Electronic Supplementary Information

Diimine-Supported Aluminum Hydride: A Versatile Hydride, Hydrogen Atom and Electron Donor

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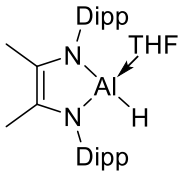
Contents

1. General Information

All manipulations were carried out on a Schlenk line or in an argon atmosphere glovebox. Solvents were dried using a MBraun solvent purification system, and stored over 3 Å sieves. Unless otherwise stated, commercial reagents were used without further purification. Compound **1** (L_{Dipp}^{2-})AlCl(THF) were synthesized according to the literature methods[1]. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Ascend 500M spectrometer. HRMS were recorded on a Thermo Scientific TM Q-Exactive PlusTM mass spectrometer. IR spectra were recorded on a Bruker ALPHA II FT-IR spectrometer. EPR spectra were collected on a CIQTEK X-band EPR spectrometer. Single-crystal X-ray diffraction data were collected on a Bruker D8 QUEST diffractometer using Cu (60W, Diamond, μKα = 12.894 mm^{-1}) micro-focus X-ray sources. Using Olex2[2] structure was solved with the XT2[3] structure solution program using Intrinsic Phasing and refined with the XL[4] refinement package using Least Squares minimization.

2. Experimental Section

Synthesis of 1:



At -30 °C a solution of α-diimine aluminum chloride (53.8 mg, 0.1 mmol) in toluene (1 mL) was added slowly to a stirring solution of $LiAlH_4$ (3.8 mg, 0.1 mmol) in toluene (1 mL). The mixture was stirred overnight. The solvent was removed under vacuum and the resulting white solid was washed with 3 x 1 mL hexane and dried in vacuo to yield white powders of the product (15.1 mg, 30 % yield). Colorless crystals suitable for X-ray diffraction studies were obtained by storage a solution of the product in hexane/toluene in -30 °C for several days.

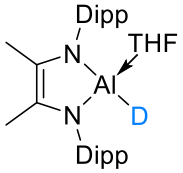
^{1}H NMR (500 MHz, C_6D_6, ppm): δ 1.02 (br, 4H, THF), 1.39 (d, *J* = 6.4 Hz, 24H, ^{i}Pr-C*H*$_3$), 1.81 (s, 6H, NCC*H*$_3$), 3.55 (br, 4H, THF), 3.72-3.89 (m, 4H, ^{i}Pr-C*H*), 4.21 (br, 1H, Al*H*), 7.21-7.31 (m, 6H, Ar*H*).

^{13}C{^{1}H} NMR (125 MHz, C_6D_6, ppm): δ 147.4 (s, N–*C*CH$_3$), 144.3(s, Ar), 124.6(s, Ar), 123.5 (s, Ar), 119.7 (s, Ar), 70.7 (s, THF), 27.9 (s, THF), 26.0 (s, *C*H), 24.9 (s, *C*H$_3$), 24.5 (s, *C*H$_3$), 14.5 (s, NC*C*H$_3$).

IR (ATR, solid, cm^{-1}): 2960, 2927, 2867, 1851 (Al-H), 1641, 1461, 1436, 1382, 1361, 1322, 1250, 1214, 1181, 1120, 7920, 762.

HRMS (*m/z*): $[M + NH_4]^+$ Calcd. for $C_{32}H_{53}AlN_3O^+$:522.3999; Found: 522.3984.

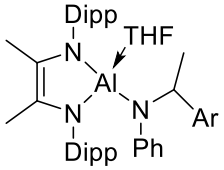
Duterium aluminum hydride of 1-D:



Using $LiAlD_4$ as starting material to react with α-diimine aluminum chloride, the procedure is same as the synthesis of **1**.

^{1}H NMR (500 MHz, C_6D_6, ppm): δ 1.03 (br, 4H, THF*H*), 1.39 (d, *J* = 5.4 Hz, 24H, ^{i}*Pr*-CH_3), 1.78 (s, 6H, NCCH_3), 3.54 (br, 4H, THF*H*), 3.80 (br, 4H, ^{i}Pr-C*H*), 7.27 (br, 6H, Ar*H*).

Synthesis of 2:



2, Ar = 4-F-C_6H_4

At -30 °C a solution of α-diimine aluminum hydride **1** (50.5 mg, 0.1 mmol) in toluene (1 mL) was added slowly to a stirring solution of 1-(4-fluorophenyl)-N-phenylethan-1-imine (21.3 mg, 0.1 mmol) in toluene (1 mL). The mixture was stirred overnight. The solvent was removed under vacuum and the resulting green solid was washed with 3 x 1 mL hexane and dried in vacuo to yield green powders of the product (50.2 mg, 70 % yield). Green crystals suitable for X-ray diffraction studies were obtained by storage a solution of the product in hexane/toluene in -30 °C for several days.

^{1}H NMR (500 MHz, C_6D_6, ppm): δ 0.91 (br, 6H, ^{i}Pr-CH_3), 1.02 (br, 4H, THF*H*), 1.14-1.19 (m, 9H, ^{i}Pr-CH_3), 1.23-1.29 (m, 9H, ^{i}Pr-CH_3), 1.36 (d, *J* = 7.0 Hz, 3H, NCHCH_3), 1.65 (s, 6H, NCCH_3), 3.40 (sept, *J* = 6.3 Hz, 1H, ^{i}Pr-C*H*), 3.48 (sept, *J* = 6.3 Hz, 1H, ^{i}Pr-C*H*), 3.64 (sept, *J* = 6.3 Hz, 1H, ^{i}Pr-C*H*), 3.67-3.80 (m, 5H, overlapped, THF*H* and ^{i}Pr-C*H*), 4.60 (q, *J* = 7.1 Hz, 1H, NC*H*), 6.29 (d, *J* = 7.8 Hz, 2H, Ar*H*), 6.36 (t, *J* = 7.4 Hz, 1H, Ar*H*), 6.61 (t, *J* = 7.7 Hz, 2H, Ar*H*), 6.67 (t, *J* = 7.2 Hz, 2H, Ar*H*), 6.80 (t, *J* = 6.3 Hz, 2H, Ar*H*), 7.04-7.09 (m, 4H, Ar*H*), 7.10-7.15 (m, 2H, Ar*H*).

^{13}C{^{1}H} NMR (125 MHz, C_6D_6, ppm): δ 162.6(s, *C*-F), 160.6(s, Ar), 150.0(s, N–*C*(Ph)), 149.0(s, N–*C*CH3), 148.9 (s, N–*C*CH3), 146.1 (s, Ar), 145.8 (s, Ar), 145.0 (s, Ar), 144.9 (s, Ar), 141.1 (s, Ar), 129.2 (s, Ar), 129.2 (s, Ar), 129.0 (s, Ar), 124.9 (s, Ar), 124.8 (s, Ar), 124.4 (s, Ar), 124.3 (s, Ar), 123.2 (s, Ar), 122.9 (s, Ar), 120.2 (s, Ar), 119.1 (s, Ar), 117.4 (s, Ar), 114.7 (s, Ar), 114.5 (s, Ar), 72.7 (s, THF), 54.0 (s, N-*C*H), 28.3 (s, *C*H), 28.0 (s, *C*H), 27.6 (s, *C*H), 27.5 (s, *C*H), 25.6 (s, *C*H_3), 25.4 (s, *C*H_3), 25.4 (s, *C*H_3), 25.3 (s, *C*H_3), 25.2 (s, *C*H_3), 25.2 (s, *C*H_3), 25.0 (s, THF), 23.9 (s, *C*H_3), 23.7 (s, *C*H_3), 21.7(s, *C*H_3), 15.6 (s, C*C*H_3), 15.0

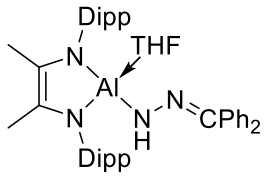
(s, C*C*H$_3$).

^{19}F{^{1}H} NMR (470 MHz, C$_6$D$_6$, ppm): δ -118.00.

IR (ATR, solid, cm^{-1}): 2967, 2864, 1596, 1506, 1493, 1460, 1434, 1382, 1315, 1256, 1244, 1210, 998, 945.83, 829, 794, 755,708, 569.

HRMS (*m/z*): [M + NH$_4$]$^+$ Calcd. for $C_{46}H_{65}AlFN_4O^+$: 735.4952; Found: 735.4955.

Synthesis of 3:



At -30 °C a solution of α-diimine aluminum hydride **1** (50.5 mg, 0.1 mmol) in toluene (1 mL) was added slowly to a stirring solution of (diphenylmethylene)hydrazine (19.6 mg, 0.1 mmol) in toluene (1 mL). The mixture was stirred overnight. The solvent was removed under vacuum and the resulting yellow solid was washed with 3 x 1 mL hexane and dried in vacuo to yield yellow powders of the product (41.8 mg, 60 % yield). Yellow crystals suitable for X-ray diffraction studies were obtained by storage a solution of the product in hexane in room temperature overnight.

^{1}H NMR (500 MHz, C$_6$D$_6$, ppm): δ 1.08-1.14 (m, 4H, THF*H*), 1.16-1.22 (m, 12H, ^{i}Pr-C*H*$_3$), 1.27 (d, *J* = 6.7Hz, 6H, ^{i}Pr-C*H*$_3$), 1.41 (d, *J* = 6.8 Hz, 6H, ^{i}Pr-C*H*$_3$), 1.74 (s, 6H, NCC*H*$_3$), 3.78 (sept, 2H, *J* = 6.3Hz, ^{i}Pr-C*H*), 3.84-3.90 (m, 6H, overlapped, THF*H* and ^{i}Pr-C*H*), 6.08 (s, 1H, N*H*), 7.01-7.04 (m, 2H, Ar*H*), 7.07-7.10 (m, 4H, Ar*H*), 7.17-7.18 (m, 2H, Ar*H*), 7.21-7.26 (m, 8H, Ar*H*).

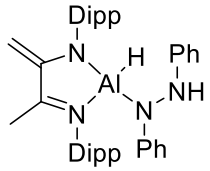
^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, ppm): δ 148.2 (s, N*C*Ph$_2$), 146.9 (s, N*C*CH$_3$), 144.3 (s, Ar), 143.9 (s, Ar), 140.7 (s, Ar), 134.1 (s, Ar), 130.1 (s, Ar), 129.6 (s, Ar), 126.6 (s, Ar), 126.2 (s, Ar), 124.4 (s, Ar), 123.9 (s, Ar), 123.1 (s, Ar), 119.0 (s, Ar), 73.3 (s, THF), 27.8 (s, *C*H), 27.7 (s, *C*H), 25.6 (s, *C*H$_3$), 25.5 (s, *C*H$_3$), 24.9 (s, *C*H$_3$), 24.9 (s, *C*H$_3$), 24.6 (s, THF) , 14.6 (s, C*C*H$_3$).

IR (ATR, solid, cm^{-1}): 2961, 2866, 2039 (N=CPh$_2$), 1641, 1587, 1461, 1439, 1361, 1322, 1254,

1183, 1159, 1120, 1060, 1026, 885, 762, 693.

HRMS (*m/z*): $[M + K]^+$ Calcd. for $C_{45}H_{59}AlN_4OK^+$:737.4136; Found: 737.4106.

Synthesis of 4:



At -30 °C a solution of α-diimine aluminum hydride **1** (50.5 mg, 0.1 mmol) in toluene (1 mL) was added slowly to a stirring solution of PhN_2Ph (18.2mg, 0.1mmol) in toluene (1 mL). The mixture was stirred overnight. The solvent was removed under vacuum and the resulting yellow solid was washed with 3 x 1 mL hexane and dried in vacuo to yield yellow powders of the product (48.1 mg, 70 % yield). Orange crystals suitable for X-ray diffraction studies were obtained by storage a solution of the product in toluene in -30 °C for several days.

^{1}H NMR (500 MHz, C_6D_6, ppm): δ 0.75-0.85 (m, 3H, ^{i}Pr-CH_3), 0.95 (dd, 6H, *J* = 11.7, 6.8 Hz, ^{i}Pr-CH_3), 1.05 (d, *J* = 6.8 Hz, 3H, ^{i}Pr-CH_3), 1.16-1.19 (m, ^{i}Pr-CH_3), 1.34 (d, *J* = 6.7 Hz, 3H, ^{i}Pr-CH_3), 1.63 (s, 3H, NCCH_3), 2.92-2.98 (m, 1H, ^{i}Pr-C*H*), 3.00-3.13 (m, 1H, ^{i}Pr-C*H*), 3.31 (sept, *J* = 5.9 Hz, 1H, ^{i}Pr-C*H*), 3.65-3.71 (m, 1H, ^{i}Pr-C*H*), 4.28 (br, 1H, Al*H*), 4.29 (s, 1H, C=CH_2), 4.60 (s, 1H, C=CH_2), 5.19 (s, 1H, N*H*), 6.41 (br, 2H, Ar*H*), 6.57 (t, *J* = 7.4 Hz, 1H, Ar*H*), 6.72 (t, *J* = 7.3 Hz, 1H, Ar*H*), 6.78-6.89 (m, 2H, Ar*H*), 6.95 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.04 (t, *J* = 7.5 Hz, 2H, Ar*H*), 7.10-7.13 (m, 3H, Ar*H*), 7.23 (br, 1H, Ar*H*), 7.26-7.31 (m, 2H, Ar*H*).

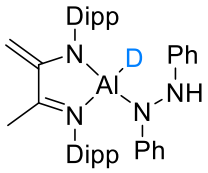
^{13}C{^{1}H} NMR (125 MHz, C_6D_6 ppm): δ 182.9 (s, N=C), 153.9 (s, Ar), 152.1 (s, *C*=CH_2), 150.6 (s, Ar), 147.9 (s, Ar), 146.4 (s, Ar), 142.1 (s, Ar), 141.9 (s, Ar), 140.7 (s, Ar), 138.0 (s, Ar), 129.2 (s, Ar), 128.7 (s, Ar), 128.4 (s, Ar), 126.6 (s, Ar), 125.1 (s, Ar), 125.1 (s, Ar), 125.0 (s, Ar), 124.4 (s, Ar), 118.6 (s, Ar), 117.3 (s, Ar), 114.0 (s, Ar), 112.2 (s, Ar), 98.3 (s, C=*C*H_2), 29.1 (s, *C*H) 28.9 (s, *C*H), 28.8 (s, *C*H), 28.5 (s, *C*H), 25.5 (s, *C*H_3), 25.0 (s, *C*H_3), 24.5 (s, *C*H_3), 24.3 (s, *C*H_3), 17.3 (s, NC*C*H_3).

IR (ATR, solid, cm^{-1}): 2961, 2925, 2865, 1849 (Al-H), 1592, 1567, 1493, 1461, 1438, 1350,

1243, 1218, 1022, 887, 795, 745, 720, 690, 584.

HRMS (*m/z*): $[M + H]^+$ Calcd. for $C_{40}H_{52}AlN_4^+$: 615.4002; Found: 615.3985.

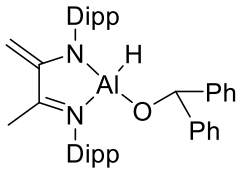
Duterium aluminum hydride of 4-D:



Using duterium compound **1-D** as starting material to react with PhC(O)Ph, the procedure is same as the synthesis of **4**.

^{1}H NMR (500 MHz, C_6D_6, ppm): δ 0.75-0.85 (m, 3H, ^{i}Pr-CH_3), 0.93-0.97 (m, 6H, ^{i}Pr-CH_3), 1.06 (d, J = 6.7 Hz, 3H, ^{i}Pr-CH_3), 1.16-1.34 (m, 9 H, ^{i}Pr-CH_3), 1.34 (d, J = 6.8 Hz, 3H, ^{i}Pr-CH_3), 1.63 (s, 3H, NCCH_3), 2.91-2.98 (m, 1H, ^{i}Pr-CH), 3.02-3.11 (m, 1H, ^{i}Pr-CH), 3.31 (m, 1H, ^{i}Pr-CH), 3.64-3.72 (m, 1H, ^{i}Pr-CH), 4.29 (s, 1H, C=CH_2), 4.59 (s, 1H, C=CH_2), 5.18 (s, 1H, NH), 6.41 (br, 2H, ArH), 6.57 (t, J = 7.4 Hz, 1H, ArH), 6.73 (t, J = 7.3 Hz, 1H, ArH), 6.78-6.88 (m, 2H, ArH), 6.95 (m, 2H, ArH), 7.04 (m, 2H, ArH), 7.10-7.13 (m, 3H, ArH), 7.23 (br, 1H, ArH), 7.21-7.29 (m, 2H, ArH).

Synthesis of 5:



At -30 °C a solution of α-diimine aluminum hydride **1** (50.5 mg, 0.1 mmol) in toluene (1 mL) was added slowly to a stirring solution of PhC(O)Ph (18.2mg, 0.1 mmol) in toluene (1 mL). The mixture was stirred overnight. The solvent was removed under vacuum and the resulting yellow solid was washed with 3 x 1 mL hexane and dried in vacuo to yield yellow powders of the product (44.7 mg, 65 % yield). Yellow crystals suitable for X-ray diffraction studies were obtained by storage a solution of the product in hexane/toluene in -30 °C for several days.

^{1}H NMR (500 MHz, C_6D_6, ppm): δ 0.94 (d, J = 6.8 Hz, 3H, ^{i}Pr-CH_3), 1.14 (d, J = 6.7 Hz, 3H,

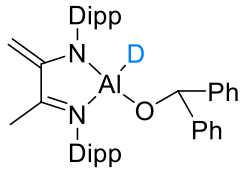
^{i}P*r*-CH_3), 1.19-1.28 (m, 12H, ^{i}Pr-CH_3), 1.36 (d, J = 6.9 Hz, 3H, ^{i}Pr-CH_3), 1.47 (d, J = 6.4Hz, 3H, ^{i}Pr-CH_3), 1.62 (s, 3H, NCCH_3), 2.89 (p, J = 7.0 Hz, 1H, ^{i}Pr-C*H*), 3.24 (p, J = 6.9 Hz, 1H, ^{i}Pr-C*H*), 3.54 (p, J = 7.2 Hz, 1H, ^{i}Pr-C*H*), 3.75 (p, J = 7.0 Hz, 1H, ^{i}Pr-C*H*), 4.18 (s, 1H, C=CH_2), 4.44 (br, 1H, AlH), 4.52 (s, 1H, C=CH_2), 5.99 (s, C*H*Ph$_2$), 6.95-7.04 (m, 10H, Ar*H*), 7.07-7.13 (m, 2H, Ar*H*), 7.25-7.35 (m, 4H, Ar*H*).

^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, ppm): δ 181.5 (s, N=*C*-CH$_3$), 151.7 (s, *C*=CH$_2$), 148.0(s, Ar), 148.0 (s, Ar), 147.0 (s, Ar), 146.9 (s, Ar), 141.8 (s, Ar), 141.3 (s, Ar), 140.4 (s, Ar), 137.7 (s, Ar), 128.6 (s, Ar), 128.5 (s, Ar), 127.2 (s, Ar), 126.9 (s, Ar), 126.4 (s, Ar), 126.3 (s, Ar), 124.8 (s, Ar), 124.7 (s, Ar), 124.5 (s, Ar), 124.4 (s, Ar), 94.9 (s, C=*C*H$_2$), 77.0 (*C*HPh$_2$), 28.9 (s, *C*H) 28.8 (s, *C*H), 28.7 (s, *C*H), 28.4 (s, *C*H) , 25.7 (s, *C*H$_3$), 25.2 (s, *C*H$_3$), 25.1 (s, *C*H$_3$), 24.9 (s, *C*H$_3$), 24.7 (s, *C*H$_3$), 24.4 (s, *C*H$_3$), 24.0 (s, *C*H$_3$), 23.7 (s, *C*H$_3$), 16.7 (s, C*C*H$_3$).

IR (ATR, solid, cm^{-1}): 2961, 2926, 2865, 1828 (Al-H), 1568, 1440, 1350, 1321, 1253, 1220, 1189, 1155, 1101, 1061, 1026, 795, 742, 693, 605.

HRMS (*m/z*): [M + H]$^+$ Calcd. for C$_{41}$H$_{52}$AlN$_2$O$^+$: 615.3890; Found: 615.3876.

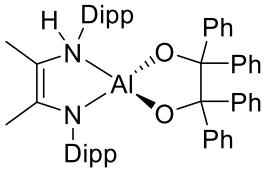
Duterium aluminum hydride of 5-D:



Using duterium compound **1-D** as starting material to react with PhC(O)Ph, the procedure is same as the synthesis of **5**.

^{1}H NMR (500 MHz, C$_6$D$_6$, ppm): δ 0.95 (br, 3H, ^{i}Pr-CH_3), 1.15 (br, 3H, ^{i}Pr-CH_3), 1.20-1.27 (m, 12H, ^{i}Pr-CH_3), 1.36 (br, 3H, ^{i}Pr-CH_3), 1.47 (br, 3H, ^{i}Pr-CH_3), 1.63 (s, 3H, NCCH_3), 2.89 (br, 1H, ^{i}Pr-C*H*), 3.23 (br, 1H, ^{i}Pr-C*H*), 3.53 (br, 1H, ^{i}Pr-C*H*), 3.75 (br, 1H, ^{i}Pr-C*H*), 4.18 (s, 1H, C=CH_2), 4.52 (s, 1H, C=CH_2), 5.95 (s, 1H, C*H*Ph$_2$), 6.96-7.04 (m, 10H, Ar*H*), 7.07-7.13 (m, 2H, Ar*H*), 7.26-7.32 (m, 4H, Ar*H*).

Synthesis of 6:



At -30 °C a solution of α-diimine aluminum hydride **1** (50.5 mg, 0.1 mmol) in toluene (1 mL) was added slowly to a stirring solution of PhC(O)Ph (36.4 mg, 0.2 mmol) in toluene (1 mL). The mixture was stirred overnight. The solvent was removed under vacuum and the resulting yellow solid was washed with 3 x 1 mL hexane and dried in vacuo to yield yellow powders of the product (43.4 mg, 50 % yield). Yellow crystals suitable for X-ray diffraction studies were obtained by storage a solution of the product in toluene in -30 °C for several days.

^{1}H NMR (500 MHz, C_6D_6, ppm): δ 0.69 (d, *J* = 6.4 Hz, 3H, ^{i}Pr-C*H*$_3$), 0.82 (d, *J* = 6.4 Hz, 3H, ^{i}Pr-C*H*$_3$), 0.98 (d, *J* = 6.5 Hz, 3H, ^{i}Pr-C*H*$_3$), 1.17 (d, *J* = 5.9 Hz, 3H, overlapped, ^{i}Pr-C*H*$_3$), 1.19 (d, *J* = 6.5 Hz, 3H, overlapped, ^{i}Pr-C*H*$_3$), 1.31 (d, *J* = 6.7 Hz, 3H, ^{i}Pr-C*H*$_3$), 1.42 (s, 3H, overlapped, NCC*H*$_3$), 1.43 (s, 3H, overlapped, NCC*H*$_3$), 1.56 (d, *J* = 6.5 Hz, 3H, overlapped, ^{i}Pr-C*H*$_3$), 1.58 (d, *J* = 6.5 Hz, 3H, overlapped, ^{i}Pr-C*H*$_3$), 2.43 (sept, *J* = 6.6 Hz, 1H, ^{i}Pr-C*H*), 3.39 (sept, *J* = 6.5 Hz, 1H, C*H*), 3.49 (sept, *J* = 6.2 Hz, 1H, C*H*), 3.17 (sept, *J* = 5.8 Hz, 1H, C*H*), 6.11 (s, N*H*), 6.37 (t, *J* = 7.5 Hz, 2H, Ar*H*), 6.52 (t, *J* = 7.7 Hz, 2H, Ar*H*), 6.59 (t, *J* = 7.7 Hz, 1H, Ar*H*), 6.72-6.76 (m, 3H, Ar*H*), 6.87-7.04 (m, 10H, Ar*H*), 7.18-7.22 (m, 4H, Ar*H*), 7.67 (d, *J* = 7.5 Hz, 2H, Ar*H*), 7.74 (d, *J* = 7.5 Hz, 2H, Ar*H*).

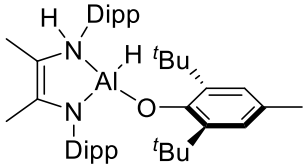
^{13}C{^{1}H} NMR (125 MHz, C_6D_6, ppm): δ 149.8 (s, N-*C*-CH$_3$), 149.5 (s, Ar), 149.2 (s, Ar), 147.7 (s, Ar), 147.6 (s, Ar), 147.1 (s, Ar), 144.4 (s, Ar), 143.2 (s, Ar), 141.6 (s, Ar), 141.0 (s, Ar), 134.4 (s, Ar), 130.5 (s, Ar), 130.4 (s, Ar), 129.5 (s, Ar), 128.7 (s, Ar), 128.4 (s, Ar),127.1 (s, Ar), 126.7 (s, Ar), 126.4 (s, Ar), 126.4 (s, Ar), 126.2 (s, Ar), 125.8 (s, Ar), 125.7 (s, Ar), 125.6 (s, Ar), 124.9 (s, Ar), 124.8 (s, Ar), 124.4 (s, Ar), 123.7 (s, Ar), 103.1 (s, NH-*C*-CH$_3$), 91.7 (*C*Ph$_2$), 91.2 (*C*Ph$_2$), 30.4 (s, *C*H) 28.5 (s, *C*H), 28.4 (s, *C*H), 28.4 (s, *C*H) , 25.6 (s, *C*H$_3$), 25.5 (s, *C*H$_3$), 24.4 (s, *C*H$_3$), 24.3 (s, *C*H$_3$), 24.2 (s, *C*H$_3$), 24.1 (s, *C*H$_3$), 24.1 (s, *C*H$_3$), 24.1 (s, *C*H$_3$), 14.8 (s, C*C*H$_3$), 13.3 (s, C*C*H$_3$).

IR (ATR, solid, cm^{-1}): 3205, 3056, 2960, 2929, 2868, 1655, 1598, 1492, 1464, 1440, 1363,

1324, 1290, 1160, 1129, 1021, 925, 752, 699.

HRMS (*m/z*): $[M + K]^+$ Calcd. for $C_{54}H_{61}AlN_2O_2K^+$: 835.4180; Found: 835.4171.

Synthesis of 7:



At -30 °C a solution of α-diimine aluminum hydride **1** (50.5 mg, 0.1 mmol) in toluene (1 mL) was added slowly to a stirring solution of BHT (22.0 mg, 0.1 mmol) in toluene (1 mL). The mixture was stirred overnight. The solvent was removed under vacuum and the resulting yellow solid was washed with 3 x 1 mL hexane and dried in vacuo to yield yellow powders of the product (50.7 mg, 70 % yield). Yellow crystals suitable for X-ray diffraction studies were obtained by storage a solution of the product in hexane/toluene in -30 °C for several days.

^{1}H NMR (500 MHz, C_6D_6, ppm): δ 0.46 (d, *J* = 6.7 Hz, 3H, ^{i}Pr-C*H*$_3$), 1.05 (d, *J* = 6.3 Hz, 3H, ^{i}Pr-C*H*$_3$), 1.12 (d, *J* = 6.7 Hz, 3H, ^{i}Pr-C*H*$_3$), 1.16 (d, *J* = 6.0 Hz, 6H, ^{i}Pr-*H*$_3$), 1.28, (d, *J* = 6.9 Hz, 3H, ^{i}Pr-C*H*$_3$), 1.36 (br, 3H, ^{i}Pr-C*H*$_3$), 1.45 (s, 6H, overlapped, NCC*H*$_3$), 1.48 (s, 18H , overlapped, BHT-C*H*$_3$), 1.56 (d, *J* = 6.7 Hz, 3H, ^{i}Pr-C*H*$_3$), 2.31 (s, 3H, BHT-C*H*$_3$), 3.34 (sept, *J* = 6.9 Hz, 1H, ^{i}Pr-C*H*), 3.47 (sept, *J* = 6.6 Hz, 1H, ^{i}Pr-C*H*), 3.71 (sept, *J* = 6.7 Hz, 1H, ^{i}Pr-C*H*), 3.84 (sept, *J* = 6.9 Hz, 1H, ^{i}Pr-C*H*), 4.92 (br, 1H, Al*H*), 6.31 (s, 1H, N*H*), 6.97 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.03 (d, *J* = 7.0 Hz, 1H, Ar*H*), 7.09 (s, 4H, overlapped, Ar*H*), 7.12 (d, *J* = 7.0 Hz, 1H, overlapped, Ar*H*), 7.20 (d, *J* = 7.6 Hz, 1H, Ar*H*).

^{13}C{^{1}H} NMR (125 MHz, C_6D_6, ppm): δ 155.1 (s, N-*C*-CH$_3$), 148.3 (s, Ar), 147.4 (s, Ar), 145.5 (s, Ar), 143.9 (s, Ar), 142.0 (s, Ar), 141.4 (s, Ar), 138.3 (s, Ar), 136.1 (s, Ar), 127.5 (s, Ar), 126.9 (s, Ar), 126.6 (s, Ar), 126.4 (s, Ar), 126.1 (s, Ar), 124.9 (s, Ar), 124.3 (s, Ar), 123.9 (s, Ar), 102.2 (s, NH-*C*-CH$_3$), 35.1 (s, BHT-*C*-(CH$_3$)$_3$), 31.4 (s, BHT-C-(*C*H$_3$)$_3$), 29.8 (s, *C*H) 28.0 (s, *C*H), 27.8 (s, *C*H), 27.6 (s, *C*H), 25.7 (s, *C*H$_3$), 25.3 (s, *C*H$_3$), 25.1 (s, *C*H$_3$), 24.8 (s, *C*H$_3$), 24.7 (s, *C*H$_3$), 24.5 (s, *C*H$_3$), 23.6 (s, *C*H$_3$), 21.4 (s, BHT-*C*H$_3$), 15.6(s, C-*C*H$_3$) 14.9 (s, C-*C*H$_3$) .

IR (ATR, solid, cm^{-1}): 3231, 2955, 2923, 2866, 1884 (AlH), 1644, 1458, 1439, 1422, 1384, 1361, 1317, 1283, 1254, 1217, 1130, 1046, 1020, 903, 860, 787, 737, 620.

HRMS (*m/z*): $[M+THF+K]^+$ Calcd. for $C_{47}H_{73}AlN_2O_2K^+$:763.5119; Found: 763.5171.

3. X-ray Crystallography

Table S1. Crystal data and structure refinement details for compounds **1**, **2, 3** and **4**

	1	**2**	**3**	**4**
CCDC	2529576	2529582	2529577	2529578
Empirical formula	$C_{35.5}H_{53}AlN_2O$	$C_{46}H_{61}AlFN_3O$	$C_{48}H_{64}AlN_4O$	$C_{40}H_{51}AlN_4$
Formula weight	550.78	717.95	740.01	614.82
Temperature, K	151	150	150	150
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	Pbca	$P2_12_12_1$	$P2_1/c$	Cc
a, Å	20.2576(4)	11.5044(8)	20.8866(6)	12.9983(5)
b, Å	15.7268(3)	17.0523(13)	14.9452(4)	28.7047(10)
c, Å	20.7217(5)	20.5884(15)	14.0417(4)	20.7415(8)
α, deg	90	90	90	90
β, deg	90	90	92.270(2)	106.764(2)
γ, deg	90	90	90	90
V, $Å^3$	6601.7(2)	4039.0(5)	4379.7(2)	7410.0(5)
Z	8	4	4	8
D_{calcd}, g/cm^3	1.108	1.181	1.122	1.102
μ/mm^{-1}	0.739	0.764	0.692	0.706
F(000)	2408.0	1552.0	1604.0	2656.0
2θ range, °	8.298 to 136.46	6.73 to 132.972	4.234 to 133.188	6.158 to 132.992
Index ranges	$-24 \le h \le 24$, $-18 \le k \le 18$, $-24 \le l \le 24$	$-13 \le h \le 8$, $-18 \le k \le 20$, $-24 \le l \le 24$	$-24 \le h \le 24$, $-17 \le k \le 17$, $-16 \le l \le 16$	$-15 \le k \le 15$, $-34 \le k \le 34$, $-24 \le l \le 24$
Reflections collected	94129	31751	104867	133486
Independent reflections	6040	7043	7739	13012
	$R_{int} = 0.1144$, $R_{sigma} = 0.0350$	$R_{int} = 0.0949$, $R_{sigma} = 0.0854$	$R_{int} = 0.1246$, $R_{sigma} = 0.0476$	$R_{int} = 0.0730$ $R_{sigma} = 0.0316$
Data/restraints/parameters	6040/42/391	7043/0/494	7739/27/530	13012/2/845
Goodness-of-fit on F^2	1.044	1.021	1.055	1.050
Final R indexes [I>=2σ (I)]	$R_1 = 0.0442$ $wR_2 = 0.1109$	$R_1 = 0.0625$, $wR_2 = 0.1455$	$R_1 = 0.0485$, $wR_2 = 0.1255$	$R_1 = 0.0418$, $wR_2 = 0.1092$
Final R indexes [all data]	$R_1 = 0.0602$, $wR_2 = 0.1210$	$R_1 = 0.0874$, $wR_2 = 0.1598$	$R_1 = 0.0650$, $wR_2 = 0.1366$	$R_1 = 0.0437$, $wR_2 = 0.1105$
Largest diff. peak/hole, $e/Å^{-3}$	0.34/-0.29	0.23/-0.28	0.29/-0.36	0.34/-0.29

Table S2. Crystal data and structure refinement details for compounds **5**, **6** and **7**

	5	**6**	**7**
CCDC	2529579	2529580	2529581
Empirical formula	$C_{89}H_{110}Al_2N_4O_2$	$C_{54}H_{61}AlN_2O_2$	$C_{43}H_{65}AlN_2O$
Formula weight	1321.76	1238.46	652.95
Temperature, K	150	150	150
Crystal system	monoclinic	triclinic	triclinic
Space group	P21/c	P-1	P-1
a, Å	19.0920(13)	11.1206(6)	10.6360(4)
b, Å	10.9609(8)	12.4290(6)	13.3704(4)
c, Å	38.346(3)	21.7777(10)	14.2491(5)
α, deg	90	93.480(3)	90.177(2)
β, deg	100.199(4)	101.068(3)	101.950(2)
γ, deg	90	94.140(3)	91.227(2)
V, Å^3	7897.7(10)	2937.8(3)	1981.90(12)
Z	4	2	2
D_{calcd}, g/cm^3	1.112	0.901	1.094
μ/mm^{-1}	0.700	0.549	0.684
F(000)	2856.0	856.0	716.0
2θ range, °	4.682 to 132.986	8.298 to 133.184	6.34 to 133.176
Index ranges	$-22 \le k \le 22$,	$-13 \le h \le 13$,	$-12 \le h \le 12$,
	$-13 \le k \le 13$,	$-14 \le k \le 14$,	$-15 \le k \le 14$,
	$-45 \le l \le 44$	$-25 \le l \le 25$	$-16 \le l \le 16$
Reflections collected	151566	43540	63261
Independent reflections	13878	10292	6983
	$R_{int} = 0.1174$,	$R_{int} = 0.1162$,	$R_{int} = 0.0841$,
	$R_{sigma} = 0.0498$	$R_{sigma} = 0.1097$	$R_{sigma} = 0.0380$
Data/restraints/parameters	13878/74/944	10292/30/577	6983/24/475
Goodness-of-fit on F^2	1.038	0.932	1.071
Final R indexes [I>=2σ (I)]	$R_1 = 0.0581$,	$R_1 = 0.0779$,	$R_1 = 0.0455$,
	$wR_2 = 0.1511$	$wR_2 = 0.2048$,	$wR_2 = 0.1198$
Final R indexes [all data]	$R_1 = 0.0779$,	$R_1 = 0.1082$,	$R_1 = 0.0556$,
	$wR_2 = 0.1639$	$wR_2 = 0.2321$	$wR_2 = 0.1266$
Largest diff. peak/hole, e/Å^{-3}	0.49/-0.35	0.37/-0.38	0.26/-0.38

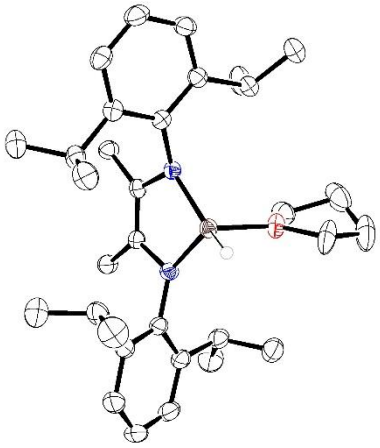


Figure S1. Thermal ellipsoid plot for **1** with the anisotropic displacement parameters depicted at the 50% probability level.

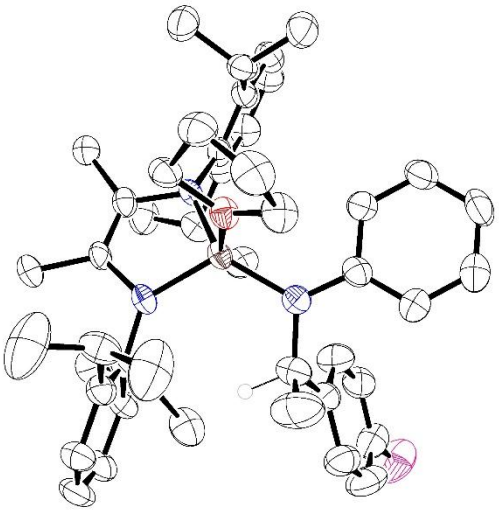


Figure S2. Thermal ellipsoid plot for **2** with the anisotropic displacement parameters depicted at the 50% probability level.

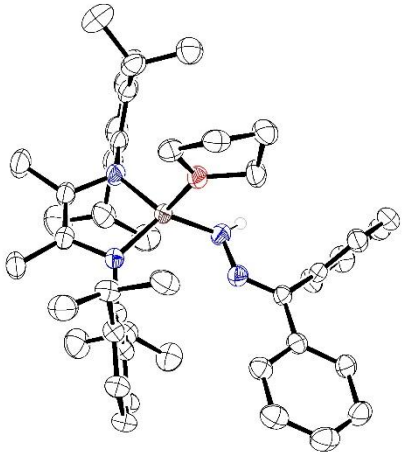


Figure S3. Thermal ellipsoid plot for **3** with the anisotropic displacement parameters depicted at the 50% probability level.

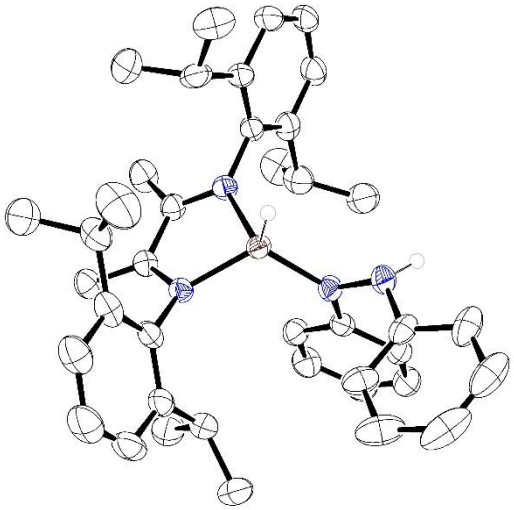


Figure S4. Thermal ellipsoid plot for **4** with the anisotropic displacement parameters depicted at the 50% probability level.

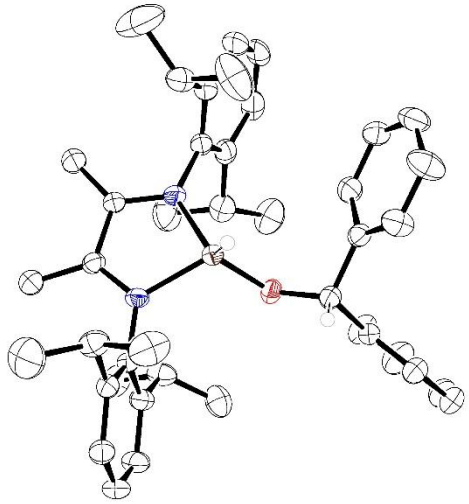


Figure S5. Thermal ellipsoid plot for **5** with the anisotropic displacement parameters depicted at the 50% probability level.

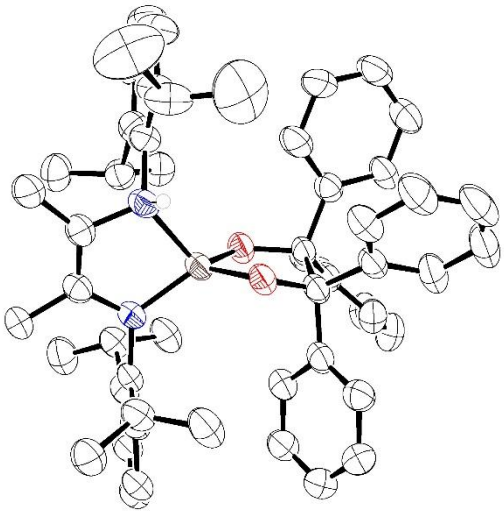


Figure S6. Thermal ellipsoid plot for **6** with the anisotropic displacement parameters depicted at the 50% probability level.

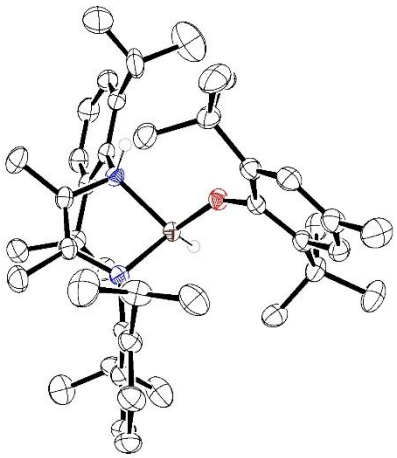


Figure S7. Thermal ellipsoid plot for **7** with the anisotropic displacement parameters depicted at the 50% probability level.

4. NMR Spectra

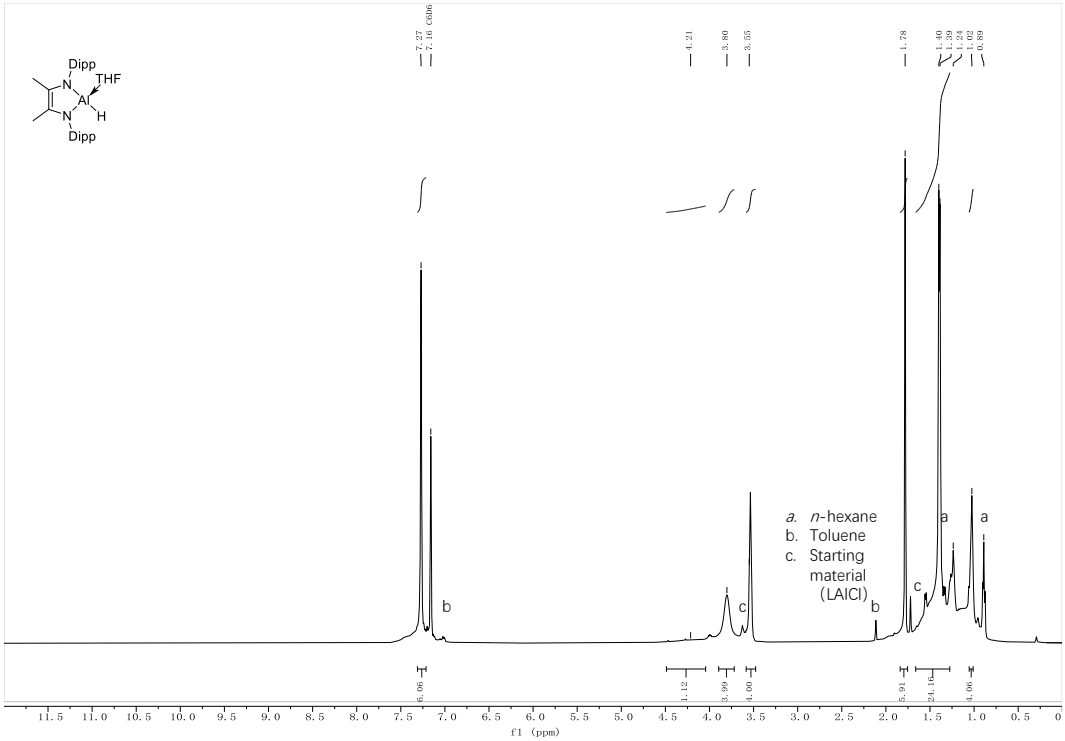


Figure S8. ^{1}H NMR spectrum of **1** in C_6D_6

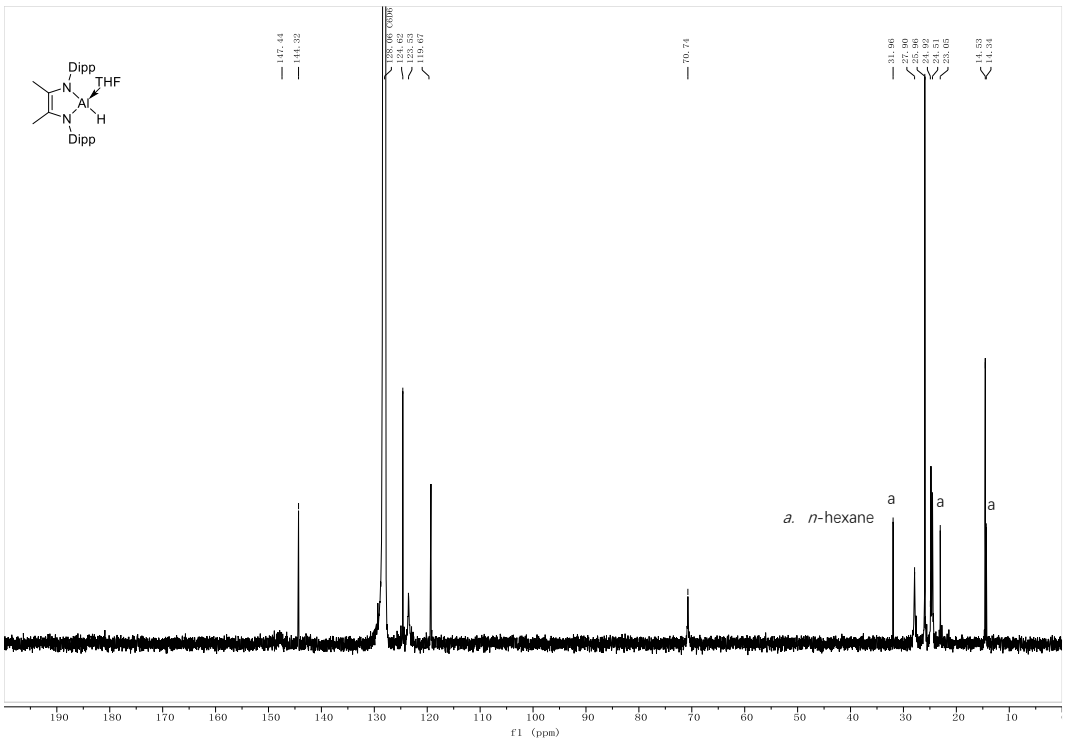


Figure S9. ^{13}C NMR spectrum of **1** in C_6D_6

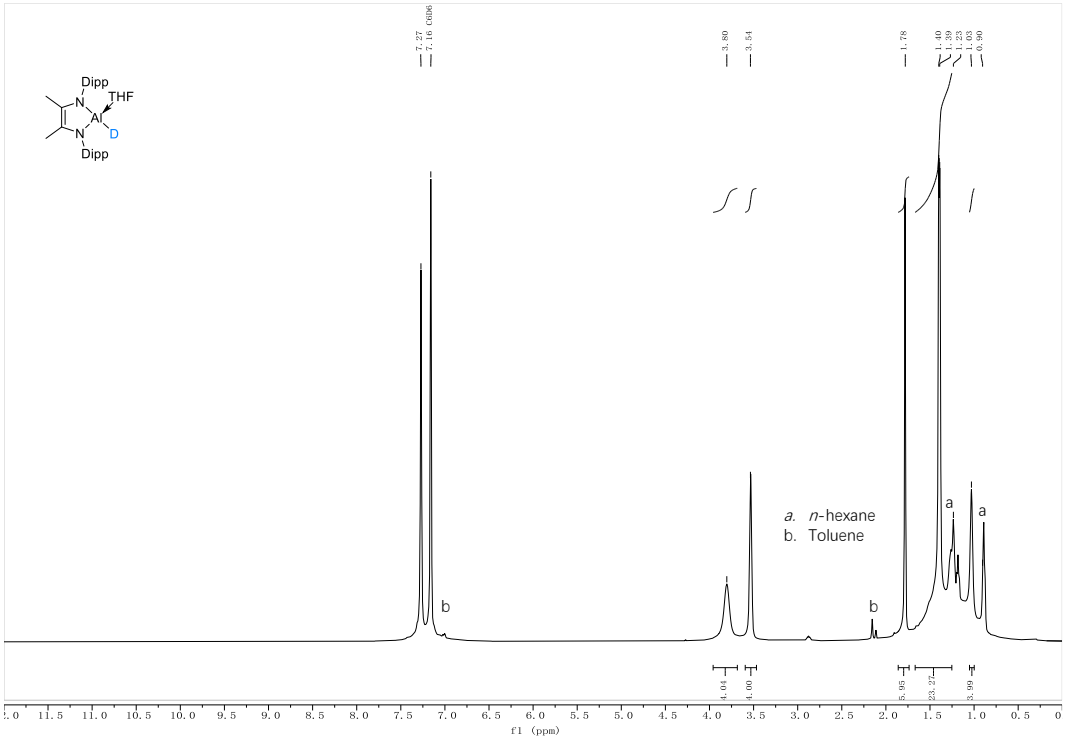


Figure S10. ^{1}H NMR spectrum of **1-D** in C_6D_6

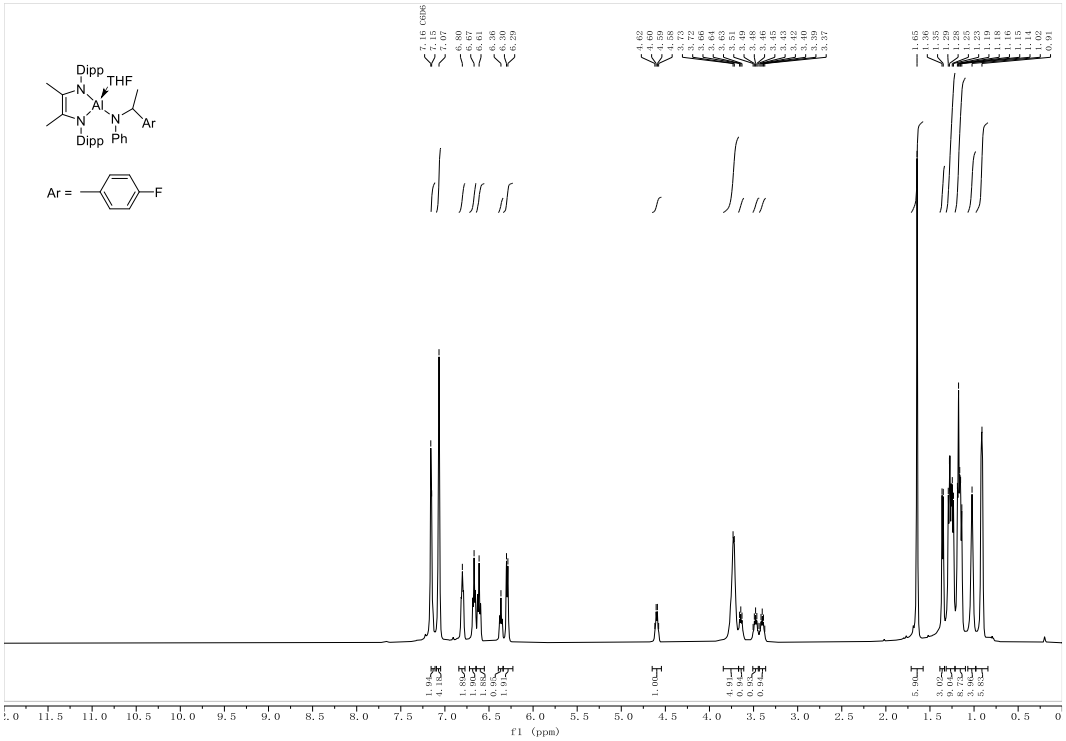


Figure S11. ^{1}H NMR spectrum of **2** in C_6D_6

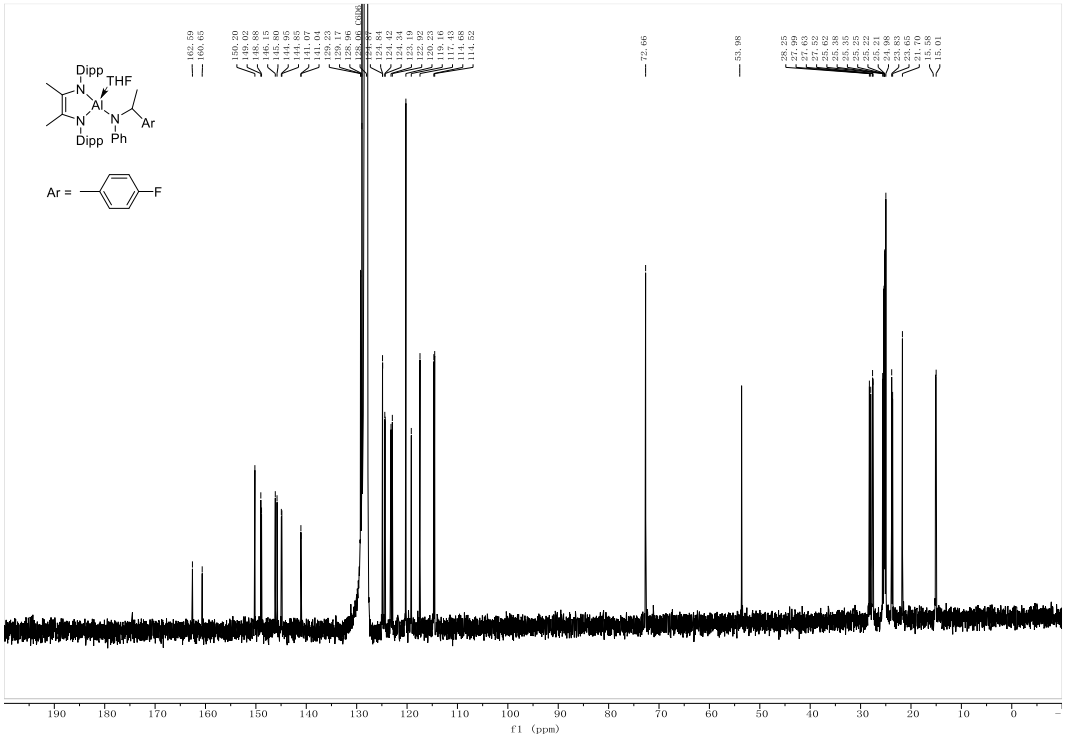


Figure S12. ^{13}C NMR spectrum of **2** in C_6D_6

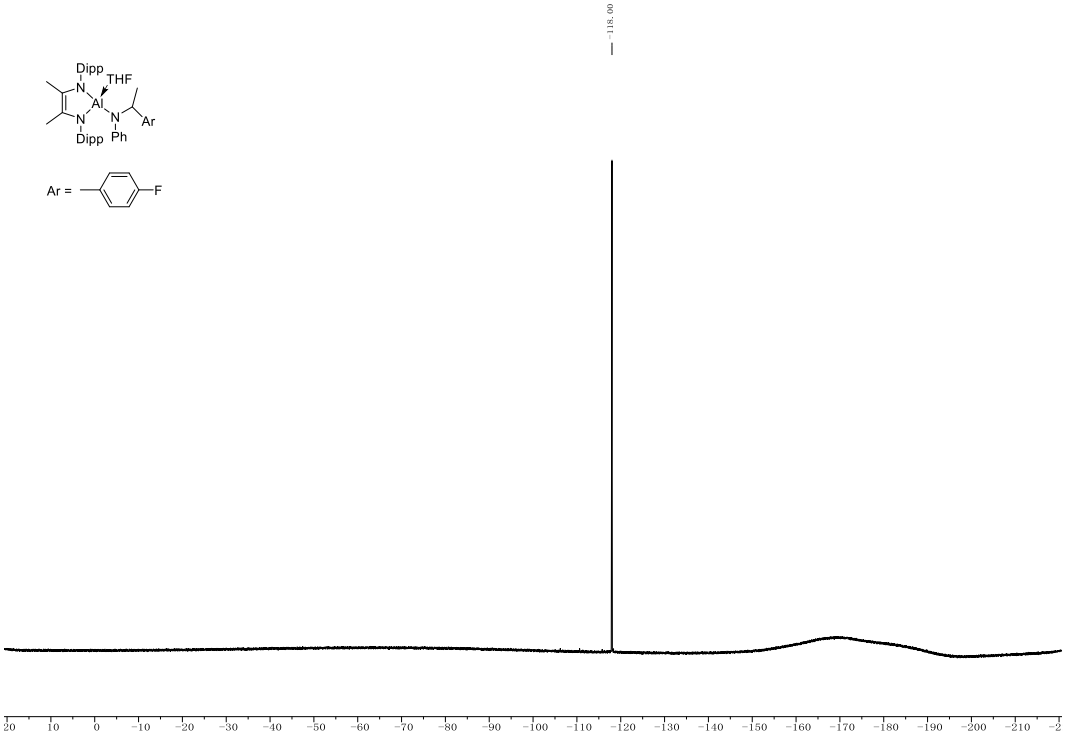


Figure S13. ^{19}F NMR spectrum of **2** in C_6D_6

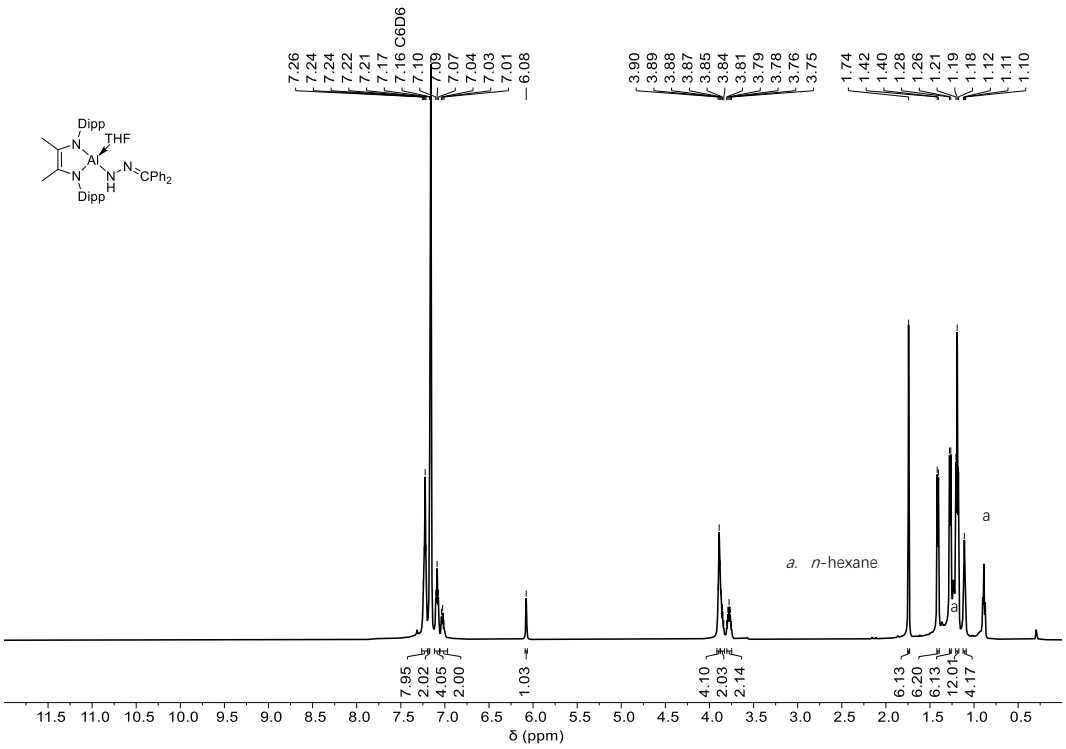


Figure S14. ^{1}H NMR spectrum of **3** in C_6D_6

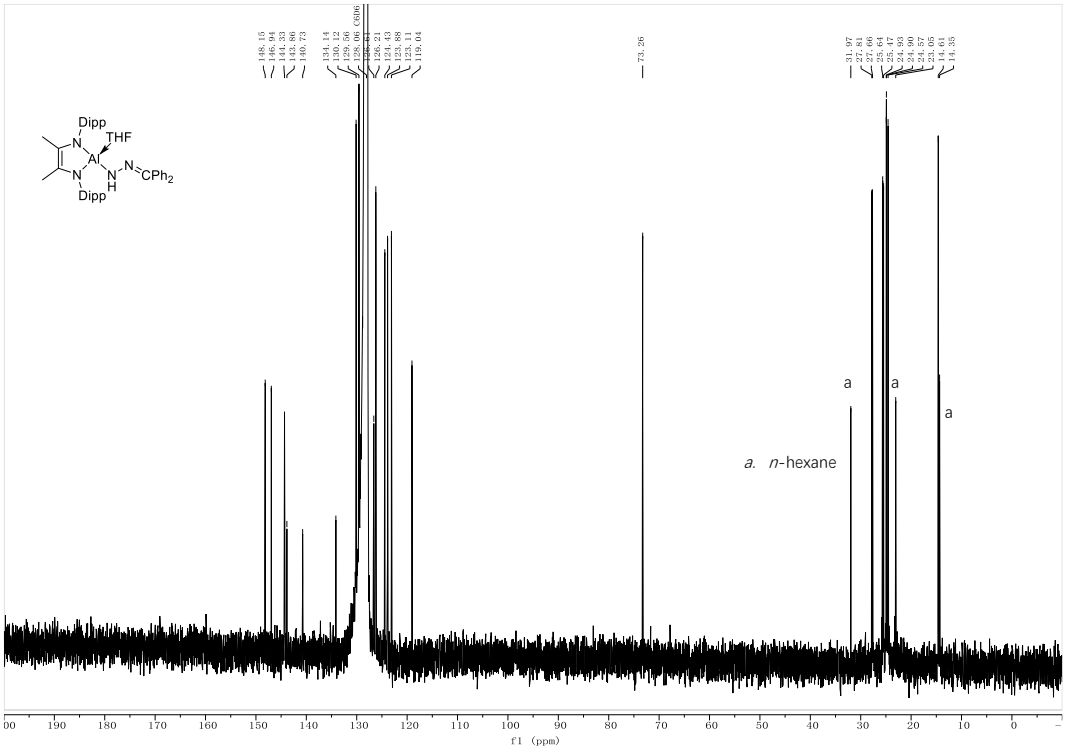


Figure S15. ^{13}C NMR spectrum of **3** in C_6D_6

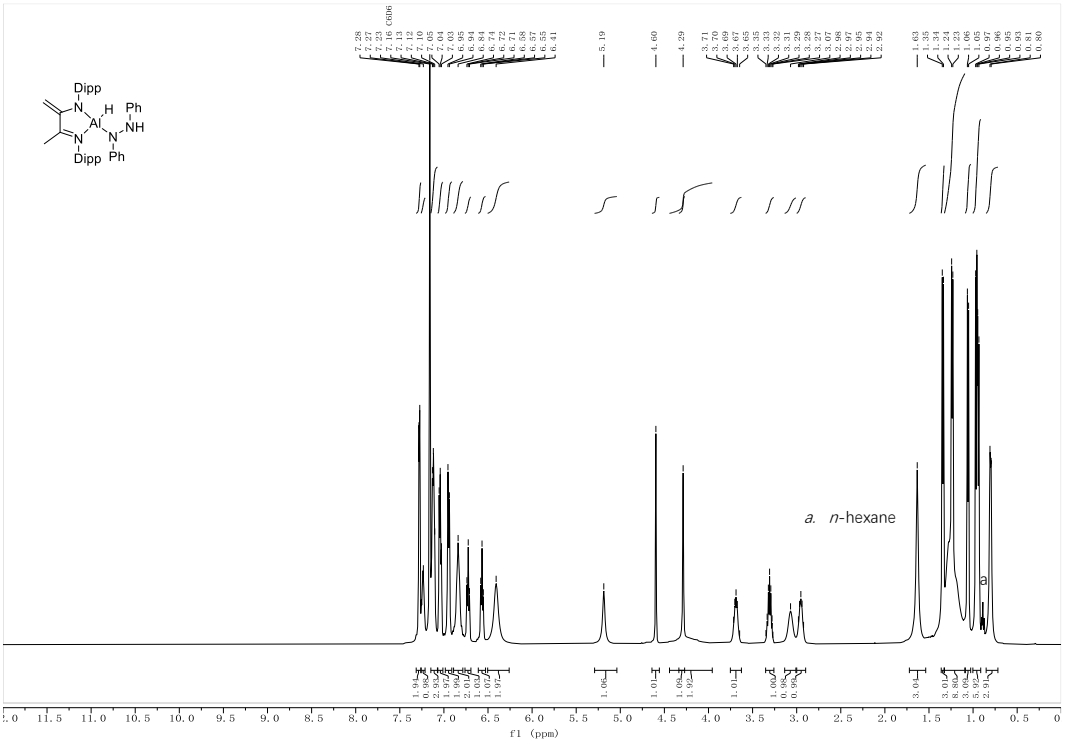


Figure S16. ^{1}H NMR spectrum of **4** in C_6D_6

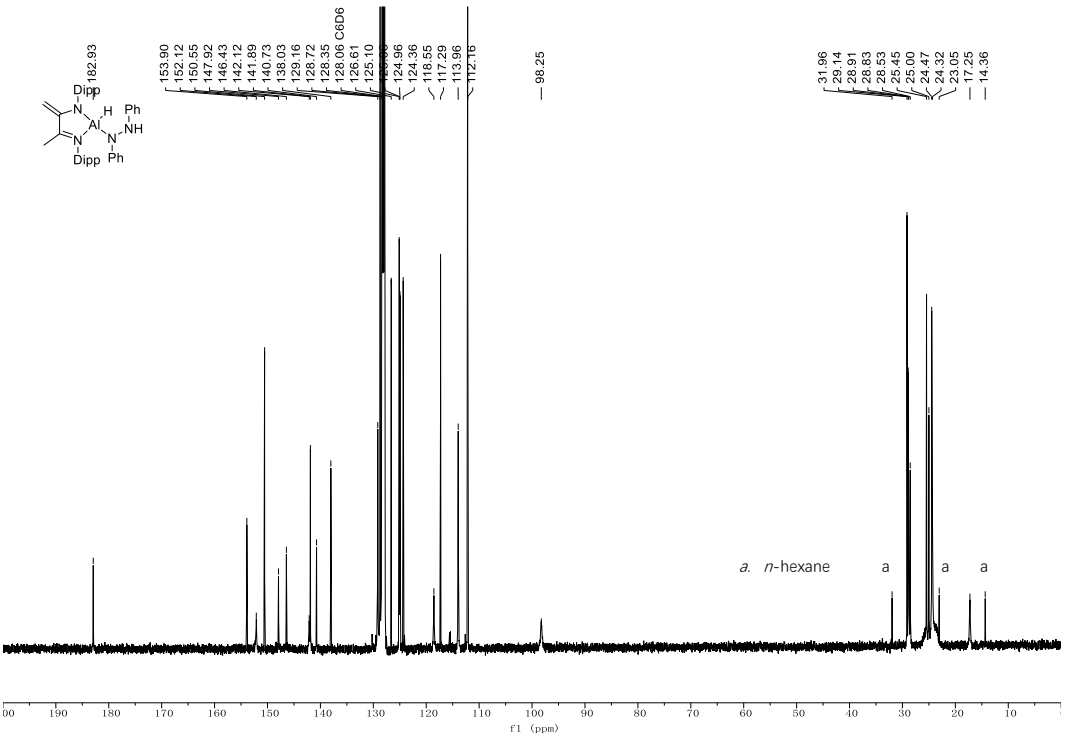


Figure S17. ^{13}C NMR spectrum of **4** in C_6D_6

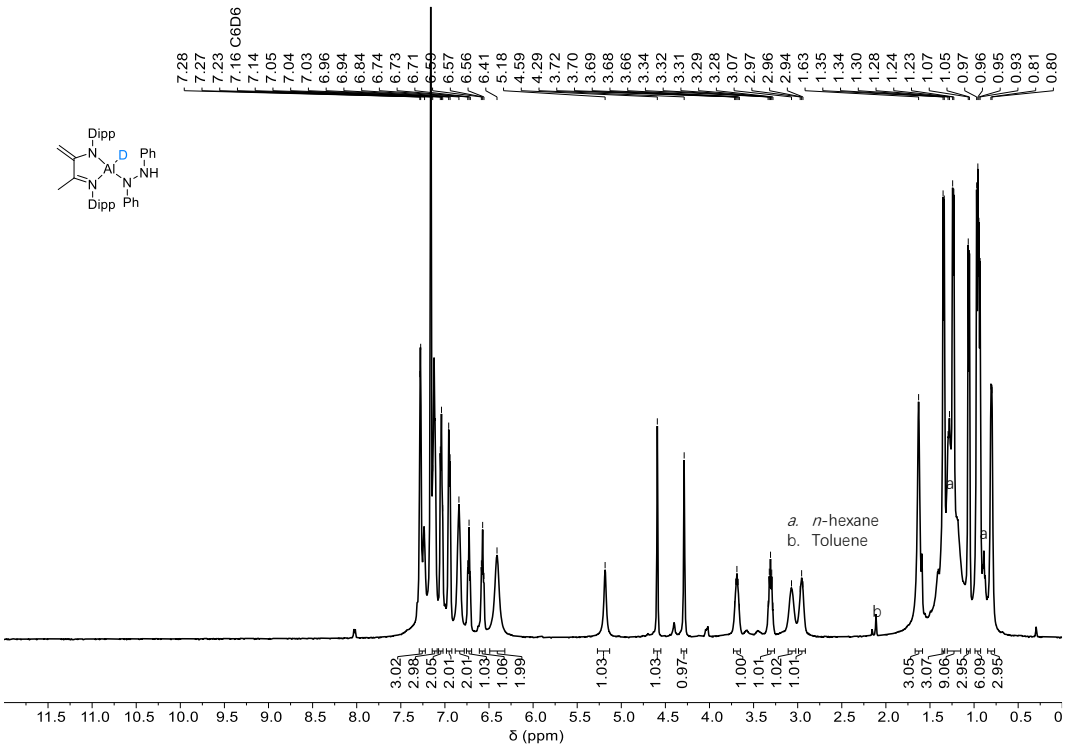


Figure S18. ^{1}H NMR spectrum of **4-D** in C_6D_6

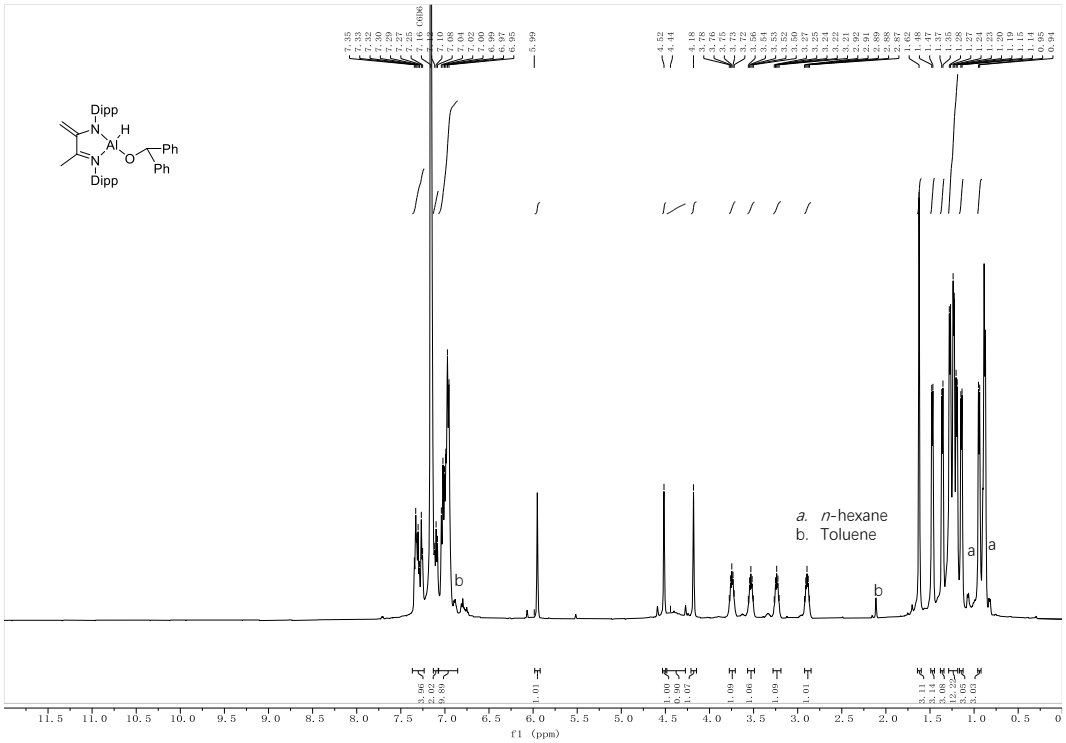


Figure S19. ^{1}H NMR spectrum of **5** in C_6D_6

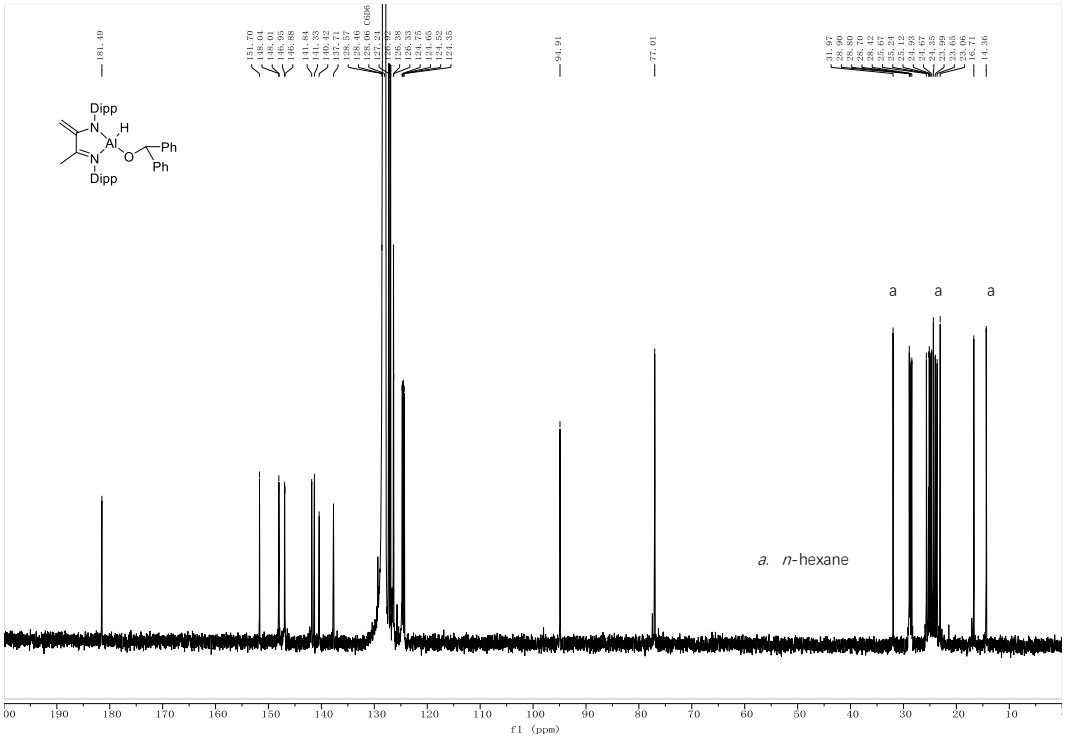


Figure S20. ^{13}C NMR spectrum of **5** in C_6D_6

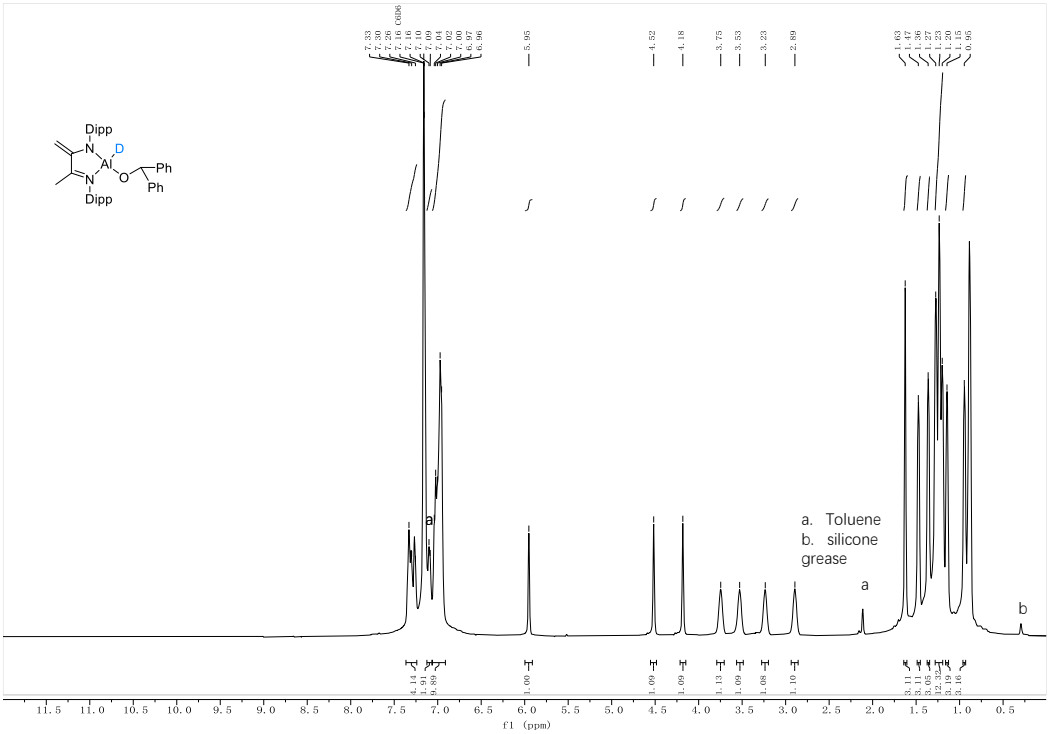


Figure S21. ^{1}H NMR spectrum of **5-D** in C_6D_6

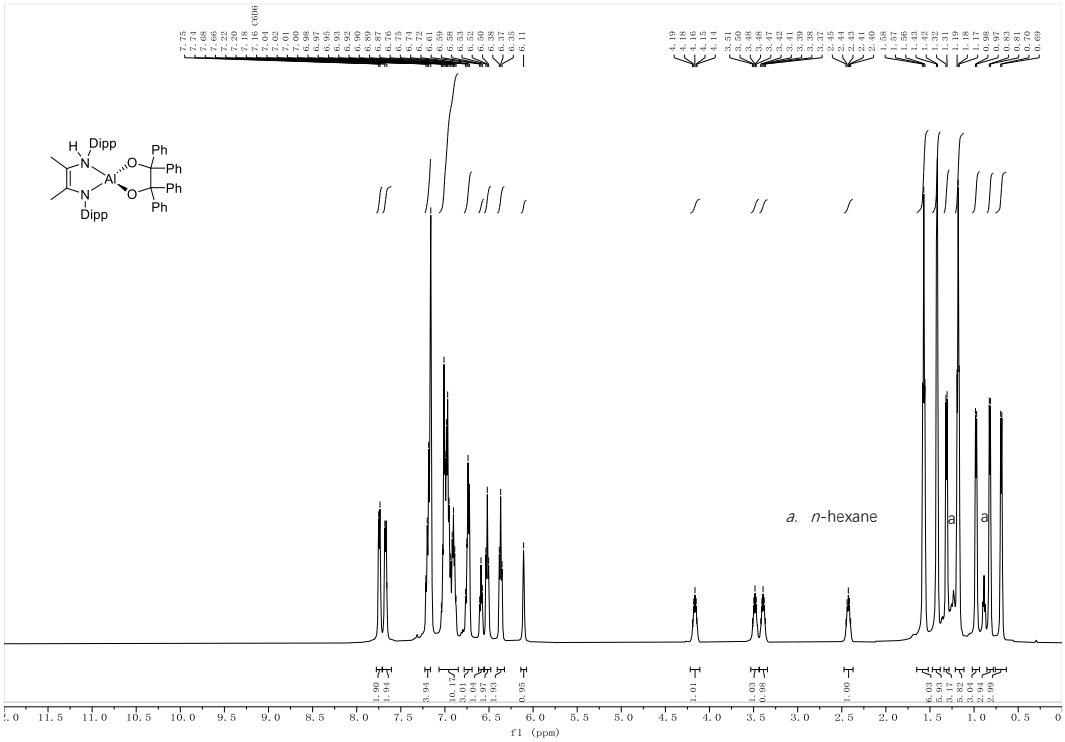


Figure S22. ^{1}H NMR spectrum of **6** in C_6D_6

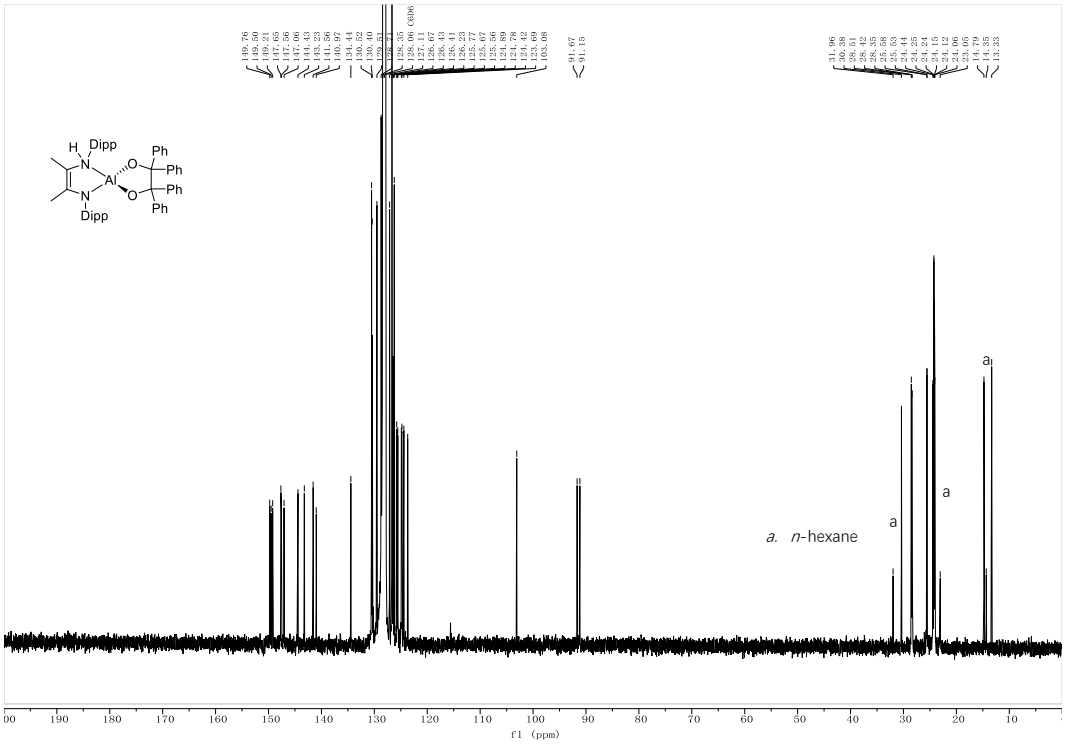


Figure S23. ^{13}C NMR spectrum of **6** in C_6D_6

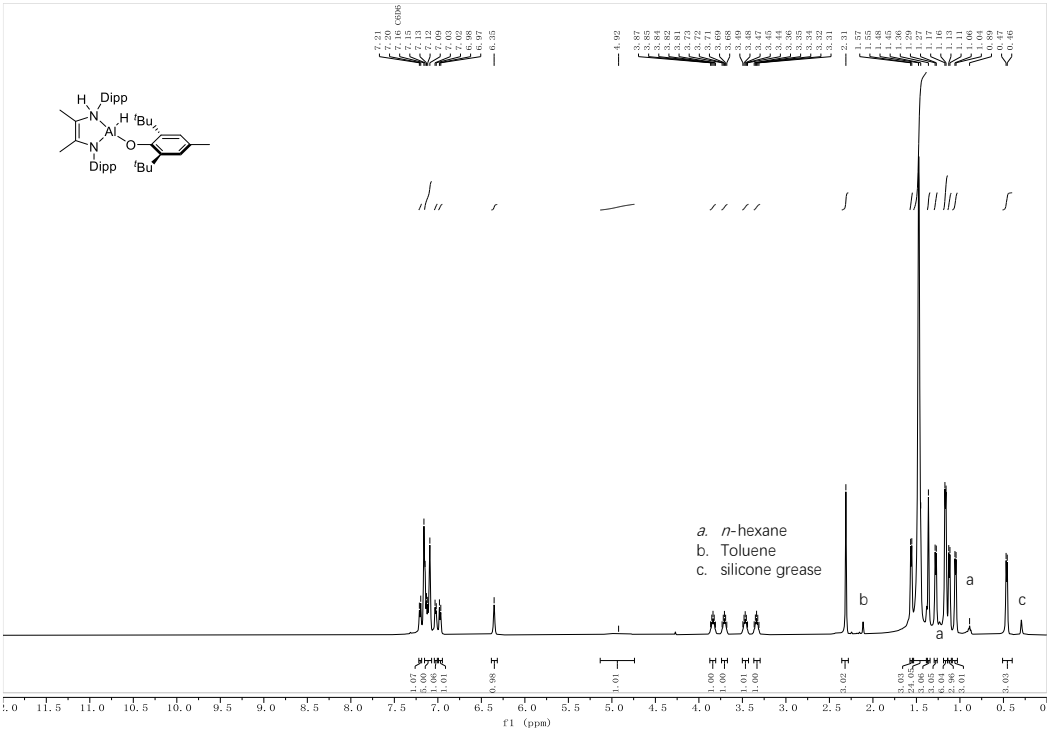


Figure S24. ^{1}H NMR spectrum of **7** in C_6D_6

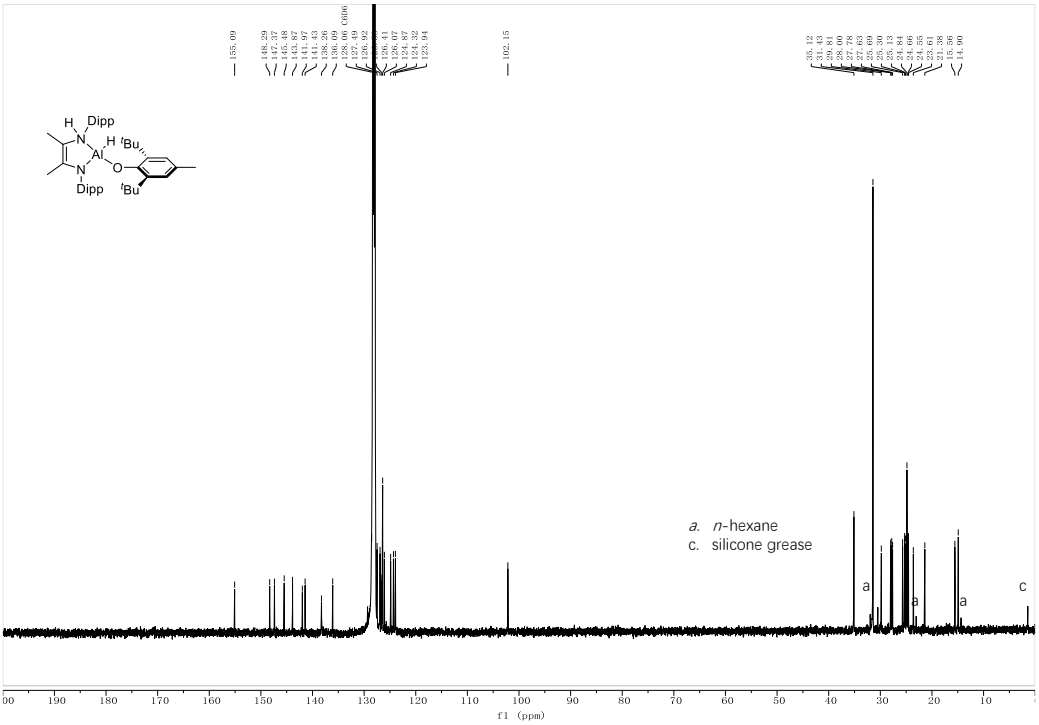


Figure S25. ^{13}C NMR spectrum of **7** in C_6D_6

5. Reference

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