Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for:

Yttrium Catalysed Dehydrocoupling of Alanes with Amines

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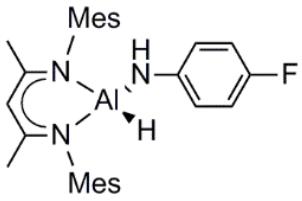
1. General Experimental

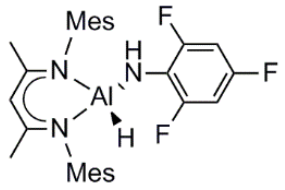
All manipulations were carried out under standard Schlenk-line or glovebox techniques under an inert atmosphere of dinitrogen. A Saffron model glovebox was employed operating under an inert atmosphere of 2-5 ppm O_2. Solvents were dried over activated alumina from an SPS (solvent purification system) based upon the Grubbs design and degassed before use. Glassware was dried for 12 hours at 150 ^oC prior to use. d_6-Benzene and d_8-toluene were dried over molten K, distilled, and stored over molecular sieves prior to use. NMR spectra were obtained on Bruker 300, 400 or 500 MHz machines, all peaks are referenced against residual solvent and values are quoted in ppm. Data were processed in Topspin or MestReNova, were NMR yields have been quoted the yields were calculated against ferrocence or durene as an internal standard and processed using the integration package in MestreNova. Infrared spectra were obtained as KBr discs, pressed by a handheld dye or as a solution in n-hexane.

Materials: $LiAlH_4$ was purified by extraction in to THF (10g in approximately 50 mL), followed by filtration and removal of the solvent under reduced pressure. The mixture was heated to 45 ^oC to remove the last traces of solvent and the colourless solid isolated proved soluble in THF and Et_2O. Amines were dried over CaH_2 and distilled before use. All other materials were purchased from Sigma-Aldrich and used without further purification. Aluminium hydrides **1a-d** were prepared according to previously published procedures.[1]

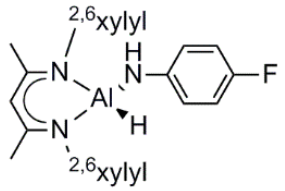
2.1 Thermal Syntheses of Aluminium Amides



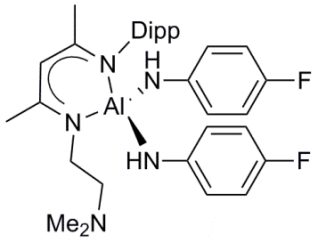
*Synthesis of [{(MesNCMe)$_2$CH}Al(H)(NH-4-C$_6$H$_4$F)] (**2a**)*: In a glovebox, [{(MesNCMe)$_2$CH}AlH$_2$] (0.707g, 1.95 mmol, 1 equiv.) was weighed out and transferred to a Schlenk tube. Dry diethyl ether (10 mL) was added followed by dropwise addition of the 4-fluoroaniline (0.184 mL, 1.95 mmol, 1 equiv.). The schlenk was sealed and removed from the box, and after 2 h at 25 ^{o}C the solvent was removed under reduced pressure. The crude reaction mixture was extracted into hexane (10 mL), filtered and stored at -20 ^{o}C. Colourless block crystals of **2a** (0.63 g, 1.33 mmol, 68%) formed overnight and were isolated by filtration. ^{1}H NMR (C$_6$D$_6$, 400 MHz, 298 K) δ 1.50 (s, 6H, C*Me*), 2.07 (s, 6H, *p*-Ar*Me*), 2.25 (s, 12H, *o*-ArMe), 3.12 (s, 1H, N*H*), 4.03 (br s, 1H, Al*H*), 5.05 (s, 1H, C*H*), 6.22-6.25 (m, 2H, -C$_6$*H*$_4$F), 6.71 (s, 2H, Ar*H*), 6.76 (s, 2H, Ar*H*), 6.80-6.85 (m, 2H, -C$_6$*H*$_4$F); ^{13}C NMR (C$_6$D$_6$, 100 MHz, 298 K) δ 18.8, 19.0, 20.8, 22.5, 97.1, 115.5 (d, $^{2}J_{13C-19F}$ = 20.0 Hz), 117.7 (d, $^{3}J_{13C-19F}$ = 7.0 Hz), 129.7, 130.0, 132.9, 135.0, 135.9, 140.1, 148.8 (d, $^{4}J_{13C-19F}$ = 2.0 Hz), 155.0 (d, $^{1}J_{13C-19F}$ = 230.0 Hz), 170.1; ^{19}F NMR (C$_6$D$_6$, 300 MHz, 298 K) δ -131.6; Infrared (solid, cm^{-1}) 2855, 1835, 1607, 1530, 1500, 1388; Elemental analysis calc. for C$_{29}$H$_{35}$AlFN$_3$ C, 73.86; H, 7.48; N, 8.91; found C, 73.77; H, 7.60; N, 8.81.



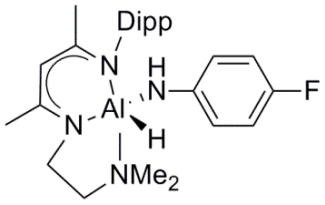
*Synthesis of [{(MesNCMe)$_2$CH}Al(H)(NH-2,4,6-C$_6$H$_2$F$_3$)] (**2b**)*: In a glovebox, [{(MesNCMe)$_2$CH}AlH$_2$] (0.500g, 1.38 mmol, 1equiv.) was weighed out and transferred to a Schlenk tube. The solid was slurried in *n*-hexane (25 mL) and 2,4,6-trifluoroaniline (0.200 g, 1.38 mmol) was added as a solid. The reaction mixture was stirred and gradually became homogeneous, after 4 h at 25 ^{o}C a colourless precipitate was observed. The mixture was stirred for 14 h in total under these conditions and then removed from the glovebox. On a vacuum line the solid was isolated by filtration and dried under vacuum and a second crop of colourless crystals of **2b** was obtained following storage of the mother liquor at -20 ^{o}C (0.440g, 0.87 mmol, 64 %). ^{1}H NMR (C$_6$D$_6$, 400 MHz, 298 K) δ 1.51 (s, 6H, C*Me*), 2.08 (s, 6H, Ar*Me*), 2.11 (s, 6H, Ar*Me*), 2.29 (s, 6H, Ar*Me*), 3.30 (s, 1H, *NH*), 4.22 (br s, 1H, Al*H*), 5.01 (s, 1H, C*H*), 6.36-6.40 (m, 2H, Ar^{F}*H*), 6.69 (s, 2H, Ar*H*), 6.77 (s, 2H, Ar*H*); ^{13}C NMR (C$_6$D$_6$, 100 MHz, 298 K) δ 18.0, 19.0, 20.9, 22.7, 98.0, 99.5 (dd, *J* = 26.3 Hz and 26.3 Hz), 127.2 (dt, J = 17.5 and 3.7 Hz), 129,9, 130.0, 133.3, 134.3, 136.0, 151.6 (dt, J = 233.8 Hz and 14.0 Hz), 152.4 (ddd, J = 237.7 Hz, 13.8 Hz and 11.3 Hz), 170.4; ^{19}F NMR (C$_6$D$_6$, 300 MHz, 298 K) δ –127.7, -128.8; Infrared (solid, cm^{-1}) 3369, 3005, 2985, 1817, 1607, 1523, 1507, 1379; Elemental analysis calc. for C$_{29}$H$_{33}$AlF$_3$N$_3$ C 68.62; H, 6.55; N, 8.28; found C, 68.73; H, 6.57; N, 8.36.



*Synthesis of [({2,6-$Me_2C_6H_3NCMe)_2CH$}Al(H)(NH-4-C_6H_4F)] (**2c**)*: In a glovebox, [({2,6-$Me_2C_6H_3NCMe)_2CH$}AlH_2] (1.0 g, 2.99 mmol, 1 equiv.) and 4-fluoroaniline (0.331g, 2.99 mmol, 1 equiv.) were weighed into separate schlenk tubes. The tubes were sealed and removed from the box and attached to a vacuum line. Diethyl ether (15 mL) was added to each tube, the solution of the dihyride was warmed gentle to aid dissolution and the solution of the aniline was then added *via* cannula at 25 ^oC. Gas evolution occurred and the mixture was left to settle for 1 h at room temperature then filtered. The filtrate was concentrated to approximately 10 mL, the product began crystallizing at 25 ^oC and following storage at -20 ^oC yielded a colourless crop of crystals. Isolation by filtration gave **2d** (0.83 g, 1.92 mmol, 62 %). ^1H NMR (C_6D_6, 400 MHz, 298 K) δ 1.43 (s, 6H, C*Me*), 2.07 (s, 6H, *o*-Ar*Me*), 2.24 (s, 6H, *o*-ArMe), 3.06 (s, 1H, N*H*), 5.00 (s, 1H, C*H*), 6.18-6.21 (m, 2H, -C_6H_4F), 6.81-6.96 (m, 8H, Ar*H*+C_6H_4F); ^{13}C NMR (C_6D_6, 75.5 MHz, 298 K) δ 18.9, 19.0, 22.5, 97.2, 115.6 (d, $^2J_{13C–19F}$ = 22.0 Hz), 117.7 (d, $^3J_{13C–19F}$ = 7.0 Hz), 126.8, 129.9, 129.3, 133.3, 135.5, 142.8, 148.7, 155.0 (d, $^1J_{13C–19F}$ = 230.0 Hz), 156.2, 170.0; ^{19}F NMR (C_6D_6, 300 MHz, 298 K) δ -131.0; Infrared (solid, cm^{-1}) 2918, 1842, 1817, 1528, 1502, 1375; Elemental analysis calc. for $C_{27}H_{31}AlFN_3$ C, 73.11; H, 7.04; N, 9.47; found C, 73.15; H, 6.97; N, 9.48.

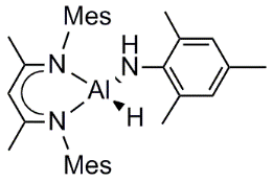


*Synthesis of [{MesNC(Me)CHC(Me)NCH$_2$CH$_2$NMe$_2$}Al(NH-4-C$_6$H$_4$F)$_2$] (**3**)*: In a glovebox, *{MesNC(Me)CHC(Me)NCH$_2$CH$_2$NMe$_2$}AlH$_2$]* (0.117g, 0.33 mmol, 1 equiv.) was weighed out and transferred to a 20 mL glass scintillation vial. Dry diethyl ether (2 mL) was added followed by dropwise addition of the 4-fluoroaniline (0.062 mL, 0.66 mmol, 2 equiv.). The vial was sealed and after 1 h at 25 ^{o}C the solution was filtered and the solvent was removed under reduced pressure. The crude reaction mixture was extracted into hot hexane (5 mL) and stored at 25 ^{o}C. Colourless needle crystals of **3** (0.129 g, 0.22 mmol, 68 %) formed overnight, were isolated by filtration and dried under vacuum. ^{1}H NMR (C$_6$D$_6$, 500 MHz, 298 K) δ 1.00 (d, 6H, $^{3}J_{1H-1H}$ = 6.5 Hz, CH*Me$_2$*), 1.10 (d, 6H, $^{3}J_{1H-1H}$ = 6.5 Hz, CH*Me$_2$*), 1.54 (s, 3H, C*Me*), 1.72 (s, 3H, C*Me*), 1.89 (s, 6H, N*Me$_2$*), 2.20 (t, 2H, $^{3}J_{1H-1H}$ = 6.5 Hz, *CH$_2$*), 3.12 (hept, 2H, $^{3}J_{1H-1H}$ = 6.5 Hz, C*H*Me$_2$), 3.29 (br s, 2H, N*H*), 3.30 (t, 2H, $^{3}J_{1H-1H}$ = 6.5 Hz, *CH$_2$*), 4.90 (s, 1H, C*H*), 6.21 (m, 4H, Ar^{F}*H*), 6.81 (m, 4H, Ar^{F}*H*), 7.04 (d, 2H, $^{3}J_{1H-1H}$ = 6.5 Hz, Ar*H*), 7.12 (m, 1H, Ar*H*); ^{13}C NMR (C$_6$D$_6$, 125 MHz, 298 K) δ 21.4, 23.3, 24.2, 25.0, 28.2, 45.8, 46.2, 60.6, 97.5, 115.6 (d, $^{2}J_{13C-19F}$ = 21.6 Hz), 116.9(d, $^{3}J_{13C-19F}$ = 6.9 Hz), 124.7, 139.4, 145.1, 148.8, 155.2 (d, $^{1}J_{13C-19F}$ = 230.0 Hz), 169.9, 171.2; ^{15}N NMR (C$_6$D$_6$, 41 MHz, 298 K) δ 22.4, 70.1, 164.1, 168.3; ^{19}F NMR (C$_6$D$_6$, 470 MHz, 298 K) δ –131.1; Infrared (solid, cm^{-1}) 3211, 2962, 2867, 2825, 2778, 1620, 1556, 1500, 1396; Elemental analysis calc. for C$_{33}$H$_{44}$AlF$_2$N$_5$ C, 68.85; H, 7.70; N, 12.16; found C, 68.74; H, 7.78; N, 11.82.

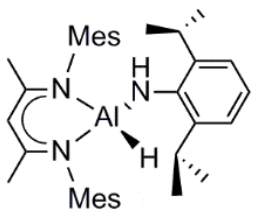


*Observation of reaction intermediate [{MesNC(Me)CHC(Me)NCH$_2$CH$_2$NMe$_2$}Al(H)(NH-4-C$_6$H$_4$F)] **(3')***: In a glovebox, *{MesNC(Me)CHC(Me)NCH$_2$CH$_2$NMe$_2$}AlH$_2$]* (0.39g, 0.1 mmol, 1 equiv.) was weighed out and dissolved in C_6D_6 (0.5 mL). The solution was transferred to a Young's tap NMR followed by addition of the 4-fluoroaniline (0.010 mL, 0.11 mmol, 1 equiv.). The tube was sealed and after 0.5 h at 25 ^{o}C ^{1}H, ^{15}N and ^{19}F NMR spectra were recorded. The mixture was predominately **3'** although both **3** and **1d** are present. *In situ data:* ^{1}H NMR (C_6D_6, 400 MHz, 298 K) δ 1.10 (d, 3H, $^{3}J_{1H-1H}$ = 6.8 Hz, CH*Me$_2$*), 1.12 (d, 3H, $^{3}J_{1H-1H}$ = 6.8 Hz, CH*Me$_2$*), 1.19 (d, 3H, $^{3}J_{1H-1H}$ = 6.8 Hz, CH*Me$_2$*), 1.48 (d, 3H, $^{3}J_{1H-1H}$ = 6.8 Hz, CH*Me$_2$*), 1.62 (s, 3H, C*Me*), 1.67 (s, 3H, C*Me*), 1.81 (s, 6H, N*Me$_2$*), 2.03 (m, 1H, *CH$_2$*), 2.14 (m, 1H, *CH$_2$*), 2.62 (m, 1H, *CH$_2$*), 2.77 (m, 1H, *CH$_2$*), 2.82 (br s, 1H, N*H*), 3.12 (hept, 1H, $^{3}J_{1H-1H}$ = 6.5 Hz, C*H*Me$_2$), 3.43 (hept, 1H, $^{3}J_{1H-1H}$ = 6.5 Hz, C*H*Me$_2$), 4.95 (s, 1H, C*H*), 6.29 (m, 2H, Ar^{F}*H*), 6.84 (m, 2H, Ar^{F}*H*), 7.18 (m, 3H, Ar*H*); ^{15}N NMR (C_6D_6, 41 MHz, 298 K) δ 29.8, 76.8, 145.2, 204.4; ^{19}F NMR (C_6D_6, 300 MHz, 298 K) δ –133.9.

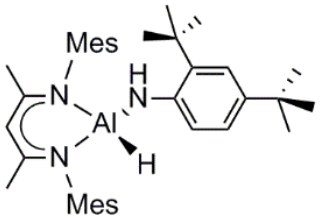
2.3 Catalytic Synthesis of Aluminium Amides



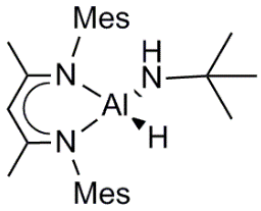
*Synthesis of [{(MesNCMe)$_2$CH}Al(H){NH-2,4,6-Mes] (**4a**)*: In a glovebox, [{(MesNCMe)$_2$CH}AlH$_2$] (0.120 g, 0.33 mmol, 1 equiv.) and [Y{N(SiMe$_3$)$_2$}$_3$] (0.009 g, 0.016 mmol, 0.05 equiv.) were weighed out into a 20 mL glass scintillation vial. Dry diethyl ether (3 mL) was added followed by addition of the 2,4,6- trimethylaniline (0.046 mL, 0.33 mmol, 1 equiv.). The vial was sealed, and after 1 h at 25 ^{o}C the mixture was passed through glass fibre filter paper and the solvent was removed under reduced pressure. The crude reaction mixture was dissolved in hexane and stored at -30 ^{o}C overnight. The solution was filtered to remove the [Y{N(SiMe$_3$)$_2$}$_3$] which recrystallized and the solvent was removed under reduced pressure. The crude reaction mixture was dissolved in pentane and stored at -30 ^{o}C. Yellow crystals of **4a** (0.114 g, 0.23 mmol, 70 %) formed over 3 days and were isolated by decanting the solvent, washing with cold pentane and drying *in vacuo*. ^{1}H NMR (C$_6$D$_6$, 500 MHz, 298 K) δ 1.49 (s, 6H, *CMe*), 2.01 (s, 6H, *ArMe*), 2.09 (s, 6H, *ArMe*), 2.19 (s, 3H, *ArMe*), 2.20 (s, 6H, *ArMe*), 2.31 (s, 6H, *ArMe*), 3.00 (s, 1H, N*H*), 4.66 (br s, 1H, Al*H*), 4.93 (s, 1H, C*H*Me$_2$), 6.68 (s, 2H, ArH), 6.74 (s, 2H, ArH), 6.76 (s, 2H, ArH); ^{13}C NMR (C$_6$D$_6$, 125 MHz, 298 K) δ 18.7, 19.0, 20.2, 20.6, 20.8, 22.6, 97.2, 123.7, 124.0, 129.6, 129.9, 133.5, 133.8, 135.8, 140.6, 146.5, 169.8; Infrared (solid, cm^{-1}) 3677, 3344, 2958, 2917, 2855, 1858, 1610, 1530, 1477, 1427, 1377; Elemental analysis calc. for C$_{32}$H$_{42}$AlN$_3$ C, 77.54; H, 8.54; N, 8.48; found C, 77.39; H, 8.60; N, 8.67.



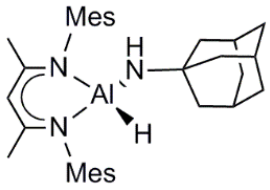
*Synthesis of [{(MesNCMe)$_2$CH}Al(H){NH-2,6-Dipp] (**4b**)*: In a glovebox, [{(MesNCMe)$_2$CH}AlH$_2$] (0.120 g, 0.33 mmol, 1 equiv.) and [Y{N(SiMe$_3$)$_2$}$_3$] (0.009 g, 0.016 mmol, 0.05 equiv.) were weighed out into a 20 mL glass scintillation vial. Dry toluene (2 mL) was added followed by addition of the 2,6, diisopropylaniline (0.061 mL, 0.33 mmol, 1 equiv.). The vial was sealed, and after 2 h at 25 ^{o}C the mixture was passed through glass fibre filter paper and the solvent was removed under reduced pressure. The crude reaction mixture was dissolved in a toluene/ hexane solution (1:2) and stored at -30 ^{o}C. Yellow tablet crystals of **4b** (0.158 g, 0.29 mmol, 89 %) formed overnight and were isolated by decanting the solvent, washing with cold hexane and drying *in vacuo*. ^{1}H NMR (C$_6$D$_6$, 400 MHz, 298 K) δ 1.07 (d, 12H, $^{3}J_{1H-1H}$ = 6.8 Hz, CH*Me$_2$*), 1.45 (s, 6H, *CMe*), 2.10 (s, 6H, *ArMe*), 2.20 (s, 6H, *ArMe*), 2.30 (s, 6H, *ArMe*), 2.59 (hept, 2H, $^{3}J_{1H-1H}$ = 6.8 Hz, C*H*Me$_2$), 3.05 (br s, 1H, N*H*), 4.70 (br s, 1H, Al*H*), 4.91 (s, 1H, C*H*Me$_2$), 6.72 (s, 2H, ArH), 6.73 (s, 2H, ArH), 6.86 (t, 1H, $^{3}J_{1H-1H}$ = 7.2 Hz, ArH), 7.05 (d, 2H, $^{3}J_{1H-1H}$ = 7.2 Hz, ArH); ^{13}C NMR (C$_6$D$_6$, 100 MHz, 298 K) δ 18.7, 19.1, 20.9, 22.7, 24.3, 28.6, 97.4, 117.6, 123.2, 129.8, 130.2, 133.2, 133.8, 135.8, 136.0, 141.0, 145.8, 169.9; Infrared (solid, cm^{-1}) 3678, 3376, 2954, 2920, 2863, 1816, 1530, 1432, 1372; Elemental analysis calc. for C$_{35}$H$_{48}$AlN$_3$ C, 78.17; H, 9.00; N, 7.81; found C, 78.40; H, 9.11; N, 8.00.



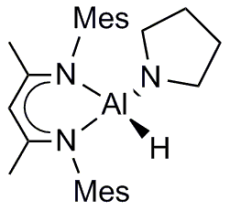
Synthesis of [{(MesNCMe)$_2$CH}Al(H){NH-2,5-di^{t}BuC$_6$H$_3$}] ***(4c)***: In a glovebox, [{(MesNCMe)$_2$CH}AlH$_2$] (0.120 g, 0.33 mmol, 1 equiv.) and [Y{N(SiMe$_3$)$_2$}$_3$] (0.009 g, 0.016 mmol, 0.05 equiv.) were weighed out into a 20 mL glass scintillation vial. Dry toluene (2 mL) was added followed by addition of the 2,5, ditert-butylaniline (0.068 mL, 0.33 mmol, 1 equiv.). The vial was sealed, and after 1 h at 25 ^{o}C the mixture was passed through glass fibre filter paper and the solvent was removed under reduced pressure. The crude reaction mixture was dissolved in a hexane solution and stored at -30 ^{o}C. Yellow crystals of **4c** (0.120 g, 0.21 mmol, 64 %) formed overnight and were isolated by decanting the solvent, washing with cold hexane and drying *in vacuo*. ^{1}H NMR (C$_6$D$_6$, 400 MHz, 298 K) δ 1.28 (s, 9H, *CMe$_3$*), 1.47 (s, 9H, *CMe$_3$*), 1.58 (s, 6H, *CMe*), 2.07 (s, 6H, *ArMe*), 2.13 (s, 6H, *ArMe*), 2.31 (s, 6H, *ArMe*), 3.84 (s, 1H, N*H*), 4.20 (br s, 1H, Al*H*), 5.19 (s, 1H, C*H*Me$_2$), 6.67 (d, 1H, ^{3}J$_{1H-1H}$ = 2 Hz, ArH), 6.73 (m, 3H, ArH), 6.78 (s, 2H, ArH), 7.23 (d, 1H, ^{3}J$_{1H-1H}$ = 8.0 Hz, ArH); ^{13}C NMR (C$_6$D$_6$, 100 MHz, 298 K) δ 18.9, 19.0, 20.8, 22.5, 29.9, 31.8, 33.7, 34.3, 98.2, 112.3, 118.2, 126.2, 129.7, 129.9, 132.9, 135.3, 135.9, 140.4, 148.5, 150.0, 170.0; Infrared (solid, cm^{-1}) 3444, 2951, 2908, 2868, 1835, 1612, 1530, 1388; Elemental analysis calc. for C$_{37}$H$_{52}$AlN$_3$ C, 78.54; H, 9.26; N, 7.43; found C, 78.45; H, 9.36; N, 7.37.



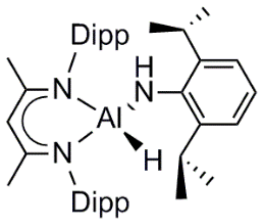
*Synthesis of [{(MesNCMe)$_2$CH}Al(H){NH-C(CH$_3$)$_3$}] (**4d**)*: In a glovebox, [{(MesNCMe)$_2$CH}AlH$_2$] (0.120 g, 0.33 mmol, 1 equiv.) and [Y{N(SiMe$_3$)$_2$}$_3$] (0.009 g, 0.016 mmol, 0.05 equiv.) were weighed out into a 20 mL glass scintillation vial. Dry toluene (2 mL) was added followed by addition of the *tert*-butylamine (0.087 mL, 0.83 mmol, 2.5 equiv.). The vial was sealed, and after 2 h at 25 ^{o}C the mixture was passed through glass fibre filter paper and the solvent was removed under reduced pressure. The crude reaction mixture was extracted into hexane (3 mL) and stored at -30 ^{o}C. Colourless tablet crystals of **4d** (0.092 g, 0.21 mmol, 64 %) formed overnight and were isolated by decanting the solvent, washing with cold hexane and drying *in vacuo*. ^{1}H NMR (C$_6$D$_6$, 400 MHz, 298 K) δ 0.56 (d, 1H, $^{3}J_{1H-1H}$ = 3.6 Hz, N*H*), 1.03 (s, 9H, *CMe$_3$*), 1.51 (s, 6H, CH*Me$_2$*), 2.13 (s, 6H, Ar*Me*), 2.32 (s, 6H, Ar*Me*), 2.39 (s, 6H, Ar*Me*), 4.53 (br s, 1H, Al*H*), 4.84 (s, 1H, C*H*Me$_2$), 6.90 (s, 2H, Ar*H*), 6.86 (s, 2H, Ar*H*); ^{13}C NMR (C$_6$D$_6$, 100 MHz, 298 K) δ 19.1, 19.3, 21.0, 22.6, 35.6, 95.9, 129.5, 129.9, 133.4, 133.9, 135.4, 140.9, 168.8; Infrared (solid, cm^{-1}) 2955, 2920, 1788, 1531, 1448, 1382; Elemental analysis calc. for C$_{27}$H$_{40}$AlN$_3$ C, 74.79; H, 9.30; N, 9.69; found C, 74.22; H, 9.82; N, 9.43.



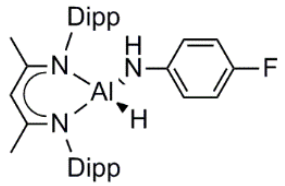
*Synthesis of [{(MesNCMe)$_2$CH}Al(H){NH-C$_{10}$H$_{15}$}] (**4e**)*: In a glovebox, [{(MesNCMe)$_2$CH}AlH$_2$] (0.120 g, 0.33 mmol, 1 equiv.) and [Y{N(SiMe$_3$)$_2$}$_3$] (0.009 g, 0.016 mmol, 0.05 equiv.) were weighed out into a 20 mL glass scintillation vial. Dry toluene (2 mL) was added followed by addition of the 1-adamantylamine (0.049 g, 0.33 mmol, 1 equiv.). The vial was sealed, and after 1 h at 25 ^{o}C the mixture was passed through glass fibre filter paper and the solvent was removed under reduced pressure. The crude reaction mixture was dissolved in toluene and stored at -30 ^{o}C. Colourless microcrystals of **4e** (0.082 g, 0.16 mmol, 48 %) formed overnight and were isolated by decanting the solvent, washing with cold hexane and drying *in vacuo*. ^{1}H NMR (C$_6$D$_6$, 400 MHz, 298 K) δ 0.36 (d, 1H, $^{3}J_{1H-1H}$ = 3.2 Hz, N*H*), 1.43 (br t, 6H, $^{3}J_{1H-1H}$ = 2.8 Hz, Ad-C*H$_2$*), 1.47 (br d, 6H, $^{3}J_{1H-1H}$ = 2.8 Hz, Ad-CH$_2$), 1.52 (s, 6H C*Me*), 1.84 (br m, 3H, Ad-C*H*), 2.13 (s, 6H, Ar*Me*), 2.37 (s, 6H, Ar*Me*), 2.40 (s, 6H, Ar*Me*), 4.52 (br s, 1H, Al*H*), 4.86 (s, 1H, C*H*Me$_2$), 6.81 (s, 2H, ArH), 6.88 (s, 2H, ArH); ^{13}C NMR (C$_6$D$_6$, 100 MHz, 298 K) δ 19.1, 19.5, 21.0, 22.6, 30.9, 37.0, 49.5, 95.9, 129.5, 129.9, 133.4, 134.1, 135.4, 140.9, 168.8; Infrared (solid, cm^{-1}) 3678, 2905, 2844, 1836, 1609, 1528, 1450, 1387; Elemental analysis calc. for C$_{33}$H$_{46}$AlN$_3$ C, 77.46; H, 9.06; N, 8.21; found C, 77.43; H, 9.12; N, 8.17.



*Synthesis of [{(MesNCMe)$_2$CH}Al(H){N-C$_4$H$_8$] (**4f**)*: In a glovebox, [{(MesNCMe)$_2$CH}AlH$_2$] (0.120 g, 0.33 mmol, 1 equiv.) and [Y{N(SiMe$_3$)$_2$}$_3$] (0.009 g, 0.016 mmol, 0.05 equiv.) were weighed out into a 20 mL glass scintillation vial. Dry diethyl ether (3 mL) was added followed by addition of the pyrrolidine (0.033 mL, 0.33 mmol, 1 equiv.). The vial was sealed, and after 0.5 h at 25 ^{o}C the mixture was passed through glass fibre filter paper and the solvent was removed under reduced pressure. The crude reaction mixture was washed with cold hexane to give **4f** as a yellow solid (0.094 g, 0.22 mmol, 66 %). ^{1}H NMR (C$_6$D$_6$, 400 MHz, 298 K) δ 1.66 (s, 6H, *CMe*), 1.69 (m, 4H, *N*CH$_2$C*H$_2$*), 2.23 (s, 6H, *ArMe*), 2.39 (s, 3H, *ArMe*), 2.42 (s, 6H, *ArMe*), 3.26 (m, 4H, *NCH$_2$*CH$_2$), 4.22 (br s, 1H, Al*H*), 5.07 (s, 1H, C*H*Me$_2$), 6.88 (s, 2H, ArH), 6.93 (s, 2H, ArH); ^{13}C NMR (C$_6$D$_6$, 100 MHz, 298 K) δ 18.2, 19.2, 20.8, 22.4, 26.9, 49.3, 97.0, 129.7, 133.1, 134.2, 135.3, 141.2, 168.7; Infrared (solid, cm^{-1}) 3677, 3680, 2955, 2918, 2862, 2790, 1849, 1610, 1527, 1452, 1383; Elemental analysis calc. for C$_{27}$H$_{38}$AlN$_3$ C, 75.14; H, 8.87; N, 9.74; found C, 74.96; H, 8.75; N, 9.63.



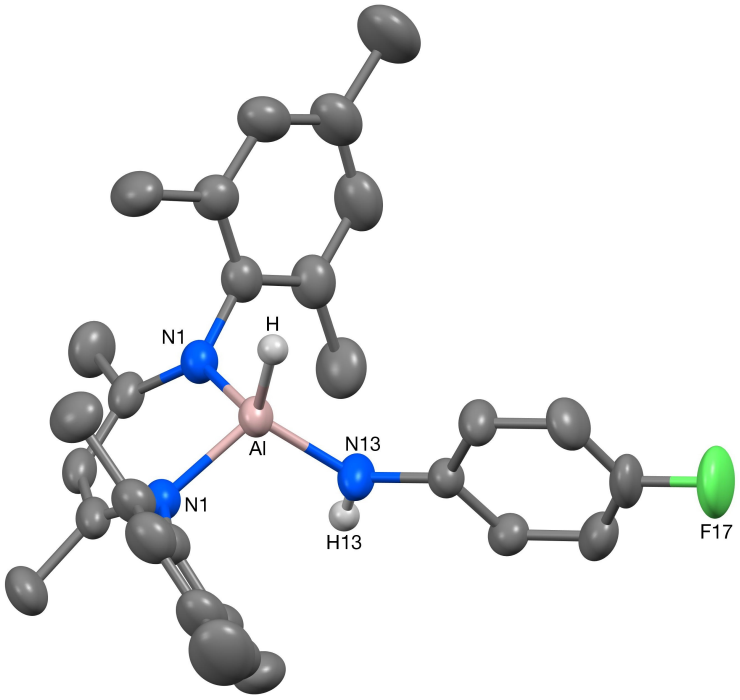
*Synthesis of [{(DippNCMe)$_2$CH}Al(H)(NH-Dipp)] (**4g**)*: In a glovebox, [{(DippNCMe)$_2$CH}AlH$_2$] (0.147 g, 0.33 mmol, 1 equiv.) and [Y{N(SiMe$_3$)$_2$}$_3$] (0.009 g, 0.016 mmol, 0.05 equiv.) were weighed out into a 20 mL glass scintillation vial. Dry toluene (3 mL) was added followed by addition of the 2,6 diisopropylaniline (0.062 mL, 0.33 mmol, 1 equiv.). The vial was sealed, and after 15 h at 25 ^{o}C the mixture was passed through glass fibre filter paper and the solvent was removed under reduced pressure. The crude reaction mixture was dissolved in a toluene/hexane mixture (1:2) and stored at -30 ^{o}C. Pale yellow microcrystals of **4g** (0.179 g, 0.29 mmol, 87 %) formed overnight and were isolated by decanting the solvent, washing with cold hexane and drying *in vacuo*. ^{1}H NMR (C$_6$D$_6$, 400 MHz, 298 K) δ 1.01 (d, 12H, $^{3}J_{1H-1H}$ = 6.8 Hz, CH*Me$_2$*), 1.11 (d, 6H, $^{3}J_{1H-1H}$ = 6.8 Hz, CH*Me$_2$*), 1.12 (d, 6H, $^{3}J_{1H-1H}$ = 6.8 Hz, CH*Me$_2$*), 1.18 (d, 6H, $^{3}J_{1H-1H}$ = 6.8 Hz, CH*Me$_2$*), 1.31 (d, 6H, $^{3}J_{1H-1H}$ = 6.8 Hz, CH*Me$_2$*), 1.53 (s, 6H, Ar*Me*), 2.49 (hept, 2H, $^{3}J_{1H-1H}$ = 6.8 Hz, C*H*Me$_2$), 3.01 (s, 1H, N*H*), 3.36 (m, C*H*Me$_2$), 4.54 (br s, 1H, Al*H*), 4.96 (s, 1H, C*H*Me$_2$), 6.82 (t, 1H, Ar*H*), 7.03-7.13 (m, 8H, ArH); ^{13}C NMR (C$_6$D$_6$, 100 MHz, 298 K) δ 23.5, 24.5, 24.5, 24.6, 24.7, 25.2, 28.4, 28.6, 28.8, 97.0, 117.5, 123.1, 124.6, 125.1, 127.7, 129.3, 135.5, 140.7, 144.0, 144.6, 145.4, 170.6. [Lit: ^{1}H NMR (C$_7$D$_8$, 300 MHz, 298 K) δ 0.95 (d, 12H, $^{3}J_{1H-1H}$ = 6.8 Hz, CH*Me$_2$*), 1.10 (d, 6H, $^{3}J_{1H-1H}$ = 6.8 Hz, CH*Me$_2$*), 1.11 (d, 6H, $^{3}J_{1H-1H}$ = 6.8 Hz, CH*Me$_2$*), 1.13 (d, 6H, $^{3}J_{1H-1H}$ = 6.8 Hz, CH*Me$_2$*), 1.26 (d, 6H, $^{3}J_{1H-1H}$ = 6.8 Hz, CH*Me$_2$*), 1.55 (s, 6H, Ar*Me*), 2.43 (hept, 2H, $^{3}J_{1H-1H}$ = 6.8 Hz, C*H*Me$_2$), 2.93 (s, 1H, N*H*), 3.32 (hept, 2H, $^{3}J_{1H-1H}$ = 6.8 Hz, C*H*Me$_2$), 4.97 (s, 1H, C*H*Me$_2$), 5.50 (br, 1H, Al*H*), 6.69-6.72, 6.92-7.10 (m, 9H, ArH); ^{13}C NMR (C$_7$D$_8$, 126 MHz, 298 K) δ 23.4, 24.4, 24.5, 24.6, 24.7, 25.2, 28.4, 28.7, 28.9, 97.9, 117.5, 123.0, 124.6, 125.0, 125.6, 128.2, 128.5, 129.2, 129.3, 135.4, 137.5 140.7, 144.0, 144.5, 145.3, 170.6.][3]



*Synthesis of [{(DippNCMe)$_2$CH}Al(H)(NH-4-C$_6$H$_4$F)] (**4h**)*: In a glovebox, [{(DippNCMe)$_2$CH}AlH$_2$] (0.147 g, 0.33 mmol, 1 equiv.) and [Y{N(SiMe$_3$)$_2$}$_3$] (0.009 g, 0.016 mmol, 0.05 equiv.) were weighed out into a 20 mL glass scintillation vial. Dry diethyl ether (3 mL) was added followed by addition of the 4-fluoroaniline (0.032 mL, 0.33 mmol, 1 equiv.). The vial was sealed, and after 1 h at 25 ^{o}C the mixture was passed through glass fibre filter paper and the solvent was removed under reduced pressure. The crude reaction mixture was washed with cold hexane to give **4h** as a pale yellow solid (0.095 g, 0.17 mmol, 52 %). ^{1}H NMR (C$_6$D$_6$, 400 MHz, 298 K) δ 0.94 (d, 6H, $^{3}J_{1H-1H}$ = 6.8 Hz, CH*Me$_2$*), 1.01 (d, 6H, $^{3}J_{1H-1H}$ = 6.8 Hz, CH*Me$_2$*), 1.13 (d, 6H, $^{3}J_{1H-1H}$ = 6.8 Hz, CH*Me$_2$*), 1.42 (d, 6H, $^{3}J_{1H-1H}$ = 6.8 Hz, CH*Me$_2$*), 1.53 (s, 6H, Ar*Me*), 3.07 (hept, 2H, $^{3}J_{1H-1H}$ = 6.8 Hz, C*H*Me$_2$), 3.09 (s, 1H, N*H*), 3.35 (hept, 2H, $^{3}J_{1H-1H}$ = 6.8 Hz, C*H*Me$_2$), 4.03 (br s, 1H, Al*H*), 5.02 (s, 1H, C*H*Me$_2$), 6.14 (br m, 2H, -C$_6$*H$_4$*F), 6.83 (m, 2H, -C$_6$*H$_4$*F), 7.08-7.18 (m, 6H, ArH); ^{13}C NMR (C$_6$D$_6$, 100 MHz, 298 K) δ 23.2, 24.2, 24.7, 25.0, 27.7, 29.0, 97.3, 115.0 (d, $^{2}J_{13C-19F}$ = 21.7 Hz), 117.6 (d, $^{3}J_{13C-19F}$ = 10.4 Hz), 124.4, 124.9, 139.8, 143.6, 146.1, 148.3, 155.0 (d, $^{1}J_{13C-19F}$ = 230.1 Hz), 170.5; ^{19}F NMR (C$_6$D$_6$, 300 MHz, 298 K) δ -131.2; Infrared (solid, cm^{-1}) 3364, 3064, 2959, 2928, 2868, 1856, 1525, 1504, 1439, 1384; Elemental analysis calc. for C$_{35}$H$_{47}$AlFN$_3$ C, 75.64; H, 8.52; N, 7.56; found C, 75.42; H, 8.69; N, 7.71.

3. Single Crystal X-ray Diffraction Data

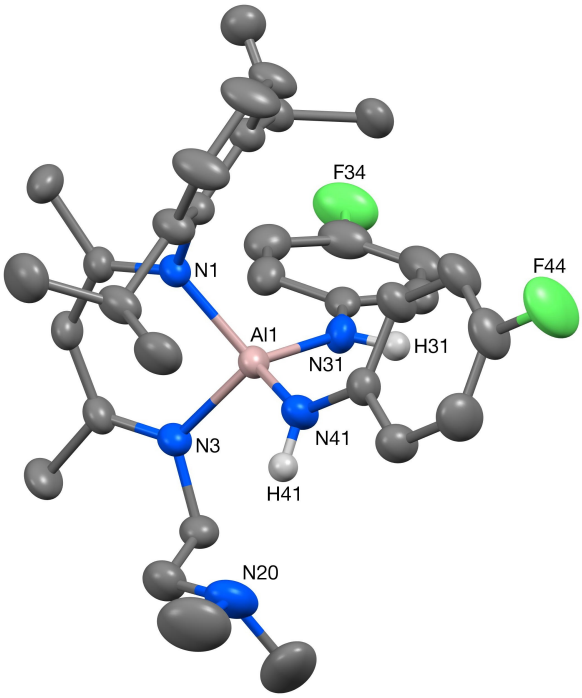
Fig. S1 The crystal structure of **2a** (50% probability ellipsoids).



The X-ray crystal structure of 2a

The structure of **2a** was found to have crystallographic C_S symmetry with Al, C(2) and the whole of the NH-4-FC_6H_4 substituent sitting on the mirror plane, as do the Al–H and N–H hydrogen atoms. These two hydrogen atoms were located from ΔF maps and refined freely, though the N–H hydrogen atom was subject to an N–H distance constraint of 0.90 Å.

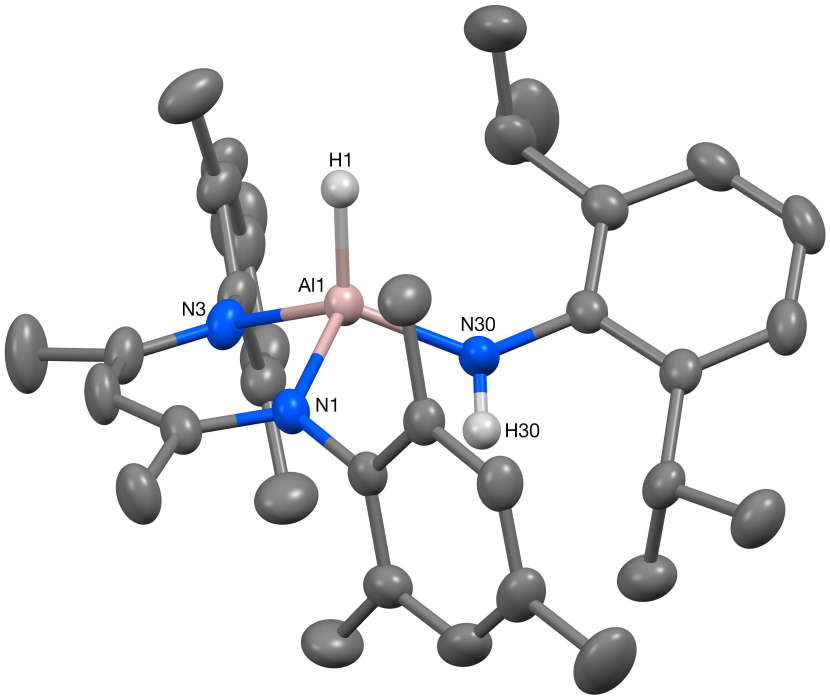
Fig. S2 The crystal structure of **3** (50% probability ellipsoids).



The X-ray crystal structure of 3

The two N–H hydrogen atoms in the structure of **3** were located from ΔF maps and refined freely subject to an N–H distance constraint of 0.90 Å.

Fig. S3 The crystal structure of **4b** (50% probability ellipsoids).



The X-ray crystal structure of 4b

The Al–H and N–H hydrogen atoms in the structure of **4b** were located from Δ*F* maps and refined freely, though the N–H hydrogen atom was subject to an N–H distance constraint of 0.90 Å. The included toluene solvent molecule was found to be disordered across a centre of symmetry. Two unique orientations were identified of *ca*. 29 and 21% occupancy, with a further two orientations of the same occupancies being generated by operation of the centre of symmetry. The geometries of the two unique orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and all of the atoms were refined isotropically.

Table S1. Crystallographic Data for compounds **2a**, **3** and **4b**.

data	**2a**	**3**	**4b**
chemical formula	$C_{29}H_{35}AlFN_3$	$C_{33}H_{44}AlF_2N_5$	$C_{35}H_{48}AlN_3$
solvent	—	—	$0.5(C_7H_8)$
fw	471.58	575.71	583.81
T (°C)	–100	–100	–100
space group	*Pnma* (no. 62)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a (Å)	15.11825(9)	9.13917(11)	10.8160(3)
b (Å)	19.66971(14)	15.5779(3)	19.4921(8)
c (Å)	9.20725(6)	22.9215(4)	16.6321(6)
α (deg)	90	90	90
β (deg)	90	94.3724(13)	90.876(3)
γ (deg)	90	90	90
V (Å^3)	2737.98(3)	3253.81(8)	3506.1(2)
Z	4 [b]	4	4
ρ_{calcd} (g cm^{-3})	1.144	1.175	1.106
λ (Å)	1.54184	1.54184	0.71073
μ (mm^{-1})	0.857	0.870	0.087
no. of unique reflns			
measured (R_{int})	2788 (0.0222)	6268 (0.0218)	6847 (0.0358)
obs, $\|F_o\| > 4\sigma(\|F_o\|)$	2591	5363	5127
R_1(obs), wR_2(all) [a]	0.0406, 0.1225	0.0384, 0.1067	0.0497, 0.1318

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$. [b] The molecule has crystallographic C_S symmetry.

Table 1 provides a summary of the crystallographic data for compounds **2a**, **3** and **4b**. Data were collected using Oxford Diffraction Xcalibur PX Ultra (**2a**), Agilent Xcalibur PX Ultra A (**3**) and Agilent Xcalibur 3E (**4**) diffractometers, and the structures were refined using the SHELXTL, SHELX-97, and SHELX-2013 program systems.[2] CCDC 1007407 to 1007409.

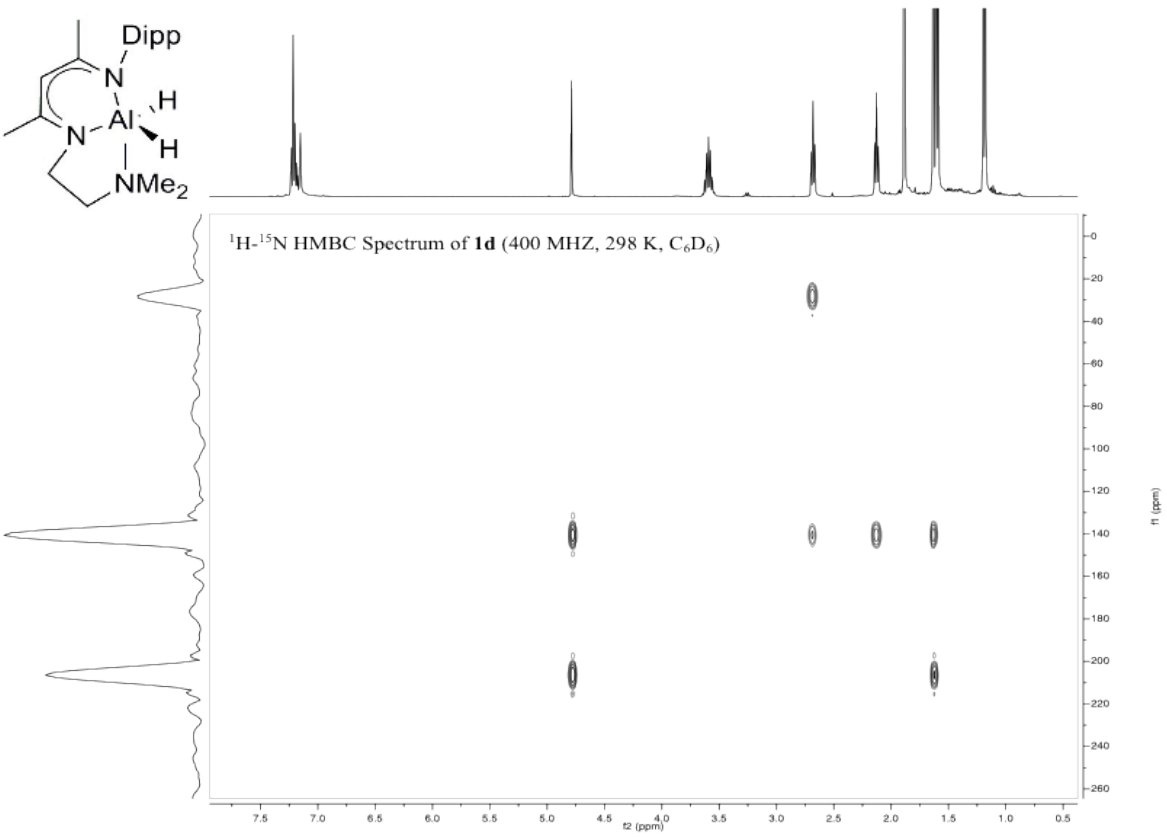
References

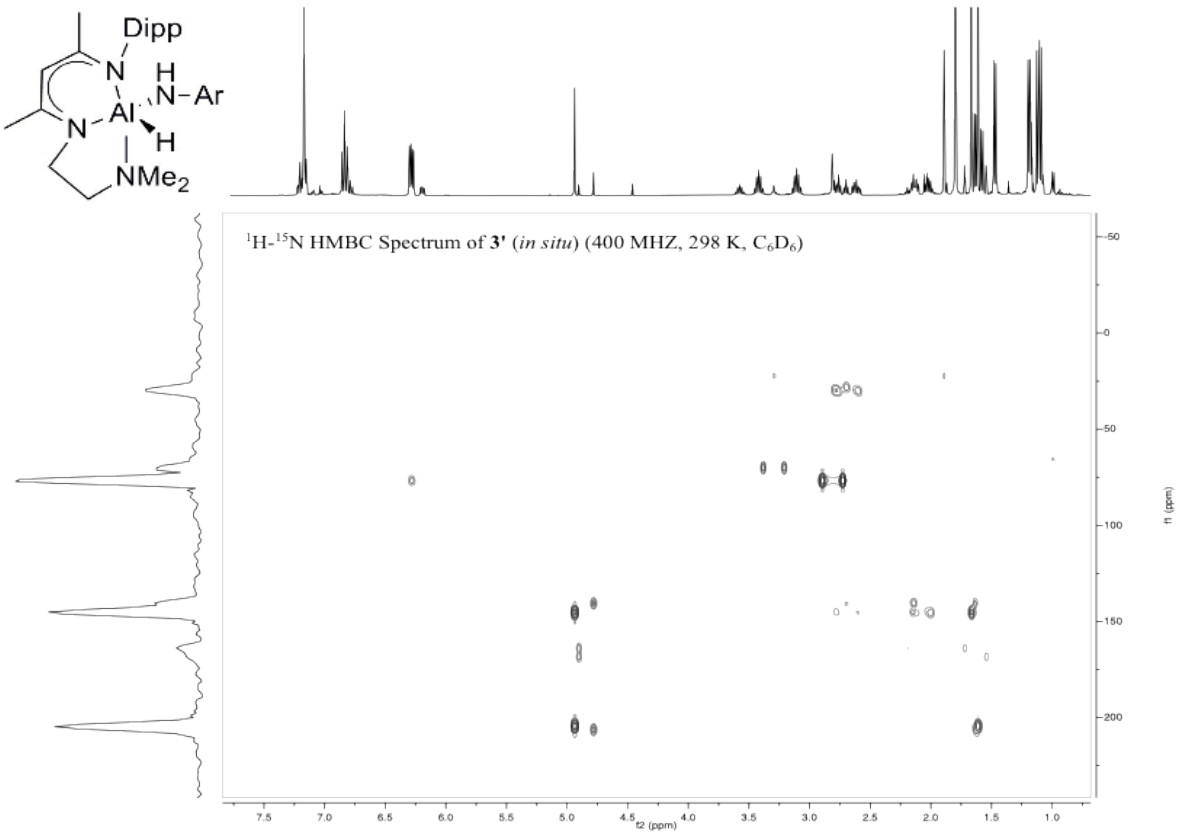
[1] A. E. Nako, S. J. Gates, A. J. P. White, M. R. Crimmin, *Dalton Trans.,* **2013**, *42*, 15199.

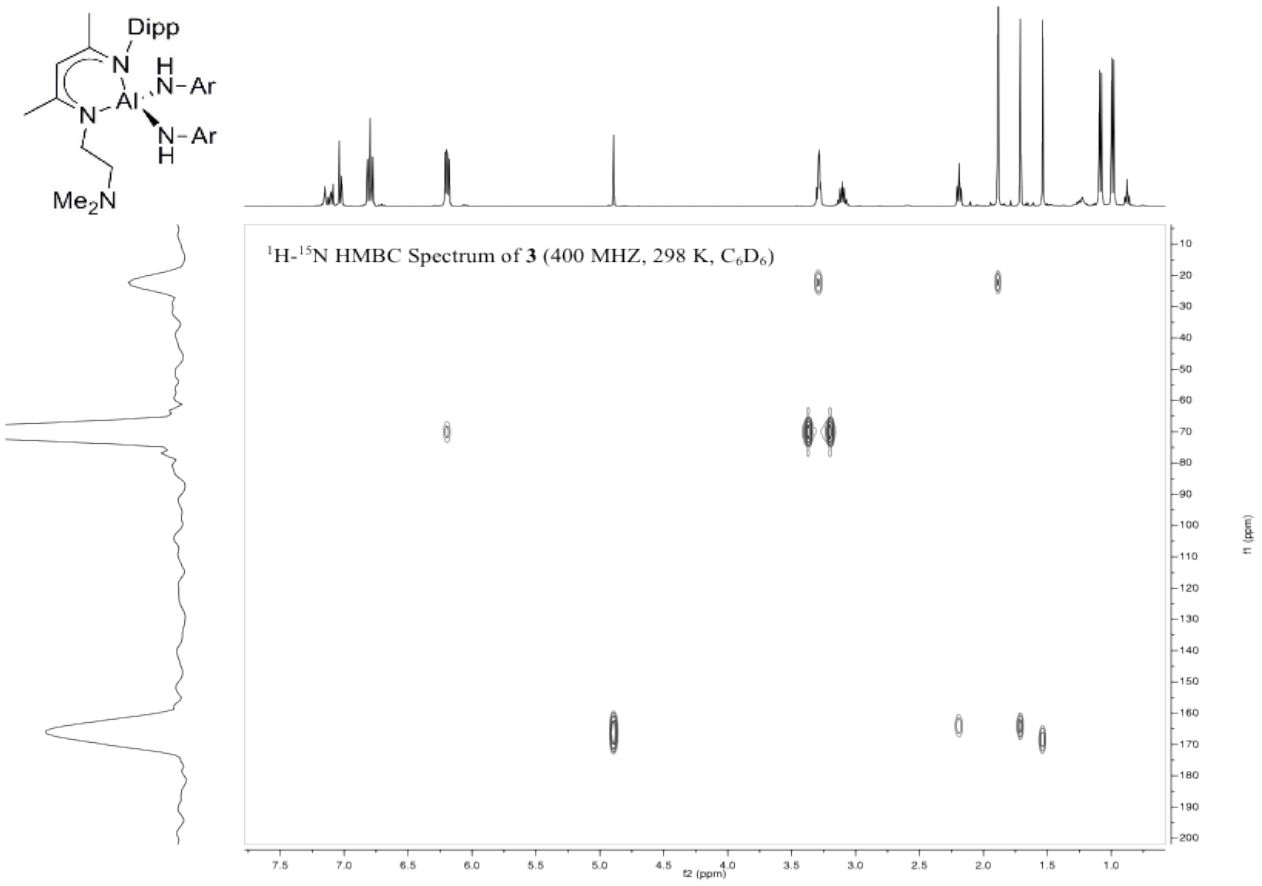
[2] SHELXTL, Bruker AXS, Madison, WI; SHELX-97, G.M. Sheldrick, *Acta Cryst.*, **2008**, *A64*, 112-122; SHELX-2013, http://shelx.uni-ac.gwdg.de/SHELX/index.php

[3] H. Zhu, Z. Yang, J. Magull, H. W. Roesky, H. Schmidt, M. Noltemeyer, *Organometallics,* **2005**, *24*, 6420.

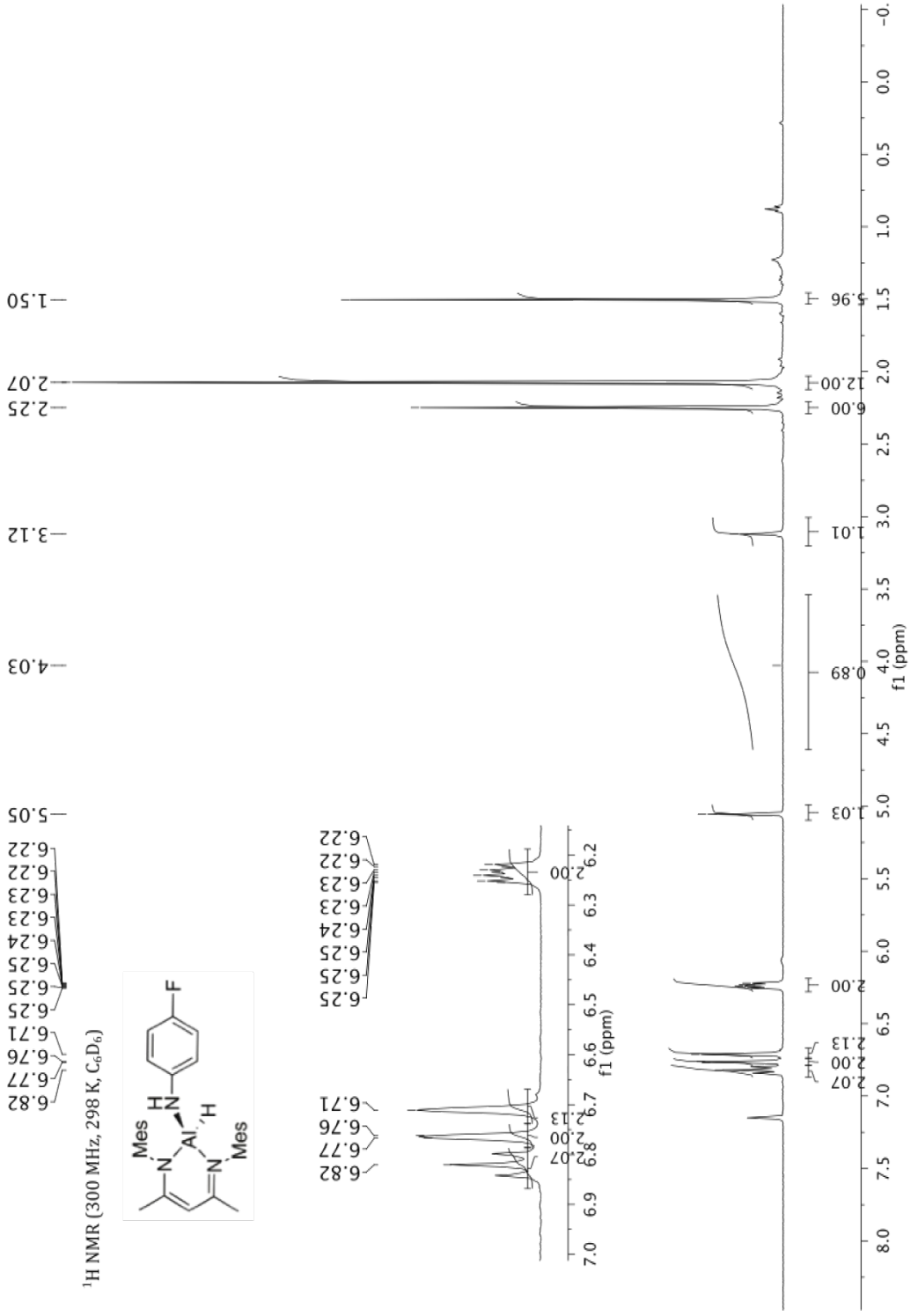
4.1 $^{1}H–^{15}N$ HMBC Experiments

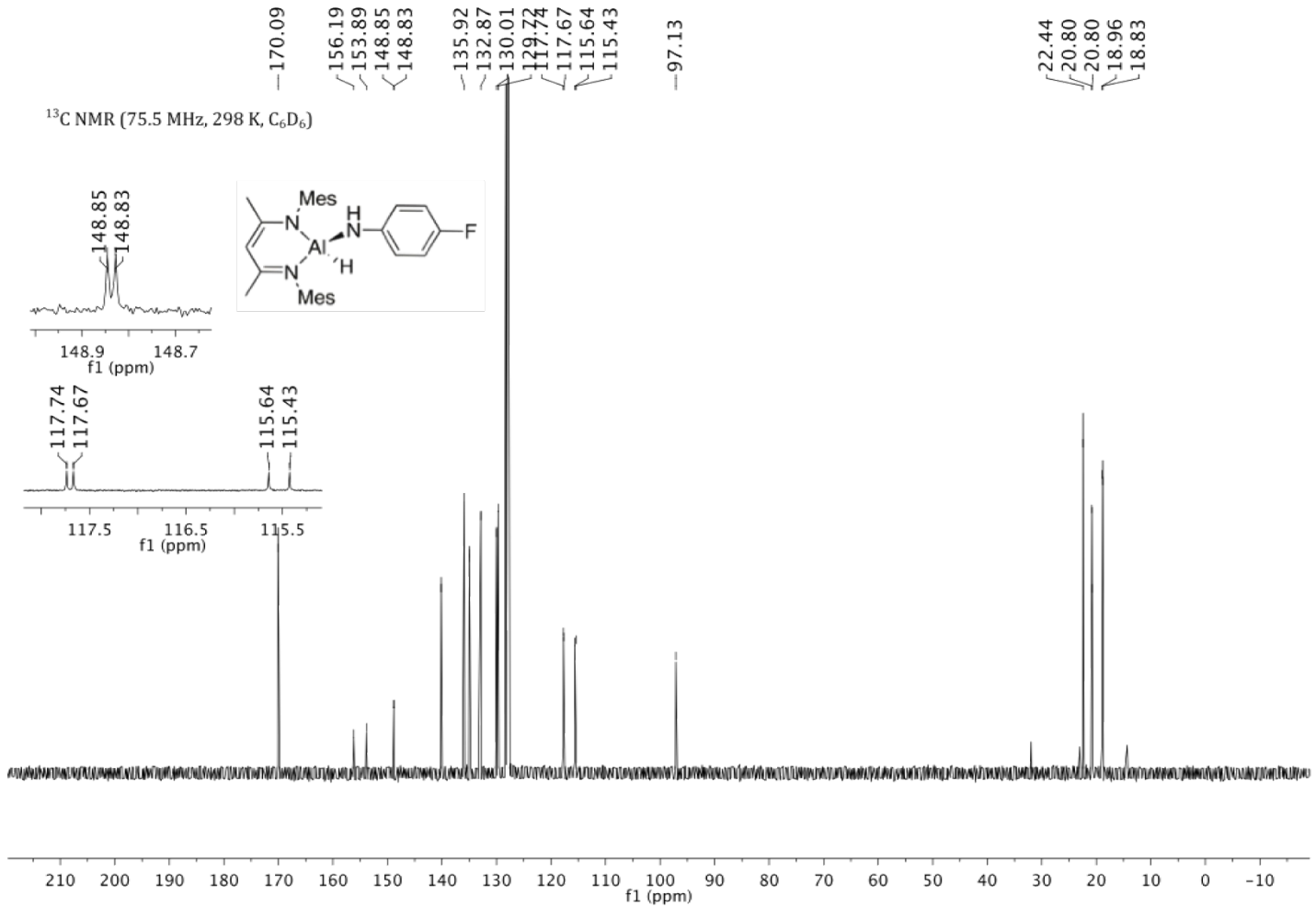



Dipp
N
H
N–Ar
Al
N
H
NMe2
^{1}H-^{15}N HMBC Spectrum of **3'** (*in situ*) (400 MHZ, 298 K, C_6D_6)
f2 (ppm)
f1 (ppm)

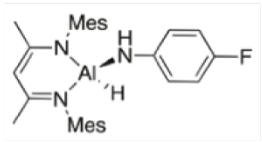

Dipp
N
H
N-Ar
Al
N
N-Ar
H
Me2N
1H-15N HMBC Spectrum of 3 (400 MHZ, 298 K, C6D6)
f1 (ppm)
f2 (ppm)

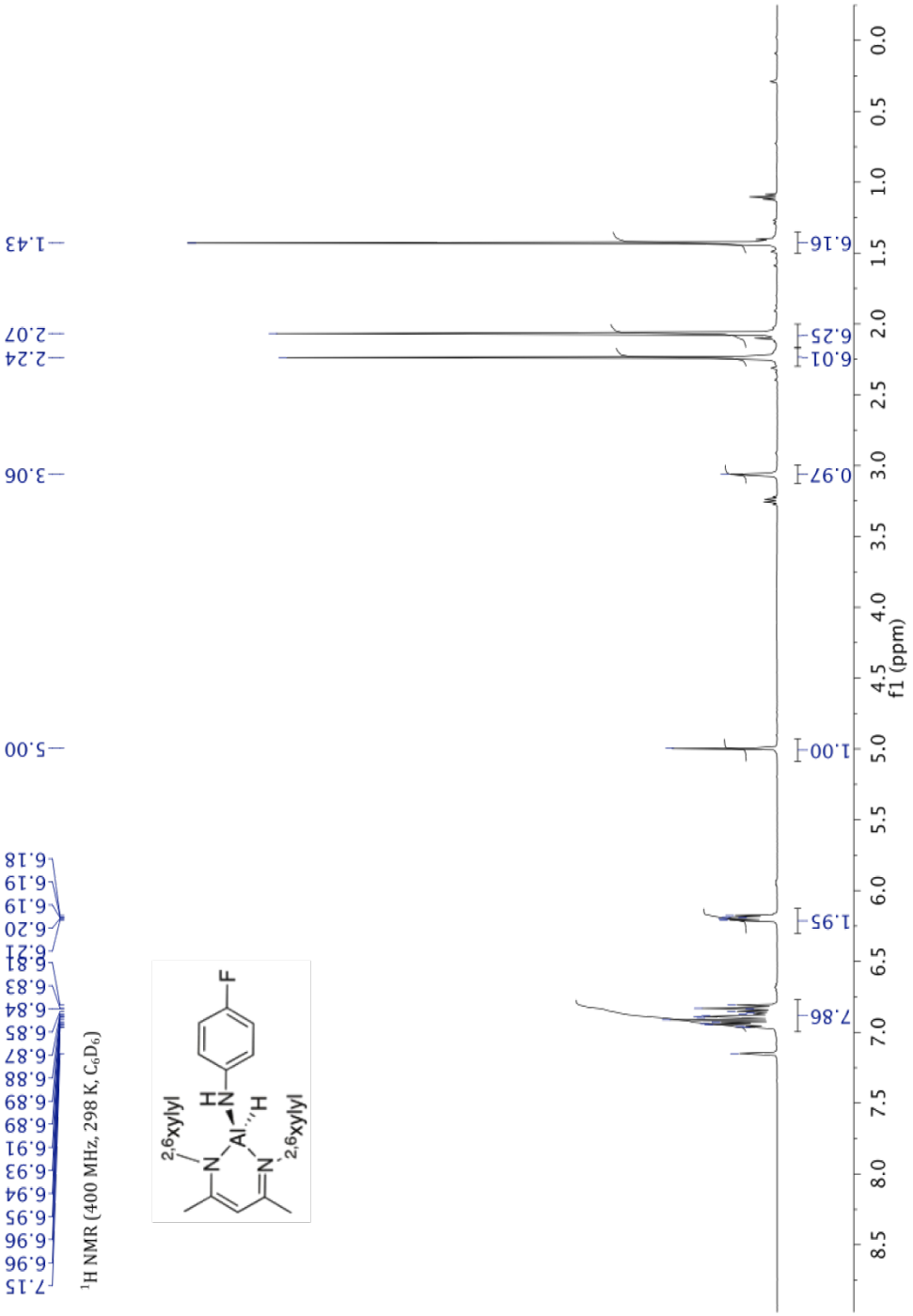
4.2 ^{1}H, ^{13}C, ^{19}F NMR data

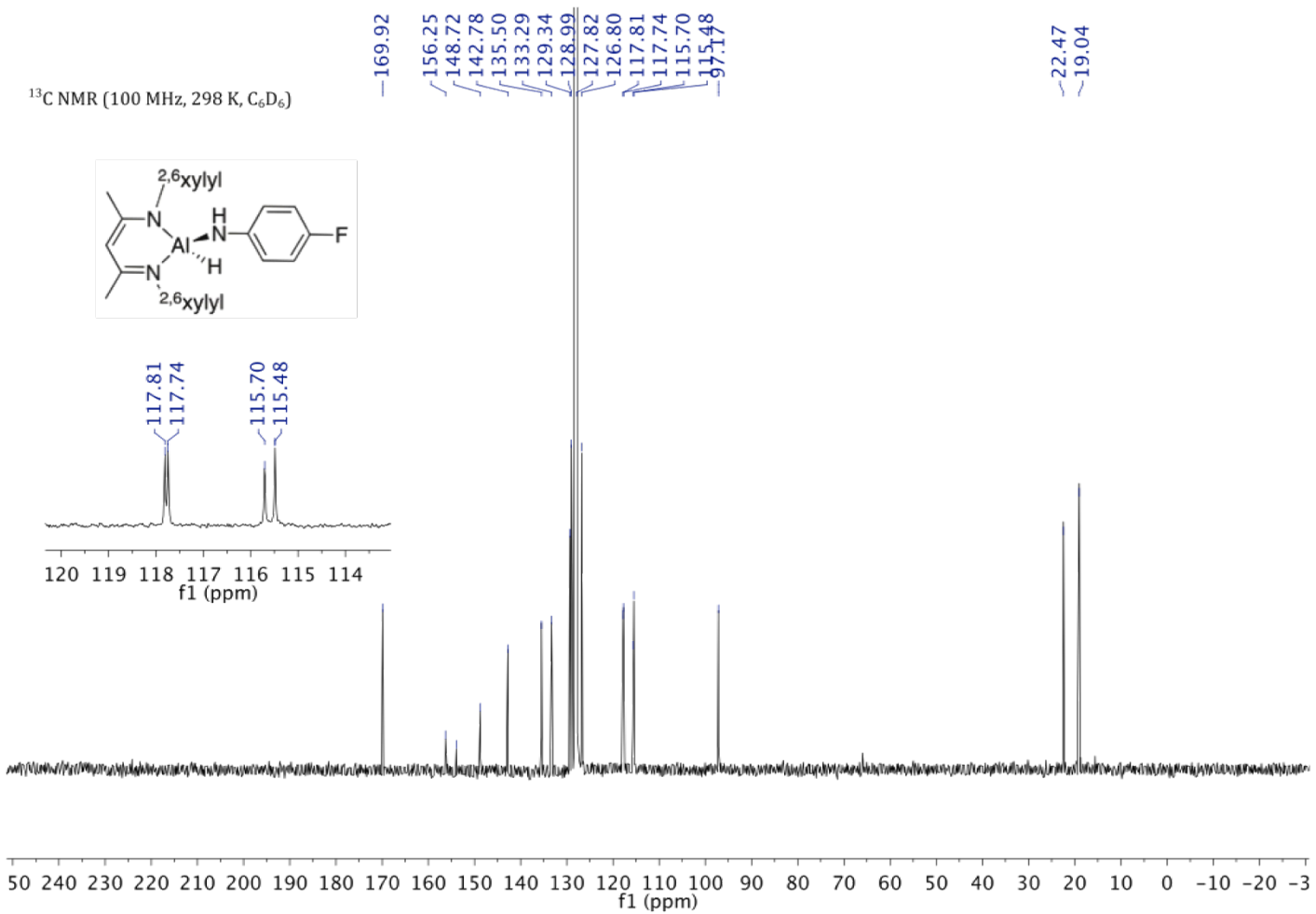



^{13}C NMR (75.5 MHz, 298 K, C_6D_6)
170.09
156.19
153.89
148.85
148.83
135.92
132.87
130.01
129.72
117.74
117.67
115.64
115.43
97.13
22.44
20.80
20.80
18.96
18.83
Mes
N
Al
H
N
H
F
N
Mes
148.85
148.83
148.9
148.7
f1 (ppm)
117.74
117.67
115.64
115.43
117.5
116.5
115.5
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{19}F NMR (75.5 MHz, 298 K, C_6D_6)




1.43
2.07
2.24
3.06
5.00
6.18
6.19
6.19
6.20
6.21
6.81
6.83
6.84
6.85
6.87
6.88
6.89
6.89
6.91
6.93
6.94
6.95
6.96
6.96
7.15
^{1}H NMR (400 MHz, 298 K, C_6D_6)
F
H
N
Al
H
N
N
2,6xylyl
2,6xylyl
6.16
6.25
6.01
0.97
1.00
1.95
7.86
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


^{13}C NMR (100 MHz, 298 K, C_6D_6)
169.92
156.25
148.72
142.78
135.50
133.29
129.34
128.99
127.82
126.80
117.81
117.74
115.70
115.48
97.17
22.47
19.04
2,6xylyl
N
Al
H
N
H
F
N
2,6xylyl
117.81
117.74
115.70
115.48
120 119 118 117 116 115 114
f1 (ppm)
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -3
f1 (ppm)

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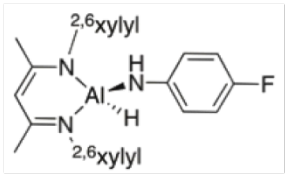
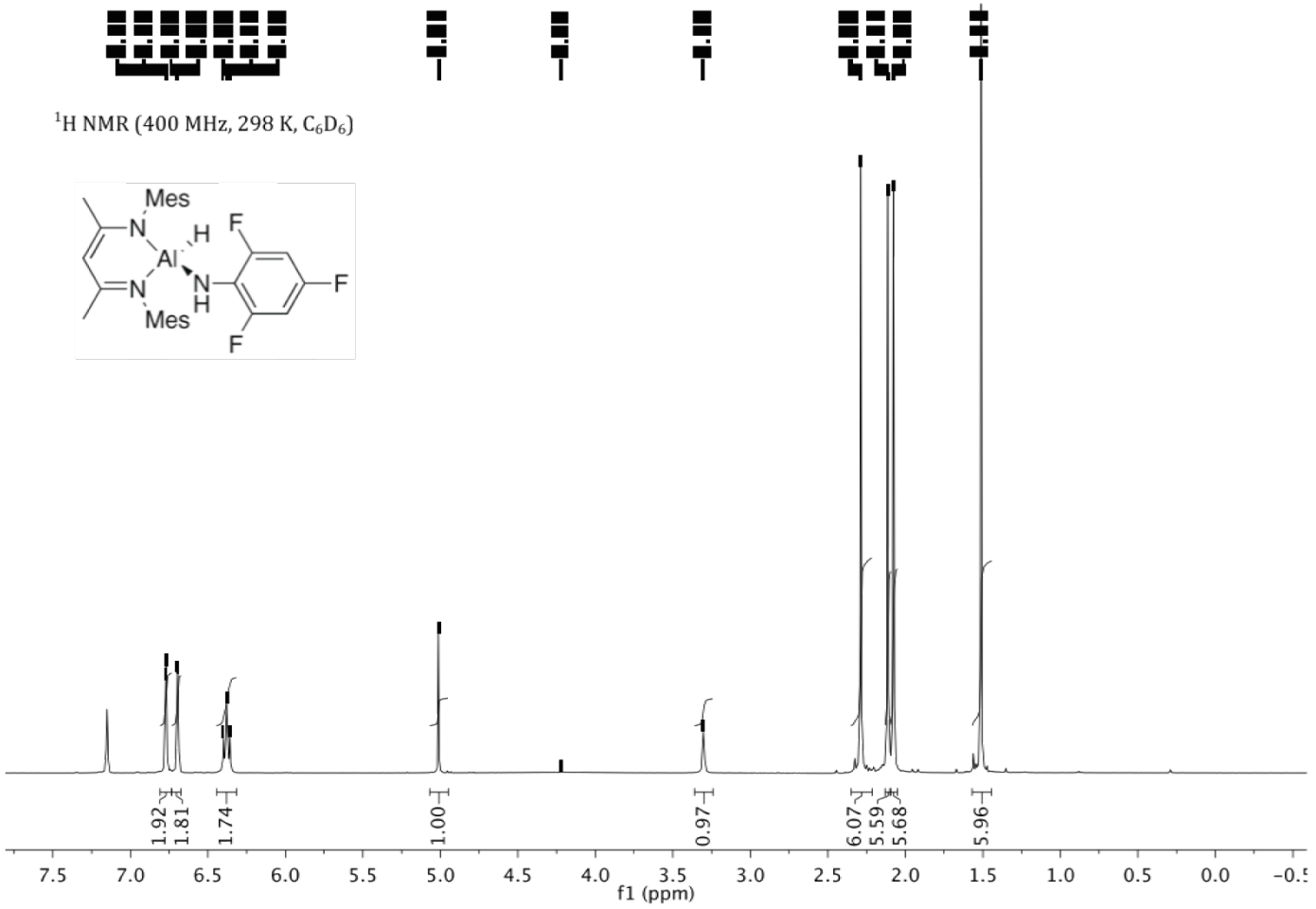
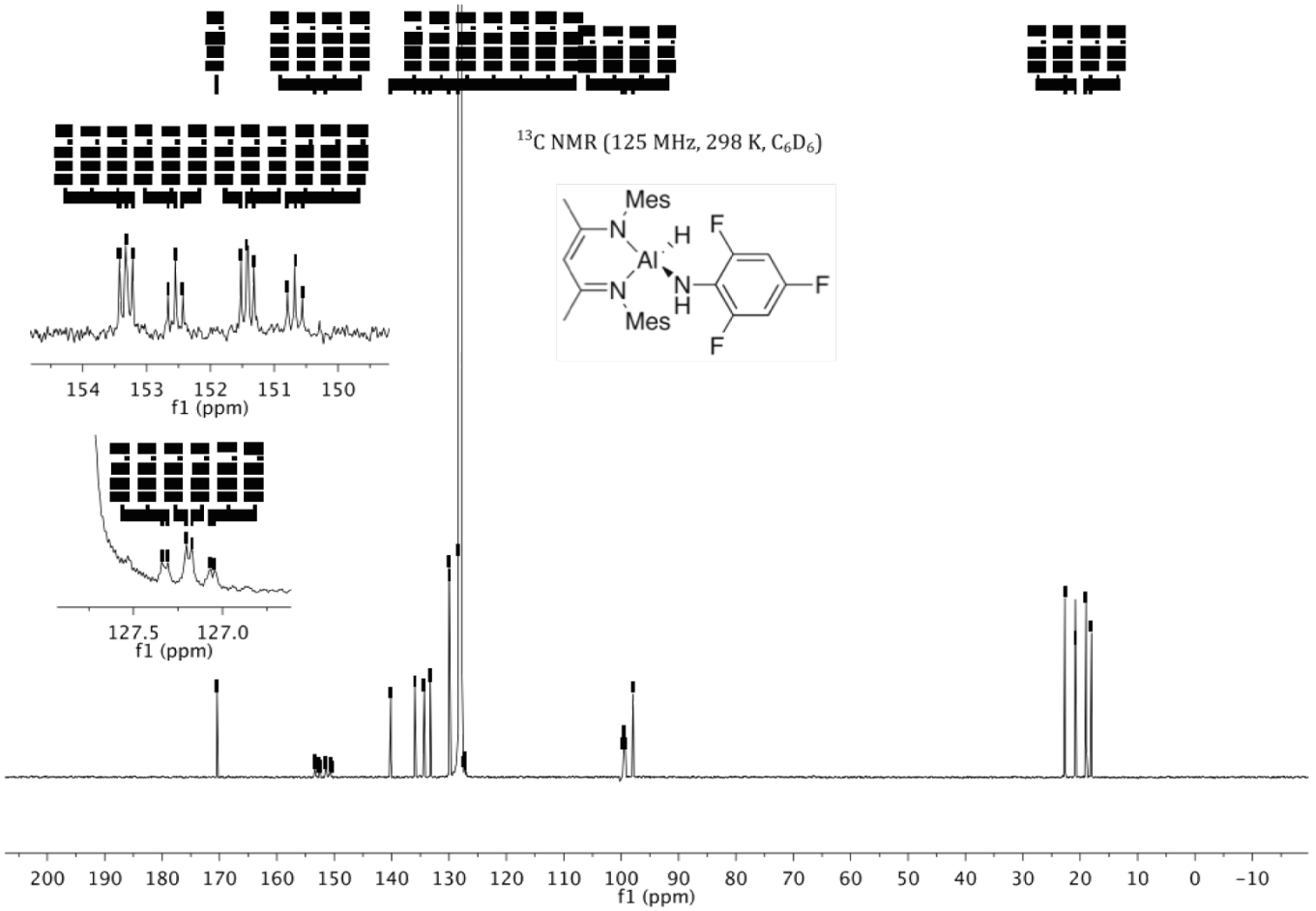
MRC_II_021A1

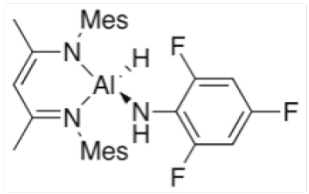
^{19F} NMR (xxx MHz, 298 K, C_6D_6)

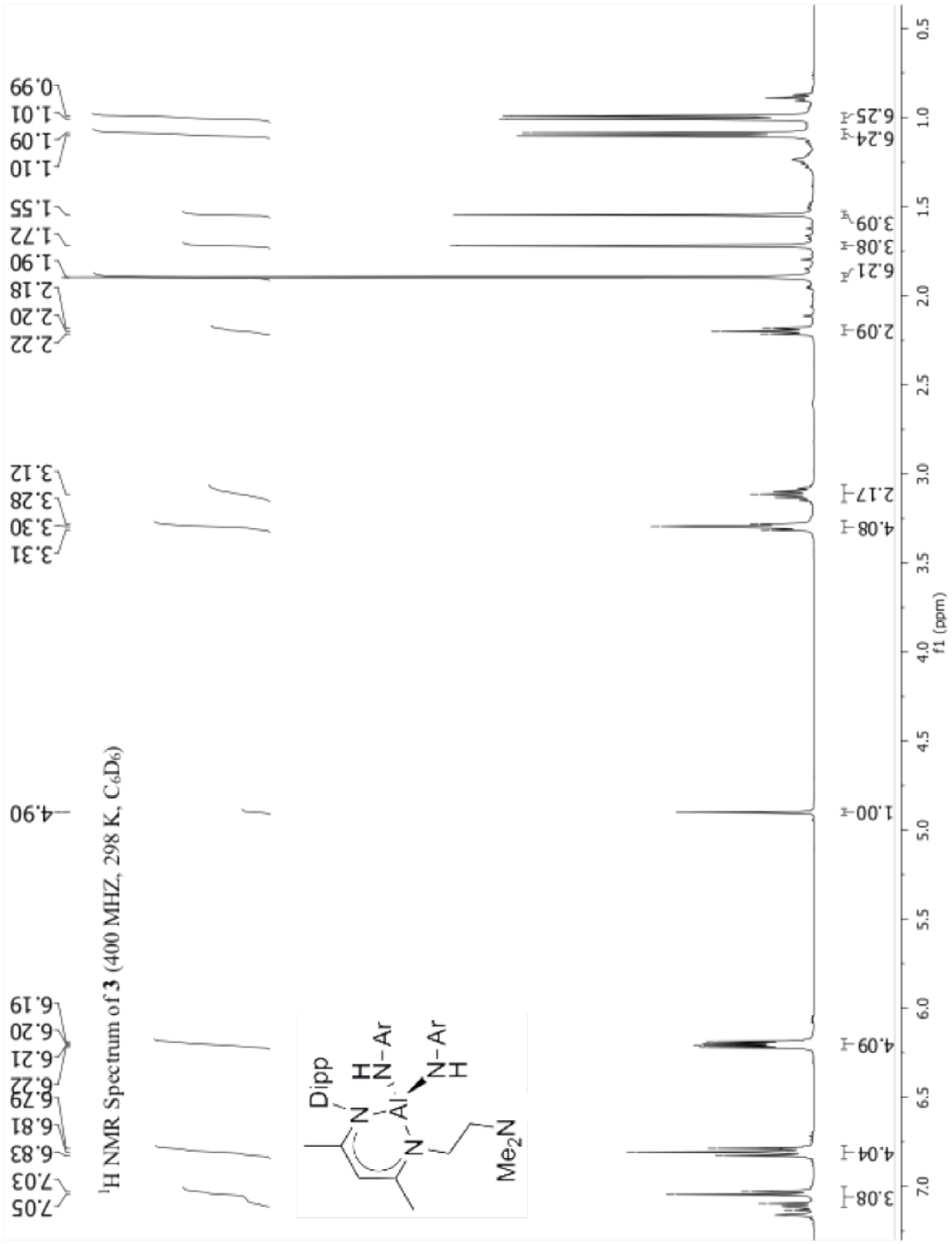


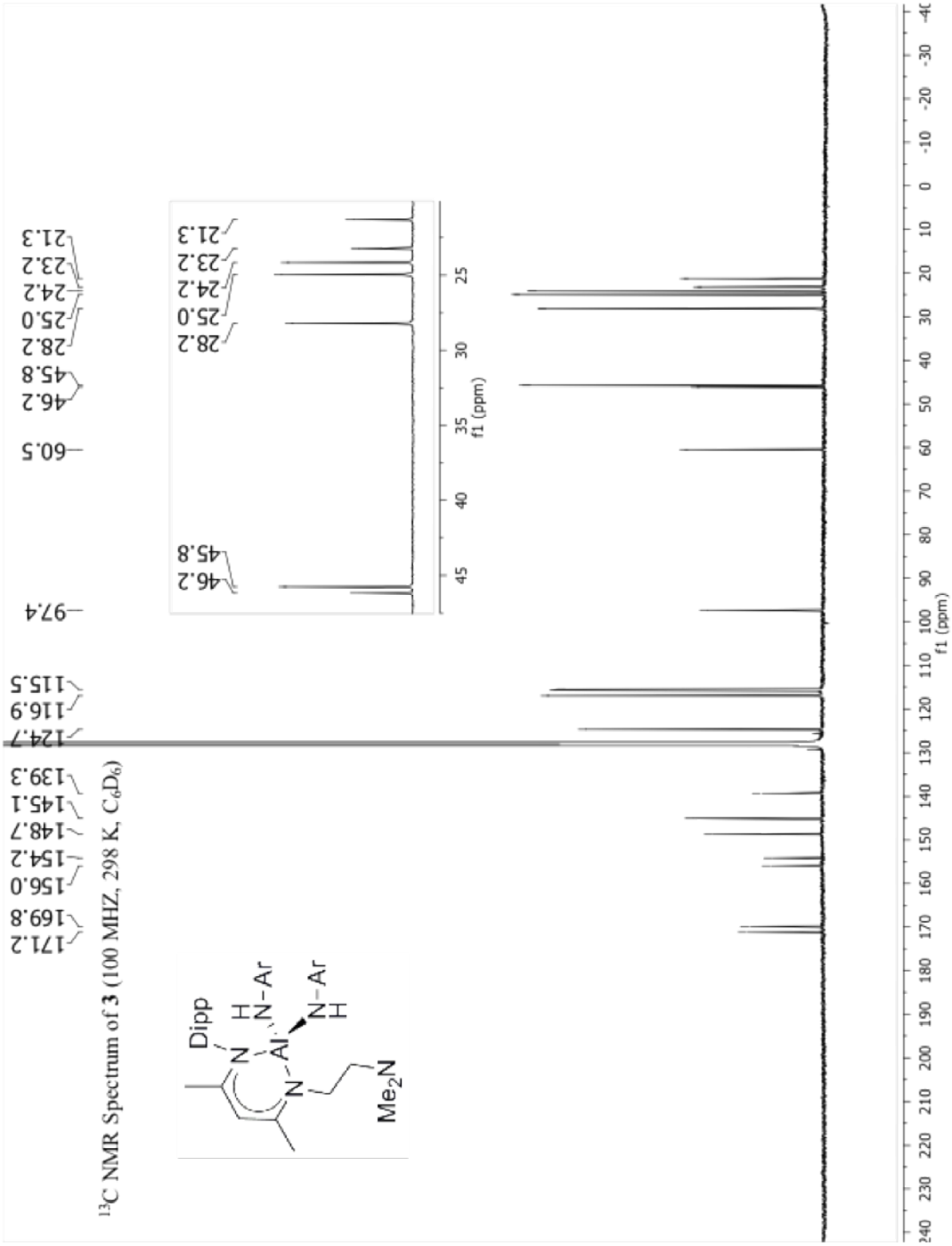

^{1}H NMR (400 MHz, 298 K, C_6D_6)
Mes
N
H
F
Al
N
H
F
N
Mes
F
1.92
1.81
1.74
1.00
0.97
6.07
5.59
5.68
5.96
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


^{13}C NMR (125 MHz, 298 K, C_6D_6)
Mes
N
Al
H
F
N
H
F
N
Mes
F
154 153 152 151 150
f1 (ppm)
127.5 127.0
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

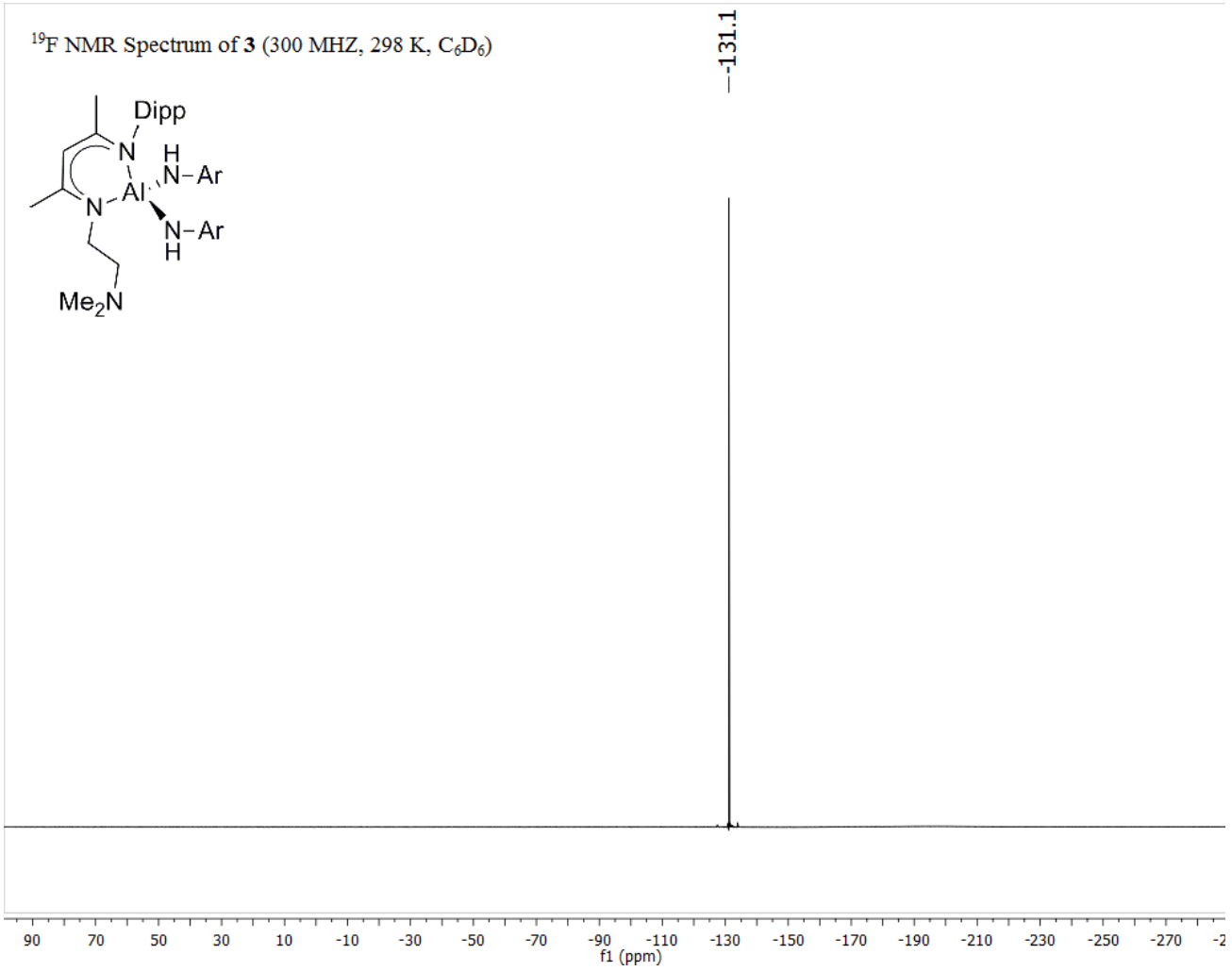
^{19F} NMR (375 MHz, 298 K, C_6D_6)

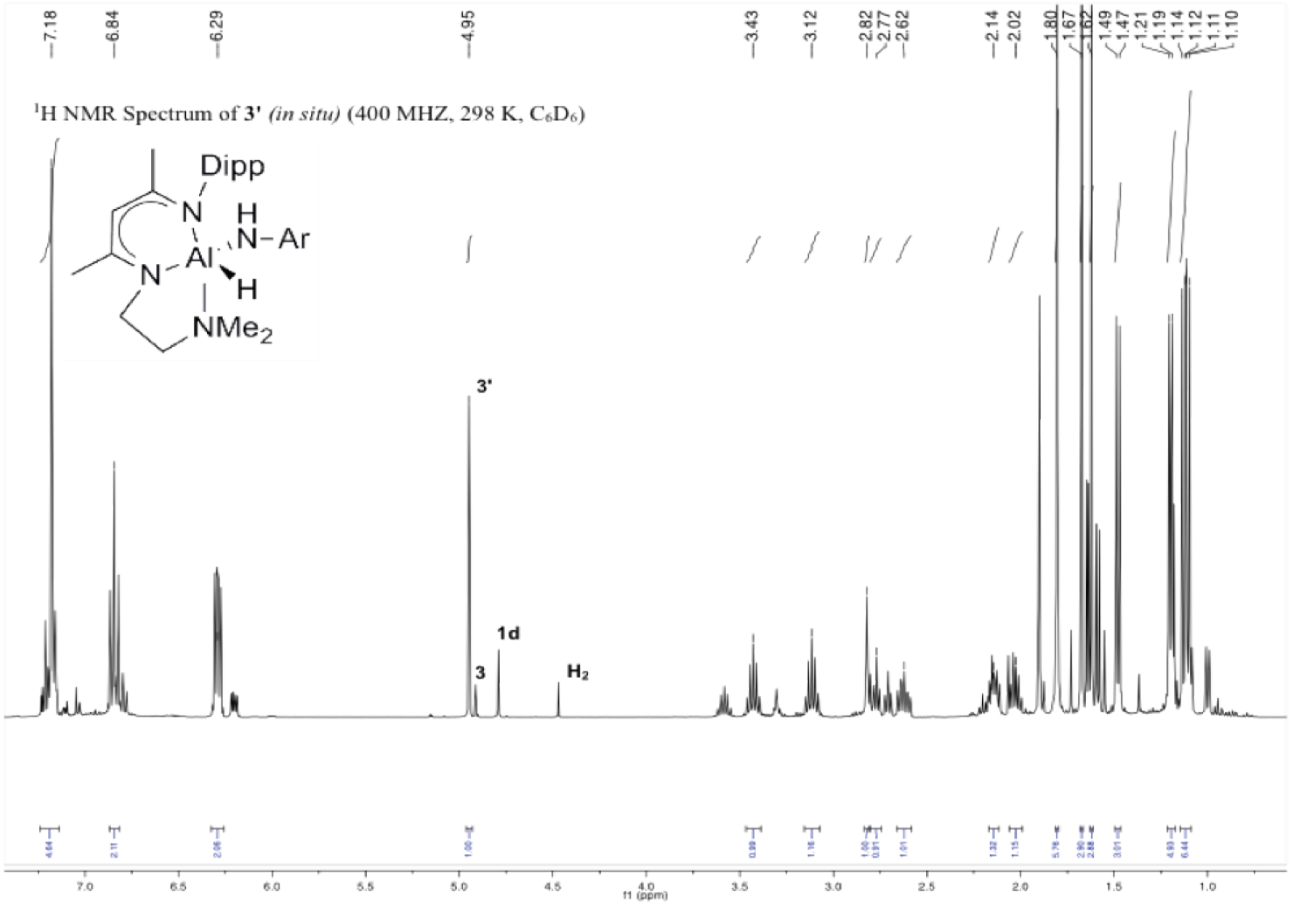



^{1}H NMR Spectrum of **3** (400 MHZ, 298 K, C_6D_6)
Dipp
N
H
N–Ar
Al
N
N–Ar
H
Me_2N
f1 (ppm)

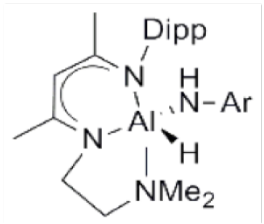

^{13}C NMR Spectrum of **3** (100 MHZ, 298 K, C_6D_6)
171.2
169.8
156.0
154.2
148.7
145.1
139.3
124.7
116.9
115.5
97.4
60.5
46.2
45.8
28.2
25.0
24.2
23.2
21.3
Dipp
N
H
N–Ar
Al
N
N–Ar
H
Me$_2$N
f1 (ppm)

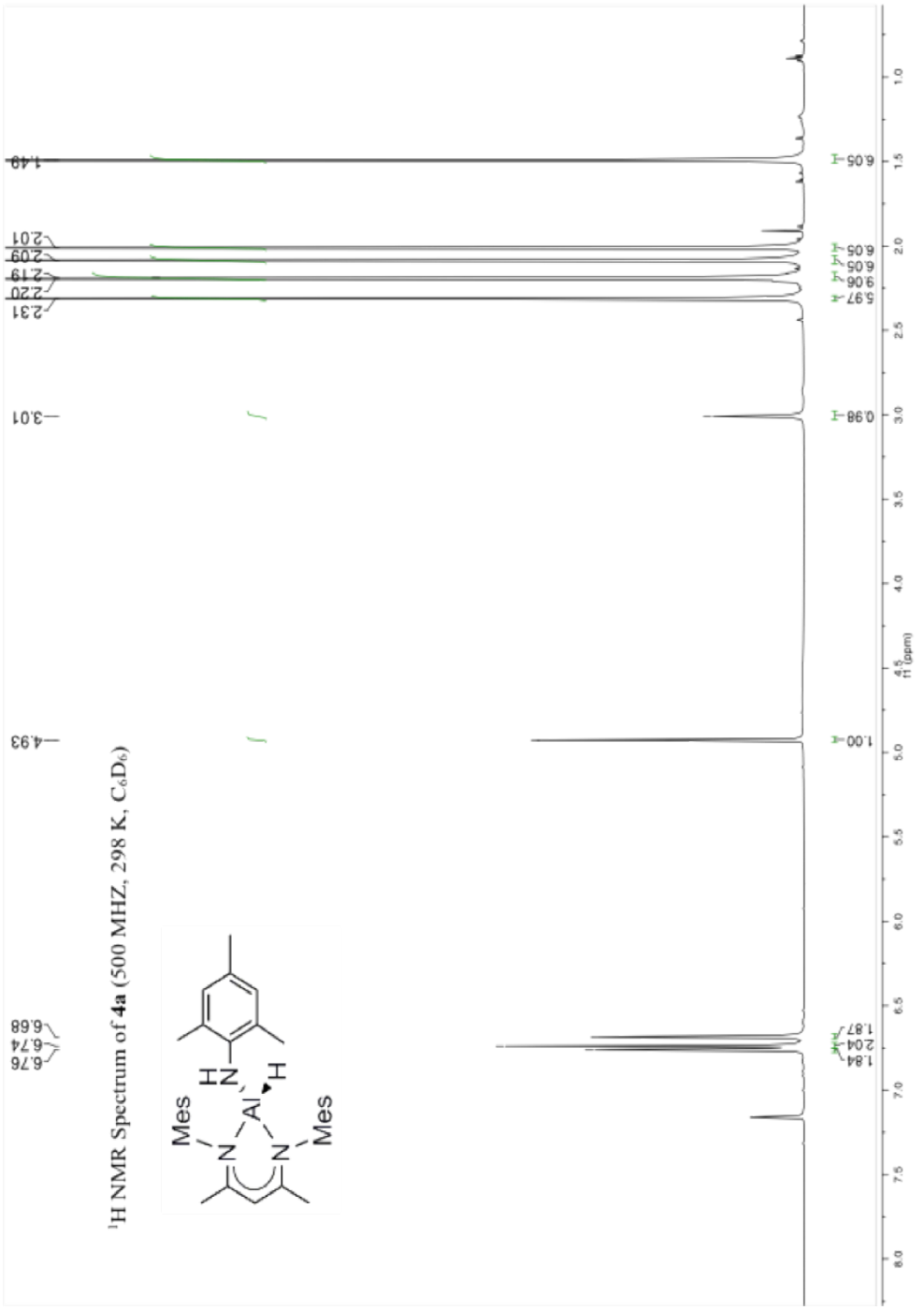
^{19}F NMR Spectrum of **3** (300 MHZ, 298 K, C_6D_6)

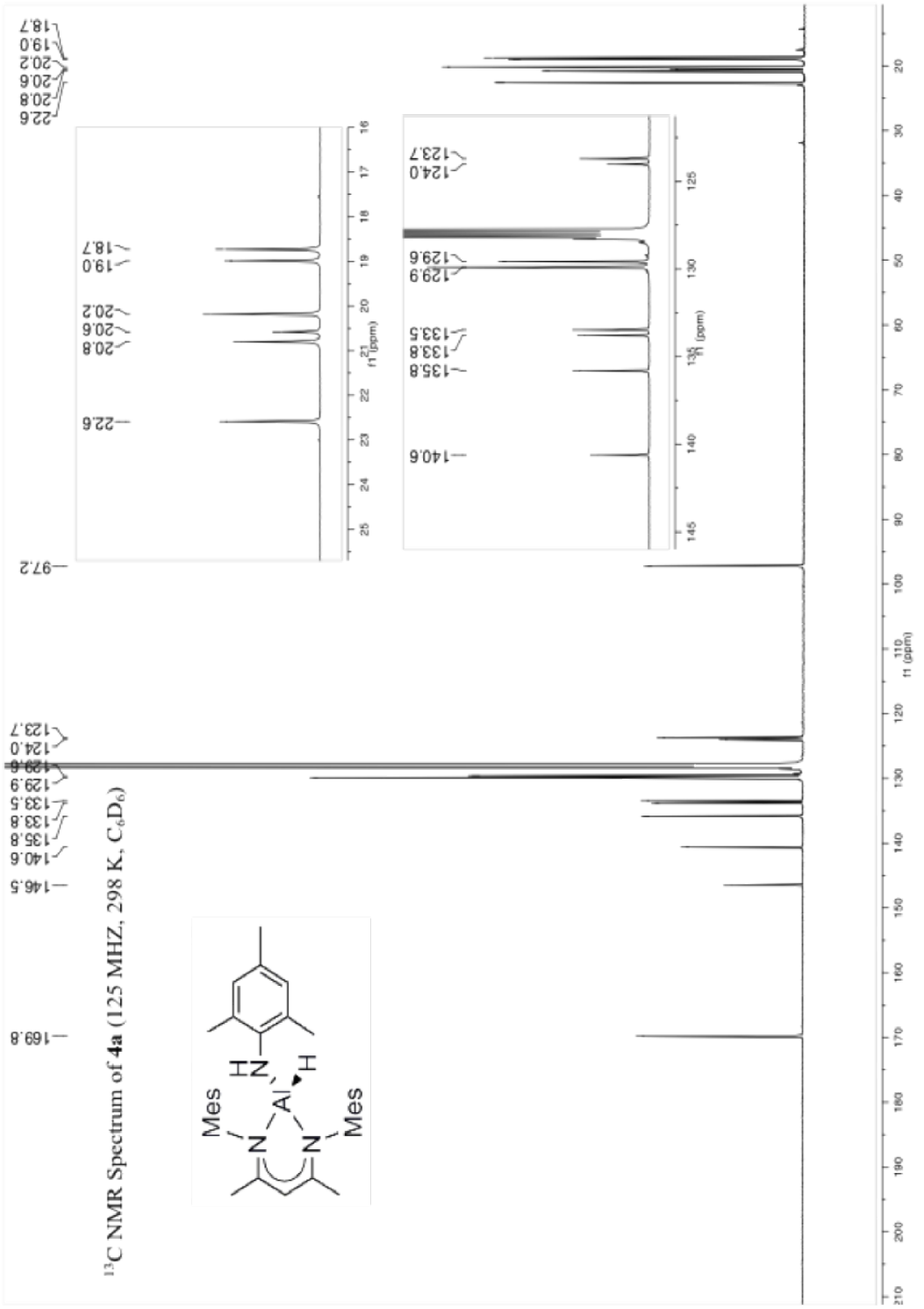


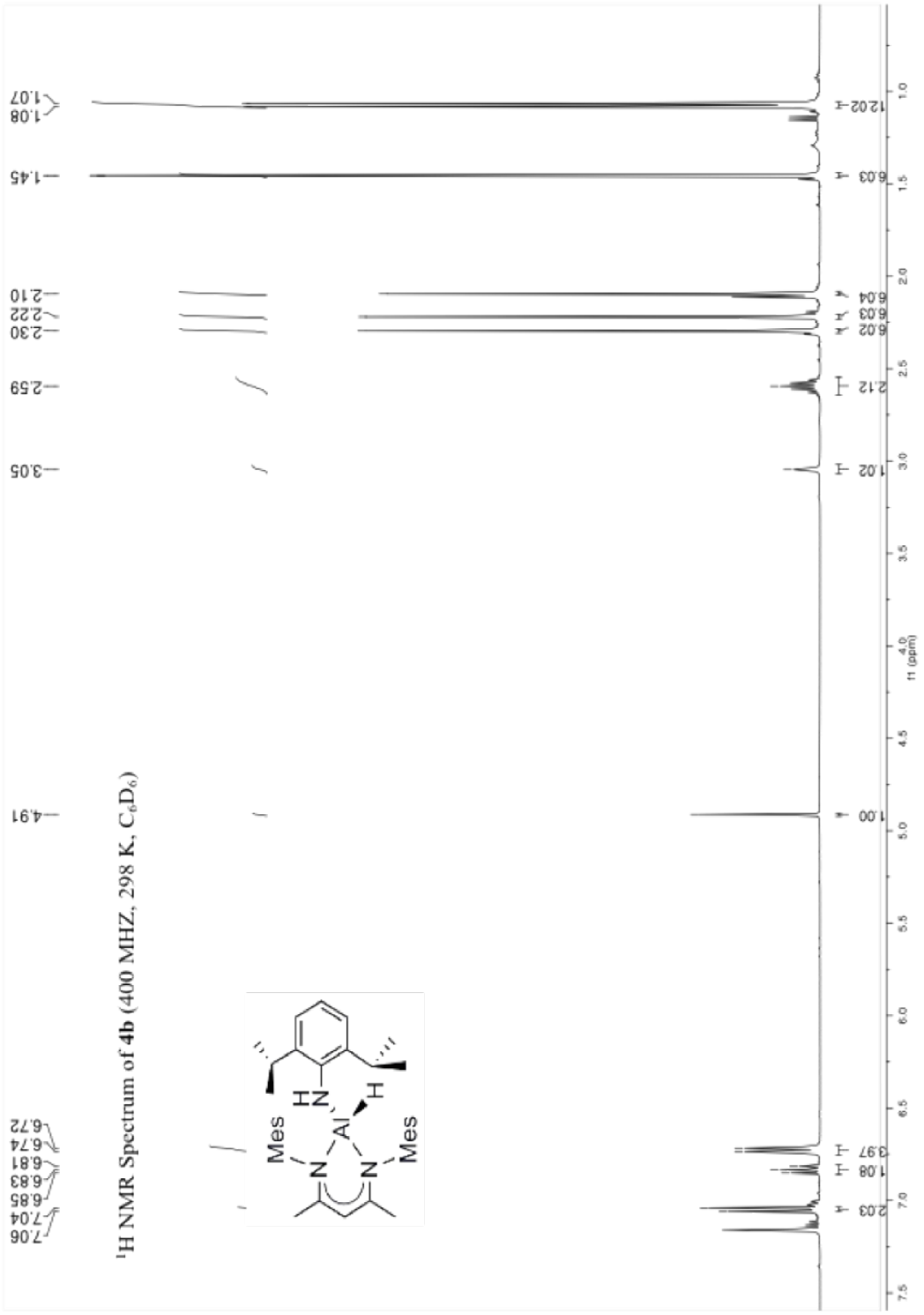

7.18
6.84
6.29
4.95
3.43
3.12
2.82
2.77
2.62
2.14
2.02
1.80
1.67
1.62
1.49
1.47
1.21
1.19
1.14
1.12
1.11
1.10
¹H NMR Spectrum of 3' (in situ) (400 MHZ, 298 K, C6D6)
Dipp
N
H
N–Ar
Al
N
H
NMe2
3'
1d
3
H2
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

^{19}F NMR Spectrum of **3'** *(in situ)* (300 MHZ, 298 K, C_6D_6)

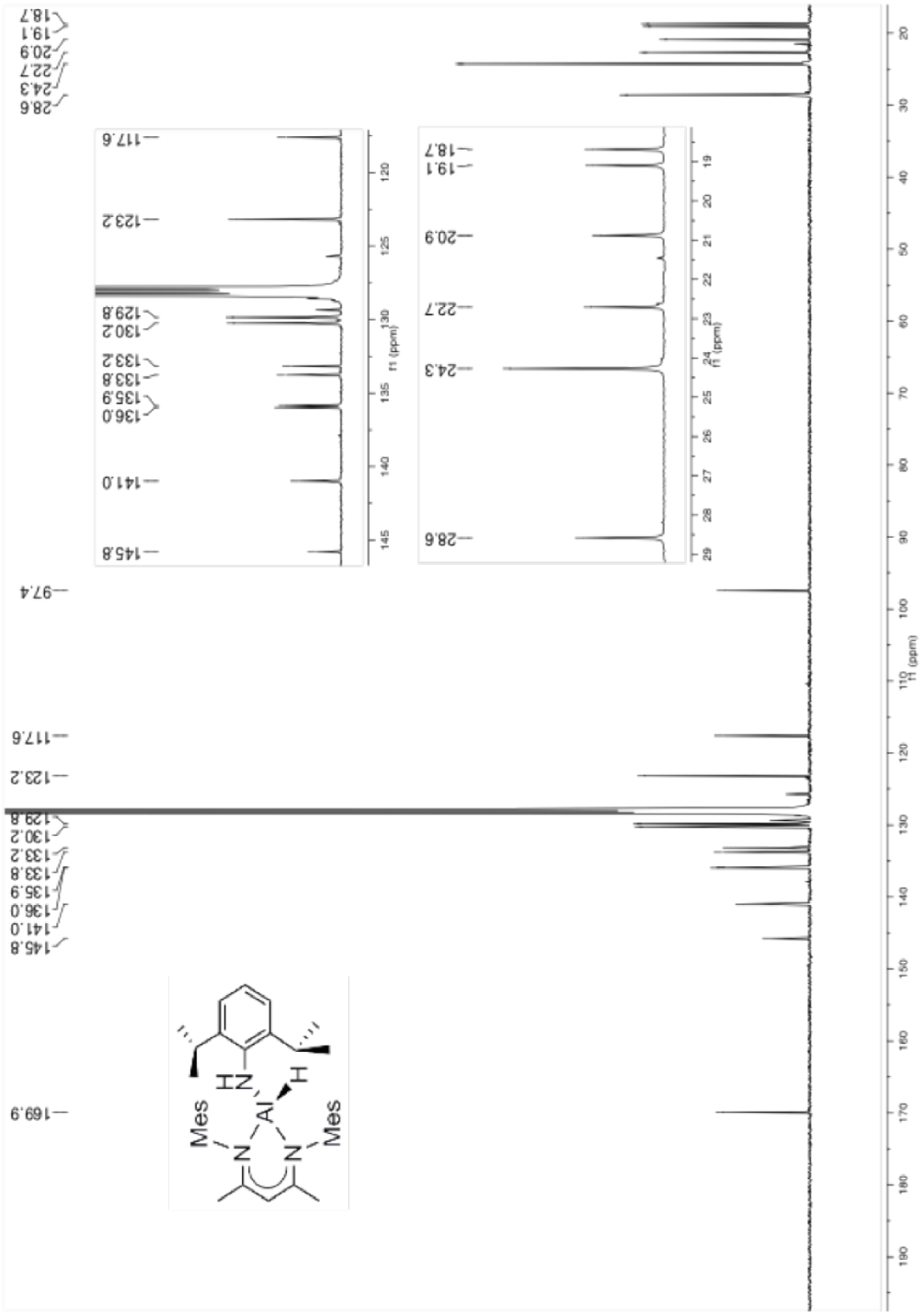


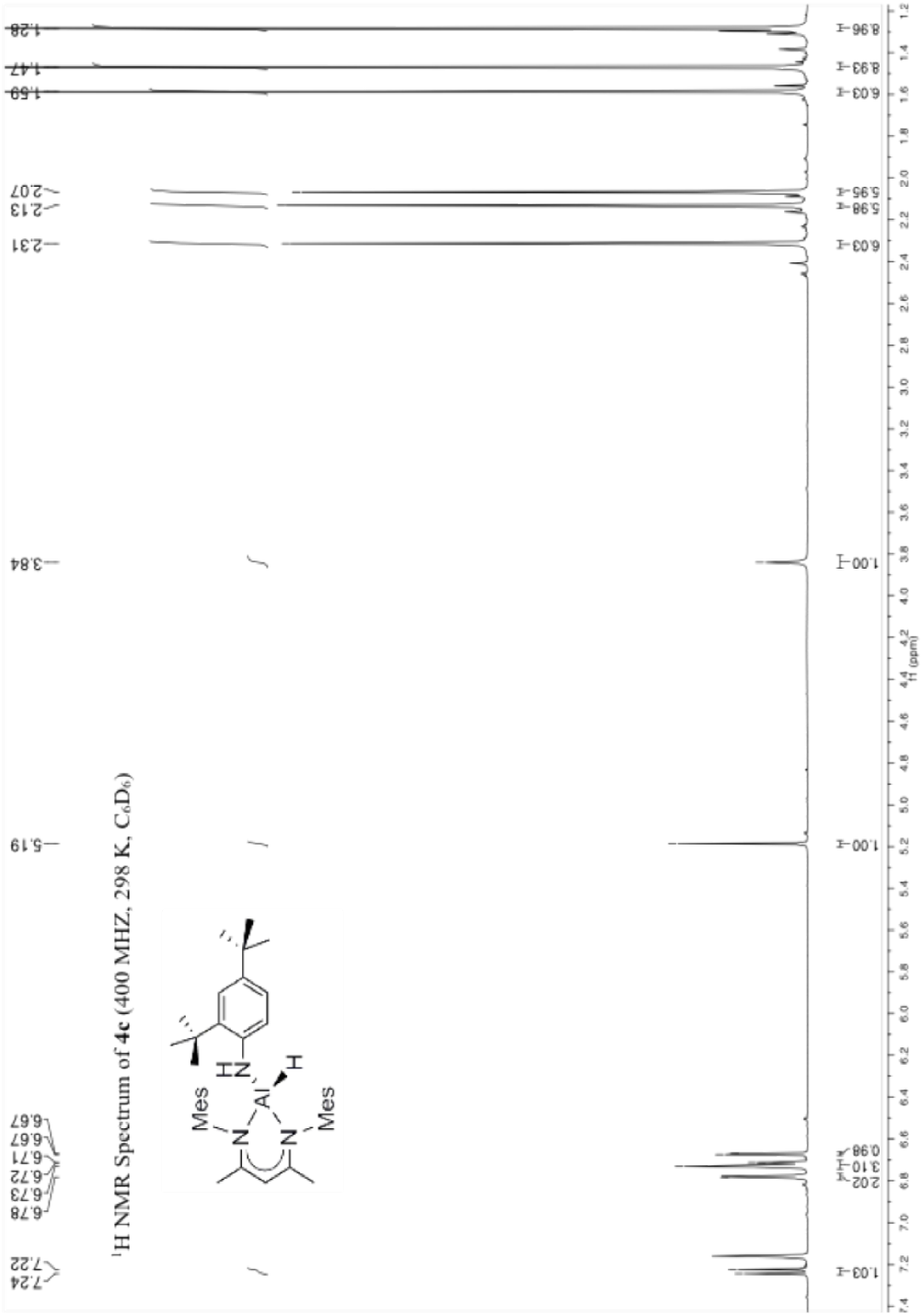

1H NMR Spectrum of 4a (500 MHZ, 298 K, C6D6)
Mes
N
H
Al
H
N
Mes
6.76
6.74
6.68
4.93
3.01
2.31
2.20
2.19
2.09
2.01
1.49
1.84
2.04
1.87
1.00
0.98
5.97
9.06
6.05
6.05
6.05
f1 (ppm)

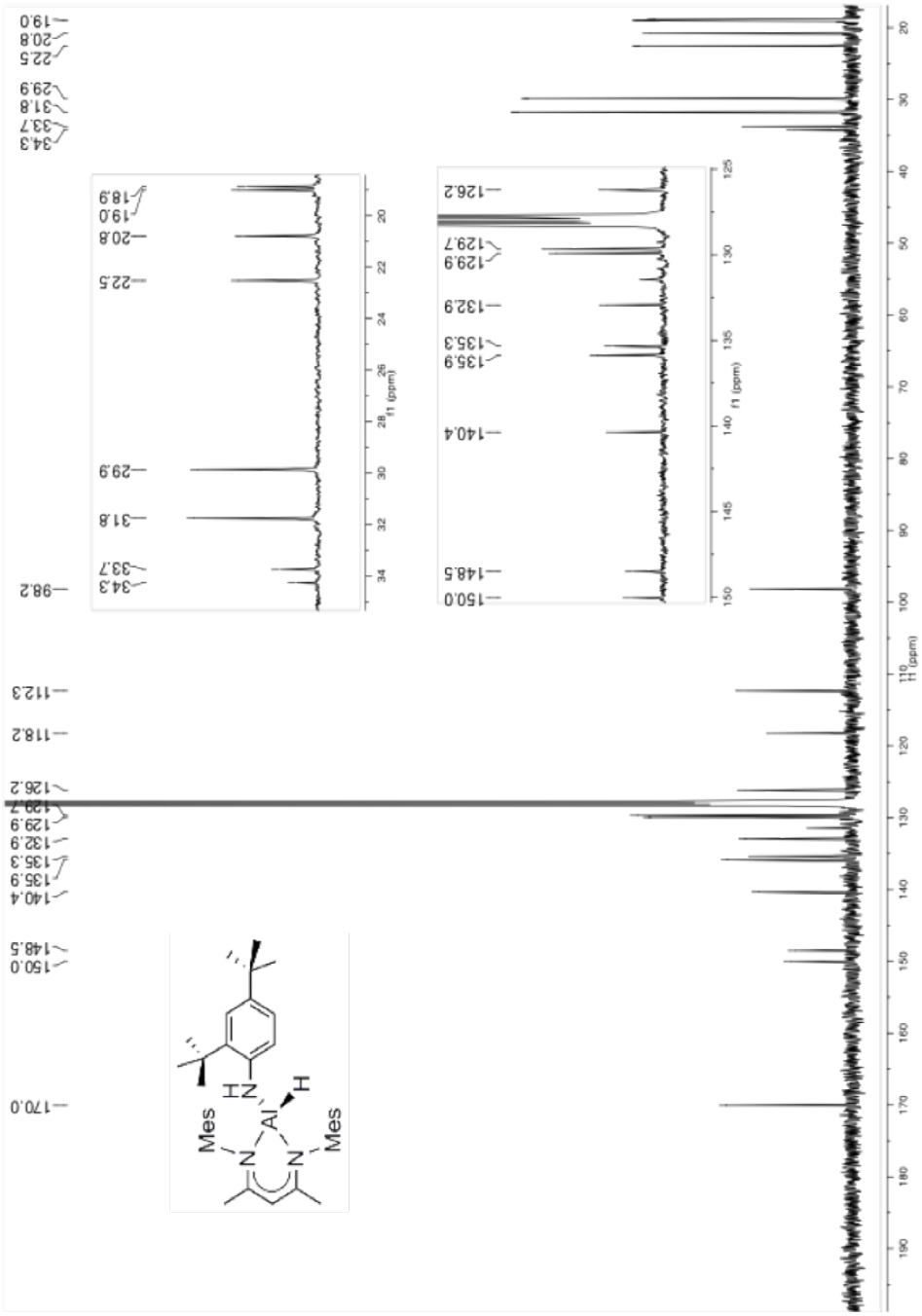

^{13}C NMR Spectrum of **4a** (125 MHZ, 298 K, C_6D_6)
Mes
Mes
N
N
Al
H
H
169.8
146.5
140.6
135.8
133.8
133.5
129.9
129.6
124.0
123.7
97.2
22.6
20.8
20.6
20.2
19.0
18.7
f1 (ppm)

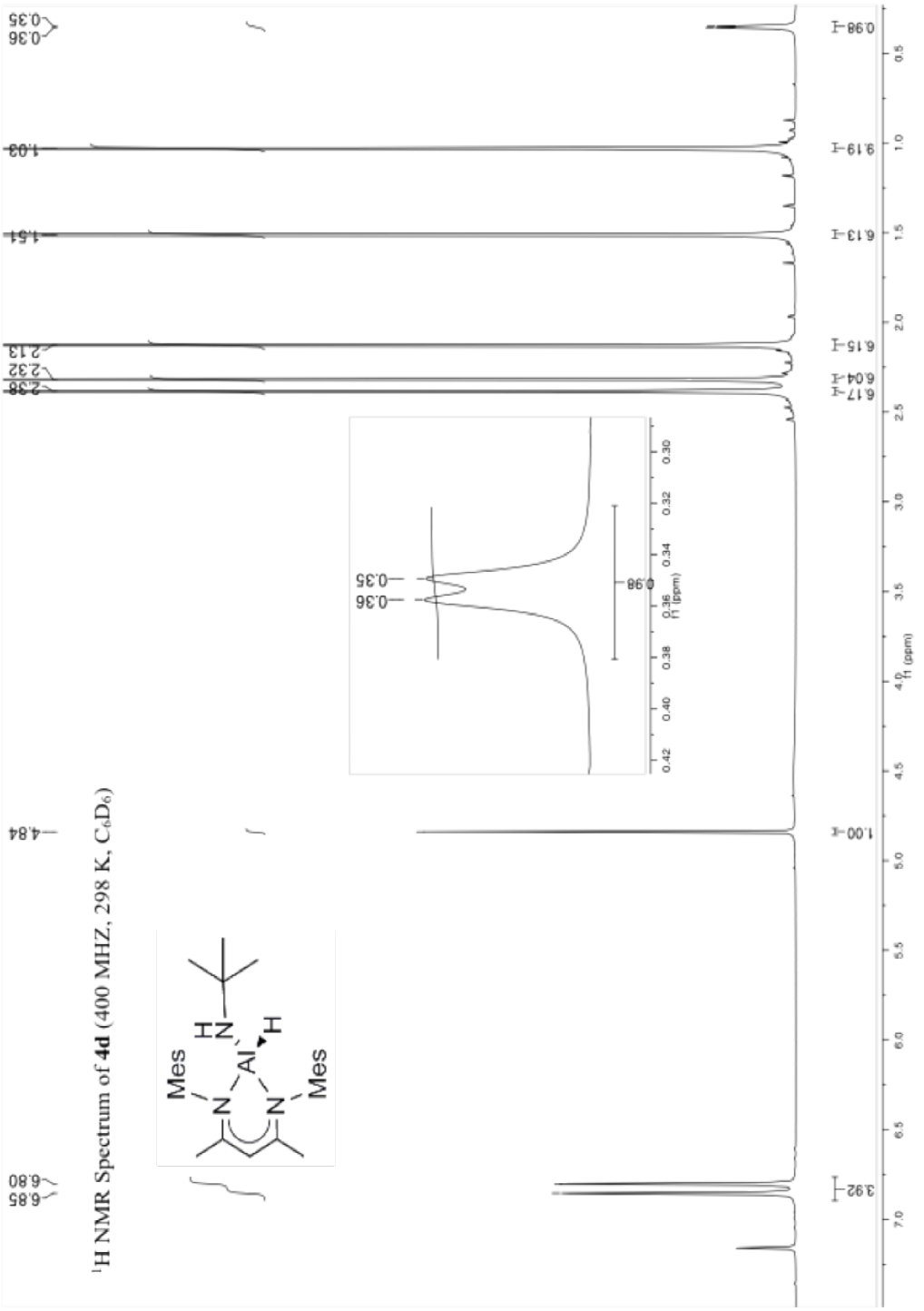


^{1}H NMR Spectrum of **4b** (400 MHZ, 298 K, C_6D_6)

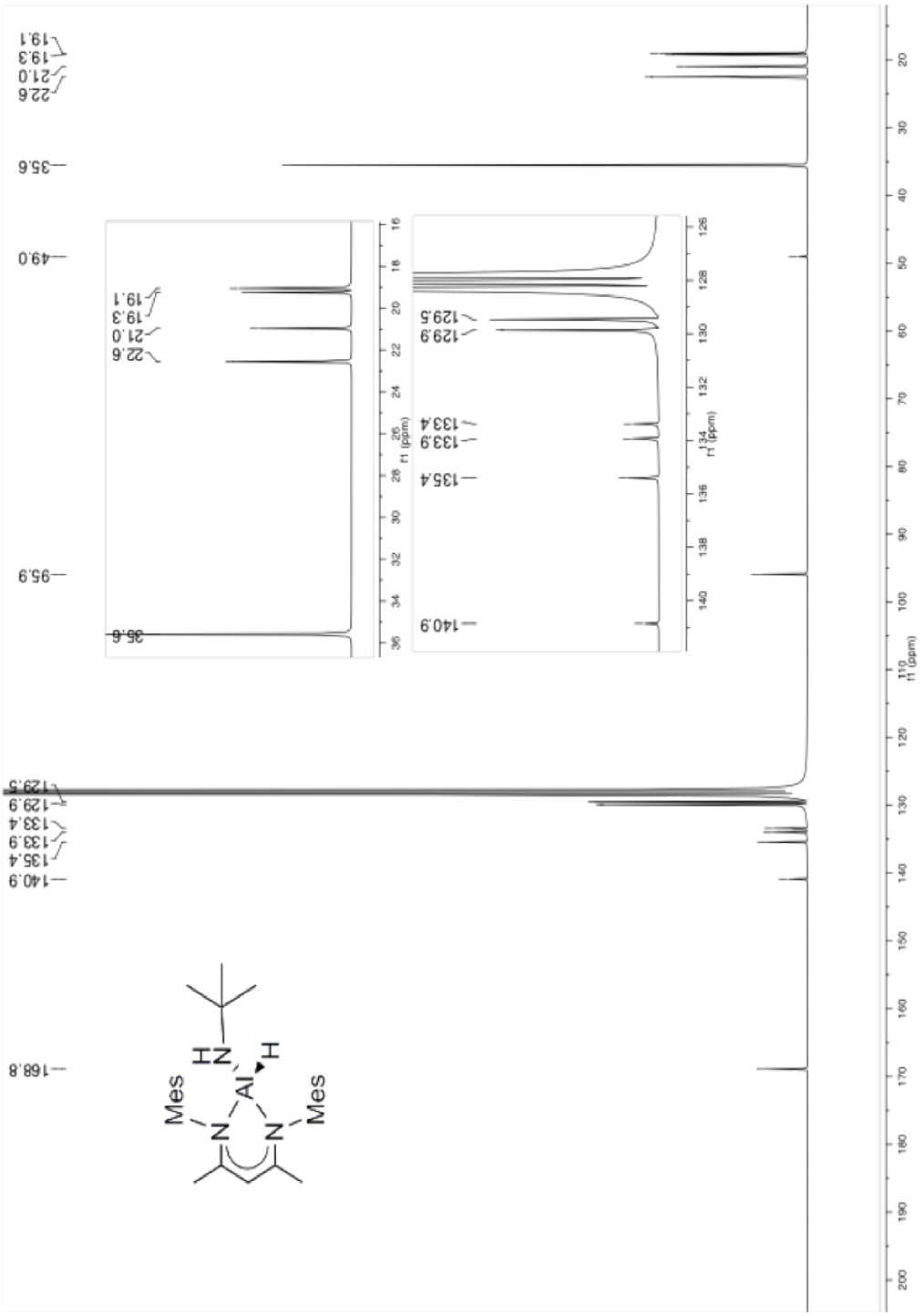

Mes
N
Al
H
N
Mes

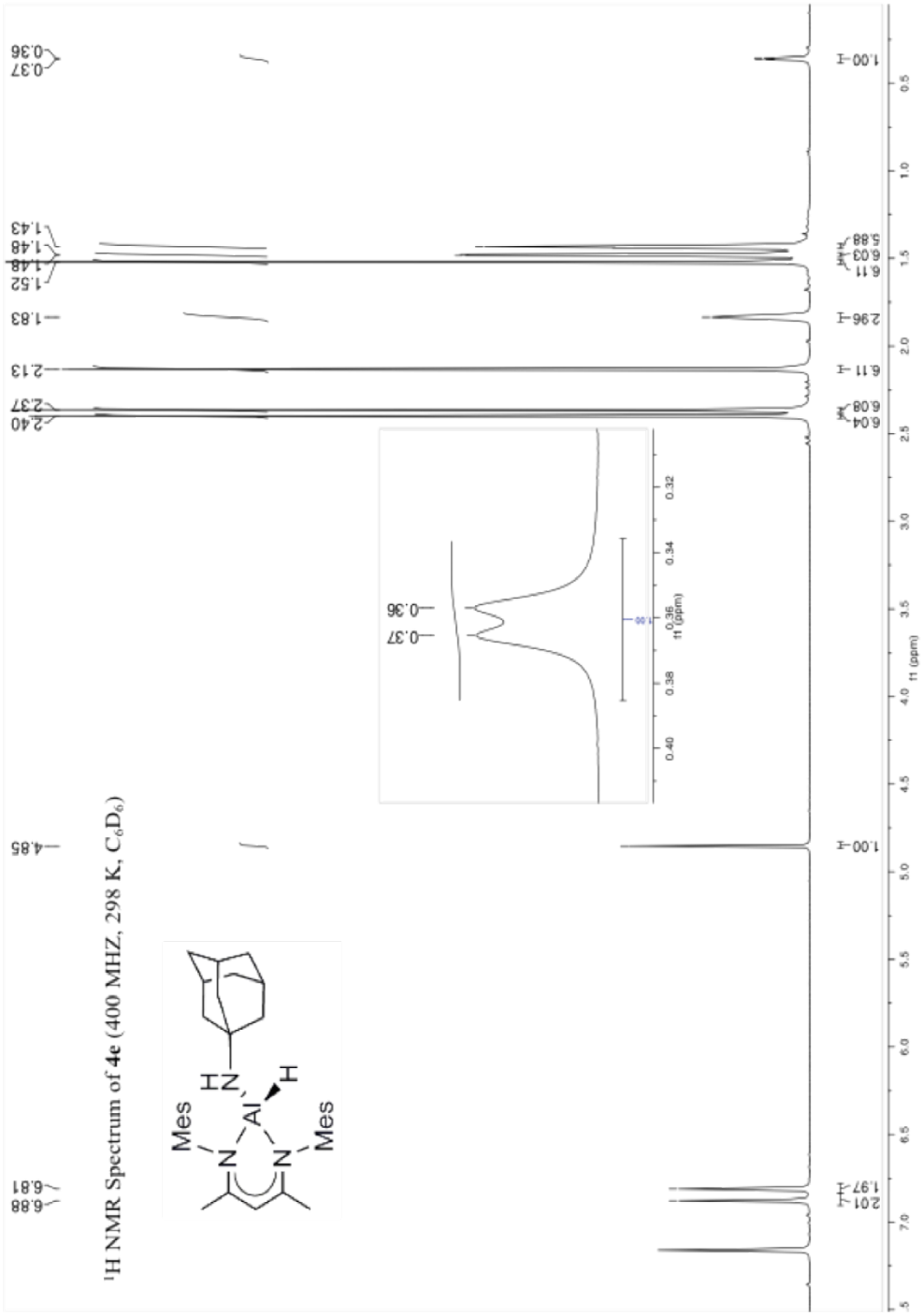

^{1}H NMR Spectrum of **4c** (400 MHZ, 298 K, C_6D_6)
Mes
Al
H
N
Mes
f1 (ppm)


170.0
150.0
148.5
140.4
135.9
135.3
132.9
129.9
129.7
126.2
118.2
112.3
98.2
34.3
33.7
31.8
29.9
22.5
20.8
19.0
18.9
f1 (ppm)
Mes
Mes
Al
H
N
N
N

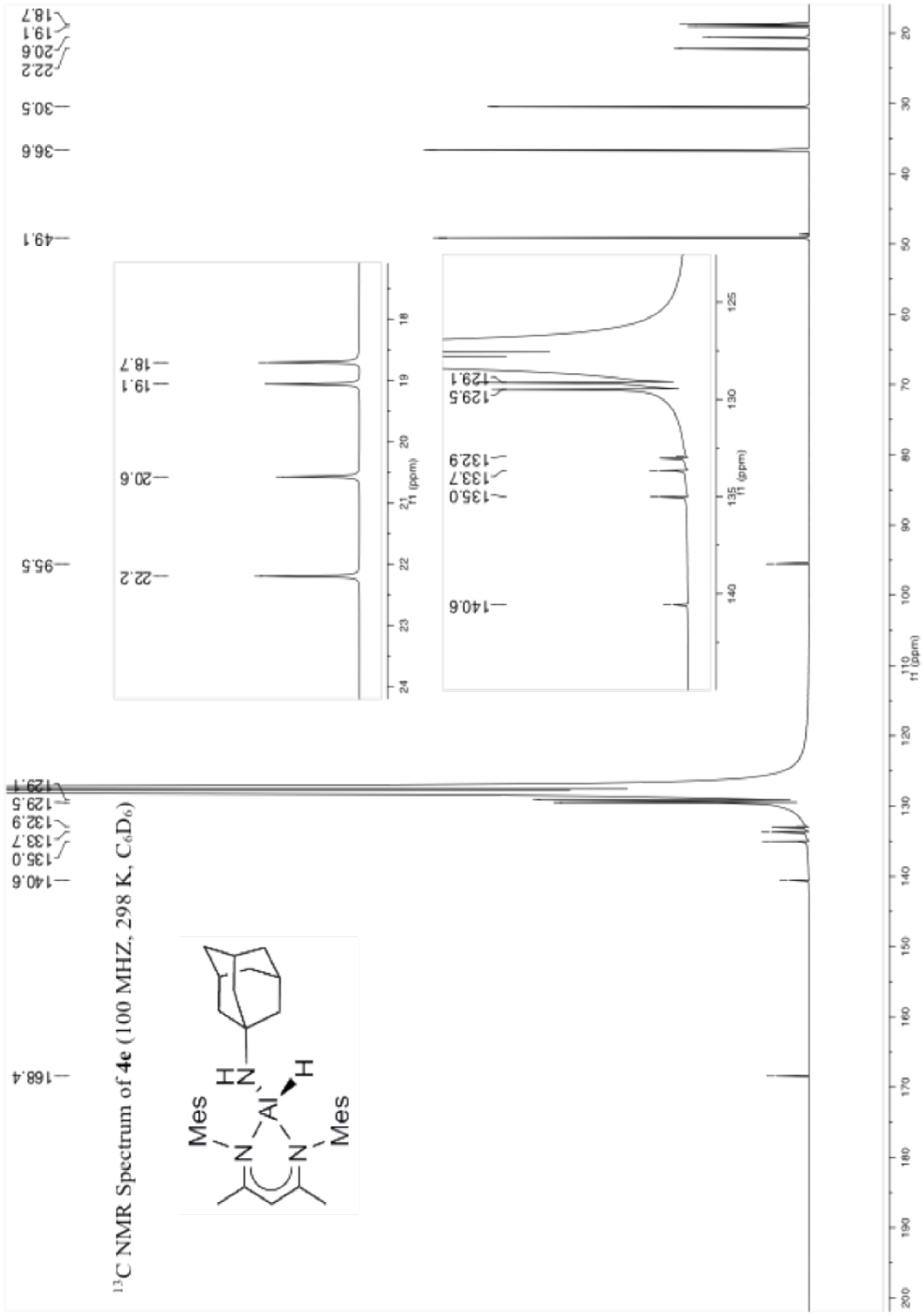


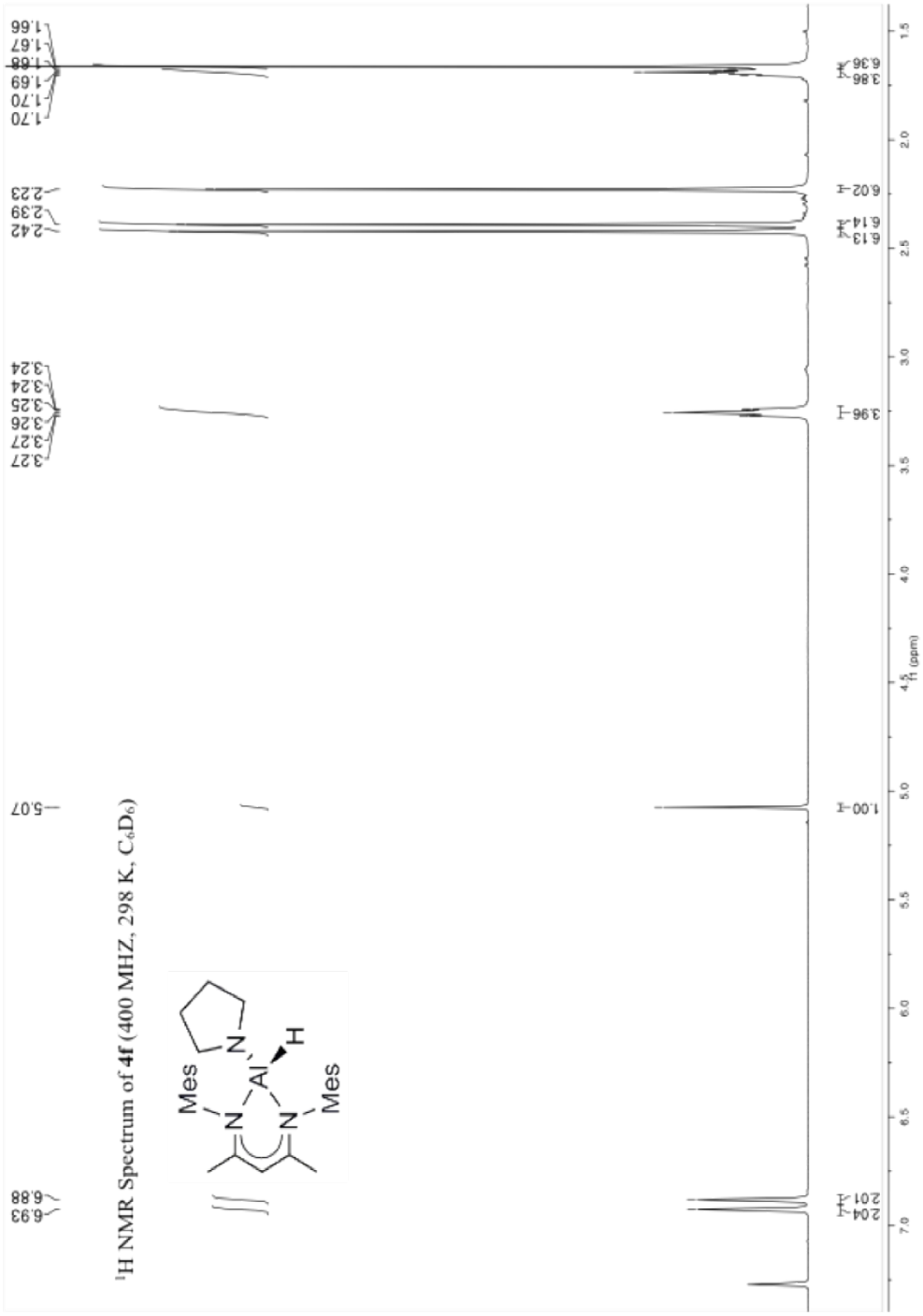
^{1}H NMR Spectrum of **4d** (400 MHZ, 298 K, C_6D_6)


168.8
140.9
135.4
133.9
133.4
129.9
129.5
95.9
49.0
35.6
22.6
21.0
19.3
19.1
Mes
Mes
N
Al
H
H
N
f1 (ppm)

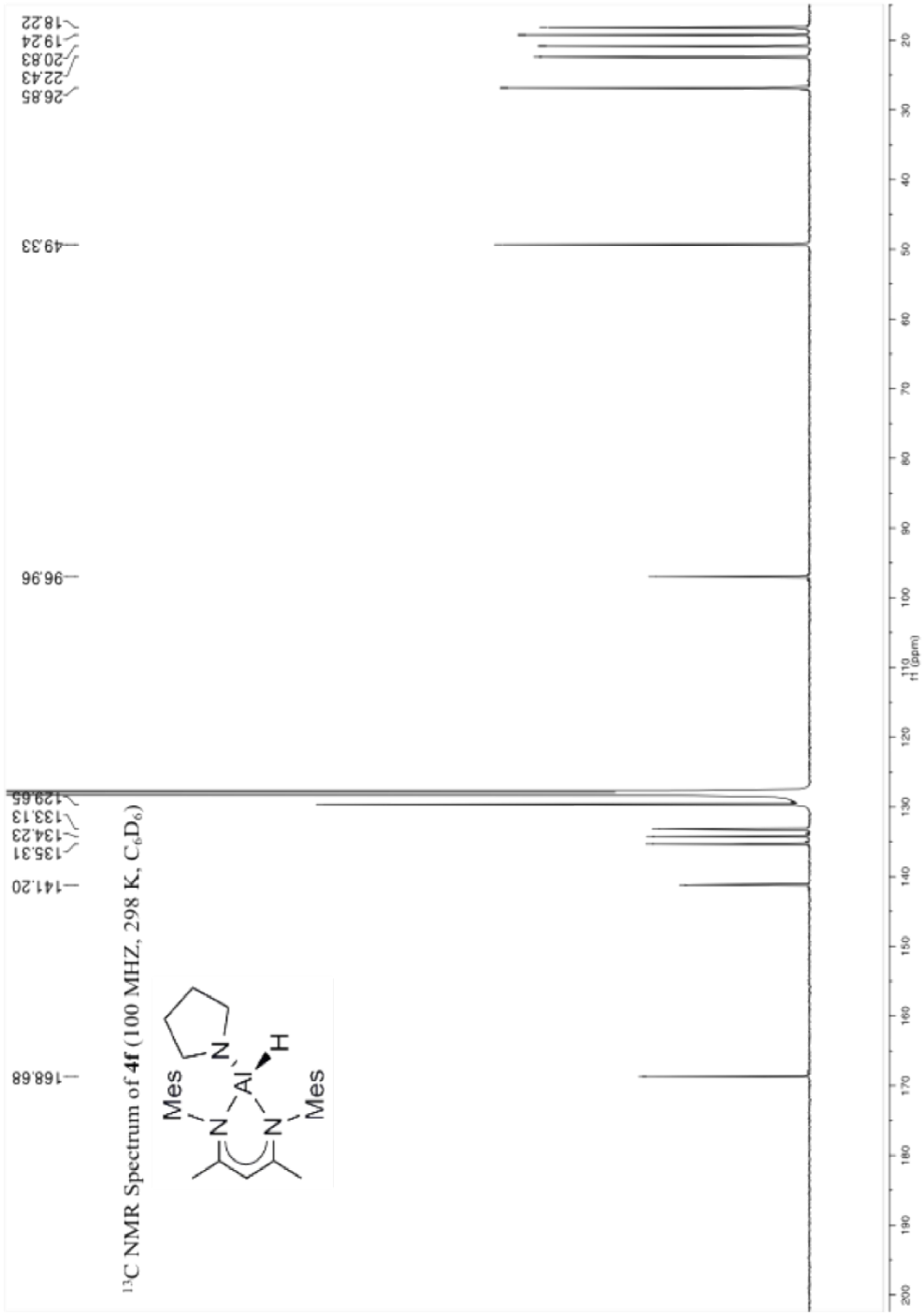


^{1}H NMR Spectrum of **4e** (400 MHZ, 298 K, C_6D_6)

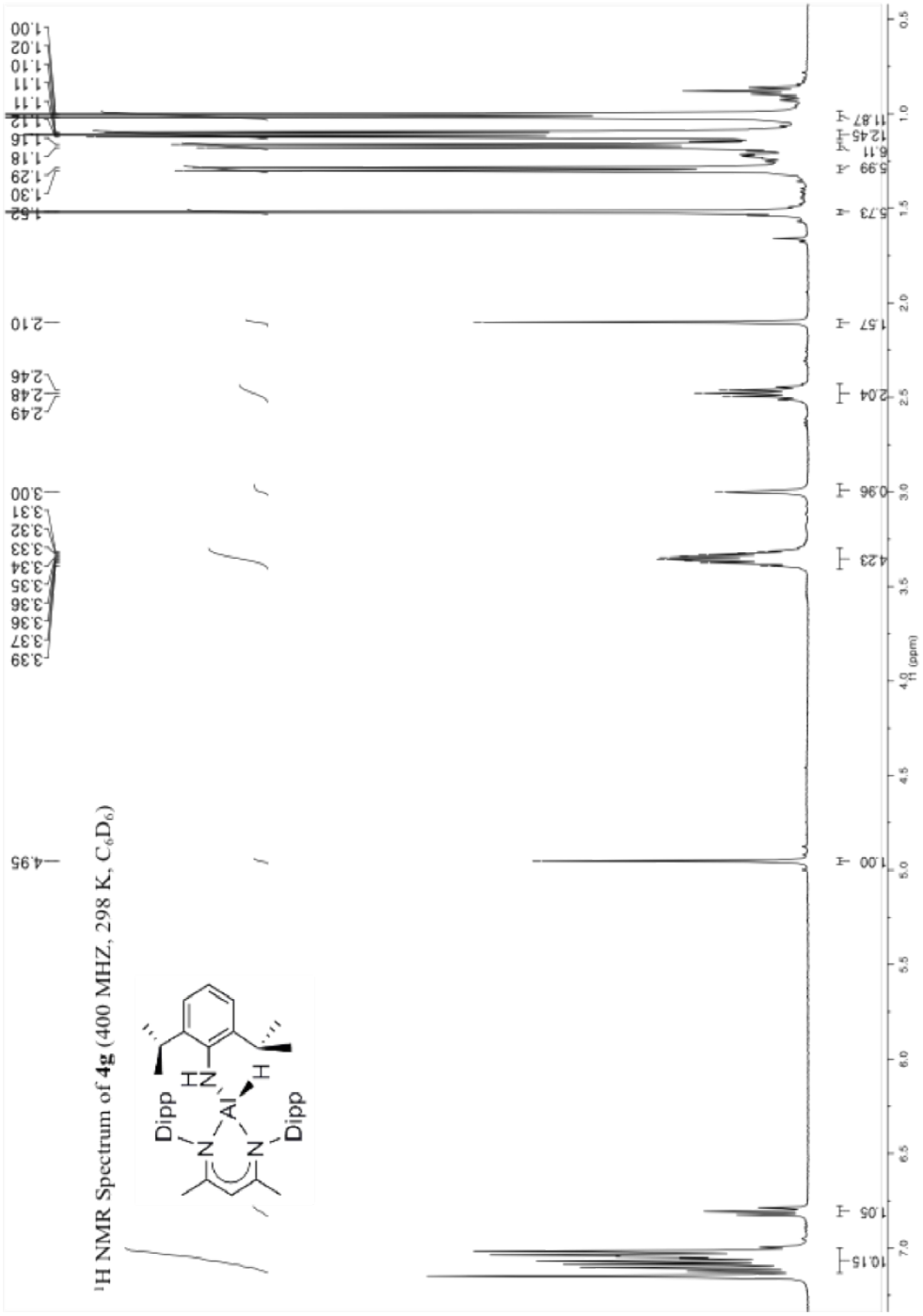

^{13}C NMR Spectrum of **4e** (100 MHZ, 298 K, C_6D_6)
Mes
N
Al
H
Mes
168.4
140.6
135.0
133.7
132.9
129.5
129.1
95.5
49.1
36.6
30.5
22.2
20.6
19.1
18.7
f1 (ppm)



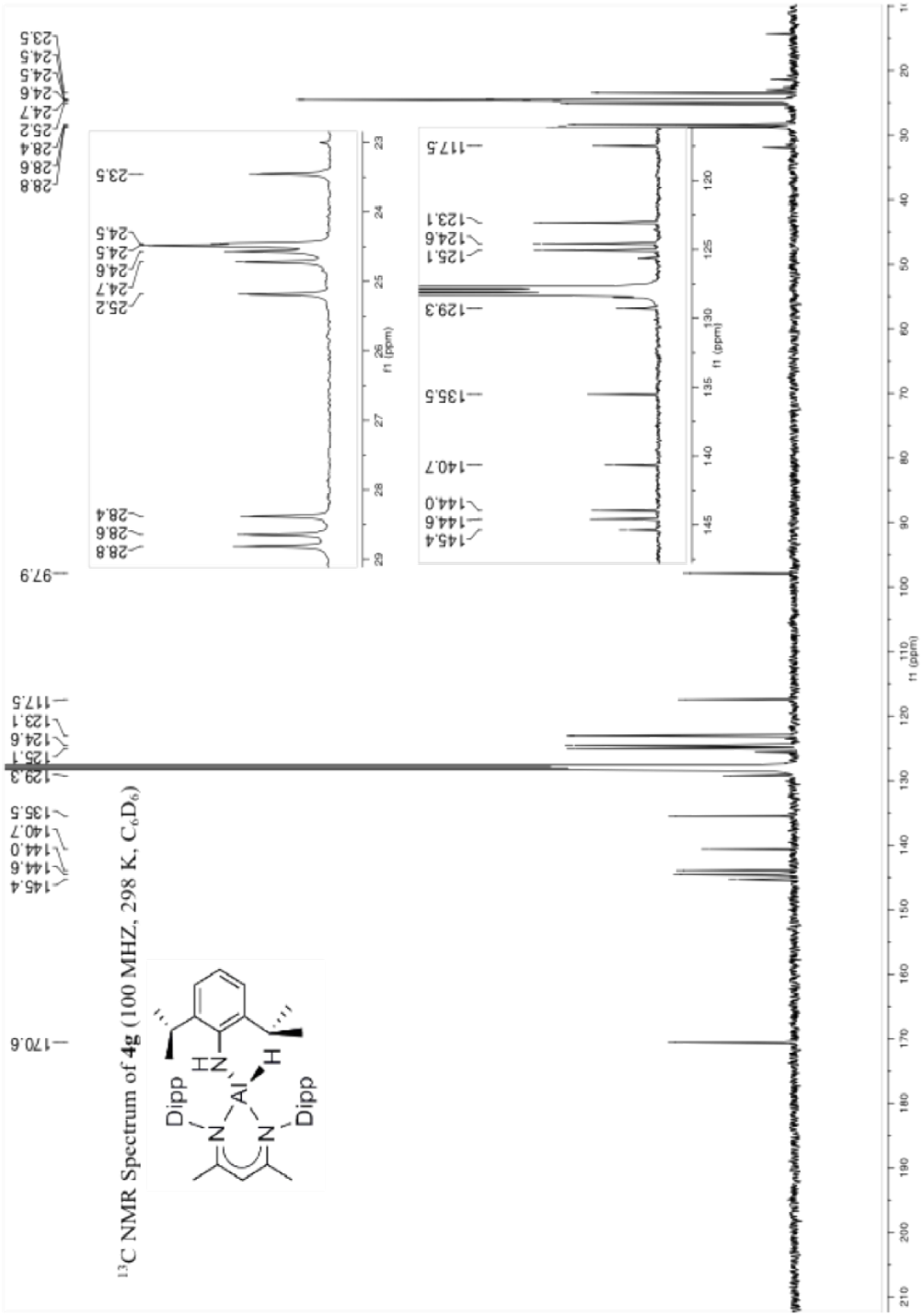
^{1}H NMR Spectrum of **4f** (400 MHZ, 298 K, C_6D_6)

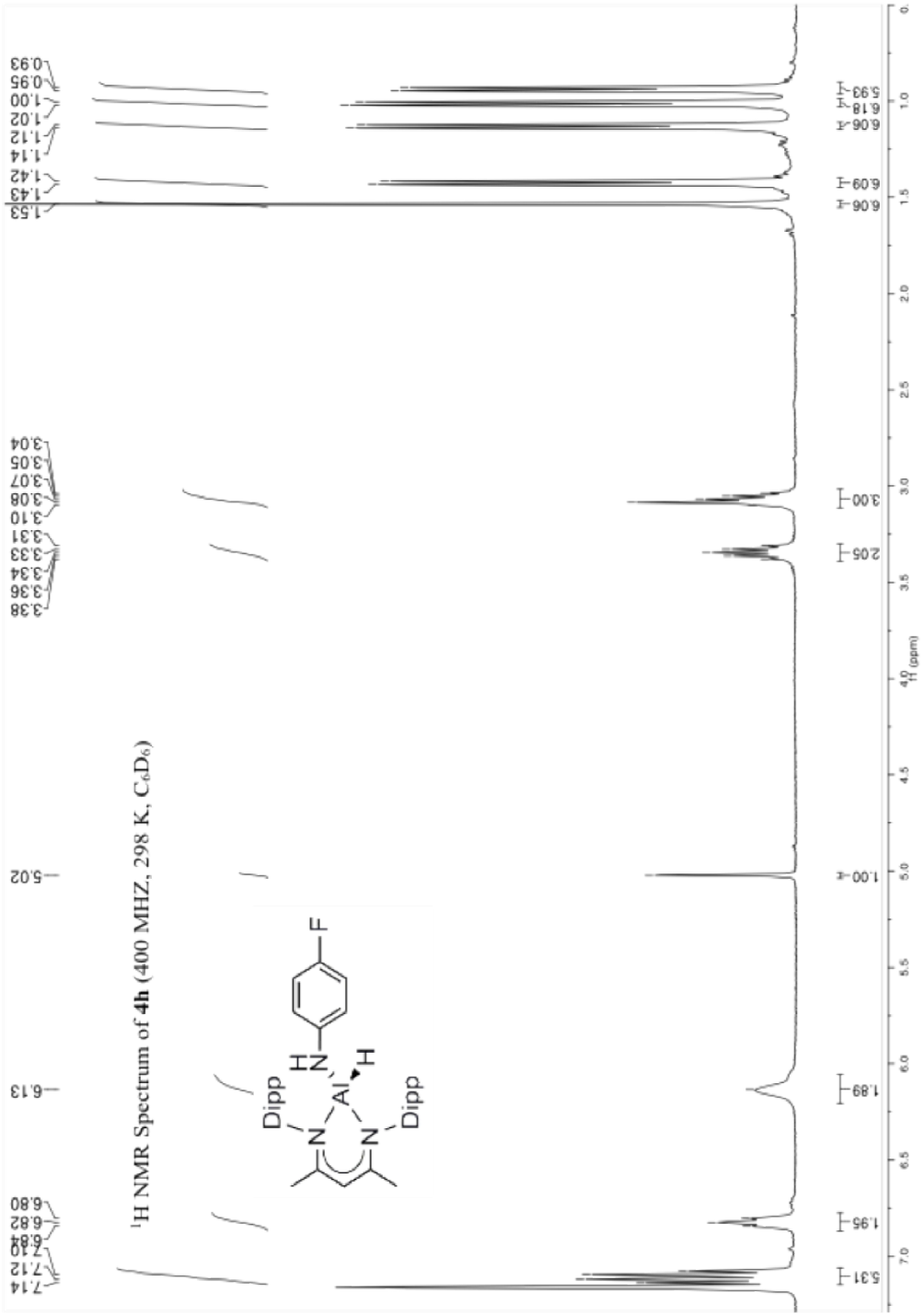


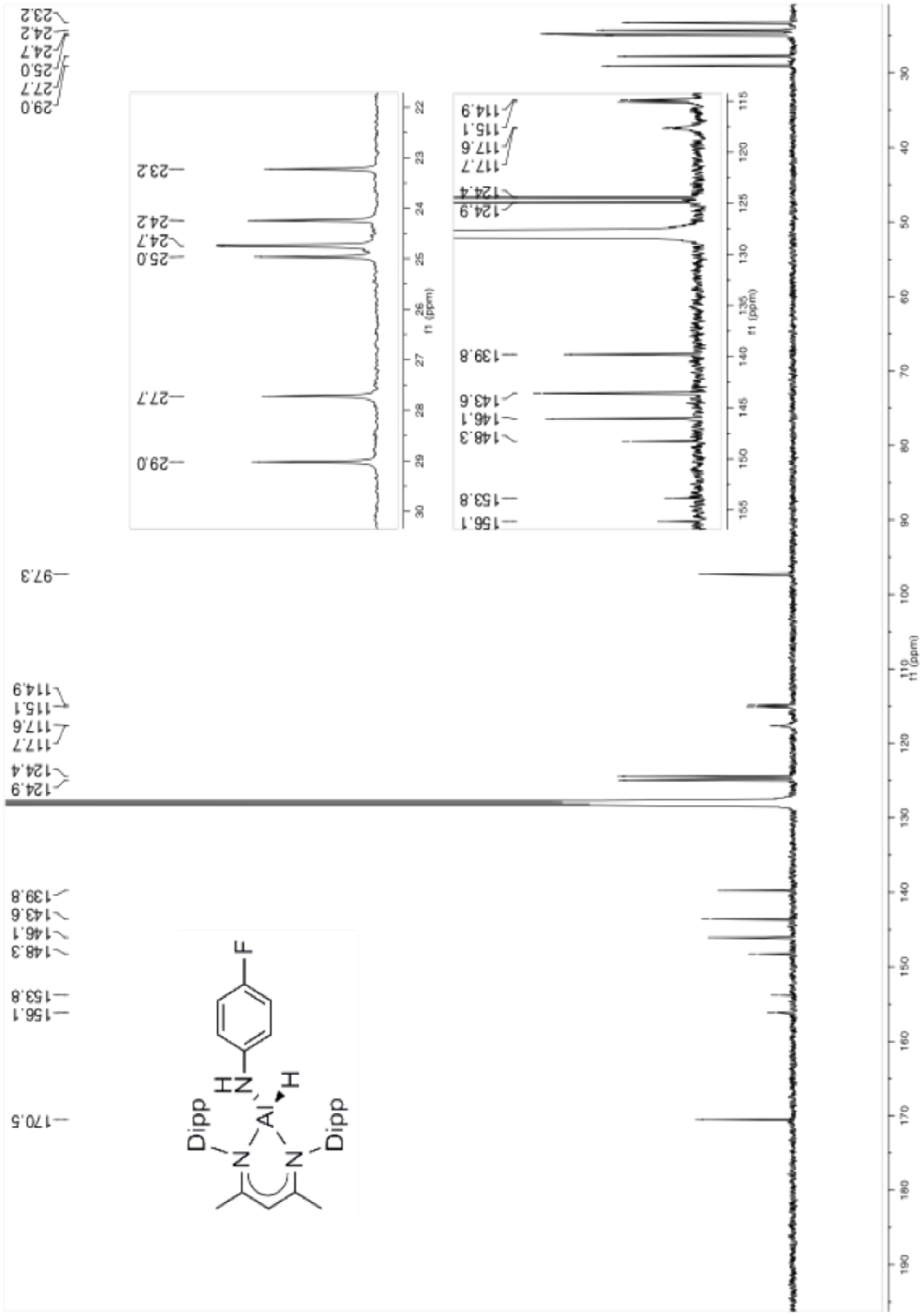
^{13}C NMR Spectrum of **4f** (100 MHZ, 298 K, C_6D_6)



^{1}H NMR Spectrum of **4g** (400 MHZ, 298 K, C_6D_6)


^{13}C NMR Spectrum of **4g** (100 MHZ, 298 K, C_6D_6)
Dipp
H
N
Al
H
N
N
Dipp
170.6
145.4
144.6
144.0
140.7
135.5
129.3
125.1
124.6
123.1
117.5
97.9
28.8
28.6
28.4
25.2
24.7
24.6
24.5
24.5
23.5
f1 (ppm)


¹H NMR Spectrum of 4h (400 MHZ, 298 K, C6D6)
F
H
N
Al
H
Dipp
N
N
Dipp
0.93
0.95
1.00
1.02
1.12
1.14
1.42
1.43
1.53
3.04
3.05
3.07
3.08
3.10
3.31
3.33
3.34
3.36
3.38
5.02
6.13
6.80
6.82
6.84
7.10
7.12
7.14
5.93
6.18
6.06
6.09
6.06
3.00
2.05
1.00
1.89
1.95
5.31
f1 (ppm)


Dipp
Al
H
N
N
Dipp
F
H

^{19}F NMR Spectrum of **4h** (300 MHZ, 298 K, C_6D_6)