585000	2.094433000
C	2.933080000	-1.373900000	1.542900000
H	1.993564000	-1.252627000	2.060546000
C	3.332998000	-2.520089000	0.777551000
H	2.741739000	-3.407871000	0.606946000
C	1.897298000	-5.448357000	-2.430201000
C	-6.212504000	-1.725197000	2.425707000
C	-5.556016000	-0.937600000	-3.729823000
B	3.289600000	3.394471000	2.302007000
C	2.406658000	5.160165000	-1.938551000
C	-4.371572000	5.562550000	0.706470000
H	-4.006238000	5.939370000	1.666776000
H	-5.148725000	6.248450000	0.351701000
H	-3.540742000	5.591057000	-0.007359000
C	-6.091186000	4.130286000	1.843530000
H	-5.761780000	4.459859000	2.833897000
H	-6.513535000	3.124227000	1.945312000
H	-6.890372000	4.803180000	1.513515000
H	1.764687000	-1.591402000	-0.794592000
H	3.239856000	0.927851000	-0.088105000
C	5.078543000	-1.006110000	0.810820000
H	6.035026000	-0.535521000	0.624590000
C	4.873370000	-0.160183000	-2.275871000
H	5.891638000	0.083524000	-2.002712000

6. Crystal data

Crystallographic details. Low-temperature diffraction data were collected on a D8 Quest APEX-III single crystal diffractometer with a Photon III detector and a IμS 3.0 microfocus X-ray source at the Instituto de Investigaciones Químicas, Sevilla. Data were collected by means of ω and φ scans using monochromatic radiation λ(Mo Kα1) = 0.71073 Å. The diffraction images collected were processed and scaled using APEX-III software. All structures were solved using SHELXT and refined against F^2 on all data by full-matrix least squares with SHELXL.[11] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). Structures **1** and **5** contain one dichloromethane and three chloroform molecules that could be located and refined. Similarly, structure **3** contains one well-behave dichloromethane molecule, but we also had to use the program SQUEEZE to compensate for the contribution of additionally disordered solvent molecules which account for three more solvent molecules in the unit cell.

A summary of the fundamental crystal and refinement data are given in Table S1 and Table S2. Atomic coordinates, anisotropic displacement parameters and bond lengths and angles can be found in the cif files, which have been deposited in the Cambridge Crystallographic Data Centre with no. 2392134-2392138. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

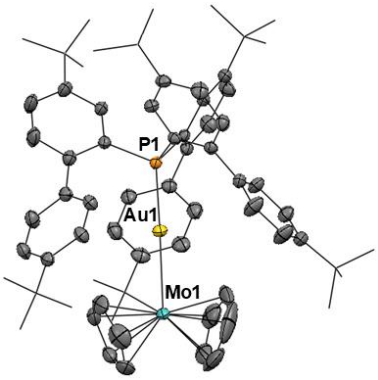

Figure S46 Molecular structure of **2**. Hydrogen atoms, solvent molecules and anion are omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond length [Å] and angles [°]: Au1-Mo1 2.7779(5), Au1-P1 2.273(1), P1-Au1-Mo1 176.67(3), $Cp_{centroid}$-Mo1-$Cp_{centroid}$ 141.87.

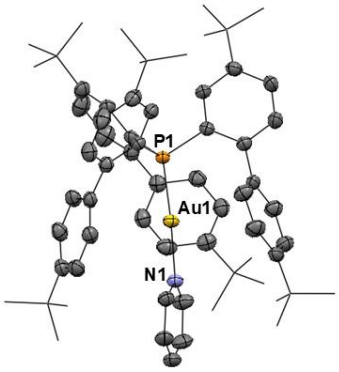

Figure S47 Molecular structure of **5**. Hydrogen atoms, solvent molecules and anion are omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond length [Å] and angles [°]: Au1-P1 2.233(1), Au1-N1 2.079(4), P1-Au1-N1 175.0(1)°.

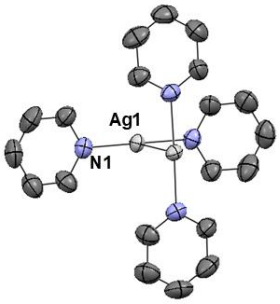

Figure S48 Molecular structure of a dimer of **[Ag(py)$_2$][SbF$_6$]**. Hydrogen atoms, solvent molecules and anion are omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond length [Å] and angles [°]: Ag1-Ag1 3.0279, Ag1-N1 2.101, N1-Ag1-N1 176.7.

Table S1. Crystal data and structure refinement for compounds **1**, **2** and **3**.

	1	**2**	**3**
formula	$C_{71}H_{87}AuBCl_2F_4PW$	$C_{71}H_{87}AuBCl_2F_4MoP$	$C_{71}H_{87}AgAuB_2Cl_2F_8PW$
Fw	1509.90	1421.99	1704.58
cryst.size, mm	0.17 × 0.17 × 0.10	0.20 × 0.18 × 0.07	0.15 × 0.12 × 0.05 mm
crystal system	Triclinic	Triclinic	Triclinic
space group	*P-1*	*P-1*	*P-1*
a, Å	12.8117(7)	12.8085(7)	13.2555(5)
b, Å	15.9264(10)	15.9405(7)	16.6165(7)
c, Å	17.4931(11)	17.4937(10)	18.5766(7)
α, deg	99.843(3)	99.952(2)	74.4560(10)
β, deg	102.329(2)	102.155(2)	85.128(2)
γ, deg	104.450(2)	104.488(2)	84.042(2)
V, Å^3	3280.5 (3)	3283.3(3)	3913.8(3)
T, K	193	193	193
Z	2	2	2
ρ_{calc}, g cm^{-3}	1.529	1.133	3.726
μ, mm^{-1} (MoKα)	4.14	2.58	2.15
F(000)	1512	1448	1688
absorption corrections	multi-scan, 0.595–0.745	multi-scan, 0.516–0.746	multi-scan, 0.489–0.746
θ range, deg	1.8-28.3	2.4-28.2	2.0-25.2
no. of rflns measd	98394	205478	126046
R_{int}	0.0794	0.0927	0.0466
no. of rflns unique	12398	14069	11676
no. of params / restraints	748 / 24	748 / 64	802 / 43
R_1 ($I > 2\sigma(I)$) [a]	0.0437	0.0428	0.0602
R_1 (all data)	0.0694	0.0564	0.0812
wR_2 ($I > 2\sigma(I)$)	0.1032	0.1037	0.1240
wR_2 (all data)	0.1251	0.1158	0.1484
Diff.Fourier.peaks min/max, eÅ^{-3}	-1.88 / 2.80	-1.82 / 2.29	-2.11/ 4.26
CCDC number	2392135	2392138	2392137

Table S2. Crystal data and structure refinement for compounds **5** and **[Ag(py)$_2$][SbF$_6$]**.

	5	**[Ag(py)$_2$][SbF$_6$]**
formula	$C_{67}H_{82}AuCl_6F_6NPSb$	$C_{20}H_{20}Ag_2F_{12}N_4Sb_2$
Fw	1577.72	1003.64
cryst.size, mm	0.14 × 0.12 × 0.04	0.19 × 0.16 × 0.14
crystal system	Triclinic	Orthorhombic
space group	*P-1*	*-I 2 2c*
a, Å	12.3268(5)	21.6055(9)
b, Å	15.5079(6)	10.8282(5)
c, Å	19.9114(8)	12.7008(5)
α, deg	104.508(2)	90
β, deg	107.310(2)	90
γ, deg	93.854(2)	90
V, Å^3	3476.4(2)	2971.3(2)
T, K	193	193
Z	2	2
ρ_{calc}, g cm^{-3}	1.507	2.244
μ, mm^{-1} (MoKα)	2.80	3.19
F(000)	1584	1888
absorption corrections	multi-scan, 0.436–0.745	multi-scan, 0.396–0.746
θ range, deg	2.0-26.5	3.1-28.3
no. of rflns measd	175234	20730
R_{int}	0.0675	0.0491
no. of rflns unique	12602	1628
no. of params / restraints	766 / 63	96 / 0
R_1 ($I > 2\sigma(I)$) [a]	0.0409	0.0469
R_1 (all data)	0.0505	0.0572
wR_2 ($I > 2\sigma(I)$)	0.1104	0.1362
wR_2 (all data)	0.1197	0.1460
Diff.Fourier.peaks min/max, eÅ^{-3}	-1.74 / 2.05	-2.01 / 2.48
CCDC number	2392136	2392134

7. References

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