

Supporting Information for:

***Oxidative Addition of Carbon–Fluorine
and Carbon–Oxygen Bonds to Al(I)***

Mark R. Crimmin, Michael J. Butler and Andrew J. P. White

Department of Chemistry, Imperial College London, South Kensington, London SW7 2AZ, U.K. Tel:
+44(0)2075942846; E-mail: m.crimmin@imperial.ac.uk

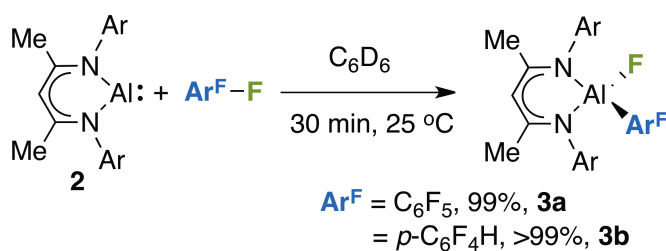
General Experimental

All manipulations were carried out under standard Schlenk-line or glovebox techniques under an inert atmosphere of nitrogen. A MBRAUN Labmaster glovebox was employed operating under an inert atmosphere of concentrations of H₂O and O₂ below 0.1 ppm. Glassware was dried for 12 hours at 120 °C prior to use. C₆D₆ and D₈-toluene were stored over molecular sieves for twelve hours before using. All other solvents were dried using a Grubbs type solvent purification system. ¹H, ¹³C, ²⁹Si NMR experiments were run within Youngs Tap NMR tubes on 400 MHz or 500 MHz BRUCKER machines. HSQC, and DEPT-135 experiments were run on a 400 MHz or 500 MHz NMR machine. The majority of ¹H spectra were recorded from + 30ppm to - 20ppm. Spectra were referenced to known solvent peaks. NMR analysis was conducted in Topspin or MestReNova with baseline corrections applied to spectra. All attempts to acquire satisfactory elemental analysis failed. Complex **2** was synthesised according to the literature procedure.¹

Synthetic Procedure for Oxidative Addition to Al(I)

Procedure for the addition of fluoroarenes, fluoroalkanes (pentafluorobenzene, cyclohexylfluoride, n-hexylfluoride, hexafluorobenzene) to 2: In a glovebox **2** (20 mg, 0.045 mmol) was weighed into a 2mL scintillation vial and dissolved in 0.5 mL of benzene-d₆, ferrocene (1-2 mg) was added to the solution and the mixture transferred to a J Youngs NMR tube. An initial time point was measured by ¹H NMR spectroscopy and the mixture returned to the glovebox, the fluorohydrocarbon or benzofuran (0.225 mmol, 5 equiv.) was added by micropipette. For the fluorocarbons, an immediate colour change from red to yellow was observed. The reactions were monitored by ¹H and ¹⁹F NMR spectroscopy and showed formation of the corresponding products **3a-d** after 30 min at 25 °C. For benzofuran the mixture was heated to 80 °C for 24h and slow conversion to **4** was observed. At the end point of the reaction, the products were isolated by removal of the solvent and recrystallisation from n-hexane. NMR yields were measured by comparison to the ferrocene internal standard.

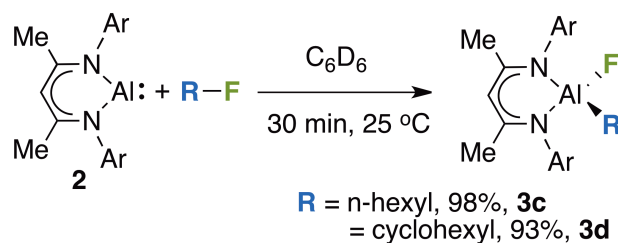
¹ C. Cui, H. W. Roesky, H.-G. Schmidt, M. Noltemeyer, H. Hao, F. Cimpoesu, *Angew. Chem., Int. Ed.* 2000, **39**, 4274.



3a (R = C₆F₅) ¹H NMR (C₆D₆, 400 MHz, 298K) δ 7.10-7.08 (m, 4H), 6.89-6.86 (m, 2H), 4.99 (s, 1H), 3.40 (hept, 2H, ³J_{H-H} = 6.8 Hz), 2.91 (hept, 2H, ³J_{H-H} = 6.8 Hz), 1.48 (s, 6H), 1.47 (d, 6H, ³J_{H-H} = 6.8 Hz), 1.09 (d, 6H, ³J_{H-H} = 6.8 Hz), 0.99 (d, 6H, ³J_{H-H} = 6.8 Hz), 0.45 (d, 6H, ³J_{H-H} = 6.8 Hz); ¹⁹F NMR (C₆D₆, 470.5 Hz, 298 K) δ -118.7 (m, 2F, *ortho*-Ar), -153.4 (t, 1F, ³J_{F-F} = 23.5 Hz, *para*-Ar), -162.1 (m, 2F, *meta*-Ar), -168.2 (broad s, 1F, Al-F). ¹³C NMR (C₆D₆, 125 MHz, 298K) δ 171.9 (C=N), 151.3 (dm, ¹J_{F-C} = 265.0 Hz, Ar^F), 136.9 (dm, ¹J_{F-F} = 313.7 Hz, Ar^F), 144.9 (q Ar), 144.2 (q Ar), 137.9 (q Ar), 128.1 (Ar), 125.0 (Ar), 124.8 (Ar), 98.7 (CHC=N), 29.0 (CHMe₂), 27.8 (CHMe₂), 24.9 (CHMe₂), 24.5 (2 signals, CHMe₂), 24.2 (CHMe₂), 23.2 (Me), *remaining carbons of C₆F₅ unit not resolved due to multiple coupling to ¹⁹F (I=1/2) and line broadening by ²⁷Al (I=5/2)*. Data match those reported previously.²

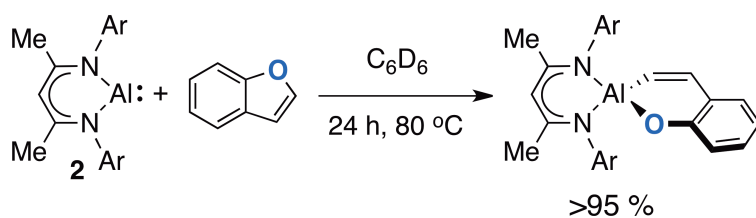
3b (R = 4-C₆F₄H) ¹H NMR (C₆D₆, 400 MHz, 298K) δ 7.10-7.08 (m, 4H), 6.92-6.89 (m, 2H), 6.49-6.40 (m, 1H), 5.01 (s, 1H), 3.43 (hept, 2H, ³J_{H-H} = 6.8 Hz), 3.01 (hept, 2H, ³J_{H-H} = 6.8 Hz), 1.51 (s, 6H), 1.48 (d, 6H, ³J_{H-H} = 6.8 Hz), 1.11 (d, 6H, ³J_{H-H} = 6.8 Hz), 1.03 (d, 6H, ³J_{H-H} = 6.8 Hz), 0.49 (d, 6H, ³J_{H-H} = 6.8 Hz); ¹³C NMR (C₆D₆, 125 MHz, 298K) δ 171.8 (C=N), 151.5 (dm, ¹J_{F-F} = 237.5 Hz, Ar^F), 146.2 (dm, ¹J_{F-F} = 250.0 Hz, Ar^F), 144.9 (q Ar), 144.4 (q Ar), 138.1 (q Ar), 128.1 (Ar), 124.9 (Ar), 124.7 (Ar), 107.3 (t, Ar^FH, ²J_{F-F} = 22.9 Hz), 97.6 (CHC=N), 29.0 (CHMe₂), 27.8 (CHMe₂), 25.0 (CHMe₂), 24.6 (CHMe₂), 24.5 (CHMe₂), 24.3 (CHMe₂), 23.2 (Me), *ipso carbon of C₆F₅H unit not resolved due to multiple coupling to ¹⁹F (I=1/2) and line broadening by ²⁷Al (I=5/2)*; ¹⁹F NMR (C₆D₆, 470.5 Hz, 298 K) δ -120.5 (m, 2F, *ortho*-Ar), -139.8 (m, 2F, *meta*-Ar), -168.5 (broad s, 1F, Al-F). Mass spec (EI, +ve) 612 (40%, M⁺), 463 (100%, [M-C₆F₅H]⁺). HRMS calc. for C₃₅H₄₂N₂F₅Al 612.3084, found 612.3076.

² S. Yow, S. J. Gates, A. J. P. White, M. R. Crimmin, *Angew. Chem., Int. Ed.* 2012, **51**, 12559.



3c (R = n-hexyl): $^1\text{H NMR}$ (C_6D_6 , 400 MHz, 298K) δ 7.15-7.13 (m, 4H), 7.08-7.06 (m, 2H), 4.97 (s, 1H), 3.62 (hept, 2H, $^3J_{\text{H-H}} = 6.8$ Hz), 3.17 (hept, 2H, $^3J_{\text{H-H}} = 6.8$ Hz), 1.57 (s, 6H), 1.47 (d, 6H, $^3J_{\text{H-H}} = 6.8$ Hz), 1.35 (d, 6H, $^3J_{\text{H-H}} = 6.8$ Hz), 1.17 (d, 6H, $^3J_{\text{H-H}} = 6.8$ Hz), 1.10-1.01 (m, 8H), 1.05 (d, 6H, $^3J_{\text{H-H}} = 6.8$ Hz), 0.76 (t, 3H, $^3J_{\text{H-H}} = 7.2$ Hz), -0.14 (m, 2H); $^{13}\text{C NMR}$ (C_6D_6 , 125 MHz, 298K) δ 170.2 (C=N), 145.5 (q Ar), 143.3 (q Ar), 140.2 (q Ar), 127.6 (Ar), 125.1 (Ar), 124.0 (Ar), 97.7 (CHC=N), 35.4 (*hex*CH₂), 31.9 (*hex*CH₂), 29.0 (CHMe₂), 27.9 (CHMe₂), 25.8 (CHMe₂), 25.1 (*hex*CH₂), 24.8 (CHMe₂), 24.4 (CHMe₂), 24.0 (CHMe₂), 23.0 (Me), 22.8 (*hex*CH₂), 14.3 (*hex*CH₃), 5.9 (broad, Al-C); $^{19}\text{F NMR}$ (C_6D_6 , 470.5 Hz, 298 K) δ -157.7 (broad s, 1F, Al-F). Mass spec (EI, +ve) 527 (100%, [M-F]⁺), 463 (95%, [M-C₆H₁₁]⁺). HRMS calc. for C₃₅H₅₂N₂Al 527.3946 found 527.3959.

3d (R = Cy): $^1\text{H NMR}$ (C_6D_6 , 400 MHz, 298K) δ 7.15-7.07 (m, 6H), 4.96 (s, 1H), 3.58 (hept, 2H, $^3J_{\text{H-H}} = 6.8$ Hz), 3.24 (hept, 2H, $^3J_{\text{H-H}} = 6.8$ Hz), 1.56 (s, 6H), 1.55-1.48 (m, 2H), 1.48 (d, 6H, $^3J_{\text{H-H}} = 6.8$ Hz), 1.39 (d, 6H, $^3J_{\text{H-H}} = 6.8$ Hz), 1.32-1.16 (m, 4H), 1.15 (d, 6H, $^3J_{\text{H-H}} = 6.8$ Hz), 1.08-1.01 (m, 2H), 1.07 (d, 6H, $^3J_{\text{H-H}} = 6.8$ Hz), 0.76-0.73 (broad m, 2H), 0.29-0.20 (broad m, 1H); $^{13}\text{C NMR}$ (C_6D_6 , 125 MHz, 298K) δ 170.2 (C=N), 145.4 (q Ar), 143.2 (q Ar), 140.6 (q Ar), 127.6 (Ar), 125.2 (Ar), 123.8 (Ar), 97.6 (CHC=N), 30.0 (*cy*CH₂), 29.4 (*cy*CH₂), 29.0 (CHMe₂), 28.0 (*cy*CH₂), 27.9 (CHMe₂), 25.5 (CHMe₂), 24.9 (CHMe₂), 24.5 (CHMe₂), 23.9 (CHMe₂), 23.0 (Me), 21.2 (broad, Al-C); $^{19}\text{F NMR}$ (C_6D_6 , 470.5 Hz, 298 K) δ -161.8 (broad s, 1F, Al-F). Mass spec (EI, +ve) 548 (100%, [M]⁺), 463 (60%, [M-C₆H₁₃]⁺). HRMS calc. for C₃₅H₅₄N₂FAI 548.40846 found 548.4077.



4 ^1H NMR (C_6D_6 , 500 MHz, 298K) δ 7.43 (d, 1H, $^3J_{\text{H-H}} = 16.0$ Hz), 7.12 (dd, 1H, $^3J_{\text{H-H}} = 8.0, 1.5$ Hz), 7.07 (ddd, 1H, $^3J_{\text{H-H}} = 8.0, 7.0, 1.5$), 7.01-6.99 (m, 4H), 6.94-6.92 (m, 2H), 6.83 (dd, 1H, $^3J_{\text{H-H}} = 7.0, 1.5$ Hz) 6.67 (ddd, 1H, $^3J_{\text{H-H}} = 8.0, 7.0, 1.5$ Hz), 5.98 (d, 1H, $^3J_{\text{H-H}} = 16.0$ Hz) 4.97 (s, 1H), 3.63 (hept, 2H, $^3J_{\text{H-H}} = 6.8$ Hz), 3.28 (hept, 2H, $^3J_{\text{H-H}} = 6.8$ Hz), 1.54 (s, 6H), 1.38 (d, 6H, $^3J_{\text{H-H}} = 6.8$ Hz), 1.15 (d, 6H, $^3J_{\text{H-H}} = 6.8$ Hz), 1.09 (d, 6H, $^3J_{\text{H-H}} = 6.8$ Hz), 1.03 (d, 6H, $^3J_{\text{H-H}} = 6.8$ Hz), ^{13}C NMR (C_6D_6 , 125 MHz, 298K) δ 170.7 (C=N), 160.1 (q, ArCH=CH), 153.6 (ArCH=CH), 144.5 (q Ar), 143.2 (q Ar), 139.6 (q Ar), 131-132 (broad, ArCH=CH), 132.1 (ArCH=CH), 128.3 (Ar), 127.7 (ArCH=CH), 127.6 (ArCH=CH), 125.0 (Ar), 124.0 (Ar), 120.8 (ArCH=CH), 118.0 (ArCH=CH), 98.3 (CHC=N), 29.1 (CHMe₂), 28.4 (CHMe₂), 26.1 (CHMe₂), 24.8 (CHMe₂), 24.7 (CHMe₂), 24.4 (CHMe₂), 23.1 (Me).

X-ray Crystallography Data

Crystal data for 3a: C₃₅H₄₁AlF₆N₂, *M* = 630.68, monoclinic, *P*2₁/*c* (no. 14), *a* = 22.5345(3), *b* = 17.93193(19), *c* = 26.6666(4) Å, β = 110.2781(15)°, *V* = 10107.8(2) Å³, *Z* = 12 [3 independent molecules], *D*_c = 1.243 g cm⁻³, μ(Cu-Kα) = 1.036 mm⁻¹, *T* = 173 K, colourless blocks, Agilent Xcalibur PX Ultra A diffractometer; 19403 independent measured reflections (*R*_{int} = 0.0289), *F*² refinement,^[X1] *R*₁(obs) = 0.0419, *wR*₂(all) = 0.1156, 14330 independent observed absorption-corrected reflections [|*F*_o| > 4σ(|*F*_o|)], 2θ_{max} = 148°, 1219 parameters. CCDC 1419650.

Crystal data for 4: C₃₇H₄₇AlN₂O, *M* = 562.74, orthorhombic, *Pna*2₁ (no. 33), *a* = 16.8019(4), *b* = 12.4929(3), *c* = 15.8089(4) Å, *V* = 3318.34(14) Å³, *Z* = 4, *D*_c = 1.126 g cm⁻³, μ(Mo-Kα) = 0.091 mm⁻¹, *T* = 173 K, colourless blocks, Agilent Xcalibur 3E diffractometer; 4227 independent measured reflections (*R*_{int} = 0.0264), *F*² refinement,³ *R*₁(obs) = 0.0365, *wR*₂(all) = 0.0865, 3752 independent observed absorption-corrected reflections [|*F*_o| > 4σ(|*F*_o|)], 2θ_{max} = 57°, 380 parameters. The absolute structure of **4** was determined by use of the Flack parameter [*x* = 0.14(12)]. CCDC 1419651.

The structure of **3a** was found to contain three crystallographically independent complexes, **3a-A**, **3a-B** and **3a-C**. The absolute structure of **4** was determined by use of the Flack parameter [*x* = 0.14(12)].

³ (a) SHELXTL, Bruker AXS, Madison, WI; (b) SHELX-2013, <http://shelx.uni-ac.gwdg.de/SHELX/index.php>

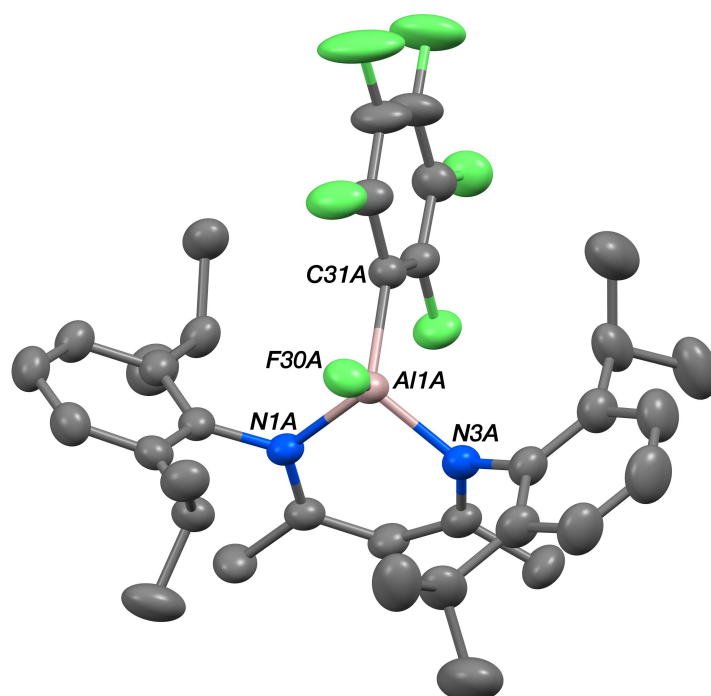


Fig. S1 The structure of one (**3a-A**) of the three independent complexes present in the crystal of **3a** (50% probability ellipsoids).

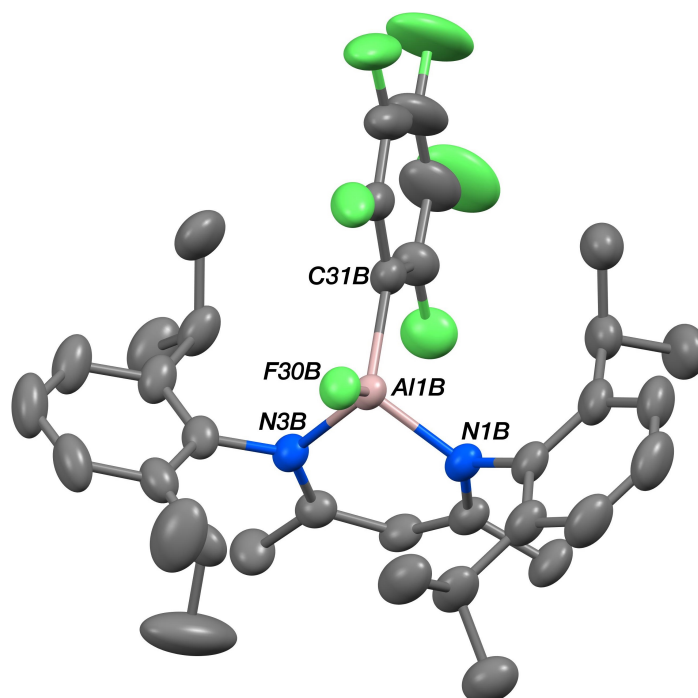


Fig. S2 The structure of one (**3a-B**) of the three independent complexes present in the crystal of **3a** (50% probability ellipsoids).

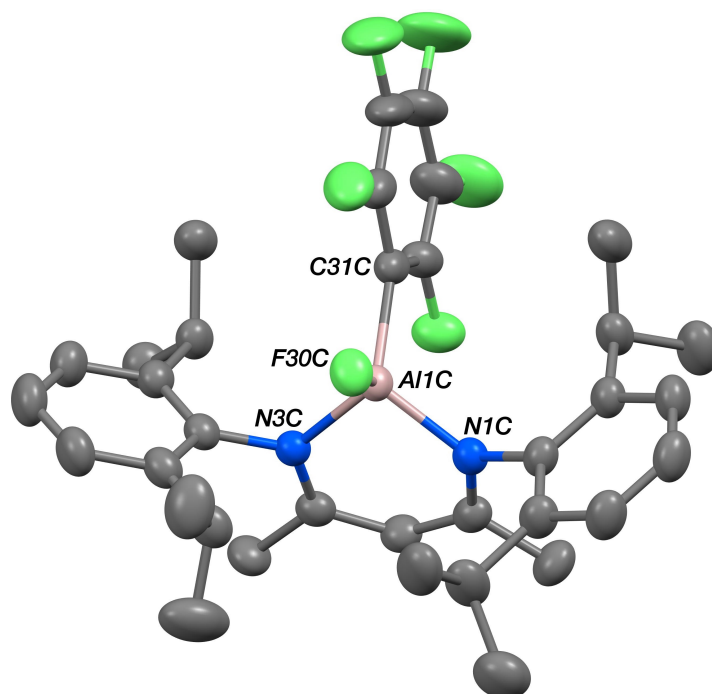


Fig. S3 The structure of one (**3a-C**) of the three independent complexes present in the crystal of **3a** (50% probability ellipsoids).

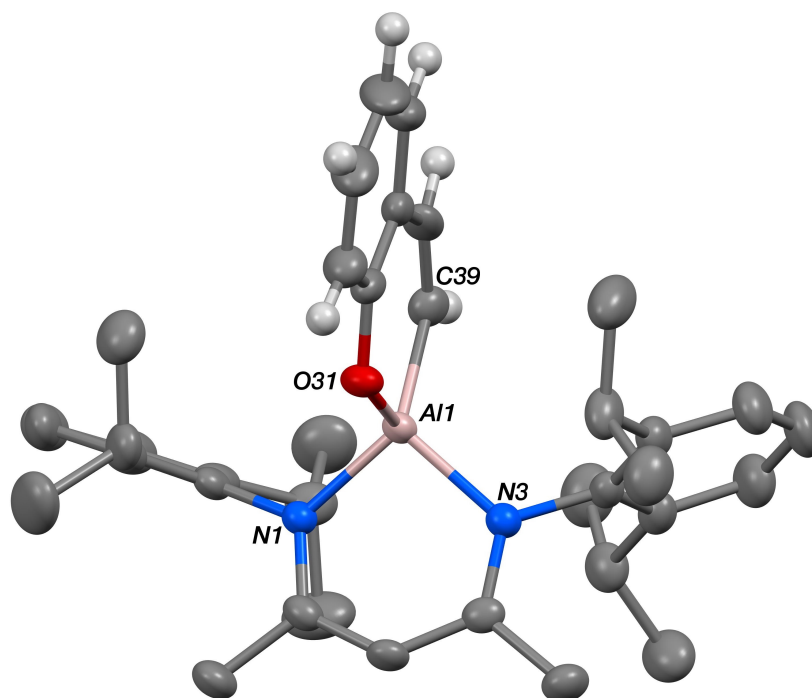
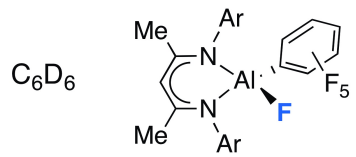


Fig. S4 The crystal structure of **4** (50% probability ellipsoids).



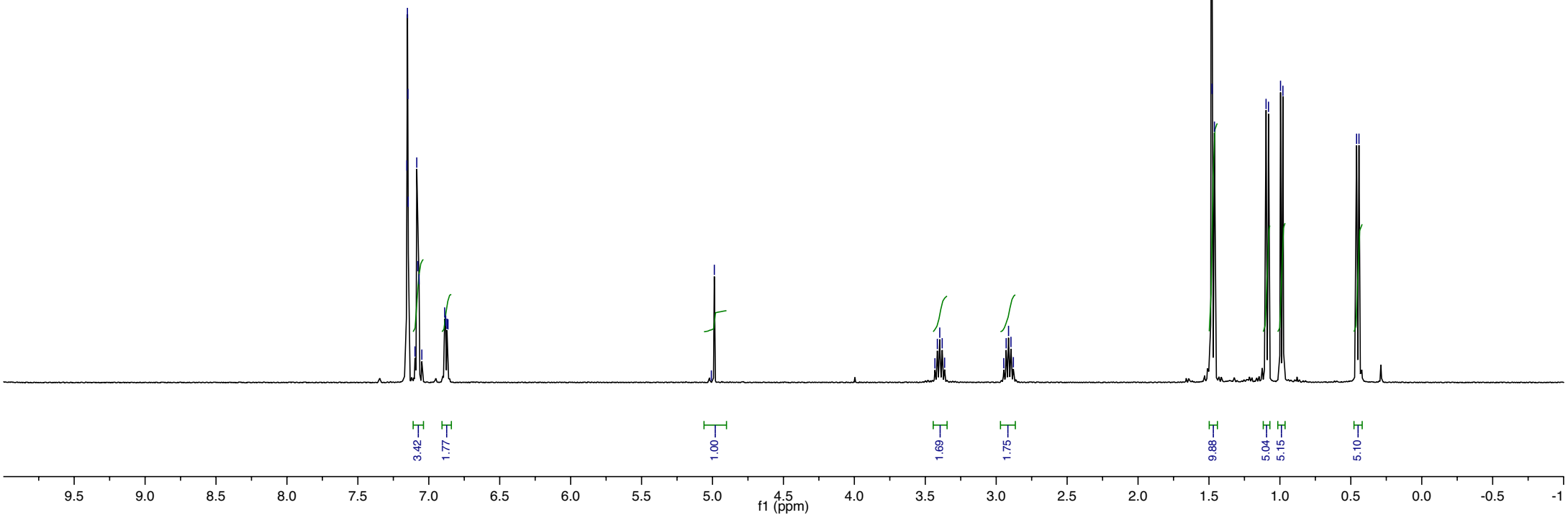
Ar = 2,6-di-iso-propylphenyl

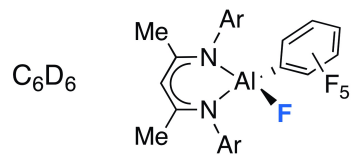
7.15
7.15
7.15
7.15
7.10
7.08
7.08
7.07
7.05
6.89
6.88
6.87
6.86

5.01
4.99

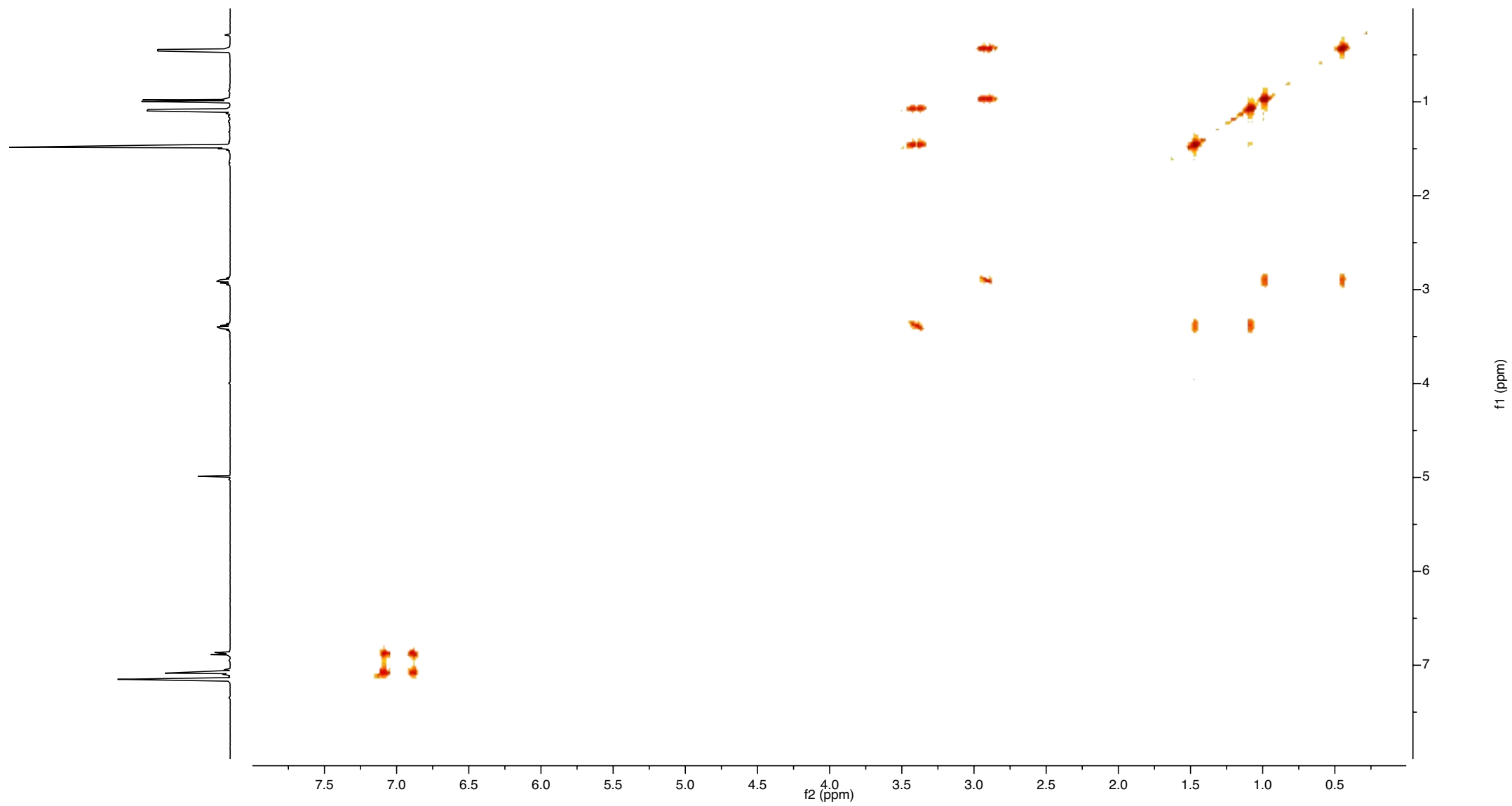
3.43
3.41
3.40
3.38
3.36
2.95
2.93
2.91
2.90
2.88

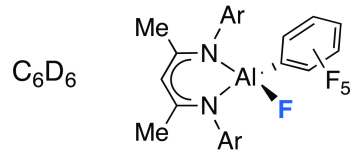
1.48
1.48
1.48
1.10
1.08
1.00
0.98
0.46
0.44



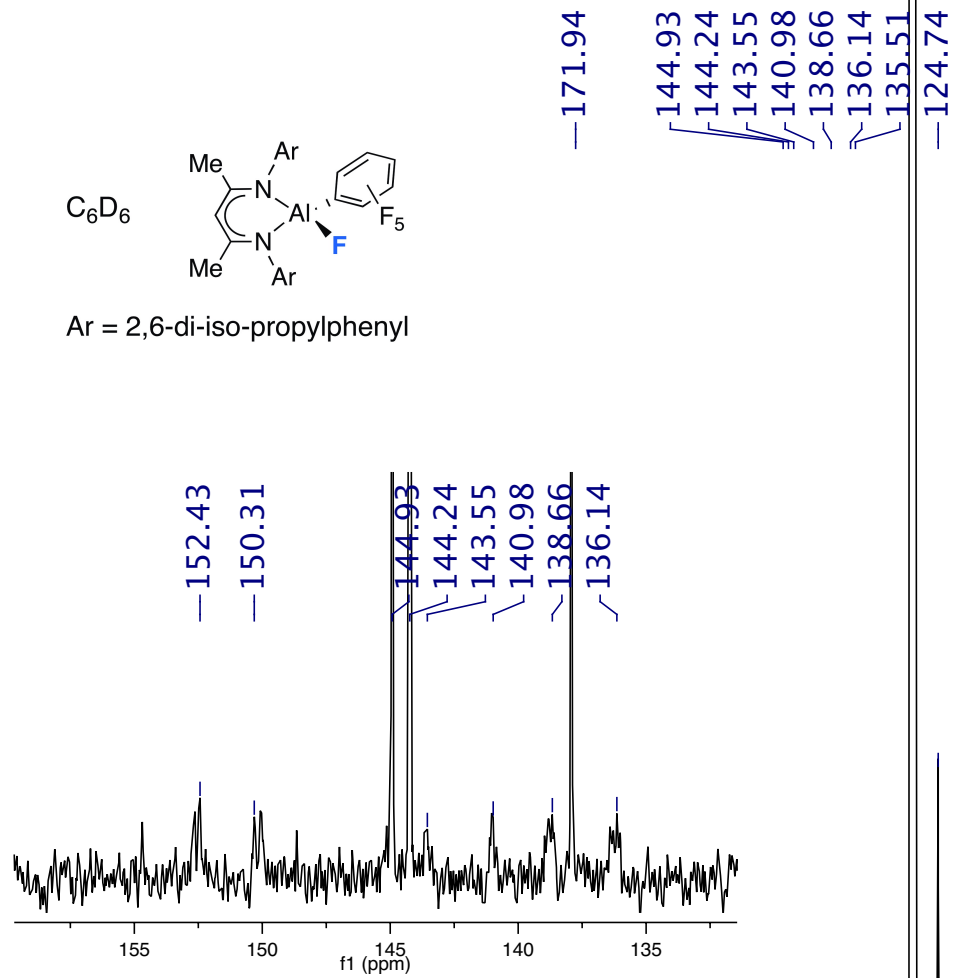


Ar = 2,6-di-iso-propylphenyl

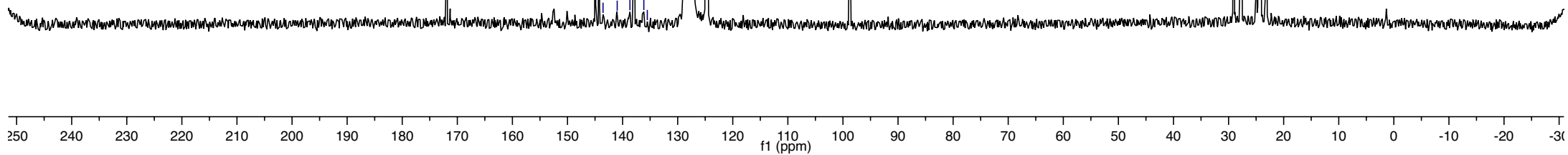
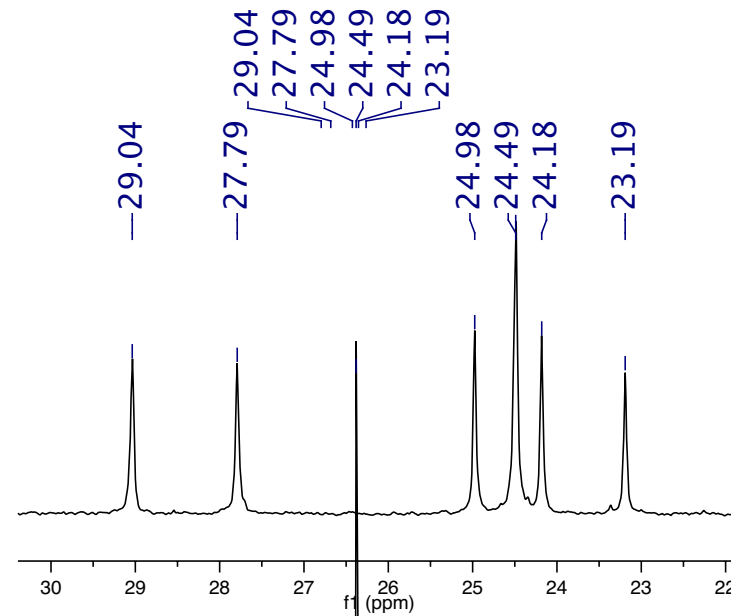


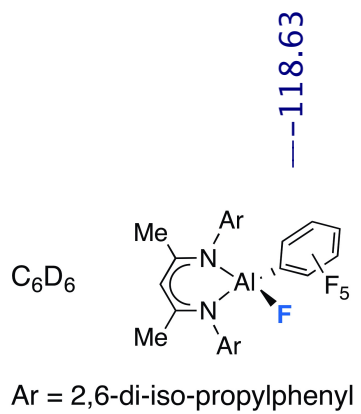


Ar = 2,6-di-iso-propylphenyl



—98.70





--118.63

--118.60
--118.63
--118.67
--118.70
--118.74

--153.32
--153.37
--153.43

--162.05
--162.09
--162.13
--162.17
--162.21

--153.37

--162.13

--168.15

--168.15

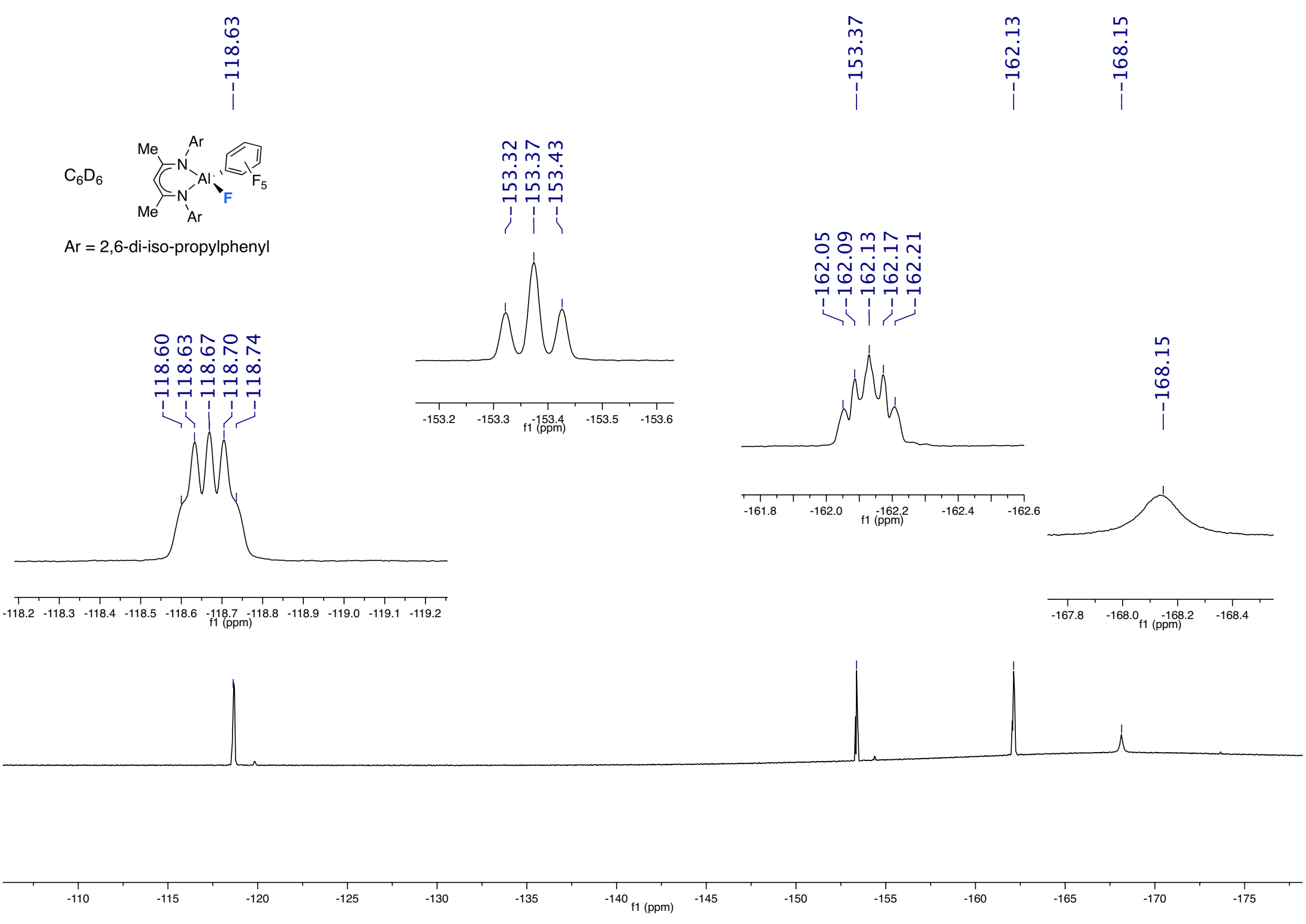
-118.2 -118.3 -118.4 -118.5 -118.6 -118.7 -118.8 -118.9 -119.0 -119.1 -119.2
f1 (ppm)

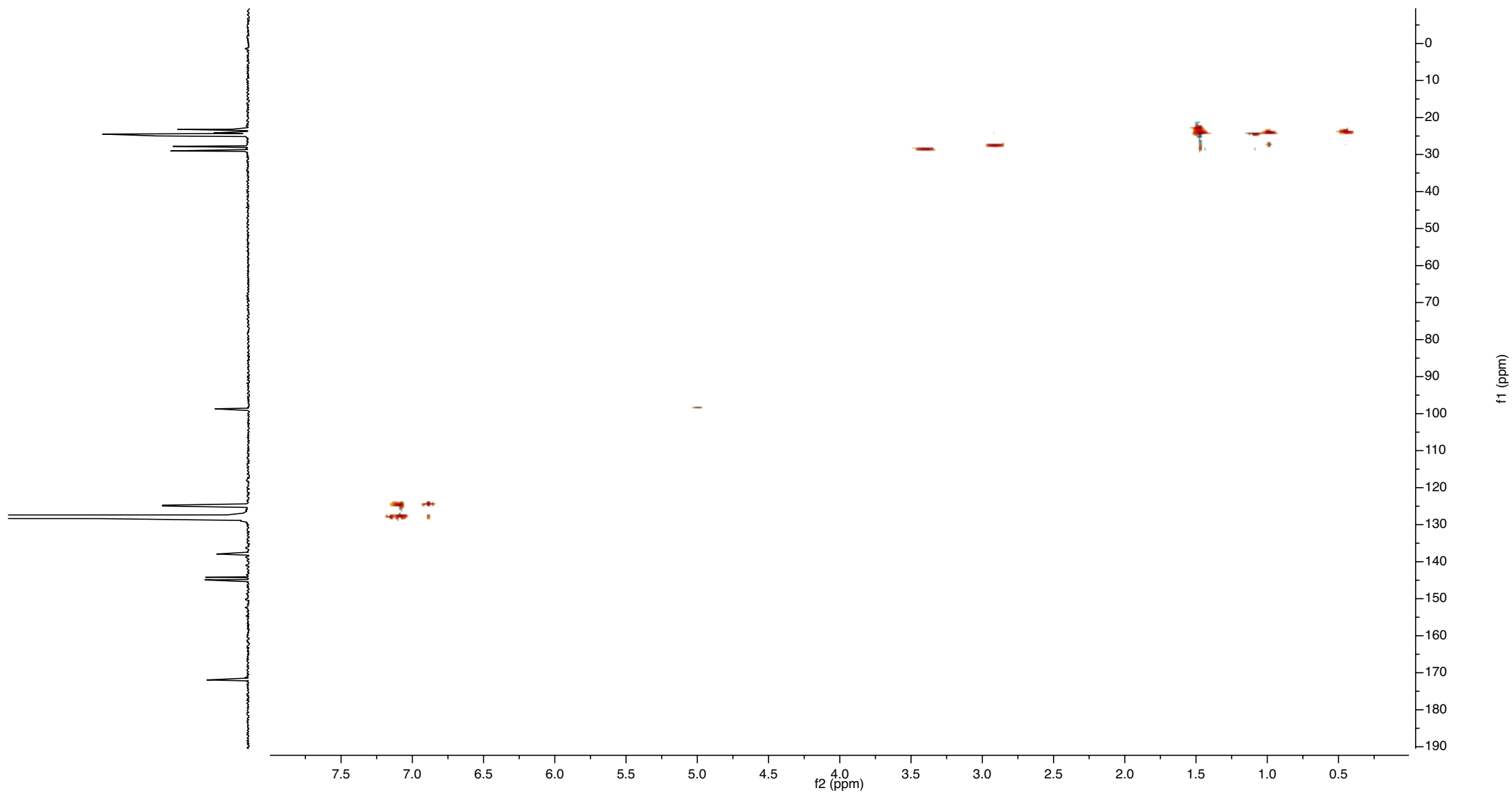
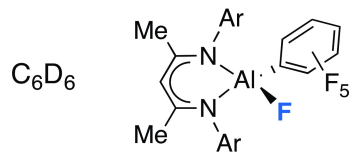
-153.2 -153.3 -153.4 -153.5 -153.6
f1 (ppm)

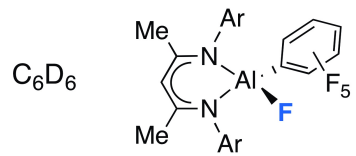
-161.8 -162.0 -162.2 -162.4 -162.6
f1 (ppm)

-167.8 -168.0 -168.2 -168.4
f1 (ppm)

-110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175
f1 (ppm)





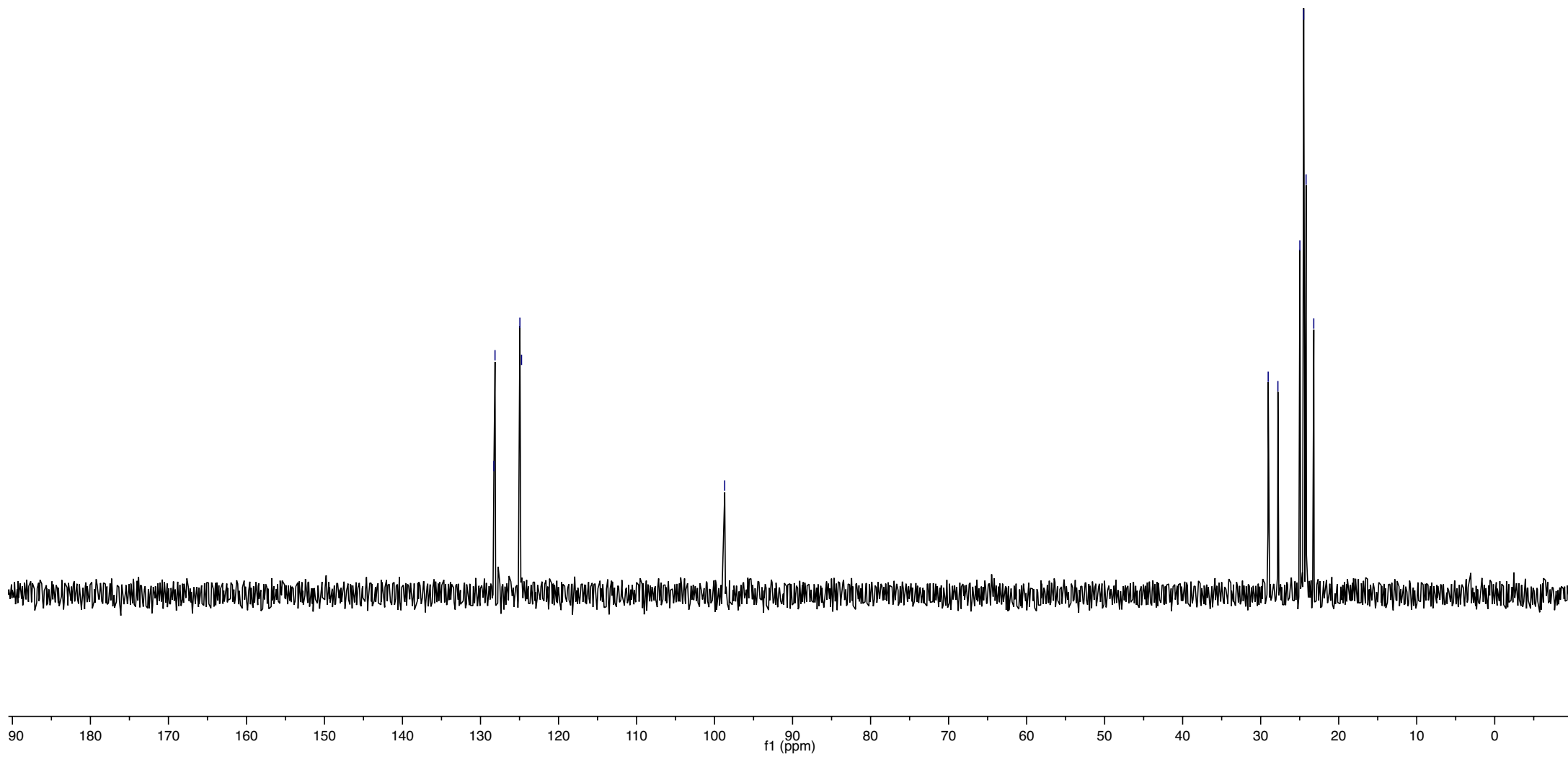


Ar = 2,6-di-iso-propylphenyl

128.28
128.14
124.95
124.74

-98.70

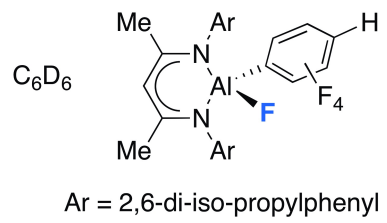
29.04
27.79
24.98
24.49
24.18
23.19



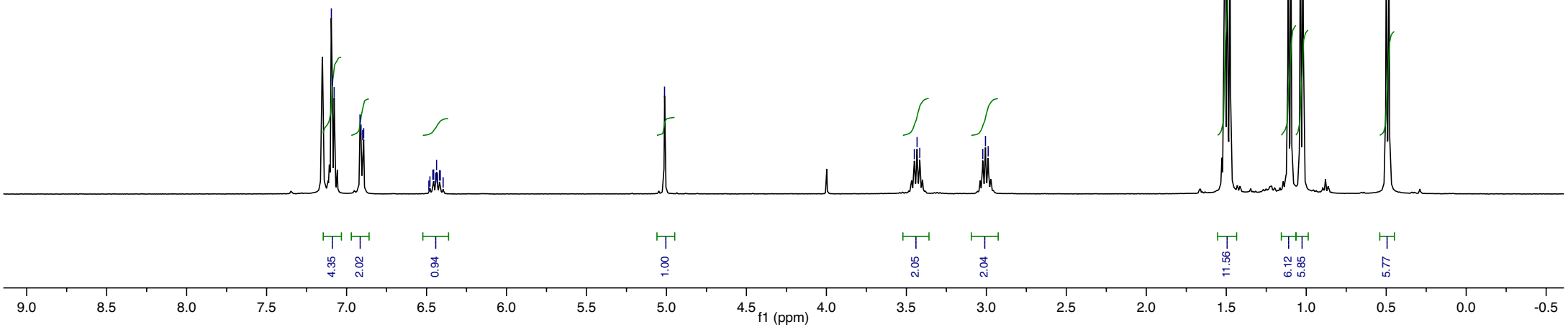
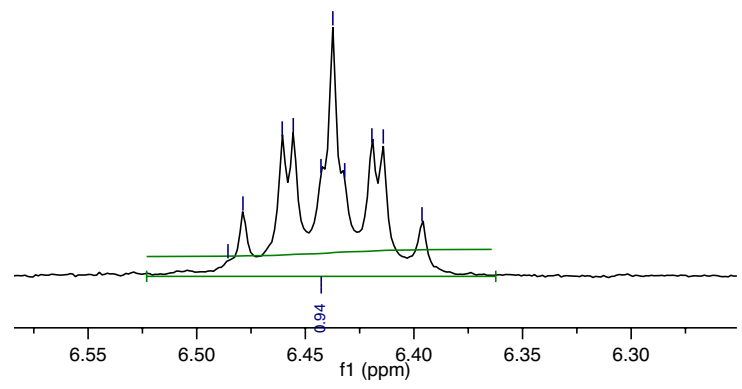
7.10
7.09
7.08
6.92
6.91
6.90
6.89
6.48
6.46
6.46
6.44
6.44
6.43
6.42
6.41
6.40

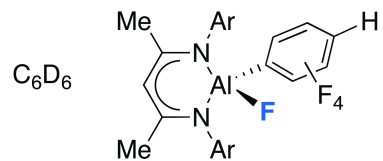
3.45
3.43
3.42
3.02
3.01
2.99

1.51
1.49
1.48
1.11
1.10
1.04
0.50
0.48

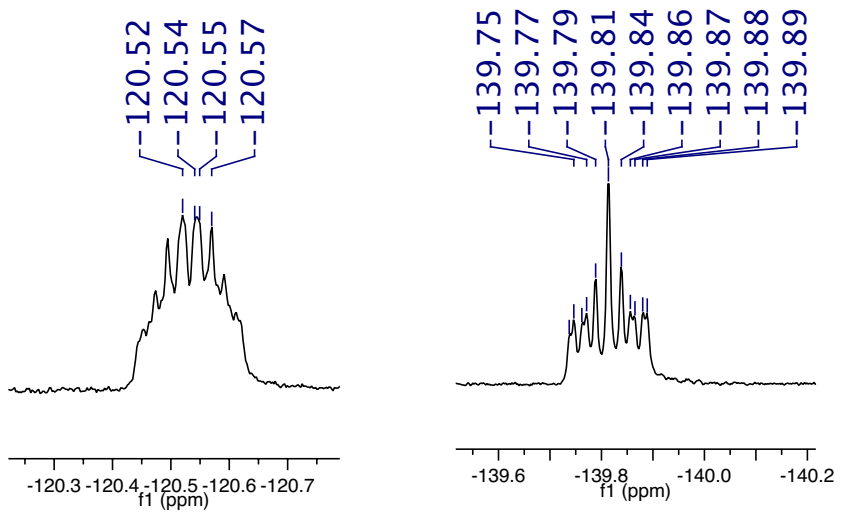


6.49
6.48
6.46
6.46
6.44
6.44
6.43
6.42
6.41
6.40





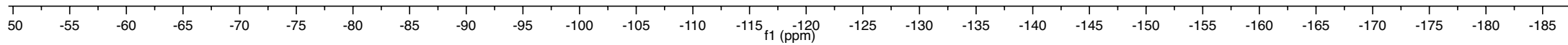
Ar = 2,6-di-iso-propylphenyl

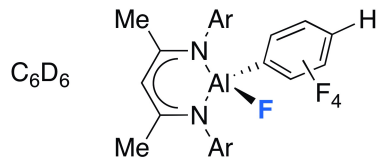


--120.49

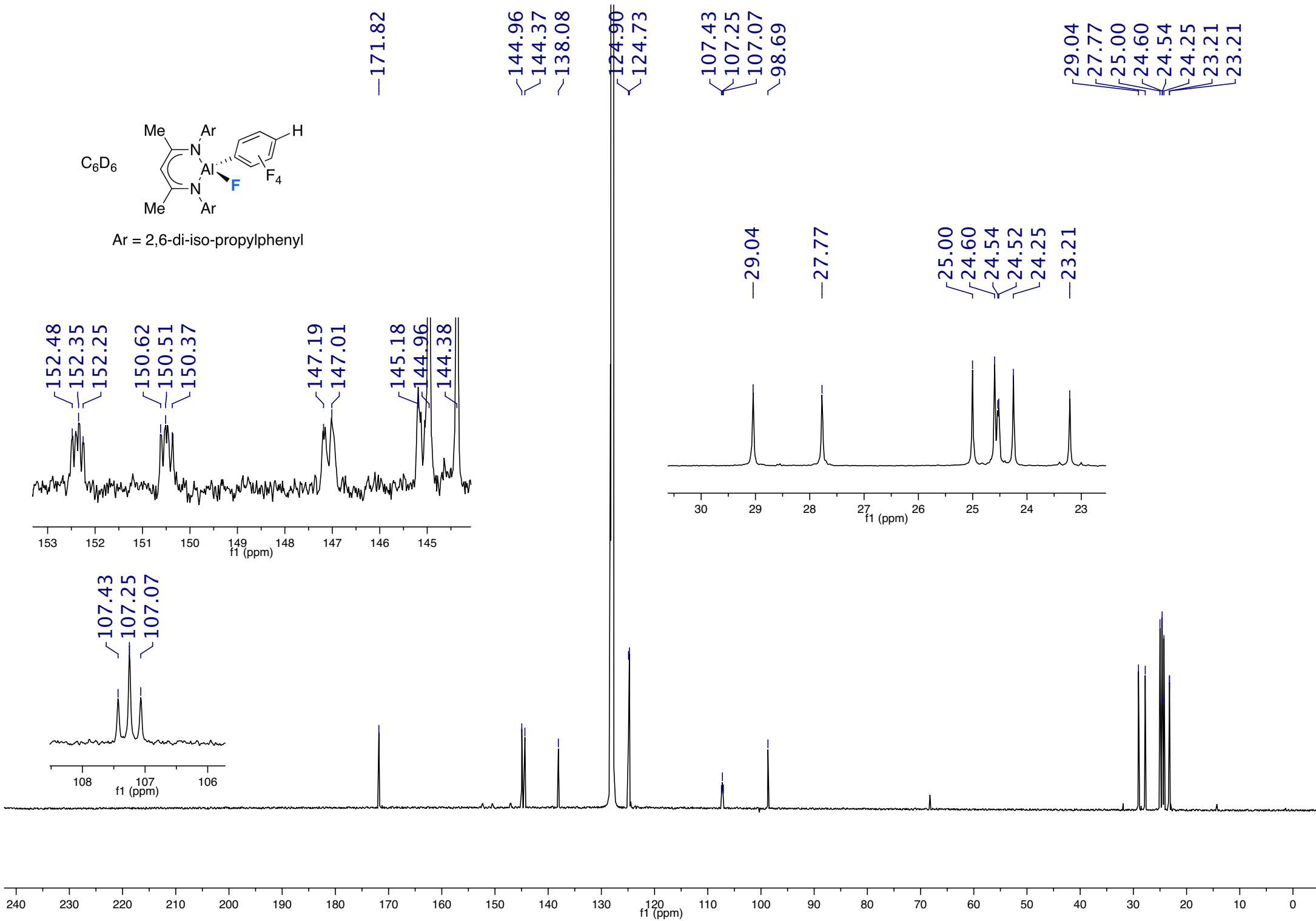
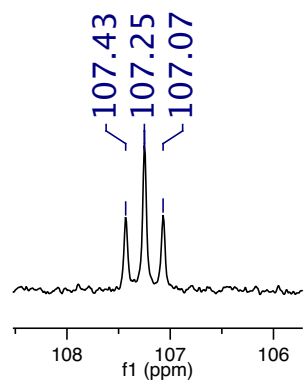
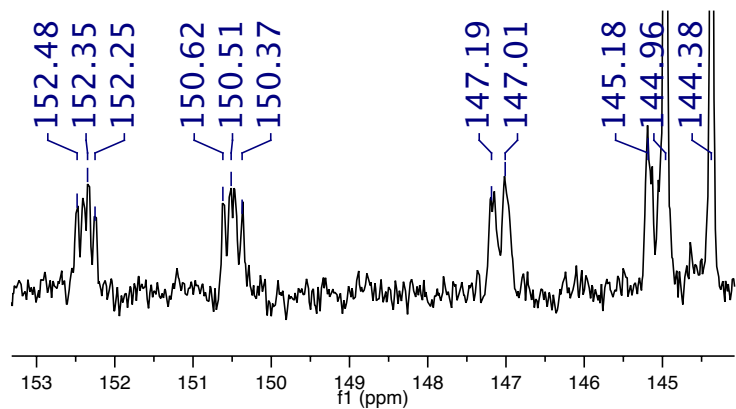
--139.84

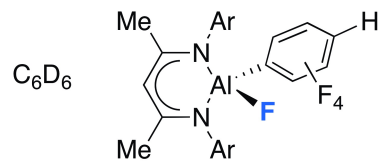
--168.47





Ar = 2,6-di-iso-propylphenyl



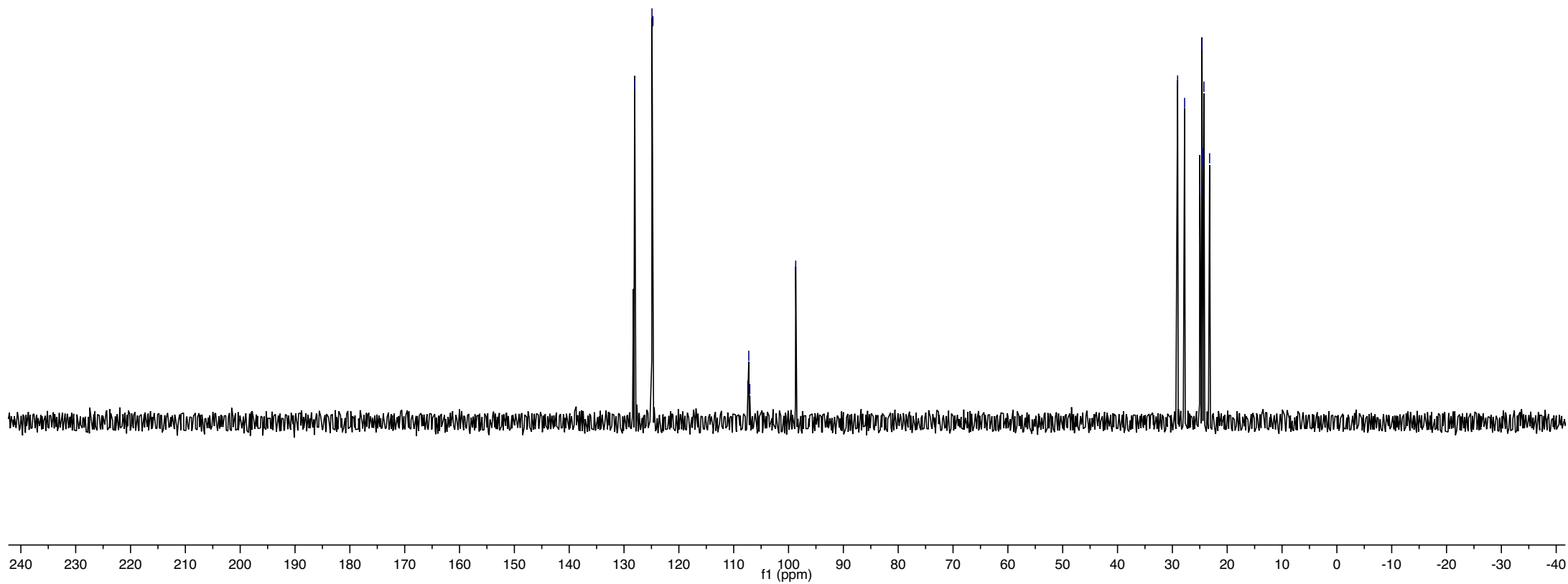


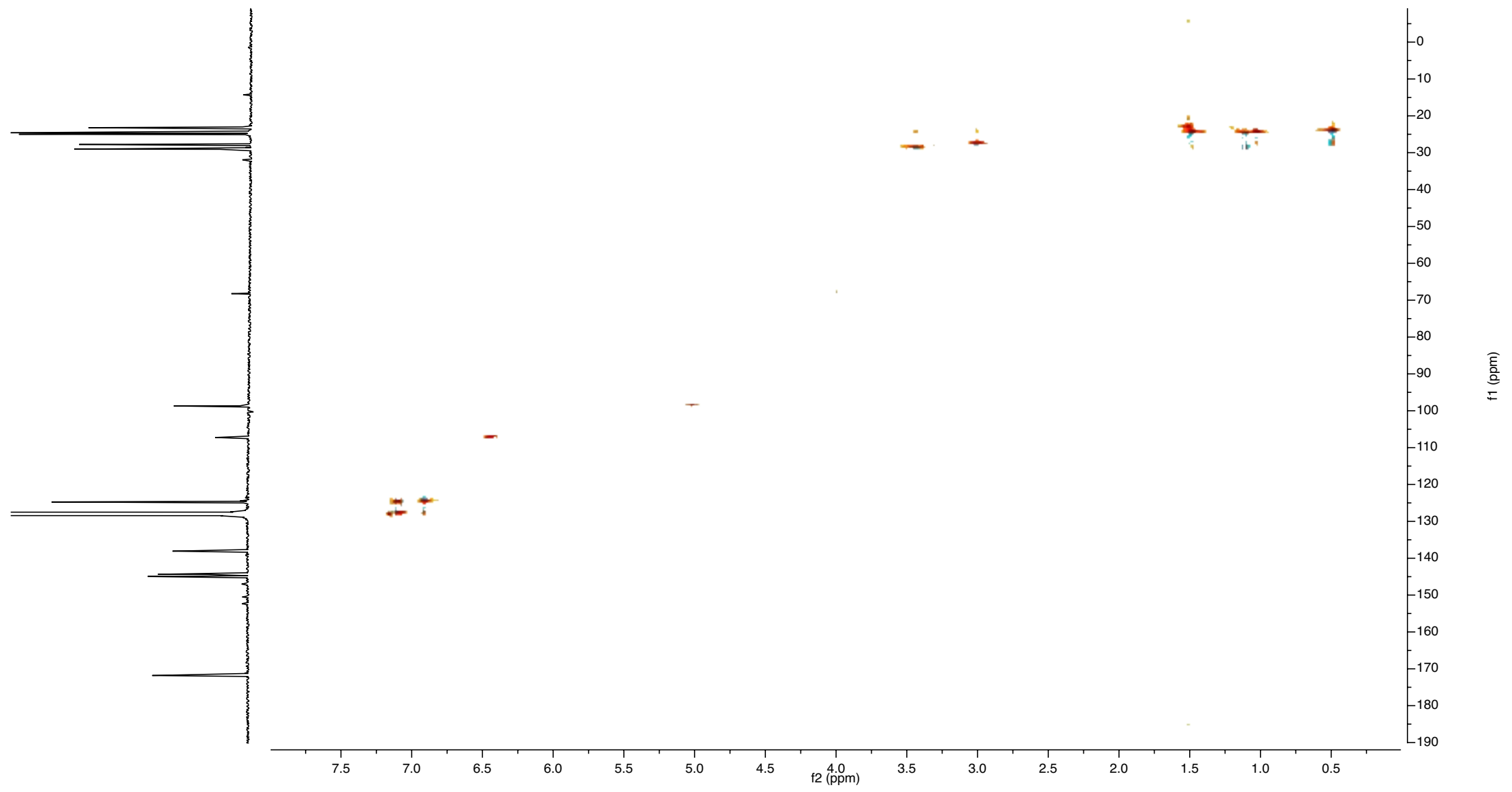
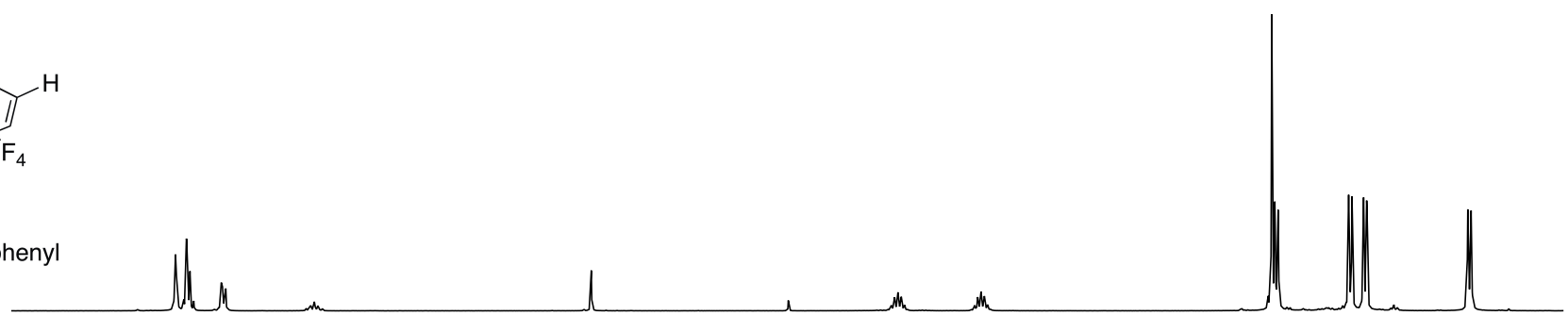
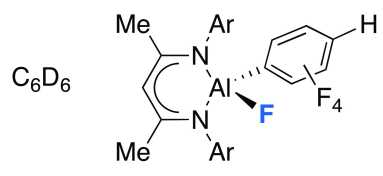
Ar = 2,6-di-iso-propylphenyl

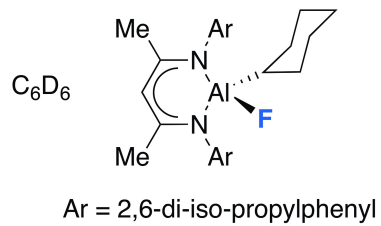
128.06
124.90
124.73

107.43
107.25
107.07
98.69

29.04
27.77
25.01
24.60
24.54
24.52
24.25
23.21





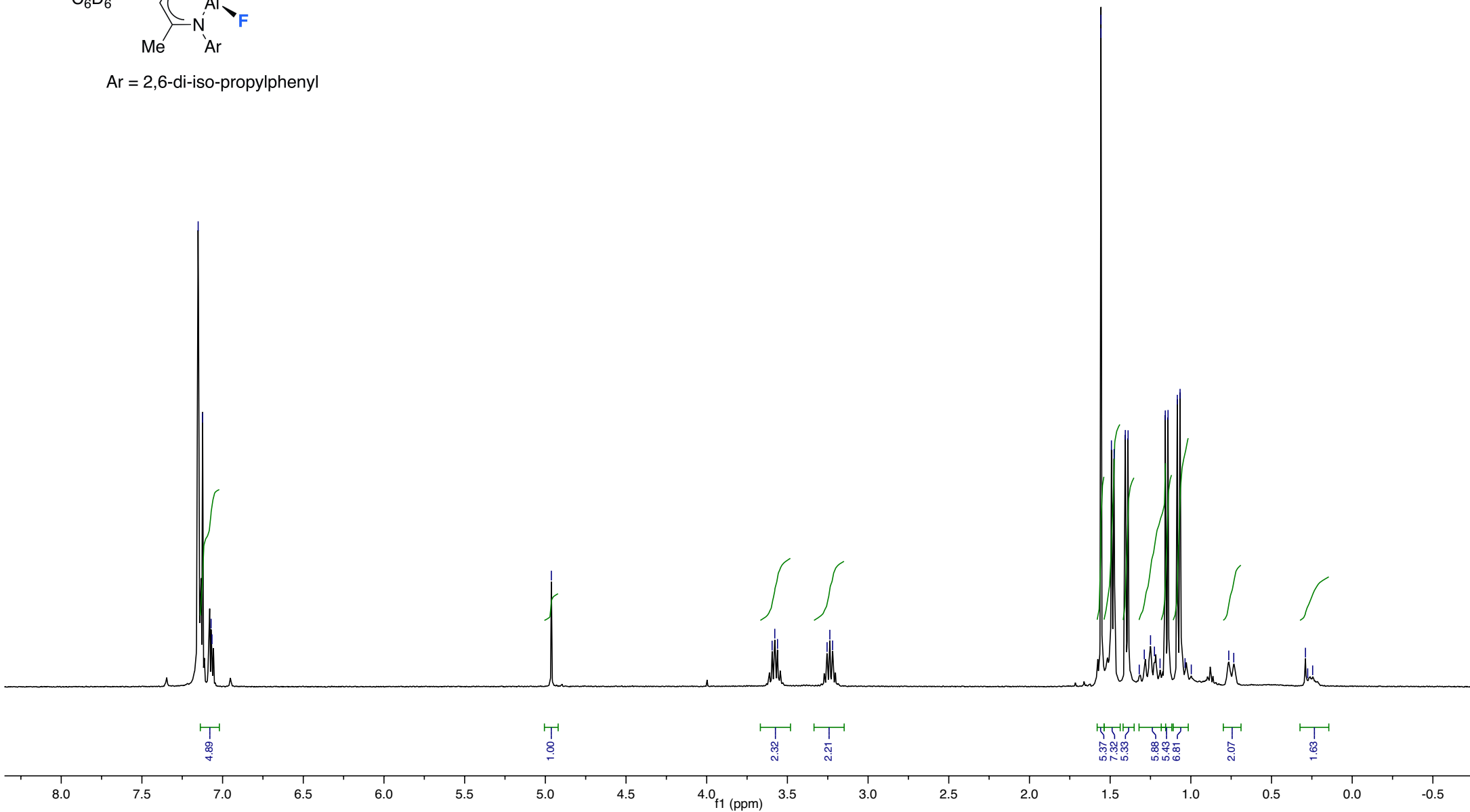


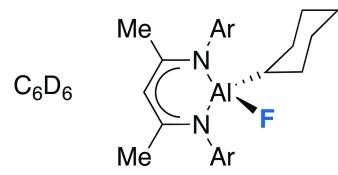
7.15
7.12
7.07
7.07

—4.96

3.59
3.58
3.56
3.25
3.24
3.22

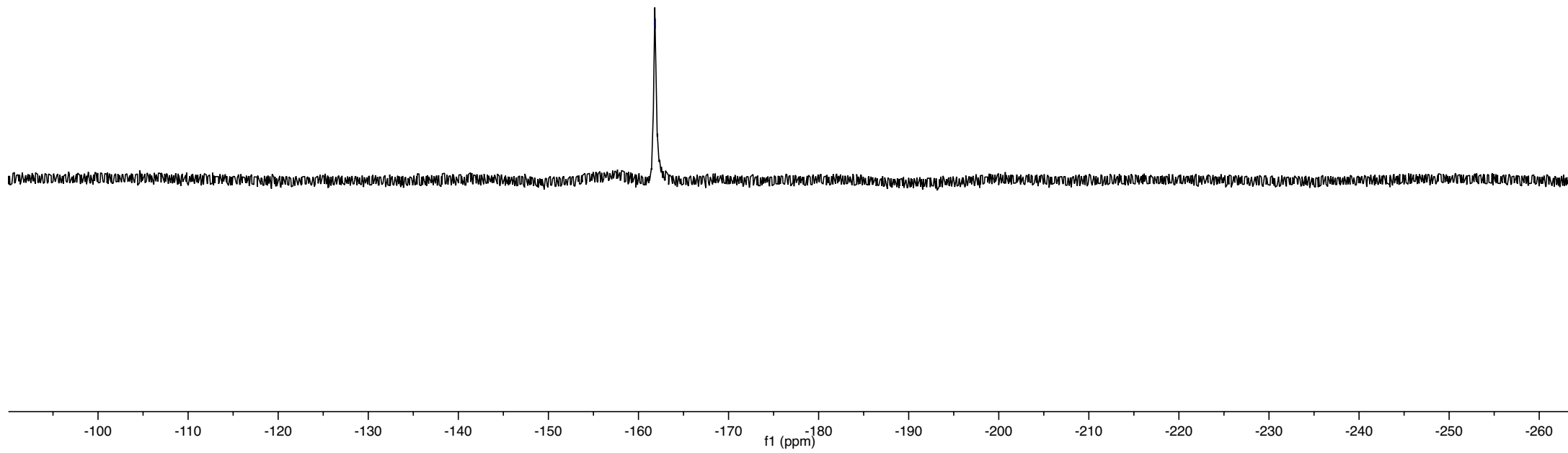
1.56
1.56
1.49
1.48
1.41
1.39
1.29
1.25
1.23
1.16
1.14
1.08
1.07
0.76
0.73
0.28
0.25

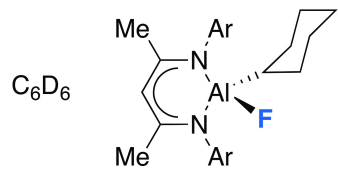




Ar = 2,6-di-iso-propylphenyl

--161.86





Ar = 2,6-di-iso-propylphenyl

—170.17

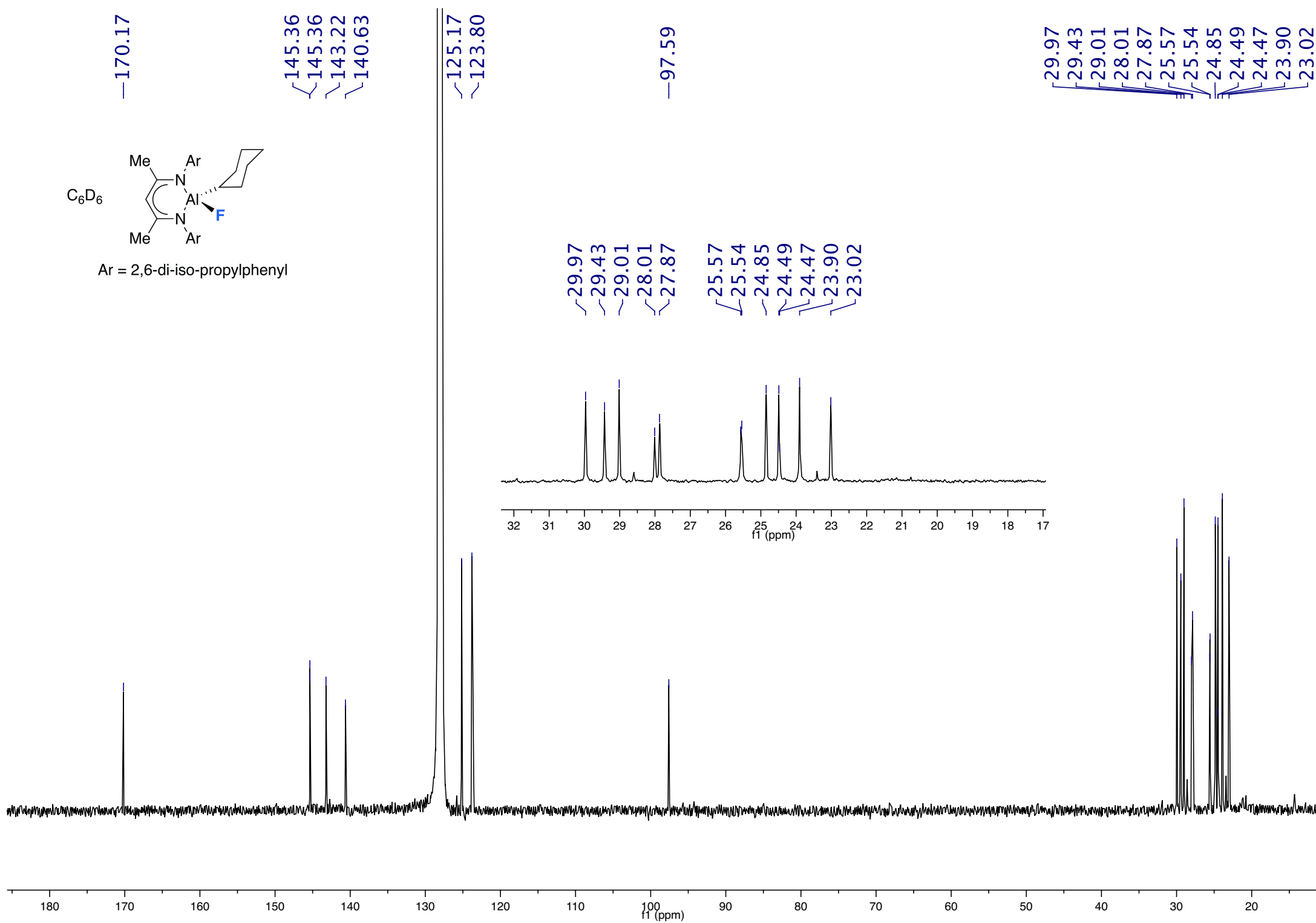
145.36
145.36
143.22
140.63

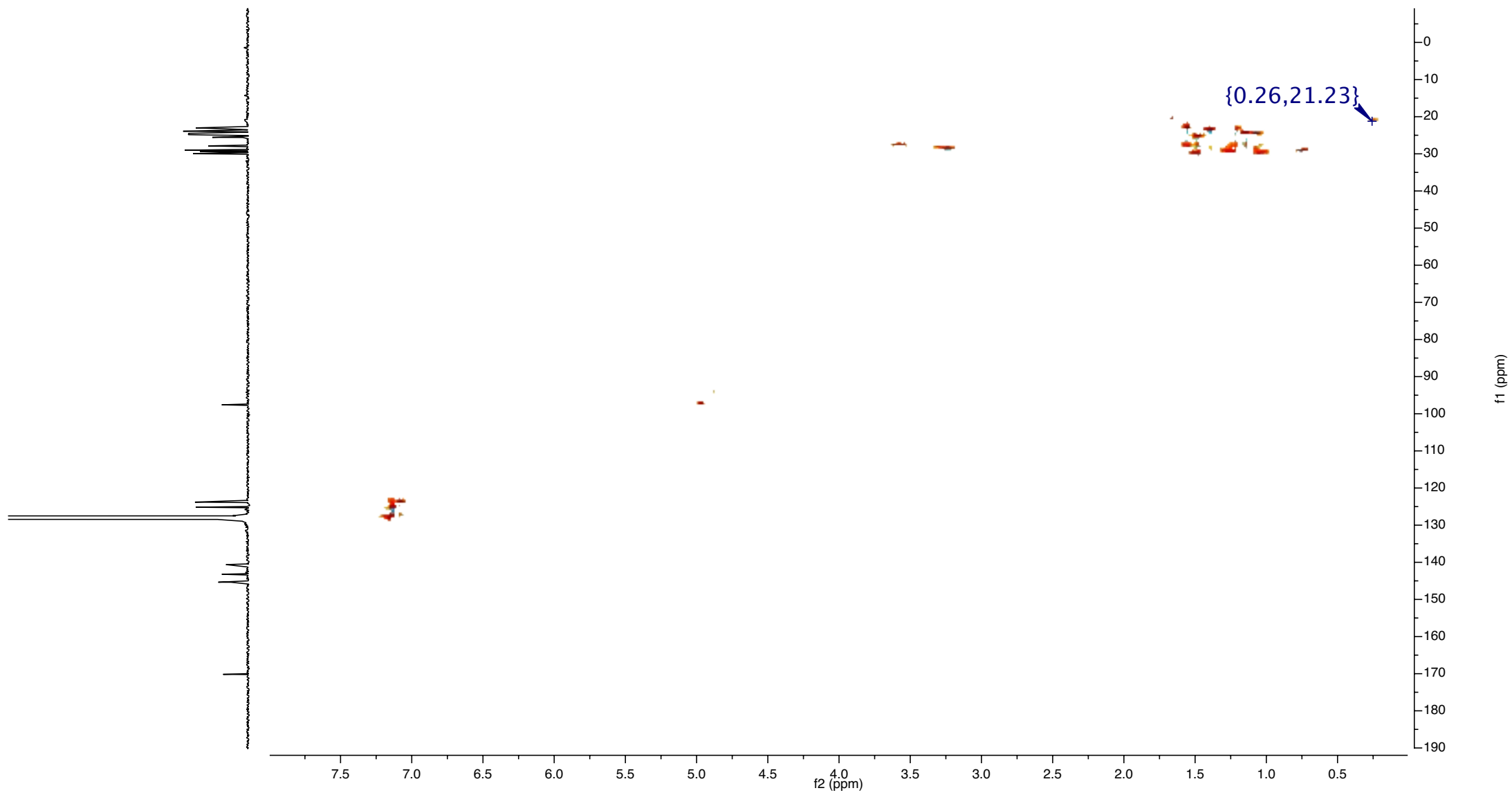
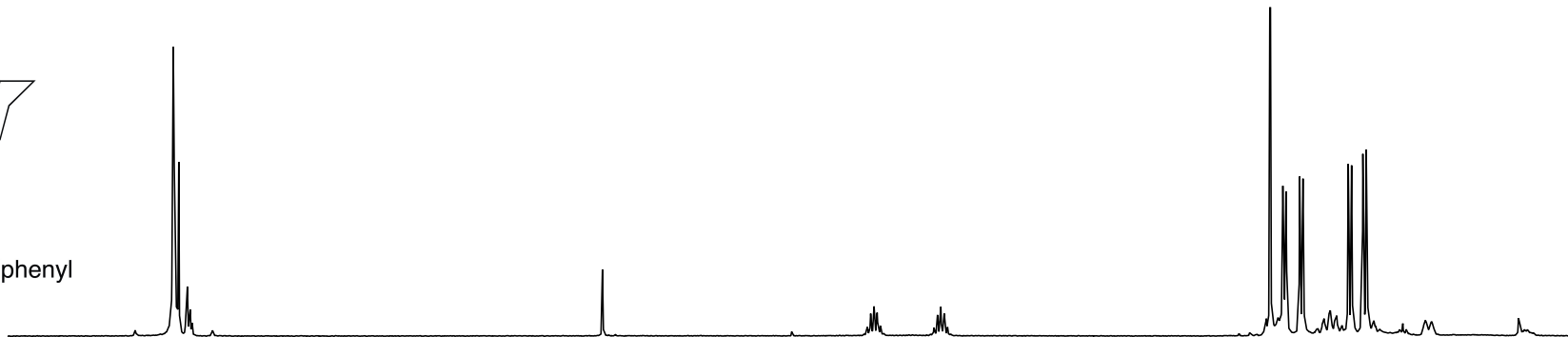
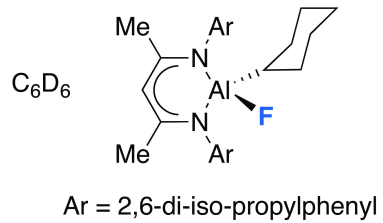
125.17
123.80

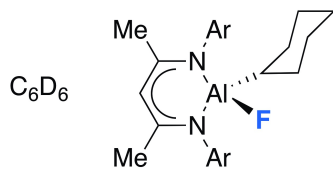
—97.59

29.97
29.43
29.01
28.01
27.87
25.57
25.54
24.85
24.49
24.47
23.90
23.02

29.97
29.43
29.01
28.01
27.87
25.57
25.54
24.85
24.49
24.47
23.90
23.02





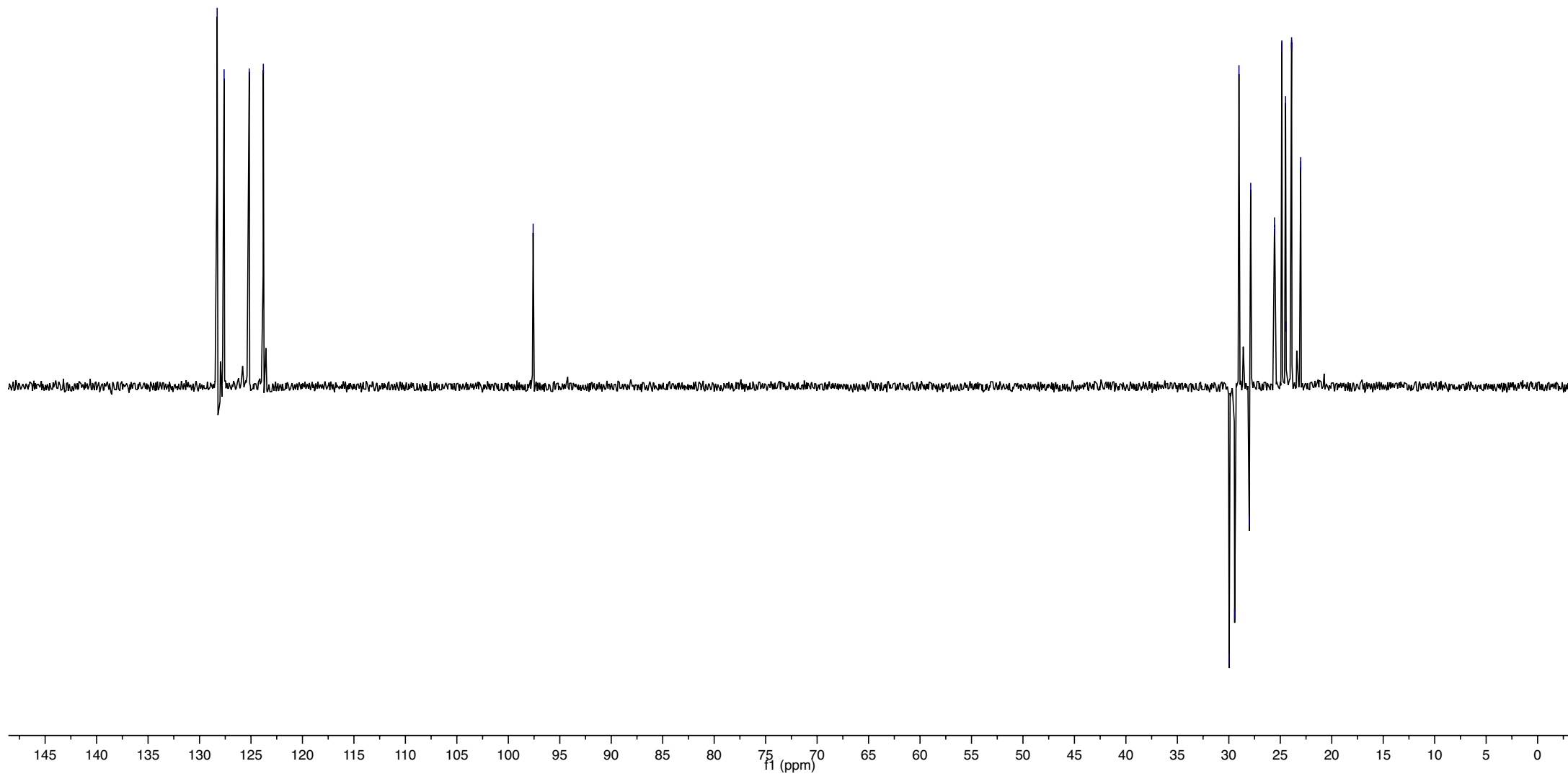


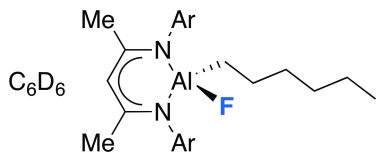
Ar = 2,6-di-iso-propylphenyl

128.29
127.61
125.17
123.80

—97.59

29.97
29.43
29.02
28.01
27.87
25.57
25.54
24.85
24.85
24.49
24.45
23.90
23.90
23.02
23.02



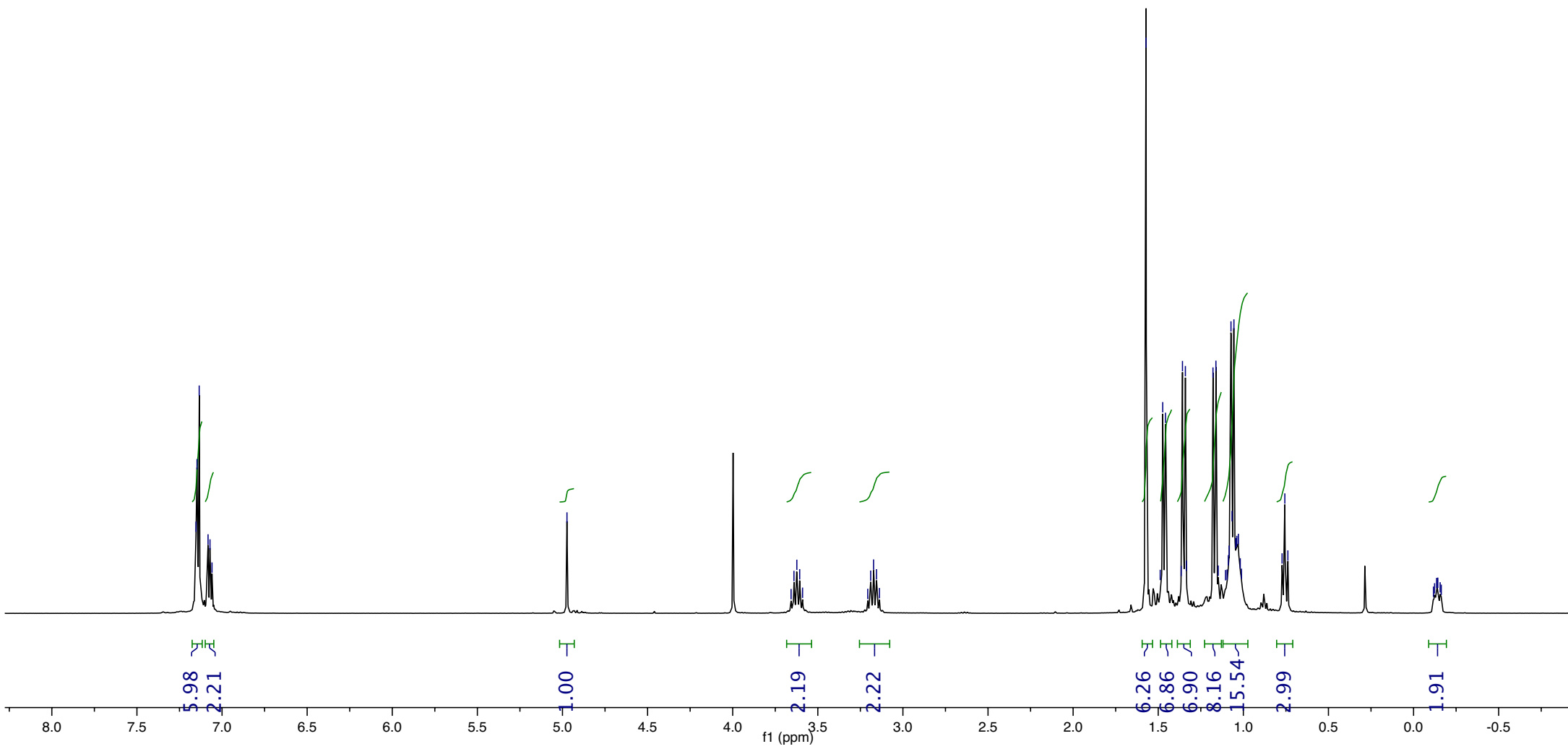


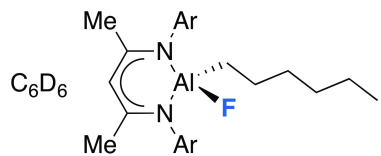
Ar = 2,6-di-iso-propylphenyl

7.15
7.15
7.13
7.08
7.07
7.06

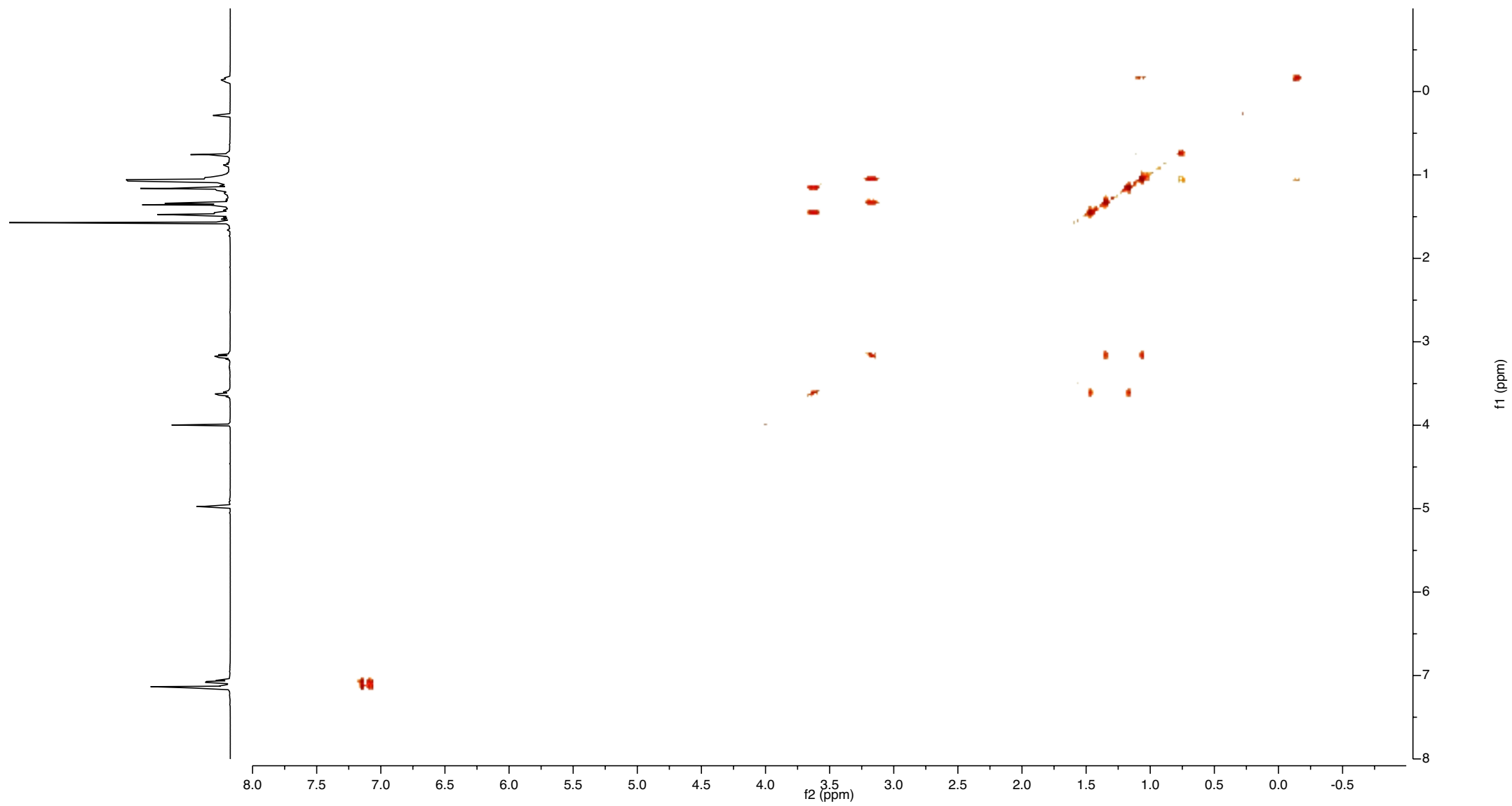
—4.97

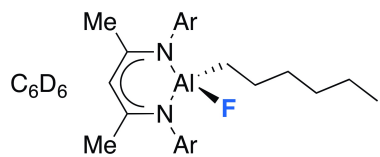
3.66
3.64
3.62
3.61
3.59
3.21
3.19
3.17
3.16
3.14
1.57
1.47
1.46
1.36
1.34
1.18
1.16
1.07
1.07
1.06
1.04
1.04
1.03
0.76
0.12
0.12
0.14
0.14
0.16
0.16





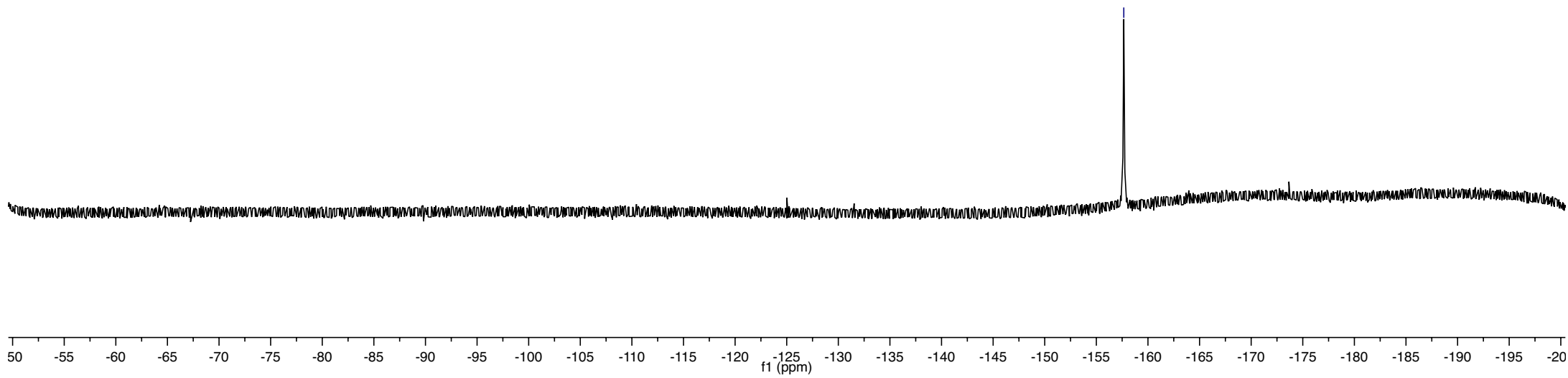
Ar = 2,6-di-iso-propylphenyl

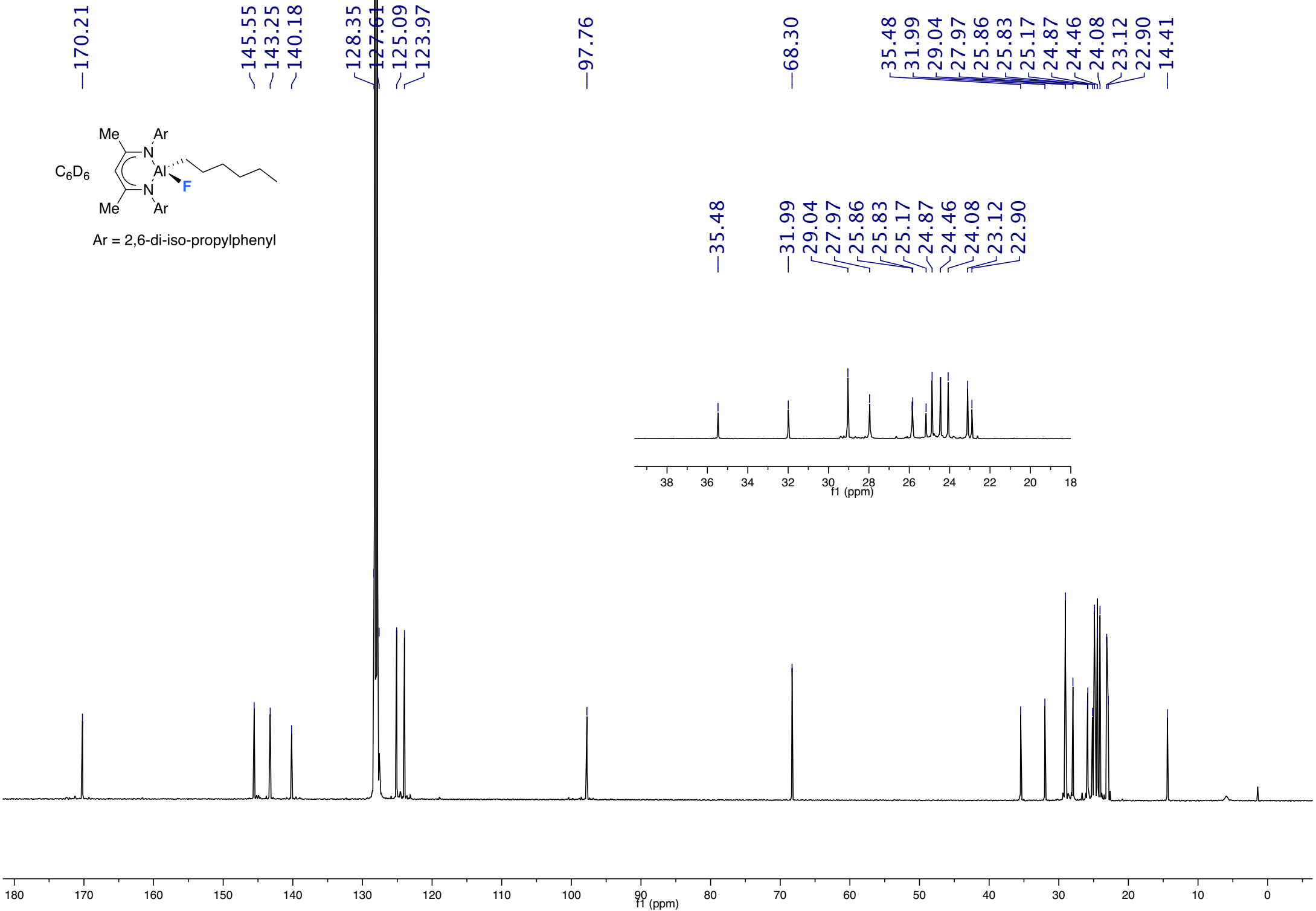
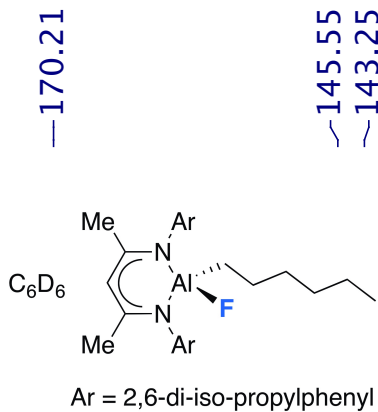


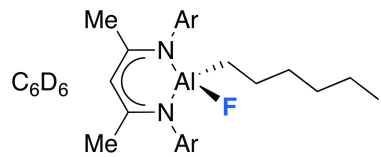


Ar = 2,6-di-iso-propylphenyl

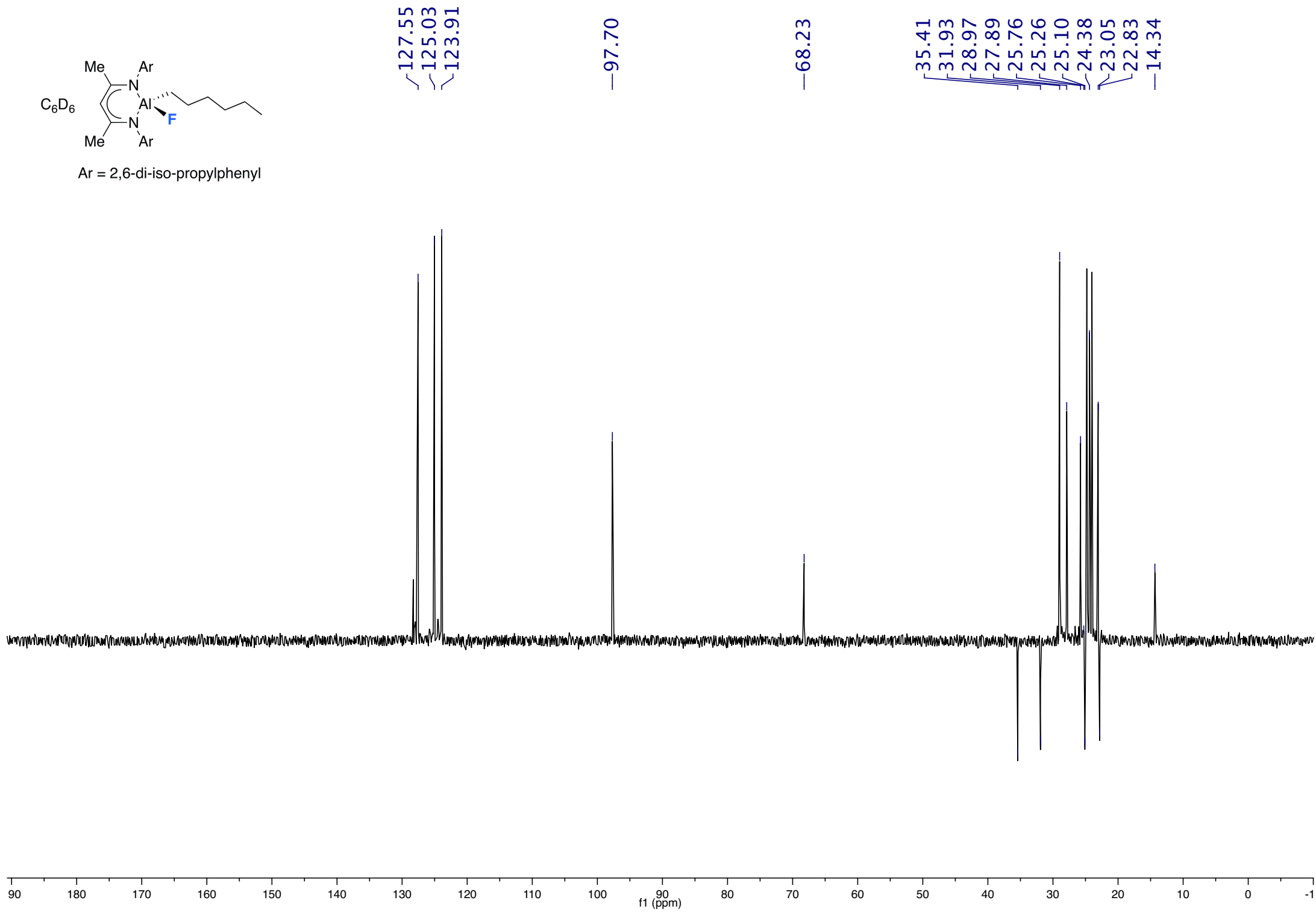
--157.66

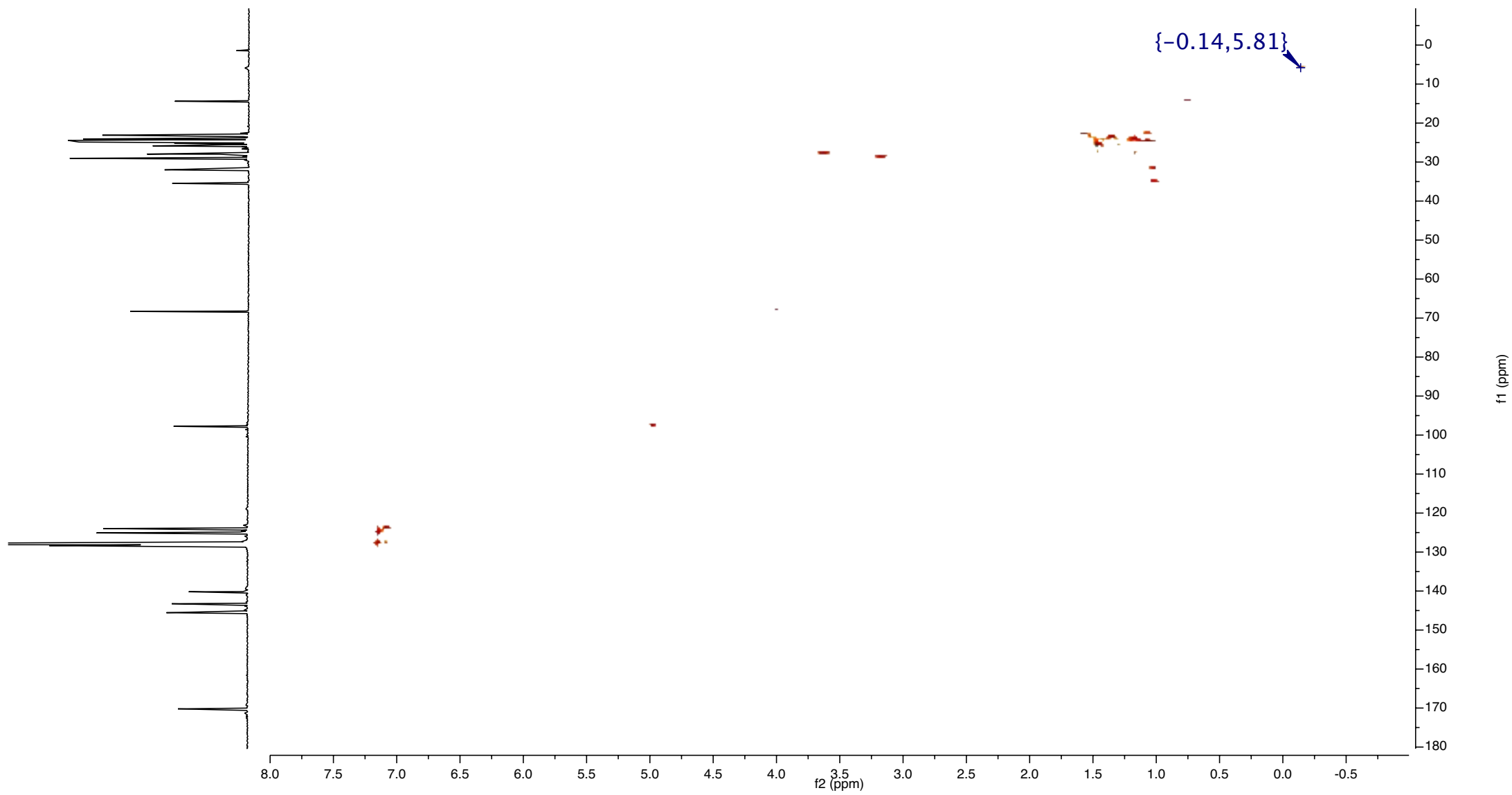
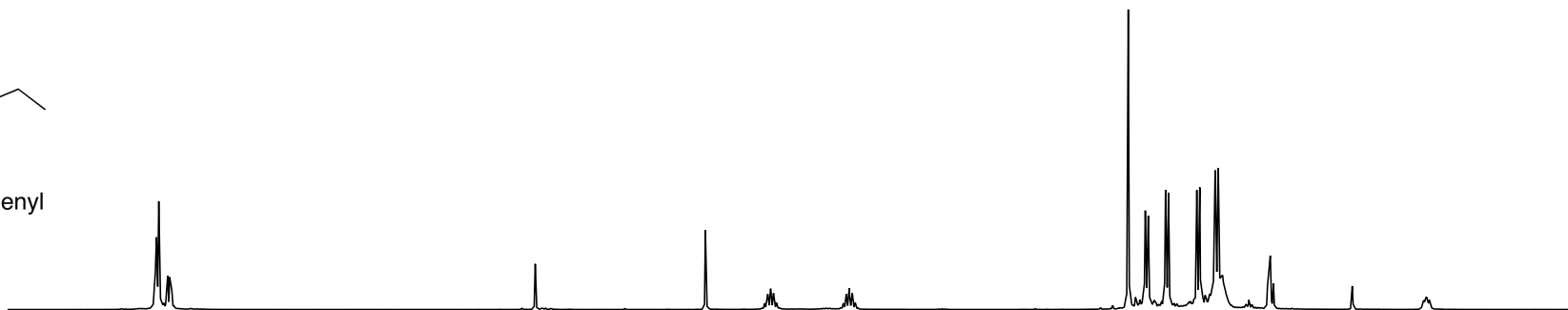
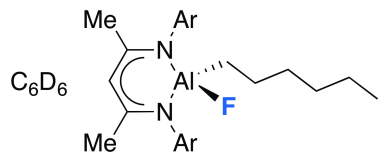






Ar = 2,6-di-iso-propylphenyl



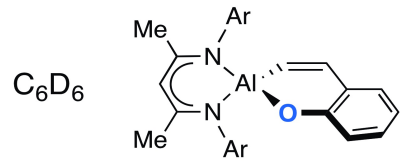


7.45
7.41
7.12
7.11
7.07
7.07
7.01
7.00
7.00
6.94
6.94
6.93
6.92
6.85
6.84
6.83
6.83
6.67
6.67
5.97

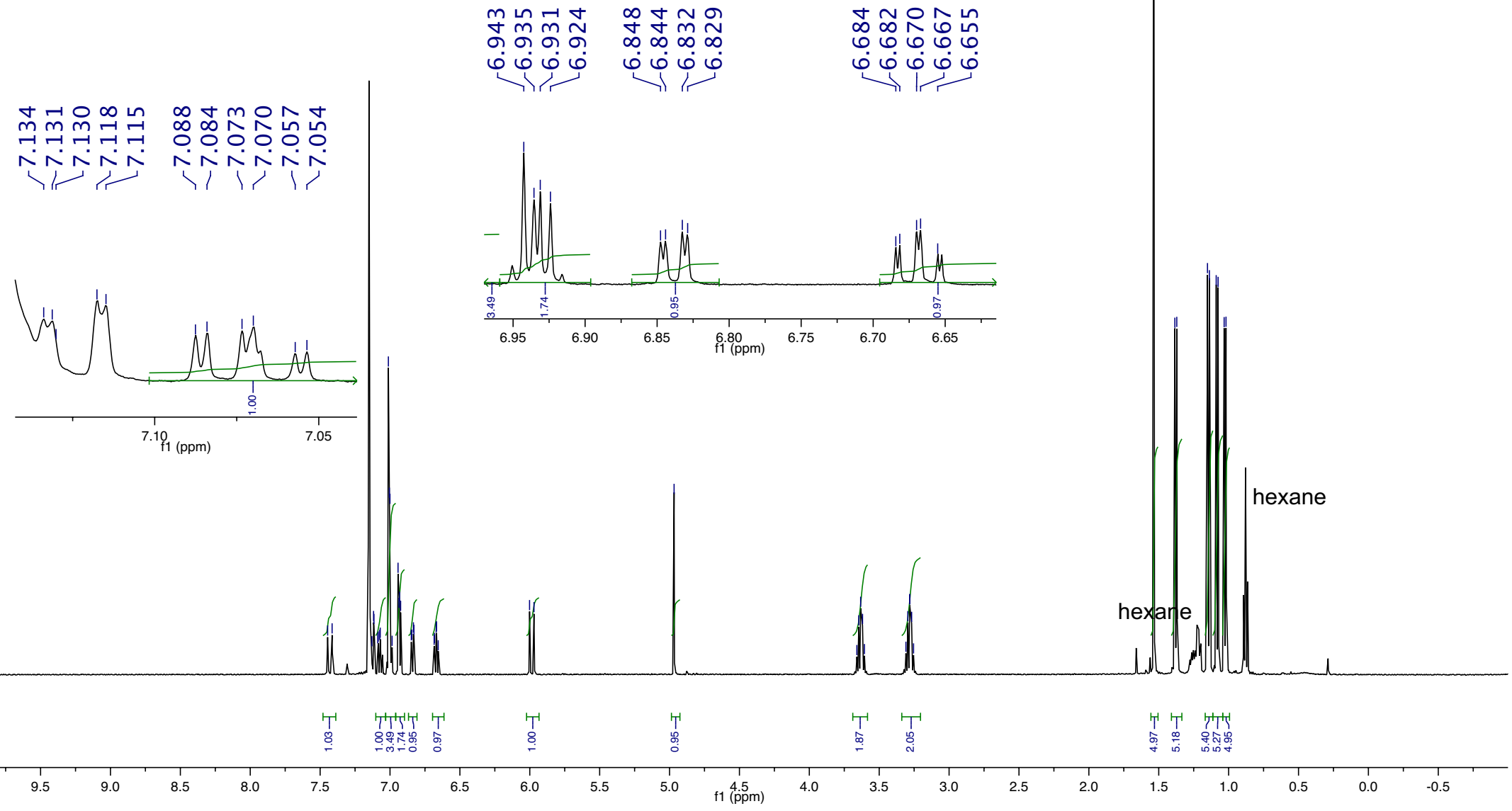
—4.97

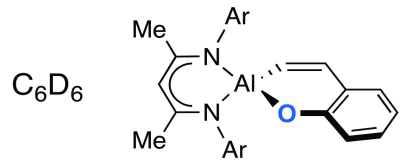
3.66
3.65
3.63
3.62
3.61
3.31
3.30
3.28
3.28
3.27
3.25

1.54
1.38
1.37
1.15
1.14
1.09
1.08
1.03
1.02

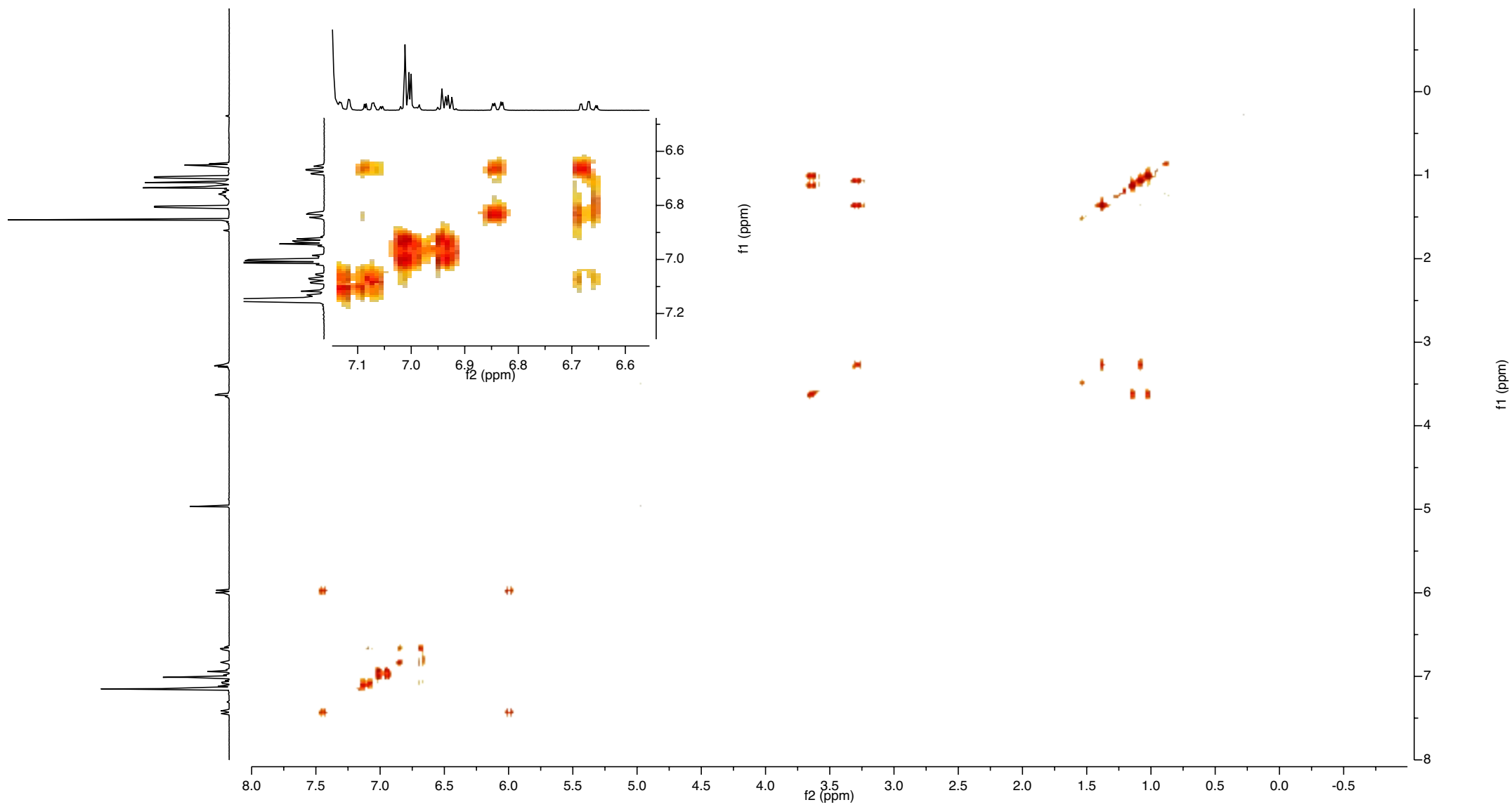


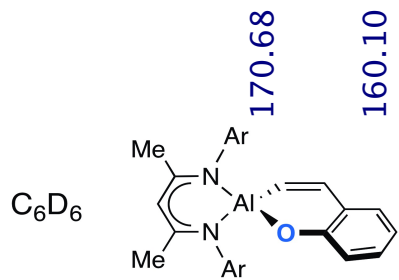
Ar = 2,6-di-iso-propylphenyl





Ar = 2,6-di-iso-propylphenyl





170.68

160.10

—153.71

~145.51

~143.22

~139.59

—132.08

124.98

123.95

~120.77

—118.03

—98.33

29.13

28.39

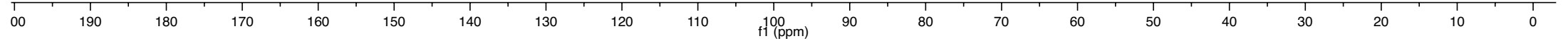
26.14

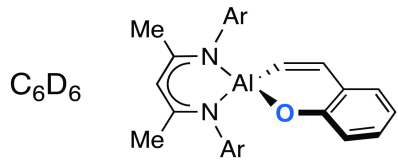
24.77

24.66

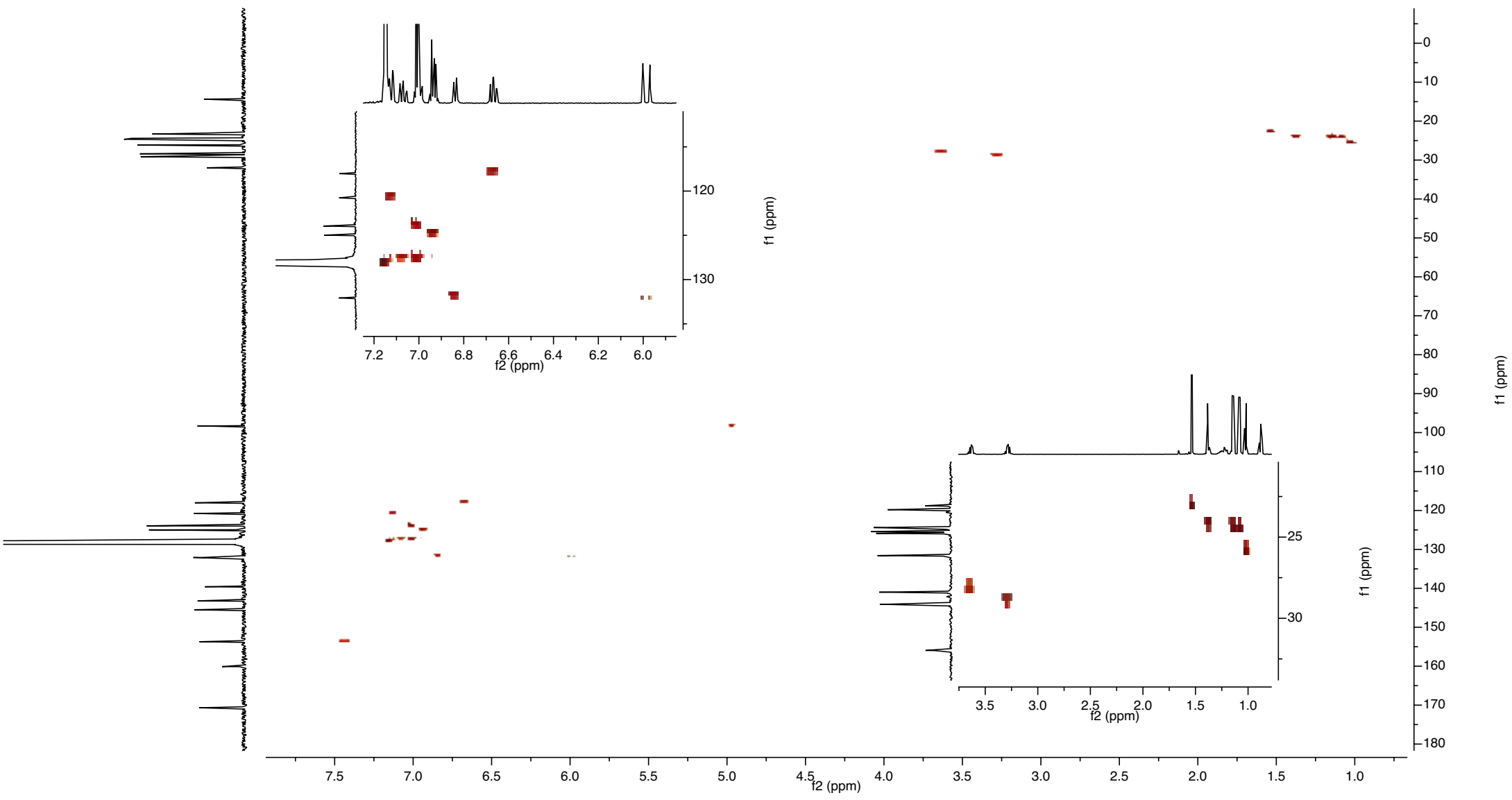
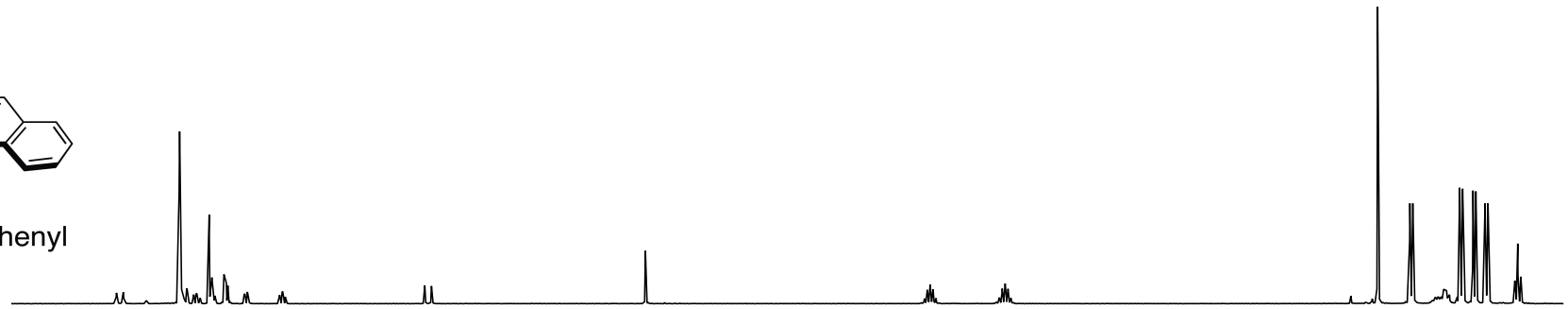
24.41

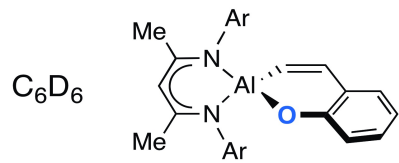
23.32





Ar = 2,6-di-iso-propylphenyl





Ar = 2,6-di-iso-propylphenyl

—161.20

—153.64

132.01
128.29
127.72
127.65
124.92
123.88
120.70
117.96

—98.26

29.07
28.33
26.07
24.71
24.60
24.35
23.25

