Reductive Activation of N_2 using a Calcium/Potassium Bimetallic System Supported by an Extremely Bulky Diamide Ligand

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Electronic Supplementary Information (33 pages)

Contents

1. Experimental

General considerations.

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Pentane was distilled over Na/K alloy (50:50), while hexane, methylcyclohexane, and toluene were distilled over molten potassium. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on either Bruker AvanceIII 600 or Bruker AvanceIII 400 spectrometers and were referenced to the resonances of the solvent used. FTIR spectra were collected for solid samples or Nujol mulls on an Agilent Cary 630 attenuated total reflectance (ATR) spectrometer. Raman spectra were acquired using a Renishaw RM2000 micro-Raman spectrometer operating at 514 nm or 782 nm. High resolution mass spectra were recorded on an Agilent 6450 QTOF MS system (Santa Clara, CA, USA) with a dual ESI source. Microanalyses were carried out using a PerkinElmer- 2400 CHNS/O Series II System. Melting points were determined in sealed glass capillaries under dinitrogen, and are uncorrected. The starting materials 2,7-diacetyl-9,9-dimethylxanthene,[1] 2,4,6-tricyclohexylaniline,[2] [Ca{N(SiMe$_3$)$_2$}$_2$],[3] [Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$][4] and 5% w/w K/KI[5] were prepared by literature procedures. All other reagents were used as received.

2,7-diethyl-9,9-dimethylxanthene. To a stirred suspension of 2,7-diacetyl-9,9-dimethylxanthene (13.9 g, 47.3 mmol) in diethylene glycol (150 mL), hydrazine hydrate (7.3 mL, 150 mmol) was added *via* a syringe. After 5 min KOH (6.3 g, 118 mmol) was added in one portion. The reaction mixture was then placed in a pre-heated oil bath at 130 °C and stirred in an open flask for 2 h. A reflux condenser was then fitted to the flask and the oil bath temperature increased to 180 °C for 6 h. After this time, the reaction mixture was cooled to room temperature and diluted with hexane (200 mL). Subsequently, the organic layer was washed thoroughly with water, 1M HCl solution, and brine, and then dried over $MgSO_4$. Volatiles were removed under reduced pressure to afford the title compound as a yellow oil (11.9 g, 95%), which was used without further purification. ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 1.28 (t, *J* = 7.5 Hz, 6H, CH_2CH_3), 1.67 (s, 6H, $C(CH_3)_2$), 2.67 (q, *J* = 7.6 Hz, 4H, CH_2CH_3), 6.99 (d, *J* = 8.2 Hz, 2H, Ar*H*), 7.05 (dd, *J* = 8.2, 2.2 Hz, 2H, Ar*H*), 7.25 (d, *J* = 2.1 Hz, 2H, Ar*H*); ^{13}C NMR (101 MHz, 298 K, $CDCl_3$) δ 16.0 (CH_2CH_3), 28.6 ($C(CH_3)_2$), 32.5 (CH_2CH_3), 34.2 ($C(CH_3)_2$), 116.2, 125.4, 126.8, 129.9, 138.6, 148.6 (Ar-*C*); IR ν/cm^{-1} (Neat): 2963 (s), 2929 (m), 2871 (m), 1452 (s), 1416 (m), 1296 (m), 1259 (s), 1218 (m), 1127 (m), 1088 (m), 1059 (m), 833 (m), 819 (s); HRMS (ESI) m/z: [M$^+$] calc. for $C_{19}H_{22}O$: 266.1671; found: 266.1686.

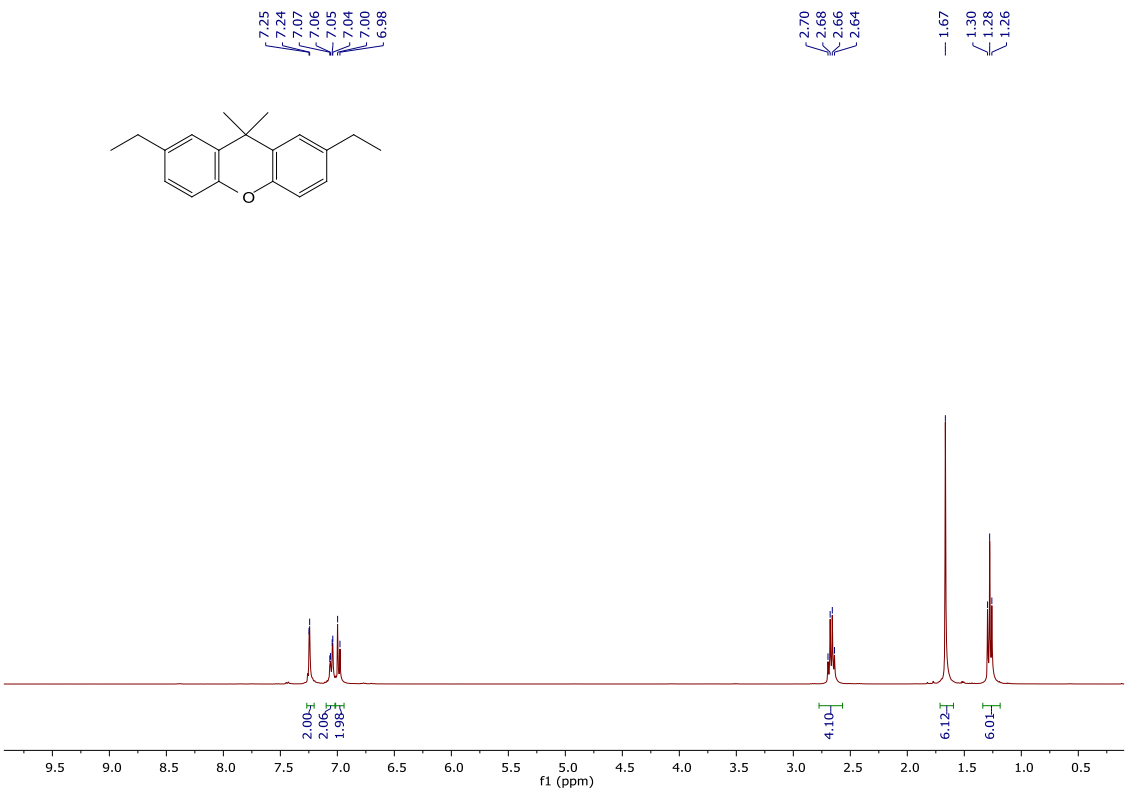

Figure S1. ^{1}H NMR spectrum (400 MHz, 298 K, $CDCl_3$) of 2,7-diethyl-9,9-dimethylxanthene.

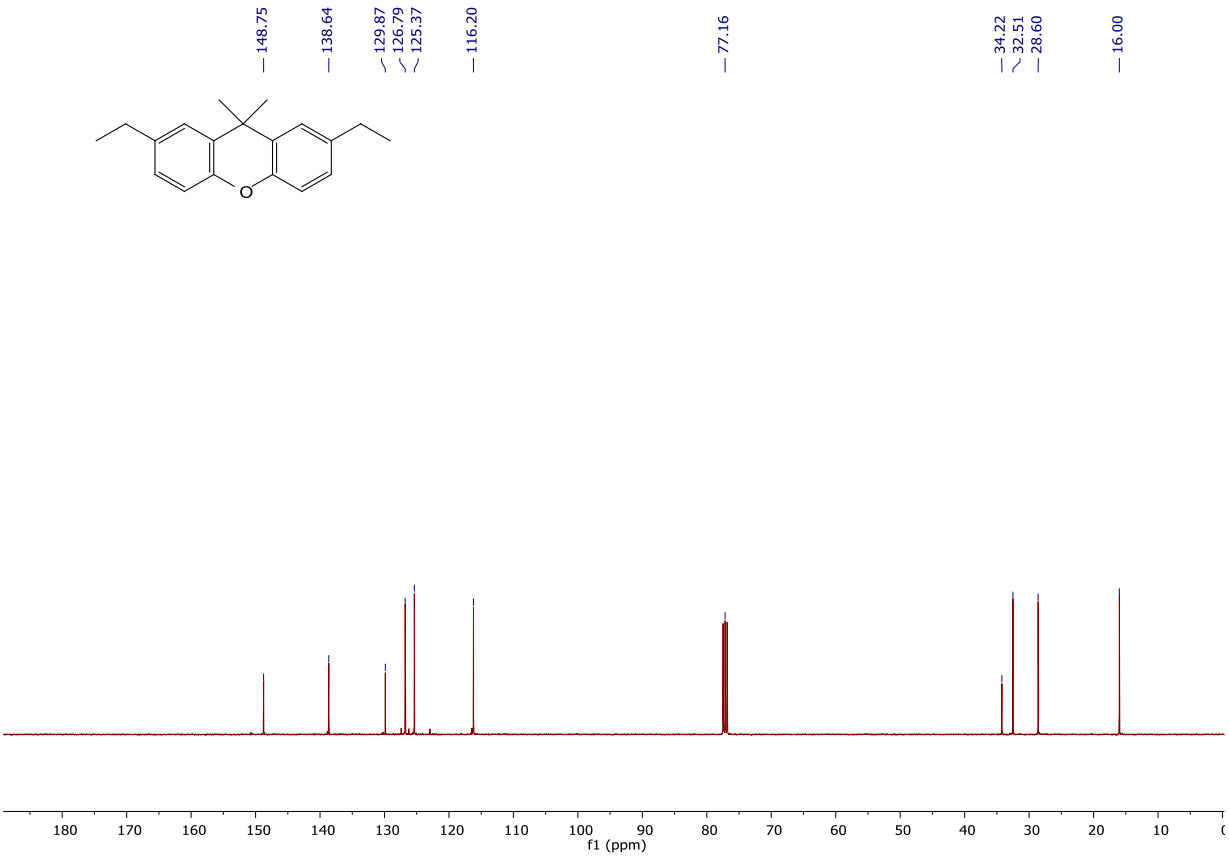

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, $CDCl_3$) of 2,7-diethyl-9,9 dimethylxanthene.

4,5-dibromo-2,7-diethyl-9,9-dimethylxanthene. To a stirred ice-cold solution of 2,7-diethyl-9,9-dimethylxanthene (11.9 g, 45 mmol) in dichloromethane (150 mL), bromine (4.9 mL 95 mmol) was added dropwise *via* a syringe over 30 min. The reaction mixture was then warmed to room temperature over 6 h, and subsequently stirred overnight. The mixture was then diluted with 100 mL dichloromethane and a saturated aq. $Na_2S_2O_3$ solution (100 mL) was added. Subsequently, the organic layer was washed with water and brine and dried over $MgSO_4$. Volatiles were evaporated under reduced pressure to obtain a yellowish-brown solid, which was purified by flash column chromatography on silica gel, using a 1:1 hexane/dichloromethane mixture as the eluent. The desired compound was obtained as a white solid (17.2 g, 90%). The compound can be recrystallized from hot hexane. M.P.: 106 – 108 °C; ^{1}H NMR (400 MHz, 298 K, C_6D_6) δ 0.98 (t, *J* = 7.6 Hz, 6H, CH_2CH_3), 1.28 (s, 6H, $C(CH_3)_2$), 2.28 (q, *J* = 7.6 Hz, 4H, CH_2CH_3), 6.89 (s, 2H, Ar*H*), 7.23 (s, 2H, Ar*H*); ^{13}C NMR (101 MHz, 298 K, C_6D_6) δ 15.8 (CH_2CH_3), 28.5 ($C(CH_3)_2$), 31.6 (CH_2CH_3), 35.5 ($C(CH_3)_2$), 111.4, 124.2, 131.0, 131.9, 140.5, 146.2 (Ar-*C*); IR *v*/cm^{-1} (Neat): 2962 (m), 2930 (m), 2875 (m), 1736 (w), 1589 (m), 1457 (s), 1325 (m), 1263 (m), 1205 (m), 1093 (m), 1060 (w), 944 (m), 866 (s), 782 (s), 734 (s); HRMS (ESI) m/z: [M$^+$] calc. for $C_{19}H_{20}Br_2O$: 423.9860; found: 424.0035.

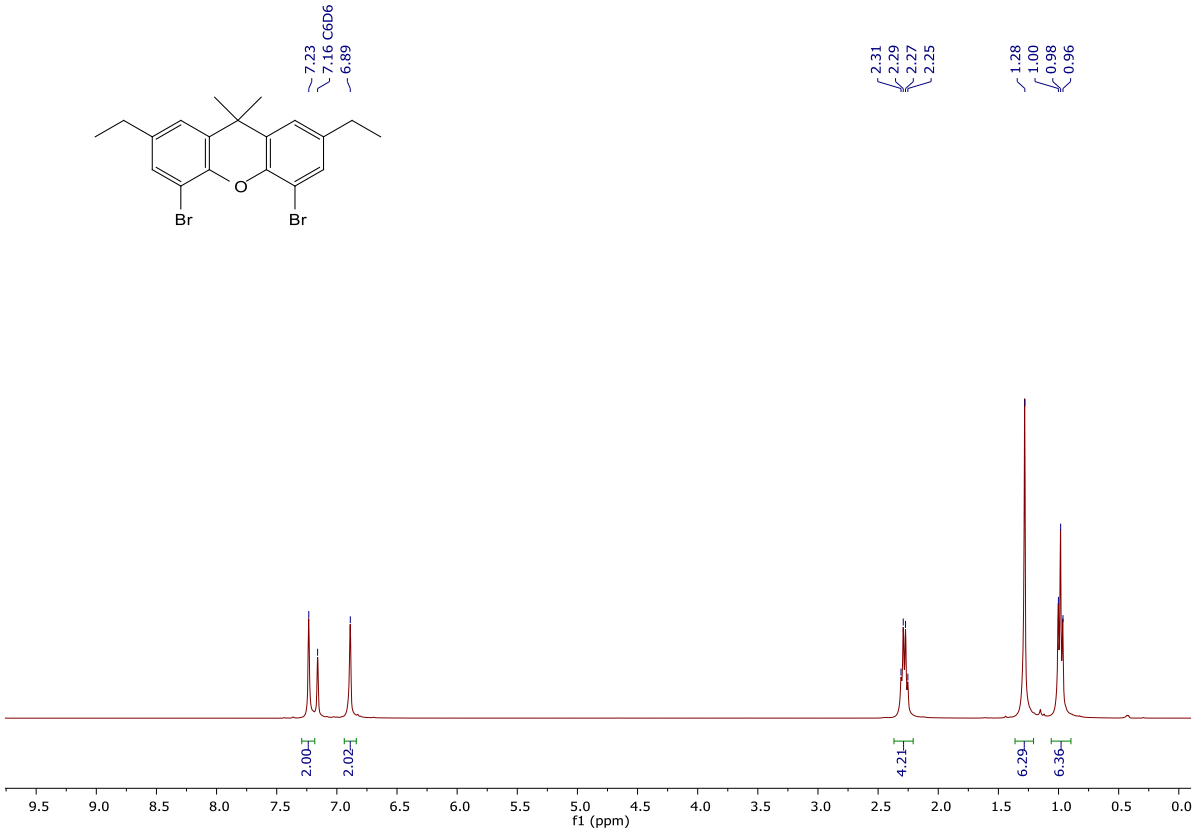

Figure S3. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of 4,5-dibromo-2,7-diethyl-9,9-dimethylxanthene.

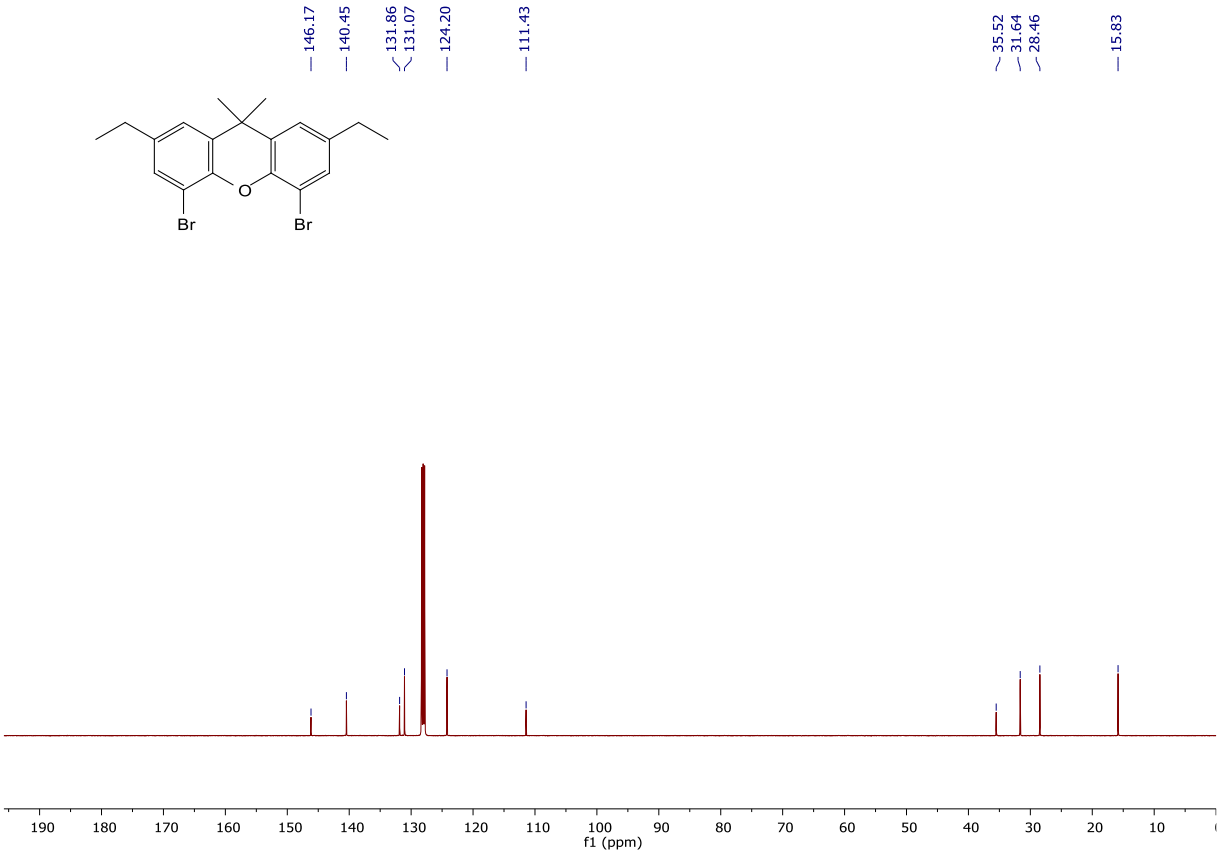

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of 4,5-dibromo-2,7-diethyl-9,9-dimethylxanthene.

4,5-bis(2,4,6-tricyclohexylanilido)-2,7-diethyl-9,9-dimethyl-xanthene, ^{TCHP}NONH$_2$. An oven-dried 250 mL Schlenk flask was charged with a magnetic stir bar, 4,5-dibromo-2,7-diethyl-9,9-dimethylxanthene (4.25 g, 10 mmol), 2,4,6-tricyclohexyl aniline (6.9 g, 20.2 mmol), NaOBu^t (2.7 g, 28 mmol), $Pd(OAc)_2$ (90 mg, 0.4 mmol), DPEPhos (324 mg, 0.6 mmol), and toluene (100 mL) under an N_2-atmosphere. The reaction mixture was then placed in a preheated oil bath at 100 °C and stirred for 5 d. The reaction was monitored by TLC. Upon completion of the reaction, the mixture was cooled to room temperature, diluted with hexane (100 mL), and filtered through celite. The organic layer was then washed with water and brine, then dried over $MgSO_4$. Solvents were removed under reduced pressure to obtain a brown solid, which was purified by flash column chromatography on neutral alumina, using hexane as eluent. Upon removal of volatiles under reduced pressure, the title compound was obtained as a white solid (8.0 g, 85%). The compound can be recrystallized from a methanol-hexane mixture at room temperature. M.P.: 121 – 125 °C; ^{1}H NMR (400 MHz, 298 K, C_6D_6) δ 1.06 (t, *J* = 7.6 Hz, 6H, CH_2CH_3), 1.17 – 1.86 (m, 54H, Cy-*H*+C(CH_3)$_2$), 1.91 – 2.08 (m, 12H, Cy-*H*), 2.29 (q, *J* = 7.6 Hz, 4H, CH_2CH_3), 2.59 (m, 2H, Cy-*H*), 3.16 – 3.30 (m, 4H, Cy-*H*), 5.96 (s, 2H, N*H*), 6.43 (d, *J* = 1.9 Hz, 2H, Ar*H*), 6.66 (d, *J* = 1.9 Hz, 2H, Ar*H*), 7.28 (s, 4H, ^{TCHP}Ar*H*); ^{13}C NMR (101 MHz, 298 k, C_6D_6) δ 16.6 (CH_2CH_3), 26.6, 26.8, 27.4, 27.4, 27.8 (Cy-*C*+C(CH_3)$_2$), 29.4

(CH_2CH_3), 32.8, 34.3, 34.7, 35.2, 35.9, 39.9, 45.4 (Cy-*C*+*C*$(CH_3)_2$), 110.7 (Ar-*C*), 114.7 (Ar-*C*), 123.4 (^{TCHP}Ar-*C*), 129.8 (Ar-*C*), 134.9 (^{TCHP}Ar-*C*), 136.4 (Ar-*C*), 137.3 (^{TCHP}Ar-*C*), 139.3 (^{TCHP}Ar-*C*), 146.4 (Ar-*C*), 146.9 (Ar-*C*); IR ν/cm^{-1} (Neat): 3438 (w), 2921 (s), 2849 (s), 1736 (m), 1619 (m), 1612 (m), 1509 (m), 1390 (m), 1348 (m), 1352 (m), 1210 (s), 1031 (m), 862 (m), 846 (m), 802 (m); HRMS (ESI) m/z: $[M + H]^+$ calc. for $C_{67}H_{93}N_2O$: 941.7282; found: 941.7283.

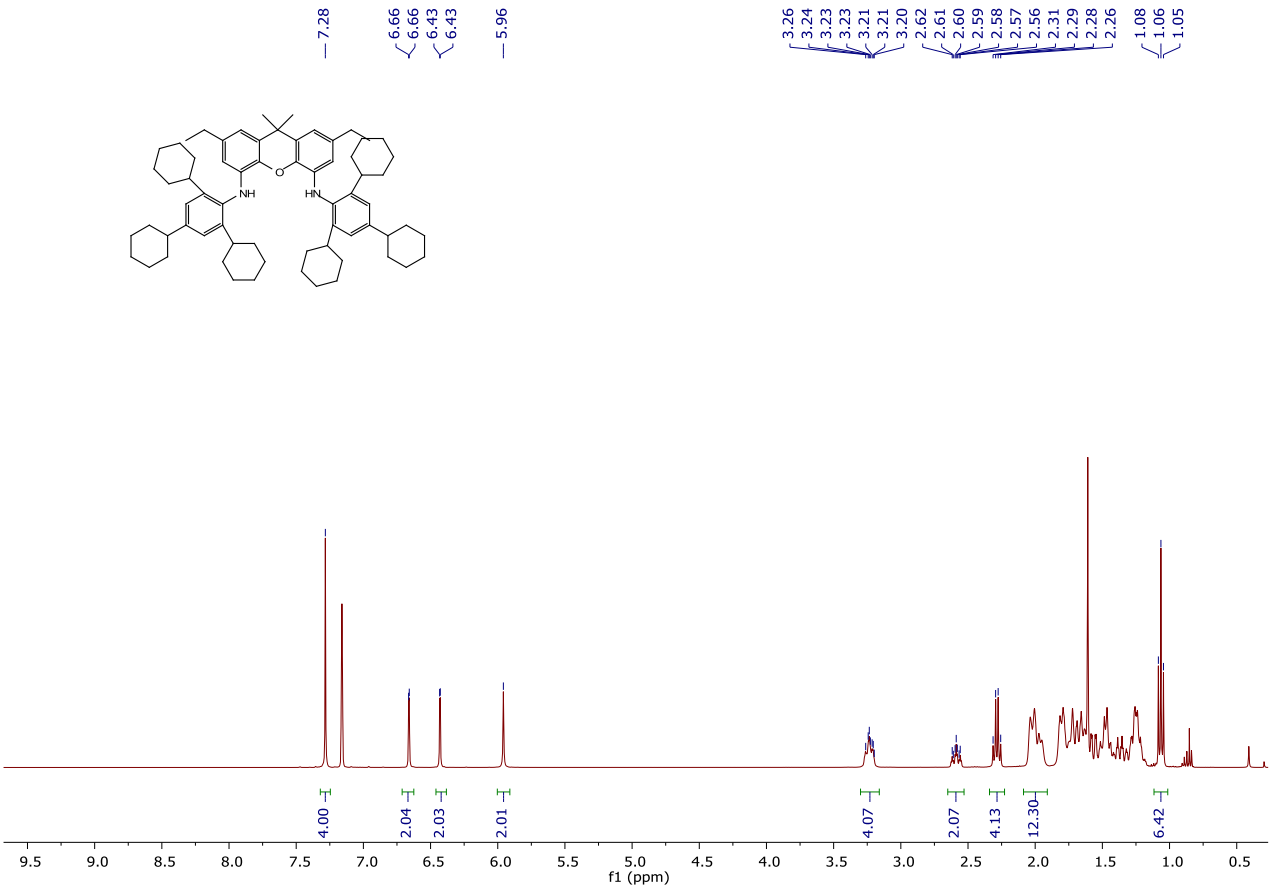

Figure S5. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of ^{TCHP}NONH$_2$.

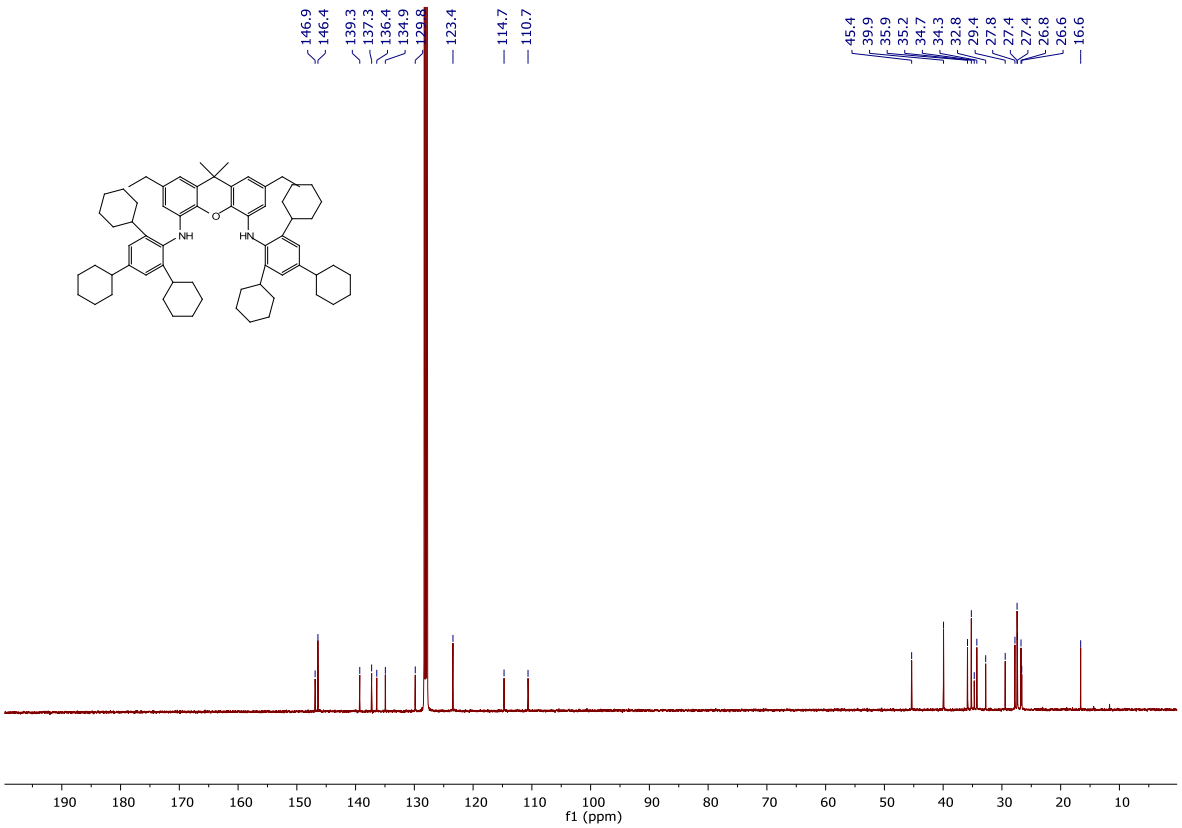

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, 298 K, C_6D_6) of $^{TCHP}NONH_2$.

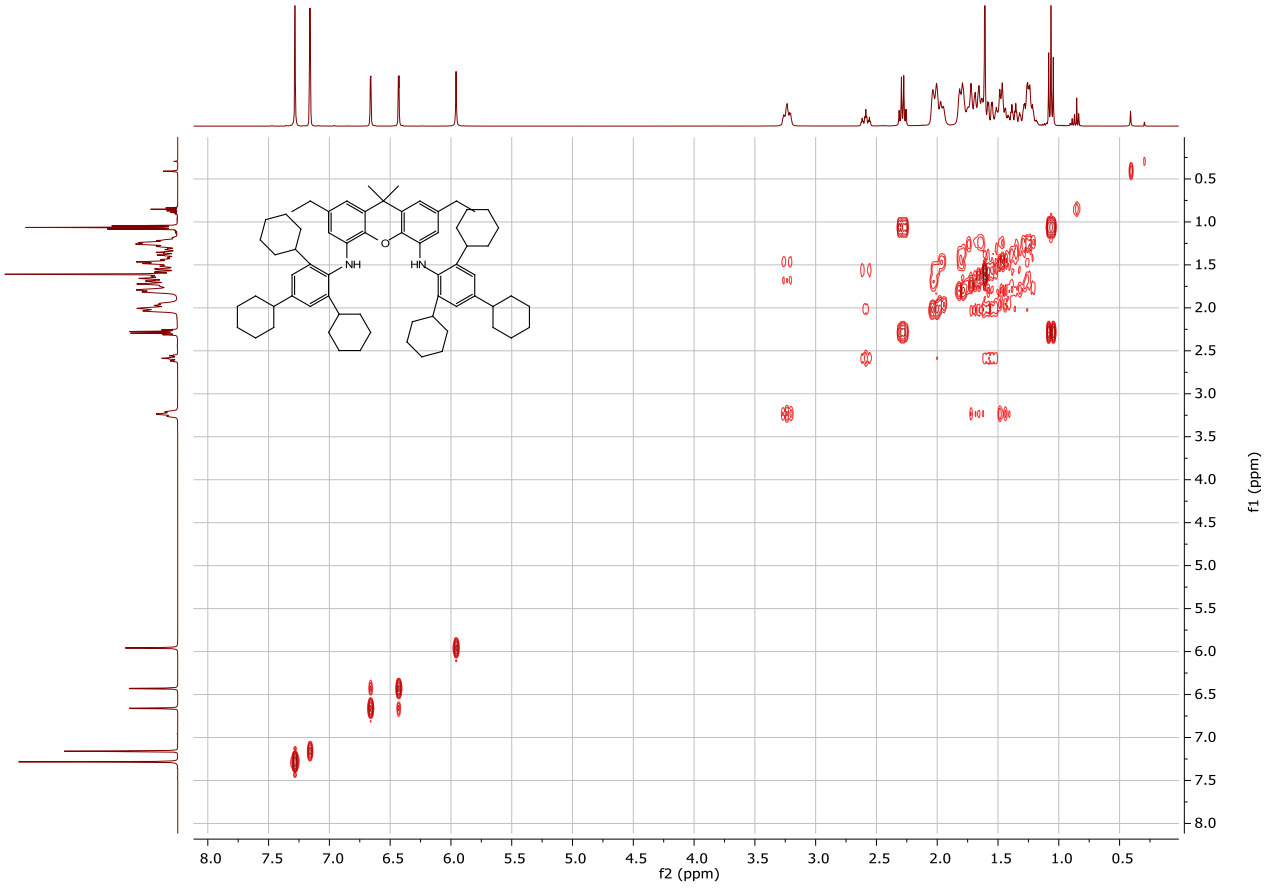

Figure S7. ^{1}H-COSY NMR spectrum (101 MHz, 298 K, C_6D_6) of $^{TCHP}NONH_2$.

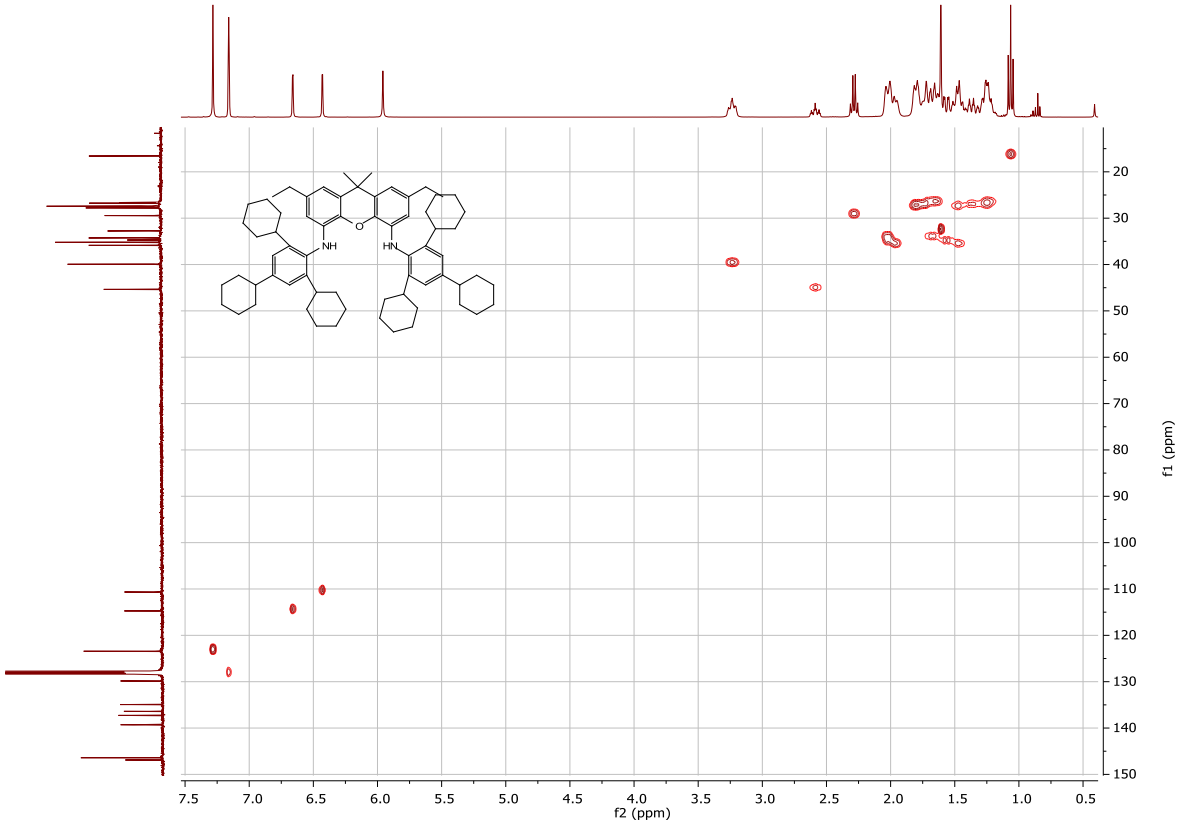

Figure S8. HSQC NMR spectrum (^{1}H: 400 MHz; ^{13}C: 101 MHz, 298 K, C_6D_6) of $^{TCHP}NONH_2$.

[(^{TCHP}NON)Ca(THF)$_2$] 3. An oven-dried Teflon screw cap Schlenk flask was charged with a magnetic stir bar, $^{TCHP}NONH_2$ (1.9 g, 2.0 mmol), [Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] (1.01 g, 2.0 mmol), and toluene (50 mL) under an N_2 atmosphere. the reaction mixture was then heated at 100 °C, with stirring, overnight. The reaction mixture was then cooled to room temperature and volatiles were removed under reduced pressure to give a solid off-white residue. This was then washed with hexane to afford the title compound as a white solid. The hexane washings were cooled to -30 °C to give colorless crysals of **3** (1.60g, 71%). M.P.: 250 – 252 °C; ^{1}H NMR (400 MHz, 298 K, C_6D_6) δ 1.17 (t, *J* = 7.6 Hz, 6H, CH$_2$*CH$_3$*), 1.24 – 1.92 (m, 66H, Cy-*H*+C(C*H$_3$*)$_2$+OCH$_2$C*H$_2$*), 1.97 – 2.03 (m, 4H, Cy-*H*), 2.21 – 2.29 (m, 4H, Cy-*H*), 2.42 (q, *J* = 7.5 Hz, 4H, C*H$_2$*CH$_3$), 2.57 (m, 2H, Cy-*H*), 3.20 (m, Cy-*H*), 3.27 – 3.37 (m, 8H, OC*H$_2$*CH$_2$), 6.11 (d, *J* = 2.0 Hz, 2H, Ar*H*), 6.41 (d, *J* = 2.0 Hz, 2H, Ar*H*), 7.19 (s, 4H, ^{TCHP}Ar*H*); ^{13}C NMR (101 MHz, 298 K, C_6D_6) δ 16.9 (CH$_2$*C*H$_3$), 25.4 (OCH$_2$*C*H$_2$), 26.8, 26.9, 27.6, 27.6, 27.9 (Cy-*C*), 30.0 (*C*H$_2$CH$_3$), 32.2 (C(*C*H$_3$)$_2$), 34.9, 35.1, 35.6, 36.7 (Cy-*C*+*C*(CH$_3$)$_2$), 38.9 (Cy-*C*), 45.2 (Cy-*C*), 69.3 (O*C*H$_2$CH$_2$), 106.4 (Ar-*C*), 111.5 (Ar-*C*), 123.0 (^{TCHP}Ar-*C*), 129.7 (Ar-*C*), 139.2 (^{TCHP}Ar-*C*), 139.8 (^{TCHP}Ar-*C*), 140.3 (^{TCHP}Ar-*C*), 143.6 (Ar-*C*), 148.3 (Ar-*C*), 149.8 (Ar-*C*); IR *ν*/cm^{-1} (Nujol): 1610 (m), 1578 (s), 1234 (s), 1184 (s), 1160 (m), 1031 (m), 997 (w), 927 (w), 918 (w), 869 (s), 780 (m); a reproducible microanalysis could not be obtained due to

traces of the protonated ligand, $^{TCHP}NONH_2$, in the product, which could not be completely removed after recrystallisation.

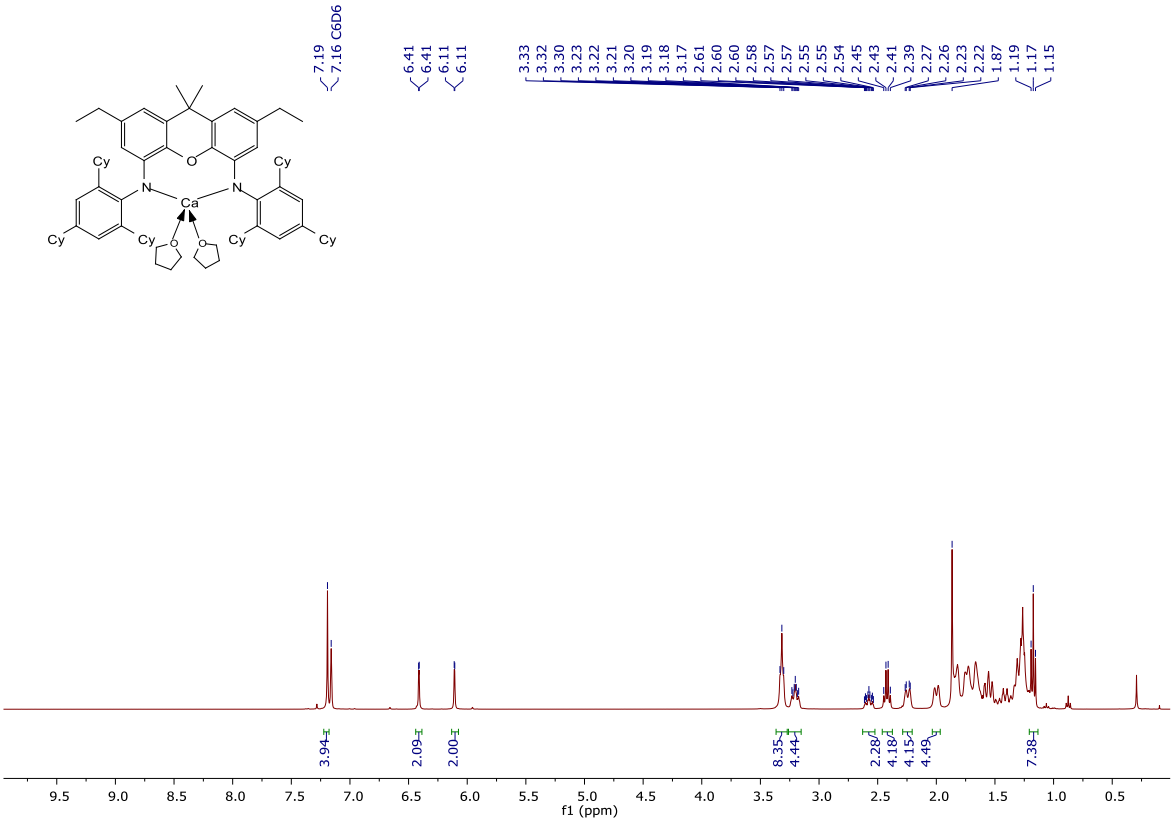

Figure S9. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of compound **3**.

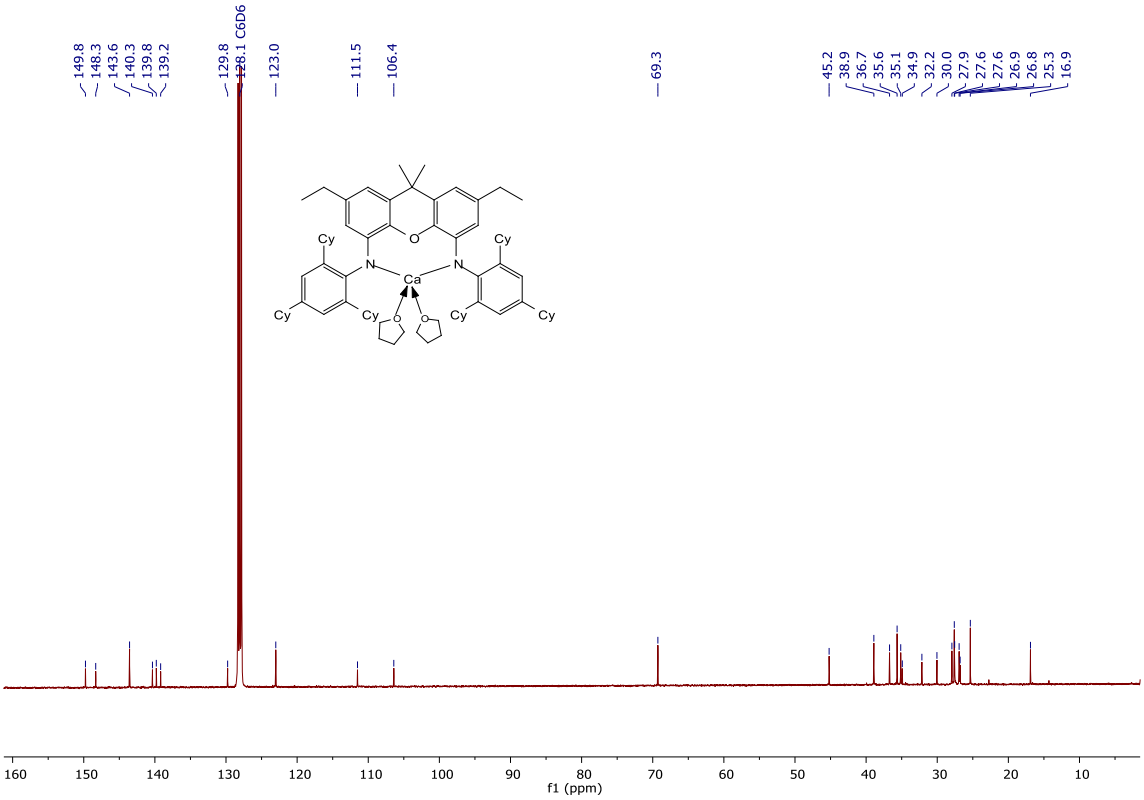

Figure S10. $^{13}C\{^{1}H\}$ NMR specturm (101 MHz, 298 K, C_6D_6) of compound **3**.

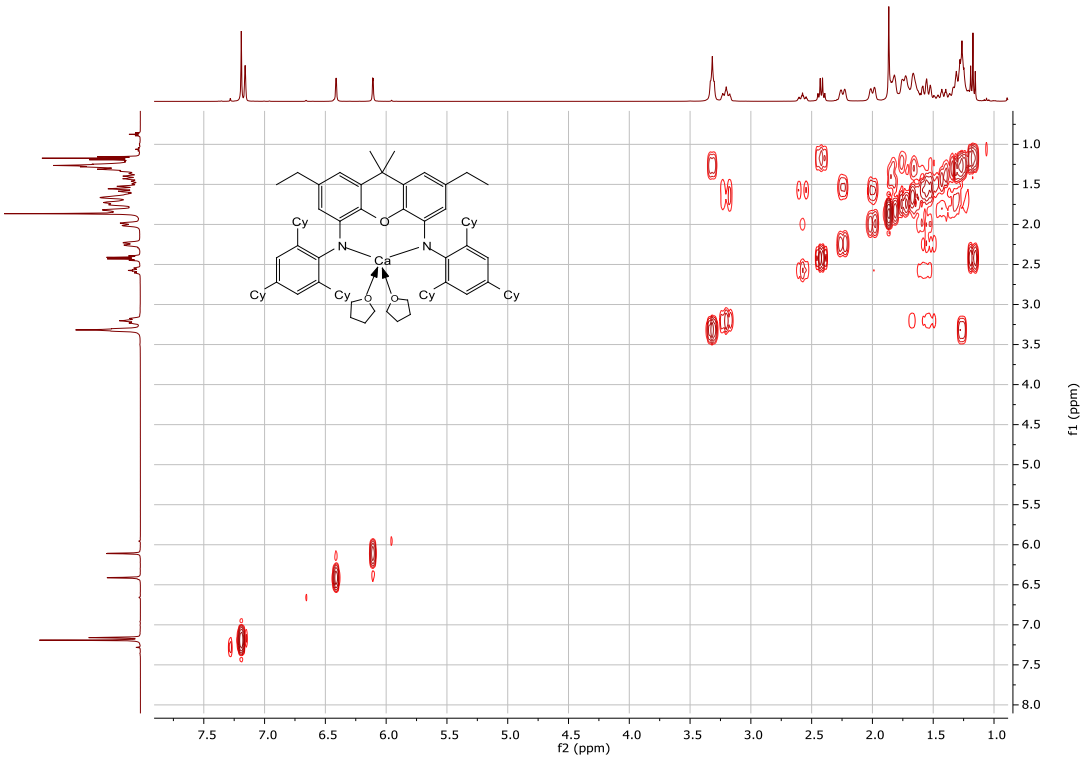

Figure S11. ^{1}H-COSY NMR specturm (101 MHz, 298 K, C_6D_6) of compound **3**.

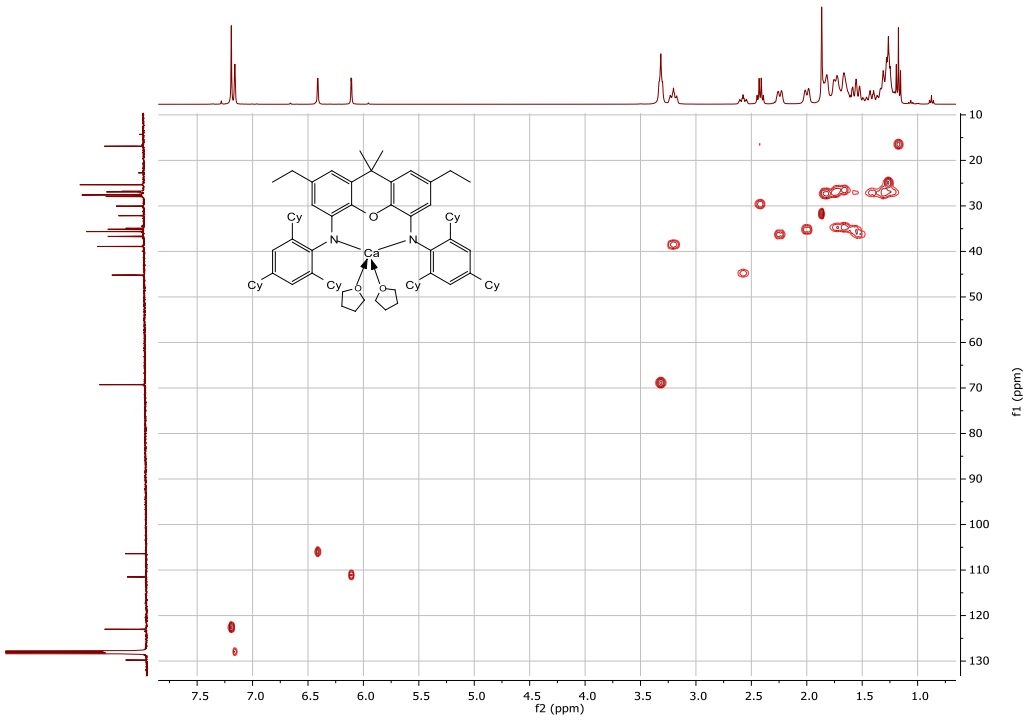

Figure S12. HSQC NMR spectrum (^{1}H: 400 MHz; ^{13}C: 101 MHz, 298 K, C_6D_6) of compound **3**.

[(^{TCHP}NON)Ca(C_7H_8)] 4. An oven-dried Teflon screw cap Schlenk flask was charged with a magnetic stir bar, $^{TCHP}NONH_2$ (2.83 g, 3.0 mmol), [Ca{N(SiMe$_3$)$_2$}$_2$](1.1 g, 3.0 mmol), and toluene (60 mL) under an N_2 atmosphere. The reaction mixture was then heated at 100 °C, with stirring, overnight. A clolor change from pale yellow to bright orange for the solution was observed. The reaction mixture was cooled to room temperature and volatiles were removed under reduced pressure to leave a solid yellow residue. The residue was extracted with hexane (100 mL), filtered, and the filtrate concentrated to *ca.* 20 mL. Upon slowly cooling of the concentrate to –30 °C, a yellow precipitate was deposited, which was isolated and dried *in vacuo* to give the title compound as a bright yellow powder (2.6 g, 80%). M.P.: 246 – 248 °C; ^{1}H NMR (400 MHz, 298 K, C_6D_6) δ 1.15 (t, *J* = 7.5 Hz, 6H, CH_2CH_3), 1.19 – 1.80 (m, 50H, Cy*H*+ $C(CH_3)_2$), 1.83 – 1.95 (m, 8H, Cy*H*), 2.12 (m, 11H, Cy*H*+PhCH_3), 2.36 (q, *J* = 7.5 Hz, 4H, CH_2CH_3), 2.67 (dd, *J* = 13.6, 10.1 Hz, 2H, Cy*H*), 2.84 – 3.00 (m, 4H, Cy*H*), 5.92 (s, 2H, Ar*H*), 6.33 (s, 2H, Ar*H*), 6.97 – 7.18 (m, 5H, $C_6H_5CH_3$), 7.28 (s, 4H, Ar*H*); ^{13}C NMR (101 MHz, 298 K, C_6D_6) δ 21.4 (PhCH_3),17.3, 26.8, 26.8, 27.6, 27.6, 28.1, 30.1, 32.5, 34.2, 35.5, 35.7, 36.2, 40.7, 45.4 (Cy-C, CH_2CH_3, CH_2CH_3, $C(CH_3)_2$, $C(CH_3)_2$), 107.9 (Ar-*C*), 109.5 (Ar-*C*), 123.1 (Ar-*C*), 125.6 (PhMe-*C*), 128.6 (PhMe-*C*), 128.8 (Ar-C), 129.3 (PhMe-*C*), 137.9 (PhMe-*C*), 138.5 (Ar-*C*), 140.1 (Ar-*C*), 142.4 (Ar-*C*), 143.9 (Ar-*C*), 148.1 (Ar-*C*), 148.2 (Ar-*C*); IR *v*/cm^{-1} (Nujol): 1619 (s), 1584 (s), 1238 (s), 1193 (s), 1159 (m), 1034 (s), 998 (m), 874 (s), 821 (m), 759 (s); anal. calc. for $C_{74}H_{98}CaN_2O$: C 82.94%, H 9.22%, N 2.61%; found: C 82.98%, H 9.49%, N 2.83%.

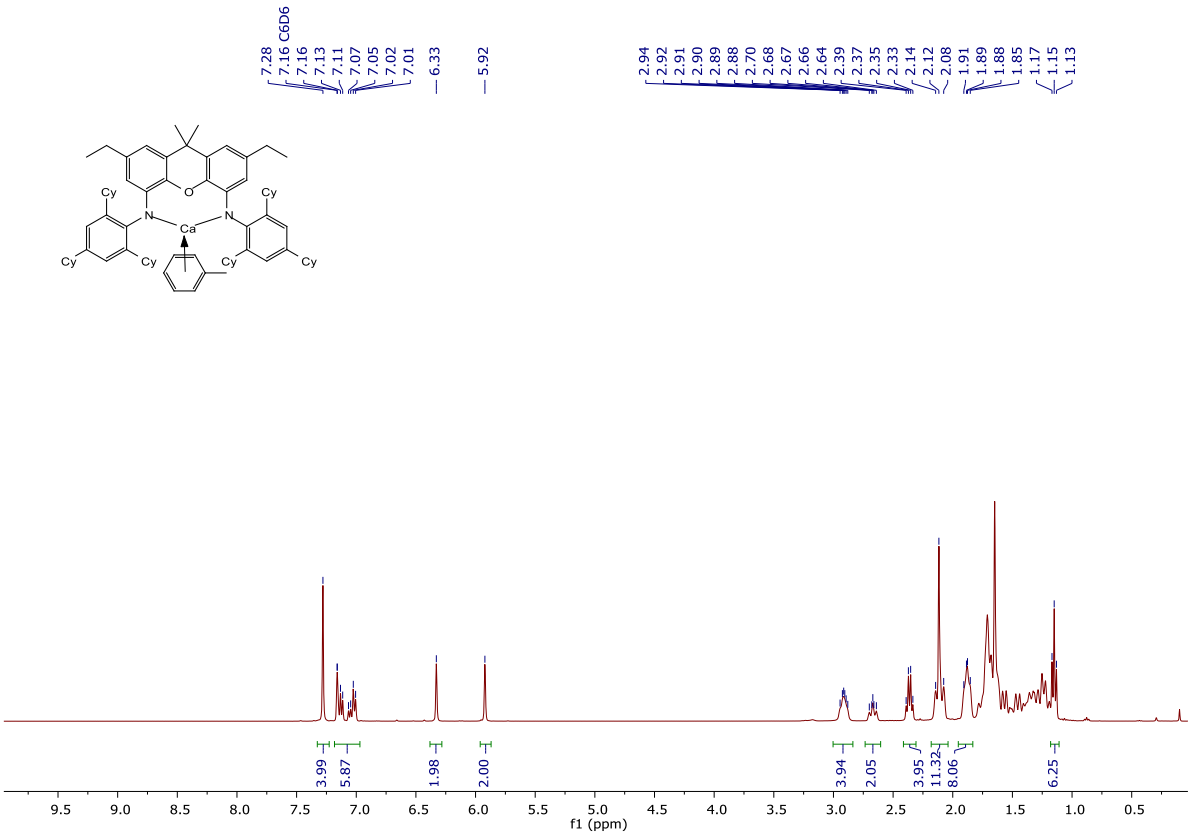

Figure S13. ^{1}H NMR spectrum (400 MHz, 298 K, C_6D_6) of compound **4**.

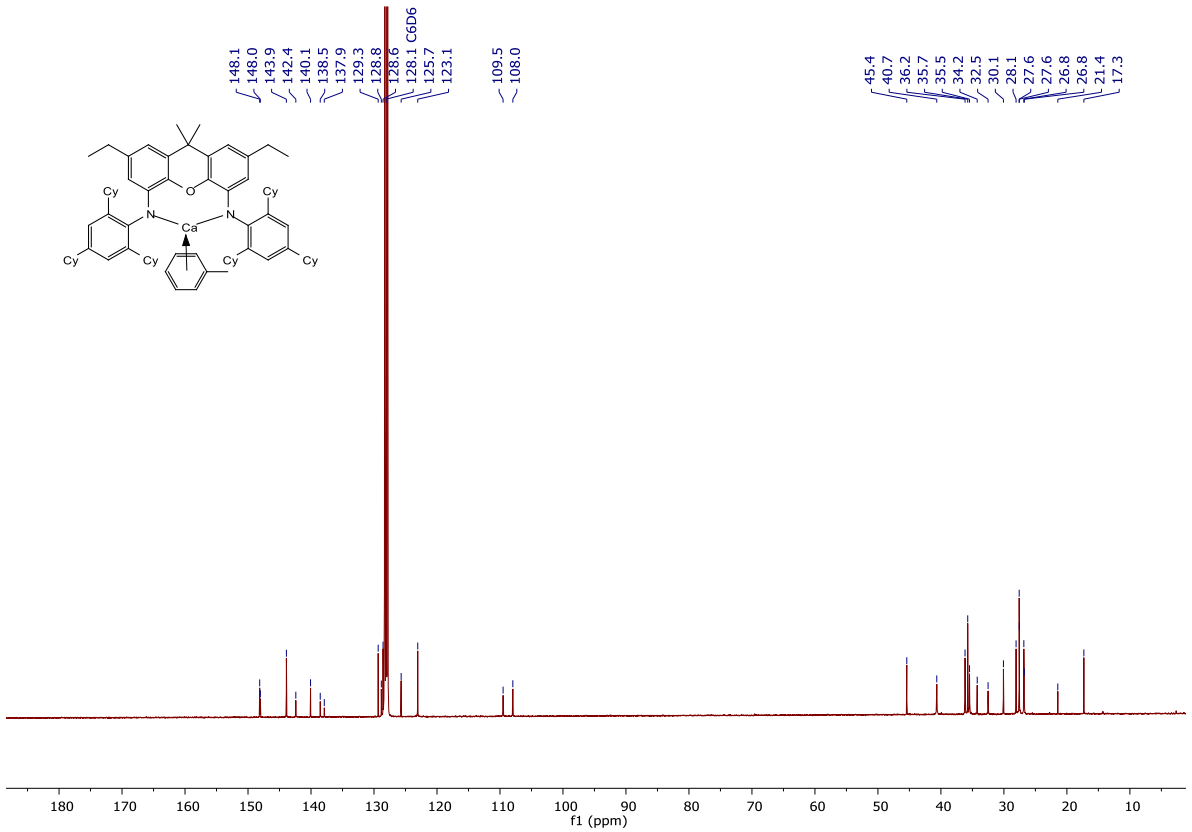

Figure S14. ^{13}C{^{1}H} NMR specturm (101 MHz, 298 K, C_6D_6) of compound **4**.

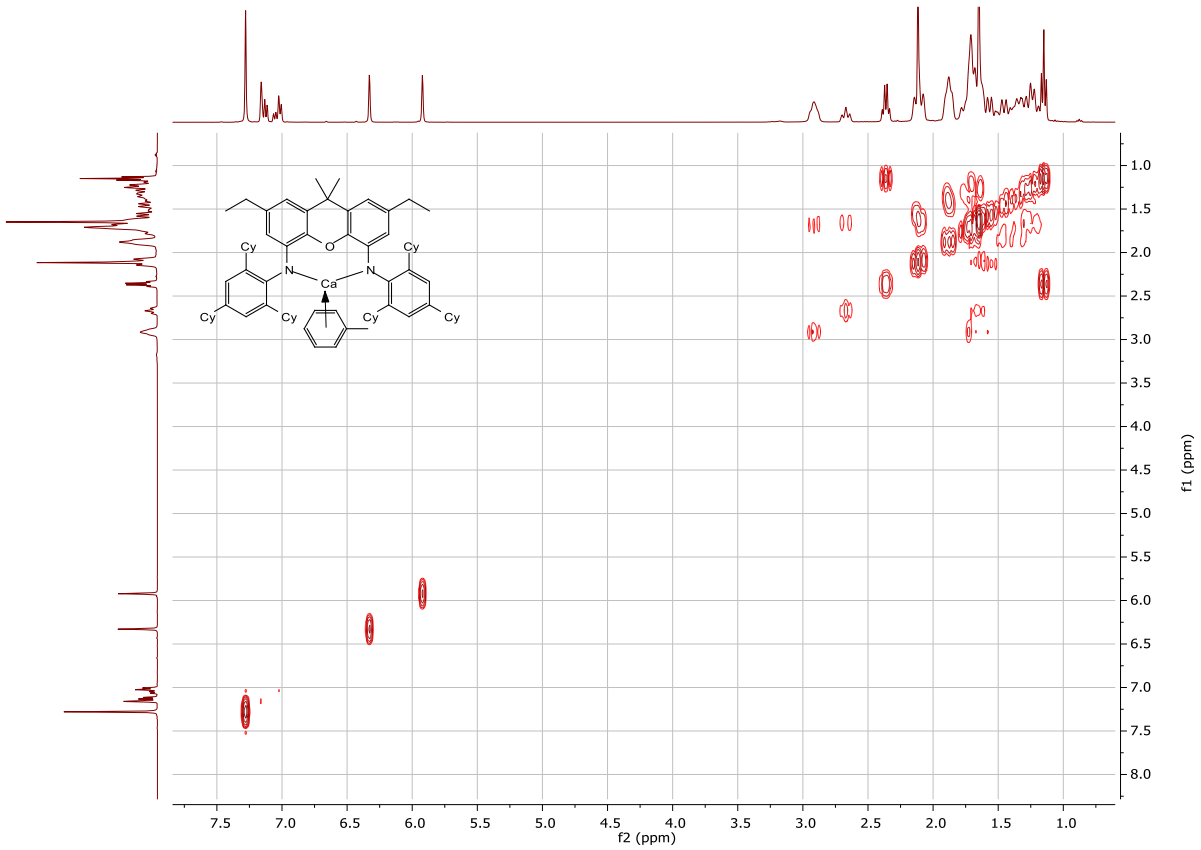

Figure S15. ^{1}H-COSY NMR specturm (101 MHz, 298 K, C_6D_6) of compound **4**.

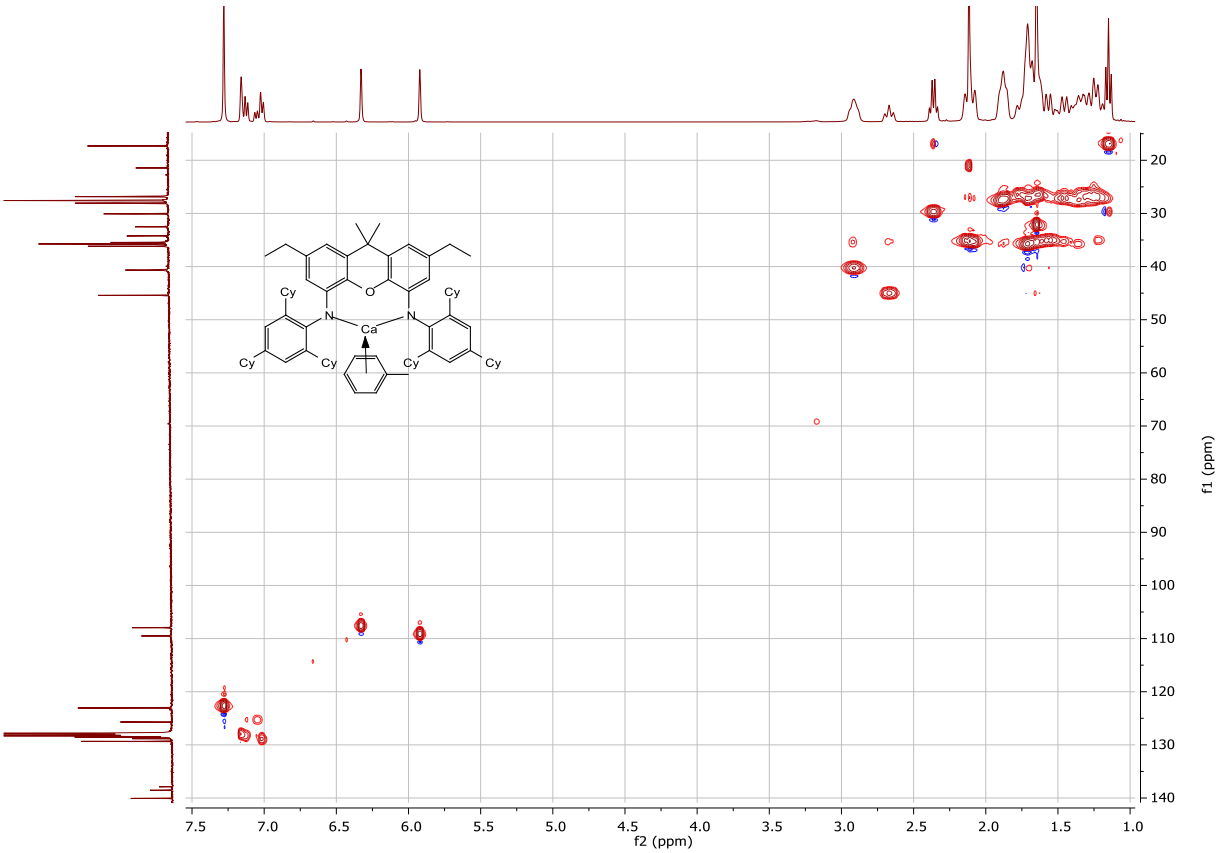

Figure S16. HSQC NMR spectrum (^{1}H: 400 MHz; ^{13}C: 101 MHz, 298 K, C_6D_6) of compound **4**.

[{K(^{TCHP}NON)Ca}$_2$(μ-η^2:η^2-N$_2$)] 5. A 100 mL oven dried Schlenk flask was charged with a magnetic stir bar, compound **4** (0.5 g, 0.5 mmol) and K/KI (5% w/w, 2.0 g, 2.5 mmol). Methylcyclohexane (20 mL) was then added and the mixture stirred overnight under an atmosphere of N_2. A color change of the solution from yellow to dark brown was observed. The reaction mixture was then filtered and volatiles removed from the filtrate to afford a brown oily solid, which was extracted with *n*-pentane (50 mL). After filtration, the dark brown filtrate was concentrated to *ca.* 15 mL and stored at room temperature to obtain dark red crystals of the title compound (75 mg, 15%). Due to the insolubility of this compound in aliphatic solvents, and its reactivity towards aromatic and ethereal solvents, NMR spectroscopic data could not be recorded. M.P.: 254 - 258 °C (decomp.); IR ν/cm^{-1} (Nujol): 1605 (w), 1579 (w), 1425 (m), 1390 (s), 1180 (m), 1162 (m), 872 (s), 840 (s), 699 (m); Raman (ν/cm^{-1}): 1419 (s, N-N str.); anal. calc. for $C_{134}H_{180}Ca_2K_2N_6O_2$ (pentane of crystallisation removed under vacuum): C 77.93%, H 8.79%, N 4.07%; found: C 77.96%, H 8.57%, N 3.95%.

N.B. Attempts to prepare the $^{15}N_2$ coordinated analogue of compound **5** by repeating the synthesis under an atmosphere of $^{15}N_2$ were not successful. It is believed this arises from the known contamination of commercially available $^{15}N_2$ with $^{15}NH_3$, $^{15}NO_x$, H_2O etc. which could react with **5**.[6] The level of these impurities is < 1% total and, therefore, should not have led to the total decomposition of **5**, if the decomposition reactions are stoichiometric. However, decomposition of **5** in the presence of the impurities could be catalytic, especially considering the extremely reactive nature of the compound. This was seemingly confirmed by the fact that when an *in situ* generated methylcyclohexane solution of $^{14}N_2$ coordinated **5** (prior to its crystallisation) was placed under an atmosphere of $^{15}N_2$, the red color of **5** in solution was lost over several minutes.

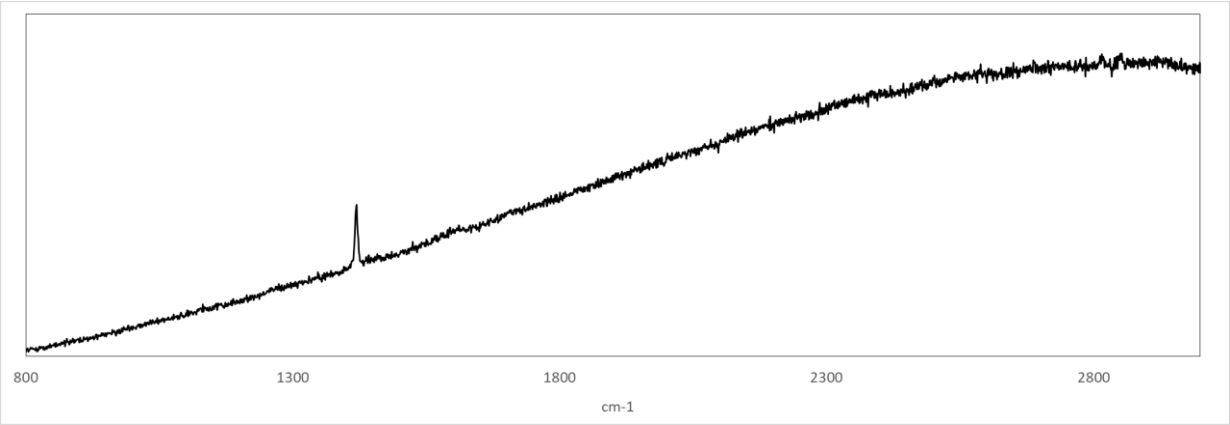

Figure S17. Raman spectrum (514 nm laser) of crystals of **5**. The strong N-N stretching absorption band for the complex is visible at ν = 1419 cm^{-1}. Less intense absorptions are presumably masked by intense fluoresence background arising from the xanthene backbone of the ligand (the spectrum collected with a 782 nm laser is very similar). The spectrum is consistent with those of related μ–η^2:η^2–N_2 bridged dilanthanide complexes, which exhibit relatively sharp, strong N–N stretching absorption bands in the typical region 1406-1473 cm^{-1}.[7]

2. X-Ray Crystallography

Crystals of compounds suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using a Rigaku Xtalab Synergy Dualflex using a graphite monochromator with either Mo Kα or Cu Kα radiation (0.71073 Å or 1.54180 Å, respectively). All structures were solved by direct methods and refined on F^2 by full matrix least squares (SHELX16[8]) using all unique data. Hydrogen atoms are typically included in calculated positions (riding model). Crystal data, details of data collections and refinements for all structures can be found in their CIF files and are summarized in Table S1.

Table S1. Crystal data for compounds $^{TCHP}NONH_2$, **3**, **5**, 4,5-dibromo-2,7-diethyl-9,9-dimethylxanthene **1S** and [{(^{TCHP}NON)K_2(μ-biphenyl)$_{0.5}$(μ-benzene)$_{0.5}$}$_\infty$] **2S**.

	$^{TCHP}NONH_2$	**3**	**5**·(pentane)
empirical formula	$C_{67}H_{92}N_2O$	$C_{75}H_{106}CaN_2O_3$	$C_{139}H_{192}Ca_2K_2N_6O_2$
formula weight	941.42	1123.69	2137.33
crystal system	Triclinic	Triclinic	Triclinic
space group	*P*-1	*P*-1	*P*-1
a (Å)	12.74090(10)	11.84030(10)	16.8905(2)
b (Å)	13.90020(10)	21.09210(10)	18.3068(3)
c (Å)	16.96350(10)	27.04330(10)	22.6963(3)
α (°)	91.6110(10)	87.156(1)	78.4640(10)
β (°)	98.2900(10)	85.1190(10)	70.1870(10)
γ (°)	106.0580(10)	75.5590(10)	70.0280(10)
V (Å^3)	2849.55(4)	6513.78(7)	6177.23(16)
Z	2	4	2
T (K)	123(2)	123(2)	123(2)
ρ_{calcd} (g·cm^3)	1.097	1.146	1.149
μ (mm^{-1})	0.473	1.189	1.802
F(000)	1032	2456	2324
reflns collected	55552	126075	126316
unique reflns	10567	23928	26441
R_{int}	0.0367	0.0409	0.0505
R1 [I > 2σ(I)]	0.0454	0.0514	0.0759
wR2 (all data)	0.1182	0.1307	0.2029
largest peak and hole (e·Å^{-3})	0.310, -0.349	1.156, -0.475	0.608, -0.554
CCDC no.	2204509	2204510	2204511

Table S1 (contd.). Crystal data for compounds $^{TCHP}NONH_2$, **3**, **5**, 4,5-dibromo-2,7-diethyl-9,9-dimethylxanthene **1S** and [{(^{TCHP}NON)K_2(μ-biphenyl)$_{0.5}$(μ-benzene)$_{0.5}$}$_\infty$] **2S**.

	1S	**2S**·(pentane)
empirical formula	$C_{19}H_{20}Br_2O$	$C_{78.5}H_{104}K_2N_2O$
formula weight	424.17	1169.83
crystal system	Triclinic	Triclinic
space group	*P*-1	*P*-1
a (Å)	9.6376(2)	12.7093(3)
b (Å)	11.1383(3)	17.6574(5)
c (Å)	17.1853(3)	18.1074(4)
α (°)	82.913(2)	113.431(3)
β (°)	82.676(2)	99.719(2)
γ (°)	68.389(2)	97.872(2)
V (Å^3)	1695.26(7)	3601.49(7)
Z	4	2
T (K)	123(2)	123(2)
ρ_{calcd} (g·cm^3)	1.662	1.085
μ (mm^{-1})	4.781	1.485
F(000)	848	1270
reflns collected	34878	64002
unique reflns	7354	13038
R_{int}	0.0467	0.0450
R1 [I > 2σ(I)]	0.0364	0.0870
wR2 (all data)	0.0749	0.2468
largest peak and hole (e·Å^{-3})	0.751, -0.467	1.564, -0.535
CCDC no.	2204507	2204508

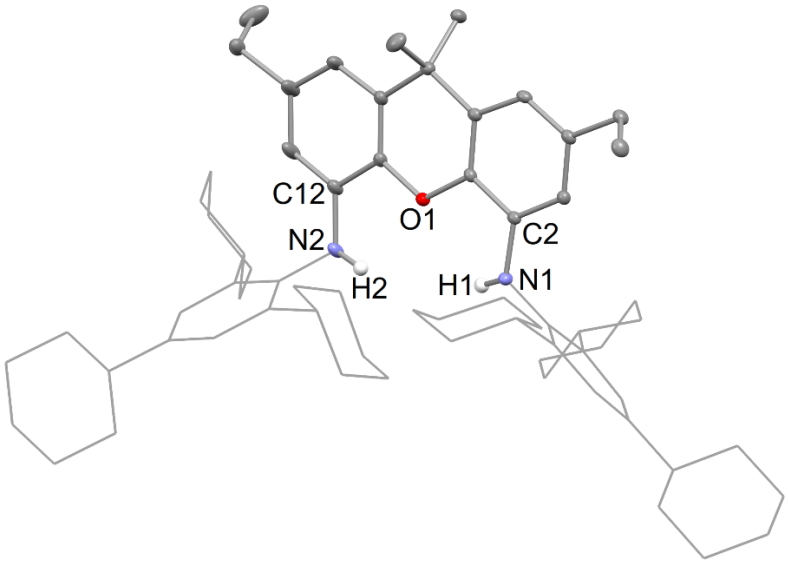

Figure S18. The molecular structure of $^{TCHP}NONH_2$ (20% ellipsoids; TCHP substituents shown as wire frame for clarity; hydrogen atoms, except aniline protons, omitted).

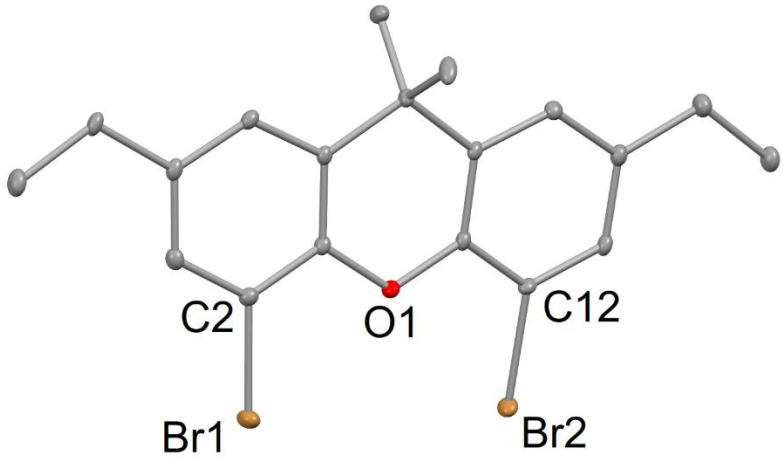

Figure S19. The molecular structure of 4,5-dibromo-2,7-diethyl-9,9-dimethylxanthene **1S** (20% ellipsoids; hydrogen atoms omitted). N.B. There are two molecules of **1S** in the asymmetric unit, with no significant geometric differences between them.

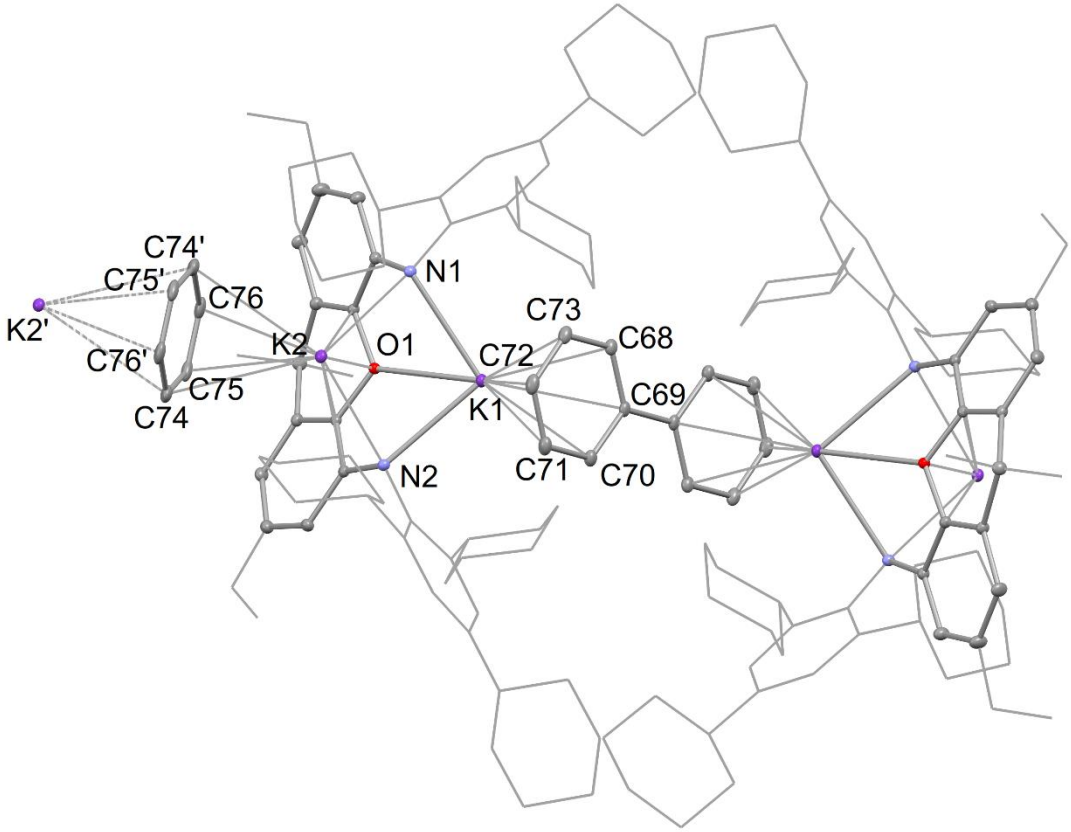

Figure S20. The molecular structure of [{(^{TCHP}NON)K_2(μ-biphenyl)$_{0.5}$(μ-benzene)$_{0.5}$}$_\infty$] **2S** (20% ellipsoids; TCHP, methyl and ethyl substituents shown as wire frame for clarity; hydrogen atoms omitted). N.B. The biphenyl and benzene ligands lie on inversion centers. Symetry operator ' = 2-x, 2-y, 2-z. Selected bond lengths (Å) and angles (°): K(1)-O(1) 2.6570(18), K(1)-N(2) 2.751(2), K(1)-N(1) 2.762(2), K(1)-cent.(C68-C73) 3.014(3), O(1)-K(2) 2.7344(19), N(1)-K(2) 2.796(2), K(2)-N(2) 2.771(2), K(2)-cent.(C74-C76') 3.049(4), O(1)-K(1)-N(2) 58.73(6), O(1)-K(1)-N(1) 58.10(6), O(1)-K(1)-cent.(C68-C73) 164.22(7), O(1)-K(2)-N(2) 57.62(6), O(1)-K(2)-N(1) 56.85(6).

3. Computational Studies

The DFT calculations were carried out by employing hybrid functional (B3PW91)[9] along with SDD basis set[10] and Pople basis sets[11] (6-311++G** for calcium, potassium atoms and 6-31G** for nitrogen, carbon, oxygen and hydrogen atoms) for the rest of the atoms. Dispersion corrections were included in our calculations by employing D3 version of Grimme's dispersion with Becke-Johnson damping.[12] Frequency calculations were performed to locate minima for the optimized structures and for obtaining thermal corrections over the energies. All the calculations were performed using Gaussian 09 suite of programs.[13] AIM analysis were carried out using Multiwfn software.[14] Natural Bonding Analyis were carried out with the NBO 06 sofware.[15]

Table S2. Computed Wiberg bond indeces for the $Ca_2N_2K_2$ core of **5**.

Atom Label	**Wiberg bond index**	**Atom Label**	**Wiberg bond index**	**Atom Label**	**Wiberg bond index**	**Atom Label**	**Wiberg bond index**
Ca1	0.0000	Ca1	0.0522	Ca1	0.1496	Ca1	0.1476
Ca2	0.0522	Ca2	0.0000	Ca2	0.1601	Ca2	0.1666
K1	0.0687	K1	0.0657	K1	0.0833	K1	0.0490
K2	0.0699	K2	0.0644	K2	0.0496	K2	0.0787
N1	0.1496	N1	0.1601	N1	0.0000	N1	1.9971
N2	0.1476	N2	0.1666	N2	1.9971	N2	0.0000

Table S3. Computed natural charges for the $Ca_2N_2K_2$ core of **5**.

Atom label	**Natural charges**
Ca1	1.46121
Ca2	1.45954
K1	0.66460
K2	0.66661
N1	-0.71561
N2	-0.72324

Table S4. Computed BCP descriptors for the $Ca_2N_2K_2$ core of **5**.

	ρ(r)	$\nabla^2\rho$(r)	G(r)	V(r)	H(r)	ε
Ca1-N1	0.042	0.203	0.047	-0.043	0.004	0.280
Ca2-N1	0.040	0.196	0.045	-0.041	0.004	0.393
Ca1-N2	0.040	0.197	0.046	-0.042	0.004	0.384
Ca2-N2	0.042	0.200	0.047	-0.043	0.004	0.278
N1-N2	0.457	-0.992	0.303	-0.854	-0.551	0.009
K1-N1	0.023	0.114	0.024	-0.020	0.004	0.369
K2-N2	0.023	0.115	0.024	-0.020	0.004	0.368

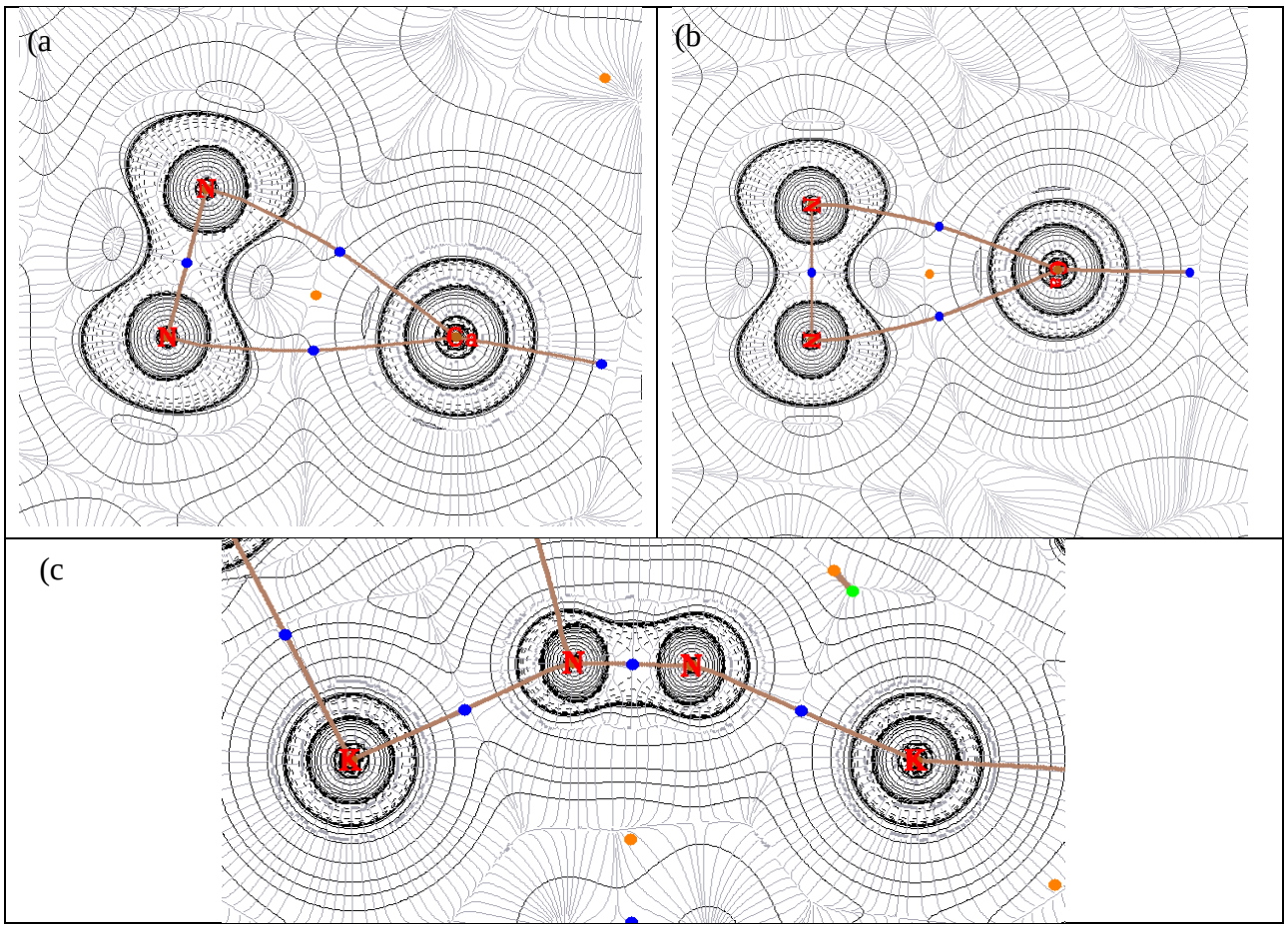

Figure S21. Laplacian distribution for the $Ca_2N_2K_2$ core of **5** (a) Ca1-N1-N2 (b) N1-N2-Ca2 (c) K1-N1-N2-K2.

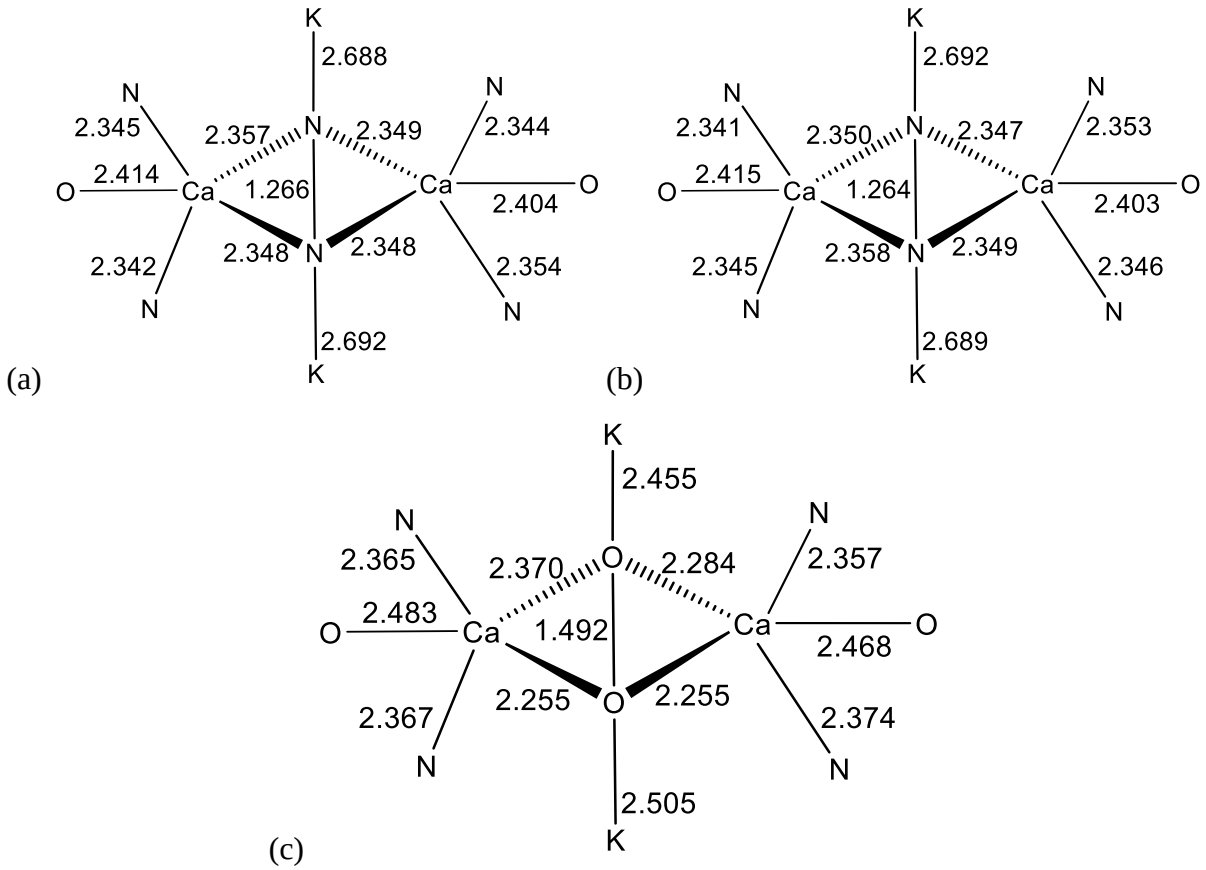

Figure S22. Comparison of the bond lengths (Å) within the first Ca coordination spheres of (a) the experimental molecular structure of **5** (esds ommitted), (b) the optimised gas phase DFT structure of **5**, and (c) the optimised gas phase DFT structure of [{K(^{TCHP}NON)Ca}$_2$(μ-η^2:η^2-O$_2$)].

Table S5. Cartesian coordinates for the optimised structures.

Compound **5**

Ca	6.686912000	7.085257000	4.619754000
Ca	9.205789000	3.487576000	4.136003000
K	5.387430000	3.386455000	5.556185000
K	10.314401000	6.745529000	6.342039000
O	5.652867000	9.144957000	3.802282000
O	10.449315000	1.731369000	2.958914000
N	7.410526000	4.855601000	4.875629000
N	8.449102000	5.545919000	5.006892000
N	5.069560000	6.658199000	2.976507000
N	6.414572000	8.677922000	6.327755000
N	9.144864000	1.430122000	5.268035000
N	11.099579000	4.340172000	3.007709000
C	5.324819000	10.118450000	4.744934000
C	5.723867000	9.841423000	6.069288000
C	5.353428000	10.805005000	7.028859000
H	5.617700000	10.621619000	8.067319000
C	4.654969000	11.962053000	6.679644000
C	4.329408000	12.201819000	5.340164000
H	3.801629000	13.112077000	5.076717000
C	4.680481000	11.280031000	4.347212000
C	4.507026000	11.505902000	2.845627000
C	4.152990000	10.163375000	2.213172000
C	3.234382000	9.987420000	1.171210000
H	2.725210000	10.843311000	0.741493000
C	2.949388000	8.709078000	0.681864000

C	3.567376000	7.594586000	1.251779000
H	3.304984000	6.595632000	0.912307000
C	4.485600000	7.715659000	2.311861000
C	4.774193000	9.033919000	2.722539000
C	5.871826000	11.968706000	2.285775000
H	6.164649000	12.919898000	2.742426000
H	5.815238000	12.097333000	1.199847000
H	6.648843000	11.231387000	2.505509000
C	3.456491000	12.572566000	2.544334000
H	2.472981000	12.282675000	2.924976000
H	3.377580000	12.740416000	1.466965000
H	3.738661000	13.527350000	2.996065000
C	4.291517000	12.981654000	7.731722000
C	5.197413000	14.215875000	7.693781000
H	6.239628000	13.939775000	7.879492000
H	4.900205000	14.952003000	8.448246000
H	5.155799000	14.698124000	6.712108000
C	1.909081000	8.521078000	-0.394328000
H	2.222613000	7.721190000	-1.076088000
H	1.834076000	9.434233000	-0.996378000
C	0.535270000	8.179455000	0.191192000
H	0.581603000	7.251261000	0.769838000
H	-0.216493000	8.054420000	-0.595488000
H	0.197225000	8.971629000	0.867010000
C	4.258670000	5.542808000	3.186023000
C	3.117045000	5.638143000	4.043402000
C	2.342490000	4.501620000	4.275740000
C	2.647487000	3.251892000	3.713452000
C	3.777959000	3.170160000	2.894671000
C	4.583490000	4.284269000	2.624723000
C	2.798129000	6.949142000	4.726064000
H	3.673855000	7.592213000	4.590853000
C	1.322727000	9.015830000	6.238500000
H	0.363038000	8.539937000	6.489203000
H	1.297930000	10.025463000	6.664116000
C	2.460669000	8.214330000	6.872135000
H	3.404595000	8.756275000	6.736844000
H	2.302318000	8.127237000	7.953857000
C	2.591755000	6.828493000	6.240113000
H	3.439897000	6.295014000	6.684401000
H	1.694739000	6.231217000	6.458209000
C	1.794138000	2.052039000	4.064257000
H	0.746974000	2.390976000	4.085149000
C	1.224109000	0.369620000	5.883327000
H	1.494002000	0.011534000	6.882801000
H	0.186004000	0.724595000	5.947805000
C	2.122542000	1.536744000	5.478173000
H	2.035180000	2.357289000	6.200961000
H	3.171868000	1.204170000	5.494585000
C	5.767832000	4.174560000	1.698796000
C	5.335118000	4.053074000	0.230558000
C	6.544672000	4.050611000	-0.703021000
C	7.571884000	2.982020000	-0.321258000
H	8.465518000	3.069414000	-0.949011000
H	7.146096000	1.987487000	-0.516004000
C	7.963751000	3.057081000	1.156136000
H	8.525792000	3.987698000	1.332657000
H	8.639927000	2.231838000	1.403467000
C	6.717142000	3.022710000	2.038446000
H	6.961765000	3.072715000	3.111247000
H	6.212202000	2.059843000	1.894091000
C	7.290975000	8.653819000	7.414922000
C	8.413933000	9.535936000	7.488957000
C	9.337636000	9.392461000	8.524625000
C	9.238164000	8.382058000	9.496583000
C	8.136775000	7.527327000	9.408907000
C	7.150866000	7.667427000	8.422048000
C	8.629838000	10.595857000	6.434666000
C	8.506923000	12.022079000	6.985456000

C	8.568451000	13.038003000	5.847789000
H	8.486450000	14.058590000	6.239598000
H	7.697933000	12.880403000	5.196433000
C	9.857667000	12.884932000	5.037629000
H	9.866902000	13.583411000	4.192816000
H	10.713888000	13.150892000	5.674384000
C	10.041418000	11.450659000	4.537691000
H	10.998177000	11.351074000	4.009569000
H	9.252723000	11.216376000	3.809274000
C	9.958982000	10.448499000	5.687531000
C	10.268850000	8.301179000	10.609731000
H	10.229282000	9.260314000	11.151791000
C	9.998644000	7.200518000	11.639445000
H	10.003807000	6.222651000	11.137592000
H	8.997988000	7.327624000	12.068334000
C	12.461335000	7.058585000	12.190984000
H	12.561582000	6.079618000	11.702228000
H	13.199103000	7.083030000	13.001043000
C	12.748557000	8.159056000	11.171319000
H	12.744466000	9.133658000	11.679704000
H	13.748915000	8.034969000	10.739919000
C	11.699903000	8.171151000	10.061582000
H	11.777649000	7.239556000	9.483944000
H	11.904764000	8.986104000	9.362597000
C	5.893629000	6.827579000	8.493555000
C	5.139434000	7.080422000	9.809891000
C	3.888597000	6.212678000	9.945840000
C	4.221472000	4.729089000	9.796903000
H	3.315239000	4.117649000	9.874889000
H	4.886605000	4.416010000	10.614290000
C	4.919257000	4.471553000	8.464997000
C	6.172299000	5.331603000	8.318154000
H	6.896131000	5.007345000	9.074263000
H	6.663301000	5.167038000	7.350168000
C	11.527567000	2.128732000	2.164729000
C	11.842551000	3.504574000	2.210703000
C	12.945792000	3.902115000	1.426663000
H	13.229916000	4.951858000	1.435062000
C	13.709991000	2.982908000	0.707326000
C	13.383184000	1.624625000	0.747221000
H	13.996126000	0.915345000	0.201842000
C	12.278332000	1.181429000	1.484791000
C	11.839162000	-0.275498000	1.593087000
C	11.347568000	-0.504185000	3.020310000
C	11.532320000	-1.686270000	3.751391000
H	12.133217000	-2.492874000	3.345567000
C	10.948423000	-1.836319000	5.011254000
C	10.144874000	-0.819484000	5.533610000
H	9.683687000	-0.941359000	6.510806000
C	9.924536000	0.384100000	4.837676000
C	10.594498000	0.502258000	3.600359000
C	12.957758000	-1.242232000	1.209881000
H	13.266835000	-1.081316000	0.173629000
H	12.610613000	-2.276365000	1.282346000
H	13.831258000	-1.120980000	1.856853000
C	10.642016000	-0.493923000	0.639187000
H	9.821658000	0.185543000	0.885071000
H	10.273508000	-1.521745000	0.723204000
H	10.943340000	-0.306381000	-0.396719000
C	14.853081000	3.468737000	-0.147986000
H	15.387315000	4.272911000	0.373125000
H	15.574046000	2.655771000	-0.294558000
C	14.374375000	3.979186000	-1.510557000
H	13.854579000	3.186043000	-2.057623000
H	15.211319000	4.328497000	-2.124753000
H	13.671576000	4.809195000	-1.385606000
C	11.231439000	-3.060313000	5.845301000
H	11.530068000	-3.889938000	5.193865000
H	10.316595000	-3.379343000	6.360605000

C	12.330697000	-2.799507000	6.880035000
H	13.260259000	-2.501119000	6.384883000
H	12.532871000	-3.688955000	7.486457000
H	12.040263000	-1.985176000	7.551833000
C	11.725854000	5.462120000	3.541535000
C	12.876680000	5.359126000	4.389060000
C	13.404148000	6.521627000	4.959191000
C	12.869161000	7.794163000	4.717504000
C	11.759519000	7.878012000	3.873741000
C	11.170592000	6.747947000	3.303327000
C	13.502267000	4.005010000	4.672963000
H	13.645595000	3.508579000	3.706155000
C	12.584211000	3.091417000	5.498977000
H	11.602074000	3.034441000	5.026326000
H	12.450504000	3.538059000	6.493189000
C	13.153706000	1.682878000	5.639258000
H	12.479157000	1.059930000	6.236960000
H	13.188597000	1.219303000	4.645331000
C	14.554896000	1.716895000	6.244301000
H	14.977078000	0.706209000	6.287500000
H	14.494504000	2.076239000	7.282646000
C	15.473550000	2.646550000	5.450388000
H	16.465812000	2.692630000	5.914772000
H	15.614730000	2.236678000	4.440797000
C	14.882525000	4.052956000	5.334425000
H	14.805336000	4.488284000	6.342479000
H	15.554879000	4.699791000	4.758104000
C	13.446231000	9.034407000	5.355128000
H	12.896354000	9.896636000	4.949794000
C	14.930875000	9.243596000	5.025528000
H	15.505925000	8.383968000	5.395881000
H	15.063728000	9.262116000	3.938042000
C	15.471588000	10.524422000	5.660505000
H	14.957414000	11.390036000	5.218997000
H	16.536198000	10.641598000	5.427775000
C	10.000505000	6.872317000	2.361455000
C	9.148242000	8.129272000	2.546185000
C	7.939707000	8.116263000	1.611677000
C	8.382156000	7.995787000	0.153662000
C	9.284337000	6.780796000	-0.059240000
C	10.469378000	6.771490000	0.901560000
C	8.203931000	1.171399000	6.268071000
C	7.063136000	0.353274000	6.020705000
C	6.070158000	0.241004000	6.998043000
C	6.146613000	0.916658000	8.224588000
C	7.291817000	1.679732000	8.468959000
C	8.326307000	1.795243000	7.535026000
C	6.906277000	-0.365570000	4.701006000
H	7.744757000	-0.064273000	4.065756000
C	6.971214000	-1.892947000	4.850389000
H	6.127227000	-2.231513000	5.469289000
H	7.889978000	-2.167521000	5.375502000
C	6.917224000	-2.575083000	3.484716000
H	7.816601000	-2.295862000	2.918893000
H	6.946585000	-3.664551000	3.602938000
C	5.671345000	-2.160206000	2.701184000
C	5.575497000	-0.639210000	2.579650000
H	6.419770000	-0.271591000	1.979701000
H	4.661926000	-0.354557000	2.043415000
C	5.624421000	0.022962000	3.955037000
H	4.743206000	-0.279357000	4.537581000
H	5.570010000	1.112108000	3.844306000
C	5.065488000	0.784482000	9.272855000
C	5.162031000	-0.560740000	10.013298000
C	4.090799000	-0.691644000	11.095122000
H	4.167743000	-1.668821000	11.585721000
H	4.271059000	0.063983000	11.873122000
C	2.688136000	-0.492023000	10.520544000
C	2.581239000	0.845333000	9.788171000

H	2.703542000	1.665118000	10.510165000
H	1.584690000	0.963899000	9.346474000
C	3.651466000	0.965913000	8.706330000
C	9.612463000	2.501117000	7.894187000
H	10.234054000	2.484575000	6.991037000
C	10.372467000	1.732620000	8.987034000
H	9.741875000	1.666580000	9.885382000
H	10.545550000	0.705737000	8.647064000
C	11.695996000	2.409780000	9.339685000
H	12.361967000	2.368859000	8.468356000
H	12.200070000	1.861286000	10.143667000
C	11.487403000	3.868742000	9.746417000
H	10.907271000	3.909151000	10.679311000
H	12.449282000	4.352019000	9.953583000
C	10.734872000	4.636390000	8.662008000
H	11.378927000	4.676648000	7.770638000
H	10.546930000	5.665254000	8.991580000
C	9.413315000	3.959238000	8.312020000
H	8.881987000	4.498619000	7.518545000
H	8.761117000	4.005332000	9.193367000
C	1.469175000	9.085051000	4.718752000
H	2.364204000	9.668107000	4.468308000
H	0.615472000	9.611414000	4.275421000
C	1.608080000	7.694423000	4.102540000
H	0.691696000	7.109692000	4.273615000
H	1.747816000	7.772462000	3.022518000
C	13.237768000	9.044700000	6.877083000
H	12.168823000	8.943337000	7.101623000
H	13.736902000	8.169238000	7.316257000
C	13.779077000	10.321274000	7.518032000
H	13.641169000	10.290418000	8.605223000
H	13.196559000	11.178455000	7.150705000
C	15.253510000	10.530816000	7.173797000
H	15.845578000	9.722893000	7.626928000
H	15.616574000	11.468546000	7.609686000
C	11.046699000	7.194397000	12.752209000
H	10.972969000	8.131912000	13.321141000
H	10.836124000	6.383403000	13.458833000
C	1.305401000	-0.766894000	4.864979000
H	0.632532000	-1.583917000	5.149328000
H	2.323847000	-1.182067000	4.869688000
C	0.976594000	-0.265914000	3.458611000
H	1.073061000	-1.080128000	2.731450000
H	-0.072325000	0.060791000	3.427427000
C	1.882797000	0.898707000	3.062161000
H	2.916906000	0.534313000	3.024376000
H	1.637412000	1.258575000	2.056347000
H	3.472995000	0.200054000	7.940942000
H	8.005442000	6.751173000	10.157591000
H	5.226661000	1.579623000	10.017183000
H	1.936050000	-0.554773000	11.315311000
H	6.164449000	-0.668234000	10.442765000
H	5.049220000	-1.370746000	9.279009000
H	2.468659000	-1.305662000	9.814373000
H	5.252818000	7.160338000	7.667979000
H	3.163305000	6.493742000	9.172022000
H	4.202711000	4.704865000	7.662575000
H	3.405112000	6.400876000	10.911471000
H	4.879660000	8.142802000	9.872781000
H	5.810071000	6.872640000	10.655005000
H	5.191116000	3.413419000	8.382683000
H	7.845289000	10.477360000	5.683154000
H	9.321266000	12.208292000	7.701177000
H	10.057883000	9.428952000	5.296944000
H	7.565915000	12.117356000	7.532749000
H	10.799813000	10.606523000	6.376175000
H	9.742634000	9.027335000	2.332020000
H	9.351110000	6.004637000	2.538945000
H	8.852196000	8.233739000	3.603709000

H	7.336953000	9.018328000	1.751137000
H	11.054860000	5.856065000	0.776389000
H	4.345278000	12.517891000	8.723383000
H	8.700091000	5.868340000	0.110144000
H	5.206605000	-0.387998000	6.790557000
H	11.137161000	7.618855000	0.690367000
H	11.358084000	8.860242000	3.643230000
H	8.928461000	8.906591000	-0.130574000
H	7.278886000	7.268933000	1.848918000
H	14.270616000	6.437955000	5.608333000
H	7.501673000	7.940903000	-0.496443000
H	7.387264000	2.179926000	9.432018000
H	3.249567000	13.295589000	7.590682000
H	9.633548000	6.738169000	-1.097535000
H	10.170668000	10.092473000	8.574238000
H	6.321402000	5.115810000	1.803719000
H	7.015169000	5.040293000	-0.661511000
H	4.757809000	3.125391000	0.106047000
H	4.664719000	4.881035000	-0.022066000
H	6.222772000	3.905132000	-1.740842000
H	3.569499000	1.933662000	8.198705000
H	4.031685000	2.223601000	2.426425000
H	4.776615000	-2.532453000	3.221084000
H	5.670895000	-2.621393000	1.706771000
H	1.472535000	4.581972000	4.926048000

$[\{K(^{TCHP}NON)Ca\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)]$

Ca	6.848269000	6.918099000	4.639131000
Ca	9.073809000	3.656994000	4.169050000
K	5.579836000	3.310352000	5.911636000
K	10.304891000	6.608644000	6.744899000
O	5.796596000	8.973679000	3.766384000
O	10.249803000	1.864734000	2.916359000
O	7.426204000	4.815800000	5.319793000
O	8.647856000	5.650330000	5.128399000
N	5.208114000	6.451470000	3.011612000
N	6.546887000	8.574650000	6.312857000
N	9.086683000	1.591384000	5.321292000
N	11.021426000	4.425124000	3.064845000
C	5.445362000	9.961091000	4.685761000
C	5.825442000	9.712064000	6.019754000
C	5.407940000	10.677453000	6.959066000
H	5.650930000	10.512487000	8.005790000
C	4.688452000	11.812496000	6.581892000
C	4.392828000	12.031549000	5.232333000
H	3.849564000	12.925209000	4.945069000
C	4.786898000	11.105295000	4.260174000
C	4.627417000	11.300615000	2.753673000
C	4.290876000	9.940259000	2.150251000
C	3.371289000	9.733168000	1.115325000
H	2.853282000	10.574991000	0.668827000
C	3.094490000	8.441761000	0.657436000
C	3.722415000	7.346986000	1.253253000
H	3.462105000	6.338605000	0.940522000
C	4.638627000	7.499587000	2.311593000
C	4.919604000	8.827816000	2.689141000
C	5.991355000	11.769801000	2.198016000
H	6.258641000	12.741714000	2.625785000
H	5.949504000	11.860234000	1.107611000
H	6.779993000	11.057934000	2.455485000
C	3.568248000	12.349183000	2.420617000
H	2.584228000	12.056099000	2.797368000
H	3.498779000	12.494458000	1.339301000
H	3.835870000	13.315698000	2.855986000
C	4.270389000	12.830621000	7.614775000
C	5.161407000	14.076226000	7.609329000
H	6.197753000	13.814931000	7.843314000
H	4.821620000	14.812879000	8.345113000
H	5.157214000	14.551696000	6.623471000

C	2.045611000	8.217063000	-0.402948000
H	2.361463000	7.406131000	-1.070518000
H	1.950315000	9.115474000	-1.023994000
C	0.685146000	7.869502000	0.209908000
H	0.757471000	6.962555000	0.818807000
H	-0.073579000	7.704365000	-0.562623000
H	0.340393000	8.677199000	0.863574000
C	4.336800000	5.373331000	3.231474000
C	3.269826000	5.502840000	4.172184000
C	2.448930000	4.401556000	4.424070000
C	2.620730000	3.170202000	3.774790000
C	3.650157000	3.069458000	2.833596000
C	4.503373000	4.144207000	2.550153000
C	3.020109000	6.825501000	4.861301000
H	3.926161000	7.429464000	4.736266000
C	1.552327000	8.935601000	6.333201000
H	0.576703000	8.480535000	6.560346000
H	1.539912000	9.945697000	6.758371000
C	2.656991000	8.110326000	6.993686000
H	3.614511000	8.631661000	6.877523000
H	2.470900000	8.031137000	8.071145000
C	2.770411000	6.719595000	6.369256000
H	3.588349000	6.161725000	6.841223000
H	1.849758000	6.151433000	6.564209000
C	1.714919000	2.011471000	4.136443000
H	0.686978000	2.402688000	4.190189000
C	1.124758000	0.333563000	5.955904000
H	1.412428000	-0.050692000	6.941217000
H	0.106347000	0.732810000	6.062547000
C	2.059544000	1.465987000	5.534379000
H	2.030026000	2.280137000	6.268544000
H	3.095164000	1.096068000	5.510816000
C	5.590026000	4.047769000	1.505412000
C	5.290645000	3.084154000	0.356152000
C	6.405159000	3.107192000	-0.690238000
C	7.761704000	2.794633000	-0.059725000
H	8.560133000	2.843404000	-0.807792000
H	7.756924000	1.765074000	0.324094000
C	8.065287000	3.751685000	1.088484000
H	8.128194000	4.775475000	0.703762000
H	9.055133000	3.529879000	1.501296000
C	6.952734000	3.715652000	2.135174000
H	7.099775000	4.456250000	2.933457000
H	6.894383000	2.715664000	2.600488000
C	7.393115000	8.633723000	7.425923000
C	8.506421000	9.533146000	7.460366000
C	9.415461000	9.467163000	8.517285000
C	9.299841000	8.530225000	9.559049000
C	8.191081000	7.681924000	9.527780000
C	7.224526000	7.741262000	8.511534000
C	8.709944000	10.544055000	6.357302000
C	8.493943000	11.984369000	6.841851000
C	8.518567000	12.951329000	5.661568000
H	8.364763000	13.980922000	6.005207000
H	7.674393000	12.710214000	5.001387000
C	9.833005000	12.840822000	4.886578000
H	9.819178000	13.496968000	4.008393000
H	10.656409000	13.189900000	5.526374000
C	10.113788000	11.398269000	4.461199000
H	11.085907000	11.333579000	3.956348000
H	9.356483000	11.084932000	3.729619000
C	10.065856000	10.442853000	5.653177000
C	10.354273000	8.486441000	10.650171000
H	10.426288000	9.500722000	11.074635000
C	10.028026000	7.537544000	11.805850000
H	9.934995000	6.512193000	11.419301000
H	9.056171000	7.797980000	12.240738000
C	12.485512000	7.224277000	12.297592000
H	12.475334000	6.188757000	11.928635000

H	13.255673000	7.272284000	13.075777000
C	12.832457000	8.163341000	11.143823000
H	12.943322000	9.186464000	11.529894000
H	13.796847000	7.890013000	10.699634000
C	11.742043000	8.150996000	10.075045000
H	11.700034000	7.150347000	9.620136000
H	11.990632000	8.851434000	9.273121000
C	5.979631000	6.887596000	8.621476000
C	5.182755000	7.237970000	9.889809000
C	3.979700000	6.319669000	10.108517000
C	4.390965000	4.848583000	10.116469000
H	3.516713000	4.202604000	10.258820000
H	5.068121000	4.657886000	10.961282000
C	5.107910000	4.494743000	8.817154000
C	6.319430000	5.394938000	8.589143000
H	7.046251000	5.181993000	9.381833000
H	6.825013000	5.164725000	7.642761000
C	11.316970000	2.252584000	2.097029000
C	11.699708000	3.608261000	2.199599000
C	12.807224000	3.985605000	1.408795000
H	13.150090000	5.016101000	1.459861000
C	13.505275000	3.063246000	0.628809000
C	13.119164000	1.719652000	0.621099000
H	13.689042000	1.005087000	0.037213000
C	12.016404000	1.298817000	1.374620000
C	11.545712000	-0.146947000	1.496010000
C	11.154113000	-0.364912000	2.956051000
C	11.393425000	-1.535074000	3.689180000
H	11.968931000	-2.345308000	3.254580000
C	10.893917000	-1.668222000	4.986653000
C	10.118985000	-0.647277000	5.543011000
H	9.716095000	-0.762503000	6.546514000
C	9.852175000	0.547456000	4.848543000
C	10.439061000	0.650269000	3.571466000
C	12.608200000	-1.139444000	1.030575000
H	12.844565000	-0.979779000	-0.024957000
H	12.240336000	-2.164770000	1.126150000
H	13.529638000	-1.042851000	1.611857000
C	10.276767000	-0.330132000	0.633292000
H	9.492600000	0.361166000	0.950813000
H	9.896497000	-1.352598000	0.730415000
H	10.501769000	-0.133110000	-0.420023000
C	14.646155000	3.534500000	-0.237580000
H	15.235616000	4.284160000	0.304888000
H	15.320118000	2.695543000	-0.447714000
C	14.152647000	4.136665000	-1.556727000
H	13.574235000	3.399625000	-2.123127000
H	14.986936000	4.472951000	-2.181783000
H	13.499098000	4.994276000	-1.367410000
C	11.230737000	-2.879461000	5.819425000
H	11.523625000	-3.708020000	5.164173000
H	10.340677000	-3.212650000	6.368274000
C	12.359144000	-2.588858000	6.814090000
H	13.264961000	-2.275446000	6.285376000
H	12.600213000	-3.469502000	7.419156000
H	12.075757000	-1.775723000	7.490350000
C	11.692245000	5.555094000	3.540688000
C	12.819628000	5.422887000	4.407779000
C	13.399841000	6.571763000	4.952923000
C	12.923234000	7.859308000	4.662952000
C	11.843479000	7.971751000	3.782582000
C	11.216149000	6.851501000	3.226484000
C	13.347528000	4.041495000	4.735714000
H	13.319907000	3.459648000	3.808895000
C	12.459426000	3.295988000	5.741711000
H	11.414251000	3.335205000	5.421476000
H	12.527100000	3.806042000	6.714828000
C	12.896576000	1.841835000	5.893696000
H	12.247370000	1.314538000	6.600576000

H	12.764470000	1.332692000	4.931095000
C	14.359036000	1.759910000	6.325793000
H	14.680225000	0.713400000	6.380895000
H	14.462456000	2.173761000	7.340569000
C	15.262722000	2.545172000	5.372948000
H	16.302234000	2.514349000	5.720416000
H	15.244118000	2.065967000	4.384422000
C	14.797831000	3.995371000	5.223920000
H	14.887364000	4.499523000	6.197957000
H	15.446085000	4.536142000	4.524418000
C	13.522772000	9.084560000	5.310554000
H	12.998241000	9.961993000	4.904535000
C	15.016987000	9.261513000	5.005324000
H	15.565371000	8.384818000	5.376238000
H	15.167295000	9.286774000	3.920276000
C	15.576662000	10.524356000	5.659968000
H	15.090304000	11.404862000	5.216459000
H	16.647524000	10.618636000	5.446123000
C	10.088949000	6.998591000	2.235496000
C	9.159921000	8.185237000	2.492379000
C	8.007333000	8.197942000	1.491873000
C	8.547279000	8.304113000	0.066293000
C	9.535883000	7.181478000	-0.246872000
C	10.643101000	7.076738000	0.800941000
C	8.147276000	1.250876000	6.299445000
C	6.987642000	0.495776000	5.953627000
C	5.998635000	0.273362000	6.913606000
C	6.105974000	0.760470000	8.225035000
C	7.273340000	1.449749000	8.562127000
C	8.300867000	1.680425000	7.638707000
C	6.850615000	-0.082151000	4.565804000
H	7.657037000	0.348022000	3.962936000
C	7.045831000	-1.607058000	4.566804000
H	6.222385000	-2.072058000	5.129130000
H	7.976235000	-1.853763000	5.083067000
C	7.073360000	-2.147599000	3.139930000
H	7.946767000	-1.724582000	2.625333000
H	7.209215000	-3.235269000	3.147223000
C	5.798486000	-1.775573000	2.383840000
C	5.551740000	-0.267898000	2.422245000
H	6.350751000	0.242638000	1.866906000
H	4.611775000	-0.024300000	1.912449000
C	5.538306000	0.262165000	3.855990000
H	4.686466000	-0.172915000	4.396675000
H	5.373189000	1.346670000	3.839200000
C	5.008338000	0.531043000	9.238010000
C	4.916102000	-0.945792000	9.656883000
C	3.807112000	-1.176698000	10.682782000
H	3.750394000	-2.239977000	10.942703000
H	4.056326000	-0.640916000	11.609801000
C	2.456475000	-0.680900000	10.165649000
C	2.532288000	0.789631000	9.756298000
H	2.727517000	1.405755000	10.645377000
H	1.571795000	1.125084000	9.347495000
C	3.642038000	1.017057000	8.733170000
C	9.585008000	2.349530000	8.067660000
H	10.230342000	2.369975000	7.182306000
C	10.304210000	1.548661000	9.163405000
H	9.632862000	1.422143000	10.024250000
H	10.524275000	0.543475000	8.787238000
C	11.585759000	2.240627000	9.627152000
H	12.299374000	2.278478000	8.793515000
H	12.063481000	1.656449000	10.421895000
C	11.303353000	3.663056000	10.110570000
H	10.648307000	3.628121000	10.992367000
H	12.230728000	4.155963000	10.424566000
C	10.619370000	4.474556000	9.013636000
H	11.334850000	4.572021000	8.183489000
H	10.383136000	5.481774000	9.380537000

C	9.346393000	3.792588000	8.520145000
H	8.875233000	4.346299000	7.698558000
H	8.616215000	3.795455000	9.338575000
C	1.740491000	9.001944000	4.818865000
H	2.650040000	9.571363000	4.595413000
H	0.908324000	9.542232000	4.351805000
C	1.870812000	7.610824000	4.204669000
H	0.936897000	7.045642000	4.343052000
H	2.046280000	7.687965000	3.129544000
C	13.293004000	9.087191000	6.830085000
H	12.218571000	9.001521000	7.033492000
H	13.772192000	8.199846000	7.267967000
C	13.849762000	10.347025000	7.489656000
H	13.693812000	10.311092000	8.574543000
H	13.291860000	11.219298000	7.119999000
C	15.333994000	10.525766000	7.169712000
H	15.900479000	9.701681000	7.626544000
H	15.711352000	11.452176000	7.617608000
C	11.113700000	7.560596000	12.881648000
H	11.150313000	8.560559000	13.336208000
H	10.858940000	6.860891000	13.685797000
C	1.118918000	-0.792194000	4.923017000
H	0.418450000	-1.580755000	5.220789000
H	2.116569000	-1.254049000	4.888315000
C	0.767838000	-0.257867000	3.534622000
H	0.799847000	-1.066164000	2.795235000
H	-0.264158000	0.119987000	3.542552000
C	1.716929000	0.865970000	3.121786000
H	2.731262000	0.453170000	3.048911000
H	1.458263000	1.246797000	2.127058000
H	3.395485000	0.475834000	7.812176000
H	8.043700000	6.970064000	10.334966000
H	5.257832000	1.114409000	10.137371000
H	1.678199000	-0.828034000	10.923093000
H	5.884848000	-1.274558000	10.049664000
H	4.720489000	-1.553453000	8.762265000
H	2.163005000	-1.281407000	9.292424000
H	5.359783000	7.126094000	7.749549000
H	3.247563000	6.475825000	9.306700000
H	4.382752000	4.616833000	7.996546000
H	3.476515000	6.581847000	11.046440000
H	4.861451000	8.283893000	9.832230000
H	5.846006000	7.163997000	10.762637000
H	5.426913000	3.445564000	8.829989000
H	7.954235000	10.347555000	5.592549000
H	9.283634000	12.246864000	7.561349000
H	10.244047000	9.415310000	5.314795000
H	7.539230000	12.048952000	7.368270000
H	10.875241000	10.690850000	6.353020000
H	9.712654000	9.128911000	2.397786000
H	9.493685000	6.079410000	2.296281000
H	8.812315000	8.175681000	3.537788000
H	7.326335000	9.026592000	1.697905000
H	11.263510000	6.195634000	0.609714000
H	4.289441000	12.370615000	8.609513000
H	8.993219000	6.229126000	-0.289412000
H	5.121259000	-0.305536000	6.632465000
H	11.302846000	7.954175000	0.735858000
H	11.492743000	8.965030000	3.516096000
H	9.052367000	9.274417000	-0.046437000
H	7.410692000	7.278889000	1.592066000
H	14.252997000	6.465067000	5.617822000
H	7.718248000	8.296510000	-0.650184000
H	7.388549000	1.805989000	9.584886000
H	3.231244000	13.130657000	7.430022000
H	9.976154000	7.326181000	-1.240646000
H	10.250270000	10.166994000	8.528325000
H	5.699554000	5.059002000	1.090358000
H	6.444987000	4.102320000	-1.154665000

H	5.195859000	2.060847000	0.741082000
H	4.326325000	3.341254000	-0.097335000
H	6.184171000	2.393500000	-1.492264000
H	3.696214000	2.078551000	8.465064000
H	3.777403000	2.144281000	2.283148000
H	4.942649000	-2.288933000	2.845457000
H	5.849322000	-2.122388000	1.345197000
H	1.632933000	4.504373000	5.137968000

4. References

1. R. P. J. Bronger, J. P. Bermon, J. Herwig, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Adv. Synth. Catal.*, 2004, **346**, 789.
2. R. Savka, H. Plenio, *Eur. J. Inorg. Chem.*, 2014, **2014**, 6246.
3. S. Krieck, P. Schüler, J. M. Peschel, M. Westerhausen, *Synthesis*, 2019, **51**, 1115.
4. M. S. Hill, M. D. Anker, A. S. S. Wilson, *Inorg. Synth.*, 2018, **37**, 24.
5. J. Hicks, M. Juckel, A. Paparo, D. Dange, C. Jones, *Organometallics*, 2018, **37**, 4810.
6. J. Choi, B. H. R. Suryanto, D. Wang, H.-L. Du, R. Y. Hodgetts, F. M. Ferrero Vallana, D. R. MacFarlane, A. N. Simonov, *Nat. Commun.*, 2020, **11**, 5546.
7. M. E. Fieser, D. H. Woen, J. F. Corbey, T. J. Mueller, J. W. Ziller, W. J. Evans, *Dalton Trans.*, 2016, **45**, 14634.
8. G. M. Sheldrick, *SHELX-16*, University of Göttingen, 2016.
9. A. D. Becke, *J. Chem. Phys*., 1993, **98**, 5648.
10. P. Fuentealba, L. von Szentpaly, H. Preuss, H. Stoll, *J. Phys. B: Atom. Mol. Phys*., 1985, **18**, 1287.
11. (a) J.-P. Blaudeau, M. P. McGrath, L. A. Curtiss, L. Radom, *J. Chem. Phys*., 1997, **107**, 5016; (b) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, D. J. DeFrees, J. A. Pople, M. S. Gordon, *J. Chem. Phys*., 1982, **77**, 3654.
12. S. Grimme, S. Ehrlich, L. Goerigk, *J. Comp. Chem.*, 2011, **32**, 1456.
13. Gaussian 09, Revision D.01: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheesman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A., Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, M. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S.

Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian Inc., 2009, Wallingford CT.

14. T. Lu, F. Chen, *J. Comput. Chem*., 2012, **33**, 580.
15. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, and F. Weinhold (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2013); http://nbo6.chem.wisc.edu/