Electronic Supporting Information

Bicyclic (alkyl)(amino)carbene stabilized zinc(0) complex with singlet biradicaloid ground state

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Table of Contents **page**

Experimental Section

General methods and instrumentation. Manipulations involving air/moisture sensitive compounds were carried out under an argon atmosphere using a Schlenk line and a glovebox. Toluene and hexane (from Na/benzophenone ketyl) were distilled fresh whenever required. Benzene-d_6 and THF-d_8 were condensed from Na/benzophenone ketyl, and $CDCl_3$ and CD_2Cl_2 were condensed from CaH_2 and stored in a glovebox. All other chemicals were purchased from Sigma-Aldrich and used as received. Elemental analyses were performed using a Perkin-Elmer 2400, Series II, CHNS/O analyser. NMR spectra were recorded on a JEOL ECS 400 MHz spectrometer and on a Bruker Avance III 500 MHz spectrometer. EPR measurements were performed on a Bruker (X-band) spectrometer. All chemical shifts were reported in ppm using tetramethylsilane as a reference.

Single-Crystal X-ray Experiments. X-ray diffraction data for complexes **1**, **2** and **3** were collected on a SuperNova, Dual, Mo at zero, Eos diffractometer. The data for complex **1** were collected at 293 K while for compounds **2** and **3** data were collected at 100 K. Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined using Olex2,[S1] and the structure was solved with the ShelXT[S2] structure solution program using Intrinsic Phasing and refined with the ShelXL[S3] refinement package using Least Squares minimization. Carbon and hydrogen atoms in bicyclo[2.2.2]octane framework (BICAAC ring) of compound **1** and **2** were disordered which were modelled using the occupancy factors with AFIX instructions. The crystal data and results of the analyses are listed in Table S1. CCDC 2033102 and 2033103, contain the supplementary crystallographic data for **1**, **2,** respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details. All geometry optimization are performed under the framework of Density functional theory. To confirm the comparison in energy among different electronic states three different functional M06-2X,[S4,S5] PBE0[S6] and B3LYP-D3[S7-S13] are used along with def2-SVP[S14] basis set for all atoms. The stationary points are characterized by vibrational analysis to recognize the structures as minima with all positive frequencies. The energies are further refined

with the larger basis set def2-TZVPP[S15] using geometries obtained from SVP basis set. All calculations are carried out with Gaussian 16 suite of program.[S16]

Synthesis of [(BICAAC)(μ-Cl)ZnCl]$_2$ (1). Toluene (20 mL) was cooled to −78 °C and added to a 1:1 mixture of BICAAC (0.516 g, 1.66 mmol) and $ZnCl_2$ (0.225 g, 1.65). The reaction mixture was slowly warmed to room temperature and stirred for 12 h. The color of the reaction mixture changed to yellow from colorless, which was then filtered over a frit using celite and then solvent was reduced to 10 mL to afford colorless block shaped crystals suitable for single-crystal X-ray analysis of **1** at 25 °C. Yield: 0.545 g, 71%. Mp: 185-186 °C dec. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.27 (1H, t, ArH), 7.19-7.11 (2H, m, ArH), 2.77-2.70 (1H, m, C*H*Me$_2$), 2.52-2.45 (1H, m, C*H*Me$_2$), 1.87-1.84 (4H, m), 1.74-1.59 (4H, m), 1.51-1.47 (1H, m), 1.25 (6H, q, CH*Me*Me), 1.16 (6H, q, CHMe*Me*), 0.99 (3H, d, C*H*$_3$), 0.96 (3H, s, C*H*$_3$). ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 144.1, 143.9, 139.5, 129.8, 129.1, 128.3, 125.3, 125.1, 65.1, 49.9, 44.0, 37.5, 32.9, 31.4, 28.9, 28.2, 25.8, 25.7, 25.0, 24.4, 24.0, 23.4, 21.5, 20.7. Elemental analysis, found (calcd) for $C_{44}H_{66}Cl_4N_2Zn_2$: C, 58.85 (59.01); H, 7.16 (7.43); N, 2.95 (3.13).

Synthesis of [(BICAAC)$_2$Zn] (2). Toluene (20 mL) was cooled to −78 °C and added to a 1:3 mixture of [(BICAAC)(μ-Cl)ZnCl]$_2$ (0.500 g, 1.66 mmol) and KC_8 (0.440 g, 3.26 mmol). The reaction mixture was slowly warmed to room temperature and stirred for 3 h resulting in a deep blue solution. The reaction mixture was filtered over a frit using celite and filtrate was dried under vacuum for several hours to obtain a black colored solid. The crude material was recrystallized from hexane at 25 °C to obtain red colored crystals. Yield: 0.14 g, 52%. UV/vis λ_{ab} = 636 nm. ^{1}H NMR (C_6D_6, 400 MHz, ppm): δ 7.21 (1H, s, ArH), 7.10-7.08 (2H, d, ArH), 3.53-3.51 (1H, m, C*H*Me$_2$), 3.35-3.32 (1H, m, C*H*Me$_2$), 1.96 (1H, br), 1.78-1.74 (4H, m), 1.64-1.60 (6H, m), 1.51 (1H, br), 1.30-1.25 (6H, m), 1.18-1.16 (3H, m), 0.8 (1H, br), 0.67 (3H, d, C*H*$_3$), 0.21 (3H, s, C*H*$_3$). ^{13}C NMR (C_6D_6, 125 MHz, ppm): δ 149.9, 149.5, 143.8, 126.0, 125.7, 125.4, 55.7, 46.6, 43.5, 38.9, 37.4, 35.5, 28.7, 28.4, 28.1, 28.0, 25.3, 24.5, 24.4, 22.9, 19.8. Elemental analysis, found (calcd) for $C_{44}H_{66}N_2Zn$: C, 76.15 (76.77); H, 10.09 (9.66); N, 4.31 (4.07).

Synthesis of [(BICAAC)CO$_2$] (3). To a Schlenk tube containing (BICAAC)$_2$Zn (**2**) (0.250 g, 1.52 mmol) in toluene (10 mL), purified CO_2 gas was condensed at −78 °C and the solution was warmed to room temperature and stirred for 1 h, whereupon a precipitate was obtained by slow

evaporation of CO_2, which was filtered using a frit, dried under vacuum. Single crystals for X-ray diffraction analysis were grown from a hexane-THF solution at -20 °C. Yield: 0.230 g, 91%. ^{1}H NMR (THF d_8 + $C_2D_2Cl_2$, 400 MHz, ppm): δ 7.37 (1H, t, ArH), 7.19-7.11 (2H, m, ArH), 2.77-2.75 (1H, m, C*H*Me$_2$), 2.56-2.53 (1H, m, C*H*Me$_2$), 2.26-2.22 (1H, m), 2.07-2.05 (1H, m), 1.93-1.89 (2H, m), 1.80-1.79 (1H, m), 1.55-1.52 (1H, m), 1.34 (3H, *s*, CH_3), 1.28-1.26 (6H, m, CH*Me*Me), 1.19-1.15 (6H, m, CH*Me*Me), 1.09 (3H, *d*, CH_3), 0.96 (3H, s, C*H*$_3$). NMR (THF d_8 + $C_2D_2Cl_2$, 100 MHz, ppm): δ 194.4, 159.7, 145.6, 145.3, 134.6, 130.6, 129.4, 129.2, 128.9, 128.4, 125.5, 64.9, 43.7, 43.4, 37.6, 34.6, 33.1, 30.1, 29.9, 29.6, 22.4, 19.3, 19.2. Elemental analysis, found (calcd) for $C_{23}H_{34}NO_2$: C, 77.18 (77.48); H, 9.35 (9.61); N, 4.05 (3.93).

Reaction of [(BICAAC)$_2$Zn] with Ph$_3$CCl. A 1:2 molar mixture of (BICAAC)$_2$Zn (0.05 g, 0.07 mmol) and Ph_3CCl (0.04 g, 0.14 mmol) was placed in a Schlenk flask and benzene (10 mL) was added at room temperature. The color of the solution immediately changed to the orange and resultant mixture was stirred for 1 h. It was filtered over a frit using celite and filtrate was dried under vacuum. Yield (filtrate): 0.03 g (crude), 88%. EPR measurement of the $Ph_3C^{\bullet}$ in toluene at 25 °C shows a sharp resonance at 3315 G. NMR measurement of precipitate (**4**)**:** ^{1}H NMR (C_6D_6, 400 MHz, ppm): δ 9.41 (1H, s, imine-H) 7.53-7.50 (1H, m, ArH), 7.34-7.31 (2H, m, ArH), 2.68-2.65 (1H, m, C*H*Me$_2$), 2.60-2.55 (1H, m, C*H*Me$_2$), 2.37-2.34 (2H, m), 2.24-2.18 (2H, m), 1.95-1.90 (1H, m), 1.84-1.79 (1H, m), 1.70-1.66 (5H, m), 1.34(3H, d), 1.30-1.25 (6H, m), 1.21-1.20 (6H, m), 1.08 (3H, d). ^{13}C NMR (C_6D_6, 125 MHz, ppm): δ 194.4, 143.8, 143.2, 135.2, 131.7, 125.7, 125.3, 69.4, 45.5, 43.7, 38.6, 33.5, 33.2, 29.7, 29.1, 25.6, 25.5, 23.8, 22.8, 22.0, 20.8, 19.7. HRMS (ESI-TOF) m/z: $[M - Cl]^+$ calcd for $C_{22}H_{34}ClN$ 312.2686, found 312.2646.

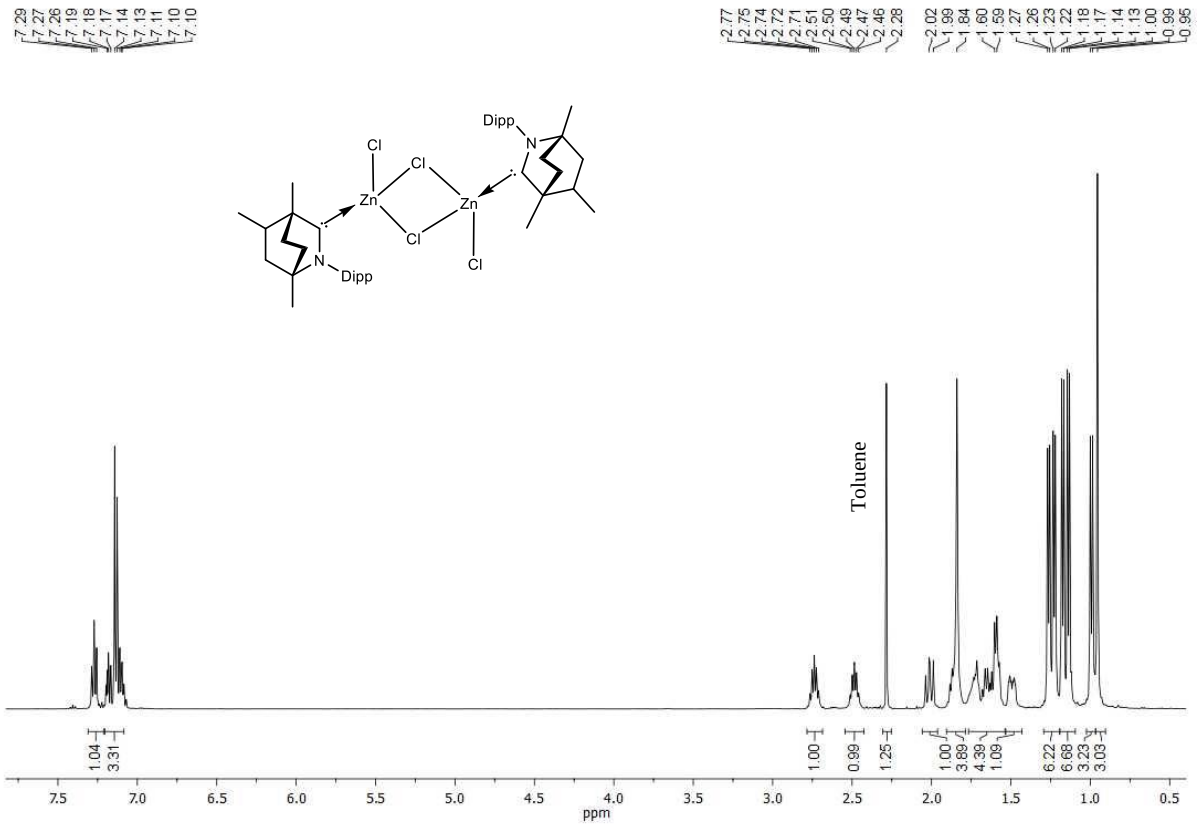

Fig. S1 ^{1}H NMR spectrum of compound **1** in $CDCl_3$

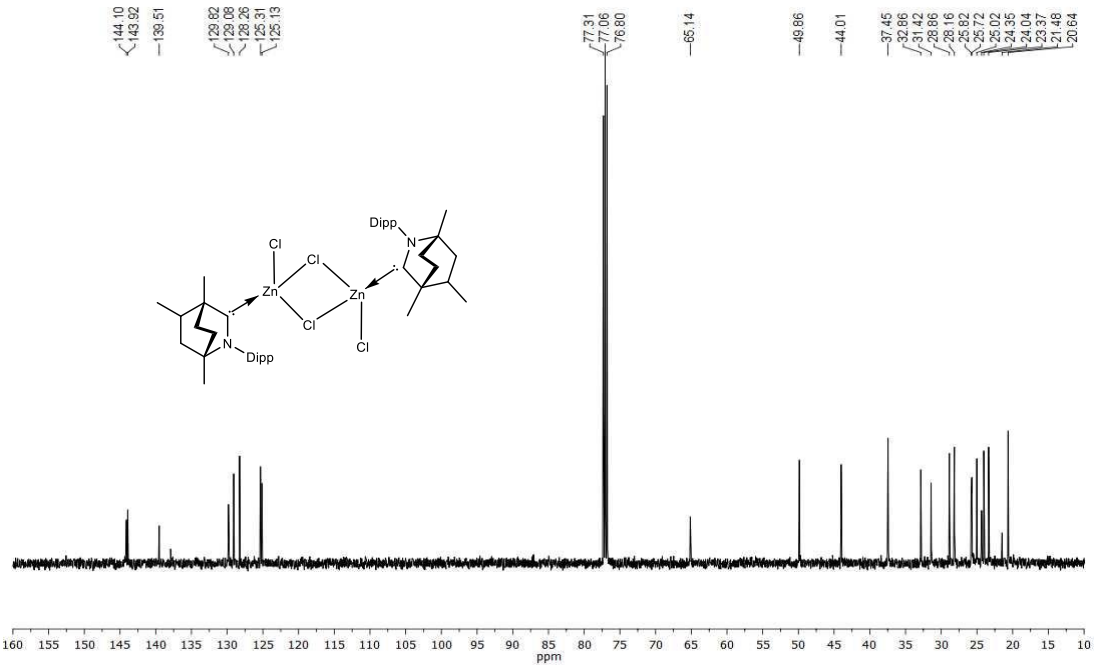

Fig. S2 ^{13}C NMR spectrum of compound **1** in $CDCl_3$

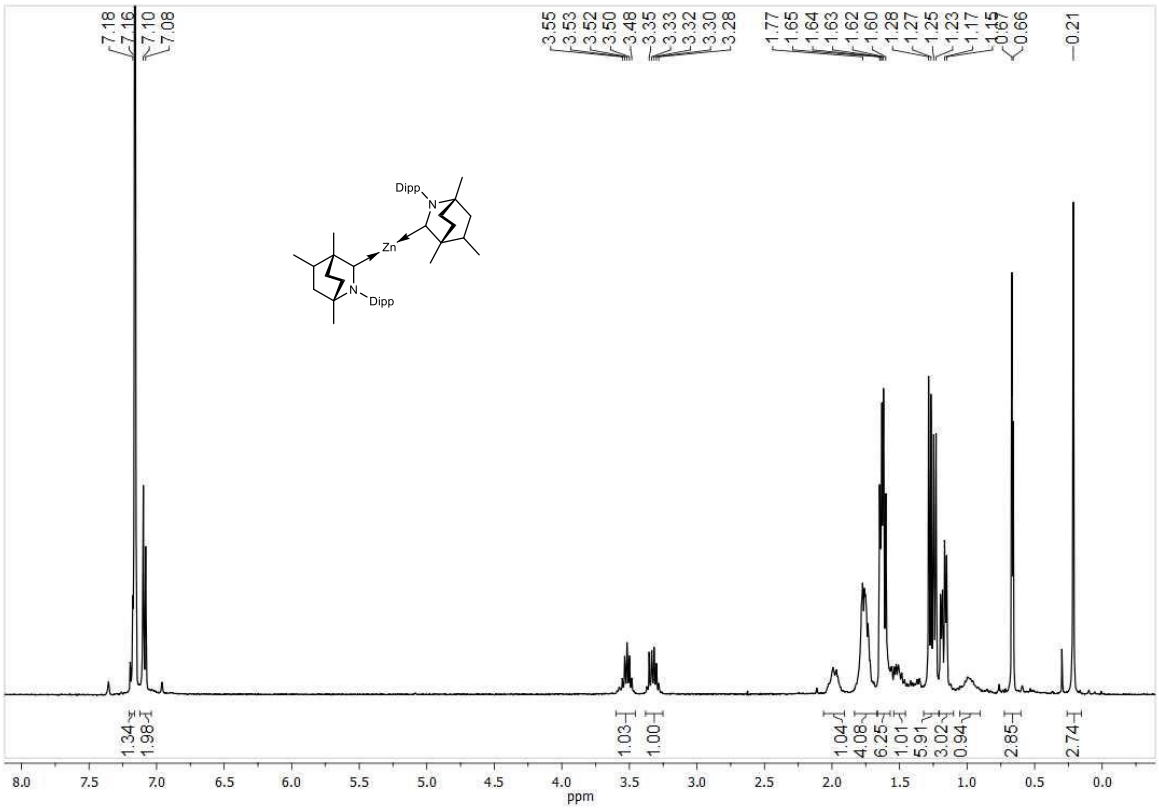

Fig. S3 ^{1}H NMR spectrum of compound **2** in C_6D_6

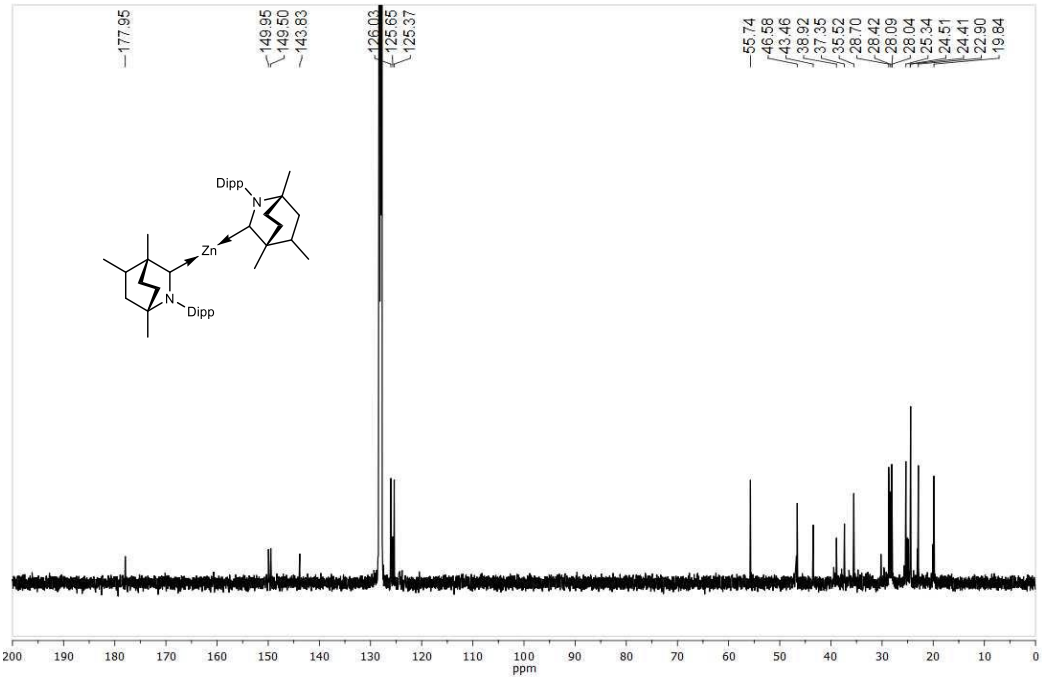

Fig. S4 ^{13}C NMR spectrum of compound **2** in C_6D_6

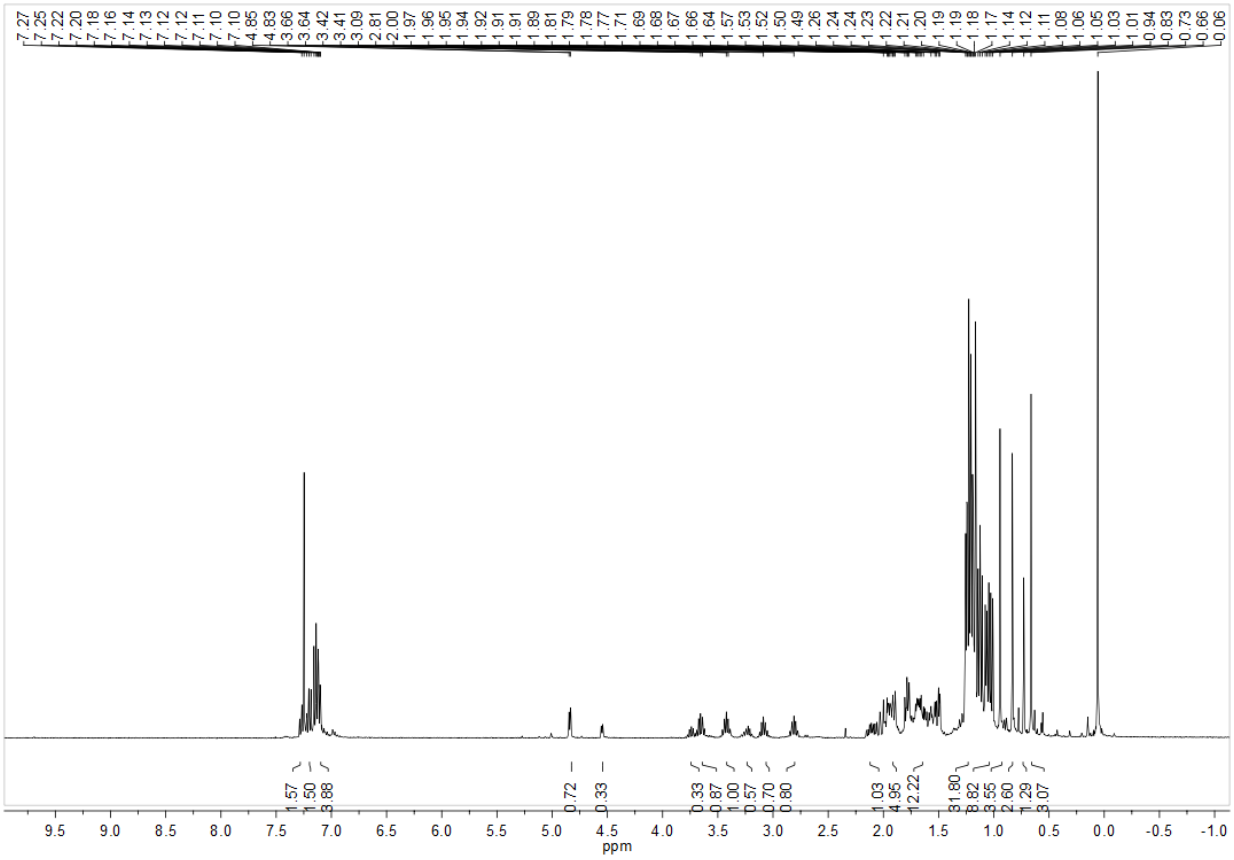

Fig. S5 ^{1}H NMR spectrum of compound **2** after exposed with oxygen in $CDCl_3$

Fig. S6 Photograph of $(BICAAC)_2Zn$ compound with degassed water.

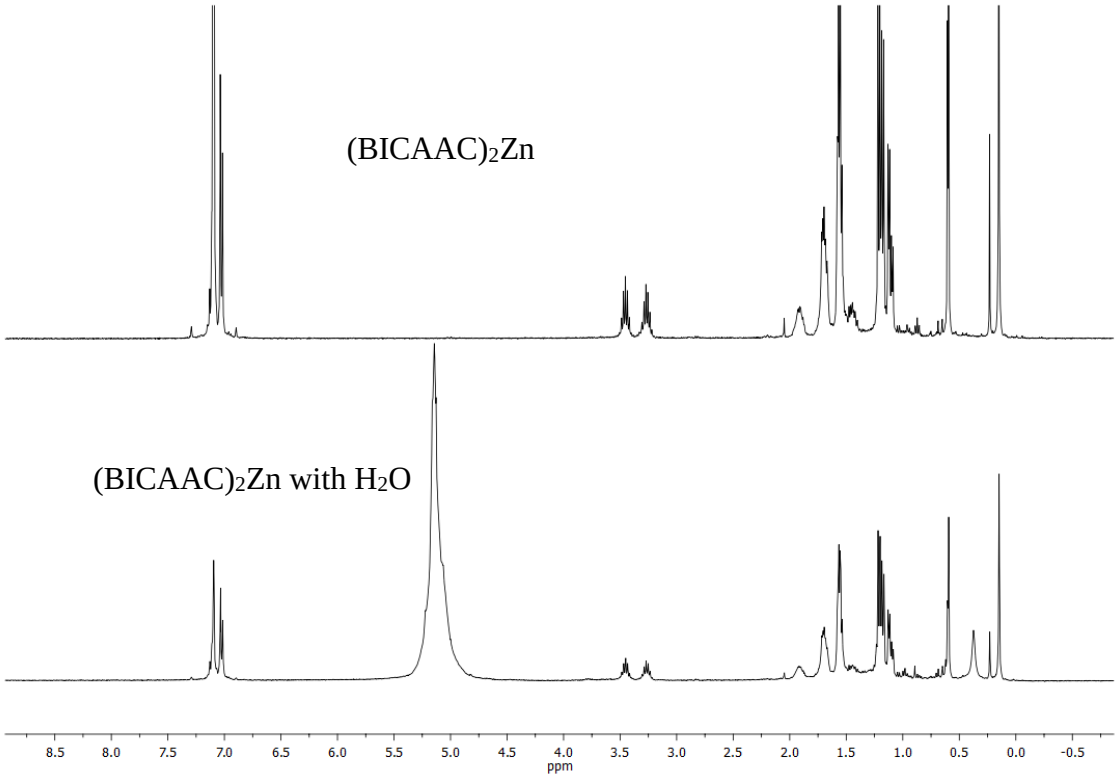

Fig. S7 NMR tube reaction of $(BICAAC)_2Zn$ compound with degassed water, recorded in C_6D_6. The top spectrum represents the ^1H NMR spectrum of **2** without H_2O treatment.

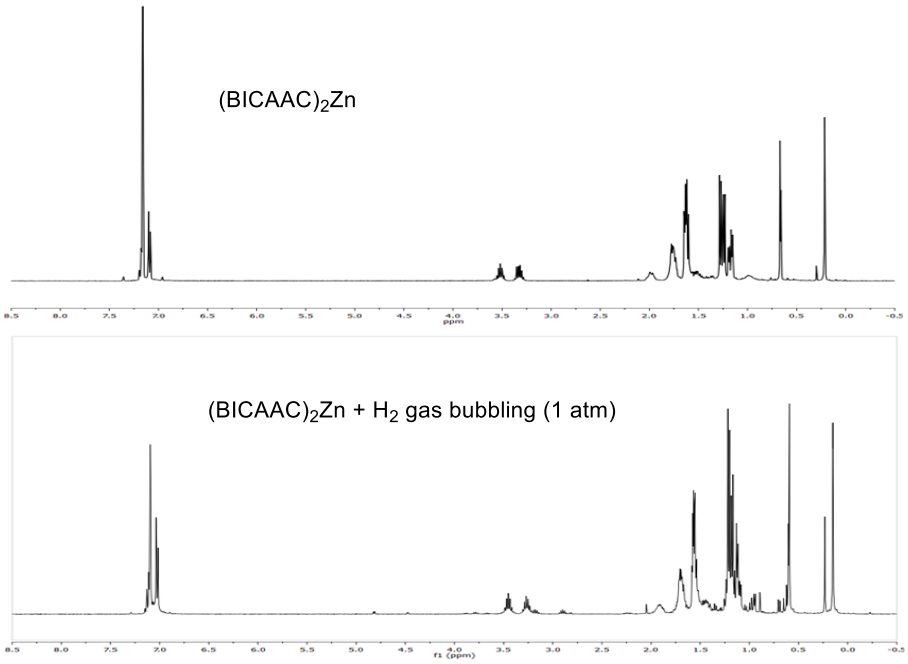

Fig. S8 ^{1}H NMR spectrum of compound **2** (without exposure to H_2 shown in the top part) and bottom spectrum shown after exposure with H_2 gas (bubbling), recorded in C_6D_6

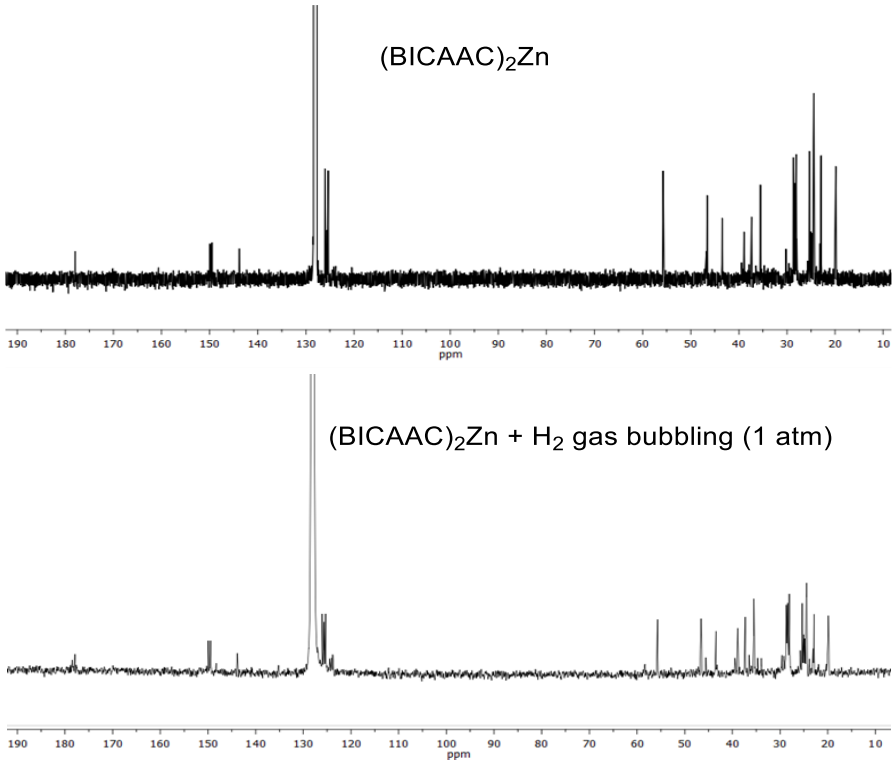

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Fig. S9 ^{13}C NMR spectrum of compound **2** (without exposure to H_2 shown in the top part) and bottom spectrum shown after exposure with H_2 gas (bubbling), recorded in C_6D_6.

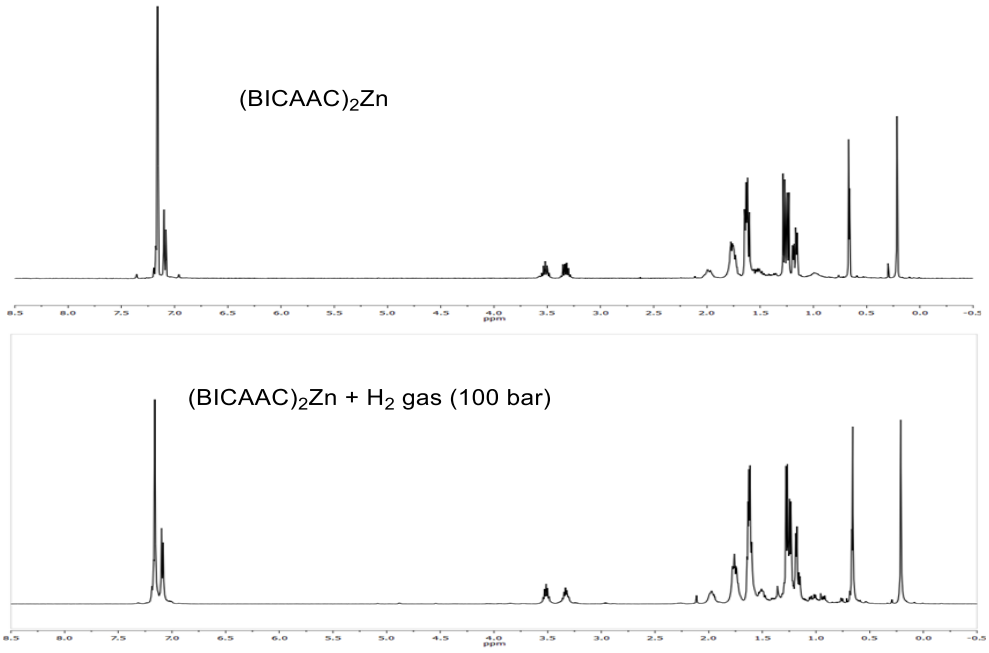

Fig. S10 ^{1}H NMR spectrum of reaction of compound **2** with H_2 gas (100 bar) in C_6D_6. The top part shows the ^{1}H NMR spectrum of **2** without exposure to H_2 gas.

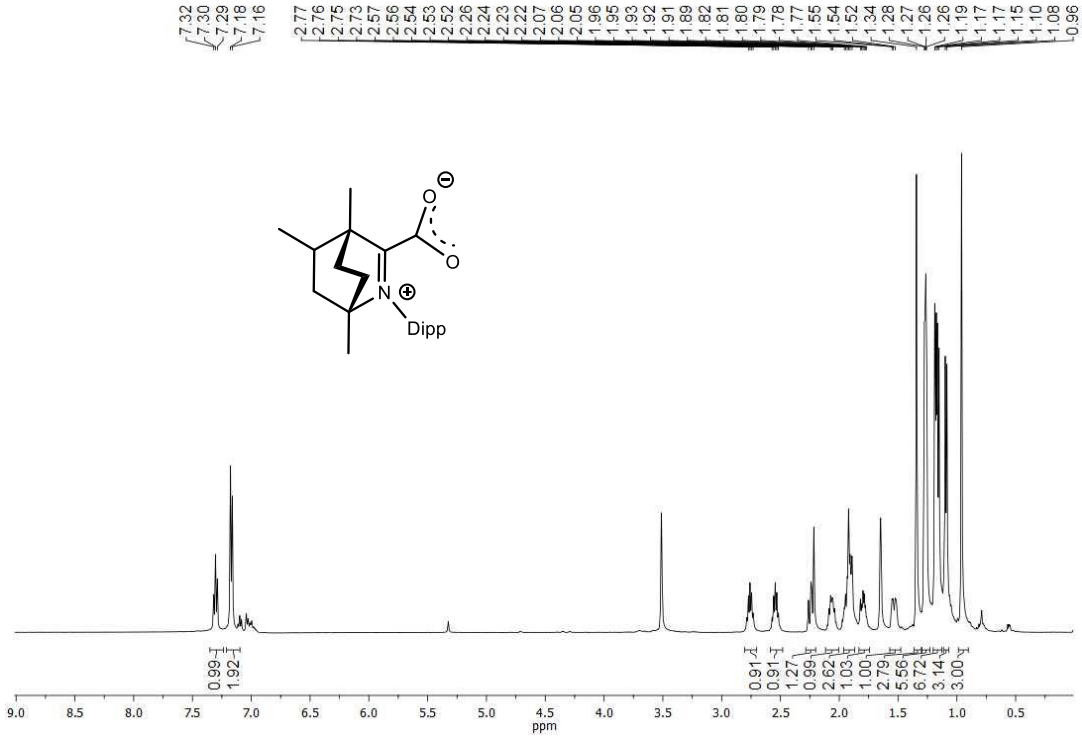

Fig. S11 ^{1}H NMR spectrum of compound **3** in CD_2Cl_2 + THF-d_8

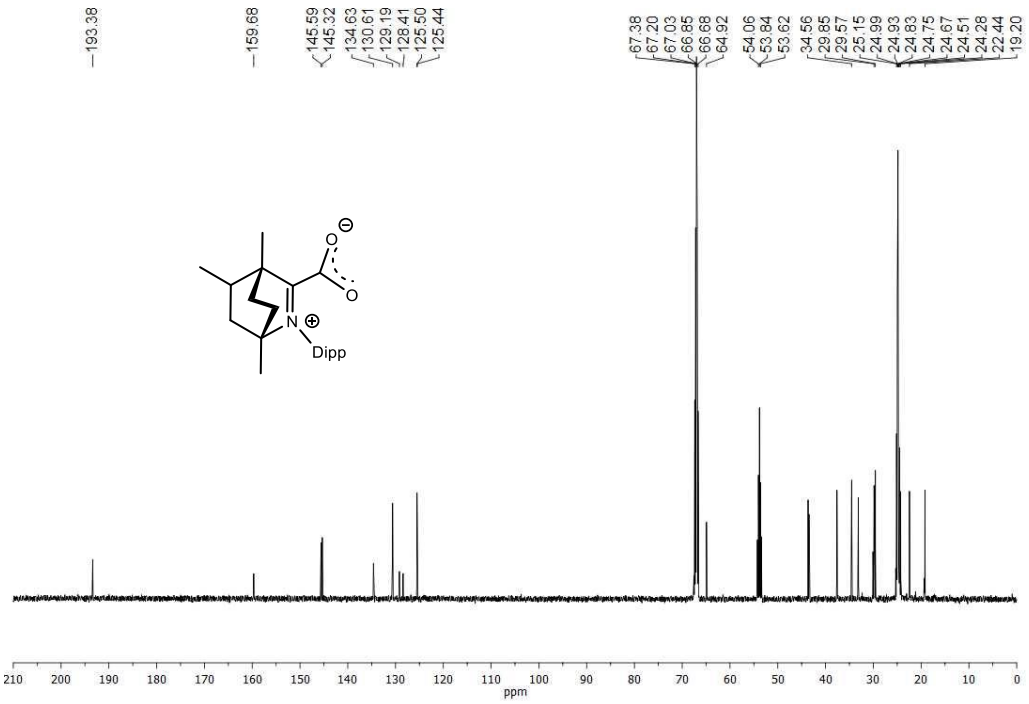

Fig. S12 ^{13}C NMR spectrum of compound **3** in CD_2Cl_2 + THF-d_8

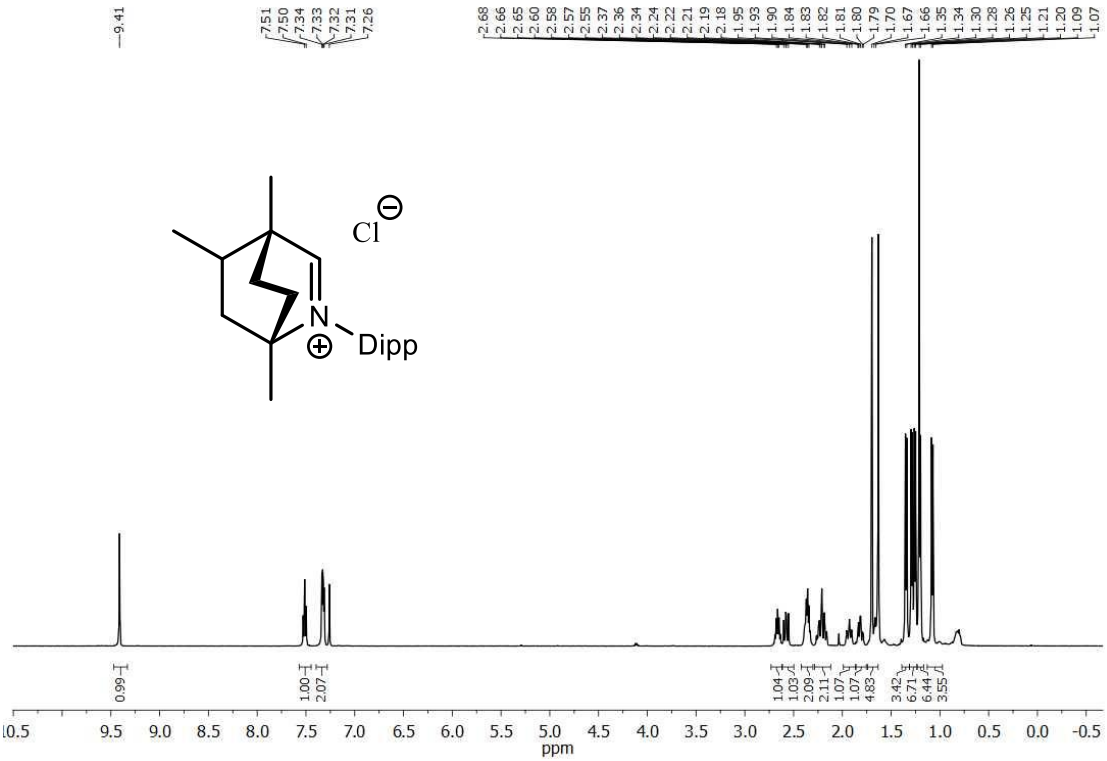

Fig. S13 ^{1}H NMR spectrum of compound **4** in $CDCl_3$

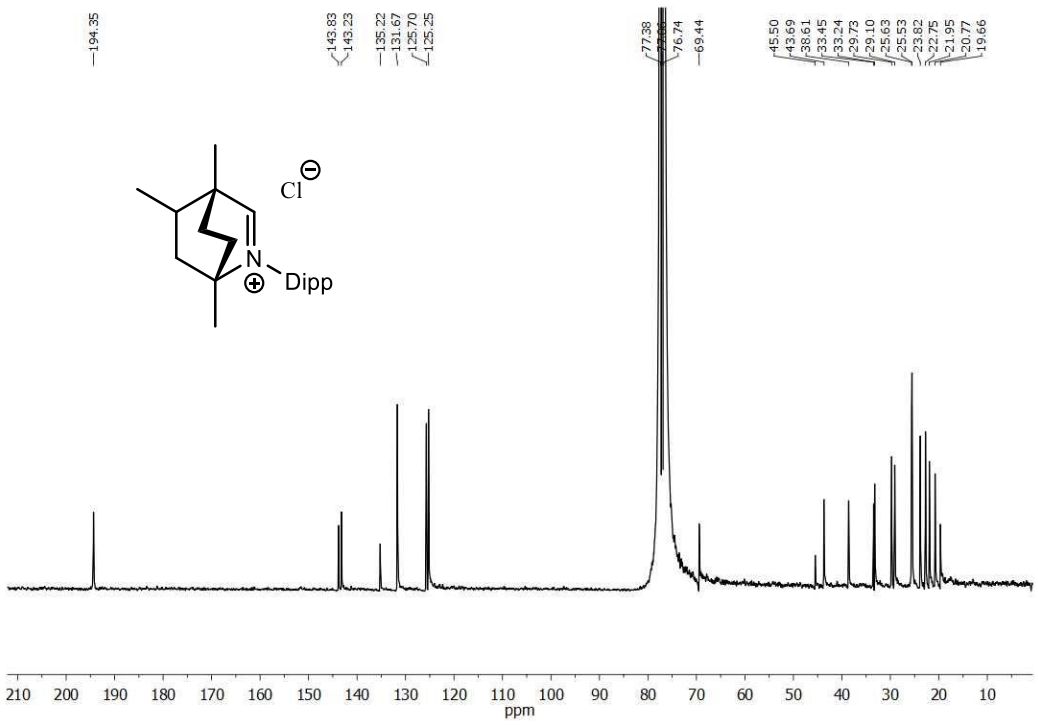

Fig. S14 ^{13}C NMR spectrum of compound **4** in $CDCl_3$

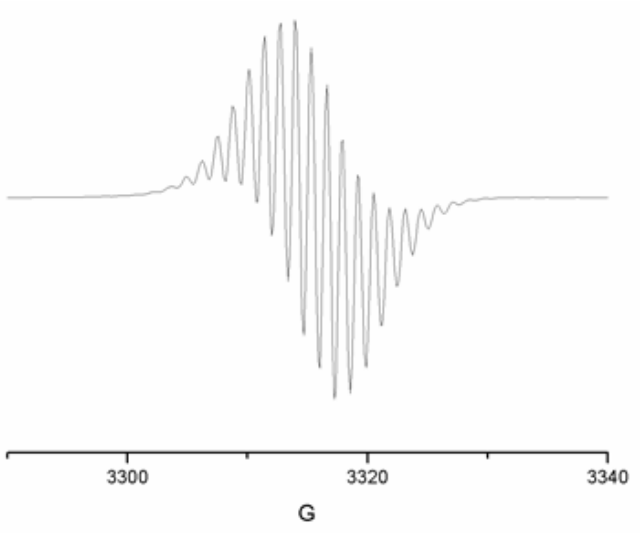

Fig. S15 EPR spectrum of $Ph_3C\cdot$ at 25 °C

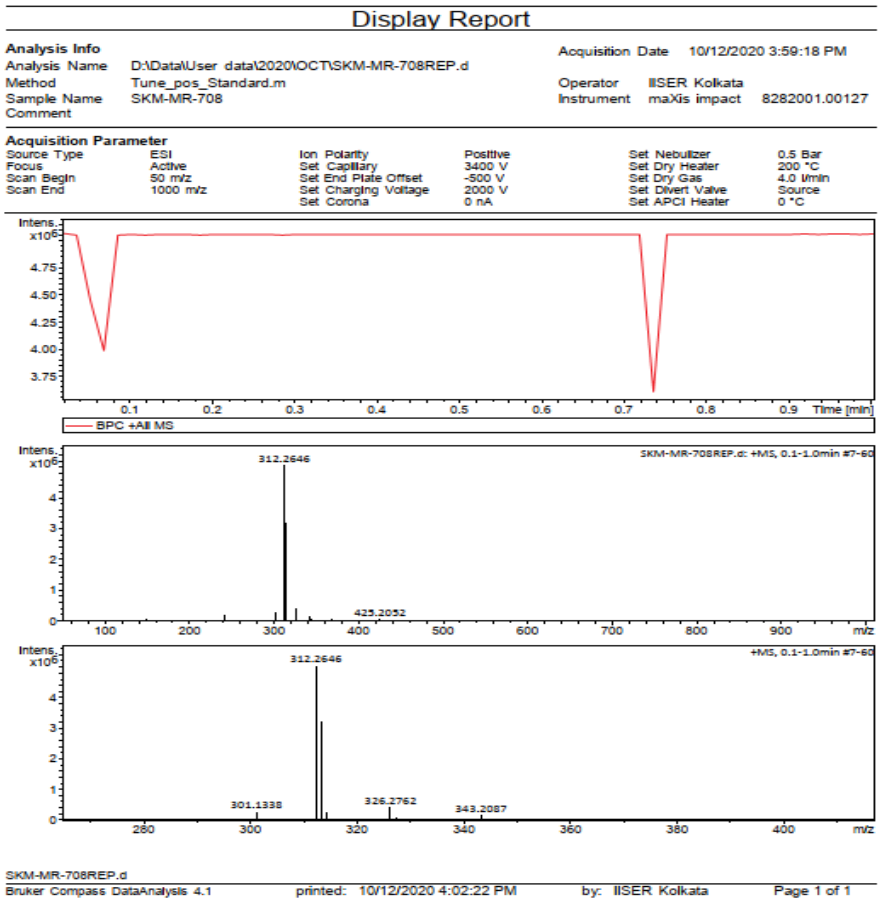

Fig. S16 HRMS spectrum of compound **4,** $[M\text{-}Cl]^+$ peak

Table S1. Crystallographic data for compounds **1** and **2**

Compound	**1**	**2**
Emprical formula	$C_{54.5}H_{78}Cl_4N_2Zn_2$	$C_{88}H_{132}N_4Zn_2$
Formula weight	1033.72	1376.71
Temperature (K)	293(2)	100.0
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	P-1
a (Å)	9.6552(7)	9.8500(4)
b (Å)	17.3124(13)	12.5419(5)
c (Å)	15.8733(13)	16.7728(6)
α (°)	90	79.912(3)
β (°)	99.979(7)	85.521(3)

γ (°)	90	70.669(4)
V(Å^3)	2613.2(4)	1924.58(14)
Z	2	1
ρ_{calc} (g/cm^3)	1.314	1.188
μ (mm^{-1})	1.159	1.105
F (000)	1094.0	748.0
Crystal size/mm^3	0.4 × 0.3 × 0.2	0.2 × 0.15 × 0.1
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)
Chemical_ formula_ sum	'C54.50 H78 Cl4 N2 Zn2'	'C88 H132 N4 Zn2'
Cell_measurement_reflns_used	3654	6719
Cell_measurement_temperature	293.0	100.00 K
Cell_measurement_theta_max	25.0730	66.1570
Cell_measurement_theta_min	2.0940	2.6460
Shelx_estimated_absorpt_T_max	0.801	0.898
Shelx_estimated_absorpt_T_min	0.654	0.809
Exptl_absorpt_coefficient_mu	1.159	1.105
Exptl_absorpt_correction_T_max	1.00000	1.00000
Exptl_absorpt_correction_T_min	0.48418	0.75632
Exptl_absorpt_correction_type	multi-scan	multi-scan
2Θ range for data collection/°	3.51 to 50.046	5.352 to 132.468
Index ranges	-11 ≤ h ≤ 11, -20 ≤ k ≤ 20, -17 ≤ l ≤ 18	-11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -19 ≤ l ≤ 19
Reflections collected	14705	18938
Independent reflections	4614 [R_{int} = 0.0745, R_{sigma} = 0.0636]	6704 [R_{int} = 0.0420, R_{sigma} = 0.0473]
Data/restraints/parameters	4614/274/291	6704/634/602
Goodness-of-fit	1.034	1.142
Final R indexes [I>=2σ (I)]	R_1 = 0.0497, wR_2 = 0.1288	R_1 = 0.0472, wR_2 = 0.1041
Final R indexes [all data]	R_1 = 0.0647, wR_2 = 0.1447	R_1 = 0.0572, wR_2 = 0.1085
Largest diff. peak/hole / e Å^{-3}	0.58/-0.56	0.38/-0.45

[a] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $wR2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$.

Coordinates and energies of $(BICAAC)_2Zn$ at different spin-state

Singlet

Zn	-0.00017900	-0.00627600	-0.02016700
N	2.82676500	0.51278300	-0.22742900
C	3.97347300	1.38907800	-0.55101800
C	3.20469900	-2.46064100	1.97888700
H	3.26421600	-2.69876500	3.04353800
C	3.00489800	-1.13227500	1.58516500
C	1.57102700	1.02924800	-0.37656400
C	2.96291700	-0.84018700	0.20445700
C	3.32493400	-3.47850500	1.03882400
H	3.49222500	-4.50662900	1.36427500
C	3.83077500	1.83091000	-2.02197300
H	4.05216100	0.98062300	-2.68349400
H	4.59497000	2.59765300	-2.22252900
C	3.20769500	-3.18642200	-0.31610800
H	3.26938800	-3.99330000	-1.05003700
C	5.30138000	0.69620000	-0.29891300
H	5.40560800	0.40985300	0.75660500
H	6.12209400	1.37939300	-0.55920900
H	5.39857800	-0.21455800	-0.90522400
C	2.83785200	-0.05855100	2.64801000
H	2.64809200	0.88736200	2.12569400
C	3.00256100	-1.87386500	-0.75698200
C	3.82672800	2.65551100	0.31149300
H	4.66489500	3.33404900	0.08968000
H	3.91834800	2.37130200	1.37173300
C	2.81239500	-1.60966700	-2.24209700
H	2.58897000	-0.54101300	-2.36032500
C	2.46461100	3.34118500	0.04578200
H	2.63952900	4.28363200	-0.50207700
C	1.62658500	2.44065800	-0.91587500
C	2.40833200	2.37712200	-2.25358500
H	2.43548100	3.38448900	-2.69955900
H	1.84566800	1.73040600	-2.94431000
C	0.22896300	2.99735900	-1.15041100
H	-0.26017400	2.46789300	-1.98223100
H	0.25852300	4.07022600	-1.39998200
H	-0.40658500	2.87239500	-0.25791900
C	1.75064800	3.68195600	1.34946600
H	1.49676300	2.76182300	1.89921900
H	0.81885200	4.23907700	1.17696200
H	2.39866600	4.29734300	1.99162900
N	-2.82661000	-0.51770000	0.22033300
C	-3.97170000	-1.39413800	0.54922500

C	-3.22368600	2.49424300	-1.93120100
H	-3.30335200	2.74962300	-2.99051900
C	-3.03395000	1.15711500	-1.56231700
C	-1.57021400	-1.03680300	0.35533100
C	-2.96231800	0.84297300	-0.18775800
C	-3.30940600	3.49872700	-0.97345700
H	-3.46956600	4.53398600	-1.27929700
C	-3.81435400	-1.84719800	2.01520500
H	-4.02059900	-0.99953800	2.68484900
H	-4.58201800	-2.60913900	2.22048800
C	-3.16787200	3.18368500	0.37412000
H	-3.20484600	3.97950000	1.12163900
C	-5.30026400	-0.69563600	0.31719300
H	-5.41414300	-0.39924000	-0.73450100
H	-6.12023900	-1.37906300	0.57919000
H	-5.38879100	0.20961600	0.93319900
C	-2.91008000	0.09794900	-2.64546900
H	-2.74090300	-0.86197600	-2.14201600
C	-2.96951300	1.86214800	0.79015800
C	-3.83826200	-2.65549000	-0.32300200
H	-4.67064100	-3.33651000	-0.08755400
H	-3.95203000	-2.36766000	-1.38000400
C	-2.75573700	1.57302600	2.26736200
H	-2.53675100	0.50151000	2.36506800
C	-2.46968000	-3.34010100	-0.08746600
H	-2.63333400	-4.29398500	0.44370100
C	-1.62338400	-2.45376500	0.87987300
C	-2.39349000	-2.40600000	2.22499400
H	-2.42311300	-3.42030100	2.65479400
H	-1.82056900	-1.77470700	2.92159400
C	-0.22510500	-3.01561200	1.09774100
H	0.27278300	-2.49316500	1.92884400
H	-0.25552400	-4.08999900	1.34048500
H	0.40348100	-2.88649400	0.20105700
C	-1.76862800	-3.64991400	-1.40599400
H	-1.52067800	-2.71620300	-1.93566900
H	-0.83458600	-4.20961400	-1.25529100
H	-2.42192800	-4.25135700	-2.05593800
C	1.59847800	-2.37667500	-2.77738200
H	1.74018100	-3.46645500	-2.70214900
H	0.69911700	-2.09813800	-2.20810900
H	1.42549700	-2.13109800	-3.83633400
C	4.06917700	-1.94346800	-3.05188100
H	3.91594600	-1.70555000	-4.11522100
H	4.94506500	-1.37969800	-2.69955700
H	4.31141500	-3.01502700	-2.98000000

C	1.61385600	-0.33601000	3.52850200
H	1.71756800	-1.28400100	4.08012900
H	1.48315500	0.47098200	4.26578800
H	0.70522000	-0.38357100	2.90848200
C	4.09834400	0.10171600	3.50383000
H	3.96731300	0.91700300	4.23104700
H	4.31400100	-0.81876300	4.06798000
H	4.98146900	0.33128700	2.89033700
C	-1.69098700	0.35701700	-3.53834200
H	-1.77505700	1.31934900	-4.06816100
H	-0.77232000	0.36499400	-2.93194400
H	-1.59547900	-0.43741300	-4.29440600
C	-4.18515300	-0.01236700	-3.48767300
H	-4.08774400	-0.82150900	-4.22687600
H	-5.06813600	-0.22219600	-2.86704800
H	-4.37858900	0.92137300	-4.03782600
C	-3.99805400	1.90043600	3.10168500
H	-3.83045200	1.64377800	4.15850400
H	-4.23508500	2.97436800	3.05109900
H	-4.88229300	1.34754200	2.75277000
C	-1.52861200	2.32388200	2.79467700
H	-1.66530300	3.41562200	2.74278800
H	-1.33710900	2.05709900	3.84529300
H	-0.64229300	2.05105800	2.20246000

Total energy = -3602.85074393

Singlet-biradical

Zn	0.00001600	-0.00007700	-0.00015500
N	2.84914300	0.48240600	-0.21562300
C	4.01087500	1.33805800	-0.53593500
C	3.16385800	-2.55538000	1.91394600
H	3.22390600	-2.82075000	2.97221200
C	3.01149000	-1.21252600	1.55231700
C	1.59354200	1.04779200	-0.34599700
C	2.95537700	-0.88224600	0.18022100
C	3.23210000	-3.55550800	0.94988600
H	3.36119000	-4.59690700	1.24928600
C	3.87142900	1.80774000	-1.99845800
H	4.06608700	0.96373900	-2.67665000
H	4.65520400	2.55639700	-2.19242900
C	3.10699800	-3.22634200	-0.39596200
H	3.12316300	-4.01783300	-1.14903200
C	5.32377600	0.60948100	-0.30439200
H	5.42713800	0.30357100	0.74628400
H	6.16073800	1.27489800	-0.55909700
H	5.39341600	-0.29383200	-0.92644900

C	2.88070600	-0.15687000	2.63714000
H	2.77311000	0.81116900	2.13283900
C	2.94685100	-1.89733300	-0.80209500
C	3.90496300	2.59726400	0.34327500
H	4.76053400	3.25492400	0.12441100
H	3.99677600	2.29964000	1.39987500
C	2.72763800	-1.58874400	-2.27374000
H	2.58000300	-0.50469100	-2.36194900
C	2.56103800	3.32760500	0.09665100
H	2.76194200	4.27459400	-0.43488600
C	1.69279100	2.46357600	-0.87002500
C	2.46294400	2.39907100	-2.21353900
H	2.51950700	3.40953800	-2.65036100
H	1.87777300	1.77716900	-2.90896900
C	0.31115400	3.06492200	-1.08912700
H	-0.20929200	2.54165500	-1.90653200
H	0.37181500	4.13282800	-1.35461400
H	-0.31594300	2.97402400	-0.18704700
C	1.86838700	3.66817100	1.41214800
H	1.58911700	2.74706300	1.94772000
H	0.95535200	4.26084000	1.25766500
H	2.54103300	4.24958100	2.06076600
N	-2.84912200	-0.48235500	0.21569100
C	-4.01087000	-1.33797800	0.53603000
C	-3.16367400	2.55555300	-1.91373700
H	-3.22368400	2.82099200	-2.97198900
C	-3.01134700	1.21266900	-1.55219400
C	-1.59355300	-1.04788700	0.34568500
C	-2.95532200	0.88230700	-0.18011600
C	-3.23196600	3.55562100	-0.94961800
H	-3.36102900	4.59703900	-1.24896500
C	-3.87129200	-1.80791100	1.99846200
H	-4.06608400	-0.96410200	2.67685600
H	-4.65493300	-2.55675000	2.19228500
C	-3.10695900	3.22637000	0.39621900
H	-3.12314800	4.01781200	1.14934000
C	-5.32375600	-0.60928800	0.30476200
H	-5.42727000	-0.30326700	-0.74586600
H	-6.16072100	-1.27467000	0.55954700
H	-5.39322800	0.29397100	0.92691700
C	-2.88065000	0.15707700	-2.63709300
H	-2.77290300	-0.81098900	-2.13287400
C	-2.94685000	1.89733200	0.80226600
C	-3.90509800	-2.59704300	-0.34339800
H	-4.76079400	-3.25462200	-0.12478100
H	-3.99672000	-2.29916600	-1.39994300

C	-2.72763100	1.58862400	2.27388300
H	-2.58008900	0.50455100	2.36200300
C	-2.56131800	-3.32764200	-0.09677100
H	-2.76239300	-4.27451100	0.43492100
C	-1.69281200	-2.46367000	0.86972600
C	-2.46271200	-2.39906000	2.21337800
H	-2.51909200	-3.40945700	2.65038200
H	-1.87746800	-1.77697400	2.90858500
C	-0.31117900	-3.06510800	1.08857500
H	0.20946300	-2.54186600	1.90587400
H	-0.37185600	-4.13300800	1.35408600
H	0.31573600	-2.97426300	0.18636500
C	-1.86886200	-3.66855000	-1.41228100
H	-1.58938100	-2.74757600	-1.94797500
H	-0.95598100	-4.26145900	-1.25781000
H	-2.54172300	-4.24983600	-2.06078700
C	1.44258500	-2.25695700	-2.77456600
H	1.51216000	-3.35528100	-2.72578000
H	0.58133800	-1.94311200	-2.16457300
H	1.24253900	-1.97663900	-3.81996700
C	3.92883700	-1.99013900	-3.13398000
H	3.75870600	-1.71484100	-4.18563300
H	4.85180700	-1.49607300	-2.79683800
H	4.09855200	-3.07726000	-3.09581300
C	1.60977700	-0.37879600	3.46545600
H	1.64096200	-1.34288300	3.99803400
H	1.49533600	0.41878200	4.21547000
H	0.71575100	-0.37210100	2.82202300
C	4.11687700	-0.09806500	3.53869700
H	4.01542600	0.71116100	4.27722700
H	4.25219900	-1.04013000	4.09202000
H	5.03290000	0.08279700	2.95780900
C	-1.60987200	0.37910800	-3.46560800
H	-1.64112200	1.34326200	-3.99805900
H	-0.71573300	0.37229400	-2.82233100
H	-1.49559200	-0.41837000	-4.21575100
C	-4.11698100	0.09826600	-3.53843300
H	-4.01558400	-0.71084100	-4.27710100
H	-5.03287100	-0.08278600	-2.95739500
H	-4.25250900	1.04040700	-4.09157800
C	-3.92874000	1.99004900	3.13422800
H	-3.75855700	1.71465300	4.18584700
H	-4.09837100	3.07718700	3.09617300
H	-4.85177700	1.49608600	2.79711500
C	-1.44250000	2.25671300	2.77468300
H	-1.51206400	3.35504600	2.72606400

H	-1.24233700	1.97622900	3.82001900
H	-0.58132900	1.94295200	2.16454300

Total energy= -3602.86944879

Triplet

Zn	-0.00000200	-0.00001400	-0.00001000
N	2.85473700	0.45313800	-0.21782100
C	4.03080200	1.28285400	-0.55047600
C	3.12273300	-2.59469100	1.90344500
H	3.18389100	-2.86375700	2.96072800
C	2.99263500	-1.24869000	1.54531000
C	1.60910900	1.05654200	-0.32368100
C	2.93419900	-0.91353800	0.17438100
C	3.16640800	-3.59384100	0.93675800
H	3.27861400	-4.63806200	1.23308400
C	3.88692700	1.75751300	-2.01112200
H	4.06049100	0.91168100	-2.69291400
H	4.68254100	2.49221600	-2.21076300
C	3.03538800	-3.25969100	-0.40728600
H	3.02830600	-4.05004200	-1.16175400
C	5.33003700	0.52598600	-0.33243100
H	5.43780700	0.21870400	0.71758600
H	6.17888000	1.17231700	-0.59679700
H	5.37309400	-0.37920300	-0.95433800
C	2.87810800	-0.19241900	2.63107800
H	2.79743000	0.77888800	2.12800500
C	2.89663100	-1.92703100	-0.80910900
C	3.96213400	2.54391500	0.33058000
H	4.83518500	3.17809500	0.11118600
H	4.04790000	2.24152300	1.38643400
C	2.66241300	-1.60984600	-2.27652700
H	2.54610500	-0.52161400	-2.36037400
C	2.63879300	3.31282100	0.08944900
H	2.86378100	4.24888000	-0.45205900
C	1.73661200	2.46455200	-0.86023600
C	2.48773400	2.37562100	-2.21325500
H	2.56000400	3.38090500	-2.65997500
H	1.88116700	1.76003400	-2.89615100
C	0.36725900	3.09782800	-1.06455200
H	-0.17971500	2.57720500	-1.86662600
H	0.44957900	4.16049200	-1.34502700
H	-0.24640800	3.03321000	-0.15139000
C	1.96995800	3.68545500	1.40854300
H	1.66216400	2.77720800	1.95063900
H	1.07803200	4.31052600	1.25828600

H	2.66841000	4.24518000	2.04895300
N	-2.85474300	-0.45317000	0.21779700
C	-4.03080800	-1.28293500	0.55032400
C	-3.12291100	2.59504600	-1.90291300
H	-3.18422000	2.86429900	-2.96014000
C	-2.99282000	1.24897400	-1.54503700
C	-1.60911600	-1.05660100	0.32353500
C	-2.93419200	0.91357600	-0.17417300
C	-3.16638400	3.59402800	-0.93604600
H	-3.27857400	4.63830800	-1.23217200
C	-3.88690900	-1.75785800	2.01088200
H	-4.06042400	-0.91213900	2.69282500
H	-4.68254200	-2.49256800	2.21041900
C	-3.03516400	3.25963600	0.40791800
H	-3.02790800	4.04985400	1.16252400
C	-5.33003800	-0.52601300	0.33243800
H	-5.43782400	-0.21854200	-0.71752200
H	-6.17888500	-1.17237900	0.59670500
H	-5.37306900	0.37906500	0.95450800
C	-2.87855200	0.19289400	-2.63101700
H	-2.79780900	-0.77850600	-2.12813800
C	-2.89641900	1.92689800	0.80948700
C	-3.96218400	-2.54384900	-0.33094700
H	-4.83521600	-3.17806900	-0.11158800
H	-4.04803400	-2.24129800	-1.38674800
C	-2.66192300	1.60945300	2.27680300
H	-2.54562600	0.52120300	2.36043700
C	-2.63882000	-3.31278700	-0.09003000
H	-2.86377700	-4.24897500	0.45126700
C	-1.73662600	-2.46471600	0.85981500
C	-2.48773000	-2.37604700	2.21286300
H	-2.56001900	-3.38142600	2.65936600
H	-1.88113700	-1.76062300	2.89588200
C	-0.36728200	-3.09805500	1.06399800
H	0.17973500	-2.57755700	1.86612500
H	-0.44962200	-4.16075500	1.34433100
H	0.24636100	-3.03333500	0.15082700
C	-1.97001000	-3.68511300	-1.40922600
H	-1.66220200	-2.77674400	-1.95111100
H	-1.07809200	-4.31023700	-1.25913000
H	-2.66847700	-4.24467700	-2.04976100
C	1.34993900	-2.23992200	-2.75607500
H	1.38779100	-3.33974600	-2.70527600
H	0.50356600	-1.90451000	-2.13623700
H	1.14245600	-1.95621900	-3.79909600
C	3.83608900	-2.04438900	-3.15808800

H	3.65720900	-1.75977400	-4.20578200
H	4.77866900	-1.57942100	-2.83408300
H	3.97359100	-3.13627000	-3.12675500
C	1.59339600	-0.38848200	3.44463000
H	1.59902000	-1.35364600	3.97614400
H	1.48604600	0.41061200	4.19405700
H	0.70420900	-0.36607800	2.79448600
C	4.10587600	-0.16358400	3.54493100
H	4.01604400	0.64699300	4.28345800
H	4.21489700	-1.10889100	4.09851500
H	5.03075300	-0.00272000	2.97215400
C	-1.59400800	0.38905000	-3.44481100
H	-1.59970900	1.35431100	-3.97614900
H	-0.70467700	0.36649200	-2.79487000
H	-1.48685600	-0.40991100	-4.19440800
C	-4.10651300	0.16427000	-3.54461700
H	-4.01688600	-0.64620200	-4.28328500
H	-5.03127900	0.00337900	-2.97166900
H	-4.21559200	1.10966700	-4.09803900
C	-3.83541100	2.04388100	3.15867200
H	-3.65632700	1.75909000	4.20628300
H	-3.97289200	3.13577100	3.12754600
H	-4.77806900	1.57899100	2.83478200
C	-1.34933400	2.23940800	2.75619000
H	-1.38717200	3.33924300	2.70561300
H	-1.14163300	1.95549600	3.79911100
H	-0.50310900	1.90409400	2.13609800

Total energy= -3602.86411255

Coordinates and energies of $(CAAC)_2Zn$ at different spin-state

Singlet-biradicaloid

Zn	0.00005000	0.00013900	-0.00024300
N	-2.75306400	-0.82693000	-0.17645100
C	-1.44227800	-1.26580800	-0.23974200
C	-1.45742200	-2.76620600	-0.46543200
C	-1.14254600	-3.52318300	0.83764700
C	-0.42725000	-3.18521500	-1.51768500
C	-2.90597900	-3.01814500	-0.95141700
C	-3.77894000	-1.87241200	-0.39680000
C	-4.49316300	-2.25985900	0.90451600
C	-4.84214800	-1.42801400	-1.40179900
C	-3.01714600	0.55399600	0.05372600
C	-3.13453100	1.04325000	1.37663800
C	-3.39324100	2.40464700	1.57116400
C	-3.48766300	3.28074400	0.49607600

C	-3.29358400	2.80617900	-0.79659100
C	-3.04647200	1.45099500	-1.04243900
C	-2.78265300	1.00613800	-2.47333200
C	-1.50337200	1.64991100	-3.02101800
C	-3.96492600	1.32179200	-3.39628400
C	-2.91091900	0.16197400	2.59523400
C	-4.11066300	0.16502100	3.54724100
C	-1.64344400	0.59618900	3.34213700
H	-0.09646800	-3.34132400	1.12782800
H	-1.77917500	-3.18895100	1.66921000
H	-1.27838600	-4.60950100	0.70603700
H	-0.63238500	-2.69762700	-2.48232900
H	0.58711900	-2.89157200	-1.19681900
H	-0.42965300	-4.27733400	-1.66666200
H	-2.92234200	-2.97235100	-2.05177200
H	-5.01958400	-1.38971500	1.32286600
H	-5.23887600	-3.04262300	0.70153800
H	-3.79513300	-2.64221200	1.66002400
H	-5.36010600	-0.52196400	-1.05007600
H	-4.40392300	-1.22320200	-2.38662900
H	-5.59239900	-2.22314300	-1.52229500
H	-3.49936000	2.78739400	2.58872800
H	-3.68742500	4.33975100	0.66725900
H	-3.32942200	3.50317700	-1.63697100
H	-2.61761600	-0.07990700	-2.45693400
H	-3.29144200	-4.00527600	-0.65403300
H	-1.60496700	2.74503400	-3.08438100
H	-0.63716400	1.42701400	-2.38007400
H	-1.28693300	1.27196900	-4.03176800
H	-4.09182800	2.40894100	-3.51319400
H	-3.79285800	0.90011200	-4.39799700
H	-4.90822900	0.91568300	-3.00695300
H	-2.74292100	-0.86074500	2.23581300
H	-5.04450900	-0.10361700	3.03461200
H	-3.95036200	-0.55022600	4.36768900
H	-4.25305600	1.15867800	3.99901700
H	-1.75003600	1.61636300	3.74403300
H	-1.44211600	-0.08284400	4.18466100
H	-0.76632600	0.58698000	2.67750800
N	2.75315400	0.82689600	0.17677200
C	1.44241800	1.26605000	0.23922300
C	1.45776600	2.76654200	0.46416400
C	1.14427200	3.52288000	-0.83963200
C	0.42677500	3.18637700	1.51526600
C	2.90600000	3.01831800	0.95118000
C	3.77912500	1.87218300	0.39763000

C	4.49462300	2.25895900	-0.90318300
C	4.84135900	1.42783400	1.40368800
C	3.01703800	-0.55407200	-0.05338500
C	3.13486200	-1.04321400	-1.37631000
C	3.39323500	-2.40466000	-1.57088700
C	3.48689000	-3.28092100	-0.49585700
C	3.29239400	-2.80644600	0.79677400
C	3.04559800	-1.45120500	1.04268500
C	2.78136500	-1.00646900	2.47354300
C	1.50194500	-1.65025200	3.02089500
C	3.96337600	-1.32226400	3.39678900
C	2.91200800	-0.16171500	-2.59488300
C	4.11202700	-0.16511900	-3.54653300
C	1.64454900	-0.59528800	-3.34218500
H	0.09836500	3.34129800	-1.13058000
H	1.78144600	3.18787600	-1.67046400
H	1.28047500	4.60921900	-0.70857200
H	0.63109300	2.69948400	2.48043200
H	-0.58734600	2.89252600	1.19379100
H	0.42908700	4.27860000	1.66345800
H	2.92150100	2.97288600	2.05156200
H	5.02095000	1.38842800	-1.32085600
H	5.24057400	3.04138000	-0.69975900
H	3.79746600	2.64150200	-1.65939900
H	5.35949300	0.52163200	1.05261500
H	4.40222500	1.22330900	2.38817300
H	5.59162800	2.22287300	1.52467300
H	3.49968700	-2.78731700	-2.58845000
H	3.68638900	-4.33997100	-0.66707800
H	3.32764300	-3.50355300	1.63709000
H	2.61634700	0.07958200	2.45717700
H	3.29193200	4.00525400	0.65375500
H	1.60347300	-2.74538300	3.08418800
H	0.63585100	-1.42726500	2.37982400
H	1.28536700	-1.27239300	4.03164600
H	4.09015700	-2.40943500	3.51362500
H	3.79106200	-0.90066400	4.39849300
H	4.90681900	-0.91619400	3.00776700
H	2.74432800	0.86102600	-2.23539900
H	5.04579200	0.10327800	-3.03363000
H	3.95215900	0.55017300	-4.36702600
H	4.25427600	-1.15881200	-3.99827200
H	1.75084000	-1.61541500	-3.74428500
H	1.44364800	0.08401600	-4.18459300
H	0.76729900	-0.58590900	-2.67774000

Triplet

Zn	0.00125300	0.00480300	-0.01100800
N	-2.75769400	-0.82015800	-0.15204800
C	-1.44850500	-1.27271500	-0.24286800
C	-1.47913300	-2.77422200	-0.44978300
C	-1.14157700	-3.52354400	0.85249100
C	-0.47719500	-3.21406500	-1.52116600
C	-2.94034700	-3.01875100	-0.90164900
C	-3.79358300	-1.86029000	-0.34138200
C	-4.48355600	-2.22993900	0.97822500
C	-4.87394000	-1.41938500	-1.32996600
C	-3.00965300	0.56535600	0.05834100
C	-3.10744200	1.07795700	1.37382300
C	-3.35992000	2.44315000	1.54903200
C	-3.46680600	3.30102400	0.46048500
C	-3.28944400	2.80425500	-0.82641300
C	-3.04966100	1.44438900	-1.05178800
C	-2.79535700	0.97288600	-2.47546400
C	-1.50655300	1.59027000	-3.03107400
C	-3.97298800	1.28937500	-3.40345800
C	-2.86085200	0.21670400	2.60200300
C	-4.03812000	0.24004500	3.58111200
C	-1.57568800	0.66095500	3.31200700
H	-0.08890700	-3.34339300	1.12007400
H	-1.76006000	-3.17924200	1.69372600
H	-1.28384200	-4.61065600	0.73367100
H	-0.69860300	-2.73138400	-2.48481300
H	0.54704100	-2.92893900	-1.22491400
H	-0.49431400	-4.30725300	-1.66135900
H	-2.97954400	-2.98453700	-2.00187700
H	-4.99734600	-1.35260300	1.39747200
H	-5.23676200	-3.01161900	0.79995200
H	-3.77127400	-2.60664000	1.72334500
H	-5.38056600	-0.50727800	-0.97723100
H	-4.45296400	-1.22580000	-2.32465000
H	-5.63049700	-2.21149100	-1.42943000
H	-3.45022200	2.84379300	2.56123300
H	-3.66145200	4.36335900	0.61618500
H	-3.33235800	3.48740100	-1.67778000
H	-2.64572800	-0.11487700	-2.44150600
H	-3.32741300	-3.99961100	-0.58582900
H	-1.59447100	2.68527200	-3.11358300
H	-0.64220700	1.37202200	-2.38555900
H	-1.29129600	1.19200000	-4.03419400
H	-4.08786100	2.37593300	-3.53699900
H	-3.80607000	0.85046600	-4.39858700

H	-4.92053500	0.89948000	-3.00754200
H	-2.70498100	-0.81276800	2.25608200
H	-4.98338900	-0.03736500	3.09479300
H	-3.85993000	-0.45959500	4.41125000
H	-4.16933600	1.24240200	4.01678700
H	-1.67272400	1.68767500	3.69926300
H	-1.35564800	-0.00412900	4.16085900
H	-0.71046500	0.64394800	2.63141700
N	2.76026600	0.81879900	0.16471400
C	1.45239700	1.28041300	0.22311900
C	1.48939400	2.78488100	0.40348600
C	1.19613200	3.51200100	-0.92196600
C	0.46087800	3.25183500	1.43731200
C	2.93979300	3.02557900	0.89083100
C	3.79900200	1.85323700	0.36954900
C	4.53058100	2.19912100	-0.93406200
C	4.84708200	1.41685900	1.39429300
C	3.00662900	-0.56791600	-0.04478000
C	3.11724300	-1.07752400	-1.36078800
C	3.36070600	-2.44402700	-1.53702800
C	3.44684900	-3.30604600	-0.44970000
C	3.25748200	-2.81162900	0.83622800
C	3.02510800	-1.45049400	1.06292800
C	2.75478200	-0.98239900	2.48486300
C	1.46138400	-1.60281100	3.02639900
C	3.92278000	-1.30003200	3.42465200
C	2.89311200	-0.21040500	-2.58922400
C	4.08015300	-0.24317600	-3.55604300
C	1.61017600	-0.63746800	-3.31354400
H	0.14977200	3.33733700	-1.21595800
H	1.83446900	3.14548300	-1.73856100
H	1.34652500	4.59973700	-0.82022500
H	0.65525900	2.79126600	2.41739200
H	-0.55592200	2.96146000	1.12094800
H	0.47684400	4.34790100	1.55275400
H	2.94917600	3.00628900	1.99202900
H	5.04264100	1.30974500	-1.32970000
H	5.29033200	2.97119400	-0.74233300
H	3.84584600	2.57898200	-1.70293200
H	5.35725700	0.49749400	1.06637500
H	4.39620300	1.23746800	2.37850500
H	5.60610500	2.20489900	1.50663800
H	3.46053900	-2.84237100	-2.54925600
H	3.63489000	-4.36945900	-0.60615900
H	3.28400800	-3.49769000	1.68593800
H	2.60395200	0.10528200	2.45144200

H	3.34268600	3.99906900	0.57195800
H	1.54972900	-2.69786200	3.10764700
H	0.60264800	-1.38452000	2.37340500
H	1.23690200	-1.20701300	4.02844600
H	4.03772300	-2.38700800	3.55494900
H	3.74391100	-0.86538700	4.41959000
H	4.87407900	-0.90708400	3.04124800
H	2.74473400	0.81948300	-2.24206000
H	5.02253300	0.02558500	-3.05938200
H	3.91672700	0.45924700	-4.38687100
H	4.20716400	-1.24592700	-3.99202400
H	1.69906600	-1.66363000	-3.70429900
H	1.40528200	0.03380300	-4.16136300
H	0.73896900	-0.61363600	-2.64102300

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