Supporting Information

Versatility and Adaptative Behavior of the (P,N) Chelating Ligand MeDalphos within Gold(I) π-complexes

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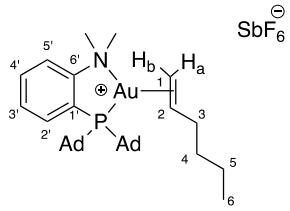
1. Synthetic procedures

General. Unless otherwise stated, all reactions and manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques or in a glovebox under an inert atmosphere. Dry, oxygen-free solvents were employed. Solution ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker Avance 300, 400 or 500 spectrometers at 298 K unless otherwise stated. Chemical shifts (δ) are expressed with a positive sign, in parts per million. ^{1}H and ^{13}C chemical shifts reported are referenced internally to residual protio (^{1}H) or deutero (^{13}C) solvent, while ^{31}P chemical shifts are relative to 85% H_3PO_4. The following abbreviations and their combinations are used: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet. The ^{1}H and ^{13}C resonance signals were attributed by means of 2D HSQC and HMBC. Mass spectra were recorded on a Waters UPLC Xevo G2 Q TOF apparatus. Melting points were determined with a calibrated Stuart SMP40 (PT1000) apparatus. Chloro-[1,2-bis(diphenylphosphino)-1,2-dicarba-closo-dodecaborane]gold(I)[S1] and MeDalphos gold(I) chloride[S2] were synthesized as reported in the literature. All other reagents were used as received from commercial suppliers.

General procedure for the preparation of gold(I) π-complexes

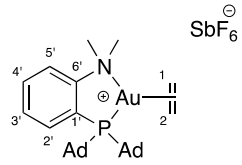
In a glovebox, a Schlenk tube was charged with silver hexafluoroantimonate (39 mg, 0.11 mmol) in dichloromethane (2 mL). MeDalphos gold(I) chloride (50 mg, 0.075 mmol) was transferred into a small glass vial and dissolved in dichloromethane (2 mL) in the presence of the olefin (0.23 mmol). The prepared solution was loaded into a plastic syringe equipped with stainless steel needle. Outside the glovebox, the Schlenk tube was cooled down to –30 ºC. At this temperature, the solution of MeDalphos gold(I) chloride and olefin was added to the $AgSbF_6$ solution. The mixture was allowed to slowly warm up to rt. Then, the mixture was filtered through a short pad of Celite and the solvents were removed under vacuum until only 1 mL of dichloromethane was left. Then Et_2O (10 mL) was added affording a solid, which was filtered, washed with Et_2O (2 x 30 mL) and dried under vacuum.

Complex 2



Complex **2** was obtained as a yellow solid following the general procedure using 1-hexene (28 µL, 0.23 mmol). Yield: 45 mg (63%). Crystals suitable for X-ray diffraction were grown by slow diffusion of pentane into a dichloromethane solution of complex **2**. **Mp**: 175–181 ºC (decomposition); **^{1}H NMR** (300 MHz, CD_2Cl_2): δ 7.83–7.76 (m, 1H, $H_{5'}$), 7.76–7.70 (m, 2H, $H_{3'}$ + $H_{4'}$), 7.56–7.47 (m, 1H, $H_{2'}$), 5.66 (m, 1H, H_2), 3.94 (dd, $^3J_{HH2}$ = 8.4 Hz, $^2J_{HH1b}$ = 6.2 Hz, 1H, H_{1a}), 3.76 (dd, $^3J_{HH2}$ = 14.7 Hz, $^2J_{HH1a}$ = 6.2 Hz, 1H, H_{1b}), 3.01 (s, 3H, NCH_3), 2.98 (s, 3H, NCH_3), 2.56 (m, 1H, H_3), 2.18 (m, 1H, H_3), 2.19–1.31 (m, 30H, H_{Ad}), 1.68 (m, 2H, H_4), 1.44 (m, 2H, H_5), 0.95 (t, $^3J_{HH5}$ = 6.5 Hz, 3H, H_6); **^{31}P{^{1}H} NMR** (121 MHz, CD_2Cl_2): δ 58.1 (s); **^{13}C{^{1}H} NMR** (75 MHz, CD_2Cl_2): δ 158.5 (d, $^2J_{CP}$ = 9.6 Hz, $C_{6'}$), 136.6 (s, $C_{5'}$), 134.7 (d, $^4J_{CP}$ = 1.4 Hz, $C_{4'}$), 128.3 (d, $^2J_{CP}$ = 5.7 Hz, $C_{2'}$), 125.5 (d, $^1J_{CP}$ = 41.5 Hz, $C_{1'}$), 125.0 (d, $^3J_{CP}$ = 4.6 Hz, $C_{3'}$), 111.1 (s, C_2), 75.2 (d, $^2J_{CP}$ = 18.9 Hz, C_1), 52.5 (s, NCH_3), 52.5 (s, NCH_3), 42.3 (d, $^2J_{CP}$ = 2.5 Hz, CH_{5Ad}), 42.2 (d, $^2J_{CP}$ = 2.5 Hz, CH_{2Ad}), 41.3 (d, $^1J_{CP}$ = 17.2 Hz, C_{qAd}), 36.5 (s, CH_{2Ad}), 35.6 (s, C_3), 32.6 (s, C_4), 29.1 (d, $^3J_{CP}$ = 10.0 Hz CH_{Ad}), 29.0 (d, $^3J_{CP}$ = 10.0 Hz CH_{Ad}), 22.8 (s, C_5), 14.2 (s, C_6).

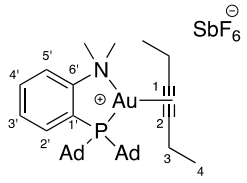
Complex 3



In a glovebox, a Schlenk was charged with silver hexafluoroantimonate (39 mg, 0.11 mmol) in dichloromethane (2 mL). MeDalphos gold(I) chloride complex (50 mg, 0.075 mmol) was transferred into a small glass vial and dissolved in dichloromethane (2 mL). The prepared solution was loaded into a plastic syringe equipped with stainless steel needle. Outside the glovebox, the Schlenk was cooled down to –30 ºC. At this temperature the solution of MeDalphos gold(I) chloride complex was added to the $AgSbF_6$ solution while bubbling ethylene. The mixture was allowed to slowly warm up to rt. Then, the mixture was filtered through a short pad of Celite and the solvents were removed under vacuum until dryness.

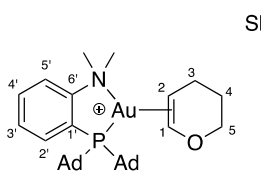
Recrystallization of the crude product with CH_2Cl_2/Pentane afforded complex **3** as a white off solid. Yield: 59 mg (89%). Crystals suitable for X-ray diffraction were grown by slow diffusion of pentane into a dichloromethane solution of complex **3**. **Mp**: 102–110 ºC (decomposition); **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.84–7.78 (m, 1H, $H_{5'}$), 7.77–7.71 (m, 2H, $H_{3'}$ + $H_{4'}$), 7.57–7.50 (m, 1H, $H_{2'}$), 4.10 (d, $^3J_{HP}$ = 2.3, 4H, H_1 + H_2), 3.14 (s, 6H, 2 x NCH_3), 2.16–1.64 (m, 30H, H_{Ad}). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2): δ 58.8 (s); **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2): δ 158.6 (d, $^2J_{CP}$ = 10.6 Hz, $C_{6'}$), 136.7 (s, $C_{5'}$), 134.8 (d, $^4J_{CP}$ = 1.5 Hz, $C_{4'}$), 128.7 (d, $^2J_{CP}$ = 5.5 Hz, $C_{2'}$), 125.7 (d, $^1J_{CP}$ = 40.7 Hz, $C_{1'}$), 124.6 (d, $^3J_{CP}$ = 4.7 Hz, $C_{3'}$), 75.1 (d, $^2J_{CP}$ = 9.8 Hz, C_1 + C_2), 53.9 (s, 2 x NCH_3), 42.2 (d, $^2J_{CP}$ = 2.6 Hz, CH_{2Ad}), 41.4 (d, $^1J_{CP}$ = 16.6 Hz, C_{qAd}), 36.5 (d, $^4J_{CP}$ = 1.5 Hz, CH_{2Ad}), 29.1 (d, $^3J_{CP}$ = 9.8 Hz, CH_{Ad}).

Complex 4



Complex **4** was obtained as a white solid following the general procedure using 3-hexyne (26 μL, 0.23 mmol). Yield: 36 mg (50%). **Mp**: 91–97 ºC (decomposition); **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 7.85–7.81 (m, 1H, $H_{5'}$), 7.76–7.72 (m, 2H, $H_{3'}$ + $H_{4'}$), 7.55–7.49 (m, 1H, $H_{2'}$), 3.02 (s, 6H, 2 x NCH_3), 2.83 (qd, $^3J_{HH4}$ = 7.3 Hz, $^4J_{HP}$ = 1.5 Hz, 4H, H_3), 2.19–1.63 (m, 30H, H_{Ad}), 1.43 (t, $^3J_{HH3}$ = 7.3 Hz, 6H, H_4); **^{31}P{^{1}H} NMR** (121 MHz, CD_2Cl_2): δ 59.4 (s); **^{13}C{^{1}H} NMR** (125 MHz, CD_2Cl_2): δ 158.9 (d, $^2J_{CP}$ = 10.0 Hz, $C_{6'}$), 136.5 (s, $C_{5'}$), 134.7 (d, $^4J_{CP}$ = 1.4 Hz, $C_{4'}$), 128.4 (d, $^2J_{CP}$ = 5.7 Hz, $C_{2'}$), 125.4 (d, $^1J_{CP}$ = 42.1 Hz, $C_{1'}$), 124.8 (d, $^3J_{CP}$ = 4.6 Hz, $C_{3'}$), 97.8 (d, $^2J_{CP}$ = 13.8 Hz, C_1 + C_2), 52.9 (s, 2 x NCH_3), 42.2 (d, $^2J_{CP}$ = 2.8 Hz, CH_{2Ad}), 40.9 (d, $^1J_{CP}$ = 17.8 Hz, C_{qAd}), 36.5 (d, $^4J_{CP}$ = 1.3 Hz, CH_{2Ad}), 29.1 (d, $^3J_{CP}$ = 9.8 Hz, CH_{Ad}), 17.6 (d, $^3J_{CP}$ = 2.7 Hz, C_3), 15.5 (d, $^4J_{CP}$ = 2.3 Hz, C_4).

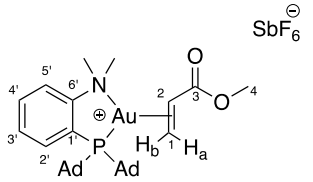
Complex 5



Complex **5** was obtained as a white solid following the general synthetic procedure using 3,4-dihydropyrane (28 μL, 0.23 mmol). Yield: 55 mg (77%). Crystals suitable for X-ray diffraction were grown by slow diffusion of pentane into a dichloromethane solution of complex **5**. **Mp**: 105–120 ºC (decomposition); **^{1}H NMR** (300 MHz, CD_2Cl_2): δ 7.81–7.77 (m, 1H, $H_{5'}$), 7.76 (d, $^3J_{HH2}$ = 4.8 Hz, 1H, H_1), 7.71–7.67 (m, 2H, $H_{3'}$ + $H_{4'}$), 7.48–7.43 (m, 1H, $H_{2'}$), 4.78 (m, 1H, H_2), 4.45 (dd, $^3J_{HH4}$ = 11.4 Hz, $^3J_{HH4}$ = 3.4 Hz, $^2J_{HH5}$ = 1.1 Hz, 1H, H_5), 4.10 (dd, $^3J_{HH4}$ = 9.1 Hz, $^3J_{HH4}$ = 2.5 Hz, 1H, H_5), 2.74 (s, 3H, NCH_3), 2.71 (s, 3H, NCH_3), 2.51 (m, 2H, H_3), 2.10 (m, 1H, H_4), 1.94 (m, 1H, H_4), 2.19–1.56 (m, 30H, H_{Ad}). **^{31}P{^{1}H} NMR** (121 MHz, CD_2Cl_2): δ 56.6 (s); **^{13}C{^{1}H} NMR** (125 MHz, CD_2Cl_2): δ 159.3 (d, $^2J_{CP}$ = 8.1 Hz, $C_{6'}$), 144.1 (s, C_1), 135.9 (s, $C_{5'}$), 134.4 (d, $^4J_{CP}$ = 1.2 Hz, $C_{4'}$), 127.3 (d, $^2J_{CP}$ = 6.4 Hz, $C_{2'}$), 126.1 (d, $^3J_{CP}$ = 4.6 Hz, $C_{3'}$), 123.2 (d, $^1J_{CP}$ = 46.3 Hz, $C_{1'}$), 76.7 (d, $^2J_{CP}$ = 19.5 Hz, C_2), 69.3 (s, C_5), 49.5 (s, NCH_3), 49.3 (s, NCH_3), 42.8 (d, $^2J_{CP}$ = 15.5 Hz, CH_{2Ad}), 42.7 (d, $^2J_{CP}$ = 15.5 Hz, CH_{2Ad}), 42.2 (d, $^1J_{CP}$ = 20.0 Hz, C_{qAd}), 41.8 (d, $^1J_{CP}$ = 20.0 Hz, C_{qAd}), 36.7 (d, $^4J_{CP}$ = 1.3 Hz, CH_{2Ad}), 36.6 (d, $^4J_{CP}$ =

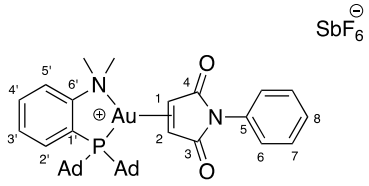
1.3 Hz, CH_{2Ad}), 29.2 (d, $^3J_{CP}$ = 9.7 Hz, CH_{Ad}), 29.1 (d, $^3J_{CP}$ = 9.7 Hz, CH_{Ad}), 21.7 (s, C_4), 21.3 (d, $^3J_{CP}$ = 2.3 Hz, C_3).

Complex 6



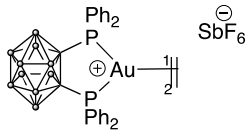
Complex **6** was obtained as a white solid following the general synthetic procedure using methyl acrylate (20 μL, 0.23 mmol). Yield: 48 mg (68%). Crystals suitable for X-ray diffraction were grown by slow diffusion of pentane into a CH_2Cl_2 solution of complex **6**. **Mp**: 165–175 ºC (decomposition); **^{1}H NMR** (300 MHz, CD_2Cl_2): δ 7.85–7.73 (m, 3H, $H_{5'}$ + $H_{3'}$ + $H_{4'}$), 7.63–7.53 (m, 1H, $H_{2'}$), 4.61 (d, $^3J_{HH2}$ = 12.7 Hz, 1H, H_{1b}), 4.35 (d, $^3J_{HH2}$ = 8.4 Hz, 1H, H_{1a}), 4.23 (m, 1H, H_2), 3.80 (s, 3H, H_4), 3.25 (s, 3H, NCH_3), 3.07 (s, 3H, NCH_3), 2.19–1.58 (m, 30H, H_{Ad}). **^{31}P{^{1}H} NMR** (121 MHz, CD_2Cl_2): δ 63.2 (s); **^{13}C{^{1}H} NMR** (75 MHz, CD_2Cl_2): δ 167.5 (d, $^3J_{CP}$ = 4.1 Hz, C_3), 158.6 (d, $^2J_{CP}$ = 10.5 Hz, $C_{6'}$), 136.6 (s, $C_{5'}$), 135.3 (d, $^4J_{CP}$ = 1.5 Hz, $C_{4'}$), 129.3 (d, $^2J_{CP}$ = 5.9 Hz, $C_{2'}$), 124.8 (d, $^1J_{CP}$ = 41.2 Hz, $C_{1'}$), 124.4 (d, $^3J_{CP}$ = 5.0 Hz, $C_{3'}$), 72.5 (d, $^2J_{CP}$ = 18.3 Hz, C_2), 68.4 (s, C_1), 54.9 (s, NCH_3), 53.8 (s, NCH_3), 52.8 (s, C_4), 42.1 (d, $^2J_{CP}$ = 5.2 Hz, CH_{2Ad}), 42.1 (d, $^2J_{CP}$ = 5.2 Hz, CH_{2Ad}), 41.8 (d, $^1J_{CP}$ = 16.4 Hz, C_{qAd}), 41.6 (d, $^1J_{CP}$ = 16.4 Hz, C_{qAd}), 36.4 (d, $^4J_{CP}$ = 1.3 Hz, CH_{2Ad}), 36.4 (d, $^4J_{CP}$ = 1.3 Hz, CH_{2Ad}), 29.1 (d, $^3J_{CP}$ = 9.9 Hz, CH_{Ad}).

Complex 7



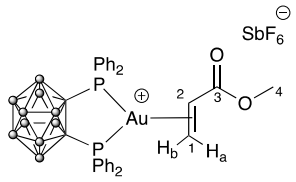
Synthesis of complex **7** was performed following the general procedure using N-Phenylmaleimide (39 mg, 0.23 mmol). Isolation of the complex **7** was not possible due to decomposition and therefore NMR characterization was recorded in a presence of excess of N-phenylmaleimide to prevent its decomposition. Crystals suitable for X-ray diffraction were grown by layering pentane into a crude dichloromethane solution of complex **7** in the presence of excess of N-phenylmaleimide. **^{1}H NMR** (500 MHz, CD_2Cl_2): δ 7.85–7.79 (m, 3H, $H_{5'}$ + $H_{3'}$ + $H_{4'}$), 7.63–7.60 (m, 1H, $H_{2'}$), 7.54–7.41 (m, 3H, H_5 + H_7), 7.17–7.14 (m, 2H, H_5), 5.67 (t, $^3J_{HH1}$ = 4.9 Hz, $^3J_{HP}$ = 4.9 Hz, 1H, H_2), 4.68 (dd, $^3J_{HP}$ = 9.7 Hz, $^3J_{HP}$ = 4.9 Hz, 1H, H_1), 3.44 (s, 3H, NCH_3), 3.34 (s, 3H, NCH_3), 2.22–1.39 (m, 30H, H_{Ad}). **^{31}P{^{1}H} NMR** (121 MHz, CD_2Cl_2): δ 65.3 (s); **^{13}C{^{1}H} NMR** (125 MHz, CD_2Cl_2): δ 170.1 (d, $^3J_{CP}$ = 5.1 Hz, C_3), 169.8 (s, C_4), 158.7 (d, $^2J_{CP}$ = 10.3 Hz, $C_{6'}$), 136.8 (s, $C_{5'}$), 135.8 (d, $^4J_{CP}$ = 1.5 Hz, $C_{4'}$), 131.5 (s, C_5), 130.2 (s, C_6), 129.9 (d, $^2J_{CP}$ = 5.8 Hz, $C_{2'}$), 129.5 (s, C_8), 126.1 (s, C_7), 124.3 (d, $^3J_{CP}$ = 5.3 Hz, $C_{3'}$), 123.9 (d, $^1J_{CP}$ = 41.6 Hz, $C_{1'}$), 72.4 (d, $^2J_{CP}$ = 4.2 Hz, C_2), 68.8 (d, $^2J_{CP}$ = 30.1 Hz, C_1), 56.5 (s, NCH_3), 54.9 (s, NCH_3), 43.0 (d, $^1J_{CP}$ = 16.8 Hz, C_{qAd}), 42.5 (d, $^1J_{CP}$ = 16.0 Hz, C_{qAd}), 42.1 (br, CH_{2Ad}), 41.5 (br, CH_{2Ad}), 36.2 (s, CH_{2Ad}), 35.9 (s, CH_{2Ad}), 29.1 (d, $^3J_{CP}$ = 10.2 Hz, CH_{Ad}), 28.7 (d, $^3J_{CP}$ = 10.2 Hz, CH_{Ad})

Complex 9



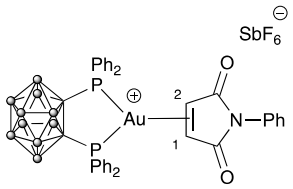
In a glovebox, a Schlenk was charged with silver hexafluoroantimonate (39 mg, 0.11 mmol) in dichloromethane (2 mL). Chloro-[1,2- bis(diphenylphosphino)-1,2-dicarba-closo-dodecaborane]gold(I) (60 mg, 0.075 mmol) was transferred into a small glass vial and dissolved in dichloromethane (2 mL). The prepared solution was loaded into a plastic syringe equipped with stainless steel needle. Outside the glovebox, the Schlenk was cooled down to –30 ºC. At this temperature the solution of Chloro-[1,2-bis(diphenylphosphino)-1,2-dicarba-closo-dodecaborane]gold(I) complex was added to the $AgSbF_6$ solution while bubbling ethylene. The mixture was allowed to slowly warm up to rt. Then, the mixture was filtered through a short pad of Celite and the solvents were removed under vacuum until dryness. Recrystallization of the crude product with CH_2Cl_2/Pentane afforded complex **9** as a yellowish solid. Yield: 65 mg (84%). Crystals suitable for X-ray diffraction were grown by slow diffusion of pentane into a dichloromethane solution of complex **8**. **Mp**: 102–110 ºC (decomposition); **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.90–7.80 (m, 8H, H_{Ar}), 7.70–7.65 (m, 4H, H_{Ar}), 7.62–7.57 (m, 8H, H_{Ar}), 4.47 (bs, 4H, H_1 + H_2), 3.09–1.27 (br, 10H, H_{BH}). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2): δ 55.4 (s); **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2): δ 135.4 (t, $^3J_{CP}$ = 9.7 Hz, C_{Ar}), 134.8 (s, C_{Ar}), 130.6 (t, $^3J_{CP}$ = 6.4 Hz, C_{Ar}), 125.7 (t, $^1J_{CP}$ = 24.0 Hz, C_{Ar}), 86.8 (pseudo t, $^1J_{CP}$ = 5.2 Hz, C_{CB}), 74.0 (t, $^2J_{CP}$ = 5.6 Hz, C_1 + C_2).

Complex 11



In a glovebox, a Schlenk was charged with silver hexafluoroantimonate (39 mg, 0.11 mmol) in dichloromethane (2 mL). Chloro-[1,2-bis(diphenylphosphino)-1,2-dicarba-closo-dodecaborane]gold(I) (60 mg, 0.075 mmol) was transferred into a small glass vial and dissolved in dichloromethane (2 mL) in the presence of methylacrylate (20 mg, 0.23 mmol). The prepared solution was loaded into a plastic syringe equipped with stainless steel needle. Outside the glovebox, the Schlenk was cooled down to –30 ºC. At this temperature the solution of Chloro-[1,2-bis(diphenylphosphino)-1,2-dicarba-closo-dodecaborane]gold(I) complex was added to the $AgSbF_6$ solution. The mixture was allowed to slowly warm up to rt. Isolation of the complex complex **11** was not possible due to decomposition and therefore NMR characterization was recorded in a presence of excess of methylacrylate to prevent its decomposition. **^{1}H NMR** (300 MHz, CD_2Cl_2): δ 7.98–7.79 (m, 6H, H_{Ar}), 7.77–7.50 (m, 14H, H_{Ar}), 5.20 (m, 1H, H_{1b}), 4.65–4.49 (m, 2H, H_{1b}+H_2), 3.53 (s, 3H, H_4), 3.10–1.25 (br, 10H, H_{BH}). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2): δ 58.7(s).

Complex 12

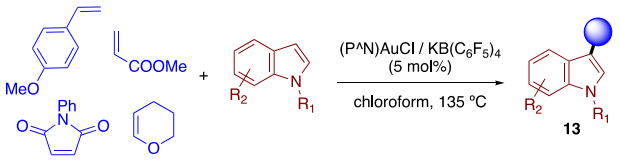


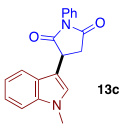
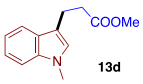
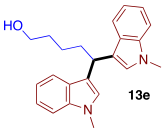
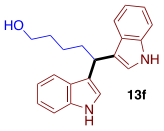
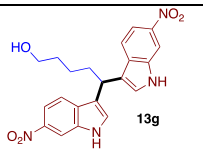
Complex **12** was prepared following the same synthetic procedure as complex **11** but using *N*-Phenylmaleimide (39 mg, 0.23 mmol). Isolation of the complex complex **12** was not possible due to decomposition and therefore NMR characterization was recorded in a presence of excess of *N*-Phenylmaleimide to prevent its decomposition. **^{1}H NMR** (300 MHz, CD_2Cl_2): δ 7.96–7.89 (m, 3H, H_{Ar}), 7.85–7.40 (m, 20H, H_{Ar}), 7.03 (dd, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 1.9 Hz, 2H, H_{Ar}), 5.71 (d, $^{3}J_{HP}$ = 2.2 Hz 2H, H_1 + H_2), 3.25–1.50 (br, 10H, H_{BH}). **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2): δ 58.7(s).

2. Catalytic experiments

General procedure for the hydroarylation of alkenes with methylindole and indoles: catalytic reactions were carried out under Ar atmosphere. MeDalphos gold(I) chloride (6 mg, 0.01 mmol, 5 mol%) and potassium tetrakis(pentafluorophenyl)borate (7 mg, 0.01 mmol, 5 mol%) were placed in a pressure NMR tube. A solution of methylindole or indole (0.04 mmol) and alkene (0.02 mmol) in 0.5 mL of $CDCl_3$ was then added to the pressure NMR tube and the reaction was set at 135 ºC.

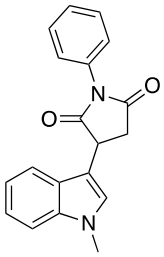
Table S1 Hydroarylation of different alkenes by indoles catalysed by the (P^N)AuCl complex.



Time (h)	 13c	 13d	 13e	 13f	 13g
1		15	30	54	
2	10	28	64	99 (60)	
3			80		
4		47	99 (80)		
6		60			
8	30	65			
16					99 (43)
24	40 (33)	75			

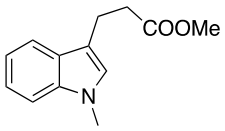
[a]Conversions determined by ^{1}H NMR spectroscopy; in brackets, yields determined after purification by SiO_2 column chromatography. [b]Control reactions were performed using same conditions in the presence of $KB(C_6F_5)_4$ without MeDalphos gold(I) chloride complex showing conversions of <5% in all cases. See ref [S3] for the hydroarylation of 4-vinylanisole by indoles.

Compound 13c



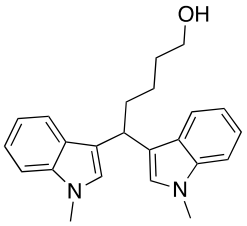
Following the general procedure from methylindole (50 μL, 0.04 mmol) and N-methylmaleimide (35 mg, 0.02 mmol). Crude product was purified by column chromatography (SiO_2; Pentane/EtOAc 4:1). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.57–7.10 (m, 1H, H_{Ar}), 4.47 (ddd, $^3J_{HH}$ = 9.6, 5.2 Hz, $^4J_{HH4}$ = 0.7 Hz 1H, CH), 3.79 (s, 3H, NCH_3), 3.43 (dd, $^2J_{HH}$ = 18.4 Hz, $^3J_{HH}$ = 9.6 Hz, 1H, CH_2), 3.07 (dd, $^2J_{HH}$ = 18.4 Hz, $^3J_{HH}$ = 5.2 Hz, 1H, CH_2); **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2): δ 177.8 (s, CO), 175.8 (s, CO), 138.0 (s, C_{Ar}), 133.0 (s, C_{Ar}), 129.7 (s, CH_{Ar}), 129.2 (s, CH_{Ar}), 127.6 (s, CH_{Ar}), 127.3 (s, CH_{Ar}), 126.7 138.0 (s, C_{Ar}), 122.7 (s, CH_{Ar}), 120.1 (s, CH_{Ar}), 119.1 (s, CH_{Ar}), 110.5 (s, C_{Ar}), 110.4 (s, CH_{Ar}), 39.0 (s, NCH_3), 37.4 (s, CH_2), 33.3 (s, CH). **HR-MS:** m/z calculated for $C_{19}H_{17}N_2O_2$ $[M+H]^+$ = 305.1290; found, 305.1283.

Compound 13d



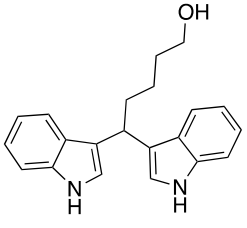
Following the general procedure from methylindole (50 μL, 0.04 mmol) and methyl acrylate (18 μL, 0.02 mmol). Crude product was purified by column chromatography (SiO_2; Pentane/EtOAc 4:1). Analytical data are consistent with those previously reported in the literature.[S4] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 (dt, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, CH_{Ar}), 7.32–7.22 (m, 2H, CH_{Ar}), 7.20–7.12 (m, 1H, CH_{Ar}), 6.89 (s, 1H, CH_{Ar}), 3.74 (s, 3H, NCH_3) 3.71 (s, 3H, OCH_3) 3.14 (t, $^3J_{HH}$ = 7.4 Hz, 2H, CH_2), 2.75 (t, $^3J_{HH}$ = 7.7 Hz, 2H, CH_2).

Compound 13e



Following the general procedure from methylindole (50 μL, 0.04 mmol) and 3,4-dihydro-2*H*-pyrane (18 μL, 0.02 mmol). Crude product was purified by column chromatography (SiO_2; Pentane/EtOAc 2:1). Analytical data are consistent with those previously reported in the literature.[S5] **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.57 (d, $^3J_{HH}$ = 8.0 Hz, 2H, CH_{Ar}), 7.28 (d, $^3J_{HH}$ = 8.3 Hz, 2H, CH_{Ar}), 7.16 (d, $^3J_{HH}$ = 7.6 Hz, 2H, CH_{Ar}), 7.00 (d, $^3J_{HH}$ = 8.0 Hz, 2H, CH_{Ar}), 6.94 (s, 2H, CH_{Ar}), 4.47 (t, $^3J_{HH}$ = 7.5 Hz, 1H, CH), 3.73 (s, 3H, NCH_3) 3.57 (t, $^3J_{HH}$ = 6.6 Hz, 2H, CH_2), 2.27–2.20 (m, 2H, CH_2), 1.65–1.57 (m, 2H, CH_2), 1.50–1.41 (m, 2H, CH_2).

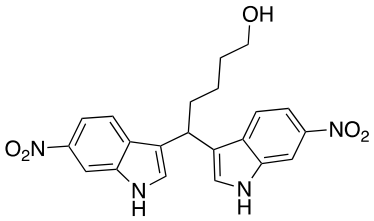
Compound 13f



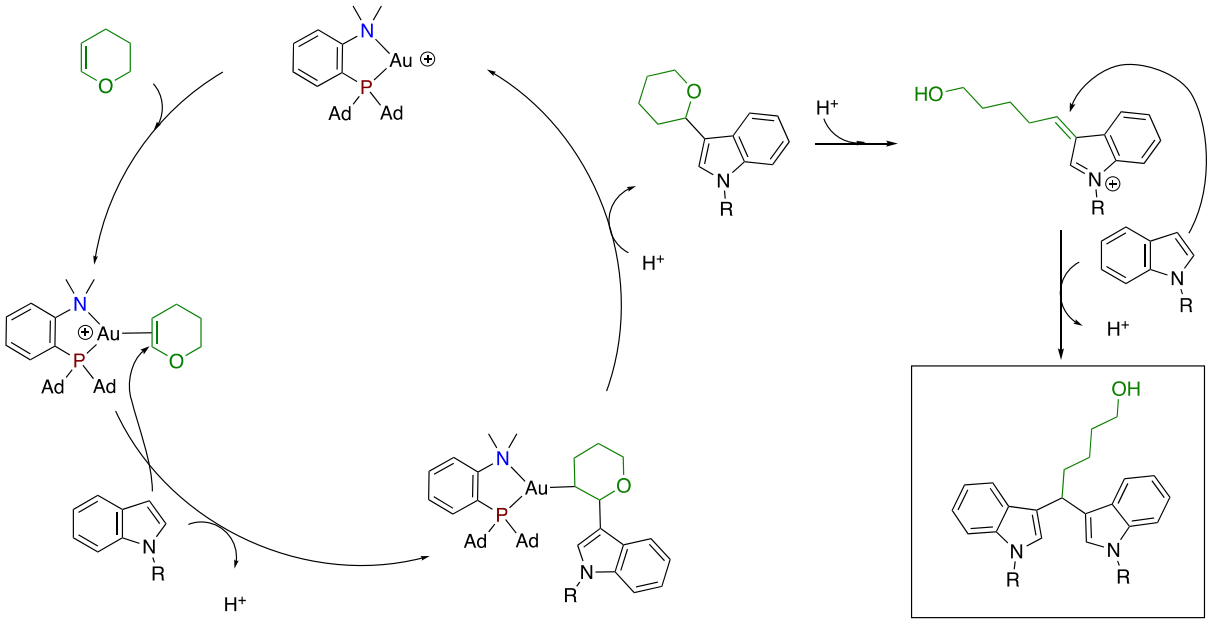
Following the general procedure from indole (57 mg, 0.04 mmol) and 3,4-dihydro-2*H*-pyrane (18 μL, 0.02 mmol). Crude product was purified by column chromatography (SiO_2; Pentane/EtOAc 2:1). Analytical data are consistent with those previously reported in the literature.[S5] **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 8.15 (bs, 1H, NH), 7.54 (d, $^3J_{HH}$ = 8.0 Hz, 2H, CH_{Ar}), 7.33 (d, $^3J_{HH}$ = 8.1 Hz, 2H, CH_{Ar}), 7.16–7.04 (m, 4H, CH_{Ar}), 6.98 (t, $^3J_{HH}$ = 8.0 Hz, 2H, CH_{Ar}), 6.94 (s, 2H, CH_{Ar}), 4.47 (t, $^3J_{HH}$ =

7.5 Hz, 1H, CH), 3.73 (s, 3H, NCH_3) 3.56 (t, $^3J_{HH}$ = 6.5 Hz, 2H, CH_2), 2.33–2.15 (m, 2H, CH_2), 1.70–1.54 (m, 2H, CH_2), 1.50–1.38 (m, 2H, CH_2).

Compound 13g



Following the general procedure from 6-nitroindole (65 mg, 0.04 mmol) and 3,4-dihydro-2*H*-pyrane (18 μL, 0.02 mmol). Crude product was purified by column chromatography (SiO_2; Cyclohexane/EtOAc 1:1). Crystals suitable for X-ray diffraction were grown by slow diffusion of pentane into a dichloromethane solution of complex **13g**. **^{1}H NMR** (400 MHz, CD_3CN): δ 9.75 (bs, 2H, NH), 8.32 (dd, $^4J_{HH}$ = 2.1, 0.5 Hz, CH_{Ar}), 7.80 (dd, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 2.1 Hz, 2H, CH_{Ar}), 7.60–7.48 (m, 4H, CH_{Ar}), 4.52 (t, $^3J_{HH}$ = 7.6 Hz, 1H, CH), 3.44 (q, $^3J_{HH}$ = 6.0 Hz, 2H, CH_2), 2.24 (q, $^3J_{HH}$ = 7.7 Hz, 2H, CH_2), 1.59–1.47 (m, 2H, CH_2), 1.43–1.31 (m, 2H, CH_2); **^{13}C{^{1}H} NMR** (100 MHz, CD_3CN): δ 169.0 (s, C_{Ar}), 143.8 (s, C_{Ar}), 136.0 (s, C_{Ar}), 129.6 (s, CH_{Ar}), 121.2 (s, C_{Ar}), 120.0 (s, CH_{Ar}), 114.8(s, CH_{Ar}), 109.3 (s, CH_{Ar}), 62.5 (s, CH_2), 35.7(s, CH_2), 34.4 (s, CH), 33.4 (s, CH_2), 25.3 (s, CH_2). **HR-MS:** m/z calculated for $C_{21}H_{19}N_4O_5$ $[M–H]^-$ = 407.1355; found, 401.1358.



Scheme S1. Proposed mechanism for the gold(I)-catalyzed hydroarylation of 3,4-dihydropyrane by indoles, followed by ring-opening of the first-formed tetrahydropyrane by addition of a second molecule of indole.[S6]

3. NMR spectra of all new compounds

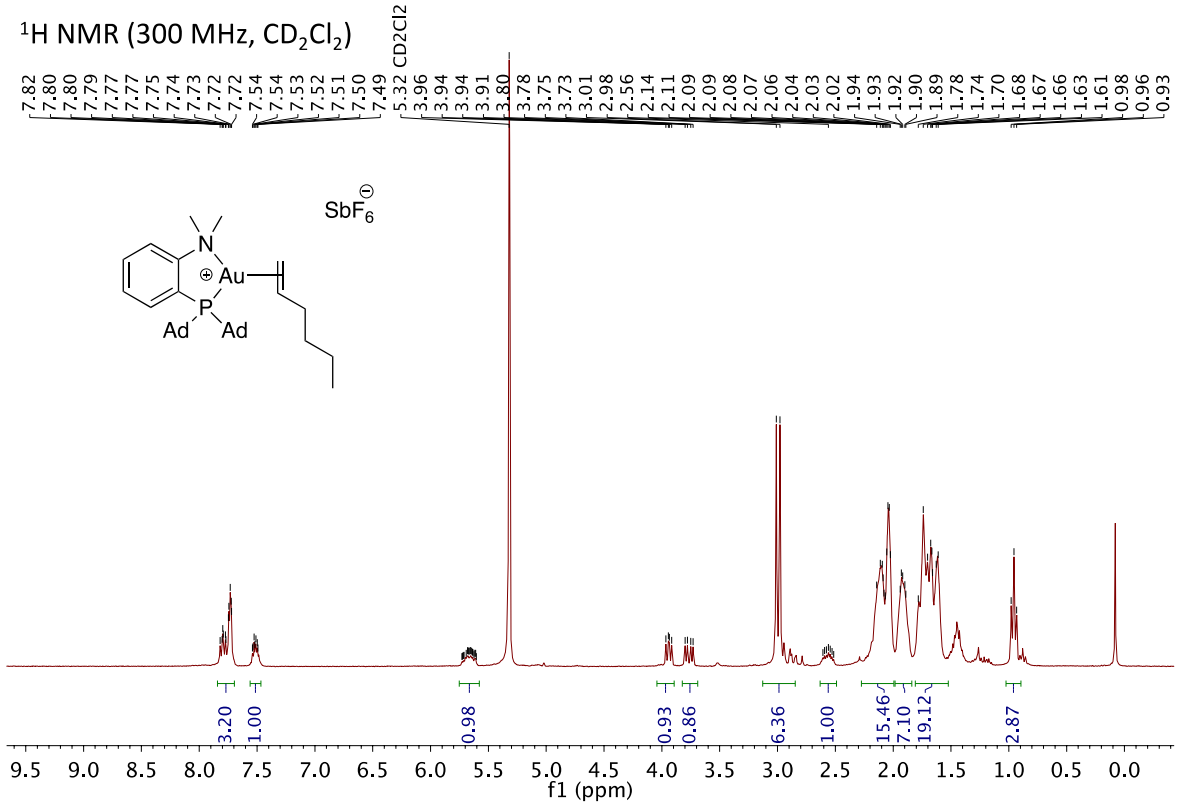


Figure S1. ^{1}H NMR of complex **2**.

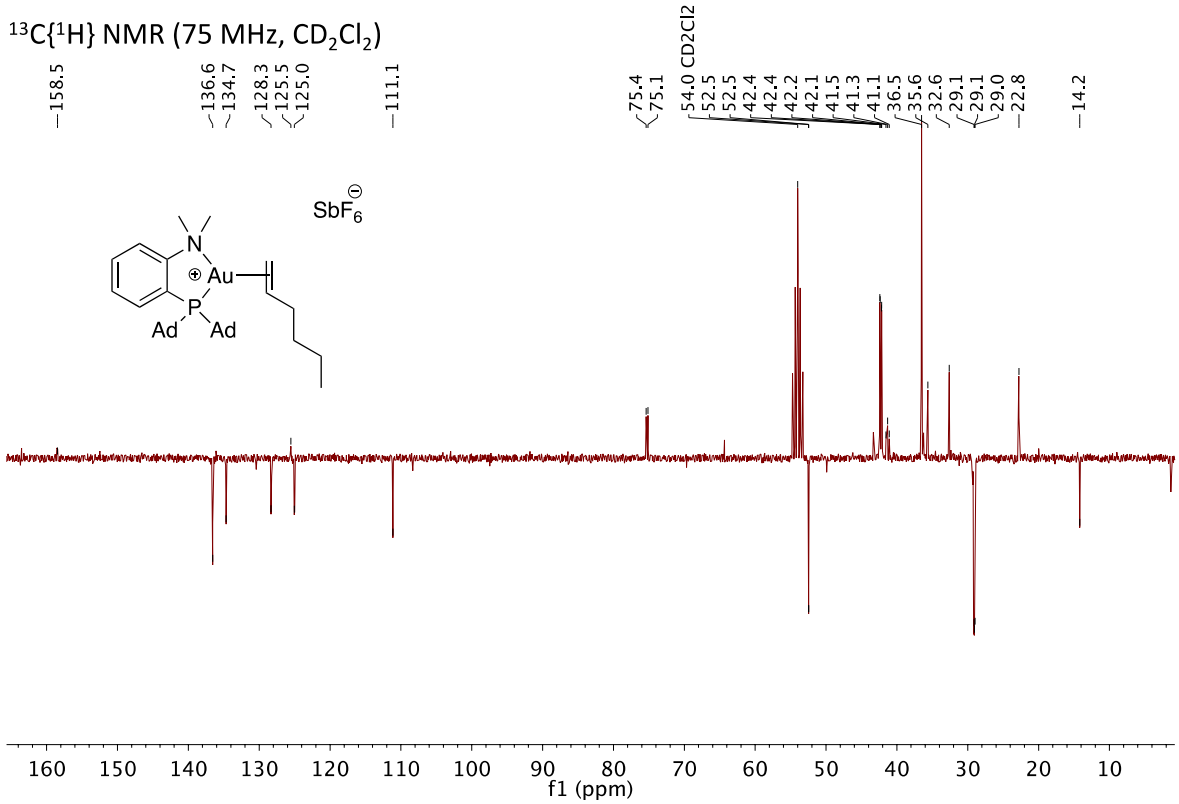


Figure S2. ^{13}C{^{1}H} NMR spectrum of complex **2**.

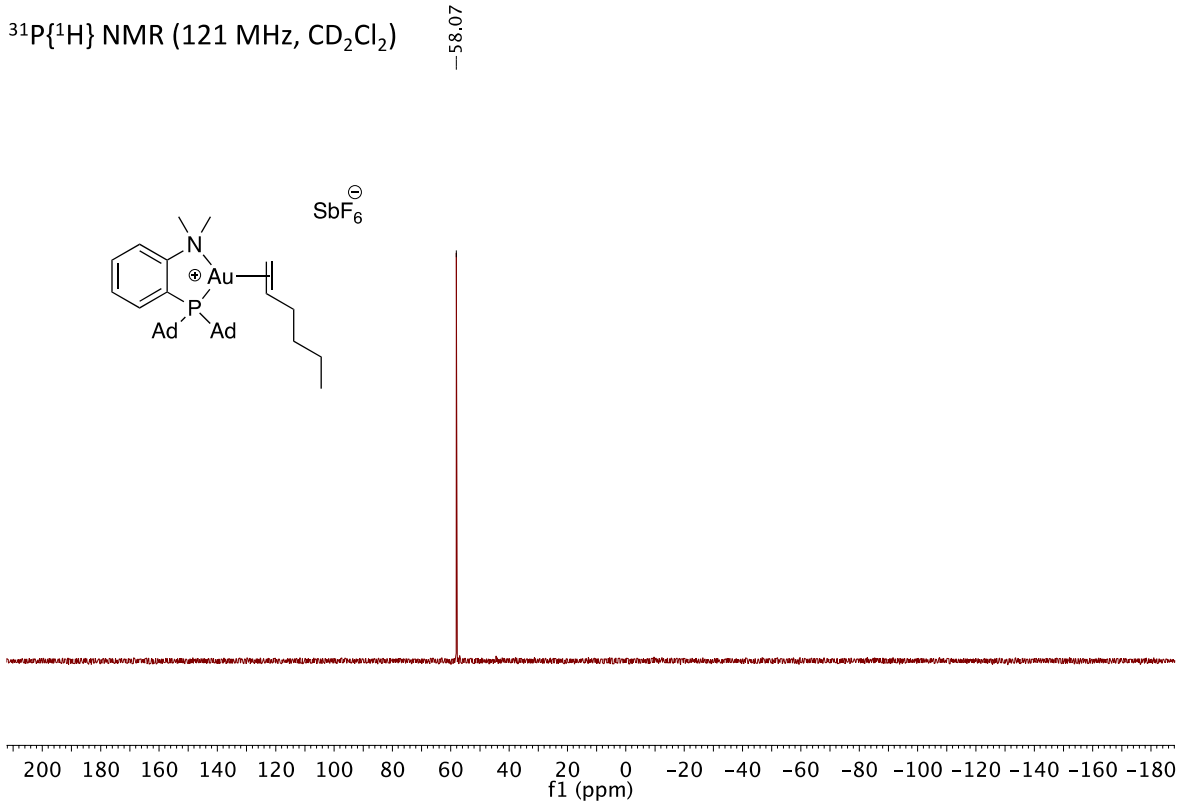


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of complex **2**.

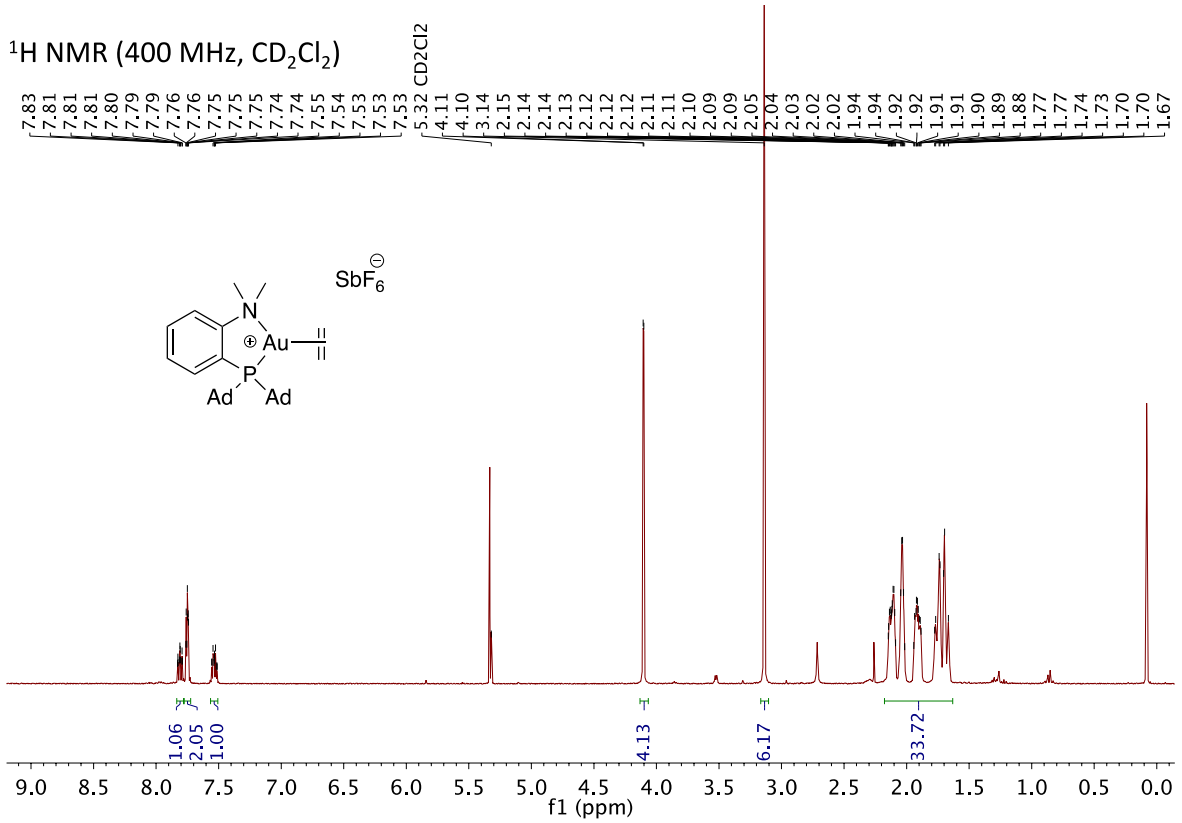


Figure S4. ^{1}H NMR spectrum of complex **3**.

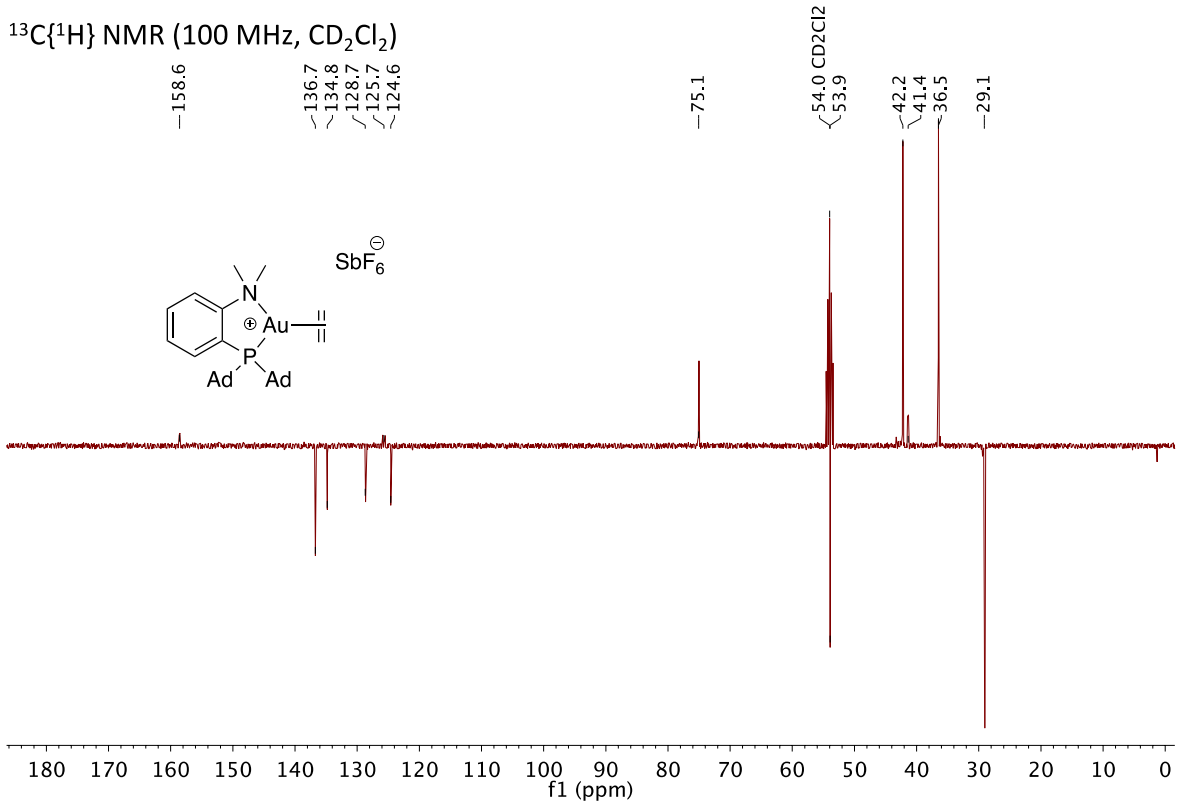


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of complex **3**.

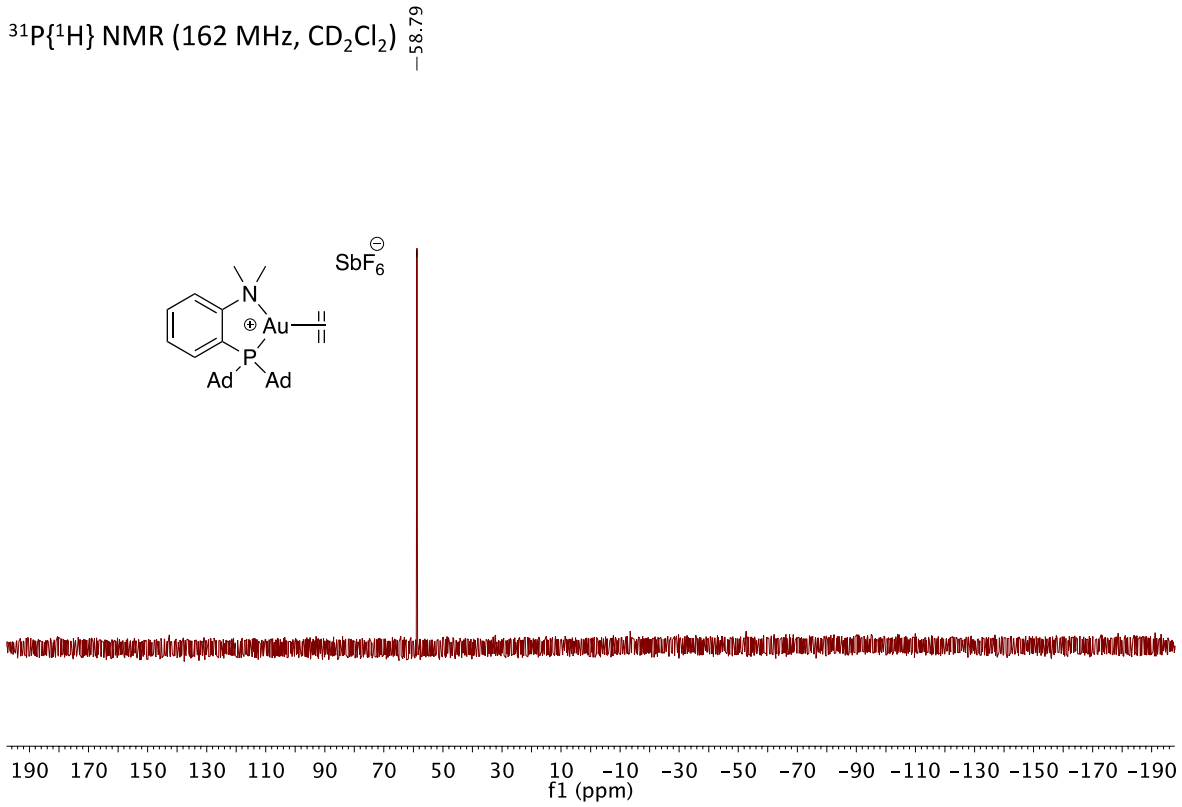


Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of complex **3**.

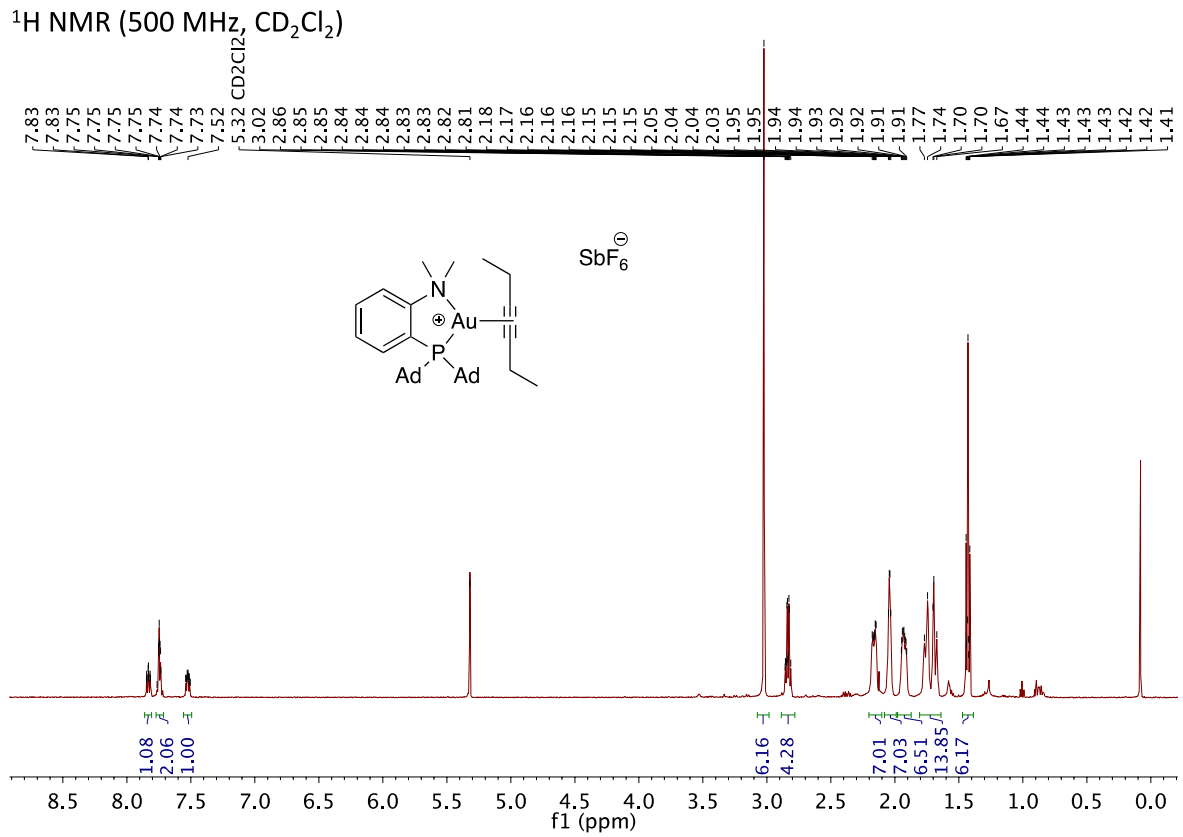


Figure S7. ^{1}H NMR spectrum of complex **4**.

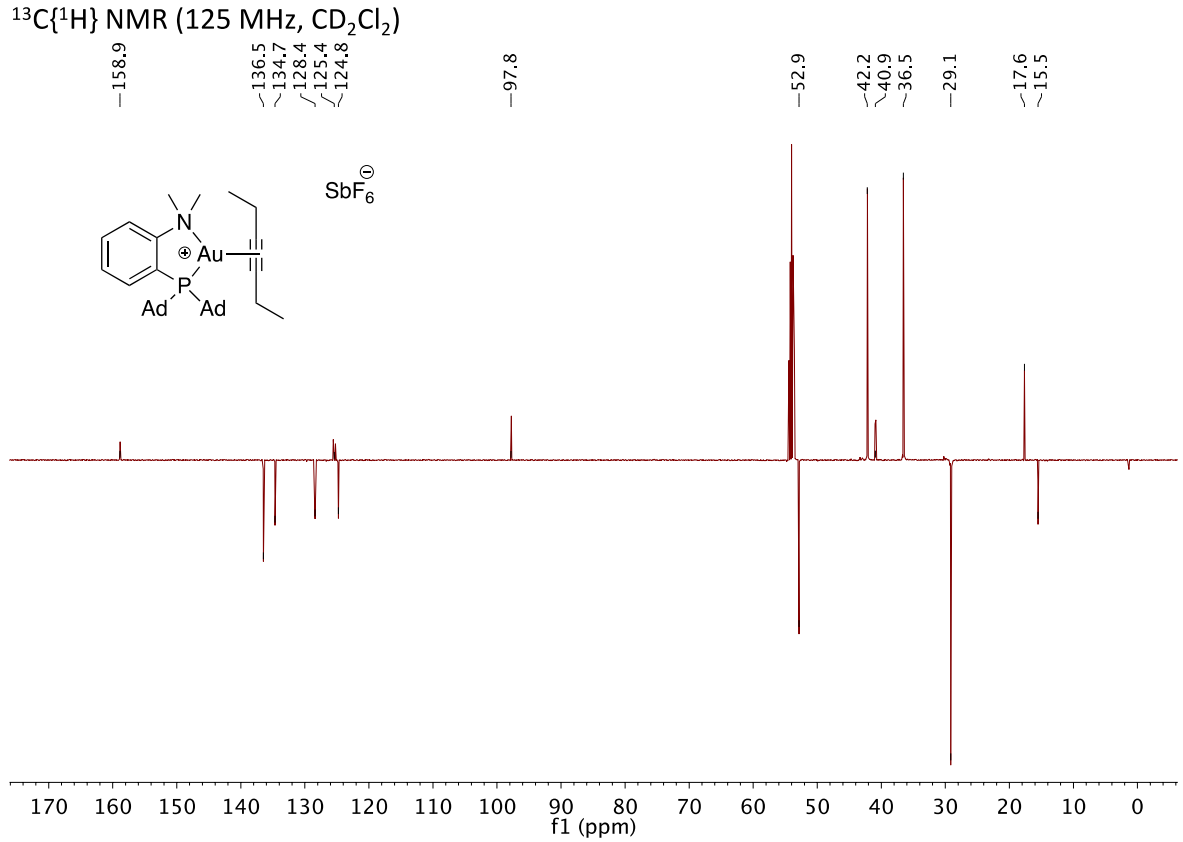


Figure S8. ^{13}C{^{1}H} NMR spectrum of complex **4**.

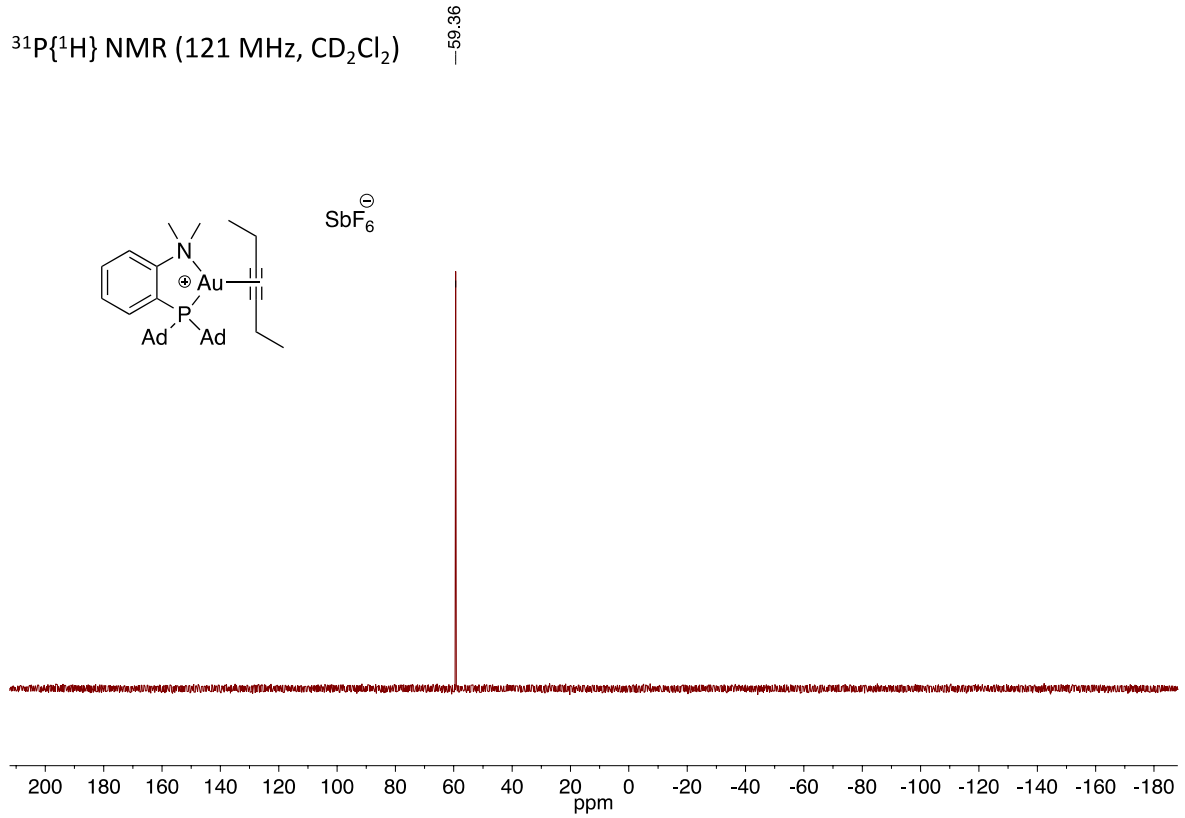


Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of complex **4**.

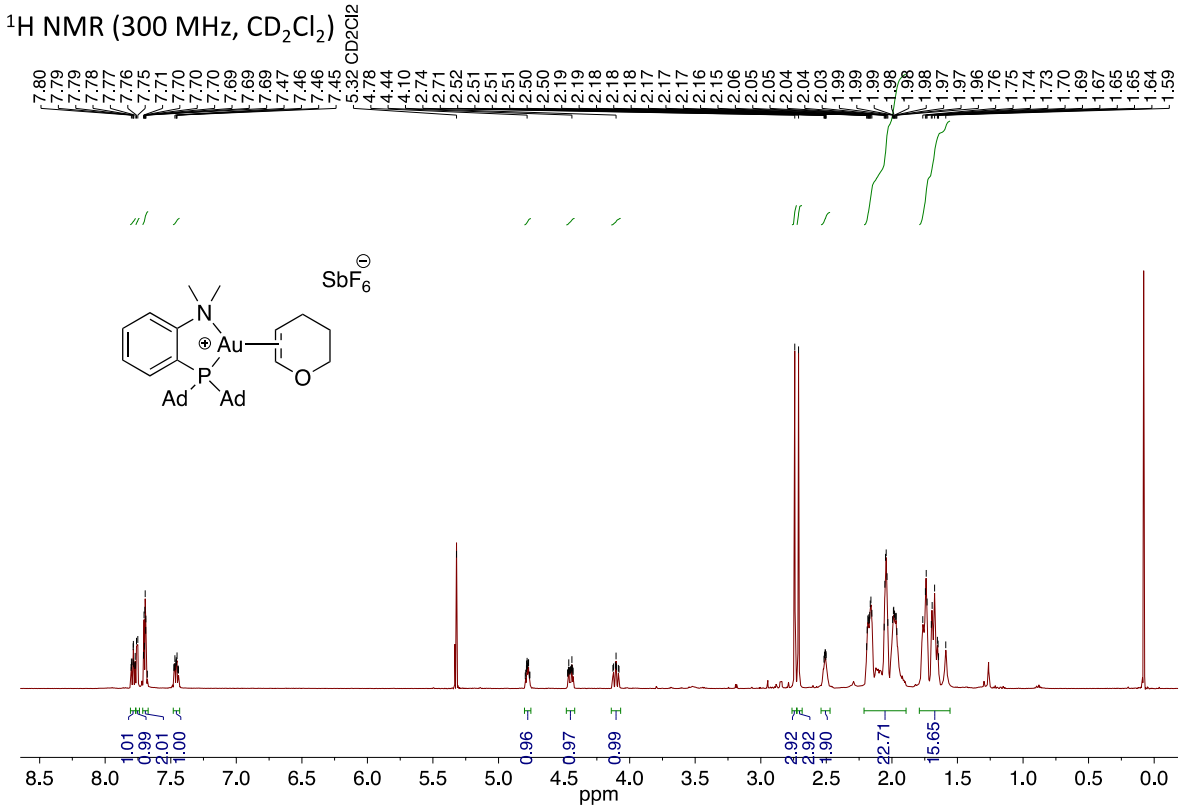


Figure S10. ^{1}H NMR spectrum of complex **5**.

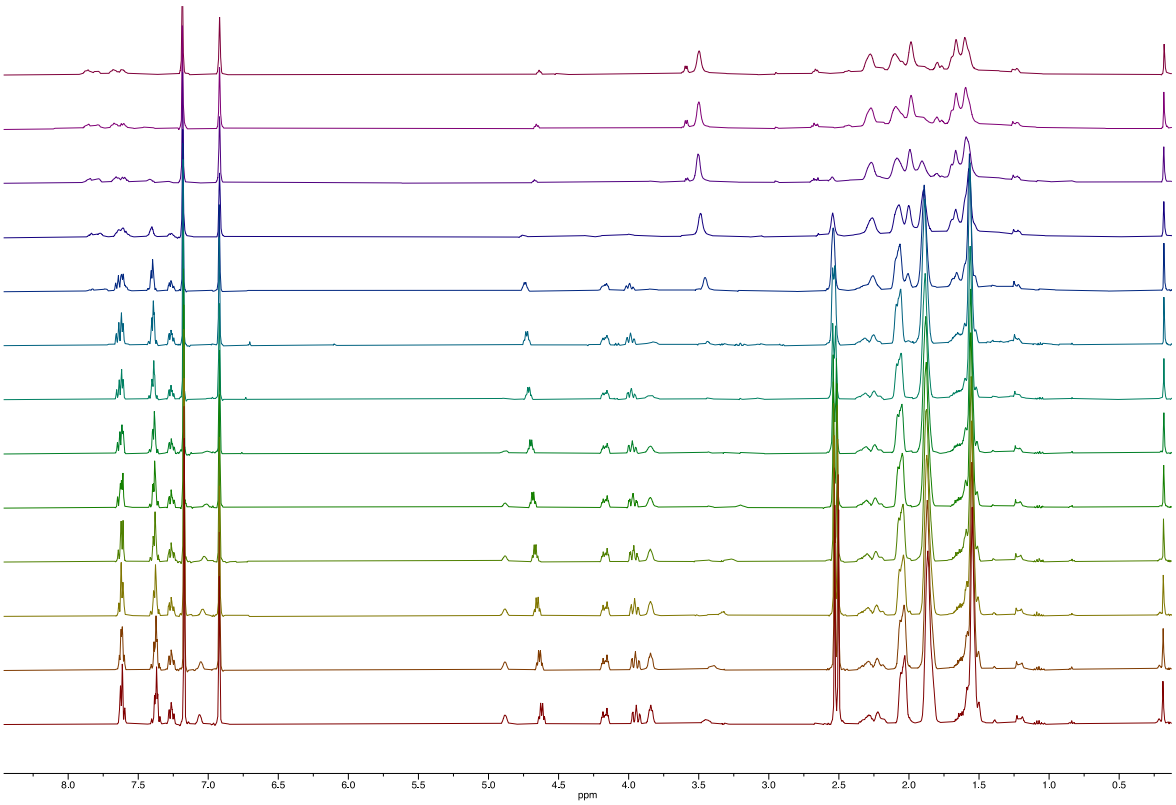


Figure S11. VT ^{1}H NMR analysis of complex **5** in the presence of a slight excess of DHP in 1,2-$Cl_2C_6D_4$ (from 298 K, bottom, to 353 K, top, with 5 K increments). Coalescence of the two NCH_3 signals is detected at 60 ºC. Above this temperature, complex **5** starts to degrade and cannot be recovered.

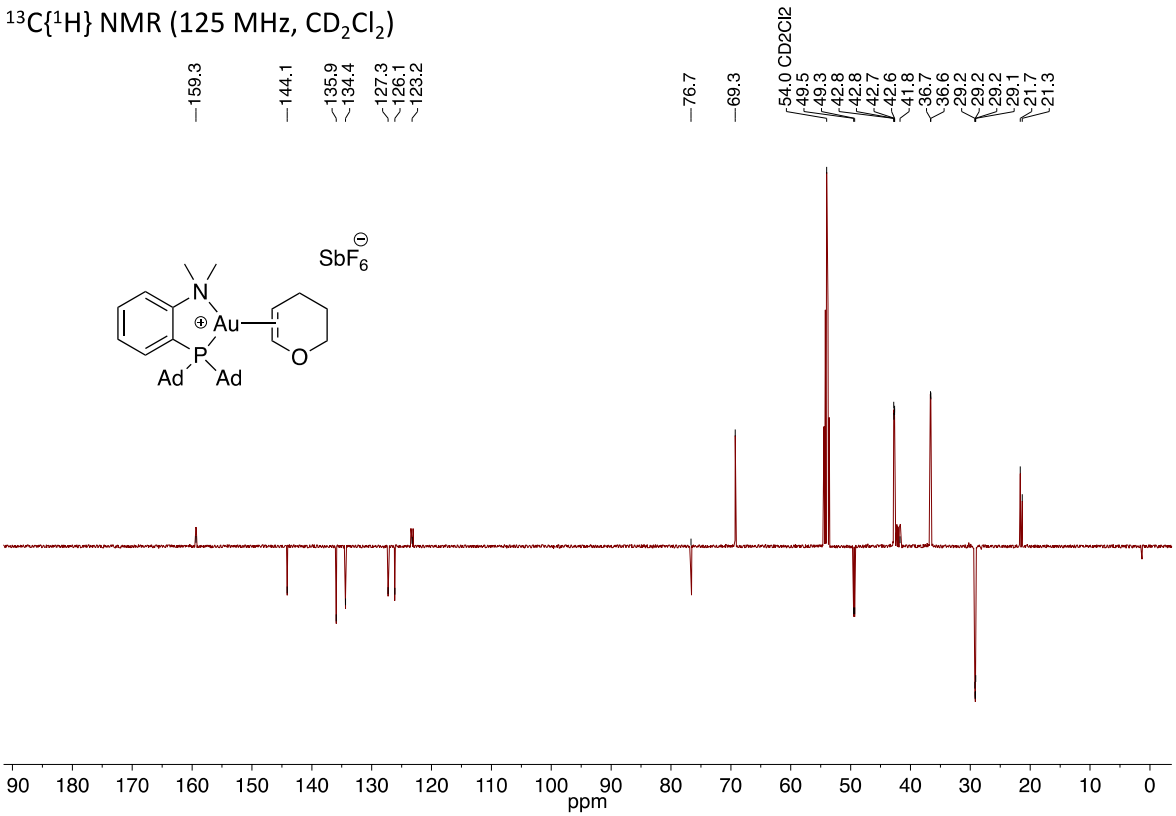


Figure S12. ^{13}C{^{1}H} NMR spectrum of complex **5**.

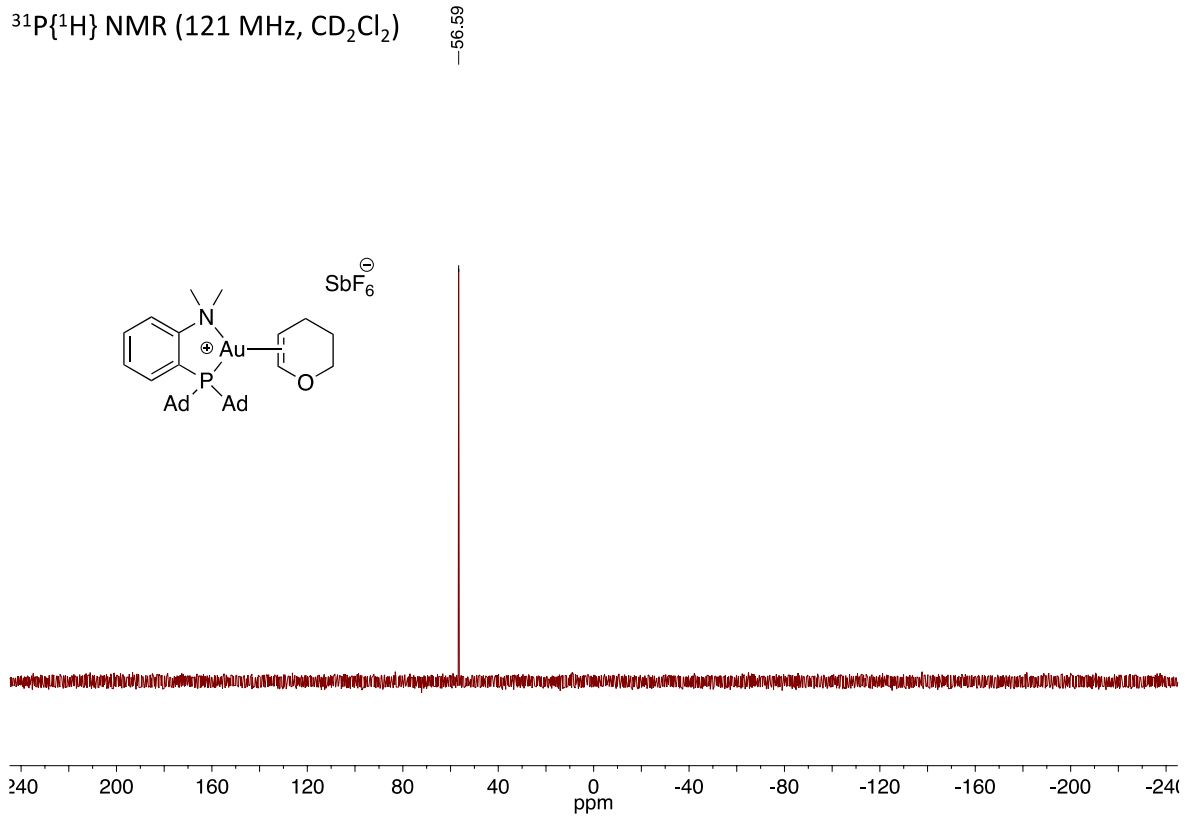


Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of complex **5**.

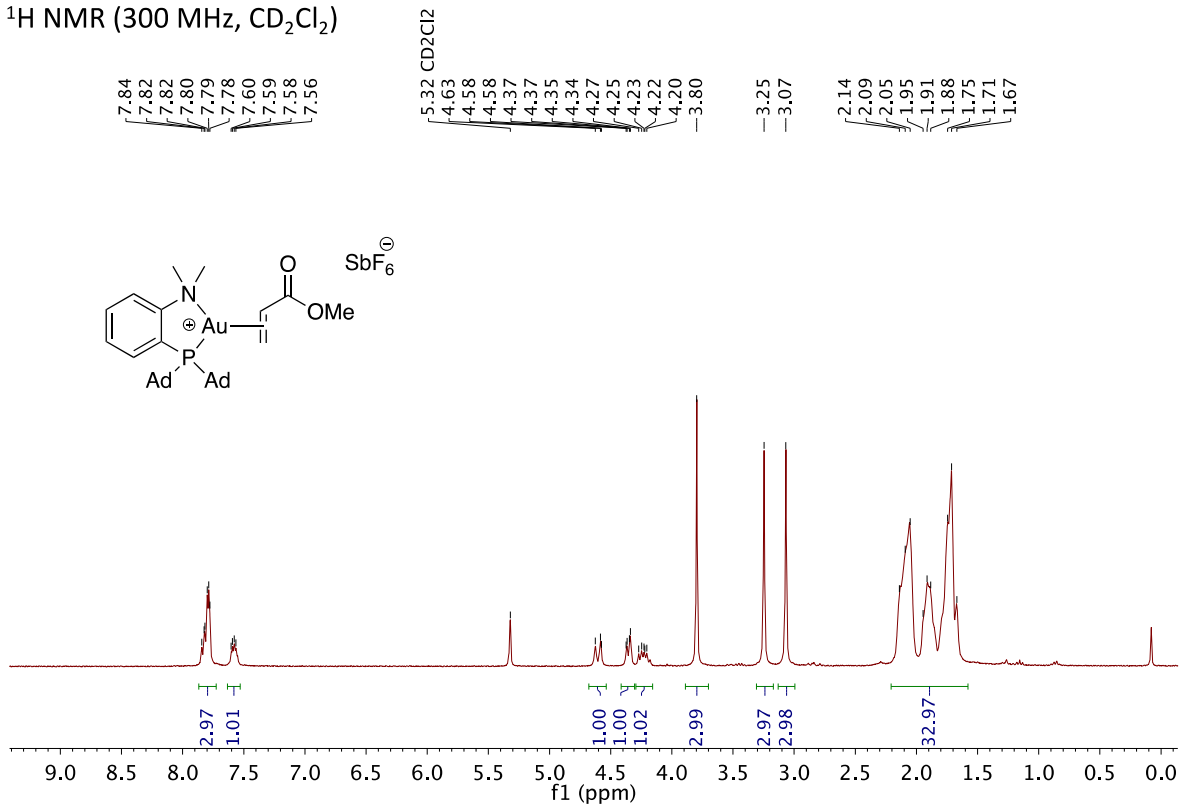


Figure S14. ^{1}H NMR spectrum of complex **6**.

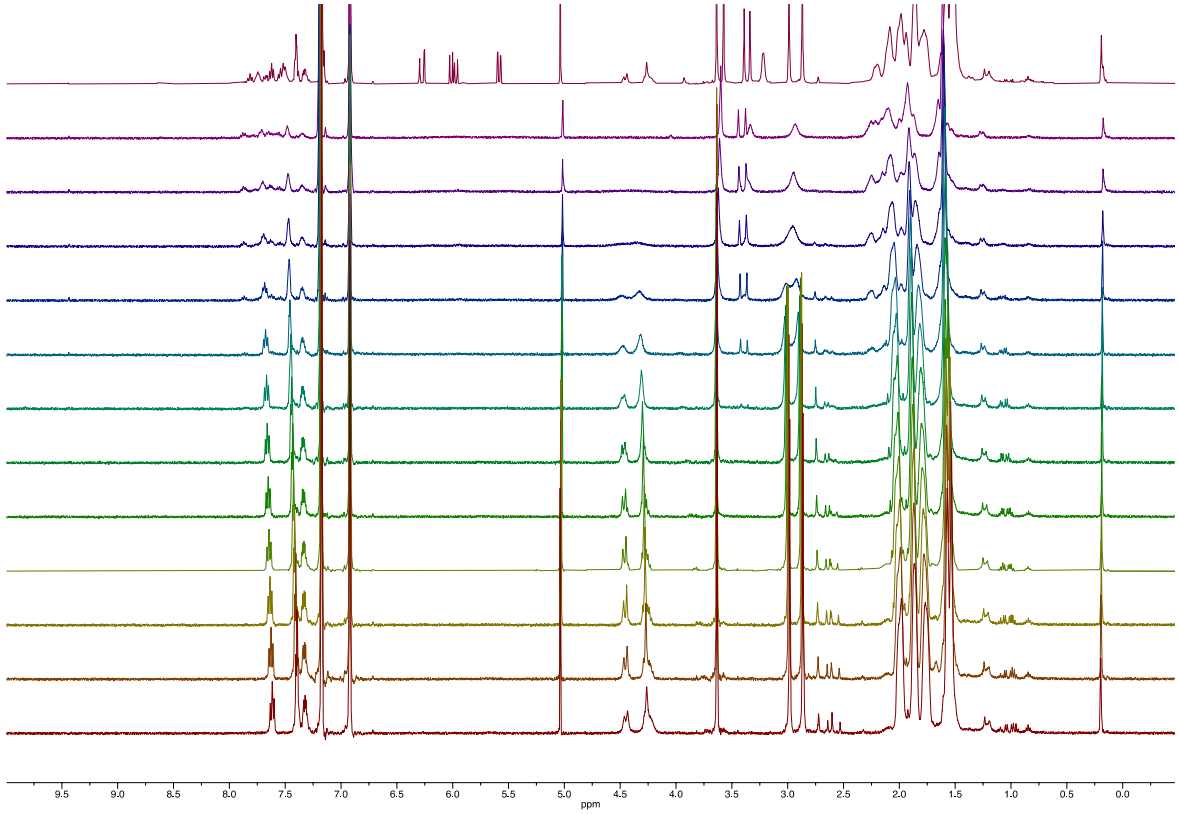


Figure S15. VT ^{1}H NMR analysis of complex **6** in 1,2-$Cl_2C_6D_4$ (from 293 K, bottom, to 403 K with 10 K increments). Coalescence of the two NCH_3 signals is detected at 110 ºC. Signs of degradation start to appear at 90 ºC. After reaching the highest temperature (130 ºC), the sample was cooled back to 25ºC (top spectrum) and the two distinct NCH_3 singlets appeared again.

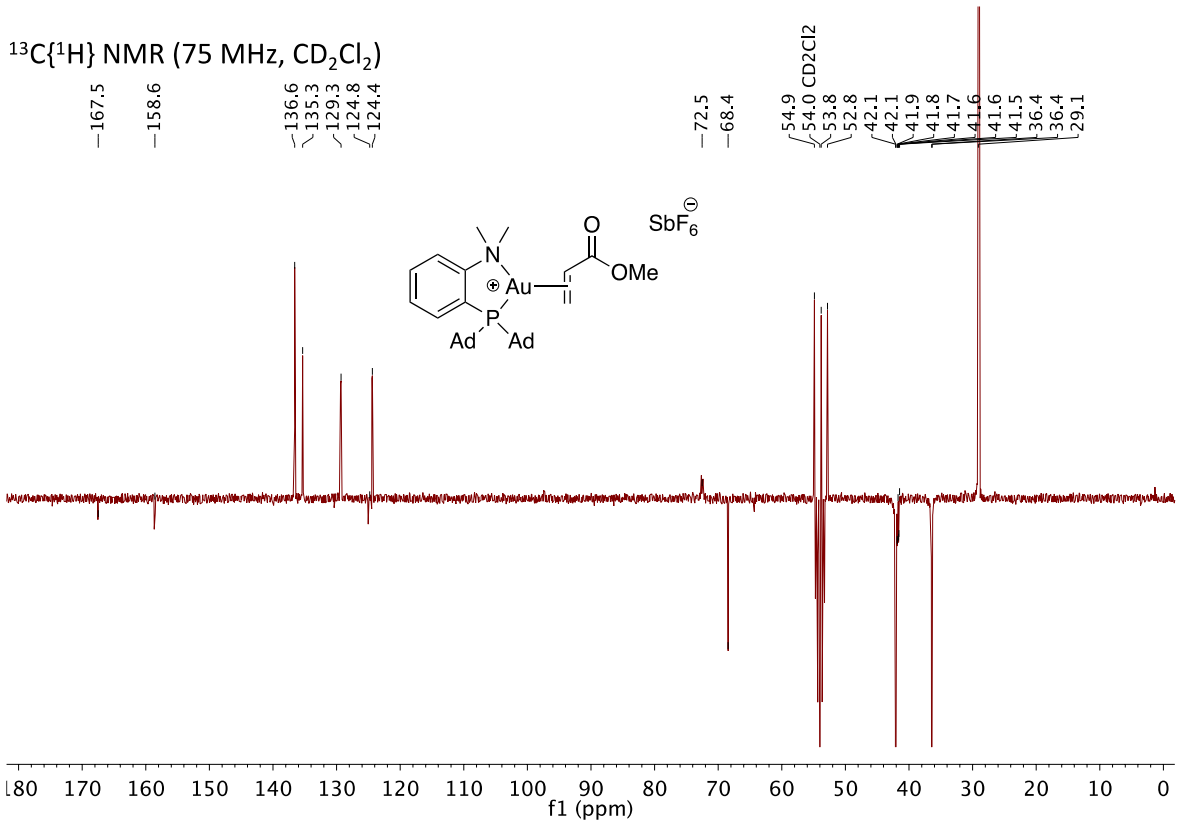


Figure S16. ^{13}C{^{1}H} NMR spectrum of complex **6**.

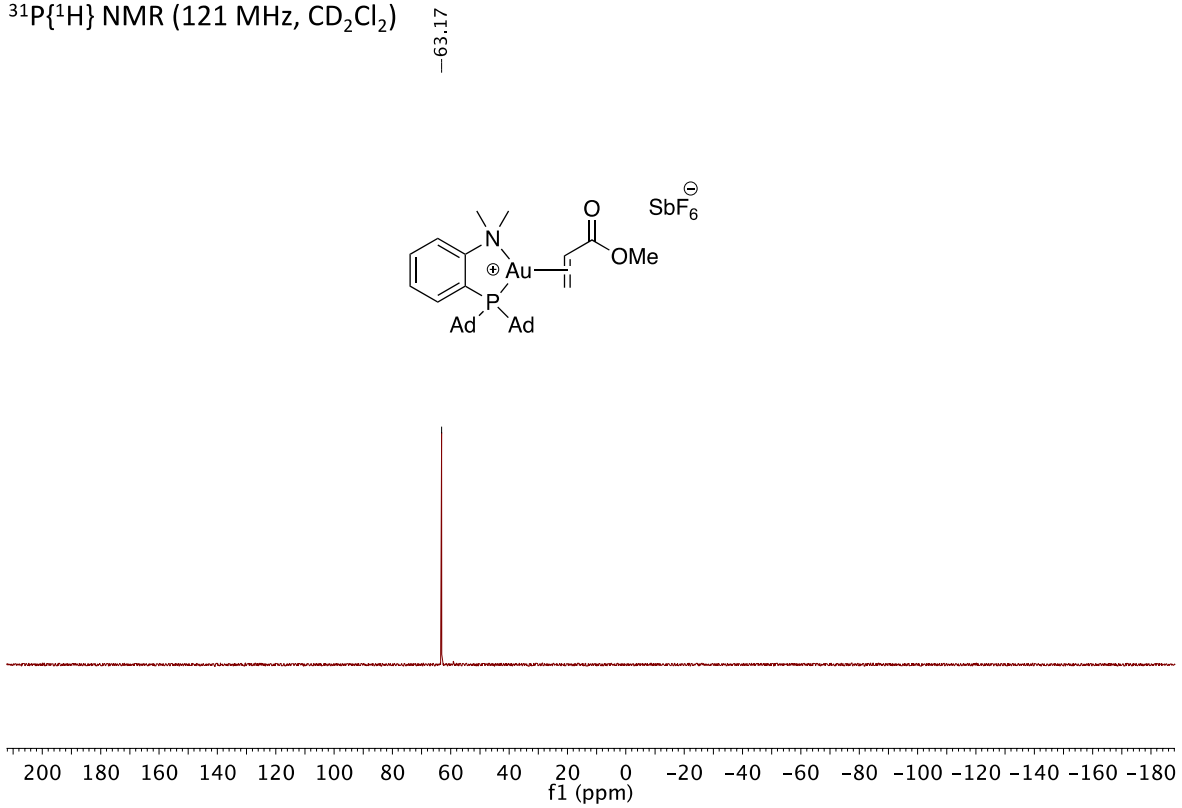


Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum of complex **6**.

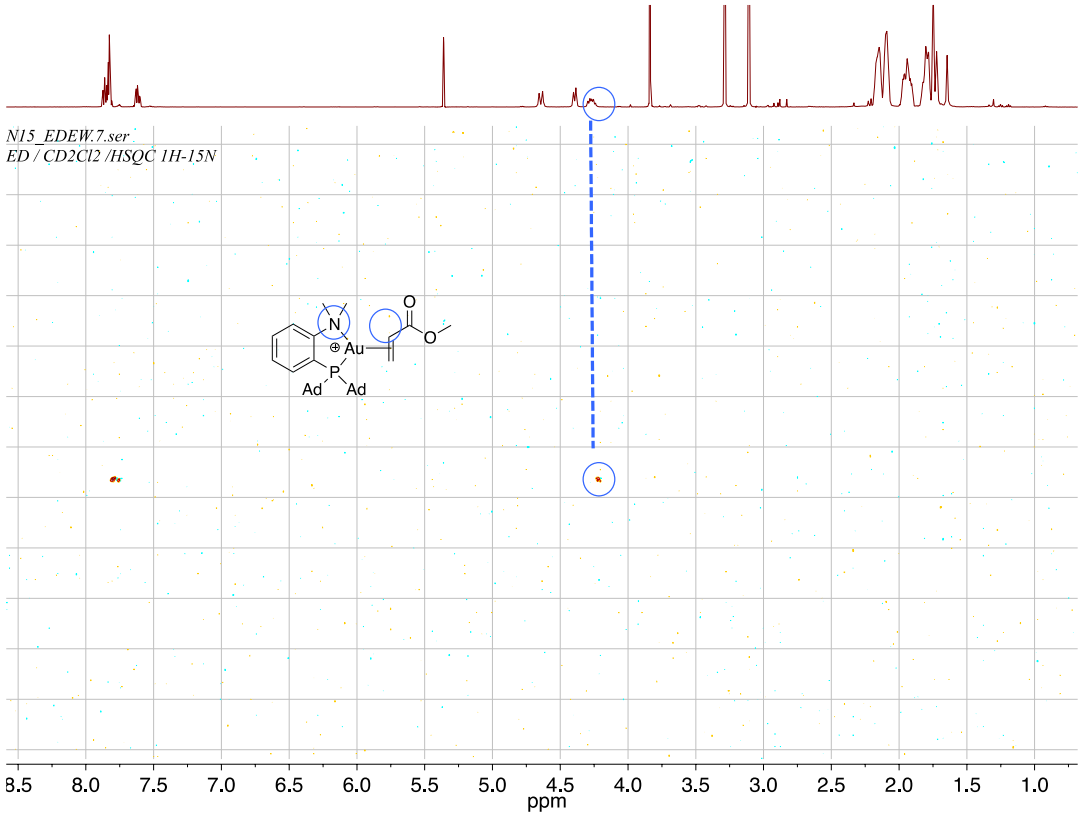


Figure S18. ^{1}H-^{15}N HSQC NMR of complex **6** in CD_2Cl_2 recorded at rt showing the correlation of one of the vinylic protons with the N atom.

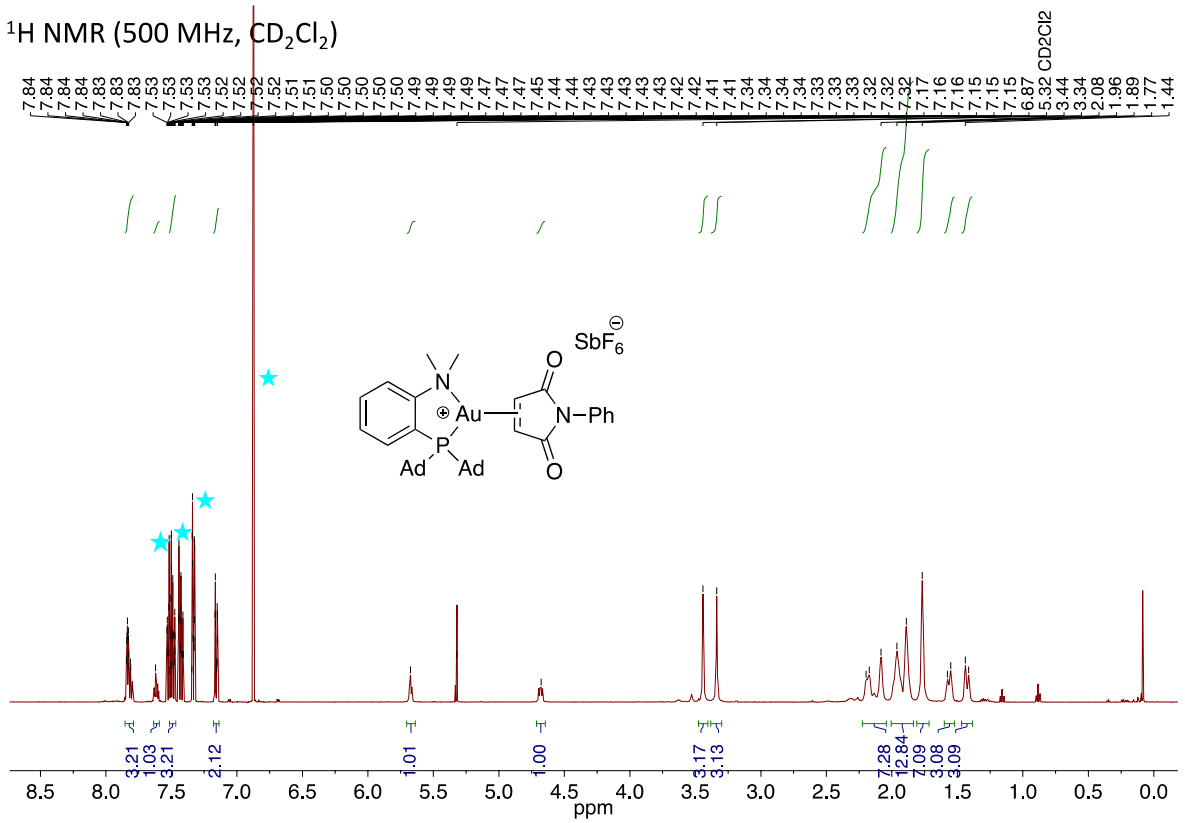


Figure S19. ^{1}H NMR spectrum of complex **7** (signals marked with a blue star correspond to the excess of *N*-Phenylmaleimide).

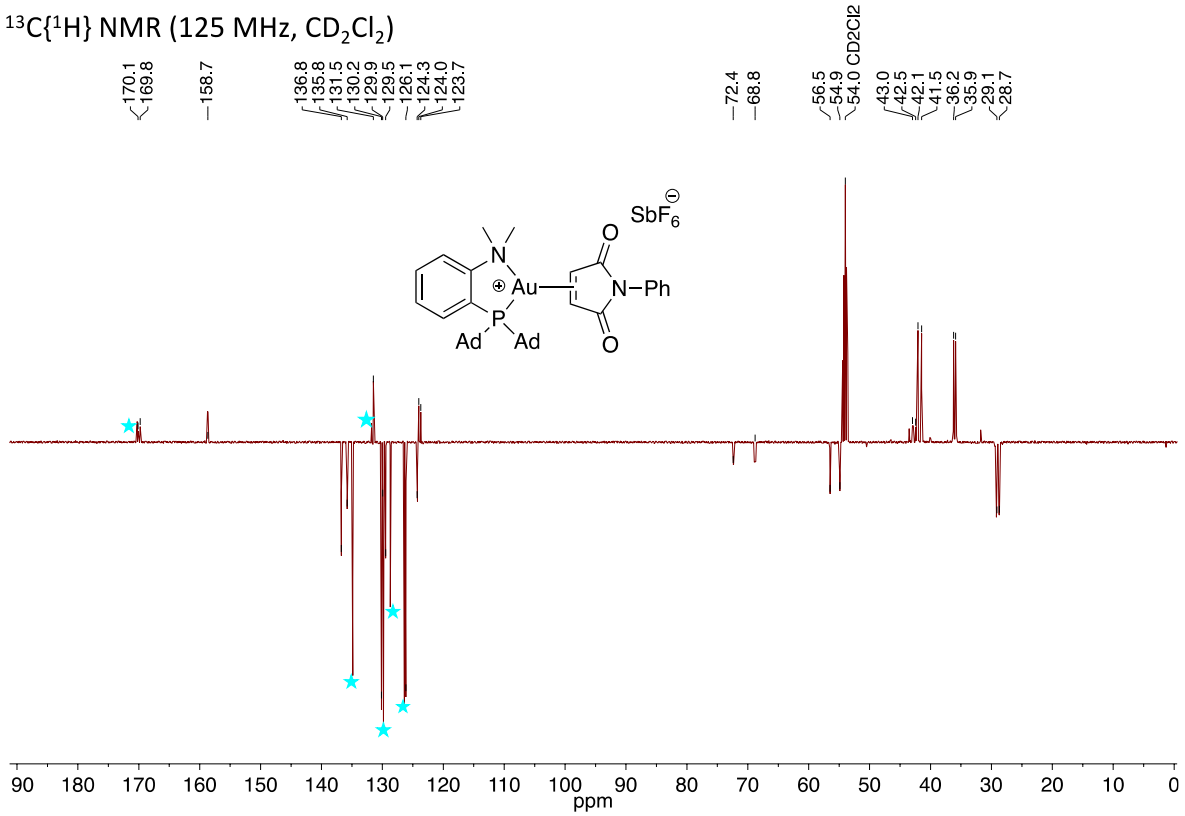


Figure S20. ^{13}C{^{1}H} NMR spectrum of complex **7** (the signals marked with a blue star correspond to the excess of *N*-Phenylmaleimide).

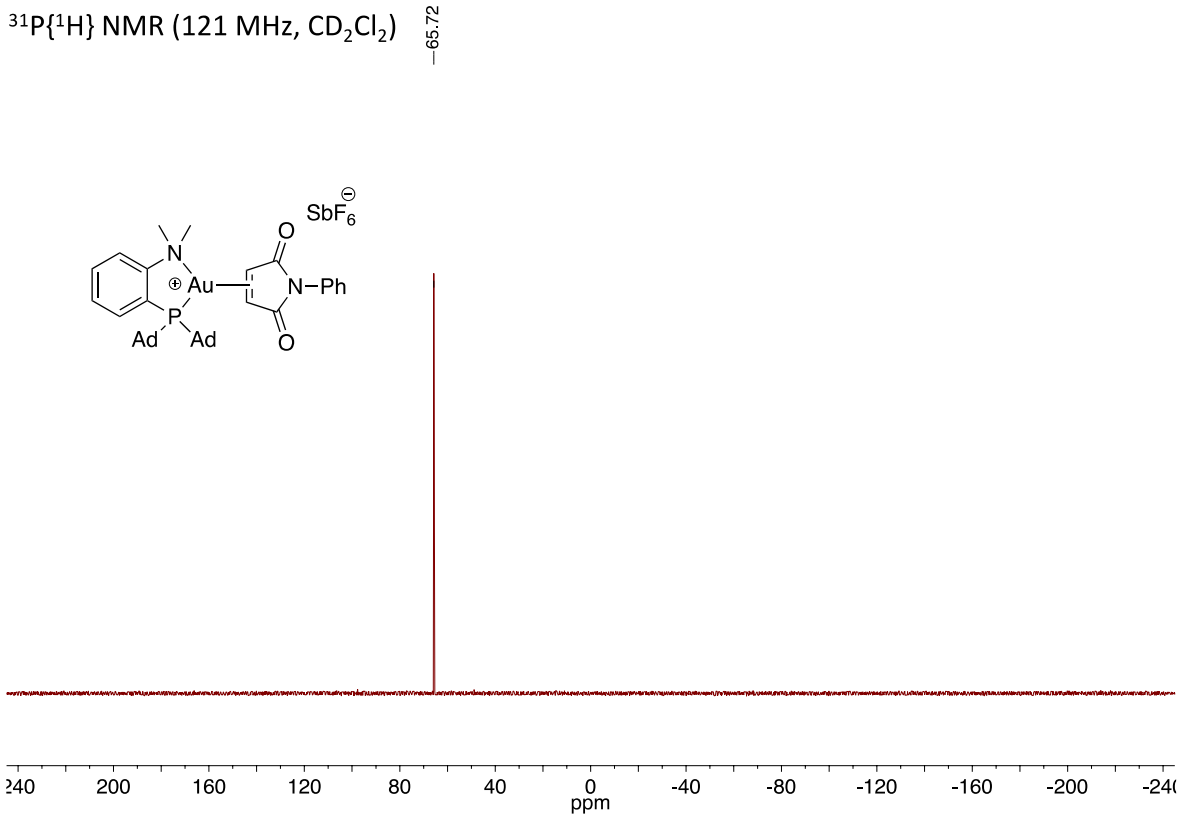


Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum of complex **7**.

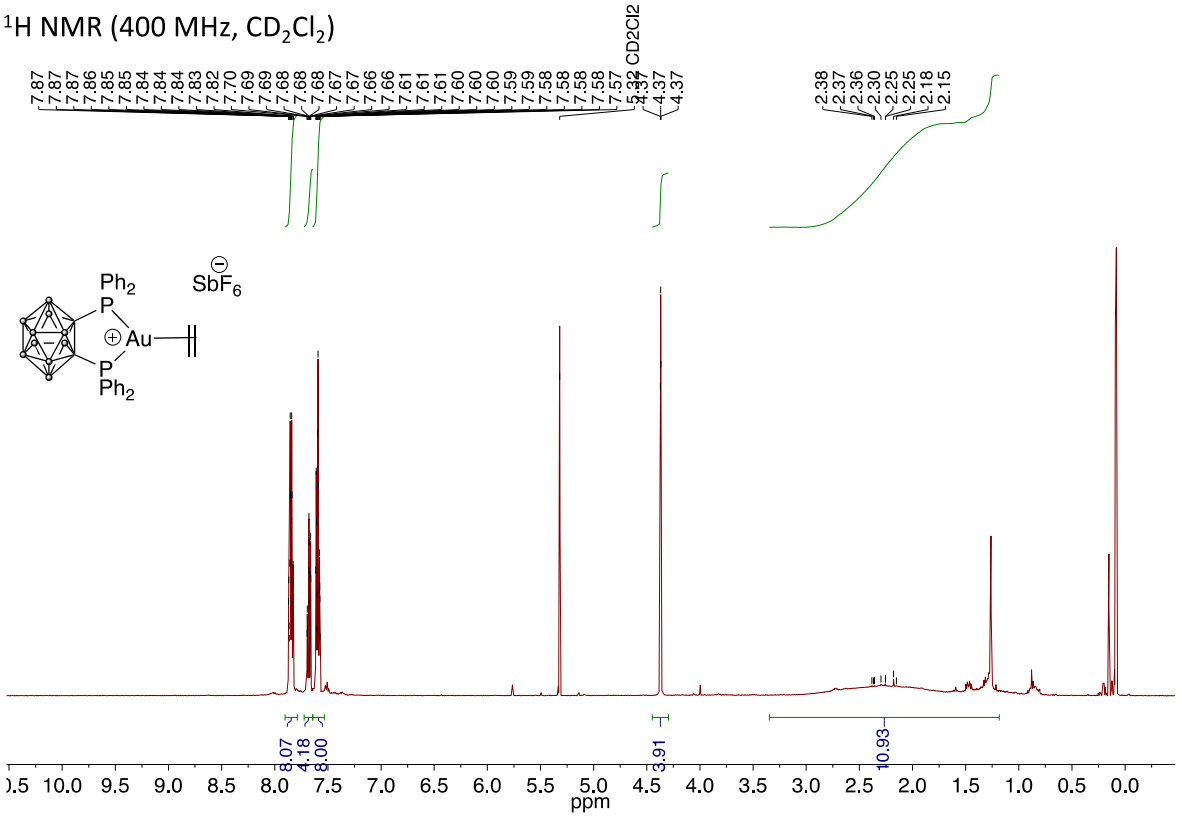


Figure S22. ^{1}H NMR spectrum of complex **9**.

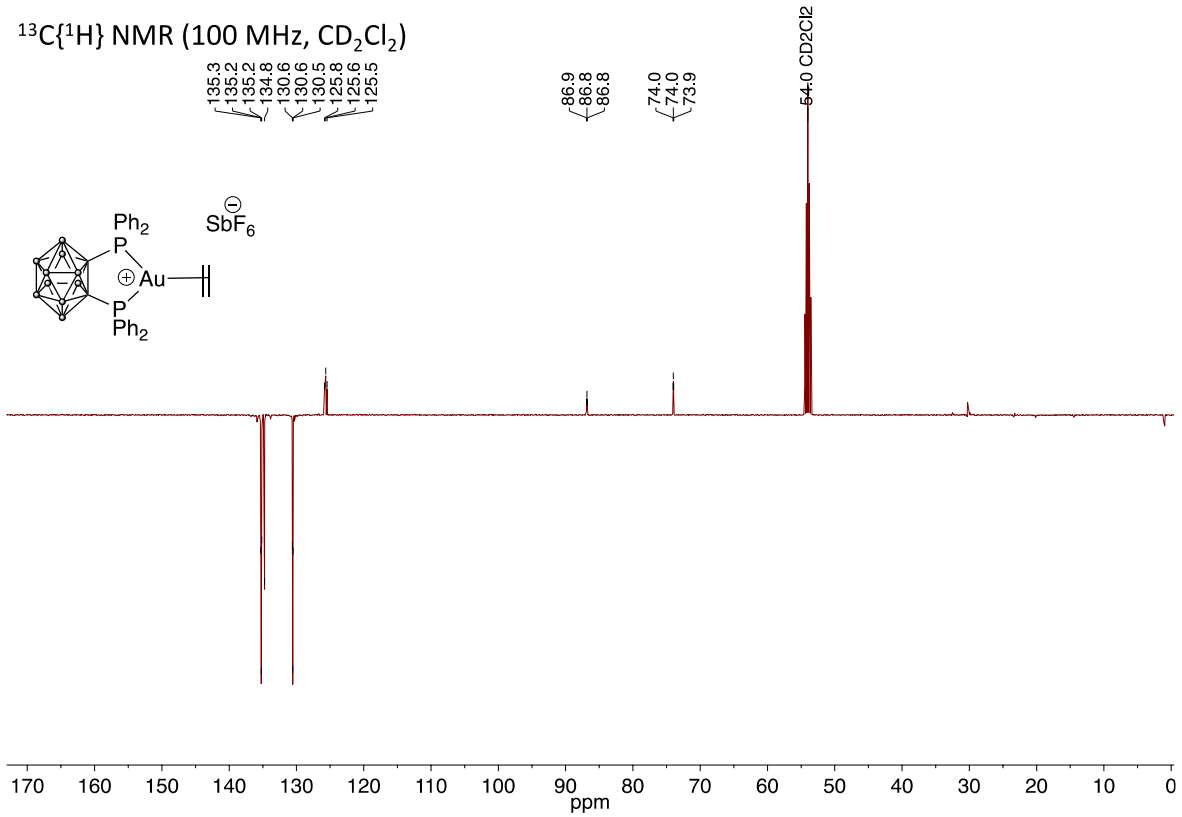


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of complex **9**.

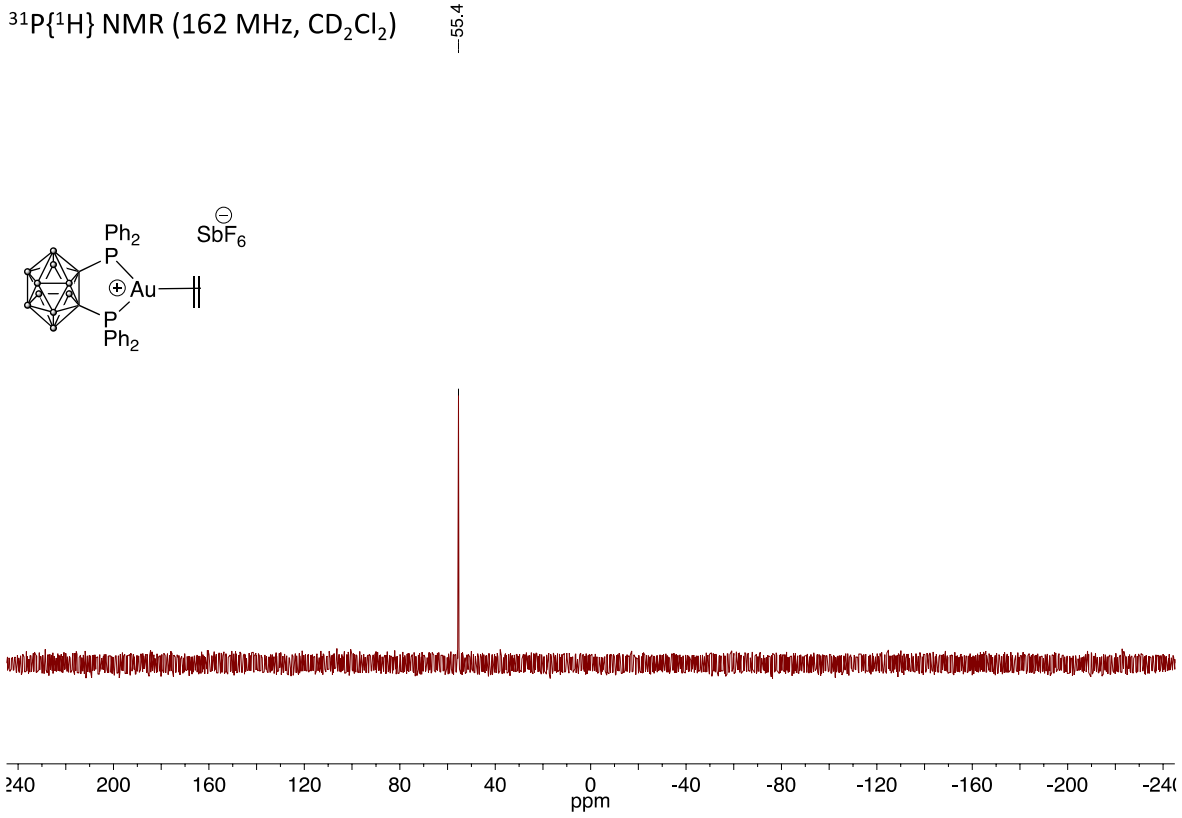


Figure S24. $^{31}P\{^{1}H\}$ NMR spectrum of complex **9**.

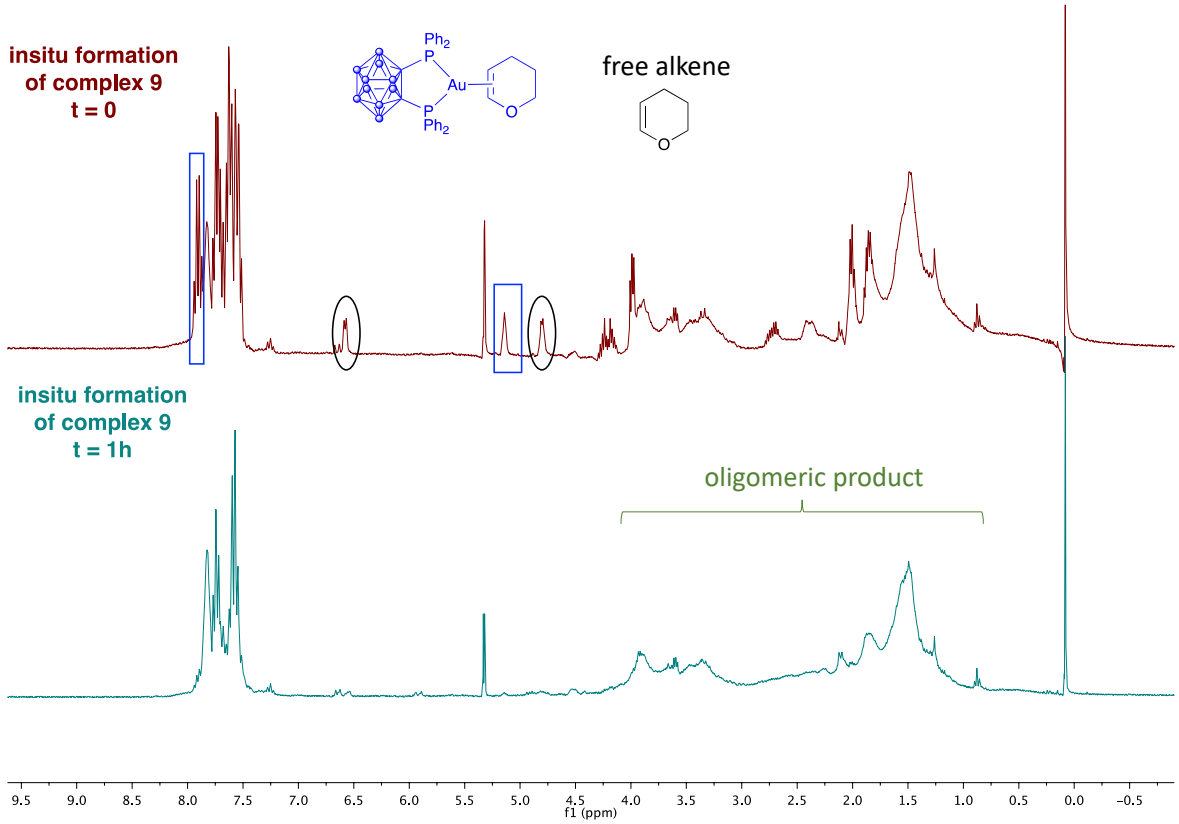


Figure S25. ^{1}H NMR spectrum of *insitu* formation of complex **10**. The olefinic signals for the free alkene are marked with black ellipsoids and the signals for the coordinated alkene are marked with blue squares.

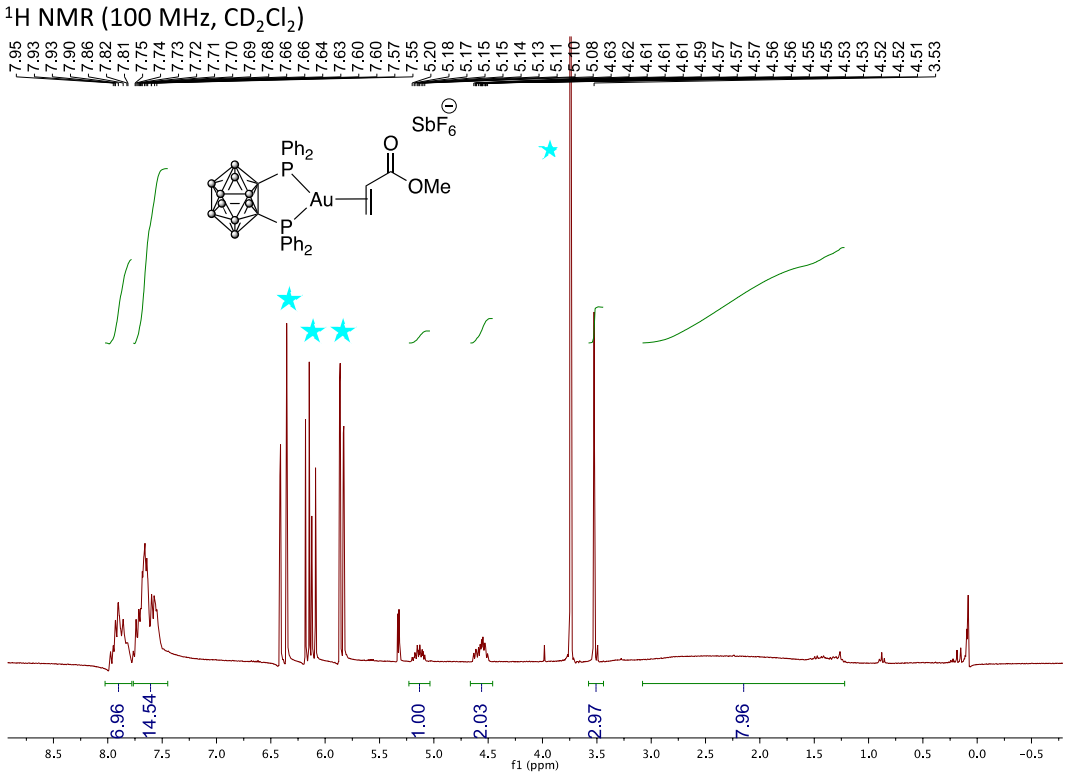


Figure S26. ^{1}H NMR spectrum of complex **11** (signals marked with a blue star correspond to the excess of methylacrylate).

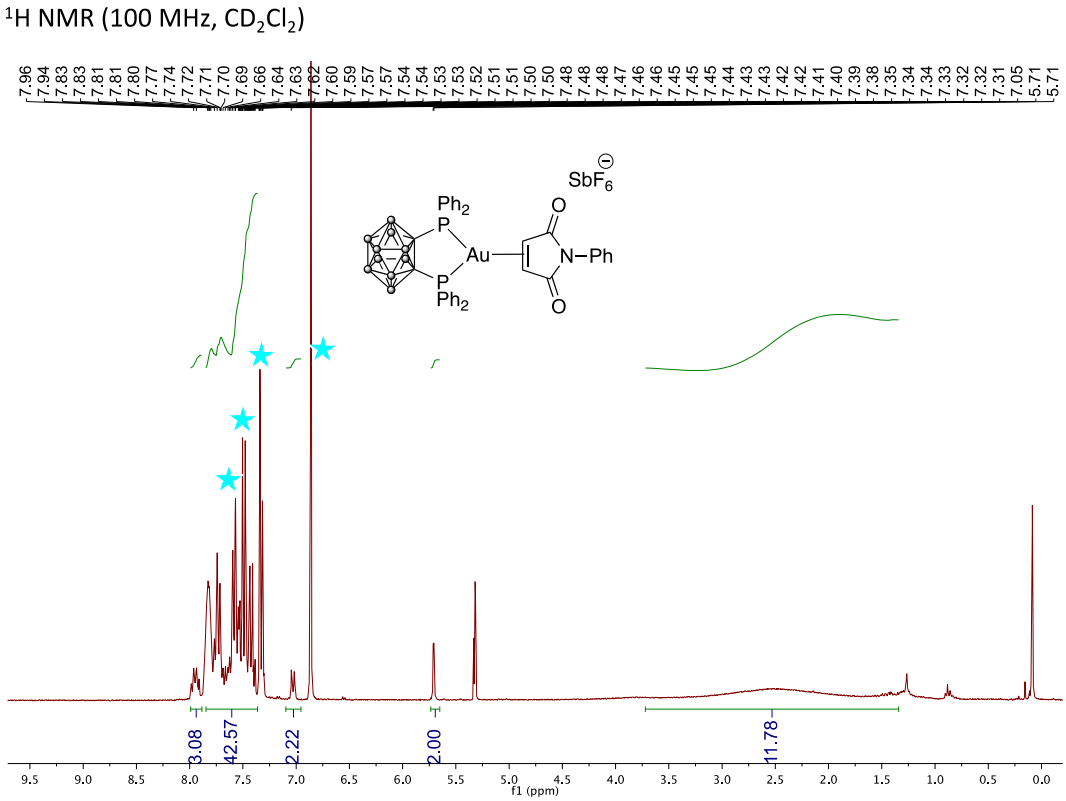
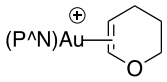
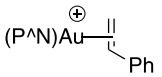
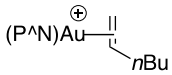
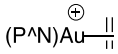
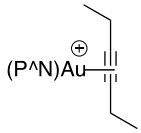
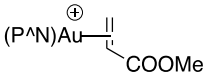
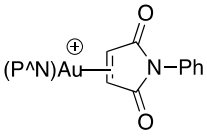


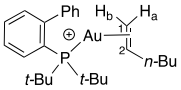
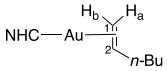
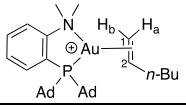
Figure S27. ^{1}H NMR spectrum of complex **12** (signals marked with a blue star correspond to the excess of *N*-phenylmaleimide).

Table S2 Selected ^{1}H, ^{13}C and ^{31}P NMR data for the (P^N)Au(I) π-complexes **1**–**7**. All data recorded in CD_2Cl_2.

	δ^{1}H (ppm)					δ^{13}C (ppm)				δ^{31}P (ppm)
	H_{1a}	H_{1b}	H_2	H_{NMe1}	H_{NMe2}	C_1	C_2	C_{NMe1}	C_{NMe2}	
(P^N)Au–Cl		-		2.57			-	47.0		53.6
		7.76 (*6.34*)	4.78 (*4.64*)	2.74	2.71	144.1 (*144.3*)	76.7 (*100.7*)	49.5	49.3	56.5
	4.33 (*5.74*)	4.17 (*5.24*)	6.03 (*6.72*)	3.09	2.82	66.4 (*113.7*)	99.9 (*136.9*)	53.0	52.8	57.3
	3.94 (*4.95*)	3.76 (*4.87*)	5.66 (*5.78*)	3.01	2.98	75.2 (*116.0*)	111.1 (*139.0*)	52.5	52.5	58.1
		4.10 (*5.43*)		3.14			75.0 (*116.8*)	53.9		58.8
		-		3.02			97.8 (*80.7*)	52.9		59.4
	4.35 (*6.40*)	4.61 (*5.82*)	4.23 (*6.13*)	3.25	3.07	68.4 (*130.6*)	72.5 (*128.5*)	54.9	53.8	63.2
		4.68 (*6.81*)	5.67 (*6.81*)	3.44	3.33	68.8 (*134.1*)	72.4 (*134.1*)	55.4	55.2	65.3

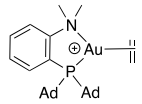
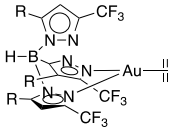
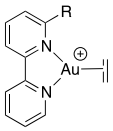
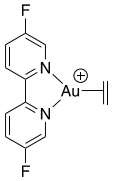
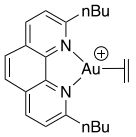
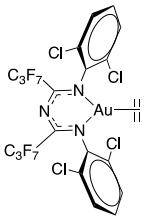
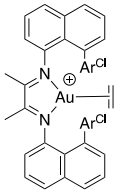
All data recorded in CD_2Cl_2. ^{1}H and ^{13}C NMR data from the free alkenes or alkyne are indicated in brackets.

Table S3 NMR comparison between reported Au(I) 1-hexene complexes and free 1-hexene. All data recorded in CD_2Cl_2.

		δ ^{1}H(ppm)			δ ^{13}C(ppm)	
Entry	Compound	H1a	H1b	H2	C1	C2
1		5.78	4.95	4.87	116.0	139.0
2[a]		6.15	4.39	4.36	100.1	141.9
3[b]		6.06	4.83	4.57	94.4	135.4
4		5.66	3.94	3.76	75.2	111.1

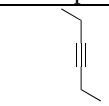
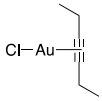
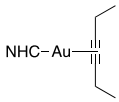
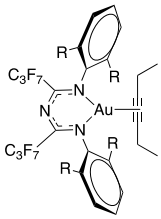
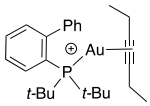
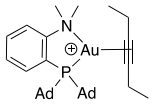
Data extracted from references: a) [S7]; b) [S8].

Table S4 Comparison of the NMR and XRD data reported for Au(I) ethylene complexes (and free ethylene). All NMR data recorded in CD_2Cl_2. For comparison of the NMR and XRD data of styrene complexes, see reference S3.

Entry	Compound	δ ^{1}H (ppm)	δ ^{13}C(ppm)	Au–C (Å)	C=C (Å)
1		5.43	116.8	-	-
2[b]		4.94	92.7	2.271(5) 2.267(6) 2.267(4) 2.263(4) 2.269(7) 2.272(4)	1.371(7) 1.351(7) 1.369(7)
3		4.10	75.0	2.141(3) 2.149(3)	1.387(5)
4[c*]		3.81 (R=CF_3) 3.69 (R=Ph)	63.7 (R=CF_3) 59.3 (R=Ph)	2.096(6) 2.108(6)	1.380(10)
5[d]		3.09	61.6	-	-
6[e]		3.90	63.8	2.086(3) 2.092(3)	1.399(5)
7[f]		3.88	60.6	2.104(7) 2.106(7)	1.411(10)
8[g*]		2.71	59.1	2.089(2) 2.098(2)	1.405(4)
9[h*]		3.31 3.28	65.4	2.094(8) 2.118(8)	1.455(13)

Data extracted from references: a) [S9]; b) [S10]; c) [S11]; d) [S12]; e) [S13]; f) [S14]; g) [S15]; h) [S16].*Data recorded in $CDCl_3$

Table S5 NMR comparison between reported Au(I) 3-hexyne complexes and free 3-hexyne. All data recorded in CD_2Cl_2.

Entry	Compound	δ ^{13}C (ppm)
1		80.7
2[a] (253K)		86.4[a]
3[b]		87.7[b]
4[c*]		90.3
5[d]		91.4
6		97.8

Data extracted from references: a) [S17]*;* b) [S18]*;* c) [S19]*;* d) [S20]. *Data recorded in $CDCl_3$

4. Crystal structure determinations

Crystallographic data were collected at low temperature (193(2) K) on a Bruker-AXS APEX II Quazar diffractometer equipped with a 30W air-cooled microfocus or on a Bruker-AXS PHOTON100 D8 VENTURE diffractometer, using MoK_α radiation (λ = 0.71073 Å). Phi- and omega-scans were used. An empirical absorption correction was performed with SADABS.[S21] The structures were solved by direct intrinsic phasing method (SHELXT),[S22] and refined using the least-squares method on F^2.[S23] All H atoms on carbon atoms were refined isotropically at calculated positions using a riding model.

CCDC 1967901 (**3**), 1967904 (**5**), 1967902 (**6**) 1967903 (**7**), 1967905 (**9**) and 1967906 (**13g**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Table S6. Crystal data and structure refinement for compounds **3**, **5** and **6**.

ID	**3**	**5**	**6**
formula	2 ($C_{30}H_{44}AuNPF_6Sb$) · CH_2Cl_2	$C_{33}H_{48}AuF_6NOPSb$· CH_2Cl_2	$C_{32}H_{46}AuF_6NO_2PSb$ · CH_2Cl_2
M_r	1849.65	1023.35	1025.32
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	P 2_1 /n	P 2_1 /c	P 2_1
a (Å)	10.4398(8)	10.9121(11)	14.8546(12)
b (Å)	18.5854(15)	17.7644(18)	12.2517(9)
c (Å)	16.9617(14)	19.509(2)	20.5946(16)
α (°)	90	90	90
β (°)	94.354(3)	104.904(3)	99.848(3)
γ (°)	90	90	90
V (Å^3)	3281.5(5)	3654.6(6)	3692.9(5)
Z	2	4	4
ρ_{calc} (g cm^{-3})	1.872	1.86	1.844
μ (mm^{-1})	5.475	4.999	4.949
F(000)	1804	2008	2008
crystal size (mm$_3$)	0.300 x 0.200 x 0.180	0.260 x 0.100 x 0.100	0.240 x 0.120 x 0.080
T/K	193(2)	193(2)	193(2)
meads rflns	124551	152131	73394
unique rflns (Rint)	13100 (0.0361)	14574 (0.0339)	12926 (0.0269)
reflns used for refinement	13100	14574	12926
refined parameters	540	434	872
GOF on F^2	1.028	1.046	1.053
R_1[a] [I>2σ(I)]	0.0257	0.0302	0.0192
wR_2[b] [all data]	0.0718	0.0790	0.0478

[a] $R_1 = \Sigma||F_o| - |F_c||/ \Sigma |F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$

Table S7. Crystal data and structure refinement for compounds **7**, **9** and **13g**.

ID	**7**	**9**	**13g**
formula	$C_{38}H_{47}AuN_2O_2PF_6Sb$	$C_{29}H_{36}AuB_{10}Cl_2F_6P_2Sb \cdot CH_2Cl_2$	$C_{21}H_{20}N_4O_5$
M_r	1027.48	1058.25	408.41
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	P 2_1 /c	Pn	P 2_1 /c
a (Å)	10.7728(7)	10.0221(4)	15.4212(12)
b (Å)	11.1430(9)	13.3021(5)	13.4652(8)
c (Å)	30.591(2)	14.7578(6)	9.4134(7)
α (°)	90	90	90
β (°)	98.974(5)	95.633(2)	102.515(4)
γ (°)	90	90	90
V (Å^3)	3627.3(5)	1957.94(13)	1908.2(2)
Z	4	2	4
ρ_{calc} (g cm^{-3})	1.881	1.795	1.422
μ (mm^{-1})	4.897	14.88	0.104
F(000)	2016	1016	856
crystal size (mm^3)	0.200 x 0.100 x 0.040	0.180 x 0.160 x 0.040	0.200 x 0.050 x 0.030
T/K	193(2)	193(2)	193(2)
meads rflns	37150	33142	43146
unique rflns (Rint)	6414 (0.0554)	6696 (0.0395)	3452 (0.1385)
reflns used for refinement	6414	6696	3452
refined parameters	535	475	317
GOF on F^2	1.079	1.036	1.053
R_1[a] [I>2σ(I)]	0.0429	0.0308	0.0611
wR_2[b] [all data]	0.1076	0.0767	0.1833

[a] $R_1 = \Sigma||F_o| - |F_c||/ \Sigma |F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$

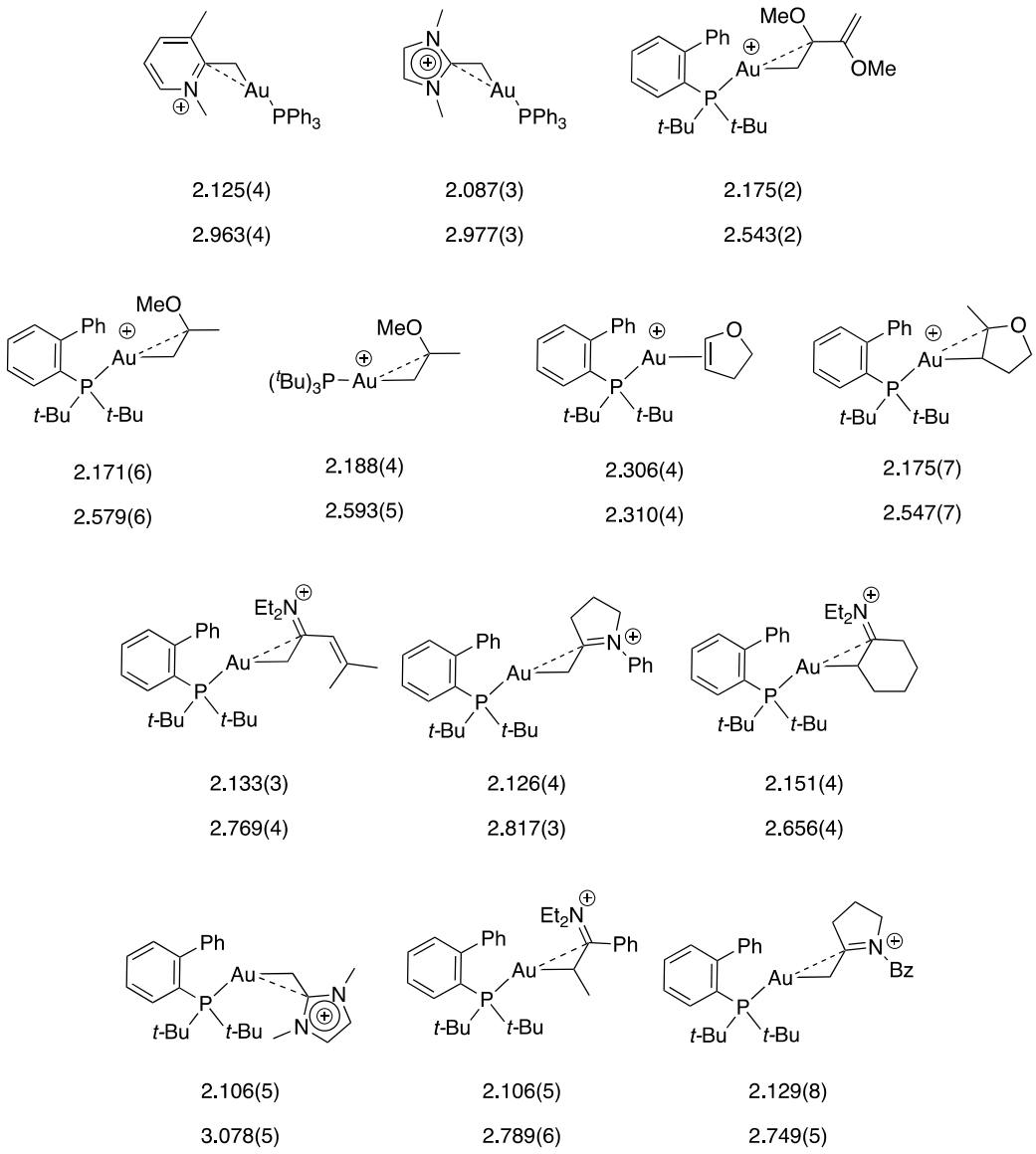


Figure S28. Reported gold(I) complexes featuring electron-rich alkenes. The two different Au–C distances (Å) extracted from references S24–S29 are indicated for each compound.

5. Computational details

All calculations were performed using the Gaussian 09 package[S30] and the B3PW91 hybrid[S31,S32] functional on the real systems taking into account solvent effect (dichloromethane, DCM) by means of the universal Solvation Model based on solute electron Density (SMD).[S33] The gold atom was described with the relativistic electron core potential SDD and associated basis set,[S34] augmented by a set of f-orbital polarization functions.[S35] The 6-31G** basis set was employed for all other atoms (C, H, P, N, O). All stationary points involved were fully optimized in solvent. Frequency calculations were undertaken to confirm the nature of the stationary points (all frequencies positive for *minima*).

In order to gain more insight into the bonding situation, in particular with respect to the Au/alkene and N→Au interactions, different approaches were used:

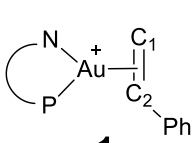
i) Natural Bond Orbital[S36–S38] analyses – NBO – were performed with NBO, 5.9 version.[S39] Stabilizing interactions ($\Delta E(2)$ in kcal·mol^{-1}), determined at second order perturbation theory, have been computed to shed light into CC→Au donation, Au→CC back-donation and N→Au interaction. Natural Localized Molecular Orbitals (NLMO) associated to $\pi_{C=C}$, n_N and d_{Au} orbitals as well as Wiberg bond indexes (WBI) have also been determined.

ii) Charge Decomposition analysis – CDA – was carried out with the CDA 2.2 program of G. Frenking[S40] in order to quantify the contributions of donation and back-donation terms. The orbital contributions to the charge distributions were divided into four parts: (i) the mixing of the occupied orbitals of the ligand and the unoccupied MOs of the metal fragment (alkene→Au donation *d*), (ii) the mixing of the unoccupied orbitals of the ligand and the occupied MOs of the metal fragment (Au→alkene back-donation *b*), (iii) the mixing of the occupied orbitals of the alkene and the occupied orbitals of the gold fragment (alkene ↔ Au repulsive polarization *r*), and (iv) the mixing of the unoccupied orbitals of the alkene and the unoccupied orbitals of the gold fragment (residual term Δ).

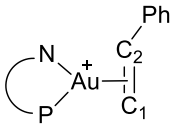
iii) Atoms In Molecules analysis – QTAIM[S41,S42] – was also performed thanks to AIMALL[S43] software in order to gain insight into the nature of the chemical bonding. Density ρ(r) was determined for Bond Critical Point (BCP) associated to C=C (complexes and free olefins), Au–C and Au–N bonds. Laplacian of the density $\nabla^2\rho(r)$ indicates the regions where the density ρ(r) is depleted or concentrated. In covalent bonding (also referred to as "open-shell" or "sharing" interactions), $\nabla^2\rho(r)$ is negative, while positive values are observed for interactions showing closed-shell (e.g, ionic, Van-der-Waals, or hydrogen). Delocalization bond indexes (δ) between the two carbon atoms of the C=C double bond and between gold and nitrogen atoms were also calculated. Bader charge analysis was also used to determine the magnitude of the charge transfer between the ligand (olefin) and the metal fragment and has been compared to Hirshfeld charge analysis (see below).

iv) Hirshfeld charge analysis was also used to determine the magnitude of the charge transfer between the alkene and the gold fragment.[S44] These calculations have been carried out with Amsterdam Density Functional 2018.01 program (ADF)[S45] at ZORA-BP86-D3/TZ2P level of theory on the geometry optimized from Gaussian 09 at B3PW91(SDM-DCM)/SDD+f(Au), 6-31G** level of theory.

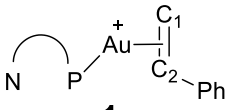
Table S8. NBO analyses for the different isomers of the styrene gold(I) complex **1**. Optimization carried out at the SMD-(Dichloromethane)-B3PW91/SDD+f(Au)/6-31G**(other atoms) level of theory and NBO analysis performed at the B3PW91/SDD+f(Au)/6-31G**(other atoms) level of theory on the geometry optimized in solvent.



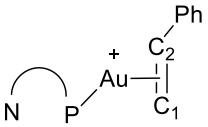
1



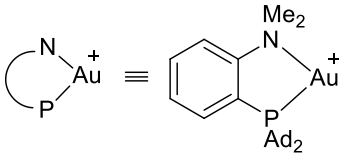
1b



1c



1d



	1	**1b**	**1c**	**1d**
Au–C (Å)	2.156 2.245	2.214 2.140	2.241 2.360	2.361 2.242
C=C (Å)	1.403	1.410	1.380	1.379
NBO analyses				
C=C/Au interaction				
WBI (C=C)[a]	1.475	1.439	1.595	1.596
styrene→Au donation				
π_{CC}→LP*(Au)[b]	143.7	161.9	88.2	87.9
NLMO[c] π_{CC} % Au % C1 % C2	 9.8 49.0 37.5	 10.6 44.3 40.8	 8.3 47.2 39.7	 8.3 47.2 39.7
Au→styrene back-donation				
LP(Au)→π^*_{CC}[b]	36.7	40.5	22.6	22.5
NLMO LP(Au) % Au % C1 % C2	 88.2 5.2 5.7	 86.7 6.0 6.3	 93.8 2.5 2.7	 93.9 2.7 2.5
N→Au interaction				
N–Au (Å)	2.456	2.385	/	/
WBI (N–Au)[a]	0.085	0.122	/	/
LP(N)→Au[b]	20.0	30.0	/	/
NLMO[c] LP(N) % Au % N	 1.1 91.7	 3.2 89.9	 / /	 / /

[a] Wiberg Bond Index. [b] Stabilizing interaction ΔE(2) at the 2nd order perturbation theory in kcal·mol^{-1}.
[c] Natural Localized Molecular Orbital with percentages of the main atoms (%) involved.

Table S9. CDA analyses for the different isomers of the styrene gold(I) complex **1** performed at the B3PW91/SDD+f(Au)/6-31G**(other atoms) level of theory on the geometry optimized in solvent at the SMD-(Dichloromethane)-B3PW91/SDD+f(Au)/6-31G**(other atoms) level of theory.

CDA analyses				
	1	**1b**	**1c**	**1d**
CC→Au donation (d)	0.416	0.407	0.368	0.367
Au→CC back-donation (b)	0.211	0.257	0.097	0.097
d/b ratio	1.97	1.58	3.79	3.78
Au↔C repulsion	-0.334	-0.350	-0.266	-0.262
Residue term Δ	-0.016	-0.020	-0.015	-0.014

Table S10. AIM analyses computed in gas phase at the B3PW91/SDD+f(Au)/6-31G**(other atoms) level of theory on the geometry optimized in solvent for the different isomers of the styrene gold(I) complex **1**. Charge transfer (CT) from the alkene to the gold fragment, density $\rho(r_c)$ in e.bohr^{-3}, Laplacian of the density $\nabla^2\rho(r_c)$ in e.bohr^{-5}, ellipticity ε and bond index δ.

AIM analyses					
		1	**1b**	**1c**	**1d**
Charge Transfer CT (CC→Au)					
		0.140	0.088	0.267	0.268
Main AIM parameters					
C1=C2	**$\rho(r_c)$**	0.313	0.302	0.319	0.319
	$\nabla^2\rho(r_c)$	-0.852	-0.775	-0.872	-0.872
	ε	0.270	0.222	0.240	0.240
	δ(C1=C2)	1.290	1.285	1.419	1.420
Au-C1	**$\rho(r_c)$**	0.090	0.091	0.083	
	$\nabla^2\rho(r_c)$	0.147	0.203	0.158	No BCP
	ε	0.270	2.972	0.548	
	δ(Au-C1)	0.571	0.582	0.543	
Au-C2	**$\rho(r_c)$**		0.104		0.082
	$\nabla^2\rho(r_c)$	No BCP	0.150	No BCP	0.157
	ε		0.471		0.553
	δ(Au-C2)		0.696		0.540
Au-N	**$\rho(r_c)$**	0.035	0.061	0.019	0.019
	$\nabla^2\rho(r_c)$	0.110	0.207	0.058	0.058
	ε	0.060	0.041	0.223	0.230
	δ(Au-N or H)	0.269	0.432	0.091[a]	0.089[a]

[a] BCP between Au and H_{phenyl}

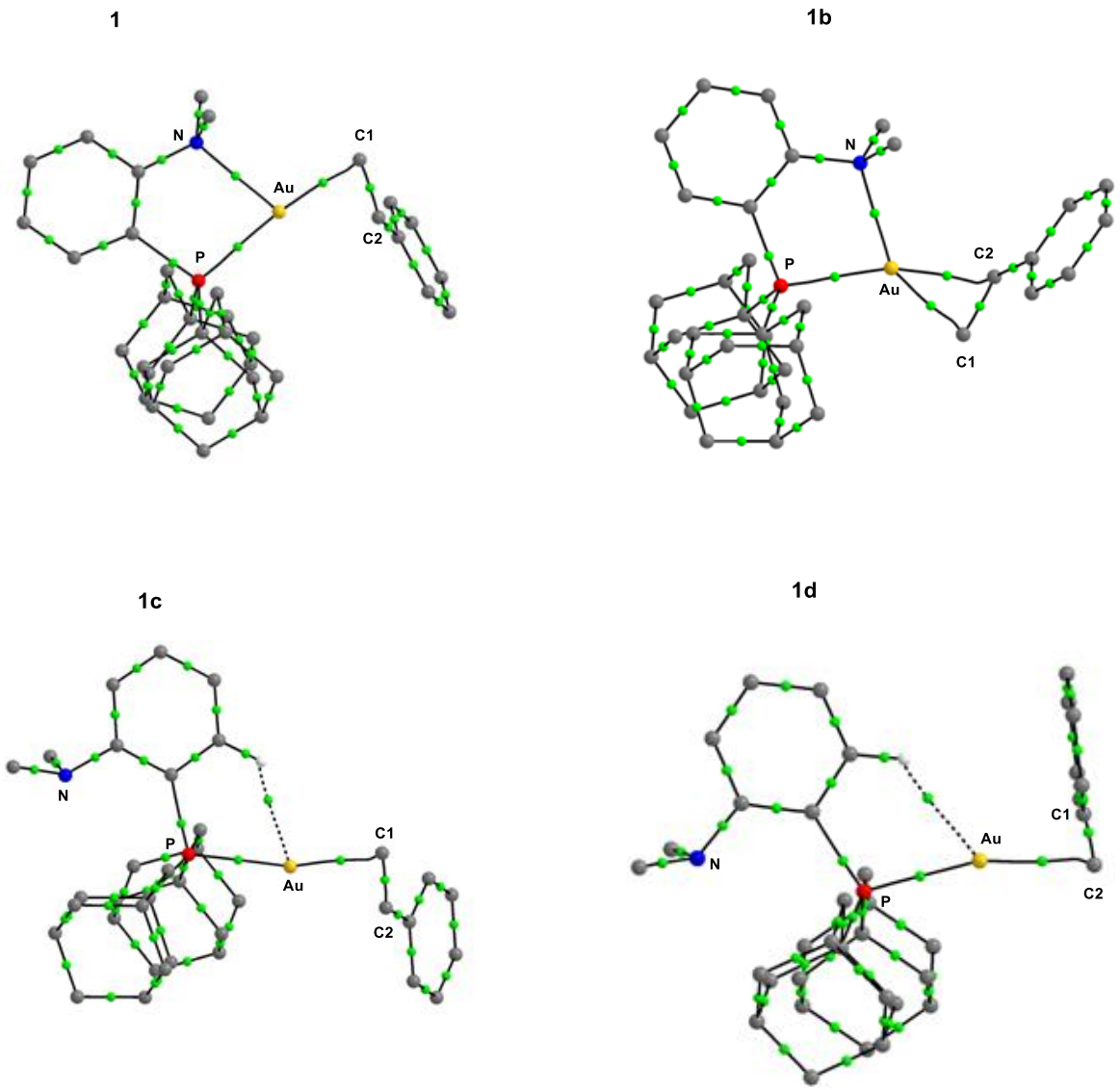


Figure S29. AIM analyses. Plot of the molecular graphs for the different isomers of styrene gold(I) complex (**1**, **1b**, **1c** and **1d)**. Green dots correspond to Bond Critical Points (BCP). Hydrogen atoms have been omitted for clarity.

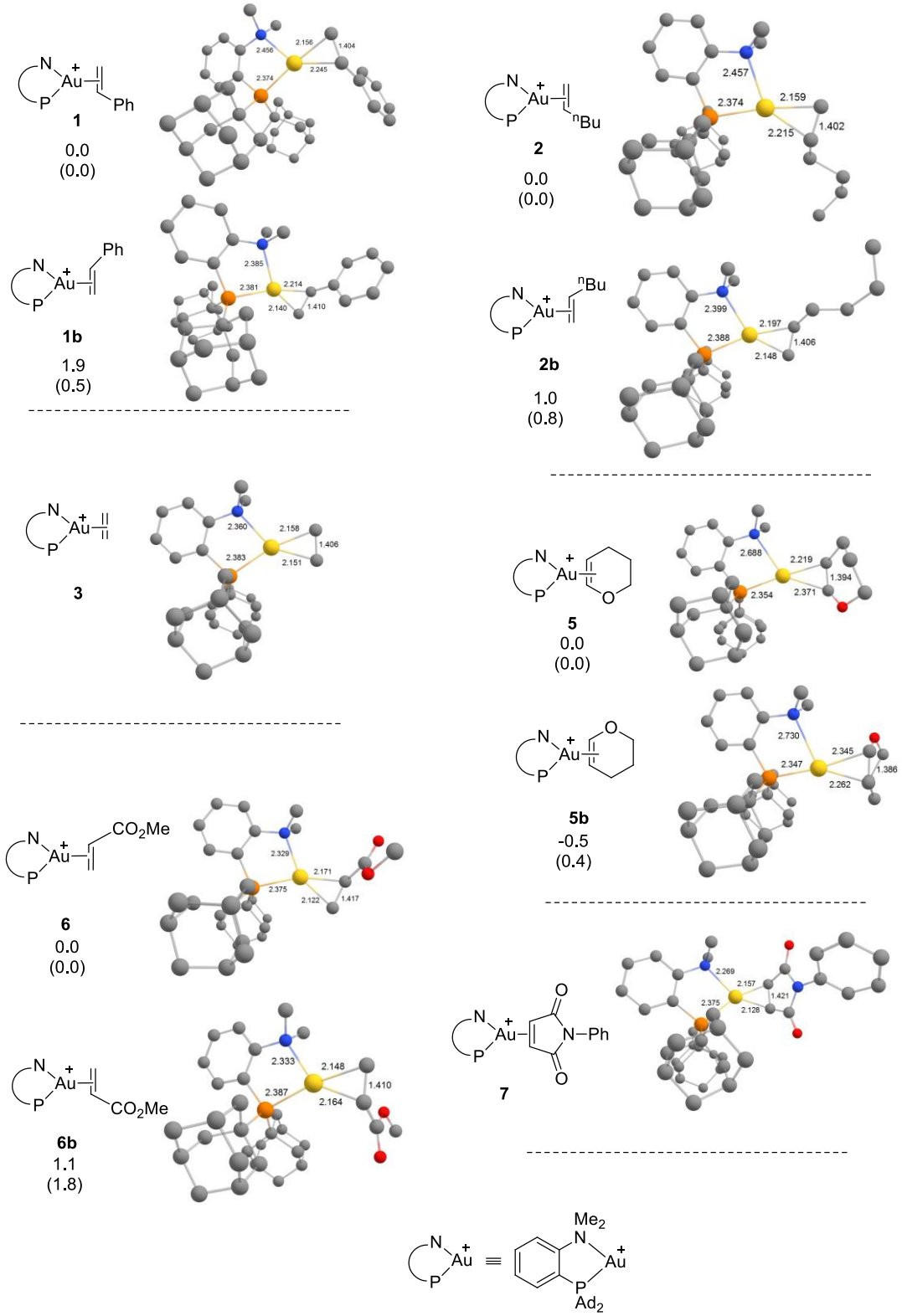
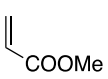
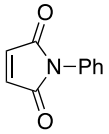


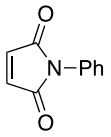
Figure S30. Geometrical structures computed at the SMD-(Dichloromethane)-B3PW91/SDD+f(Au)/6-31G**(other atoms) level of theory for the different alkene gold(I) complexes **1**–**3** and **5**–**7**. Main distances in Å. Relative stability (ΔG) in kcal·mol^{-1} and ΔE into brackets. Hydrogen atoms have been omitted for clarity.

Table S11. Main geometrical parameters computed at the SMD-(Dichloromethane)-B3PW91/ SDD+f(Au)/6-31G**(other atoms) level of theory for the different alkene gold(I) complexes **1**–**3** and **5**–**7**. Main distances in Å and bond angles in °. Comparison with the corresponding free olefin.

						
P–Au	2.354	2.374	2.378	2.385	2.375	2.375
N–Au	2.688	2.456	2.457	2.360	2.333	2.269
C=C	1.394	1.404	1.402	1.406	1.417	1.421
C=C^{olefin,a}	(1.339)	(1.339)	(1.334)	(1.331)	(1.335)	(1.334)
ΔC=C^{b}	0.055	0.075	0.063	0.067	0.082	0.087
Au–C1	2.219	2.156	2.159	2.158	2.171	2.157
Au–C2	2.371	2.245	2.215	2.151	2.122	2.128
Δ(Au–C)^{c}	0.152	0.089	0.056	0.007	0.049	0.029
N-Au-C1	106.92	105.96	107.35	110.78	114.80	112.02
N-Au-C2	141.74	143.05	144.54	148.85	153.29	150.73
P-Au-C1	175.61	172.27	171.48	166.66	161.89	163.25
P-Au-C2	140.48	135.73	134.20	128.59	123.37	124.73

[a] C=C bond computed for the free olefin. [b] Difference between C=C bond length in the complex and free olefin. [c] Difference between the two Au-C bond lengths.

Table S12. NBO analyses carried out at the B3PW91/SDD+f(Au)/6-31G**(other atoms) level of theory for the different alkene gold(I) complexes **1**–**3** and **5**–**7** on the geometry optimized in solvent.

NBO analysis						
						
C=C/Au interaction						
WBI (C=C)[a]	1.477	1.475	1.501	1.489	1.437	1.341
alkene → Au donation						
π_{CC}→ LP*(Au)[b]	119.8	143.7	158.2	175.0	168.1	178.3
NLMO[c] π_{CC}						
% Au	9.3	9.8	10.7	11.3	10.4	9.8
% C1	53.0	49.0	48.7	46.9	44.5	46.3
% C2	33.8	37.5	37.4	39.1	40.8	37.6
Au → alkene back-donation						
LP(Au)→π^*_{CC}[b]	23.0	36.7	38.9	45.1	45.1	48.9
NLMO[c] LP(Au)						
% Au	93.5	88.2	88.3	86.2	85.0	82.0
% C1	3.2	5.2	5.1	6.4	7.3	7.7
% C2	2.2	5.7	5.9	6.7	6.5	8.3
N→Au interaction						
N–Au (Å)	2.688	2.456	2.457	2.360	2.333	2.269
WBI (N–Au)[a]	0.048	0.085	0.093	0.125	0.138	0.167
LP(N)→Au[b]	10.8	20.0	22.0	32.4	34.0	44.0
NLMO[c] LP(N)						
% Au	1.1	2.0	2.2	3.3	3.6	4.4
% N	91.7	90.7	90.6	89.7	88.9	87.5

[a] Wiberg Bond Index. [b] Stabilizing interaction ΔE(2) at the 2nd order perturbation theory in kcal·mol^{-1}.
[c] Natural Localized Molecular Orbital with percentages of the main atoms (%) involved.

Table S13. CDA analyses carried out at the B3PW91/SDD+f(Au)/6-31G**(other atoms) level of theory for the different alkene gold(I) complexes **1**–**3** and **5**–**7** on the geometry optimized in solvent.

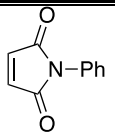
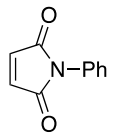
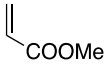
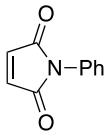
CDA analysis						
						
CC→Au donation (d)	0.411	0.416	0.529	0.477	0.485	0.399
Au→CC back-donation (b)	0.146	0.211	0.230	0.262	0.274	0.323
d/b ratio	2.82	1.97	2.30	1.82	1.77	1.24
Au↔C repulsion	-0.283	-0.334	-0.337	-0.355	-0.366	-0.386
Residue term	-0.027	-0.016	-0.017	-0.011	-0.017	-0.028

Table S14. AIM analyses carried out in gas phase at the B3PW91/SDD+f(Au)/6-31G**(other atoms) level of theory for the different alkene gold(I) complexes **1**–**3** and **5**–**7** on the geometry optimized in solvent. Charge transfer (CT) from ligand to metal fragment, density $\rho(r_c)$ in e.bohr^{-3}, Laplacian of the density $\nabla^2\rho(r_c)$ in e.bohr^{-5}, ellipticity ε and bond index δ.

AIM analysis							
							
Charge Transfer CT (CC→Au)							
		0.25	0.14	0.14	0.07	-0.02	-0.10
Main AIM parameters							
C=C	**$\rho(r_c)$**	0.313 (0.342)[a]	0.305 (0.341)[a]	0.307 (0.343)[a]	0.303 (0.344)[a]	0.297 (0.344)[a]	0.297 (0.347)[a]
	$\Delta(\rho(r_c))$[b]	0.029	0.036	0.036	0.041	0.047	0.050
	$\nabla^2\rho(r_c)$	-0.852	-0.797	-0.08	-0.786	-0.751	-0.739
	ε	0.27	0.22	0.23	0.23	0.21	0.19
	δ(C1=C2)	1.29 (1.70)[a]	1.31 (1.80)[a]	1.32 (1.85)[a]	1.32 (1.92)[a]	1.26 (1.82)[a]	1.22 (1.75)[a]
Au-C1	**$\rho(r_c)$**	0.09	0.010	0.090	0.102	0.099	0.102
	$\nabla^2\rho(r_c)$	0.147	0.152	0.212	0.172	0.192	0.182
	ε	0.27	0.38	5.40	0.79	1.16	0.81
	δ(Au-C1)	0.571	0.649	0.603	0.667	0.628	0.644
Au-C2	**$\rho(r_c)$**			0.101	0.102	0.108	0.108
	$\nabla^2\rho(r_c)$			0.160	0.166	0.142	0.153
	ε	No BCP	No BCP	0.51	0.83	0.48	0.52
	δ(Au-C2)			0.652	0.697	0.722	0.702
Au-N	**$\rho(r_c)$**	0.035	0.054	0.053	0.064	0.068	0.078
	$\nabla^2\rho(r_c)$	0.110	0.178	0.178	0.219	0.231	0.212
	ε	0.06	0.04	0.04	0.04	0.05	0.04
	δ(Au-N)	0.269	0.383	0.385	0.448	0.474	0.516

[a] Value for free olefin. [b] Difference between density in the complex and in the free olefin

Table S15. Charge transfer (CT) computed from Hirshfeld or Bader charges for the different alkene gold(I) complexes **1**–**3** and **5**–**7**.

Charge transfer CT (CC→Au)						
						
Compound	**5**	**1**	**2**	**3**	**6**	**7**
BADER	0.25	0.14	0.14	0.07	-0.02	-0.10
Hirshfield	0.16	0.06	0.05	-0.003	-0.06	-0.12

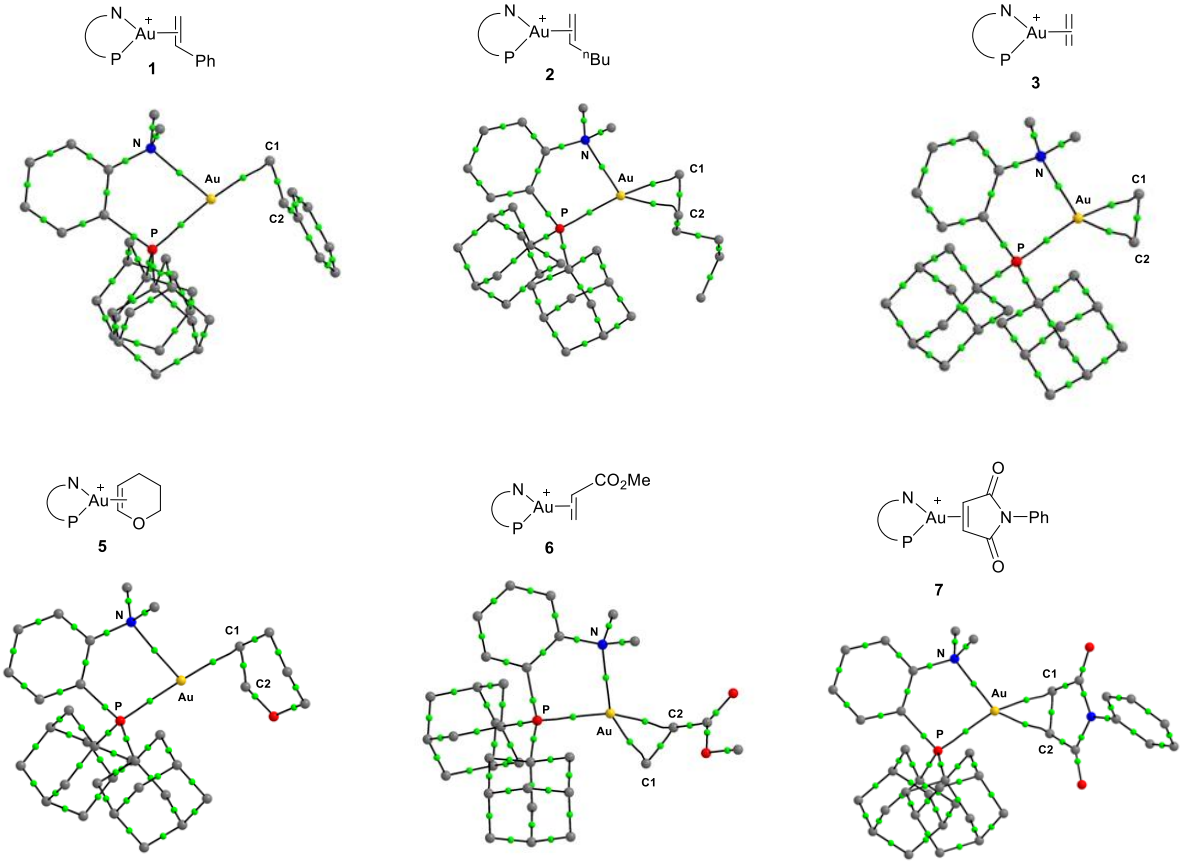
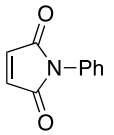


Figure S31. AIM analyses. Molecular graphs for the different alkene gold(I) complexes **1**–**3** and **5**–**7**. Green dots correspond to Bond Critical Points (BCP). Hydrogen atoms have been omitted for clarity.

Table S16. NBO and AIM analyses computed at the B3PW91/6-31G**(other atoms) level of theory for the different olefins on the geometry optimized in solvent.

						
C1=C2 (Å)	1.339	1.339	1.334	1.331	1.335	1.335
NBO analysis						
WBI (C=C)[a]	1.841	1.900	1.979	2.040	1.923	1.875
Δ(WBI)[b]	0.364	0.425	0.478	0.551	0.486	0.510
AIM analysis						
$\rho(r_c)$[c]	0.342	0.341	0.343	0.344	0.344	0.347
$\Delta(\rho(r_c))$[b,c]	0.029	0.036	0.036	0.041	0.047	0.050
δ(C1-C2)[a]	1.698	1.796	1.850	1.917	1.816	1.753
Δδ(C1-C2)[a,b]	0.41	0.49	0.53	0.60	0.56	0.53

[a] Bond Indexes. [b] Difference between the gold complex and the free olefin. [c] Density $\rho(r_c)$ in e.bohr^{-3}.

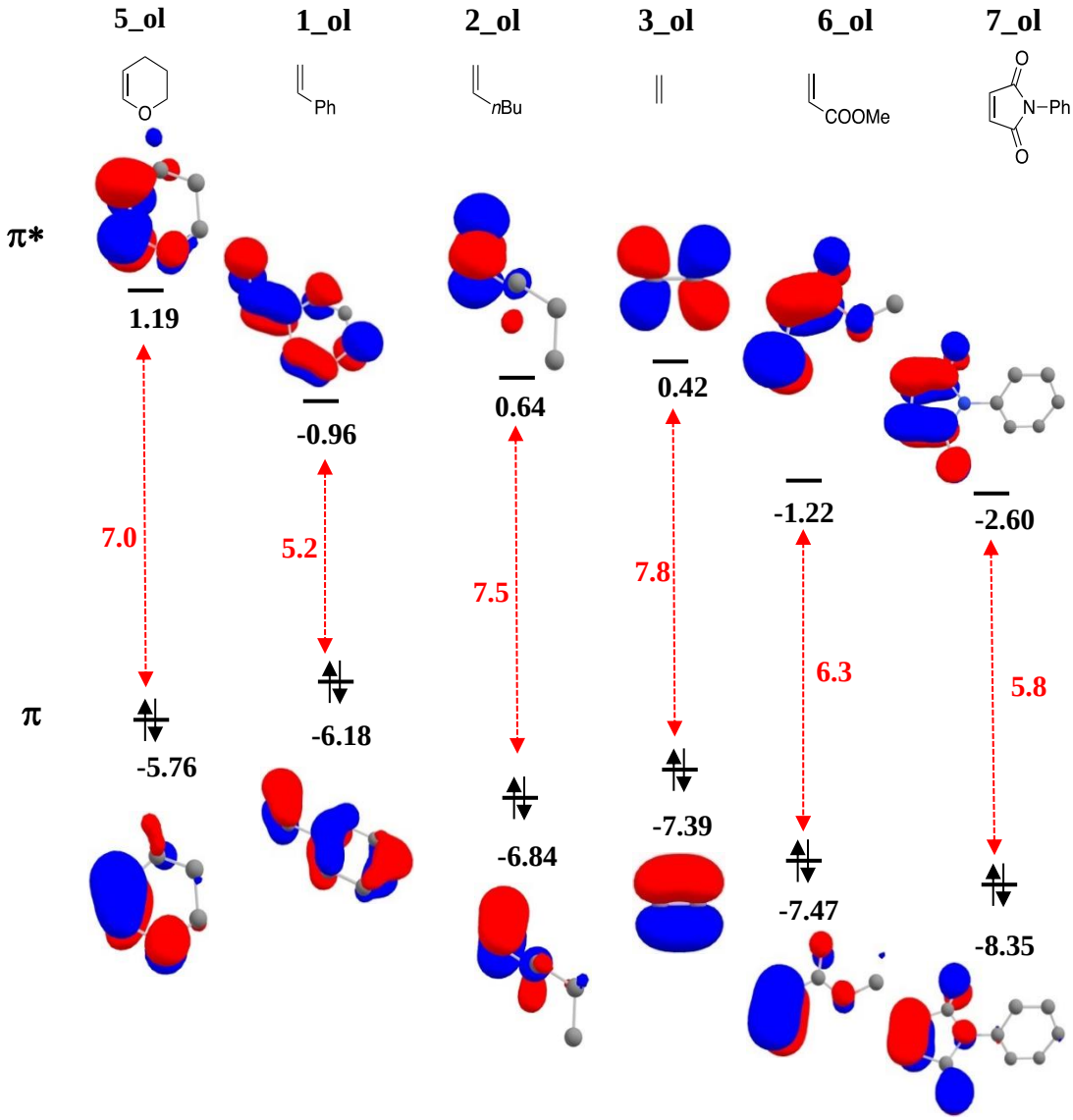


Figure S32. Energetic positions (Kohn-Sham energies in eV) of the $\pi_{C=C}$ and $\pi^*_{C=C}$ orbitals of the different olefins computed at the SMD-(Dichloromethane)-B3PW91/SDD+f(Au)/6-31G**(other atoms) level of theory.

6. Z-matrices and energies in au

(P^N)Au(alkene)$^+$ complexes

1

Sum of electronic and zero-point Energies= -1931.372433
Sum of electronic and thermal Enthalpies = -1931.336238
Sum of electronic and thermal Free Energies = -1931.439716

C	-1.79669	-0.07375	1.74950
C	-2.70766	0.85515	2.28496
H	-2.80687	1.83128	1.82599
C	-3.48674	0.55930	3.39719
H	-4.17965	1.30021	3.78502
C	-3.37114	-0.68921	4.00337
H	-3.97544	-0.93961	4.87065
C	-2.47048	-1.61917	3.49784
H	-2.38278	-2.58772	3.98108
C	-1.67615	-1.32863	2.38134
C	-1.44026	-3.56075	1.46906
H	-1.98696	-4.04419	2.29000
H	-0.70452	-4.26907	1.08096
H	-2.14522	-3.31036	0.67358
C	0.25347	-2.67037	2.95780
H	0.78257	-1.76452	3.26134
H	0.97333	-3.38292	2.54804
H	-0.21233	-3.12263	3.84346
C	0.21296	1.90807	0.67138
C	0.75154	1.74813	2.11256
H	1.30762	0.80389	2.19859
H	-0.07874	1.70330	2.82597
C	1.67202	2.92848	2.47054
H	2.03042	2.78928	3.49843
C	1.42547	1.96293	-0.28862
H	1.98687	1.02377	-0.22051
H	1.09097	2.06351	-1.32660
C	0.36611	4.41580	0.93379
H	-0.21087	5.34603	0.85736
C	1.55465	4.45909	-0.03594
H	2.20585	5.30956	0.20453
H	1.19914	4.60611	-1.06449
C	2.34223	3.14542	0.07086
H	3.18428	3.15533	-0.63219
C	-0.55941	3.23968	0.56260
H	-0.92581	3.37870	-0.46046
H	-1.43059	3.24134	1.22632
C	2.86235	2.97127	1.50360
H	3.53137	3.80072	1.76707
H	3.44859	2.04645	1.58324
C	0.87866	4.23952	2.37016
H	0.03753	4.22878	3.07616
H	1.51883	5.08735	2.64660
C	-1.99379	0.49594	-1.18156
C	-2.66887	-0.45908	-3.90815
H	-3.31061	-0.47732	-4.79842
H	-1.82942	-1.14016	-4.10255
C	-4.11719	1.43009	-2.18586
H	-4.95682	2.10962	-1.99207
C	-1.22449	0.97581	-2.43233
H	-0.85069	1.99361	-2.27540
H	-0.35492	0.33012	-2.61185
C	-3.45889	-0.93141	-2.67923
H	-3.82183	-1.95438	-2.84087
C	-3.20273	1.42755	-0.94491
H	-3.78095	1.08046	-0.08191
H	-2.87160	2.44880	-0.73181
C	-2.14949	0.96416	-3.66238
H	-1.57486	1.30610	-4.53236
C	-4.64544	0.01129	-2.43487
H	-5.23125	-0.33096	-1.57146
H	-5.31749	0.00471	-3.30299
C	-2.53669	-0.92954	-1.44734
H	-1.70108	-1.62354	-1.61263
H	-3.08885	-1.28689	-0.56862
C	-3.33288	1.91073	-3.41402
H	-3.98908	1.93362	-4.29369
H	-2.97026	2.93524	-3.25652
Au	0.59007	-1.57932	-0.00631
N	-0.73805	-2.34094	1.91443
P	-0.78142	0.33917	0.27008
C	2.22326	-2.19812	-1.41673
H	1.73907	-2.19576	-2.39232
C	1.87539	-3.22874	-0.52969
H	2.51931	-3.48922	0.30728
H	1.21724	-4.01979	-0.88372
C	3.43521	-1.35612	-1.34334
C	4.27858	-1.32325	-0.21964
C	3.77789	-0.58087	-2.46198
C	5.42704	-0.53859	-0.22098
C	4.92898	0.20408	-2.46234
C	5.75753	0.22802	-1.34147
H	4.03867	-1.91225	0.66113
H	3.13667	-0.60149	-3.34021
H	6.07043	-0.52686	0.65460
H	5.17989	0.79303	-3.34015
H	6.65713	0.83702	-1.33869

1b

Sum of electronic and zero-point Energies= -1931.371662
Sum of electronic and thermal Enthalpies = -1931.336081
Sum of electronic and thermal Free Energies = -1931.436665

C	0.95937	-0.16052	2.07416
C	2.04674	0.19550	2.89289
H	2.92195	0.65513	2.44966
C	2.03361	-0.03048	4.26409
H	2.89022	0.25462	4.86772
C	0.91769	-0.62179	4.85110
H	0.88820	-0.80224	5.92182
C	-0.16414	-0.99048	4.06020
H	-1.02507	-1.45769	4.52857
C	-0.15707	-0.77485	2.67680
C	-2.54068	-0.50149	2.33560
H	-2.79427	-0.72992	3.37877
H	-3.37379	-0.81003	1.70028
H	-2.39555	0.57553	2.23359
C	-1.50438	-2.67343	2.01580
H	-0.60735	-3.18790	1.66533
H	-2.35173	-2.97132	1.39513
H	-1.70811	-2.97887	3.04991
C	2.45812	-0.79759	-0.46648
C	2.43933	-2.20838	0.17020
H	1.45870	-2.67756	0.00656
H	2.59135	-2.13944	1.25317
C	3.54462	-3.08582	-0.44439
H	3.50749	-4.07365	0.03226
C	2.23856	-0.96306	-1.99061
H	1.26351	-1.43164	-2.17113
H	2.22671	0.01165	-2.48853
C	4.94473	-1.04519	-0.83947
H	5.91499	-0.56920	-0.64974
C	4.71844	-1.18305	-2.35089
H	5.51358	-1.79415	-2.79747
H	4.76211	-0.19720	-2.83281
C	3.35140	-1.83499	-2.59973
H	3.17109	-1.91936	-3.67888
C	3.84137	-0.15484	-0.23404
H	3.88013	0.83519	-0.70231
H	4.03316	-0.02300	0.83597
C	3.31886	-3.22681	-1.95587
H	4.09617	-3.86537	-2.39515
H	2.35372	-3.71320	-2.15219
C	4.90993	-2.43391	-0.18490
H	5.08889	-2.34823	0.89512
H	5.71102	-3.06221	-0.59517

C	0.99873	2.02925	0.02464
C	-0.38234	4.33517	-1.22881
H	-0.49361	5.40967	-1.42369
H	-1.19062	3.82582	-1.77075
C	1.98083	4.30305	0.51887
H	2.78660	4.81518	1.05954
C	1.12132	2.33446	-1.48395
H	2.09569	1.99775	-1.85511
H	0.34922	1.78840	-2.04161
C	-0.49784	4.05774	0.27675
H	-1.47686	4.39128	0.64328
C	2.10631	2.78982	0.78421
H	2.01728	2.61109	1.86087
H	3.09748	2.44415	0.47367
C	0.98310	3.84733	-1.73235
H	1.07001	4.03158	-2.81051
C	0.61933	4.79826	1.02532
H	0.53149	4.62459	2.10596
H	0.52691	5.88013	0.86402
C	-0.37266	2.54418	0.52607
H	-1.18219	2.01475	0.00413
H	-0.48192	2.33496	1.59776
C	2.10375	4.58419	-0.98509
H	2.03754	5.66388	-1.17189
H	3.08403	4.25461	-1.35454
Au	-1.09655	-0.78296	-0.43769
N	-1.31629	-1.20904	1.89892
P	0.98005	0.14834	0.26157
C	-2.84941	-1.49768	-1.58653
H	-2.85502	-2.58012	-1.46041
C	-1.85741	-0.95843	-2.43063
H	-1.97580	0.02253	-2.88517
H	-1.20053	-1.63772	-2.96843
C	-4.11487	-0.83492	-1.20278
C	-4.37845	0.52327	-1.45201
C	-5.10956	-1.60025	-0.57171
C	-5.59214	1.09129	-1.07644
C	-6.32448	-1.03017	-0.19685
C	-6.57027	0.31957	-0.44511
H	-3.63447	1.14132	-1.94731
H	-4.92834	-2.65648	-0.38507
H	-5.77848	2.14209	-1.28174
H	-7.08074	-1.64353	0.28564
H	-7.51692	0.76685	-0.15541

1c

Sum of electronic and zero-point Energies= -1931.356536
Sum of electronic and thermal Enthalpies = -1931.320389
Sum of electronic and thermal Free Energies = -1931.423562

C	1.66571	0.50998	-1.74720
C	1.07432	-0.02999	-2.90849
H	0.15776	-0.60726	-2.81528
C	1.61492	0.14109	-4.17798
H	1.12070	-0.30074	-5.03832
C	2.78457	0.87797	-4.32656
H	3.22732	1.02727	-5.30750
C	3.38181	1.43079	-3.20041
H	4.29044	2.01522	-3.31500
C	2.85293	1.26696	-1.91184
C	3.47695	3.35140	-0.88217
H	4.05225	3.75754	-1.73107
H	3.89386	3.77408	0.03806
H	2.44450	3.68991	-0.97871
C	4.94832	1.48750	-0.72324
H	5.05008	0.40463	-0.82147
H	5.34336	1.78574	0.25363
H	5.57759	1.95795	-1.49641
C	0.15940	1.63827	0.74154
C	-0.27069	2.64292	-0.35333
H	-1.02423	2.17785	-1.00425
H	0.57930	2.90551	-0.98960
C	-0.85069	3.91407	0.29009
H	-1.12605	4.61253	-0.51011
C	-1.10212	1.28667	1.57083
H	-1.85965	0.82868	0.92125
H	-0.86079	0.55875	2.35256
C	0.59729	3.56588	2.30904
H	1.35687	4.01829	2.95904
C	-0.64376	3.20227	3.13543
H	-1.06298	4.10057	3.60713
H	-0.37110	2.51171	3.94469
C	-1.68872	2.55722	2.21509
H	-2.57286	2.26922	2.79760
C	1.18887	2.28571	1.68887
H	1.43491	1.58392	2.49443
H	2.11556	2.50360	1.15267
C	-2.09074	3.55085	1.11640
H	-2.52427	4.45431	1.56449
H	-2.86106	3.10960	0.47014
C	0.20627	4.55532	1.20167
H	1.09046	4.83852	0.61667
H	-0.19216	5.47701	1.64541
C	1.78733	-1.15672	0.84000
C	1.89947	-3.94415	1.84870
H	2.39548	-4.76131	2.38797
H	0.93976	-4.33558	1.48473
C	3.86820	-1.77872	2.12423
H	4.82734	-1.38800	2.48695
C	0.93538	-1.62959	2.04048
H	0.75929	-0.79452	2.72777
H	-0.04588	-1.98241	1.69215
C	2.76680	-3.48800	0.66716
H	2.92978	-4.32609	-0.02206
C	3.14447	-0.65196	1.36202
H	3.75774	-0.32194	0.52337
H	3.01073	0.20928	2.02288
C	1.66375	-2.75758	2.79304
H	1.03603	-3.07173	3.63642
C	4.11457	-2.96725	1.18520
H	4.74992	-2.66171	0.34351
H	4.64782	-3.76494	1.71849
C	2.04315	-2.36508	-0.09629
H	1.08902	-2.74151	-0.49119
H	2.64818	-2.05202	-0.95583
C	3.01069	-2.23428	3.31275
H	3.53015	-3.02310	3.87217
H	2.84906	-1.39918	4.00727
Au	-1.17901	-1.12369	-0.76774
N	3.53938	1.88838	-0.80871
P	0.76834	0.08431	-0.16899
C	-3.29411	-2.16452	-0.65778
H	-3.11083	-2.90152	0.12411
C	-2.67694	-2.36991	-1.87433
H	-2.94413	-1.79780	-2.75979
H	-2.11846	-3.28824	-2.03949
C	-4.32804	-1.16996	-0.33329
C	-4.78151	-0.20513	-1.25044
C	-4.90261	-1.21038	0.94762
C	-5.78165	0.68963	-0.88942
C	-5.90551	-0.31340	1.30583
C	-6.34682	0.63883	0.38831
H	-4.35555	-0.15513	-2.24840
H	-4.56100	-1.95623	1.66128
H	-6.12751	1.42840	-1.60683
H	-6.34301	-0.36011	2.29890
H	-7.13023	1.33903	0.66411

1d

Sum of electronic and zero-point Energies= -1931.356552
Sum of electronic and thermal Enthalpies = -1931.320304
Sum of electronic and thermal Free Energies = -1931.424069

C	0.67888	0.46933	1.94192
C	-0.49639	0.05925	2.60507
H	-1.27538	-0.44287	2.03763
C	-0.71237	0.27835	3.96075

H	-1.63835	-0.05551	4.41968
C	0.26506	0.92298	4.71055
H	0.12283	1.10397	5.77240
C	1.43484	1.33351	4.08358
H	2.20233	1.83252	4.66847
C	1.66748	1.12593	2.71605
C	4.05736	0.85020	2.69541
H	4.23699	1.06192	3.76289
H	4.95846	1.13524	2.14209
H	3.90902	-0.22504	2.58194
C	3.12640	3.02244	2.37294
H	2.23756	3.59200	2.09237
H	3.96247	3.35417	1.74828
H	3.37140	3.27006	3.41861
C	2.15104	-1.00063	-0.40138
C	2.31887	-2.04087	0.73062
H	1.37077	-2.57545	0.88551
H	2.56299	-1.54047	1.67276
C	3.42991	-3.04351	0.37247
H	3.53281	-3.75816	1.19859
C	1.78546	-1.76344	-1.70071
H	0.83704	-2.30254	-1.57199
H	1.64891	-1.06229	-2.53093
C	4.59210	-1.28204	-0.97999
H	5.53098	-0.73292	-1.12556
C	4.22240	-2.02829	-2.26882
H	5.01351	-2.74117	-2.53554
H	4.13195	-1.32023	-3.10319
C	2.89609	-2.77078	-2.05611
H	2.60707	-3.28933	-2.97903
C	3.48251	-0.26502	-0.64770
H	3.36927	0.41753	-1.49683
H	3.74924	0.34032	0.22082
C	3.05386	-3.78610	-0.91626
H	3.82994	-4.51960	-1.17052
H	2.11914	-4.34456	-0.77192
C	4.75154	-2.28814	0.16811
H	5.03852	-1.76950	1.09177
H	5.55668	-2.99696	-0.06486
C	0.44374	1.71239	-0.85473
C	-1.46467	3.34437	-2.43922
H	-1.73249	4.25201	-2.99558
H	-2.33852	2.67974	-2.47009
C	1.28770	3.96559	-1.61671
H	2.15718	4.63436	-1.58847
C	0.09679	1.37618	-2.32456
H	0.94892	0.88739	-2.81045
H	-0.74973	0.67621	-2.36382
C	-1.12020	3.69932	-0.98649
H	-1.98341	4.17490	-0.50417
C	1.64298	2.67896	-0.84792
H	1.92279	2.91834	0.17844
H	2.51158	2.20899	-1.31735
C	-0.25513	2.66324	-3.09429
H	-0.49617	2.39070	-4.12955
C	0.08314	4.65212	-0.95844
H	0.32211	4.92788	0.07718
H	-0.15990	5.58070	-1.49089
C	-0.77478	2.41826	-0.20948
H	-1.63999	1.74039	-0.20520
H	-0.55634	2.67088	0.83461
C	0.94784	3.61704	-3.07225
H	0.71535	4.53004	-3.63567
H	1.81169	3.14788	-3.56164
Au	-1.23775	-1.20176	-0.34646
N	2.91073	1.58795	2.15669
P	0.68509	0.09831	0.11234
C	-3.31426	-2.31005	-0.16098
H	-3.08612	-3.02480	0.62979
C	-2.72202	-2.51945	-1.38903
H	-3.03142	-1.97511	-2.27817
H	-2.13651	-3.42137	-1.55057
C	-4.37310	-1.34491	0.17207
C	-4.87464	-0.40702	-0.74779
C	-4.92431	-1.39044	1.46289
C	-5.89794	0.45776	-0.37933
C	-5.95138	-0.52415	1.82838
C	-6.43940	0.40255	0.90835
H	-4.46765	-0.35466	-1.75343
H	-4.54662	-2.11732	2.17812
H	-6.28014	1.17651	-1.09863
H	-6.37102	-0.57498	2.82892
H	-7.24147	1.07898	1.18973

2

Sum of electronic and zero-point Energies= -1857.574602
Sum of electronic and thermal Enthalpies = -1857.537813
Sum of electronic and thermal Free Energies = -1857.641503

C	2.15067	0.11986	-1.28398
C	3.32415	0.89051	-1.19094
H	3.43582	1.59803	-0.37767
C	4.34852	0.77738	-2.12379
H	5.24152	1.38725	-2.02340
C	4.21907	-0.12028	-3.18103
H	5.01165	-0.22410	-3.91665
C	3.06222	-0.88108	-3.30044
H	2.96401	-1.57127	-4.13300
C	2.02104	-0.76938	-2.37048
C	1.13104	-3.01679	-2.53276
H	1.80810	-3.31550	-3.34455
H	0.20007	-3.57919	-2.63655
H	1.59422	-3.26932	-1.57669
C	0.14861	-1.22230	-3.83527
H	-0.09858	-0.15861	-3.83632
H	-0.77502	-1.80052	-3.91454
H	0.77225	-1.44171	-4.71246
C	0.23378	2.08998	-0.05447
C	0.20222	2.54243	-1.53368
H	-0.42155	1.85496	-2.12238
H	1.21016	2.51377	-1.96127
C	-0.35778	3.97109	-1.64247
H	-0.35987	4.26312	-2.70026
C	-1.21268	2.14728	0.49304
H	-1.84544	1.45594	-0.07716
H	-1.23924	1.82025	1.53841
C	0.54331	4.49997	0.63456
H	1.18604	5.17518	1.21340
C	-0.88585	4.53736	1.19309
H	-1.28693	5.55754	1.13545
H	-0.88508	4.25160	2.25339
C	-1.77032	3.57764	0.38480
H	-2.79117	3.58437	0.78719
C	1.10675	3.07081	0.75609
H	1.12179	2.77866	1.81183
H	2.14140	3.05828	0.39658
C	-1.78779	4.01220	-1.08747
H	-2.19791	5.02650	-1.17656
H	-2.44030	3.34919	-1.67133
C	0.53401	4.92907	-0.83949
H	1.55572	4.92257	-1.24198
H	0.15929	5.95685	-0.93065
C	1.52422	-0.32945	1.61239
C	1.16911	-2.24436	3.84802
H	1.48803	-2.69918	4.79480
H	0.23066	-2.73505	3.55627
C	3.32056	-0.29714	3.38927
H	4.25846	0.19022	3.68371
C	0.46425	-0.11362	2.71523
H	0.28885	0.95772	2.86374
H	-0.49049	-0.56328	2.41263
C	2.23989	-2.46637	2.77031
H	2.39757	-3.54154	2.61797
C	2.85460	0.31749	2.05405
H	3.62620	0.14412	1.29665
H	2.74236	1.39978	2.16822
C	0.94173	-0.73804	4.03784
H	0.17012	-0.57235	4.80030
C	3.55376	-1.80275	3.20528

H	4.33295	-1.97547	2.45115
H	3.90839	-2.24853	4.14372
C	1.76378	-1.84973	1.44405
H	0.83447	-2.34077	1.12327
H	2.51370	-2.02460	0.66211
C	2.25415	-0.06858	4.46996
H	2.59306	-0.48530	5.42737
H	2.09604	1.00685	4.62616
Au	-0.85533	-1.23081	-0.80755
N	0.82266	-1.57373	-2.56882
P	0.80824	0.27687	-0.03520
C	-2.79659	-1.93226	-0.00396
H	-2.52882	-2.46456	0.91021
C	-2.50592	-2.55876	-1.22364
H	-3.01645	-2.23743	-2.13103
H	-2.09737	-3.56779	-1.23446
C	-3.84995	-0.86997	0.16511
H	-3.99219	-0.32539	-0.77624
H	-3.52267	-0.14597	0.91826
C	-5.18434	-1.50024	0.60190
H	-5.49173	-2.23045	-0.15758
H	-5.02977	-2.06542	1.53167
C	-6.31230	-0.48394	0.81010
H	-7.24415	-1.03826	0.97945
H	-6.46238	0.08640	-0.11686
C	-6.09130	0.47938	1.97399
H	-5.94022	-0.06364	2.91473
H	-5.21880	1.12270	1.81768
H	-6.95790	1.13574	2.10838

2b

Sum of electronic and zero-point Energies= -1857.573280
Sum of electronic and thermal Enthalpies = -1857.536467
Sum of electronic and thermal Free Energies = -1857.639898

C	1.02656	-0.02690	2.05373
C	2.21623	0.23617	2.75761
H	3.10432	0.53617	2.21481
C	2.28962	0.12065	4.14060
H	3.22439	0.32969	4.65244
C	1.15850	-0.26010	4.85823
H	1.19540	-0.35014	5.94009
C	-0.02620	-0.52977	4.18392
H	-0.90189	-0.82660	4.75273
C	-0.10780	-0.42435	2.78987
C	-2.43461	0.19875	2.59413
H	-2.62260	0.11237	3.67232
H	-3.36120	-0.02873	2.06367
H	-2.13693	1.22427	2.36700
C	-1.78676	-2.13141	2.42269
H	-1.01108	-2.81589	2.07362
H	-2.71476	-2.34193	1.88671
H	-1.95812	-2.30387	3.49300
C	2.22283	-1.08342	-0.50447
C	2.07623	-2.41305	0.27313
H	1.03369	-2.75798	0.22343
H	2.32182	-2.26434	1.33042
C	3.00619	-3.48440	-0.32239
H	2.88286	-4.40969	0.25454
C	1.85919	-1.35827	-1.98479
H	0.81921	-1.70140	-2.04848
H	1.93345	-0.44043	-2.57629
C	4.61780	-1.69769	-1.02263
H	5.65352	-1.34232	-0.95132
C	4.25103	-1.94156	-2.49254
H	4.92369	-2.68975	-2.93155
H	4.37732	-1.01644	-3.07069
C	2.79650	-2.42572	-2.57775
H	2.51861	-2.58580	-3.62719
C	3.69126	-0.61474	-0.43546
H	3.81834	0.31491	-1.00123
H	3.98585	-0.41541	0.60013
C	2.64131	-3.73438	-1.79158
H	3.29251	-4.51054	-2.21429
H	1.60954	-4.10302	-1.86907
C	4.46072	-3.00184	-0.22720
H	4.73755	-2.84100	0.82319
H	5.13810	-3.76896	-0.62429
C	1.20163	1.94535	-0.19711
C	0.11504	4.30362	-1.63563
H	0.14727	5.36233	-1.92377
H	-0.76611	3.86434	-2.12247
C	2.49113	4.09875	0.08461
H	3.37077	4.54155	0.56860
C	1.32489	2.10045	-1.72901
H	2.23366	1.60259	-2.08365
H	0.47062	1.62204	-2.22616
C	-0.00238	4.17483	-0.11037
H	-0.91904	4.66863	0.23614
C	2.41688	2.61124	0.48096
H	2.32300	2.54056	1.56970
H	3.34563	2.10594	0.19632
C	1.38963	3.59076	-2.10710
H	1.47751	3.66864	-3.19802
C	1.22085	4.81803	0.55788
H	1.13342	4.75333	1.65052
H	1.27281	5.88422	0.30144
C	-0.07586	2.68539	0.27120
H	-0.96095	2.22911	-0.19385
H	-0.18809	2.58575	1.35856
C	2.61687	4.22785	-1.43977
H	2.69313	5.28585	-1.72227
H	3.53405	3.73450	-1.78813
Au	-1.29559	-0.58579	-0.24919
N	-1.38112	-0.73581	2.14386
P	0.93794	0.11624	0.22059
C	-3.19700	-1.20220	-1.16112
H	-3.30766	-2.26114	-0.91876
C	-2.25626	-0.86469	-2.14959
H	-2.32993	0.08982	-2.66902
H	-1.70219	-1.64086	-2.67296
C	-4.39214	-0.33905	-0.83547
H	-4.15094	0.71765	-1.00815
H	-4.64933	-0.44394	0.22438
C	-5.60649	-0.73217	-1.69384
H	-5.32687	-0.64472	-2.75177
H	-5.83925	-1.79268	-1.52282
C	-6.85994	0.11050	-1.43559
H	-7.61735	-0.16785	-2.17944
H	-6.62849	1.16853	-1.62048
C	-7.45739	-0.04572	-0.03895
H	-7.69139	-1.09514	0.17747
H	-6.77880	0.31167	0.74319
H	-8.38767	0.52512	0.05468

3

Sum of electronic and zero-point Energies= -1700.471377
Sum of electronic and thermal Enthalpies= -1700.440193
Sum of electronic and thermal Free Energies= -1700.530672

C	-0.097067000	-0.480048000	1.940464000
C	0.189210000	0.266367000	3.097816000
H	0.532265000	1.289945000	3.002213000
C	0.054633000	-0.278287000	4.369410000
H	0.286518000	0.322896000	5.243591000
C	-0.375589000	-1.595637000	4.509629000
H	-0.488833000	-2.036593000	5.495799000
C	-0.656426000	-2.354503000	3.379465000
H	-0.984682000	-3.382045000	3.502205000
C	-0.517139000	-1.816941000	2.094263000
C	-2.215696000	-3.121249000	0.953731000
H	-2.447666000	-3.721776000	1.842437000
H	-2.397900000	-3.730589000	0.066011000
H	-2.875038000	-2.251726000	0.930526000
C	0.096406000	-3.852665000	0.932365000
H	1.135495000	-3.518817000	0.909235000
H	-0.110123000	-4.443277000	0.037425000
H	-0.054383000	-4.489202000	1.813121000

C	1.900002000	0.784963000	0.064132000
C	2.787913000	-0.313907000	0.694706000
H	2.549335000	-1.289516000	0.248428000
H	2.591872000	-0.390313000	1.769700000
C	4.275677000	0.010383000	0.468282000
H	4.877381000	-0.781372000	0.932178000
C	2.218849000	0.845515000	-1.450666000
H	1.978617000	-0.119980000	-1.912628000
H	1.597927000	1.601051000	-1.943784000
C	3.745063000	2.458905000	0.474478000
H	3.968428000	3.426835000	0.940521000
C	4.035483000	2.527488000	-1.031248000
H	5.090712000	2.778076000	-1.200292000
H	3.437916000	3.322325000	-1.497181000
C	3.705787000	1.172469000	-1.672781000
H	3.894543000	1.215872000	-2.752976000
C	2.252940000	2.145322000	0.699880000
H	1.647156000	2.939692000	0.251182000
H	2.042339000	2.135548000	1.775007000
C	4.570449000	0.075756000	-1.036613000
1	5.634172000	0.289111000	-1.203902000
1	4.359330000	-0.893852000	-1.507428000
6	4.606417000	1.362526000	1.116858000
H	4.420250000	1.319542000	2.198312000
H	5.671280000	1.593595000	0.983483000
C	-1.194115000	1.629846000	0.108072000
C	-3.499888000	2.631611000	-1.469157000
H	-4.308618000	3.350273000	-1.654592000
H	-3.540865000	1.886600000	-2.275106000
C	-2.312353000	3.717363000	0.990475000
H	-2.274056000	4.462894000	1.794713000
C	-1.010393000	2.334162000	-1.254351000
H	-0.047981000	2.857216000	-1.283699000
H	-1.005417000	1.593396000	-2.064375000
C	-3.700501000	1.950084000	-0.108180000
H	-4.660899000	1.419475000	-0.094515000
C	-1.188992000	2.689423000	1.231829000
H	-1.351465000	2.209129000	2.202532000
H	-0.225617000	3.206774000	1.276642000
C	-2.143703000	3.350404000	-1.481117000
H	-1.987201000	3.832861000	-2.454076000
C	-3.671292000	3.005139000	1.006504000
H	-3.838491000	2.529917000	1.982137000
H	-4.480726000	3.731845000	0.859248000
C	-2.574169000	0.927285000	0.117336000
H	-2.607375000	0.167580000	-0.675566000
H	-2.725088000	0.412867000	1.075080000
C	-2.107944000	4.405689000	-0.366200000
H	-2.893788000	5.154563000	-0.529487000
H	-1.148043000	4.938767000	-0.381420000
Au	-0.466871000	-1.608892000	-1.132179000
N	-0.803476000	-2.676196000	0.945039000
P	0.091146000	0.242301000	0.260084000
C	-0.498884000	-1.710193000	-3.280276000
H	-1.245662000	-1.012594000	-3.653337000
C	-0.886435000	-2.958498000	-2.763224000
H	-0.176168000	-3.782796000	-2.740699000
H	-1.938710000	-3.234863000	-2.737413000
H	0.509740000	-1.560607000	-3.658880000

5

Sum of electronic and zero-point Energies= -1892.292661
Sum of electronic and thermal Enthalpies = -1892.257923
Sum of electronic and thermal Free Energies = -1892.356297

C	1.06316	0.17327	2.08335
C	2.27351	0.70928	2.56206
H	2.98185	1.13892	1.86395
C	2.59690	0.69852	3.91391
H	3.54149	1.11841	4.24710
C	1.70348	0.14687	4.82948
H	1.93862	0.13321	5.89011
C	0.50518	-0.39216	4.37792
H	-0.18904	-0.82488	5.09279
C	0.16889	-0.39337	3.01723
C	-2.23404	-0.23940	3.15729
H	-2.28257	-0.27707	4.25653
H	-3.15859	-0.67080	2.76372
H	-2.17853	0.80699	2.84815
C	-1.16891	-2.40342	2.96526
H	-0.33056	-2.94327	2.51791
H	-2.10061	-2.81603	2.56766
H	-1.15720	-2.57887	4.05176
C	2.12406	-0.67176	-0.62176
C	2.53611	-1.89573	0.22889
H	1.65845	-2.52767	0.42326
H	2.92407	-1.57136	1.20026
C	3.61545	-2.71421	-0.50252
H	3.89031	-3.56807	0.12957
C	1.58856	-1.19150	-1.97938
H	0.70384	-1.81717	-1.80683
H	1.26834	-0.35525	-2.61048
C	4.44831	-0.63102	-1.61750
H	5.32133	0.01170	-1.78773
C	3.89966	-1.12805	-2.96168
H	4.66949	-1.70023	-3.49565
H	3.63173	-0.27549	-3.59976
C	2.66906	-2.00924	-2.70803
H	2.25589	-2.35578	-3.66389
C	3.36988	0.19920	-0.89278
H	3.09916	1.05989	-1.51355
H	3.78644	0.58766	0.04248
C	3.06692	-3.21435	-1.84540
H	3.82595	-3.81495	-2.36324
H	2.19835	-3.86605	-1.68017
C	4.84710	-1.82968	-0.74635
H	5.25911	-1.48219	0.21038
H	5.63472	-2.41120	-1.24284
C	0.44655	2.02255	-0.18640
C	-1.39988	4.00294	-1.40446
H	-1.66494	5.02708	-1.69779
H	-2.23051	3.35456	-1.71410
C	1.23008	4.42463	-0.16336
H	2.05659	5.07764	0.14406
C	0.24519	2.12575	-1.71417
H	1.15807	1.82085	-2.23719
H	-0.55523	1.44494	-2.03287
C	-1.20416	3.92391	0.11615
H	-2.13157	4.21190	0.62730
C	1.57817	2.97957	0.24539
H	1.70951	2.93870	1.33189
H	2.52926	2.69224	-0.21319
C	-0.10342	3.57270	-2.10551
H	-0.23744	3.61612	-3.19368
C	-0.06358	4.85995	0.53826
H	0.06752	4.82921	1.62807
H	-0.30865	5.89648	0.27216
C	-0.85700	2.47855	0.51404
H	-1.68151	1.80794	0.23409
H	-0.73796	2.41326	1.60309
C	1.04314	4.50359	-1.68499
H	0.81862	5.53602	-1.98283
H	1.97098	4.21569	-2.19708
Au	-1.32325	-0.97459	-0.06433
N	-1.09018	-0.98017	2.61329
P	0.68738	0.19994	0.28107
C	-4.45292	-1.38892	-0.16310
C	-3.17520	-2.09395	-0.55376
C	-2.63628	-1.87645	-1.82106
O	-3.10711	-1.01555	-2.72857
C	-4.38967	-0.39287	-2.45346
C	-4.60520	-0.10674	-0.98028
H	-4.46795	-1.17083	0.90891
H	-2.93812	-3.05157	-0.09078
H	-1.87207	-2.52574	-2.24146
H	-4.39499	0.51730	-3.05563
H	-3.87889	0.64234	-0.64261
H	-5.30070	-2.06012	-0.35685
H	-5.60290	0.32593	-0.85516

H	-5.15993	-1.07162	-2.83817

5b

Sum of electronic and zero-point Energies= -1892.292051
Sum of electronic and thermal Enthalpies= -1892.256968
Sum of electronic and thermal Free Energies= -1892.357068

C	-0.927933000	-0.049186000	2.097074000
C	-2.061395000	0.493948000	2.731227000
H	-2.795128000	1.037674000	2.149206000
C	-2.272556000	0.358083000	4.098574000
H	-3.158006000	0.792319000	4.553566000
C	-1.343570000	-0.333557000	4.871944000
H	-1.494204000	-0.450166000	5.941620000
C	-0.214728000	-0.873197000	4.267189000
H	0.511017000	-1.407117000	4.874144000
C	0.013985000	-0.740706000	2.890606000
C	1.249792000	-2.768180000	2.449351000
H	1.315703000	-3.107109000	3.495046000
H	2.125286000	-3.149926000	1.915653000
H	0.353009000	-3.201817000	2.000025000
C	2.427222000	-0.697223000	2.874789000
H	2.383379000	0.387892000	2.750276000
H	3.295158000	-1.071945000	2.325299000
H	2.572837000	-0.920016000	3.943496000
C	-0.638083000	2.044973000	-0.051482000
C	0.288907000	2.662126000	1.023124000
H	1.266102000	2.159324000	1.005728000
H	-0.135535000	2.513208000	2.022024000
C	0.473799000	4.167942000	0.766450000
H	1.129085000	4.574388000	1.547150000
C	0.008464000	2.285765000	-1.437658000
H	0.981238000	1.778633000	-1.480243000
H	-0.611725000	1.855726000	-2.230935000
C	-1.806926000	4.275213000	-0.264132000
H	-2.790691000	4.760045000	-0.224441000
C	-1.175585000	4.492576000	-1.644755000
H	-1.056153000	5.566006000	-1.840861000
H	-1.832585000	4.092954000	-2.428630000
C	0.190924000	3.793182000	-1.690566000
H	0.644172000	3.926246000	-2.681082000
C	-2.001593000	2.766659000	-0.018259000
H	-2.661367000	2.356172000	-0.790544000
H	-2.495035000	2.626003000	0.948601000
C	1.107693000	4.387900000	-0.613200000
H	1.254943000	5.460821000	-0.792637000
H	2.098829000	3.916900000	-0.653921000
C	-0.893943000	4.863682000	0.821005000
H	-1.347787000	4.729859000	1.811886000
H	-0.773212000	5.943653000	0.665650000
C	-2.114537000	-0.771084000	-0.560686000
C	-2.774869000	-2.913938000	-2.504201000
H	-3.490338000	-3.548950000	-3.042623000
H	-1.771119000	-3.198053000	-2.848446000
C	-4.572502000	-1.289923000	-0.839544000
H	-5.575244000	-1.006759000	-0.495415000
C	-2.018225000	-0.551314000	-2.086414000
H	-2.215674000	0.499625000	-2.326835000
H	-1.002240000	-0.783242000	-2.433434000
C	-2.899831000	-3.143194000	-0.990955000
H	-2.695377000	-4.195281000	-0.754927000
C	-3.542665000	-0.419352000	-0.091407000
H	-3.643108000	-0.603124000	0.983185000
H	-3.761846000	0.638113000	-0.269549000
C	-3.043854000	-1.435764000	-2.816786000
H	-2.947422000	-1.260239000	-3.895614000
C	-4.313909000	-2.769667000	-0.526547000
H	-4.419456000	-2.952191000	0.551053000
H	-5.056432000	-3.398841000	-1.034170000
C	-1.867181000	-2.269718000	-0.257368000
H	-0.854001000	-2.551807000	-0.576060000
H	-1.931641000	-2.446331000	0.823728000
C	-4.457262000	-1.057063000	-2.352153000
H	-5.204314000	-1.661288000	-2.883071000
H	-4.664445000	-0.005649000	-2.592391000
Au	1.331316000	-0.818379000	-0.360161000
N	1.213443000	-1.308083000	2.322982000
P	-0.697119000	0.172026000	0.282009000
C	3.465114000	-0.281626000	-2.636351000
C	2.845485000	-1.450398000	-1.916913000
C	3.381772000	-1.897288000	-0.719527000
O	4.422888000	-1.334447000	-0.078654000
C	5.161552000	-0.320794000	-0.804542000
C	4.266096000	0.566033000	-1.649142000
H	2.696038000	0.314242000	-3.136943000
H	2.224047000	-2.150437000	-2.471400000
H	3.109363000	-2.857761000	-0.286181000
H	5.694672000	0.243100000	-0.037027000
H	3.584154000	1.122988000	-0.994593000
H	4.124386000	-0.669081000	-3.425618000
H	4.891243000	1.297164000	-2.171292000
H	5.897097000	-0.841714000	-1.429960000

6

Sum of electronic and zero-point Energies= -1928.224158
Sum of electronic and thermal Enthalpies = -1928.188744
Sum of electronic and thermal Free Energies = -1928.288831

C	0.71994	-0.23651	2.07499
C	1.75131	0.17028	2.94042
H	2.57331	0.76079	2.55346
C	1.74753	-0.17035	4.28782
H	2.55872	0.15738	4.93110
C	0.70098	-0.93327	4.79968
H	0.68245	-1.20883	5.85007
C	-0.32690	-1.34965	3.96125
H	-1.13265	-1.94830	4.37368
C	-0.33066	-1.01298	2.60305
C	-2.72717	-0.93192	2.23763
H	-2.95710	-1.24837	3.26205
H	-3.52354	-1.28228	1.57772
H	-2.68360	0.15835	2.20385
C	-1.49458	-2.97542	1.77717
H	-0.54453	-3.37827	1.42157
H	-2.29580	-3.29967	1.11031
H	-1.69664	-3.36707	2.78117
C	2.28766	-0.63047	-0.46548
C	2.34331	-2.07537	0.08738
H	1.39582	-2.59239	-0.12135
H	2.47519	-2.06132	1.17501
C	3.50919	-2.84636	-0.55700
H	3.52526	-3.86070	-0.13901
C	2.10025	-0.71533	-2.00071
H	1.15353	-1.22144	-2.22671
H	2.04421	0.28538	-2.43853
C	4.78636	-0.70443	-0.80470
H	5.72339	-0.18319	-0.57174
C	4.58832	-0.76248	-2.32578
H	5.42813	-1.29111	-2.79479
H	4.57192	0.25249	-2.74486
C	3.27007	-1.48414	-2.63890
H	3.11188	-1.51502	-3.72429
C	3.62392	0.07665	-0.15999
H	3.60892	1.09978	-0.55127
H	3.78995	0.13752	0.92124
C	3.31266	-2.91082	-2.07752
H	4.13196	-3.47615	-2.54003
H	2.38085	-3.44047	-2.31790
C	4.82914	-2.13047	-0.23711
H	4.99136	-2.10159	0.84857
H	5.67109	-2.68326	-0.67333
C	0.63474	2.06829	0.13065
C	-0.78477	4.32009	-1.17601
H	-0.96033	5.39115	-1.33954
H	-1.48614	3.77637	-1.82291
C	1.37294	4.38328	0.81846
H	2.07346	4.92763	1.46410
C	0.88581	2.45243	-1.34335

H	1.91503	2.20555	-1.62482
H	0.21605	1.88153	-2.00011
C	-1.03748	3.96499	0.29681
H	-2.07407	4.20507	0.56553
C	1.59291	2.87150	1.03593
H	1.40111	2.63423	2.08766
H	2.63678	2.61708	0.82233
C	0.65995	3.96074	-1.54438
H	0.84690	4.20145	-2.59848
C	-0.06934	4.75183	1.19051
H	-0.25852	4.52300	2.24756
H	-0.22817	5.83018	1.06072
C	-0.81643	2.45556	0.50606
H	-1.52607	1.89102	-0.11321
H	-1.01292	2.19371	1.55403
C	1.63377	4.74184	-0.65087
H	1.50246	5.82078	-0.80366
H	2.67079	4.50264	-0.92172
Au	-1.24419	-0.86740	-0.46553
N	-1.43654	-1.49321	1.76942
P	0.74739	0.18342	0.28811
C	-2.85330	-1.56128	-1.74701
H	-2.80381	-2.64593	-1.80781
C	-1.92294	-0.77779	-2.47401
H	-2.16257	0.24883	-2.73841
H	-1.20972	-1.27571	-3.12620
C	-4.17122	-1.07207	-1.27601
O	-5.01052	-1.79603	-0.76978
O	-4.34804	0.24815	-1.45560
C	-5.61009	0.77070	-1.01379
H	-6.43242	0.30444	-1.56178
H	-5.74681	0.60157	0.05717
H	-5.57604	1.83933	-1.22529

6b

Sum of electronic and zero-point Energies= -1928.221274
Sum of electronic and thermal Enthalpies = -1928.185662
Sum of electronic and thermal Free Energies = -1928.287008

C	-1.16000	0.02536	2.01641
C	-2.06418	0.89653	2.65051
H	-2.42826	1.76792	2.11924
C	-2.49772	0.67678	3.95248
H	-3.19603	1.36828	4.41436
C	-2.02764	-0.43025	4.65446
H	-2.35547	-0.61777	5.67281
C	-1.12471	-1.29859	4.05191
H	-0.75904	-2.15131	4.61525
C	-0.68161	-1.08365	2.74169
C	-0.24817	-3.40330	2.15587
H	-0.44740	-3.77366	3.16854
H	0.48588	-4.06001	1.68507
H	-1.17412	-3.42742	1.57827
C	1.56063	-1.98229	2.93994
H	1.96031	-0.96658	2.93069
H	2.27877	-2.65497	2.46665
H	1.41362	-2.30110	3.97913
C	0.29006	2.02567	0.30245
C	1.12062	2.11892	1.60398
H	1.79716	1.25598	1.67721
H	0.46167	2.09156	2.47833
C	1.93553	3.42441	1.62166
H	2.50696	3.46318	2.55762
C	1.27100	2.06830	-0.89370
H	1.95240	1.21109	-0.83624
H	0.72863	1.98485	-1.84103
C	0.16951	4.54725	0.24381
H	-0.52528	5.39459	0.18818
C	1.12331	4.57635	-0.95853
H	1.69441	5.51378	-0.96411
H	0.55255	4.54139	-1.89596
C	2.07897	3.37795	-0.87496
H	2.75377	3.38035	-1.74005
C	-0.65228	3.24428	0.21649
H	-1.23676	3.20698	-0.70883
H	-1.35937	3.24494	1.05329
C	2.89327	3.45856	0.42311
H	3.48530	4.38274	0.44141
H	3.60231	2.62173	0.47954
C	0.97718	4.62222	1.54705
H	0.30070	4.62114	2.41194
H	1.54600	5.56035	1.58439
C	-2.08509	0.18880	-0.83911
C	-3.20758	-1.17871	-3.22103
H	-4.01564	-1.37191	-3.93820
H	-2.35505	-1.80303	-3.52091
C	-4.46602	0.78988	-1.43784
H	-5.31721	1.41399	-1.13793
C	-1.65778	0.56372	-2.27588
H	-1.37993	1.62231	-2.32180
H	-0.77704	-0.01922	-2.57341
C	-3.66177	-1.54929	-1.80208
H	-3.93037	-2.61254	-1.76179
C	-3.31602	1.03119	-0.43901
H	-3.65425	0.74843	0.56365
H	-3.06923	2.09677	-0.41772
C	-2.81495	0.30486	-3.25709
H	-2.48058	0.57617	-4.26623
C	-4.86935	-0.68996	-1.40462
H	-5.21622	-0.96482	-0.39962
H	-5.70408	-0.87128	-2.09418
C	-2.50392	-1.30244	-0.81882
H	-1.65024	-1.93418	-1.09897
H	-2.81024	-1.59127	0.19490
C	-4.01789	1.17003	-2.85597
H	-4.84360	1.02088	-3.56371
H	-3.74796	2.23369	-2.89605
Au	0.88935	-1.52220	-0.02470
N	0.29039	-2.02199	2.17385
P	-0.57472	0.33455	0.30150
C	1.96664	-2.14821	-1.79392
H	1.23068	-2.35132	-2.56787
C	2.17153	-3.08186	-0.75713
H	3.11145	-3.09097	-0.21159
H	1.60846	-4.01252	-0.76616
C	2.99688	-1.16559	-2.23951
O	2.90623	-0.53342	-3.27377
O	4.03962	-1.07981	-1.40170
C	5.10224	-0.20727	-1.81869
H	5.52119	-0.54350	-2.77028
H	4.74386	0.81930	-1.92239
H	5.85576	-0.26572	-1.03350

7

Sum of electronic and zero-point Energies= -2212.087161
Sum of electronic and thermal Enthalpies = -2212.048346
Sum of electronic and thermal Free Energies = -2212.155658

C	1.988027000	-0.239193000	1.925508000
C	3.110475000	0.364449000	2.520032000
H	3.629732000	1.160414000	1.999811000
C	3.576932000	-0.036687000	3.766243000
H	4.448513000	0.445575000	4.198420000
C	2.917880000	-1.053816000	4.452255000
H	3.264997000	-1.374906000	5.429946000
C	1.808865000	-1.667506000	3.881865000
H	1.306148000	-2.460355000	4.426419000
C	1.342287000	-1.277791000	2.622270000
C	-1.023642000	-1.751380000	2.903564000
H	-0.885267000	-2.160734000	3.910760000
H	-1.878490000	-2.245610000	2.436860000
H	-1.218011000	-0.679911000	2.976469000
C	0.452835000	-3.440339000	1.964085000
H	1.332995000	-3.604520000	1.340021000
H	-0.411480000	-3.926023000	1.508337000
H	0.622269000	-3.883114000	2.951388000
C	2.762776000	0.076740000	-0.982947000
C	3.404841000	-1.304652000	-0.709885000

H	2.634155000	-2.088305000	-0.738800000
H	3.853704000	-1.324607000	0.289489000
C	4.487401000	-1.603594000	-1.761858000
H	4.927228000	-2.583226000	-1.537038000
C	2.144412000	0.049209000	-2.403110000
H	1.362010000	-0.717354000	-2.451685000
H	1.670602000	1.007369000	-2.636390000
C	4.943124000	0.850189000	-1.990320000
H	5.711336000	1.631618000	-1.934143000
C	4.314510000	0.836952000	-3.390315000
H	5.085396000	0.643198000	-4.147213000
H	3.877999000	1.817925000	-3.619901000
C	3.232244000	-0.250642000	-3.449006000
H	2.763665000	-0.255163000	-4.441016000
C	3.861019000	1.160804000	-0.937420000
H	3.430983000	2.148889000	-1.133262000
H	4.327072000	1.195291000	0.052727000
C	3.858794000	-1.621105000	-3.161544000
H	4.621897000	-1.854300000	-3.915194000
H	3.094967000	-2.408008000	-3.224132000
C	5.572508000	-0.518797000	-1.695351000
H	6.041917000	-0.514273000	-0.702742000
H	6.364158000	-0.732851000	-2.424848000
C	0.678350000	2.041986000	0.473525000
C	-1.614762000	3.860182000	0.009017000
H	-2.109131000	4.835888000	0.099167000
H	-2.304356000	3.197600000	-0.529780000
C	0.936905000	4.387624000	1.369067000
H	1.622528000	5.054203000	1.906992000
C	0.371396000	2.629791000	-0.920736000
1	1.298406000	2.743225000	-1.492705000
1	-0.283847000	1.953564000	-1.483787000
6	-1.314609000	3.293730000	1.404592000
1	-2.249294000	3.171364000	1.965971000
6	1.608561000	3.006683000	1.238990000
1	1.813096000	2.616272000	2.241444000
1	2.568156000	3.108856000	0.720660000
6	-0.302368000	4.005758000	-0.772572000
1	-0.509317000	4.397570000	-1.776032000
6	-0.373413000	4.245973000	2.155545000
1	-0.170463000	3.863289000	3.164571000
1	-0.850160000	5.227588000	2.273668000
6	-0.647037000	1.914107000	1.261275000
1	-1.326653000	1.229775000	0.735541000
1	-0.453988000	1.488109000	2.254409000
6	0.642955000	4.957058000	-0.025430000
1	0.184866000	5.950561000	0.062953000
1	1.577364000	5.082936000	-0.588625000
79	-0.351008000	-1.323388000	-0.041571000
7	0.181223000	-1.981213000	2.064113000
15	1.364666000	0.287884000	0.278825000
6	-1.447319000	-1.584229000	-1.846340000
6	-2.553220000	-0.572272000	-1.936140000
7	-3.553984000	-0.990401000	-1.044785000
6	-3.211917000	-2.209951000	-0.424292000
6	-1.860724000	-2.585068000	-0.925735000
1	-0.799303000	-1.728200000	-2.704474000
1	-1.564898000	-3.628547000	-0.939067000
8	-3.916220000	-2.814369000	0.359367000
8	-2.600155000	0.416647000	-2.638289000
6	-4.758674000	-0.274443000	-0.793769000
C	-5.552468000	0.143338000	-1.864357000
C	-5.138792000	0.001866000	0.521881000
C	-6.725121000	0.851733000	-1.611561000
C	-6.321425000	0.697195000	0.762946000
C	-7.114523000	1.126782000	-0.300926000
H	-5.253250000	-0.083571000	-2.881706000
H	-4.517964000	-0.330134000	1.347059000
H	-7.340138000	1.180716000	-2.444362000
H	-6.619106000	0.906955000	1.786410000
H	-8.033537000	1.673317000	-0.109096000

Alkenes

1_ol

Sum of electronic and zero-point Energies= -309.417719
Sum of electronic and thermal Enthalpies= -309.410027
Sum of electronic and thermal Free Energies= -309.448892

C	-1.952172000	-0.531973000	-0.000221000
H	-2.184508000	-1.597167000	-0.000743000
C	-2.970823000	0.336722000	0.000277000
H	-2.828477000	1.414655000	0.000914000
H	-3.998499000	-0.015425000	0.000140000
C	-0.514605000	-0.221401000	-0.000115000
C	-0.011476000	1.091776000	-0.000179000
C	0.406368000	-1.281839000	0.000014000
C	1.358698000	1.329321000	-0.000063000
C	1.779401000	-1.044732000	0.000133000
C	2.261859000	0.263025000	0.000100000
H	-0.697335000	1.934353000	-0.000335000
H	0.035464000	-2.304421000	0.000041000
H	1.726351000	2.352187000	-0.000121000
H	2.471739000	-1.882564000	0.000259000
H	3.331767000	0.452994000	0.000167000

2_ol

Sum of electronic and zero-point Energies= -235.618297
Sum of electronic and thermal Enthalpies= -235.609543
Sum of electronic and thermal Free Energies= -235.650301

C	-1.903620000	-0.261623000	0.391196000
H	-1.944606000	-0.434801000	1.468805000
C	-3.035356000	0.013269000	-0.259533000
H	-3.046597000	0.195893000	-1.333150000
H	-3.992472000	0.063476000	0.254483000
C	-0.541243000	-0.345551000	-0.230550000
H	-0.618628000	-0.197305000	-1.315574000
H	-0.144546000	-1.359070000	-0.076788000
C	0.442467000	0.674886000	0.362506000
H	0.025823000	1.681116000	0.224878000
H	0.514190000	0.518810000	1.448393000
C	1.846567000	0.627291000	-0.249248000
H	2.423340000	1.474679000	0.143601000
H	1.773618000	0.787969000	-1.333867000
C	2.615559000	-0.663656000	0.023932000
H	2.704415000	-0.851329000	1.100902000
H	2.129130000	-1.536377000	-0.424948000
H	3.630094000	-0.610753000	-0.386552000

3_ol

Sum of electronic and zero-point Energies= -78.512655
Sum of electronic and thermal Enthalpies= -78.508668
Sum of electronic and thermal Free Energies= -78.534840

C	0.665410000	-0.000002000	-0.000182000
H	1.237997000	-0.925193000	0.000534000
C	-0.665477000	-0.000002000	-0.000167000
H	-1.237774000	0.925342000	0.000510000
H	-1.237796000	-0.925331000	0.000513000
H	1.237976000	0.925204000	0.000537000

5_ol

Sum of electronic and zero-point Energies= -270.340231
Sum of electronic and thermal Enthalpies= -270.334053
Sum of electronic and thermal Free Energies= -270.368642

C	-1.449517000	0.292532000	0.126091000
C	-0.395033000	1.362187000	0.062109000
C	0.903585000	1.070213000	-0.081068000
O	1.436336000	-0.181300000	-0.111676000

C	0.532021000	-1.219622000	0.289026000
C	-0.849830000	-1.043665000	-0.320971000
H	-2.297577000	0.560932000	-0.516785000
H	-0.682663000	2.409467000	0.090592000
H	1.675409000	1.827464000	-0.195648000
H	1.002103000	-2.155538000	-0.024196000
H	-0.758270000	-1.066432000	-1.413613000
H	-1.859694000	0.206992000	1.142925000
H	-1.483438000	-1.887490000	-0.027722000
H	0.466093000	-1.214866000	1.386736000

6-ol

Sum of electronic and zero-point Energies= -306.266075
Sum of electronic and thermal Enthalpies= -306.258471
Sum of electronic and thermal Free Energies= -306.296601

C	1.486548000	0.381675000	-0.000868000
H	1.990964000	1.343933000	-0.000949000
C	2.169207000	-0.765281000	0.000720000
H	1.667942000	-1.728737000	0.001373000
H	3.255807000	-0.768602000	0.000250000
C	0.010438000	0.481754000	-0.000322000
O	-0.587015000	1.542918000	0.000640000
O	-0.603073000	-0.713012000	-0.000525000
C	-2.035394000	-0.672816000	0.000085000
H	-2.409130000	-0.165394000	0.893479000
H	-2.409812000	-0.158727000	-0.889158000
H	-2.359861000	-1.713707000	-0.003597000

7_ol

Sum of electronic and zero-point Energies= -590.132081
Sum of electronic and thermal Enthalpies= -590.121171
Sum of electronic and thermal Free Energies= -590.168512

C	-2.984639000	0.648157000	-0.159517000
C	-1.570814000	1.115265000	-0.274427000
N	-0.763047000	0.000016000	0.000467000
C	-1.571006000	-1.115035000	0.274541000
C	-2.984750000	-0.647912000	0.158621000
H	-3.822285000	1.313782000	-0.325014000
H	-3.822482000	-1.313234000	0.324866000
O	-1.175410000	-2.226596000	0.554190000
O	-1.174811000	2.226657000	-0.553927000
C	0.657733000	-0.000071000	0.000292000
C	1.351342000	0.978100000	0.717139000
C	1.351022000	-0.978276000	-0.716833000
C	2.744310000	0.979109000	0.704902000
C	2.744009000	-0.979323000	-0.705200000
C	3.443794000	-0.000108000	-0.000308000
H	0.803748000	1.728644000	1.276953000
H	0.803235000	-1.728904000	-1.276350000
H	3.282618000	1.743947000	1.257603000
H	3.282060000	-1.744195000	-1.258106000
H	4.530191000	-0.000078000	-0.000582000

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