Supporting Information

Flexible Bidentate Aluminum Lewis Acids for Host–Guest Complex Formation

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1. NMR characterizations for all compounds

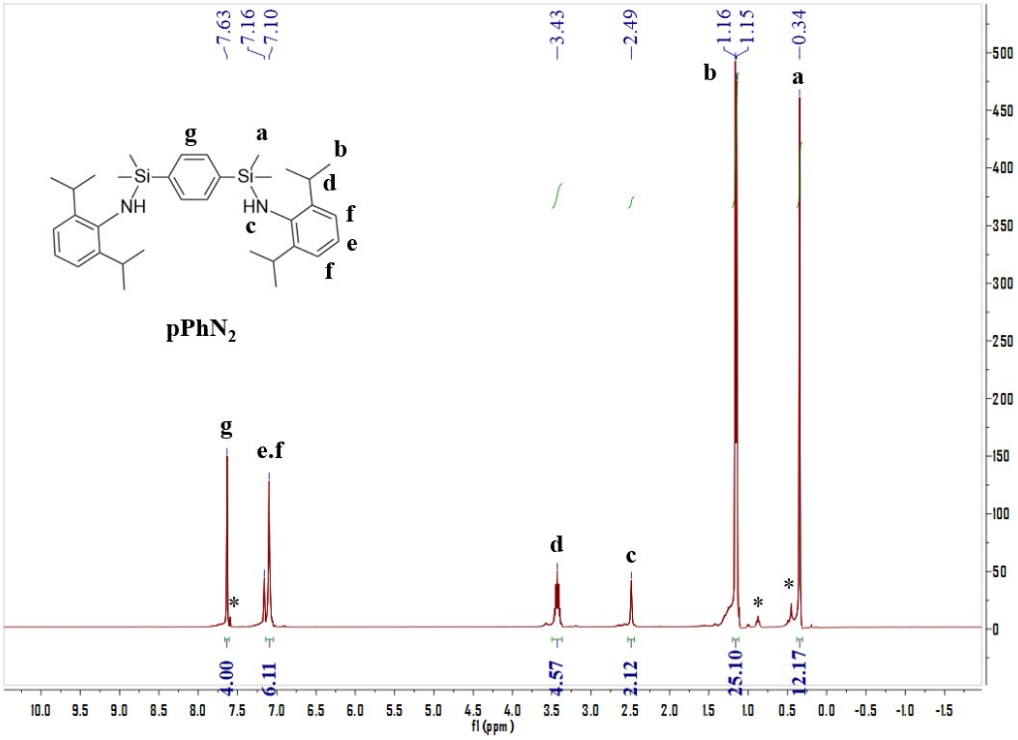


Figure S1. ^{1}H NMR spectrum of **H_2L1** in C_6D_6.

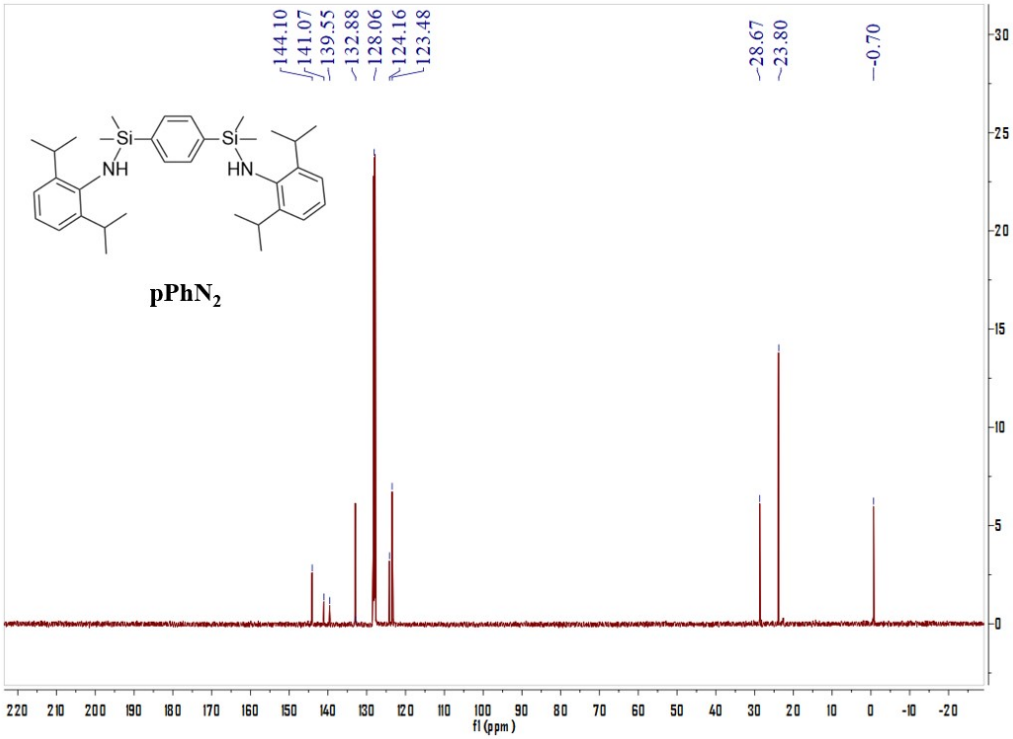


Figure S2. ^{13}C{^{1}H} NMR spectrum of **H_2L1** in C_6D_6.

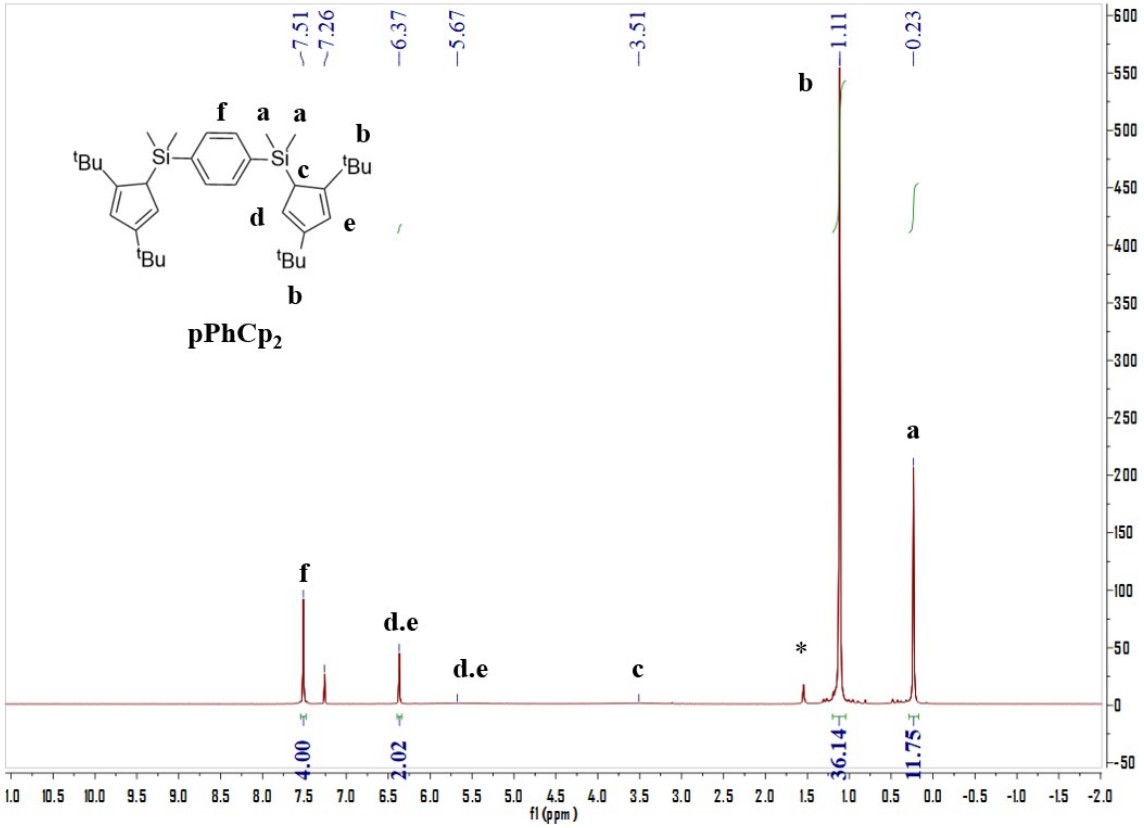


Figure S3. ^{1}H NMR spectrum of **H_2L2** in $CDCl_3$.

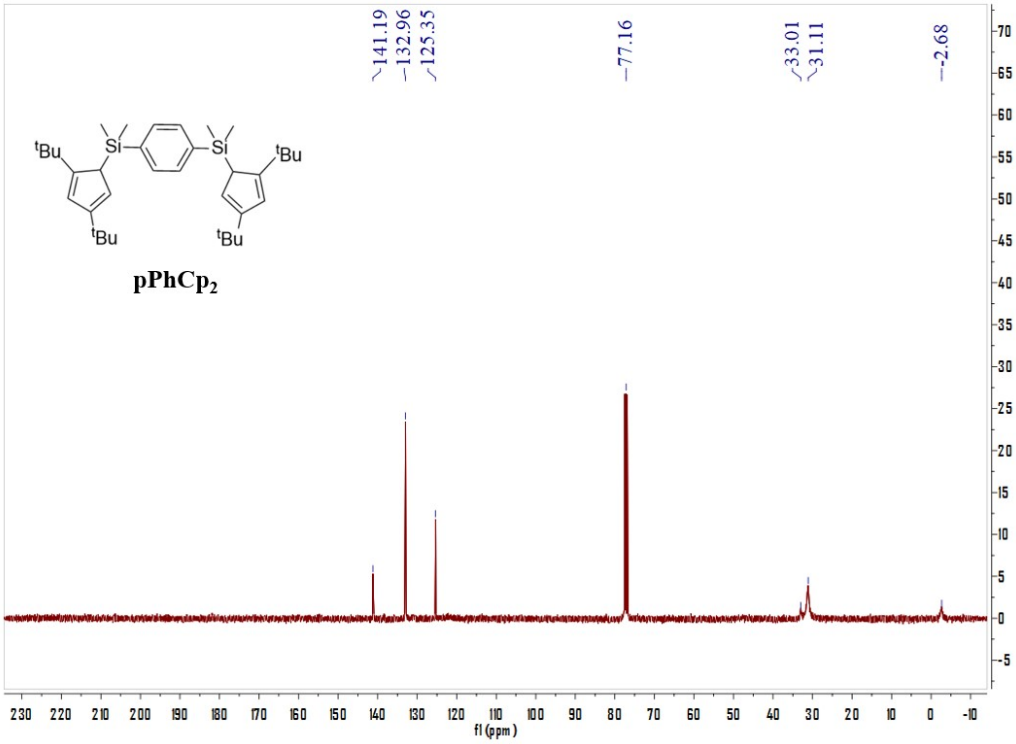


Figure S4. ^{13}C{^{1}H} NMR spectrum of **H_2L2** in $CDCl_3$.

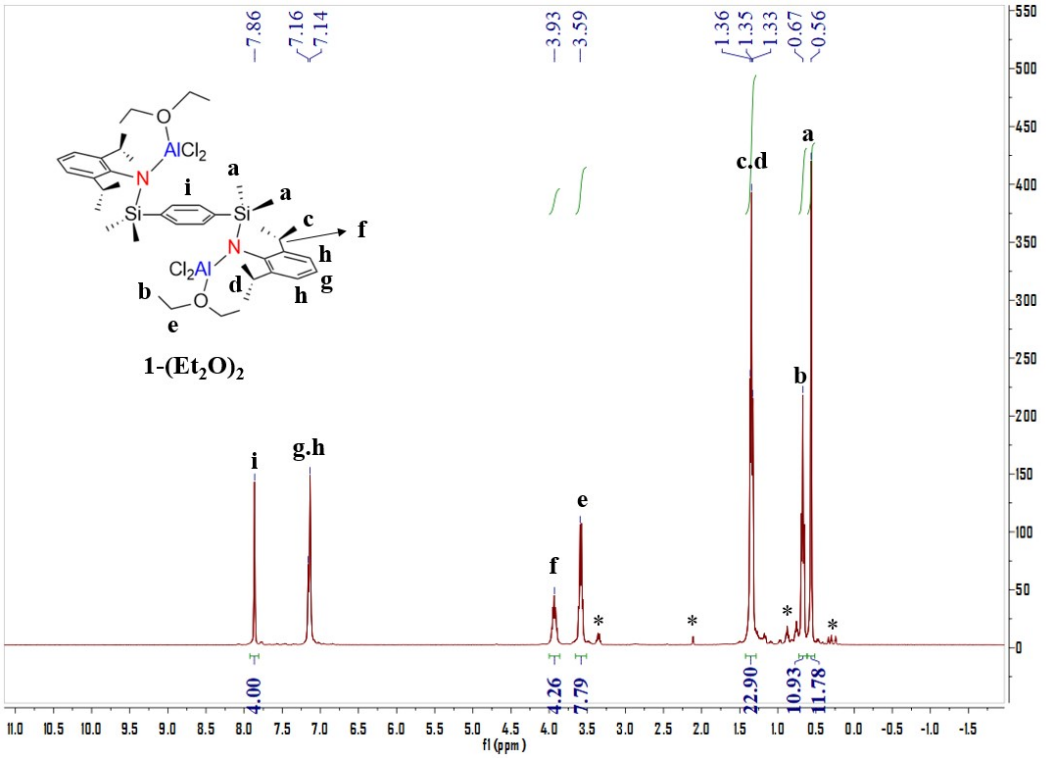


Figure S5. ^{1}H NMR spectrum of **1-(Et$_2$O)$_2$** in C_6D_6.

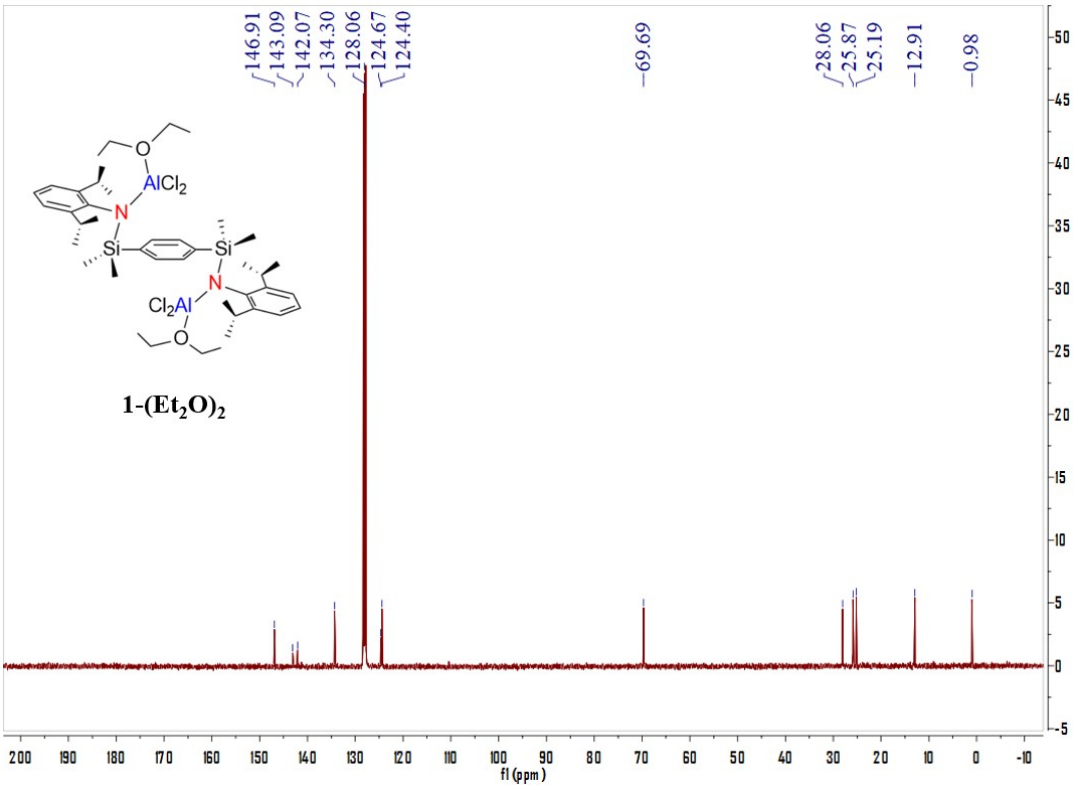


Figure S6. ^{13}C{^{1}H} NMR spectrum of **1-(Et$_2$O)$_2$** in C_6D_6.

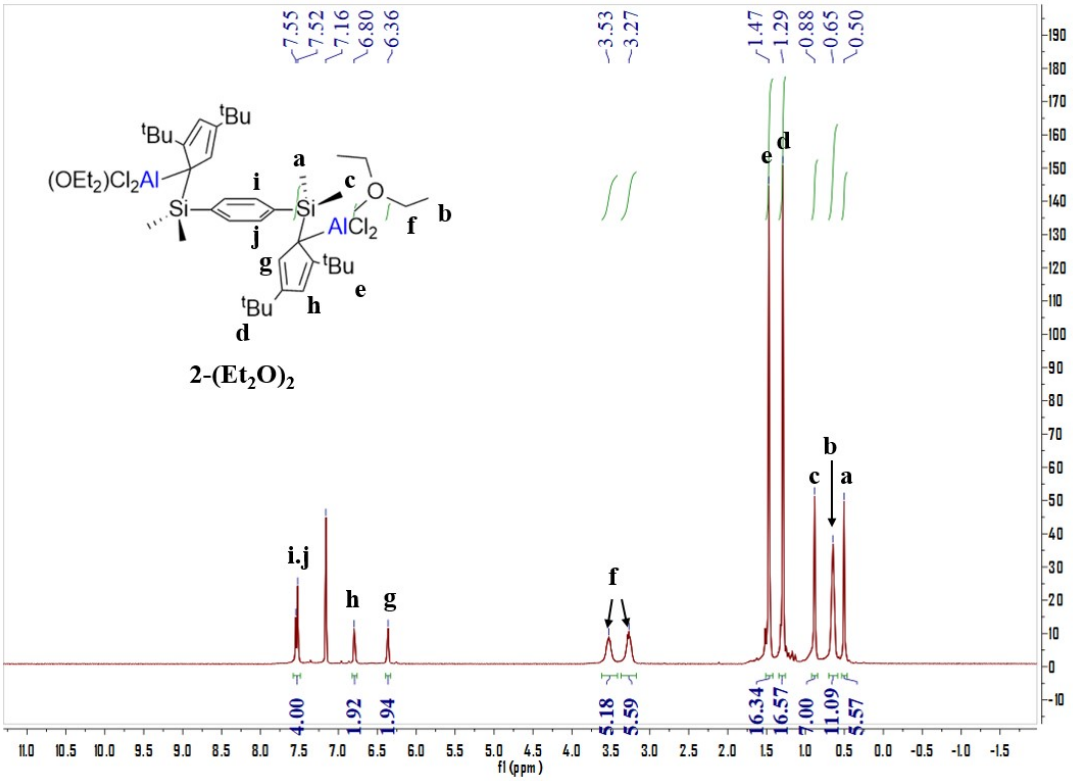


Figure S7. ^{1}H NMR spectrum of **2-$(Et_2O)_2$** in C_6D_6.

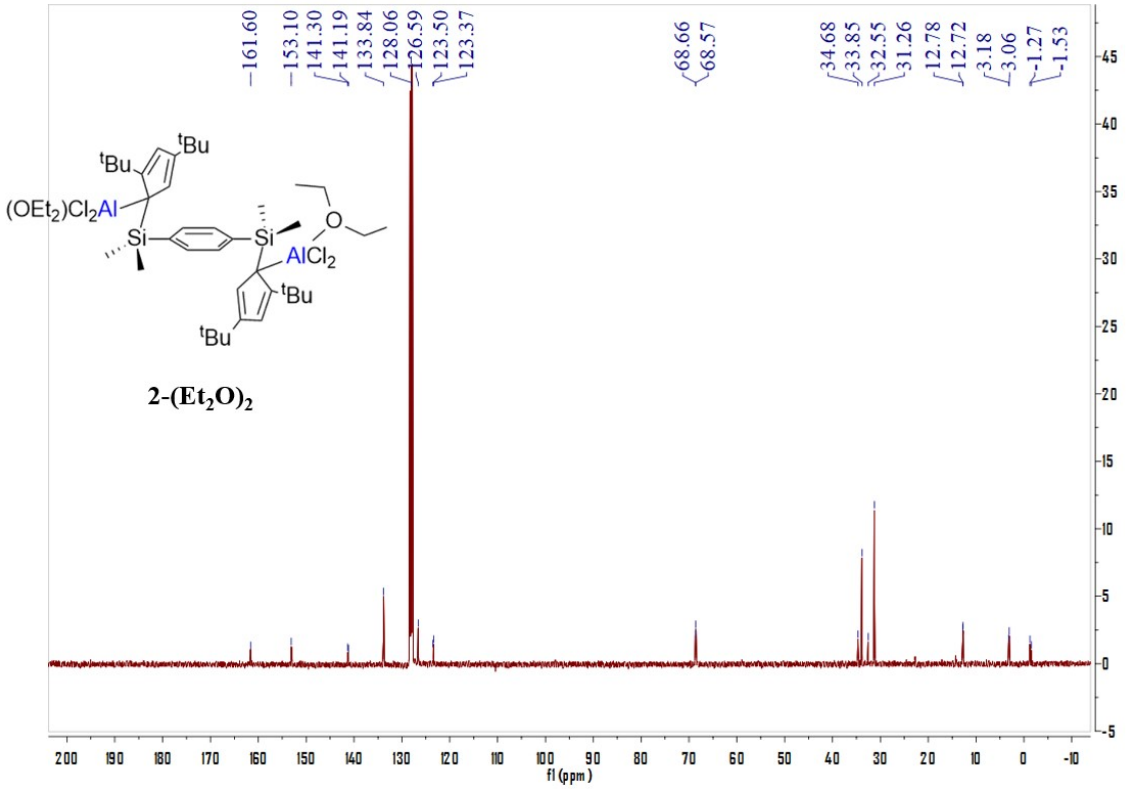


Figure S8. ^{13}C{^{1}H} NMR spectrum of **2-$(Et_2O)_2$** in C_6D_6.

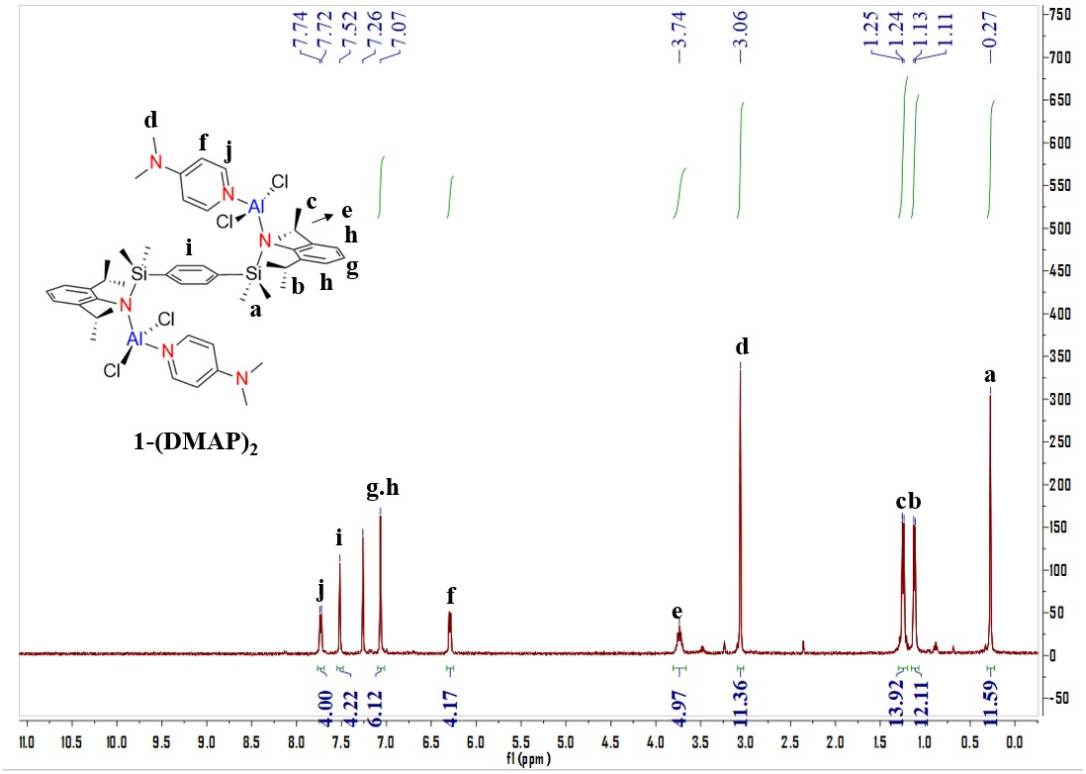


Figure S9. ^{1}H NMR spectrum of **1-(DMAP)$_2$** in $CDCl_3$.

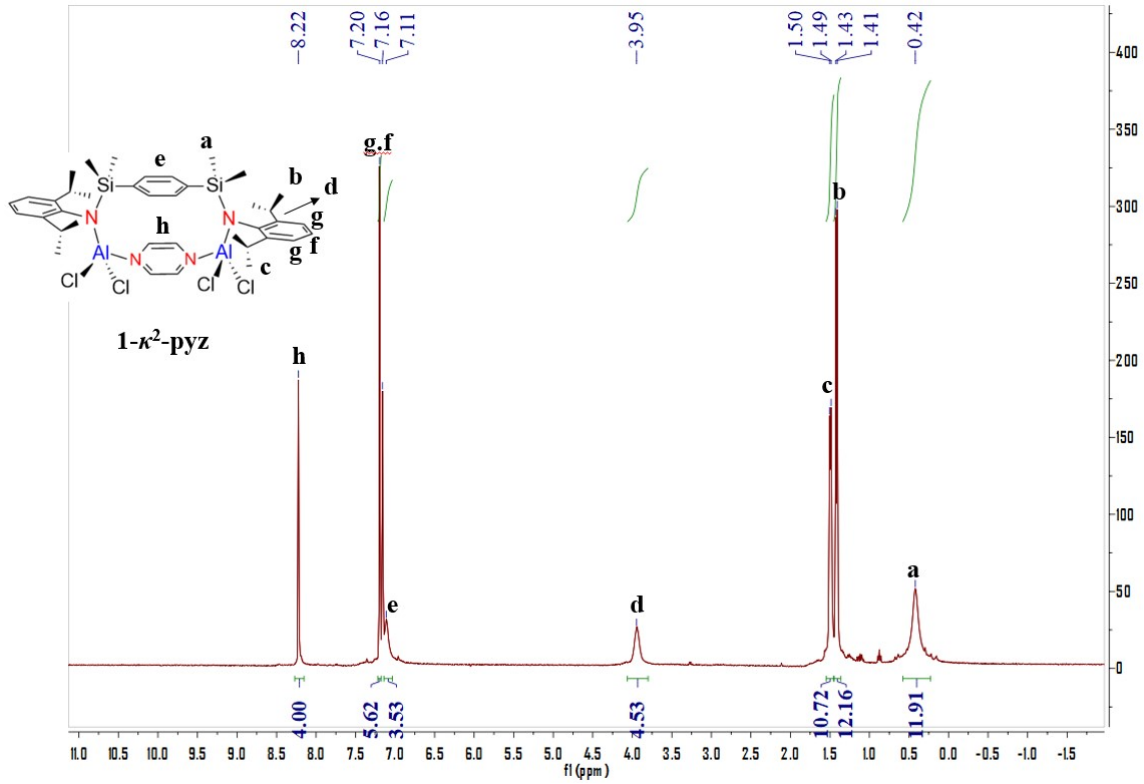


Figure S10. ^{1}H NMR spectrum of **1-κ^2-pyz** in benzene-d_6.

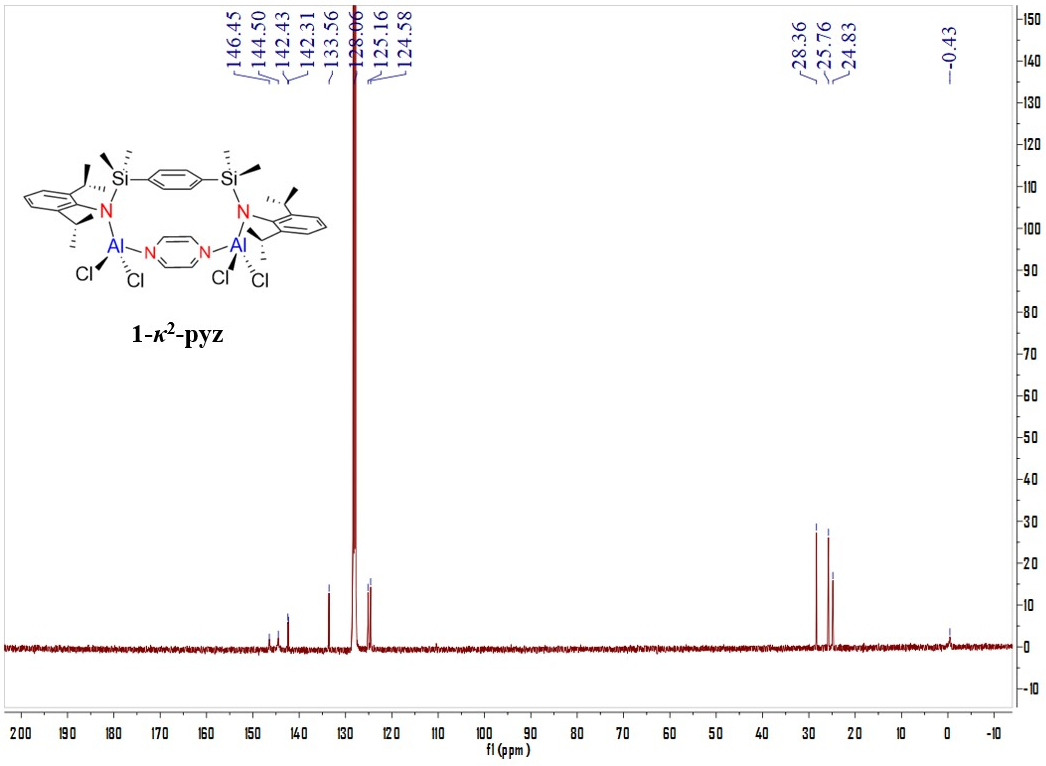
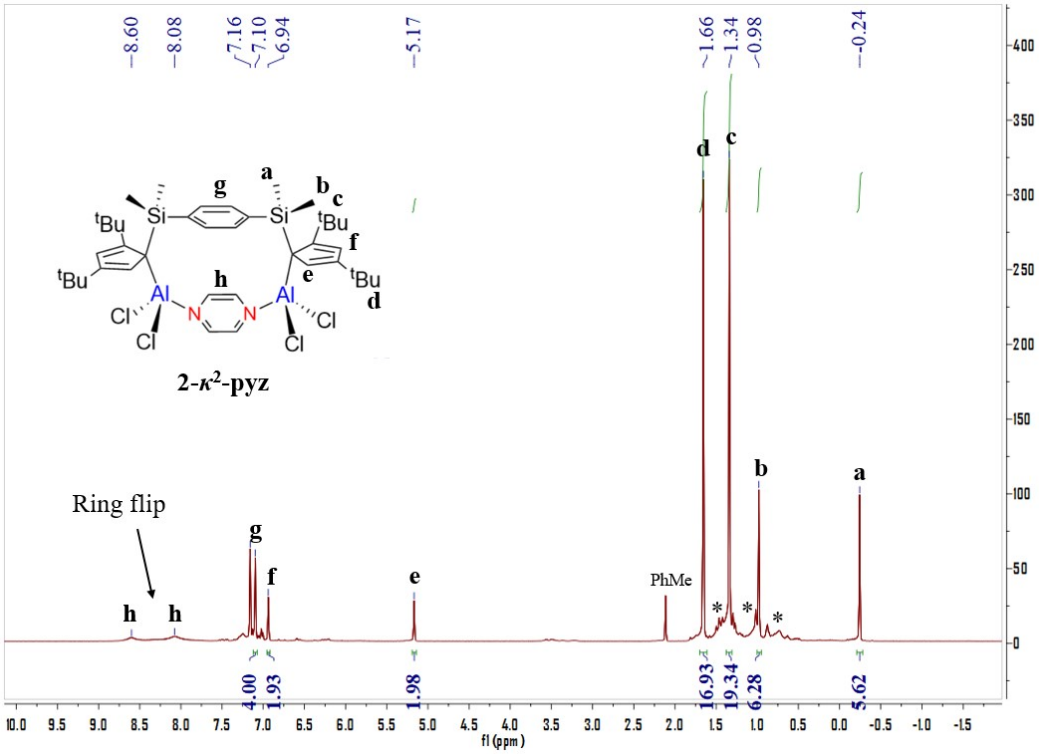


Figure S11. ^{13}C{^{1}H} NMR spectrum of **1-κ^2-pyz** in benzene-d_6.



2-κ^2-pyz

Figure S12. ^{1}H NMR spectrum of **2-κ^2-pyz** in benzene-d_6.

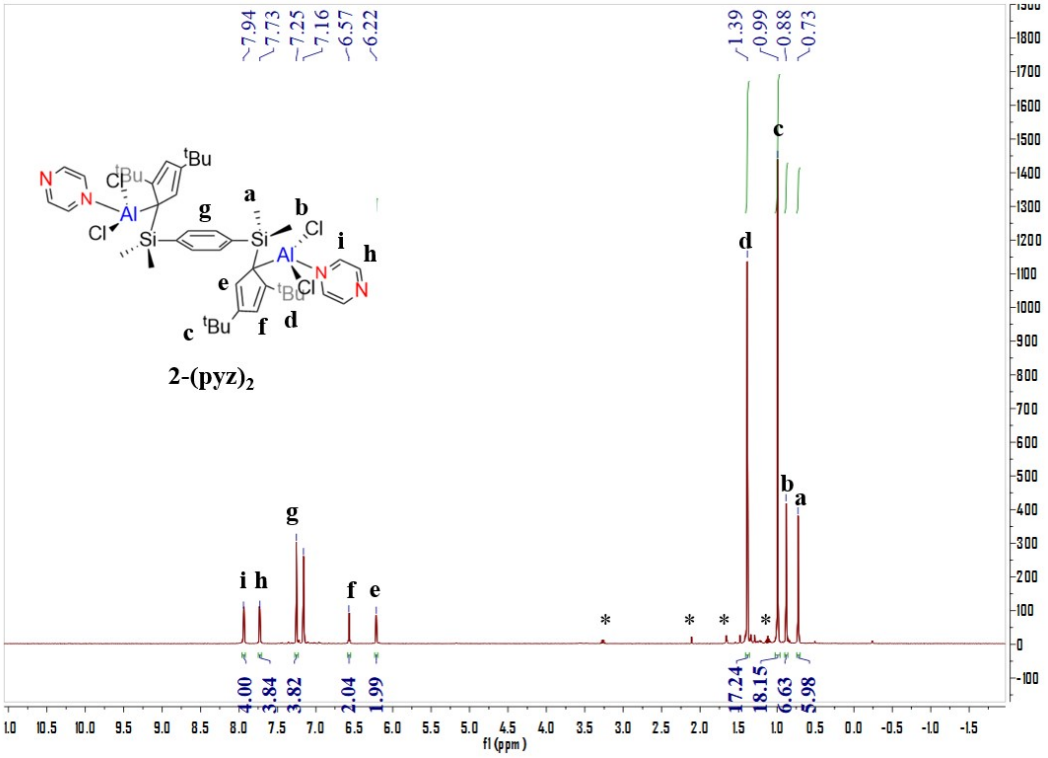


Figure S13. ^{1}H NMR spectrum of **2-(pyz)$_2$** in benzene-d_6.

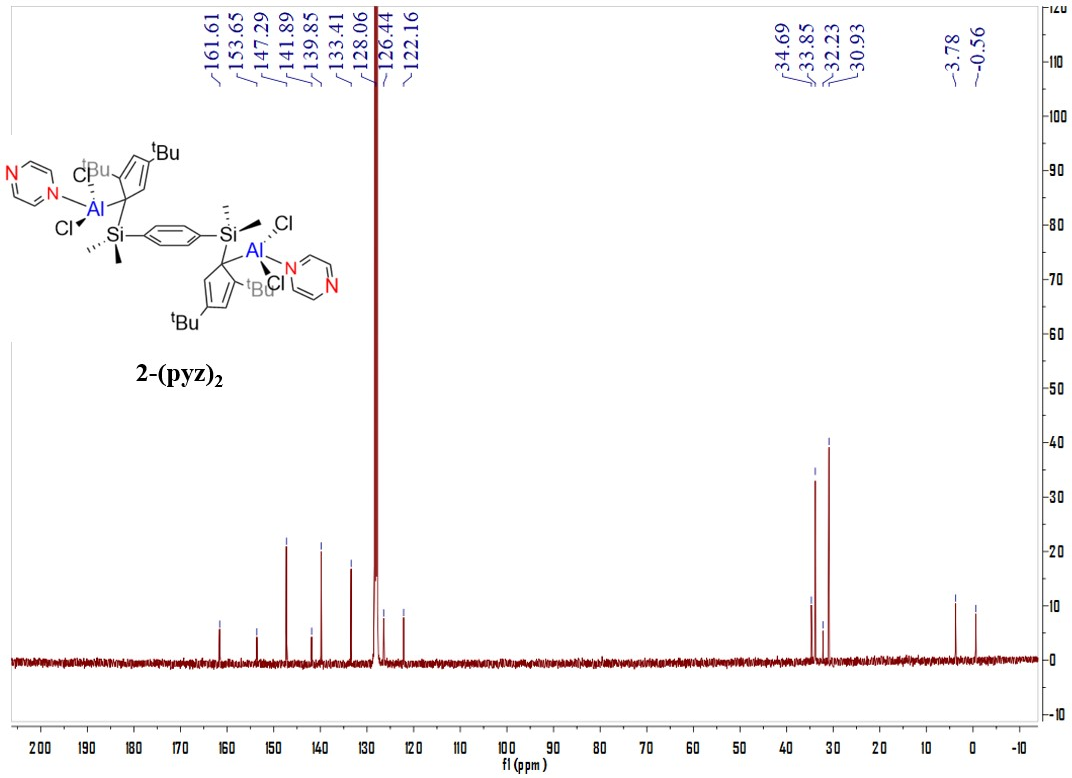


Figure S14. ^{13}C{^{1}H} NMR spectrum of **2-(pyz)$_2$** in benzene-d_6.

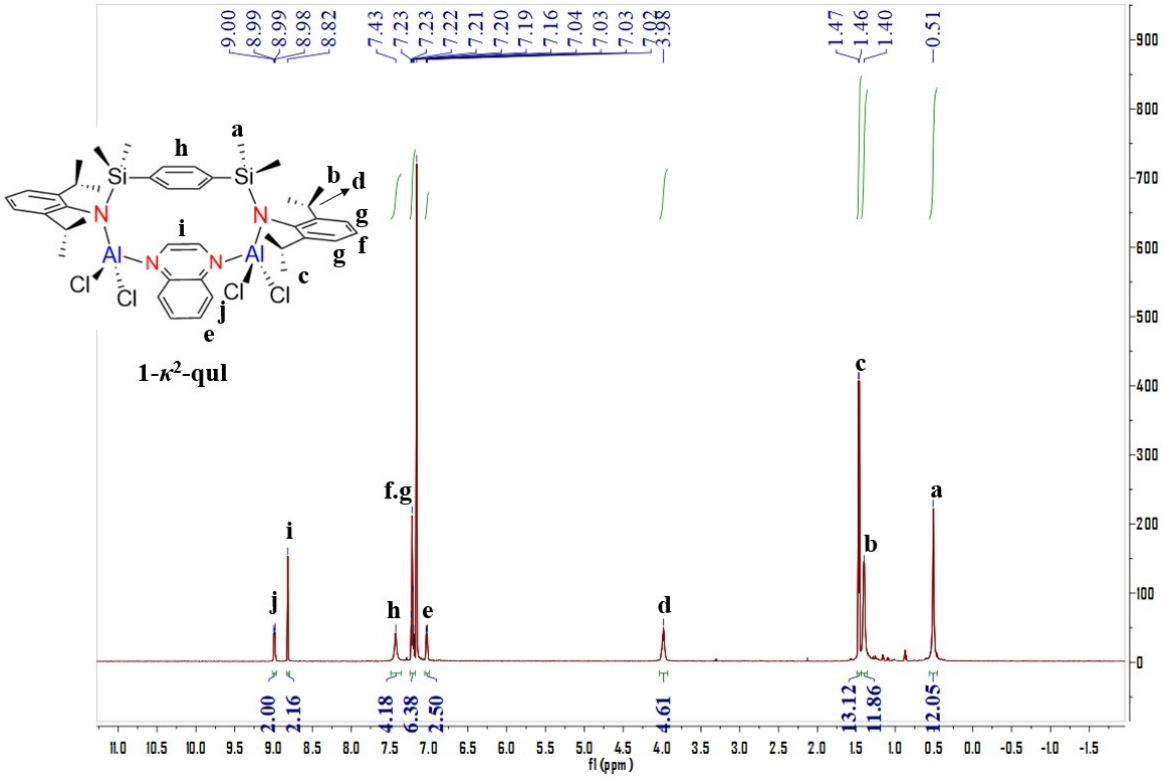


Figure S15. ^{1}H NMR spectrum of **1-κ^2-qul** in benzene-d_6.

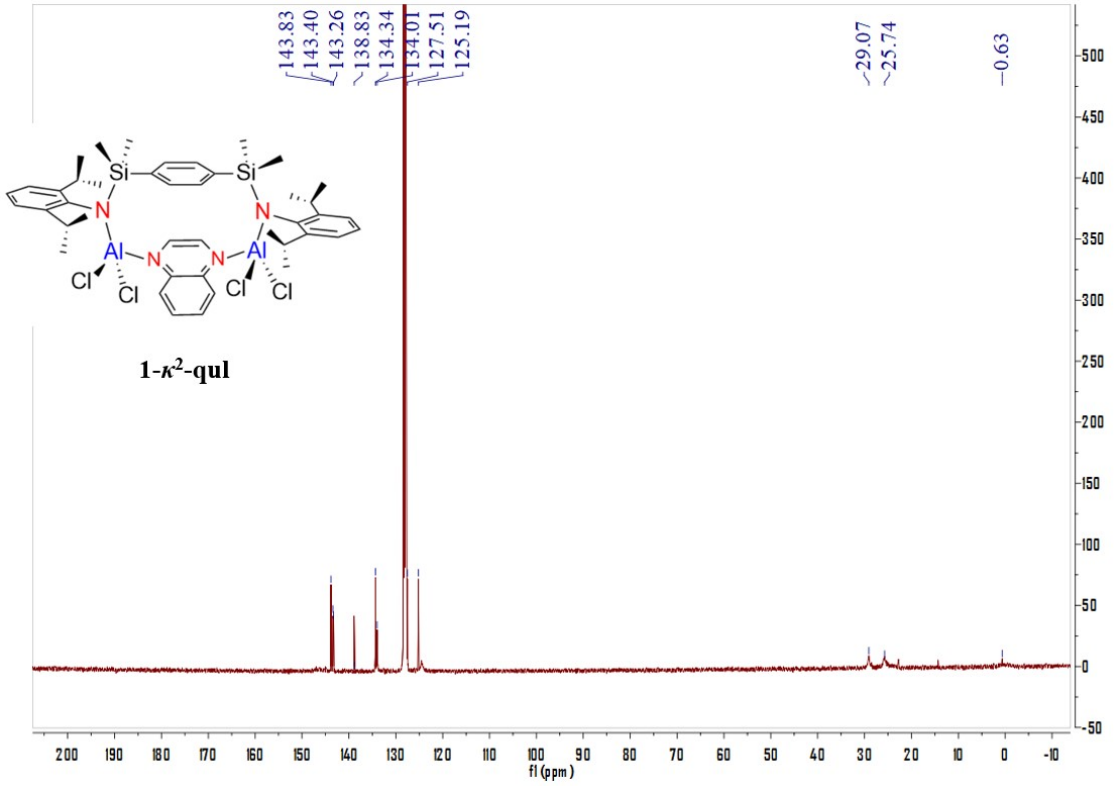


Figure S16. ^{13}C{^{1}H} NMR spectrum of **1-κ^2-qul** in benzene-d_6.

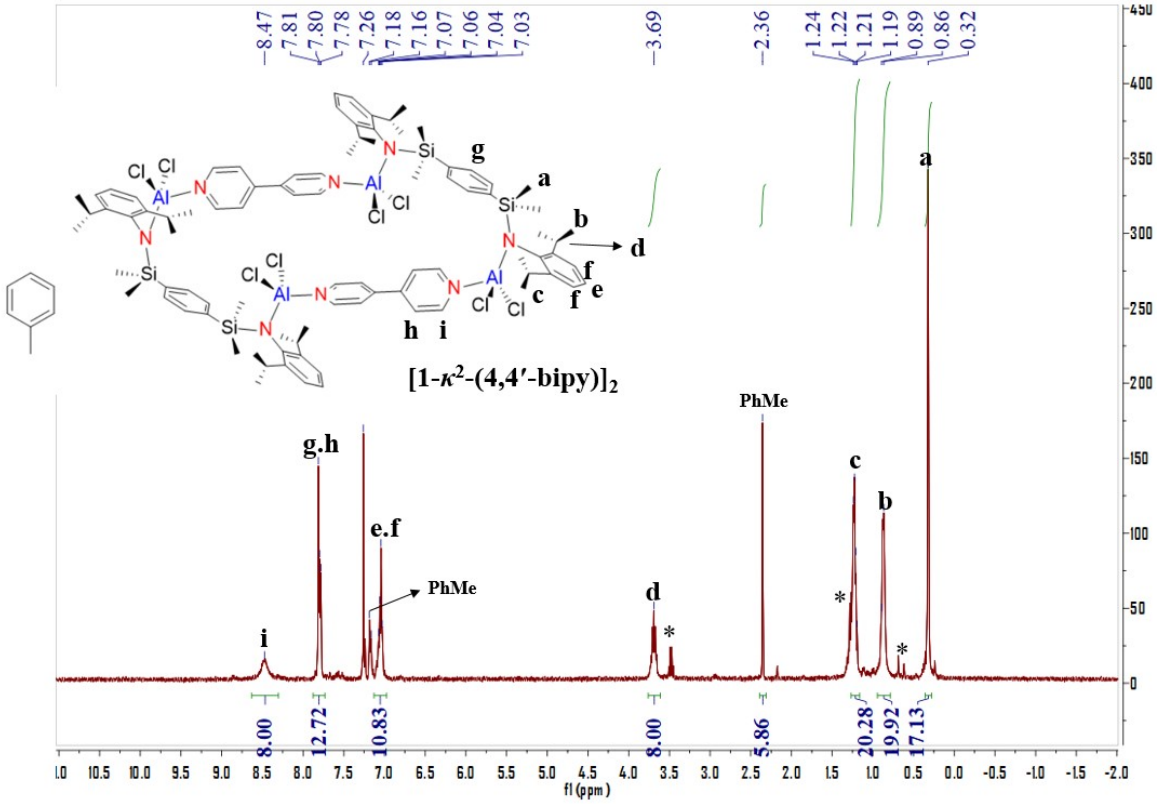


Figure S17. ^{1}H NMR spectrum of **1_2-μ-(bipy)$_2$** in $CDCl_3$.

2. Single-crystal X-ray diffraction crystal structure figures and data tables

Single-crystal X-ray diffraction for all complexes were performed on a Bruker APEX DUO diffractometer with APEX II 4K and multi-layer mirror monochromated Mo K_α radiation (λ = 0.71073 Å) at 200(2) K. Data collection and reduction were performed with Bruker APEX II software. All of non-hydrogen atoms are refined anisotropically. Hydrogen atoms attached to the carbons were fixed at calculated positions and refined using a riding mode. Multiple disordered solvent molecules were observed in the crystal structures of all complexes. Whenever possible, co-crystallizing solvent molecules were modeled. Otherwise, SQUEEZE was employed to treat diffuse solvent contribution in the voids. The structures were solved using direct methods, which yielded the positions of all non-hydrogen atoms. Hydrogen atoms on carbons were placed in calculated positions in the final structure refinement.

All cif files have been deposited on CCDC (2390325 (**1-(Et$_2$O)$_2$**), 2390330 (**2-(Et$_2$O)$_2$**), 2390331 (**1-(DMAP)$_2$**), 2390335 (**1-κ^2-pyz**), 2390401 (**2-κ^2-pyz**), 2390404 (**1-(pyz)$_2$**), 2390405 (**2-(pyz)$_2$**), 2390403 (**1-κ^2-qul**), and 2390402 (**1$_2$-μ-(bipy)$_2$**)).

Table S1. Crystal data and structure refinement for **1-$(Et_2O)_2$**

Empirical formula	$C_{84}H_{140}Al_4Cl_8N_4O_4Si_4$	
Formula weight	1773.87	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 20.154(4) Å	a= 90°.
	b = 12.249(3) Å	b= 111.568(6)°.
	c = 21.588(5) Å	g = 90°.
Volume	4956(2) $Å^3$	
Z	2	
Density (calculated)	1.189 Mg/m^3	
Absorption coefficient	0.357 mm^{-1}	
F(000)	1896	
Crystal size	0.220 x 0.160 x 0.100 mm^3	
Theta range for data collection	2.173 to 25.141°.	
Index ranges	-23<=h<=23, -14<=k<=14, -25<=l<=25	
Reflections collected	59068	
Independent reflections	8764 [R(int) = 0.1485]	
Completeness to theta = 25.141°	98.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8764 / 0 / 464	
Goodness-of-fit on F2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.1230, wR2 = 0.3386	
R indices (all data)	R1 = 0.2031, wR2 = 0.4032	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.407 and -0.573 $e.Å^{-3}$	

Table S2. Crystal data and structure refinement for **2-$(Et_2O)_2$**

Empirical formula	$C_{44}H_{76}Al_2Cl_4O_2Si_2$	
Formula weight	888.99	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 30.424(2) Å	a= 90°.
	b = 13.1426(9) Å	b= 107.722(2)°.
	c = 13.4477(10) Å	g = 90°.
Volume	5121.8(6) $Å^3$	
Z	4	
Density (calculated)	1.153 Mg/m^3	
Absorption coefficient	0.344 mm^{-1}	
F(000)	1912	
Crystal size	0.130 x 0.110 x 0.030 mm^3	
Theta range for data collection	2.178 to 25.054°.	
Index ranges	-36<=h<=36, -15<=k<=15, -16<=l<=16	
Reflections collected	38274	
Independent reflections	4518 [R(int) = 0.0920]	
Completeness to theta = 25.054°	99.4 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4518 / 0 / 254	
Goodness-of-fit on F2	1.085	
Final R indices [I>2sigma(I)]	R1 = 0.0782, wR2 = 0.1807	
R indices (all data)	R1 = 0.1069, wR2 = 0.1967	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.174 and -0.270 $e.Å^{-3}$	

Table S3. Crystal data and structure refinement for **1-(DMAP)$_2$**

Empirical formula	$C_{48}H_{70}Al_2Cl_4N_6Si_2$	
Formula weight	983.04	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 14.257(6) Å	α= 90°.
	b = 8.838(4) Å	β= 90.02(1)°.
	c = 21.438(9) Å	γ = 90°.
Volume	2701.3(19) Å^3	
Z	2	
Density (calculated)	1.209 Mg/m^3	
Absorption coefficient	0.333 mm^{-1}	
F(000)	1044	
Crystal size	0.110 x 0.050 x 0.040 mm^3	
Theta range for data collection	2.304 to 25.239°.	
Index ranges	-16<=h<=14, -10<=k<=9, -25<=l<=19	
Reflections collected	9570	
Independent reflections	4524 [R(int) = 0.1243]	
Completeness to theta = 25.239°	97.1 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4524 / 0 / 281	
Goodness-of-fit on F2	1.017	
Final R indices [I>2sigma(I)]	R1 = 0.0870, wR2 = 0.1791	
R indices (all data)	R1 = 0.2157, wR2 = 0.2432	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.537 and -0.560 e.Å^{-3}	

Table S4. Crystal data and structure refinement for **1-κ^2-pyz**

Identification code	shelx	
Empirical formula	$C_{38}H_{54}Al_2Cl_4N_4Si_2$	
Formula weight	818.79	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.1488(7) Å	a= 104.981(2)°.
	b = 13.9273(10) Å	b= 90.704(2)°.
	c = 14.8262(11) Å	g = 96.782(2)°.
Volume	2206.1(3) Å^3	
Z	2	
Density (calculated)	1.233 Mg/m^3	
Absorption coefficient	0.393 mm^{-1}	
F(000)	864	
Crystal size	0.200 x 0.160 x 0.070 mm^3	
Theta range for data collection	2.239 to 25.017°.	
Index ranges	-13<=h<=13, -16<=k<=16, -17<=l<=17	
Reflections collected	60691	
Independent reflections	7780 [R(int) = 0.0752]	
Completeness to theta = 25.017°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7780 / 0 / 451	
Goodness-of-fit on F2	1.124	
Final R indices [I>2sigma(I)]	R1 = 0.0403, wR2 = 0.0960	
R indices (all data)	R1 = 0.0695, wR2 = 0.1214	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.379 and -0.417 e.Å^{-3}	

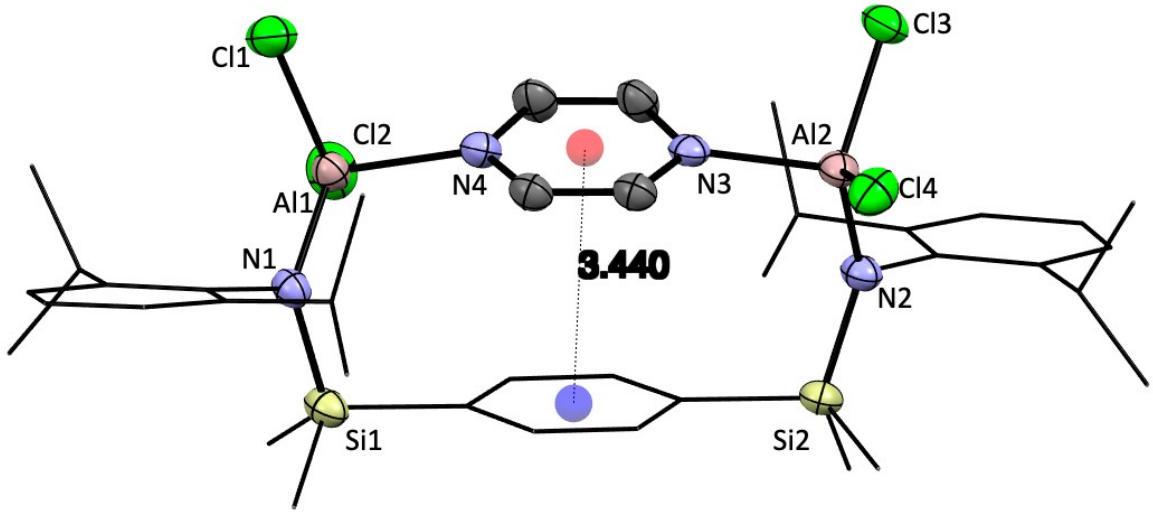


Figure S18. ORTEP of **1-κ^2-pyz** (50% thermal ellipsoids; all hydrogen atoms are omitted for clarity).

Table S5. Crystal data and structure refinement for **2-κ^2-pyz**

Identification code	shelx	
Empirical formula	$C_{40}H_{60}Al_2Cl_4N_2Si_2$	
Formula weight	820.84	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 18.694(3) Å	a= 90°.
	b = 11.3202(16) Å	b= 91.315(4)°.
	c = 21.709(3) Å	g = 90°.
Volume	4592.8(11) Å^3	
Z	4	
Density (calculated)	1.187 Mg/m^3	
Absorption coefficient	0.377 mm^{-1}	
F(000)	1744	
Crystal size	0.170 x 0.110 x 0.070 mm^3	
Theta range for data collection	2.179 to 25.048°.	
Index ranges	-22<=h<=22, -13<=k<=13, -25<=l<=25	
Reflections collected	45645	
Independent reflections	8110 [R(int) = 0.0520]	
Completeness to theta = 25.048°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8110 / 0 / 467	
Goodness-of-fit on F2	1.058	
Final R indices [I>2sigma(I)]	R1 = 0.0461, wR2 = 0.1097	
R indices (all data)	R1 = 0.0741, wR2 = 0.1285	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.351 and -0.293 e.Å^{-3}	

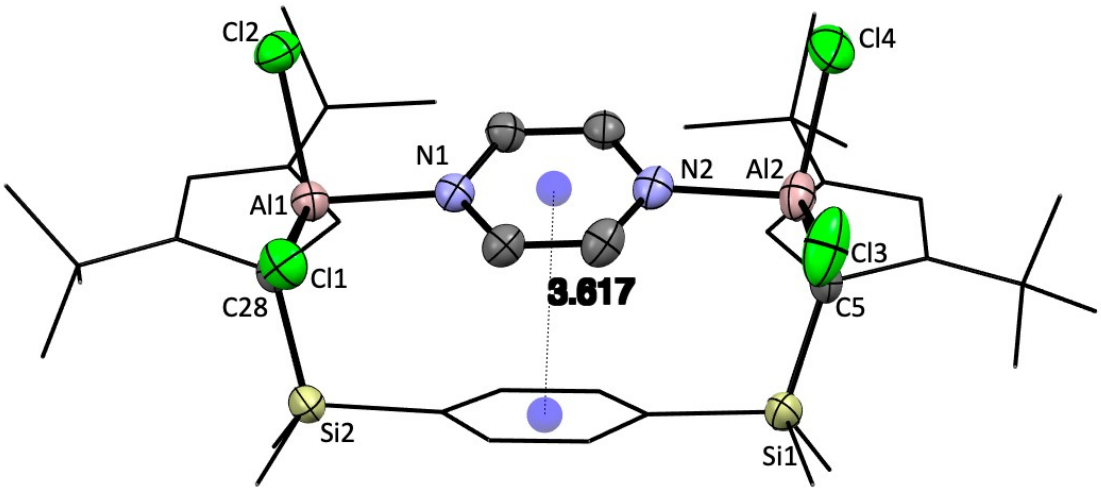


Figure S19. ORTEP of **2-κ^2-pyz** (50% thermal ellipsoids; all hydrogen atoms are omitted for clarity).

Table S6. Crystal data and structure refinement for **1-(pyz)$_2$**

Empirical formula	$C_{42}H_{58}Al_2Cl_4N_6Si_2$	
Formula weight	898.88	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 9.898(3) Å	a= 90°.
	b = 14.727(4) Å	b= 90.300(12)°.
	c = 16.692(4) Å	g = 90°.
Volume	2432.9(11) Å^3	
Z	2	
Density (calculated)	1.227 Mg/m^3	
Absorption coefficient	0.364 mm^{-1}	
F(000)	948	
Crystal size	0.230 x 0.080 x 0.040 mm^3	
Theta range for data collection	2.398 to 25.029°.	
Index ranges	-11<=h<=11, -17<=k<=16, -19<=l<=19	
Reflections collected	15600	
Independent reflections	4256 [R(int) = 0.0658]	
Completeness to theta = 25.029°	99.1 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4256 / 0 / 253	
Goodness-of-fit on F2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0438, wR2 = 0.0902	
R indices (all data)	R1 = 0.0782, wR2 = 0.1112	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.276 and -0.321 e.Å^{-3}	

Table S7. Crystal data and structure refinement for **2-(pyz)$_2$**

Empirical formula	$C_{44}H_{64}Al_2Cl_4N_4Si_2$	
Formula weight	900.93	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 29.643(4) Å	a= 90°.
	b = 11.0482(13) Å	b= 94.938(4)°.
	c = 15.368(2) Å	g = 90°.
Volume	5014.3(12) Å^3	
Z	4	
Density (calculated)	1.193 Mg/m^3	
Absorption coefficient	0.352 mm^{-1}	
F(000)	1912	
Crystal size	0.470 x 0.030 x 0.020 mm^3	
Theta range for data collection	2.342 to 25.039°.	
Index ranges	-35<=h<=35, -13<=k<=12, -18<=l<=18	
Reflections collected	31182	
Independent reflections	4436 [R(int) = 0.1782]	
Completeness to theta = 25.039°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4436 / 0 / 261	
Goodness-of-fit on F2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0748, wR2 = 0.1255	
R indices (all data)	R1 = 0.1456, wR2 = 0.1498	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.296 and -0.369 e.Å^{-3}	

Table S8. Crystal data and structure refinement for **1-κ^2-quI**

Empirical formula	$C_{42}H_{56}Al_2Cl_4N_4Si_2$	
Formula weight	868.84	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P 1	
Unit cell dimensions	a = 8.9257(9) Å	a= 83.306(3)°.
	b = 10.0525(10) Å	b= 79.441(3)°.
	c = 13.5513(16) Å	g = 80.105(3)°.
Volume	1173.0(2) $Å^3$	
Z	1	
Density (calculated)	1.230 Mg/m^3	
Absorption coefficient	0.374 mm^{-1}	
F(000)	458	
Crystal size	0.200 x 0.140 x 0.020 mm^3	
Theta range for data collection	2.349 to 25.080°.	
Index ranges	-10<=h<=10, -11<=k<=11, -16<=l<=16	
Reflections collected	29810	
Independent reflections	8256 [R(int) = 0.0742]	
Completeness to theta = 25.080°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8256 / 3 / 501	
Goodness-of-fit on F2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0920, wR2 = 0.2850	
R indices (all data)	R1 = 0.1080, wR2 = 0.2992	
Absolute structure parameter	0.01(4)	
Extinction coefficient	0.025(10)	
Largest diff. peak and hole	1.247 and -0.529 $e.Å^{-3}$	

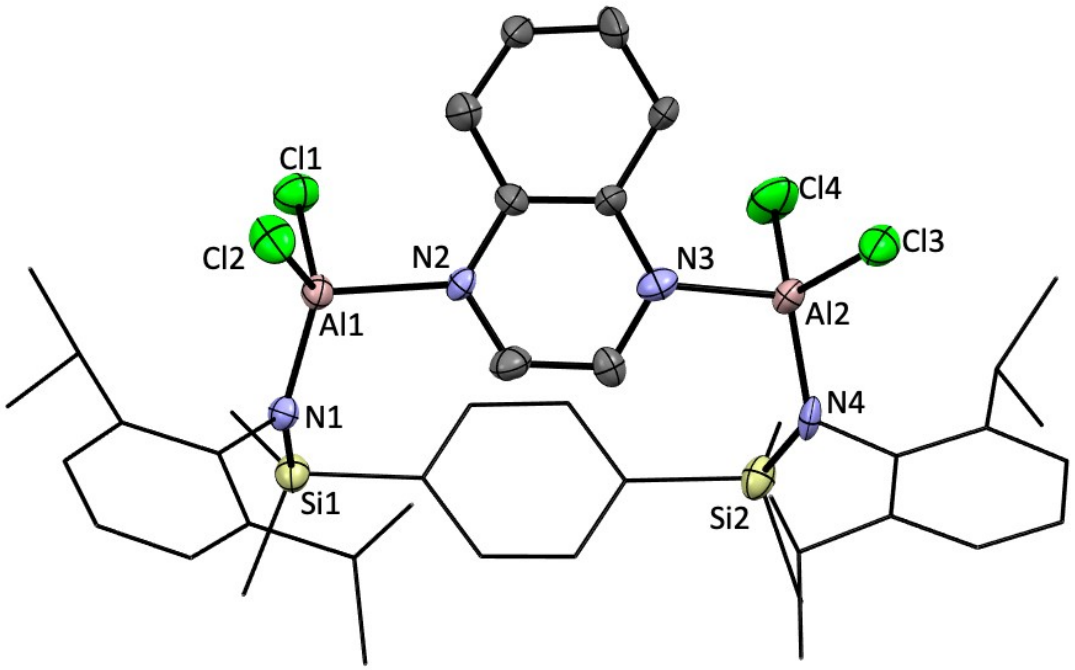


Figure S19. ORTEP of **1-κ^2-qul** (50% thermal ellipsoids; all hydrogen atoms are omitted for clarity).

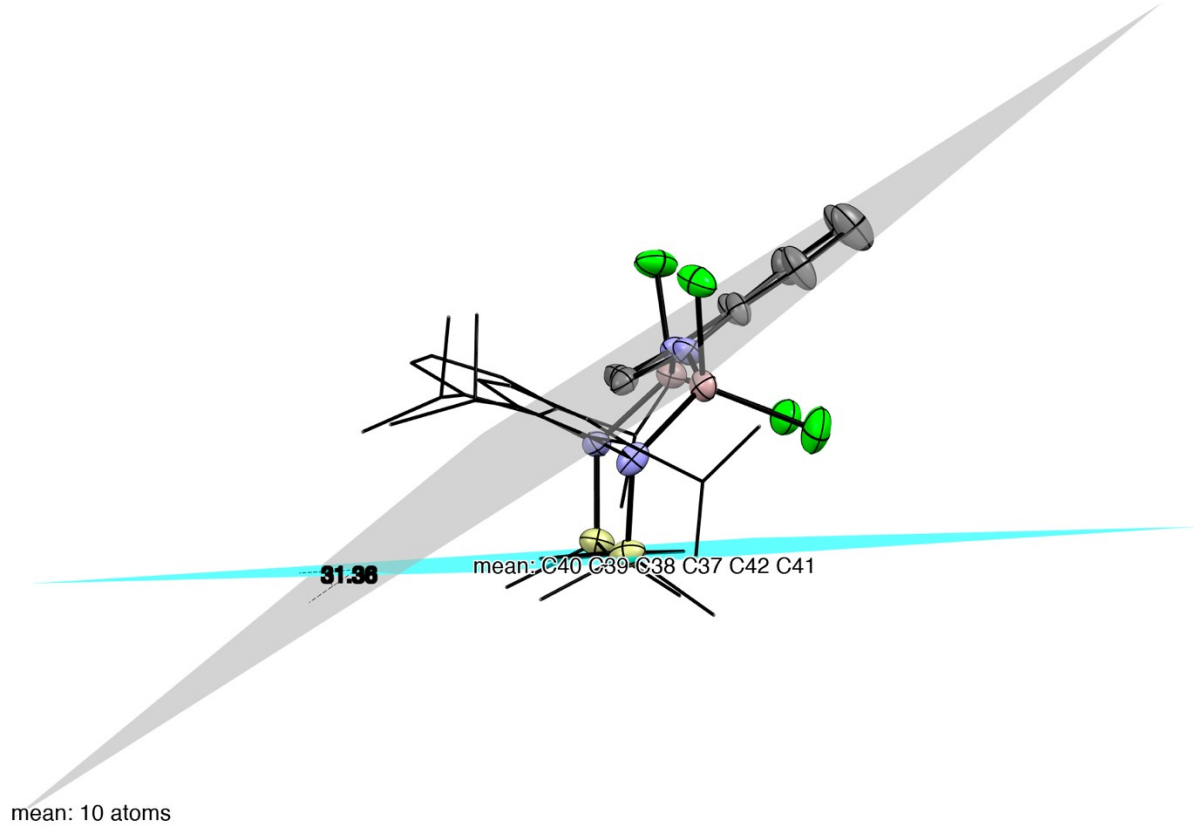


Figure S20. The side view of the molecular structure of **1-κ^2-qul** (50% thermal ellipsoids; all hydrogen atoms are omitted for clarity) showing the inclined quinoxaline plane (gray) relative to the central phenyl plane (cyan).

Table S9. Crystal data and structure refinement for **1_2-*μ*-(bipy)$_2$**

Empirical formula	$C_{95}H_{124}Al_4Cl_8N_8Si_4$	
Formula weight	1881.89	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 18.184(2) Å	a= 90°.
	b = 10.2631(12) Å	b= 94.243(3)°.
	c = 27.735(3) Å	g = 90°.
Volume	5161.9(10) Å^3	
Z	2	
Density (calculated)	1.211 Mg/m^3	
Absorption coefficient	0.345 mm^{-1}	
F(000)	1988	
Crystal size	0.310 x 0.090 x 0.020 mm^3	
Theta range for data collection	2.280 to 25.112°.	
Index ranges	-21<=h<=20, -12<=k<=12, -33<=l<=33	
Reflections collected	70763	
Independent reflections	9167 [R(int) = 0.1097]	
Completeness to theta = 25.112°	99.6 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9167 / 0 / 554	
Goodness-of-fit on F2	1.050	
Final R indices [I>2sigma(I)]	R1 = 0.0575, wR2 = 0.1182	
R indices (all data)	R1 = 0.1250, wR2 = 0.1499	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.386 and -0.465 e.Å^{-3}	

3. Computational details and results

Density Functional Theory (DFT) calculations were carried out using the Gaussian 16 suite of programs.[1] Geometry optimizations were conducted at the M06-2X[2-3]/def2-SVP[4] level of theory, incorporating Grimme's D3 dispersion correction with Becke-Johnson (BJ) damping.[5-6]

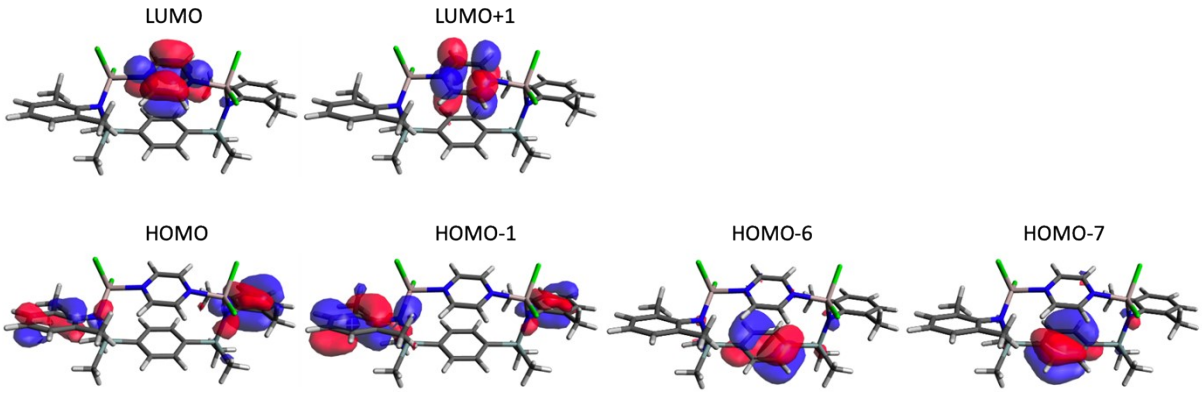


Figure S21. Frontier orbitals of **1-κ^2-pyz**.

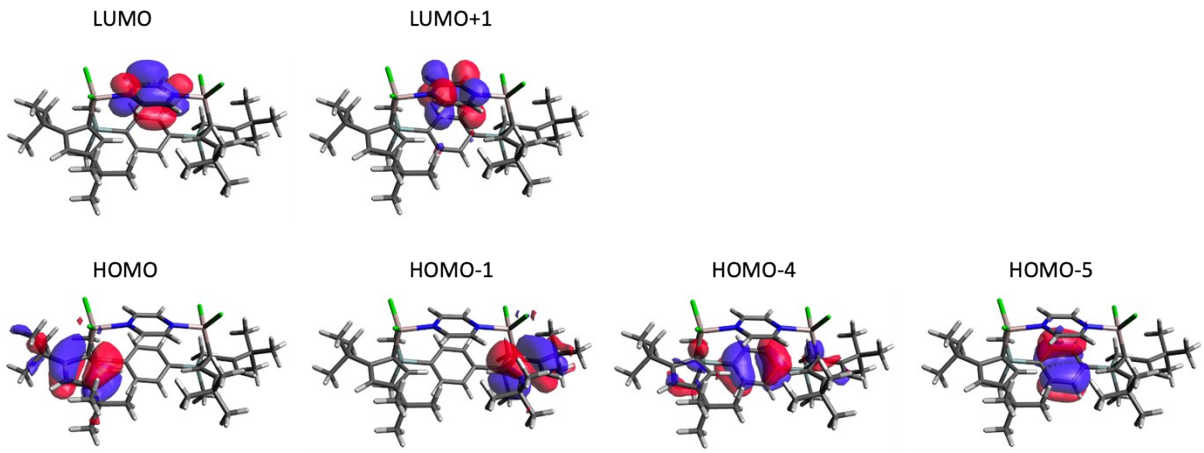


Figure S22. Frontier orbitals of **2-κ^2-pyz**.

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