

## Supporting Information for:

# A Highly Chemoselective, Zr-Catalyzed C–O Bond Functionalization of Benzofuran

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## 1. General Experimental

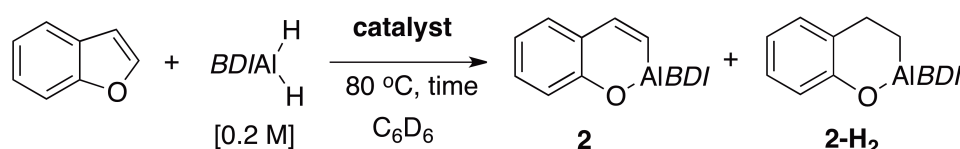
All manipulations were carried out under standard Schlenk-line or glovebox techniques under an inert atmosphere of dinitrogen. A Saffron 2P/O/H<sub>2</sub>O type glovebox was employed operating under an inert atmosphere of 2–5 ppm O<sub>2</sub> or an MBraun Labmaster glovebox operating at <0.1 ppm O<sub>2</sub> and <0.1 H<sub>2</sub>O. 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 120 °C prior to use. d<sub>6</sub>-Benzene and d<sub>8</sub>-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. Infrared spectra were obtained as KBr discs, pressed by a handheld dye, on an ATR cell or as a solution in *n*-hexane. All ethers, including benzofuran, were dried over CaH<sub>2</sub>, distilled and freeze-pump-thaw degassed before use. Ferrocene was sublimed before use. Cp<sub>2</sub>ZrCl<sub>2</sub> and Cp<sub>2</sub>TiCl<sub>2</sub> were purchased from Sigma-Aldrich and used without purification. Indenyl<sub>2</sub>ZrCl<sub>2</sub> was prepared from reaction of indenylLi with ZrCl<sub>4</sub> as described in the literature.<sup>1</sup> *BDI*AlH<sub>2</sub> was prepared according to our previously reported method from the reaction of LiAlH<sub>4</sub> with [{MesNC(Me)}<sub>2</sub>CH]H.<sup>2</sup>

## 2.1 Screening of Catalysts and Additives for C–O bond Alumination

**Experimental Procedure for Screening with Group 4-11 Catalysts:** In a glovebox,  $BDIAlH_2$  (40 mg, 0.11 mmol) was weighed into a 2 mL scintillation vial and dissolved in 550  $\mu$ L of  $C_6D_6$ , benzofuran (10-17.5  $\mu$ L added with a 200  $\mu$ L pipette, due to volatility and measuring inaccuracies the exact ratio of alane to benzofuran was measured by  $^1H$  NMR spectroscopy). The catalyst (5-10 mol%) and internal standard ferrocene (1-2 mg) were weighed into separate scintillation vials, and the reaction mixture added to dissolve each solid. The reaction mixture was transferred to a Youngs tap NMR tube, the NMR tube removed from the box and the reaction monitored by  $^1H$  NMR spectroscopy. The mixture was heated to 80  $^{\circ}C$  on an oil bath and removed periodically to monitor the progress of the reaction.

**Table S1.** Catalysts for the C–O bond Functionalization of Benzofuran

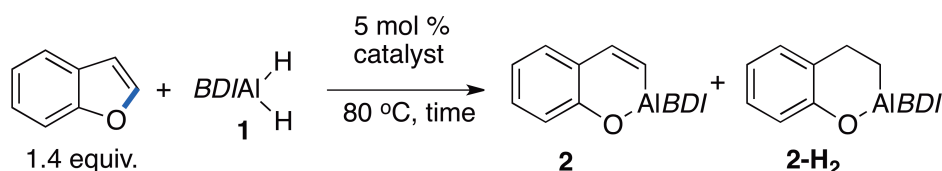


Benzofuran	catalyst (mol%)	time / h	yield / % <sup>[a]</sup>	2 : 2-H <sub>2</sub> <sup>[b]</sup>
1.3 equiv. <sup>[c]</sup>	–	168	0%	–
1.3 equiv.	Cp <sub>2</sub> ZrCl <sub>2</sub> (5)	1	75 % <sup>[d]</sup>	1.1 : 1
1.4 equiv.	Ind <sub>2</sub> ZrCl <sub>2</sub> (5)	3	82 % <sup>[d]</sup>	1.7 : 1
1.2 equiv.	RuH <sub>2</sub> (CO)(PPh <sub>3</sub> ) <sub>3</sub> (10)	20	0%	–
1.0 equiv.	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (10)	20	0%	–
1.0 equiv.	$BDI^2Cu$ (10)	20	0%	–
0.7 equiv.	IrH(CO)(PPh <sub>3</sub> ) <sub>3</sub> (2)	20	0%	–

[a] yield determined by  $^1H$  NMR spectroscopy using ferrocene as an internal standard. [b] ratio determined by  $^1H$  NMR spectroscopy. [c] measured by  $^1H$  NMR spectroscopy. [d] unidentified minor by-product present.  $BDI = \kappa^2\text{-}\{MesNC(Me)\}_2CH$ ,  $BDI^2 = \kappa^2\text{-}\{2,6\text{-}Cl_2C_6H_3NC(Me)\}_2CH$

*Screening with Group 4 Catalysts:* In a glovebox,  $BDIAI\text{H}_2$  (40 mg, 0.11 mmol) was weighed into a 2 mL scintillation vial and dissolved in 500  $\mu\text{L}$  of  $\text{C}_6\text{D}_6$ , benzofuran (10-20  $\mu\text{L}$  was added by micropipette, with the exact ratio of alane to benzofuran, see table, measured by  $^1\text{H}$  NMR spectroscopy). A stock solution of the catalyst (0.5 equiv.),  $BDIAI\text{H}_2$  (0.5 equiv.) and ferrocene (40 mg) was made up in  $\text{C}_6\text{D}_6$  (500  $\mu\text{L}$ ). Upon mixing fast reaction occurred between the hydride and the Group 4 chloride, 50  $\mu\text{L}$  of this stock solution (representing 5 mol % catalyst) was removed and added to the benzofuran/alane reaction mixture. The reaction mixture was transferred to a Youngs tap NMR tube, removed from the box and the reaction monitored by  $^1\text{H}$  NMR spectroscopy.

The above procedure was used and the reaction mixtures were heated to the desired temperature (Table S2).



time / h	Catalyst	Yield	Temp / $^\circ\text{C}$	2 : 2-H <sub>2</sub>
1	$\text{Cp}_2\text{ZrCl}_2$	75 %	80	1.1 : 1
40	$\text{Cp}_2\text{ZrCl}_2$	69 %	60	1.1 : 1
96	$\text{Cp}_2\text{ZrCl}_2$	72%	40	1.3 : 1

*Screening with  $\text{H}_2$  as an additive:* The above procedure was followed exactly, following removal of the Youngs tap NMR tube from the box, the tube was attached a double vacuum manifold and reaction mixture was freeze-pump-thaw degassed over three cycles. On the final cycle the mixture was left to warm to room temperature under vacuum. The manifold was pressurized with 1 atm of  $\text{H}_2$  and the tube opened to the manifold. Following sealing of the NMR tube, the tube was inverted 10 times to ensure thorough mixing and the reaction mixture was monitored by  $^1\text{H}$  NMR spectroscopy.

**Screening with Group 4 Catalysts with alkene additives:** In a glovebox,  $BDIAlH_2$  (40 mg, 0.11 mmol) was weighed into a 2 mL scintillation vial, the alkene (3-7.5 equiv. see table S2) and  $C_6D_6$  was added by micropipette such that the total volume as made up to 500  $\mu$ L. Benzofuran (15-30  $\mu$ L the exact ratio of alkene to benzofuran, see table, measured by  $^1H$  NMR spectroscopy) was added to this mixture by micropipette. A stock solution of the catalyst (0.5 equiv.),  $BDIAlH_2$  (0.5 equiv.) and ferrocene (40 mg) was made up in  $C_6D_6$  (500  $\mu$ L). Upon mixing a fast reaction occurred between the hydride and the group IV chloride, 50  $\mu$ L of this stock solution (representing 5 mol % catalyst) was removed and added to the benzofuran/alkene reaction mixture. The reaction mixture was transferred to a Youngs tap NMR tube, removed from the box and the reaction monitored by  $^1H$  NMR spectroscopy.

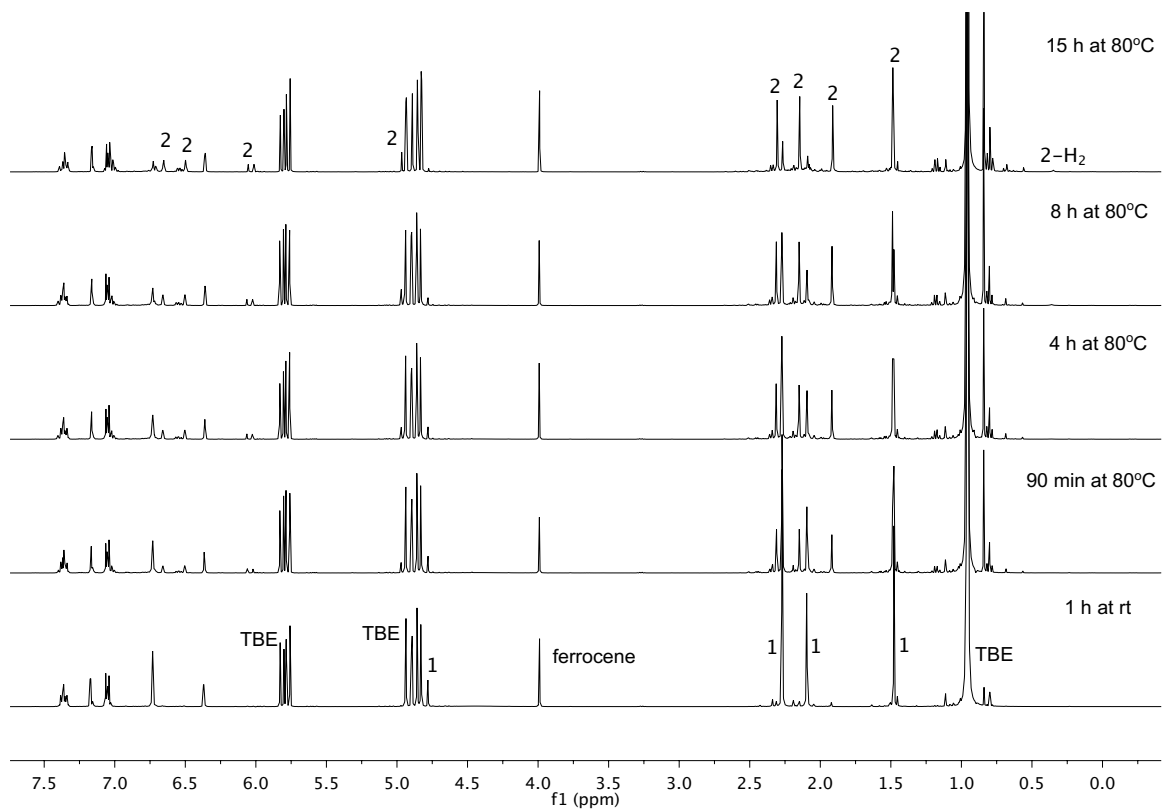
**Table S2:** Additives for the Catalytic C–O bond Functionalization of Benzofuran

Reaction scheme: Benzofuran +  $BDIAlH_2$  (0.2 M)  $\xrightarrow[80\text{ }^\circ\text{C, time}]{5\text{ mol \% catalyst, } C_6D_6}$  **2** + **2-H<sub>2</sub>**

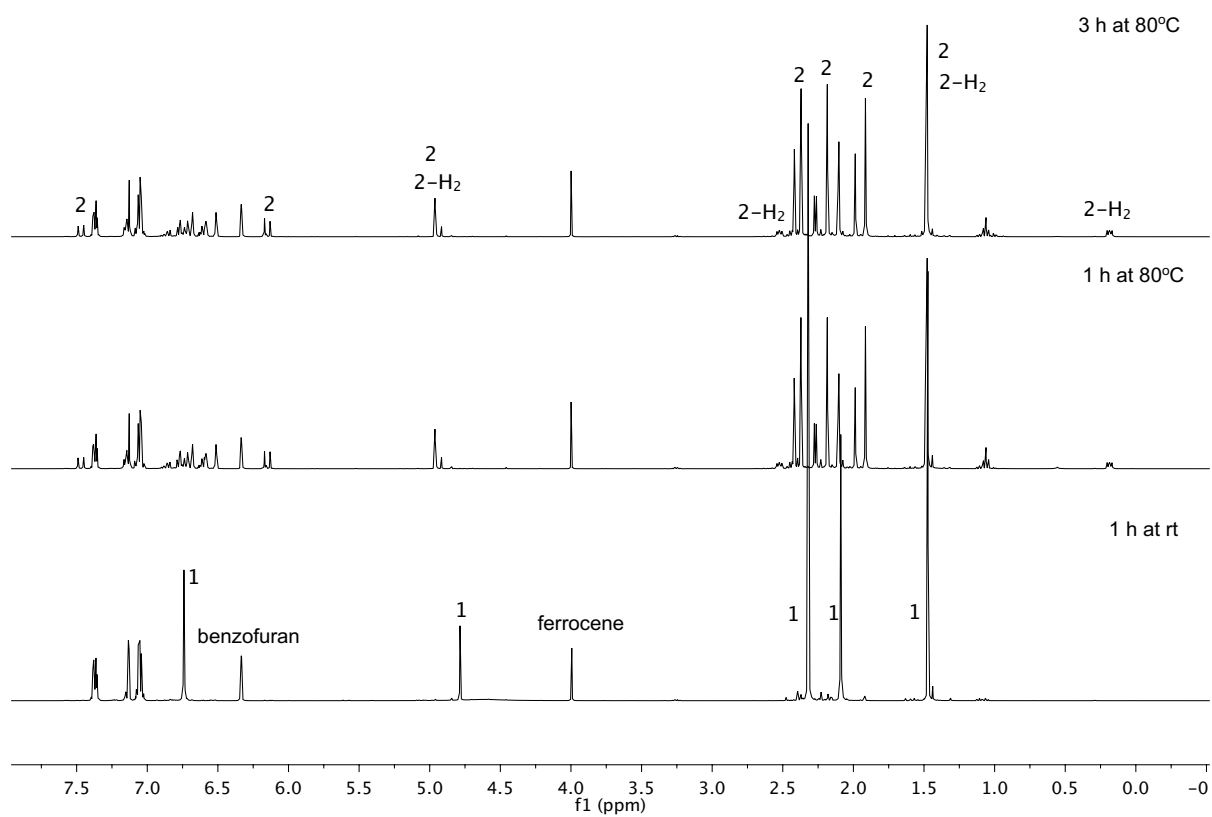
Benzofuran	Catalyst	time / h	yield <sup>[a]</sup>	<b>2</b> : <b>2-H<sub>2</sub></b> <sup>[b]</sup>	additive
2.5 equiv.	$Cp_2ZrCl_2$	3	56 %	3.5 : 1	t-Bu 4.8 equiv.
1.8 equiv.	$Ind_2ZrCl_2$	1	82 %	7.9 : 1	t-Bu 3 equiv.
2.3 equiv.	$Ind_2ZrCl_2$	8	76 %	15 : 1	t-Bu 4.4 equiv.
1.6 equiv.	$Ind_2ZrCl_2$	15	60 %	>50 : 1	t-Bu 7.5 equiv.
2.2 equiv.	$Ind_2ZrCl_2$	1.5	26 %	>20 : 1	nBu 5.5 equiv.
1.4 equiv.	$Cp_2ZrCl_2$	1	75 % <sup>[c]</sup>	1.1 : 1	–
1.1 equiv.	$Cp_2ZrCl_2$	2	76 % <sup>[c]</sup>	1.7 : 1	$H_2$ (1 atm)

[a] yield determined by  $^1H$  NMR spectroscopy using ferrocene as an internal standard. [b] ratio determined by  $^1H$  NMR spectroscopy. [c] unidentified minor by-product present.  $BDI = \kappa^2\text{-}\{MesNC(Me)\}_2CH$ .

(a)

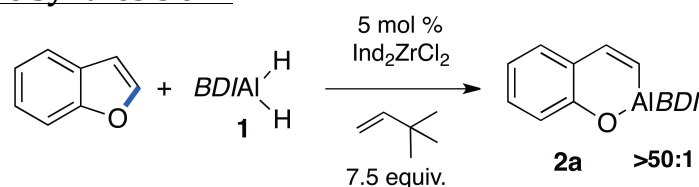


(b)



**Figure S1:**  $^1\text{H}$  NMR stackplot for the reaction of **1** with benzofuran to form **2** catalyzed by (a)  $\text{indenyl}_2\text{ZrCl}_2$  with 7.5 equiv. 3,3-dimethylbut-1-ene (TBE) and (b)  $\text{indenyl}_2\text{ZrCl}_2$ . Reactions conducted at 80 °C based on a 0.2 M concentration of  $\text{BDIAlH}_2$  in  $\text{C}_6\text{D}_6$ .

## 2.2 Preparative Scale Synthesis of **2**

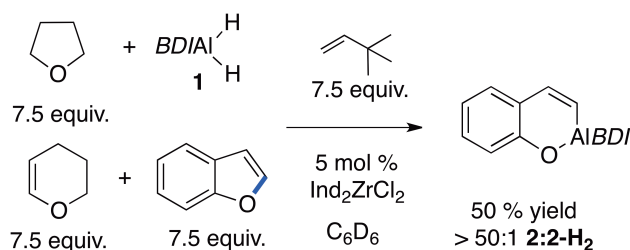


**Synthesis of **2**:** In a glovebox benzofuran (163 mg, 1.38 mmol, 1.25 equiv.),  $BDIALH_2$  (400 mg, 1.1 mmol, 1 equiv.)  $Ind_2ZrCl_2$  (21 mg, 0.053 mmol, 5 mol %), and 3,3-dimethylbut-1-ene (694 mg, 8.25 mmol, 7.5 equiv.) were weighed into separate snap cap vials. The alane,  $BDIALH_2$  and zirconium catalyst were loaded into a Youngs tap schlenk and dissolved in toluene (3 mL). The benzofuran and alkene were added, the reaction vessel sealed and removed from the glovebox. The mixture was heated in this sealed system to 80 °C for 22 h. Following cooling to room temperature the reaction mixture was concentrated to 2 mL *in vacuo*. n-Hexane (10 mL) was then added, upon which point the product began to crystallize. The reaction mixture was stored at -20 °C overnight and the product isolated by filtration and dried under vacuum. Colorless crystals of **2** were collected (250 mg, 0.52 mmol, 47%).  $^1H$  NMR ( $C_6D_6$ , 400 MHz, 298 K)  $\delta$  1.48 (s, 6H), 1.93 (s, 6H), 2.19 (s, 6H), 2.38 (s, 6H), 4.96 (s, 1H), 6.16 (d, 1H,  $J$  = 16.0 Hz), 6.52 (s, 2H), 6.61 (dt, 1H,  $J$  = 6.0 and 1.2 Hz), 6.69 (s, 2H), 6.80 (dd,  $J$  = 7.2 and 1.2 Hz), 7.08 (dt, 1H,  $J$  = 7.6 and 1.2 Hz), 7.16-7.18 (m, 1H), 7.49 (d, 1H,  $J$  = 16.0 Hz);  $^{13}C$  NMR ( $C_6D_6$ , 125 MHz, 298 K)  $\delta$  18.3, 18.6, 20.8, 22.3, 97.5, 118.0, 119.7, 127.8, 129.4, 130.2, 132.1 ( $\alpha$ -Al), 132.3, 134.1, 135.9, 139.6, 153.1, 159.1 ( $\beta$ -Al), 170.1; EI Mass Spec (+ve ion) 319 (30%  $[M-H]^+$ ); Elemental Analysis calc. for  $C_{31}H_{35}AlN_2O$  C, 77.80; H, 7.37; N, 5.85 found C, 77.87; H, 7.40; N, 5.92.

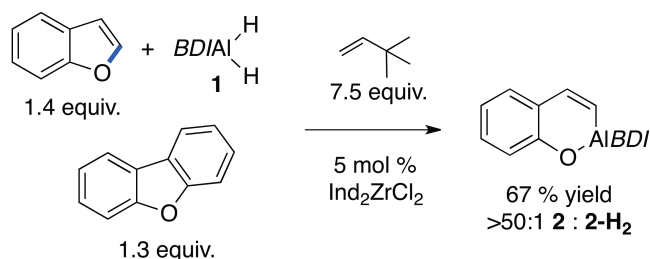
**Synthesis of **2/2-H<sub>2</sub>**:** In a glovebox benzofuran (163 mg, 1.38 mmol, 1equiv.),  $BDIALH_2$  (500 mg, 1.1 mmol, 1 equiv.) and  $Cp_2ZrCl_2$  (19.9 mg, 0.068 mmol, 5 mol %) were weighed into separate snap cap vials. The alane,  $BDIALH_2$  and zirconium catalyst were loaded into a Youngs tap schlenk and dissolved in toluene (5 mL). The benzofuran was then added, the reaction vessel sealed and removed from the glovebox. The mixture was heated in this sealed system to 80 °C for 24 h. The hot mixture was transferred to a Schlenk tube and crystallization of a mixture of **2/2-H<sub>2</sub>** occurred upon cooling to room temperature. The mixture was stored at -20 °C for a further 24 h and the product isolated by filtration as colorless crystals of **2/2-H<sub>2</sub>** (290 mg, 0.60 mmol, 44 %). Recrystallization of an aliquot from toluene allowed isolation of a product enriched in **2-H<sub>2</sub>** 1:3 ratio of **2/2-H<sub>2</sub>**.

*In situ* NMR data for **2** are identical to those above. *In situ* NMR data for **2-H<sub>2</sub>** <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 298 K) δ 0.18 – 0.21 (m, 2H), 1.48 (s, 6 H), 1.99 (s, 6H), 2.10 (s, 6H), 2.42 (s, 6H), 4.95 (s, 1H), 6.58 (s, 2H), 6.60-6.63 (m, 1H), 6.71 (s, 2H), 6.86 (d, 1H, *J* = 7.2 Hz), 7.15-7.17 (m, 2H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 100 MHz, 298 K) δ 18.5 (2 signals), 20.9, 22.2, 31.2 (β-Al), 97.6, 118.1, 119.5, 127.2, 129.4, 130.1, 130.3, 132.4, 132.7, 134.6, 136.0, 139.8, 160.1, 170.4 (α-Al not observed).

### 2.3 <sup>1</sup>H NMR Competition Experiments



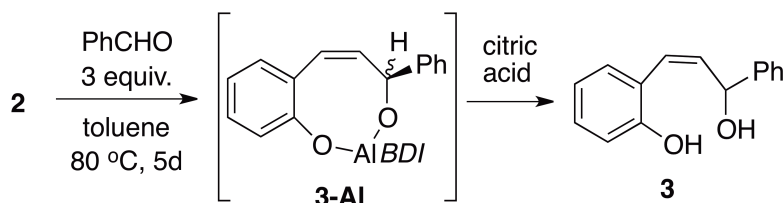
*Competition Experiment between excess THF, 2H-pyran and benzofuran:* In a glovebox, BDIALH<sub>2</sub> (40 mg, 0.11 mmol) was weighed into a 2mL scintillation vial and dissolved in 50 μL of C<sub>6</sub>D<sub>6</sub>, benzofuran (91 μL, 0.825 mmol, 7.5 equiv.), THF (67 μL, 0.825 mmol, 7.5 equiv.), 3,4-dihydro-2H-pyran (75 μL, 0.825 mmol, 7.5 equiv.) and 3,3-dimethylbut-1-ene (~100 μL) were added by micropipette. A stock solution of Indenyl<sub>2</sub>ZrCl<sub>2</sub> (0.5 equiv.), BDIALH<sub>2</sub> (0.5 equiv.) and ferrocene (40 mg) was made up in C<sub>6</sub>D<sub>6</sub> (500 μL). Upon mixing a fast reaction occurred between the hydride and the Group 4 chloride, 50 μL of this stock solution (representing 5 mol % catalyst) was removed and added to the benzofuran/alane reaction mixture. The reaction mixture was transferred to a Youngs tap NMR tube, removed from the box and the reaction monitored by <sup>1</sup>H NMR spectroscopy. Following 2d at 80 °C **2** was observed in 50 % yield and >50:1 selectivity of **2**:**2-H<sub>2</sub>**.



*Competition Experiment between benzofuran and dibenzofuran:* In a glovebox, BDIALH<sub>2</sub> (40 mg, 0.11 mmol) was weighed into a 2 mL scintillation vial and dissolved in 300 μL of C<sub>6</sub>D<sub>6</sub>, benzofuran (17.5 μL, 0.16 mmol, 1.4 equiv.), dibenzofuran (24.1 mg, 0.143 mmol, 1.3 equiv.), and 3,3-dimethylbut-1-ene (~100 μL) were added by micropipette. A stock solution of Indenyl<sub>2</sub>ZrCl<sub>2</sub> (0.5 equiv.), BDIALH<sub>2</sub> (0.5 equiv.) and ferrocene (40 mg) was made up in C<sub>6</sub>D<sub>6</sub>

(500  $\mu$ L). Upon mixing a fast reaction occurred between the hydride and the Group 4 chloride, 50  $\mu$ L of this stock solution (representing 5 mol % catalyst) was removed and added to the benzofuran/alane reaction mixture. The reaction mixture was transferred to a Youngs tap NMR tube, removed from the box and the reaction monitored by  $^1\text{H}$  NMR spectroscopy. Following 24 h at 80  $^\circ\text{C}$  **2** was observed in 67 % yield and >50:1 selectivity of **2:2-H<sub>2</sub>**.

## 2.4 Reaction of **2** with Benzaldehyde

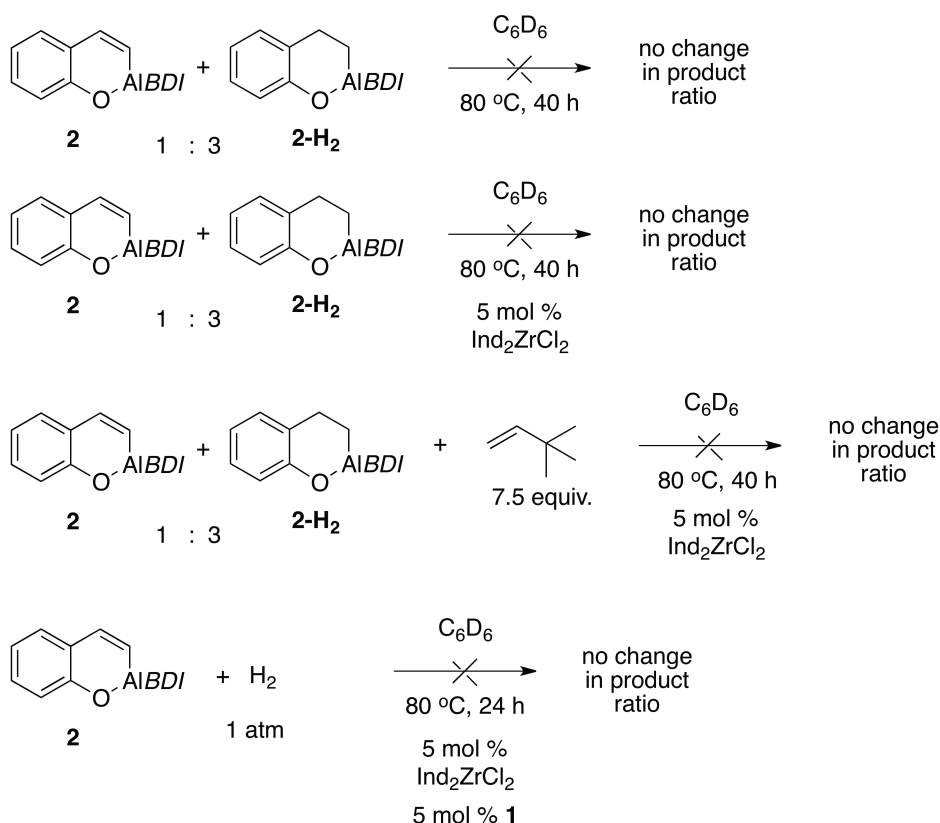


The reaction of **2** with benzaldehyde to form **3-Al** could be monitored by  $^1\text{H}$  NMR spectroscopy and proceed cleanly at 80  $^\circ\text{C}$  over the course of 5 days at 80  $^\circ\text{C}$ . Inclusion of ferrocene as an internal standard gave 61 % yield of **3-Al** by  $^1\text{H}$  NMR.

**Synthesis of 3:** In a glovebox, the aluminium complex **2** (200 mg, 0.418 mmol) was weighed out and dissolved in benzene (2mL). Benzaldehyde (143 mg, 1.347 mmol, 3.2 equiv.) was added to the solution and the reaction mixture transferred to a Youngs ampoule. The ampoule was sealed, removed from the box and heated to 80  $^\circ\text{C}$  for 5 d. The solvent was removed *in vacuo* and the crude redissolved in DCM (50 mL) and washed with an aqueous solution of citric acid (3 x 10 mL), followed by water (10 mL), the organic layer was dried over  $\text{MgSO}_4$  and the solvent removed. The crude was purified by column chromatography using a hexane to 3:1 hexane : ethyl acetate gradient. The product was isolated as a yellow oil (31 mg, 0.137 mmol, 33 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, 298 K)  $\delta$  5.39 (d, 1H,  $J$  = 9.6 Hz), 6.08 (dd, 1H,  $J$  = 11.2 and 9.6 Hz), 6.59 (d, 1H,  $J$  = 11.2 Hz), 6.87 – 6.95 (m, 2H), 7.13 (d, 1H,  $J$  = 8.0 Hz), 7.21 (dt, 1H,  $J$  = 8.0 Hz, 1.6 Hz), 7.29-7.37 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, 298 K)  $\delta$  70.7, 116.3, 120.6, 123.3, 126.3, 126.5, 127.9, 128.8, 129.3, 130., 135.5, 142.6, 153.1; HR-MS calc. for  $\text{C}_{15}\text{H}_{13}\text{O}$  209.0966 found 209.0958. [Lit.<sup>4</sup>  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.31 (br. s, 2H, OH), 5.78 (dd, 1H,  $J$  = 9.7, 3.4 Hz, ArCH=CH), 5.91 (m, 1H, HOCH), 6.52 (dd, 1H,  $J$  = 9.7, 1.8 Hz, ArCH), 6.77-6.88, 6.98-7.13, 7.30-7.37 (m, 9H, ArH). IR (film,  $\text{cm}^{-1}$ ) 3404, 3061, 3029, 1642, 1228. HRMS for  $\text{C}_{15}\text{H}_{12}\text{O}$  calc. 208.0888 found 208.0893 ( $\text{M}^+ - \text{H}_2\text{O}$ )].



## 2.5 Control Experiments



## 3. X-Ray Crystallography Data

*Crystal data for 2:* C<sub>31</sub>H<sub>35</sub>AlN<sub>2</sub>O, *M* = 478.59, monoclinic, *C*2/*c* (no. 15), *a* = 35.1731(10), *b* = 16.6491(4), *c* = 18.7399(5) Å, β = 96.397(3)°, *V* = 10905.8(5) Å<sup>3</sup>, *Z* = 16 (two independent molecules), *D<sub>c</sub>* = 1.166 g cm<sup>-3</sup>, μ(Mo-Kα) = 0.100 mm<sup>-1</sup>, *T* = 173 K, pale yellow blocks, Oxford Diffraction Xcalibur 3 diffractometer; 12565 independent measured reflections (*R*<sub>int</sub> = 0.0245), *F*<sup>2</sup> refinement,<sup>3</sup> *R*<sub>1</sub>(obs) = 0.0496, *wR*<sub>2</sub>(all) = 0.1386, 9156 independent observed absorption-corrected reflections [*|F<sub>o</sub>|* > 4σ(*|F<sub>o</sub>|*)], 2θ<sub>max</sub> = 58°, 648 parameters. CCDC 942589.

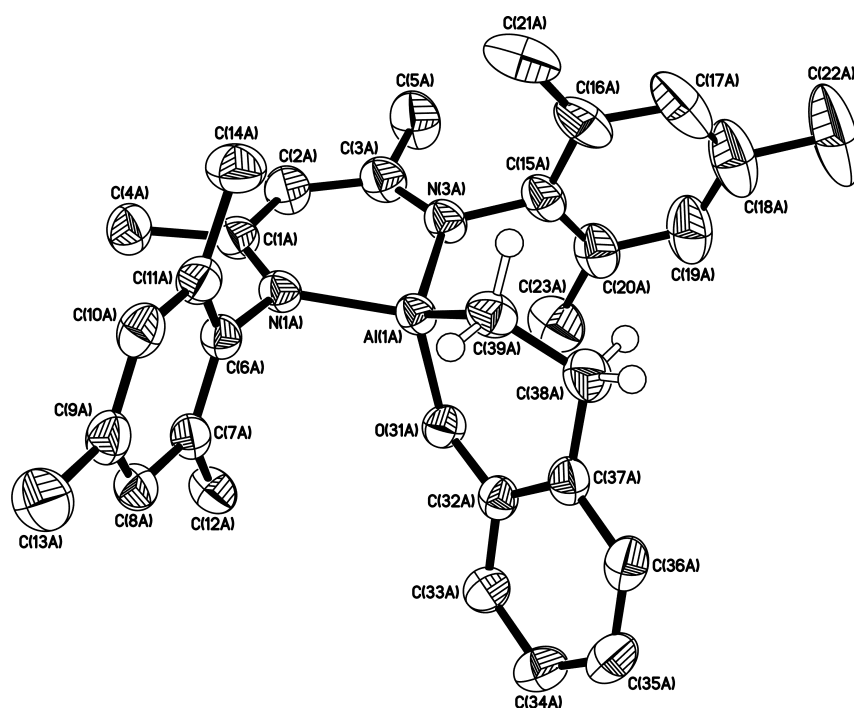
*The X-ray crystal structure of 2:* The crystal structure of **2** was found to contain two independent complexes (**A** and **B**) in the asymmetric unit, shown in pictures S2 and S3 respectively. In view of the “co-crystallisation disorder” seen for the structure of **2-H<sub>2</sub>/2** (see below), which was determined prior to that of **2**, the Hirshfeld test alert in the checkCIF report for the C(38)–C(39) bond in molecule **B** of this structure was investigated as a possible sign of something similar happening here. However, when modeled in this fashion, the second

component was both unconvincing and of low site occupancy (*ca.* 11%), and so this component was not included in the final structure. Additionally, when omitted from the final structure, the four C(38)/C(39) hydrogen atoms across the two independent complexes were clearly visible from a  $\Delta F$  map, appearing as the four largest residual electron density peaks.

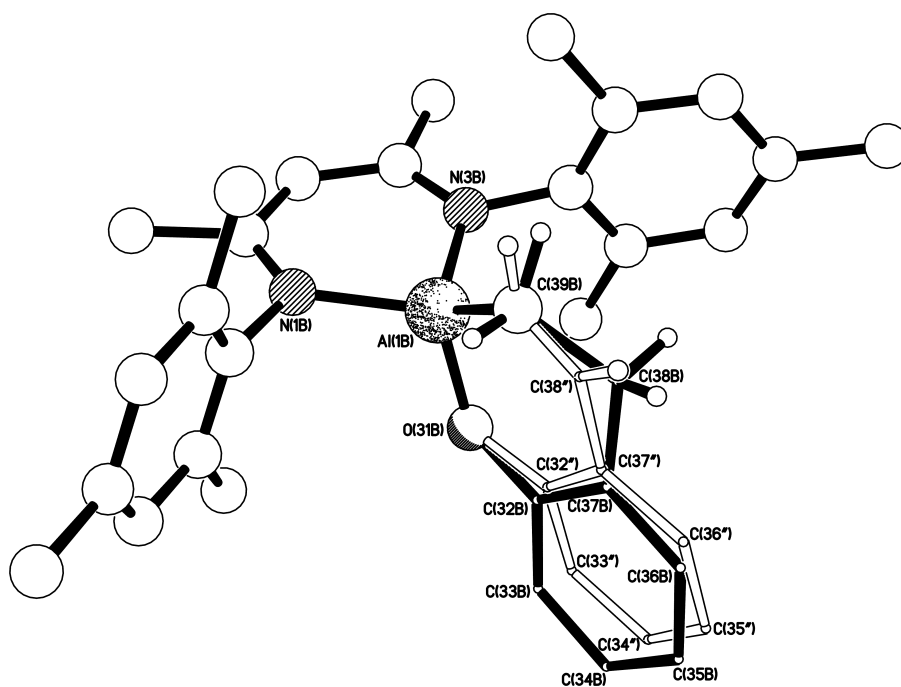
Crystal data for **2-H<sub>2</sub>/2**: 0.85(C<sub>31</sub>H<sub>37</sub>AlN<sub>2</sub>O)·0.15(C<sub>31</sub>H<sub>35</sub>AlN<sub>2</sub>O), *M* = 480.30, monoclinic, *C*2/*c* (no. 15), *a* = 35.7739(4), *b* = 16.53506(17), *c* = 18.7014(2) Å,  $\beta$  = 97.8415(11)°, *V* = 10958.9(2) Å<sup>3</sup>, *Z* = 16 (two independent molecules), *D<sub>c</sub>* = 1.164 g cm<sup>-3</sup>,  $\mu$ (Cu-K $\alpha$ ) = 0.829 mm<sup>-1</sup>, *T* = 173 K, colourless needles, Oxford Diffraction Xcalibur PX Ultra diffractometer; 10493 independent measured reflections (*R*<sub>int</sub> = 0.0260), *F*<sup>2</sup> refinement,<sup>[1]</sup> *R*<sub>1</sub>(obs) = 0.0439, *wR*<sub>2</sub>(all) = 0.1247, 8506 independent observed absorption-corrected reflections [*|F<sub>o</sub>|* > 4σ(*|F<sub>o</sub>|*), 2θ<sub>max</sub> = 145°], 653 parameters. CCDC 942590.

*The X-ray crystal structure of 2-H<sub>2</sub>/2*: The crystal structure of **2-H<sub>2</sub>/2** was found to contain two independent complexes (**A** and **B**) in the asymmetric unit, shown in pictures S4 and S6 respectively. The O(31)/C(39) ligand of the second complex was found to be disordered, and modelling of this disorder suggested that the best fit was a mixture of **2-H<sub>2</sub>** and **2** in a *ca.* 69:31 ratio (Figure S5); this makes the overall ratio throughout the crystal *ca.* 85:15 for **2-H<sub>2</sub>** and **2**. For both components of the disorder the aryl ring was treated as an idealized rigid body, and the oxygen atom O(31B) (which is common to both components) and the appropriate C(38) site were restrained to be coplanar with applicable aryl ring. The thermal parameters of adjacent atoms across the two components were restrained to be similar, and only the non-hydrogen atoms of the major occupancy component were refined anisotropically. When omitted from the final structure, the four C(38)/C(39) hydrogen atoms for complex **2-H<sub>2</sub>(A)** were clearly visible from a  $\Delta F$  map, though understandably those for the two partial occupancy components of the second independent complex were not so evident.

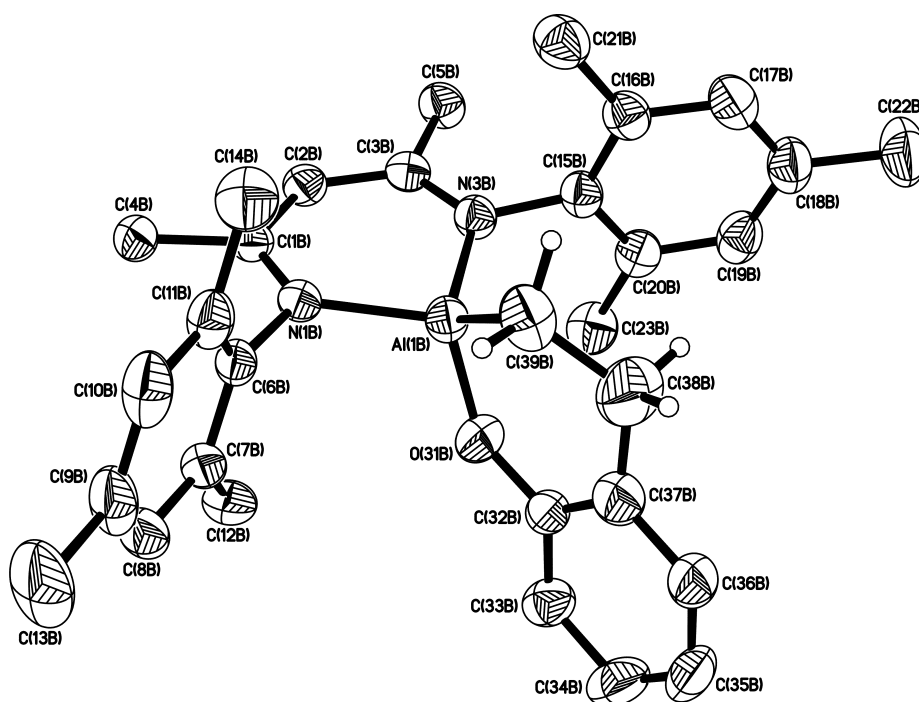




**Figure S4:** The structure of **2-H<sub>2</sub>(A)**, one of the two independent complexes present in the crystal of **2-H<sub>2</sub>/2** (50% probability ellipsoids).



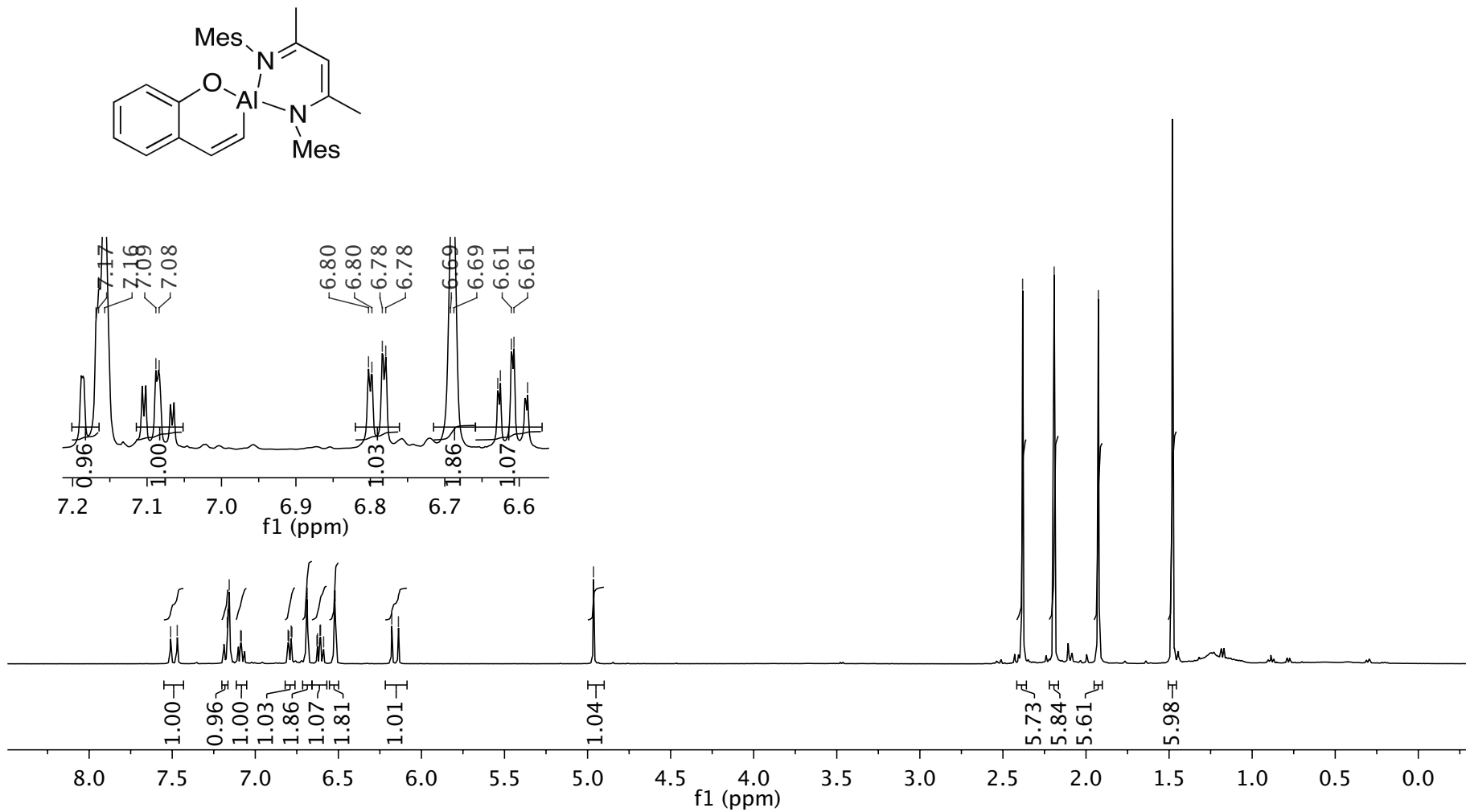
**Figure S5:** The structure of the second independent molecule in the crystal of **2-H<sub>2</sub>/2** showing the co-crystallisation of **2-H<sub>2</sub>** and **2** that manifests as disorder in the O(31)/C(39) ligand. The major occupancy component (**2-H<sub>2</sub>**, ca. 69%) has been drawn with dark bonds, whilst the minor occupancy component (**2**, ca. 31%) has been drawn with open bonds.



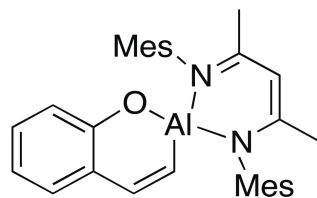
**Figure S6:** The structure of **2-H<sub>2</sub>(B)**, the major occupancy component of the second of the two independent complexes present in the crystal of **2-H<sub>2</sub>/2** (50% probability ellipsoids).

#### 4. References

1. (a) P. Courtot, R. Pichon, J. Y. Salaun, L. Toupet, *Can. J. Chem.* **1991**, 69, 661. (b) A. Lapczuk-Krygier, K. Baranowska, L. Ponikiewski, E. Matern, J. Pikies, *Inorg. Chim. Acta* **2012**, 387, 361.
2. S. Yow, S. J. Gates, A. J. P. White, M. R. Crimmin, *Angew. Chem. Int. Ed.* **2012**, 51, 12559.
3. G.M. Sheldrick, *Acta Cryst.*, **2008**, A64, 112.
4. M. Yus, F. Foubelo, J. V. Ferrández, *Eur. J. Org. Chem.* **2001**, 2809.

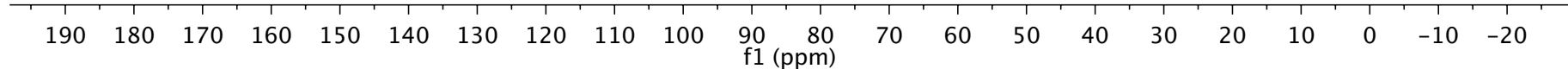


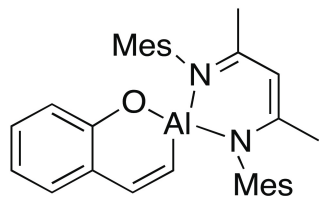
$^{13}\text{C}$  NMR (125 MHz, 298 K,  $\text{C}_6\text{D}_6$ )



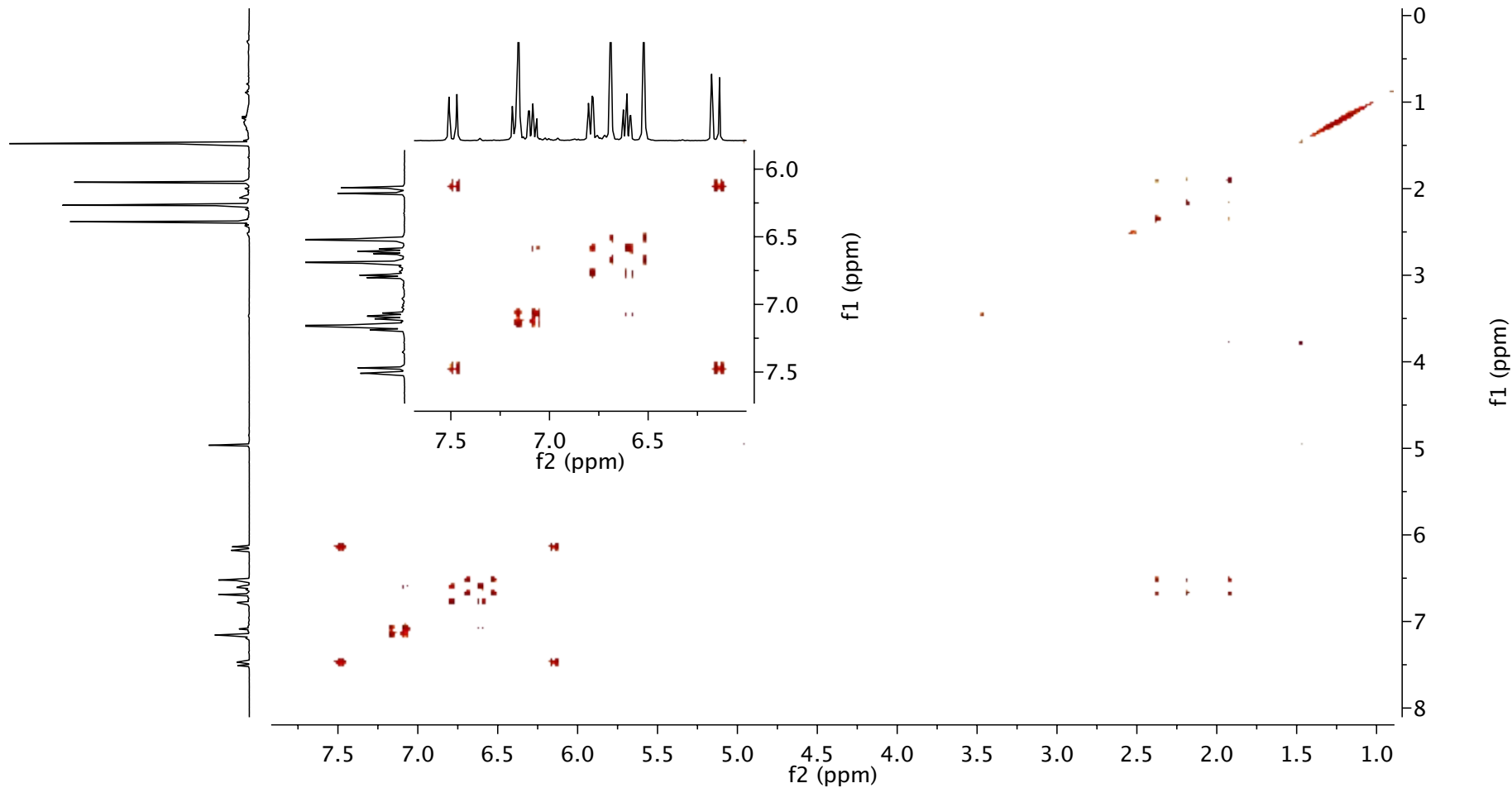
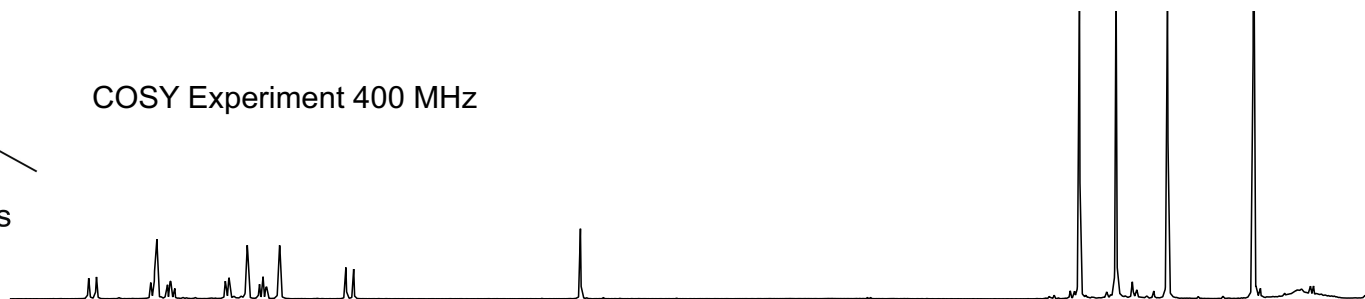
—170.2  
—159.1  
—153.1  
132.3  
132.1  
130.2  
129.4  
128.3  
128.2  
128.1  
128.0  
127.9  
127.8  
119.7  
97.5

22.3  
20.8  
18.6  
18.3



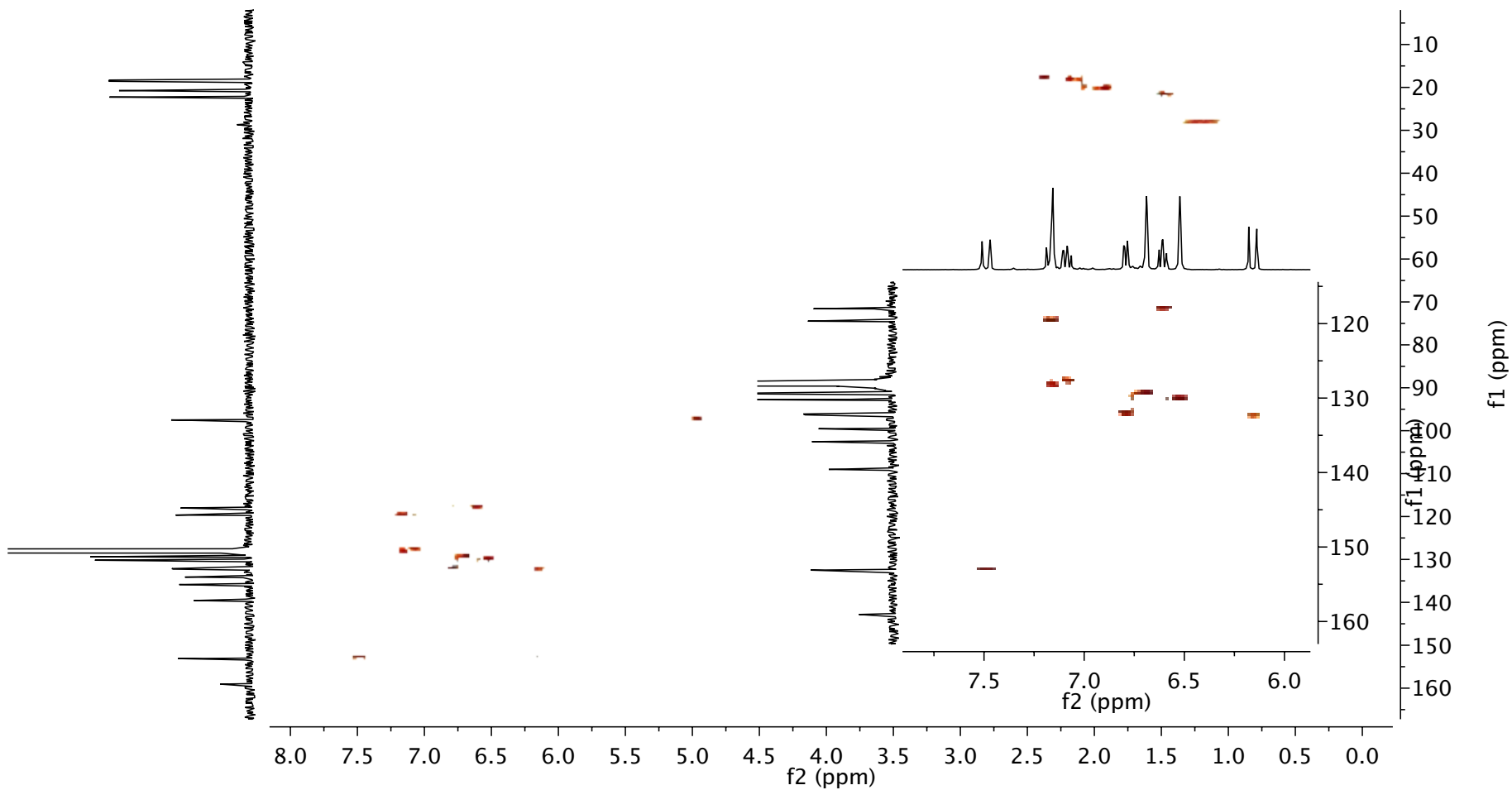
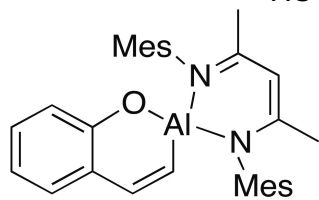


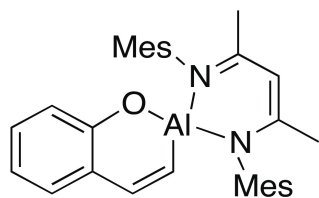
COSY Experiment 400 MHz



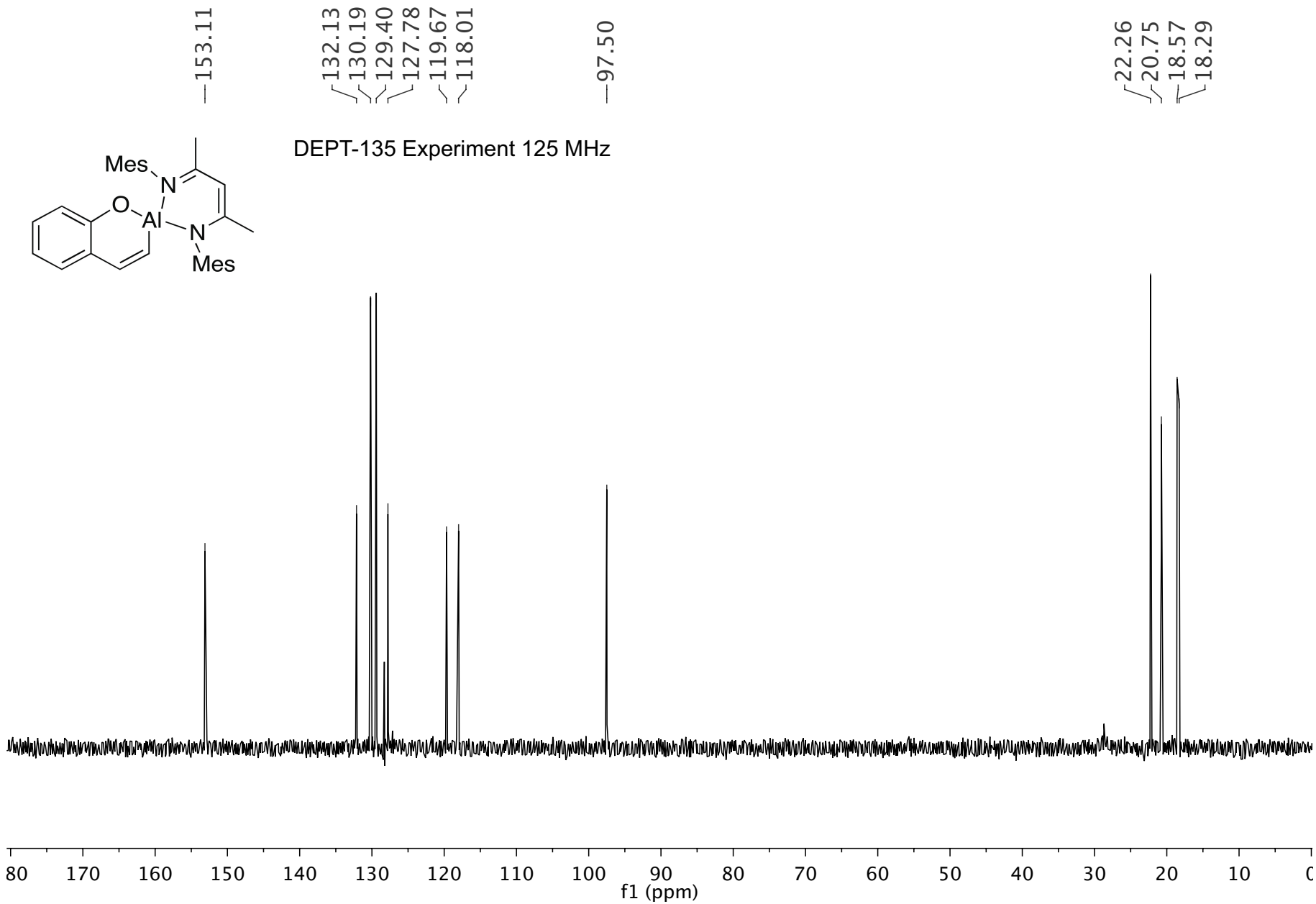


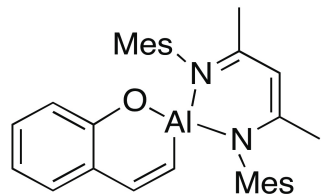
# HSQC Experiment



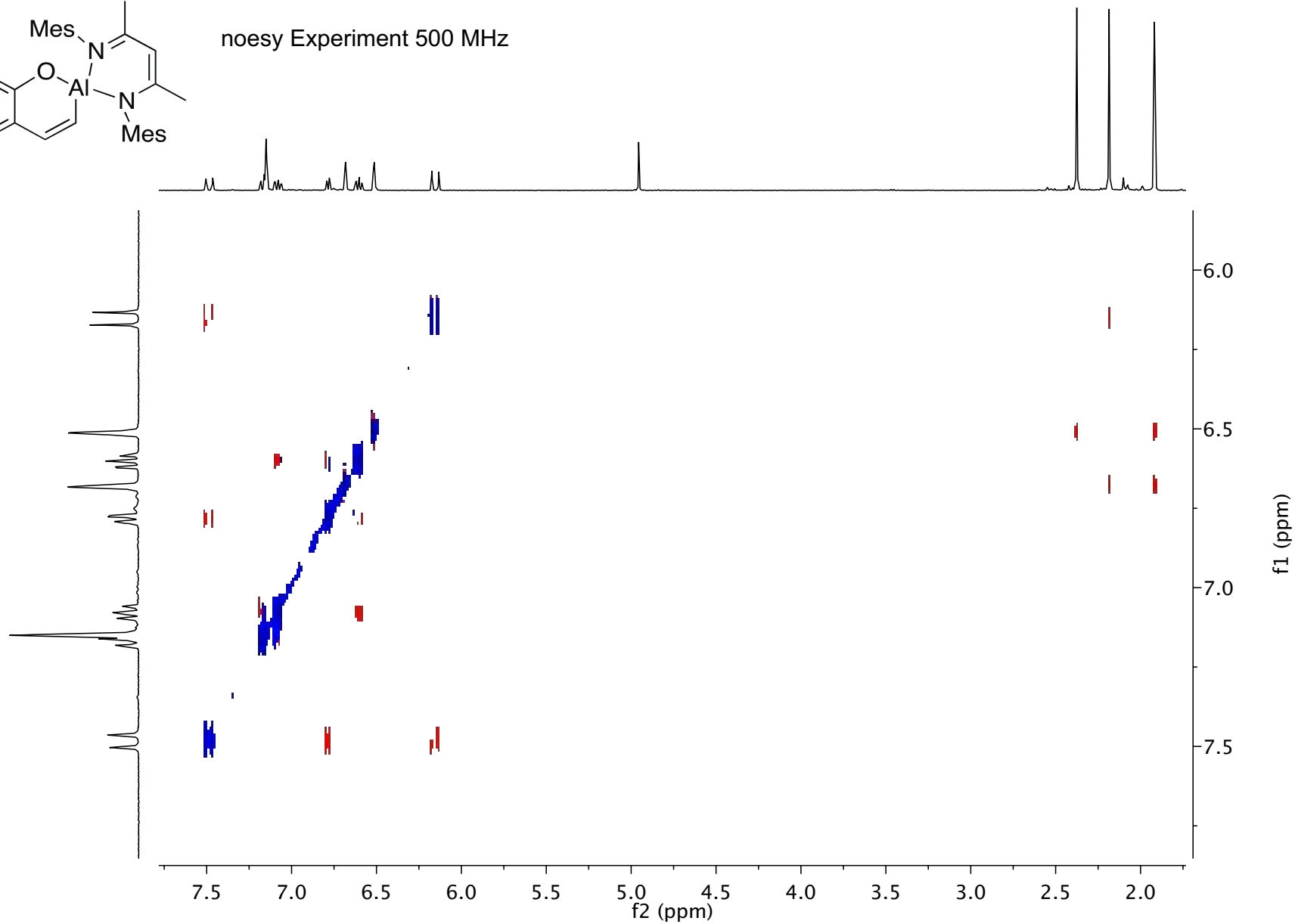


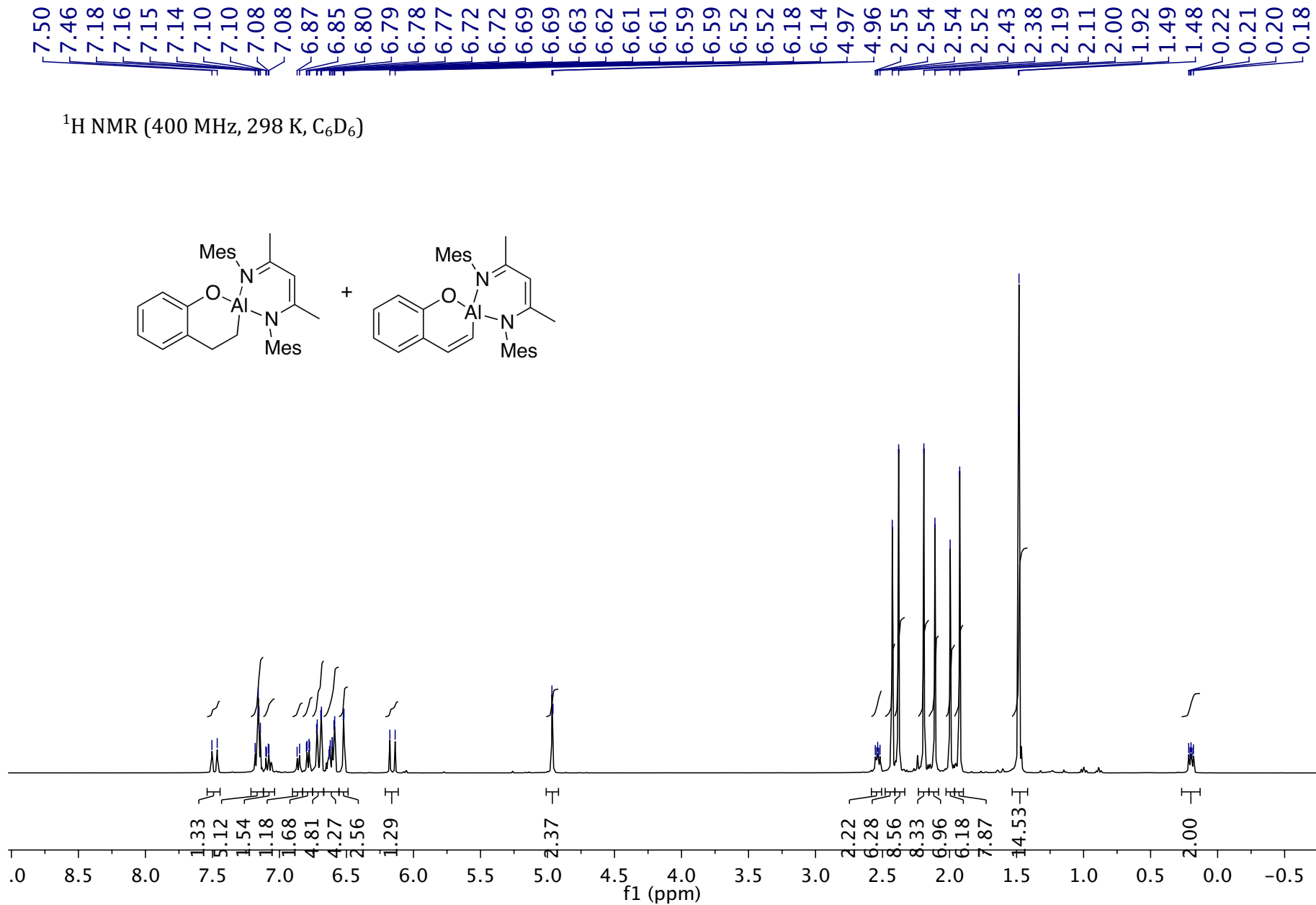
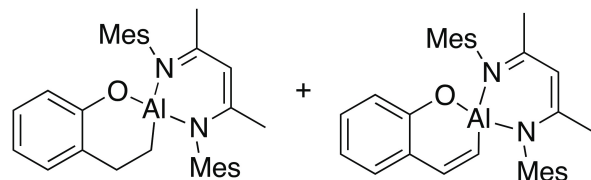
DEPT-135 Experiment 125 MHz

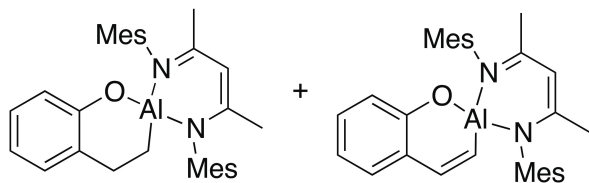




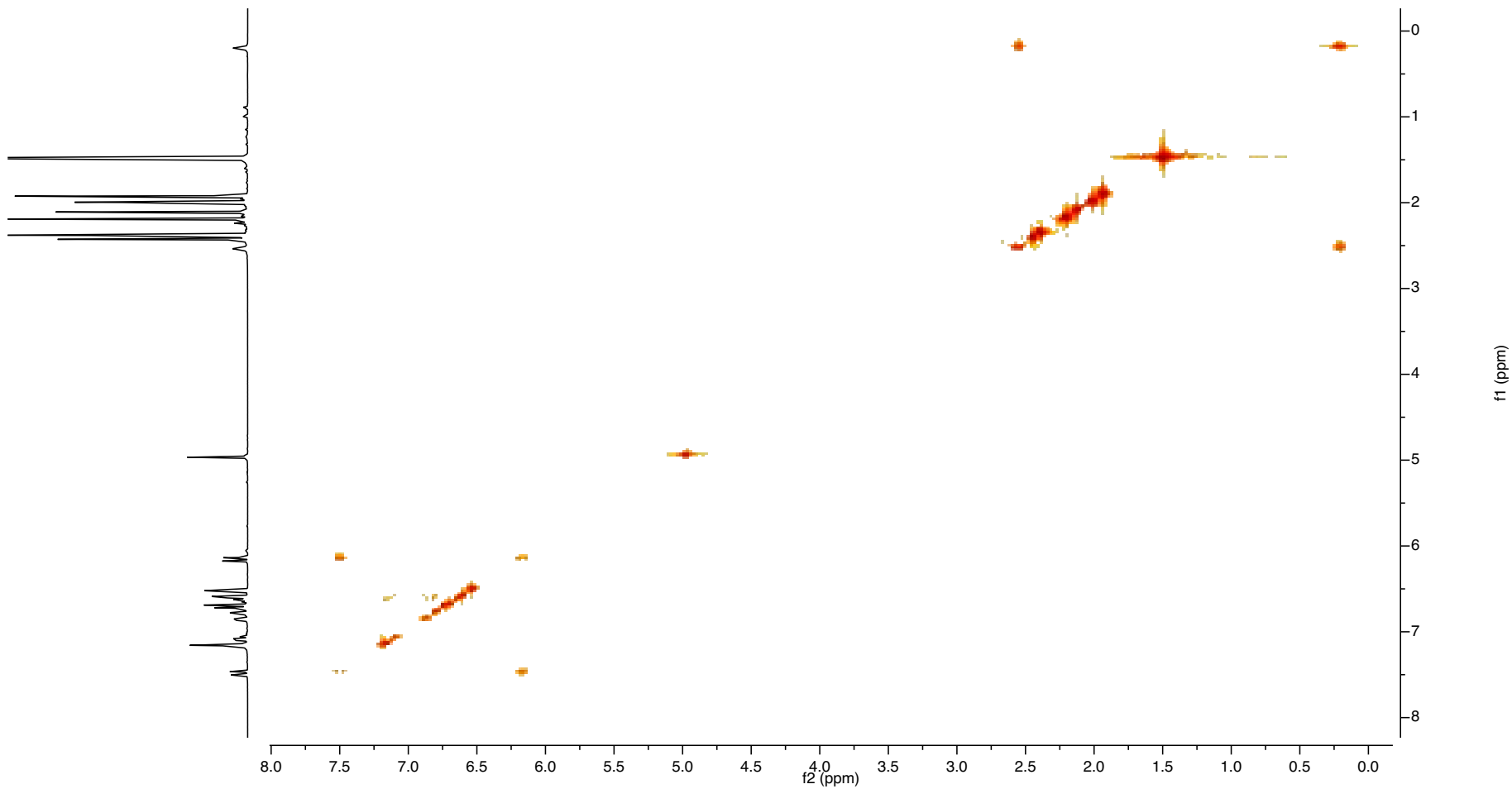
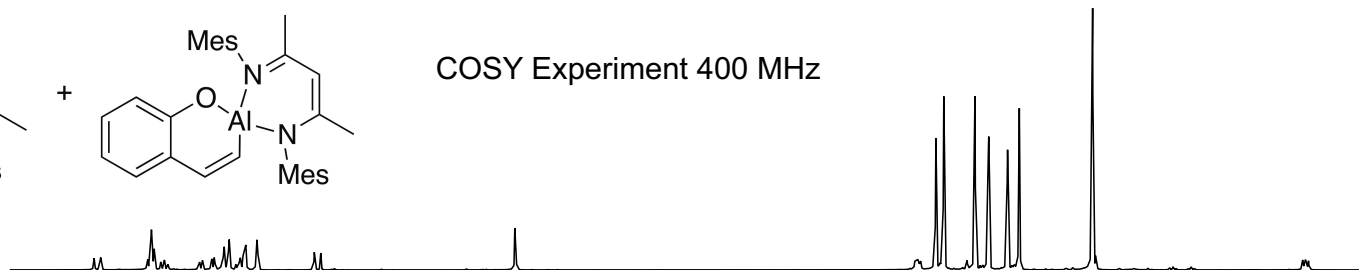
noesy Experiment 500 MHz



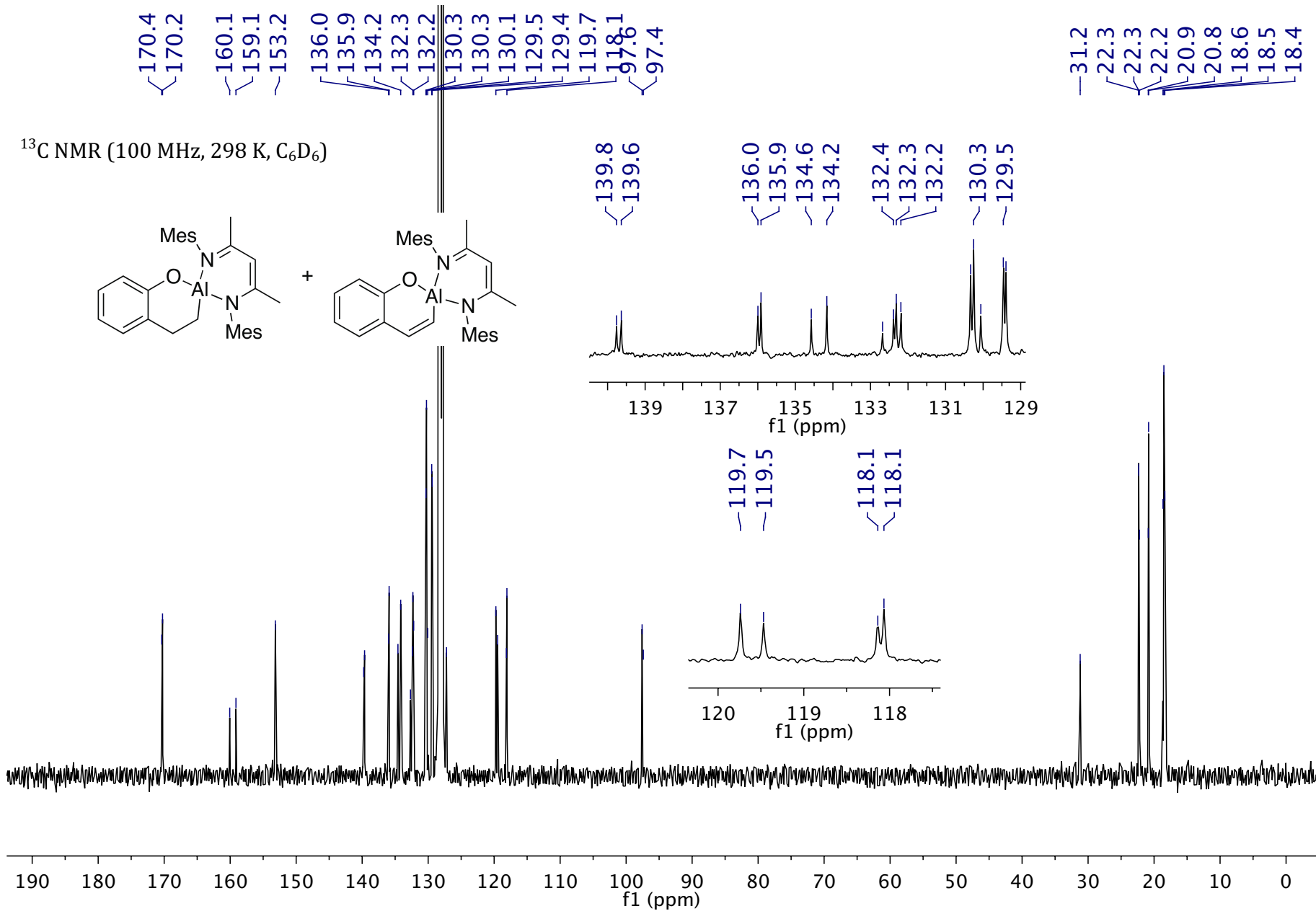
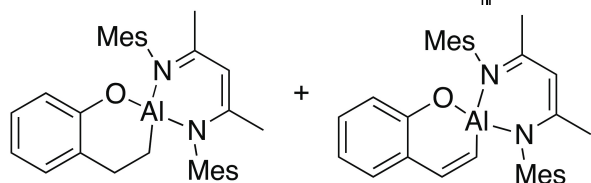




COSY Experiment 400 MHz



$^{13}\text{C}$  NMR (100 MHz, 298 K,  $\text{C}_6\text{D}_6$ )



$^1\text{H}$  NMR (400 MHz, 298 K,  $\text{C}_6\text{D}_6$ ) Recrystallised from Toluene 3:1 Mixture

