Electronic Supplementary Information

Activation of alkynes by an α-diimine-stabilized Al−Al-bonded compound: Insertion to Al−Al bond or cycloaddition to AlN_2C_2 ring

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S1. Experimental

General Considerations

All of the reactions and manipulations of air- and moisture-sensitive compounds were carried out under argon or nitrogen with standard Schlenk or drybox techniques. The solvents (toluene and THF) were dried using appropriate methods and were distilled under argon prior to use. Benzene-d_6 was dried over Na/K alloy. The α-diimine ligand L was prepared according to literature procedures.[1] Sodium metal, anhydrous aluminum chloride ($AlCl_3$), diphenylacetylene, phenylacetylene and 4-ethynyltoluene were purchased from Alfa Aesar. NMR spectra were recorded on a Mercury Plus-400 spectrometer in benzene-d_6. Elemental analyses were performed with an Elementar VarioEL III instrument. IR spectra were recorded using a Nicolet AVATAR 360 FT-IR spectrometer. Raman spectrum was obtained in the region 100−3500 cm^{-1} using a Renishaw Raman microscope system excited at 785 nm. Laser power used was 500 mW. The solid sample was sealed in glass tube in an inert atmosphere.

Synthesis

$[L^{2-}Al^{III}(PhC{=}CPh)^{2-}Al^{III}L^{2-}]$ (2). Diphenylacetylene (0.89 g, 0.50 mmol) was added to a solution of $[L^{2-}Al(THF)]_2$ (**1**) [2] (0.50 mmol) in THF (30 mL). The resultant brown-green solution was stirred at ambient temperature for 5 days, and the mixture was filtered. The filtrate was concentrated to about 5 mL and stored at ca. −20 °C to yield red crystals of compound **2** (crystal yield: 0.22 g, 37%) after 1 week. ^{1}H NMR (400 MHz, C_6D_6, δ/ppm): 1.21 (d, J = 7.2 Hz, 48H, CH(CH_3)$_2$), 1.32 (THF), 1.82 (s, 12H, CCH_3), 3.32 (THF), 3.68 (m, 8H, CH(CH$_3$)$_2$), 6.92−7.34 (m, 22H, Ar-H). ^{13}C NMR (C_6D_6, δ/ppm): 16.2 (N-CCH_3), 24.0 (CH(CH_3)$_2$), 26.8 (CH(CH$_3$)$_2$), 28.3 (THF), 68.6 (THF), 120.6, 123.2, 124.6, 126.9, 128.3, 136.2, 137.1 (Ar-C), 146.3 (N-CCH$_3$), 148.8 (Al−C=). IR (KBr, ν/cm^{-1}): 1643, 1604，1586, 1435, 1376, 1358, 1211, 1179, 1083, 1030, 908, 860, 729. Anal. Calcd for $C_{78}H_{106}Al_2N_4O_2$ (1185.63): C, 79.01; H, 9.01; N, 4.73. Found: C, 78.92; H, 9.01; N, 4.64.

$[L^{-}(CPh{=}CH)^{-}Al^{II}{-}Al^{II}(CH{=}CPh)^{-}L^{-}]$ (3a). To a solution of $[L^{2-}Al(THF)]_2$ (**1**) (0.50 mmol) in 30 mL of toluene was added phenylacetylene (0.100 g, 1.0 mmol). A yellow-brown solution was generated, which was stirred at ambient temperature for 5 days. The mixture was filtered and the reddish filtrate was concentrated to about 5 mL and stored at ca. −20 °C to yield light yellow crystals of the product **3a** (crystl yield: 0.22 g, 33%) after one week. ^{1}H NMR (400 MHz, C_6D_6, δ/ppm): 1.11 (d, J = 7.2 Hz, 48H, CH(CH_3)$_2$), 1.40 (s, 6H, CCH_3), 1.66 (s, 6H, CCH_3), 2.10 (s, 4H, CH_2C(CH$_3$)), 3.57 (m, 4H, CH(CH$_3$)$_2$), 6.78−7.40 (m, 22H, Ar-H), 7.60 (s, 1H, (AlCH=CPh). ^{13}C NMR ($CDCl_3$, δ/ppm): 15.4 (N-CCH_3), 22.9 (CH(CH_3)$_2$), 23.6 (CH(CH_3)$_2$), 28.1 (CH(CH$_3$)$_2$), 70.5 (N-CCH$_3$), 122.5, 123.2, 123.6, 125.2, 127.7, 127.9, 140.3 (=CPh, Ar-C), 146.3 (Al−C=), 149.2 (N=CCH$_3$). IR (KBr ν/cm^{-1}): 3300, 1640, 1593, 1461, 1362, 1254, 1119, 1087, 912, 789, 759, 730, 693. Anal. Calcd for $C_{72}H_{92}Al_2N_4{\cdot}3C_7H_8$ (1343.86): C, 83.12; H, 8.70; N, 4.17. Found: C, 83.68; H, 8.69; N, 4.01.

$[L^{-}(C(C_6H_4{-}Me){=}CH)^{-}Al^{II}{-}Al^{II}(CH{=}C(C_6H_4{-}Me))^{-}L^{-}]$ (3b). Complex **3b** was prepared by a similar procedure to that employed for **3a** by using 2.0 equiv of 4-ethynyltoluene (0.116 g, 1.0 mmol). Light yellow

crystals of **3b** (crystal yield: 0.24 g, 38%) were isolated. IR (KBr ν/cm^{-1}): 3294, 1642, 1587, 1460, 1437, 1381, 1360, 1256, 1118, 1038, 816, 789, 729, 693. Anal. Calcd for $C_{74}H_{96}Al_2N_4{\cdot}2C_7H_8$ (1279.78): C, 82.59; H, 8.82; N, 4.38. Found: C, 82.56; H, 8.43; N, 4.25.

X-ray Crystal Structure Determination. Diffraction data for the complexes **2**, **3a** and **3b** (sealed in thin glass tubes) were collected on a Bruker SMART APEX II diffractometer at low temperature (153 K) with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction using SADABS was applied for all data.[3] The structures were solved by direct methods using the SHELXS program.[4] All non-hydrogen atoms were refined anisotropically by full-matrix least squares on F^2 by the use of the program SHELXL.[4] Hydrogen atoms bonded to carbon were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Crystallographic data and refinement details for **2**, **3a** and **3b** are given in Table S1. CCDC 923250–923252 contain the the crystallographic data for complexes **2**, **3a** and **3b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data and refinement details for compounds **2, 3a** and **3b.**

	2	**3a**	**3b**
empirical formula	$C_{78}H_{106}Al_2N_4O_2$	$C_{72}H_{92}Al_2N_4{\cdot}3C_7H_8$	$C_{74}H_{96}Al_2N_4{\cdot}2C_7H_8$
*F*w	1185.63	1343.86	1279.78
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	*P*2(1)/*n*	*C*2/*c*	*C*2/*c*
a /Å	11.941(5)	24.135(4)	19.133 (4)
b /Å	20.210(8)	12.756(2)	18.651 (4)
c /Å	14.884(6)	27.140(5)	20.965 (5)
α /°	90	90	90
β /°	20.210(8)	109.968(2)	95.545 (3)
γ /°	90	90	90
V /Å^3	3481(2)	7853(2)	7446 (3)
Z	2	4	4
D_{calc} /g cm^{-3}	1.131	1.137	1.142
F (000)	1288	2912	2776
μ /mm^{-1}	0.09	0.09	0.09
θ range	1.73−25.03	1.80−25.05	1.53−25.07
reflns collected	16820	25243	23989
independent reflns	5879	4862	6573
observed reflns	2562	4195	4281
R(int)	0.090	0.076	0.068
R_1; wR_2 ($I > 2\sigma(I)$)	0.0603, 0.1185	0.0819, 0.1654	0.0559, 0.1126
R_1; wR_2 (all data)	0.1725, 0.1577	0.1388, 0.1894	0.0980, 0.1290
GOF (F^2)	1.003	1.188	1.025

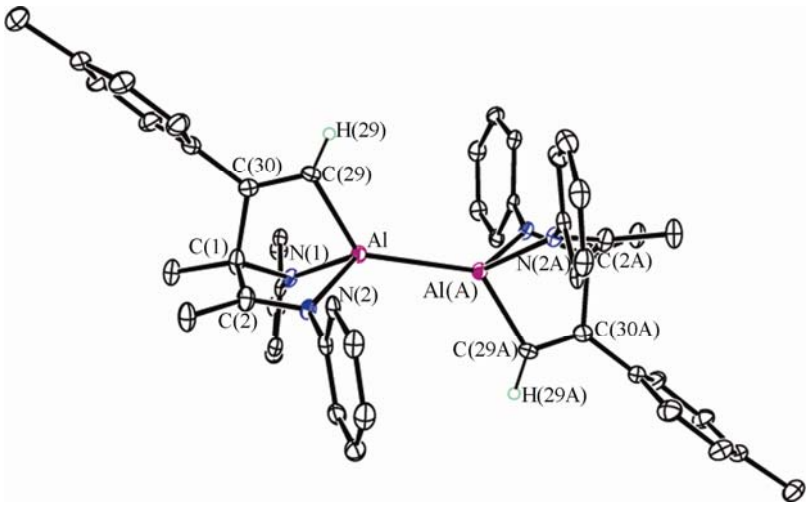

Fig. S1. Molecular structure of **3b**. Thermal ellipsoids are set at the 30% probability level; the acetylenic hydrogen atoms are presented, and the other ones as well as isopropyl groups of the ligand L are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Al−Al(A) 2.6006(15), Al–N(1) 1.881(2), Al–N(2) 2.068(2), Al–C(29) 2.004(3), C(29)−C(30) 1.324(4), N(1)–C(1) 1.466(3), N(2)–C(2) 1.315(3), C(1)–C(2) 1.519(4), C(1)–C(30) 1.664(4); N(1)–Al–N(2) 82.38(8), N(1)–Al–C(29) 90.45(10), N(2)−Al−C(29) 90.31(9), C(29)–Al–Al(A) 129.91(9), C(30)–C(29)–Al 105.72(19), C(1)–N(1)–Al 98.56(15), C(2)–N(2)–Al 104.27(16), C(31)−C(30)−C(29)−H(29) (torsion) = 5.70. Symmetry code: A) −*x*, *y*, 0.5−*z*.

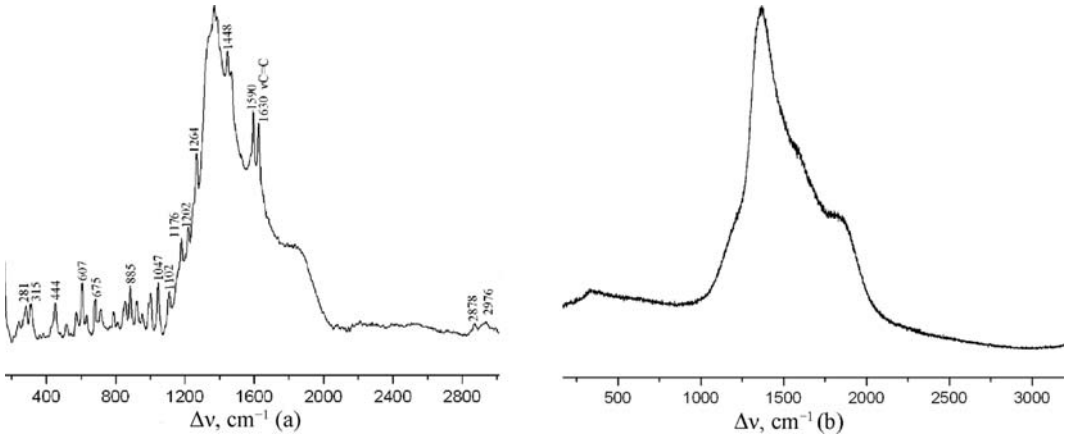

Fig. S2. (a) Raman spectrum of **2** (solid sample, RT); (b) Raman spectrum of the glass tube.

S2. DFT computations

The model compounds [L'(H_2O)Al(CPh=CPh)Al(H_2O)L′] (**2H**; L′ = [PhNCMe]$_2$)), wherein the 2,6-diisopropylphenyl groups on the nitrogen atoms were replaced by phenyl groups and the THF molecules by H_2O, and the full molecules of **3a** and **3b** were corroborated by DFT computations. The structure optimization and NBO bonding analysis for the compounds **2H, 3a** and **3b** were carried out at the DFT (B3LYP) level with the 6-31G* basis sets using the Gaussian 03 program.[5] The B3LYP method is a hybrid

of the HF and DFT methods, incorporating Becke's three-parameter exchange functional (B3)[6] with the Lee, Yang, and Parr (LYP) correlation functional. Geometry optimizations gave bond distances that were in good agreement with the X-ray structures.

All reported structural parameters refer to singlet ground state structures. Bonding analyses were performed by means of natural bond orbital (NBO) analysis and natural population analysis (NPA). Wiberg bond indices (WBI) were evaluated with Weinhold's natural bond orbital method.[7]

In the computed structure of **3b** (Fig. S3), the Al−C (2.017 Å) bond distances compare well with the experimental values (2.004(3 Å), with an average σ-bond order of 0.53. The C(1)–C(30) (1.604 Å) bond distance is somewhat shorter than the experimental value (1.664(4) Å), with a σ-bond order of 0.90. The erstwhile C(29)−C(30) triple bond now displays the double bond order of 1.88 with bond distances of 1.350 Å. Meanwhile, the C(C_6H_4Me)=CH fragment accumulates a negative partial charge of −0.58, which is essentially the same with that in **3a** (−0.59). The sum of NPA charges on Al (1.20) is comparable with that in **1H** (1.13), and the negative partial charge on the ligand L decreases from −1.79 (in **1H**) to −0.63 (in **3b**), as in the case of **3a**. The dissociation energy of one alkyne molecule from the AlN_2C_2 cycle was calculated to be 12.7 and 13.1 kcal mol^{-1} for **3a** and **3b**, respectively, indicating the dissociation of the acetylene is a low-energy process (the bond dissociation energie of typical C−C single bond (1.54 Å) is generally higher than 80 kcal mol^{-1}).[8] This may lead to the long C(1)−C(30) bond distances (1.600(6) and 1.664(4) Å) in the compounds.

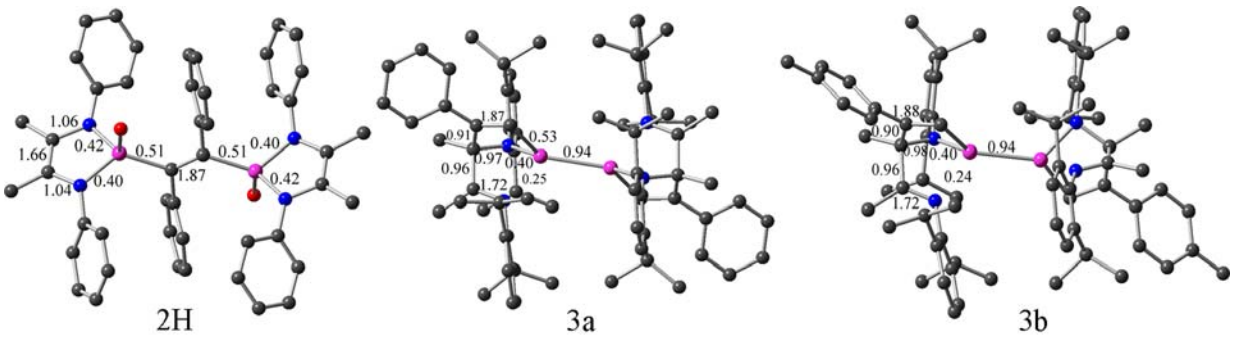

Fig. S3. Optimized structures of **2H, 3a** and **3b** and selected bond orders.

Table S2. Natural charges of the model compounds **1H**, **2H**, **3a**, and **3b** at B3LYP/6-31G* level.

	1H	**2H**	**3a**	**3b**
Al	1.13	1.92	1.20	1.20
L	−1.79	−1.58	−0.87	−0.63
Alkyne		−1.19	−0.59	−0.58

Table S3. Cartesian coordinates of the optimized geometry for **2H**.

Al	-2.42474600	0.01634000	0.43629300	H	0.31434300	-2.85677100	-0.21103500
O	-2.18861800	0.48699500	2.34978600	Al	2.42473200	-0.01634100	-0.43628000
N	-3.65413400	-1.35234500	0.67608800	O	2.18855700	-0.48697300	-2.34977900
N	-3.73302900	1.10274600	-0.27574100	N	3.65409000	1.35236300	-0.67613600
C	-4.93762600	-0.87073100	0.26118200	N	3.73306300	-1.10272300	0.27569500
C	-4.98151600	0.41534000	-0.19092900	C	4.93761000	0.87076400	-0.26129800
C	-6.14917200	-1.73875100	0.49773700	C	4.98153800	-0.41530600	0.19081200
H	-6.04179400	-2.27372800	1.44972300	C	6.14912900	1.73880200	-0.49792600
H	-6.31372800	-2.50572100	-0.27029100	H	6.04171600	2.27372300	-1.44994100
H	-7.06038200	-1.13980900	0.56263100	H	6.31367600	2.50582100	0.27005400
C	-6.22782500	1.09148900	-0.70197800	H	7.06035400	1.13988400	-0.56280400
H	-7.00911600	0.36088500	-0.92088300	C	6.22787700	-1.09145400	0.70178600
H	-6.00842000	1.62666600	-1.63394000	H	7.00919700	-0.36085500	0.92060700
H	-6.65095100	1.83278600	-0.01148000	H	6.00853600	-1.62659600	1.63378400
C	-3.34508900	-2.72558500	0.66975100	H	6.65093600	-1.83278100	0.01128000
C	-3.78240000	-3.60857800	-0.33974000	C	3.34503200	2.72560100	-0.66976800
C	-3.41830500	-4.95283200	-0.32378800	C	3.78236000	3.60857900	0.33973000
H	-3.77074500	-5.60741300	-1.11763400	C	3.41825500	4.95283000	0.32381200
C	-2.59060900	-5.46025700	0.68132300	H	3.77070900	5.60739800	1.11766200
H	-2.30724100	-6.50897800	0.68719300	C	2.59053200	5.46026800	-0.68126900
C	-2.13338400	-4.59593800	1.67748200	H	2.30715600	6.50898700	-0.68711300
H	-1.49240500	-4.96974400	2.47263400	C	2.13328900	4.59596500	-1.67743400
C	-2.51422500	-3.25478700	1.67779900	H	1.49229100	4.96978300	-2.47256600
C	-3.64917000	2.49816400	-0.45970900	C	2.51414000	3.25481700	-1.67778600
C	-4.40027100	3.41870000	0.29980300	C	3.64923100	-2.49814100	0.45968400
C	-4.24845100	4.79193400	0.11636800	C	4.40025600	-3.41867600	-0.29990400
H	-4.84179300	5.47780800	0.71670600	C	4.24846200	-4.79191000	-0.11644600
C	-3.32955100	5.29192600	-0.80983500	H	4.84174200	-5.47778500	-0.71684400
H	-3.21044800	6.36331100	-0.94527800	C	3.32966500	-5.29190000	0.80986000
C	-2.56646600	4.39326100	-1.55789100	H	3.21058200	-6.36328600	0.94532100
H	-1.84851600	4.76254200	-2.28651500	C	2.56665700	-4.39323600	1.55799600
C	-2.73158300	3.01817200	-1.39361000	H	1.84879000	-4.76251800	2.28670100
C	-0.57448900	-0.26818600	-0.24814500	C	2.73174900	-3.01814700	1.39368700
C	-0.51522300	-1.24511800	-1.38135100	C	0.57448800	0.26815100	0.24820700
C	-0.95931600	-0.88521100	-2.67242900	C	0.51522200	1.24506600	1.38143100
H	-1.37503300	0.10671600	-2.83335900	C	0.95921600	0.88509800	2.67252600
C	-0.88197100	-1.78847300	-3.73881300	H	1.37485400	-0.10686200	2.83345400
H	-1.22513900	-1.48500400	-4.72476200	C	0.88187300	1.78834000	3.73892700
C	-0.37670900	-3.07496100	-3.53585100	H	1.22496500	1.48482500	4.72488800
H	-0.32079300	-3.77716500	-4.36289300	C	0.37670900	3.07486600	3.53596600
C	0.04944300	-3.45038300	-2.26090800	H	0.32079300	3.77705500	4.36302200
H	0.44318400	-4.44769400	-2.08709200	C	-0.04934700	3.45034600	2.26100800
C	-0.01686100	-2.54836800	-1.19725500	H	-0.44301500	4.44768600	2.08719500

C	0.01695700	2.54835300	1.19733700	H	-2.18562600	-2.60116100	2.48390300
H	-0.31417800	2.85679800	0.21110800	H	-2.15917400	2.32167700	-2.00034300
H	2.65309800	0.19319800	-2.87150100	H	-5.08477400	3.04624900	1.05542800
H	1.27319100	-0.61066000	-2.69090400	H	2.18552700	2.60120300	-2.48389500
H	-1.27325500	0.61065900	2.69093500	H	4.37987700	3.21929100	1.15750200
H	-2.65320100	-0.19313400	2.87152300	H	5.08467600	-3.04622400	-1.05560300
H	-4.37989400	-3.21930300	-1.15753500	H	2.15940500	-2.32164900	2.00047800

Table S4. Cartesian coordinates of the optimized geometry for **3a**.

Al	0.98366400	-0.85545700	-0.11140400	C	1.67561800	0.54039500	4.38625500
N	2.66354500	-0.90157700	0.74211700	H	2.23541800	1.24443600	5.01354400
N	0.79599000	-2.81532600	0.75916500	H	0.98864100	-0.00697500	5.04207500
C	3.10250200	-2.25634600	0.28772000	H	1.07678000	1.12672900	3.68148800
C	2.01947100	-3.22428500	0.85734800	C	3.37616500	-1.31810900	4.65100700
C	4.51651500	-2.61668000	0.74788600	H	4.02239900	-2.04050800	4.13857100
H	5.23852500	-1.93022800	0.30368300	H	2.67813700	-1.87714800	5.28648300
H	4.80595100	-3.62655300	0.45283800	H	4.01568700	-0.71960900	5.31076500
H	4.60482400	-2.52901700	1.83510900	C	-0.33074000	-3.66850500	1.08689300
C	2.41141400	-4.54740900	1.45196700	C	-0.79081800	-3.79367000	2.41876100
H	2.95601700	-4.36980300	2.38788800	C	-1.87762300	-4.64177200	2.67046700
H	3.09493900	-5.09213400	0.79584500	H	-2.23669000	-4.74557600	3.69041900
H	1.54408800	-5.17317700	1.66377400	C	-2.50318300	-5.34906200	1.65208500
C	3.58830700	0.03454400	1.30358800	H	-3.34174900	-6.00402400	1.87281500
C	4.53037900	0.75644200	0.51065400	C	-2.04585600	-5.20716900	0.34736400
C	5.39156600	1.67888800	1.11830300	H	-2.53163900	-5.75934600	-0.45156400
H	6.09813300	2.22580700	0.49938400	C	-0.96675100	-4.37243400	0.03434000
C	5.35983600	1.92203900	2.48574000	C	-0.16741000	-3.05898800	3.60043700
H	6.03814500	2.64245200	2.93620600	H	0.68916600	-2.49058300	3.23452900
C	4.44366700	1.22862500	3.26560800	C	0.35122200	-4.03708200	4.67461000
H	4.41178800	1.40976700	4.33740900	H	-0.46677100	-4.60850500	5.12811600
C	3.56401300	0.29371500	2.70555200	H	0.85381100	-3.48775000	5.47890500
C	4.62468700	0.60710600	-1.00360900	H	1.06517900	-4.75600300	4.25814200
H	3.97909200	-0.21904000	-1.29711400	C	-1.15825500	-2.05395200	4.22029400
C	6.05153400	0.28775600	-1.49188100	H	-2.06038200	-2.55926900	4.58422200
H	6.74434200	1.11616600	-1.30207700	H	-1.46891200	-1.29776200	3.49232200
H	6.04944300	0.10356700	-2.57265700	H	-0.69969200	-1.53906700	5.07178200
H	6.46213300	-0.60376200	-1.00545400	C	-0.49151100	-4.30431400	-1.41404000
C	4.09187600	1.86854800	-1.70733500	H	0.23352200	-3.49239300	-1.50032900
H	3.06056400	2.08451100	-1.41160000	C	-1.63859000	-3.99645300	-2.39405700
H	4.11400900	1.74396700	-2.79729600	H	-2.36894100	-4.81267600	-2.44157000
H	4.69463500	2.75031700	-1.45947800	H	-1.23799800	-3.85948300	-3.40517400
C	2.61391500	-0.43143300	3.64671600	H	-2.17663100	-3.08519200	-2.11547000
H	1.99899600	-1.07891400	3.01919400	C	0.23277100	-5.60511600	-1.81781000

H	1.08301800	-5.81641000	-1.15964700	H	-6.46213300	0.60376200	1.00545400
H	0.61397400	-5.52905200	-2.84253300	C	-4.09187600	-1.86854800	1.70733500
H	-0.44472500	-6.46652100	-1.77077100	H	-3.06056400	-2.08451100	1.41160000
C	1.81722700	-1.67217400	-1.74208200	H	-4.11400900	-1.74396700	2.79729600
H	1.59456500	-1.69495400	-2.80912600	H	-4.69463500	-2.75031700	1.45947800
C	2.89353300	-2.35349600	-1.29756500	C	-2.61391500	0.43143300	-3.64671600
C	3.80253100	-3.12492600	-2.19089400	H	-1.99899600	1.07891400	-3.01919400
C	4.15217800	-4.47183300	-1.98386700	C	-1.67561800	-0.54039500	-4.38625500
H	3.75738900	-5.00751200	-1.12695500	H	-2.23541800	-1.24443600	-5.01354400
C	4.96576200	-5.15945900	-2.88448100	H	-0.98864100	0.00697500	-5.04207500
H	5.20754800	-6.20300500	-2.69842600	H	-1.07678000	-1.12672900	-3.68148800
C	5.45886200	-4.51877700	-4.02154700	C	-3.37616500	1.31810900	-4.65100700
H	6.09651200	-5.05296500	-4.72066300	H	-4.02239900	2.04050800	-4.13857100
C	5.11962400	-3.18404900	-4.25023500	H	-2.67813700	1.87714800	-5.28648300
H	5.49371700	-2.66962900	-5.13193800	H	-4.01568700	0.71960900	-5.31076500
C	4.30481800	-2.50055100	-3.34945900	C	0.33074000	3.66850500	-1.08689300
H	4.04972900	-1.46135500	-3.53379000	C	0.79081800	3.79367000	-2.41876100
Al	-0.98366400	0.85545700	0.11140400	C	1.87762300	4.64177200	-2.67046700
N	-2.66354500	0.90157700	-0.74211700	H	2.23669000	4.74557600	-3.69041900
N	-0.79599000	2.81532600	-0.75916500	C	2.50318300	5.34906200	-1.65208500
C	-3.10250200	2.25634600	-0.28772000	H	3.34174900	6.00402400	-1.87281500
C	-2.01947100	3.22428500	-0.85734800	C	2.04585600	5.20716900	-0.34736400
C	-4.51651500	2.61668000	-0.74788600	H	2.53163900	5.75934600	0.45156400
H	-5.23852500	1.93022800	-0.30368300	C	0.96675100	4.37243400	-0.03434000
H	-4.80595100	3.62655300	-0.45283800	C	0.16741000	3.05898800	-3.60043700
H	-4.60482400	2.52901700	-1.83510900	H	-0.68916600	2.49058300	-3.23452900
C	-2.41141400	4.54740900	-1.45196700	C	-0.35122200	4.03708200	-4.67461000
H	-2.95601700	4.36980300	-2.38788800	H	0.46677100	4.60850500	-5.12811600
H	-3.09493900	5.09213400	-0.79584500	H	-0.85381100	3.48775000	-5.47890500
H	-1.54408800	5.17317700	-1.66377400	H	-1.06517900	4.75600300	-4.25814200
C	-3.58830700	-0.03454400	-1.30358800	C	1.15825500	2.05395200	-4.22029400
C	-4.53037900	-0.75644200	-0.51065400	H	2.06038200	2.55926900	-4.58422200
C	-5.39156600	-1.67888800	-1.11830300	H	1.46891200	1.29776200	-3.49232200
H	-6.09813300	-2.22580700	-0.49938400	H	0.69969200	1.53906700	-5.07178200
C	-5.35983600	-1.92203900	-2.48574000	C	0.49151100	4.30431400	1.41404000
H	-6.03814500	-2.64245200	-2.93620600	H	-0.23352200	3.49239300	1.50032900
C	-4.44366700	-1.22862500	-3.26560800	C	1.63859000	3.99645300	2.39405700
H	-4.41178800	-1.40976700	-4.33740900	H	2.36894100	4.81267600	2.44157000
C	-3.56401300	-0.29371500	-2.70555200	H	1.23799800	3.85948300	3.40517400
C	-4.62468700	-0.60710600	1.00360900	H	2.17663100	3.08519200	2.11547000
H	-3.97909200	0.21904000	1.29711400	C	-0.23277100	5.60511600	1.81781000
C	-6.05153400	-0.28775600	1.49188100	H	-1.08301800	5.81641000	1.15964700
H	-6.74434200	-1.11616600	1.30207700	H	-0.61397400	5.52905200	2.84253300
H	-6.04944300	-0.10356700	2.57265700	H	0.44472500	6.46652100	1.77077100

C	-1.81722700	1.67217400	1.74208200	H	-5.20754800	6.20300500	2.69842600
H	-1.59456500	1.69495400	2.80912600	C	-5.45886200	4.51877700	4.02154700
C	-2.89353300	2.35349600	1.29756500	H	-6.09651200	5.05296500	4.72066300
C	-3.80253100	3.12492600	2.19089400	C	-5.11962400	3.18404900	4.25023500
C	-4.15217800	4.47183300	1.98386700	H	-5.49371700	2.66962900	5.13193800
H	-3.75738900	5.00751200	1.12695500	C	-4.30481800	2.50055100	3.34945900
C	-4.96576200	5.15945900	2.88448100	H	-4.04972900	1.46135500	3.53379000

Table S5. Cartesian coordinates of the optimized geometry for **3b**.

Al	0.19502000	1.29994100	0.11987600	H	-1.00277500	2.87970600	2.42369900
N	1.17769600	2.36464900	1.31636300	C	-1.35964400	4.00860000	4.20491400
N	1.51736600	2.22631900	-1.31332800	H	-1.35127400	3.89774800	5.29601100
C	1.09668100	3.66118800	0.58984000	H	-2.38916600	4.23825600	3.90508700
C	1.73655700	3.39499900	-0.80543800	H	-0.73550100	4.87540700	3.96012700
C	1.79777400	4.81111000	1.31825700	C	-1.73655700	1.52956800	3.91150700
H	1.39550700	4.91948500	2.32704400	H	-1.44564500	0.61555600	3.38424000
H	1.67242100	5.76271100	0.79732400	H	-2.79305900	1.72609300	3.69255100
H	2.86714500	4.60789400	1.42175500	H	-1.65218600	1.32394700	4.98522100
C	2.46846300	4.50197100	-1.50723500	C	1.93298400	1.86746100	-2.65091500
H	2.83364400	4.19793900	-2.48885200	C	1.15931500	2.26829500	-3.76750500
H	3.31227900	4.84328900	-0.89840900	C	1.57567500	1.86730400	-5.04344800
H	1.79734600	5.36178700	-1.62506500	H	0.98640100	2.16637600	-5.90580200
C	1.56238700	2.31907600	2.69318300	C	2.72373500	1.10783800	-5.23130800
C	2.92462000	2.08866400	3.04645400	H	3.03234700	0.81619400	-6.23169000
C	3.29297700	1.99603500	4.39406600	C	3.47720600	0.73029500	-4.12566600
H	4.33382000	1.81235000	4.64925100	H	4.38171600	0.14710500	-4.27126200
C	2.35772700	2.12547900	5.41336700	C	3.10009900	1.08691900	-2.82515000
H	2.66062400	2.04729600	6.45467500	C	-0.09519100	3.12930400	-3.65415200
C	1.02967900	2.35732400	5.07953200	H	-0.24241400	3.38446700	-2.60319900
H	0.29298900	2.45844300	5.87251300	C	0.04512900	4.44836000	-4.44172700
C	0.61208300	2.46600400	3.74634200	H	0.92910400	5.01586600	-4.13158900
C	4.01915000	1.90762600	2.00194000	H	-0.83402500	5.08300400	-4.28108700
H	3.56460700	2.10802900	1.02848000	H	0.12815400	4.26794000	-5.51978800
C	5.19224600	2.88920300	2.19329900	C	-1.34974800	2.36060400	-4.10685700
H	4.85027300	3.92989400	2.22837100	H	-1.28656700	2.06979400	-5.16193200
H	5.91023600	2.79582300	1.36911700	H	-2.24377600	2.98487100	-3.98663500
H	5.73782400	2.69486300	3.12413900	H	-1.49295500	1.44791900	-3.52191300
C	4.53496300	0.45506400	1.99149500	C	3.99850900	0.68294800	-1.66172000
H	4.94770800	0.17610100	2.96825200	H	3.45349700	0.87144800	-0.73337900
H	5.33075000	0.32536000	1.24818600	C	4.36113100	-0.81335500	-1.68190500
H	3.73004900	-0.25010800	1.75961100	H	3.46404700	-1.43821500	-1.72509100
C	-0.86799100	2.73094700	3.49508000	H	4.91475500	-1.07821800	-0.77472200

H	4.99444700	-1.07179300	-2.53862300	C	-4.01915000	-1.90762600	2.00194000
C	5.27446500	1.55043400	-1.64817100	H	-3.56460700	-2.10802900	1.02848000
H	5.85179800	1.40854500	-2.56963500	C	-5.19224600	-2.88920300	2.19329900
H	5.91927500	1.28289000	-0.80375300	H	-4.85027300	-3.92989400	2.22837100
H	5.03625900	2.61690400	-1.56774800	H	-5.91023600	-2.79582300	1.36911700
C	-1.10050200	2.82232100	-0.14689100	H	-5.73782400	-2.69486300	3.12413900
H	-2.14585200	2.91587900	-0.44034600	C	-4.53496300	-0.45506400	1.99149500
C	-0.42762500	3.94605600	0.17832200	H	-4.94770800	-0.17610100	2.96825200
C	-0.99105800	5.32159000	0.04160400	H	-5.33075000	-0.32536000	1.24818600
C	-0.95293600	6.28574200	1.06707000	H	-3.73004900	0.25010800	1.75961100
H	-0.47894800	6.04936000	2.01201500	C	0.86799100	-2.73094700	3.49508000
C	-1.55444300	7.53328800	0.91530700	H	1.00277500	-2.87970600	2.42369900
H	-1.51578900	8.24292900	1.73948200	C	1.35964400	-4.00860000	4.20491400
C	-2.21822800	7.88707000	-0.26631900	H	1.35127400	-3.89774800	5.29601100
C	-2.27230100	6.92997800	-1.28585500	H	2.38916600	-4.23825600	3.90508700
H	-2.79051500	7.16494400	-2.21357200	H	0.73550100	-4.87540700	3.96012700
C	-1.67507200	5.67970300	-1.13530700	C	1.73655700	-1.52956800	3.91150700
H	-1.74501700	4.95673000	-1.94174400	H	1.44564500	-0.61555600	3.38424000
C	-2.83653000	9.25472100	-0.43666700	H	2.79305900	-1.72609300	3.69255100
H	-3.62712700	9.24577000	-1.19448500	H	1.65218600	-1.32394700	4.98522100
H	-2.08970700	9.99540300	-0.75371900	C	-1.93298400	-1.86746100	-2.65091500
H	-3.27129300	9.61812200	0.50121200	C	-1.15931500	-2.26829500	-3.76750500
Al	-0.19502000	-1.29994100	0.11987600	C	-1.57567500	-1.86730400	-5.04344800
N	-1.17769600	-2.36464900	1.31636300	H	-0.98640100	-2.16637600	-5.90580200
N	-1.51736600	-2.22631900	-1.31332800	C	-2.72373500	-1.10783800	-5.23130800
C	-1.09668100	-3.66118800	0.58984000	H	-3.03234700	-0.81619400	-6.23169000
C	-1.73655700	-3.39499900	-0.80543800	C	-3.47720600	-0.73029500	-4.12566600
C	-1.79777400	-4.81111000	1.31825700	H	-4.38171600	-0.14710500	-4.27126200
H	-1.39550700	-4.91948500	2.32704400	C	-3.10009900	-1.08691900	-2.82515000
H	-1.67242100	-5.76271100	0.79732400	C	0.09519100	-3.12930400	-3.65415200
H	-2.86714500	-4.60789400	1.42175500	H	0.24241400	-3.38446700	-2.60319900
C	-2.46846300	-4.50197100	-1.50723500	C	-0.04512900	-4.44836000	-4.44172700
H	-2.83364400	-4.19793900	-2.48885200	H	-0.92910400	-5.01586600	-4.13158900
H	-3.31227900	-4.84328900	-0.89840900	H	0.83402500	-5.08300400	-4.28108700
H	-1.79734600	-5.36178700	-1.62506500	H	-0.12815400	-4.26794000	-5.51978800
C	-1.56238700	-2.31907600	2.69318300	C	1.34974800	-2.36060400	-4.10685700
C	-2.92462000	-2.08866400	3.04645400	H	1.28656700	-2.06979400	-5.16193200
C	-3.29297700	-1.99603500	4.39406600	H	2.24377600	-2.98487100	-3.98663500
H	-4.33382000	-1.81235000	4.64925100	H	1.49295500	-1.44791900	-3.52191300
C	-2.35772700	-2.12547900	5.41336700	C	-3.99850900	-0.68294800	-1.66172000
H	-2.66062400	-2.04729600	6.45467500	H	-3.45349700	-0.87144800	-0.73337900
C	-1.02967900	-2.35732400	5.07953200	C	-4.36113100	0.81335500	-1.68190500
H	-0.29298900	-2.45844300	5.87251300	H	-3.46404700	1.43821500	-1.72509100
C	-0.61208300	-2.46600400	3.74634200	H	-4.91475500	1.07821800	-0.77472200

H	-4.99444700	1.07179300	-2.53862300	C	1.10050200	-2.82232100	-0.14689100
C	-5.27446500	-1.55043400	-1.64817100	H	2.14585200	-2.91587900	-0.44034600
H	-5.85179800	-1.40854500	-2.56963500	C	0.42762500	-3.94605600	0.17832200
H	-5.91927500	-1.28289000	-0.80375300	C	0.99105800	-5.32159000	0.04160400
H	-5.03625900	-2.61690400	-1.56774800	C	0.95293600	-6.28574200	1.06707000

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