Supporting Information

for

Switching On Emission in Zn(II) Coordination Complexes by Tempering N$_{\text{amido}}$ Character

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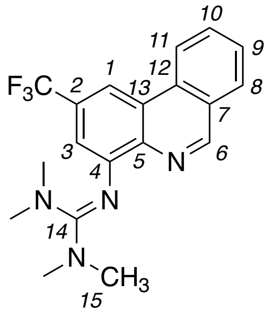
Experimental Details

General considerations

Air-sensitive manipulations were carried either in a N_2-filled glovebox or using standard Schlenk techniques under Ar. Chloroformamidinium chloride,{Citation} (4-aminophenyl)(2-*tert*-butyl)phenanthridine (**$^{t\text{Bu}}$L3**)[1] and *bis*(4-aminophenyl)(2-*tert*-butyl)phenanthridine zinc(II) ((**$^{t\text{Bu}}$L3**)$_2$Zn)[1] were synthesized according to literature procedure. Diethyl zinc (1.0 M in *n*-hexanes), tetramethyl urea (99 % purity), palladium(II) acetate (98 % purity), and DPEPhos (98 % purity) were purchased from Sigma Aldrich. Sodium hydroxide (97 % purity) and zinc dichloride (97 % purity) were purchased from Fisher Scientific. Oxalyl chloride (98 % purity) was purchased from Thermo Scientific. 2-bromopyrimidine (98 % purity) was purchased from Combi Blocks. Triethylamine (99 % purity) was purchased from Millipore. All other reagents and solvents were purchased from commercial suppliers and used without further purification. For moisture-sensitive manipulations, organic solvents were dried and distilled using appropriate drying agents. 1D and 2D NMR spectra were recorded on Bruker Avance 400 or 500 MHz spectrometers. ^{1}H and ^{13}C NMR spectra were referenced to residual solvent peaks. High resolution mass spectra (HRMS) were recorded using a Bruker microOTOF-QIII mass spectrometer.

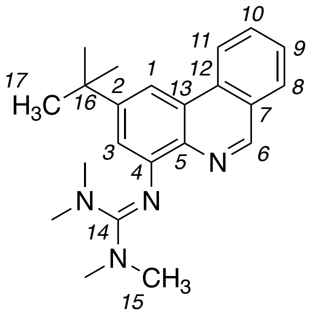
Absorption spectra were measured on an Agilent Technologies Cary series UV-Vis-NIR spectrometer. Emission spectra in solution were measured using either a Photo Technology International Xenoflash fluorimeter or Jobin Yvon FluoroMax-2 spectrometer, in quartz cuvettes of 1 cm pathlength. Spectral data are corrected for the wavelength dependence of the detector, a Hamamatsu R928 photomultiplier tube (PMT). Fluorescence quantum yields in solution were measured using fluorescein in 0.1 M aqueous NaOH ($\Phi = 0.90$) and cross-checked with aqueous $[Ru(bpy)_3]Cl_2$ ($\Phi = 0.04$). Fluorescence lifetimes were measured by time-correlated single-photon counting, following excitation at 405 nm with a pulsed laser diode. The emitted light was detected at 90° using an R928 PMT Peltier-cooled to –20°C, after passage through a monochromator. The estimated uncertainty in the lifetimes is ±10% or better. The fluorescence spectra in the solid state were recorded using an integrating sphere attached to a Jobin Yvon Fluorolog instrument through optical fibres. Finely powdered samples were contained within Spectralon sample holders of 10 mm diameter. Quantum yields were determined using a sample of finely powedered $BaSO_4$ as a non-emissive blank.

Preparation of (4-tetramethylguanidino)(2-trifluoromethyl)phenanthridine, $^{\mathbf{CF3}}$L1



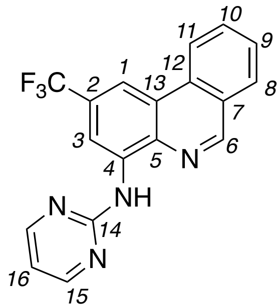
A solution of 4-amino-2-(trifluoromethyl)phenanthridine (0.39 g, 1.5 mmol) in acetonitrile (10 mL) was added dropwise under positive pressure of argon to chloroformamidinium chloride (0.26 g, 1.5 mmol) in a Teflon-stoppered flask and stirred for ~ 5 min. Triethylamine (0.21 mL, 1.5 mmol) was then added also under positive pressure and the mixture was heated in an oil bath set to 80 °C for 16 h. The flask was then cooled to ambient temperature and an aqueous solution of NaOH (0.060 g, 1.5 mmol; 3 mL H_2O) was added and allowed to stir for ~ 5 min. The volatiles were removed *in vacuo*. The organic product was then taken up in ethyl acetate and washed with distilled water (3x 70 mL), stirred over Na_2SO_4 (10 g), and dried *in vacuo* to leave a tacky dark brown solid. Isolated yield: 0.47 g (87 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 22 °C): δ 9.26 (s, 1H; C_6H), 8.56 (d, $^3J_{HH}$ = 8.3 Hz, 1H; $C_{11}H$), 8.26 (s, 1H; C_1H), 7.99 (d, $^3J_{HH}$ = 6.6 Hz, 1H; C_8H), 7.81 (ddd, $^3J_{HH}$ = 8.4, 7.1 Hz; $^4J_{HH}$ = 1.5 Hz, 1H; C_9H), 7.67 (ddd, $^3J_{HH}$ = 7.4, 7.2 Hz; $^3J_{HH}$ = 1.0 Hz, 1H; $C_{10}H$), 7.10 (s, 1H; C_3H), 2.73 ppm (s, 12H; $C_{15}H_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, 22 °C): δ 162.4 (C_{14}), 153.1 (C_6), 151.9 (C_{12}) , 139.6 (C_4), 133.0 (C_{13}), 131.0 (C_{11}), 129.1 (q, $^2J_{CF}$ = 31.4 Hz, C_2), 128.7 (C_8) 127.8 (C_{10}) 126.6 (C_5), 124.7 (q, $^1J_{CF}$ = 273 Hz, C_{CF3}), 124.7 (C_7), 122.4 (C_{11}), 115.5 (q, $^3J_{CF}$ = 3 Hz; C_3), 110.1 (q, $^3J_{CF}$ = 4 Hz; C_1), 39.7 ppm (C_{15}). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 377 MHz, 22 °C): -62.1 ppm (F_{CF3}). HR-MS (APCI/MS, m/z) calculated for $M+H^+$ ($M = C_{19}H_{19}F_3N_4$) 361.1635; found 361.1657.

Preparation of (2-tert-butyl)(4-tetramethylguanidino)phenanthridine, $^{\mathbf{\textit{t}Bu}}$L1



A suspension of 4-amino-2-(*tert*-butyl)phenanthridine (0.37 g, 1.5 mmol) in acetonitrile (15 mL) was added dropwise under positive pressure of argon to a Teflon-stoppered flask charged with chloroformamidinium chloride (0.26 g, 1.5 mmol) and stirred for ~ 5 min. Triethylamine (0.21 mL, 2.5 mmol) was then added under positive pressure of argon and the mixture was heated in an oil bath set to 80 °C for 16 h. The flask was then cooled to ambient temperature and an aqueous solution of NaOH (0.060 g, 1.5 mmol; 3 mL H_2O) was added and allowed to stir for ~ 5 min. The volatiles were removed *in vacuo*, and the organic product was then taken up in ethyl acetate and washed with distilled water (3x 70 mL), stirred over Na_2SO_4 (10 g), and dried *in vacuo* to leave a dark brown powder. Isolated yield: 0.45 g (89 %). ^{1}H NMR (CDCl$_3$, 400 MHz, 22 °C): δ 9.12 (s, 1H; C_6H), 8.60 (d, $^3J_{HH}$ = 8.3 Hz, 1H; $C_{11}H$), 8.09 (s, 1H; C_1H), 7.94 (d, $^3J_{HH}$ = 7.9 Hz, 1H; C_8H), 7.76 (ddd, $^3J_{HH}$ = 8.4, 7.0 Hz; $^4J_{HH}$ = 1.4 Hz, 1H; C_9H), 7.60 (ddd, $^3J_{HH}$ = 7.4, 7.2 Hz; $^4J_{HH}$ = 1.0 Hz, 1H; $C_{10}H$), 7.22 (s, 1H; C_3H), 2.74 (s, 12H; $C_{15}H_3$), 1.44 ppm (s, 9H, $C_{17}H_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, 22 °C): δ 161.81 (C_{14}), 150.8 (C_6), 150.5 (C_2), 136.5 (C_4), 133.2 (C_{13}), 130.2 (C_9), 128.5 (C_8) 126.8 (C_{10}) 126.6 (C_5), 124.1 (C_7), 122.2 (C_{11}), 119.2 (C_3), 110.2 (C_1), 39.7 (C_{15}), 35.1 (C_{16}) 31.6 (C_{17}) ppm. Not observed: C_{12}. HR-MS (APCI/MS, m/z) calculated for M+H$^+$ (M = $C_{22}H_{28}N_4$) 349.2387; found 349.2349.

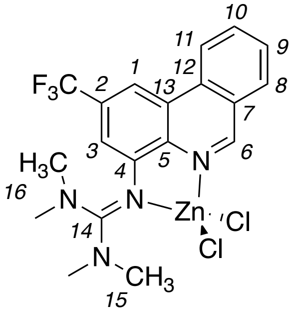
Preparation of (4-aminopyrimidino)(2-trifluoromethyl)phenanthridine, ^{CF3}L2



Pd(OAc)$_2$ (0.017 g, 0.075 mmol) and DPEPhos (0.083 g, 0.15 mmol) were combined with dry toluene (10 mL) in a Teflon-stoppered flask and stirred for ~ 5 min. Under positive pressure of argon, 2-Bromopyrimidine (0.12 g, 0.75 mmol) was added, followed by 4-amino-2-(trifluoromethyl)phenanthridine (0.20 g, 0.75 mmol) and Cs$_2$CO$_3$ (0.29 g, 0.90 mmol), with brief stirring (~ 5 min) following each addition. The mixture was then heated in an oil bath set to 130 °C. After 16 h, the mixture was cooled to room temperature, filtered over celite, and the solvents removed *in vacuo*. The residue was taken up in methanol and filtered, and the precipitate was washed thoroughly with methanol, leaving a purple-brown solid. Isolated yield: 0.11 g (42%). ^{1}H NMR (CDCl$_3$, 500 MHz, 22 °C): δ 10.00 (s, 1H; NH), 9.22 (overlapped s, 2H; C_1H, C_6H), 8.57 (d, $^3J_{HH}$ = 4.9 Hz, 2H; $C_{15}H_2$), 8.55 (d, $^3J_{HH}$ = 8.1 Hz, 1H; $C_{11}H$), 8.33 (s, 1H; C_3H), 8.06 (d, $^3J_{HH}$ = 7.9 Hz, 1H; C_8H), 7.87 (ddd, $^3J_{HH}$ = 8.4, 7.0 Hz; $^4J_{HH}$ = 1.4 Hz, 1H; $C_{10}H$), 7.72 (ddd, $^3J_{HH}$ = 7.9, 7.0 Hz; $^4J_{HH}$ = 1.1 Hz, 1H; C_9H), 6.84 (t, $^3J_{HH}$ = 4.8 Hz, 1H; $C_{16}H$). ^{13}C{^{1}H} NMR (CDCl$_3$, 126 MHz, 22 °C): δ 159.7 (C_{14}), 158.1 (C_{15}), 152.7 (C_6), 137.8 (C_{12}), 134.7 (C_4), 132.6 (C_{13}), 131.7 (C_{10}), 129.3 (q, $^2J_{CF}$ = 32 Hz; C_2), 129.1 (C_8), 128.3 (C_9), 126.8 (C_7), 124.6 (q, $^1J_{CF}$ = 273 Hz; C_{CF3}), 123.5 (C_5), 122.3 (C_{11}), 113.4 (C_{16}), 111.2 (q, $^3J_{CF}$ = 5 Hz; C_3),110.6 ppm (q, $^3J_{CF}$ = 4 Hz; C_1). ^{19}F{^{1}H} NMR (CDCl$_3$, 471 MHz, 22 °C): -62.0 ppm (F_{CF3}). HR-MS (APCI/MS, m/z) calculated for M+H$^+$ (M = $C_{18}H_{11}F_3N_4$) 341.1009; found 341.1025.

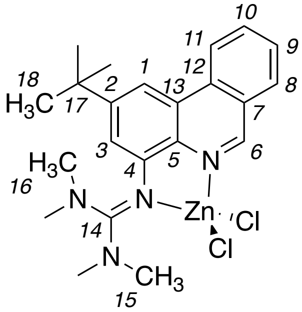
Preparation of (4-tetramethylguanidino)(2-trifluoromethyl)phenanthridine zinc chloride, (^{CF3}L1)ZnCl$_2$

A solution of (4-tetramethylguanidino)(2-trifluoromethyl)phenanthridine (0.14 g, 0.39 mmol) in dichloromethane (10 mL) was added to a stirring solution of ZnCl$_2$ (0.047 g, 0.35 mmol) in methanol (10 mL) in a round bottom flask, and continued to stir at room temperature for 16 h. The solvents were then evaporated *in vacuo* and the residue taken up in methanol and filtered. The precipitate was washed thoroughly with methanol, leaving a bright yellow-green solid. Isolated yield: 0.091 g (46 %). ^{1}H NMR (CDCl$_3$, 400 MHz, 22 °C): δ 9.39 (s, 1H; C$_6$*H*), 8.66 (d, $^3J_{HH}$ = 8.3 Hz, 1H; C$_{11}$*H*), 8.38 (s, 1H; C$_1$*H*), 8.21 (d, $^3J_{HH}$ = 8.0 Hz, 1H; C$_8$*H*), 8.07 (ddd, $^3J_{HH}$ = 8.5, 7.1 Hz; $^4J_{HH}$ = 1.4 Hz, 1H; C$_9$*H*), 7.88 (ddd, $^3J_{HH}$ = 8.1, 7.2 Hz; $^4J_{HH}$ = 0.8 Hz, 1H; C$_{10}$*H*), 6.99 (s, 1H; C$_3$*H*), 3.11 (s, 6H; C$_{15}$*H*$_3$), 2.93 ppm (s, 6H; C$_{16}$*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, 22 °C): δ 165.6 (*C*$_{14}$), 154.8 (*C*$_6$), 145.3 (*C*$_{12}$), 135.4 (*C*$_{13}$), 134.4 (*C*$_9$), 133.8 (*C*$_4$) 130.8 (q, $^2J_{CF}$ = 32.7 Hz; *C*$_2$), 130.7 (*C*$_8$), 129.7 (*C*$_{10}$), 126.6 (*C*$_5$), 125.7 (*C*$_7$), 124.0 (q, $^1J_{CF}$ = 276 Hz; *C*$_{CF3}$), 122.7 (*C*$_{11}$), 112.8 (q, $^3J_{CF}$ = 3 Hz; *C*$_3$), 111.7 (q, $^3J_{CF}$ = 4 Hz; *C*$_1$), 41.1 (*C*$_{15}$), 40.5 ppm (*C*$_{16}$). ^{19}F{^{1}H} NMR (CDCl$_3$, 377 MHz, 22 °C): -62.5 ppm (*F*$_{CF3}$).

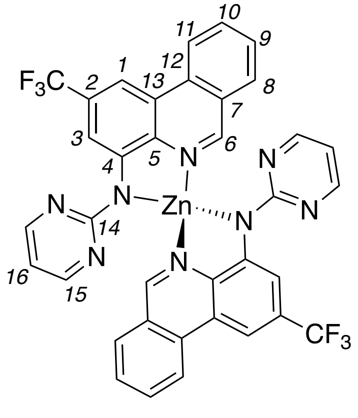


Preparation of (2-*tert*-butyl)(4-tetramethylguanidino)phenanthridine zinc chloride, (^{tBu}L1)ZnCl$_2$

A solution of (2-*tert*-butyl)(4-tetramethylguanidino)phenanthridine (0.11 g, 0.32 mmol) in dichloromethane (10 mL) was added to a stirring solution of ZnCl$_2$ (0.040 g, 0.29 mmol) in methanol (10 mL) in a round bottom flask, with stirring then continued at room temperature for 16 h. The solvents were next evaporated *in vacuo* and the residue taken up in methanol and filtered. The precipitate was washed thoroughly with methanol, leaving a bright green solid. Isolated yield: 0.79 g (56 %). ^{1}H NMR (CDCl$_3$, 400 MHz, 22 °C): δ 9.23 (s, 1H; C$_6$*H*), 8.66 (d, $^3J_{HH}$ = 8.1 Hz, 1H; C$_{11}$*H*), 8.14 (d, $^3J_{HH}$ = 1.9 Hz, 1H; C$_1$*H*), 8.12 (d, $^3J_{HH}$ = 8.0 Hz, 1H; C$_8$*H*), 7.98 (ddd, $^3J_{HH}$ = 8.5, 7.1 Hz; $^4J_{HH}$ = 1.4 Hz, 1H; C$_9$*H*), 7.78 (ddd, $^3J_{HH}$ = 8.0, 7.1 Hz; $^4J_{HH}$ = 1.1 Hz, 1H; C$_{10}$*H*), 6.96 (s, 1H; C$_3$*H*), 3.08 (s, 6H; C$_{15}$*H*$_3$), 2.39 (s, 6H; C$_{16}$*H*$_3$), 1.47 ppm (s, 9H, C$_{18}$*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, 22 °C): δ 165.5 (*C*$_{14}$), 152.2 (*C*$_6$), 152.0 (*C*$_2$), 143.6 (*C*$_{12}$), 133.7 (*C*$_4$), 133.2 (*C*$_9$), 132.8 (*C*$_{13}$) 130.4 (*C*$_8$) 128.6 (*C*$_{10}$), 126.5 (*C*$_5$), 125.3 (*C*$_7$), 122.5 (*C*$_{11}$), 116.0 (*C*$_3$), 110.0 (*C*$_1$), 40.9 (*C*$_{15}$) 40.3 (*C*$_{16}$), 35.5 (*C*$_{17}$), 31.6 (*C*$_{18}$) ppm.



Preparation of *bis*(4-aminopyrimidino)(2-trifluoromethyl)phenanthridine zinc, $^{\mathbf{CF3}}\mathbf{L2})_2\mathbf{Zn}$



In a glovebox of N_2 atmosphere, a solution of (4-aminopyrimidino)(2-trifluoromethyl)phenanthridine (0.025 g, 0.073 mmol) in benzene-d_6 (1 mL) was cooled to -18 °C. Diethylzinc (0.038 mL, 0.035 mmol) was then added to the frozen solution and the mixture allowed to warm to room temperature. Upon thawing, the solution was transferred to an NMR tube, and immediately following NMR analysis of the reactive compound, the solvent was evaporated *in vacuo*, revealing a bright yellow solid. NMR showed that reaction conversion was quantitative (> 95 %). Note: this compound is susceptible to proto-deligation and decomposes in the presence of protic solvents/impurities, including chloroform. ^{1}H NMR (C_6D_6, 500 MHz, 22 °C): δ 10.58 (s, 1H; C_1H_2), 8.55 (s, 1H; C_6H_2), 8.11 (s, 1H; C_3H_2), 8.05 (d, $^{3}J_{HH}$ = 4.7 Hz, 2H; $C_{15}H_4$), 7.81 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H; C_8H_2), 7.17 (d, $^{3}J_{HH}$ = 7.5 Hz, 1H; $C_{11}H_2$), 6.94 (ddd, $^{3}J_{HH}$ = 8.1, 6.9 Hz; $^{4}J_{HH}$ = 0.8 Hz, 1H; $C_{10}H_2$), 6.90 (d, $^{3}J_{HH}$ = 7.9 Hz, 1H; C_9H_2), 5.84 (t, $^{3}J_{HH}$ = 4.6 Hz, 1H; $C_{16}H_2$). ^{13}C{^{1}H} NMR (C_6D_6, 126 MHz, 22 °C): *δ* 165.8 (C_{14}), 158.1 (C_{15}), 151.3 (C_6), 146.5 (C_{13}), 136.5 (C_5), 134.2 (C_7), 132.7 (C_{11}), 132.0 (C_{12}), 131.7 (C_4), 129.6 (C_9), 127.7 (C_{10}), 125.8 (q, $^{2}J_{CF}$ = 103 Hz; C_2), 122.7 (C_8), 113.7 (q, $^{3}J_{CF}$ = 4 Hz; C_1), 110.8 (C_{16}), 107.3 ppm (q, $^{3}J_{CF}$ = 3 Hz; C_3). Not observed: C_{CF3}. ^{19}F{^{1}H} NMR ($CDCl_3$, 471 MHz, 22 °C): -61.8 ppm (F_{CF3}).

X-ray crystallography

Single crystals of each compound were selected using an optical microscope and were mounted on MiTeGen loops. Data collection was carried out using the Bruker D8 QUEST ECO diffractometer and Bruker APEX4 software.[2] Structure solution was performed using XS, XT, and XL[3] embedded in Olex2.[4] Mercury was used to visualize solid-state structures.[5] Details of growth, data collection, solution, and refinement specific to each crystal are given below.

Crystal structure of ($^{\mathbf{CF3}}\mathbf{L1}$)ZnCl₂ (CCDC 2320600)

X-ray quality crystals of yellow, plate-like habit were obtained through slow cooling (60 °C to 22 °C) and slow evaporation of a saturated solution of ($^{\mathbf{CF3}}\mathbf{L1}$)$ZnCl_2$ in 3:1 methanol:water. The data collection was performed under a cold stream of nitrogen (150 K). Crystal structure parameters:

$C_{19}H_{19}Cl_2F_3N_4Zn$ (248.34 g/mol): monoclinic, space group *C*2/*c*, *a* = 31.5266(16) Å, *b* = 16.1610(8) Å, *c* = 13.1152(6) Å, *β* = 114.276(2)°, *V* = 6091.3(5) Å^3, *Z* = 16; crystal dimensions 0.39 x 0.21 x 0.05 mm; diffractometer Bruker D8 QUEST ECO CMOS, Mo K_α radiation, 2θ = 2.45 to 26.53°, 55874 reflections measured, 6320 unique (R_{int} = 0.0684, R_{sigma} = 0.0343) which were used in all calculations, intrinsic phasing; μ(MoKα) = 1.009 mm^{-1}, absorption correction semiempirical (multi-scan); refinement with olex2.refine 1.5, 294 parameters, 73 restraints, the final R_1 was 0.0406 (I > 2σ(I)) and wR_2 was 0.0984 (all data), GooF = 1.0331, residual electron density 0.54 Å^{-3}.

Crystal structure of $(^{CF3}\mathbf{L2})_2$Zn (CCDC 2320601)

X-ray quality crystals of yellow, block-habit were obtained through layering dry hexanes over a solution of $(^{CF3}\mathbf{L2})_2$Zn in tetrahydrofuran in a glovebox of N_2 atmosphere. The data collection was performed under a cold stream of nitrogen (168 K). Crystal structure parameters $C_{36}H_{20}F_6N_8Zn$, C_4H_8O (*M* =816.07 g/mol): monoclinic, space group *C*2/*c*, *a* = 22.2606(14) Å, *b* = 21.5288(14) Å, *c* = 10.5400(7) Å, *β* = 115.087(2)°, *V* = 4574.7(5) Å^3, *Z* = 4; crystal dimensions 0.22 x 0.2 x 0.09 mm; diffractometer Bruker D8 QUEST ECO CMOS, Mo K_α radiation, 2θ = 2.77 to 24.79°, 50165 reflections measured, 3912 unique (R_{int} = 0.0594, R_{sigma} = 0.0249) which were used in all calculations, intrinsic phasing; μ(MoKα) = 0.598 mm^{-1}, absorption correction semiempirical (multi-scan); refinement with SHELXL, 276 parameters, 75 restraints, the final R_1 was 0.0514 (I > 2σ(I)) and wR_2 was 0.1537 (all data), GooF = 1.080, residual electron density 0.71 Å^{-3}.

Computational Modelling

All calculations were carried out on Orca v.5.0.1.[6,7] within the framework of Kohn-Sham density functional theory (KS-DFT); restricted and unrestricted KS were used for closed-shell and open-shell calculations, respectively. Solvent effects were accounted for implicitly using the SMD solvent model.[8] Furthermore, we used the resolution-of-identity approximation to speed up all our calculations. Note that for the hybrid and range-separated functionals used in this study, we used the resolution-of-identity 'chains of spheres' approximation (RIJCOSX). Additional auxiliary basis sets were therefore used (def2/J). The ground state geometries of the complexes were optimized at the M06-L/def2-SVP and B3LYP/def2-SVP level of theories in the gas phase and in CH_2Cl_2. The coordinates from the crystal structures of the complexes were used as initial inputs for the optimization. Subsequent frequency analyses on the optimized geometries did not show any imaginary frequencies indicating the structures are minima on the ground state potential energy surface. A comparison of the solid-state vs computationally optimized bond lengths and angles can be found in Tables S1-S3.

We then carried out natural bond orbital (NBO) analyses on the complexes using the NBO 7.0 program[9] to interrogate the bonding around the amido/imino nitrogen donors. Here, we used the geometries obtained using M06-L/def2-SVP both in the gas phase and in solution. We varied the amount of Hartree-Fock exchange to understand its impact on the bonding character. The following functionals were used M06-L (0%),[10] TPSSh (10%),[11] O3LYP (11.16%),[12] B3LYP (20%),[13] PBE0 (25%),[14] M06 (27%),[10] M06-2X (54%),[10] and CAM-B3LYP (range-separated; HF% is variational).[15] A larger basis set was also implemented, using the triple-zeta and doubly polarized def2-TZVPP basis set. A summary of the NBO results can be found in Figures S25 and S26, and a collection of the relevant NBO raw output data can be found in Tables S33-S120.

For the excited states, we used the B3LYP/def2-SVP level of theory to optimize the excited S_1 and T_1 states in CH_2Cl_2. We additionally optimized the geometries in Et_2O, toluene and *n*-hexane. Time-dependent DFT (TD-DFT) was used to optimize the S_1 state. Similarly, frequency analyses did not reveal any imaginary frequencies. We further performed TD-DFT on the ground state geometries to simulate the optical spectra of the complexes in the four solvents used in this study. The simulated optical spectra were generated using Multiwfn version 3.7[16] applying 0.35 eV broadening (Figures S14, S16, and S19). Ground state molecular orbital isosurfaces were generated on Avogadro with isovalue of 0.04. The electron-hole density maps were obtained from the changes in the electron densities obtained from the TDDFT calculations. To do this, we first generated molden files using the orca_2mkl module, which were subsequently fed into Multiwfn v.3.7. After choosing the electronic excitation of interest, we then created cube files that were opened on VESTA 3.5.8 to plot the relevant electron-hole density maps (isovalue = 0.001). Spin density maps were generated using the orca_plot module and visualized using Gabedit.[17] Orbital composition analysis (Hirshfeld method)[18] and fragment contribution analysis were done using Multiwfn version 3.7.[16] Mercury was used to visualize S_0, S_1,and T_1 states.[5]

Electronic Absorption and Emission Spectroscopy Figures

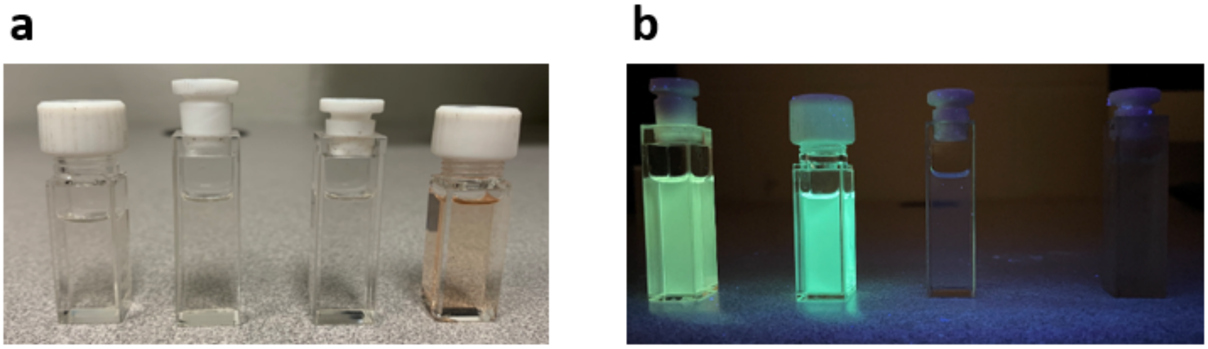


Figure S1. Equimolar solutions (approx. 0.10 mM) of proligands (a) in ambient light and (b) under UV irradiation (355 nm). For each image, from left to right: $^{t\mathrm{Bu}}$**L1**, $^{\mathrm{CF3}}$**L1**, $^{\mathrm{CF3}}$**L2**, $^{t\mathrm{Bu}}$**L3**.

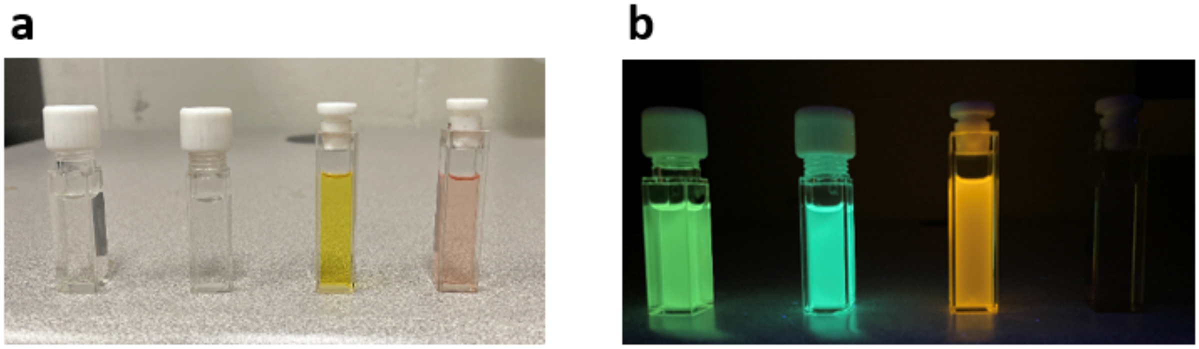


Figure S2. Equimolar solutions (approx. 0.10 mM) of complexes (a) in ambient light and (b) under UV irradiation (355 nm). For each image, from left to right: ($^{t\mathrm{Bu}}$**L1**)$ZnCl_2$, ($^{\mathrm{CF3}}$**L1**)$ZnCl_2$, ($^{\mathrm{CF3}}$**L2**)$_2$Zn, ($^{t\mathrm{Bu}}$**L3**)$_2$Zn.

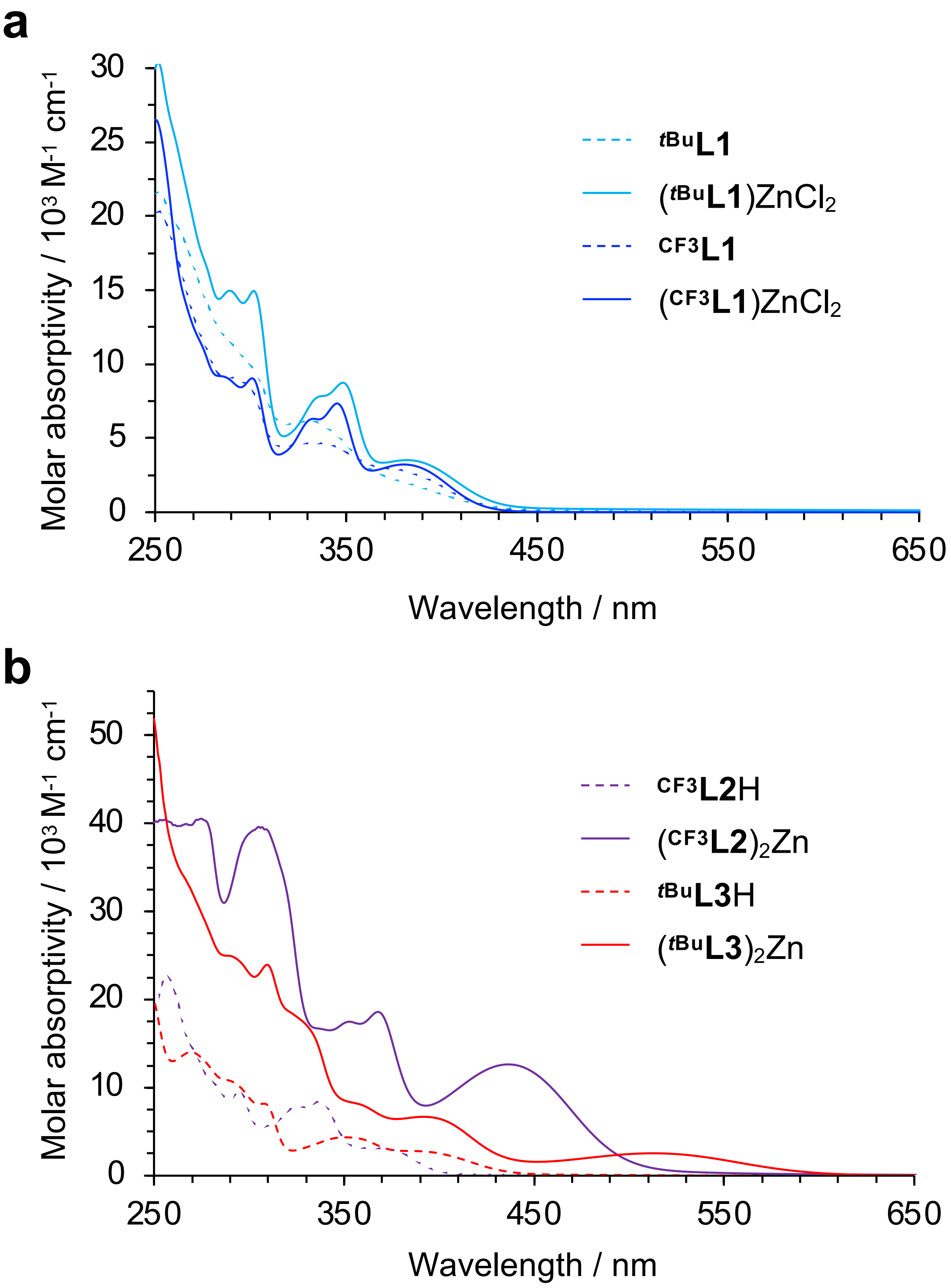


Figure S3. Molar absorptivity of (a) $^{\mathbf{R}}$**L1** / ($^{\mathbf{R}}$**L1**)ZnCl$_2$ and (b) $^{\mathbf{CF3}}$**L2** / ($^{\mathbf{CF3}}$**L2**)$_2$Zn / $^{\boldsymbol{t}\mathbf{Bu}}$**L3** / ($^{\boldsymbol{t}\mathbf{Bu}}$**L3**)$_2$Zn in CH$_2Cl_2$ at 295 K.

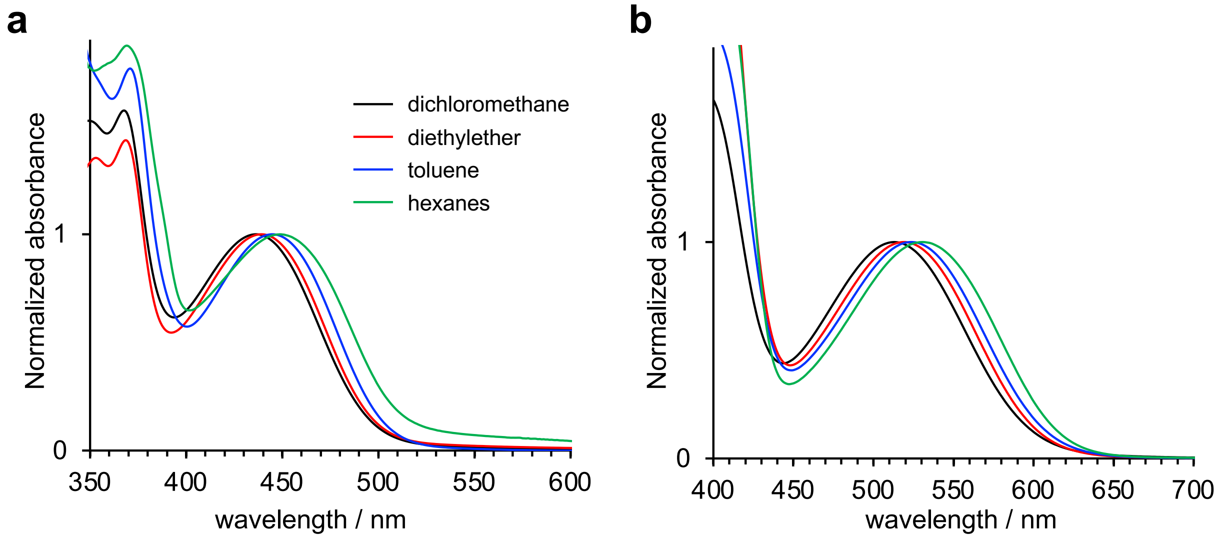


Figure S4. Normalized UV-Vis absorption spectra of equimolar solutions (1.0 x 10^{-4} M) of (a) $(^{\mathrm{CF3}}\mathbf{L2})_2\mathrm{Zn}$ and (b) $(^{t\mathrm{Bu}}\mathbf{L3})_2\mathrm{Zn}$ in solvents of varying polarities at 295 K.

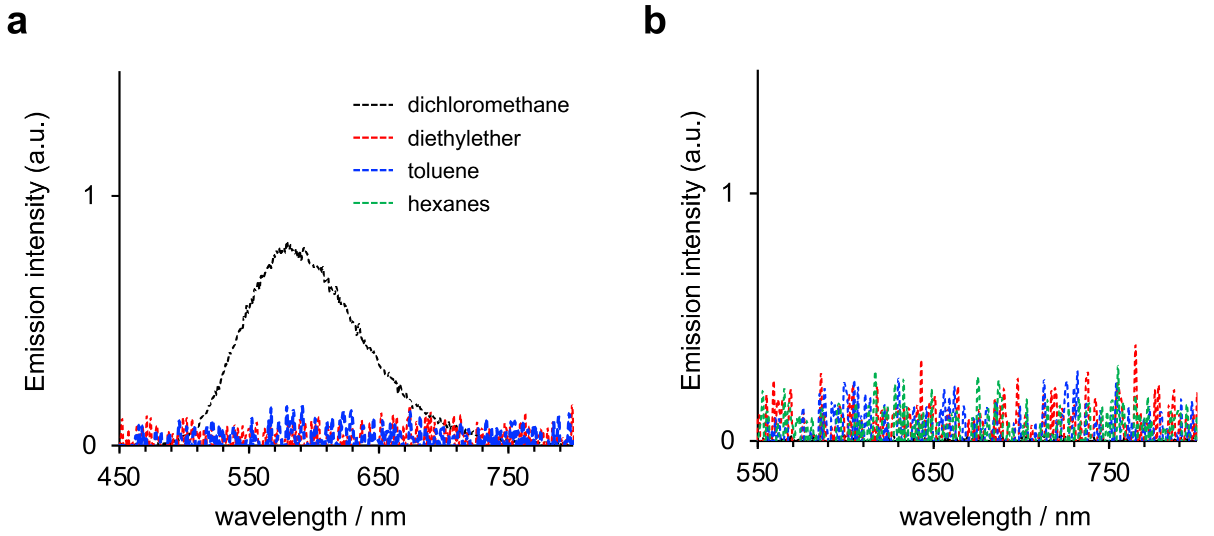


Figure S5. Emission spectra of equimolar solutions (1.0 x 10^{-4} M) of (a) $(^{\mathrm{CF3}}\mathbf{L2})_2\mathrm{Zn}$ and (b) $(^{t\mathrm{Bu}}\mathbf{L3})_2\mathrm{Zn}$ in solvents of varying polarities at 295 K.

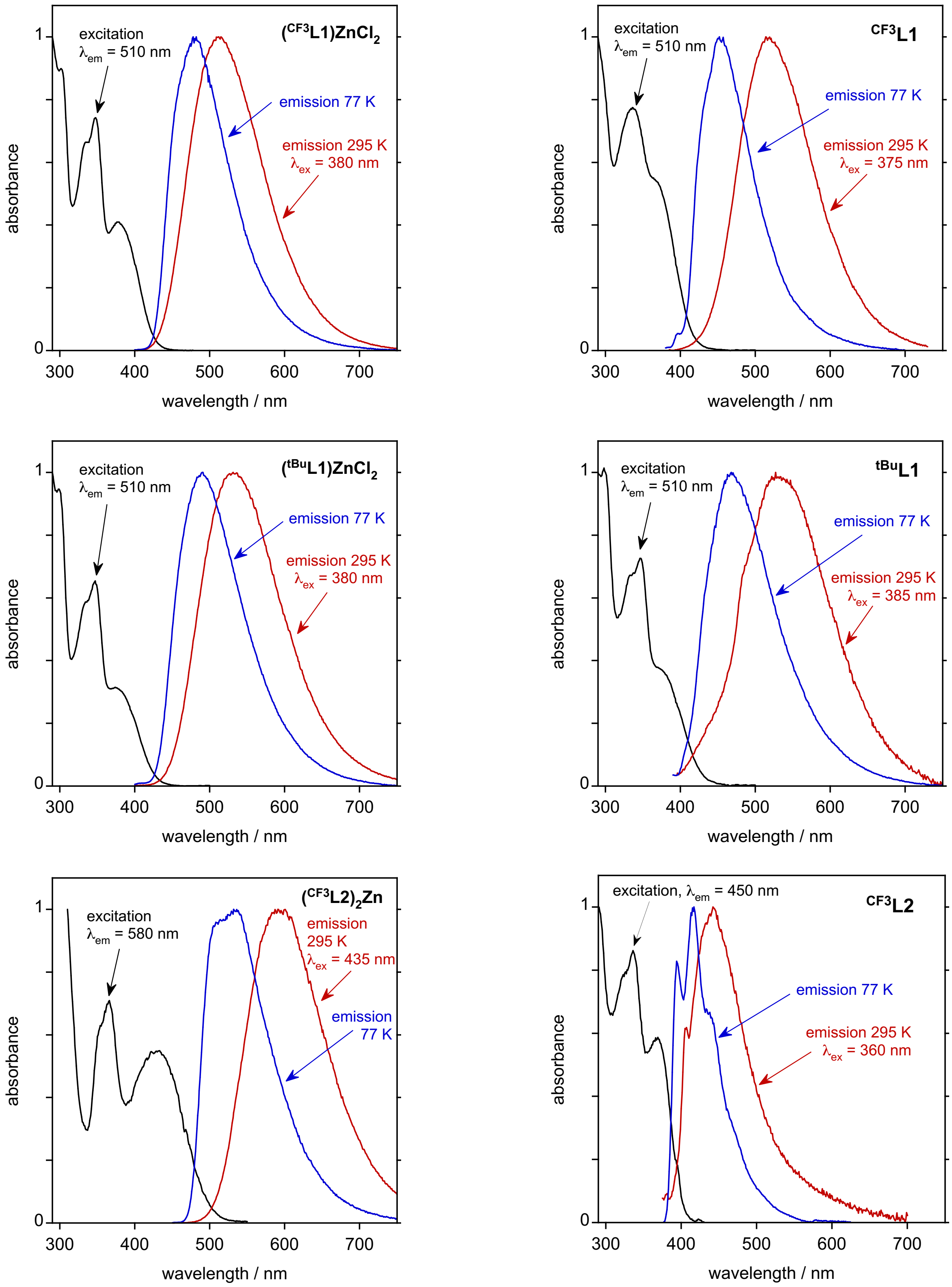


Figure S6. Emission and excitation spectra in CH_2Cl_2 at 295 K (red and black lines respectively, registered at the λ_{ex} and λ_{em} values shown), and emission in EPA at 77 K (blue lines, at the same λ_{ex}), for the zinc complexes indicated (left) and for the corresponding proligands (right).

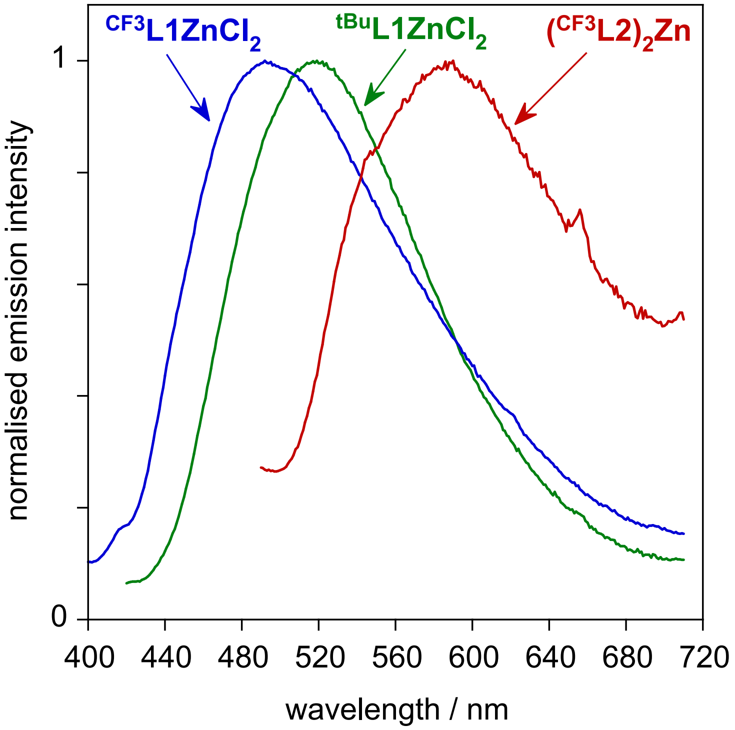


Figure S7. Normalized emission spectra in the solid state at 295 K: (^{CF3}**L1**)ZnCl$_2$ (λ_{ex} = 380 nm, blue line), (^{tBu}**L1**)ZnCl$_2$ (λ_{ex} = 400 nm, green line), and (^{CF3}**L2**)$_2$Zn (λ_{ex} = 400 nm, red line).

Table S1. Comparison of selected photophysical properties of Zn(II) systems.

Compound	**λ_{max} (abs)**	**λ_{em}**	**ϕ**	**Ref.**
[(PNNP)Zn]$_2$	425 (sh)	525	0.93	[1]
bis(*bis*-imidazo[1,2-*a*]pyridine)Zn(II) [BF$_4$]$_2$	341	450	0.50	[2]
(*meta*-(2-hydroxyphenyl)benzoxazole di(anisyl)amino)Zn(II)	400	500	0.50	[3]
(*para*-(2-hydroxyphenyl)benzoxazole di(anisyl)amino)Zn(II)	375	450	0.86	[3]
heteroleptic bis(dipyrrinato)zinc(II)	495	578	0.76	[4]
(N^N^O)$_2$Zn	366	593	0.06	[5]
(**^{CF3}L1**)ZnCl$_2$	380	512	0.64	*this work*
(**^{tBu}L1**)ZnCl$_2$	383	530	0.41	*this work*
(**^{CF3}L2**)$_2$Zn	436	595	0.26	*this work*

References for Table S1:

1 P. W. Roesky, Intensely Photoluminescent Diamidophosphines of the Alkaline-Earth Metals, Aluminum, and Zinc, *Angew. Chem., Int. Ed.*, 2018, **57**, 14265–14269.

2 V. Giuso, E. Jouaiti, C. Cebrián, S. Parant-Aury, N. Kyritsakas, C. Gourlaouen and M. Mauro, Symmetry-Broken Charge-Transfer Excited State in Homoleptic Zinc(II) Imidazo[1,2-a]pyridine Complexes, *ChemPhotoChem*, 2023, **7**, e202300092.

3 J. A. Kübler, B. Pfund and O. S. Wenger, Zinc(II) Complexes with Triplet Charge-Transfer Excited States Enabling Energy-Transfer Catalysis, Photoinduced Electron Transfer, and Upconversion, *JACS Au*, 2022, **2**, 2367–2380.

4 S. Kusaka, R. Sakamoto, Y. Kitagawa, M. Okumura and H. Nishihara, An Extremely Bright Heteroleptic Bis(dipyrrinato)zinc(II) Complex, *Chemistry – An Asian Journal*, 2012, **7**, 907–910.

5 I. B. Lozada, J. D. Braun, J. A. G. Williams and D. E. Herbert, Yellow-Emitting, Pseudo-Octahedral Zinc Complexes of Benzannulated N^N^O Pincer-Type Ligands, *Inorg. Chem.*, 2022, **61**, 17568–17578.

Structural Figures and Tables

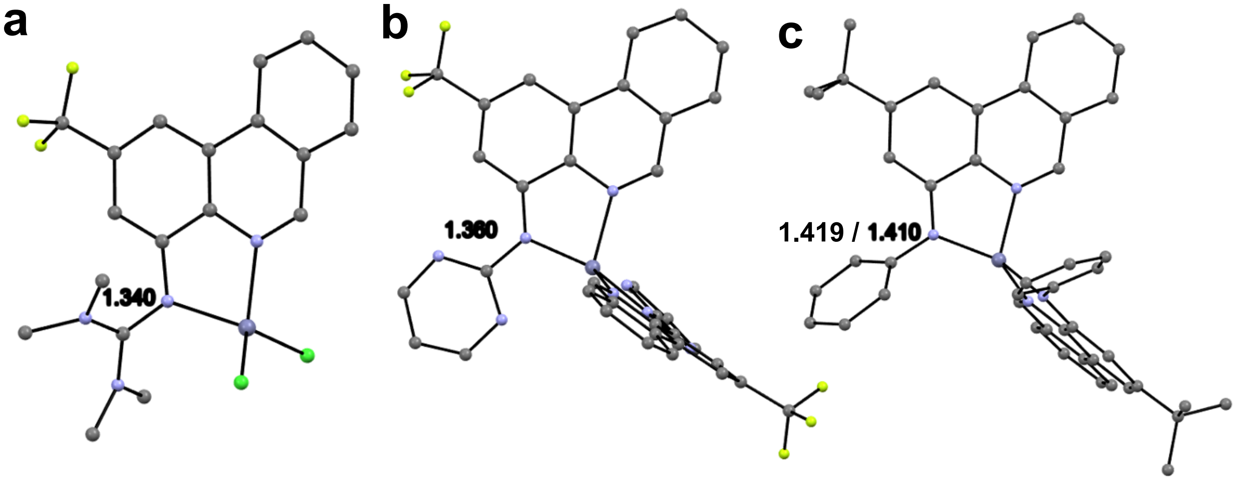


Figure S8. Comparison of C–N bond lengths of (a) (^{CF3}**L1**)ZnCl$_2$, (b) (^{CF3}**L2**)$_2$Zn, and (c) (^{tBu}**L3**)$_2$Zn in the solid state. Hydrogen atoms and solvent molecules omitted for clarity. Solid-state structure of (^{tBu}**L3**)$_2$Zn reproduced from Reference 1.

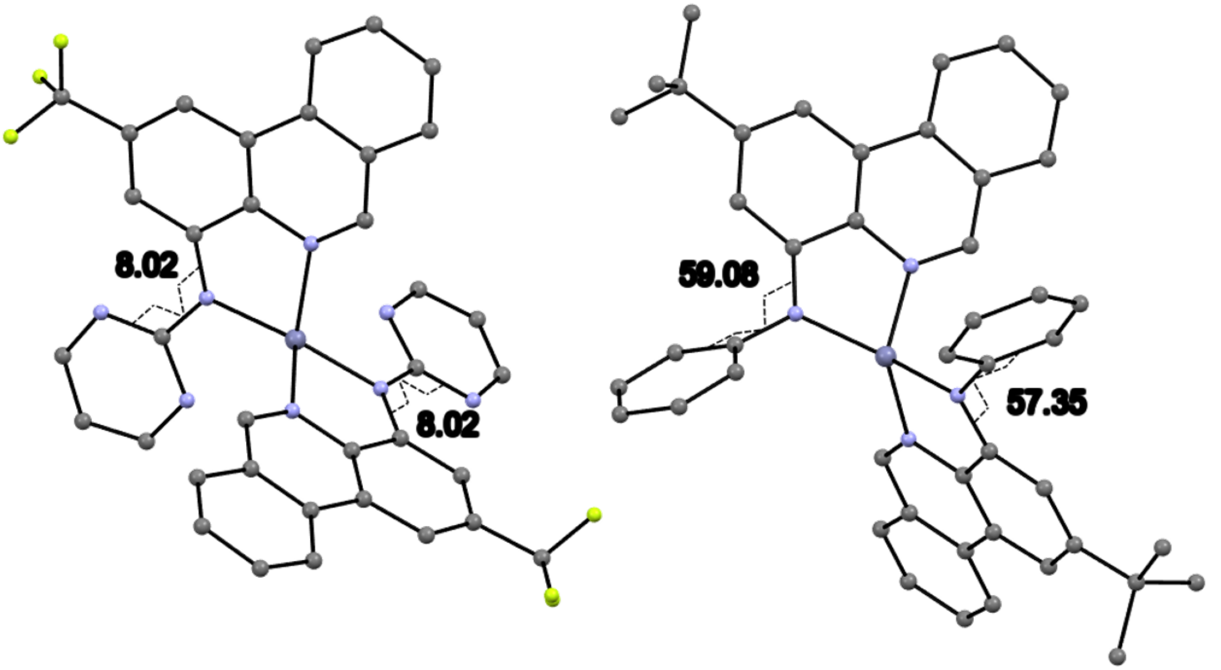


Figure S9. Torsion angles between ring fragments and phenanthridinyl planes in solid-state structures of (^{CF3}**L2**)$_2$Zn (C-N-C-N) and (^{tBu}**L3**)$_2$Zn (C-N-C-C). Hydrogen atoms and solvent molecules omitted for clarity. Solid-state structure of (^{tBu}**L3**)$_2$Zn reproduced from Reference 2.

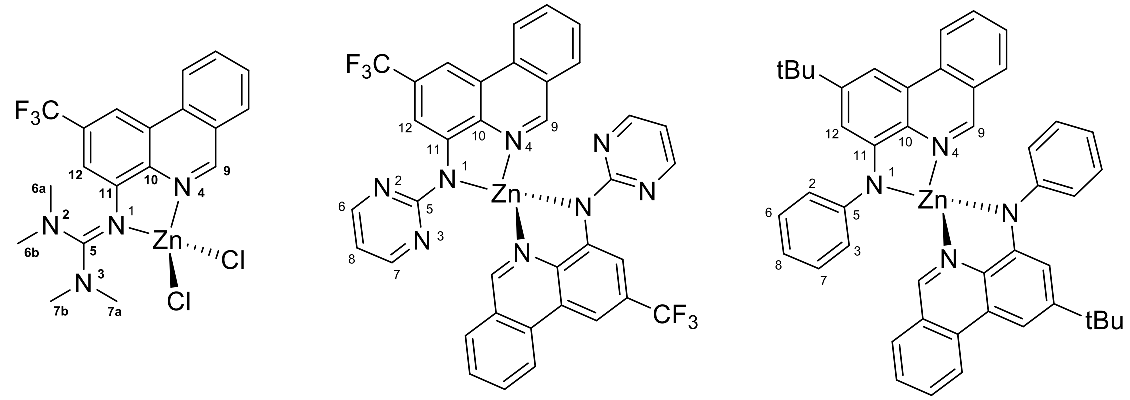


Figure S10. Atomic labels for Tables S2-S5.

Table S2. Comparison of experimentally determined and calculated[a] bond distances (Å) and angles (°) for (^{CF3}**L1**)ZnCl$_2$. See Figure S10 for numbering scheme.

Bond/Å	**(^{CF3}L1)ZnCl$_2$**		
	XRD	**DFT**	**|Δd|[b]**
N1-Zn	2.017	2.085	0.068
N4-Zn	2.067	2.109	0.042
N1-C5	1.340	1.341	0.001
N1-C11	1.402	1.388	0.014
N2-C5	1.347	1.362	0.015
N2-C6a	1.455	1.457	0.002
N2-C6b	1.451	1.459	0.008
N3-C5	1.336	1.355	0.019
N3-C7a	1.459	1.460	0.001
N3-C7b	1.451	1.459	0.008
C11-C12	1.370	1.400	0.030
C11-C10	1.417	1.440	0.023
N4-C9	1.297	1.306	0.009
N4-C10	1.380	1.380	0.000
MAD[c]			0.017
Angle/(°)	**XRD**	**DFT**	**|Δ angle|[b]**
N1-Zn-N4	81.31	80.03	1.3
C11-N1-Zn	112.8	113.1	0.3
C5-N1-Zn	118.9	118.3	0.6
Zn-N4-C9	128.7	126.4	2.3
Zn-N4-C10	112.1	112.7	0.6
C11-N1-C5	119.8	124.0	4.2
N1-C5-N2	122.4	123.0	0.6
N1-C5-N3	117.8	118.3	0.5
N2-C5-N3	119.7	118.5	1.2
C5-N2-C6a	126.4	121.4	5.0
C5-N2-C6b	123.1	122.9	0.2
C6a-N2-C6b	115.4	115.6	0.2
C5-N3-C7a	122.8	122.4	0.4
C5-N3-C7b	121.1	121.2	0.1
C7a-N3-C7b	115.7	115.2	0.5
N1-C11-C12	124.2	125.1	0.9
N1-C11-C10	116.6	117.1	0.5
C10-C11-C12	119.2	117.7	1.5
C11-C10-N4	116.5	116.9	0.4
C10-N4-C9	119.1	120.7	1.6
MAD[c]			1.1

[a] B3LYP (SMD “dichloromethane”/ def2-svp def2/j)

[b] Absolute difference between experimentally determined and calculated bond distances or angles

[c] Mean absolute deviation

Table S3. Comparison of experimentally determined and calculated[a] bond distances (Å) and angles (°) for (^{CF3}**L2**)$_2$Zn. See Figure S10 for numbering scheme.

Bond/Å	**(^{CF3}L2)$_2$Zn**		
	XRD	**DFT**	**|Δd|**[b]
N1-Zn	1.944	1.995	0.051
N4-Zn	2.097	2.126	0.029
N1-C5	1.360	1.359	0.001
N1-C11	1.375	1.373	0.002
N2-C5	1.343	1.350	0.007
N2-C6	1.335	1.335	0.000
N3-C5	1.355	1.365	0.01
N3-C7	1.328	1.326	0.002
C6-C8	1.366	1.394	0.028
C7-C8	1.378	1.402	0.024
C11-C12	1.396	1.402	0.006
C11-C10	1.439	1.451	0.012
N4-C9	1.291	1.307	0.016
N4-C10	1.391	1.379	0.012
MAD[c]			0.014
Angle/(°)	**XRD**	**DFT**	**|Δ angle|**[b]
N1-Zn-N4	81.23	80.44	0.8
C11-N1-Zn	117.0	116.4	0.6
C5-N1-Zn	116.1	114.7	1.4
Zn-N4-C9	129.5	128.2	1.3
Zn-N4-C10	110.6	110.9	0.3
C11-N1-C5	126.9	129.0	2.1
N1-C5-N2	122.4	123.5	1.1
N1-C5-N3	112.8	112.8	0.0
N2-C5-N3	124.9	123.6	1.3
C5-N2-C6	116.2	117.4	1.2
N2-C6-C8	123.5	123.1	0.4
C6-C8-C7	116.1	115.6	0.5
C5-N3-C7	116.3	117.9	1.6
N3-C7-C8	123.1	122.4	0.7
N1-C11-C12	128.2	127.5	0.7
N1-C11-C10	114.8	115.4	0.6
C10-C11-C12	117.0	117.2	0.2
C11-C10-N4	116.2	116.9	0.7
C10-N4-C9	119.9	120.9	1.0
MAD[c]			0.87

[a] B3LYP (SMD “dichloromethane”/ def2-svp def2/j)

[b] Absolute difference between experimentally determined and calculated bond distances or angles

[c] Mean absolute deviation

Table S4. Comparison of experimentally determined and calculated[a] bond distances (Å) and angles (°) for $({}^{t\mathrm{Bu}}\mathbf{L3})_2$Zn. Solid state structure of $({}^{t\mathrm{Bu}}\mathbf{L3})_2$Zn reproduced from Reference [1]. See Figure S10 for numbering scheme.

Bond/Å	**$({}^{\mathrm{tBu}}\mathrm{L3})_2\mathrm{Zn}$**		
	XRD	**DFT**	**|Δd|[b]**
N1-Zn	1.946	1.991	0.045
N4-Zn	2.060	2.075	0.015
N1-C5	1.410	1.397	0.013
N1-C11	1.372	1.371	0.001
C2-C5	1.397	1.417	0.020
C2-C6	1.388	1.398	0.010
C3-C5	1.386	1.417	0.031
C3-C7	1.384	1.396	0.012
C6-C8	1.378	1.400	0.022
C7-C8	1.390	1.401	0.011
C11-C12	1.392	1.407	0.015
C11-C10	1.435	1.450	0.015
N4-C9	1.307	1.309	0.002
N4-C10	1.382	1.378	0.004
MAD[c]			0.015
Angle/(°)	**XRD**	**DFT**	**|Δ angle|[b]**
N1-Zn-N4	82.72	83.20	0.5
C11-N1-Zn	114.1	112.6	1.5
C5-N1-Zn	125.9	122.0	3.9
Zn-N4-C9	129.4	128.9	0.5
Zn-N4-C10	110.5	106.7	3.8
C11-N1-C5	120.0	124.9	4.9
N1-C5-C2	122.6	124.4	1.8
N1-C5-C3	119.1	118.5	0.6
C2-C5-C3	118.2	117.0	1.2
C5-C2-C6	120.4	121.1	0.7
C2-C6-C8	120.8	121.1	0.3
C6-C8-C7	119.1	118.6	0.5
C5-C3-C7	121.0	121.6	0.6
C3-C7-C8	120.6	120.7	0.1
N1-C11-C12	126.8	126.6	0.2
N1-C11-C10	116.6	117.0	0.4
C10-C11-C12	116.5	116.3	0.2
C11-C10-N4	115.7	117.0	1.3
C10-N4-C9	119.8	121.2	1.4
MAD[c]			1.3

[a] B3LYP (SMD “dichloromethane”/ def2-svp def2/j)

[b] Absolute difference between experimentally determined and calculated bond distances or angles

[c] Mean absolute deviation

Table S5. Comparison of solid-state structure bond distances (Å) and angles (°) of complexes of varying N_{amido} character. Solid state structure of $(^{tBu}\mathbf{L3})_2Zn$ reproduced from Reference [1]. See Figure S10 for numbering scheme.

Bond/Å	**$(^{CF3}\mathbf{L1})ZnCl_2$**	**$(^{CF3}\mathbf{L2})_2Zn$**	**$(^{tBu}\mathbf{L3})_2Zn$**	**|Δd|**[a]	**|Δd|**[b]	**|Δd|**[c]
N1-Zn	2.017	1.944	1.946	0.073	0.071	0.002
N4-Zn	2.067	2.097	2.060	0.03	0.007	0.037
N1-C5	1.340	1.360	1.410	0.02	0.07	0.05
N1-C11	1.402	1.375	1.372	0.027	0.03	0.003
C2-C5/ N2-C5	1.347	1.343	1.397	0.004	0.05	0.054
C2-C6/ N2-C6	n/a	1.335	1.388	n/a	n/a	0.053
C3-C5/ N3-C5	1.336	1.355	1.386	0.019	0.05	0.031
C3-C7/ N3-C7	n/a	1.328	1.384	n/a	n/a	0.056
N2-C6a	1.455	n/a	n/a	n/a	n/a	n/a
N2-C6b	1.451	n/a	n/a	n/a	n/a	n/a
N3-C7a	1.459	n/a	n/a	n/a	n/a	n/a
N3-Cb	1.451	n/a	n/a	n/a	n/a	n/a
C6-C8	n/a	1.366	1.378	n/a	n/a	0.012
C7-C8	n/a	1.378	1.390	n/a	n/a	0.012
C11-C12	1.370	1.396	1.392	0.026	0.022	0.004
C11-C10	1.417	1.439	1.435	0.022	0.018	0.004
N4-C9	1.297	1.291	1.307	0.006	0.01	0.016
N4-C10	1.380	1.391	1.382	0.011	0.002	0.009
MAD[d]				0.023	0.033	0.0245
Angle/(°)	**$(^{CF3}\mathbf{L1})ZnCl_2$**	**$(^{CF3}\mathbf{L2})_2Zn$**	**$(^{tBu}\mathbf{L3})_2Zn$**	**|Δ angle|**[a]	**|Δ angle|**[b]	**|Δ angle|**[c]
N1-Zn-N4	81.3	81.2	82.7	0.1	1.4	1.5
C11-N1-Zn	112.8	117.0	114.1	4.2	1.3	2.9
C5-N1-Zn	118.9	116.1	125.9	2.8	7	9.8
Zn-N4-C9	128.7	129.5	129.4	0.8	0.7	0.1
Zn-N4-C10	112.1	110.6	110.5	1.5	1.6	0.1
C11-N1-C5	119.8	126.9	120.0	7.1	0.2	6.9
N1-C5-C2/ N1-C5-N2/	122.4	122.4	122.6	0	0.2	0.2
N1-C5-C3/ N1-C5-N3	117.8	112.8	119.1	5	1.3	6.3
C2-C5-C3/ N2-C5-N3	119.7	124.9	118.2	5.2	1.5	6.7
C5-C2-C6/ C5-N2-C6	n/a	116.2	120.4	n/a	n/a	4.2
C2-C6-C8/ N2-C6-C8	n/a	123.5	120.8	n/a	n/a	2.7
C5-N2-C6a	126.4	n/a	n/a	n/a	n/a	
C5-N2-C6b	123.1	n/a	n/a	n/a	n/a	
C6a-N2-C6b	115.4	n/a	n/a	n/a	n/a	
C5-N3-C7a	122.8	n/a	n/a	n/a	n/a	
C5-N3-C7b	121.1	n/a	n/a	n/a	n/a	
C7a-N3-C7b	115.7	n/a	n/a	n/a	n/a	
C6-C8-C7	n/a	116.1	119.1	n/a	n/a	3
C5-C3-C7/ C5-N3-C7	n/a	116.3	121.0	n/a	n/a	4.7

C3-C7-C8/ N3-C7-C8	n/a	123.1	120.6	n/a	n/a	2.5
N1-C11-C12	124.2	128.2	126.8	4	2.6	1.4
N1-C11-C10	116.6	114.8	116.6	1.8	0	1.8
C10-C11-C12	119.2	117.0	116.5	2.2	2.7	0.5
C11-C10-N4	116.5	116.2	115.7	0.3	0.8	0.5
C10-N4-C9	119.1	119.9	119.8	0.8	0.7	0.1
MAD[d]				2.557	1.571	2.942

[a] Absolute difference between solid-state structure bond distances or angles of ($^{\mathrm{CF3}}$**L1**)ZnCl$_2$ and ($^{\mathrm{CF3}}$**L2**)$_2$Zn

[b] Absolute difference between solid-state structure bond distances or angles of ($^{\mathrm{CF3}}$**L1**)ZnCl$_2$ and ($^{t\mathrm{Bu}}$**L3**)$_2$Zn

[c] Absolute difference between solid-state structure bond distances or angles of ($^{\mathrm{CF3}}$**L2**)$_2$Zn and ($^{t\mathrm{Bu}}$**L3**)$_2$Zn

[d] Mean absolute deviation

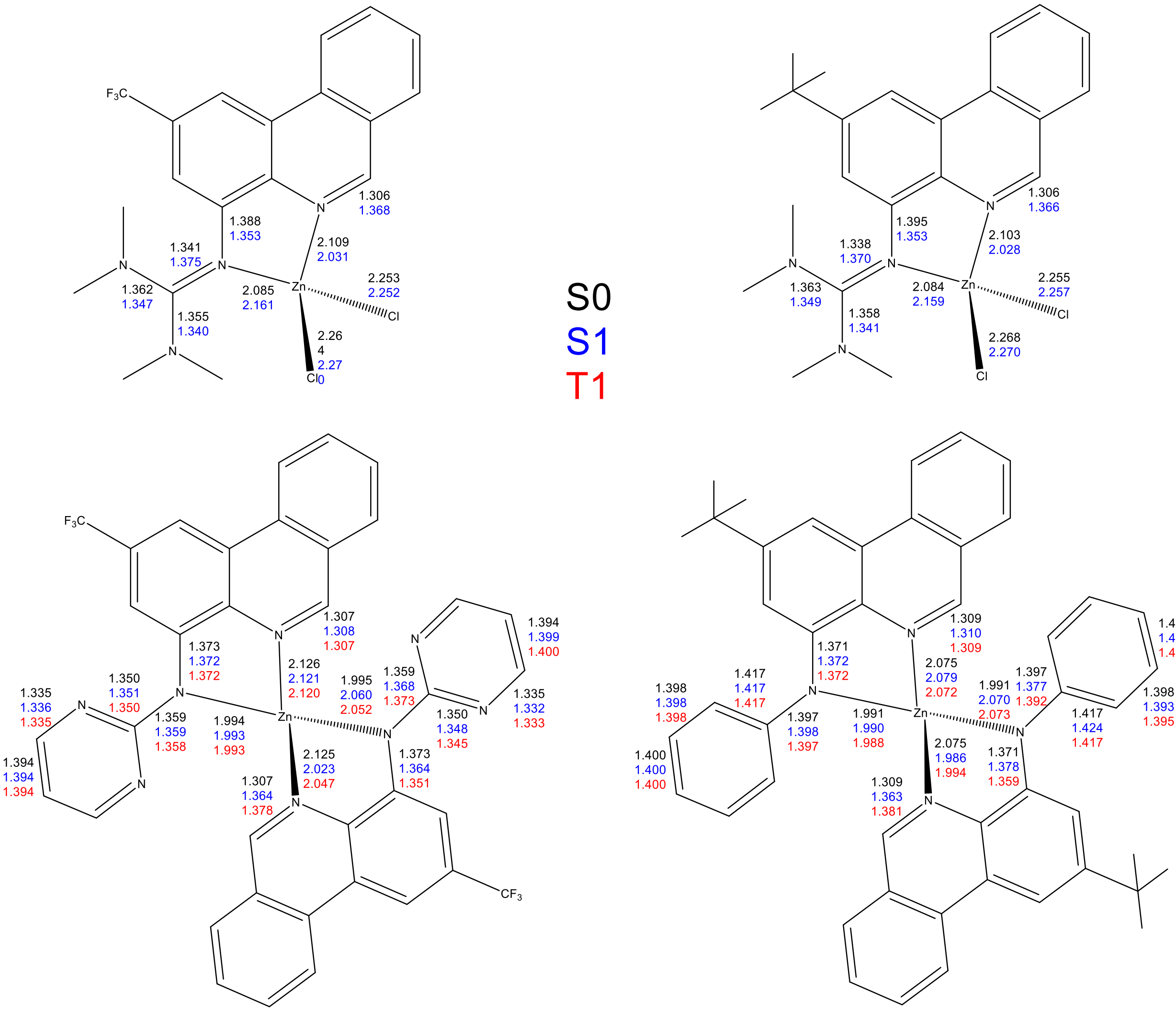


Figure S11. Select calculated bond distances (Å) at the S0, S1, and T1 optimized[a] geometries.
[a] B3LYP (SMD "dichloromethane"/ def2-svp def2/j)

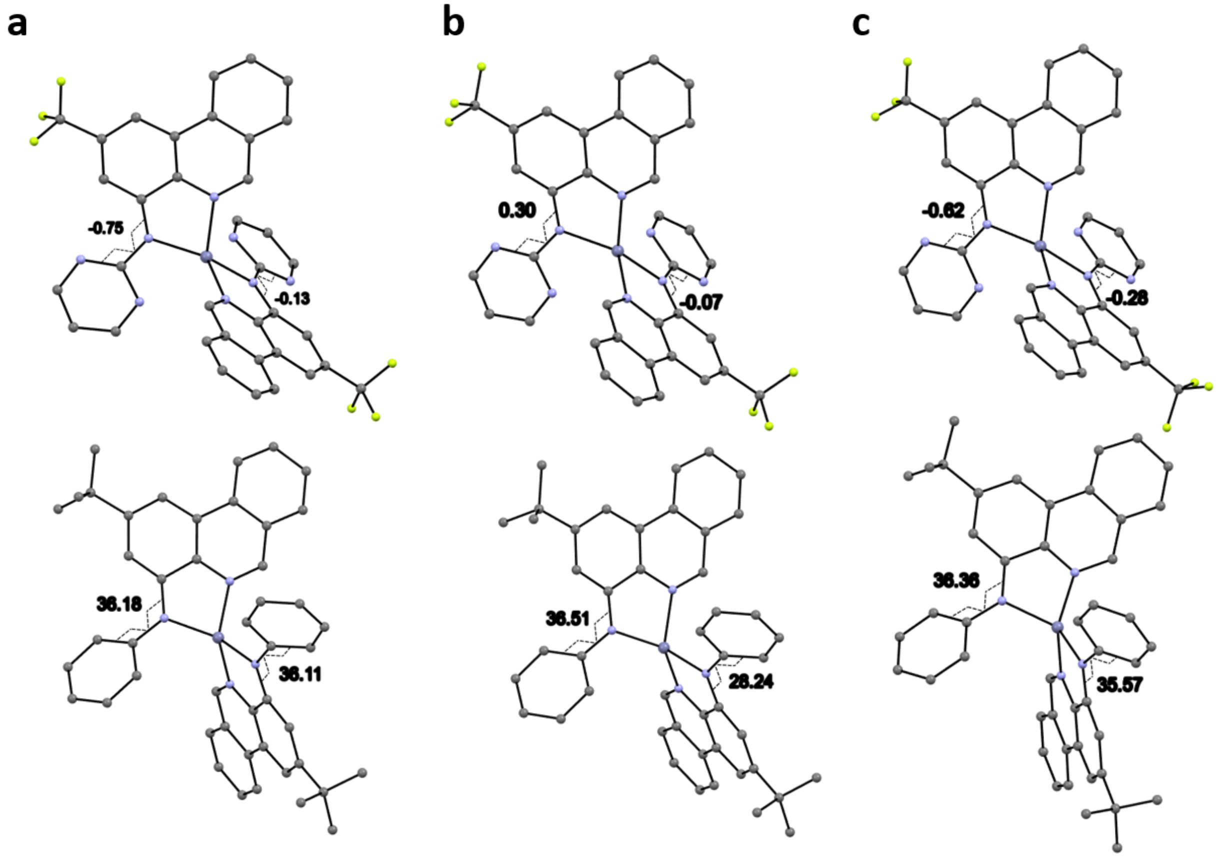


Figure S12. Torsion angles between ring fragments and phenanthridinyl planes in (a) S_0, (b) S_1, and (c) T_1 optimized geometies of $(^{CF3}\mathbf{L2})_2$Zn (C-N-C-N) and $(^{tBu}\mathbf{L3})_2$Zn (C-N-C-C). Hydrogens omitted for clarity.

Computational Figures and Tables

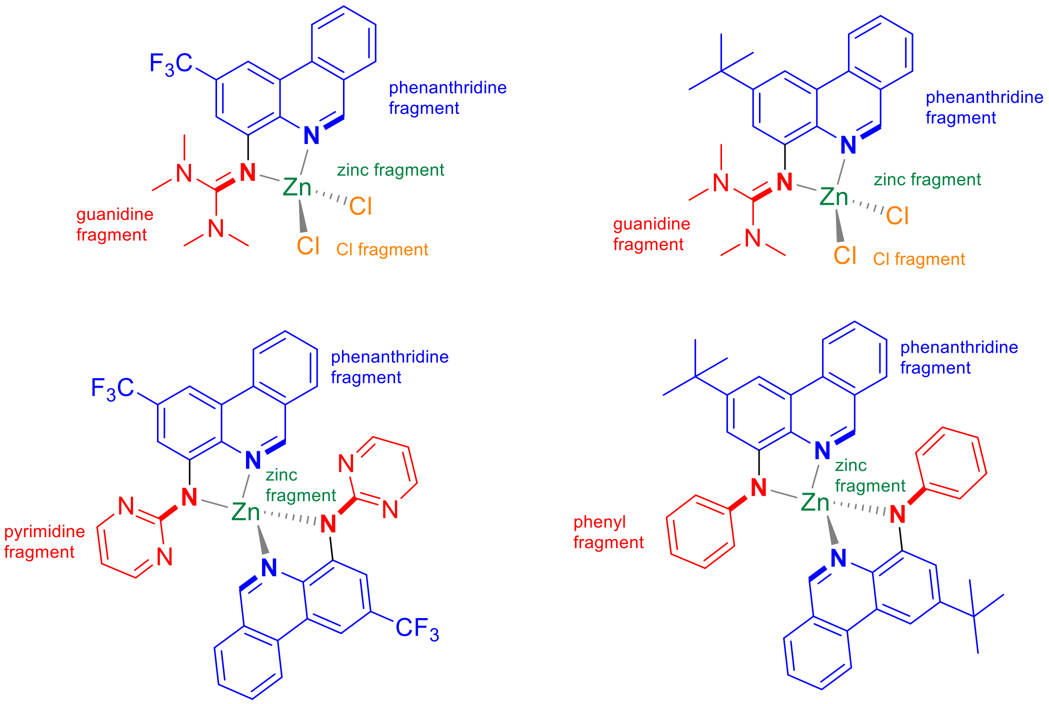


Figure S13. Defined fragments for Tables S8, S10, S12, and S14. C=N sub-fragments are indicated in figure by bolded line and lettering.

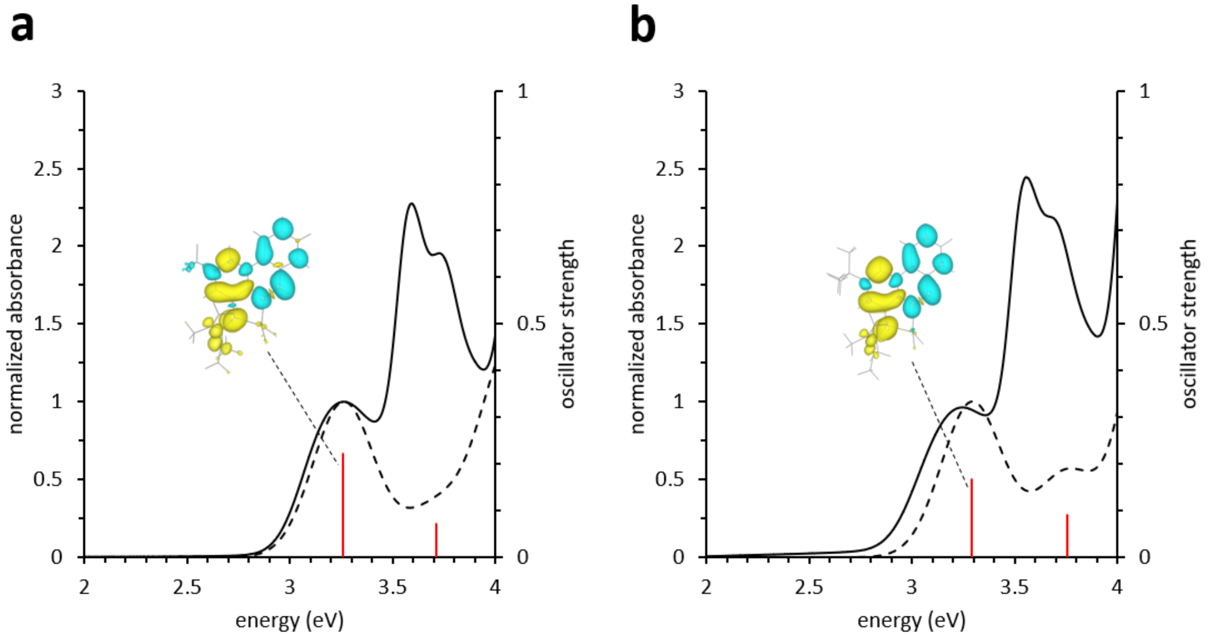


Figure S14. Normalized experimental UV-Vis absorption spectrum (solid trace, dichloromethane), normalized TD-DFT simulated spectrum (dotted trace, FWHM = 0.35 eV, SMD "dichloromethane"), predicted singlet-singlet vertical excitation energies ($f_{\mathrm{osc}} > 0.07$), and electron-hole density maps (yellow = hole; blue = electron; isosurface value = 0.001) for the lowest-energy vertical electronic transitions of (a) (**^{CF3}L1**)ZnCl$_2$ and (b) (**^{tBu}L1**)ZnCl$_2$.

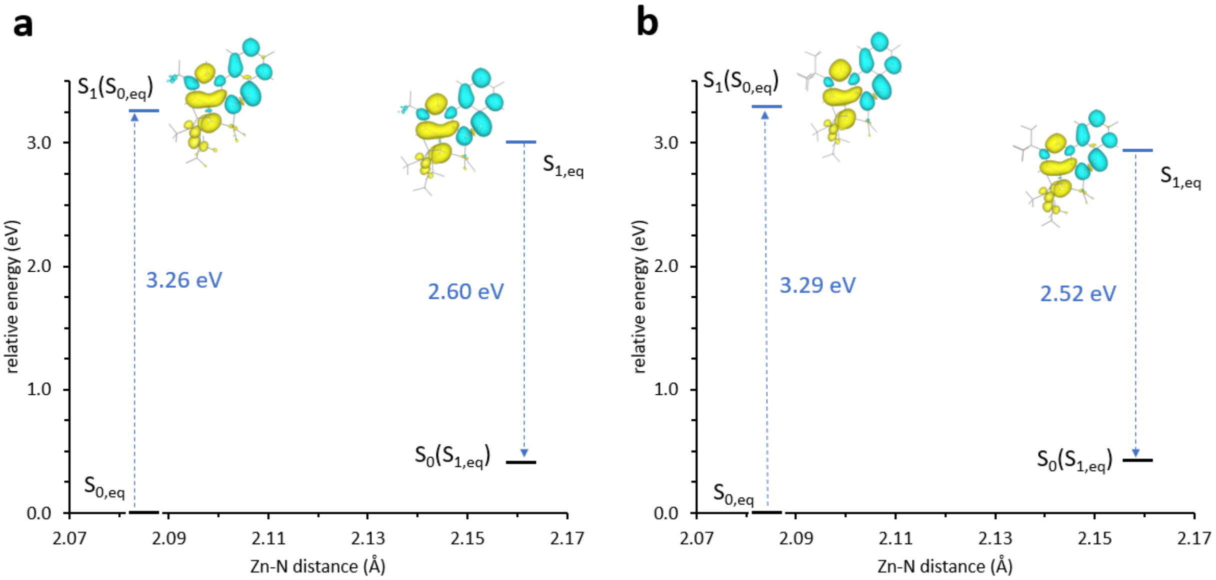


Figure S15. Jablonski diagram for (a) (**^{CF3}L1**)ZnCl$_2$ and (b) (**^{tBu}L1**)ZnCl$_2$ along the Zn-N$_{guanidine}$ bond at the equilibrium S$_0$ and S$_1$ optimized geometries, with electron-hole density maps (yellow = hole; blue = electron; isosurface value = 0.001).

Table S6. TD-DFT predicted singlet-singlet vertical excitation energies, oscillator strengths (f_{osc} > 0.07), and MO pair contributions (>10%) below 4 eV for (**^{CF3}L1**)ZnCl$_2$ in dichloromethane. H=HOMO; L=LUMO

No.	E (eV)	f_{osc}	MO contributions
1	3.26	0.22	H→L 97%
2	3.71	0.07	H-1→L 48%, H→L+1 49%

Table S7. Fragment contributions to select ground-state MOs of (**^{CF3}L1**)ZnCl$_2$ in dichloromethane.

MO	E (eV)	Zn (%)	Phenanthridine (%)			Guanidine (%)		Cl (%)
			full	C=N	CF3	full	C=N	
LUMO+1	-1.55	0	93	3	1	5	3	0
LUMO	-2.14	1	95	33	2	2	2	0
HOMO	-6.33	1	63	4	1	31	22	2
HOMO-1	-7.01	0	98	8	1	1	0	1

Table S8. TD-DFT predicted singlet-singlet vertical excitation energies, oscillator strengths (f_{osc} > 0.07), and MO pair contributions (>10%) below 4 eV for ($^{t\text{Bu}}$**L1**)ZnCl$_2$ in dichloromethane. H=HOMO; L=LUMO

No.	**E (eV)**	f_{osc}	**MO contributions**
1	3.29	0.17	H→L 95%
2	3.76	0.09	H-1→L 42%, H→L+1 50%

Table S9. Fragment contributions to select ground-state MOs of ($^{t\text{Bu}}$**L1**)ZnCl$_2$ in dichloromethane.

MO	**E (eV)**	**Zn (%)**	**Phenanthridine (%)**			**Guanidine (%)**		**Cl (%)**
			full	**C=N**	**tBu**	**full**	**C=N**	
LUMO+1	-1.37	0	93	3	2	6	3	0
LUMO	-1.93	1	95	33	1	3	1	1
HOMO	-6.11	1	67	5	2	30	19	1
HOMO-1	-6.74	0	99	9	3	1	0	0

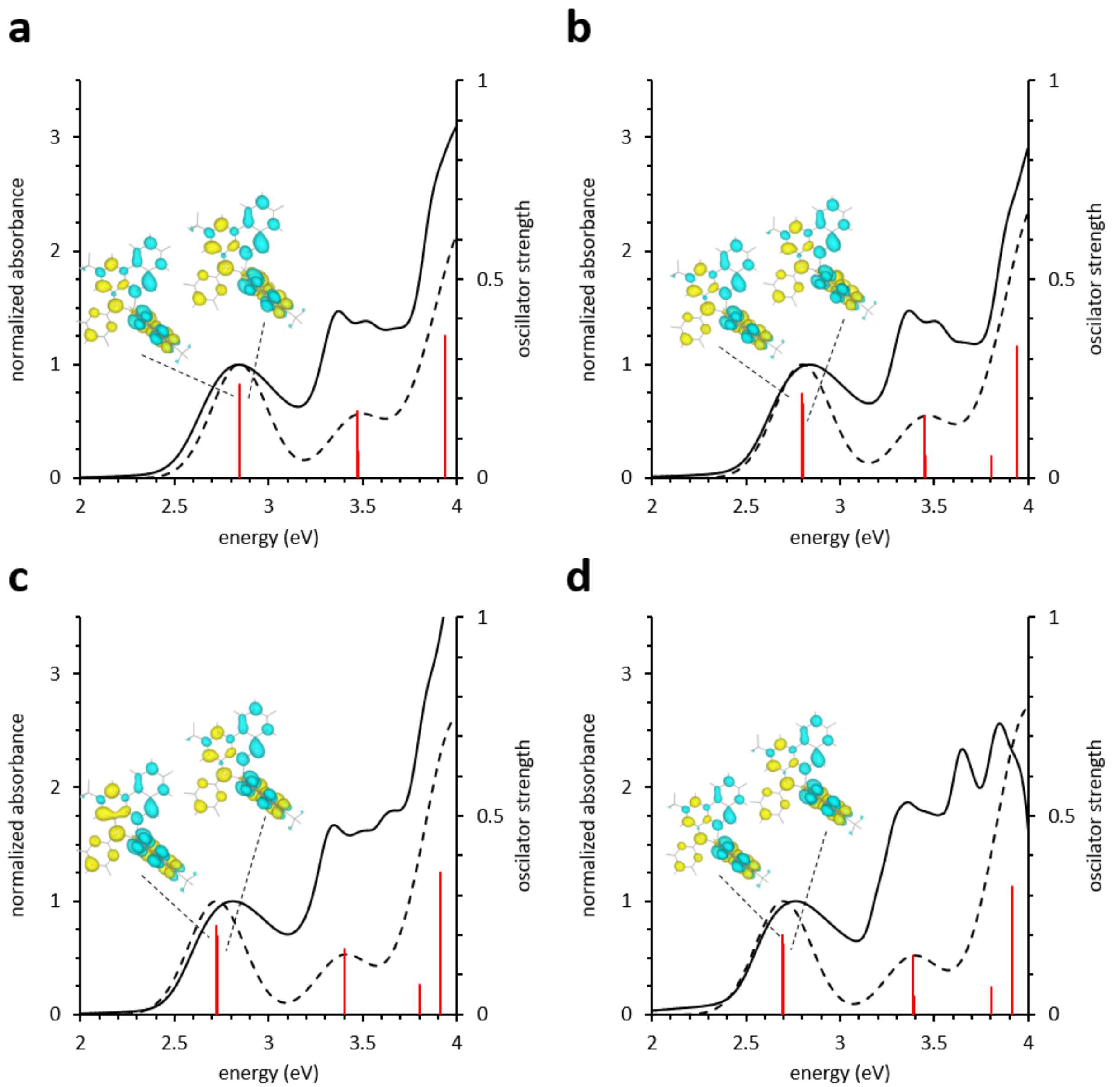


Figure S16. Normalized experimental UV-Vis absorption spectrum (solid trace), normalized TD-DFT simulated spectrum (dotted trace, FWHM = 0.35 eV), predicted singlet-singlet vertical excitation energies ($f_{\mathrm{osc}} > 0.05$), and electron-hole density maps (yellow = hole; blue = electron; isosurface value = 0.001) for the lowest-energy vertical electronic transitions of $(^{\mathbf{CF3}}\mathbf{L2})_2$Zn in (a) dichloromethane, (b) diethyl ether, (c) toluene, and (d) n-hexane.

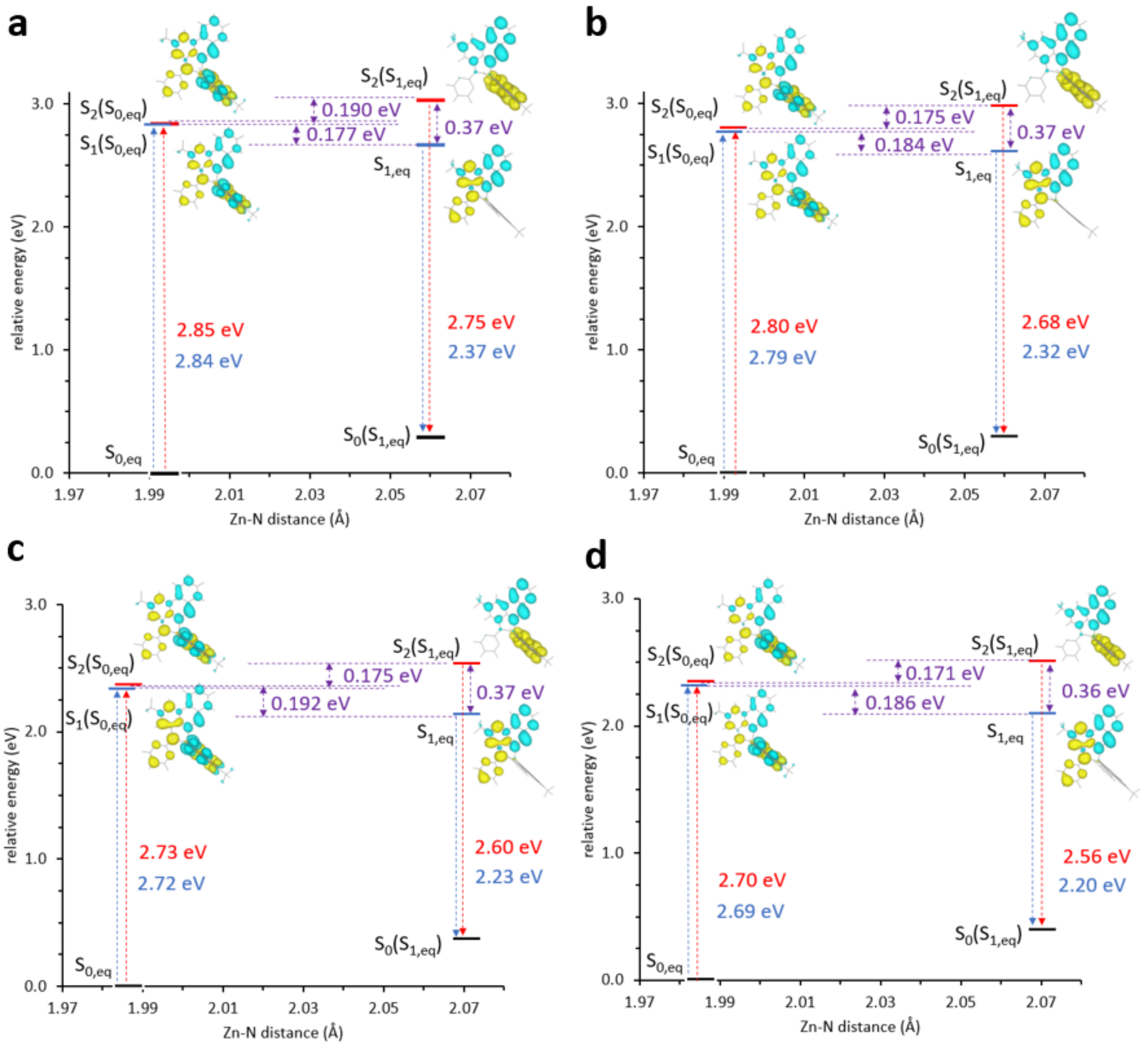


Figure S17. Jablonski diagram in the singlet manifold for $(^{CF3}\mathbf{L2})_2$Zn along the Zn-N$_{pyrimidine}$ bond at the equilibrium S_0 and S_1 optimized geometries, with electron-hole density maps (yellow = hole; blue = electron; isosurface value = 0.001) in (a) dichloromethane, (b) diethyl ether, (c) toluene, and (d) n-hexane.

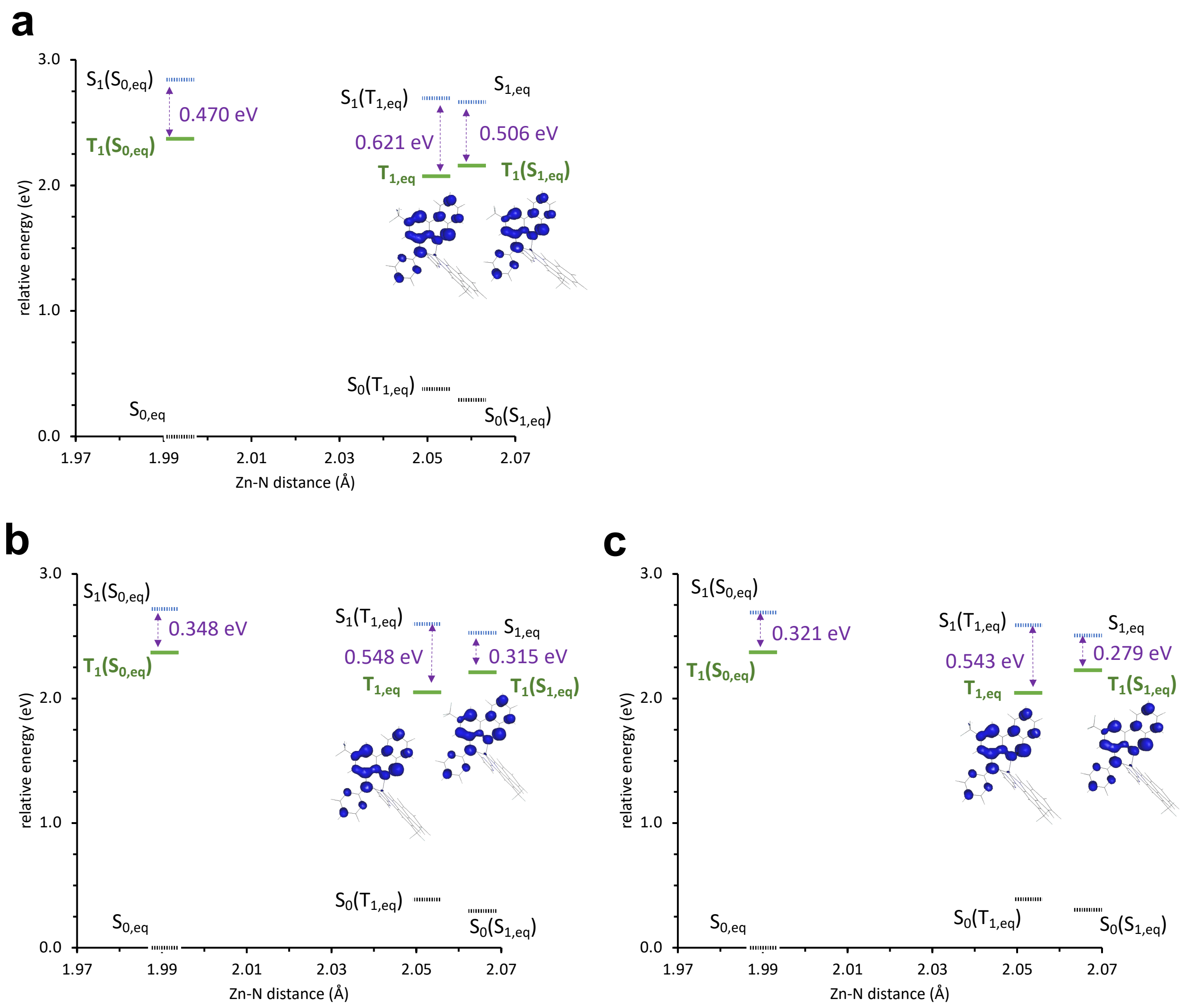


Figure S18. Jablonski diagram with T_1 states for $(^{\mathbf{CF3}}\mathbf{L2})_2$Zn along the Zn-N$_{\text{pyrimidine}}$ bond at the equilibrium S_0, S_1, and T_1 optimized geometries, with spin density maps (isosurface value = 0.004) in (a) dichloromethane, (b) toluene and (c) n-hexane.

Table S10. TD-DFT predicted singlet-singlet vertical excitation energies, oscillator strengths ($f_{\text{osc}} > 0.05$), and MO pair contributions (>10%) for $(^{\mathbf{CF3}}\mathbf{L2})_2$Zn in dichloromethane. H=HOMO; L=LUMO

No.	**E (eV)**	$\boldsymbol{f_{\text{osc}}}$	**MO contributions**
1	2.84	0.23	H-1→L 49%, H→L+1 49%
2	2.85	0.21	H→L 53%, H-1→L+1 45%
5	3.47	0.17	H-1→L+2 42%, H→L+3 38%
6	3.48	0.065	H-1→L+3 39%, H→L+2 39%
12	3.94	0.36	H-3→L+1 36%, H-2→L 39%

Table S11. Fragment contributions to select ground-state MOs of $(^{\mathrm{CF3}}\mathbf{L2})_2$Zn in dichloromethane.

MO	E	Zn	Phen 1 (%)			Pyrim 1 (%)		Phen 2 (%)			Pyrim 2 (%)	
	(eV)	(%)	full	C=N	CF3	full	C-N	full	C=N	CF3	full	C-N
LUMO+3	-1.41	0	40	1	0	4	1	51	5	0	5	2
LUMO+2	-1.41	0	51	2	0	5	2	40	4	0	4	1
LUMO+1	-2.04	1	49	16	1	2	1	47	8	1	2	1
LUMO	-2.05	1	47	16	1	2	1	49	8	1	2	1
HOMO	-5.77	2	26	2	0	30	13	23	3	0	23	11
HOMO-1	-5.78	2	23	2	0	26	11	26	4	0	26	13
HOMO-2	-6.91	0	49	4	1	0	0	51	6	1	0	0
HOMO-3	-6.91	0	51	4	2	0	0	49	6	1	0	0

Table S12. TD-DFT predicted singlet-singlet vertical excitation energies, oscillator strengths ($f_{\mathrm{osc}} > 0.05$), and MO pair contributions (>10%) for $(^{\mathrm{CF3}}\mathbf{L2})_2$Zn in diethyl ether. H=HOMO; L=LUMO

No.	E (eV)	f_{osc}	MO contributions
1	2.79	0.21	H-1→L 49%, H→L+1 49%
2	2.80	0.19	H→L 52%, H-1→L+1 45%
5	3.45	0.16	H-1→L+2 42%, H→L+3 37%
6	3.45	0.056	H-1→L+3 40%, H→L+2 38%
10	3.80	0.056	H-1→L+4 45%, H→L+5 35%
12	3.94	0.33	H-3→L+1 36%, H-2→L 39%

Table S13. Fragment contributions to select ground-state MOs of $(^{\mathrm{CF3}}\mathbf{L2})_2$Zn in diethyl ether.

MO	E	Zn	Phen 1 (%)			Pyrim 1 (%)		Phen 2 (%)			Pyrim 2 (%)	
	(eV)	(%)	full	C=N	CF3	full	C-N	full	C=N	CF3	full	C-N
LUMO+3	-1.43	0	40	1	0	4	1	52	2	0	4	1
LUMO+2	-1.43	0	52	2	0	5	1	39	1	0	3	1
LUMO+1	-2.07	1	50	17	1	2	1	36	15	1	1	1
LUMO	-2.08	1	45	16	1	2	1	40	17	1	2	1
HOMO	-5.76	2	24	2	0	33	12	25	2	0	25	13
HOMO-1	-5.76	2	26	2	0	35	12	23	2	0	23	11
HOMO-2	-6.94	0	49	4	1	1	0	47	4	1	1	0
HOMO-3	-6.94	0	50	4	1	1	0	47	4	1	1	0

Table S14. TD-DFT predicted singlet-singlet vertical excitation energies, oscillator strengths (f_{osc} > 0.05), and MO pair contributions (>10%) for (^{CF3}**L2**)$_2$Zn in toluene. H=HOMO; L=LUMO

No.	E (eV)	f_{osc}	MO contributions
1	2.72	0.22	H-1→L 49%, H→L+1 48%
2	2.73	0.20	H→L 51%, H-1→L+1 46%
5	3.40	0.17	H-1→L+2 42%, H→L+3 36%
6	3.40	0.052	H-1→L+3 42%, H→L+2 38%
10	3.80	0.076	H-1→L+4 50%, H→L+5 37%
12	3.91	0.36	H-3→L+1 32%, H-2→L 25%, H-4→L 16%

Table S15. Fragment contributions to select ground-state MOs of (^{CF3}**L2**)$_2$Zn in toluene.

MO	E	Zn	Phen 1 (%)			Pyrim 1 (%)		Phen 2 (%)			Pyrim 2 (%)	
	(eV)	(%)	full	C=N	CF3	full	C-N	full	C=N	CF3	full	C-N
LUMO+3	-1.47	0	40	1	0	3	1	53	2	0	4	1
LUMO+2	-1.47	0	54	2	0	4	1	39	1	0	3	1
LUMO+1	-2.11	1	48	16	1	1	1	38	16	1	1	1
LUMO	-2.12	1	48	16	1	1	1	38	16	1	1	1
HOMO	-5.75	2	45	3	0	44	22	5	1	0	5	3
HOMO-1	-5.75	2	5	1	0	5	2	42	3	0	39	21
HOMO-2	-6.97	0	48	4	1	2	0	46	4	1	1	0
HOMO-3	-6.98	0	49	4	1	1	0	46	4	1	1	0

Table S16. TD-DFT predicted singlet-singlet vertical excitation energies, oscillator strengths (f_{osc} > 0.05), and MO pair contributions (>10%) for (^{CF3}**L2**)$_2$Zn in n-hexane. H=HOMO; L=LUMO

No.	E (eV)	f_{osc}	MO contributions
1	2.69	0.20	H-1→L 48%, H→L+1 48%
2	2.70	0.18	H→L 51%, H-1→L+1 46%
5	3.39	0.15	H-1→L+2 42%, H→L+3 36%
10	3.81	0.070	H-1→L+4 50%, H→L+5 37%
12	3.92	0.32	H-4→L+1 39%, H-5→L+1 35%

Table S17. Fragment contributions to select ground-state MOs of $(^{\mathrm{CF3}}\mathbf{L2})_2\mathrm{Zn}$ in n-hexane.

MO	**E**	**Zn**	**Phen 1 (%)**			**Pyrim 1 (%)**		**Phen 2 (%)**			**Pyrim 2 (%)**	
	(eV)	**(%)**	**full**	**C=N**	**CF3**	**full**	**C-N**	**full**	**C=N**	**CF3**	**full**	**C-N**
LUMO+3	-1.49	0	22	1	0	2	1	71	2	0	5	2
LUMO+2	-1.49	0	71	2	0	5	2	22	1	0	2	1
LUMO+1	-2.13	1	47	16	1	1	1	49	17	1	1	1
LUMO	-2.15	1	49	17	1	1	1	47	16	1	1	1
HOMO	-5.74	2	30	2	0	30	15	19	1	0	19	9
HOMO-1	-5.75	2	19	1	0	19	10	29	2	0	30	15
HOMO-2	-7.00	0	41	3	1	8	1	43	4	1	7	1
HOMO-3	-7.00	0	47	4	1	3	0	45	4	1	5	0

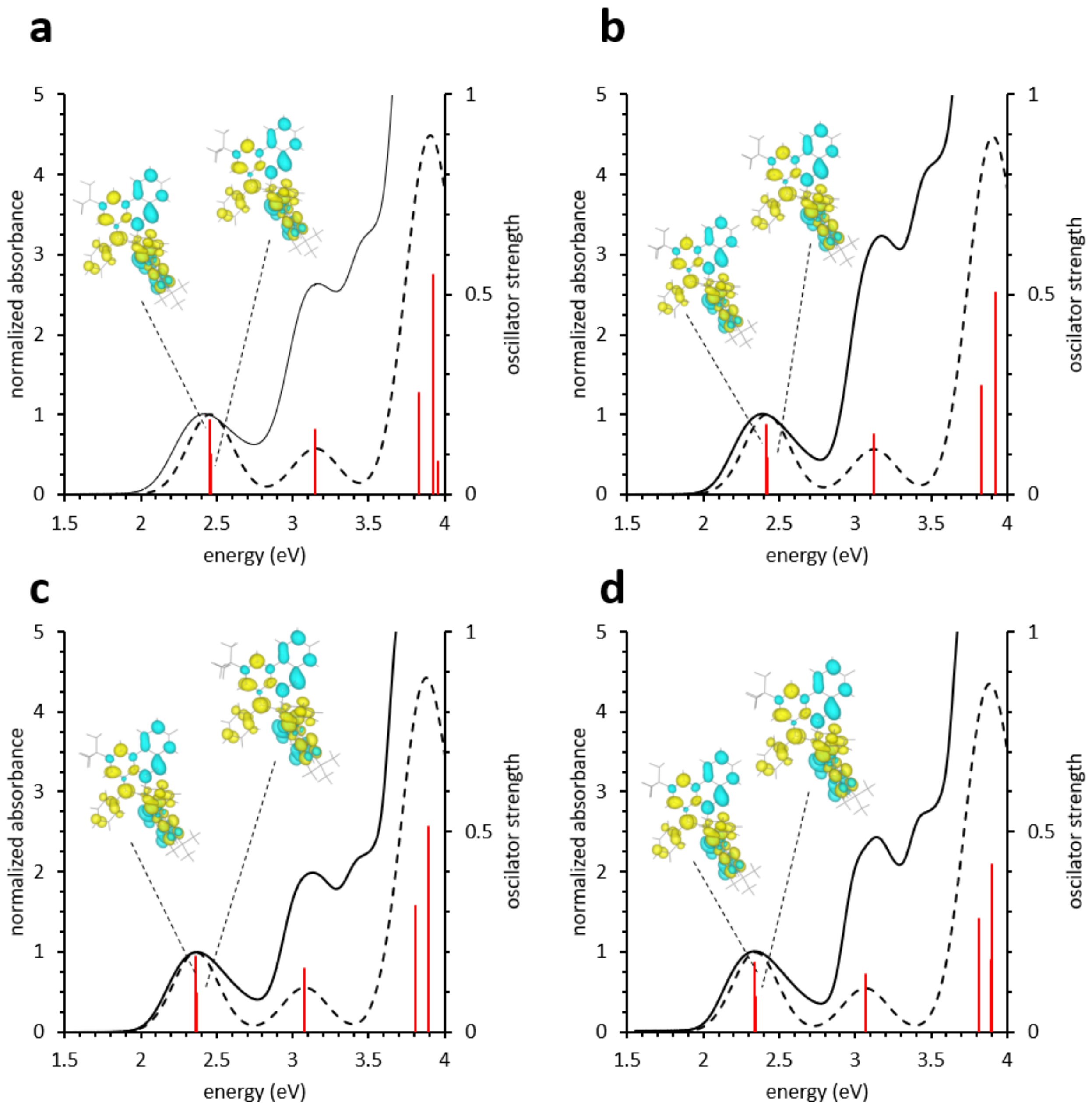


Figure S19. Normalized experimental UV-Vis absorption spectrum (solid trace), normalized TD-DFT simulated spectrum (dotted trace, FWHM = 0.35 eV), predicted singlet-singlet vertical excitation energies ($f_{\mathrm{osc}} > 0.08$), and electron-hole density maps (yellow = hole; blue = electron; isosurface value = 0.001) for the lowest-energy vertical electronic transitions of ($^{t\mathrm{Bu}}$**L3**)$_2$Zn (a) dichloromethane, (b) diethyl ether, (c) toluene, and (d) n-hexane.

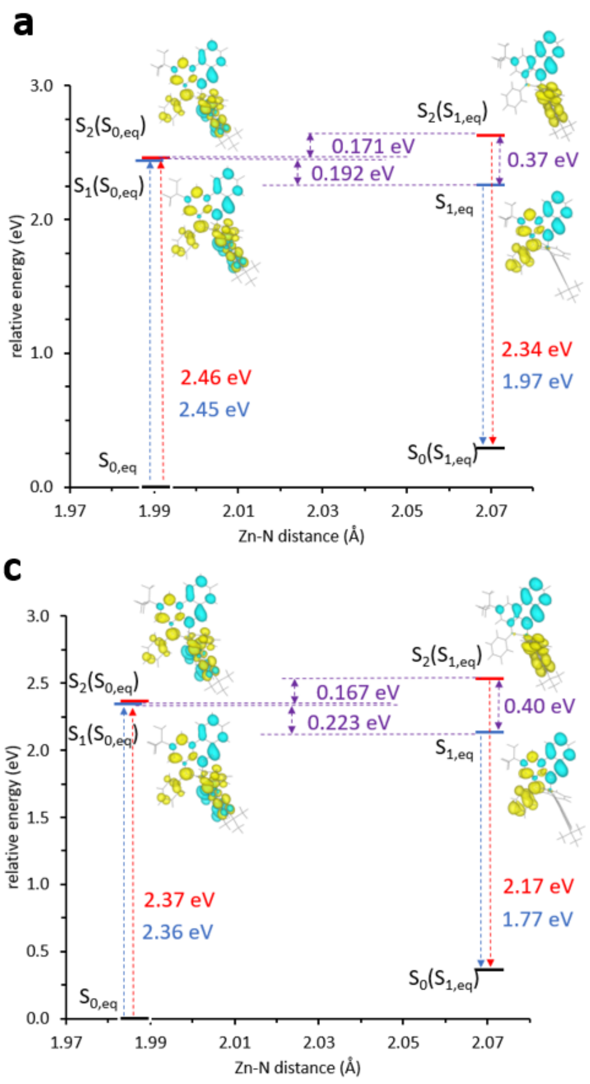


Figure S20. Jablonski diagram in the singlet manifold for (**$^{t\mathrm{Bu}}$L3**)$_2$Zn along the Zn-N$_{\mathrm{phenyl}}$ bond at the equilibrium S_0 and S_1 optimized geometries, with electron-hole density maps (yellow = hole; blue = electron; isosurface value = 0.001) in (a) dichloromethane, (b) diethyl ether, (c) toluene, and (d) n-hexane.

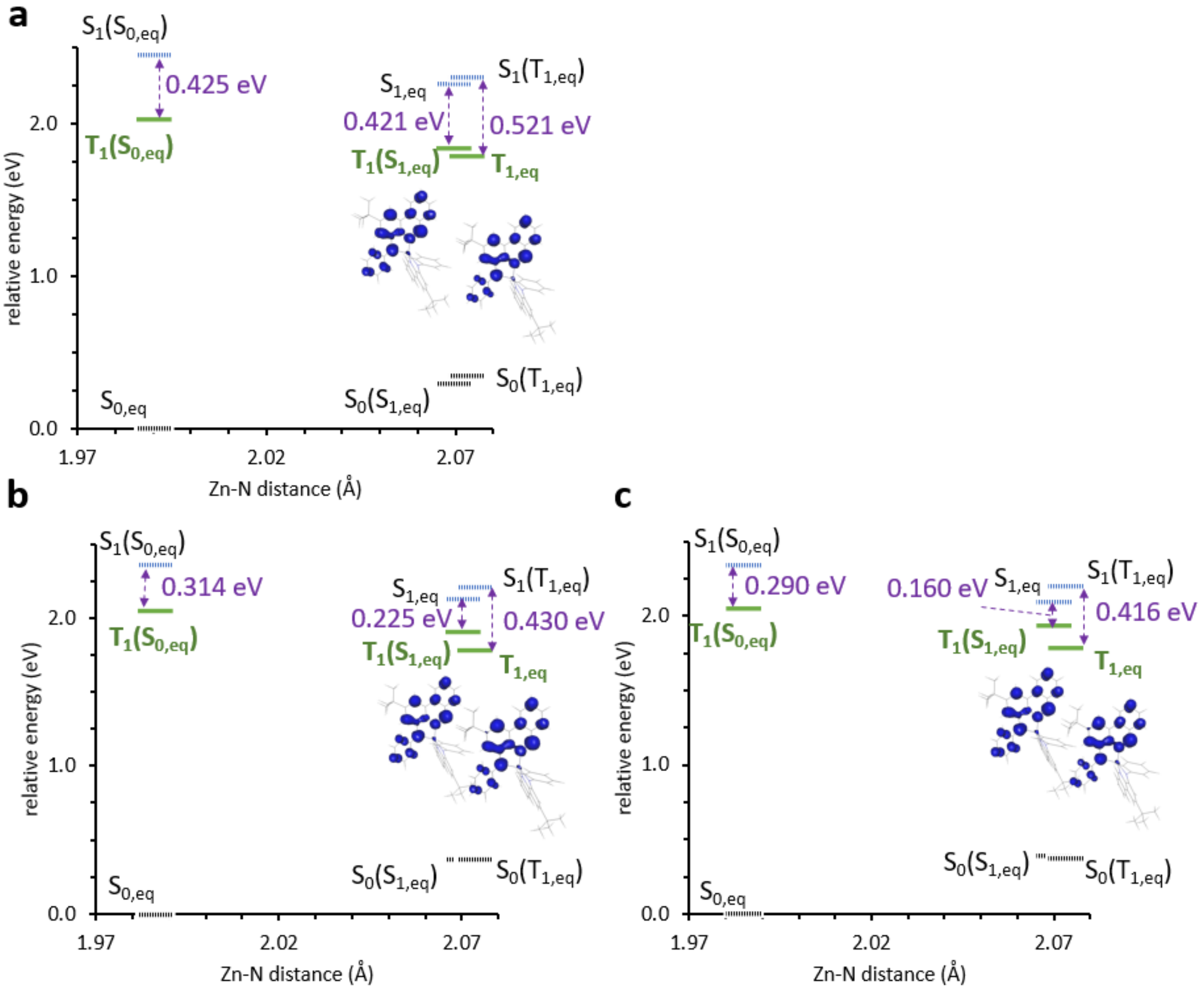


Figure S21. Jablonski diagram with T_1 states for ($^{t\mathbf{Bu}}$**L3**)$_2$Zn along the Zn-N$_{phenyl}$ bond at the equilibrium S_0, S_1, and T_1 optimized geometries, with spin density maps (isosurface value = 0.004) in (a) dichloromethane, (b) toluene, and (c) n-hexane. Diethyl ether is omitted due to complications with calculations.

Table S18. TD-DFT predicted singlet-singlet vertical excitation energies, oscillator strengths (f_{osc} > 0.08), and MO pair contributions (>10%) for (^{tBu}**L3**)$_2$Zn in dichloromethane. H=HOMO; L=LUMO

No.	E (eV)	f_{osc}	MO contributions
1	2.45	0.19	H→L 58%, H-1→L+1 40%
2	2.46	0.099	H-1→L 57%, H→L+1 42%
5	3.15	0.16	H→L+2 48%, H-1→L+3 46%
9	3.83	0.16	H-3→L 34%, H-2→L+1 30%
10	3.83	0.25	H-2→L 34%, H-3→L+1 29%
11	3.92	0.26	H-1→L+4 53%, H→L+5 38%
12	3.93	0.55	H→L+4 58%, H-1→L+5 34%
14	3.96	0.082	H→L+7 38%, H-1→L+6 27%, H-1→L+7 20%

Table S19. Fragment contributions to select ground-state MOs of (^{tBu}**L3**)$_2$Zn in dichloromethane.

MO	E	Zn	Phenan 1 (%)			Phenyl 1 (%)		Phenan 2 (%)			Phenyl 2 (%)	
	(eV)	(%)	full	C=N	CF3	full	C-N	full	C=N	CF3	full	C-N
LUMO+3	-1.19	0	47	2	1	3	1	48	2	1	3	1
LUMO+2	-1.20	0	48	2	1	2	1	47	2	1	2	1
LUMO+1	-1.83	2	48	17	1	1	1	47	17	1	1	1
LUMO	-1.86	2	48	17	1	1	1	46	17	1	1	1
HOMO	-5.18	2	27	2	1	27	15	22	1	0	22	13
HOMO-1	-5.19	3	21	2	0	23	12	25	2	0	28	15
HOMO-2	-6.61	0	50	5	2	1	1	48	5	2	1	0
HOMO-3	-6.62	0	49	5	2	1	0	49	5	2	1	0

Table S20. TD-DFT predicted singlet-singlet vertical excitation energies, oscillator strengths (f_{osc} > 0.08), and MO pair contributions (>10%) for (^{tBu}**L3**)$_2$Zn in diethyl ether. H=HOMO; L=LUMO

No.	E (eV)	f_{osc}	MO contributions
1	2.41	0.17	H→L 58%, H-1→L+1 40%
2	2.42	0.09	H-1→L 57%, H→L+1 42%
5	3.12	0.15	H→L+2 49%, H-1→L+3 46%
9	3.83	0.12	H-3→L 41%, H-2→L+1 35%
10	3.83	0.27	H-2→L 40%, H-3→L+1 34%
11	3.92	0.23	H-1→L+4 55%, H→L+5 36%
12	3.92	0.51	H→L+4 59%, H-1→L+5 32%

Table S21. Fragment contributions to select ground-state MOs of ($^{t\mathrm{Bu}}$**L3**)$_2$Zn in diethyl ether.

MO	E (eV)	Zn (%)	Phenan 1 (%)			Phenyl 1 (%)		Phenan 2 (%)			Phenyl 2 (%)	
			full	C=N	CF3	full	C-N	full	C=N	CF3	full	C-N
LUMO+3	-1.20	0	47	2	1	2	1	44	2	1	2	1
LUMO+2	-1.20	0	48	2	1	2	1	43	2	1	2	1
LUMO+1	-1.84	2	48	17	1	1	1	47	17	1	1	1
LUMO	-1.87	2	47	17	1	1	1	46	17	1	1	1
HOMO	-5.15	2	25	2	0	25	14	22	2	0	25	14
HOMO-1	-5.16	3	23	2	0	25	14	21	2	0	26	14
HOMO-2	-6.61	0	48	6	2	2	1	41	5	2	2	1
HOMO-3	-6.61	0	48	5	2	2	1	42	5	2	2	1

Table S22. TD-DFT predicted singlet-singlet vertical excitation energies, oscillator strengths (f_{osc} > 0.08), and MO pair contributions (>10%) for ($^{t\mathrm{Bu}}$**L3**)$_2$Zn in toluene. H=HOMO; L=LUMO

No.	E (eV)	f_{osc}	MO contributions
1	2.36	0.19	H→L 59%, H-1→L+1 40%
2	2.37	0.097	H-1→L 56%, H→L+1 42%
5	3.08	0.16	H→L+2 50%, H-1→L+3 46%
9	3.81	0.13	H-3→L 37%, H-2→L+1 28%, H-4→L+1 14%, H-5→L 10%
10	3.81	0.32	H-2→L 33%, H-3→L+1 31%, H-4→L 15%, H-5→L+1 10%,
11	3.89	0.23	H-1→L+4 55%, H→L+5 35%
12	3.89	0.51	H→L+4 59%, H-1→L+5 31%

Table S23. Fragment contributions to select ground-state MOs of ($^{t\mathrm{Bu}}$**L3**)$_2$Zn in toluene.

MO	E (eV)	Zn (%)	Phenan 1 (%)			Phenyl 1 (%)		Phenan 2 (%)			Phenyl 2 (%)	
			full	C=N	CF3	full	C-N	full	C=N	CF3	full	C-N
LUMO+3	-1.21	0	48	2	1	2	1	47	2	1	2	1
LUMO+2	-1.21	0	47	2	1	2	1	48	2	1	2	1
LUMO+1	-1.86	2	48	17	1	1	1	48	17	1	1	1
LUMO	-1.89	2	48	17	1	1	1	47	17	1	1	1
HOMO	-5.11	2	24	2	0	25	14	24	2	0	25	14
HOMO-1	-5.13	3	23	2	0	25	14	23	2	0	25	14
HOMO-2	-6.61	1	43	5	2	6	2	43	6	2	6	2
HOMO-3	-6.62	1	46	6	3	4	1	46	6	3	4	1

Table S24. TD-DFT predicted singlet-singlet vertical excitation energies, oscillator strengths (f_{osc} > 0.08), and MO pair contributions (>10%) for $({}^{t\mathrm{Bu}}\mathbf{L3})_2\mathrm{Zn}$ in n-hexane. H=HOMO; L=LUMO

No.	**E (eV)**	f_{osc}	**MO contributions**
1	2.34	0.17	H→L 60%, H-1→L+1 39%
2	2.35	0.088	H-1→L 56%, H→L+1 42%
5	3.07	0.14	H→L+2 50%, H-1→L+3 46%
9	3.81	0.11	H-3→L 31%, H-4→L+1 25%, H-5→L 17%, H-2→L+1 17%
10	3.82	0.28	H-4→L 28%, H-3→L+1 24%, H-2→L 20%, H-5→L+1 16%
11	3.90	0.18	H-1→L+4 54%, H→L+5 34%
12	3.90	0.42	H→L+4 57%, H-1→L+5 29%

Table S25. Fragment contributions to select ground-state MOs of $({}^{t\mathrm{Bu}}\mathbf{L3})_2\mathrm{Zn}$ in n-hexane.

MO	**E**	**Zn**	**Phenan 1 (%)**			**Phenyl 1 (%)**		**Phenan 2 (%)**			**Phenyl 2 (%)**	
	(eV)	**(%)**	**full**	**C=N**	**CF3**	**full**	**C-N**	**full**	**C=N**	**CF3**	**full**	**C-N**
LUMO+3	-1.22	0	48	2	1	2	1	47	2	3	2	1
LUMO+2	-1.22	0	48	2	1	2	1	48	2	4	2	1
LUMO+1	-1.87	2	48	16	1	1	1	48	17	2	1	1
LUMO	-1.90	2	48	16	1	1	1	47	16	2	1	1
HOMO	-5.10	2	24	2	0	25	14	24	2	2	28	14
HOMO-1	-5.11	3	23	2	0	25	14	23	2	2	28	14
HOMO-2	-6.61	1	37	5	2	12	4	38	5	4	15	4
HOMO-3	-6.61	1	43	6	3	6	2	44	6	4	8	2

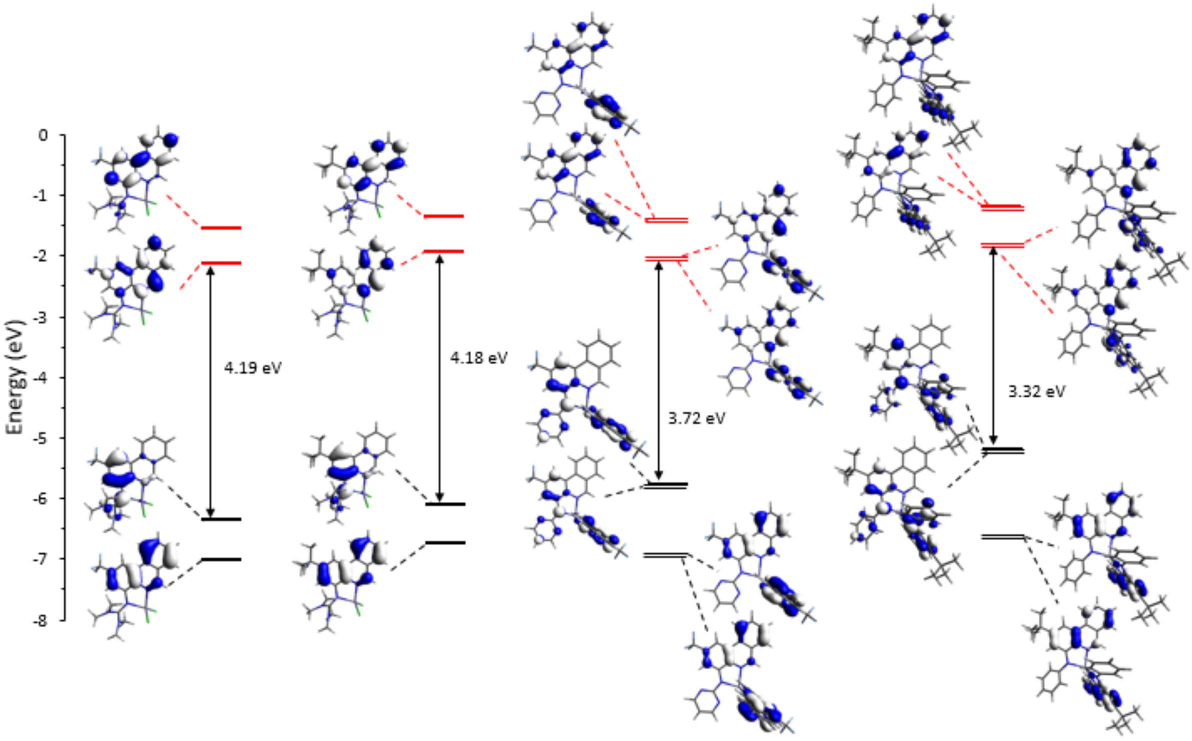


Figure S22. Ground-state frontier molecular orbital energy level diagram and isosurfaces (isovalue = 0.04) of the four complexes calculated in dichloromethane. From left to right: ($^{\mathrm{CF3}}$**L1**)ZnCl$_2$ (HOMO – 1 to LUMO +1), ($^{t\mathrm{Bu}}$**L1**)ZnCl$_2$ (HOMO – 1 to LUMO +1), ($^{\mathrm{CF3}}$**L2**)$_2$Zn (HOMO – 3 to LUMO +3), ($^{t\mathrm{Bu}}$**L3**)$_2$Zn (HOMO – 3 to LUMO +3).

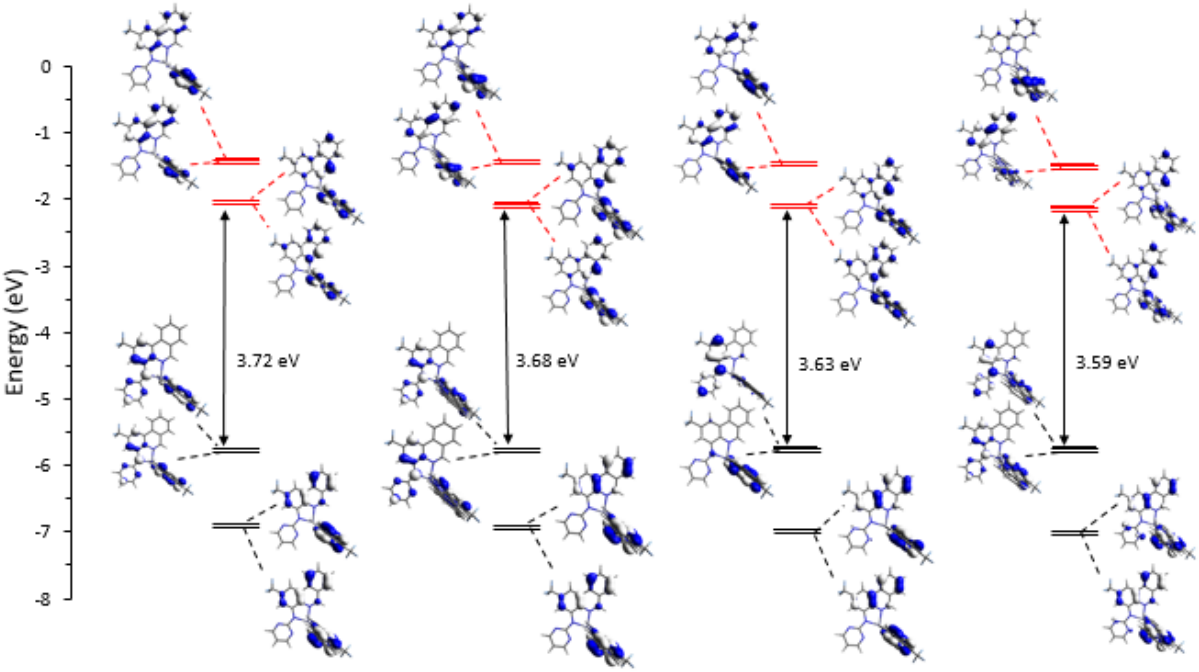


Figure S23. Ground-state frontier molecular orbital energy level diagram and isosurfaces (isovalue = 0.04) of (^{CF3}**L2**)$_2$Zn (HOMO – 3 to LUMO +3). From left to right: dichloromethane, diethyl ether, toluene, n-hexane.

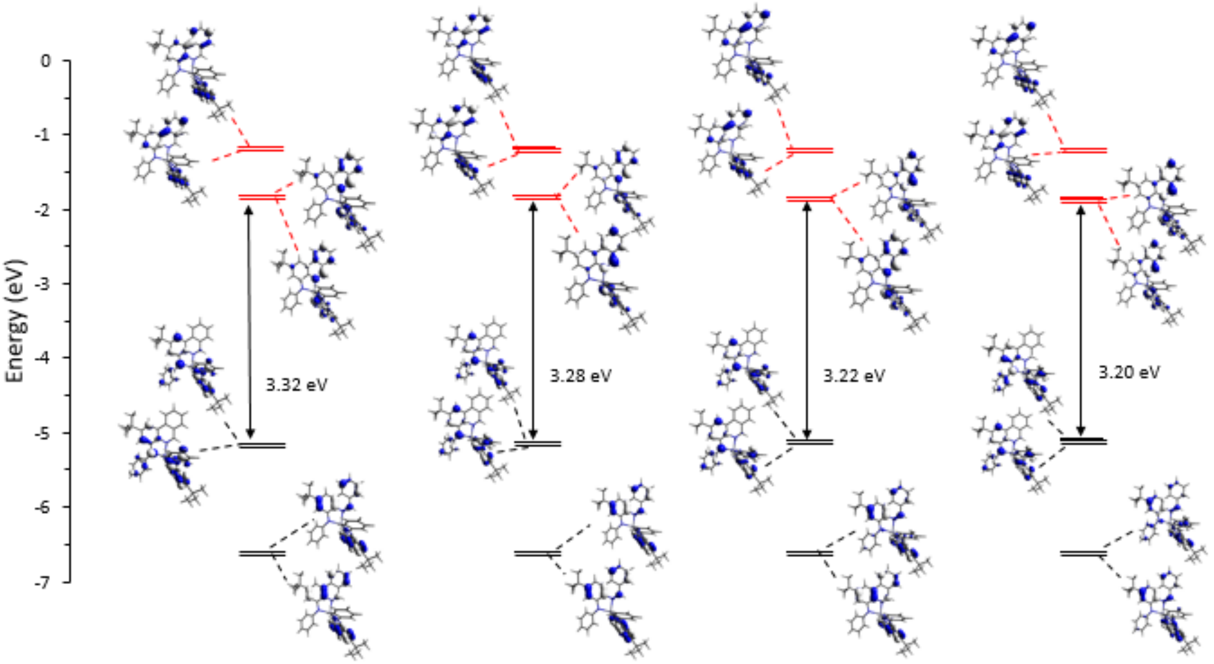


Figure S24. Ground-state frontier molecular orbital energy level diagram and isosurfaces (isovalue = 0.04) of (^{tBu}**L3**)$_2$Zn (HOMO – 3 to LUMO +3). From left to right: dichloromethane, diethyl ether, toluene, n-hexane.

Table S26. Spin-orbit coupling matrix elements for ($^{\mathbf{CF3}}$**L2**)$_2$Zn between the five lowest-lying excited triplet states with the ground state and two lowest-lying excited singlet states calculated in dichloromethane at the optimized ground state geometry.

Root		**<T|H$_{SO}$|S> (Re, Im) cm^{-1}**		
T	**S**	**Z**	**X**	**Y**
1	0	(0, -0.08)	(0, 0.12)	(0, 1.39)
1	1	(0, 0.04)	(0, -0.23)	(0, -0.04)
1	2	(0, 0.01)	(0, -0.06)	(0, -0.34)
2	0	(0, -0.18)	(0, 1.1)	(0, -0.18)
2	1	(0, 0)	(0, 0.05)	(0, -0.32)
2	2	(0, 0.04)	(0, -0.38)	(0, 0.04)
3	0	(0, 0)	(0, 0.08)	(0, 0.1)
3	1	(0, 0.05)	(0, 0.1)	(0, 0.02)
3	2	(0, 0.03)	(0, 0.1)	(0, 0.02)
4	0	(0, 0.02)	(0, 0.34)	(0, -0.04)
4	1	(0, -0.01)	(0, -0.02)	(0, 0.25)
4	2	(0, 0.24)	(0, 0.33)	(0, -0.03)
5	0	(0, -0.05)	(0, 0.36)	(0, -0.47)
5	1	(0, -0.3)	(0, -1.57)	(0, -0.1)
5	2	(0, 0.79)	(0, 0.37)	(0, 0.19)

Table S27. Spin-orbit coupling matrix elements for ($^{\mathbf{CF3}}$**L2**)$_2$Zn between the five lowest-lying excited triplet states with the ground state and two lowest-lying excited singlet states calculated in diethyl ether at the optimized ground state geometry.

Root		**<T|H$_{SO}$|S> (Re, Im) cm^{-1}**		
T	**S**	**Z**	**X**	**Y**
1	0	(0.00, -0.04)	(0.00, -0.10)	(-0.00, 1.49)
1	1	(0.00, -0.04)	(0.00, 0.23)	(-0.00, -0.03)
1	2	(0.00, -0.00)	(0.00, -0.01)	(-0.00, 0.33)
2	0	(0.00, 0.20)	(0.00, -1.17)	(-0.00, -0.11)
2	1	(0.00, 0.00)	(0.00, 0.01)	(-0.00, -0.31)
2	2	(0.00, 0.05)	(0.00, -0.39)	(-0.00, -0.04)
3	0	(0.00, 0.01)	(0.00, 0.26)	(-0.00, -0.10)
3	1	(0.00, -0.02)	(0.00, 0.06)	(-0.00, -0.19)
3	2	(0.00, -0.22)	(0.00, -0.25)	(-0.00, 0.18)
4	0	(0.00, 0.00)	(0.00, -0.32)	(-0.00, -0.07)
4	1	(0.00, -0.05)	(0.00, 0.03)	(-0.00, 0.17)
4	2	(0.00, 0.22)	(0.00, 0.28)	(-0.00, 0.19)
5	0	(0.00, 0.07)	(0.00, -0.40)	(-0.00, 0.49)
5	1	(0.00, -0.30)	(0.00, -1.56)	(-0.00, -0.11)
5	2	(0.00, 0.91)	(0.00, 0.38)	(-0.00, 0.20)

Table S28. Spin-orbit coupling matrix elements for $(^{\mathbf{CF3}}\mathbf{L2})_2\mathrm{Zn}$ between the five lowest-lying excited triplet states with the ground state and two lowest-lying excited singlet states calculated in toluene at the optimized ground state geometry.

Root		**<T|H$_{SO}$|S> (Re, Im) cm^{-1}**		
T	**S**	**Z**	**X**	**Y**
1	0	(0.00, -0.01)	(0.00, 0.39)	(-0.00, -1.53)
1	1	(0.00, -0.05)	(0.00, 0.21)	(-0.00, -0.10)
1	2	(0.00, -0.01)	(0.00, 0.09)	(-0.00, -0.29)
2	0	(0.00, 0.22)	(0.00, -1.20)	(-0.00, -0.48)
2	1	(0.00, -0.01)	(0.00, 0.02)	(-0.00, 0.27)
2	2	(0.00, 0.05)	(0.00, -0.35)	(-0.00, -0.12)
3	0	(0.00, 0.01)	(0.00, -0.35)	(-0.00, 0.08)
3	1	(0.00, -0.00)	(0.00, 0.03)	(-0.00, -0.21)
3	2	(0.00, 0.36)	(0.00, 0.34)	(-0.00, -0.16)
4	0	(0.00, -0.02)	(0.00, 0.36)	(-0.00, 0.07)
4	1	(0.00, -0.08)	(0.00, -0.04)	(-0.00, 0.14)
4	2	(0.00, -0.32)	(0.00, -0.31)	(-0.00, -0.22)
5	0	(0.00, -0.08)	(0.00, 0.43)	(-0.00, -0.52)
5	1	(0.00, -0.32)	(0.00, -1.54)	(-0.00, -0.13)
5	2	(0.00, -1.01)	(0.00, -0.39)	(-0.00, -0.19)

Table S29. Spin-orbit coupling matrix elements for $(^{\mathbf{CF3}}\mathbf{L2})_2\mathrm{Zn}$ between the five lowest-lying excited triplet states with the ground state and two lowest-lying excited singlet states calculated in n-hexane at the optimized ground state geometry.

Root		**<T|H$_{SO}$|S> (Re, Im) cm^{-1}**		
T	**S**	**Z**	**X**	**Y**
1	0	(0.00, -0.03)	(0.00, 0.51)	(-0.00, -1.54)
1	1	(0.00, -0.05)	(0.00, 0.21)	(-0.00, -0.14)
1	2	(0.00, -0.01)	(0.00, 0.12)	(-0.00, -0.27)
2	0	(0.00, 0.23)	(0.00, 0.23)	(-0.00, -0.63)
2	1	(0.00, -0.02)	(0.00, 0.03)	(-0.00, 0.26)
2	2	(0.00, 0.05)	(0.00, -0.35)	(-0.00, -0.15)
3	0	(0.00, -0.03)	(0.00, 0.42)	(-0.00, -0.06)
3	1	(0.00, -0.02)	(0.00, -0.02)	(-0.00, 0.22)
3	2	(0.00, -0.51)	(0.00, -0.42)	(-0.00, 0.14)
4	0	(0.00, 0.03)	(0.00, -0.39)	(-0.00, -0.06)
4	1	(0.00, 0.11)	(0.00, 0.11)	(-0.00, -0.11)
4	2	(0.00, 0.42)	(0.00, 0.34)	(-0.00, 0.24)
5	0	(0.00, 0.08)	(0.00, -0.41)	(-0.00, 0.55)
5	1	(0.00, 0.32)	(0.00, 1.54)	(-0.00, 0.13)
5	2	(0.00, 0.99)	(0.00, 0.34)	(-0.00, 0.18)

Table S30. Spin-orbit coupling matrix elements for (^{tBu}**L3**)$_2$Zn between the five lowest-lying excited triplet states with the ground state and two lowest-lying excited singlet states calculated in dichloromethane at the optimized ground state geometry.

Root		<T|H$_{SO}$|S> (Re, Im) cm^{-1}		
T	**S**	**Z**	**X**	**Y**
1	0	(0.00, -1.47)	(0.00, 0.91)	(-0.00, -0.23)
1	1	(0.00, -0.02)	(0.00, 0.09)	(-0.00, 0.03)
1	2	(0.00, -0.13)	(0.00, 0.27)	(-0.00, -0.24)
2	0	(0.00, 0.54)	(0.00, 2.48)	(-0.00, -0.65)
2	1	(0.00, -0.04)	(0.00, -0.01)	(-0.00, -0.03)
2	2	(0.00, 0.05)	(0.00, 0.77)	(-0.00, -0.67)
3	0	(0.00, 1.42)	(0.00, 0.16)	(-0.00, 0.03)
3	1	(0.00, 0.02)	(0.00, 3.24)	(-0.00, 0.05)
3	2	(0.00, -0.25)	(0.00, -0.17)	(-0.00, 0.24)
4	0	(0.00, 0.04)	(0.00, -3.53)	(-0.00, -0.61)
4	1	(0.00, 0.01)	(0.00, 0.20)	(-0.00, -0.13)
4	2	(0.00, -0.03)	(0.00, 1.51)	(-0.00, -4.75)
5	0	(0.00, -0.01)	(0.00, 0.56)	(-0.00, -0.55)
5	1	(0.00, -0.33)	(0.00, 0.20)	(-0.00, -0.10)
5	2	(0.00, 0.05)	(0.00, 0.45)	(-0.00, -1.15)

Table S31. Spin-orbit coupling matrix elements for (^{tBu}**L3**)$_2$Zn between the five lowest-lying excited triplet states with the ground state and two lowest-lying excited singlet states calculated in diethyl ether at the optimized ground state geometry.

Root		<T|H$_{SO}$|S> (Re, Im) cm^{-1}		
T	**S**	**Z**	**X**	**Y**
1	0	(0.00, 1.56)	(0.00, 0.42)	(-0.00, -0.11)
1	1	(0.00, 0.01)	(0.00, 0.07)	(-0.00, 0.08)
1	2	(0.00, 0.13)	(0.00, 0.12)	(-0.00, -0.11)
2	0	(0.00, 0.24)	(0.00, -2.67)	(-0.00, 0.71)
2	1	(0.00, -0.04)	(0.00, 0.01)	(-0.00, 0.01)
2	2	(0.00, 0.02)	(0.00, -0.80)	(-0.00, 0.71)
3	0	(0.00, 1.37)	(0.00, 0.04)	(-0.00, 0.01)
3	1	(0.00, -0.00)	(0.00, -3.40)	(-0.00, 0.08)
3	2	(0.00, -0.20)	(0.00, -0.01)	(-0.00, 0.05)
4	0	(0.00, -0.01)	(0.00, 3.49)	(-0.00, 0.70)
4	1	(0.00, -0.04)	(0.00, 0.03)	(-0.00, 0.01)
4	2	(0.00, 0.00)	(0.00, -1.50)	(-0.00, 4.87)
5	0	(0.00, -0.02)	(0.00, -0.84)	(-0.00, 0.49)
5	1	(0.00, -0.31)	(0.00, -0.05)	(-0.00, 0.03)
5	2	(0.00, 0.02)	(0.00, -0.30)	(-0.00, 0.68)

Table S32. Spin-orbit coupling matrix elements for $(^{t\mathrm{Bu}}\mathbf{L3})_2$Zn between the five lowest-lying excited triplet states with the ground state and two lowest-lying excited singlet states calculated in toluene at the optimized ground state geometry.

Root		**$\langle$T|H$_{SO}$|S$\rangle$ (Re, Im) cm^{-1}**		
T	**S**	**Z**	**X**	**Y**
1	0	(0.00, 0.06)	(0.00, -2.78)	(-0.00, 0.72)
1	1	(0.00, -0.04)	(0.00, 0.00)	(-0.00, 0.01)
1	2	(0.00, -0.00)	(0.00, 0.78)	(-0.00, -0.70)
2	0	(0.00, 1.59)	(0.00, 0.10)	(-0.00, -0.03)
2	1	(0.00, 0.00)	(0.00, 0.04)	(-0.00, 0.16)
2	2	(0.00, -0.13)	(0.00, -0.03)	(-0.00, 0.03)
3	0	(0.00, 1.33)	(0.00, -0.01)	(-0.00, -0.00)
3	1	(0.00, 0.00)	(0.00, -3.52)	(-0.00, 0.17)
3	2	(0.00, 0.18)	(0.00, -0.00)	(-0.00, 0.02)
4	0	(0.00, 0.01)	(0.00, 3.45)	(-0.00, 0.83)
4	1	(0.00, -0.06)	(0.00, -0.01)	(-0.00, -0.00)
4	2	(0.00, 0.00)	(0.00, 1.51)	(-0.00, -4.91)
5	0	(0.00, -0.01)	(0.00, 0.96)	(-0.00, -0.44)
5	1	(0.00, 0.28)	(0.00, -0.02)	(-0.00, 0.01)
5	2	(0.00, -0.01)	(0.00, -0.22)	(-0.00, 0.40)

Table S33. Spin-orbit coupling matrix elements for $(^{t\mathrm{Bu}}\mathbf{L3})_2$Zn between the five lowest-lying excited triplet states with the ground state and two lowest-lying excited singlet states calculated in n-hexane at the optimized ground state geometry.

Root		**$\langle$T|H$_{SO}$|S$\rangle$ (Re, Im) cm^{-1}**		
T	**S**	**Z**	**X**	**Y**
1	0	(0.00, -0.08)	(0.00, 2.83)	(-0.00, -0.73)
1	1	(0.00, -0.04)	(0.00, 0.00)	(-0.00, 0.01)
1	2	(0.00, -0.01)	(0.00, 0.79)	(-0.00, -0.71)
2	0	(0.00, -1.59)	(0.00, -0.15)	(-0.00, 0.04)
2	1	(0.00, 0.00)	(0.00, 0.03)	(-0.00, 0.21)
2	2	(0.00, -0.13)	(0.00, -0.04)	(-0.00, 0.04)
3	0	(0.00, -1.31)	(0.00, 0.01)	(-0.00, 0.00)
3	1	(0.00, 0.00)	(0.00, -3.55)	(-0.00, 0.20)
3	2	(0.00, 0.16)	(0.00, 0.00)	(-0.00, 0.01)
4	0	(0.00, 0.00)	(0.00, 3.43)	(-0.00, 0.91)
4	1	(0.00, 0.07)	(0.00, 0.01)	(-0.00, 0.01)
4	2	(0.00, -0.00)	(0.00, -1.51)	(-0.00, 4.93)
5	0	(0.00, 0.00)	(0.00, -1.51)	(-0.00, 0.43)
5	1	(0.00, 0.27)	(0.00, -0.01)	(-0.00, 0.00)
5	2	(0.00, -0.00)	(0.00, -0.20)	(-0.00, 0.33)

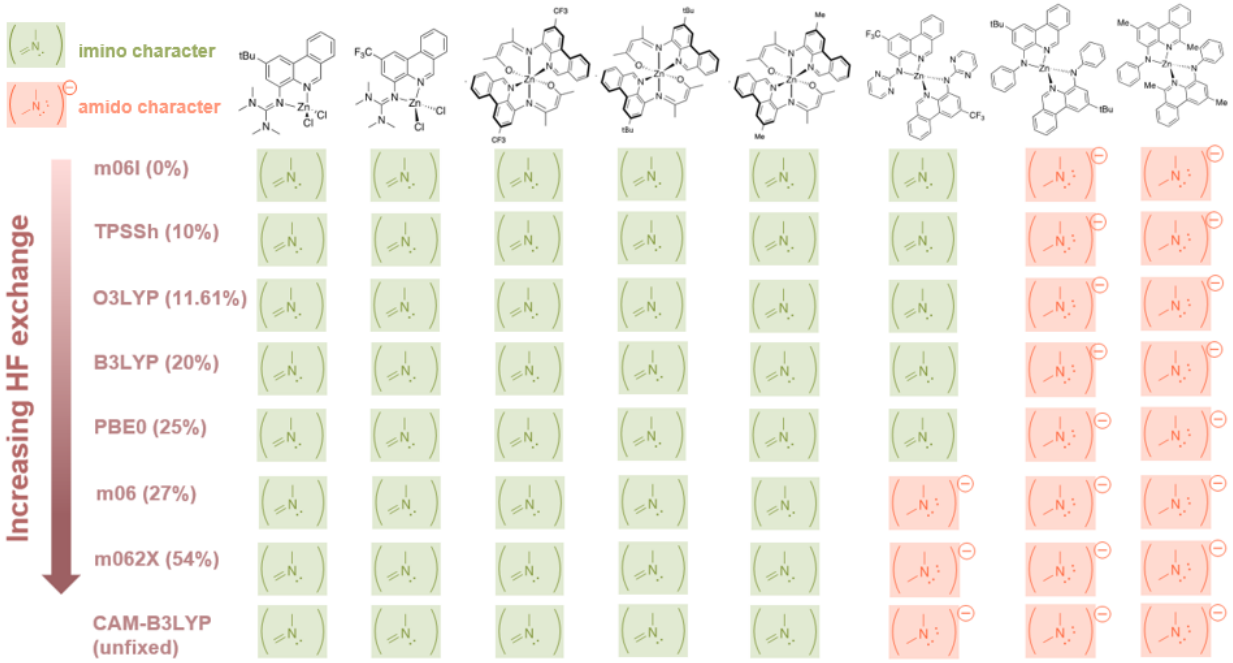


Figure S25. NBO results for complexes of varying N_{amido} character.

^{a} For all functionals, gas phase/ def2-tzvpp def2/j

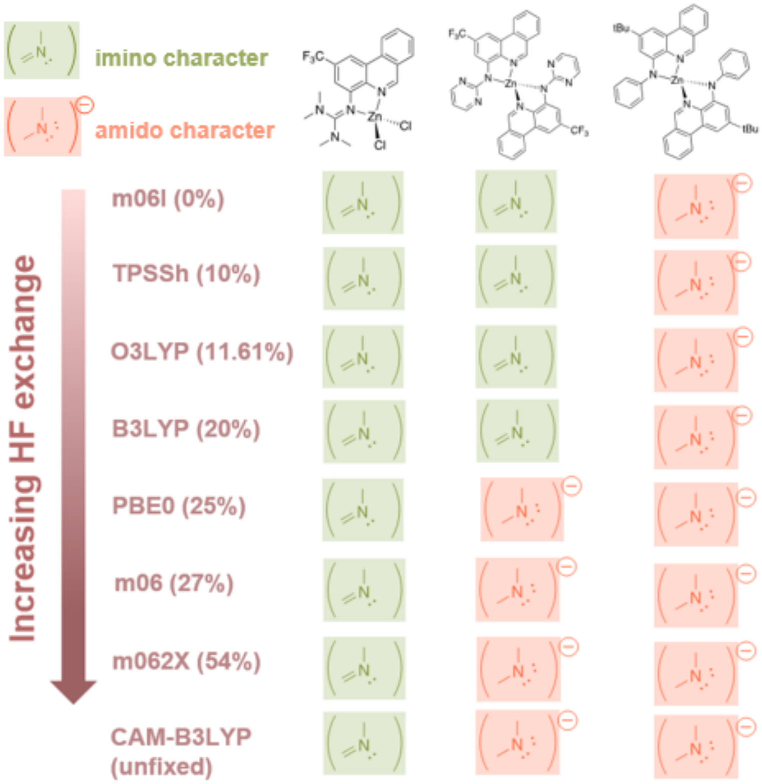


Figure S26. Solvated NBO results for select complexes of varying N_{amido} character.

^{a} For all functionals, SMD “dichloromethane”/ def2-tzvpp def2/j

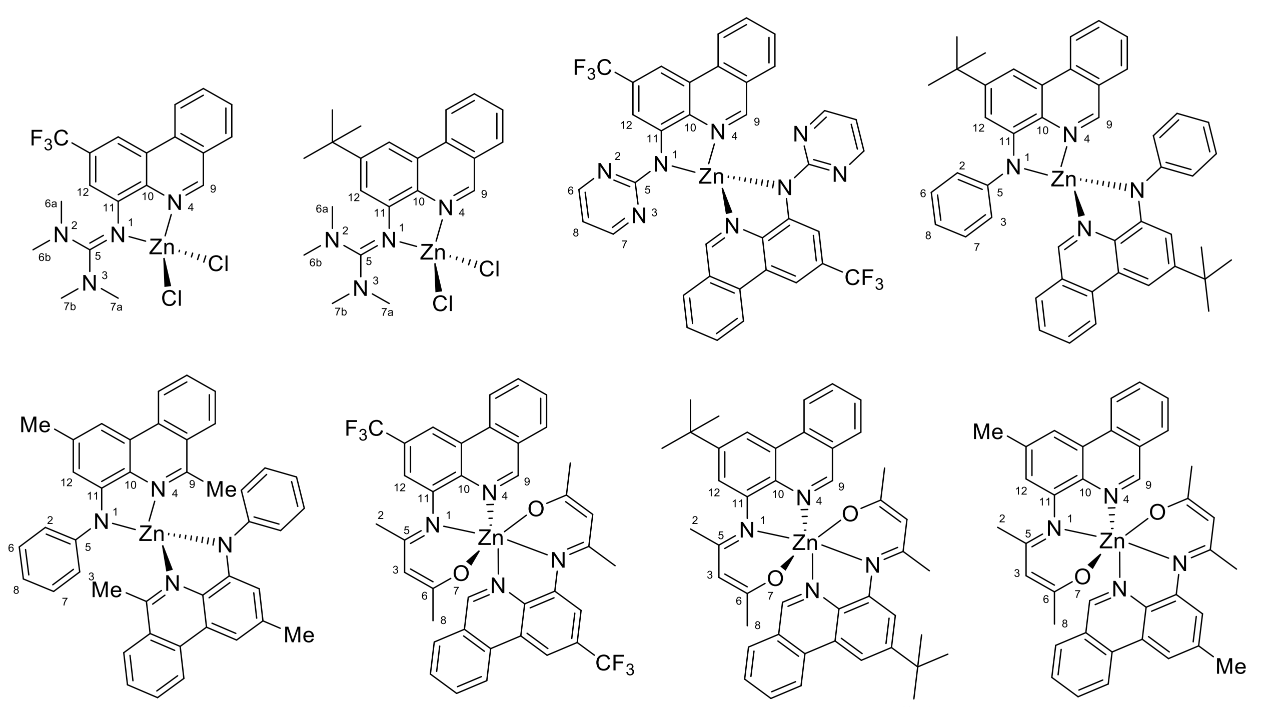


Figure S27. Atomic labels for NBO tables. Top, from left to right: ($^{\mathbf{CF3}}$**L1**)ZnCl$_2$, ($^{\boldsymbol{t}\mathbf{Bu}}$**L1**)ZnCl$_2$, ($^{\mathbf{CF3}}$**L2**)$_2$Zn, ($^{\boldsymbol{t}\mathbf{Bu}}$**L3**)$_2$Zn. Bottom, from left to right: ($^{\mathbf{Me\wedge Me}}$**L3**)$_2$Zn, ($^{\mathbf{CF3}}$**L4**)$_2$Zn, ($^{\boldsymbol{t}\mathbf{Bu}}$**L4**)$_2$Zn, ($^{\mathbf{Me}}$**L4**)$_2$Zn.

Table S34. NBO analysis[a] of $(^{\mathrm{CF3}}\mathbf{L1})\mathrm{ZnCl_2}$ with the M06-L functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.83456	$sp^{2.30}$	*s*(30.32%)*p*(69.60%)
σ(N1-C5)	1.98066	$sp^{1.84}$ at N1 $sp^{1.85}$ at C5	N1 (59.03%): *s*(35.06%)*p*(64.62%) C5 (40.97%): *s*(35.11%)*p*(64.80%)
π(N1-C5)	1.85196	n/a	N1 (74.22%): *s*(0.12%)*p*(99.74%) C5 (25.78%): *s*(0.29%)*p*(99.50%)
σ(N1-C11)	1.98049	$sp^{2.15}$ at N1 $sp^{1.90}$ at C11	N1 (58.87%): *s*(34.38%)*p*(65.33%) C11 (41.13%): *s*(31.69%)*p*(68.22%)
Lone pair 1 (N2)	1.68044	n/a	*s*(0.00%)*p*(99.94%)
σ(N2-C5)	1.98077	$sp^{2.08}$ at N2 $sp^{1.80}$ at C5	N2 (61.40%): *s*(35.64%)*p*(64.20%) C5 (38.60%): *s*(32.39%)*p*(67.51%)
σ(N2-C6a)	1.98313	$sp^{2.10}$ at N2 $sp^{2.89}$ at C6a	N2 (62.19%): *s*(32.22%)*p*(67.67%) C6a (37.81%): *s*(25.71%)*p*(74.22%)
σ(N2-C6b)	1.98404	$sp^{2.12}$ at N2 $sp^{2.78}$ at C6b	N2 (61.62%): *s*(32.01%)*p*(67.88%) C6b (38.38%): *s*(26.47%)*p*(73.46%)
Lone pair 1 (N3)	1.65321	n/a	*s*(2.78%)*p*(97.15%)
σ(N3-C5)	1.97954	$sp^{2.11}$ at N3 $sp^{1.81}$ at C5	N3 (61.19%): *s*(35.49%)*p*(64.32%) C5 (38.81%): *s*(32.13%)*p*(67.77%)
σ(N3-C7a)	1.97996	$sp^{2.28}$ at N3 $sp^{2.87}$ at C7a	N3 (61.98%): *s*(30.46%)*p*(69.42%) C7a (38.02%): *s*(25.80%)*p*(74.13%)
σ(N3-C7b)	1.98497	$sp^{2.21}$ at N3 $sp^{2.92}$ at C7b	N3 (62.23%): *s*(31.13%)*p*(68.75%) C7b (37.77%): *s*(25.50%)*p*(74.43%)
σ(C11-C12)	1.97853	$sp^{1.76}$ at C11 $sp^{1.77}$ at C12	C11 (50.60%): *s*(36.24%)*p*(63.64%) C12 (49.40%): *s*(36.09%)*p*(63.74%)
π(C11-C12)	1.65401	n/a	C11 (46.89%): *s*(0.02%)*p*(99.88%) C12 (53.11%): *s*(0.01%)*p*(99.90%)
σ(C11-C10)	1.97226	$sp^{1.94}$ at C10 $sp^{2.12}$ at C11	C10 (50.67%): *s*(34.01%)*p*(65.86%) C11 (49.33%): *s*(31.99%)*p*(67.88%)
Lone pair 1 (N4)	1.87149	$sp^{2.42}$	*s*(29.19%)*p*(70.78%)
σ(N4-C9)	1.98871	$sp^{1.65}$ at N4 $sp^{1.91}$ at C9	N4 (59.91%): *s*(37.63%)*p*(62.03%) C9 (40.09%): *s*(34.28%)*p*(65.62%)
π(N4-C9)	1.84705	n/a	N4 (63.43%): *s*(0.00%)*p*(99.82%) C9 (36.57%): *s*(0.00%)*p*(99.85%)
σ(N4-C10)	1.98163	$sp^{2.02}$ at N4 $sp^{2.29}$ at C10	N4 (58.91%): *s*(33.04%)*p*(66.65%) C10 (41.09%): *s*(30.38%)*p*(69.54%)

[a] Calculated in gas phase at the optimized S0 geometry using M06-L (gas phase/ def2-tzvpp def2/j). The M06-L functional uses 0 % Hartree-Fock exchange.[19]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S35. NBO analysis[a] of (^{CF3}**L1**)$ZnCl_2$ with the TPSSh functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.83499	$sp^{2.50}$	s(28.58%)p(71.34%)
σ(N1-C5)	1.98116	$sp^{1.76}$ at N1 $sp^{1.85}$ at C5	N1 (58.85%): s(36.05%)p(63.59%) C5 (41.15%): s(35.05%)p(64.84%)
π(N1-C5)	1.85365	n/a	N1 (74.39%): s(0.11%)p(99.75%) C5 (25.61%): s(0.24%)p(99.56%)
σ(N1-C11)	1.98091	$sp^{2.14}$ at N1 $sp^{1.84}$ at C11	N1 (58.59%): s(35.14%)p(64.55%) C11 (41.41%): s(31.82%)p(68.08%)
Lone pair 1 (N2)	1.68049	n/a	s(0.00%)p(99.95%)
σ(N2-C5)	1.98089	$sp^{2.07}$ at N2 $sp^{1.80}$ at C5	N2 (61.27%): s(35.65%)p(64.17%) C5 (38.73%): s(32.50%)p(67.38%)
σ(N2-C6a)	1.98342	$sp^{2.10}$ at N2 $sp^{2.91}$ at C6a	N2 (62.44%): s(32.20%)p(67.68%) C6a (37.56%): s(25.58%)p(74.33%)
σ(N2-C6b)	1.98439	$sp^{2.12}$ at N2 $sp^{2.79}$ at C6b	N2 (61.83%): s(31.99%)p(67.88%) C6b (38.17%): s(26.37%)p(73.54%)
Lone pair 1 (N3)	1.65192	n/a	s(2.51%)p(97.43%)
σ(N3-C5)	1.97956	$sp^{2.11}$ at N3 $sp^{1.81}$ at C5	N3 (61.06%): s(35.57%)p(64.22%) C5 (38.94%): s(32.11%)p(67.77%)
σ(N3-C7a)	1.98064	$sp^{2.27}$ at N3 $sp^{2.89}$ at C7a	N3 (62.21%): s(30.54%)p(69.33%) C7a (37.79%): s(25.67%)p(74.24%)
σ(N3-C7b)	1.98547	$sp^{2.20}$ at N3 $sp^{2.94}$ at C7b	N3 (62.49%): s(31.22%)p(68.66%) C7b (37.51%): s(25.37%)p(74.54%)
σ(C11-C12)	1.97790	$sp^{1.76}$ at C11 $sp^{1.78}$ at C12	C11 (50.75%): s(36.25%)p(63.64%) C12 (49.25%): s(35.97%)p(63.86%)
π(C11-C12)	1.65477	n/a	C11 (47.41%): s(0.02%)p(99.90%) C12 (52.59%): s(0.01%)p(99.90%)
σ(C11-C10)	1.97223	$sp^{1.94}$ at C10 $sp^{2.14}$ at C11	C10 (50.71%): s(33.96%)p(65.93%) C11 (49.29%): s(31.85%)p(68.02%)
Lone pair 1 (N4)	1.87196	$sp^{2.45}$	s(27.99%)p(71.99%)
σ(N4-C9)	1.98877	$sp^{1.61}$ at N4 $sp^{1.92}$ at C9	N4 (59.84%): s(38.22%)p(61.41%) C9 (40.16%): s(34.25%)p(65.63%)
π(N4-C9)	1.84686	n/a	N4 (63.55%): s(0.00%)p(99.82%) C9 (36.45%): s(0.00%)p(99.86%)
σ(N4-C10)	1.98235	$sp^{1.96}$ at N4 $sp^{2.28}$ at C10	N4 (58.67%): s(33.65%)p(66.03%) C10 (41.33%): s(30.46%)p(69.44%)

[a] Calculated in gas phase at the optimized S0 geometry using TPSSh (gas phase/ def2-tzvpp def2/j). The TPSSh functional uses 10 % Hartree-Fock exchange.[11]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S36. NBO analysis[a] of ($^{\mathrm{CF3}}$**L1**)ZnCl$_2$ with the O3LYP functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.83262	$sp^{2.52}$	*s*(28.40%)*p*(71.51%)
σ(N1-C5)	1.98112	$sp^{1.76}$ at N1 $sp^{1.85}$ at C5	N1 (58.69%): *s*(36.15%)*p*(63.50%) C5 (41.31%): *s*(35.02%)*p*(64.87%)
π(N1-C5)	1.85224	n/a	N1 (74.20%): *s*(0.10%)*p*(99.77%) C5 (25.80%): *s*(0.23%)*p*(99.58%)
σ(N1-C11)	1.98082	$sp^{2.13}$ at N1 $sp^{1.83}$ at C11	N1 (58.43%): *s*(35.23%)*p*(64.47%) C11 (41.57%): *s*(31.87%)*p*(68.04%)
Lone pair 1 (N2)	1.67790	n/a	*s*(0.00%)*p*(99.95%)
σ(N2-C5)	1.98070	$sp^{2.07}$ at N2 $sp^{1.81}$ at C5	N2 (61.12%): *s*(35.59%)*p*(64.24%) C5 (38.88%): *s*(32.56%)*p*(67.33%)
σ(N2-C6a)	1.98358	$sp^{2.10}$ at N2 $sp^{2.89}$ at C6a	N2 (62.18%): *s*(32.22%)*p*(67.67%) C6a (37.82%): *s*(25.67%)*p*(74.24%)
σ(N2-C6b)	1.98457	$sp^{2.12}$ at N2 $sp^{2.78}$ at C6b	N2 (61.59%): *s*(32.04%)*p*(67.84%) C6b (38.41%): *s*(26.45%)*p*(73.47%)
Lone pair 1 (N3)	1.64944	n/a	*s*(2.42%)*p*(97.52%)
σ(N3-C5)	1.97947	$sp^{2.11}$ at N3 $sp^{1.81}$ at C5	N3 (60.92%): *s*(35.53%)*p*(64.27%) C5 (39.08%): *s*(32.10%)*p*(67.79%)
σ(N3-C7a)	1.98103	$sp^{2.26}$ at N3 $sp^{2.88}$ at C7a	N3 (61.95%): *s*(30.63%)*p*(69.25%) C7a (38.05%): *s*(25.75%)*p*(74.16%)
σ(N3-C7b)	1.98551	$sp^{2.20}$ at N3 $sp^{2.92}$ at C7b	N3 (62.23%): *s*(31.25%)*p*(68.62%) C7b (37.77%): *s*(25.46%)*p*(74.45%)
σ(C11-C12)	1.97748	$sp^{1.76}$ at C11 $sp^{1.78}$ at C12	C11 (50.75%): *s*(36.24%)*p*(63.65%) C12 (49.25%): *s*(35.92%)*p*(63.92%)
π(C11-C12)	1.65331	n/a	C11 (47.42%): *s*(0.01%)*p*(99.90%) C12 (52.58%): *s*(0.01%)*p*(99.91%)
σ(C11-C10)	1.97177	$sp^{1.95}$ at C10 $sp^{2.14}$ at C11	C10 (50.69%): *s*(33.91%)*p*(65.98%) C11 (49.31%): *s*(31.81%)*p*(68.08%)
Lone pair 1 (N4)	1.86998	$sp^{2.45}$	*s*(27.87%)*p*(72.11%)
σ(N4-C9)	1.98860	$sp^{1.60}$ at N4 $sp^{1.92}$ at C9	N4 (59.72%): *s*(38.32%)*p*(61.31%) C9 (40.28%): *s*(34.24%)*p*(65.63%)
π(N4-C9)	1.84779	n/a	N4 (63.49%): *s*(0.00%)*p*(99.82%) C9 (36.51%): *s*(0.00%)*p*(99.86%)
σ(N4-C10)	1.98214	$sp^{1.96}$ at N4 $sp^{2.27}$ at C10	N4 (58.51%): *s*(33.67%)*p*(66.01%) C10 (41.49%): *s*(30.53%)*p*(69.38%)

[a] Calculated in gas phase at the optimized S0 geometry using O3LYP (gas phase/ def2-tzvpp def2/j). The O3LYP functional uses 11.61 % Hartree-Fock exchange.[21]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_Ah_A + c_Bh_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S37. NBO analysis[a] of (^{CF3}**L1**)ZnCl$_2$ with the B3LYP functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.83797	$sp^{2.56}$	*s*(28.05%)*p*(71.86%)
σ(N1-C5)	1.98138	$sp^{1.75}$ at N1 $sp^{1.85}$ at C5	N1 (58.81%): *s*(36.29%)*p*(63.34%) C5 (41.19%): *s*(35.00%)*p*(64.88%)
π(N1-C5)	1.85799	n/a	N1 (74.92%): *s*(0.10%)*p*(99.76%) C5 (25.08%): *s*(0.22%)*p*(99.59%)
σ(N1-C11)	1.98121	$sp^{2.14}$ at N1 $sp^{1.81}$ at C11	N1 (58.56%): *s*(35.43%)*p*(64.25%) C11 (41.44%): *s*(31.84%)*p*(68.05%)
Lone pair 1 (N2)	1.68743	n/a	*s*(0.00%)*p*(99.95%)
σ(N2-C5)	1.98103	$sp^{2.07}$ at N2 $sp^{1.81}$ at C5	N2 (61.24%): *s*(35.55%)*p*(64.26%) C5 (38.76%): *s*(32.57%)*p*(67.31%)
σ(N2-C6a)	1.98389	$sp^{2.10}$ at N2 $sp^{2.88}$ at C6a	N2 (62.32%): *s*(32.23%)*p*(67.65%) C6a (37.68%): *s*(25.73%)*p*(74.17%)
σ(N2-C6b)	1.98482	$sp^{2.12}$ at N2 $sp^{2.77}$ at C6b	N2 (61.75%): *s*(32.06%)*p*(67.81%) C6b (38.25%): *s*(26.50%)*p*(73.41%)
Lone pair 1 (N3)	1.65887	n/a	*s*(2.34%)*p*(97.60%)
σ(N3-C5)	1.97978	$sp^{2.11}$ at N3 $sp^{1.81}$ at C5	N3 (61.03%): *s*(35.51%)*p*(64.27%) C5 (38.97%): *s*(32.12%)*p*(67.76%)
σ(N3-C7a)	1.98152	$sp^{2.26}$ at N3 $sp^{2.87}$ at C7a	N3 (62.11%): *s*(30.68%)*p*(69.19%) C7a (37.89%): *s*(25.81%)*p*(74.09%)
σ(N3-C7b)	1.98584	$sp^{2.19}$ at N3 $sp^{2.91}$ at C7b	N3 (62.40%): *s*(31.30%)*p*(68.57%) C7b (37.60%): *s*(25.53%)*p*(74.37%)
σ(C11-C12)	1.97783	$sp^{1.76}$ at C11 $sp^{1.77}$ at C12	C11 (50.73%): *s*(36.24%)*p*(63.64%) C12 (49.27%): *s*(35.98%)*p*(63.84%)
π(C11-C12)	1.65602	n/a	C11 (47.08%): *s*(0.01%)*p*(99.90%) C12 (52.92%): *s*(0.01%)*p*(99.91%)
σ(C11-C10)	1.97229	$sp^{1.95}$ at C10 $sp^{2.14}$ at C11	C10 (50.72%): *s*(33.91%)*p*(65.97%) C11 (49.28%): *s*(31.82%)*p*(68.05%)
Lone pair 1 (N4)	1.87462	$sp^{2.45}$	*s*(27.39%)*p*(72.59%)
σ(N4-C9)	1.98855	$sp^{1.58}$ at N4 $sp^{1.91}$ at C9	N4 (59.81%): *s*(38.54%)*p*(61.07%) C9 (40.19%): *s*(34.29%)*p*(65.58%)
π(N4-C9)	1.85028	n/a	N4 (63.66%): *s*(0.00%)*p*(99.82%) C9 (36.34%): *s*(0.00%)*p*(99.86%)
σ(N4-C10)	1.98237	$sp^{1.94}$ at N4 $sp^{2.27}$ at C10	N4 (58.68%): *s*(33.93%)*p*(65.73%) C10 (41.32%): *s*(30.52%)*p*(69.38%)

[a] Calculated in gas phase at the optimized S0 geometry using B3LYP (gas phase/ def2-tzvpp def2/j). The B3LYP functional uses 20 % Hartree-Fock exchange.[22]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S38. NBO analysis[a] of ($^{\mathbf{CF3}}$**L1**)$ZnCl_2$ with the PBE0 functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.83982	$sp^{2.57}$	s(27.99%)p(71.92%)
σ(N1-C5)	1.98150	$sp^{1.74}$ at N1 $sp^{1.85}$ at C5	N1 (58.83%): s(36.35%)p(63.27%) C5 (41.17%): s(34.99%)p(64.89%)
π(N1-C5)	1.85878	n/a	N1 (75.22%): s(0.11%)p(99.75%) C5 (24.78%): s(0.23%)p(99.56%)
σ(N1-C11)	1.98127	$sp^{2.13}$ at N1 $sp^{1.81}$ at C11	N1 (58.49%): s(35.42%)p(64.25%) C11 (41.51%): s(31.87%)p(68.03%)
Lone pair 1 (N2)	1.68825	n/a	s(0.00%)p(99.95%)
σ(N2-C5)	1.98111	$sp^{2.07}$ at N2 $sp^{1.80}$ at C5	N2 (61.25%): s(35.59%)p(64.22%) C5 (38.75%): s(32.56%)p(67.32%)
σ(N2-C6a)	1.98393	$sp^{2.10}$ at N2 $sp^{2.89}$ at C6a	N2 (62.30%): s(32.22%)p(67.65%) C6a (37.70%): s(25.68%)p(74.23%)
σ(N2-C6b)	1.98488	$sp^{2.12}$ at N2 $sp^{2.78}$ at C6b	N2 (61.70%): s(32.02%)p(67.85%) C6b (38.30%): s(26.46%)p(73.45%)
Lone pair 1 (N3)	1.66022	n/a	s(2.38%)p(97.56%)
σ(N3-C5)	1.97984	$sp^{2.11}$ at N3 $sp^{1.81}$ at C5	N3 (61.04%): s(35.54%)p(64.24%) C5 (38.96%): s(32.12%)p(67.76%)
σ(N3-C7a)	1.98150	$sp^{2.26}$ at N3 $sp^{2.88}$ at C7a	N3 (62.07%): s(30.66%)p(69.21%) C7a (37.93%): s(25.76%)p(74.15%)
σ(N3-C7b)	1.98589	$sp^{2.20}$ at N3 $sp^{2.92}$ at C7b	N3 (62.34%): s(31.25%)p(68.61%) C7b (37.66%): s(25.48%)p(74.42%)
σ(C11-C12)	1.97794	$sp^{1.76}$ at C11 $sp^{1.78}$ at C12	C11 (50.71%): s(36.24%)p(63.64%) C12 (49.29%): s(35.96%)p(63.86%)
π(C11-C12)	1.65719	n/a	C11 (47.10%): s(0.01%)p(99.90%) C12 (52.90%): s(0.01%)p(99.90%)
σ(C11-C10)	1.97250	$sp^{1.94}$ at C10 $sp^{2.14}$ at C11	C10 (50.74%): s(33.94%)p(65.94%) C11 (49.26%): s(31.80%)p(68.07%)
Lone pair 1 (N4)	1.87641	$sp^{2.63}$	s(27.52%)p(72.46%)
σ(N4-C9)	1.98876	$sp^{1.59}$ at N4 $sp^{1.91}$ at C9	N4 (59.76%): s(38.45%)p(61.16%) C9 (40.24%): s(34.28%)p(65.59%)
π(N4-C9)	1.85124	n/a	N4 (63.77%): s(0.00%)p(99.81%) C9 (36.23%): s(0.00%)p(99.85%)
σ(N4-C10)	1.98253	$sp^{1.94}$ at N4 $sp^{2.27}$ at C10	N4 (58.58%): s(33.89%)p(65.77%) C10 (41.42%): s(30.51%)p(69.40%)

[a] Calculated in gas phase at the optimized S0 geometry using PBE0 (gas phase/ def2-tzvpp def2/j). The PBE0 functional uses 25 % Hartree-Fock exchange.[14]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S39. NBO analysis[a] of $(^{\mathbf{CF3}}\mathbf{L1})\mathrm{ZnCl_2}$ with the M06 functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.83617	$sp^{2.54}$	*s*(28.23%)*p*(71.66%)
σ(N1-C5)	1.98120	$sp^{1.76}$ at N1 $sp^{1.85}$ at C5	N1 (59.04%): *s*(36.13%)*p*(63.56%) C5 (40.96%): *s*(35.01%)*p*(64.90%)
π(N1-C5)	1.86288	n/a	N1 (75.62%): *s*(0.14%)*p*(99.70%) C5 (24.38%): *s*(0.24%)*p*(99.53%)
σ(N1-C11)	1.98091	$sp^{2.14}$ at N1 $sp^{1.82}$ at C11	N1 (58.82%): *s*(35.39%)*p*(64.34%) C11 (41.18%): *s*(31.78%)*p*(68.14%)
Lone pair 1 (N2)	1.69707	n/a	*s*(0.00%)*p*(99.94%)
σ(N2-C5)	1.98082	$sp^{2.07}$ at N2 $sp^{1.81}$ at C5	N2 (61.42%): *s*(35.58%)*p*(64.28%) C5 (38.58%): *s*(32.55%)*p*(67.36%)
σ(N2-C6a)	1.98350	$sp^{2.10}$ at N2 $sp^{2.89}$ at C6a	N2 (62.46%): *s*(32.24%)*p*(67.66%) C6a (37.54%): *s*(25.70%)*p*(74.23%)
σ(N2-C6b)	1.98439	$sp^{2.12}$ at N2 $sp^{2.78}$ at C6b	N2 (61.88%): *s*(32.04%)*p*(67.86%) C6b (38.12%): *s*(26.46%)*p*(73.47%)
Lone pair 1 (N3)	1.66908	n/a	*s*(2.32%)*p*(97.60%)
σ(N3-C5)	1.97943	$sp^{2.11}$ at N3 $sp^{1.81}$ at C5	N3 (61.21%): *s*(35.54%)*p*(64.29%) C5 (38.79%): *s*(32.12%)*p*(67.79%)
σ(N3-C7a)	1.98112	$sp^{2.26}$ at N3 $sp^{2.88}$ at C7a	N3 (62.26%): *s*(30.69%)*p*(69.21%) C7a (37.74%): *s*(25.78%)*p*(74.15%)
σ(N3-C7b)	1.98550	$sp^{2.19}$ at N3 $sp^{2.92}$ at C7b	N3 (62.53%): *s*(31.30%)*p*(68.60%) C7b (37.47%): *s*(25.51%)*p*(74.42%)
σ(C11-C12)	1.97768	$sp^{1.76}$ at C11 $sp^{1.77}$ at C12	C11 (50.63%): *s*(36.26%)*p*(63.64%) C12 (49.37%): *s*(36.03%)*p*(63.76%)
π(C11-C12)	1.65789	n/a	C11 (46.62%): *s*(0.02%)*p*(99.89%) C12 (53.38%): *s*(0.01%)*p*(99.90%)
σ(C11-C10)	1.97190	$sp^{1.94}$ at C10 $sp^{2.13}$ at C11	C10 (50.71%): *s*(33.96%)*p*(65.93%) C11 (49.29%): *s*(31.88%)*p*(68.00%)
Lone pair 1 (N4)	1.87264	$sp^{2.63}$	*s*(27.53%)*p*(72.43%)
σ(N4-C9)	1.98857	$sp^{1.60}$ at N4 $sp^{1.91}$ at C9	N4 (59.87%): *s*(38.38%)*p*(61.29%) C9 (40.13%): *s*(34.38%)*p*(65.52%)
π(N4-C9)	1.85486	n/a	N4 (64.35%): *s*(0.00%)*p*(99.79%) C9 (35.65%): *s*(0.00%)*p*(99.84%)
σ(N4-C10)	1.98198	$sp^{1.94}$ at N4 $sp^{2.28}$ at C10	N4 (58.90%): *s*(33.96%)*p*(65.75%) C10 (41.10%): *s*(30.45%)*p*(69.47%)

[a] Calculated in gas phase at the optimized S0 geometry using M06 (gas phase/ def2-tzvpp def2/j). The M06 functional uses 27 % Hartree-Fock exchange.[23]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|$>0.95), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S40. NBO analysis[a] of ($^{\mathrm{CF3}}$**L1**)ZnCl$_2$ with the M06-2X functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.85336	$sp^{2.65}$	*s*(27.36%)*p*(72.54%)
σ(N1-C5)	1.98161	$sp^{1.72}$ at N1 $sp^{1.86}$ at C5	N1 (58.94%): *s*(36.67%)*p*(62.97%) C5 (41.06%): *s*(34.96%)*p*(64.95%)
π(N1-C5)	1.86651	n/a	N1 (76.02%): *s*(0.11%)*p*(99.73%) C5 (23.98%): *s*(0.24%)*p*(99.54%)
σ(N1-C11)	1.98125	$sp^{2.14}$ at N1 $sp^{1.79}$ at C11	N1 (58.59%): *s*(35.72%)*p*(63.96%) C11 (41.41%): *s*(31.84%)*p*(68.08%)
Lone pair 1 (N2)	1.69821	n/a	*s*(0.00%)*p*(99.94%)
σ(N2-C5)	1.98108	$sp^{2.06}$ at N2 $sp^{1.81}$ at C5	N2 (61.44%): *s*(35.51%)*p*(64.31%) C5 (38.56%): *s*(32.61%)*p*(67.29%)
σ(N2-C6a)	1.98373	$sp^{2.10}$ at N2 $sp^{2.90}$ at C6a	N2 (62.64%): *s*(32.26%)*p*(67.62%) C6a (37.36%): *s*(25.65%)*p*(74.27%)
σ(N2-C6b)	1.98461	$sp^{2.12}$ at N2 $sp^{2.78}$ at C6b	N2 (62.02%): *s*(32.06%)*p*(67.82%) C6b (37.98%): *s*(26.42%)*p*(73.51%)
Lone pair 1 (N3)	1.67034	n/a	*s*(2.27%)*p*(97.65%)
σ(N3-C5)	1.97986	$sp^{2.11}$ at N3 $sp^{1.81}$ at C5	N3 (61.23%): *s*(35.50%)*p*(64.30%) C5 (38.77%): *s*(32.12%)*p*(67.78%)
σ(N3-C7a)	1.98146	$sp^{2.25}$ at N3 $sp^{2.89}$ at C7a	N3 (62.42%): *s*(30.75%)*p*(69.12%) C7a (37.58%): *s*(25.71%)*p*(74.21%)
σ(N3-C7b)	1.98583	$sp^{2.19}$ at N3 $sp^{2.93}$ at C7b	N3 (62.66%): *s*(31.30%)*p*(68.57%) C7b (37.34%): *s*(25.45%)*p*(74.47%)
σ(C11-C12)	1.97829	$sp^{1.75}$ at C11 $sp^{1.77}$ at C12	C11 (50.72%): *s*(36.30%)*p*(63.59%) C12 (49.28%): *s*(36.00%)*p*(63.82%)
π(C11-C12)	1.66363	n/a	C11 (46.88%): *s*(0.02%)*p*(99.90%) C12 (53.12%): *s*(0.01%)*p*(99.90%)
σ(C11-C10)	1.97303	$sp^{1.94}$ at C10 $sp^{2.14}$ at C11	C10 (50.78%): *s*(33.94%)*p*(65.95%) C11 (49.22%): *s*(31.78%)*p*(68.10%)
Lone pair 1 (N4)	1.88916	$sp^{2.71}$	*s*(26.95%)*p*(73.02%)
σ(N4-C9)	1.98869	$sp^{1.57}$ at N4 $sp^{1.92}$ at C9	N4 (59.92%): *s*(38.71%)*p*(60.91%) C9 (40.08%): *s*(34.23%)*p*(65.65%)
π(N4-C9)	1.85752	n/a	N4 (63.69%): *s*(0.00%)*p*(99.79%) C9 (36.31%): *s*(0.00%)*p*(99.85%)
σ(N4-C10)	1.98248	$sp^{1.91}$ at N4 $sp^{2.28}$ at C10	N4 (58.78%): *s*(34.20%)*p*(65.47%) C10 (41.22%): *s*(30.47%)*p*(69.44%)

[a] Calculated in gas phase at the optimized S0 geometry using M06-2X (gas phase/ def2-tzvpp def2/j). The M06-2X functional uses 54 % Hartree-Fock exchange.[23]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \le x \le 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp$^{\lambda}$, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp$^{\infty}$) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S41. NBO analysis[a] of ($^{\mathbf{CF3}}$**L1**)ZnCl$_2$ with the CAM-B3LYP functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.84523	$sp^{2.68}$	s(27.16%)p(72.75%)
σ(N1-C5)	1.98181	$sp^{1.71}$ at N1 $sp^{1.86}$ at C5	N1 (58.87%): s(36.73%)p(62.89%) C5 (41.13%): s(34.94%)p(64.94%)
π(N1-C5)	1.86885	n/a	N1 (76.13%): s(0.13%)p(99.73%) C5 (23.87%): s(0.21%)p(99.57%)
σ(N1-C11)	1.98156	$sp^{2.14}$ at N1 $sp^{1.78}$ at C11	N1 (58.54%): s(35.85%)p(63.81%) C11 (41.46%): s(31.82%)p(68.07%)
Lone pair 1 (N2)	1.69995	n/a	s(0.00%)p(99.95%)
σ(N2-C5)	1.98149	$sp^{2.06}$ at N2 $sp^{1.81}$ at C5	N2 (61.30%): s(35.52%)p(64.28%) C5 (38.70%): s(32.61%)p(67.27%)
σ(N2-C6a)	1.98436	$sp^{2.10}$ at N2 $sp^{2.89}$ at C6a	N2 (62.38%): s(32.24%)p(67.63%) C6a (37.62%): s(25.71%)p(74.19%)
σ(N2-C6b)	1.98526	$sp^{2.11}$ at N2 $sp^{2.78}$ at C6b	N2 (61.80%): s(32.07%)p(67.79%) C6b (38.20%): s(26.46%)p(73.44%)
Lone pair 1 (N3)	1.67140	n/a	s(2.18%)p(97.75%)
σ(N3-C5)	1.98015	$sp^{2.11}$ at N3 $sp^{1.81}$ at C5	N3 (61.08%): s(35.51%)p(64.27%) C5 (38.92%): s(32.13%)p(67.74%)
σ(N3-C7a)	1.98233	$sp^{2.24}$ at N3 $sp^{2.88}$ at C7a	N3 (62.18%): s(30.79%)p(69.07%) C7a (37.82%): s(25.78%)p(74.12%)
σ(N3-C7b)	1.98632	$sp^{2.19}$ at N3 $sp^{2.92}$ at C7b	N3 (62.45%): s(31.35%)p(68.51%) C7b (37.55%): s(25.51%)p(74.39%)
σ(C11-C12)	1.97797	$sp^{1.75}$ at C11 $sp^{1.77}$ at C12	C11 (50.69%): s(36.28%)p(63.60%) C12 (49.31%): s(36.01%)p(63.80%)
π(C11-C12)	1.66410	n/a	C11 (46.69%): s(0.01%)p(99.89%) C12 (53.31%): s(0.01%)p(99.90%)
σ(C11-C10)	1.97308	$sp^{1.94}$ at C10 $sp^{2.14}$ at C11	C10 (50.78%): s(33.95%)p(65.92%) C11 (49.22%): s(31.80%)p(68.06%)
Lone pair 1 (N4)	1.88134	$sp^{2.45}$	s(26.72%)p(73.26%)
σ(N4-C9)	1.98852	$sp^{1.57}$ at N4 $sp^{1.91}$ at C9	N4 (59.79%): s(38.81%)p(60.79%) C9 (40.21%): s(34.28%)p(65.59%)
π(N4-C9)	1.85902	n/a	N4 (63.96%): s(0.00%)p(99.81%) C9 (36.04%): s(0.00%)p(99.85%)
σ(N4-C10)	1.98272	$sp^{1.90}$ at N4 $sp^{2.28}$ at C10	N4 (58.71%): s(34.33%)p(65.32%) C10 (41.29%): s(30.45%)p(69.45%)

[a] Calculated in gas phase at the optimized S0 geometry using CAM-B3LYP (gas phase/ def2-tzvpp def2/j). The CAM-B3LYP functional is a range-separated functional, and uses 19 % Hartree-Fock exchange at short range, 33 % Hartree-Fock exchange at intermediate range, and 65 % Hartree-Fock exchange at long range.[15]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S42. Solvated NBO analysis[a] of (^{CF3}**L1**)ZnCl$_2$ with the M06-L functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.83271	$sp^{2.34}$	s(29.95%)p(69.97%)
σ(N1-C5)	1.98087	$sp^{1.83}$ at N1 $sp^{1.85}$ at C5	N1 (59.17%): s(35.22%)p(64.47%) C5 (40.83%): s(35.04%)p(64.87%)
π(N1-C5)	1.85422	n/a	N1 (74.96%): s(0.11%)p(99.75%) C5 (25.04%): s(0.26%)p(99.53%)
σ(N1-C11)	1.98075	$sp^{1.88}$ at N1 $sp^{2.15}$ at C11	N1 (58.98%): s(34.60%)p(65.12%) C11 (41.02%): s(31.69%)p(68.23%)
Lone pair 1 (N2)	1.67085	n/a	s(0.00%)p(99.94%)
σ(N2-C5)	1.98059	$sp^{1.82}$ at N2 $sp^{2.07}$ at C5	N2 (61.20%): s(35.41%)p(64.42%) C5 (38.80%): s(32.55%)p(67.35%)
σ(N2-C6a)	1.98313	$sp^{2.11}$ at N2 $sp^{2.88}$ at C6a	N2 (62.14%): s(32.16%)p(67.73%) C6a (37.86%): s(25.75%)p(74.18%)
σ(N2-C6b)	1.98339	$sp^{2.09}$ at N2 $sp^{2.81}$ at C6b	N2 (62.03%): s(32.30%)p(67.58%) C6b (37.97%): s(26.26%)p(73.67%)
Lone pair 1 (N3)	1.65168	n/a	s(2.84%)p(97.09%)
σ(N3-C5)	1.97970	$sp^{1.82}$ at N3 $sp^{2.11}$ at C5	N3 (61.13%): s(35.41%)p(64.40%) C5 (38.87%): s(32.08%)p(67.82%)
σ(N3-C7a)	1.97984	$sp^{2.27}$ at N3 $sp^{2.89}$ at C7a	N3 (62.13%): s(30.58%)p(69.30%) C7a (37.87%): s(25.70%)p(74.23%)
σ(N3-C7b)	1.98520	$sp^{2.22}$ at N3 $sp^{2.90}$ at C7b	N3 (62.05%): s(31.03%)p(68.86%) C7b (37.95%): s(25.64%)p(74.30%)
σ(C11-C12)	1.97814	$sp^{1.75}$ at C11 $sp^{1.77}$ at C12	C11 (50.66%): s(36.29%)p(63.59%) C12 (49.34%): s(36.02%)p(63.81%)
π(C11-C12)	1.65328	n/a	C11 (47.32%): s(0.01%)p(99.89%) C12 (52.68%): s(0.01%)p(99.90%)
σ(C11-C10)	1.97254	$sp^{1.94}$ at C10 $sp^{2.13}$ at C11	C10 (50.69%): s(33.98%)p(65.90%) C11 (49.31%): s(31.94%)p(67.92%)
Lone pair 1 (N4)	1.86794	$sp^{2.46}$	s(28.93%)p(71.05%)
σ(N4-C9)	1.98873	$sp^{1.64}$ at N4 $sp^{1.93}$ at C9	N4 (60.07%): s(37.71%)p(61.96%) C9 (39.93%): s(34.12%)p(65.78%)
π(N4-C9)	1.85210	n/a	N4 (64.33%): s(0.00%)p(99.83%) C9 (35.67%): s(0.00%)p(99.85%)
σ(N4-C10)	1.98192	$sp^{2.00}$ at N4 $sp^{2.29}$ at C10	N4 (59.05%): s(33.23%)p(66.47%) C10 (40.95%): s(30.34%)p(69.58%)

[a] Calculated in solution at the optimized S0 geometry using M06-L (gas phase/ def2-tzvpp def2/j). The M06-L functional uses 0 % Hartree-Fock exchange.[19]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}| > 0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S43. Solvated NBO analysis[a] of ($^{\mathbf{CF3}}$**L1**)ZnCl$_2$ with the TPSSh functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.83294	$sp^{2.54}$	*s*(28.21%)*p*(71.72%)
σ(N1-C5)	1.98135	$sp^{1.75}$ at N1 $sp^{1.86}$ at C5	N1 (59.00%): *s*(36.21%)*p*(63.44%) C5 (41.00%): *s*(34.96%)*p*(64.93%)
π(N1-C5)	1.85585	n/a	N1 (75.18%): *s*(0.12%)*p*(99.76%) C5 (24.82%): *s*(0.21%)*p*(99.59%)
σ(N1-C11)	1.98113	$sp^{1.82}$ at N1 $sp^{2.14}$ at C11	N1 (58.69%): *s*(35.36%)*p*(64.34%) C11 (41.31%): *s*(31.82%)*p*(68.08%)
Lone pair 1 (N2)	1.67009	n/a	*s*(0.00%)*p*(99.95%)
σ(N2-C5)	1.98071	$sp^{1.82}$ at N2 $sp^{2.06}$ at C5	N2 (61.06%): *s*(35.42%)*p*(64.40%) C5 (38.94%): *s*(32.67%)*p*(67.22%)
σ(N2-C6a)	1.98339	$sp^{2.11}$ at N2 $sp^{2.90}$ at C6a	N2 (62.39%): *s*(32.14%)*p*(67.74%) C6a (37.61%): *s*(25.61%)*p*(74.30%)
σ(N2-C6b)	1.98373	$sp^{2.09}$ at N2 $sp^{2.82}$ at C6b	N2 (62.26%): *s*(32.29%)*p*(67.59%) C6b (37.74%): *s*(26.14%)*p*(73.77%)
Lone pair 1 (N3)	1.65034	n/a	*s*(2.57%)*p*(97.37%)
σ(N3-C5)	1.97970	$sp^{1.81}$ at N3 $sp^{2.11}$ at C5	N3 (60.99%): *s*(35.50%)*p*(64.30%) C5 (39.01%): *s*(32.07%)*p*(67.82%)
σ(N3-C7a)	1.98047	$sp^{2.26}$ at N3 $sp^{2.91}$ at C7a	N3 (62.38%): *s*(30.67%)*p*(69.20%) C7a (37.62%): *s*(25.55%)*p*(74.35%)
σ(N3-C7b)	1.98569	$sp^{2.21}$ at N3 $sp^{2.92}$ at C7b	N3 (62.32%): *s*(31.10%)*p*(68.77%) C7b (37.68%): *s*(25.50%)*p*(74.40%)
σ(C11-C12)	1.97750	$sp^{1.75}$ at C11 $sp^{1.78}$ at C12	C11 (50.83%): *s*(36.31%)*p*(63.58%) C12 (49.17%): *s*(35.89%)*p*(63.94%)
π(C11-C12)	1.65385	n/a	C11 (47.91%): *s*(0.01%)*p*(99.91%) C12 (52.09%): *s*(0.01%)*p*(99.90%)
σ(C11-C10)	1.97251	$sp^{1.94}$ at C10 $sp^{2.14}$ at C11	C10 (50.74%): *s*(33.92%)*p*(65.96%) C11 (49.26%): *s*(31.80%)*p*(68.07%)
Lone pair 1 (N4)	1.86842	$sp^{2.61}$	*s*(27.72%)*p*(72.26%)
σ(N4-C9)	1.98880	$sp^{1.60}$ at N4 $sp^{1.93}$ at C9	N4 (60.01%): *s*(38.30%)*p*(61.33%) C9 (39.99%): *s*(34.07%)*p*(65.81%)
π(N4-C9)	1.85179	n/a	N4 (64.52%): *s*(0.00%)*p*(99.83%) C9 (35.48%): *s*(0.00%)*p*(99.86%)
σ(N4-C10)	1.98264	$sp^{1.95}$ at N4 $sp^{2.29}$ at C10	N4 (58.81%): *s*(33.84%)*p*(65.84%) C10 (41.19%): *s*(30.41%)*p*(69.49%)

[a] Calculated in solution at the optimized S0 geometry using TPSSh (gas phase/ def2-tzvpp def2/j). The TPSSh functional uses 10 % Hartree-Fock exchange.[11]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S44. Solvated NBO analysis[a] of (**^{CF3}L1**)ZnCl$_2$ with the O3LYP functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.83061	$sp^{2.56}$	*s*(28.03%)*p*(71.88%)
σ(N1-C5)	1.98131	$sp^{1.74}$ at N1 $sp^{1.86}$ at C5	N1 (58.84%): *s*(36.32%)*p*(63.34%) C5 (41.16%): *s*(34.94%)*p*(64.95%)
π(N1-C5)	1.85393	n/a	N1 (75.00%): *s*(0.10%)*p*(99.78%) C5 (25.00%): *s*(0.20%)*p*(99.60%)
σ(N1-C11)	1.98103	$sp^{1.81}$ at N1 $sp^{2.13}$ at C11	N1 (58.52%): *s*(35.43%)*p*(64.27%) C11 (41.48%): *s*(31.87%)*p*(68.03%)
Lone pair 1 (N2)	1.67734	n/a	*s*(0.00%)*p*(99.95%)
σ(N2-C5)	1.98051	$sp^{1.82}$ at N2 $sp^{2.05}$ at C5	N2 (60.91%): *s*(35.36%)*p*(64.46%) C5 (39.09%): *s*(32.72%)*p*(67.17%)
σ(N2-C6a)	1.98357	$sp^{2.11}$ at N2 $sp^{2.89}$ at C6a	N2 (62.13%): *s*(32.15%)*p*(67.74%) C6a (37.87%): *s*(25.70%)*p*(74.21%)
σ(N2-C6b)	1.98393	$sp^{2.09}$ at N2 $sp^{2.81}$ at C6b	N2 (62.01%): *s*(32.33%)*p*(67.55%) C6b (37.99%): *s*(26.23%)*p*(73.68%)
Lone pair 1 (N3)	1.64766	n/a	*s*(2.47%)*p*(97.47%)
σ(N3-C5)	1.97959	$sp^{1.81}$ at N3 $sp^{2.12}$ at C5	N3 (60.85%): *s*(35.46%)*p*(64.34%) C5 (39.15%): *s*(32.05%)*p*(67.84%)
σ(N3-C7a)	1.98086	$sp^{2.25}$ at N3 $sp^{2.90}$ at C7a	N3 (62.12%): *s*(30.76%)*p*(69.12%) C7a (37.88%): *s*(25.65%)*p*(74.27%)
σ(N3-C7b)	1.98573	$sp^{2.21}$ at N3 $sp^{2.90}$ at C7b	N3 (62.06%): *s*(31.14%)*p*(68.73%) C7b (37.94%): *s*(25.60%)*p*(74.31%)
σ(C11-C12)	1.97708	$sp^{1.75}$ at C11 $sp^{1.79}$ at C12	C11 (50.83%): *s*(36.30%)*p*(63.60%) C12 (49.17%): *s*(35.84%)*p*(64.00%)
π(C11-C12)	1.65192	n/a	C11 (47.90%): *s*(0.01%)*p*(99.91%) C12 (52.10%): *s*(0.01%)*p*(99.91%)
σ(C11-C10)	1.97206	$sp^{1.95}$ at C10 $sp^{2.15}$ at C11	C10 (50.73%): *s*(33.88%)*p*(66.02%) C11 (49.27%): *s*(31.76%)*p*(68.13%)
Lone pair 1 (N4)	1.86661	$sp^{2.62}$	*s*(27.60%)*p*(72.38%)
σ(N4-C9)	1.98863	$sp^{1.59}$ at N4 $sp^{1.93}$ at C9	N4 (59.88%): *s*(38.40%)*p*(61.24%) C9 (40.12%): *s*(34.07%)*p*(65.81%)
π(N4-C9)	1.85261	n/a	N4 (64.41%): *s*(0.00%)*p*(99.83%) C9 (35.59%): *s*(0.00%)*p*(99.86%)
σ(N4-C10)	1.98242	$sp^{1.94}$ at N4 $sp^{2.28}$ at C10	N4 (58.64%): *s*(33.86%)*p*(65.83%) C10 (41.36%): *s*(30.48%)*p*(69.43%)

[a] Calculated in solution at the optimized S0 geometry using O3LYP (gas phase/ def2-tzvpp def2/j). The O3LYP functional uses 11.61 % Hartree-Fock exchange.[21]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp$^{\lambda}$, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp$^{\infty}$) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S45. Solvated NBO analysis[a] of ($^{\mathbf{CF3}}$**L1**)ZnCl$_2$ with the B3LYP functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.83578	$sp^{2.61}$	s(27.69%)p(72.22%)
σ(N1-C5)	1.98155	$sp^{1.73}$ at N1 $sp^{1.86}$ at C5	N1 (58.95%): s(36.43%)p(63.20%) C5 (41.05%): s(34.92%)p(64.96%)
π(N1-C5)	1.86028	n/a	N1 (75.69%): s(0.11%)p(99.77%) C5 (24.31%): s(0.19%)p(99.62%)
σ(N1-C11)	1.98140	$sp^{1.80}$ at N1 $sp^{2.14}$ at C11	N1 (58.67%): s(35.65%)p(64.04%) C11 (41.33%): s(31.84%)p(68.05%)
Lone pair 1 (N2)	1.67725	n/a	s(0.00%)p(99.95%)
σ(N2-C5)	1.98085	$sp^{1.83}$ at N2 $sp^{2.05}$ at C5	N2 (61.03%): s(35.33%)p(64.48%) C5 (38.97%): s(32.73%)p(67.15%)
σ(N2-C6a)	1.98387	$sp^{2.11}$ at N2 $sp^{2.88}$ at C6a	N2 (62.28%): s(32.16%)p(67.71%) C6a (37.72%): s(25.77%)p(74.13%)
σ(N2-C6b)	1.98422	$sp^{2.09}$ at N2 $sp^{2.80}$ at C6b	N2 (62.16%): s(32.34%)p(67.53%) C6b (37.84%): s(26.29%)p(73.61%)
Lone pair 1 (N3)	1.65761	n/a	s(2.39%)p(97.55%)
σ(N3-C5)	1.97992	$sp^{1.81}$ at N3 $sp^{2.11}$ at C5	N3 (60.97%): s(35.45%)p(64.34%) C5 (39.03%): s(32.07%)p(67.81%)
σ(N3-C7a)	1.98139	$sp^{2.24}$ at N3 $sp^{2.89}$ at C7a	N3 (62.28%): s(30.81%)p(69.06%) C7a (37.72%): s(25.71%)p(74.19%)
σ(N3-C7b)	1.98605	$sp^{2.20}$ at N3 $sp^{2.89}$ at C7b	N3 (62.21%): s(31.19%)p(68.68%) C7b (37.79%): s(25.68%)p(74.23%)
σ(C11-C12)	1.97744	$sp^{1.75}$ at C11 $sp^{1.78}$ at C12	C11 (50.80%): s(36.29%)p(63.59%) C12 (49.20%): s(35.91%)p(63.91%)
π(C11-C12)	1.65505	n/a	C11 (47.59%): s(0.01%)p(99.91%) C12 (52.41%): s(0.01%)p(99.90%)
σ(C11-C10)	1.97255	$sp^{1.95}$ at C10 $sp^{2.14}$ at C11	C10 (50.74%): s(33.87%)p(66.00%) C11 (49.26%): s(31.78%)p(68.09%)
Lone pair 1 (N4)	1.87092	$sp^{2.69}$	s(27.13%)p(72.85%)
σ(N4-C9)	1.98857	$sp^{1.58}$ at N4 $sp^{1.93}$ at C9	N4 (59.98%): s(38.62%)p(61.00%) C9 (40.02%): s(34.12%)p(65.75%)
π(N4-C9)	1.85506	n/a	N4 (64.65%): s(0.00%)p(99.83%) C9 (35.35%): s(0.00%)p(99.86%)
σ(N4-C10)	1.98262	$sp^{1.92}$ at N4 $sp^{2.28}$ at C10	N4 (58.81%): s(34.11%)p(65.55%) C10 (41.19%): s(30.47%)p(69.42%)

[a] Calculated in solution at the optimized S0 geometry using B3LYP (gas phase/ def2-tzvpp def2/j). The B3LYP functional uses 20 % Hartree-Fock exchange.[22]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S46. Solvated NBO analysis[a] of ($^{\mathbf{CF3}}$**L1**)ZnCl$_2$ with the PBE0 functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.83794	$sp^{2.61}$	*s*(27.62%)*p*(72.29%)
σ(N1-C5)	1.98168	$sp^{1.73}$ at N1 $sp^{1.86}$ at C5	N1 (58.98%): *s*(36.51%)*p*(63.12%) C5 (41.02%): *s*(34.91%)*p*(64.98%)
π(N1-C5)	1.86079	n/a	N1 (76.00%): *s*(0.12%)*p*(99.75%) C5 (24.00%): *s*(0.20%)*p*(99.59%)
σ(N1-C11)	1.98147	$sp^{1.80}$ at N1 $sp^{2.13}$ at C11	N1 (58.59%): *s*(35.63%)*p*(64.04%) C11 (41.41%): *s*(31.87%)*p*(68.03%)
Lone pair 1 (N2)	1.67812	n/a	*s*(0.00%)*p*(99.95%)
σ(N2-C5)	1.98093	$sp^{1.82}$ at N2 $sp^{2.05}$ at C5	N2 (61.04%): *s*(35.36%)*p*(64.44%) C5 (38.96%): *s*(32.73%)*p*(67.16%)
σ(N2-C6a)	1.98392	$sp^{2.11}$ at N2 $sp^{2.89}$ at C6a	N2 (62.24%): *s*(32.15%)*p*(67.72%) C6a (37.76%): *s*(25.71%)*p*(74.19%)
σ(N2-C6b)	1.98425	$sp^{2.09}$ at N2 $sp^{2.81}$ at C6b	N2 (62.12%): *s*(32.31%)*p*(67.56%) C6b (37.88%): *s*(26.24%)*p*(73.67%)
Lone pair 1 (N3)	1.65870	n/a	*s*(2.43%)*p*(97.50%)
σ(N3-C5)	1.97997	$sp^{1.81}$ at N3 $sp^{2.11}$ at C5	N3 (60.97%): *s*(35.47%)*p*(64.31%) C5 (39.03%): *s*(32.07%)*p*(67.81%)
σ(N3-C7a)	1.98135	$sp^{2.24}$ at N3 $sp^{2.89}$ at C7a	N3 (62.24%): *s*(30.79%)*p*(69.08%) C7a (37.76%): *s*(25.65%)*p*(74.25%)
σ(N3-C7b)	1.98610	$sp^{2.21}$ at N3 $sp^{2.90}$ at C7b	N3 (62.16%): *s*(31.14%)*p*(68.73%) C7b (37.84%): *s*(25.62%)*p*(74.29%)
σ(C11-C12)	1.97757	$sp^{1.75}$ at C11 $sp^{1.78}$ at C12	C11 (50.79%): *s*(36.29%)*p*(63.59%) C12 (49.21%): *s*(35.88%)*p*(63.93%)
π(C11-C12)	1.65628	n/a	C11 (47.62%): *s*(0.01%)*p*(99.90%) C12 (52.38%): *s*(0.01%)*p*(99.90%)
σ(C11-C10)	1.97277	$sp^{1.95}$ at C10 $sp^{2.14}$ at C11	C10 (50.76%): *s*(33.90%)*p*(65.98%) C11 (49.24%): *s*(31.76%)*p*(68.11%)
Lone pair 1 (N4)	1.87318	$sp^{2.67}$	*s*(27.26%)*p*(72.72%)
σ(N4-C9)	1.98879	$sp^{1.59}$ at N4 $sp^{1.93}$ at C9	N4 (59.93%): *s*(38.53%)*p*(61.08%) C9 (40.07%): *s*(34.10%)*p*(65.77%)
π(N4-C9)	1.85577	n/a	N4 (64.79%): *s*(0.00%)*p*(99.82%) C9 (35.21%): *s*(0.00%)*p*(99.85%)
σ(N4-C10)	1.98280	$sp^{1.93}$ at N4 $sp^{2.28}$ at C10	N4 (58.71%): *s*(34.07%)*p*(65.59%) C10 (41.29%): *s*(30.46%)*p*(69.44%)

[a] Calculated in solution at the optimized S0 geometry using PBE0 (gas phase/ def2-tzvpp def2/j). The PBE0 functional uses 25 % Hartree-Fock exchange.[14]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \le x \le 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp$^\lambda$, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp$^\infty$) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S47. Solvated NBO analysis[a] of ($^{\mathbf{CF3}}$**L1**)ZnCl$_2$ with the M06 functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.83409	$sp^{2.59}$	s(27.86%)p(72.04%)
σ(N1-C5)	1.98139	$sp^{1.75}$ at N1 $sp^{1.86}$ at C5	N1 (59.18%): s(36.27%)p(63.42%) C5 (40.82%): s(34.94%)p(64.97%)
π(N1-C5)	1.86533	n/a	N1 (76.39%): s(0.15%)p(99.71%) C5 (23.61%): s(0.21%)p(99.57%)
σ(N1-C11)	1.98114	$sp^{1.80}$ at N1 $sp^{2.15}$ at C11	N1 (58.93%): s(35.62%)p(64.11%) C11 (41.07%): s(31.77%)p(68.15%)
Lone pair 1 (N2)	1.68745	n/a	s(0.00%)p(99.94%)
σ(N2-C5)	1.98065	$sp^{1.82}$ at N2 $sp^{2.05}$ at C5	N2 (61.22%): s(35.35%)p(64.50%) C5 (38.78%): s(32.72%)p(67.19%)
σ(N2-C6a)	1.98348	$sp^{2.10}$ at N2 $sp^{2.88}$ at C6a	N2 (62.42%): s(32.18%)p(67.72%) C6a (37.58%): s(25.73%)p(74.19%)
σ(N2-C6b)	1.98374	$sp^{2.09}$ at N2 $sp^{2.81}$ at C6b	N2 (62.31%): s(32.33%)p(67.57%) C6b (37.69%): s(26.25%)p(73.68%)
Lone pair 1 (N3)	1.66770	n/a	s(2.37%)p(97.56%)
σ(N3-C5)	1.97959	$sp^{1.81}$ at N3 $sp^{2.12}$ at C5	N3 (61.15%): s(35.47%)p(64.36%) C5 (38.85%): s(32.07%)p(67.84%)
σ(N3-C7a)	1.98099	$sp^{2.24}$ at N3 $sp^{2.89}$ at C7a	N3 (62.43%): s(30.82%)p(69.08%) C7a (37.57%): s(25.67%)p(74.26%)
σ(N3-C7b)	1.98572	$sp^{2.20}$ at N3 $sp^{2.90}$ at C7b	N3 (62.35%): s(31.19%)p(68.70%) C7b (37.65%): s(25.64%)p(74.29%)
σ(C11-C12)	1.97729	$sp^{1.75}$ at C11 $sp^{1.77}$ at C12	C11 (50.69%): s(36.31%)p(63.58%) C12 (49.31%): s(36.02%)p(63.83%)
π(C11-C12)	1.65771	n/a	C11 (47.16%): s(0.01%)p(99.90%) C12 (52.84%): s(0.01%)p(99.90%)
σ(C11-C10)	1.97213	$sp^{1.94}$ at C10 $sp^{2.14}$ at C11	C10 (50.72%): s(33.92%)p(65.97%) C11 (49.28%): s(31.84%)p(68.04%)
Lone pair 1 (N4)	1.86877	$sp^{2.67}$	s(27.27%)p(72.70%)
σ(N4-C9)	1.98860	$sp^{1.59}$ at N4 $sp^{1.92}$ at C9	N4 (60.04%): s(38.46%)p(61.22%) C9 (39.96%): s(34.21%)p(65.70%)
π(N4-C9)	1.85971	n/a	N4 (65.45%): s(0.00%)p(99.81%) C9 (34.55%): s(0.00%)p(99.84%)
σ(N4-C10)	1.98255	$sp^{1.92}$ at N4 $sp^{2.29}$ at C10	N4 (59.04%): s(34.15%)p(65.56%) C10 (40.96%): s(30.40%)p(69.51%)

[a] Calculated in solution at the optimized S0 geometry using M06 (gas phase/ def2-tzvpp def2/j). The M06 functional uses 27 % Hartree-Fock exchange.[23]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S48. Solvated NBO analysis[a] of ($^{\mathbf{CF3}}$**L1**)ZnCl$_2$ with the M06-2X functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.85205	$sp^{2.70}$	*s*(27.00%)*p*(72.91%)
σ(N1-C5)	1.98178	$sp^{1.71}$ at N1 $sp^{1.87}$ at C5	N1 (59.09%): *s*(36.83%)*p*(62.81%) C5 (40.91%): *s*(34.87%)*p*(65.04%)
π(N1-C5)	1.86873	n/a	N1 (76.78%): *s*(0.12%)*p*(99.74%) C5 (23.22%): *s*(0.21%)*p*(99.56%)
σ(N1-C11)	1.98142	$sp^{1.77}$ at N1 $sp^{2.14}$ at C11	N1 (58.69%): *s*(35.93%)*p*(63.76%) C11 (41.31%): *s*(31.84%)*p*(68.08%)
Lone pair 1 (N2)	1.68836	n/a	*s*(0.00%)*p*(99.94%)
σ(N2-C5)	1.98088	$sp^{1.83}$ at N2 $sp^{2.05}$ at C5	N2 (61.23%): *s*(35.29%)*p*(64.53%) C5 (38.77%): *s*(32.78%)*p*(67.13%)
σ(N2-C6a)	1.98370	$sp^{2.10}$ at N2 $sp^{2.89}$ at C6a	N2 (62.59%): *s*(32.19%)*p*(67.69%) C6a (37.41%): *s*(25.68%)*p*(74.24%)
σ(N2-C6b)	1.98397	$sp^{2.09}$ at N2 $sp^{2.82}$ at C6b	N2 (62.47%): *s*(32.35%)*p*(67.53%) C6b (37.53%): *s*(26.19%)*p*(73.73%)
Lone pair 1 (N3)	1.66902	n/a	*s*(2.32%)*p*(97.60%)
σ(N3-C5)	1.97996	$sp^{1.82}$ at N3 $sp^{2.12}$ at C5	N3 (61.17%): *s*(35.43%)*p*(64.36%) C5 (38.83%): *s*(32.07%)*p*(67.83%)
σ(N3-C7a)	1.98130	$sp^{2.23}$ at N3 $sp^{2.90}$ at C7a	N3 (62.60%): *s*(30.88%)*p*(68.99%) C7a (37.40%): *s*(25.60%)*p*(74.32%)
σ(N3-C7b)	1.98601	$sp^{2.20}$ at N3 $sp^{2.91}$ at C7b	N3 (62.49%): *s*(31.19%)*p*(68.68%) C7b (37.65%): *s*(25.58%)*p*(74.34%)
σ(C11-C12)	1.97794	$sp^{1.75}$ at C11 $sp^{1.78}$ at C12	C11 (50.80%): *s*(36.35%)*p*(63.54%) C12 (49.20%): *s*(35.93%)*p*(63.90%)
π(C11-C12)	1.66333	n/a	C11 (47.40%): *s*(0.01%)*p*(99.91%) C12 (52.60%): *s*(0.01%)*p*(99.90%)
σ(C11-C10)	1.97327	$sp^{1.95}$ at C10 $sp^{2.15}$ at C11	C10 (50.79%): *s*(33.91%)*p*(65.99%) C11 (49.21%): *s*(31.74%)*p*(68.14%)
Lone pair 1 (N4)	1.88658	$sp^{2.75}$	*s*(26.69%)*p*(73.29%)
σ(N4-C9)	1.98872	$sp^{1.57}$ at N4 $sp^{1.93}$ at C9	N4 (60.11%): *s*(38.81%)*p*(60.82%) C9 (39.89%): *s*(34.04%)*p*(65.85%)
π(N4-C9)	1.86154	n/a	N4 (64.78%): *s*(0.00%)*p*(99.80%) C9 (35.22%): *s*(0.00%)*p*(99.84%)
σ(N4-C10)	1.98273	$sp^{1.90}$ at N4 $sp^{2.28}$ at C10	N4 (58.90%): *s*(34.37%)*p*(65.30%) C10 (41.10%): *s*(30.43%)*p*(69.48%)

[a] Calculated in solution at the optimized S0 geometry using M06-2X (gas phase/ def2-tzvpp def2/j). The M06-2X functional uses 54 % Hartree-Fock exchange.[23]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}| > 0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S49. Solvated NBO analysis[a] of (**^{CF3}L1**)ZnCl$_2$ with the CAM-B3LYP functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.84325	$sp^{2.73}$	*s*(26.80%)*p*(73.11%)
σ(N1-C5)	1.98195	$sp^{1.70}$ at N1 $sp^{1.87}$ at C5	N1 (59.01%): *s*(36.87%)*p*(62.75%) C5 (40.99%): *s*(34.86%)*p*(65.02%)
π(N1-C5)	1.87117	n/a	N1 (76.90%): *s*(0.14%)*p*(99.73%) C5 (23.10%): *s*(0.18%)*p*(99.59%)
σ(N1-C11)	1.98172	$sp^{1.76}$ at N1 $sp^{2.14}$ at C11	N1 (58.66%): *s*(36.07%)*p*(63.59%) C11 (41.34%): *s*(31.81%)*p*(68.08%)
Lone pair 1 (N2)	1.68996	n/a	*s*(0.00%)*p*(99.94%)
σ(N2-C5)	1.98132	$sp^{1.83}$ at N2 $sp^{2.05}$ at C5	N2 (61.09%): *s*(35.30%)*p*(64.50%) C5 (38.91%): *s*(32.77%)*p*(67.10%)
σ(N2-C6a)	1.98434	$sp^{2.10}$ at N2 $sp^{2.88}$ at C6a	N2 (62.34%): *s*(32.17%)*p*(67.69%) C6a (37.66%): *s*(25.74%)*p*(74.15%)
σ(N2-C6b)	1.98469	$sp^{2.09}$ at N2 $sp^{2.81}$ at C6b	N2 (62.22%): *s*(32.35%)*p*(67.52%) C6b (37.78%): *s*(26.25%)*p*(73.65%)
Lone pair 1 (N3)	1.67036	n/a	*s*(2.22%)*p*(97.71%)
σ(N3-C5)	1.98028	$sp^{1.81}$ at N3 $sp^{2.11}$ at C5	N3 (61.03%): *s*(35.45%)*p*(64.33%) C5 (38.97%): *s*(32.08%)*p*(67.80%)
σ(N3-C7a)	1.98223	$sp^{2.23}$ at N3 $sp^{2.89}$ at C7a	N3 (62.34%): *s*(30.92%)*p*(68.94%) C7a (37.66%): *s*(25.68%)*p*(74.22%)
σ(N3-C7b)	1.98651	$sp^{2.20}$ at N3 $sp^{2.89}$ at C7b	N3 (62.26%): *s*(31.23%)*p*(68.62%) C7b (37.74%): *s*(25.65%)*p*(74.24%)
σ(C11-C12)	1.97762	$sp^{1.75}$ at C11 $sp^{1.78}$ at C12	C11 (50.77%): *s*(36.33%)*p*(63.55%) C12 (49.23%): *s*(35.94%)*p*(63.87%)
π(C11-C12)	1.66358	n/a	C11 (47.26%): *s*(0.01%)*p*(99.90%) C12 (52.74%): *s*(0.01%)*p*(99.90%)
σ(C11-C10)	1.97330	$sp^{1.94}$ at C10 $sp^{2.14}$ at C11	C10 (50.79%): *s*(33.92%)*p*(65.96%) C11 (49.21%): *s*(31.77%)*p*(68.10%)
Lone pair 1 (N4)	1.87784	$sp^{2.78}$	*s*(26.46%)*p*(73.52%)
σ(N4-C9)	1.98854	$sp^{1.56}$ at N4 $sp^{1.93}$ at C9	N1 (59.96%): *s*(38.89%)*p*(60.72%) C5 (40.04%): *s*(34.09%)*p*(65.77%)
π(N4-C9)	1.86320	n/a	N1 (65.06%): *s*(0.00%)*p*(99.82%) C5 (34.94%): *s*(0.00%)*p*(99.85%)
σ(N4-C10)	1.98294	$sp^{1.89}$ at N4 $sp^{2.29}$ at C10	N4 (58.83%): *s*(34.51%)*p*(65.14%) C10 (41.17%): *s*(30.41%)*p*(69.49%)

[a] Calculated in solution at the optimized S0 geometry using CAM-B3LYP (gas phase/ def2-tzvpp def2/j). The CAM-B3LYP functional is a range-separated functional, and uses 19 % Hartree-Fock exchange at short range, 33 % Hartree-Fock exchange at intermediate range, and 65 % Hartree-Fock exchange at long range.[15]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp$^\lambda$, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp$^\infty$) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S50. NBO analysis[a] of (^{tBu}**L1**)ZnCl_2 with the M06-L functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.83269	$sp^{2.29}$	*s*(30.35%)*p*(69.56%)
σ(N1-C5)	1.98071	$sp^{1.84}$ at N1 $sp^{1.84}$ at C5	N1 (59.02%): *s*(35.14%)*p*(64.53%) C5 (40.98%): *s*(35.20%)*p*(64.71%)
π(N1-C5)	1.86750	n/a	N1 (73.65%): *s*(0.19%)*p*(99.67%) C5 (26.35%): *s*(0.35%)*p*(99.44%)
σ(N1-C11)	1.97991	$sp^{1.92}$ at N1 $sp^{2.21}$ at C11	N1 (59.03%): *s*(34.19%)*p*(65.53%) C11 (40.97%): *s*(31.14%)*p*(68.77%)
Lone pair 1 (N2)	1.68704	n/a	*s*(0.00%)*p*(99.95%)
σ(N2-C5)	1.98083	$sp^{1.81}$ at N2 $sp^{2.09}$ at C5	N2 (61.47%): *s*(35.57%)*p*(64.27%) C5 (38.53%): *s*(32.29%)*p*(67.61%)
σ(N2-C6a)	1.98303	$sp^{2.10}$ at N2 $sp^{2.88}$ at C6a	N2 (62.12%): *s*(32.20%)*p*(67.69%) C6a (37.88%): *s*(25.78%)*p*(74.15%)
σ(N2-C6b)	1.98462	$sp^{2.11}$ at N2 $sp^{2.75}$ at C6b	N2 (61.49%): *s*(32.10%)*p*(67.78%) C6b (38.51%): *s*(26.64%)*p*(73.29%)
Lone pair 1 (N3)	1.65904	n/a	*s*(3.20%)*p*(96.73%)
σ(N3-C5)	1.97958	$sp^{1.82}$ at N3 $sp^{2.11}$ at C5	N3 (61.23%): *s*(35.36%)*p*(64.45%) C5 (38.77%): *s*(32.09%)*p*(67.82%)
σ(N3-C7a)	1.97991	$sp^{2.29}$ at N3 $sp^{2.87}$ at C7a	N3 (61.92%): *s*(30.33%)*p*(69.55%) C7a (38.08%): *s*(25.85%)*p*(74.09%)
σ(N3-C7b)	1.98482	$sp^{2.23}$ at N3 $sp^{2.91}$ at C7b	N3 (62.15%): *s*(30.96%)*p*(68.92%) C7b (37.85%): *s*(25.57%)*p*(74.36%)
σ(C11-C12)	1.97726	$sp^{1.71}$ at C11 $sp^{1.82}$ at C12	C11 (50.84%): *s*(36.82%)*p*(63.07%) C12 (49.16%): *s*(35.45%)*p*(64.37%)
π(C11-C12)	1.67213	n/a	C11 (46.62%): *s*(0.03%)*p*(99.88%) C12 (53.38%): *s*(0.02%)*p*(99.89%)
σ(C11-C10)	1.97156	$sp^{1.93}$ at C10 $sp^{2.13}$ at C11	C10 (50.74%): *s*(34.08%)*p*(65.79%) C11 (49.26%): *s*(31.95%)*p*(67.92%)
Lone pair 1 (N4)	1.87040	$sp^{2.44}$	*s*(29.07%)*p*(70.91%)
σ(N4-C9)	1.98868	$sp^{1.65}$ at N4 $sp^{1.91}$ at C9	N4 (59.91%): *s*(37.66%)*p*(62.00%) C9 (40.09%): *s*(34.31%)*p*(65.59%)
π(N4-C9)	1.85216	n/a	N4 (64.03%): *s*(0.00%)*p*(99.82%) C9 (36.97%): *s*(0.00%)*p*(99.86%)
σ(N4-C10)	1.98137	$sp^{2.01}$ at N4 $sp^{2.29}$ at C10	N4 (58.97%): *s*(33.13%)*p*(66.58%) C10 (41.03%): *s*(30.34%)*p*(69.57%)

[a] Calculated in gas phase at the optimized S0 geometry using M06-L (gas phase/ def2-tzvpp def2/j). The M06-L functional uses 0 % Hartree-Fock exchange. [19]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \le x \le 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S51. NBO analysis[a] of (**^{tBu}L1**)ZnCl$_2$ with the TPSSh functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.83320	$sp^{2.49}$	*s*(28.61%)*p*(71.31%)
σ(N1-C5)	1.98120	$sp^{1.76}$ at N1 $sp^{1.84}$ at C5	N1 (58.83%): *s*(36.14%)*p*(63.50%) C5 (41.17%): *s*(35.15%)*p*(64.74%)
π(N1-C5)	1.86941	n/a	N1 (73.79%): *s*(0.18%)*p*(99.69%) C5 (26.21%): *s*(0.29%)*p*(99.51%)
σ(N1-C11)	1.98039	$sp^{1.85}$ at N1 $sp^{2.20}$ at C11	N1 (58.76%): *s*(34.96%)*p*(64.73%) C11 (41.24%): *s*(31.26%)*p*(68.64%)
Lone pair 1 (N2)	1.68732	n/a	*s*(0.00%)*p*(99.95%)
σ(N2-C5)	1.98098	$sp^{1.81}$ at N2 $sp^{2.08}$ at C5	N2 (61.34%): *s*(35.58%)*p*(64.24%) C5 (38.66%): *s*(32.40%)*p*(67.49%)
σ(N2-C6a)	1.98332	$sp^{2.10}$ at N2 $sp^{2.90}$ at C6a	N2 (62.37%): *s*(32.18%)*p*(67.70%) C6a (37.63%): *s*(25.65%)*p*(74.26%)
σ(N2-C6b)	1.98498	$sp^{2.11}$ at N2 $sp^{2.76}$ at C6b	N2 (61.68%): *s*(32.08%)*p*(67.79%) C6b (38.32%): *s*(26.54%)*p*(73.37%)
Lone pair 1 (N3)	1.65808	n/a	*s*(2.91%)*p*(97.03%)
σ(N3-C5)	1.97965	$sp^{1.81}$ at N3 $sp^{2.11}$ at C5	N3 (61.09%): *s*(35.46%)*p*(64.34%) C5 (38.91%): *s*(32.07%)*p*(67.82%)
σ(N3-C7a)	1.98062	$sp^{2.28}$ at N3 $sp^{2.88}$ at C7a	N3 (62.14%): *s*(30.42%)*p*(69.45%) C7a (37.86%): *s*(25.72%)*p*(74.19%)
σ(N3-C7b)	1.98534	$sp^{2.22}$ at N3 $sp^{2.93}$ at C7b	N3 (62.42%): *s*(31.06%)*p*(68.81%) C7b (37.58%): *s*(25.44%)*p*(74.47%)
σ(C11-C12)	1.97670	$sp^{1.71}$ at C11 $sp^{1.83}$ at C12	C11 (50.98%): *s*(36.82%)*p*(63.07%) C12 (49.02%): *s*(35.33%)*p*(64.49%)
π(C11-C12)	1.67280	n/a	C11 (47.19%): *s*(0.02%)*p*(99.89%) C12 (52.81%): *s*(0.02%)*p*(99.90%)
σ(C11-C10)	1.97149	$sp^{1.93}$ at C10 $sp^{2.14}$ at C11	C10 (50.78%): *s*(34.04%)*p*(65.85%) C11 (49.22%): *s*(31.82%)*p*(68.05%)
Lone pair 1 (N4)	1.87078	$sp^{2.59}$	*s*(27.87%)*p*(72.11%)
σ(N4-C9)	1.98873	$sp^{1.60}$ at N4 $sp^{1.91}$ at C9	N4 (59.83%): *s*(38.25%)*p*(61.38%) C9 (40.17%): *s*(34.29%)*p*(65.59%)
π(N4-C9)	1.85227	n/a	N4 (63.12%): *s*(0.00%)*p*(99.83%) C9 (36.88%): *s*(0.00%)*p*(99.86%)
σ(N4-C10)	1.98209	$sp^{1.95}$ at N4 $sp^{2.28}$ at C10	N4 (58.74%): *s*(33.74%)*p*(65.94%) C10 (41.26%): *s*(30.42%)*p*(69.48%)

[a] Calculated in gas phase at the optimized S0 geometry using TPSSh (gas phase/ def2-tzvpp def2/j). The TPSSh functional uses 10 % Hartree-Fock exchange.[11]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S52. NBO analysis[a] of (^{tBu}**L1**)ZnCl$_2$ with the O3LYP functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.83085	$sp^{2.51}$	*s*(28.43%)*p*(71.47%)
σ(N1-C5)	1.98116	$sp^{1.75}$ at N1 $sp^{1.84}$ at C5	N1 (58.68%): *s*(36.23%)*p*(63.41%) C5 (41.32%): *s*(35.12%)*p*(64.77%)
π(N1-C5)	1.86849	n/a	N1 (73.59%): *s*(0.16%)*p*(99.71%) C5 (26.41%): *s*(0.28%)*p*(99.53%)
σ(N1-C11)	1.98030	$sp^{1.84}$ at N1 $sp^{2.19}$ at C11	N1 (58.59%): *s*(35.05%)*p*(64.65%) C11 (41.41%): *s*(31.32%)*p*(68.59%)
Lone pair 1 (N2)	1.68491	n/a	*s*(0.00%)*p*(99.95%)
σ(N2-C5)	1.98081	$sp^{1.81}$ at N2 $sp^{2.08}$ at C5	N2 (61.19%): *s*(35.52%)*p*(64.31%) C5 (38.81%): *s*(32.46%)*p*(67.44%)
σ(N2-C6a)	1.98348	$sp^{2.10}$ at N2 $sp^{2.88}$ at C6a	N2 (62.11%): *s*(32.19%)*p*(67.69%) C6a (37.89%): *s*(25.74%)*p*(74.18%)
σ(N2-C6b)	1.98516	$sp^{2.11}$ at N2 $sp^{2.75}$ at C6b	N2 (61.45%): *s*(32.13%)*p*(67.75%) C6b (38.55%): *s*(26.62%)*p*(73.30%)
Lone pair 1 (N3)	1.65568	n/a	*s*(2.81%)*p*(97.13%)
σ(N3-C5)	1.97957	$sp^{1.82}$ at N3 $sp^{2.12}$ at C5	N3 (60.96%): *s*(35.42%)*p*(64.38%) C5 (39.04%): *s*(32.05%)*p*(67.84%)
σ(N3-C7a)	1.98101	$sp^{2.27}$ at N3 $sp^{2.87}$ at C7a	N3 (61.88%): *s*(30.51%)*p*(69.37%) C7a (38.12%): *s*(25.80%)*p*(74.11%)
σ(N3-C7b)	1.98538	$sp^{2.21}$ at N3 $sp^{2.91}$ at C7b	N3 (62.16%): *s*(31.10%)*p*(68.78%) C7b (37.84%): *s*(25.53%)*p*(74.38%)
σ(C11-C12)	1.97630	$sp^{1.71}$ at C11 $sp^{1.83}$ at C12	C11 (50.97%): *s*(36.80%)*p*(63.10%) C12 (49.03%): *s*(35.28%)*p*(64.55%)
π(C11-C12)	1.67176	n/a	C11 (47.24%): *s*(0.02%)*p*(99.90%) C12 (52.76%): *s*(0.02%)*p*(99.90%)
σ(C11-C10)	1.97106	$sp^{1.94}$ at C10 $sp^{2.14}$ at C11	C10 (50.76%): *s*(33.99%)*p*(65.91%) C11 (49.24%): *s*(31.79%)*p*(68.09%)
Lone pair 1 (N4)	1.86882	$sp^{2.60}$	*s*(27.75%)*p*(72.23%)
σ(N4-C9)	1.98856	$sp^{1.60}$ at N4 $sp^{1.91}$ at C9	N4 (59.71%): *s*(38.35%)*p*(61.29%) C9 (40.29%): *s*(34.29%)*p*(65.59%)
π(N4-C9)	1.85325	n/a	N4 (63.06%): *s*(0.00%)*p*(99.83%) C9 (36.94%): *s*(0.00%)*p*(99.87%)
σ(N4-C10)	1.98187	$sp^{1.95}$ at N4 $sp^{2.28}$ at C10	N4 (58.58%): *s*(33.76%)*p*(65.93%) C10 (41.42%): *s*(30.49%)*p*(69.42%)

[a] Calculated in gas phase at the optimized S0 geometry using O3LYP (gas phase/ def2-tzvpp def2/j). The O3LYP functional uses 11.61 % Hartree-Fock exchange.[21]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_Ah_A + c_Bh_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S53. NBO analysis[a] of (^{tBu}**L1**)ZnCl$_2$ with the B3LYP functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.83631	$sp^{2.56}$	*s*(28.07%)*p*(71.84%)
σ(N1-C5)	1.98142	$sp^{1.74}$ at N1 $sp^{1.85}$ at C5	N1 (58.79%): *s*(36.38%)*p*(63.25%) C5 (41.21%): *s*(35.10%)*p*(64.78%)
π(N1-C5)	1.87368	n/a	N1 (74.28%): *s*(0.17%)*p*(99.70%) C5 (25.72%): *s*(0.26%)*p*(99.55%)
σ(N1-C11)	1.98071	$sp^{1.83}$ at N1 $sp^{2.19}$ at C11	N1 (58.73%): *s*(35.26%)*p*(64.42%) C11 (41.27%): *s*(31.29%)*p*(68.60%)
Lone pair 1 (N2)	1.69436	n/a	*s*(0.00%)*p*(99.95%)
σ(N2-C5)	1.98113	$sp^{1.81}$ at N2 $sp^{2.08}$ at C5	N2 (61.31%): *s*(35.48%)*p*(64.33%) C5 (38.69%): *s*(32.47%)*p*(67.41%)
σ(N2-C6a)	1.98380	$sp^{2.10}$ at N2 $sp^{2.87}$ at C6a	N2 (62.25%): *s*(32.20%)*p*(67.67%) C6a (37.75%): *s*(25.80%)*p*(74.10%)
σ(N2-C6b)	1.98539	$sp^{2.11}$ at N2 $sp^{2.75}$ at C6b	N2 (61.60%): *s*(32.15%)*p*(67.72%) C6b (38.40%): *s*(26.67%)*p*(73.24%)
Lone pair 1 (N3)	1.66500	n/a	*s*(2.71%)*p*(97.23%)
σ(N3-C5)	1.97988	$sp^{1.82}$ at N3 $sp^{2.11}$ at C5	N3 (61.07%): *s*(35.40%)*p*(64.39%) C5 (38.93%): *s*(32.07%)*p*(67.81%)
σ(N3-C7a)	1.98151	$sp^{2.27}$ at N3 $sp^{2.86}$ at C7a	N3 (62.05%): *s*(30.57%)*p*(69.30%) C7a (37.95%): *s*(25.86%)*p*(74.04%)
σ(N3-C7b)	1.98572	$sp^{2.21}$ at N3 $sp^{2.90}$ at C7b	N3 (62.32%): *s*(31.15%)*p*(68.71%) C7b (37.68%): *s*(25.60%)*p*(74.30%)
σ(C11-C12)	1.97664	$sp^{1.71}$ at C11 $sp^{1.82}$ at C12	C11 (50.96%): *s*(36.80%)*p*(63.09%) C12 (49.04%): *s*(35.33%)*p*(64.47%)
π(C11-C12)	1.67459	n/a	C11 (46.87%): *s*(0.02%)*p*(99.90%) C12 (53.13%): *s*(0.02%)*p*(99.90%)
σ(C11-C10)	1.97155	$sp^{1.94}$ at C10 $sp^{2.14}$ at C11	C10 (50.79%): *s*(33.99%)*p*(65.89%) C11 (49.21%): *s*(31.80%)*p*(68.07%)
Lone pair 1 (N4)	1.87345	$sp^{2.67}$	*s*(27.26%)*p*(72.72%)
σ(N4-C9)	1.98850	$sp^{1.58}$ at N4 $sp^{1.91}$ at C9	N4 (59.80%): *s*(38.57%)*p*(61.04%) C9 (40.20%): *s*(34.33%)*p*(65.53%)
π(N4-C9)	1.85575	n/a	N4 (63.20%): *s*(0.00%)*p*(99.83%) C9 (36.80%): *s*(0.00%)*p*(99.87%)
σ(N4-C10)	1.98210	$sp^{1.93}$ at N4 $sp^{2.28}$ at C10	N4 (58.75%): *s*(34.02%)*p*(65.65%) C10 (41.25%): *s*(30.47%)*p*(69.42%)

[a] Calculated in gas phase at the optimized S0 geometry using B3LYP (gas phase/ def2-tzvpp def2/j). The B3LYP functional uses 20 % Hartree-Fock exchange.[22]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S54. NBO analysis[a] of ($^{t\mathrm{Bu}}$**L1**)ZnCl$_2$ with the PBE0 functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.83821	$sp^{2.57}$	*s*(28.00%)*p*(71.90%)
σ(N1-C5)	1.98154	$sp^{1.73}$ at N1 $sp^{1.85}$ at C5	N1 (58.82%): *s*(36.43%)*p*(63.18%) C5 (41.18%): *s*(35.10%)*p*(64.79%)
π(N1-C5)	1.87417	n/a	N1 (74.57%): *s*(0.18%)*p*(99.68%) C5 (25.43%): *s*(0.27%)*p*(99.52%)
σ(N1-C11)	1.98076	$sp^{1.83}$ at N1 $sp^{2.19}$ at C11	N1 (58.66%): *s*(35.25%)*p*(64.42%) C11 (41.34%): *s*(31.31%)*p*(68.59%)
Lone pair 1 (N2)	1.69507	n/a	*s*(0.00%)*p*(99.95%)
σ(N2-C5)	1.98121	$sp^{1.81}$ at N2 $sp^{2.08}$ at C5	N2 (61.32%): *s*(35.52%)*p*(64.29%) C5 (38.68%): *s*(32.46%)*p*(67.42%)
σ(N2-C6a)	1.98384	$sp^{2.10}$ at N2 $sp^{2.88}$ at C6a	N2 (62.23%): *s*(32.20%)*p*(67.67%) C6a (37.77%): *s*(25.74%)*p*(74.16%)
σ(N2-C6b)	1.98544	$sp^{2.11}$ at N2 $sp^{2.75}$ at C6b	N2 (61.55%): *s*(32.12%)*p*(67.75%) C6b (38.45%): *s*(26.63%)*p*(73.28%)
Lone pair 1 (N3)	1.66633	n/a	*s*(2.75%)*p*(97.18%)
σ(N3-C5)	1.97995	$sp^{1.82}$ at N3 $sp^{2.11}$ at C5	N3 (61.08%): *s*(35.43%)*p*(64.35%) C5 (38.92%): *s*(32.07%)*p*(67.81%)
σ(N3-C7a)	1.98149	$sp^{2.27}$ at N3 $sp^{2.87}$ at C7a	N3 (62.00%): *s*(30.55%)*p*(69.32%) C7a (38.00%): *s*(25.81%)*p*(74.10%)
σ(N3-C7b)	1.98577	$sp^{2.21}$ at N3 $sp^{2.91}$ at C7b	N3 (62.26%): *s*(31.10%)*p*(68.76%) C7b (37.74%): *s*(25.55%)*p*(74.35%)
σ(C11-C12)	1.97672	$sp^{1.71}$ at C11 $sp^{1.83}$ at C12	C11 (50.94%): *s*(36.82%)*p*(63.08%) C12 (49.06%): *s*(35.31%)*p*(64.50%)
π(C11-C12)	1.67573	n/a	C11 (46.89%): *s*(0.02%)*p*(99.89%) C12 (53.11%): *s*(0.02%)*p*(99.90%)
σ(C11-C10)	1.97175	$sp^{1.94}$ at C10 $sp^{2.14}$ at C11	C10 (50.81%): *s*(34.02%)*p*(65.87%) C11 (49.19%): *s*(31.78%)*p*(68.09%)
Lone pair 1 (N4)	1.87532	$sp^{2.65}$	*s*(27.39%)*p*(72.59%)
σ(N4-C9)	1.98870	$sp^{1.59}$ at N4 $sp^{1.91}$ at C9	N4 (59.75%): *s*(38.48%)*p*(61.13%) C9 (40.25%): *s*(34.33%)*p*(65.55%)
π(N4-C9)	1.85662	n/a	N4 (63.30%): *s*(0.00%)*p*(99.82%) C9 (36.70%): *s*(0.00%)*p*(99.86%)
σ(N4-C10)	1.98225	$sp^{1.93}$ at N4 $sp^{2.28}$ at C10	N4 (58.66%): *s*(33.98%)*p*(65.68%) C10 (41.34%): *s*(30.46%)*p*(69.44%)

[a] Calculated in gas phase at the optimized S0 geometry using PBE0 (gas phase/ def2-tzvpp def2/j). The PBE0 functional uses 25 % Hartree-Fock exchange.[14]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|$>0.95), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp$^{\lambda}$, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp$^{\infty}$) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S55. NBO analysis[a] of ($^{t\text{Bu}}$**L1**)ZnCl$_2$ with the M06 functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.83458	$sp^{2.54}$	*s*(28.24%)*p*(71.65%)
σ(N1-C5)	1.98124	$sp^{1.75}$ at N1 $sp^{1.85}$ at C5	N1 (59.03%): *s*(36.21%)*p*(63.48%) C5 (40.97%): *s*(35.12%)*p*(64.80%)
π(N1-C5)	1.87742	n/a	N1 (74.98%): *s*(0.22%)*p*(99.63%) C5 (25.02%): *s*(0.29%)*p*(99.49%)
σ(N1-C11)	1.98036	$sp^{1.83}$ at N1 $sp^{2.20}$ at C11	N1 (59.00%): *s*(35.22%)*p*(64.51%) C11 (41.00%): *s*(31.22%)*p*(68.70%)
Lone pair 1 (N2)	1.70357	n/a	*s*(0.00%)*p*(99.94%)
σ(N2-C5)	1.98088	$sp^{1.81}$ at N2 $sp^{2.08}$ at C5	N2 (61.49%): *s*(35.50%)*p*(64.36%) C5 (38.51%): *s*(32.45%)*p*(67.45%)
σ(N2-C6a)	1.98342	$sp^{2.10}$ at N2 $sp^{2.88}$ at C6a	N2 (62.40%): *s*(32.22%)*p*(67.68%) C6a (37.60%): *s*(25.77%)*p*(74.16%)
σ(N2-C6b)	1.98496	$sp^{2.11}$ at N2 $sp^{2.75}$ at C6b	N2 (61.74%): *s*(32.14%)*p*(67.76%) C6b (38.26%): *s*(26.63%)*p*(73.30%)
Lone pair 1 (N3)	1.67463	n/a	*s*(2.68%)*p*(97.24%)
σ(N3-C5)	1.97951	$sp^{1.82}$ at N3 $sp^{2.12}$ at C5	N3 (61.25%): *s*(35.44%)*p*(64.40%) C5 (38.75%): *s*(32.07%)*p*(67.84%)
σ(N3-C7a)	1.98112	$sp^{2.27}$ at N3 $sp^{2.87}$ at C7a	N3 (62.20%): *s*(30.58%)*p*(69.31%) C7a (37.80%): *s*(25.83%)*p*(74.10%)
σ(N3-C7b)	1.98539	$sp^{2.21}$ at N3 $sp^{2.91}$ at C7b	N3 (62.46%): *s*(31.15%)*p*(68.74%) C7b (37.54%): *s*(25.57%)*p*(74.35%)
σ(C11-C12)	1.97640	$sp^{1.71}$ at C11 $sp^{1.82}$ at C12	C11 (50.87%): *s*(36.85%)*p*(63.05%) C12 (49.13%): *s*(35.40%)*p*(64.43%)
π(C11-C12)	1.67744	n/a	C11 (46.28%): *s*(0.03%)*p*(99.89%) C12 (53.72%): *s*(0.02%)*p*(99.89%)
σ(C11-C10)	1.97166	$sp^{1.93}$ at C10 $sp^{2.14}$ at C11	C10 (50.77%): *s*(34.04%)*p*(65.85%) C11 (49.23%): *s*(31.84%)*p*(68.04%)
Lone pair 1 (N4)	1.87149	$sp^{2.65}$	*s*(27.41%)*p*(72.56%)
σ(N4-C9)	1.98851	$sp^{1.59}$ at N4 $sp^{1.90}$ at C9	N4 (59.86%): *s*(38.42%)*p*(61.26%) C9 (40.14%): *s*(34.42%)*p*(65.48%)
π(N4-C9)	1.86011	n/a	N4 (63.85%): *s*(0.00%)*p*(99.80%) C9 (36.15%): *s*(0.00%)*p*(99.85%)
σ(N4-C10)	1.98169	$sp^{1.93}$ at N4 $sp^{2.29}$ at C10	N4 (58.97%): *s*(34.05%)*p*(65.67%) C10 (41.03%): *s*(30.41%)*p*(69.51%)

[a] Calculated in gas phase at the optimized S0 geometry using M06 (gas phase/ def2-tzvpp def2/j). The M06 functional uses 27 % Hartree-Fock exchange.[23]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S56. NBO analysis[a] of (**$^{t\mathrm{Bu}}$L1**)ZnCl$_2$ with the M06-2X functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.85191	$sp^{2.65}$	s(27.36%)p(72.54%)
σ(N1-C5)	1.98164	$sp^{1.71}$ at N1 $sp^{1.85}$ at C5	N1 (58.92%): s(36.75%)p(62.88%) C5 (41.08%): s(35.05%)p(64.85%)
π(N1-C5)	1.88150	n/a	N1 (75.31%): s(0.18%)p(99.66%) C5 (24.69%): s(0.29%)p(99.49%)
σ(N1-C11)	1.98073	$sp^{1.80}$ at N1 $sp^{2.20}$ at C11	N1 (58.79%): s(35.58%)p(64.11%) C11 (41.21%): s(31.26%)p(68.66%)
Lone pair 1 (N2)	1.70539	n/a	s(0.00%)p(99.94%)
σ(N2-C5)	1.98148	$sp^{1.82}$ at N2 $sp^{2.07}$ at C5	N2 (61.51%): s(35.44%)p(64.38%) C5 (38.49%): s(32.51%)p(67.39%)
σ(N2-C6a)	1.98365	$sp^{2.10}$ at N2 $sp^{2.89}$ at C6a	N2 (62.57%): s(32.24%)p(67.64%) C6a (37.43%): s(25.71%)p(74.21%)
σ(N2-C6b)	1.98517	$sp^{2.11}$ at N2 $sp^{2.76}$ at C6b	N2 (61.87%): s(32.15%)p(67.73%) C6b (38.13%): s(26.59%)p(73.33%)
Lone pair 1 (N3)	1.67668	n/a	s(2.63%)p(97.29%)
σ(N3-C5)	1.97999	$sp^{1.82}$ at N3 $sp^{2.12}$ at C5	N3 (61.27%): s(35.39%)p(64.40%) C5 (38.73%): s(32.07%)p(67.83%)
σ(N3-C7a)	1.98148	$sp^{2.26}$ at N3 $sp^{2.88}$ at C7a	N3 (62.35%): s(30.65%)p(69.23%) C7a (37.65%): s(25.76%)p(74.16%)
σ(N3-C7b)	1.98572	$sp^{2.21}$ at N3 $sp^{2.92}$ at C7b	N3 (62.58%): s(31.16%)p(68.72%) C7b (37.42%): s(25.52%)p(74.40%)
σ(C11-C12)	1.97699	$sp^{1.71}$ at C11 $sp^{1.83}$ at C12	C11 (51.01%): s(36.91%)p(62.99%) C12 (48.99%): s(35.28%)p(64.53%)
π(C11-C12)	1.68206	n/a	C11 (46.71%): s(0.02%)p(99.90%) C12 (53.29%): s(0.02%)p(99.90%)
σ(C11-C10)	1.97225	$sp^{1.94}$ at C10 $sp^{2.15}$ at C11	C10 (50.85%): s(34.03%)p(65.87%) C11 (49.15%): s(31.75%)p(68.13%)
Lone pair 1 (N4)	1.88835	$sp^{2.73}$	s(26.83%)p(73.14%)
σ(N4-C9)	1.98862	$sp^{1.57}$ at N4 $sp^{1.91}$ at C9	N4 (59.90%): s(38.73%)p(60.89%) C9 (40.10%): s(34.28%)p(65.61%)
π(N4-C9)	1.86271	n/a	N4 (63.19%): s(0.00%)p(99.79%) C9 (36.81%): s(0.00%)p(99.85%)
σ(N4-C10)	1.98218	$sp^{1.90}$ at N4 $sp^{2.28}$ at C10	N4 (58.86%): s(34.40%)p(65.38%) C10 (41.14%): s(30.42%)p(69.50%)

[a] Calculated in gas phase at the optimized S0 geometry using M06-2X (gas phase/ def2-tzvpp def2/j). The M06-2X functional uses 54 % Hartree-Fock exchange.[23]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \le x \le 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S57. NBO analysis[a] of ($^{t\mathrm{Bu}}$**L1**)ZnCl$_2$ with the CAM-B3LYP functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.84386	$sp^{2.68}$	s(27.16%)p(72.75%)
σ(N1-C5)	1.98184	$sp^{1.71}$ at N1 $sp^{1.85}$ at C5	N1 (58.85%): s(36.81%)p(62.80%) C5 (41.15%): s(35.05%)p(64.83%)
π(N1-C5)	1.88346	n/a	N1 (75.43%): s(0.21%)p(99.65%) C5 (24.57%): s(0.26%)p(99.53%)
σ(N1-C11)	1.98108	$sp^{1.79}$ at N1 $sp^{2.20}$ at C11	N1 (58.74%): s(35.70%)p(63.97%) C11 (41.26%): s(31.25%)p(68.64%)
Lone pair 1 (N2)	1.70690	n/a	s(0.00%)p(99.95%)
σ(N2-C5)	1.98159	$sp^{1.82}$ at N2 $sp^{2.07}$ at C5	N2 (61.37%): s(35.45%)p(64.35%) C5 (38.63%): s(32.51%)p(67.37%)
σ(N2-C6a)	1.98427	$sp^{2.10}$ at N2 $sp^{2.88}$ at C6a	N2 (62.31%): s(32.21%)p(67.65%) C6a (37.69%): s(25.77%)p(74.13%)
σ(N2-C6b)	1.98579	$sp^{2.11}$ at N2 $sp^{2.75}$ at C6b	N2 (61.65%): s(32.16%)p(67.70%) C6b (38.35%): s(26.63%)p(73.27%)
Lone pair 1 (N3)	1.67749	n/a	s(2.53%)p(97.40%)
σ(N3-C5)	1.98027	$sp^{1.82}$ at N3 $sp^{2.11}$ at C5	N3 (61.12%): s(35.41%)p(64.37%) C5 (38.88%): s(32.08%)p(67.79%)
σ(N3-C7a)	1.98234	$sp^{2.25}$ at N3 $sp^{2.87}$ at C7a	N3 (62.11%): s(30.69%)p(69.17%) C7a (37.89%): s(25.82%)p(74.07%)
σ(N3-C7b)	1.98622	$sp^{2.20}$ at N3 $sp^{2.91}$ at C7b	N3 (62.38%): s(31.20%)p(68.65%) C7b (37.62%): s(25.58%)p(74.32%)
σ(C11-C12)	1.97679	$sp^{1.71}$ at C11 $sp^{1.82}$ at C12	C11 (50.94%): s(36.86%)p(63.03%) C12 (49.06%): s(35.34%)p(64.46%)
π(C11-C12)	1.68288	n/a	C11 (46.46%): s(0.02%)p(99.89%) C12 (53.54%): s(0.02%)p(99.89%)
σ(C11-C10)	1.97232	$sp^{1.93}$ at C10 $sp^{2.14}$ at C11	C10 (50.85%): s(34.03%)p(65.84%) C11 (49.15%): s(31.78%)p(68.08%)
Lone pair 1 (N4)	1.88028	$sp^{2.76}$	s(26.59%)p(73.39%)
σ(N4-C9)	1.98844	$sp^{1.56}$ at N4 $sp^{1.91}$ at C9	N4 (59.78%): s(38.84%)p(60.77%) C9 (40.22%): s(34.32%)p(65.55%)
π(N4-C9)	1.86436	n/a	N4 (63.42%): s(0.00%)p(99.81%) C9 (36.58%): s(0.00%)p(99.85%)
σ(N4-C10)	1.98243	$sp^{1.89}$ at N4 $sp^{2.29}$ at C10	N4 (58.79%): s(34.43%)p(65.23%) C10 (41.21%): s(30.39%)p(69.50%)

[a] Calculated in gas phase at the optimized S0 geometry using CAM-B3LYP (gas phase/ def2-tzvpp def2/j). The CAM-B3LYP functional is a range-separated functional, and uses 19 % Hartree-Fock exchange at short range, 33 % Hartree-Fock exchange at intermediate range, and 65 % Hartree-Fock exchange at long range.[15]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S58. NBO analysis[a] of $(^{\mathbf{CF3}}\mathbf{L2})_2$Zn with the M06-L functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.82184	$sp^{2.60}$	*s*(27.78%)*p*(72.20%)
σ(N1-C5)	1.98430	$sp^{1.86}$ at N1 $sp^{2.02}$ at C5	N1 (59.34%): *s*(34.85%)*p*(64.92%) C5 (40.66%): *s*(33.14%)*p*(66.78%)
π(N1-C5)	1.81422	n/a	N1 (76.46%): *s*(0.00%)*p*(99.92%) C5 (23.54%): *s*(0.00%)*p*(99.80%)
σ(N1-C11)	1.98564	$sp^{1.68}$ at N1 $sp^{2.11}$ at C11	N1 (59.03%): *s*(37.23%)*p*(62.54%) C11 (40.97%): *s*(32.11%)*p*(67.81%)
Lone pair 1 (N2)	1.90026	$sp^{1.92}$	*s*(34.22%)*p*(65.60%)
σ(N2-C5)	1.98343	$sp^{2.20}$ at N2 $sp^{1.91}$ at C5	N2 (57.68%): *s*(31.09%)*p*(68.48%) C5 (42.32%): *s*(34.39%)*p*(65.52%)
σ(N2-C6)	1.98482	$sp^{1.88}$ at N2 $sp^{1.99}$ at C6	N2 (58.81%): *s*(34.56%)*p*(64.98%) C6 (41.19%): *s*(33.47%)*p*(66.44%)
π(N2-C6)	1.75322	n/a	N2 (63.60%): *s*(0.00%)*p*(99.68%) C6 (36.40%): *s*(0.00%)*p*(99.86%)
Lone pair 1 (N3)	1.89354	$sp^{1.94}$	*s*(33.97%)*p*(65.88%)
σ(N3-C5)	1.98098	$sp^{2.33}$ at N3 $sp^{1.96}$ at C5	N3 (58.01%): *s*(29.93%)*p*(69.67%) C5 (41.99%): *s*(32.35%)*p*(67.57%)
σ(N3-C7)	1.98735	$sp^{1.77}$ at N3 $sp^{1.96}$ at C7	N3 (58.91%): *s*(35.95%)*p*(63.60%) C7 (41.09%): *s*(33.72%)*p*(66.18%)
π(N3-C7)	1.78624	n/a	N3 (63.29%): *s*(0.00%)*p*(99.70%) C7 (36.71%): *s*(0.00%)*p*(99.86%)
σ(C6-C8)	1.98865	$sp^{1.84}$ at C8 $sp^{1.62}$ at C6	C8 (50.54%): *s*(35.15%)*p*(64.67%) C6 (49.46%): *s*(38.10%)*p*(61.74%)
σ(C7-C8)	1.98759	$sp^{1.88}$ at C8 $sp^{1.77}$ at C7	C8 (50.35%): *s*(34.72%)*p*(65.10%) C7 (49.65%): *s*(37.89%)*p*(61.95%)
σ(C11-C12)	1.97802	$sp^{1.73}$ at C11 $sp^{1.85}$ at C12	C11 (50.99%): *s*(36.57%)*p*(63.32%) C12 (49.01%): *s*(35.02%)*p*(64.81%)
π(C11-C12)	1.62363	n/a	C11 (47.33%): *s*(0.00%)*p*(99.90%) C12 (52.67%): *s*(0.00%)*p*(99.91%)
σ(C11-C10)	1.97256	$sp^{2.20}$ at C11 $sp^{1.95}$ at C10	C11 (49.31%): *s*(31.26%)*p*(68.62%) C10 (50.69%): *s*(33.81%)*p*(66.07%)
Lone pair 1 (N4)	1.87739	$sp^{2.45}$	*s*(28.96%)*p*(71.00%)
σ(N4-C9)	1.98810	$sp^{1.63}$ at N4 $sp^{1.90}$ at C9	N4 (59.70%): *s*(37.82%)*p*(61.83%) C9 (40.30%): *s*(34.46%)*p*(65.44%)
π(N4-C9)	1.85103	n/a	N4 (62.24%): *s*(0.00%)*p*(99.82%) C9 (37.76%): *s*(0.00%)*p*(99.86%)
σ(N4-C10)	1.98075	$sp^{2.08}$ at N4 $sp^{2.30}$ at C10	N4 (59.02%): *s*(32.09%)*p*(66.60%) C10 (40.98%): *s*(30.30%)*p*(69.62%)

[a] Calculated in gas phase at the optimized S0 geometry using M06-L (gas phase/ def2-tzvpp def2/j). The M06-L functional uses 0 % Hartree-Fock exchange.[19]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S59. NBO analysis[a] of $(^{\mathbf{CF3}}\mathbf{L2})_2\mathrm{Zn}$ with the TPSSh functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.82187	$sp^{2.81}$	*s*(26.21%)*p*(73.77%)
σ(N1-C5)	1.98465	$sp^{1.80}$ at N1 $sp^{2.02}$ at C5	N1 (59.12%): *s*(35.63%)*p*(64.12%) C5 (40.88%): *s*(33.04%)*p*(66.86%)
π(N1-C5)	1.81683	n/a	N1 (76.56%): *s*(0.00%)*p*(99.93%) C5 (23.44%): *s*(0.00%)*p*(99.80%)
σ(N1-C11)	1.98547	$sp^{1.62}$ at N1 $sp^{2.10}$ at C11	N1 (58.78%): *s*(38.02%)*p*(61.74%) C11 (41.22%): *s*(32.19%)*p*(67.70%)
Lone pair 1 (N2)	1.90289	$sp^{2.04}$	*s*(32.82%)*p*(67.02%)
σ(N2-C5)	1.98447	$sp^{2.13}$ at N2 $sp^{1.90}$ at C5	N2 (57.46%): *s*(31.79%)*p*(67.75%) C5 (42.54%): *s*(34.47%)*p*(65.42%)
σ(N2-C6)	1.98568	$sp^{1.82}$ at N2 $sp^{2.00}$ at C6	N2 (58.76%): *s*(35.26%)*p*(64.25%) C6 (41.24%): *s*(33.34%)*p*(66.53%)
π(N2-C6)	1.75111	n/a	N2 (63.61%): *s*(0.00%)*p*(99.68%) C6 (36.39%): *s*(0.00%)*p*(99.86%)
Lone pair 1 (N3)	1.89464	$sp^{2.06}$	*s*(32.68%)*p*(67.18%)
σ(N3-C5)	1.98220	$sp^{2.26}$ at N3 $sp^{2.09}$ at C5	N3 (57.77%): *s*(30.55%)*p*(69.02%) C5 (42.23%): *s*(32.36%)*p*(67.55%)
σ(N3-C7)	1.98791	$sp^{1.72}$ at N3 $sp^{1.97}$ at C7	N3 (58.86%): *s*(36.61%)*p*(62.92%) C7 (41.14%): *s*(33.58%)*p*(66.29%)
π(N3-C7)	1.78412	n/a	N3 (63.19%): *s*(0.00%)*p*(99.71%) C7 (36.81%): *s*(0.00%)*p*(99.85%)
σ(C6-C8)	1.98857	$sp^{1.85}$ at C8 $sp^{1.63}$ at C6	C8 (50.54%): *s*(35.01%)*p*(64.79%) C6 (49.46%): *s*(37.99%)*p*(61.84%)
σ(C7-C8)	1.98757	$sp^{1.89}$ at C8 $sp^{1.64}$ at C7	C8 (50.37%): *s*(34.58%)*p*(65.23%) C7 (49.63%): *s*(37.78%)*p*(62.05%)
σ(C11-C12)	1.97723	$sp^{1.73}$ at C11 $sp^{1.86}$ at C12	C11 (51.16%): *s*(36.63%)*p*(63.26%) C12 (48.84%): *s*(34.87%)*p*(64.95%)
π(C11-C12)	1.62402	n/a	C11 (47.85%): *s*(0.00%)*p*(99.91%) C12 (52.15%): *s*(0.00%)*p*(99.90%)
σ(C11-C10)	1.97253	$sp^{2.21}$ at C11 $sp^{1.96}$ at C10	C11 (49.28%): *s*(31.11%)*p*(68.78%) C10 (50.72%): *s*(33.73%)*p*(66.15%)
Lone pair 1 (N4)	1.87776	$sp^{2.59}$	*s*(27.81%)*p*(72.16%)
σ(N4-C9)	1.98807	$sp^{1.60}$ at N4 $sp^{1.90}$ at C9	N4 (59.60%): *s*(38.36%)*p*(61.27%) C9 (40.40%): *s*(34.43%)*p*(65.45%)
π(N4-C9)	1.85065	n/a	N4 (62.24%): *s*(0.00%)*p*(99.83%) C9 (37.56%): *s*(0.00%)*p*(99.87%)
σ(N4-C10)	1.98158	$sp^{1.96}$ at N4 $sp^{2.29}$ at C10	N4 (58.78%): *s*(33.69%)*p*(65.97%) C10 (41.22%): *s*(30.39%)*p*(69.51%)

[a] Calculated in gas phase at the optimized S0 geometry using TPSSh (gas phase/ def2-tzvpp def2/j). The TPSSh functional uses 10 % Hartree-Fock exchange.[11]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + cB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S60. NBO analysis[a] of ($^{\mathbf{CF3}}$**L2**)$_2$Zn with the O3LYP functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.82080	$sp^{2.86}$	s(25.88%)p(74.10%)
σ(N1-C5)	1.98451	$sp^{1.79}$ at N1 $sp^{2.03}$ at C5	N1 (59.01%): s(35.79%)p(63.96%) C5 (40.99%): s(32.98%)p(66.92%)
π(N1-C5)	1.81607	n/a	N1 (76.42%): s(0.00%)p(99.93%) C11 (23.58%): s(0.00%)p(99.80%)
σ(N1-C11)	1.98525	$sp^{1.61}$ at N1 $sp^{2.10}$ at C11	N1 (58.66%): s(38.18%)p(61.58%) C11 (41.34%): s(32.24%)p(67.66%)
Lone pair 1 (N2)	1.89989	$sp^{2.06}$	s(32.61%)p(67.21%)
σ(N2-C5)	1.98442	$sp^{2.12}$ at N2 $sp^{1.89}$ at C5	N2 (57.37%): s(31.87%)p(67.67%) C5 (42.63%): s(34.55%)p(65.35%)
σ(N2-C6)	1.98558	$sp^{1.81}$ at N2 $sp^{2.00}$ at C6	N2 (58.65%): s(35.39%)p(64.13%) C6 (41.35%): s(33.34%)p(66.54%)
π(N2-C6)	1.75211	n/a	N2 (63.48%): s(0.00%)p(99.67%) C6 (36.52%): s(0.00%)p(99.87%)
Lone pair 1 (N3)	1.89241	$sp^{2.07}$	s(32.50%)p(67.35%)
σ(N3-C5)	1.98208	$sp^{2.25}$ at N3 $sp^{2.09}$ at C5	N3 (57.65%): s(30.62%)p(68.96%) C5 (42.35%): s(32.34%)p(67.57%)
σ(N3-C7)	1.98775	$sp^{1.71}$ at N3 $sp^{1.98}$ at C7	N3 (58.74%): s(36.72%)p(62.81%) C7 (41.26%): s(33.57%)p(66.31%)
π(N3-C7)	1.78465	n/a	N3 (63.05%): s(0.00%)p(99.70%) C7 (36.95%): s(0.00%)p(99.86%)
σ(C6-C8)	1.98799	$sp^{1.85}$ at C8 $sp^{1.63}$ at C6	C8 (50.55%): s(34.98%)p(64.84%) C6 (49.45%): s(37.98%)p(61.86%)
σ(C7-C8)	1.98701	$sp^{1.89}$ at C8 $sp^{1.64}$ at C7	C8 (50.39%): s(34.56%)p(65.26%) C7 (49.61%): s(37.77%)p(62.08%)
σ(C11-C12)	1.97670	$sp^{1.73}$ at C11 $sp^{1.87}$ at C12	C11 (51.14%): s(36.64%)p(63.25%) C12 (48.86%): s(34.82%)p(65.01%)
π(C11-C12)	1.62356	n/a	C11 (47.89%): s(0.00%)p(99.92%) C12 (52.11%): s(0.00%)p(99.91%)
σ(C11-C10)	1.97207	$sp^{2.22}$ at C11 $sp^{1.96}$ at C10	C11 (49.32%): s(31.05%)p(68.85%) C10 (50.68%): s(33.69%)p(66.20%)
Lone pair 1 (N4)	1.87570	$sp^{2.61}$	s(27.68%)p(72.29%)
σ(N4-C9)	1.98786	$sp^{1.59}$ at N4 $sp^{1.90}$ at C9	N4 (59.49%): s(38.47%)p(61.17%) C9 (40.51%): s(34.42%)p(65.46%)
π(N4-C9)	1.85161	n/a	N4 (62.41%): s(0.00%)p(99.82%) C9 (37.59%): s(0.00%)p(99.87%)
σ(N4-C10)	1.98136	$sp^{1.96}$ at N4 $sp^{2.28}$ at C10	N4 (58.62%): s(33.72%)p(65.96%) C10 (41.38%): s(30.46%)p(69.45%)

[a] Calculated in gas phase at the optimized S0 geometry using O3LYP (gas phase/ def2-tzvpp def2/j). The O3LYP functional uses 11.61 % Hartree-Fock exchange.[21]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}| > 0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S61. NBO analysis[a] of $(^{\mathrm{CF3}}\mathbf{L2})_2\mathrm{Zn}$ with the B3LYP functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.82542	$sp^{2.90}$	*s*(25.67%)*p*(74.32%)
σ(N1-C5)	1.98458	$sp^{1.78}$ at N1 $sp^{2.03}$ at C5	N1 (59.07%): *s*(35.89%)*p*(63.85%) C5 (40.93%): *s*(32.99%)*p*(66.90%)
π(N1-C5)	1.82035	n/a	N1 (77.22%): *s*(0.00%)*p*(99.93%) C11 (22.78%): *s*(0.00%)*p*(99.81%)
σ(N1-C11)	1.98533	$sp^{1.60}$ at N1 $sp^{2.10}$ at C11	N1 (58.75%): *s*(38.31%)*p*(61.44%) C11 (41.25%): *s*(32.25%)*p*(67.64%)
Lone pair 1 (N2)	1.90434	$sp^{2.13}$	*s*(31.91%)*p*(67.91%)
σ(N2-C5)	1.98457	$sp^{2.09}$ at N2 $sp^{1.89}$ at C5	N2 (57.52%): *s*(32.19%)*p*(67.33%) C5 (42.48%): *s*(34.52%)*p*(65.37%)
σ(N2-C6)	1.98609	$sp^{1.78}$ at N2 $sp^{1.99}$ at C6	N2 (58.78%): *s*(35.77%)*p*(63.73%) C6 (41.22%): *s*(33.39%)*p*(66.48%)
π(N2-C6)	1.75163	n/a	N2 (63.98%): *s*(0.00%)*p*(99.68%) C6 (36.02%): *s*(0.00%)*p*(99.87%)
Lone pair 1 (N3)	1.89692	$sp^{2.13}$	*s*(31.87%)*p*(67.99%)
σ(N3-C5)	1.98240	$sp^{2.22}$ at N3 $sp^{2.09}$ at C5	N3 (57.81%): *s*(30.93%)*p*(68.62%) C5 (42.19%): *s*(32.35%)*p*(67.55%)
σ(N3-C7)	1.98801	$sp^{1.69}$ at N3 $sp^{1.97}$ at C7	N3 (58.85%): *s*(37.05%)*p*(62.47%) C7 (41.15%): *s*(33.62%)*p*(66.24%)
π(N3-C7)	1.78543	n/a	N3 (63.50%): *s*(0.00%)*p*(99.71%) C7 (36.50%): *s*(0.00%)*p*(99.86%)
σ(C6-C8)	1.98798	$sp^{1.85}$ at C8 $sp^{1.62}$ at C6	C8 (50.51%): *s*(35.01%)*p*(64.78%) C6 (49.49%): *s*(38.05%)*p*(61.78%)
σ(C7-C8)	1.98709	$sp^{1.88}$ at C8 $sp^{1.64}$ at C7	C8 (50.35%): *s*(34.59%)*p*(65.20%) C7 (49.65%): *s*(37.83%)*p*(62.00%)
σ(C11-C12)	1.97702	$sp^{1.73}$ at C11 $sp^{1.86}$ at C12	C11 (51.13%): *s*(36.61%)*p*(63.28%) C12 (48.87%): *s*(34.89%)*p*(64.92%)
π(C11-C12)	1.62598	n/a	C11 (47.44%): *s*(0.00%)*p*(99.92%) C12 (52.56%): *s*(0.00%)*p*(99.91%)
σ(C11-C10)	1.97261	$sp^{2.22}$ at C11 $sp^{1.96}$ at C10	C11 (49.29%): *s*(31.06%)*p*(68.82%) C10 (50.71%): *s*(33.70%)*p*(66.17%)
Lone pair 1 (N4)	1.88070	$sp^{2.67}$	*s*(27.21%)*p*(72.76%)
σ(N4-C9)	1.98779	$sp^{1.58}$ at N4 $sp^{1.90}$ at C9	N4 (59.58%): *s*(38.68%)*p*(60.94%) C9 (40.42%): *s*(34.47%)*p*(65.40%)
π(N4-C9)	1.85387	n/a	N4 (62.49%): *s*(0.00%)*p*(99.83%) C9 (37.51%): *s*(0.00%)*p*(99.88%)
σ(N4-C10)	1.98159	$sp^{1.93}$ at N4 $sp^{2.28}$ at C10	N4 (58.79%): *s*(33.98%)*p*(65.67%) C10 (41.21%): *s*(30.45%)*p*(69.45%)

[a] Calculated in gas phase at the optimized S0 geometry using B3LYP (gas phase/ def2-tzvpp def2/j). The B3LYP functional uses 20 % Hartree-Fock exchange.[22]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S62. NBO analysis[a] of $(^{\mathbf{CF3}}\mathbf{L2})_2$Zn with the PBE0 functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.82844	$sp^{2.90}$	s(25.62%)p(74.37%)
σ(N1-C5)	1.98484	$sp^{1.78}$ at N1 $sp^{2.03}$ at C5	N1 (59.08%): s(35.93%)p(63.80%) C5 (40.92%): s(33.00%)p(66.90%)
π(N1-C5)	1.82213	n/a	N1 (77.56%): s(0.00%)p(99.92%) C11 (22.44%): s(0.00%)p(99.79%)
σ(N1-C11)	1.98545	$sp^{1.60}$ at N1 $sp^{2.10}$ at C11	N1 (58.69%): s(38.31%)p(61.43%) C11 (41.31%): s(32.26%)p(67.64%)
Lone pair 1 (N2)	1.90459	$sp^{2.10}$	s(32.22%)p(67.60%)
σ(N2-C5)	1.98479	$sp^{2.10}$ at N2 $sp^{1.89}$ at C5	N2 (57.46%): s(32.08%)p(67.43%) C5 (42.54%): s(34.52%)p(65.38%)
σ(N2-C6)	1.98610	$sp^{1.77}$ at N2 $sp^{1.99}$ at C6	N2 (58.69%): s(35.55%)p(63.03%) C6 (41.31%): s(33.36%)p(66.51%)
π(N2-C6)	1.75137	n/a	N2 (64.13%): s(0.00%)p(99.65%) C6 (35.87%): s(0.00%)p(99.85%)
Lone pair 1 (N3)	1.89734	$sp^{2.11}$	s(32.10%)p(67.75%)
σ(N3-C5)	1.98259	$sp^{2.23}$ at N3 $sp^{2.09}$ at C5	N3 (57.75%): s(30.84%)p(68.70%) C5 (42.25%): s(32.35%)p(67.56%)
σ(N3-C7)	1.98812	$sp^{1.70}$ at N3 $sp^{1.97}$ at C7	N3 (58.79%): s(36.89%)p(62.61%) C7 (41.21%): s(33.60%)p(66.27%)
π(N3-C7)	1.78515	n/a	N3 (63.67%): s(0.00%)p(99.68%) C7 (36.33%): s(0.00%)p(99.85%)
σ(C6-C8)	1.98821	$sp^{1.85}$ at C8 $sp^{1.63}$ at C6	C8 (50.57%): s(34.98%)p(64.82%) C6 (49.43%): s(37.97%)p(61.86%)
σ(C7-C8)	1.98730	$sp^{1.89}$ at C8 $sp^{1.64}$ at C7	C8 (50.40%): s(34.56%)p(65.25%) C7 (49.60%): s(37.76%)p(62.08%)
σ(C11-C12)	1.97720	$sp^{1.73}$ at C11 $sp^{1.86}$ at C12	C11 (51.10%): s(36.62%)p(63.27%) C12 (48.90%): s(34.87%)p(64.94%)
π(C11-C12)	1.62749	n/a	C11 (47.39%): s(0.00%)p(99.91%) C12 (52.61%): s(0.00%)p(99.90%)
σ(C11-C10)	1.97279	$sp^{2.22}$ at C11 $sp^{1.96}$ at C10	C11 (49.27%): s(31.05%)p(68.83%) C10 (50.73%): s(33.72%)p(66.16%)
Lone pair 1 (N4)	1.88191	$sp^{2.65}$	s(27.36%)p(72.61%)
σ(N4-C9)	1.98801	$sp^{1.58}$ at N4 $sp^{1.90}$ at C9	N4 (59.52%): s(38.58%)p(61.03%) C9 (40.48%): s(34.46%)p(65.41%)
π(N4-C9)	1.85470	n/a	N4 (62.64%): s(0.00%)p(99.81%) C9 (37.36%): s(0.00%)p(99.86%)
σ(N4-C10)	1.98177	$sp^{1.94}$ at N4 $sp^{2.28}$ at C10	N4 (58.69%): s(33.92%)p(65.72%) C10 (41.31%): s(30.44%)p(69.46%)

[a] Calculated in gas phase at the optimized S0 geometry using PBE0 (gas phase/ def2-tzvpp def2/j). The PBE0 functional uses 25 % Hartree-Fock exchange.[14]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S63. NBO analysis[a] of ($^{\mathbf{CF3}}$**L2**)$_2$Zn with the M06 functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.81960	$sp^{2.87}$	*s*(25.83%)*p*(74.15%)
Lone pair 2 (N1)	1.55936	n/a	*s*(0.00%)*p*(99.91%)
σ(N1-C5)	1.98445	$sp^{1.79}$ at N1 $sp^{2.02}$ at C5	N1 (59.30%): *s*(35.80%)*p*(63.99%) C5 (40.70%): *s*(33.06%)*p*(66.86%)
σ(N1-C11)	1.98535	$sp^{1.61}$ at N1 $sp^{2.10}$ at C11	N1 (58.96%): *s*(38.24%)*p*(61.55%) C11 (41.04%): *s*(32.22%)*p*(67.69%)
Lone pair 1 (N2)	1.90261	$sp^{2.08}$	*s*(32.35%)*p*(67.43%)
σ(N2-C5)	1.98394	$sp^{2.10}$ at N2 $sp^{1.90}$ at C5	N2 (57.74%): *s*(32.08%)*p*(67.50%) C5 (42.26%): *s*(34.50%)*p*(65.42%)
σ(N2-C6)	1.98555	$sp^{1.81}$ at N2 $sp^{1.99}$ at C6	N2 (58.83%): *s*(35.44%)*p*(64.11%) C6 (41.17%): *s*(33.44%)*p*(66.47%)
π(N2-C6)	1.75275	n/a	N2 (64.89%): *s*(0.00%)*p*(99.64%) C6 (35.11%): *s*(0.00%)*p*(99.85%)
Lone pair 1 (N3)	1.89556	$sp^{2.09}$	*s*(32.29%)*p*(67.52%)
σ(N3-C5)	1.98177	$sp^{2.23}$ at N3 $sp^{2.09}$ at C5	N3 (58.02%): *s*(30.85%)*p*(68.76%) C5 (41.98%): *s*(32.34%)*p*(67.59%)
σ(N3-C7)	1.98771	$sp^{1.71}$ at N3 $sp^{1.96}$ at C7	N3 (58.87%): *s*(36.71%)*p*(62.86%) C7 (41.13%): *s*(33.71%)*p*(66.19%)
π(N3-C7)	1.78691	n/a	N3 (64.45%): *s*(0.00%)*p*(99.67%) C7 (35.55%): *s*(0.00%)*p*(99.84%)
σ(C6-C8)	1.98778	$sp^{1.62}$ at C6 $sp^{1.85}$ at C8	C6 (49.49%): *s*(38.09%)*p*(61.76%) C8 (50.51%): *s*(35.05%)*p*(64.77%)
σ(C7-C8)	1.98679	$sp^{1.64}$ at C7 $sp^{1.88}$ at C8	C7 (49.64%): *s*(37.84%)*p*(62.01%) C8 (50.36%): *s*(34.64%)*p*(65.19%)
σ(C11-C12)	1.97678	$sp^{1.73}$ at C11 $sp^{1.85}$ at C12	C11 (51.01%): *s*(36.59%)*p*(63.31%) C12 (48.99%): *s*(35.00%)*p*(64.84%)
π(C11-C12)	1.62792	n/a	C11 (46.85%): *s*(0.00%)*p*(99.91%) C12 (53.15%): *s*(0.00%)*p*(99.90%)
σ(C11-C10)	1.97228	$sp^{2.21}$ at C11 $sp^{1.96}$ at C10	C11 (49.30%): *s*(31.12%)*p*(68.77%) C10 (50.70%): *s*(33.74%)*p*(66.14%)
Lone pair 1 (N4)	1.87927	$sp^{2.66}$	*s*(27.32%)*p*(72.63%)
σ(N4-C9)	1.98779	$sp^{1.59}$ at N4 $sp^{1.89}$ at C9	N4 (59.65%): *s*(38.55%)*p*(61.12%) C9 (40.35%): *s*(34.55%)*p*(65.36%)\
π(N4-C9)	1.85836	n/a	N4 (63.10%): *s*(0.00%)*p*(99.80%) C9 (39.90%): *s*(0.00%)*p*(99.85%)
σ(N4-C10)	1.98120	$sp^{1.93}$ at N4 $sp^{2.29}$ at C10	N4 (59.01%): *s*(34.01%)*p*(65.69%) C10 (40.99%): *s*(30.38%)*p*(69.54%)

[a] Calculated in gas phase at the optimized S0 geometry using M06 (gas phase/ def2-tzvpp def2/j). The M06 functional uses 27 % Hartree-Fock exchange.[23]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S64. NBO analysis[a] of ($^{\mathbf{CF3}}$**L2**)$_2$Zn with the M06-2X functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.84913	$sp^{2.97}$	s(25.20%)p(74.78%)
Lone pair 2 (N1)	1.56422	n/a	s(0.00%)p(99.91%)
σ(N1-C5)	1.98480	$sp^{1.76}$ at N1 $sp^{2.03}$ at C5	N1 (59.09%): s(36.19%)p(63.56%) C5 (40.91%): s(32.96%)p(66.95%)
σ(N1-C11)	1.98507	$sp^{1.59}$ at N1 $sp^{2.10}$ at C11	N1 (58.71%): s(38.49%)p(61.26%) C11 (41.29%): s(32.27%)p(67.64%)
Lone pair 1 (N2)	1.90970	$sp^{2.16}$	s(31.59%)p(68.22%)
σ(N2-C5)	1.98502	$sp^{2.07}$ at N2 $sp^{1.89}$ at C5	N2 (57.59%): s(32.39%)p(67.13%) C5 (42.41%): s(34.58%)p(65.34%)
σ(N2-C6)	1.98641	$sp^{1.77}$ at N2 $sp^{1.99}$ at C6	N2 (58.86%): s(35.89%)p(63.61%) C6 (41.14%): s(33.36%)p(66.52%)
π(N2-C6)	1.74943	n/a	N2 (64.38%): s(0.00%)p(99.62%) C6 (35.62%): s(0.00%)p(99.85%)
Lone pair 1 (N3)	1.90350	$sp^{2.18}$	s(31.38%)p(68.46%)
σ(N3-C5)	1.98290	$sp^{2.19}$ at N3 $sp^{2.09}$ at C5	N3 (57.93%): s(31.22%)p(68.34%) C5 (42.07%): s(32.35%)p(67.57%)
σ(N3-C7)	1.98826	$sp^{1.67}$ at N3 $sp^{1.97}$ at C7	N3 (58.94%): s(37.25%)p(62.26%) C7 (41.06%): s(33.59%)p(66.29%)
π(N3-C7)	1.78600	n/a	N3 (63.94%): s(0.00%)p(99.65%) C7 (36.06%): s(0.00%)p(99.84%)
σ(C6-C8)	1.98822	$sp^{1.85}$ at C8 $sp^{1.63}$ at C6	C8 (50.54%): s(34.96%)p(64.85%) C6 (49.46%): s(38.01%)p(61.84%)
σ(C7-C8)	1.98735	$sp^{1.89}$ at C8 $sp^{1.64}$ at C7	C8 (50.36%): s(34.53%)p(65.28%) C7 (49.64%): s(37.79%)p(62.05%)
σ(C11-C12)	1.97763	$sp^{1.73}$ at C11 $sp^{1.86}$ at C12	C11 (51.11%): s(36.63%)p(63.26%) C12 (48.89%): s(34.94%)p(64.88%)
π(C11-C12)	1.63427	n/a	C11 (46.84%): s(0.00%)p(99.92%) C12 (53.16%): s(0.00%)p(99.90%)
σ(C11-C10)	1.97340	$sp^{2.22}$ at C11 $sp^{1.96}$ at C10	C11 (49.19%): s(31.04%)p(68.85%) C10 (50.81%): s(33.75%)p(66.14%)
Lone pair 1 (N4)	1.89318	$sp^{2.73}$	s(26.80%)p(73.16%)
σ(N4-C9)	1.98794	$sp^{1.57}$ at N4 $sp^{1.90}$ at C9	N4 (59.68%): s(38.83%)p(60.79%) C9 (40.32%): s(34.43%)p(65.46%)
π(N4-C9)	1.86067	n/a	N4 (62.56%): s(0.00%)p(99.79%) C9 (37.44%): s(0.00%)p(99.86%)
σ(N4-C10)	1.98180	$sp^{1.91}$ at N4 $sp^{2.29}$ at C10	N4 (58.91%): s(34.24%)p(65.42%) C10 (41.09%): s(30.40%)p(69.52%)

[a] Calculated in gas phase at the optimized S0 geometry using M06-2X (gas phase/ def2-tzvpp def2/j). The M06-2X functional uses 54 % Hartree-Fock exchange.[23]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + cB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S65. NBO analysis[a] of ($^{\mathbf{CF3}}$**L2**)$_2$Zn with the CAM-B3LYP functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.83248	$sp^{2.89}$	*s*(24.96%)*p*(75.02%)
Lone pair 2 (N1)	1.56898	n/a	*s*(0.00%)*p*(99.92%)
σ(N1-C5)	1.98489	$sp^{1.75}$ at N1 $sp^{2.03}$ at C5	N1 (59.04%): *s*(36.25%)*p*(63.48%) C5 (40.96%): *s*(32.97%)*p*(66.92%)
σ(N1-C11)	1.98526	$sp^{1.58}$ at N1 $sp^{2.10}$ at C11	N1 (58.70%): *s*(38.66%)*p*(61.07%) C11 (41.30%): *s*(32.24%)*p*(67.65%)
Lone pair 1 (N2)	1.90874	$sp^{2.20}$	*s*(31.17%)*p*(68.65%)
σ(N2-C5)	1.98512	$sp^{2.05}$ at N2 $sp^{1.89}$ at C5	N2 (57.56%): *s*(32.58%)*p*(66.92%) C5 (42.44%): *s*(34.53%)*p*(65.36%)
σ(N2-C6)	1.98655	$sp^{1.75}$ at N2 $sp^{2.00}$ at C6	N2 (58.78%): *s*(36.12%)*p*(63.36%) C6 (41.22%): *s*(33.34%)*p*(66.52%)
π(N2-C6)	1.75029	n/a	N2 (64.78%): *s*(0.00%)*p*(99.66%) C6 (35.22%): *s*(0.00%)*p*(99.85%)
Lone pair 1 (N3)	1.90193	$sp^{2.21}$	*s*(31.15%)*p*(68.70%)
σ(N3-C5)	1.98307	$sp^{2.18}$ at N3 $sp^{2.09}$ at C5	N3 (57.84%): *s*(31.32%)*p*(68.22%) C5 (42.16%): *s*(32.36%)*p*(67.54%)
σ(N3-C7)	1.98825	$sp^{1.66}$ at N3 $sp^{1.97}$ at C7	N3 (58.84%): *s*(37.37%)*p*(62.12%) C7 (41.16%): *s*(33.58%)*p*(66.28%)
π(N3-C7)	1.78608	n/a	N3 (64.24%): *s*(0.00%)*p*(99.68%) C7 (35.76%): *s*(0.00%)*p*(99.85%)
σ(C6-C8)	1.98783	$sp^{1.85}$ at C8 $sp^{1.62}$ at C6	C8 (50.51%): *s*(34.98%)*p*(64.81%) C6 (49.49%): *s*(38.06%)*p*(61.76%)
σ(C7-C8)	1.98708	$sp^{1.89}$ at C8 $sp^{1.64}$ at C7	C8 (50.35%): *s*(34.56%)*p*(65.23%) C7 (49.65%): *s*(37.83%)*p*(61.99%)
σ(C11-C12)	1.97714	$sp^{1.73}$ at C11 $sp^{1.86}$ at C12	C11 (51.09%): *s*(36.63%)*p*(63.26%) C12 (48.91%): *s*(34.93%)*p*(64.87%)
π(C11-C12)	1.63466	n/a	C11 (46.75%): *s*(0.00%)*p*(99.91%) C12 (53.25%): *s*(0.00%)*p*(99.90%)
σ(C11-C10)	1.97336	$sp^{2.22}$ at C11 $sp^{1.96}$ at C10	C11 (49.22%): *s*(31.05%)*p*(68.82%) C10 (50.78%): *s*(33.74%)*p*(66.13%)
Lone pair 1 (N4)	1.88705	$sp^{2.76}$	*s*(26.60%)*p*(73.37%)
σ(N4-C9)	1.98770	$sp^{1.56}$ at N4 $sp^{1.90}$ at C9	N4 (59.54%): *s*(38.91%)*p*(60.69%) C9 (40.46%): *s*(34.46%)*p*(65.41%)
π(N4-C9)	1.86193	n/a	N4 (62.71%): *s*(0.00%)*p*(99.81%) C9 (37.29%): *s*(0.00%)*p*(99.86%)
σ(N4-C10)	1.98194	$sp^{1.90}$ at N4 $sp^{2.29}$ at C10	N4 (58.82%): *s*(34.35%)*p*(65.28%) C10 (41.18%): *s*(30.38%)*p*(69.51%)

[a] Calculated in gas phase at the optimized S0 geometry using CAM-B3LYP (gas phase/ def2-tzvpp def2/j). The CAM-B3LYP functional is a range-separated functional, and uses 19 % Hartree-Fock exchange at short range, 33 % Hartree-Fock exchange at intermediate range, and 65 % Hartree-Fock exchange at long range.[15]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+cB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S66. Solvated NBO analysis[a] of ($^{\mathbf{CF3}}$**L2**)$_2$Zn with the M06-L functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.82237	$sp^{2.60}$	*s*(27.75%)*p*(72.23%)
σ(N1-C5)	1.98439	$sp^{1.87}$ at N1 $sp^{2.02}$ at C5	N1 (59.30%): *s*(34.79%)*p*(64.98%) C5 (40.70%): *s*(33.08%)*p*(66.83%)
π(N1-C5)	1.81909	n/a	N1 (76.40%): *s*(0.00%)*p*(99.92%) C11 (23.60%): *s*(0.00%)*p*(99.80%)
σ(N1-C11)	1.98565	$sp^{1.67}$ at N1 $sp^{2.12}$ at C11	N1 (59.07%): *s*(37.32%)*p*(62.46%) C11 (40.93%): *s*(32.05%)*p*(67.87%)
Lone pair 1 (N2)	1.90248	$sp^{1.94}$	*s*(33.94%)*p*(65.88%)
σ(N2-C5)	1.98378	$sp^{2.19}$ at N2 $sp^{1.90}$ at C5	N2 (57.76%): *s*(31.25%)*p*(68.32%) C5 (42.24%): *s*(34.41%)*p*(65.51%)
σ(N2-C6)	1.98500	$sp^{1.87}$ at N2 $sp^{2.00}$ at C6	N2 (58.99%): *s*(34.69%)*p*(64.86%) C6 (41.01%): *s*(33.28%)*p*(66.62%)
π(N2-C6)	1.75701	n/a	N2 (64.49%): *s*(0.00%)*p*(99.69%) C6 (35.51%): *s*(0.00%)*p*(99.86%)
Lone pair 1 (N3)	1.89496	$sp^{1.96}$	*s*(33.77%)*p*(66.08%)
σ(N3-C5)	1.98144	$sp^{2.31}$ at N3 $sp^{2.08}$ at C5	N3 (58.04%): *s*(30.07%)*p*(69.53%) C5 (41.96%): *s*(32.39%)*p*(67.53%)
σ(N3-C7)	1.98749	$sp^{1.76}$ at N3 $sp^{1.98}$ at C7	N3 (59.07%): *s*(36.02%)*p*(63.54%) C7 (40.93%): *s*(33.54%)*p*(66.36%)
π(N3-C7)	1.78850	n/a	N3 (64.08%): *s*(0.00%)*p*(99.71%) C7 (35.92%): *s*(0.00%)*p*(99.85%)
σ(C6-C8)	1.98873	$sp^{1.85}$ at C8 $sp^{1.62}$ at C6	C8 (50.44%): *s*(34.97%)*p*(64.84%) C6 (49.56%): *s*(38.08%)*p*(61.76%)
σ(C7-C8)	1.98758	$sp^{1.89}$ at C8 $sp^{1.64}$ at C7	C8 (50.29%): *s*(34.55%)*p*(65.27%) C7 (49.71%): *s*(37.84%)*p*(62.00%)
σ(C11-C12)	1.97779	$sp^{1.73}$ at C11 $sp^{1.85}$ at C12	C11 (50.89%): *s*(36.55%)*p*(63.33%) C12 (49.11%): *s*(35.07%)*p*(64.76%)
π(C11-C12)	1.63950	n/a	C11 (46.74%): *s*(0.00%)*p*(99.91%) C12 (53.26%): *s*(0.00%)*p*(99.91%)
σ(C11-C10)	1.97252	$sp^{2.19}$ at C11 $sp^{1.96}$ at C10	C11 (49.48%): *s*(31.33%)*p*(68.55%) C10 (50.52%): *s*(33.70%)*p*(66.18%)
Lone pair 1 (N4)	1.87718	$sp^{2.45}$	*s*(28.96%)*p*(71.00%)
σ(N4-C9)	1.98809	$sp^{1.63}$ at N4 $sp^{1.92}$ at C9	N4 (59.84%): *s*(37.90%)*p*(61.76%) C9 (40.16%): *s*(34.27%)*p*(65.63%)
π(N4-C9)	1.84913	n/a	N4 (63.34%): *s*(0.00%)*p*(99.82%) C9 (36.66%): *s*(0.00%)*p*(99.86%)
σ(N4-C10)	1.97252	$sp^{2.02}$ at N4 $sp^{2.29}$ at C10	N4 (58.92%): *s*(33.01%)*p*(66.67%) C10 (41.08%): *s*(30.39%)*p*(69.53%)

[a] Calculated in solution at the optimized S0 geometry using M06-L (SMD “dichloromethane”/ def2-tzvpp def2/j). The M06-L functional uses 0 % Hartree-Fock exchange.[19]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized “bond” is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S67. Solvated NBO analysis[a] of ($^{\mathbf{CF3}}$**L2**)$_2$Zn with the TPSSh functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.82218	$sp^{2.82}$	*s*(26.18%)*p*(73.80%)
σ(N1-C5)	1.98474	$sp^{1.80}$ at N1 $sp^{2.03}$ at C5	N1 (59.08%): *s*(35.57%)*p*(64.17%) C5 (40.92%): *s*(32.98%)*p*(66.92%)
π(N1-C5)	1.82168	n/a	N1 (76.52%): *s*(0.00%)*p*(99.93%) C11 (23.48%): *s*(0.00%)*p*(99.80%)
σ(N1-C11)	1.98548	$sp^{1.62}$ at N1 $sp^{2.11}$ at C11	N1 (58.82%): *s*(38.10%)*p*(61.65%) C11 (41.18%): *s*(32.14%)*p*(67.76%)
Lone pair 1 (N2)	1.90474	$sp^{2.06}$	*s*(32.58%)*p*(67.26%)
σ(N2-C5)	1.98472	$sp^{2.12}$ at N2 $sp^{1.90}$ at C5	N2 (57.73%): *s*(31.91%)*p*(67.63%) C5 (42.27%): *s*(34.49%)*p*(65.41%)
σ(N2-C6)	1.98586	$sp^{1.81}$ at N2 $sp^{2.01}$ at C6	N2 (58.96%): *s*(35.39%)*p*(64.13%) C6 (41.04%): *s*(33.14%)*p*(66.73%)
π(N2-C6)	1.75431	n/a	N2 (64.52%): *s*(0.00%)*p*(99.69%) C6 (35.48%): *s*(0.00%)*p*(99.85%)
Lone pair 1 (N3)	1.89582	$sp^{2.07}$	*s*(32.49%)*p*(67.38%)
σ(N3-C5)	1.98255	$sp^{2.25}$ at N3 $sp^{2.08}$ at C5	N3 (57.79%): *s*(30.66%)*p*(68.91%) C5 (42.21%): *s*(32.40%)*p*(67.51%)
σ(N3-C7)	1.98807	$sp^{1.71}$ at N3 $sp^{1.99}$ at C7	N3 (59.05%): *s*(36.70%)*p*(62.84%) C7 (40.95%): *s*(33.39%)*p*(66.48%)
π(N3-C7)	1.78626	n/a	N3 (64.03%): *s*(0.00%)*p*(99.72%) C7 (35.97%): *s*(0.00%)*p*(99.85%)
σ(C6-C8)	1.98876	$sp^{1.86}$ at C8 $sp^{1.63}$ at C6	C8 (50.44%): *s*(34.84%)*p*(64.97%) C6 (49.56%): *s*(37.99%)*p*(61.84%)
σ(C7-C8)	1.98255	$sp^{1.90}$ at C8 $sp^{1.64}$ at C7	C8 (50.29%): *s*(34.42%)*p*(65.39%) C7 (49.71%): *s*(37.76%)*p*(62.08%)
σ(C11-C12)	1.97707	$sp^{1.73}$ at C11 $sp^{1.86}$ at C12	C11 (51.07%): *s*(36.61%)*p*(63.28%) C12 (48.93%): *s*(34.93%)*p*(64.89%)
π(C11-C12)	1.64008	n/a	C11 (47.31%): *s*(0.00%)*p*(99.92%) C12 (52.69%): *s*(0.00%)*p*(99.91%)
σ(C11-C10)	1.97250	$sp^{2.20}$ at C11 $sp^{1.97}$ at C10	C11 (49.46%): *s*(31.18%)*p*(68.70%) C10 (50.54%): *s*(33.62%)*p*(66.26%)
Lone pair 1 (N4)	1.87731	$sp^{2.60}$	*s*(27.80%)*p*(72.17%)
σ(N4-C9)	1.98811	$sp^{1.59}$ at N4 $sp^{1.92}$ at C9	N4 (59.78%): *s*(38.46%)*p*(61.17%) C9 (40.22%): *s*(34.22%)*p*(65.65%)
π(N4-C9)	1.84868	n/a	N4 (63.61%): *s*(0.00%)*p*(99.83%) C9 (36.39%): *s*(0.00%)*p*(99.86%)
σ(N4-C10)	1.98190	$sp^{1.97}$ at N4 $sp^{2.28}$ at C10	N4 (58.67%): *s*(33.60%)*p*(66.06%) C10 (41.33%): *s*(30.48%)*p*(69.42%)

[a] Calculated in solution at the optimized S0 geometry using TPSSh (SMD "dichloromethane"/ def2-tzvpp def2/j). The TPSSh functional uses 10 % Hartree-Fock exchange.[11]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}| > 0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S6. Solvated NBO analysis[a] of ($^{\mathbf{CF3}}$**L2**)$_2$Zn with the O3LYP functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.82122	$sp^{2.87}$	*s*(25.86%)*p*(74.13%)
σ(N1-C5)	1.98461	$sp^{1.79}$ at N1 $sp^{2.03}$ at C5	N1 (58.97%): *s*(35.74%)*p*(64.01%) C5 (41.03%): *s*(32.93%)*p*(66.97%)
π(N1-C5)	1.82080	n/a	N1 (76.36%): *s*(0.00%)*p*(99.93%) C11 (23.64%): *s*(0.00%)*p*(99.81%)
σ(N1-C11)	1.98526	$sp^{1.61}$ at N1 $sp^{2.10}$ at C11	N1 (58.69%): *s*(38.26%)*p*(61.50%) C11 (41.31%): *s*(32.19%)*p*(67.71%)
Lone pair 1 (N2)	1.90188	$sp^{2.08}$	*s*(32.38%)*p*(67.44%)
σ(N2-C5)	1.98469	$sp^{2.11}$ at N2 $sp^{1.89}$ at C5	N2 (57.43%): *s*(31.99%)*p*(67.56%) C5 (42.57%): *s*(34.56%)*p*(65.34%)
σ(N2-C6)	1.98576	$sp^{1.80}$ at N2 $sp^{2.01}$ at C6	N2 (58.85%): *s*(35.51%)*p*(64.01%) C6 (41.15%): *s*(33.14%)*p*(66.74%)
π(N2-C6)	1.75524	n/a	N2 (64.36%): *s*(0.00%)*p*(99.68%) C6 (35.64%): *s*(0.00%)*p*(99.86%)
Lone pair 1 (N3)	1.89378	$sp^{2.09}$	*s*(32.32%)*p*(67.53%)
σ(N3-C5)	1.98243	$sp^{2.24}$ at N3 $sp^{2.09}$ at C5	N3 (57.68%): *s*(30.73%)*p*(68.85%) C5 (42.32%): *s*(32.38%)*p*(67.53%)
σ(N3-C7)	1.98791	$sp^{1.70}$ at N3 $sp^{1.99}$ at C7	N3 (58.92%): *s*(36.80%)*p*(62.74%) C7 (41.08%): *s*(33.37%)*p*(66.50%)
π(N3-C7)	1.78670	n/a	N3 (63.85%): *s*(0.00%)*p*(99.71%) C7 (36.15%): *s*(0.00%)*p*(99.86%)
σ(C6-C8)	1.98819	$sp^{1.87}$ at C8 $sp^{1.63}$ at C6	C8 (50.45%): *s*(34.81%)*p*(65.01%) C6 (49.55%): *s*(37.98%)*p*(61.87%)
σ(C7-C8)	1.98713	$sp^{1.90}$ at C8 $sp^{1.65}$ at C7	C8 (50.31%): *s*(34.40%)*p*(65.43%) C7 (49.69%): *s*(37.74%)*p*(62.11%)
σ(C11-C12)	1.97654	$sp^{1.73}$ at C11 $sp^{1.86}$ at C12	C11 (51.05%): *s*(36.63%)*p*(63.27%) C12 (48.95%): *s*(34.87%)*p*(64.96%)
π(C11-C12)	1.63934	n/a	C11 (47.38%): *s*(0.00%)*p*(99.92%) C12 (52.62%): *s*(0.00%)*p*(99.91%)
σ(C11-C10)	1.97204	$sp^{2.21}$ at C11 $sp^{1.97}$ at C10	C11 (49.49%): *s*(31.12%)*p*(68.78%) C10 (50.51%): *s*(33.58%)*p*(66.31%)
Lone pair 1 (N4)	1.87537	$sp^{2.61}$	*s*(27.67%)*p*(72.29%)
σ(N4-C9)	1.98791	$sp^{1.58}$ at N4 $sp^{1.92}$ at C9	N4 (59.66%): *s*(38.57%)*p*(61.07%) C9 (40.34%): *s*(34.21%)*p*(65.67%)
π(N4-C9)	1.84951	n/a	N4 (63.54%): *s*(0.00%)*p*(99.83%) C9 (36.46%): *s*(0.00%)*p*(99.87%)
σ(N4-C10)	1.98168	$sp^{1.96}$ at N4 $sp^{2.27}$ at C10	N4 (58.51%): *s*(33.62%)*p*(66.05%) C10 (41.49%): *s*(30.54%)*p*(69.36%)

[a] Calculated in solution at the optimized S0 geometry using O3LYP (SMD "dichloromethane"/ def2-tzvpp def2/j). The O3LYP functional uses 11.61 % Hartree-Fock exchange.[21]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}| > 0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S69. Solvated NBO analysis[a] of ($^{\mathbf{CF3}}$**L2**)$_2$Zn with the B3LYP functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.82588	$sp^{2.90}$	*s*(25.64%)*p*(74.34%)
σ(N1-C5)	1.98466	$sp^{1.78}$ at N1 $sp^{2.03}$ at C5	N1 (59.03%): *s*(35.83%)*p*(63.91%) C5 (40.97%): *s*(32.94%)*p*(66.95%)
π(N1-C5)	1.82511	n/a	N1 (77.14%): *s*(0.00%)*p*(99.93%) C11 (22.86%): *s*(0.00%)*p*(99.81%)
σ(N1-C11)	1.98534	$sp^{1.60}$ at N1 $sp^{2.10}$ at C11	N1 (58.79%): *s*(38.39%)*p*(61.36%) C11 (41.21%): *s*(32.19%)*p*(67.70%)
Lone pair 1 (N2)	1.90611	$sp^{2.15}$	*s*(31.69%)*p*(68.14%)
σ(N2-C5)	1.98479	$sp^{2.08}$ at N2 $sp^{1.89}$ at C5	N2 (57.59%): *s*(32.31%)*p*(67.21%) C5 (42.41%): *s*(34.53%)*p*(65.36%)
σ(N2-C6)	1.98624	$sp^{1.77}$ at N2 $sp^{2.01}$ at C6	N2 (58.98%): *s*(35.88%)*p*(63.62%) C6 (41.02%): *s*(33.20%)*p*(66.67%)
π(N2-C6)	1.75515	n/a	N2 (64.90%): *s*(0.00%)*p*(99.69%) C6 (35.10%): *s*(0.00%)*p*(99.87%)
Lone pair 1 (N3)	1.89808	$sp^{2.15}$	*s*(31.70%)*p*(68.16%)
σ(N3-C5)	1.98271	$sp^{2.21}$ at N3 $sp^{2.08}$ at C5	N3 (57.84%): *s*(31.04%)*p*(68.52%) C5 (42.16%): *s*(32.39%)*p*(67.51%)
σ(N3-C7)	1.98815	$sp^{1.68}$ at N3 $sp^{1.99}$ at C7	N3 (59.03%): *s*(37.11%)*p*(62.40%) C7 (40.97%): *s*(33.43%)*p*(66.43%)
π(N3-C7)	1.78761	n/a	N3 (64.34%): *s*(0.00%)*p*(99.72%) C7 (35.66%): *s*(0.00%)*p*(99.86%)
σ(C6-C8)	1.98816	$sp^{1.86}$ at C8 $sp^{1.62}$ at C6	C8 (50.41%): *s*(34.85%)*p*(64.94%) C6 (49.59%): *s*(38.05%)*p*(61.78%)
σ(C7-C8)	1.98721	$sp^{1.90}$ at C8 $sp^{1.64}$ at C7	C8 (50.28%): *s*(34.44%)*p*(65.36%) C7 (49.72%): *s*(37.80%)*p*(62.02%)
σ(C11-C12)	1.97685	$sp^{1.73}$ at C11 $sp^{1.86}$ at C12	C11 (51.03%): *s*(36.59%)*p*(63.29%) C12 (48.97%): *s*(34.95%)*p*(64.85%)
π(C11-C12)	1.64238	n/a	C11 (46.89%): *s*(0.00%)*p*(99.92%) C12 (53.11%): *s*(0.00%)*p*(99.91%)
σ(C11-C10)	1.97257	$sp^{2.21}$ at C11 $sp^{1.97}$ at C10	C11 (49.47%): *s*(31.13%)*p*(68.75%) C10 (50.53%): *s*(33.59%)*p*(66.29%)
Lone pair 1 (N4)	1.88023	$sp^{2.67}$	*s*(27.21%)*p*(72.76%)
σ(N4-C9)	1.98784	$sp^{1.57}$ at N4 $sp^{1.91}$ at C9	N4 (59.74%): *s*(38.78%)*p*(60.84%) C9 (40.26%): *s*(34.27%)*p*(65.60%)
π(N4-C9)	1.85177	n/a	N4 (63.69%): *s*(0.00%)*p*(99.83%) C9 (36.31%): *s*(0.00%)*p*(99.87%)
σ(N4-C10)	1.98188	$sp^{1.94}$ at N4 $sp^{2.27}$ at C10	N4 (58.68%): *s*(33.89%)*p*(65.77%) C10 (41.32%): *s*(30.54%)*p*(69.36%)

[a] Calculated in solution at the optimized S0 geometry using B3LYP (SMD "dichloromethane"/ def2-tzvpp def2/j). The B3LYP functional uses 20 % Hartree-Fock exchange.[22]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}| > 0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S70. Solvated NBO analysis[a] of ($^{\mathbf{CF3}}$**L2**)$_2$Zn with the PBE0 functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.82887	$sp^{2.91}$	*s*(25.59%)*p*(74.39%)
Lone pair 2 (N1)	1.55029	n/a	*s*(0.00%)*p*(99.92%)
σ(N1-C5)	1.98493	$sp^{1.78}$ at N1 $sp^{2.03}$ at C5	N1 (59.04%): *s*(35.88%)*p*(63.85%) C5 (40.96%): *s*(32.95%)*p*(66.95%)
σ(N1-C11)	1.98545	$sp^{1.60}$ at N1 $sp^{2.10}$ at C11	N1 (58.72%): *s*(38.39%)*p*(61.35%) C11 (41.28%): *s*(32.20%)*p*(67.70%)
Lone pair 1 (N2)	1.90638	$sp^{2.12}$	*s*(32.00%)*p*(67.82%)
σ(N2-C5)	1.98503	$sp^{2.09}$ at N2 $sp^{1.89}$ at C5	N2 (57.52%): *s*(32.19%)*p*(67.32%) C5 (42.48%): *s*(34.54%)*p*(65.36%)
σ(N2-C6)	1.98626	$sp^{1.79}$ at N2 $sp^{2.01}$ at C6	N2 (58.90%): *s*(35.67%)*p*(63.81%) C6 (41.10%): *s*(33.16%)*p*(66.71%)
π(N2-C6)	1.75429	n/a	N2 (65.07%): *s*(0.00%)*p*(99.67%) C6 (34.93%): *s*(0.00%)*p*(99.85%)
Lone pair 1 (N3)	1.89349	$sp^{2.13}$	*s*(31.92%)*p*(67.93%)
σ(N3-C5)	1.98503	$sp^{2.09}$ at N3 $sp^{1.89}$ at C5	N3 (57.52%): *s*(32.19%)*p*(67.32%) C5 (42.48%): *s*(34.54%)*p*(65.36%)
σ(N3-C7)	1.98827	$sp^{1.69}$ at N3 $sp^{1.99}$ at C7	N3 (58.97%): *s*(36.97%)*p*(62.53%) C7 (41.03%): *s*(33.39%)*p*(66.47%)
π(N3-C7)	1.78714	n/a	N3 (64.54%): *s*(0.00%)*p*(99.69%) C7 (35.46%): *s*(0.00%)*p*(99.84%)
σ(C6-C8)	1.98841	$sp^{1.87}$ at C8 $sp^{1.63}$ at C6	C8 (50.46%): *s*(34.80%)*p*(65.00%) C6 (49.54%): *s*(37.97%)*p*(61.86%)
σ(C7-C8)	1.98743	$sp^{1.90}$ at C8 $sp^{1.65}$ at C7	C8 (50.33%): *s*(34.39%)*p*(65.42%) C7 (49.67%): *s*(37.73%)*p*(62.10%)
σ(C11-C12)	1.97704	$sp^{1.73}$ at C11 $sp^{1.86}$ at C12	C11 (51.01%): *s*(36.60%)*p*(63.29%) C12 (48.99%): *s*(34.93%)*p*(64.89%)
π(C11-C12)	1.64397	n/a	C11 (46.89%): *s*(0.00%)*p*(99.91%) C12 (53.11%): *s*(0.00%)*p*(99.91%)
σ(C11-C10)	1.97277	$sp^{2.21}$ at C11 $sp^{1.97}$ at C10	C11 (49.45%): *s*(31.13%)*p*(68.76%) C10 (50.55%): *s*(33.60%)*p*(66.28%)
Lone pair 1 (N4)	1.88150	$sp^{2.66}$	*s*(27.35%)*p*(72.62%)
σ(N4-C9)	1.98807	$sp^{1.57}$ at N4 $sp^{1.92}$ at C9	N4 (59.70%): *s*(38.68%)*p*(60.92%) C9 (40.30%): *s*(34.25%)*p*(65.62%)
π(N4-C9)	1.85266	n/a	N4 (63.87%): *s*(0.00%)*p*(99.82%) C9 (36.13%): *s*(0.00%)*p*(99.85%)
σ(N4-C10)	1.98208	$sp^{1.95}$ at N4 $sp^{2.27}$ at C10	N4 (58.57%): *s*(33.83%)*p*(65.82%) C10 (41.43%): *s*(30.53%)*p*(69.37%)

[a] Calculated in solution at the optimized S0 geometry using PBE0 (SMD "dichloromethane"/ def2-tzvpp def2/j). The PBE0 functional uses 25 % Hartree-Fock exchange.[14]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S71. Solvated NBO analysis[a] of ($^{\mathbf{CF3}}$**L2**)$_2$Zn with the M06 functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.82004	$sp^{2.88}$	s(25.79%)p(74.19%)
Lone pair 2 (N1)	1.56231	n/a	s(0.00%)p(99.91%)
σ(N1-C5)	1.98452	$sp^{1.79}$ at N1 $sp^{2.03}$ at C5	N1 (59.27%): s(35.74%)p(64.05%) C5 (40.73%): s(33.00%)p(66.92%)
σ(N1-C11)	1.98536	$sp^{1.60}$ at N1 $sp^{2.11}$ at C11	N1 (59.00%): s(38.34%)p(61.45%) C11 (41.00%): s(32.16%)p(67.76%)
Lone pair 1 (N2)	1.90455	$sp^{2.11}$	s(32.13%)p(67.66%)
σ(N2-C5)	1.98417	$sp^{2.09}$ at N2 $sp^{1.90}$ at C5	N2 (57.80%): s(32.20%)p(67.39%) C5 (42.20%): s(34.51%)p(65.41%)
σ(N2-C6)	1.98570	$sp^{1.80}$ at N2 $sp^{2.00}$ at C6	N2 (59.03%): s(35.56%)p(64.00%) C6 (40.97%): s(33.25%)p(66.66%)
π(N2-C6)	1.75575	n/a	N2 (65.86%): s(0.00%)p(99.66%) C6 (34.14%): s(0.00%)p(99.84%)
Lone pair 1 (N3)	1.89679	$sp^{2.11}$	s(32.11%)p(67.72%)
σ(N3-C5)	1.98212	$sp^{2.22}$ at N3 $sp^{2.09}$ at C5	N3 (58.05%): s(30.97%)p(68.64%) C5 (41.95%): s(32.38%)p(67.55%)
σ(N3-C7)	1.98786	$sp^{1.70}$ at N3 $sp^{1.98}$ at C7	N3 (59.05%): s(36.97%)p(62.79%) C7 (40.95%): s(33.53%)p(66.37%)
π(N3-C7)	1.78919	n/a	N3 (65.38%): s(0.00%)p(99.68%) C7 (34.62%): s(0.00%)p(99.84%)
σ(C6-C8)	1.98797	$sp^{1.86}$ at C8 $sp^{1.62}$ at C6	C8 (50.42%): s(34.89%)p(64.94%) C6 (49.58%): s(38.09%)p(61.77%)
σ(C7-C8)	1.98690	$sp^{1.90}$ at C8 $sp^{1.64}$ at C7	C8 (50.28%): s(34.48%)p(65.35%) C7 (49.72%): s(37.81%)p(62.04%)
σ(C11-C12)	1.97661	$sp^{1.73}$ at C11 $sp^{1.85}$ at C12	C11 (50.92%): s(36.59%)p(63.31%) C12 (49.08%): s(35.06%)p(64.78%)
π(C11-C12)	1.64542	n/a	C11 (46.33%): s(0.00%)p(99.91%) C12 (53.67%): s(0.00%)p(99.91%)
σ(C11-C10)	1.97221	$sp^{2.20}$ at C11 $sp^{1.97}$ at C10	C11 (49.48%): s(31.19%)p(68.70%) C10 (50.52%): s(33.63%)p(66.26%)
Lone pair 1 (N4)	1.87873	$sp^{2.66}$	s(27.31%)p(72.64%)
σ(N4-C9)	1.98785	$sp^{1.58}$ at N4 $sp^{1.91}$ at C9	N4 (59.81%): s(38.65%)p(61.03%) C9 (40.19%): s(34.35%)p(65.55%)
π(N4-C9)	1.85680	n/a	N4 (64.40%): s(0.00%)p(99.80%) C9 (35.60%): s(0.00%)p(99.84%)
σ(N4-C10)	1.98152	$sp^{1.94}$ at N4 $sp^{2.28}$ at C10	N4 (58.90%): s(33.93%)p(65.77%) C10 (41.10%): s(30.47%)p(69.45%)

[a] Calculated in solution at the optimized S0 geometry using M06 (SMD "dichloromethane"/ def2-tzvpp def2/j). The M06 functional uses 27 % Hartree-Fock exchange.[23]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S72. Solvated NBO analysis[a] of ($^{\mathbf{CF3}}$**L2**)$_2$Zn with the M06-2X functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.84978	$sp^{2.97}$	*s*(25.17%)*p*(74.81%)
Lone pair 2 (N1)	1.56655	n/a	*s*(0.00%)*p*(99.91%)
σ(N1-C5)	1.98488	$sp^{1.76}$ at N1 $sp^{2.04}$ at C5	N1 (59.06%): *s*(36.13%)*p*(63.61%) C5 (40.94%): *s*(32.90%)*p*(67.01%)
σ(N1-C11)	1.98507	$sp^{1.59}$ at N1 $sp^{2.10}$ at C11	N1 (58.74%): *s*(38.57%)*p*(61.18%) C11 (41.26%): *s*(32.20%)*p*(67.71%)
Lone pair 1 (N2)	1.91136	$sp^{2.18}$	*s*(31.36%)*p*(68.45%)
σ(N2-C5)	1.98523	$sp^{2.06}$ at N2 $sp^{1.89}$ at C5	N2 (57.64%): *s*(32.49%)*p*(67.03%) C5 (42.36%): *s*(34.60%)*p*(65.32%)
σ(N2-C6)	1.98656	$sp^{1.76}$ at N2 $sp^{2.01}$ at C6	N2 (59.09%): *s*(36.02%)*p*(63.48%) C6 (40.91%): *s*(33.14%)*p*(66.74%)
π(N2-C6)	1.75212	n/a	N2 (65.38%): *s*(0.00%)*p*(99.63%) C6 (34.62%): *s*(0.00%)*p*(99.84%)
Lone pair 1 (N3)	1.90447	$sp^{2.20}$	*s*(31.19%)*p*(68.65%)
σ(N3-C5)	1.98320	$sp^{2.18}$ at N3 $sp^{2.08}$ at C5	N3 (57.95%): *s*(31.32%)*p*(68.24%) C5 (42.05%): *s*(32.39%)*p*(67.53%)
σ(N3-C7)	1.98839	$sp^{1.66}$ at N3 $sp^{1.99}$ at C7	N3 (59.15%): *s*(37.34%)*p*(62.17%) C7 (40.85%): *s*(33.37%)*p*(66.51%)
π(N3-C7)	1.78784	n/a	N3 (64.86%): *s*(0.00%)*p*(99.66%) C7 (35.14%): *s*(0.00%)*p*(99.83%)
σ(C6-C8)	1.98844	$sp^{1.87}$ at C8 $sp^{1.63}$ at C6	C8 (50.43%): *s*(34.78%)*p*(65.02%) C6 (49.57%): *s*(38.00%)*p*(61.84%)
σ(C7-C8)	1.98750	$sp^{1.90}$ at C8 $sp^{1.64}$ at C7	C8 (50.28%): *s*(34.36%)*p*(65.45%) C7 (49.72%): *s*(37.76%)*p*(62.08%)
σ(C11-C12)	1.97746	$sp^{1.73}$ at C11 $sp^{1.85}$ at C12	C11 (51.01%): *s*(36.61%)*p*(63.28%) C12 (48.99%): *s*(34.99%)*p*(64.83%)
π(C11-C12)	1.65133	n/a	C11 (46.37%): *s*(0.00%)*p*(99.92%) C12 (53.63%): *s*(0.00%)*p*(99.91%)
σ(C11-C10)	1.97338	$sp^{2.21}$ at C11 $sp^{1.97}$ at C10	C11 (49.39%): *s*(31.12%)*p*(68.77%) C10 (50.61%): *s*(33.62%)*p*(66.27%)
Lone pair 1 (N4)	1.89290	$sp^{2.73}$	*s*(26.79%)*p*(73.17%)
σ(N4-C9)	1.98800	$sp^{1.56}$ at N4 $sp^{1.92}$ at C9	N4 (59.87%): *s*(38.95%)*p*(60.67%) C9 (40.13%): *s*(34.20%)*p*(65.68%)
π(N4-C9)	1.85866	n/a	N4 (63.85%): *s*(0.00%)*p*(99.79%) C9 (36.15%): *s*(0.00%)*p*(99.85%)
σ(N4-C10)	1.98209	$sp^{1.92}$ at N4 $sp^{2.28}$ at C10	N4 (58.77%): *s*(34.14%)*p*(65.52%) C10 (41.23%): *s*(30.50%)*p*(69.41%)

[a] Calculated in solution at the optimized S0 geometry using M06-2X (SMD "dichloromethane"/ def2-tzvpp def2/j). The M06-2X functional uses 54 % Hartree-Fock exchange.[23]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}| > 0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S73. Solvated NBO analysis[a] of ($^{\mathrm{CF3}}$**L2**)$_2$Zn with the CAM-B3LYP functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.83300	$sp^{3.01}$	*s*(24.93%)*p*(75.05%)
Lone pair 2 (N1)	1.57089	n/a	*s*(0.00%)*p*(99.92%)
σ(N1-C5)	1.98497	$sp^{1.76}$ at N1 $sp^{2.03}$ at C5	N1 (59.00%): *s*(36.18%)*p*(63.54%) C5 (41.00%): *s*(32.92%)*p*(66.97%)
σ(N1-C11)	1.98526	$sp^{1.57}$ at N1 $sp^{2.10}$ at C11	N1 (58.74%): *s*(38.75%)*p*(60.98%) C11 (41.26%): *s*(32.18%)*p*(67.71%)
Lone pair 1 (N2)	1.91037	$sp^{2.22}$	*s*(30.96%)*p*(68.86%)
σ(N2-C5)	1.98532	$sp^{2.04}$ at N2 $sp^{1.89}$ at C5	N2 (57.62%): *s*(32.69%)*p*(66.82%) C5 (42.38%): *s*(34.54%)*p*(65.35%)
σ(N2-C6)	1.98668	$sp^{1.75}$ at N2 $sp^{2.01}$ at C6	N2 (58.99%): *s*(36.23%)*p*(63.25%) C6 (41.01%): *s*(33.14%)*p*(66.72%)
π(N2-C6)	1.75344	n/a	N2 (65.77%): *s*(0.00%)*p*(99.67%) C6 (34.23%): *s*(0.00%)*p*(99.85%)
Lone pair 1 (N3)	1.90294	$sp^{2.22}$	*s*(30.99%)*p*(68.87%)
σ(N3-C5)	1.98335	$sp^{2.17}$ at N3 $sp^{2.08}$ at C5	N3 (57.86%): *s*(31.42%)*p*(68.12%) C5 (42.14%): *s*(32.40%)*p*(67.50%)
σ(N3-C7)	1.98838	$sp^{1.66}$ at N3 $sp^{1.99}$ at C7	N3 (59.03%): *s*(37.44%)*p*(62.06%) C7 (40.97%): *s*(33.38%)*p*(66.48%)
π(N3-C7)	1.78815	n/a	N3 (65.15%): *s*(0.00%)*p*(99.70%) C7 (34.85%): *s*(0.00%)*p*(99.84%)
σ(C6-C8)	1.98802	$sp^{1.87}$ at C8 $sp^{1.62}$ at C6	C8 (50.41%): *s*(34.81%)*p*(64.97%) C6 (49.59%): *s*(38.06%)*p*(61.77%)
σ(C7-C8)	1.98721	$sp^{1.90}$ at C8 $sp^{1.64}$ at C7	C8 (50.28%): *s*(34.40%)*p*(65.40%) C7 (49.72%): *s*(37.80%)*p*(62.02%)
σ(C11-C12)	1.97697	$sp^{1.73}$ at C11 $sp^{1.85}$ at C12	C11 (50.99%): *s*(36.61%)*p*(63.27%) C12 (49.01%): *s*(34.99%)*p*(64.81%)
π(C11-C12)	1.65180	n/a	C11 (46.27%): *s*(0.00%)*p*(99.91%) C12 (53.73%): *s*(0.00%)*p*(99.91%)
σ(C11-C10)	1.97332	$sp^{2.21}$ at C11 $sp^{1.97}$ at C10	C11 (49.42%): *s*(31.13%)*p*(68.75%) C10 (50.58%): *s*(33.62%)*p*(66.25%)
Lone pair 1 (N4)	1.88647	$sp^{2.76}$	*s*(26.59%)*p*(73.38%)
σ(N4-C9)	1.98777	$sp^{1.55}$ at N4 $sp^{1.92}$ at C9	N4 (59.72%): *s*(39.03%)*p*(60.58%) C9 (40.28%): *s*(34.25%)*p*(65.61%)
π(N4-C9)	1.85990	n/a	N4 (64.03%): *s*(0.00%)*p*(99.81%) C9 (35.97%): *s*(0.00%)*p*(99.85%)
σ(N4-C10)	1.98221	$sp^{1.91}$ at N4 $sp^{2.28}$ at C10	N4 (58.69%): *s*(34.25%)*p*(65.39%) C10 (41.31%): *s*(30.48%)*p*(69.41%)

[a] Calculated in solution at the optimized S0 geometry using CAM-B3LYP (SMD "dichloromethane"/ def2-tzvpp def2/j). The CAM-B3LYP functional is a range-separated functional, and uses 19 % Hartree-Fock exchange at short range, 33 % Hartree-Fock exchange at intermediate range, and 65 % Hartree-Fock exchange at long range.[15]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|$>0.95), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S74. NBO analysis[a] of ($^{t\mathrm{Bu}}$**L3**)$_2$Zn with the M06-L functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.80939	$sp^{2.18}$	*s*(31.48%)*p*(68.50%)
Lone pair 2 (N1)	1.60384	n/a	*s*(0.07%)*p*(99.88%)
σ(N1-C5)	1.98378	$sp^{1.97}$ at N1 $sp^{2.23}$ at C5	N1 (59.22%): *s*(33.65%)*p*(66.15%) C5 (40.78%): *s*(30.94%)*p*(68.98%)
σ(N1-C11)	1.98288	$sp^{1.88}$ at N1 $sp^{2.08}$ at C11	N1 (58.51%): *s*(34.68%)*p*(65.09%) C11 (41.49%): *s*(32.41%)*p*(67.50%)
σ(C2-C5)	1.97772	$sp^{1.84}$ at C2 $sp^{1.87}$ at C5	C2 (49.60%): *s*(35.10%)*p*(64.73%) C5 (50.40%): *s*(34.76%)*p*(65.13%)
σ(C2-C6)	1.98213	$sp^{1.74}$ at C2 $sp^{1.75}$ at C6	C2 (50.23%): *s*(36.50%)*p*(63.33%) C6 (49.77%): *s*(36.25%)*p*(63.60%)
π(C2-C6)	1.70484	n/a	C2 (52.02%): *s*(0.01%)*p*(99.92%) C6 (47.98%): *s*(0.00%)*p*(99.92%)
σ(C3-C5)	1.97754	$sp^{1.83}$ at C3 $sp^{1.93}$ at C5	C3 (49.45%): *s*(35.32%)*p*(64.50%) C5 (50.55%): *s*(34.20%)*p*(65.86%)
π(C3-C5)	1.62648	n/a	C3 (52.77%): *s*(0.00%)*p*(99.92%) C5 (47.23%): *s*(0.01%)*p*(99.91%)
σ(C3-C7)	1.98321	$sp^{1.74}$ at C3 $sp^{1.77}$ at C7	C3 (50.25%): *s*(36.43%)*p*(63.39%) C7 (49.75%): *s*(36.08%)*p*(63.76%)
σ(C6-C8)	1.98417	$sp^{1.77}$ at C6 $sp^{1.79}$ at C8	C6 (50.15%): *s*(36.01%)*p*(63.82%) C8 (49.85%): *s*(35.73%)*p*(64.11%)
σ(C7-C8)	1.98402	$sp^{1.77}$ at C7 $sp^{1.79}$ at C8	C7 (50.10%): *s*(36.02%)*p*(63.81%) C8 (49.90%): *s*(35.74%)*p*(64.10%)
π(C7-C8)	1.67304	n/a	C7 (48.16%): *s*(0.00%)*p*(99.92%) C8 (51.84%): *s*(0.00%)*p*(99.92%)
σ(C11-C12)	1.97698	$sp^{1.75}$ at C11 $sp^{1.87}$ at C12	C11 (50.94%): *s*(36.30%)*p*(63.59%) C12 (49.06%): *s*(34.76%)*p*(65.06%)
π(C11-C12)	1.63613	n/a	C11 (44.36%): *s*(0.00%)*p*(99.90%) C12 (55.64%): *s*(0.01%)*p*(99.90%)
σ(C11-C10)	1.97095	$sp^{2.20}$ at C11 $sp^{1.94}$ at C10	C11 (49.09%): *s*(31.21%)*p*(68.66%) C10 (50.91%): *s*(34.01%)*p*(65.87%)
Lone pair 1 (N4)	1.86702	$sp^{2.43}$	*s*(29.12%)*p*(70.86%)
σ(N4-C9)	1.98844	$sp^{1.66}$ at N4 $sp^{1.94}$ at C9	N4 (59.97%): *s*(37.45%)*p*(62.24%) C9 (40.03%): *s*(34.02%)*p*(65.89%)
π(N4-C9)	1.86261	n/a	N4 (62.68%): *s*(0.00%)*p*(99.86%) C9 (37.32%): *s*(0.00%)*p*(99.87%)
σ(N4-C10)	1.98149	$sp^{1.99}$ at N4 $sp^{2.34}$ at C10	N4 (59.48%): *s*(33.31%)*p*(66.42%) C10 (40.52%): *s*(29.90%)*p*(70.03%)

[a] Calculated in gas phase at the optimized S0 geometry using M06-L (gas phase/ def2-tzvpp def2/j). The M06-L functional uses 0 % Hartree-Fock exchange.[19]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S75. NBO analysis[a] of $({}^{t\mathrm{Bu}}\mathbf{L3})_2$Zn with the TPSSh functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.80893	$sp^{2.37}$	*s*(29.70%)*p*(70.27%)
Lone pair 2 (N1)	1.61047	n/a	*s*(0.07%)*p*(99.88%)
σ(N1-C5)	1.98428	$sp^{1.89}$ at N1 $sp^{2.22}$ at C5	N1 (59.00%): *s*(34.50%)*p*(65.28%) C5 (41.00%): *s*(31.02%)*p*(68.88%)
σ(N1-C11)	1.98325	$sp^{1.80}$ at N1 $sp^{2.08}$ at C11	N1 (58.25%): *s*(35.61%)*p*(64.15%) C11 (41.75%): *s*(32.48%)*p*(67.41%)
σ(C2-C5)	1.97775	$sp^{1.86}$ at C2 $sp^{1.87}$ at C5	C2 (49.47%): *s*(34.94%)*p*(64.88%) C5 (50.53%): *s*(34.76%)*p*(65.13%)
σ(C2-C6)	1.98200	$sp^{1.74}$ at C2 $sp^{1.76}$ at C6	C2 (50.24%): *s*(36.40%)*p*(63.42%) C6 (49.76%): *s*(36.11%)*p*(63.72%)
π(C2-C6)	1.70324	n/a	C2 (51.83%): *s*(0.01%)*p*(99.92%) C6 (48.17%): *s*(0.00%)*p*(99.93%)
σ(C3-C5)	1.97766	$sp^{1.84}$ at C3 $sp^{1.93}$ at C5	C3 (49.30%): *s*(35.18%)*p*(64.64%) C5 (50.70%): *s*(34.12%)*p*(65.77%)
π(C3-C5)	1.62719	n/a	C3 (52.29%): *s*(0.00%)*p*(99.93%) C5 (47.71%): *s*(0.02%)*p*(99.91%)
σ(C3-C7)	1.98307	$sp^{1.75}$ at C3 $sp^{1.78}$ at C7	C3 (50.27%): *s*(36.31%)*p*(63.51%) C7 (49.73%): *s*(35.93%)*p*(63.90%)
σ(C6-C8)	1.98432	$sp^{1.78}$ at C6 $sp^{1.80}$ at C8	C6 (50.14%): *s*(35.88%)*p*(63.94%) C8 (49.86%): *s*(35.61%)*p*(64.21%)
σ(C7-C8)	1.98364	$sp^{1.78}$ at C7 $sp^{1.80}$ at C8	C7 (50.08%): *s*(35.96%)*p*(63.86%) C8 (49.92%): *s*(35.70%)*p*(64.12%)
π(C7-C8)	1.67297	n/a	C7 (48.20%): *s*(0.00%)*p*(99.93%) C8 (51.80%): *s*(0.00%)*p*(99.93%)
σ(C11-C12)	1.97605	$sp^{1.75}$ at C11 $sp^{1.88}$ at C12	C11 (51.10%): *s*(36.35%)*p*(63.54%) C12 (48.90%): *s*(34.66%)*p*(65.15%)
π(C11-C12)	1.63577	n/a	C11 (44.82%): *s*(0.00%)*p*(99.91%) C12 (55.18%): *s*(0.01%)*p*(99.91%)
σ(C11-C10)	1.97063	$sp^{2.22}$ at C11 $sp^{1.94}$ at C10	C11 (49.08%): *s*(31.00%)*p*(68.88%) C10 (50.92%): *s*(33.96%)*p*(65.93%)
Lone pair 1 (N4)	1.86723	$sp^{2.58}$	*s*(27.91%)*p*(72.07%)
σ(N4-C9)	1.98843	$sp^{1.60}$ at N4 $sp^{1.93}$ at C9	N4 (59.91%): *s*(38.40%)*p*(61.25%) C9 (40.09%): *s*(34.11%)*p*(65.77%)
π(N4-C9)	1.86265	n/a	N4 (62.80%): *s*(0.00%)*p*(99.87%) C9 (37.20%): *s*(0.00%)*p*(99.88%)
σ(N4-C10)	1.98196	$sp^{1.92}$ at N4 $sp^{2.33}$ at C10	N4 (59.27%): *s*(34.14%)*p*(65.56%) C10 (40.73%): *s*(29.98%)*p*(69.92%)

[a] Calculated in gas phase at the optimized S0 geometry using TPSSh (gas phase/ def2-tzvpp def2/j). The TPSSh functional uses 10 % Hartree-Fock exchange.[11]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S76. NBO analysis[a] of (**$^{t\mathrm{Bu}}$L3**)$_2$Zn with the O3LYP functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.80815	$sp^{2.40}$	*s*(29.41%)*p*(70.56%)
Lone pair 2 (N1)	1.60716	n/a	*s*(0.06%)*p*(99.89%)
σ(N1-C5)	1.98429	$sp^{1.88}$ at N1 $sp^{2.22}$ at C5	N1 (58.85%): *s*(34.65%)*p*(65.14%) C5 (41.15%): *s*(31.06%)*p*(68.84%)
σ(N1-C11)	1.98316	$sp^{1.79}$ at N1 $sp^{2.07}$ at C11	N1 (58.13%): *s*(35.74%)*p*(64.01%) C11 (41.87%): *s*(32.53%)*p*(67.36%)
σ(C2-C5)	1.97733	$sp^{1.86}$ at C2 $sp^{1.87}$ at C5	C2 (49.47%): *s*(34.90%)*p*(64.93%) C5 (50.53%): *s*(34.77%)*p*(65.13%)
σ(C2-C6)	1.98150	$sp^{1.74}$ at C2 $sp^{1.77}$ at C6	C2 (50.23%): *s*(36.38%)*p*(63.45%) C6 (49.77%): *s*(36.09%)*p*(63.75%)
π(C2-C6)	1.70356	n/a	C2 (51.77%): *s*(0.01%)*p*(99.93%) C6 (48.23%): *s*(0.00%)*p*(99.93%)
σ(C3-C5)	1.97717	$sp^{1.84}$ at C3 $sp^{1.93}$ at C5	C3 (49.31%): *s*(35.15%)*p*(64.69%) C5 (50.69%): *s*(34.07%)*p*(65.82%)
π(C3-C5)	1.62685	n/a	C3 (52.28%): *s*(0.00%)*p*(99.93%) C5 (47.72%): *s*(0.02%)*p*(99.92%)
σ(C3-C7)	1.98256	$sp^{1.75}$ at C3 $sp^{1.78}$ at C7	C3 (50.27%): *s*(36.30%)*p*(63.53%) C7 (49.73%): *s*(35.90%)*p*(63.94%)
σ(C6-C8)	1.98374	$sp^{1.78}$ at C6 $sp^{1.81}$ at C8	C6 (50.14%): *s*(35.87%)*p*(63.96%) C8 (49.86%): *s*(35.59%)*p*(64.24%)
σ(C7-C8)	1.98360	$sp^{1.78}$ at C7 $sp^{1.80}$ at C8	C7 (50.08%): *s*(35.88%)*p*(63.96%) C8 (49.92%): *s*(35.61%)*p*(64.23%)
π(C7-C8)	1.67379	n/a	C7 (48.30%): *s*(0.00%)*p*(99.94%) C8 (51.70%): *s*(0.00%)*p*(99.94%)
σ(C11-C12)	1.97605	$sp^{1.75}$ at C11 $sp^{1.89}$ at C12	C11 (51.08%): *s*(36.34%)*p*(63.56%) C12 (48.92%): *s*(34.58%)*p*(65.25%)
π(C11-C12)	1.63506	n/a	C11 (45.02%): *s*(0.00%)*p*(99.92%) C12 (54.98%): *s*(0.01%)*p*(99.92%)
σ(C11-C10)	1.97062	$sp^{2.22}$ at C11 $sp^{1.95}$ at C10	C11 (49.11%): *s*(31.06%)*p*(68.83%) C10 (50.89%): *s*(33.90%)*p*(66.00%)
Lone pair 1 (N4)	1.86538	$sp^{2.60}$	*s*(27.77%)*p*(72.22%)
σ(N4-C9)	1.98834	$sp^{1.61}$ at N4 $sp^{1.94}$ at C9	N4 (59.76%): *s*(38.13%)*p*(61.54%) C9 (40.24%): *s*(34.01%)*p*(65.88%)
π(N4-C9)	1.86369	n/a	N4 (62.78%): *s*(0.00%)*p*(99.87%) C9 (37.22%): *s*(0.00%)*p*(99.88%)
σ(N4-C10)	1.98204	$sp^{1.93}$ at N4 $sp^{2.32}$ at C10	N4 (59.10%): *s*(33.98%)*p*(65.72%) C10 (40.90%): *s*(30.06%)*p*(69.85%)

[a] Calculated in gas phase at the optimized S0 geometry using O3LYP (gas phase/ def2-tzvpp def2/j). The O3LYP functional uses 11.61 % Hartree-Fock exchange.[21]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + cB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S77. NBO analysis[a] of ($^{t\mathrm{Bu}}$**L3**)$_2$Zn with the B3LYP functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.81183	$sp^{2.44}$	*s*(29.08%)*p*(70.89%)
Lone pair 2 (N1)	1.62131	n/a	*s*(0.07%)*p*(99.88%)
σ(N1-C5)	1.98457	$sp^{1.86}$ at N1 $sp^{2.21}$ at C5	N1 (58.94%): *s*(34.83%)*p*(64.94%) C5 (41.06%): *s*(31.09%)*p*(68.80%)
σ(N1-C11)	1.98343	$sp^{1.78}$ at N1 $sp^{2.07}$ at C11	N1 (58.22%): *s*(35.90%)*p*(63.84%) C11 (41.78%): *s*(32.55%)*p*(67.33%)
σ(C2-C5)	1.97752	$sp^{1.85}$ at C2 $sp^{1.88}$ at C5	C2 (49.50%): *s*(34.96%)*p*(64.85%) C5 (50.50%): *s*(34.72%)*p*(65.16%)
σ(C2-C6)	1.98185	$sp^{1.74}$ at C2 $sp^{1.76}$ at C6	C2 (50.23%): *s*(36.43%)*p*(63.38%) C6 (49.77%): *s*(36.13%)*p*(63.69%)
π(C2-C6)	1.70328	n/a	C2 (51.94%): *s*(0.01%)*p*(99.93%) C6 (48.06%): *s*(0.00%)*p*(99.93%)
σ(C3-C5)	1.97750	$sp^{1.84}$ at C3 $sp^{1.93}$ at C5	C3 (49.33%): *s*(35.20%)*p*(64.60%) C5 (50.67%): *s*(34.06%)*p*(65.82%)
π(C3-C5)	1.62671	n/a	C3 (52.66%): *s*(0.00%)*p*(99.93%) C5 (47.34%): *s*(0.02%)*p*(99.91%)
σ(C3-C7)	1.98284	$sp^{1.75}$ at C3 $sp^{1.78}$ at C7	C3 (50.25%): *s*(36.34%)*p*(63.47%) C7 (49.75%): *s*(35.96%)*p*(63.86%)
σ(C6-C8)	1.98384	$sp^{1.78}$ at C6 $sp^{1.80}$ at C8	C6 (50.14%): *s*(35.91%)*p*(63.90%) C8 (49.86%): *s*(35.64%)*p*(64.18%)
σ(C7-C8)	1.98371	$sp^{1.78}$ at C7 $sp^{1.80}$ at C8	C7 (50.08%): *s*(35.92%)*p*(63.89%) C8 (49.92%): *s*(35.65%)*p*(64.17%)
π(C7-C8)	1.67455	n/a	C7 (48.13%): *s*(0.00%)*p*(99.94%) C8 (51.87%): *s*(0.00%)*p*(99.94%)
σ(C11-C12)	1.97634	$sp^{1.75}$ at C11 $sp^{1.88}$ at C12	C11 (51.07%): *s*(36.31%)*p*(63.58%) C12 (48.93%): *s*(34.64%)*p*(65.16%)
π(C11-C12)	1.63757	n/a	C11 (44.36%): *s*(0.00%)*p*(99.91%) C12 (55.64%): *s*(0.00%)*p*(99.92%)
σ(C11-C10)	1.97118	$sp^{2.22}$ at C11 $sp^{1.95}$ at C10	C11 (49.06%): *s*(31.04%)*p*(68.83%) C10 (50.94%): *s*(33.91%)*p*(65.97%)
Lone pair 1 (N4)	1.87037	$sp^{2.66}$	*s*(27.31%)*p*(72.68%)
σ(N4-C9)	1.98827	$sp^{1.60}$ at N4 $sp^{1.93}$ at C9	N4 (59.84%): *s*(38.33%)*p*(61.32%) C9 (40.16%): *s*(34.06%)*p*(65.81%)
π(N4-C9)	1.86588	n/a	N4 (62.85%): *s*(0.00%)*p*(99.87%) C9 (37.15%): *s*(0.00%)*p*(99.88%)
σ(N4-C10)	1.98226	$sp^{1.91}$ at N4 $sp^{2.32}$ at C10	N4 (59.27%): *s*(34.24%)*p*(65.44%) C10 (40.73%): *s*(30.05%)*p*(69.85%)

[a] Calculated in gas phase at the optimized S0 geometry using B3LYP (gas phase/ def2-tzvpp def2/j). The B3LYP functional uses 20 % Hartree-Fock exchange.[22]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S78. NBO analysis[a] of ($^{t\mathrm{Bu}}$**L3**)$_2$Zn with the PBE0 functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.81558	$sp^{2.44}$	*s*(29.03%)*p*(70.94%)
Lone pair 2 (N1)	1.62561	n/a	*s*(0.07%)*p*(99.88%)
σ(N1-C5)	1.98475	$sp^{1.86}$ at N1 $sp^{2.21}$ at C5	N1 (58.90%): *s*(34.87%)*p*(64.90%) C5 (41.10%): *s*(31.09%)*p*(68.80%)
σ(N1-C11)	1.98357	$sp^{1.78}$ at N1 $sp^{2.07}$ at C11	N1 (58.16%): *s*(35.91%)*p*(63.83%) C11 (41.84%): *s*(32.56%)*p*(67.33%)
σ(C2-C5)	1.97780	$sp^{1.86}$ at C2 $sp^{1.88}$ at C5	C2 (49.53%): *s*(34.94%)*p*(64.88%) C5 (50.47%): *s*(34.73%)*p*(65.16%)
σ(C2-C6)	1.98194	$sp^{1.74}$ at C2 $sp^{1.77}$ at C6	C2 (50.24%): *s*(36.37%)*p*(63.45%) C6 (49.76%): *s*(36.10%)*p*(63.73%)
π(C2-C6)	1.70297	n/a	C2 (51.98%): *s*(0.01%)*p*(99.93%) C6 (48.02%): *s*(0.00%)*p*(99.93%)
σ(C3-C5)	1.97776	$sp^{1.84}$ at C3 $sp^{1.93}$ at C5	C3 (49.35%): *s*(35.18%)*p*(64.63%) C5 (50.65%): *s*(34.06%)*p*(65.82%)
π(C3-C5)	1.62719	n/a	C3 (52.67%): *s*(0.00%)*p*(99.93%) C5 (47.33%): *s*(0.02%)*p*(99.91%)
σ(C3-C7)	1.98296	$sp^{1.75}$ at C3 $sp^{1.78}$ at C7	C3 (50.27%): *s*(36.29%)*p*(63.53%) C7 (49.73%): *s*(35.92%)*p*(63.91%)
σ(C6-C8)	1.98407	$sp^{1.78}$ at C6 $sp^{1.80}$ at C8	C6 (50.14%): *s*(35.86%)*p*(63.96%) C8 (49.86%): *s*(35.59%)*p*(64.23%)
σ(C7-C8)	1.98394	$sp^{1.78}$ at C7 $sp^{1.80}$ at C8	C7 (50.07%): *s*(35.87%)*p*(63.95%) C8 (49.93%): *s*(35.60%)*p*(64.22%)
π(C7-C8)	1.67432	n/a	C7 (48.10%): *s*(0.00%)*p*(99.93%) C8 (51.90%): *s*(0.00%)*p*(99.94%)
σ(C11-C12)	1.97648	$sp^{1.75}$ at C11 $sp^{1.88}$ at C12	C11 (51.04%): *s*(36.33%)*p*(63.56%) C12 (48.96%): *s*(34.60%)*p*(65.20%)
π(C11-C12)	1.63888	n/a	C11 (44.30%): *s*(0.00%)*p*(99.91%) C12 (55.70%): *s*(0.01%)*p*(99.91%)
σ(C11-C10)	1.97135	$sp^{2.22}$ at C11 $sp^{1.94}$ at C10	C11 (49.03%): *s*(31.03%)*p*(68.85%) C10 (50.97%): *s*(33.93%)*p*(65.95%)
Lone pair 1 (N4)	1.87229	$sp^{2.64}$	*s*(27.45%)*p*(72.53%)
σ(N4-C9)	1.98850	$sp^{1.61}$ at N4 $sp^{1.93}$ at C9	N4 (59.78%): *s*(38.23%)*p*(61.41%) C9 (40.22%): *s*(34.05%)*p*(65.83%)
π(N4-C9)	1.86650	n/a	N4 (62.98%): *s*(0.00%)*p*(99.86%) C9 (37.02%): *s*(0.00%)*p*(99.87%)
σ(N4-C10)	1.98243	$sp^{1.92}$ at N4 $sp^{2.33}$ at C10	N4 (59.17%): *s*(34.19%)*p*(65.49%) C10 (40.83%): *s*(30.03%)*p*(69.87%)

[a] Calculated in gas phase at the optimized S0 geometry using PBE0 (gas phase/ def2-tzvpp def2/j). The PBE0 functional uses 25 % Hartree-Fock exchange.[14]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S79. NBO analysis[a] of ($^{t\mathrm{Bu}}$**L3**)$_2$Zn with the M06 functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.80780	$sp^{2.42}$	*s*(29.26%)*p*(70.72%)
Lone pair 2 (N1)	1.63460	n/a	*s*(0.08%)*p*(99.85%)
σ(N1-C5)	1.98440	$sp^{1.87}$ at N1 $sp^{2.22}$ at C5	N1 (59.23%): *s*(34.80%)*p*(65.01%) C5 (40.77%): *s*(31.06%)*p*(68.85%)
σ(N1-C11)	1.98333	$sp^{1.79}$ at N1 $sp^{2.07}$ at C11	N1 (58.43%): *s*(35.75%)*p*(64.04%) C11 (41.57%): *s*(32.52%)*p*(67.38%)
σ(C2-C5)	1.97705	$sp^{1.85}$ at C2 $sp^{1.88}$ at C5	C2 (49.59%): *s*(35.08%)*p*(64.76%) C5 (50.41%): *s*(34.73%)*p*(65.16%)
σ(C2-C6)	1.98156	$sp^{1.74}$ at C2 $sp^{1.76}$ at C6	C2 (50.20%): *s*(36.41%)*p*(63.42%) C6 (49.80%): *s*(36.21%)*p*(63.64%)
π(C2-C6)	1.70283	n/a	C2 (52.25%): *s*(0.01%)*p*(99.92%) C6 (47.75%): *s*(0.00%)*p*(99.92%)
σ(C3-C5)	1.97710	$sp^{1.83}$ at C3 $sp^{1.93}$ at C5	C3 (49.41%): *s*(35.32%)*p*(64.51%) C5 (50.59%): *s*(34.09%)*p*(65.80%)
π(C3-C5)	1.62772	n/a	C3 (53.02%): *s*(0.00%)*p*(99.93%) C5 (46.98%): *s*(0.02%)*p*(99.91%)
σ(C3-C7)	1.98263	$sp^{1.75}$ at C3 $sp^{1.77}$ at C7	C3 (50.22%): *s*(36.32%)*p*(63.52%) C7 (49.78%): *s*(36.03%)*p*(63.81%)
σ(C6-C8)	1.98350	$sp^{1.78}$ at C6 $sp^{1.80}$ at C8	C6 (50.15%): *s*(35.93%)*p*(63.91%) C8 (49.85%): *s*(35.67%)*p*(64.18%)
σ(C7-C8)	1.98339	$sp^{1.78}$ at C7 $sp^{1.80}$ at C8	C7 (50.09%): *s*(35.94%)*p*(63.90%) C8 (49.91%): *s*(35.68%)*p*(64.17%)
π(C7-C8)	1.67390	n/a	C7 (47.91%): *s*(0.00%)*p*(99.93%) C8 (52.09%): *s*(0.00%)*p*(99.93%)
σ(C11-C12)	1.97604	$sp^{1.75}$ at C11 $sp^{1.88}$ at C12	C11 (50.98%): *s*(36.32%)*p*(63.58%) C12 (49.02%): *s*(34.69%)*p*(65.13%)
π(C11-C12)	1.64011	n/a	C11 (43.42%): *s*(0.00%)*p*(99.91%) C12 (56.58%): *s*(0.01%)*p*(99.91%)
σ(C11-C10)	1.97086	$sp^{2.21}$ at C11 $sp^{1.94}$ at C10	C11 (49.07%): *s*(31.07%)*p*(68.81%) C10 (50.93%): *s*(33.96%)*p*(65.93%)
Lone pair 1 (N4)	1.86833	$sp^{2.64}$	*s*(27.44%)*p*(72.53%)
σ(N4-C9)	1.98829	$sp^{1.61}$ at N4 $sp^{1.93}$ at C9	N4 (59.92%): *s*(38.19%)*p*(61.52%) C9 (40.08%): *s*(34.14%)*p*(65.77%)
π(N4-C9)	1.87004	n/a	N4 (63.44%): *s*(0.00%)*p*(99.84%) C9 (36.56%): *s*(0.00%)*p*(99.86%)
σ(N4-C10)	1.98194	$sp^{1.91}$ at N4 $sp^{2.33}$ at C10	N4 (59.50%): *s*(34.26%)*p*(65.47%) C10 (40.50%): *s*(29.98%)*p*(69.94%)

[a] Calculated in gas phase at the optimized S0 geometry using M06 (gas phase/ def2-tzvpp def2/j). The M06 functional uses 27 % Hartree-Fock exchange.[23]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+cB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp$^{\lambda}$, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp$^{\infty}$) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S80. NBO analysis[a] of (${}^{t\mathrm{Bu}}$**L3**)$_2$Zn with the M06-2X functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.83539	$sp^{2.51}$	*s*(28.47%)*p*(71.50%)
Lone pair 2 (N1)	1.64322	n/a	*s*(0.04%)*p*(99.89%)
σ(N1-C5)	1.98488	$sp^{1.83}$ at N1 $sp^{2.21}$ at C5	N1 (58.94%): *s*(35.22%)*p*(64.56%) C5 (41.06%): *s*(31.13%)*p*(68.79%)
σ(N1-C11)	1.98351	$sp^{1.76}$ at N1 $sp^{2.07}$ at C11	N1 (58.21%): *s*(36.15%)*p*(63.60%) C11 (41.79%): *s*(32.58%)*p*(67.32%)
σ(C2-C5)	1.97800	$sp^{1.85}$ at C2 $sp^{1.88}$ at C5	C2 (49.52%): *s*(34.97%)*p*(64.86%) C5 (50.48%): *s*(34.71%)*p*(65.19%)
σ(C2-C6)	1.98224	$sp^{1.75}$ at C2 $sp^{1.77}$ at C6	C2 (50.23%): *s*(36.36%)*p*(63.46%) C6 (49.77%): *s*(36.10%)*p*(63.74%)
π(C2-C6)	1.70225	n/a	C2 (52.06%): *s*(0.01%)*p*(99.93%) C6 (47.94%): *s*(0.00%)*p*(99.93%)
σ(C3-C5)	1.97800	$sp^{1.83}$ at C3 $sp^{1.93}$ at C5	C3 (49.31%): *s*(35.21%)*p*(64.61%) C5 (50.69%): *s*(34.06%)*p*(65.83%)
π(C3-C5)	1.62899	n/a	C3 (52.91%): *s*(0.00%)*p*(99.93%) C5 (47.09%): *s*(0.02%)*p*(99.92%)
σ(C3-C7)	1.98319	$sp^{1.75}$ at C3 $sp^{1.78}$ at C7	C3 (50.25%): *s*(36.26%)*p*(63.56%) C7 (49.75%): *s*(35.93%)*p*(63.90%)
σ(C6-C8)	1.98421	$sp^{1.78}$ at C6 $sp^{1.81}$ at C8	C6 (50.14%): *s*(35.86%)*p*(63.97%) C8 (49.86%): *s*(35.59%)*p*(64.25%)
σ(C7-C8)	1.98407	$sp^{1.78}$ at C7 $sp^{1.80}$ at C8	C7 (50.07%): *s*(35.85%)*p*(63.97%) C8 (49.93%): *s*(35.60%)*p*(64.23%)
π(C7-C8)	1.67529	n/a	C7 (48.01%): *s*(0.00%)*p*(99.94%) C8 (51.99%): *s*(0.00%)*p*(99.94%)
σ(C11-C12)	1.97674	$sp^{1.75}$ at C11 $sp^{1.88}$ at C12	C11 (51.08%): *s*(36.38%)*p*(63.52%) C12 (48.92%): *s*(34.60%)*p*(65.21%)
π(C11-C12)	1.64397	n/a	C11 (43.70%): *s*(0.00%)*p*(99.91%) C12 (56.30%): *s*(0.01%)*p*(99.91%)
σ(C11-C10)	1.97194	$sp^{2.23}$ at C11 $sp^{1.94}$ at C10	C11 (48.94%): *s*(30.97%)*p*(68.91%) C10 (51.06%): *s*(33.97%)*p*(65.93%)
Lone pair 1 (N4)	1.88594	$sp^{2.71}$	*s*(26.92%)*p*(73.06%)
σ(N4-C9)	1.98841	$sp^{1.59}$ at N4 $sp^{1.94}$ at C9	N4 (59.91%): *s*(38.46%)*p*(61.19%) C9 (40.09%): *s*(34.03%)*p*(65.86%)
π(N4-C9)	1.87186	n/a	N4 (62.85%): *s*(0.00%)*p*(99.84%) C9 (37.15%): *s*(0.00%)*p*(99.87%)
σ(N4-C10)	1.98240	$sp^{1.89}$ at N4 $sp^{2.33}$ at C10	N4 (59.39%): *s*(34.50%)*p*(65.19%) C10 (40.61%): *s*(29.99%)*p*(69.93%)

[a] Calculated in gas phase at the optimized S0 geometry using M06-2X (gas phase/ def2-tzvpp def2/j). The M06-2X functional uses 54 % Hartree-Fock exchange.[23]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S81. NBO analysis[a] of $({}^{t\mathrm{Bu}}\mathbf{L3})_2\mathrm{Zn}$ with the CAM-B3LYP functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.81921	$sp^{2.55}$	*s*(28.15%)*p*(71.82%)
Lone pair 2 (N1)	1.64835	n/a	*s*(0.07%)*p*(99.88%)
σ(N1-C5)	1.98511	$sp^{1.82}$ at N1 $sp^{2.21}$ at C5	N1 (58.90%): *s*(35.33%)*p*(64.43%) C5 (41.10%): *s*(31.10%)*p*(68.79%)
σ(N1-C11)	1.98375	$sp^{1.75}$ at N1 $sp^{2.07}$ at C11	N1 (58.16%): *s*(36.33%)*p*(63.40%) C11 (41.84%): *s*(32.55%)*p*(67.33%)
σ(C2-C5)	1.97802	$sp^{1.85}$ at C2 $sp^{1.88}$ at C5	C2 (49.55%): *s*(34.97%)*p*(64.83%) C5 (50.45%): *s*(34.73%)*p*(65.16%)
σ(C2-C6)	1.98192	$sp^{1.74}$ at C2 $sp^{1.76}$ at C6	C2 (50.23%): *s*(36.41%)*p*(63.39%) C6 (49.77%): *s*(36.11%)*p*(63.71%)
π(C2-C6)	1.70191	n/a	C2 (52.18%): *s*(0.01%)*p*(99.93%) C6 (47.82%): *s*(0.00%)*p*(99.93%)
σ(C3-C5)	1.97803	$sp^{1.83}$ at C3 $sp^{1.93}$ at C5	C3 (49.36%): *s*(35.22%)*p*(64.59%) C5 (50.64%): *s*(34.05%)*p*(65.83%)
π(C3-C5)	1.62730	n/a	C3 (53.12%): *s*(0.00%)*p*(99.92%) C5 (46.88%): *s*(0.02%)*p*(99.91%)
σ(C3-C7)	1.98285	$sp^{1.75}$ at C3 $sp^{1.78}$ at C7	C3 (50.25%): *s*(36.31%)*p*(63.50%) C7 (49.75%): *s*(35.94%)*p*(63.88%)
σ(C6-C8)	1.98382	$sp^{1.78}$ at C6 $sp^{1.80}$ at C8	C6 (50.14%): *s*(35.89%)*p*(63.92%) C8 (49.86%): *s*(35.62%)*p*(64.20%)
σ(C7-C8)	1.98373	$sp^{1.78}$ at C7 $sp^{1.80}$ at C8	C7 (50.07%): *s*(35.89%)*p*(63.92%) C8 (49.93%): *s*(35.63%)*p*(64.18%)
π(C7-C8)	1.67570	n/a	C7 (47.90%): *s*(0.00%)*p*(99.93%) C8 (52.10%): *s*(0.00%)*p*(99.94%)
σ(C11-C12)	1.97653	$sp^{1.75}$ at C11 $sp^{1.88}$ at C12	C11 (51.04%): *s*(36.34%)*p*(63.55%) C12 (48.96%): *s*(34.65%)*p*(65.15%)
π(C11-C12)	1.64470	n/a	C11 (43.35%): *s*(0.00%)*p*(99.90%) C12 (56.65%): *s*(0.00%)*p*(99.91%)
σ(C11-C10)	1.97203	$sp^{2.22}$ at C11 $sp^{1.94}$ at C10	C11 (48.98%): *s*(31.01%)*p*(68.86%) C10 (51.02%): *s*(33.97%)*p*(65.91%)
Lone pair 1 (N4)	1.87748	$sp^{2.75}$	*s*(26.68%)*p*(73.31%)
σ(N4-C9)	1.98823	$sp^{1.58}$ at N4 $sp^{1.93}$ at C9	N4 (59.79%): *s*(38.56%)*p*(61.08%) C9 (40.21%): *s*(34.07%)*p*(65.81%)
π(N4-C9)	1.87353	n/a	N4 (62.98%): *s*(0.00%)*p*(99.86%) C9 (37.02%): *s*(0.00%)*p*(99.87%)
σ(N4-C10)	1.98260	$sp^{1.88}$ at N4 $sp^{2.33}$ at C10	N4 (59.31%): *s*(34.64%)*p*(65.03%) C10 (40.69%): *s*(29.97%)*p*(69.92%)

[a] Calculated in gas phase at the optimized S0 geometry using CAM-B3LYP (gas phase/ def2-tzvpp def2/j). The CAM-B3LYP functional is a range-separated functional, and uses 19 % Hartree-Fock exchange at short range, 33 % Hartree-Fock exchange at intermediate range, and 65 % Hartree-Fock exchange at long range.[15]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}| > 0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S82. Solvated NBO analysis[a] of (^{tBu}**L3**)$_2$Zn with the M06-L functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.81111	$sp^{2.18}$	s(31.41%)p(68.57%)
Lone pair 2 (N1)	1.60880	n/a	s(0.10%)p(99.84%)
σ(N1-C5)	1.98383	$sp^{1.97}$ at N1 $sp^{2.22}$ at C5	N1 (59.11%): s(33.58%)p(66.22%) C5 (40.89%): s(31.02%)p(68.90%)
σ(N1-C11)	1.98283	$sp^{1.87}$ at N1 $sp^{2.09}$ at C11	N1 (58.58%): s(34.80%)p(64.97%) C11 (41.42%): s(32.33%)p(67.58%)
σ(C2-C5)	1.97805	$sp^{1.85}$ at C2 $sp^{1.88}$ at C5	C2 (49.59%): s(35.00%)p(64.82%) C5 (50.41%): s(34.72%)p(65.16%)
σ(C2-C6)	1.98224	$sp^{1.74}$ at C2 $sp^{1.76}$ at C6	C2 (50.22%): s(36.43%)p(63.40%) C6 (49.78%): s(36.14%)p(63.70%)
π(C2-C6)	1.70514	n/a	C2 (51.93%): s(0.01%)p(99.91%) C6 (48.07%): s(0.00%)p(99.92%)
σ(C3-C5)	1.97785	$sp^{1.83}$ at C3 $sp^{1.92}$ at C5	C3 (49.49%): s(35.26%)p(64.56%) C5 (50.51%): s(34.16%)p(65.72%)
π(C3-C5)	1.62661	n/a	C3 (53.06%): s(0.00%)p(99.92%) C5 (46.94%): s(0.01%)p(99.91%)
σ(C3-C7)	1.98329	$sp^{1.75}$ at C3 $sp^{1.77}$ at C7	C3 (50.26%): s(36.36%)p(63.46%) C7 (49.74%): s(35.98%)p(63.86%)
σ(C6-C8)	1.98437	$sp^{1.78}$ at C6 $sp^{1.80}$ at C8	C6 (50.12%): s(35.91%)p(63.91%) C8 (49.88%): s(35.64%)p(64.20%)
σ(C7-C8)	1.98423	$sp^{1.78}$ at C7 $sp^{1.80}$ at C8	C7 (50.11%): s(35.94%)p(63.88%) C8 (49.89%): s(35.65%)p(64.19%)
π(C7-C8)	1.67794	n/a	C7 (48.02%): s(0.00%)p(99.92%) C8 (51.98%): s(0.00%)p(99.93%)
σ(C11-C12)	1.97700	$sp^{1.75}$ at C11 $sp^{1.88}$ at C12	C11 (50.96%): s(36.33%)p(63.57%) C12 (49.04%): s(34.65%)p(65.17%)
π(C11-C12)	1.64755	n/a	C11 (44.36%): s(0.00%)p(99.91%) C12 (55.64%): s(0.00%)p(99.91%)
σ(C11-C10)	1.97095	$sp^{2.19}$ at C11 $sp^{1.94}$ at C10	C11 (49.20%): s(31.27%)p(68.60%) C10 (50.80%): s(33.93%)p(65.95%)
Lone pair 1 (N4)	1.86668	$sp^{2.43}$	s(29.15%)p(70.83%)
σ(N4-C9)	1.98848	$sp^{1.66}$ at N4 $sp^{1.95}$ at C9	N4 (60.08%): s(37.50%)p(62.19%) C9 (39.92%): s(33.84%)p(66.06%)
π(N4-C9)	1.86174	n/a	N4 (63.51%): s(0.00%)p(99.86%) C9 (36.49%): s(0.00%)p(99.86%)
σ(N4-C10)	1.98183	$sp^{2.00}$ at N4 $sp^{2.34}$ at C10	N4 (59.37%): s(33.22%)p(66.50%) C10 (40.63%): s(29.95%)p(69.97%)

[a] Calculated in solution at the optimized S0 geometry using M06-L (SMD "dichloromethane"/ def2-tzvpp def2/j). The M06-L functional uses 0 % Hartree-Fock exchange.[19]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \le x \le 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp$^\lambda$, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp$^\infty$) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S83. Solvated NBO analysis[a] of (^{tBu}**L3**)$_2$Zn with the TPSSh functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.81076	$sp^{2.38}$	*s*(29.62%)*p*(70.35%)
Lone pair 2 (N1)	1.61582	n/a	*s*(0.10%)*p*(99.85%)
σ(N1-C5)	1.98436	$sp^{1.90}$ at N1 $sp^{2.21}$ at C5	N1 (58.89%): *s*(34.43%)*p*(65.35%) C5 (41.11%): *s*(31.10%)*p*(68.80%)
σ(N1-C11)	1.98322	$sp^{1.79}$ at N1 $sp^{2.08}$ at C11	N1 (58.32%): *s*(35.73%)*p*(64.03%) C11 (41.68%): *s*(32.40%)*p*(67.49%)
σ(C2-C5)	1.97825	$sp^{1.87}$ at C2 $sp^{1.89}$ at C5	C2 (49.44%): *s*(34.82%)*p*(65.00%) C5 (50.56%): *s*(34.74%)*p*(65.15%)
σ(C2-C6)	1.98212	$sp^{1.75}$ at C2 $sp^{1.77}$ at C6	C2 (50.24%): *s*(36.32%)*p*(63.49%) C6 (49.76%): *s*(35.99%)*p*(63.84%)
π(C2-C6)	1.70270	n/a	C2 (51.69%): *s*(0.01%)*p*(99.92%) C6 (48.31%): *s*(0.00%)*p*(99.92%)
σ(C3-C5)	1.97796	$sp^{1.84}$ at C3 $sp^{1.93}$ at C5	C3 (49.33%): *s*(35.10%)*p*(64.72%) C5 (50.67%): *s*(34.07%)*p*(65.82%)
σ(C3-C7)	1.98316	n/a	C3 (50.28%): *s*(36.24%)*p*(63.58%) C7 (49.72%): *s*(35.82%)*p*(64.00%)
π(C3-C7)	1.69983	n/a	C3 (51.73%): *s*(0.01%)*p*(99.92%) C7 (48.27%): *s*(0.00%)*p*(99.93%)
σ(C6-C8)	1.98455	$sp^{1.79}$ at C6 $sp^{1.81}$ at C8	C6 (50.11%): *s*(35.76%)*p*(64.05%) C8 (49.89%): *s*(35.51%)*p*(64.31%)
σ(C7-C8)	1.98442	$sp^{1.79}$ at C7 $sp^{1.81}$ at C8	C7 (50.10%): *s*(35.80%)*p*(64.02%) C8 (49.90%): *s*(35.52%)*p*(64.31%)
Lone pair 1 (C31)	1.04616	n/a	*s*(0.00%)*p*(99.95%)
σ(C11-C12)	1.97651	$sp^{1.75}$ at C11 $sp^{1.89}$ at C12	C11 (51.14%): *s*(36.38%)*p*(63.51%) C12 (48.86%): *s*(34.49%)*p*(65.32%)
π(C11-C12)	1.64701	n/a	C11 (45.00%): *s*(0.00%)*p*(99.92%) C12 (55.00%): *s*(0.00%)*p*(99.91%)
σ(C11-C10)	1.97106	$sp^{2.21}$ at C11 $sp^{1.95}$ at C10	C11 (49.17%): *s*(31.14%)*p*(68.74%) C10 (50.83%): *s*(33.88%)*p*(66.01%)
Lone pair 1 (N4)	1.86686	$sp^{2.58}$	*s*(27.93%)*p*(72.06%)
σ(N4-C9)	1.98858	$sp^{1.62}$ at N4 $sp^{1.95}$ at C9	N4 (60.01%): *s*(38.07%)*p*(61.59%) C9 (39.99%): *s*(33.81%)*p*(66.07%)
π(N4-C9)	1.86186	n/a	N4 (63.72%): *s*(0.00%)*p*(99.87%) C9 (36.28%): *s*(0.00%)*p*(99.87%)
σ(N4-C10)	1.98257	$sp^{1.94}$ at N4 $sp^{2.33}$ at C10	N4 (59.15%): *s*(33.88%)*p*(65.82%) C10 (40.85%): *s*(30.03%)*p*(69.88%)

[a] Calculated in solution at the optimized S0 geometry using TPSSh (SMD "dichloromethane"/ def2-tzvpp def2/j). The TPSSh functional uses 10 % Hartree-Fock exchange.[11]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + cB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S84. Solvated NBO analysis[a] of (^{tBu}**L3**)$_2$Zn with the O3LYP functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.81000	$sp^{2.41}$	*s*(29.34%)*p*(70.63%)
Lone pair 2 (N1)	1.61221	n/a	*s*(0.09%)*p*(99.86%)
σ(N1-C5)	1.98434	$sp^{1.88}$ at N1 $sp^{2.21}$ at C5	N1 (58.74%): *s*(34.59%)*p*(65.20%) C5 (41.26%): *s*(31.13%)*p*(68.77%)
σ(N1-C11)	1.98313	$sp^{1.78}$ at N1 $sp^{2.08}$ at C11	N1 (58.19%): *s*(35.85%)*p*(63.90%) C11 (41.81%): *s*(32.42%)*p*(67.44%)
σ(C2-C5)	1.97770	$sp^{1.87}$ at C2 $sp^{1.88}$ at C5	C2 (49.44%): *s*(34.78%)*p*(65.05%) C5 (50.56%): *s*(34.73%)*p*(65.16%)
σ(C2-C6)	1.98163	$sp^{1.75}$ at C2 $sp^{1.78}$ at C6	C2 (50.23%): *s*(36.30%)*p*(63.53%) C6 (49.77%): *s*(35.97%)*p*(63.88%)
π(C2-C6)	1.70301	n/a	C2 (51.60%): *s*(0.01%)*p*(99.93%) C6 (48.40%): *s*(0.00%)*p*(99.93%)
σ(C3-C5)	1.97754	$sp^{1.85}$ at C3 $sp^{1.94}$ at C5	C3 (49.34%): *s*(35.06%)*p*(64.77%) C5 (50.66%): *s*(34.03%)*p*(65.87%)
π(C3-C5)	1.62735	n/a	C3 (52.50%): *s*(0.00%)*p*(99.93%) C5 (47.50%): *s*(0.02%)*p*(99.91%)
σ(C3-C7)	1.98265	$sp^{1.76}$ at C3 $sp^{1.79}$ at C7	C3 (50.28%): *s*(36.22%)*p*(63.61%) C7 (49.72%): *s*(35.80%)*p*(64.04%)
σ(C6-C8)	1.98400	$sp^{1.79}$ at C6 $sp^{1.81}$ at C8	C6 (50.11%): *s*(35.75%)*p*(64.08%) C8 (49.89%): *s*(35.49%)*p*(64.35%)
σ(C7-C8)	1.98387	$sp^{1.79}$ at C7 $sp^{1.81}$ at C8	C7 (50.09%): *s*(35.79%)*p*(64.04%) C8 (49.91%): *s*(35.50%)*p*(64.34%)
π(C7-C8)	1.67905	n/a	C7 (48.21%): *s*(0.00%)*p*(99.94%) C8 (51.79%): *s*(0.00%)*p*(99.94%)
σ(C11-C12)	1.97608	$sp^{1.75}$ at C11 $sp^{1.90}$ at C12	C11 (51.13%): *s*(36.37%)*p*(63.53%) C12 (48.87%): *s*(34.44%)*p*(65.39%)
π(C11-C12)	1.64562	n/a	C11 (45.19%): *s*(0.00%)*p*(99.92%) C12 (54.81%): *s*(0.00%)*p*(99.92%)
σ(C11-C10)	1.97068	$sp^{2.21}$ at C11 $sp^{1.95}$ at C10	C11 (49.20%): *s*(31.10%)*p*(68.79%) C10 (50.80%): *s*(33.83%)*p*(66.07%)
Lone pair 1 (N4)	1.86514	$sp^{2.60}$	*s*(27.78%)*p*(72.20%)
σ(N4-C9)	1.98840	$sp^{1.61}$ at N4 $sp^{1.95}$ at C9	N4 (59.89%): *s*(38.19%)*p*(61.48%) C9 (40.11%): *s*(33.81%)*p*(66.07%)
π(N4-C9)	1.86292	n/a	N4 (63.64%): *s*(0.00%)*p*(99.87%) C9 (36.36%): *s*(0.00%)*p*(99.88%)
σ(N4-C10)	1.98238	$sp^{1.94}$ at N4 $sp^{2.32}$ at C10	N4 (58.98%): *s*(33.90%)*p*(65.80%) C10 (41.02%): *s*(30.10%)*p*(69.81%)

[a] Calculated in solution at the optimized S0 geometry using O3LYP (SMD "dichloromethane"/ def2-tzvpp def2/j). The O3LYP functional uses 11.61 % Hartree-Fock exchange.[21]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + cB^2)}$, exceeds a fixed limit ($|i_{AB}| > 0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S85. Solvated NBO analysis[a] of (^{tBu}**L3**)$_2$Zn with the B3LYP functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.81367	$sp^{2.45}$	s(29.02%)p(70.96%)
Lone pair 2 (N1)	1.62637	n/a	s(0.10%)p(99.85%)
σ(N1-C5)	1.98460	$sp^{1.87}$ at N1 $sp^{2.20}$ at C5	N1 (58.82%): s(34.75%)p(65.03%) C5 (41.18%): s(31.17%)p(68.72%)
σ(N1-C11)	1.98340	$sp^{1.77}$ at N1 $sp^{2.08}$ at C11	N1 (58.29%): s(36.02%)p(63.72%) C11 (41.71%): s(32.47%)p(67.41%)
σ(C2-C5)	1.97784	$sp^{1.86}$ at C2 $sp^{1.88}$ at C5	C2 (49.48%): s(34.84%)p(64.96%) C5 (50.52%): s(34.69%)p(65.20%)
σ(C2-C6)	1.98196	$sp^{1.75}$ at C2 $sp^{1.77}$ at C6	C2 (50.22%): s(36.35%)p(63.46%) C6 (49.78%): s(36.02%)p(63.81%)
π(C2-C6)	1.70278	n/a	C2 (51.78%): s(0.01%)p(99.93%) C6 (48.22%): s(0.00%)p(99.93%)
σ(C3-C5)	1.97782	$sp^{1.84}$ at C3 $sp^{1.94}$ at C5	C3 (49.37%): s(35.13%)p(64.67%) C5 (50.63%): s(34.01%)p(65.86%)
π(C3-C5)	1.62686	n/a	C3 (52.93%): s(0.00%)p(99.93%) C5 (47.07%): s(0.02%)p(99.91%)
σ(C3-C7)	1.98291	$sp^{1.75}$ at C3 $sp^{1.78}$ at C7	C3 (50.26%): s(36.27%)p(63.55%) C7 (49.74%): s(35.86%)p(63.96%)
σ(C6-C8)	1.98405	$sp^{1.79}$ at C6 $sp^{1.81}$ at C8	C6 (50.11%): s(35.81%)p(64.00%) C8 (49.89%): s(35.54%)p(64.28%)
σ(C7-C8)	1.98393	$sp^{1.78}$ at C7 $sp^{1.81}$ at C8	C7 (50.09%): s(35.84%)p(63.97%) C8 (49.91%): s(35.55%)p(64.27%)
π(C7-C8)	1.67996	n/a	C7 (48.01%): s(0.00%)p(99.94%) C8 (51.99%): s(0.00%)p(99.94%)
σ(C11-C12)	1.97635	$sp^{1.75}$ at C11 $sp^{1.89}$ at C12	C11 (51.11%): s(36.34%)p(63.55%) C12 (48.89%): s(34.51%)p(65.29%)
π(C11-C12)	1.64854	n/a	C11 (44.51%): s(0.00%)p(99.92%) C12 (55.49%): s(0.00%)p(99.92%)
σ(C11-C10)	1.97119	$sp^{2.21}$ at C11 $sp^{1.95}$ at C10	C11 (49.17%): s(31.10%)p(68.77%) C10 (50.83%): s(33.84%)p(66.05%)
Lone pair 1 (N4)	1.86995	$sp^{2.66}$	s(27.33%)p(72.66%)
σ(N4-C9)	1.98834	$sp^{1.60}$ at N4 $sp^{1.95}$ at C9	N4 (59.97%): s(38.40%)p(61.25%) C9 (40.03%): s(33.88%)p(65.99%)
π(N4-C9)	1.86510	n/a	N4 (63.78%): s(0.00%)p(99.87%) C9 (36.22%): s(0.00%)p(99.88%)
σ(N4-C10)	1.98257	$sp^{1.92}$ at N4 $sp^{2.32}$ at C10	N4 (59.15%): s(34.16%)p(65.53%) C10 (40.85%): s(30.10%)p(69.80%)

[a] Calculated in solution at the optimized S0 geometry using B3LYP (SMD "dichloromethane"/ def2-tzvpp def2/j). The B3LYP functional uses 20 % Hartree-Fock exchange.[22]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S86. Solvated NBO analysis[a] of (^{tBu}**L3**)$_2$Zn with the PBE0 functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.81745	$sp^{2.45}$	*s*(28.96%)*p*(71.01%)
Lone pair 2 (N1)	1.63057	n/a	*s*(0.09%)*p*(99.85%)
σ(N1-C5)	1.98479	$sp^{1.87}$ at N1 $sp^{2.21}$ at C5	N1 (58.79%): *s*(34.80%)*p*(64.97%) C5 (41.21%): *s*(31.17%)*p*(68.73%)
σ(N1-C11)	1.98355	$sp^{1.77}$ at N1 $sp^{2.08}$ at C11	N1 (58.22%): *s*(36.03%)*p*(63.71%) C11 (41.78%): *s*(32.47%)*p*(67.41%)
σ(C2-C5)	1.97813	$sp^{1.87}$ at C2 $sp^{1.88}$ at C5	C2 (49.50%): *s*(34.81%)*p*(65.00%) C5 (50.50%): *s*(34.70%)*p*(65.19%)
σ(C2-C6)	1.98207	$sp^{1.75}$ at C2 $sp^{1.78}$ at C6	C2 (50.24%): *s*(36.29%)*p*(63.52%) C6 (49.76%): *s*(35.97%)*p*(63.86%)
π(C2-C6)	1.70206	n/a	C2 (51.85%): *s*(0.01%)*p*(99.92%) C6 (48.15%): *s*(0.00%)*p*(99.92%)
σ(C3-C5)	1.97808	$sp^{1.84}$ at C3 $sp^{1.94}$ at C5	C3 (49.38%): *s*(35.10%)*p*(64.71%) C5 (50.62%): *s*(34.02%)*p*(65.86%)
π(C3-C5)	1.62815	n/a	C3 (52.89%): *s*(0.00%)*p*(99.92%) C5 (47.11%): *s*(0.02%)*p*(99.91%)
σ(C3-C7)	1.98304	$sp^{1.76}$ at C3 $sp^{1.79}$ at C7	C3 (50.28%): *s*(36.21%)*p*(63.60%) C7 (49.72%): *s*(35.80%)*p*(64.02%)
σ(C6-C8)	1.98431	$sp^{1.79}$ at C6 $sp^{1.81}$ at C8	C6 (50.11%): *s*(35.74%)*p*(64.07%) C8 (49.89%): *s*(35.49%)*p*(64.34%)
σ(C7-C8)	1.98418	$sp^{1.79}$ at C7 $sp^{1.81}$ at C8	C7 (50.09%): *s*(35.78%)*p*(64.04%) C8 (49.91%): *s*(35.49%)*p*(64.33%)
π(C7-C8)	1.67909	n/a	C7 (48.01%): *s*(0.00%)*p*(99.93%) C8 (51.99%): *s*(0.00%)*p*(99.94%)
σ(C11-C12)	1.97649	$sp^{1.75}$ at C11 $sp^{1.90}$ at C12	C11 (51.09%): *s*(36.36%)*p*(63.53%) C12 (48.91%): *s*(34.47%)*p*(65.34%)
π(C11-C12)	1.65006	n/a	C11 (44.47%): *s*(0.00%)*p*(99.91%) C12 (55.53%): *s*(0.00%)*p*(99.91%)
σ(C11-C10)	1.97138	$sp^{2.21}$ at C11 $sp^{1.95}$ at C10	C11 (49.15%): *s*(31.08%)*p*(68.79%) C10 (50.85%): *s*(33.85%)*p*(66.03%)
Lone pair 1 (N4)	1.87193	$sp^{2.64}$	*s*(27.47%)*p*(72.52%)
σ(N4-C9)	1.98857	$sp^{1.60}$ at N4 $sp^{1.95}$ at C9	N4 (59.92%): *s*(38.30%)*p*(61.34%) C9 (40.08%): *s*(33.85%)*p*(66.03%)
π(N4-C9)	1.86570	n/a	N4 (63.95%): *s*(0.00%)*p*(99.86%) C9 (36.05%): *s*(0.00%)*p*(99.86%)
σ(N4-C10)	1.98276	$sp^{1.92}$ at N4 $sp^{2.32}$ at C10	N4 (59.04%): *s*(34.10%)*p*(65.57%) C10 (40.96%): *s*(30.08%)*p*(69.82%)

[a] Calculated in solution at the optimized S0 geometry using PBE0 (SMD "dichloromethane"/ def2-tzvpp def2/j). The PBE0 functional uses 25 % Hartree-Fock exchange.[14]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S87. Solvated NBO analysis[a] of (^{tBu}**L3**)$_2$Zn with the M06 functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.80959	$sp^{2.43}$	s(29.16%)p(70.81%)
Lone pair 2 (N1)	1.64041	n/a	s(0.12%)p(99.82%)
σ(N1-C5)	1.98442	$sp^{1.87}$ at N1 $sp^{2.21}$ at C5	N1 (59.12%): s(34.72%)p(65.09%) C5 (40.88%): s(31.14%)p(68.78%)
σ(N1-C11)	1.98331	$sp^{1.78}$ at N1 $sp^{2.08}$ at C11	N1 (58.51%): s(35.89%)p(63.89%) C11 (41.49%): s(32.43%)p(67.48%)
σ(C2-C5)	1.97730	$sp^{1.85}$ at C2 $sp^{1.88}$ at C5	C2 (49.57%): s(34.97%)p(64.86%) C5 (50.43%): s(34.70%)p(65.20%)
σ(C2-C6)	1.98167	$sp^{1.75}$ at C2 $sp^{1.77}$ at C6	C2 (50.21%): s(36.34%)p(63.49%) C6 (49.79%): s(36.09%)p(63.77%)
π(C2-C6)	1.70203	n/a	C2 (52.19%): s(0.01%)p(99.92%) C6 (47.81%): s(0.00%)p(99.92%)
σ(C3-C5)	1.97737	$sp^{1.83}$ at C3 $sp^{1.93}$ at C5	C3 (49.45%): s(35.25%)p(64.58%) C5 (50.55%): s(34.05%)p(65.84%)
π(C3-C5)	1.62941	n/a	C3 (53.32%): s(0.00%)p(99.93%) C5 (46.68%): s(0.01%)p(99.91%)
σ(C3-C7)	1.98270	$sp^{1.75}$ at C3 $sp^{1.78}$ at C7	C3 (50.24%): s(36.26%)p(63.58%) C7 (49.76%): s(35.93%)p(63.92%)
σ(C6-C8)	1.98371	$sp^{1.79}$ at C6 $sp^{1.81}$ at C8	C6 (50.12%): s(35.82%)p(64.02%) C8 (49.88%): s(35.57%)p(64.28%)
σ(C7-C8)	1.98358	$sp^{1.78}$ at C7 $sp^{1.81}$ at C8	C7 (50.11%): s(35.86%)p(63.98%) C8 (49.89%): s(35.57%)p(64.27%)
π(C7-C8)	1.67803	n/a	C7 (47.79%): s(0.00%)p(99.93%) C8 (52.21%): s(0.00%)p(99.93%)
σ(C11-C12)	1.97603	$sp^{1.75}$ at C11 $sp^{1.89}$ at C12	C11 (51.01%): s(36.36%)p(63.55%) C12 (48.99%): s(34.57%)p(65.26%)
π(C11-C12)	1.65233	n/a	C11 (43.55%): s(0.00%)p(99.91%) C12 (56.45%): s(0.00%)p(99.91%)
σ(C11-C10)	1.97084	$sp^{2.21}$ at C11 $sp^{1.95}$ at C10	C11 (49.19%): s(31.13%)p(68.75%) C10 (50.81%): s(33.87%)p(66.02%)
Lone pair 1 (N4)	1.86763	$sp^{2.64}$	s(27.45%)p(72.53%)
σ(N4-C9)	1.98836	$sp^{1.61}$ at N4 $sp^{1.94}$ at C9	N4 (60.05%): s(38.26%)p(61.45%) C9 (39.95%): s(33.95%)p(65.96%)
π(N4-C9)	1.86970	n/a	N4 (64.51%): s(0.00%)p(99.84%) C9 (35.49%): s(0.00%)p(99.85%)
σ(N4-C10)	1.98226	$sp^{1.92}$ at N4 $sp^{2.33}$ at C10	N4 (59.38%): s(34.19%)p(65.55%) C10 (40.62%): s(30.03%)p(69.89%)

[a] Calculated in solution at the optimized S0 geometry using M06 (SMD "dichloromethane"/ def2-tzvpp def2/j). The M06 functional uses 27 % Hartree-Fock exchange.[23]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S88. Solvated NBO analysis[a] of ($^{t\mathrm{Bu}}$**L3**)$_2$Zn with the M06-2X functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.83696	$sp^{2.52}$	*s*(28.42%)*p*(71.55%)
Lone pair 2 (N1)	1.64833	n/a	*s*(0.06%)*p*(99.87%)
σ(N1-C5)	1.98489	$sp^{1.84}$ at N1 $sp^{2.20}$ at C5	N1 (58.83%): *s*(35.14%)*p*(64.64%) C5 (41.17%): *s*(31.20%)*p*(68.72%)
σ(N1-C11)	1.98348	$sp^{1.75}$ at N1 $sp^{2.08}$ at C11	N1 (58.28%): *s*(36.27%)*p*(63.47%) C11 (41.72%): *s*(32.49%)*p*(67.42%)
σ(C2-C5)	1.97827	$sp^{1.87}$ at C2 $sp^{1.88}$ at C5	C2 (49.48%): *s*(34.84%)*p*(64.98%) C5 (50.52%): *s*(34.68%)*p*(65.22%)
σ(C2-C6)	1.98235	$sp^{1.75}$ at C2 $sp^{1.78}$ at C6	C2 (50.25%): *s*(36.29%)*p*(63.53%) C6 (49.75%): *s*(35.96%)*p*(63.88%)
π(C2-C6)	1.70105	n/a	C2 (51.98%): *s*(0.01%)*p*(99.92%) C6 (48.02%): *s*(0.00%)*p*(99.93%)
σ(C3-C5)	1.97827	$sp^{1.84}$ at C3 $sp^{1.94}$ at C5	C3 (49.34%): *s*(35.12%)*p*(64.70%) C5 (50.66%): *s*(34.02%)*p*(65.87%)
π(C3-C5)	1.63046	n/a	C3 (53.13%): *s*(0.00%)*p*(99.93%) C5 (46.87%): *s*(0.01%)*p*(99.92%)
σ(C3-C7)	1.98326	$sp^{1.76}$ at C3 $sp^{1.79}$ at C7	C3 (50.28%): *s*(36.19%)*p*(63.63%) C7 (49.72%): *s*(35.81%)*p*(64.02%)
σ(C6-C8)	1.98443	$sp^{1.79}$ at C6 $sp^{1.81}$ at C8	C6 (50.11%): *s*(35.74%)*p*(64.09%) C8 (49.89%): *s*(35.48%)*p*(64.36%)
σ(C7-C8)	1.98429	$sp^{1.79}$ at C7 $sp^{1.81}$ at C8	C7 (50.10%): *s*(35.77%)*p*(64.06%) C8 (49.90%): *s*(35.48%)*p*(64.35%)
π(C7-C8)	1.67921	n/a	C7 (47.93%): *s*(0.00%)*p*(99.94%) C8 (52.07%): *s*(0.00%)*p*(99.94%)
σ(C11-C12)	1.97673	$sp^{1.74}$ at C11 $sp^{1.90}$ at C12	C11 (51.13%): *s*(36.41%)*p*(63.50%) C12 (48.87%): *s*(34.47%)*p*(65.35%)
π(C11-C12)	1.65589	n/a	C11 (43.87%): *s*(0.00%)*p*(99.92%) C12 (56.13%): *s*(0.00%)*p*(99.91%)
σ(C11-C10)	1.97194	$sp^{2.22}$ at C11 $sp^{1.95}$ at C10	C11 (49.07%): *s*(31.04%)*p*(68.85%) C10 (50.93%): *s*(33.87%)*p*(66.03%)
Lone pair 1 (N4)	1.88562	$sp^{2.71}$	*s*(26.93%)*p*(73.05%)
σ(N4-C9)	1.98849	$sp^{1.58}$ at N4 $sp^{1.95}$ at C9	N4 (60.08%): *s*(38.55%)*p*(61.10%) C9 (39.92%): *s*(33.81%)*p*(66.08%)
π(N4-C9)	1.87103	n/a	N4 (63.91%): *s*(0.00%)*p*(99.84%) C9 (36.09%): *s*(0.00%)*p*(99.86%)
σ(N4-C10)	1.98271	$sp^{1.90}$ at N4 $sp^{2.32}$ at C10	N4 (59.24%): *s*(34.40%)*p*(65.29%) C10 (40.76%): *s*(30.05%)*p*(69.86%)

[a] Calculated in solution at the optimized S0 geometry using M06-2X (SMD "dichloromethane"/ def2-tzvpp def2/j). The M06-2X functional uses 54 % Hartree-Fock exchange.[23]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S89. Solvated NBO analysis[a] of (**$^{t\mathrm{Bu}}$L3**)$_2$Zn with the CAM-B3LYP functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.82111	$sp^{2.56}$	*s*(28.09%)*p*(71.88%)
Lone pair 2 (N1)	1.65342	n/a	*s*(0.10%)*p*(99.85%)
σ(N1-C5)	1.98511	$sp^{1.83}$ at N1 $sp^{2.20}$ at C5	N1 (58.78%): *s*(35.24%)*p*(64.52%) C5 (41.22%): *s*(31.18%)*p*(68.71%)
σ(N1-C11)	1.98372	$sp^{1.74}$ at N1 $sp^{2.08}$ at C11	N1 (58.24%): *s*(36.46%)*p*(63.27%) C11 (41.76%): *s*(32.46%)*p*(67.42%)
σ(C2-C5)	1.97829	$sp^{1.86}$ at C2 $sp^{1.88}$ at C5	C2 (49.52%): *s*(34.85%)*p*(64.95%) C5 (50.48%): *s*(34.69%)*p*(65.19%)
σ(C2-C6)	1.98204	$sp^{1.75}$ at C2 $sp^{1.77}$ at C6	C2 (50.23%): *s*(36.33%)*p*(63.47%) C6 (49.77%): *s*(35.99%)*p*(63.83%)
π(C2-C6)	1.70085	n/a	C2 (52.05%): *s*(0.01%)*p*(99.92%) C6 (47.95%): *s*(0.00%)*p*(99.92%)
σ(C3-C5)	1.97830	$sp^{1.84}$ at C3 $sp^{1.94}$ at C5	C3 (49.40%): *s*(35.14%)*p*(64.66%) C5 (50.60%): *s*(34.00%)*p*(65.87%)
π(C3-C5)	1.62799	n/a	C3 (53.40%): *s*(0.00%)*p*(99.92%) C5 (46.60%): *s*(0.02%)*p*(99.91%)
σ(C3-C7)	1.98292	$sp^{1.75}$ at C3 $sp^{1.79}$ at C7	C3 (50.26%): *s*(36.24%)*p*(63.57%) C7 (49.74%): *s*(35.83%)*p*(63.98%)
σ(C6-C8)	1.98404	$sp^{1.79}$ at C6 $sp^{1.81}$ at C8	C6 (50.11%): *s*(35.78%)*p*(64.03%) C8 (49.89%): *s*(35.52%)*p*(64.30%)
σ(C7-C8)	1.98393	$sp^{1.79}$ at C7 $sp^{1.81}$ at C8	C7 (50.09%): *s*(35.81%)*p*(64.00%) C8 (49.91%): *s*(35.52%)*p*(64.29%)
π(C7-C8)	1.68053	n/a	C7 (47.79%): *s*(0.00%)*p*(99.93%) C8 (52.21%): *s*(0.00%)*p*(99.94%)
σ(C11-C12)	1.97653	$sp^{1.75}$ at C11 $sp^{1.89}$ at C12	C11 (51.08%): *s*(36.37%)*p*(63.52%) C12 (48.92%): *s*(34.52%)*p*(65.28%)
π(C11-C12)	1.65623	n/a	C11 (43.56%): *s*(0.00%)*p*(99.91%) C12 (56.44%): *s*(0.00%)*p*(99.91%)
σ(C11-C10)	1.97203	$sp^{2.21}$ at C11 $sp^{1.95}$ at C10	C11 (49.10%): *s*(31.07%)*p*(68.79%) C10 (50.90%): *s*(33.88%)*p*(66.00%)
Lone pair 1 (N4)	1.87690	$sp^{2.75}$	*s*(26.69%)*p*(73.30%)
σ(N4-C9)	1.98832	$sp^{1.58}$ at N4 $sp^{1.95}$ at C9	N4 (59.94%): *s*(38.64%)*p*(60.99%) C9 (40.06%): *s*(33.86%)*p*(66.00%)
π(N4-C9)	1.87280	n/a	N4 (64.05%): *s*(0.00%)*p*(99.85%) C9 (35.95%): *s*(0.00%)*p*(99.86%)
σ(N4-C10)	1.98288	$sp^{1.89}$ at N4 $sp^{2.33}$ at C10	N4 (59.18%): *s*(34.54%)*p*(65.13%) C10 (40.82%): *s*(30.03%)*p*(69.86%)

[a] Calculated in solution at the optimized S0 geometry using CAM-B3LYP (SMD "dichloromethane"/ def2-tzvpp def2/j). The CAM-B3LYP functional is a range-separated functional, and uses 19 % Hartree-Fock exchange at short range, 33 % Hartree-Fock exchange at intermediate range, and 65 % Hartree-Fock exchange at long range.[15]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|$>0.95), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S90. NBO analysis[a] of $(^{\mathrm{Me}}\mathbf{L3}^{\mathrm{Me}})_2\mathrm{Zn}$ with the M06-L functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.81477	$sp^{2.23}$	*s*(30.94%)*p*(69.04%)
Lone pair 2 (N1)	1.60621	n/a	*s*(0.05%)*p*(99.89%)
σ(N1-C5)	1.98380	$sp^{1.94}$ at N1 $sp^{2.23}$ at C5	N1 (59.27%): *s*(33.95%)*p*(65.84%) C5 (40.73%): *s*(30.95%)*p*(68.96%)
σ(N1-C11)	1.98284	$sp^{1.86}$ at N1 $sp^{2.08}$ at C11	N1 (58.61%): *s*(34.94%)*p*(64.83%) C11 (41.39%): *s*(32.41%)*p*(67.50%)
σ(C2-C5)	1.97734	$sp^{1.84}$ at C2 $sp^{1.88}$ at C5	C2 (49.61%): *s*(35.11%)*p*(64.71%) C5 (50.39%): *s*(34.73%)*p*(65.15%)
σ(C2-C6)	1.98211	$sp^{1.74}$ at C2 $sp^{1.75}$ at C6	C2 (50.22%): *s*(36.50%)*p*(63.33%) C6 (49.78%): *s*(36.27%)*p*(63.57%)
π(C2-C6)	1.70618	n/a	C2 (52.06%): *s*(0.01%)*p*(99.92%) C6 (47.94%): *s*(0.00%)*p*(99.92%)
σ(C3-C5)	1.97750	$sp^{1.82}$ at C3 $sp^{1.92}$ at C5	C3 (49.45%): *s*(35.35%)*p*(64.47%) C5 (50.55%): *s*(34.20%)*p*(65.67%)
π(C3-C5)	1.62631	n/a	C3 (52.79%): *s*(0.00%)*p*(99.92%) C5 (47.21%): *s*(0.02%)*p*(99.90%)
σ(C3-C7)	1.98313	$sp^{1.74}$ at C3 $sp^{1.77}$ at C7	C3 (50.25%): *s*(36.38%)*p*(63.45%) C7 (49.75%): *s*(36.10%)*p*(63.74%)
σ(C6-C8)	1.98416	$sp^{1.77}$ at C6 $sp^{1.80}$ at C8	C6 (50.15%): *s*(36.01%)*p*(63.82%) C8 (49.85%): *s*(35.72%)*p*(64.12%)
σ(C7-C8)	1.98403	$sp^{1.77}$ at C7 $sp^{1.79}$ at C8	C7 (50.09%): *s*(36.02%)*p*(63.81%) C8 (49.91%): *s*(35.75%)*p*(64.09%)
π(C7-C8)	1.67382	n/a	C7 (48.10%): *s*(0.00%)*p*(99.92%) C8 (51.90%): *s*(0.00%)*p*(99.93%)
σ(C11-C12)	1.97725	$sp^{1.77}$ at C11 $sp^{1.85}$ at C12	C11 (50.88%): *s*(36.05%)*p*(63.84%) C12 (49.12%): *s*(35.02%)*p*(64.80%)
π(C11-C12)	1.63884	n/a	C11 (44.53%): *s*(0.01%)*p*(99.90%) C12 (55.47%): *s*(0.01%)*p*(99.91%)
σ(C11-C10)	1.97095	$sp^{2.17}$ at C11 $sp^{1.95}$ at C10	C11 (49.10%): *s*(31.47%)*p*(68.40%) C10 (50.90%): *s*(33.91%)*p*(65.97%)
Lone pair 1 (N4)	1.86727	$sp^{2.47}$	*s*(28.84%)*p*(71.13%)
σ(N4-C9)	1.98753	$sp^{1.65}$ at N4 $sp^{2.04}$ at C9	N4 (59.71%): *s*(37.65%)*p*(62.04%) C9 (40.29%): *s*(32.87%)*p*(67.03%)
π(N4-C9)	1.85386	n/a	N4 (64.03%): *s*(0.00%)*p*(99.85%) C9 (35.97%): *s*(0.00%)*p*(99.85%)
σ(N4-C10)	1.98131	$sp^{1.99}$ at N4 $sp^{2.33}$ at C10	N4 (59.58%): *s*(33.34%)*p*(66.38%) C10 (40.42%): *s*(30.01%)*p*(69.91%)

[a] Calculated in gas phase at the optimized S0 geometry using M06-L (gas phase/ def2-tzvpp def2/j). The M06-L functional uses 0 % Hartree-Fock exchange.[19]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S91. NBO analysis[a] of $(^{\mathrm{Me}}\mathbf{L3}^{\mathrm{Me}})_2$Zn with the TPSSh functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.81409	$sp^{2.42}$	*s*(29.21%)*p*(70.76%)
Lone pair 2 (N1)	1.61272	n/a	*s*(0.05%)*p*(99.90%)
σ(N1-C5)	1.98419	$sp^{1.87}$ at N1 $sp^{2.22}$ at C5	N1 (59.06%): *s*(34.78%)*p*(65.00%) C5 (40.94%): *s*(31.03%)*p*(68.87%)
σ(N1-C11)	1.98310	$sp^{1.78}$ at N1 $sp^{2.08}$ at C11	N1 (58.36%): *s*(35.84%)*p*(63.91%) C11 (41.64%): *s*(32.48%)*p*(67.41%)
σ(C2-C5)	1.97742	$sp^{1.86}$ at C2 $sp^{1.88}$ at C5	C2 (49.46%): *s*(34.94%)*p*(64.87%) C5 (50.54%): *s*(34.74%)*p*(65.15%)
σ(C2-C6)	1.98196	$sp^{1.74}$ at C2 $sp^{1.76}$ at C6	C2 (50.24%): *s*(36.41%)*p*(63.41%) C6 (49.76%): *s*(36.14%)*p*(63.70%)
π(C2-C6)	1.70434	n/a	C2 (51.86%): *s*(0.01%)*p*(99.93%) C6 (48.14%): *s*(0.00%)*p*(99.93%)
σ(C3-C5)	1.97768	$sp^{1.84}$ at C3 $sp^{1.93}$ at C5	C3 (49.29%): *s*(35.20%)*p*(64.62%) C5 (50.71%): *s*(34.12%)*p*(65.77%)
π(C3-C5)	1.62681	n/a	C3 (52.29%): *s*(0.00%)*p*(99.93%) C5 (47.71%): *s*(0.02%)*p*(99.91%)
σ(C3-C7)	1.98300	$sp^{1.75}$ at C3 $sp^{1.78}$ at C7	C3 (50.27%): *s*(36.27%)*p*(63.56%) C7 (49.73%): *s*(35.94%)*p*(63.88%)
σ(C6-C8)	1.98431	$sp^{1.78}$ at C6 $sp^{1.80}$ at C8	C6 (50.15%): *s*(35.87%)*p*(63.95%) C8 (49.85%): *s*(35.61%)*p*(64.22%)
σ(C7-C8)	1.98420	$sp^{1.78}$ at C7 $sp^{1.80}$ at C8	C7 (50.07%): *s*(35.89%)*p*(63.93%) C8 (49.93%): *s*(35.63%)*p*(64.20%)
π(C7-C8)	1.67406	n/a	C7 (48.21%): *s*(0.00%)*p*(99.93%) C8 (51.79%): *s*(0.00%)*p*(99.94%)
σ(C11-C12)	1.97683	$sp^{1.77}$ at C11 $sp^{1.86}$ at C12	C11 (51.04%): *s*(36.10%)*p*(63.79%) C12 (48.96%): *s*(34.89%)*p*(64.93%)
π(C11-C12)	1.63882	n/a	C11 (44.94%): *s*(0.00%)*p*(99.91%) C12 (55.06%): *s*(0.01%)*p*(99.91%)
σ(C11-C10)	1.97093	$sp^{2.19}$ at C11 $sp^{1.95}$ at C10	C11 (49.07%): *s*(31.35%)*p*(68.53%) C10 (50.93%): *s*(33.85%)*p*(66.04%)
Lone pair 1 (N4)	1.86647	$sp^{2.63}$	*s*(27.57%)*p*(72.42%)
σ(N4-C9)	1.98757	$sp^{1.60}$ at N4 $sp^{2.03}$ at C9	N4 (59.51%): *s*(38.31%)*p*(61.35%) C9 (40.49%): *s*(32.93%)*p*(66.95%)
π(N4-C9)	1.85470	n/a	N4 (63.82%): *s*(0.00%)*p*(99.86%) C9 (36.18%): *s*(0.00%)*p*(99.87%)
σ(N4-C10)	1.98153	$sp^{1.99}$ at N4 $sp^{2.32}$ at C10	N4 (59.38%): *s*(33.96%)*p*(65.75%) C10 (40.62%): *s*(30.10%)*p*(69.80%)

[a] Calculated in gas phase at the optimized S0 geometry using TPSSh (gas phase/ def2-tzvpp def2/j). The TPSSh functional uses 10 % Hartree-Fock exchange.[11]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}| > 0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S92. NBO analysis[a] of ($^{\mathbf{Me}}$**L3**$^{\mathbf{Me}}$)$_2$Zn with the O3LYP functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.81331	$sp^{2.45}$	*s*(28.94%)*p*(71.03%)
Lone pair 2 (N1)	1.60961	n/a	*s*(0.05%)*p*(99.90%)
σ(N1-C5)	1.98418	$sp^{1.86}$ at N1 $sp^{2.22}$ at C5	N1 (58.91%): *s*(34.93%)*p*(64.86%) C5 (41.09%): *s*(31.07%)*p*(68.84%)
σ(N1-C11)	1.98297	$sp^{1.77}$ at N1 $sp^{2.07}$ at C11	N1 (58.24%): *s*(35.96%)*p*(63.79%) C11 (41.76%): *s*(32.52%)*p*(67.38%)
σ(C2-C5)	1.97701	$sp^{1.86}$ at C2 $sp^{1.87}$ at C5	C2 (49.46%): *s*(34.90%)*p*(64.93%) C5 (50.54%): *s*(34.75%)*p*(65.15%)
σ(C2-C6)	1.98145	$sp^{1.74}$ at C2 $sp^{1.76}$ at C6	C2 (50.23%): *s*(36.38%)*p*(63.44%) C6 (49.77%): *s*(36.11%)*p*(63.73%)
π(C2-C6)	1.70459	n/a	C2 (51.79%): *s*(0.01%)*p*(99.93%) C6 (48.21%): *s*(0.00%)*p*(99.93%)
σ(C3-C5)	1.97720	$sp^{1.84}$ at C3 $sp^{1.93}$ at C5	C3 (49.30%): *s*(35.16%)*p*(64.67%) C5 (50.70%): *s*(34.08%)*p*(65.82%)
π(C3-C5)	1.62651	n/a	C3 (52.27%): *s*(0.00%)*p*(99.93%) C5 (47.73%): *s*(0.02%)*p*(99.91%)
σ(C3-C7)	1.98248	$sp^{1.75}$ at C3 $sp^{1.78}$ at C7	C3 (50.27%): *s*(36.26%)*p*(63.58%) C7 (49.73%): *s*(35.91%)*p*(63.93%)
σ(C6-C8)	1.98373	$sp^{1.78}$ at C6 $sp^{1.81}$ at C8	C6 (50.14%): *s*(35.87%)*p*(63.97%) C8 (49.86%): *s*(35.59%)*p*(64.25%)
σ(C7-C8)	1.98363	$sp^{1.78}$ at C7 $sp^{1.80}$ at C8	C7 (50.07%): *s*(35.88%)*p*(63.95%) C8 (49.93%): *s*(35.61%)*p*(64.23%)
π(C7-C8)	1.67436	n/a	C7 (48.27%): *s*(0.00%)*p*(99.94%) C8 (51.73%): *s*(0.00%)*p*(99.94%)
σ(C11-C12)	1.97638	$sp^{1.77}$ at C11 $sp^{1.87}$ at C12	C11 (51.02%): *s*(36.10%)*p*(63.80%) C12 (48.98%): *s*(34.84%)*p*(65.00%)
π(C11-C12)	1.63859	n/a	C11 (45.02%): *s*(0.00%)*p*(99.92%) C12 (54.98%): *s*(0.01%)*p*(99.92%)
σ(C11-C10)	1.97056	$sp^{2.19}$ at C11 $sp^{1.95}$ at C10	C11 (49.11%): *s*(31.31%)*p*(68.58%) C10 (50.89%): *s*(33.81%)*p*(66.09%)
Lone pair 1 (N4)	1.86463	$sp^{2.64}$	*s*(27.44%)*p*(72.54%)
σ(N4-C9)	1.98742	$sp^{1.59}$ at N4 $sp^{2.03}$ at C9	N4 (59.40%): *s*(38.41%)*p*(61.25%) C9 (40.60%): *s*(32.94%)*p*(66.95%)
π(N4-C9)	1.85538	n/a	N4 (63.85%): *s*(0.00%)*p*(99.86%) C9 (36.15%): *s*(0.00%)*p*(99.88%)
σ(N4-C10)	1.98129	$sp^{1.93}$ at N4 $sp^{2.31}$ at C10	N4 (59.21%): *s*(33.98%)*p*(65.73%) C10 (40.79%): *s*(30.17%)*p*(69.74%)

[a] Calculated in gas phase at the optimized S0 geometry using O3LYP (gas phase/ def2-tzvpp def2/j). The O3LYP functional uses 11.61 % Hartree-Fock exchange.[21]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S93. NBO analysis[a] of $(^{\mathrm{Me}}\mathbf{L3}^{\mathrm{Me}})_2$Zn with the B3LYP functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.81718	$sp^{2.49}$	*s*(28.63%)*p*(71.35%)
Lone pair 2 (N1)	1.62314	n/a	*s*(0.04%)*p*(99.91%)
σ(N1-C5)	1.98444	$sp^{1.84}$ at N1 $sp^{2.21}$ at C5	N1 (58.99%): *s*(35.10%)*p*(64.68%) C5 (41.01%): *s*(31.10%)*p*(68.79%)
σ(N1-C11)	1.98323	$sp^{1.76}$ at N1 $sp^{2.07}$ at C11	N1 (58.33%): *s*(36.11%)*p*(63.63%) C11 (41.67%): *s*(32.53%)*p*(67.35%)
σ(C2-C5)	1.97719	$sp^{1.85}$ at C2 $sp^{1.88}$ at C5	C2 (49.50%): *s*(34.96%)*p*(64.85%) C5 (50.50%): *s*(34.71%)*p*(65.17%)
σ(C2-C6)	1.98180	$sp^{1.74}$ at C2 $sp^{1.76}$ at C6	C2 (50.22%): *s*(36.44%)*p*(63.37%) C6 (49.78%): *s*(36.16%)*p*(63.67%)
π(C2-C6)	1.70428	n/a	C2 (51.97%): *s*(0.01%)*p*(99.93%) C6 (48.03%): *s*(0.00%)*p*(99.93%)
σ(C3-C5)	1.97753	$sp^{1.83}$ at C3 $sp^{1.93}$ at C5	C3 (49.32%): *s*(35.22%)*p*(64.59%) C5 (50.68%): *s*(34.07%)*p*(65.81%)
π(C3-C5)	1.62629	n/a	C3 (52.66%): *s*(0.00%)*p*(99.93%) C5 (47.34%): *s*(0.02%)*p*(99.91%)
σ(C3-C7)	1.98277	$sp^{1.75}$ at C3 $sp^{1.78}$ at C7	C3 (50.26%): *s*(36.30%)*p*(63.52%) C7 (49.74%): *s*(35.97%)*p*(63.85%)
σ(C6-C8)	1.98383	$sp^{1.78}$ at C6 $sp^{1.80}$ at C8	C6 (50.14%): *s*(35.91%)*p*(63.90%) C8 (49.86%): *s*(35.63%)*p*(64.19%)
σ(C7-C8)	1.98373	$sp^{1.78}$ at C7 $sp^{1.80}$ at C8	C7 (50.07%): *s*(35.92%)*p*(63.89%) C8 (49.93%): *s*(35.65%)*p*(64.16%)
π(C7-C8)	1.67507	n/a	C7 (48.09%): *s*(0.00%)*p*(99.94%) C8 (51.91%): *s*(0.00%)*p*(99.94%)
σ(C11-C12)	1.97670	$sp^{1.77}$ at C11 $sp^{1.86}$ at C12	C11 (51.00%): *s*(36.08%)*p*(63.81%) C12 (49.00%): *s*(34.90%)*p*(64.91%)
π(C11-C12)	1.64069	n/a	C11 (44.39%): *s*(0.00%)*p*(99.91%) C12 (55.61%): *s*(0.01%)*p*(99.92%)
σ(C11-C10)	1.97113	$sp^{2.19}$ at C11 $sp^{1.95}$ at C10	C11 (49.07%): *s*(31.30%)*p*(68.57%) C10 (50.93%): *s*(33.83%)*p*(66.06%)
Lone pair 1 (N4)	1.86992	$sp^{2.70}$	*s*(27.02%)*p*(72.97%)
σ(N4-C9)	1.98740	$sp^{1.58}$ at N4 $sp^{2.03}$ at C9	N4 (59.49%): *s*(38.58%)*p*(61.07%) C9 (40.51%): *s*(32.94%)*p*(66.94%)
π(N4-C9)	1.85774	n/a	N4 (64.00%): *s*(0.00%)*p*(99.86%) C9 (36.00%): *s*(0.00%)*p*(99.88%)
σ(N4-C10)	1.98159	$sp^{1.91}$ at N4 $sp^{2.31}$ at C10	N4 (59.39%): *s*(34.24%)*p*(65.46%) C10 (40.61%): *s*(30.15%)*p*(69.74%)

[a] Calculated in gas phase at the optimized S0 geometry using B3LYP (gas phase/ def2-tzvpp def2/j). The B3LYP functional uses 20 % Hartree-Fock exchange.[22]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp$^\lambda$, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp$^\infty$) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S94. NBO analysis[a] of ($^{\mathbf{Me}}$**L3**$^{\mathbf{Me}}$)$_2$Zn with the PBE0 functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.82096	$sp^{2.50}$	*s*(28.56%)*p*(71.41%)
Lone pair 2 (N1)	1.62756	n/a	*s*(0.05%)*p*(99.90%)
σ(N1-C5)	1.98460	$sp^{1.84}$ at N1 $sp^{2.21}$ at C5	N1 (58.95%): *s*(35.14%)*p*(64.63%) C5 (41.05%): *s*(31.10%)*p*(68.80%)
σ(N1-C11)	1.98335	$sp^{1.76}$ at N1 $sp^{2.07}$ at C11	N1 (58.27%): *s*(36.13%)*p*(63.61%) C11 (41.73%): *s*(32.54%)*p*(67.34%)
σ(C2-C5)	1.97746	$sp^{1.86}$ at C2 $sp^{1.88}$ at C5	C2 (49.52%): *s*(34.94%)*p*(64.87%) C5 (50.48%): *s*(34.71%)*p*(65.17%)
σ(C2-C6)	1.98190	$sp^{1.74}$ at C2 $sp^{1.76}$ at C6	C2 (50.23%): *s*(36.37%)*p*(63.44%) C6 (49.77%): *s*(36.12%)*p*(63.71%)
π(C2-C6)	1.70396	n/a	C2 (52.01%): *s*(0.01%)*p*(99.93%) C6 (47.99%): *s*(0.00%)*p*(99.93%)
σ(C3-C5)	1.97777	$sp^{1.84}$ at C3 $sp^{1.93}$ at C5	C3 (49.34%): *s*(35.20%)*p*(64.62%) C5 (50.66%): *s*(34.07%)*p*(65.81%)
π(C3-C5)	1.62672	n/a	C3 (52.66%): *s*(0.00%)*p*(99.93%) C5 (47.34%): *s*(0.02%)*p*(99.91%)
σ(C3-C7)	1.98289	$sp^{1.75}$ at C3 $sp^{1.78}$ at C7	C3 (50.27%): *s*(36.24%)*p*(63.57%) C7 (49.73%): *s*(35.93%)*p*(63.90%)
σ(C6-C8)	1.98407	$sp^{1.78}$ at C6 $sp^{1.81}$ at C8	C6 (50.14%): *s*(35.86%)*p*(63.96%) C8 (49.86%): *s*(35.59%)*p*(64.24%)
σ(C7-C8)	1.98396	$sp^{1.78}$ at C7 $sp^{1.80}$ at C8	C7 (50.07%): *s*(35.87%)*p*(63.95%) C8 (49.93%): *s*(35.61%)*p*(64.21%)
π(C7-C8)	1.67481	n/a	C7 (48.07%): *s*(0.00%)*p*(99.93%) C8 (51.93%): *s*(0.00%)*p*(99.94%)
σ(C11-C12)	1.97682	$sp^{1.77}$ at C11 $sp^{1.86}$ at C12	C11 (50.98%): *s*(36.09%)*p*(63.80%) C12 (49.02%): *s*(34.87%)*p*(64.94%)
π(C11-C12)	1.64185	n/a	C11 (44.36%): *s*(0.00%)*p*(99.91%) C12 (55.64%): *s*(0.01%)*p*(99.91%)
σ(C11-C10)	1.97129	$sp^{2.19}$ at C11 $sp^{1.95}$ at C10	C11 (49.05%): *s*(31.29%)*p*(68.59%) C10 (50.95%): *s*(33.84%)*p*(66.05%)
Lone pair 1 (N4)	1.87152	$sp^{2.69}$	*s*(27.09%)*p*(72.90%)
σ(N4-C9)	1.98761	$sp^{1.58}$ at N4 $sp^{2.03}$ at C9	N4 (59.45%): *s*(38.56%)*p*(61.08%) C9 (40.55%): *s*(32.97%)*p*(66.92%)
π(N4-C9)	1.85875	n/a	N4 (64.10%): *s*(0.00%)*p*(99.85%) C9 (35.90%): *s*(0.00%)*p*(99.87%)
σ(N4-C10)	1.98169	$sp^{1.92}$ at N4 $sp^{2.31}$ at C10	N4 (59.28%): *s*(34.19%)*p*(65.50%) C10 (40.72%): *s*(30.15%)*p*(69.76%)

[a] Calculated in gas phase at the optimized S0 geometry using PBE0 (gas phase/ def2-tzvpp def2/j). The PBE0 functional uses 25 % Hartree-Fock exchange.[14]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+cB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S95. NBO analysis[a] of ($^{\mathrm{Me}}$**L3**$^{\mathrm{Me}}$)$_2$Zn with the M06 functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.81339	$sp^{2.48}$	*s*(28.75%)*p*(71.22%)
Lone pair 2 (N1)	1.63612	n/a	*s*(0.05%)*p*(99.88%)
σ(N1-C5)	1.98429	$sp^{1.84}$ at N1 $sp^{2.22}$ at C5	N1 (59.29%): *s*(35.09%)*p*(64.71%) C5 (40.71%): *s*(31.07%)*p*(68.84%)
σ(N1-C11)	1.98316	$sp^{1.77}$ at N1 $sp^{2.07}$ at C11	N1 (58.55%): *s*(35.99%)*p*(63.80%) C11 (41.45%): *s*(32.50%)*p*(67.41%)
σ(C2-C5)	1.97663	$sp^{1.85}$ at C2 $sp^{1.88}$ at C5	C2 (49.60%): *s*(35.09%)*p*(64.75%) C5 (50.40%): *s*(34.72%)*p*(65.18%)
σ(C2-C6)	1.98154	$sp^{1.74}$ at C2 $sp^{1.76}$ at C6	C2 (50.19%): *s*(36.41%)*p*(63.42%) C6 (49.81%): *s*(36.24%)*p*(63.62%)
π(C2-C6)	1.70394	n/a	C2 (52.29%): *s*(0.01%)*p*(99.92%) C6 (47.71%): *s*(0.00%)*p*(99.92%)
σ(C3-C5)	1.97705	$sp^{1.82}$ at C3 $sp^{1.93}$ at C5	C3 (49.42%): *s*(35.35%)*p*(64.48%) C5 (50.58%): *s*(34.10%)*p*(65.79%)
π(C3-C5)	1.62726	n/a	C3 (53.03%): *s*(0.00%)*p*(99.93%) C5 (46.97%): *s*(0.02%)*p*(99.91%)
σ(C3-C7)	1.98255	$sp^{1.75}$ at C3 $sp^{1.77}$ at C7	C3 (50.21%): *s*(36.27%)*p*(63.57%) C7 (49.79%): *s*(36.06%)*p*(63.79%)
σ(C6-C8)	1.98350	$sp^{1.78}$ at C6 $sp^{1.80}$ at C8	C6 (50.15%): *s*(35.93%)*p*(63.91%) C8 (49.85%): *s*(35.66%)*p*(64.18%)
σ(C7-C8)	1.98340	$sp^{1.78}$ at C7 $sp^{1.80}$ at C8	C7 (50.08%): *s*(35.93%)*p*(63.90%) C8 (49.92%): *s*(35.69%)*p*(64.16%)
π(C7-C8)	1.67434	n/a	C7 (47.86%): *s*(0.00%)*p*(99.93%) C8 (52.14%): *s*(0.00%)*p*(99.93%)
σ(C11-C12)	1.97641	$sp^{1.77}$ at C11 $sp^{1.85}$ at C12	C11 (50.91%): *s*(36.07%)*p*(63.83%) C12 (49.09%): *s*(34.98%)*p*(64.85%)
π(C11-C12)	1.64266	n/a	C11 (43.57%): *s*(0.01%)*p*(99.90%) C12 (56.43%): *s*(0.01%)*p*(99.91%)
σ(C11-C10)	1.97079	$sp^{2.19}$ at C11 $sp^{1.95}$ at C10	C11 (49.08%): *s*(31.35%)*p*(68.53%) C10 (50.92%): *s*(33.86%)*p*(66.03%)
Lone pair 1 (N4)	1.86836	$sp^{2.69}$	*s*(27.08%)*p*(72.90%)
σ(N4-C9)	1.98740	$sp^{1.59}$ at N4 $sp^{2.03}$ at C9	N4 (59.66%): *s*(38.50%)*p*(61.21%) C9 (40.34%): *s*(32.96%)*p*(66.95%)
π(N4-C9)	1.86262	n/a	N4 (64.73%): *s*(0.00%)*p*(99.83%) C9 (35.27%): *s*(0.00%)*p*(99.85%)
σ(N4-C10)	1.98155	$sp^{1.91}$ at N4 $sp^{2.32}$ at C10	N4 (59.61%): *s*(34.28%)*p*(65.46%) C10 (40.39%): *s*(30.08%)*p*(69.84%)

[a] Calculated in gas phase at the optimized S0 geometry using M06 (gas phase/ def2-tzvpp def2/j). The M06 functional uses 27 % Hartree-Fock exchange.[23]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+cB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S96. NBO analysis[a] of $(^{\mathbf{Me}}\mathbf{L3}^{\mathbf{Me}})_2$Zn with the M06-2X functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.84154	$sp^{2.57}$	*s*(28.04%)*p*(71.93%)
Lone pair 2 (N1)	1.64418	n/a	*s*(0.03%)*p*(99.91%)
σ(N1-C5)	1.98461	$sp^{1.81}$ at N1 $sp^{2.21}$ at C5	N1 (59.00%): *s*(35.47%)*p*(64.31%) C5 (41.00%): *s*(31.13%)*p*(68.79%)
σ(N1-C11)	1.98320	$sp^{1.74}$ at N1 $sp^{2.07}$ at C11	N1 (58.32%): *s*(36.35%)*p*(63.40%) C11 (41.68%): *s*(32.56%)*p*(67.34%)
σ(C2-C5)	1.97761	$sp^{1.85}$ at C2 $sp^{1.83}$ at C5	C2 (49.52%): *s*(34.98%)*p*(64.85%) C5 (50.48%): *s*(34.70%)*p*(65.20%)
σ(C2-C6)	1.98221	$sp^{1.75}$ at C2 $sp^{1.76}$ at C6	C2 (50.23%): *s*(36.36%)*p*(63.46%) C6 (49.77%): *s*(36.13%)*p*(63.71%)
π(C2-C6)	1.70318	n/a	C2 (52.11%): *s*(0.01%)*p*(99.93%) C6 (47.89%): *s*(0.00%)*p*(99.93%)
σ(C3-C5)	1.97799	$sp^{1.83}$ at C3 $sp^{1.93}$ at C5	C3 (49.31%): *s*(35.23%)*p*(64.60%) C5 (50.69%): *s*(34.07%)*p*(65.82%)
π(C3-C5)	1.62827	n/a	C3 (52.91%): *s*(0.00%)*p*(99.93%) C5 (47.09%): *s*(0.02%)*p*(99.92%)
σ(C3-C7)	1.98313	$sp^{1.76}$ at C3 $sp^{1.78}$ at C7	C3 (50.26%): *s*(36.22%)*p*(63.61%) C7 (49.74%): *s*(35.95%)*p*(63.89%)
σ(C6-C8)	1.98421	$sp^{1.78}$ at C6 $sp^{1.81}$ at C8	C6 (50.14%): *s*(35.85%)*p*(63.97%) C8 (49.86%): *s*(35.58%)*p*(64.26%)
σ(C7-C8)	1.98408	$sp^{1.78}$ at C7 $sp^{1.80}$ at C8	C7 (50.07%): *s*(35.85%)*p*(63.97%) C8 (49.93%): *s*(35.60%)*p*(64.23%)
π(C7-C8)	1.67559	n/a	C7 (47.97%): *s*(0.00%)*p*(99.94%) C8 (52.03%): *s*(0.00%)*p*(99.94%)
σ(C11-C12)	1.97716	$sp^{1.77}$ at C11 $sp^{1.86}$ at C12	C11 (51.02%): *s*(36.13%)*p*(63.77%) C12 (48.98%): *s*(34.88%)*p*(64.94%)
π(C11-C12)	1.64551	n/a	C11 (43.87%): *s*(0.01%)*p*(99.91%) C12 (56.13%): *s*(0.01%)*p*(99.91%)
σ(C11-C10)	1.97182	$sp^{2.20}$ at C11 $sp^{1.95}$ at C10	C11 (48.96%): *s*(31.24%)*p*(68.64%) C10 (51.04%): *s*(33.87%)*p*(66.03%)
Lone pair 1 (N4)	1.88574	$sp^{2.77}$	*s*(26.55%)*p*(73.43%)
σ(N4-C9)	1.98749	$sp^{1.57}$ at N4 $sp^{2.04}$ at C9	N4 (59.61%): *s*(38.83%)*p*(60.82%) C9 (40.39%): *s*(32.91%)*p*(66.99%)
π(N4-C9)	1.86514	n/a	N4 (63.91%): *s*(0.00%)*p*(99.83%) C9 (36.09%): *s*(0.00%)*p*(99.86%)
σ(N4-C10)	1.98158	$sp^{1.89}$ at N4 $sp^{2.32}$ at C10	N4 (59.50%): *s*(34.47%)*p*(65.23%) C10 (40.50%): *s*(30.10%)*p*(69.82%)

[a] Calculated in gas phase at the optimized S0 geometry using M06-2X (gas phase/ def2-tzvpp def2/j). The M06-2X functional uses 54 % Hartree-Fock exchange.[23]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S97. NBO analysis[a] of (^{Me}**L3**^{Me})$_2$Zn with the CAM-B3LYP functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.82481	$sp^{2.61}$	*s*(27.72%)*p*(72.25%)
Lone pair 2 (N1)	1.64981	n/a	*s*(0.04%)*p*(99.91%)
σ(N1-C5)	1.98489	$sp^{1.80}$ at N1 $sp^{2.21}$ at C5	N1 (58.95%): *s*(35.59%)*p*(64.17%) C5 (41.05%): *s*(31.10%)*p*(68.79%)
σ(N1-C11)	1.98347	$sp^{1.73}$ at N1 $sp^{2.07}$ at C11	N1 (58.27%): *s*(36.53%)*p*(63.20%) C11 (41.73%): *s*(32.53%)*p*(67.35%)
σ(C2-C5)	1.97768	$sp^{1.85}$ at C2 $sp^{1.88}$ at C5	C2 (49.54%): *s*(34.97%)*p*(64.83%) C5 (50.46%): *s*(34.71%)*p*(65.17%)
σ(C2-C6)	1.98188	$sp^{1.74}$ at C2 $sp^{1.76}$ at C6	C2 (50.22%): *s*(36.42%)*p*(63.39%) C6 (49.78%): *s*(36.14%)*p*(63.69%)
π(C2-C6)	1.70280	n/a	C2 (52.21%): *s*(0.01%)*p*(99.93%) C6 (47.79%): *s*(0.00%)*p*(99.93%)
σ(C3-C5)	1.97804	$sp^{1.83}$ at C3 $sp^{1.93}$ at C5	C3 (49.35%): *s*(35.23%)*p*(64.57%) C5 (50.65%): *s*(34.06%)*p*(65.82%)
π(C3-C5)	1.62675	n/a	C3 (53.12%): *s*(0.00%)*p*(99.92%) C5 (46.88%): *s*(0.02%)*p*(99.91%)
σ(C3-C7)	1.98279	$sp^{1.75}$ at C3 $sp^{1.78}$ at C7	C3 (50.25%): *s*(36.27%)*p*(63.54%) C7 (49.75%): *s*(35.95%)*p*(63.87%)
σ(C6-C8)	1.98382	$sp^{1.78}$ at C6 $sp^{1.80}$ at C8	C6 (50.14%): *s*(35.89%)*p*(63.92%) C8 (49.86%): *s*(35.61%)*p*(64.21%)
σ(C7-C8)	1.98375	$sp^{1.78}$ at C7 $sp^{1.80}$ at C8	C7 (50.07%): *s*(35.89%)*p*(63.91%) C8 (49.93%): *s*(35.63%)*p*(64.18%)
π(C7-C8)	1.67613	n/a	C7 (47.86%): *s*(0.00%)*p*(99.93%) C8 (52.14%): *s*(0.00%)*p*(99.94%)
σ(C11-C12)	1.97692	$sp^{1.77}$ at C11 $sp^{1.86}$ at C12	C11 (50.98%): *s*(36.11%)*p*(63.78%) C12 (49.02%): *s*(34.91%)*p*(64.89%)
π(C11-C12)	1.64732	n/a	C11 (43.43%): *s*(0.00%)*p*(99.90%) C12 (56.57%): *s*(0.01%)*p*(99.91%)
σ(C11-C10)	1.97197	$sp^{2.19}$ at C11 $sp^{1.95}$ at C10	C11 (49.00%): *s*(31.27%)*p*(68.60%) C10 (51.00%): *s*(33.88%)*p*(66.00%)
Lone pair 1 (N4)	1.87689	$sp^{2.80}$	*s*(26.31%)*p*(73.67%)
σ(N4-C9)	1.98743	$sp^{1.56}$ at N4 $sp^{2.03}$ at C9	N4 (59.48%): *s*(38.90%)*p*(60.74%) C9 (40.52%): *s*(32.92%)*p*(66.96%)
π(N4-C9)	1.86648	n/a	N4 (64.21%): *s*(0.00%)*p*(99.85%) C9 (35.79%): *s*(0.00%)*p*(99.86%)
σ(N4-C10)	1.98189	$sp^{1.88}$ at N4 $sp^{2.32}$ at C10	N4 (59.43%): *s*(34.63%)*p*(65.05%) C10 (40.57%): *s*(30.08%)*p*(69.82%)

[a] Calculated in gas phase at the optimized S0 geometry using CAM-B3LYP (gas phase/ def2-tzvpp def2/j). The CAM-B3LYP functional is a range-separated functional, and uses 19 % Hartree-Fock exchange at short range, 33 % Hartree-Fock exchange at intermediate range, and 65 % Hartree-Fock exchange at long range.[15]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}| > 0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S98. NBO analysis[a] of $(^{\mathbf{CF3}}\mathbf{L4})_2$Zn with the M06-L functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.84126	$sp^{2.35}$	s(29.86%)p(70.11%)
σ(N1-C5)	1.98732	$sp^{1.63}$ at N1 $sp^{2.01}$ at C5	N1 (59.81%): s(37.86%)p(61.84%) C5 (40.19%): s(33.19%)p(66.72%)
π(N1-C5)	1.85812	n/a	N1 (70.41%): s(0.08%)p(99.78%) C5 (29.59%): s(0.13%)p(99.70%)
σ(N1-C11)	1.98192	$sp^{2.11}$ at N1 $sp^{2.15}$ at C11	N1 (58.27%): s(32.05%)p(67.68%) C11 (41.73%): s(31.71%)p(68.21%)
σ(C2-C5)	1.98404	$sp^{2.85}$ at C2 $sp^{2.18}$ at C5	C2 (51.83%): s(25.91%)p(73.94%) C5 (48.17%): s(31.45%)p(68.48%)
σ(C3-C5)	1.97761	$sp^{1.83}$ at C3 $sp^{1.84}$ at C5	C3 (49.98%): s(35.22%)p(64.59%) C5 (50.02%): s(35.21%)p(64.71%)
σ(C3-C6)	1.98633	$sp^{1.90}$ at C3 $sp^{1.67}$ at C6	C3 (51.52%): s(34.36%)p(65.45%) C6 (48.48%): s(37.38%)p(62.52%)
π(C3-C6)	1.63358	n/a	C3 (67.89%): s(0.01%)p(99.91%) C6 (32.11%): s(0.02%)p(99.88%)
σ(C6-C8)	1.98547	$sp^{2.16}$ at C6 $sp^{2.92}$ at C8	C6 (47.50%): s(31.59%)p(68.32%) C8 (52.50%): s(25.48%)p(74.36%)
σ(C6-O7)	1.99359	$sp^{2.21}$ at C6 $sp^{1.73}$ at O7	C6 (35.13%): s(31.09%)p(68.81%) O7 (64.87%): s(36.44%)p(63.12%)
Lone pair 1 (O7)	1.95984	n/a	s(58.05%)p(41.88%)
Lone pair 2 (O7)	1.88638	n/a	s(5.46%)p(94.41%)
Lone pair 3 (O7)	1.57135	n/a	s(0.01%)p(99.78%)
σ(C11-C12)	1.97730	$sp^{1.78}$ at C11 $sp^{1.90}$ at C12	C11 (49.98%): s(35.93%)p(63.97%) C12 (50.02%): s(34.44%)p(65.39%)
π(C11-C12)	1.64782	n/a	C11 (46.63%): s(0.01%)p(99.90%) C12 (53.37%): s(0.02%)p(99.90%)
σ(C11-C10)	1.97462	$sp^{2.09}$ at C11 $sp^{1.94}$ at C10	C11 (49.39%): s(32.28%)p(67.60%) C10 (50.61%): s(33.92%)p(65.94%)
Lone pair 1 (N4)	1.88662	$sp^{2.16}$	s(31.67%)p(68.25%)
σ(N4-C9)	1.98633	$sp^{1.72}$ at N4 $sp^{1.95}$ at C9	N4 (59.00%): s(36.59%)p(63.09%) C9 (41.00%): s(33.86%)p(66.04%)
π(N4-C9)	1.84619	n/a	N4 (61.90%): s(0.01%)p(99.82%) C9 (38.10%): s(0.01%)p(99.85%)
σ(N4-C10)	1.98145	$sp^{2.15}$ at N4 $sp^{2.31}$ at C10	N4 (58.48%): s(31.61%)p(68.09%) C10 (41.52%): s(30.17%)p(69.75%)

[a] Calculated in gas phase at the optimized S0 geometry using M06-L (gas phase/ def2-tzvpp def2/j). The M06-L functional uses 0 % Hartree-Fock exchange.[19]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S99. NBO analysis[a] of ($^{\mathbf{CF3}}$**L4**)$_2$Zn with the TPSSh functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.84094	$sp^{2.53}$	s(28.29%)p(71.68%)
σ(N1-C5)	1.98736	$sp^{1.57}$ at N1 $sp^{2.01}$ at C5	N1 (59.59%): s(38.72%)p(60.94%) C5 (40.41%): s(33.22%)p(66.66%)
π(N1-C5)	1.86062	n/a	N1 (70.16%): s(0.07%)p(99.79%) C5 (29.84%): s(0.10%)p(99.75%)
σ(N1-C11)	1.98219	$sp^{2.04}$ at N1 $sp^{2.14}$ at C11	N1 (58.01%): s(32.76%)p(66.95%) C11 (41.99%): s(31.82%)p(68.09%)
σ(C2-C5)	1.98387	$sp^{2.88}$ at C2 $sp^{2.16}$ at C5	C2 (51.34%): s(25.73%)p(74.11%) C5 (48.66%): s(31.60%)p(68.34%)
σ(C3-C5)	1.97714	$sp^{1.84}$ at C3 $sp^{1.85}$ at C5	C3 (49.82%): s(35.17%)p(64.64%) C5 (50.18%): s(35.07%)p(64.85%)
σ(C3-C6)	1.98567	$sp^{1.91}$ at C3 $sp^{1.68}$ at C6	C3 (51.38%): s(34.27%)p(65.54%) C6 (48.62%): s(37.34%)p(62.56%)
π(C3-C6)	1.63303	n/a	C3 (67.61%): s(0.01%)p(99.92%) C6 (32.39%): s(0.01%)p(99.88%)
σ(C6-C8)	1.98525	$sp^{2.15}$ at C6 $sp^{2.94}$ at C8	C6 (48.05%): s(31.70%)p(68.23%) C8 (51.95%): s(25.34%)p(74.49%)
σ(C6-O7)	1.99358	$sp^{2.22}$ at C6 $sp^{1.66}$ at O7	C6 (35.36%): s(31.04%)p(68.84%) O7 (64.64%): s(37.46%)p(62.08%)
Lone pair 1 (O7)	1.95806	n/a	s(55.98%)p(43.94%)
Lone pair 2 (O7)	1.88647	n/a	s(6.52%)p(93.36%)
Lone pair 3 (O7)	1.56978	n/a	s(0.02%)p(99.78%)
σ(C11-C12)	1.97662	$sp^{1.78}$ at C11 $sp^{1.90}$ at C12	C11 (50.17%): s(35.93%)p(63.97%) C12 (49.83%): s(34.37%)p(65.45%)
π(C11-C12)	1.64900	n/a	C11 (47.17%): s(0.01%)p(99.91%) C12 (52.83%): s(0.01%)p(99.91%)
σ(C11-C10)	1.97442	$sp^{2.10}$ at C11 $sp^{1.95}$ at C10	C11 (49.38%): s(32.17%)p(67.71%) C10 (50.62%): s(33.85%)p(66.02%)
Lone pair 1 (N4)	1.88565	$sp^{2.27}$	s(30.52%)p(69.41%)
σ(N4-C9)	1.98626	$sp^{1.68}$ at N4 $sp^{1.95}$ at C9	N4 (58.94%): s(37.15%)p(62.51%) C9 (41.06%): s(33.84%)p(66.03%)
π(N4-C9)	1.84524	n/a	N4 (62.15%): s(0.01%)p(99.82%) C9 (37.85%): s(0.02%)p(99.86%)
σ(N4-C10)	1.98202	$sp^{2.10}$ at N4 $sp^{2.30}$ at C10	N4 (58.22%): s(32.20%)p(67.47%) C10 (41.78%): s(30.27%)p(69.63%)

[a] Calculated in gas phase at the optimized S0 geometry using TPSSh (gas phase/ def2-tzvpp def2/j). The TPSSh functional uses 10 % Hartree-Fock exchange.[11]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+cB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S100. NBO analysis[a] of ($^{\mathbf{CF3}}$**L4**)$_2$Zn with the O3LYP functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.83866	$sp^{2.56}$	*s*(28.05%)*p*(71.92%)
σ(N1-C5)	1.98724	$sp^{1.56}$ at N1 $sp^{2.01}$ at C5	N1 (59.46%): *s*(38.86%)*p*(60.80%) C5 (40.54%): *s*(33.24%)*p*(66.65%)
π(N1-C5)	1.85993	n/a	N1 (70.07%): *s*(0.06%)*p*(99.80%) C5 (29.93%): *s*(0.09%)*p*(99.76%)
σ(N1-C11)	1.98202	$sp^{2.03}$ at N1 $sp^{2.14}$ at C11	N1 (57.89%): *s*(32.86%)*p*(66.85%) C11 (42.11%): *s*(31.86%)*p*(68.05%)
σ(C2-C5)	1.98352	$sp^{2.88}$ at C2 $sp^{2.16}$ at C5	C2 (51.53%): *s*(25.73%)*p*(74.13%) C5 (48.47%): *s*(31.65%)*p*(68.30%)
σ(C3-C5)	1.97664	$sp^{1.84}$ at C3 $sp^{1.85}$ at C5	C3 (49.84%): *s*(35.16%)*p*(64.67%) C5 (50.16%): *s*(35.01%)*p*(64.92%)
σ(C3-C6)	1.98522	$sp^{1.91}$ at C3 $sp^{1.68}$ at C6	C3 (51.41%): *s*(34.25%)*p*(65.57%) C6 (48.59%): *s*(37.32%)*p*(62.60%)
π(C3-C6)	1.63054	n/a	C3 (67.49%): *s*(0.01%)*p*(99.92%) C6 (32.51%): *s*(0.01%)*p*(99.89%)
σ(C6-C8)	1.98503	$sp^{2.16}$ at C6 $sp^{2.94}$ at C8	C6 (47.84%): *s*(31.67%)*p*(68.27%) C8 (52.16%): *s*(25.36%)*p*(74.49%)
σ(C6-O7)	1.99350	$sp^{2.21}$ at C6 $sp^{1.65}$ at O7	C6 (35.56%): *s*(31.10%)*p*(68.78%) O7 (64.44%): *s*(37.53%)*p*(62.00%)
Lone pair 1 (O7)	1.95717	n/a	*s*(56.30%)*p*(43.63%)
Lone pair 2 (O7)	1.88491	n/a	*s*(6.13%)*p*(93.74%)
Lone pair 3 (O7)	1.56970	n/a	*s*(0.02%)*p*(99.77%)
σ(C11-C12)	1.97612	$sp^{1.78}$ at C11 $sp^{1.90}$ at C12	C11 (50.15%): *s*(35.94%)*p*(63.97%) C12 (49.85%): *s*(34.31%)*p*(65.35%)
π(C11-C12)	1.64816	n/a	C11 (47.13%): *s*(0.01%)*p*(99.92%) C12 (52.87%): *s*(0.01%)*p*(99.91%)
σ(C11-C10)	1.97400	$sp^{2.11}$ at C11 $sp^{1.95}$ at C10	C11 (49.39%): *s*(32.12%)*p*(67.77%) C10 (50.61%): *s*(33.82%)*p*(66.07%)
Lone pair 1 (N4)	1.88373	$sp^{2.28}$	*s*(30.42%)*p*(69.50%)
σ(N4-C9)	1.98599	$sp^{1.68}$ at N4 $sp^{1.95}$ at C9	N4 (58.81%): *s*(37.23%)*p*(62.44%) C9 (41.19%): *s*(33.82%)*p*(66.05%)
π(N4-C9)	1.84617	n/a	N4 (62.09%): *s*(0.01%)*p*(99.81%) C9 (37.91%): *s*(0.02%)*p*(99.86%)
σ(N4-C10)	1.98177	$sp^{2.09}$ at N4 $sp^{2.29}$ at C10	N4 (58.06%): *s*(32.22%)*p*(67.46%) C10 (41.94%): *s*(30.32%)*p*(69.58%)

[a] Calculated in gas phase at the optimized S0 geometry using O3LYP (gas phase/ def2-tzvpp def2/j). The O3LYP functional uses 11.61 % Hartree-Fock exchange.[21]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S101. NBO analysis[a] of ($^{\mathbf{CF3}}$**L4**)$_2$Zn with the B3LYP functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.84533	$sp^{2.61}$	*s*(27.71%)*p*(72.26%)
σ(N1-C5)	1.98722	$sp^{1.55}$ at N1 $sp^{2.01}$ at C5	N1 (59.57%): *s*(39.02%)*p*(60.63%) C5 (40.43%): *s*(33.22%)*p*(66.66%)
π(N1-C5)	1.86389	n/a	N1 (70.71%): *s*(0.06%)*p*(99.80%) C5 (29.29%): *s*(0.08%)*p*(99.77%)
σ(N1-C11)	1.98233	$sp^{2.02}$ at N1 $sp^{2.14}$ at C11	N1 (58.00%): *s*(33.05%)*p*(66.65%) C11 (42.00%): *s*(31.86%)*p*(68.04%)
σ(C2-C5)	1.98394	$sp^{2.85}$ at C2 $sp^{2.16}$ at C5	C2 (51.46%): *s*(25.91%)*p*(73.93%) C5 (48.54%): *s*(31.64%)*p*(68.29%)
σ(C3-C5)	1.97700	$sp^{1.84}$ at C3 $sp^{1.85}$ at C5	C3 (49.81%): *s*(35.20%)*p*(64.60%) C5 (50.19%): *s*(35.04%)*p*(64.87%)
σ(C3-C6)	1.98515	$sp^{1.91}$ at C3 $sp^{1.68}$ at C6	C3 (51.36%): *s*(34.29%)*p*(65.51%) C6 (48.64%): *s*(37.31%)*p*(62.59%)
π(C3-C6)	1.63648	n/a	C3 (68.58%): *s*(0.01%)*p*(99.92%) C6 (31.42%): *s*(0.01%)*p*(99.88%)
σ(C6-C8)	1.98541	$sp^{2.16}$ at C6 $sp^{2.91}$ at C8	C6 (47.96%): *s*(31.65%)*p*(68.28%) C8 (52.04%): *s*(25.53%)*p*(74.30%)
σ(C6-O7)	1.99352	$sp^{2.21}$ at C6 $sp^{1.62}$ at O7	C6 (35.32%): *s*(31.11%)*p*(68.76%) O7 (64.68%): *s*(37.98%)*p*(61.55%)
Lone pair 1 (O7)	1.95701	n/a	*s*(55.12%)*p*(44.80%)
Lone pair 2 (O7)	1.89219	n/a	*s*(6.87%)*p*(93.02%)
Lone pair 3 (O7)	1.57926	n/a	*s*(0.02%)*p*(99.78%)
σ(C11-C12)	1.97651	$sp^{1.78}$ at C11 $sp^{1.90}$ at C12	C11 (50.13%): *s*(35.91%)*p*(63.99%) C12 (49.87%): *s*(34.39%)*p*(65.42%)
π(C11-C12)	1.65025	n/a	C11 (46.84%): *s*(0.01%)*p*(99.91%) C12 (53.16%): *s*(0.01%)*p*(99.91%)
σ(C11-C10)	1.97442	$sp^{2.11}$ at C11 $sp^{1.95}$ at C10	C11 (49.37%): *s*(32.13%)*p*(67.74%) C10 (50.63%): *s*(33.82%)*p*(66.05%)
Lone pair 1 (N4)	1.88890	$sp^{2.34}$	*s*(29.89%)*p*(70.04%)
σ(N4-C9)	1.98595	$sp^{1.66}$ at N4 $sp^{1.95}$ at C9	N4 (58.91%): *s*(37.47%)*p*(62.18%) C9 (41.09%): *s*(33.87%)*p*(65.99%)
π(N4-C9)	1.84883	n/a	N4 (62.21%): *s*(0.01%)*p*(99.82%) C9 (37.79%): *s*(0.02%)*p*(99.86%)
σ(N4-C10)	1.98203	$sp^{2.07}$ at N4 $sp^{2.30}$ at C10	N4 (58.24%): *s*(32.51%)*p*(67.15%) C10 (41.76%): *s*(30.31%)*p*(69.59%)

[a] Calculated in gas phase at the optimized S0 geometry using B3LYP (gas phase/ def2-tzvpp def2/j). The B3LYP functional uses 20 % Hartree-Fock exchange.[22]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S102. NBO analysis[a] of $(^{\mathbf{CF3}}\mathbf{L4})_2$Zn with the PBE0 functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.84708	$sp^{2.61}$	*s*(27.69%)*p*(72.28%)
σ(N1-C5)	1.98740	$sp^{1.55}$ at N1 $sp^{2.01}$ at C5	N1 (59.55%): *s*(39.06%)*p*(60.58%) C5 (40.45%): *s*(33.24%)*p*(66.65%)
π(N1-C5)	1.86532	n/a	N1 (70.96%): *s*(0.07%)*p*(99.78%) C5 (29.04%): *s*(0.08%)*p*(99.75%)
σ(N1-C11)	1.98244	$sp^{2.02}$ at N1 $sp^{2.13}$ at C11	N1 (57.91%): *s*(33.02%)*p*(66.67%) C11 (42.09%): *s*(31.88%)*p*(68.02%)
σ(C2-C5)	1.98400	$sp^{2.86}$ at C2 $sp^{2.16}$ at C5	C2 (51.51%): *s*(25.84%)*p*(74.00%) C5 (48.49%): *s*(31.61%)*p*(68.33%)
σ(C3-C5)	1.97706	$sp^{1.84}$ at C3 $sp^{1.85}$ at C5	C3 (49.86%): *s*(35.18%)*p*(64.63%) C5 (50.14%): *s*(35.06%)*p*(64.86%)
σ(C3-C6)	1.98529	$sp^{1.91}$ at C3 $sp^{1.68}$ at C6	C3 (51.48%): *s*(34.27%)*p*(65.53%) C6 (48.52%): *s*(37.31%)*p*(62.60%)
π(C3-C6)	1.63672	n/a	C3 (69.03%): *s*(0.01%)*p*(99.92%) C6 (30.97%): *s*(0.01%)*p*(99.87%)
σ(C6-C8)	1.98548	$sp^{2.16}$ at C6 $sp^{2.92}$ at C8	C6 (47.86%): *s*(31.64%)*p*(68.29%) C8 (52.14%): *s*(25.44%)*p*(74.39%)
σ(C6-O7)	1.99365	$sp^{2.21}$ at C6 $sp^{1.63}$ at O7	C6 (35.49%): *s*(31.14%)*p*(68.75%) O7 (64.51%): *s*(37.89%)*p*(61.62%)
Lone pair 1 (O7)	1.95775	n/a	*s*(55.59%)*p*(44.33%)
Lone pair 2 (O7)	1.89201	n/a	*s*(6.49%)*p*(93.39%)
Lone pair 3 (O7)	1.57904	n/a	*s*(0.02%)*p*(99.77%)
σ(C11-C12)	1.97663	$sp^{1.78}$ at C11 $sp^{1.90}$ at C12	C11 (50.11%): *s*(35.91%)*p*(64.00%) C12 (49.89%): *s*(34.38%)*p*(65.44%)
π(C11-C12)	1.65181	n/a	C11 (46.82%): *s*(0.01%)*p*(99.91%) C12 (53.18%): *s*(0.01%)*p*(99.90%)
σ(C11-C10)	1.97459	$sp^{2.11}$ at C11 $sp^{1.95}$ at C10	C11 (49.35%): *s*(32.12%)*p*(67.75%) C10 (50.65%): *s*(33.83%)*p*(66.04%)
Lone pair 1 (N4)	1.88872	$sp^{2.33}$	*s*(30.05%)*p*(69.88%)
σ(N4-C9)	1.98617	$sp^{1.67}$ at N4 $sp^{1.95}$ at C9	N4 (58.85%): *s*(37.37%)*p*(62.26%) C9 (41.15%): *s*(33.87%)*p*(66.00%)
π(N4-C9)	1.84971	n/a	N4 (62.35%): *s*(0.01%)*p*(99.80%) C9 (37.65%): *s*(0.02%)*p*(99.85%)
σ(N4-C10)	1.98214	$sp^{2.07}$ at N4 $sp^{2.30}$ at C10	N4 (58.12%): *s*(32.44%)*p*(67.21%) C10 (41.88%): *s*(30.31%)*p*(69.59%)

[a] Calculated in gas phase at the optimized S0 geometry using PBE0 (gas phase/ def2-tzvpp def2/j). The PBE0 functional uses 25 % Hartree-Fock exchange.[14]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}| > 0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S103. NBO analysis[a] of ($^{\mathbf{CF3}}$**L4**)$_2$Zn with the M06 functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.84368	$sp^{2.59}$	*s*(27.82%)*p*(72.15%)
σ(N1-C5)	1.98723	$sp^{1.56}$ at N1 $sp^{2.01}$ at C5	N1 (59.79%): *s*(38.94%)*p*(60.77%) C5 (40.21%): *s*(33.20%)*p*(66.71%)
π(N1-C5)	1.86794	n/a	N1 (71.97%): *s*(0.08%)*p*(99.76%) C5 (28.03%): *s*(0.10%)*p*(99.72%)
σ(N1-C11)	1.98221	$sp^{2.02}$ at N1 $sp^{2.14}$ at C11	N1 (58.25%): *s*(33.02%)*p*(66.72%) C11 (41.75%): *s*(31.81%)*p*(68.11%)
σ(C2-C5)	1.98371	$sp^{2.84}$ at C2 $sp^{2.16}$ at C5	C2 (51.67%): *s*(26.02%)*p*(73.83%) C5 (48.33%): *s*(31.59%)*p*(68.34%)
σ(C3-C5)	1.97679	$sp^{1.83}$ at C3 $sp^{1.85}$ at C5	C3 (49.88%): *s*(35.27%)*p*(64.56%) C5 (50.12%): *s*(35.10%)*p*(64.83%)
σ(C3-C6)	1.98530	$sp^{1.90}$ at C3 $sp^{1.68}$ at C6	C3 (51.51%): *s*(34.36%)*p*(65.45%) C6 (48.49%): *s*(37.31%)*p*(62.60%)
π(C3-C6)	1.63823	n/a	C3 (70.25%): *s*(0.01%)*p*(99.92%) C6 (29.75%): *s*(0.02%)*p*(99.87%)
σ(C6-C8)	1.98528	$sp^{2.16}$ at C6 $sp^{2.90}$ at C8	C6 (47.66%): *s*(31.58%)*p*(68.34%) C8 (52.34%): *s*(25.60%)*p*(74.24%)
σ(C6-O7)	1.99362	$sp^{2.20}$ at C6 $sp^{1.64}$ at O7	C6 (35.09%): *s*(31.18%)*p*(68.73%) O7 (64.91%): *s*(37.73%)*p*(61.83%)
Lone pair 1 (O7)	1.95855	n/a	*s*(55.77%)*p*(44.15%)
Lone pair 2 (O7)	1.89108	n/a	*s*(6.46%)*p*(93.40%)
Lone pair 3 (O7)	1.58647	n/a	*s*(0.01%)*p*(99.75%)
σ(C11-C12)	1.97631	$sp^{1.78}$ at C11 $sp^{1.90}$ at C12	C11 (49.99%): *s*(35.91%)*p*(64.00%) C12 (50.01%): *s*(34.47%)*p*(65.38%)
π(C11-C12)	1.65207	n/a	C11 (46.37%): *s*(0.01%)*p*(99.91%) C12 (53.63%): *s*(0.02%)*p*(99.90%)
σ(C11-C10)	1.97415	$sp^{2.10}$ at C11 $sp^{1.95}$ at C10	C11 (49.36%): *s*(32.19%)*p*(67.69%) C10 (50.64%): *s*(33.88%)*p*(66.00%)
Lone pair 1 (N4)	1.88803	$sp^{2.33}$	*s*(29.97%)*p*(69.94%)
σ(N4-C9)	1.98589	$sp^{1.67}$ at N4 $sp^{1.94}$ at C9	N4 (58.97%): *s*(37.35%)*p*(62.34%) C9 (41.03%): *s*(33.93%)*p*(65.97%)
π(N4-C9)	1.85400	n/a	N4 (62.80%): *s*(0.01%)*p*(99.79%) C9 (37.20%): *s*(0.01%)*p*(99.84%)
σ(N4-C10)	1.98166	$sp^{2.06}$ at N4 $sp^{2.31}$ at C10	N4 (58.49%): *s*(32.56%)*p*(67.14%) C10 (41.51%): *s*(30.23%)*p*(69.69%)

[a] Calculated in gas phase at the optimized S0 geometry using M06 (gas phase/ def2-tzvpp def2/j). The M06 functional uses 27 % Hartree-Fock exchange.[23]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S104. NBO analysis[a] of ($^{\mathrm{CF3}}$**L4**)$_2$Zn with the M06-2X functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.86365	$sp^{2.69}$	s(27.12%)p(72.85%)
σ(N1-C5)	1.98721	$sp^{1.53}$ at N1 $sp^{2.02}$ at C5	N1 (59.71%): s(39.41%)p(60.24%) C5 (40.29%): s(33.13%)p(66.77%)
π(N1-C5)	1.87230	n/a	N1 (71.48%): s(0.08%)p(99.75%) C5 (28.52%): s(0.09%)p(99.74%)
σ(N1-C11)	1.98243	$sp^{2.00}$ at N1 $sp^{2.13}$ at C11	N1 (57.97%): s(33.25%)p(66.45%) C11 (42.03%): s(31.90%)p(68.02%)
σ(C2-C5)	1.98438	$sp^{2.86}$ at C2 $sp^{2.16}$ at C5	C2 (51.38%): s(25.89%)p(73.97%) C5 (48.62%): s(31.67%)p(68.27%)
σ(C3-C5)	1.97710	$sp^{1.84}$ at C3 $sp^{1.85}$ at C5	C3 (49.79%): s(35.17%)p(64.65%) C5 (50.21%): s(35.12%)p(64.81%)
σ(C3-C6)	1.98483	$sp^{1.91}$ at C3 $sp^{1.68}$ at C6	C3 (51.44%): s(34.27%)p(65.55%) C6 (48.56%): s(37.33%)p(62.58%)
π(C3-C6)	1.64449	n/a	C3 (70.61%): s(0.02%)p(99.92%) C6 (29.39%): s(0.02%)p(99.87%)
σ(C6-C8)	1.98582	$sp^{2.15}$ at C6 $sp^{2.92}$ at C8	C6 (48.04%): s(31.69%)p(68.24%) C8 (51.96%): s(25.44%)p(74.40%)
σ(C6-O7)	1.99393	$sp^{2.21}$ at C6 $sp^{1.57}$ at O7	C6 (35.24%): s(31.08%)p(68.82%) O7 (64.76%): s(38.71%)p(60.80%)
Lone pair 1 (O7)	1.95772	n/a	s(55.16%)p(44.76%)
Lone pair 2 (O7)	1.90563	n/a	s(6.10%)p(93.77%)
Lone pair 3 (O7)	1.58655	n/a	s(0.02%)p(99.74%)
σ(C11-C12)	1.97701	$sp^{1.78}$ at C11 $sp^{1.90}$ at C12	C11 (50.10%): s(35.92%)p(63.99%) C12 (49.90%): s(34.45%)p(65.38%)
π(C11-C12)	1.65791	n/a	C11 (46.56%): s(0.01%)p(99.91%) C12 (53.44%): s(0.02%)p(99.91%)
σ(C11-C10)	1.97497	$sp^{2.11}$ at C11 $sp^{1.95}$ at C10	C11 (49.30%): s(32.11%)p(67.78%) C10 (50.70%): s(33.85%)p(66.03%)
Lone pair 1 (N4)	1.90053	$sp^{2.40}$	s(29.41%)p(70.51%)
σ(N4-C9)	1.98621	$sp^{1.64}$ at N4 $sp^{1.95}$ at C9	N4 (59.02%): s(37.68%)p(61.96%) C9 (40.98%): s(33.84%)p(66.04%)
π(N4-C9)	1.85696	n/a	N4 (62.23%): s(0.01%)p(99.77%) C9 (37.77%): s(0.01%)p(99.85%)
σ(N4-C10)	1.98215	$sp^{2.04}$ at N4 $sp^{2.30}$ at C10	N4 (58.33%): s(32.78%)p(66.88%) C10 (41.67%): s(30.28%)p(69.64%)

[a] Calculated in gas phase at the optimized S0 geometry using M06-2X (gas phase/ def2-tzvpp def2/j). The M06-2X functional uses 54 % Hartree-Fock exchange.[23]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + cB^2)}$, exceeds a fixed limit ($|i_{AB}| > 0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S105. NBO analysis[a] of $({}^{\mathbf{CF3}}\mathbf{L4})_2$Zn with the CAM-B3LYP functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.85329	$sp^{2.72}$	s(26.90%)p(73.07%)
σ(N1-C5)	1.98722	$sp^{1.52}$ at N1 $sp^{2.01}$ at C5	N1 (59.59%): s(39.47%)p(60.17%) C5 (40.41%): s(33.15%)p(66.73%)
π(N1-C5)	1.87425	n/a	N1 (71.92%): s(0.08%)p(99.77%) C5 (28.08%): s(0.07%)p(99.75%)
σ(N1-C11)	1.98271	$sp^{1.98}$ at N1 $sp^{2.14}$ at C11	N1 (57.95%): s(33.40%)p(66.29%) C11 (42.05%): s(31.86%)p(68.04%)
σ(C2-C5)	1.98436	$sp^{2.83}$ at C2 $sp^{2.16}$ at C5	C2 (51.49%): s(26.04%)p(73.79%) C5 (48.51%): s(31.67%)p(68.26%)
σ(C3-C5)	1.97712	$sp^{1.83}$ at C3 $sp^{1.85}$ at C5	C3 (49.80%): s(35.21%)p(64.59%) C5 (50.20%): s(35.09%)p(64.82%)
σ(C3-C6)	1.98488	$sp^{1.91}$ at C3 $sp^{1.67}$ at C6	C3 (51.38%): s(34.29%)p(65.50%) C6 (48.62%): s(37.35%)p(62.55%)
π(C3-C6)	1.64903	n/a	C3 (70.55%): s(0.02%)p(99.91%) C6 (29.45%): s(0.01%)p(99.86%)
σ(C6-C8)	1.98590	$sp^{2.15}$ at C6 $sp^{2.90}$ at C8	C6 (47.97%): s(31.68%)p(68.24%) C8 (52.03%): s(25.61%)p(74.20%)
σ(C6-O7)	1.99363	$sp^{2.22}$ at C6 $sp^{1.58}$ at O7	C6 (35.31%): s(31.05%)p(68.82%) O7 (64.69%): s(38.64%)p(60.87%)
Lone pair 1 (O7)	1.95679	n/a	s(53.64%)p(46.28%)
Lone pair 2 (O7)	1.89895	n/a	s(7.68%)p(92.19%)
Lone pair 3 (O7)	1.58800	n/a	s(0.02%)p(99.76%)
σ(C11-C12)	1.97664	$sp^{1.78}$ at C11 $sp^{1.90}$ at C12	C11 (50.07%): s(35.91%)p(63.99%) C12 (49.93%): s(34.46%)p(65.35%)
π(C11-C12)	1.65874	n/a	C11 (46.37%): s(0.01%)p(99.90%) C12 (53.63%): s(0.01%)p(99.90%)
σ(C11-C10)	1.97501	$sp^{2.11}$ at C11 $sp^{1.95}$ at C10	C11 (49.31%): s(32.13%)p(67.74%) C10 (50.69%): s(33.86%)p(66.00%)
Lone pair 1 (N4)	1.89480	$sp^{2.42}$	s(29.22%)p(70.70%)
σ(N4-C9)	1.98587	$sp^{1.64}$ at N4 $sp^{1.95}$ at C9	N4 (58.87%): s(37.73%)p(61.90%) C9 (41.13%): s(33.88%)p(65.98%)
π(N4-C9)	1.85807	n/a	N4 (62.46%): s(0.01%)p(99.80%) C9 (37.54%): s(0.02%)p(99.85%)
σ(N4-C10)	1.98232	$sp^{2.03}$ at N4 $sp^{2.30}$ at C10	N4 (58.25%): s(32.91%)p(66.74%) C10 (41.75%): s(30.25%)p(69.64%)

[a] Calculated in gas phase at the optimized S0 geometry using CAM-B3LYP (gas phase/ def2-tzvpp def2/j). The CAM-B3LYP functional is a range-separated functional, and uses 19 % Hartree-Fock exchange at short range, 33 % Hartree-Fock exchange at intermediate range, and 65 % Hartree-Fock exchange at long range.[15]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S106. NBO analysis[a] of $({}^{t\mathrm{Bu}}\mathbf{L4})_2$Zn with the M06-L functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.83908	$sp^{2.31}$	*s*(30.21%)*p*(69.74%)
σ(N1-C5)	1.98649	$sp^{1.67}$ at N1 $sp^{2.02}$ at C5	N1 (59.69%): *s*(37.34%)*p*(62.36%) C5 (40.31%): *s*(33.06%)*p*(66.85%)
π(N1-C5)	1.87061	n/a	N1 (70.02%): *s*(0.18%)*p*(99.67%) C5 (29.98%): *s*(0.25%)*p*(99.58%)
σ(N1-C11)	1.98126	$sp^{2.10}$ at N1 $sp^{2.21}$ at C11	N1 (58.19%): *s*(32.14%)*p*(67.59%) C11 (41.81%): *s*(31.14%)*p*(68.78%)
σ(C2-C5)	1.98373	$sp^{2.85}$ at C2 $sp^{2.26}$ at C5	C2 (52.08%): *s*(25.97%)*p*(73.89%) C5 (47.92%): *s*(30.63%)*p*(69.29%)
σ(C3-C5)	1.97829	$sp^{1.80}$ at C3 $sp^{1.77}$ at C5	C3 (50.14%): *s*(35.60%)*p*(64.21%) C5 (49.86%): *s*(36.02%)*p*(63.89%)
σ(C3-C6)	1.98583	$sp^{1.94}$ at C3 $sp^{1.66}$ at C6	C3 (51.43%): *s*(33.91%)*p*(65.89%) C6 (48.57%): *s*(37.51%)*p*(62.39%)
π(C3-C6)	1.64582	n/a	C3 (67.94%): *s*(0.01%)*p*(99.91%) C6 (32.06%): *s*(0.01%)*p*(99.89%)
σ(C6-C8)	1.98636	$sp^{2.13}$ at C6 $sp^{2.83}$ at C8	C6 (47.32%): *s*(31.87%)*p*(68.04%) C8 (52.68%): *s*(26.04%)*p*(73.79%)
σ(C6-O7)	1.99333	$sp^{2.26}$ at C6 $sp^{1.80}$ at O7	C6 (35.29%): *s*(30.67%)*p*(69.23%) O7 (64.71%): *s*(35.58%)*p*(64.00%)
Lone pair 1 (O7)	1.95992	n/a	*s*(58.02%)*p*(41.91%)
Lone pair 2 (O7)	1.89031	n/a	*s*(6.36%)*p*(93.53%)
Lone pair 3 (O7)	1.58118	n/a	*s*(0.01%)*p*(99.80%)
σ(C11-C12)	1.97550	$sp^{1.76}$ at C11 $sp^{1.92}$ at C12	C11 (50.19%): *s*(36.16%)*p*(63.75%) C12 (49.81%): *s*(34.16%)*p*(65.66%)
π(C11-C12)	1.66357	n/a	C11 (46.22%): *s*(0.02%)*p*(99.90%) C12 (53.78%): *s*(0.04%)*p*(99.87%)
σ(C11-C10)	1.97282	$sp^{2.06}$ at C11 $sp^{1.93}$ at C10	C11 (49.18%): *s*(32.61%)*p*(67.25%) C10 (50.82%): *s*(34.10%)*p*(65.75%)
Lone pair 1 (N4)	1.88963	$sp^{2.03}$	*s*(32.99%)*p*(66.97%)
σ(N4-C9)	1.98607	$sp^{1.83}$ at N4 $sp^{1.98}$ at C9	N4 (58.78%): *s*(35.28%)*p*(64.42%) C9 (41.22%): *s*(33.57%)*p*(66.33%)
π(N4-C9)	1.84226	n/a	N4 (61.26%): *s*(0.00%)*p*(99.83%) C9 (38.74%): *s*(0.00%)*p*(99.86%)
σ(N4-C10)	1.98147	$sp^{2.16}$ at N4 $sp^{2.30}$ at C10	N4 (58.23%): *s*(31.60%)*p*(68.10%) C10 (41.77%): *s*(30.26%)*p*(69.65%)

[a] Calculated in gas phase at the optimized S0 geometry using M06-L (gas phase/ def2-tzvpp def2/j). The M06-L functional uses 0 % Hartree-Fock exchange.[19]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S107. NBO analysis[a] of ($^{t\mathrm{Bu}}$**L4**)$_2$Zn with the TPSSh functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.83910	$sp^{2.49}$	s(28.64%)p(71.32%)
σ(N1-C5)	1.98661	$sp^{1.61}$ at N1 $sp^{2.02}$ at C5	N1 (59.45%): s(38.21%)p(61.45%) C5 (40.55%): s(33.12%)p(66.77%)
π(N1-C5)	1.87312	n/a	N1 (69.74%): s(0.16%)p(99.70%) C5 (30.26%): s(0.19%)p(99.66%)
σ(N1-C11)	1.98158	$sp^{2.03}$ at N1 $sp^{2.20}$ at C11	N1 (57.93%): s(32.86%)p(66.85%) C11 (42.07%): s(31.23%)p(68.67%)
σ(C2-C5)	1.98353	$sp^{2.87}$ at C2 $sp^{2.25}$ at C5	C2 (51.60%): s(25.78%)p(74.07%) C5 (48.40%): s(30.79%)p(69.15%)
σ(C3-C5)	1.97779	$sp^{1.81}$ at C3 $sp^{1.78}$ at C5	C3 (49.99%): s(35.56%)p(64.25%) C5 (50.01%): s(35.89%)p(64.03%)
σ(C3-C6)	1.98515	$sp^{1.95}$ at C3 $sp^{1.67}$ at C6	C3 (51.28%): s(33.83%)p(65.98%) C6 (48.72%): s(37.48%)p(62.44%)
π(C3-C6)	1.64490	n/a	C3 (67.62%): s(0.01%)p(99.92%) C6 (32.38%): s(0.00%)p(99.89%)
σ(C6-C8)	1.98613	$sp^{2.13}$ at C6 $sp^{2.86}$ at C8	C6 (47.84%): s(31.97%)p(67.96%) C8 (52.16%): s(25.89%)p(73.93%)
σ(C6-O7)	1.99334	$sp^{2.26}$ at C6 $sp^{1.72}$ at O7	C6 (35.52%): s(30.63%)p(69.26%) O7 (64.48%): s(36.58%)p(62.98%)
Lone pair 1 (O7)	1.95815	n/a	s(55.85%)p(44.08%)
Lone pair 2 (O7)	1.89029	n/a	s(7.54%)p(92.36%)
Lone pair 3 (O7)	1.57928	n/a	s(0.01%)p(99.81%)
σ(C11-C12)	1.97484	$sp^{1.76}$ at C11 $sp^{1.93}$ at C12	C11 (50.38%): s(36.17%)p(63.74%) C12 (49.62%): s(34.07%)p(65.75%)
π(C11-C12)	1.66500	n/a	C11 (46.80%): s(0.02%)p(99.91%) C12 (53.20%): s(0.04%)p(99.88%)
σ(C11-C10)	1.97256	$sp^{2.07}$ at C11 $sp^{1.93}$ at C10	C11 (49.16%): s(32.51%)p(67.37%) C10 (50.84%): s(34.04%)p(65.83%)
Lone pair 1 (N4)	1.88853	$sp^{2.15}$	s(31.78%)p(68.18%)
σ(N4-C9)	1.98610	$sp^{1.78}$ at N4 $sp^{1.98}$ at C9	N4 (58.72%): s(35.86%)p(63.82%) C9 (41.28%): s(33.55%)p(66.32%)
π(N4-C9)	1.84135	n/a	N4 (61.51%): s(0.00%)p(99.83%) C9 (38.49%): s(0.00%)p(99.87%)
σ(N4-C10)	1.98200	$sp^{2.09}$ at N4 $sp^{2.29}$ at C10	N4 (57.99%): s(32.22%)p(67.46%) C10 (42.01%): s(30.34%)p(69.55%)

[a] Calculated in gas phase at the optimized S0 geometry using TPSSh (gas phase/ def2-tzvpp def2/j). The TPSSh functional uses 10 % Hartree-Fock exchange.[11]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp$^{\lambda}$, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp$^{\infty}$) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S108. NBO analysis[a] of ($^{t\mathrm{Bu}}$**L4**)$_2$Zn with the O3LYP functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.83659	$sp^{2.52}$	*s*(28.41%)*p*(71.54%)
σ(N1-C5)	1.98651	$sp^{1.60}$ at N1 $sp^{2.01}$ at C5	N1 (59.31%): *s*(38.35%)*p*(61.31%) C5 (40.69%): *s*(33.15%)*p*(66.74%)
π(N1-C5)	1.87282	n/a	N1 (69.65%): *s*(0.15%)*p*(99.71%) C5 (30.35%): *s*(0.18%)*p*(99.67%)
σ(N1-C11)	1.98142	$sp^{2.03}$ at N1 $sp^{2.19}$ at C11	N1 (57.80%): *s*(32.95%)*p*(66.76%) C11 (42.20%): *s*(31.28%)*p*(68.63%)
σ(C2-C5)	1.98319	$sp^{2.88}$ at C2 $sp^{2.24}$ at C5	C2 (51.78%): *s*(25.77%)*p*(74.09%) C5 (48.22%): *s*(30.82%)*p*(69.13%)
σ(C3-C5)	1.97729	$sp^{1.81}$ at C3 $sp^{1.79}$ at C5	C3 (50.01%): *s*(35.54%)*p*(64.28%) C5 (49.99%): *s*(35.84%)*p*(64.09%)
σ(C3-C6)	1.98464	$sp^{1.95}$ at C3 $sp^{1.67}$ at C6	C3 (51.32%): *s*(33.81%)*p*(66.01%) C6 (48.68%): *s*(37.45%)*p*(62.47%)
π(C3-C6)	1.64303	n/a	C3 (67.50%): *s*(0.01%)*p*(99.92%) C6 (32.50%): *s*(0.00%)*p*(99.90%)
σ(C6-C8)	1.98589	$sp^{2.13}$ at C6 $sp^{2.85}$ at C8	C6 (47.64%): *s*(31.95%)*p*(67.99%) C8 (52.36%): *s*(25.92%)*p*(73.92%)
σ(C6-O7)	1.99325	$sp^{2.25}$ at C6 $sp^{1.72}$ at O7	C6 (35.73%): *s*(30.69%)*p*(69.20%) O7 (64.27%): *s*(36.67%)*p*(62.89%)
Lone pair 1 (O7)	1.95721	n/a	*s*(56.20%)*p*(43.73%)
Lone pair 2 (O7)	1.88895	n/a	*s*(7.10%)*p*(92.79%)
Lone pair 3 (O7)	1.57910	n/a	*s*(0.01%)*p*(99.80%)
σ(C11-C12)	1.97434	$sp^{1.76}$ at C11 $sp^{1.93}$ at C12	C11 (50.36%): *s*(36.16%)*p*(63.76%) C12 (49.64%): *s*(34.02%)*p*(65.81%)
π(C11-C12)	1.66436	n/a	C11 (46.82%): *s*(0.01%)*p*(99.91%) C12 (53.18%): *s*(0.04%)*p*(99.89%)
σ(C11-C10)	1.97210	$sp^{2.08}$ at C11 $sp^{1.94}$ at C10	C11 (49.18%): *s*(32.47%)*p*(67.42%) C10 (50.82%): *s*(34.00%)*p*(65.88%)
Lone pair 1 (N4)	1.88679	$sp^{2.15}$	*s*(31.69%)*p*(68.27%)
σ(N4-C9)	1.98582	$sp^{1.77}$ at N4 $sp^{1.98}$ at C9	N4 (58.60%): *s*(35.94%)*p*(63.74%) C9 (41.40%): *s*(33.54%)*p*(66.33%)
π(N4-C9)	1.84223	n/a	N4 (61.44%): *s*(0.00%)*p*(99.82%) C9 (38.56%): *s*(0.00%)*p*(99.88%)
σ(N4-C10)	1.98174	$sp^{2.09}$ at N4 $sp^{2.29}$ at C10	N4 (57.83%): *s*(32.23%)*p*(67.46%) C10 (42.17%): *s*(30.40%)*p*(69.49%)

[a] Calculated in gas phase at the optimized S0 geometry using O3LYP (gas phase/ def2-tzvpp def2/j). The O3LYP functional uses 11.61 % Hartree-Fock exchange.[21]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + cB^2)}$, exceeds a fixed limit ($|i_{AB}| > 0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S109. NBO analysis[a] of $({}^{t\mathrm{Bu}}\mathbf{L4})_2$Zn with the B3LYP functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.84339	$sp^{2.56}$	*s*(28.04%)*p*(71.91%)
σ(N1-C5)	1.98657	$sp^{1.59}$ at N1 $sp^{2.01}$ at C5	N1 (59.42%): *s*(38.53%)*p*(61.12%) C5 (40.58%): *s*(33.13%)*p*(66.75%)
π(N1-C5)	1.87655	n/a	N1 (70.27%): *s*(0.15%)*p*(99.71%) C5 (29.73%): *s*(0.16%)*p*(99.69%)
σ(N1-C11)	1.98176	$sp^{2.01}$ at N1 $sp^{2.19}$ at C11	N1 (57.93%): *s*(33.15%)*p*(66.54%) C11 (42.07%): *s*(31.28%)*p*(68.62%)
σ(C2-C5)	1.98358	$sp^{2.85}$ at C2 $sp^{2.24}$ at C5	C2 (51.72%): *s*(25.95%)*p*(73.89%) C5 (48.28%): *s*(30.82%)*p*(69.11%)
σ(C3-C5)	1.97760	$sp^{1.80}$ at C3 $sp^{1.79}$ at C5	C3 (49.98%): *s*(35.58%)*p*(64.22%) C5 (50.02%): *s*(35.85%)*p*(64.06%)
σ(C3-C6)	1.98460	$sp^{1.95}$ at C3 $sp^{1.67}$ at C6	C3 (51.26%): *s*(33.86%)*p*(65.94%) C6 (48.74%): *s*(37.44%)*p*(62.47%)
π(C3-C6)	1.64794	n/a	C3 (68.57%): *s*(0.01%)*p*(99.92%) C6 (31.43%): *s*(0.00%)*p*(99.89%)
σ(C6-C8)	1.98623	$sp^{2.13}$ at C6 $sp^{2.83}$ at C8	C6 (47.76%): *s*(31.93%)*p*(68.00%) C8 (52.24%): *s*(26.07%)*p*(73.74%)
σ(C6-O7)	1.99329	$sp^{2.25}$ at C6 $sp^{1.68}$ at O7	C6 (35.49%): *s*(30.71%)*p*(69.17%) O7 (64.51%): *s*(37.10%)*p*(62.45%)
Lone pair 1 (O7)	1.95715	n/a	*s*(54.86%)*p*(45.07%)
Lone pair 2 (O7)	1.89597	n/a	*s*(8.02%)*p*(91.88%)
Lone pair 3 (O7)	1.58856	n/a	*s*(0.01%)*p*(99.80%)
σ(C11-C12)	1.97479	$sp^{1.76}$ at C11 $sp^{1.93}$ at C12	C11 (50.35%): *s*(36.15%)*p*(63.76%) C12 (49.65%): *s*(34.09%)*p*(65.72%)
π(C11-C12)	1.66702	n/a	C11 (46.48%): *s*(0.01%)*p*(99.91%) C12 (53.52%): *s*(0.03%)*p*(99.89%)
σ(C11-C10)	1.97253	$sp^{2.08}$ at C11 $sp^{1.94}$ at C10	C11 (49.15%): *s*(32.47%)*p*(67.40%) C10 (50.85%): *s*(34.00%)*p*(65.86%)
Lone pair 1 (N4)	1.89182	$sp^{2.21}$	*s*(31.13%)*p*(68.83%)
σ(N4-C9)	1.98580	$sp^{1.75}$ at N4 $sp^{1.97}$ at C9	N4 (58.70%): *s*(36.20%)*p*(63.47%) C9 (41.30%): *s*(33.60%)*p*(66.27%)
π(N4-C9)	1.84491	n/a	N4 (61.51%): *s*(0.00%)*p*(99.83%) C9 (38.49%): *s*(0.00%)*p*(99.88%)
σ(N4-C10)	1.98197	$sp^{2.06}$ at N4 $sp^{2.29}$ at C10	N4 (58.01%): *s*(32.53%)*p*(67.14%) C10 (41.99%): *s*(30.39%)*p*(69.50%)

[a] Calculated in gas phase at the optimized S0 geometry using B3LYP (gas phase/ def2-tzvpp def2/j). The B3LYP functional uses 20 % Hartree-Fock exchange.[22]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S110. NBO analysis[a] of $({}^{t\mathrm{Bu}}\mathbf{L4})_2$Zn with the PBE0 functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.84525	$sp^{2.57}$	*s*(28.03%)*p*(71.92%)
σ(N1-C5)	1.98672	$sp^{1.58}$ at N1 $sp^{2.01}$ at C5	N1 (59.41%): *s*(38.55%)*p*(61.08%) C5 (40.59%): *s*(33.14%)*p*(66.74%)
π(N1-C5)	1.87778	n/a	N1 (70.51%): *s*(0.16%)*p*(99.69%) C5 (29.49%): *s*(0.17%)*p*(99.66%)
σ(N1-C11)	1.98186	$sp^{2.01}$ at N1 $sp^{2.19}$ at C11	N1 (57.84%): *s*(33.12%)*p*(66.56%) C11 (42.16%): *s*(31.30%)*p*(68.61%)
σ(C2-C5)	1.98363	$sp^{2.86}$ at C2 $sp^{2.24}$ at C5	C2 (51.76%): *s*(25.88%)*p*(73.97%) C5 (48.24%): *s*(30.80%)*p*(69.14%)
σ(C3-C5)	1.97766	$sp^{1.81}$ at C3 $sp^{1.79}$ at C5	C3 (50.04%): *s*(35.56%)*p*(64.24%) C5 (49.96%): *s*(35.87%)*p*(64.05%)
σ(C3-C6)	1.98477	$sp^{1.95}$ at C3 $sp^{1.67}$ at C6	C3 (51.38%): *s*(33.83%)*p*(65.97%) C6 (48.62%): *s*(37.44%)*p*(62.47%)
π(C3-C6)	1.64783	n/a	C3 (69.01%): *s*(0.01%)*p*(99.92%) C6 (30.99%): *s*(0.00%)*p*(99.89%)
σ(C6-C8)	1.98631	$sp^{2.13}$ at C6 $sp^{2.84}$ at C8	C6 (47.66%): *s*(31.92%)*p*(68.01%) C8 (52.34%): *s*(25.98%)*p*(73.83%)
σ(C6-O7)	1.99343	$sp^{2.25}$ at C6 $sp^{1.69}$ at O7	C6 (35.66%): *s*(30.73%)*p*(69.16%) O7 (64.34%): *s*(37.01%)*p*(62.52%)
Lone pair 1 (O7)	1.95789	n/a	*s*(55.41%)*p*(44.52%)
Lone pair 2 (O7)	1.89583	n/a	*s*(7.55%)*p*(92.34%)
Lone pair 3 (O7)	1.58841	n/a	*s*(0.01%)*p*(99.79%)
σ(C11-C12)	1.97485	$sp^{1.76}$ at C11 $sp^{1.93}$ at C12	C11 (50.32%): *s*(36.15%)*p*(63.76%) C12 (49.68%): *s*(34.06%)*p*(65.75%)
π(C11-C12)	1.66885	n/a	C11 (46.46%): *s*(0.01%)*p*(99.91%) C12 (53.54%): *s*(0.04%)*p*(99.88%)
σ(C11-C10)	1.97271	$sp^{2.08}$ at C11 $sp^{1.94}$ at C10	C11 (49.13%): *s*(32.46%)*p*(67.41%) C10 (50.87%): *s*(34.02%)*p*(65.85%)
Lone pair 1 (N4)	1.89264	$sp^{2.19}$	*s*(31.29%)*p*(68.67%)
σ(N4-C9)	1.98600	$sp^{1.76}$ at N4 $sp^{1.97}$ at C9	N4 (58.63%): *s*(36.10%)*p*(63.56%) C9 (41.37%): *s*(33.60%)*p*(66.27%)
π(N4-C9)	1.84578	n/a	N4 (61.66%): *s*(0.00%)*p*(99.81%) C9 (38.34%): *s*(0.00%)*p*(99.87%)
σ(N4-C10)	1.98209	$sp^{2.07}$ at N4 $sp^{2.29}$ at C10	N4 (57.89%): *s*(32.46%)*p*(67.20%) C10 (42.11%): *s*(30.39%)*p*(69.50%)

[a] Calculated in gas phase at the optimized S0 geometry using PBE0 (gas phase/ def2-tzvpp def2/j). The PBE0 functional uses 25 % Hartree-Fock exchange.[14]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + cB^2)}$, exceeds a fixed limit ($|i_{AB}| > 0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S111. NBO analysis[a] of ($^{t\text{Bu}}$**L4**)$_2$Zn with the M06 functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.84204	$sp^{2.55}$	*s*(28.16%)*p*(71.78%)
σ(N1-C5)	1.98652	$sp^{1.60}$ at N1 $sp^{2.02}$ at C5	N1 (59.66%): *s*(38.39%)*p*(61.31%) C5 (40.34%): *s*(33.10%)*p*(66.81%)
π(N1-C5)	1.87994	n/a	N1 (71.47%): *s*(0.19%)*p*(99.65%) C5 (28.53%): *s*(0.20%)*p*(99.62%)
σ(N1-C11)	1.98155	$sp^{2.01}$ at N1 $sp^{2.20}$ at C11	N1 (58.18%): *s*(33.14%)*p*(66.60%) C11 (41.82%): *s*(31.23%)*p*(68.69%)
σ(C2-C5)	1.98337	$sp^{2.83}$ at C2 $sp^{2.25}$ at C5	C2 (51.92%): *s*(26.06%)*p*(73.79%) C5 (48.08%): *s*(30.79%)*p*(69.14%)
σ(C3-C5)	1.97737	$sp^{1.80}$ at C3 $sp^{1.78}$ at C5	C3 (50.06%): *s*(35.65%)*p*(64.17%) C5 (49.94%): *s*(35.88%)*p*(64.04%)
σ(C3-C6)	1.98483	$sp^{1.94}$ at C3 $sp^{1.67}$ at C6	C3 (51.40%): *s*(33.92%)*p*(65.90%) C6 (48.60%): *s*(37.44%)*p*(62.47%)
π(C3-C6)	1.64874	n/a	C3 (70.17%): *s*(0.01%)*p*(99.92%) C6 (29.83%): *s*(0.01%)*p*(99.88%)
σ(C6-C8)	1.98614	$sp^{2.14}$ at C6 $sp^{2.82}$ at C8	C6 (47.49%): *s*(31.86%)*p*(68.06%) C8 (52.51%): *s*(26.13%)*p*(73.69%)
σ(C6-O7)	1.99341	$sp^{2.25}$ at C6 $sp^{1.70}$ at O7	C6 (35.27%): *s*(30.77%)*p*(69.14%) O7 (64.73%): *s*(36.84%)*p*(62.74%)
Lone pair 1 (O7)	1.95878	n/a	*s*(55.54%)*p*(44.39%)
Lone pair 2 (O7)	1.89473	n/a	*s*(7.59%)*p*(92.30%)
Lone pair 3 (O7)	1.59620	n/a	*s*(0.01%)*p*(99.78%)
σ(C11-C12)	1.97446	$sp^{1.76}$ at C11 $sp^{1.92}$ at C12	C11 (50.20%): *s*(36.16%)*p*(63.76%) C12 (49.80%): *s*(34.16%)*p*(65.68%)
π(C11-C12)	1.66961	n/a	C11 (45.93%): *s*(0.02%)*p*(99.90%) C12 (54.07%): *s*(0.04%)*p*(99.88%)
σ(C11-C10)	1.97217	$sp^{2.07}$ at C11 $sp^{1.93}$ at C10	C11 (49.14%): *s*(32.52%)*p*(67.36%) C10 (50.86%): *s*(34.06%)*p*(65.81%)
Lone pair 1 (N4)	1.89090	$sp^{1.90}$	*s*(31.23%)*p*(68.71%)
σ(N4-C9)	1.98565	$sp^{1.76}$ at N4 $sp^{1.97}$ at C9	N4 (58.77%): *s*(36.08%)*p*(63.63%) C9 (41.23%): *s*(33.67%)*p*(66.24%)
π(N4-C9)	1.85015	n/a	N4 (62.04%): *s*(0.00%)*p*(99.80%) C9 (37.96%): *s*(0.00%)*p*(99.86%)
σ(N4-C10)	1.98154	$sp^{2.06}$ at N4 $sp^{2.30}$ at C10	N4 (58.25%): *s*(32.56%)*p*(67.14%) C10 (41.75%): *s*(30.32%)*p*(69.59%)

[a] Calculated in gas phase at the optimized S0 geometry using M06 (gas phase/ def2-tzvpp def2/j). The M06 functional uses 27 % Hartree-Fock exchange.[23]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + cB^2)}$, exceeds a fixed limit ($|i_{AB}| > 0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S112. NBO analysis[a] of $(^{t\mathrm{Bu}}\mathbf{L4})_2\mathrm{Zn}$ with the M06-2X functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.86136	$sp^{2.65}$	s(27.38%)p(72.57%)
σ(N1-C5)	1.98663	$sp^{1.56}$ at N1 $sp^{2.02}$ at C5	N1 (59.57%): s(38.94%)p(60.71%) C5 (40.43%): s(33.04%)p(66.86%)
π(N1-C5)	1.88457	n/a	N1 (70.99%): s(0.18%)p(99.65%) C5 (29.01%): s(0.18%)p(99.65%)
σ(N1-C11)	1.98194	$sp^{1.99}$ at N1 $sp^{2.19}$ at C11	N1 (57.94%): s(33.39%)p(66.31%) C11 (42.06%): s(31.29%)p(68.63%)
σ(C2-C5)	1.98392	$sp^{2.85}$ at C2 $sp^{2.24}$ at C5	C2 (51.63%): s(25.93%)p(73.93%) C5 (48.37%): s(30.88%)p(69.07%)
σ(C3-C5)	1.97766	$sp^{1.81}$ at C3 $sp^{1.78}$ at C5	C3 (49.97%): s(35.56%)p(64.26%) C5 (50.03%): s(35.90%)p(64.02%)
σ(C3-C6)	1.98435	$sp^{1.95}$ at C3 $sp^{1.67}$ at C6	C3 (51.34%): s(33.83%)p(65.98%) C6 (48.66%): s(37.46%)p(62.46%)
π(C3-C6)	1.65426	n/a	C3 (70.55%): s(0.01%)p(99.92%) C6 (29.45%): s(0.00%)p(99.88%)
σ(C6-C8)	1.98667	$sp^{2.13}$ at C6 $sp^{2.84}$ at C8	C6 (47.84%): s(31.96%)p(67.98%) C8 (52.16%): s(25.98%)p(73.85%)
σ(C6-O7)	1.99376	$sp^{2.26}$ at C6 $sp^{1.63}$ at O7	C6 (35.42%): s(30.68%)p(69.23%) O7 (64.58%): s(37.82%)p(61.71%)
Lone pair 1 (O7)	1.95796	n/a	s(54.90%)p(45.02%)
Lone pair 2 (O7)	1.90938	n/a	s(7.26%)p(92.63%)
Lone pair 3 (O7)	1.59601	n/a	s(0.01%)p(99.77%)
σ(C11-C12)	1.97522	$sp^{1.76}$ at C11 $sp^{1.93}$ at C12	C11 (50.36%): s(36.19%)p(63.72%) C12 (49.64%): s(34.08%)p(65.74%)
π(C11-C12)	1.67593	n/a	C11 (46.24%): s(0.02%)p(99.91%) C12 (53.76%): s(0.04%)p(99.88%)
σ(C11-C10)	1.97309	$sp^{2.08}$ at C11 $sp^{1.93}$ at C10	C11 (49.07%): s(32.43%)p(67.45%) C10 (50.93%): s(34.03%)p(65.84%)
Lone pair 1 (N4)	1.90351	$sp^{2.26}$	s(30.65%)p(69.31%)
σ(N4-C9)	1.98599	$sp^{1.74}$ at N4 $sp^{1.97}$ at C9	N4 (58.80%): s(36.42%)p(63.25%) C9 (41.20%): s(33.58%)p(66.31%)
π(N4-C9)	1.85275	n/a	N4 (61.50%): s(0.00%)p(99.78%) C9 (38.50%): s(0.00%)p(99.87%)
σ(N4-C10)	1.98206	$sp^{2.04}$ at N4 $sp^{2.29}$ at C10	N4 (58.11%): s(32.81%)p(66.87%) C10 (41.89%): s(30.35%)p(69.56%)

[a] Calculated in gas phase at the optimized S0 geometry using M06-2X (gas phase/ def2-tzvpp def2/j). The M06-2X functional uses 54 % Hartree-Fock exchange.[23]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}| > 0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S113. NBO analysis[a] of (${}^{t\mathrm{Bu}}$**L4**)$_2$Zn with the CAM-B3LYP functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.85169	$sp^{2.67}$	*s*(27.21%)*p*(72.74%)
σ(N1-C5)	1.98665	$sp^{1.56}$ at N1 $sp^{2.02}$ at C5	N1 (59.44%): *s*(38.96%)*p*(60.67%) C5 (40.56%): *s*(33.07%)*p*(66.80%)
π(N1-C5)	1.88627	n/a	N1 (71.41%): *s*(0.18%)*p*(99.67%) C5 (28.59%): *s*(0.16%)*p*(99.67%)
σ(N1-C11)	1.98218	$sp^{1.97}$ at N1 $sp^{2.19}$ at C11	N1 (57.90%): *s*(33.52%)*p*(66.16%) C11 (42.10%): *s*(31.27%)*p*(68.63%)
σ(C2-C5)	1.98395	$sp^{2.83}$ at C2 $sp^{2.24}$ at C5	C2 (51.74%): *s*(26.08%)*p*(73.75%) C5 (48.26%): *s*(30.87%)*p*(69.06%)
σ(C3-C5)	1.97764	$sp^{1.80}$ at C3 $sp^{1.79}$ at C5	C3 (49.99%): *s*(35.59%)*p*(64.20%) C5 (50.01%): *s*(35.87%)*p*(64.04%)
σ(C3-C6)	1.98437	$sp^{1.95}$ at C3 $sp^{1.67}$ at C6	C3 (51.27%): *s*(33.86%)*p*(65.93%) C6 (48.73%): *s*(37.48%)*p*(62.43%)
π(C3-C6)	1.65833	n/a	C3 (70.48%): *s*(0.01%)*p*(99.92%) C6 (29.52%): *s*(0.00%)*p*(99.88%)
σ(C6-C8)	1.98662	$sp^{2.13}$ at C6 $sp^{2.82}$ at C8	C6 (47.77%): *s*(31.95%)*p*(67.97%) C8 (52.23%): *s*(26.14%)*p*(73.66%)
σ(C6-O7)	1.99343	$sp^{2.26}$ at C6 $sp^{1.64}$ at O7	C6 (35.49%): *s*(30.65%)*p*(69.23%) O7 (64.51%): *s*(37.76%)*p*(61.77%)
Lone pair 1 (O7)	1.95703	n/a	*s*(53.19%)*p*(46.73%)
Lone pair 2 (O7)	1.90255	n/a	*s*(9.02%)*p*(90.87%)
Lone pair 3 (O7)	1.59672	n/a	*s*(0.01%)*p*(99.79%)
σ(C11-C12)	1.97496	$sp^{1.76}$ at C11 $sp^{1.92}$ at C12	C11 (50.30%): *s*(36.17%)*p*(63.74%) C12 (49.70%): *s*(34.13%)*p*(65.67%)
π(C11-C12)	1.67659	n/a	C11 (46.01%): *s*(0.01%)*p*(99.90%) C12 (53.99%): *s*(0.03%)*p*(99.88%)
σ(C11-C10)	1.97314	$sp^{2.08}$ at C11 $sp^{1.93}$ at C10	C11 (49.08%): *s*(32.45%)*p*(67.41%) C10 (50.92%): *s*(34.04%)*p*(65.82%)
Lone pair 1 (N4)	1.89761	$sp^{2.28}$	*s*(30.44%)*p*(69.52%)
σ(N4-C9)	1.98573	$sp^{1.73}$ at N4 $sp^{1.97}$ at C9	N4 (58.66%): *s*(36.48%)*p*(63.17%) C9 (41.34%): *s*(33.61%)*p*(66.25%)
π(N4-C9)	1.85412	n/a	N4 (61.70%): *s*(0.00%)*p*(99.81%) C9 (38.30%): *s*(0.00%)*p*(99.87%)
σ(N4-C10)	1.98225	$sp^{2.03}$ at N4 $sp^{2.29}$ at C10	N4 (58.04%): *s*(32.94%)*p*(66.71%) C10 (41.96%): *s*(30.32%)*p*(69.56%)

[a] Calculated in gas phase at the optimized S0 geometry using CAM-B3LYP (gas phase/ def2-tzvpp def2/j). The CAM-B3LYP functional is a range-separated functional, and uses 19 % Hartree-Fock exchange at short range, 33 % Hartree-Fock exchange at intermediate range, and 65 % Hartree-Fock exchange at long range.[15]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S114. NBO analysis[a] of $(^{\mathbf{Me}}\mathbf{L4})_2$Zn with the M06-L functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.83925	$sp^{2.31}$	*s*(30.22%)*p*(69.73%)
σ(N1-C5)	1.98656	$sp^{1.67}$ at N1 $sp^{2.02}$ at C5	N1 (59.70%): *s*(37.36%)*p*(62.33%) C5 (40.30%): *s*(33.05%)*p*(66.86%)
π(N1-C5)	1.86924	n/a	N1 (70.04%): *s*(0.18%)*p*(99.67%) C5 (29.96%): *s*(0.25%)*p*(99.58%)
σ(N1-C11)	1.98131	$sp^{2.11}$ at N1 $sp^{2.20}$ at C11	N1 (58.20%): *s*(32.11%)*p*(67.61%) C11 (41.80%): *s*(31.25%)*p*(68.67%)
σ(C2-C5)	1.98378	$sp^{2.85}$ at C2 $sp^{2.26}$ at C5	C2 (52.06%): *s*(25.96%)*p*(73.90%) C5 (47.94%): *s*(30.64%)*p*(69.29%)
σ(C3-C5)	1.97835	$sp^{1.80}$ at C3 $sp^{1.77}$ at C5	C3 (50.14%): *s*(35.60%)*p*(64.21%) C5 (49.86%): *s*(36.02%)*p*(63.88%)
σ(C3-C6)	1.98586	$sp^{1.94}$ at C3 $sp^{1.66}$ at C6	C3 (51.43%): *s*(33.91%)*p*(65.89%) C6 (48.57%): *s*(37.51%)*p*(62.39%)
π(C3-C6)	1.64456	n/a	C3 (67.94%): *s*(0.01%)*p*(99.91%) C6 (32.06%): *s*(0.01%)*p*(99.89%)
σ(C6-C8)	1.98636	$sp^{2.13}$ at C6 $sp^{2.83}$ at C8	C6 (47.33%): *s*(31.87%)*p*(68.04%) C8 (52.67%): *s*(26.03%)*p*(73.79%)
σ(C6-O7)	1.99333	$sp^{2.26}$ at C6 $sp^{1.80}$ at O7	C6 (35.29%): *s*(30.67%)*p*(69.23%) O7 (64.71%): *s*(35.58%)*p*(64.00%)
Lone pair 1 (O7)	1.95994	n/a	*s*(58.03%)*p*(41.91%)
Lone pair 2 (O7)	1.89028	n/a	*s*(6.36%)*p*(93.54%)
Lone pair 3 (O7)	1.58082	n/a	*s*(0.01%)*p*(99.80%)
σ(C11-C12)	1.97599	$sp^{1.78}$ at C11 $sp^{1.92}$ at C12	C11 (50.19%): *s*(35.96%)*p*(63.94%) C12 (49.81%): *s*(34.17%)*p*(65.65%)
π(C11-C12)	1.65857	n/a	C11 (46.25%): *s*(0.02%)*p*(99.89%) C12 (53.75%): *s*(0.05%)*p*(99.86%)
σ(C11-C10)	1.97296	$sp^{2.05}$ at C11 $sp^{1.93}$ at C10	C11 (49.16%): *s*(32.70%)*p*(67.17%) C10 (50.84%): *s*(34.08%)*p*(65.77%)
Lone pair 1 (N4)	1.88961	$sp^{2.03}$	*s*(33.00%)*p*(66.96%)
σ(N4-C9)	1.98610	$sp^{1.83}$ at N4 $sp^{1.98}$ at C9	N4 (58.78%): *s*(35.28%)*p*(64.42%) C9 (41.22%): *s*(33.57%)*p*(66.33%)
π(N4-C9)	1.84264	n/a	N4 (61.25%): *s*(0.00%)*p*(99.83%) C9 (38.75%): *s*(0.00%)*p*(99.86%)
σ(N4-C10)	1.98154	$sp^{2.16}$ at N4 $sp^{2.30}$ at C10	N4 (58.23%): *s*(31.59%)*p*(68.11%) C10 (41.77%): *s*(30.31%)*p*(69.60%)

[a] Calculated in gas phase at the optimized S0 geometry using M06-L (gas phase/ def2-tzvpp def2/j). The M06-L functional uses 0 % Hartree-Fock exchange.[19]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S115. NBO analysis[a] of $(^{\mathbf{Me}}\mathbf{L4})_2$Zn with the TPSSh functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.83920	$sp^{2.49}$	s(28.65%)p(71.31%)
σ(N1-C5)	1.98669	$sp^{1.61}$ at N1 $sp^{2.02}$ at C5	N1 (59.46%): s(38.23%)p(61.43%) C5 (40.54%): s(33.11%)p(66.78%)
π(N1-C5)	1.87155	n/a	N1 (69.78%): s(0.16%)p(99.70%) C5 (30.22%): s(0.19%)p(99.66%)
σ(N1-C11)	1.98164	$sp^{2.04}$ at N1 $sp^{2.19}$ at C11	N1 (57.95%): s(32.83%)p(66.87%) C11 (42.05%): s(31.34%)p(68.56%)
σ(C2-C5)	1.98360	$sp^{2.87}$ at C2 $sp^{2.25}$ at C5	C2 (51.59%): s(25.78%)p(74.07%) C5 (48.41%): s(30.79%)p(69.15%)
σ(C3-C5)	1.97784	$sp^{1.81}$ at C3 $sp^{1.78}$ at C5	C3 (49.99%): s(35.56%)p(64.25%) C5 (50.01%): s(35.89%)p(64.02%)
σ(C3-C6)	1.98517	$sp^{1.95}$ at C3 $sp^{1.67}$ at C6	C3 (51.28%): s(33.82%)p(65.98%) C6 (48.72%): s(37.47%)p(62.44%)
π(C3-C6)	1.64334	n/a	C3 (67.63%): s(0.01%)p(99.92%) C6 (32.37%): s(0.00%)p(99.89%)
σ(C6-C8)	1.98613	$sp^{2.12}$ at C6 $sp^{2.86}$ at C8	C6 (47.86%): s(31.98%)p(67.95%) C8 (52.14%): s(25.88%)p(73.94%)
σ(C6-O7)	1.99334	$sp^{2.26}$ at C6 $sp^{1.72}$ at O7	C6 (35.52%): s(30.63%)p(69.26%) O7 (64.48%): s(36.58%)p(62.98%)
Lone pair 1 (O7)	1.95817	n/a	s(55.85%)p(44.08%)
Lone pair 2 (O7)	1.89026	n/a	s(7.55%)p(92.36%)
Lone pair 3 (O7)	1.57883	n/a	s(0.01%)p(99.81%)
σ(C11-C12)	1.97540	$sp^{1.78}$ at C11 $sp^{1.93}$ at C12	C11 (50.38%): s(35.96%)p(63.94%) C12 (49.62%): s(34.08%)p(65.73%)
π(C11-C12)	1.66017	n/a	C11 (46.78%): s(0.02%)p(99.90%) C12 (53.22%): s(0.05%)p(99.87%)
σ(C11-C10)	1.97267	$sp^{2.06}$ at C11 $sp^{1.94}$ at C10	C11 (49.14%): s(32.60%)p(67.28%) C10 (50.86%): s(34.02%)p(65.85%)
Lone pair 1 (N4)	1.88851	$sp^{2.14}$	s(31.80%)p(68.17%)
σ(N4-C9)	1.98613	$sp^{1.78}$ at N4 $sp^{1.98}$ at C9	N4 (58.72%): s(35.86%)p(63.81%) C9 (41.28%): s(33.55%)p(66.32%)
π(N4-C9)	1.84172	n/a	N4 (61.51%): s(0.00%)p(99.83%) C9 (38.49%): s(0.00%)p(99.87%)
σ(N4-C10)	1.98206	$sp^{2.10}$ at N4 $sp^{2.29}$ at C10	N4 (57.99%): s(32.20%)p(67.48%) C10 (42.01%): s(30.39%)p(69.50%)

[a] Calculated in gas phase at the optimized S0 geometry using TPSSh (gas phase/ def2-tzvpp def2/j). The TPSSh functional uses 10 % Hartree-Fock exchange.[11]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+cB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S116. NBO analysis[a] of $(^{\mathbf{Me}}\mathbf{L4})_2$Zn with the O3LYP functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.83665	$sp^{2.52}$	*s*(28.42%)*p*(71.53%)
σ(N1-C5)	1.98659	$sp^{1.60}$ at N1 $sp^{2.01}$ at C5	N1 (59.32%): *s*(38.37%)*p*(61.29%) C5 (40.68%): *s*(33.14%)*p*(66.75%)
π(N1-C5)	1.87110	n/a	N1 (69.69%): *s*(0.15%)*p*(99.71%) C5 (30.31%): *s*(0.18%)*p*(99.67%)
σ(N1-C11)	1.98147	$sp^{2.03}$ at N1 $sp^{2.18}$ at C11	N1 (57.82%): *s*(32.93%)*p*(66.78%) C11 (42.18%): *s*(31.39%)*p*(68.52%)
σ(C2-C5)	1.98325	$sp^{2.88}$ at C2 $sp^{2.24}$ at C5	C2 (51.76%): *s*(25.77%)*p*(74.10%) C5 (48.24%): *s*(30.82%)*p*(69.13%)
σ(C3-C5)	1.97733	$sp^{1.81}$ at C3 $sp^{1.79}$ at C5	C3 (50.01%): *s*(35.54%)*p*(64.28%) C5 (49.99%): *s*(35.84%)*p*(64.08%)
σ(C3-C6)	1.98466	$sp^{1.95}$ at C3 $sp^{1.67}$ at C6	C3 (51.32%): *s*(33.81%)*p*(66.01%) C6 (48.68%): *s*(37.45%)*p*(62.48%)
π(C3-C6)	1.64136	n/a	C3 (67.51%): *s*(0.01%)*p*(99.92%) C6 (32.49%): *s*(0.00%)*p*(99.90%)
σ(C6-C8)	1.98588	$sp^{2.13}$ at C6 $sp^{2.85}$ at C8	C6 (47.66%): *s*(31.96%)*p*(67.98%) C8 (52.34%): *s*(25.91%)*p*(73.93%)
σ(C6-O7)	1.99326	$sp^{2.25}$ at C6 $sp^{1.72}$ at O7	C6 (35.73%): *s*(30.69%)*p*(69.20%) O7 (64.27%): *s*(36.66%)*p*(62.89%)
Lone pair 1 (O7)	1.95723	n/a	*s*(56.20%)*p*(43.73%)
Lone pair 2 (O7)	1.88893	n/a	*s*(7.11%)*p*(92.79%)
Lone pair 3 (O7)	1.57862	n/a	*s*(0.01%)*p*(99.80%)
σ(C11-C12)	1.97486	$sp^{1.78}$ at C11 $sp^{1.93}$ at C12	C11 (50.35%): *s*(35.96%)*p*(63.95%) C12 (49.65%): *s*(34.02%)*p*(65.80%)
π(C11-C12)	1.65979	n/a	C11 (46.75%): *s*(0.02%)*p*(99.91%) C12 (53.25%): *s*(0.05%)*p*(99.87%)
σ(C11-C10)	1.97220	$sp^{2.07}$ at C11 $sp^{1.94}$ at C10	C11 (49.16%): *s*(32.56%)*p*(67.33%) C10 (50.84%): *s*(33.98%)*p*(65.90%)
Lone pair 1 (N4)	1.88675	$sp^{2.15}$	*s*(31.70%)*p*(68.25%)
σ(N4-C9)	1.98585	$sp^{1.77}$ at N4 $sp^{1.98}$ at C9	N4 (58.60%): *s*(35.94%)*p*(63.74%) C9 (41.40%): *s*(33.54%)*p*(66.33%)
π(N4-C9)	1.84263	n/a	N4 (61.44%): *s*(0.00%)*p*(99.82%) C9 (38.56%): *s*(0.00%)*p*(99.88%)
σ(N4-C10)	1.98178	$sp^{2.09}$ at N4 $sp^{2.28}$ at C10	N4 (57.83%): *s*(32.21%)*p*(67.47%) C10 (42.17%): *s*(30.45%)*p*(69.45%)

[a] Calculated in gas phase at the optimized S0 geometry using O3LYP (gas phase/ def2-tzvpp def2/j). The O3LYP functional uses 11.61 % Hartree-Fock exchange.[21]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S117. NBO analysis[a] of $(^{\mathrm{Me}}\mathbf{L4})_2\mathrm{Zn}$ with the B3LYP functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.84344	$sp^{2.56}$	*s*(28.05%)*p*(71.90%)
σ(N1-C5)	1.98665	$sp^{1.58}$ at N1 $sp^{2.01}$ at C5	N1 (59.43%): *s*(38.55%)*p*(61.09%) C5 (40.57%): *s*(33.13%)*p*(66.75%)
π(N1-C5)	1.87491	n/a	N1 (70.31%): *s*(0.14%)*p*(99.71%) C5 (29.69%): *s*(0.17%)*p*(99.69%)
σ(N1-C11)	1.98182	$sp^{2.01}$ at N1 $sp^{2.18}$ at C11	N1 (57.94%): *s*(33.12%)*p*(66.57%) C11 (42.06%): *s*(31.39%)*p*(68.51%)
σ(C2-C5)	1.98364	$sp^{2.85}$ at C2 $sp^{2.24}$ at C5	C2 (51.70%): *s*(25.95%)*p*(73.89%) C5 (48.30%): *s*(30.83%)*p*(69.11%)
σ(C3-C5)	1.97764	$sp^{1.80}$ at C3 $sp^{1.79}$ at C5	C3 (49.98%): *s*(35.58%)*p*(64.22%) C5 (50.02%): *s*(35.85%)*p*(64.06%)
σ(C3-C6)	1.98462	$sp^{1.95}$ at C3 $sp^{1.67}$ at C6	C3 (51.26%): *s*(33.85%)*p*(65.94%) C6 (48.74%): *s*(37.44%)*p*(62.47%)
π(C3-C6)	1.64634	n/a	C3 (68.57%): *s*(0.01%)*p*(99.92%) C6 (31.43%): *s*(0.00%)*p*(99.89%)
σ(C6-C8)	1.98623	$sp^{2.13}$ at C6 $sp^{2.83}$ at C8	C6 (47.77%): *s*(31.93%)*p*(67.99%) C8 (52.23%): *s*(26.07%)*p*(73.75%)
σ(C6-O7)	1.99329	$sp^{2.25}$ at C6 $sp^{1.68}$ at O7	C6 (35.49%): *s*(30.71%)*p*(69.17%) O7 (64.51%): *s*(37.09%)*p*(62.45%)
Lone pair 1 (O7)	1.95717	n/a	*s*(54.85%)*p*(45.07%)
Lone pair 2 (O7)	1.89595	n/a	*s*(8.02%)*p*(91.88%)
Lone pair 3 (O7)	1.58811	n/a	*s*(0.01%)*p*(99.80%)
σ(C11-C12)	1.97530	$sp^{1.78}$ at C11 $sp^{1.93}$ at C12	C11 (50.34%): *s*(35.95%)*p*(63.96%) C12 (49.66%): *s*(34.10%)*p*(65.70%)
π(C11-C12)	1.66217	n/a	C11 (46.42%): *s*(0.02%)*p*(99.91%) C12 (53.58%): *s*(0.05%)*p*(99.88%)
σ(C11-C10)	1.97265	$sp^{2.07}$ at C11 $sp^{1.94}$ at C10	C11 (49.13%): *s*(32.56%)*p*(67.31%) C10 (50.87%): *s*(33.98%)*p*(65.88%)
Lone pair 1 (N4)	1.89180	$sp^{2.21}$	*s*(31.15%)*p*(68.81%)
σ(N4-C9)	1.98583	$sp^{1.75}$ at N4 $sp^{1.97}$ at C9	N4 (58.70%): *s*(36.20%)*p*(63.46%) C9 (41.30%): *s*(33.60%)*p*(66.27%)
π(N4-C9)	1.84534	n/a	N4 (61.51%): *s*(0.00%)*p*(99.83%) C9 (38.49%): *s*(0.00%)*p*(99.88%)
σ(N4-C10)	1.98201	$sp^{2.07}$ at N4 $sp^{2.28}$ at C10	N4 (58.01%): *s*(32.51%)*p*(67.16%) C10 (41.99%): *s*(30.43%)*p*(69.46%)

[a] Calculated in gas phase at the optimized S0 geometry using B3LYP (gas phase/ def2-tzvpp def2/j). The B3LYP functional uses 20 % Hartree-Fock exchange.[22]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + cB^2)}$, exceeds a fixed limit ($|i_{AB}| > 0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S118. NBO analysis[a] of (^{Me}**L4**)$_2$Zn with the PBE0 functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.84533	$sp^{2.56}$	s(28.04%)p(71.91%)
σ(N1-C5)	1.98680	$sp^{1.58}$ at N1 $sp^{2.01}$ at C5	N1 (59.41%): s(38.57%)p(61.06%) C5 (40.59%): s(33.14%)p(66.75%)
π(N1-C5)	1.87625	n/a	N1 (70.55%): s(0.16%)p(99.69%) C5 (29.45%): s(0.17%)p(99.66%)
σ(N1-C11)	1.98191	$sp^{2.01}$ at N1 $sp^{2.18}$ at C11	N1 (57.86%): s(33.09%)p(66.59%) C11 (42.14%): s(31.41%)p(68.50%)
σ(C2-C5)	1.98370	$sp^{2.86}$ at C2 $sp^{2.24}$ at C5	C2 (51.75%): s(25.88%)p(73.97%) C5 (48.25%): s(30.80%)p(69.14%)
σ(C3-C5)	1.97771	$sp^{1.81}$ at C3 $sp^{1.79}$ at C5	C3 (50.04%): s(35.56%)p(64.24%) C5 (49.96%): s(35.87%)p(64.04%)
σ(C3-C6)	1.98480	$sp^{1.95}$ at C3 $sp^{1.67}$ at C6	C3 (51.38%): s(33.83%)p(65.97%) C6 (48.62%): s(37.44%)p(62.47%)
π(C3-C6)	1.64636	n/a	C3 (69.02%): s(0.01%)p(99.92%) C6 (30.98%): s(0.00%)p(99.89%)
σ(C6-C8)	1.98631	$sp^{2.13}$ at C6 $sp^{2.84}$ at C8	C6 (47.67%): s(31.92%)p(68.01%) C8 (52.33%): s(25.98%)p(73.84%)
σ(C6-O7)	1.99343	$sp^{2.25}$ at C6 $sp^{1.69}$ at O7	C6 (35.66%): s(30.73%)p(69.16%) O7 (64.34%): s(37.01%)p(62.52%)
Lone pair 1 (O7)	1.95791	n/a	s(55.41%)p(44.52%)
Lone pair 2 (O7)	1.89582	n/a	s(7.56%)p(92.34%)
Lone pair 3 (O7)	1.58800	n/a	s(0.01%)p(99.79%)
σ(C11-C12)	1.97537	$sp^{1.78}$ at C11 $sp^{1.93}$ at C12	C11 (50.32%): s(35.95%)p(63.96%) C12 (49.68%): s(34.08%)p(65.73%)
π(C11-C12)	1.66402	n/a	C11 (46.41%): s(0.02%)p(99.90%) C12 (53.59%): s(0.05%)p(99.87%)
σ(C11-C10)	1.97283	$sp^{2.07}$ at C11 $sp^{1.94}$ at C10	C11 (49.11%): s(32.55%)p(67.32%) C10 (50.89%): s(34.00%)p(65.87%)
Lone pair 1 (N4)	1.89263	$sp^{2.19}$	s(31.31%)p(68.65%)
σ(N4-C9)	1.98603	$sp^{1.76}$ at N4 $sp^{1.97}$ at C9	N4 (58.63%): s(36.10%)p(63.55%) C9 (41.37%): s(33.59%)p(66.28%)
π(N4-C9)	1.84623	n/a	N4 (61.66%): s(0.00%)p(99.81%) C9 (38.34%): s(0.00%)p(99.87%)
σ(N4-C10)	1.98215	$sp^{2.07}$ at N4 $sp^{2.28}$ at C10	N4 (57.89%): s(32.44%)p(67.21%) C10 (42.11%): s(30.43%)p(69.46%)

[a] Calculated in gas phase at the optimized S0 geometry using PBE0 (gas phase/ def2-tzvpp def2/j). The PBE0 functional uses 25 % Hartree-Fock exchange.[14]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^λ, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^∞) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S119. NBO analysis[a] of (^{Me}**L4**)$_2$Zn with the M06 functional.

NBO[b]	**Occupancy**[c]	**Hybridization**[d]	**Atomic Orbital Contributions (%)**[e]
Lone pair 1 (N1)	1.84214	$sp^{2.55}$	*s*(28.17%)*p*(71.77%)
σ(N1-C5)	1.98659	$sp^{1.60}$ at N1 $sp^{2.02}$ at C5	N1 (59.67%): *s*(38.42%)*p*(61.29%) C5 (40.33%): *s*(33.10%)*p*(66.81%)
π(N1-C5)	1.87865	n/a	N1 (71.50%): *s*(0.19%)*p*(99.65%) C5 (28.50%): *s*(0.20%)*p*(99.62%)
σ(N1-C11)	1.98161	$sp^{2.01}$ at N1 $sp^{2.19}$ at C11	N1 (58.20%): *s*(33.11%)*p*(66.63%) C11 (41.80%): *s*(31.34%)*p*(68.58%)
σ(C2-C5)	1.98343	$sp^{2.83}$ at C2 $sp^{2.25}$ at C5	C2 (51.90%): *s*(26.06%)*p*(73.80%) C5 (48.10%): *s*(30.79%)*p*(69.14%)
σ(C3-C5)	1.97743	$sp^{1.80}$ at C3 $sp^{1.78}$ at C5	C3 (50.07%): *s*(35.65%)*p*(64.17%) C5 (49.93%): *s*(35.88%)*p*(64.04%)
σ(C3-C6)	1.98486	$sp^{1.94}$ at C3 $sp^{1.67}$ at C6	C3 (51.40%): *s*(33.91%)*p*(65.90%) C6 (48.60%): *s*(37.44%)*p*(62.47%)
π(C3-C6)	1.64763	n/a	C3 (70.18%): *s*(0.01%)*p*(99.92%) C6 (29.82%): *s*(0.01%)*p*(99.88%)
σ(C6-C8)	1.98614	$sp^{2.14}$ at C6 $sp^{2.82}$ at C8	C6 (47.50%): *s*(31.86%)*p*(68.06%) C8 (52.50%): *s*(26.13%)*p*(73.69%)
σ(C6-O7)	1.99341	$sp^{2.25}$ at C6 $sp^{1.70}$ at O7	C6 (35.26%): *s*(30.77%)*p*(69.14%) O7 (64.74%): *s*(36.84%)*p*(62.74%)
Lone pair 1 (O7)	1.95880	n/a	*s*(55.54%)*p*(44.39%)
Lone pair 2 (O7)	1.89472	n/a	*s*(7.59%)*p*(92.29%)
Lone pair 3 (O7)	1.59593	n/a	*s*(0.01%)*p*(99.78%)
σ(C11-C12)	1.97500	$sp^{1.78}$ at C11 $sp^{1.92}$ at C12	C11 (50.19%): *s*(35.95%)*p*(63.97%) C12 (49.81%): *s*(34.19%)*p*(65.65%)
π(C11-C12)	1.66459	n/a	C11 (45.90%): *s*(0.02%)*p*(99.90%) C12 (54.10%): *s*(0.05%)*p*(99.87%)
σ(C11-C10)	1.97231	$sp^{2.06}$ at C11 $sp^{1.93}$ at C10	C11 (49.12%): *s*(32.62%)*p*(67.26%) C10 (50.88%): *s*(34.03%)*p*(65.84%)
Lone pair 1 (N4)	1.89088	$sp^{2.20}$	*s*(31.24%)*p*(68.70%)
σ(N4-C9)	1.98569	$sp^{1.76}$ at N4 $sp^{1.97}$ at C9	N4 (58.76%): *s*(36.08%)*p*(63.63%) C9 (41.24%): *s*(33.67%)*p*(66.24%)
π(N4-C9)	1.85071	n/a	N4 (62.02%): *s*(0.00%)*p*(99.80%) C9 (37.98%): *s*(0.00%)*p*(99.86%)
σ(N4-C10)	1.98160	$sp^{2.06}$ at N4 $sp^{2.29}$ at C10	N4 (58.25%): *s*(32.55%)*p*(67.16%) C10 (41.75%): *s*(30.37%)*p*(69.55%)

[a] Calculated in gas phase at the optimized S0 geometry using M06 (gas phase/ def2-tzvpp def2/j). The M06 functional uses 27 % Hartree-Fock exchange.[23]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2-cB^2)}{(cA^2+cB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S120 NBO analysis[a] of ($^{\mathbf{Me}}$**L4**)$_2$Zn with the M06-2X functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.86149	$sp^{2.65}$	*s*(27.39%)*p*(72.56%)
σ(N1-C5)	1.98670	$sp^{1.56}$ at N1 $sp^{2.02}$ at C5	N1 (59.58%): *s*(38.96%)*p*(60.69%) C5 (40.42%): *s*(33.04%)*p*(66.86%)
π(N1-C5)	1.88341	n/a	N1 (71.03%): *s*(0.18%)*p*(99.65%) C5 (28.97%): *s*(0.18%)*p*(99.64%)
σ(N1-C11)	1.98200	$sp^{1.99}$ at N1 $sp^{2.18}$ at C11	N1 (57.95%): *s*(33.36%)*p*(66.33%) C11 (42.05%): *s*(31.40%)*p*(68.52%)
σ(C2-C5)	1.98399	$sp^{2.85}$ at C2 $sp^{2.24}$ at C5	C2 (51.62%): *s*(25.93%)*p*(73.93%) C5 (48.38%): *s*(30.88%)*p*(69.07%)
σ(C3-C5)	1.97772	$sp^{1.81}$ at C3 $sp^{1.78}$ at C5	C3 (49.97%): *s*(35.56%)*p*(64.26%) C5 (50.03%): *s*(35.91%)*p*(64.01%)
σ(C3-C6)	1.98437	$sp^{1.95}$ at C3 $sp^{1.67}$ at C6	C3 (51.34%): *s*(33.83%)*p*(65.98%) C6 (48.66%): *s*(37.46%)*p*(62.46%)
π(C3-C6)	1.65312	n/a	C3 (70.56%): *s*(0.01%)*p*(99.92%) C6 (29.44%): *s*(0.00%)*p*(99.88%)
σ(C6-C8)	1.98667	$sp^{2.13}$ at C6 $sp^{2.84}$ at C8	C6 (47.85%): *s*(31.96%)*p*(67.97%) C8 (52.15%): *s*(25.98%)*p*(73.85%)
σ(C6-O7)	1.99376	$sp^{2.26}$ at C6 $sp^{1.63}$ at O7	C6 (35.42%): *s*(30.68%)*p*(69.23%) O7 (64.58%): *s*(37.81%)*p*(61.71%)
Lone pair 1 (O7)	1.95797	n/a	*s*(54.90%)*p*(45.02%)
Lone pair 2 (O7)	1.90938	n/a	*s*(7.26%)*p*(92.63%)
Lone pair 3 (O7)	1.59570	n/a	*s*(0.01%)*p*(99.77%)
σ(C11-C12)	1.97576	$sp^{1.78}$ at C11 $sp^{1.93}$ at C12	C11 (50.36%): *s*(35.98%)*p*(63.93%) C12 (49.64%): *s*(34.09%)*p*(65.73%)
π(C11-C12)	1.67051	n/a	C11 (46.25%): *s*(0.02%)*p*(99.91%) C12 (53.75%): *s*(0.05%)*p*(99.88%)
σ(C11-C10)	1.97322	$sp^{2.07}$ at C11 $sp^{1.94}$ at C10	C11 (49.05%): *s*(32.53%)*p*(67.35%) C10 (50.95%): *s*(34.01%)*p*(65.86%)
Lone pair 1 (N4)	1.90351	$sp^{2.26}$	*s*(30.66%)*p*(69.29%)
σ(N4-C9)	1.98602	$sp^{1.74}$ at N4 $sp^{1.97}$ at C9	N4 (58.80%): *s*(36.42%)*p*(63.24%) C9 (41.20%): *s*(33.58%)*p*(66.31%)
π(N4-C9)	1.85335	n/a	N4 (61.49%): *s*(0.00%)*p*(99.78%) C9 (38.51%): *s*(0.00%)*p*(99.87%)
σ(N4-C10)	1.98213	$sp^{2.04}$ at N4 $sp^{2.29}$ at C10	N4 (58.10%): *s*(32.79%)*p*(66.88%) C10 (41.90%): *s*(30.40%)*p*(69.51%)

[a] Calculated in gas phase at the optimized S0 geometry using M06-2X (gas phase/ def2-tzvpp def2/j). The M06-2X functional uses 54 % Hartree-Fock exchange.[23]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}| > 0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp$^{\lambda}$, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp$^{\infty}$) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

Table S121. NBO analysis[a] of ($^{\mathbf{Me}}$**L4**)$_2$Zn with the CAM-B3LYP functional.

NBO[b]	Occupancy[c]	Hybridization[d]	Atomic Orbital Contributions (%)[e]
Lone pair 1 (N1)	1.85171	$sp^{2.67}$	*s*(27.22%)*p*(72.73%)
σ(N1-C5)	1.98672	$sp^{1.56}$ at N1 $sp^{2.02}$ at C5	N1 (59.45%): *s*(38.99%)*p*(60.64%) C5 (40.55%): *s*(33.07%)*p*(66.81%)
π(N1-C5)	1.88489	n/a	N1 (71.46%): *s*(0.18%)*p*(99.67%) C5 (28.54%): *s*(0.16%)*p*(99.67%)
σ(N1-C11)	1.98223	$sp^{1.98}$ at N1 $sp^{2.18}$ at C11	N1 (57.92%): *s*(33.49%)*p*(66.18%) C11 (42.08%): *s*(31.38%)*p*(68.52%)
σ(C2-C5)	1.98401	$sp^{2.83}$ at C2 $sp^{2.24}$ at C5	C2 (51.73%): *s*(26.08%)*p*(73.75%) C5 (48.27%): *s*(30.87%)*p*(69.06%)
σ(C3-C5)	1.97768	$sp^{1.80}$ at C3 $sp^{1.79}$ at C5	C3 (49.99%): *s*(35.59%)*p*(64.20%) C5 (50.01%): *s*(35.87%)*p*(64.04%)
σ(C3-C6)	1.98439	$sp^{1.95}$ at C3 $sp^{1.67}$ at C6	C3 (51.27%): *s*(33.85%)*p*(65.94%) C6 (48.73%): *s*(37.47%)*p*(62.43%)
π(C3-C6)	1.65697	n/a	C3 (70.49%): *s*(0.01%)*p*(99.92%) C6 (29.51%): *s*(0.00%)*p*(99.88%)
σ(C6-C8)	1.98662	$sp^{2.13}$ at C6 $sp^{2.82}$ at C8	C6 (47.78%): *s*(31.96%)*p*(67.96%) C8 (52.22%): *s*(26.14%)*p*(73.66%)
σ(C6-O7)	1.99344	$sp^{2.26}$ at C6 $sp^{1.64}$ at O7	C6 (35.48%): *s*(30.65%)*p*(69.23%) O7 (64.52%): *s*(37.76%)*p*(61.78%)
Lone pair 1 (O7)	1.95705	n/a	*s*(53.19%)*p*(46.73%)
Lone pair 2 (O7)	1.90253	n/a	*s*(9.03%)*p*(90.87%)
Lone pair 3 (O7)	1.59635	n/a	*s*(0.01%)*p*(99.79%)
σ(C11-C12)	1.97548	$sp^{1.78}$ at C11 $sp^{1.92}$ at C12	C11 (50.30%): *s*(35.97%)*p*(63.93%) C12 (49.70%): *s*(34.14%)*p*(65.66%)
π(C11-C12)	1.67159	n/a	C11 (45.94%): *s*(0.02%)*p*(99.90%) C12 (54.06%): *s*(0.04%)*p*(99.87%)
σ(C11-C10)	1.97326	$sp^{2.07}$ at C11 $sp^{1.94}$ at C10	C11 (49.06%): *s*(32.54%)*p*(67.32%) C10 (50.94%): *s*(34.02%)*p*(65.84%)
Lone pair 1 (N4)	1.89760	$sp^{2.28}$	*s*(30.45%)*p*(69.51%)
σ(N4-C9)	1.98576	$sp^{1.73}$ at N4 $sp^{1.97}$ at C9	N4 (58.66%): *s*(36.48%)*p*(63.17%) C9 (41.34%): *s*(33.61%)*p*(66.25%)
π(N4-C9)	1.85466	n/a	N4 (61.69%): *s*(0.00%)*p*(99.81%) C9 (38.31%): *s*(0.00%)*p*(99.87%)
σ(N4-C10)	1.98231	$sp^{2.03}$ at N4 $sp^{2.29}$ at C10	N4 (58.03%): *s*(32.92%)*p*(66.73%) C10 (41.97%): *s*(30.37%)*p*(69.52%)

[a] Calculated in gas phase at the optimized S0 geometry using CAM-B3LYP (gas phase/ def2-tzvpp def2/j). The CAM-B3LYP functional is a range-separated functional, and uses 19 % Hartree-Fock exchange at short range, 33 % Hartree-Fock exchange at intermediate range, and 65 % Hartree-Fock exchange at long range.[15]

[b] The general formulation of a sigma natural bond orbital (NBO) is $\sigma_{AB} = c_A h_A + c_B h_B$, where h_A and h_B are the atom-centered hybrid orbitals of atoms A and B, and c_A and c_B are the normalized polarization coefficients of atoms A and B. If the natural ionicity of an NBO, given by $i_{AB} = \frac{(cA^2 - cB^2)}{(cA^2 + CB^2)}$, exceeds a fixed limit ($|i_{AB}|>0.95$), this extremely polarized "bond" is identified instead as a lone pair.[20]

[c] Orbital occupancy ($0 \leq x \leq 2$) is the number of electrons in the specified NBO. Lower orbital occupancy values are indicative of stronger delocalization.[20]

[d] Hybridization of a given NBO is of the form sp^{λ}, where $\lambda = (\frac{\%p}{\%s})$.[20] Hybridizations with a very high value of λ (for example, sp^{∞}) have been denoted as non-applicable.

[e] Atomic orbital contributions denote the percent contribution of s, p, d, and f orbitals from atom A, and the percent contribution of s, p, d, and f orbitals from atom B, to their shared NBO σ_{AB} or π_{AB}.[20] Contributions from d and f orbitals are negligible and are omitted for simplicity. The percent contributions from each atom A (c_A^2 x 100%) and B (c_B^2 x 100%) to their shared NBO are also shown.

NMR spectra

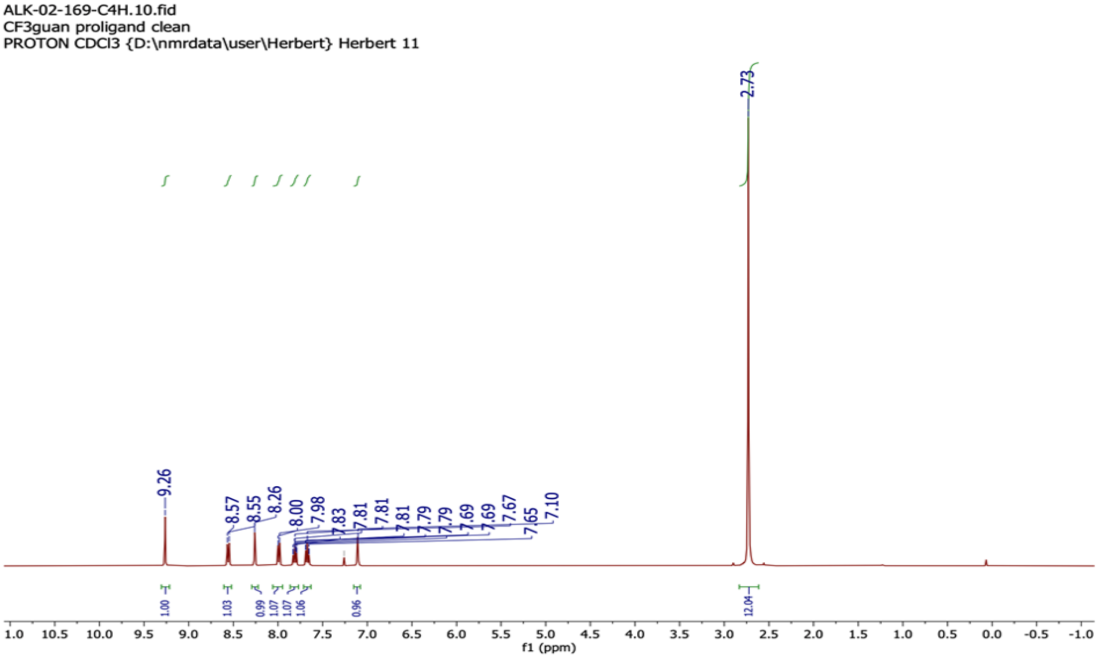


Figure S28. ^{1}H NMR (400 MHz, CDCl$_3$, 22 °C) of (4-tetramethylguanidino)(2-trifluoromethyl)phenanthridine ($^{\text{CF3}}$**L1**).

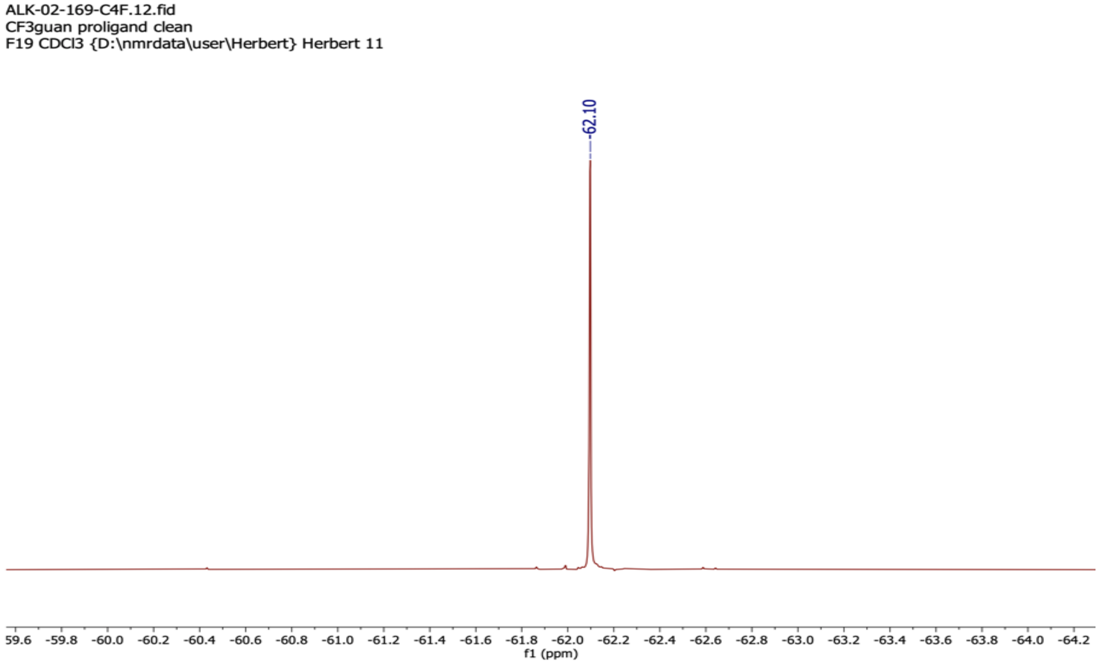


Figure S29. ^{19}F{^{1}H} NMR (377 MHz, CDCl$_3$, 22 °C) of (4-tetramethylguanidino)(2-trifluoromethyl)phenanthridine ($^{\text{CF3}}$**L1**).

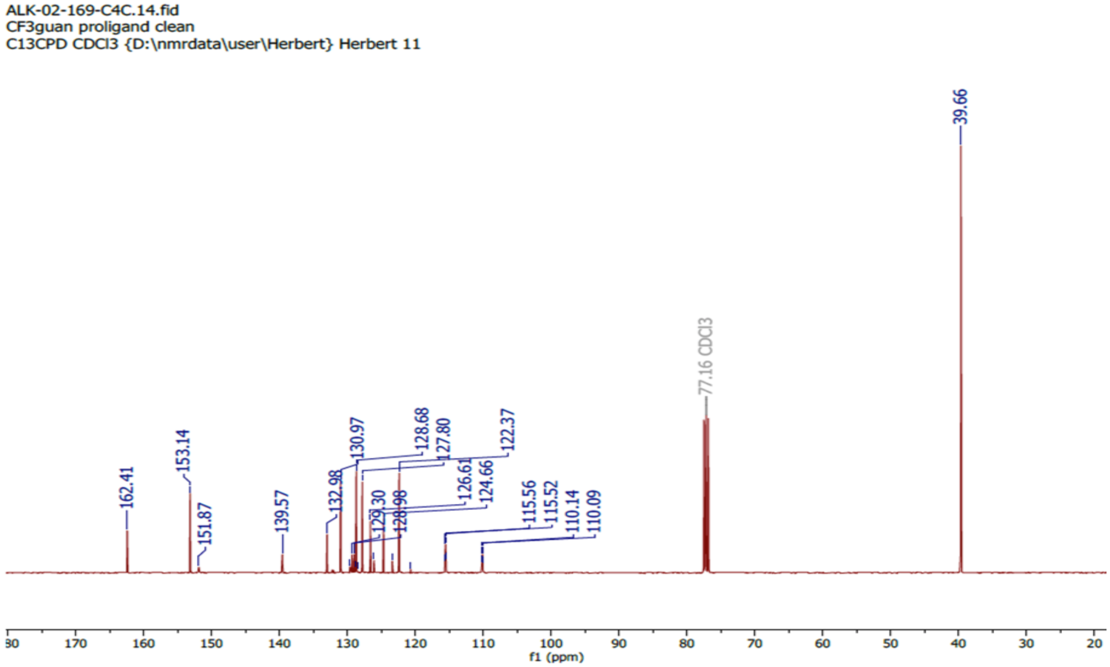


Figure S30. ^{13}C NMR (101 MHz, CDCl$_3$, 22 °C) of (4-tetramethylguanidino)(2-trifluoromethyl)phenanthridine ($^{\mathbf{CF3}}$**L1**).

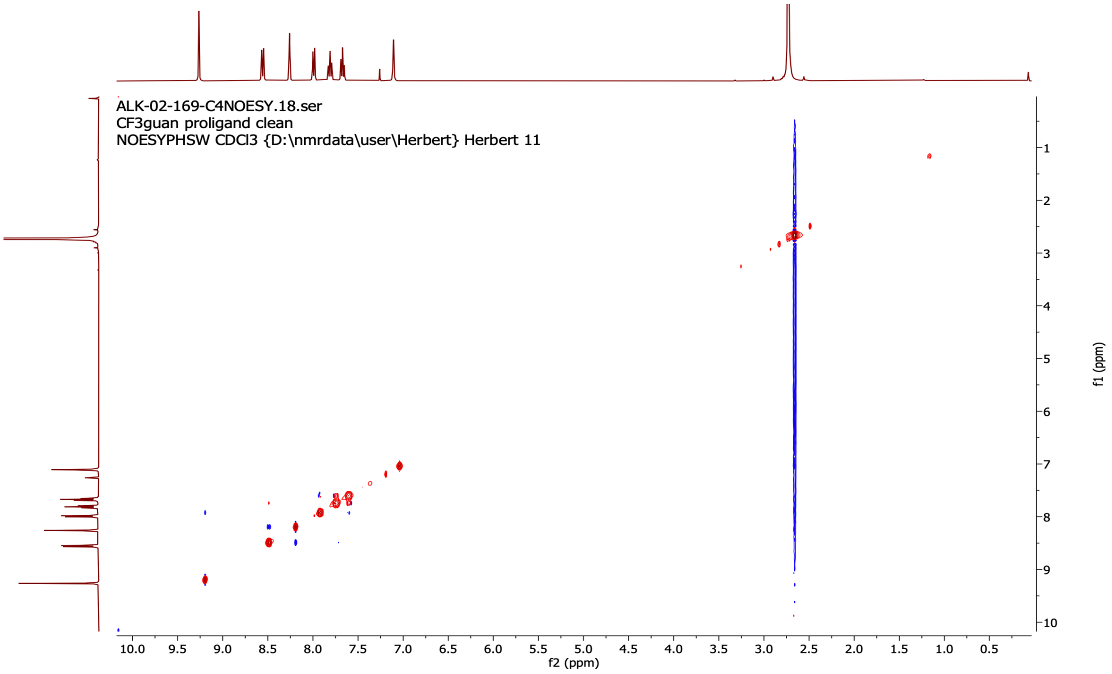


Figure S31. ^{1}H-^{13}C HSQC NMR (101 MHz, CDCl$_3$, 22 °C) of (4-tetramethylguanidino)(2-trifluoromethyl)phenanthridine ($^{\mathbf{CF3}}$**L1**).

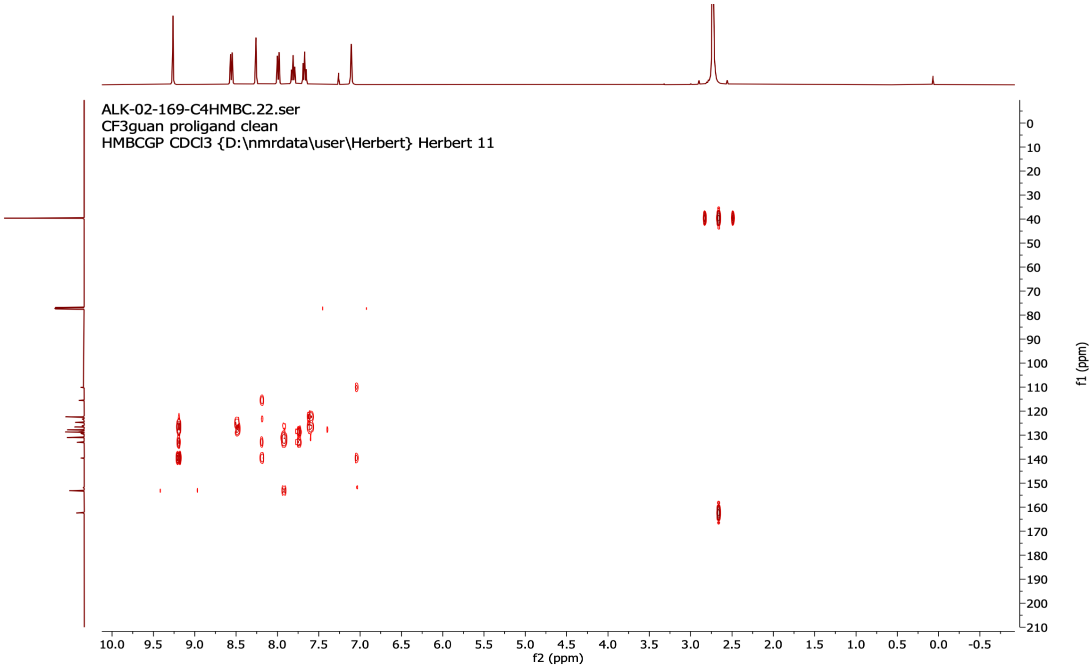


Figure S32. ^{1}H-^{13}C HMBC NMR (101 MHz, CDCl$_3$, 22 °C) of (4-tetramethylguanidino)(2-trifluoromethyl)phenanthridine ($^{\mathbf{CF3}}$**L1**).

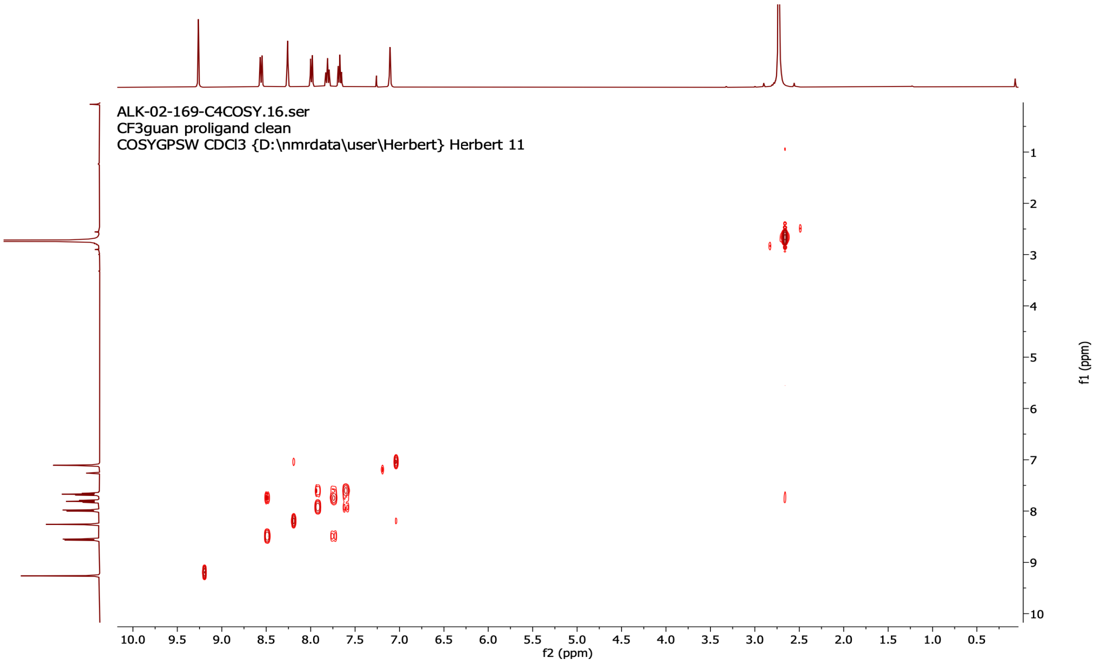


Figure S33. ^{1}H-^{1}H COSY NMR (400 MHz, CDCl$_3$, 22 °C) of (4-tetramethylguanidino)(2-trifluoromethyl)phenanthridine ($^{\mathbf{CF3}}$**L1**).

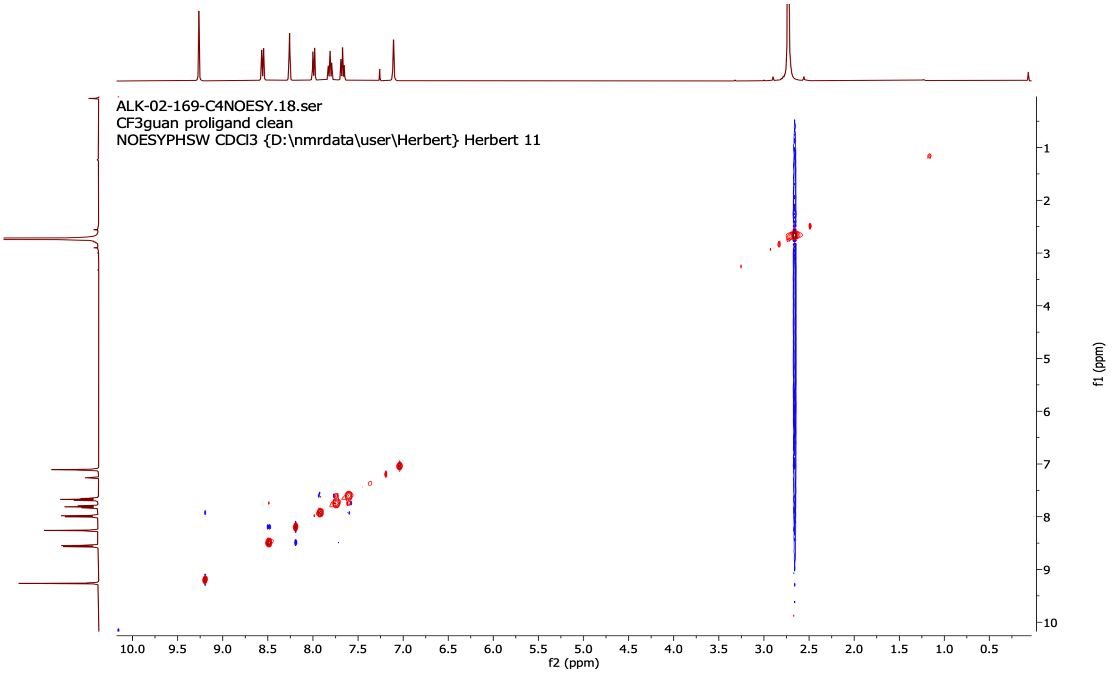


Figure S34. ^{1}H-^{1}H NOESY NMR (400 MHz, CDCl$_3$, 22 °C) of (4-tetramethylguanidino)(2-trifluoromethyl)phenanthridine ($^{\mathbf{CF3}}$**L1**).

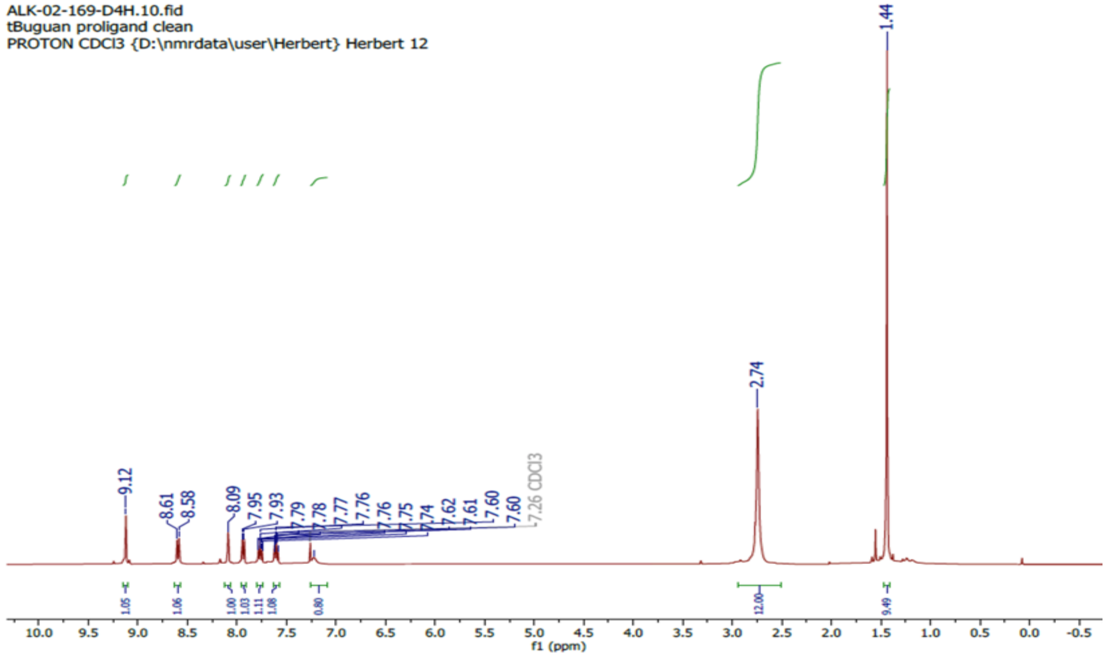


Figure S35. ^{1}H NMR (400 MHz, CDCl$_3$, 22 °C) of (2-tert-butyl)(4-tetramethylguanidino)phenanthridine ($^{\mathbf{\mathit{t}Bu}}$**L1**).

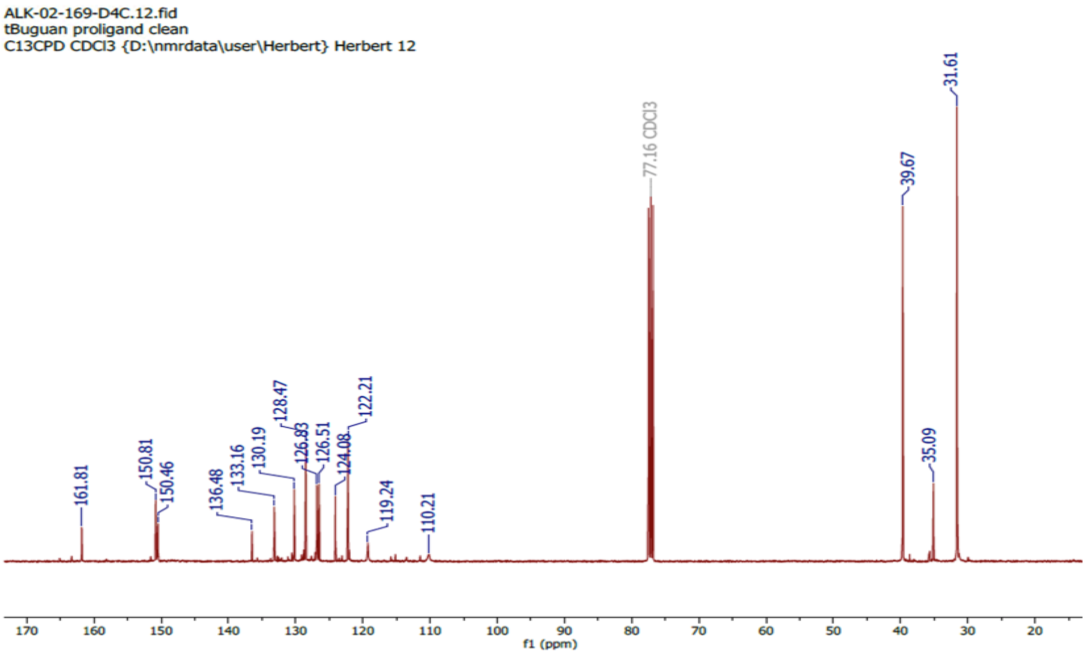


Figure S36. ^{13}C NMR (101 MHz, $CDCl_3$, 22 °C) of (2-tert-butyl)(4-tetramethylguanidino)phenanthridine (^{tBu}**L1**).

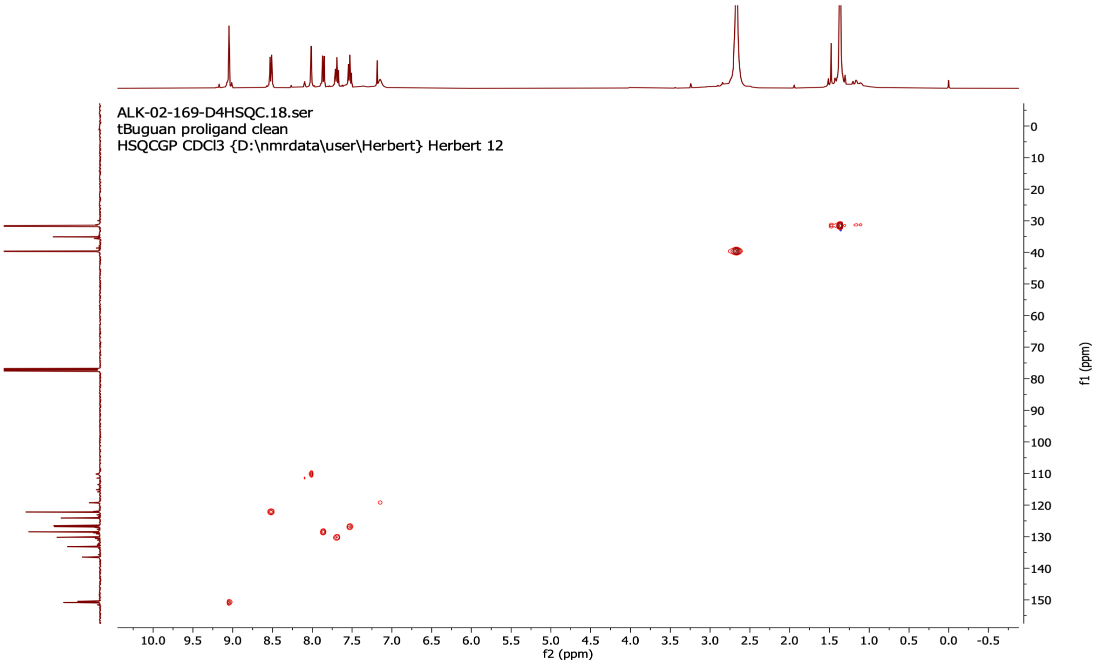


Figure S37. ^{1}H-^{13}C HSQC NMR (101 MHz, $CDCl_3$, 22 °C) of (2-tert-butyl)(4-tetramethylguanidino)phenanthridine (^{tBu}**L1**).

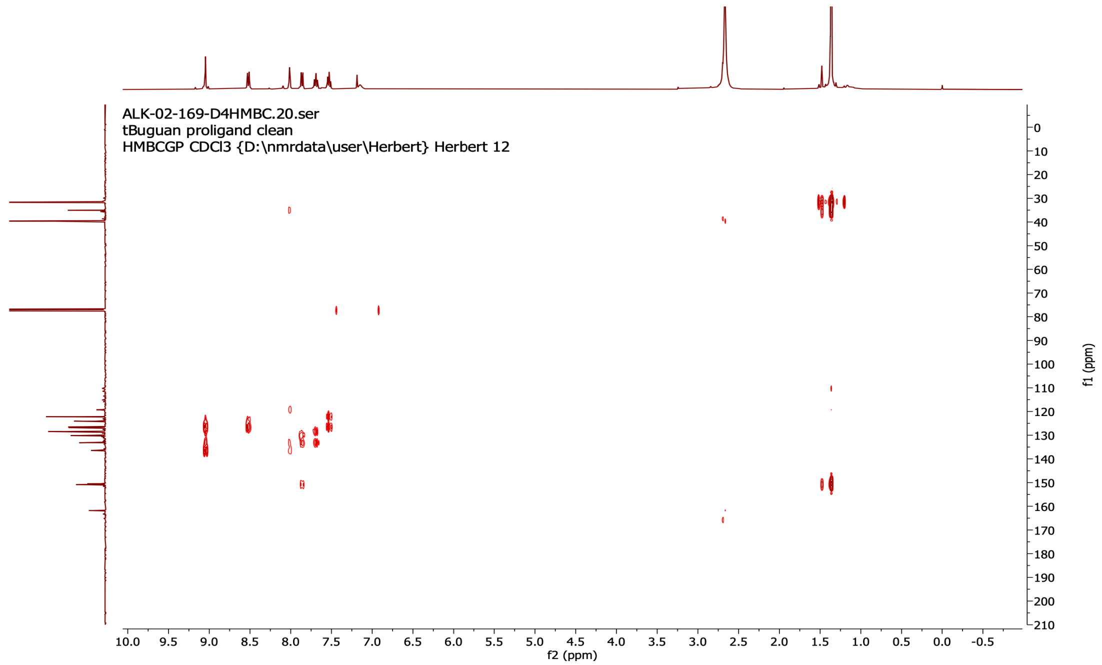


Figure S38. ^{1}H-^{13}C HMBC NMR (101 MHz, $CDCl_3$, 22 °C) of (2-tert-butyl)(4-tetramethylguanidino)phenanthridine (^{tBu}**L1**).

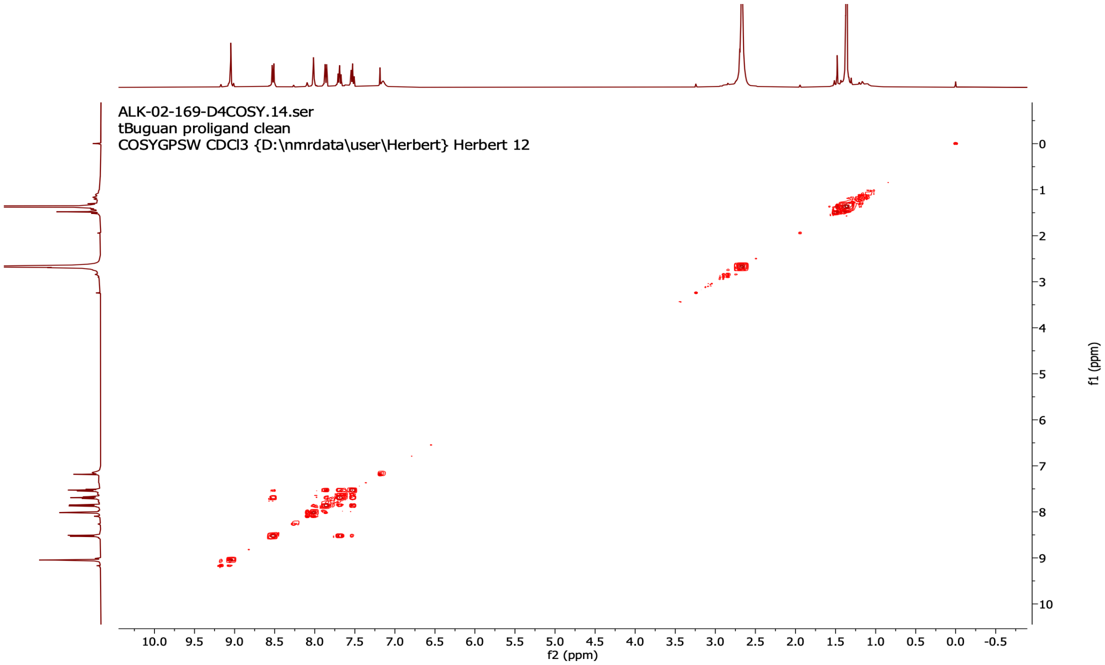


Figure S39. ^{1}H-^{1}H COSY NMR (400 MHz, $CDCl_3$, 22 °C) of (2-tert-butyl)(4-tetramethylguanidino)phenanthridine (^{tBu}**L1**).

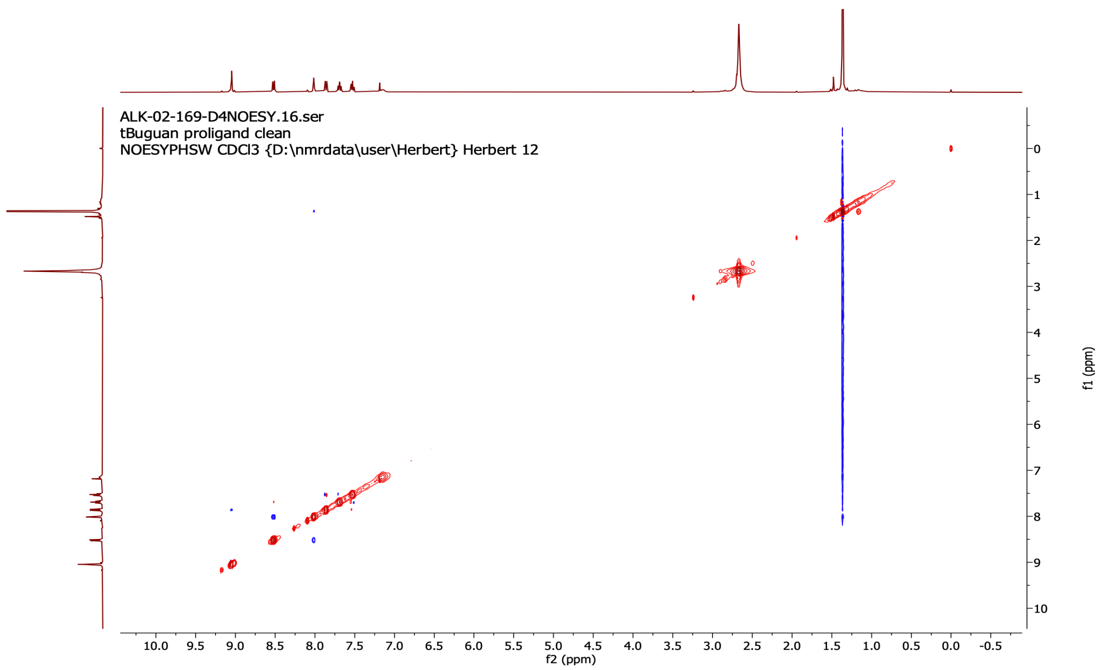


Figure S40. ^{1}H-^{1}H NOESY NMR (400 MHz, $CDCl_3$, 22 °C) of (2-tert-butyl)(4-tetramethylguanidino)phenanthridine (***^{tBu}*L1**).

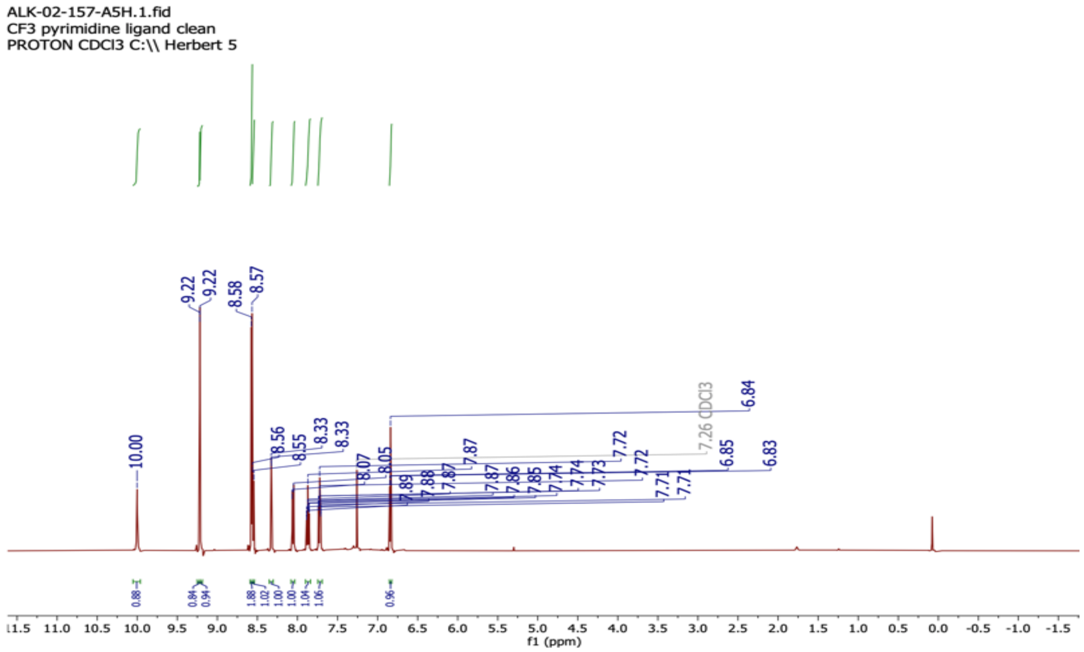


Figure S41. ^{1}H NMR (500 MHz, $CDCl_3$, 22 °C) of (4-aminopyrimidino)(2-trifluoromethyl)phenanthridine (**^{CF3}L2**).

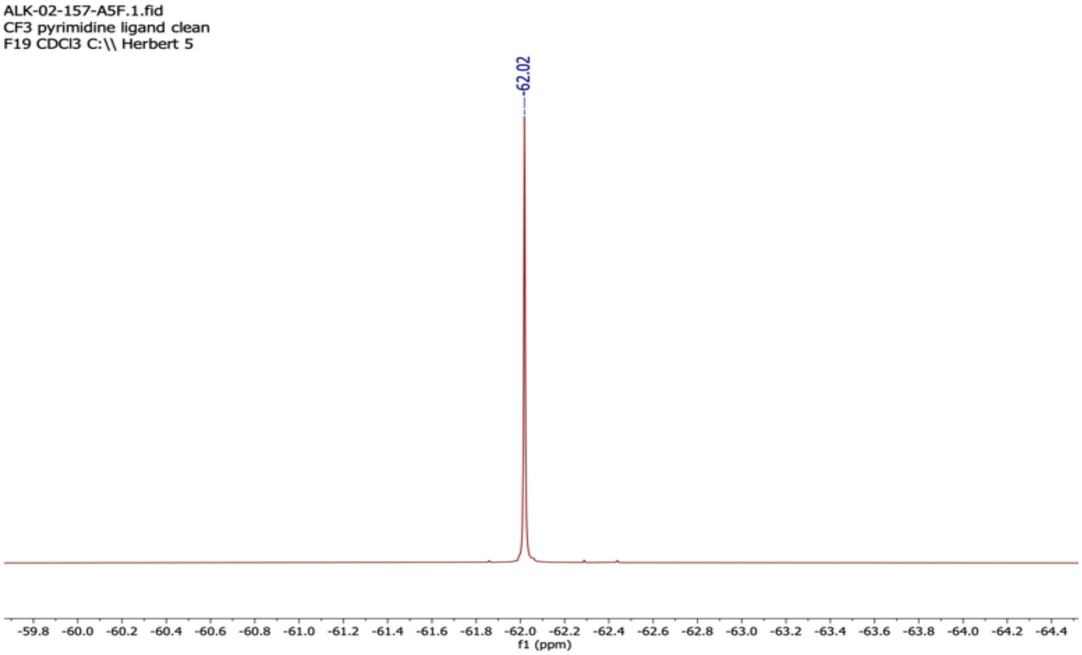


Figure S42. $^{19}F\{^{1}H\}$ NMR (471 MHz, $CDCl_3$, 22 °C) of (4-aminopyrimidino)(2-trifluoromethyl)phenanthridine (**^{CF3}L2**).

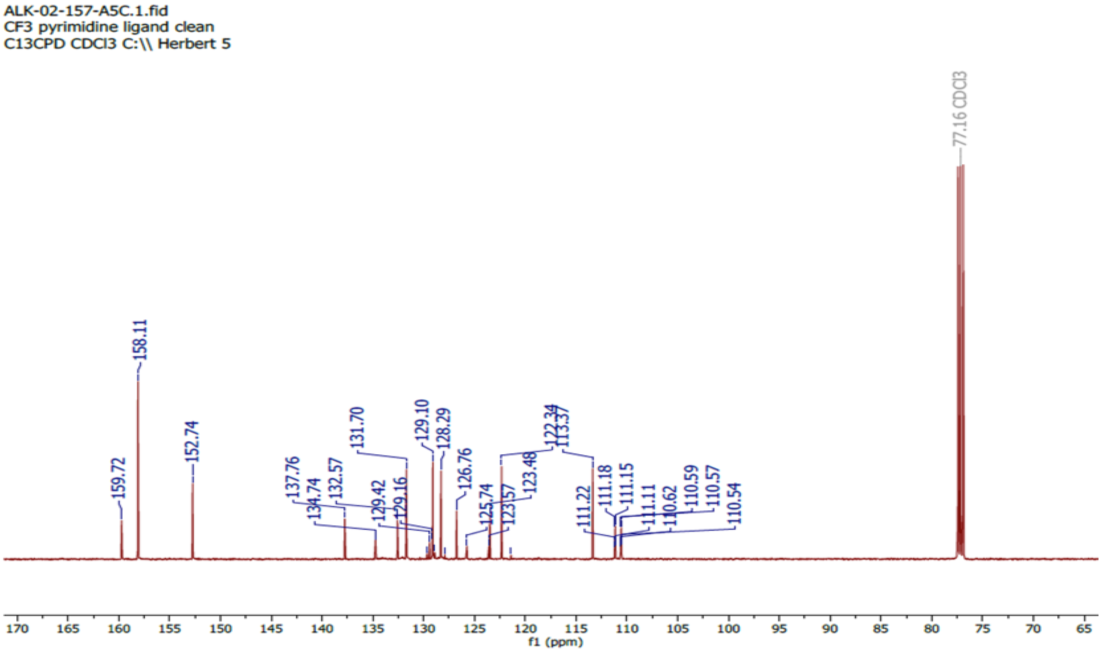


Figure S43. ^{13}C NMR (126 MHz, $CDCl_3$, 22 °C) of (4-aminopyrimidino)(2-trifluoromethyl)phenanthridine (**^{CF3}L2**).

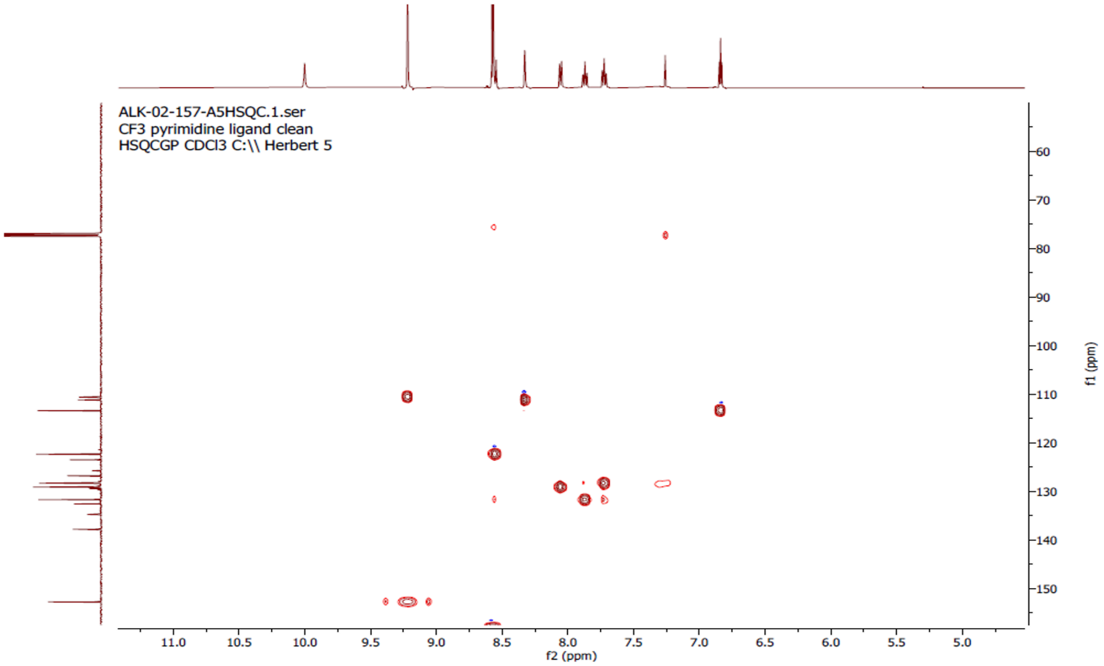


Figure S44. ^{1}H-^{13}C HSQC NMR (126 MHz, $CDCl_3$, 22 °C) of (4-aminopyrimidino)(2-trifluoromethyl)phenanthridine (**^{CF3}L2**).

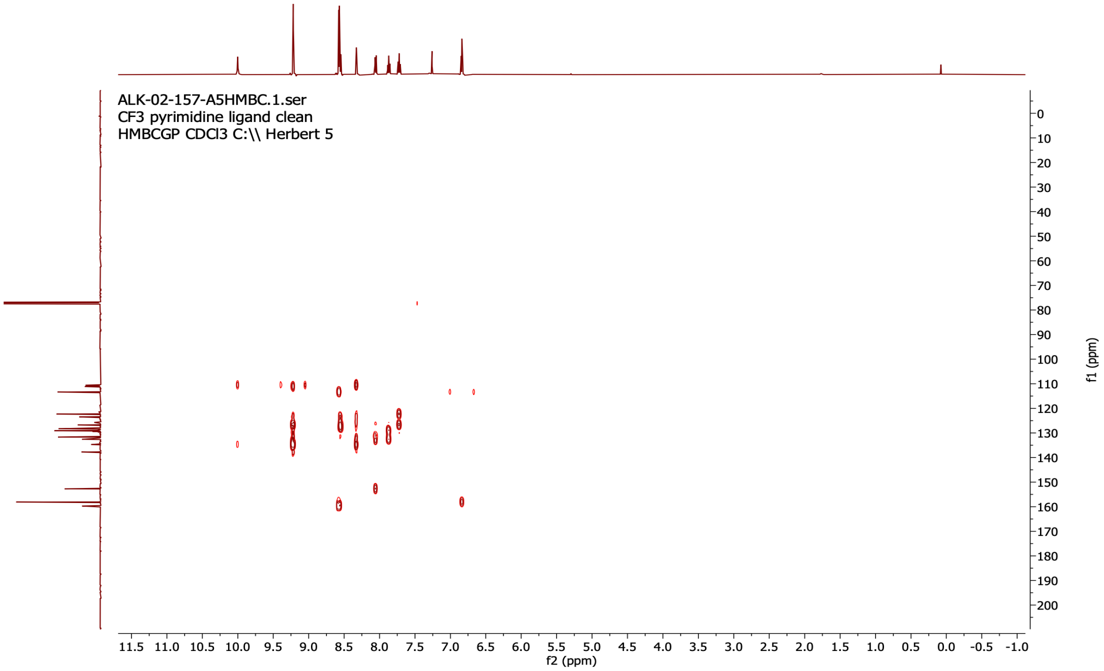


Figure S45. ^{1}H-^{13}C HMBC NMR (126 MHz, $CDCl_3$, 22 °C) of (4-aminopyrimidino)(2-trifluoromethyl)phenanthridine (**^{CF3}L2**).

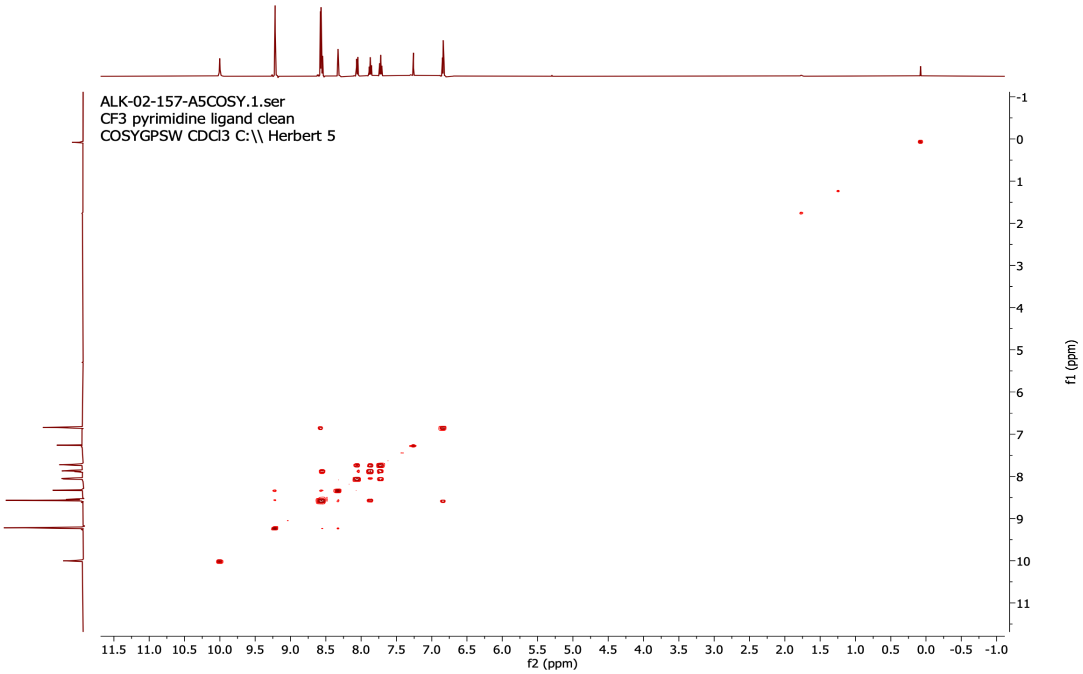


Figure S46. ^{1}H-^{1}H COSY NMR (500 MHz, $CDCl_3$, 22 °C) of (4-aminopyrimidino)(2-trifluoromethyl)phenanthridine ($^{\mathbf{CF3}}$**L2**).

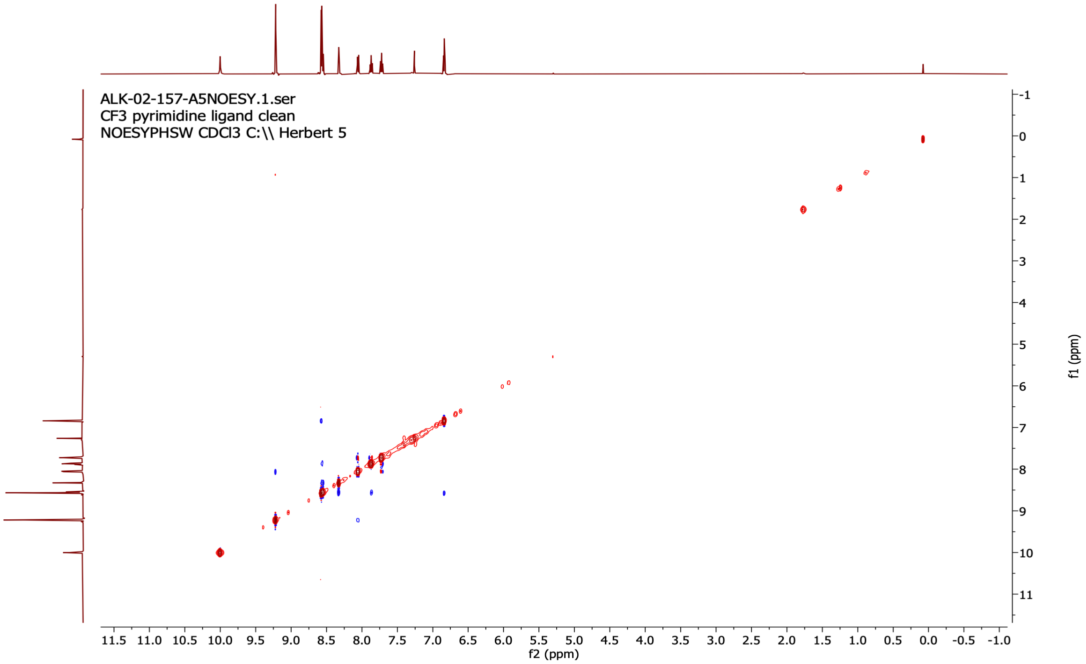


Figure S47. ^{1}H-^{1}H NOESY NMR (500 MHz, $CDCl_3$, 22 °C) of (4-aminopyrimidino)(2-trifluoromethyl)phenanthridine ($^{\mathbf{CF3}}$**L2**).

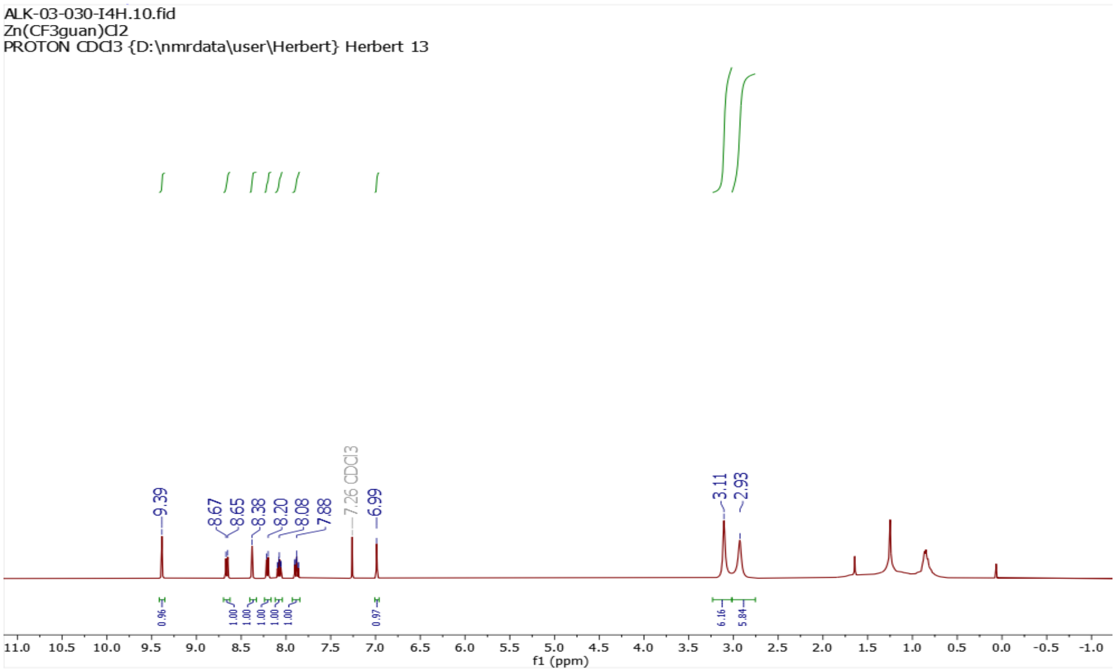


Figure S48. ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C) of (4-tetramethylguanidino)(2-trifluoromethyl)phenanthridine zinc chloride (($^{\mathbf{CF3}}$**L1**)$ZnCl_2$).

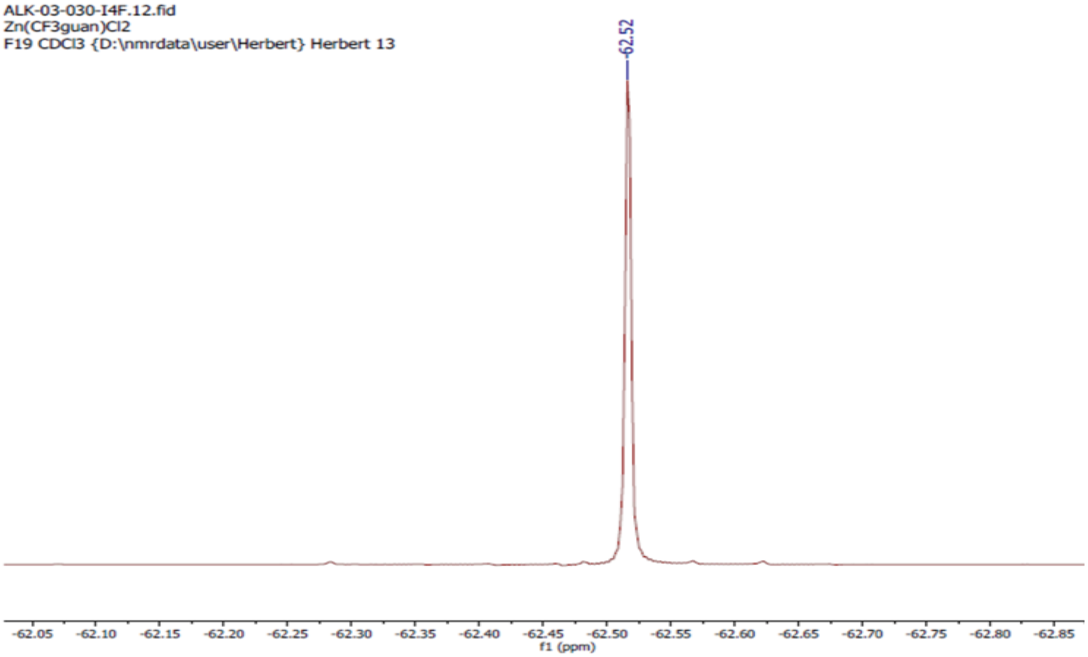


Figure S49. ^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$, 22 °C) of (4-tetramethylguanidino)(2-trifluoromethyl)phenanthridine zinc chloride (($^{\mathbf{CF3}}$**L1**)$ZnCl_2$).

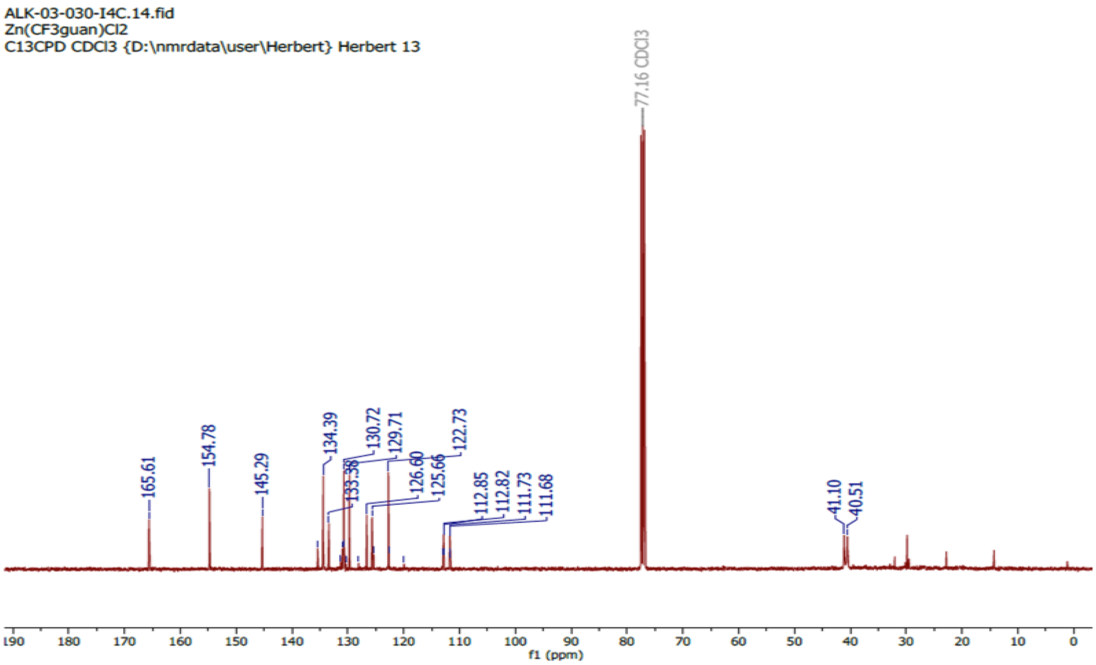


Figure S50. ^{13}C NMR (101 MHz, $CDCl_3$, 22 °C) of (4-tetramethylguanidino)(2-trifluoromethyl)phenanthridine zinc chloride ((^{CF3}**L1**)$ZnCl_2$).

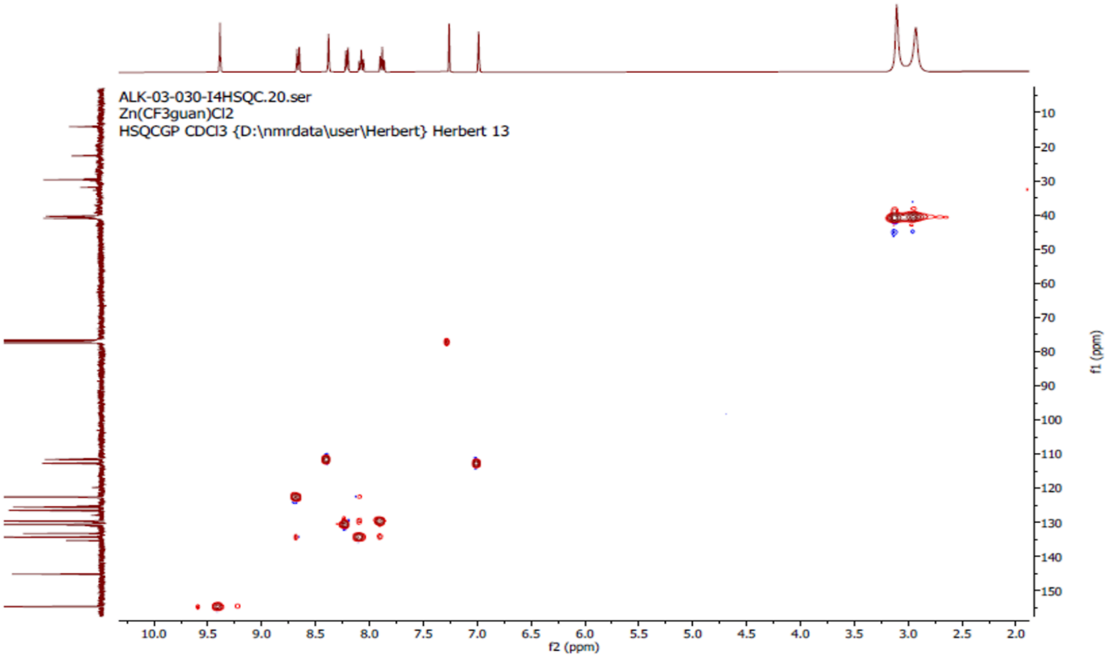


Figure S51. ^{1}H-^{13}C HSQC NMR (101 MHz, $CDCl_3$, 22 °C) of (4-tetramethylguanidino)(2-trifluoromethyl)phenanthridine zinc chloride ((^{CF3}**L1**)$ZnCl_2$).

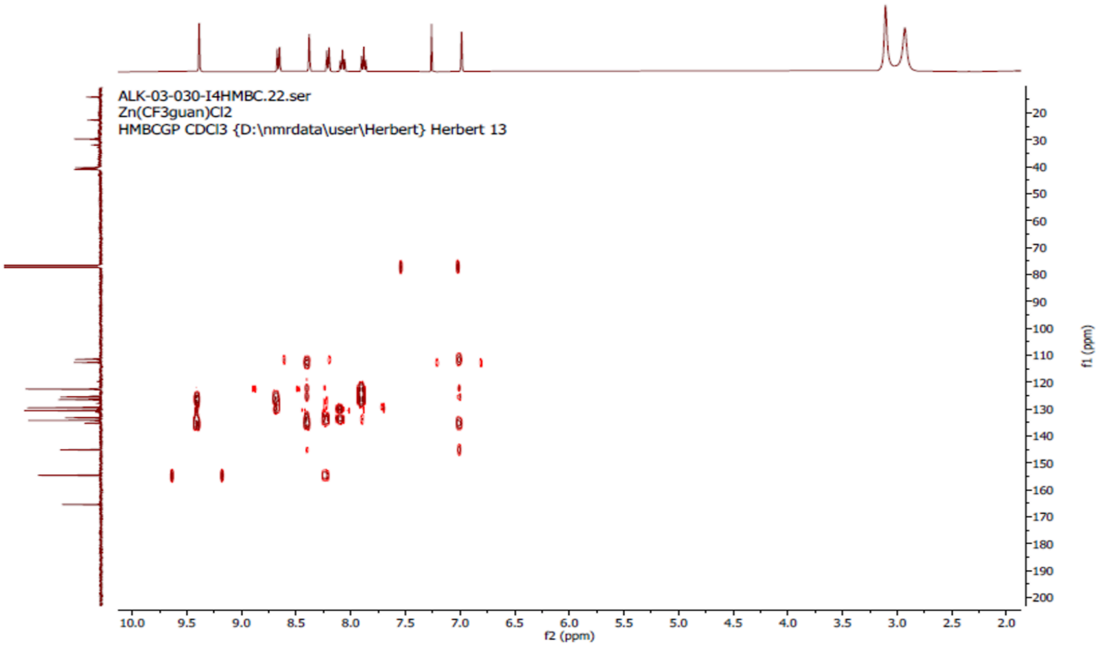


Figure S52. ^{1}H-^{13}C HMBC NMR (101 MHz, $CDCl_3$, 22 °C) of (4-tetramethylguanidino)(2-trifluoromethyl)phenanthridine zinc chloride (($^{\mathbf{CF3}}$**L1**)$ZnCl_2$).

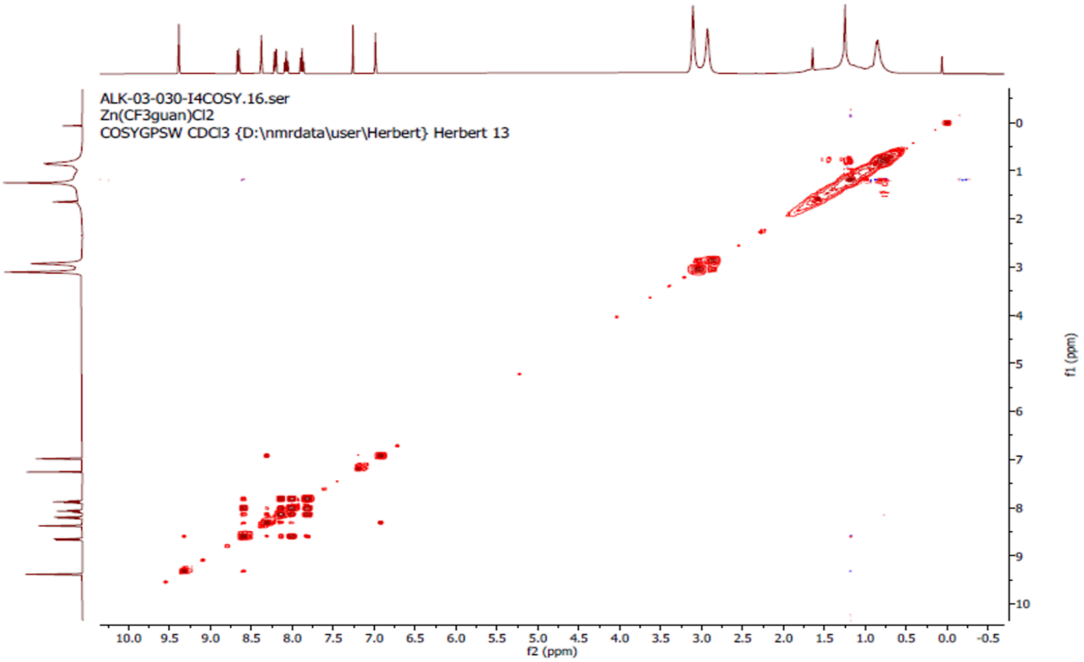


Figure S53. ^{1}H-^{1}H COSY NMR (400 MHz, $CDCl_3$, 22 °C) of (4-tetramethylguanidino)(2-trifluoromethyl)phenanthridine zinc chloride (($^{\mathbf{CF3}}$**L1**)$ZnCl_2$).

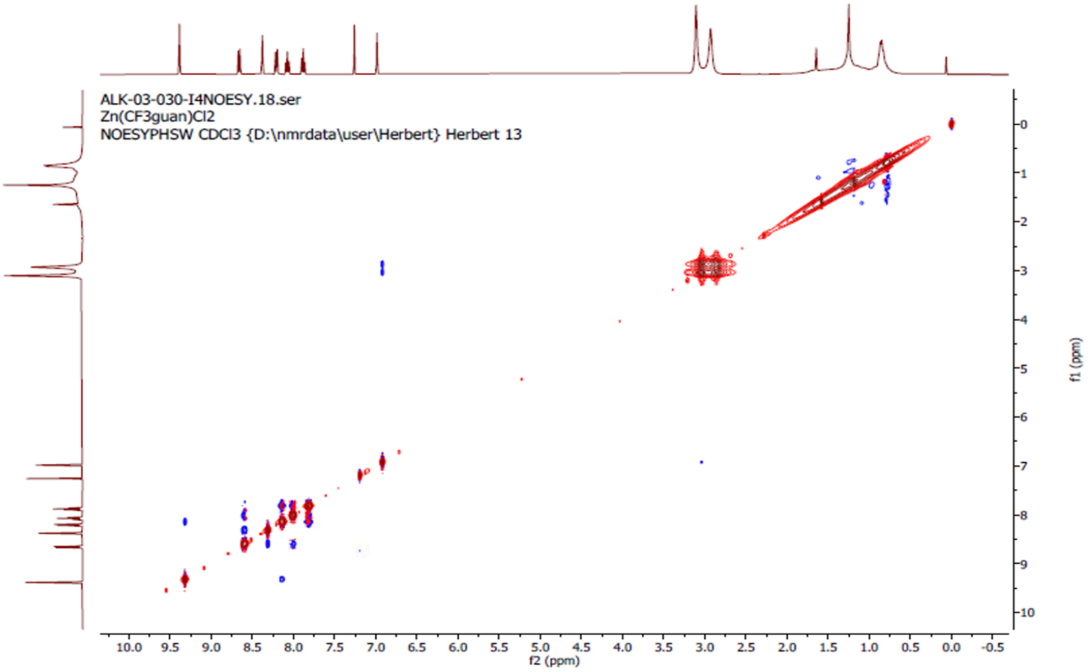


Figure S54. ^{1}H-^{1}H NOESY NMR (400 MHz, $CDCl_3$, 22 °C) of (4-tetramethylguanidino)(2-trifluoromethyl)phenanthridine zinc chloride ((^{CF3}**L1**)$ZnCl_2$).

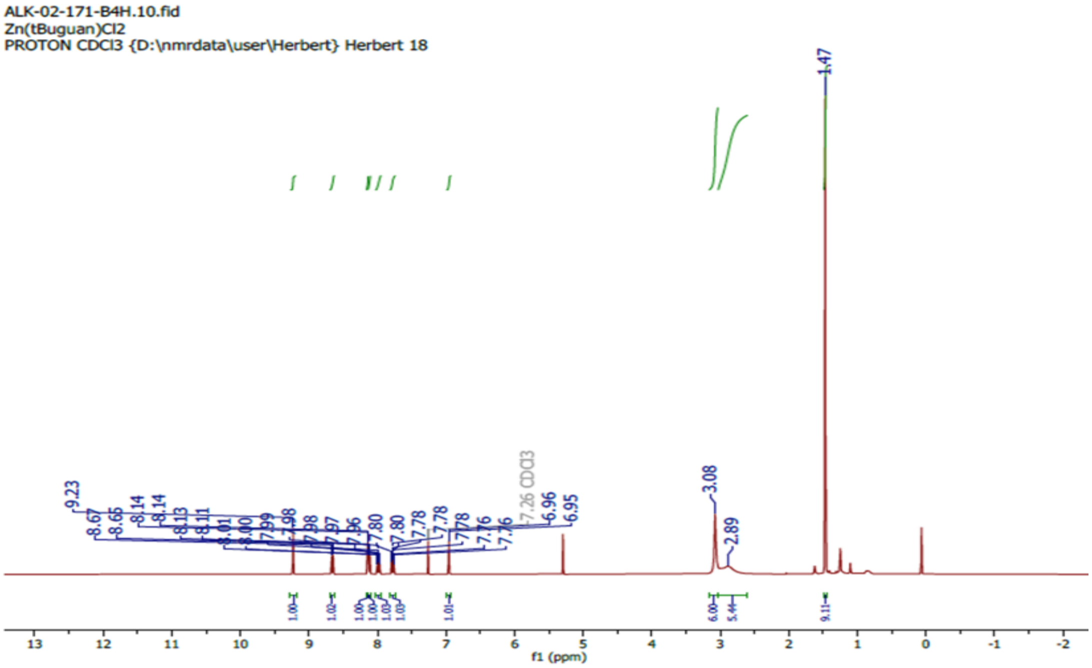


Figure S55. ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C) of (2-tert-butyl)(4-tetramethylguanidino)phenanthridine zinc chloride ((^{tBu}**L1**)$ZnCl_2$).

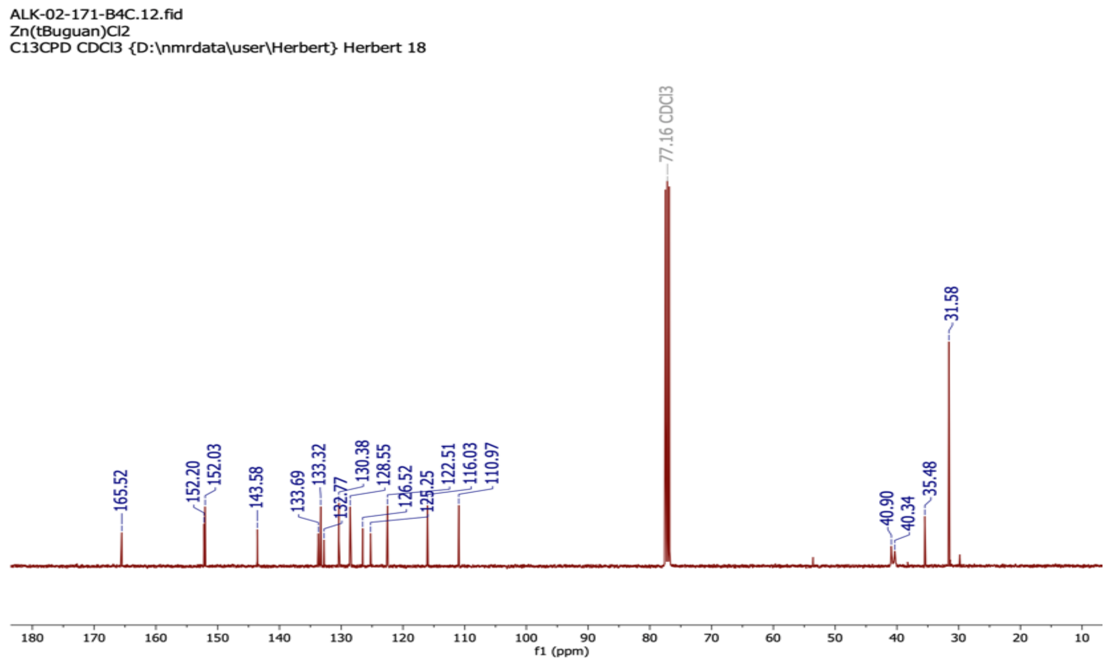


Figure S56. ^{13}C NMR (101 MHz, $CDCl_3$, 22 °C) of (2-tert-butyl)(4-tetramethylguanidino)phenanthridine zinc chloride ((^{tBu}**L1**)$ZnCl_2$).

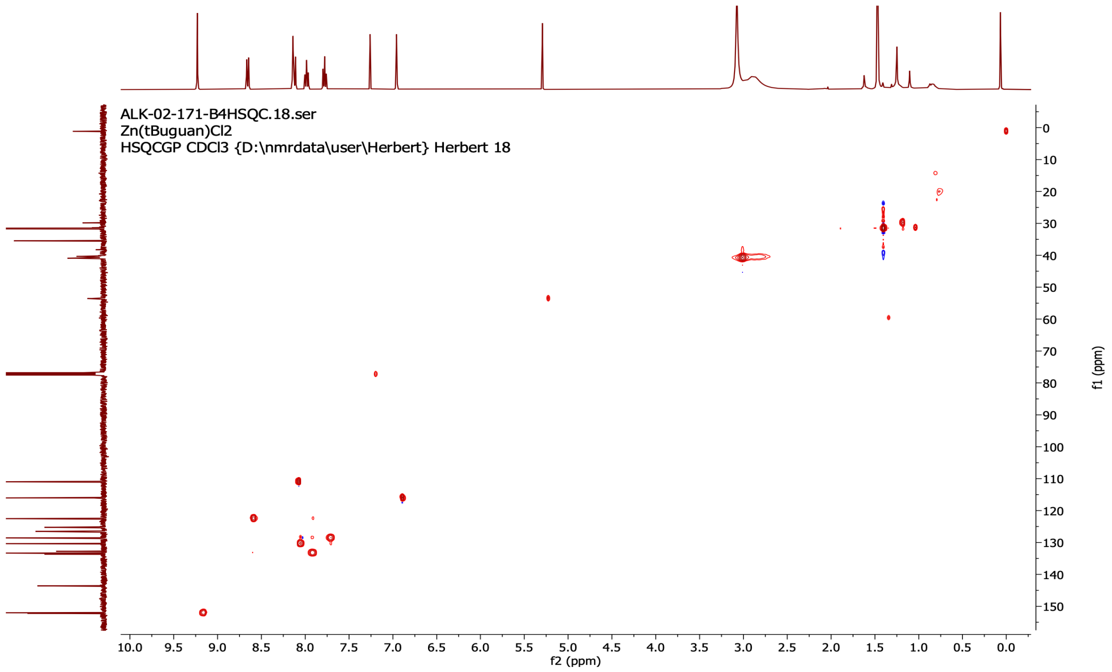


Figure S57. ^{1}H-^{13}C HSQC NMR (101 MHz, $CDCl_3$, 22 °C) of (2-tert-butyl)(4-tetramethylguanidino)phenanthridine zinc chloride ((^{tBu}**L1**)$ZnCl_2$).

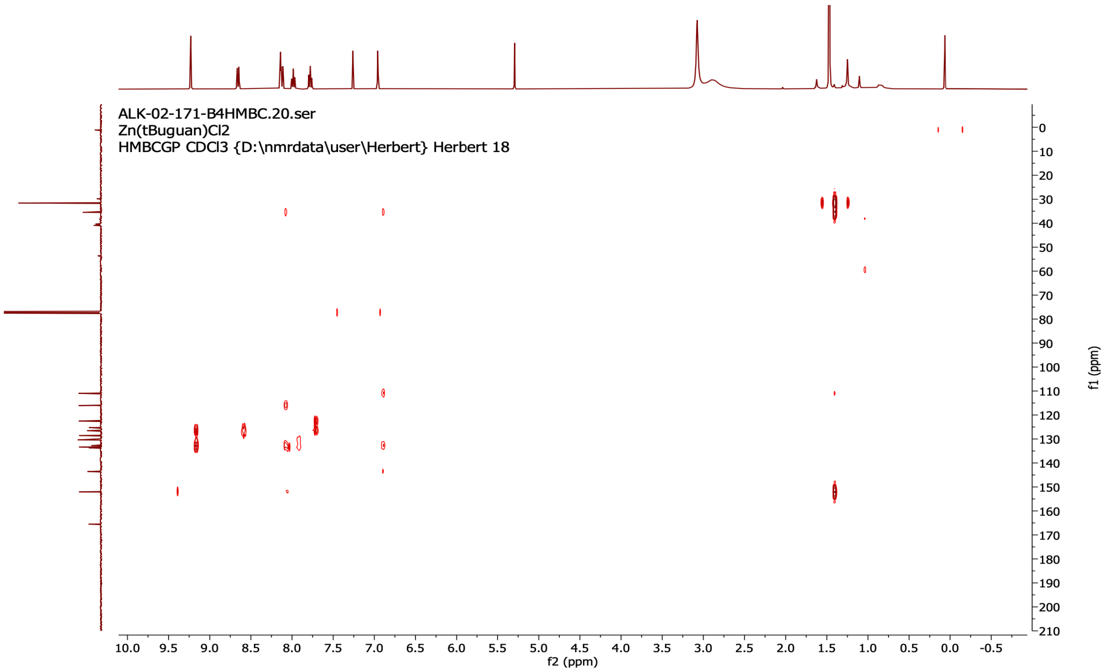


Figure S58. ^{1}H-^{13}C HMBC NMR (101 MHz, $CDCl_3$, 22 °C) of (2-tert-butyl)(4-tetramethylguanidino)phenanthridine zinc chloride ((*^{t}*$^{\mathbf{Bu}}$**L1**)$ZnCl_2$).

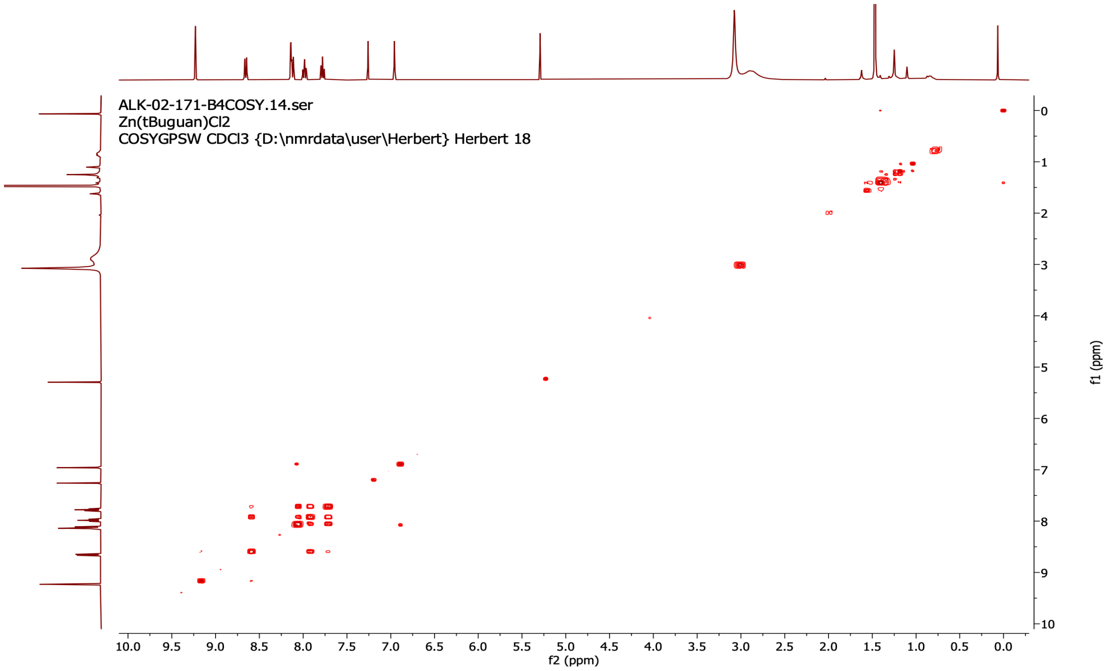


Figure S59. ^{1}H-^{1}H COSY NMR (400 MHz, $CDCl_3$, 22 °C) of (2-tert-butyl)(4-tetramethylguanidino)phenanthridine zinc chloride ((*^{t}*$^{\mathbf{Bu}}$**L1**)$ZnCl_2$).

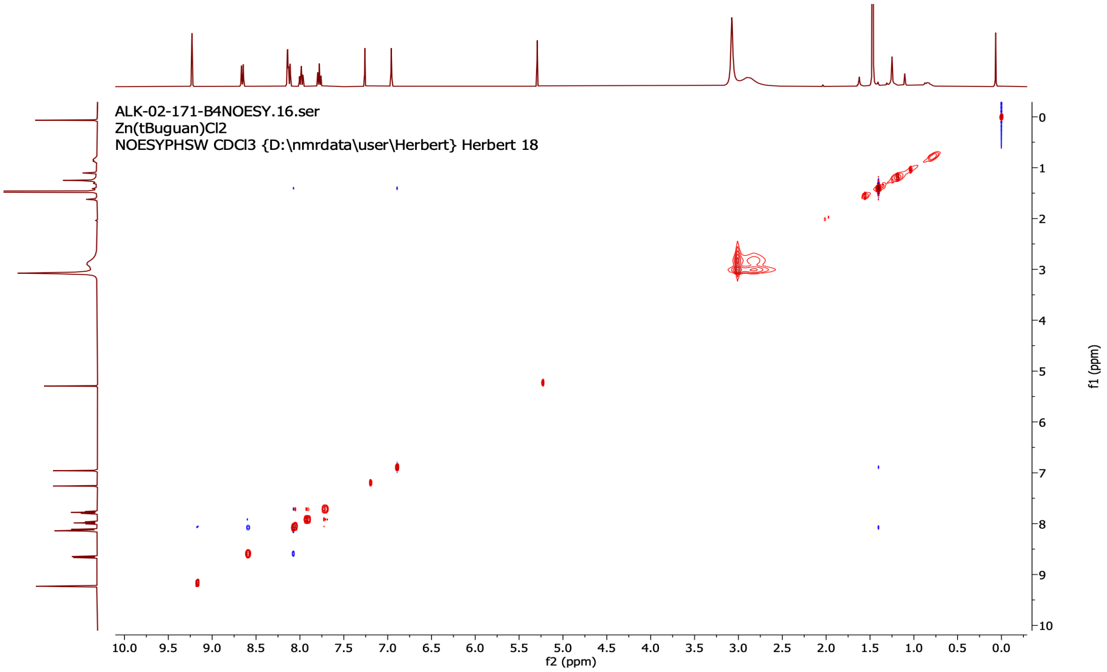


Figure S60. ^{1}H-^{1}H NOESY NMR (400 MHz, $CDCl_3$, 22 °C) of (2-tert-butyl)(4-tetramethylguanidino)phenanthridine zinc chloride (($^{t\mathbf{Bu}}$**L1**)$ZnCl_2$).

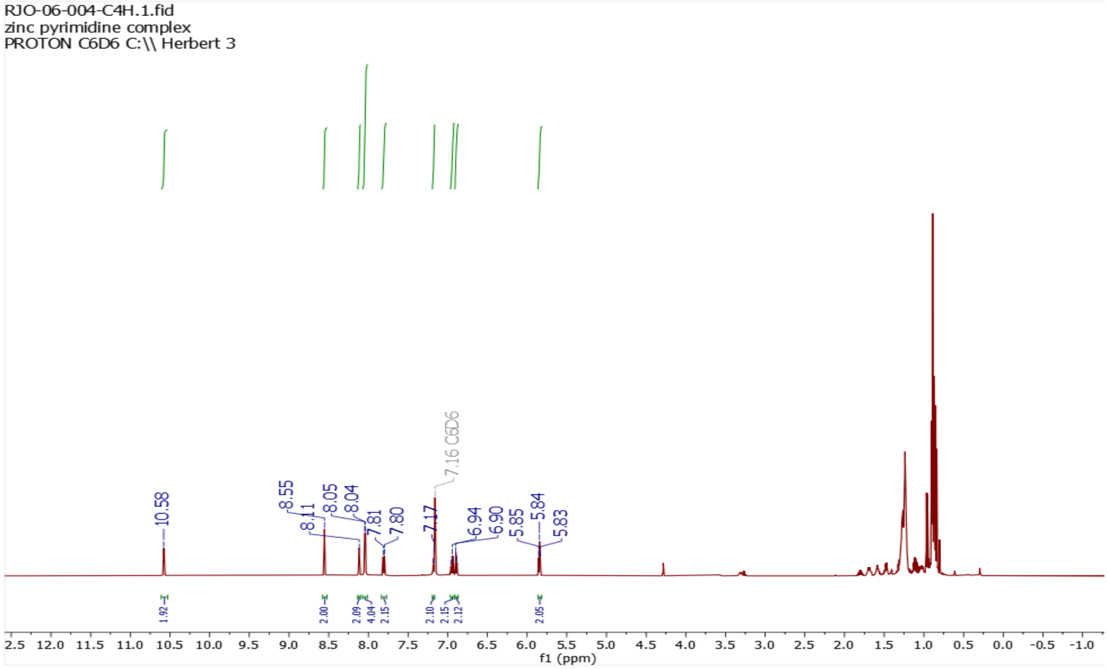


Figure S61. ^{1}H NMR (400 MHz, C_6D_6, 22 °C) of bis-(4-aminopyrimidino)(2-trifluoromethyl)phenanthridine zinc (($^{\mathbf{CF3}}$**L2**)$_2$Zn).

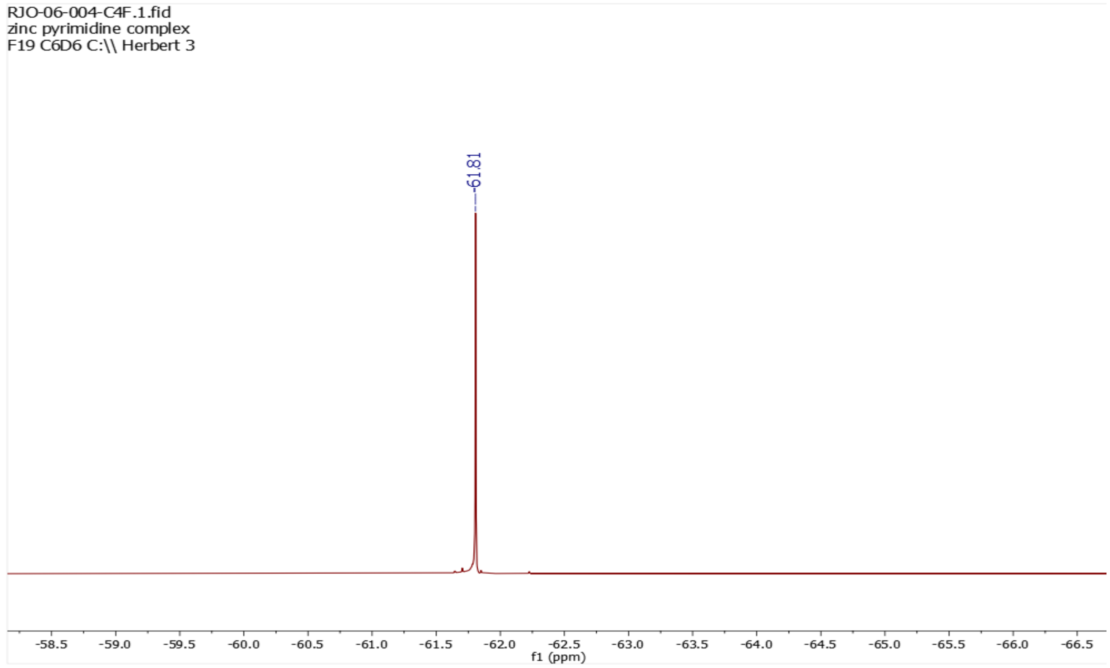


Figure S62. $^{19}F\{^{1}H\}$ NMR (377 MHz, C_6D_6, 22 °C) of bis-(4-aminopyrimidino)(2-trifluoromethyl)phenanthridine zinc $((^{\mathbf{CF3}}\mathbf{L2})_2Zn)$.

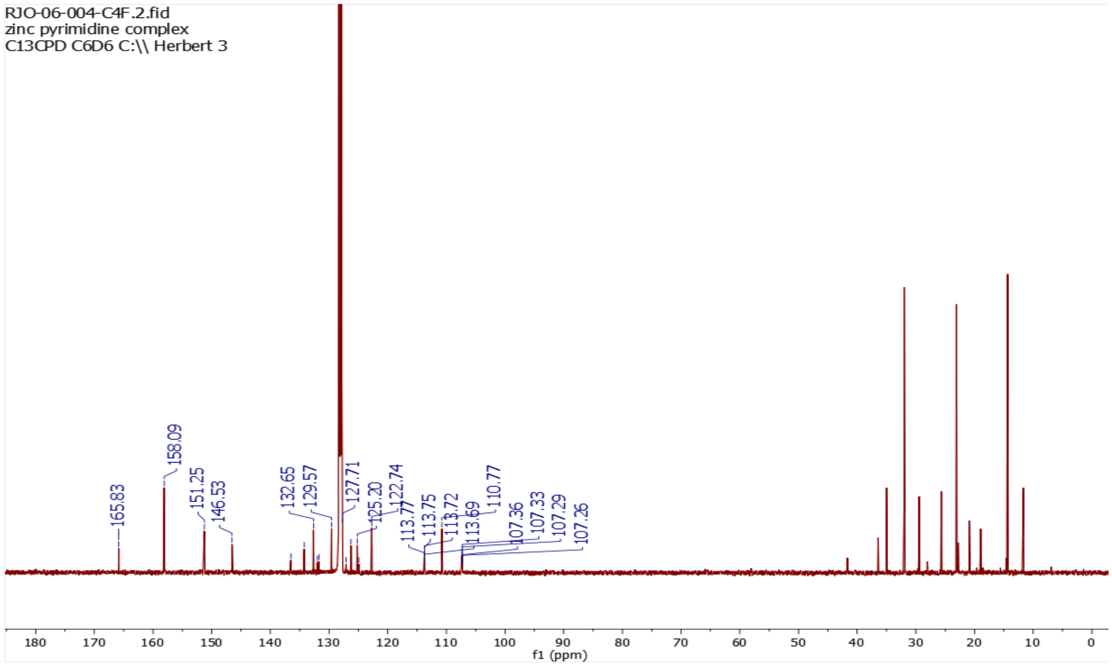


Figure S63. ^{13}C NMR (101 MHz, C_6D_6, 22 °C) of bis-(4-aminopyrimidino)(2-trifluoromethyl)phenanthridine zinc $((^{\mathbf{CF3}}\mathbf{L2})_2Zn)$.

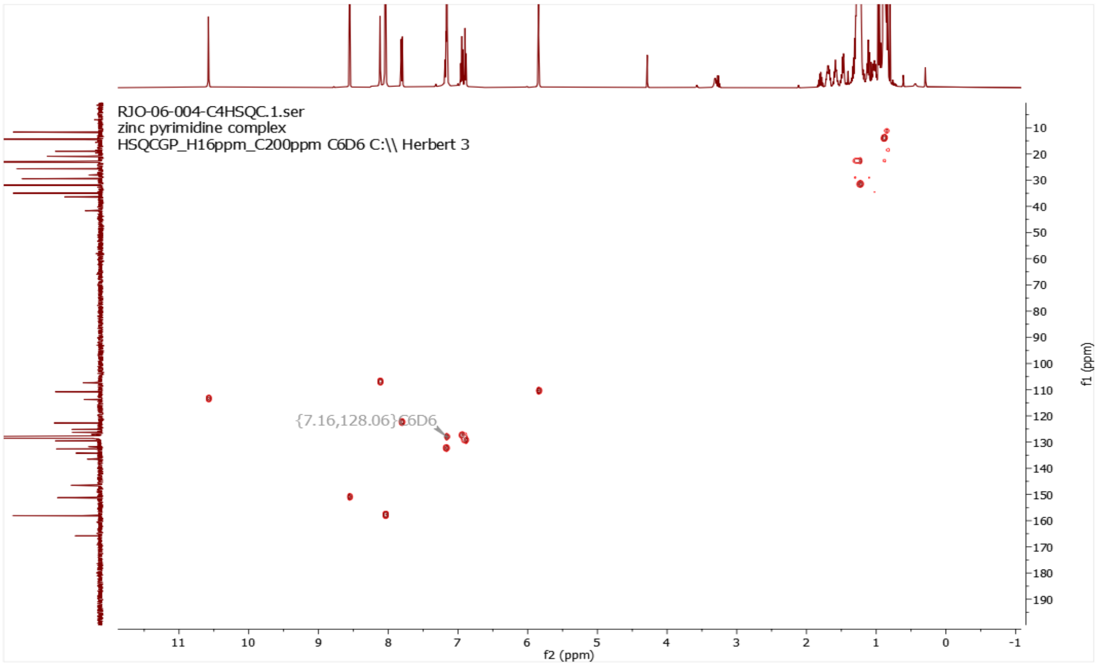


Figure S64. ^{1}H-^{13}C HSQC NMR (101 MHz, CDCl$_3$, 22 °C) of bis-(4-aminopyrimidino)(2-trifluoromethyl)phenanthridine zinc (($^{\mathbf{CF3}}$**L2**)$_2$Zn).

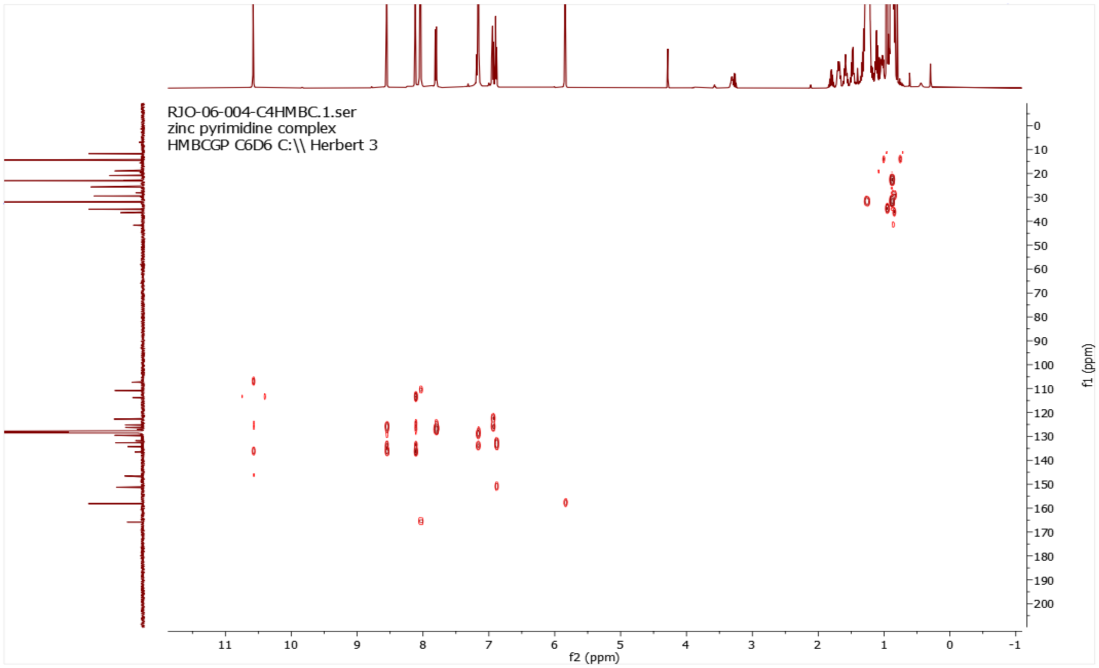


Figure S65. ^{1}H-^{13}C HMBC NMR (101 MHz, CDCl$_3$, 22 °C) of bis-(4-aminopyrimidino)(2-trifluoromethyl)phenanthridine zinc (($^{\mathbf{CF3}}$**L2**)$_2$Zn).

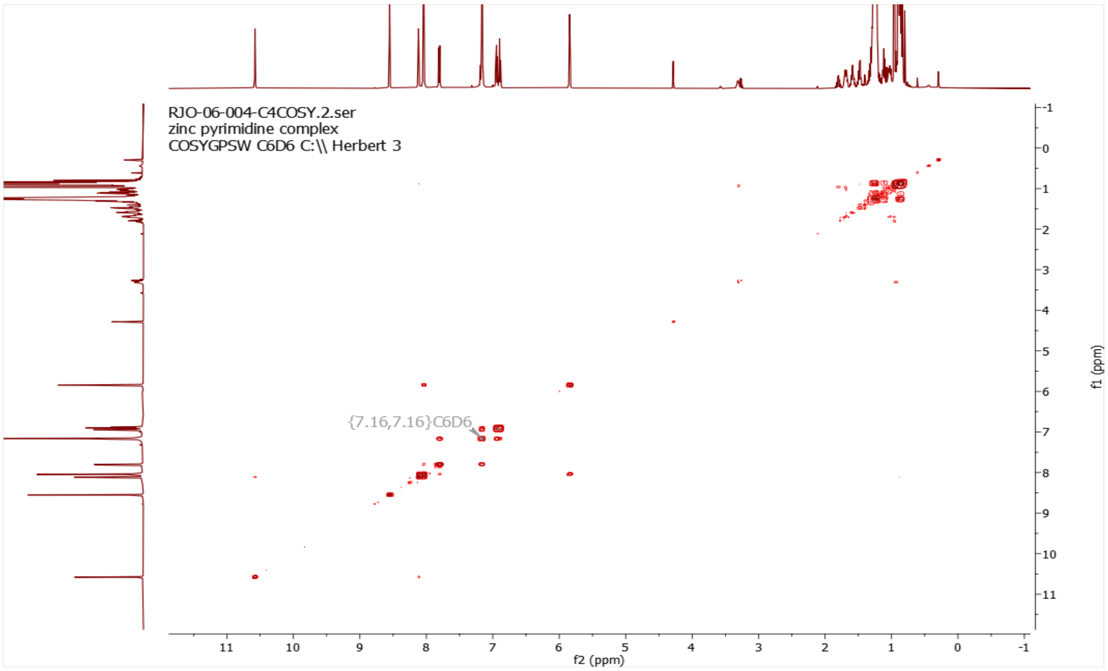


Figure S66. ^{1}H-^{1}H COSY NMR (400 MHz, $CDCl_3$, 22 °C) of bis-(4-aminopyrimidino)(2-trifluoromethyl)phenanthridine zinc ((^{CF3}**L2**)$_2$Zn).

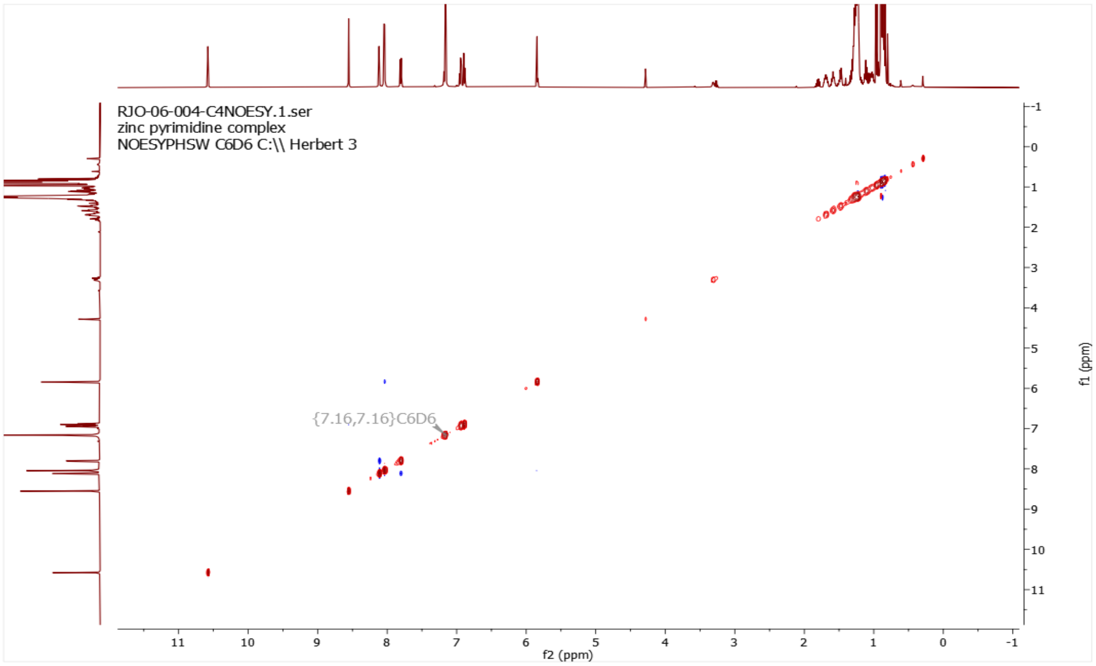


Figure S67. ^{1}H-^{1}H NOESY NMR (400 MHz, $CDCl_3$, 22 °C) of bis-(4-aminopyrimidino)(2-trifluoromethyl)phenanthridine zinc ((^{CF3}**L2**)$_2$Zn).

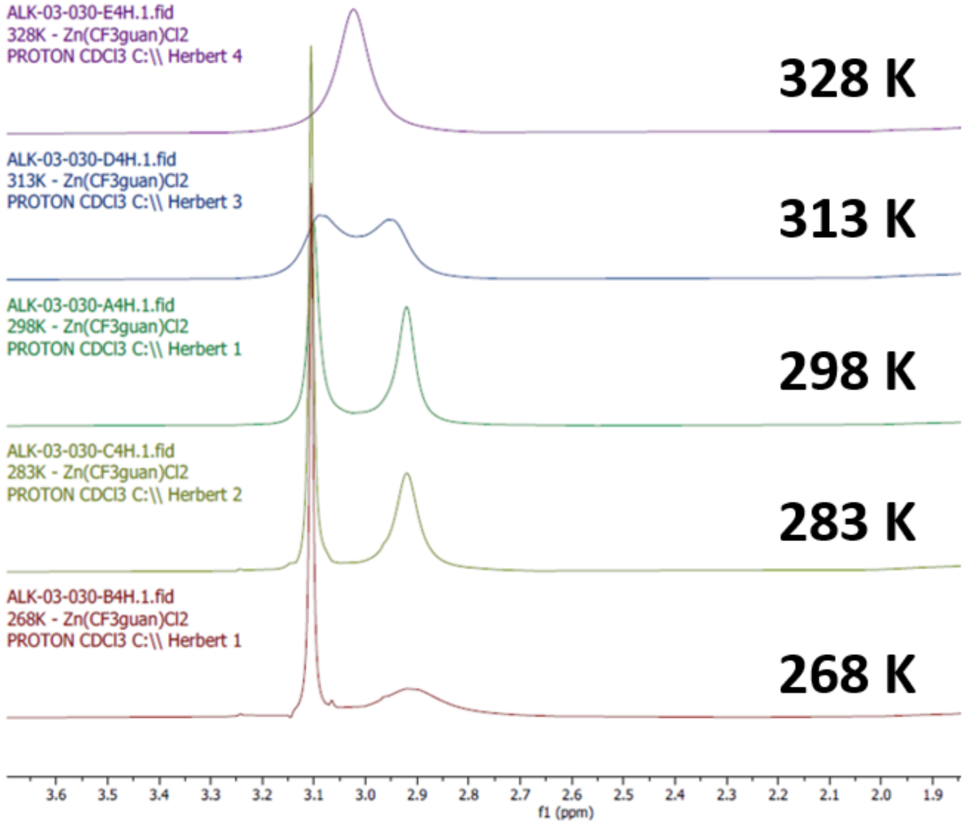


Figure S68. Variable-temperature ^{1}H NMR (500 MHz, $CDCl_3$) of (4-tetramethylguanidino)(2-trifluoromethyl)phenanthridine zinc chloride (zoom of tetramethyl region) (($^{\mathrm{CF3}}$**L2**)$_2$Zn).

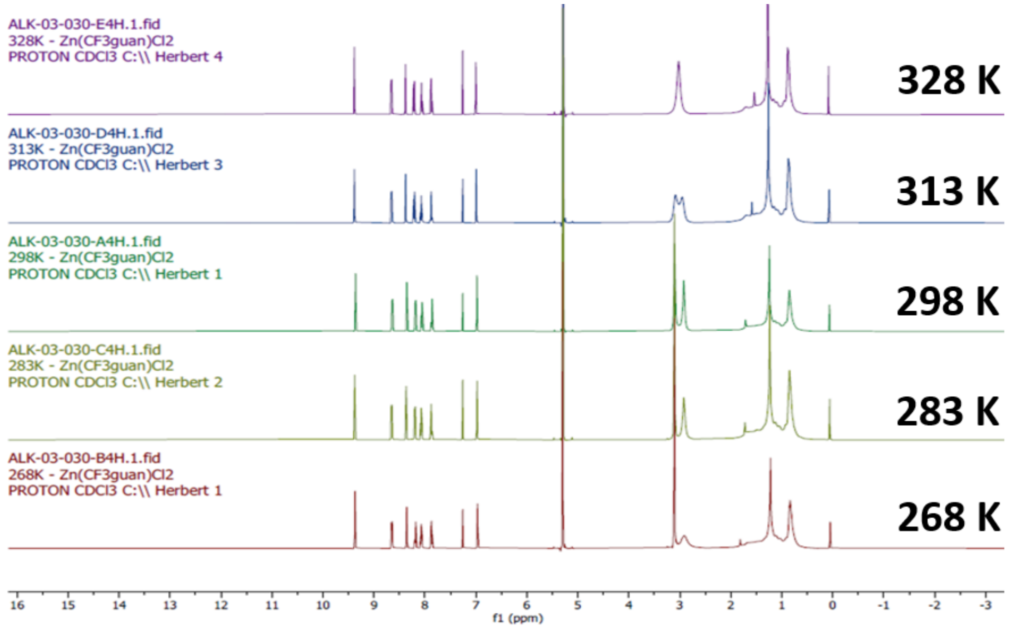


Figure S69. Variable-temperature ^{1}H NMR (500 MHz, $CDCl_3$) of (4-tetramethylguanidino)(2-trifluoromethyl)phenanthridine zinc chloride (full spectra) (($^{\mathrm{CF3}}$**L2**)$_2$Zn).

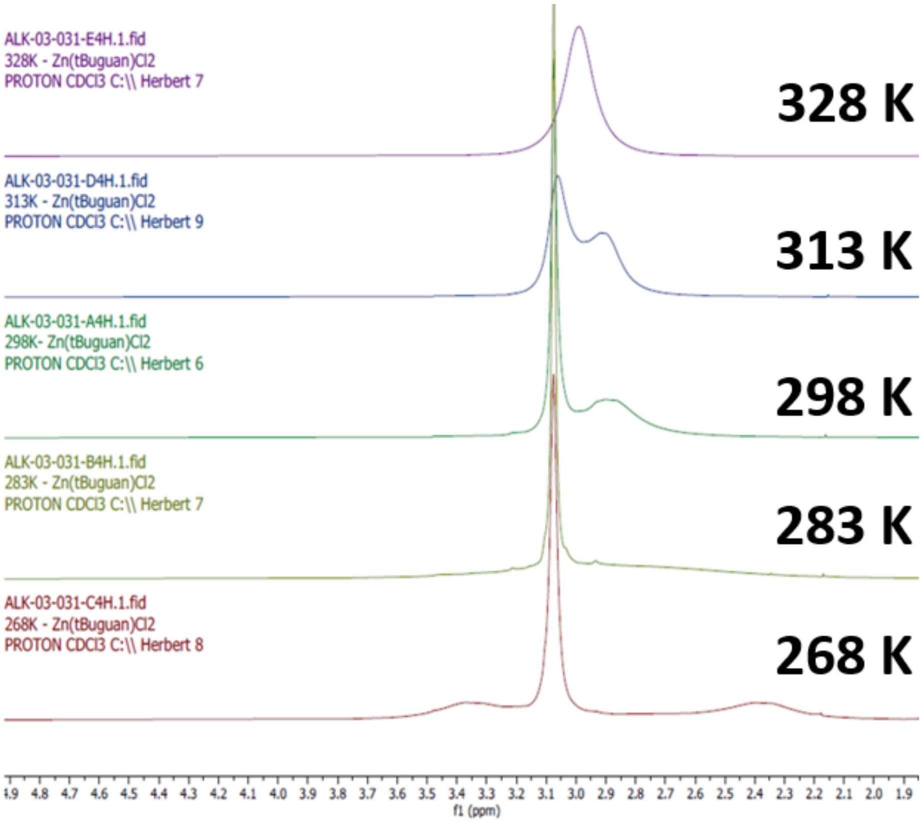


Figure S70. Variable-temperature ^{1}H NMR (500 MHz, $CDCl_3$) of (2-tert-butyl)(4-tetramethylguanidino)phenanthridine zinc chloride (zoom of tetramethyl region) (($^{t\mathbf{Bu}}$**L1**)$ZnCl_2$).

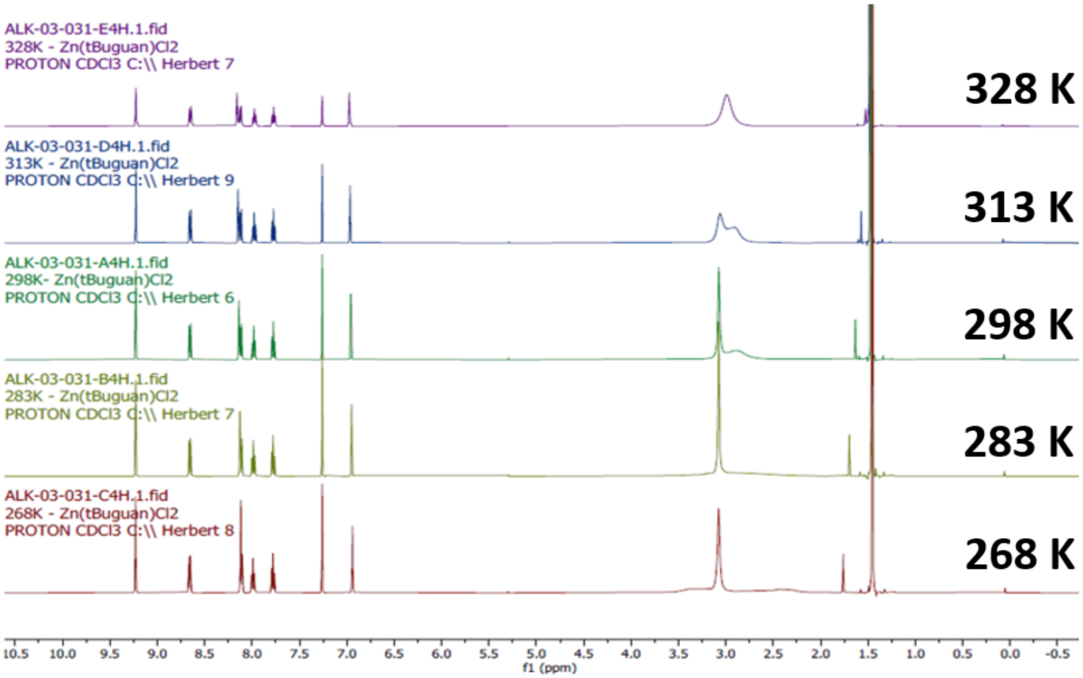


Figure S71. Variable-temperature ^{1}H NMR (500 MHz, $CDCl_3$) of (2-tert-butyl)(4-tetramethylguanidino)phenanthridine zinc chloride (full spectra) (($^{t\mathbf{Bu}}$**L1**)$ZnCl_2$).

HRMS figures

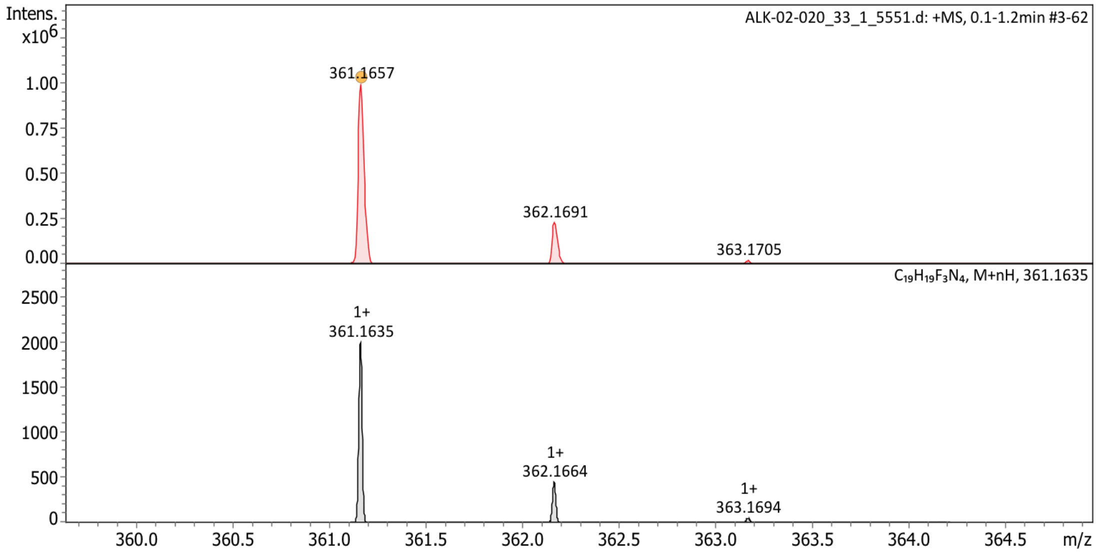


Figure S72. APCI high-resolution mass spectrum of (4-tetramethylguanidino)(2-trifluoromethyl)phenanthridine (^{CF3}**L1**).

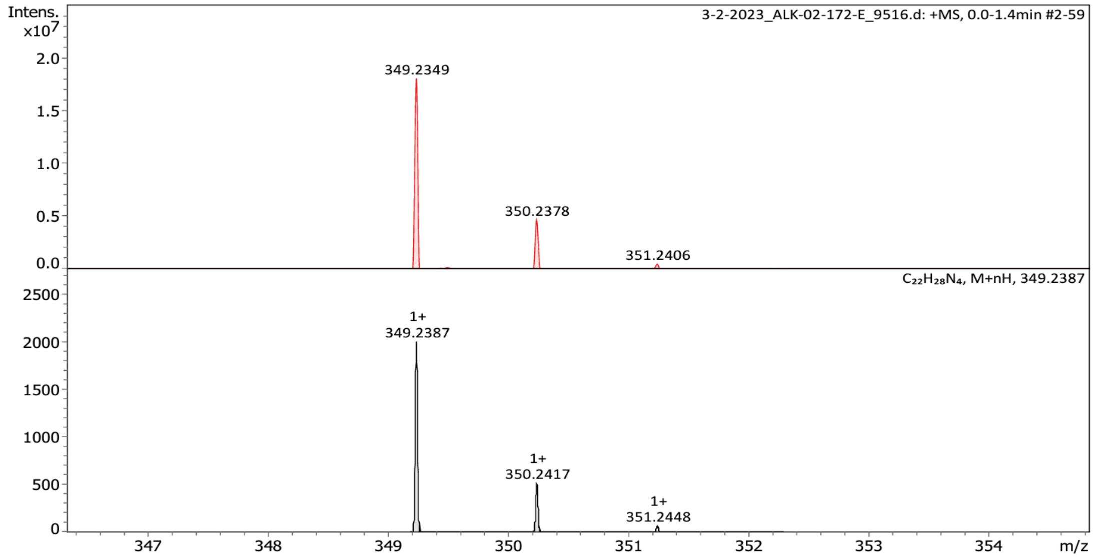


Figure S73. APCI high-resolution mass spectrum of (2-tert-butyl)(4-tetramethylguanidino)phenanthridine (^{tBu}**L1**).

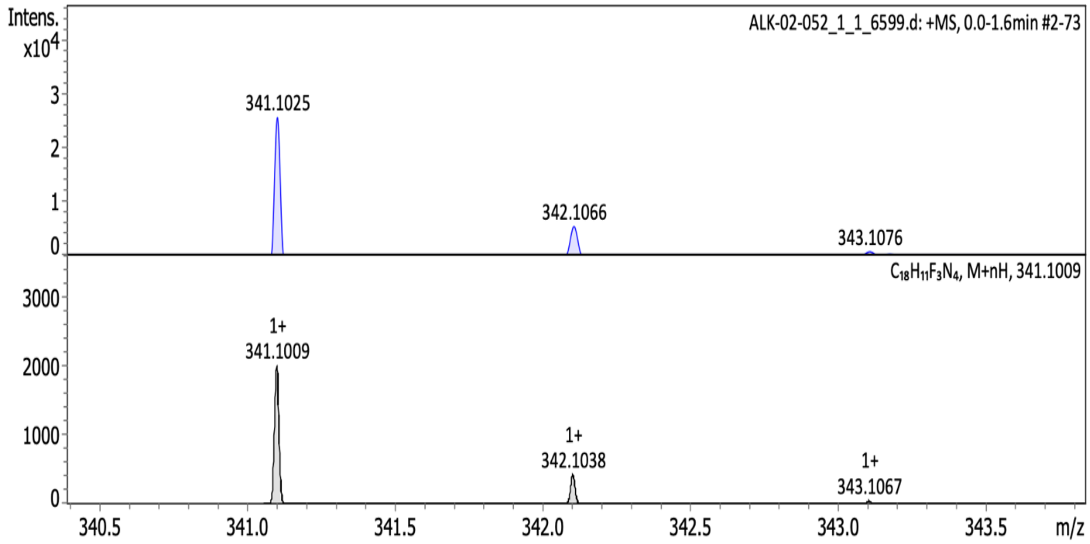


Figure S74. APCI high-resolution mass spectrum of (4-aminopyrimidino)(2-trifluoromethyl)phenanthridine ($^{\mathbf{CF3}}$**L2**).

Coordinates of optimized geometries

($^{\mathbf{CF3}}$**L1**)$ZnCl_2$ ($S_{0,eq}$) M06-L (gas phase/ def2-tzvpp def2/j)

Zn	8.85735	10.12510	6.22951
Cl	8.44462	9.08804	4.33155
Cl	10.81542	10.20198	7.32627
N	7.73977	11.93012	6.14475
N	7.64754	9.98392	7.97050
N	8.52473	7.97841	8.69628
N	8.51987	9.78284	10.16841
C	6.85201	11.08474	8.19320
C	5.99416	11.25357	9.27797
H	5.93885	10.48605	10.05293
C	6.04258	13.25558	7.29158
C	5.21394	13.39427	8.42291
H	4.58044	14.27153	8.54688
C	6.87476	12.11167	7.19339
C	6.09946	14.22517	6.22013
C	5.20569	12.40687	9.39297
C	8.20005	9.27025	8.94436
C	5.32173	15.40045	6.18551
H	4.63255	15.62300	7.00147
C	7.96623	7.29962	7.54331
H	6.97239	7.69379	7.30912
H	8.59709	7.42622	6.64569
H	7.88610	6.22565	7.76103
C	6.98425	13.97322	5.13344
F	3.64445	13.66901	10.64408
C	5.41714	16.27987	5.12212
H	4.80442	17.18409	5.11544
C	7.78108	12.79322	5.16660

H	8.46629	12.57333	4.33936
C	8.46313	8.99545	11.37756
H	7.84992	9.51789	12.13060
H	7.99832	8.02367	11.17812
H	9.45864	8.82314	11.81962
C	8.92267	11.16369	10.32000
H	9.21966	11.57141	9.34619
H	8.13082	11.79041	10.76765
H	9.80645	11.20698	10.97385
F	3.52158	11.51435	10.77483
C	9.74972	7.39949	9.21681
H	10.34098	8.15924	9.73680
H	9.55578	6.55120	9.89239
H	10.36200	7.04456	8.37525
C	4.36945	12.54492	10.63090
C	6.29068	16.02426	4.04970
H	6.35314	16.72759	3.21708
C	7.06560	14.88242	4.05667
H	7.75049	14.66547	3.23319
F	5.14606	12.55629	11.73277

$(^{\mathbf{CF3}}\mathbf{L1})ZnCl_2$ $(S_{0,eq})$ B3LYP (SMD “dichloromethane”/ def2-tzvpp def2/j)

Zn	8.87197	10.20603	6.22852
Cl	8.35755	9.04304	4.36848
Cl	11.03535	10.29404	6.88882
N	7.79920	12.01915	6.13694
C	7.84597	12.90009	5.17342
H	8.55934	12.72243	4.36111
C	7.01073	14.05991	5.13406
C	7.10651	14.98849	4.06796
H	7.83344	14.80729	3.27175
C	6.28839	16.10340	4.04421
H	6.35812	16.82284	3.22458
C	5.35780	16.31036	5.08633
H	4.71161	17.19198	5.06468
C	5.24947	15.41195	6.13759
H	4.51958	15.60131	6.92577
C	6.07362	14.26247	6.19000
C	6.02152	13.27243	7.25602
C	6.90817	12.16436	7.17993
C	6.91526	11.13847	8.18990
C	6.01460	11.26419	9.24981
H	5.97379	10.49654	10.02328
C	5.15085	12.37306	9.32752
C	5.14019	13.36406	8.35803
H	4.45413	14.20420	8.45128
C	4.25132	12.47448	10.53305
F	3.33965	13.45548	10.42367
F	3.57626	11.32847	10.75629
F	4.95992	12.72141	11.65803
N	7.77321	10.06515	7.99520
C	8.25827	9.30296	8.98681
N	8.50335	7.99483	8.73187
C	7.79586	7.28736	7.66982
H	6.83015	7.76661	7.46901
H	8.37427	7.27215	6.73025
H	7.62053	6.24812	7.99149
C	9.66054	7.29416	9.28085
H	10.32354	7.99392	9.80219
H	9.36594	6.48702	9.97214

H	10.22914	6.84762	8.44835
N	8.58672	9.79944	10.21184
C	8.45717	9.02594	11.44183
H	7.88900	9.61951	12.17853
H	7.90766	8.09510	11.25592
H	9.43788	8.78186	11.88428
C	9.03996	11.17458	10.37732
H	9.40324	11.56803	9.41954
H	8.24633	11.83347	10.77102
H	9.87960	11.18396	11.09145

(^{CF3}**L1**)ZnCl$_2$ (S$_{1,eq}$) B3LYP (SMD “dichloromethane”/ def2-tzvpp def2/j)

Zn	9.17824	10.46120	6.26268
Cl	9.04752	8.98536	4.56683
Cl	11.20504	10.72920	7.24829
N	7.92757	12.05570	6.12758
N	7.95844	10.18006	8.02427
N	8.38619	8.01187	8.72542
N	8.76615	9.78758	10.21467
C	7.05749	11.17467	8.19323
C	6.14432	11.25084	9.27359
H	6.15760	10.47917	10.04457
C	6.07502	13.21992	7.21596
C	5.18539	13.26093	8.32742
H	4.45360	14.06483	8.39811
C	7.01941	12.17950	7.13849
C	6.04360	14.23120	6.15177
C	5.21818	12.29740	9.33731
C	8.35315	9.31878	9.02115
C	5.16270	15.31850	6.11728
H	4.43735	15.46205	6.92075
C	7.54788	7.47317	7.64896
H	6.63441	8.07040	7.54307
H	8.09073	7.47496	6.68957
H	7.26803	6.44245	7.91197
C	6.99960	14.05647	5.07870
F	3.35534	13.32813	10.37678
C	5.18540	16.24202	5.05900
H	4.48766	17.08244	5.05224
C	7.89080	12.97518	5.11578
H	8.61097	12.83176	4.30605
C	8.69103	8.99726	11.44464
H	8.27864	9.64456	12.23440
H	8.02000	8.14148	11.30885
H	9.68266	8.64273	11.76722
C	9.28853	11.14834	10.37465
H	9.62579	11.53953	9.40775
H	8.53358	11.81542	10.82160
H	10.15770	11.10147	11.04814
F	3.64672	11.20834	10.72913
C	9.39791	7.09947	9.26310
H	10.22413	7.66804	9.70506
H	8.97795	6.40816	10.01023
H	9.79544	6.50914	8.42328
C	4.29053	12.37503	10.51835
C	6.11204	16.07418	4.00835
H	6.12967	16.79303	3.18344
C	7.00031	15.01132	4.00774
H	7.71804	14.88554	3.19251
F	4.96164	12.64520	11.66080

($^{t\mathrm{Bu}}$**L1**)ZnCl$_2$ (S$_{0,\mathrm{eq}}$) M06-L (gas phase/ def2-tzvpp def2/j)

Zn	8.77870	10.05365	6.18620
Cl	8.27089	8.97853	4.33184
Cl	10.79380	10.08421	7.18694
N	7.73826	11.89825	6.12699
N	7.62904	9.95715	7.96691
N	8.53203	7.97606	8.73006
N	8.59605	9.84137	10.12744
C	6.84763	11.07611	8.18608
C	5.99032	11.25436	9.26800
H	5.94615	10.46708	10.02536
C	6.06859	13.24577	7.29474
C	5.23515	13.38083	8.42384
H	4.61517	14.27141	8.51580
C	6.88523	12.09352	7.18333
C	6.14404	14.22394	6.23142
C	5.18637	12.40278	9.41083
C	8.22030	9.27985	8.93903
C	5.39264	15.41749	6.20749
H	4.71040	15.64766	7.02720
C	7.93214	7.26516	7.61825
H	6.92301	7.64123	7.42198
H	8.51771	7.38167	6.68871
H	7.87873	6.19498	7.86170
C	7.02211	13.96563	5.13989
C	3.50290	13.82770	10.66111
C	5.50557	16.30644	5.15397
H	4.91296	17.22418	5.15823
C	7.79289	12.76783	5.15529
H	8.46583	12.54053	4.32017
C	8.58977	9.10891	11.36994
H	8.00268	9.65684	12.12655
H	8.12589	8.12612	11.22949
H	9.60257	8.95992	11.78129
C	9.02113	11.22210	10.18822
H	9.30418	11.56358	9.18484
H	8.24815	11.89135	10.60591
H	9.91856	11.29174	10.82107
C	3.30136	11.35348	10.66905
C	9.78274	7.41723	9.20912
H	10.37955	8.18515	9.70992
H	9.62185	6.56707	9.89130
H	10.37475	7.07248	8.34858
C	4.29293	12.52233	10.64650
C	6.37194	16.04343	4.07752
H	6.44922	16.75369	3.25192
C	7.12109	14.88459	4.07270
H	7.80026	14.66102	3.24605
C	5.16890	12.47239	11.90439
H	2.82958	13.91293	9.79573
H	4.16028	14.70953	10.66716
H	2.87818	13.88179	11.56407
H	5.90266	13.29243	11.91493
H	5.72703	11.52791	11.98455
H	4.55239	12.56411	12.81129
H	2.65884	11.35686	9.77658
H	2.64795	11.41664	11.55226
H	3.80785	10.37861	10.70587

(${}^{t\mathrm{Bu}}$**L1**)ZnCl$_2$ (S$_{0,\mathrm{eq}}$) B3LYP (SMD “dichloromethane”/ def2-tzvpp def2/j)

Zn	8.84287	10.16366	6.19944
Cl	8.27707	8.97220	4.37081
Cl	11.03286	10.22975	6.78513
N	7.81070	11.99389	6.11472
N	7.79254	10.05557	7.99645
N	8.52158	7.98464	8.73166
N	8.72762	9.81594	10.16739
C	6.96390	11.15760	8.20621
C	6.09008	11.31198	9.28395
H	6.07572	10.53978	10.05382
C	6.08666	13.28481	7.27958
C	5.22986	13.39128	8.40067
H	4.56632	14.24967	8.47030
C	6.95481	12.16535	7.18333
C	6.12766	14.26595	6.20364
C	5.21665	12.42115	9.40103
C	8.31654	9.30516	8.97247
C	5.32411	15.43185	6.16408
H	4.62301	15.64238	6.97269
C	7.74035	7.27485	7.72478
H	6.76717	7.76090	7.58467
H	8.25340	7.24756	6.74795
H	7.57811	6.23950	8.06577
C	7.02824	14.03895	5.12018
C	3.40355	13.77466	10.59994
C	5.41500	16.31972	5.10254
H	4.78441	17.21292	5.09357
C	7.84404	12.86426	5.14128
H	8.52698	12.66639	4.30782
C	8.66787	9.06500	11.41554
H	8.16334	9.67891	12.18114
H	8.09040	8.14199	11.28221
H	9.67168	8.80745	11.79473
C	9.22226	11.18222	10.27186
H	9.54818	11.53828	9.28642
H	8.46663	11.87476	10.68167
H	10.09597	11.18927	10.94393
C	3.33662	11.27553	10.62824
C	9.70555	7.27735	9.20973
H	10.40320	7.97239	9.69017
H	9.44817	6.47245	9.91857
H	10.22223	6.82624	8.34600
C	4.27440	12.50556	10.62083
C	6.30846	16.08695	4.03354
H	6.36552	16.79752	3.20513
C	7.10639	14.95741	4.04337
H	7.80462	14.75608	3.22638
C	5.11107	12.51657	11.92133
H	2.75191	13.81584	9.71263
H	4.01087	14.69373	10.62147
H	2.75120	13.78968	11.48776
H	5.80096	13.37642	11.94552
H	5.70861	11.59913	12.03693
H	4.44827	12.59118	12.79966
H	2.71931	11.23972	9.71539
H	2.65548	11.32043	11.49455
H	3.89594	10.32921	10.69502

($^{t\text{Bu}}$**L1**)ZnCl$_2$ (S$_{1,eq}$) B3LYP (SMD “dichloromethane”/ def2-tzvpp def2/j)

Zn	8.99271	10.30373	6.14446
Cl	8.48543	8.84925	4.49477
Cl	11.12763	10.32505	6.91560
N	7.91328	12.01924	6.09102
N	7.91639	10.15905	8.01034
N	8.36731	8.02512	8.80839
N	8.88215	9.88178	10.14734
C	7.05327	11.18625	8.18725
C	6.16148	11.29717	9.28724
H	6.19045	10.51669	10.04884
C	6.13177	13.24919	7.23572
C	5.24888	13.30387	8.36228
H	4.54766	14.13376	8.41243
C	7.02866	12.17974	7.12808
C	6.12919	14.27973	6.19076
C	5.23934	12.34756	9.38942
C	8.36779	9.34943	9.01973
C	5.30852	15.41422	6.19442
H	4.61330	15.58378	7.01917
C	7.45495	7.43132	7.82696
H	6.54097	8.03183	7.74610
H	7.92804	7.37054	6.83304
H	7.18706	6.42088	8.16920
C	7.05409	14.07476	5.09325
C	3.33478	13.62865	10.50901
C	5.35564	16.35541	5.15120
H	4.70454	17.23214	5.17471
C	7.89078	12.95150	5.09284
H	8.58280	12.78833	4.26201
C	8.87775	9.17703	11.42925
H	8.53229	9.88209	12.20175
H	8.18317	8.32969	11.39652
H	9.88197	8.82025	11.70822
C	9.44617	11.23419	10.17054
H	9.74714	11.53230	9.15925
H	8.73274	11.96263	10.58889
H	10.34389	11.21742	10.80684
C	3.39241	11.12640	10.58438
C	9.41711	7.14227	9.32148
H	10.27620	7.73384	9.65836
H	9.05840	6.50380	10.14393
H	9.74743	6.49608	8.49382
C	4.26495	12.40429	10.58092
C	6.24863	16.15590	4.07600
H	6.28594	16.88707	3.26231
C	7.07951	15.04924	4.03709
H	7.77185	14.90158	3.20355
C	5.07182	12.47951	11.89864
H	2.71008	13.61635	9.60168
H	3.89926	14.57460	10.52534
H	2.65945	13.62721	11.37897
H	5.69762	13.38650	11.92668
H	5.73028	11.60581	12.02614
H	4.38557	12.51068	12.76089
H	2.80379	11.04842	9.65574
H	2.68986	11.14988	11.43365
H	4.00272	10.21452	10.67918

$(^{\mathrm{CF3}}\mathbf{L2})_2\mathrm{Zn}$ ($S_{0,\mathrm{eq}}$) M06-L (gas phase/ def2-tzvpp def2/j)

Zn	10.04516	7.34683	2.39085
N	9.51023	7.69062	4.26095
N	11.33713	5.98224	3.46464
F	9.08485	6.07313	9.26318
N	7.99012	9.03812	5.49407
F	11.16086	5.75514	9.75878
N	8.19417	9.08905	3.10638
C	8.54040	8.62557	4.33964
C	10.13043	7.00509	5.25816
F	10.43007	7.75067	9.38447
C	11.13582	6.07571	4.81661
C	11.87997	5.30229	5.73264
C	11.61605	5.44152	7.10233
H	12.16387	4.86656	7.83282
C	6.63244	10.51177	4.19343
H	5.86758	11.27169	4.14083
C	12.24052	5.17502	2.98972
H	12.35888	5.14779	1.90862
C	9.90677	7.10327	6.62857
H	9.15765	7.79010	6.99103
C	10.64640	6.32586	7.51882
C	7.05148	9.97129	5.39558
H	6.61279	10.30160	6.33407
C	13.05763	4.35211	3.80220
C	12.87904	4.40825	5.20604
C	7.25672	10.01510	3.05608
H	6.99101	10.37771	2.06657
C	14.63055	2.75908	5.43704
H	15.24632	2.13655	6.07347
C	14.02243	3.49810	3.24198
H	14.13781	3.47645	2.16491
C	10.33828	6.47321	8.97971
C	14.80173	2.70936	4.04821
H	15.54521	2.05185	3.61786
C	13.69227	3.58799	6.00425
H	13.58381	3.60564	7.07975
N	10.60978	7.67442	0.52629
N	8.66857	6.08689	1.30397
F	10.63280	7.39471	-4.51712
N	12.21550	8.93528	-0.69053
F	9.97064	5.35523	-4.75770
N	12.01985	8.96259	1.69820
C	11.64081	8.54284	0.45893
C	9.94264	7.04506	-0.47706
F	8.54931	6.96854	-4.88303
C	8.87950	6.18047	-0.04686
C	8.08704	5.46589	-0.97286
C	8.36078	5.60627	-2.33661
H	7.77840	5.07606	-3.07663
C	13.67009	10.29570	0.62843
H	14.48333	11.00288	0.69017
C	7.71380	5.33623	1.77000
H	7.59088	5.30810	2.85061
C	10.17385	7.14919	-1.84938
H	10.96488	7.79061	-2.20151
C	9.38729	6.43456	-2.74541
C	13.21433	9.80250	-0.58049
H	13.67261	10.11695	-1.51506

C	6.84777	4.57348	0.94790
C	7.03255	4.63018	-0.45468
C	13.01661	9.82371	1.75989
H	13.30776	10.15244	2.75409
C	5.18381	3.09386	-0.70362
H	4.53343	2.51492	-1.34666
C	5.83074	3.77651	1.49872
H	5.71147	3.75285	2.57532
C	9.64379	6.54738	-4.22020
C	5.00651	3.04340	0.68401
H	4.22295	2.42920	1.10717
C	6.17302	3.86876	-1.26159
H	6.28598	3.88889	-2.33665

$(^{\mathbf{CF3}}\mathbf{L2})_2$Zn ($S_{0,eq}$) B3LYP (SMD “dichloromethane”/ def2-tzvpp def2/j)

Zn	10.03615	7.15726	2.38825
N	9.52103	7.69030	4.23990
N	11.31461	5.86941	3.49471
F	9.19211	6.49485	9.36549
N	8.08959	9.15160	5.46932
F	11.23919	5.97220	9.83701
N	8.15180	9.07805	3.07889
C	8.56976	8.65814	4.30809
C	10.16686	7.04146	5.26254
F	10.72186	8.02013	9.36327
C	11.14388	6.05068	4.85123
C	11.88921	5.30096	5.79922
C	11.66719	5.52977	7.17752
H	12.22150	4.97096	7.92905
C	6.67296	10.59832	4.18283
H	5.91191	11.37860	4.13587
C	12.17585	4.99876	3.03783
H	12.26790	4.90164	1.95025
C	9.98675	7.22949	6.64061
H	9.26075	7.96606	6.97695
C	10.73262	6.47650	7.56721
C	7.15818	10.10509	5.39280
H	6.77975	10.49543	6.34597
C	12.98740	4.18470	3.88718
C	12.85002	4.32870	5.29932
C	7.22611	10.02601	3.02905
H	6.90381	10.35087	2.03186
C	14.55260	2.61119	5.58296
H	15.16655	1.99393	6.24439
C	13.90811	3.25374	3.34371
H	13.99241	3.16505	2.25714
C	10.47818	6.73456	9.03070
C	14.68323	2.47444	4.18273
H	15.39457	1.75524	3.76910
C	13.65758	3.51662	6.13247
H	13.58171	3.59762	7.21775
N	10.57467	7.68071	0.54132
N	8.69113	5.94683	1.27196
F	10.82474	6.58997	-4.59573
N	12.09894	9.05550	-0.67605
F	8.76906	6.10345	-5.06917
N	12.01612	8.98273	1.71382
C	11.58155	8.59102	0.48107

C	9.89204	7.07932	-0.48635
F	9.31831	8.13819	-4.57552
C	8.86497	6.13714	-0.08297
C	8.07596	5.44164	-1.03695
C	8.30338	5.67722	-2.41322
H	7.71556	5.16027	-3.16929
C	13.59560	10.40779	0.62257
H	14.40397	11.13848	0.67600
C	7.78661	5.11732	1.72170
H	7.69443	5.01045	2.80837
C	10.07678	7.27519	-1.86272
H	10.84139	7.97454	-2.19296
C	9.28668	6.57657	-2.79527
C	13.08804	9.94829	-0.59151
H	13.49659	10.31560	-1.54139
C	6.92870	4.35947	0.86588
C	7.06686	4.51533	-0.54495
C	12.99929	9.87041	1.77161
H	13.33421	10.17344	2.77152
C	5.27337	2.89550	-0.84235
H	4.62413	2.32116	-1.50872
C	5.96197	3.47184	1.40178
H	5.87826	3.37279	2.48751
C	9.54317	6.84549	-4.25642
C	5.14201	2.74697	0.55660
H	4.39486	2.06154	0.96441
C	6.21335	3.75884	-1.38453
H	6.28907	3.84952	-2.46901

$(^{\mathbf{CF3}}\mathbf{L2})_2$Zn (S$_{1,eq}$) B3LYP (SMD “dichloromethane”/ def2-tzvpp def2/j)

Zn	9.95754	6.97332	2.40522
N	9.56458	7.67490	4.22933
N	11.28406	5.76251	3.53376
F	9.28502	6.64567	9.39582
N	8.26831	9.28729	5.41772
F	11.34148	6.15739	9.86396
N	8.22600	9.06668	3.03334
C	8.67009	8.69742	4.27046
C	10.21497	7.05697	5.26745
F	10.80156	8.18390	9.32320
C	11.15483	6.01996	4.88338
C	11.90386	5.29856	5.85011
C	11.71172	5.59130	7.22086
H	12.26329	5.04895	7.98638
C	6.87808	10.73202	4.09799
H	6.15822	11.54910	4.03195
C	12.11086	4.84556	3.10273
H	12.16522	4.68175	2.02065
C	10.06636	7.31064	6.63874
H	9.36780	8.08138	6.95534
C	10.80572	6.57554	7.58456
C	7.38760	10.28629	5.31680
H	7.07265	10.75499	6.25777
C	12.93113	4.06312	3.97317
C	12.83465	4.28454	5.37833
C	7.35067	10.06082	2.96165
H	7.00457	10.34289	1.95931
C	14.51769	2.55600	5.70972

H	15.14072	1.96560	6.38698
C	13.82084	3.08771	3.45616
H	13.87254	2.93960	2.37403
C	10.56605	6.88503	9.04011
C	14.60687	2.34122	4.31531
H	15.29487	1.58843	3.92259
C	13.65180	3.50486	6.23299
H	13.60783	3.64729	7.31364
N	10.53532	7.63888	0.54311
N	8.72215	5.85323	1.26039
F	10.04963	8.18205	-4.49700
N	12.01503	9.10457	-0.61981
F	9.98971	6.06060	-4.92167
N	12.01516	8.84919	1.76259
C	11.54672	8.55939	0.52076
C	9.82789	7.09800	-0.48975
F	8.15778	7.20346	-4.90713
C	8.83336	6.11272	-0.07852
C	8.03875	5.47389	-1.05390
C	8.22165	5.82013	-2.41695
H	7.60627	5.34070	-3.17934
C	13.55114	10.35413	0.72575
H	14.36128	11.08052	0.80476
C	7.80259	4.93306	1.67179
H	7.74158	4.75865	2.74946
C	9.97396	7.40374	-1.86056
H	10.71568	8.14191	-2.15326
C	9.16915	6.76663	-2.81331
C	13.00402	9.99007	-0.50880
H	13.37969	10.43005	-1.43977
C	6.96310	4.22626	0.79775
C	7.04980	4.47352	-0.62367
C	13.00072	9.73301	1.85614
H	13.37181	9.96097	2.86187
C	5.28954	2.82161	-1.01321
H	4.64639	2.28180	-1.71199
C	6.01285	3.25937	1.26525
H	5.94235	3.06944	2.33995
C	9.34276	7.05940	-4.27702
C	5.20017	2.57843	0.37340
H	4.48129	1.84398	0.74926
C	6.21235	3.76534	-1.49371
H	6.26784	3.94104	-2.57009

(^{CF3}**L2**)$_2$Zn (T$_{1,eq}$) B3LYP (SMD “dichloromethane”/ def2-tzvpp def2/j)

Zn	9.93363	6.94764	2.43083
N	9.52135	7.60813	4.26512
N	11.25054	5.71580	3.54501
F	9.38297	6.65429	9.45112
N	8.19723	9.19030	5.46419
F	11.44961	6.16524	9.87039
N	8.14587	8.97040	3.08237
C	8.60585	8.61050	4.31563
C	10.20134	7.00609	5.29324
F	10.90119	8.18532	9.31846
C	11.14461	5.97763	4.89569
C	11.92135	5.27040	5.85105
C	11.75987	5.57554	7.22308
H	12.33566	5.04722	7.98053
C	6.76722	10.60298	4.15468

H	6.02874	11.40369	4.09347
C	12.07543	4.80334	3.10177
H	12.11279	4.63800	2.01929
C	10.08263	7.27155	6.66518
H	9.38224	8.03736	6.99063
C	10.85450	6.55548	7.59955
C	7.29369	10.16865	5.37008
H	6.97340	10.62972	6.31293
C	12.91619	4.02917	3.95968
C	12.84850	4.25905	5.36546
C	7.24806	9.94375	3.01510
H	6.88990	10.21841	2.01505
C	14.54775	2.54200	5.67071
H	15.18843	1.95937	6.33815
C	13.79988	3.05514	3.43023
H	13.83008	2.89982	2.34830
C	10.65424	6.88416	9.05743
C	14.60772	2.31848	4.27682
H	15.29096	1.56668	3.87395
C	13.68875	3.48952	6.20657
H	13.66815	3.63809	7.28707
N	10.53651	7.62241	0.58905
N	8.68217	5.83925	1.24976
F	10.35213	8.02217	-4.46990
N	12.06316	9.07908	-0.52933
F	9.75836	5.99534	-4.95679
N	11.99254	8.82664	1.84634
C	11.55850	8.53928	0.59479
C	9.85091	7.09386	-0.44836
F	8.26256	7.54254	-4.79464
C	8.82732	6.10589	-0.05480
C	8.03523	5.47271	-1.07091
C	8.25721	5.81891	-2.40285
H	7.66307	5.34974	-3.18916
C	13.57279	10.31638	0.85577
H	14.38708	11.03543	0.95771
C	7.74020	4.92358	1.66694
H	7.67021	4.75521	2.74402
C	10.02504	7.40071	-1.82972
H	10.78139	8.13178	-2.10297
C	9.24614	6.77958	-2.78273
C	13.05770	9.95623	-0.39152
H	13.46282	10.39136	-1.31258
C	6.90669	4.23623	0.77105
C	7.02697	4.48886	-0.64400
C	12.98345	9.70183	1.96872
H	13.32600	9.92767	2.98516
C	5.24683	2.87035	-1.06815
H	4.60605	2.34338	-1.77946
C	5.93520	3.28660	1.21984
H	5.84469	3.09653	2.29321
C	9.41123	7.09002	-4.23871
C	5.12593	2.62135	0.31692
H	4.38802	1.89842	0.67680
C	6.18817	3.79387	-1.53028
H	6.26449	3.97100	-2.60539

($^{\mathbf{CF3}}$**L2**)$_2$Zn (S$_{0,eq}$) B3LYP (SMD “diethyl ether”/ def2-tzvpp def2/j)

Zn	10.03478	7.17792	2.38893

N	9.51488	7.68745	4.24377
N	11.31642	5.87843	3.49277
F	9.18439	6.46808	9.36404
N	8.07631	9.14018	5.47483
F	11.23387	5.95292	9.83387
N	8.14923	9.07760	3.08437
C	8.56211	8.65350	4.31361
C	10.16108	7.03708	5.26396
F	10.70709	8.00062	9.36895
C	11.14252	6.05220	4.84953
C	11.88947	5.30130	5.79570
C	11.66418	5.52356	7.17414
H	12.21934	4.96483	7.92504
C	6.66594	10.59247	4.18831
H	5.90521	11.37314	4.14156
C	12.18303	5.01513	3.03338
H	12.27804	4.92518	1.94528
C	9.97780	7.21881	6.64258
H	9.24840	7.95174	6.98000
C	10.72525	6.46517	7.56668
C	7.14541	10.09336	5.39844
H	6.76237	10.47853	6.35199
C	12.99682	4.20004	3.88009
C	12.85515	4.33584	5.29255
C	7.22408	10.02534	3.03421
H	6.90645	10.35387	2.03664
C	14.56454	2.62394	5.57159
H	15.17931	2.00576	6.23146
C	13.92330	3.27609	3.33467
H	14.01173	3.19313	2.24789
C	10.46877	6.71611	9.03158
C	14.69963	2.49558	4.17115
H	15.41530	1.78194	3.75526
C	13.66418	3.52242	6.12306
H	13.58487	3.59716	7.20852
N	10.58002	7.67651	0.53848
N	8.68733	5.95653	1.27373
F	10.83801	6.56241	-4.59214
N	12.10941	9.04450	-0.67995
F	8.78255	6.07482	-5.06614
N	12.02055	8.97803	1.70988
C	11.58877	8.58448	0.47699
C	9.89782	7.07351	-0.48729
F	9.33283	8.11213	-4.58387
C	8.86577	6.13808	-0.08141
C	8.07616	5.44085	-1.03402
C	8.30871	5.66823	-2.41040
H	7.72150	5.15038	-3.16624
C	13.60136	10.40095	0.61917
H	14.40901	11.13250	0.67267
C	7.77710	5.13519	1.72570
H	7.68100	5.03653	2.81295
C	10.08731	7.26164	-1.86424
H	10.85567	7.95674	-2.19527
C	9.29697	6.56163	-2.79476
C	13.09764	9.93736	-0.59523
H	13.50883	10.30140	-1.54535
C	6.91769	4.37608	0.87201
C	7.06145	4.52252	-0.53920
C	13.00263	9.86610	1.76831
H	13.33467	10.17097	2.76869
C	5.26073	2.90960	-0.83291

H	4.61092	2.33441	-1.49806
C	5.94447	3.49662	1.40945
H	5.85565	3.40427	2.49544
C	9.55678	6.82195	-4.25745
C	5.12378	2.77054	0.56631
H	4.37174	2.09158	0.97601
C	6.20678	3.76482	-1.37664
H	6.28667	3.84860	-2.46135

$(^{\mathrm{CF3}}\mathbf{L2})_2$Zn (S$_{1,\mathrm{eq}}$) B3LYP (SMD “diethyl ether”/ def2-tzvpp def2/j)

Zn	9.88616	6.99678	2.42339
N	9.52913	7.68226	4.25639
N	11.24623	5.78235	3.52304
F	9.37591	6.67991	9.42435
N	8.22238	9.26583	5.47124
F	11.43863	6.17837	9.84936
N	8.15633	9.06006	3.08587
C	8.62024	8.69081	4.31564
C	10.20819	7.07114	5.27896
F	10.90033	8.20836	9.32000
C	11.14763	6.04172	4.87435
C	11.92608	5.32890	5.82472
C	11.76397	5.62352	7.19848
H	12.33748	5.08853	7.95287
C	6.78497	10.68745	4.17782
H	6.04649	11.48876	4.12598
C	12.06817	4.87044	3.07409
H	12.09672	4.70471	1.99117
C	10.08984	7.32652	6.65298
H	9.39050	8.09098	6.98301
C	10.85756	6.60036	7.58197
C	7.32019	10.24625	5.38749
H	7.00826	10.70340	6.33514
C	12.91576	4.09596	3.92551
C	12.85308	4.32136	5.33193
C	7.25859	10.03451	3.03133
H	6.89540	10.31601	2.03488
C	14.55813	2.60694	5.62581
H	15.20303	2.02399	6.28886
C	13.79951	3.12541	3.38972
H	13.82498	2.97317	2.30718
C	10.64991	6.91176	9.04269
C	14.61301	2.38780	4.23043
H	15.29622	1.63887	3.82229
C	13.69832	3.55074	6.16743
H	13.68060	3.69685	7.24832
N	10.51441	7.63193	0.56717
N	8.66140	5.88037	1.27004
F	10.01027	8.18526	-4.48093
N	12.06529	9.02288	-0.59281
F	10.38699	6.07884	-4.79009
N	11.96055	8.87336	1.79641
C	11.53871	8.53566	0.54945
C	9.83182	7.07166	-0.47564
F	8.38094	6.85332	-5.01289
C	8.81293	6.11039	-0.07401
C	8.03852	5.46503	-1.05643
C	8.26746	5.77891	-2.42535
H	7.66626	5.29283	-3.19421
C	13.56754	10.30307	0.76079

H	14.38802	11.01745	0.84224
C	7.71525	4.98329	1.66896
H	7.61731	4.83030	2.74730
C	10.02429	7.34497	-1.84413
H	10.78449	8.06713	-2.12969
C	9.23928	6.69751	-2.81137
C	13.06547	9.89392	-0.47890
H	13.48835	10.28472	-1.41170
C	6.88956	4.27257	0.78543
C	7.02116	4.48928	-0.63767
C	12.95717	9.74295	1.89277
H	13.28893	10.00999	2.90268
C	5.24662	2.85706	-1.04473
H	4.61529	2.31296	-1.75079
C	5.91055	3.33053	1.24430
H	5.80553	3.16377	2.31996
C	9.49937	6.95706	-4.26891
C	5.11325	2.64440	0.34255
H	4.37184	1.92933	0.71192
C	6.19857	3.77676	-1.51728
H	6.28824	3.92866	-2.59487

$(^{CF3}\mathbf{L2})_2$Zn ($T_{1,eq}$) B3LYP (SMD "diethyl ether"/ def2-tzvpp def2/j)

Zn	9.91927	6.95589	2.43376
N	9.51769	7.61022	4.27044
N	11.23945	5.71426	3.54497
F	9.40008	6.66864	9.45739
N	8.20682	9.20202	5.47074
F	11.46595	6.16800	9.86733
N	8.14365	8.97390	3.08999
C	8.60702	8.61672	4.32254
C	10.20077	7.00898	5.29573
F	10.92648	8.19099	9.31670
C	11.13992	5.97801	4.89543
C	11.91907	5.27011	5.84878
C	11.76386	5.57785	7.22050
H	12.34084	5.05005	7.97733
C	6.77874	10.61707	4.16245
H	6.04404	11.42134	4.10171
C	12.05988	4.79943	3.09950
H	12.09159	4.63279	2.01691
C	10.08839	7.27706	6.66789
H	9.39092	8.04542	6.99407
C	10.86229	6.56068	7.59957
C	7.30839	10.18428	5.37730
H	6.99493	10.64998	6.32028
C	12.90260	4.02385	3.95462
C	12.84125	4.25596	5.36024
C	7.25085	9.95124	3.02296
H	6.88976	10.22340	2.02319
C	14.53715	2.53440	5.66127
H	15.17877	1.95092	6.32713
C	13.78160	3.04650	3.42364
H	13.80757	2.88863	2.34189
C	10.67008	6.89180	9.05849
C	14.59085	2.30877	4.26761
H	15.27021	1.55445	3.86280
C	13.68300	3.48500	6.19865
H	13.66691	3.63514	7.27901
N	10.53220	7.62313	0.59201

N	8.67907	5.83741	1.24922
F	10.36083	8.01717	-4.46845
N	12.05415	9.08656	-0.52373
F	9.76436	5.99073	-4.95523
N	11.98368	8.83032	1.85149
C	11.55071	8.54298	0.59943
C	9.85007	7.09301	-0.44666
F	8.27050	7.54003	-4.79344
C	8.82758	6.10282	-0.05486
C	8.04026	5.46606	-1.07261
C	8.26537	5.81215	-2.40379
H	7.67496	5.34099	-3.19161
C	13.55719	10.32876	0.86377
H	14.36807	11.05153	0.96713
C	7.73805	4.92015	1.66454
H	7.66420	4.75421	2.74171
C	10.02708	7.39968	-1.82819
H	10.78192	8.13296	-2.10001
C	9.25267	6.77578	-2.78228
C	13.04424	9.96764	-0.38425
H	13.44746	10.40548	-1.30507
C	6.90948	4.22914	0.76723
C	7.03398	4.47995	-0.64763
C	12.97008	9.70935	1.97556
H	13.31062	9.93464	2.99297
C	5.26010	2.85597	-1.07509
H	4.62321	2.32605	-1.78769
C	5.93906	3.27785	1.21408
H	5.84482	3.08935	2.28740
C	9.41875	7.08633	-4.23842
C	5.13494	2.60902	0.30981
H	4.39761	1.88484	0.66830
C	6.20014	3.78105	-1.53538
H	6.27904	3.95623	-2.61047

($^{\mathrm{CF3}}$**L2**)$_2$Zn (S$_{0,\mathrm{eq}}$) B3LYP (SMD “toluene”/ def2-tzvpp def2/j)

Zn	10.03697	7.20854	2.38887
N	9.50926	7.68682	4.24815
N	11.32077	5.89326	3.48950
F	9.17078	6.43353	9.35976
N	8.05817	9.12477	5.48141
F	11.22140	5.92161	9.82871
N	8.14745	9.07952	3.09130
C	8.55307	8.64887	4.32034
C	10.15454	7.03275	5.26513
F	10.68833	7.97089	9.37742
C	11.14150	6.05553	4.84652
C	11.88896	5.30098	5.79004
C	11.65818	5.51325	7.16868
H	12.21289	4.95316	7.91881
C	6.65228	10.58124	4.19546
H	5.88962	11.35993	4.14919
C	12.19340	5.03883	3.02645
H	12.29290	4.95979	1.93778
C	9.96587	7.20458	6.64448
H	9.23205	7.93259	6.98350
C	10.71393	6.44843	7.56518
C	7.12523	10.07488	5.40551
H	6.73481	10.45149	6.35947
C	13.00818	4.22007	3.86924

C	12.86017	4.34377	5.28220
C	7.22010	10.02416	3.04101
H	6.90904	10.35809	2.04322
C	14.57585	2.63636	5.55442
H	15.19027	2.01541	6.21185
C	13.94109	3.30445	3.32096
H	14.03496	3.23040	2.23400
C	10.45391	6.68890	9.03203
C	14.71733	2.52024	4.15372
H	15.43766	1.81331	3.73469
C	13.66951	3.52651	6.10876
H	13.58475	3.59240	7.19429
N	10.58873	7.67372	0.53366
N	8.68467	5.97227	1.27712
F	10.85631	6.52309	-4.58794
N	12.12490	9.03220	-0.68660
F	8.80085	6.03453	-5.06112
N	12.02290	8.98055	1.70294
C	11.59832	8.58021	0.47005
C	9.90738	7.06672	-0.48886
F	9.35369	8.07509	-4.59489
C	8.86897	6.14067	-0.07849
C	8.07853	5.43987	-1.02844
C	8.31773	5.65494	-2.40518
H	7.73125	5.13535	-3.16029
C	13.60923	10.39623	0.61259
H	14.41644	11.12815	0.66592
C	7.76749	5.16171	1.73287
H	7.66689	5.07496	2.82086
C	10.10329	7.24280	-1.86666
H	10.87689	7.93148	-2.19941
C	9.31231	6.54009	-2.79373
C	13.11201	9.92513	-0.60195
H	13.52787	10.28306	-1.55234
C	6.90615	4.39973	0.88313
C	7.05677	4.53227	-0.52877
C	13.00430	9.86835	1.76188
H	13.32995	10.17872	2.76263
C	5.24708	2.92742	-0.81547
H	4.59665	2.35028	-1.47817
C	5.92504	3.53111	1.42363
H	5.83038	3.44902	2.50994
C	9.57593	6.78818	-4.25869
C	5.10341	2.80218	0.58421
H	4.34558	2.13185	0.99719
C	6.20057	3.77181	-1.36226
H	6.28589	3.84581	-2.44717

($^{\mathbf{CF3}}$**L2**)$_2$Zn (S$_{1,eq}$) B3LYP (SMD “toluene”/ def2-tzvpp def2/j)

Zn	9.85534	7.03100	2.43066
N	9.53834	7.70590	4.27227
N	11.20972	5.77727	3.51728
F	9.39949	6.66173	9.43595
N	8.31197	9.34566	5.49539
F	11.46152	6.14145	9.84158
N	8.19833	9.12150	3.11322
C	8.66798	8.74666	4.33897
C	10.21270	7.07802	5.28629
F	10.93509	8.17871	9.32832
C	11.12623	6.03075	4.86995

C	11.89479	5.29529	5.81169
C	11.74709	5.58615	7.18741
H	12.31170	5.03488	7.93670
C	6.91381	10.81343	4.21110
H	6.20781	11.64369	4.16366
C	12.00716	4.84985	3.05783
H	12.02267	4.68874	1.97376
C	10.10916	7.32992	6.66218
H	9.43041	8.10971	6.99951
C	10.86538	6.58150	7.58205
C	7.44958	10.36055	5.41647
H	7.17119	10.83717	6.36503
C	12.84358	4.05139	3.89843
C	12.79558	4.27054	5.30640
C	7.34074	10.13093	3.06341
H	6.97200	10.41638	2.07012
C	14.46372	2.51616	5.57899
H	15.09957	1.91494	6.23435
C	13.70149	3.06399	3.35194
H	13.71629	2.91621	2.26855
C	10.67140	6.88672	9.04677
C	14.50397	2.30355	4.18236
H	15.16681	1.54153	3.76509
C	13.62936	3.47609	6.13110
H	13.62200	3.61666	7.21277
N	10.49707	7.65371	0.56868
N	8.65498	5.89604	1.27937
F	9.35375	8.18405	-4.57337
N	11.96337	9.12884	-0.59505
F	10.86357	6.63969	-4.58946
N	11.91756	8.92740	1.79309
C	11.48317	8.59450	0.54802
C	9.83750	7.06238	-0.47750
F	8.81108	6.14823	-5.08533
C	8.82704	6.09524	-0.07164
C	8.08481	5.41435	-1.04747
C	8.34391	5.68839	-2.42524
H	7.77480	5.16368	-3.19163
C	13.42452	10.45958	0.75446
H	14.20713	11.21542	0.83410
C	7.71143	4.99694	1.67602
H	7.59412	4.86574	2.75549
C	10.05663	7.30049	-1.84430
H	10.81375	8.02591	-2.13395
C	9.30451	6.60571	-2.81436
C	12.91859	10.04761	-0.48318
H	13.30078	10.47754	-1.41648
C	6.90873	4.25784	0.79520
C	7.06755	4.43999	-0.62947
C	12.86967	9.84385	1.88671
H	13.21078	10.10490	2.89522
C	5.31264	2.78632	-1.03184
H	4.69890	2.22130	-1.73672
C	5.92762	3.31966	1.25749
H	5.80120	3.17824	2.33433
C	9.57620	6.88838	-4.26491
C	5.15368	2.60646	0.35648
H	4.40977	1.89540	0.72832
C	6.26805	3.70164	-1.50774
H	6.37668	3.82878	-2.58665

($^{\mathbf{CF3}}$**L2**)$_2$Zn (T$_{1,eq}$) B3LYP (SMD “toluene”/ def2-tzvpp def2/j)

Zn	9.90509	6.97019	2.43600
N	9.51375	7.61289	4.27648
N	11.22865	5.71479	3.54488
F	9.41852	6.68518	9.46498
N	8.20833	9.20833	5.47728
F	11.48342	6.17121	9.86385
N	8.14445	8.97892	3.09689
C	8.60645	8.62195	4.32969
C	10.19961	7.01231	5.29867
F	10.95391	8.19731	9.31444
C	11.13495	5.97937	4.89517
C	11.91635	5.27023	5.84648
C	11.76742	5.58054	7.21780
H	12.34558	5.05352	7.97414
C	6.78267	10.62432	4.16823
H	6.04921	11.42960	4.10721
C	12.04447	4.79771	3.09701
H	12.07095	4.63084	2.01419
C	10.09346	7.28278	6.67109
H	9.39854	8.05329	6.99815
C	10.86974	6.56635	7.59982
C	7.31222	10.19155	5.38350
H	7.00037	10.65813	6.32655
C	12.88852	4.01951	3.94891
C	12.83316	4.25305	5.35456
C	7.25352	9.95702	3.02893
H	6.89334	10.22848	2.02869
C	14.52455	2.52553	5.65088
H	15.16632	1.94037	6.31496
C	13.76245	3.03861	3.41630
H	13.78423	2.87905	2.33471
C	10.68678	6.90052	9.06012
C	14.57236	2.29868	4.25737
H	15.24735	1.54174	3.85042
C	13.67568	3.47943	6.18990
H	13.66332	3.63069	7.27004
N	10.53061	7.62435	0.59376
N	8.67637	5.83960	1.24911
F	10.37347	8.00762	-4.46904
N	12.05209	9.08998	-0.51929
F	9.77483	5.98079	-4.95294
N	11.97658	8.83457	1.85571
C	11.54676	8.54548	0.60286
C	9.85227	7.09192	-0.44592
F	8.28261	7.53180	-4.79411
C	8.82930	6.10141	-0.05480
C	8.04646	5.46053	-1.07368
C	8.27592	5.80489	-2.40433
H	7.68899	5.33184	-3.19344
C	13.54586	10.33928	0.87147
H	14.35311	11.06578	0.97657
C	7.73471	4.92281	1.66334
H	7.65595	4.76158	2.74078
C	10.03341	7.39644	-1.82798
H	10.78793	8.13048	-2.09902
C	9.26298	6.76976	-2.78254
C	13.03780	9.97451	-0.37764
H	13.44159	10.41248	-1.29825
C	6.91084	4.22754	0.76540
C	7.04084	4.47390	-0.64962

C	12.95823	9.71721	1.98201
H	13.29465	9.94333	3.00067
C	5.27173	2.84557	-1.07862
H	4.63878	2.31211	-1.79188
C	5.94009	3.27652	1.21129
H	5.84141	3.09185	2.28475
C	9.43047	7.07830	-4.23962
C	5.14103	2.60339	0.30642
H	4.40329	1.87952	0.66429
C	6.21179	3.77026	-1.53800
H	6.29463	3.94165	-2.61334

(^{CF3}**L2**)$_2$Zn (S$_{0,eq}$) B3LYP (SMD “n-hexane”/ def2-tzvpp def2/j)

Zn	10.03812	7.22508	2.38901
N	9.50518	7.68600	4.25022
N	11.32249	5.90089	3.48807
F	9.16038	6.41772	9.35686
N	8.04748	9.11634	5.48431
F	11.21030	5.90278	9.82632
N	8.14749	9.08204	3.09409
C	8.54782	8.64672	4.32322
C	10.14964	7.02991	5.26575
F	10.67875	7.95420	9.38233
C	11.13978	6.05693	4.84521
C	11.88721	5.30050	5.78761
C	11.65305	5.50743	7.16627
H	12.20731	4.94657	7.91611
C	6.64634	10.57741	4.19834
H	5.88336	11.35576	4.15226
C	12.19844	5.05093	3.02364
H	12.30083	4.97750	1.93474
C	9.95747	7.19627	6.64539
H	9.22088	7.92138	6.98479
C	10.70568	6.43897	7.56464
C	7.11433	10.06579	5.40832
H	6.71940	10.43753	6.36236
C	13.01332	4.23019	3.86470
C	12.86154	4.34764	5.27781
C	7.21978	10.02597	3.04385
H	6.91320	10.36385	2.04597
C	14.58042	2.64256	5.54718
H	15.19448	2.02018	6.20356
C	13.94969	3.31884	3.31527
H	14.04672	3.24936	2.22827
C	10.44362	6.67408	9.03249
C	14.72564	2.53270	4.14639
H	15.44848	1.82917	3.72604
C	13.67079	3.52846	6.10265
H	13.58287	3.58984	7.18814
N	10.59180	7.67527	0.53127
N	8.68436	5.98050	1.27924
F	10.86242	6.50889	-4.58546
N	12.13190	9.02657	-0.69175
F	8.80726	6.01793	-5.05838
N	12.02692	8.98210	1.69808
C	11.60326	8.57941	0.46566
C	9.91054	7.06603	-0.48945
F	9.35936	8.06049	-4.59957
C	8.87031	6.14330	-0.07664
C	8.07960	5.44025	-1.02506

C	8.32081	5.65017	-2.40204
H	7.73486	5.12910	-3.15651
C	13.61690	10.39169	0.60555
H	14.42527	11.12239	0.65766
C	7.76509	5.17375	1.73698
H	7.66302	5.09219	2.82533
C	10.10827	7.23705	-1.86773
H	10.88359	7.92342	-2.20137
C	9.31719	6.53250	-2.79297
C	13.12030	9.91769	-0.60833
H	13.53790	10.27179	-1.55943
C	6.90319	4.40968	0.88941
C	7.05591	4.53640	-0.52281
C	13.00958	9.86820	1.75569
H	13.33422	10.18065	2.75614
C	5.24358	2.93337	-0.80561
H	4.59302	2.35480	-1.46690
C	5.91974	3.54486	1.43169
H	5.82322	3.46707	2.51817
C	9.58208	6.77536	-4.25904
C	5.09786	2.81394	0.59435
H	4.33837	2.14665	1.00913
C	6.19924	3.77398	-1.35412
H	6.28631	3.84394	-2.43912

(^{CF3}**L2**)$_2$Zn (S$_{1,eq}$) B3LYP (SMD “n-hexane”/ def2-tzvpp def2/j)

Zn	9.84578	7.03326	2.43278
N	9.53508	7.70692	4.27610
N	11.20325	5.77709	3.51953
F	9.41674	6.68962	9.44324
N	8.31305	9.34889	5.49989
F	11.47632	6.15309	9.84115
N	8.19379	9.12137	3.11821
C	8.66581	8.74831	4.34345
C	10.21287	7.08172	5.28875
F	10.96444	8.19310	9.32410
C	11.12392	6.03277	4.87175
C	11.89415	5.29771	5.81285
C	11.75222	5.59305	7.18796
H	12.31816	5.04331	7.93736
C	6.91226	10.81480	4.21675
H	6.20617	11.64499	4.16984
C	11.99628	4.84643	3.05957
H	12.00825	4.68403	1.97556
C	10.11505	7.33781	6.66447
H	9.43817	8.11943	7.00156
C	10.87383	6.59141	7.58335
C	7.45096	10.36347	5.42157
H	7.17513	10.84124	6.37034
C	12.83258	4.04646	3.89895
C	12.78987	4.26909	5.30658
C	7.33639	10.13061	3.06905
H	6.96550	10.41441	2.07605
C	14.45277	2.50916	5.57775
H	15.08843	1.90708	6.23247
C	13.68527	3.05469	3.35235
H	13.69624	2.90391	2.26929
C	10.68826	6.90293	9.04837
C	14.48774	2.29323	4.18159
H	15.14629	1.52782	3.76377

C	13.62369	3.47331	6.13000
H	13.62000	3.61632	7.21134
N	10.49316	7.65591	0.57149
N	8.65836	5.89007	1.27894
F	9.35081	8.19438	-4.56980
N	11.96341	9.12714	-0.59138
F	10.86150	6.65082	-4.58906
N	11.90780	8.93346	1.79782
C	11.47731	8.59623	0.55177
C	9.83459	7.06403	-0.47816
F	8.80961	6.15970	-5.08841
C	8.82854	6.09324	-0.07469
C	8.08888	5.41287	-1.04977
C	8.34634	5.69115	-2.42946
H	7.77873	5.16566	-3.19627
C	13.41858	10.46235	0.76009
H	14.20086	11.21845	0.84049
C	7.71841	4.98644	1.67024
H	7.60065	4.85050	2.74924
C	10.05230	7.30701	-1.84266
H	10.80664	8.03588	-2.13075
C	9.30158	6.61143	-2.81606
C	12.91785	10.04567	-0.47835
H	13.30428	10.47180	-1.41177
C	6.91801	4.24674	0.78812
C	7.07522	4.43389	-0.63588
C	12.85871	9.84999	1.89212
H	13.19538	10.11402	2.90144
C	5.32576	2.77595	-1.04207
H	4.71319	2.21138	-1.74822
C	5.94064	3.30356	1.24840
H	5.81532	3.15801	2.32476
C	9.57391	6.89824	-4.26600
C	5.16870	2.59092	0.34549
H	4.42752	1.87607	0.71541
C	6.27778	3.69613	-1.51595
H	6.38448	3.82697	-2.59453

($^{\mathbf{CF3}}$**L2**)$_2$Zn (T$_{1,eq}$) B3LYP (SMD “n-hexane”/ def2-tzvpp def2/j)

Zn	9.89596	6.97516	2.43754
N	9.51058	7.61299	4.27966
N	11.22170	5.71312	3.54551
F	9.43392	6.70291	9.47054
N	8.20972	9.21154	5.48089
F	11.49798	6.17922	9.86194
N	8.14257	8.97970	3.10055
C	8.60528	8.62372	4.33336
C	10.19928	7.01423	5.30032
F	10.97633	8.20690	9.31019
C	11.13227	5.97979	4.89550
C	11.91581	5.27121	5.84586
C	11.77187	5.58486	7.21671
H	12.35160	5.05933	7.97282
C	6.78399	10.62751	4.17192
H	6.05131	11.43345	4.11102
C	12.03464	4.79413	3.09686
H	12.05759	4.62586	2.01407
C	10.09804	7.28785	6.67260
H	9.40478	8.05986	6.99978
C	10.87680	6.57287	7.59998

C	7.31486	10.19542	5.38708
H	7.00500	10.66321	6.33021
C	12.87992	4.01541	3.94733
C	12.82904	4.25155	5.35270
C	7.25273	9.95847	3.03267
H	6.89185	10.22895	2.03240
C	14.51784	2.52075	5.64729
H	15.16011	1.93535	6.31063
C	13.75043	3.03172	3.41428
H	13.76895	2.86995	2.33294
C	10.70111	6.91133	9.06071
C	14.56126	2.29145	4.25404
H	15.23338	1.53241	3.84634
C	13.67249	3.47736	6.18670
H	13.66307	3.63059	7.26656
N	10.52872	7.62404	0.59586
N	8.67370	5.83902	1.24844
F	10.37964	8.00617	-4.46796
N	12.04998	9.09112	-0.51529
F	9.78051	5.97924	-4.95200
N	11.97265	8.83479	1.85984
C	11.54398	8.54570	0.60642
C	9.85246	7.09124	-0.44492
F	8.28861	7.53071	-4.79387
C	8.82925	6.10015	-0.05520
C	8.04907	5.45788	-1.07538
C	8.28096	5.80251	-2.40544
H	7.69600	5.32903	-3.19568
C	13.54012	10.34272	0.87744
H	14.34588	11.07072	0.98354
C	7.73164	4.92183	1.66090
H	7.65003	4.76186	2.73829
C	10.03591	7.39579	-1.82704
H	10.79025	8.13046	-2.09691
C	9.26779	6.76846	-2.78256
C	13.03387	9.97698	-0.37223
H	13.43778	10.41543	-1.29265
C	6.91063	4.22499	0.76177
C	7.04388	4.47036	-0.65304
C	12.95233	9.71888	1.98719
H	13.28716	9.94475	3.00650
C	5.27777	2.83967	-1.08495
H	4.64727	2.30484	-1.79927
C	5.93978	3.27346	1.20601
H	5.83852	3.08974	2.27937
C	9.43634	7.07721	-4.23992
C	5.14377	2.59867	0.29996
H	4.40589	1.87443	0.65660
C	6.21781	3.76485	-1.54268
H	6.30305	3.93525	-2.61799

$(^{t\mathbf{Bu}}\mathbf{L3})_2$Zn ($S_{0,eq}$) M06-L (gas phase/ def2-tzvpp def2/j)

Zn	0.00000	0.00000	0.27705
N	-1.07684	-1.40509	-0.81680
N	0.95159	-1.60696	0.93135
C	0.44037	-2.78204	0.43793
C	-0.65593	-2.67970	-0.49748
C	-0.80653	-5.11190	-0.65277
H	-1.27077	-5.99525	-1.07048
C	0.83400	-4.08116	0.80546

H	1.62347	-4.18701	1.54100
C	-1.27244	-3.83671	-1.04291
C	-2.76616	-2.29840	-2.28018
C	-2.07425	-1.21940	-1.65364
C	0.23057	-5.23950	0.27425
C	-2.36720	-3.63439	-1.97827
C	2.15279	-1.54395	1.65546
C	-3.06870	-4.69118	-2.60759
H	-2.79637	-5.72088	-2.40463
C	3.31013	-2.28212	1.31520
H	3.28064	-2.96470	0.47130
C	0.73583	-6.61477	0.74728
C	-3.83209	-2.05043	-3.18115
H	-4.11673	-1.02282	-3.39014
C	-4.49740	-3.10423	-3.78038
H	-5.31417	-2.91761	-4.47035
C	-4.10805	-4.43049	-3.48794
H	-4.63014	-5.25842	-3.95825
C	2.25122	-0.63064	2.72843
H	1.37472	-0.04522	2.99594
C	4.49951	-2.12030	2.03010
H	5.37446	-2.69650	1.73952
C	4.57932	-1.21789	3.09865
H	5.50637	-1.09607	3.65079
C	3.44478	-0.46912	3.43542
H	3.48490	0.24175	4.25663
N	1.07684	1.40509	-0.81680
N	-0.95159	1.60696	0.93135
C	-0.44037	2.78204	0.43793
C	0.65593	2.67970	-0.49748
C	0.80653	5.11190	-0.65277
H	1.27077	5.99525	-1.07048
C	-0.83400	4.08116	0.80546
H	-1.62347	4.18701	1.54100
C	1.27244	3.83671	-1.04291
C	2.76616	2.29840	-2.28018
C	2.07425	1.21940	-1.65364
C	-0.23057	5.23950	0.27425
C	2.36720	3.63439	-1.97827
C	-2.15279	1.54395	1.65546
C	3.06870	4.69118	-2.60759
H	2.79637	5.72088	-2.40463
C	-3.31013	2.28212	1.31520
H	-3.28064	2.96470	0.47130
C	-0.73583	6.61477	0.74728
C	3.83209	2.05043	-3.18115
H	4.11673	1.02282	-3.39014
C	4.49740	3.10423	-3.78038
H	5.31417	2.91761	-4.47035
C	4.10805	4.43049	-3.48794
H	4.63014	5.25842	-3.95825
C	-2.25122	0.63064	2.72843
H	-1.37472	0.04522	2.99594
C	-4.49951	2.12030	2.03010
H	-5.37446	2.69650	1.73952
C	-4.57932	1.21789	3.09865
H	-5.50637	1.09607	3.65079
C	-3.44478	0.46912	3.43542
H	-3.48490	-0.24175	4.25663
H	-2.36605	-0.19253	-1.85902
H	2.36605	0.19253	-1.85902
C	-0.52303	6.74064	2.27555

H	-0.88315	7.71567	2.62455
H	-1.06504	5.96427	2.82460
H	0.53970	6.65693	2.52808
C	-2.24482	6.74810	0.43150
H	-2.83408	5.97540	0.93506
H	-2.61228	7.72487	0.76755
H	-2.42457	6.66637	-0.64620
C	0.00000	7.78216	0.06307
H	1.07399	7.76886	0.27917
H	-0.13630	7.76614	-1.02412
H	-0.40261	8.73037	0.43548
C	0.52303	-6.74064	2.27555
H	0.88315	-7.71567	2.62455
H	1.06504	-5.96427	2.82460
H	-0.53970	-6.65693	2.52808
C	2.24482	-6.74810	0.43150
H	2.83408	-5.97540	0.93506
H	2.61228	-7.72487	0.76755
H	2.42457	-6.66637	-0.64620
C	0.00000	-7.78216	0.06307
H	-1.07399	-7.76886	0.27917
H	0.13630	-7.76614	-1.02412
H	0.40261	-8.73037	0.43548

(${}^{t\mathrm{Bu}}$**L3**)$_2$Zn (S$_{0,\mathrm{eq}}$) B3LYP (SMD “dichloromethane”/ def2-tzvpp def2/j)

Zn	0.02117	0.05096	-0.00948
N	-1.04985	-1.40535	-1.02766
N	0.97936	-1.51996	0.74987
C	0.42598	-2.71353	0.36219
C	-0.66424	-2.65510	-0.59233
C	-0.89887	-5.08783	-0.53499
H	-1.39857	-5.98792	-0.88321
C	0.76415	-3.99120	0.84571
H	1.54724	-4.06605	1.59841
C	-1.31081	-3.83597	-1.04656
C	-2.73083	-2.36658	-2.44862
C	-2.01946	-1.25803	-1.89507
C	0.12011	-5.17240	0.41646
C	-2.38124	-3.68353	-2.02354
C	2.17534	-1.38552	1.45905
C	-3.10113	-4.77027	-2.57996
H	-2.86377	-5.79266	-2.28293
C	3.30897	-2.21713	1.28053
H	3.27037	-3.04156	0.56676
C	0.56213	-6.52122	1.02680
C	-3.76673	-2.16580	-3.39633
H	-4.01280	-1.14501	-3.70176
C	-4.44973	-3.24734	-3.92097
H	-5.24823	-3.09626	-4.65177
C	-4.10974	-4.55476	-3.50668
H	-4.64977	-5.40987	-3.92238
C	2.31004	-0.29751	2.35669
H	1.45557	0.36922	2.50563
C	4.49561	-1.97865	1.97937
H	5.35277	-2.63808	1.81072
C	4.60407	-0.90748	2.87418
H	5.53463	-0.72806	3.41916
C	3.49933	-0.06456	3.04881
H	3.56026	0.78439	3.73664
N	1.10653	1.49470	-1.03112

N	-0.94582	1.63154	0.71789
C	-0.38632	2.82009	0.32379
C	0.71624	2.74973	-0.61559
C	0.95247	5.18276	-0.58296
H	1.45780	6.07833	-0.93468
C	-0.72958	4.10342	0.78822
H	-1.52241	4.18743	1.52969
C	1.36966	3.92482	-1.07495
C	2.80691	2.43828	-2.44085
C	2.08755	1.33670	-1.88369
C	-0.07864	5.27907	0.35420
C	2.45248	3.76035	-2.03617
C	-2.15129	1.50622	1.41255
C	3.17992	4.84014	-2.59628
H	2.93885	5.86614	-2.31506
C	-3.28217	2.33557	1.20808
H	-3.23360	3.15096	0.48459
C	-0.52714	6.63509	0.94347
C	3.85521	2.22581	-3.37221
H	4.10485	1.20135	-3.66209
C	4.54560	3.30076	-3.90072
H	5.35370	3.14064	-4.61893
C	4.20062	4.61319	-3.50689
H	4.74635	5.46307	-3.92585
C	-2.29833	0.42967	2.32194
H	-1.44593	-0.23496	2.49085
C	-4.47830	2.10585	1.89356
H	-5.33304	2.76297	1.70481
C	-4.59913	1.04602	2.80025
H	-5.53711	0.87342	3.33460
C	-3.49698	0.20544	3.00068
H	-3.56742	-0.63474	3.69830
H	-2.28496	-0.23864	-2.19477
H	2.35641	0.31371	-2.16778
C	-0.30302	6.62655	2.47400
H	-0.61540	7.58954	2.91213
H	-0.88079	5.83207	2.97152
H	0.76115	6.47418	2.71958
C	-2.02918	6.85718	0.65013
H	-2.65970	6.07641	1.10312
H	-2.35887	7.82724	1.05880
H	-2.22664	6.86414	-0.43482
C	0.25612	7.82078	0.35115
H	1.33607	7.74849	0.55659
H	0.12082	7.90303	-0.73925
H	-0.10138	8.76168	0.79977
C	0.31629	-6.49621	2.55382
H	0.62370	-7.45385	3.00694
H	0.88583	-5.69543	3.05074
H	-0.75147	-6.34279	2.78256
C	2.06844	-6.74437	0.75721
H	2.69152	-5.95785	1.21054
H	2.39345	-7.70945	1.18114
H	2.28127	-6.76294	-0.32468
C	-0.21106	-7.71451	0.43646
H	-1.29392	-7.64172	0.62576
H	-0.06018	-7.80844	-0.65094
H	0.14134	-8.64991	0.90037

($^{t\text{Bu}}$**L3**)$_2$Zn (S$_{1,\text{eq}}$) B3LYP (SMD “dichloromethane”/ def2-tzvpp def2/j)

Zn	-0.24665	0.01131	-0.17492
N	-1.11468	-1.49119	-1.14176
N	0.85117	-1.52353	0.67616
C	0.34458	-2.75276	0.31450
C	-0.70661	-2.73068	-0.67746
C	-0.81234	-5.16426	-0.52430
H	-1.26166	-6.09105	-0.87445
C	0.70476	-3.97793	0.90119
H	1.42312	-3.96741	1.72040
C	-1.25480	-3.94110	-1.12108
C	-2.67346	-2.60471	-2.65274
C	-2.08895	-1.45814	-2.09493
C	0.13841	-5.20808	0.49041
C	-2.27173	-3.91289	-2.18265
C	2.06233	-1.32364	1.29924
C	-2.85971	-5.05161	-2.74715
H	-2.56220	-6.04519	-2.40553
C	3.18881	-2.18460	1.16269
H	3.12764	-3.05910	0.51432
C	0.58012	-6.51329	1.17993
C	-3.67510	-2.52767	-3.67922
H	-3.98590	-1.54158	-4.03618
C	-4.23663	-3.67789	-4.20862
H	-4.99885	-3.59667	-4.98997
C	-3.83685	-4.95194	-3.75338
H	-4.28234	-5.85583	-4.17516
C	2.22126	-0.13754	2.07080
H	1.36974	0.53956	2.17041
C	4.39006	-1.88236	1.79906
H	5.24764	-2.54750	1.66624
C	4.51488	-0.72924	2.58753
H	5.46072	-0.50238	3.08548
C	3.42126	0.14224	2.71376
H	3.51067	1.04932	3.31727
N	0.89055	1.46790	-1.12680
N	-1.07873	1.58292	0.71809
C	-0.47510	2.76715	0.37837
C	0.58289	2.70882	-0.61081
C	0.93861	5.12101	-0.43116
H	1.46983	6.01450	-0.74852
C	-0.73657	4.03062	0.93989
H	-1.49514	4.10053	1.71790
C	1.27386	3.88049	-1.02098
C	2.56997	2.42657	-2.55241
C	1.82041	1.32420	-2.03776
C	-0.04873	5.20198	0.55358
C	2.30446	3.73180	-2.03999
C	-2.26417	1.47432	1.45092
C	3.06310	4.81204	-2.55656
H	2.88999	5.82504	-2.19081
C	-3.35776	2.36802	1.33601
H	-3.29077	3.22285	0.66100
C	-0.41292	6.53548	1.24180
C	3.56191	2.23002	-3.54711
H	3.74222	1.21791	-3.92005
C	4.28420	3.30500	-4.03234
H	5.04872	3.15747	-4.79928
C	4.02852	4.60135	-3.52979
H	4.59989	5.45098	-3.91355
C	-2.43261	0.35434	2.30161
H	-1.60751	-0.35678	2.40260
C	-4.54107	2.15428	2.04884

H	-5.36788	2.86151	1.93005
C	-4.68482	1.04720	2.89441
H	-5.61286	0.88626	3.44925
C	-3.61891	0.14519	3.00722
H	-3.70838	-0.73133	3.65619
H	-2.41135	-0.46729	-2.42704
H	2.02036	0.31261	-2.40702
C	-0.14313	6.41819	2.76099
H	-0.39627	7.36566	3.26556
H	-0.74396	5.62016	3.22377
H	0.92012	6.20169	2.95645
C	-1.91148	6.84278	1.01053
H	-2.56111	6.05829	1.42830
H	-2.18212	7.79591	1.49476
H	-2.13348	6.93215	-0.06575
C	0.40860	7.71945	0.69858
H	1.48894	7.57896	0.86151
H	0.24191	7.87420	-0.37931
H	0.11014	8.64345	1.21908
C	0.22442	-6.44052	2.68407
H	0.54040	-7.36532	3.19494
H	0.72442	-5.59508	3.18252
H	-0.86265	-6.32579	2.82641
C	2.10926	-6.68857	1.02398
H	2.66615	-5.85320	1.47659
H	2.43774	-7.61709	1.51980
H	2.39204	-6.75101	-0.03979
C	-0.11203	-7.74856	0.57605
H	-1.20692	-7.70145	0.68810
H	0.11829	-7.86381	-0.49520
H	0.23773	-8.65601	1.09344

(${}^{t\mathrm{Bu}}$**L3**)$_2$Zn (T$_{1,\mathrm{eq}}$) B3LYP (SMD “dichloromethane”/ def2-tzvpp def2/j)

Zn	0.23929	-0.01158	-0.18827
N	-0.91650	-1.43950	-1.14700
N	1.08788	-1.59920	0.65604
C	0.47050	-2.77427	0.30772
C	-0.60644	-2.69123	-0.65947
C	-0.97824	-5.10276	-0.51320
H	-1.52405	-5.98614	-0.83385
C	0.73215	-4.04917	0.84274
H	1.50416	-4.13855	1.60525
C	-1.31453	-3.85038	-1.07611
C	-2.63363	-2.35954	-2.55199
C	-1.86546	-1.27225	-2.03358
C	0.02605	-5.20810	0.45156
C	-2.36514	-3.67616	-2.07070
C	2.28951	-1.50472	1.36297
C	-3.14135	-4.74134	-2.59192
H	-2.96663	-5.76279	-2.25127
C	3.37253	-2.40773	1.22314
H	3.28646	-3.25786	0.54469
C	0.38670	-6.55567	1.11587
C	-3.64632	-2.13804	-3.51996
H	-3.82929	-1.11810	-3.86938
C	-4.38568	-3.19887	-4.00934
H	-5.16644	-3.03189	-4.75568
C	-4.12648	-4.50582	-3.53883
H	-4.71104	-5.34456	-3.92670
C	2.48683	-0.38901	2.21346

H	1.67239	0.33161	2.33292
C	4.57102	-2.20849	1.91394
H	5.38838	-2.92323	1.77603
C	4.74186	-1.10736	2.76126
H	5.68168	-0.95831	3.29940
C	3.68801	-0.19507	2.89703
H	3.79880	0.67829	3.54698
N	1.14098	1.51014	-1.10812
N	-0.85548	1.51534	0.68858
C	-0.35924	2.73147	0.33872
C	0.72500	2.71538	-0.63683
C	0.81151	5.14406	-0.47512
H	1.26208	6.08016	-0.79955
C	-0.76124	3.97378	0.90807
H	-1.51189	3.95491	1.69768
C	1.28569	3.95235	-1.05630
C	2.76474	2.62510	-2.55496
C	2.15612	1.47170	-2.04397
C	-0.19444	5.18470	0.52192
C	2.34646	3.92589	-2.07922
C	-2.04351	1.30271	1.38287
C	2.96175	5.07052	-2.60542
H	2.65505	6.06079	-2.26132
C	-3.20907	2.08886	1.20323
H	-3.20461	2.91058	0.48554
C	-0.64366	6.49958	1.19524
C	3.80192	2.56186	-3.54399
H	4.12266	1.57999	-3.90459
C	4.38698	3.71561	-4.03565
H	5.17664	3.64439	-4.79005
C	3.97231	4.98316	-3.57318
H	4.43490	5.89277	-3.96425
C	-2.11451	0.18704	2.25279
H	-1.22818	-0.43865	2.38232
C	-4.38056	1.78289	1.89631
H	-5.27351	2.39266	1.73263
C	-4.42519	0.69917	2.78244
H	-5.34565	0.46812	3.32484
C	-3.28498	-0.09834 `	2.95209
H	-3.31023	-0.95390	3.63252
H	-2.06665	-0.25255	-2.37881
H	2.46844	0.48017	-2.38091
C	-0.29867	6.44434	2.70198
H	-0.61456	7.37427	3.20453
H	-0.80334	5.60532	3.20700
H	0.78664	6.32837	2.85813
C	-2.17097	6.67435	1.03046
H	-2.73339	5.85076	1.49775
H	-2.50314	7.61237	1.50632
H	-2.45522	6.71697	-0.03413
C	0.04863	7.73216	0.58545
H	1.14270	7.69971	0.71132
H	-0.16839	7.83925	-0.48970
H	-0.31176	8.64457	1.08723
C	0.13994	-6.45702	2.63971
H	0.38761	-7.41345	3.13042
H	0.75642	-5.67420	3.10843
H	-0.91691	-6.23020	2.85798
C	1.87773	-6.87698	0.86101
H	2.54516	-6.11133	1.28610
H	2.14485	-7.84232	1.32307
H	2.09095	-6.94980	-0.21849

C	-0.45440	-7.72355	0.56910
H	-1.53161	-7.57946	0.74978
H	-0.30644	-7.86961	-0.51292
H	-0.15946	-8.65911	1.07121

(${}^{t\mathrm{Bu}}$**L3**)$_2$Zn ($S_{0,\mathrm{eq}}$) B3LYP (SMD “diethyl ether”/ def2-tzvpp def2/j)

Zn	0.00001	-0.00000	0.00478
N	-1.06985	-1.46234	-1.01079
N	0.98326	-1.56536	0.73899
C	0.43682	-2.76138	0.35314
C	-0.66607	-2.70971	-0.58726
C	-0.87559	-5.14452	-0.53861
H	-1.37060	-6.04826	-0.88384
C	0.79399	-4.03802	0.82604
H	1.58668	-4.10703	1.56926
C	-1.30694	-3.89511	-1.03863
C	-2.76223	-2.43261	-2.41172
C	-2.05402	-1.32005	-1.86231
C	0.15643	-5.22297	0.39947
C	-2.39216	-3.74809	-1.99962
C	2.18518	-1.42467	1.43815
C	-3.10828	-4.83898	-2.55265
H	-2.85519	-5.86040	-2.26554
C	3.32720	-2.23737	1.23187
H	3.29025	-3.04983	0.50420
C	0.61890	-6.56999	0.99844
C	-3.81429	-2.23819	-3.34266
H	-4.07696	-1.21861	-3.63835
C	-4.49309	-3.32370	-3.86398
H	-5.30410	-3.17684	-4.58180
C	-4.13254	-4.62958	-3.46303
H	-4.66901	-5.48824	-3.87610
C	2.31480	-0.35018	2.35157
H	1.45272	0.30143	2.52207
C	4.51862	-1.99417	1.92037
H	5.38292	-2.63844	1.73081
C	4.62274	-0.93641	2.83114
H	5.55725	-0.75291	3.36792
C	3.50904	-0.11214	3.03307
H	3.56675	0.72602	3.73424
N	1.06986	1.46234	-1.01078
N	-0.98325	1.56534	0.73899
C	-0.43682	2.76138	0.35314
C	0.66608	2.70972	-0.58726
C	0.87559	5.14452	-0.53861
H	1.37060	6.04826	-0.88384
C	-0.79399	4.03801	0.82604
H	-1.58668	4.10702	1.56925
C	1.30694	3.89511	-1.03863
C	2.76224	2.43262	-2.41171
C	2.05404	1.32005	-1.86231
C	-0.15643	5.22297	0.39946
C	2.39216	3.74809	-1.99962
C	-2.18518	1.42467	1.43815
C	3.10828	4.83898	-2.55265
H	2.85518	5.86040	-2.26553
C	-3.32719	2.23737	1.23187
H	-3.29025	3.04983	0.50420
C	-0.61891	6.56998	0.99843
C	3.81431	2.23820	-3.34266

H	4.07698	1.21862	-3.63834
C	4.49310	3.32371	-3.86397
H	5.30411	3.17685	-4.58179
C	4.13254	4.62960	-3.46303
H	4.66901	5.48825	-3.87610
C	-2.31479	0.35018	2.35157
H	-1.45272	-0.30144	2.52207
C	-4.51862	1.99416	1.92038
H	-5.38292	2.63844	1.73081
C	-4.62273	0.93641	2.83114
H	-5.55725	0.75291	3.36792
C	-3.50903	0.11214	3.03308
H	-3.56674	-0.72602	3.73424
H	-2.33431	-0.30140	-2.15117
H	2.33433	0.30140	-2.15116
C	-0.39001	6.55411	2.52812
H	-0.71214	7.51017	2.97447
H	-0.95624	5.74948	3.02250
H	0.67647	6.41207	2.76959
C	-2.12405	6.77670	0.71027
H	-2.74487	5.98651	1.16022
H	-2.46460	7.74054	1.12489
H	-2.32480	6.78694	-0.37403
C	0.14883	7.76846	0.41163
H	1.23004	7.70828	0.61446
H	0.01003	7.85612	-0.67795
H	-0.21822	8.70286	0.86622
C	0.38999	-6.55411	2.52812
H	0.71212	-7.51017	2.97448
H	0.95623	-5.74949	3.02251
H	-0.67649	-6.41207	2.76959
C	2.12404	-6.77672	0.71028
H	2.74485	-5.98653	1.16024
H	2.46459	-7.74055	1.12491
H	2.32479	-6.78695	-0.37401
C	-0.14885	-7.76847	0.41164
H	-1.23006	-7.70827	0.61446
H	-0.01004	-7.85612	-0.67795
H	0.21820	-8.70286	0.86623

($^{t\mathrm{Bu}}$**L3**)$_2$Zn (S$_{1,\mathrm{eq}}$) B3LYP (SMD “diethyl ether”/ def2-tzvpp def2/j)

Zn	-0.26442	0.00953	-0.16471
N	-1.10471	-1.49077	-1.15444
N	0.83566	-1.52163	0.69002
C	0.33302	-2.75618	0.31928
C	-0.70045	-2.73463	-0.68716
C	-0.80720	-5.16810	-0.53615
H	-1.24927	-6.09436	-0.89644
C	0.68126	-3.97657	0.91433
H	1.38514	-3.96476	1.74612
C	-1.23956	-3.94260	-1.14106
C	-2.62996	-2.60800	-2.69724
C	-2.05969	-1.46137	-2.12476
C	0.12220	-5.21086	0.49339
C	-2.23573	-3.91584	-2.22124
C	2.04784	-1.32287	1.30252
C	-2.81128	-5.05444	-2.79734
H	-2.51955	-6.04796	-2.45092
C	3.16948	-2.19489	1.17709
H	3.10020	-3.07750	0.54093

C	0.55650	-6.51440	1.19045
C	-3.61169	-2.53052	-3.74240
H	-3.91717	-1.54452	-4.10392
C	-4.16164	-3.68081	-4.28322
H	-4.90918	-3.59985	-5.07855
C	-3.76942	-4.95445	-3.82186
H	-4.20626	-5.85814	-4.25279
C	2.21964	-0.12561	2.05736
H	1.37343	0.55906	2.14911
C	4.37348	-1.89274	1.80655
H	5.22591	-2.56596	1.68171
C	4.50916	-0.72902	2.57794
H	5.45766	-0.50258	3.07080
C	3.42266	0.15333	2.69303
H	3.52072	1.06834	3.28298
N	0.87096	1.46499	-1.12567
N	-1.07751	1.58266	0.74146
C	-0.47753	2.76482	0.39295
C	0.57067	2.70559	-0.60688
C	0.92900	5.11757	-0.43417
H	1.45686	6.01081	-0.75750
C	-0.73412	4.03003	0.95369
H	-1.48593	4.10037	1.73822
C	1.25867	3.87671	-1.02492
C	2.53819	2.41957	-2.56789
C	1.79080	1.31907	-2.04617
C	-0.05021	5.20001	0.55896
C	2.27977	3.72533	-2.05291
C	-2.25354	1.48027	1.49253
C	3.03620	4.80381	-2.57621
H	2.86809	5.81684	-2.20838
C	-3.35276	2.36502	1.37125
H	-3.29769	3.20480	0.67637
C	-0.40918	6.53505	1.24712
C	3.52081	2.22198	-3.57148
H	3.69611	1.20984	-3.94683
C	4.24099	3.29533	-4.06287
H	4.99828	3.14640	-4.83666
C	3.99259	4.59191	-3.55775
H	4.56226	5.44050	-3.94623
C	-2.40381	0.37802	2.36795
H	-1.57326	-0.32602	2.47264
C	-4.52599	2.16007	2.10260
H	-5.35877	2.85925	1.97862
C	-4.65223	1.07061	2.97309
H	-5.57265	0.91595	3.54211
C	-3.58024	0.17725	3.09214
H	-3.65710	-0.68583	3.76033
H	-2.38261	-0.47158	-2.46001
H	1.98334	0.30690	-2.41801
C	-0.12839	6.42124	2.76446
H	-0.37809	7.36942	3.26947
H	-0.72499	5.62393	3.23373
H	0.93615	6.20516	2.95287
C	-1.90923	6.84185	1.02542
H	-2.55607	6.05814	1.44878
H	-2.17759	7.79583	1.50930
H	-2.13874	6.92852	-0.04942
C	0.40835	7.71793	0.69563
H	1.48989	7.57777	0.85070
H	0.23336	7.87121	-0.38116
H	0.11457	8.64335	1.21628

C	0.17738	-6.44246	2.68879
H	0.48779	-7.36590	3.20553
H	0.66643	-5.59565	3.19573
H	-0.91193	-6.33044	2.81435
C	2.08823	-6.68644	1.05782
H	2.63702	-5.85046	1.51921
H	2.41224	-7.61423	1.55796
H	2.38760	-6.74742	-0.00142
C	-0.12324	-7.75145	0.57650
H	-1.21985	-7.70634	0.67068
H	0.12468	-7.86732	-0.49072
H	0.21912	-8.65847	1.09960

$({}^{t\mathrm{Bu}}\mathbf{L3})_2$Zn ($\mathrm{T}_{1,\mathrm{eq}}$) B3LYP (SMD “diethyl ether”/ def2-tzvpp def2/j)

Zn	0.25350	-0.01157	-0.18766
N	-0.89637	-1.44591	-1.14883
N	1.08543	-1.59266	0.68028
C	0.47212	-2.76872	0.33306
C	-0.59327	-2.69327	-0.64765
C	-0.96699	-5.10333	-0.48797
H	-1.50857	-5.98942	-0.80810
C	0.72796	-4.04016	0.87973
H	1.49143	-4.12269	1.65163
C	-1.29704	-3.85571	-1.06362
C	-2.59835	-2.37535	-2.56593
C	-1.83450	-1.28493	-2.04781
C	0.02683	-5.20132	0.48873
C	-2.33639	-3.68815	-2.07079
C	2.27595	-1.49829	1.40814
C	-3.10846	-4.75642	-2.59173
H	-2.93863	-5.77506	-2.24044
C	3.36509	-2.39313	1.27056
H	3.29255	-3.23304	0.57764
C	0.38023	-6.54407	1.16643
C	-3.60018	-2.16149	-3.54672
H	-3.77881	-1.14459	-3.90729
C	-4.33543	-3.22527	-4.03528
H	-5.10778	-3.06358	-4.79151
C	-4.08294	-4.52829	-3.55096
H	-4.66425	-5.36973	-3.93797
C	2.45338	-0.39405	2.27616
H	1.63330	0.32049	2.39316
C	4.55211	-2.19759	1.98128
H	5.37586	-2.90523	1.84497
C	4.70373	-1.10777	2.84634
H	5.63490	-0.96095	3.39989
C	3.64347	-0.20329	2.97965
H	3.74028	0.66143	3.64320
N	1.14884	1.50546	-1.11927
N	-0.85009	1.51748	0.67488
C	-0.35730	2.73224	0.31644
C	0.72696	2.71198	-0.65945
C	0.80275	5.14175	-0.51953
H	1.24915	6.07670	-0.85276
C	-0.76286	3.97794	0.87674
H	-1.51133	3.96158	1.66851
C	1.28080	3.94823	-1.09170
C	2.76521	2.61472	-2.57876
C	2.16427	1.46310	-2.05524
C	-0.20145	5.18719	0.48032

C	2.33888	3.91734	-2.11673
C	-2.03743	1.30621	1.37033
C	2.94488	5.06005	-2.65742
H	2.63158	6.05223	-2.32492
C	-3.20479	2.08873	1.18682
H	-3.20216	2.90632	0.46436
C	-0.65172	6.50591	1.14537
C	3.80158	2.54747	-3.56757
H	4.12944	1.56397	-3.91703
C	4.37759	3.69919	-4.07325
H	5.16707	3.62499	-4.82749
C	3.95405	4.96877	-3.62523
H	4.40930	5.87705	-4.02783
C	-2.10667	0.19512	2.24612
H	-1.21942	-0.42874	2.37836
C	-4.37559	1.78425	1.88154
H	-5.26979	2.39142	1.71458
C	-4.41826	0.70535	2.77325
H	-5.33824	0.47537	3.31694
C	-3.27658	-0.08887	2.94660
H	-3.30001	-0.94127	3.63108
H	-2.02946	-0.26768	-2.40396
H	2.48329	0.46993	-2.38052
C	-0.29553	6.46545	2.64998
H	-0.61095	7.39824	3.14765
H	-0.79264	5.62889	3.16646
H	0.79120	6.35437	2.79927
C	-2.18078	6.67351	0.98977
H	-2.73748	5.85298	1.46921
H	-2.51412	7.61486	1.45831
H	-2.47304	6.70395	-0.07305
C	0.03082	7.73629	0.52019
H	1.12576	7.71087	0.63998
H	-0.19310	7.83287	-0.55457
H	-0.33055	8.65200	1.01527
C	0.11608	-6.43482	2.68657
H	0.35808	-7.38741	3.18759
H	0.72650	-5.64842	3.15710
H	-0.94308	-6.20615	2.89113
C	1.87398	-6.86663	0.93005
H	2.53682	-6.09822	1.35721
H	2.13713	-7.82890	1.40086
H	2.09928	-6.94572	-0.14651
C	-0.45427	-7.71617	0.61857
H	-1.53353	-7.57170	0.78650
H	-0.29413	-7.87010	-0.46065
H	-0.16506	-8.64851	1.12998

($^{t\text{Bu}}$**L3**)$_2$Zn (S$_{0,\text{eq}}$) B3LYP (SMD “toluene”/ def2-tzvpp def2/j)

Zn	0.00000	0.00000	0.02193
N	-1.07930	-1.45945	-0.99337
N	0.98914	-1.56711	0.73742
C	0.44104	-2.76112	0.35173
C	-0.67002	-2.70735	-0.57930
C	-0.87565	-5.14220	-0.53994
H	-1.37195	-6.04548	-0.88414
C	0.80410	-4.03976	0.81516
H	1.60265	-4.10973	1.55183
C	-1.31373	-3.89190	-1.03005
C	-2.78639	-2.42448	-2.37979

C	-2.07336	-1.31406	-1.83252
C	0.16488	-5.22305	0.38867
C	-2.40889	-3.74133	-1.97887
C	2.19427	-1.42822	1.43304
C	-3.12912	-4.83029	-2.53035
H	-2.87004	-5.85233	-2.25129
C	3.33731	-2.23481	1.21269
H	3.29812	-3.04001	0.47716
C	0.63408	-6.57213	0.97803
C	-3.84956	-2.22804	-3.29749
H	-4.11851	-1.20764	-3.58454
C	-4.53194	-3.31175	-3.81716
H	-5.35151	-3.16250	-4.52454
C	-4.16387	-4.61884	-3.42774
H	-4.70293	-5.47645	-3.83937
C	2.32429	-0.36203	2.35501
H	1.46055	0.28450	2.53574
C	4.53136	-1.99395	1.89696
H	5.39697	-2.63318	1.69721
C	4.63625	-0.94429	2.81636
H	5.57285	-0.76236	3.34976
C	3.52119	-0.12595	3.03192
H	3.57997	0.70592	3.74020
N	1.07931	1.45945	-0.99337
N	-0.98914	1.56712	0.73743
C	-0.44103	2.76112	0.35172
C	0.67002	2.70735	-0.57930
C	0.87566	5.14220	-0.53995
H	1.37195	6.04548	-0.88414
C	-0.80409	4.03976	0.81516
H	-1.60264	4.10974	1.55183
C	1.31373	3.89190	-1.03006
C	2.78639	2.42448	-2.37979
C	2.07336	1.31406	-1.83252
C	-0.16487	5.22305	0.38867
C	2.40889	3.74134	-1.97888
C	-2.19428	1.42823	1.43303
C	3.12912	4.83030	-2.53036
H	2.87003	5.85233	-2.25130
C	-3.33731	2.23481	1.21267
H	-3.29812	3.04001	0.47715
C	-0.63407	6.57214	0.97803
C	3.84956	2.22803	-3.29749
H	4.11851	1.20764	-3.58454
C	4.53194	3.31175	-3.81717
H	5.35151	3.16249	-4.52455
C	4.16387	4.61884	-3.42775
H	4.70293	5.47645	-3.83938
C	-2.32430	0.36202	2.35499
H	-1.46056	-0.28451	2.53573
C	-4.53137	1.99394	1.89694
H	-5.39698	2.63317	1.69718
C	-4.63626	0.94428	2.81633
H	-5.57287	0.76235	3.34971
C	-3.52121	0.12594	3.03189
H	-3.57998	-0.70594	3.74016
H	-2.35805	-0.29384	-2.11155
H	2.35804	0.29384	-2.11155
C	-0.41609	6.56410	2.50935
H	-0.74389	7.52108	2.94957
H	-0.98308	5.76017	3.00368
H	0.64871	6.42549	2.75932

C	-2.13733	6.77536	0.67799
H	-2.76049	5.98651	1.12678
H	-2.48309	7.74036	1.08552
H	-2.33064	6.77987	-0.40756
C	0.13559	7.76955	0.39142
H	1.21523	7.71318	0.60321
H	0.00495	7.85208	-0.69955
H	-0.23650	8.70571	0.83814
C	0.41609	-6.56410	2.50935
H	0.74390	-7.52108	2.94956
H	0.98309	-5.76017	3.00368
H	-0.64870	-6.42548	2.75932
C	2.13734	-6.77536	0.67799
H	2.76050	-5.98651	1.12678
H	2.48310	-7.74036	1.08552
H	2.33065	-6.77987	-0.40756
C	-0.13558	-7.76955	0.39141
H	-1.21522	-7.71317	0.60321
H	-0.00495	-7.85207	-0.69955
H	0.23650	-8.70570	0.83815

(${}^{\mathit{t}\mathrm{Bu}}$**L3**)$_2$Zn (S$_{1,\mathrm{eq}}$) B3LYP (SMD “toluene”/ def2-tzvpp def2/j)

Zn	-0.30693	0.00583	-0.14607
N	-1.10668	-1.49503	-1.16135
N	0.80185	-1.51632	0.71497
C	0.31225	-2.76082	0.32969
C	-0.69797	-2.74361	-0.69513
C	-0.79007	-5.17790	-0.55482
H	-1.21611	-6.10514	-0.93118
C	0.65229	-3.97415	0.93130
H	1.33749	-3.95912	1.77868
C	-1.21692	-3.95024	-1.16617
C	-2.57779	-2.62223	-2.74992
C	-2.03533	-1.47390	-2.15393
C	0.11127	-5.21644	0.49334
C	-2.18486	-3.92850	-2.27066
C	2.01459	-1.31184	1.31167
C	-2.73569	-5.06848	-2.86610
H	-2.44494	-6.06133	-2.51735
C	3.13663	-2.18935	1.19826
H	3.06270	-3.08184	0.57701
C	0.54448	-6.51676	1.19631
C	-3.53294	-2.54666	-3.81908
H	-3.83804	-1.56152	-4.18297
C	-4.05931	-3.69857	-4.37885
H	-4.78744	-3.61986	-5.19207
C	-3.66847	-4.97068	-3.91409
H	-4.08724	-5.87543	-4.36020
C	2.19568	-0.10042	2.04699
H	1.35111	0.58714	2.13113
C	4.34247	-1.87968	1.81790
H	5.19303	-2.55675	1.70155
C	4.48480	-0.70296	2.56884
H	5.43563	-0.47121	3.05444
C	3.40104	0.18510	2.67210
H	3.50437	1.10961	3.24595
N	0.83065	1.45586	-1.12365
N	-1.09604	1.58676	0.76402
C	-0.49179	2.76339	0.40921
C	0.54492	2.69770	-0.60241

C	0.92121	5.10672	-0.43445
H	1.45009	5.99700	-0.76383
C	-0.73281	4.03057	0.97301
H	-1.47550	4.10478	1.76583
C	1.23591	3.86449	-1.02881
C	2.48619	2.39789	-2.58723
C	1.73737	1.30313	-2.05566
C	-0.04609	5.19524	0.57004
C	2.24329	3.70527	-2.06874
C	-2.25988	1.49824	1.53827
C	3.00142	4.77799	-2.60127
H	2.84455	5.79180	-2.23080
C	-3.35914	2.38129	1.41510
H	-3.31309	3.20506	0.70045
C	-0.38864	6.53276	1.26169
C	3.45504	2.19448	-3.60283
H	3.61893	1.18155	-3.98130
C	4.17689	3.26237	-4.10275
H	4.92337	3.10810	-4.88589
C	3.94415	4.56030	-3.59414
H	4.51502	5.40496	-3.98926
C	-2.39551	0.41548	2.43828
H	-1.56377	-0.28698	2.54324
C	-4.52027	2.19383	2.16941
H	-5.35479	2.89053	2.04397
C	-4.63254	1.12340	3.06456
H	-5.54380	0.98165	3.65126
C	-3.56015	0.23156	3.18537
H	-3.62749	-0.61711	3.87264
H	-2.36627	-0.48636	-2.48886
H	1.91658	0.28889	-2.42891
C	-0.09100	6.41793	2.77569
H	-0.32958	7.36719	3.28409
H	-0.68580	5.62378	3.25230
H	0.97424	6.19563	2.95198
C	-1.88900	6.84929	1.05664
H	-2.53661	6.07031	1.48720
H	-2.14661	7.80518	1.54262
H	-2.13017	6.93633	-0.01550
C	0.42970	7.71057	0.70057
H	1.51209	7.56451	0.84387
H	0.24346	7.86485	-0.37417
H	0.14783	8.63843	1.22344
C	0.12997	-6.45427	2.68563
H	0.43945	-7.37490	3.20794
H	0.59566	-5.60304	3.20693
H	-0.96306	-6.35560	2.78613
C	2.08060	-6.67242	1.09830
H	2.61102	-5.83404	1.57659
H	2.40370	-7.59919	1.60091
H	2.40535	-6.72438	0.04616
C	-0.10711	-7.75925	0.56325
H	-1.20595	-7.72665	0.63260
H	0.16632	-7.86883	-0.49833
H	0.23253	-8.66495	1.09041

($^{t\mathrm{Bu}}$**L3**)$_2$Zn (T$_{1,\mathrm{eq}}$) B3LYP (SMD “toluene”/ def2-tzvpp def2/j)

Zn	0.27636	-0.00959	-0.17916
N	-0.87787	-1.43802	-1.15068
N	1.09215	-1.59519	0.69040

C	0.47629	-2.76694	0.33778
C	-0.58291	-2.68642	-0.64960
C	-0.96631	-5.09500	-0.49689
H	-1.50833	-5.97904	-0.82149
C	0.72409	-4.04083	0.88309
H	1.48269	-4.12644	1.65933
C	-1.28866	-3.84590	-1.07205
C	-2.57504	-2.35744	-2.57990
C	-1.80930	-1.27150	-2.05531
C	0.02155	-5.19801	0.48560
C	-2.32122	-3.67193	-2.08488
C	2.27617	-1.50908	1.43220
C	-3.09506	-4.73582	-2.61210
H	-2.93096	-5.75523	-2.26070
C	3.36513	-2.40276	1.29307
H	3.29742	-3.23274	0.58782
C	0.36611	-6.54339	1.16299
C	-3.57029	-2.13897	-3.56626
H	-3.74304	-1.12113	-3.92702
C	-4.30715	-3.19864	-4.06054
H	-5.07423	-3.03256	-4.82103
C	-4.06294	-4.50311	-3.57640
H	-4.64530	-5.34170	-3.96771
C	2.44525	-0.41625	2.31479
H	1.62459	0.29752	2.43158
C	4.54516	-2.21749	2.01744
H	5.37001	-2.92342	1.87997
C	4.68870	-1.13895	2.89731
H	5.61462	-0.99967	3.46125
C	3.62848	-0.23531	3.03187
H	3.72001	0.62105	3.70666
N	1.15591	1.50894	-1.12066
N	-0.83394	1.51476	0.68389
C	-0.34968	2.73102	0.31931
C	0.72865	2.71340	-0.66384
C	0.79007	5.14338	-0.53460
H	1.22823	6.07952	-0.87496
C	-0.75795	3.97682	0.87847
H	-1.49981	3.95804	1.67627
C	1.27119	3.95193	-1.10599
C	2.75477	2.62204	-2.59655
C	2.16616	1.46888	-2.06294
C	-0.20687	5.18721	0.47402
C	2.32108	3.92325	-2.13901
C	-2.01531	1.29797	1.38737
C	2.91345	5.06744	-2.69133
H	2.59399	6.05897	-2.36296
C	-3.18722	2.07620	1.21486
H	-3.19244	2.89538	0.49436
C	-0.65708	6.50604	1.13933
C	3.78472	2.55739	-3.59128
H	4.11870	1.57461	-3.93650
C	4.34737	3.71026	-4.10797
H	5.13241	3.63810	-4.86678
C	3.91592	4.97871	-3.66507
H	4.36043	5.88810	-4.07665
C	-2.07472	0.18453	2.26085
H	-1.18460	-0.43705	2.38361
C	-4.35164	1.76588	1.91737
H	-5.24920	2.37019	1.75862
C	-4.38403	0.68473	2.80635
H	-5.29903	0.45002	3.35616

C	-3.23836	-0.10560	2.96874
H	-3.25364	-0.96029	3.65041
H	-1.99641	-0.25252	-2.41092
H	2.49129	0.47634	-2.38346
C	-0.28043	6.47544	2.63925
H	-0.59510	7.40814	3.13759
H	-0.76436	5.63806	3.16665
H	0.80866	6.37167	2.77479
C	-2.18906	6.66431	1.00385
H	-2.73510	5.84367	1.49513
H	-2.52226	7.60590	1.47194
H	-2.49657	6.68715	-0.05472
C	0.00871	7.73844	0.49988
H	1.10507	7.72240	0.60681
H	-0.22880	7.82856	-0.57248
H	-0.35294	8.65437	0.99428
C	0.09148	-6.43681	2.68145
H	0.32814	-7.39052	3.18286
H	0.69943	-5.65234	3.15807
H	-0.96837	-6.20612	2.87925
C	1.86035	-6.87049	0.93641
H	2.52296	-6.10524	1.36925
H	2.11786	-7.83432	1.40709
H	2.09331	-6.94789	-0.13850
C	-0.46787	-7.71213	0.60710
H	-1.54782	-7.56548	0.76827
H	-0.30068	-7.86477	-0.47119
H	-0.18522	-8.64668	1.11808

$(^{t\mathrm{Bu}}\mathbf{L3})_2$Zn ($S_{0,\mathrm{eq}}$) B3LYP (SMD “n-hexane”/ def2-tzvpp def2/j)

Zn	0.00000	0.00000	0.02981
N	-1.08520	-1.45829	-0.98394
N	0.99236	-1.56790	0.73579
C	0.44313	-2.76089	0.35065
C	-0.67286	-2.70637	-0.57453
C	-0.87622	-5.14128	-0.53903
H	-1.37332	-6.04450	-0.88207
C	0.80984	-4.04036	0.80920
H	1.61227	-4.11026	1.54164
C	-1.31842	-3.89071	-1.02386
C	-2.80135	-2.42147	-2.36055
C	-2.08517	-1.31186	-1.81581
C	0.16971	-5.22304	0.38358
C	-2.41973	-3.73881	-1.96516
C	2.20019	-1.43095	1.42812
C	-3.14283	-4.82703	-2.51436
H	-2.88048	-5.84922	-2.23913
C	3.34391	-2.23250	1.19520
H	3.30232	-3.03140	0.45289
C	0.64346	-6.57294	0.96741
C	-3.87120	-2.22436	-3.27028
H	-4.14353	-1.20365	-3.55307
C	-4.55617	-3.30738	-3.78774
H	-5.38090	-3.15721	-4.48886
C	-4.18398	-4.61494	-3.40396
H	-4.72494	-5.47222	-3.81375
C	2.33118	-0.37248	2.35819
H	1.46624	0.26969	2.54826
C	4.54053	-1.99432	1.87569
H	5.40698	-2.62937	1.66665

C	4.64675	-0.95205	2.80312
H	5.58542	-0.77192	3.33339
C	3.53072	-0.13869	3.03109
H	3.59084	0.68733	3.74599
N	1.08521	1.45829	-0.98394
N	-0.99236	1.56790	0.73579
C	-0.44313	2.76089	0.35065
C	0.67287	2.70637	-0.57453
C	0.87622	5.14128	-0.53903
H	1.37332	6.04449	-0.88208
C	-0.80984	4.04036	0.80919
H	-1.61227	4.11026	1.54163
C	1.31842	3.89071	-1.02386
C	2.80136	2.42148	-2.36055
C	2.08518	1.31186	-1.81581
C	-0.16971	5.22304	0.38357
C	2.41973	3.73882	-1.96516
C	-2.20019	1.43094	1.42812
C	3.14284	4.82704	-2.51436
H	2.88048	5.84922	-2.23913
C	-3.34391	2.23250	1.19519
H	-3.30232	3.03140	0.45288
C	-0.64347	6.57295	0.96740
C	3.87120	2.22436	-3.27028
H	4.14355	1.20366	-3.55306
C	4.55618	3.30739	-3.78774
H	5.38091	3.15720	-4.48886
C	4.18398	4.61495	-3.40396
H	4.72494	5.47222	-3.81376
C	-2.33118	0.37248	2.35819
H	-1.46624	-0.26970	2.54825
C	-4.54053	1.99431	1.87568
H	-5.40698	2.62936	1.66664
C	-4.64675	0.95204	2.80311
H	-5.58542	0.77191	3.33338
C	-3.53072	0.13868	3.03109
H	-3.59084	-0.68734	3.74598
H	-2.37236	-0.29104	-2.09023
H	2.37237	0.29104	-2.09022
C	-0.43360	6.56866	2.49998
H	-0.76518	7.52606	2.93637
H	-1.00174	5.76478	2.99287
H	0.63001	6.43182	2.75548
C	-2.14533	6.77403	0.65846
H	-2.76994	5.98516	1.10500
H	-2.49459	7.73932	1.06224
H	-2.33214	6.77598	-0.42815
C	0.12809	7.77004	0.38232
H	1.20651	7.71517	0.60047
H	0.00330	7.84967	-0.70952
H	-0.24746	8.70685	0.82468
C	0.43360	-6.56866	2.49998
H	0.76517	-7.52607	2.93637
H	1.00174	-5.76479	2.99289
H	-0.63001	-6.43182	2.75549
C	2.14532	-6.77403	0.65846
H	2.76994	-5.98516	1.10500
H	2.49458	-7.73932	1.06224
H	2.33213	-6.77597	-0.42815
C	-0.12809	-7.77004	0.38232
H	-1.20652	-7.71516	0.60048
H	-0.00332	-7.84966	-0.70952

H	0.24745	-8.70685	0.82469

($^{t\mathrm{Bu}}$**L3**)$_2$Zn ($\mathrm{S}_{1,\mathrm{eq}}$) B3LYP (SMD “n-hexane”/ def2-tzvpp def2/j)

Zn	-0.32537	0.00364	-0.13761
N	-1.10178	-1.49672	-1.16827
N	0.78556	-1.51366	0.72859
C	0.30061	-2.76359	0.33663
C	-0.69398	-2.74806	-0.70034
C	-0.78418	-5.18215	-0.56204
H	-1.20200	-6.10967	-0.94667
C	0.63133	-3.97238	0.94517
H	1.30488	-3.95576	1.80192
C	-1.20301	-3.95358	-1.18039
C	-2.53799	-2.62808	-2.78611
C	-2.01159	-1.47920	-2.17636
C	0.09830	-5.21851	0.49895
C	-2.15080	-3.93362	-2.30161
C	2.00029	-1.30793	1.31294
C	-2.68798	-5.07387	-2.90811
H	-2.40152	-6.06653	-2.55553
C	3.11994	-2.19199	1.20608
H	3.03937	-3.09165	0.59635
C	0.52604	-6.51685	1.20848
C	-3.47345	-2.55267	-3.87221
H	-3.77445	-1.56783	-4.24014
C	-3.98706	-3.70494	-4.44272
H	-4.70065	-3.62681	-5.26868
C	-3.60189	-4.97640	-3.97262
H	-4.01084	-5.88136	-4.42720
C	2.19171	-0.08750	2.03410
H	1.35010	0.60404	2.11463
C	4.32907	-1.87997	1.81649
H	5.17628	-2.56200	1.70486
C	4.48035	-0.69454	2.55237
H	5.43429	-0.46133	3.03096
C	3.40070	0.19983	2.64938
H	3.51085	1.13063	3.21163
N	0.81064	1.45293	-1.12363
N	-1.10244	1.58697	0.77722
C	-0.49809	2.76171	0.41880
C	0.53131	2.69473	-0.60026
C	0.91339	5.10266	-0.43446
H	1.44100	5.99237	-0.76725
C	-0.73229	4.02933	0.98487
H	-1.46934	4.10392	1.78290
C	1.22141	3.86050	-1.03155
C	2.45643	2.39151	-2.60018
C	1.70941	1.29841	-2.06284
C	-0.04647	5.19241	0.57721
C	2.22030	3.69916	-2.07916
C	-2.25820	1.50391	1.56548
C	2.97669	4.77023	-2.61739
H	2.82467	5.78409	-2.24517
C	-3.35942	2.38390	1.44287
H	-3.32089	3.19886	0.71764
C	-0.38166	6.53040	1.27155
C	3.41683	2.18694	-3.62344
H	3.57585	1.17400	-4.00403
C	4.13701	3.25329	-4.12861
H	4.87686	3.09764	-4.91771

C	3.91108	4.55133	-3.61757
H	4.48052	5.39503	-4.01676
C	-2.38228	0.43174	2.47884
H	-1.54833	-0.26815	2.58280
C	-4.51227	2.20404	2.21123
H	-5.34925	2.89782	2.08635
C	-4.61339	1.14399	3.11969
H	-5.51838	1.00779	3.71726
C	-3.53890	0.25504	3.23990
H	-3.59829	-0.58565	3.93756
H	-2.34395	-0.49279	-2.51374
H	1.88262	0.28357	-2.43752
C	-0.07369	6.41480	2.78339
H	-0.30741	7.36401	3.29414
H	-0.66581	5.62120	3.26410
H	0.99233	6.19082	2.95230
C	-1.88272	6.84989	1.07669
H	-2.52910	6.07208	1.51109
H	-2.13581	7.80606	1.56451
H	-2.13105	6.93739	0.00629
C	0.43487	7.70697	0.70520
H	1.51798	7.55912	0.84102
H	0.24136	7.86228	-0.36809
H	0.15866	8.63541	1.23005
C	0.09177	-6.45481	2.69214
H	0.39716	-7.37384	3.21965
H	0.54726	-5.60180	3.21947
H	-1.00271	-6.35937	2.77818
C	2.06374	-6.66861	1.13058
H	2.58624	-5.82928	1.61590
H	2.38326	-7.59446	1.63714
H	2.40255	-6.71931	0.08287
C	-0.11370	-7.76160	0.56791
H	-1.21342	-7.73160	0.62230
H	0.17442	-7.87169	-0.48968
H	0.22053	-8.66634	1.10014

($^{t\mathrm{Bu}}$**L3**)$_2$Zn (T$_{1,\mathrm{eq}}$) B3LYP (SMD “n-hexane”/ def2-tzvpp def2/j)

Zn	0.28898	-0.00817	-0.17604
N	-0.86684	-1.43398	-1.15365
N	1.09574	-1.59595	0.69521
C	0.47822	-2.76543	0.34019
C	-0.57700	-2.68268	-0.65137
C	-0.96629	-5.09024	-0.50052
H	-1.50857	-5.97334	-0.82703
C	0.72110	-4.04015	0.88606
H	1.47672	-4.12677	1.66507
C	-1.28387	-3.84075	-1.07666
C	-2.56080	-2.34898	-2.58959
C	-1.79411	-1.26515	-2.06206
C	0.01783	-5.19542	0.48569
C	-2.31209	-3.66398	-2.09329
C	2.27650	-1.51507	1.44412
C	-3.08687	-4.72579	-2.62335
H	-2.92640	-5.74534	-2.27082
C	3.36543	-2.40773	1.30189
H	3.29978	-3.23120	0.58879
C	0.35709	-6.54166	1.16405
C	-3.55184	-2.12860	-3.57975
H	-3.72085	-1.11051	-3.94162

C	-4.28961	-3.18630	-4.07661
H	-5.05336	-3.01833	-4.84001
C	-4.05056	-4.49122	-3.59120
H	-4.63354	-5.32848	-3.98440
C	2.44129	-0.43001	2.33629
H	1.62015	0.28285	2.45479
C	4.54211	-2.22919	2.03314
H	5.36759	-2.93385	1.89338
C	4.68162	-1.15821	2.92266
H	5.60502	-1.02390	3.49182
C	3.62129	-0.25544	3.06018
H	3.71019	0.59517	3.74245
N	1.15930	1.51159	-1.12333
N	-0.82447	1.51309	0.68819
C	-0.34505	2.73038	0.32063
C	0.72945	2.71476	-0.66698
C	0.78299	5.14479	-0.54197
H	1.21635	6.08180	-0.88593
C	-0.75435	3.97578	0.88041
H	-1.49196	3.95501	1.68207
C	1.26560	3.95474	-1.11390
C	2.74777	2.62793	-2.60825
C	2.16613	1.47357	-2.06979
C	-0.20932	5.18711	0.47197
C	2.31057	3.92800	-2.15168
C	-2.00264	1.29299	1.39572
C	2.89552	5.07337	-2.70938
H	2.57316	6.06427	-2.38197
C	-3.17672	2.06948	1.22989
H	-3.18588	2.89014	0.51118
C	-0.65962	6.50548	1.13821
C	3.77359	2.56540	-3.60696
H	4.11042	1.58328	-3.95117
C	4.32899	3.71923	-4.12879
H	5.11111	3.64869	-4.89065
C	3.89383	4.98676	-3.68703
H	4.33253	5.89704	-4.10272
C	-2.05705	0.17739	2.26681
H	-1.16562	-0.44345	2.38357
C	-4.33775	1.75572	1.93636
H	-5.23693	2.35890	1.78265
C	-4.36491	0.67251	2.82288
H	-5.27726	0.43506	3.37581
C	-3.21735	-0.11633	2.97851
H	-3.22854	-0.97293	3.65781
H	-1.97655	-0.24555	-2.41849
H	2.49421	0.48168	-2.38905
C	-0.27309	6.47881	2.63583
H	-0.58756	7.41124	3.13476
H	-0.75055	5.64062	3.16769
H	0.81711	6.37852	2.76409
C	-2.19302	6.65897	1.01217
H	-2.73339	5.83720	1.50773
H	-2.52642	7.59998	1.48123
H	-2.50696	6.67929	-0.04449
C	-0.00204	7.73929	0.49264
H	1.09492	7.72725	0.59331
H	-0.24626	7.82649	-0.57843
H	-0.36395	8.65487	0.98741
C	0.07628	-6.43509	2.68149
H	0.30972	-7.38913	3.18374
H	0.68294	-5.65125	3.16057

H	-0.98403	-6.20288	2.87450
C	1.85169	-6.87158	0.94319
H	2.51386	-6.10733	1.37826
H	2.10578	-7.83576	1.41495
H	2.08829	-6.94915	-0.13082
C	-0.47675	-7.70887	0.60444
H	-1.55697	-7.56015	0.76158
H	-0.30538	-7.86115	-0.47322
H	-0.19782	-8.64415	1.11605

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