Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

for

Synthesis and structural characterization of arsinoamide - early transition metal (Zr, Hf) and main group metal (Al, In, Sn, Pb) complexes

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Content

1. Experimental Section

All manipulations of air-sensitive materials were performed under nitrogen atmosphere by using either Schlenk line or argon-filled MBraun glovebox. All the Solvents were dried from a MBraun solvent purification system (SPS-800) or degassed, dried and stored in vacuum over $LiAlH_4$. Deuterated solvents were obtained from Aldrich GmbH (99 atom % D) and were degassed, dried, and stored in vacuum with Na/K alloy. IR spectra were obtained on a Bruker Tensor 37 instrument. NMR spectra were recorded with a Bruker Avance III 300 MHz or Avance III 400 MHz NMR spectrometer. Chemical shifts are referenced to the residual protio solvent (^1H) or the deuterated solvent ($^{13}C\{^1H\}$), and are reported relative to tetramethylsilane (^1H and $^{13}C\{^1H\}$). The ^{119}Sn and ^{207}Pb NMR data were referenced to $SnMe_4$ and $PbMe_4$, respectively. Elemental analyses were carried out with an Elementar Vario micro cube.

All the reagents were purchased from Acros Organics, Alfa Aesar and ABCR, and used without further purification. $[(Mes_2AsNPh)\{Li(OEt_2)_2\}]$[1] and $[(Me_2N)_2MCl_2(THF)_2]$ (M = Zr, Hf)[2] were prepared according to the literature.

All new compounds are air and moisture sensitive.

Safety and hazards

Considering their toxicity towards human and environmental hazard, arsenic compounds should be handled carefully by trained persons only.

Synthesis

$[(Mes_2AsNPh)_2ZrCl_2(THF)]$ (1)

$[(Mes_2AsNPh)\{Li(OEt_2)_2\}]$ (0.448 g, 0.8 mmol) dissolved in THF (15 ml) was added dropwise to a suspension of $ZrCl_4$ (0.093 g, 0.4 mmol) in THF (30 ml). After stirring overnight at room temperature, the volatiles were removed under vacuum and toluene (20 ml) was added. The white solid was removed by filtration. The target compound can be obtained from filtrate after removing toluene and washing with n-pentane (3×5 ml). Single crystals were crystallized from DCM by slow evaporation. Yield: 0.307 g, 68 %.

^{1}H NMR (300 MHz, d_8-THF, 298 K): δ(ppm) = 7.26-7.22 (m, 2H, Ph), 7.17-6.99 (m, 8H, Ph), 6.79 (s, 8H, ring CH Mes), 2.30 (s, 24H, o-CH_3 Mes), 2.20 (s, 12H, p-CH_3 Mes).

$^{13}C\{^1H\}$ NMR (75 MHz, d_8-THF, 298 K): δ(ppm) = 148.7, 143.4, 139.3, 138.3, 129.2, 128.1, 124.4, 22.6(o-Me), 20.7(p-Me).

IR (ATR, cm^{-1}): 3017(w), 2966(m), 2922(m), 2860(w), 1595(s), 1559(w), 1468(s), 1448(w), 1377(w), 1286(m), 1198(vs), 1172(m), 1072(w), 1028(m), 1000(m), 917(m), 848(vs), 789(vs), 737(m), 685(vs), 603(m), 583(m), 554(m), 498(s), 448(s).

Anal. calcd. (%) for [$C_{49}H_{56}As_2Cl_4N_2Zr$ = 1 - THF] (1052.07): C, 55.74; H, 5.35; N, 2.65. Found: C, 55.43; H, 5.22; N, 2.44.

[$(Mes_2AsNPh)_2HfCl_2(THF)$] (2)

Compound 2 was synthesized following the same synthetic approach carried out for 1 but using $HfCl_4$ instead of $ZrCl_4$.Yield: 0.316 g, 65 %.

^{1}H NMR (300 MHz, d_8-THF, 298 K): δ(ppm) = 7.12-6.93 (m, 4H, Ph), 6.77 (s, 8H, ring CH Mes), 6.74-6.68 (m, 2H, Ph), 6.58-6.41 (m, 4H, Ph), 2.27 (s, 24H, o-CH_3 Mes), 2.17 (s, 12H, p-CH_3 Mes).

$^{13}C\{^1H\}$ NMR (75 MHz, d_8-THF, 298 K): δ(ppm) = 151.1, 143.3, 141.0, 137.8, 129.8, 127.5, 123.4, 22.8(o-Me), 20.7(p-Me).

IR (ATR, cm^{-1}): 3016(w), 2965(m), 2922(m), 2860(w), 1595(s), 1558(w), 1467(s), 1377(w), 1286(m), 1198(vs), 1172(m), 1072(w), 1028(m), 1000(m), 917(m), 848(vs), 789(vs), 738(m), 686(vs), 603(m), 554(m), 497(s), 448(s).

Anal. calcd. (%) for [$C_{52}H_{62}As_2Cl_2HfN_2O$] (1130.21): C, 55.26; H, 5.53; N, 2.48. Found: C, 55.54; H, 5.23; N, 2.45.

[$(Mes_2AsNPh)_2Zr(NMe_2)_2$] (3)

[$(Mes_2AsNPh)\{Li(OEt_2)_2\}$] (0.448 g, 0.8 mmol) dissolved in THF (15 ml) was added dropwise to a solution of [$(Me_2N)_2ZrCl_2\cdot(THF)_2$] (0.158 g, 0.4 mmol) in THF (15 ml) and the mixture was stirred overnight at room temperature. After removing the volatiles under vacuum, n-pentane (10 ml) and diethyl ether (10 ml) were added by cannula. The white solid was removed by filtration. After keeping the filtrate under -30 ^{o}C overnight, crystals suitable for single crystal diffraction were obtained. Yield: 0.308 g, 78 %.

^{1}H NMR (300 MHz, C_6D_6, 298 K): δ(ppm) = 7.04-6.95 (m, 8H, m,o-H Ph), 6.84-6.80 (m, 2H, p-H Ph), 6.63 (s, 8H, ring CH Mes), 2.95 (s, 12H, NMe_2), 2.32(s, 24H, o-CH_3 Mes), 2.07(s, 12H, p-CH_3 Mes).

^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ(ppm) = 153.8, 142.2, 138.8, 138.1, 130.1, 128.3, 126.0, 122.2, 44.0(NMe_2), 22.9(o-Me), 21.0(p-Me).

IR (ATR, cm^{-1}): 3020(w), 2961(m), 2919(m), 2856(w), 1594(s), 1490(s), 1461(s), 1377(w), 1358(w), 1282(s), 1224(m), 1174(m), 1145(w), 1025(m), 991(w), 941(w), 903(w), 846(vs), 772(m), 747(s), 693(s), 659(s), 611(w), 582(w), 542(m), 498(m), 417(w).

Anal. calcd. (%) for [$C_{52}H_{66}As_2N_4Zr$] (986.28): C, 63.20; H, 6.73; N, 5.67. Found: C, 63.61; H, 6.88; N, 5.23.

[$(Mes_2AsNPh)_2Hf(NMe_2)_2$] (4)

Compound 4 was synthesized following the same synthetic approach carried out for 3 but using [$(Me_2N)_2HfCl_2\cdot(THF)_2$] instead of [$(Me_2N)_2ZrCl_2\cdot(THF)_2$]. Yield: 0.288 g, 67 %.

^{1}H NMR (300 MHz, C_6D_6, 298 K): δ(ppm) = 7.05-6.97 (m, 8H, m,o-H Ph), 6.84-6.77 (m, 2H, p-H Ph), 6.62 (s, 8H, ring CH Mes), 2.97 (s, 12H, NMe_2), 2.31(s, 24H, o-CH_3 Mes), 2.07(s, 12H, p-CH_3 Mes).

^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ(ppm) = 153.5, 142.3, 138.6, 138.1, 130.1, 128.1, 126.7, 122.5, 43.5(NMe_2), 22.9(o-Me), 20.9(p-Me).

IR (ATR, cm^{-1}): 3022(w), 2961(m), 2920(m), 2855(w), 2770(w), 1595(vs), 1493(vs), 1465(s), 1445(s), 1376(m), 1357(m), 1283(vs), 1244(m), 1225(m), 1176(w), 1139(w), 1075(m), 1027(m), 993(w), 948(w), 934(w), 903(w), 870(w), 847(vs), 771(m), 748(s), 690(s), 657(m), 657(w), 611(w), 583(w), 543(m), 501(m), 416(w).

Anal. calcd. (%) for [$C_{52}H_{66}As_2HfN_4$] (1076.32): C, 58.07; H, 6.19; N, 5.21. Found: C, 58.43; H, 6.03; N, 4.77.

[(Mes_2AsNPh)$AlCl_2$(THF)] (5)

[(Mes_2AsNPh){Li(OEt_2)$_2$}] (0.889 g, 1.6 mmol) dissolved in 20 ml THF was added dropwise to a suspension of $AlCl_3$ (0.213 g, 1.6 mmol) in THF (15 ml) and the mixture was stirred overnight at room temperature. After filtration, the volatiles were removed under vacuum. The residue was extracted with toluene (20 ml). The target compound was obtained after removing toluene and washing with cold n-pentane (3×5 ml). Single crystals of 5 could be obtained from slow evaporation of the DCM solution. Yield: 0.521 g (57 %).

^1H NMR (300 MHz, C_6D_6, 298 K): δ(ppm) = 7.29-7.26 (m, 2H, m-H Ph), 7.01-6.96 (m, 2H, o-H Ph), 6.79 (s, 4H, ring CH Mes), 6.79-6.78 (m, 1H, p-H Ph), 2.62 (s, 12H, o-CH_3 Mes), 2.11 (s, 6H, p-CH_3 Mes).

$^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 298 K): δ(ppm) = 142.8, 138.8, 138.4, 130.5, 128.8, 125.9, 121.5, 120.4, 23.0(o-CH_3), 21.0(p-CH_3).

IR (ATR, cm^{-1}): 3015(w), 2959(w), 2916(w), 2863(w), 1587(m), 1481(m), 1446(m), 1229(s), 1179(w), 1081(w), 1029(m), 992(m), 956(m), 897(m), 861(s), 846(s), 805(vs), 749(m), 698(m), 610(m), 585(w), 519(vs), 473(s).

Anal. calcd. (%) for [$C_{24}H_{27}AlAsCl_2N$, = 5 -THF] (502.29): C, 57.39; H, 5.42; N, 2.79. Found: C, 57.40; H, 5.81; N, 2.50.

[(Mes_2AsNPh)$InCl_3$][Li$(THF)_4$] (6)

[(Mes_2AsNPh){Li(OEt_2)$_2$}] (0.889 g, 1.6 mmol) dissolved in 20 ml THF was added dropwise to a suspension of $InCl_3$ (0.354 g, 1.6 mmol) in THF (15 ml). After stirring at room temperature overnight, the mixture was filtered and the resulting colorless solution was slowly evaporated until crystallization. The target compound was isolated after washing with cold n-pentane (2×5 ml). Yield: 0.632 g (43 %).

^{1}H NMR (300 MHz, d_8-THF, 298 K): δ(ppm) = 6.72-6.64 (m, 2H, m-H Ph), 6.64 (s, 4H, ring CH Mes), 6.32-6.30 (m, 2H, o-H Ph), 5.98-5.94 (m, 1H, p-H Ph), 2.36 (s, 12H, o-CH_3 Mes), 2.13 (s, 6H, p-CH_3 Mes).

^{13}C{^{1}H} NMR (75 MHz, d_8-THF, 298 K): δ(ppm) = 164.5, 143.2, 142.8, 136.7, 129.7, 128.7, 118.3, 109.7, 21.7(o-CH_3), 20.7(p-CH_3).

IR (ATR, cm^{-1}): 3016(w), 2963(w), 2918(w), 2866(w), 1588(m), 1480(m), 1446(m), 1403(w), 1378(w), 1287(w), 1229(s), 1179(w), 1080(w), 1029(m), 992(w), 956(w), 897(m), 847(s), 805(s), 748(s), 697(s), 609(s), 585(w), 518(vs), 472(vs).

Anal. calcd. (%) for [$C_{32}H_{43}AsCl_3InLiNO_2$, = 6 - 2 THF] (776.73): C, 49.48; H, 5.58; N, 1.80. Found: C, 49.46; H, 5.83; N, 1.58.

[($Mes_2AsNPh)_2Sn$] (7)

Toluene (20 ml) was condensed onto a mixture of $SnCl_2$ (0.076 g, 0.4 mmol) and [(Mes_2AsNPh){$Li(OEt_2)_2$}] (0.448 g, 0.8 mmol). The mixture was then stirred at room temperature overnight. The solid formed was removed by filtration. Compound 7 was isolated as a red solid after removing volatiles under vacuum and washing with cold n-pentane (5 ml). Single crystals were crystallized by diffusion of n-pentane and diethyl ether (1/1) into a solution of 7 in toluene. Yield: 0.267 g (72 %).

^{1}H NMR (300 MHz, C_6D_6, 298 K): δ(ppm) = 7.14-7.11 (m, 4H, m-H Ph), 7.01-6.98 (m, 4H, o-H Ph), 6.84-6.80 (m, 2H, p-H Ph), 6.61 (s, 8H, ring CH Mes), 2.35 (s, 24H, o-CH_3 Mes), 2.05 (s, 12H, p-CH_3 Mes).

^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ(ppm) = 155.6, 143.3, 139.0, 136.6, 130.5, 129.2, 122.3, 120.1, 22.6(o-CH_3), 20.9(p-CH_3).

^{119}Sn{^{1}H} NMR (112 MHz, C_6D_6, 298 K): δ(ppm) = 319.

IR (ATR, cm^{-1}): 3017(w), 2961(w), 2917(w), 2854(w), 1595(vs), 1493(vs), 1465(s), 1442(s), 1375(m), 1356(m), 1283(vs), 1227(s), 1174(m), 1075(m), 1026(m), 848(s), 760(vs), 749(s), 684(vs), 611(w), 583(w), 558(w), 543(m), 512(m), 463(w).

Anal. calcd. (%) for [$C_{48}H_{54}As_2N_2Sn$] (927.53): C, 62.16; H, 5.87; N, 3.02. Found: C, 62.51; H, 5.56; N, 2.65.

[($Mes_2AsNPh)_2Pb$] (8)

Toluene (20 ml) was condensed into a mixture of $PbCl_2$ (0.111 g, 0.4 mmol) and [(Mes_2AsNPh){Li($OEt_2)_2$}] (0.448 g, 0.8 mmol). The mixture was then stirred overnight at room temperature. The solid formed was removed by filtration and compound 8 was obtained as a deep violated powder after removing volatiles and washing with cold n-pentane (5 ml) and diethyl ether (5 ml). Single crystals were obtained by diffusion of a mixture of n-pentane and diethyl ether (1/1) into a solution of 8 in toluene. Yield: 0.229 g (56 %).

^{1}H NMR (300 MHz, C_6D_6, 298 K): δ(ppm) = 7.36-7.31 (m, 4H, m-H Ph), 7.13-7.10 (m, 4H, o-H Ph), 6.78-6.71 (m, 2H, p-H Ph), 6.60 (s, 8H, ring CH Mes), 2.34 (s, 24H, o-CH_3 Mes), 2.04 (s, 12H, p-CH_3 Mes).

^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 298 K): δ(ppm) = 157.7, 143.6, 139.0, 137.0, 130.3, 129.3, 121.4, 119.1, 22.1(o-CH_3), 20.9(p-CH_3).

^{207}Pb{^{1}H} NMR (62.8MHz, C_6D_6, 298 K): δ(ppm) = 3244.

IR (ATR, cm^{-1}): 3021(w), 2958(m), 2918(m), 2866(w), 1595(vs), 1492(vs), 1465(s), 1443(s), 1357(m), 1283(vs), 1228(m), 1152(m), 1027(m), 847(s), 750(s), 691(s), 543(m), 507(s).

Anal. calcd. (%) for [$C_{48}H_{54}As_2N_2Pb$] (1016.02): C, 56.74; H, 5.36; N, 2.76. Found: C, 57.18; H, 5.34; N, 2.83.

2. NMR spectra.

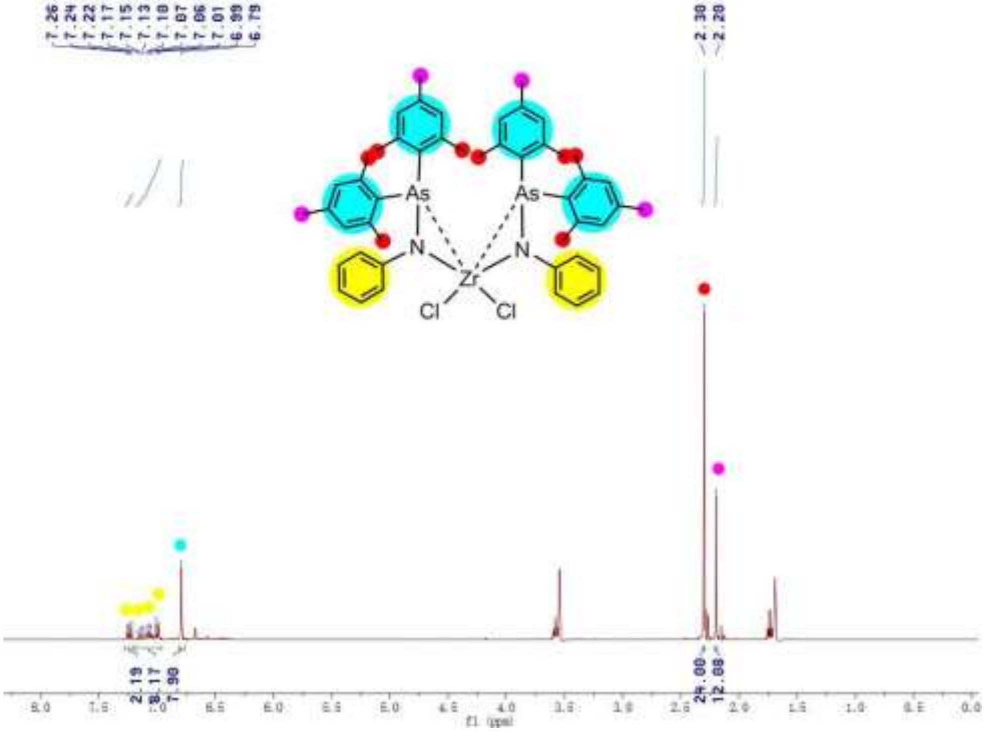

Figure S1: ^{1}H NMR spectrum of 1 (300 MHz, d$_8$-THF, 298K).

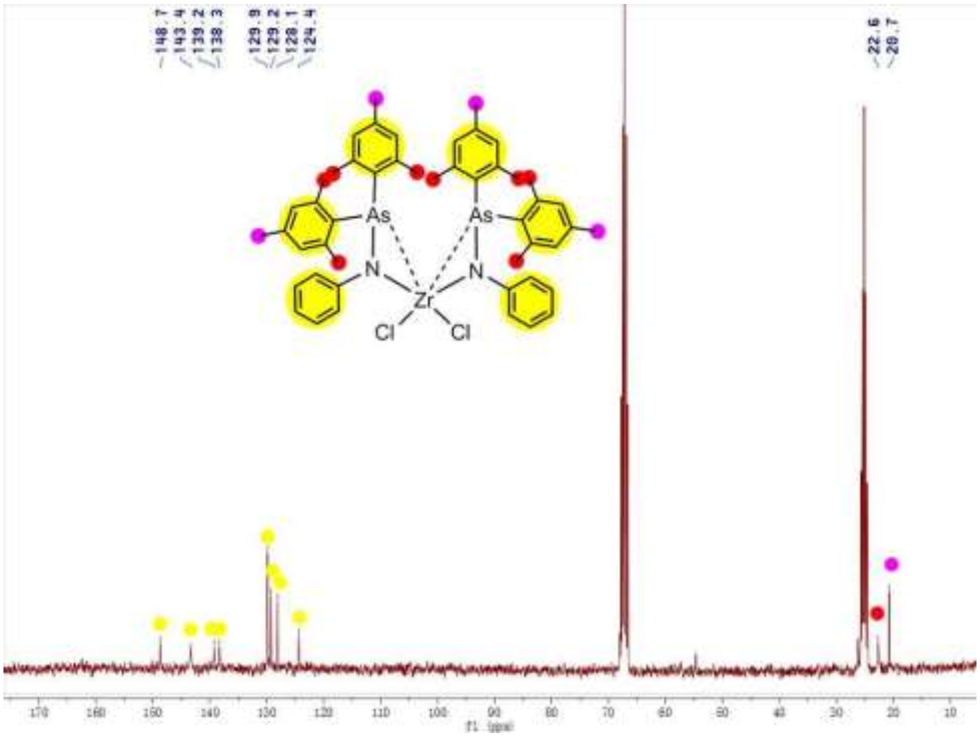

Figure S2: ^{13}C{^{1}H} NMR spectrum of 1 (75 MHz, d$_8$-THF, 298K).

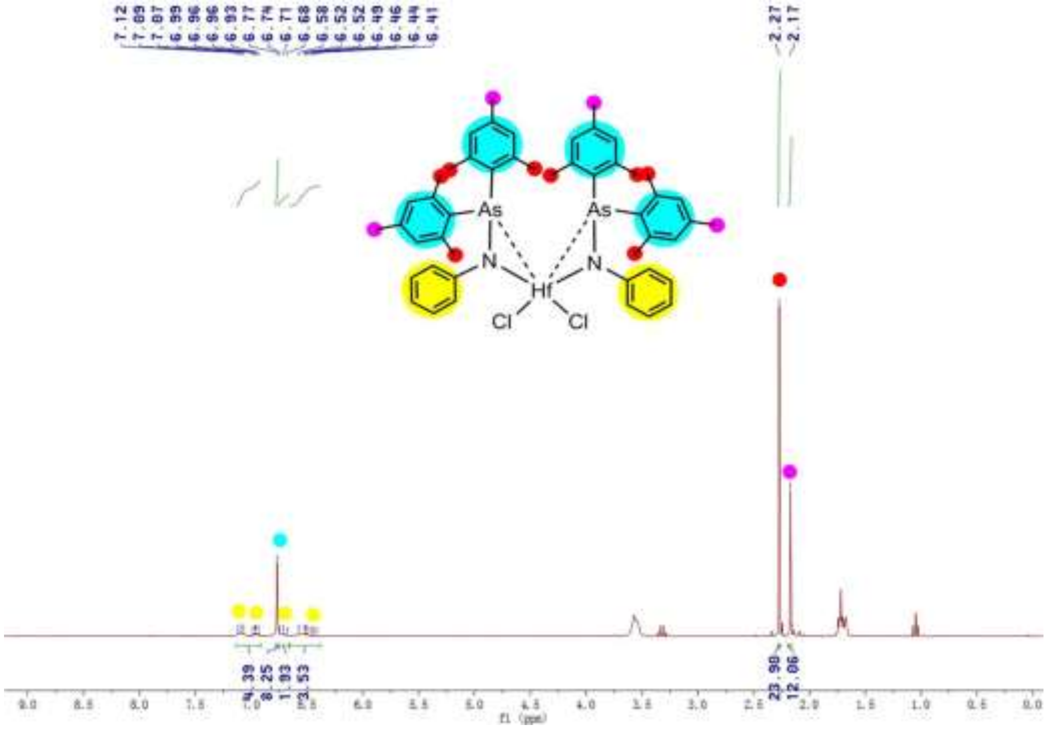

Figure S3: ^{1}H NMR spectrum of 2 (300 MHz, d_8-THF, 298K).

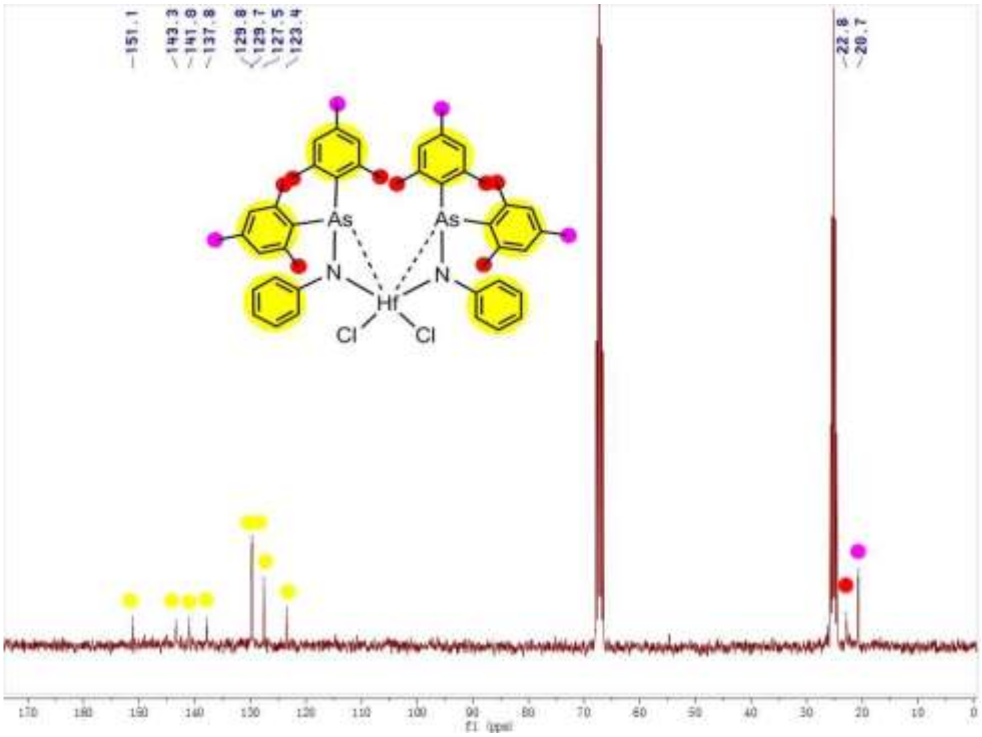

Figure S4: $^{13}C\{^1H\}$ NMR spectrum of 2 (75 MHz, d_8-THF, 298K).

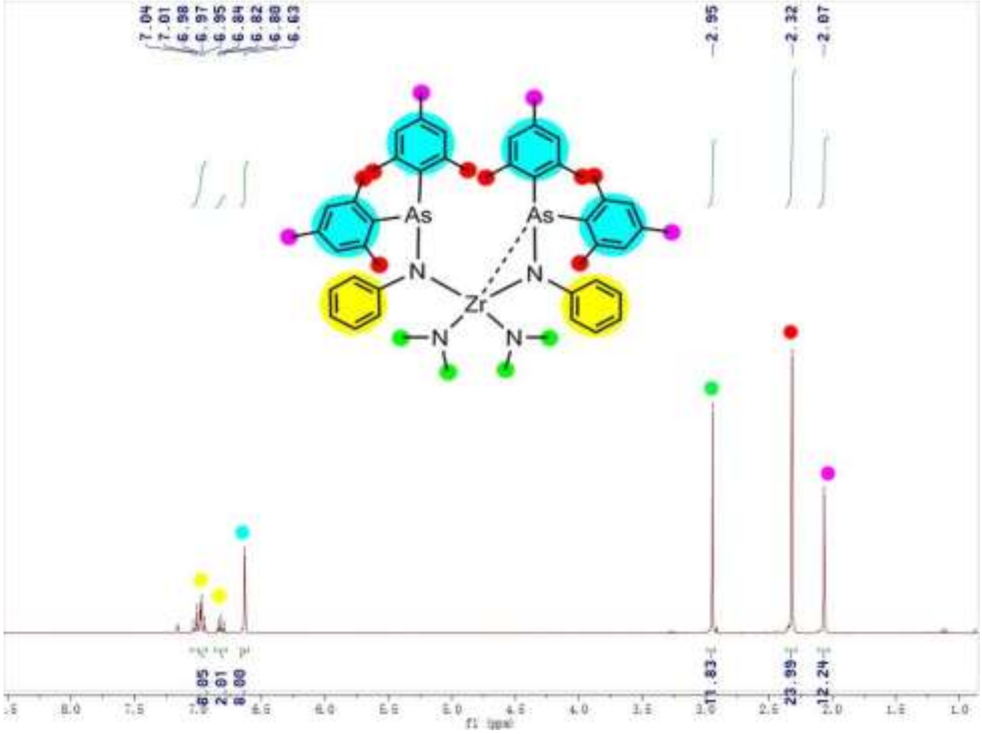

Figure S5: ^{1}H NMR spectrum of 3 (300 MHz, C_6D_6, 298K).

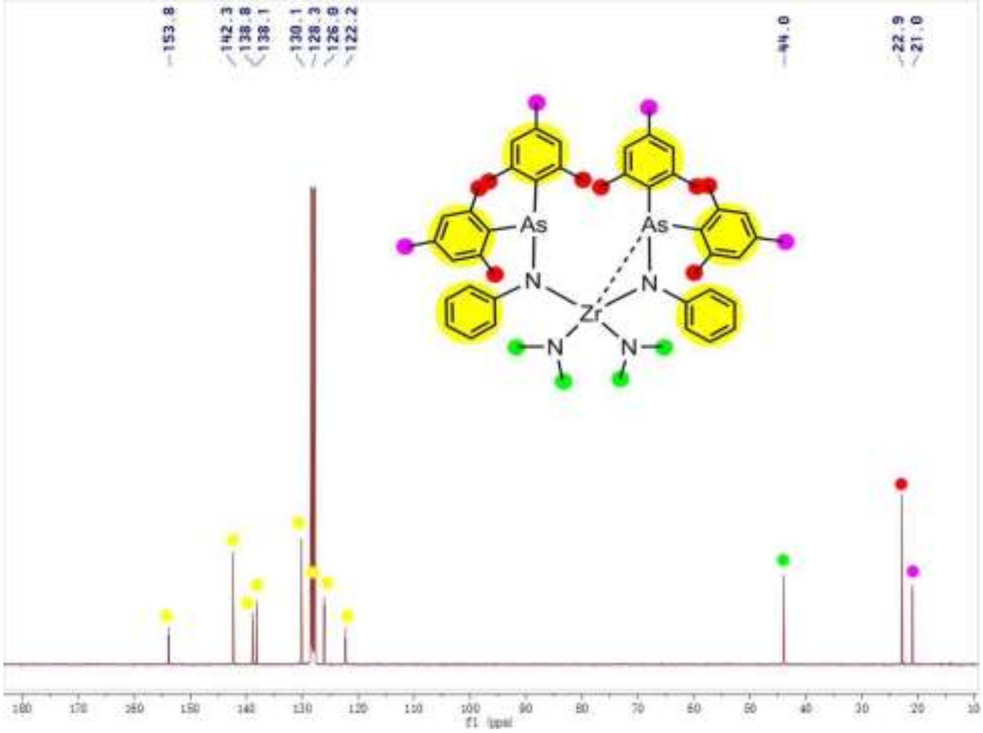

Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum of 3 (75 MHz, C_6D_6, 298K).

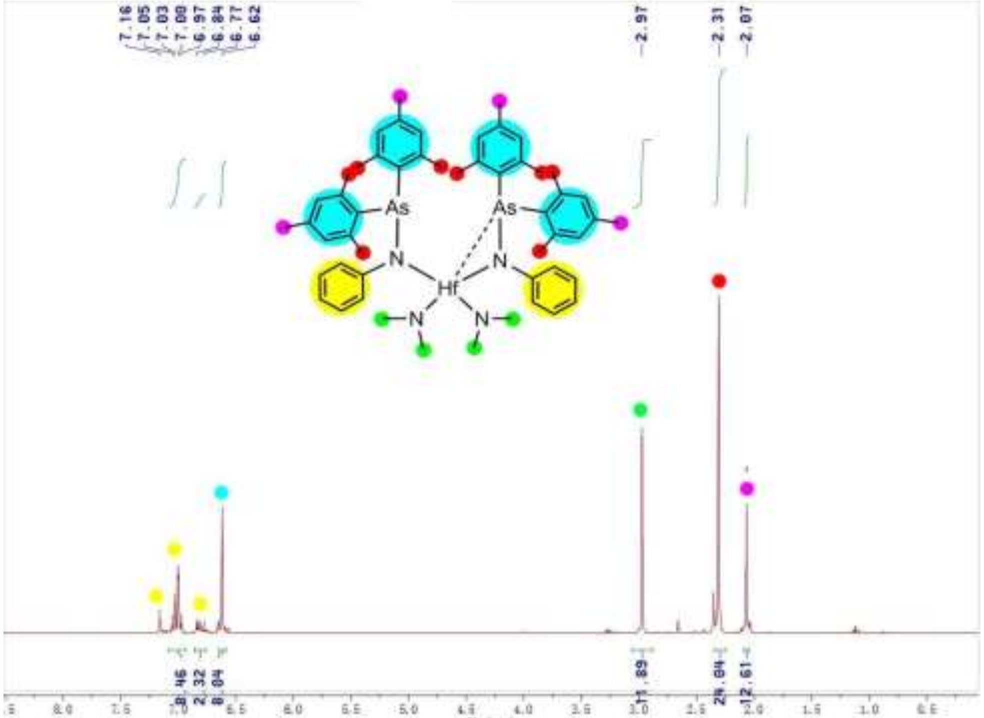

Figure S7: ^{1}H NMR spectrum of 4 (300 MHz, C_6D_6, 298K).

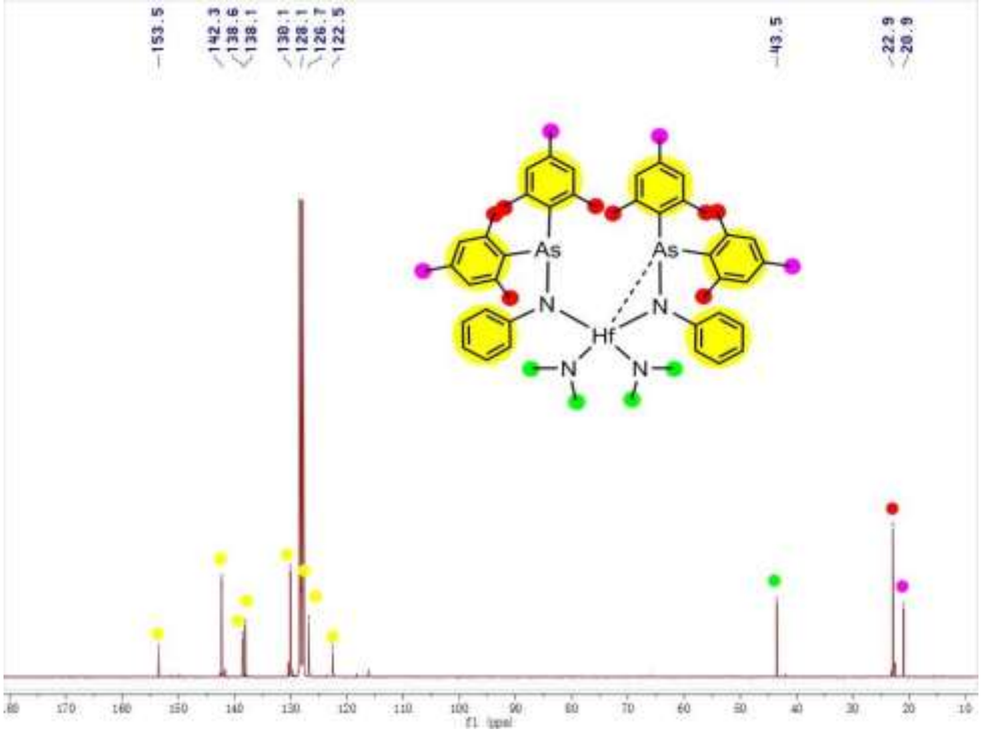

Figure S8: ^{13}C{^{1}H} NMR spectrum of 4 (75 MHz, C_6D_6, 298K).

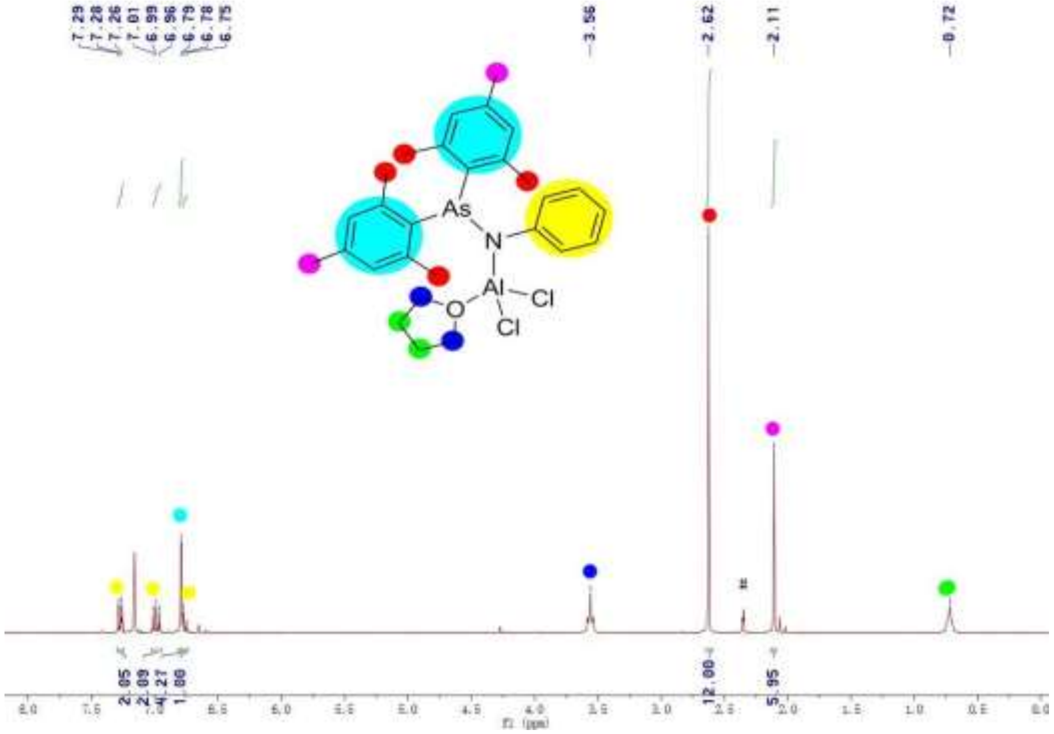

Figure S9: ^{1}H NMR spectrum of 5 (300 MHz, C_6D_6, 298K) (# stands for solvent peak).

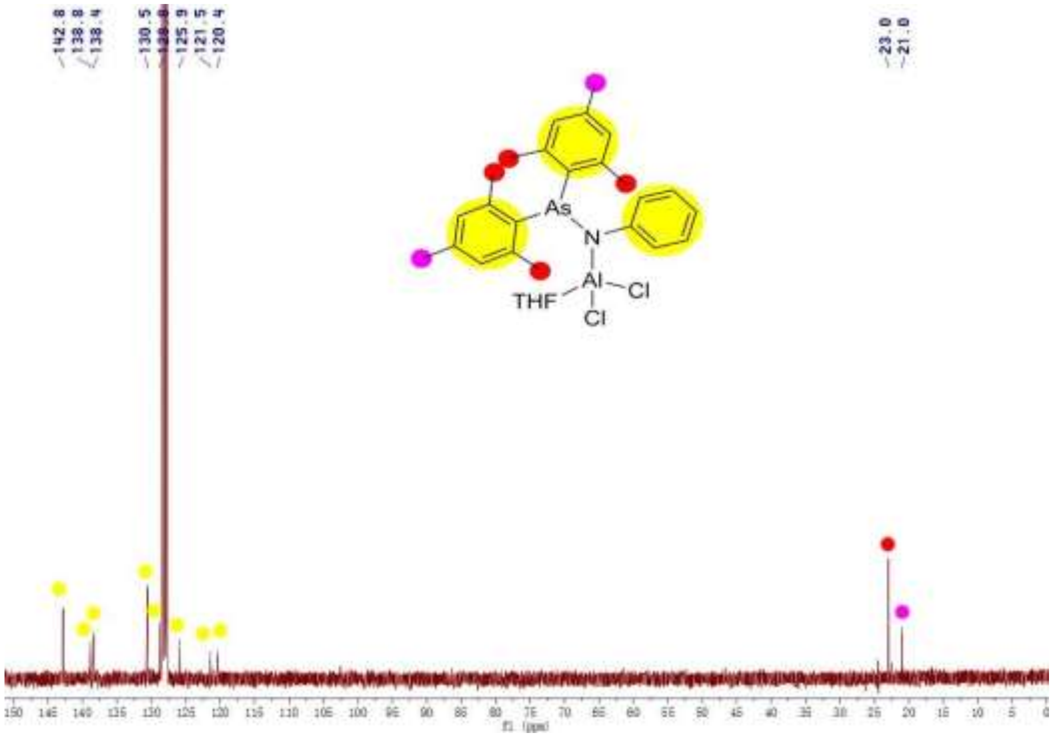

Figure S10: $^{13}C\{^{1}H\}$ NMR spectrum of 5 (75 MHz, C_6D_6, 298K).

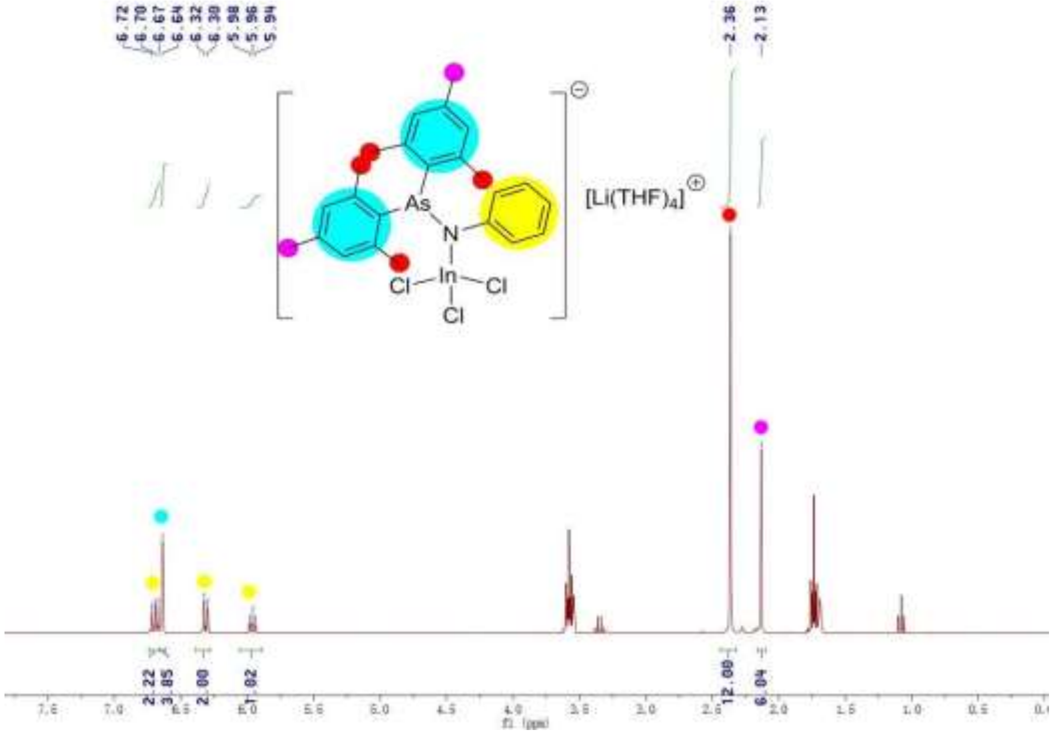

Figure S11: ^{1}H NMR spectrum of 6 (300 MHz, d_8-THF, 298K).

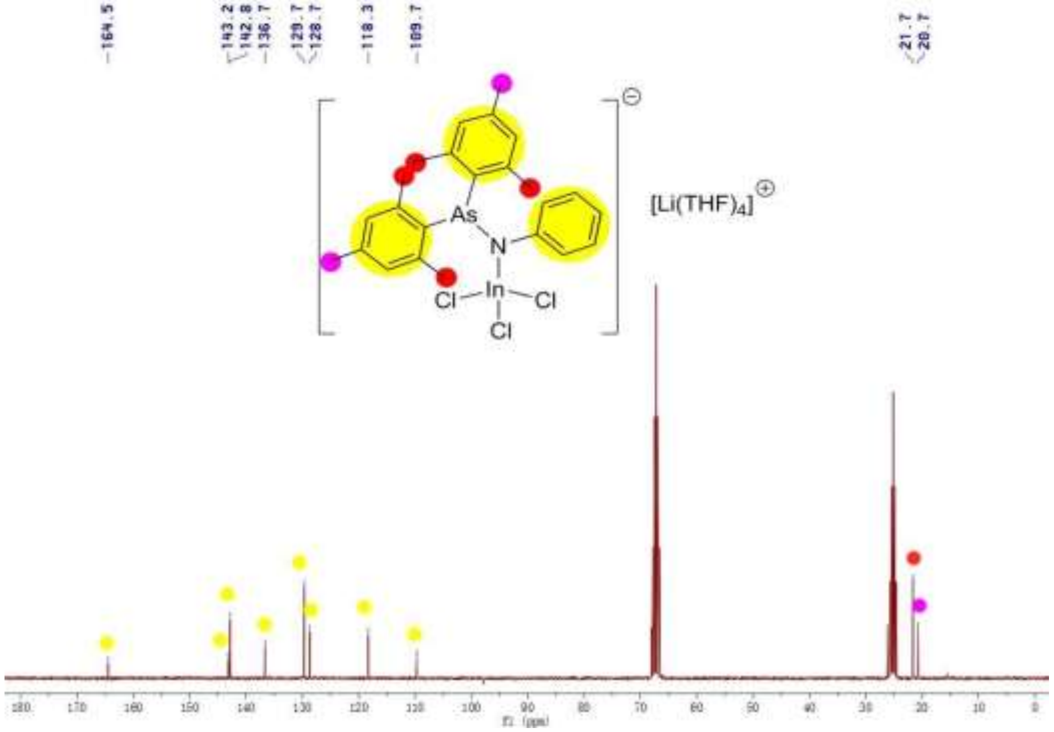

Figure S12: ^{13}C{^{1}H} NMR spectrum of 6 (75 MHz, d_8-THF, 298K).

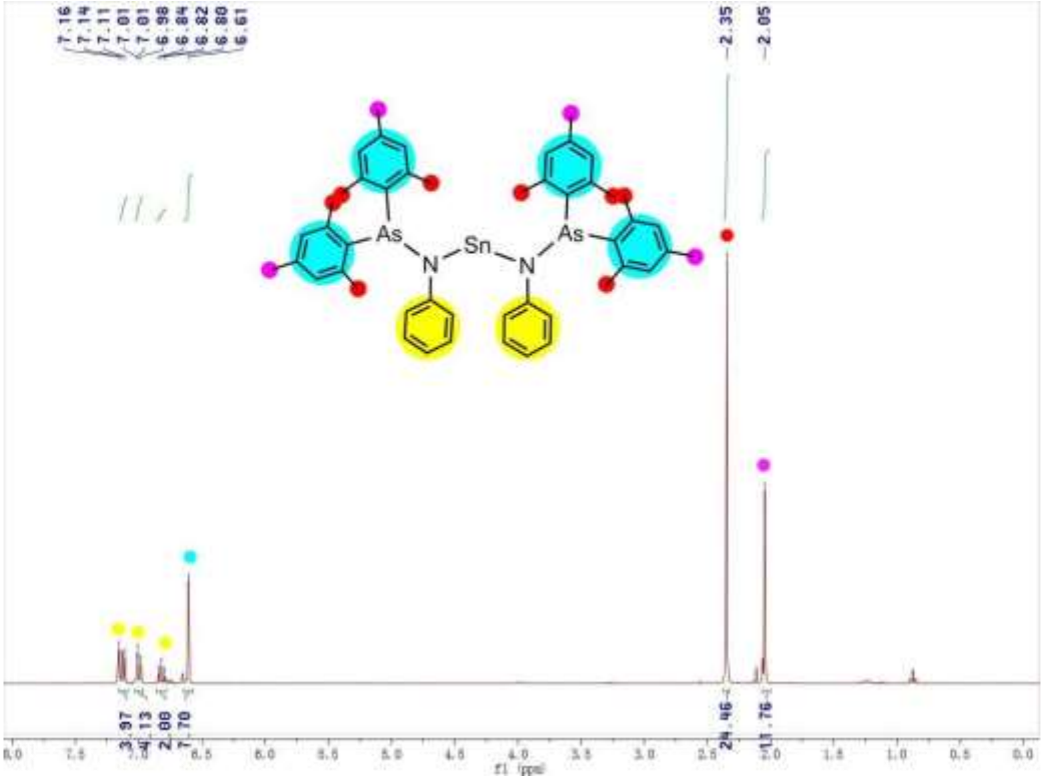

Figure S13: ^{1}H NMR spectrum of 7 (300 MHz, C_6D_6, 298K).

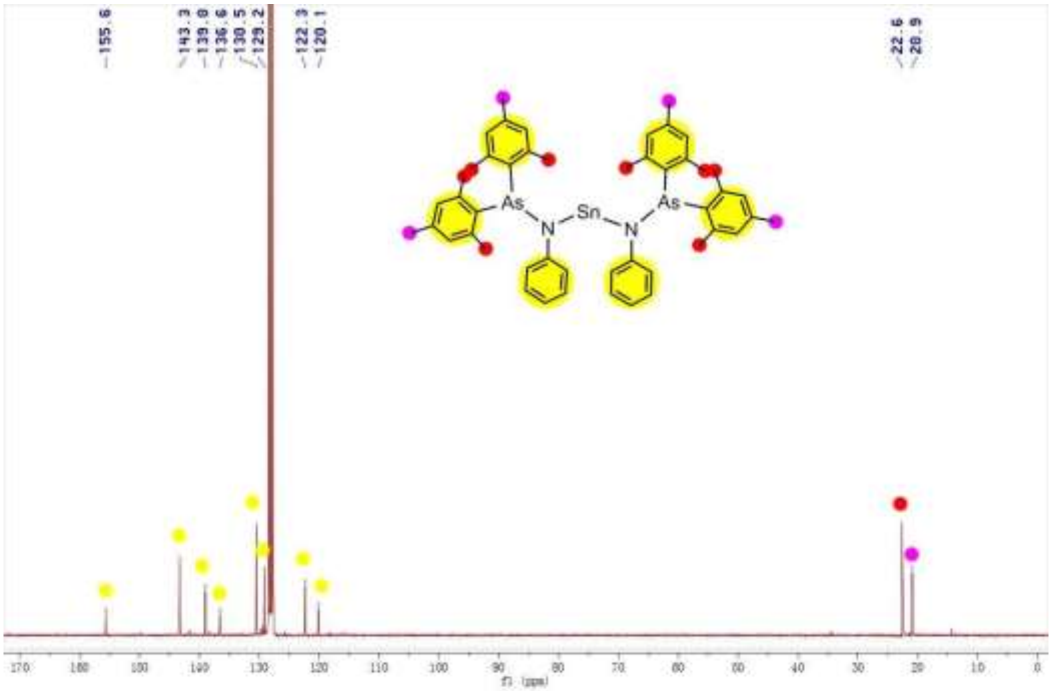

Figure S14: ^{13}C{^{1}H} NMR spectrum of 7 (75 MHz, C_6D_6, 298K).

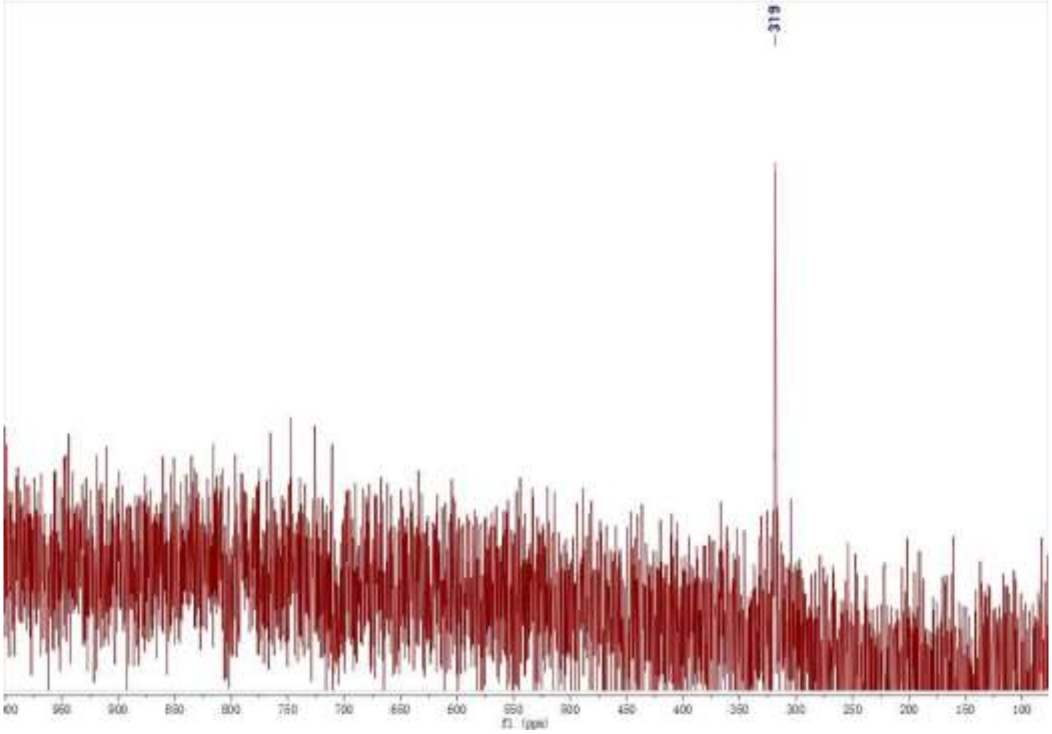

Figure S15: ^{119}Sn{^{1}H} NMR spectrum of 7 (112 MHz, C_6D_6, 298K).

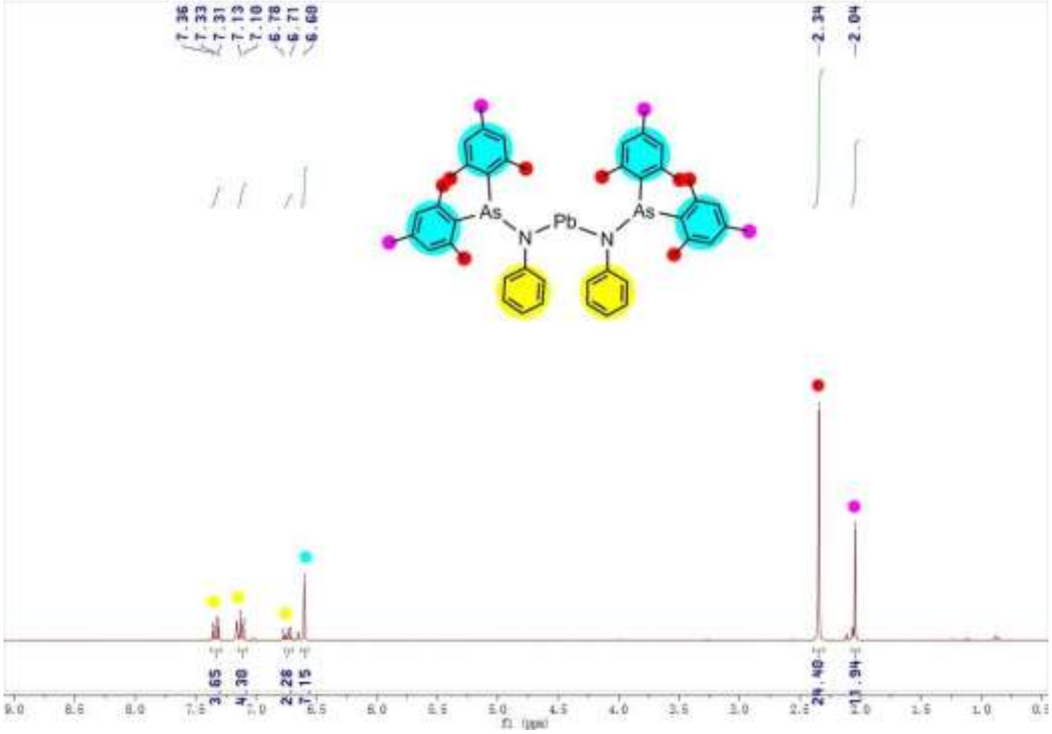

Figure S16: ^{1}H NMR spectrum of 8 (300 MHz, C_6D_6, 298K).

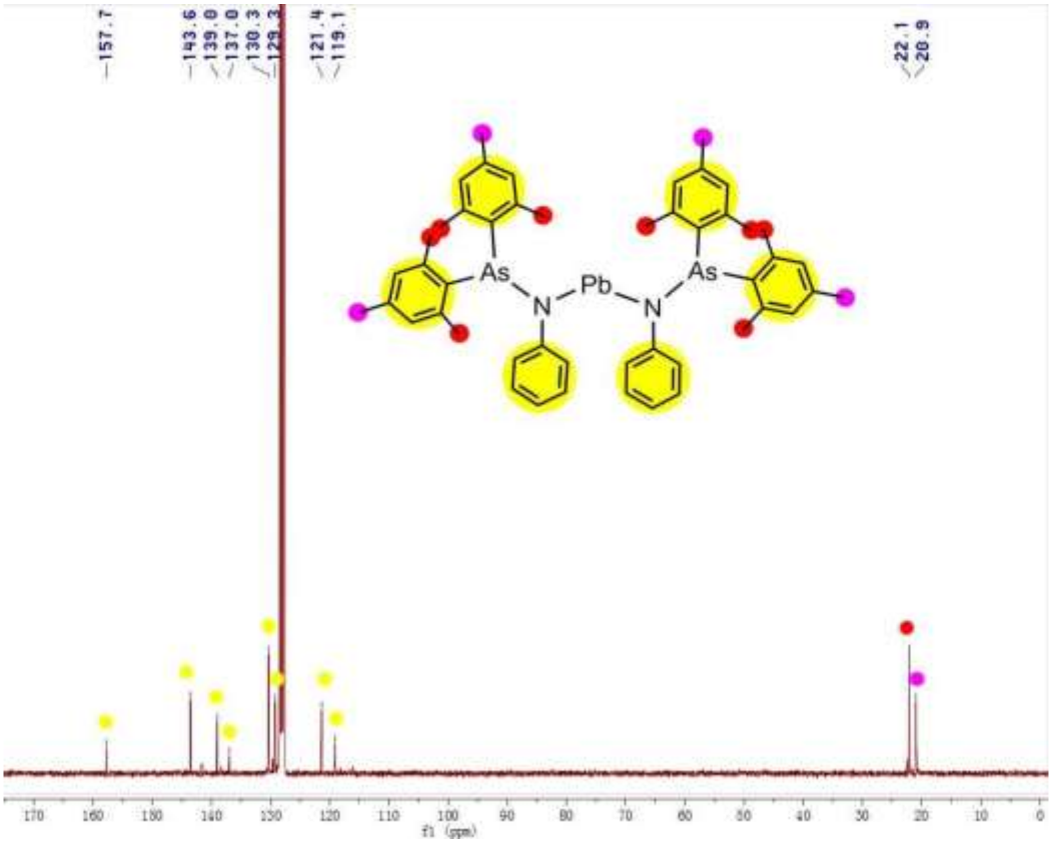

Figure S17: $^{13}C\{^{1}H\}$ NMR spectrum of 8 (75 MHz, C_6D_6, 298K).

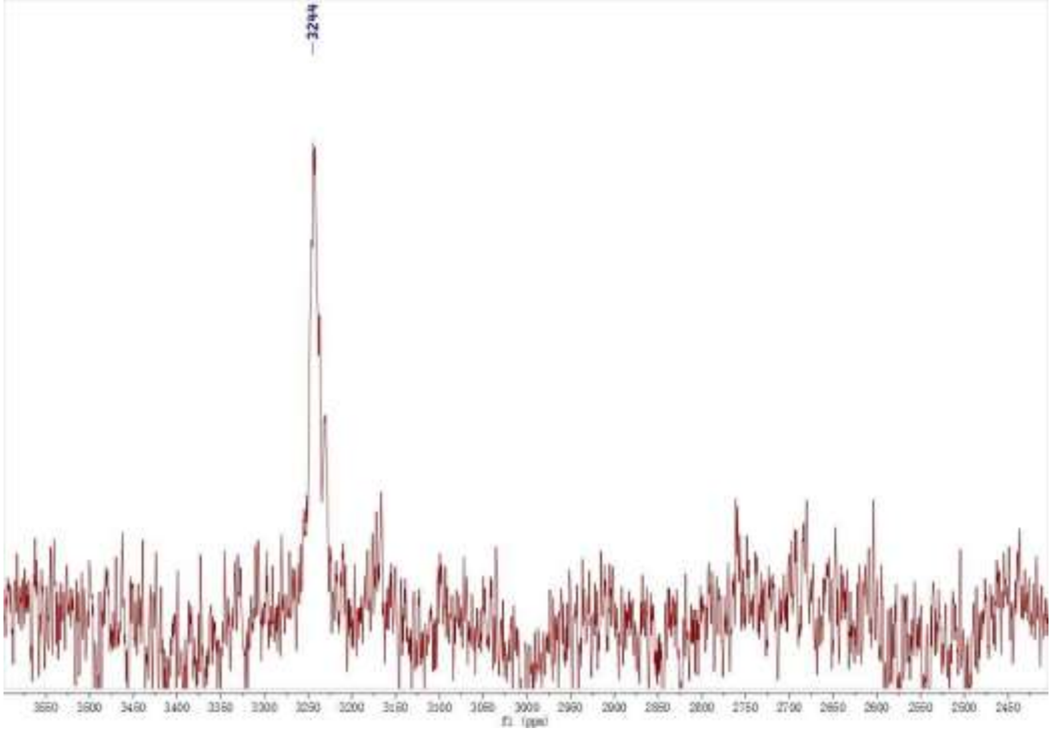

Figure S18: $^{207}Pb\{^{1}H\}$ NMR spectrum of 8 (62.8 MHz, C_6D_6, 298K).

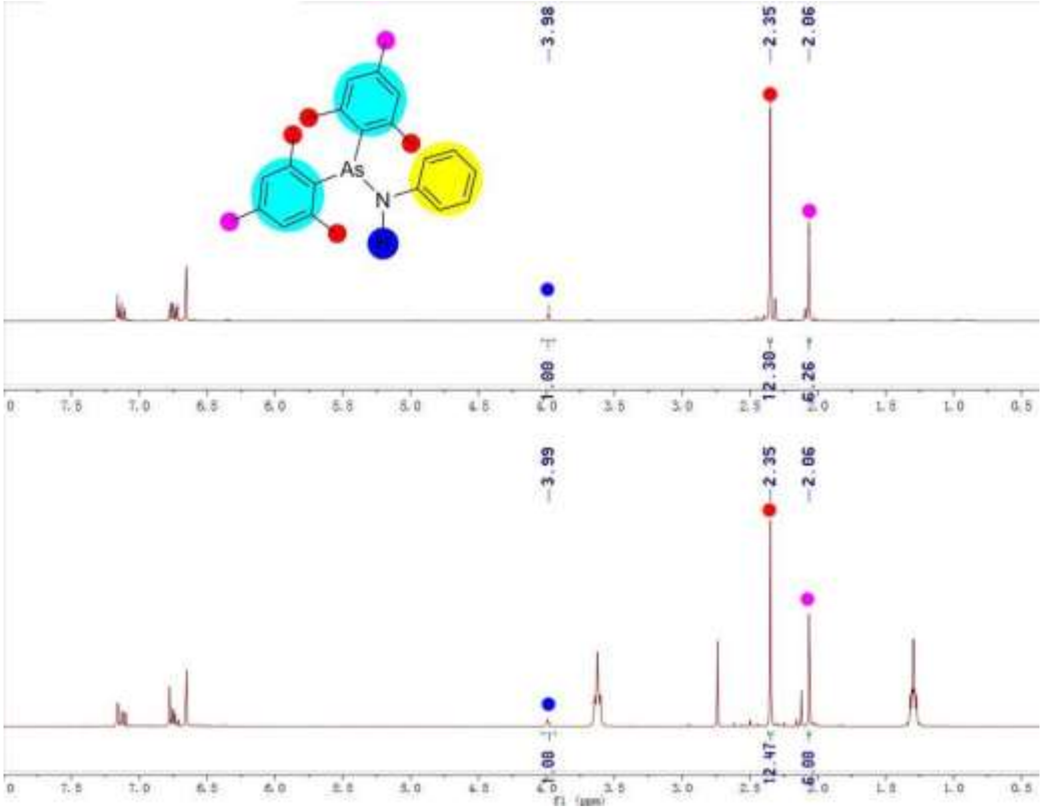

Figure S19: ^{1}H NMR spectra of $Mes_2AsN(H)Ph$ (top) and the decomposed 6 (bottom) (300 MHz, C_6D_6, 298K).

3. IR spectra

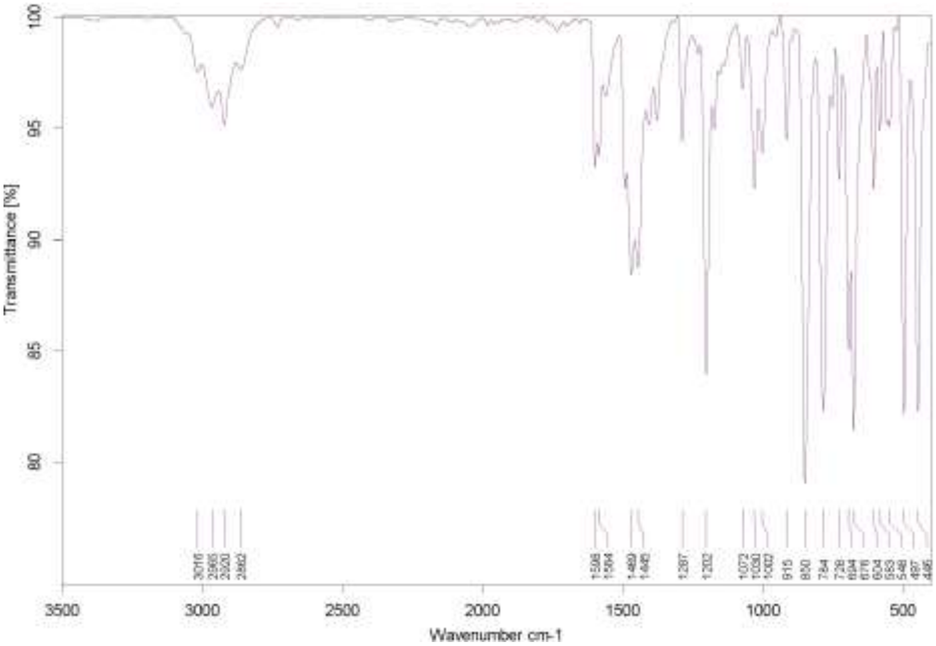

Figure S20: IR spectrum of compound 1.

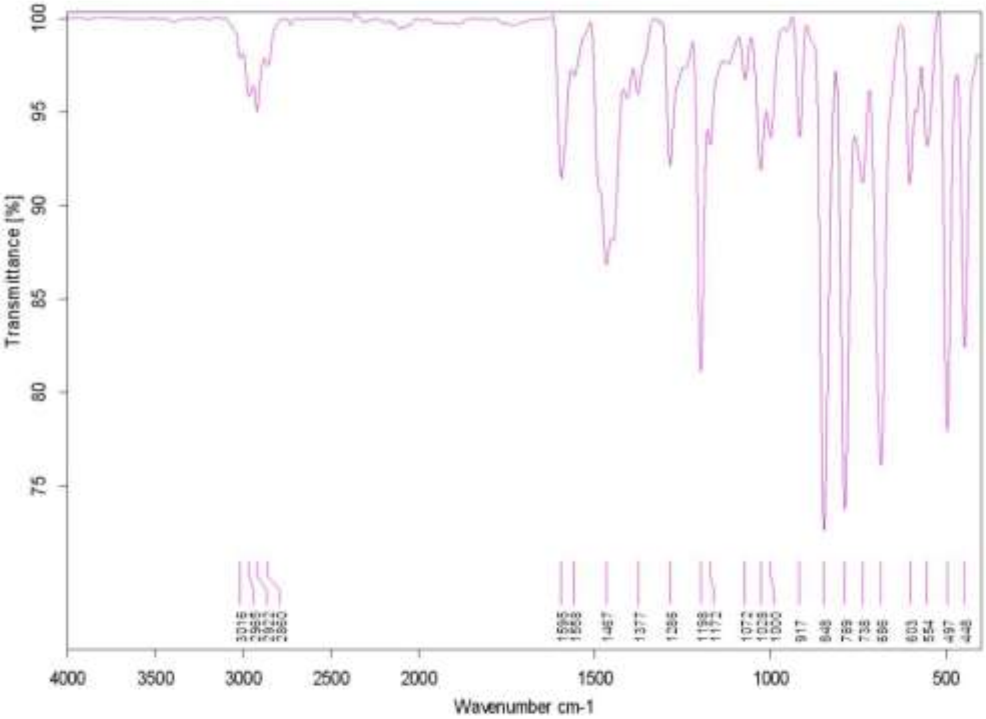

Figure S21: IR spectrum of compound 2.

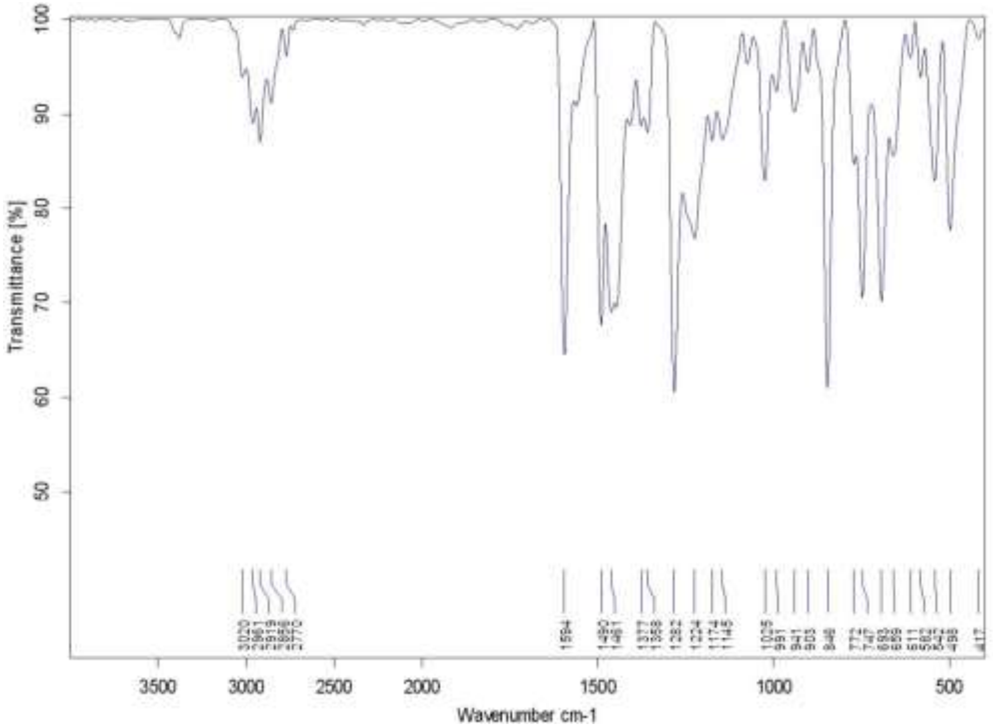

Figure S22: IR spectrum of compound 3.

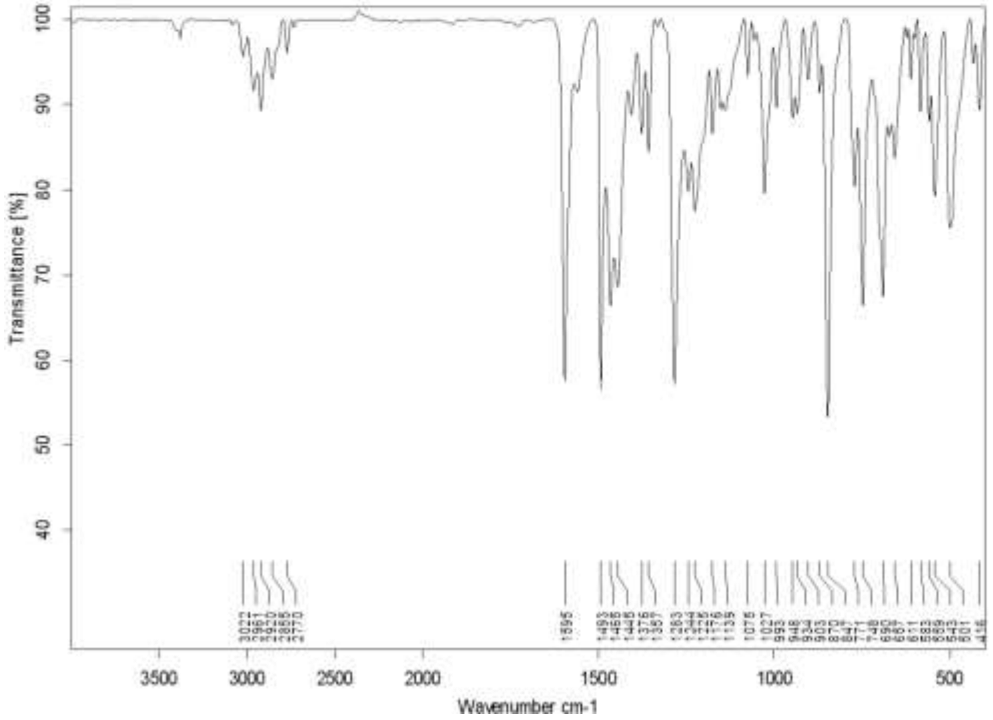

Figure S23: IR spectrum of compound 4.

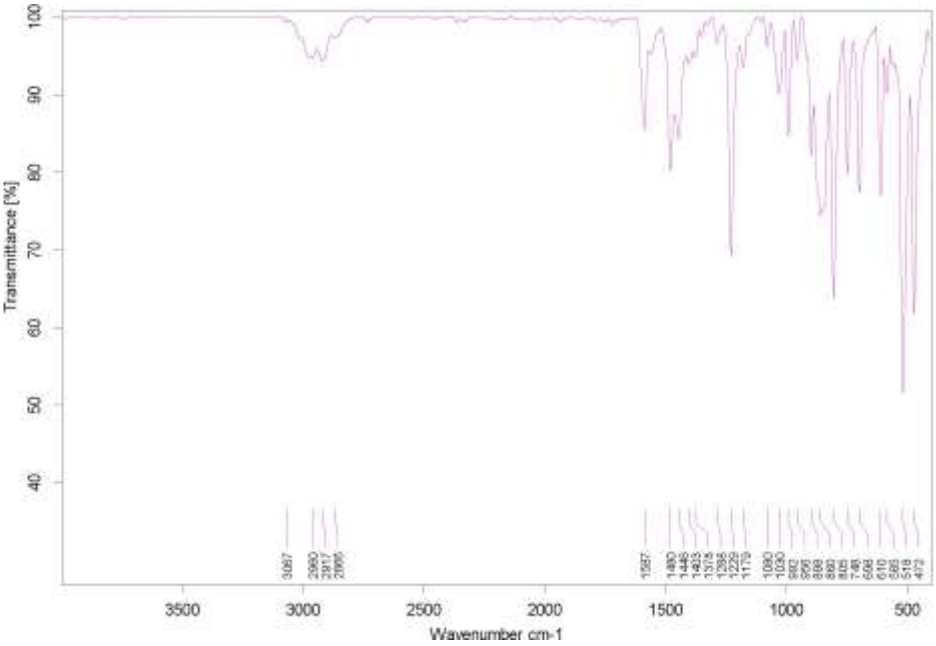

Figure S24: IR spectrum of compound 5.

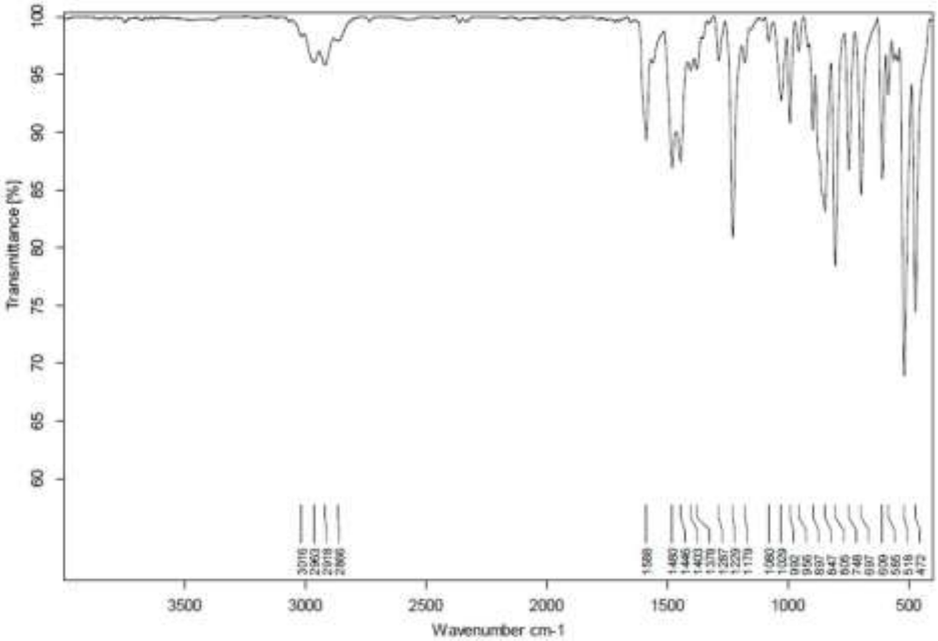

Figure S25: IR spectrum of compound 6.

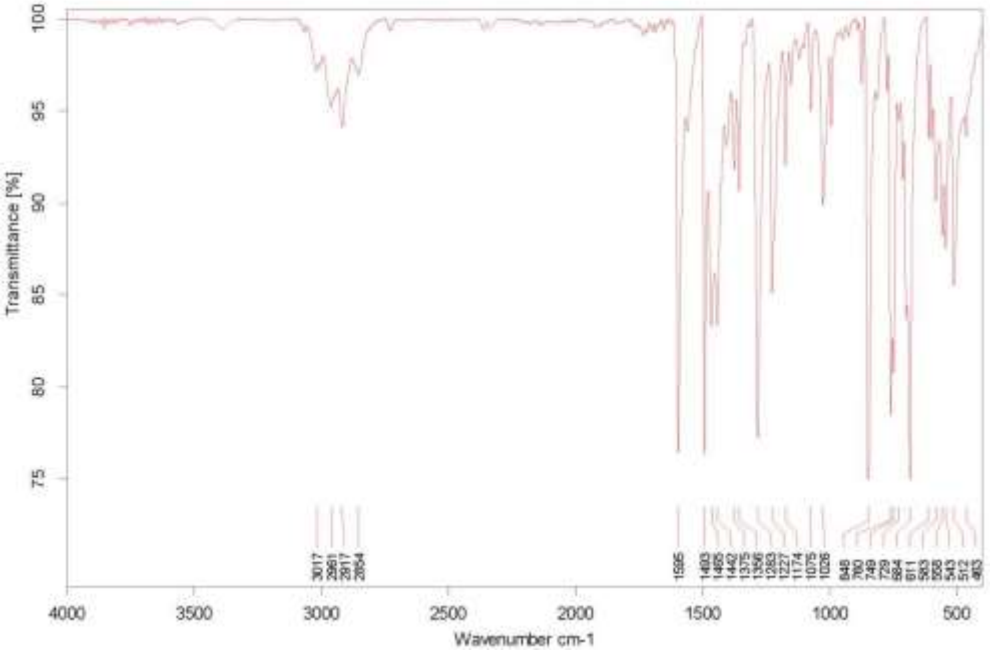

Figure S26: IR spectrum of compound 7.

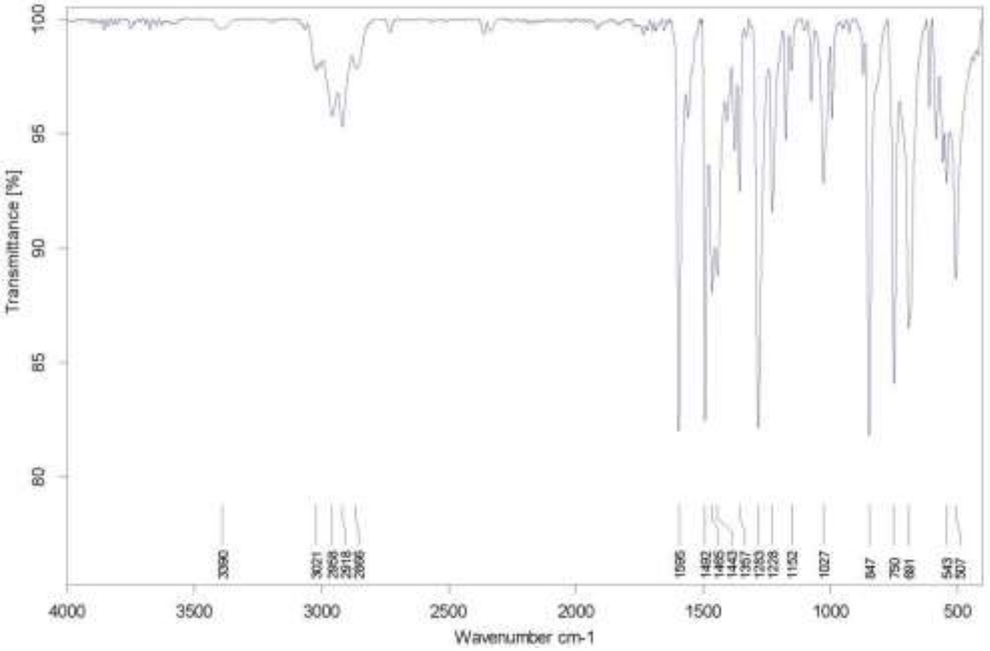

Figure S27: IR spectrum of compound 8.

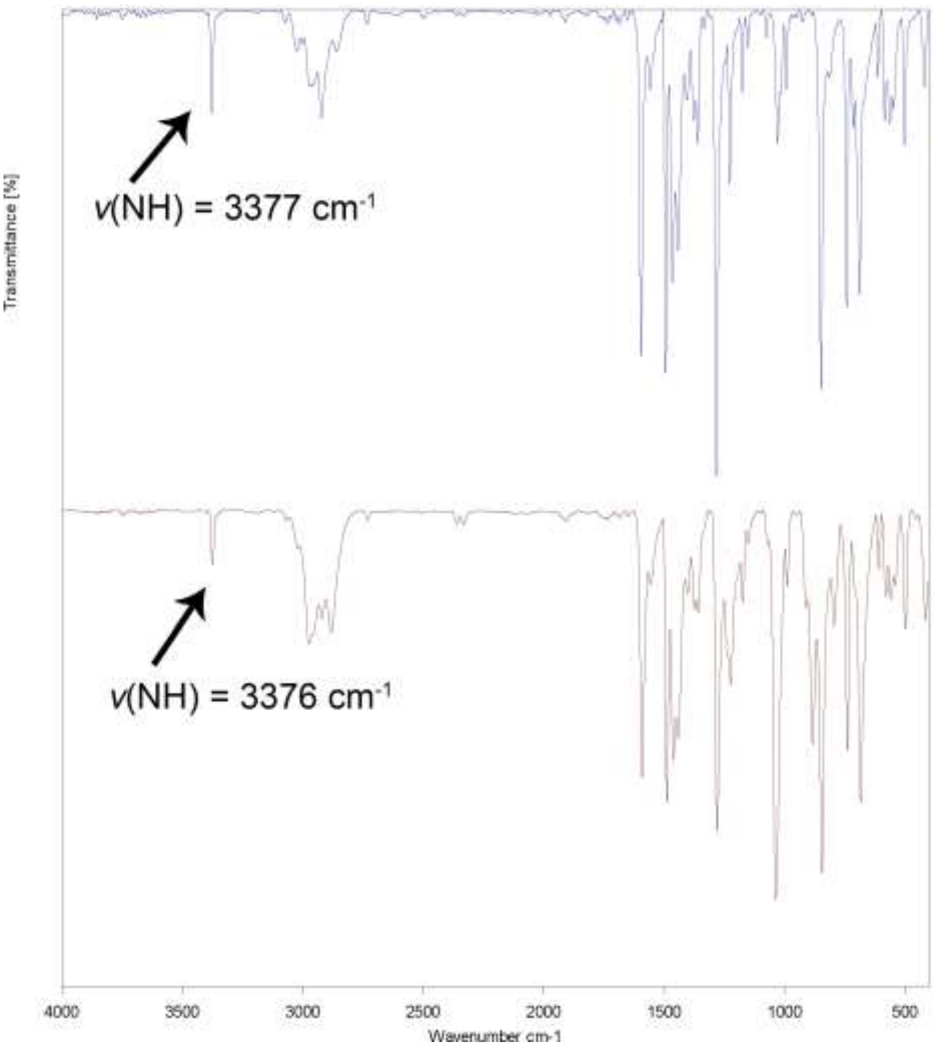

Figure S28: IR spectra of $Mes_2AsN(H)Ph$ (top) and the decomposed 6 (bottom).

4. Crystallographic Investigations

A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fibre or a mylar loop. The crystal was transferred directly to the cold stream of a STOE IPDS 2 (150 or 210 K) or STADIVARI (100 K) diffractometer.

All structures were solved by using the programs SHELXS/T[3, 4] and Olex2.[5] The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F^2 by using the program SHELXL.[3, 4] In each case, the locations of the largest peaks in the final difference Fourier map calculations, as well as the magnitude of the residual electron densities, were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, bond distances and angles have been deposited as supporting information.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC-1949410-1949417. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

Table S1: Crystal data, data collection and refinement for compounds 1-8.

	1·DCM	2·DCM	3	4	5	6	7	8
Empirical formula	$C_{53}H_{64}As_2Cl_4N_2OZr$	$C_{53}H_{64}As_2Cl_4N_2OHf$	$C_{52}H_{66}As_2N_4Zr$	$C_{52}H_{66}As_2N_4Hf$	$C_{28}H_{35}AlAsCl_2NO$	$C_{40}H_{59}AsCl_3InLiNO_4$	$C_{101}H_{120}As_4N_4Sn_2$	$C_{103}H_{116}As_4N_4Pb_2$
Formula weight	1127.92	1215.19	988.14	1075.41	574.37	920.91	1927.06	2124.05
Temperature/K	100	100	100	150	210	100	100	100
Crystal system	monoclinic	monoclinic	triclinic	triclinic	triclinic	monoclinic	tetragonal	tetragonal
Space group	$P2_1/n$	$P2_1/n$	P-1	P-1	P-1	$P2_1/n$	$I4_1/a$	$I4_1/a$
a/Å	12.3693(6)	12.3504(5)	9.3140(6)	9.3307(4)	8.3091(7)	15.2723(8)	23.6642(5)	23.7152(8)
b/Å	16.8828(5)	16.8952(5)	13.5043(8)	13.5735(6)	12.8303(10)	13.4957(5)	23.6642(5)	23.7152(8)
c/Å	25.0260(11)	24.8854(10)	19.5598(12)	19.6583(9)	13.3272(10)	20.3619(11)	31.7406(8)	31.4568(12)
α/°			95.792(5)	95.723(3)	86.646(6)			
β/°	102.369(4)	102.520(3)	95.805(5)	96.008(4)	87.317(6)	95.307(4)		
γ/°			103.161(5)	103.085(4)	85.587(6)			
V/Å^3	5104.8(4)	5069.2(3)	2363.7(3)	2392.1(2)	1412.9(2)	4178.8(4)	17774.6(9)	17691.6(14)
Z	4	4	2	2	2	4	8	8
ρ_{calc}g/cm^3	1.468	1.592	1.388	1.493	1.350	1.464	1.440	1.595
μ/mm^{-1}	1.751	3.60	1.661	3.592	1.444	1.583	2.089	5.337
F(000)	2312.0	2440.0	1024.0	1088.0	596.0	1896.0	7888.0	8464.0
Crystal size/mm^3	0.162 0.131 0.077	0.404 0.211 0.078	0.373 0.336 0.314	0.438 0.31 0.182	0.259 0.195 0.121	0.409 0.315 0.22	0.4 0.215 0.067	0.386 0.159 0.041
Reflections collected	22922	29684	23999	26320	14629	27310	114872	26155
2Θ range /°	4.068 to 59.338	4.822 to 62.02	3.538 to 63.258	3.52 to 59.034	3.188 to 59.098	3.626 to 67.816	4.216 to 59.45	4.858 to 62.04
Independent reflections	12038 [R_{int} = 0.0467, R_{sigma} = 0.0843]	13188 [R_{int} = 0.0265, R_{sigma} = 0.0390]	12895 [R_{int} = 0.0347, R_{sigma} = 0.0446]	13191 [R_{int} = 0.0323, R_{sigma} = 0.0420]	7780 [R_{int} = 0.0639, R_{sigma} = 0.1076]	14135 [R_{int} = 0.0351, R_{sigma} = 0.0488]	114872 [R_{int} = 0.0686, R_{sigma} = 0.0903]	11522 [R_{int} = 0.0555, R_{sigma} = 0.0775]
Data/restraints/parameters	12038/0/580	13188/0/580	12895/0/548	13191/0/548	7780/0/331	14135/0/466	114872/24/537	11522/0/490
GOOF	1.012	1.025	1.055	1.037	0.923	1.052	0.985	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0523, wR_2 = 0.1107	R_1 = 0.0335, wR_2 = 0.0778	R_1 = 0.0392, wR_2 = 0.0985	R_1 = 0.0311, wR_2 = 0.0751	R_1 = 0.0575, wR_2 = 0.1028	R_1 = 0.0415, wR_2 = 0.0914	R_1 = 0.0539, wR_2 = 0.1158	R_1 = 0.0582, wR_2 = 0.1391
Final R indexes [all data]	R_1 = 0.1011, wR_2 = 0.1305	R_1 = 0.0469, wR_2 = 0.0843	R_1 = 0.0526, wR_2 = 0.1053	R_1 = 0.0436, wR_2 = 0.0789	R_1 = 0.1089, wR_2 = 0.1172	R_1 = 0.0706, wR_2 = 0.1060	R_1 = 0.1052, wR_2 = 0.1352	R_1 = 0.0969, wR_2 = 0.1620
Largest diff. peak/hole / eÅ^{-3}	0.65/-0.64	1.16/-1.23	0.73/-0.79	1.92/-1.44	0.67/-0.61	0.93/-1.50	0.82/-0.82	1.56/-2.36

ORTEP-Plots of solid-state structures

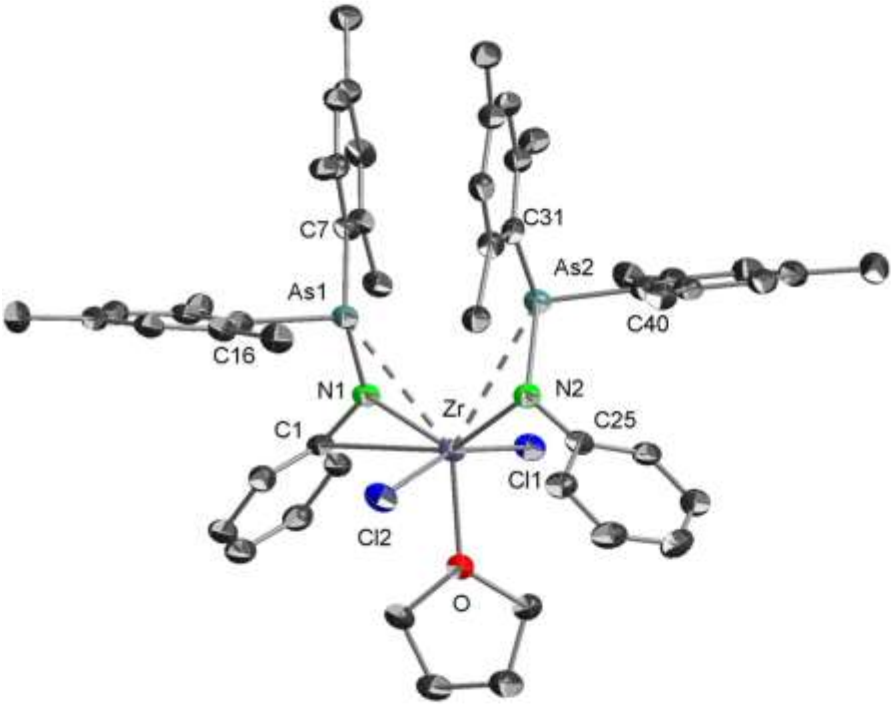

Figure S29: Molecular structure of 1 in the solid-state. Hydrogen atoms and DCM molecule are omitted for clarity. Ellipsoids displayed at 50% probability. Selected bond lengths (Å) and angles (°): Zr-As1 3.2101(6), Zr-As2 3.2216(6), Zr-Cl1 2.4846(12), Zr-Cl2 2.4932(12), Zr-O 2.204(3), Zr-N1 2.039(4), Zr-N2 2.036(4), Zr-C1 2.827(5), As1-N1 1.867(3), As1-C7 1.977(4), As1-C16 1.990(4), As2-N2 1.891(3), As2-C31 1.998(4), As2-C40 1.995(5), N1-C1 1.428(5), N2-C25 1.417(6); As1-Zr-As2 68.047(15), Cl1-Zr-Cl2 160.84(4), N2-Zr-N1 118.42(14), C7-As1-C16 99.39(18), As1-N1-Zr 110.5(2), C1-N1-Zr 107.9(3), C1-N1-As1 131.3(3), As2-N2-Zr 110.2(2), C25-N2-Zr 111.4(3), C25-N2-As2 129.4(3).

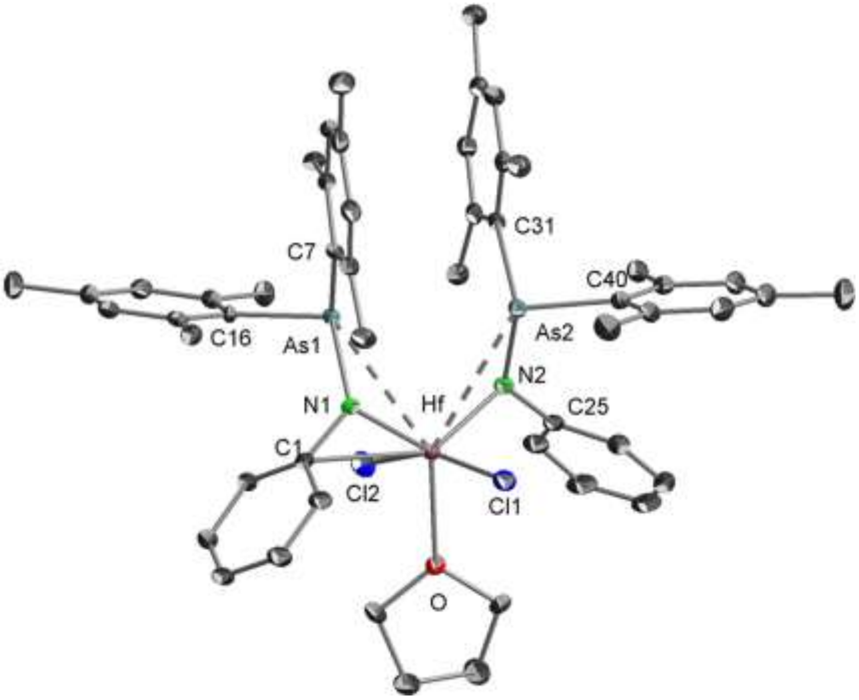

Figure S30: Molecular structure of 2 in the solid-state. Hydrogen atoms and DCM molecule are omitted for clarity. Ellipsoids displayed at 50% probability. Selected bond lengths (Å) and angles (°): Hf-As1 3.2423(4), Hf-As2 3.2342(4), Hf-Cl1 2.4543(8), Hf-Cl2 2.4650(9), Hf-O 2.175(2), Hf-N1 2.020(3), Hf-N2 2.018(3), Hf-C1 2.794(3), As1-N1 1.870(3), As1-C7 1.974(3), As1-C16 1.982(3), As2-N2 1.877(3), As2-C31 1.984(3), As2-C40 1.984(3), N1-C1 1.421(4), N2-C25 1.427(4); As2-Hf-As1 66.812(9), Cl1-Hf-Cl2 161.21(3), N2-Hf-N1 115.30(11), C7-As1-C16 99.26(13), C31-As2-C40 99.22(13), As1-N1-Hf 112.90(13), C1-N1-Hf 107.3(2), C1-N1-As1 130.2(2), As2-N2-Hf 112.24(13), C25-N2-Hf 109.7(2), C25-N2-As2 129.3(2).

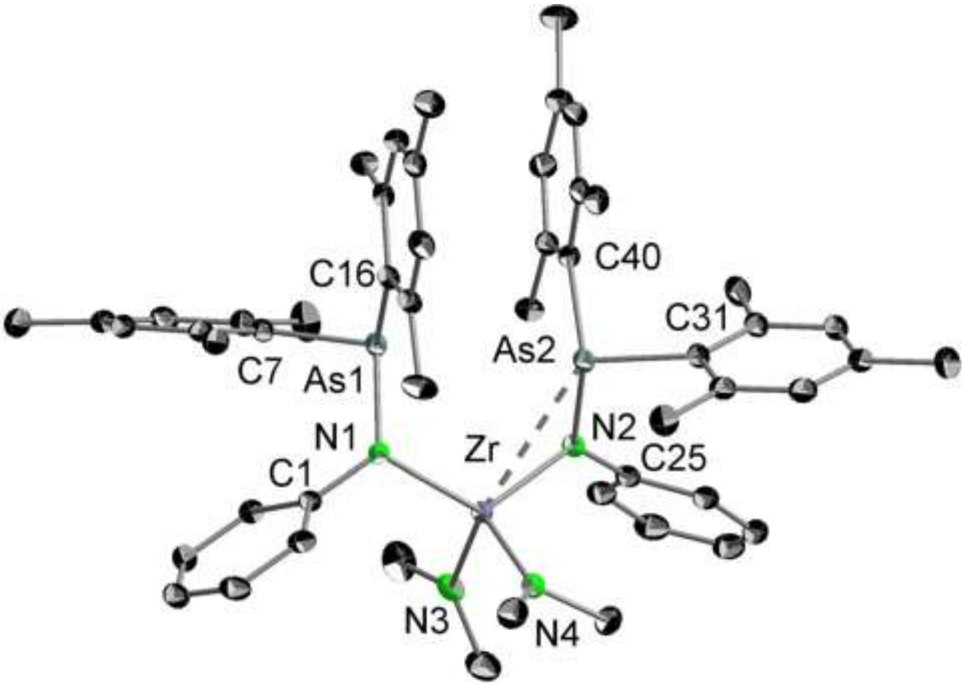

Figure S31: Molecular structure of 3 in the solid-state. Hydrogen atoms are omitted for clarity. Ellipsoids displayed at 50% probability. Selected bond lengths (Å) and angles (°): Zr-As2 3.0798(4), Zr-N1 2.081(2), Zr-N2 2.096(2), Zr-N3 2.040(2), Zr-N4 2.035(2), As1-N1 1.878(2), As1-C7 1.966(2), As1-C16 1.988(2), As2-N2 1.863(2), As2-C31 1.966(2), As2-C40 1.979(2), N1-C1 1.425(3), N2-C25 1.412(3); N1-Zr-N2 118.94(7), N4-Zr-N3 103.33(9), C7-As1-C16 101.46(9), C31-As2-C40 100.14(9), As1-N1-Zr 114.45(9), C1-N1-Zr 117.66(14), C1-N1-As1 124.24(14), As2-N2-Zr 101.98(8), C25-N2-Zr 124.63(14), C25-N2-As2 129.9(2).

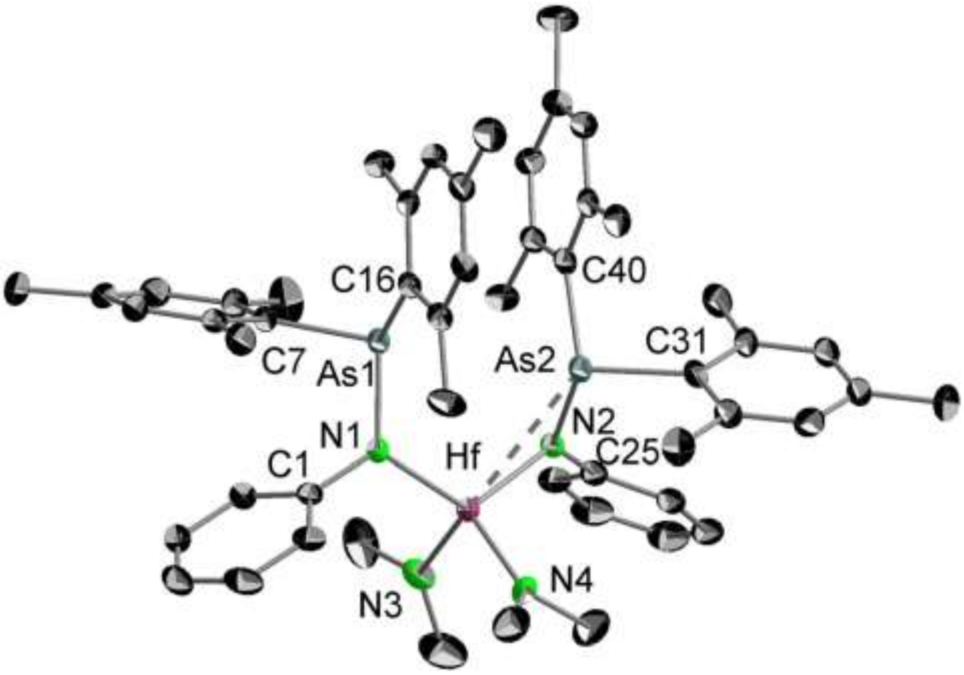

Figure S32: Molecular structure of 4 in the solid-state. Hydrogen atoms are omitted for clarity. Ellipsoids displayed at 50% probability. Selected bond lengths (Å) and angles (°): Hf-As2 3.0892(3), Hf-N1 2.069(2), Hf-N2 2.078(2), Hf-N3 2.028(3), Hf-N4 2.037(3), As1-N1 1.885(2), As1-C7 1.982(3), As1-C16 1.984(3), As2-N2 1.870(2), As2-C31 1.978(3), As2-C40 1.986(3), N1-C1 1.432(4), N2-C25 1.418(4); N1-Hf-N2 118.94(9), N3-Hf-N4 103.67(12), C7-As1-C16 101.81(12), C31-As2-C40 100.44(12), As1-N1-Hf 114.88(11), C1-N1-Hf 118.3(2), C1-N1-As1 123.8(2), As2-N2-Hf 102.84(11), C25-N2-Hf 124.3 (2), C25-N2-As2 129.7(2).

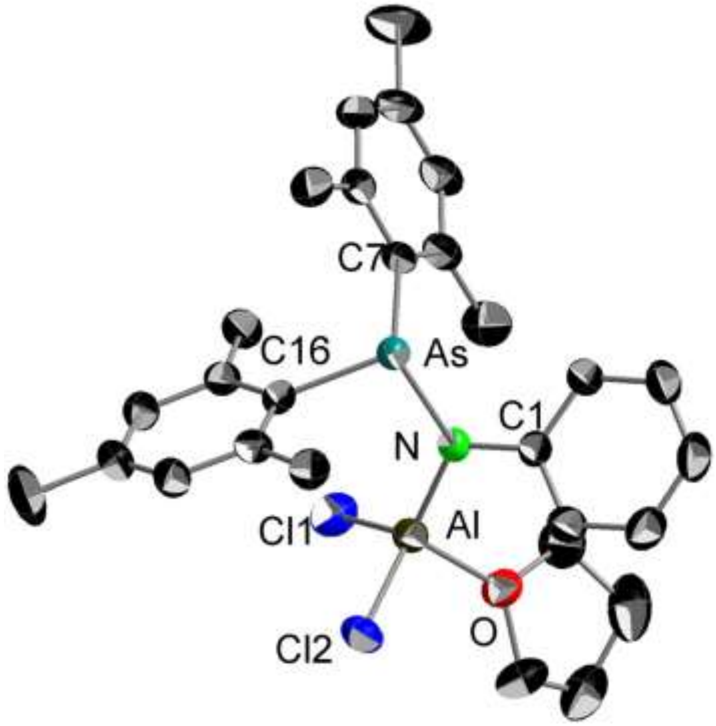

Figure S33: Molecular structure of 5 in the solid-state. Hydrogen atoms are omitted for clarity. Ellipsoids displayed at 50% probability. Selected bond lengths (Å) and angles (°): As-N 1.884(3), As-C7 1.989(4), As-C16 1.985(3), Cl1-Al 2.119(2), Cl2-Al 2.1411(14), Al-O 1.869(3), Al-N 1.819(3), N-C1 1.429(4); N-As-C7 110.6(2), N-As-C16 99.18(13), C16-As-C7 104.04(14), Cl1-Al-Cl2 111.07(6), Al-N-As 125.9(2), C1-N-As 110.9(2), C1-N-Al 120.6(2).

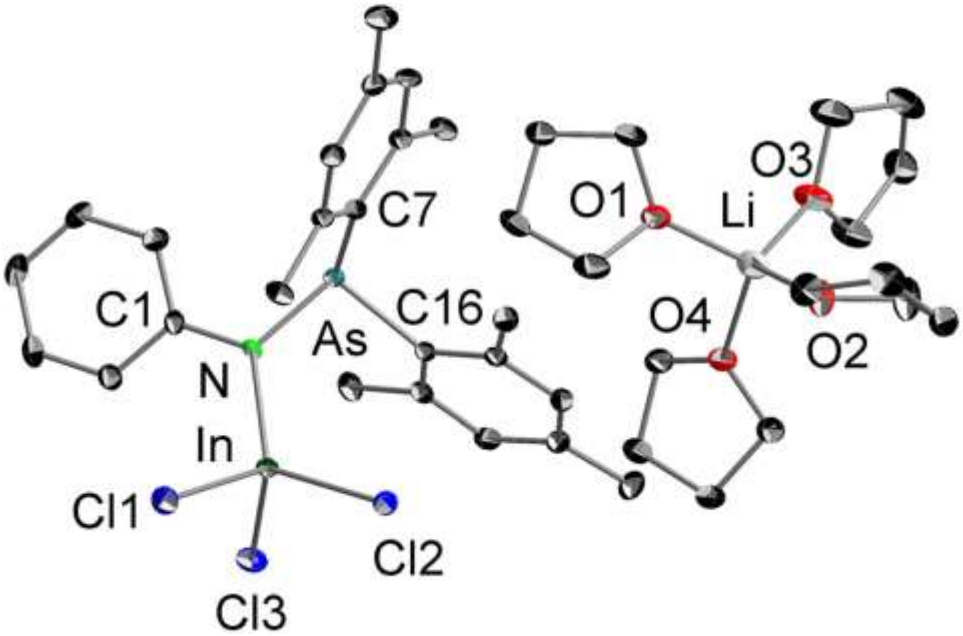

Figure S34: Molecular structure of 6 in the solid-state. Hydrogen atoms are omitted for clarity. Ellipsoids displayed at 50% probability. Selected bond lengths (Å) and angles (°): In-Cl1 2.3884(7), In-Cl2 2.3540(7), In-Cl3 2.3906(7), In-N 2.078(2), As-N 1.861(2), As-C7 1.976(3), As-C16 1.961(3), N-C1 1.400(3); N-In-Cl1 109.89(6), N-In-Cl2 119.51(6), N-In-Cl3 110.27(7), N-As-C7 106.81(10), N-As-C16 101.13(10), C16-As-C7 108.39(11), As-N-In 126.3(1), C1-N-In 118.6(2), C1-N-As 114.4(2).

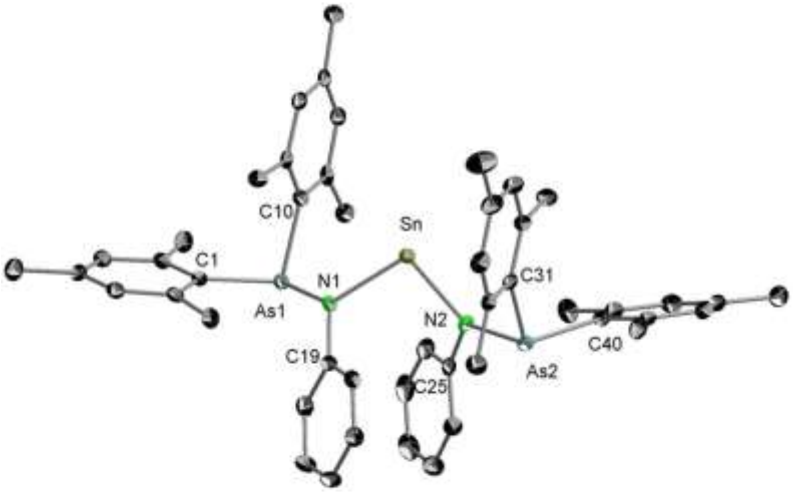

Figure S35: Molecular structure of 7 in the solid-state. Hydrogen atoms are omitted for clarity. Ellipsoids displayed at 50% probability. Selected bond lengths (Å) and angles (°): Sn-N1 2.120(4), Sn-N2 2.115(4), As1-N1 1.880(4), As2-N2 1.880(4), As1-C1 1.996(5), As1-C10 1.985(5), As2-C31 1.981(5), As2-C40 1.995(5), N1-C19 1.419(6), N2-C25 1.416(7); N2-Sn-N1 97.8(2), N1-As1-C1 109.8(2), N1-As1-C10 97.0(2), C10-As1-C1 99.9(2), N2-As2-C31 96.9(2), N2-As2-C40 109.7(2), C31-As2-C40 101.4(2), As1-N1-Sn 116.0(2), C19-N1-Sn 119.2(3), C19-N1-As1 116.3(3), As2-N2-Sn 121.5(2), C25-N2-Sn 118.4(3), C25-N2-As2 116.5(3).

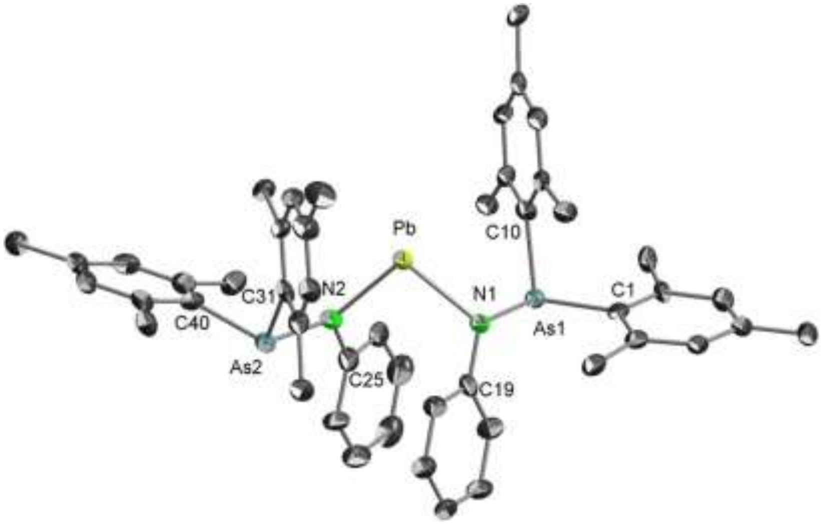

Figure S36: Molecular structure of 8 in the solid-state. Hydrogen atoms are omitted for clarity. Ellipsoids displayed at 50% probability. Selected bond lengths (Å) and angles (°): Pb-N1 2.236(6), Pb-N2 2.211(6), As1-N1 1.872(6), As2-N2 1.873(6), As1-C1 1.994(7), As1-C10 1.989(7), As2-C31 1.972(7), As2-C40 1.986(7), N1-C19 1.403(9), N2-C25 1.420(9); N2-Pb-N1 97.4(2), N1-As1-C1 109.0(3), N1-As1-C10 97.1(3), C10-As1-C1 100.3(3), N2-As2-C31 96.0(3), N2-As2-C40 108.7(3), C31-As2-C40 100.8(3), As1-N1-Pb 113.8(3), C19-N1-Pb 118.4(4), C19-N1-As1 116.7(5), As2-N2-Pb 121.4(3), C25-N2-Pb 116.6(5), C25-N2-As2 116.5(5).

5. Reference

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