Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2021

A bis(imino)carbazolate pincer ligand stabilized mononuclear gallium(I) compound: Synthesis, characterization, and reactivity

Hao Li,[†] *Yuhao He,*[†] *Chunmeng Liu,*[‡] *Gengwen Tan*[†*]

[†]College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China. E-mail: gwtan@suda.edu.cn.

[‡]Center for Molecular Imaging and Nuclear Medicine, School for Radiological and Interdisciplinary Sciences (RAD-X), Collaborative Innovation Center of Radiation Medicine of Jiangsu Higher Education Institutions, and State Key Laboratory of Radiation Medicine and Protection, Soochow University, Suzhou 215123, China

Content

Table S1. Crystal data and refinement of **2**-**6** S2

Table S2. Crystal data and refinement of **6**-**8** S3

Selected experimental spectra.....S4

Calculation details.....S10

Coordinate of **3** S11

Table S1. Crystal data and refinement of 2-6

	2	**3**	**4**	**5**
formula	$C_{46}H_{58}Cl_2GaN_3$	$C_{46}H_{58}Ga_{0.6}K_{0.4}N_3$	$C_{92}H_{116}Ga_2N_6Se_2$	$C_{51}H_{58}CrGaN_3O_5$
formula weight	793.57	722.67	1603.26	914.72
crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
space group	*P*2(1)/*c*	*P*2(1)/*n*	*C*2/*c*	*P*-1
a/Å	12.5642(10)	12.4878(7)	46.899(2)	12.9201(3)
b/Å	14.3473(12)	11.6830(6)	15.2306(8)	13.5764(4)
c/Å	23.322(2)	28.9149(15)	33.5912(17)	14.9197(4)
α/deg				83.9920(10)
β/deg	100.111(2)	99.338(2)	124.4080(10)	66.2460(10)
γ/deg				84.9710(10)
V/Å^3	4138.8(6)	4162.6(4)	19796.0(17)	2379.20(11)
Z	4	4	8	2
ρ_{calcd}/g·cm^{-3}	1.273	1.153	1.076	1.277
μ/mm^{-1}	0.829	0.481	1.320	0.843
F(000)	1680	1525	6720	960
crystal size/mm^3	0.38 x 0.36 x 0.08	0.26 x 0.06 x 0.05	0.26 x 0.22 x 0.20	0.20 x 0.16 x 0.14
θ range/deg	1.774–24.999	2.253–26.00	1.954–27.486	2.043–25.999
index ranges	-14 ≤ h ≤ 14	–15 ≤ *h* ≤ 15	–60 ≤ *h* ≤ 60	–15 ≤ *h* ≤ 15
	–17 ≤ *k* ≤ 17	–14 ≤ *k* ≤ 14	–19 ≤ *k* ≤ 19	–16 ≤ *k* ≤ 16
	–27 ≤ *l* ≤ 27	–35 ≤ *l* ≤ 35	–43 ≤ *l* ≤ 43	–18 ≤ *l* ≤ 18
collected data	66934	39788	363906	69446
unique data	7271 (R_{int} = 0.1141)	8177 (R_{int} = 0.0929)	22673 (R_{int} = 0.1128)	9334 (R_{int} = 0.0680)
completeness to *θ*	99.9%	99.8%	99.9%	99.8%
GOF on F^2	1.022	1.059	0.996	1.045
final *R* indices [*I*>2□(*I*)]	R_1 = 0.0553	R_1 = 0.0716	R_1 = 0.0458	R_1 = 0.0363
	wR_2 = 0.1372	wR_2 = 0.1701	wR_2 = 0.1144	wR_2 = 0.0909
R indices (all data)	R_1 = 0.0800	R_1 = 0.1179	R_1 = 0.0727	R_1 = 0.0454
	wR_2 = 0.1574	wR_2 = 0.1876	wR_2 = 0.1302	wR_2 = 0.0909
Largest diff peak/hole (e·Å^{-3})	1.471/–0.943	0.918/–0.865	1.805/–0.953	0.563/–0.399

Table S2. Crystal data and refinement of 6-8

	6	**7**	**8**
formula	$C_{48}H_{64}AlN_3$	$C_{53}H_{66}AlI_2N_3$	$C_{92}H_{116}Al_2I_2N_6$
formula weight	710.00	1025.86	1613.66
crystal system	Monoclinic	Orthorhombic	Monoclinic
space group	*P*2(1)/*c*	*Fdd*2	*P*2(1)/*c*
a/Å	12.4884(7)	20.312(2)	18.3541(17)
b/Å	14.4969(7)	48.543(4)	21.0425(19)
c/Å	23.4665(12)	19.898(2)	24.667(2)
α/deg			
β/deg	99.594(2)		108.628(4)
γ/deg			
V/Å^3	4189.0(4)	19620(3)	9027.9(14)
Z	4	16	4
ρ_{calcd}/g·cm^{-3}	1.126	1.389	1.187
μ/mm^{-1}	0.084	1.337	4.094
F(000)	1544	8384	3368
crystal size/mm^3	0.38 x 0.26 x 0.16	0.22 x 0.16 x 0.14	0.13 x 0.11 x 0.10
θ range/deg	2.170–26.000	2.212–25.998	2.210–53.836
index ranges	-15 ≤ h ≤ 15	–25 ≤ *h* ≤ 25	–22 ≤ *h* ≤ 20
	–17 ≤ *k* ≤ 17	–57 ≤ *k* ≤ 57	–25 ≤ *k* ≤ 22
	–28 ≤ *l* ≤ 28	–23 ≤ *l* ≤ 23	–29 ≤ *l* ≤ 29
collected data	42054	111731	67435
unique data	8219 (R_{int} = 0.0878)	8629 (R_{int} = 0.1594)	16410 (R_{int} = 0.0560)
completeness to *θ*	99.8%	99.8%	99.8%
GOF on F^2	1.049	1.039	1.005
final *R* indices [*I*>2□(*I*)]	R_1 = 0.0543	R_1 = 0.0450	R_1 = 0.0373
	wR_2 = 0.1299	wR_2 = 0.1041	wR_2 = 0.0789
R indices (all data)	R_1 = 0.0806	R_1 = 0.0567	R_1 = 0.0549
	wR_2 = 0.1422	wR_2 = 0.1115	wR_2 = 0.0866
Largest diff peak/hole (e·Å^{-3})	0.356/–0.316	0.797/–1.196	0.620/–0.567

Selected experimental spectra

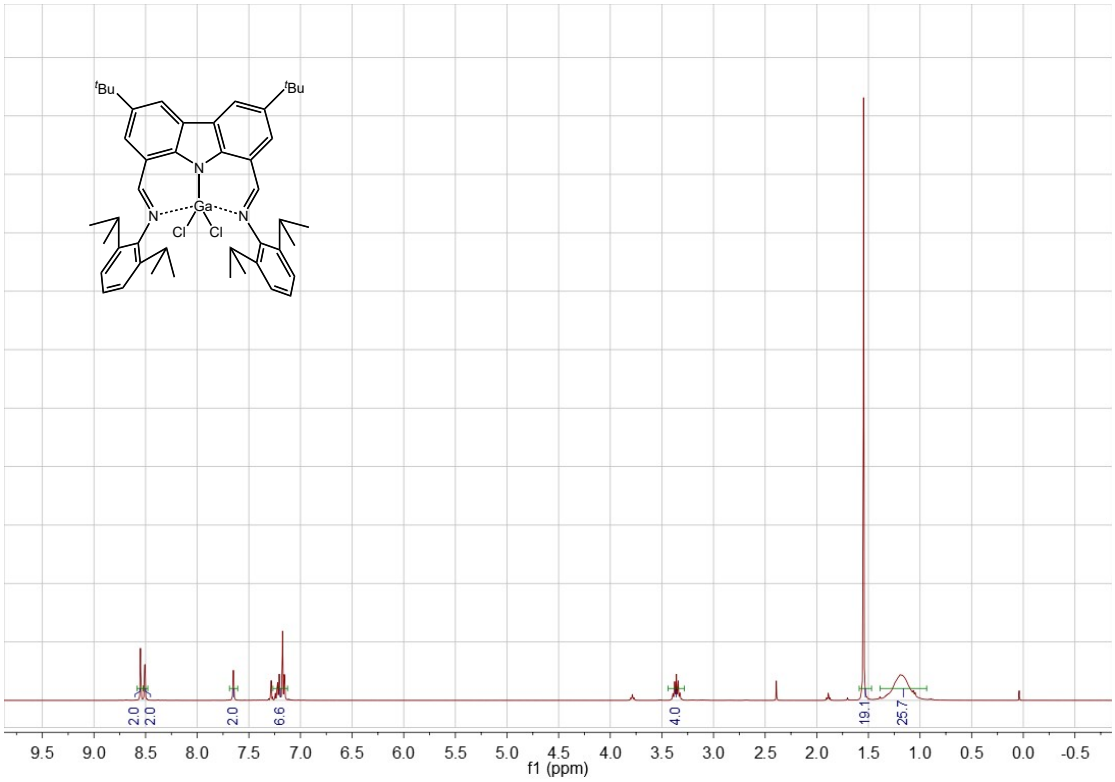

Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) of **2** at room temperature.

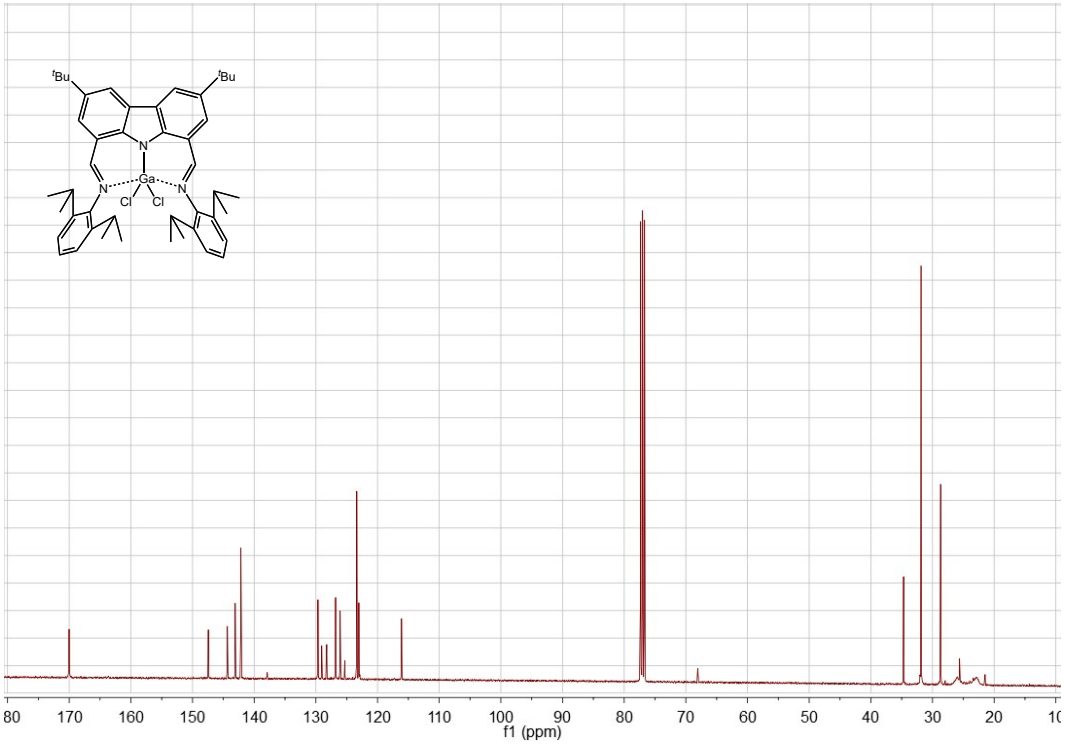

Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$) of **2** at room temperature.

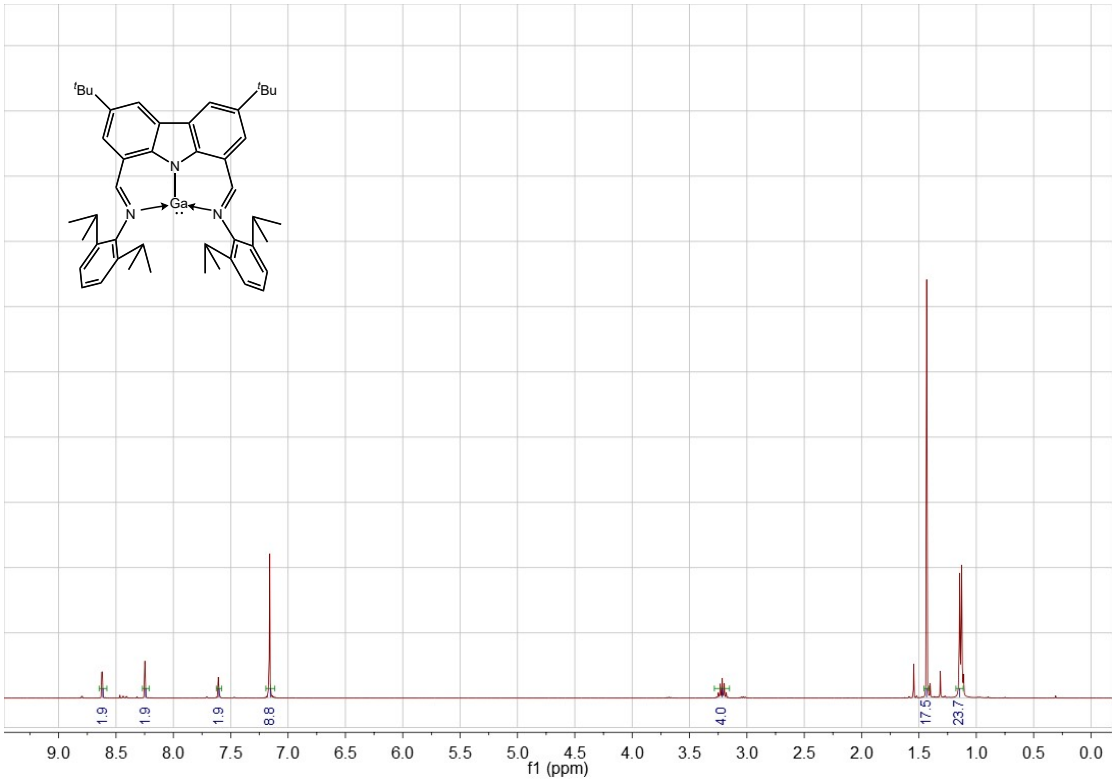

Figure S3. ^{1}H NMR (400 MHz, C_6D_6) of **3** at room temperature.

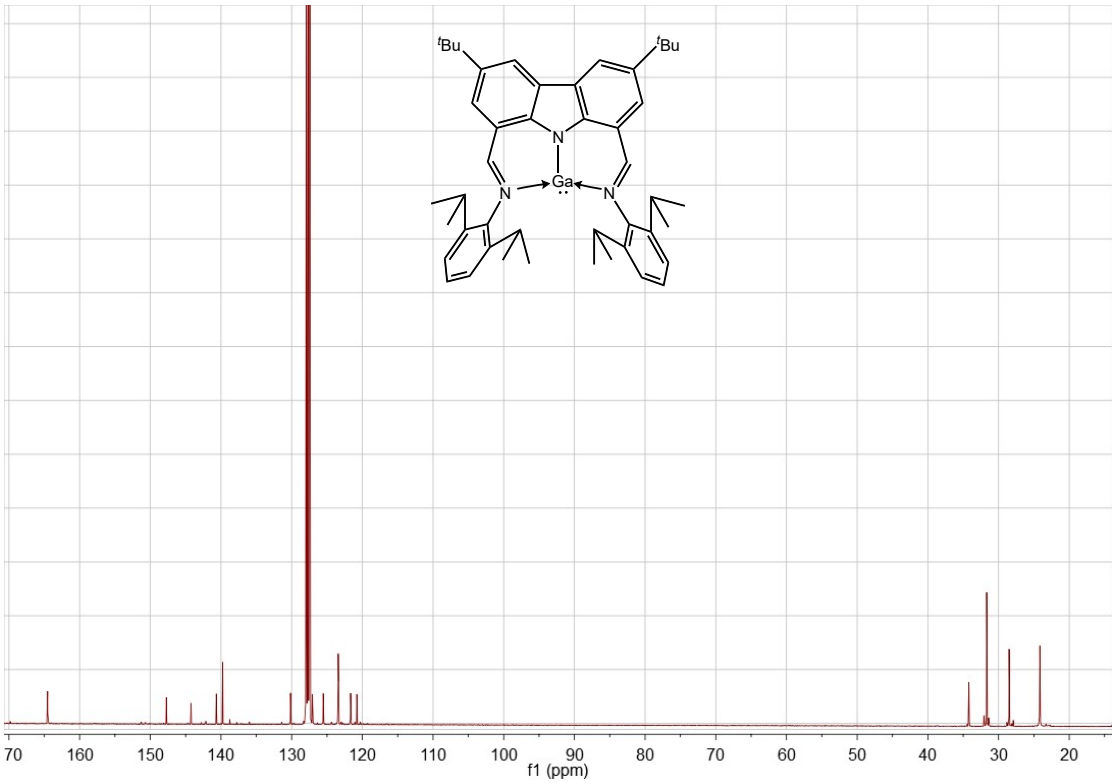

Figure S4. ^{13}C NMR (100 MHz, C_6D_6) of **3** at room temperature.

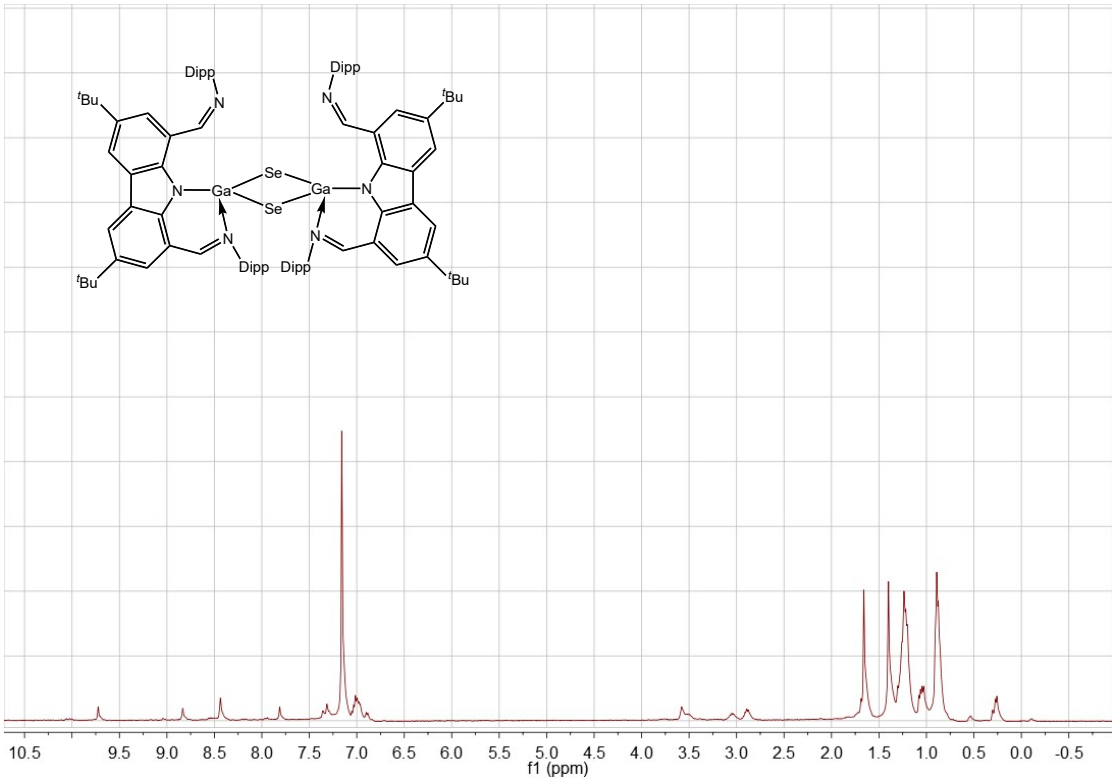

Figure S5. ^{1}H NMR (400 MHz, C_6D_6) of **4** at room temperature. Due to low solubility, very weak signals were observed.

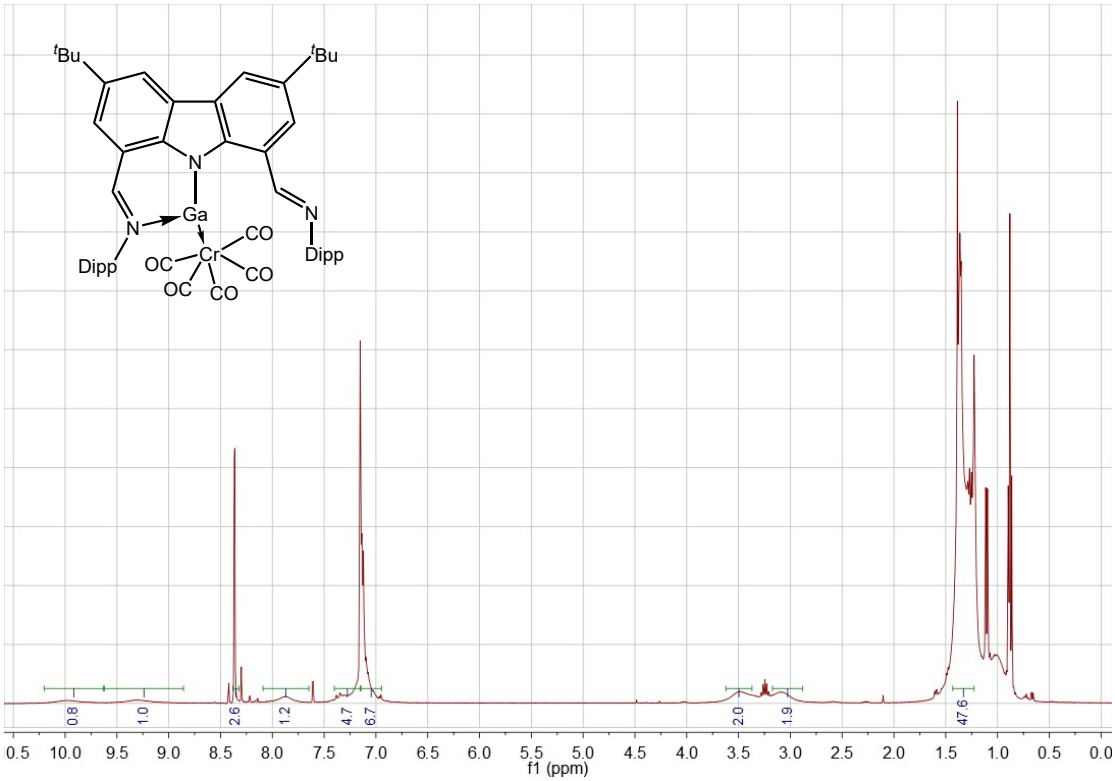

Figure S6. ^{1}H NMR (400 MHz, C_6D_6) of **5** at room temperature.

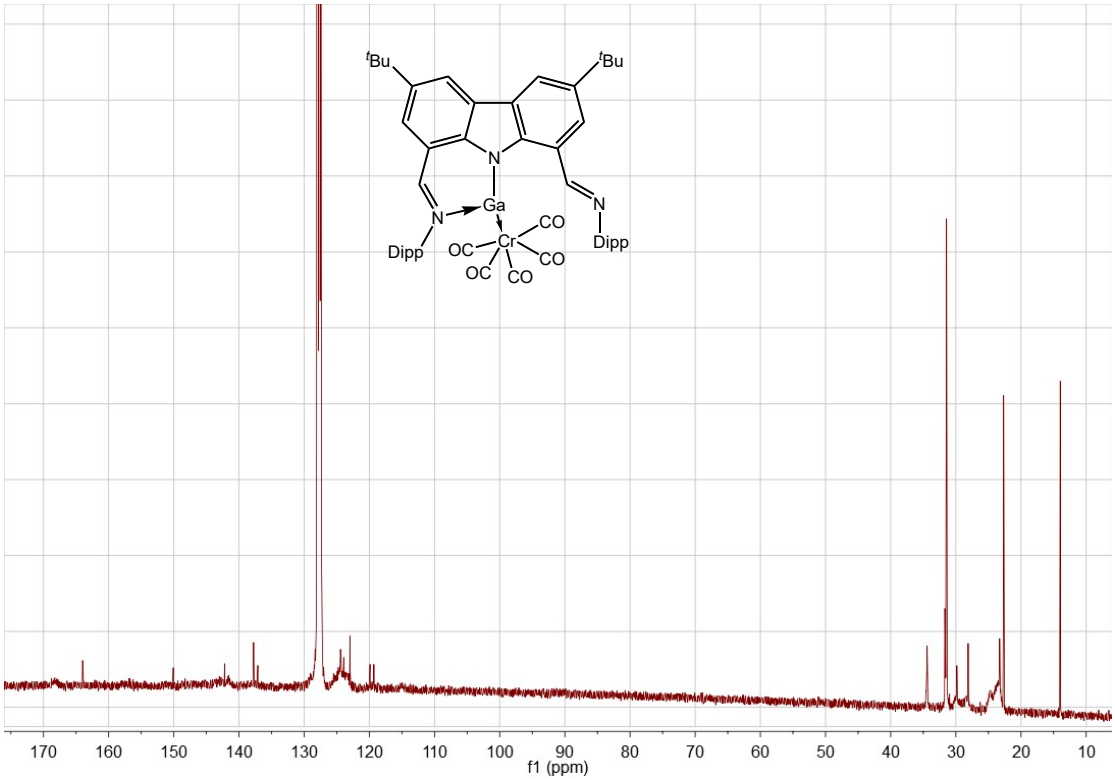

Figure S7. ^{13}C NMR (400 MHz, C_6D_6) of **5** at room temperature.

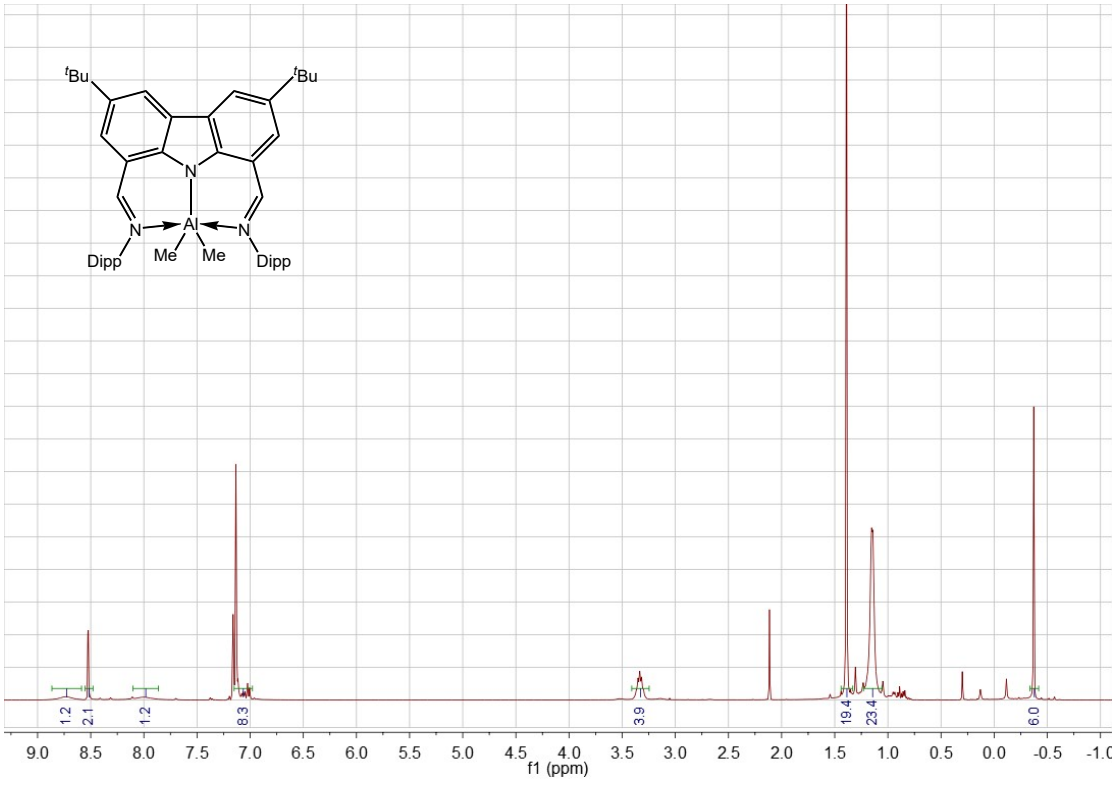

Figure S8. ^{1}H NMR (400 MHz, C_6D_6) of **6** at room temperature.

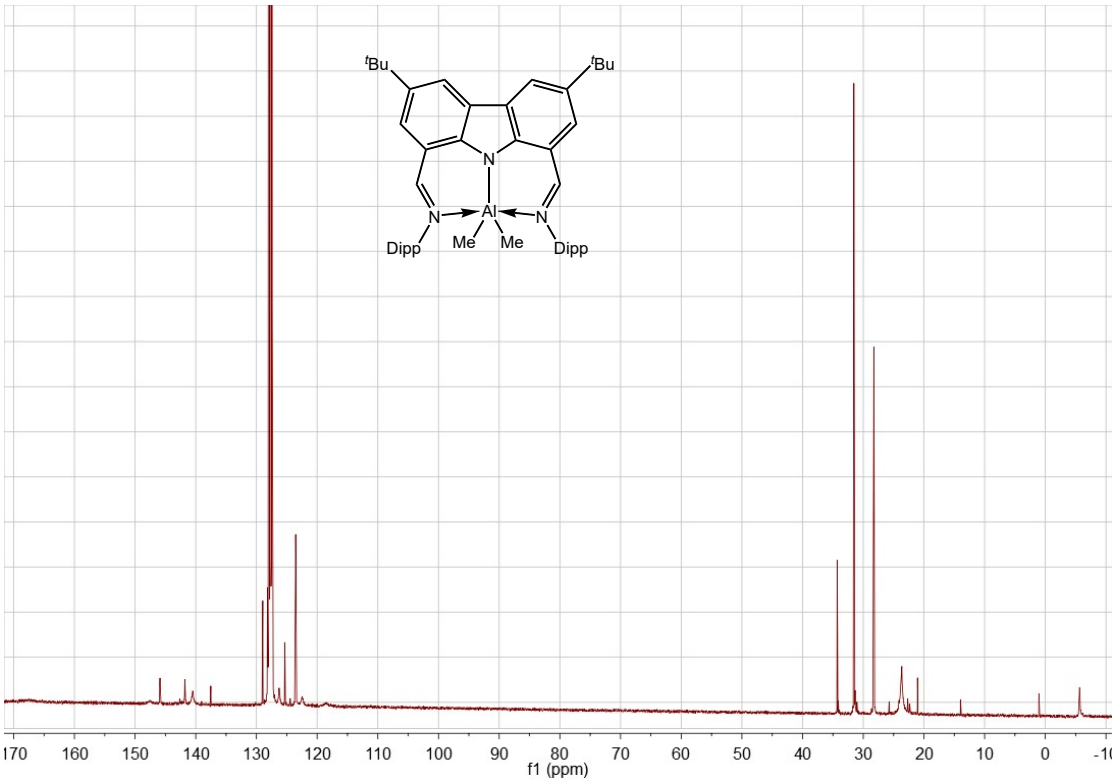

Figure S9. ^{13}C NMR (100 MHz, C_6D_6) of **6** at room temperature.

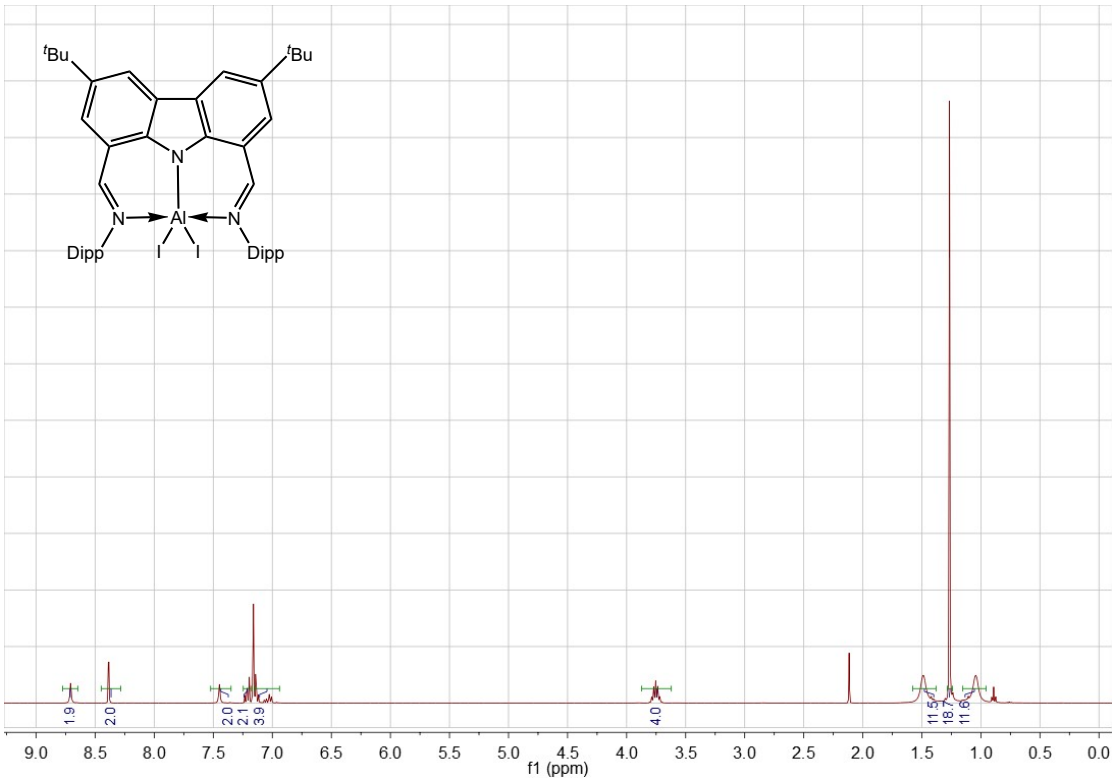

Figure S10. ^{1}H NMR (400 MHz, C_6D_6) of **7** at room temperature.

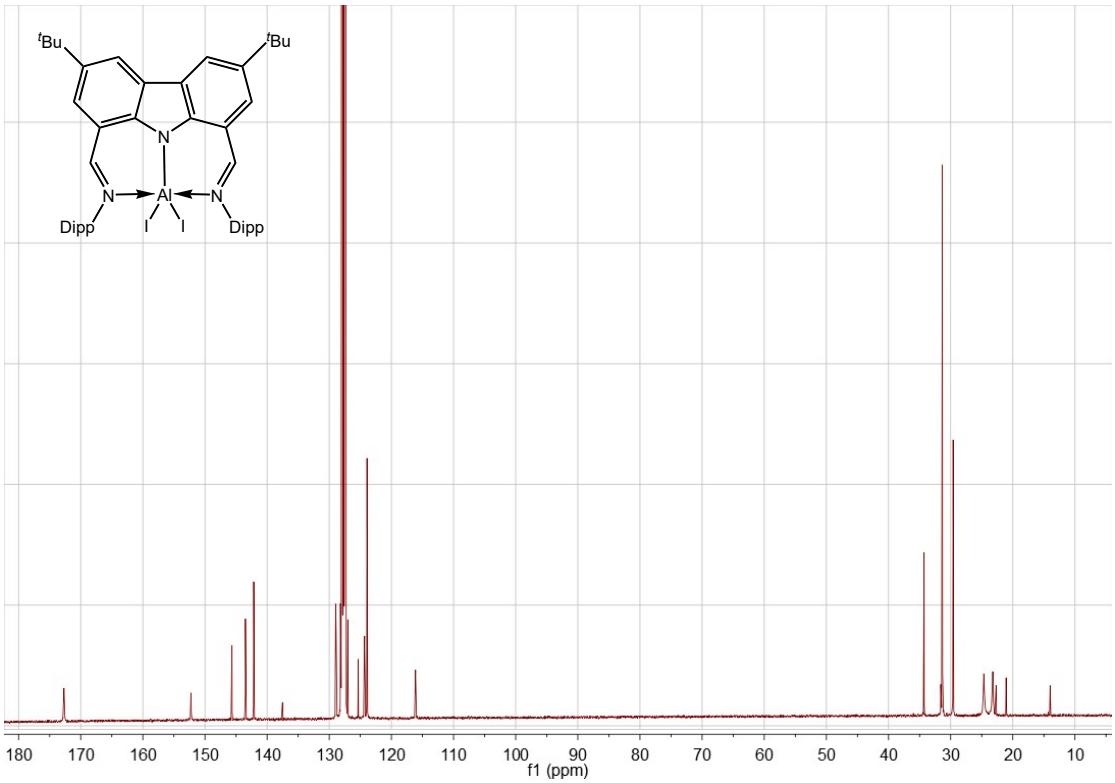

Figure S11. ^{13}C NMR (100 MHz, C_6D_6) of **7** at room temperature.

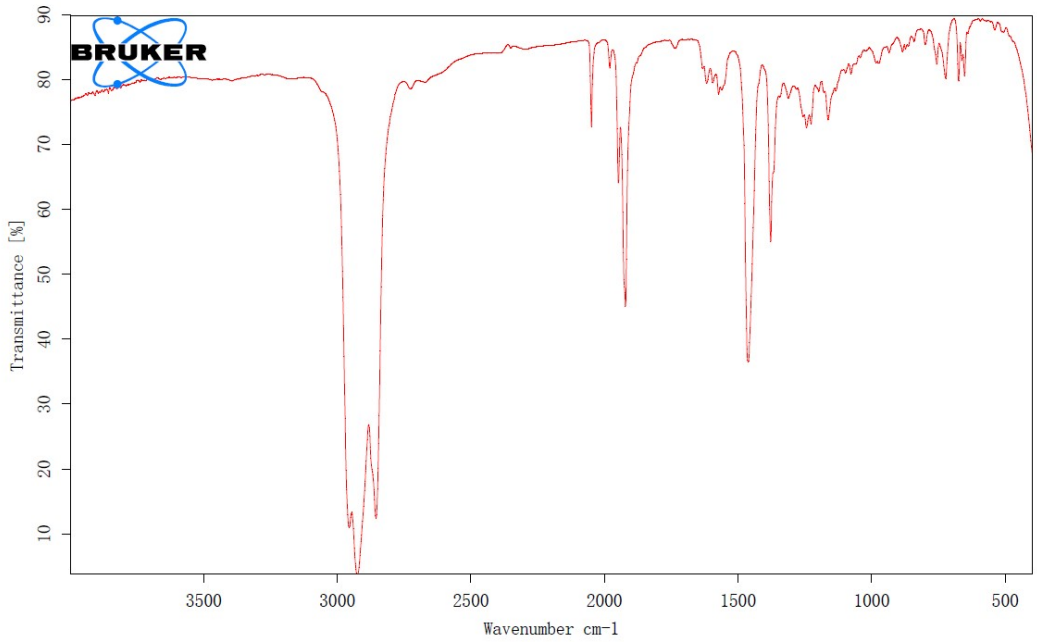

Figure S12. IR spectrum of **5**.

Calculation details

Geometry optimizations of the studied compound were performed with the density functional theory (DFT) method by using the B3LYP[S1] and 6-31G* basis set[S2] at the Gaussian 16 program.[S3]

References

(S1) Ernzerhof, M.; Scuseria, G. E. Assessment of the Perdew-Burke-Ernzerhof exchange-correlation functional, *J. Chem. Phys.* **1999**, *110*, 5029-5036.

(S2) Ditchfield, R.; Hehre, W. J.; and Pople, J. A. Self-Consistent Molecular Orbital Methods. 9. Extended Gaussian-type basis for molecular-orbital studies of organic molecules, *J. Chem. Phys.*, **1971**, *54*, 724.

(S3) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A.; Jr., Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016, Revision B.01.

Coordinate of 3

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-1.097712537	2.758317492	-0.026347669
6	-2.488016066	2.463328349	0.069384377
6	-3.393924145	3.542948354	0.105920430
1	-4.454394347	3.314984912	0.189165846
6	-2.988325124	4.876629372	0.028295725
6	-1.630758575	5.172461399	-0.092316521
1	-1.295702559	6.205288159	-0.156375475
6	-0.705705022	4.127695876	-0.114881691
6	0.729273375	4.123978226	-0.202260796
6	1.654992787	5.161128862	-0.314447319
1	1.320035495	6.195359788	-0.351372646
6	3.015942509	4.857626860	-0.377106300
6	3.421974482	3.523791931	-0.325892231
1	4.483209969	3.289241180	-0.373445235
6	2.513515334	2.450929922	-0.210565343
6	1.122350538	2.752267822	-0.148540043
6	-3.077691165	1.138180696	0.097629165
1	-4.161242115	1.108775147	0.278933310
6	3.093918095	1.125667559	-0.162632240
1	4.190841078	1.087781875	-0.216322033
6	-3.109048320	-1.202109609	-0.026297274
6	-3.488905762	-1.743177524	1.223515808
6	-4.131149610	-2.990088290	1.229234124
1	-4.438679248	-3.425098437	2.177096259
6	-4.373964061	-3.688117575	0.049625053
1	-4.877402293	-4.651286103	0.078831504
6	-3.956420875	-3.153144951	-1.169977432
1	-4.138608389	-3.710679004	-2.084262361
6	-3.307361219	-1.916160238	-1.232358900
6	-3.185695893	-1.044800628	2.547702137
1	-2.652611082	-0.116253338	2.324093645
6	-2.251079392	-1.894656888	3.432451847
1	-1.985478886	-1.344237236	4.343917293
1	-1.326373916	-2.140577943	2.899492976
1	-2.726555925	-2.835070546	3.736680430
6	-4.466970307	-0.661982789	3.314591723
1	-5.044624812	-1.550213898	3.598879981
1	-5.121211339	-0.021846449	2.710859633

1	-4.214509272	-0.119562188	4.234282181
6	-2.880968163	-1.306569119	-2.564341820
1	-2.054022903	-0.618958848	-2.349253499
6	-4.018568351	-0.465331142	-3.181975459
1	-4.352662846	0.323196146	-2.498455590
1	-4.886195806	-1.095881716	-3.414683271
1	-3.684841782	0.012177433	-4.112021270
6	-2.364998665	-2.341146768	-3.578810548
1	-1.579525226	-2.970554485	-3.145860027
1	-1.947792533	-1.828826465	-4.454190026
1	-3.165195381	-2.998092948	-3.941060490
6	3.101894934	-1.214220974	0.020108048
6	3.511706163	-1.705021664	1.280122438
6	4.157826144	-2.947718486	1.323057536
1	4.491422339	-3.341521114	2.280097832
6	4.377360914	-3.690706754	0.165248447
1	4.885421011	-4.650290493	0.220155835
6	3.931814599	-3.203981316	-1.063295304
1	4.096288651	-3.794939601	-1.960231262
6	3.275693030	-1.971166382	-1.161394220
6	3.254108880	-0.933205931	2.572038634
1	2.719091017	-0.015848056	2.309440504
6	2.345738920	-1.725018235	3.533679116
1	2.818711994	-2.659492154	3.859455759
1	1.394751443	-1.978122544	3.052631109
1	2.128689130	-1.130060296	4.429876972
6	4.563306512	-0.514756953	3.269694965
1	5.147919756	-1.388663111	3.582881365
1	4.346796488	0.080779991	4.165342260
1	5.196688324	0.086464111	2.606543912
6	2.802032222	-1.442971953	-2.512723738
6	2.077940952	-2.508736255	-3.355634334
1	1.661917230	-2.051528737	-4.261752370
1	2.754684262	-3.309446157	-3.677440736
1	1.255029377	-2.967155510	-2.796075935
6	3.963861912	-0.814329606	-3.310241764
1	3.602040460	-0.400424030	-4.259946087
1	4.444823784	-0.004662466	-2.749078666
1	4.733269159	-1.563196224	-3.537349669
7	0.014901849	1.918469642	-0.037663616
7	-2.430834654	0.046588844	-0.097333589
7	2.421512271	0.037106244	-0.053167318
31	0.009772465	-0.183496151	0.210257533
1	2.078207578	-0.644827021	-2.313232541

1	3.754618877	5.648931255	-0.464777111
1	-3.726763754	5.672568491	0.056144169