New Journal of Chemistry

Syntheses and ligand exchange experiments of *N*,*N*-dialkylcarbamate bridged $\{Al_3(\mu_3\text{–}O)\}^{7+}$ complexes

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Electronic Supplementary Information

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Synthetic procedures

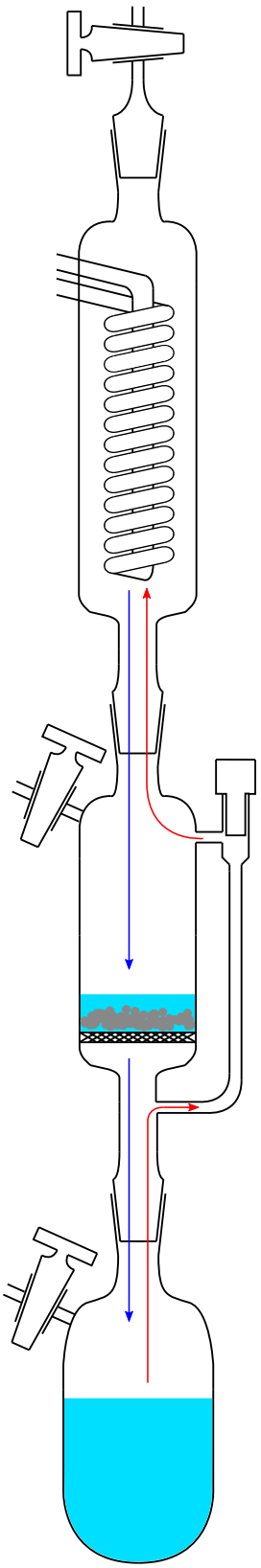

Figure ESI.1: Illustration of the extraction procedure with diethyl ether (blue coloured liquid) with a SCHLENK-type extractor.

Crystal structures of compounds (1a) and (2a)

distance	value, Å
Al1–O5	1.8110(7)
Al1–O3	1.8885(19)
Al1–O1	1.906(2)
Al1–O2#1	1.9138(19)
Al1–O4#2	1.9146(19)
Al1–N1	2.107(2)
O1–C1	1.275(3)
O2–C1	1.275(3)
O3–C2	1.278(3)
O4–C2	1.279(3)
N2–C1	1.348(3)
N2–C8	1.460(4)
N2–C12	1.464(4)
N3–C2	1.348(3)
N3–C13	1.459(4)
N3–C17	1.464(4)
N1–C3A	1.471(7)
N1–C3B	1.497(18)
N1–C7B	1.350(11)
N1–C7A	1.463(4)

angle	value, °
O5–Al1–O3	94.14(10)
O5–Al1–O1	93.74(10)
O5–Al1–O2#1	96.92(8)
O5–Al1–O4#2	96.10(8)
O3–Al1–N1	89.43(10)
O1–Al1–N1	82.68(10)
O2#1–Al1–N1	80.82(9)
O4#2–Al1–N1	86.21(9)
Al1#1–O5–Al1#2	119.995(3)
O2–C1–O1	123.9(2)
O3–C2–O4	123.8(2)

Symmetry transformations used to generate equivalent atoms:
#1 -y+1,x-y,z
#2 -x+y+1,-x+1,z

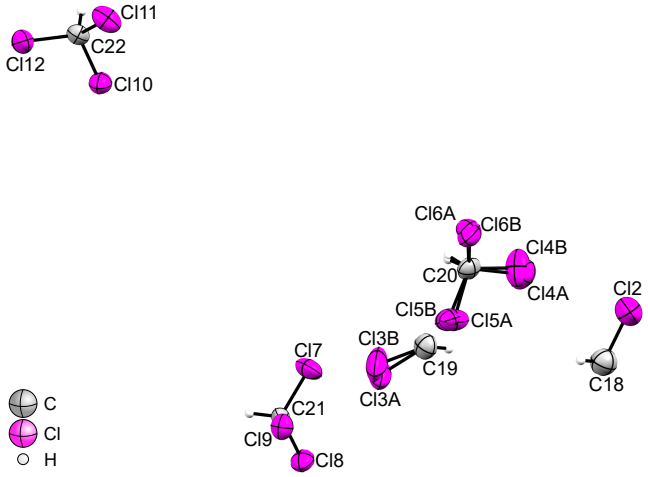

Figure ESI.2: Left: selected distances; middle: selected angles; right: chloroform molecules in the asymmetric unit of the crystal structure of compound **(2a)**; C18-Cl2 and C19-Cl3A/B are chloroform molecules on special positions of symmetry, thermal ellipsoids with 50% probability.

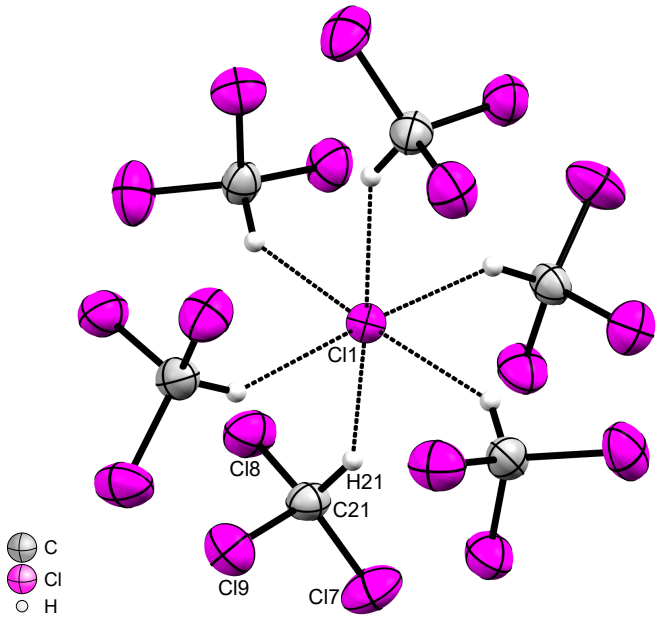

Figure ESI.3: Detailed illustration of the octahedral arrangement of the chloroform molecules around the chloride ion of compound **(2a)** through hydrogen bonds, thermal ellipsoids with 50% probability.

distance	value, Å
Al1–O13	1.8186(15)
Al2–O13	1.8458(16)
Al3–O13	1.8416(16)
Al1–O3	1.8867(19)
Al1–O10	1.8994(18)
Al1–O1	1.9007(18)
Al1–O12	1.9079(18)
Al1–N1	2.158(2)
Al2–O2	1.8753(19)
Al2–O5	1.8900(18)
Al2–O7	1.8961(18)
Al2–O4	1.9002(17)
Al2–N2	2.1197(19)
Al3–O6	1.8651(19)
Al3–O11	1.8944(17)
Al3–O9	1.9007(19)
Al3–O8	1.9068(17)
Al3–N3	2.113(2)
O1–C1	1.266(3)
O2–C1	1.260(3)
O3–C2	1.263(3)
O4–C2	1.260(3)
O5–C3	1.248(3)
O6–C3	1.258(3)
O7–C4	1.253(3)
O8–C4	1.258(3)
O9–C5	1.255(3)
O10–C5	1.271(3)
O11–C6	1.265(3)
O12–C6	1.261(3)
N1–C7B	1.362(16)
N1–C7A	1.413(9)
N1–C10	1.452(4)
N2–C11	1.492(3)
N2–C14	1.493(3)
N2–H2	0.88(3)
N3–C15	1.496(3)
N3–C18	1.500(3)
N3–H3	0.85(3)
N4–C1	1.340(3)
N4–C19	1.455(3)
N4–C22	1.461(3)
N5–C2	1.347(3)
N5–C23	1.460(3)
N5–C26	1.460(4)
N6–C3	1.345(3)
N6–C27	1.449(3)
N6–C30	1.463(3)
N7–C4	1.356(3)
N7–C31	1.456(3)
N7–C34	1.459(3)
N8–C5	1.339(3)
N8–C35	1.466(3)
N8–C38	1.459(3)
N9–C6	1.350(3)
N9–C39	1.462(4)
N9–C42	1.460(3)

angle	value, °
O13–Al1–O3	96.66(8)
O13–Al1–O10	98.66(7)
O13–Al1–O1	97.46(7)
O13–Al1–O12	97.49(7)
O13–Al2–O2	96.79(8)
O13–Al2–O5	94.90(8)
O13–Al2–O7	97.20(7)
O13–Al2–O4	94.02(7)
O13–Al3–O6	93.84(8)
O13–Al3–O11	95.08(7)
O13–Al3–O9	97.31(8)
O13–Al3–O8	96.31(7)
O3–Al1–N1	83.85(9)
O10–Al1–N1	80.97(9)
O1–Al1–N1	79.75(9)
O12–Al1–N1	85.29(9)
O2–Al2–N2	83.64(8)
O5–Al2–N2	85.69(8)
O7–Al2–N2	82.39(8)
O4–Al2–N2	85.39(7)
O6–Al3–N3	84.82(8)
O11–Al3–N3	86.42(8)
O9–Al3–N3	84.83(8)
O8–Al3–N3	81.57(8)
Al1–O13–Al3	119.78(8)
Al1–O13–Al2	120.02(8)
Al3–O13–Al2	120.17(8)
O2–C1–O1	124.3(2)
O4–C2–O3	125.2(2)
O5–C3–O6	124.5(2)
O7–C4–O8	125.2(2)
O9–C5–O10	124.4(2)
O12–C6–O11	125.8(2)

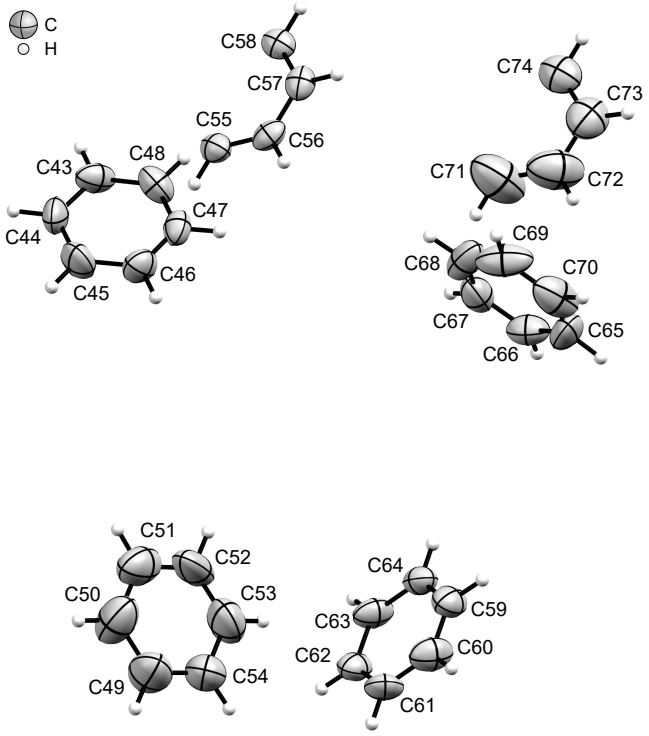

Figure ESI.4: Left: selected distances; middle: selected angles; right: benzene molecules in the asymmetric unit of the crystal structure of compound **(1a)**, thermal ellipsoids with 50% probability.

NMR investigations and ligand exchange

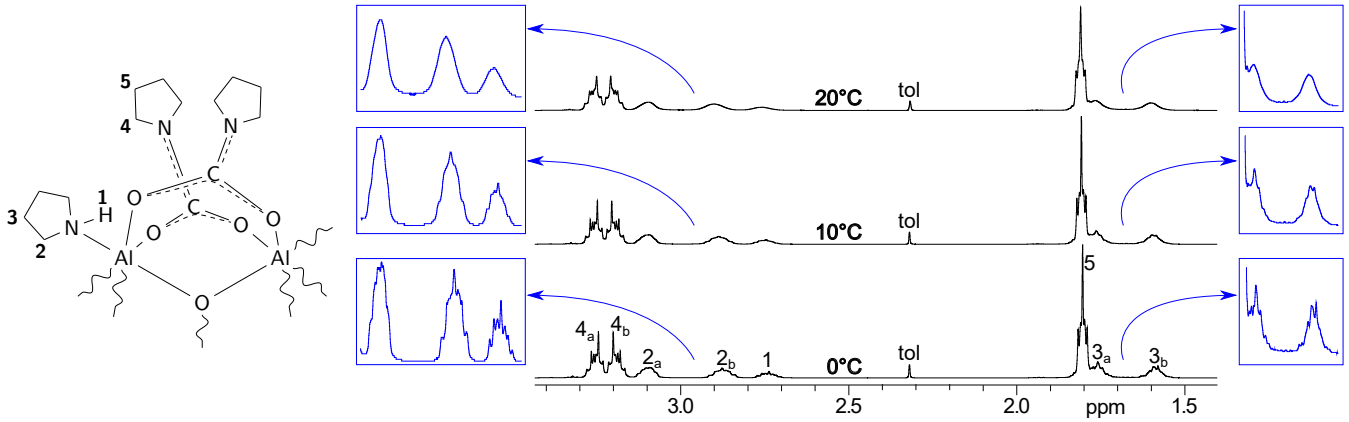

Figure ESI.5: Temperature-dependent ^{1}H NMR ($CDCl_3$) spectra of compound **(1a)**.

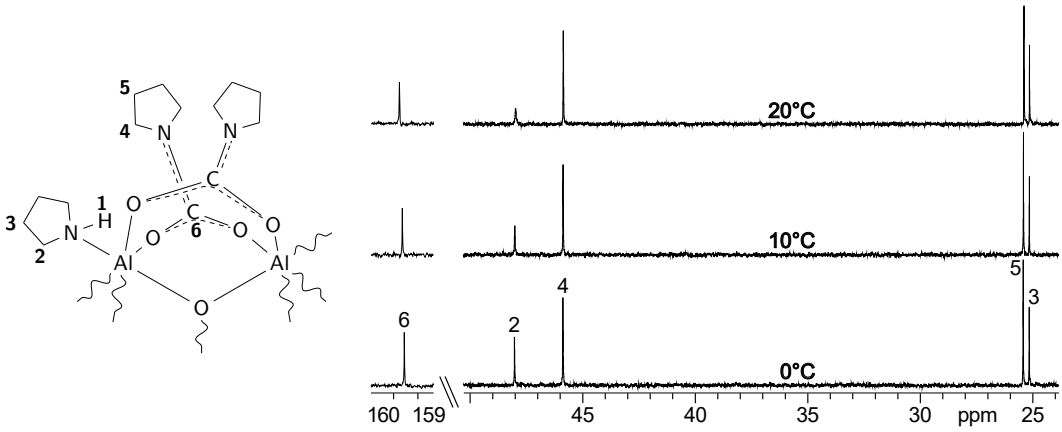

Figure ESI.6: Temperature-dependent ^{13}C NMR ($CDCl_3$) spectra of compound **(1a)**.

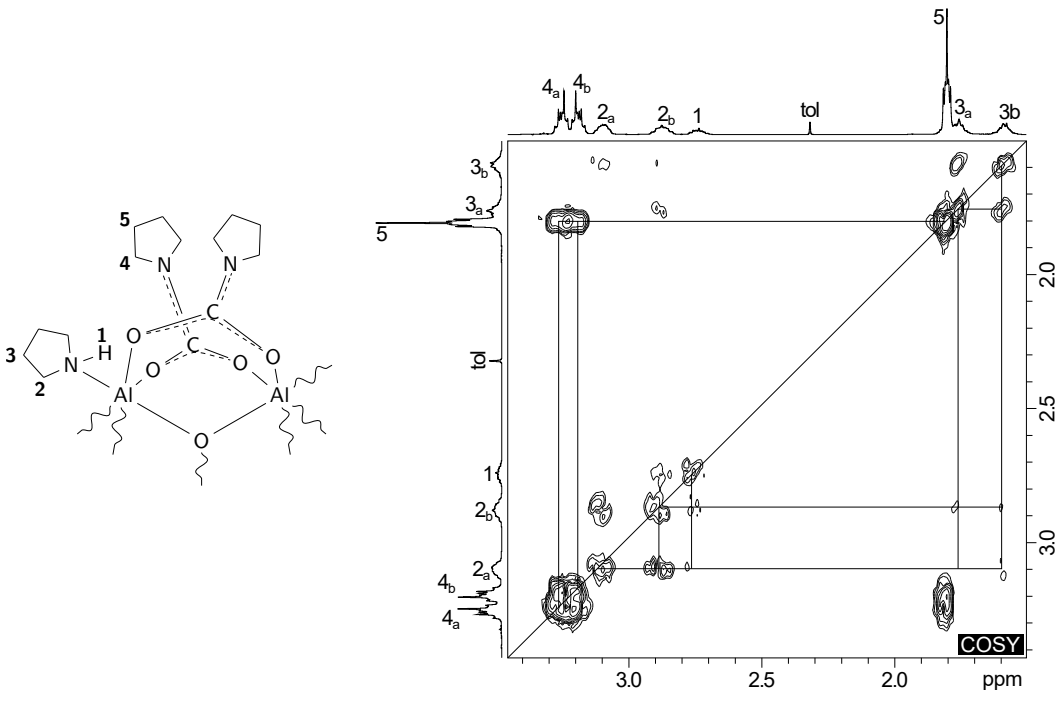

Figure ESI.7: H,H COSY spectrum ($CDCl_3$) of compound **(1a)** at 0°C.

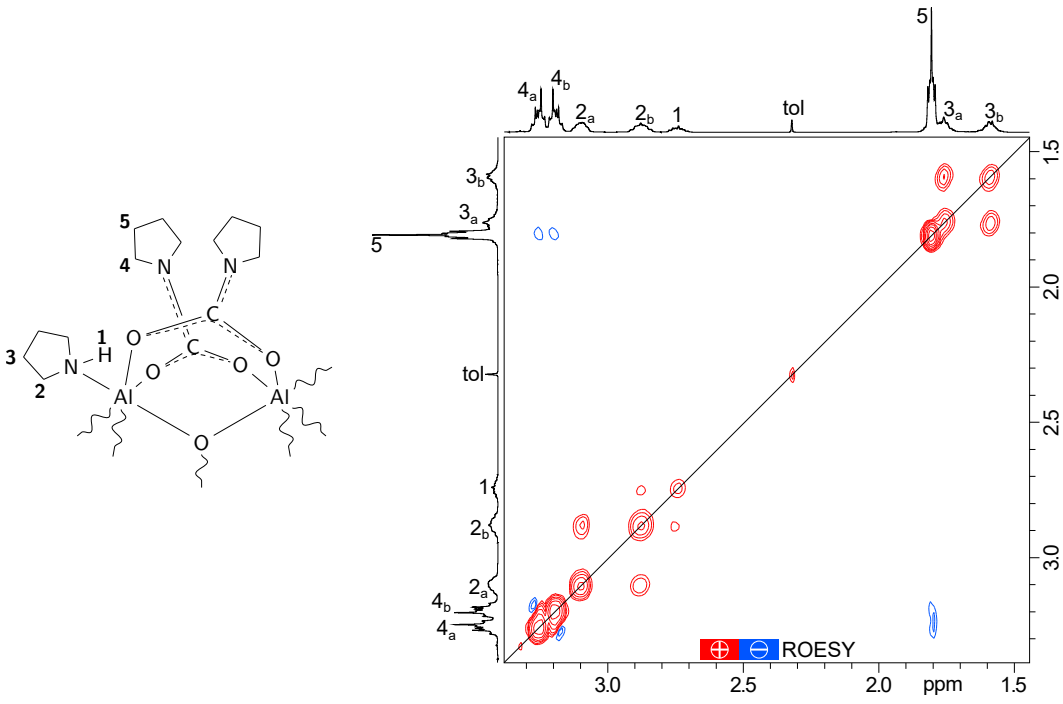

Figure ESI.8: H,H ROESY spectrum ($CDCl_3$) of compound **(1a)**; red coloured positive intensity; blue coloured negative intensity at 0°C.

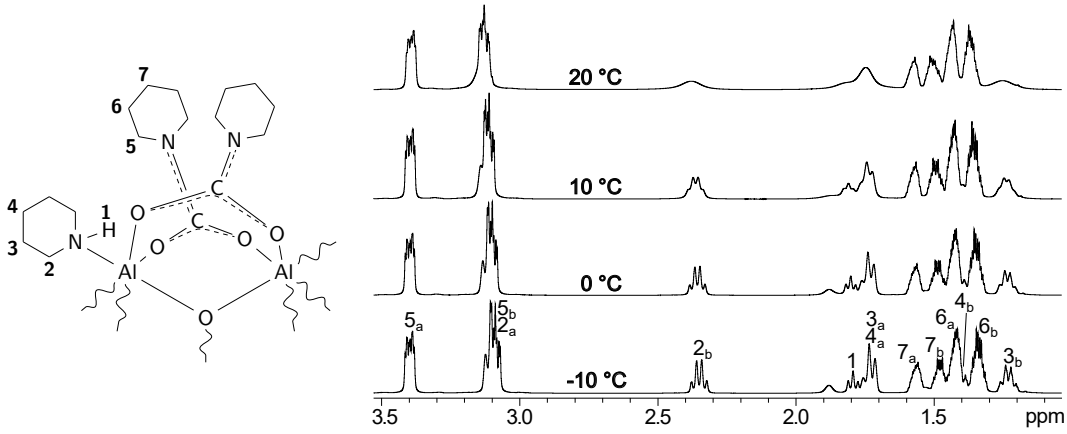

Figure ESI.9: Temperature-dependent ^{1}H NMR ($CDCl_3$) spectra of compound **(2a)**.

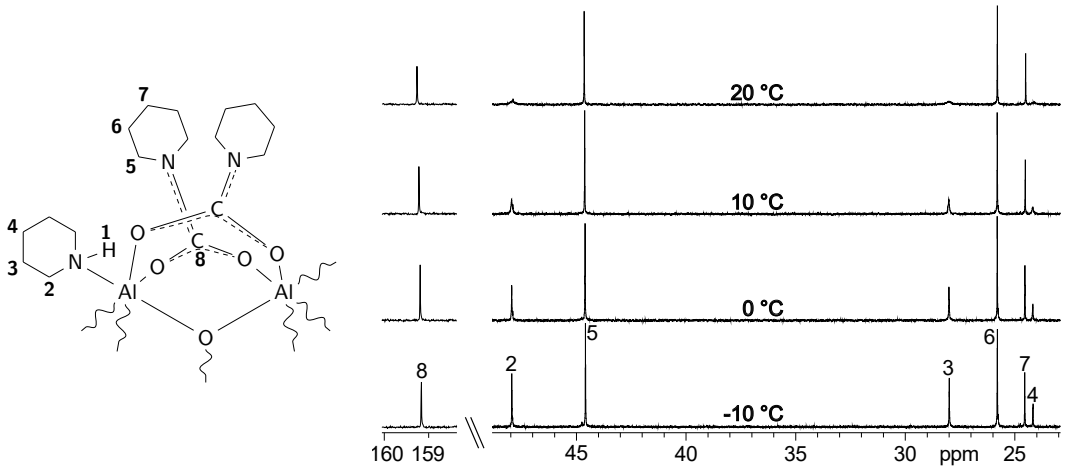

Figure ESI.10: Temperature-dependent ^{13}C NMR ($CDCl_3$) spectra of compound **(2a)**.

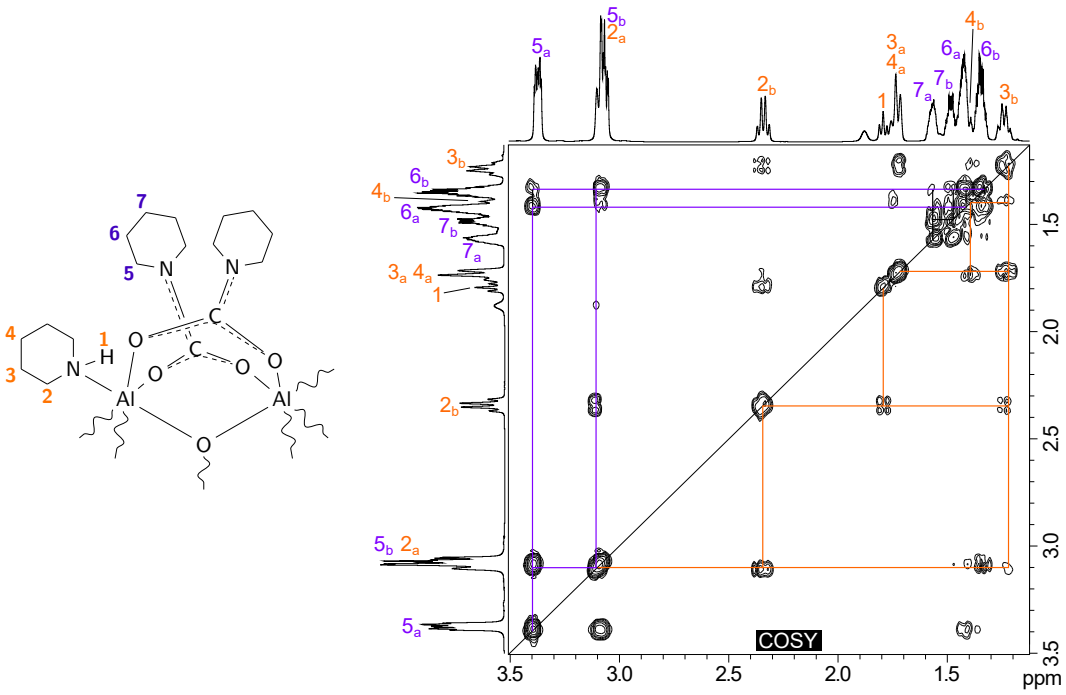

Figure ESI.11: H,H COSY spectrum ($CDCl_3$) of compound **(2a)** at 0°C.

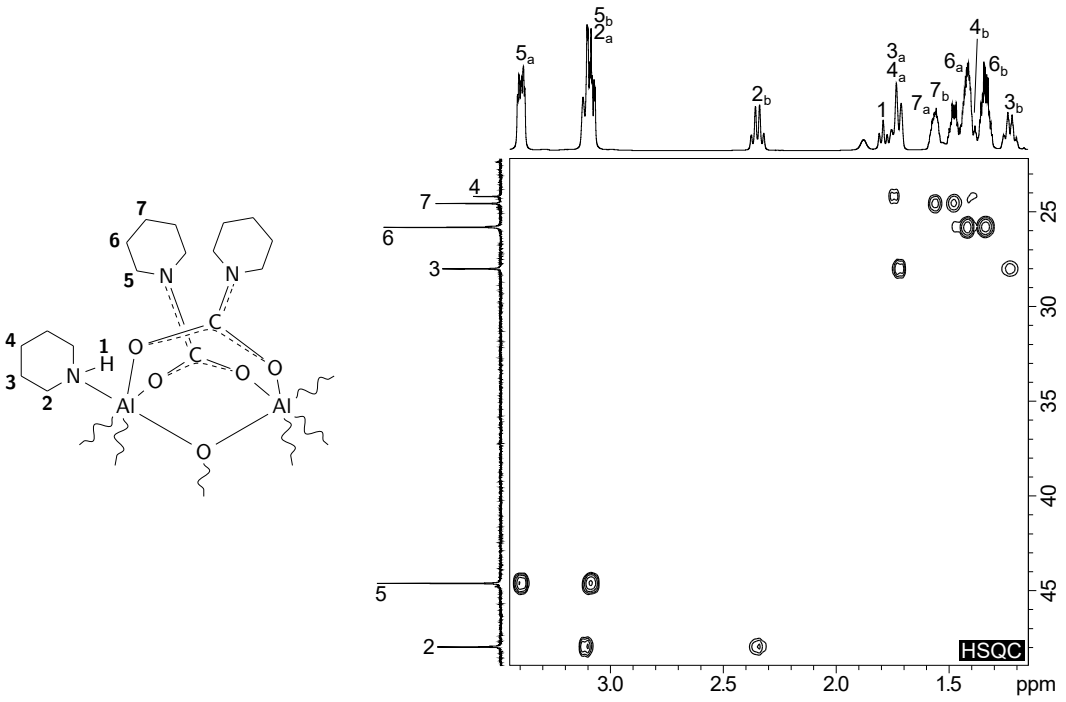

Figure ESI.12: HSQC spectrum ($CDCl_3$) of compound **(2a)** at 0°C.

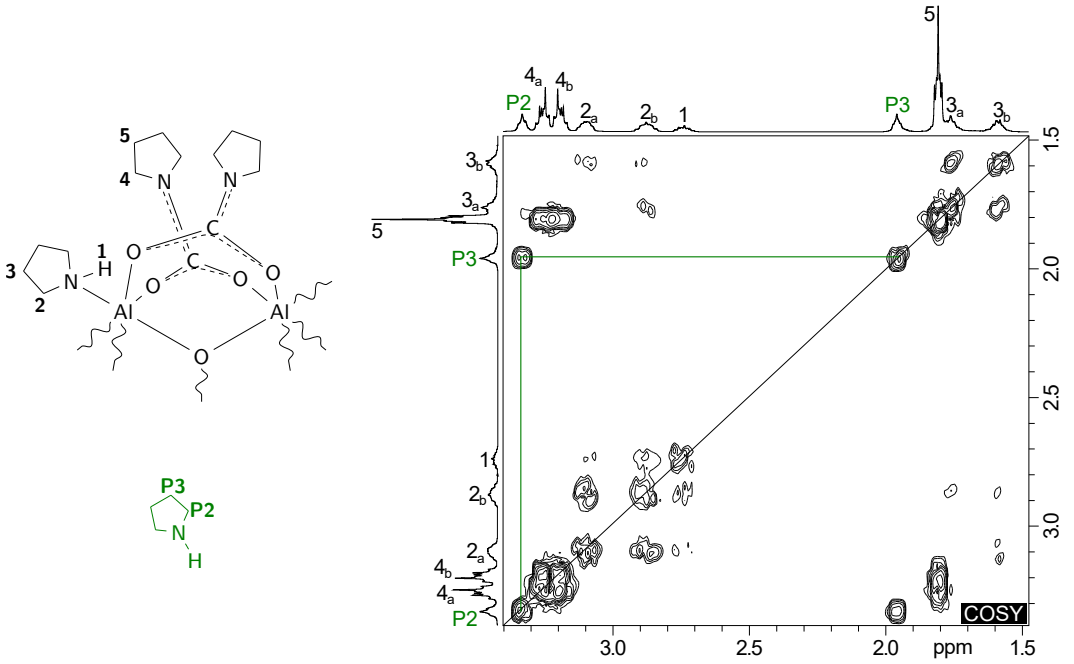

Figure ESI.13: H,H COSY spectrum ($CDCl_3$) of a compound **(1a)** sample that contains residual pyrrolidine (green marked labels P2 and P3); spectrum was measured at 0°C.

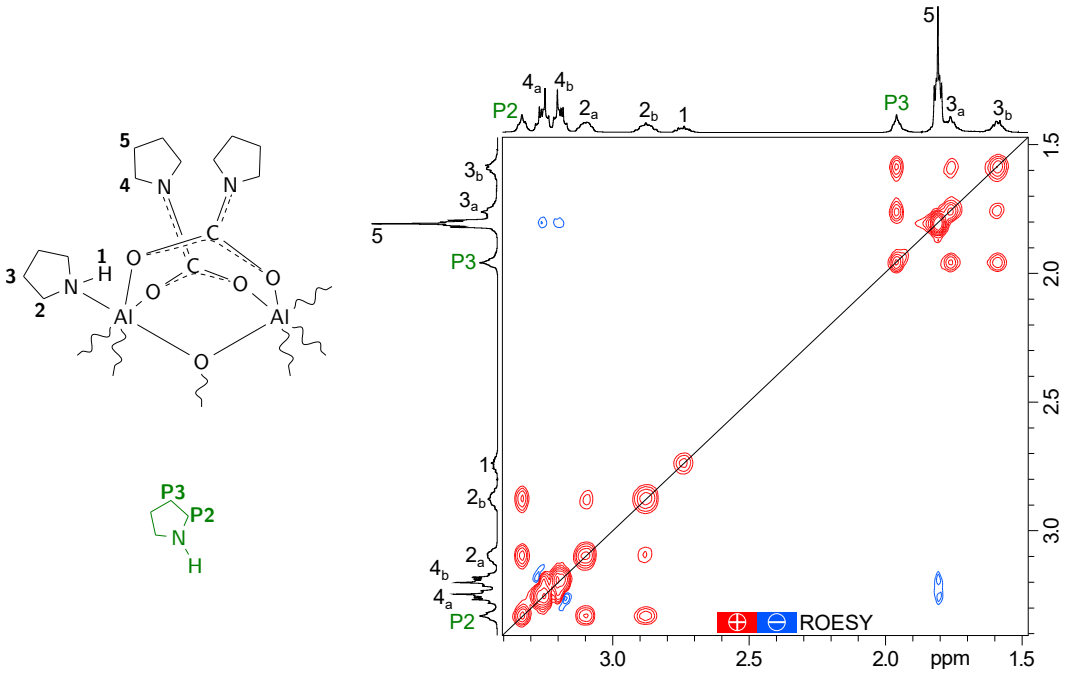

Figure ESI.14: H,H ROESY spectrum ($CDCl_3$) of a compound **(1a)** sample that that contains residual pyrrolidine (green marked labels P2 and P3); red coloured positive intensity; blue coloured negative intensity; spectrum was measured at 0°C.

Analyses of compounds (1b) and (2b)

distance	value, Å
Al1–O13	1.8135(12)
Al2–O13	1.8165(12)
Al3–O13	1.8220(11)
Al1–O1	1.8831(12)
Al1–O12	1.8835(13)
Al1–O3	1.8940(13)
Al1–O10	1.8954(13)
Al2–O7	1.8798(13)
Al2–O5	1.8895(13)
Al2–O2	1.8960(13)
Al2–O4	1.8965(13)
Al3–O8	1.8802(13)
Al3–O11	1.8851(13)
Al3–O9	1.8919(13)
Al3–O6	1.8932(13)
Al1–N1	2.1175(14)
Al2–N2	2.1301(14)
Al3–N3	2.1275(14)
O1–C1	1.265(2)
O2–C1	1.2692(19)
O3–C2	1.270(2)
O4–C2	1.267(2)
O5–C3	1.272(2)
O6–C3	1.272(2)
O7–C4	1.2726(19)
O8–C4	1.2645(19)
O9–C5	1.268(2)
O10–C5	1.273(2)
O11–C6	1.271(2)
O12–C6	1.266(2)
N1–C11	1.341(2)
N1–C7	1.344(2)
N2–C16	1.340(2)
N2–C12	1.346(2)
N3–C21	1.340(2)
N3–C17	1.346(2)
N4–C1	1.340(2)
N4–C25	1.461(2)
N4–C22	1.462(2)
N5–C2	1.338(2)
N5–C26	1.463(2)
N5–C29	1.463(3)
N6–C3	1.338(2)
N6–C30	1.461(2)
N6–C33	1.463(2)
N7–C4	1.336(2)
N7–C34	1.461(2)
N7–C37	1.464(2)
N8–C5	1.339(2)
N8–C41	1.460(2)
N8–C38	1.460(2)
N9–C6	1.338(2)
N9–C42	1.461(2)
N9–C45	1.462(2)

angle	value, °
O13–Al1–O1	97.69(5)
O13–Al1–O12	97.43(5)
O13–Al1–O3	96.69(5)
O13–Al1–O10	95.75(5)
O13–Al2–O7	97.37(5)
O13–Al2–O5	97.55(5)
O13–Al2–O2	96.35(5)
O13–Al2–O4	96.39(5)
O13–Al3–O8	96.69(5)
O13–Al3–O11	97.13(5)
O13–Al3–O6	95.10(5)
O13–Al3–O9	97.67(5)
O1–Al1–N1	81.85(5)
O12–Al1–N1	83.05(5)
O3–Al1–N1	83.72(6)
O10–Al1–N1	83.85(6)
O7–Al2–N2	83.41(6)
O5–Al2–N2	84.24(5)
O2–Al2–N2	82.88(5)
O4–Al2–N2	81.81(5)
O8–Al3–N3	81.14(5)
O11–Al3–N3	83.95(5)
O9–Al3–N3	84.51(5)
O6–Al3–N3	83.89(5)
Al1–O13–Al2	119.95(6)
Al1–O13–Al3	119.93(6)
Al2–O13–Al3	120.11(6)
O1–C1–O2	124.90(14)
O4–C2–O3	124.77(15)
O5–C3–O6	125.01(15)
O8–C4–O7	124.76(15)
O9–C5–O10	125.13(15)
O12–C6–O11	125.16(15)

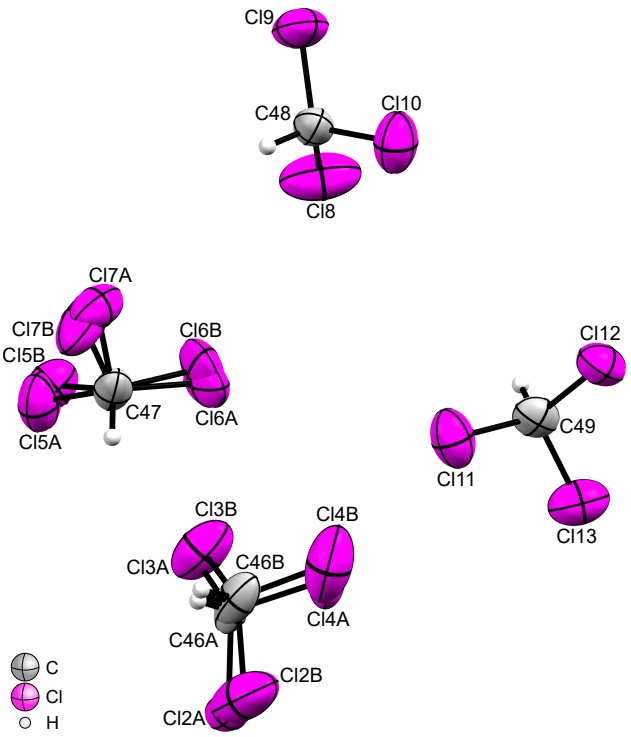

Figure ESI.15: Left: selected distances; middle: selected angles; right: chloroform molecules of the asymmetric unit of the crystal structure of compound **(1b)**, thermal ellipsoids with 50% probability.

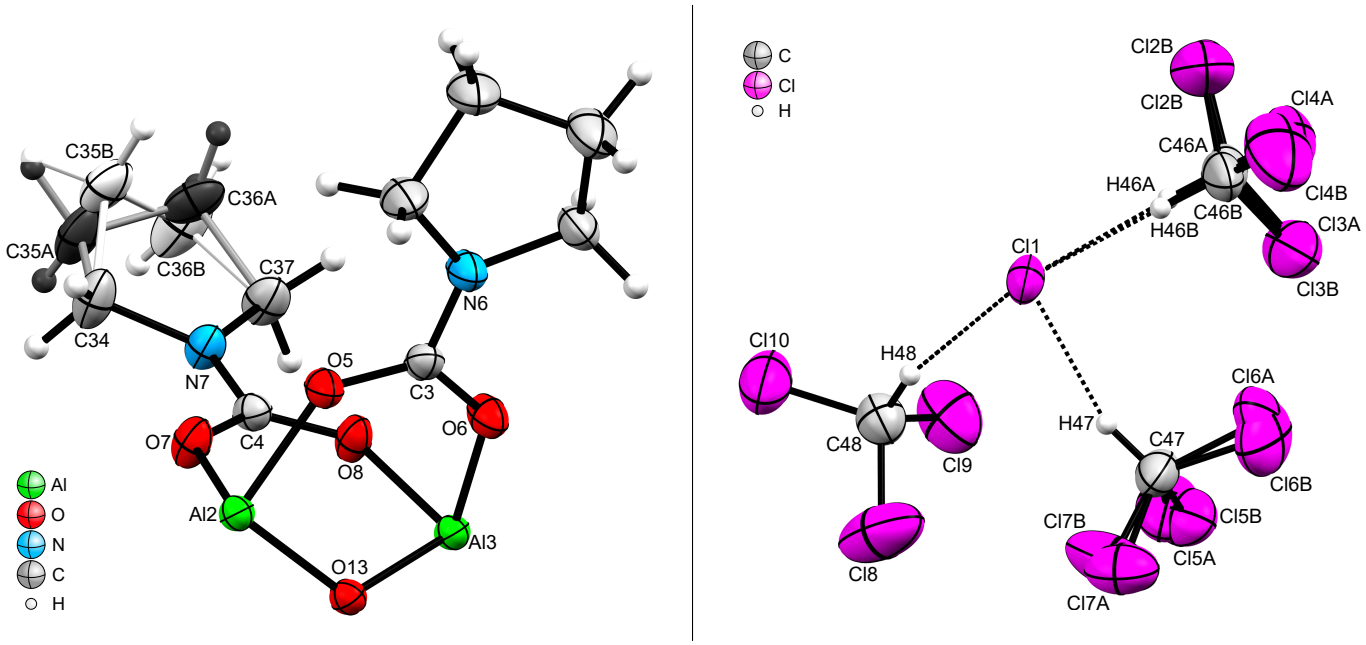

Figure ESI.16: Left: Detailed illustration of the disordered carbon atoms C35 and C36 of a carbamate bridge of compound **(1b)**, thermal ellipsoids with 50% probability; right: arrangement of the chloroform molecules around the chloride ion of compound **(1b)** through hydrogen bonds, thermal ellipsoids with 50% probability.

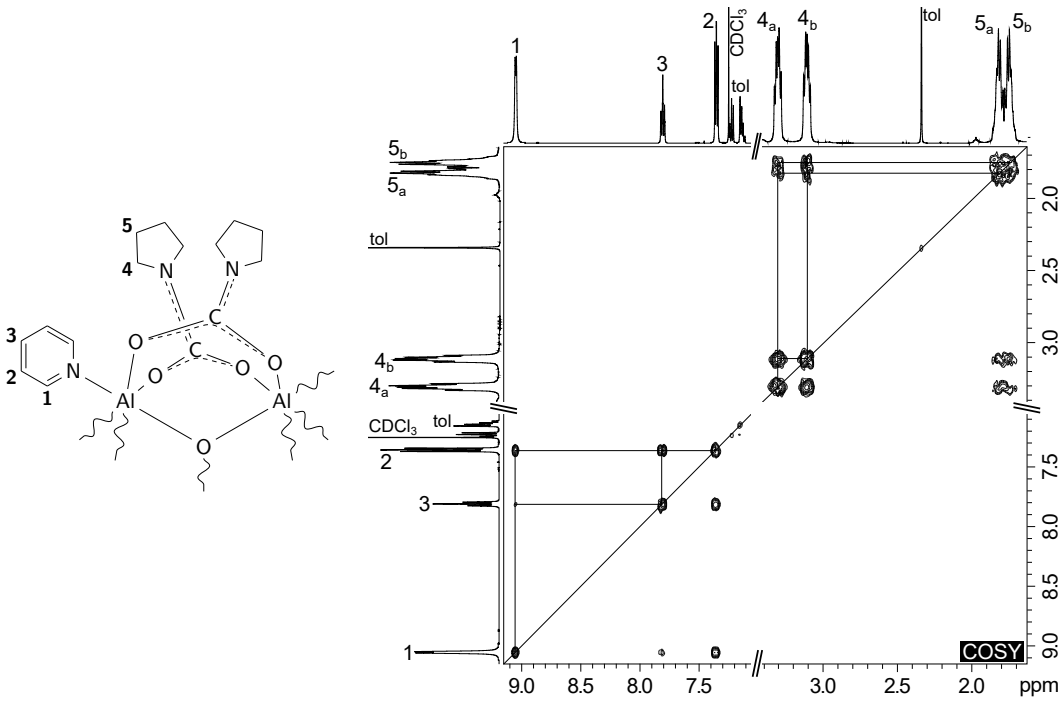

Figure ESI.17: H,H COSY spectrum ($CDCl_3$) of compound **(1b)**.

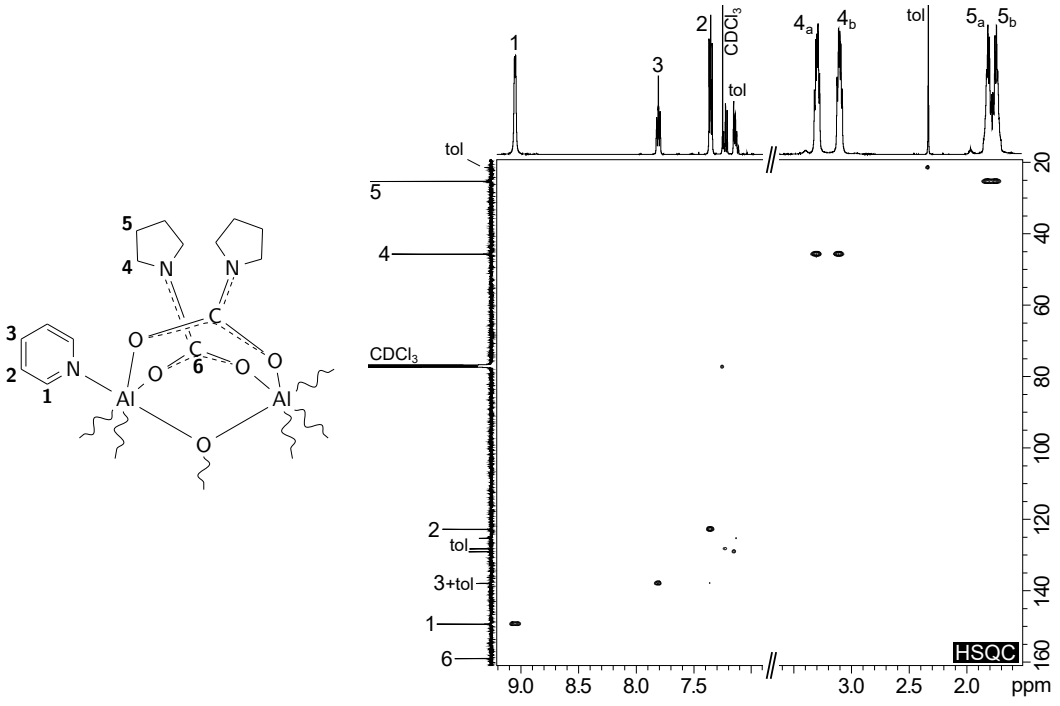

Figure ESI.18: HSQC spectrum ($CDCl_3$) of compound **(1b)**.

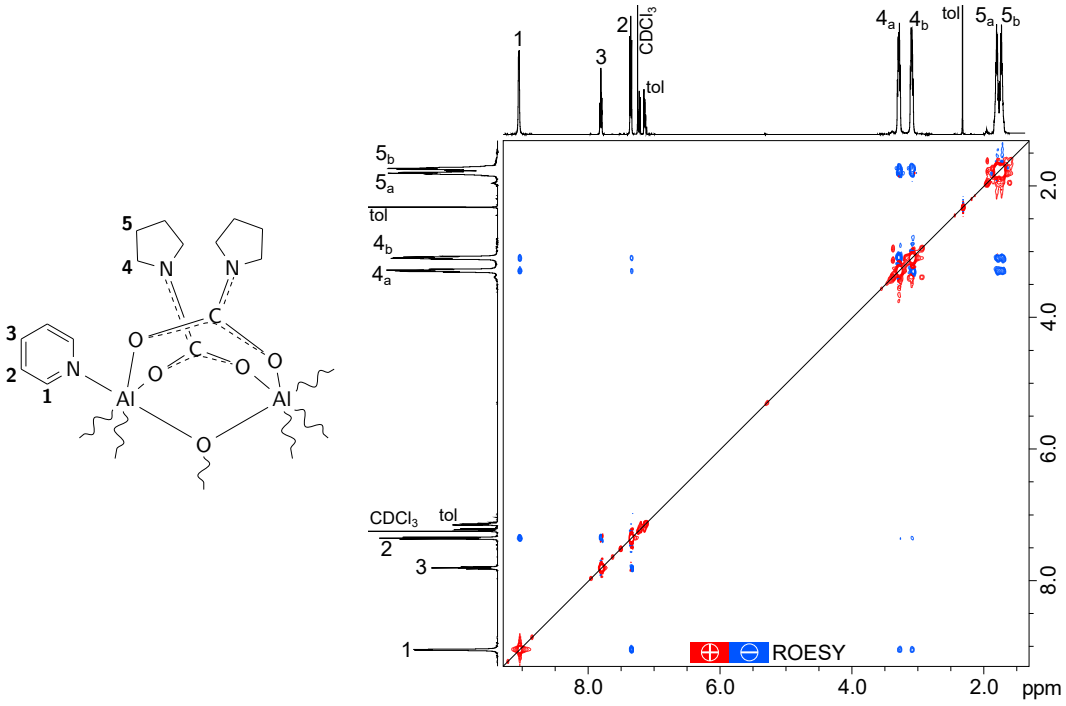

Figure ESI.19: H,H ROESY spectrum ($CDCl_3$) of compound **(1b)**; red coloured positive intensity; blue coloured negative intensity.

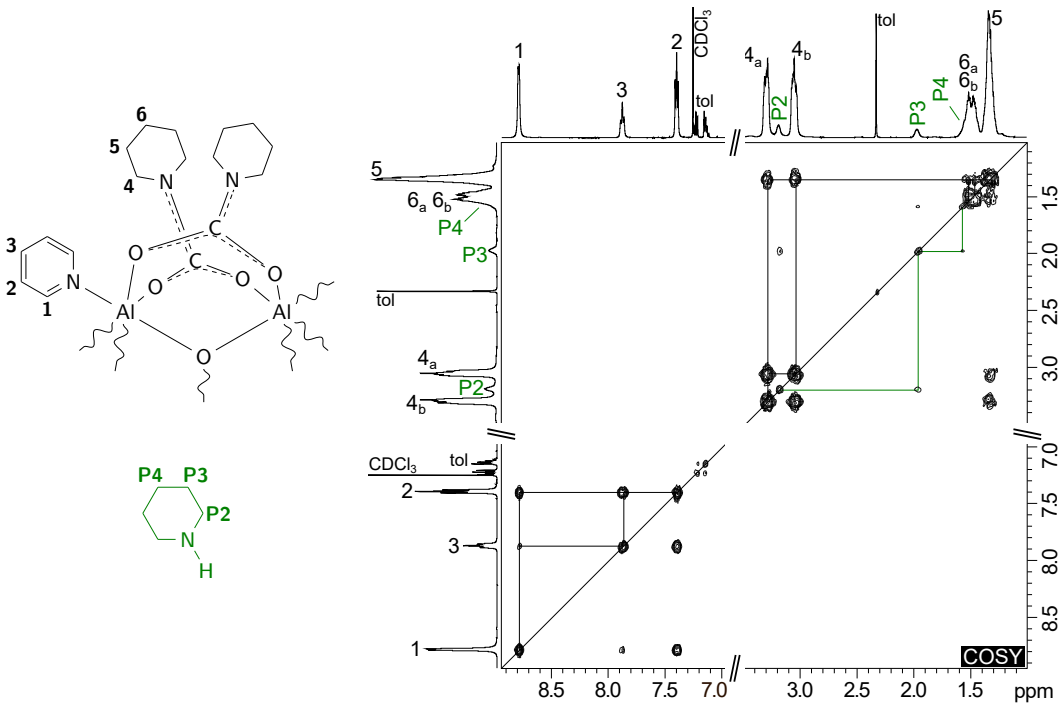

Figure ESI.20: H,H COSY spectrum ($CDCl_3$) of compound **(2b)** containing residual piperidine (green marked labels P2, P3 and P4);

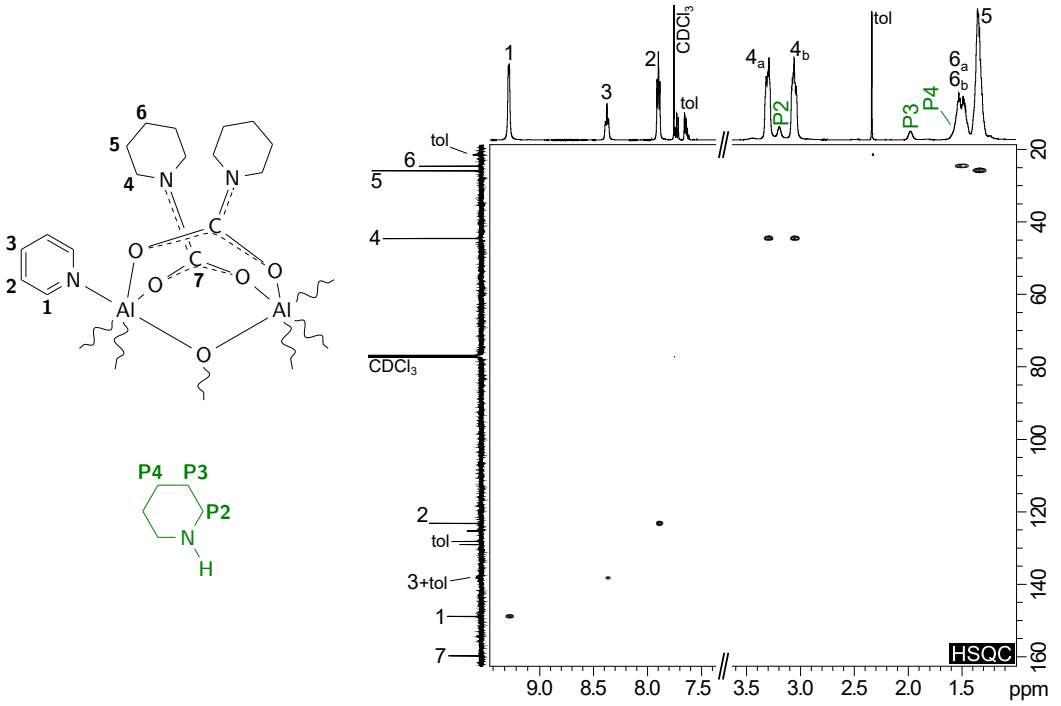

Figure ESI.21: HSQC spectrum ($CDCl_3$) of compound **(2b)** containing residual piperidine (green marked labels P2, P3 and P4); red coloured positive intensity; blue colourednegative intensity.

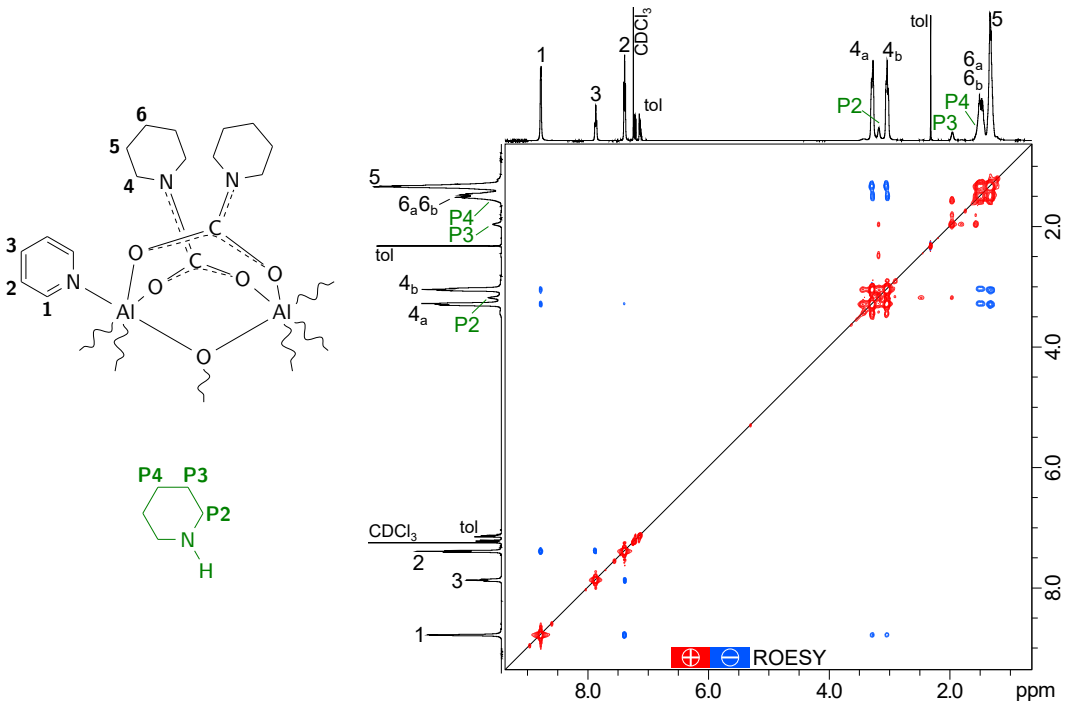

Figure ESI.22: H,H ROESY spectrum ($CDCl_3$) of compound **(2b)** containing residual piperidine (green marked labels P2, P3 and P4); red coloured positive intensity; blue coloured negative intensity.