N-Heterocyclic Olefin-Based Dianionic [^{OArCH2}*NHO*^{ArO}]$^{2-}$ and Neutral [^{MeOArCH2}*NHO*^{ArOMe}] *O,C,O'*-Pincer Ligands.

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1. General Methods and Instrumentation.

All experiments were carried out under dry and oxygen-free nitrogen atmosphere using standard Schlenk techniques or in an argon-filled glovebox (MBraun), unless otherwise stated. Prior to use, glassware were dried overnight at 130 °C and solvents were dried, distilled and degassed using standard methods and stored on activated 4 Å molecule sieves in the glovebox. The phenolic imidazole $^{\mathbf{HOAr}}$**Imd**,[1] the benzyl bromide $^{\mathbf{HOAr}}$**CH_2Br**,[2] and their methylated versions $^{\mathbf{MeOAr}}$**Imd**[3] and $^{\mathbf{MeOAr}}$**CH_2Br**[4] were made following literature procedure. $AlMe_3$ (2 M in toluene) and $KN(SiMe_3)_2$ were purchased from Sigma-Aldrich and used inside the glovebox as received. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Avance NEO (500 MHz) or Avance III (500 MHz) or Jeol (400 MHz) spectrometer at ambient temperature unless otherwise mentioned. Abbreviations for NMR spectra: s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), br (broad). High-resolution mass spectrometric analyses were done either on a Bruker micrOTOF–Q II or Waters Xevo G2-XS QTof Spectrometers. X-ray diffraction data were collected on either a Rigaku Synergy i xtalab or a Bruker D8 QUEST diffractometer. The crystallographic data for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre, under the deposition numbers 2541598 (**1**), 2541599 (**2**), 2541600 (**3**), 2541601 (**4**). The data are available free of charge via https://www.ccdc.cam.ac.uk/structures/

2. Synthesis and Characterization Data.

$^{\mathbf{Me}}$**L*H_3*Br:** A 50 mL storage tube fitted with a magnetic stir bar was charged with $^{\mathbf{HOAr}}$**Imd** (3.000 g, 9.985 mmol) and $^{\mathbf{HOAr}}$**CH_2Br** (2.988 g, 9.985 mmol) and evacuated for 30 min before adding 20 mL of acetonitrile. The mixture was heated at 110 °C under constant stirring for 3 d. Upon cooling to room temperature, the volatiles were removed under vacuum and the residue was washed with ether (2 × 50 mL) to get $^{\mathbf{Me}}$**L*H_3*Br** (5.367 g, 8.950 mmol, 90%) as a white powder.

^{1}H NMR (DMSO-*d*$_6$, 400 MHz): δ 8.48 (s, 1 H, Ar-*H*), 8.27 (s, 1 H, Ar-*H*), 7.70 (s, 1 H, Ar-*H*), 7.55 (s, 1 H, Ar-*H*), 7.18 (s, 1 H, ArO*H*), 7.13 (s, 1 H, ArO*H*), 6.85 (s, 1 H, NC*H*CHN), 6.18 (s, 1 H, NCHC*H*N), 5.37 (s, 2 H, NCC*H*$_2$Ar), 4.52 (s, 2 H, NC*H*$_2$Ar), 3.62 (s, 3 H, N-*Me*), 1.37 (s, 9 H, *^{t}Bu*), 1.32 (s, 9 H, *^{t}Bu*), 1.11 (s, 9 H, *^{t}Bu*), 1.06 (s, 9 H, *^{t}Bu*). **^{13}C{^{1}H} NMR** (DMSO-*d*$_6$, 100 MHz): δ 151.5, 151.0, 145.9, 143.0, 139.2, 124.8, 124.6, 123.5, 123.0, 122.9, 122.1, 48.2, 35.4, 35.2, 34.3, 34.2, 31.7, 30.3. HRMS-(m/z): [M+nH] calc. for $[C_{17}H_{23}N_3]$, 519.3945, Found 519.3922.

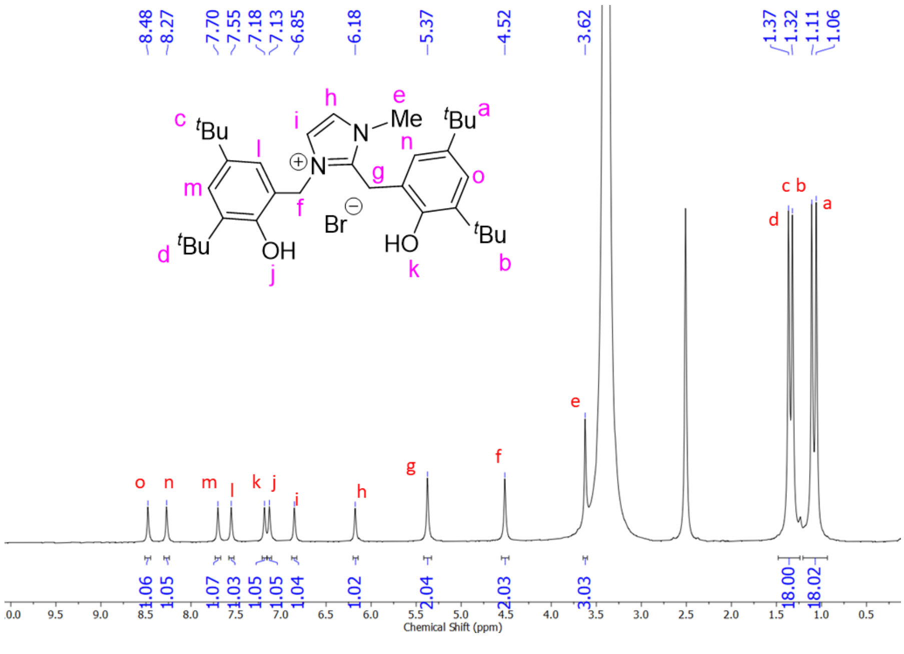

Figure S1. ^{1}H NMR spectrum of $^{\mathbf{Me}}$**L*H_3*Br** in DMSO-*d*$_6$.

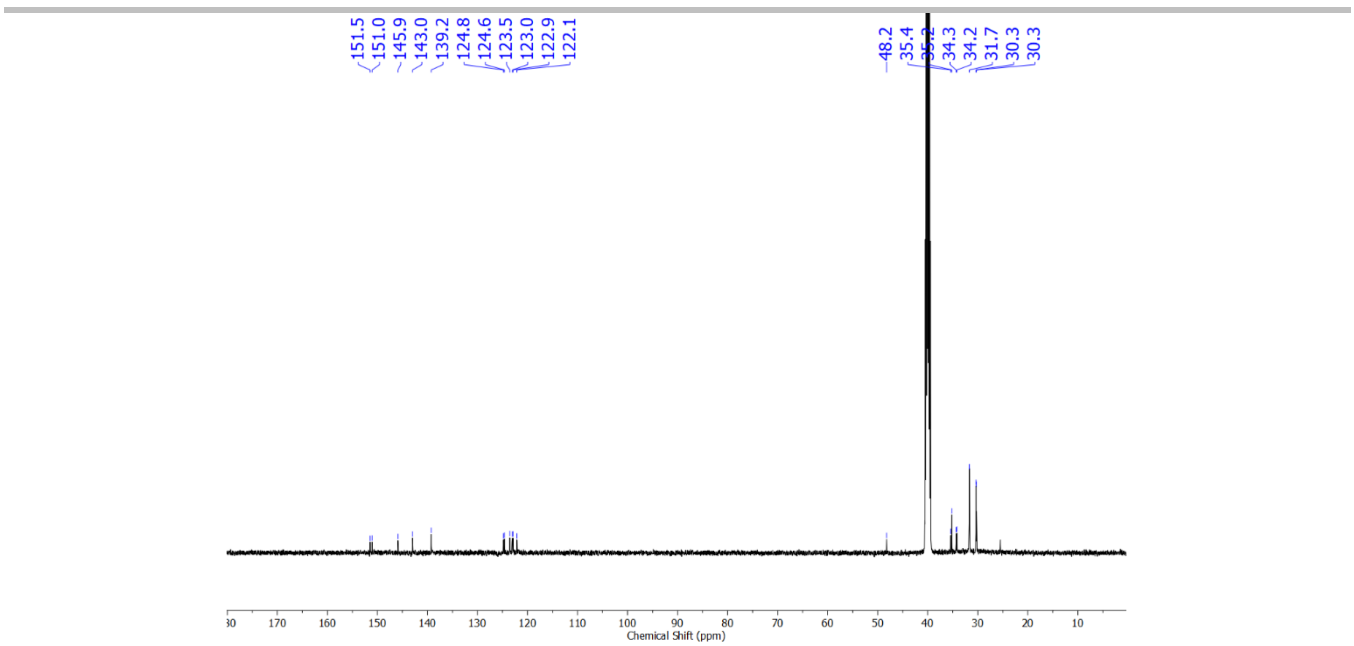

Figure S2. $^{13}C\{^1H\}$ NMR spectrum of ^{Me}**L*H*$_3$Br** in DMSO-d_6.

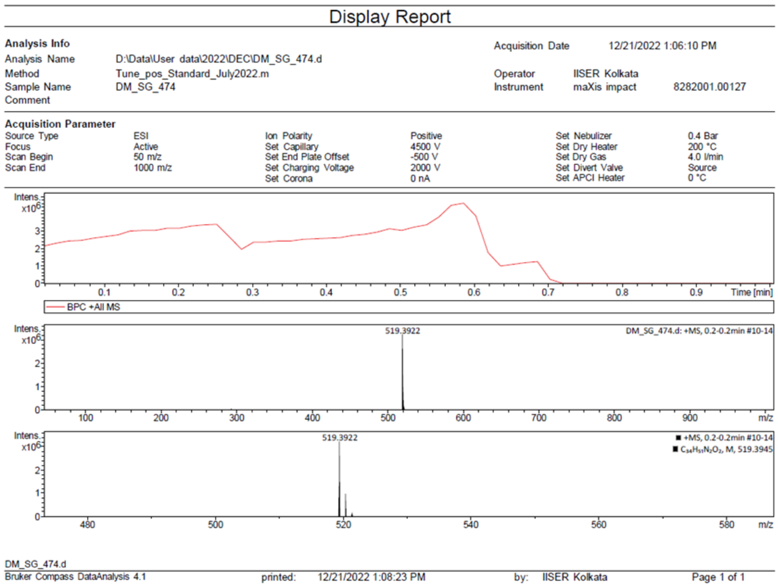

Figure S3. HRMS data of ^{Me}**L*H*$_3$Br**.

1: A 10 mL screw-cap vial equipped with a magnetic stir bar was charged with ^{Me}**L*H*$_3$Br** (0.300 g, 0.500 mmol) and 1 mL of toluene. To this suspension, a 3 mL toluene solution of $KN(SiMe_3)_2$ (0.300 g, 1.5 mmol) was added dropwise under constant stirring. The reaction mixture was continued to stir for an additional 12 h at room temperature. Volatiles were then removed under reduced pressure and the residue was extracted in 5 mL of THF and filtered. Evaporating the filtrate under reduced pressure gave a white solid that was purified by recrystallization from THF followed by washing with hexane (3 × 2 mL). Finally, drying the solid under vacuum afforded 0.165 g (0.176 mmol, 70% yield) of **1** as an analytically pure white solid. X-ray quality single crystals were grown from diffusing hexane into a concentrated THF solution at −35 °C.
^{1}**H NMR** (C_6D_6/THF-d_8 (2:1); 500 MHz): δ 7.00-7.59 (m, 6 H, Ar-*H*), 6.99 (s, 1 H, NC*H*CHN), 6.95 (s, 1 H, NCHC*H*N), 6.32 (s, 1 H, NC*H*CHN), 6.28 (s, 1 H, NCHC*H*N), 4.19 (s, 1 H, ArCH$_2$C*H*(Ar)(Imd)), 3.48 (s, 3 H, N-*Me*), 3.20 (br, 4 H, ArC*H*$_2$CH(Ar)(Imd) & ArC*H*$_2$Imd), 3.06 (s, 3 H, N-*Me*), 1.34-2.12 (54 H, ^{t}*Bu*). ^{13}**C{^{1}H} NMR** (C_6D_6/THF-d_8 (2:1); 126 MHz): δ 150.9, 135.6, 128.0, 127.9, 127.8, 127.5, 125.5, 124.9, 123.2, 120.8, 67.4, 67.2, 35.2, 33.9, 33.7, 33.6, 32.9, 32.2, 30.0, 29.8, 25.4, 24.9, 24.8, 24.6, 24.4, 24.2, 24.0. Elemental analysis for $C_{73}H_{115}N_4O_8K_3$: Calcd. C, 67.76; H, 8.96; N, 4.33; Found C, 67.20; H, 8.88; N, 4.27.

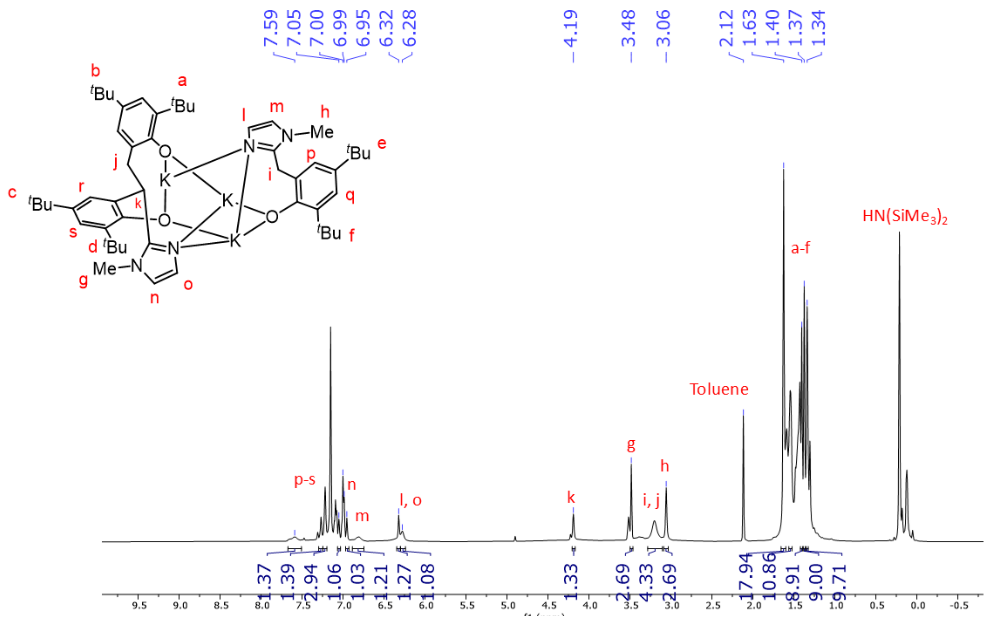

Figure S4. ^{1}H NMR spectrum of **1** in C_6D_6/THF-d_8 (2:1).

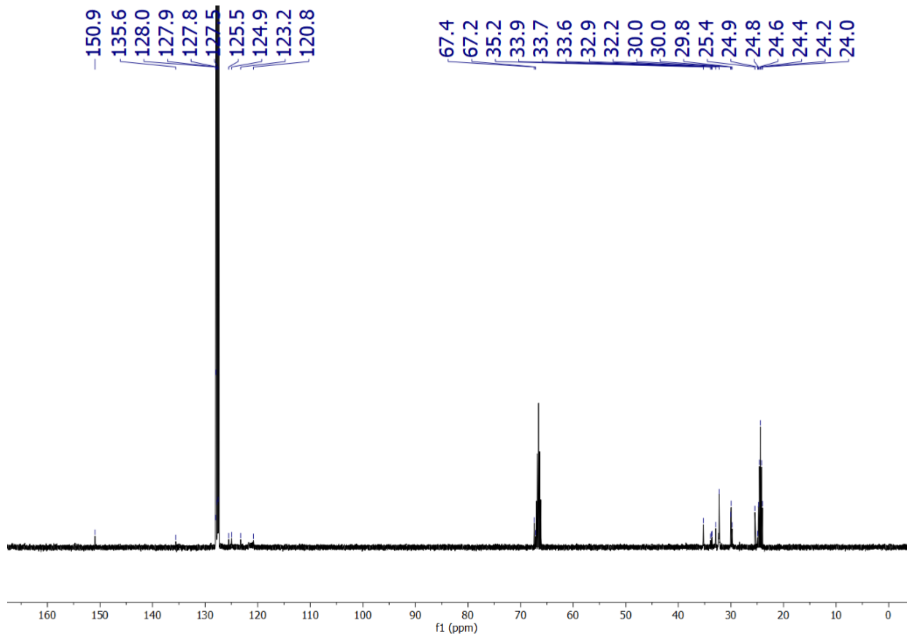

Figure S5. ^{13}C{^{1}H} NMR spectrum of **1** in C_6D_6/THF-d_8 (2:1).

^{Me}L^{OMe}*H*Br: A 50 mL storage tube fitted with a magnetic stir bar was charged with **^{MeOAr}Imd** (1.500 g, 4.770 mmol) and **^{MeOAr}CH$_2$Br** (1.494 g, 4.770 mmol) and evacuated for 30 min before adding 10 mL of acetonitrile. The mixture was heated at 110 °C under constant stirring for 3 d. Upon cooling to room temperature, the volatiles were removed under reduced pressure and the residue was washed with ether (2 × 50 mL) to get **^{Me}L^{OMe}*H*Br** (2.820 g, 4.520 mmol, 95%) as a white powder.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 (s, 1 H, Ar-*H*), 7.35 (s, 2 H, Ar-*H*), 7.27 (s, 1 H, Ar-*H*), 7.09 (d, $^3J_{HH}$ = 2.4 Hz, 1 H, NC*H*CHN), 6.29 (d, $^3J_{HH}$ =2.4 Hz, 1 H, NCHC*H*N), 5.42 (s, 2 H, NC*H*$_2$Ar), 4.72 (s, 2 H, NCC*H*$_2$Ar), 3.86 (s, 3 H, O*Me*), 3.85 (s, 3 H, O*Me*), 3.62 (s, 3 H, N-*Me*), 1.36 (s, 9 H, *^{t}Bu*), 1.29 (s, 9 H, *^{t}Bu*), 1.22 (s, 9 H, *^{t}Bu*), 1.13 (s, 9 H, *^{t}Bu*). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz): δ 155.9, 155.5, 147.4, 147.0, 146.4, 143.2, 143.1, 126.3, 126.1, 125.8, 125.6, 124.6, 123.2, 121.4, 63.1, 62.4, 48.4, 36.2, 35.5, 35.4, 34.7, 34.4, 31.5, 31.4, 31.1, 31.0. [M+nH] calc. for [$C_{17}H_{23}N_3$], 547.4258, Found 547.4233.

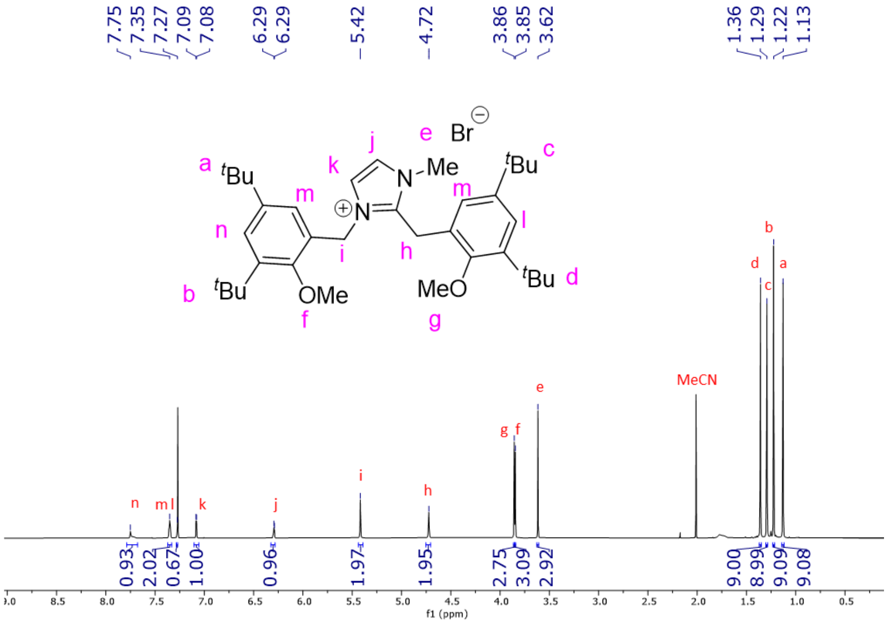

Figure S6. ^{1}H NMR spectrum of $^{Me}L^{OMe}$***H*****Br** in $CDCl_3$.

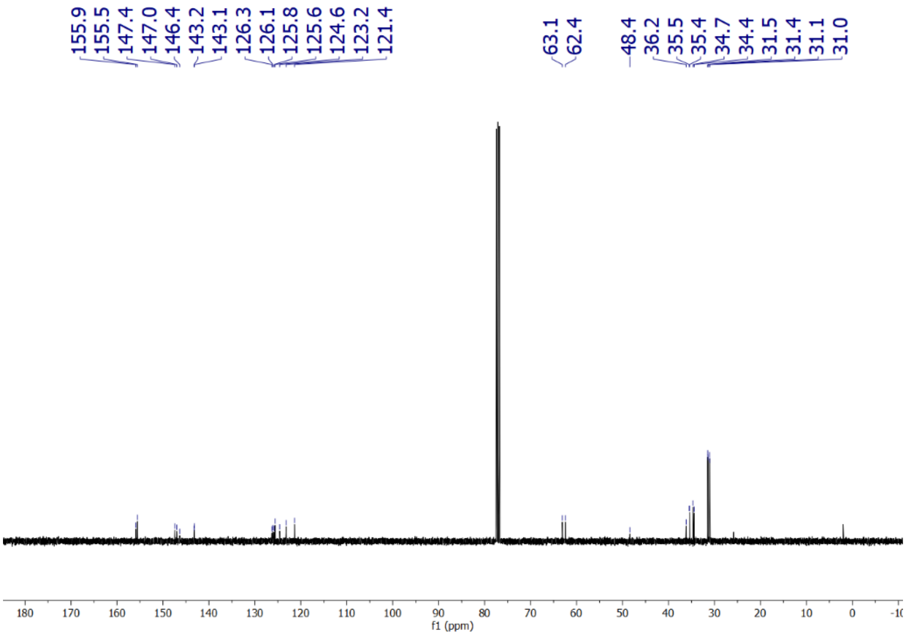

Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of $^{Me}L^{OMe}$***H*****Br** in $CDCl_3$.

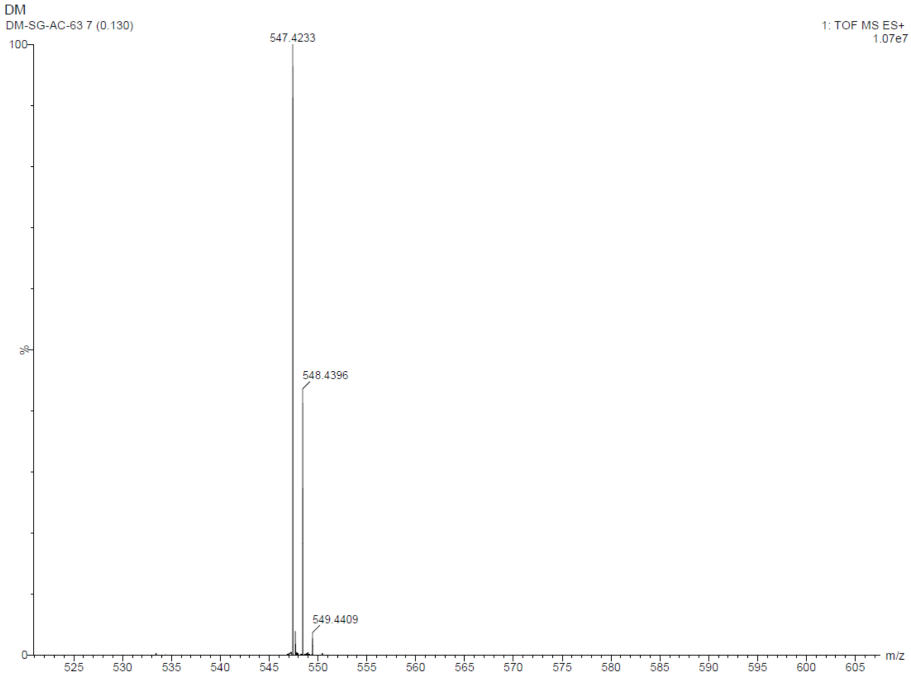

Figure S8. HRMS of **$^{Me}L^{OMe}$*H*Br**.

$^{Me}L^{OMe}$: In an argon-filled glovebox, a 10 mL screw-cap vial equipped with a magnetic stir bar was charged with **$^{Me}L^{OMe}$*H*Br** (0.200 g, 0.318 mmol) and 1 mL of toluene. To this suspension, a 2 mL toluene solution of KHMDS (0.064 g, 0.318 mmol) was added dropwise under constant stirring. The reaction mixture was continued to stir for an additional 1 h at room temperature. It was then filtered and the filtrate was evaporated under reduce pressure to obtain a white solid. It was purified by recrystallization from toluene followed by washing with chilled hexane (3 × 2 mL). Finally, drying the solid under vacuum afforded 0.156 g (0.285 mmol, 90% yield) of **$^{Me}L^{OMe}$** as a white solid.
^1H NMR (C_6D_6, 400 MHz): δ 7.37 (br, 1 H, Ar-*H*), 7.17 (br, 1 H, Ar-*H*), 7.07 (br, 2 H, Ar-*H*), 5.63 (s, 1 H, NC*H*CHN), 5.51 (s, 1 H, NCHC*H*N), 4.90 (br, 1 H, NCC*H*Ar), 4.44 (br, 2 H, NC*H*$_2$Ar), 3.76 (br, 3 H, O*Me*), 3.24 (br, 3 H, O*Me*), 2.47 (br, 3 H, N-*Me*), 1.53 (s, 9 H, *^{t}Bu*), 1.40 (s, 9 H, *^{t}Bu*), 1.30 (s, 9 H, *^{t}Bu*), 1.22 (s, 9 H, *^{t}Bu*). **$^{13}C\{^1H\}$ NMR** (C_6D_6, 100 MHz): δ 156.0, 145.7, 143.9, 141.9, 137.6, 129.0, 128.3, 128.1, 128.0, 127.9, 127.6, 125.4, 58.0, 35.2, 35.0, 34.4, 34.3, 31.7, 31.4, 31.1, 31.0, 26.9. Elemental analysis for $C_{36}H_{54}N_2O_2$: Calcd. C, 79.07; H, 9.95; N, 5.12; Found C, 78.77; H, 10.10; N, 5.08.

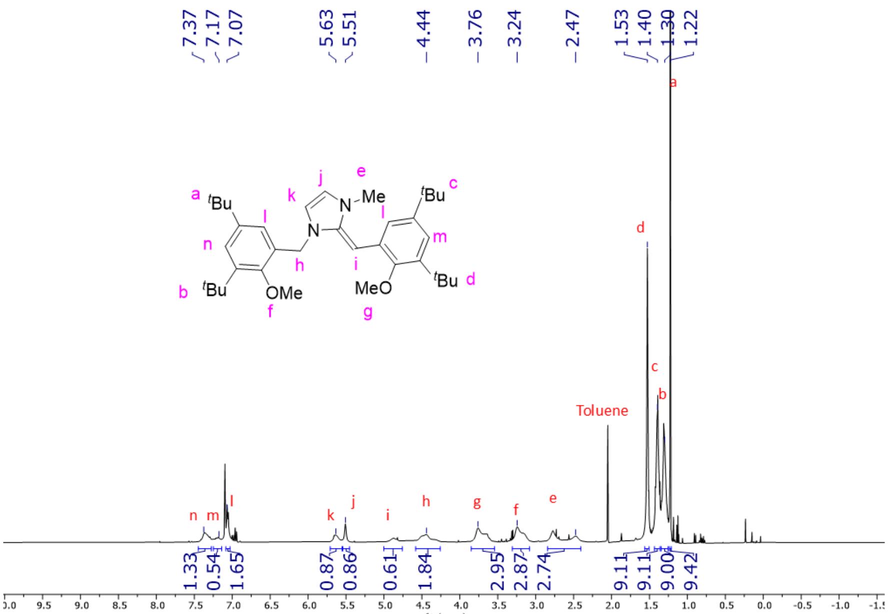

Figure S9. ^1H NMR spectrum of **$^{Me}L^{OMe}$** in C_6D_6.

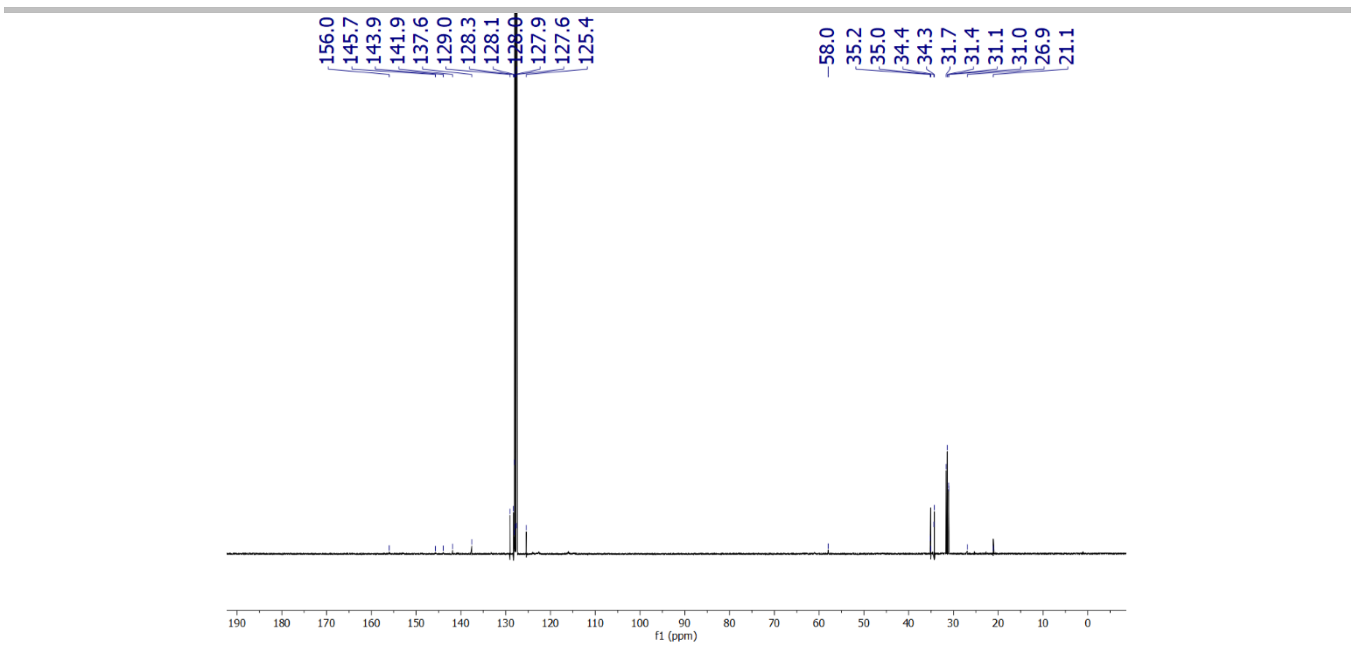

Figure S10. $^{13}C\{^1H\}$ NMR spectrum of ^{Me}**L**^{OMe} in C_6D_6.

2: A 10 mL screw-cap vial fitted with a magnetic stir bar was charged with ^{Me}**L**^{OMe} (0.165 g, 0.300 mmol) and dissolved in 2 mL of toluene. 150 µL of $AlMe_3$ solution (2 M toluene) was added dropwise into it under constant stirring. The reaction mixture was stirred for an additional 2 h at room temperature. All the volatiles were then removed under reduced pressure to obtain a white solid which was washed with hexane (3 × 5 mL) and dried under vacuum to obtain 0.183 g of **2** (0.295 mmol, 98%) as an analytically pure white solid. X-ray quality single crystals were grown from a concentrated toluene solution at −30 °C.

^{1}H NMR (C_6D_6, 400 MHz): δ 8.33 (s, 1 H, Ar-*H*), 7.38 (s, 1 H, Ar-*H*), 7.33 (s, 1 H, Ar-*H*), 7.20 (s, 1 H, Ar-*H*), 5.76 (s, 1 H, NC*H*CHN), 5.40 (s, 1 H, NCHC*H*N), 4.90 (d, $^3J_{HH}$ = 14.8 Hz, 1 H, NCH_2Ar), 4.63 (d, $^3J_{HH}$ = 14.8 Hz, 1 H, NCH_2Ar), 3.76 (s, 1 H, NCC*H*Al), 3.17 (s, 3 H, O*Me*), 2.93 (s, 3 H, O*Me*), 2.67 (s, 3 H, N-*Me*), 1.42 (s, 9 H, ^{t}*Bu*), 1.39 (s, 9 H, ^{t}*Bu*), 1.33 (s, 9 H, ^{t}*Bu*), 1.23 (s, 9 H, ^{t}*Bu*), –0.26 (s, 6 H, Al-*Me*), –0.45 (s, 3 H, Al-*Me*). **^{13}C{^{1}H} NMR** (C_6D_6, 100 MHz): δ 159.3, 156.3, 155.7, 146.4, 146.0, 142.0, 140.6, 133.4, 130.7, 126.2, 124.2, 121.4, 117.1, 115.8, 61.9, 59.3, 46.4, 35.2, 35.1, 31.6, 31.3, 30.9, –1.1, –5.4. Elemental analysis for $C_{39}H_{63}N_2O_2Al$: Calcd. C, 75.68; H, 10.26; N, 4.53; Found C, 75.79; H, 10.40; N, 4.40.

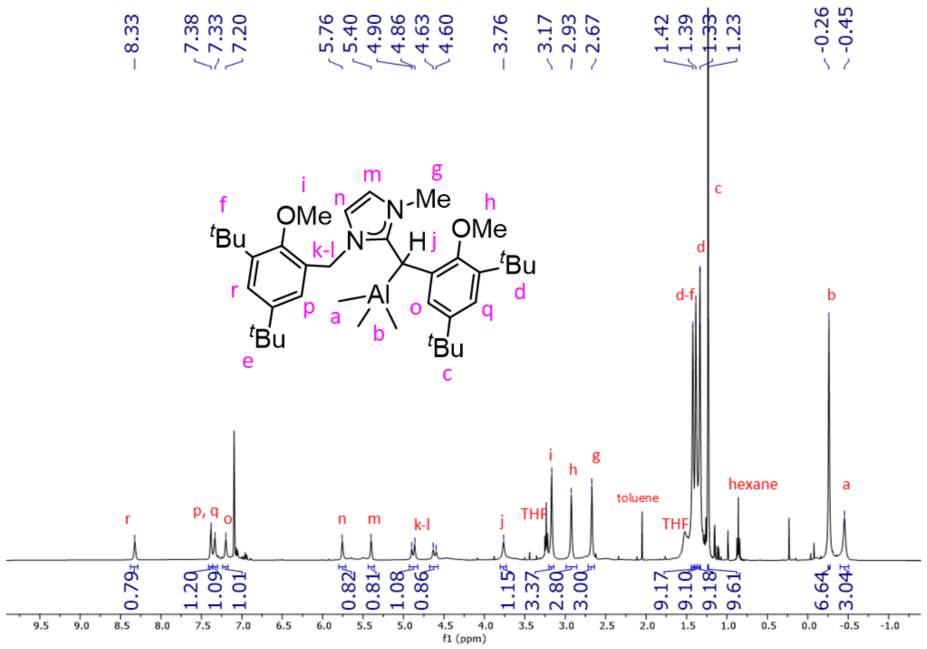

Figure S11. ^{1}H NMR spectrum of **2** in C_6D_6.

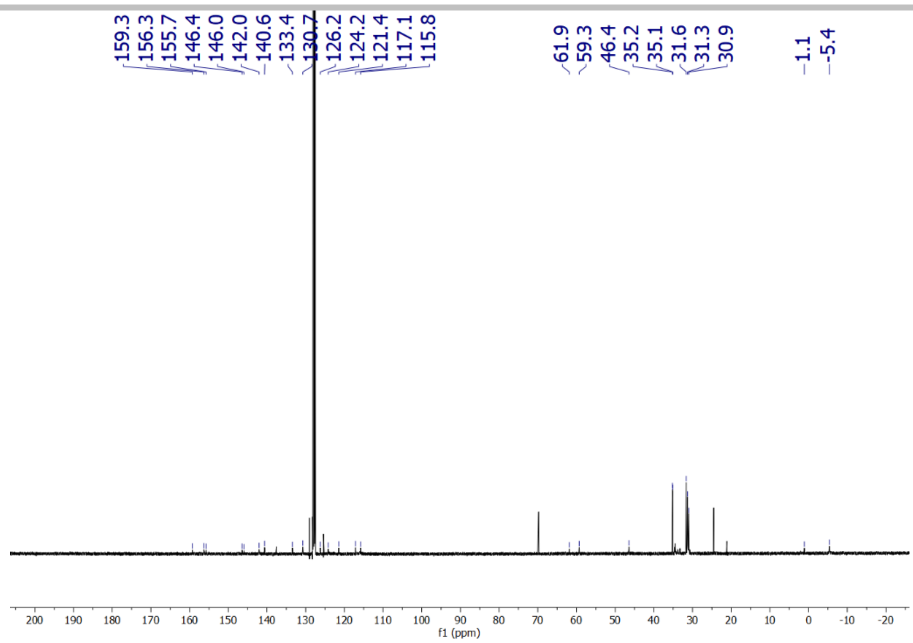

Figure S12. $^{13}C\{^1H\}$ NMR spectrum of **2** in C_6D_6.

3: A 10 mL screw-cap vial fitted with a magnetic stir bar was charged with ^{Me}**L*H*$_3$Br** (0.600 g, 1.000 mmol) and 2 mL of toluene to get a suspension. 0.5 mL of $AlMe_3$ solution (2 M toluene) was added dropwise into it under constant stirring that resulted in an immediate gas evolution. The reaction mixture was stirred for an additional 30 min at room temperature. All the volatiles were then removed under reduced pressure to obtain a white solid which was washed with hexane (3 × 5 mL) and dried under vacuum to obtain 0.607 g of **3** (0.950 mmol, 95%) as an analytically pure white solid. X-ray quality single crystals were grown from a concentrated solution in THF/toluene (5:1) mixture at −30 °C.

^{1}H NMR (C_6D_6/THF-d_8 (2:1); 500 MHz): δ 7.39 (s, 1 H, Ar-*H*), 7.36 (s, 1 H, Ar-*H*), 7.00 (s, 1 H, Ar-*H*),6.85 (s, 1 H, Ar-*H*), 6.76 (br, 1 H, NC*H*CHN), 6.32 (s, 1 H, NCHC*H*N), 5.56 (s, 1 H, NC*H*$_2$Ar), 4.90 (s, 1 H, NC*H*$_2$Ar), 3.49 n(s, 1 H, NCC*H*$_2$Ar), 3.13 (s, 3 H, N-*Me*), 3.08 (s, 1 H, NCC*H*$_2$Ar), 1.58 (s, 9 H, ^{t}*Bu*), 1.58 (s, 9 H, ^{t}*Bu*), 1.58 (s, 9 H, ^{t}*Bu*), 1.58 (s, 9 H, ^{t}*Bu*), −0.15 (s, 3 H, Al-*Me*). **^{13}C{^{1}H} NMR** (C_6D_6/THF-d_8 (2:1); 126 MHz): δ 154.9, 154.7, 147.0, 140.2, 140.0, 138.9, 138.7, 124.9, 124.0, 123.8, 121.9, 121.2, 120.2, 67.3, 67.0, 49.7, 35.2, 34.6, 33.8, 33.7, 31.3, 30.0, −0.7. Elemental analysis for $C_{25}H_{52}N_2O_2BrAl$: Calcd. C, 65.72; H, 8.19; N, 4.38; Found C, 65.50; H, 8.15; N, 4.46.

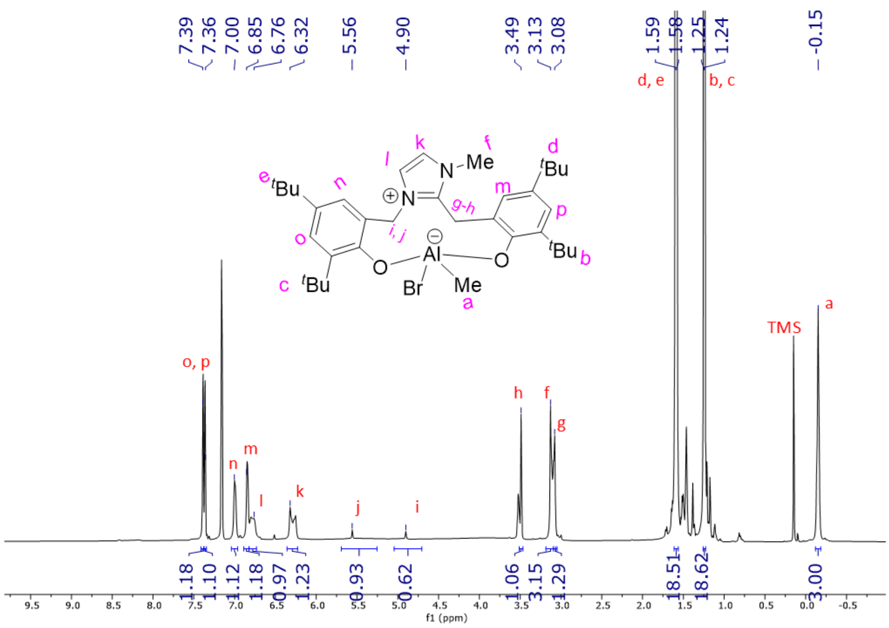

Figure S13. ^{1}H NMR spectrum of **3** in C_6D_6/THF-d_8 (2:1).

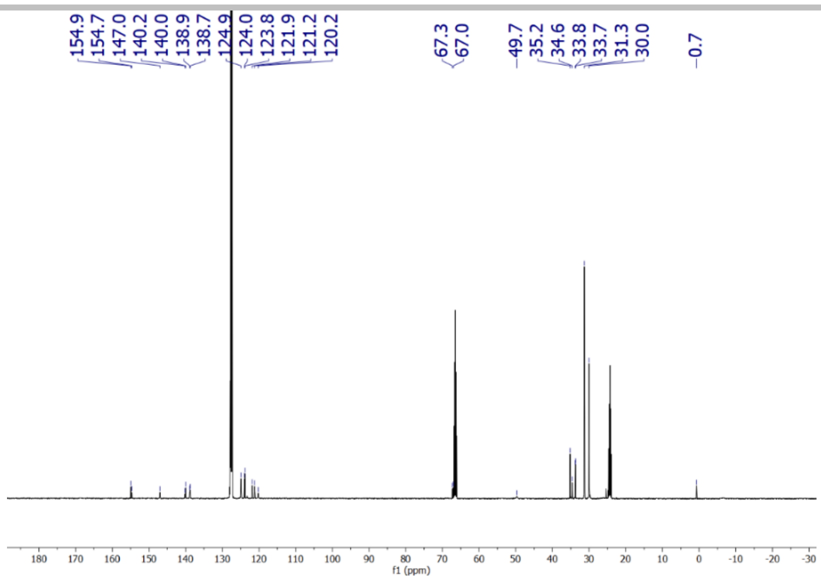

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6/THF-d_8 (2:1).

4: A 10 mL screw-cap vial fitted with a magnetic stir bar was charged with **^{Me}L*H*$_3$Br** (0.600 g, 1.000 mmol) and 2 mL of toluene to get a white suspension. 0.5 mL of $AlMe_3$ solution (2 M toluene) was added dropwise into it under constant stirring that resulted in an immediate gas evolution. The reaction mixture was stirred for an additional 30 min at room temperature. A 2.5 mL toluene solution of $KN(SiMe_3)_2$ (0.200 g, 1 mmol) was then added dropwise under constant stirring and the stirring was continued for an additional 2 h at room temperature. The mixture was then filtered using a pad of celite. All the volatiles were removed from the filtrate under reduced pressure to obtain a white solid which was washed with hexane (3 × 5 mL) and dried under vacuum to obtain 0.502 g of **4** (0.900 mmol, 90%) as an analytically pure white solid. X-ray quality single crystals were grown from its concentrated toluene solution at –30 °C.

Alternatively, a 10 mL screw cap vial fitted with a stir bar was charged with **3** (0.250 g, 0.390 mmol) and 1.5 mL dry toluene. To this suspension a 2 mL toluene solution of $KN(SiMe_3)_2$ (0.078 g, 0.390 mmol) was added dropwise. The reaction mixture was then further stirred for additional 2 h before filtering through a pad of celite. The filtrate was concentrated under vacuum and 5 mL hexane was added to the residue to obtain a white precipitate. Washing the precipitate with fresh hexane (2 × 5 mL) and dried under vacuum gave analytically pure **4** (0.195 g, 0.350 mmol, 90%) as a white solid.

^{1}H NMR (C_6D_6, 400 MHz): δ 7.50 (s, 1 H, Ar-*H*), 7.49 (s, 1H, Ar-*H*), 6.77 (s, 1 H, Ar-*H*), 6.61 (s, 1 H, Ar-*H*), 5.69 (s, 1 H, NCHCHN), 5.26 (d, $^{3}J_{HH}$ = 14.8 Hz, N-C*H*H-Ar), 5.07 (s, 1 H, NCHC*H*N), 3.37 (d, $^{3}J_{HH}$ = 14.8 Hz, N-CH*H*-Ar), 2.74 (s, 1 H, NCC*H*Al), 2.19 (s, 3 H, N-*Me*), 1.69 (s, 9 H, *^{t}Bu*), 1.57 (s, 9 H, *^{t}Bu*), 1.39 (s, 9 H, *^{t}Bu*), 1.29 (s, 9 H, *^{t}Bu*), –0.05 (s, 3 H, Al-*Me*). **$^{13}C\{^{1}H\}$ NMR** (C_6D_6, 100 MHz): δ 161.0, 157.0, 155.4, 138.9, 138.4, 138.0, 137.1, 128.9, 124.9, 124.6, 124.3, 124.2, 122.6, 117.8, 116.7, 49.2, 35.4, 35.2, 33.9, 32.7, 32.0, 31.7, 29.7, 29.6. Elemental analysis for $C_{35}H_{51}N_2O_2Al$: Calcd. C, 75.23; H, 9.20; N, 5.01; Found C, 75.13; H, 9.16; N, 5.10.

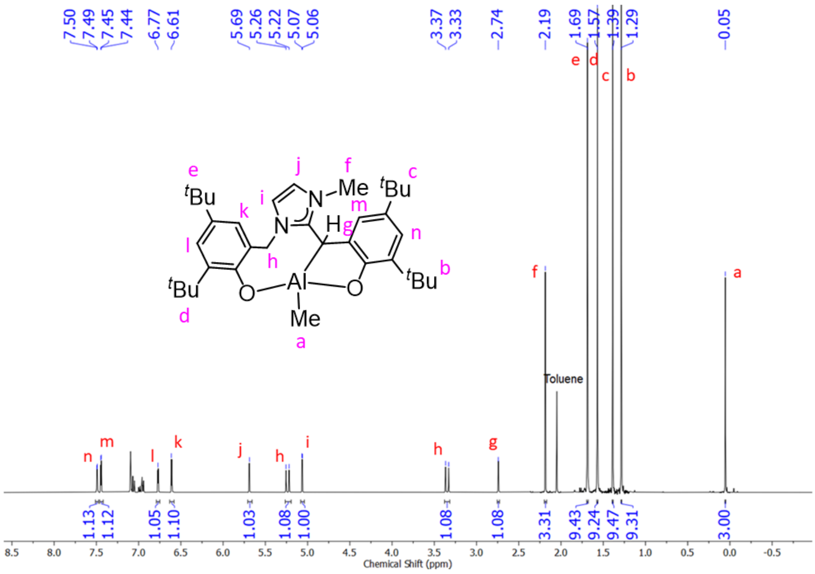

Figure S15. ^{1}H NMR spectrum of **4** in C_6D_6.

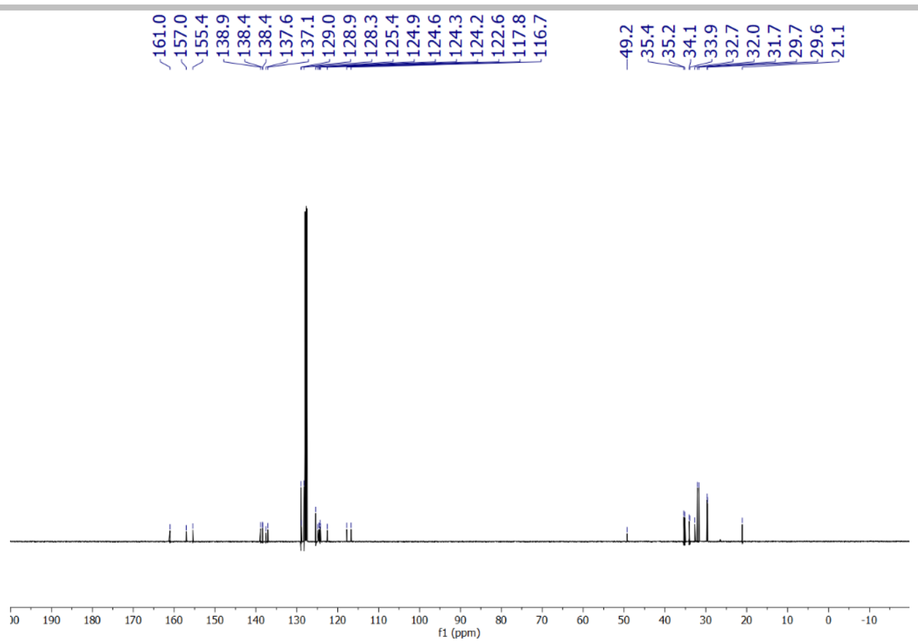

Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in C_6D_6.

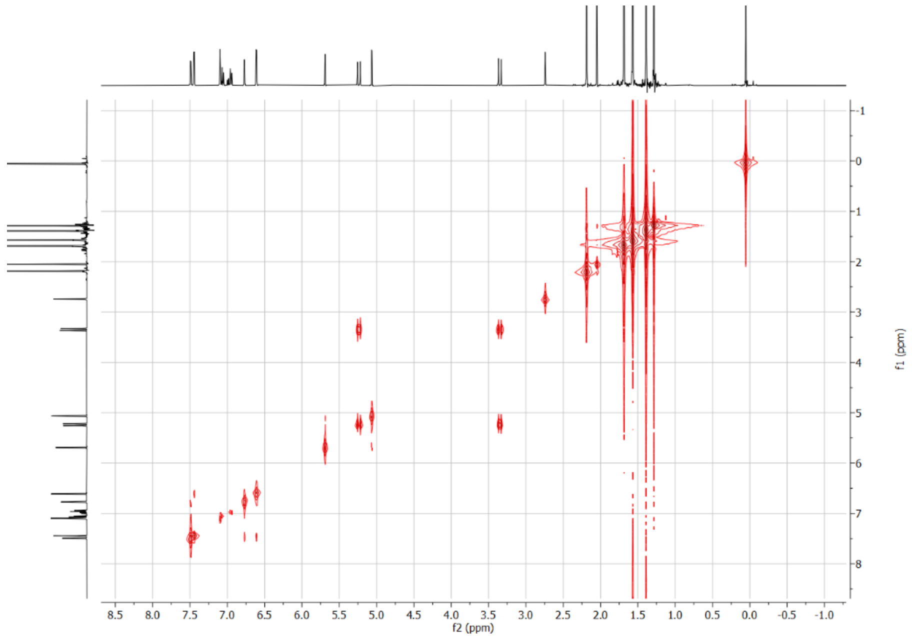

Figure S17. ^{1}H-^{1}H COSY NMR spectrum of **4** in C_6D_6.

3. Crystallographic Data.

X-ray diffraction data of **1, 3** and **4** were collected on a Rigaku XtaLAB Synergy i, Dualflex four-circle diffractometer with HyPix3000 detector and Cu-K_α radiation at 100 K. X-ray diffraction data of **2** was collected on a Bruker D8 three-circle diffractometer, Bruker smart CCD 6000 area detector, and Mo-K_α radiation at 100 K. The structures were solved by intrinsic phasing using SHELXT.[5] All refinements were carried out against F^2 with ShelXL[6] as implemented in the program system Olex2.[7] The non-hydrogen atoms were refined with anisotropic displacement parameters. In the case of **3**, potential solvent accessible area or void space was calculated using PLATON[8] executable in Olex2. In the case of **1**, significant disorder was observed in multiple phenyl ring-*C* and alkyl chain-*C* atoms. Appropriate restraints such as SADI, RIGU, DELU, SIMU, DANG, ISOR and DFIX and AFIX were applied to maintain chemically reasonable bond lengths (for geometry), and physically meaningful anisotropic displacement parameters for all thermal ellipsoids, resulting in a satisfactory structural model. All hydrogen atoms were included in calculated positions and treated as riding throughout the refinement. Refinement results are given in Tables S1. Graphical representations were performed with the program DIAMOND.[9] The crystallographic data can be obtained free of charge from the Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif using the CCDC numbers (given in the tables S1 and S2) as reference.

Table S1: Crystallographic data of **1**-**4**.

	1	**2**	**3**	**4**
Formula	$C_{81}H_{130}K_3N_4O_{10}$	$C_{46}H_{71}AlN_2O_2$	$C_{43}H_{68}AlBrN_2O_4$	$C_{42}H_{59}AlN_2O_2$
Fw /g·mol^{-1}	1437.18	711.02	783.88	650.89
cryst. color, habit	White	White	White	White
crystal size / mm^3	0.16 × 0.141 × 0.116	0.07 × 0.06 × 0.03	0.21 × 0.08 × 0.05	0.0228 × 0.0224 × 0.0198
crystal system	triclinic	triclinic	triclinic	monoclinic
space group	P-1	P-1	P-1	P2$_1$/c
a / Å	13.4375(3)	9.922(3)	10.6048(2)	12.4150(2)
b / Å	16.7453(4)	17.188(5)	15.8261(3)	16.7769(3)
c / Å	19.3647(5)	26.042(7)	28.5773(4)	19.3270(3)
α / °	92.178(2)	89.435(11)	76.5860(10)	90
β / °	105.282(2)	89.895(11)	87.7380(10)	103.195(2)
γ / °	95.822(2)	78.034(10)	71.836(2)	90
V / Å^3	4172.06(18)	4344(2)	4430.08(14)	3919.25(12)
Z	2	4	4	4
d_{calc}/Mg·m^{-3}	1.144	1.087	1.175	1.103
μ/mm^{-1}	1.884 (CuKα)	0.083 (CuKα)	1.760 (MoKα)	0.713 (CuKα)
F(000)	1562.0	1560.0	1680.0	1416.0
2θ range for data collection/ °	4.742 to 137.69	3.938 to 50.054	6.042 to 136.3	7.06 to 136.712
index ranges	-16 ≤ h ≤ 14, -20 ≤ k ≤ 19, -22 ≤ l ≤ 23	-11 ≤ h ≤ 11, -20 ≤ k ≤ 20, -31 ≤ l ≤ 31	-12 ≤ h ≤ 12, -18 ≤ k ≤ 19, -34 ≤ l ≤ 27	-14 ≤ h ≤ 14, -19 ≤ k ≤ 20, -19 ≤ l ≤ 23
Reflections collected	53388	128933	59330	41208
independ.reflns (R_{int})	14954 [R_{int} = 0.0468, R_{sigma} = 0.0429]	15287 [R_{int} = 0.2369, R_{sigma} = 0.1283]	16044 [R_{int} = 0.0429, R_{sigma} = 0.0387]	7089 [R_{int} = 0.0616, R_{sigma} = 0.0348]
observed reflns	11427	9852	13591	5777
data/ restr./ param.	14954/41/864	15287/222/905	16044/266/887	7089/0/439
R_1, wR_2 [$I > 2\sigma(I)$]	R_1 = 0.0944, wR_2 = 0.2739	R_1 = 0.1855, wR_2 = 0.4152	*R_1 = 0.0831, wR_2 = 0.2322*	*R_1 = 0.0657, wR_2 = 0.1725*
R_1, wR_2 (all data)	R_1 = 0.1136, wR_2 = 0.2989	R_1 = 0.2344, wR_2 = 0.4410	*R_1 = 0.0917, wR_2 = 0.2376*	*R_1 = 0.0799, wR_2 = 0.1938*
GooF-of-fit on F^2	1.083	1.075	1.089	1.108
largest diff. peak, hole/ e·Å^3	1.64/-1.33	0.91/-0.62	0.56/-0.42	1.08/-0.57
CCDC number	2541598	2541599	2541600	2541601

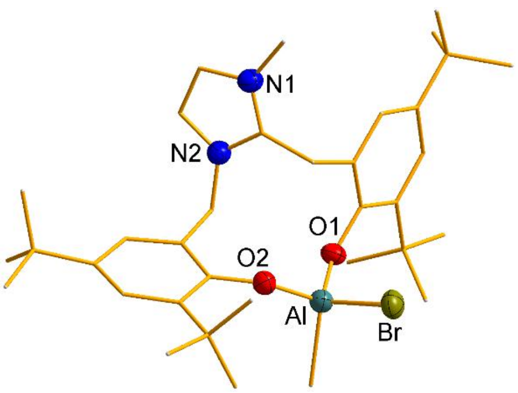

Figure S18. DIAMOND-rendered molecular structure of **3**. Relevant ellipsoids are set at 50% probability level while the rest of the skeleton is shown in sticks for better viewing. H atoms are omitted for clarity. Selected bond distances (Å): Al-C2 2.059(3), Al-O1 1.748(3), Al-O2 1.737(3).

4. DFT Analyses.

Density Functional Theory (DFT) studies were undertaken using ORCA 6.0 program.[10] The structures were optimized using the B3LYP[11] functional with Grimme's D3 parameter set with Becke-Johnson (BJ) damping (D3BJ) for the dispersion correction.[12] The Resolution of the Identity J-Integral, Chain-Of-Spheres Exchange (RIJCOSX)[13] method was used to speed up the calculations with minimum loss of accuracy. The minimally augmented ma-def2-SVP basis set was used to describe all atoms except Al, for which def2-TZVP was used.[14] This combination is referred to as the B3LYP-D3BJ/BS1 level of theory. The stationary point was characterized by vibrational frequency analysis. The natural bond orbital (NBO)[15] analyses were performed at B3LYP-D3BJ/def2-TZVP//B3LYP-D3BJ/BS1 level of theory using Gaussian 16.[16]

Table S2: Selected Natural Charges on **4**.

Atom	Natural Charge
Al	+1.947
C_{α}	+0.478
C_{β}	–0.757
O1	–0.881
O2	–0.917

Table S3: Selected Wiberg Bond Indices (WBI) on **4**.

Bond	Natural Charge
C_{α}–C_{β}	1.20
C_{β}–Al	0.33
Al–O1	0.35
Al–O2	0.36

Table S4: Selected Donor-Acceptor Stabilization energy from Second-order perturbation theory analysis of Fock matrix in NBO basis.

Donor NBO / occupancy	Acceptor NBO / occupancy	$E^{(2)}$ in kcal/mol
C_{β}: LP (13.5% s, 86.4% p) / 1.559	Al: LP* (93.2% s, 6.7% p) / 0.453	96.02

Cartesian Coordinates of the optimized geometry:

4

Al	0.223317000	2.253884000	1.062347000
O	-1.201970000	1.496277000	0.402262000
O	1.171757000	1.084190000	2.002069000
N	0.669986000	3.084475000	-2.559133000
N	0.147071000	1.008818000	-2.151564000
C	2.670375000	-0.789026000	1.724337000
C	-3.991307000	-0.837298000	0.127250000
H	-4.978639000	-0.994430000	0.549417000
C	2.081287000	0.416359000	1.275139000
C	-3.542027000	-1.730148000	-0.853900000
C	3.594775000	-1.411402000	0.871344000
H	4.052122000	-2.335865000	1.210345000
C	0.887633000	2.053088000	-1.694556000
C	-1.954100000	0.459869000	0.045480000
C	3.950714000	-0.919310000	-0.393868000
C	3.328251000	0.261774000	-0.816653000
H	3.546309000	0.679281000	-1.803126000
C	-3.242774000	0.250851000	0.601129000
C	-1.471638000	-0.440883000	-0.934847000
C	4.959621000	-1.627305000	-1.311961000
C	2.401180000	0.922387000	-0.010524000

C	2.259614000	-1.404583000	3.070954000
C	1.636128000	2.146736000	-0.468505000
H	2.239886000	3.063613000	-0.443500000
C	-2.261797000	-1.504379000	-1.370639000
H	-1.849828000	-2.175193000	-2.129301000
C	-0.075719000	-0.282044000	-1.478418000
H	0.677151000	-0.369583000	-0.690085000
H	0.136468000	-1.074470000	-2.210064000
C	-0.549394000	1.394206000	-3.286891000
H	-1.223520000	0.712345000	-3.794261000
C	5.528084000	-2.906504000	-0.675484000
H	6.055490000	-2.692174000	0.266927000
H	6.249424000	-3.376919000	-1.362145000
H	4.738410000	-3.644699000	-0.465256000
C	-3.792276000	1.177167000	1.701218000
C	0.747385000	-1.729733000	3.037984000
H	0.146769000	-0.828629000	2.862683000
H	0.432671000	-2.176482000	3.995802000
H	0.525357000	-2.453297000	2.236892000
C	-0.229353000	2.686802000	-3.543438000
H	-0.547247000	3.357247000	-4.335297000
C	-4.381445000	-2.913060000	-1.360626000
C	1.234756000	4.412742000	-2.413927000
H	0.843708000	4.909070000	-1.512031000
H	0.965293000	5.008434000	-3.294459000
H	2.330770000	4.359032000	-2.342810000
C	3.016061000	-2.712030000	3.363410000
H	2.815364000	-3.484463000	2.604195000
H	2.691579000	-3.113080000	4.336381000
H	4.105231000	-2.554999000	3.415932000
C	-3.868785000	2.631601000	1.184237000
H	-2.886168000	3.006731000	0.877761000
H	-4.262778000	3.294523000	1.972316000
H	-4.548131000	2.693028000	0.318403000
C	-5.751715000	-2.990680000	-0.667636000
H	-5.651545000	-3.125038000	0.420672000
H	-6.319871000	-3.849727000	-1.057821000
H	-6.352614000	-2.085274000	-0.846595000
C	6.136933000	-0.674904000	-1.614295000
H	5.798291000	0.244202000	-2.116616000
H	6.875334000	-1.163656000	-2.272064000
H	6.647452000	-0.379299000	-0.684019000
C	-3.627098000	-4.232698000	-1.088271000
H	-2.650935000	-4.257260000	-1.596486000
H	-4.212231000	-5.096329000	-1.446091000
H	-3.445650000	-4.362889000	-0.009579000
C	-2.885112000	1.091296000	2.949510000
H	-2.868910000	0.063498000	3.345143000
H	-3.261245000	1.757729000	3.743153000
H	-1.851091000	1.379792000	2.730952000
C	4.263006000	-2.015169000	-2.635313000
H	3.410121000	-2.685731000	-2.443382000
H	4.964717000	-2.535283000	-3.308484000
H	3.882281000	-1.130110000	-3.167988000
C	-5.211261000	0.773325000	2.142461000
H	-5.932540000	0.824937000	1.311577000
H	-5.558478000	1.464772000	2.925793000
H	-5.241103000	-0.243779000	2.563278000
C	2.564335000	-0.414111000	4.216987000
H	3.644152000	-0.196931000	4.261679000
H	2.265269000	-0.849932000	5.185160000
H	2.025825000	0.531441000	4.078688000
C	-0.150542000	4.008092000	1.833166000

H	-0.663163000	4.666900000	1.109080000
H	0.769346000	4.523521000	2.159299000
H	-0.812235000	3.931649000	2.713314000
C	-4.616785000	-2.761492000	-2.879632000
H	-5.147764000	-1.821592000	-3.100041000
H	-5.223210000	-3.597885000	-3.265467000
H	-3.668765000	-2.751228000	-3.439486000

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