Electronic Supplementary Information for:

N-Heterocyclic Carbene Complexes of Molybdenum(IV) and Tungsten(IV)

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Content:

1) Synthesis and characterization of the compounds

Synthesis of [MoCl$_4$(IMes)$_2$] 1:
A solution of [MoCl$_4$(SEt$_2$)$_2$] (2.88 g, 6.89 mmol) and IMes (4.20 g, 13.8 mmol) in 30 mL toluene was stirred overnight whereby the color changed from red to dark orange. All volatiles were removed *in vacuo* and the residue was suspended in 20 mL of *n*-hexane. After filtration, the remaining solid was washed with *n*-hexane (2 x 10 mL portions) and dried *in vacuo*.
Yield: 5.37 g (6.34 mmol, 92 %) of an orange solid. Orange crystals of [MoCl$_4$(IMes)$_2$] suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a saturated solution of the compound in benzene. $C_{42}H_{48}Cl_4MoN_4$ [846.63 g/mol] found (calcd.): C 59.18 (59.59), H 6.09 (5.71), N 5.98 (6.62). **Magnetic Moment (Evans-Method)[S1]:** μ_{eff} = 2.11 μ_B. **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = 1.77 (s, 12 H, CH_{3para}), 2.92 (s, 24 H, CH_{3ortho}), 4.66 (s, 4 H, NC*H*C*H*N), 6.76 (s, 8 H, CH_{meta}) ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 21.2 (CH_{3para}), 44.4 (CH_{3ortho}), 81.3 (N*C*H*C*HN), 121.4 (C_{para}), 135.5 (C_{ipso}), 140.5 (CH_{meta}), 159.1 (C_{ortho}) ppm. **IR** (ATR[cm^{-1}]): 473 (m), 523 (w), 551 (w), 576 (m), 592 (w), 614 (w), 643 (m), 674 (m), 697 (s), 738 (s), 806 (m), 850 (vs), 892 (w), 926 (s), 1035 (vs), 1071 (vs), 1208 (m), 1227 (m), 1257 (s), 1292 (m), 1388 (s), 1483 (s), 1543 (m), 1608 (s), 2001 (vw), 2075 (vw), 2170 (vw), 2736 (w), 2859 (m), 2918 (m), 2951 (m), 3138 (w.).

Synthesis of [MoCl$_4$(IDipp)$_2$] 2: A solution of [MoCl$_4$(SEt$_2$)$_2$] (600 mg, 1.43 mmol) and IDipp (1.11 g, 2.87 mmol) in 20 mL toluene was stirred overnight whereby the color changed from red to dark orange. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. After filtration the remaining solid was washed with *n*-hexane (2 x 5 mL portions) and dried *in vacuo*. **Yield:** 1.21 g (1.19 mmol, 83 %) of an orange solid. Orange crystals of [MoCl$_4$(IDipp)$_2$] suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a saturated solution of the compound in benzene. $C_{54}H_{72}Cl_4MoN_4$ [1014.95 g/mol] found (calcd.): C 63.82 (63.90), H 7.24 (7.15), N 5.33 (5.52). **Magnetic Moment (Evans-Method)[S1]:** μ_{eff} = 2.53 μ_B. **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = 1.06 (s_{br}, 24 H, *i*PrCH_3), 1.96 (s_{br},24 H, *i*PrCH_3), 4.52 (s_{br}, 8 H, *i*PrC*H*), 5.16 (s, 4 H, NC*H*C*H*N), 7.12 (t, 4 H, $^3J_{HH}$ = 6.7 Hz, CH_{para}), 7.34 (d, 8 H, $^3J_{HH}$ = 7.3 Hz, CH_{meta}) ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 22.4 (*i*Pr*C*H$_3$), 39.1 (*i*Pr*C*H$_3$), 64.4 (*i*Pr*C*H), 85.9 (N*C*H*C*HN), 126.8 (C_{ipso}), 128.6 (CH_{para}), 131.8 (CH_{meta}), 166.4 (C_{ortho}) ppm. **IR** (ATR[cm^{-1}]): 441 (w), 461 (w), 523 (vw), 635 (m), 757 (vs), 803 (s), 850 (s), 1060 (m), 1101 (m), 1116 (m), 1181 (w), 1196 (w), 1235 (w), 1262 (m), 1330 (m), 1361 (s), 1389 (s), 1445 (s), 1464 (s), 1594 (w), 2868 (m), 2929 (s), 2964 (s), 3071 (w).

Synthesis of [WCl$_4$(IMes)$_2$] 3: A solution of [WCl$_4$(SEt$_2$)$_2$] (2.00 g, 3.95 mmol) and IMes (2.41 g, 7.90 mmol) in 30 mL toluene was stirred overnight whereby the color changed from red-orange to dark yellow. All volatiles were removed *in vacuo* and the residue was suspended in 15 mL of *n*-hexane. After filtration the remaining solid was washed with *n*-hexane (2 x 10 mL portions) and dried *in vacuo*. **Yield:** 3.63 g (3.88 mmol, 98 %) of a pale-yellow solid. Yellow crystals of [WCl$_4$(IMes)$_2$] suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a saturated solution of the compound in benzene. $C_{42}H_{48}Cl_4N_4W$ (934.51 g/mol): found (calcd.): C 53.45 (53.98), H 5.54 (5.18), N: 5.86 (6.00). **Magnetic Moment (Evans-Method)[S1]:** μ_{eff} = 1.76 μ_B. **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = 2.41 (s, 12 H, CH_{3para}), 2.51 (s, 4 H, NC*H*C*H*N) 2.62 (s, 24 H, CH_{3ortho}), 7.78 (s, 8 H, CH_{meta}) ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 21.6 (CH_{3para}), 37.5 (CH_{3ortho}), 92.6 (NCHCHN), 107.6 (C_{ipso}), 137.3 (C_{para}), 138.7 (CH_{meta}), 158.6 (C_{ortho}) ppm. **IR** (ATR[cm^{-1}]): 578 (m), 593 (w), 643 (w), 698 (s), 740 (s), 751 (m), 851 (vs), 926 (m), 960 (w), 1034 (m), 1206 (m), 1257 (s), 1389 (m), 1483 (s), 1608 (w), 2737 (vw), 2857 (w), 2917 (m), 2949 (w), 3141 (vw).

Synthesis of [WCl_4(IDipp)$_2$] 4: A solution of [WCl_4(SEt_2)$_2$] (500 mg, 0.99 mmol) and IDipp (768 mg, 1.98 mmol) in 15 mL toluene was stirred overnight whereby the color changed from red orange to dark yellow. All volatiles were removed *in vacuo* and the residue was suspended in 15 mL of *n*-hexane. After filtration the remaining solid was washed with *n*-hexane (2 x 5 mL portions) and dried *in vacuo*. **Yield:** 880 mg (798 µmol, 81 %) of a pale yellow solid. Yellow crystals of [WCl_4(IDipp)$_2$] suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a saturated solution of the compound in benzene. $C_{54}H_{72}Cl_4N_4W$ (1102.84 g/mol): found (calcd.): C 58.89 (58.81), H 7.00 (6.58), N 5.10 (5.08). **Magnetic Moment (Evans-Method)[S1]:** μ_{eff} = 1.69 μ_B. **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = 0.72 (d, 24 H, $^3J_{HH}$ = 6.3 Hz, *i*PrCH_3), 1.46 (sept, 8 H, $^3J_{HH}$ = 6.3 Hz, *i*PrC*H*), 2.76 (s, 4 H, NC*H*C*H*N), 4.18 (d, 24 H, $^3J_{HH}$ = 5.9 Hz, *i*PrCH_3), 7.72 (t, 4 H, $^3J_{HH}$ = 7.6 Hz, CH_{para}), 8.39 (d, 8 H, $^3J_{HH}$ = 7.6 Hz, CH_{meta}), ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 25.6 (*i*PrCH_3), 35.2 (*i*PrCH_3), 55.3 (*i*Pr*C*H), 96.1 (N*C*H*C*HN), 110.3 (C_{ipso}), 129.9 (CH_{para}), 130.8 (CH_{meta}), 167.0 (C_{ortho}) ppm. **IR** (ATR[cm^{-1}]): 461 (m), 636 (m), 700 (s), 729 (m), 758 (vs), 802 (s), 937 (s), 1060 (m), 1100 (m), 1117 (m), 1181 (m), 1195 (m), 1234 (m), 1262 (m), 1330 (m), 1362 (m), 1391 (s), 1444 (s), 1464 (s), 1594 (w), 2867 (m), 2929 (m), 2964 (s).

Synthesis of [WCl_4(I*i*Pr^{Me})$_2$] 5: A solution of [WCl_4(SEt_2)$_2$] (300 mg, 593 µmol) and I*i*Pr^{Me} (214 mg, 1.19 mmol) in 10 mL toluene was stirred overnight whereby a yellow precipitate was formed. The product was filtered off, washed with *n*-hexane (2 x 5 mL portions) and dried *in vacuo*. **Yield:** 286 mg (416 µmol, 70 %) of a yellow solid. Dark yellow crystals of [WCl_4(I*i*Pr^{Me})$_2$] suitable for single-crystal X-ray diffraction were obtained by storing a saturated solution of the compound in chloroform at -30 °C. $C_{22}H_{40}Cl_4N_4W$ (686.23 g/mol): found (calcd.): C 38.83 (38.51), H 5.85 (5.88), N 7.78 (8.16). **^{1}H NMR** (400 MHz, thf-d_8, 298 K): δ = 6.25 (d, 24 H, $^3J_{HH}$ = 6.3 Hz, *i*PrCH_3), 13.62 (s, 12 H, CH_3), 21.36 (m_{br}, 4 H, *i*PrC*H*) ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, thf-d_8, 298 K): δ = -22.6 (CH_3, *via* HSQC), 57.7 (N*CC*N, *via* HMBC), 171.1 (*i*PrCH_3, *via* HSQC), 213.7 (*i*PrC*H*, *via* HMBC) ppm. **IR** (ATR[cm^{-1}]): 439 (m), 467 (w), 543 (m), 588 (w), 652 (m), 697 (w), 753 (m), 823 (w), 899 (s), 959 (w), 1068 (s), 1111 (m), 1142 (m), 1163 (m), 1197 (s), 1230 (m), 1319 (s), 1341 (vs), 1369 (vs), 1380 (m), 1443 (m), 1456 (m), 1551 (m), 1641 (m), 2879 (w), 2938 (m), 2977 (s), 3057 (w), 3129 (w).

General procedure for the synthesis of the *mono*-NHC complexes 6-8:

A solution of [MCl_4(SEt_2)$_2$] (M = Mo, W) and the corresponding *bis*-NHC complex (**1**-**3**) in toluene was heated at 100 °C for 24 h whereby the color changed from orange to red. All volatiles were removed *in vacuo* and the residue was suspended in 12 mL of *n*-hexane. After filtration the remaining solid was washed with *n*-hexane (2 x 7 mL portions) and dried *in vacuo*.

Synthesis of [$MoCl_4$(IMes)(SEt_2)] 6: A solution of [$MoCl_4$(SEt_2)$_2$] (350 mg, 837 µmol) and [$MoCl_4$(IMes)$_2$] (709 mg, 837 µmol) in 15 mL toluene was heated at 100 °C for 24 h whereby the color changed from orange to red. All volatiles were removed *in vacuo* and the residue was suspended in 12 mL of *n*-hexane. After filtration the remaining solid was washed with *n*-hexane (2 x 7 mL portions) and dried *in vacuo*. **Yield:** 708 mg (1.12 mmol, 67 %) of a red solid. Red crystals of [$MoCl_4$(IMes)(SEt_2)] suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a saturated solution of the compound in benzene. $C_{25}H_{35}Cl_4MoN_2S$ [632.37 g/mol] found (calcd.): C 47.06 (47.48), H 5.18 (5.42), N 4.52 (4.43). **Magnetic Moment (Evans-Method)[S1]:** $\mu_{eff} = 2.61\ \mu_B$. **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = -4.23 (s, 2 H, $NC\mathit{H}C\mathit{H}N$), 1.92 (s, 6 H, $C\mathit{H}_{3\mathrm{para}}$), 4.08 (s, 12 H, $C\mathit{H}_{3\mathrm{ortho}}$), 7.78 (s, 4 H, $C\mathit{H}_{\mathrm{meta}}$) ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 20.6 ($\mathit{C}H_{3\mathrm{para}}$), 42.5 ($\mathit{C}H_{3\mathrm{ortho}}$), 66.7 ($N\mathit{C}H\mathit{C}HN$), 80.1 ($\mathit{C}_{\mathrm{ipso}}$), 137.0 ($\mathit{C}_{\mathrm{para}}$), 143.5 ($\mathit{C}H_{\mathrm{meta}}$), 195.0 ($\mathit{C}_{\mathrm{ortho}}$) ppm. **IR** (ATR[$cm^{-1}$]): 426 (w), 477 (w), 501 (w), 577 (m), 592 (m), 643 (w), 676 (m), 700 (vs), 733 (s), 749 (vs), 765 (m), 856 (m), 909 (m), 928 (m), 979 (vs), 1000 (m), 1035 (m), 1056 (m), 1078 (m), 1104 (m), 1148 (m), 1164 (m), 1228 (s), 1263 (s), 1378 (s), 1393 (s), 1421 (m), 1450 (s), 1483 (s), 1557 (m), 1567 (m), 1607 (m), 1685 (w), 1744 (w), 2872 (m), 2927 (m), 2970 (m), 3139 (w), 3170 (w).

Synthesis of [$MoCl_4$(IDipp)(SEt_2)] 7: A solution of [$MoCl_4(SEt_2)_2$] (168 mg, 402 µmol) and [$MoCl_4(IDipp)_2$] (409 mg, 402 µmol) in 10 mL toluene was heated at 100 °C for 24 h whereby the color changed from orange to red. All volatiles were removed *in vacuo* and the residue was suspended in 8 mL of *n*-hexane. After filtration the remaining solid was washed with *n*-hexane (2 x 5 mL portions) and dried *in vacuo*. **Yield:** 431 mg (601 µmol, 75 %) of a red solid. Red crystals of [$MoCl_4$(IDipp)(SEt_2)] suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a saturated solution of the compound in benzene. $C_{31}H_{46}Cl_4MoN_2S$ [716.53 g/mol] found (calcd.): C 51.94 (51.96), H 6.76 (6.47), N 4.09 (3.91). **Magnetic Moment (Evans-Method)[S1]:** $\mu_{eff} = 2.24\ \mu_B$. **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = -2.92 (s, 2 H, $NC\mathit{H}C\mathit{H}N$), 1.31 (s_{br}, 12 H, *i*Pr$C\mathit{H}_3$), 1.97 (s_{br}, 12 H, *i*Pr$C\mathit{H}_3$), 5.42 (s_{br}, 4 H, *i*Pr$C\mathit{H}$), 6.75 (t, 4 H, $^3J_{HH}$ = 7.0 Hz, $C\mathit{H}_{\mathrm{para}}$), 8.63 (d, 4 H, $^3J_{HH}$ = 7.4 Hz, $C\mathit{H}_{\mathrm{meta}}$) ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 23.8 (*i*Pr$\mathit{C}H_3$), 39.7 (*i*Pr$\mathit{C}H_3$), 44.0 (*i*Pr$\mathit{C}H$), 83.3 ($N\mathit{C}H\mathit{C}HN$), 95.4 ($\mathit{C}_{\mathrm{ipso}}$), 131.0 ($\mathit{C}H_{\mathrm{meta}}$), 131.7 ($\mathit{C}H_{\mathrm{para}}$), 187.5 ($\mathit{C}_{\mathrm{ortho}}$) ppm. **IR** (ATR[$cm^{-1}$]): 422 (w), 460 (w), 552 (vw), 635 (w), 699 (m), 729 (m), 757 (vs), 802 (s), 938 (s), 975 (m), 1015 (m), 1060 (m), 1076 (w), 1104 (m), 1117 (m), 1150 (m), 1181 (m), 1199 (m), 1265 (m), 1328 (m), 1363 (s), 1385 (s), 1445 (s), 1463 (s), 1569 (w), 1596 (w), 2868 (m), 2929 (s), 2964 (s), 3068 (w), 3171 (w).

Synthesis of [WCl_4(IMes)(SEt_2)] 8: A solution of [$WCl_4(IMes)_2$] (368 mg, 394 µmol) and [$WCl_4(SEt_2)_2$] (199 mg, 394 µmol) in 15 mL toluene was heated at 100 °C for 24 h whereby the color changed from dark yellow to red. All volatiles were removed *in vacuo* and the residue was suspended in 8 mL of *n*-hexane. After filtration the remaining solid was washed with *n*-hexane (2 x 4 mL portions) and dried *in vacuo*. **Yield:** 489 mg (679 µmol, 86 %) of a red-brown solid. Red crystals of [WCl_4(IMes)(SEt_2)] suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a saturated solution of the compound in benzene. $C_{25}H_{34}Cl_4N_2SW$ (720.26 g/mol): found (calcd.) C 42.35 (41.69), H 4.62 (4.76), N 3.98 (3.89). **Magnetic Moment (Evans-Method)[S1]:** $\mu_{eff} = 1.73\ \mu_B$. **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = -15.5 (s_{br}, 4 H, $C\mathit{H}_{2\mathrm{SEt2}}$), -5.52 (s, 2 H, $NC\mathit{H}C\mathit{H}N$), 2.99 (s, 6 H, $C\mathit{H}_{3\mathrm{para}}$), 3.38 (s, 12 H, $C\mathit{H}_{3\mathrm{ortho}}$), 3.85 (t, 6 H, $^3J_{HH}$ = 7.3 Hz, $C\mathit{H}_{3\mathrm{SEt2}}$), 9.34 (s, 4 H, $C\mathit{H}_{\mathrm{meta}}$) ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 21.4 ($\mathit{C}H_{3\mathrm{para}}$), 33.4 ($\mathit{C}H_{3\mathrm{ortho}}$), 64.0 ($\mathit{C}_{\mathrm{ipso}}$), 75.8 ($N\mathit{C}H\mathit{C}HN$), 139.6 ($\mathit{C}_{\mathrm{para}}$), 141.9 ($\mathit{C}H_{\mathrm{meta}}$), 178.6 ($\mathit{C}H_{3\mathrm{SEt2}}$), 198.0 ($\mathit{C}_{\mathrm{ortho}}$) ppm. **IR** (ATR[$cm^{-1}$]): 424 (vw), 476 (w), 578 (m), 592 (w), 645 (w), 677 (vw), 701 (s), 734 (m), 751 (s), 766 (w), 776 (w), 854 (vs), 891 (vw), 927 (m), 978 (m), 1005 (m), 1034 (m), 1055 (m), 1075 (m), 1106 (m), 1164 (w), 1215 (m), 1262 (s), 1379 (s), 1391 (s), 1449 (s), 1483 (s), 1568 (w), 1607 (w), 2871 (w), 2928 (m), 2968 (m), 3139 (w), 3170 (w.).

Synthesis of [WCl$_4$(IDipp)(SEt$_2$)] 9: A solution of [WCl$_4$(IDipp)$_2$] (500 mg, 453 µmol) and [WCl$_4$(SEt$_2$)$_2$] (229 mg, 453 µmol) in 15 mL toluene was heated at 100 °C for 24 h whereby the color changed from dark yellow to red. All volatiles were removed and the remaining solid was dried *in vacuo*. **Yield:** 692 mg (861 µmol, 95 %) of a red solid. $C_{31}H_{46}Cl_4N_2SW$ [804.42 g/mol] found (calcd.): C 46.19 (46.29), H 5.75 (5.76), N 3.45 (3.48). **Magnetic Moment (Evans-Method)[S1]:** μ_{eff} = 1.69 μ_B. **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = -16.3 (s$_{br}$, 4 H, C*H*$_{2SEt2}$), -4.60 (s, 2 H, NC*H*C*H*N), 0.70 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, *i*PrC*H*$_3$), 2.23 (sept, 4 H, $^3J_{HH}$ = 6.8 Hz, *i*PrC*H*), 3.96 (t, 6 H, $^3J_{HH}$ = 7.3 Hz, C*H*$_{3SEt2}$), 5.37 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, *i*PrC*H*$_3$), 7.66 (t, 2 H, $^3J_{HH}$ = 7.7 Hz, C*H*$_{para}$), 9.87 (d, 4 H, $^3J_{HH}$ = 7.7 Hz, C*H*$_{meta}$) ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 27.3 (*i*Pr*C*H$_3$), 35.3 (*i*Pr*C*H$_3$), 36.6 (*i*Pr*C*H), 74.3 (*C*$_{ipso}$), 89.4 (N*C*H*C*HN), 132.2 (*C*H$_{para}$), 132.7 (*C*H$_{meta}$), 177.2 (*C*H$_{3SEt2}$), 189.6 (*C*$_{ortho}$) ppm. **IR** (ATR[cm^{-1}]): 461 (m), 635 (m), 701 (m), 729 (m), 758 (vs), 802 (vs), 937 (s), 975 (m), 1018 (m), 1060 (m), 1076 (m), 1104 (m), 1117 (m), 1181 (m), 1199 (s), 1260 (m), 1328 (m), 1363 (m), 1384 (s), 1464 (s), 1569 (w), 1596 (w), 2868 (m), 2929 (s), 2964 (vs), 3173 (w).

Synthesis of [MoCl$_4$(IMes)(cAAC^{Me})] 10: A solution of [MoCl$_4$(IMes)(SEt$_2$)] (70.0 mg, 111 µmol) and cAAC^{Me} (31.7 mg, 111 µmol) in 10 mL toluene was stirred overnight whereby the color changed from red to yellow. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. After filtration the remaining solid was washed with *n*-hexane (2 x 10 mL portions) and dried *in vacuo*. **Yield:** 56.0 mg (67.7 µmol, 61 %) of a yellow solid. $C_{41}H_{55}Cl_4N_3Mo$ (827.66 g/mol): found (calcd.) C 59.50 (59.50), H 6.98 (6.70), N 4.62 (5.08). **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = -0.86 (s, 6 H, C-C*H*$_{3,\ cAAC}$), -0.71 (s, 6 H, *i*PrC*H*$_3$), 1.33 (s, 6 H, C-C*H*$_{3,\ cAAC}$), 1.40 (s, 6 H, *i*PrC*H*$_3$), 1.98 (s, 6 H, C*H*$_{3para}$), 3.12 (s, 12 H, C*H*$_{3ortho}$), 3.73 (s$_{br}$, 2 H, *i*PrC*H*), 5.17 (s, 2 H, NC*H*C*H*N), 6.74 (m, 5 H, C*H*$_{meta,\ Mes,}$ C*H*$_{para,\ cAAC}$)), 8.93 (d, 2 H, $^3J_{HH}$ = 7.6 Hz, C*H*$_{meta,\ cAAC}$), 14.08 (s, 2 H, C*H*$_{2,\ cAAC}$) ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 12.4 (*i*Pr*C*H$_{3,\ cAAC}$), 20.9 (*C*H$_{3para,\ Mes}$), 30.3 (*i*Pr*C*H$_{3,\ cAAC}$), 48.8 (*C*H$_{3ortho,\ Mes}$), 58.0 (*i*Pr*C*H$_{,\ cAAC}$), 77.1 (C-*C*H$_{3,\ cAAC}$), 83.9 (N*C*H*C*HN), 116.8 (*C*$_{ipso,\ Mes}$), 119.3 (*C*$_{ipso,\ cAAC}$), 120.7 (*C*-CH$_{3,\ cAAC,}$ *via* HMBC), 129.3 (*C*H$_{meta,\ cAAC}$), 131.1 (*C*H$_{para,\ cAAC}$), 137.2 (*C*$_{para,\ Mes}$), 142.2 (*C*H$_{meta,\ Mes}$), 160.2 (*C*$_{ortho,\ Mes}$), 170.5 (*C*H$_{2,\ cAAC,}$ *via* HSQC), 173.3 (C-*C*H$_{3,\ cAAC}$, *via* HSQC), 174.7 (*C*$_{ortho,\ cAAC}$), 220.4 (*C*-CH$_{3,\ cAAC}$, *via* HMBC) ppm. **IR** (ATR[cm^{-1}]): 4.07 (w), 415 (w), 478 (w), 510 (m), 523 (w), 524 (w), 547 (m), 579 (w), 597 (w), 673 (w), 699 (w), 720 (w), 744 (w), 772 (m), 804 (vs), 819 (vs), 824 (s), 842 (w), 912 (vw), 915 (w), 1011 (m), 1034 (s), 1060 (s), 1085 (s), 1087 (s), 1118 (s), 1167 (w), 1231 (m), 1252 (m), 1345 (s), 1379 (m), 1387 (m), 1441 (s), 1452 (s), 1458 (s), 1495 (m), 1533 (m), 1587 (vs), 1680 (w), 2866 (m), 2911 (s), 2921 (s), 2961 (m).

Synthesis of [MoCl$_4$(IDipp)(cAAC^{Me})] 11: A solution of [MoCl$_4$(IDipp)(SEt$_2$)] (75.0 mg, 105 µmol) and cAAC^{Me} (29.9 mg, 105 µmol) in 10 mL toluene was stirred overnight whereby the color changed from red to yellow. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. After filtration the remaining solid was washed with *n*-hexane (2 x 10 mL portions) and dried *in vacuo*. **Yield:** 60.1 mg (65.9 µmol, 63 %) of a yellow solid. Yellow crystals of [MoCl$_4$(IDipp)(cAAC^{Me})] suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a saturated solution of the compound in benzene. $C_{47}H_{67}Cl_4N_3Mo$ (911.83 g/mol): found (calcd.) C 62.83 (61.91), 7.64 (7.41), N 4.61 (4.02). **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = -0.73 (s, 6 H, C-C*H*$_{3,\ \text{cAAC}}$), -0.60 (s, 6 H, *i*PrC*H*$_{3\text{cAAC}}$), 1.41 (s, 6 H, *i*PrC*H*$_{3\text{cAAC}}$), 1.58 (s$_{\text{br}}$, 12 H, *i*PrC*H*$_{3\text{Dipp}}$), 1.92 (s$_{\text{br}}$, 12 H, *i*PrC*H*$_{3\text{Dipp}}$), 1.96 (s, 6 H, C-C*H*$_{3,\ \text{cAAC}}$), 4.10 (s$_{\text{br}}$, 2 H, *i*PrC*H*$_{\text{cAAC}}$), 4.57 (s$_{\text{br}}$, 4 H, *i*PrCH$_{\text{Dipp}}$), 5.92 (s, 2 H, NC*H*C*H*N), 6.67 (t, 1 H, $^3J_{\text{HH}}$ = 7.7 Hz, C*H*$_{\text{para, cAAC}}$), 6.98 (d, 4 H, $^3J_{\text{HH}}$ = 7.6 Hz, C*H*$_{\text{meta, Dipp}}$), 7.34 (d, 2 H, C*H*$_{\text{para, Dipp}}$), 8.80 (d, 2 H, $^3J_{\text{HH}}$ = 7.7 Hz, C*H*$_{\text{meta, cAAC}}$), 13.16 (s, 2 H, C*H*$_{2,\ \text{cAAC}}$) ppm. **^{13}C{^{1}H} NMR** (125.8 MHz, C_6D_6, 298 K): δ = 13.1 (*i*Pr*C*H$_{3,\ \text{cAAC}}$), 30.7 (*i*Pr*C*H$_{3,\ \text{cAAC}}$), 32.0 (*i*Pr*C*H$_{3,\ \text{Dipp}}$), 38.9 (*i*Pr*C*H$_{3,\ \text{Dipp}}$), 39.1 (C-*C*H$_{3,\ \text{cAAC}}$), 60.7 (*i*Pr*C*H$_{,\ \text{Dipp}}$), 60.8 (*i*Pr*C*H$_{,\ \text{cAAC}}$), 78.0 (C-*C*H$_{3,\ \text{cAAC}}$), 92.2 (N*C*H*C*HN), 103.0 (*C*$_{\text{ipso, cAAC}}$), 124.2 (*C*$_{\text{ipso, Dipp}}$), 130.0 (*C*H$_{\text{meta, cAAC}}$), 131.1 (*C*H$_{\text{para, cAAC}}$), 131.8 (*C*H$_{\text{para, Dipp}}$), 134.7 (*C*H$_{\text{meta, Dipp}}$), 145.7 (*C*H$_{2,\ \text{cAAC,}}$ *via* HSQC), 162.9 (*C*$_{\text{ortho, Dipp}}$), 166.4 (*C*-CH$_{3,\ \text{cAAC}}$), 174.8 (*C*$_{\text{ortho, cAAC}}$) ppm. **IR** (ATR[cm^{-1}]): 404 (w), 413 (m), 419 (w), 428 (vw), 440 (vw), 474 (w), 496 (w), 505 (vw), 570 (w), 605 (w), 633 (w), 698 (m), 730 (vs), 755 (vs), 768 (s), 800 (vs), 937 (m), 1009 (w), 1060 (w), 1099 (w), 1117 (w), 1181 (w), 1261 (w), 1330 (m), 1362 (s), 1384 (s), 1456 (s), 1593 (w), 2866 (m), 2928 (m), 2965 (m).

Synthesis of [WCl_4(IMes)(cAAC$^{\text{Me}}$)] 12: A solution of [WCl_4(IMes)(SEt_2)] (70.0 mg, 97.0 µmol) and cAAC$^{\text{Me}}$ (27.8 mg, 97.0 µmol) in 10 mL toluene was stirred overnight whereby the color changed from red to yellow. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. After filtration the remaining solid was washed with *n*-hexane (2 x 5 mL portions) and dried *in vacuo*. **Yield:** 51.7 mg (56.5 µmol, 58 %) of a yellow solid. $C_{41}H_{55}Cl_4N_3W$ (934.51 g/mol): found (calcd.): C 53.96 (53.79), H 5.97 (6.06), N: 4.20 (4.59). **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = -2.18 (s, 6 H, C-C*H*$_{3,\ \text{cAAC}}$), 0.43 (s, 6 H, C-C*H*$_{3,\ \text{cAAC}}$), 1.17 (d, 6 H, $^3J_{\text{HH}}$ = 6.4 Hz, *i*PrC*H*$_3$), 2.25 (sept, 2 H, $^3J_{\text{HH}}$ = 6.4 Hz, *i*PrC*H*), 2.53 (s, 6 H, C*H*$_{3\text{para}}$), 2.74 (s, 12 H, C*H*$_{3\text{ortho}}$), 2.80 (s, 2 H, NC*H*C*H*N), 6.36 (d, 6 H, $^3J_{\text{HH}}$ = 6.1 Hz, *i*PrC*H*$_3$), 7.34 (t, 1 H, $^3J_{\text{HH}}$ = 7.6 Hz, C*H*$_{\text{para, cAAC}}$), 7.73 (s, 4 H, C*H*$_{\text{meta, Mes}}$), 8.45 (s, 2 H, C*H*$_{2,\ \text{cAAC}}$), 9.99 (d, 2 H, $^3J_{\text{HH}}$ = 7.7 Hz, C*H*$_{\text{meta, cAAC}}$) ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 21.4 (*C*H$_{3\text{para, Mes}}$), 23.1 (*i*Pr*C*H$_{3,\ \text{cAAC}}$), 29.9 (*i*Pr*C*H$_{3,\ \text{cAAC}}$), 40.3 (*C*H$_{3\text{ortho, Mes}}$), 50.9 (*i*Pr*C*H$_{,\ \text{cAAC}}$), 90.7 (C-*C*H$_{3,\ \text{cAAC}}$), 90.7 (*C*$_{\text{ipso, cAAC}}$), 95.5 (N*C*H*C*HN), 107.3 (*C*$_{\text{ipso, Mes}}$), 130.7 (*C*H$_{\text{para, cAAC}}$), 132.0 (*C*H$_{\text{meta, cAAC}}$), 138.1 (*C*$_{\text{para, Mes}}$), 140.4 (*C*H$_{\text{meta, Mes}}$), 154.7 (*C*H$_{2,\ \text{cAAC}}$), 161.5 (*C*$_{\text{ortho, Mes}}$), 173.3 (C-*C*H$_{3,\ \text{cAAC}}$, *via* HSQC), 186.6 (*C*$_{\text{ortho, cAAC}}$), 191.3 (*C*-CH$_{3,\ \text{cAAC}}$, *via* HMBC), 273.9 (*C*-CH$_{3,\ \text{cAAC}}$) ppm. **IR** (ATR[cm^{-1}]): 423 (vw), 426 (w), 434 (w), 438 (w), 441 (w), 450 (w), 464 (w), 450 (w), 452 (w), 468 (w), 485 (w), 499 (w), 502 (w), 511 (w), 518 (w), 530 (w), 550 (w), 569 (w), 594 (m), 635 (w), 645 (w), 678 (w), 701 (s), 735 (m), 747 (s), 773 (w), 805 (s), 849 (vs), 881 (w), 928 (m), 966 (m), 1018 (m), 1035 (m), 1051 (m), 1065 (m), 1102 (w), 1129 (w), 1164 (w), 1193 (w), 1213 (m), 1232 (m), 1261 (m), 1293 (s), 1351 (m), 1371 (m), 1386 (s), 1451 (s), 1478 (s), 1542 (m), 1569 (m), 1616 (w), 1627 (w), 2868 (m), 2918 (m), 2967 (m).

Synthesis of [WCl_4(IDipp)(cAAC$^{\text{Me}}$)] 13: A solution of [WCl_4(IDipp)(SEt_2)] (75.0 mg, 93.2 µmol) and cAAC$^{\text{Me}}$ (26.6 mg, 93.2 µmol) in 10 mL toluene was stirred overnight whereby the color changed from red to yellow. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. After filtration the remaining solid was washed with *n*-hexane (2 x 10 mL portions) and dried *in vacuo*. **Yield:** 47.5 mg (47.5 µmol, 51 %) of a yellow solid. Yellow crystals of [WCl_4(IDipp)(cAAC$^{\text{Me}}$)] suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a saturated solution of the compound in benzene. $C_{47}H_{67}Cl_4N_3W$ (999.71 g/mol): found (calcd.) C 56.10 (56.47), H 6.70 (6.76), N 3.91 (4.20). **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = -2.28 (s, 6 H, C-C*H*$_{3,\ \text{cAAC}}$), 0.76 (d, 12 H, $^3J_{HH}$ = 6.0 Hz, *i*PrC*H*$_{3,\ \text{Dipp}}$), 1.03 (d, 6 H, $^3J_{HH}$ = 5.8 Hz, *i*PrC*H*$_{3,\ \text{cAAC}}$), 1.13 (s, 6 H, C-C*H*$_{3,\ \text{cAAC}}$), 1.77 (m, 6 H, *i*PrC*H*$_{\text{cAAC, Dipp}}$), 3.30 (s, 2 H, NC*H*C*H*N), 4.38 (d, 12 H, $^3J_{HH}$ = 5.4 Hz, *i*PrC*H*$_{3,\ \text{Dipp}}$), 6.31 (s, 6 H, C-C*H*$_{3,\ \text{cAAC}}$), 7.16 (m, 1 H C*H*$_{\text{para, cAAC,}}$ *via* HSQC), 7.57 (t, 2 H, $^3J_{HH}$ = 7.5 Hz, C*H*$_{\text{para, Dipp}}$), 7.76 (s, 2 H, C*H*$_{2,\ \text{cAAC}}$), 8.04 (d, 4 H, $^3J_{HH}$ = 7.3 Hz, C*H*$_{\text{meta, Dipp}}$), 9.82 (d, 2 H, $^3J_{HH}$ = 7.4 Hz, C*H*$_{\text{meta, cAAC}}$) ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 24.8 (*i*Pr*C*H$_{3,\ \text{cAAC}}$), 29.0 (*i*Pr*C*H$_{3,\ \text{Dipp}}$), 29.8 (*i*Pr*C*H$_{3,\ \text{cAAC}}$), 35.3 (*i*Pr*C*H$_{3,\ \text{Dipp}}$), 51.7 (*i*Pr*C*H$_{,\ \text{Dipp}}$), 53.3 (*i*Pr*C*H$_{,\ \text{cAAC}}$), 76.0 (*C*$_{\text{ipso, cAAC}}$), 91.4 (C-*C*H$_{3,\ \text{cAAC}}$), 101.5 (N*C*H*C*HN), 114.5 (*C*$_{\text{ipso, Dipp}}$), 129.8 (*C*H$_{\text{para, Dipp}}$), 130.8 (*C*H$_{\text{para, cAAC}}$), 132.1 (*C*H$_{\text{meta, cAAC}}$), 132.6 (*C*H$_{\text{meta, Dipp}}$), 134.5 (*C*-CH$_{3,\ \text{cAAC}}$, *via* HMBC) 135.6 (*C*H$_{2,\ \text{cAAC}}$), 163.8 (*C*$_{\text{ortho, Dipp}}$), 178.0 (C-*C*H$_{3,\ \text{cAAC}}$, *via* HSQC) 187.6 (*C*$_{\text{ortho, cAAC}}$), 217.3 (*C*-CH$_{3,\ \text{cAAC}}$, *via* HMBC) ppm. **IR** (ATR[cm^{-1}]): 417 (w), 423 (w), 429 (w), 441 (w), 461 (vw), 481 (w), 494 (w), 556 (w), 567 (w), 608 (w), 636 (w), 702 (m), 730 (w), 754 (vs), 758 (vs), 770 (s), 801 (s), 883 (w), 936 (m), 962 (w), 1061 (w) 1102 (w), 1118 (w), 1162 (vw), 1181 (w), 1198 (w), 1235 (vw), 1262 (w), 1330 (w), 1362 (w), 1372 (w), 1391 (m), 1443 (m), 1456 (m), 1464 (m), 1571 (vw), 1594 (vw), 2868 (w), 2928 (w), 2962 (m), 3063 (vw).

Synthesis of [WCl$_4$(IMes)(PMe$_3$)] 14: To a solution of [WCl$_4$(IMes)(SEt$_2$)] (80.0 mg, 111 µmol) in 5 mL toluene was added trimethylphosphine (8.44 mg, 11.3 µL, 111 µmol). The solution was stirred overnight whereby the color changed from red to yellow. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. After filtration the remaining solid was washed with *n*-hexane (2 x 5 mL portions) and dried *in vacuo*. **Yield:** 48.6 mg (68.8 µmol, 62 %) of a pale yellow solid. $C_{24}H_{33}Cl_4N_2WP$ (706.16 g/mol): found (calcd.) C 40.98 (40.82), H 4.64 (4.71), N 3.96 (3.97). **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = -24.7 (s, 9 H, PC*H*$_3$), -4.02 (s, 2 H, NC*H*C*H*N), 3.00 (s, 6 H, C*H*$_{3\text{para}}$), 3.05 (s, 12 H, C*H*$_{3\text{ortho}}$), 8.87 (s, 4 H, C*H*$_{\text{meta}}$) ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 21.5 (*C*H$_{3\text{para}}$), 34.8 (*C*H$_{3\text{ortho}}$), 78.1 (*C*$_{\text{ipso}}$), 81.9 (N*C*H*C*HN), 110.0 (P*C*H$_3$, *via* HSQC), 139.5 (*C*$_{\text{para}}$), 142.2 (*C*H$_{\text{meta}}$), 185.9 (*C*$_{\text{ortho}}$) ppm. **^{31}P{^{1}H} NMR** (162.1 MHz, C_6D_6, 298 K) not observed. **IR** (ATR[cm^{-1}]): 412 (vw), 448 (vw), 497 (vw), 573 (w), 579 (w), 592 (vw), 672 (w), 699 (s), 734 (m), 742 (s), 748 (m), 813 (w), 861 (s), 928 (m), 959 (vs), 963 (vs), 1036 (w), 1076 (vw), 1111 (w), 1164 (w), 1218 (w), 1263 (m), 1281 (w), 1301 (w), 1378 (w), 1394 (w), 1429 (w), 1485 (m), 1538 (w), 1567 (w), 1606 (w), 2912 (w), 3130 (w), 3165 (w).

Synthesis of [WCl$_4$(IMes)(PPh$_3$)] 15: A solution of [WCl$_4$(IMes)(SEt$_2$)] (80.0 mg, 111 µmol) and triphenylphosphine (29.1 mg, 111 µmol) in 10 mL toluene was stirred overnight whereby the color changed from red to yellow. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. After filtration the remaining solid was washed with *n*-hexane (2 x 5 mL portions) and dried *in vacuo*. **Yield:** 45.9 mg (51.4 µmol, 46 %) of a yellow solid. Yellow crystals of [WCl$_4$(IMes)(PPh$_3$)] suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a saturated solution of the compound in benzene. $C_{39}H_{39}Cl_4N_2WP$ (892.37 g/mol): found (calcd.) C 50.19 (52.49), H 4.43 (4.41), N 2.74 (3.14). **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = -3.46 (s, 2 H, NC*H*C*H*N), 2.80 (s, 6 H, C*H*$_{3\text{para}}$), 3.00 (s, 12 H, C*H*$_{3\text{ortho}}$), 7.05 (m, 9 H, C*H*$_{\text{arom., PPh3}}$), 8.76 (s, 4 H, C*H*$_{\text{meta}}$), 10.76 (m, 6 H, C*H*$_{\text{arom., PPh3}}$) ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 21.7 (*C*H$_{3\text{para}}$), 35.0 (*C*H$_{3\text{ortho}}$), 85.1 (*C*$_{\text{ipso}}$), 85.9 (N*C*H*C*HN), 91.8 (*C*$_{\text{ipso, PPh3}}$, *via* HMBC) 119.2 (*C*H$_{\text{arom., PPh3}}$), 121.6

(*C*H$_{\text{arom., PPh3}}$), 128.9 (*C*H$_{\text{arom., PPh3}}$), 132.4 (*C*H$_{\text{arom., PPh3}}$), 138.8 (*C*$_{\text{para, Mes}}$), 141.6 (*C*H$_{\text{meta, Mes}}$), 179.7 (*C*$_{\text{ortho, Mes}}$) ppm. **^{31}P{^{1}H} NMR** (162.1 MHz, C_6D_6, 298 K) not observed. **IR** (ATR[cm^{-1}]): 417 (w), 430 (w), 445 (m), 491 (s), 507 (s), 522 (vs), 581 (w), 592 (vw), 619 (w), 691 (s), 701 (s), 740 (m), 852 (s), 928 (w), 961 (w), 1005 (w), 1029 (w), 1090 (m), 1161 (w), 1188 (vw), 1217 (w), 1263 (m), 1379 (w), 1392 (m), 1435 (s), 1456 (w), 1483 (m), 1571 (w), 1609 (vw), 2857 (w), 2920 (w), 2954 (w).

Synthesis of [WCl$_4$(IDipp)(PMe$_3$)] 16: To a solution of [WCl$_4$(IDipp)(SEt$_2$)] (75.0 mg, 93.2 µmol) in 5 mL toluene was added trimethylphosphine (7.09 mg, 9.60 µL, 93.2 µmol). The solution was stirred overnight whereby the color changed from red to yellow. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. After filtration the remaining solid was washed with *n*-hexane (2 x 5 mL portions) and dried *in vacuo*. **Yield:** 43.2 mg (54.7 µmol, 58 %) of a yellow solid. Yellow crystals of [WCl$_4$(IDipp)(PMe$_3$)] suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a saturated solution of the compound in toluene. $C_{30}H_{45}Cl_4N_2WP$ (790.32 g/mol): found (calcd.) C 44.83 (45.59), H 5.71 (5.74), N 3.22 (3.54). **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = -25.16 (s, 9 H, P*C*H$_3$), -3.25 (s, 2 H, NC*H*C*H*N), 0.57 (d, 12 H, $^{3}J_{\text{HH}}$ = 6.8 Hz, *i*PrC*H*$_3$), 1.63 (sept, 4 H, $^{3}J_{\text{HH}}$ = 6.8 Hz, *i*PrC*H*), 5.40 (d, 12 H, $^{3}J_{\text{HH}}$ = 6.4 Hz, *i*PrC*H*$_3$), 7.79 (t, 2 H, $^{3}J_{\text{HH}}$ = 7.6 Hz, C*H*$_{\text{para}}$), 9.46 (d, 4 H, $^{3}J_{\text{HH}}$ = 7.6 Hz, C*H*$_{\text{meta}}$) ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 29.4 (*i*Pr*C*H$_3$), 33.8 (*i*Pr*C*H$_3$), 36.1 (*i*Pr*C*H), 87.8 (*C*$_{\text{ipso}}$), 94.4 (N*C*H*C*HN), 115.5 (P*C*H$_3$, *via* HSQC), 132.5 (*C*H$_{\text{para}}$), 132.9 (*C*H$_{\text{meta}}$), 180.6 (*C*$_{\text{ortho}}$) ppm. **^{31}P{^{1}H} NMR** (162.1 MHz, C_6D_6, 298 K) not observed. **IR** (ATR[cm^{-1}]): 412 (w), 417 (w), 425 (w), 440 (w), 459 (w), 635 (w), 678 (vw), 698 (s), 730 (m), 740 (vs), 749 (m), 760 (s), 770 (w), 803 (s), 846 (vw), 959 (m), 966 (s), 1044 (vw), 1062 (w), 1100 (vw), 1119 (w), 1182 (w), 1200 (w), 1239 (w), 1282 (m), 1301 (w), 1328 (m), 1364 (w), 1384 (w), 1391 (w), 1416 (w), 1442 (m), 1466 (m), 1477 (w), 1569 (vw), 2869 (w), 2928 (w), 2964 (m), 3138 (vw).

Synthesis of [WCl$_4$(IDipp)(PPh$_3$)] 17: A solution of [WCl$_4$(IDipp)(SEt$_2$)] (75.0 mg, 93.2 µmol) and triphenylphosphine (24.5 mg, 93.2 µmol) in 10 mL toluene was stirred overnight whereby the color changed from red to yellow. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. After filtration the remaining solid was washed with *n*-hexane (2 x 5 mL portions) and dried *in vacuo*. **Yield:** 62.0 mg (63.4 µmol, 68 %) of a yellow solid. $C_{45}H_{51}Cl_4N_2WP$ (976.53 g/mol): found (calcd.) C 54.67 (55.35), H 5.35 (5.26), N 2.87 (2.87). **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = -2.88 (s, 2 H, NC*H*C*H*N), 0.66 (d, 12 H, $^{3}J_{\text{HH}}$ = 6.7 Hz, *i*PrC*H*$_3$), 1.64 (sept, 4 H, $^{3}J_{\text{HH}}$ = 6.8 Hz, *i*PrC*H*), 6.41 (d, 12 H, $^{3}J_{\text{HH}}$ = 6.4 Hz, *i*PrC*H*$_3$), 7.09 (m, 9 H, C*H*$_{\text{arom., PPh3}}$), 7.69 (t, 2 H, $^{3}J_{\text{HH}}$ = 7.6 Hz, C*H*$_{\text{para}}$), 9.42 (d, 4 H, $^{3}J_{\text{HH}}$ = 7.6 Hz, C*H*$_{\text{meta}}$), 10.42 (d, 6 H, $^{3}J_{\text{HH}}$ = 7.3 Hz, C*H*$_{\text{arom., PPh3}}$) ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 27.3 (*i*Pr*C*H$_3$), 36.2 (*i*Pr*C*H$_3$), 41.7 (*i*Pr*C*H), 93.1 (*C*$_{\text{ipso}}$), 96.9 (N*C*H*C*HN), 106.6 (*C*$_{\text{ipso, PPh3}}$, *via* HMBC), 121.2 (*C*H$_{\text{arom., PPh3}}$), 121.7 (*C*H$_{\text{arom., PPh3}}$), 131.8 (*C*H$_{\text{meta, Dipp}}$), 132.4 (*C*H$_{\text{para, Dipp}}$), 132.7 (*C*H$_{\text{arom., PPh3}}$), 179.8 (*C*$_{\text{ortho}}$) ppm. **^{31}P{^{1}H} NMR** (162.1 MHz, C_6D_6, 298 K) not observed. **IR** (ATR[cm^{-1}]): 407 (w), 416 (w), 421 (w), 425 (w), 428 (w), 431 (w), 437 (w), 444 (w), 447 (w), 452 (w), 462 (w), 470 (s), 474 (s), 490 (s), 504 (vs), 525 (w), 617 (w), 638 (w), 694 (vs), 742 (vs), 748 (vs), 759 (m), 763 (s), 803 (m), 810 (w), 847 (w), 937 (w), 962 (w), 998 (m), 1019 (w), 1030 (w), 1060 (w), 1089 (w), 1117 (w), 1182 (vw), 1267 (w), 1329 (w), 1362 (w), 1383 (w), 1394 (w), 1434 (m), 1439 (m), 1456 (m), 1482 (w), 1549 (w), 1575 (w), 1616 (w), 2864 (w), 2929 (w), 2960 (m).

Synthesis of [MoCl$_4$(IMes)(Py)] 18: To a solution of [MoCl$_4$(IMes)(SEt$_2$)] (75 mg, 119 µmol) in 10 mL toluene was added pyridine (9.42 mg, 9.60 µL, 119 µmol). The solution was stirred overnight whereby the color changed from red to yellow. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. After filtration the remaining solid was washed with *n*-hexane (2 x 7 mL portions) and dried *in vacuo*. **Yield:** 54.8 mg (88.2 µmol, 74 %) of a yellow solid. Yellow crystals of [MoCl$_4$(IMes)(Py)] suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a saturated solution of the compound in benzene. $C_{26}H_{29}Cl_4N_3Mo$ (621.29 g/mol): found (calcd.) C 50.56 (50.26), H 4.74 (4.71), N 6.67 (6.76). **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = -28.73 (s_{br}, 2 H, C$H_{\text{ortho, Py}}$), -17.30 (s, 1 H, C$H_{\text{para, Py}}$), -4.34 (s, 2 H, NC*H*C*H*N), 1.90 (s, 6 H, C$H_{3\text{para}}$), 4.31 (s, 12 H, C$H_{3\text{ortho}}$), 7.82 (s, 4 H, CH_{meta}), 19.50 (s, 2 H, C$H_{\text{meta, Py}}$) ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 20.7 (CH$_{3\text{para}}$), 44.2 (CH$_{3\text{ortho}}$), 59.1 (N*C*H*C*HN), 77.5 (C_{ipso}), 136.5 (C_{para}), 142.5 (CH$_{\text{meta}}$), 199.0 (C_{ortho}) ppm. Despite several attempts with measurements from -200 – 400 ppm, no signals for the pyridine carbon atoms were detected. **IR** (ATR[cm^{-1}]): 404 (w), 410 (w), 413 (w), 416 (w), 419 (w), 423 (w), 429 (w), 433 (w), 442 (w), 447 (w), 477 (w), 501 (w), 525 (w), 546 (w), 575 (w), 580 (w), 591 (w), 609 (m), 638 (m), 679 (m), 693 (vs), 735 (w), 749 (w), 756 (s), 765 (s), 802 (w), 855 (s), 918 (w), 955 (m), 975 (w), 1000 (m), 1013 (m), 1042 (m), 1071 (m), 1158 (w), 1221 (s), 1266 (m), 1380 (w), 1396 (w), 1446 (s), 1485 (m), 1530 (w), 1575 (w), 1605 (m), 1634 (w), 1700 (vw), 2920 (w), 3108 (w), 3173 (w).

Synthesis of [MoCl$_4$(IMes)(DMAP)] 19: A solution of [WCl$_4$(IMes)(SEt$_2$)] (75.0 mg, 119 µmol) and 4-Dimethylaminopyridine (DMAP) (14.5 mg, 119 µmol) in 10 mL toluene was stirred overnight whereby the color changed from red to yellow. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. After filtration the remaining solid was washed with *n*-hexane (2 x 5 mL portions) and dried *in vacuo*. **Yield:** 54.4 mg (81.3 µmol, 69 %) of a yellow solid. $C_{28}H_{34}Cl_4N_4Mo$ (664.36 g/mol): found (calcd.) C 50.33 (50.62), H 5.90 (5.16), N 7.08 (8.43). **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = -24.78 (s_{br}, 2 H, C$H_{\text{ortho, DMAP}}$), -3.14 (s, 2 H, NC*H*C*H*N), 1.84 (s, 6 H, C$H_{3\text{para}}$), 4.16 (s, 12 H, C$H_{3\text{ortho}}$), 7.70 (s, 4 H, CH_{meta}), 14.20 (s_{br}, 2 H, C$H_{\text{meta, DMAP}}$), 18.87 (s, 6 H, N(CH_3)$_2$) ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 20.7 (CH$_{3\text{para}}$), 41.8 (CH$_{3\text{ortho}}$), 61.6 (N*C*H*C*HN), 83.0 (C_{ipso}), 136.2 (C_{para}), 141.3 (CH$_{\text{meta}}$), 193.8 (C_{ortho}) ppm. Despite several attempts with measurements from -200 – 400 ppm, no signals for the DMAP carbon atoms were detected. **IR** (ATR[cm^{-1}]): 404 (w), 410 (w), 413 (w), 418 (w), 421 (w), 428 (w), 432 (w), 448 (w), 465 (w), 477 (w), 486 (w), 526 (s), 549 (w), 579 (w), 593 (w), 646 (w), 700 (m), 733 (m), 752 (m), 761 (m), 771 (s), 851 (s), 928 (m), 950 (s), 954 (s), 1035 (vs), 1065 (w), 1108 (s), 1232 (vs), 1265 (w), 1349 (w), 1391 (s), 1436 (s), 1443 (s), 1484 (s), 1533 (m), 1544 (m), 1557 (s), 1564 (s), 1616 (s), 1627 (vs), 1695 (vw), 1699 (vw), 1927 (vw), 1976 (vw), 2049 (vw), 2151 (vw), 2162 (vw), 2878 (w), 2921 (m), 2969 (w).

Synthesis of [MoCl$_4$(IDipp)(Py)] 20: To a solution of [MoCl$_4$(IDipp)(SEt$_2$)] (75 mg, 105 µmol) in 10 mL toluene was added pyridine (8.28 mg, 8.43 µL, 105 µmol). The solution was stirred overnight whereby the color changed from red to yellow. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. After filtration the remaining solid was washed with *n*-hexane (2 x 7 mL portions) and dried *in vacuo*. **Yield:** 52.6 mg (74.6 µmol, 71 %) of a yellow solid. $C_{32}H_{41}Cl_4N_3Mo$ (705.45 g/mol): found (calcd.) C 54.19 (54.48), H 5.87 (5.86), N 5.43 (5.96). **^{1}H NMR**

(400 MHz, C_6D_6, 298 K): δ = -29.50 (s$_{\text{br}}$, 2 H, C*H*$_{\text{ortho, Py}}$), -17.96 (s, 1 H, C*H*$_{\text{para, Py}}$), -2.94 (s, 2 H, NC*H*C*H*N), 1.26 (*i*PrC*H*$_3$), 1.95 (*i*PrC*H*$_3$), 5.46 (s$_{\text{br}}$, 4 H, *i*PrC*H*), 6.75 (t, 2 H, $^3J_{\text{HH}}$ = 7.4 Hz, C*H*$_{\text{para}}$), 8.62 (d, 4 H, $^3J_{\text{HH}}$ = 7.4 Hz, C*H*$_{\text{meta}}$), 19.71 (C*H*$_{\text{meta, Py}}$) ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 22.9 (*i*Pr*C*H$_3$), 39.1 (*i*Pr*C*H$_3$), 42.5 (*i*Pr*C*H), 78.4 (N*C*H*C*HN), 94.6 (*C*$_{\text{ipso}}$), 130.4 (*C*H$_{\text{meta}}$), 131.4 (*C*H$_{\text{para}}$), 186.4 (*C*$_{\text{ortho}}$) ppm. Despite several attempts with measurements from -200 – 400 ppm, no signals for the pyridine carbon atoms were detected. **IR** (ATR[cm^{-1}]): 404 (w), 408 (w), 419 (w), 426 (w), 436 (w), 442 (w), 446 (vw), 453 (w), 462 (w), 473 (vw), 496 (w), 544 (m), 609 (s), 636 (s), 678 (s), 691 (vs), 803 (s), 937 (w), 974 (w), 1012 (m), 1043 (m), 1060 (w), 1071 (w), 1117 (w), 1181 (w), 1199 (w), 1222 (m), 1257 (w), 1328 (w), 1362 (m), 1386 (m), 1446 (m), 1464 (m), 1486 (w), 1531 (w), 1605 (w), 2868 (w), 2928 (m), 2964 (m), 3070 (w).

Synthesis of [MoCl$_4$(IDipp)(DMAP)] 21: A solution of [MoCl$_4$(IDipp)(SEt$_2$)] (75.0 mg, 106 µmol) and 4-Dimethylaminopyridine (DMAP) (13.0 mg, 106 µmol) in 10 mL toluene was stirred overnight whereby the color changed from red to yellow. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. After filtration the remaining solid was washed with *n*-hexane (2 x 5 mL portions) and dried *in vacuo*. **Yield:** 51.0 mg (68.1 µmol, 65 %) of a yellow solid. **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = -25.66 (s$_{\text{br}}$, 2 H, C*H*$_{\text{ortho, DMAP}}$), -1.97 (s, 2 H, NC*H*C*H*N), 1.29 (s, 12 H, *i*PrC*H*$_3$), 1.92 (s, 12 H, *i*PrC*H*$_3$), 5.47 (s$_{\text{br}}$, 4 H, *i*PrC*H*), 6.76 (s$_{\text{br}}$, 2 H, C*H*$_{\text{para}}$), 8.52 (d, 4 H, $^3J_{\text{HH}}$ = 6.4 Hz, C*H*$_{\text{meta}}$), 14.25 (s, 2 H, C*H*$_{\text{meta, DMAP}}$), 19.28 (s, 6 H, N(C*H*$_3$)$_2$) ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 22.7 (*i*Pr*C*H$_3$), 38.2 (*i*Pr*C*H$_3$), 41.2 (*i*Pr*C*H), 78.6 (N*C*H*C*HN), 98.6 (*C*$_{\text{ipso}}$), 129.6 (*C*H$_{\text{meta}}$), 131.1 (*C*H$_{\text{para}}$), 184.5 (*C*$_{\text{ortho}}$) ppm. Despite several attempts with measurements from -200 – 400 ppm, no signals for the DMAP carbon atoms were detected. $C_{34}H_{46}Cl_4N_4Mo$ (748.52 g/mol): found (calcd.) C 54.98 (54.56), H 6.34 (6.19), N 7.26 (7.49). **IR** (ATR[cm^{-1}]): 406 (w), 409 (w), 414 (w), 416 (w), 420 (w), 431 (w), 435 (w), 439 (vw), 444 (vw), 449 (w), 462 (vw), 481 (w), 488 (w), 502 (vw), 508 (w), 529 (w), 546 (m), 587 (w), 635 (w), 663 (w), 699 (w), 730 (w), 758 (s), 802 (s), 937 (w), 950 (w), 1014 (vs), 1065 (m), 1117 (w), 1180 (w), 1234 (s), 1262 (w), 1329 (w), 1350 (w), 1362 (w), 1385 (m), 1443 (m), 1464 (m), 1538 (m), 1623 (s), 2866 (w), 2927 (m), 2962 (m).

Synthesis of [WCl$_4$(IMes)(Py)] 22: To a solution of [WCl$_4$(IMes)(SEt$_2$)] (80.0 mg, 111 µmol) in 5 mL toluene was added pyridine (8.80 mg, 8.95 µL, 111 µmol). The solution was stirred overnight whereby the color changed from red to yellow. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. After filtration the remaining solid was washed with *n*-hexane (2 x 5 mL portions) and dried *in vacuo*. **Yield:** 51.5 mg (72.6 µmol, 65 %) of a yellow solid. Yellow crystals of [WCl$_4$(IMes)(Py)] suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a saturated solution of the compound in benzene. $C_{26}H_{29}Cl_4N_3W$ (709.18 g/mol): found (calcd.) C 44.46 (44.03), H 4.01 (4.12), N 5.76 (5.93). **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = -32.60 (d, 2 H, $^3J_{\text{HH}}$ = 5.4 Hz, C*H*$_{\text{ortho, Py}}$), -24.22 (t, 1 H, $^3J_{\text{HH}}$ = 7.3 Hz, C*H*$_{\text{para, Py}}$), -5.31 (s, 2 H, NC*H*C*H*N), 2.99 (s, 6 H, C*H*$_{3\text{para}}$), 3.53 (s, 12 H, C*H*$_{3\text{ortho}}$), 9.34 (s, 4 H, C*H*$_{\text{meta}}$), 15.92 (t, 2 H, $^3J_{\text{HH}}$ = 6.5 Hz, C*H*$_{\text{meta, Py}}$) ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 21.4 (*C*H$_{3\text{para}}$), 34.1 (*C*H$_{3\text{ortho}}$), 62.5 (*C*$_{\text{ipso}}$), 70.6 (N*C*H*C*HN), 139.3 (*C*$_{\text{para}}$), 140.8 (*C*H$_{\text{meta}}$), 202.2 (*C*$_{\text{ortho}}$) ppm. Despite several attempts with measurements from -200 – 400 ppm, no signals for the pyridine carbon atoms were detected. **IR** (ATR[cm^{-1}]): 444 (m), 465 (w), 574 (w), 580 (w), 590 (w), 639 (m), 693 (vs), 702 (m), 735 (m), 755 (s), 766 (s), 855 (s), 862 (m), 875 (w), 928 (w), 961 (w), 967 (m), 981 (m), 1013 (w), 1034 (w), 1045 (m), 1071 (w), 1160 (w), 1221 (m), 1265 (m), 1380 (w), 1395 (m), 1436 (w), 1446 (s), 1456 (w), 1464 (w), 1487 (m), 1575 (w), 1606 (m), 2918 (w), 3113 (w), 3141 (w), 3176 (w).

Synthesis of [WCl_4(IMes)(DMAP)] 23: A solution of [WCl_4(IMes)(SEt_2)] (70.0 mg, 97.0 µmol) and 4-Dimethylaminopyridine (DMAP) (11.9 mg, 97.0 µmol) in 10 mL toluene was stirred overnight whereby the color changed from red to yellow. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. After filtration the remaining solid was washed with *n*-hexane (2 x 5 mL portions) and dried *in vacuo*. **Yield:** 42.8 mg (56.9 µmol, 59 %) of a yellow solid. Yellow crystals of [WCl_4(IMes)(DMAP)] suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a saturated solution of the compound in toluene. $C_{28}H_{34}Cl_4N_4W$ (752.25 g/mol): found (calcd.) C 45.19 (44.71), H 4.27 (4.56), N 6.56 (7.45). **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = -25.95 (d, 2 H, $^3J_{HH}$ = 6.9 Hz, $CH_{\text{ortho, DMAP}}$), -4.04 (s, 2 H, NC*H*C*H*N), 2.86 (s, 6 H, $CH_{3\text{para}}$), 3.45 (s, 12 H, $CH_{3\text{ortho}}$), 9.13 (s, 4 H, CH_{meta}), 11.12 (d, 2 H, $^3J_{HH}$ = 6.8 Hz, $CH_{\text{meta, DMAP}}$), 14.02 (s, 6 H, $N(CH_3)_2$) ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 13.5 ($N(CH_3)_2$), 21.4 ($CH_{3\text{para}}$), 32.3 ($CH_{3\text{ortho}}$), 68.2 (C_{ipso}), 71.8 (N*C*H*C*HN), 138.9 (C_{para}), 140.1 (CH_{meta}), 196.7 (C_{ortho}) ppm. Despite several attempts with measurements from -200 – 400 ppm, no resonances for the DMAP aryl carbon atoms were detected. **IR** (ATR[cm^{-1}]): 422 (vw), 429 (w), 465 (w), 489 (w), 526 (m), 549 (w), 647 (vw), 702 (m), 732 (w), 751 (m), 763 (w), 802 (s), 808 (s), 850 (s), 897 (w), 928 (w), 949 (w), 965 (w), 1017 (vs), 1035 (w), 1064 (s), 1107 (w), 1163 (vw), 1233 (s), 1265 (m), 1289 (w), 1350 (w), 1380 (m), 1392 (s), 1419 (w), 1436 (m), 1443 (s), 1456 (m), 1486 (m), 1533 (m), 1539 (m), 1542 (m), 1545 (m), 1557 (s), 1571 (w), 1616 (s), 1627 (vs). 2856 (w), 2915 (m), 3169 (vw).

Synthesis of [WCl_4(IDipp)(Py)] 24: To a solution of [WCl_4(IDipp)(SEt_2)] (75.0 mg, 93.2 µmol) in 5 mL toluene was added pyridine (7.37 mg, 7.51 µL, 93.2 µmol). The solution was stirred overnight whereby the color changed from red to yellow. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. After filtration the remaining solid was washed with *n*-hexane (2 x 7 mL portions) and dried *in vacuo*. **Yield:** 39.8 mg (50.2 µmol, 54 %) of a yellow solid. $C_{32}H_{41}Cl_4N_3W$ (793.34 g/mol): found (calcd.) C 48.75 (48.45), H 5.22 (5.21), N 4.93 (5.30). **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = -33.49 (d, 2 H, $^3J_{HH}$ = 5.5 Hz, $CH_{\text{ortho, Py}}$), -25.01 (t, 1 H, $^3J_{HH}$ = 7.4 Hz, $CH_{\text{para, Py}}$), -4.26 (s, 2 H, NC*H*C*H*N), 0.74 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, *i*PrCH_3), 2.51 (sept, 4 H, $^3J_{HH}$ = 6.6 Hz, *i*PrC*H*), 5.21 (d, 12 H, $^3J_{HH}$ = 6.5 Hz, *i*PrCH_3), 7.62 (t, 2 H, $^3J_{HH}$ = 7.6 Hz, CH_{para}), 9.78 (d, 4 H, $^3J_{HH}$ = 7.6 Hz, CH_{meta}), 16.01 (t, 2 H, $^3J_{HH}$ = 6.5 Hz, $CH_{\text{meta, Py}}$) ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 26.8 (*i*PrCH_3), 34.5 (*i*PrCH_3), 34.8 (*i*Pr*C*H), 73.9 (C_{ipso}), 85.9 (N*C*H*C*HN), 131.8 (CH_{meta}), 132.4 (CH_{para}), 188.5 (C_{ortho}). Despite several attempts with measurements from -200 – 400 ppm, no resonances for the pyridine carbon atoms were detected. **IR** (ATR[cm^{-1}]): 429 (w), 439 (w), 445 (w), 450 (w), 462 (w), 637 (m), 689 (vs), 701 (m), 729 (w), 758 (vs), 772 (w), 804 (s), 937 (m), 969 (w), 1011 (w), 1045 (w), 1061 (w), 1071 (w), 1116 (w), 1155 (w), 1180 (w), 1199 (m), 1222 (w), 1267 (w), 1328 (w), 1362 (w), 1385 (w), 1447 (s), 1467 (m), 1488 (w), 1575 (w), 1607 (w), 2867 (w), 2930 (w), 2964 (m).

Synthesis of [WCl_4(IDipp)(DMAP)] 25: A solution of [WCl_4(IDipp)(SEt_2)] (75.0 mg, 93.2 µmol) and 4-Dimethylaminopyridine (DMAP) (11.3 mg, 93.2 µmol) in 10 mL toluene was stirred overnight whereby the color changed from red to yellow. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. After filtration the remaining solid was washed with *n*-hexane (2 x 5 mL portions) and dried *in vacuo*. **Yield:** 40.4 mg (48.3 µmol, 52 %) of a yellow solid. Yellow crystals of [WCl_4(IDipp)(DMAP)] suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a saturated solution of the compound in toluene. $C_{28}H_{34}Cl_4N_4W$ (836.41 g/mol): found (calcd.) C 48.82 (48.82), H 5.61 (5.54), N 6.09 (6.70). **^{1}H NMR** (400 MHz, C_6D_6, 298 K): δ = -26.87 (d, 2 H, $^3J_{HH}$ = 6.9 Hz, C$H_{ortho, DMAP}$), -3.19 (s, 2 H, NC*H*C*H*N), 0.80 (d, 12 H, $^3J_{HH}$ = 6.5 Hz, *i*PrCH_3), 2.73 (sept, 4 H, $^3J_{HH}$ = 6.5 Hz, *i*PrC*H*), 5.03 (d, 12 H, $^3J_{HH}$ = 6.2 Hz, *i*PrCH_3), 7.54 (t, 2 H, $^3J_{HH}$ = 7.5 Hz, CH_{para}), 9.59 (d, 4 H, $^3J_{HH}$ = 7.6 Hz, CH_{meta}), 11.04 (d, 2 H, $^3J_{HH}$ = 5.3 Hz, C$H_{meta, DMAP}$), 14.02 (s, 6 H, N(CH_3)$_2$) ppm. **^{13}C{^{1}H} NMR** (100.7 MHz, C_6D_6, 298 K): δ = 11.9 (N(CH_3)$_2$), 26.7 (*i*PrCH_3), 34.0 (*i*PrCH_3), 34.1 (*i*Pr*C*H), 78.0 (C_{ipso}), 85.5 (N*C*H*C*HN), 131.1 (CH_{meta}), 132.0 (CH_{para}), 186.6 (C_{ortho}) ppm. Despite several attempts with measurements from -200 – 400 ppm, no signals for the DMAP aryl carbon atoms were detected. **IR** (ATR[cm^{-1}]): 417 (vw), 420 (w), 423 (w), 446 (w), 462 (m), 527 (m), 634 (w), 702 (w), 729 (w), 754 (s), 760 (s), 801 (vs), 936 (m), 951 (w), 966 (w), 1017 (vs), 1063 (s), 1118 (w), 1181 (w), 1198 (w), 1234 (s), 1268 (w), 1327 (w), 1351 (w), 1362 (w), 1393 (m), 1442 (m), 1456 (w), 1464 (m), 1548 (m), 1569 (m), 1616 (m), 1631 (s), 2865 (w), 2930 (w), 2960 (m).

2) NMR spectra of compounds

$[MoCl_4(IMes)_2]$ **1**

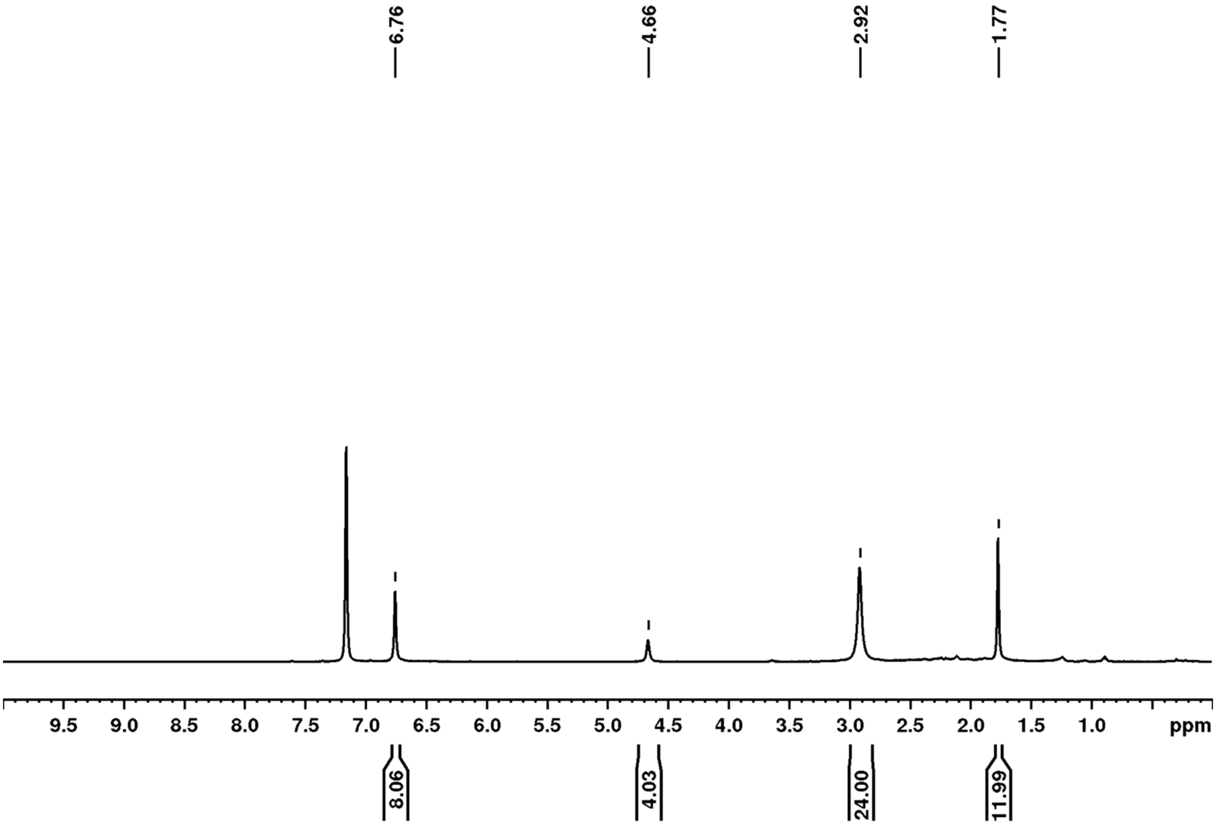

Figure S1: ^1H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of $[MoCl_4(IMes)_2]$ **1**.

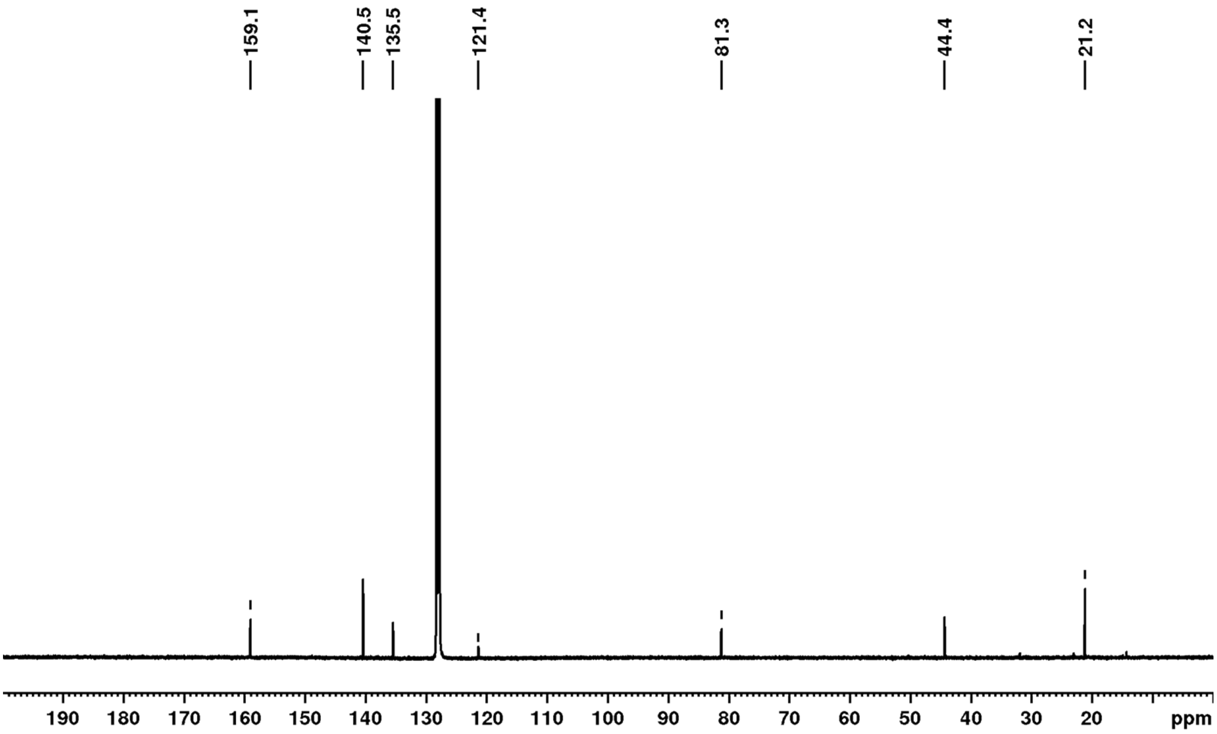

Figure S2: $^{13}C\{^1H\}$ NMR spectrum (100.6 MHz, C_6D_6, 298 K) of $[MoCl_4(IMes)_2]$ **1**.

[$MoCl_4(IDipp)_2$] **2**

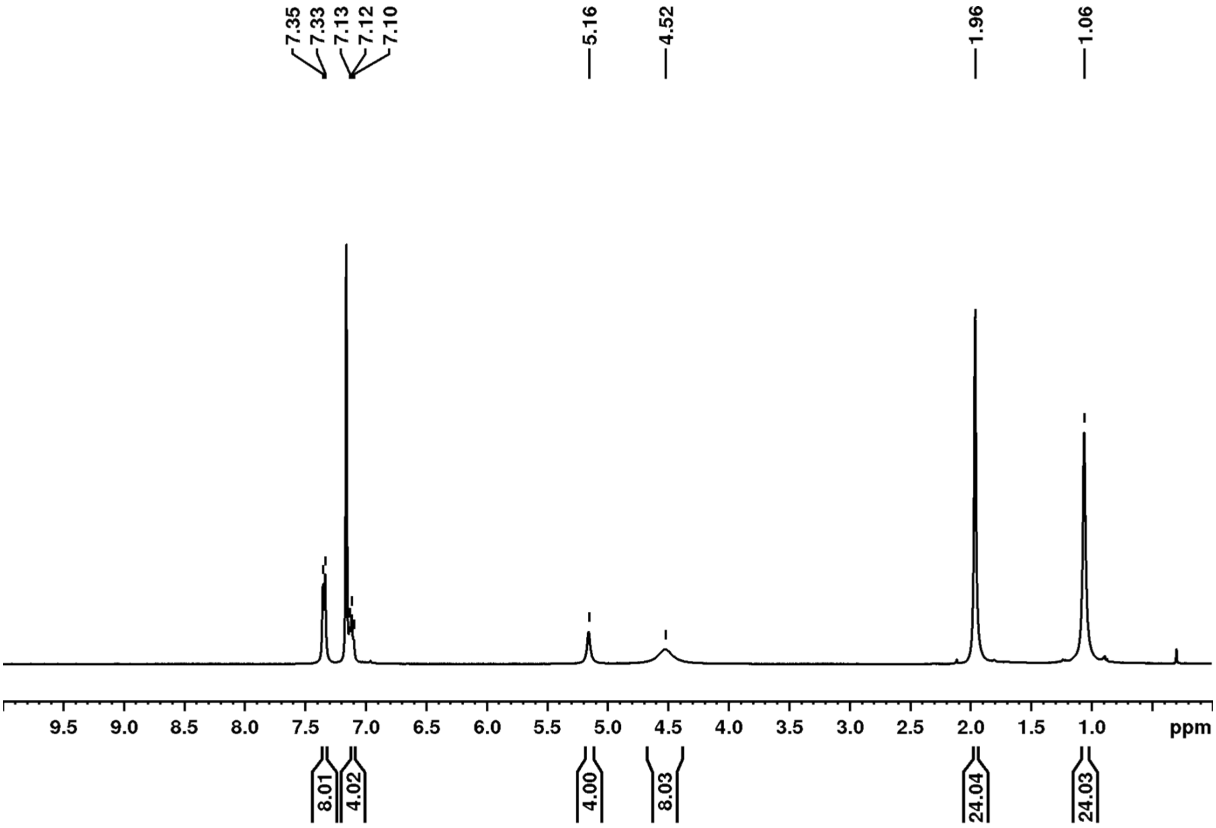

Figure S3: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [$MoCl_4(IDipp)_2$] **2**.

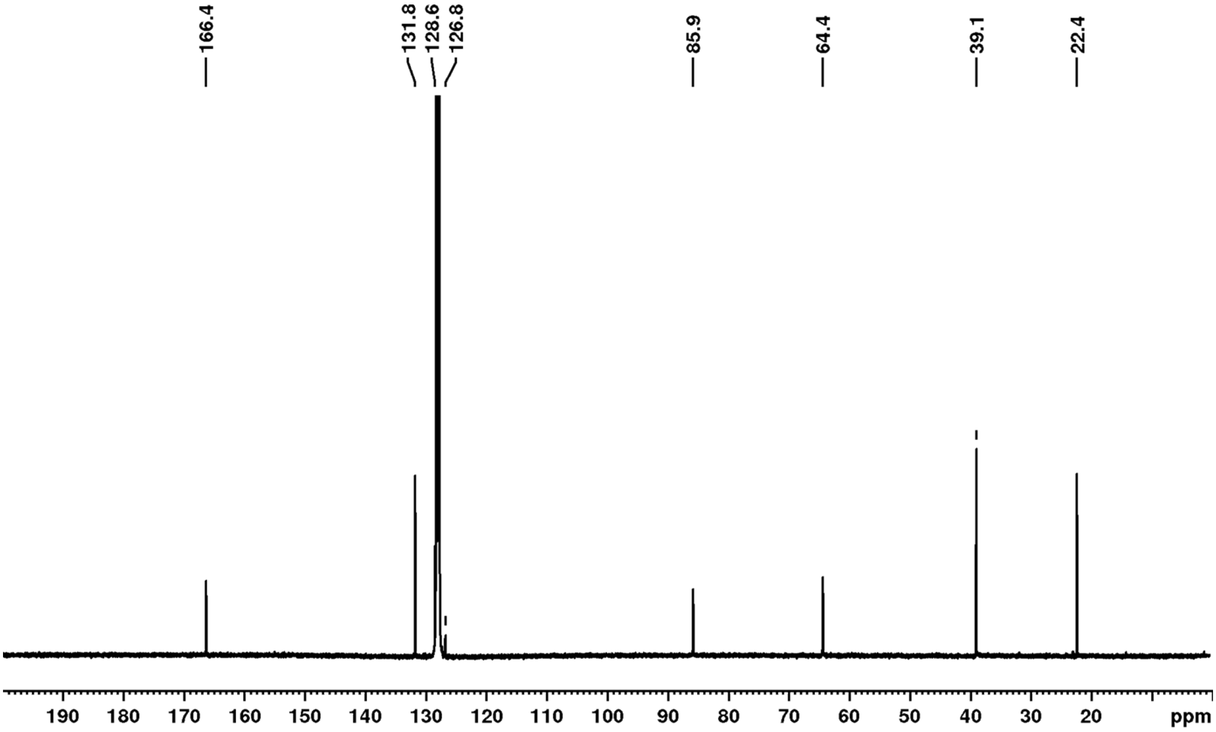

Figure S4: $^{13}C\{^1H\}$ NMR spectrum (100.6 MHz, C_6D_6, 298 K) of [$MoCl_4(IDipp)_2$] **2**.

[WCl$_4$(IMes)$_2$] **3**

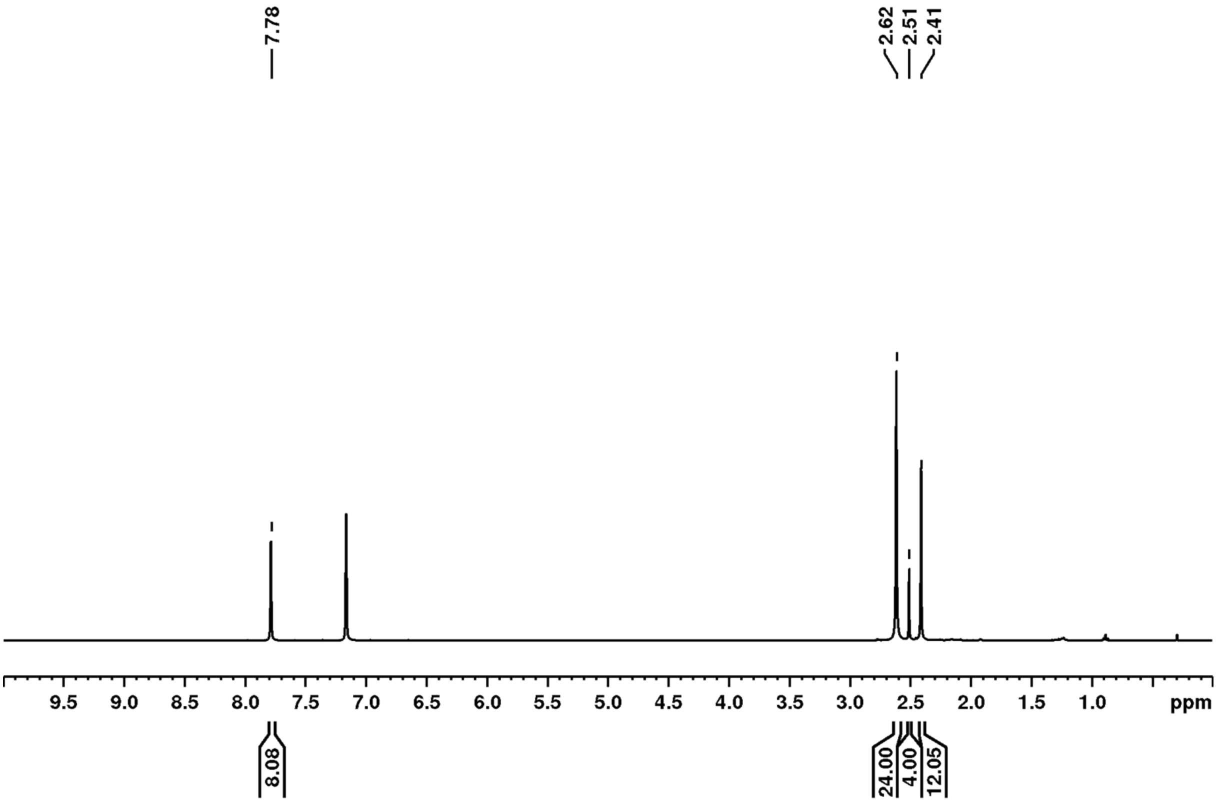

Figure S5: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [WCl$_4$(IMes)$_2$] **3**.

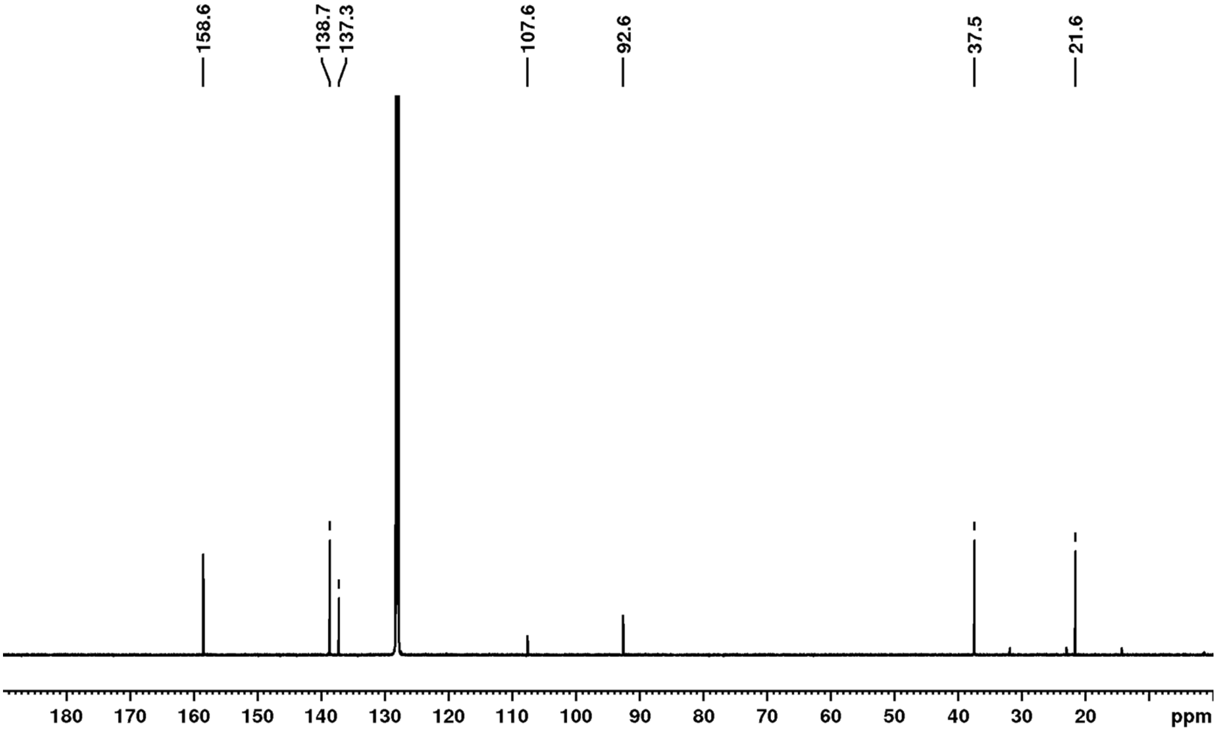

Figure S6: ^{13}C{^{1}H} NMR spectrum (100.6 MHz, C_6D_6, 298 K) of [WCl$_4$(IMes)$_2$] **3**.

[WCl$_4$(IDipp)$_2$] **4**

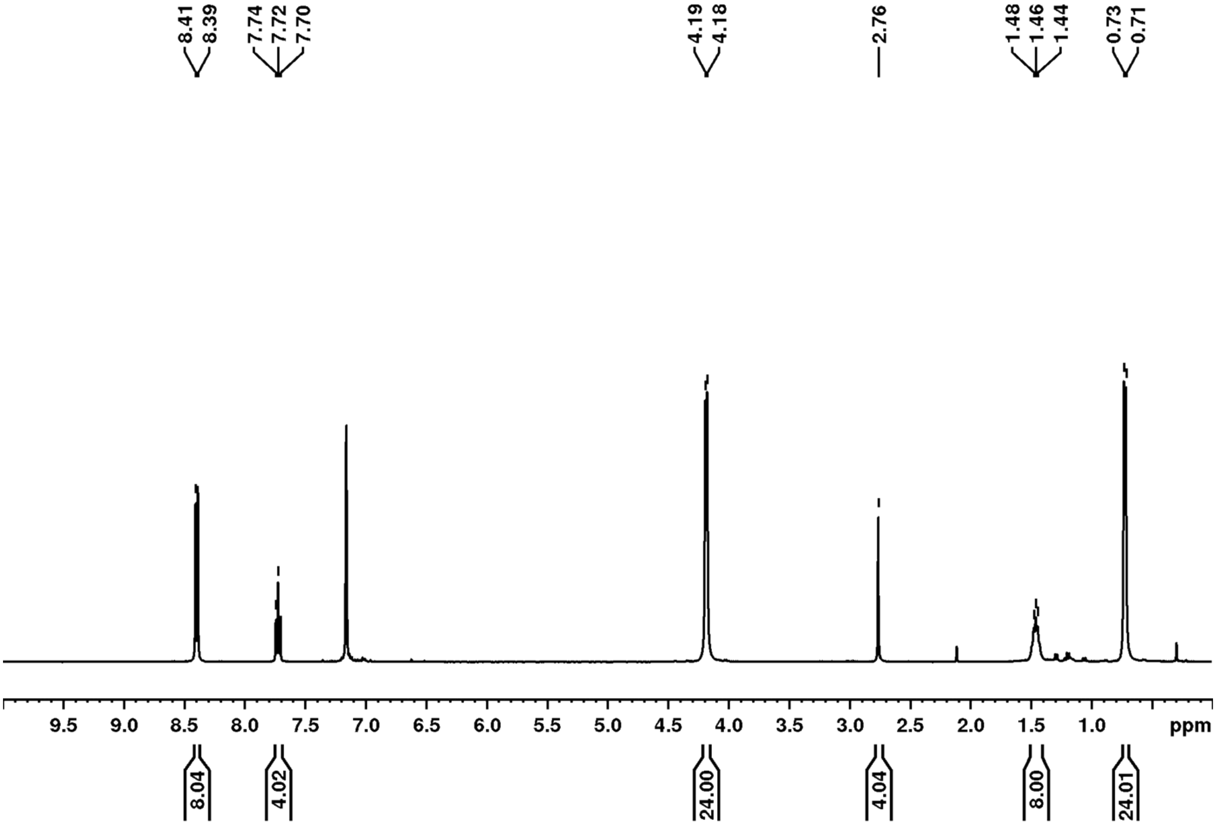

Figure S7: ^{1}H NMR spectrum (400.1 MHz, C$_6$D$_6$, 298 K) of [WCl$_4$(IDipp)$_2$] **4**.

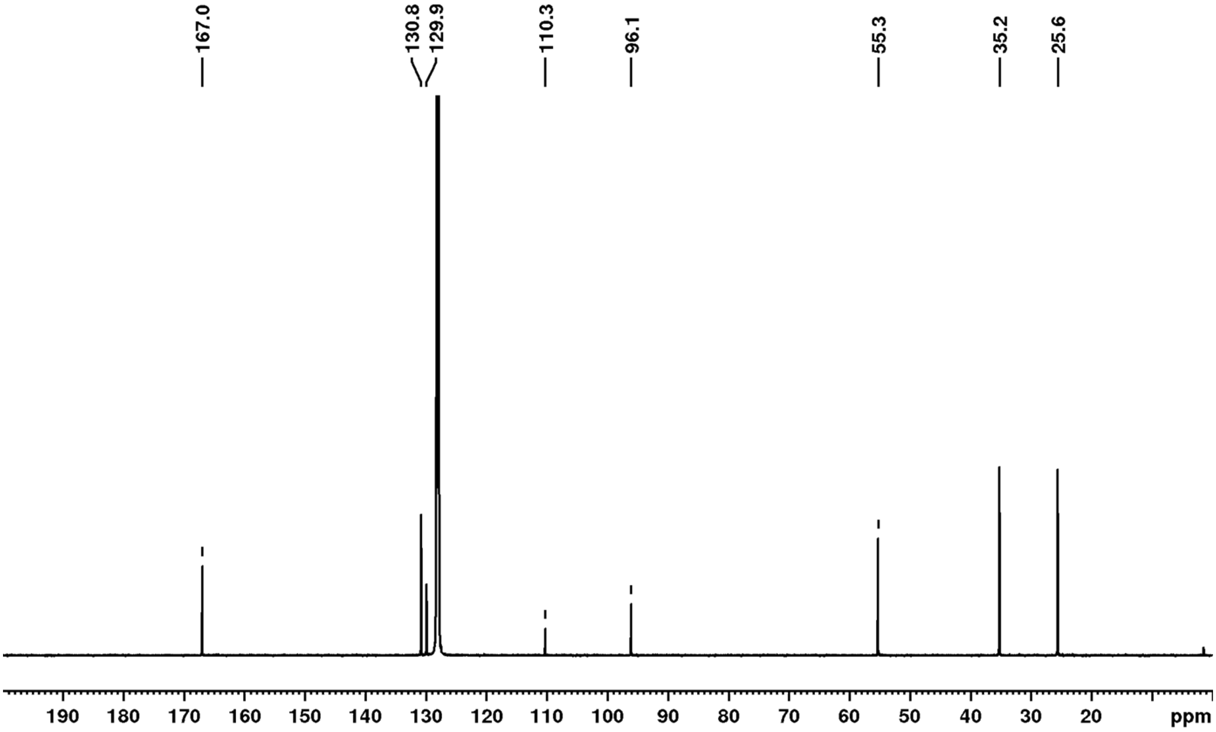

Figure S8: ^{13}C{^{1}H} NMR spectrum (100.6 MHz, C$_6$D$_6$, 298 K) of [WCl$_4$(IDipp)$_2$] **4**.

[WCl$_4$(I*i*Pr^{Me})$_2$] **5**

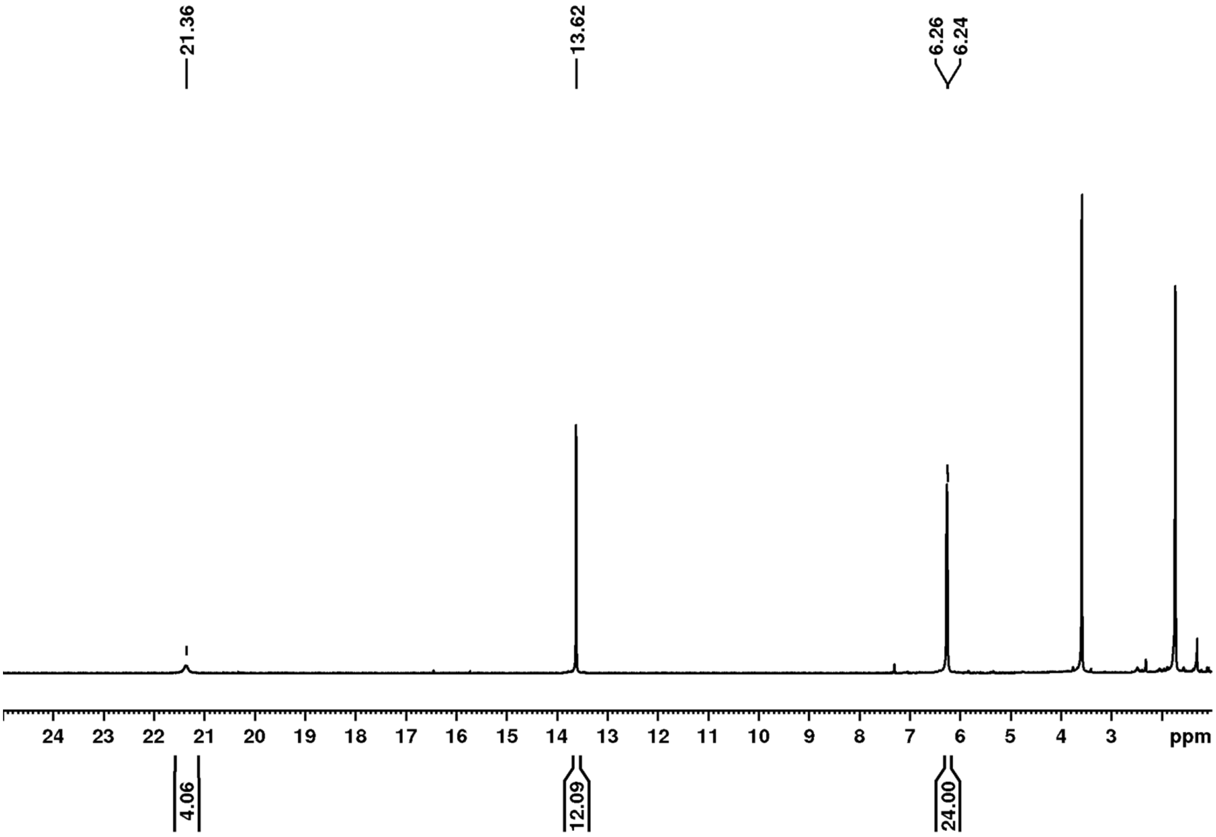

Figure S9: ^{1}H NMR spectrum (400.1 MHz, thf-d$_8$, 298 K) of [WCl$_4$(I*i*Pr^{Me})$_2$] **5**.

[MoCl$_4$(IMes)(SEt$_2$)] **6**

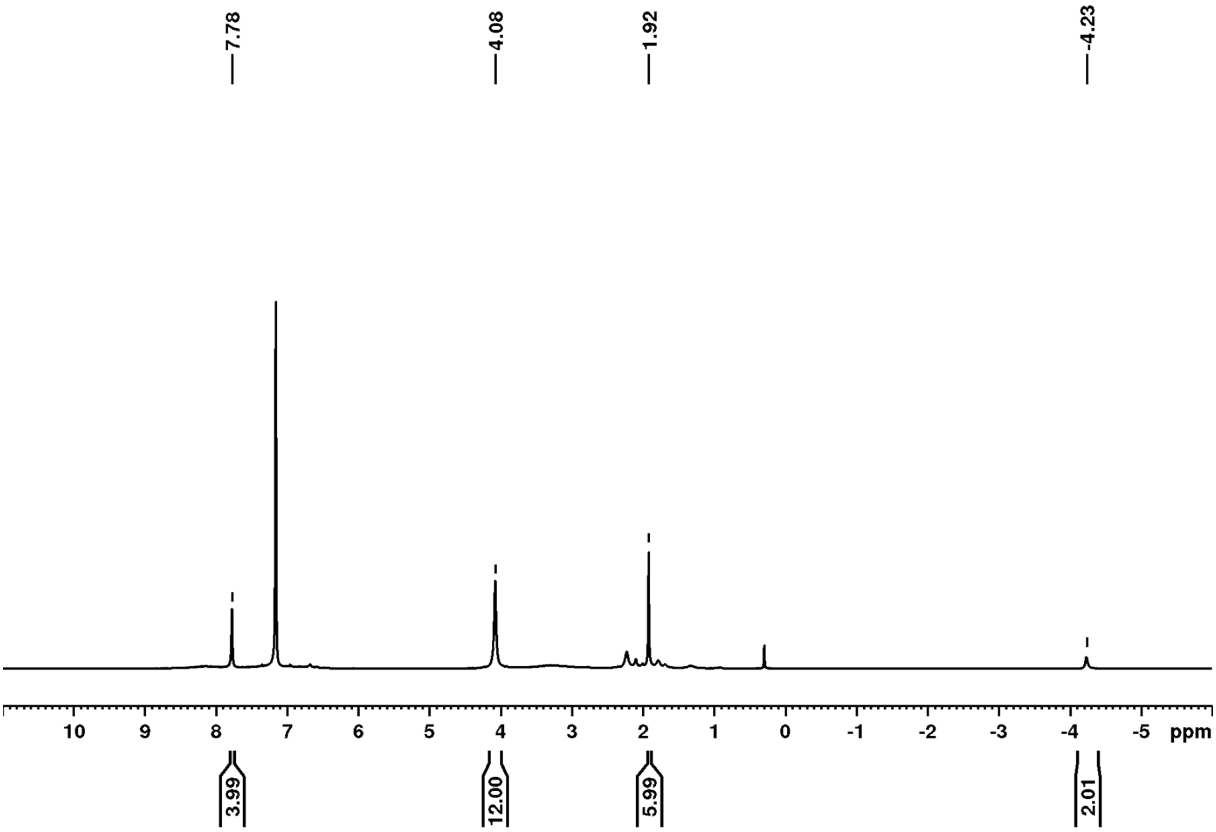

Figure S10: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [MoCl$_4$(IMes)(SEt$_2$)] **6**.

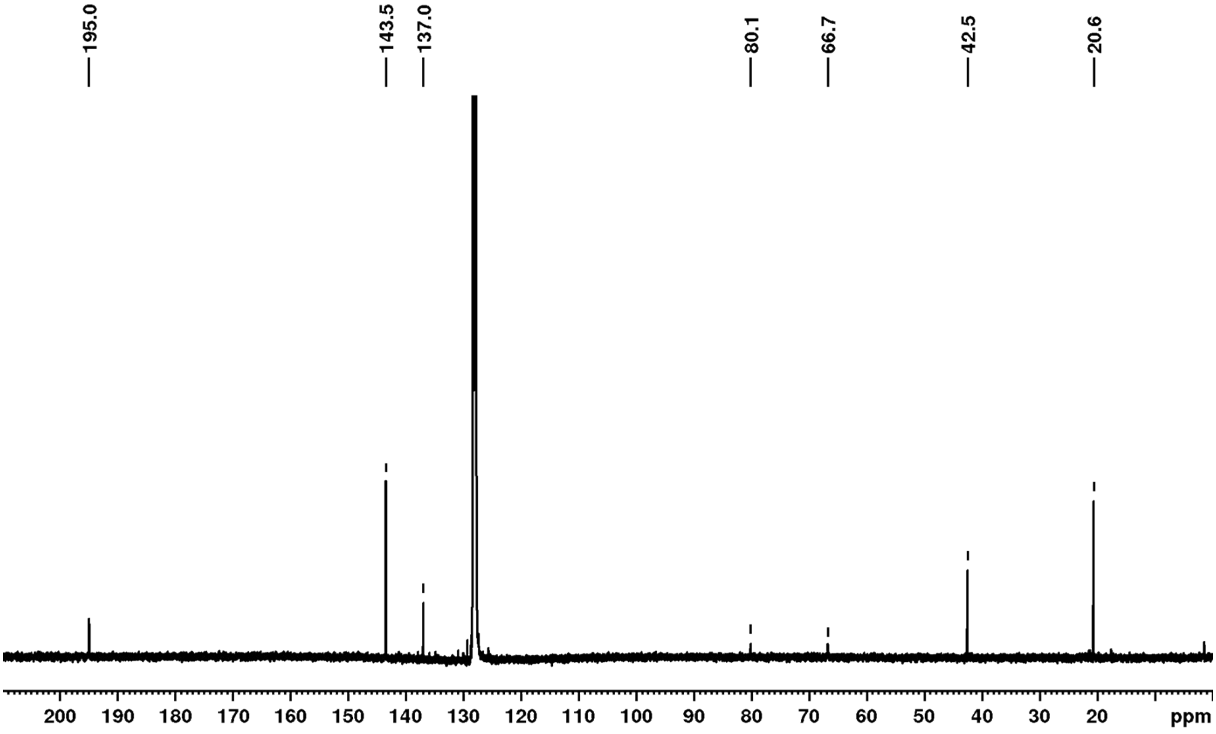

Figure S11: $^{13}C\{^1H\}$ NMR spectrum (100.6 MHz, C_6D_6, 298 K) of [MoCl$_4$(IMes)(SEt$_2$)] **6**.

[MoCl$_4$(IDipp)(SEt$_2$)] **7**

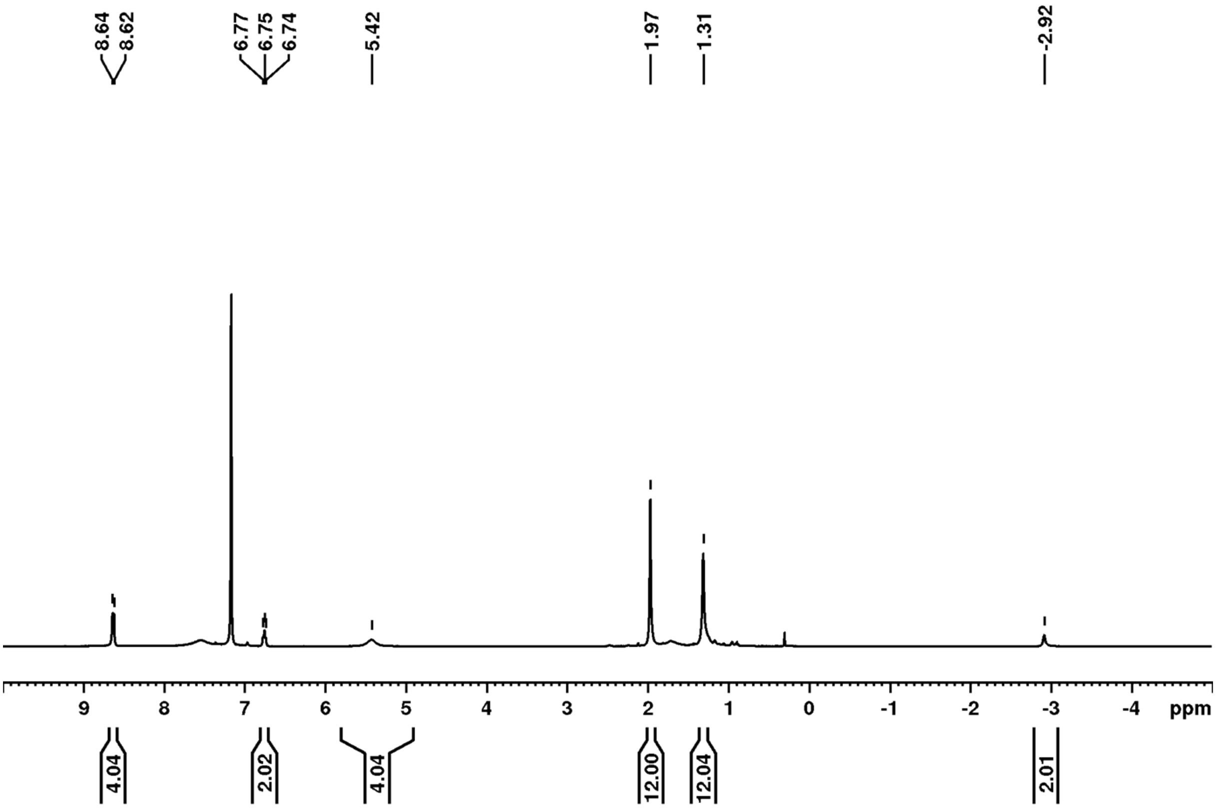

Figure S12: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [MoCl$_4$(IDipp)(SEt$_2$)] **7**.

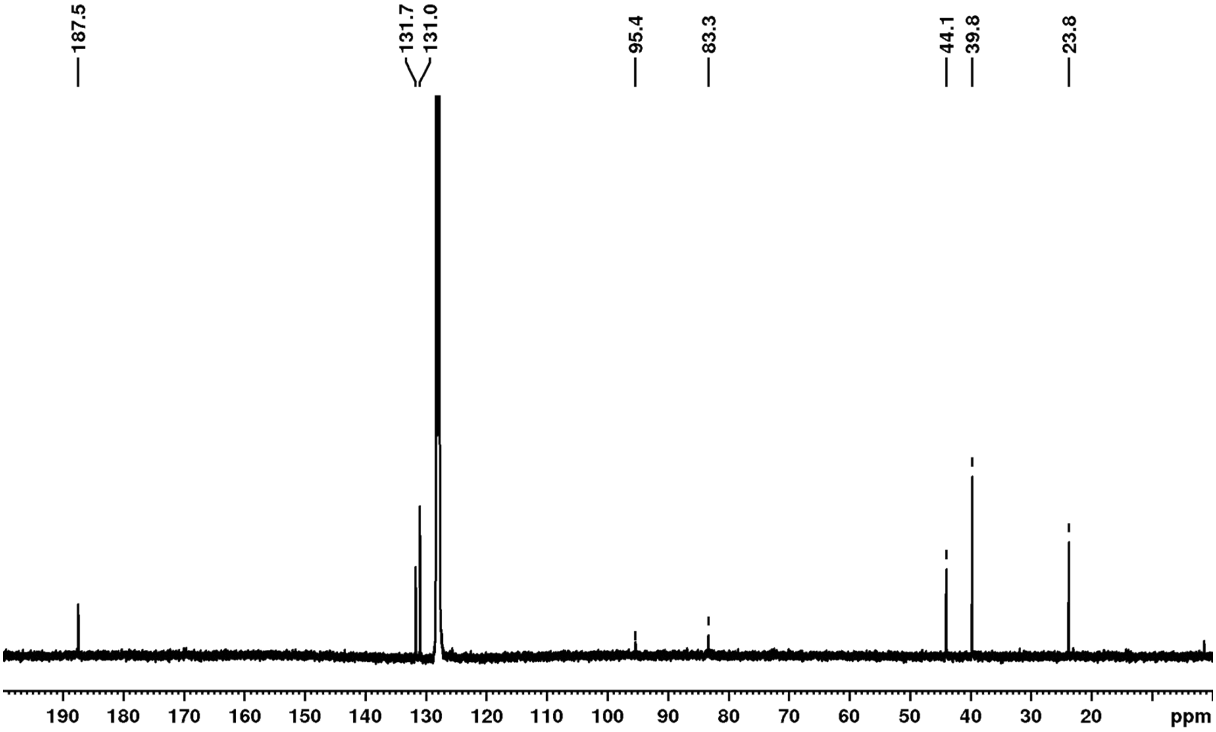

Figure S13: $^{13}C\{^1H\}$ NMR spectrum (100.6 MHz, C_6D_6, 298 K) of [MoCl$_4$(IDipp)(SEt$_2$)] **7**.

[WCl$_4$(IMes)(SEt$_2$)] **8**

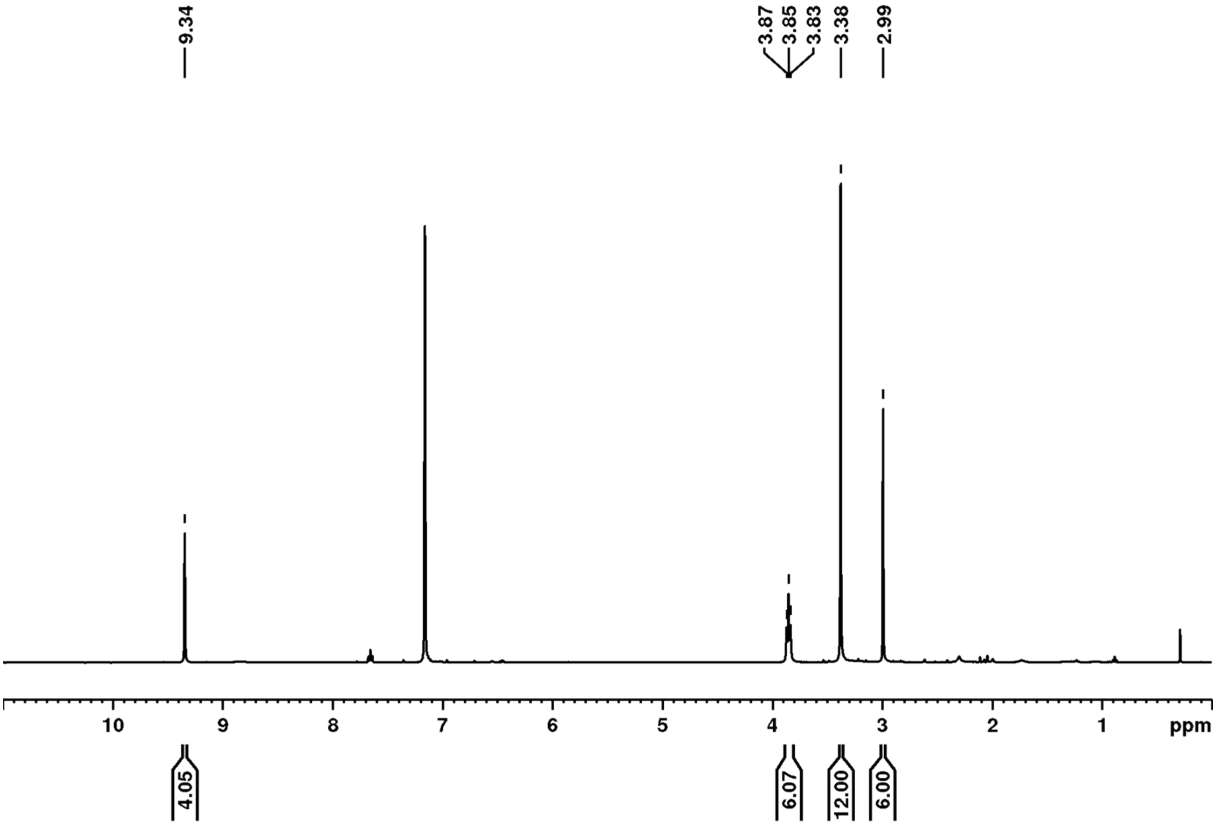

Figure S14: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [WCl$_4$(IMes)(SEt$_2$)] **8** from 0 to 12 ppm.

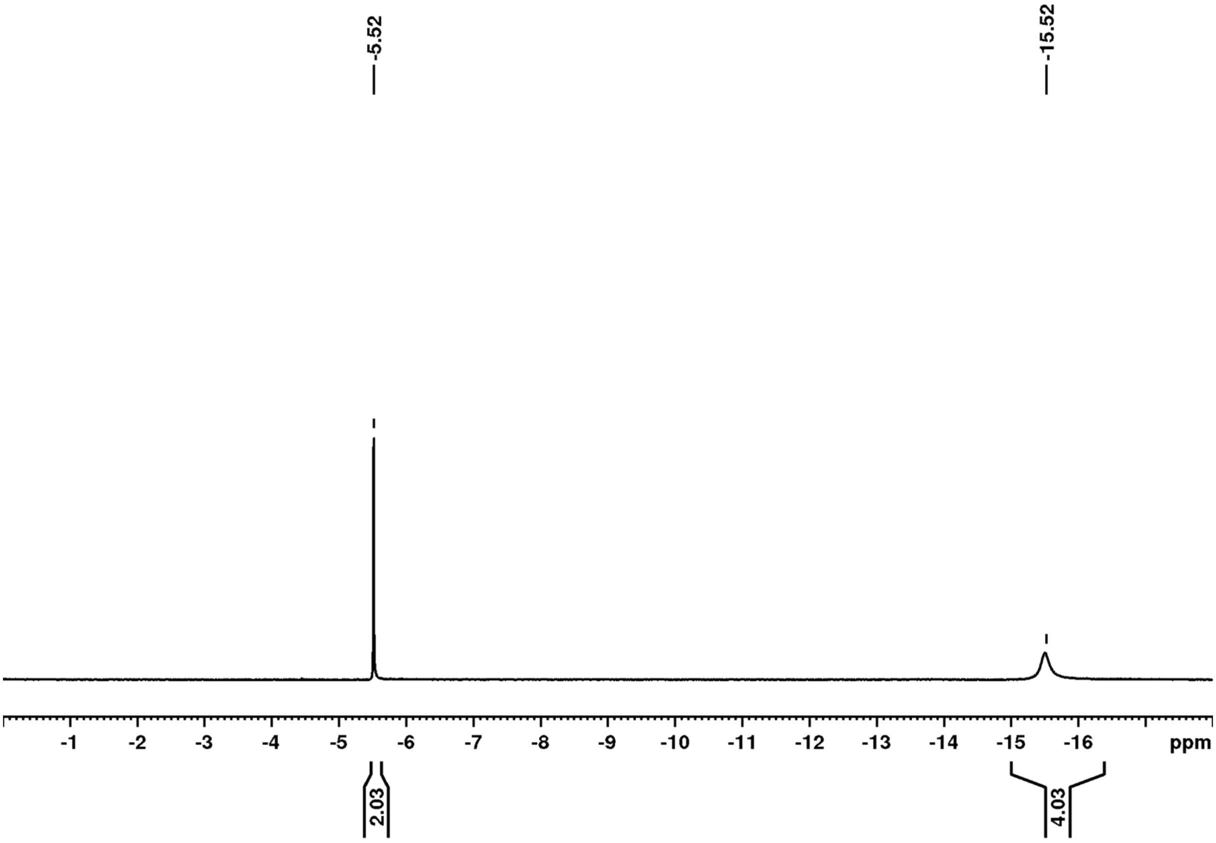

Figure S15: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [WCl$_4$(IMes)(SEt$_2$)] **8** from -18 to 0 ppm.

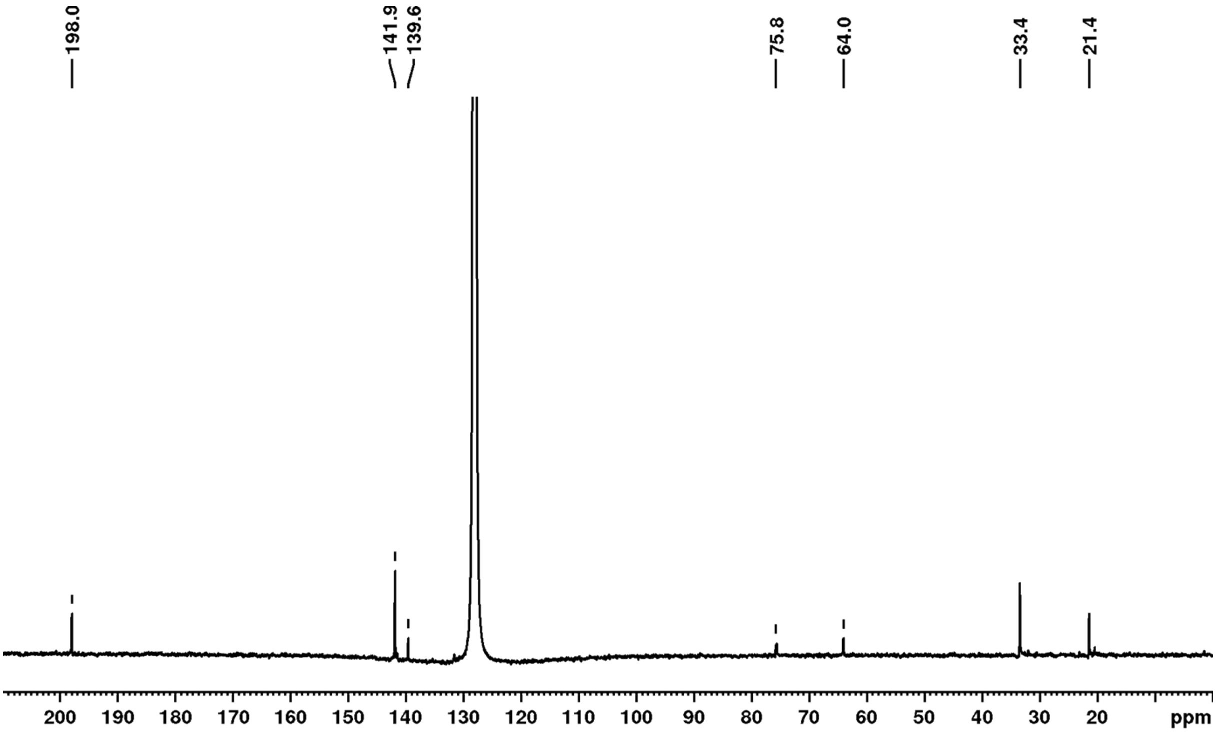

Figure S16: $^{13}C\{^1H\}$ NMR spectrum (100.6 MHz, C_6D_6, 298 K) of $[WCl_4(\textbf{I}Mes)(SEt_2)]$ **8**.

$[WCl_4(IDipp)(SEt_2)]$ **9**

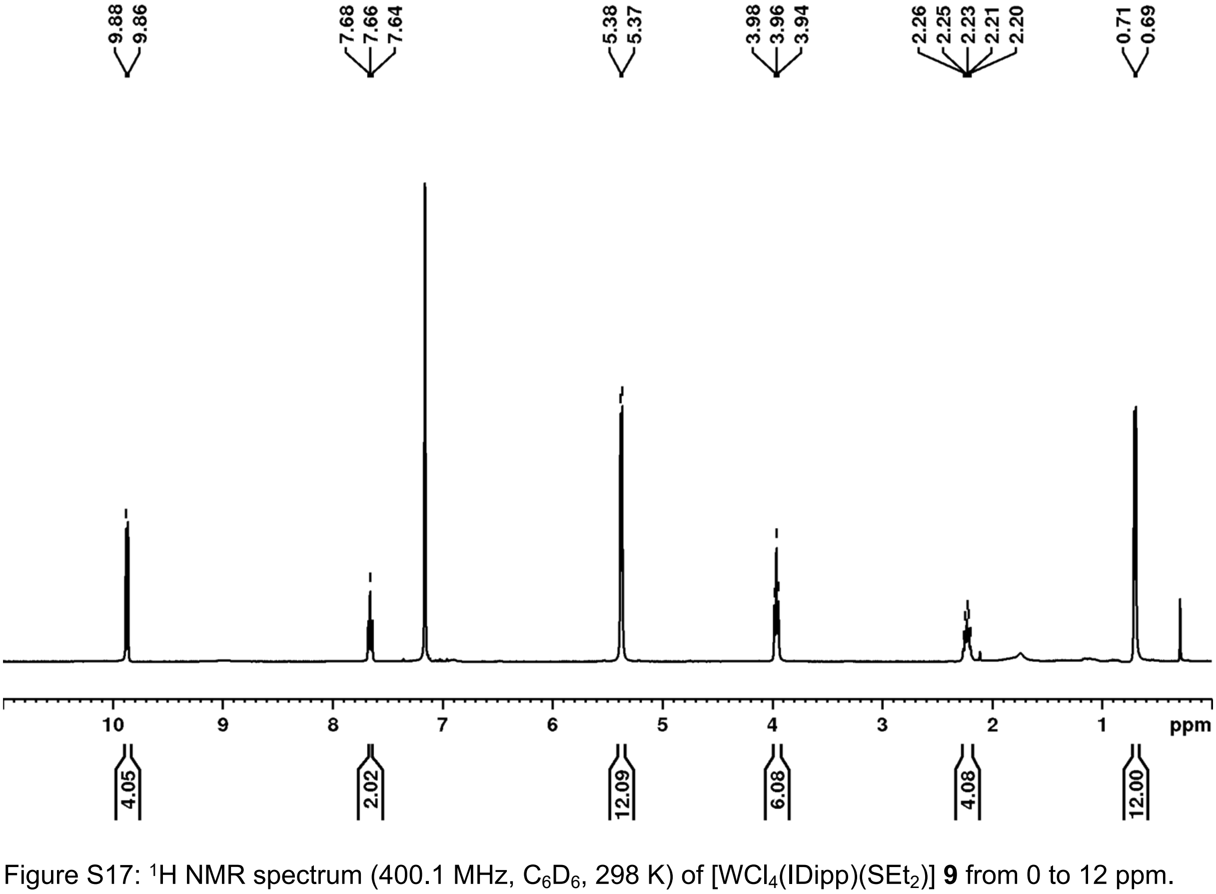

Figure S17: ^1H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of $[WCl_4(\textbf{I}Dipp)(SEt_2)]$ **9** from 0 to 12 ppm.

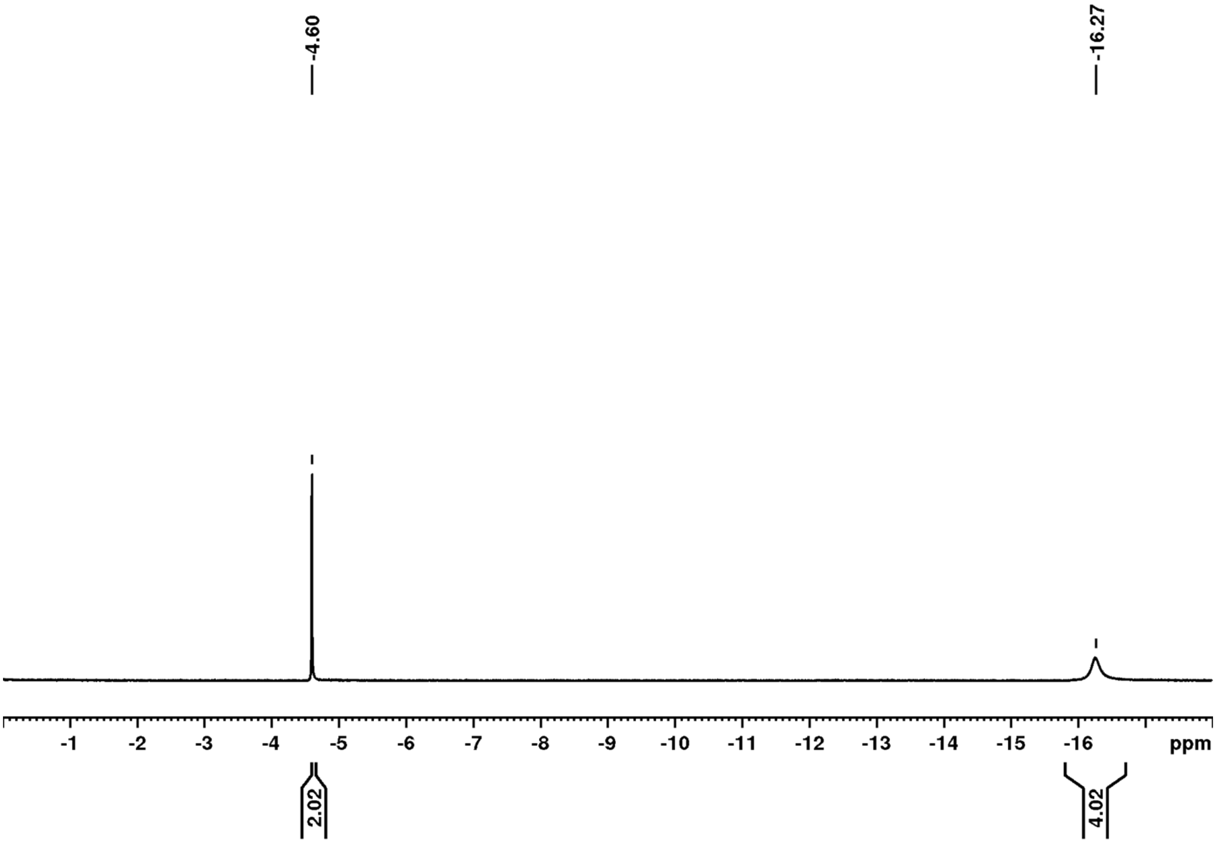

Figure S18: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [WCl_4(IDipp)(SEt_2)] **9** from -18 to 0 ppm.

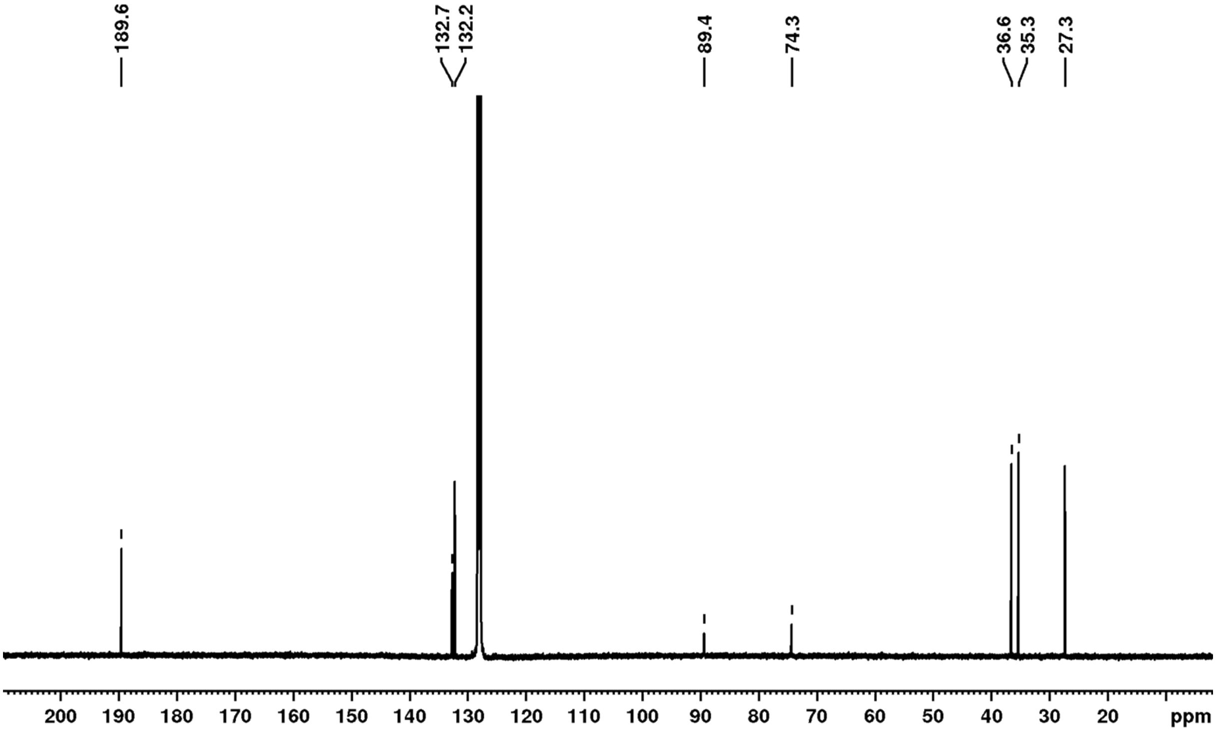

Figure S19: $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, C_6D_6, 298 K) of [WCl_4(IDipp)(SEt_2)] **9**.

$[\mathrm{MoCl_4(IMes)(cAAC^{Me})}]$ **10**

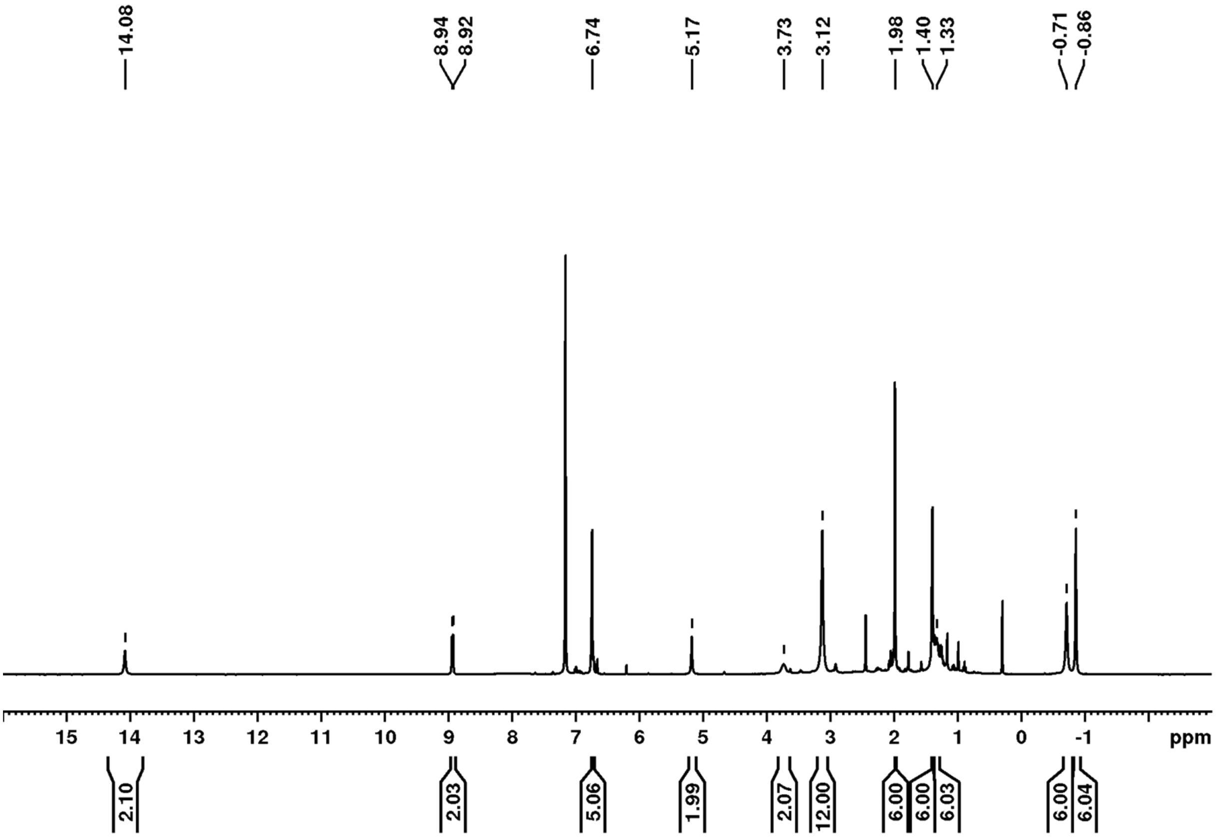

Figure S20: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of $[\mathrm{MoCl_4(IMes)(cAAC^{Me})}]$ **10**.

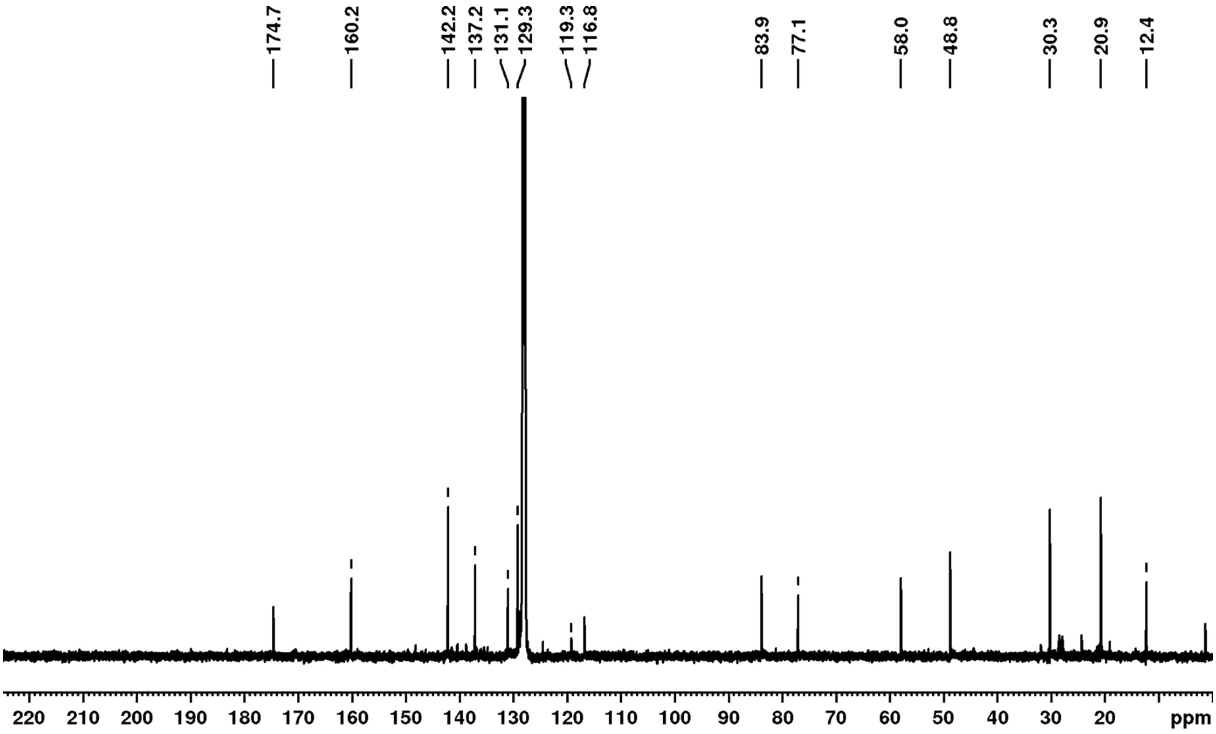

Figure S21: $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, C_6D_6, 298 K) of $[\mathrm{MoCl_4(IMes)(cAAC^{Me})}]$ **10**.

[MoCl$_4$(IDipp)(cAAC^{Me})] **11**

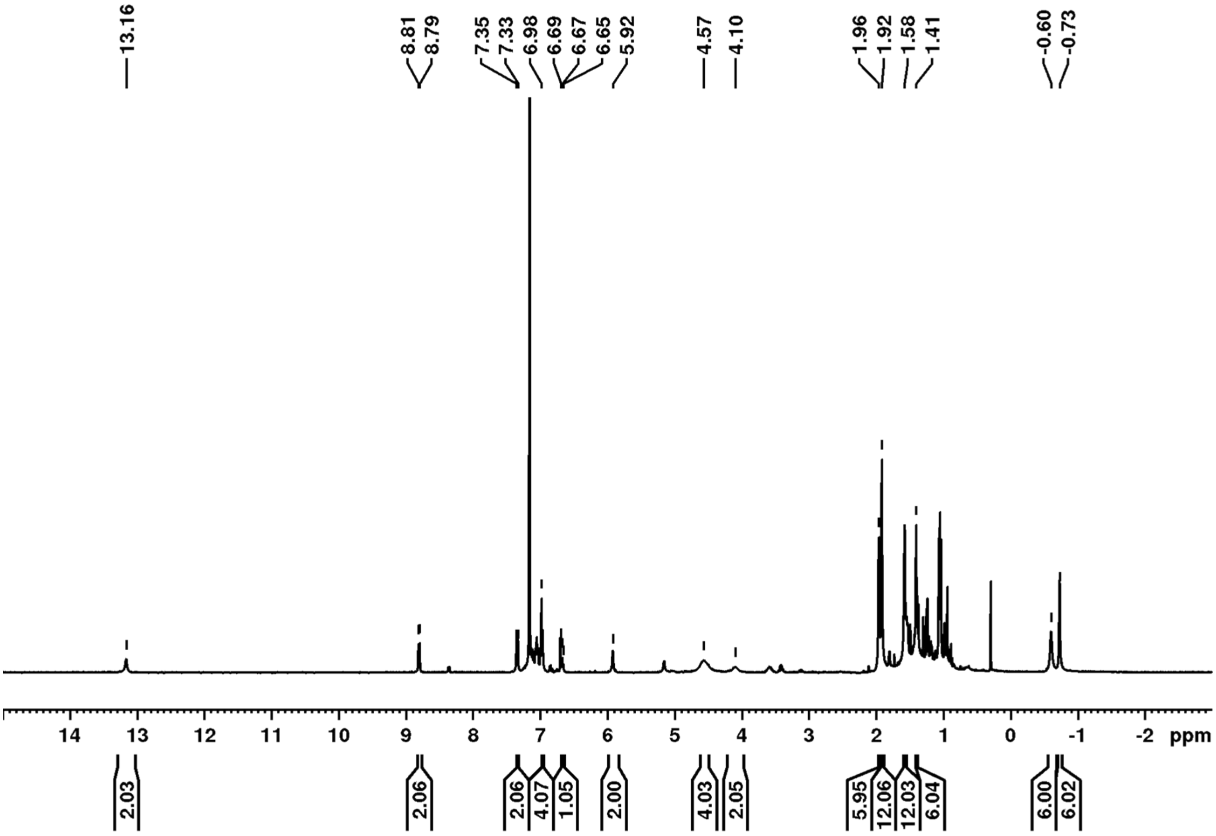

Figure S22: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [MoCl$_4$(IDipp)(cAAC^{Me})] **11**.

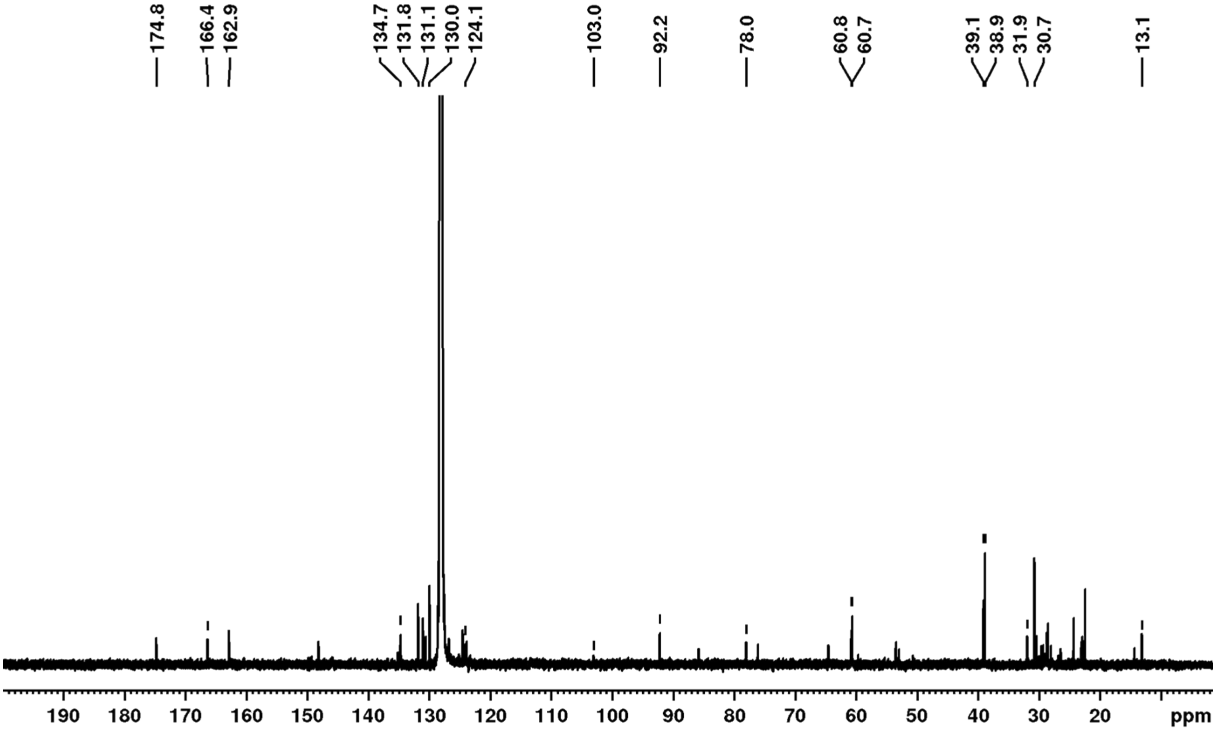

Figure S23: $^{13}C\{^1H\}$ NMR spectrum (100.6 MHz, C_6D_6, 298 K) of [MoCl$_4$(IDipp)(cAAC^{Me})] **11**.

[WCl_4(IMes)(cAAC^{Me})] **12**

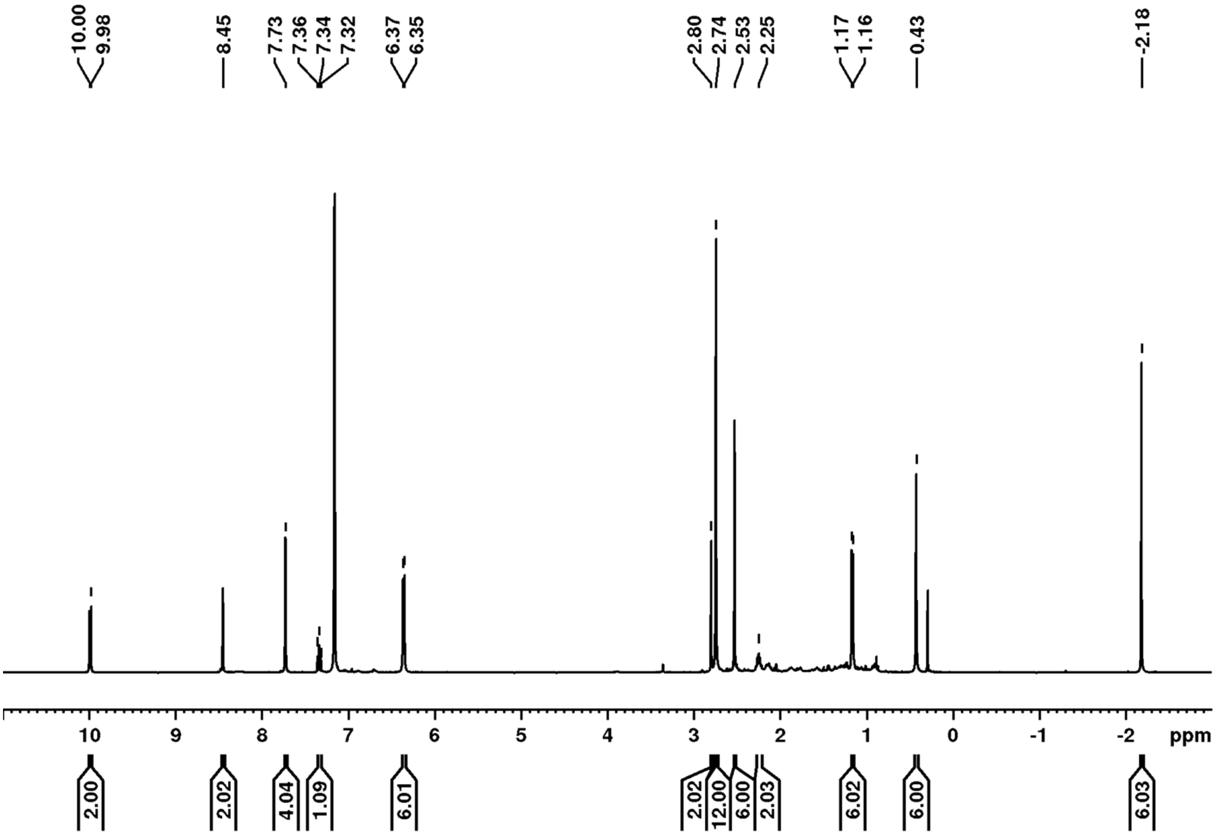

Figure S24: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [WCl_4(IMes)(cAAC^{Me})] **12**.

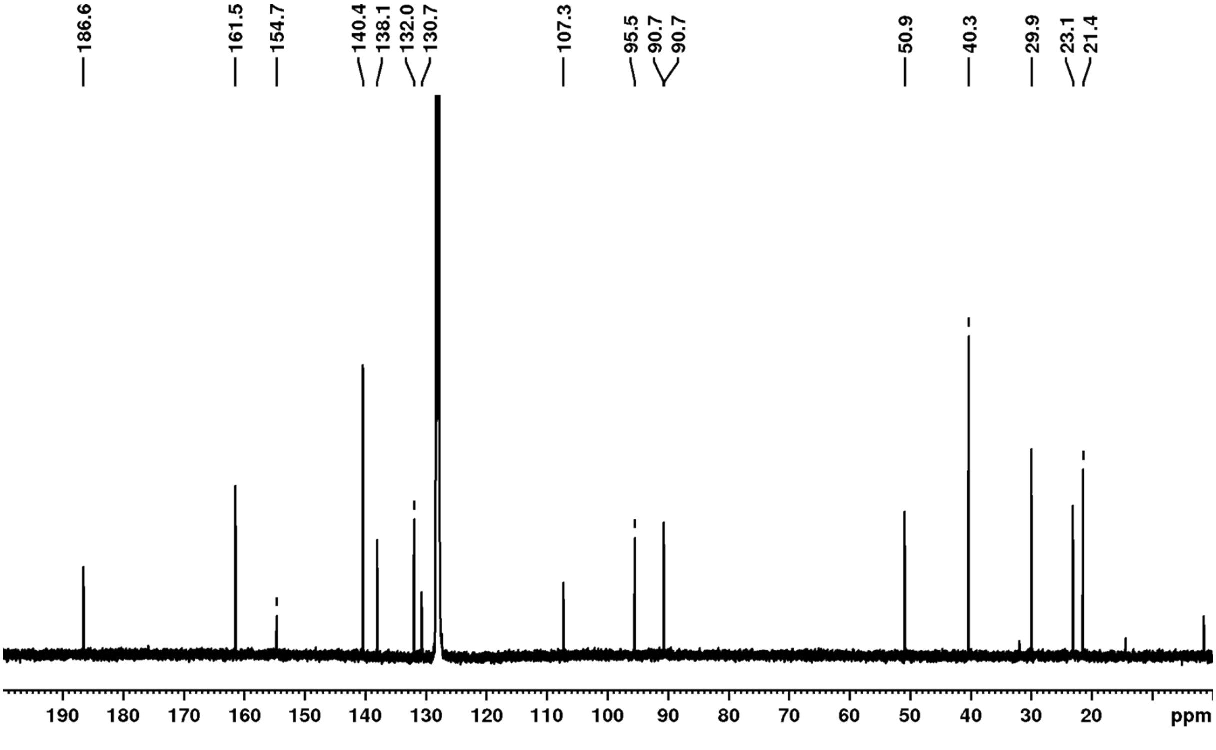

Figure S25: $^{13}C\{^1H\}$ NMR spectrum (100.6 MHz, C_6D_6, 298 K) of [WCl_4(IMes)(cAAC^{Me})] **12**.

[WCl_4(IDipp)(cAAC^{Me})] **13**

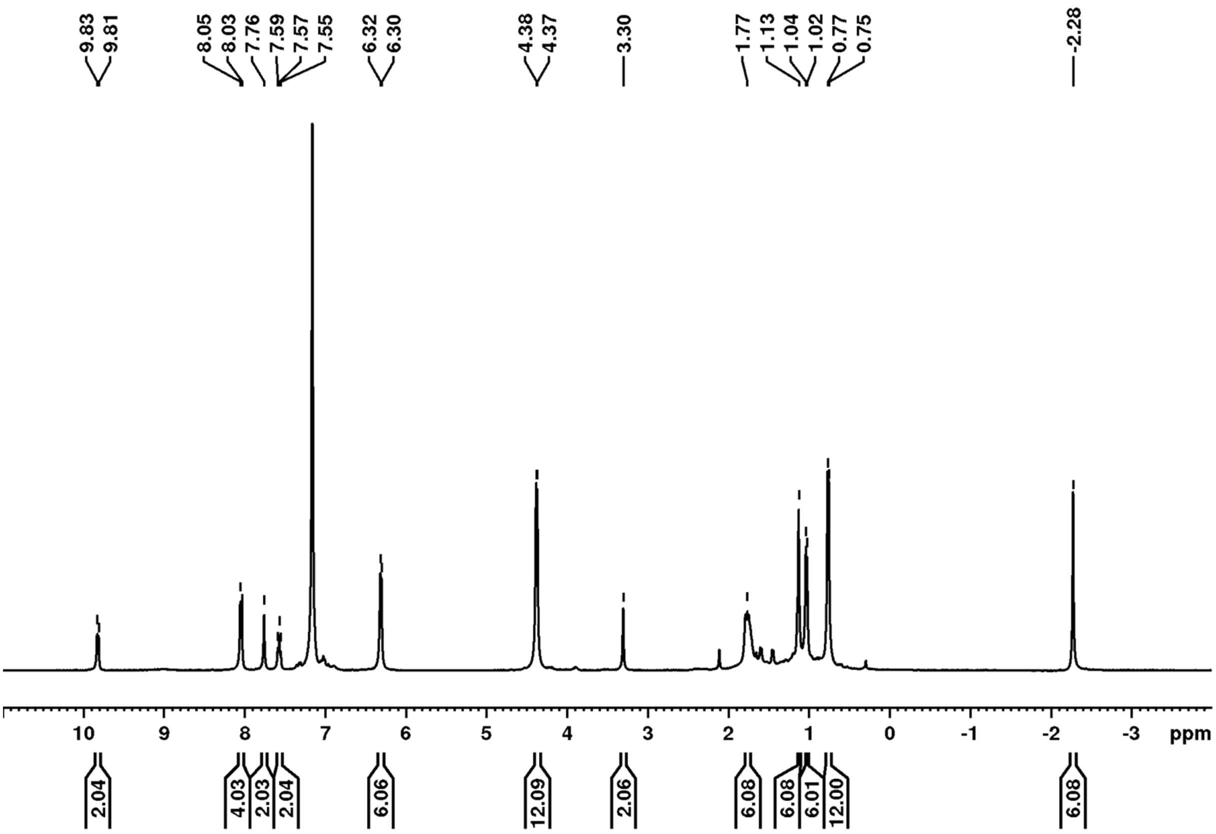

Figure S26: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [WCl_4(IDipp)(cAAC^{Me})] **13**.

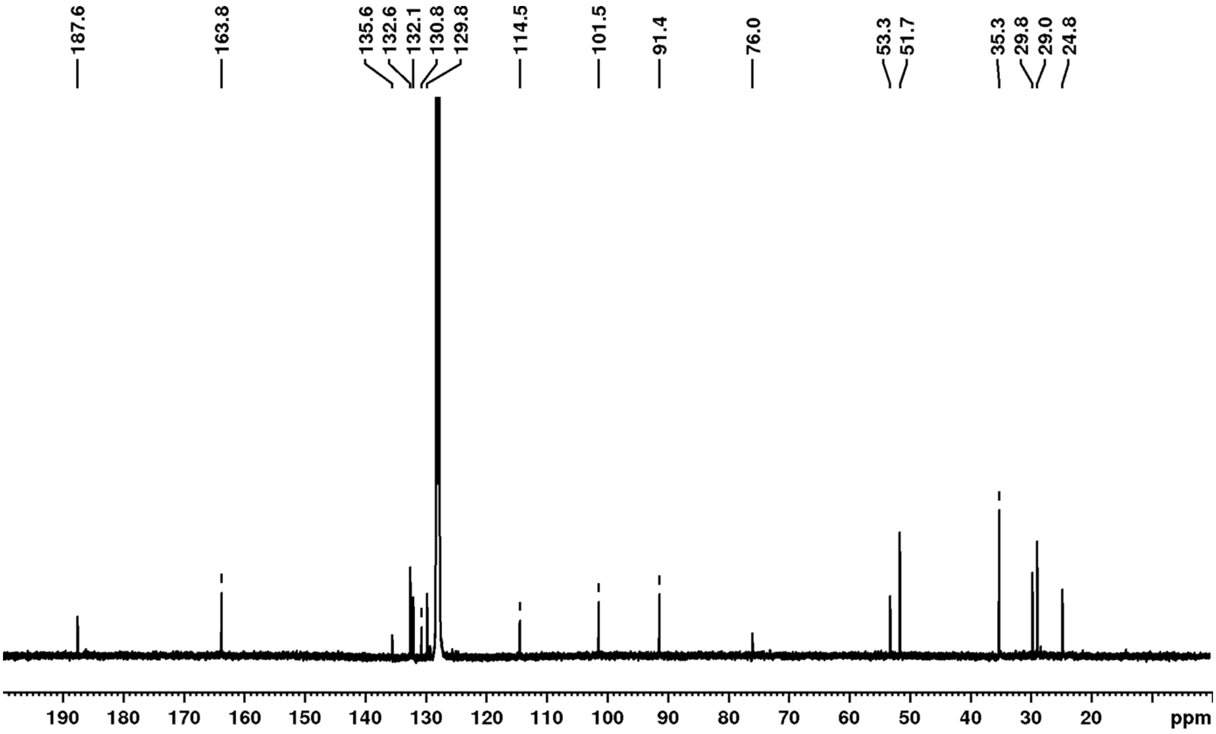

Figure S27: ^{13}C{^{1}H} NMR spectrum (100.6 MHz, C_6D_6, 298 K) of [WCl_4(IDipp)(cAAC^{Me})] **13**.

[WCl$_4$(IMes)(PMe$_3$)] **15**

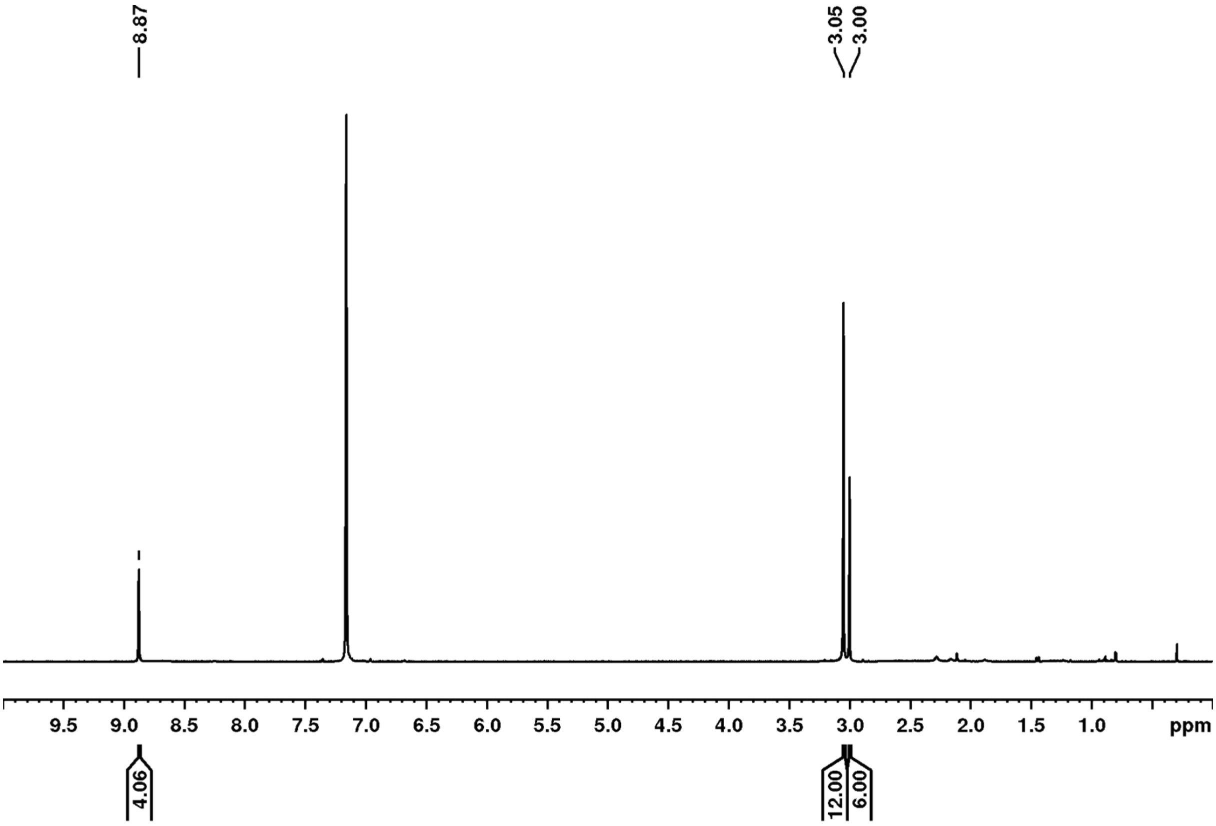

Figure S28: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [WCl$_4$(IMes)(PMe$_3$)] **14** from 0 to 10 ppm.

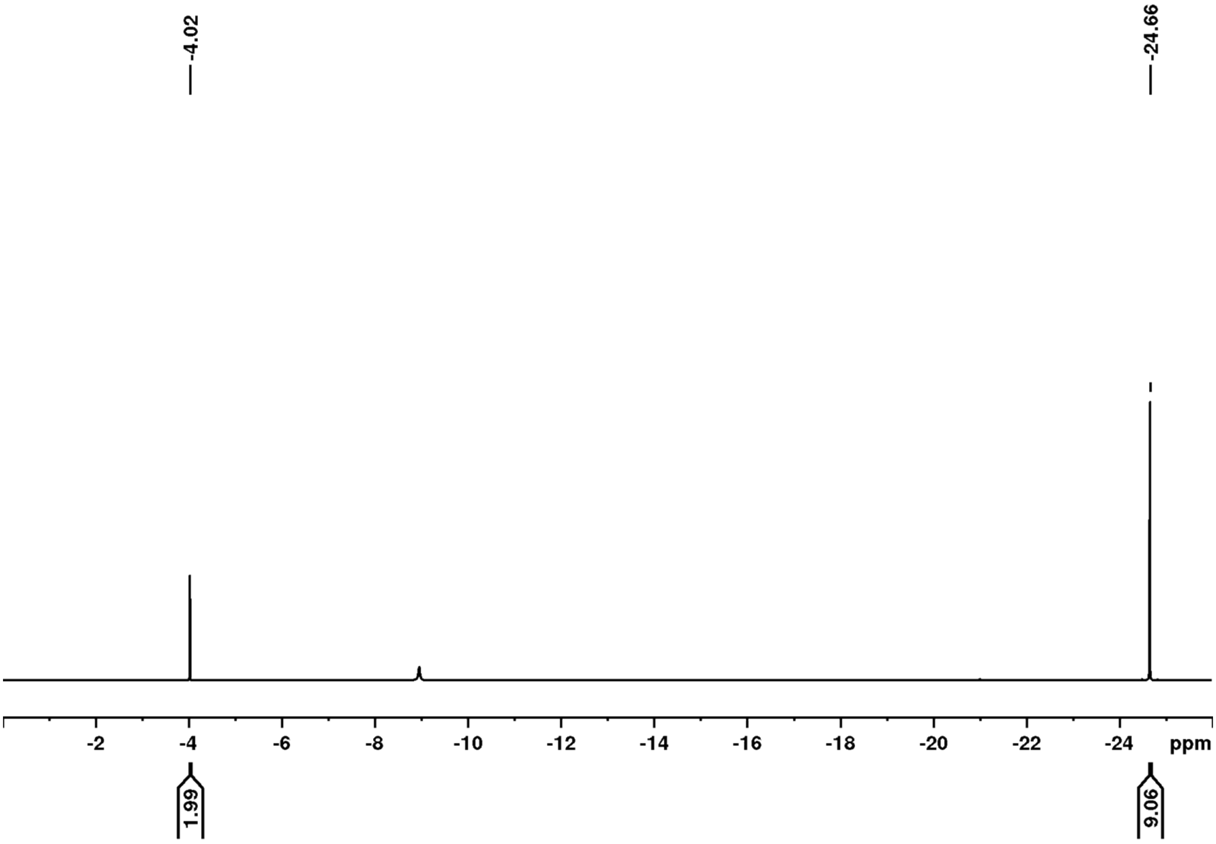

Figure S29: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [WCl$_4$(IMes)(PMe$_3$)] **14** from -26 to 0 ppm.

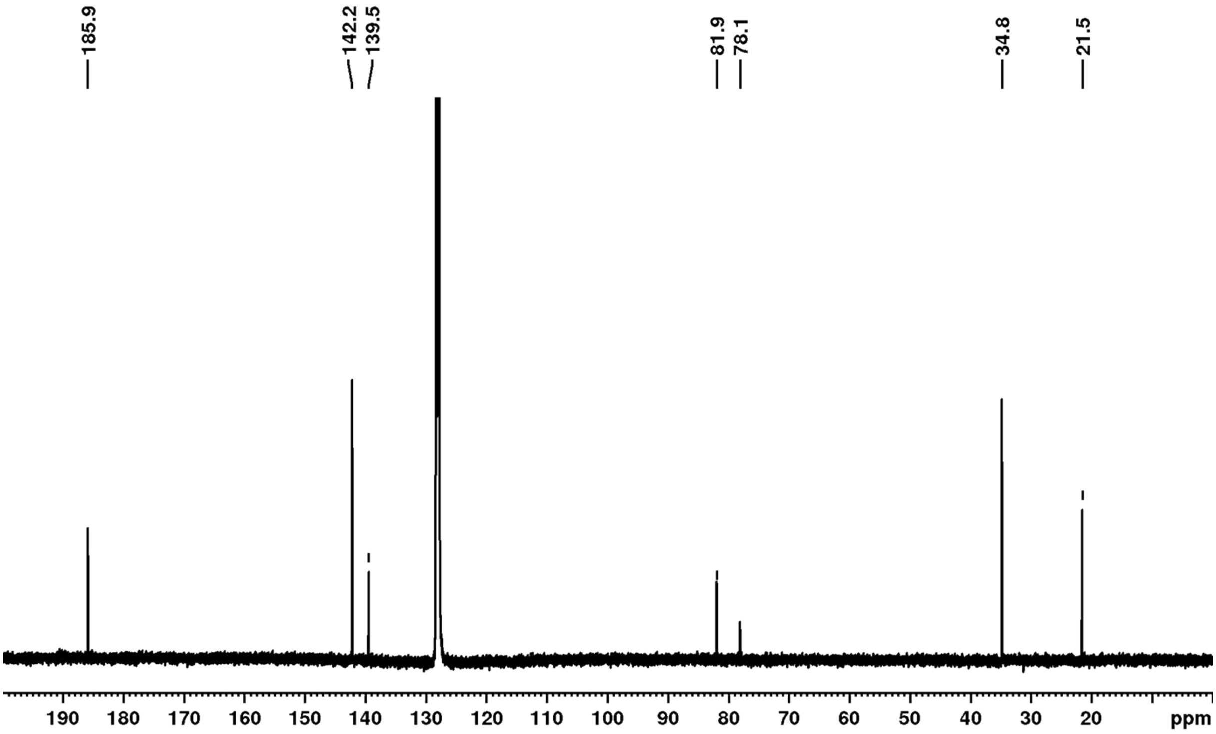

Figure S30: $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, C_6D_6, 298 K) of [WCl_4(IMes)(PMe_3)] **14**.

[WCl_4(IMes)(PPh_3)] **15**

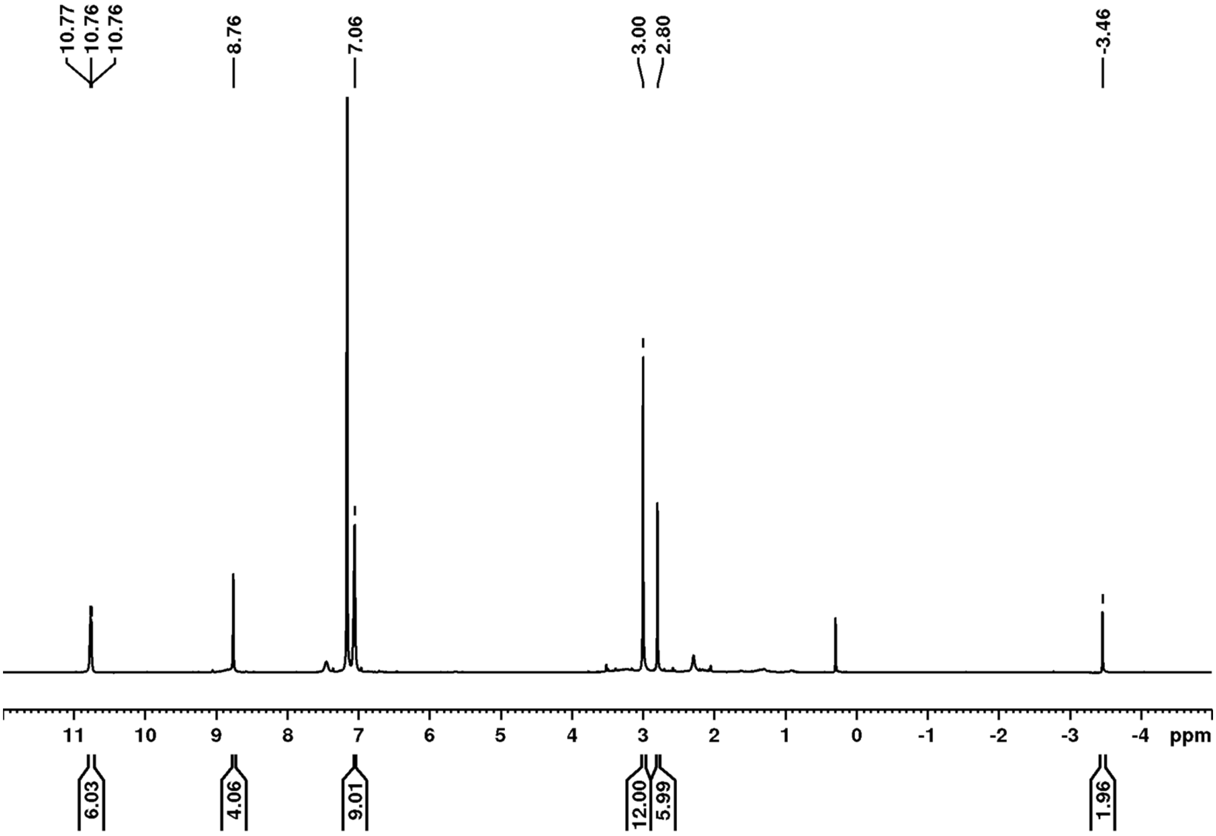

Figure S31: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [WCl_4(IMes)(PPh_3)] **15**.

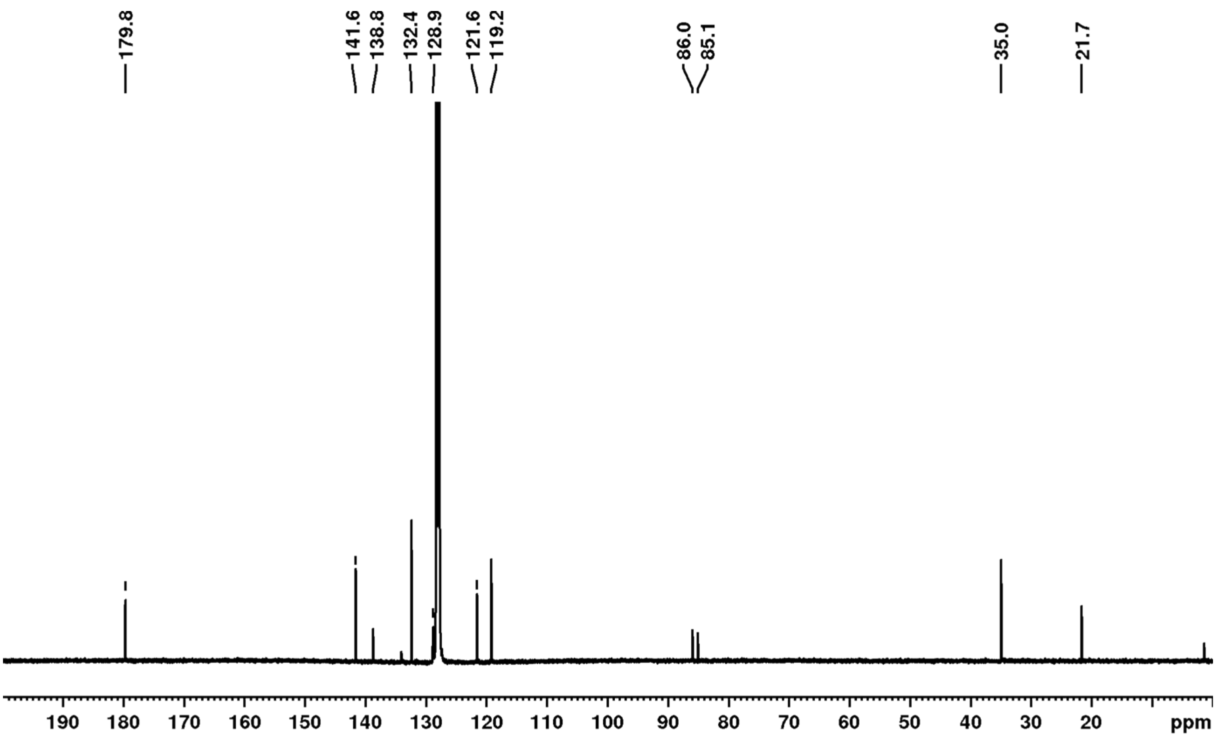

Figure S32: $^{13}C\{^1H\}$ NMR spectrum (100.6 MHz, C_6D_6, 298 K) of [WCl$_4$(IMes)(PPh$_3$)] **15**.

[WCl$_4$(IDipp)(PMe$_3$)] **16**

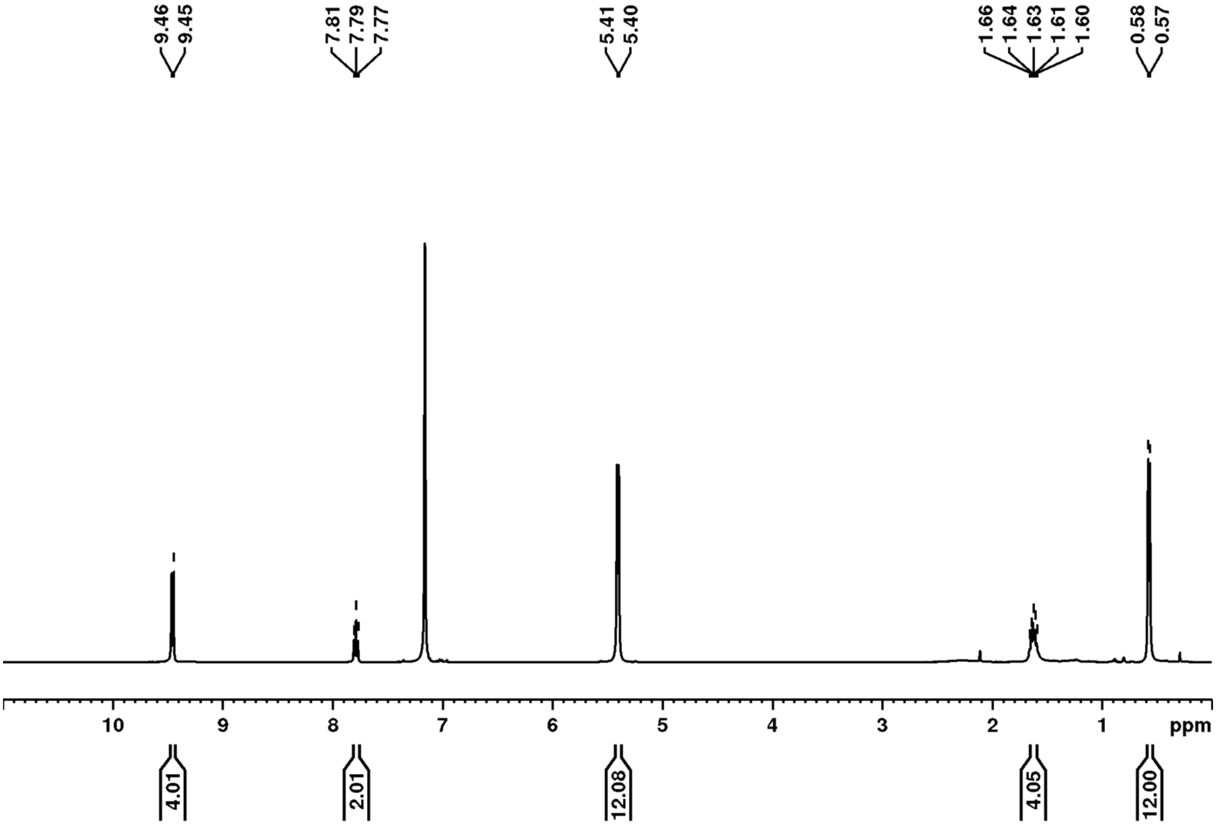

Figure S33: ^1H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [WCl$_4$(IDipp)(PMe$_3$)] **16** from 0 to 11 ppm.

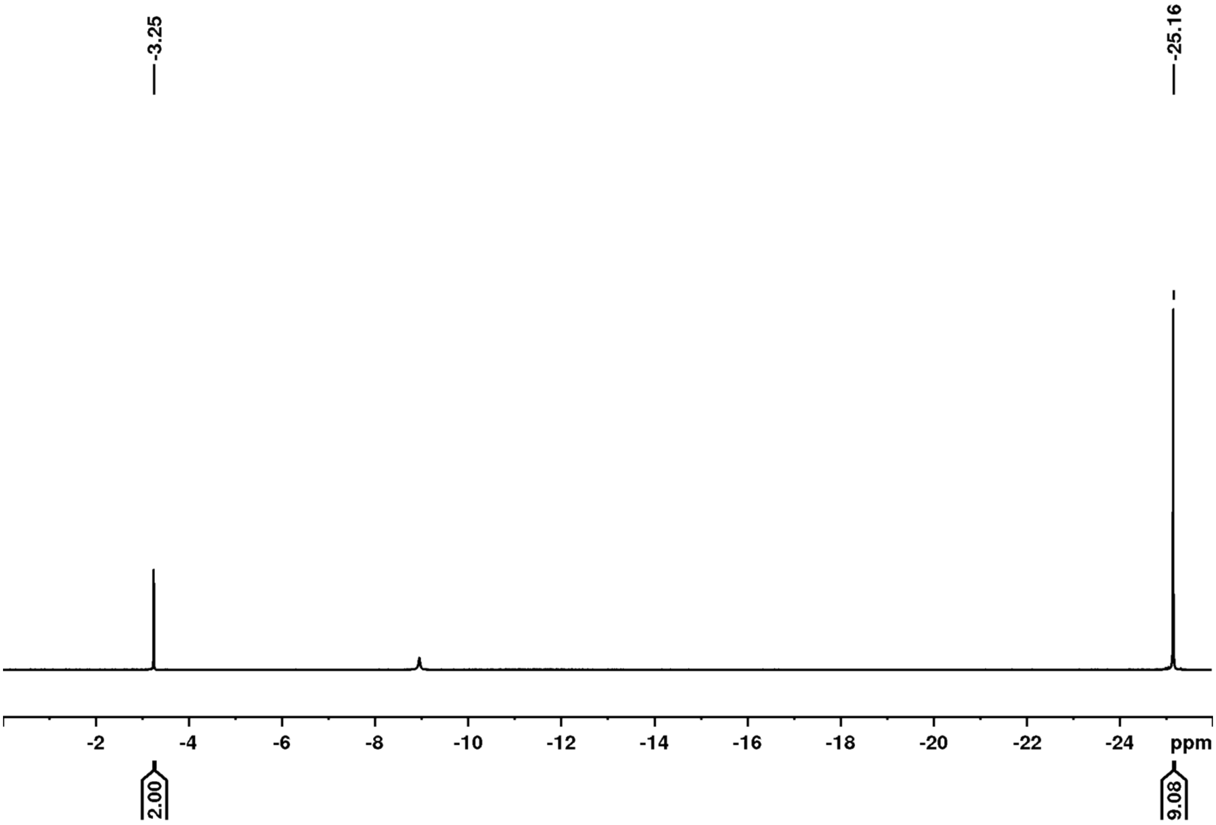

Figure S34: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [WCl_4(IDipp)(PMe_3)] **16** from -26 to 0 ppm.

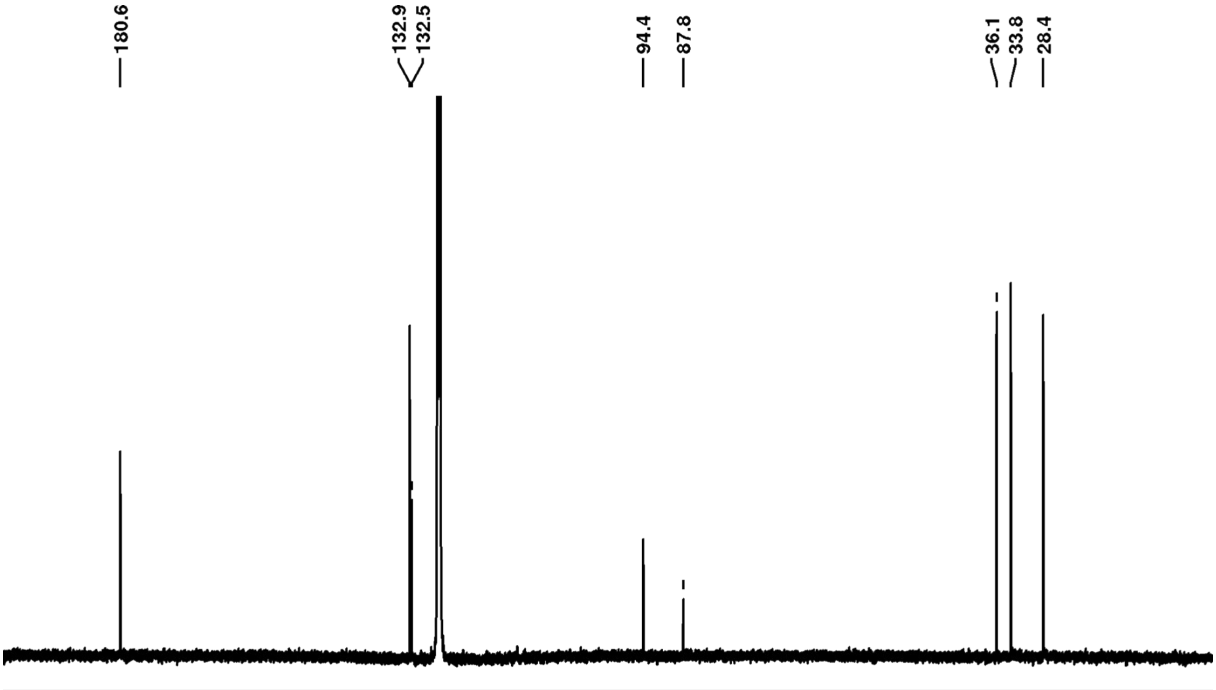

Figure S35: ^{13}C{^{1}H} NMR spectrum (100.6 MHz, C_6D_6, 298 K) of [WCl_4(IDipp)(PMe_3)] **16**.

[WCl$_4$(IDipp)(PPh$_3$)] **17**

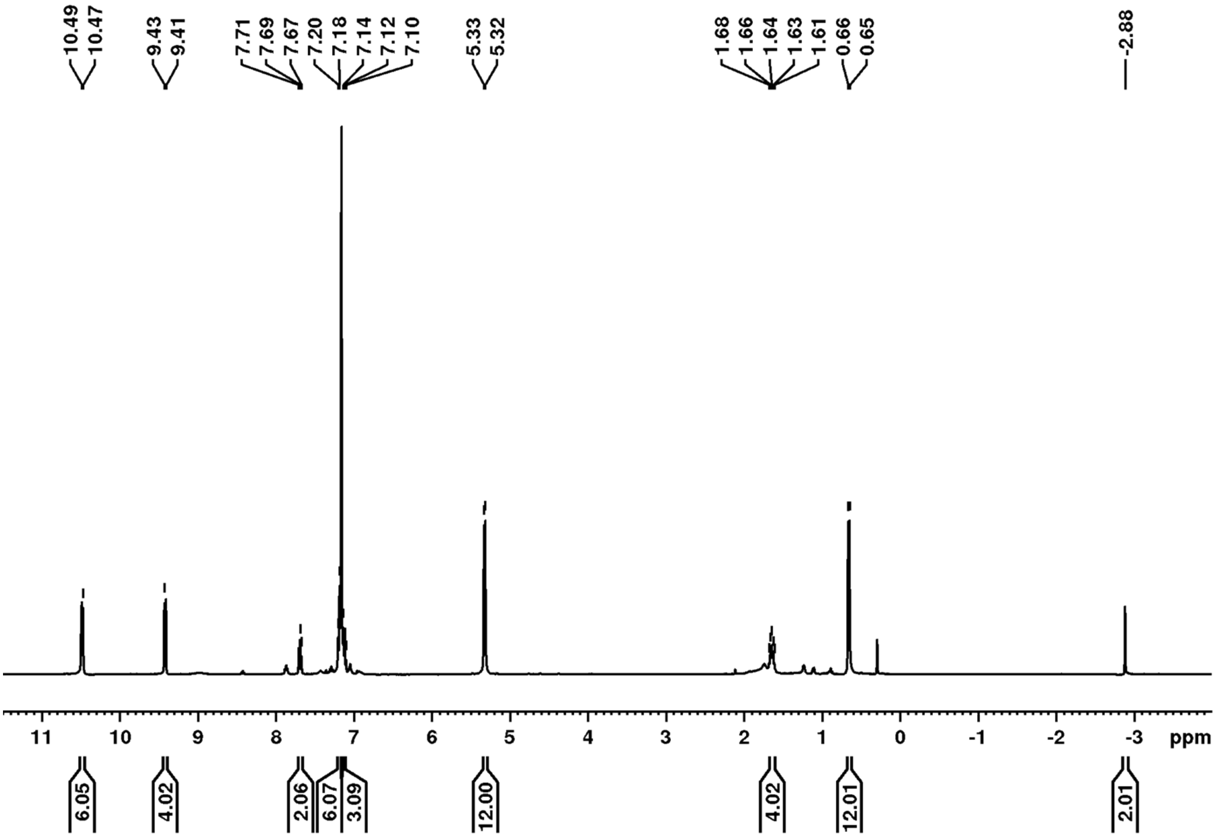

Figure S36: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [WCl$_4$(IDipp)(PPh$_3$)] **17**.

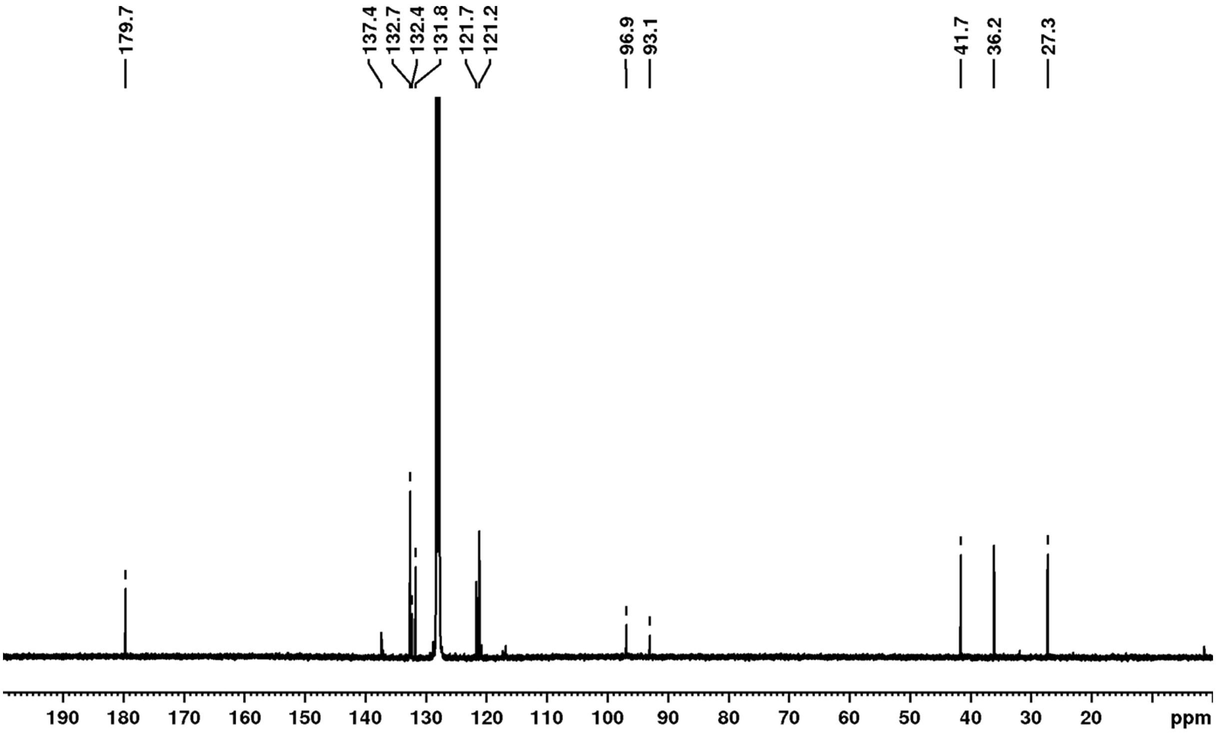

Figure S37: $^{13}C\{^1H\}$ NMR spectrum (100.6 MHz, C_6D_6, 298 K) of [WCl$_4$(IDipp)(PPh$_3$)] **17**.

[MoCl$_4$(IMes)(Py)] **18**

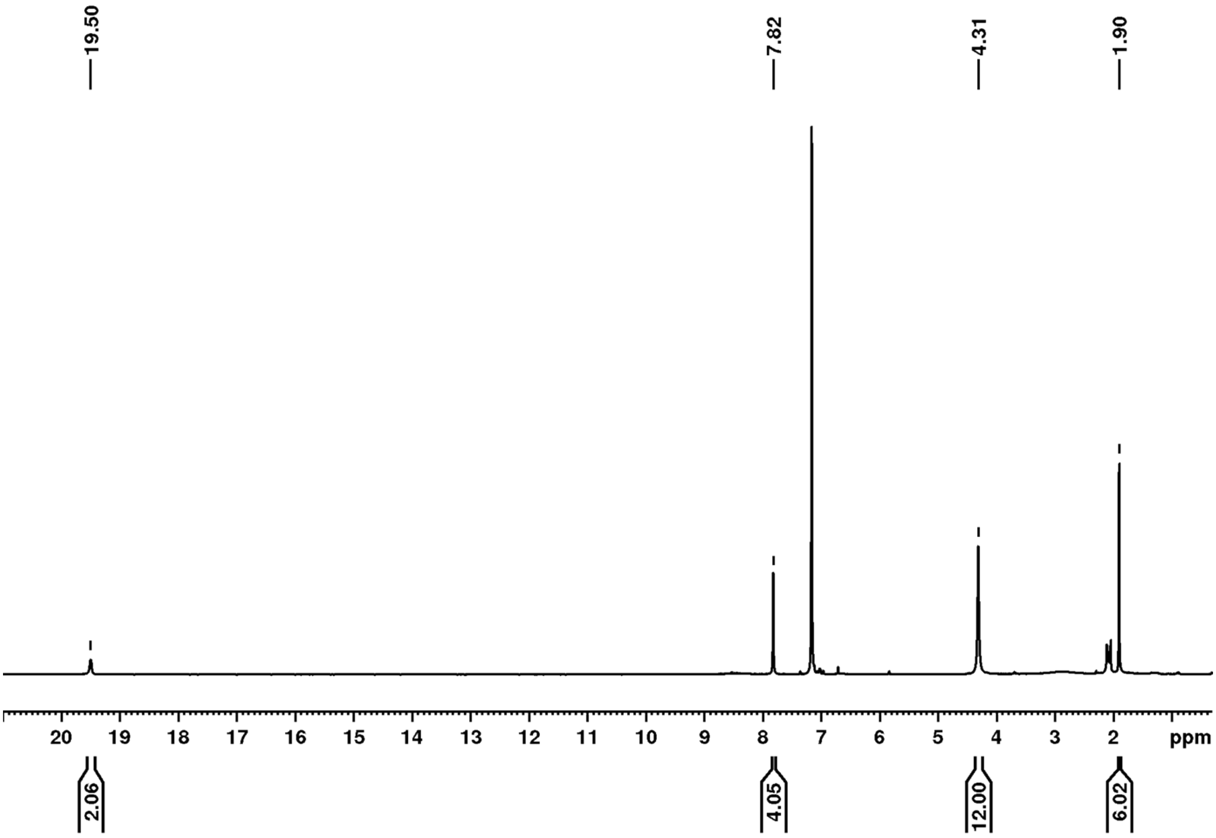

Figure S38: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [MoCl$_4$(IMes)(Py)] **18** from 0 to 21 ppm.

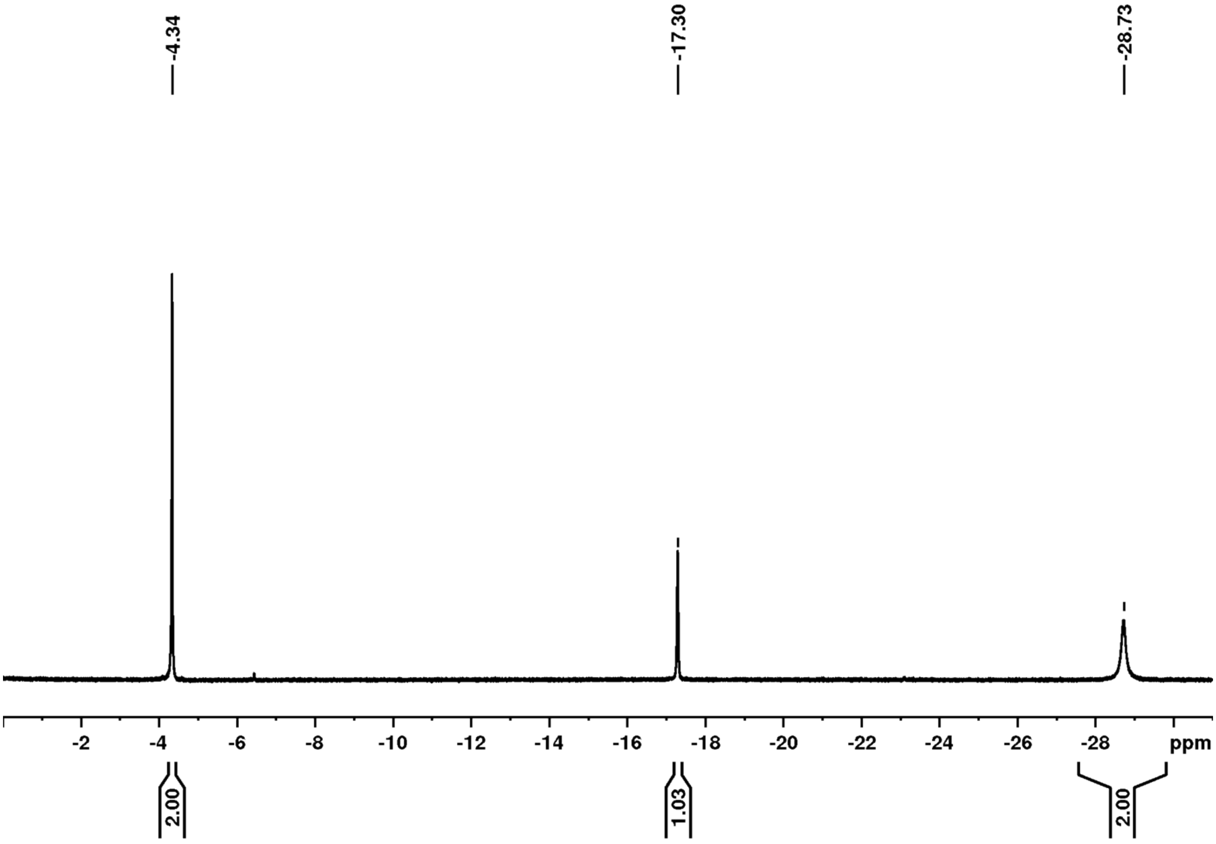

Figure S39: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [MoCl$_4$(IMes)(Py)] **18** from -31 to 0 ppm.

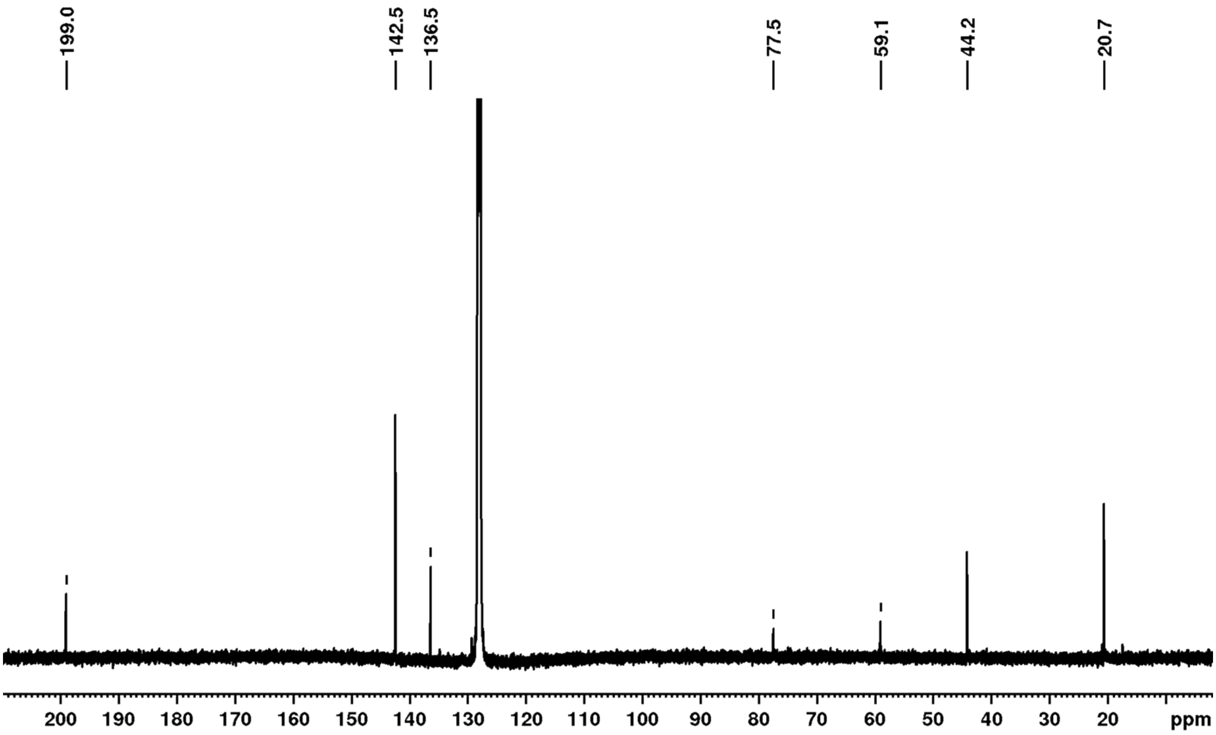

Figure S40: $^{13}C\{^1H\}$ NMR spectrum (100.6 MHz, C_6D_6, 298 K) of [$MoCl_4$(IMes)(Py)] **18**.

[$MoCl_4$(IMes)(DMAP)] **19**

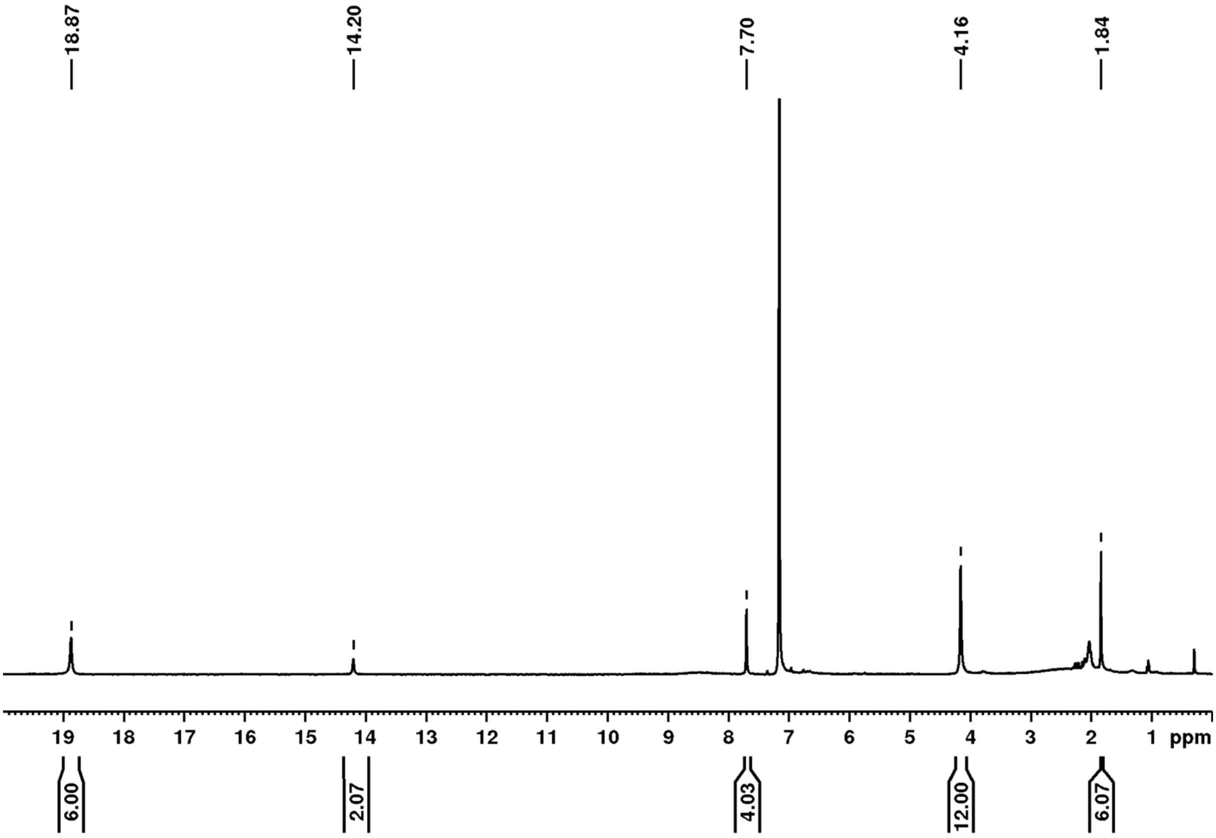

Figure S41: ^1H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [$MoCl_4$(IMes)(DMAP)] **19** from 0 to 20 ppm.

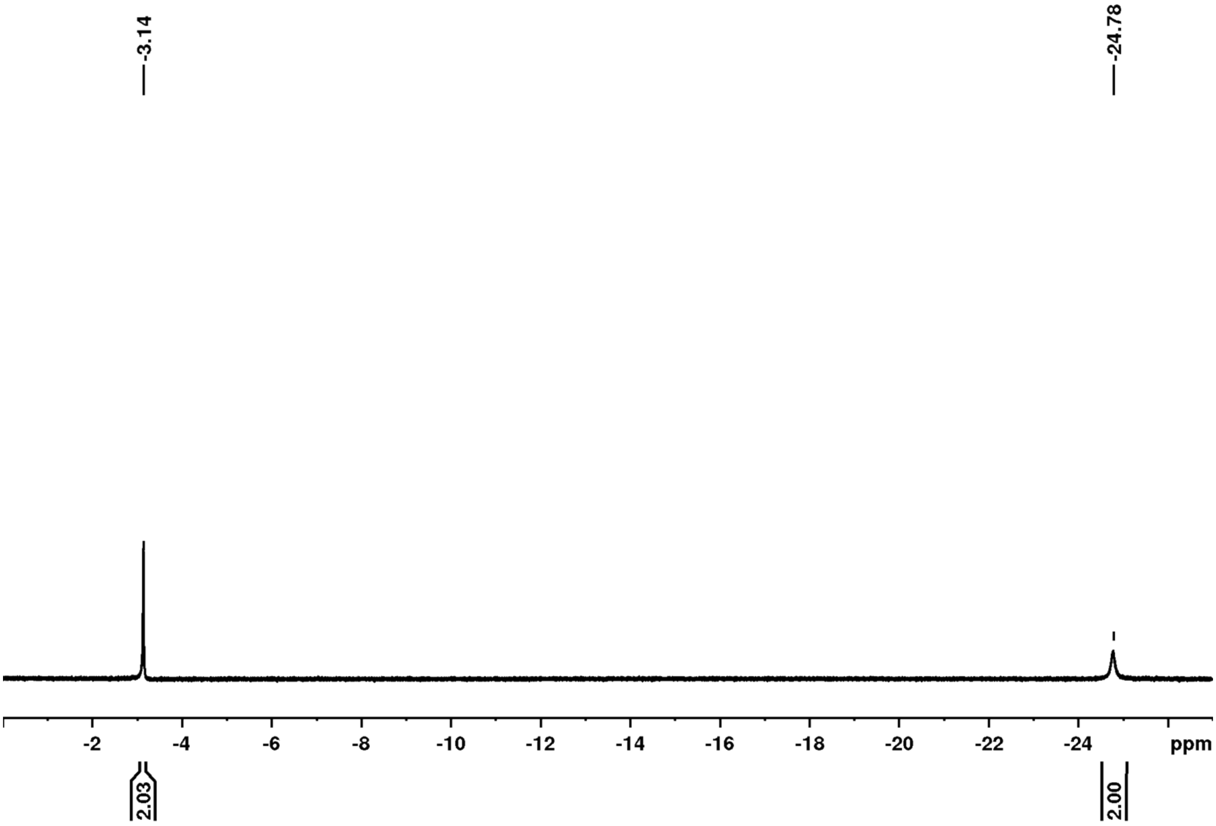

Figure S42: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [MoCl$_4$(IMes)(DMAP)] **19** from -27 to 0 ppm.

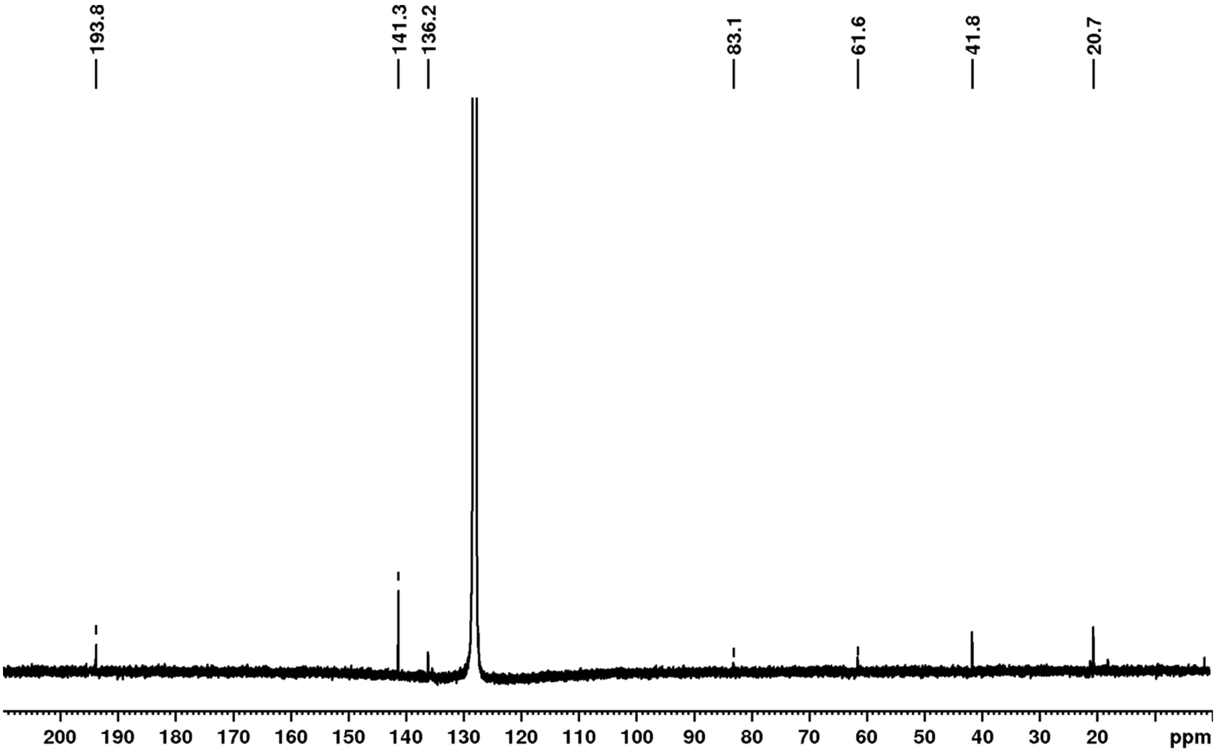

Figure S43: ^{13}C{^{1}H} NMR spectrum (100.6 MHz, C_6D_6, 298 K) of [MoCl$_4$(IMes)(DMAP)] **19**.

[MoCl$_4$(IDipp)(Py)] **20**

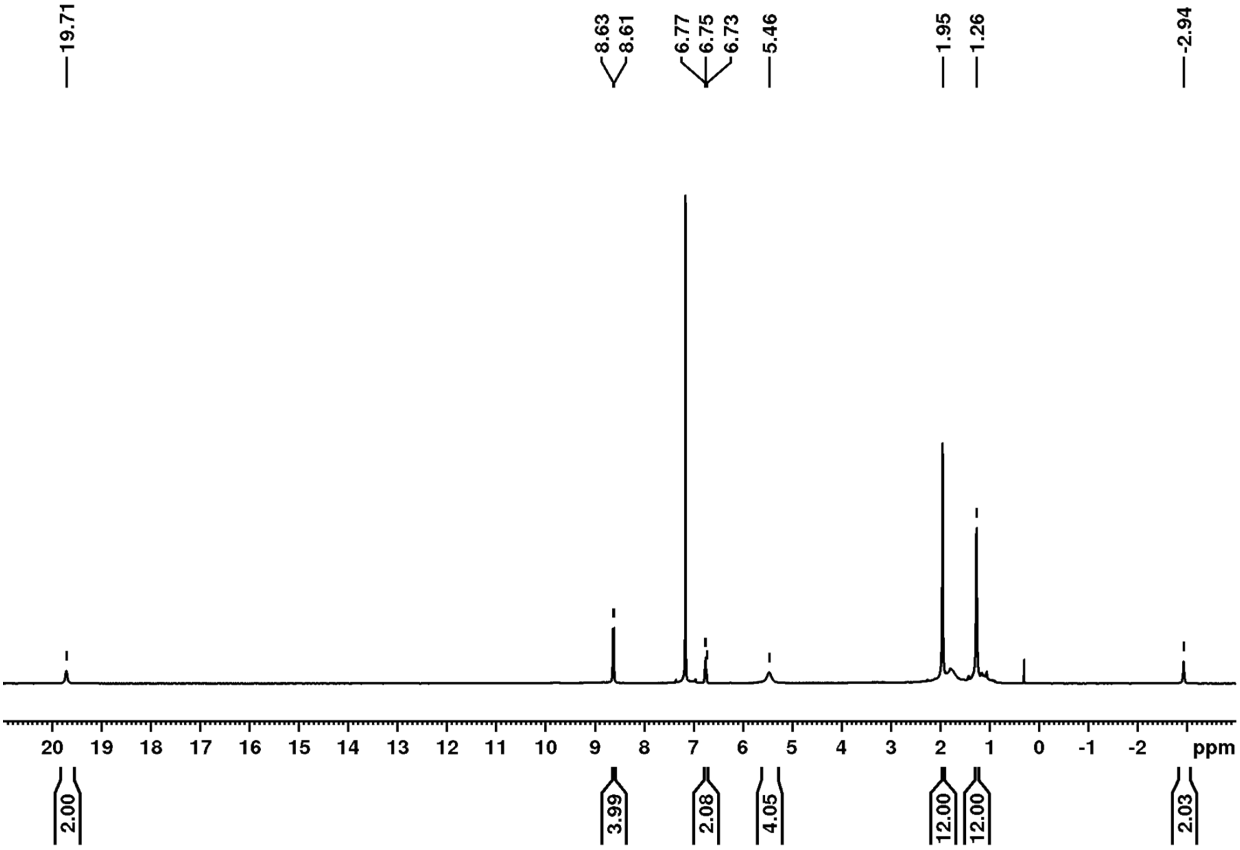

Figure S44: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [MoCl$_4$(IDipp)(Py)] **20** from -4 to 21 ppm.

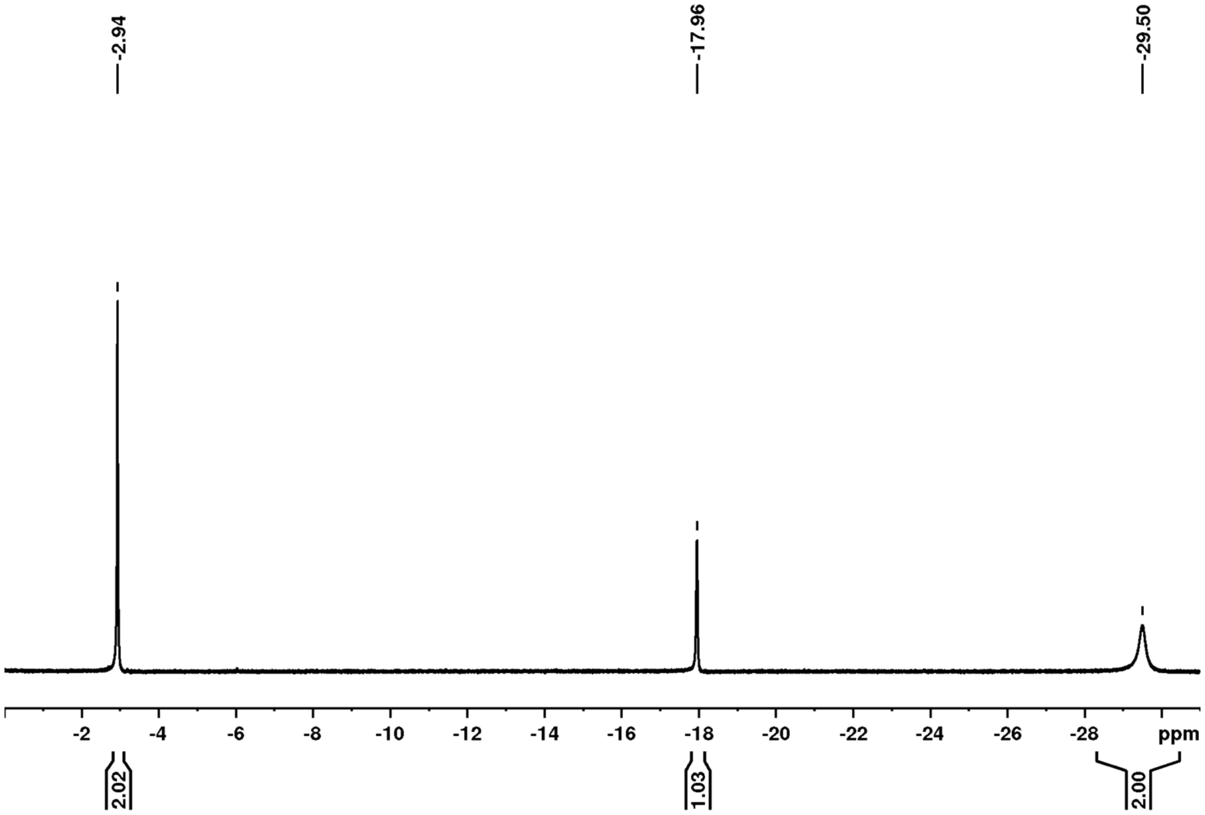

Figure S45: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [MoCl$_4$(IDipp)(Py)] **20** from -31 to 0 ppm.

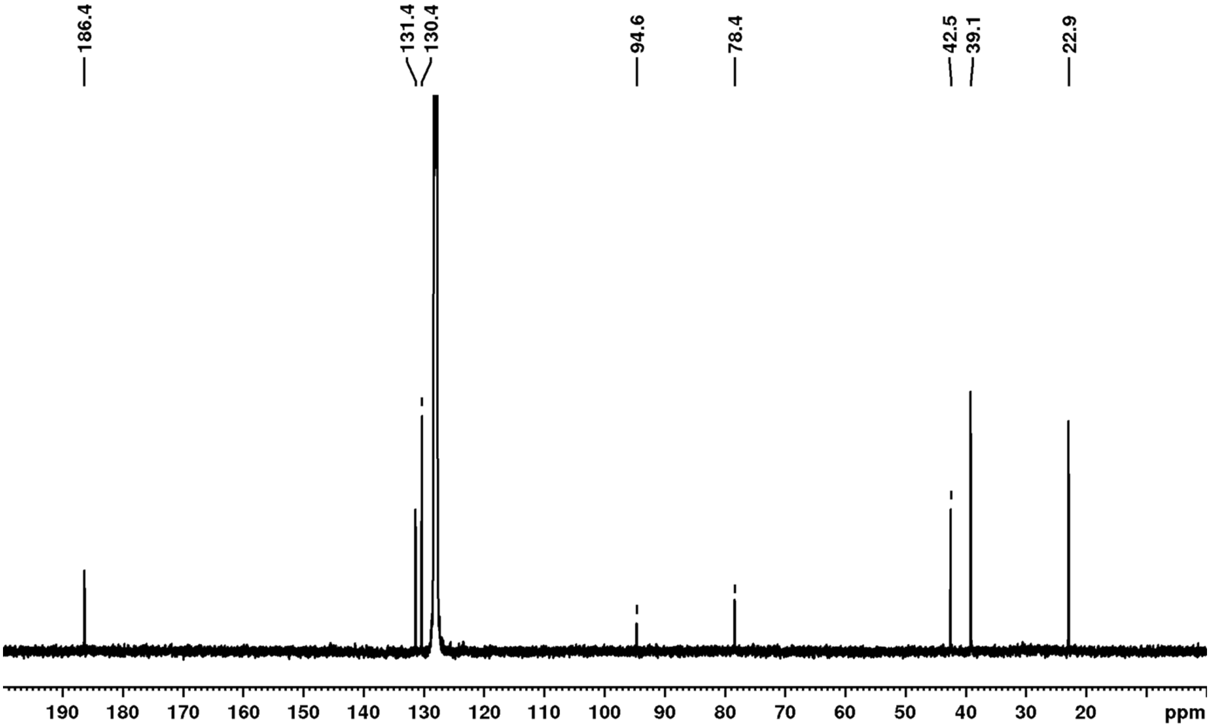

Figure S46: $^{13}C\{^1H\}$ NMR spectrum (100.6 MHz, C_6D_6, 298 K) of $[MoCl_4(IDipp)(Py)]$ **20**.

$[MoCl_4(IDipp)(DMAP)]$ **21**

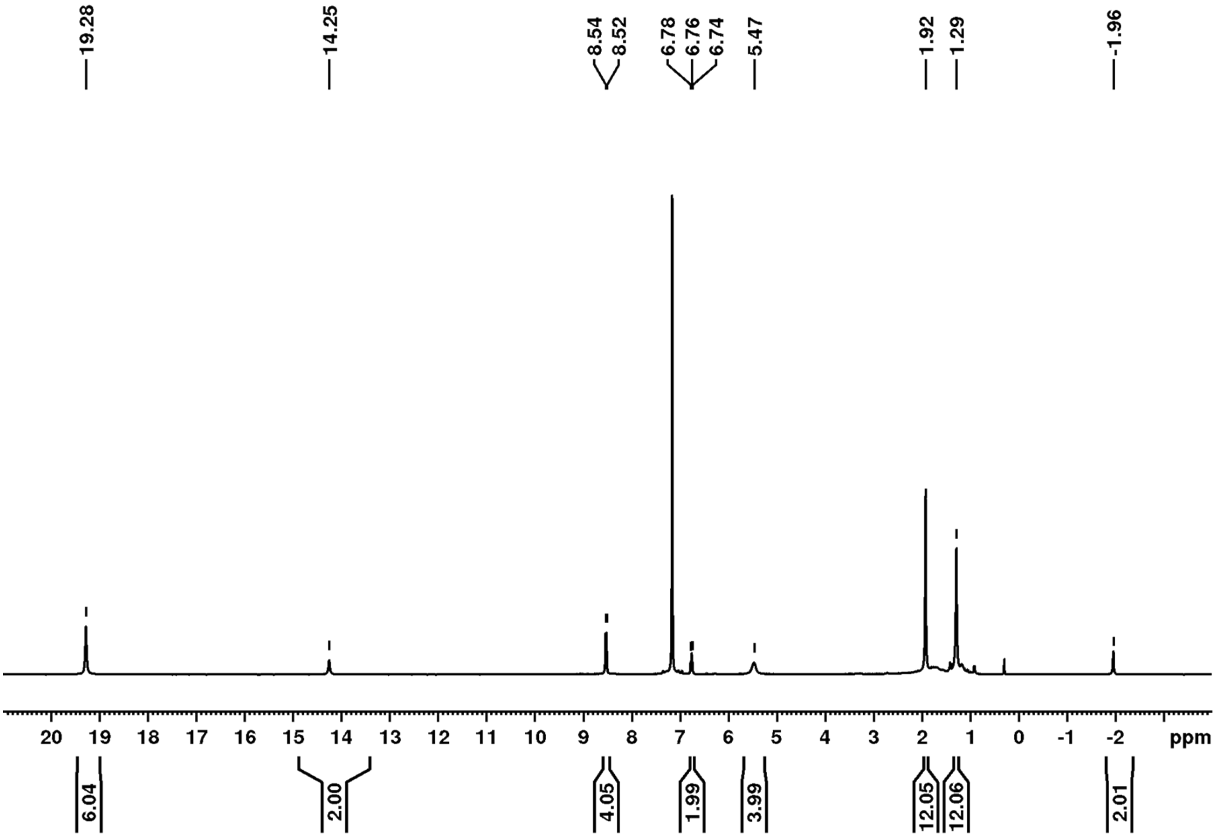

Figure S47: ^1H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of $[MoCl_4(IDipp)(DMAP)]$ **21** from -4 to 21.

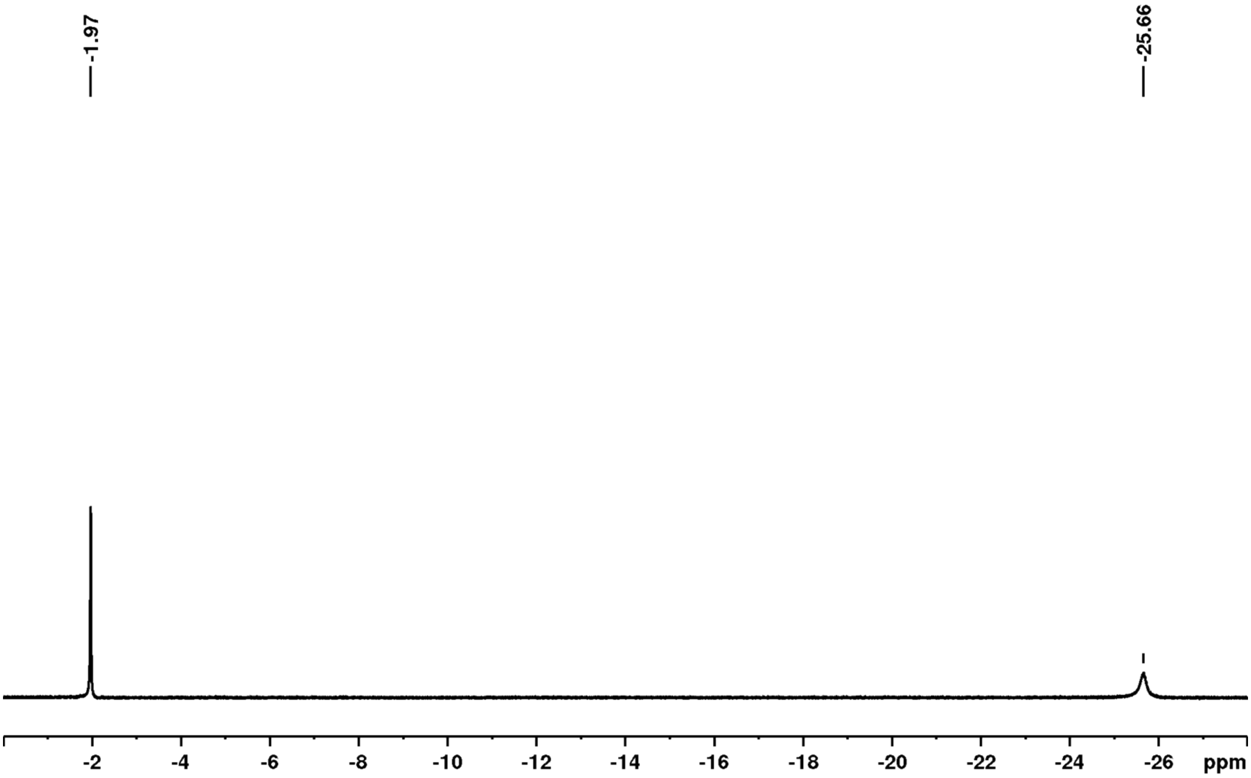

Figure S48: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [$MoCl_4$(IDipp)(DMAP)] **21** from -27 to 0.

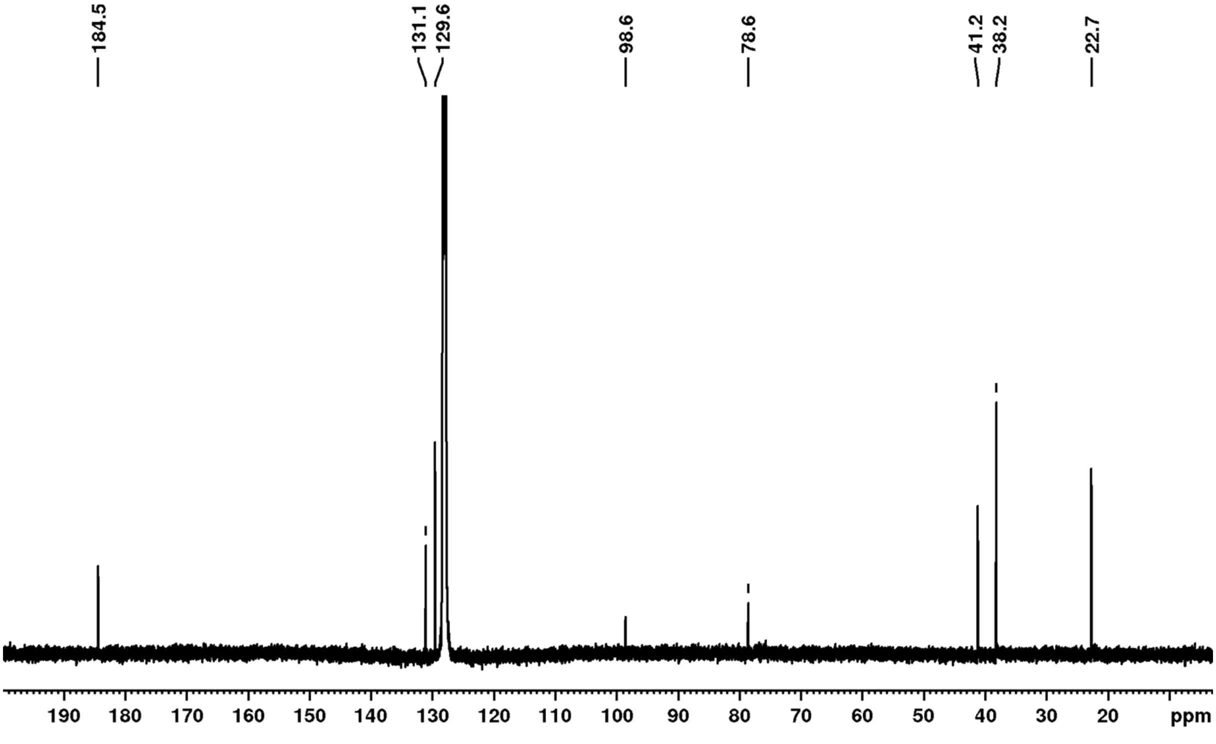

Figure S49: $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, C_6D_6, 298 K) of [$MoCl_4$(IDipp)(DMAP)] **21**.

[WCl$_4$(IMes)(Py)] **22**

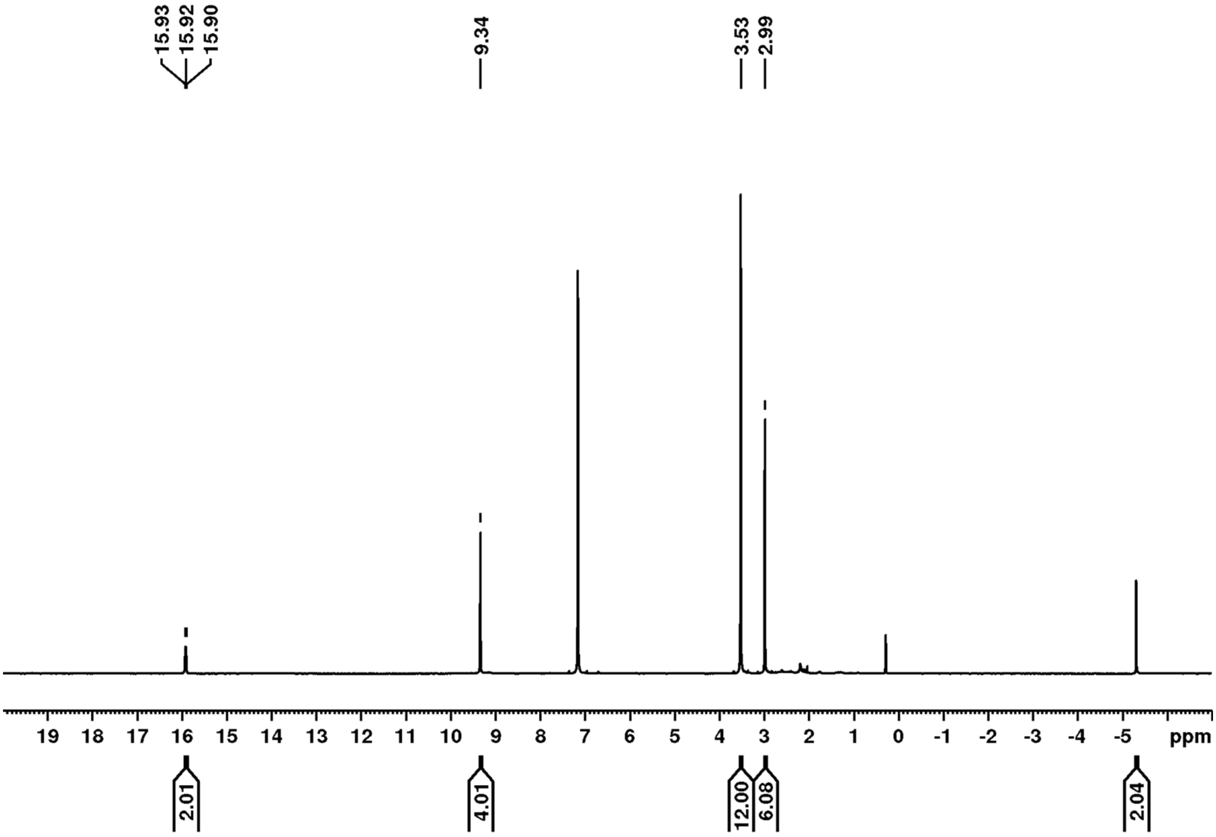

Figure S50: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [WCl$_4$(IMes)(Py)] **22** from 0 to 20 ppm.

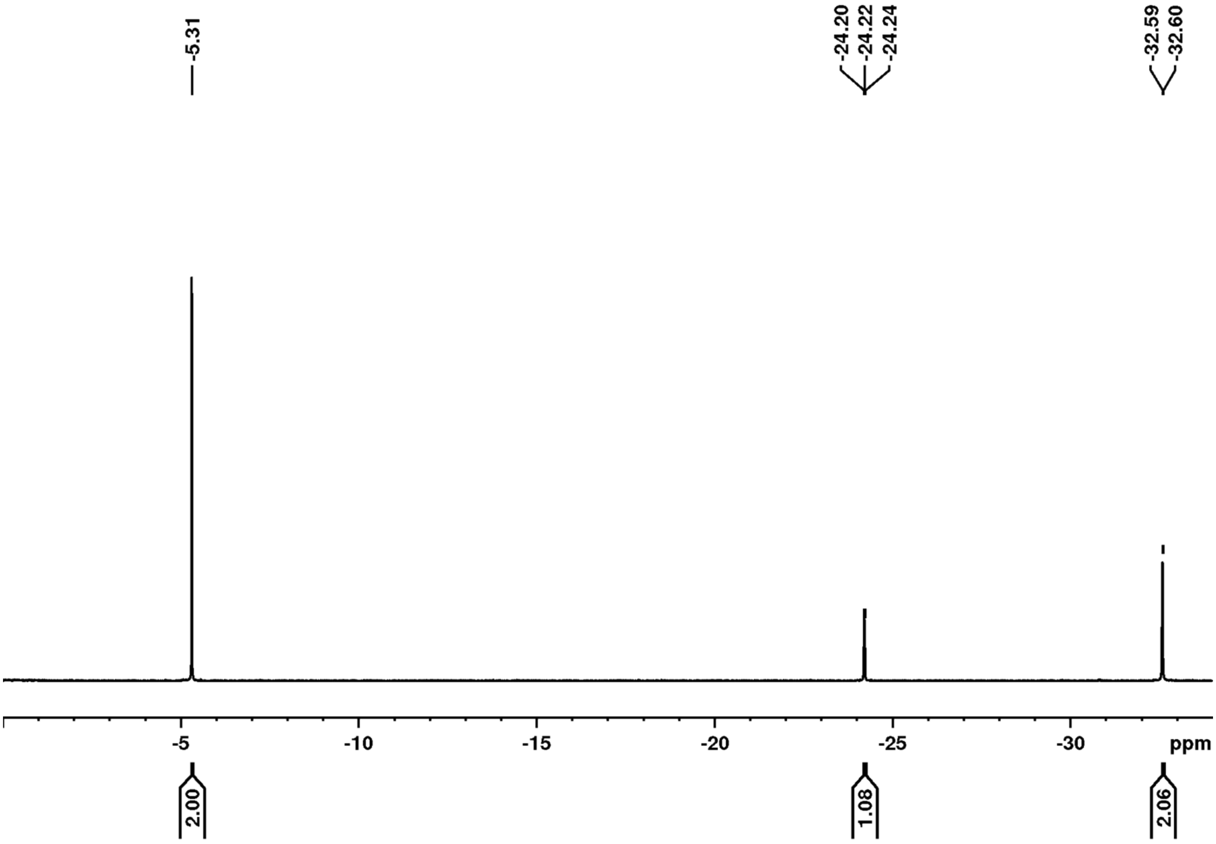

Figure S51: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [WCl$_4$(IMes)(Py)] **22** from -33 to 0 ppm.

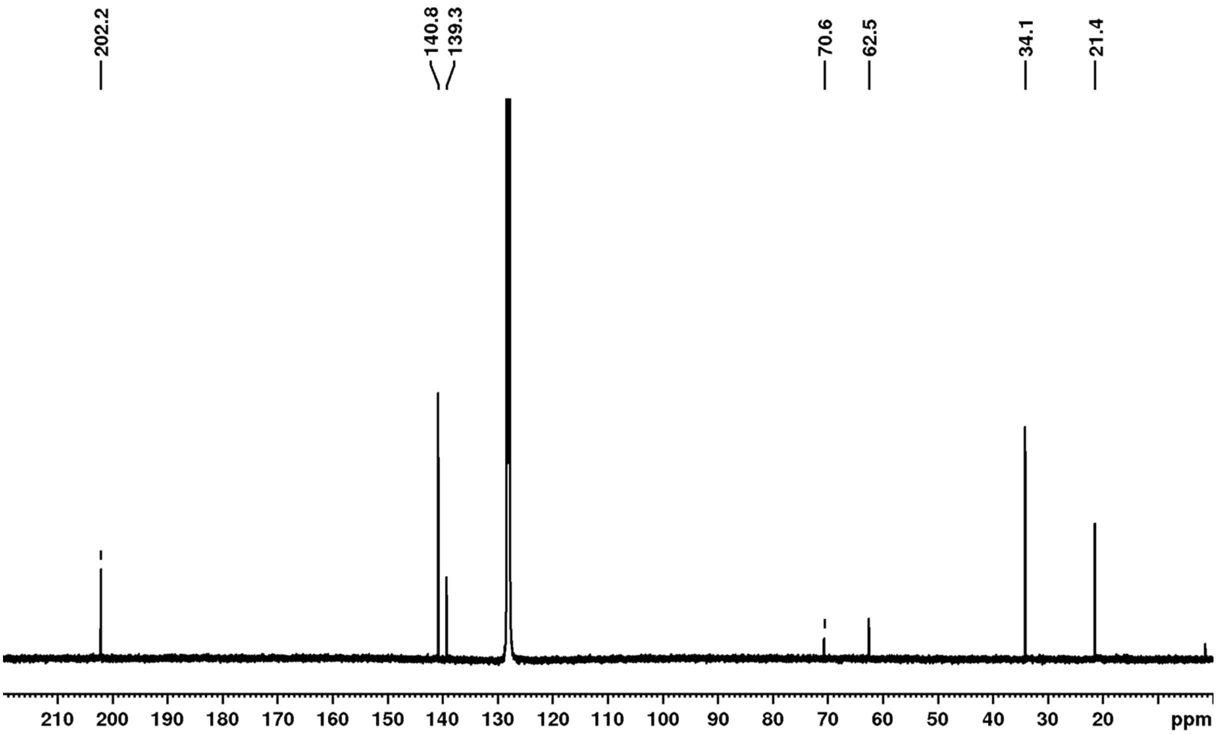

Figure S52: $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, C_6D_6, 298 K) of [WCl_4(IMes)(Py)] **22**.

[WCl_4(IMes)(DMAP)] **23**

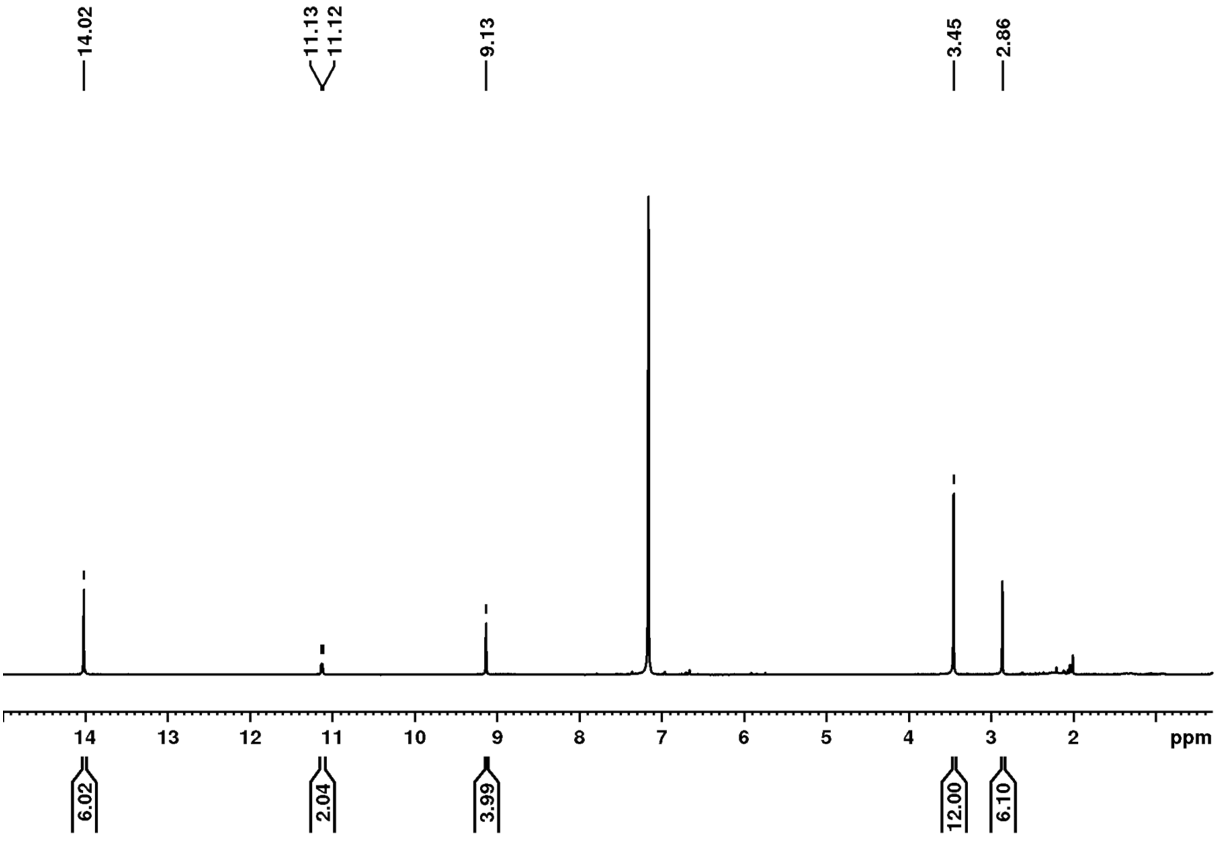

Figure S53: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [WCl_4(IMes)(DMAP)] **23** from 0 to 15 ppm.

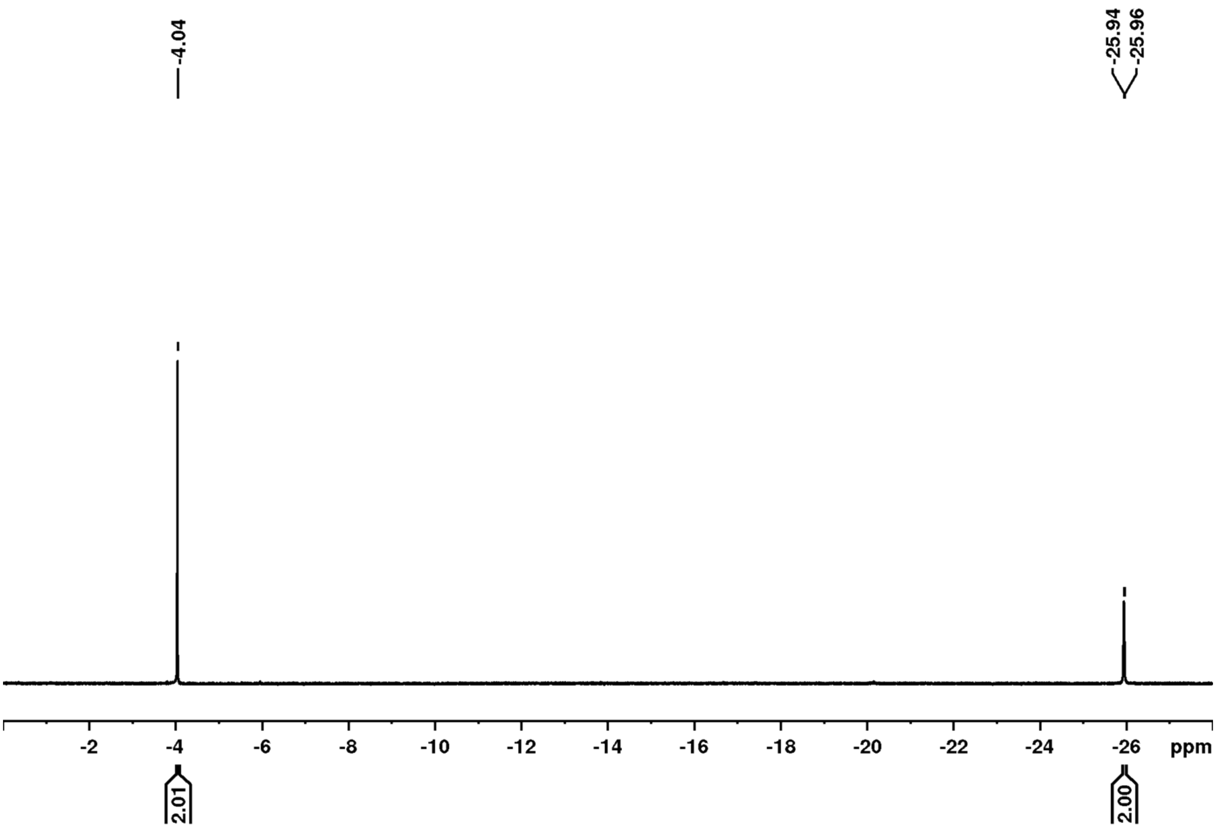

Figure S54: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [WCl_4(IMes)(DMAP)] **23** from -28 to 0 ppm.

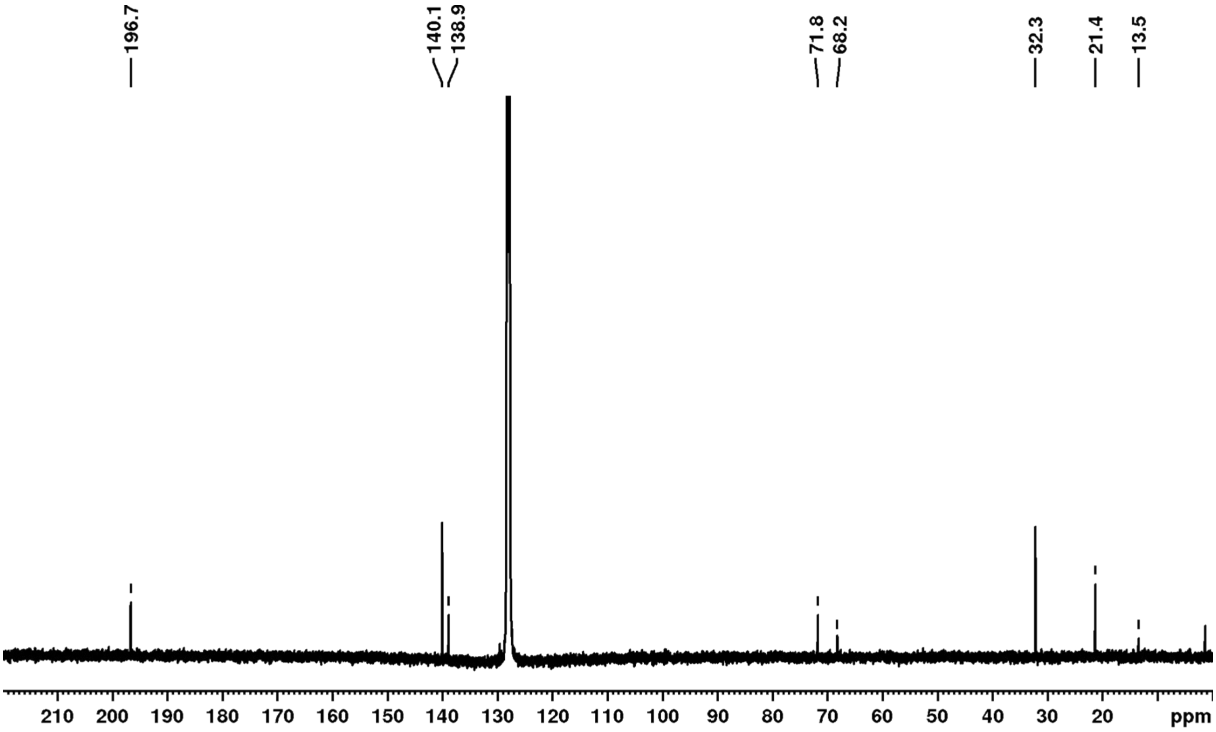

Figure S55: $^{13}C\{^1H\}$ NMR spectrum (100.6 MHz, C_6D_6, 298 K) of [WCl_4(IMes)(DMAP)] **23**.

[WCl$_4$(IDipp)(Py)] **24**

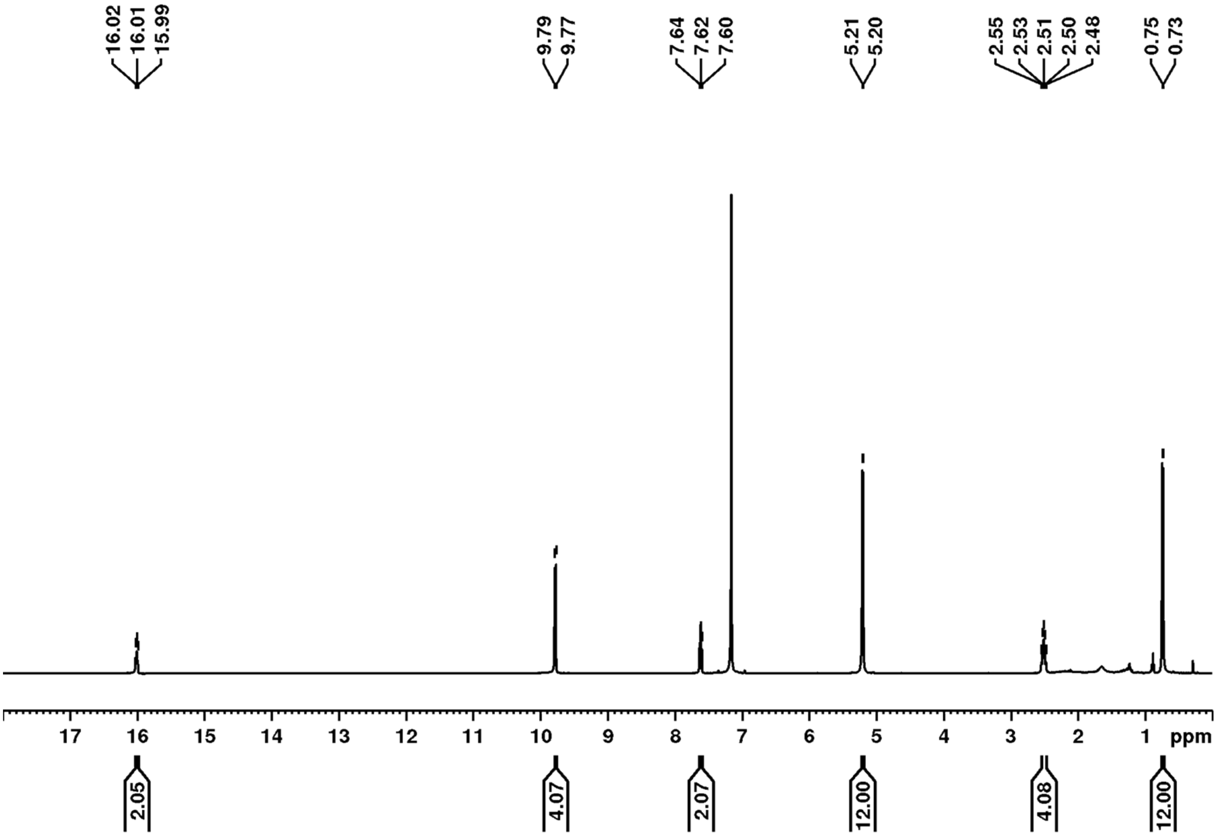

Figure S56: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [WCl$_4$(IDipp)(Py)] **24** from 0 to 18 ppm.

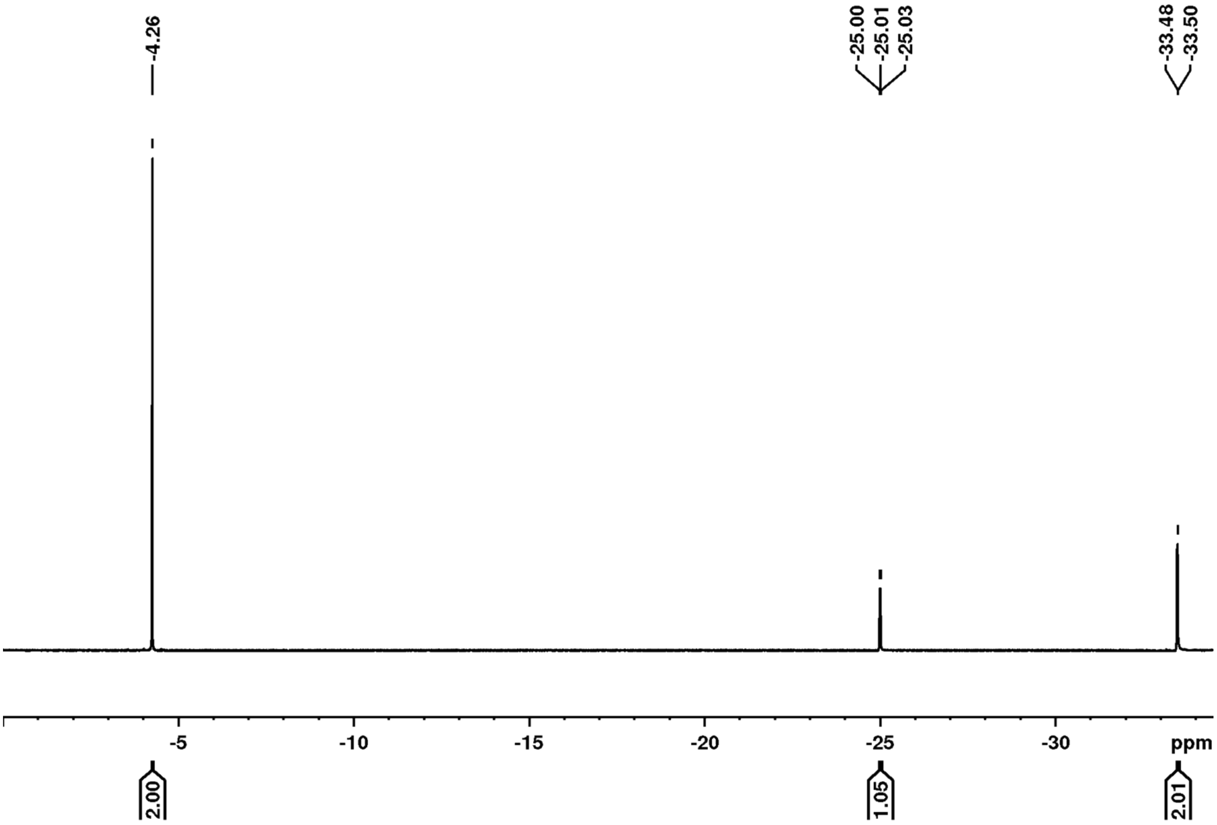

Figure S57: ^{1}H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [WCl$_4$(IDipp)(Py)] **24** from -34.5 to 0 ppm.

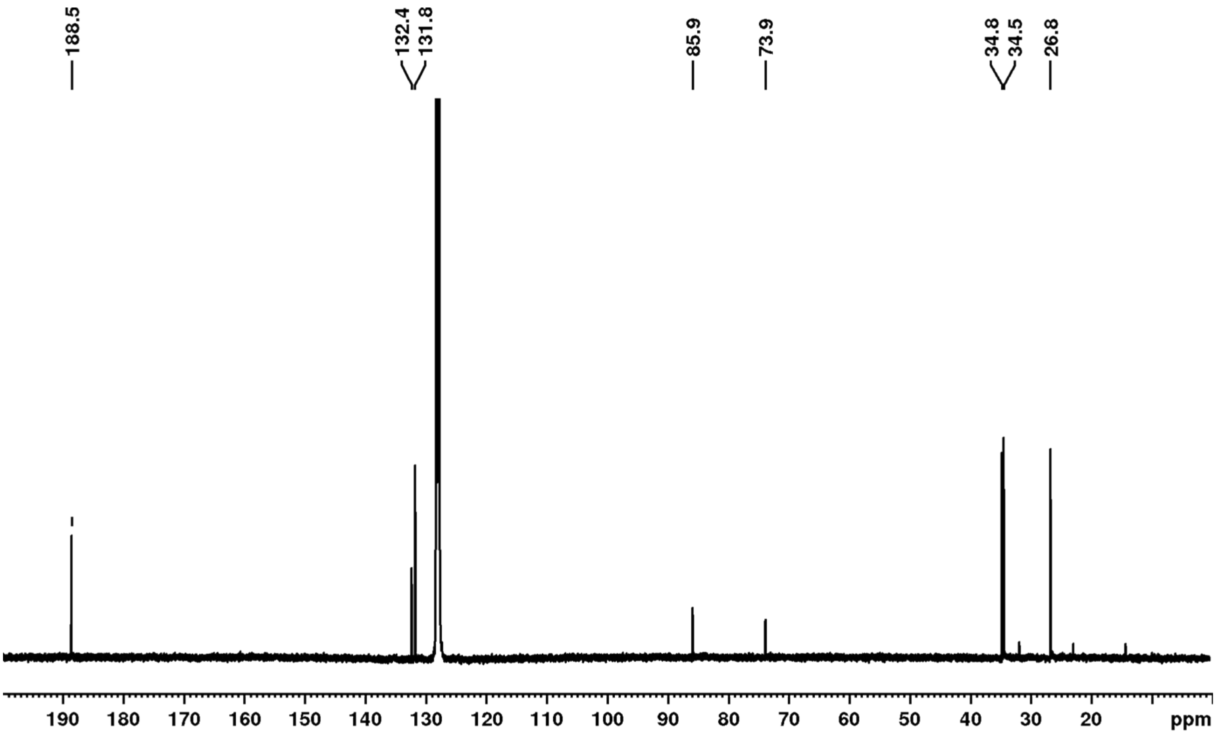

Figure S58: $^{13}C\{^1H\}$ NMR spectrum (100.6 MHz, C_6D_6, 298 K) of [WCl_4(IDipp)(Py)] **24**.

[WCl_4(IDipp)(DMAP)] **25**

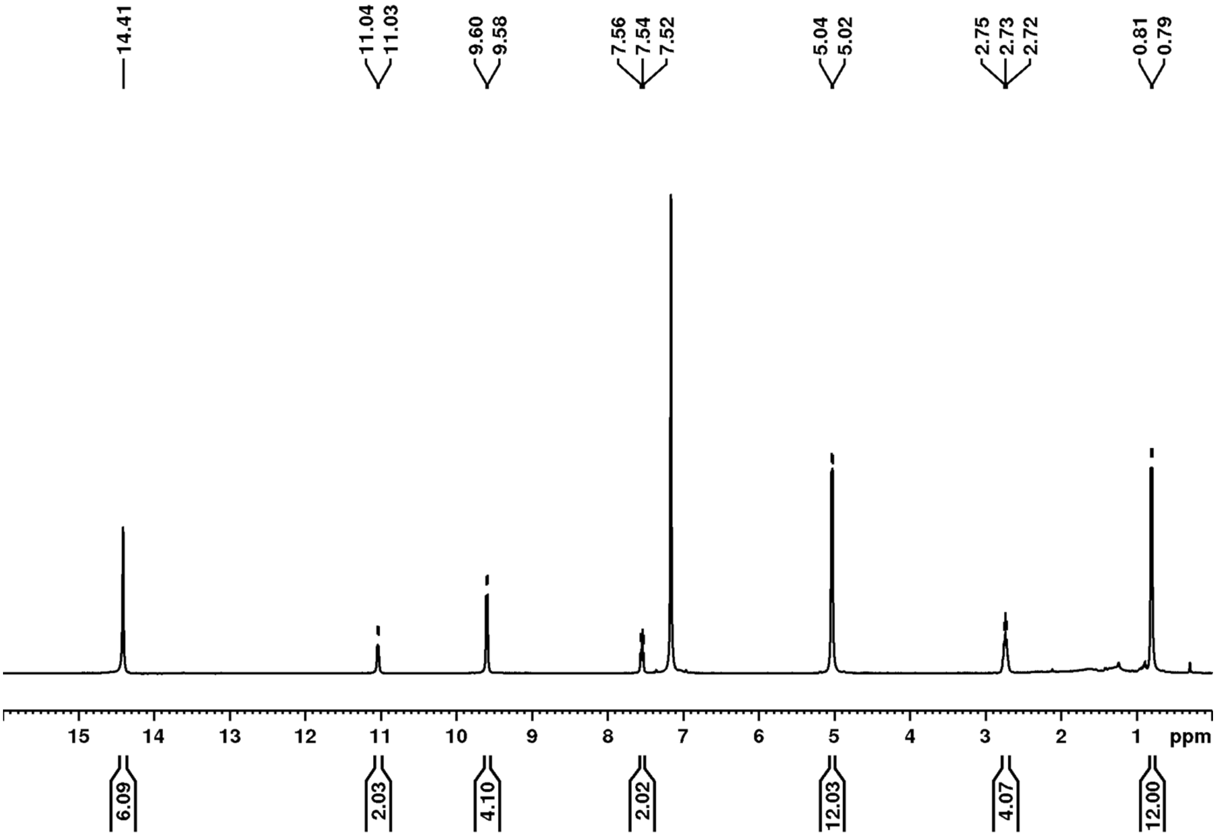

Figure S59: ^1H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [WCl_4(IDipp)(DMAP)] **25** from 0 to 16 ppm.

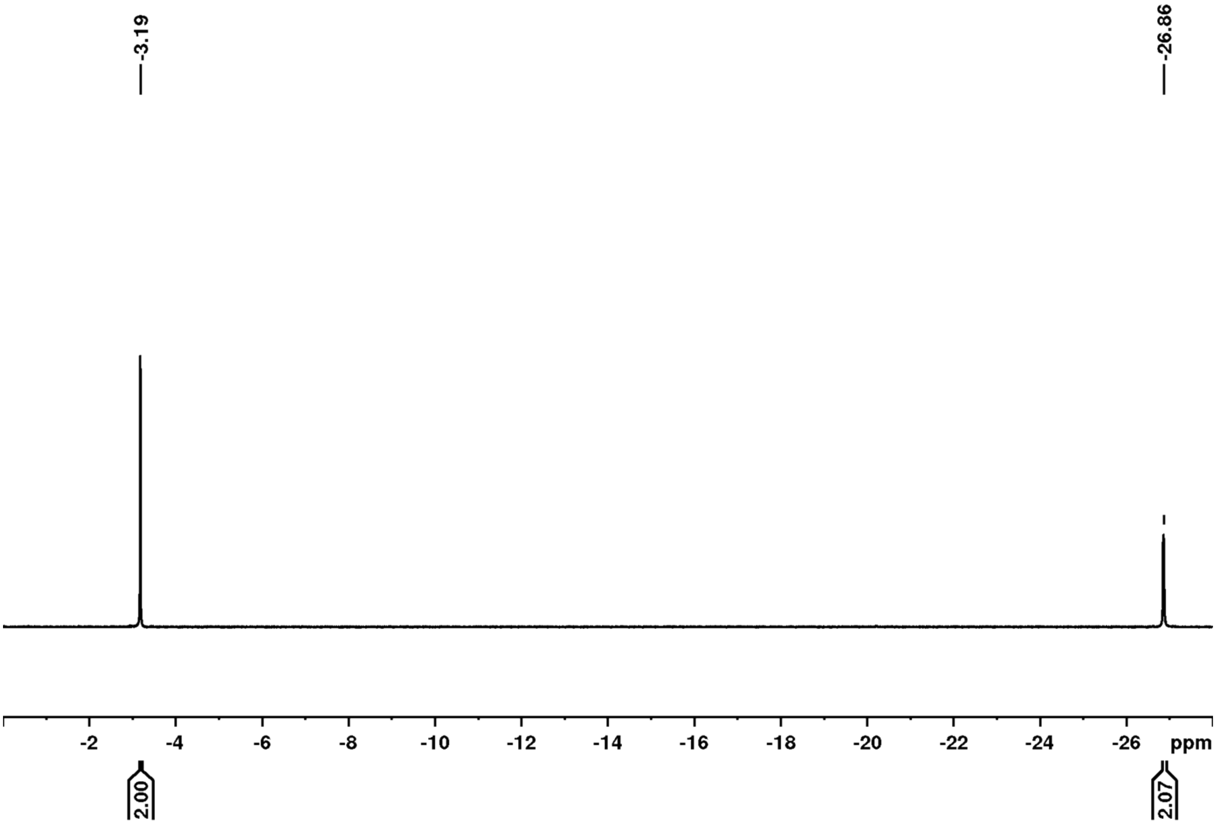

Figure S60: ^1H NMR spectrum (400.1 MHz, C_6D_6, 298 K) of [WCl_4(IDipp)(DMAP)] **25** from -27 to 0 ppm.

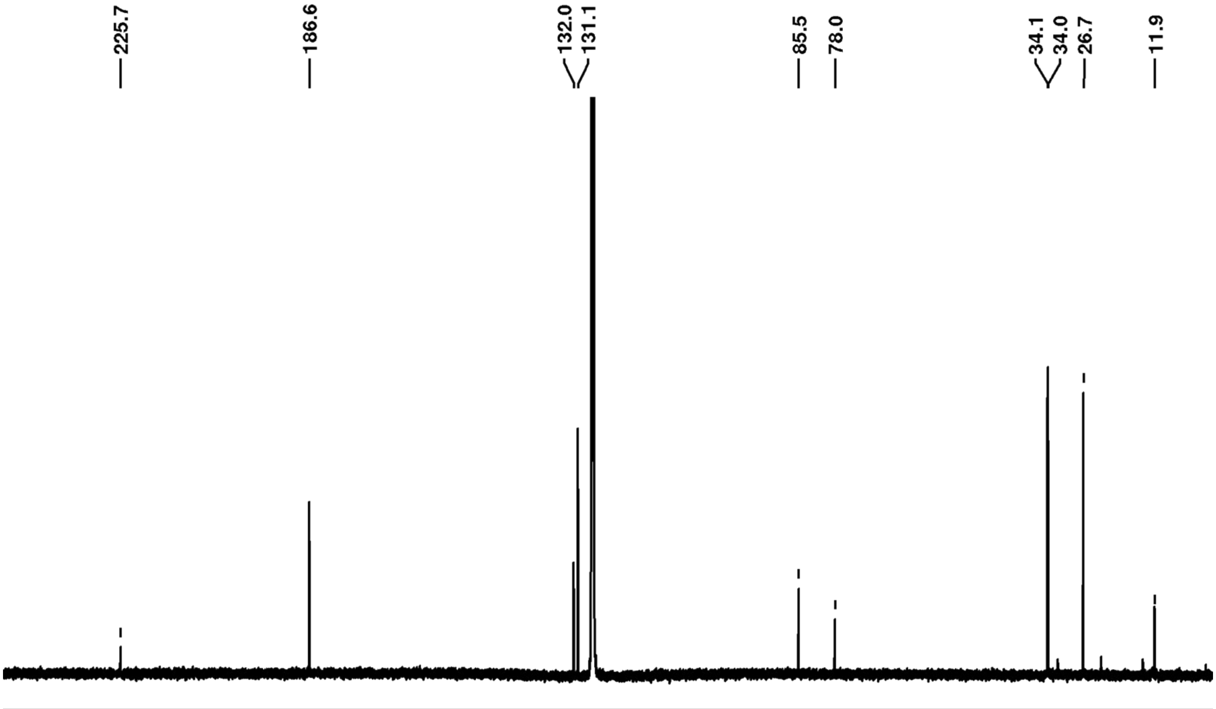

Figure S61: $^{13}C\{^1H\}$ NMR spectrum (100.6 MHz, C_6D_6, 298 K) of [WCl_4(IDipp)(DMAP)] **25**.

2) Crystallographic details

Crystals were immersed in a film of perfluoropolyether oil on a glass fiber MicroMount™ (MiTeGen) and transferred to a Rigaku XtaLAB Synergy-DW diffractometer with HyPix-6000HE detector and monochromated Cu-K_α or Mo-K_α equipped with an Oxford Cryo 800 cooling unit. Data were collected at 100 K. The images were processed with the Crysalis software packages and equivalent reflections were merged. Corrections for Lorentz-polarization effects and absorption were performed if necessary and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. The structures were solved by using the ShelXTL software package.[S1] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were usually assigned to idealized positions and were included in structure factors calculations.
Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no.s CCDC 2214150 (**1**), CCDC 2214149 (**2**), CCDC 2214163 (**3**), CCDC 2214155 (**4**), CCDC 2214148 (**5**), CCDC 2214152 (**6**), CCDC 2214154 (**7**), CCDC 2214151 (**8**), CCDC 2214153 (**11**), CCDC 2214156 (**13**), CCDC 2214162 (**15**), CCDC 2214160 (**16**), CCDC 2214161 (**18**), CCDC 2214157 (**22**), CCDC 2214158 (**23**), CCDC 2214159 (**25**).

Experimental crystal data collection of **[MoCl$_4$(IMes)$_2$] 1**
$C_{48}H_{54}Cl_4MoN_4$, M$_r$ = 924.69, T = 100.00(2) K, wavelength = 1.54184 Å, triclinic space group P$\bar{1}$, a = 12.4857(1) Å, b = 12.6008(2) Å, c = 15.2630(2) Å, α = 76.030(1)°, β = 82.051(1)°, γ = 75.788(1)°, V = 2250.99(5) Å^3, Z = 2, *ρ(calcd)* = 1.364 g/cm^3, *μ* = 4.851 mm^{-1}, F(000) = 960, 46566 reflections in -15 ≤ h ≤ 15, -15 ≤ k ≤ 14,-19 ≤ l ≤ 18 measured in 2.994 < θ < 77.612°, completeness 99.9 %, 9443 independent reflections, 8913 reflections observed in [I>2sigma(I)], 526 parameters, 0 restraints, R indices (all data) R^1 = 0.0313, wR^2 = 0.0796, final R indices [I>2sigma(I)] R$_1$ = 0.0299, wR$_2$ = 0.0786, largest difference peak and hole 0.388 and -0.791 eA^{-3}, GooF = 1.084.

Experimental crystal data collection of **[MoCl$_4$(IDipp)$_2$] 2**
$C_{60}H_{78}Cl_4MoN_4$, M$_r$ = 1093.00, T = 100.00(2) K, wavelength = 1.54184 Å, trigonal space group R$\bar{3}$, a = 47.2641(3) Å, b = 47.2641(3) Å, c = 14.0081(1) Å, α = 90°, β = 90°, γ = 120°, V = 27100.2(4) Å^3, Z = 18, *ρ(calcd)* = 1.206 g/cm^3, *μ* = 3.699 mm^{-1}, F(000) = 10368, 59825 reflections in -58 ≤ h ≤ 53, -45 ≤ k ≤ 58, -14 ≤ l ≤ 17 measured in 3.239 < θ < 77.740°, completeness 99.6 %, 12565 independent reflections, 11652 reflections observed in [I>2sigma(I)], 598 parameters, 31 restraints, R indices (all data) R^1 = 0.0366, wR^2 = 0.0906, final R indices [I>2sigma(I)] R$_1$ = 0.0341, wR$_2$ = 0.0891, largest difference peak and hole 0 1.422 and -0.509 eA^{-3}, GooF = 1.030.

Experimental crystal data collection of **[WCl$_4$(IMes)$_2$] 3**
$C_{48}H_{54}Cl_4N_4W$, M$_r$ = 1012.59, T = 100.00(10) K, wavelength = 0.71073 Å, triclinic space group P$\bar{1}$, a = 12.5166(1) Å, b = 12.6137(1) Å, c = 15.29640(10) Å, α = 76.148(1)°, β = 81.794(1)°, γ = 75.425(1)°, V = 2260.55(3) Å^3, Z = 2, *ρ(calcd)* = 1.488 g/cm^3, *μ* = 2.829 mm^{-1}, F(000) = 1024, 94116 reflections in -15 ≤ h ≤ 15, -15 ≤ k ≤ 15,-19 ≤ l ≤ 19 measured in 1.952 < θ < 26.371°, completeness 100.0 %, 9248 independent reflections, 9002 reflections observed in [I>2sigma(I)], 526 parameters, 0 restraints, R indices (all

data) R^1 = 0.0232, wR^2 = 0.0457, final R indices [I>2sigma(I)] R$_1$ = 0.0224, wR$_2$ = 0.0454, largest difference peak and hole 0.943 and -1.385 eA^{-3}, GooF = 1.030.

Experimental crystal data collection of **[WCl$_4$(IDipp)$_2$] 4**
C$_{60}$H$_{78}$Cl$_4$N$_4$W, M$_r$ = 1180.91, T = 100.00(2) K, wavelength = 0.71073 Å, trigonal space group R$\bar{3}$, a = 47.1426(4) Å, b = 47.1426(4) Å, c = 13.9660(1) Å, α = 90°, β = 90°, γ = 120°, V = 26880.0(5) Å^3, Z = 18, *ρ(calcd)* = 1.313 g/cm^3, *μ* = 2.151 mm^{-1}, F(000) = 10944, 66288 reflections in -59≤ h≤58, -64≤k≤ 60, -19 ≤ l ≤ 17 measured in 1.967 < θ < 29.683°, completeness 99.9 %, 14819 independent reflections, 13840 reflections observed in [I>2sigma(I)], 608 parameters, 0 restraints, R indices (all data) R^1 = 0.0211, wR^2 = 0.0478, final R indices [I>2sigma(I)] R$_1$ = 0.0187, wR$_2$ = 0.0472, largest difference peak and hole 1.442 and -0.443 eA^{-3}, GooF = 1.039.

Experimental crystal data collection of **[WCl$_4$(I*i*Pr^{Me})$_2$] 5**
C$_{26}$H$_{44}$Cl$_4$N$_4$W, M$_r$ = 1163.69, T = 100(2) K, wavelength = 1.54184 Å, triclinic space group P$\bar{1}$, a = 9.1142(2) Å, b = 11.0375(2) Å, c = 12.2193(3) Å, α = 116.175(2)°, β = 98.184(2)°, γ = 95.091(2)°, V = 1075.94(4) Å^3, Z = 1, *ρ(calcd)* = 1.796 g/cm^3, *μ* = 14.331 mm^{-1}, F(000) = 574, 22370 reflections in -11 ≤ h ≤ 11, -14 ≤ k ≤ 12, -12 ≤ l ≤ 15 measured in 4.117 < θ < 80.227°, completeness 100 %, 4589 independent reflections, 4529 reflections observed in [I>2sigma(I)], 228 parameters, 0 restraints, R indices (all data) R^1 = 0.0253, wR^2 = 0.0653, final R indices [I>2sigma(I)] R$_1$ = 0.0251, wR$_2$ = 0.0652, largest difference peak and hole 0.981 and -0.940 eA^{-3}, GooF = 1.124.

Experimental crystal data collection of **[MoCl$_4$(IMes)(SEt$_2$)] 6**
C$_{25}$H$_{34}$Cl$_4$MoN$_2$S, M$_r$ = 632.34, T = 100(2) K, wavelength = 1.54184 Å, monoclinic space group P2$_1$/n, a = 9.9710(1) Å, b = 12.7873(2) Å, c = 22.6725(3) Å, α = 90°, β = 99.933(1)°, γ = 90°, V = 2847.46(7) Å^3, Z = 4, *ρ(calcd)* = 1.475 g/cm^3, *μ* = 8.028 mm^{-1}, F(000) = 1296, 28083 reflections in -12 ≤ h ≤12, -13 ≤ k ≤ 16, -28 ≤ l ≤ 25 measured in 3.959 < θ < 77.438°, completeness 99.7 %, 5930 independent reflections, 5252 reflections observed in [I>2sigma(I)], 325 parameters, 18 restraints, R indices (all data) R^1 = 0.0443, wR^2 = 0.1070, final R indices [I>2sigma(I)] R$_1$ = 0.0398, wR$_2$ = 0.1039, largest difference peak and hole 0.746 and -1.189 eA^{-3}, GooF = 1.073.

Experimental crystal data collection of **[MoCl$_4$(IDipp)(SEt$_2$)] 7**
C$_{31}$H$_{46}$Cl$_4$MoN$_2$S, M$_r$ = 716.50, T = 100(2) K, wavelength = 1.54184 Å, monoclinic space group P2$_1$/c, a = 11.6290(2) Å, b = 19.3196(2) Å, c = 16.1826(2) Å, α = 90°, β = 105.230(2)°, γ = 90°, V = 3508.02(9) Å^3, Z = 4, *ρ(calcd)* = 1.357 g/cm^3, *μ* = 6.578 mm^{-1}, F(000) = 1488, 36072 reflections in -14 ≤ h ≤14, -14 ≤ k ≤ 14, -20 ≤ l ≤ 19 measured in 3.640 < θ < 77.594°, completeness 99.9 %, 7360 independent reflections, 6496 reflections observed in [I>2sigma(I)], 535 parameters, 221 restraints, R indices (all data) R^1 = 0.0447, wR^2 = 0.1048, final R indices [I>2sigma(I)] R$_1$ = 0.0391, wR$_2$ = 0.1003, largest difference peak and hole 0.380 and -0.658 eA^{-3}, GooF = 1.047.

Experimental crystal data collection of **[WCl$_4$(IMes)(SEt$_2$)] 8**
C$_{25}$H$_{34}$Cl$_4$N$_2$SW, M$_r$ = 720.24, T = 100(2) K, wavelength = 0.71073 Å, monoclinic space group P2$_1$/n, a = 10.8901(1) Å, b = 20.5337(1) Å, c = 13.2841(1) Å, α = 90°, β = 103.976(1)°, γ = 90°, V = 2882.57(4) Å^3, Z = 4, *ρ(calcd)* = 1.660 g/cm^3, *μ* = 4.467 mm^{-1}, F(000) = 1424, 127644 reflections in -15 ≤ h ≤ 14, -27 ≤ k ≤ 27, -27 ≤ l ≤ 17 measured

in $1.865 < \theta < 29.661°$, completeness 100 %, 7625 independent reflections, 7252 reflections observed in [I>2sigma(I)], 306 parameters, 0 restraints, R indices (all data) $R^1 = 0.0173$, $wR^2 = 0.0360$, final R indices [I>2sigma(I)] $R_1 = 0.0155$, $wR_2 = 0.0356$, largest difference peak and hole 0.789 and -0.511 eA^{-3}, GooF = 1.074.

Experimental crystal data collection of **[MoCl$_4$(IDipp)(cAAC^{Me})] 11**
$C_{47}H_{67}Cl_4N_3Mo$, $M_r = 911.77$, T = 100(2) K, wavelength = 1.54184 Å, monoclinic space group P2$_1$/n, a = 17.6541(1) Å, b = 13.2397(1) Å, c = 19.8834(1) Å, α = 90°, β = 93.568(1)°, γ = 90°, V = 4638.44(5) Å^3, Z = 4, $\rho(calcd)$ = 1.306 g/cm^3, μ = 4.687 mm^{-1}, F(000) = 1920, 29352 reflections in $-19 \le h \le 22$, $-16 \le k \le 14$, $-25 \le l \le 24$ measured in $3.240 < \theta < 80.025°$, completeness 99.8 %, 48884 independent reflections, 9867 reflections observed in [I>2sigma(I)], 512 parameters, 0 restraints, R indices (all data) $R^1 = 0.0372$, $wR^2 = 0.01204$, final R indices [I>2sigma(I)] $R_1 = 0.0348$, $wR_2 = 0.01167$, largest difference peak and hole 1.568 and -1.070 eA^{-3}, GooF = 1.021.

Experimental crystal data collection of **[WCl$_4$(IDipp)(cAAC^{Me})] 13**
$C_{53}H_{73}Cl_4N_3W$, $M_r = 1077.79$, T = 100(2) K, wavelength = 0.71073 Å, monoclinic space group P2$_1$/m, a = 10.4290(3) Å, b = 19.2372(5) Å, c = 13.3968(4) Å, α = 90°, β = 106.711(3)°, γ = 90°, V = 2574.22(13) Å^3, Z = 2, $\rho(calcd)$ = 1.390 g/cm^3, μ = 2.488 mm^{-1}, F(000) = 1108, 29352 reflections in $-14 \le h \le 13$, $-24 \le k \le 26$, $-17 \le l \le 16$ measured in $1.908 < \theta < 30.802°$, completeness 100 %, 6656 independent reflections, 5812 reflections observed in [I>2sigma(I)], 301 parameters, 0 restraints, R indices (all data) $R^1 = 0.0404$, $wR^2 = 0.0728$, final R indices [I>2sigma(I)] $R_1 = 0.0303$, $wR_2 = 0.0680$, largest difference peak and hole 2.017 and -1.507 eA^{-3}, GooF = 1.030.

Experimental crystal data collection of **[WCl$_4$(IMes)(PPh$_3$)] 15**
$C_{177}H_{180}Cl_{16}N_8P_4W_4$, $M_r = 3845.73$, T = 100(2) K, wavelength = 1.54184 Å, triclinic space group P$\bar{1}$, a = 10.0173(1) Å, b = 17.6425(2) Å, c = 25.2649(3) Å, α = 69.869(1)°, β = 80.720(1)°, γ = 81.980(1)°, V = 4120.38(8) Å^3, Z = 1, $\rho(calcd)$ = 1.550 g/cm^3, μ = 8.202 mm^{-1}, F(000) = 1926, 127644 reflections in $-12 \le h \le 12$, $-22 \le k \le 22$, $-31 \le l \le 32$ measured in $2.679 < \theta < 77.823°$, completeness 98.7 %, 17379 independent reflections, 15707 reflections observed in [I>2sigma(I)], 1144 parameters, 830 restraints, R indices (all data) $R^1 = 0.0401$, $wR^2 = 0.0803$, final R indices [I>2sigma(I)] $R_1 = 0.0345$, $wR_2 = 0.0780$, largest difference peak and hole 2.284 and -0.936 eA^{-3}, GooF = 1.082.

Experimental crystal data collection of **[WCl$_4$(IDipp)(PMe$_3$)] 16**
$C_{67}H_{98}Cl_8N_4P_2W_2$, $M_r = 1672.71$, T = 100(2) K, wavelength = 1.54184 Å, monoclinic space group P2$_1$/n, a = 8.7752(1) Å, b = 21.0448(2) Å, c = 19.7355(2) Å, α = 90°, β = 95.969(1)°, γ = 90°, V = 3624.84 Å^3, Z = 2, $\rho(calcd)$ = 1.533 g/cm^3, μ = 9.217 mm^{-1}, F(000) = 1684, 38319 reflections in $-11 \le h \le 11$, $-20 \le k \le 26$, $-22 \le l \le 24$ measured in $3.079 < \theta < 77.759°$, completeness 98.2 %, 7593 independent reflections, 6886 reflections observed in [I>2sigma(I)], 380 parameters, 7 restraints, R indices (all data) $R^1 = 0.0356$, $wR^2 = 0.0852$, final R indices [I>2sigma(I)] $R_1 = 0.0321$, $wR_2 = 0.0830$, largest difference peak and hole 1.494 and -1.504 eA^{-3}, GooF = 1.063.

Experimental crystal data collection of **[MoCl$_4$(IMes)(Py)] 18**
$C_{26}H_{29}Cl_4N_3Mo$, $M_r = 621.26$, T = 100(2) K, wavelength = 1.54184 Å, monoclinic space group P2$_1$/c, a = 10.9151(1) Å, b = 13.0793(1) Å, c = 19.4782(2) Å, α = 90°, β = 94.371(1)°, γ = 90°, V = 2772.66(4) Å^3, Z = 4, $\rho(calcd)$ = 1.488 g/cm^3, μ = 7.565 mm^{-1},

F(000) = 1264, 29009 reflections in -13 ≤ h ≤ 13, -16 ≤ k ≤ 14, -24 ≤ l ≤ 24 measured in 4.062 < θ < 77.509°, completeness 100 %, 5800 independent reflections, 5511 reflections observed in [I>2sigma(I)], 313 parameters, 0 restraints, R indices (all data) R^1 = 0.0412, wR^2 = 0.01051, final R indices [I>2sigma(I)] R_1 = 0.0396, wR_2 = 0.01039, largest difference peak and hole 2.017 and -1.535 eA^{-3}, GooF = 1.047.

Experimental crystal data collection of **[WCl$_4$(IMes)(Py)] 22**
$C_{26}H_{29}Cl_4N_3W$, M_r = 709.17, T = 100(2) K, wavelength = 0.71073 Å, monoclinic space group P2(1)/c, a = 10.9513(2) Å, b = 13.1018(2) Å, c = 19.4111(3) Å, α = 90°, β = 94.394(1)°, γ = 90°, V = 2776.95(8) Å^3, Z = 4, *ρ(calcd)* = 1.696 g/cm^3, *μ* = 4.564 mm^{-1}, F(000) = 1392, 122731 reflections in -15 ≤ h ≤ 14, -18 ≤ k ≤ 18, -27 ≤ l ≤ 28 measured in 1.877 < θ < 31.295°, completeness 100 %, 8149 independent reflections, 6988 reflections observed in [I>2sigma(I)], 313 parameters, 0 restraints, R indices (all data) R^1 = 0.0391, wR^2 = 0.0676, final R indices [I>2sigma(I)] R_1 = 0.0293, wR_2 = 0.0640, largest difference peak and hole 1.864 and -1.625 eA^{-3}, GooF = 1.042.

Experimental crystal data collection of **[WCl$_4$(IMes)(DMAP)] 23**
$C_{63}H_{76}Cl_8N_8W_2$, M_r = 1596.67, T = 100(2) K, wavelength = 1.54184 Å, monoclinic space group $P2_1/c$, a = 11.7070(1) Å, b = 13.8984(1) Å, c = 20.9439(2) Å, α = 90°, β = 104.642(1)°, γ = 90°, V = 3297.08(5) Å^3, Z = 2, *ρ(calcd)* = 1.608 g/cm^3, *μ* = 9.682 mm^{-1}, F(000) = 1588, 38491 reflections in -14 ≤ h ≤ 14, -13 ≤ k ≤ 17, -26 ≤ l ≤ 26 measured in 3.857 < θ < 77.653°, completeness 100 %, 6978 independent reflections, 6442 reflections observed in [I>2sigma(I)], 439 parameters, 344 restraints, R indices (all data) R^1 = 0.0361, wR^2 = 0.0885, final R indices [I>2sigma(I)] R_1 = 0.0335, wR_2 = 0.0860, largest difference peak and hole 1.018 and -2.436 eA^{-3}, GooF = 1.034.

Experimental crystal data collection of **[WCl$_4$(IDipp)(DMAP)] 25**
$C_{109}H_{146}Cl_{12}N_{12}W_3$, M_r = 2601.30, T = 100(2) K, wavelength = 1.54184 Å, triclinic space group $P\bar{1}$, a = 20.5525(1) Å, b = 25.8044(2) Å, c = 25.9330(2) Å, α = 114.5430(1)°, β = 105.947(1)°, γ = 94.478(1)°, V = 11735.30(17) Å^3, Z = 4, *ρ(calcd)* = 1.472 g/cm^3, *μ* = 8.206 mm^{-1}, F(000) = 5240, 243807 reflections in -24 ≤ h ≤ 26, -32 ≤ k ≤ 32, -32 ≤ l ≤ 32 measured in 2.046 < θ < 77.706°, completeness 99.8 %, 49142 independent reflections, 43799 reflections observed in [I>2sigma(I)], 2465 parameters, 14 restraints, R indices (all data) R^1 = 0.0411, wR^2 = 0.0868, final R indices [I>2sigma(I)] R_1 = 0.0349, wR_2 = 0.0840, largest difference peak and hole 2.056 and -1.868 eA^{-3}, GooF = 1.010.

3) Crystal structures of the compounds

Crystal structure of [MoCl$_4$(IMes)$_2$] 1

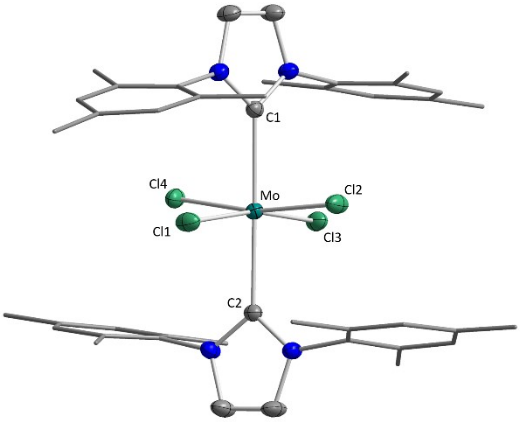

Figure S62: Molecular structure of [MoCl$_4$(IMes)$_2$] **1** in the solid state. Hydrogen atoms and a co-crystallized molecule of benzene were omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **1**: Mo-C1/C2 2.3006(17)/2.3068(17), C1-Cl1/Cl3 3.0665(19)/3.1489(16), C2-Cl2/Cl4 3.1196(16)/3.1400(18), C1-Mo-C2 177.22(6), Cl1-Mo-Cl3 167.801(17), Cl2-Mo-Cl4 168.521(16), C1-Mo-Cl1/Cl3 83.02(4)/85.26(4), C2-Mo-Cl2/Cl4 84.56(4)/84.54(4).

Crystal structure of [MoCl$_4$(IDipp)$_2$] 2

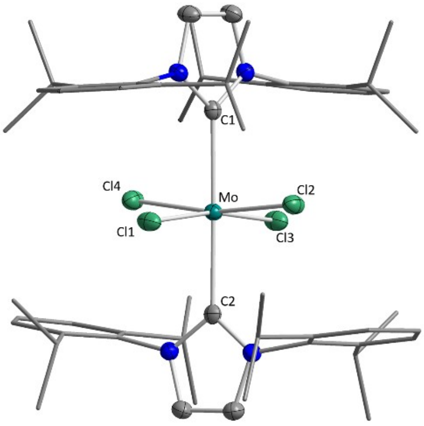

Figure S63: Molecular structure of [MoCl$_4$(IDipp)$_2$] **2** in the solid state. Hydrogen atoms and a co-crystallized molecule of benzene were omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **2**: Mo-C1/C2 2.318(2)/2.306(2), C1-Cl1/Cl3 3.108(2)/3.185(2), C2-Cl2/Cl4 3.177(3)/3.086(2), C1-Mo-C2 178.89(8), Cl1-Mo-Cl3 169.834(19), Cl2-Mo-Cl4 169.376(19), C1-Mo-Cl1/Cl3 83.49(5)/86.38(5), C2-Mo-Cl2/Cl4 86.40(5)/82.98(5).

Crystal structure of [WCl$_4$(IMes)$_2$] 3

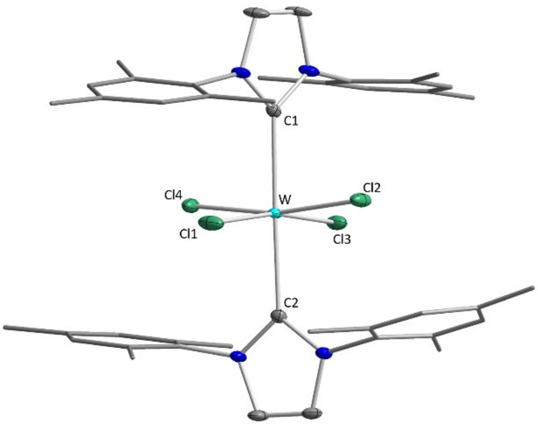

Figure S64: Molecular structure of [WCl$_4$(IMes)$_2$] **3** in the solid state. Hydrogen atoms and a co-crystallized molecule of benzene were omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **3**: W-C1/C2 2.288(2)/2.283(2), C1-Cl1/Cl3 3.1225(19)/3.1406(23), C2-Cl2/Cl4 3.0617(21)/3.1534(21), C1-W-C2 177.46(6), Cl1-W-Cl3 169.361(18), Cl2-W-Cl4 168.504(19), C1-W-Cl1/Cl3 84.80(6)/84.87(6), C2-W-Cl2/Cl4 82.99(5)/85.74(5).

Crystal structure of [WCl$_4$(IDipp)$_2$] 4

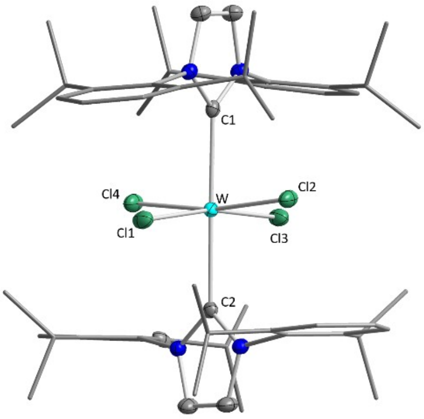

Figure S65: Molecular structure of [WCl$_4$(IDipp)$_2$] **4** in the solid state. Hydrogen atoms and a co-crystallized molecule of benzene were omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **4**: W-C1/C2 2.2958(16)/2.3023(17), C1-Cl1/Cl3 3.0766(19)/3.1931(19), C2-Cl2/Cl4 3.1023(17)/3.1928(20), C1-W-C2 178.71(6), Cl1-W-Cl3 169.847(15), Cl2-W-Cl4 170.403(15), C1-W-Cl1/Cl3 82.82(4)/87.03(4), C2-W-Cl2/Cl4 83.60(4)/86.82(4).

Crystal structure of [WCl$_4$(I*i*Pr^{Me})$_2$] 5

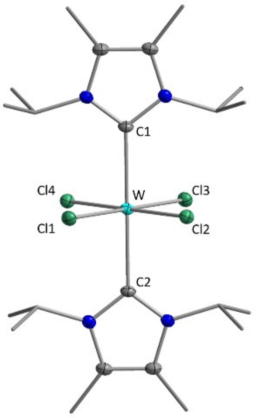

Figure S66: Molecular structure of [WCl$_4$(I*i*Pr^{Me})$_2$] **5** in the solid state. Hydrogen atoms and two co-crystallized molecule of chloroform were omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **5**: W-C1/C1' 2.283(2), C1-Cl1 3.272(3), C1-Cl2 3.300(3), C1-Cl1' 3.315(3), C1-Cl2' 3.273(3), C1-W-C1' 180.000.

Crystal structure of [MoCl$_4$(IMes)(SEt$_2$)] 6

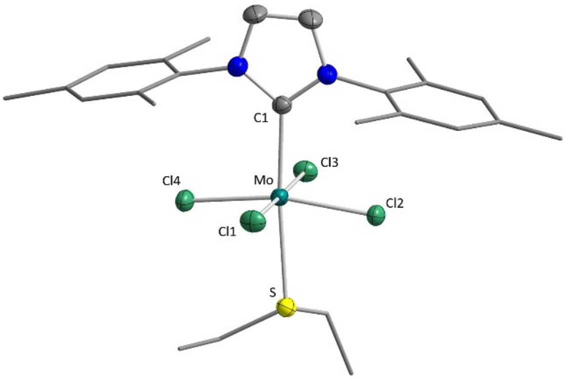

Figure S67: Molecular structure of [MoCl$_4$(IMes)(SEt$_2$)] **6** in the solid state. Hydrogen atoms were omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **6**: Mo-C1 2.236(3), Mo-S 2.6140(7), C1-Cl1/Cl3 3.194(3)/3.293(3), C1-Cl2/Cl4 3.386(3)/3.455(3), C1-Mo-S 171.84(8), C1-Mo-Cl1 88.78(7), C1-Mo-Cl2 95.84(8), C1-W-Cl3 90.84(7), C1-W-Cl4 98.45(8).

Crystal structure of [MoCl$_4$(IDipp)(SEt$_2$)] 7

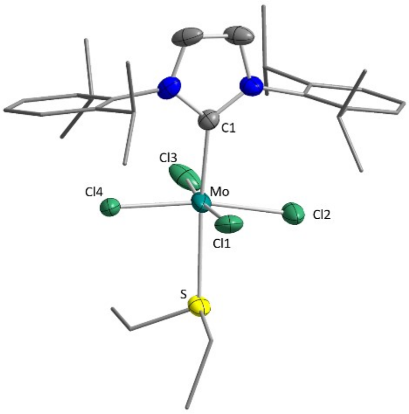

Figure S68: Molecular structure of [MoCl$_4$(IDipp)(SEt$_2$)] **7** in the solid state. Hydrogen atoms were omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **7**: Mo-C1 2.266(3), Mo-S 2.655(2), C1-Cl1/Cl3 3.157(5)/3.310(4), C1-Cl2/Cl4 3.452(5)/3.421(4), C1-Mo-S 170.21(12), C1-Mo-Cl1 86.87(12), C1-Mo-Cl2 98.62(14), C1-W-Cl3 91.55(9), C1-W-Cl4 96.80(9).

Crystal structure of [WCl$_4$(IMes)(SEt$_2$)] 8

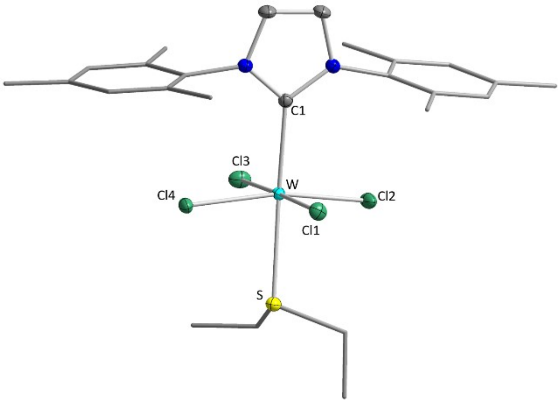

Figure S69: Molecular structure of [WCl$_4$(IMes)(SEt$_2$)] **8** in the solid state. Hydrogen atoms were omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **8**: W-C1 2.2170(15), W-S 2.5844(4), C1-Cl1/Cl3 3.3389(15)/3.1878(15), C1-Cl2/Cl4 3.4090(14)/3.3519(16), C1-W-S 171.58(4), C1-W-Cl1 93.48(4), C1-W-Cl2 96.61(4), C1-W-Cl3 88.58(4), C1-W-Cl4 94.98(4).

$[MoCl_4(IDipp)(cAAC^{Me})]$ 11

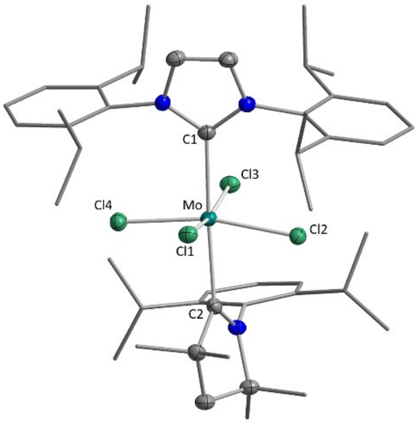

Figure S70: Molecular structure of $[MoCl_4(IDipp)(cAAC^{Me})]$ **11** in the solid state. Hydrogen atoms were omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **11**: Mo-C1 2.314(2), Mo-C2 2.288(2), C1-Cl1/Cl3 3.2368(18)/3.0068(18), C1-Cl2/Cl4 3.4865(18)/3.4195(18), C2-Cl1/Cl3 3.4413(18)/3.4666(18), C2-Cl2/Cl4 2.9610(18)/3.2190(18), C1-Mo-C2 173.65(6), Cl1-Mo-Cl3 167.878(16), Cl2-Mo-Cl4 167.056(16).

$[WCl_4(IDipp)(cAAC^{Me})]$ 13

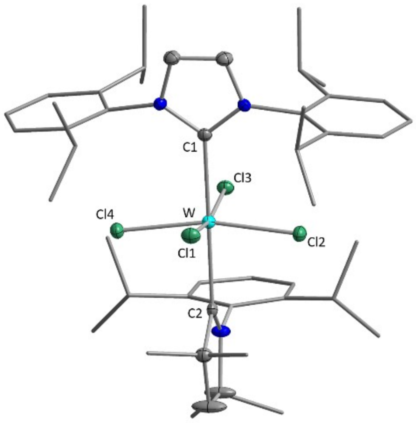

Figure S71: Molecular structure of $[WCl_4(IDipp)(cAAC^{Me})]$ **8** in the solid state. Hydrogen atoms were omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **8**: W-C1 2.305(4), W-C2 2.304(4), C1-Cl1/Cl3 3.011(4)/3.194(5), C1-Cl2/Cl2' 3.451(3), C2-Cl1/Cl3 3.563(5)/3.407(4), C2-Cl2/Cl2' 3.116(3), C1-W-C2 178.15(13), Cl1-W-Cl3 166.77(3), Cl2-W-Cl2' 167.07(3).

[WCl$_4$(IMes)(PPh$_3$)] 15

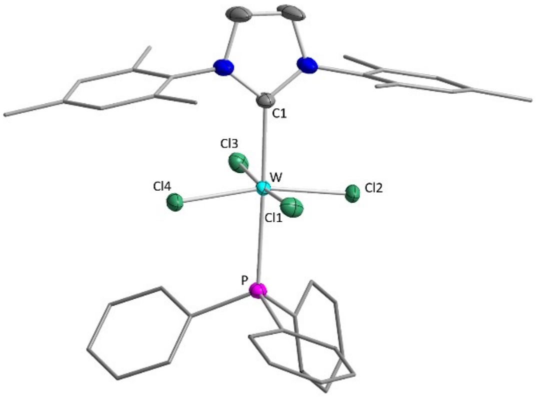

Figure S72: Molecular structure of [WCl$_4$(IMes)(PPh$_3$)] **15** in the solid state. Hydrogen atoms and a co-crystallized molecule of toluene were omitted for clarity. Only one of two independent molecules of the asymmetric unit is shown. Due to disorder in the structure of **15** at the metal center in one of the two molecules only the data of the not disordered molecule is given. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **15** (molecule 1): W-C1 2.237(3), W-P 2.6431(9), C1-W-P 177.77(10).

[WCl$_4$(IDipp)(PMe$_3$)] 16

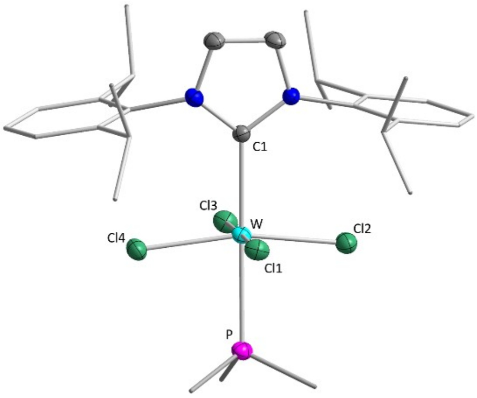

Figure S73: Molecular structure of [WCl$_4$(IDipp)(PMe$_3$)] **16** in the solid state. Hydrogen atoms and a co-crystallized molecule of toluene were omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **16**: W-C1 2.258(3), W-P 2.549(1), C1-W-P 173.83(8).

[MoCl$_4$(IMes)(Py)] 18

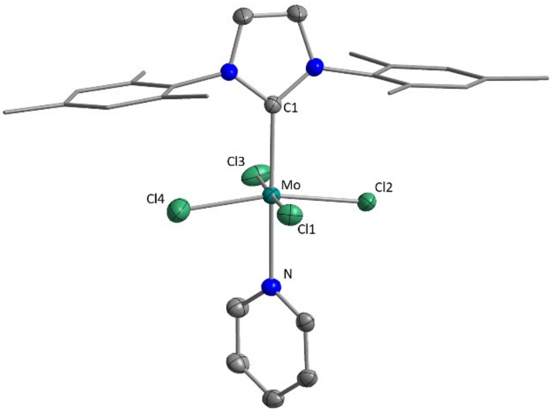

Figure S74: Molecular structure of [MoCl$_4$(IMes)(Py)] **18** in the solid state. Hydrogen atoms were omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **18**: Mo-C1 2.228(3), Mo-N 2.260(2), C1-Mo-N 177.77(9).

[WCl$_4$(IMes)(Py)] 22

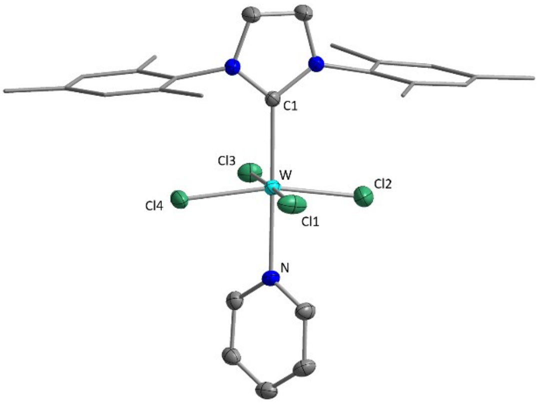

Figure S75: Molecular structure of [WCl$_4$(IMes)(Py)] **22** in the solid state. Hydrogen atoms were omitted for clarity. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **22**: W-C1 2.216(3), W-N 2.249(2), C1-W-N 177.63(9).

[WCl$_4$(IMes)(DMAP)] 23

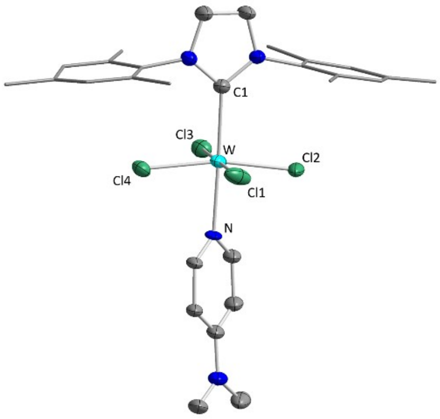

Figure S76: Molecular structure of [WCl$_4$(IMes)(DMAP)] **23** in the solid state. Hydrogen atoms were omitted for clarity. The crystal structure of **23** showed disorder of the DMAP ligand and due to this both bond lengths are given. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **23**: W-C1 2.232(3), W-N 2.224(4)/ 2.223(4), C1-W-N 174.9(4) / 175.6(3).

[WCl$_4$(IDipp)(DMAP)] 25

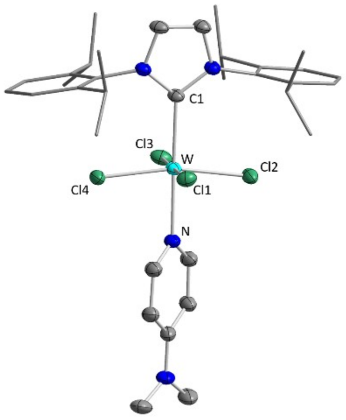

Figure S77: Molecular structure of [WCl$_4$(IDipp)(DMAP)] **25** in the solid state. Hydrogen atoms and two co-crystallized molecules of toluene were omitted for clarity. Only one of six independent molecules of the asymmetric unit is shown. Atomic displacement ellipsoids are set at 50 % probability. Selected bond lengths [Å] and angles [°] for **25**: W-C1 2.218(3) – 2.239(3), W-N 2.208(3) – 2.219(3), C1-W-N 176.11(12) – 179.50(12).

4) References

[S1] D. F. Evans, *J. Chem. Soc.* **1959**, 2003-2005.

[S2] G. Sheldrick, *Acta Cryst. A* **2014**, *70*, C1437.