Supporting Information

Reactivity of Aluminum Complexes of Redox-Active Ligand toward N-Heterocyclic Carbene and Its Thione

Vladimir G. Sokolov,[a] Tatyana S. Koptseva,[a] Roman V. Rumyantcev,[a]
Xiao-Juan Yang,[b] Yanxia Zhao,[b] Igor L. Fedushkin*[,a,b]

[a] G.A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Tropinina str. 49, 603950, Nizhny Novgorod, Russian Federation

[b] College of Chemistry and Materials Science, Northwest University, Xi'an 710069, China

X-ray crystallographic data for compounds 3-6. The X-ray diffraction data were collected on a Bruker D8 Quest Photon (for **3** and **4**) and Oxford Xcalibur Eos (**5**, **6**) diffractometers (Mo-K_α radiation, ω-scan technique, λ = 0.71073 Å). The intensity data were integrated by SAINT (**2**, **3**)[1] and CrysAlisPro (**5**, **6**)[2] programs. The structures were solved by using a dual-space algorithm (**3** and **5**)[3] and direct methods (**4** and **6**). All structures were refined on F_{hkl}^2 using SHELXTL package.[4] Samples of **4** and **6** were refined as two-component twins (HKLF4 and HKLF5 were used for final refinement of complex **4** and **6**, respectively). The refined BASF parameter for the prevailing component equals 0.5438(1) (for **4**) and 0.6181(1) (**6**). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms except H(1) in complex **6** were placed in calculated positions and were refined in the riding model ($U_{iso}(H)$ = $1.5U_{eq}(C)$ in CH_3-groups and $U_{iso}(H) = 1.2U_{eq}(C)$ in other groups). The hydrogen atom H(1) in complex **6** was localized from the difference Fourier synthesis and refined in the isotropic approximation. SADABS (**3**, **4**)[5] and and SCALE3 ABSPACK scaling algorithm into CrysAlisPro (**5**, **6**)[2] were used to perform absorption corrections. The crystals of **3**-**6** contains solvate molecules. There are 0.5 toluene molecule per one complex molecule in **3**, 1.5 toluene molecules in **4**, two DME molecules in **5** and 0.5 toluene molecule in **6**. The main crystallographic data and structure refinement details for **3**-**6** are presented in Table 1. CCDC 1949240 (**3**), 1949241 (**4**), 1949242 (**5**) and 1949243 (**6**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via ccdc.cam.ac.uk/structures/.

DFT Calculations. Structure optimization for the model compounds (dpp-bian)Al–Al(dpp-bian) (**1**), (dpp-bian)AlH(THF) (**2**), (dpp-bian)(NHC)Al–Al(dpp-bian) (**3**) and (dpp-bian)AlH(NHC) (**6**) were carried out at the DFT (B3LYP) level with a 6-31G*[6,7] basis set using the Gaussian 09 program.[8]

(1) SAINT. Data Reduction and Correction Program v. 8.37A, Bruker AXS, Madison, Wisconsin, USA, **2017**.

(2) Rigaku Oxford Diffraction, CrysAlisPro Software system, v. 1.171.38.46, Rigaku Corporation, Oxford, UK, **2015**.

(3) Sheldrick, G. SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst*. **2015**, *A 71*, 3–8.

(4) Sheldrick, G. Crystal structure refinement with SHELXL. *Acta Cryst*. **2015**, *C 71*, 3–8.

(5) Krause, L.; Herbst-Irmer, R.; Sheldrick, G.M.; Stalke, D. Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination. *J. Appl. Cryst*. **2015**, *48,* 3–10.

(6) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(7) Lee, C.; Yang W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B.*, **1988**, *37*, 785−789.

(8) Gaussian 09, Revision C.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

Table 1. Crystal data and structure refinement details for compounds **3**-**6**.

	3	**4**	**5**	**6**
Empirical Formula	$C_{86.50}H_{104}Al_2N_6$	$C_{104.50}H_{134}Al_2N_8S_2$	$C_{102}H_{140}A_2N_8O_4S$	$C_{50.50}H_{65}AlN_4$
M	1281.71	1620.27	1628.23	755.04
T/K	100(2)	100(2)	100(2)	100(2)
Crystal System	monoclinic	triclinic	Triclinic	triclinic
Space Group	$P2_1/n$	P-1	P-1	P-1
a/Å	12.4899(4)	13.247(2)	12.73595(19)	12.8299(5)
b/Å	27.2515(9)	16.392(4)	18.5631(3)	18.2822(4)
c/Å	21.6359(7)	23.630(4)	19.6627(3)	20.0455(4)
α/deg	90	81.347(4)	79.6121(12)	93.108(2)
β/deg	92.4570(16)	73.784(3)	85.9195(12)	96.587(2)
γ/deg	90	66.231(3)	86.5802(12)	107.085(3)
V/Å^3	7357.4(4)	4504.8(14)	4555.67(12)	4445.5(2)
Z	4	2	2	4
d_{calc}/Mg m^{-3}	1.157	1.195	1.187	1.128
μ(Mo Kα)/mm^{-1}	0.089	0.132	0.111	0.084
F(000)	2764	1750	1764	1636
Crystal Size/mm	0.33×0.17×0.11	0.36×0.23×0.015	0.27×0.20×0.17	0.74×0.40×0.21
θ range/deg	1.994–25.027	2.206–24.676	2.834–26.022	2.824–26.029
h, k, l	–14 ≤ h ≤ 14 –32 ≤ k ≤ 32 –25 ≤ l ≤ 25	–15 ≤ h ≤ 15 –19 ≤ k ≤ 19 –27 ≤ l ≤ 27	–15 ≤ h ≤ 15 –22 ≤ k ≤ 22 –24 ≤ l ≤ 23	–15 ≤ h ≤ 15 –22 ≤ k ≤ 22 –24 ≤ l ≤ 24
Reflections Collect.	65052	35325	59992	31921
Indep. Reflections	12887	15027	17717	31921
R_{int}	0.0654	0.0940	0.0363	0.0499
Data/Restr./Param.	12887 / 19 / 906	15027 / 43 / 1094	17717 / 0 / 1086	31921 / 104 / 1075
GooF	1.015	1.054	1.030	0.991
R_1 / wR_2 (I>2σ(I))	0.0477 / 0.1327	0.0674 / 0.1609	0.0436 / 0.0939	0.0503 / 0.1113
R_1 / wR_2 (all data)	0.0693 / 0.1462	0.0925 / 0.1745	0.0633 / 0.1016	0.0755 / 0.1164
Larg. Diff. Peak and Hole/e Å^{-3}	0.332 / –0.356	0.554 / –0.559	0.332 / –0.267	0.350 / –0.335

Table 2. Selected bond lengths [Å] and angles [°] for complexes **3**-**6**.

Bond	**3**	**4**	**5**	**6**
Al(1)–N(1)	1.8796(16)	1.873(4)	1.8989(14)	1.8715(17)
Al(1)–N(2)	1.8889(16)	1.866(4)	1.8943(15)	1.8759(17)
Al(2)–N(3)	1.8743(16)	1.894(4)	1.9025(15)	
Al(2)–N(4)	1.8535(17)	1.854(4)	1.9014(14)	
N(1)–C(1)	1.415(2)	1.408(5)	1.400(2)	1.400(2)
N(2)–C(2)	1.391(2)	1.393(5)	1.398(2)	1.409(2)
C(1)–C(2)	1.369(3)	1.364(6)	1.370(2)	1.369(3)
N(3)–C(37)	1.407(2)	1.396(5)	1.397(2)	
N(4)–C(38)	1.386(2)	1.405(5)	1.414(2)	
C(37)–C(38)	1.366(3)	1.360(7)	1.370(2)	
Al–C(carb)	2.094(2)	2.071(4)	2.0762(17), 2.0710(17)	2.057(2)
Al(1)–S(1)		2.2062(16)	2.2760(6)	
Al(2)–S(1)		2.2397(16)	2.2670(6)	
Al(1)–S(2)		2.3341(16)		
Al–H(1)				1.524(18)
Angle				
N(1)–Al(1)–N(2)	91.81(7)	91.58(15)	90.03(6)	91.48(7)
N(4)–Al(2)–N(3)	91.10(7)	90.53(17)	90.80(6)	
Al(1)–S(1)–Al(2)		138.16(6)	150.52(3)	
C(carb)–Al(2)–S(1)		92.93(12)	95.35(5), 110.55(5)	
S(1)–Al(1)–S(2)		96.71(6)		
C(carb)–Al(1)–Al(2)	102.27(5)			
C(carb)–Al–H(1)				99.5(7)

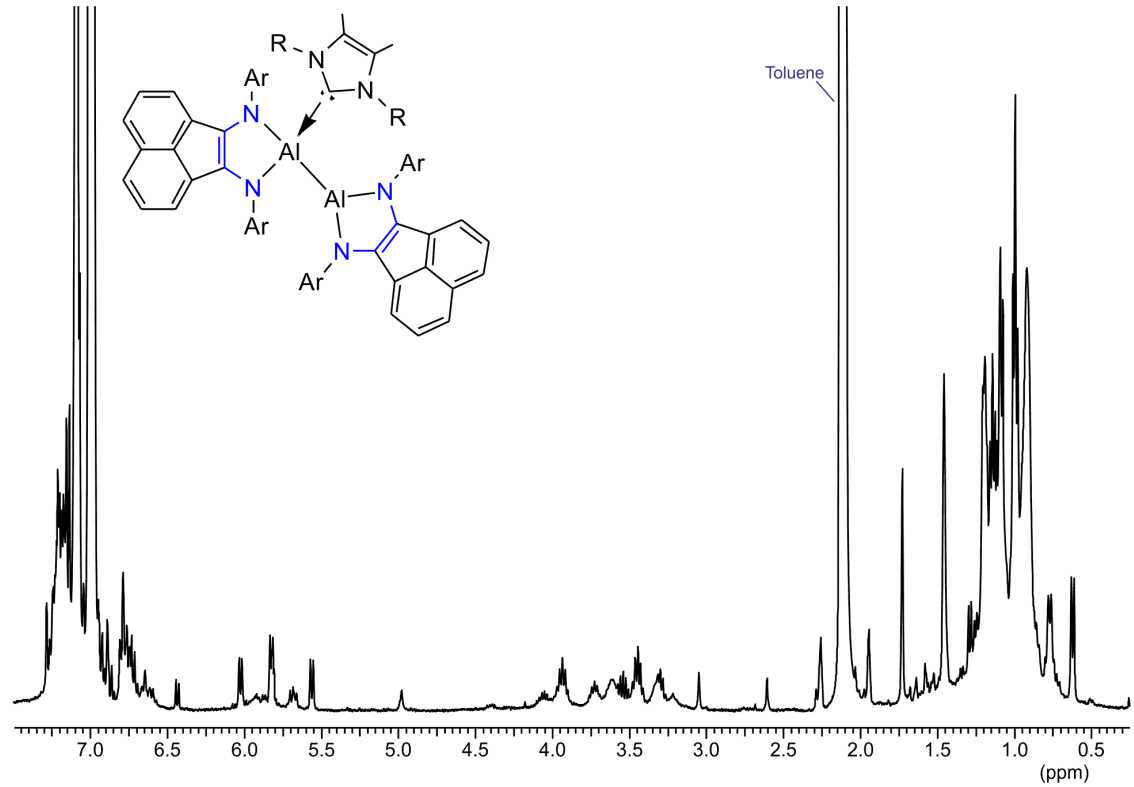

Fig. S1. ^{1}H NMR spectrum of complex **3**.

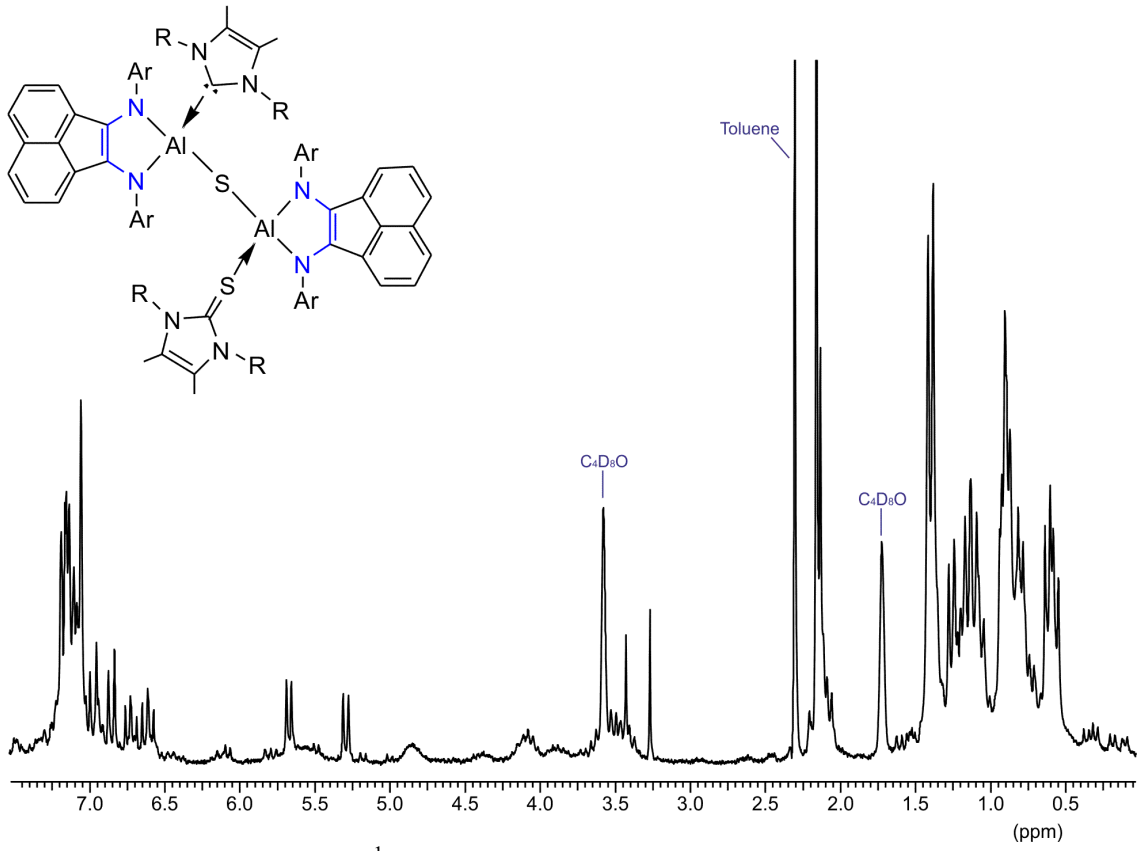

Fig. S2. ^{1}H NMR spectrum of complex **4**.

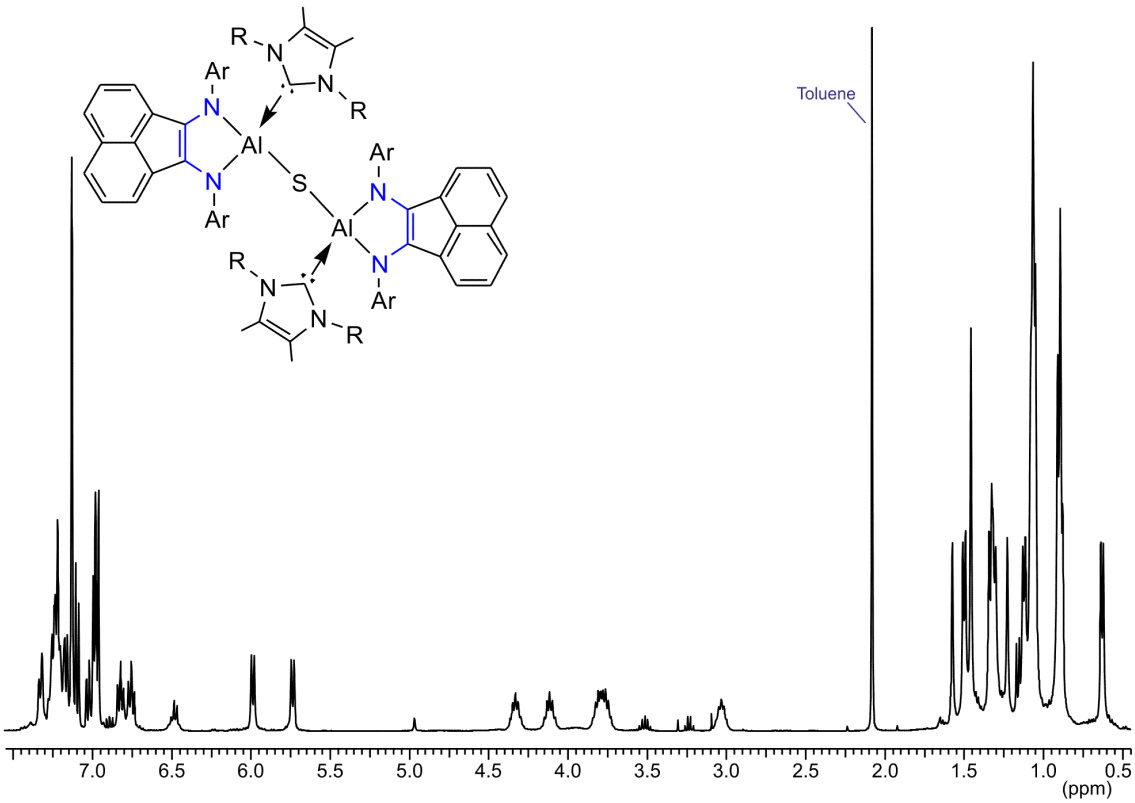

Fig. S3. ^{1}H NMR spectrum of complex **5**.

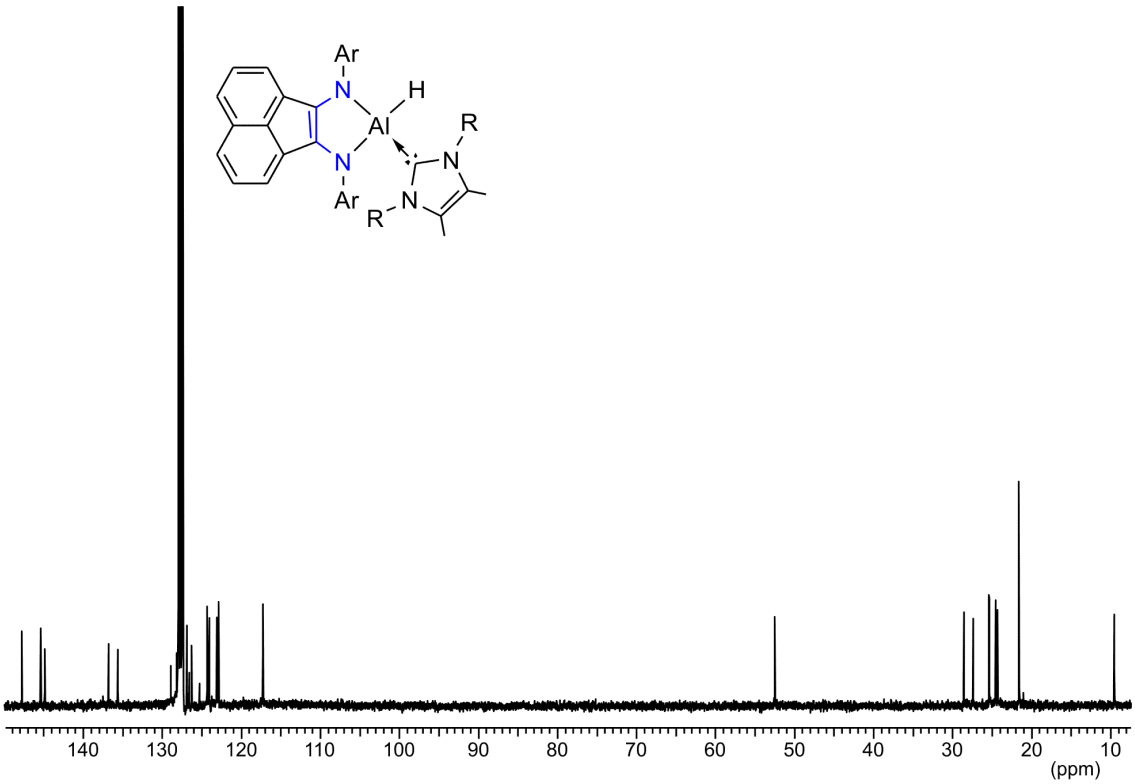

Fig. S4. ^{13}C NMR spectrum of complex **6**.

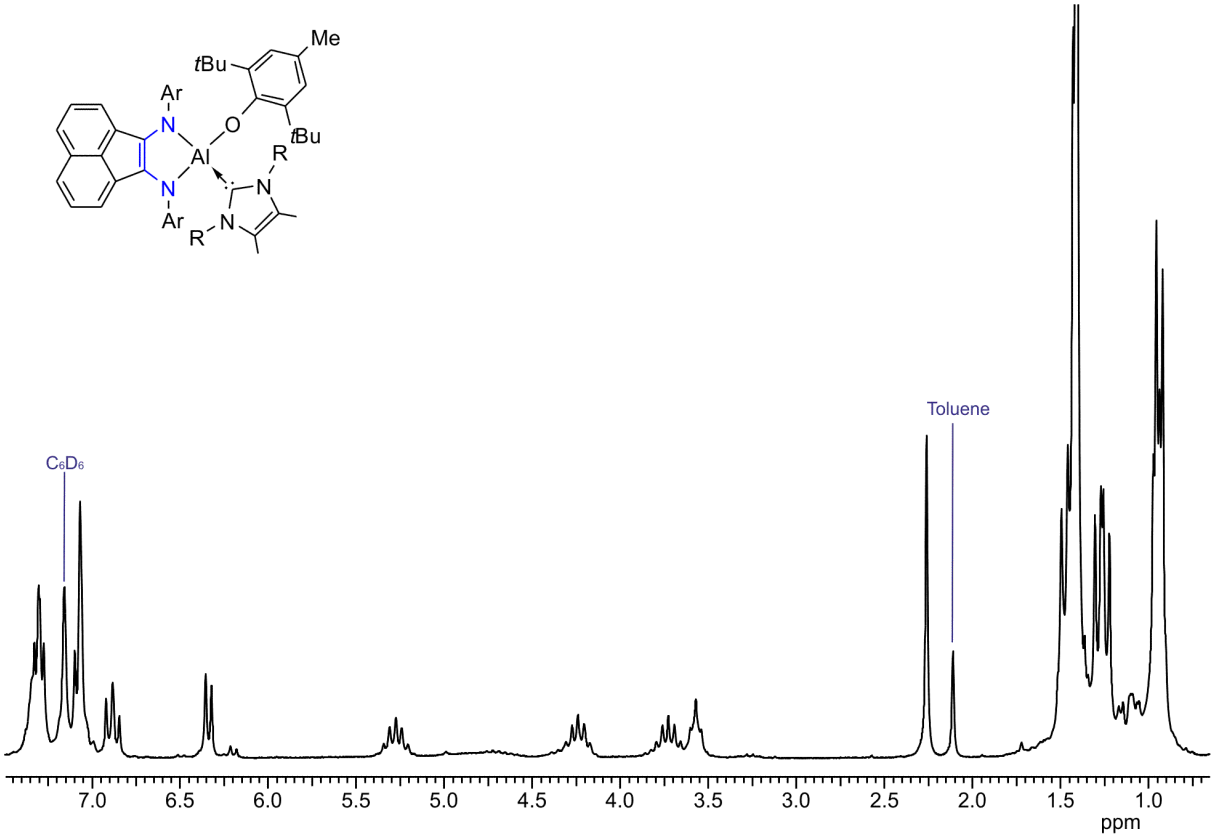

Fig. S5. ^{1}H NMR spectrum of complex **7**.

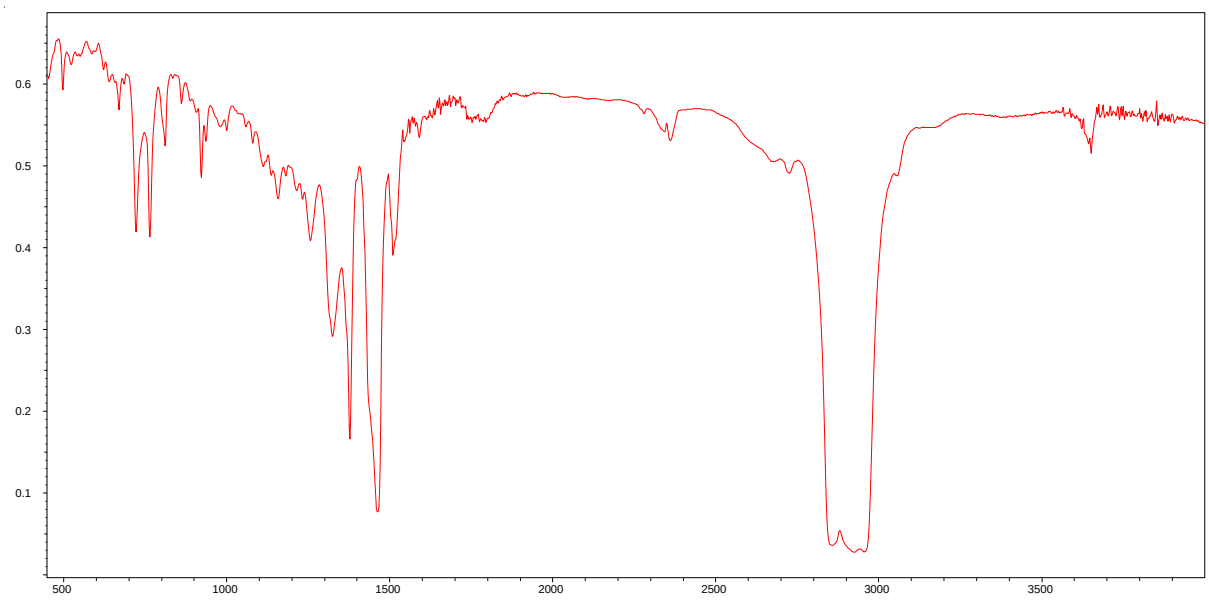

Fig. S6. IR spectrum of complex **7**.