Supporting Information

Shunichiro Ito, Kazuo Tanaka and Yoshiki Chujo*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University,

Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

E-mail: tanaka@poly.synchem.kyoto-u.ac.jp

Table of Contents

1. Methods

^{1}H (400 MHz) and $^{13}C\{^{1}H\}$ (100 MHz) NMR spectra were recorded on a JEOL JNM-AL400 spectrometer. In ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra, tetramethylsilane (TMS) and/or residual solvent peaks were used as an internal standard. $^{27}Al\{^{1}H\}$ NMR (130 MHz) spectra were recorded on a JEOL JNM-ECZ500 spectrometer and referenced to 1.1 M $Al(NO_3)_3$ in D_2O (0 ppm) as an external standard. The peak in $^{27}Al\{^{1}H\}$ NMR spectra at around 60 ppm was attributed to the signal from the probe. High-resolution mass (HRMS) spectrometry was performed at the Technical Support Office (Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University), and the HRMS spectra were obtained on a Thermo Fisher Scientific EXACTIVE spectrometer for electrospray ionization (ESI) and for direct analysis in real time (DART). UV−vis absorption spectra were recorded on a SHIMADZU UV-3600 spectrophotometer. Fluorescence and phosphorescence emission spectra and phosphorescence decay were measured with a HORIBA JOBIN YVON Fluorolog-3 spectrofluorometer and an Oxford Optistat DN for temperature control. Absolute photoluminescence quantum yields were measured with a Hamamatsu Photonics Quantaurus-QY Plus C13534-01 and a sample holder for low temperature, A11238-05, was used for the measurements at 77 K. Photoluminescence (PL) lifetimes were measured by a Horiba FluoroCube spectrofluorometer system and excitation was carried out at 375 nm using UV diode laser (NanoLED 375 nm). Single-crystal X-ray diffraction data were collected using a Rigaku R-AXIS RAPID-F. Dara were collected at 93 K with graphite-monochromated Mo Kα radiation diffractometer and an imaging plate. Equivalent reflections were merged and a symmetry related absorption correction was carried out with the program ABSCOR.[1] The structures were solved with SHELXT 2014[2] and refined on F^2 with SHELXL[3] on Yadokari-XG[4] or Shelxle.[5] The program ORTEP-3[6] was used to generate the X-ray structural diagram. Elemental analysis was performed at the Microanalytical Center of Kyoto University.

2. Materials

All reactions were performed under argon atmosphere using modified Schlenk line techniques and an MBRAUN glove box system (UNIlab), unless otherwise noted. Analytical thin layer chromatography (TLC) was performed with silica gel 60 Merck F254 plates. Column chromatography was performed with Wakogel C-200 SiO_2. *n*-BuLi (1.55 M in hexane, Kanto Chemical Co., Inc,), deoxygenated toluene (Fujifilm Wako Pure Chemical Industries, Ltd.; Wako), and deoxygenated hexane (Wako) were purchased from commercial sources and used as received. $AlCl_3$ (99.999% trace metal basis, Sigma-Aldrich Co., LLC.), $GaCl_3$ (anhydrous, Tokyo Chemical Industry Co., Ltd.; TCI), and $InCl_3$ (anhydrous (99.999%-In), Strem Chemicals, Inc.) were purified by sublimation under inert atmosphere before use. **LH** was synthesized according to the reported literatures.[7] **LMCl** (M = Al, Ga, In) was synthesized by using modified procedures of the literature for the related compounds.[8]

3. Synthesis

General Procedure for Synthesis of LMCl

To a slurry of **LH** in hexane (0.1 M) was added *n*-BuLi (1.55 M in hexane, 1.1 eq.) dropwise at –78 °C. The mixture was stirred for 10 min at –78 °C, then allowed to slowly warm to r.t. and stirred for 5 h. The slurry showed green emission under UV irradiation. The slurry was added to a slurry of freshly sublimed MCl_3 (2 eq.) in hexane (0.3 M) at –78 °C. The mixture was warmed to 50 °C and stirred for 19 h at the same temperature. The product was extracted with hexane then filtered with Merck Millipore 0.20 μm hydrophobic PTFE filter repeatedly. The filtrate was concentrated under reduced pressure. Analytically pure product was obtained by repeated crystallization from hexane with a slow-evaporation method. The crystals were collected and washed with hexane to give the spectroscopically pure and X-ray quality product.

LAlCl: Colorless crystals (87 mg, 18%). Anal. Calcd. for $C_{39}H_{45}AlCl_2N_2$: C, 73.23; H, 7.09; N, 4.38; Cl, 11.08. Found: C, 73.27; H, 7.19; N, 4.33; Cl, 10.78. ^{1}H NMR ($CDCl_3$): δ 7.24–7.07 (m, 16H), 5.86 (s, 1H), 3.64 (sept, 4H, $^3J_{H–H}$ = 6.70 Hz), 1.28 (d, 12H, $^3J_{H–H}$ = 6.70 Hz), 0.88 (d, 12H, $^3J_{H–H}$ = 6.70 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 172.2, 144.6, 138.1, 137.9, 129.5, 129.0, 127.7, 127.6, 124.4, 103.6 (C=*C*H–C), 28.7, 26.1, 23.6. ^{27}Al{^{1}H} NMR (C_6D_6): δ 100.7. HRMS (DART) $[M+H]^+$; Found: 639.2828. Calcd.: 639.2848.

LGaCl: Yellow crystals (57 mg, 46% yield). ^{1}H NMR (C_6D_6): δ 7.25–7.07 (m, 16H), 5.70 (s, 1H), 3.37 (sept, 4H, $^3J_{H–H}$ = 6.7 Hz), 1.28 (d, 12H, $^3J_{H–H}$ = 6.7 Hz), 0.91 (d, 12H, $^3J_{H–H}$ = 6.8 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 171.8, 144.4, 138.3, 137.7, 129.5, 128.9, 127.8, 127.6, 124.3, 102.1, 28.5, 26.1, 23.5. HRMS (DART) $[M+H]^+$; Found: 681.2295. Calcd.: 681.2288.

LInCl: Yellow crystals (135 mg, 34% yield). ^{1}H NMR ($CDCl_3$) δ 7.21–7.03 (m, 16H), 5.47 (s, 1H), 3.36 (7, $^3J_{H–H}$ = 6.7 Hz, 4H), 1.27 (d, $^3J_{H–H}$ = 6.7 Hz, 12H), 0.99 (d, $^3J_{H–H}$ = 6.7 Hz, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 173.4, 143.3, 140.0, 138.7, 129.3, 127.5, 127.4, 124.1, 101.3, 28.4, 26.2, 23.3. HRMS (DART) $[M+H]^+$; Found: 727.2046. Calcd.: 727.2071.

4. Single Crystal X-ray Analysis

Table S1. Selected X-ray data collection and refinement parameters

CCDC Deposition Number			
Crystal data			
Chemical formula	$C_{39}H_{45}Cl_2AlN_2$	$C_{39}H_{45}Cl_2GaN_2$	$C_{39}H_{45}Cl_2InN_2$
M_r	639.65	682.39	727.49
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Temperature (K)	93(2)	93(2)	93(2)
a, b, c (Å)	8.878(3), 16.177(2), 24.527(2)	11.2754(4), 16.0756(5), 19.9006(6)	11.2370(4), 16.2519(5), 19.9080(7)
β (°)	91.897(16)	99.934(7)	100.753(7)
V (Å^3)	3520.6(14)	3553.1(2)	3571.8(2)
Z	4	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.239	0.954	0.839
Crystal size (mm)	0.40 × 0.40 × 0.40	0.50 × 0.20 × 0.10	0.49 × 0.35 × 0.29
Data collection			
Diffractometer	Rigaku Raxis Rapid	Rigaku Raxis Rapid	Rigaku Raxis Rapid
Absorption correction	Empirical, *ABSCOR* (Rigaku, 1995)	Empirical, *ABSCOR* (Rigaku, 1995)	Empirical, *ABSCOR* (Rigaku, 1995)
T_{min}, T_{max}	0.7374, 1.0000	0.5416, 1.0000	0.6612, 1.0000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	60564, 8072, 6360	31821, 8094, 6213	33694, 8168, 7377
R_{int}	0.1235	0.0513	0.0327
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.1081, 0.2582, 1.084	0.0582, 0.1432, 1.214	0.0259, 0.0623, 1.065
No. of reflections	8072	8094	8168
No. of parameters	405	405	405

H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.005, –0.493	1.868, –3.835*	0.912, –0.286

* The A-level alert arises from the imperfect absorption correction of heavy metal (Ga ion) compound. Although some crystals have been subjected to X-ray analyses, the reported result is the best one.

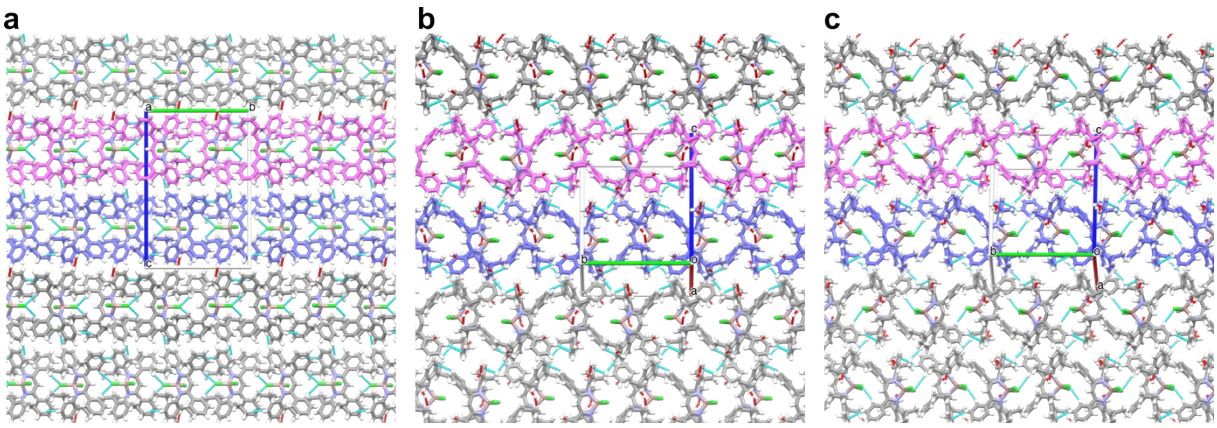

Figure S1. Packing structures of (a) **LAlCl**, (b) **LGaCl** and (c) **LInCl**. Cyan and red dotted lines represent short contacts within shown molecules and with outside molecules, respectively.

5. Photophysical Properties

Table S2. Onset wavelengths of fluorescence and phosphorescence spectra at 77 K in solutions and the corresponding energies of singlet and triplet excited states

	λ_{onset}^{FL} / nm	λ_{onset}^{FL} / nm	E_g^S / eV	E_g^T / eV
LAlCl	409.9	495.4	3.02	2.50
LGaCl	420.4	503.5	2.95	2.46
LInCl	422.1	510.7	2.94	2.43

6. Theoretical Calculations

Table S3. Results of TD-DFT calculations[a]

	$\lambda_{S0–S1}$ / nm	$E_{S0–S1}$ / eV	f	E_{HOMO} / eV	E_{LUMO} / eV	NPA Charge on the ligand
LAlCl	345.96	3.5838	0.3861	–6.44898	–2.16109	1.72299
LGaCl[a]	349.99	3.5425	0.3611	–6.4049	–2.13143	1.57002
	(347.85)	(3.5643)	(0.3763)	(–6.40626)	(–2.12435)	(1.67214)
LInCl	351.24	3.5299	0.3788	–6.38531	–2.12082	1.63705

[a]PBE1PBE/def2-TZVP level of theory until otherwise noted. [b]The value in the parentheses was obtained with the Lanl2DZ pseudopotential for Ga.

Table S4. Optimized geometry of **LAlCl** at S_0 state

Center Number	Atomic Number	Coordinates (Angstroms)		
		x	y	z
1	13	0.000003	-0.766291	1.15576
2	7	-1.456959	-0.125661	0.119647
3	7	1.456963	-0.125662	0.119643
4	6	1.273334	1.040211	-0.513956
5	6	-3.03864	-1.832937	-0.661734
6	6	-2.765515	-0.747764	0.197884
7	6	2.410078	1.884492	-1.013369
8	6	-2.410084	1.884479	-1.013375
9	6	2.765522	-0.747762	0.197883
10	6	-1.273335	1.040209	-0.513956
11	6	3.038659	-1.832926	-0.661744
12	6	-3.725929	-0.294626	1.122435
13	6	-0.000001	1.59529	-0.738883
14	1	-0.000002	2.528163	-1.279547
15	6	-3.448818	1.402242	-1.81398
16	1	-3.492005	0.35729	-2.083993
17	6	3.725925	-0.29463	1.122448
18	6	2.403731	3.245014	-0.679766
19	1	1.620082	3.634134	-0.03902
20	6	-2.40375	3.245001	-0.679772
21	1	-1.620105	3.634129	-0.039025
22	6	-5.280143	-1.947125	0.257316
23	1	-6.263338	-2.406823	0.273782
24	6	-4.310041	-2.403556	-0.622336
25	1	-4.543772	-3.226741	-1.288607
26	6	-4.977615	-0.913599	1.127282
27	1	-5.730169	-0.573481	1.830812
28	6	-3.477807	0.81891	2.129072
29	1	-2.483245	1.231556	1.952776
30	6	-4.441193	2.259368	-2.27761
31	1	-5.233725	1.863819	-2.904358
32	6	4.97761	-0.913606	1.127309
33	1	5.730156	-0.573491	1.83085
34	6	3.477796	0.818904	2.129084
35	1	2.483229	1.231539	1.952787
36	6	3.448818	1.402265	-1.813972
37	1	3.492014	0.357314	-2.083986
38	6	4.441188	2.259399	-2.277598
39	1	5.233724	1.863857	-2.904345
40	6	2.016024	-2.400724	-1.638871

41	1	1.036145	-2.016836	-1.353003
42	6	-2.015988	-2.400747	-1.638836
43	1	-1.036106	-2.016905	-1.352919
44	6	-3.40227	4.098149	-1.133205
45	1	-3.381929	5.145583	-0.850386
46	6	4.424202	3.608385	-1.939904
47	1	5.204045	4.272006	-2.299186
48	6	-4.494849	1.960669	1.990381
49	1	-4.536915	2.348618	0.970793
50	1	-4.224032	2.784355	2.658423
51	1	-5.501562	1.633032	2.267965
52	6	3.402245	4.098169	-1.133195
53	1	3.381895	5.145603	-0.850374
54	6	-4.424219	3.608355	-1.939918
55	1	-5.204067	4.271968	-2.299203
56	6	4.310055	-2.403556	-0.622321
57	1	4.543794	-3.226745	-1.288585
58	6	5.280145	-1.947134	0.257349
59	1	6.263337	-2.406838	0.273831
60	6	-3.496247	0.269229	3.563005
61	1	-4.489452	-0.110535	3.823903
62	1	-3.240699	1.061139	4.273456
63	1	-2.775498	-0.539831	3.693641
64	6	4.494829	1.96067	1.990385
65	1	5.50154	1.633052	2.267998
66	1	4.22399	2.784374	2.658396
67	1	4.536912	2.348588	0.970786
68	17	-0.000034	-2.869707	1.43669
69	6	-2.275747	-1.95614	-3.086073
70	1	-3.27969	-2.246871	-3.413161
71	1	-1.555315	-2.42998	-3.760307
72	1	-2.177718	-0.875056	-3.211167
73	6	-1.946486	-3.931063	-1.564187
74	1	-1.767318	-4.269831	-0.5419
75	1	-1.130791	-4.298633	-2.192454
76	1	-2.867195	-4.397301	-1.92712
77	6	3.496244	0.269229	3.563019
78	1	2.775521	-0.539855	3.693653
79	1	3.240665	1.061132	4.273466
80	1	4.489459	-0.110502	3.823926
81	17	0.000006	0.271628	3.030471
82	6	1.94646	-3.931036	-1.564183
83	1	2.867176	-4.397315	-1.927044

84	1	1.130792	-4.298591	-2.192495
85	1	1.767213	-4.269771	-0.541899
86	6	2.275856	-1.956181	-3.086116
87	1	2.177931	-0.875093	-3.211252
88	1	1.555397	-2.429979	-3.76035
89	1	3.279778	-2.247019	-3.413169

Table S5. Optimized geometry of **LGaCl** at S_0 state

Center Number	Atomic Number	Coordinates (Angstroms)		
		x	y	z
1	7	-1.472602	-0.081058	0.036955
2	7	1.472567	-0.081152	0.036919
3	6	1.27613	1.111289	-0.530039
4	6	-3.034222	-1.768958	-0.794135
5	6	-2.774127	-0.706133	0.09615
6	6	2.410761	1.978826	-0.990131
7	6	-2.410648	1.978923	-0.990237
8	6	2.774054	-0.706296	0.096079
9	6	-1.276088	1.111356	-0.530037
10	6	3.03409	-1.769169	-0.794162
11	6	-3.728858	-0.301273	1.045697
12	6	0.000036	1.670302	-0.728667
13	1	0.00006	2.631994	-1.216452
14	6	-3.437763	1.537685	-1.827628
15	1	-3.470469	0.509156	-2.156419
16	6	3.72882	-0.301396	1.045564
17	6	2.415251	3.316431	-0.576123
18	1	1.640432	3.67015	0.09529
19	6	-2.414932	3.316632	-0.576565
20	1	-1.640027	3.670415	0.094715
21	6	-5.275617	-1.924218	0.115397
22	1	-6.256899	-2.388273	0.113538
23	6	-4.301309	-2.348213	-0.777216
24	1	-4.529736	-3.152548	-1.467325
25	6	-4.978485	-0.924292	1.02558
26	1	-5.731493	-0.617667	1.743919
27	6	-3.468536	0.756164	2.107087
28	1	-2.47652	1.179454	1.940135
29	6	-4.431454	2.414376	-2.249459
30	1	-5.216268	2.051825	-2.905203
31	6	4.97843	-0.924449	1.025456
32	1	5.731471	-0.61779	1.743745
33	6	3.468531	0.756175	2.106828
34	1	2.476525	1.179466	1.939815
35	6	3.437785	1.537656	-1.827671
36	1	3.470342	0.509204	-2.156716
37	6	4.431571	2.414319	-2.249334
38	1	5.216306	2.051825	-2.905205
39	6	1.987703	-2.290696	-1.771019
40	1	1.012744	-2.006335	-1.374883

41	6	-1.987869	-2.290481	-1.77103
42	1	-1.012891	-2.006239	-1.374856
43	6	-3.413489	4.189638	-0.990632
44	1	-3.402118	5.219132	-0.64778
45	6	4.425098	3.741665	-1.833967
46	1	5.205277	4.420969	-2.161843
47	6	-4.488961	1.901033	2.052224
48	1	-4.544609	2.350647	1.058686
49	1	-4.210038	2.68309	2.765394
50	1	-5.491555	1.555295	2.322724
51	6	3.413912	4.189402	-0.990011
52	1	3.402701	5.21881	-0.646897
53	6	-4.424779	3.741826	-1.834425
54	1	-5.20488	4.421154	-2.162434
55	6	4.30116	-2.348465	-0.777236
56	1	4.529549	-3.15284	-1.467311
57	6	5.275503	-1.924447	0.11533
58	1	6.256773	-2.388528	0.11347
59	6	-3.459904	0.119737	3.504718
60	1	-4.445879	-0.281983	3.760132
61	1	-3.193287	0.866915	4.2582
62	1	-2.732894	-0.69138	3.570485
63	6	4.488963	1.90103	2.05181
64	1	5.491567	1.555314	2.3223
65	1	4.210074	2.683161	2.764911
66	1	4.544568	2.350545	1.058222
67	17	-0.000038	-2.947598	1.265445
68	6	-2.113055	-1.665205	-3.167559
69	1	-3.110592	-1.835611	-3.586797
70	1	-1.383638	-2.115306	-3.848233
71	1	-1.926886	-0.588654	-3.156529
72	6	-2.001278	-3.819652	-1.873714
73	1	-1.944251	-4.284094	-0.886737
74	1	-1.141909	-4.159242	-2.457922
75	1	-2.898978	-4.188349	-2.37914
76	6	3.45986	0.119925	3.504538
77	1	2.7328	-0.691141	3.570405
78	1	3.193284	0.867214	4.257925
79	1	4.44581	-0.281823	3.760007
80	17	0.000043	0.19411	2.999032
81	6	2.00099	-3.819877	-1.873565
82	1	2.898677	-4.188692	-2.378929
83	1	1.141613	-4.159448	-2.457774

84	1	1.943894	-4.284225	-0.886548
85	6	2.112957	-1.665553	-3.167603
86	1	1.926887	-0.588984	-3.156666
87	1	1.383507	-2.115647	-3.848245
88	1	3.110483	-1.836085	-3.586818
89	31	-0.000024	-0.803671	1.051763

Table S6. Optimized geometry of **LInCl** at S_0 state

Center Number	Atomic Number	Coordinates (Angstroms)		
		x	y	z
1	7	-1.539121	-0.037315	-0.016413
2	7	1.539093	-0.037302	-0.016441
3	6	1.290291	1.185124	-0.494463
4	6	-3.124184	-1.602126	-1.034025
5	6	-2.85722	-0.628791	-0.04709
6	6	2.395484	2.11855	-0.905528
7	6	-2.395519	2.1183	-0.906109
8	6	2.857184	-0.628789	-0.047411
9	6	-1.290343	1.185037	-0.494617
10	6	3.124197	-1.601508	-1.034937
11	6	-3.827704	-0.281483	0.91241
12	6	-0.000029	1.739924	-0.634759
13	1	-0.000025	2.735382	-1.049723
14	6	-3.410412	1.771508	-1.801416
15	1	-3.454222	0.776062	-2.219269
16	6	3.827632	-0.282062	0.912333
17	6	2.383725	3.417036	-0.380691
18	1	1.616412	3.697864	0.332754
19	6	-2.383811	3.417018	-0.381848
20	1	-1.616577	3.698167	0.331554
21	6	-5.386645	-1.788736	-0.179879
22	1	-6.376526	-2.230461	-0.238769
23	6	-4.403756	-2.153711	-1.088591
24	1	-4.633536	-2.88953	-1.85199
25	6	-5.088083	-0.874762	0.817719
26	1	-5.849989	-0.613352	1.544827
27	6	-3.567561	0.682152	2.06078
28	1	-2.560836	1.090864	1.94989
29	6	-4.376863	2.701807	-2.170448
30	1	-5.15165	2.412749	-2.873225
31	6	5.087971	-0.875391	0.817424
32	1	5.849841	-0.614428	1.544731
33	6	3.567491	0.681068	2.061124
34	1	2.560765	1.089821	1.950409
35	6	3.410456	1.772147	-1.800889
36	1	3.454293	0.776883	-2.219171
37	6	4.376947	2.702606	-2.16942
38	1	5.151799	2.413855	-2.872252
39	6	2.080403	-2.07118	-2.042478
40	1	1.106337	-1.708071	-1.70782

41	6	-2.080264	-2.072503	-2.041108
42	1	-1.106071	-1.710274	-1.705875
43	6	-3.356224	4.342524	-0.741925
44	1	-3.333058	5.339225	-0.313038
45	6	4.355877	3.989489	-1.641477
46	1	5.114966	4.710531	-1.927513
47	6	-4.555069	1.8577	2.064121
48	1	-4.570667	2.379262	1.105037
49	1	-4.277051	2.577386	2.840608
50	1	-5.573359	1.519836	2.281182
51	6	3.356179	4.342695	-0.740265
52	1	3.332977	5.339208	-0.310942
53	6	-4.355836	3.988926	-1.643077
54	1	-5.114894	4.709845	-1.929505
55	6	4.403723	-2.153179	-1.08969
56	1	4.63352	-2.888542	-1.853531
57	6	5.386544	-1.788844	-0.18065
58	1	6.37639	-2.230626	-0.23969
59	6	-3.617226	-0.052237	3.409211
60	1	-4.620375	-0.445626	3.603609
61	1	-3.358274	0.632819	4.22185
62	1	-2.912268	-0.885384	3.444529
63	6	4.554974	1.856636	2.064919
64	1	5.573295	1.518696	2.281717
65	1	4.277011	2.575957	2.841763
66	1	4.570457	2.378639	1.10607
67	17	0.000042	-3.271861	1.072079
68	6	-2.316921	-1.496662	-3.445639
69	1	-3.311076	-1.766007	-3.817694
70	1	-1.578409	-1.898131	-4.146853
71	1	-2.230287	-0.407554	-3.467127
72	6	-2.003671	-3.603689	-2.10669
73	1	-1.841664	-4.03651	-1.117546
74	1	-1.173606	-3.908926	-2.750218
75	1	-2.916049	-4.035593	-2.528874
76	6	3.617179	-0.053877	3.409248
77	1	2.912264	-0.887078	3.444215
78	1	3.358179	0.630826	4.222168
79	1	4.620341	-0.447304	3.603498
80	17	-0.000075	-0.061154	3.242858
81	6	2.002683	-3.602327	-2.107821
82	1	2.915116	-4.034975	-2.529125
83	1	1.172953	-3.907071	-2.752021

84	1	1.839525	-4.034844	-1.118736
85	6	2.318297	-1.495821	-3.447
86	1	2.232741	-0.406633	-3.468743
87	1	1.579726	-1.8967	-4.148489
88	1	3.312359	-1.766197	-3.818548
89	49	0.000012	-0.953998	1.078078

7. NMR Spectra

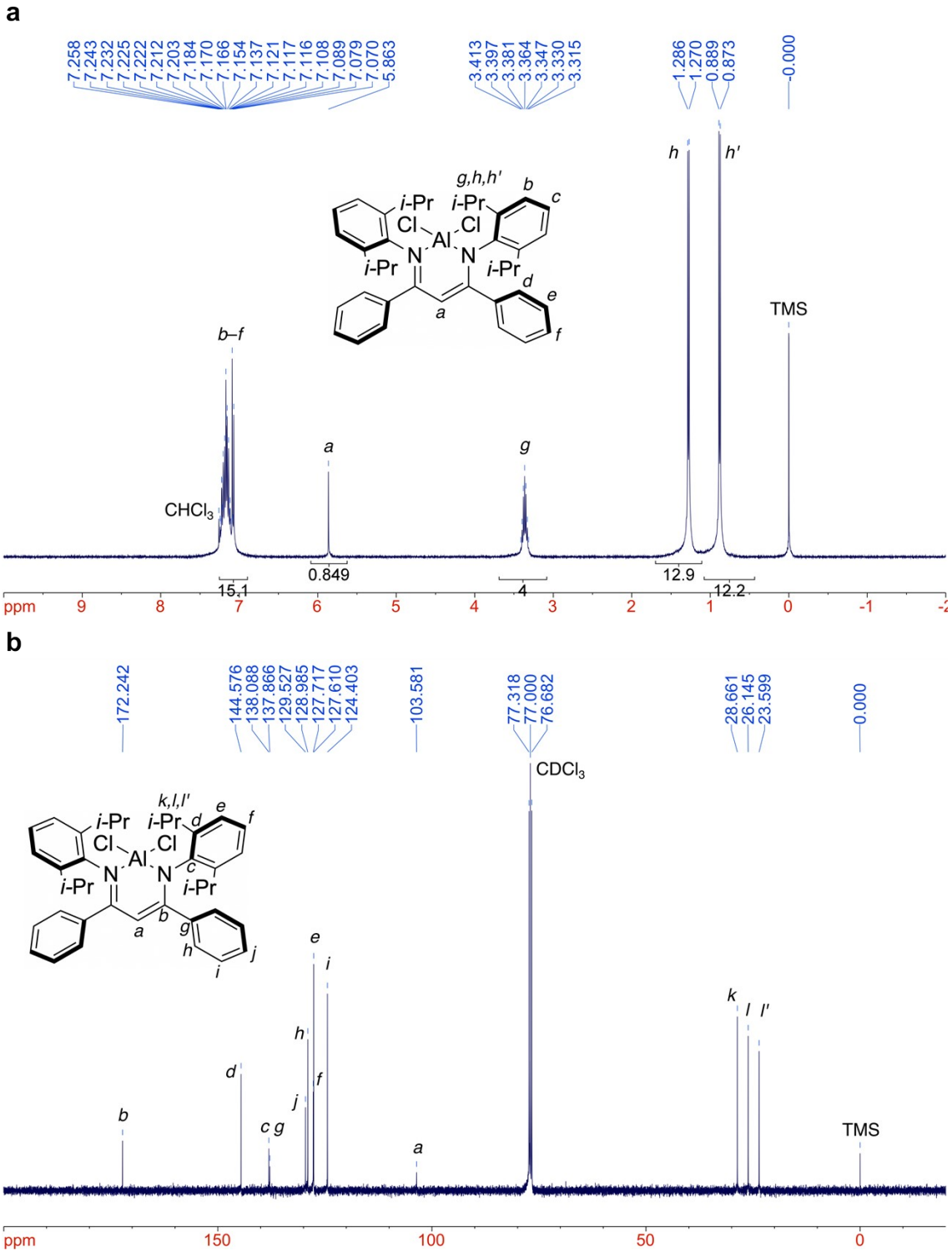

Figure S2. (a) ^{1}H and (b) $^{13}C\{^{1}H\}$ NMR spectra of **LAlCl** in $CDCl_3$.

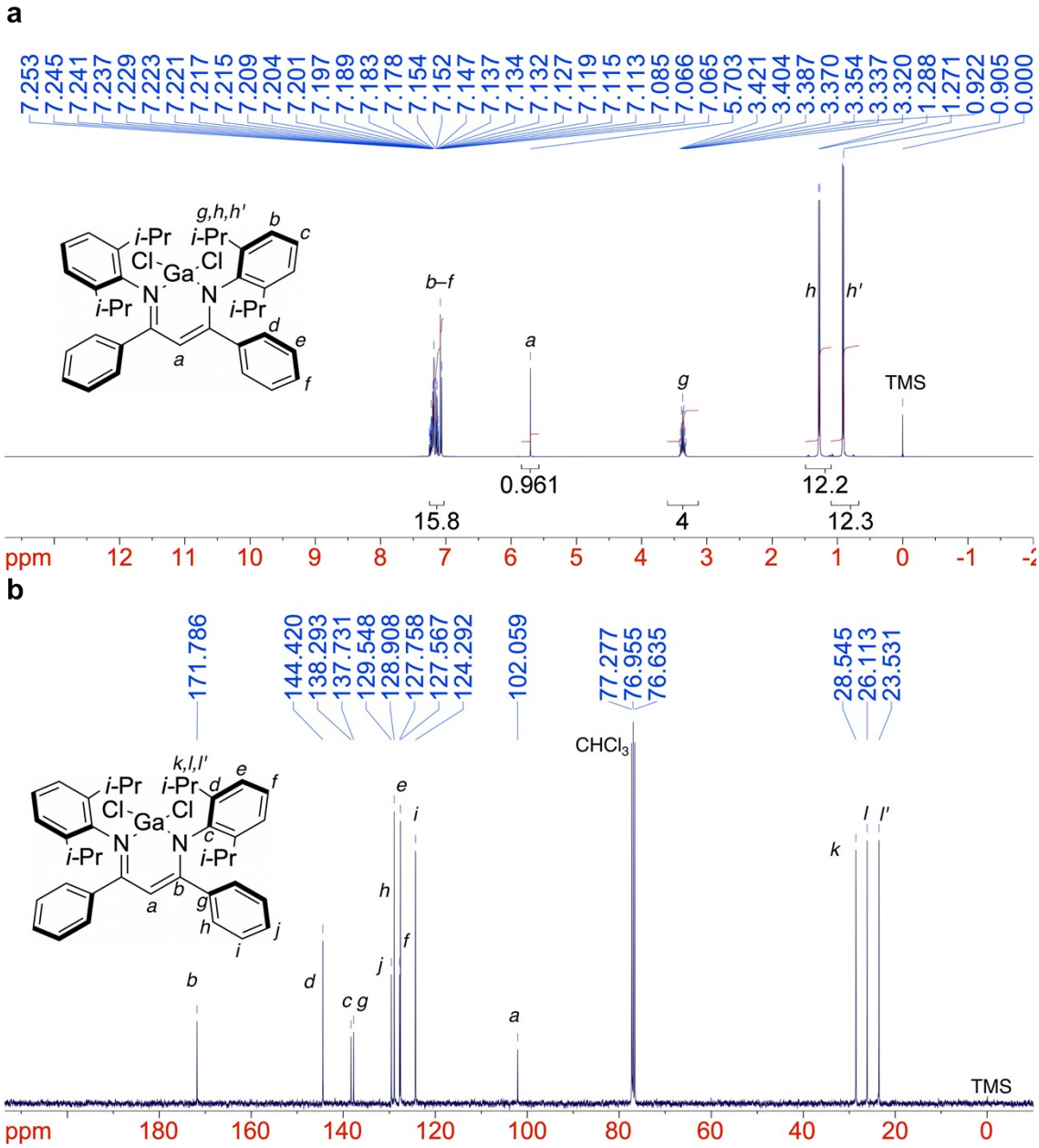

Figure S3. (a) ^{1}H and (b) $^{13}C\{^{1}H\}$ NMR spectra of **LGaCl** in $CDCl_3$.

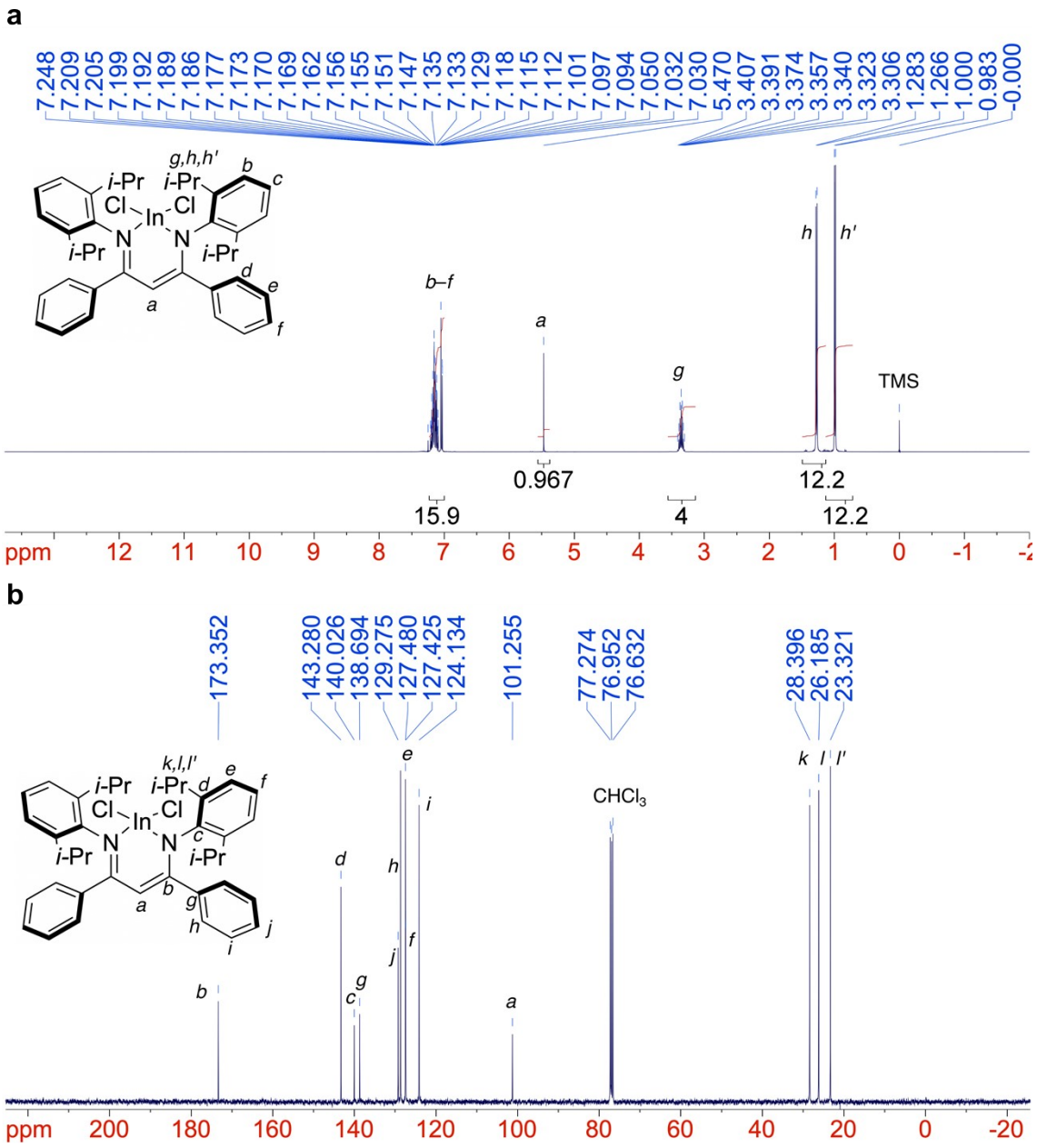

Figure S4. (a) ^{1}H and (b) $^{13}C\{^{1}H\}$ NMR spectra of **LInCl** in $CDCl_3$.

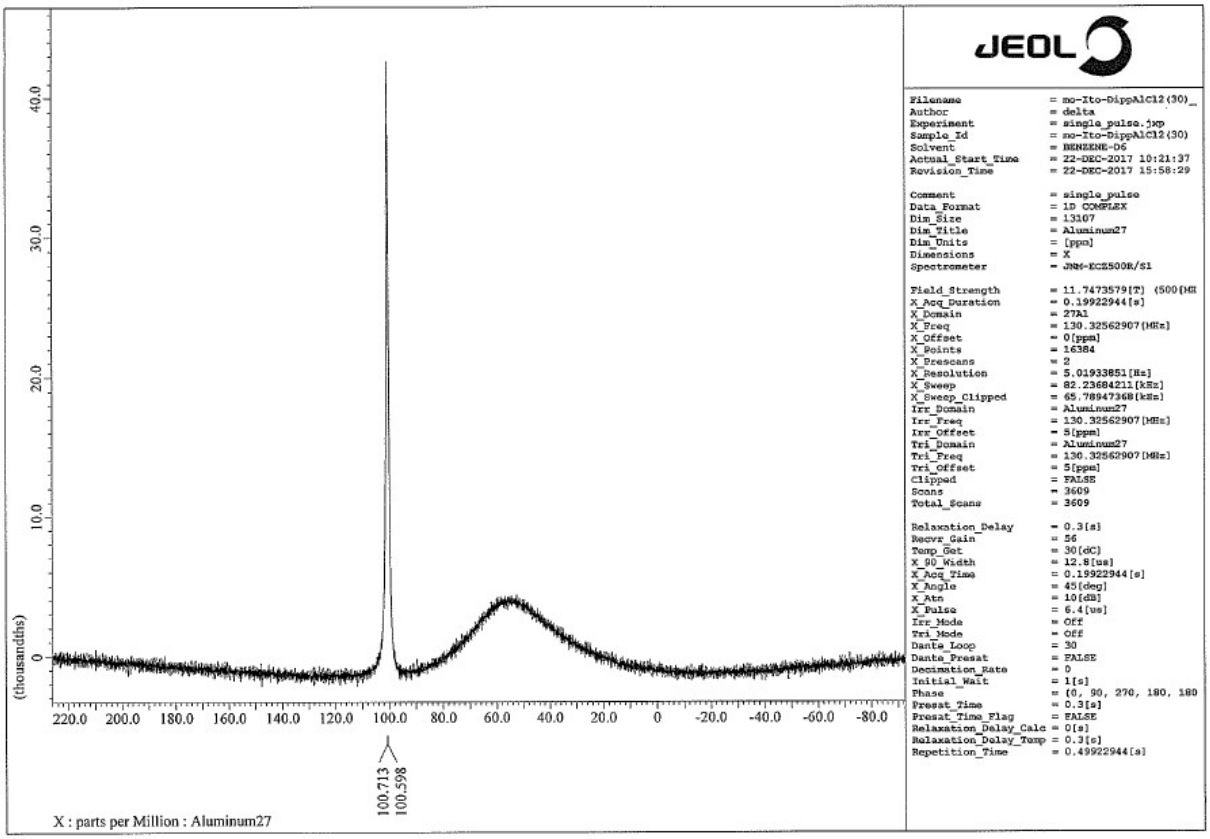

Figure S5. $^{27}Al\{^{1}H\}$ NMR spectra of **LAlCl** in C_6D_6. The broad peak around 60 ppm is attributed to the signal from the NMR tube.

8. References

1. Higashi, T. *ABSCOR. Program for Absorption Correction*; Rigaku Corporation, 1995.
2. Sheldrick, G. M. *Acta Crystallogr. Sect. A Found. Adv.* **2014**, *A71*, 3.
3. Sheldrick, G. M. *Acta Crystallogr. Sect. C Struct. Chem.* **2014**, *C71*, 3.
4. Wakita, K. *Yadokari-XG. Program for Crystal Structure Analysis*; 2000.
5. Hübschle, C. B.; Sheldrick, G. M.; Dittrich, B. *J. Appl. Crystallogr.* **2011**, *44*, 1281.
6. Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.
7. Arrowsmith, M.; Crimmin, M. R.; Hill, M. S.; Kociok-Köhn, G. *Dalton Trans.* **2013**, *42*, 9720.
8. Qian, B.; Ward, D. L.; Smith, M. R. *Organometallics* **1998**, *17*, 3070.