Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for:

Adamantyl Metal Complexes: New Routes to Adamantyl Anions and New Transmetallations

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General Specifications:

All manipulations were carried out under an inert (N_2 or Ar) atmosphere using standard glove box (M Braun UniLab) and Schlenk techniques except where noted, and using oven-dried glassware. All reagents for which synthesis is not given were commercially available from Sigma Aldrich, Alfa Aesar, or STREM, and were used as received without further purification. 1- and 2-Adamantylzinc bromide solutions (0.5 M in THF) were commercially available from Rieke metals via Sigma Aldrich. These compounds can alternatively be synthesized by reaction of 1- and 2-bromoadamantane with Rieke zinc in THF.[i] Solvents were purified prior to use by passing through a column of activated alumina using an MBRAUN SPS. NMR solvents were obtained from Cambridge Isotope Laboratories. Diethyl ether (Et_2O), tetrahydrofuran (THF), and benzene-d_6 (C_6D_6) were further purified using by vacuum distillation from purple sodium benzophenone ketyl. Toluene and pentane were freshly distilled from activated molecular sieves. NMR data was obtained on a Bruker Avance III 400 MHz spectrometer. Chemical shifts are reported in ppm and referenced to residual solvent resonance peaks. Adamantane was present as a common contaminant in NMR spectra and was difficult to remove completely. Chemical shifts for adamantane are:

^1H NMR (C_6D_6, 400 MHz): 1.86 (bs, 4H, CH); 1.74 (bs, 12H, CH_2)

^{13}C NMR (C_6D_6, 100.6 MHz): 38.02 (CH_2); 28.76 (CH)

It should be noted that α-carbon peaks for the 1-adamantyl species could not be located by ^{13}C NMR. This is likely due to slow relaxation of the quaternary-like carbon bound to a metal center with no nuclear spin.

Some elemental analysis results for organometallic species were outside the range traditionally associated with analytical purity. Those data (deviation > 0.5 % points) are indicated with a "*" and they are provided here to illustrate the best values obtained.

Isolation of 1-adamantylzinc bromide as its THF adduct [1-AdZnBr(THF)$_x$] (1a, THF-solvate):

2 mL (1 mmol) of 1-AdZnBr solution (0.5M in THF) were diluted to 5 mL with toluene. The solvent was removed in vacuo. The residue was extracted with 3 mL of toluene and placed in a freezer at -40 ^{0}C for 7 days, after which 1-AdZnBr(THF) had precipitated out as a soft, amorphous, white solid.

^{1}H NMR (C_6D_6, 400 MHz): 3.64 (bs, THF); 2.54 (s, 6H, CH_2); 2.18 (d, 3H, CH_2, $^2J_{HH}$ =10.8 Hz); 2.05 (d, 3H, CH_2, coupling constant obscured by overlapping peaks); 2.02 (s, 3H, CH); 1.32 (bs, THF)

^{13}C NMR (C_6D_6, 100.6 MHz): 69.22 (THF); 45.37 (CH); 39.40 (CH_2); 30.25 (CH_2); 25.42 (THF)

Isolation of 2-adamantylzinc bromide as its THF adduct [2-AdZnBr(THF)$_x$] (1b, THF-solvate):

The procedure performed was analogous to that for **1a**, THF-solvate, above.

^{1}H NMR (C_6D_6, 400 MHz): 3.63 (bs, THF); 1.85-2.45 (m, 15H, 2-AdZnBr); 1.28 (bs, THF)

^{13}C NMR (C_6D_6, 100.6 MHz): 69.14 (THF); 43.76 (CH); 41.80 (CH_2); 40.00 (CH_2); 39.19 (CH); 34.16 (CH_2); 30.05 (CH); 29.74 (CH); 25.34 (THF)

Synthesis of 1-adamantylmagnesium bromide as its THF adduct [1-AdMgBr(THF)$_x$] (2a, THF-solvate):

6 mL (3 mmol) of 1-AdZnBr solution (0.5M in THF) were stirred over excess magnesium turnings for 2 days. The mixture was allowed to settle over a period of 8 hours, and the supernatant was decanted off. The concentration of the solution was determined by titration against diphenyl ditelluride.[ii] (Yield 81%)

^{1}H NMR (C_6D_6, 400 MHz): 3.68 (bs, 12H, THF); 2.65 (s, 6H, CH_2); 2.39 (d, 3H, CH_2, $^2J_{HH}$ =11.4 Hz); 2.31 (d, 3H, CH_2, $^2J_{HH}$ =11.7 Hz); 2.09 (s, 3H, CH); 1.35 (bs, THF)

^{13}C NMR (C_6D_6, 100.6 MHz): 69.14 (THF); 46.89 (CH); 40.67 (CH_2); 30.40 (CH_2); 26.51 (C-Mg); 25.39 (THF)

Synthesis of 2-adamantylmagnesium bromide as its THF adduct [2-AdMgBr(THF)$_x$] (2b, THF-solvate):

The procedure performed was analogous to that for **2a**, THF-solvate, above. (Yield 82%)

^{1}H NMR (C_6D_6, 400 MHz): 3.70 (bs, THF); 2.14-2.51 (m, 14H, 2-AdMgBr); 1.27 (bs, 1H, 2-AdMgBr, α-CH); 1.17 (bs, 6H, THF)

^{13}C NMR (C_6D_6, 100.6 MHz): 69.79 (THF); 43.51 (CH_2); 41.48 (CH_2); 39.92 (CH); 39.71 (CH); 35.12 (CH_2); 30.97 (CH); 30.61 (CH); 25.06 (THF)

Synthesis of bis(1-adamantyl)zinc [1-Ad$_2$Zn] (3a):

A) 154 mg (1 mmol) of biphenyl were dissolved in 15 mL of THF. 30 mg (4.3 mmol) of lithium pieces were added, and the solution was stirred for one hour, until a deep blue-green solution of lithium biphenylide was formed. The solution was transferred off of the excess lithium into a solution of 2 mL (1 mmol) of 1-adamantylzinc bromide solution (0.5 M in THF) which had been diluted to 10 mL with THF and cooled to -40^{0}C. The mixture was allowed to come to room temperature and stirred for 24 hours, then the solvent was removed *in vacuo*, and the residue was heated to 40 ^{0}C under vacuum for 16 hours to remove the biphenyl by sublimation. The residue was extracted with 15 mL of toluene. The volume of the toluene solution was reduced until the solution became cloudy and was placed in a freezer at -40 ^{0}C for 2 days. The product was collected as an off-white microcrystalline powder. (Yield 130 mg, 77%)

B) 69 mg (0.4 mmol) of 2,2,-bipyridine were dissolved in 10mL of THF. 10mg (1.43 mmol) of lithium pieces were added, the solution was stirred for one hour, until a deep green solution of lithium 2,2'-bipyridylide was formed. The solution was transferred off the excess lithium into a solution of 0.8 mL (0.4 mmol) of 1-adamantylzinc bromide solution (0.5 M in THF) which had been diluted to 5mL with THF. The mixture was allowed to react with stirring for 24 hours, then filtered through a coarse frit, followed by removal of the solvent *in vacuo*. The residue was extracted with 15 mL of toluene. The volume of the toluene solution was reduced until the solution became cloudy and was placed in the freezer at -40^{0}C for 2 days. The product was collected as an off-white microcrystalline powder. (Yield 55 mg, 78%)

C) 10 mL of 1-AdZnBr solution (0.5 M in THF) was stirred over excess magnesium turnings at room temperature for 3 days. To this mixture was added 10 mL of 1-AdZnBr solution (0.5 M in THF) and 1 mL of dioxane with vigorous stirring. The mixture was stirred for 10 minutes and then filtered through a course frit. The solvent was removed in vacuo with gentle heating, then the residue was extracted with 80 mL of toluene. The toluene slurry was again filtered through a course frit and the solvent was removed in vacuo to give an off-white powder. This crude product is contaminated with ~5% adamantane by NMR integration, which can be removed by recrystallization with significant loss of yield. (Crude yield 1.61 g, 96%)

^{1}H NMR (C_6D_6, 400 MHz): 2.10 (m, 12H, CH_2); 1.97 (d, 6H, CH_2, $^2J_{HH}$ =12.2 Hz); 1.92 (d, 6H, CH_2, $^2J_{HH}$ =11.9 Hz); 1.80 (s, 6H, CH)

^{13}C NMR (C_6D_6, 100.6 MHz): 43.66 (CH); 39.10 (CH_2); 29.55 (CH_2)

HRMS (EI-TOF+): mass [M] calc'd for $C_{20}H_{30}Zn$ 334.1639 Da, measured 334.1641 Da.

IR Absorptions: ν_{max}/cm^{-1} 2885 (CH_2), 2841 and 2824 (CH), 1443 (CH_2)

MP 220 ^{0}C (decomp)

Synthesis of bis(2-adamantyl)zinc [2-Ad$_2$Zn] (3b):

The procedure performed was analogous to that for **3a**, above. Yield 86% for the lithium biphenylide method, 76% for the lithium 2,2'-bipyridylide method, and 95% for the Grignard method.

^{1}H NMR (C_6D_6, 400 MHz): 1.79-2.07 (m, 28H, 2-Ad$_2$Zn); 1.38 (bs, 2H, 2-Ad$_2$Zn, α-CH)

^{13}C NMR (C_6D_6, 100.6 MHz): 46.50 (CH); 42.13 (CH_2); 40.91 (CH_2); 38.56 (CH); 33.04 (CH_2); 29.76 (CH); 29.41 (CH)

HRMS (EI-TOF+): mass [M] calc'd for C20H30Zn 334.1639 Da, measured 334.1644 Da.

IR Absorptions: ν_{max}/cm^{-1} 2889 (CH_2), 2833 (CH), 1443 (CH_2)

MP 230 ^{0}C (decomp)

Synthesis of 2,2'bipyridyl-bis(1-adamantyl)zinc [1-Ad$_2$Zn(bipy)] (4a):

84 mg (0.25 mmol) of 1-Ad$_2$Zn were dissolved in 5 mL of pentane and cooled to –40 ^{0}C. A solution of 40 mg (0.25 mmol) of 2,2'-bipyridyl in 5 mL of pentane at –40 ^{0}C was added dropwise. A dark blue solution formed from which olive crystals precipitated out of solution immediately. The solution was allowed to stand in a freezer at –40 ^{0}C overnight, after which crystals suitable for X-ray analysis were collected. (Yield 111 mg, 89%).

^{1}H NMR (C_6D_6, 400 MHz): 8.33 (d, 2H, bipy, $^3J_{HH}$ =5.3 Hz); 7.20 (m, 2H, bipy); 6.91 (t, 2H, bipy, $^3J_{HH}$ =7.9 Hz); 6.57 (t, 2H, bipy, $^3J_{HH}$ =5.8 Hz); 2.39 (bs, 12H, CH_2); 2.22 (d, 6H, CH_2, $^2J_{HH}$ =11.0 Hz); 2.17 (d, 6H, CH_2, $^2J_{HH}$ =12.1 Hz); 2.01 (bs, 6H, CH)

^{13}C NMR (C_6D_6, 100.6 MHz): 47.28 (CH); 40.22 (CH_2); 30.68 (CH_2)

** We were unable to acquire the peaks corresponding to the bipyridine ligand by ^{13}C NMR although they were fully visible by ^{1}H NMR. We attribute this to the presence of radical character localized on the bipy ligand.

*EA $C_{30}H_{38}N_2Zn$ (492.03): calc'd C 73.23, H 7.78, N 5.69; found C 69.90, H 7.39, N 5.32 (extremely air sensitive compound).

EI-TOF+ MS resulted in complete fragmentation to (1-Ad)$_2$Zn and 2,2'-bipyridyl.

IR Absorptions: ν_{max}/cm^{-1} 2866 (CH_2), 2848, 2829, and 2804 (CH), 1594 (Aromatic C=C) , 1443 (CH_2)

MP 190 ^{0}C (decomp)

Synthesis of 2,2'bipyridyl-bis(2-adamantyl)zinc [2-Ad_2Zn(bipy)] (4b):

The procedure performed was analogous to that for **4a**, above. The product was collected from a red solution as red crystals, which were suitable for X-ray analysis. (Yield 93%)

^1H NMR (C_6D_6, 400 MHz): 8.47 (d, 2H, bipy, $^3J_{HH}$ =4.9 Hz); 7.62 (d, 2H, bipy, $^3J_{HH}$ =7.9 Hz); 6.97 (t, 2H, bipy, $^3J_{HH}$ =7.8 Hz); 6.57 (m, 2H, bipy) 2.00-2.30 (m, 28H, 2-Ad); 1.44 (bs, 2H, 2-Ad α-CH)

^{13}C NMR (C_6D_6, 100.6 MHz): 149.06 (bipy); 136.94 (bipy); 124.11 (bipy); 120.89 (bipy); 44.93 (2-Ad); 42.76 (2-Ad); 41.03 (2-Ad); 39.63 (2-Ad); 35.04 (2-Ad); 30.57 (2-Ad); 30.30 (2-Ad).

* EA $C_{30}H_{38}N_2Zn$ (492.03): calc'd C 73.23, H 7.78, N 5.69; found C 73.94, H 7.41, N 6.73

EI-TOF+ MS resulted in complete fragmentation to $(2\text{-Ad})_2Zn$ and 2,2'-bipyridyl.

IR Absorptions: ν_{max}/cm^{-1} 2885 (CH_2), 2829 (b, CH), 1594 (Aromatic C=C), 1437 (CH_2)

MP 180 ^0C (decomp)

Synthesis of bis(1-adamantyl)mercury [1-Ad_2Hg] (5a):

135 mg (0.5 mmol) of $HgCl_2$ was slurried in 5 mL of toluene. 2 mL (1 mmol) of 1-AdZnBr (0.5 M in THF) was added slowly, with stirring. The mixture was stirred at room temperature for 24 h, and then the solvent was removed in vacuo. The residue was extracted with 10 mL of pentane and the volume was reduced in vacuo until the solution became cloudy. The solution was placed in a freezer at -40 ^0C and the product was isolated as a white powder. (Yield 184 mg, 78%)

^1H NMR (C_6D_6, 400 MHz): 2.09 (s, 6H, CH_2); 1.89 (d, 3H, CH_2, $^2J_{HH}$ =12.0 Hz); 1.87 (d, 3H, CH_2, $^2J_{HH}$ = 12.0 Hz); 1.68 (s, 3H, CH)

^{13}C NMR (C_6D_6, 100.6 MHz): 46.44 (CH); 38.95 (CH_2); 31.60 (CH_2)

* EA $C_{20}H_{30}Hg$ (471.05): calc'd C 51.00, H 6.42; found C 56.18, H 7.21 (contaminated with adamantane)

HRMS (EI-TOF+): mass [M] calc'd for C20H30Hg 472.2054 Da, measured 472.2054 Da.

IR Absorptions: ν_{max}/cm^{-1} 2897 (CH_2), 2845 (CH), 1447 (CH_2)

MP 250 ^{0}C (decomp)

Synthesis of bis(2-adamantyl)mercury [2-Ad_2Hg] (5b):

The procedure performed was analogous to that for **5a**, above. (Yield 80%)

^{1}H NMR (C_6D_6, 400 MHz): 1.80-2.10 (m, 30H, 2-Ad_2Hg)

^{13}C NMR (C_6D_6, 100.6 MHz): 74.06 (CH); 42.77 (CH_2); 40.89 (CH_2); 38.66 (CH); 35.29 (CH_2); 29.56 (CH); 29.25 (CH)

EA $C_{20}H_{30}Hg$ (471.05): calc'd C 51.00, H 6.42; found C 51.25, H 6.38

HRMS (EI-TOF+): mass [M] calc'd for C20H30Hg 472.2054 Da, measured 472.2063 Da.

IR Absorptions: ν_{max}/cm^{-1} 2885 (CH_2), 2841 (CH)

MP 210 ^{0}C (decomp)

Synthesis of bis(2-adamantyl)bismuth(III) bromide [2-Ad_2BiBr] (6b):

45 mg (0.1 mmol) of $BiBr_3$ was slurried in 5 mL of diethyl ether and cooled to –40 ^{0}C. A solution of 34 mg (0.1 mmol) of 2-Ad_2Zn in 5 mL of diethyl ether at –40 ^{0}C was added dropwise. The yellow solution gradually turned black and was allowed to come to room temperature with stirring and was stirred for 16h. The solution was filtered through a medium frit giving a clear yellow

solution. The solvent was removed in vacuo to give an orange residue which was extracted with 10 mL of pentane. The pentane solution was filtered through a coarse frit and the solvent was removed in vacuo to give an orange powder. (Yield 40 mg, 72%) Crystals suitable for single crystal XRD were obtained by slow evaporation of a pentane solution of 2-Ad_2BiBr.

^{1}H NMR (C_6D_6, 400 MHz):

4.22 (t, 1H, Bi-CH, $^3J_{HH}$ = 13.3 Hz); 3.10 (s, 1H, CH); 2.36 (d, 1H, CH_2, $^2J_{HH}$ = 12.3 Hz); 2.22 (d, 1H, CH_2, $^2J_{HH}$ = 12.2 Hz); 2.02 (d, 1H, CH_2, $^2J_{HH}$ = 13.0 Hz); 1.98 (s, 2H, CH); 1.91 (s, 1H, CH); 1.77-1.56 (m, 6H, CH_2); 1.44 (d, 1H, CH_2, $^2J_{HH}$ = 12.2 Hz);

^{13}C NMR (C_6D_6, 100.6 MHz):

81.28 (1C, Bi-C); 45.54 (1C, CH_2); 42.64 (1C, CH); 38.59 (1C, CH); 37.95 (1C, CH_2); 37.44 (1C, CH); 37.19 (1C, CH_2); 33.62 (1C, CH); 28.51 (1C, CH_2); 27.80 (1C, CH_2)

EA $C_{20}H_{30}BiBr$ (559.34): calc'd C 42.95, H 5.41; found C 43.32, H 5.49

HRMS (EI-TOF+): mass [M] calc'd for C20H30BiBr 558.1335 Da, measured 558.1328 Da.

IR Absorptions: ν_{max}/cm^{-1} 2897 (CH_2), 2842 (CH), 1446 (CH_2)

MP 120 ^{0}C (decomp)

Attempted Synthesis of bis(1-adamantyl)bismuth(III) bromide [1-Ad_2BiBr] (6a):

Under analogous reaction conditions as used for the synthesis of **6b** but using 1-Ad_2Zn, no **6a** could be isolated. ^{1}H and ^{13}C NMR of the reaction contained a complex mixture of decomposition products, including large quantities of adamantane.

Generation of 1-adamantylgold(triphenylphosphine) [1-AdAu(PPh_3)] (7a):

100 mg (0.20 mmol) of ClAu(PPh_3) was slurried in 5 mL of THF. 0.500 mL (0.2mmol) of 1-AdMgBr (0.4 M in THF) was added slowly, with stirring. The mixture was stirred at room temperature for 24 h, and then the solvent was removed in vacuo. The residue was extracted with 10 mL of benzene and filtered through a coarse frit. The solvent was removed in vacuo to yield the product as an off white oil. Product decomposed rapidly and could not be isolated.

^{1}H NMR (C_6D_6, 400 MHz): 7.46 (broad s, 6H, PPh_3); 7.32 (broad s, 8H, PPh_3); 6.94 (broad s, 21H, PPh_3); 3.00 (s, 6H, CH_2); 2.31 (d, 3H, CH_2); 2.11 (s, 3H, CH); 2.01 (d, 3H, CH_2).

^{31}P NMR (C_6D_6, 161.98 MHz): 44.00 (PPh_3); 40.00 (PPh_3) *

*The major phosphorus peak at 40 ppm corresponds to the major 1-AdAu(PPh_3) species. A secondary peak from the decomposition appears at 44 ppm. This corresponds with the presence of various triphenylphosphine species in the ^{1}H NMR where broad singlets of the PPh_3 peaks are observed with higher than expected integrations.

* EA $C_{28}H_{30}AuP$ (594.49): calc'd C 56.57, H 5.09; found C 52.88, H 5.37

** EA Sample contaminated with $MgBr_2(THF)_n$ which could not be sufficiently removed.

Synthesis of 2-adamantylgold(triphenylphosphine) [2-AdAu(PPh_3)] (7b):

100 mg (0.20 mmol) of ClAu(PPh_3) was slurried in 5 mL of THF. 0.670 mL (0.2mmol) of 2-AdMgBr (0.3 M in THF) was added slowly, with stirring. The mixture was stirred at room temperature for 24 h, and then the solvent was removed in vacuo. The residue was extracted with 10 mL of benzene and filtered through a coarse frit. The solvent was removed in vacuo to yield the product as an off white oil.

Alternatively; 50 mg (0.10 mmol) of $ClAu(PPh_3)$ was slurried in 5 mL of Toluene. 17 mg (0.05 mmol) of 2-Ad_2Zn was added slowly, with stirring. The mixture was stirred at room temperature for 2 h, and then the product was filtered through a medium frit. Solvent was removed in vacuo to yield the product as a light purple solid (minor amounts of gold metal). (Yield 62%). This complex could similarly be synthesized using 2-Ad_2Zn(bipy).

Crystals suitable for single crystal XRD were obtained by slow evaporation of a diethyl ether solution of 2-$AdAu(PPh_3)$.

^1H NMR (C_6D_6, 400 MHz): 7.48 (m, 6H, PPh_3); 6.95 (m, 9H, PPh_3); 3.17 (dt, $^3J_{HP}$ = 8.55 Hz, $^3J_{HH}$ = 4.85 Hz, 1H, Au-CH); 2.99 (d, $^2J_{HH}$ = 11.44, 2H, CH_2); 2.88 (s, 2H, CH); 2.07 (m, 10H, adamantyl)

^{31}P NMR (C_6D_6, 161.98 MHz): 43.44 (PPh_3)

^{13}C NMR (C_6D_6, 100.6 MHz): 134.04 (d, $^2J_{CP}$ = 13.74 Hz , PPh_3); 132.06, (d, $^1J_{CP}$ = 42.96 Hz , PPh_3); 130.17 (d, $^4J_{CP}$ = 1.72 Hz , PPh_3); 128.57 (d, $^3J_{CP}$ = 10.19 Hz , PPh_3); 63.19 (d, $^2J_{CP}$ = 97.24 Hz , Au-C); 42.72; 42.64; 39.11; 37.86; 37.82; 29.90; 29.66.

* EA $C_{28}H_{30}AuP$ (594.49): calc'd C 56.57, H 5.09; found C 55.52, H 4.84, N 0.46

** EA sample contaminated with a small amount (~2.5%) of 2,2'-bipyridyl

HRMS (EI-TOF+): mass [M] calc'd for C28H30AuP 594.1751 Da, measured 594.1734 Da.

IR Absorptions: ν_{max}/cm^{-1} 2885 (CH_2), 2831 (b, CH), 1464 (Aromatic C=C), 1434 (CH_2)

MP 145 ^0C (decomp)

Generation of 1-adamantylgold(tricyclohexylphosphine) [1-$AdAu(PCy_3)$] (8a):

50 mg (0.10 mmol) of $ClAu(PCy_3)$ was slurried in 5 mL of benzene. 17 mg (0.05 mmol) of 1-Ad_2Zn was added slowly, with stirring. The mixture was stirred at room temperature for 2 h, and

then the product was filtered through a medium frit. Solvent was removed in vacuo to yield the product as a dark purple solid. The resulting compound was not isolable. NMR data indicates the presence of 1-AdAu(PCy$_3$), but the product cannot be fully characterized.

^{1}H NMR (C_6D_6, 400 MHz): 2.92 (broad s, 6H, CH$_2$); 2.31-0.86 (m, cyclohexyl and adamantyl); 1.87 (d, 3H, CH$_2$); 1.68 (s, 3H, CH) ^{31}P NMR (C_6D_6, 161.98 MHz): 63.08; 55.02. **

** The ^{31}P NMR spectrum indicates that two products are present, not one.

Synthesis of 2-adamantylgold(tricyclohexylphosphine) [2-AdAu(PCy$_3$)] (8b):

50 mg (0.10 mmol) of ClAu(PCy$_3$) was slurried in 5 mL of benzene. 17 mg (0.05 mmol) of 2-Ad$_2$Zn was added slowly, with stirring. The mixture was stirred at room temperature for 2 h, and then the product was filtered through a medium frit. Solvent was removed in vacuo to yield the product as a dark purple solid likely due to presence of gold metal. (Yield 67%)

Crystals suitable for single crystal XRD were obtained by slow evaporation of a benzene solution of 2-AdAu(PCy$_3$).

^{1}H NMR (C_6D_6, 400 MHz): 2.97-1.04 (multiple signals that cannot be assigned, adamantyl and cyclohexyl); 1.89 (d, 3H, CH$_2$); 1.87 (d, 3H, CH$_2$); 1.68 (s, 3H, CH).

^{13}C NMR (C_6D_6, 100.6 MHz): 70.05; 64.40 (d, J_{CP} = 94.69 Hz); 43.62 (d, J_{CP} = 7.61 Hz); 42.11; 39.78; 38.40; 33.58 (d, J_{CP} = 20.12 Hz); 30.81; 30.46 (d, J_{CP} = 15.04 Hz); 27.45 (d, $^2J_{CP}$ = 10.80 Hz); 26.42; 25.07.

^{31}P NMR (C_6D_6, 161.98 MHz): 57.61 (PCy$_3$)

HRMS (EI-TOF+): mass [M] calc'd for C28H48AuP 612.3159 Da, measured 612.3146 Da.

IR Absorptions: ν_{max}/cm^{-1} 2891 (CH$_2$), 2831 (b, CH), 1444 (CH$_2$)

MP 165 ^{0}C (decomp)

NMR Spectra

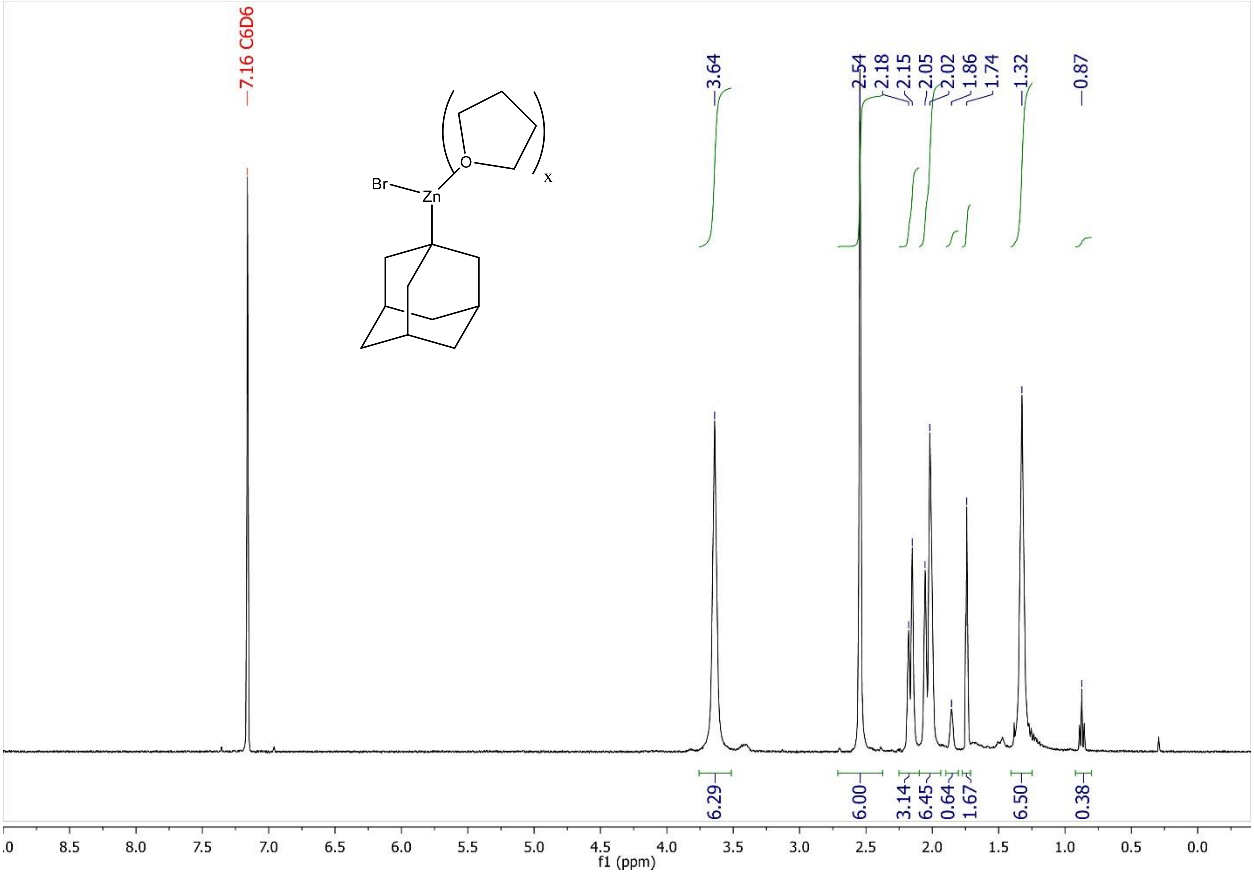

Figure S1. ^{1}H NMR spectrum of **1a**, THF-solvate, in C_6D_6 at 25 °C.

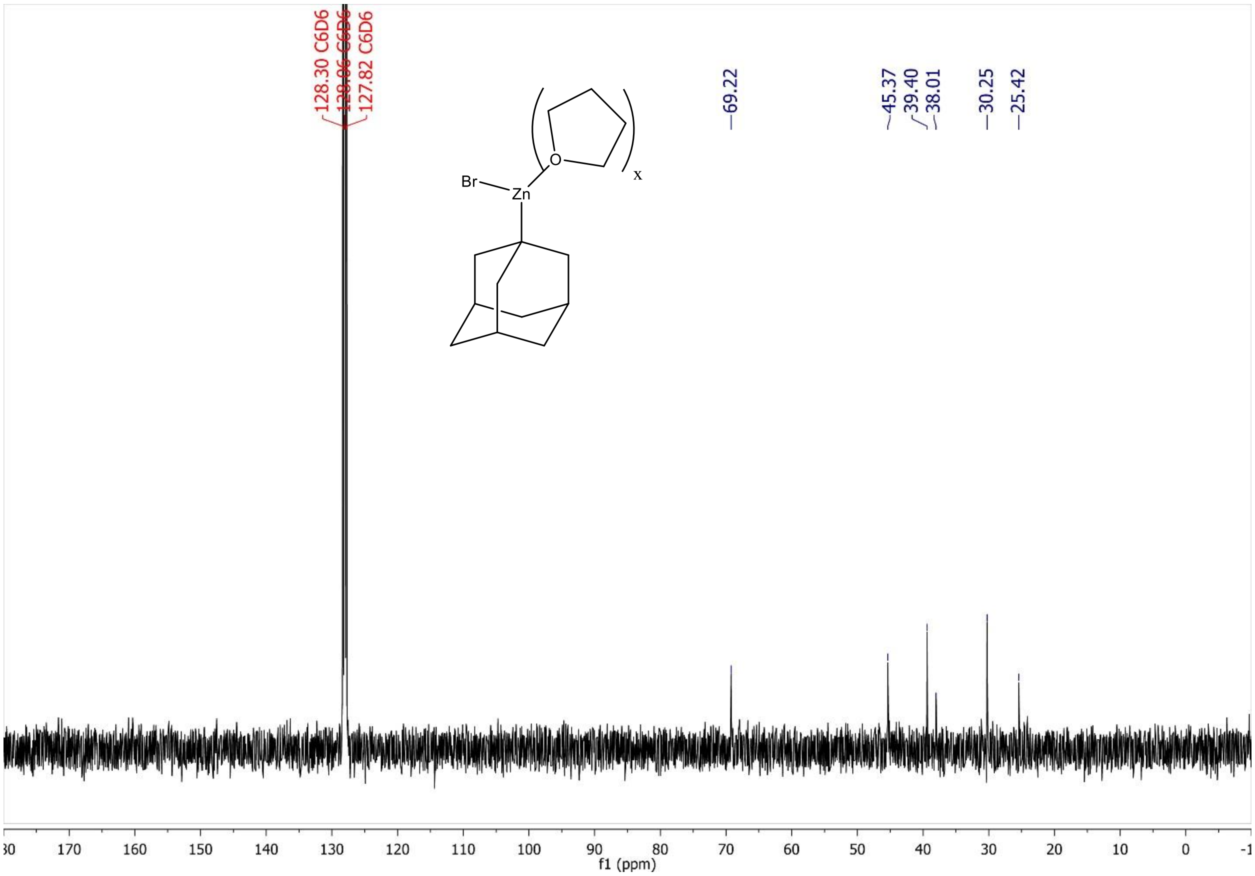

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **1a**, THF-solvate, in C_6D_6 at 25 °C.

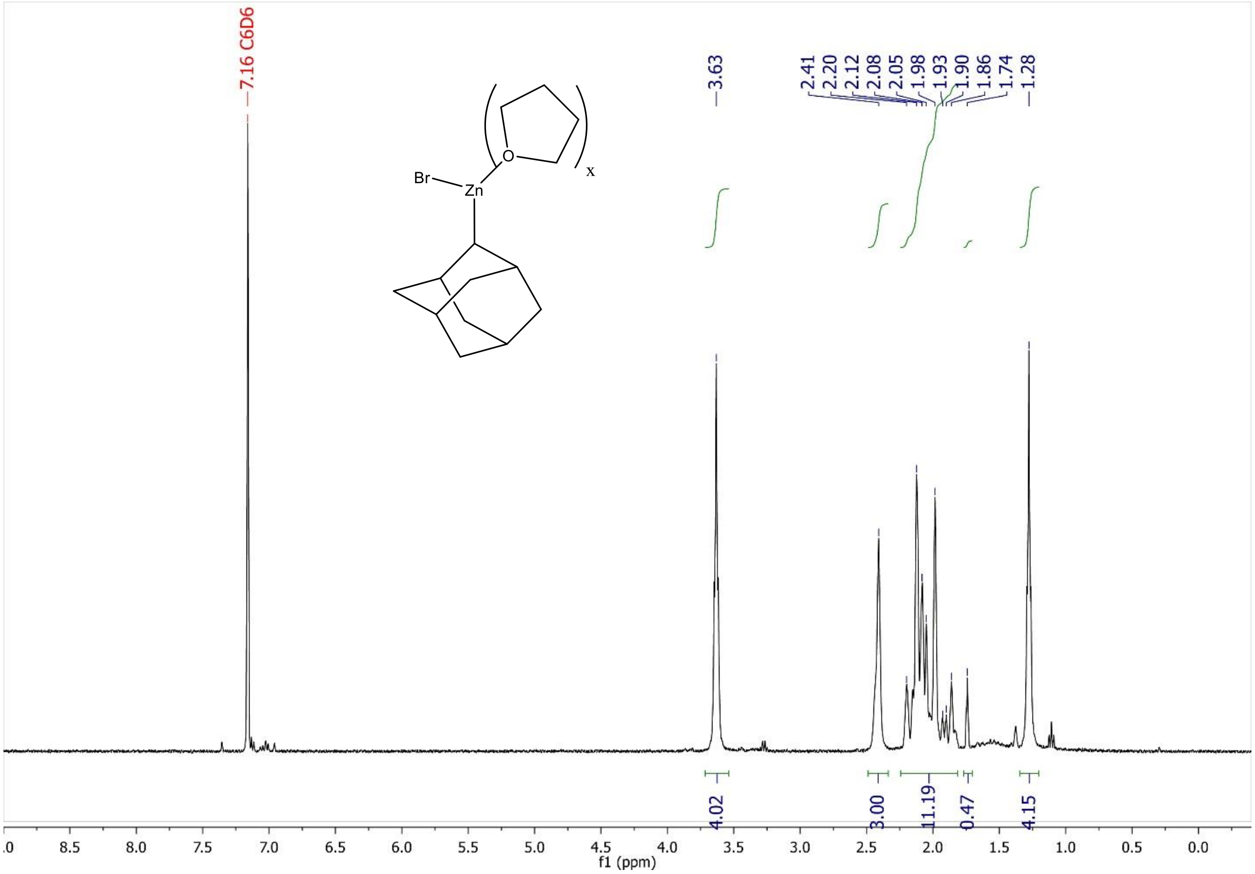

Figure S3. ^{1}H NMR spectrum of **1b**, THF-solvate, in C_6D_6 at 25 °C.

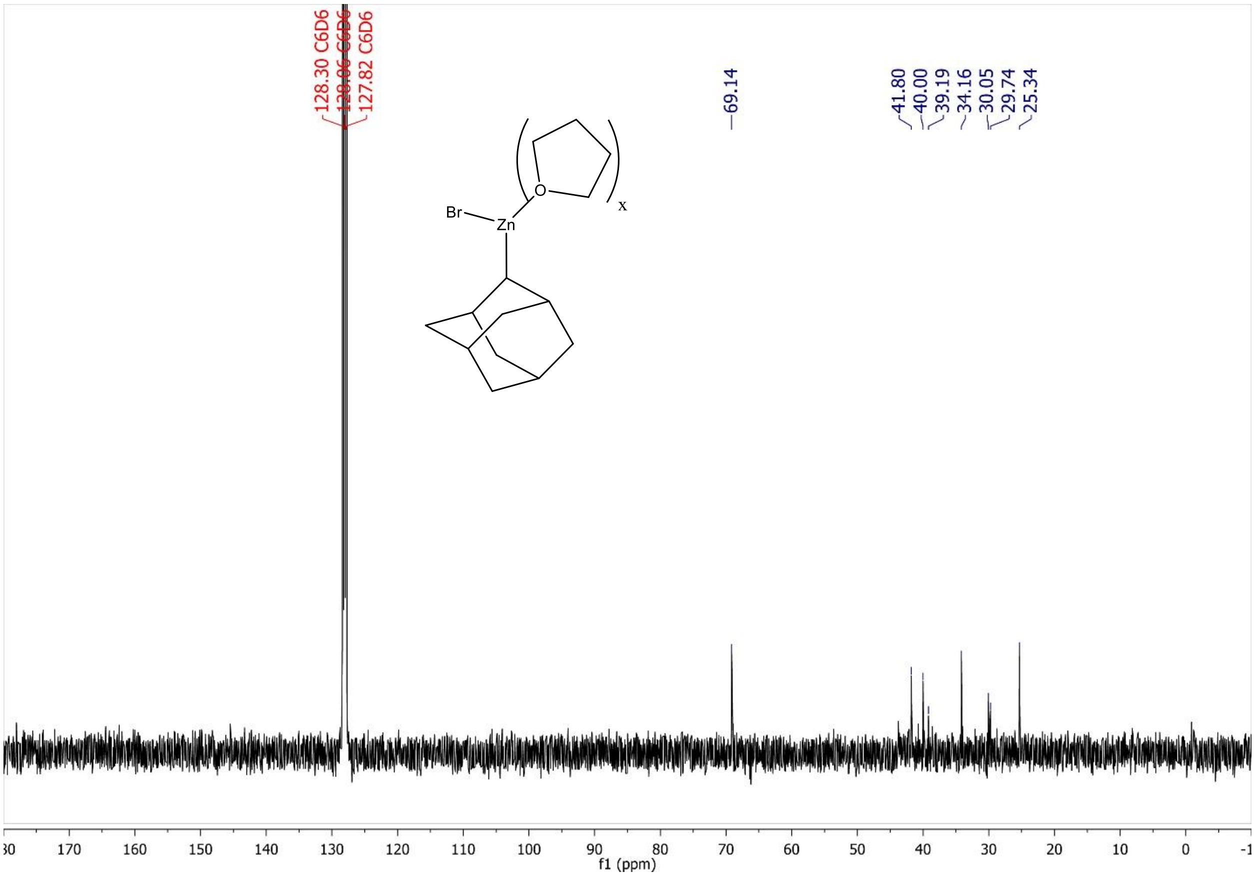

Figure S4. $^{13}C\{^1H\}$ NMR spectrum of **1b**, THF-solvate, in C_6D_6 at 25 °C.

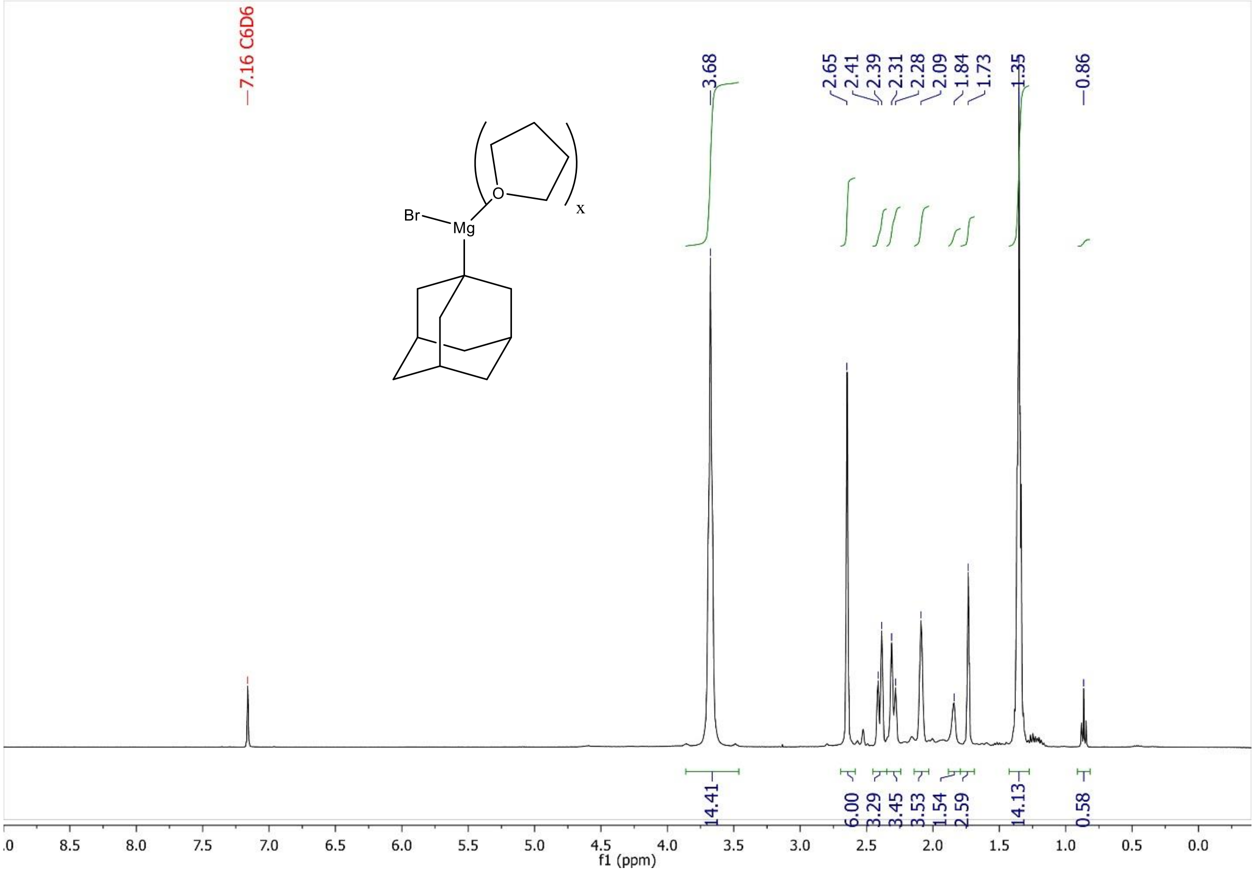

Figure S5. ^{1}H NMR spectrum of **2a**, THF-solvate, in C_6D_6 at 25 °C.

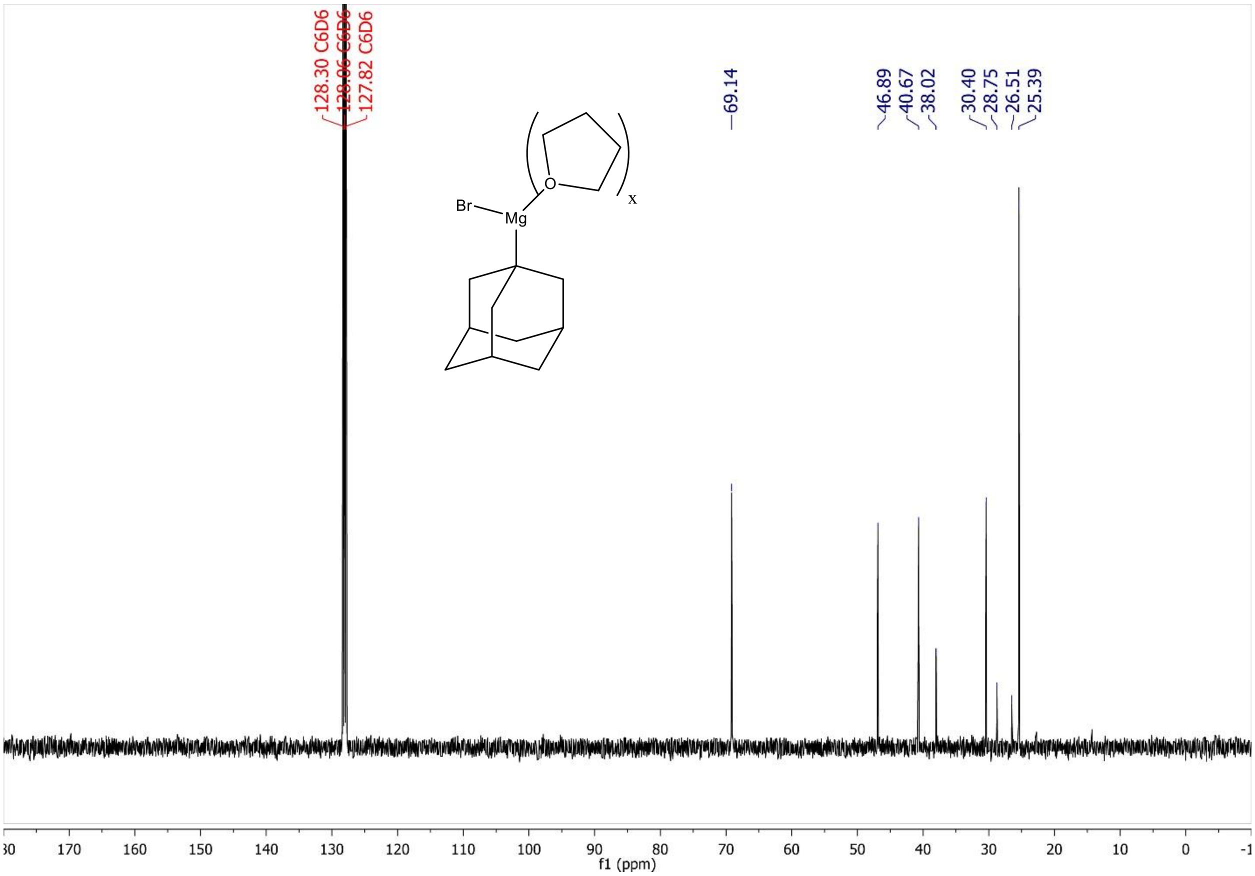

Figure S6. ^{13}C{^{1}H} NMR spectrum of **2a**, THF-solvate, in C_6D_6 at 25 °C.

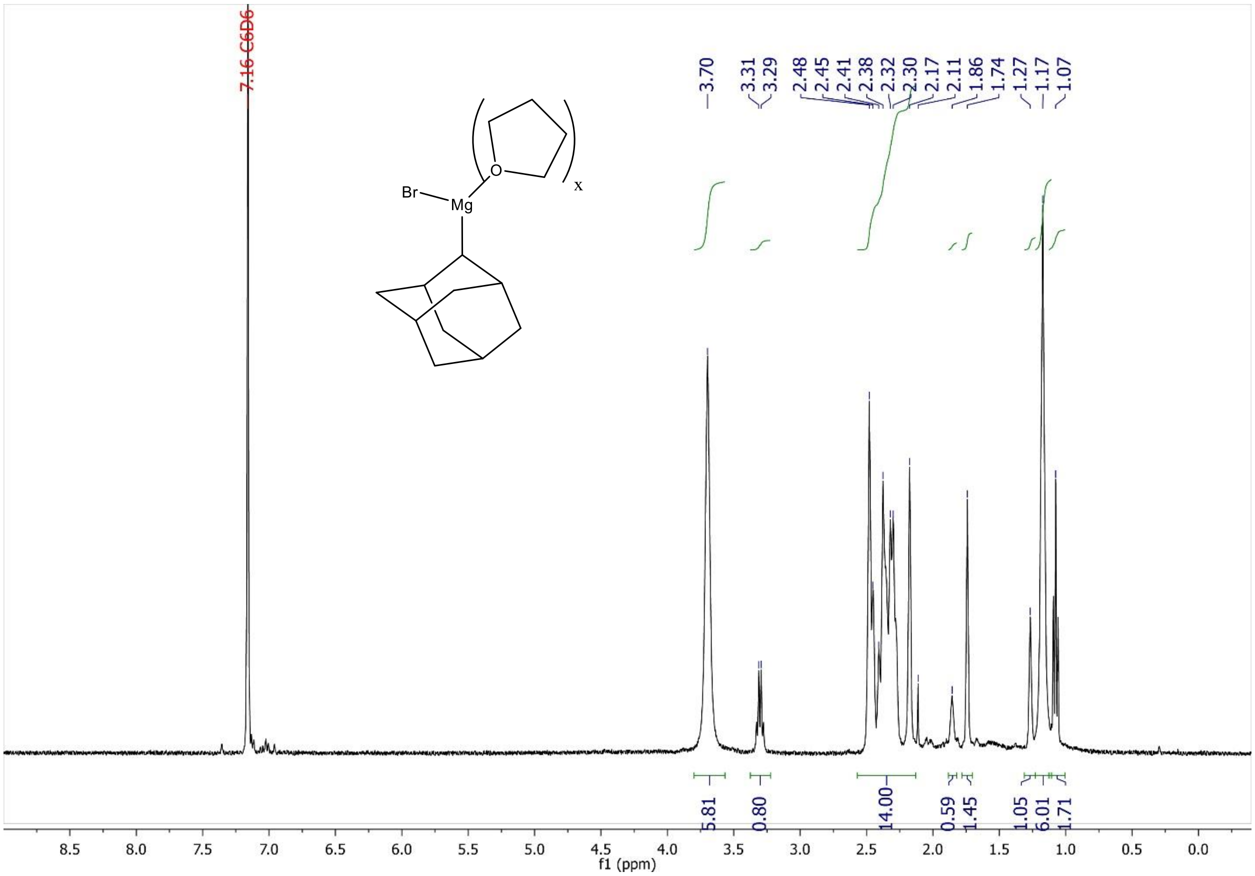

Figure S7. ^{1}H NMR spectrum of **2b**, THF-solvate, in C_6D_6 at 25 °C.

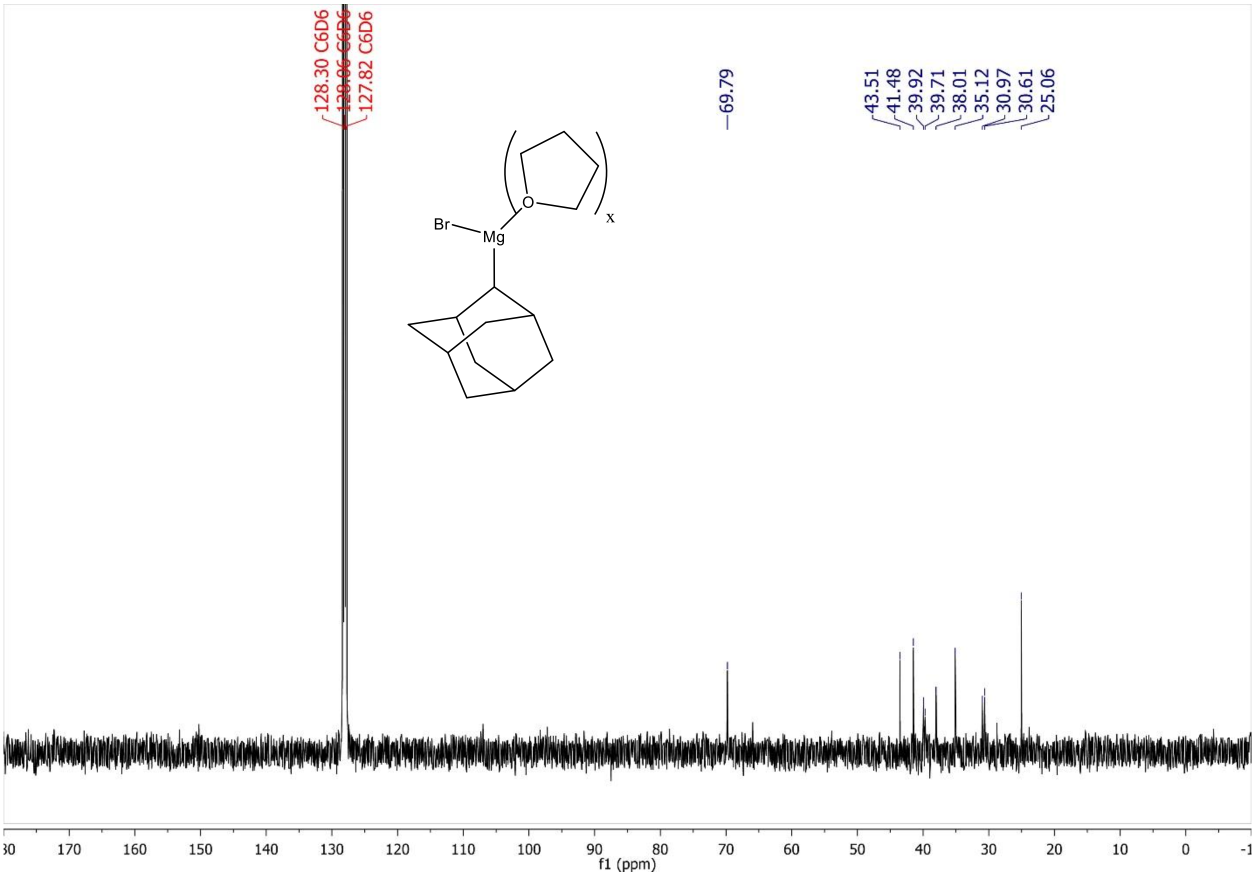

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **2b**, THF-solvate, in C_6D_6 at 25 °C.

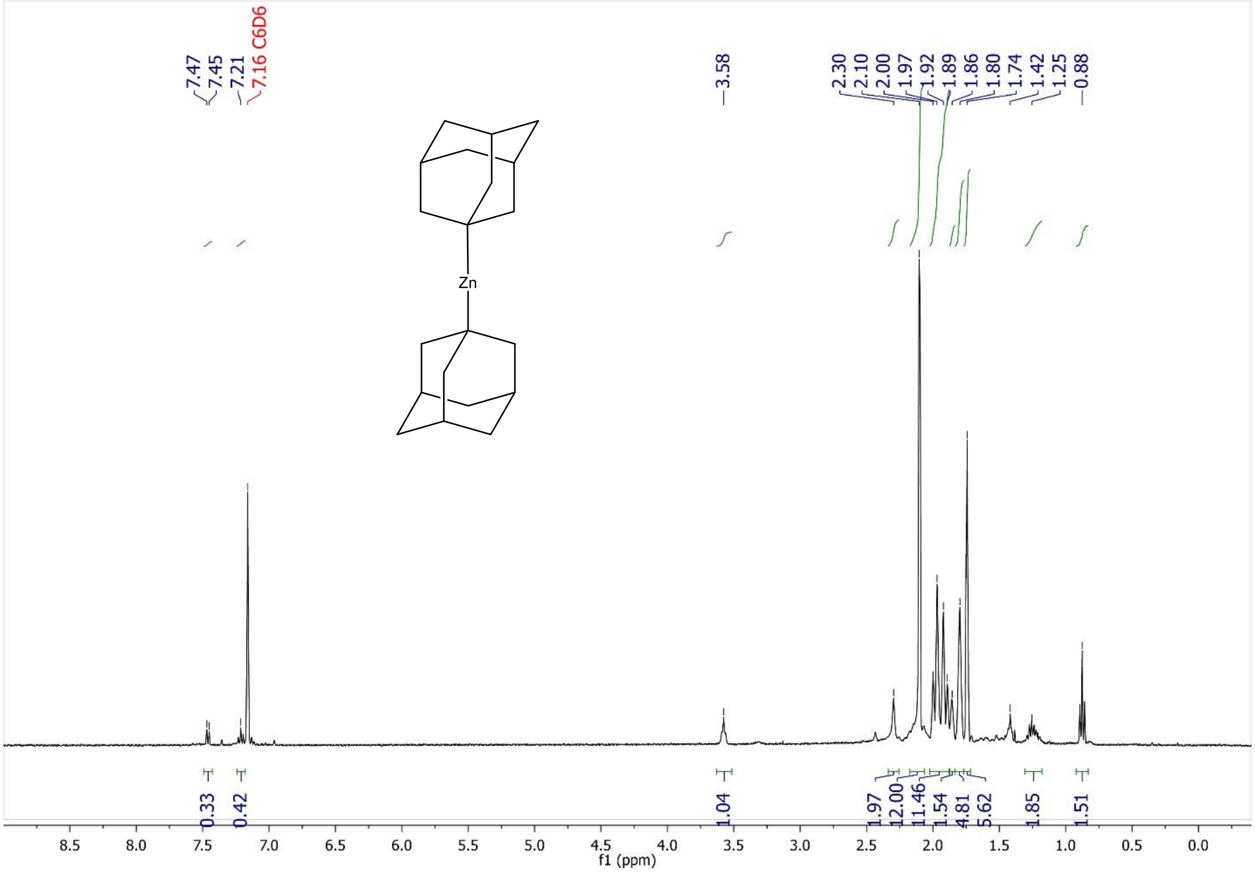

Figure S9. ^{1}H NMR spectrum of **3a** in C_6D_6 at 25 °C.

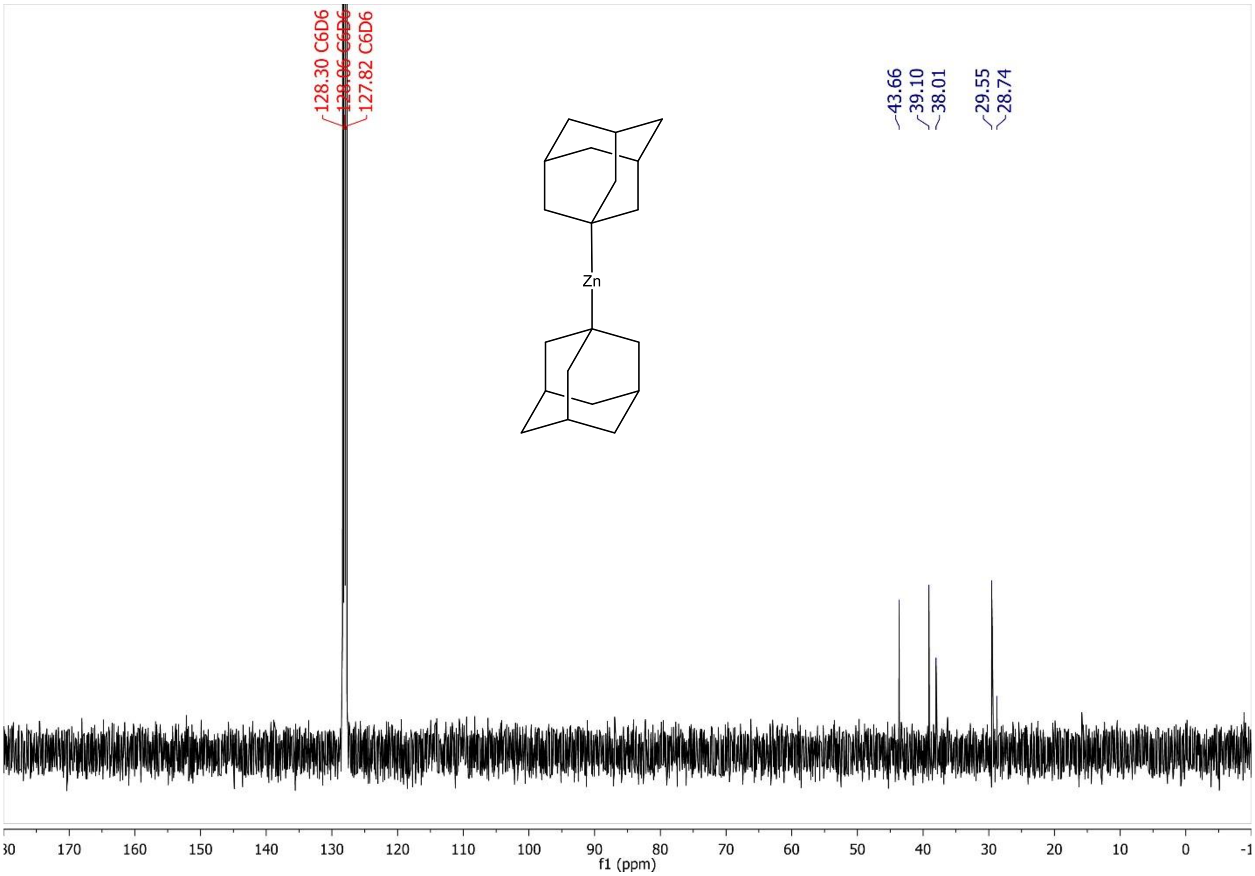

Figure S10. $^{13}C\{^1H\}$ NMR spectrum of **3a** in C_6D_6 at 25 °C.

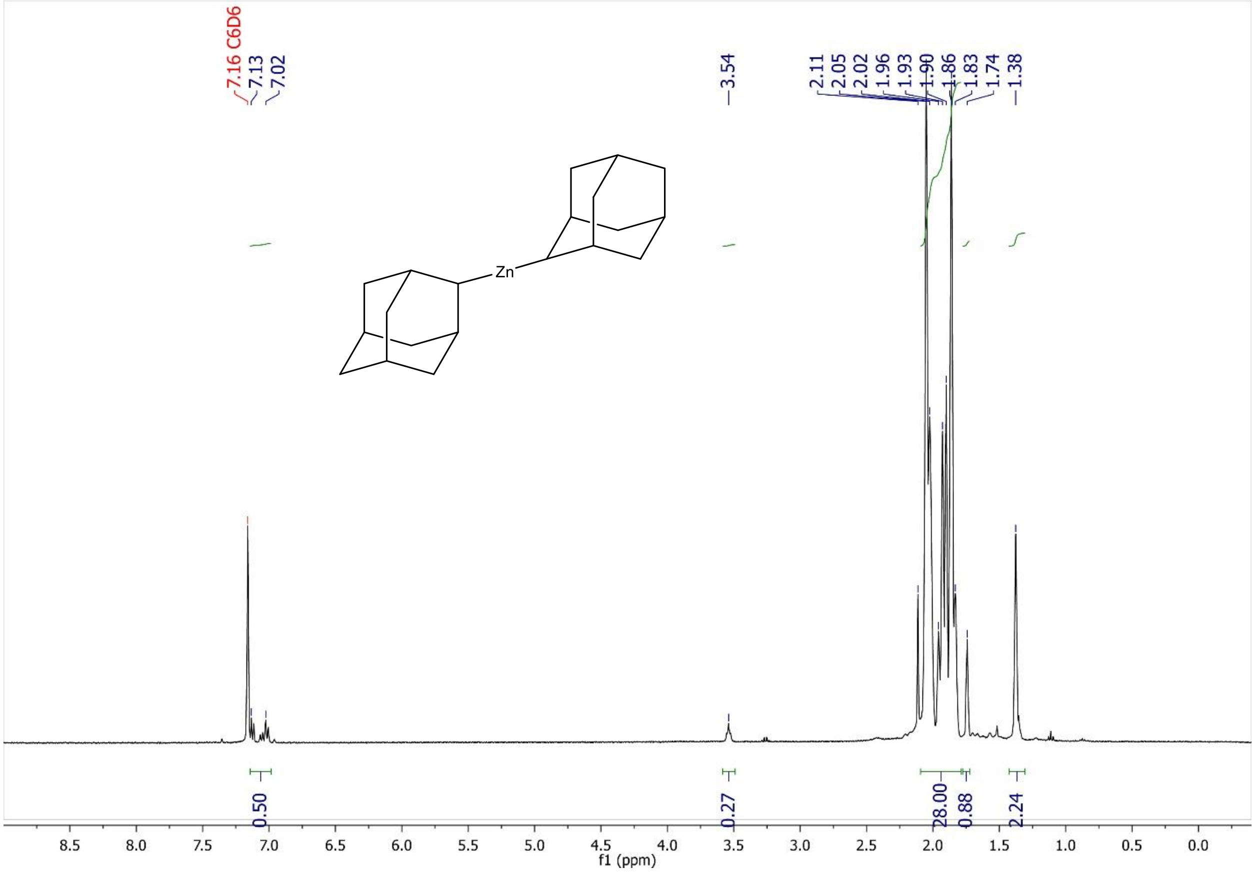

Figure S11. ^{1}H NMR spectrum of **3b** in C_6D_6 at 25 °C.

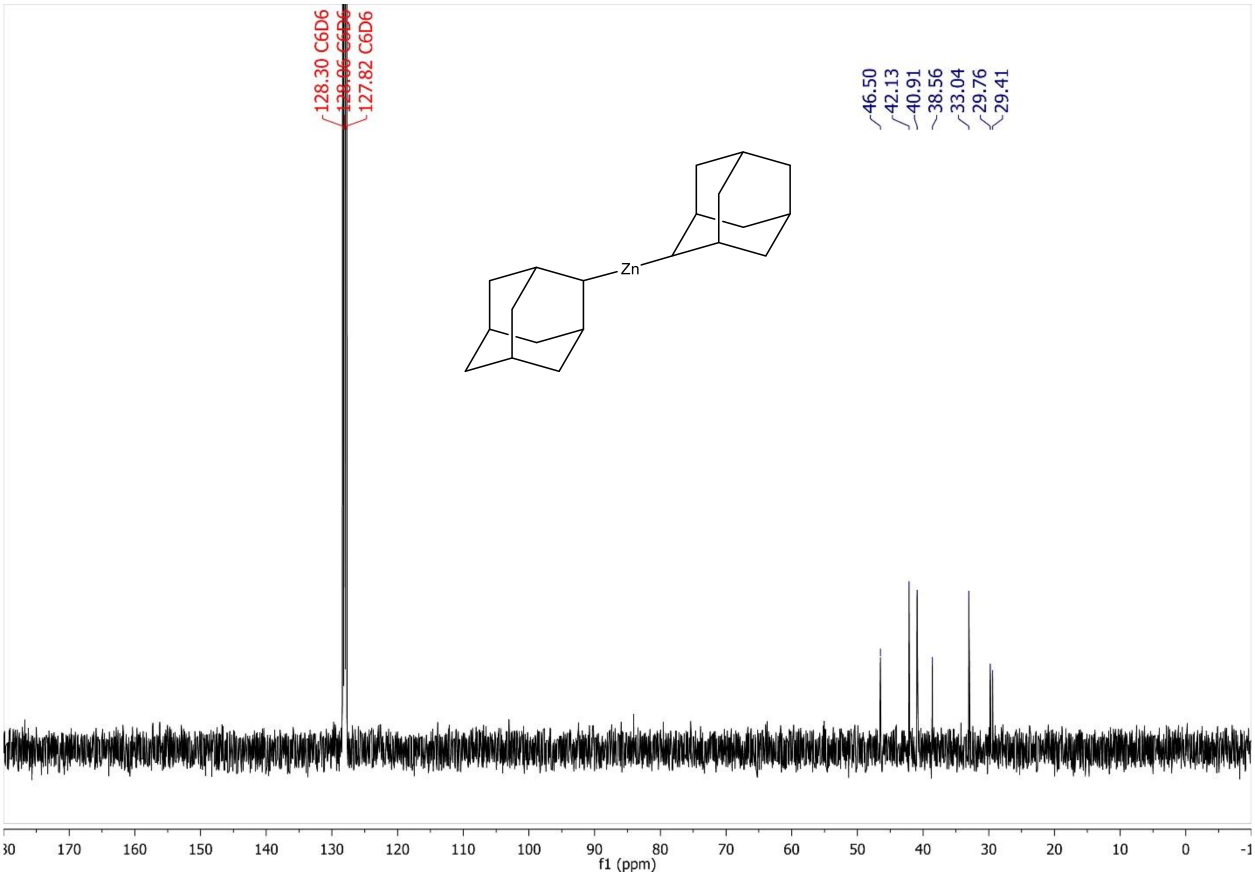

Figure S12. $^{13}C\{^1H\}$ NMR spectrum of **3b** in C_6D_6 at 25 °C.

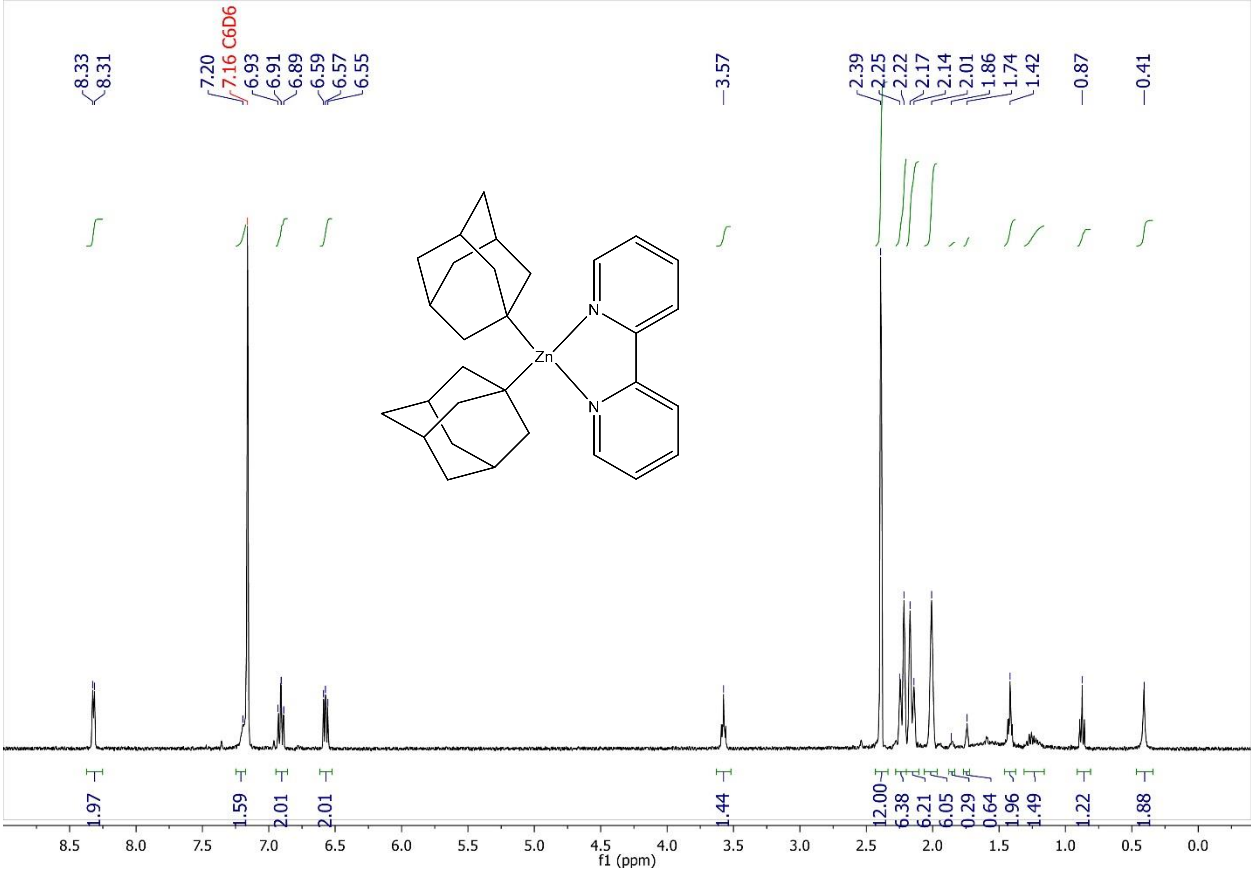

Figure S13. ^{1}H NMR spectrum of **4a** in C_6D_6 at 25 °C.

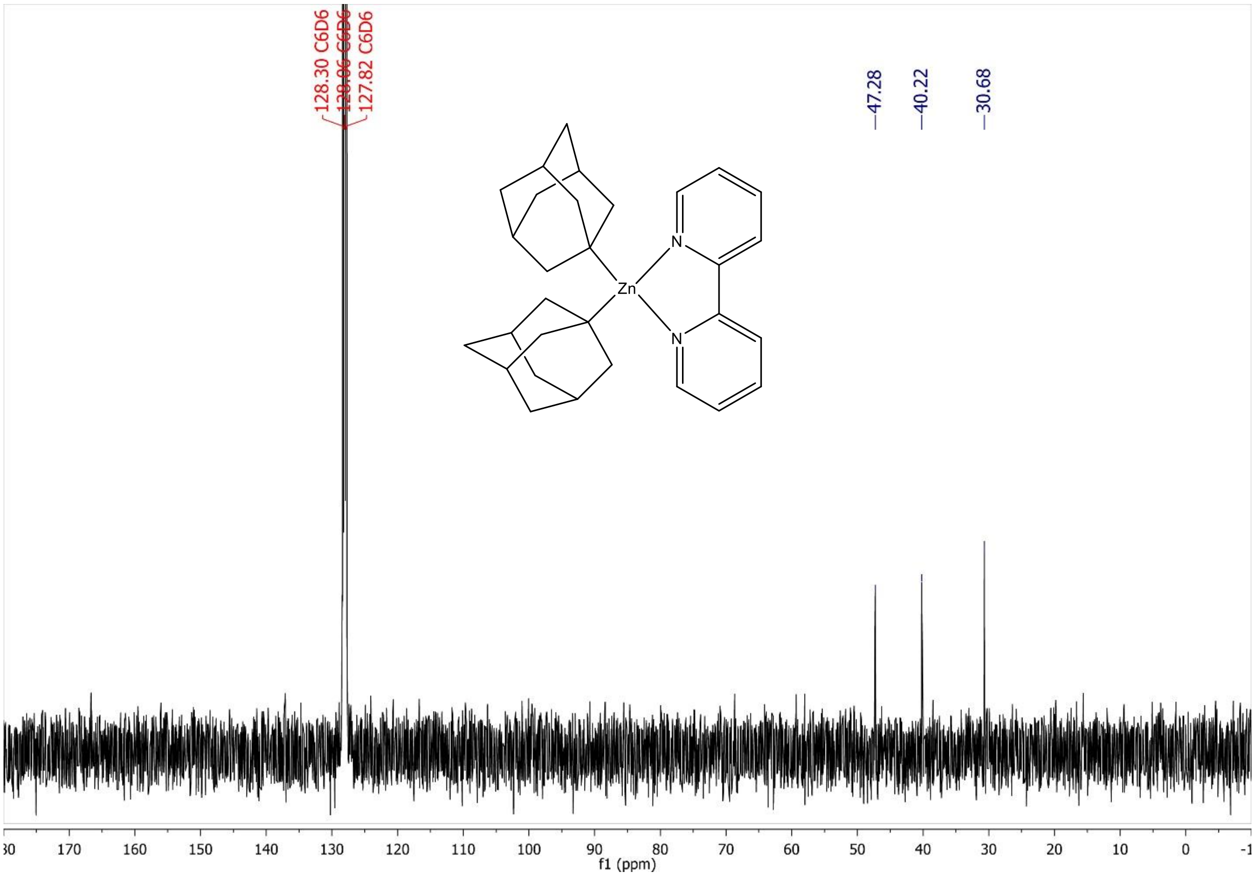

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **4a** in C_6D_6 at 25 °C.

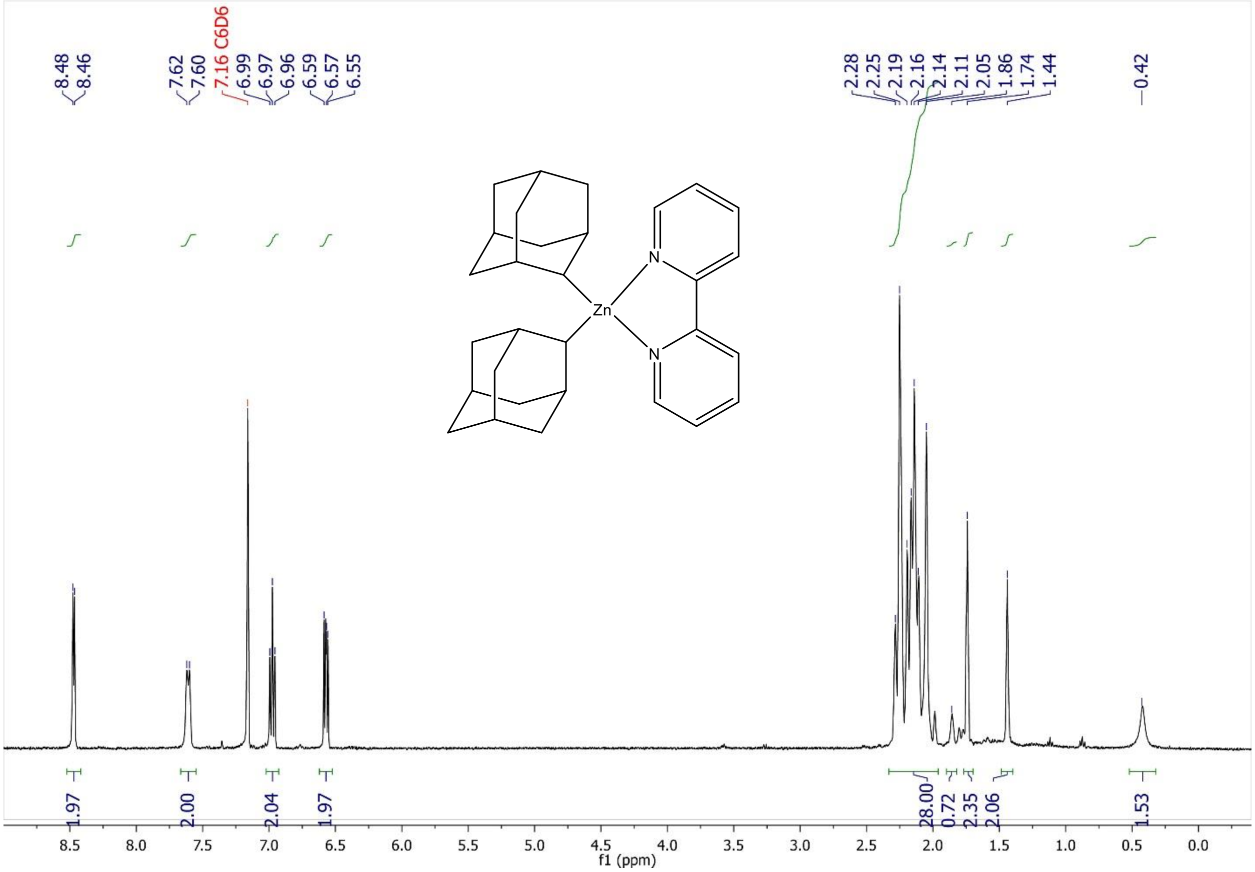

Figure S15. ^{1}H NMR spectrum of **4b** in C_6D_6 at 25 °C.

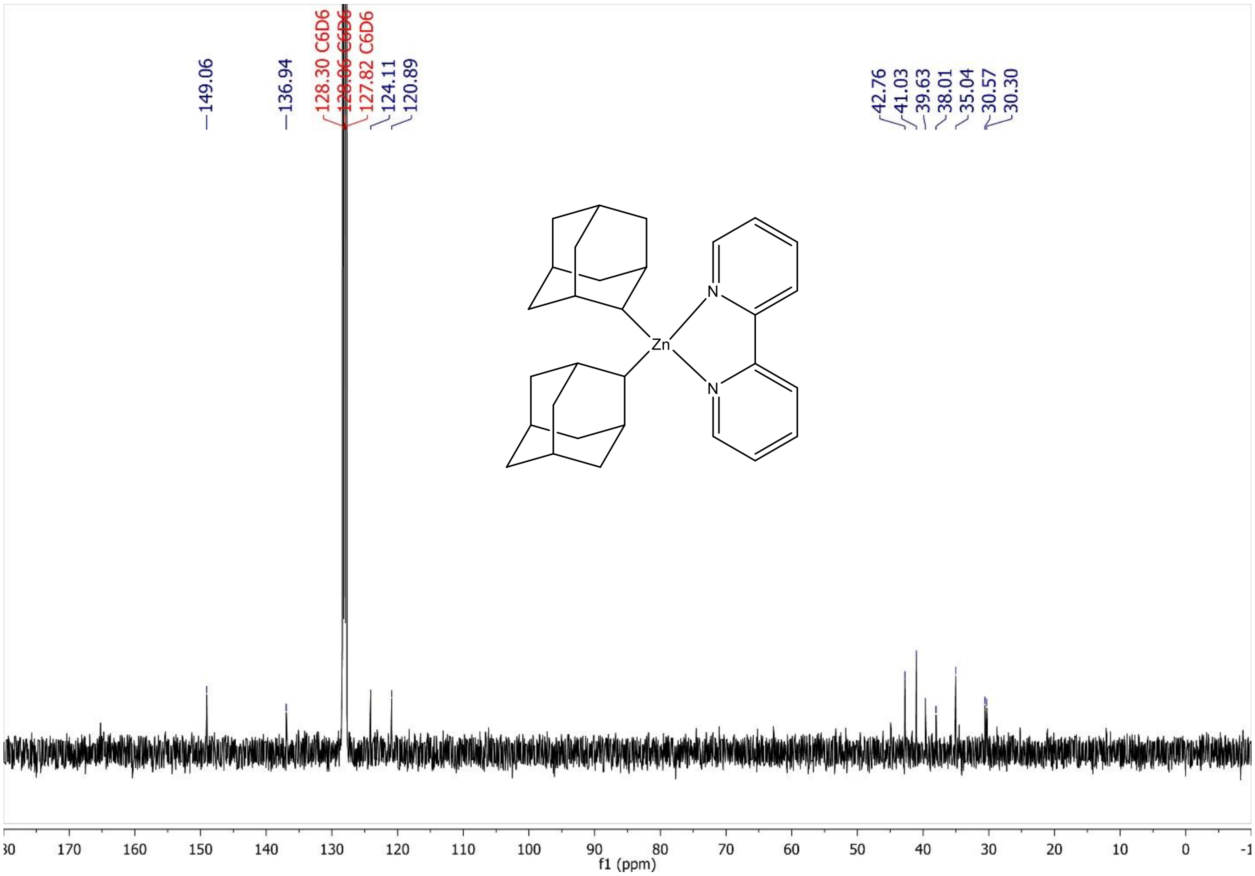

Figure S16. $^{13}C\{^1H\}$ NMR spectrum of **4b** in C_6D_6 at 25 °C.

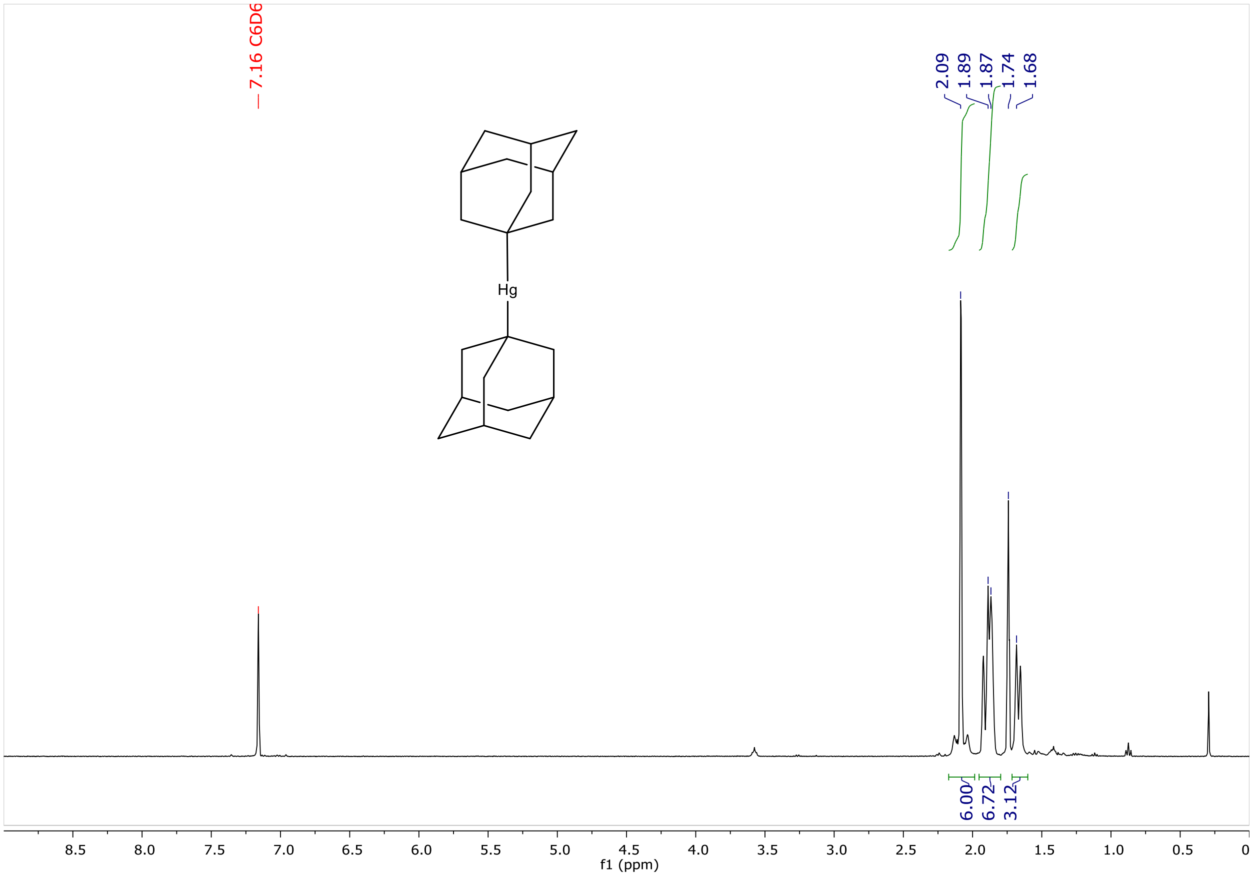

Figure S17. ^{1}H NMR spectrum of **5a** in C_6D_6 at 25 °C.

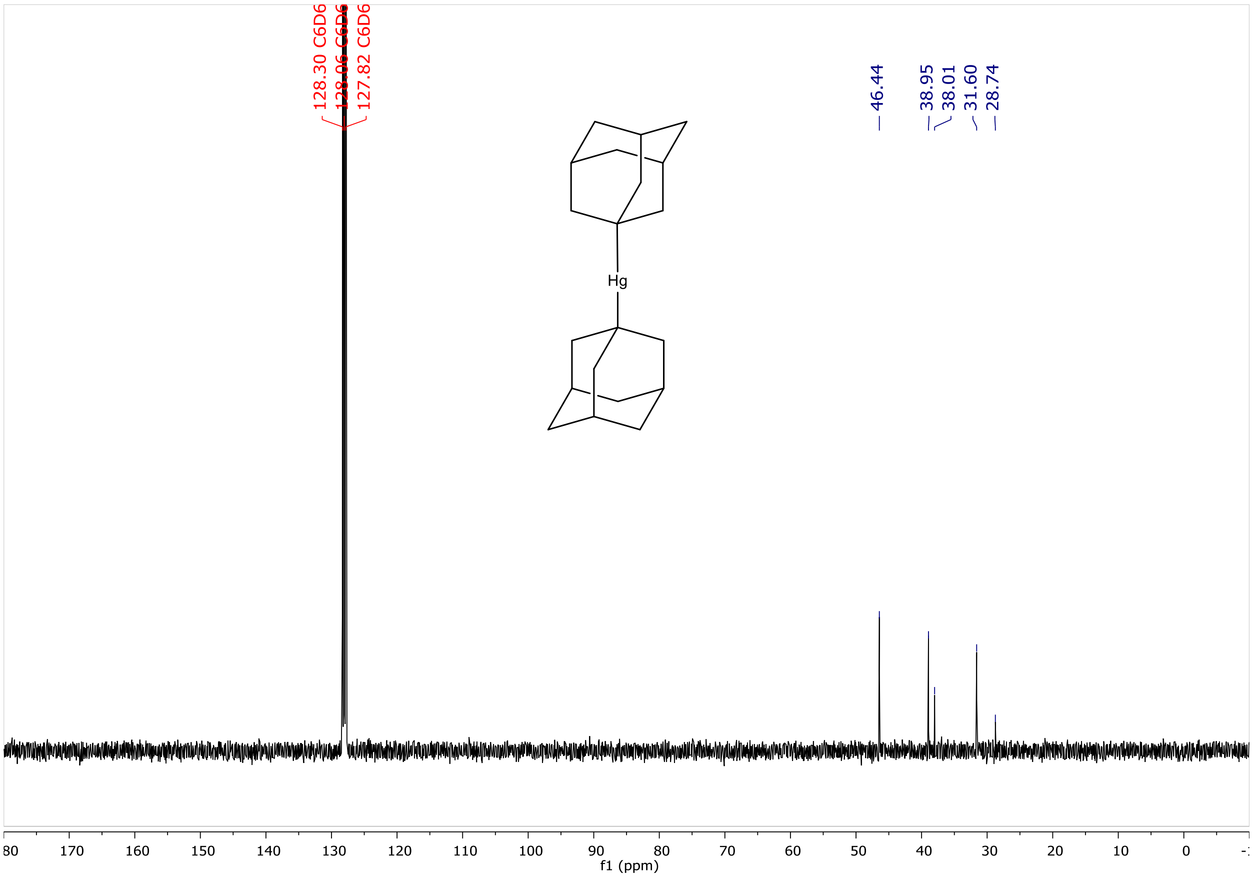

Figure S18. $^{13}C\{^1H\}$ NMR spectrum of **5a** in C_6D_6 at 25 °C.

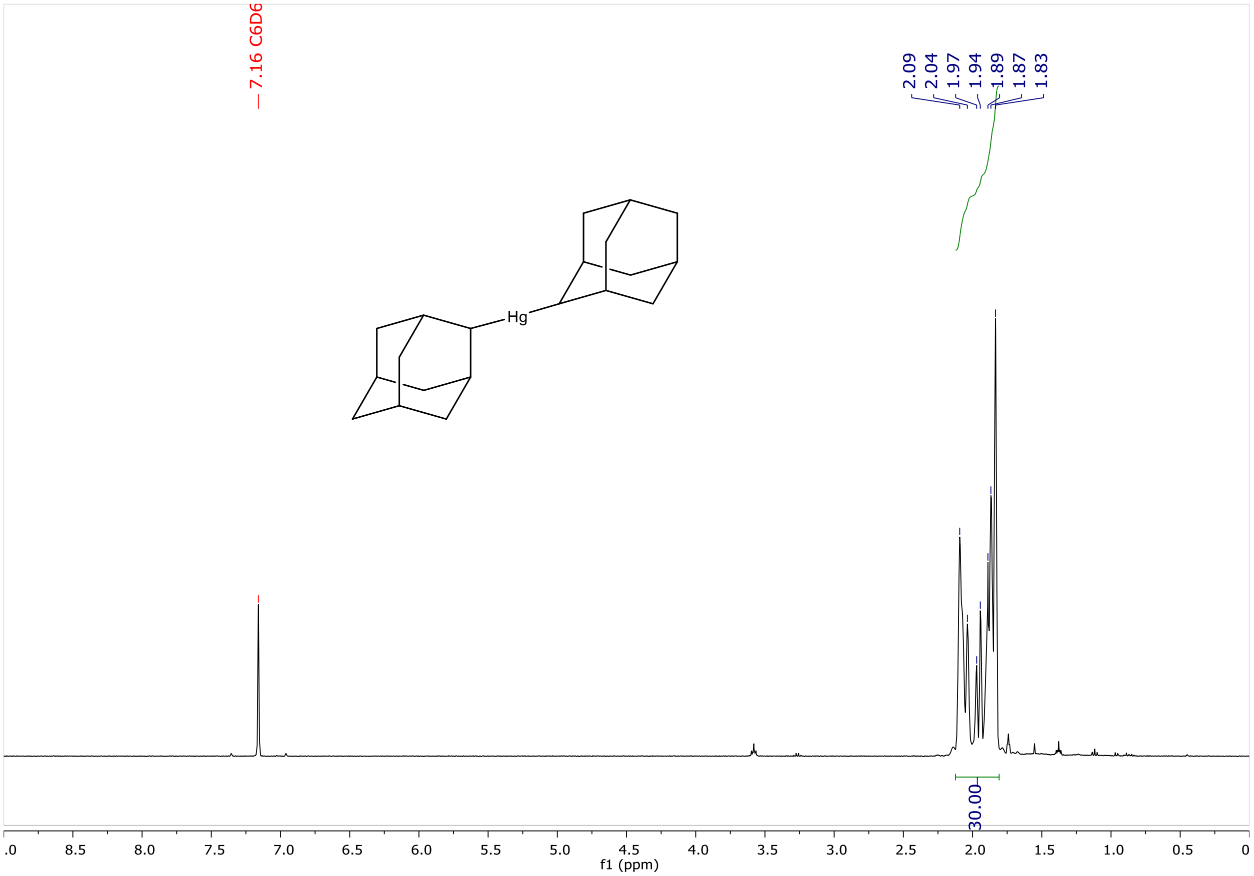

Figure S19. ^{1}H NMR spectrum of **5b** in C_6D_6 at 25 °C.

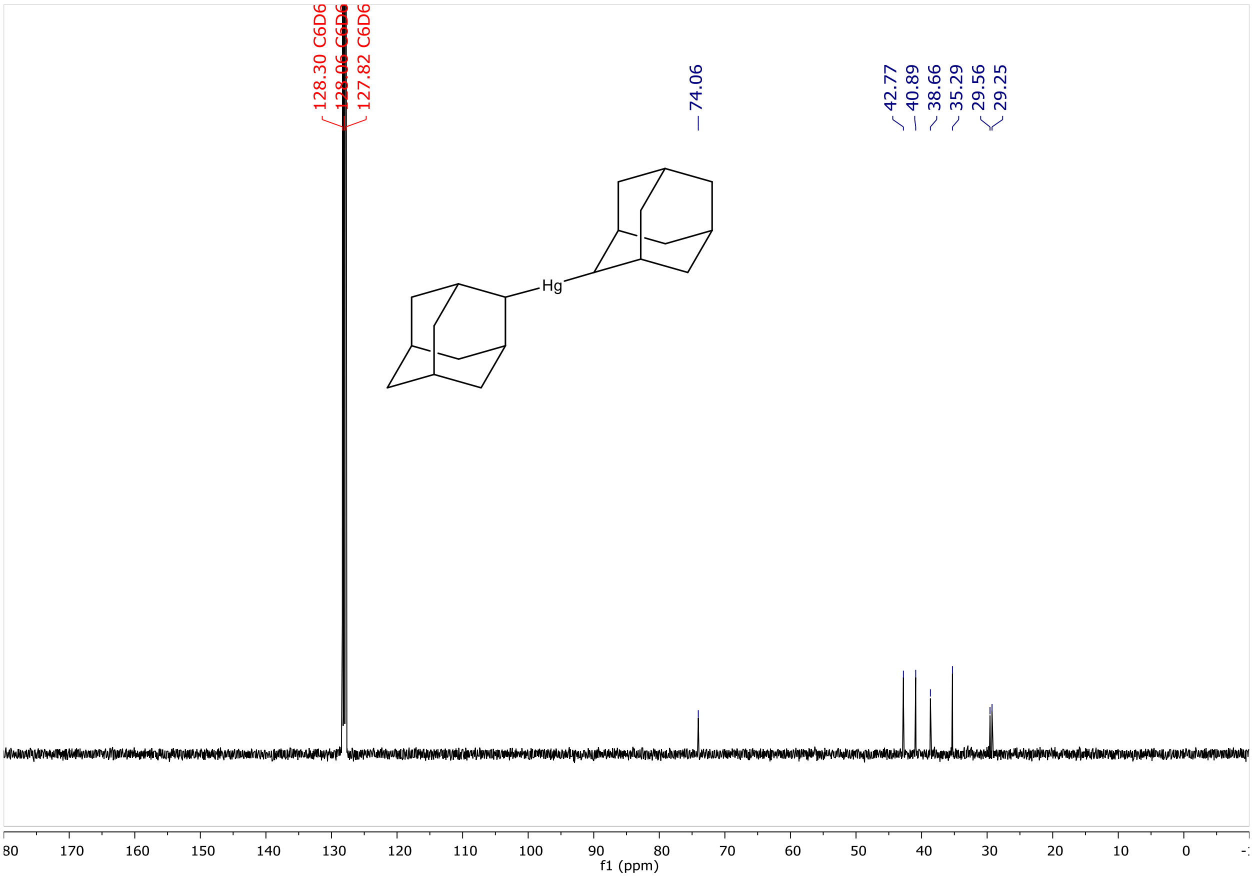

Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of **5b** in C_6D_6 at 25 °C.

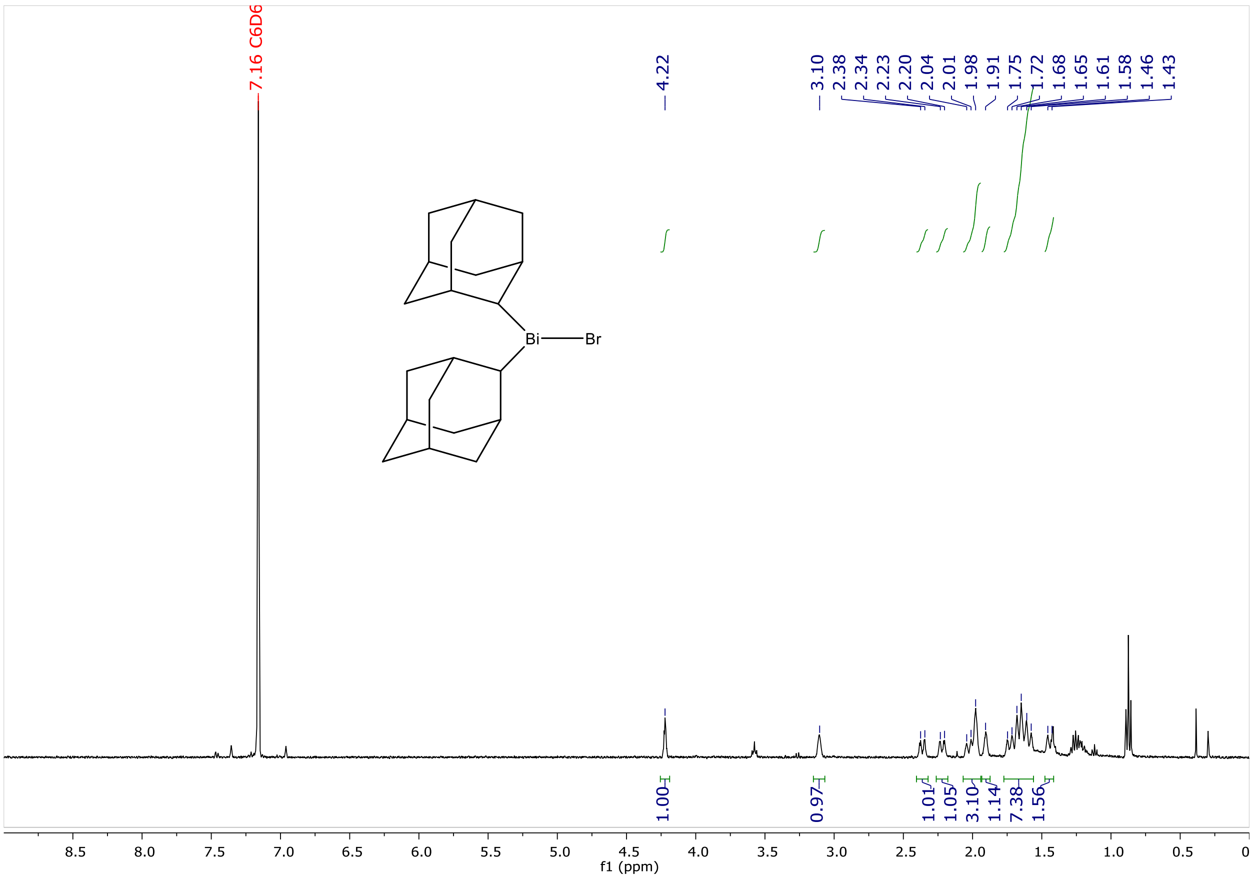

Figure S21. ^{1}H NMR spectrum of **6b** in C_6D_6 at 25 °C. (Contaminated with pentane, THF, and silicone grease).

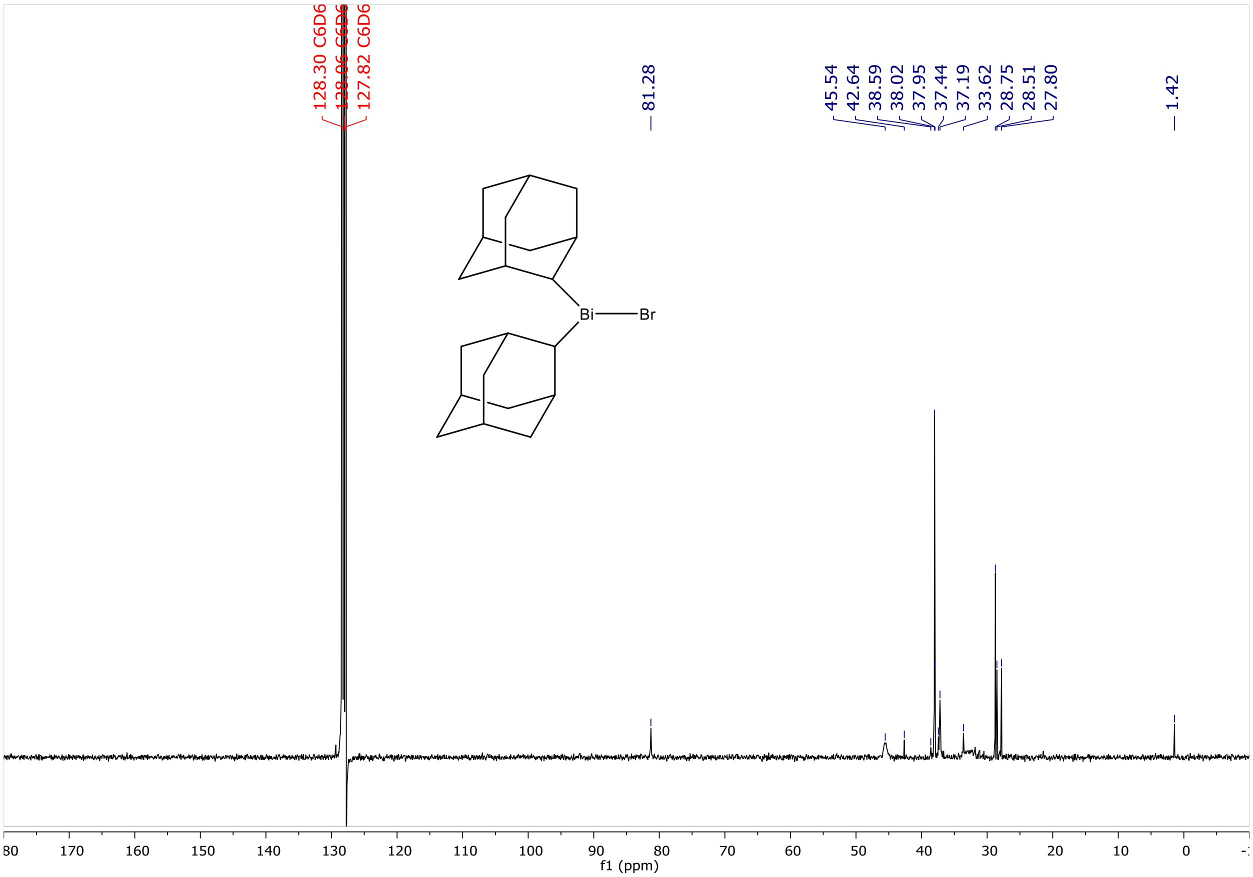

Figure S22. ^{13}C{^{1}H} NMR spectrum of **6b** in C_6D_6 at 25 °C. (Contaminated with adamantane)

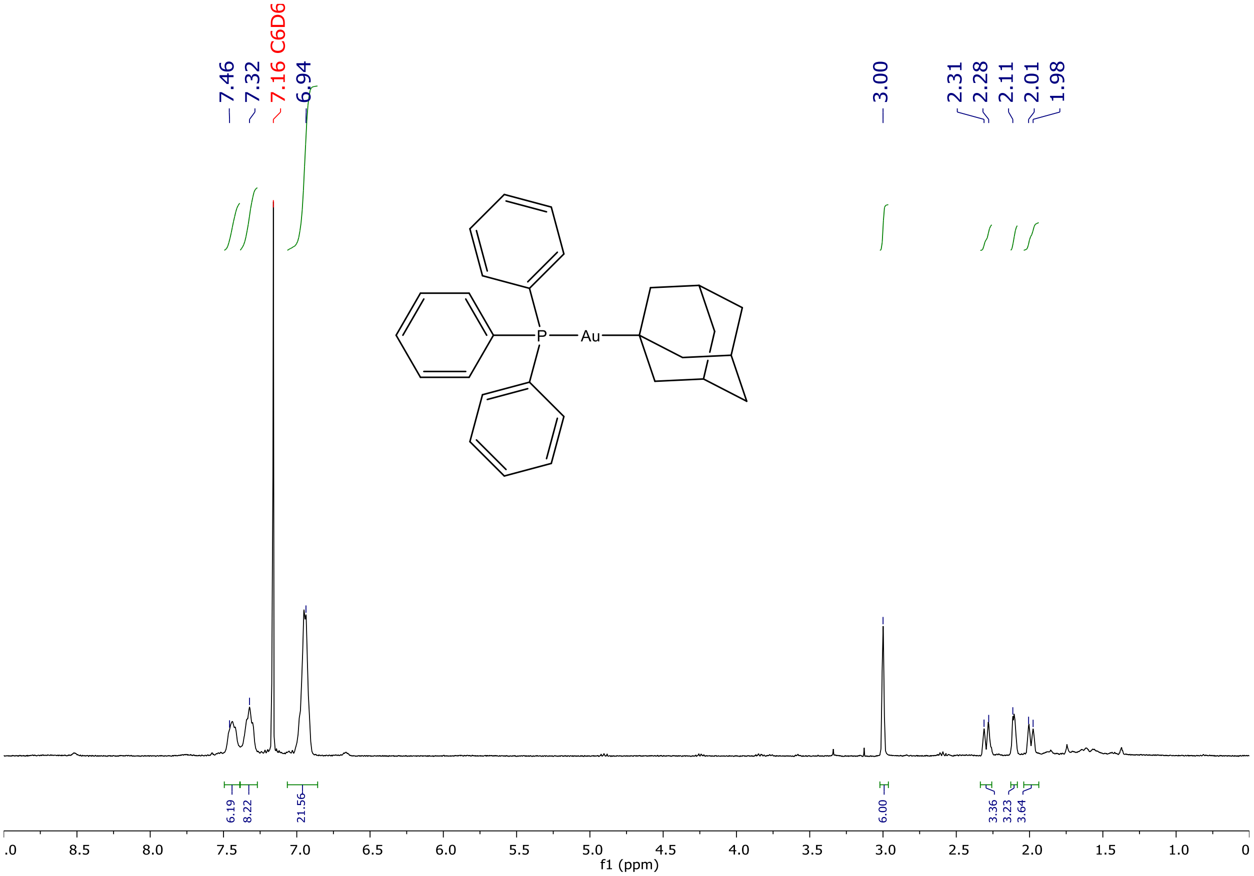

Figure S23. ^{1}H NMR spectrum of **7a** in C_6D_6 at 25 °C.

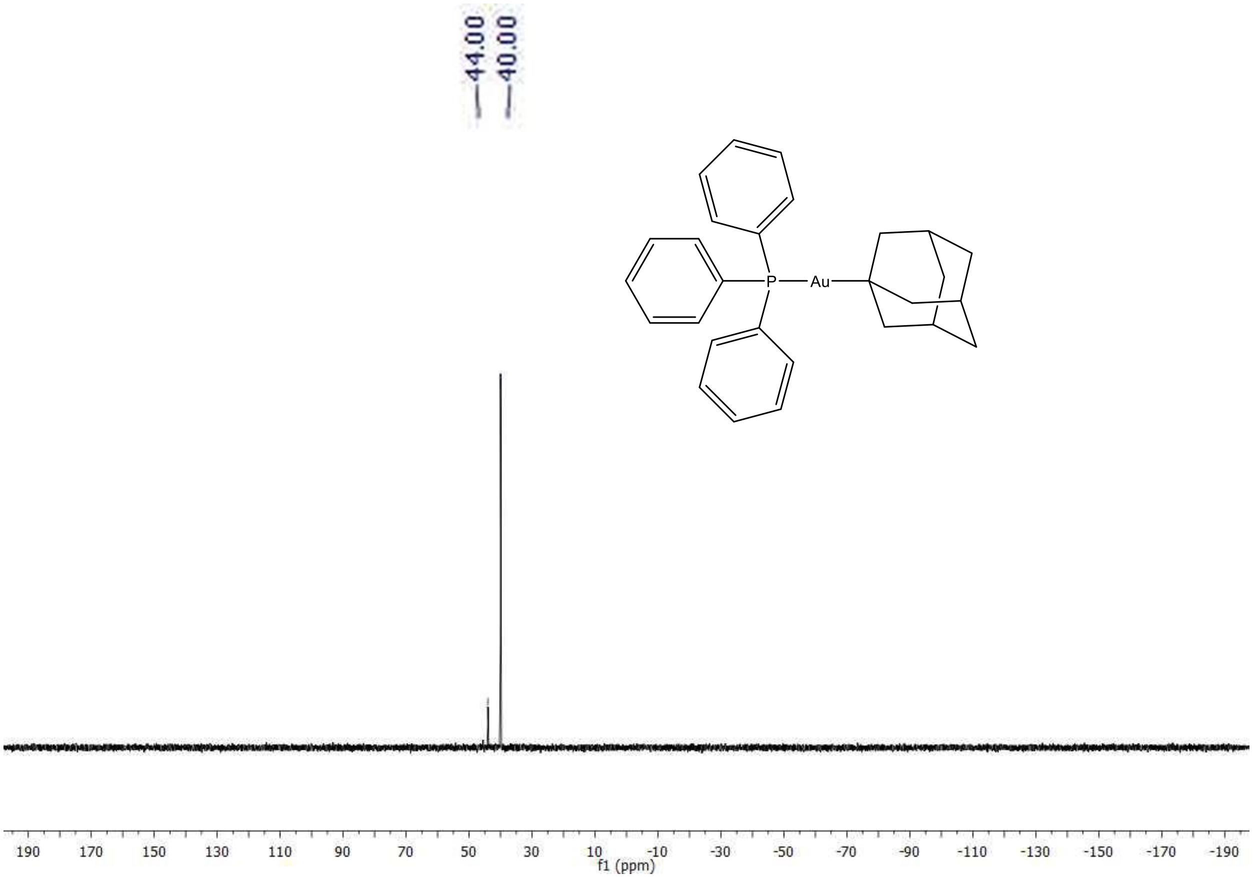

Figure S24. $^{31}P\{^{1}H\}$ NMR spectrum of **7a** in C_6D_6 at 25 °C.

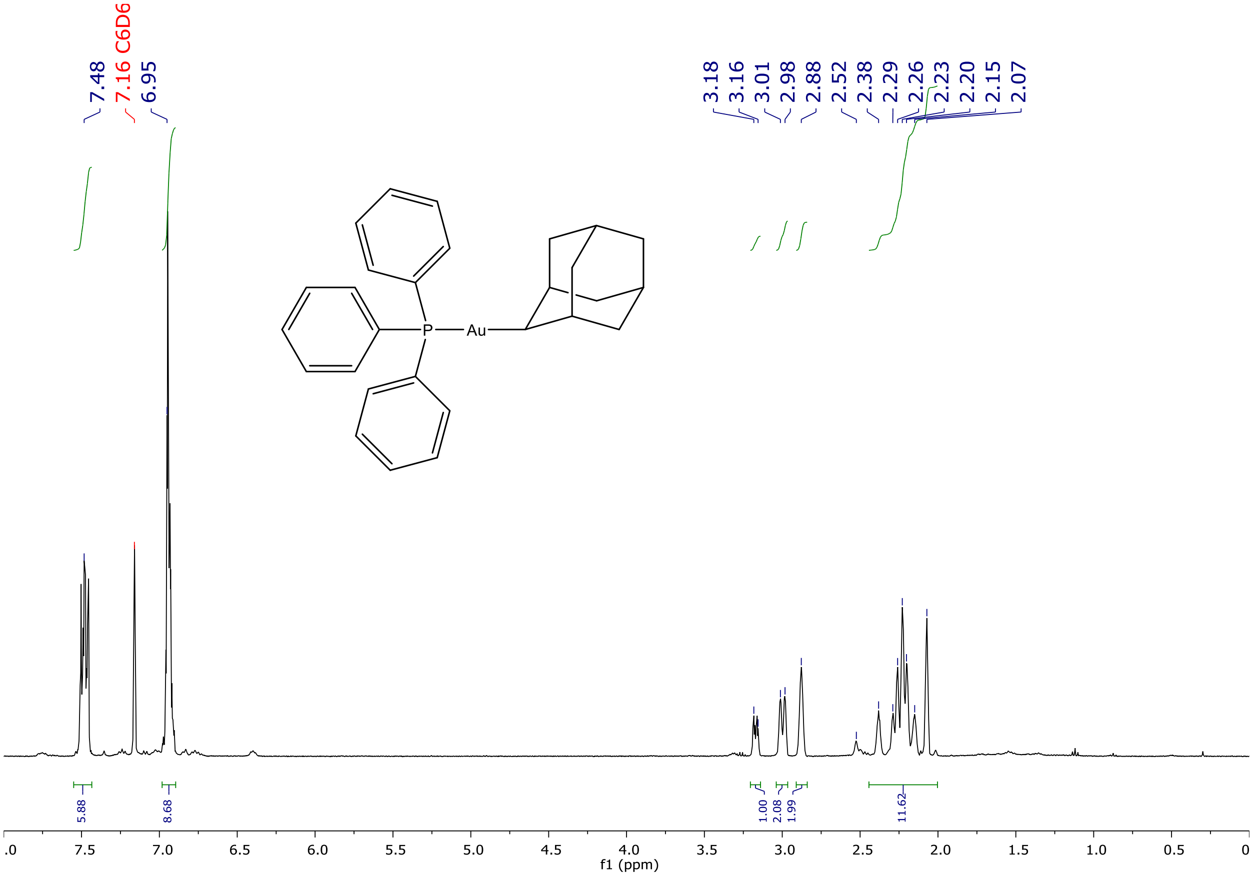

Figure S25. ^{1}H NMR spectrum of **7b** in C_6D_6 at 25 °C.

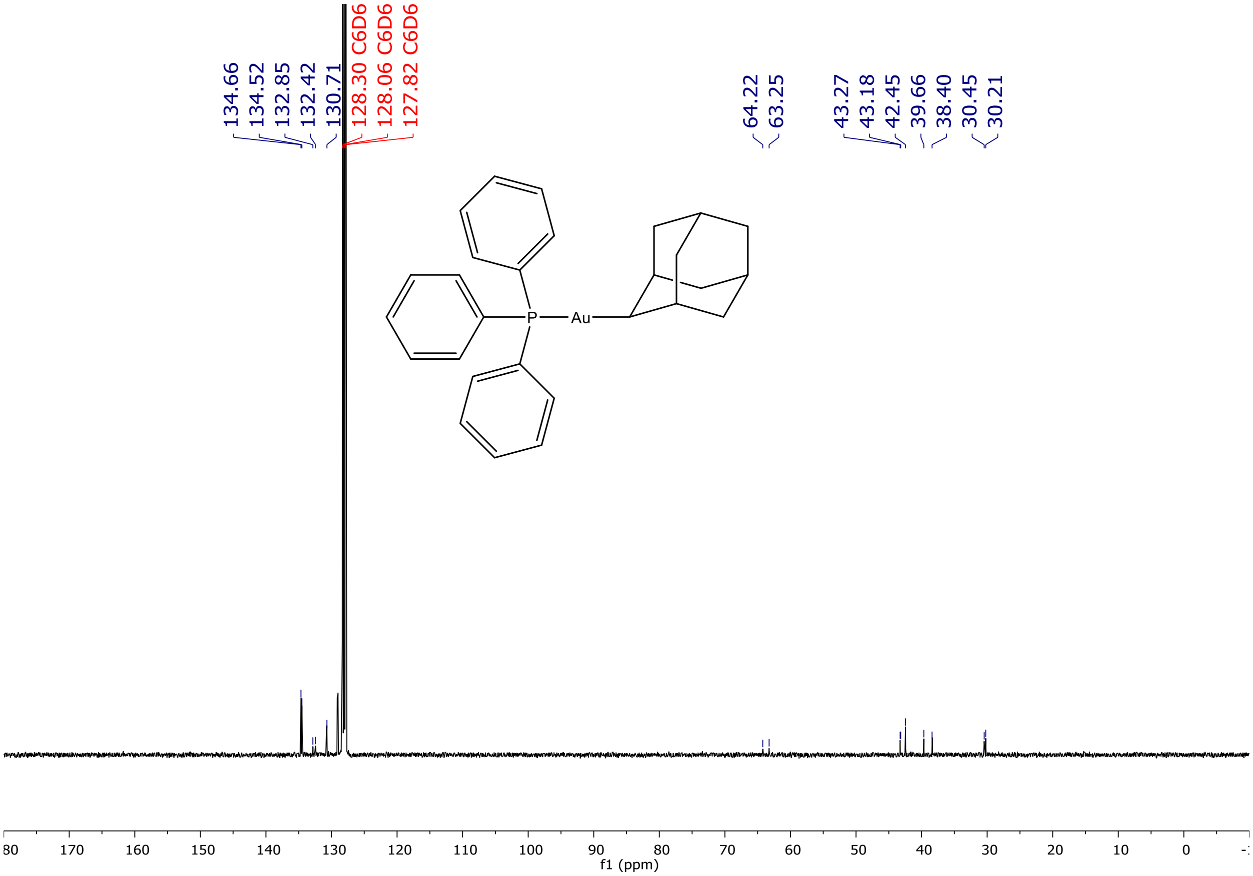

Figure S26. $^{13}C\{^1H\}$ NMR spectrum of **7b** in C_6D_6 at 25 °C.

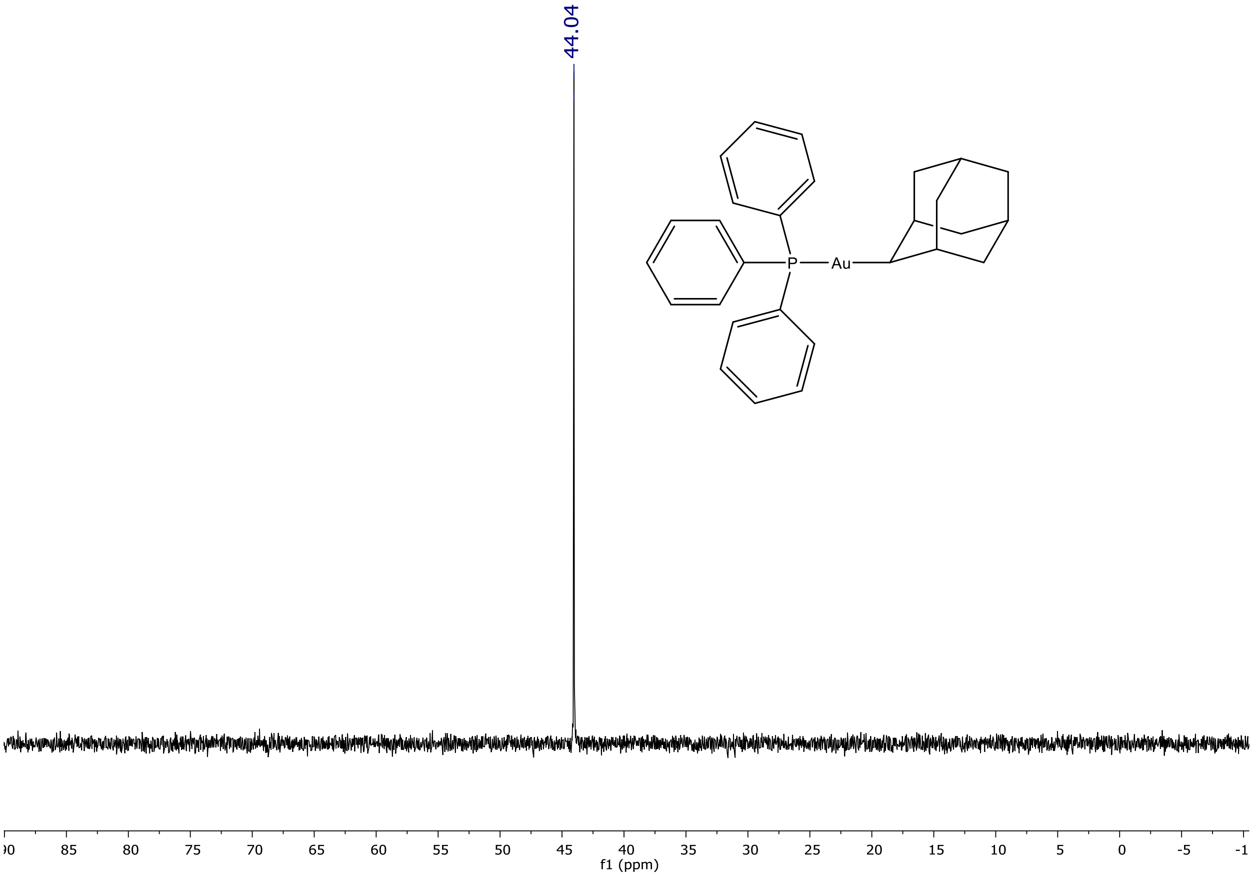

Figure S27. ^{31}P{^{1}H} NMR spectrum of **7b** in C_6D_6 at 25 °C.

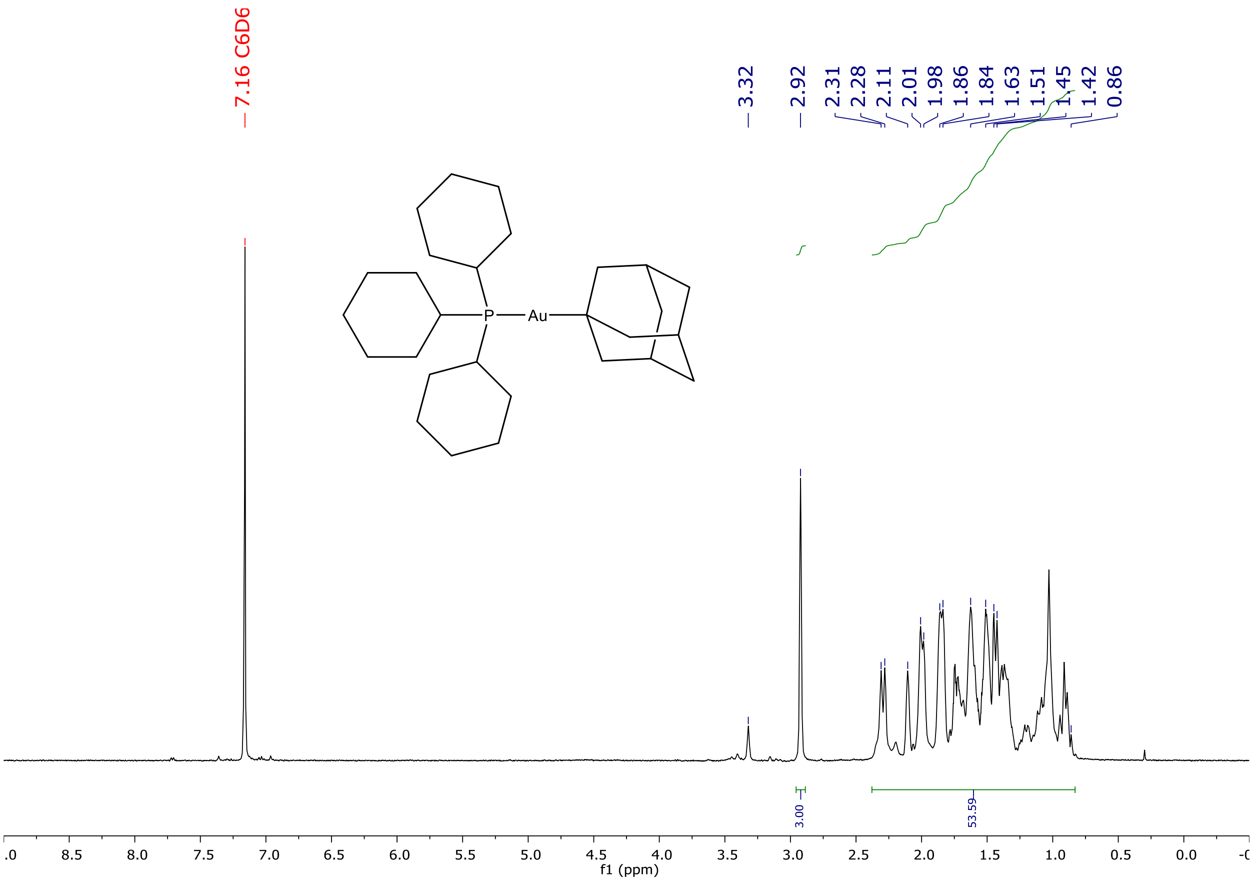

Figure S28. ^{1}H NMR spectrum of **8a** in C_6D_6 at 25 °C.

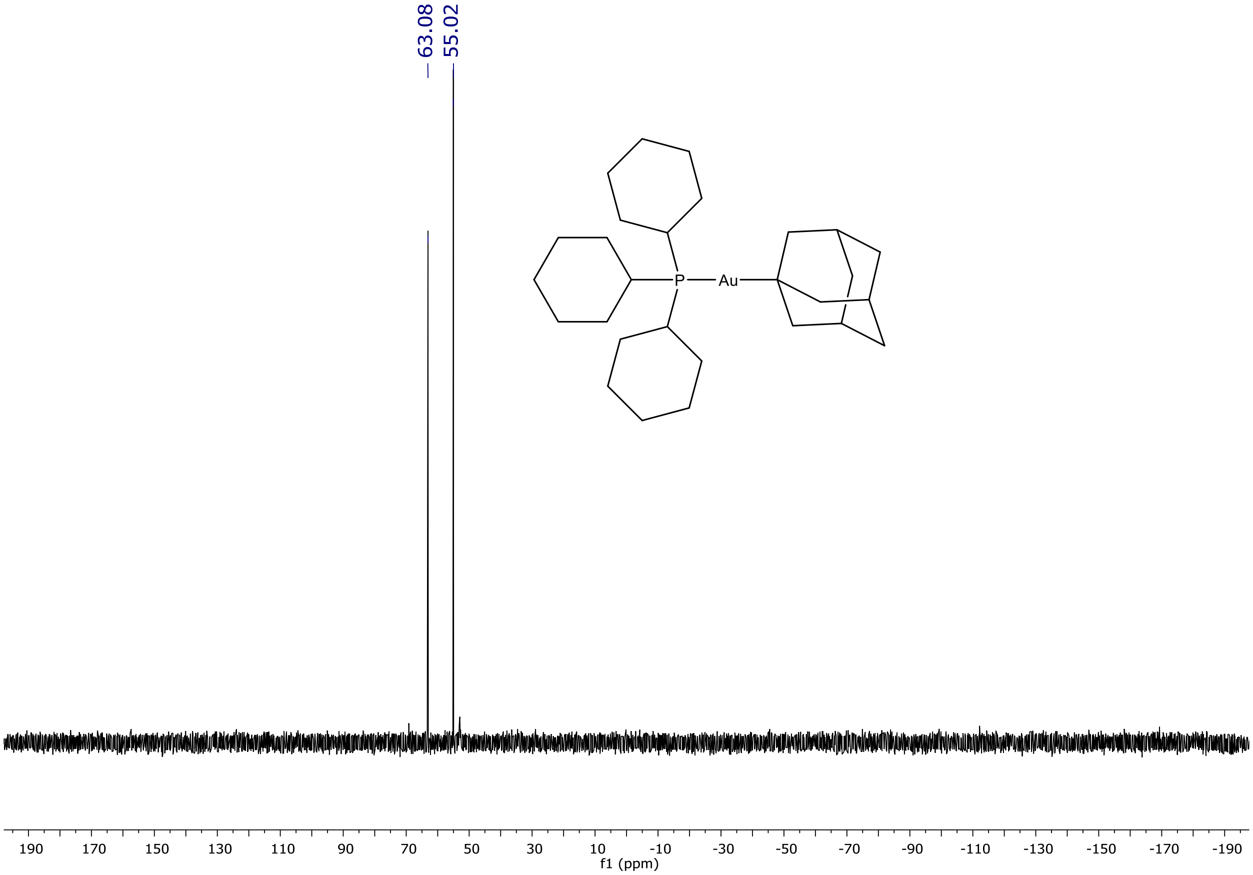

Figure S29. $^{31}P\{^{1}H\}$ NMR spectrum of **8a** in C_6D_6 at 25 °C.

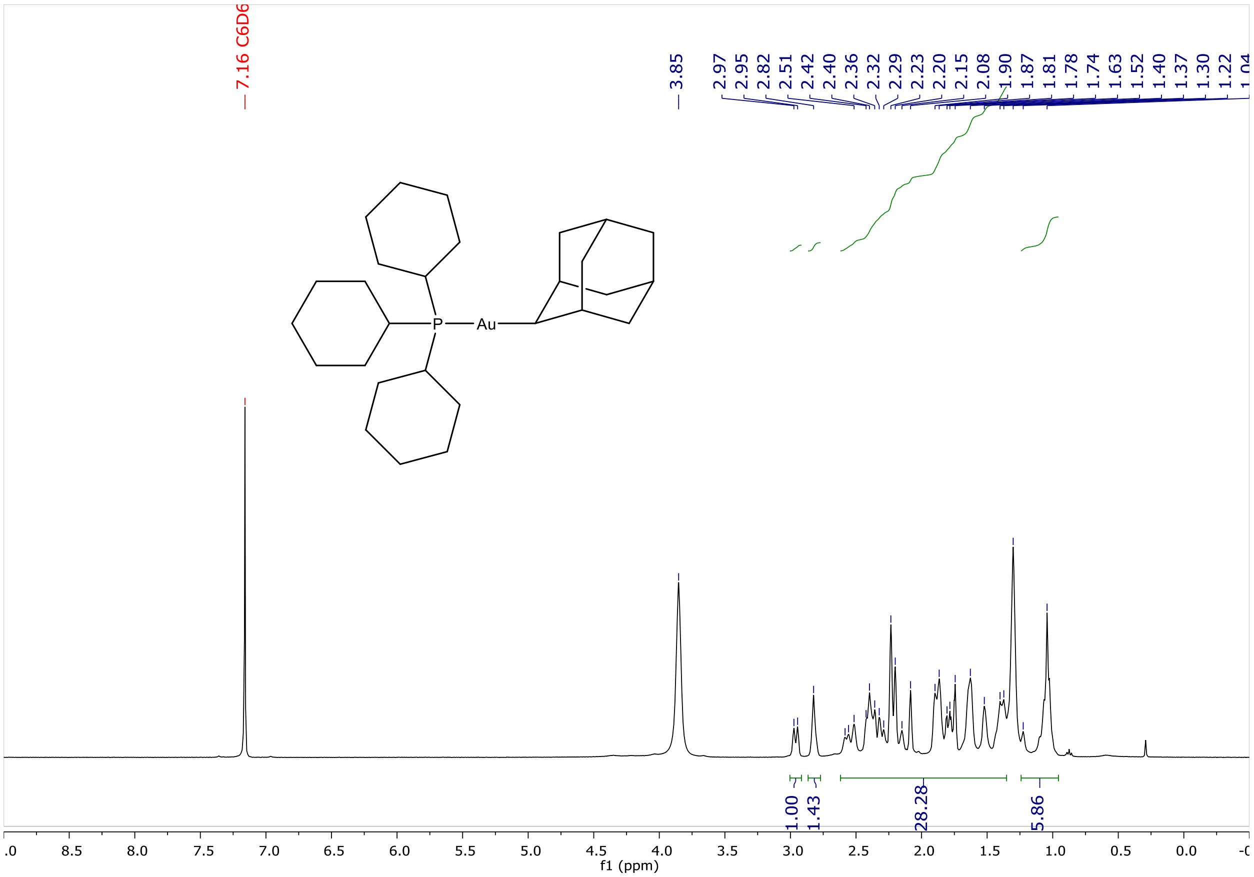

Figure S30. ^{1}H NMR spectrum of **8b** in C_6D_6 at 25 °C. (Contaminated with THF)

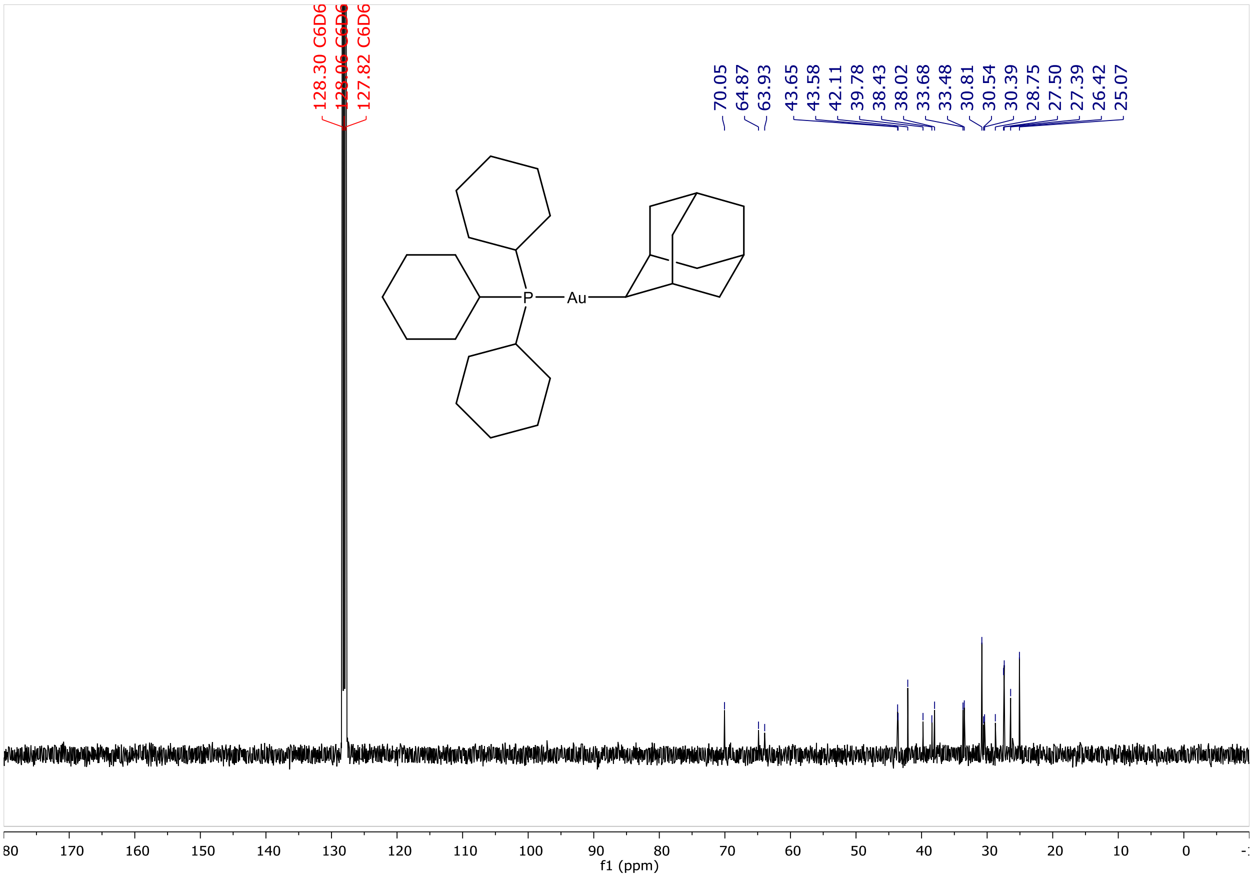

Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of **8b** in C_6D_6 at 25 °C. (Contaminated with THF)

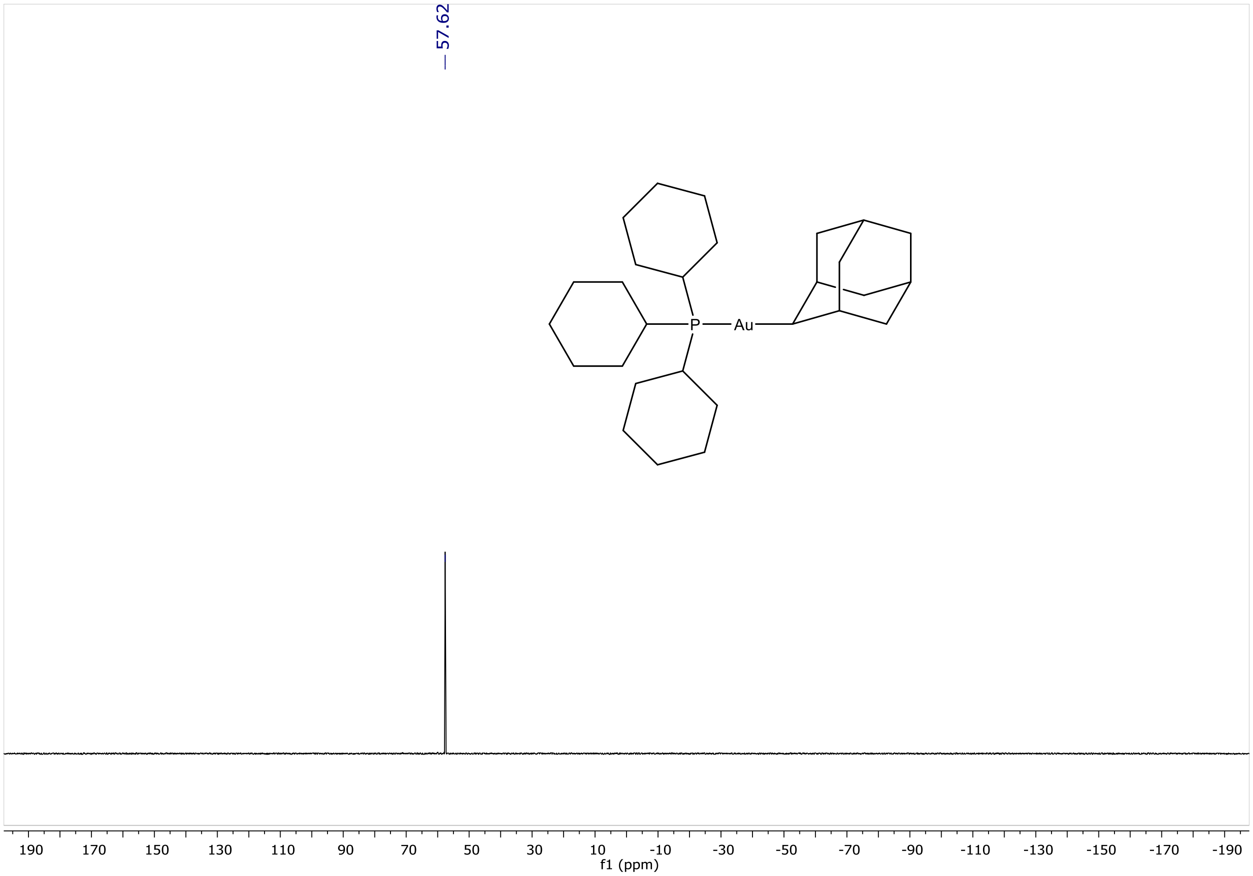

Figure S32. $^{31}P\{^{1}H\}$ NMR spectrum of **8b** in C_6D_6 at 25 °C.

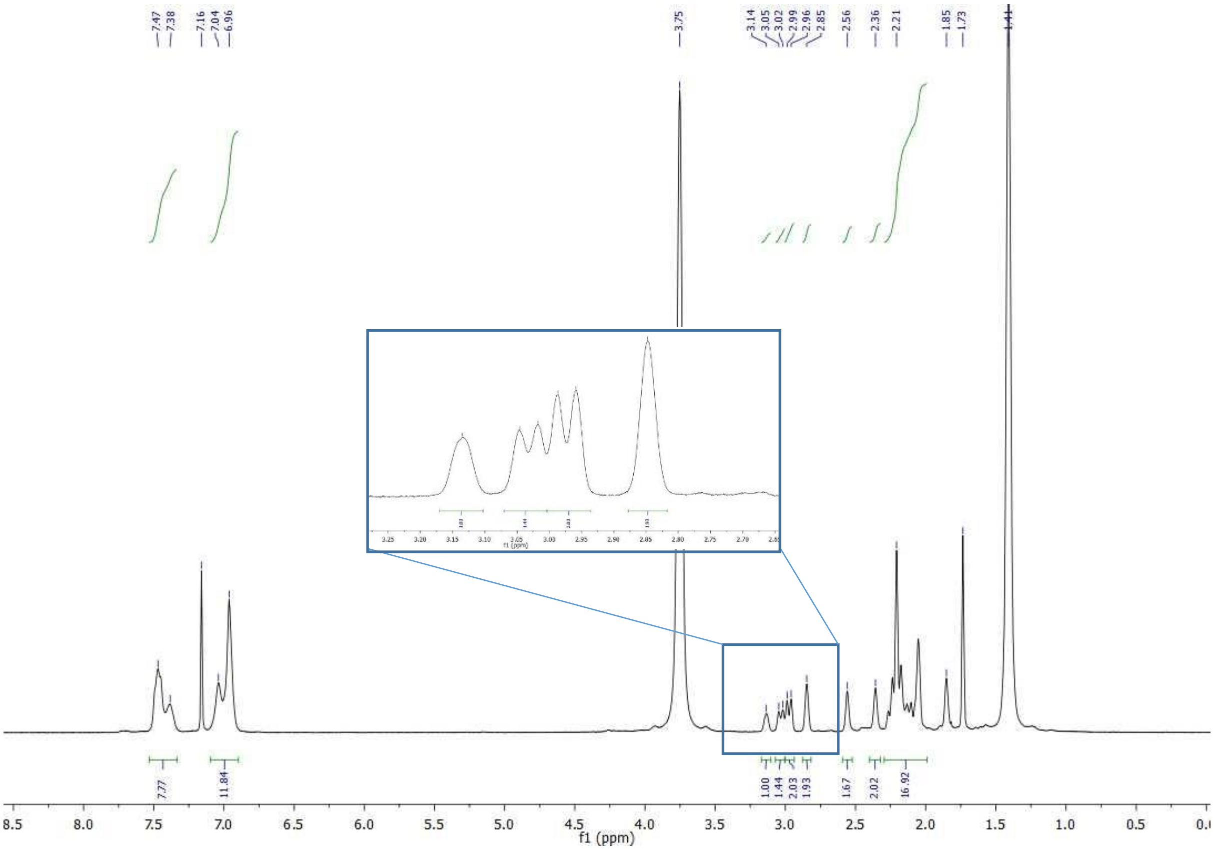

Figure S33. ^{1}H NMR spectrum in C_6D_6 showing the decomposition of **7b**; a new doublet at 3.02 emerges over time.

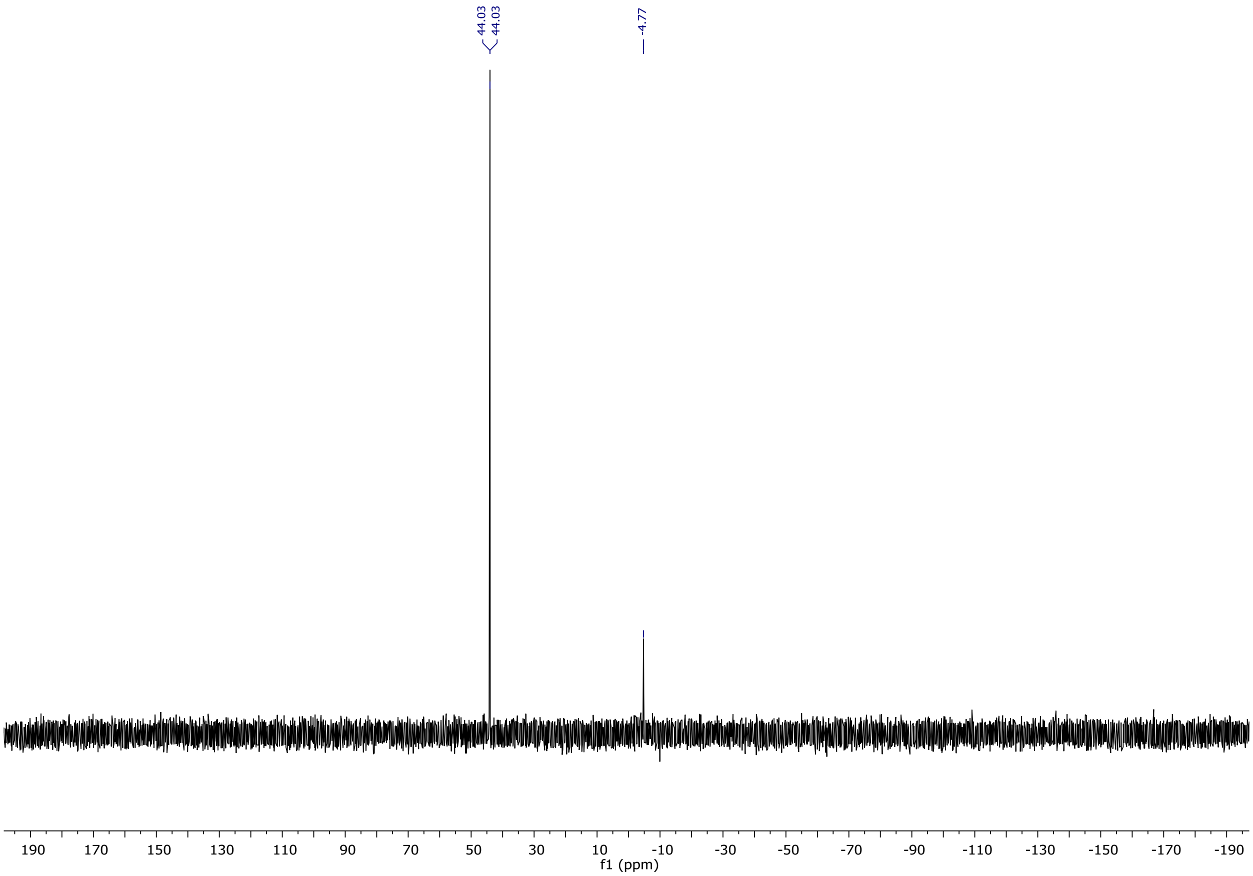

Figure S34. $^{31}P\{^1H\}$ NMR in C_6D_6 showing the decomposition of **7b**; free PPh_3 is observed at -4.77 ppm.

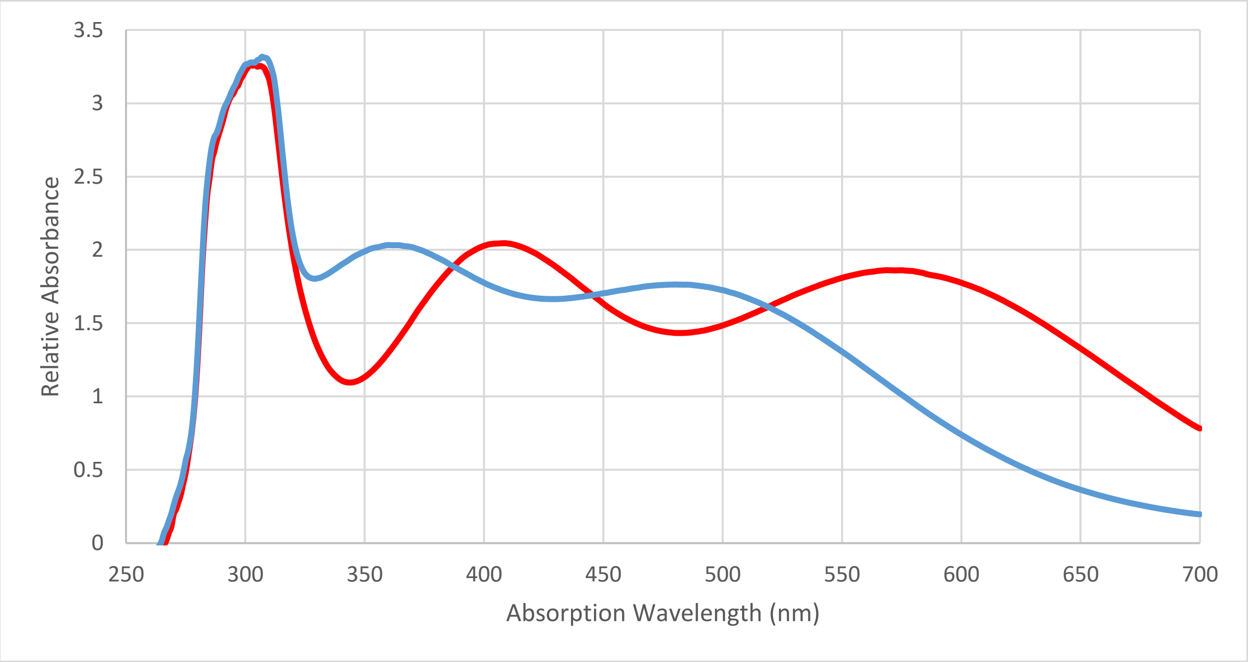

Figure S35. UV-Vis spectra of **4a** (red) and **4b** (blue) in toluene.

References

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[i] Sämann, C.; Dhayalan, V.; Schreiner, P. R.; Knochel, P. *Org. Lett.* **2014**, *16*, 2418-2421.

[ii] Aso, Y.; Yamashita, H.; Otsubo, T.; Ogura, F. *J. Org. Chem.*, **1989**, *54*, 5627-5629.