A Tris(triphenylphosphine)aluminum Ambiphilic Precatalyst for the Reduction of Carbon Dioxide with Catecholborane.

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Figure S1. ^{1}H NMR spectrum of (2), selected regions (500 MHz, C_6D_6)

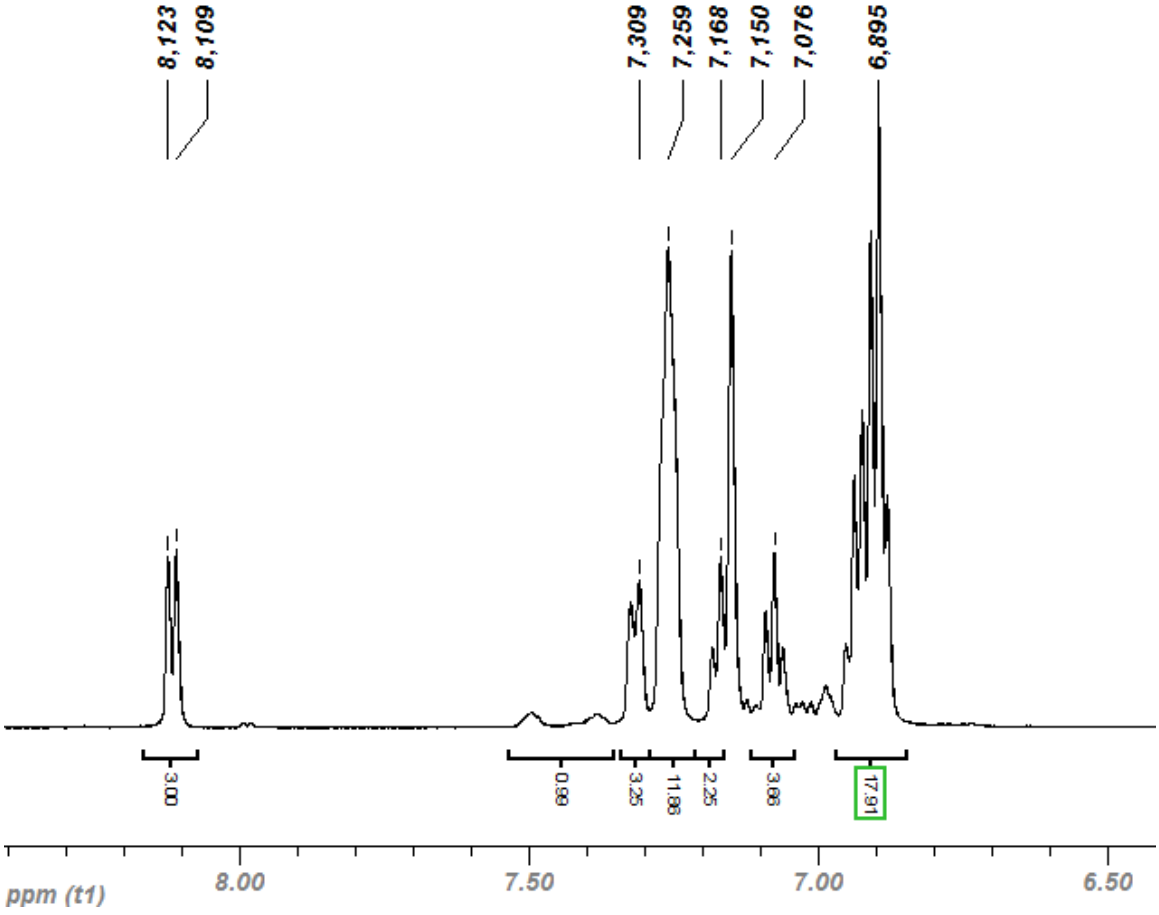

Figure S2. ^{13}C NMR spectrum of (2) (126 MHz, C_6D_6)

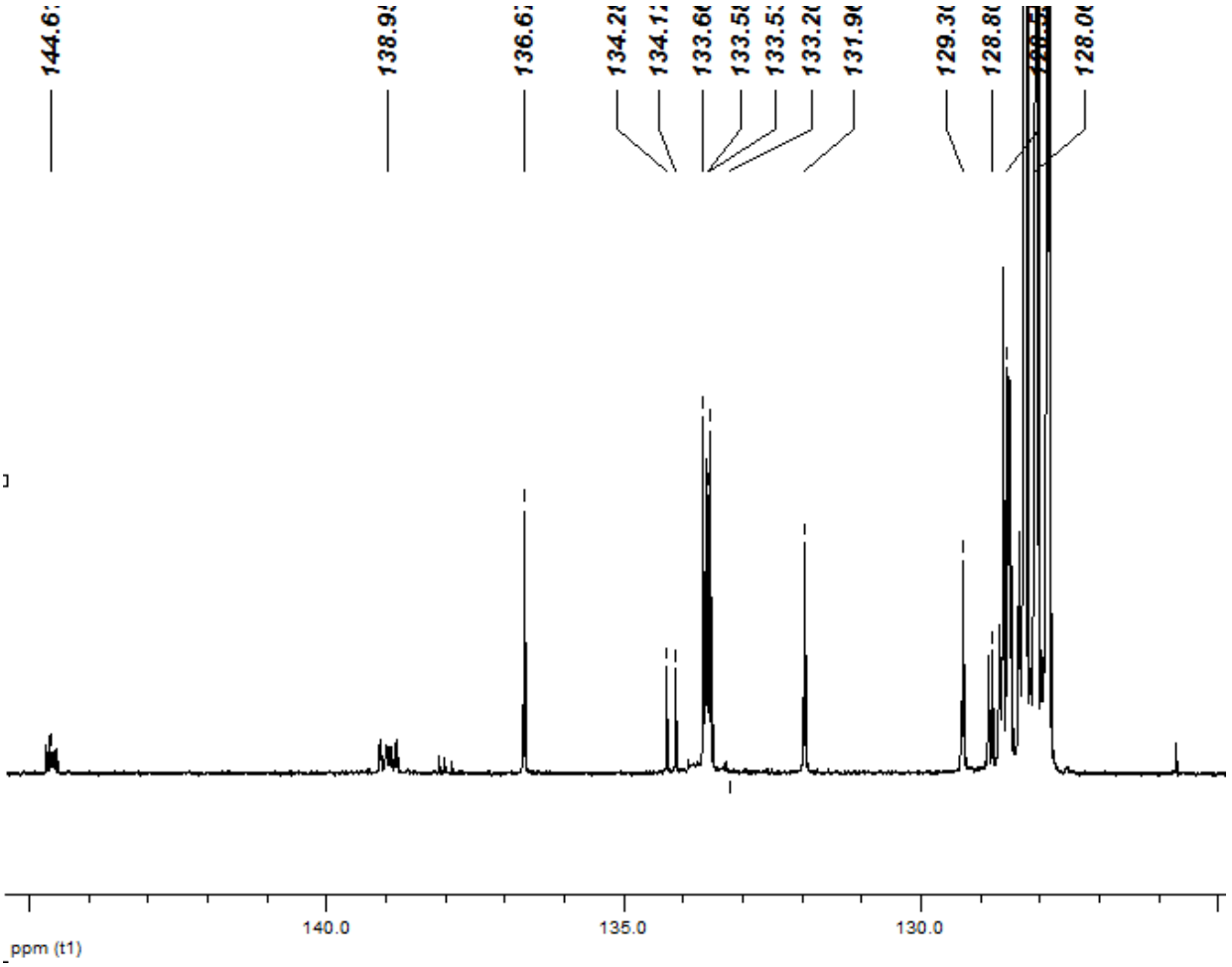

Figure S3. ^{31}P NMR spectrum of (2) (203 MHz, C_6D_6)

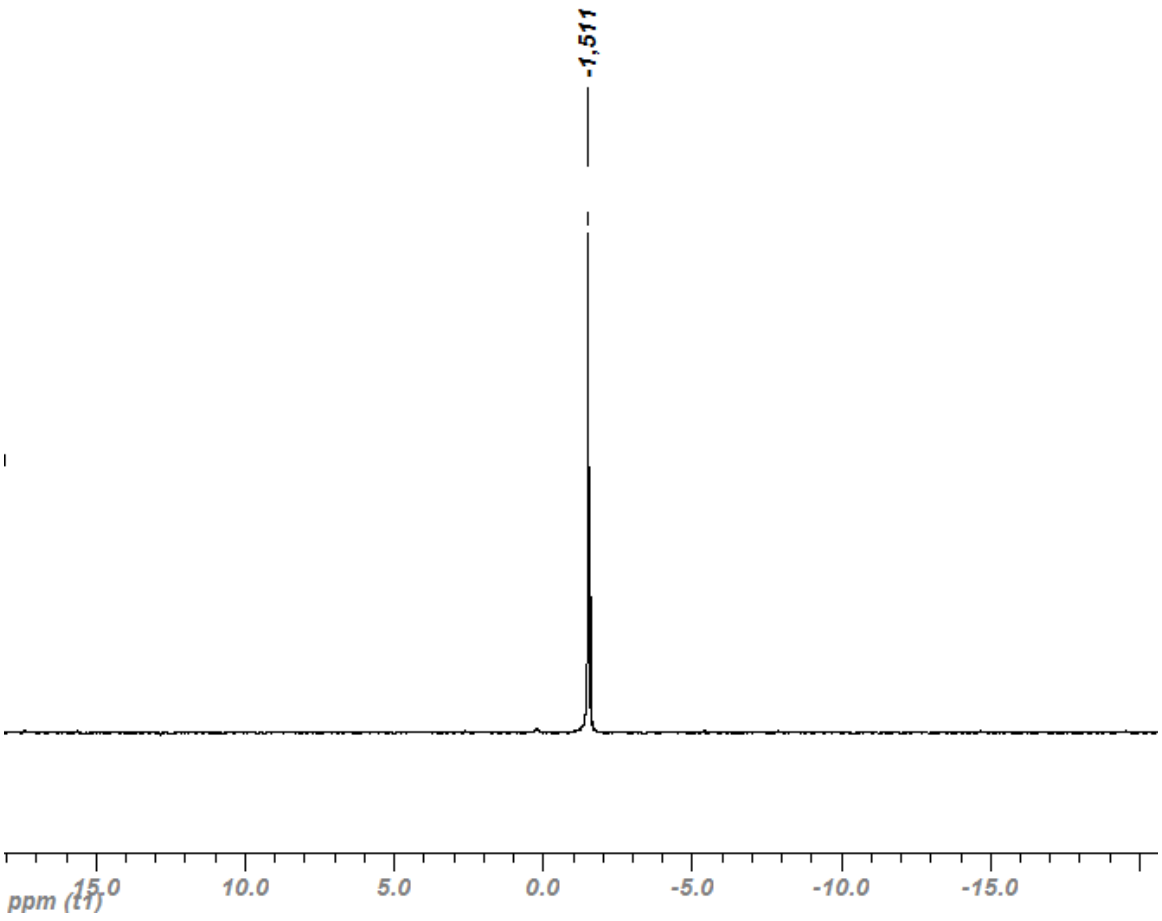

Figure S4. ^{1}H NMR spectrum of (3) (500 MHz, C_6D_6)

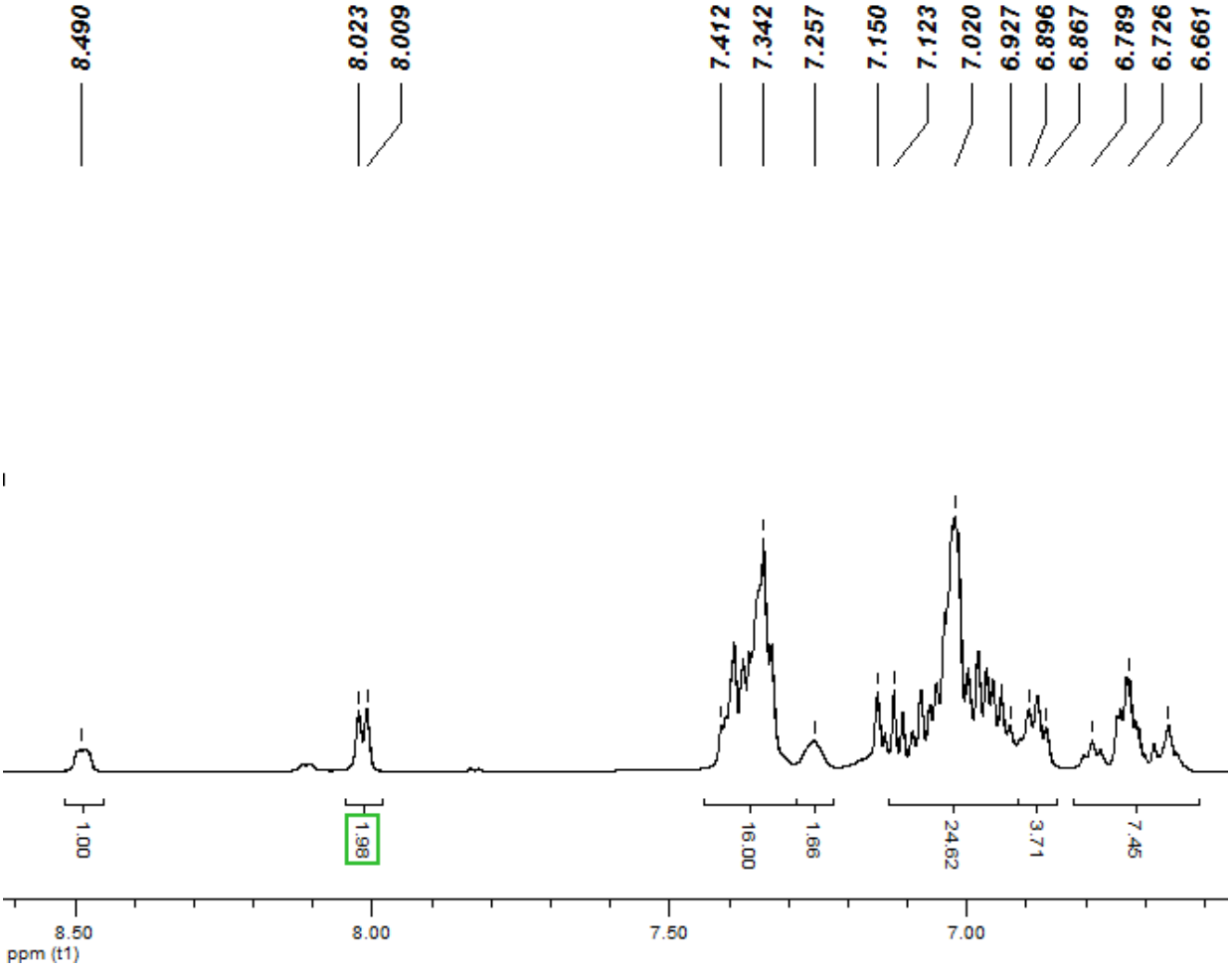

Fig. S5 ^{13}C NMR spectrum of (3) (126 MHz, C_6D_6)

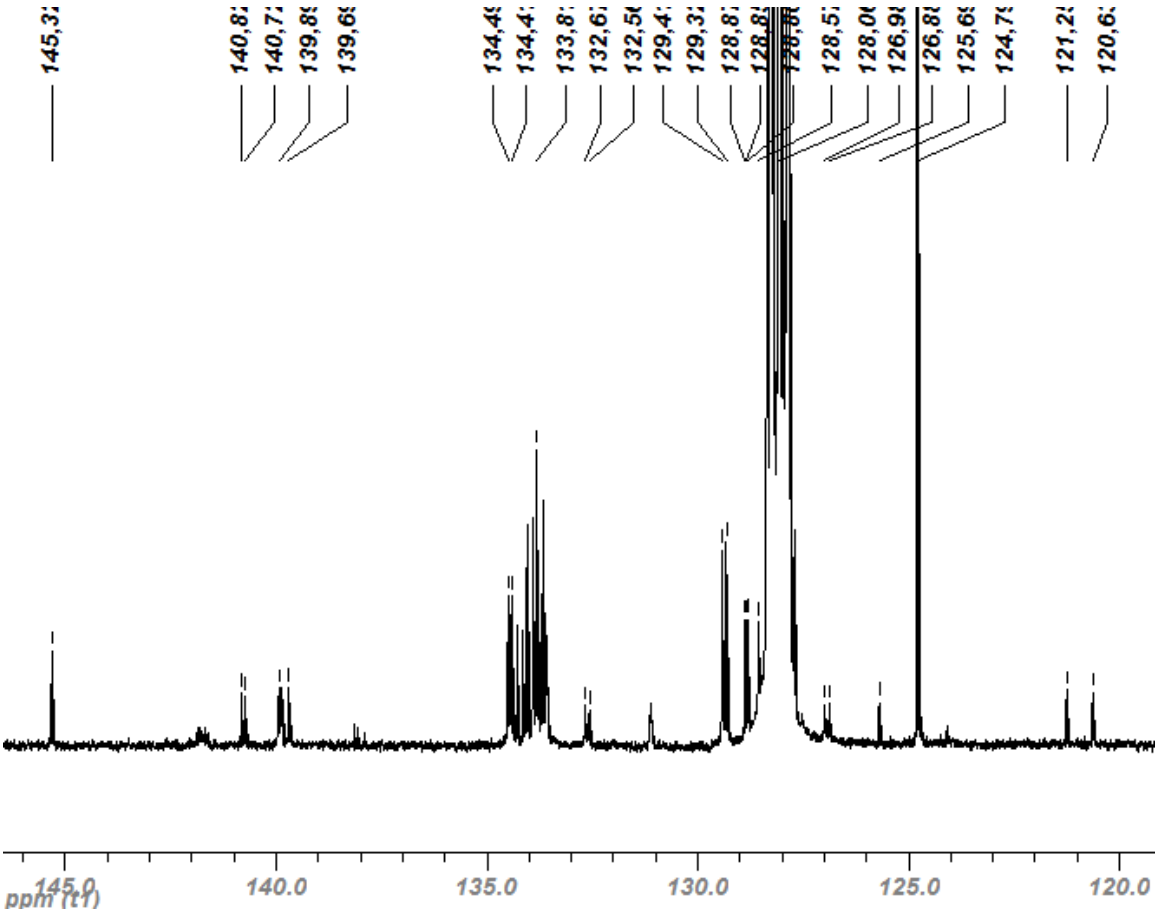

Figure S6. ^{31}P NMR spectrum of (3) (203 MHz, C_6D_6)

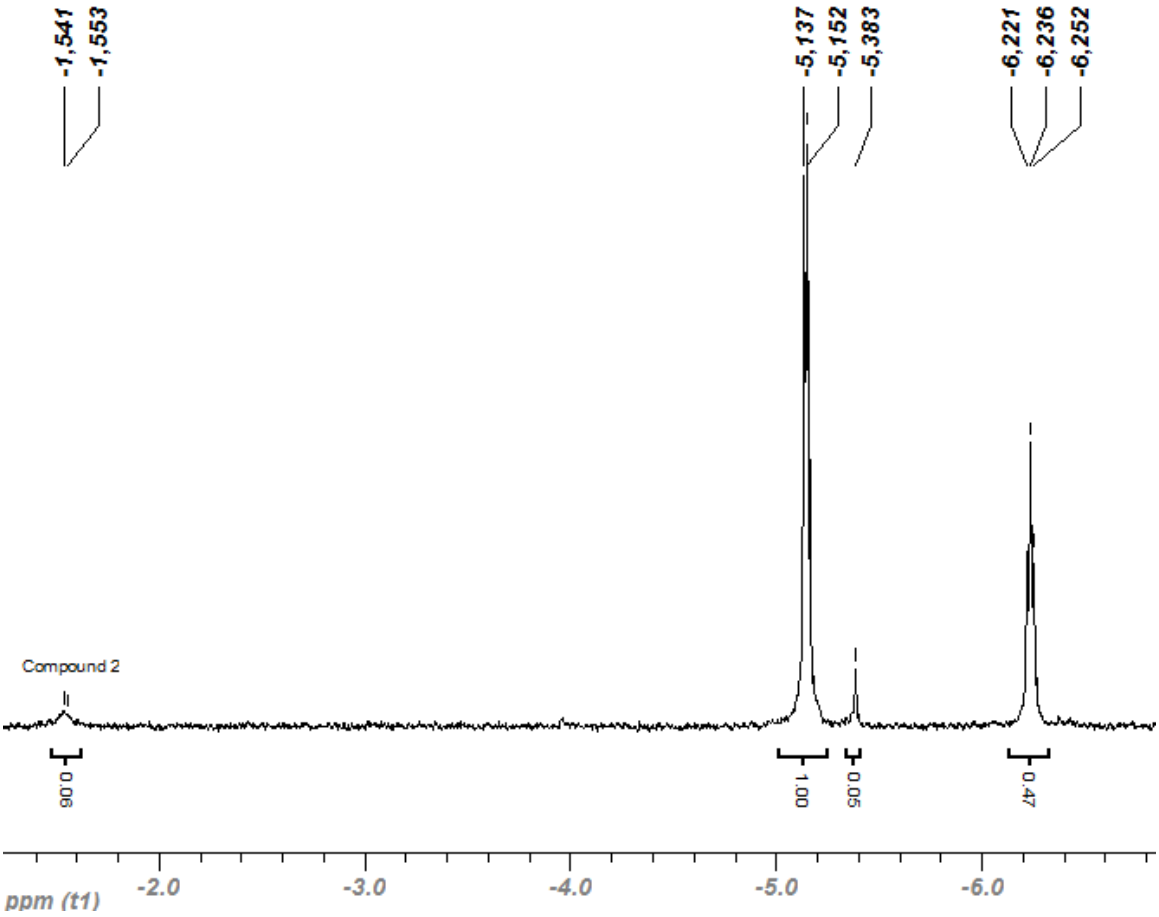

Figure S7. ^{1}H NMR spectrum of (4) (500 MHz, C_6D_6)

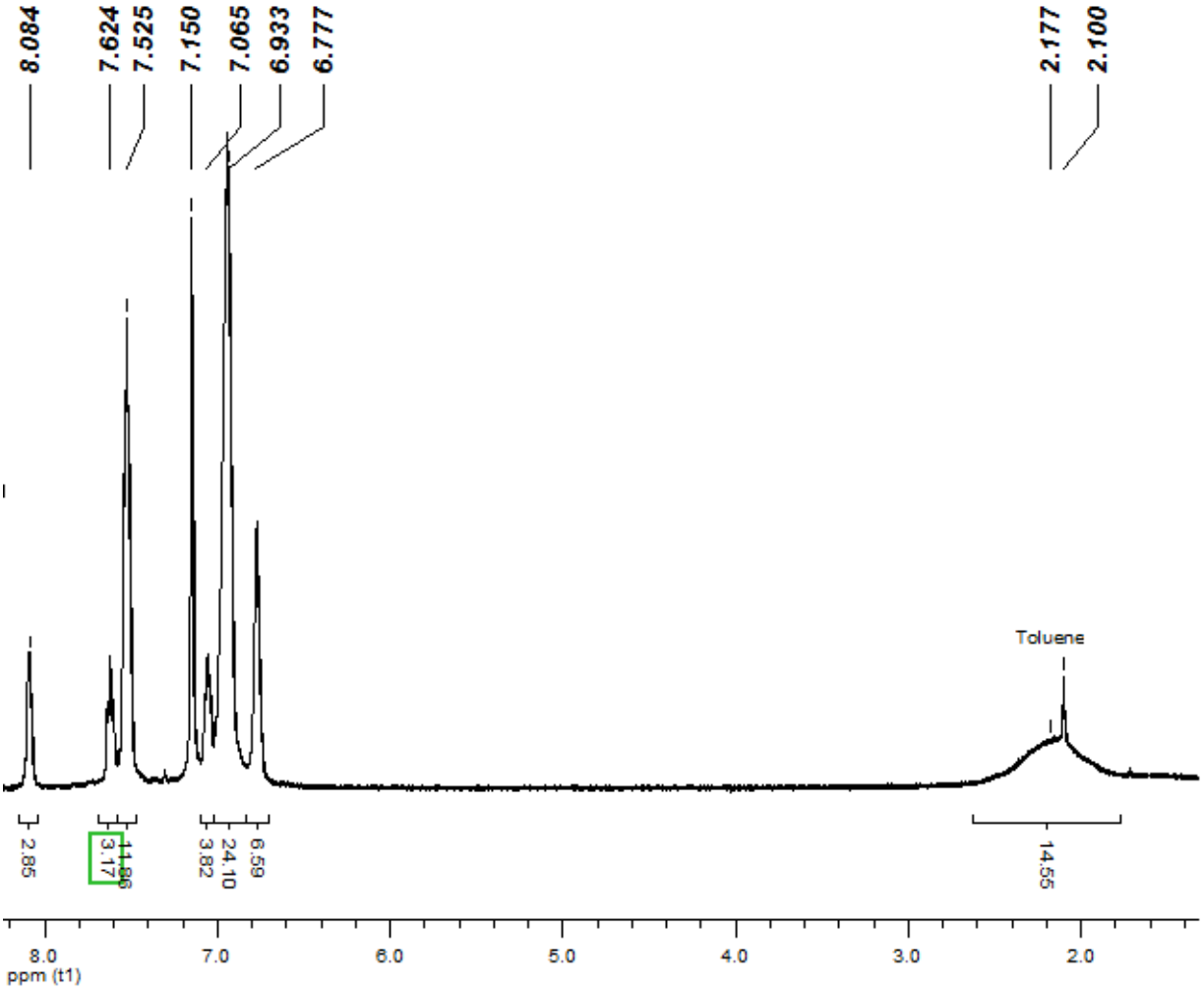

Figure S8. ^{13}C NMR spectrum of (4) (126 MHz, C_6D_6)

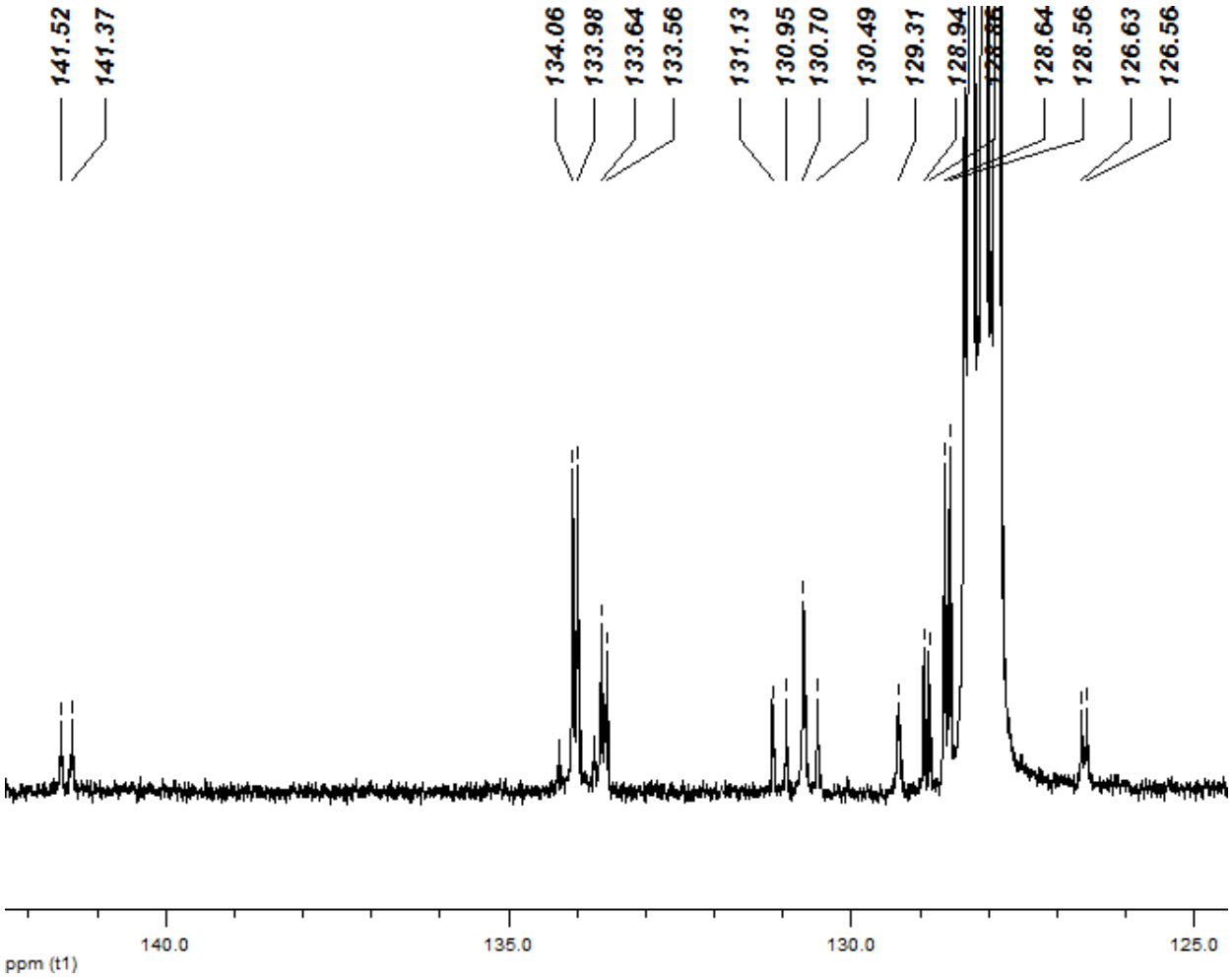

Figure S9. ^{31}P NMR spectrum of (4) (203 MHz, C_6D_6)

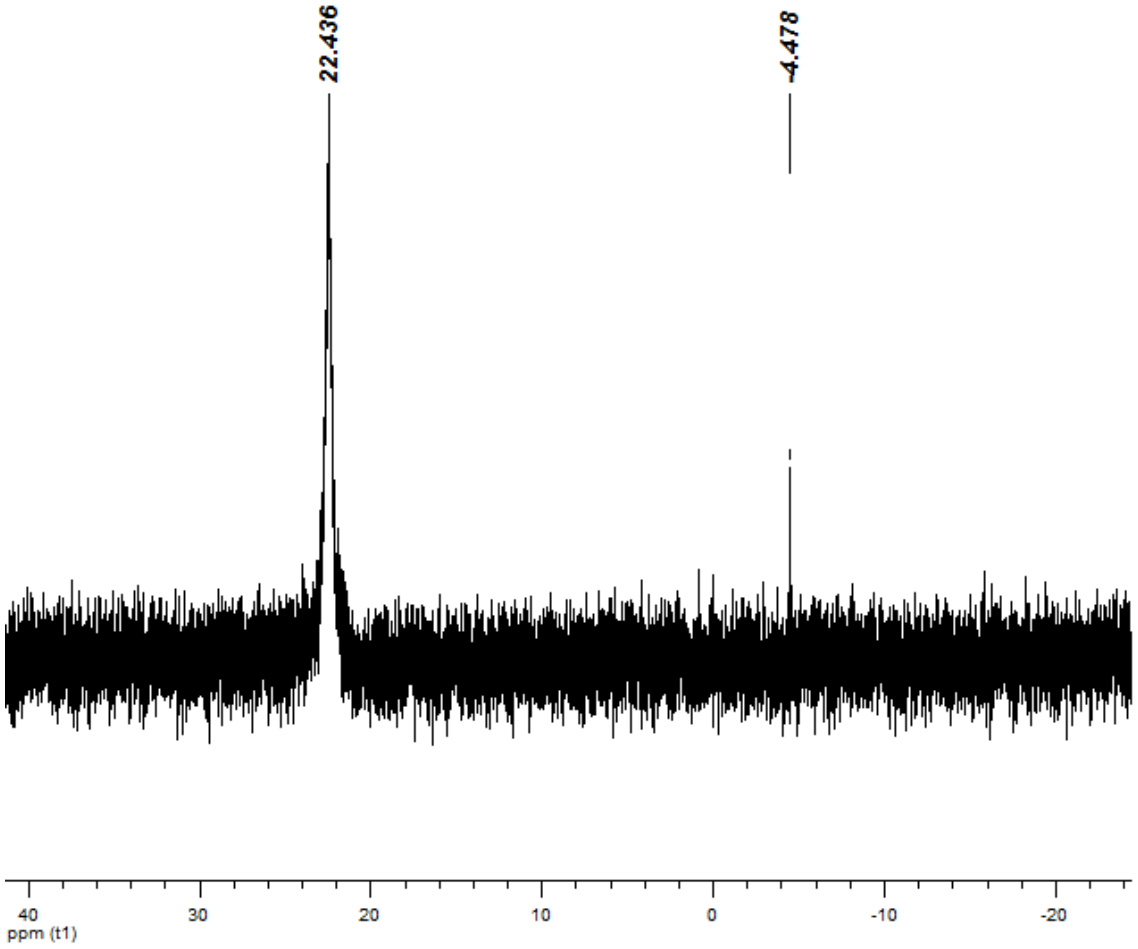

Figure S10. ^{11}B NMR spectrum of (4) (161 MHz, C_6D_6)

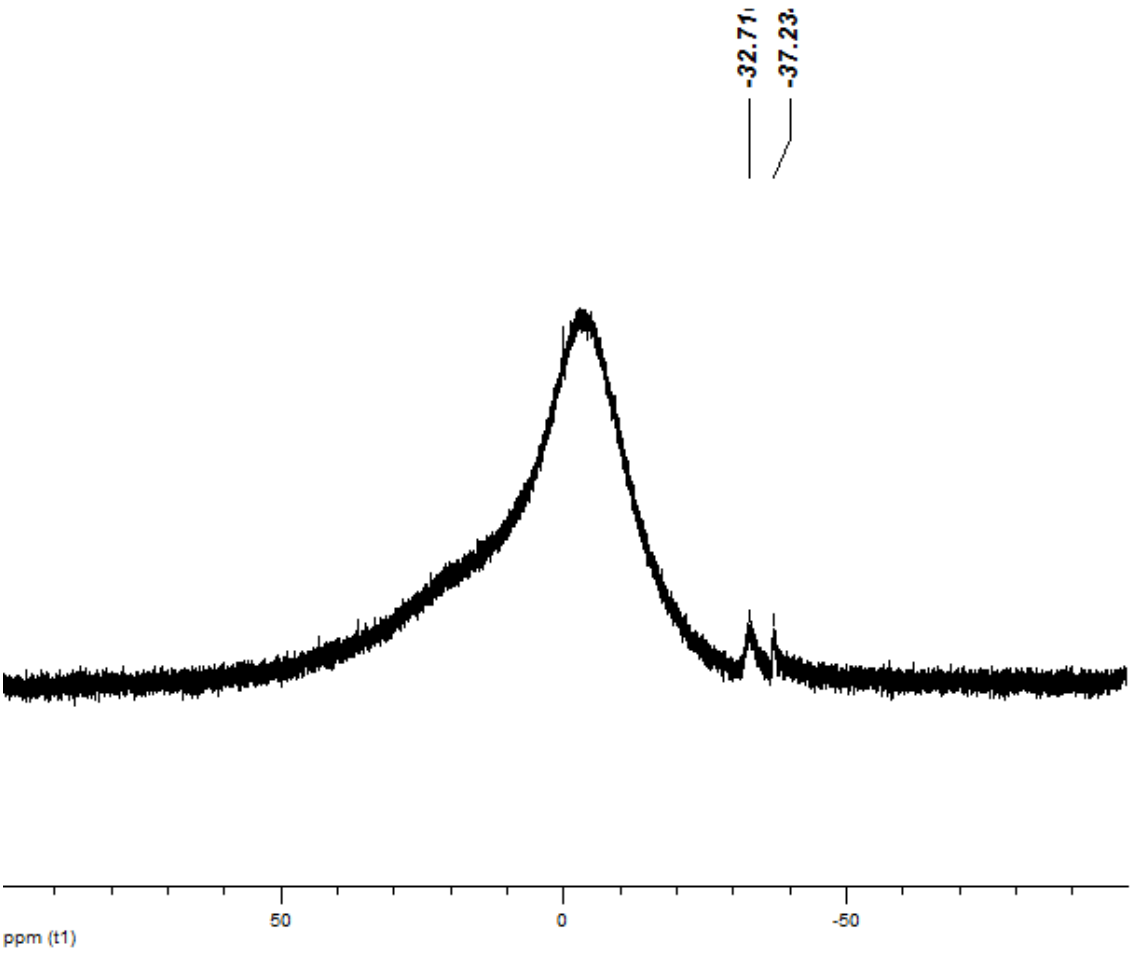

Table S1. Crystal Data and Structural Refinements for Compounds 2 and 5[a]

Compound	**2**	**5**
Formula	$C_{54}H_{42}AlP_3$	$C_{25.75}H_{31.75}O_{16}B_3Al$
M_r (g mol^{-1})	810.77	592.67
Crystal size	0.20 × 0.16 × 0.06	0.42 × 0.40 × 0.38
Crystal color	Colorless	Colorless
Crystal system	Triclinic	Triclinic
Space group	*P* -1	*P* -1
λ (Å)	0.71073	0.71073
T (K)	150(2)	150(2)
a (Å)	11.0020(2)	12.49960(10)
b (Å)	13.1765(2)	13.9779(2)
c (Å)	31.9414(6)	16.8699(2)
α (^{o})	87.5550(10)	95.1040(10)
β (^{o})	82.8900 (10)	96.6310(10)
γ (^{o})	77.3160 (10)	90.8690(10)
V (Å^3)	4482.16(14)	2915.19(6)
Z	4	1
$\rho_{cal.}$ (g cm^{-3})	1.201	1.350
F(000)	1696	1241
μ (mm^{-1})	0.188	0.131
θ for data collection (^{o})	1.9 to 26.4	1.5 to 26.4
Reflection collected	18131	46769
Data /parameters	18131 / 1045	11901 / 770
GOOF	1.049	1.038
$R_1(wR_2)$ ($I > 2\sigma(I)$)	0.0526 (0.1277)	0.0431 (0.1049)
$R_1(wR_2)$ (all data)	0.0878 (0.1402)	0.0615 (0.1151)
largest diff. peak / hole (eÅ^{-3})	0.347 / -0.473	0.384 / -0.303

a $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{0.5}$

Crystallographic data for 2.

A colorless bloc crystal with approximate dimensions of 0.20 x 0.12 x 0.06 mm was mounted on a cryoloop with Paratone-N hydrocarbon oil. The diffraction data were collected at 150(2) K on a Bruker SMART APEX II CCD area detector diffractometer equipped with graphite monochromated MoK_α radiation. Frames were collected using ω and φ scans of 0.5º counted for a total of 20 seconds per frame. An orientation matrix corresponding to cell constants listed in Table S1 was obtained from a least-squares refinement using the measured positions of 9852 centered reflections in the range $2.4º < \theta < 25.8º$. The program used for retrieving cell parameters and data collection was APEX 2. [S3] Data were integrated and reduced using the program SAINT [S4] and the multi-scan absorption correction was performed by using SADABS. The structure was solved in direct methods using SHELXS-97 and refined using the SHELXTL6.14[S5]software package. All non-H atoms were refined anisotropically. The hydrogen atoms were placed in ideal positions and refined in riding mode. The heavily disordered guest molecule of toluene was squeezed out by the routine of SQUEEZE in Platon.

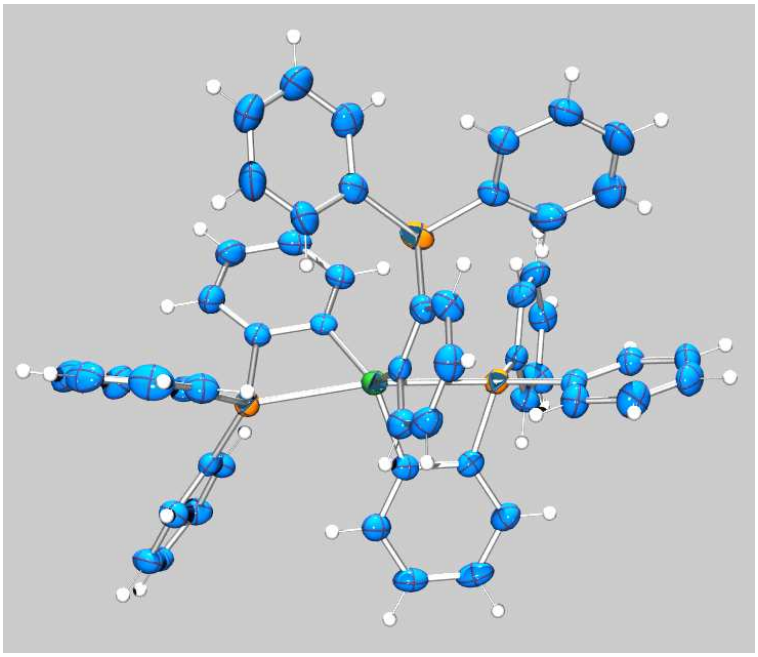

Figure S11. the general ORTEP plot of **2**.

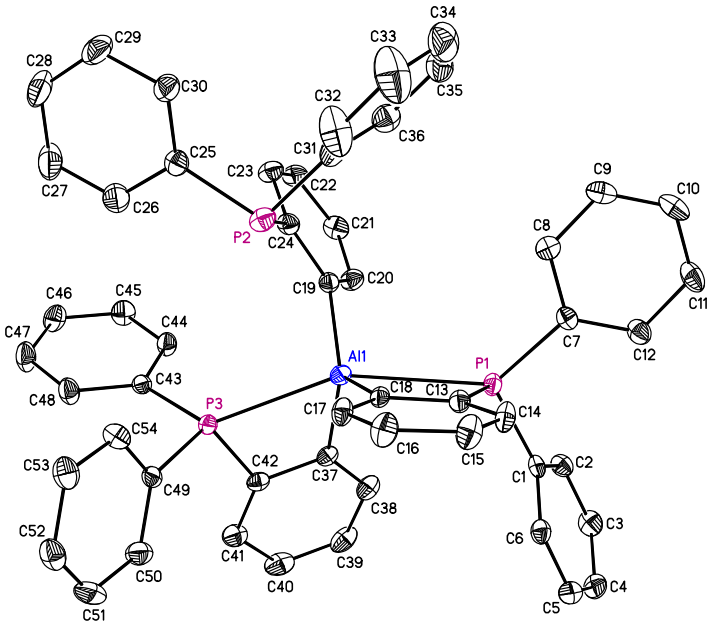

Figure S12 - ORTEP drawing of the first molecule of **2** in the asymmetric unit cell, with anisotropic atomic displacement ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

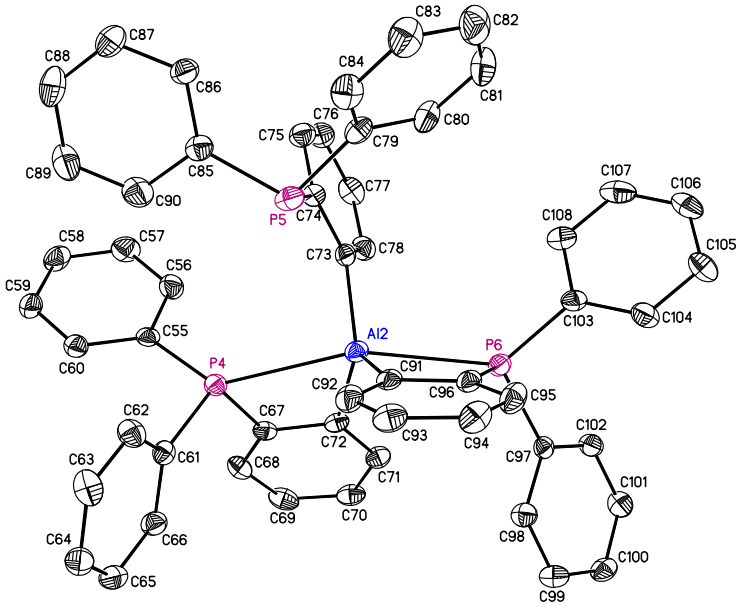

Figure S13 - ORTEP drawing of the second molecule of **2** in the asymmetric unit cell, with anisotropic atomic displacement ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

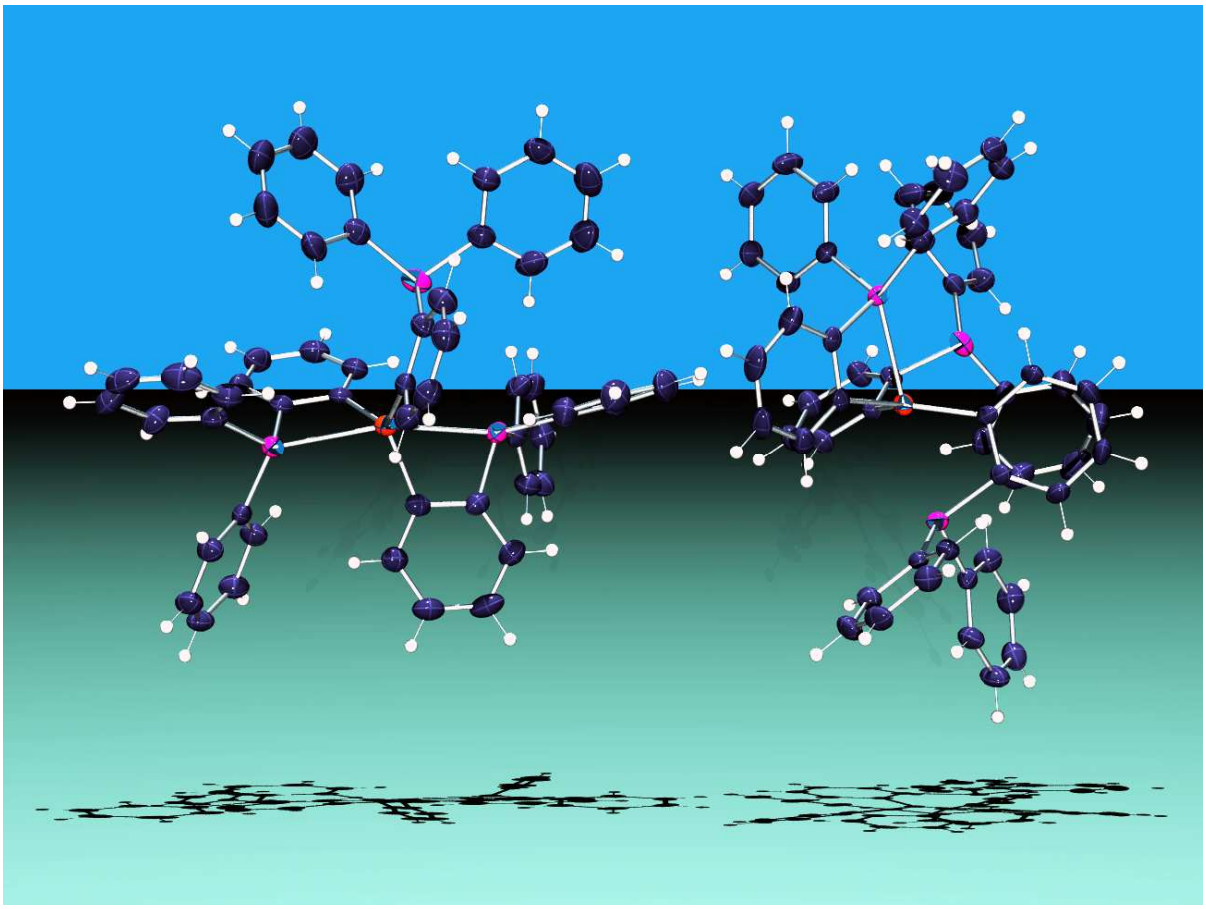

Figure S14 The ORTEP plot of 2 in the asymmetry unit cell.

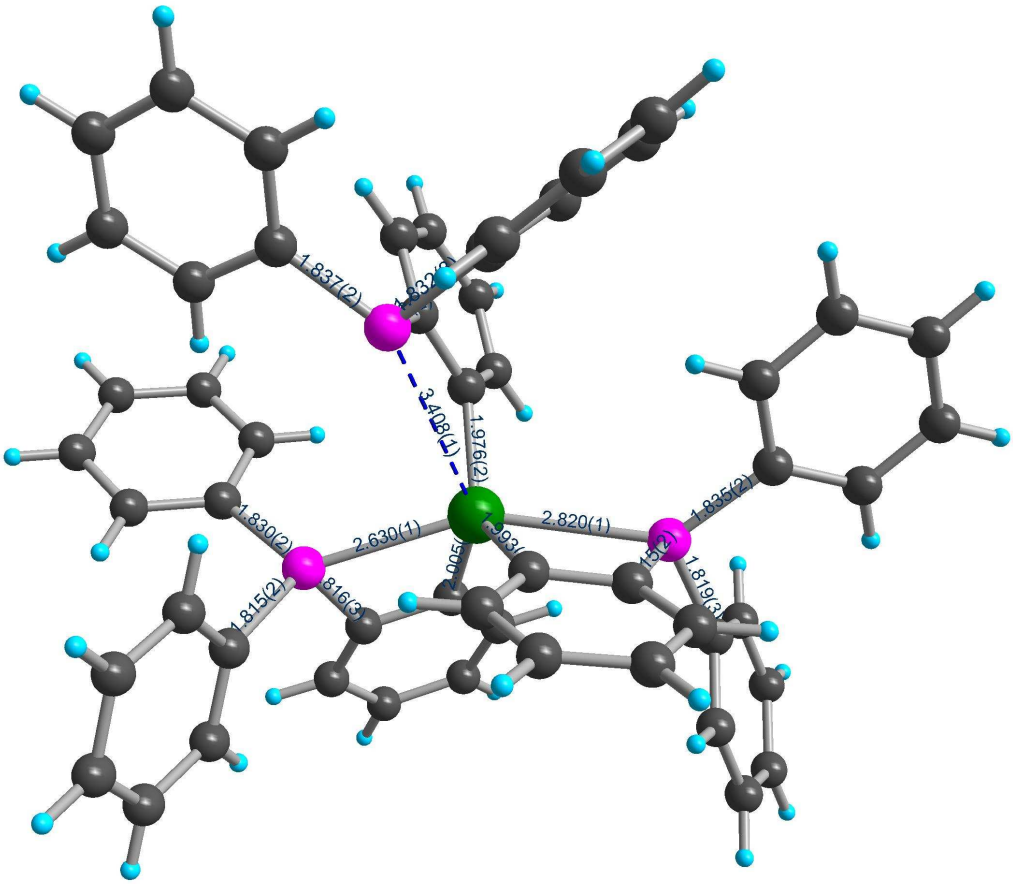

Figure S15 The Coordination environment of Al1 in 2.

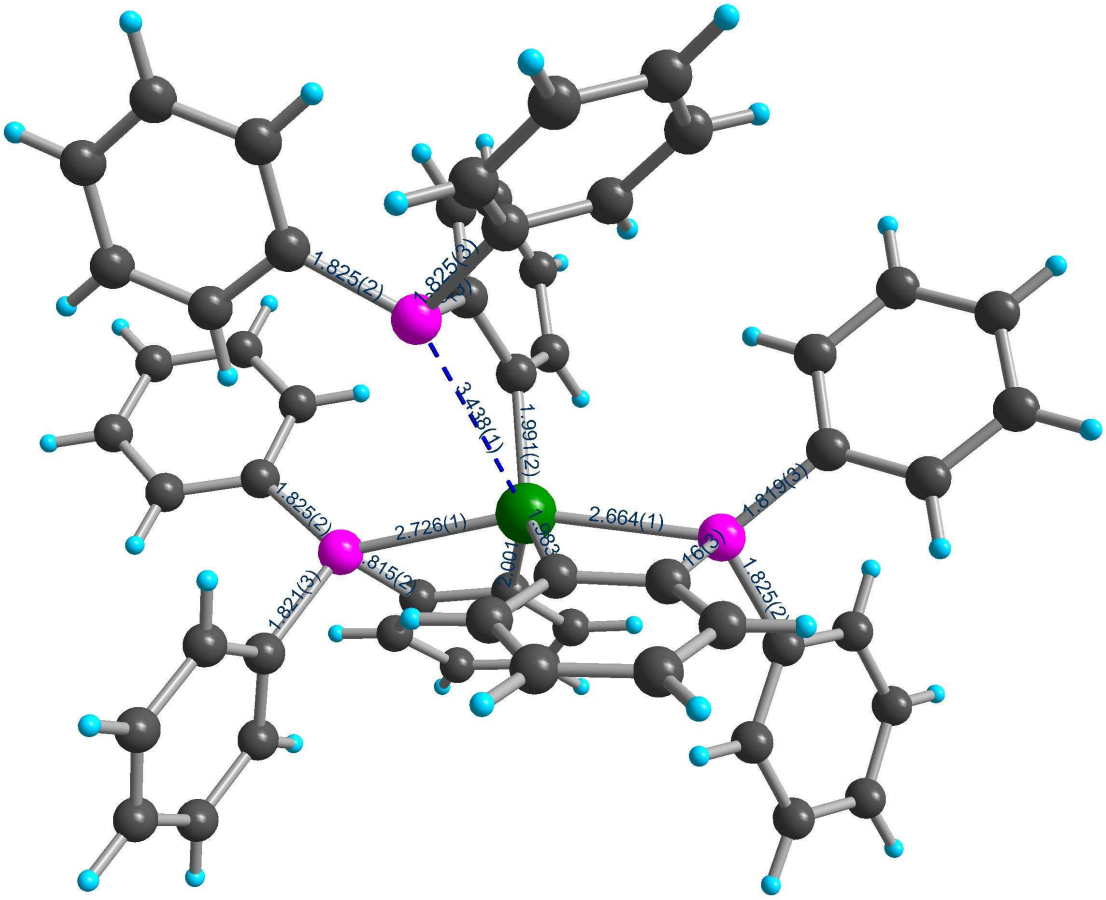

Figure S16 The Coordination environment of Al2 in 2.

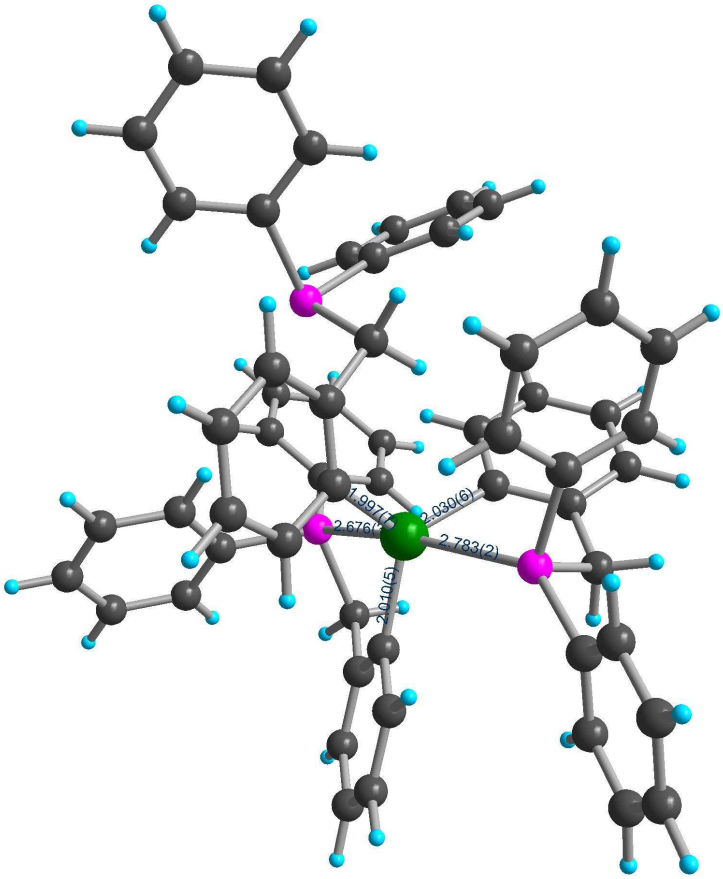

Figure S17 The Coordination environment of Al in UVMPIC (Müller's structure).

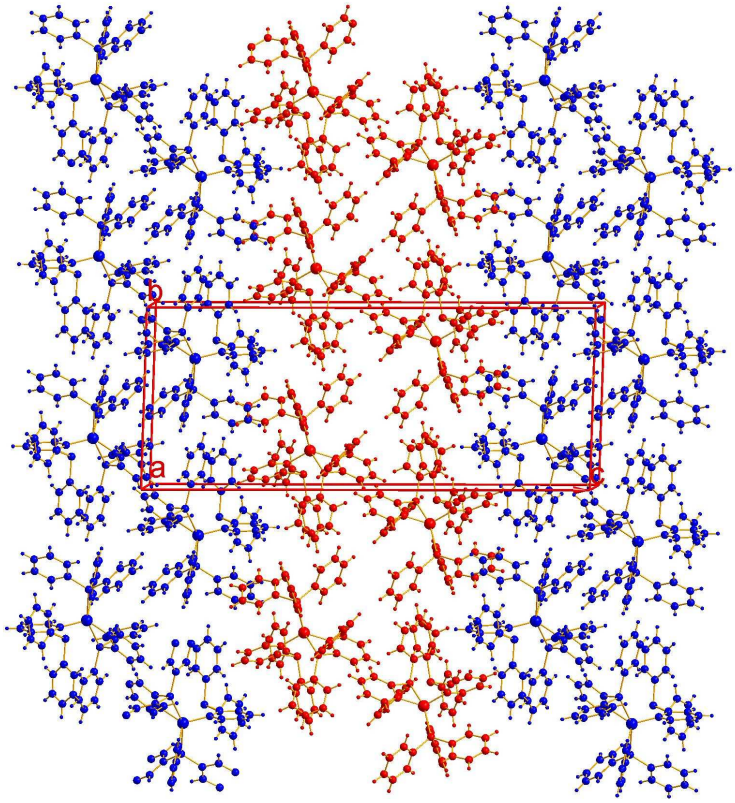

Figure S18 The arrangement of the different double-layered sheets in 1 viewing along *a* axis. Sheet of Al_1 molecules in blue; Sheet of Al_2 molecules in red.

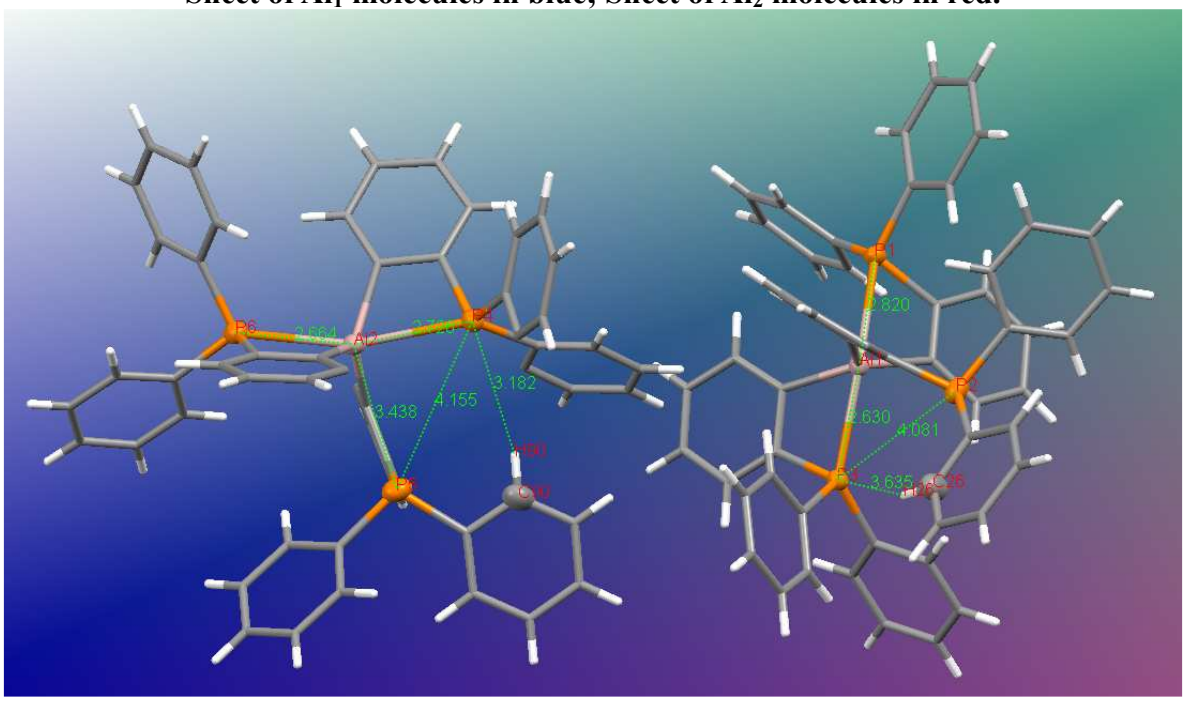

Figure S19 The distances between P and C-H of side Ph groups in 2.

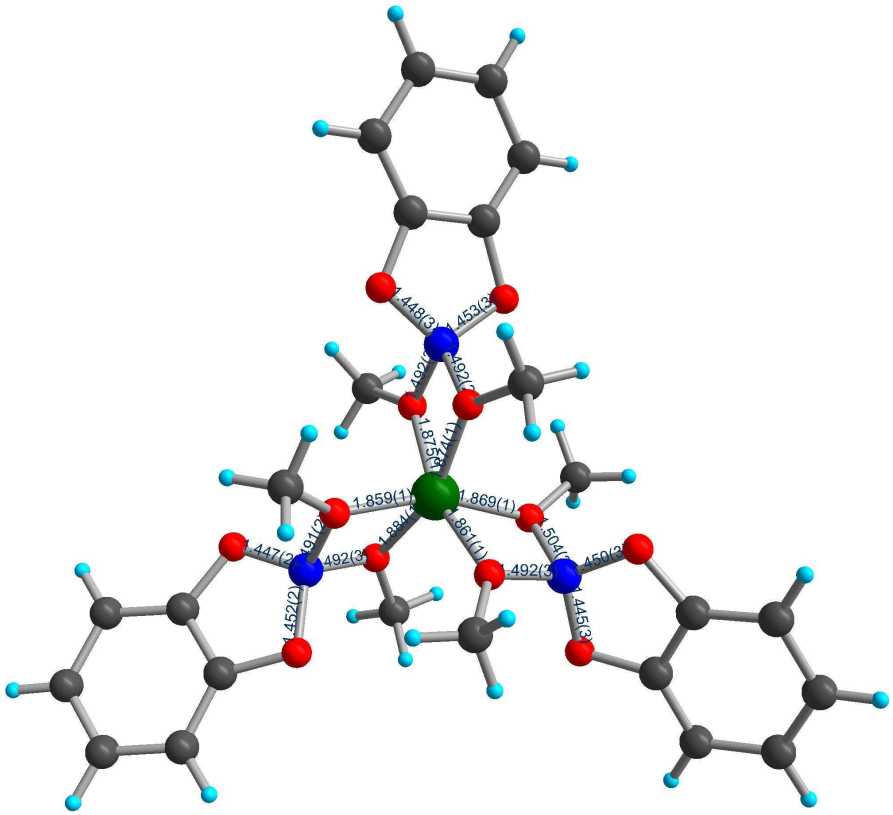

Figure S20: Selected bond lengths in the first molecule of 5. (Al1 cluster)

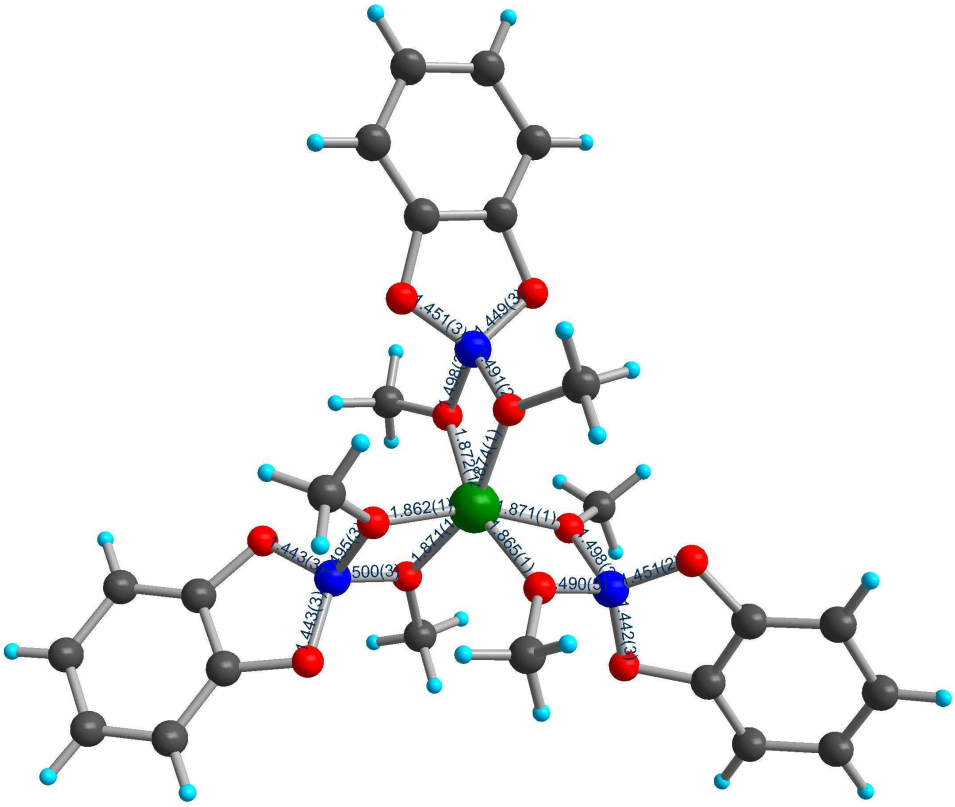

Figure S21: Selected bond lengths in the second molecule of 5. (Al2 cluster)

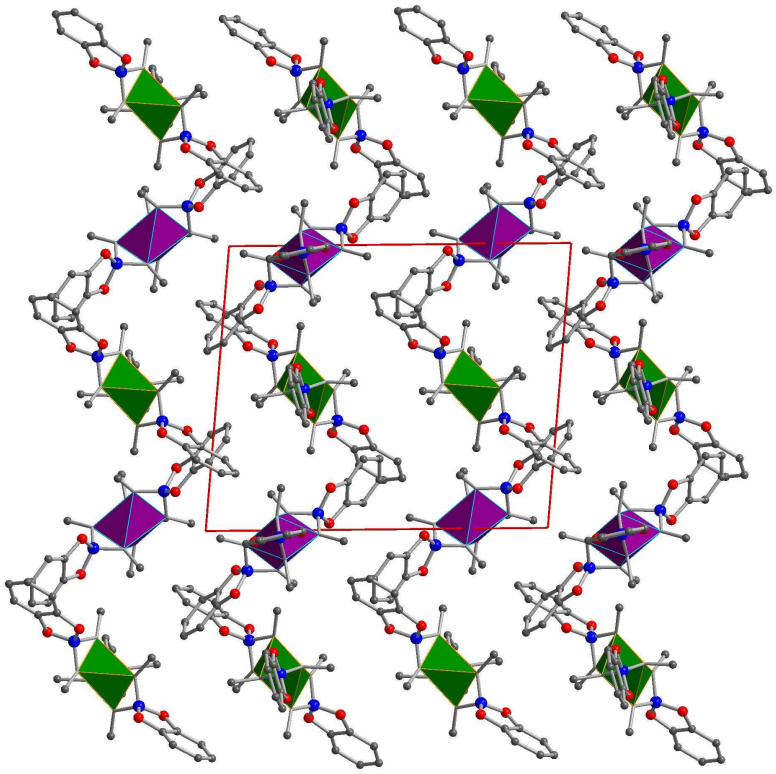

Figure S22: The packing pattern of 5 viewing along *a* axis. Different octahedra of AlO_6 clusters are shown in different colors (Al1 in green, Al2 in purple). H atoms and guest solvent molecules are omitted for clarity.

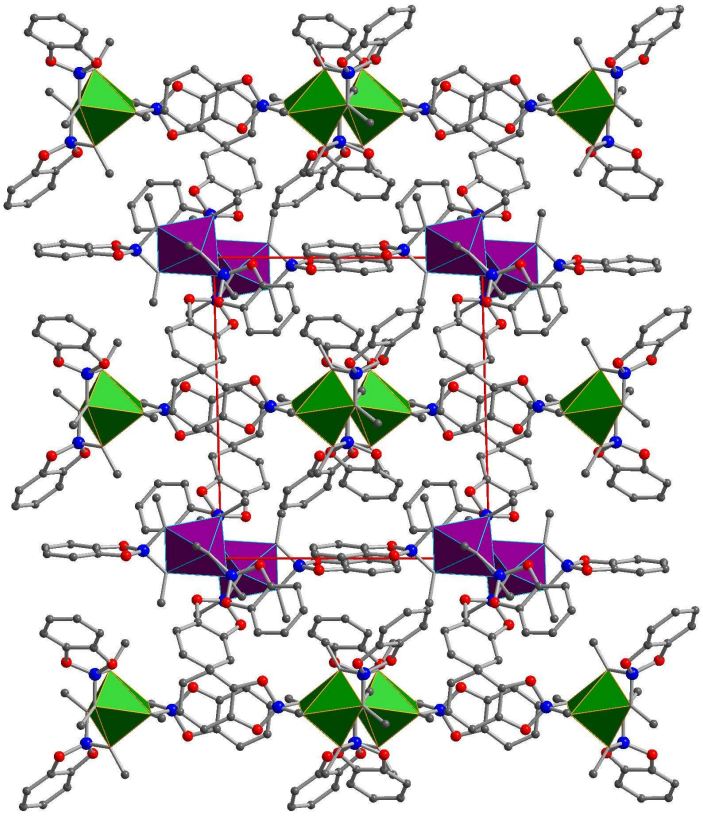

Figure S23: The packing pattern of 5 viewing along *c* axis. Different octahedra of AlO_6 clusters are shown in different colors (Al1 in green, Al2 in purple). H atoms and guest solvent molecules are omitted for clarity.

Computational details

Calculations were performed with the GAUSSIAN 03 suite of programs.[S6] The B3PW91[S7,S8]functional was used in combination with the 6-31+G** basis set for B,C,H, and O atoms,[S9,S10] and the SDD basis set with an additional polarization function (one d function with a 0.34 exponent and a 1.0 contraction coefficient) for P atoms,[S11] and for aluminum[S12] . The stationary points were characterized as minima by full vibration frequencies calculations (no imaginary frequency). All geometry optimization were carried out without any symmetry constraints.

Cartesian coordinates of all optimized structures

$Al(C_6H_4(o\text{-}PPh_2))_3$ **(2):** -2104.009509

P	6.802569	5.159062	11.097485	C	4.597700	7.023343	10.669932
P	8.193202	1.215790	10.690245	H	5.293077	7.845065	10.516274
P	3.212407	1.415352	12.635421	C	3.224855	7.233070	10.576241
Al	5.285404	2.958708	11.414706	H	2.839500	8.225333	10.355467
C	7.674997	5.768782	9.580270	C	2.341986	6.164259	10.762102
C	7.584034	4.981914	8.423808	H	1.270568	6.336353	10.687965
H	7.050358	4.035359	8.453379	C	2.821858	4.883731	11.035517
C	8.173618	5.409812	7.235343	H	2.109155	4.073735	11.175368
H	8.095729	4.791686	6.345301	C	4.200537	4.628965	11.132858
C	8.865112	6.619861	7.192117	C	5.629969	1.890863	9.760272
H	9.327568	6.950657	6.266111	C	6.811181	1.180250	9.437353
C	8.964768	7.402838	8.341634	C	6.940646	0.513511	8.210660
H	9.503661	8.346233	8.313736	H	7.862935	-0.011058	7.974930
C	8.373009	6.981671	9.531523	C	5.899273	0.525188	7.284402
H	8.459129	7.595429	10.423341	H	6.011171	0.006056	6.335549
C	7.593890	6.098481	12.479862	C	4.721307	1.208589	7.580560
C	8.965894	5.920534	12.715270	H	3.905733	1.229935	6.861416
H	9.554122	5.293077	12.050075	C	4.598592	1.876742	8.799180
C	9.582727	6.547086	13.794901	H	3.675143	2.417735	9.003289
H	10.647003	6.405918	13.962865	C	8.047864	-0.440200	11.528620
C	8.836182	7.347297	14.660734	C	7.225847	-1.482816	11.087122
H	9.317558	7.833081	15.505009	H	6.625249	-1.351873	10.192053
C	7.471096	7.517020	14.440294	C	7.170706	-2.686729	11.790139
H	6.882934	8.135850	15.112585	H	6.520703	-3.484235	11.440127
C	6.850169	6.896357	13.356130	C	7.941164	-2.867211	12.937032
H	5.785671	7.032300	13.190975	H	7.896062	-3.805714	13.483057
C	5.062199	5.733922	10.953301	C	8.761964	-1.833209	13.387154

H	9.359229	-1.962017	14.285998
C	8.805672	-0.626228	12.693892
H	9.430802	0.183964	13.061868
C	9.698668	0.946282	9.618921
C	10.342393	-0.286054	9.452867
H	9.948787	-1.170166	9.945508
C	11.487505	-0.386836	8.661695
H	11.976024	-1.350912	8.544358
C	12.002419	0.739196	8.022447
H	12.894562	0.658502	7.407123
C	11.369180	1.972136	8.182106
H	11.765199	2.857447	7.691375
C	10.233142	2.075529	8.980870
H	9.753385	3.043252	9.108645
C	5.679912	2.300166	13.259968
C	6.818072	2.490867	14.062529
H	7.651421	3.077653	13.683410
C	6.907447	1.931370	15.335543
H	7.797580	2.094802	15.938854
C	5.862860	1.152809	15.842865
H	5.943375	0.709889	16.832449
C	4.719681	0.943967	15.077892
H	3.906814	0.335273	15.465613
C	4.635110	1.523675	13.806079
C	1.763865	2.114644	13.560974
C	1.934408	2.972062	14.654586
H	2.931917	3.168506	15.035778
C	0.829952	3.569614	15.261804
H	0.978339	4.229056	16.112837
C	-0.455714	3.322212	14.785376
H	-1.314518	3.787081	15.261781
C	-0.634088	2.474906	13.691363
H	-1.632938	2.276620	13.311619
C	0.466631	1.880178	13.079923
H	0.315117	1.220513	12.229054
C	2.771715	-0.381150	12.486723
C	2.061276	-1.084086	13.469327
H	1.712334	-0.567392	14.358921
C	1.782352	-2.438498	13.301918
H	1.232236	-2.974988	14.070562
C	2.202906	-3.103542	12.149542
H	1.979576	-4.159034	12.018875
C	2.901056	-2.409216	11.163587
H	3.220299	-2.919364	10.258745
C	3.183230	-1.053376	11.329291
H	3.720593	-0.511108	10.555617

$Al(C_6H_4(o\text{-}PPh_2))_3.CO2$ **(3):** -2292.519823

Al	-0.268454	0.148741	0.245017
C	-0.037998	-0.971683	1.889881
C	1.501308	0.910104	-0.302695
C	-1.184761	-0.525255	-1.418018
P	-1.296550	-3.282795	0.882890
P	0.240800	3.058373	-1.603383
O	-1.425451	1.473446	0.859629
C	-2.559166	1.921600	0.507437
O	-3.206311	2.857784	0.922546
C	-2.469969	-0.177219	-1.878767
C	-2.993337	-0.600829	-3.111879
C	-2.222082	-1.415409	-3.931499
C	-0.938169	-1.779404	-3.519719
C	-0.437974	-1.335672	-2.297856
H	-3.983369	-0.286641	-3.432933
H	-2.613204	-1.751431	-4.887792
H	-0.322417	-2.406378	-4.159811
H	0.573294	-1.624925	-2.019943
P	-3.507982	0.899289	-0.846710
C	-0.435317	-2.292320	2.206964
C	-0.204525	-2.836535	3.478677
C	0.422145	-2.085116	4.470166
C	0.830256	-0.784284	4.188740
C	0.606304	-0.252489	2.919181
H	-0.520579	-3.852448	3.697947
H	0.590727	-2.517052	5.453711
H	1.318491	-0.184327	4.953148
H	0.941121	0.766970	2.727444
C	2.646133	0.171132	0.058283
C	3.924993	0.491231	-0.399351
C	4.103800	1.583095	-1.244723
C	3.001171	2.350988	-1.614407
C	1.720613	2.025457	-1.147259
H	2.534862	-0.688294	0.717457
H	4.777894	-0.114332	-0.101183
H	5.093618	1.839651	-1.614559
H	3.136342	3.204820	-2.273488
C	0.119649	-4.189125	0.076866
C	-2.090018	-4.657292	1.866182
C	-0.138713	-4.828083	-1.144849
C	0.868455	-5.517826	-1.816605
C	2.157921	-5.561695	-1.286050
C	2.429215	-4.919258	-0.079047
C	1.417022	-4.240775	0.600712
H	-1.137372	-4.779678	-1.572936
H	0.649095	-6.013575	-2.758847
H	2.947648	-6.090419	-1.813124
H	3.432049	-4.947911	0.339398
H	1.633864	-3.748562	1.544220
C	-1.596678	-5.964835	1.947942
C	-2.285385	-6.940370	2.670333
C	-3.471685	-6.623177	3.328487
C	-3.971586	-5.322366	3.256094
C	-3.291966	-4.352350	2.523789

H	-0.668377	-6.222982	1.447457	H	2.455898	6.218273	1.641092
H	-1.887137	-7.950578	2.722445	H	2.427841	4.247268	0.149873
H	-4.004362	-7.383381	3.893570	C	-4.396299	2.082489	-1.919670
H	-4.895396	-5.064097	3.767684	C	-4.735483	-0.073111	0.101005
H	-3.694631	-3.343727	2.464530	C	-4.923237	-1.431291	-0.175999
C	0.380614	4.526049	-0.465452	C	-5.869291	-2.155571	0.548321
C	0.748450	3.789822	-3.242238	C	-6.617964	-1.530546	1.544171
C	1.139306	5.120811	-3.429581	C	-6.417613	-0.179141	1.828917
C	1.445251	5.597386	-4.705409	C	-5.475217	0.554965	1.114020
C	1.370303	4.751522	-5.809868	H	-4.323797	-1.922219	-0.935850
C	0.981634	3.422591	-5.634306	H	-6.009907	-3.211607	0.338885
C	0.664852	2.949539	-4.363795	H	-7.352981	-2.099238	2.106937
H	1.206633	5.788057	-2.575466	H	-6.989931	0.304614	2.615056
H	1.747918	6.633739	-4.832755	H	-5.300393	1.601384	1.346526
H	1.611200	5.124048	-6.801922	C	-3.627999	2.900148	-2.760204
H	0.919272	2.754856	-6.489819	C	-4.262017	3.815758	-3.594469
H	0.354028	1.914509	-4.237840	C	-5.654159	3.915741	-3.596326
C	-0.764385	5.319140	-0.305295	C	-6.415619	3.098714	-2.763147
C	-0.746655	6.435779	0.527613	C	-5.790345	2.179374	-1.922040
C	0.412813	6.764971	1.228305	H	-2.543121	2.821740	-2.757157
C	1.551531	5.972752	1.090223	H	-3.665817	4.450729	-4.243120
C	1.537753	4.861216	0.248029	H	-6.145116	4.631520	-4.249720
H	-1.681948	5.052624	-0.823718	H	-7.499179	3.173690	-2.765623
H	-1.644084	7.037831	0.641671	H	-6.385534	1.544265	-1.273787
H	0.425596	7.629187	1.887142				

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