Supplementary Materials: Syntheses and Structures of Novel λ^3,λ^3-Phosphanylalumanes Fully Bearing Carbon Substituents and Their Substituent Effects

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1. Spectroscopic Data

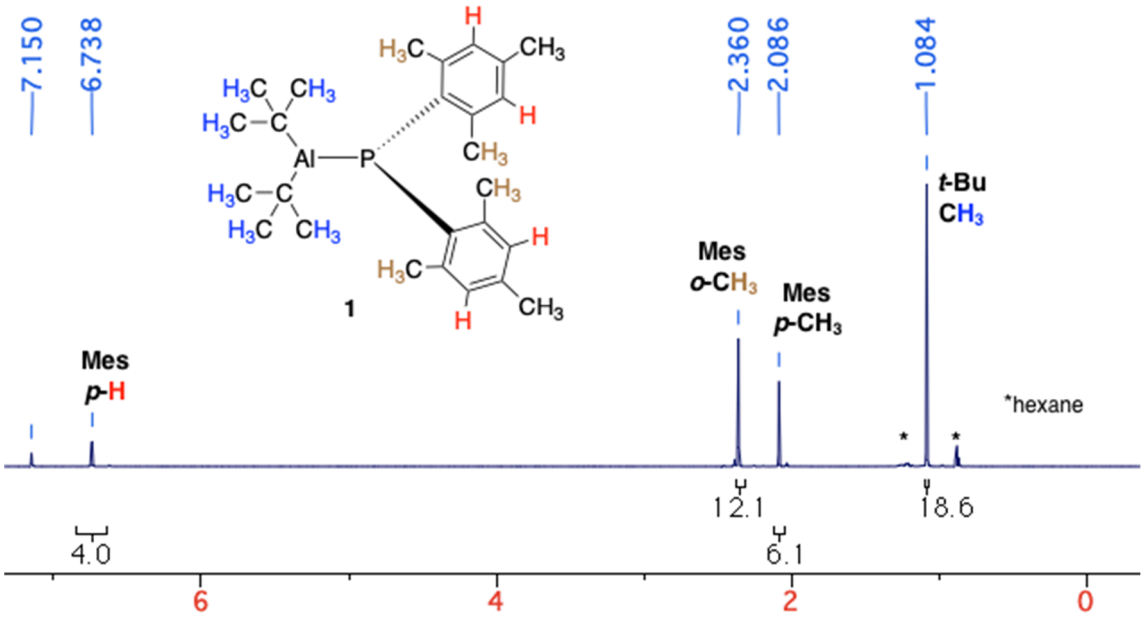

Figure S1. ^{1}H NMR spectrum of 1 (600 MHz, C_6D_6, 298 K).

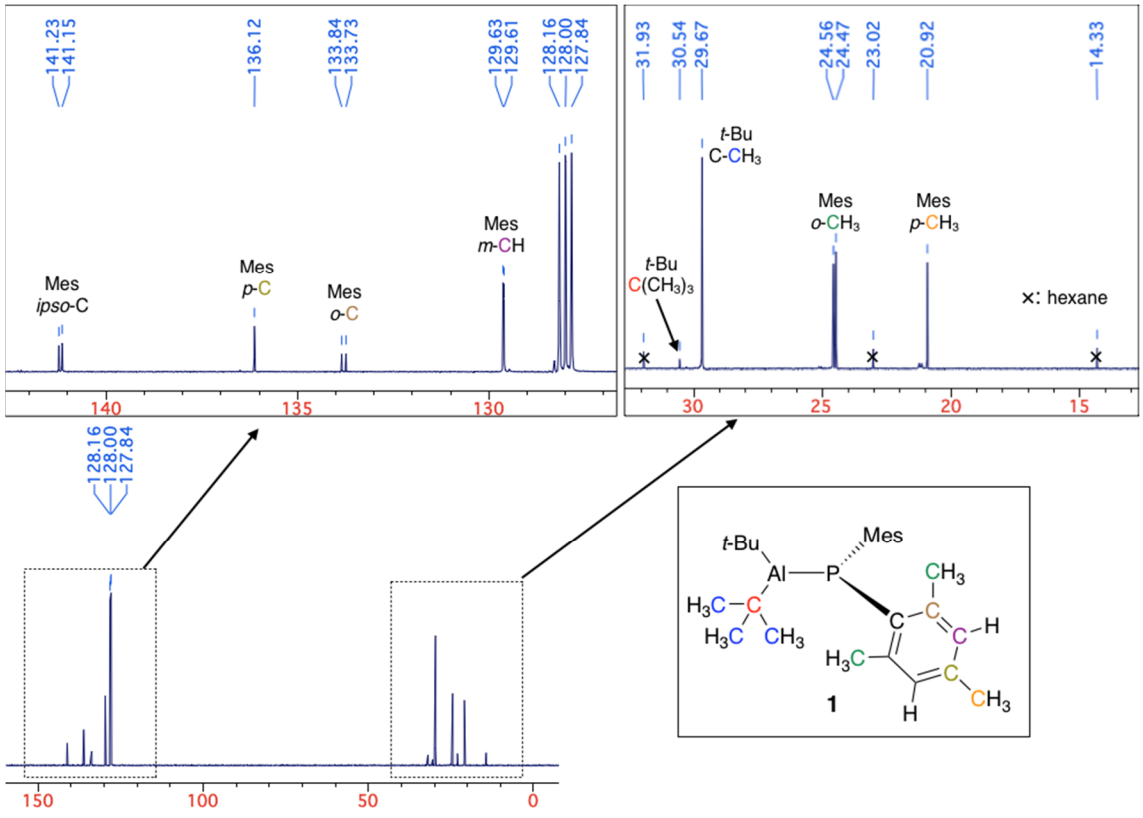

Figure S2. ^{13}C{^{1}H} NMR spectrum of **1** (151 MHz, C_6D_6, 298 K).

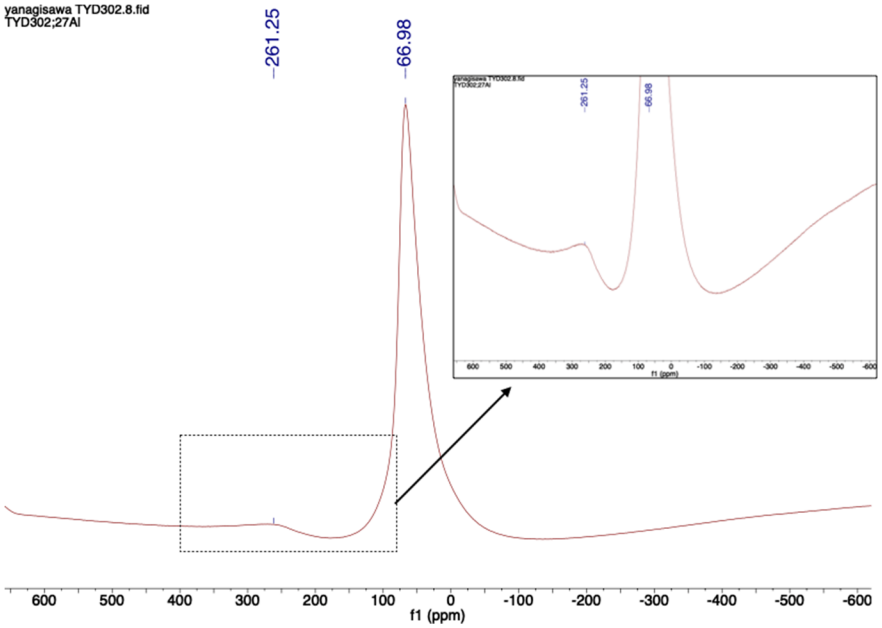

Figure S3. $^{27}Al\{^{1}H\}$ NMR spectrum of **1** (156 MHz, C_6D_6, 298 K).

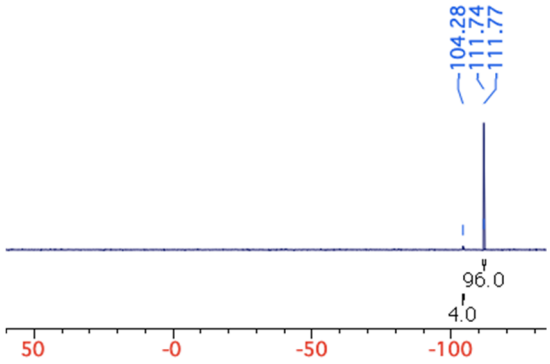

Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum of **1** (242 MHz, C_6D_6, 298 K).

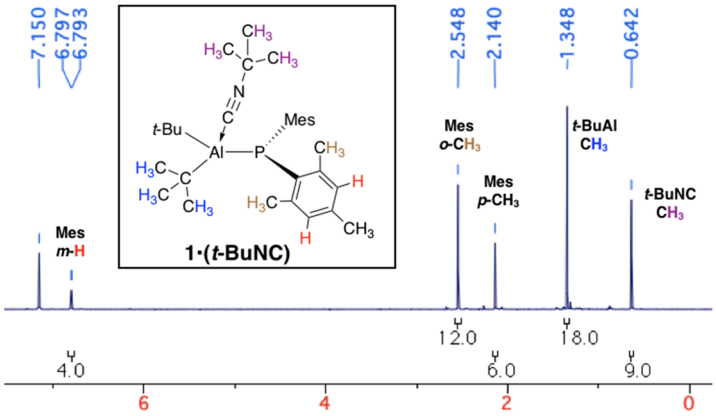

Figure S5. ^{1}H NMR spectrum of **1·(*t*-BuNC)** (600 MHz, C_6D_6, 298 K).

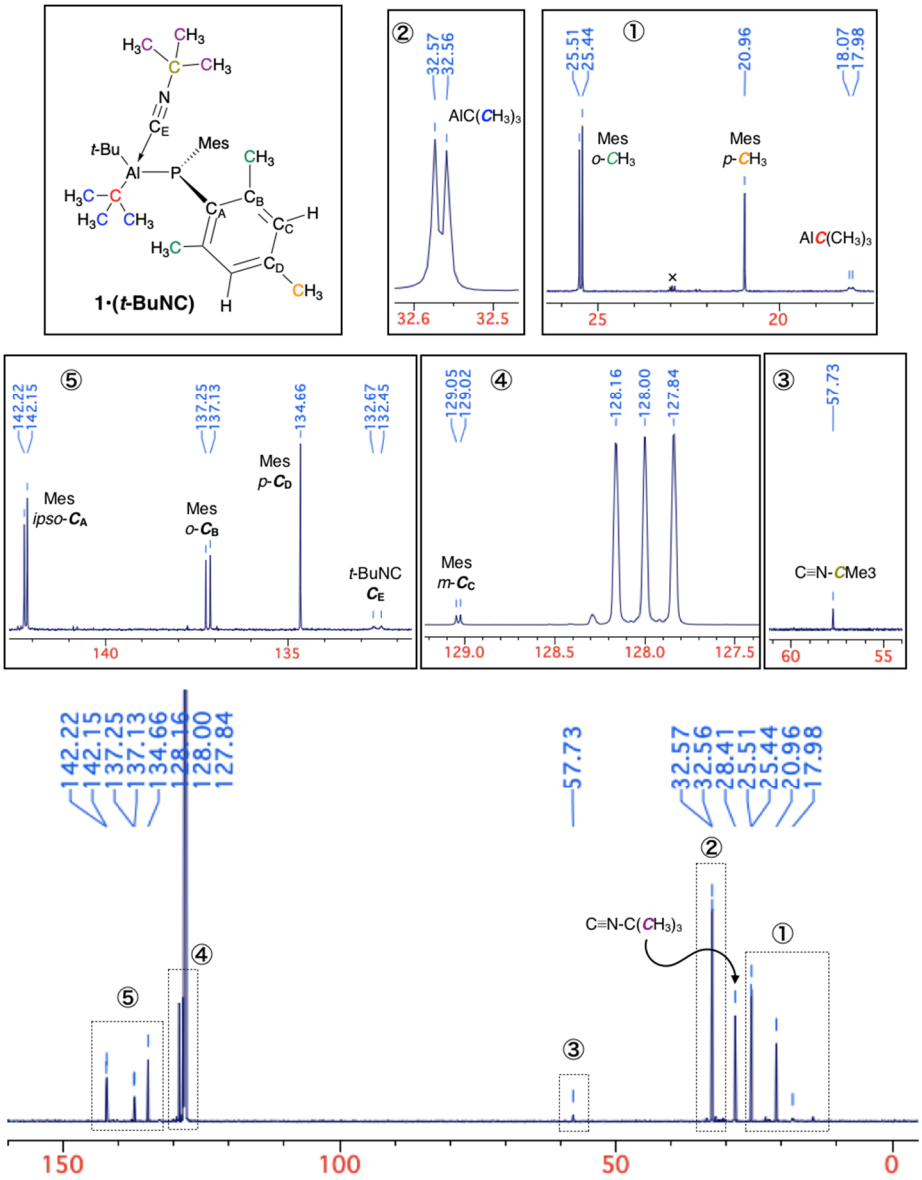

Figure S6. ^{13}C{^{1}H} NMR spectrum of **1·(*t*-BuNC)** (151 MHz, C_6D_6, 298 K).

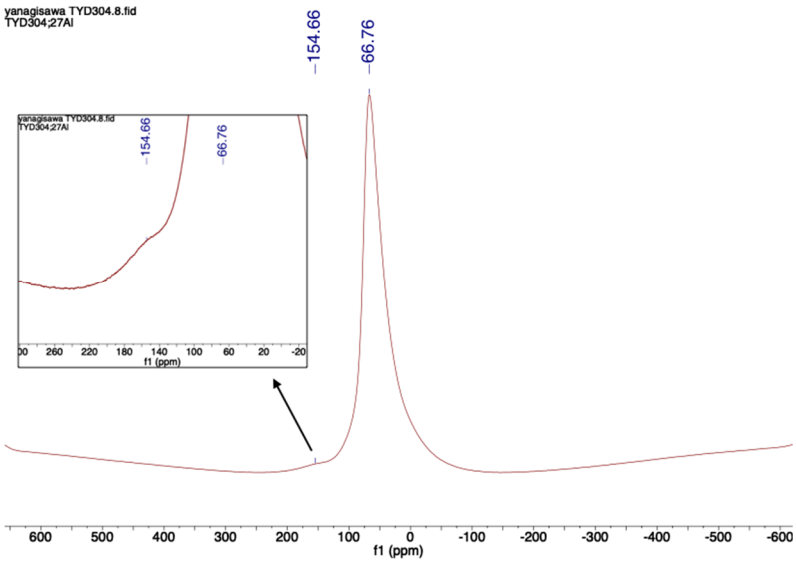

Figure S7. ^{27}Al{^{1}H} NMR spectrum of **1·(*t*-BuNC)** (156 MHz, C_6D_6, 298 K).

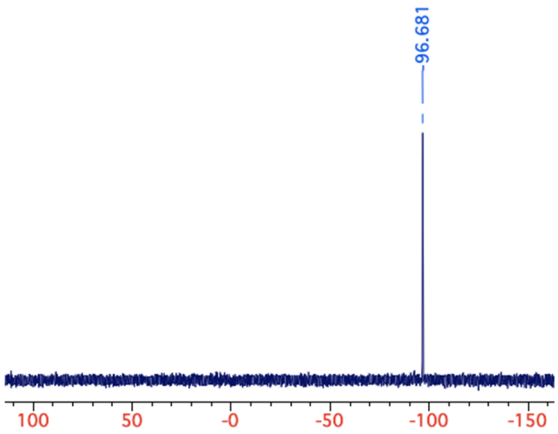

Figure S8. ^{31}P{^{1}H} NMR spectrum of **1·(*t*-BuNC)** (242 MHz, C_6D_6, 298 K).

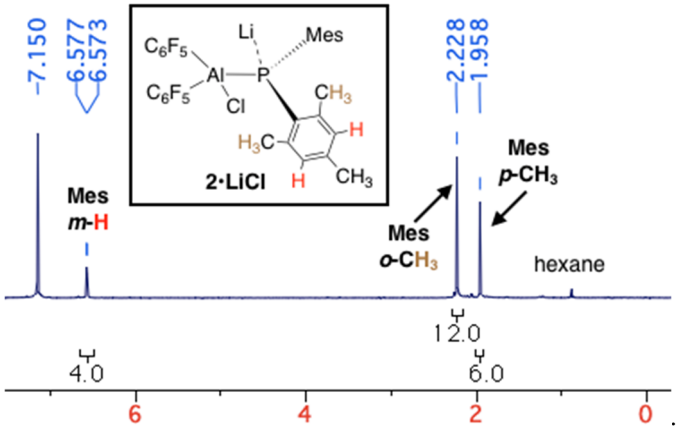

Figure S9. ^{1}H NMR spectrum of **2·LiCl** (600 MHz, C_6D_6, 298 K).

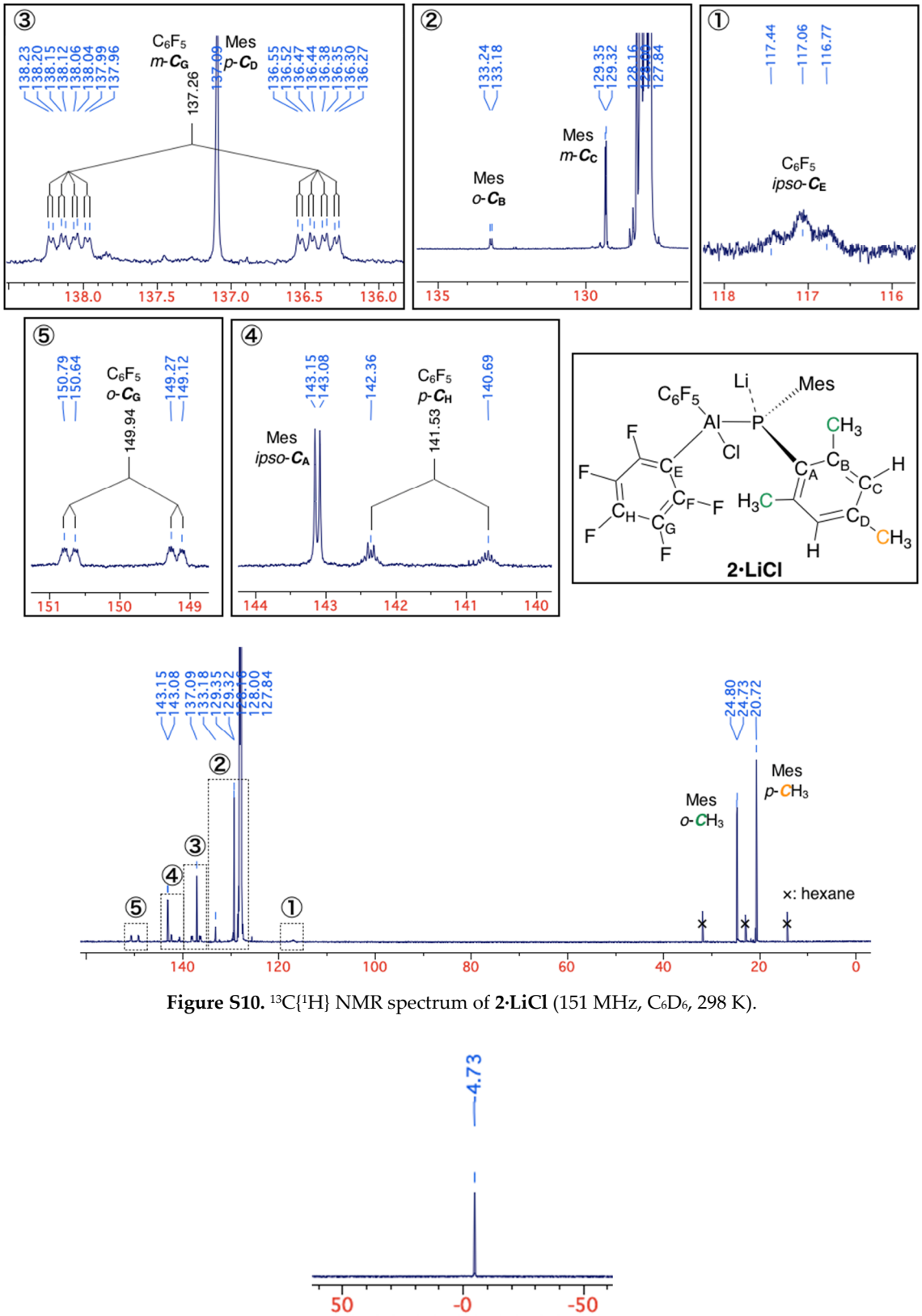

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **2·LiCl** (151 MHz, C_6D_6, 298 K).

Figure S11. $^{7}Li\{^{1}H\}$ NMR spectrum of **2·LiCl** (233 MHz, C_6D_6 298 K).

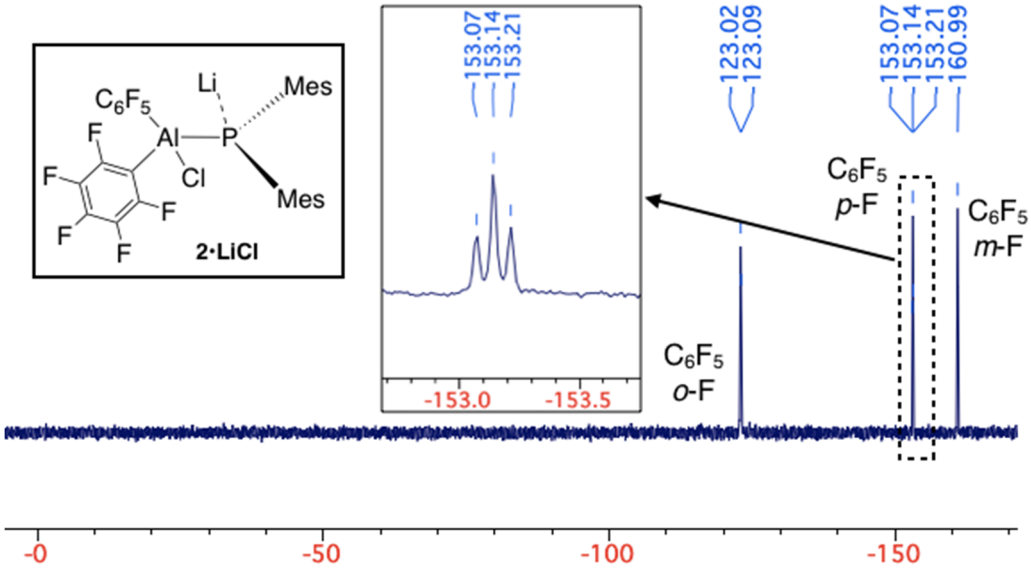

Figure S12. ^{19}F NMR spectrum of **2·LiCl** (282 MHz, C_6D_6, 298 K).

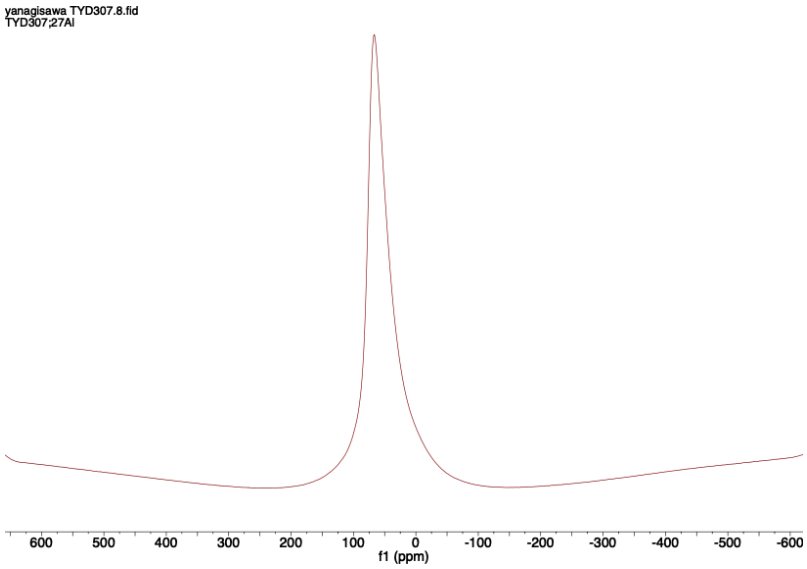

Figure S13. ^{27}Al{^{1}H} NMR spectrum of **2·LiCl** (156 MHz, C_6D_6, 298 K).

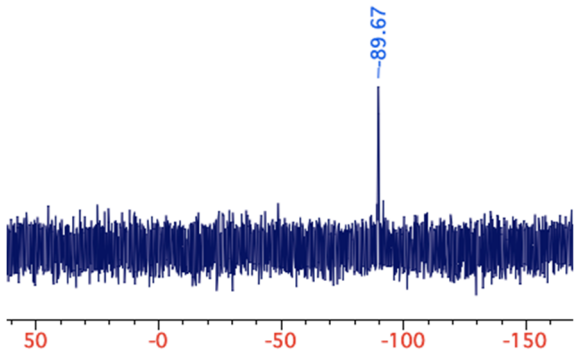

Figure S14. ^{31}P{^{1}H} NMR spectrum of **2·LiCl** (121 MHz, C_6D_6, 298 K).

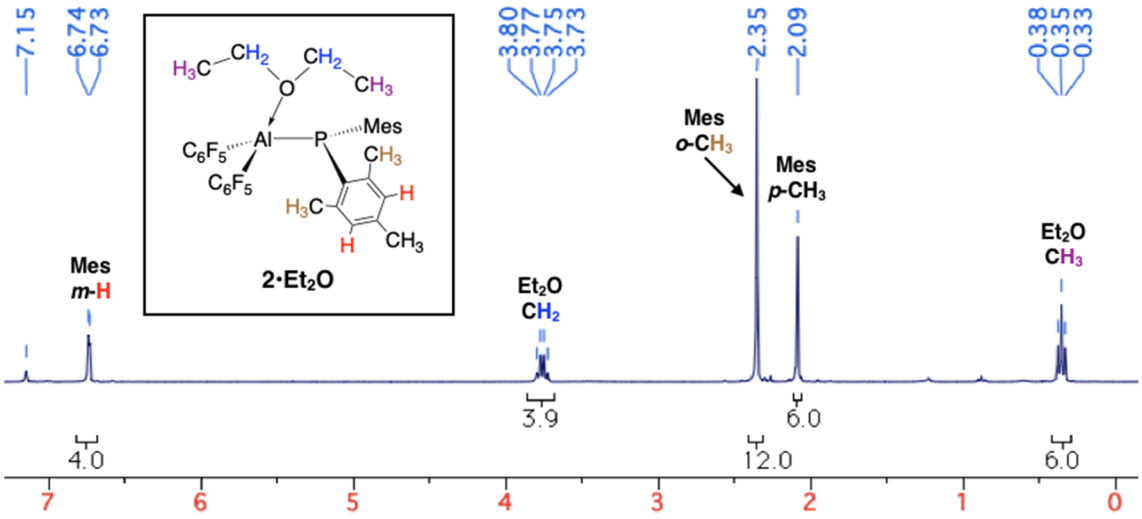

Figure S15. ^{1}H NMR spectrum of **2·Et₂O** (300 MHz, C_6D_6, 298 K).

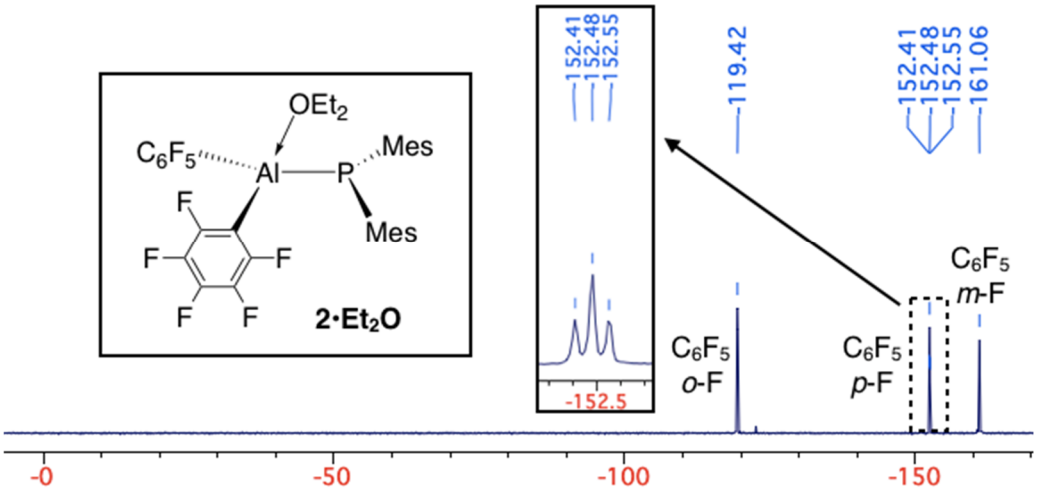

Figure S16. ^{19}F NMR spectrum of **2·Et₂O** (282 MHz, C_6D_6, 298 K).

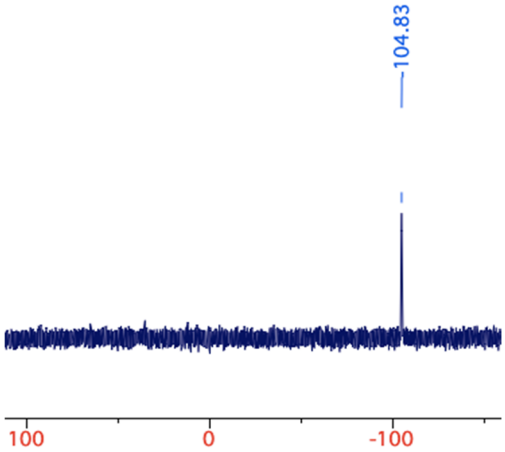

Figure S17. ^{31}P{^{1}H} NMR spectrum of **2·Et₂O** (121 MHz, C_6D_6, 298 K).

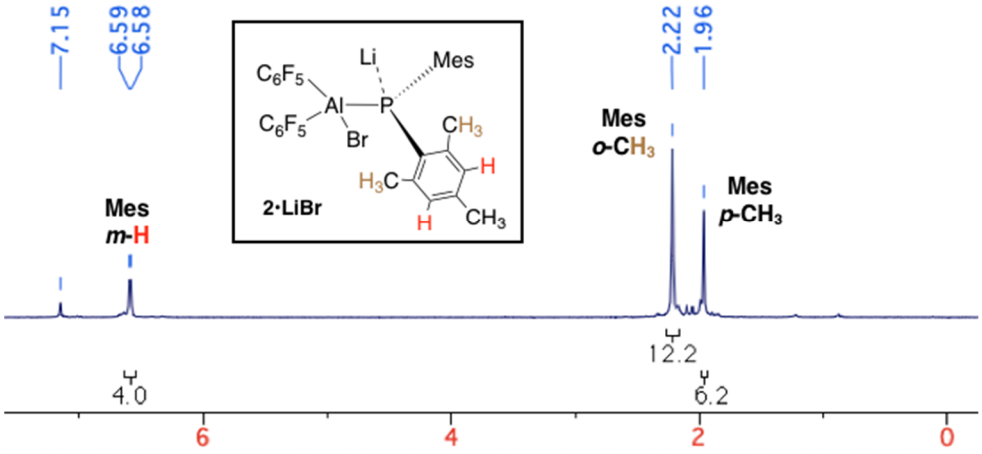

Figure S18. ^{1}H NMR spectrum of a crude material **2·LiBr** (300 MHz, C_6D_6, 298 K).

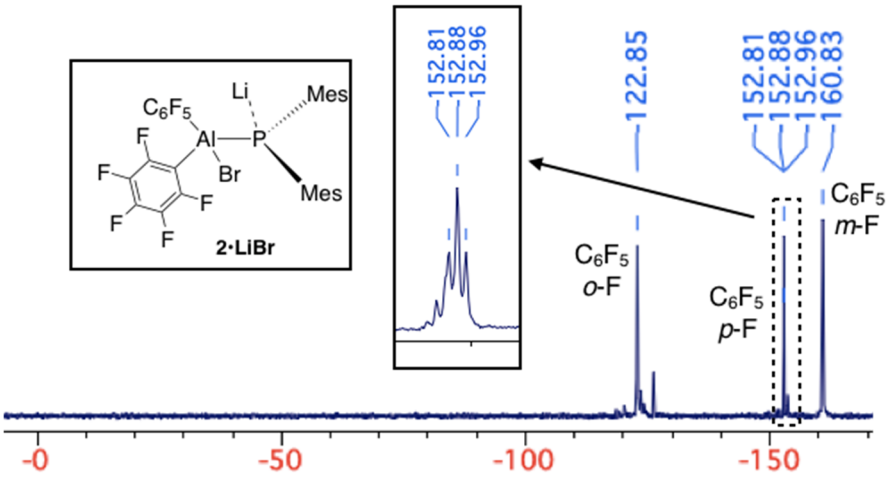

Figure S19. ^{19}F NMR spectrum of a crude material **2·LiBr** (282 MHz, C_6D_6, 298 K).

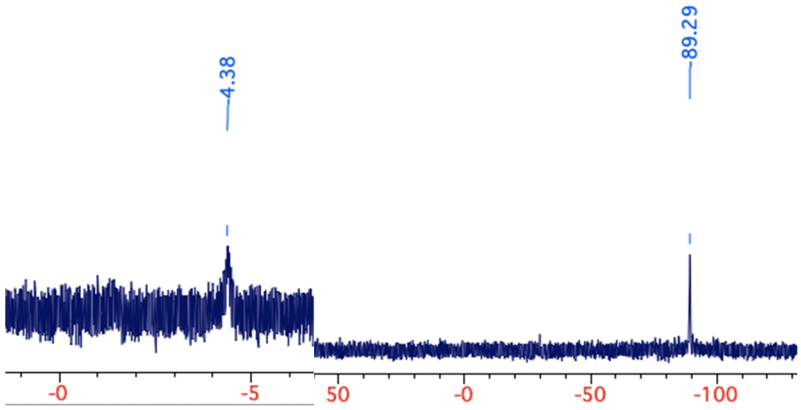

Figure S20. ^{7}Li{^{1}H} (left, 117 MHz) and ^{31}P{^{1}H} (right, 121 MHz) NMR spectrum of a crude material **2·LiBr** (C_6D_6, 298 K).

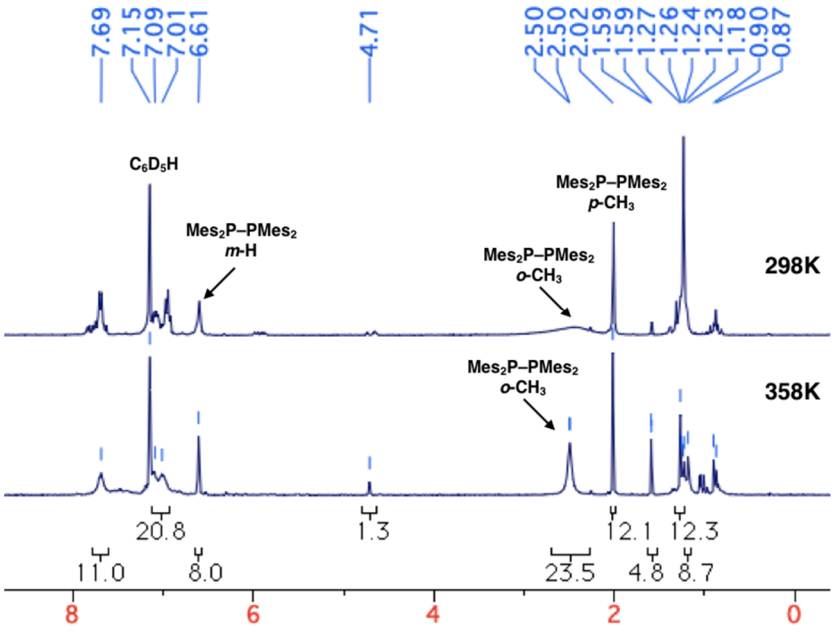

Figure S21. ^{1}H NMR spectrum of the reaction mixture of **1** and benzophenone (300 MHz, C_6D_6, 298 and 358 K). Due to the broadening of *o*-CH_3 parts in Mes groups, ^{1}H NMR spectrum was also recorded at elevated temperature.

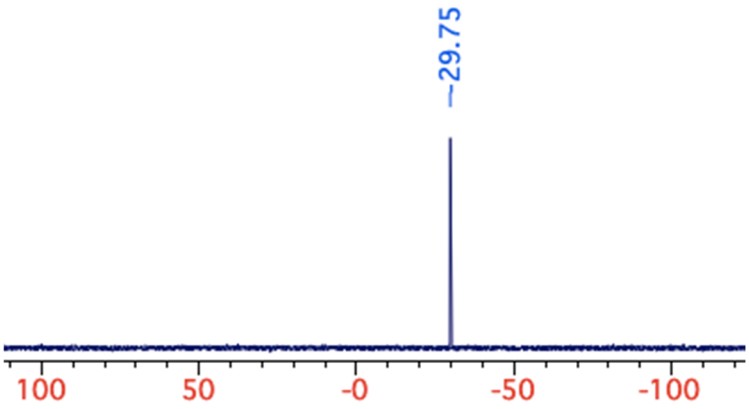

Figure S22. ^{31}P{^{1}H} NMR spectrum of the reaction mixture of **1** with benzophenone (121 MHz, C_6D_6, 298 K).

2. X-Ray Crystallographic Analysis

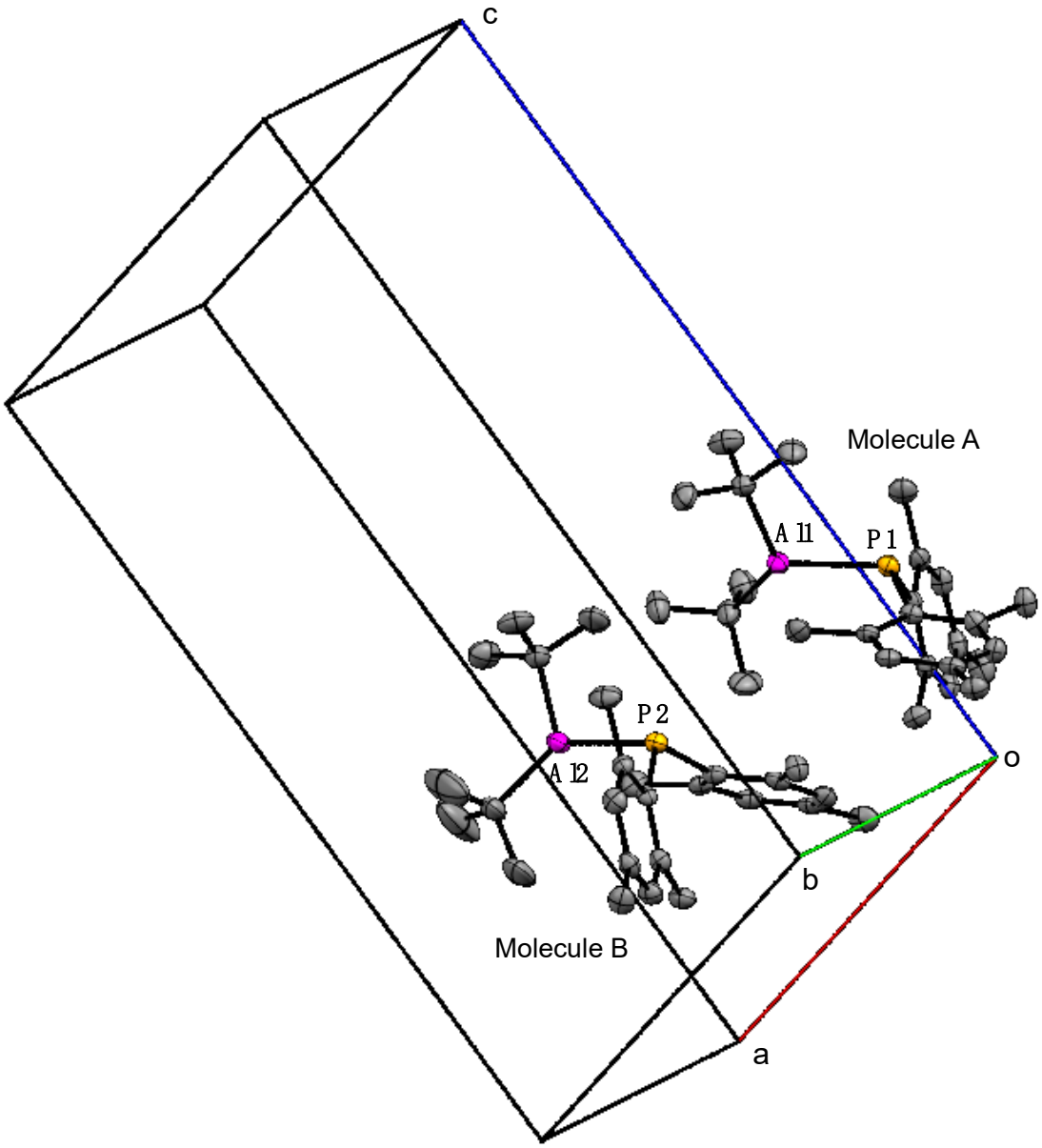

Figure S23. Molecular structure of 1 (right Molecule A, left: Molecule B) at 50% probability. Two crystallographically independent molecules were found in the unit cell. Hydrogen atoms, solvent molecule and the disorder part of a *t*-Bu group in the Molecule B are omitted for clarity.

Table S1. Crystallographic data for 1, 1·(*t*-BuNC), 2·LiCl, and 2·Et_2O.

	1	**1·(*t*-BuNC)**	**2·Et_2O**	**2·LiCl**
Empirical formula	$C_{55}H_{87}Al_2P_2$	$C_{31}H_{49}AlNP$	$C_{34}H_{32}AlF_{10}OP$	$C_{40.5}H_{34}AlClF_{10}LiP$
Formula weight	864.14	493.66	704.54	811.01
Temperature (K)	103(2)	103(2)	103(2)	103(2)
Crystal system	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Crystal size (mm)	0.100 × 0.080 × 0.050	0.230 × 0.160 × 0.080	0.120 × 0.100 × 0.100	0.120 × 0.100 × 0.100
Space group	*P*–1 (#2)	$P2_1/c$ (#14)	$P2_12_12_1$ (#19)	$P2_1/c$ (#14)
a (Å)	8.4522(1)	19.9406(6)	12.6870(4)	27.6951(9)
b (Å)	15.9446(3)	8.6565(2)	15.9515(5)	9.7813(3)
c (Å)	20.8805(4)	20.1247(6)	16.0665(5)	14.2023(5)
α (°)	71.211(2)	90	90	90
b (°)	85.691(2)	116.119(4)	90	103.951(3)
γ (°)	89.948(2)	90	90	90
V (Å^3)	2655.71(8)	3119.01(18)	3251.48(18)	3733.8(2)
Z	2	4	4	4
$D_{calcd.}$ (g·cm^{-3})	1.081	1.051	1.439	1.443
μ (mm^{-1})	0.148	0.134	0.197	0.249
F(000)	946	1080	1448	1660
θ range (°)	1.947 to 25.250	2.029 to 25.245	1.799 to 25.248	2.216 to 25.250
Reflections collected	45144	34738	34942	41517
Independent reflections	9579 [R_{int} = 0.0475]	5641 [R_{int} = 0.0272]	5889 [R_{int} = 0.0560]	6745 [R_{int} = 0.0752]
Completeness to θ_{max}	99.6%	99.8%	100%	99.8%
Data / restraints / parameters	9579 / 6 / 573	1850 / 0 / 322	5889 / 0 / 432	6745 / 0 / 531
Goodness of fit	1.144	1.035	1.048	1.050
R_1 [$I > 2\sigma(I)$]	0.0562	0.0381	0.0336	0.0841
wR_2 [$I > 2\sigma(I)$]	0.1261	0.0979	0.0678	0.2126
R_1 (all data)	0.0795	0.0439	0.0437	0.0947
wR_2 (all data)	0.1338	0.1028	0.0714	0.2188
Largest diff. peak (e·Å)	0.510	0.720	0.253	1.139
Largest diff. hole (e·Å)	−0.469	−0.236	−0.174	−0.441
CCDC number	1959322	1959323	1959324	1959325

3. Computational Studies

Coordinates (xyz) for the Calculated Structures

Table S2. λ^3,λ^3-phosphanylalumane (**2**).

2	−1718544.8416 kcal·mol^{-1}										
Atom	***x***	***y***	***z***	**Atom**	***x***	***y***	***z***	**Atom**	***x***	***y***	***z***
P	−0.1636	1.4709	−1.232	C	4.6865	−2.0955	0.2846	C	−1.1061	−0.2113	−3.6199
Al	0.8639	−0.1832	0.0322	C	5.5606	−1.1456	−0.2416	H	−0.8341	0.7986	−3.9415
F	−0.2827	−2.4966	−1.4117	C	−2.6289	1.3599	1.0509	H	−1.5625	−0.7338	−4.4667
F	3.2857	1.5643	−0.9679	H	−2.7368	2.4348	0.8785	H	−0.1711	−0.7343	−3.384
F	2.5261	−2.74	0.8887	H	−1.6556	1.2159	1.5277	C	−1.9756	3.8229	−2.0466
F	−0.5921	−0.6145	2.9085	H	−3.3918	1.0543	1.7735	H	−2.7595	3.0622	−1.9511
F	5.9201	1.0032	−1.1636	C	−0.7457	5.4554	1.1683	H	−1.3094	3.488	−2.851
F	6.8632	−1.4179	−0.3344	C	3.3305	−1.7891	0.374	H	−2.4495	4.7571	−2.3627
F	5.1581	−3.2794	0.6923	C	−2.1276	−2.2784	2.2625	C	−2.6166	−3.1436	1.2839
F	−2.4911	−4.036	−0.9022	C	−1.2218	4.0126	−0.7504	C	−4.0805	−1.1188	−1.4332
F	−2.7519	−2.1864	3.4439	C	−1.398	5.2039	−0.0402	C	−3.1672	−1.0408	−2.4825
F	−3.7181	−3.8669	1.5178	H	−2.0659	5.9602	−0.4482	H	−3.311	−1.6701	−3.3581
C	−0.8684	−2.4442	−0.1859	C	−0.3693	3.009	−0.2244	C	−0.9282	6.7658	1.8956
C	5.0766	0.0919	−0.6653	C	0.1049	4.4663	1.6643	H	−0.2221	7.5226	1.5285
C	−0.36	−1.5506	0.7465	H	0.6242	4.6394	2.6046	H	−0.7569	6.6554	2.9718
C	3.7135	0.3484	−0.5582	C	0.3068	3.2564	0.993	H	−1.9373	7.167	1.7516
C	−1.8181	0.5975	−1.2839	C	−2.0517	−0.1954	−2.4366	C	−5.2079	−2.1217	−1.4394
C	2.7953	−0.567	−0.0403	C	1.2464	2.2544	1.6206	H	−6.1163	−1.7127	−0.9834
C	−2.7647	0.559	−0.2243	H	0.7314	1.3013	1.8561	H	−4.9238	−3.012	−0.8635
C	−1.0103	−1.5011	1.9697	H	1.6307	2.6088	2.5823	H	−5.4514	−2.4512	−2.4546
C	−3.873	−0.2861	−0.3314	H	2.1146	2.0566	0.9846				
H	−4.5812	−0.3218	0.4943	C	−1.9838	−3.2369	0.0455				

Table S3. Anion part of 2·LiCl ($2Cl^-$).

$2Cl^-$	−2007201.5083 kcal·mol^{-1}									
Atom	***x***	***y***	***z***	**Atom**	***x***	***y***	***z***	**Atom**	***x***	***y***	***z***
Al	0.6369	0.3775	0.7642	H	−3.9888	−2.4646	1.4546	C	2.7025	2.1138	−0.7166
P	−1.0866	1.0098	−0.7986	C	−3.1565	−3.191	−0.3842	F	3.4368	−0.3601	1.7918
Cl	0.4004	0.7893	2.9106	C	−2.3946	−2.8344	−1.4978	F	5.932	0.461	1.1993
C	−2.2711	2.3774	−0.3755	H	−2.2038	−3.5795	−2.269	F	6.3263	2.3998	−0.6887
C	−1.8749	3.519	0.3702	C	−1.8462	−1.5568	−1.6429	F	4.1836	3.5025	−1.978
C	−2.7925	4.5447	0.6185	C	−3.1542	0.0513	1.6013	F	1.6938	2.6985	−1.4082
H	−2.4652	5.402	1.2054	H	−3.8491	0.8348	1.2779	C	0.7153	−1.6304	0.4931
C	−4.1031	4.5102	0.1425	H	−2.2504	0.5567	1.9514	C	−0.0156	−2.5417	1.2536
C	−4.4606	3.4262	−0.6571	H	−3.5982	−0.4701	2.4555	C	−0.0923	−3.9005	0.9583
H	−5.4594	3.3955	−1.0916	C	−3.6334	−4.6104	−0.1896	C	0.5954	−4.4008	−0.1413
C	−3.576	2.3796	−0.9443	H	−3.8011	−5.117	−1.1473	C	1.351	−3.5364	−0.926
C	−5.0901	5.6038	0.4764	H	−4.5659	−4.6497	0.3858	C	1.3926	−2.1866	−0.5858
H	−4.5937	6.576	0.5813	H	−2.8813	−5.1868	0.3641	F	−0.7433	−2.1281	2.311
H	−5.6083	5.4033	1.4252	C	−1.0303	−1.2746	−2.888	F	−0.8526	−4.7351	1.6976
H	−5.8607	5.7007	−0.2978	H	−1.3716	−0.3648	−3.3939	F	0.5161	−5.7076	−0.4515
C	−4.0662	1.3086	−1.8948	H	−1.1026	−2.1137	−3.5899	F	2.0089	−4.0111	−2.0019
H	−4.3473	0.3848	−1.3789	H	0.0298	−1.1202	−2.6643	F	2.1019	−1.387	−1.4286
H	−3.2921	1.0353	−2.6206	C	2.4386	1.1433	0.244	C	−0.4714	3.6958	0.8983
H	−4.9424	1.6657	−2.4482	C	3.5703	0.6134	0.8606	H	−0.3351	4.7061	1.2999
C	−2.0478	−0.5828	−0.6294	C	4.8739	1.0096	0.5721	H	0.2776	3.5498	0.1153
C	−2.8573	−0.921	0.4837	C	5.0792	1.9934	−0.3909	H	−0.2517	2.9922	1.7065
C	−3.3964	−2.2103	0.5772	C	3.9857	2.5534	−1.0427				